INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

UMI

A Bell & Howell Information Company
300 North Zeeb Road, Ann Arbor MI 48106-1346 USA
313/761-4700 800/521-0600

Dicationic Dihydrogen Complexes
of Osmium and Ruthenium

by

Thomas Alan Luther

A dissertation submitted in partial fulfillment
of the requirements for the degree of

Doctor of Philosophy

University of Washington

1997

Approved by D.M. Heinekey
(Chairperson of Supervisory Committee)

Program Authorized
to Offer Degree Chemistry

Date June 26, 1997

UMI
300 North Zeeb Road
Ann Arbor, MI 48103

Doctoral Dissertation

Signature __________________________________

Date 6/26/97

University of Washington

Abstract

Dicationic Dihydrogen Complexes of Osmium and Ruthenium

by Thomas Alan Luther

Chairperson of the Supervisory Committee: Professor Dennis Michael Heinekey
Department of Chemistry

The dicationic complexes $[Os(H_2)(PR_3)_2(bpy)(CO)]^{2+}$ ($PR_3 = PPh_3$, $PMePh_2$), $[Os(H_2)(PPh_3)_2(phen)(CO)]^{2+}$, $[Ru(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$, and $[Os(H_2)(bpy)_2(CO)]^{2+}$ (bpy = 2,2'-bipyridine; phen = 1,10-phenanthroline) have been prepared by the protonation of the corresponding monocationic hydrides using an excess of trifluoromethanesulfonic acid. The presence of a bound dihydrogen ligand is indicated by short T_1 minimum values consistent with H-H distances of 0.92–1.04 Å. In the partially deuterated derivatives J_{HD} values of 25.3–31.0 Hz were observed. The dicationic complexes are strong acids indicating that the bound H_2 is substantially activated toward heterolytic cleavage. The H_2 ligand is tightly bound to the metal center, and does not undergo exchange with D_2 over the course of several weeks at room temperature. The complex $[Os(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$ has been shown to be very stable in solution at room temperature. In contrast, the ruthenium analogue, $[Ru(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$ irreversibly loses H_2 in solution at room temperature but is relatively stable to H_2 loss at temperatures less than 245 K.

The complexes $[Os(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$ and $[Os(H_2)(PPh_3)_2(phen)(CO)]^{2+}$ and the corresponding HD complexes were studied by solution NMR spectroscopy in magnetic fields of 11.75 and 17.63 T (^{1}H: 500 and 750 MHz). The effects of the partial alignment of these complexes with the magnetic field were large enough to be observable in the NMR spectra. The total splitting of the HD resonance of the partially deuterated

complexes was measured in several magnetic fields to determine the field independent spin coupling (J_{HD}) value and the magnitude and sign of the field dependent residual dipolar coupling (D_{HD}).

TABLE OF CONTENTS

Chapter 2 Synthesis, Characterization, and Reactivity of Neutral and Monocationic Hydrides of Osmium and Ruthenium

Chapter 3 Synthesis and Characterization of Dicationic Dihydrogen Complexes of Ruthenium and Osmium

LIST OF FIGURES

Chapter 1

Chapter 2

Chapter 3

Chapter 4

Chapter 5

LIST OF TABLES

Chapter 2

Chapter 3

Chapter 5

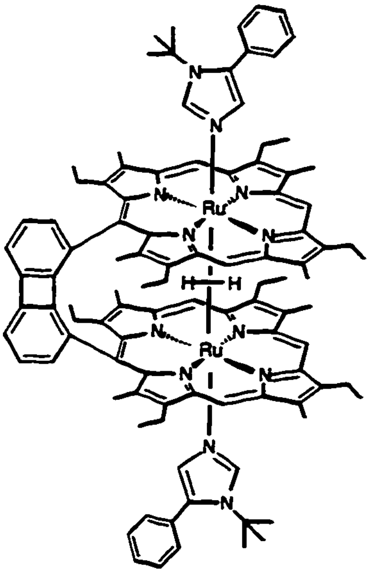
Appendix

ABBREVIATIONS AND SYMBOLS

Å	angstrom
A	Boltzmann factor
A	correlation constant
{aromatic ^{1}H}	aromatic protons selectively decoupled
atm	atmosphere
BAr'$_4^-$	B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4^-$
B_0	magnetic field strength
bpy	2,2'-bipyridine
bq	7,8-benzoquinolinate
cht	cycloheptatriene
Cp	cyclopentadienyl, (η^5-C$_5$H$_5^-$)
Cp*	pentamethylcyclopentadienyl, (η^5-C$_5$(CH$_3$)$_5^-$)
CSA	chemical shift anisotropy
Cy	cyclohexyl
d	doublet
D	dipolar coupling
°C	degrees Celsius
δ	chemical shift in ppm
$\delta\chi$	molecular diamagnetic susceptibility asymmetry
$\Delta\chi$	molecular diamagnetic susceptibility anisotropy
$\Delta\delta$	isotope shift
$\Delta G^‡$	free energy of activation
$\Delta\nu_{1/2}$	half-height line width

dcpe	1,2-bis(dicyclohexylphosphino)ethane
dmpe	1,2-bis(dimethylphosphino)ethane
DPB	1,8-bis[5-(2,8,13,17-tetraethyl-3,7,12,18-tetramethyl)porphyrin]biphenylene dianion
dppe	1,2-bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
dppp	1,3-bis(diphenylphosphino)propane
E_a	activation energy
$E_{1/2}$	electrochemical potential (V)
en	ethylenediamine
eq	equation
equiv	equivalents
Et	ethyl
η	hapticity
g_2	intermolecular interaction correction factor
γ	gyromagnetic ratio
h	Plank's constant
h	hour
$\{^1H\}$	broadband proton decoupling
HETCOR	heteronuclear shift correlation
Hz	hertz
*Im	1-*tert*-butyl-5-phenylimidazole
^{i}Pr	isopropyl
IPR	isotopic perturbation of resonance
IR	infrared

J	coupling constant
$J(\omega)$	spectral density function
k	Boltzmann constant
K	Kelvin
L	ligand
m	multiplet
	medium absorbance
M	molarity
	metal atom
Me	methyl
mL	milliliter
µL	microliter
mmol	millimole
MP2	second order Møller-Plesset perturbation theory
ms	millisecond
µs	microsecond
ν	frequency
n	neutron
NBS	*N*-bromosuccinimide
NCS	*N*-chlorosuccinimide
NMR	nuclear magnetic resonance
N-N	chelating nitrogen ligand
ω	Larmor frequency
OAc	acetate, (CH_3COO^-)
OEP	octaethylporphyrin

OTf	trifluoromethanesulfonate, (triflate, $OSO_2CF_3^-$)
Ph	phenyl
phen	1,10-phenanthroline
P-P	chelating phosphine ligand
ppm	parts per million
R	alkyl
	gas constant
r_{HH}	internuclear H-H distance
R_{CSA}	relaxation rate due to CSA
R_{HH}	homonuclear dipole-dipole relaxation rate
R_{HX}	heteroatom-proton dipole relaxation rate
R_{obs}	observed relaxation rate
$Ru_2(H_2)(DPB)(*Im)_2$	
s	singlet
	strong absorbance

S	nuclear spin state
	degree of alignment
SCF	Hartree-Fock self-consistent field
ss	solid state
Stang's sponge	2,6-di-*tert*-butyl-4methylpyridine
t	triplet
τ	lifetime
	delay time (ms)
τ_c	correlation time of the molecule
τ_{H_2}	correlation time of the H_2 ligand
T	temperature (K)
	Tesla
T_1	spin-lattice relaxation time
T_2	spin-spin relaxation time
Tp	hydridotris(pyrazolyl)borate
^{t}Bu	*tert*-butyl
tetraphos-II	tris[2-(diphenylphosphino)ethyl]phosphine
THF	tetrahydrofuran
TMS	tetramethylsilane
V	volts
X	anion

ACKNOWLEDGMENTS

As I reach the end of another chapter in my life, I look back and realize that the earning of a Ph.D. is a communal effort and this acknowledgment is for those that provided help and support along the way. A great amount of thanks is due to Mike Heinekey for the encouragement and guidance over the past five years. When I first joined the Heinekey group in the Summer of 1992, Beth Schomber and Greg Harper provided much appreciated technical expertise and support that allowed me to get started down this road. The four "senior" members of the group, Amber Hinkle, Mark Voges, Warren Oldham, and David Fine, will always be remembered for their openness in allowing a "youngster" to join the "gang of four" at the beginning stages of the University of Washington edition of the Heinekey research group. Along with the original cast of characters, Cathy Radzewich, Mirjam van Roon, Diane Nagahara, Jack Wiley, Heather Mellows, and James Law, deserve many thanks for the many countless hours of discussions and encouragement. All the rough times with the chemistry were definitely balanced with the "happy dances", chocolate, coffee, and general camaraderie.

Many thanks are due to the other members of the Inorganic Division which over the years have provided exposure to a large amount of interesting chemistry and helpful discussions. Dr. Tom Pratum for his understanding and helpfulness with the NMR spectrometers and Bob Morley for keeping the glassware in one piece. Diane Hunn and Nancy Cooper for making sure all the paperwork that goes along with this endeavor was properly taken care of and filed with the Graduate School. Jack Norton and Dan Gately for their mentoring and guidance during my initial exposure to inorganic chemistry at Colorado State University.

My parents, Howard and Dorothy Luther for their unwavering support throughout the years with all the career changes that I have made them endure. Most of all, this work is dedicated to my wife and our son, this degree is as much theirs as it is mine, thank you.

To Yvonne & Branum

"I'll love you forever..."

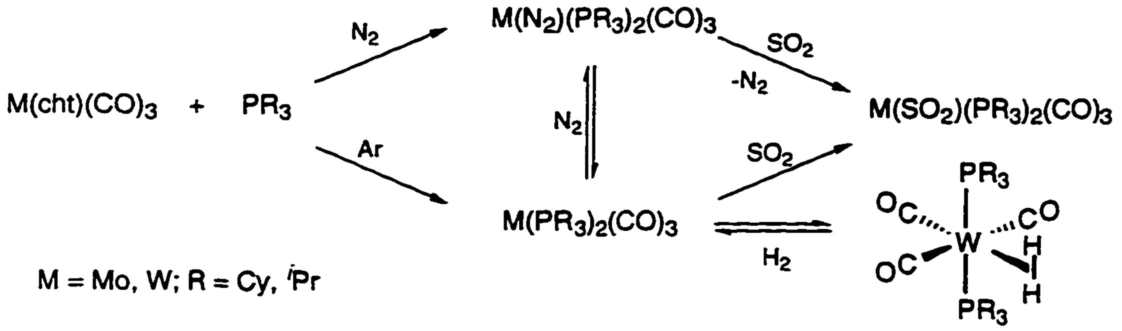
"Wow, it really snowed last night! Isn't it wonderful?
Everything familiar has disappeared! The world looks brand-new!
A new year...a fresh clean start!
It's like having a big white sheet of paper to draw on!
A day full of possibilities! It's a magical world Hobbes, ol' buddy...
...let's go exploring!"

Bill Watterson

Chapter 1

Introduction

Initial Discovery of an Intact Dihydrogen Ligand. In the early 1980's Kubas and coworkers were studying the structure and bonding characteristics of $M(SO_2)(PR_3)_2(CO)_3$ (M = Mo, W; PR_3 = bulky phosphines).[1] The preparation of $M(SO_2)(PR_3)_2(CO)_3$ (R = Cy, ^{i}Pr) involves the addition of SO_2 to the product of the reaction of $M(cht)(CO)_3$ (cht = cycloheptatriene) with PR_3. They observed that under N_2 the phosphine substitution reaction results in an orange complex with a labile dinitrogen ligand. The subsequent addition of SO_2 displaces the N_2 which is observable by gas evolution. If $M(cht)(CO)_3$ is reacted with excess PR_3 under Ar, a purple complex with an agostic interaction with a phosphine C-H group forms and no gas evolves with the addition of SO_2 (Scheme 1.1).



Scheme 1.1

The addition of H_2 to $M(H_2)(PR_3)_2(CO)_3$ in solution or in the solid state results in the formation of a yellow complex $M(H_2)(PR_3)_2(CO)_3$ that is stable under an H_2 atmosphere.[2] Suitable crystals of $W(H_2)(P{\it i}Pr_3)_2(CO)_3$ were examined by low temperature X-ray and neutron diffraction which indicate an intact H_2 ligand aligned with the P–W–P axis. Solid state NMR data[3] has determined the H-H bond length to be 0.89 Å which is slightly longer than the H-H bond length in H_2 gas (0.74 Å).

The coordination of the H_2 ligand to the metal center has been modeled in a similar fashion as the binding interaction between a metal center and an ethylene ligand.[4] The M-H_2 bond results from a combination of electron donation from the σ orbital of the dihydrogen molecule to an empty metal d orbital of σ symmetry and π back-donation from filled metal d orbitals to the σ^* orbital of H_2 (Figure 1.1).

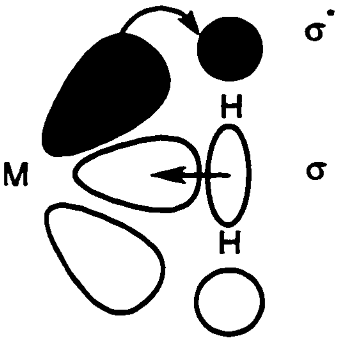


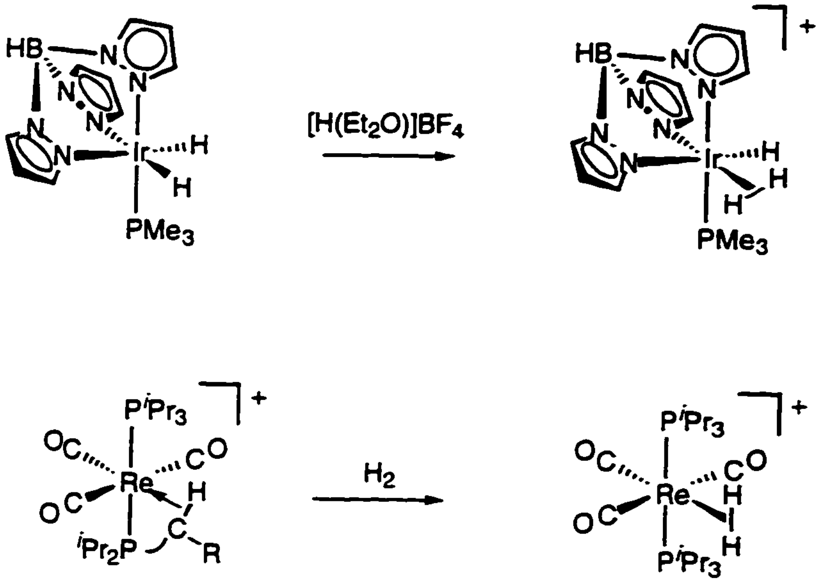
Figure 1.1. Bonding model of an H_2 ligand with a metal center. The arrows indicate the flow of electrons from filled orbitals donating into empty orbitals.

Both interactions will lead to a weakening and therefore lengthening of the H-H bond when H_2 coordinates to a metal center. A strong metal to H_2 back donation into the σ^* orbital of H_2 may eventually lead to homolytic cleavage and oxidative addition of the H_2 ligand.

Preparation of Dihydrogen Complexes. Since the discovery of the first transition metal complex with an intact H_2 ligand, $W(H_2)(P^iPr_3)_2(CO)_3$, in 1984 this area of research has been actively pursued by several research groups.[5] Examples of dihydrogen complexes are now known for every metal in the vanadium, chromium, manganese, iron, and cobalt triads and recently a platinum H_2 complex has been reported.[6] The most common electronic configuration of stable H_2 complexes is d^6 with just a few examples of d^2, d^4, and d^8 configuration.[5,6,7] The vast majority of these complexes have been found to be singly charged cationic species.[5] The plethora of monocationic complexes suggests that positive charge confers additional stability to the H_2 complexes. An assessment of the effect of charge on the binding of H_2 requires the preparation of charged complexes of the form $[M(H_2)(L)_5]^{n+}$ with ligands L comparable to those employed in the tungsten complexes.

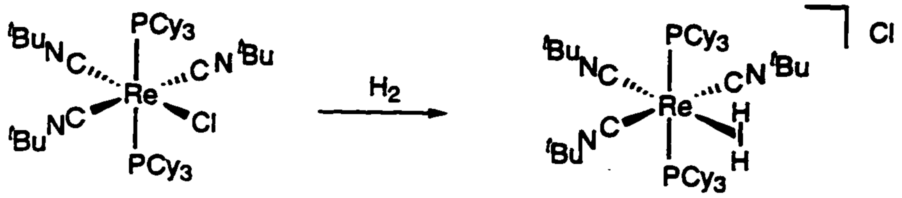
Recently, the preparation of rhenium cationic analogues, $[Re(H_2)(PR_3)_2(CO)_3]^+$ and $[Re(H_2)(PR_3)_2(CN^tBu)_3]^+$ and comparative studies with the neutral tungsten complexes have been reported.[8,9,10] At the outset of this study the only well characterized dicationic complexes belonged to the osmium series, $[Os(H_2)(NH_3)_4(L)]^{2+}$ and $[Os(H_2)(en)_2(L)]^{2+}$ (en = ethylenediamine) which had been reported by Taube and coworkers.[11,12,13]

The synthetic route to H_2 complexes generally involves the protonation of a metal hydride[14] or the complexation of dihydrogen with a metal species possessing either a labile neutral ligand or an "open" coordination site[15] (Scheme 1.2).



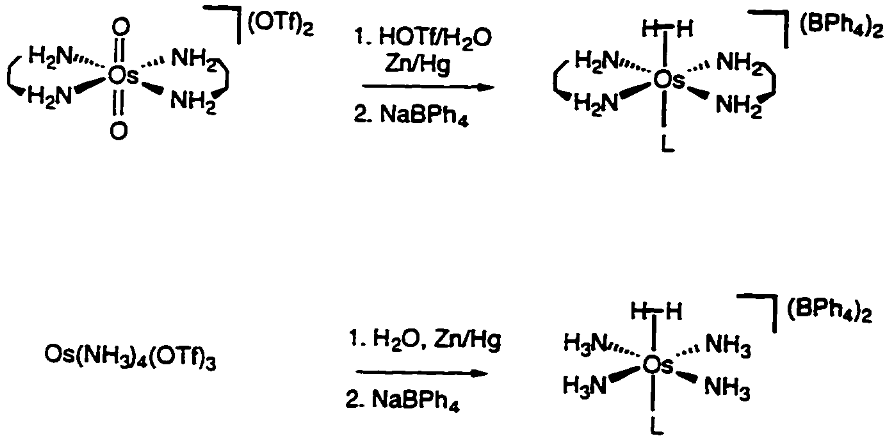
Scheme 1.2

Recently, the preparation of a H_2 complex by the novel method of unassisted chloride displacement by dihydrogen was reported[9] (Scheme 1.3).



Scheme 1.3

Taube and coworkers[12,13] have prepared a series of interesting H_2 complexes by the reduction of $Os(NH_3)_4(OTf)_3$ (OTf = OSO_2CF_3) or $[Os(O)_2(en)_2](OTf)_2$ (en = ethylenediamine) using a zinc/mercury amalgam under acidic conditions (Scheme 1.4).



L = solvent

Scheme 1.4

The ligand L, *trans* to the H_2, in these complexes is quite labile and can be displaced by a variety of neutral or anionic ligands producing a series of monocationic and dicationic complexes. The basicity of the metal center results in a wide range of elongated H-H bond lengths on the verge of homolytic cleavage (1.09–1.34 Å).

Characterization as Dihydrogen Complexes. Unequivocal determination of an intact dihydrogen ligand is by single crystal neutron diffraction analysis.[16] The difficulty in obtaining large high quality crystals suitable for neutron study and the limited number of facilities limits its general use as a spectroscopic tool. Other methods include low temperature single crystal X-ray diffraction data and infrared and raman spectroscopy. However, X-ray diffraction suffers from the difficulty in obtaining high quality crystals and accurate distances between the hydrogen atoms in the H_2 ligand. The vibrational data has not been widely used due to the inherent weakness in the coordinated H_2 vibrational modes. The most widely used methods that have been developed are solution NMR experiments to determine the minimum spin-lattice relaxation time (T_1 minimum) of the H_2 ligand and the measurement of the H-D coupling (J_{HD}) in the corresponding HD complex.

Spin-Lattice Relaxation (T_1). Hamilton and Crabtree[17] were the first to propose that the T_1 minimum of the H_2 resonance could be used as evidence of an intact H_2 ligand. Assuming that the molecule is tumbling isotropically in solution and that the rate of relaxation of the dihydrogen ligand is primarily due to the homonuclear dipolar interaction (R_{HH}), the observed rate of relaxation for a proton is given by eq 1.1.[18]

$$R_{HH} = T_1^{-1} = \frac{3\gamma_H{}^4 h^2}{20\pi\, r_{HH}^6} \left\{ \frac{\tau_c}{1+\omega^2\tau_c{}^2} + \frac{4\tau_c}{1+4\omega^2\tau_c{}^2} \right\} \qquad (1.1)$$

Where γ_H is the gyromagnetic ratio of the proton, h is Plank's constant, ω is the Larmor frequency, r_{HH} is the internuclear distance of the two hydrogen atoms, and τ_c is the rotational correlation time of the molecule in solution (at room temperature a typical $\tau_c \approx 1 \times 10^{-10}$ s). At low temperatures when the molecule is tumbling slowly in solution and $\omega^2\tau_c{}^2 \gg 1$, the term in the brackets reduces to $2/\omega^2\tau_c$ and the rate of relaxation is inversely proportional to τ_c and the strength of the magnetic field squared. At high temperatures and $\omega^2\tau_c{}^2 \ll 1$, when the molecule is tumbling quickly, the bracketed term reduces to $5\tau_c$ and the rate of relaxation is proportional to τ_c and is independent of the strength of the magnetic field. This equation predicts that the rate of relaxation will increase, proceed through a maximum, and then decrease as the temperature is increased. The first derivative of eq 1.1 with respect to τ_c yields the maximum rate of relaxation, which will occur when $\omega\tau_c = 0.6158$. Since the rate of relaxation is proportional to the inverse sixth power of the distance between the hydrogen nuclei, the maximum rate of relaxation (T_1 minimum) can be used to calculate the H-H distance in the dihydrogen ligand. Examination of the T_1 minimum of some known metal polyhydrides and some of the early reported H_2 complexes suggested that a range of T_1 minimum values (at 250 MHz) could be used to determine between a dihydride (> 150 ms) and a dihydrogen (< 80 ms) structure. Halpern and coworkers[18] refined this method to include other sources of relaxation. They showed that in certain complexes the interactions between the metal center and the ancillary coligands with the hydride ligands added to the relaxation rate producing T_1 minimum values that were misinterpreted as evidence for a bound H_2.

This "static" model assumes the rotation of H_2 ligand around the M-H_2 axis does not contribute to the rate of relaxation. Woessner[19] has shown that corrections to the spectral density function in the relaxation rate equation (eq 1.1) are needed to account for the rotation of a methyl group attached to a molecule that is tumbling isotropically in solution. Morris and coworkers have adapted this work to include the rotation of the H_2 ligand in the homonuclear dipole interaction relaxation rate equation (eq 1.2).[20]

$$R_{HH} = \frac{3\gamma_H{}^4\hbar^2}{20\pi r_{HH}{}^6}\left\{\frac{0.25\tau_c}{1+\omega^2\tau_c{}^2} + \frac{0.75\left(\frac{\tau_c}{2+{}^{\tau_{H_2}}/_{\tau_c}}\right)}{1+\omega^2\left(\frac{\tau_c}{2+{}^{\tau_{H_2}}/_{\tau_c}}\right)^2} + \frac{\tau_c}{1+4\omega^2\tau_c{}^2} + \frac{3\left(\frac{\tau_c}{2+{}^{\tau_{H_2}}/_{\tau_c}}\right)}{1+4\omega^2\left(\frac{\tau_c}{2+{}^{\tau_{H_2}}/_{\tau_c}}\right)^2}\right\} \qquad (1.2)$$

Where τ_c is the correlation time of the molecule and τ_{H_2} is the correlation time of the rotation of the H_2 ligand around the $M\text{-}H_2$ axis. This "fast" rotation model effectively produces a relaxation rate that is 4 times the rate of the "static" model (eq 1.3).

$$R_{HH} = (0.25)\ \frac{3\gamma_H{}^4\hbar^2}{20\pi\ r_{HH}^6}\left\{\frac{\tau_c}{1+\omega^2\tau_c{}^2} + \frac{4\tau_c}{1+4\omega^2\tau_c{}^2}\right\} \tag{1.3}$$

The internuclear H-H distance in the H_2 ligand is obtained from T_1 minimum measurements using eq 1.4 (static model) or eq 1.5 (fast rotation model), where v is the operating frequency of the spectrometer in MHz.[18]

$$r_{HH} = 5.817\ \text{Å}\ s^{-1/3}\left(\frac{1}{R_{HH}\ v}\right)^{\frac{1}{6}} \tag{1.4}$$

$$r_{HH} = 4.617\ \text{Å}\ s^{-1/3}\left(\frac{1}{R_{HH}\ v}\right)^{\frac{1}{6}} \tag{1.5}$$

The choice of which rotation model to use for the determination of the H-H bond length should be fairly straightforward. However, the rotational barrier of the H_2 ligand in $W(H_2)(P^iPr_3)_2(CO)_3$ has been measured by inelastic neutron scattering and found to be lower (1.9–2.2 kcal mol^{-1}) than the barrier for molecular tumbling (2.6–3.8 kcal mol^{-1}).[21] When the fast rotation model is used for the determination of r_{HH}, unlikely distances of 0.76 and 0.77 Å are obtained[22] (the H-H bond length in H_2 gas is 0.74 Å). Gusev and coworkers[23] have recently examined the reported T_1 minimum data of dihydrogen complexes possessing short H-H bond lengths, determined by neutron, X-ray, or J_{HD} data, indicating that the H_2 ligand should have low barriers to rotation. The static model was found to provide reasonable H-H distances in most of these complexes not the fast rotation model as predicted.

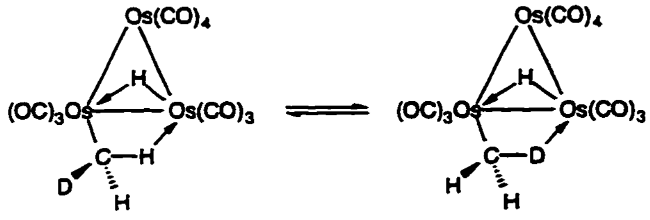
H-D Coupling (J_{HD}) in the Partially Deuterated Complexes. More definitive solution NMR evidence of a bound dihydrogen ligand is the observation of H-D coupling in the HD analogue. Typically, J_{HD} values range from 20–34 Hz in the coordinated HD ligand (HD gas has a J_{HD} value of 43.2 Hz[24]). In comparison, *cis*-dihydrides normally have J_{HD} values of less than 3 Hz.[25] Taube and coworkers[13] have prepared a series of dicationic H_2 complexes of the type $[Os(H_2)(en)_2L^z]^{(2+z)}$ (L^z = various neutral or anionic ligands; $z = 0$ or -1) with J_{HD} values of 3–21 Hz. Neutron diffraction data of $[Os(H_2)(en)_2(OAc)]^+$ (OAc = CH_3COO^-) support the existence of an elongated H-H bond (1.34 Å) in a complex with $J_{HD} = 8.1$ Hz.[26]

When the J_{HD} values of the HD complexes are plotted versus the most reliable r_{HH} values (corrected neutron diffraction and solid state NMR data) of the H_2 species a roughly inverse linear relationship is observed (eq 1.6).[27]

$$r_{HH} = 1.44 - 0.0168(J_{HD}) \tag{1.6}$$

This is in contrast with what is predicted for HD gas, where J_{HD} values *increase* with increases in r_{HH}.[28]

Isotopic Perturbation of Resonance. Partial substitution of deuterium into the H_2 ligand may result in the observation of temperature dependent isotope effects on the hydride resonance in the solution NMR spectra due to isotopic perturbation of resonance (IPR). Calvert and Shapley[29] used IPR to model a C•••H•••Os interaction in $HOs_3(CO)_{10}CH_3$. Upon deuteration, the solution NMR spectra show separate resonances for CH_2D and CHD_2 that are shifted significantly upfield from the CH_3 resonance and the isotope shifts, $\Delta\delta_1 = \delta_{CH_3} - \delta_{CH_2D}$ and $\Delta\delta_2 = \delta_{CH_2D} - \delta_{CHD_2}$, were found to have a strong temperature dependence. These observations are consistent with rapid dynamic averaging of two structures. In structure **A**, the deuterium in the methyl group is located in a terminal position. In structure **B**, the deuterium is located in the bridging position.

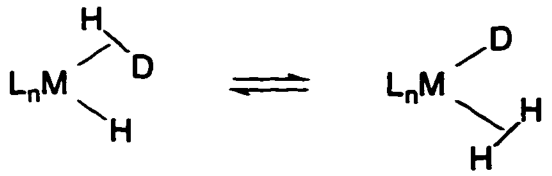


A **B**

The stretching force constant of the bridging C-H or C-D bond should be lower than the analogous noninteracting terminal C-H or C-D bond. The deuterium should therefore show a preference for the terminal position resulting in an observable temperature dependent isotope shift in the ^{1}H NMR spectrum. This is a manifestation of the non-statistical occupation of the bridging and terminal sites by deuterium.

This model can be adapted for dihydrogen complexes that are in equilibrium with a dihydride tautomer (eq 1.7) or polyhydride complexes that have a fluxional dihydrogen/hydride equilibrium process occurring (eq 1.8).

(1.7)



(1.8)

The observed chemical shift in the ^{1}H NMR spectrum of the dihydrogen complex in eq 1.7 would be a weighted average of the chemical shift of the H_2 resonance and the chemical shift of the hydride resonance. The partially deuterated complex should exhibit a temperature dependent isotope shift due to the slight perturbation of the equilibrium populations of the two tautomers. This equilibrium should also be manifested by temperature dependent J_{HD} values.

An example of a fluxional dihydrogen/hydride equilibrium as shown in eq 1.8 has recently been reported for the complex $[Ir(H_2)H(Tp)(PMe_3)]^+$ (Tp =

hydridotris(pyrazolyl)borate).[14] The ^{1}H NMR spectra of the partially deuterated complex exhibit large temperature dependent isotope shifts. The isotope shifts were found to vary from 228 to 149 ppb for $\Delta\delta_1 = \delta_{H_3} - \delta_{H_2D}$ and from 122 to 72 ppb for $\Delta\delta_2 = \delta_{H_2D} - \delta_{HD_2}$ over the temperature range 215–281 K. The H-D coupling of the monodeuterated complex also exhibited a temperature dependence which varied from 6.87 to 7.63 Hz over the same temperature range. The analysis of the data provided for the determination of limiting chemical shifts for the dihydrogen ligand and the terminal hydride, J_{HD} of the HD ligand, and the equilibrium constants for eq 1.8 and for the dideuterated species. The activation energy for the proton exchange was calculated to be $\Delta G^\ddagger \leq 5$ kcal mol^{-1}.

Organization of the Thesis. The preparation and reactivity of the monocationic hydrides, $[OsH(PR_3)_2(bpy)(CO)]^+$ ($PR_3 = PPh_3$, $PMePh_2$), $[OsH(PPh_3)_2(phen)(CO)]^+$, $[RuH(PPh_3)_2(bpy)(CO)]^+$ (bpy = 2,2'-bipyridine, phen = 1,10-phenanthroline), and the neutral precursors, $OsH(Cl)(PR_3)_3(CO)$ ($PR_3 = PPh_3$, $PMePh_2$) and $RuH(Cl)(PPh_3)_3(CO)$, along with the preparation of $[OsH(bpy)_2(CO)]^+$ are described in Chapter 2. The protonation of the monocationic hydrides to generate the dications, $[Os(H_2)(PR_3)_2(bpy)(CO)]^{2+}$ ($PR_3 = PPh_3$, $PMePh_2$), $[Os(H_2)(PPh_3)_2(phen)(CO)]^{2+}$, $[Ru(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$, and $[Os(H_2)(bpy)_2(CO)]^{2+}$ and a review of the known dicationic dihydrogen complexes are discussed in Chapter 3. The availability of high field NMR spectrometers (^{1}H: ≥ 500 MHz) allow the potential of observations of the effects caused by the partial alignment of H_2 complexes with the magnetic field. Chapter 4 investigates some manifestations caused by the effects of partial alignment of $[Os(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$ and $[Os(H_2)(PPh_3)_2(phen)(CO)]^{2+}$ with the magnetic field and implications concerning some reported anomalous behavior. The results of an investigation concerning a possible dihydrogen/dihydride equilibrium process occurring in the complexes by Taube and coworkers[13,26] are presented in Chapter 5.

Notes to Chapter 1.

1 Kubas, G. J.; Jarvinen, G. D.; Ryan, R. R. *J. Am. Chem. Soc.* **1983**, *105*, 1883.

2 Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451-452.

3 Zilm, K. W.; Millar, J. M. *Adv. Magn. Opt. Reson.* **1990**, *15*, 163-200.

4 (a) Hay, P. J. *Chem. Phys. Lett.* **1984**, *103*, 466-469. (b) Saillard, J.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006-2026. (c) Jean, Y.; Eisenstein, O.; Volatron, F.; Maouche, B.; Sefta, F. *J. Am. Chem. Soc.* **1986**, *108*, 6587-6592.

5 (a) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913-926. (b) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155-289. (c) Crabtree, R. H. *Accts. Chem. Res.* **1990**, *23*, 95-101. (d) Kubas, G. J. *Accts. Chem. Res.* **1988**, *21*, 120-128.

6 Gusev, D. G.; Notheis, J. U.; Rambo, J. R.; Hauger, B. E.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1994**, *116*, 7409-7410.

7 (a) Sabo-Etienne, S.; Chaudret, B.; el Makarim, H. A.; Barthelat, J.; Daudey, J.; Ulrich, S.; Limbach, H.; Moïse, C. *J. Am. Chem. Soc.* **1995**, *117*, 11602-11603. (b) Jalón, F. A.; Otero, A.; Manzano, B. R.; Villaseñor, E.; Chaudret, B. *J. Am. Chem. Soc.* **1995**, *117*, 10123-10124. (c) Gusev, D. G.; Kuznetsov, V. F.; Eremenko, I. L.; Berke, H. *J. Am. Chem. Soc.* **1993**, *115*, 5831-5832. (d) Neuner, B.; Schrock, R. R. *Organometallics* **1996**, *15*, 5-6. (e) Vigalok, A.; Ben-David, Y.; Milstein, D. *Organometallics* **1996**, *15*, 1839-1844.

8 Heinekey, D. M.; Schomber, B. M.; Radzewich, C. E. *J. Am. Chem. Soc.* **1994**, *116*, 4515-4516.

9 Heinekey, D. M.; Voges, M. H.; Barnhart, D. M. *J. Am. Chem. Soc.* **1996**, *118*, 10792-10802.

---

10 Heinekey, D. M.; Radzewich, C. E.; Voges, M. H.; Schomber, B. M. *J. Am. Chem. Soc.* **1997**, *119*, 4172-4181.

11 Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1990**, *112*, 2261-2263.

12 Li, Z.-W.; Taube, H. *J. Am. Chem. Soc.* **1991**, *113*, 8946-8947.

13 Li, Z.-W.; Taube, H. *J. Am. Chem. Soc.* **1994**, *116*, 9506-9513.

14 Heinekey, D. M.; Oldham, W. J., Jr. *J. Am. Chem. Soc.* **1994**, *116*, 3137-3138.

15 The "open" coordination site is more correctly described as an agostic interaction with a phosphine C–H bond.[10]

16 Bau, R.; Teller, R. G.; Kirtley, S. W.; Koetzle, T. F. *Accts. Chem. Res.* **1979**, *12*, 176-183.

17 Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126-4133.

18 Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173-4184.

19 (a) Woessner, D. E. *J. Chem. Phys.* **1962**, *36*, 1-4. (b) Woessner, D. E. *J. Chem. Phys.* **1962**, *37*, 647-654.

20 Bautista, M. T.; Earl, K. A.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T.; Sella, A. *J. Am. Chem. Soc.* **1988**, *110*, 7031-7036.

21 Kubas, G. J.; Nelson, J. E.; Bryan, J. C.; Eckert, J.; Wisniewski, L; Zilm, K. *Inorg. Chem.* **1994**, *33*, 2954-2960.

22 T_1 minimum values of 5.9 and 6.2 ms at 300 MHz in CD_2Cl_2 and toluene-d_8, respectively.

23 Gusev, D. G.; Kuhlman, R. L.; Renkema, K. B.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1996**, *35*, 6775-6783.

24 Evans, D. F. *Chem. Ind.* **1961**, 1960.

25 Heinekey, D. M.; Hinkle, A. S.; Close, J. D. *J. Am. Chem. Soc.* **1996**, *118*, 5353-5361.

26 Hasegawa, T.; Li, Z.-W.; Parkin, S.; Hope, H.; McMullan, R. K.; Koetzle, T. F.; Taube, H. *J. Am. Chem. Soc.* **1994**, *116*, 4352-5356.

27 Heinekey, D. M.; Luther, T. A. *Inorg. Chem.* **1996**, *35*, 4396-4399.

28 Jameson, C. J.; Osten, H.-J. *J. Am. Chem. Soc.* **1986**, *108*, 2497-2503.

29 Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726-7727.

Chapter 2

Synthesis, Characterization, and Reactivity of Neutral and Monocationic Hydrides of Osmium and Ruthenium

Introduction

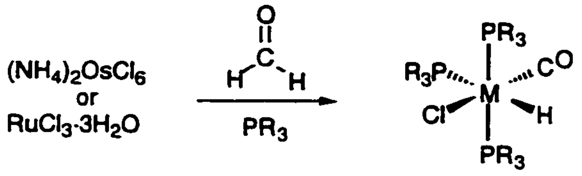
The protonation of a neutral transition metal hydride resulting in the formation of a cationic dihydrogen complex was first reported by Crabtree and Lavin in 1985.[1] Since that time, numerous research groups have utilized this methodology as a synthetic tool for the preparation of transition metal dihydrogen complexes.[2] However, the preparation of the only known dicationic dihydrogen complexes involved the reduction of osmium(III) and osmium(IV) dications under acidic conditions.[3]

We have found that dicationic dihydrogen complexes could be prepared by the protonation of monohydride cations of osmium(II) and ruthenium(II). The preparation of the monocationic hydrides followed the synthetic route developed by Uttley and Robinson and coworkers[4] to generate neutral carbonyl trisphosphine hydride complexes $MH(Cl)(PR_3)_3(CO)$ ($M = Os$, $PR_3 = PPh_3$, $PMePh_2$ (**1a,b**); $M = Ru$, $PR_3 = PPh_3$ (**4a**)). The catalytic activity of these complexes and related compounds has been studied and reported elsewhere.[5] These neutral complexes react with a chelating ligand to produce the desired monocationic hydrides $[MH(PR_3)_2(N\text{-}N)(CO)]^+$ ($M = Os$, $PR_3 = PPh_3$, $PMePh_2$, N-N = bpy (**2a,b**); $M = Os$, $PR_3 = PPh_3$, N-N = phen (**9a**); $M = Ru$, $PR_3 = PPh_3$, N-N = bpy (**5a**)) (bpy = 2,2'-bipyridine, phen = 1,10-phenanthroline).

This chapter will cover the preparation and some of the reactivity of the neutral carbonyl trisphosphine hydrides and the monocationic hydrides that will be used in protonation reactions to produce dihydrogen dications (Chapter 3). The preparation of a related compound $[OsH(bpy)_2(CO)]^+$ will also be discussed.

Results and Discussion

Synthesis and Characterization of the Neutral Hydrides: MH(Cl)(PR$_3$)$_3$(CO) [M = Os, PR$_3$ = PPh$_3$, PMePh$_2$ (1a,b); M = Ru, PR$_3$ = PPh$_3$ (4a)]. The synthetic procedure developed by Robinson and coworkers to prepare triphenylphosphine complexes of ruthenium and osmium serves as a useful method for the preparation of a series of neutral carbonyl trisphosphine hydrides (Scheme 2.1).[4]



M = Os, PR$_3$ = PPh$_3$, PMePh$_2$ **(1a,b)**
M = Ru, PR$_3$ = PPh$_3$ **(4a)**

Scheme 2.1

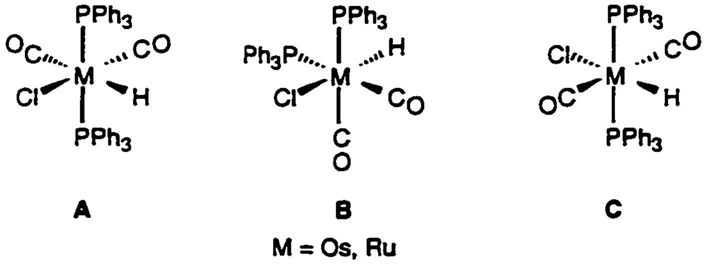
The general procedure requires the addition, in rapid succession, of a 2-methoxyethanol solution of the metal halide followed by the addition of aqueous formaldehyde to a boiling solution of excess triphenylphosphine in 2-methoxyethanol. The manner in which the reagents are added is the critical factor in the synthesis, if the addition is not carried out properly, an insoluble precipitate forms instead of the desired product. The triphenylphosphine products are generally insoluble in 2-methoxyethanol and will precipitate quickly out of solution as they are formed or when the reaction mixture is cooled to room temperature. This technique allows for a one-pot synthesis with short reaction times and high yields of the products without need of further purification.

The hydride region of the ^{1}H NMR spectrum recorded at room temperature of the osmium complex OsH(Cl)(PPh$_3$)$_3$(CO) (**1a**) shows a doublet of triplets (J_{HPcis} = 24.7 Hz, $J_{HPtrans}$ = 86.3 Hz) centered at δ -6.95. The ^{31}P{aromatic ^{1}H} NMR spectrum of **1a** exhibits a doublet of doublets at δ +7.83 (J_{PHcis} = 22 Hz, J_{PP} = 11 Hz) and a doublet of triplets δ -9.14 ($J_{PHtrans}$ = 76 Hz, J_{PP} = 11 Hz) in a 2:1 ratio, consistent with two equivalent phosphine ligands *trans* to each other and a third phosphine ligand *trans* to the hydride ligand. The ^1H and $^{31}P\{$aromatic $^1H\}$ NMR spectra are consistent with the structure shown in Scheme 2.1. The structure of **1a** has also been confirmed by X-ray crystallography.[6]

The ^1H and $^{31}P\{$aromatic $^1H\}$ NMR spectra at room temperature of the ruthenium analogue, $RuH(Cl)(PPh_3)_3(CO)$ (**4a**), indicate a dynamic system. The coupling in the hydride resonance in the ^1H NMR spectrum is unresolved. However, the resonances in the $^{31}P\{$aromatic $^1H\}$ NMR spectrum exhibit couplings to the hydride ligand but the coupling to each other is not resolvable. When the temperature is lowered to 5 °C, the spectra of **4a** is consistent with a static structure, similar to **1a**. The hydride resonance in the ^1H NMR spectrum recorded at 5 °C is a doublet of triplets centered at δ -7.18 ($J_{HPtrans}$ = 104.1 Hz, J_{HPcis} = 24.0 Hz). The $^{31}P\{$aromatic $^1H\}$ NMR spectrum at this temperature exhibits two resonances, a doublet of doublets at δ +40.3 (J_{PHcis} = 23 Hz, J_{PP} = 15 Hz) and a doublet of triplets at δ +12.8 ($J_{PHtrans}$ = 103 Hz, J_{PP} = 15 Hz).

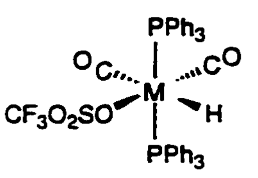
The previously unknown analogue $OsH(Cl)(PMePh_2)_3(CO)$ (**1b**) was prepared following the same synthetic procedure as **1a** and **4a**, substituting methyldiphenylphosphine for triphenylphosphine. The increased solubility of **1b** in 2-methoxyethanol resulted in the complex not precipitating when the reaction mixture cooled to room temperature. However, precipitation did occur when the solvent volume was reduced. The hydride region of the ^1H NMR spectrum exhibits a doublet of triplets at δ -6.45 (J_{HPcis} = 22.2 Hz, $J_{HPtrans}$ = 85.3 Hz). The $^{31}P\{^1H\}$ NMR spectrum shows two resonances, a doublet at δ -20.1 (J_{PP} = 13 Hz) and a second doublet at δ -23.3 (J_{PP} = 13 Hz).

Reactivity of $MH(Cl)(PPh_3)_3(CO)$ [M = Os, Ru (1a, 4a)]. When solutions of **1a** and **4a** are exposed to CO at room temperature, the labile phosphine *trans* to the hydride is displaced[5a] and new complexes are observed by NMR. The NMR data is consistent with the complexes formulated as $MH(Cl)(PPh_3)_2(CO)_2$ (M = Os, Ru). The ^1H NMR spectrum for the new osmium species shows a triplet in the hydride region at δ -3.63 with a J_{HP} value of 20.2 Hz. The $^{31}P\{aromatic\ ^1H\}$ NMR spectrum exhibits a doublet at δ +8.97 with a J_{PH} value of 19 Hz and a resonance for "free" triphenylphosphine at δ -4.98. The ^1H NMR spectrum recorded in benzene-d_6 for the new ruthenium complex shows a triplet in the hydride region at δ -3.89 with a J_{HP} value 19.2 Hz. The $^{31}P\{aromatic\ ^1H\}$ NMR spectrum exhibits a doublet at δ +39.8 with a J_{PH} value of 16 Hz and also a resonance for "free" triphenylphosphine at δ -4.69. The NMR spectra indicate equivalent phosphines. Three reasonable structures for these complexes that can be envisioned are shown below.

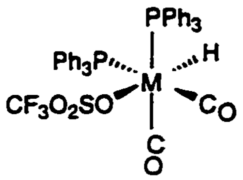


Previously reported infrared data[7] along with the NMR spectra support the assignment of the ruthenium species as the structure shown for **B**. The similarity of the NMR spectra suggest that the osmium analogue has the same stereochemistry.

When silver triflate (AgOTf) is added to solutions of these new species under a CO atmosphere, or to solutions of **1a** and **4a** under a CO atmosphere, the ^1H and ^{31}P NMR spectra show new resonances that are consistent with new complexes resulting from the abstraction of chloride. The ^1H NMR spectrum of the osmium species exhibits a triplet resonance at δ -4.70 with J_{HP} = 14.8 Hz. The $^{31}P\{aromatic\ ^1H\}$ NMR spectrum shows a doublet at δ +4.56 with J_{PH} = 12 Hz. The ^1H and $^{31}P\{aromatic\ ^1H\}$ NMR spectra of the ruthenium reaction indicate that two species are formed in *ca.* 3:1 ratio. The ^1H NMR spectrum in the hydride region exhibits two triplets with the major resonance at δ -3.29 with J_{HP} = 18.5 Hz and the minor resonance at δ -4.43 with J_{HP} = 17.5 Hz. The ^{31}P{aromatic ^{1}H} NMR spectrum shows two resonances, the major resonance as a doublet at δ +41.08 with J_{PH} = 15 Hz and a minor broad resonance at δ +14.41 with no observable coupling.



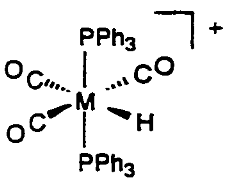
D



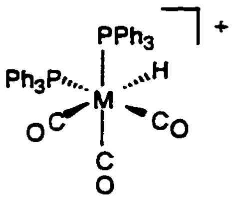
E

M = Os, Ru

Since only a small change is observed in the chemical shift of the resonance in the ^{31}P NMR spectra of the osmium complex and the major ruthenium species the most likely possibility is a new neutral complex. The possible structures that can be reasonably proposed are **D** and **E** resulting from the abstraction of chloride and subsequent coordination of the triflate anion to form a metal triflate species. A larger change in the ^{31}P NMR chemical shifts would be expected from this reaction if a cationic species was generated (structures **F** and **G**).



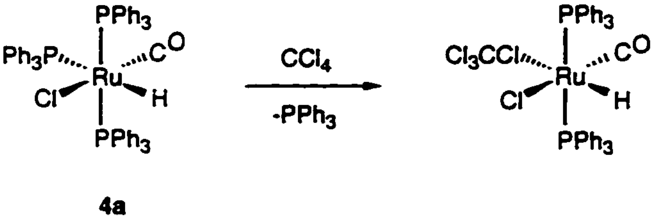
F



G

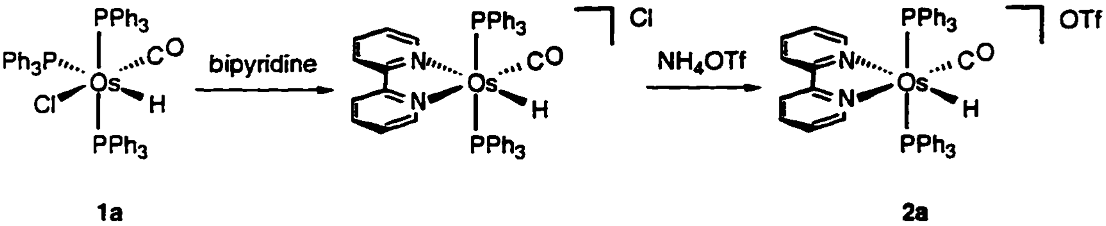
The minor resonance in the ^{31}P NMR spectrum of the ruthenium reaction would be consistent with this reasoning.

When CCl_4 was added to a methylene chloride-d_2 solution of **4a**, the ^{31}P{aromatic ^{1}H} NMR spectrum shows a singlet resonance growing in at δ +28.09. After a day this becomes the major resonance with a dozen minor resonances (combining for ≈ 10% of the intensity of the major resonance) in the ^{31}P NMR spectrum. The hydride region of the ^{1}H NMR spectrum originally exhibits a minor new triplet resonance appearing at δ -4.49 with a J_{HP} value of 19.0 Hz. After a day, there are no observable signals in the hydride region of the spectrum. This new hydride resonance is consistent with initial loss of phosphine followed by coordination of CCl_4 occurring before the hydride abstraction (Scheme 2.2).



Scheme 2.2

Synthesis and Characterization of the Monocationic Bisphosphine Hydrides: $[MH(PR_3)_2(N\text{-}N)(CO)]^+$ [M = Os, PR_3 = PPh_3, $PMePh_2$, N-N = bpy (2a,b); M = Ru, PR_3 = PPh_3, N-N = bpy (5a); M = Os, PR_3 = PPh_3, N-N = phen (9a)]. The monocationic hydrides were prepared as the triflate salts as outlined in Scheme 2.3 for the synthesis of $[OsH(PPh_3)_2(bpy)(CO)](OTf)$ (**2a**). Meyer and coworkers[8] previously reported the synthesis of **2a**(PF_6) using ammonium hexafluorophosphate to precipitate the cationic hydride complex. The ^{1}H and ^{31}P{aromatic ^{1}H} NMR spectra indicate that the triflate and hexafluorophosphate anions have no observable effect on the structure of the cation.



Scheme 2.3

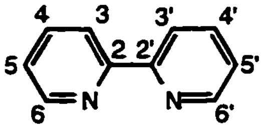
As described earlier, the phosphine ligand *trans* to the hydride ligand in **1a** is labile and therefore it can be substituted with a variety of chelating ligands. The neutral osmium hydride **1a** and bipyridine are heated in ethylene glycol at reflux for 15 min or 2-methoxyethanol for 1 h. The displaced chloride anion is exchanged for a triflate or hexafluorophosphate anion using the appropriate ammonium salt. The desired complex precipitates as a yellow solid with the ammonium chloride remaining in solution. When an excess of bipyridine is used and with longer reaction times (greater than 1 week), the NMR spectra indicate that **2a** is still the only product formed. The ^{1}H NMR spectrum of **2a** exhibits eight resonances in the aromatic region for the bipyridyl protons, a narrow region of triphenylphosphine aromatic protons and a well resolved triplet in the hydride region at δ -12.19 with a J_{HP} = 18.4 Hz. The ^{31}P{aromatic ^{1}H} NMR spectrum shows a single doublet resonance at δ +18.76 with a J_{PH} = 17 Hz. The NMR spectra are consistent with two equivalent *trans* phosphines and a bipyridyl ligand with eight inequivalent protons as depicted in Scheme 2.3. The complexes **2b**, **5a** and **9a**, were prepared in this manner, and exhibit similar ^{1}H and ^{31}P{aromatic ^{1}H} NMR spectra (Table 2.1).

Table 2.1. Comparison of the NMR Data of the Hydride Bisphosphine Monocation Complexes.[a]

compound		^{1}H δ_H (ppm)	J_{HP} (Hz)[b]	^{31}P δ (ppm)
$[OsH(PPh_3)_2(bpy)(CO)]^+$	**(2a)**	-12.19	18.4	+18.76
$[OsH(PMePh_2)_2(bpy)(CO)]^+$	**(2b)**	-12.22	17.6	+0.08
$[OsH(PPh_3)_2(phen)(CO)]^+$	**(9a)**	-11.98	18.1	+19.25
$[RuH(PPh_3)_2(bpy)(CO)]^+$	**(5a)**	-11.31	19.6	+46.53

[a] In methylene chloride-d_2. [b] ^{1}H NMR data.

T. J. Meyer and coworkers synthesized a series of dimethylbipyridyl derivatives of **2a**(PF_6) to compare by ^1H NMR spectroscopy with the parent complex that enabled the assignment of the proton resonances of the bipyridyl ligand.[8] The numbering scheme for the bipyridyl ligand is depicted in the following figure:



The assignment of the bipyridyl proton resonances of $[OsH(PPh_3)_2(bpy)(CO)]^+$ (**2a**) are shown in Figure 2.1. Examination of the chemical shifts of the proton resonances of the bipyridyl ligand show that the individual protons of the 3,3' and 4,4' pairs experience very similar magnetic environments while the resonances of the 5,5' and 6,6' pairs are more widely split, 0.67 ppm and 1.08 ppm, respectively. The 6,6' proton pair is situated such that one proton is directed into the carbonyl ligand causing an upfield shift while the other one is directed at the hydride ligand. Similarly, the 5,5' pair has one proton-carbon bond of the pair roughly parallel to the CO ligand resulting in less shielding than the other accounting for the split in the chemical shifts. The ^1H NMR spectrum of $[RuH(PPh_3)_2(bpy)(CO)]^+$ (**5a**) is shown in Figure 2.2 that shows that the similarity of the complexes allow the same proton assignments to be made for the bipyridyl proton resonances in **5a**.

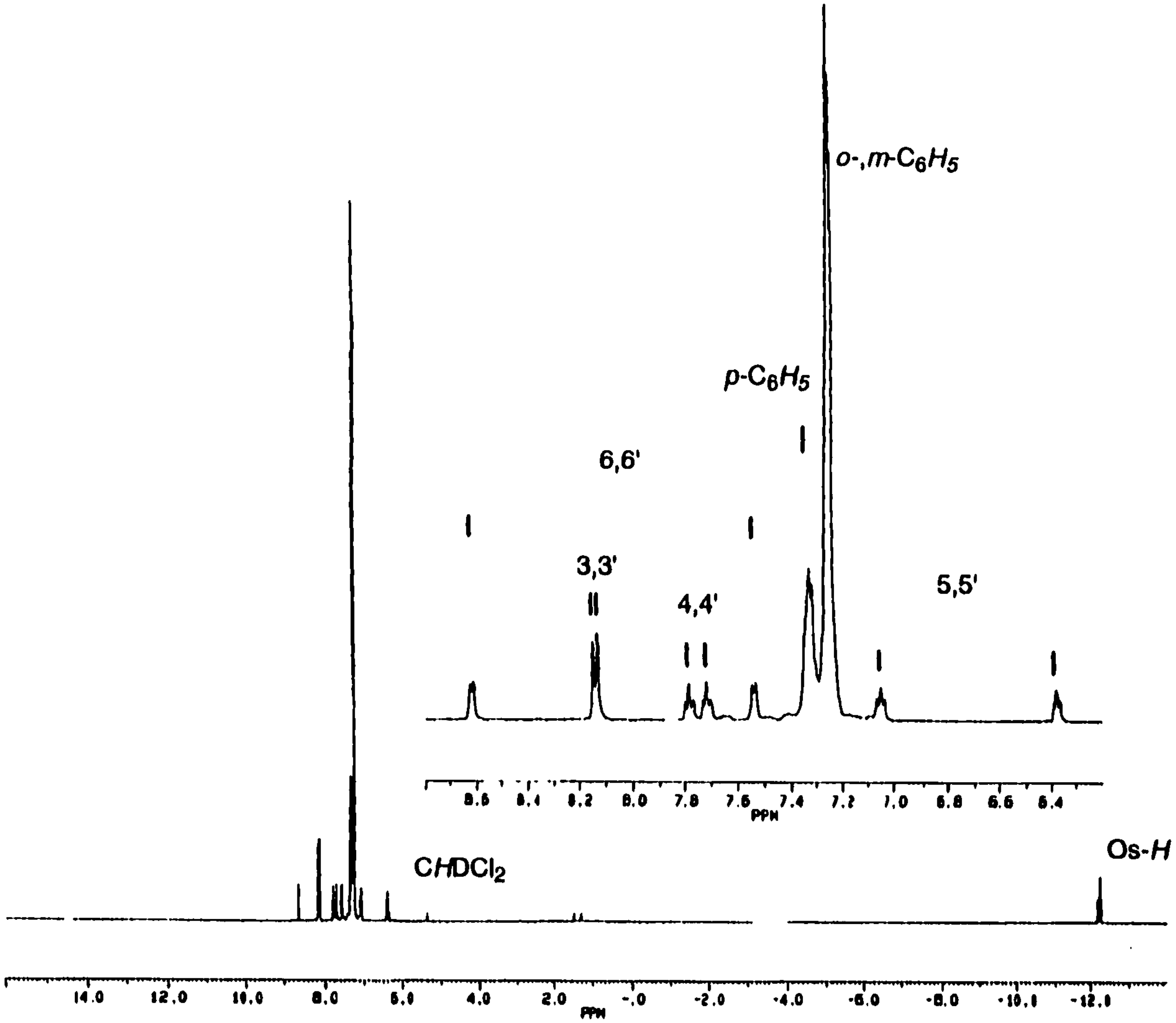


Figure 2.1. ^{1}H NMR spectrum of $[OsH(PPh_3)_2(bpy)(CO)]^+$ (**2a**) (500 MHz, CD_2Cl_2).

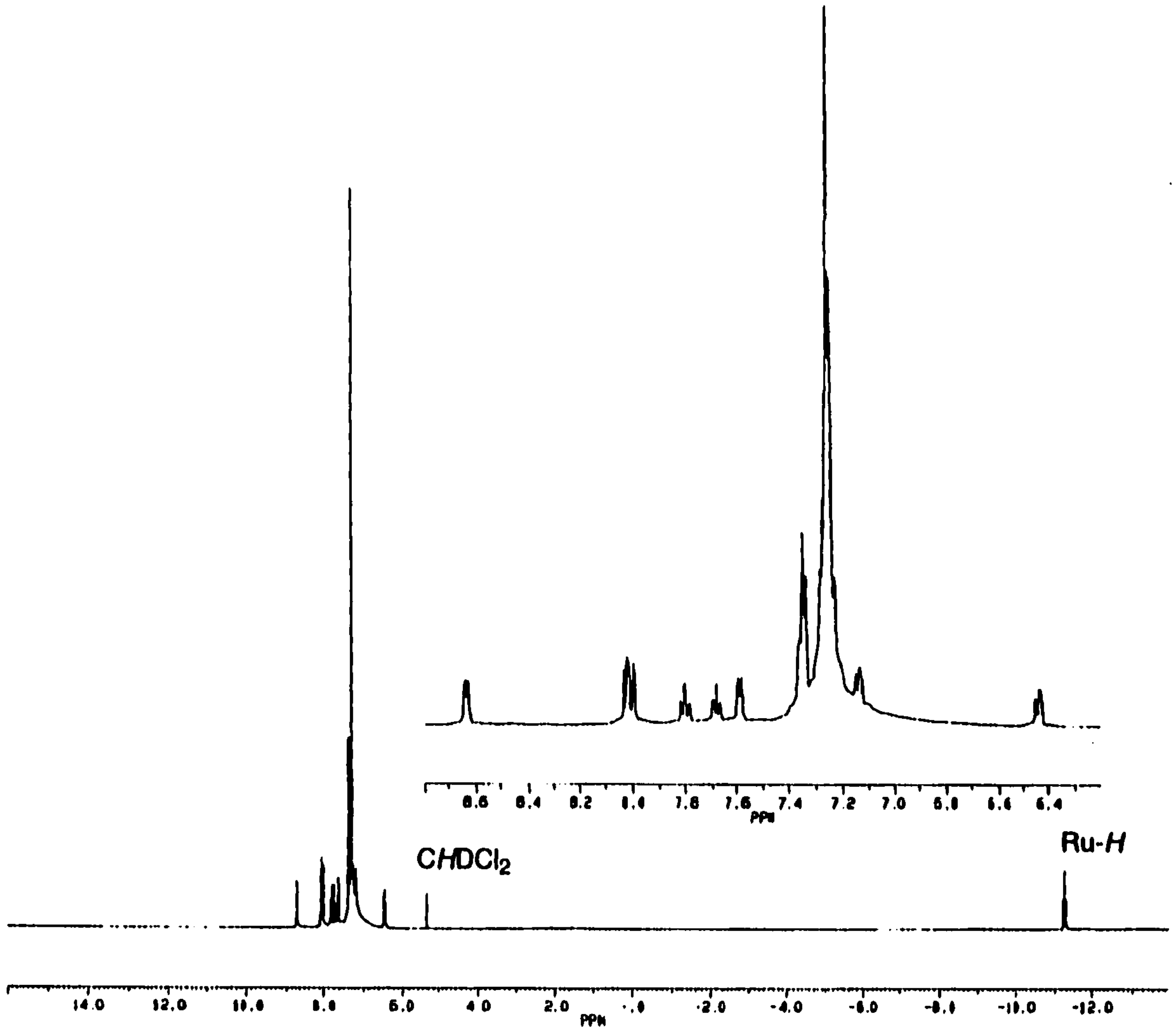


Figure 2.2. ^{1}H NMR spectrum of $[RuH(PPh_3)_2(bpy)(CO)]^+$ (**5a**) (500 MHz, CD_2Cl_2).

Structural Assignment of $[RuH(PPh_3)_2(bpy)(CO)]^+$ (5a) with $^1H,^{13}C$ HETCOR NMR. The assignment of the bipyridyl proton resonances allow for a $^1H,^{13}C$ HETCOR NMR experiment to assign the corresponding carbon resonances (Figure 2.3). The ten inequivalent ^{13}C resonances of the bipyridyl ligand in the $^{13}C\{^1H\}$ NMR spectrum along with the ^{13}C resonances in the phosphine ligands and the carbonyl can now be assigned and are shown in Figure 2.4. Inspection of the ^{13}C chemical shifts show the difference that exists in the magnetic environments for the proton 6,6' pair is also observed in the $^{13}C\{^1H\}$ NMR spectrum. Since the $^1H,^{13}C$ HETCOR NMR spectrum shows resonances for carbons that are coupled to protons, the resonances for the 2,2' carbons of the bipyridyl ligand along with the *ipso*-carbons of the phenyl groups in the phosphine ligands do not appear.

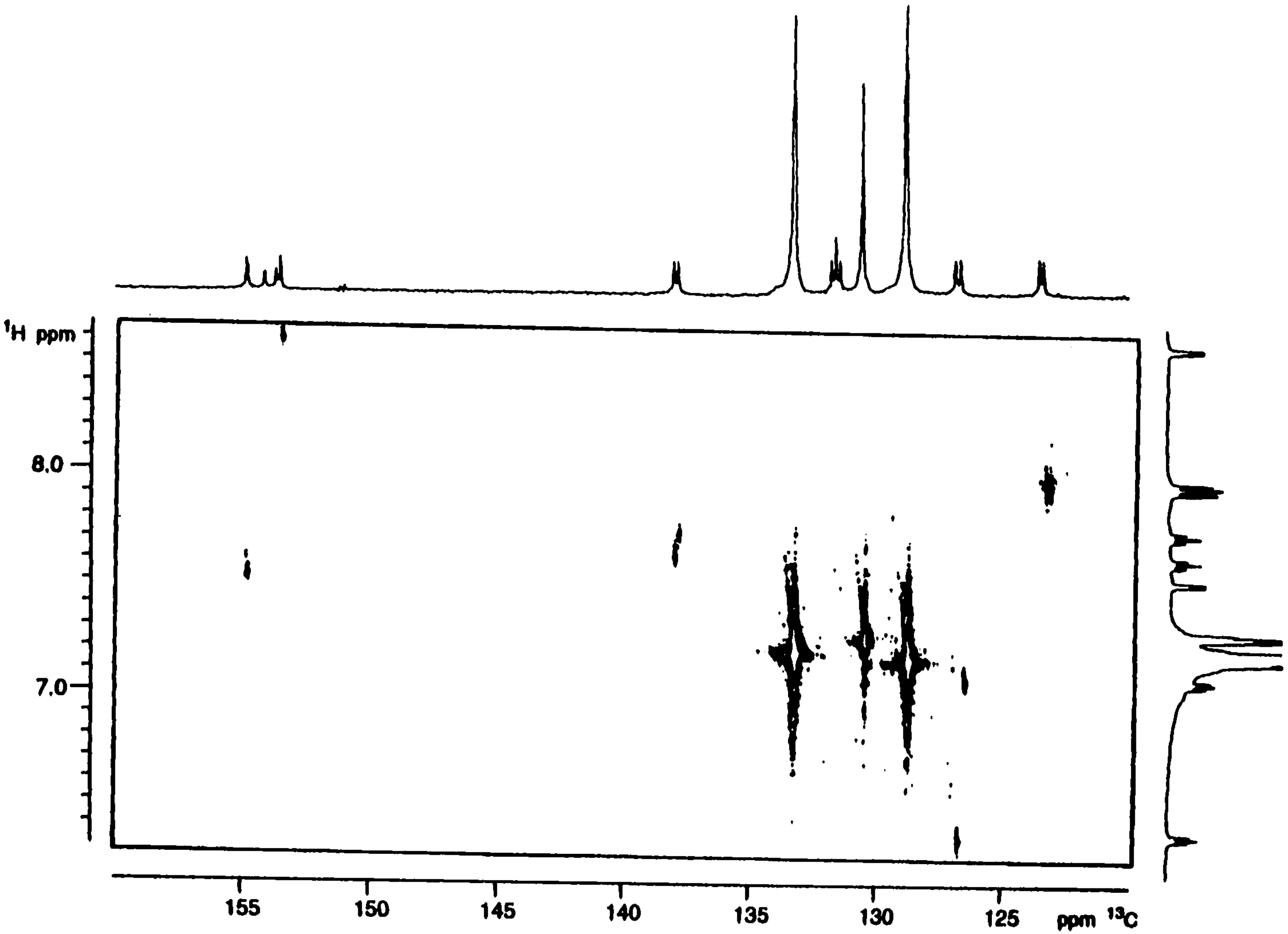


Figure 2.3. $^{1}H,^{13}C$ HETCOR NMR spectrum of $[RuH(PPh_3)_2(bpy)(CO)]^+$ (**5a**) (CD_2Cl_2).

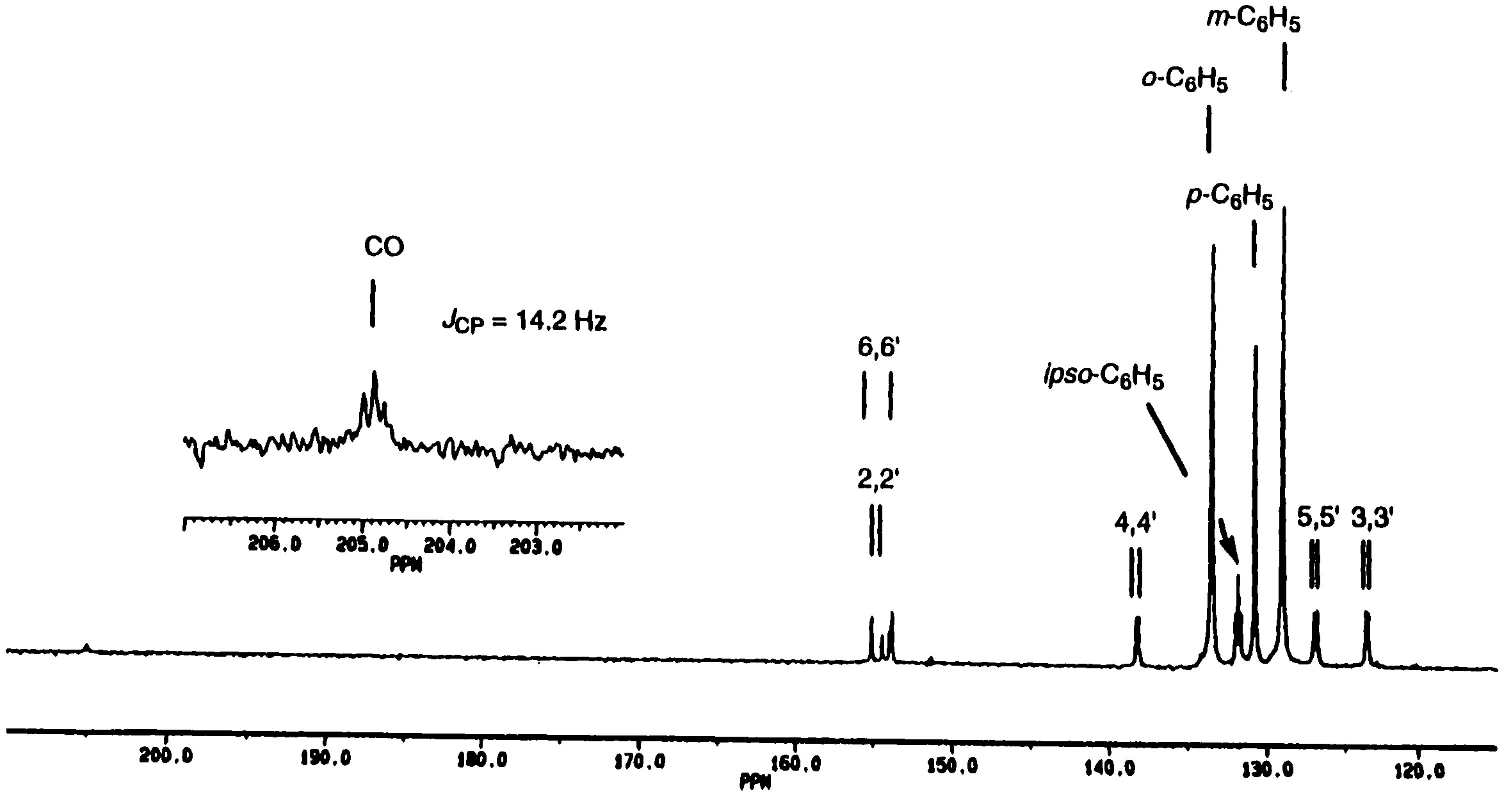
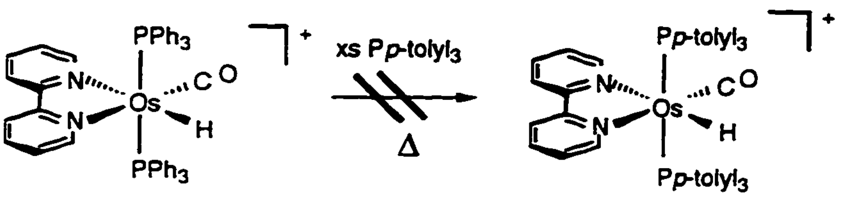


Figure 2.4. $^{13}C\{^1H\}$ NMR spectrum of $[RuH(PPh_3)_2(bpy)(CO)]^+$ (**5a**) (125 MHz, CD_2Cl_2).

Reactivity of $[MH(PPh_3)_2(bpy)(CO)]^+$ [M = Os, Ru (2a, 5a)]. The reactivity of the complexes **2a** and **5a** was examined to determine the feasibility of a ligand exchange that could lead to a change in the electronic or steric character of the complex. It was hoped that the substitution of the phosphine ligands or the displacement of the carbonyl ligand would provide a route to create changes in the basicity of the complex.

A two and a half-fold excess of tri-*p*-tolylphosphine was added to **2a** and monitored by ^1H and ^{31}P NMR spectroscopy. The added phosphine, due to its increased basicity, was expected to replace the triphenylphosphine ligands in **2a** (Scheme 2.4).



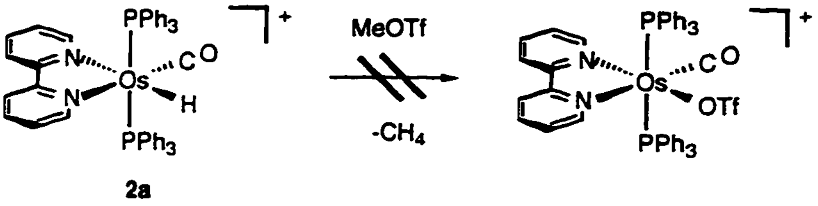
2a

Scheme 2.4

No effect was observed when the sample was kept at room temperature for several days. The sample was heated at 55 °C and over the course of a month, only the apparent decomposition of the tri-*p*-tolylphosphine was evident by NMR.

The displacement of a coordinated carbonyl ligand under the proper conditions can result in the coordination of a more desired ligand. Gladysz and coworkers[9] used this methodology for the preparation of $[ReCp(NO)(PPh_3)_2]^+$. They reported $[ReCp(NO)(PPh_3)(CO)]^+$ was treated with $(CH_3)_3NO$ in the presence of PPh_3 to generate the desired product as a result of loss of CO_2 and coordination of PPh_3. Another method for displacement of a coordinated CO ligand is with hydroxide ion. This methodology primarily works when the carbonyl ligand is strongly activated towards nucleophilic attack as noted by Graham and Sweet[10] in the generation of $ReHCp^*(NO)(CO)$ from $[ReCp^*(NO)(CO)_2]^+$ treated with OH^-. Oxygen atom donors, pyridine-*N*-oxide (C_5H_5NO) and trimethylamine-*N*-oxide ($(CH_3)_3NO$), were reacted with **2a** in acetonitrile in an attempt to displace the carbonyl ligand by forming carbon dioxide followed by coordination of a solvent molecule. The IR stretching frequency of the CO ligand in **2a** is 1923 cm^{-1}. The low frequency is an indication that the carbon does not have a large partial positive charge and nucleophilic attack at the carbonyl is not likely to occur. The ^{1}H and ^{31}P NMR spectra indicated that no new products were formed when **2a** was treated with $(CH_3)_3NO$ or C_5H_5NO.

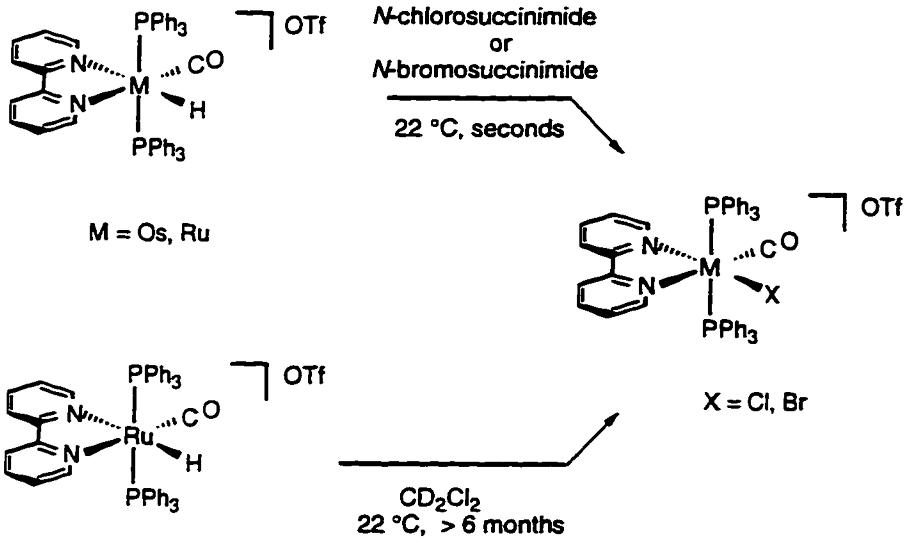
The methylating agent, methyl triflate (MeOTf) was added to a solution of **2a** with the expectation that loss of methane would lead to the triflate cation, $[Os(OTf)(PPh_3)_2(bpy)(CO)]^+$ (Scheme 2.5).



Scheme 2.5

No reaction was observed by NMR spectroscopy after two weeks at room temperature. The sample was heated to 55 °C and monitored by NMR for a period of two months. The ^{1}H and ^{31}P{aromatic ^{1}H} NMR spectra indicate that essentially no reaction occurred. However, when MeOTf was added to a solution of $[RuH(PPh_3)_2(bpy)(CO)]^+$ (**5a**) and heated at 45 °C for two weeks, new resonances were observed in the ^{1}H and ^{31}P{aromatic ^{1}H} NMR spectra. The ^{31}P{aromatic ^{1}H} NMR spectrum reveals two new resonances at δ +46.49 and +21.76 appearing in equal intensity as the resonance for **5a** decreases, indicating two new species are being formed at the expense of the monohydride cation. The identity of one of these new resonances (δ +21.76) has been confirmed as the methylphosphonium cation, $MePPh_3^+$. The other resonance is a singlet that corresponds to an unidentified new ruthenium complex with only one phosphine ligand and no hydride ligand. The ^{1}H NMR spectrum indicates that the expected product of the methylation, methane, is only formed in a trace amount along with a minor amount of triflic acid.

The preparation of the chloride cation analogues of **2a** and **5a**, $[OsCl(PPh_3)_2(bpy)(CO)]^+$ and $[RuCl(PPh_3)_2(bpy)(CO)]^+$, were of interest to explore a possible route for the isolation of the dihydrogen dication complexes $[Os(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$ (**3a**) and $[Ru(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$ (**6a**) (Chapter 3). Meyer and coworkers developed a synthetic route to the chloride cation derivative of **2a** that involves pyrolyzing an acidic mixture of the osmium halide and bipyridine to produce $Os(bpy)Cl_4$. Reduction of this species with triphenylphosphine under a CO atmosphere finally generates the cationic chloride $[OsCl(PPh_3)_2(bpy)(CO)]^+$. A simpler, more direct synthetic route was desired. The addition of carbon tetrachloride to a metal hydride is normally a useful technique to confirm its presence resulting in the formation of a metal chloride.[11] The generation of the metal chloride is proposed to occur by electron transfer from the CCl_4 to the metal hydride forming a radical pair and quickly followed by chlorine atom transfer and hydride abstraction producing a metal chloride species and chloroform. Unfortunately, when CCl_4 is added to a solution of **2a** no reaction occurs even after heating at 55 °C for a period of two months. However, when CCl_4 is added to a solution of **5a** and heated gently (45 °C), the resonance for the chloride cation $[RuCl(PPh_3)_2(bpy)(CO)]^+$ is observable by $^{31}P\{aromatic\ ^1H\}$ NMR in a minor amount. After a couple of weeks several other unidentified resonances begin to appear. A second route involving the reaction of the precursor **4a** with CCl_4 was explored due to the more labile ligands in this complex that may be utilize to develop a route to the chloride cation. The addition of CCl_4 to **4a**, even though the hydride ligand was replaced, did not cleanly produce a single product to react with bipyridine to generate the desired chloride cation. However, when *N*-chlorosuccinimide (NCS) is added to solutions of **2a** and **5a** as a chlorine atom donor, succinimide is generated along with a single new complex that is formed cleanly and quantitatively by NMR. The aromatic region in the ^1H NMR spectra for these complexes exhibit the expected eight resonances for the inequivalent bipyridyl protons and a narrow band for the triphenylphosphine protons and are now lacking observable resonances in the hydride region. The $^{31}P\{aromatic\ ^1H\}$ NMR spectra reveal only a singlet resonance, δ -1.17 for the osmium complex and at δ +27.39 for the ruthenium analogue. The NMR spectra are consistent with the formulation of these complexes as $[OsCl(PPh_3)_2(bpy)(CO)]^+$ and $[RuCl(PPh_3)_2(bpy)(CO)]^+$ (Scheme 2.6). The complex **2a** was also reacted with *N*-bromosuccinimide (NBS) with similar results, the generation of succinimide and a single new complex characterized as $[OsBr(PPh_3)_2(bpy)(CO)]^+$. The ^1H and $^{31}P\{aromatic\ ^1H\}$ NMR spectra for this species are very similar to the others with a singlet resonance at δ -1.97 in the $^{31}P\{aromatic\ ^1H\}$ NMR spectrum.

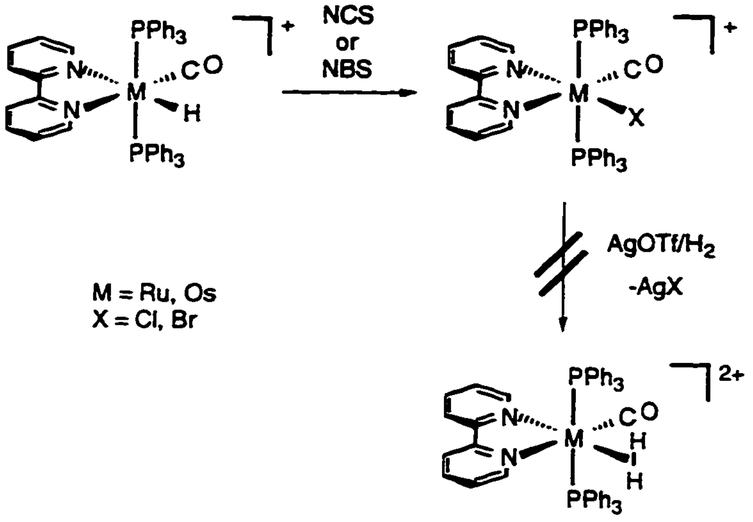


5a

Scheme 2.6

$[RuCl(PPh_3)_2(bpy)(CO)]^+$ was also found to be formed when a methylene chloride-*d*$_2$ solution of **5a** was allowed to stand at room temperature for an extended period (Scheme 2.6). After six months the concentration of the chloride cation is approximately the same as the concentration of **5a** as determined by the intensity of the resonances in the ^{31}P\{aromatic ^{1}H\} NMR spectrum.

A solution of the ruthenium chloride cation $[RuCl(PPh_3)_2(bpy)(CO)]^+$ was reacted with silver triflate (AgOTf) under an hydrogen atmosphere in an attempt to produce the dicationic dihydrogen complex $[Ru(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$ (**6a**) as shown in Scheme 2.7.



Scheme 2.7

The NMR spectra confirmed that a reaction occurred and a new complex was formed. The ^{31}P\{aromatic ^{1}H\} NMR spectrum exhibits a new resonance at δ +15.7 with no observable resonance for the expected dihydrogen species (at δ +32.8). After 24 h this resonance decreased in intensity and several new unidentified resonances emerged. Since the observed trend in the iron triad is that the ruthenium compounds are found to be less stable to H_2 loss than the iron or osmium analogues, the cationic osmium chloride and bromide complexes were also reacted with AgOTf and H_2. No changes were observed in the ^{31}P\{aromatic ^{1}H\} NMR spectra for these reactions.

Correlation time for $[RuH(PPh_3)_2(bpy)(CO)]^+$ (5a). The observed rate of relaxation for a proton is given by eq 2.1 (also discussed in Chapters 1 and 4).[12]

$$R_{HH} = T_1^{-1} = \frac{3\gamma_H^4 \hbar^2}{20\pi r_{HH}^6} \left\{ \frac{\tau_c}{1+\omega^2\tau_c^2} + \frac{4\tau_c}{1+4\omega^2\tau_c^2} \right\} \tag{2.1}$$

The first derivative of eq 2.1 with respect to τ_c yields the maximum rate of relaxation, which will occur when $\omega\tau_c = 0.6158$. The Larmor frequency is directly proportional to the strength of the magnetic field, $\omega = \gamma_H B_o$, therefore the maximum rate of relaxation (minimum value of T_1) is expected to occur at higher temperatures with increases in magnetic fields and the T_1 minimum value will also increase in direct proportion with an increase in field.

Assuming the rate of relaxation of the resonance in the ^{31}P NMR spectrum is primarily due to the ^{31}P-^{1}H heteroatom-proton dipole interaction, the relaxation rate (R_{HP}) is given by eq 2.2.[12]

$$R_{HP} = \frac{\gamma_H^2 \gamma_P^2 \hbar^2}{15\pi r_{HP}^6} S(S+1) \left\{ \frac{\tau_c}{1+\tau_c^2\omega_-^2} + \frac{3\tau_c}{1+\tau_c^2\omega_H^2} + \frac{6\tau_c}{1+\tau_c^2\omega_+^2} \right\} \tag{2.2}$$

Where γ_P is the gyromagnetic ratio of the phosphorus nuclei, S is the nuclear spin state (^{31}P: $S = 1/2$), and ω_- and ω_+ are defined as $\omega_H - \omega_P$ and $\omega_H + \omega_P$, respectively. By differentiating eq 2.2 with respect to τ_c and setting $\partial R_{HP}/\partial\tau_c = 0$, the value of $\omega_P\tau_c$ is found to be equal to 0.7202.[12] In a magnetic field of 11.75 T (^{31}P: 202 MHz), ω_P is 1.27×10^{-9} s^{-1} and the minimum value of τ_c will be 5.66×10^{-10} s.

The measurement of the T_1 minimum of the hydride resonance in different fields and the T_1 minimum of the phosphorus resonance provide the temperature dependence of τ_c for $[RuH(PPh_3)_2(bpy)(CO)]^+$ (**5a**). Since an Arrhenius equation can be written as $\tau_c^{-1} = Ae^{-E_a/RT}$, the activation parameters of the correlation time of the molecule can be determined by plotting $-\ln(\tau_c)$ versus $1/T$, where T is the temperature of the T_1 minimum in K (Figure 2.5). The activation parameters derived from the linear relationship are A = 2.5 (±0.9) × 10^{11} s and E_a = 2.0 (±0.2) kcal/mol. The range of possible temperatures for the τ_c minimum for the ^{31}P 202 MHz (±5 °C) and the ^{1}H 200 MHz (±4 °C) data provide a rough estimate of the error in the activation parameters.

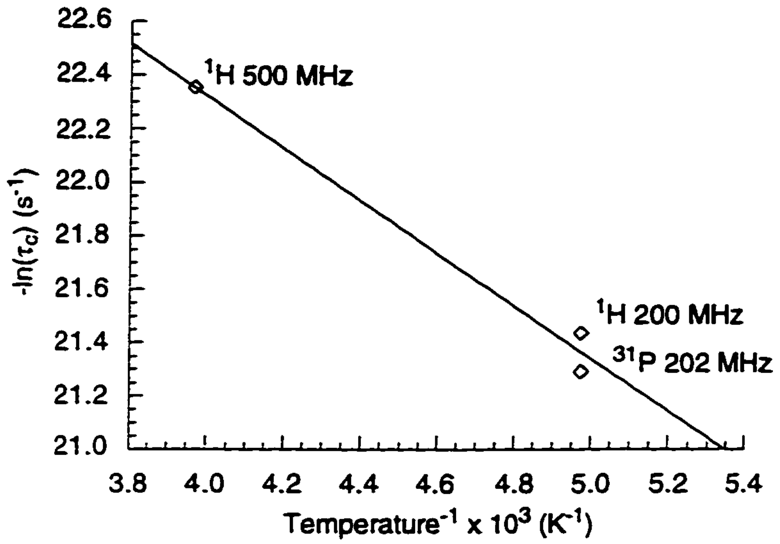
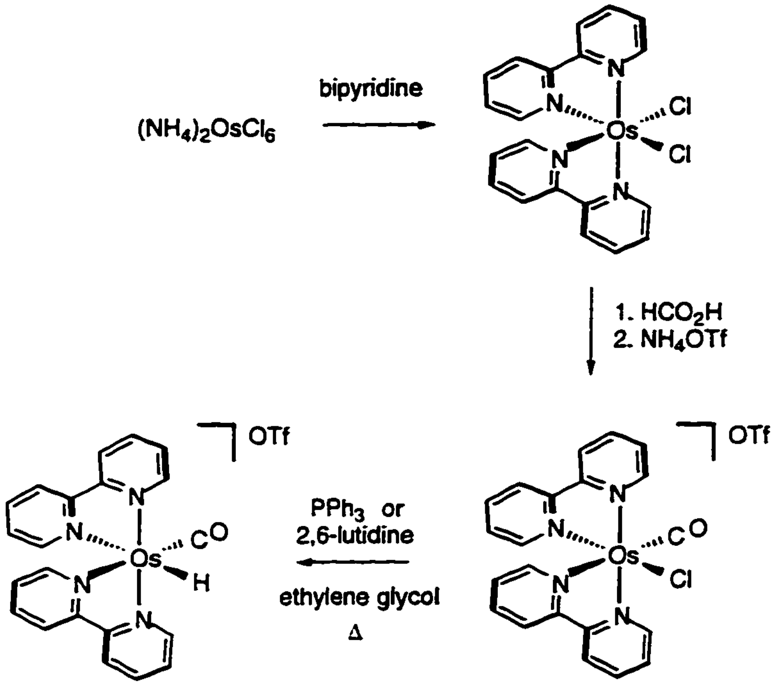


Figure 2.5. Temperature dependence of τ_c minimum for $[RuH(PPh_3)_2(bpy)(CO)]^+$ (**5a**) in CD_2Cl_2.

The linear relationship and the small activation barrier provide evidence that the molecule is tumbling isotropically in solution and the relaxation rate is predominately due to dipolar interactions (eqs 2.1 and 2.2). However, higher magnetic fields would lead to partial alignment of the molecule with the magnetic field affecting the rate of relaxation (Chapter 4) and produce nonlinear results with a larger activation energy. Halpern and coworkers reported a similar set of activation parameters for $Os(H)_4(Pp\text{-tolyl}_3)_3$ ($A = 5.1 \times 10^{11}$ s and $E_a = 2.53$ kcal/mol).[12]

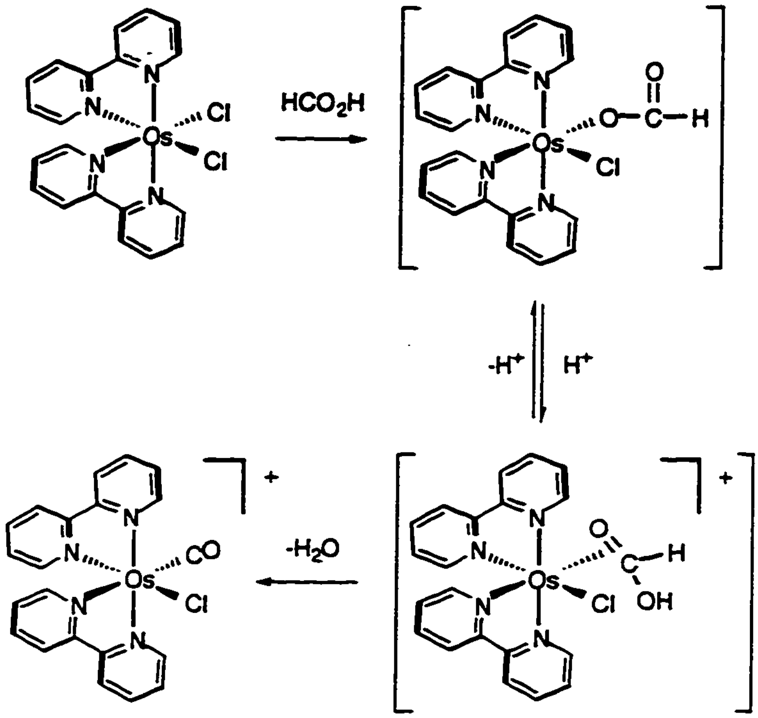
Synthesis and Characterization of $[OsH(bpy)_2(CO)]^+$ (7). The monocationic bisbipyridyl hydride $[OsH(bpy)_2(CO)]^+$ (**7**) was synthesized as the triflate salt following the procedure developed by Meyer and coworkers[13,14] for the synthesis of $7(PF_6)$ (Scheme 2.8). Osmium halide is reacted with 2 equiv of bipyridine in ethylene glycol and heated at reflux for 45 min under Ar. The crude reaction mixture consists of $OsCl_2(bpy)_2$ and $[OsCl_2(bpy)_2]^+$ to which an equal volume of aqueous sodium dithionite is added to reduced the Os(III) to Os(II) and causing $OsCl_2(bpy)_2$ to precipitate as a dark solid. A suspension of $OsCl_2(bpy)_2$ in ethylene glycol and formic acid is heated at reflux for 12 h under an Ar atmosphere.



7

Scheme 2.8

The formic acid is removed on the rotary evaporator and $[OsCl(bpy)_2(CO)]OTf$ is precipitated by addition of aqueous NH_4OTf. The chloride cation is reduced to the cationic hydride, $[OsH(bpy)_2(CO)]OTf$ (7), by heating in ethylene glycol at reflux with either PPh_3 or 2,6-lutidine for 12 h. When PPh_3 is used, prolonged reaction times will produce $[OsH(PPh_3)_2(bpy)(CO)]^+$ (**2a**) as an impurity. The generation of the carbonyl chloride cation is proposed to proceed through the initial binding of formate with subsequent loss of water (Scheme 2.9).[14]



Scheme 2.9

The subsequent reduction of [OsCl(bpy)$_2$(CO)]OTf to the hydride monocation **7** presumably occurs via an alkoxide intermediate followed by β-hydride elimination. The ^{1}H NMR spectrum of **7** shows 16 inequivalent resonances in the aromatic region for the bipyridyl protons and a singlet resonance in the hydride region at δ -11.52. The ^{1}H NMR data is in agreement with the data reported by T. J. Meyer and coworkers for **7**(PF$_6$).[8]

Conclusion

The generation of a series of monocationic hydrides, [OsH(PR$_3$)$_2$(bpy)(CO)]$^+$ (PR$_3$ = PPh$_3$, PMePh$_2$ (**2a**,**b**)), [RuH(PPh$_3$)$_2$(bpy)(CO)]$^+$ (**5a**), and [OsH(PPh$_3$)$_2$(phen)(CO)]$^+$ (**9a**), was accomplished following the synthetic route developed by Robinson and Uttley to produce neutral trisphosphine complexes and reacting these complexes with a chelating ligand. The catalytic behavior of MH(Cl)(PPh$_3$)$_3$(CO) (M = Os, Ru (**1a**, **4a**)) has been extensively studied and is manifested by the lability of a phosphine ligand *trans* to the hydride.[5a] The dissociation of the phosphine *trans* to the hydride generates a 16-electron complex with an open coordination site which allows for a variety of substitution reactions. We have found that the addition of a chelating ligand such as bipyridine or phenanthroline results in a complex that is mostly inert to further substitutions.

Experimental

General procedures. Manipulations of air sensitive complexes were performed under argon using standard vacuum line, Schlenk, or syringe techniques. Argon was deoxygenated and dried by passage through Schweitzerhall Inc. (BASF) R3-11 CuO catalyst followed by Mallinckrodt Aquasorb containing P_2O_5. CD_2Cl_2 and CD_3NO_2 were purchased from Cambridge Isotope Laboratories and were degassed and stored over CaH_2. OsO_4 was acquired from Stevens Metallurgical Inc. $RuCl_3{\cdot}3H_2O$ was purchased from Alfa Products. All other solvents and reagents were used without further purification, except for CH_2Cl_2 which was vacuum distilled from CaH_2.

Elemental analysis were performed by Canadian Microanalytical Services of Delta, British Columbia, Canada.

Infrared spectra were recorded on a Perkin-Elmer model 1600 Fourier transform spectrophotometer (2.0 cm^{-1} resolution). Samples were examined on NaCl cells as Nujol mulls.

^1H NMR spectra were recorded on Bruker AC 200 (^1H: 200.13 MHz), DPX 200 (^1H: 200.13 MHz), AF 300 (^1H: 300.12 MHz), AM 500 (^1H: 500.14 MHz), and DMX 750 (^1H: 750.00 MHz) spectrometers and referenced internally to the residual proton resonance of the deuterated solvent with respect to TMS. $^{31}P\{$aromatic $^1H\}$ NMR spectra were recorded on Bruker AC 200 (^{31}P: 81.02 MHz) and AM 500 (^{31}P: 202.46 MHz) spectrometers with the aromatic protons selectively decoupled and referenced externally to 85% H_3PO_4. $^1H\{^{31}P\}$ NMR spectra were recorded on a Bruker AM 500 spectrometer using a broadband decoupling procedure to decouple the ^{31}P nuclei. $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker AF 300 (^{13}C: 75.47 MHz) and AM 500 (^{13}C: 125.76 MHz) spectrometers and referenced internally to the carbon resonance of the solvent relative to TMS. Variable temperature ^1H NMR experiments were conducted using a AM 500 spectrometer equipped with a Bruker B-VT 1000 temperature control module with a copper-constantan thermocouple. Proton T_1 studies were performed using the standard inversion recovery 180°-τ-90° pulse sequence method.[15] Temperature calibration was accomplished following the Van Geet methanol calibration method.[16]

$(NH_4)_2OsCl_6$.[17] A 1 g ampule of OsO_4 was broken and dropped into a 125 Erlenmeyer flask. HCl (30 mL, 12M) and $FeCl_2{\cdot}4H_2O$ (10 g, 50 mmol) were added and the flask was stoppered loosely and gently stirred while heated on a water bath for 2 h, during which time the color of the solution changed from green to dark orange-red. The solution was cooled to room temperature and decanted into a 125 mL beaker. The flask was rinsed with HCl (10 mL, 12M) and added to the solution. An aqueous 20% solution of NH_4Cl (10 mL, 40 mmol) was added to the solution and the mixture was further cooled in an ice bath. The solid that precipitated was collected on a fritted glass filter and washed with absolute ethanol and dried in vacuo overnight. Yield was 1.6 g (94%).

$OsH(Cl)(PPh_3)_3(CO)$ (1a).[4] Solutions of $(NH_4)_2OsCl_6$ (500 mg, 1.14 mmol) in 35 mL of 2-methoxyethanol and aqueous formaldehyde (15 mL, 37% solution) were added in rapid succession to a vigorously stirred, boiling solution of PPh_3 (1.96 g, 7.75 mmol) in 75 mL of 2-methoxyethanol. The red-brown reaction mixture was heated at reflux for 45 min under Ar. The clear yellow solution was cooled to room temperature and the ivory solid that precipitated was collected on a fritted glass filter and washed with ethanol, water, ethanol, and finally n-hexanes and dried overnight in vacuo. Yield was 950 mg (80%). ^{1}H NMR (CD_2Cl_2): δ 7.32–7.00 (m, 45 H, $P(C_6\mathit{H}_5)_3$), -6.95 (dt, 1 H, J_{HPtrans} = 86.3 Hz, J_{HPcis} = 24.7 Hz, Os*H*). ^{31}P{aromatic ^{1}H} NMR (CD_2Cl_2): δ 7.83 (dd, J_{PP} = 11 Hz, J_{PHcis} = 23 Hz), -9.14 (dt, J_{PP} = 11 Hz, J_{PHtrans} = 83 Hz). IR (Nujol): ν(OsH) = 2095 cm^{-1}, ν(CO) = 1910 cm^{-1} (s), 1892 cm^{-1} (m).

[OsH(PPh$_3$)$_2$(bpy)(CO)](OSO$_2$CF$_3$) (2a).[8] OsH(Cl)(PPh$_3$)$_3$(CO) (**1a**) (250 mg, 0.25 mmol) and 1 eq of bipyridine (40 mg, 0.26 mmol) were added to 10 mL of 2-methoxyethanol in a 100 mL round bottom flask and heated at reflux for 1 h under Ar. The solution was cooled to room temperature and 10 mL of a saturated aqueous solution of NH_4OTf (416 mg, 2.50 mmol) were added. The resulting yellow precipitate was collected by filtration using a Büchner funnel and washed with warer and ether and dried overnight in vacuo. Traces of excess water were removed by dissolving the solid in CH_2Cl_2 and removing the solvent under vacuum using a LN_2 trap with further drying overnight in vacuo. Yield was 200 mg (77%). ^{1}H NMR (CD_2Cl_2): δ 8.62 (1 H, d, J_{HH} = 5.3 Hz), 7.54 (1 H, d, J_{HH} = 5.3 Hz) *6,6′*-bipyridyl, 8.13 (2 H, d, J_{HH} = 8.1 Hz) *3,3′*-bipyridyl, 7.79 (1 H, t, J_{HH} = 7.9 Hz), 7.72 (1 H, t, J_{HH} = 7.9 Hz) *4,4′*-bipyridyl, 7.05 (1 H, t, J_{HH} = 6.5 Hz), 6.38 (1 H, t, J_{HH} = 6.5 Hz) *5,5′*-bipyridyl, 7.33–7.23 (m, 30 H, $P(C_6\mathit{H}_5)_3$), -12.19 (t, 1 H, J_{HP} = 18.4 Hz, Os*H*, T_1 min = 500 ms (247 K, 500 MHz)). ^{31}P{aromatic ^{1}H} NMR (CD_2Cl_2): δ 18.76 (d, J_{PH} = 17 Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 186.56 (t, J_{CP} = 10.8 Hz, *C*O), 155.6, 154.9 (*2,2′*-bipyridyl), 155.2, 153. 7 (*6,6′*-bipyridyl), 138.1, 137.3 (*4,4′*-bipyridyl), 127.6, 127.2 (*5,5′*-bipyridyl), 124.2, 123.8 (*3,3′*-bipyridyl), 133. 4 (t, J_{CP} = 5.4 Hz, *o-C*$_6$H$_5$), 131.2 (t, J_{CP} = 25.4 Hz, *ipso-C*$_6$H$_5$), 130.7 (s, *p-C*$_6$H$_5$), 128.9 (t, J_{CP} = 4.5 Hz, *m-C*$_6$H$_5$). Anal calcd for $C_{48}H_{39}N_2F_3O_4P_2SOs$: C, 54.96; H, 3.75; N, 2.67. Found: C, 54.52; H, 3.80; N, 2.66. IR (Nujol): ν(OsH) = 2081 cm^{-1}, ν(CO) = 1923 cm^{-1} (s).

$OsH(Cl)(PMePh_2)_3(CO)$ (1b). Solutions of $(NH_4)_2OsCl_6$ (499 mg, 1.14 mmol) in 35 mL of 2-methoxyethanol and aqueous formaldehyde (15 mL, 37% solution) were added in rapid succession to a vigorously stirred, boiling solution of $PMePh_2$ (1.2 mL, 6.4 mmol) in 75 mL of 2-methoxyethanol. The moss-green reaction mixture was heated at reflux for 1 h under Ar. The solution was cooled to room temperature and the volume was reduced, the solids that precipitated were collected on a fritted glass filter and wash with water, ethanol, and n-hexanes and dried in vacuo. Yield was 300 mg (31%). ^1H NMR (C_6D_6): δ 7.82–6.63 (m, 30 H, $PCH_3(C_6\mathit{H}_5)_2$), 2.30 (s, 6 H, $PC\mathit{H}_3(C_6H_5)_2$), 1.90 (s, 3 H, $PC\mathit{H}_3(C_6H_5)_2$), -6.45 (dt, 1 H, $J_{HPtrans} = 85.3$ Hz, $J_{HPcis} = 22.2$ Hz, $Os\mathit{H}$). ^{31}P\{aromatic ^1H\} NMR (C_6D_6): δ -20.1 (t, $J_{PP} = 13$ Hz), -23.3 (d, $J_{PP} = 13$ Hz).

$[OsH(PMePh_2)_2(bpy)(CO)](OSO_2CF_3)$ (2b). $OsH(Cl)(PMePh_2)_3(CO)$ (**1b**) (152 mg, 0.18 mmol) and bipyridine (40 mg, 0.26 mmol) were added to 15 mL of ethylene glycol in a 100 mL round bottom flask and heated at reflux for 6 days under Ar. The solution was cooled to room temperature and 10 mL of a saturated aqueous solution of NH_4OTf (502 mg, 3.00 mmol) were added. The golden-yellow precipitate that formed was collected by filtration using a Büchner funnel and washed with ethanol, water, and ethanol and dried overnight in vacuo. Further drying was performed by dissolving the solid in CH_2Cl_2 and removing the solvent under vacuum using a LN_2 trap with drying overnight in vacuo. ^1H NMR (CD_2Cl_2): δ 8.61–6.92 (m, 28 H, bipyridyl and $PCH_3(C_6\mathit{H}_5)_2$), 1.75 (t, 6 H, $J_{HP} = 3.2$ Hz, $PC\mathit{H}_3(C_6H_5)_2$), -12.22 (t, 1 H, $J_{HP} = 17.6$ Hz, $Os\mathit{H}$). ^{31}P NMR (CD_2Cl_2): δ 0.08 (d, $J_{PH} = 14$ Hz).

$RuH(Cl)(PPh_3)_3(CO)$ (4a). Solutions of $RuCl_3 \cdot 3H_2O$ (270 mg, 1.03 mmol) in 20 mL of 2-methoxyethanol and aqueous formaldehyde (20 mL, 37% solution) were added in rapid succession to a vigorously stirred, boiling solution of PPh_3 (1.64 g, 6.16 mmol) in 75 mL of 2-methoxyethanol. The reaction mixture was heated at reflux for 30 min under Ar. The clear solution was cooled to room temperature and the dusty-grey solid that precipitated was collected on a fritted glass filter and washed with ethanol, water, ethanol, and finally n-hexanes and dried overnight in vacuo. Yield was 764 mg (78%). ^{1}H NMR (CD_2Cl_2, 271 K): δ 7.32–6.95 (m, 45 H, P(C_6H_5)$_3$), -7.18 (dt, 1 H, $J_{HPtrans}$ = 104.1 Hz, J_{HPcis} = 24.0 Hz, Ru*H*). ^{31}P{aromatic ^{1}H} NMR (CD_2Cl_2, 271 K): δ 40.3 (dd, J_{PP} = 15 Hz, J_{PHcis} = 23 Hz), 12.8 (dt, J_{PP} = 15 Hz, $J_{PHtrans}$ = 103 Hz).

[RuH(PPh$_3$)$_2$(bpy)(CO)](OSO$_2$CF$_3$) (5a). RuH(Cl)(PPh$_3$)$_3$(CO) (**4a**) (449 mg, 0.47 mmol) and bipyridine (107 mg, 0.69 mmol) were added to 20 mL of 2-methoxyethanol in a 100 mL round bottom flask and heated at reflux for 1 h under Ar. The solution was cooled to room temperature and 10 mL of a saturated aqueous solution of NH_4OTf (416 mg, 2.50 mmol) were added. The yellow precipitate that formed was collected by filtration using a Büchner funnel and washed with water and ether and dried overnight in vacuo. Traces of excess water were removed by dissolving the solid in CH_2Cl_2 and removing the solvent under vacuum using a LN_2 trap with further drying overnight in vacuo. ^{1}H NMR (CD_2Cl_2): δ 8.64 (1 H, d, J_{HH} = 4.8 Hz), 7.59 (1 H, d, J_{HH} = 5.0 Hz) *6,6'*-bipyridyl, 8.05 (1 H, d, J_{HH} = 9.1 Hz), 8.03 (1 H, d, J_{HH} = 9.7 Hz) *3,3'*-bipyridyl, 7.81 (1 H, t, J_{HH} = 7.7 Hz), 7.69 (1 H, t, J_{HH} = 7.7 Hz) *4,4'*-bipyridyl, 7.15 (1 H, t, J_{HH} = 6.2 Hz), 6.44 (1 H, t, J_{HH} = 6.4 Hz) *5,5'*-bipyridyl, 7.35–7.25 (m, 30 H, P(C_6H_5)$_3$), -11.31 (t, 1 H, J_{HP} = 19.6 Hz, Ru*H*, T_1 min = 193 ms (205 K, 200 MHz), T_1 min = 475 ms (252 K, 500 MHz)). ^{31}P{aromatic ^{1}H} NMR (CD_2Cl_2): δ46.5 (d, J_{PH} = 18 Hz, T_1 min = 616 ms (202 K, 202 MHz)). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ204.9 (t, J_{CP} = 14.9 Hz, *CO*), 155.0, 153.7 (*6,6'*-bipyridyl), 154.3, 153.9 (*2,2'*-bipyridyl), 138.1, 137.9 (*4,4'*-bipyridyl), 126.8, 126.6 (*5,5'*-bipyridyl), 123.5, 123.4 (*3,3'*-bipyridyl), 133. 4 (t, J_{CP} = 5.7 Hz, *o-C$_6$*H$_5$), 131.7 (t, J_{CP} = 22.1 Hz, *ipso-C$_6$*H$_5$), 130.6 (s, *p-C$_6$*H$_5$), 128.9 (t, J_{CP} = 4.4

Hz, *m*-C_6H_5). Anal calcd for $C_{48}H_{39}N_2F_3O_4P_2SRu\cdot CH_2Cl_2$: C, 56.33; H, 3.96; N, 2.68. Found: C, 56.64; H, 3.93; N, 2.75.

$Os(bpy)_2Cl_2$.[13] $(NH_4)_2OsCl_6$ (1 g, 2.28 mmol) and 2 eq bipyridine (0.72 g, 4.6 mmol) were added to a 50 mL of ethylene glycol and heated at reflux for 45 min. The reaction mixture was cooled to room temperature and 50 mL of a saturated aqueous solution of sodium dithionite (12.2 g) was added to reduce any $[Os(bpy)_2Cl_2]^+$ formed during the reaction. The dark purple-black precipitate was collected on a fritted glass filter and washed with water followed by a large volume of ether and dried overnight in vacuo. Yield was 1.01 g (77%).

$[OsCl(bpy)_2(CO)](OSO_2CF_3)$.[14] $Os(bpy)_2Cl_2$ (250 mg, 0.44 mmol) was added to deoxygenated formic acid (30 mL, 88% solution) and heated at reflux for 12 h under Ar. The solution was cooled to room temperature and the formic acid was removed using a rotary evaporator. Water (25 mL) and a saturated aqueous solution of ammonium trifluoromethanesulfonate (5 mL) were added to the residue. The resulting red precipitate was collected on a fritted glass filter and washed with a large volume of water followed by ether. Yield was 100 mg (41%).

$[OsH(bpy)_2(CO)](OSO_2CF_3)$ (7).[14] $[OsCl(bpy)_2(CO)](OSO_2CF_3)$ (100 mg, 0.18 mmol) and triphenylphosphine (300 mg, 1.14 mmol) were added to ethylene glycol (30 mL) and vigorously stirred while heated at reflux for 12 h (prolonged reaction times cause the formation of **2a**). The deep red reaction mixture was cooled to room temperature and 30 mL of water were added. The precipitate was collected on a Büchner funnel and washed with water. Purification was accomplished with column chromatography using neutral alumina and toluene:acetonitrile (1:1) as the eluent, collecting the dark red band that was the first to elute from the column. The solvent was removed using a rotary evaporator. The residue was further purified by dissolving in a minimal amount of acetonitrile and the resulting solution was added dropwise to a large volume of stirring ether. The precipitate was collected on a fritted glass filter and washed with ether and dried in vacuo. ^{1}H NMR (CD_2Cl_2): δ 9.46 (s, 2 H), 8.50 (d, 1 H, J_{HH} = 8.2 Hz), 8.40 (d, 1 H, J_{HH} = 8.0 Hz), 8.34 (d, 1 H, J_{HH} = 8.2 Hz), 8.29 (d, 1 H, J_{HH} = 8.2 Hz), 8.21 (t, 1 H, J_{HH} = 7.8 Hz), 8.01 (t, 1 H, J_{HH} = 8.7 Hz), 7.97 (t, 1 H, J_{HH} = 8.5 Hz), 7.86 (t, 1 H, J_{HH} = 7.7 Hz), 7.70 (d, 1 H, J_{HH} = 5.0 Hz), 7.55 (t, 1 H, J_{HH} = 6.5 Hz), 7.39–7.32 (m, 3 H), 7.27 (d, 1 H, J_{HH} = 5.2 Hz), bipyridyl, -11.52 (s, 1 H, Os*H*).

[OsH(PPh$_3$)$_2$(phen)(CO)](OSO$_2$CF$_3$) (9a).[8] OsH(Cl)(PPh$_3$)$_3$(CO) (**1a**) (253 mg, 0.24 mmol) and phenanthroline (87 mg, 0.44 mmol) were added to 15 mL of ethylene glycol in a 100 mL round bottom flask and heated at reflux for 1 h under Ar. The solution was cooled to room temperature and 10 mL of a saturated aqueous solution of NH_4OTf (800 mg, 4.79 mmol) were added. The yellow precipitate that formed was collected by filtration using a Büchner funnel and washed with water and ether and dried overnight in vacuo. ^{1}H NMR (CD_2Cl_2): δ 9.02 (1 H, d, J_{HH} = 4.9 Hz), 7.95 (1 H, d, J_{HH} = 5.2 Hz) *2,9*-phenanthroline, 8.28 (1 H, d, J_{HH} = 8.1 Hz), 8.21(1 H, d, J_{HH} = 8.1 Hz) *4,7*-phenanthroline, 7.91 (2 H, s) *5,6*-phenanthroline, 6.84 (1 H, d, J_{HH} = 5.3 Hz), 6.83 (1 H, d, J_{HH} = 5.3 Hz) *3,8*-phenanthroline, 7.29–7.10 (m, 30 H, P(C_6H_5)$_3$), -11.98 (t, 1 H, J_{HP} = 18.1 Hz, Os*H*). ^{31}P{aromatic ^{1}H} NMR (CD_2Cl_2): δ 19.25 (d, J_{PH} = 17 Hz). IR (Nujol): ν(OsH) = 2063 cm^{-1}, ν(CO) = 1929 cm^{-1} (s).

OsH(Cl)(PPh$_3$)$_2$(CO)$_2$. A sealable NMR tube was charged with OsH(Cl)(PPh$_3$)$_3$(CO) (**1a**) (12 mg, 0.01 mmol) and evacuated. CD_2Cl_2 (0.5 mL) was vacuum transferred to the solid and the tube was flame-sealed after 1 atm CO (760 Torr) was added. ^{1}H NMR

(CD_2Cl_2): δ 7.71–7.31 (m, bound and "free" $P(C_6H_5)_3$), -3.63 (t, 1 H, J_{HP} = 20.2 Hz). $^{31}P\{aromatic\ ^1H\}$ NMR (CD_2Cl_2): δ 8.97 (d, J_{PH} = 19 Hz), -4.98 (s, $P(C_6H_5)_3$).

$RuH(Cl)(PPh_3)_2(CO)_2$. An NMR tube equipped with a J. Young Teflon valve was charged with $RuH(Cl)(PPh_3)_3(CO)$ (**4a**) (12 mg, 0.01 mmol) and evacuated. C_6D_6 (0.5 mL) was vacuum transferred to the solid and 1 atm CO (760 Torr) was added. ^1H NMR (C_6D_6): δ 7.98–6.97 (m, bound and "free" $P(C_6H_5)_3$), -3.89 (t, 1 H, J_{HP} = 19.2 Hz). $^{31}P\{aromatic\ ^1H\}$ NMR (C_6D_6): δ 39.8 (d, J_{PH} = 16 Hz), -4.69 (s, $P(C_6H_5)_3$).

Reaction of $OsH(Cl)(PPh_3)(CO)_2$ and $AgOSO_2CF_3$. A sealable NMR tube was charged with $OsH(Cl)(PPh_3)_3(CO)$ (**1a**) (12 mg, 0.01 mmol) and 1 equiv $AgOSO_2CF_3$ (3 mg, 0.01 mmol) and evacuated. CD_2Cl_2 (0.5 mL) was vacuum transferred to the solid and the tube was flame-sealed after 1 atm CO (760 Torr) was added. ^1H NMR (CD_2Cl_2): δ 7.57–7.07 (m, $P(C_6H_5)_3$), -4.70 (t, 1 H, J_{HP} = 20.2 Hz). $^{31}P\{aromatic\ ^1H\}$ NMR (CD_2Cl_2): δ 8.97 (d, J_{PH} = 19 Hz).

Reaction of $RuH(Cl)(PPh_3)(CO)_2$ and $AgOSO_2CF_3$. An NMR tube equipped with a J. Young Teflon valve was charged with $RuH(Cl)(PPh_3)_3(CO)$ (**4a**) (11 mg, 0.01 mmol) and $AgOSO_2CF_3$ (8 mg, 0.03 mmol) and evacuated. C_6D_6 (0.5 mL) was vacuum transferred to the solid and 1 atm CO (760 Torr) was added. ^1H NMR (C_6D_6): δ 7.86–6.97 (m, $P(C_6H_5)_3$), -3.29 (t, J_{HP} = 19.2 Hz), -4.43 (t, J_{HP} = 17.5 Hz). $^{31}P\{aromatic\ ^1H\}$ NMR (C_6D_6): δ 41.08 (d, J_{PH} = 15 Hz), 14.41 (s).

Reaction of $[OsH(PPh_3)_2(bpy)(CO)](OSO_2CF_3)$ (2a) with P*p*-tolyl$_3$. $[OsH(PPh_3)_2(bpy)(CO)](OSO_2CF_3)$ (**2a**) (20 mg, 0.02 mmol) and P*p*-tolyl$_3$ (30 mg, 0.10 mmol) were added to a sealable NMR tube. CD_2Cl_2 (0.5 mL) was vacuum transferred to the solids and the tube was evacuated and flame-sealed. The sample was kept in a oil bath at 55 °C and monitored by NMR.

Reaction of [OsH(PPh$_3$)$_2$(bpy)(CO)](OSO$_2$CF$_3$) (2a) with Pyridine-*N*-oxide. [OsH(PPh$_3$)$_2$(bpy)(CO)](OSO$_2$CF$_3$) (**2a**) (10 mg, 0.01 mmol) and C$_5$H$_5$NO (6 mg, 0.06 mmol) were added to a sealable NMR tube. CD$_3$CN (0.5 mL) was vacuum transferred to the solids and the tube was evacuated and flame-sealed.

Reaction of [OsH(PPh$_3$)$_2$(bpy)(CO)](OSO$_2$CF$_3$) (2a) with (CH$_3$)$_3$N-*N*-oxide. [OsH(PPh$_3$)$_2$(bpy)(CO)](OSO$_2$CF$_3$) (**2a**) (7 mg, 0.01 mmol) and (CH$_3$)$_3$NO (7 mg, 0.09 mmol) were added to a sealable NMR tube. CD$_3$CN (0.5 mL) was vacuum transferred to the solids and the tube was evacuated and flame-sealed.

Reaction of [OsH(PPh$_3$)$_2$(bpy)(CO)](OSO$_2$CF$_3$) (2a) with MeOSO$_2$CF$_3$. [OsH(PPh$_3$)$_2$(bpy)(CO)](OSO$_2$CF$_3$) (**2a**) (20 mg, 0.02 mmol) was added to a sealable NMR tube. CD$_2$Cl$_2$ (0.5 mL) was vacuum transferred to the solids and methyl triflate (4 µL, 0.04 mmol) was added via syringe under Ar. The tube was evacuated and flame-sealed. The sample was kept in a oil bath at 55 °C and monitored by NMR.

Reaction of [RuH(PPh$_3$)$_2$(bpy)(CO)](OSO$_2$CF$_3$) (5a) with MeOSO$_2$CF$_3$. [RuH(PPh$_3$)$_2$(bpy)(CO)](OSO$_2$CF$_3$) (**5a**) (8 mg, 0.01 mmol) was added to a sealable NMR tube. CD$_2$Cl$_2$ (0.5 mL) was vacuum transferred to the solids and methyl triflate (9 µL, 0.08 mmol) was added via syringe under Ar. The tube was evacuated and flame-sealed. The sample was kept in a oil bath at 45 °C and monitored by NMR. ^{1}H NMR (CD$_2$Cl$_2$): δ 8.65–6.44 (bipyridyl and P(C$_6$$H_5$)$_3$), 4.26 (C$H_3OSO_2CF_3$$^+$), 2.82 (d, J_{HP} =

13.3 Hz, $CH_3P(C_6H_5)_3^+$), -11.31 (t, J_{HP} = 19.5 Hz). $^{31}P\{aromatic\ ^1H\}$ NMR (CD_2Cl_2): δ 51.78 (s), 46.49 (d, J_{PH} = 18 Hz, **5a**), 21.76 ($[CH_3P(C_6H_5)_3]^+$).

Reaction of $[OsH(PPh_3)_2(bpy)(CO)](OSO_2CF_3)$ (2a) with CCl_4. $[OsH(PPh_3)_2(bpy)(CO)](OSO_2CF_3)$ (**2a**) (19 mg, 0.02 mmol) was added to a sealable NMR tube. CD_2Cl_2 (0.5 mL) and CCl_4 (0.5 mL) were vacuum transferred to the solids. The tube was evacuated and flame-sealed.

$[RuCl(PPh_3)_2(bpy)(CO)](OSO_2CF_3)$. $[RuH(PPh_3)_2(bpy)(CO)](OSO_2CF_3)$ (**5a**) (8 mg, 0.01 mmol) and *N*-chlorosuccinimide (2 mg, 0.02 mmol) were added to a sealable NMR tube. CD_2Cl_2 (0.5 mL) was vacuum transferred to the solids. Diethyl ether (2 mL) was added to the solution via syringe under a flow of Ar. The resulting precipitate was washed with diethyl ether (2 x 2 mL) with the excess solvent removed with a pipet. The solids were dried in vacuo overnight. CD_2Cl_2 (0.5 mL) was added via vacuum transfer and the tube was flame-sealed. ^1H NMR (CD_2Cl_2): δ 8.47–6.43 (bipyridyl and $P(C_6H_5)_3$). $^{31}P\{aromatic\ ^1H\}$ NMR (CD_2Cl_2): δ 27.38 (s).

$[OsCl(PPh_3)_2(bpy)(CO)](OSO_2CF_3)$. $[OsH(PPh_3)_2(bpy)(CO)](OSO_2CF_3)$ (**2a**) (12 mg, 0.01 mmol) and *N*-chlorosuccinimide (3 mg, 0.02 mmol) were added to a sealable NMR tube. CD_2Cl_2 (0.5 mL) was vacuum transferred to the solids. Diethyl ether (2 mL) was added to the solution via syringe under a flow of Ar. The resulting precipitate was washed with diethyl ether (2 x 2 mL) with the excess solvent removed with a pipet. The solids were dried in vacuo overnight. CD_2Cl_2 (0.5 mL) was added via vacuum transfer and the tube was flame-sealed. ^1H NMR (CD_2Cl_2): δ 8.40 (1 H, d, J_{HH} = 8.0 Hz), 8.25 (1 H, d, J_{HH} = 8.0 Hz) *3,3'*-bipyridyl, 8.32 (1 H, d, J_{HH} = 5.2 Hz), 7.62 (1 H, d, J_{HH} = 5.7 Hz) *6,6'*-bipyridyl, 7.96 (1 H, t, J_{HH} = 7.5 Hz), 7.65 (1 H, t, J_{HH} = 7.7 Hz) *4,4'*-bipyridyl, 6.97 (1 H, t, J_{HH} = 6.3 Hz), 6.48 (1 H, t, J_{HH} = 6.5 Hz) *5,5'*-bipyridyl, 7.35–7.23 (m, 30 H, $P(C_6H_5)_3$). $^{31}P\{$aromatic $^1H\}$ NMR (CD_2Cl_2): δ -0.33 (s).

$[OsBr(PPh_3)_2(bpy)(CO)](OSO_2CF_3)$. $[OsH(PPh_3)_2(bpy)(CO)](OSO_2CF_3)$ (**2a**) (10 mg, 0.01 mmol) and *N*-bromosuccinimide (11 mg, 0.06 mmol) were added to a sealable NMR tube. CD_2Cl_2 (0.5 mL) was vacuum transferred to the solids and the tube was evacuated and flame-sealed. ^1H NMR (CD_2Cl_2): δ 8.50 (1 H, d, J_{HH} = 8.0 Hz), 8.34 (1 H, d, J_{HH} = 7.9 Hz) *3,3'*-bipyridyl, 8.42 (1 H, d, J_{HH} = 5.1 Hz), 7.65 (1 H, d, J_{HH} = 6.6 Hz) *6,6'*-bipyridyl, 7.96 (1 H, t, J_{HH} = 7.6 Hz), 7.66 (1 H, t, J_{HH} = 8.0 Hz) *4,4'*-bipyridyl, 6.89 (1 H, t, J_{HH} = 6.4 Hz), 6.46 (1 H, t, J_{HH} = 6.4 Hz) *5,5'*-bipyridyl, 7.34–7.21 (m, 30 H, $P(C_6H_5)_3$). $^{31}P\{$aromatic $^1H\}$ NMR (CD_2Cl_2): δ -1.97 (s).

Reaction of $[RuCl(PPh_3)_2(bpy)(CO)](OSO_2CF_3)$ with $AgOSO_2CF_3$ and H_2. $[RuH(PPh_3)_2(bpy)(CO)](OSO_2CF_3)$ (**5a**) (8 mg, 0.01 mmol) and *N*-chlorosuccinimide (2 mg, 0.02 mmol) were added to a NMR tube equipped with a J. Young Teflon valve. CD_2Cl_2 (0.5 mL) was vacuum transferred to the solids. Diethyl ether was added to the resulting solution (2 mL) via pipet under Ar. The solvents were removed from the precipitate via syringe. The solids were washed with diethyl ether (2 x 2 mL) and the sample was placed under dynamic vacuum overnight. Silver triflate (2 mg, 1 mmol) was added to the solids under Ar. The NMR tube was evacuated and CD_3NO_2 (0.5 mL) was vacuum transferred to the sample and H_2 (800 Torr) was added. ^1H NMR (CD_3NO_2): δ 8.74–7.09 (bipyridyl and $P(C_6H_5)_3$). $^{31}P\{$aromatic $^1H\}$ NMR (CD_3NO_2): δ 15.7 (s).

Reaction of $[OsCl(PPh_3)_2(bpy)(CO)](OSO_2CF_3)$ and $[OsBr(PPh_3)_2(bpy)(CO)](OSO_2CF_3)$ with $AgOSO_2CF_3$ and H_2. $[OsH(PPh_3)_2(bpy)(CO)](OSO_2CF_3)$ (**2a**) and *N*-chlorosuccinimide or *N*-

bromosuccinimide were added to a NMR tube equipped with a J. Young Teflon valve. CD_2Cl_2 (0.5 mL) was vacuum transferred to the solids. Diethyl ether was added to the resulting solution (2 mL) via pipet under Ar. The solvents were removed from the precipitate via syringe. The solids were washed with diethyl ether (2 x 2 mL) and the sample was placed under dynamic vacuum overnight. Silver triflate (2 mg, 1 mmol) was added to the solids under Ar. The NMR tube was evacuated and CD_3NO_2 (0.5 mL) was vacuum transferred to the sample and H_2 (1 atm) was added.

Notes to Chapter 2.

---

1 Crabtree, R. H.; Lavin, M. *J. Chem. Soc., Chem. Commun.* **1985**, 794-795.

2 (a) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913-926. (b) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155-289.

3 (a) Li, Z.-W.; Taube, H. *J. Am. Chem. Soc.* **1994**, *116*, 9506-9513. (b) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1990**, *112*, 2261-2263.

4 Ahmad, N.; Robinson, S. D.; Uttley, M. F. *J. Chem. Soc.* **1972**, 843-847.

5 (a) Sánchez-Delgado, R. A.; Valencia, N.; Márquez-Silva, R-L.; Andriollo, A.; Medina, M. *Inorg. Chem.* **1986**, *25*, 1106-1111. (b) Sánchez-Delgado, R. A.; Bradley, J. S.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1976**, 399-404. (c) Tsuji, J.; Suzuki, H. *Chem. Lett.* **1977**, 1085-1086. (d) Hallman, P. S.; McGarvey, B. R.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 3143.

6 Orioli, P. L.; Vaska, L. *Proc. Chem. Soc., London* **1962**, 333.

7 (a) Geoffroy, G. L.; Bradley, M. G. *Inorg. Chem.* **1977**, *16*, 744-748. (b) James, B. R.; Markham, L. D.; Hui, B. C.; Rempel, G. L. *J. Chem. Soc., Dalton Trans.* **1973**, 2247-2252.

8 Sullivan, B. P.; Lumpkin, R. S.; Meyer, T. J. *Inorg. Chem.* **1987**, *26*, 1247-1252.

9 Gladysz, J. A.; Selover, J. C.; Strouse, C. E. *J. Am. Chem. Soc.* **1978**, *100*, 6766-6767.

10 Sweet, J. R.; Graham, W. A. G. *Organometallics* **1982**, *1*, 982-986.

11 Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, 1987.

12 Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173-4184.

---

13 Kober, E. M.; Caspar, J. V.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1988**, *27*, 4587-4598.

14 Sullivan, B. P.; Caspar, J. V.; Johnson, S. R.; Meyer, T. J. *Organometallics* **1984**, *3*, 1241-1251.

15 Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126-4133.

16 Van Geet, A. L. *Analytical Chemistry* **1970**, *42*, 679-680.

17 Dwyer, F. P.; Hogarth, J. W. *Inorganic Synthesis*, **1957**, *5*, 206-207.

Chapter 3

Synthesis and Characterization of Dicationic Dihydrogen Complexes of Ruthenium and Osmium

Introduction

Since the initial discovery by Kubas and coworkers of the transition metal dihydrogen complex $W(H_2)(P^iPr_3)_2(CO)_3$,[1] a large number of isolable H_2 complexes have been prepared, the majority of which have been found to be singly charged cationic species.[2] The plethora of monocationic complexes suggests that positive charge confers additional stability to the H_2 complexes. An assessment of the effect of charge on the binding of H_2 requires the preparation of charged complexes of the form $[M(H_2)(L)_5]^{n+}$ with ligands L comparable to those employed in the tungsten complexes.

Recently, the preparation of rhenium cationic analogues, $[Re(H_2)(PR_3)_2(CO)_3]^+$ and $[Re(H_2)(PR_3)_2(CN^tBu)_3]^+$ and comparative studies with the neutral tungsten complexes have been reported.[3,4,5] At the outset of this study the only well characterized dicationic complexes belonged to the osmium series, $[Os(H_2)(NH_3)_4(L)]^{2+}$ and $[Os(H_2)(en)_2(L)]^{2+}$ (en = ethylenediamine) which had been reported by Taube and coworkers.[6,7,8]

The bis(ethylenediamine) complex was initially formulated in 1971 as a *cis* dihydride of osmium(IV), $[Os(H)_2(en)_2]Cl_2$.[9] Further research with this complex and $[Os(H_2)(NH_3)_4(L)]^{2+}$ indicated that the data supporting the original structural assignment were misinterpreted and these complexes are more properly formulated as dihydrogen complexes of osmium(II). The preparation and properties of these osmium dihydrogen dications (and monocations when L is anionic) are quite unique compared to other known dihydrogen complexes. The cationic complexes are surprisingly nonacidic and monohydride analogues are unknown. The basicity of the complexes results in very strong M-H_2 interactions and H-H bond lengths in the H_2 ligand that are on the verge of homolytic cleavage (1.09–1.34 Å).[8]

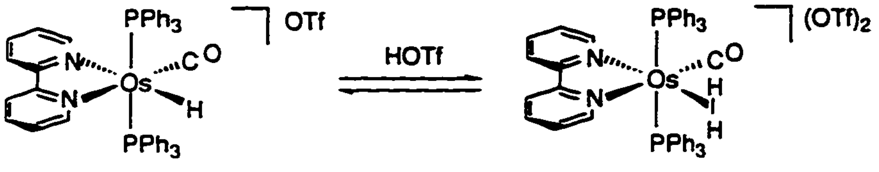
A search for relevant chemistry for comparison to the tungsten and rhenium systems led us to the 1987 report by Sullivan, Lumpkin and Meyer[10] on the protonation of $[OsH(PPh_3)_2(bpy)(CO)]PF_6$ (bpy = 2,2'-bipyridine). The product was characterized as a dihydride dication of osmium(IV), $[Os(H)_2(PPh_3)_2(bpy)(CO)]^{2+}$. The results of further investigations (T_1 measurements and H-D coupling) on this dication and its analogues, $[Os(H_2)(PMePh_2)_2(bpy)(CO)]^{2+}$, $[Ru(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$, $[Os(H_2)(PPh_3)_2(phen)(CO)]^{2+}$ (phen = 1,10-phenanthroline), as well as a related complex $[Os(H_2)(bpy)_2(CO)]^{2+}$, will be discussed along with the proposition that the data are most consistent with the structural assignment of these dications as dihydrogen complexes.

During the course of this study, the preparation of the dicationic complexes, $[Os(H_2)(P^iPr_3)_2(NCMe)_3]^{2+}$ by Caulton, Tilset, and coworkers,[11] $[Os(H_2)(dppe)_2(NCMe)]^{2+}$ (dppe = 1,2-bis(diphenylphosphino)ethane) by Morris and coworkers,[12] and $[M(H_2)(dppp)_2(CO)]^{2+}$ (M = Ru, Os; dppp = 1,3-bis(diphenylphosphino)propane) by Mezzetti and coworkers[13] has been reported. A review of these dihydrogen dications and the complexes reported by Taube and coworkers[6,7,8] will also be presented.

Results

Protonation of $[MH(PR_3)_2(N\text{-}N)(CO)]^+$ [M = Os, N-N = bpy, PR_3 = PPh_3, $PMePh_2$ (2a,b); M = Ru, N-N = bpy, PR_3 = PPh_3 (5a); M = Os, N-N = phen, PR_3 = PPh_3 (9a)]. It was reported by Meyer and coworkers[10] that protonation of **2a** (PF_6 salt) with triflic acid (HOTf) in CH_2Cl_2 affords an insoluble oil with no gas evolution. A homogeneous system was achieved using HOTf/CF_3COOH mixtures as solvent. In this solvent system, ^1H NMR spectra were obtained which exhibit a broad resonance at -6.4 ppm in contrast with the sharp triphenylphosphine and bipyridyl proton resonances. Studies that confirmed the protonation site as the metal center rather than the ancillary ligands, along with the presence of a single slightly broadened resonance in the ^{31}P NMR spectrum led them to characterize the complex as a dihydride of osmium(IV), $[Os(H)_2(PPh_3)_2(bpy)(CO)]^{2+}$.

We find that protonation can be conveniently carried out using the triflate salt of **2a** and excess triflic acid in nitromethane or in methylene chloride (Scheme 3.1).



2a **3a**

Scheme 3.1

The dicationic product, $[Os(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$ (**3a**), is soluble in these solvents and thermally robust, showing no loss of H_2 with only minor (estimated to be < 10% as determined by ^{31}P NMR) decomposition occurring over a period of 18 months in methylene chloride-d_2 at room temperature. When the protonation of **2a** is attempted with less than 4 equiv of triflic acid or with protonated ethers, **3a** is only partially generated (*vide infra*). The presence of bases such as diethyl ether or water will immediately deprotonate the dication and regenerate **2a** without any loss to decomposition.

In the ^1H NMR spectrum of **3a** recorded in CD_2Cl_2 (Figure 3.1), the hydride resonance at -5.78 ppm is fairly broad, with a half-height line width ($\Delta\nu_{1/2}$) = 170 Hz. The ^{31}P NMR spectrum of **3a** with the aromatic protons selectively decoupled exhibits a single resonance at +8.54 ppm ($\Delta\nu_{1/2}$ = 6.5 Hz), consistent with a structure containing equivalent phosphines as postulated by Meyer and coworkers, and shows no evidence of

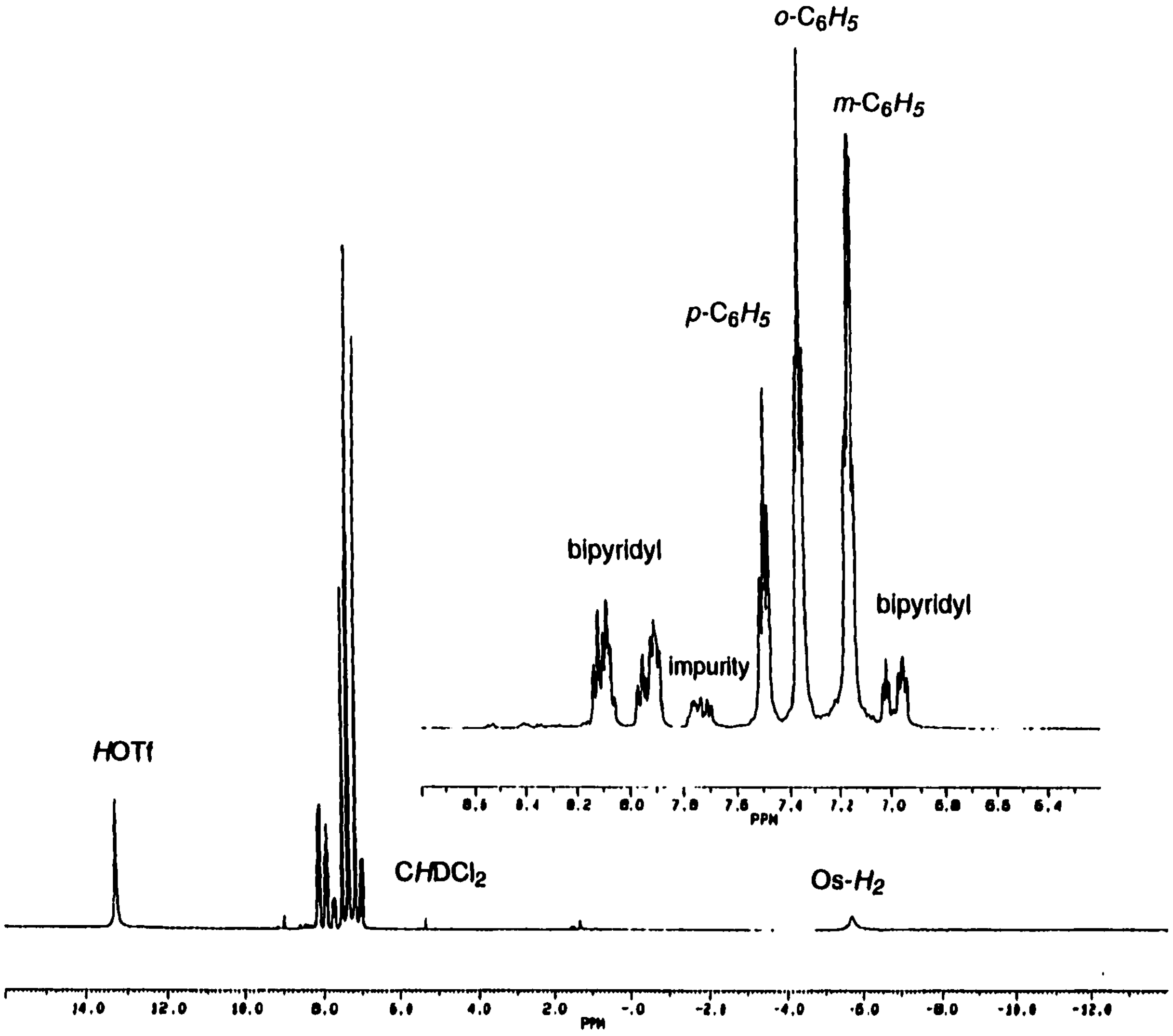


Figure 3.1. ^{1}H NMR spectrum of $[Os(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$ (**3a**) (500 MHz, CD_2Cl_2).

H-P coupling. An investigation of the T_1 of the hydride resonance as a function of temperature shows that at 500 MHz a minimum value of 15.2 ms is reached at 263 K.

The previously unknown analogues, $[Os(H_2)(PMePh_2)_2(bpy)(CO)]^{2+}$ (**3b**), $[Os(H_2)(PPh_3)_2(phen)(CO)]^{2+}$ (**10a**), and $[Ru(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$ (**6a**), were prepared from the hydride monocations under similar conditions. As expected, the properties of the protonated dications **3b** and **10a** are very similar to **3a**. The slight increase in basicity of the phosphine ligands and the size of the chelating ligand are manifested in slight changes in chemical shifts in the ^{1}H NMR spectra ($\delta(H_2)$ -6.23 for **3b** and -5.63 for **10a**) and changes in chemical shifts in the ^{31}P{aromatic ^{1}H} NMR spectra (δ -6.02 for **3b** and +8.60 for **10a**). The T_1 minimum of the H_2 resonance in **3b** was found to be 16.5 ms (500 MHz, 260 K) which is slightly longer than that found in **3a**, and suggests a slightly longer H-H bond (*vide infra*). Due to contributions to the relaxation rate arising from the effects caused by interactions with the magnetic field (Chapter 4), a variable temperature T_1 study of the H_2 resonance of **10a** was performed in a magnetic field of 4.70 T (^{1}H: 200 MHz). A minimum T_1 value of 6.3 ms at 200 K was observed which extrapolates to 15.8 ms at 500 MHz.

The ^{1}H and ^{31}P{aromatic ^{1}H} NMR spectra for the ruthenium analogue, **6a**, are similar to the other dihydrogen dications and are most consistent with the same structural assignment as a dihydrogen complex. The ^{1}H NMR spectrum exhibits an H_2 resonance at δ -6.70 ($\Delta\nu_{1/2}$ = 110 Hz) and in the ^{31}P{aromatic ^{1}H} NMR spectrum a single resonance at δ +32.81 ($\Delta\nu_{1/2}$ = 12.6 Hz). However, **6a** is not as robust as the other dications. In fact, **6a** will irreversibly lose H_2 at room temperature, but appears to be relatively stable for longer periods (> 2 months) when stored at -28 °C. The ^{31}P{aromatic ^{1}H} NMR spectrum (in CD_2Cl_2) indicates that the decomposition of **6a** results initially with the formation of the chloride cation, $[RuCl(PPh_3)_2(bpy)(CO)]OTf$, and several other complexes that have not been identified. The irreversible loss of H_2 at room temperature made it necessary to investigate the T_1 of the H_2 resonance at a lower magnetic field. The T_1 minimum of the H_2 resonance was found to be 3.9 ms (200 MHz, 240 K), which extrapolates to a value of 9.8 ms at 500 MHz, an indication of a shorter H-H bond in the H_2 ligand than what is observed for **3a,b** and **10a**.

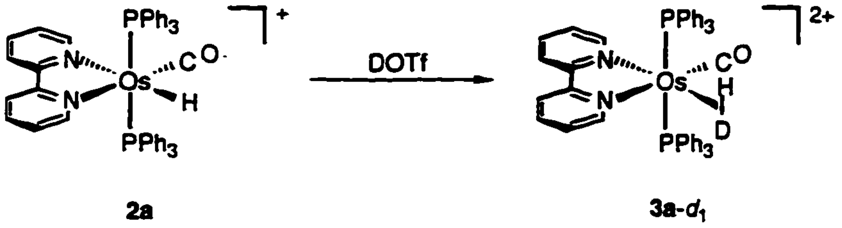
Table 3.1. NMR Properties of the Dicationic Dihydrogen Complexes.

compound		^{1}H δ^a ($\Delta\nu_{1/2}$)^c	T_1 minimum	^{31}P δ^b ($\Delta\nu_{1/2}$)^c
$[Os(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$	(**3a**)	-5.78 (170)	15.2 ms (263 K, 500 MHz)	+8.54 (6.5)
$[Os(H_2)(PMePh_2)_2(bpy)(CO)]^{2+}$	(**3b**)	-6.23 (41)	16.5 ms (260 K, 500 MHz)	-6.02 (8.4)
$[Os(H_2)(PPh_3)_2(phen)(CO)]^{2+}$	(**10a**)	-5.63 (39)	6.3 ms (200 K, 200 MHz)	+8.60 (7.0)
$[Ru(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$	(**6a**)	-6.70^d (110)	3.9 ms (240 K, 200 MHz)	+32.81^d (12.6)

[a] ^{1}H NMR chemical shift of the H_2 resonance in ppm. [b] ^{31}P NMR chemical shift in ppm. [c] Half-height line width in Hz. [d] Recorded at 253 K.

Partial Deuterium Incorporation into $[M(H_2)(PR_3)_2(N\text{-}N)(CO)]^{2+}$ [M = Os, N-N = bpy, PR_3 = PPh_3, $PMePh_2$ (3a,b); M = Ru, N-N = bpy, PR_3 = PPh_3 (6a); M = Os, N-N = phen, PR_3 = PPh_3 (10a)]. A common route for partial incorporation of deuterium into the H_2 ligand of dihydrogen complexes is to expose the complex to deuterium for a few hours or a few days.[4,5] A sealed NMR tube containing **3a** in methylene chloride-d_2 and 1 atm of D_2 was monitored for a period of 2 weeks. A similar sample was prepared containing **6a** in methylene chloride-d_2 with 1 atm of D_2 and stored at -28 °C and monitored by NMR for a period of 2 months. No evidence of deuterium incorporation was observed by ^{1}H and ^{31}P NMR spectroscopy in either sample, indicating that even though **3a** and **6a** are extremely acidic (*vide infra*), the H_2 ligand is not labile.

The HD complex **3a**-d_1, was prepared by addition of excess deuterated triflic acid (DOTf) to a solution of **2a** in CD_2Cl_2 (Scheme 3.2).



Scheme 3.2

The hydride region of the ^1H NMR spectrum of **3a**-d_1 exhibits a sharp "triplet" resonance, as opposed to the broad singlet in **3a**. The intensity ratio of the three resonances is *ca.* 1:1.2:1, with a separation of 25.3 Hz. This intensity ratio was unexpected since coupling to two equivalent ^{31}P nuclei would give a 1:2:1 triplet, whereas coupling to a single deuteron would give three lines with the intensity ratio 1:1:1. The $^1H\{^{31}P\}$ NMR spectrum of **3a**-d_1 is identical to the spectrum recorded without phosphorus decoupling, an indication that the coupling is not due to the phosphines. When the ^{31}P\{aromatic ^1H\} NMR spectrum of **3a**-d_1 is recorded at 81 MHz a single resonance is observed. However, at 202 MHz a second resonance is clearly visible which is separated from the major resonance by +80 ppb. These results are consistent with contamination of **3a**-d_1 by a minor amount of **3a**, arising from the incomplete deuteration of the triflic acid. To confirm this hypothesis, a ^1H NMR 180°-τ-90° inversion recovery pulse sequence experiment was performed on a sample of **3a**-d_1 with a delay, $\tau = T_1(\ln 2)$, designed to null the signal from the minor amount of **3a** present.[14,15] A clean 1:1:1 triplet was obtained confirming H-D coupling (Figure 3.2). The small upfield shift of the HD resonance from the H_2 signal ($\Delta\delta = +18$ ppb) is typical of reported dihydrogen complexes and smaller than what is observed in H_2/HD gas ($\Delta\delta =$

+36 ppb).[16] Consistent with a single structure,[17] we find that the ^{1}H NMR spectra of **3a** and **3a**-d_1 are essentially independent of temperature (including J_{HD} values) down to 165 K.

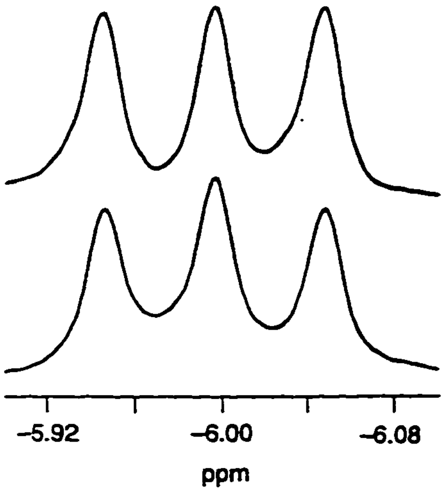


Figure 3.2. ^{1}H NMR (hydride region) of **3a**-d_1 at 298 K (CD_2Cl_2, 500 MHz). The lower trace is the normal spectrum showing the increased intensity of the center resonance due to a minor amount of **3a**. The upper trace is the inverted spectrum of **3a**-d_1 using a 180°-τ-90° pulse sequence with $\tau = 21$ ms. Under these conditions, the signal due to **3a** is nulled.

Similar results were obtained for the other HD complexes which were prepared under comparable conditions with the exception of **6a**-d_1, where the sample was maintained at temperatures of less than 0 °C (Table 3.2).

Table 3.2. Comparison of the HD Complexes.

compound		^{1}H δ_{HD}[a] $\Delta\delta$[b]	J_{HD}[c]	^{31}P δ_{HD}[d] $\Delta\delta$[b]
$[Os(HD)(PPh_3)_2(bpy)(CO)]^{2+}$	(**3a**-d_1)	-6.01 +18 ppb	25.3	+7.89 +80 ppb
$[Os(HD)(PMePh_2)_2(bpy)(CO)]^{2+}$	(**3b**-d_1)	-6.32 +20 ppb	25.5	-6.30 +99 ppb
$[Os(HD)(PPh_3)_2(phen)(CO)]^{2+}$	(**10a**-d_1)	-5.72 < +20 ppb	25.5	+8.36 +81 ppb
$[Ru(HD)(PPh_3)_2(bpy)(CO)]^{2+}$	(**6a**-d_1)	-6.84[e] < +20 ppb	31.0[e]	+32.45[e] +40 ppb

[a] ^{1}H NMR chemical shift of the HD resonance (ppm). [b] Chemical shift difference between the H_2 and HD resonances (δ_{H_2} - δ_{HD}). [c] Measured at 500 MHz (Hz). [d] ^{31}P NMR chemical shift (ppm). [e] Measured at 265 K.

Basicity of $[MH(PPh_3)_2(bpy)(CO)]^+$ [M = Os, Ru (2a, 5a)]. The hydride monocations were found to be very weak bases in that excess triflic acid (HOTf) is required to generate the dication species completely, as determined by the ^{1}H and ^{31}P NMR spectra. When the dications are exposed to weak bases such as diethyl ether or water, they are immediately deprotonated to regenerate the hydride monocations. We have found the dicationic complexes to be soluble only in methylene chloride and nitromethane. Protonation of the hydride monocations by other strong acids produces varying results as shown in Tables 3.3 and 3.4.

Table 3.3. Protonation of $[OsH(PPh_3)_2(bpy)(CO)]^+$ (**2a**) with Various Strong Acids to Produce $[Os(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$ (**3a**).[a]

Acid	# of equiv	% **2a**	% **3a**
HOTf	2.2	50	50
	3.8	5	95
	5.6	0	100
$[H(Et_2O)]BF_4$	3.3	> 99	trace
	10.0	25	75
$[H(Et_2O)_x]BAr'_4$	8.6	100	0

[a] Relative concentrations were determined by integration of the resonances in the $^{31}P\{aromatic\ ^1H\}$ NMR spectra recorded at 298 K.

Table 3.4. Protonation of $[RuH(PPh_3)_2(bpy)(CO)]^+$ (**5a**) with Various Strong Acids to Produce $[Ru(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$ (**6a**).[a]

Acid	# of equiv	% **5a**	% **6a**
HOTf	3.5	trace	> 99
	7.0	0	100
$[H(Et_2O)]BF_4$	2.0	92	8
	4.0	49	51
	10.0	10	90

[a] Samples prepared and maintained at temperatures of 195–265 K and relative concentrations were determined by integration of the resonances in the $^{31}P\{aromatic\ ^1H\}$ NMR spectra recorded at 265 K.

The data indicate that the monohydride cations **2a** and **5a**, are extremely weak bases and are similar in strength to OTf^-. A large excess of the protonated etherate, $[H(Et_2O)]BF_4$ will only partially generate the dications, presumably due to the presence of diethyl ether. No evidence of the dication **3a** was observed when $[H(Et_2O)_x]BAr'_4$ (Ar' = 3,5-$(CF_3)_2C_6H_3$) was used due to the larger amount of diethyl ether associated with the acid and the water that is inevitably present.[18]

A direct comparison of basicity was performed in an NMR tube with equimolar amounts of **2a** and **5a**. Incremental amounts of HOTf were added and the percentages of the cations and dications were determined by ^{31}P NMR spectroscopy. The data indicate that the ruthenium complex **6a** is slightly more acidic than the osmium analogue **3a** (Table 3.5).

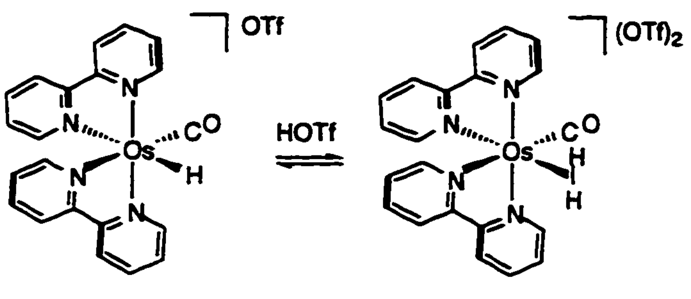
Table 3.5. Protonation Comparison of $[OsH(PPh_3)_2(bpy)(CO)]^+$ (**2a**) and $[RuH(PPh_3)_2(bpy)(CO)]^+$ (**5a**) with Triflic Acid.[a]

# of equiv of HOTf	% **2a**	% **3a**	% **5a**	% **6a**
1	100	0	100	0
2	58	42	79	21
3	16	84	40	60
4	0	100	0	100

[a] Samples prepared and maintained at temperatures of 195–265 K and relative concentrations were determined by integration of the resonances in the $^{31}P\{aromatic\ ^1H\}$ NMR spectra recorded at 222 K.

Various attempts to isolate the dication **3a** were unsuccessful. Addition of pentane to a methylene chloride solution of **3a** resulted in precipitation of a gummy residue. NMR spectra of this residue show it to consist of **3a** and HOTf. Repeated additions of methylene chloride followed by pentane resulted in the hydride monocation **2a** being regenerated. When a methylene chloride solution of **3a** is placed under dynamic vacuum, an oily film is observed with the removal of solvent. The ^1H and ^{31}P NMR spectra indicate that only **3a**, **2a** and HOTf are present. There is no evidence of any product that involves the loss of H_2.

Synthesis and Protonation of $[OsH(bpy)_2(CO)]^+$ (7). The closely related species, $[OsH(bpy)_2(CO)]^+$ (7), was prepared as the triflate salt (Chapter 2).[19] The protonated dication **8** can be generated in either a methylene chloride or nitromethane solution of **7** with excess HOTf (Scheme 3.3).



7 8

Scheme 3.3

The hydride resonance in the ^{1}H NMR spectrum of **8** in nitromethane-d_3 is a broad singlet at -4.2 ppm. The aromatic region in the ^{1}H NMR spectra for **7** and **8** exhibit sixteen resonances, indicating that the two bipyridyl ligands remain inequivalent, consistent with the structures shown in Scheme 3.3. A T_1 study of the hydride resonance as a function of temperature shows a minimum of 12 ms at 230 K at 500 MHz (in CD_2Cl_2). The partially deuterated analogue, **8**-d_1 was prepared and a sharp "triplet" in the hydride region appears with a J_{HD} value of 29.0 Hz. The intensity of the central resonance is slightly increased due to a small contamination of **8** resulting from the incomplete deuteration of the DOTf. The small isotope shift and the H-D coupling do not appear to be temperature dependent. Complex **8** is less thermally robust than **3a**. We have found that **8** is stable in methylene chloride-d_2 at room temperature as a dihydrogen species for less than a day before forming the metal triflate complex as noted by Meyer and coworkers.[19] The loss of H_2 from **8** will also occur in a period of 1 to 2 weeks when the sample is stored at -28 °C. In contrast to the extremely acidic nature of the bisphosphine complexes, **8** is unaffected by the presence of diethyl ether but will be deprotonated to regenerate **7** with the addition of water.

Discussion

Characterization of the Complexes as Dihydrogen Species. Complex **3a**(PF_6) was structurally characterized by Meyer and coworkers as a dihydride of Os(IV).[10] This assignment was based on limited spectroscopic data due to the poor solubility of **3a**(PF_6). Their data indicate that no major rearrangement of the ancillary ligands occurs upon protonation. However, their assignment of the structure as a dihydride dication is inconsistent with our new data.

The mixed acidic solvent, HOTf/CF_3COOH, has many drawbacks for the study of this particular complex. This solvent system only allows the exploration of the spin-lattice relaxation at temperatures that are above the temperature of the T_1 minimum. Trifluoroacetic acid also provides a stronger base, CF_3COO^-, that allows for proton exchange with the dication that not only results in increased broadness in the ^1H and ^{31}P NMR spectra, it also makes the observation of the HD complex **3a**(PF_6)-d_1 highly unlikely. Meyer and coworkers observed that when deuterated trifluoroacetic acid was used in the solvent system, no hydride resonance was observed in the ^1H NMR spectrum. When the hydride cation was regenerated by deprotonation, the hydride resonance was one-eighth of its original intensity. This is in agreement with the large excess of deuterium in the solvent pool. The most prevalent species under these conditions would be **3a**(PF_6)-d_2 due to proton/deuteron exchange with the solvent and would not show any H-D coupling.

We find that protonation of **2a**(PF_6) in nitromethane results in the product, **3a**(PF_6), remaining soluble. However, the properties of this solvent are not conducive to low temperature NMR spectroscopy (freezing point of CH_3NO_2 = -29 °C). The accessibility of lower temperatures was accomplished by preparing samples of **3a**(PF_6) in nitromethane-d_3 and adding methylene chloride-d_2 (volume ratios of CD_3NO_2:CD_2Cl_2 were typically 1:9). For ease of preparation and avoidance of possible errors resulting from concentration effects, a single solvent system was desired. We anticipated that the preparation of the triflate salt of **2a** would provide the necessary solubility characteristics by avoiding the mixed anion product that results from the protonation of **2a**(PF_6) by

HOTf. The triflate salt of **3a** and several analogues have been prepared and are soluble in methylene chloride.

The $^{31}P\{aromatic\ ^1H\}$ NMR spectra of these bisphosphine dications display a single sharp resonance for the equivalent phosphines as expected for a *trans* structure. A bound dihydrogen ligand often lacks observable coupling to adjacent bound phosphines.[20] The narrowness of the line widths ($\Delta\nu_{1/2}$) in the $^{31}P\{aromatic\ ^1H\}$ NMR spectra for the bisphosphine dications (6.5–12.6 Hz) imply that any H-P coupling must be less than 3 Hz. More definitive NMR evidence of a bound dihydrogen ligand is the observation of a large H-D coupling in the partially deuterated analogues. The increased intensity of the center peak of the triplet of the HD resonances are due to the presence of a small amount of the H_2 species, indicating that the isotope effect on the chemical shift of the proton in the HD ligand is very small, and is consistent with the limited data in the literature. This small chemical shift difference and the magnitude of the H-D coupling are essentially independent of temperature, suggesting that there is only one structure for these bisphosphine complexes. A rapid equilibrium between a dihydride and a dihydrogen structure would likely lead to temperature dependent isotope effects resulting from isotopic perturbation of equilibrium.[17] The rapid relaxation shown by the hydride resonance of the dicationic H_2 complexes from the T_1 studies and the observed H-D coupling in the partially deuterated analogues are most consistent with the dications being formulated as dihydrogen complexes.

A related complex, $[Os(H_2)(bpy)_2(CO)]^{2+}$ (**8**), was postulated by Meyer and coworkers[19] as an intermediate in forming a metal triflate species. The structure of **8** was considered to be either a seven coordinate Os(IV) dihydride or a six coordinate Os(II) dihydrogen species but the issue was not further investigated.

The ^1H NMR spectrum of the partially deuterated **8**-d_1 clearly shows a sharp "triplet" in the hydride region indicating a bound dihydrogen ligand with a J_{HD} value of

29.0 Hz. The isotope shift and the H-D coupling appear to be independent of temperature as was observed for the bisphosphine dications, suggesting only one structure for **8**. The H-D coupling of **8**-d_1 and the rapid relaxation of the H_2 resonance in the ^{1}H NMR spectrum is most consistent with the formulation of **8** as a dihydrogen complex.

Determination of the H-H Internuclear Distance. When appropriate crystals for X-ray or neutron diffraction studies are unobtainable, the observation of short spin-lattice relaxation times (T_1 minimum) and/or a large value of the spin coupling in the HD resonance of the partially deuterated complex is taken as good evidence of a bound dihydrogen ligand. The H-H distance (r_{HH}) in the bound H_2 ligand can be determined from the maximum rate of relaxation (minimum value of T_1), assuming that the rate of relaxation is dominated by the homonuclear dipole interaction (Chapter 4). Quantitative analysis by the method of Halpern and coworkers[21] leads to two possible values for the H-H distance in the dihydrogen complexes, depending upon the relative rate of the H_2 ligand rotation.[22] A choice between these two rotation regimes for the determination of the H-H distance can be made based on other data as outlined below.

In reported dihydrogen complexes which have been structurally characterized by neutron diffraction or solid state NMR methods, an inverse correlation between J_{HD} and the H-H distance is observed (Table 3.6 and Figure 3.3).

Table 3.6. Structural and Solution Data for Dihydrogen Complexes.

compound	r_{HH} (Å)	J_{HD} (Hz)	ref.
$Mo(H_2)(CO)(dppe)_2$	0.88 (ss NMR)[a] 0.85 (n)[b,c]	34	23, 24
$W(H_2)(P^iPr_3)_2(CO)_3$	0.89 (ss NMR) 0.82 (n)	33.5	14, 23
$[Fe(H_2)H(dppe)_2]^+$	0.82 (n)	32	25
$[Ir(H_2)H(PPh_3)_2(bq)]^+$	0.94 (ss NMR)	29.5	23
$[Ru(H_2)Cp(CO)(PCy_3)]^+$	0.97 (ss NMR)	28	23
$[Ru(H_2)Cp(dmpe)]^+$	1.02 (ss NMR)	22	23
$[Ru(H_2)Cp^*(dppm)]^+$	1.10 (n)[c]	20.9	26
$Ir(H_2)H(Cl)_2(P^iPr_3)_2$	1.11 (n)	12	27
$[Os(H_2)(en)_2OAc]^+$	1.34 (n)	9.1	28
$Cr(H_2)(P^iPr_3)_2(CO)_3$	0.85 (ss NMR)	35	29
$[Os(H_2)Cl(dppe)_2]^+$	1.22 (n)[d]	13.9	30
$[Mn(H_2)(CO)(dppe)_2]^+$	0.89 (ss NMR)	32	31

[a] ss NMR = solid state NMR. [b] n = neutron diffraction. [c] Distance corrected by the Maverick/Trueblood method.[32] [d] Distance corrected using the rigid-body analysis method.[33]

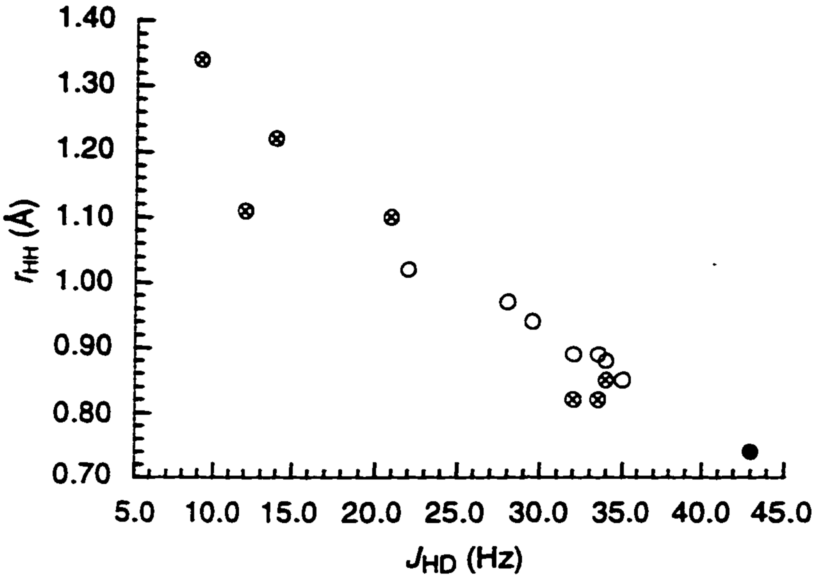


Figure 3.3. Plot of H-H bond length versus J_{HD}. The symbols are as follows: ⊗ = neutron diffraction; o = solid state NMR; ● = HD gas.

Only the bond lengths of the H_2 ligand that are considered to be the most accurate should be included when comparing H-H distances obtained from T_1 studies (using static and fast rotation models). Single crystal neutron diffraction studies of dihydrogen complexes clearly indicate the existence of a bound H_2 ligand. However, the distances obtained from neutron diffraction data can be underestimated by approximately 10% due to the large libration of the H_2 ligand[32] and only the distances corrected for this motion are therefore considered to be accurate. The neutron diffraction study of one complex, $Ir(H_2)H(Cl)_2(P^iPr_3)_2$ has further complications consisting of apparent structural differences in solution versus the solid state in this complex that affect the H-H bond length.[27] The large dipolar couplings between the hydrogen atoms in the H_2 ligand of dihydrogen complexes provide an accurate determination of r_{HH} by solid state NMR (Chapter 4). Figure 3.4 shows the inverse linear relationship between r_{HH} and J_{HD} values for the H-H bond length distances obtained from solid state NMR and corrected neutron diffraction data.[34]

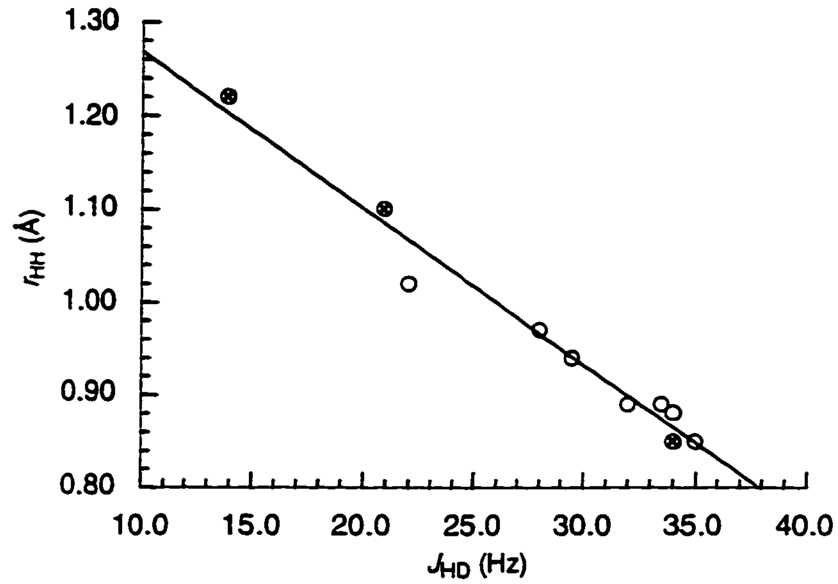


Figure 3.4. Plot of H-H bond length versus J_{HD} shown with a linear fit ($R^2 = 0.9733$). The symbols are as follows: ⊗ = corrected neutron diffraction; o = solid state NMR.

The barrier to rotation around the M-H_2 axis for the complex $W(H_2)(P^iPr_3)_2(CO)_3$ has been determined by inelastic neutron scattering spectroscopy to be lower (1.9–2.2 kcal/mol) than the barrier to molecular tumbling (2.6–3.8 kcal/mol) indicative of fast rotation.[29] However, if the fast rotation model is used in the calculation of the H-H distance in the H_2 ligand for $W(H_2)(P^iPr_3)_2(CO)_3$, unlikely values of 0.76 and 0.77 Å are obtained[35] (the H-H distance in H_2 gas is 0.74 Å). The H-H distance determined from the neutron diffraction study of 0.82 Å (uncorrected)[36] and the distance calculated from solid state NMR of 0.89 Å provide more evidence that the distance obtained from the fast rotation model is inconsistent. Other complexes, $Mo(H_2)(CO)(dppe)_2$, $Cr(H_2)(CO)_3(P^iPr_3)_2$, and $Ir(H_2)(H)_2I(P^iPr_3)_2$ that have short H-H distances (determined by neutron diffraction or solid state NMR studies) and low rotational barriers (determined by inelastic neutron scattering to be *ca.* 0.7, 1.17, and 0.98 kcal/mol, respectively) provide a reasonable minimum H-H distance in a coordinated H_2 ligand (Table 3.7).[37]

Table 3.7. Shortest Measured H-H Distances for Coordinated H_2.

compound	r_{HH} (Å)
$W(H_2)(P^iPr_3)_2(CO)_3$	0.89[a] 0.82[b]
$Mo(H_2)(CO)(dppe)_2$	0.88[a] 0.85[b,c]
$Cr(H_2)(CO)_3(P^iPr_3)_2$	0.86[a]
$Ir(H_2)(H)_2I(P^iPr_3)_2$	0.86[b]

[a] Determined from solid state NMR. [b] Determined from neutron diffraction. [c] Corrected by the Maverick/Trueblood Method.[32]

Gusev and coworkers[38] have analyzed the T_1 minimum and J_{HD} data of reported dihydrogen complexes that have J_{HD} values ≥ 25 Hz. In only a few cases, namely those with the general formula *trans*-$M(H_2)H(P\text{-}P)_2^+$ (M = Fe, Ru; P-P = chelating phosphine), is it necessary to invoke the fast rotation model to produce a reasonable H-H distance in the H_2 ligand. This suggests that when the dominant source of relaxation is due to the homonuclear dipolar interaction, the determination of the H-H distance in the H_2 ligand using T_1 minimum data should consider the rotation around the $M\text{-}H_2$ axis as static.

Based on comparison to the data as shown in Figure 3.4, the observed J_{HD} values and T_1 minima for the dicationic dihydrogen complexes, $[Os(H_2)(PR_3)_2(bpy)(CO)]^{2+}$ (PR_3 = PPh_3, $PMePh_2$) (**3a,b**), $[Os(H_2)(PPh_3)_2(phen)(CO)]^{2+}$ (**10a**), $[Os(H_2)(bpy)_2(CO)]^{2+}$ (**8**), and $[Ru(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$ (**6a**), are in agreement with the static model for the H_2 ligand rotation with calculated H-H distances of 0.95 to 1.04

Å (Figures 3.5 and 3.6). The alternative possibility of rapid rotation would require H-H distances of 0.76 to 0.83 Å, which is inconsistent with the inverse linear relationship depicted in Figure 3.4.

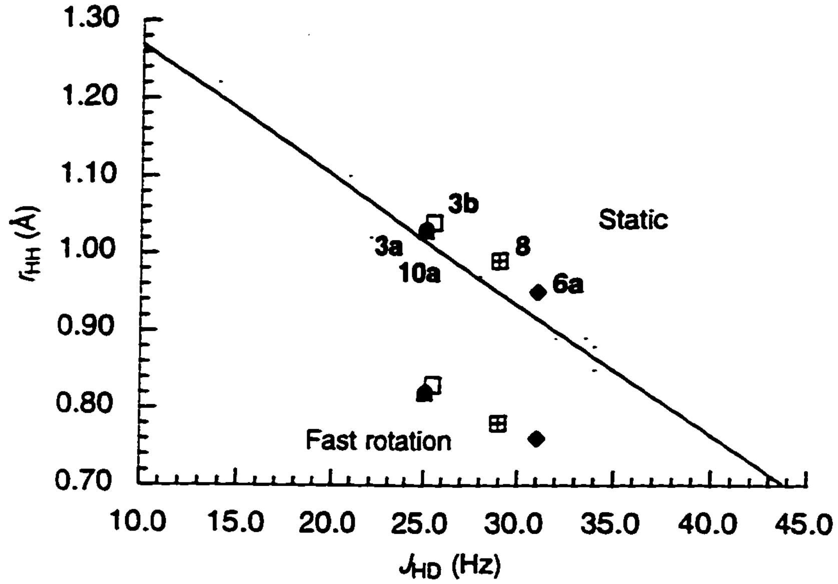


Figure 3.5. Plot of H-H distance versus J_{HD}. The line represents the inverse linear relationship between r_{HH} and J_{HD} values from the corrected neutron diffraction and solid state NMR data (Figure 3.4). H-H distances for the dicationic species, $[Os(H_2)(PR_3)_2(bpy)(CO)]^{2+}$ ($PR_3 = PPh_3$, $PMePh_2$) (**3a,b**), $[Os(H_2)(PPh_3)_2(phen)(CO)]^{2+}$ (**10a**), $[Os(H_2)(bpy)_2(CO)]^{2+}$ (**8**), and $[Ru(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$ (**6a**), are calculated from the T_1 minimum values using static and fast rotation models for the H_2 ligand. The J_{HD} values for **3a**-d_1 and **10a**-d_1 have been corrected for the field dependent D_{HD} (Chapter 4).

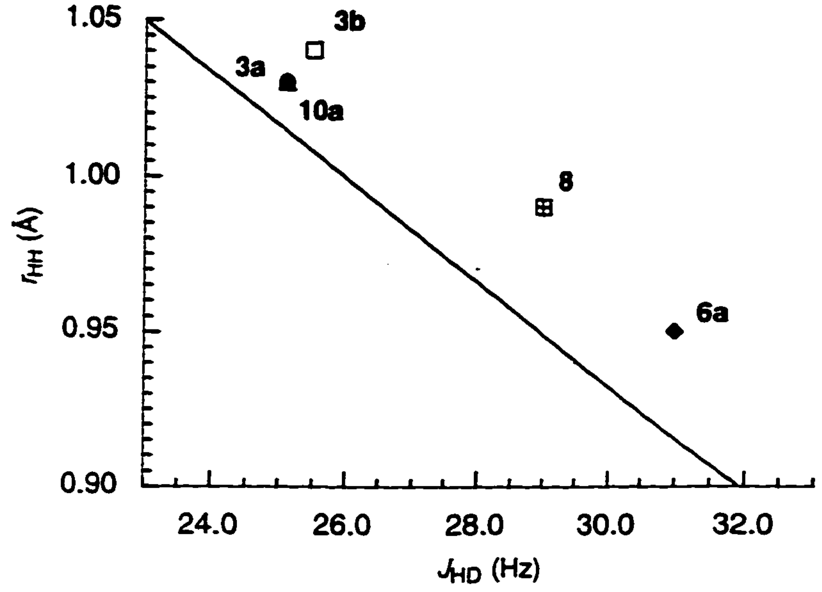


Figure 3.6. Expanded view of Figure 3.5. H-H distance versus J_{HD}. H-H distances calculated from T_1 minimum values of **3a,b**, **6a**, **8**, and **10a** using the static model.

Using the static model, the calculated H-H distances in **3a,b**, **6a**, **8**, and **10a** are slightly overestimated when compared to the corrected neutron diffraction and solid state NMR data (Figure 3.6). The J_{HD} values for **3a**-d_1 and **10a**-d_1 have been corrected for the small residual dipolar coupling (D_{HD}) that is field dependent (Chapter 4).

Alternatively, an empirical method based on the inverse linear relationship between r_{HH} and J_{HD} values would provide a straightforward determination of the H-H bond length in the H_2 ligand. The equation corresponding to the inverse relationship between r_{HH} and J_{HD} from the corrected neutron diffraction and solid state NMR data shown in Figure 3.4 is (eq 3.1):

$$r_{HH} = 1.44 - 0.0168(J_{HD}) \qquad (3.1)$$

Morris and coworkers[12] have used a larger set of distances versus J_{HD} values to develop a similar equation for the H-H bond length. They have also included the uncorrected neutron data and distances determined from X-ray diffraction data along with the most reliable distances from the solid state NMR and corrected neutron data. While X-ray diffraction data can accurately determine distances between heavier atoms, the data suffer from the inability to precisely locate the relatively small electron density due to the hydrogen atoms and inaccurate distances between two hydrogen atoms are obtained. However, with this larger data set the equation is surprisingly similar to eq 3.1 (eq 3.2).

$$r_{HH} = 1.42 - 0.0167(J_{HD}) \qquad (3.2)$$

The determination of the H-H bond lengths in the H_2 ligand of the dications, **3a,b**, **6a**, **8**, and **10a**, by the T_1 minimum method using a static model is in general agreement with the distances calculated from the J_{HD} values (Table 3.8).

Table 3.8. Determination of the H-H Distance in the H_2 Ligand of the Dicationic Dihydrogen Complexes from T_1 Minimum (Fast Rotation and Static Models) and J_{HD} Values of the HD Analogues.

compound		r_{HH} (Å)	
$[Os(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$	**(3a)**	0.82/1.03[a]	1.02[b,c]
$[Os(H_2)(PMePh_2)_2(bpy)(CO)]^{2+}$	**(3b)**	0.83/1.04	1.01
$[Os(H_2)(PPh_3)_2(phen)(CO)]^{2+}$	**(10a)**	0.82/1.03	1.02[c]
$[Ru(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$	**(6a)**	0.76/0.95	0.92
$[Os(H_2)(bpy)_2(CO)]^{2+}$	**(8)**	0.78/0.99	0.95

[a] H-H distance calculated from the T_1 minimum values for fast rotation/static regimes of the H_2 ligand. [b] H-H distance calculated from the J_{HD} value of the HD complex and eq 3.1. [c] Distance calculated from the corrected J_{HD} value (Chapter 4).

The slight overestimation of the bond length by the T_1 minimum method using the static model (< 4% in these complexes) was also reported for $W(H_2)(P^iPr_3)_2(CO)_3$. The longer distances obtained from solution data are believed to be manifested in the torsional and vibrational motion of the $M\text{-}H_2$ fragment that would affect the T_1 minimum data.[38]

A relatively long H-H distance is also consistent with the tight binding of H_2 to the metal center observed in **3a**. No exchange of D_2 for H_2 occurs in complex **3a** after several weeks of exposure to D_2 at room temperature in methylene chloride-d_2. This result is in contrast to the observations on the neutral tungsten complexes of Kubas[39] and the cationic rhenium analogues[3,4,5] which undergo rapid D_2/H_2 exchange.

The coordination of a dihydrogen ligand to a metal center is considered to result from the σ donation of the dihydrogen molecule to an empty metal orbital and π back-donation from filled metal d orbitals to the σ^* orbital of H_2.[2d] The right combination of both interactions will produce an elongated H-H bond that does not necessarily lead to oxidative addition. In these formally Os(II) and Ru(II) d^6 complexes, formation of the Os(IV) and Ru(IV) dihydride species is presumably disfavored by the 2+ charge on the metal center.

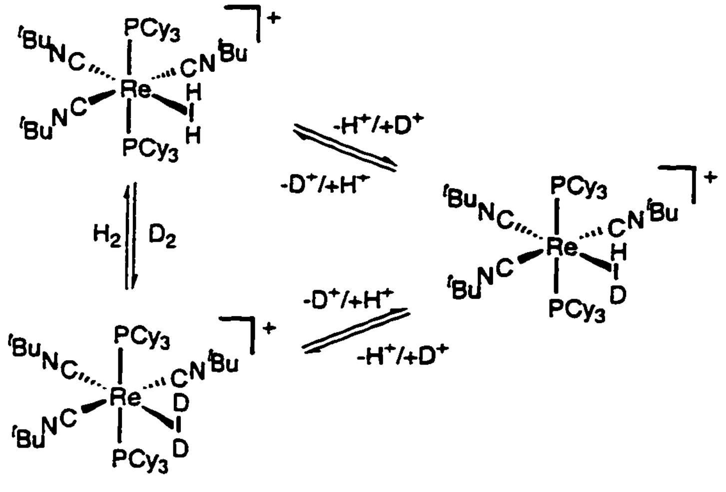
Stability and Acidity of the Dihydrogen Dications. Complex **3a** is remarkably robust in methylene chloride at room temperature. This stability is surprising in light of Morris' ligand additivity study in which it was predicted that both complexes **3a** and **8**, if formulated as dihydrogen complexes, would be unstable with respect to loss of dihydrogen at 25 °C.[40] This prediction was based on the generalization that if the calculated $E_{1/2}$ value of the corresponding N_2 complex was > 2.0 V, the H_2 complex would be unstable at room temperature.[41] The calculated $E_{1/2}$ value for **3a**(N_2) is slightly larger than **8**(N_2) (2.6 V and 2.4 V respectively)[40] and given that **3a** is significantly more acidic than **8**, it would be expected that **3a**, on the basis of this information, would be less stable with respect to H_2 loss than **8**. However, **8** is stable in solution at room temperature for less than a day, while **3a** has been relatively stable in solution at room temperature for over 18 months. The calculated $E_{1/2}$ values for the corresponding N_2 dicationic complexes are shown in Table 3.9.[40,42]

Table 3.9. Calculated $E_{1/2}$ Values of the Dicationic Dinitrogen Analogues of the Dihydrogen Complexes.

compound		$E_{1/2}$ (V)	stability[a]
$[Os(N_2)(PPh_3)_2(bpy)(CO)]^{2+}$	**3a**(N_2)	2.6	stable
$[Os(N_2)(PMePh_2)_2(bpy)(CO)]^{2+}$	**3b**(N_2)	2.6	stable
$[Os(N_2)(PPh_3)_2(phen)(CO)]^{2+}$	**10a**(N_2)	2.6	stable
$[Ru(N_2)(PPh_3)_2(bpy)(CO)]^{2+}$	**6a**(N_2)	2.9	$- H_2$[b]
$[Os(N_2)(bpy)_2(CO)]^{2+}$	**8**(N_2)	2.4	$- H_2$[c]

[a] Stability of the dihydrogen complex with respect to loss of H_2. [b] Irreversible loss of H_2 occurs immediately at room temperature but is stable at lower temperatures. [c] Irreversible loss of H_2 occurs within 24 h at room temperature or within 2 weeks at 245 K.

The preparation of the HD analogues is commonly performed by exposure of the H_2 complex to D_2. The incorporation is proposed to occur by isotopic scrambling due to the combination of the lability and the acidity of the H_2 ligand.[43] The reaction of $[Re(H_2)(PCy_3)_2(CN^tBu)_3]^+$ with D_2 provides experimental evidence for deuterium incorporation by this route (Scheme 3.4).[4]

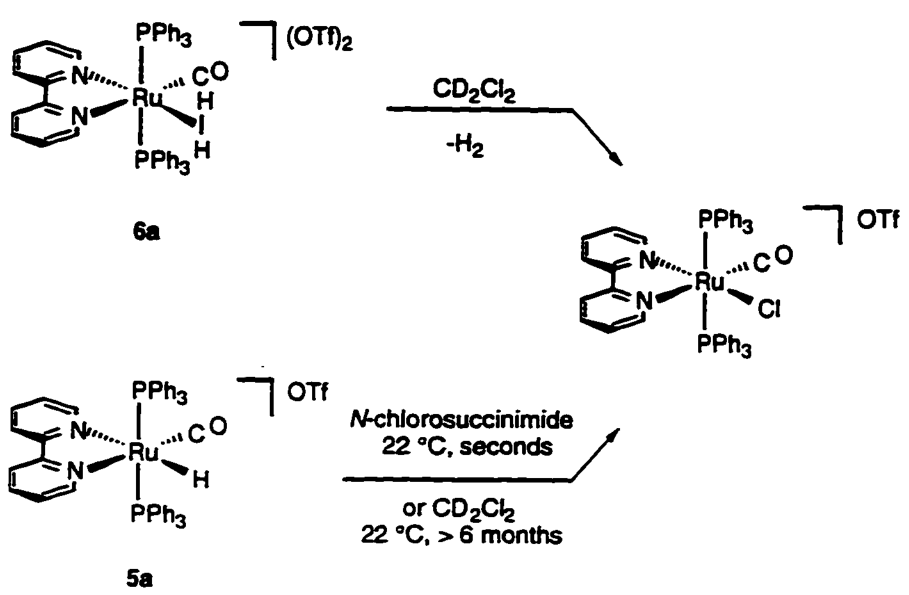


Scheme 3.4

The ^{31}P NMR spectra show that the resonance corresponding to the D_2 species, $[Re(D_2)(PCy_3)_2(CN^tBu)_3]^+$ grows in before the resonance for $[Re(HD)(PCy_3)_2(CN^tBu)_3]^+$ appears. Samples of **3a** and **6a** were exposed to D_2 for extended periods with no observable deuterium incorporation indicating that the H_2 ligand is not labile.

The presence of a nonlabile dihydrogen ligand in the osmium bisphosphine dications (or the ruthenium analogue if maintained at low temperatures) has a beneficial experimental aspect. When the HD complex is generated in the presence of an excess of DOTf there is no proton/deuteron exchange with the weak base OTf^- and no isotopic scrambling occurs. This allows the preparation of samples that can be studied over long periods, thereby removing possible errors arising from concentration effects and other variables when different samples are used to study the effects of different magnetic fields on the H-D coupling (Chapter 4).

The instability of $[Ru(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$ (**6a**) with respect to H_2 loss at room temperature in comparison with the osmium analogues is consistent with the observed trend in the iron triad as noted by Morris and coworkers[44] and also in the complexes, $[M(H_2)(dppp)_2(CO)]^{2+}$ (M = Ru, Os) by Mezzetti and coworkers.[13] The H-H distance in the H_2 ligand of **6a**, as determined by T_1 minimum and J_{HD} data, is shorter than the distance in the osmium analogues, indicative of a weaker M-H_2 interaction. The loss of H_2 from **6a** presumably generates the highly reactive 16-electron Lewis acid, $[Ru(PPh_3)_2(bpy)(CO)]^{2+}$ which can abstract chloride from the solvent (CD_2Cl_2) forming the chloride cation, $[RuCl(PPh_3)_2(bpy)(CO)]^+$ (Scheme 3.5).

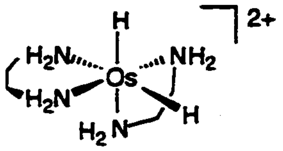


Scheme 3.5

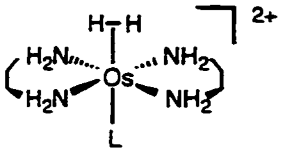
The chloride cation can also be generated from the monohydride cation $[RuH(PPh_3)_2(bpy)(CO)]^+$ (**5a**) either by the immediate and quantitative reaction with *N*-chlorosuccinimide or by a slow reaction with the methylene chloride-d_2 solvent over a period in excess of six months (Chapter 2). The generation of a similar chloride cation was observed by Mezzetti and coworkers[13] in the decomposition of $[Ru(H_2)(dppp)_2(CO)]^{2+}$.

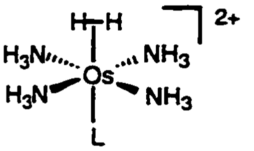
It is important to note that the protonation of the monohydride cations were performed in methylene chloride-d_2 and assignment of pK_a values would be qualitative at best.[45] Morris and coworkers have attempted to assign pK_a values to complexes in nonaqueous solvents and subsequently extrapolate to aqueous pK_a values.[46,47] Unfortunately, due to the extreme acidity of these complexes, the assignment of specific pK_a values cannot reasonably be made. Qualitatively, these complexes, **3a,b**, **6a**, and **10a**, are extremely acidic since they will protonate diethyl ether ($[H(Et_2O)]^+$ pK_a = -2.6)[48] and are similar in strength to HOTf (estimated aqueous pK_a = -4.9).[45,49,50]

Comparison to Other Dicationic Dihydrogen Complexes. In 1971, Taube and coworkers reported the synthesis and characterization of an osmium complex that they originally formulated as a dihydride, *cis*-$[Os(H)_2(en)_2]^{2+}$ (en = ethylenediamine).[9] The ^1H NMR spectrum revealed two separate amine resonances in equal intensity which was structurally interpreted as a *cis* configuration.

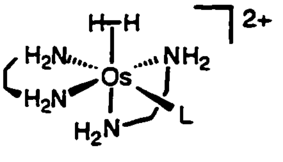


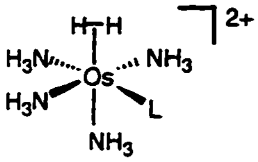
Further research with this system and the analogous $[Os(H_2)(NH_3)_4L]^{2+}$ (L = various neutral ligands or solvent) provided the evidence that a *trans* configuration is the correct formulation for these complexes.[7]



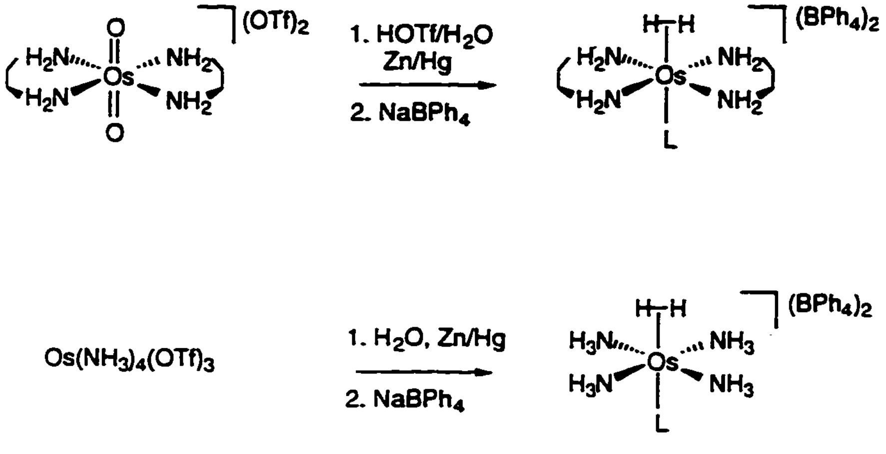


The separate amine proton resonances arise from the different magnetic environments that exists above and below the equatorial plane in the bis(ethylenediamine) complex. Depending on the nature of the ligand L, a *trans* to *cis* isomerization will usually occur at room temperature over the course of a few hours or days.[8] The observation of this isomerization provided the basis for the correct structural configuration assignment. In the bis(ethylenediamine) complexes, the lower symmetry in the *cis* isomer leads to the doubling of the number of amine resonances as well as the number of methylene resonances compared to the *trans* isomer. In the ^1H NMR spectrum of the tetraammine complex after isomerization, the 12 ammine protons appear in a ratio of 2:1:1, the pattern expected for a *cis* configuration.





The synthetic route to these dihydrogen complexes is quite different from the other dicationic complexes. The formation of the dihydrogen complex is the result of the reduction of the bis(ethylenediamine)dioxo osmium(VI) complex, $[Os(O)_2(en)_2]^{2+}$, or the tetraammine osmium(III) complex, $Os(NH_3)_4(OTf)_3$ (Scheme 3.6).



Scheme 3.6

The ligand L *trans* to the H_2 ligand in these dicationic (when L is neutral) or monocationic (when L is anionic) complexes is quite labile and can be exchanged readily by changing the solvent or by the addition of a reagent that will displace the coordinated ligand or solvent molecule. However, in contrast with the ligand L, the H_2 ligand is quite nonlabile and partial incorporation of deuterium into the H_2 ligand is accomplished by the addition of a trace amount of HOTf to a solution of the complex in D_2O. The dihydrogen species are unusually weak acids and there are no monohydride analogues of these complexes known. In fact, when these complexes are exposed to a variety of bases there is no reaction. However, the addition of a very strong base will lead to decomposition.

The data indicate that the presence of a π-acid ligand tends to compete for the d_π electron density and reduces the back-bonding to the H_2 ligand resulting in larger J_{HD} values (shorter H-H bond lengths) (Table 3.10). In the presence of a strong π-acid, such as benzyl isonitrile, the competition for this π electron density is severe and loss of H_2 is observed.

Table 3.10. Properties of the Dicationic Dihydrogen Complexes by Taube.[7,8]

compound	L	T_1 minimum	J_{HD} (Hz)[f]	$E_{1/2}$ (V)[h]
$[Os(H_2)(NH_3)_4L]^{2+}$	pyridine[a]	38 ms[c,d] 28 ms[c,e]	19.6[d] 20.2[e]	0.8
	imidazole[a]	63 ms[c,d]	17.1[d]	0.7
	D_2O[b]	77 ms[c,d]	8.1[d]	0.6
$[Os(H_2)(en)_2L]^{2+}$	pyrazine[a]	[g]	21.1[d] 18.6[e]	0.9
	pyridine[b]	[g]	19.2[d] 18.1[e]	0.8
	pyridine[a]	32 ms (212 K)[d] 27 ms (215 K)[e]	19.0[d] 18.0[e]	0.8
	MeCN[a]	54 ms (233 K)[d] 41 ms (243 K)[e]	17.7[d] 18.5[e]	0.9
	NH_3[a]	[g]	14.0[d] 14.8[e]	0.6
	D_2O[b]	[g]	8.8[d]	0.6

[a] In acetone-d_6 at 400 MHz. [b] In D_2O at 400 MHz. [c] No temperature of the T_1 minimum reported. [d] *trans* isomer. [e] *cis* isomer. [f] J_{HD} of the HD complex. [g] No T_1 minimum reported. [h] $E_{1/2}$ of the N_2 analogue.

The H-H bond distances in the elongated H_2 ligands in these complexes determined from T_1 minimum data using the fast rotation and static models and the J_{HD} values of the corresponding HD complexes are shown in Table 3.11.

Table 3.11. H-H Distances in the H_2 Ligand Determined by T_1 Minimum Data (Fast Rotation/Static Models) and J_{HD} Values (of the HD Complexes) for the H_2 Complexes by Taube.

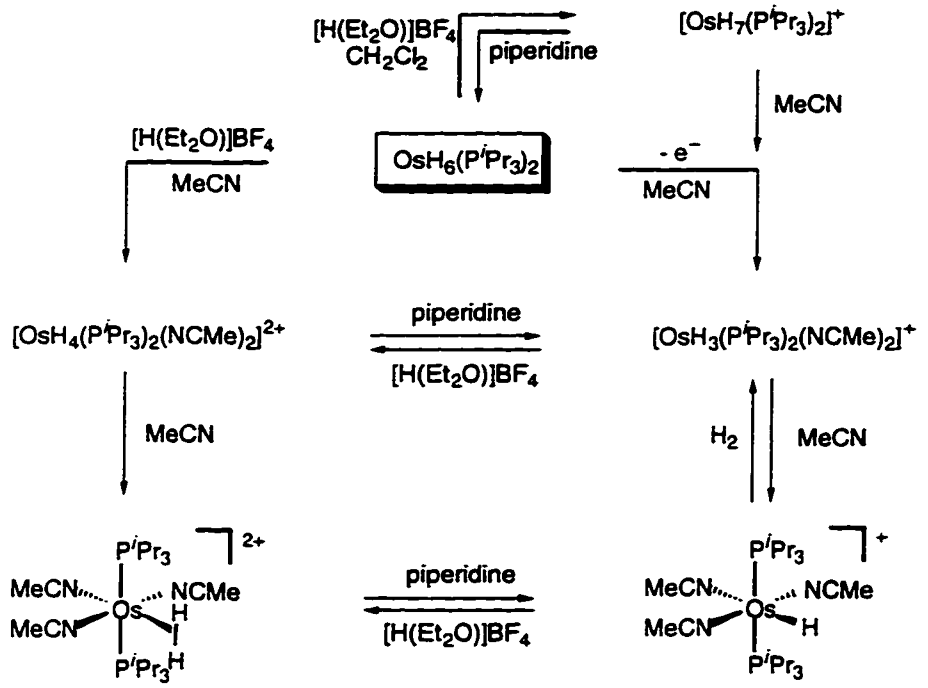
compound	L		r_{HH} (Å)		
$[Os(H_2)(NH_3)_4L]^{2+}$	pyridine	*trans*	0.99[a]	1.24[b]	1.11[c]
		cis	0.94	1.18	1.10
	imidazole	*trans*	1.07	1.35	1.15
	D_2O	*trans*	1.11	1.40	1.31
$[Os(H_2)(en)_2L]^{2+}$	pyrazine	*trans*			1.09
		cis			1.13
	pyridine	*trans*			1.12
		cis			1.14
	pyridine	*trans*	0.96	1.21	1.12
		cis	0.93	1.17	1.14
	MeCN	*trans*	1.05	1.32	1.14
		cis	1.00	1.26	1.13
	NH_3	*trans*			1.20
		cis			1.19
	D_2O	*trans*			1.29

[a] Distance determined from T_1 minimum fast rotation model. [b] Distance determined from T_1 minimum static model. [c] Distance determined from J_{HD} of the HD complex.

It is important to note that there does not seem to be a strong correlation between the rotation model and J_{HD} for these complexes with elongated H_2 ligands.

Tilset, Caulton and coworkers[11] reported on the electrochemical oxidation of $OsH_6(P^iPr_3)_2$ in acetonitrile that results in the loss of H_2 and produces the trihydride cation, $[OsH_3(P^iPr_3)_2(NCMe)_2]^+$. If the protonation of $OsH_6(P^iPr_3)_2$ is performed in methylene chloride, the product is $[OsH_7(P^iPr_3)_2]^+$. When the solvent is replaced with acetonitrile, loss of H_2 occurs and once again, $[OsH_3(P^iPr_3)_2(NCMe)_2]^+$ is formed. The protonation of this cationic species or the neutral complex, $OsH_6(P^iPr_3)_2$, in acetonitrile results in the formation of a dicationic complex, $[OsH_4(P^iPr_3)_2(NCMe)_2]^{2+}$. The T_1

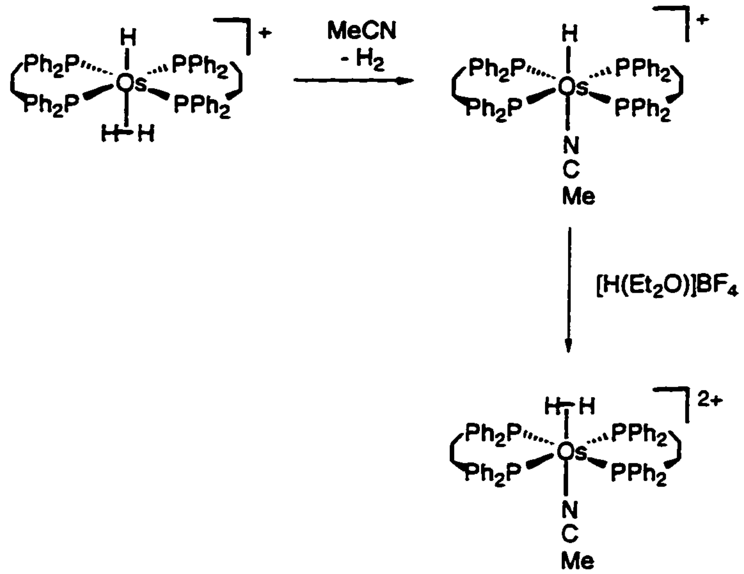
minimum is consistent with a complex that has either one or two dihydrogen ligands. This dication is easily deprotonated when exposed to piperidine to reform the trihydride cation. Deuterium incorporation into this dication, $[OsH_4(P^iPr_3)_2(NCMe)_2]^{2+}$, was insufficient to observe H-D couplings. The dication will undergo further reaction in solution and slowly convert to form another dicationic species, $[Os(H_2)(P^iPr_3)_2(NCMe)_3]^{2+}$. This dihydrogen dication can also be generated by the protonation of the monohydride cation that results from the loss of H_2 from the trihydride cation, $[OsH_3(P^iPr_3)_2(NCMe)_2]^+$ (Scheme 3.7).



Scheme 3.7

The trihydride cation can be readily protonated but it reportedly shows no tendency to deprotonate when exposed to a Brønsted base, such as triethylamine, which is often indicative of the absence of an H_2 ligand. The characterization of the dication $[Os(H_2)(P^iPr_3)_2(NCMe)_3]^{2+}$, as a dihydrogen complex is due to a rapid spin-lattice relaxation rate (short T_1 minimum) and a large J_{HD} value of the HD analogue. The dication will readily deprotonate when exposed to piperidine to reform the monohydride cation. Attempts to isolate the dication with diethyl ether led to the precipitation of the monohydride cation.

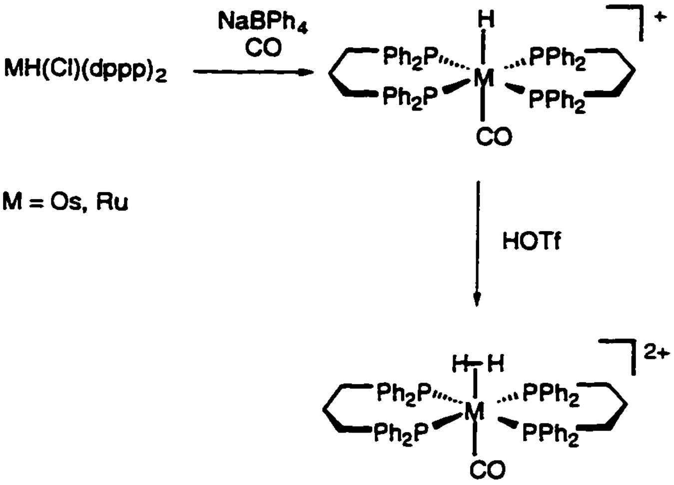
Morris and coworkers[12] reported that the dihydrogen hydride cation complex, $[Os(H_2)H(dppe)_2]^+$ (dppe = 1,2-bis(diphenylphosphino)ethane) will lose H_2 in acetonitrile and coordinate a solvent molecule forming $[OsH(dppe)_2(NCMe)]^+$. The protonation of $[OsH(dppe)_2(NCMe)]^+$ produces the dihydrogen dication complex, $[Os(H_2)(dppe)_2(NCMe)]^{2+}$ (Scheme 3.8).



Scheme 3.8

The short T_1 minimum and large J_{HD} value are consistent with its characterization as a dihydrogen complex. The partial deuterium incorporation was accomplished by exposure of a methylene chloride-d_2 solution of the dication to D_2 over several days. When a methylene chloride-d_2 solution of the dication was exposed to H_2, no incorporation was observed, establishing the source of the partial incorporation of deuterium as the D_2. The protonation of the cation can be successfully completed using $[H(Et_2O)]BF_4$, but when the resultant dication is exposed to an excess of diethyl ether or water, it is immediately deprotonated and the monohydride cation is regenerated.

Recently, Mezzetti and coworkers[13] have reported osmium and ruthenium dihydrogen dicationic complexes with a strong π-acid CO *trans* to the H_2 ligand, $[M(H_2)(dppp)_2(CO)]^{2+}$ (M = Ru, Os; dppp = 1,3-bis(diphenylphosphino)propane). The monohydride carbonyl cations are created by a substitution reaction of $MH(Cl)(dppp)_2$ with $NaBPh_4$ under a CO atmosphere. The dications are extremely acidic and are only produced when the monohydride carbonyl cations are treated with an excess of HOTf under dry conditions (Scheme 3.9).



Scheme 3.9

There is no reaction of $[MH(dppp)_2(CO)]^+$ with $[H(Et_2O)]BF_4$, even when 5 equiv are used for protonation. When an excess of HOTf is added to a methylene chloride-d_2 solution of $[RuH(dppp)_2(CO)]^+$ at room temperature, gas evolution occurs immediately. The ^{31}P NMR spectrum indicates a series of products are formed including $[RuCl(dppp)_2(CO)]^+$. The ruthenium dihydrogen dication is only observable at low temperatures, but the osmium dihydrogen dication is stable at room temperature under Ar or H_2. Isolation attempts of either complex resulted in decomposition.

Table 3.12. Properties of the Acidic Dicationic Dihydrogen Complexes.

compound		T_1[a]	J_{HD}[b]	$E_{1/2}$[c]	r_{HH}[d]	stability[e]
$[Os(H_2)(P^iPr_3)_2(NCMe)_3]^{2+}$		20.7 ms[f]	25.5	1.9	1.01	[g]
$[Os(H_2)(dppe)_2(NCMe)]^{2+}$		35 ms[h]	21.4	2.1	1.08	H_2/D_2[i]
$[Os(H_2)(bpy)_2(CO)]^{2+}$	**8**	12 ms	29.0	2.4	0.95	24 h[j]
$[Os(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$	**3a**	15.2 ms	25.1[k]	2.6	1.02	stable
$[Os(H_2)(PMePh_2)_2(bpy)(CO)]^{2+}$	**3b**	16.5 ms	25.5	2.6	1.01	stable
$[Os(H_2)(PPh_3)_2(phen)(CO)]^{2+}$	**10a**	15.8 ms	25.1[k]	2.6	1.02	stable
$[Os(H_2)(dppp)_2(CO)]^{2+}$		13.8 ms[l]	32.0	2.7	0.90	stable
$[Ru(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$	**6a**	9.8 ms	31.0[m]	2.9	0.92	$-H_2$
$[Ru(H_2)(dppp)_2(CO)]^{2+}$		12.5 ms[l]	34.2[n]	3.0	0.87	$-H_2$

[a] T_1 minimum extrapolated to 500 MHz. [b] J_{HD} of the HD complex (Hz). [c] $E_{1/2}$ of the N_2 analogue (V). [d] Calculated from the J_{HD} value of the HD complex (Å). [e] Stability with respect to loss of H_2 at room temperature. [f] Reference 11. [g] Not reported. [h] Reference 12. [i] Exchanges slowly with D_2. [j] Loss of H_2 occurs after 24 h. [k] Corrected J_{HD} value. [l] Reference 13. [m] Measured at 253 K. [n] Measured at 193 K.

Although ligand exchange is slow, the complexes $[Os(H_2)(PR_3)_2(bpy)(CO)]^{2+}$ ($PR_3 = PPh_3$, $PMePh_2$) (**3a,b**), $[Ru(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$ (**6a**), and $[Os(H_2)(PPh_3)_2(phen)(CO)]^{2+}$ (**10a**) are strong acids, as demonstrated by their immediate deprotonation by a variety of bases, including diethyl ether. Thus **3a,b**, **6a**, and **10a** along with the recently reported complexes by Mezzetti and coworkers,[13] $[M(H_2)(dppp)_2(CO)]^{2+}$ (M = Ru, Os) represent an interesting combination of high reactivity towards heterolysis combined with very tight binding of H_2. In contrast to the properties of this group of dihydrogen dications, highly acidic dihydrogen complexes such as $[Ru(H_2)Cp^*(CO)_2]^+$ are very labile with respect to loss of H_2,[15] and the dicationic H_2 complexes such as $[Os(H_2)(NH_3)_4L]^{2+}$ and $[Os(H_2)(en)_2(L)]^{2+}$ reported by Taube and coworkers,[6,8] which tightly bind H_2, are not acidic. The two other dicationic complexes, $[Os(H_2)(P^iPr_3)_2(NCMe)_3]^{2+}$ by Tilset/Caulton and coworkers[11] and

$[Os(H_2)(dppe)_2(NCMe)]^{2+}$ by Morris and coworkers[12] represent an intermediate level of reactivity towards heterolysis and binding of the H_2 ligand. The two complexes, while strongly acidic, are fully generated by the protonation of the hydride monocation with $[H(Et_2O)]BF_4$, which does not occur for the other extremely acidic dications due to the presence of diethyl ether. The lability of the H_2 ligand has been demonstrated in the generation of the HD complex, $[Os(HD)(dppe)_2(NCMe)]^{2+}$ by slow, reversible H_2/D_2 ligand exchange. Due to the similarity in the properties of the two complexes, $[Os(H_2)(P^iPr_3)_2(NCMe)_3]^{2+}$ may also show reversible H_2 loss comparable with $[Os(H_2)(dppe)_2(NCMe)]^{2+}$.

Conclusion

The complexes $[Os(H_2)(PR_3)_2(bpy)(CO)]^{2+}$ ($PR_3 = PPh_3$, $PMePh_2$) (**3a,b**), $[Ru(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$ (**6a**), $[Os(H_2)(bpy)_2(CO)]^{2+}$ (**8**), and $[Os(H_2)(PPh_3)_2(phen)(CO)]^{2+}$ (**10a**) are best formulated as dihydrogen complexes, not as dihydrides as originally suggested by Meyer and coworkers for **3a**(PF_6).[10] Determination of the H-H distance (r_{HH}) in the H_2 ligand of dihydrogen complexes by the T_1 minimum method should in most cases utilize the static model of the rotation regime of the H_2 ligand. A more straightforward determination can be achieved through the use of an empirical inverse linear relationship between the J_{HD} value of the HD complex and r_{HH}. The acidity of the dihydrogen dicationic complexes and the stability of the H_2 ligand does follow the trend as predicted by the calculated redox potential of the analogous dinitrogen complexes. However, the complexes show a very strong M-H_2 interaction as evident by the long H-H distances and the nonlability of the H_2 ligand, which is primarily due to the σ donation from the ligand because of the high redox potential of the complexes. The upper limit of the redox potential with respect to H_2 loss for the dihydrogen dications appears to be in the vicinity of 3 V (2.9 V for **6a**(N_2) and 3.0 V for $[Ru(N_2)(dppp)_2(CO)]^{2+}$).

Experimental

General procedures. The general procedures followed are outlined in Chapter 2. Deuterated trifluoromethanesulfonic acid (DOTf) was prepared by reacting equimolar quantities of trifluoromethanesulfonic anhydride and D_2O which was deoxygenated by three freeze-pump-thaw cycles and stored under Ar. $[H(Et_2O)_x](BAr'_4)$ was prepared following published procedures.[51]

$[Os(H_2)(PPh_3)_2(bpy)(CO)](OSO_2CF_3)_2$ (3a). In a typical protonation reaction, CD_2Cl_2 (0.5 mL) was vacuum transferred to an NMR tube that was charged with **2a** (20 mg, 0.02 mmol). Trifluoromethanesulfonic acid (HOTf) (10 µL, 0.1 mmol) was added via syringe under Ar. The sample was degassed (freeze-pump-thaw, 3 cycles) and sealed under vacuum. ^1H NMR (CD_2Cl_2): δ 13.28 (s, *H*OTf), 8.13–6.96 (m, 8 H, bipyridyl), 7.49 (t, 6 H, J_{HH} = 7.4 Hz, *p*-P(C_6H_5)$_3$), 7.36 (t, 12 H, J_{HH} = 7.5 Hz, *o*-P(C_6H_5)$_3$), 7.16 (dt, 12 H, J_{HH} = 6.3 Hz J_{HH} = 6.3 Hz, *m*-P(C_6H_5)$_3$), -5.78 (s, 2 H, Os(H_2), $\Delta\nu_{1/2}$ = 170 Hz, T_1 min = 15.2 ms (263 K, 500MHz)). $^{31}P\{aromatic\ ^1H\}$ NMR (CD_2Cl_2): δ 8.54 (s, $\Delta\nu_{1/2}$ = 6.5 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 175.6 (*C*O), 155.0, 154.6, 154.3, 141.8, 141.3, 125.5, 125.3 (bipyridyl), 133. 2 (t, J_{CP} = 5.2 Hz, *o*-C_6H_5), 132.9 (s, *p*-C_6H_5), 130.2 (t, J_{CP} = 5.2 Hz, *m*-C_6H_5), 126.1 (t, J_{CP} = 28.7 Hz, *ipso*-C_6H_5), 119.3 (q, J_{CF} = 238.0 Hz, OSO_2CF_3).

$[Os(HD)(PPh_3)_2(bpy)(CO)](OSO_2CF_3)_2$ (3a-d_1). Prepared as above for **3a** using deuterated trifluoromethanesulfonic acid (DOTf). ^1H NMR (CD_2Cl_2): δ 11.60 (s, *H*OTf), 8.08–6.96 (m, 8 H, bipyridyl), 7.52 (t, 6 H, J_{HH} = 7.2 Hz, *p*-P(C_6H_5)$_3$), 7.37 (t, 12 H, J_{HH} = 7.2 Hz, *o*-P(C_6H_5)$_3$), 7.12 (dt, 12 H, J_{HH} = 6.0 Hz, J_{HH} = 6.2 Hz, *m*-P(C_6H_5)$_3$), -6.01 (t, J_{HD} = 25.3 Hz, Os(*HD*), Δδ = +18 ppb). $^{31}P\{$aromatic $^1H\}$ NMR (CD_2Cl_2): δ +7.89 (s, Δδ = +80 ppb).

[Os(H_2)($PMePh_2$)$_2$(bpy)(CO)](OSO_2CF_3)$_2$ (3b). In a typical protonation reaction, CD_2Cl_2 (0.5 mL) was vacuum transferred to an NMR tube that was charged with **2b** (8 mg, 0.01 mmol). Trifluoromethanesulfonic acid (HOTf) (6 μL, 0.07 mmol) was added via syringe under Ar at 195 K. The sample was degassed (freeze-pump-thaw, 3 cycles) and sealed under vacuum. ^1H NMR (CD_2Cl_2): δ 11.87 (s, *H*OTf), 8.46–7.03 (m, 28 H, bipyridyl and $PCH_3(C_6H_5)_2$), 1.81 (t, 6 H, J_{HP} = 3.8 Hz, $PCH_3(C_6H_5)_2$), -6.23 (s, 2 H, Os(H_2), $\Delta\nu_{1/2}$ = 41 Hz, T_1 min = 16.5 ms (260 K, 500MHz)). ^{31}P NMR (CD_2Cl_2): δ -6.02 (s, $\Delta\nu_{1/2}$ = 8.4 Hz).

[Os(HD)($PMePh_2$)$_2$(bpy)(CO)](OSO_2CF_3)$_2$ (3b-d_1). Prepared as above for **3b** using deuterated trifluoromethanesulfonic acid (DOTf). ^1H NMR (CD_2Cl_2): δ 10.88 (s, *H*OTf), 8.41–7.01 (m, 28 H, bipyridyl and $PCH_3(C_6H_5)_2$), 1.77 (t, 6 H, J_{HP} = 3.8 Hz, $PCH_3(C_6H_5)_2$), -6.32 (t, J_{HD} = 25.5 Hz, Os(*HD*), Δδ = +20 ppb). ^{31}P NMR (CD_2Cl_2): δ -6.30 (s, Δδ = +99 ppb).

[Ru(H_2)(PPh_3)$_2$(bpy)(CO)](OSO_2CF_3)$_2$ (6a). In a typical protonation reaction, CD_2Cl_2 (0.5 mL) was vacuum transferred to an NMR tube that was charged with **5a** (9 mg, 0.01 mmol). Trifluoromethanesulfonic acid (HOTf) (8 μL, 0.09 mmol) was added via syringe under Ar at 195 K. The sample was degassed (freeze-pump-thaw, 3 cycles) and sealed under vacuum. The sample was kept at 195 K until inserted into the precooled NMR probe and spectra were recorded at temperatures less than 273 K. ^1H NMR (CD_2Cl_2, 253 K): δ 12.52 (s, *H*OTf), 8.02–7.01 (m, 8 H, bipyridyl), 7.50 (t, 6 H, J_{HH} =

7.4 Hz, *p*-P(C_6H_5)$_3$), 7.33 (t, 12 H, J_{HH} = 7.7 Hz, *o*-P(C_6H_5)$_3$), 7.08 (dt, 12 H, J_{HH} = 6.5 Hz, J_{HH} = 6.7 Hz, *m*-P(C_6H_5)$_3$), -6.70 (s, 2 H, Ru(H_2), $\Delta\nu_{1/2}$ = 110 Hz, T_1 min = 3.9 ms (240 K, 200 MHz)). ^{31}P{aromatic ^{1}H} NMR (CD_2Cl_2, 253 K): δ 32.81 (s, $\Delta\nu_{1/2}$ = 12.6 Hz).

[Ru(HD)(PPh$_3$)$_2$(bpy)(CO)](OSO$_2$CF$_3$)$_2$ (6a-*d*$_1$). Prepared as above for **6a** using deuterated trifluoromethanesulfonic acid (DOTf). ^{1}H NMR (CD_2Cl_2, 265 K): δ 12.25 (s, *H*OTf), 8.03–7.01 (m, 8 H, bipyridyl), 7.52 (t, 6 H, J_{HH} = 7.0 Hz, *p*-P(C_6H_5)$_3$), 7.35 (t, 12 H, J_{HH} = 6.9 Hz, *o*-P(C_6H_5)$_3$), 7.05 (dt, 12 H, J_{HH} = 5.8 Hz, J_{HH} = 5.8 Hz, *m*-P(C_6H_5)$_3$), -6.84 (t, J_{HD} = 31.0 Hz, Ru(*HD*), Δδ < +20 ppb). ^{31}P{aromatic ^{1}H} NMR (CD_2Cl_2, 265 K): δ 32.45 (s, Δδ = +40 ppb).

[Os(H$_2$)(bpy)$_2$(CO)](OSO$_2$CF$_3$)$_2$ (8). In a typical protonation reaction, **7** (10 mg, 0.01 mmol) was added to an NMR tube and CD_3NO_2 or CD_2Cl_2 (0.5 mL) was vacuum transferred to the solid. HOTf (10 μL) was added via syringe under Ar. The sample was degassed (freeze-pump-thaw, 3 cycles) and sealed under vacuum. ^{1}H NMR (CD_3NO_2): δ 9.61–7.53 (m, 16 H, bipyridyl), -4.23 (s, 2 H, Os(H_2), T_1(min) = 12.1 ms (230 K, 500 MHz)).

[Os(HD)(bpy)$_2$(CO)](OSO$_2$CF$_3$)$_2$ (8-*d*$_1$). Prepared as above for **8** using CD_3NO_2 as the solvent and deuterating with DOTf. ^{1}H NMR (CD_3NO_2): δ 9.62–7.51 (m, 16 H, bipyridyl), -4.23 (t, J_{HD} = 29.0 Hz, Os(*HD*)).

[Os(H$_2$)(PPh$_3$)$_2$(phen)(CO)](OSO$_2$CF$_3$)$_2$ (10a). In a typical protonation reaction, CD_2Cl_2 (0.5 mL) was vacuum transferred to an NMR tube that was charged with **9a** (20 mg, 0.02 mmol). Trifluoromethanesulfonic acid (HOTf) (10 μL, 0.1 mmol) was added via syringe under Ar. The sample was degassed (freeze-pump-thaw, 3 cycles) and sealed under vacuum. ^1H NMR (CD_2Cl_2): δ 11.97 (s, *H*OTf), 8.58 (d, 1 H, J_{HH} = 8.2 Hz), 8.49 (d, 1 H, J_{HH} = 8.2 Hz), 8.44 (d, 1 H, J_{HH} = 4.7 Hz), 8.28 (d, 1 H, J_{HH} = 4.8 Hz), 8.09 (m, 2 H), 7.37 (dd, 2H, J_{HH} = 5.4 Hz, J_{HH} = 5.5 Hz), 7.45 (t, 6 H, J_{HH} = 7.5 Hz, *p*-$P(C_6H_5)_3$), 7.26 (t, 12 H, J_{HH} = 7.3 Hz, *o*-$P(C_6H_5)_3$), 6.94 (dt, 12 H, J_{HH} = 6.0 Hz J_{HH} = 6.1 Hz, *m*-$P(C_6H_5)_3$), -5.63 (s, 2 H, Os(H_2), $\Delta\nu_{1/2}$ = 39 Hz, T_1 min = 6.3 ms (200 K, 200MHz)). $^{31}P\{$aromatic $^1H\}$ NMR (CD_2Cl_2): δ8.60 (s, $\Delta\nu_{1/2}$ = 7.0 Hz).

[Os(HD)(PPh$_3$)$_2$(phen)(CO)](OSO$_2$CF$_3$)$_2$ (10a-d_1). Prepared as above for **10a** using deuterated trifluoromethanesulfonic acid (DOTf). ^1H NMR (CD_2Cl_2): δ 11.47 (s, *H*OTf), 8.58 (d, 1 H, J_{HH} = 8.3 Hz), 8.50 (d, 1 H, J_{HH} = 8.2 Hz), 8.47 (d, 1 H, J_{HH} = 5.3 Hz), 8.20 (d, 1 H, J_{HH} = 5.3 Hz), 8.10 (m, 2 H), 7.36 (dd, 2H, J_{HH} = 5.3 Hz, J_{HH} = 5.3 Hz), 7.45 (t, 6 H, J_{HH} = 7.5 Hz, *p*-$P(C_6H_5)_3$), 7.26 (t, 12 H, J_{HH} = 7.8 Hz, *o*-$P(C_6H_5)_3$), 6.92 (dt, 12 H, J_{HH} = 6.5 Hz, J_{HH} = 6.7 Hz, *m*-$P(C_6H_5)_3$), -5.72 (t, J_{HD} = 25.5 Hz, Os(*HD*), Δδ < +20 ppb). $^{31}P\{$aromatic $^1H\}$ NMR (CD_2Cl_2): δ8.36 (s, Δδ = +81 ppb).

Basicity Measurements of [OsH(PPh$_3$)$_2$(bpy)(CO)](OSO$_2$CF$_3$) (2a) and [RuH(PPh$_3$)$_2$(bpy)(CO)](OSO$_2$CF$_3$) (5a). The individual basicity studies were performed by adding either **2a** (20–22 mg, 0.019–0.021 mmol) or **5a** (20–22 mg, 0.021–0.023 mmol) to an NMR tube equipped with a J. Young Teflon valve. CD_2Cl_2 (0.5 mL) was vacuum transferred to the tube and the solids were dissolved. Incremental amounts of HOTf (4–12 μL) or $[H(Et_2O)]BF_4$ (8–33 μL) were added via gas-tight microsyringe under a flow of Ar and sealed. The basicity study with $[H(Et_2O)_x]BAr'_4$ (Ar' = 3,5-$(CF_3)_2C_6H_3$) (174 mg) and **2a** (21 mg, 0.020 mmol) was performed by adding both solids to a sealable NMR tube and vacuum transferring CD_2Cl_2(0.5 mL) to the solids. The tube was evacuated and flame-sealed. The direct basicity study was prepared by adding

2a (30 mg, 0.029 mmol) and **5a** (28 mg, 0.029 mmol) to an NMR tube equipped with a J. Young Teflon valve. CD_2Cl_2 (0.5 mL) was vacuum transferred to the solids and dissolved. Incremental amounts of HOTf (5–20 μL) were added via a gas-tight microsyringe under a flow of Ar and sealed. The concentrations were obtained from integration of the $^{31}P\{aromatic\ ^{1}H\}$ NMR spectra. Due to the loss of H_2 at room temperature, the basicity measurements involving **5a** were performed at 222 K. Multiple spectra were taken to insure equilibrium conditions.

Notes to Chapter 3.

---

1 Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451-452.

2 Review articles: (a) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913-926. (b) Morris, R. H.; Jessop, P. G. *Coord. Chem. Rev.* **1992**, *121*, 155-289. (c) Crabtree, R. H. *Accts. Chem. Res.* **1990**, *23*, 95-101. (d) Kubas, G. J. *Accts. Chem. Res.* **1988**, *21*, 120-128.

3 Heinekey, D. M.; Schomber, B. M.; Radzewich, C. E. *J. Am. Chem. Soc.* **1994**, *116*, 4515-4516.

4 Heinekey, D. M.; Voges, M. H.; Barnhart, D. M. *J. Am. Chem. Soc.* **1996**, *118*, 10792-10802.

5 Heinekey, D. M.; Radzewich, C. E.; Voges, M. H.; Schomber, B. M. *J. Am. Chem. Soc.* **1997**, *119*, 4172-4181.

6 Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1990**, *112*, 2261-2263.

7 Li, Z.-W.; Taube, H. *J. Am. Chem. Soc.* **1991**, *113*, 8946-8947.

8 Li, Z.-W.; Taube, H. *J. Am. Chem. Soc.* **1994**, *116*, 9506-9513.

9 Malin, J.; Taube, H. *Inorg. Chem.* **1971**, *10*, 2403-2406.

10 Sullivan, B. P.; Lumpkin, R. S.; Meyer, T. J. *Inorg. Chem.* **1987**, *26*, 1247-1252.

11 Smith, K.-T.; Tilset, M.; Kuhlman, R.; Caulton, K. G. *J. Am. Chem. Soc.* **1995**, *117*, 9473-9480.

12 Schalf, M.; Lough, A. J.; Maltby, P. A.; Morris, R. H. *Organometallics* **1996**, *15*, 2270-2278.

13 Rocchini, E.; Mezzetti, A.; Rüegger, H.; Burckhardt, U.; Gramlich, V.; Del Zotto, A.; Martinuzzi, P.; Rigo, P. *Inorg. Chem.* **1997**, *36*, 711-720.

---

14 Kubas, G. J.; Unkefer, C. J.; Swanson, B. I.; Fukushima, E. *J. Am. Chem. Soc.* **1986**, *108*, 7000-7009.

15 Chinn, M.S.; Heinekey, D. M.; Payne, N. G.; Sofield, C. D. *Organometallics* **1989**, *8*, 1824-1826.

16 Evans, D. F. *Chem. Ind.* **1961**, 1960.

17 Heinekey, D. M.; Oldham, W. J., Jr. *J. Am. Chem. Soc.* **1994**, *116*, 3137-3138.

18 Radzewich, C. E., Ph.D. Thesis, University of Washington, 1997.

19 Sullivan, B. P.; Caspar, J. V.; Johnson, S. R.; Meyer, T. J. *Organometallics* **1984**, *3*, 1241-1251.

20 Heinekey, D. M.; Liegeois, A.; van Roon, M. *J. Am. Chem. Soc.* **1994**, *116*, 8388-8389.

21 Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173-4184.

22 Bautista, M. T.; Earl, K. A.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T.; Sella, A. *J. Am. Chem. Soc.* **1988**, *110*, 7031-7036.

23 Zilm, K. W.; Millar, J. M. *Adv. Magn. Opt. Reson.* **1990**, *15*, 163-200.

24 Kubas, G. J.; Burns, C. J.; Eckert, J.; Johnson, S. W.; Larson, A. C.; Vergamini, P. J.; Unkefer, C. J.; Khalsa, G. R. K.; Jackson, S. A.; Eisenstein, O. *J. Am. Chem. Soc.* **1993**, *115*, 569-581.

25 Ricci, J. S.; Koetzle, T. F.; Bautista, M. T.; Hofstede, T. M.; Morris, R. H.; Sawyer, J. F. *J. Am. Chem. Soc.* **1989**, *111*, 8823-8827.

26 Klooster, W. T.; Koetzle, T. F.; Jia, G.; Fong, T. P.; Morris, R. H.; Albinati, A. *J. Am. Chem. Soc.* **1994** *116*, 7677-7681.

27 Albinati, A.; Bakhmutov, V. I.; Caulton, K. G.; Clot, E.; Eckert, J.; Eisenstein, O.; Gusev, D. G.; Grushin, V. V.; Hauger, B. E.; Klooster, W. T.; Koetzle, T. F.;

McMullan, R. K.; O'Loughlin, T. J.; Pélissier, M.; Ricci, J. S.; Sigalas, M. P.; Vymenits, A. B. *J. Am. Chem. Soc.* **1993**, *115*, 7300-7312.

28 Hasegawa, T.; Li, Z.-W.; Parkin, S.; Hope, H.; McMullan, R. K.; Koetzle, T. F.; Taube, H. *J. Am. Chem. Soc.* **1994**, *116*, 4352-5356.

29 Kubas, G. J.; Nelson, J. E.; Bryan, J. C.; Eckert, J.; Wisniewski, L; Zilm, K. *Inorg. Chem.* **1994**, *33*, 2954-2960.

30 Maltby, P. A.;Schlaf, M.; Steinbeck, M.; Lough, A. J.; Morris, R. H.; Klooster, W. T.; Koetzle, T. F.; Srivastava, R. C. *J. Am. Chem. Soc.* **1996**, *118*, 5396-5407.

31 King, W. A.; Luo, X-L.; Scott, B. L.; Kubas, G. J.; Zilm, K. W. *J. Am. Chem. Soc.* **1996**, *118*, 6782-6783.

32 Eckert, J.; Albinati, A.; White, R. P.; Bianchini, C.; Peruzzini, M. *Inorg. Chem.* **1992**, *31*, 4241-4244.

33 Craven, B. M. Program EKRT, University of Pittsburgh, 1992.

34 Also excluded from the calculation is HD gas, since there is no expectation that when coordinated it would produce a linear fit.

35 T_1 minimum values of 5.9 and 6.2 ms at 300 MHz (in CD_2Cl_2 and toluene-d_8 respectively).

36 The distances that have been corrected for the librations of the hydrogen atom in the H_2 ligand have been found to be approximately 10% longer.[32]

37 Eckert, J.; Jensen, C. M.; Koetzle, T. F.; Husebo, T. L.; Nicol, J.; Wu, P. *J. Am. Chem. Soc.* **1995**, *117*, 7271-7272.

38 Gusev, D. G.; Kuhlman, R. L.; Renkema, K. B.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1996**, *35*, 6775-6783.

39 Kubas, G. J.; Burns, C. J.; Khalsa, G. R. K.; Van Der Sluys, L. S.; Kiss, G.; Hoff, C. D. *Organometallics* **1992**, *11*, 3390-3404.

40 Morris, R. H. *Inorg. Chem.* **1992**, *31*, 1471-1478.

41 The $E_{1/2}$ values are determined for the complexes using N_2 in place of H_2 since there is less uncertainty with the binding mode of the N_2 ligand and its effect on the redox potential.[40]

42 Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 1271-1285.

43 Albeniz, A. C.; Heinekey, D. M.; Crabtree, R. H. *Inorg. Chem.* **1991**, *30*, 3632-3632.

44 Schalf, M.; Lough, A. J.; Morris, R. H. *Organometallics* **1993**, *12*, 3808-3809.

45 Kristjánsdóttir, S. S.; Norton, J. R. In Transition Metal Hydrides; Dedieu, A.; Ed.; VCH: New York, 1992, Chapter 9, pp 324-334.

46 Jia, G.; Lough, A. L.; Morris, R. H. *Organometallics* **1992**, *11*, 161-171.

47 Jia, G.; Morris, R. H. *Inorg. Chem.* **1990**, *29*, 581-582.

48 The pK_a of protonated diethyl ether in aqueous sulfuric acid. Perdoncin, G.; Scorrano, G. *J. Am. Chem. Soc.* **1977**, *99*, 6983-6986.

49 Fujinaga, T.; Sakamoto, I *J. Electroanal. Chem.* **1977**, *85*, 185-201.

50 The aqueous pK_a of HOTf has also been estimated to be < -10: (a) Fine, D. A., Ph.D. Thesis, University of Washington, 1996. (b) Cox, R. A.; Krull, U. J.; Thompson, M.; Yates, K. *Anal. Chim. Acta.* **1979**, *106*, 51-57.

51 Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11* 3920-3922.

Chapter 4

NMR Spectroscopy of Transition Metal Dihydrogen Complexes at Very High Field

Introduction

Since the isolation and characterization of the first transition metal dihydrogen complexes,[1] there have been more than 300 complexes reported.[2] Only a very limited number of these have been structurally characterized by neutron diffraction or solid state NMR. The H-H bond length in the H_2 ligand can be measured directly from neutron diffraction studies. However, uncorrected neutron diffraction data can underestimate the H-H bond length by approximately 10% due to large librations of the hydrogen atoms in the H_2 ligand. In solid state NMR, the proximity of the hydrogen atoms in the H_2 ligand of dihydrogen complexes produce large dipolar couplings of hundreds of kilohertz. The dipolar couplings provide for an accurate determination of the H-H bond length, since deviations of a few hundredths of an angstrom in the bond length will cause observable changes of tens of kilohertz in the solid state NMR spectra. When the distances determined from neutron diffraction have been corrected[3] they are in agreement with the distances obtained from solid state NMR spectra. These techniques have provided for accurate measurements of the H-H bond distance in dihydrogen complexes, ranging from 0.85 to 1.22 Å (Chapter 3).[4,5,6]

More routine solution NMR techniques have broader applicability. In solution NMR, a bound H_2 ligand will exhibit a fast spin-lattice relaxation rate (T_1^{-1}). The spin-lattice relaxation rate is comprised of various contributions to the relaxation process, including the homonuclear dipolar interaction, dipolar interactions from ancillary ligands, chemical shift anisotropy (CSA), spin-rotation, quadrupolar interactions, and others.[7]

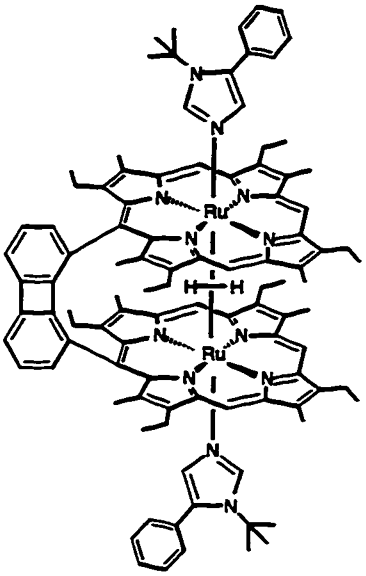
Assuming that the molecule is tumbling isotropically in solution and the rate of relaxation of the dihydrogen ligand is primarily due to the homonuclear dipolar interaction (R_{HH}), the internuclear H-H distance (r_{HH}) can be determined from the observed maximum rate of relaxation (minimum value of T_1).[8]

The characterization of some transition metal dihydrogen complexes have been plague by unobservable T_1 minimum due to line broadening of the H_2 resonance or by solvent restrictions because of the low temperatures. The line broadening may result from a dihydrogen/dihydride equilibrium or from efficient spin-spin relaxation times (T_2) due to the low temperatures. Solution NMR studies of these complexes at higher magnetic fields should therefore benefit from the increased sharpness of the H_2 resonance resulting from increases in T_1 and T_2 along with an increase in the temperature of the T_1 minimum. The higher magnetic fields may allow the observation of a decoalescence of the H_2 resonance if a dihydrogen/dihydride equilibrium is in effect.

There is an increasing amount of empirical[6,9] and theoretical[10] evidence that an inverse relationship exists between the J_{HD} value of the HD complex and r_{HH} (Chapter 3). Determination of r_{HH} from the J_{HD} value has the advantage that correction factors concerning the rotation regime of the dihydrogen ligand and other sources of relaxation do not have to be considered.[11,12] However, the growing availability of NMR spectrometers with high magnetic fields increases the possibility of observing the effects of partial alignment with the magnetic field of the complex in solution. Low temperatures, when combined with relatively high magnetic fields, may enhance the partial alignment, thereby affecting the relaxation data and the observed spin coupling values.

Partial alignment of a transition metal dihydrogen complex with the magnetic field in solution NMR has been observed. Collman and coworkers have reported a unique transition metal dihydrogen compound, $Ru_2(H_2)(DPB)(*Im)_2$ (DPB = 1,8-bis[5-

(2,8,13,17-tetraethyl-3,7,12,18-tetramethyl)porphyrin]biphenylene, *Im = 1-*tert*-butyl-5-phenylimidazole) that has two porphyrin rings that are parallel to each other and perpendicular to the Ru-Ru axis.[13]



The extensive aromatic ring system of this complex provides for a large anisotropic diamagnetic susceptibility leading to a significant degree of alignment in the magnetic field. The partial orientation allows for the observation of residual dipolar H-H and H-D couplings in high field solution NMR spectra of $Ru_2(H_2)(DPB)(*Im)_2$ and $Ru_2(HD)(DPB)(*Im)_2$.

Results and Discussion

High Field Effects on Relaxation Rates. Assuming that the molecule is tumbling isotropically in solution and that the rate of relaxation of the dihydrogen ligand is primarily due to the homonuclear dipolar interaction (R_{HH}), the observed rate of relaxation for a proton is given by eq 4.1.[11]

$$R_{HH} = T_1^{-1} = \frac{3\gamma_H{}^4\hbar^2}{20\pi\, r_{HH}^6}\left\{\frac{\tau_c}{1+\omega^2\tau_c{}^2} + \frac{4\tau_c}{1+4\omega^2\tau_c{}^2}\right\} \qquad (4.1)$$

The rate of relaxation is proportional to the inverse sixth power of the distance between the hydrogen nuclei, therefore the maximum rate of relaxation can be used to calculate the H-H distance in the dihydrogen ligand. Since the Larmor frequency is directly proportional to the strength of the magnetic field, $\omega = \gamma_H B_0$, the maximum rate of relaxation (minimum value of T_1) is expected to occur at higher temperatures with increases in magnetic fields and the T_1 minimum value will also increase in direct proportion with an increase in field (Figure 4.1).

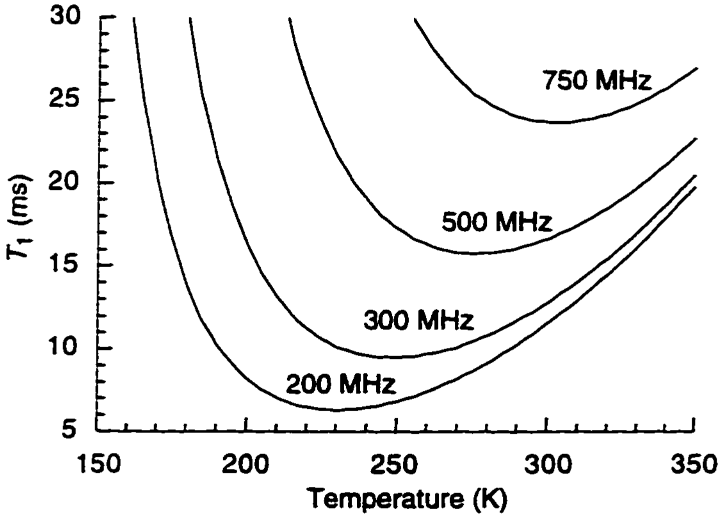
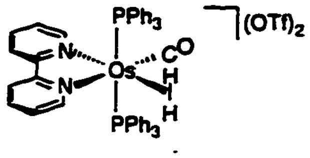


Figure 4.1. Simulated T_1 (ms) versus temperature (K), assuming the homonuclear dipole interaction as the dominant source of relaxation with r_{HH} of approximately 1.00 Å at 200, 300, 500, and 750 MHz.

High Field Effects on the Relaxation Rate of $[Os(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$ (3a). Variable temperature studies of the spin-lattice relaxation (T_1) of the dihydrogen resonance of $[Os(H_2)(PPh_3)_2(bpy)(CO)](OTf)_2$ (**3a**) (bpy = 2,2'-bipyridine; OTf = OSO_2CF_3)[9] were performed in magnetic fields of 11.75 and 17.63 T (^1H: 500 and 750

MHz) to demonstrate the effects of magnetic field strength on the relaxation rate with respect to temperature.



3a

The measured T_1 of the dihydrogen resonance in **3a** exhibits a minimum value of 15.2 ms at 263 K in an 11.75 T field (^1H: 500 MHz). With the assumption that the H_2 ligand is in the slow rotation regime, r_{HH} is calculated to be 1.03 Å.[9] The T_1 minimum of the hydride resonance in the monohydride precursor to **3a**, $[OsH(PPh_3)_2(bpy)(CO)]OTf$ (**2a**) was found to be 500 ms at 247 K (500 MHz). The relaxation of the hydride resonance resulting from the homonuclear dipolar interactions in **2a** must be entirely due to the ancillary coligands and the metal center. This T_1 minimum value indicates that the other dipolar interactions contribute approximately 3% to the rate of relaxation of the protons in the dihydrogen ligand in **3a**.

The T_1 minimum of the dihydrogen resonance of **3a** at 750 MHz is found to be 25.2 ms, which is approximately 10% longer than the expected value of 22.8 ms as extrapolated from the 500 MHz data.[9] Typical error occurring in the measurement of the temperature and the T_1 values accounts for less than half of this observed difference. The temperature of maximum relaxation was found to be essentially identical to that previously reported at 500 MHz (Figure 4.2).[9]

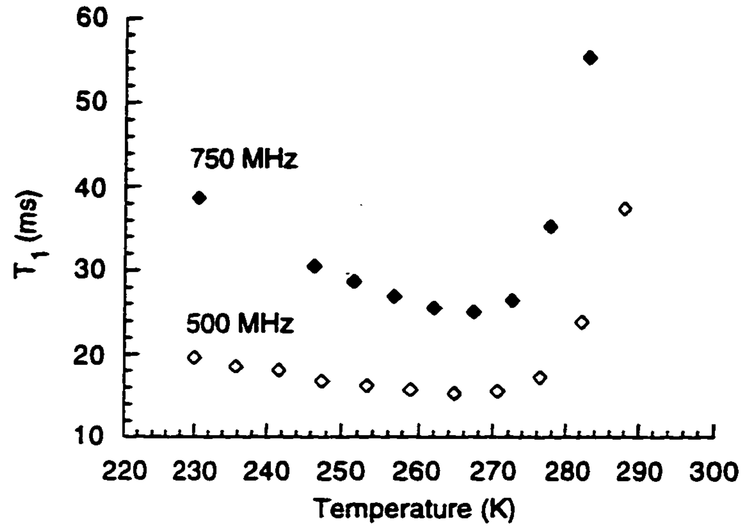


Figure 4.2. Variable temperature relaxation studies of the dihydrogen resonance of $[Os(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$ (**3a**) performed in magnetic fields of 11.75 and 17.63 T (^1H: 500 and 750 MHz) (CD_2Cl_2).

Since the expected increase in temperature of the T_1 minimum did not occur and the T_1 minimum is longer than expected, other sources of relaxation may now be significant and seem to be affecting the observed rate (R_{obs}). The unexpected behavior was manifested by an increase in magnetic field strength, indicating that partial alignment of the molecule with the magnetic field may be occurring.

Chemical Shift Anisotropy Effects on Rates of Relaxation. Anisotropic diamagnetic susceptibilities may provide significant interactions with the magnetic field and affect the relaxation rate if the anisotropic diamagnetic susceptibility is large enough. R_{CSA} is dependent on the square of the magnetic field strength (B_o) and the molecular diamagnetic susceptibility (eq 4.2).[14]

$$R_{CSA} = \frac{\gamma_H^2 B_o^2}{15} (\Delta\chi)^2 \left(1 + \frac{\eta_{CSA}^2}{3}\right) \left\{ \frac{2\tau_c}{1 + \omega^2 \tau_c^2} \right\} \qquad (4.2)$$

Where the quantities $\Delta\chi = \chi_z - (\chi_x + \chi_y)/2$ and $\delta\chi = \chi_x - \chi_y$ are the anisotropy and asymmetry of the diamagnetic susceptibility tensor, respectively and $\eta_{CSA} = 3(\delta\chi)/2(\Delta\chi)$. The molecular axes are chosen such that $|\Delta\chi| > |\delta\chi|$ where x, y, and z represent the molecular axes in relation to the laboratory axes.

The bracketed term involving the correlation time of the molecule will display a similar response to the variations in temperature as the related term for R_{HH} in eq 4.1 and will reach a maximum value when $\omega\tau_c = 1$.[15] However, at low temperatures when the molecule is in the slow rotation regime, $\omega^2\tau_c^2 \gg 1$, and the correlation term reduces to $2/\omega^2\tau_c$, R_{CSA} will actually be independent of field strength since $\omega = \gamma B_o$. At high temperatures when the molecule is in the fast rotation regime, $\omega^2\tau_c^2 \ll 1$, the correlation term reduces to $2\tau_c$ but R_{CSA} will be dependent on the magnetic field. The general shape of the T_1 versus temperature curve due to R_{CSA} will initially decrease with an increase in temperature, reach a minimum and then increase as what is observed for the T_1 versus temperature curve for R_{HH}. However, at low temperatures the curves represented by increasing fields will now converge and at higher temperatures where the relaxation times are field dependent, will possess shorter T_1 values as the field is increased (Figure 4.3).

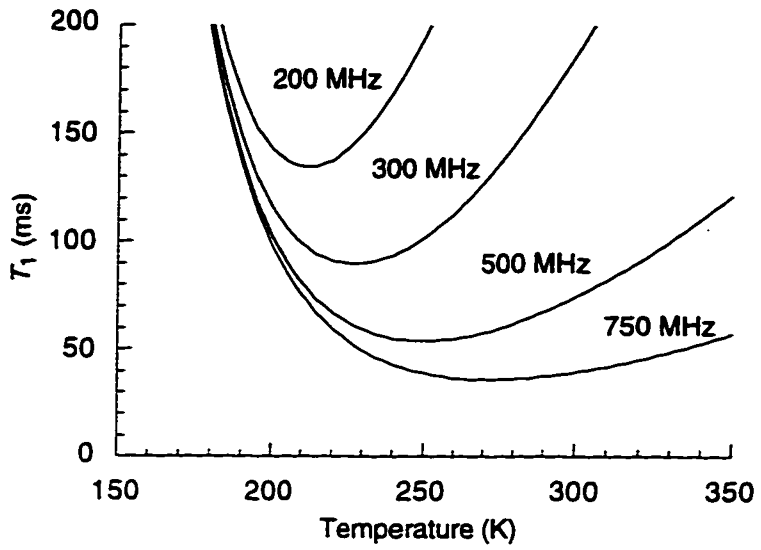


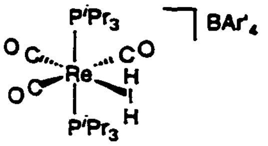
Figure 4.3. Simulated T_1 (ms) versus temperature (K) for CSA contributions to the relaxation rate at 200, 300, 500, and 750 MHz.

Anisotropic Rotational Diffusion. When the non-random reorientation of the molecule is significant, the reduced spectral density function ($J(\omega)$) for the rate of relaxation is given by eq 4.3.[14]

$$J(\omega) = \left\{ \frac{2S^2\tau_c}{1 + \omega^2\tau_c^2} + \frac{2(1 - S^2)\tau}{1 + \omega^2\tau^2} \right\} \tag{4.3}$$

Where S is the anisotropic degree of alignment of the molecule (*vide infra*), $\tau^{-1} = \tau_c^{-1} + \tau_{H_2}^{-1}$, and τ_{H_2} is the correlation time of the rotation of the H_2 ligand around the M-H_2 axis. This will result in having a greater effect on the rate of relaxation when the degree of alignment increases are due to a change in $\Delta\chi$ of the molecule, higher magnetic fields, or lower temperatures (*vide infra*).

High Field Effects on the Relaxation Rates of Related Compounds. To support our contention that partial alignment of $[Os(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$ (**3a**) with the field was affecting R_{obs} rather than uncertainties in measurement, we investigated a similar complex with a ligand environment that lacks significant anisotropic diamagnetic susceptibility ($\Delta\chi$) and a complex with a larger molecular $\Delta\chi$ than **3a**. From the absence of ligands with significant $\Delta\chi$ in $[Re(H_2)(P^iPr_3)_2(CO)_3]BAr'_4$ (**11**) (Ar' = 3,5-$(CF_3)_2C_6H_3$),[16] we would predict that this complex should show no influence due to partial alignment effects on the relaxation rate of the H_2 resonance with variations of the magnetic field strength.



11

T_1 studies of the dihydrogen resonance in **11** as a function of temperature were performed at 500 and 750 MHz. The T_1 minimum at 500 MHz was found to be 9.7 ms. This value extrapolates to an expected T_1 minimum of 14.6 ms at 750 MHz, which matches the observed value. The expected increase in temperature of the T_1 minimum with the increase in field was also observed (Figure 4.4).[17]

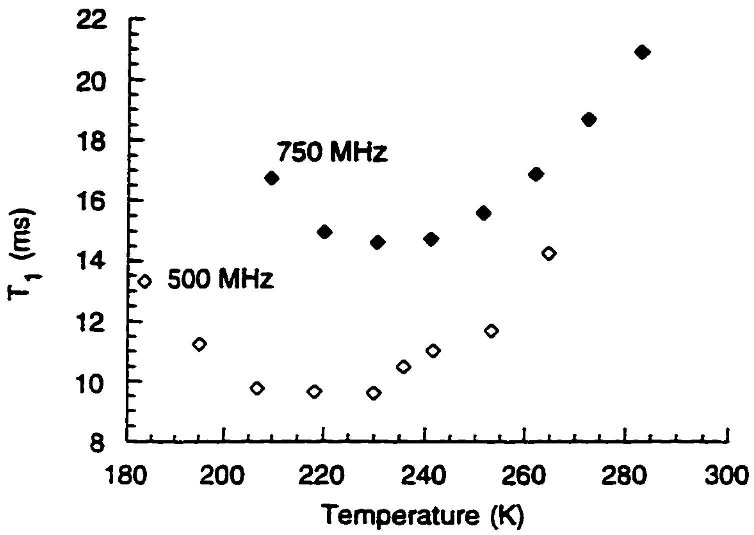
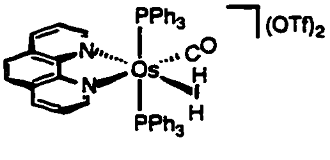


Figure 4.4. Variable temperature relaxation studies of the dihydrogen resonance in $[Re(H_2)(P^iPr_3)_2(CO)_3]^+$ (**11**) performed at 500 and 750 MHz (CD_2Cl_2).

Variable temperature T_1 studies of an analogue of **3a**, $[Os(H_2)(PPh_3)_2(phen)(CO)](OTf)_2$ (**10a**) (phen = 1,10-phenanthroline) were performed in various magnetic fields to investigate the effects caused by an increase in the anisotropic diamagnetic susceptibility due to the phenanthroline ligand.



10a

The observance of double minima at 500 MHz was unexpected, but is consistent with our contention that **10a** should show greater alignment with the field and thus affecting the rate of relaxation. At lower field (200 MHz), the calculated H-H distance in the H_2 ligand from the T_1 minimum value for **10a** is identical, as expected, to the distance determined for **3a** (1.03 Å).[9] However, the flatness of the curve (at 200 MHz) suggests that R_{HH} may not be the dominant interaction, and that the low temperature is enhancing the effects of alignment. At 750 MHz the T_1 data exhibit a curve with a single minimum (Figure 4.5).

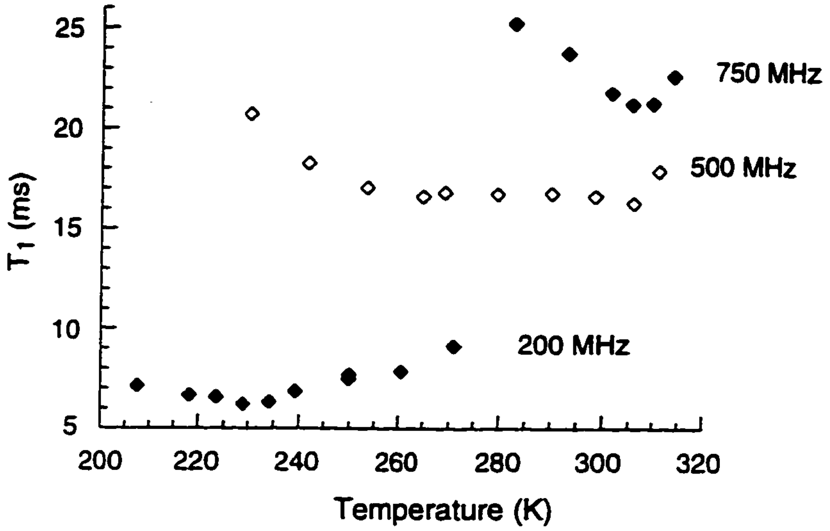


Figure 4.5. Variable temperature relaxation studies of the dihydrogen ligand in $[Os(H_2)(PPh_3)_2(phen)(CO)]^{2+}$ (**10a**) performed at 200, 500, and 750 MHz (CD_2Cl_2).

Solution NMR and the Observation of Dipolar Couplings. Zilm and coworkers have used solid state NMR to measure the dipolar coupling (D_{HH}) of the hydrogen atoms in the H_2 ligand in several transition metal dihydrogen complexes.[4] The H-H bond length in the dihydrogen ligand can be determined with a high degree of accuracy from the dipolar coupling (eq 4.4).[18]

$$\frac{3}{2} D_{HH} = \frac{3\gamma_H^2 h}{8\pi^2 r_{HH}^3} \tag{4.4}$$

Since an internuclear H-H distance of 1 Å produces a dipolar coupling of 120 kHz, deviations of a few hundredths of an angstrom will result in observable changes of tens of kilohertz. In solution NMR, the rapid molecular tumbling normally averages the dipolar tensors with respect to the magnetic field so that the dipolar couplings are not observable. However, an incomplete averaging of the dipolar tensors will result in small residual dipolar couplings that may be observable in solution NMR if the anisotropic degree of alignment, $|S_z|$, is large enough (eq 4.5).[19]

$$S_z = \left\langle \frac{3}{2}\cos^2\theta - \frac{1}{2} \right\rangle = g_2 \frac{\Delta\chi B_0^2}{15kT} \tag{4.5}$$

Where, θ is the angle between the magnetic field direction and the axis of the maximum diamagnetic susceptibility of the molecule, $\Delta\chi$ is the anisotropy of the effective molecular diamagnetic susceptibility, g_2 is a correction factor for intermolecular interactions (in a dilute solution in a solvent where $\Delta\chi = 0$, then $g_2 = 1$), k is the Boltzmann constant, and T is the absolute temperature. The degree of alignment for molecules experiencing random tumbling gives $\langle 3/2 \cos^2\theta - 1/2 \rangle = 0$, but as alignment occurs $\langle 3/2 \cos^2\theta - 1/2 \rangle \neq 0$, with fully oriented molecules having values of -1/2 or +1. Partial alignment of diamagnetic molecules in magnetic fields of 10–14 T typically have $\langle 3/2 \cos^2\theta - 1/2 \rangle$ values of 10^{-6}–10^{-5}.[19] The diamagnetic susceptibilities of aromatic organic compounds have been measured[20] and the molecular anisotropy can be estimated fairly accurately from the sum of the anisotropies of the ligands (eq 4.6), where θ_g is the angle between the molecular z axis and the normal to the plane of the rings.[20a]

$$\Delta\chi = \Sigma\Delta\chi_i \left(\frac{3}{2}\cos^2\theta_g - \frac{1}{2} \right) \tag{4.6}$$

When the molecular axes are such that $\delta\chi \neq 0$, then the asymmetry term for the degree of alignment $(S_x - S_y)$ is shown in eq 4.7.

$$\frac{2}{3}(S_x - S_y) = \left\langle \sin^2\theta \cos 2\phi \right\rangle = \frac{\delta\chi B_0^2}{15kT} \tag{4.7}$$

High field solution ^{1}H NMR spectra of dihydrogen complexes that align with the field may exhibit a residual dipolar coupling of the hydrogen atoms in the H_2 ligand (eq 4.8).[19]

$$D_{HH} = -\frac{\gamma_H^2 h}{2\pi^2 r_{HH}^3}\left[S_z\left(\frac{3}{2}\cos^2\theta_z - \frac{1}{2}\right) + \frac{3}{4}\left(S_x - S_y\right)\left(\sin^2\theta_z \cos 2\phi_{xy}\right)\right] \tag{4.8}$$

Where θ_z and ϕ_{xy} represent the angles between the molecular axes and the H-H internuclear axis. If the line widths are narrow enough, this coupling may be observed as a small splitting of the H_2 resonance with the frequency difference of the doublet given by eq 4.9.[19]

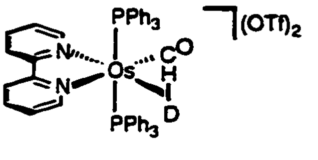
$$\Delta\nu_D = \frac{3}{2} D_{HH} \tag{4.9}$$

The HD resonance in the ^{1}H NMR spectrum of the partially deuterated analogue will exhibit a coupling that is comprised of the field independent spin coupling (J_{HD}) and the field dependent residual dipolar coupling (D_{HD}) given by equation 4.10.[19]

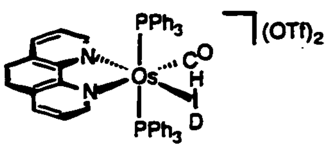
$$\Delta\nu_c = J_{HD} + D_{HD} \tag{4.10}$$

Since the residual dipolar coupling is proportional to the square of the magnetic field strength, the measurement of the H-D coupling at several field strengths allows the straightforward determination of the sign and the magnitude of D_{HD} and the magnitude of J_{HD}. Plotting the total splitting versus the square of the NMR frequency will produce a linear relationship with the intercept of the y axis (zero field) yielding the magnitude of J_{HD}, while the slope of the line affords the sign of the dipolar coupling. Since the one bond J_{HD} (and J_{HH}) is always positive,[7] a negative slope indicates a negative D_{HD} (and D_{HH}) and a positive slope is indicative of a positive value of the dipolar coupling.

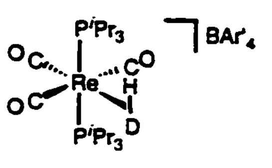
Partial Alignment Observed in HD Complexes. The HD complexes $[Os(HD)(PPh_3)_2(bpy)(CO)](OTf)_2$ (**3a**-d_1), $[Os(HD)(PPh_3)_2(phen)(CO)](OTf)_2$ (**10a**-d_1), and $[Re(HD)(P^iPr_3)_2(CO)_3]BAr'_4$ (**11**-d_1), were studied in several magnetic fields to determine the field dependence of the total splitting of the HD resonance.



3a-d_1



10a-d_1



11-d_1

Since the bidentate ligands are rigidly bound to the metal center, a greater degree of alignment should result at higher fields. Due to the similarity of the complexes, the spin coupling of the HD complexes is expected to be the same for **3a**-d_1 and **10a**-d_1, with only the field dependent residual dipolar coupling exhibiting the influence of alignment with respect to magnetic field strength. The maximum difference in the anisotropic diamagnetic susceptibility ($\Delta\chi$) of these complexes can be estimated by the difference of the measured values of the anisotropic diamagnetic susceptibilities for the bipyridyl and phenanthroline ligands.[21] Assuming the contribution of the triphenylphosphine ligands to the $\Delta\chi$ of the molecule is the same for both complexes and that the molecular z axis is defined by the P–Os–P axis, the maximum difference in the molecular anisotropic diamagnetic susceptibility is 1.34×10^{-28} cm^3 and the maximum difference in S_z is 6.75×10^{-6} measured in a magnetic field of 17.63 T at 298 K. The larger value of $|\Delta\chi|$ of **10a**-d_1 in comparison to **3a**-d_1 is expected to add to the observed effects of alignment. The $[J + D]_{HD}$ of the HD resonance in **3a**-d_1 measured at 750 MHz is 25.52 (±0.02) Hz and in **10a**-d_1 is 25.90 (±0.05) Hz. Careful measurement of the total splitting in other fields allows the determination of the sign and magnitude of the residual dipolar coupling (D_{HD}) and the magnitude of the spin coupling (J_{HD}) for these complexes. The field independent value of J_{HD} is found to be +25.10 Hz in both complexes (Figure 4.6). At

750 MHz the values of D_{HD} in **3a**-d_1 and **10a**-d_1 are +0.42 Hz and +0.80 Hz, respectively. The inverse linear relationship between J_{HD} and r_{HH} allows the H-H distance of the dihydrogen ligand in **3a** and **10a** to be calculated as 1.02 Å (Chapter 3).[22,23]

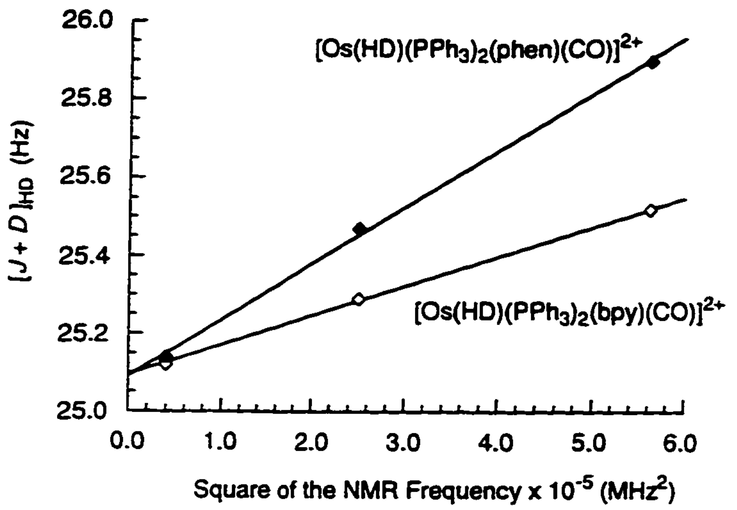


Figure 4.6. Total splitting, $[J + D]_{HD}$, of $[Os(HD)(PPh_3)_2(bpy)(CO)]^{2+}$ (**3a**-d_1) and $[Os(HD)(PPh_3)_2(phen)(CO)]^{2+}$ (**10a**-d_1) versus the square of the NMR frequency. Values of $[J + D]_{HD}$ were measured at 200, 500, and 750 MHz (CD_2Cl_2).

The plot of the total splitting of the HD resonance in $[Re(HD)(P^{i}Pr_3)_2(CO)_3]^+$ (**11**-d_1) versus the square of the NMR frequency is shown in Figure 4.7 and indicates that the magnetic field has no effect on the H-D coupling.

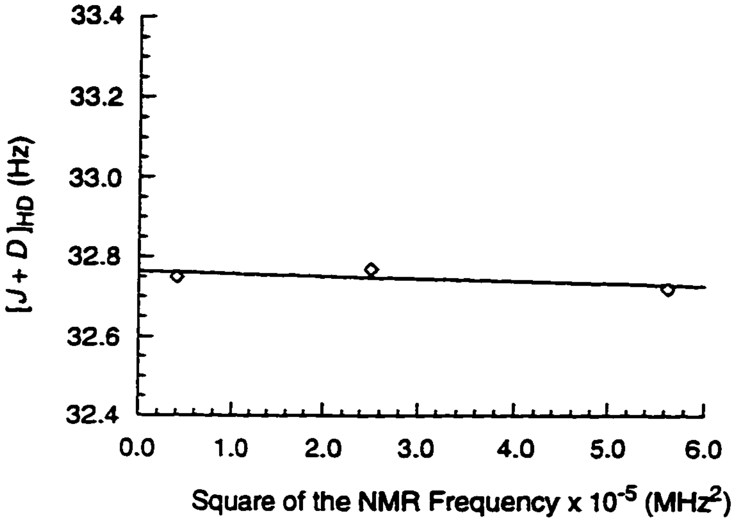
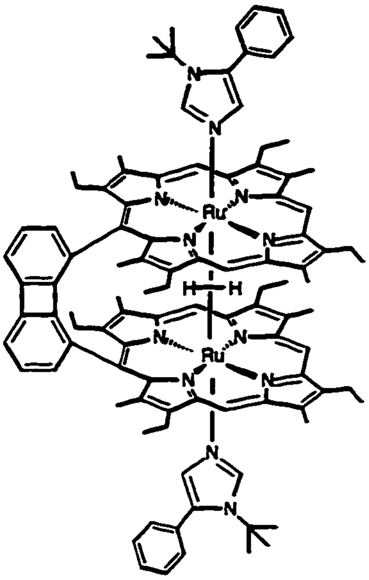


Figure 4.7. Total splitting, $[J + D]_{HD}$, of $[Re(HD)(P^iPr_3)_2(CO)_3]^+$ (**11**-d_1) versus the square of the NMR frequency. Values of $[J + D]_{HD}$ were measured in fields of 200, 500, and 750 MHz (CD_2Cl_2).

We can estimate the residual dipolar coupling of **3a** and **10a** at 750 MHz since D_{HH} should be D_{HD} times γ_H/γ_D or +2.7 Hz for **3a** and +5.2 Hz for **10a**. The splitting of the H_2 resonances in the ^1H NMR spectra are therefore only expected to be 4.1 Hz for **3a** and 7.8 Hz for **10a** at 750 MHz and thus were not detected due to the relatively broad lines observed for the dihydrogen resonances in **3a** and **10a** (line widths are in excess of 70 Hz).

According to equation 4.8, the internuclear H-H distance of the H_2 ligand can be calculated if the anisotropy and asymmetry of the diamagnetic susceptibility of the complex can be accurately ascertained, which allows the measurement of the alignment with the field. This will provide another method for the determination of r_{HH} in the H_2 ligand to verify the distance calculated from T_1 minimum data or from the J_{HD} value of the HD complex. Alternatively, the use of solvents with high viscosity or that have a significant anisotropic diamagnetic susceptibility coupled with the use of chelating ligands that possess a more extensive aromatic system will increase the partial alignment with the magnetic field. This increase in the alignment in the field may be large enough to observe residual dipolar H-H couplings of neighboring protons in the chelating nitrogen ligand in the dihydrogen complex or in the monohydride precursor.[24] The dipolar coupling and the known distance between the protons will provide the magnitude of the alignment parameters in eq 4.8. The alignment parameters can then be used in conjunction with the residual dipolar coupling of the hydrogen atoms in the H_2 ligand in the dihydrogen complex to determine the H-H internuclear distance. However, due to the extreme acidity of **3a** and **10a** (Chapter 3), the choice of solvents is severely limited. The synthetic route to these complexes (Chapter 2) allows the straightforward addition of a variety of chelating ligands so that the size of the aromatic "raft" can be systematically adjusted. Other synthetic routes will need to be developed to provide a template for a dihydrogen complex that will be lower in acidity if a different solvent is necessary to enhance the partial alignment with the magnetic field.

Partial Alignment with the Magnetic Field in Other Reported Dihydrogen Complexes. The extensive aromatic ring system of $Ru_2(H_2)(DPB)(*Im)_2$ prompted Collman and coworkers[13] to study the complex at high field with the expectation that they would be able to observe the effects of partial alignment.



The narrow line width of the dihydrogen resonance enabled the observation of a doublet with a splitting of 7.37 Hz in a 14.57 T field (^{1}H: 620 MHz). Since the splitting of the H_2 resonance is $3D_{HH}/2$, the residual dipolar coupling at 620 MHz is ±4.91 Hz. The determination of the sign of the coupling was accomplished by measuring the field dependency of the H-D coupling of the partially deuterated analogue, $Ru_2(HD)(DPB)(^*Im)_2$. ^{1}H NMR spectra of the HD complex were recorded at varying magnetic fields and the residual H-D dipolar coupling was found to be -0.93 Hz at 620 MHz which also indicated that the sign of D_{HH} is negative.

The orientation of the H_2 ligand with respect to the molecular axis was determined by eq 4.8.[20a] Due to the symmetry of the complex, the asymmetry degree of alignment term $(S_x - S_y) = 0$ and θ_z is the angle between the internuclear H-H axis and the molecular z axis. Substituting the known values along with the D_{HH} obtained from the ^{1}H NMR spectrum at 620 MHz yields eq 4.11.

$$\frac{\left(\frac{3}{2}\cos^2\theta_z - \frac{1}{2}\right)}{r_{HH}{}^3} = -0.309 \times 10^{24}\ \mathrm{cm}^{-3} \qquad (4.11)$$

Plotting θ_z versus the internuclear H-H distance (Å), produces two curves that correspond to positive or negative values of D_{HH}. Since the sign of the dipolar coupling was found to be negative, and using the T_1 minimum value that was obtained at a lower magnetic field (132 ms, 400 MHz) to calculate an H-H bond distance (1.21/1.53 Å, fast rotation/static regimes),[11,25] they determined that the H_2 ligand is oriented at right angles to the molecular axis (Figure 4.9).[26]

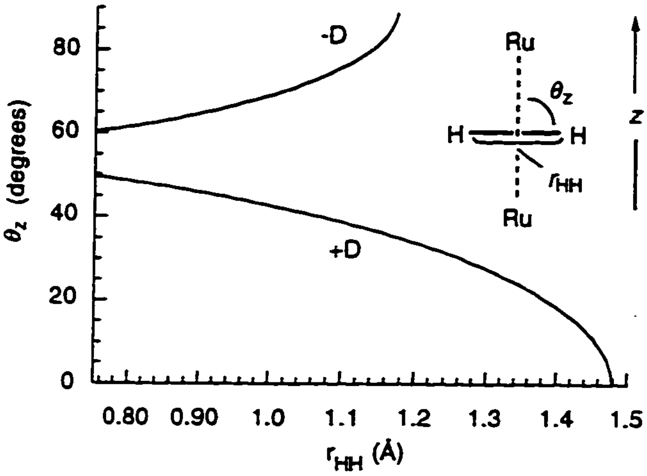


Figure 4.8. Plot of the possible values of θ_z versus r_{HH} for $Ru_2(H_2)(DPB)(*Im)_2$.

Examples of Possible Partial Alignment with the Magnetic Field. Other examples of partial alignment of transition metal dihydrogen complexes with the magnetic field have not been reported. However, the vast majority of dihydrogen complexes[2] have ancillary ligands that have significant anisotropic diamagnetic susceptibilities, such as triphenylphosphine, that may have a considerable effect due to partial alignment in high magnetic fields or at low temperatures. The temperature dependence of the rotation around the P-C and the M-P axes could induce the occurrence of partial alignment with the magnetic field with decreases in temperature, thereby affecting the observed T_1 and J_{HD} data.[27]

Some reported cases of anomalous behavior concerning relaxation data and J_{HD} values may have been due to partial alignment of the complex with the magnetic field. Relaxation data have been used extensively for the determination of the H-H distance in the H_2 ligand of transition metal dihydrogen complexes.[2] Morris and coworkers have attempted to determine the barrier to rotation of the H_2 ligand with the use of the "fast" rotation model of the spectral density function in the homonuclear dipole interaction relaxation rate equation (eq 4.12).[28]

$$R_{HH} = \frac{3\gamma_H^4\hbar^2}{20\pi r_{HH}^6}\left\{\frac{0.25\tau_c}{1+\omega^2\tau_c^2} + \frac{0.75\left(\frac{\tau_c}{2+\tau_{H_2}/\tau_c}\right)}{1+\omega^2\left(\frac{\tau_c}{2+\tau_{H_2}/\tau_c}\right)^2} + \frac{\tau_c}{1+4\omega^2\tau_c^2} + \frac{3\left(\frac{\tau_c}{2+\tau_{H_2}/\tau_c}\right)}{1+4\omega^2\left(\frac{\tau_c}{2+\tau_{H_2}/\tau_c}\right)^2}\right\} \qquad (4.12)$$

Where τ_c is the correlation time of the molecule and τ_{H_2} is the correlation time of the rotation of the H_2 ligand around the $M\text{-}H_2$ axis. With this two parameter model and the known correlation time of the molecule, they proposed that the correlation time of the dihydrogen ligand can be determined from the shape of the T_1 curve. Since an Arrhenius equation can be written for the correlation time for the rotation of the H_2 ligand, $\tau_{H_2} = Ae^{Ea/RT}$, the activation barrier for the rotation of the H_2 ligand could also be determined. Using the activation parameters for the molecular correlation time determined from relaxation measurements of the methylene hydrogens in the dppe backbone in $[Os(H_2)Cl(dppe)_2]^+$ (dppe = 1,2-bis(diphenylphosphino)ethane) and equation 4.10, they calculated the activation parameters of the rotational correlation time of the H_2 ligand at 500 MHz. However, using these activation parameters they were not successful at generating the calculated T_1 curves that match their observed data for the complex recorded at 300 and 400 MHz at temperatures of 175–300 K.[6] They propose that the rotation of the H_2 ligand may be better described as "hopping" between orientations instead of free spinning.[29] However, the magnitude of these fields in conjunction with the low temperatures, may enhance the partial alignment with the field of the phenyl groups in the phosphine ligands. This partial alignment may result in significant contributions to the rate of relaxation of the H_2 resonance which may explain the observed behavior.

Other examples of anomalous behavior involve the HD analogue, $[Os(HD)Cl(dppe)_2]^+$ and two other complexes, $[Os(HD)Cl(dcpe)_2]^+$ (dcpe = 1,2-bis(dicyclohexylphosphino)ethane)[6] and $[Ru(HD)Cp^*(dppm)]^+$ (dppm = bis(diphenylphosphino)methane),[30] show temperature dependent J_{HD} values. The H-D couplings increase with an increase in temperature for the complexes $[Os(HD)Cl(dppe)_2]^+$ and $[Os(HD)Cl(dcpe)_2]^+$, and decrease in value with an increase in temperature for $[Ru(HD)Cp^*(dppm)]^+$.[6] To account for the increase in J_{HD} value with an increase in temperature, they proposed a rapid equilibration between a dihydride and a dihydrogen species with the dihydrogen tautomer dominant at higher temperatures.

The J_{HD} values would be the weighted average of the two species and increase with temperature. However, the NMR spectra exhibited no other evidence to support this theory. They also pointed out that if this were the case, then the T_1 measurements at low temperatures should show a much longer relaxation time, due to the influence of the dihydride tautomer, than was observed. The decrease in the H-D coupling for $[Ru(HD)Cp^*(dppm)]^+$ was proposed to be a thermal property of stretched dihydrogen complexes, that an increase in temperature causes the H-D bond length to increase resulting in a decrease in J_{HD}.[30] However, the temperature range employed is not likely to be large enough to cause the thermal excitation necessary to account for the behavior.[31]

An alternative explanation for these anomalous observations is partial alignment with the magnetic field that is being enhanced at the lower temperatures. This hypothesis would require the complexes, $[Os(H_2)Cl(dppe)_2]^+$ and $[Os(H_2)Cl(dcpe)_2]^+$, to have negative dipolar couplings and $[Ru(H_2)Cp^*(dppm)]^+$ to have a positive dipolar coupling.

Conclusion

The proximity of the hydrogen atoms in the H_2 ligand in transition metal dihydrogen complexes provide for dipolar couplings of 100–300 kHz as measured by solid state NMR.[4] Such large couplings allow the possibility of observable residual H-H and H-D dipolar couplings in solution NMR that are five orders of magnitude smaller. Accurate measurement of the total splitting of the HD resonance is important since the effect is small and the observation could be easily overlooked. Low temperatures, combined with relatively high magnetic fields, may enhance the partial alignment, thereby affecting the relaxation data and the observed spin coupling values. The field dependence of J_{HD} values or T_1 minimum studies should be considered in the determination of the H-H bond distance. The growing availability of NMR spectrometers with high magnetic fields increases the possibility of observing the effects of partial alignment in solution.

The observations presented here demonstrate that partial alignment can have a small but significant effect on the solution NMR parameters of transition metal dihydrogen complexes with commonly employed coligands. Such observations of field dependent partial alignment are not restricted to complex porphyrin ligands.[13] The design of dihydrogen complexes with significant anisotropic diamagnetic susceptibilities may provide a third method for the determination of the bond length in the H_2 ligand to collaborate distances obtained from J_{HD} values or T_1 minimum data.

Experimental

General procedures

The general procedures followed are outlined in Chapter 2. The syntheses of the cationic hydride precursors and the dicationic dihydrogen complexes are described in Chapters 2 and 3. Dilute solutions of the complexes (typically $< 4.0 \times 10^{-2}$ M) were used to prevent concentration effects for the NMR experiments concerning the relaxation studies of the dihydrogen complexes and the total splitting measurements of the HD complexes. The same sample was used for each measurement of the total splitting of the H-D coupling at different magnetic fields and was temperature equilibrated at 298 K. The same sample of the corresponding dihydrogen complex was used for the variable temperature ^{1}H relaxation studies at 200, 500, and 750 MHz to prevent any concentration dependent errors. Methylene chloride-d_2 was used as the solvent ($\Delta\chi = 0$) to prevent anisotropy effects due to the solvent for the H-D coupling measurements and the relaxation studies. Proper acquisition parameters and processing of the spectra resulted in spectral resolutions typically better than ± 0.05 Hz. The determination of the total splitting was accomplished by expansion of the region of the triplet splitting of the HD resonance in the ^{1}H NMR spectra and then taking the average of the splitting of the outer resonances.

$[Re(HD)(P^iPr_3)_2(CO)_3](BAr'_4)$[16] was prepared by published methods from $[Re(P^iPr_3)_2(CO)_3](BAr'_4)$ that was generously provided by Dr. Catherine Radzewich.

Notes to Chapter 4.

1 Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451-452.

2 (a) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913-926. (b) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155-289. (c) Kubas, G. J. *Accts. Chem. Res.* **1988**, *21*, 120-128.

3 Eckert, J.; Albinati, A.; White, R. P.; Bianchini, C.; Peruzzini, M. *Inorg. Chem.* **1992**, *31*, 4241-4244.

4 Zilm, K. W.; Millar, J. M. *Adv. Magn. Opt. Reson.* **1990**, *15*, 163-200.

5 Hasegawa, T.; Li, Z.-W.; Parkin, S.; Hope, H.; McMullan, R. K.; Koetzle, T. F.; Taube, H. *J. Am. Chem. Soc.* **1994**, *116*, 4352-5356.

6 Maltby, P. A.; Schlaf, M.; Steinbeck, M.; Lough, A. J.; Morris, R. H.; Klooster, W. T.; Koetzle, T. F.; Srivastava, R. C. *J. Am. Chem. Soc.* **1996**, *118*, 5396-5407.

7 Günther, H. In *NMR Spectroscopy: Basic Principles, Concepts, and Applications in Chemistry*, John Wiley & Sons: Chichester, 1995.

8 Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126-4133.

9 Heinekey, D. M.; Luther, T. A. *Inorg. Chem.* **1996**, *35*, 4396-4399.

10 Hush, N. S. *J. Am. Chem. Soc.* **1997**, *119*, 1717-1719.

11 Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173-4184.

12 Gusev, D. G.; Kuhlman, R. L.; Renkema, K. B.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1996**, *35*, 6775-6783.

13 Collman, J. P.; Wagenknecht, P. S.; Hutchison, J. E.; Lewis, N. S.; Lopez, M. A.; Guilard, R.; L'Her, M.; Bothner-By, A. A.; Mishra, P. K. *J. Am. Chem. Soc.* **1992**, *114*, 5654-5664.

---

14 Canet, D.; Robert, J. B. In *NMR Basic Principles and Progress, Vol. 25: NMR at Very High Field*; Diehl, P., Fluck, E., Günther, H., Kosfeld, R., Seelig, J., Eds.; Springer-Verlag: New York, 1991; pp 45-89.

15 Abragam, A. In *The Principles of Nuclear Magnetism*; Clarendon: Oxford, 1961.

16 Heinekey, D. M.; Schomber, B. M.; Radzewich, C. E. *J. Am. Chem. Soc.* **1994**, *116*, 4515-4516.

17 $[Re(H_2)(P^iPr_3)_2(CO)_3]BAr'_4$ was supplied by Dr. Catherine Radzewich for the 750 MHz variable temperature ^1H NMR spin-lattice relaxation study. 500 MHz data: Heinekey, D. M.; Radzewich, C. E.; Voges, M. H.; Schomber, B. M. *J. Am. Chem. Soc.* **1997**, *119*, 4172-4181.

18 Zilm, K. M.; Merrill, R. A.; Kummer, M. W.; Kubas, G. J. *J. Am. Chem. Soc.* **1986**, *108*, 7837-7839.

19 Bastiaan, E. W.; MacLean, C. In *NMR Basic Principles and Progress, Vol. 25: NMR at Very High Field*; Diehl, P., Fluck, E., Günther, H., Kosfeld, R., Seelig, J., Eds.; Springer-Verlag: New York, 1991; pp 17-43.

20 (a) Bastiaan, E. W.; MacLean, C.; van Zijl, P. C. M.; Bothner-By, A. A. In *Annual Reports on NMR Spectroscopy*, Vol. 19; Webb, G. A., Ed.; Academic: London, 1987; pp 35-77. (b) van Zijl, P. C. M.; Ruessink, B. H.; Bulthuis, J.; MacLean, C. *Accts. Chem. Res.* **1984**, *17*, 172-180. (c) Bastiaan, E. W.; Bulthuis, J.; MacLean, C. *Magn. Reson. Chem.* **1986**, *24*, 723-728.

21 $\Delta\chi$ values of -1.64×10^{-28} cm^3 and -2.98×10^{-28} cm^3 were used for the bipyridine and phenanthroline ligands, respectively.[20a]

22 The H-H bond distance is calculated using eq 3.1: $r_{HH} = 1.44 - 0.0168(J_{HD})$.

23 With the field dependent D_{HD} included in the calculation, the H-H distance is calculated to be 1.01 Å for **10a** at 500 MHz.

---

24 Residual dipolar H-H couplings of 0.20 Hz at 750 MHz have recently been observed in $C_{60}H_2$: Alemany, L. B.; Gonzalez, A.; Luo, W.; Billups, W. E.; Willcott, M. R.; Ezell, E.; Gozansky, E. *J. Am. Chem. Soc.* **1997**, *119*, 5047-5048.

25 Alternatively, the H-H bond length can be determined from the J_{HD} value of 15 Hz to yield a distance of 1.18 Å, which is in agreement with the fast rotation regime of the H_2 ligand (Chapter 3).

26 Using the inverse linear relationship between the H-H bond distance in the H_2 ligand and the J_{HD} value of the HD complex, produces an H-H bond distance of 1.17 Å (Chapter 3).

27 The barrier to rotation around the P-C axis ($\Delta H^{\ddagger} = 2.6$-$3.58$ kcal/mol) for triphenylphosphine, when combined with steric demands when complexed to a metal center are expected to be greater. Bushweller, C. H.; Brunelle, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 5949-5955.

28 Bautista, M. T.; Earl, K. A.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T.; Sella, A. *J. Am. Chem. Soc.* **1988**, *110*, 7031-7036.

29 Schalf, M.; Lough, A. J.; Maltby, P. A.; Morris, R. H. *Organometallics* **1996**, *15*, 2270-2278.

30 Klooster, W. T.; Koetzle, T. F.; Jia, G.; Fong, T. P.; Morris, R. H.; Albinati, A. *J. Am. Chem. Soc.* **1994** *116*, 7677-7681.

31 Drago, R. S. In *Physical Methods for Chemists, 2nd ed.*, Harcourt Brace Jovanovich, Orlando, 1977, p 218.

Chapter 5

Investigation of Possible Dihydrogen/Dihydride Equilibrium

Introduction

In 1994 Taube and coworkers reported NMR and low temperature neutron diffraction data for $[Os(H_2)(en)_2(OAc)](PF_6)$ (**13d**) (en = ethylenediamine, OAc = CH_3COO^-).[1] The low temperature neutron diffraction data show an intact dihydrogen ligand bonded sideways in an η^2 fashion with the osmium metal center and is oriented parallel to an axis bisecting the ethylenediamine ligands. The H-H bond distance in the H_2 ligand as determined from the neutron diffraction study is 1.34 Å, almost twice the distance in H_2 gas. This is in sharp contrast to the neutron and low temperature X-ray diffraction data of the neutral tungsten complex $W(H_2)(P^iPr_3)(CO)_3$ by Kubas which indicate that the H-H axis lies roughly parallel to the P–W–P axis[2] and solid state NMR data that indicate a "normal" H-H bond length of 0.89 Å.[3]

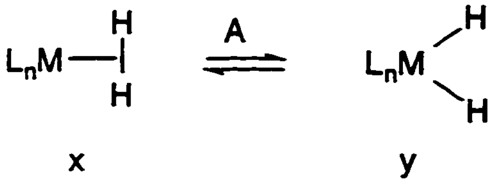
The reported[1] T_1 minimum of **13d** in CD_3OD is 61 ms (233 K, 400 MHz) and the J_{HD} value of 8.1 Hz in the HD analogue $[Os(HD)(en)_2(OAc)](PF_6)$ (**13d**-d_1) support such a "stretched" dihydrogen ligand (Chapter 3). The ^1H NMR spectrum of **13d**-d_1 recorded at 400 MHz also indicated an isotope shift of the HD resonance of +80 ppb ($\Delta\delta = \delta_{H_2} - \delta_{HD}$). This large isotope shift[4] relative to HD gas ($\Delta\delta$ = +36 ppb)[5] along with the apparent elongated dihydrogen bond length suggested to us the possibility of a dihydrogen/dihydride equilibrium that could account for these observations.

Several theoretical papers have been published concerning the nature of the Os-H_2 interaction[6,7] in the series of dihydrogen complexes reported by Taube and coworkers.[1,8] However, there is some disagreement about the bonding interaction of the H_2 ligand with the metal center. Hush and coworkers[7] have used the experimental data along with quantum chemical calculations[9] to support the configuration of these complexes as a single species dihydrogen complexes. The calculations show that an unusually flat potential energy curve exists resulting from strong electronic coupling between a *cis*-dihydride tautomer and a dihydrogen species. This leads to a single minimum potential energy surface indicating the existence of the H_2 complex only. This also implies that the stretching force constant in the H_2 ligand is very low which agrees with the observation of large changes in the J_{HD} values corresponding to changes of the ligand, L, *trans* to the H_2 ligand. Recently, Maseras and coworkers[6] have used the "atoms in molecules" model of Bader and coworkers[10,11] to locate the chemical bonds, as electron density, between the metal center and the hydrogen atoms of a known dihydrogen complex and a known dihydride complex and two complexes having an elongated H_2 ligand (one of which is **13d**). This study supports the classification of **13d** as a dihydride with a close H-H interaction but not as an intact dihydrogen ligand.

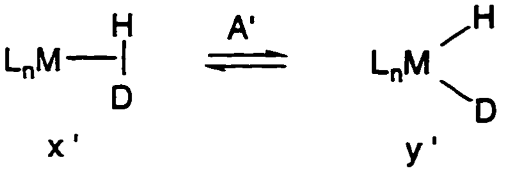
The existence of a continuum of J_{HD} values ranging from 21 Hz to 8 Hz is consistent with the classification of these species as dihydrogen complexes only or as complexes that are experiencing a rapid dihydrogen/dihydride equilibrium. Evidence of such an equilibrium would be the existence of a temperature dependence of the isotope shift and in the H-D coupling of the HD complex.[4d]

Results and Discussion

Equilibrium Between a Dihydrogen and a Dihydride. An equilibrium between $[Os(H_2)(en)_2L^z]^{(2+z)}$ and $[Os(H)_2(en)_2L^z]^{(2+z)}$ (L^z = various neutral or anionic ligands with $z = 0$ or -1) should be observable in the temperature dependence of the isotope shift of the HD complex and also in the J_{HD} value even if a decoalescence of the resonance was unobservable in the ^1H NMR spectrum of the H_2 complex. A single species dihydrogen complex will have a distinct chemical shift for the H_2 resonance and the corresponding HD complex is normally expected to have a J_{HD} value of 20–34 Hz.[12] A single species *cis*-dihydride complex will have a distinct chemical shift for the hydride resonance and a J_{HD} value < 3 Hz for the HD analogue.[13] The temperature dependence of the isotope shift evolves from the equilibrium population difference between a dihydrogen configuration and a dihydride form in the H_2 complex and in the HD complex (eqs 5.1 and 5.2).



(5.1)



(5.2)

The Boltzmann factor, A defined as $e^{-\Delta E/RT}$, in the H_2 species should not have the same temperature dependence profile as the corresponding Boltzmann factor, A', in the HD complex due to intrinsic isotope effects. The observed chemical shifts of the H_2 resonance and the HD resonance would be a weighted average of the actual chemical shifts for the dihydrogen resonance and the dihydride resonance, where x, y, x', and y' are the relative concentrations of the different forms (eq 5.3 and 5.4).

$$\begin{aligned}\delta_{H_2\,obs} &= x\delta_{H_2} + y\delta_H \\ &= \frac{\delta_{H_2} + A\delta_H}{1 + A} \qquad (5.3)\end{aligned}$$

$$\begin{aligned}\delta_{HD\,obs} &= x'\delta_{H_2} + y'\delta_H \\ &= \frac{\delta_{H_2} + A'\delta_H}{1 + A'} \qquad (5.4)\end{aligned}$$

In eqs 5.3 and 5.4, δ_{H_2} and δ_H denote the actual chemical shifts of the dihydrogen and hydride resonances, respectively. The observed isotope shift is the difference of the observed chemical shifts of the H_2 resonance and the HD resonance which is expected to be temperature dependent (eq 5.5).

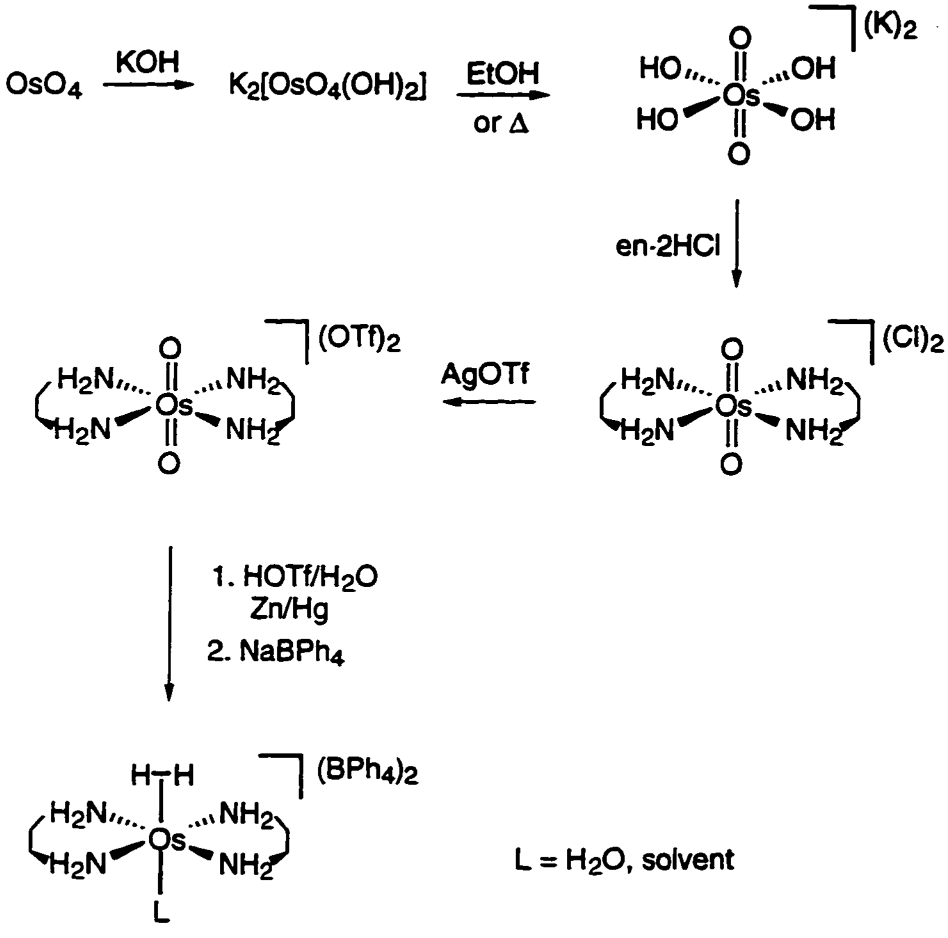
$$\begin{aligned}\delta_{H_2\,obs} - \delta_{HD\,obs} &= \frac{\delta_{H_2} + A\delta_H}{1 + A} - \frac{\delta_{H_2} + A'\delta_H}{1 + A'} \\ &= \frac{(A' - A)(\delta_{H_2} + \delta_H)}{(1 + A)\,(1 + A')} \qquad (5.5)\end{aligned}$$

A similar expression can be written for the H-D coupling equilibrium between a dihydrogen complex and a dihydride that also indicate a dependency with temperature (eq 5.6)

$$J_{HD\,obs} = \frac{{}^1J_{HD} + A'[{}^2J_{HD}]}{1 + A'} \qquad (5.6)$$

Where $J_{HD\,obs}$ is the observed H-D coupling and ${}^1J_{HD}$ and ${}^2J_{HD}$ denote the one- and two-bond coupling between the hydrogen and deuterium nuclei in the dihydrogen and dihydride, respectively.

Synthesis of [Os(H_2)(en)$_2$L](X_2) [X = BPh_4, OTf, BAr'$_4$, PF_6 (12a-d)] (L = H_2O or solvent; Ar' = 3,5-$(CF_3)_2C_6H_5$). The synthetic route to the dihydrogen dications [Os(H_2)(en)$_2$L]$^{2+}$ (**12a-d**) (L = H_2O or solvent) begins with the reduction of OsO_4 to the Os(VI) species $K_2[Os(O)_2(OH)_4]$. The potassium osmate is reacted with ethylenediamine dihydrochloride to form the dioxo dichloride species [Os(O)$_2$(en)$_2$]Cl_2. Silver triflate (AgOTf) is added to generate [Os(O)$_2$(en)$_2$](OTf)$_2$ and AgCl. The dioxo complex $[Os(O)_2(en)_2](OTf)_2$ is finally reduced to Os(II) with a zinc/mercury amalgam under acidic conditions followed by addition of sodium tetraphenylborate to precipitate the dihydrogen dication $[Os(H_2)(en)_2L](BPh_4)_2$ (**12a**) (L = H_2O or solvent) (Scheme 5.1).

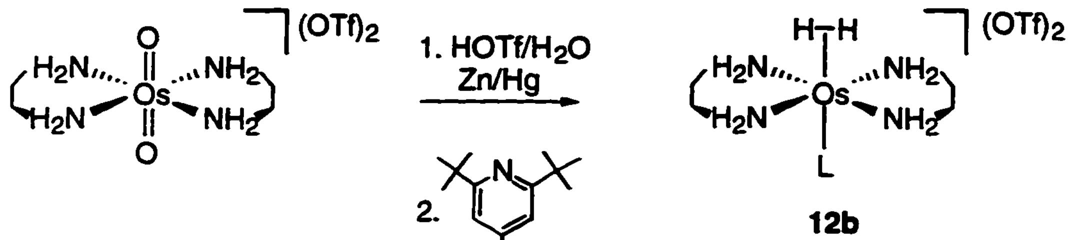


12a

Scheme 5.1

The ^1H NMR spectrum of **12a** shows two broad resonances for the amine protons (δ +5.52 and +3.83) and two multiplets for the methylene protons (δ +2.39 and +2.08) as well as a broad H_2 resonance in the hydride region (δ -13.57).[8a,14] The "open" coordination site *trans* to the H_2 ligand is very labile and can be occupied by a solvent molecule or a variety of other ligands including the counter ion if it can coordinate and compete with the solvent (Chapter 3).

The complex, $[Os(H_2)(en)_2L](OTf)_2$ (**12b**) is prepared by the reduction of the dioxo species, as shown in Scheme 5.1, followed by neutralization of the acidic mixture with 2,6-di-*tert*-butyl-4methylpyridine (Stang's sponge) (Scheme 5.2).



12b

L = H_2O, solvent

Scheme 5.2

Similar conditions were used (Scheme 5.1) to prepare $[Os(H_2)(en)_2L](BAr'_4)_2$ (12c) substituting $NaBAr'_4$ after the reduction of the dioxo complex to precipitate **12c**. The preparation of the PF_6 complex $[Os(H_2)(en)_2L](PF_6)_2$ (**12d**) followed the synthetic route reported by Taube and coworkers with the substitution of the dianion in **12a** with PF_6 using $TlPF_6$ (Scheme 5.3).[8a]

12a

12d

Scheme 5.3

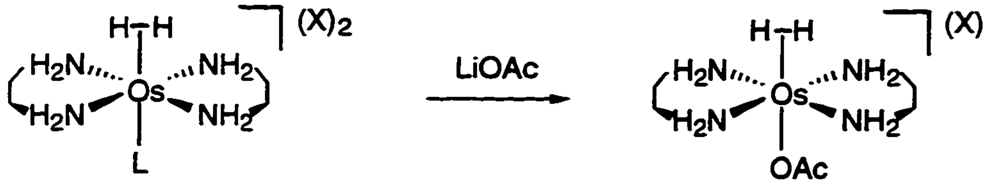
Table 5.1 compares the ^1H NMR data for the complexes, **12a-d**, and suggests that the coordination ability of a solvent molecule in the *trans* position is more effective than X.

Table 5.1. ^{1}H NMR Chemical Shifts for $[Os(H_2)(en)_2L](X)_2$.[a]

X	δ_{NH_2}		δ_{CH_2}		δ_{H_2}	solvent
BPh_4 **12a**	+5.52	+3.83	+2.39	+2.08	-13.57	CD_3OD
OTf **12b**	+5.83	+4.14	+2.54	+2.22	-13.51	CD_3OD
BAr'_4 **12c**	+5.83	+4.14	+2.55	+2.33	-13.51	CD_3OD
	+4.54	+3.93	+2.80	+2.33	-13.87	CD_2Cl_2
	+4.26	+3.83	+2.80	+2.23	-13.87	$CDFCl_2$
PF_6 **12d**	+5.70	+3.99	+2.54	+2.21	-13.39	CD_3OD

[a] In ppm recorded at 300 MHz.

Synthesis of $[Os(H_2)(en)_2(OAc)](X)$ ($X = OTf$, BAr'_4, (13b,c)). The acetate complexes are prepared by the reaction of the dihydrogen dications, **12b,c**, with lithium acetate in a methanol solution (Scheme 5.4).



12b,c **13b,c**

Scheme 5.4

Partial Incorporation of Deuterium into the H_2 Ligand. A sample of $[Os(H_2)(en)_2(OAc)](OTf)$ (**13b**) was dissolved in methanol-d_4 and monitored by ^{1}H NMR for a period of 2 weeks. During this time no deuterium incorporation into the H_2 ligand was observed. However, a methanol-d_4 solution of **12b** was found to partially incorporate deuterium into the H_2 ligand over the course of 10 days to generate $[Os(H_2)(en)_2L](OTf)_2$:$[Os(HD)(en)_2L](OTf)_2$ in an approximate 50:50 ratio. By reacting this mixture with LiOAc, a 50:50 mixture of **13b**:**13b**-d_1 is produced.

Table 5.2. ^{1}H NMR Chemical Shifts for [Os(HD)(en)$_2$L](X)$_2$ (**12**-d_1) and [Os(HD)(en)$_2$(OAc)](X) (**13**-d_1).[a]

X		δ_{HD}	J_{HD} (Hz)	$\Delta\delta$ (ppb)[b]	solvent
OTf	**12b**-d_1	-13.56	8.8	+48	CD_3OD
BAr'$_4$	**12c**-d_1	-13.56	9.1	+47	CD_3OD
		-13.92	9.0	+59	CD_2Cl_2
		-13.93	9.3	+56	$CDFCl_2$
OTf	**13b**-d_1	-12.84	9.2	+92	CD_3OD
BAr'$_4$	**13c**-d_1	-12.82	8.3	+86	CD_3OD

[a] In ppm recorded at 300 MHz. [b] $\delta_{H_2} - \delta_{HD}$.

Variable Temperature Studies. The H-D coupling and the isotope shift ($\Delta\delta$) of the HD dications [Os(HD)(en)$_2$L](OTf)$_2$ (**12b**-d_1) and [Os(HD)(en)$_2$L](BAr'$_4$)$_2$ (**12c**-d_1) were examined by variable temperature ^{1}H NMR spectroscopy. If a rapid equilibrium between a dihydrogen and a dihydride in these complexes was occurring, there should be an observable change in the parameters J_{HD} and $\Delta\delta$ that is temperature dependent (eqs 5.5 and 5.6). The variable temperature results of **12b**-d_1 (300 MHz, CD_3OD) indicate that there is a temperature dependence of the J_{HD} value (Figure 5.1). However, the isotope shift ($\Delta\delta$) remains unchanged throughout this temperature range.

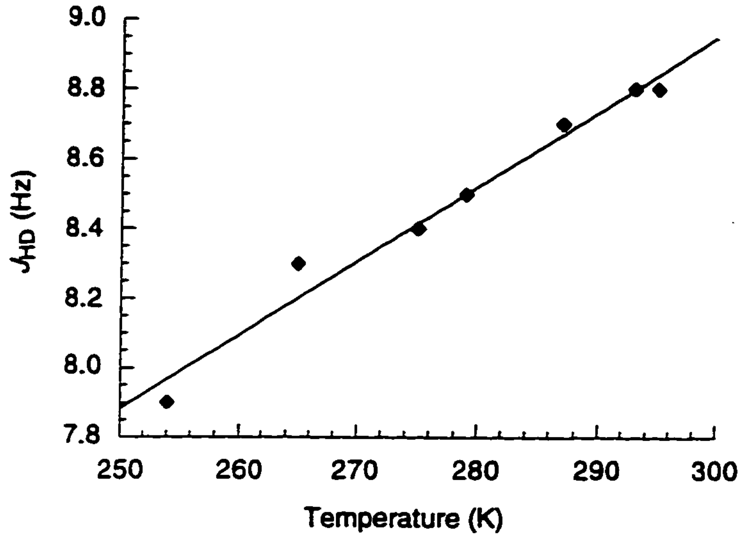


Figure 5.1. The value of J_{HD} in $[Os(HD)(en)_2L](OTf)_2$ (**12b**-d_1) versus temperature (300 MHz, CD_3OD).

The variable temperature study of **12c**-d_1 (300 MHz, CD_2Cl_2) measured in the same temperature range as **12b**-d_1 shows no temperature dependence of the H-D coupling or of the isotope shift. The similarity of the complexes by ^1H NMR shows that the nature of the anion, OTf^- or $BAr'_4{}^-$, does not greatly affect the chemical shifts indicating the anion is not coordinating at the site *trans* to the H_2 ligand at room temperature (Table 5.1). A reasonable explanation of this change in behavior in response to temperature may be due to an increased ability of the OTf^- anion to coordinate *trans* to the H_2 ligand at lower temperatures. The observed J_{HD} would reflect the equilibrium between OTf^- and a solvent molecule as the ligand *trans* to the H_2 ligand.

Conclusion

The dihydrogen complexes, $[Os(H_2)(en)_2L^z]^{(2+z)}$ reported by Taube and coworkers[1,8a,15] all have elongated H-H bonds in the H_2 ligand as determined by T_1 minimum or J_{HD} values[8a] (Chapter 3). The H-H distance in the H_2 ligand of one compound, $[Os(H_2)(en)_2(OAc)]^+$ has been determined by neutron diffraction to be 1.34 Å,[1] almost twice the distance in H_2 gas. The temperature dependence of the H-D coupling and of the isotope shift of the HD resonance from the H_2 resonance was investigated. An equilibrium between a dihydrogen species and a dihydride should show observable changes in these parameters due to isotopic perturbation of equilibrium.[4d,16] The lack of a temperature dependence of the isotope shift in **12b**-d_1 and **12c**-d_1 indicates that an equilibrium between a dihydrogen and a dihydride tautomer is most likely not occurring and these are single species complexes.

Experimental

General Procedures. The general conditions that were followed are described in Chapter 2. All manipulations involving the dihydrogen complexes were performed using Schlenk, vacuum line, and dry box techniques. The zinc/mercury amalgam was prepared from granular Zn (2 g, 20 mesh) which was washed with 3 M HCl and treated with a saturated aqueous $HgCl_2$ solution for 30 min.[17] The preparation of NaBAr'$_4$ followed published procedures.[18] For the dicationic dihydrogen complexes, L = H_2O or solvent.

$K_2[OsO_2(OH)_4]$. A glass ampule of OsO_4 (1 g, 3.9 mmol) was broken and dropped into a 100 mL beaker containing 50 mL of cold aqueous KOH (619 mg, 11.0 mmol) and dissolved. The addition of a small amount of ethanol (≈ 5 mL) to reduce $K_2[OsO_4(OH)_2]$, caused the color of the red solution to immediately change to purple. The solvent was removed via a rotary evaporator and the solid was placed under dynamic vacuum overnight.

$[Os(O)_2(en)_2]Cl_2$.[15] A minimum amount of H_2O (≈ 80 mL) was added to dissolve the $K_2[OsO_2(OH)_4]$ and added dropwise to aqueous solution (minimal amount of H_2O ≈ 10 mL) of ethylenediamine dihydrochloride (2.62 g, 19.7 mmol). The solids are collected on a glass frit and dried in vacuo. Yield 788 mg (49% based on OsO_4).

$[Os(O)_2(en)_2](OSO_2CF_3)_2$.[8a] $[Os(O)_2(en)_2]Cl_2$ (788 mg, 1.9 mmol) was dissolved in water and 2.0 equiv of silver triflate $AgOSO_2CF_3$ (992 mg, 3.9 mmol) was added slowly to the solution. The solution was filtered using a fritted glass funnel and a golden yellow solution was obtained and then dried by a rotary evaporator. Yield 1.150 g (95%).

$[Os(H_2)(en)_2L](BPh_4)_2$ (12a).[8a] $[Os(O)_2(en)_2](OSO_2CF_3)_2$ (514 mg, 0.80 mmol) was dissolved in 10 mL of water (previously sparged with Ar) and triflic acid (HOTf) (0.9 mL, 10 mmol) in an 150 mL Schlenk flask. While under a flow of Ar, a zinc/mercury amalgam (2 g) was added to the solution and stirred for approximately 3 h, during which time the color of the solution changed from yellow to dark purple and back to yellow. The reaction mixture was filtered and $NaBPh_4$ (712 mg, 2.1 mmol) was dissolved in 10 mL of water and added dropwise to the yellow solution via syringe. The white precipitate was transferred via cannula to a fritted glass filter and dried in vacuo. ^1H NMR (CD_3OD): δ 5.52 (4 H, NH_2), 3.83 (4 H, NH_2), 2.39 (4 H, CH_2), 2.08 (4 H, CH_2), -13.57 (2 H, Os-H_2).

$[Os(H_2)(en)_2L](OSO_2CF_3)_2$ (12b). Prepared as above for **12a** except 10 mL of an aqueous solution 2,6-di-*tert*-butyl-4-methylpyridine (Stang's sponge) (470 mg, 2.3 mmol) was added via cannula to the solution and stirred for 30 min (instead of addition of $NaBPh_4$). The solution was transferred via cannula to a fritted glass filter and the solvent was reduced using dynamic vacuum. The addition of diethyl ether (30 mL) resulted in the precipitation of ivory solids which were dried in vacuo. ^1H NMR

(CD_3OD): δ 5.83 (4 H, N*H*$_2$), 4.14 (4 H, N*H*$_2$), 2.54 (4 H, C*H*$_2$), 2.22 (4 H, C*H*$_2$), -13.51 (2 H, Os-*H*$_2$).

[Os(H_2)(en)$_2$L](BAr'$_4$)$_2$ (12c) (Ar' = 3,5-(CF_3)$_2$$C_6H_3$). Prepared as above for **12a** using 10 mL of an aqueous suspension of NaBAr'$_4$ (904 mg, 1.0 mmol) in place of $NaBPh_4$. ^{1}H NMR (CD_3OD): δ 5.83 (4 H, N*H*$_2$), 4.14 (4 H, N*H*$_2$), 2.55 (4 H, C*H*$_2$), 2.33 (4 H, C*H*$_2$), -13.51 (2 H, Os-*H*$_2$).

[Os(H_2)(en)$_2$L](PF_6)$_2$ (12d). Two methods were used to generate **12d**. Method A: Prepared as above for **12a** using an aqueous solution of $NaPF_6$ (0.2 M, 10 mL). The volume of the solution was reduced to ≈ 3 mL and 50 mL of diethyl ether was added. The resulting solids were collected and dried in vacuo. Method B: [Os(H_2)(en)$_2$](BPh_4)$_2$ (**12a**) (201 mg, 0.21 mmol) was dissolved in 5 mL of acetone and a 5 mL acetone solution of $TlPF_6$ (152 mg, 0.44 mmol) was added. The white precipitate was removed by filtration and the solution was reduced in volume to 3 mL and treated with 50 mL of diethyl ether. The resulting solids were collected and dried in vacuo. ^{1}H NMR (CD_3OD): δ 5.70 (4 H, N*H*$_2$), 3.99 (4 H, N*H*$_2$), 2.54 (4 H, C*H*$_2$), 2.21 (4 H, C*H*$_2$), -13.39 (2 H, Os-*H*$_2$).

[Os(H_2)(en)$_2$(OAc)](X) [X = OSO_2CF_3, BAr'$_4$ (13b,c)].[1] Lithium acetate dihydrate (100 mg, 0.98 mmol) was dissolved in methanol (2 mL) and transferred via cannula to a methanol (5 mL) solution of **12b** (99 mg, 0.16 mmol) or **12c** (100 mg, 0.15 mmol). The reaction mixture was stirred for 30 min and 50 mL of diethyl ether was added. The precipitate was collected of a glass filter frit and washed with diethyl ether. ^{1}H NMR (**13b**, CD_3OD): δ 5.46 (4 H, N*H*$_2$), 4.60 (4 H, N*H*$_2$), 2.46 (4 H, C*H*$_2$), 2.01 (4 H, C*H*$_2$), 2.05 (3 H, CH_2COO$^-$), -12.75 (2 H, Os-H_2). **(13c, CD_3OD):** δ 5.44 (4 H, NH_2), 4.57 (4 H, NH_2), 2.46 (4 H, CH_2), 2.14 (4 H, CH_2), 2.14 (3 H, CH_2COO$^-$), -12.73 (2 H, Os-H_2).

Deuterium Incorporation into [Os(H_2)(en)$_2$L](X)$_2$ [X = OSO_2CF_3, BAr'$_4$ (12b,c)] and [Os(H_2)(en)$_2$(OAc)](X) [X = OSO_2CF_3, BAr'$_4$ (13b,c)]. The HD analogues **12b**-*d*$_1$ and **12c**-*d*$_1$ were prepared by allowing the NMR samples (CD_3OD or D_2O) of **12b,c** to stand at room temperature for 2 to 10 days. The HD complexes **13b**-*d*$_1$ and **13c**-*d*$_1$ were prepared by dissolving **12b,c** (≈ 300 mg) in CD_3OD for a period of 10 days and using the resultant mixtures of **12b**;**12b**-*d*$_1$ and **12c**;**12c**-*d*$_1$ to react with lithium acetate as described above. ^{1}H NMR (**12b**-*d*$_1$, CD_3OD), δ -13.56 (t, J_{HD} = 8.8 Hz, Os-*HD*, Δδ = 48 ppb). ^{1}H NMR (**13b**-*d*$_1$, CD_3OD), δ -12.84 (t, J_{HD} = 9.2 Hz, Os-*HD*, Δδ = 92 ppb).

Notes to Chapter 5.

---

1 Hasegawa, T.; Li, Z.-W.; Parkin, S.; Hope, H.; McMullan, R. K.; Koetzle, T. F.; Taube, H. *J. Am. Chem. Soc.* **1994**, *116*, 4352-5356.

2 Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451-452.

3 Zilm, K. W.; Millar, J. M. *Adv. Magn. Opt. Reson.* **1990**, *15*, 163-200.

4 Reported isotope shifts in dihydrogen complexes are generally < 40 ppb, reported exceptions are: (a) $\Delta\delta = +60$ ppb for $[Fe(H_2)H(\text{tetraphos-II})]^+$ (tetraphos-II = tris[2-(diphenylphosphino)ethyl]phosphine). [Bianchini, C.; Peruzzini, M.; Zanobini, F. *J. Organomet. Chem.* **1988**, *354*, C19-C22.] (b) $\Delta\delta = +90$ ppb for $Ru(H_2)(OEP)(THF)$ (OEP = octaethylporphyrin), +130 ppb for $Os(H_2)(OEP)(^*Im)$ (*Im = 3-*tert*-butyl-4-phenylimidazole), and -200 ppb for $Ru_2(H_2)(DPB)(^*Im)_2$ (DPB = 1,8-bis[5-(2,8,13,17-tetraethyl-3,7,12,18-tetramethyl)porphyrin]biphenylene). [Collman, J. P.; Wagenknecht, P. S.; Hutchison, J. E.; Lewis, N. S.; Lopez, M. A.; Guilard, R.; L'Her, M.; Bothner-By, A. A.; Mishra, P. K. *J. Am. Chem. Soc.* **1992**, *114*, 5654-5664.] (c) $\Delta\delta = +200$ ppb for $[Ta(H_2)Cp_2(CO)]^+$. [Moreno, B.; Sabo-Etienne, S.; Chaudret, B.; Rodriguez, A.; Jalón, F.; Trofimenko, S. *J. Am. Chem. Soc.* **1994**, *116*, 2635-2636.] (d) $\Delta\delta = -228$ ppb for $Ir(H_2)HTp(PMe_3)]^+$. [Heinekey, D. M.; Oldham, W. J., Jr. *J. Am. Chem. Soc.* **1994**, *116*, 3137-3138.]

5 Evans, D. F. *Chem. Ind.* **1961**, 1960.

6 Maseras, F.; Lledós, A.; Costas, M.; Poblet, J. P. *Organometallics*, **1996**, *15*, 2947-2953.

7 (a) Hush, N. S. *J. Am. Chem. Soc.* **1997**, *119*, 1717-1719. (c) Bacskay, G. B.; Bytheway, I.; Hush, N. S. *J. Am. Chem. Soc.* **1996**, *118*, 3753-3756. (c) Craw, J.

S.; Bacskay, G. B.; Hush, N. S. *J. Am. Chem. Soc.* **1994**, *116*, 5937-5948. (d) Craw, J. S.; Bacskay, G. B.; Hush, N. S. *Inorg. Chem.* **1993**, *32*, 2230-2231.

8 (a) Li, Z.-W.; Taube, H. *J. Am. Chem. Soc.* **1994**, *116*, 9506-9513. (b) Hasegawa, T.; Li, Z.-W.; Parkin, S.; Hope, H.; McMullan, R. K.; Koetzle, T. F.; Taube, H. *J. Am. Chem. Soc.* **1994**, *116*, 4352-5356. (c) Li, Z.-W.; Taube, H. *J. Am. Chem. Soc.* **1991**, *113*, 8946-8947.

9 Primarily Hartree-Fock self-consistent field (SCF) and second order Møller-Plesset (MP2) perturbation theory.

10 Bader, R. F. W. *Atoms in Molecules. A Quantum Theory*; Oxford University: Oxford, 1994.

11 Bader, R. F. W.: Anderson, S. G.; Duke, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 1389-1395. (b) Bader, R. F. W. *Chem. Rev.* **1991**, *91*, 893-928.

12 (a) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913-926. (b) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155-289. (c) Kubas, G. J. *Accts. Chem. Res.* **1988**, *21*, 120-128.

13 Heinekey, D. M.; Hinkle, A. S.; Close, J. D. *J. Am. Chem. Soc.* **1996**, *118*, 5353-5361.

14 The chemical shifts are similar to those reported by Taube and coworkers for **12a** in acetone-d_6.

15 Malin, J.; Taube, H. *Inorg. Chem.* **1971**, *10*, 2403-2406.

16 Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726-7727.

17 Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1990**, *112*, 2261-2263.

18 Brookhart, M.; Grant. B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11* 3920-3922.

Bibliography

Abragam, A. *The Principles of Nuclear Magnetism*; Clarendon: Oxford, 1961.

Ahmad, N.; Levinson, J. J.; Robinson, S. D.; Uttley, M. F. *Inorg. Synth.* **1974**, *15*, 45-64.

Ahmad, N.; Robinson, S. D.; Uttley, M. F. *J. Chem. Soc.* **1972**, 843-847.

Albeniz, A. C.; Heinekey, D. M.; Crabtree, R. H. *Inorg. Chem.* **1991**, *30*, 3632-3632.

Albinati, A.; Bakhmutov, V. I.; Caulton, K. G.; Clot, E.; Eckert, J.; Eisenstein, O.; Gusev, D. G.; Grushin, V. V.; Hauger, B. E.; Klooster, W. T.; Koetzle, T. F.; McMullan, R. K.; O'Loughlin, T. J.; Pélissier, M.; Ricci, J. S.; Sigalas, M. P.; Vymenits, A. B. *J. Am. Chem. Soc.* **1993**, *115*, 7300-7312.

Alemany, L. B.; Gonzalez, A.; Luo, W.; Billups, W. E.; Willcott, M. R.; Ezell, E.; Gozansky, E. *J. Am. Chem. Soc.* **1997**, *119*, 5047-5048.

Bacskay, G. B.; Bytheway, I.; Hush, N. S. *J. Am. Chem. Soc.* **1996**, *118*, 3753-3756.

Bader, R. F. W. *Chem. Rev.* **1991**, *91*, 893-928.

Bader, R. F. W. *Atoms in Molecules. A Quantum Theory*; Oxford University: Oxford, 1994.

Bader, R. F. W.; Anderson, S. G.; Duke, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 1389-1395.

Bastiaan, E. W.; Bulthuis, J.; MacLean, C. *Magn. Reson. Chem.* **1986**, *24*, 723-728.

Bastiaan, E. W.; MacLean, C. In *NMR Basic Principles and Progress, Vol. 25: NMR at Very High Field*; Diehl, P., Fluck, E., Günther, H., Kosfeld, R., Seelig, J., Eds.; Springer-Verlag: New York, 1991; pp 17-43.

Bastiaan, E. W.; MacLean, C.; van Zijl, P. C. M.; Bothner-By, A. A. In *Annual Reports on NMR Spectroscopy,* Vol. 19; Webb, G. A., Ed.; Academic: London, 1987; pp 35-77.

Bau, R.; Teller, R. G.; Kirtley, S. W.; Koetzle, T. F. *Accts. Chem. Res.* **1979**, *12*, 176-183.

Bautista, M. T.; Earl, K. A.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T.; Sella, A. *J. Am. Chem. Soc.* **1988**, *110*, 7031-7036.

Bianchini, C.; Peruzzini, M.; Zanobini, F. *J. Organomet. Chem.* **1988**, *354*, C19-C22.

Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920-3922.

Bushweller, C. H.; Brunelle, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 5949-5955.

Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726-7727.

Canet, D.; Robert, J. B. In *NMR Basic Principles and Progress, Vol. 25: NMR at Very High Field*; Diehl, P., Fluck, E., Günther, H., Kosfeld, R., Seelig, J., Eds.; Springer-Verlag: New York, 1991; pp 45-89.

Caspar, J. V.; Sullivan, B. P.; Meyer, T. J. *Organometallics* **1983**, *2*, 551-554.

Chinn, M.S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5166-5175.

Chinn, M.S.; Heinekey, D. M.; Payne, N. G.; Sofield, C. D. *Organometallics* **1989**, *8*, 1824-1826.

Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, 1987.

Collman, J. P.; Hutchison, J. E.; Lopez, M. A.; Guilard, R.; Reed, R. A. *J. Am. Chem. Soc.* **1991**, *113*, 2794-2796.

Collman, J. P.; Wagenknecht, P. S.; Hutchison, J. E.; Lewis, N. S.; Lopez, M. A.; Guilard, R.; L'Her, M.; Bothner-By, A. A.; Mishra, P. K. *J. Am. Chem. Soc.* **1992**, *114*, 5654-5664.

Cox, R. A.; Krull, U. J.; Thompson, M.; Yates, K. *Anal. Chim. Acta.* **1979**, *106*, 51-57.

Crabtree, R. H. *Inorg. Chim. Acta.* **1986**, *125*, L7-L8.

Crabtree, R. H. In *Comprehensive Coordination Chemistry*; Wilkinson, G. Ed.; Pergamon: Oxford, 1987; Vol. 2, pp 689-714.

Crabtree, R. H. *Accts. Chem. Res.* **1990**, *23*, 95-101.

Crabtree, R. H.; Lavin, M. *J. Chem. Soc., Chem. Commun.* **1985**, 794-795.

Craven, B. M. Program EKRT, University of Pittsburgh, 1992.

Craw, J. S.; Bacskay, G. B.; Hush, N. S. *Inorg. Chem.* **1993**, *32*, 2230-2231.

Craw, J. S.; Bacskay, G. B.; Hush, N. S. *J. Am. Chem. Soc.* **1994**, *116*, 5937-5948.

Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173-4184.

Drago, R. S. In *Physical Methods for Chemists, 2nd ed.*; Harcourt Brace Jovanovich: Orlando, 1977; p 218.

Dwyer, F. P.; Hogarth, J. W. *Inorganic Synthesis* **1957**, *5*, 206-207.

Eckert, J.; Albinati, A.; White, R. P.; Bianchini, C.; Peruzzini, M. *Inorg. Chem.* **1992**, *31*, 4241-4244.

Eckert, J.; Jensen, C. M.; Koetzle, T. F.; Husebo, T. L.; Nicol, J.; Wu, P. *J. Am. Chem. Soc.* **1995**, *117*, 7271-7272.

Evans, D. F. *Chem. Ind.* **1961**, 1960.

Fine, D. A. Ph.D. Thesis, University of Washington, Fall 1996.

Fujinaga, T.; Sakamoto, I *J. Electroanal. Chem.* **1977**, *85*, 185-201.

Geoffroy, G. L.; Bradley, M. G. *Inorg. Chem.* **1977**, *16*, 744-748.

Gladysz, J. A.; Selover, J. C.; Strouse, C. E. *J. Am. Chem. Soc.* **1978**, *100*, 6766-6767.

Günther, H. *NMR Spectroscopy: Basic Principles, Concepts, and Applications in Chemistry*, John Wiley & Sons: Chichester, 1995.

Gusev, D. G.; Kuhlman, R. L.; Renkema, K. B.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1996**, *35*, 6775-6783.

Gusev, D. G.; Kuznetsov, V. F.; Eremenko, I. L.; Berke, H. *J. Am. Chem. Soc.* **1993**, *115*, 5831-5832.

Gusev, D. G.; Notheis, J. U.; Rambo, J. R.; Hauger, B. E.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1994**, *116*, 7409-7410.

Hallman, P. S.; McGarvey, B. R.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 3143.

Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126-4133.

Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1990**, *112*, 2261-2263.

Hasegawa, T.; Li, Z.-W.; Parkin, S.; Hope, H.; McMullan, R. K.; Koetzle, T. F.; Taube, H. *J. Am. Chem. Soc.* **1994**, *116*, 4352-5356.

Hay, P. J. *Chem. Phys. Lett.* **1984**, *103*, 466-469.

Heinekey, D. M.; Hinkle, A. S.; Close, J. D. *J. Am. Chem. Soc.* **1996**, *118*, 5353-5361.

Heinekey, D. M.; Liegeois, A.; van Roon, M. *J. Am. Chem. Soc.* **1994**, *116*, 8388-8389.

Heinekey, D. M.; Luther, T. A. *Inorg. Chem.* **1996**, *35*, 4396-4399.

Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913-926.

Heinekey, D. M.; Oldham, W. J., Jr. *J. Am. Chem. Soc.* **1994**, *116*, 3137-3138.

Heinekey, D. M.; Oldham, W. J., Jr.; Wiley, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 12842-12843.

Heinekey, D. M.; Radzewich, C. E.; Voges, M. H.; Schomber, B. M. *J. Am. Chem. Soc.* **1997**, *119*, 4172-4181.

Heinekey, D. M.; Schomber, B. M.; Radzewich, C. E. *J. Am. Chem. Soc.* **1994**, *116*, 4515-4516.

Heinekey, D. M.; van Roon, M. *J. Am. Chem. Soc.* **1996**, *118*, 12134-12140.

Heinekey, D. M.; Voges, M. H.; Barnhart, D. M. *J. Am. Chem. Soc.* **1996**, *118*, 10792-10802.

Hush, N. S. *J. Am. Chem. Soc.* **1997**, *119*, 1717-1719.

Jalón, F. A.; Otero, A.; Manzano, B. R.; Villaseñor, E.; Chaudret, B. *J. Am. Chem. Soc.* **1995**, *117*, 10123-10124.

James, B. R.; Markham, L. D.; Hui, B. C.; Rempel, G. L. *J. Chem. Soc., Dalton Trans.* **1973**, 2247-2252.

Jameson, C. J.; Osten, H.-J. *J. Am. Chem. Soc.* **1986**, *108*, 2497-2503.

Jean, Y.; Eisenstein, O.; Volatron, F.; Maouche, B.; Sefta, F. *J. Am. Chem. Soc.* **1986**, *108*, 6587-6592.

Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155-289.

Jia, G.; Lough, A. L.; Morris, R. H. *Organometallics* **1992**, *11*, 161-171.

Jia, G.; Morris, R. H. *Inorg. Chem.* **1990**, *29*, 581-582.

King, W. A.; Luo, X-L.; Scott, B. L.; Kubas, G. J.; Zilm, K. W. *J. Am. Chem. Soc.* **1996**, *118*, 6782-6783.

Klooster, W. T.; Koetzle, T. F.; Jia, G.; Fong, T. P.; Morris, R. H.; Albinati, A. *J. Am. Chem. Soc.* **1994**, *116*, 7677-7681.

Kober, E. M.; Caspar, J. V.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1988**, *27*, 4587-4598.

Kristjánsdóttir, S. S.; Norton, J. R. In *Transition Metal Hydrides*; Dedieu, A.; Ed.; VCH: New York, 1992; pp 324-334.

Kubas, G. J. *Accts. Chem. Res.* **1988**, *21*, 120-128.

Kubas, G. J.; Burns, C. J.; Eckert, J.; Johnson, S. W.; Larson, A. C.; Vergamini, P. J.; Unkefer, C. J.; Khalsa, G. R. K.; Jackson, S. A.; Eisenstein, O. *J. Am. Chem. Soc.* **1993**, *115*, 569-581.

Kubas, G. J.; Burns, C. J.; Khalsa, G. R. K.; Van Der Sluys, L. S.; Kiss, G.; Hoff, C. D. *Organometallics* **1992**, *11*, 3390-3404.

Kubas, G. J.; Jarvinen, G. D.; Ryan, R. R. *J. Am. Chem. Soc.* **1983**, *105*, 1883.

Kubas, G. J.; Nelson, J. E.; Bryan, J. C.; Eckert, J.; Wisniewski, L; Zilm, K. *Inorg. Chem.* **1994**, *33*, 2954-2960.

Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451-452.

Kubas, G. J.; Unkefer, C. J.; Swanson, B. I.; Fukushima, E. *J. Am. Chem. Soc.* **1986**, *108*, 7000-7009.

Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 1271-1285.

Li, Z.-W.; Taube, H. *J. Am. Chem. Soc.* **1991**, *113*, 8946-8947.

Li, Z.-W.; Taube, H. *J. Am. Chem. Soc.* **1994**, *116*, 9506-9513.

Malin, J.; Taube, H. *Inorg. Chem.* **1971**, *10*, 2403-2406.

Maltby, P. A.; Schlaf, M.; Steinbeck, M.; Lough, A. J.; Morris, R. H.; Klooster, W. T.; Koetzle, T. F.; Srivastava, R. C. *J. Am. Chem. Soc.* **1996**, *118*, 5396-5407.

Maseras, F.; Lledós, A.; Costas, M.; Poblet, J. P. *Organometallics*, **1996**, *15*, 2947-2953.

Moreno, B.; Sabo-Etienne, S.; Chaudret, B.; Rodriguez, A.; Jalón, F.; Trofimenko, S. *J. Am. Chem. Soc.* **1994**, *116*, 2635-2636.

Morris, R. H. *Inorg. Chem.* **1992**, *31*, 1471-1478.

Neuner, B.; Schrock, R. R. *Organometallics* **1996**, *15*, 5-6.

Oldham, W. J., Jr.; Heinekey, D. M. *Organometallics* **1997**, *16*, 467-474.

Orioli, P. L.; Vaska, L. *Proc. Chem. Soc., London* **1962**, 333.

Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*; 2nd ed.; John Wiley & Sons: New York, 1992.

Perdoncin, G.; Scorrano, G. *J. Am. Chem. Soc.* **1977**, *99*, 6983-6986.

Radzewich, C. E. Ph.D. Thesis, University of Washington, Winter 1997.

Ricci, J. S.; Koetzle, T. F.; Bautista, M. T.; Hofstede, T. M.; Morris, R. H.; Sawyer, J. F. *J. Am. Chem. Soc.* **1989**, *111*, 8823-8827.

Rocchini, E.; Mezzetti, A.; Rüegger, H.; Burckhardt, U.; Gramlich, V.; Del Zotto, A.; Martinuzzi, P.; Rigo, P. *Inorg. Chem.* **1997**, *36*, 711-720.

Sabo-Etienne, S.; Chaudret, B.; el Makarim, H. A.; Barthelat, J.; Daudey, J.; Ulrich, S.; Limbach, H.; Moïse, C. *J. Am. Chem. Soc.* **1995**, *117*, 11602-11603.

Saillard, J.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006-2026.

Salvatore, B. A.; Ghose, R.; Prestegard, J. H. *J. Am. Chem. Soc.* **1996**, *118*, 4001-4008.

Sánchez-Delgado, R. A.; Bradley, J. S.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1976**, 399-404.

Sánchez-Delgado, R. A.; Thewalt, U.; Valencia, N.; Andriollo, A.; Márquez-Silva, R-L.; Puga, J.; Schöllhorn, H.; Klein, H-P.; Fontal, B. *Inorg. Chem.* **1986**, *25*, 1097-1106.

Sánchez-Delgado, R. A.; Valencia, N.; Márquez-Silva, R-L.; Andriollo, A.; Medina, M. *Inorg. Chem.* **1986**, *25*, 1106-1111.

Schalf, M.; Lough, A. J.; Maltby, P. A.; Morris, R. H. *Organometallics* **1996**, *15*, 2270-2278.

Schalf, M.; Lough, A. J.; Morris, R. H. *Organometallics* **1993**, *12*, 3808-3809.

Smith, K.-T.; Tilset, M.; Kuhlman, R.; Caulton, K. G. *J. Am. Chem. Soc.* **1995**, *117*, 9473-9480.

Sullivan, B. P.; Caspar, J. V.; Johnson, S. R.; Meyer, T. J. *Organometallics* **1984**, *3*, 1241-1251.

Sullivan, B. P.; Lumpkin, R. S.; Meyer, T. J. *Inorg. Chem.* **1987**, *26*, 1247-1252.

Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334-3341.

Sweet, J. R.; Graham, W. A. G. *Organometallics* **1982**, *1*, 982-986.

Tsuji, J.; Suzuki, H. *Chem. Lett.* **1977**, 1085-1086.

Van Geet, A. L. *Analytical Chemistry* **1970**, *42*, 679-680.

van Zijl, P. C. M.; Ruessink, B. H.; Bulthuis, J.; MacLean, C. *Accts. Chem. Res.* **1984**, *17*, 172-180.

Vigalok, A.; Ben-David, Y.; Milstein, D. *Organometallics* **1996**, *15*, 1839-1844.

Winemiller, M. D.; Kopach, M. E.; Harman, W. D. *J. Am. Chem. Soc.* **1997**, *119*, 2096-2102.

Woessner, D. E. *J. Chem. Phys.* **1962**, *36*, 1-4.

Woessner, D. E. *J. Chem. Phys.* **1962**, *37*, 647-654.

Zilm, K. M.; Merrill, R. A.; Kummer, M. W.; Kubas, G. J. *J. Am. Chem. Soc.* **1986**, *108*, 7837-7839.

Zilm, K. W.; Millar, J. M. *Adv. Magn. Opt. Reson.* **1990**, *15*, 163-200.

APPENDIX

Compilation of ^1H and ^{31}P {aromatic ^1H} NMR Chemical Shifts and Coupling Constants

Table A.1. Compilation of ^1H and $^{31}P\{aromatic\ ^1H\}$ NMR Data.[a]

compound	$^1H\ \delta$ ($\Delta\delta$ ppb)	m	J_{HP} or J_{HD} (Hz)	$^{31}P\ \delta$ ($\Delta\delta$ ppb)	m	J_{PP} (Hz)	J_{PH}
$Os(H)(Cl)(PPh_3)_3(CO)$	-6.95	dt	24.7 *cis*	+7.83	dd	11	23 *cis*
			86.3 *trans*	-9.14	dt	11	83 *trans*
$[OsH(PPh_3)_2(bpy)(CO)]^+$	-12.19	t	18.4	+18.76	d		17
$[Os(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$	-5.78	s		+8.54	s		
$[Os(HD)(PPh_3)_2(bpy)(CO)]^{2+}$	-6.01 (+18)	t	25.3	+7.89 (+80)	s		
$Os(H)(Cl)(PMePh_2)_3(CO)$	-6.45	dt	22.2 *cis*	-20.1		13	
			85.3 *trans*	-23.1		13	
$[OsH(PMePh_2)_2(bpy)(CO)]^+$	-12.22	t	17.6	+0.08	d		14
$[Os(H_2)(PMePh_2)_2(bpy)(CO)]^{2+}$	-6.23	s		-6.02			
$[Os(HD)(PMePh_2)_2(bpy)(CO)]^{2+}$	-6.32 (+20)	t	25.5	-6.30 (+99)	s		
$[OsH(PPh_3)_2(phen)(CO)]^+$	-11.98	t	18.1	+19.25	d		17
$[Os(H_2)(PPh_3)_2(phen)(CO)]^{2+}$	-5.63	s		+8.60	s		
$[Os(HD)(PPh_3)_2(phen)(CO)]^{2+}$	-5.72 (< +20)	t	25.5	+8.36 (+81)	s		

compound	$^1H\ \delta$ ($\Delta\delta$ ppb)	m	J_{HP} or J_{HD} (Hz)	$^{31}P\ \delta$ ($\Delta\delta$ ppb)	m	J_{PP} (Hz)	J_{PH}
$[OsCl(PPh_3)_2(bpy)(CO)]^+$				-0.33	s		
$[OsBr(PPh_3)_2(bpy)(CO)]^+$				-1.97	s		
$Ru(H)(Cl)(PPh_3)_3(CO)$	-7.18	dt	24.0 *cis*	+40.30	dd	15	23 *cis*
			104.1 *trans*	+12.80	dt	15	103 *trans*
$[RuH(PPh_3)_2(bpy)(CO)]^+$	-11.31	t	19.6	+46.53	d		18
$[Ru(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$	-6.70	s		+32.81	s		
$[Ru(HD)(PPh_3)_2(bpy)(CO)]^{2+}$	-6.84 (< +20)	t	31.0	+32.45 (+40)	s		
$[RuCl(PPh_3)_2(bpy)(CO)]^+$				+27.38			
$OsH(bpy)_2(CO)]^+$	-11.52	s					
$[Os(H_2)(bpy)_2(CO)]^{2+}$	-4.23	s					
$[Os(HD)(bpy)_2(CO)]^{2+}$	-4.23	t	29.0				

[a] NMR spectra were recorded at 500 MHz (^1H) and 202 MHz (^{31}P). Solvent used was CD_2Cl_2 except for $OsH(bpy)_2(CO)]^+$, $[Os(H_2)(bpy)_2(CO)]^{2+}$, and $[Os(HD)(bpy)_2(CO)]^{2+}$ which were dissolved in CD_3NO_2.

Thomas Alan Luther was born December 7, 1953 in Turlock, California. He attended California State College, Stanislaus in 1972-1973 before transferring to Colorado State University in Fort Collins, Colorado where he attended until the Spring of 1975. During the extended absence from education he was involved in concert production work in the Denver, Colorado area before moving in March of 1978 to Geyser, Montana for 11 years where he managed the local grain elevator. In 1989 he returned to Fort Collins to continue his undergraduate education at Colorado State University and received a Bachelor of Science in Chemistry in May of 1992. He began graduate research with D. Michael Heinekey at the University of Washington in July of 1992 and completed his Doctor of Philosophy in Inorganic/Organometallic Chemistry in June of 1997.