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Ligand effects on the heats of protonation of metal-metal bonds in organometallic complexes

by

Chip Nataro

A dissertation submitted to the graduate faculty

in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Inorganic Chemistry

Major Professor: Robert J. Angelici

Iowa State University

Ames, Iowa

1997

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For the Major Program

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For the Graduate College

To the people who have always been there for me:

Marthur Anne Nataro, Sidney Leigh Nataro and

Charlene Ann Hoell

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ABBREVIATIONS

Cp, η^5-C_5H_5 ligand

MeCp, η^5-C_5MeH_4 ligand

Cp*, η^5-C_5Me_5 ligand

Cp‡, η^5-$C_5Me_4CF_3$ ligand

Cp', subsituted cyclopentadienyl ligand

Ind, η^5-C_9H_7 ligand

Fv, η^5: $\eta^{5'}$ $C_{10}H_8$ lignad

HBpz$_3$, $HB(C_3H_3N_2)_3$ ligand

Me, -CH_3 group

Et, -CH_2CH_3

^{i}Pr, -$CH(CH_3)_2$

^{t}Bu, -$C(CH_3)_3$

Ph, -C6H5 group

p-tol, *p*-$C_6H_4CH_3$

Cy, -C_6H_{11} group

dppm, $Ph_2PCH_2PPh_2$

dppe, $Ph_2PCH_2CH_2PPh_2$

dmpm, $Me_2PCH_2PMe_2$

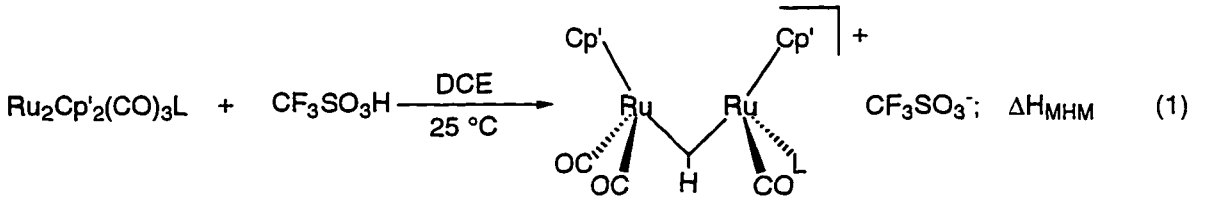
L∩L, bidentate phosphine

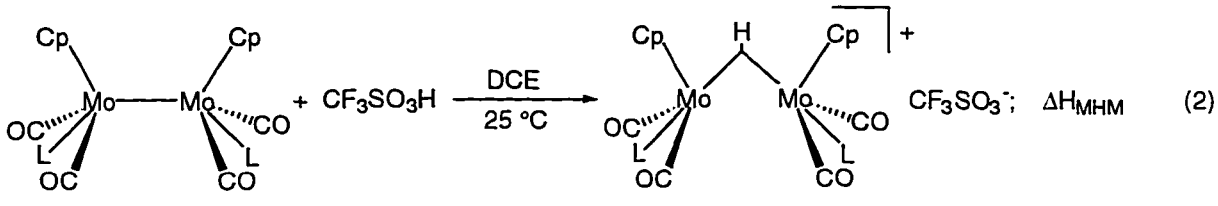
PNP, $R_2PN(R')PR_2$ ligand

POP, R_2POPR_2 ligand

ABSTRACT

Calorimetric determination of the metal center basicity in organometallic complexes has proven to be a useful tool for understanding reactivity trends. Similar studies conducted on metal-metal bonded species to determine discrete metal-metal bond basicity could offer a simple model of reactivity for transition metal surfaces. However, few examples of dinuclear compounds exist in which protonation occurs at the metal-metal bond to form the bridging hydride. In this research, the basicities of the metal-metal bond in $Ru_2Cp'_2(CO)_3L$ and $Mo_2Cp_2(CO)_4L_2$ have been determined. Basicities have been measured by the heat evolved (ΔH_{MHM}) when a metal complex is protonated by CF_3SO_3H in 1,2-dichloroethane (DCE) to form either $Ru_2Cp'_2(CO)_3L(\mu\text{-}H)^+$ (eq 1) or $Mo_2Cp_2(CO)_4L_2(\mu\text{-}H)^+$ (eq 2) at 25 °C.

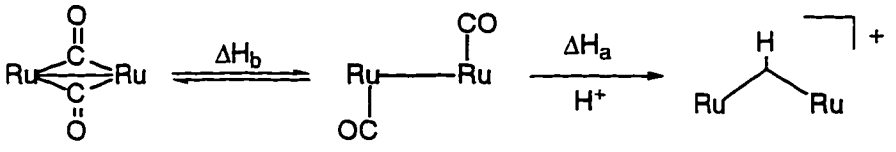




Previous protonation studies of mononuclear cyclopentadienyl complexes have found that the basicity of a metal center is increased by replacing Cp with a more electron donating Cp' ligand. Complexes which contain a Cp* ligand have been found to be significantly more basic than the Cp analog. Similarly, the basicity of the metal center in mononuclear complexes when L = PR_3 has been found to be substantially more basic than when L = CO. In these studies it was found that the metal-metal bond basicity is affected by the electron donor ability of the Cp' or L ligands. However, the observed data could not be explained based solely on

electronic arguments. Another factor, which could not be observed in mononuclear species, was found to influence the overall metal-metal bond basicity.

In the ruthenium system, the complexes can have either four terminal carbonyls, two bridging and two terminal carbonyls or there can be a mixture of these two isomers. The ΔH_{MHM} can be considered to be the sum of H_a and H_b (eq3).



(3)

The relative amounts of the bridging and non-bridging isomers affect the overall basicity of the complex. This can be seen in complexes that are expected to have similar basicity based on electronic arguments, but in fact have very different heats of protonation. It was determined that the Ru-Ru bond in $Cp_2Ru_2(CO)_4$ is substantially more basic than the Ru in the related mononuclear $CpRu(CO)_2H$.

GENERAL INTRODUCTION

Dissertation Organization

This dissertation contains two papers in the format required for journal publication, describing the research I performed at Iowa State University. Preceding these papers is a literature review of the protonation of metal-metal bonded, bimetallic organometallic complexes. In the literature review as well as the papers, the literature citations, schemes, tables and figures pertain only to the chapters in which they appear. After the final paper is a general summary.

PROTONATION OF METAL-METAL BONDED BIMETALLIC ORGANOMETALLIC COMPLEXES

Introduction

The study of transition metal complexes in which there is a hydride ligand bound to the metal has been a topic of considerable interest.[1] Hydride ligands can be bonded terminally to a single metal atom (M-H) or bridge between two or more metal centers (μ-H).[2] Bridging hydride complexes have been prepare by a variety of means, but protonation of a M-M bond is a particularly interesting method, as it gives insight into the basicity of the metal-metal bond. Metal-metal bond protonation also provides the opportunity to study the basicity of the bonding pair of electrons in a metal-metal bond.

The purpose of this review is to summarize the presently available information relating to the protonation of metal-metal bonds in bimetallic organometallic complexes. Complexes that contain more than two metal centers and complexes that protonate at a site other than the metal-metal bond will not be discussed. Unless otherwise stated, protonation of these complexes occurs quantitatively with one equivalent of the appropriate acid. In some cases, the protonated products rearrange further to give additional products. However, by using a variety of techniques, the species in which there is a protonated metal-metal bond was characterized.

The present survey covers the literature through the end of 1996.

Protonation of Metal-Metal Bonds

Chromium-Chromium

There are only a few examples of protonation of Cr-Cr bonds in dimeric complexes. In THF, the compound $Cr_2(CO)_{10}^{2-}$ is readily protonated at the Cr-Cr bond by 1 equivalent of

HCl in ether.[3] This results in the formation of the complex $(\mu\text{-H})Cr_2(CO)_{10}^-$. X-ray and neutron determined structures of these compounds have been obtained with a variety of counter cations, all of which show that the hydride is symmetrically located between the Cr atoms and that the Cr-H-Cr unit is not linear.[4]

Protonation of the compounds $M_2Cp_2(CO)_6$ (M = Mo or W) has been studied and will be discussed in a following section. However, protonation of the Cr analog $Cr_2Cp_2(CO)_6$ has not been reported. This may be due in part to the tendency of the dimer to undergo homolytic Cr-Cr bond cleavage to form the 17 electron species $Cp(CO)_3Cr$.[5]

Molybdenum-Molybdenum

The protonation of Mo-Mo bonds in dimeric complexes has received slightly more attention than the Cr analogs. Similar to the Cr compound, a THF solution of $Mo_2(CO)_{10}^{2-}$ can be protonated with 1 equivalent of HCl in ether to give $(\mu\text{-H})Mo_2(CO)_{10}^-$.[3] Surprisingly, Behrens and Haag[6] discovered that the compound $Mo_2(CO)_{10}^{2-}$ could also be protonated by water. This implies that the Mo complex is more basic than the Cr analog, which is not protonated by water.

Protonation of $Mo_2Cp_2(CO)_6$ occurs with excess 98% H_2SO_4 to give the hydride bridged species, $(\mu\text{-H})Mo_2Cp_2(CO)_6^+$.[7] This compound has also been protonated in 1,2-dichloroethane with triflic acid (CF_3SO_3H), and requires a three-fold excess of acid.[8] A variety of related complexes $Mo_2Cp_2(CO)_4L_2$ have also been studied. Riera[9] found that $Mo_2Cp_2(CO)_4(\mu\text{-dppm})$ in toluene is protonated with an excess of HBF_4 to give $(\mu\text{-H})Mo_2Cp_2(CO)_4(\mu\text{-dppm})^+$. Protonation of the monodentate phosphine complexes $Mo_2Cp_2(CO)_4L_2$ (where L = PMe_3, PMe_2Ph, $PMePh_2$ or PPh_3) have also been studied.[8]

Tungsten-Tungsten

Compounds of W behave quite similarly to their Mo analogs. Protonation of the W-W bond in $W_2(CO)_{10}^{2-}$ can be carried out with water[10] or HCl in acetone[3] to give $(\mu\text{-H})W_2(CO)_{10}^-$. Protonation of $W_2Cp_2(CO)_6$ occurs with excess 98% H_2SO_4 to give $(\mu\text{-H})W_2Cp_2(CO)_6^+$.[7] Tilset, Vollhardt and Boese[11] have performed a qualitative comparison of the effect of Cp and fv ligands on the basicity of a W-W bond. Using excess HBF_4, a CH_2Cl_2 solution of $W_2fv(CO)_6$ protonates to give $(\mu\text{-H})W_2fv(CO)_6$. However, under the same conditions, the Cp analog does not protonate, leading to the conclusion that the fv ligand makes the W-W bond more basic than the Cp ligands.

Manganese-Manganese

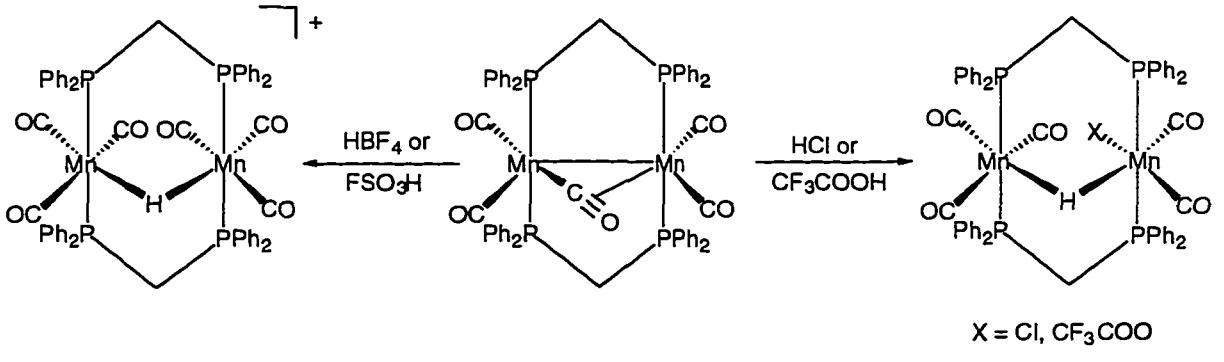
A variety of anionic Mn-Mn bonded dimers have been found to protonate at the metal-metal bond. In CH_2Cl_2, $Mn_2(CO)_8(\mu\text{-PCy}_2)^-$ reacts with HBF_4 to give the bridging-hydrido, bridging-phosphido complex $Mn_2(CO)_8(\mu\text{-PCy}_2)(\mu\text{-H})$.[12] A variety of compounds of the general form $Mn_2(\mu\text{-L}\frown\text{L})_n(CO)_{8-2n}(\mu\text{-X})^-$ (μ-L$\frown$L = dppm or POP; n = 1 or 2) are protonated in THF by H_3PO_4. These compounds are summarized in Table 1.[13]

Deeming has studied the protonation of $Mn_2(CO)_4(\mu\text{-dppm})_2L$ where L = CO[14, 15] or CNR (R = *p*-tol) in CH_2Cl_2.[15] The products of the reaction depend greatly on which acid is used for the protonation (Scheme 1). With all acids used, a protonated complex, $Mn_2(CO)_4(\mu\text{-dppm})_2(\mu\text{-CO})(\mu\text{-H})^+$ was postulated as the initial intermediate. This intermediate could then either coordinate the counter anion (in the case of HCl or CF_3COOH) or abstract a CO from another dimer (as was the case with HBF_4 or FSO_3H). In this later case, only partial formation of the final product was observed. NMR studies of the protonation reaction with HBF_4 at -80 °C allowed for identification of the intermediate.[14] The protonation of a similar

Table 1. Protonation of $Mn_2(\mu\text{-}L\frown L)_n(CO)_{8-2n}(\mu\text{-}X)^-$ (n = 1 or 2) complexes.

Starting Complex	Protonated Product
$Mn_2(CO)_6(\mu\text{-POP})(\mu\text{-X})^-$	$Mn_2(CO)_6(\mu\text{-POP})(\mu\text{-X})(\mu\text{-H})$
R = OEt	R = OEt
X = Br, I	X = Br, I
$Mn_2(CO)_4(\mu\text{-POP})_2(\mu\text{-X})^-$	$Mn_2(CO)_4(\mu\text{-POP})_2(\mu\text{-X})(\mu\text{-H})$
R = OEt	R = OEt
X = Br, I	X = Br, I
$Mn_2(CO)_6(\mu\text{-dppm})(\mu\text{-Cl})^-$	$Mn_2(CO)_6(\mu\text{-dppm})(\mu\text{-Cl})(\mu\text{-H})$

complex in which the bridging carbonyl was substituted with a bridging iso-cyanide was also studied. Protonation at -80 °C allowed for NMR characterization of the analogous intermediate, $Mn_2(CO)_4(\mu\text{-dppm})_2(\mu\text{-CNR})(\mu\text{-H})^+$ (R = *p*-tol), however, the protonation was not complete.



Scheme 1. Protonation of $Mn_2(CO)_5(\mu\text{-dppm})_2$

Rhenium-Rhenium

Anionic rhenium dimers have not been as thoroughly studied as the analogous Mn complexes. Riera[13] has protonated the compound $Re_2(CO)_6(\mu\text{-}(EtO)_2POP(OEt)_2)(\mu\text{-}Br)^-$ in THF with excess H_3PO_4. Similar to the manganese analog (Table 1), the protonation occurs at the Re-Re bond.

Protonation of the neutral compounds $Re_2Cp'_2(CO)_4(\mu\text{-}CO)$ (Cp' = Cp or MeCp), has been carried out by Lewis and Caulton.[16] This reaction was done in CH_2Cl_2 with excess CF_3SO_3H at -70 °C and resulted in the formation of $Re_2Cp'_2(CO)_4(\mu\text{-}CO)(\mu\text{-}H)^+$.

Iron-Iron

Three dimeric iron complexes of the type $Fe_2Cp_2(CO)_4$ and the related phosphine substituted complexes $Fe_2Cp_2(CO)_{4-n}L_n$ (n = 0, 1 or 2) have been protonated. The unprotonated complexes exist as either a carbonyl bridged isomer (two terminal CO's and two bridging), an all terminal isomer, or as a mixture of the two isomers, depending on the nature of the Cp' ligand and the L groups. Protonation of these compounds occurs at the Fe-Fe bond to give a bridging hydride with all of the carbonyl ligands in terminal positions. The available data on the protonation of this series of compounds are displayed in Table 2

Protonation of compounds of the general type $[Fe_2(CO)_{8-2n}(\mu\text{-}L\frown L)_n(\mu\text{-}CO)]$ (μ-L$\frown$L = dppm, dmpm or PNP; n = 1 or 2) has also been studied. The majority of these studies has focused on the complexes where n = 2. Again, all of these dimers undergo protonation at the Fe-Fe bond to give a bridging hydride with all terminal carbonyl ligands. The complexes that were protonated, as well as the acids used for the protonation are presented in Table 3.

Table 2. Protonation of $Fe_2Cp'_2(CO)_{4-n}L_n$

Compound	Acid	Ref.
$Fe_2Cp_2(CO)_4$	excess HF + PCl_5[a]	7
	excess 98% H_2SO_4	7, 17
	excess HBF_4	18
$Fe_2Cp_2(CO)_3(P(OMe)_3)$	excess 98% H_2SO_4	17
$Fe_2Cp_2(CO)_2(\mu\text{-dppm})$	HBF_4	19

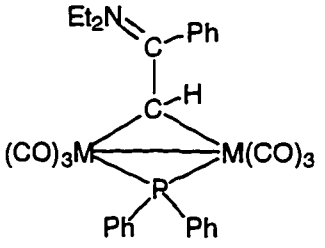
[a] PCl_5 was used to form the PF_6^- salt.

The protonation of complexes with bridging phosphido and sulfido ligands has also been investigated. Walther, *et. al.*[23] have studied the protonation of $Fe_2(CO)_6(\mu\text{-CO})(\mu\text{-PR}_2)^-$ (R = ^{t}Bu or Ph) in THF. When R = ^{t}Bu, the complex protonates completely with acetic acid. However, when R = Ph, CF_3COOH must be used for complete protonation. The exact location of the hydride ligand in the product was not determined. However, addition of $MPPh_3^+$ (M = Cu, Ag, Au), which is isolobal with H^+, led to the formation of $Fe_2(CO)_6(\mu\text{-CO})(\mu\text{-PR}_2)(\mu\text{-MPPh}_3)$ which was characterized completely. This result leads to the conclusion that protonation most likely occurs at the Fe-Fe bond to form $Fe_2(CO)_6(\mu\text{-CO})(\mu\text{-PR}_2)(\mu\text{-H})$. Poilblanc, *et. al.* have studied the protonation of $Fe_2(CO)_4(\mu\text{-A})(\mu\text{-A}')L_2$ complexes in MeOH with excess $HClO_4$.[24,25] Protonation occurs at the Fe-Fe bond to form $Fe_2(CO)_4(\mu\text{-A})(\mu\text{-A}')L_2(\mu\text{-H})^+$. For each combination of A and A', four different complexes were studied where L = PMe_3, PMe_2Ph, $PMePh_2$ or PPh_3. The different A and A' groups studied are listed below (Table 4). The extent of protonation and the final geometry of the protonated complexes are greatly affected by the properties of both L and A/A'. In EtOH solution, the compound with two μ-SMe groups protonates completely at the

Fe-Fe bond with excess HCl when L = PMe_3 or PMe_2Ph.[24] However, when L = $PMePh_2$ or PPh_3 only partial protonation of the Fe-Fe bond occurred. The protonated products of the compounds with μ-SR groups all have L groups that are *trans-* to the protonated Fe-Fe bond. However, with the stronger electron donating μ-PR_2 groups the L group is not *trans-* to the protonated Fe-Fe bond.

Table 3. Protonation of $Fe_2(CO)_{8-2n}(\mu\text{-}L\frown L)_n(\mu\text{-}CO)$ complexes.

Compound	Acid	Solvent	Ref.
$Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}dppm)$	HBF_4	CH_2Cl_2	20
$Fe_2(CO)_4(\mu\text{-}CO)(\mu\text{-}dppm)_2$	HBF_4 or HPF_6	C_6H_6 or Et_2O	21
$Fe_2(CO)_4(\mu\text{-}CO)(\mu\text{-}dmpm)_2$	HBF_4 or HPF_6	C_6H_6 or Et_2O	21
$Fe_2(CO)_4(\mu\text{-}CO)(\mu\text{-}PNP)_2$	HBF_4 or HPF_6	C_6H_6 or Et_2O	21
R' = Et			
R = OMe, OEt, O^{i}Pr or OPh			
$Fe_2(CO)_4(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}dmpm)$	HBF_4	Et_2O	22
$Fe_2(CO)_4(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}PNP)$	HBF_4	Et_2O	22
R' = Et			
R = OMe or Ph			
$Fe_2(CO)_4(\mu\text{-}CO)(\mu\text{-}dmpm)(\mu\text{-}PNP)$	HBF_4	Et_2O	22
R' = Et, R = OMe			
R' = Me, R = OEt			



M = Fe, Ru or Os

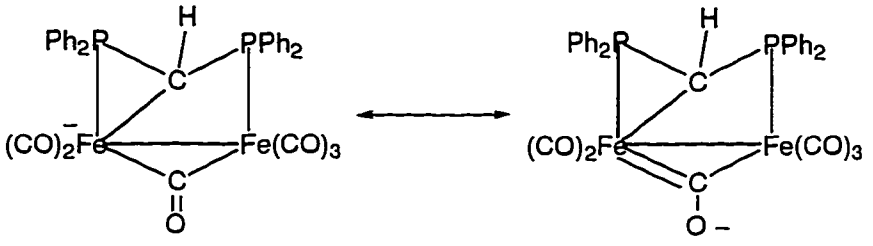
Figure 1. Group 8 dimers with bridging phosphido and carbene ligands.

The complex with both a bridging phosphido and a carbene ligand (Figure 1) was found to protonate in CH_2Cl_2 with excess HBF_4 at -78 °C. Protonation occured at the Fe-Fe bond to give the μ-H cationic complex,which still contains a bridging phosphido ligand and the bridging carbene group.[26]

Table 4. Variation of A and A' groups in $Fe_2(CO)_4(\mu\text{-}A)(\mu\text{-}A')L_2$.

A	A'
SMe	SMe
SPh	SPh
SPh	PPh_2
PPh_2	PPh_2
PMe_2	PPh_2

Several anionic iron dimers have been protonated at the Fe-Fe bond. The compound $Fe_2(CO)_8^{2-}$ is protonated with acetic acid to give $Fe_2(CO)_8(\mu\text{-}H)^-$.[27,28] A related anionic iron dimer (Scheme 2) was also found to undergo protonation at the Fe-Fe bond with CF_3COOH to give the (μ-H) species.[29] This is somewhat unexpected, since resonance structures can be drawn as in Scheme 2, which show the anionic charge delocalized between an iron atom and the oxygen atom of the bridging carbonyl.

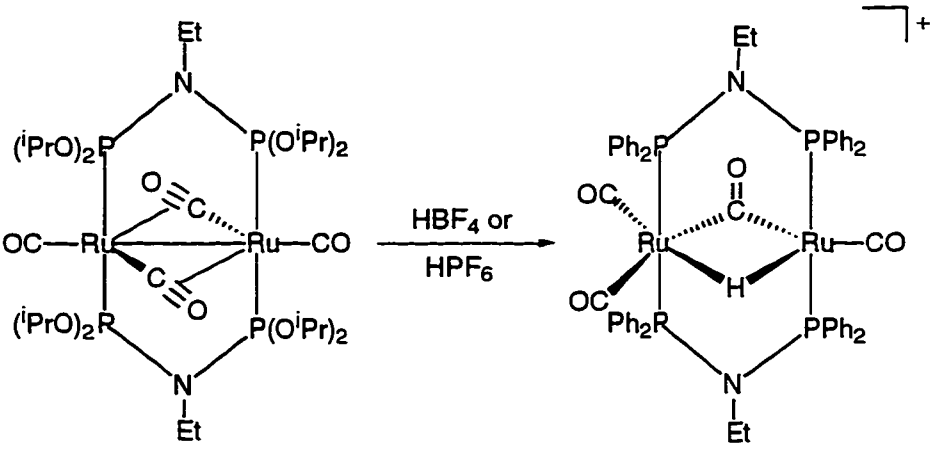


Scheme 2. Resonance structures.

Ruthenium-Ruthenium

The protonation of the Ru-Ru bond in dimeric ruthenium complexes is quite similar to the protonation of the analogous iron dimers. $Ru_2Cp_2(CO)_4$ has been protonated with excess 98% H_2SO_4[7,17] and HCl in liquid Xe[30] to give $Ru_2Cp_2(CO)_4(\mu\text{-}H)^+$. The Cp* analog has also been found to protonate at the Ru-Ru bond in CH_2Cl_2 with HBF_4.[31] The protonation of additional substituted Cp complexes $Ru_2Cp'_2(CO)_4$ has also been studied,[32] and has shown analogous results.

Compared to the iron complexes discussed previously, very few ruthenium complexes of the type $Ru_2(CO)_4(\mu\text{-}CO)(\mu\text{-}L\frown L)_2$ have been protonated. Only the dppm[21] (in C_6H_6 or Et_2O) and dmpm[33] (in CH_2Cl_2) complexes have been protonated, and both protonate with HBF_4 to give $Ru_2(CO)_4(\mu\text{-}CO)(\mu\text{-}L\frown L)_2(\mu\text{-}H)^+$. The protonation of a closely related complex has been studied by Field, *et. al.*[34] (Scheme 3).



Scheme 3. Protonation of $Ru_2(CO)_4(\mu\text{-PNP})_2$.

The Ru complex shown in Figure 1 was found to protonate at the Ru-Ru bond in CH_2Cl_2 with an excess of HBF_4.[26]

Osmium-Osmium

The osmium compound shown in Figure 1 is the only known osmium dimer to undergo protonation at the Os-Os bond. Similar to the iron and ruthenium complexes, a CH_2Cl_2 solution of the compound requires an excess of HBF_4 to be protonated completely.[26]

Cobalt-Cobalt

A majority of the Co-Co dimers that have been protonated are in complexes of the general type $Co_2Cp'_2(\mu\text{-}PR_2)_2$. Protonation occurs at the Co-Co bond, forming a cationic μ-H species while maintaining the bridging phosphido groups. The complexes that have been protonated are summarized in Table 5.

Field, *et. al.*[39] reported the only other cobalt dimers that protonate at the Co-Co bond. In those studies, solutions of the compounds $Co_2(CO)_4(\mu\text{-PNP})_2$ (R' = Et; R = Me or ^{i}Pr) in methanol were found to protonate with aqueous HPF_6.

Table 5. Protonation of $Co_2Cp'_2(\mu\text{-}PR_2)_2$ complexes.

Compound	Acid	Ref.
$Co_2Cp_2(\mu\text{-}PMe_2)_2$	excess CF_3COOH	35, 36
$Co_2Cp_2(\mu\text{-}PPh_2)_2$	excess CF_3COOH or HBF_4	36
$Co_2Cp_2(\mu\text{-}PEt_2)_2$	HBF_4	37
$Co_2Cp_2(\mu\text{-}PMePh)_2$	HBF_4	37
$Co_2Cp_2(\mu\text{-}PhPCH_2CH_2PPh)$	HBF_4	37
$Co_2Cp_2(\mu\text{-}PhPCH_2CH_2CH_2PPh)$	HBF_4	37
$Co_2Cp^*_2(\mu\text{-}PMe_2)_2$	CF_3COOH	38

Rhodium-Rhodium

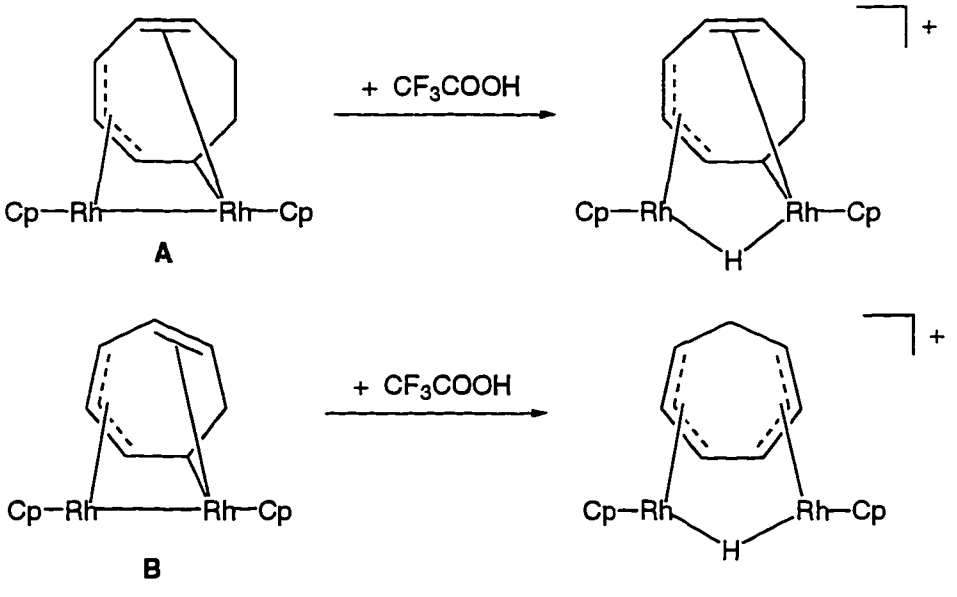
A variety of complexes of the type $Rh_2Cp'_2(CO)_2(\mu\text{-}L)$ (L = CO or CH_2) are known which protonate at the Rh-Rh bond. These complexes are summarized in Table 6.

The protonation of a number of compounds of the type $Rh_2(CO)_n(\mu\text{-}L\frown L)(L)$ has also been studied. The compound $Rh_2(CO)_2(\mu\text{-dppm})_2$ protonates in Et_2O with HPF_6 or *p*-$tolSO_3H$.[46,47] Protonation of $(CO)_2Rh(\mu\text{-dmpm})_2Rh(CO)$ occurs in Et_2O with HBF_4 to give the complex $Rh_2(CO)_2(\mu\text{-dmpm})_2(\mu\text{-CO})(\mu\text{-H})^+$.[48] In a similar complex which contains a bridging alkyne $Rh_2(CO)_2(\mu\text{-dppm})_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}C_2(CO_2Me)_2)$, protonation occurs in THF at the Rh-Rh bond with HBF_4 giving $Rh_2(CO)_2(\mu\text{-dppm})_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}C_2(CO_2Me)_2)(\mu\text{-H})^+$.[48]

Table 6. Protonation of $Rh_2Cp'_2(CO)_2(\mu\text{-L})$ complexes.

Compound	Acid	Ref.
$Rh_2Cp_2(CO)_2(\mu\text{-}CH_2)$	HCl or HBr	40, 41
	HBF_4, CF_3SO_3H or FSO_3H	42
$Rh_2Cp_2(CO)_2(\mu\text{-CO})$	HBF_4	41-43
$Rh_2Cp^*_2(CO)_2(\mu\text{-CO})$	HBF_4	44
$Rh_2(Cp_2CH_2)(CO)_2(\mu\text{-CO})$	CF_3SO_3H	45

One of the more thoroughly studied metal-metal bond protonation reactions is depicted in Scheme 4.[49] In both of the examples shown, deuterium labeling experiments have shown that the initial site of protonation is the C_8 (**A**) or C_7 (**B**) ring. This short lived intermediate then transfers a proton to the Rh-Rh bond forming the cationic bridging hydride species.



Scheme 4. Protonation of $Rh_2Cp_2(\mu\text{-cycloalkene})$

Iridium-Iridium

A solution of the compound $Ir_2(CO)_4(\mu\text{-dppm})_2$ in CH_2Cl_2 can be protonated with HBF_4 to give $Ir_2(CO)_4(\mu\text{-dppm})_2(\mu\text{-H})^+$.[50] Bonnet, *et. al.*[51] have studied the series of complexes $Ir_2L_2(H)_2(CO)_2(\mu\text{-S}^t\text{Bu})_2$ where L = $P(OMe)_3$, PMe_3 or PPh_3. Protonation occurs at the Ir-Ir bond in EtOH when the compounds are reacted with excess $HClO_4$. Surprisingly, H_2 is not eliminated from the complex upon protonation. Protonation of $Ir_2Cp^*_2(CO)_2(\mu\text{-L})$ (L = CO or CH_2) has also been carried out.[52] When L = CO, protonation of the Ir-Ir bond occurs with excess $CH_2(SO_2CF_3)_2$in CH_2Cl_2. When L = CH_2 use of either excess HBF_4 or excess $CH_2(SO_2CF_3)_2$ in CH_2Cl_2 will protonate the Ir-Ir bond.

Palladium-Palladium

The protonation of one palladium dimer has been studied. The compound $Pd_2(CH_3)_2(\mu\text{-dppm})_2$ is protonated by ethanol at -40 °C to give the bridging hydride species, $Pd_2(CH_3)_2(\mu\text{-dppm})_2(\mu\text{-H})^+$.[53]

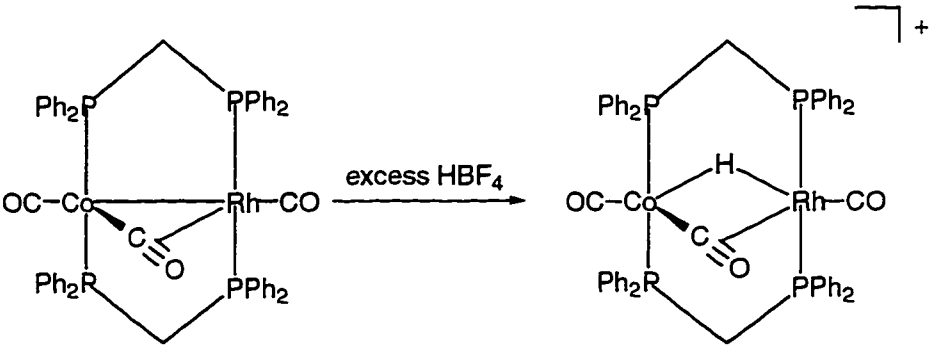
Platinum-Platinum

The compound $Pt_2Cl_2(\mu\text{-dppm})_2$ can be protonated at the Pt-Pt bond.[54] Protonation occurs with HCl in $CHCl_3$ and unlike the previously discussed palladium analog, the reaction does not have to be carried out at low temperature.

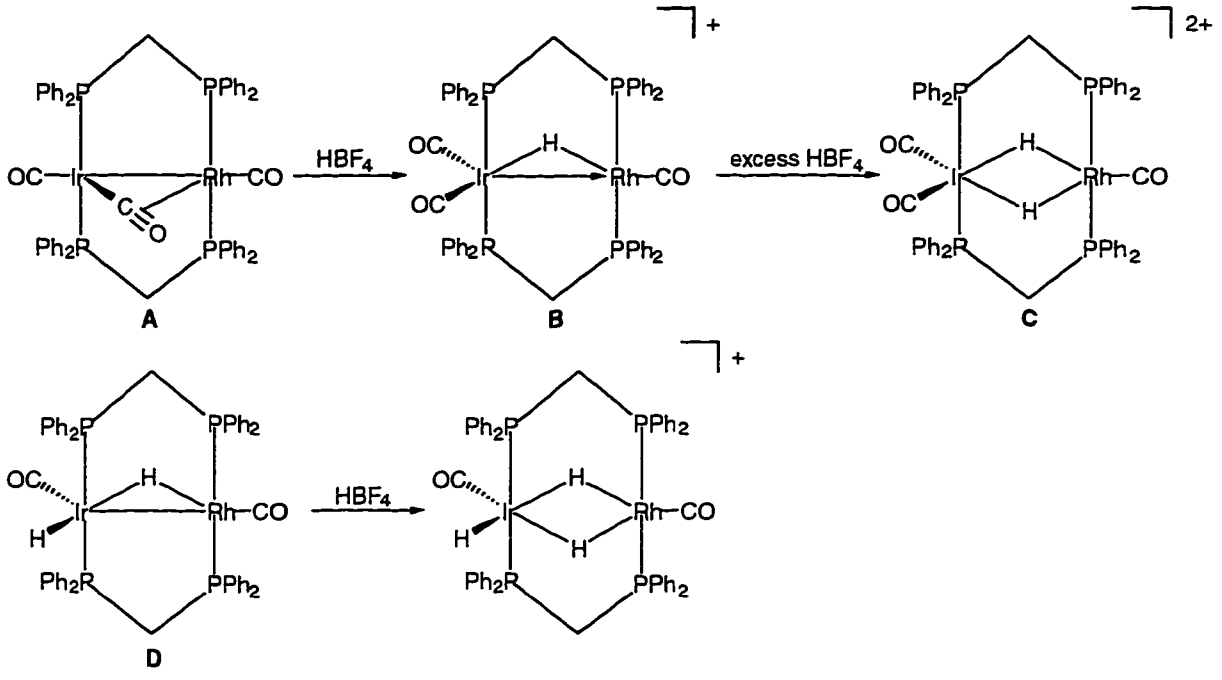
Mixed Metal Dimers from the Same Group

Several compounds containing metal-metal bonds between two different metals of the same group have been protonated. Similar to the di-molybdenum and di-tungsten compounds discussed above, $MoWCp_2(CO)_6$ has been protonated at the Mo-W bond by excess 98% H_2SO_4.[7] In Scheme 5, an example of the protonation of a mixed Co-Rh complex

$(CO)_2Co(\mu\text{-dppm})_2Rh(CO)$ in CH_2Cl_2 is shown.[55,56] Protonation of the mixed Rh-Ir cationic complex $(CO)Rh(\mu\text{-dppm})_2Ir(CO)_2(CH_3)^+$ has been accomplished in CH_2Cl_2 with CF_3SO_3H to form $(CO)Rh(\mu\text{-dppm})_2(\mu\text{-CO})(\mu\text{-H})Ir(CO)(CH_3)^{2+}$.[57] McDonald and Cowie[58] studied the protonation of similar Rh-Ir complexes in CH_2Cl_2(Scheme 6). Complex **A** is quite interesting. After protonation occurs at the Rh-Ir bond the compound undergoes ligand rearrangement, and a dative bond is formed in **B**. This bond is then protonated with excess acid to give the bis-μ-hydride product **C**. Compound **D** is similar to **B** as it also contains a bridging hydride, and upon protonation of the Ir-Rh bond a cationic complex with two bridging hydride ligands is obtained.



Scheme 5. Protonation of $CoRh(CO)_3(\mu\text{-dppm})_2$.



Scheme 6. Protonation of mixed a Ir-Rh system.

Mixed Metal Dimers from Different Groups

A variety of different mixed-metal complexes from different groups have been protonated. A listing of these complexes is provided in Table 7. Most of these compounds simply undergo protonation at the metal-metal bond to form the bridging hydride complex. However, in some of these compounds, rearrangement of the ligands occurs. Compounds that undergo rearrangement will be discussed further.

The protonation of $Cp(CO)Ru(\mu\text{-}PPh_2)Pt(PCy_3)(CO)$ in CH_2Cl_2 gives two separate initial products, which both rearrange into the same final product. In the first product, protonation occurs at the ruthenium center, while in the second product protonation occurs at the Ru-Pt bond. In the second product, the CO ligand on the Pt is *trans-* to the bridging phosphido group. Both the first and second products slowly rearrange to give $Cp(CO)Ru(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PCy_3)(CO)^+$, in which the CO ligand on the Pt is *cis-* to the bridging phosphido group and *trans-* to the bridging hydride.

Table 7. Protonation of mixed metal complexes.

Compound	Acid	Ref.
$Cp(CO)_2Fe\text{-}Mn(CO)_5$	98% H_2SO_4	7
$Cp(CO)Ru(\mu\text{-}PPh_2)Pt(PPh_3)_2$	HBF_4	59
$Cp(CO)Ru(\mu\text{-}PPh_2)Pt(PCy_3)(CO)$	HBF_4	59
$Cp(CO)_2M(\mu\text{-}PPh_2)Pt(PPh_3)(CO)$	HBF_4	60
M = Mo or W		
$Cp(CO)_2M(\mu\text{-}PPh_2)Pt(PPh_3)_2$	HBF_4	60
M = Mo or W		
$Cp(CO)_2M(\mu\text{-}PPh_2)Pt(PPh_3)(CO)$	HCl	60
M = Mo or W		
$Cp(CO)_2Mo(\mu\text{-}P(p\text{-tol})_2)Mn(CO)_4^-$	excess HBF_4	61
$(CO)Rh(\mu\text{-dppm})_2Re(CO)_3$	HBF_4	62
$(CO)Rh(\mu\text{-dppm})_2Os(CO)_2(H)$	HBF_4	63
$(CO)Rh(\mu\text{-dppm})_2Os(CO)_3^+$	excess HBF_4	63
$MM'(CO)_{10}^-$	H_3PO_4	64
M = Mn; M' = W or M = Re; M' = Cr or W		
$(CO)_3(SiPhMe_2)Fe(\mu\text{-}PPh_2)Pt(PPh_3)_2$	CF_3COOH	65
$(CO)Rh(\mu\text{-dppm})_2(\mu\text{-}\eta^1\text{:}\eta^1C_2(CF_3)_2)Mn(CO)_2$	excess HBF_4	66
$(CO)Rh(\mu\text{-dppm})_2(\mu\text{-}\eta^2\text{:}\eta^2C_2(CF_3)_2)Mn(CO)_2$	excess HBF_4	66

The initial site of protonation in $Cp(CO)_2M(\mu\text{-}PPh_2)Pt(PPh_3)(CO)$ depends on M. When M = Mo, protonation occurs at the Mo-Pt bond to form a bridging hydride complex in which the CO ligand on Pt is *trans-* to the bridging phosphido group. However, when M = W, protonation initially occurs at the W. Both the Mo and W complexes rearrange over the course of two days to give $Cp(CO)_2M(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PPh_3)(CO)^+$, in which the CO ligand on Pt is *cis-* to the bridging phosphido group and *trans-* to the bridging hydride. When $Cp(CO)_2M(\mu\text{-}PPh_2)Pt(PPh_3)(CO)$ (M = Mo or W) is protonated with HCl, the initial complex that is formed in the reaction is $Cp(CO)_2M(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PPh_3)(Cl)$, in which the Cl^- has replaced the CO on platinum. The Cl ligand is *cis-* to the hydride and *trans-* to the phosphido group. These complexes rearrange to give a complex where the Cl ligand is *trans-* to the hydride and *cis-* to the phosphido group.

Protonation of $(CO)Rh(\mu\text{-}dppm)_2Os(CO)_2(H)$ occurs at the Rh-Os bond. However, the final product $(CO)Rh(\mu\text{-}dppm)_2Os(CO)_2(\mu\text{-}H)_2^+$, contains two bridging hydride ligands. This is due to the hydride ligand, initially on the osmium, rearranging to a bridging position between the two metal centers. Protonation of $(CO)Rh(\mu\text{-}dppm)_2Os(CO)_3^+$ also occurs at the Rh-Os bond. However, due to the lack of a terminal hydride on osmium, the protonated complex has only a single bridging hydride, $(CO)Rh(\mu\text{-}dppm)_2(\mu\text{-}H)Os(CO)_3^{2+}$.

References

[1] (a) Pearson, R. G. *Chem. Rev.* **1985**, *85*, 41. (b) Martinho Simões, J. A.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629. (c) Bullock, R. M. *Comments Inorg. Chem.* **1991**, *12*, 1.

[2] (a) Kristjánsdóttir, S. S.; Norton, J. R. in *Transition Metal Hydrides: Recent Advances in Theory and Experiment*; Dedieu, A., *ed.*; VCH: New York, 1991; Chap 10. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and*

Applications of Organotransition Metal Chemistry; University Science Books: Mill Valley, CA, 1987.

[3] Hayter, R. G. *J. Am. Chem. Soc.* **1966**, *88*, 4376.

[4] (a) Rozier, J.; Williams, J. M.; Stewart, R. P., Jr.; Petersen, J. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1977**, *99*, 4497. (b) Petersen, J. L.; Johnson, P. L.; O'Connor, J.; Dahl, L. F.; Williams, J. M. *Inorg. Chem.* **1978**, *17*, 3460.

[5] Watkins, W. C.; Jaeger, T.; Kidd, C. E.; Fortier, S.; Baird, M. C.; Kiss, G.; Roper, G. C.; Hoff, C. D. *J. Am. Chem. Soc.* **1992**, *114*, 907.

[6] Behrens, H.; Haag, W. *Chem. Ber.* **1961**, *94*, 312.

[7] Davison, A.; McFarlane, M.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1962**, 3653.

[8] Nataro, C; Angelici, R. J. *manuscript in preparation.*

[9] Riera, V.; Ruiz, M. A.; Villafañe, F. *Organometallics*, **1992**, *11*, 2854.

[10] Behrens, H.; Vogl, J. *Chem. Ber.* **1963**, *96*, 2220.

[11] Tilset, M.; Vollhardt, K. P. C.; Boese, R. *Organometallics* **1994**, *13*, 3146.

[12] Braunstein, P.; de Jesús, E.; Dedieu, A.; Lanfranchi, M.; Tiripicchio, A. *Inorg. Chem.* **1992**, *31*, 399.

[13] Riera, V.; Ruiz, M. A.; Tiripicchio, A.; Camellini, M. T. *J. Chem. Soc: Dalton Trans.* **1987**, 1551.

[14] Aspinall, H. C.; Deeming, A. J. *J. Chem. Soc.: Dalton Trans.* **1985**. 743.

[15] Deeming, A. J.; Donovan-Mtunzi, S. *Organometallics* **1985**, *4*, 693.

[16] Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1981**, *20*, 1139.

[17] Harris, D. C.; Gray, H. B. *Inorg. Chem.* **1975**, *14*, 1215.

[18] Legzdins, P.; Martin, D. T.; Nurse, C. R.; Wassink, B. *Organometallics* **1983**, *2*, 1238.

[19] LaCroce, S. J.; Menard, K. P.; Cutler, A. R. *J. Organomet. Chem.* **1980**, *190*, C79.

[20] Boothman, J.; Hogarth, G. *J. Organomet. Chem.* **1992**, *437*, 201.

[21] Field, J. S.; Haines, R. J.; Sampson, C. N.; Sundermeyer, T.; Moodley, K. G. *J. Organomet. Chem.* **1987**, *322*, C7.

[22] Moodley, K. G.; Engel, D. W.; Field, J. S.; Haines, R. J. *Polyhedron* **1993**, *12*, 533.

[23] Walther, B.; Hartung, H.; Böttcher, H-C.; Baumeister, U.; Böhland, U.; Reinhold, J.; Sieler, J.; Ladriere, J.; Schiebel, H-M. *Polyhedron* **1991**, *10*, 2423.

[24] Fauvel, K.; Mathieu, R.; Poilblanc, R. *Inorg. Chem.* **1976**, *15*, 976.

[25] Arabi, M. S.; Mathieu, R.; Poilblanc, R. *J. Organomet. Chem.* **1979**, *177*, 199.

[26] Cherkas, A. A.; Hoffman, D.; Taylor, N. J.; Carty, A. J. *Organometallics* **1987**, *6*, 1466.

[27] Collman, J. P.; Finke, R. G.; Matlock, P. L.; Wahren, R.; Komoto, R. G.; Brauman, J. I. *J. Am. Chem. Soc.* **1978**, *100*, 1119.

[28] Farmery, K.; Kilner, M.; Greatrex, R.; Greenwood, N. N. *J. Chem. Soc. (A)* **1969**, 2339.

[29] Dawkins, G. M.; Green, M.; Jeffery, J. C.; Sambale, C.; Stone, F. G. A. *J. Chem. Soc.: Dalton Trans.* **1983**, 499.

[30] Lokshin, B. V.; Ginzburg, A.; Kazaryan, S. G. *J. Organomet. Chem.* **1990**, *397*, 203.

[31] Stasunik, A.; Malisch, W. *J. Organomet. Chem.* **1984**, *270*, C56.

[32] Nataro, C.; Thomas, L. M.; Angelici, R. J. *submitted to Inorganic Chemistry.*

[33] Johnson, K. A.; Gladfelter, W. L. *Organometallics* **1989**, *8*, 2866.

[34] Field, J. S.; Haines, R. J.; Stewart, M. W.; Woollam, S. F. *S. Afr. J. Chem.* **1993**, *46*, 75.

[35] Werner, H.; Hofmann, W. *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 158.

[36] Werner, H.; Hofmann, W.; Zolk, R.; Dahl, L. F.; Kocal, J.; Kühn, A. *J. Organomet. Chem.* **1985**, *289*, 173.

[37] Chen, L.; Kountz, D. J.; Meek, D. W. *Organometallics* **1985**, *4*, 598.

[38] Klingert, B.; Werner, H. *J. Organomet. Chem.* **1983**, *252*, C47.

[39] Field, J. S.; Haines, R. J.; Rix, L. A. *J. Chem. Soc.: Dalton Trans.* **1990**, 2311.

[40] Herrmann, W. A.; Plank, J.; Ziegler, M. L.; Balbach, B. *J. Am. Chem. Soc.* **1980**, *102*, 5906.

[41] Herrmann, W. A.; Plank, J.; Riedel, D.; Ziegler, M. L.; Weidenhammer, K.; Guggolz, E.; Balbach, B. *J. Am. Chem. Soc.* **1981**, *103*, 63.

[42] Herrmann, W. A.; Plank, J.; Guggolz, E.; Ziegler, M. L. *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 651.

[43] Herrmann, W. A.; Plank, J.; Riedel, D. *J. Organomet. Chem.* **1980**, *190*, C47.

[44] Plank, J.; Riedel, D.; Herrmann, W. A. *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 937.

[45] Bitterwolf, T. E.; Spink, W. C.; Rausch, M. D. *J. Organomet. Chem.* **1989**, *363*, 189.

[46] Kubiak, C. P.; Woodcock, C.; Eisenberg, R. *Inorg. Chem.* **1982**, *21*, 2119.

[47] Kubiak, C. P.; Eisenberg, R. *J. Am. Chem. Soc.* **1980**, *102*, 3637.

[48] Jenkins, J. A.; Cowie, M. *Organometallics* **1992**, *11*, 2767.

[49] Evans, J.; Johnson, B. F. G.; Lewis, J.; Watt, R. *J. Shem. Soc.: Dalton Trans.* **1974**, 2368.

[50] McDonald, R.; Sutherland, B. R.; Cowie, M. *Inorg. Chem.* **1987**, *26*, 3333.

[51] Bonnet, J. J.; Thorez, A.; Maisonnat, A.; Galy, J.; Poilblanc, R. *J. Am. Chem. Soc.* **1979**, *101*, 5940.

[52] Heinekey, D. M.; Michel, S. T.; Schultz, G. K. *Organometallics* **1989**, *8*, 1241.

[53] Young, S. J.; Kellenberger, B.; Reibenspies, J. H.; Himmel, S. E.; Manning, M.; Anderson, O. P.; Stille, J. K. *J. Am. Chem. Soc.* **1988**, *110*, 5744.

[54] Brown, M. P.; Puddephatt, R. J.; Rashidi, M.; Seddon, K. R. *Inorg. Chim. Acta* **1977**, *23*, L27.

[55] Elliot, D. J.; Vittal, J. J.; Puddephatt, R. J.; Holah, D. G.; Hughes, A. N. *Inorg. Chem.* **1992**, *31*, 1247.

[56] Elliot, D. J.; Ferguson, G.; Holah, D. G.; Hughes, A. N.; Jennings, M. C.; Magnuson, V. R.; Potter, D.; Puddephatt, R. J. *Organometallics* **1990**, *9*, 1336.

[57] Antwi-Nsiah, F. H.; Oke, O.; Cowie, M. *Organometallics* **1996**, *15*, 1042.

[58] McDonald, R.; Cowie, M. *Inorg. Chem.* **1990**, *29*, 1564.

[59] Powell, J.; Fuchs, E.; Gregg, M. R.; Phillips, J.; Stainer, M. U. R. *Organometallics* **1990**, *9*, 387.

[60] Powell, J.; Sawyer, J. F.; Smith, S. J. *J. Chem. Soc.: Dalton Trans.* **1992**, 2793.

[61] Casey, C. P.; Bullock, R. M. *Organometallics* **1984**, *3*, 1100.

[62] Antonelli, D. M.; Cowie, M. *Inorg. Chem.* **1990**, *29*, 4039.

[63] Hilts, R. W.; Franchuk, R. A.; Cowie, M. *Organometallics* **1991**, *10*, 304.

[64] Foust, A. S.; Grahan, W. A. G.; Stewart, R. P., Jr. *J. Organomet. Chem.* **1973**, *54*, C22.

[65] Knorr, M.; Stährfeldt, T.; Braunstein, P.; Reinhard, G.; Hauenstein, P.; Mayer, B.; Schubert, V.; Khan, S.; Kaesz, H. D. *Chem. Ber.* **1994**, *127*, 295.

[66] Wang, L-S.; Cowie, M. *Can. J. Chem.* **1995**, *73*, 1058.

CYCLOPENTADIENYL LIGAND EFFECTS ON ENTHALPIES OF PROTONATION OF THE Ru-Ru BOND IN $Cp'_2Ru_2(CO)_4$ COMPLEXES†

A paper submitted to *Inorganic Chemistry*

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Abstract

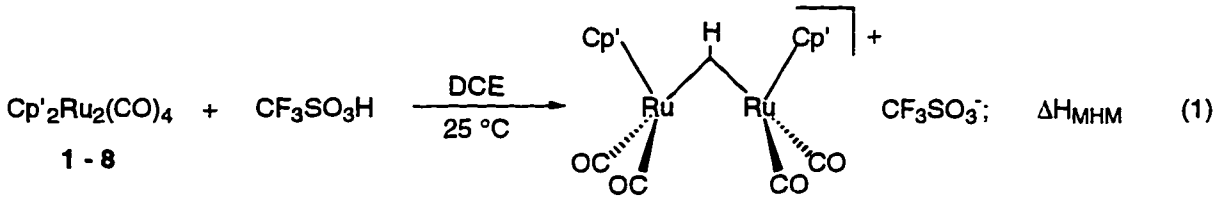
Basicities of a series of $Cp'_2Ru_2(CO)_4$ complexes were established by measuring the heats evolved (ΔH_{MHM}) when the complexes were protonated by CF_3SO_3H in 1,2-dichloroethane at 25.0 °C. Spectroscopic studies show that the protonation occurs at the metal-metal bond to form $[Cp'_2Ru_2(CO)_4(\mu\text{-}H)]^+ CF_3SO_3^-$, in which all of the CO ligands are terminal. The basicities ($-\Delta H_{MHM}$) increase with the Cp'_2 ligands in the following order: $C_5Me_4CF_3 < C_9H_7 < C_5H_4C_5H_4 < C_5H_4CH_2CH_2C_5H_4 < (C_5H)_2 < (C_5Me_5)_2 < C_5H_4CH_2C_5H_4$. This trend can be understood in part by considering that more strongly donating Cp' ligands increase the basicity of the Ru-Ru bond. Another important factor is the CO-bridging or non-bridging form of each $Cp'_2Ru_2(CO)_4$ complex. A dimer with bridging CO groups is significantly less basic than another dimer with only terminal CO groups although the donor abilities of their Cp' ligands are nearly equal. The Ru-Ru bond in $Cp_2Ru_2(CO)_4$ is substantially more basic than the Ru in the related mononuclear $CpRu(CO)_2H$. Molecular structures of $[Cp_2Ru_2(CO)_4(\mu\text{-}H)]^+CF_3SO_3^-$, $[(C_5H_4CH_2C_5H_4)Ru_2(CO)_4(\mu\text{-}H)]^+CF_3SO_3^-$ and $(C_5H_4CH_2CH_2C_5H_4)Ru_2(CO)_4$ as determined by X-ray diffraction studies are also presented.

Introduction

Basicities of the metal in mononuclear organometallic complexes are of great interest because they are indicators of other reactivities that depend on electron richness at the metal center.[1] Metal-metal bonded species are also a topic of considerable interest as they provide small molecule models of multiple metal sites on metal surfaces.[2] There are, however, surprisingly few studies on the basicities of metal-metal bonds. Walker, Pearson and Ford[3] found that $H_4Os_4(CO)_{12}$ is more acidic than $H_2Os(CO)_4$ (pK_a values in methanol are 12.0 and 15.2, respectively). From this, they concluded that bridging hydrides are more acidic than terminal hydrides in analogous complexes of the same element. In the same paper, the authors showed that in the series of complexes $H_4Ru_4(CO)_{12}$, $H_4Ru_4(CO)_{11}[P(OMe)_3]$ and $H_4Ru_4(CO)_{10}[P(OMe)_3]_2$, the acidities decreased (pK_a values in methanol are 11.7, 14.7 and >15, respectively) as CO ligands were replaced by $P(OMe)_3$. Norton[4] also studied $H_4Ru_4(CO)_{11}[P(OMe)_3]$ and $H_4Ru_4(CO)_{10}[P(OMe)_3]_2$, but in acetonitrile solvent, and found the same trend (pK_a values are 12.4, and 15.4, respectively).

In this paper, we report values for basicities of the metal-metal bonds in a series of $Cp'_2Ru_2(CO)_4$ complexes containing a variety of cyclopentadienyl-type ligands. These basicities are defined as the enthalpies of protonation (ΔH_{MHM}) of the metal complexes with triflic acid (CF_3SO_3H) in 1,2-dichloroethane (DCE) solution at 25.0 °C (eq 1). These heats of protonation are determined by titration calorimetry.

Previously, our heat of protonation studies (ΔH_{HM}) focused on mononuclear metal complexes (eq 2).[5-8] One aspect of these investigations was the effect of methyl-substituted cyclopentadienyl ligands on the ΔH_{HM} of a series of (η^5-$C_5Me_xH_{5-x}$)Ir(1,5-cyclooctadiene)



1, Cp' = Cp* = η^5-C_5Me_5
2, Cp' = Cp = η^5-C_5H_5
3, Cp' = $HBpz_3$
4, Cp' = Ind = η^5-C_9H_7
5, Cp' = Cp‡ = η^5-$C_5Me_4CF_3$
6, Cp'$_2$ = Cp_2CH_2 = η^5:$\eta^{5'}$-$C_5H_4CH_2C_5H_4$
7, Cp'$_2$ = $Cp_2(CH_2)_2$ = η^5:$\eta^{5'}$-$C_5H_4(CH_2)_2C_5H_4$
8, Cp'$_2$ = Fv = η^5:$\eta^{5'}$-$C_{10}H_8$

1H$^+$ - 8H$^+$

complexes.[8a] In this series, $-\Delta H_{HM}$ increased regularly by 1.1 kcal/mol for each added methyl group from CpIr(1,5-COD) (22.8 kcal/mol) to Cp*Ir(1,5-COD) (28.5 kcal/mol). The indenyl

$$ML_n + CF_3SO_3H \xrightarrow[25\ °C]{DCE} HML_n^+\ CF_3SO_3^-; \qquad \Delta H_{HM} \qquad (2)$$

ligand in these complexes had essentially the same effect as Cp on the basicity of the metal center. A similar trend was noted in the related Cp'Ir(CO)(PR_3) (Cp' = Cp or Cp*).[7c] In that system, the Cp* complexes were found to be 4.8 to 7.7 kcal/mol more basic then the analogous Cp compounds.

More directly relevant to the dinuclear ruthenium complexes reported in this paper are the Cp'Ru(PR_3)$_2$X complexes.[8h] For Cp'Ru(PPh_3)$_2$H, the Cp* complex is 5.5 kcal/mol more basic then the Cp derivative. For Cp'Ru(PMe_3)$_2$Cl, the Cp* complex is 9.0 kcal/mol more basic than the Cp analog.[8g] In the present studies, we sought to compare the influence of Cp' ligands in these mononuclear complexes with the effect of a variety of Cp' ligands on basicities of the metal-metal bonds in the Cp'$_2$Ru$_2$(CO)$_4$ complexes (eq 1). We also wished to gain some general understanding of the Ru-Ru bond basicity as compared with basicities of related mononuclear complexes.

Experimental Section

General Procedures. All preparative reactions, chromatography and manipulations were carried out under an atmosphere of nitrogen or argon using standard Schlenk techniques. Solvents were purified under nitrogen using standard methods.[9] Hexanes, heptane, decane and methylene chloride were refluxed over CaH_2 and then distilled. 1,2-Dimethoxyethane was refluxed over CaH_2 and vacuum distilled. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium benzophenone. Methanol was dried over magnesium methoxide and distilled. CD_2Cl_2 was stored over molecular sieves under nitrogen. 1,2-Dichloroethane (DCE) was purified by washing with concentrated sulfuric acid, distilled deionized water, 5% NaOH, and again with water. The solvent was then predried over anhydrous $MgSO_4$ and stored in amber bottles over molecular sieves (4 Å). The DCE was distilled from P_4O_{10} under argon immediately before use. Triflic acid (CF_3SO_3H) was purchased from 3M Co. and purified by fractional distillation under argon prior to use. Neutral Al_2O_3 (Brockmann, activity I) used for chromatography was deoxygenated at room temperature under vacuum for 12 h, deactivated with 3% (w/w) N_2-saturated water, and stored under N_2. Silica gel (40 μm) used for chromatography was deoxygenated under vacuum for 12 h and stored under N_2.

Triruthenium dodecacarbonyl ($Ru_3(CO)_{12}$) and biscyclopentadienyl magnesium (Cp_2Mg) were purchased from Strem. Dicyclopentadiene, pentamethylcyclopentadiene and indene were purchased from Aldrich. *centa*-$Ru(CO)_2(O_2CCH_3)$ was prepared according to the literature procedure.[10] The ^1H NMR spectra were obtained on samples in CD_2Cl_2 solvent on a Nicolet NT 300-MHz or a Bruker AC 200 MHz spectrometer with TMS ($\delta = 0.00$ ppm) as the internal reference. Solution infrared spectra were recorded on a Nicolet 710 FT-IR

spectrometer using sodium chloride cells with 0.1 mm spacers. Elemental microanalyses were performed on a Perkin Elmer 2400 Series II CHNS/O analyzer.

Ligand Syntheses. Dicyclopentadiene was cracked over iron filings.[11] Methylenebis(cyclopentadiene),[12] fulvalene,[13] 1,2-ethylenebis(cyclopentadiene)[14] and potassium hydrotris(1-pyrazolyl)borate[15] [K(HBpz$_3$)] were prepared by literature methods.

Dimer Syntheses. The dimers Cp*$_2$Ru$_2$(CO)$_4$ (**1**),[16] Cp$_2$Ru$_2$(CO)$_4$ (**2**),[11] (HBpz$_3$)$_2$Ru$_2$(CO)$_4$ (**3**),[17] Ind$_2$Ru$_2$(CO)$_4$ (**4**),[18] (Cp$_2$CH$_2$)Ru$_2$(CO)$_4$ (**6**)[19] and (Fv)Ru$_2$(CO)$_4$ (**8**)[13] were prepared by literature methods. Cp$^{\ddagger}_2$Ru$_2$(CO)$_4$ (**5**) was generously provided by J. H. Nelson at the University of Nevada-Reno.[20]

(Ind)$_2$Ru$_2$(CO)$_4$ (4). Although some spectroscopic data were reported[18, 21] previously for this compound, ^{1}H NMR and IR data in CD_2Cl_2 and CH_2Cl_2 are given below. Proton assignments in the ^{1}H NMR spectrum of **4** are based on those of Ind$_2$Ru.[18,22] ^{1}H (CD_2Cl_2): δ 7.29 (m, 8H, H4-H7), 5.69 (d, $^3J_{H\text{-}H}$ 3.0 Hz, 4H, H1, H3), 5.58 (d, $^3J_{H\text{-}H}$ 2.9 Hz, 2H, H2). IR (CH_2Cl_2): ν(CO) (cm^{-1}) 2001 (s), 1956 (m), 1763 (s).

(Cp$_2$(CH$_2$)$_2$)Ru$_2$(CO)$_4$ (7). A suspension of Ru$_3$(CO)$_{12}$ (677 mg, 1.05 mmol) and 1,2-ethylenebis(cyclopentadiene) (621 mg, 3.92 mmol) in 20 mL of heptane was heated to reflux. After 1 h at reflux the solution had a deep red color which, by analogy to the Cp$_2$Ru$_2$(CO)$_4$ synthesis,[11] was presumed to be a hydride intermediate, (Cp$_2$(CH$_2$)$_2$)(Ru(CO)$_2$H)$_2$. Refluxing for an additional 2 h turned the solution bright yellow, and a yellow precipitate was noted. The solution was cooled to room temperature and transferred to an alumina column (1.5 x 30 cm) packed in hexanes. Any unreacted Ru$_3$(CO)$_{12}$ was removed by eluting with 40 mL of a 5:1 (v/v) mixture of hexanes and CH_2Cl_2. A bright

yellow band was eluted using a 3:2 (v/v) mixture of hexanes and CH_2Cl_2. Solvent was removed from the eluent under vacuum, and the product was recrystallized by dissolving in a minimal amount of CH_2Cl_2 and layering with a ten-fold excess of hexanes. The mixture was then cooled to -20 °C for 48 h to yield yellow crystals of $(Cp_2(CH_2)_2)Ru_2(CO)_4$ (**7**) (352 mg, 74%). ^1H (CD_2Cl_2): δ 5.55, 5.21 ([AB]$_2$ system, 8H, C_5H_4), 2.45 (s, 4H, CH_2). IR (CH_2Cl_2): ν(CO) (cm^{-1}) 1998 (s), 1956 (m), 1770 (s). Anal. Calcd. for $C_{16}H_{12}O_4Ru_2$: C, 40.85; H, 2.57. Found: C, 40.77; H, 2.34. Crystals of **7** were obtained by layering a solution of **7** in CH_2Cl_2 with a ten-fold excess of ether and allowing the solvents to slowly mix at -78 °C.

Protonation Reactions. Compounds **1-8** were protonated for characterization of the $[Cp'_2Ru_2(CO)_4(\mu\text{-}H)]^+CF_3SO_3^-$ products by dissolving approximately 10 mg of the complex in 0.50 mL of either CD_2Cl_2 (for NMR) or CH_2Cl_2 (for IR) in an NMR tube under nitrogen. To the solution was added 1 equivalent of CF_3SO_3H through the rubber septum using a gastight microliter syringe. The solutions immediately changed color from bright yellow to feint yellow with the exception of **3** which turned orange and **5** which was orange and turned bright yellow. Yields of the protonated products were determined to be quantitative by IR and ^1H NMR spectroscopy. Compound $\mathbf{1H^+BF_4^-}$ was previously reported;[23] its IR and ^1H NMR data compare favorably with that of $\mathbf{1H^+CF_3SO_3^-}$ in these studies. Compound $\mathbf{2H^+}$ has been characterized by ^1H NMR in H_2SO_4[24] and by IR and ^1H NMR in acetic acid.[25] Crystals of $\mathbf{2H^+CF_3SO_3^-}$ were obtained by layering the protonation reaction solution with a ten-fold excess of ether. The solvents were allowed to mix slowly at room temperature.

Crystals of **$6H^+CF_3SO_3^-$** were formed by slow evaporation of CD_2Cl_2 from its solution at room temperature. ^1H NMR data for **$1H^+$-$8H^+$** are given below; IR data are presented in Table 1.

$[Cp^*_2Ru_2(CO)_4(\mu\text{-}H)]^+ CF_3SO_3^-$ ($1H^+CF_3SO_3^-$). ^1H NMR (CD_2Cl_2): δ 2.07 (s, 30H, Me), -17.71 (s, 1H, μ-H).

$[Cp_2Ru_2(CO)_4(\mu\text{-}H)]^+CF_3SO_3^-$ ($2H^+CF_3SO_3^-$). ^1H NMR (CD_2Cl_2): δ 5.74 (s, 10H, Cp), -19.27 (s, 1H, μ-H).

$[(HBpz_3)_2Ru_2(CO)_4(\mu\text{-}H)]^+ CF_3SO_3^-$ ($3H^+CF_3SO_3^-$). Assignments of the ^1H NMR peaks for **$3H^+CF_3SO_3^-$** are based upon those for $(HBpz_3)W(CO)_2[C(H)SMe]^+$ $CF_3SO_3^-$,[26a] which undergoes slow rotation on the ^1H NMR timescale around the H-B-W axis.[26b] ^1H NMR (CD_2Cl_2): δ 8.22 (d, $^3J_{H\text{-}H}$ 2.35 Hz, 4H, H3 of pz), 8.02 (d, $^3J_{H\text{-}H}$ 2.02 Hz, 2H, H3 of pz), 7.86 (d, $^3J_{H\text{-}H}$ 2.56 Hz, 4H, H5 of pz), 7.56 (d, $^3J_{H\text{-}H}$ 2.23 Hz, 2H, H5 of pz), 6.86 (t, $^3J_{H\text{-}H}$ 2.52 Hz, 4H, H4 of pz), 6.53 (t, $^3J_{H\text{-}H}$ 2.14 Hz, 2H, H4 of pz), -25.53 (s, 1H, μ-H). IR (CH_2Cl_2): ν(BH) (cm^{-1}) 2087 (m).

$[Ind_2Ru_2(CO)_4(\mu\text{-}H)]^+ CF_3SO_3^-$ ($4H^+CF_3SO_3^-$). ^1H NMR (CD_2Cl_2): δ 7.45 (m, 8H, H4-H7), 5.95 (m, 4H, H1 and H3), 5.65 (m, 2H, H2), -17.98 (s, 1H, μ-H).

$[Cp^‡_2Ru_2(CO)_4(\mu\text{-}H)]^+ CF_3SO_3^-$ ($5H^+CF_3SO_3^-$). ^1H NMR (CD_2Cl_2): δ 2.26 (s, 12H, 2,5-Me), 2.12 (s, 12H, 3,4-Me), -18.44 (s, 1H, μ-H).

$[(Cp_2CH_2)Ru_2(CO)_4(\mu\text{-}H)]^+ CF_3SO_3^-$ ($6H^+CF_3SO_3^-$). ^1H NMR (CD_2Cl_2): δ 5.73, 5.22 ($[AB]_2$ system, 8H, C_5H_4), 4.02 (s, 2H, CH_2), -17.95 (s, 1H, μ-H).

$[(Cp_2(CH_2)_2)Ru_2(CO)_4(\mu\text{-}H)]^+ CF_3SO_3^-$ ($7H^+CF_3SO_3^-$). ^1H NMR (CD_2Cl_2): δ 5.68, 5.63 ($[AB]_2$ system, 8H, C_5H_4), 2.65 (s, 4H, CH_2), -17.79 (s, 1H, μ-H).

$[FvRu_2(CO)_4(\mu\text{-}H)]^+ CF_3SO_3^-$ ($8H^+CF_3SO_3^-$). ^1H NMR (CD_2Cl_2): δ 6.10, 4.99 ($[AB]_2$ system, 8H, C_5H_4), -19.46 (s, 1H, μ-H).

Calorimetric Studies. Heats of protonation (ΔH_{MHM}) of the $Cp'_2Ru_2(CO)_4$ complexes were determined with 0.1 M CF_3SO_3H in DCE solvent at 25.0 °C. Titrations were performed using a Tronac Model 458 isoperibol calorimeter as originally described[7a] and then modified.[8a] A typical calorimetric run consisted of three sections:[27] initial heat capacity calibration, titration and final heat capacity calibration. Each section was preceded by a baseline acquisition period. During the titration, 1.2 mL of a 0.1 M CF_3SO_3H solution (standardized to a precision of ±0.0002 M) in DCE was added at a rate of 0.3962 mL/min to 50 mL of a 2.6 mM solution of the complex (5-10% excess) in DCE at 25.0 °C. Infrared spectra of the titrated solutions indicated ν(CO) bands for the $Cp'_2Ru_2(CO)_4(\mu\text{-}H)^+$ products as well as small bands for the excess starting material.

Two separate standardized acid solutions were used for determining the ΔH_{MHM} of each complex. The reported values are the average of at least four titrations and as many as five. The reaction enthalpies were corrected for the heat of dilution (ΔH_{dil}) of the acid in DCE (-0.2 kcal/mol).[8a] The reported error in ΔH_{MHM} is the average deviation from the mean of all of the determinations. Titrations of 1,3-diphenylguanidine (GFS Chemicals) with CF_3SO_3H in DCE (-36.9 ± 0.3 kcal/mol; lit.[7a] -37.2 ± 0.4 kcal/mol) were used to monitor the performance of the calorimeter before each set of determinations.

X-ray Diffraction Studies. The crystals were mounted on glass fibers and transferred to a Siemens P4RA ($\mathbf{6H^+CF_3SO_3^-}$) or an Enraf-Nonius CAD4 diffractometer ($\mathbf{2H^+CF_3SO_3^-}$ and **7**). Data were collected at 20 ± 2 °C for $\mathbf{2H^+CF_3SO_3^-}$ and **7**, and at 25 ± 1 °C for $\mathbf{6H^+CF_3SO_3^-}$. The cell constants for $\mathbf{6H^+CF_3SO_3^-}$ were determined from reflections found from a random search routine, while those for $\mathbf{2H^+CF_3SO_3^-}$ and **7** were determined from reflections found from a 360° rotation photograph. Pertinent data collection and reduction information are given in Table 2. Lorentz and polarization corrections were applied. Nonlinear corrections based on decay in the standard reflections were applied to the data for $\mathbf{2H^+CF_3SO_3^-}$ and **7**. A series of azimuthal reflections was collected and a semi-empirical absorption correction based on the azimuthal scan was applied. For $\mathbf{2H^+CF_3SO_3^-}$, data reductions were done using ICE, a suite of crystallographic programs developed at Iowa State University by Robert A. Jacobson.[28] The space groups were determined by systematic absences and intensity statistics, and the structures were solved by direct methods.[29] All non-hydrogen atoms were placed directly from the E-map and refined with anisotropic displacement parameters. Hydrogen atoms were treated as riding-atoms with individual isotropic displacement parameters. The hydride atom of $\mathbf{6H^+CF_3SO_3^-}$ was located and refined anisotropically. The bridging hydrides of the two crystallographically independent molecules of $\mathbf{2H^+CF_3SO_3^-}$ were placed from the E-map and their coordinates were refined. Selected bond distances, angles and atomic coordinates are listed in Tables 5 and 6 for $\mathbf{2H^+}$, Tables 7 and 8 for $\mathbf{6H^+}$ and Tables 3 and 4 for **7**. The ORTEP drawing of $\mathbf{2H^+}$ is shown in Figure 3, that of $\mathbf{6H^+}$ is in Figure 4, and **7** is in Figure 2.

Results

$Cp'_2Ru_2(CO)_4$ Syntheses. The previously unknown dimer **7** was prepared in 74% yield by refluxing $Ru_3(CO)_{12}$ and 1,2-ethylenebis(cyclopentadiene) in heptanes for three hours (eq 3).

$$^2/_3\ Ru_3(CO)_{12} + HCpCH_2CH_2CpH \xrightarrow[\text{reflux}]{C_7H_{16}} (Cp_2(CH_2)_2)Ru_2(CO)_4 \quad (3)$$

This synthesis is based upon a general procedure for the synthesis of $Cp'_2Ru_2(CO)_4$ complexes developed by Knox[11] (eq 4).

$$^2/_3\ Ru_3(CO)_{12} + 2\ HCp' \xrightarrow[\text{reflux}]{C_nH_{2n+2}} Cp'_2Ru_2(CO)_4 \quad (4)$$

The hydride complex $Cp'Ru(CO)_2H$ was proposed as an intermediate in this reaction.[11]

Characterization of Complexes 1-8 and Their Protonated Products. Complexes **1-8** may exist in any or all of the four isomeric forms in Figure 1. The *cisoid*, non-bridged isomer is drawn with eclipsed ligands but may exist in the staggered form depending on the Cp' ligands. The solid state structures of compounds **1-3** and **5-8** have all been determined by X-ray diffraction studies. Compounds **3**, **6** and **8** are all non-bridged in the solid state, while compounds **1**, **2**, **5** and **7** exist in the bridged form. The structure of **3** is staggered *cisoid* with a B-Ru-Ru-B torsion angle of 44.4°.[17] The structures of compounds **6**[19] and **8**[30] both show *cis*-geometry which is imposed by the link between the Cp ligands. In **6**, the Cp_{cent}-Ru-Ru-Cp_{cent} torsion angle (39.9°)[19] indicates that the Cp rings have a staggered *cisoid* structure. Compound **8** is truly *cis* as shown by the 0.0° Cp_{cent}-Ru-Ru-Cp_{cent} torsion angle.[30] The bridged compounds **1**,[31] **2**[32] and **5**[20] all adopt the *trans* structure in the solid state. Compound **7** (Figure 2) exists as the *cis* isomer as demonstrated by the 0.9° Cp_{cent}-Ru-Ru-Cp_{cent} torsion angle. The Ru-Ru bond length of 2.7037(10) Å in **7** is comparable to that

(2.735(2) Å) in **2**.[32] The bridging carbonyls and the ruthenium atoms are not planar as indicated by the angle (156.6°) between the Ru(1)-C(3)-Ru(2) and Ru(1)-C(4)-Ru(2) planes. This bending is presumably due to the bridging carbonyls maximizing the overlap with the metal orbitals in the π^* HOMO, as proposed for $Cp_2Fe_2(CO)_4$.[33]

Since the calorimetric measurements are performed in solution, it is of importance to know the isomers (Fig. 1) that are present in solution prior to protonation. IR data for compounds **1-8** are shown in Table 1. Complex **1** has been characterized in CH_2Cl_2 solution by IR and NMR, and at room temperature it exists as the *trans*, bridged isomer.[16] Complex **2** in solution has been thoroughly studied by IR,[34a] NMR,[18,34b-c] electronic[34d] and Raman[34e] spectroscopy. In CH_2Cl_2 at room temperature, all four isomers occur in nearly equal quantities.[18, 34] Complex **3** exists solely in the non-bridged form in CH_2Cl_2 solution.[17] The *cis/trans* ratio was not determined; however, NMR studies show that only at -70 °C is the rotation about the metal-metal bond slow enough to distinguish between the two forms.[17] From ^{13}C NMR studies, it was shown that **4** exists as both *cis* and *trans* bridged forms in solution.[18] Manning[21] determined that there are approximately equal amounts of the *cis* and *trans* isomers in $CHCl_3$ and THF at room temperature. Preliminary studies of compound **5** indicate that it exists as the *trans*, bridged structure in CH_2Cl_2 at room temperature.[20] Compounds **6**, **7** and **8** can only be *cis* due to the linking of the Cp rings. In compound **6**, both bridged and non-bridged forms are observed in CH_2Cl_2 at room temperature with the non-bridged being the dominant ($\geq$ 90%) form.[19] The IR spectrum of compound **7** in the ν(CO) region exhibits a strong and a medium band in the terminal region and a strong band in the bridging region (Table 1). This is indicative of a *cis*, bridged carbonyl structure.[34a,f] Complex **8** is present as only the non-bridged isomer in CH_2Cl_2 at room temperature as determined by IR spectroscopy.[30]

Upon protonation with 1 equivalent of triflic acid, complexes **1-8** are converted to the hydride-bridged complexes $\mathbf{1H^+CF_3SO_3^-}$-$\mathbf{8H^+CF_3SO_3^-}$ in which all of the CO ligands are non-bridging. A singlet resonance in the ^{1}H NMR spectrum of these compounds in the range from δ -17.71 to -25.53 is assigned to the bridging hydride ligand. Protonation of **2**, **4**, **6**, **7** and **8** causes the Cp' resonances to shift downfield by approximately 0.7 ppm. At the same time, the terminal ν(CO) bands move approximately 100 cm^{-1} to higher wavenumbers, and there is no evidence for ν(CO) bands in the region (1750-1850 cm^{-1}) characteristic of bridging CO groups. IR data for the protonated compounds are shown in Table 1.

No X-ray diffraction studies of the protonated dimers $Cp'_2Ru_2(CO)_4(\mu\text{-}H)^+$ have been previously reported. The structure of $\mathbf{2H^+CF_3SO_3^-}$ (Figure 3) shows two crystallographically independent molecules of $\mathbf{2H^+}$. In both, the Cp ligands are *trans* and all of the CO ligands are terminal. The average Ru-Ru distance in $\mathbf{2H^+}$ (3.037 Å) is considerably longer than in **2** (2.735(2) Å).[32] The structure of $\mathbf{6H^+CF_3SO_3^-}$ (Figure 4) has *cis* Cp ligands due to the methylene link, and all of the CO groups are terminal. The Ru-Ru distance is substantially longer in $\mathbf{6H^+}$ (3.019(1) Å) than in **6** (2.767(1) Å).[19] The Cp_{cent}-Ru-Ru-Cp_{cent} torsion angle in $\mathbf{6H^+}$ (11.6°) is smaller than that (39.9°) in **6**.[19] The hydride in $\mathbf{6H^+}$ is not equidistant from the two Ru atoms (Ru-H, 1.49(8) Å and Ru'-H, 2.0(1)). This feature, although unexpected due to the symmetry of the molecule, is not uncommon. A neutron diffraction study of $[Et_4N][HW_2(CO)_{10}]$ shows the hydride to be asymmetric (W(1)-H, 1.72(1) Å and W(2)-H, 2.07(1) Å),[35a] and in the X-ray structure of $Pd_2(^iPr_2P(CH_2)_3P^iPr_2)_2(\mu\text{-}H)_2$, the hydride ligands asymmetrically bridge the palladium atoms (Pd_a-H_a 1.67(5) Å, Pd_b-H_a 2.13 (4) Å, Pd_a-H_b 2.11(5) Å and Pd_b-H_b 1.73(4) Å).[35b]

Calorimetry Studies. Table 9 contains the heats of protonation (ΔH_{MHM}) of complexes **1-8** as determined by calorimetric titration. Titrations were carried out in DCE

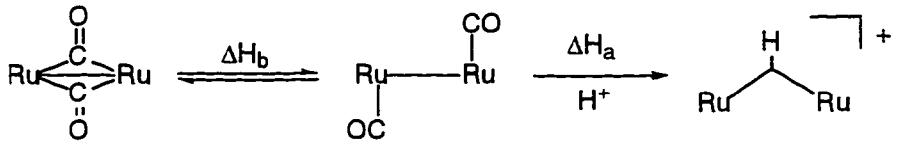
solvent at 25.0 °C according to eq 1. Plots of temperature vs. amount of acid added were linear, indicating that the protonations occur rapidly and stoichiometrically,[27] conclusions that are supported by the IR and ^{1}H NMR studies. Normal pre- and post-titration traces were evidence that no decomposition of the neutral or protonated species occurred. The protonated complexes in DCE solution were deprotonated with 1 equiv. of diphenylguanidine. The pure, unprotonated complexes were recovered by passing these solutions through an alumina column while eluting with CH_2Cl_2, evaporating the eluent solutions to dryness and recrystallizing the residue from CH_2Cl_2 layered with hexanes.

Discussion

Basicities of $Cp'_2Ru_2(CO)_4$ Complexes without Linked Cp' Ligands. Enthalpies (ΔH_{MHM}) of protonation (eq 1) of the $Cp'_2Ru_2(CO)_4$ complexes, together with that of $(HBpz_3)_2Ru_2(CO)_4$, increase (Table 9) with the Cp' ligand in the following order ($-\Delta H_{MHM}$, kcal/mol, in parentheses): $Cp^‡$(12.0) < Ind(14.1) < $HBpz_3$(16.6) < Cp(18.4) < Cp*(19.2). It is expected that this trend would be strongly influenced by the donor ability of the Cp' ligand. As noted in the introduction, the basicity of a metal center in mononuclear complexes increases as Cp is replaced by methyl-substituted cyclopentadienyl ligands, e.g. Cp*. For complexes **1-5**, the relative donor abilities of the Cp' ligands may be estimated from average ν(CO) values for the protonated complexes $Cp'_2Ru_2(CO)_4(\mu\text{-}H)^+$. These Aν values (Table 1) are averages of the three observed ν(CO) values. This ν(CO) averaging procedure has been used previously for the purpose of estimating ligand donor ability.[36] For complexes **1-5**, the ν(CO) values show that the Cp' ligand donor abilities increase in the following order (average ν(CO) values, cm^{-1}, in parentheses): Cp(2046) ~ Ind(2046) < $Cp^‡$(2042) < $HBpz_3$(2039) << Cp*(2019). The similar donor abilities of Cp, Ind and $Cp^‡$ are consistent with previous comparisons of these ligands.[8c, 37, 38] The $HBpz_3$ ligand is known to be a

somewhat stronger donor than Cp,[37,39] as is also found in the present trend. The Cp* ligand is a significantly stronger donor than any of the other ligands. It is evident that the Cp' donor trend is very different than the basicity trend ($-\Delta H_{MHM}$) for the complexes. Another feature of the basicity ($-\Delta H_{MHM}$) trend that is not understandable in terms of the Cp' ligand donor ability is the small difference between the $-\Delta H_{MHM}$ values for the Cp(18.4 kcal/mol) and Cp*(19.2) complexes (**2** and **1**).

In order to provide an understanding of the observed $-\Delta H_{MHM}$ trend, it is necessary to consider that while all of the protonated products $Cp'_2Ru_2(CO)_4(\mu\text{-}H)^+$ have the same structure (all terminal CO ligands), the reacting Ru dimers may have structures with bridging CO's, no bridging CO's or an equilibrium mixture of bridged and non-bridged forms. In solution, the Cp*(**1**), Ind(**4**), and Cp‡(**5**) complexes are present only as the bridged isomer; the $HBpz_3$ complex (**3**) is all non-bridged; and the Cp(**2**) analog is an equilibrium mixture of bridged and non-bridged forms. One might consider the protonation of bridged isomers as being comprised of two steps (eq 5): (i) opening of the bridge to give the non-bridged form, a step which requires energy (ΔH_b) and (ii) protonation of the non-bridged isomer which is exothermic (ΔH_a). The overall measured ΔH_{MHM} is then the sum of ΔH_b and ΔH_a. If one



(5)

considers only the complexes with Cp' ligands that have similar donor abilities (Cp, Ind, and Cp‡), their ΔH_a values should be similar and the overall ΔH_{MHM} should be controlled by ΔH_b. Unfortunately, the only reported ΔH_b values for $Cp'_2Ru_2(CO)_4$ complexes are for $Cp_2Ru_2(CO)_4$. An IR study[40] in CS_2 solvent gave $\Delta H_b = +1.32$ kcal/mol, while a ^{13}C investigation[18] yielded a value of +2.6 kcal/mol. Since $Cp_2Ru_2(CO)_4$ exists as an equilibrium mixture, the ΔH_b values for the Ind(**4**) and Cp‡(**5**) complexes, which are present as only the

bridged isomers, are very likely to have ΔH_b values that are even more endothermic than that (+1.3 or +2.6 kcal/mol) of the Cp complex (**2**); in addition, since **4** and **5** exist only in the bridged form, more of the bridged form must be converted to the non-bridged form. Thus, the ΔH_{MHM} values of the Ind(**4**) and $Cp^{\ddagger}$(**5**) dimers are expected to be less exothermic than that for Cp(**2**), which is the observed trend.

Complex **1** with Cp* ligands might be expected to be substantially more basic than **2** with Cp ligands. In mononuclear complexes, the replacement of a Cp by Cp* increases the basicity by 5-9 kcal/mol;[5] the replacement of two Cp ligands by two Cp* groups in the dimeric ruthenium complexes should presumably increase the basicity even more. The results (Table 9). however, show that the Cp* complex (**1**) is only 0.8 kcal/mol more basic than **2**. This unexpectedly low value of $-\Delta H_{MHM}$ for **1** can easily be understood by considering the energy (ΔH_b) that is required to convert the dimer from its existing bridging form to the non-bridged form (eq 5). The small difference in $-\Delta H_{MHM}$ values between **1** and **2** must mean that the replacement of Cp by Cp* increases $-\Delta H_a$ by an amount that is only 0.8 kcal/mol greater than the increase in ΔH_b. For all of the $Cp'_2Ru_2(CO)_4$ complexes, it is therefore possible to understand the observed $-\Delta H_{MHM}$ trend: $Cp^{\ddagger} < Ind < Cp < Cp^*$. Only the relative ordering of the $Cp^{\ddagger}$ and Ind dimers cannot be predicted because ΔH_b values (or estimates) are not available for their bridged to non-bridged conversions.

The relative basicity of the $HBpz_3$ dimer (**3**) is somewhat of a special case as compared with the Cp' dimers. Since **3** exists in the non-bridged form only, there is no bridge to non-bridge reaction (ΔH_b) to reduce its basicity ($-\Delta H_{MHM}$). Therefore, the stronger donor ability of $HBpz_3$ as compared with Cp should make **3** more basic than **2**.[39] However, **3** is 1.8 kcal/mol *less* basic than **2**. This unexpectedly lower basicity of a $HBpz_3$ complex as compared with its Cp analog has been observed by Tilset[41] in the mononuclear complexes $(L)M(CO)_3H$ (M = Cr, Mo, W and L = Cp or $HBpz_3$). For example, $CpMo(CO)_3H$ (pK_a = 13.9 in

CH_3CN) is less acidic than $(HBpz_3)Mo(CO)_3H$(pK_a = 10.7). The authors rationalize this trend by suggesting that the $(HBpz_3)Mo(CO)_3^-$ ion resists formation of the seven-coordinate $(HBpz_3)Mo(CO)_3H$ due to a combination of steric and stereoelectronic effects. Although the precise nature of the effects that lead to a lower basicity for $(HBpz_3)Mo(CO)_3^-$ as compared with $CpMo(CO)_3^-$ are not known, they may also be responsible for the lower basicity of **3** relative to **2**.

The availability of ΔH_{MHM} values for the $Cp'_2Ru_2(CO)_4$ complexes offers the possibility of comparing basicities of Ru-Ru bonds with Ru in mononuclear complexes. Such comparisons are ambiguous because of the quite different natures of dinuclear and mononuclear complexes. For comparison with $Cp_2Ru_2(CO)_4$, one might choose mononuclear $CpRu(CO)_2X$, where the X group replaces the $Ru(CO)_2Cp$ group in the dimer. The choice of X could greatly affect the basicity of the Ru. For example, in the $CpOs(PPh_3)_2X$ complexes, $-\Delta H_{HM}$ is 37.3 kcal/mol for X = H but only 19.7 kcal/mol for X = Cl.[8h] If we choose the strongly donating H ligand for our comparison, we need ΔH_{HM} for $CpRu(CO)_2H$. In the absence of a ΔH_{HM} value for this complex, or any other $CpRu(CO)_2X$ complexes, it is necessary to estimate it. Since $Cp^*Ru(CO)_2H$ is mostly protonated by Et_2OH^+,[1g, 42] it is estimated that $Cp^*Ru(CO)_2(\eta^2\text{-}H_2)^+$ has about the same pK_a (H_2O) = -2 as Et_2OH^+. In order to convert this pK_a (H_2O) value into a ΔH_{HM}, we note that pK_a (H_2O) of $(p\text{-}CF_3C_6H_4)_3P$ is -1.3 and its ΔH_{HP} is -13.6 kcal/mol.[5] From this, one can estimate the ΔH_{HM} for $Cp^*Ru(CO)_2H$ as -13 kcal/mol. Since the replacement of a Cp* by Cp reduces the basicity of $Cp'Ru(L)_2X$ complexes by 5-9 kcal/mol,[5] the ΔH_{HM} for $CpRu(CO)_2H$ can be very roughly approximated as -6 kcal/mol.

Another approach to estimating ΔH_{HM} for $CpRu(CO)_2H$ involves replacing both PPh_3 groups in $CpRu(PPh_3)_2H$ (ΔH_{HM} = -29.7 kcal/mol)[8h] with CO. Substitution of the PPh_3 in $Cp^*Ir(CO)(PPh_3)$ by a CO reduces the basicity of the Ir by 15.7 kcal/mol.[7c] The replacement

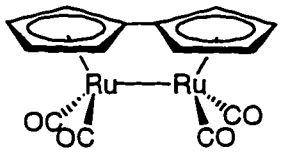
of both PPh_3 ligands in $CpRu(PPh_3)_2H$ with CO may not reduce the basicity of the metal by 31.4 kcal/mol (2 x 15.7), in which case ΔH_{HM} for $CpRu(CO)_2H$ would be +1.7 kcal/mol, but the reduction could be 23.6 kcal/mol if replacement of one PPh_3 by CO reduces $-\Delta H_{HM}$ by 15.7 kcal/mol and the second replacement reduces it by one-half that amount (7.9 kcal/mol). This would yield an estimated ΔH_{HM} value of -6 kcal/mol for $CpRu(CO)_2H$. Although very approximate, these two estimates (-6 kcal/mol) for the ΔH_{HM} value of $CpRu(CO)_2H$ indicate that this mononuclear complex is much less basic than $Cp_2Ru_2(CO)_4$ (ΔH_{MHM} = -18.4 kcal/mol). Subtracting the ΔH_b (~1 kcal/mol) for the conversion of the bridged to the non-bridged form (eq 5) gives a basicity for the non-bridged Ru-Ru bond in $Cp_2Ru_2(CO)_4$ of -19 kcal/mol. This estimating procedure suggests that the unbridged Ru-Ru bond in $Cp_2Ru_2(CO)_4$ is much more basic (~13 kcal/mol) than the Ru in the mononuclear $CpRu(CO)_2H$. If instead of $CpRu(CO)_2H$ we had chosen $CpRu(CO)_2Cl$, with the weakly donating Cl ligand, for comparison with $Cp_2Ru_2(CO)_4$, the Ru-Ru bond would have been relatively even more basic than Ru in a mononuclear complex.

Basicities of $Cp'_2Ru_2(CO)_4$ Complexes with Linked Cp' Ligands. Because of the *cisoid* geometry imposed on the complexes with $-CH_2-$ or $-CH_2CH_2-$ linking groups, it seemed possible that the basicities of compounds **6** and **7** would not follow trends observed for the unlinked $Cp'_2Ru_2(CO)_4$ complexes. The values (Table 9) of $-\Delta H_{MHM}$ for **6**, **7**, as well as $Cp_2Ru_2(CO)_4$(**2**), increase in the order ($-\Delta H_{MHM}$, kcal/mol, in parentheses): $Cp_2(CH_2)_2$ (16.9) < Cp_2 (18.4) < Cp_2CH_2 (21.0). The CH_2 groups attached to the Cp rings of the linked complexes make these ligands slightly stronger donors than Cp. This factor clearly does not account for **7** being less basic than **2** and **6** being more basic. The observed trend can, however, be readily understood in terms of the bridging vs. non-bridging forms of the complexes. The Cp_2 complex (**2**) is approximately 50% each of the bridged and

non-bridged isomers in CH_2Cl_2 solution.[34] On the other hand, the $Cp_2(CH_2)_2$ complex (**7**) is completely bridged which suggests that its ΔH_b (eq 5) will be more endothermic than that (~2 kcal/mol) for **2**. Since ΔH_a is expected to be about the same for these complexes, the sum of $\Delta H_a + \Delta H_b = \Delta H_{MHM}$ should be less exothermic for **7** than **2**, as observed.

The higher basicity ($-\Delta H_{MHM}$) of Cp_2CH_2 (**6**) than Cp_2 (**2**) may be due in part to the slightly stronger donating ability of the Cp' groups in Cp_2CH_2, but it is probably influenced more by the fact that **6** exists in solution primarily (≥90%) as the non-bridged isomer. This means that ΔH_b is likely to be less endothermic for **6** than for **2** and the overall ΔH_{MHM} will be more exothermic for **6** than **2**. Another possible explanation is that the Cp_2CH_2 ligand in **6** introduces some strain within the molecule that favors protonation because it causes lengthening of the Ru-Ru bond in $\mathbf{6H^+}$. Molecular models indicate that the Cp_2CH_2 ligand geometry forces the Cp ligands to be staggered with respect to each other; this is evident in the Cp_{cent}-Ru-Ru-Cp_{cent} torsion angle (39.9°)[19] in the solid state structures of the non-bridged isomer. Such a torsion angle would disfavor the bridged isomer, because of the difficulty in forming CO bridges in this twisted geometry. This may account for the fact that **6** exists primarily (≥90%) in the non-bridged form in solution. Thus, three factors could contribute to the larger $-\Delta H_{MHM}$ for **6** than **2**: (a) the higher donor ability of Cp_2CH_2, (b) the more endothermic ΔH_b, and/or (c) strain in **6** induced by the Cp_2CH_2 ligand. These factors provide an understanding of the overall observed trend $Cp_2(CH_2)_2 < Cp_2 < Cp_2CH_2$.

The fulvalene complex $FvRu_2(CO)_4$ (**8**) has some unusual features as compared with the other linked Cp complexes.[44] Perhaps the most important is strain within the molecule; a



planar Fv ligand places the Cp centroids at a distance of 4.0 Å from each other, but the Ru-Ru bond in the unstrained $Cp_2Ru_2(CO)_4$ complex is only 2.735(2) Å.[32] The donor ability of the Fv ligand, as measured (Table 1) by the average ν(CO) value (2055 cm^{-1}) for $FvRu_2(CO)_4(\mu\text{-}H)^+$, is substantially less than that of Cp in **2** (2046 cm^{-1}) or any of the other Cp' ligands in this study. This comparison suggests that **8** should be the least basic of the Ru dimers, which is not observed (Table 9). On the other hand, there is no endothermic ΔH_b contribution, as there is in some of the other dimers, since **8** exists only as the non-bridged isomer. In addition, the release in strain upon protonation and lengthening of the Ru-Ru bond (from 2.821(1)[30] to approximately 3.0 Å) should make **8** more basic than the other Ru dimers. It is presumably a balance of these factors which leads to its intermediate (16.1 kcal/mol) $-\Delta H_{MHM}$ value. It might be noted that while the cyclopentadienyl complex $Cp_2Ru_2(CO)_4$ (**2**) is more basic than fulvalene $FvRu_2(CO)_4$ (**8**) in the present studies, qualitative investigations[44] of $Cp_2W_2(CO)_6$ and $FvW_2(CO)_6$ (both non-bridged) show that the Fv complex is protonated by $HBF_4 \bullet Et_2O$ in acetonitrile but the Cp derivative is not. This suggests that the Fv complex is more basic than the Cp, which is just the opposite order of the Ru dimer system. Presumably the relative magnitudes of the factors contributing to the basicities of the two systems change sufficiently to cause this reversal in order of basicity.

Conclusion

Considering all of the $Cp'_2Ru_2(CO)_4$ complexes in this study, the $-\Delta H_{MHM}$ values increase in the following order, where the compound number, $-\Delta H_{MHM}$ value, and bridging(b) or non-bridging(nb) form present in solution are indicated in parentheses: $Cp^{\ddagger}_2$(**5**, 12.0, b) < Ind_2(**4**, 14.1, b) < Fv(**8**, 16.1, nb) < $Cp_2(CH_2)_2$(**7**, 16.9, b) < Cp_2(**2**, 18.4, 50% nb) < Cp^*_2(**1**, 19.2, b) < Cp_2CH_2(**6**, 21.0, ≥ 90% nb). For the complexes that have Cp' ligands with approximately the same donor ability the basicities increase, **5**(b) < **4**(b) < **7**(b) <

2(50%nb) < **6** (90%nb), as the non-bridged form of the $Cp'_2Ru_2(CO)_4$ becomes more predominant. *Thus, in general, one expects that M-M bonds with bridging CO ligands to be less basic than bonds in related compounds without bridging CO ligands*; this assumes that all of the CO groups in the protonated product are non-bridging, as they are in the present investigation.

Complexes **1** and **8** in the above series also deserve comment. The Cp* complex **1** is quite basic for a bridged isomer, but this is due to the stronger donor ability of Cp* as compared with Cp, i.e., ΔH_a in eq 5 is more exothermic for Cp* than Cp. On the other hand, the Fv complex **8** is unusually weakly basic for a non-bridged complex; this is due to the weakly donating nature of the Fv ligand.

Although one can understand how the existence of bridging and non-bridging isomers affect the $-\Delta H_{MHM}$ values, it is not so clear why some of the $Cp'_2Ru_2(CO)_4$ dimers are bridged while others are non-bridged. There appear to be two factors: (a) a high electron density on the Ru favors the bridging form; (b) bulky Cp' ligands favor the bridging form. The Cp' steric effect may be seen in the comparison of complex **4** with **2**. Both Cp' ligands in these complexes have very similar electron donor properties[8a] but **4** with the bulky indenyl ligand is completely bridged while the Cp analog **2** is only 50% bridged. Similarly, $Cp^‡$ and Cp have similar donor abilities,[38] but **5** with the bulky $Cp^‡$ ligand exists only as the bridged isomer, while **2** with the Cp ligand is only 50% bridged. Evidence for electronic effects on the bridging vs. non-bridging isomer distribution is less direct. While $Cp^*_2Ru_2(CO)_4$ (**1**) is completely bridged and $Cp_2Ru_2(CO)_4$ (**2**) is only 50% bridged, either the bulkiness or the higher donor ability of the Cp* group could account for the greater preference of **1** for the bridged form. In a comparison of **2** and **8**, Cp is a stronger electron donor than fulvalene (on the basis of average ν(CO) values) which accounts for it being 50% bridged but **8** is completely non-bridged. On the other hand, the Fv ligand imposes special structural features on **8** which may influence its isomer preference. As noted in the linked-Cp section above, the

isomer distribution for **6** is probably affected by the strain imposed by the Cp_2CH_2 ligand. Thus, a variety of factors probably contribute to the bridging vs. non-bridging isomer distribution in specific Ru dimer complexes.

An attempt to compare the basicity of the metal-metal bond in $Cp_2Ru_2(CO)_4$(**2**) with that of the metal in a related mononuclear complex $CpRu(CO)_2H$ shows that the Ru-Ru bond in **2** is much more basic than the metal in $CpRu(CO)_2H$. This conclusion may depend, of course, on the particular complexes that are compared.

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References

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[1] (a) Pearson, R. G. *Chem. Rev.* **1985**, *85*, 41. (b) Martinho Simões, J. A.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629. (c) Kristjánsdóttir, S. S.; Norton, J. R. in *Transition Metal Hydrides: Recent Advances in Theory and Experiment*; Dedieu, A., *ed.*; VCH: New York, 1991; Chap 10. (d) Bullock, R. M. *Comments Inorg. Chem.* **1991**, *12*, 1. (e) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; Universtiy Science Books: Mill Valley, CA, 1987. (f) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.*

1992, *121*, 155. (g) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913. (h) Kramarz, K.; Norton, J. R. *Prog. Inorg. Chem.* **1994**, *42*, 1.

[2] (a) Hogarth, G. *Organomet. Chem.* **1994**, *24*, 184. (b) Powell, J; Sawyer, J. F.; Smith, S. J. *J. Chem. Soc.: Dalton Trans.* **1992**, 2793. (c) Field, J. S.; Haines, R. J.; Stewart, M. W.; Sundermeyer, J.; Woollam ,S. F. *J. Chem. Soc.: Dalton Trans.* **1993**, 947. (d) Mirza, H. A.; Vittal, J. J.; Puddephatt, R. J. *Inorg. Chem.* **1993**, *32*, 1327. (e) Moldes, I.; Delavaux-Nicot, B.; Lugan, N.; Mathieu, R. *Inorg. Chem.* **1994**, *33*, 3510. (f) Field, J. S.; Haines, R. J.; Stewart, M. W.; Woollman, S. F. *S. Afr. J. Chem.* **1993**, *46*, 75. (g) Schreiner, S.; Gallaher, T. N. *Organometallics* **1993**, *12*, 4201. (h) He, Z.; Nefedov, S.; Lugan, N.; Neibecker, D.; Mathieu, R. *Organometallics* **1993**, *12*, 3837.

[3] Walker, H. W.; Pearson, R. G.; Ford, P. C. *J. Am. Chem. Soc.* **1983**, *105*, 1179.

[4] Kristjánsdóttir, S. S.; Moody, A. E.; Weberg, R. T.; Norton, J. R. *Organometallics* **1988**, *7*, 1983.

[5] Angelici, R. J. *Acc. Chem. Res.***1995**, *28*, 51.

[6] Sowa, J. R., Jr.; Bonanno, J. B.; Zanotti, V.; Angelici, R. J. *Inorg. Chem.* **1992**, *31*, 1370.

[7] (a) Bush, R. C.; Angelici, R. J. *Inorg. Chem.* **1988**, *27*, 681. (b) Rottink, M. K.; Angelici, R. J. *Inorg. Chem.* **1993**, *32*, 2421. (c) Wang, D.; Angelici, R. J. *Inorg. Chem.* **1996**, *35*, 1321.

[8] (a) Sowa, J. R., Jr.; Angelici, R. J. *J Am. Chem. Soc.* **1991**, *113*, 2537. (b) Sowa, J. R., Jr.; Zanotti, V.; Angelici, R. J. *Inorg. Chem.* **1991**, *30*, 4109. (c) Sowa, J. R., Jr.; Zanotti, V.; Facchin, G.; Angelici, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 9185. (d) Sowa, J. R., Jr.; Zanotti, V.; Facchin, G.; Angelici, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 160. (e) Sowa, J. R., Jr.; Zanotti, V.; Angelici, R. J. *Inorg. Chem.* **1993**, *32*, 848. (f) Rottink, M. K.; Angelici, R. J. *J. Am. Chem. Soc.* **1992**, *114*,

8296. (g) Rottink, M. K.; Angelici, R. J. *Inorg. Chem.* **1993**, *32*, 3282. (h) Rottink, M. K.; Angelici, R. J. *J. Am. Chem. Soc.* **1993**, *115*, 7267.

[9] Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon: New York, 1980.

[10] Crooks, G. R.; Johnson, B. F. G.; Lewis, J.; Williams, I.G.; Gamlen, G. *J. Chem. Soc. (A)* **1969**, 2761.

[11] Doherty, N.M.; Knox, S. A. R.; Morris, M. J. *Inorg. Synth.* **1990**, *28*, 189.

[12] Schore, N. E.; Ilenda, C. S.; White, M. A.; Bryndza, H. E.; Matturro, M. G.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 7451.

[13] Vollhardt, K. P. C.; Weldman, T. W. *Organometallics* **1984**, *3*, 189.

[14] Collins, S.; Hong, Y.; Taylor, N.J. *Organometallics* **1990**, *9*, 2695.

[15] Trofimenko, S. *Inorg. Synth.* **1970**, *12*, 99.

[16] King, R. B.; Iqbal, M. Z.; King, A. D. *J. Organomet. Chem.* **1979**, *171*, 53.

[17] Steyn, M. M. de V.; Singleton, E.; Hietkamp, S.; Liles, D. C. *J. Chem. Soc.: Dalton Trans.* **1990**, 2991.

[18] Gansow, O. A.; Burke, A. R.; Vernon, W. D. *J. Am. Chem. Soc.* **1976**, *98*, 5817.

[19] Knox, S. A. R.; Macpherson, K. A.; Orpen, A. G.; Rendle, M. C. *J. Chem. Soc.: Dalton Trans.* **1989**, 1807.

[20] Barthel-Rosa, L. P.; Sowa, J. R., Jr.; Gassman, P. G.; Fischer, J.; McCarty, B. M.; Goldsmith, S. L.; Giboon, M. T.; Nelson, J. H. *Organometallics* submitted.

[21] McArdle, P.; Manning, A. R. *J. Chem. Soc. (A)* **1970**, 2128.

[22] Osiecki, J. H.; Hoffman, C.J.; Hollins, D. P. *J. Organomet. Chem.* **1965**, *3*, 107.

[23] Stasunik, A.; Malisch, W. *J. Organomet. Chem.* **1984**, *270*, C56.

[24] Davidson, A.; McFarlane, W.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1962**, 3653.

[25] Harris, D. C.; Gray, H. B. *Inorg. Chem.* **1975**, *14*, 1215.

[26] (a) Kim, H. P.; Angelici, R. J. *Organometallics* **1986**, *5*, 2481. (b) Kim, H. P.; Angelici, R. J. *Organometallics* **1986**, *5*, 2489 and references there in.

[27] Eatough, D. J., Christensen, J. J., Izatt, R. M. *Experiments in Thermometric and Titration Calorimetry*; Brigham Young University: Provo, UT, 1974.

[28] Jacobson, R. A., **1994**. ICE An Integrated Crystallographic Program Suite, Ames Laboratory, Iowa State University, Ames, IA.

[29] SHELXTL-PLUS, Siemens Analytical Xray, Inc., Madison, WI.

[30] Vollhardt, K. P. C.; Weidman, T. W. *J. Am. Chem. Soc.* **1983**, *105*, 1676.

[31] Steiner, A.; Gornitzka, H.; Stalke, D.; Edlelmann, F. T. *J. Organomet. Chem.* **1992**, *431*, C21.

[32] Mills, O. S.; Nice, J. P. *J. Organomet. Chem.* **1967**, *9*, 339.

[33] Jemmis, E. D.; Pinhas, A. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 2576 and references therein.

[34] (a) Fischer, R. D.; Vogler, A.; Noack, K. *J. Organomet. Chem.* **1967**, *7*, 135. (b) Bullitt, J. G.; Cotton, F. A.; Marks, J. D. *J. Am. Chem. Soc.* **1970**, *92*, 2155. (c) Bullitt, J. G.; Cotton, F. A.; Marks, J. D. *Inorg. Chem.* **1972**, *11*, 671. (d) Abrahamson, H. B.; Palazzotto, M. C.; Reichel, C. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 4123. (e) Onaka, S.; Shriver, D. F. *Inorg. Chem.* **1976**, *15*, 915. (f) Wnuk, T. A.; Angelici, R. J. *Inorg. Chem.* **1977**, *16*, 1173.

[35] (a) Bau, R.; Teller, R.G.; Kirtley, S.W.; Koetzle, T.F. *Acc. Chem. Res.* **1979**, *12*, 176. (b) Fryzuk, M. D.; Lloyd, B. R.; Clentsmith, G. K. B.; Rettig, S. T. *J. Am. Chem. Soc.* **1994**, *116*, 3804.

[36] Jolly, W. L.; Avanzino, S. C.; Rietz, R. R. *Inorg. Chem.* **1977**, *16*, 964.

[37] (a) Frankcom, T. M.; Green, J. C.; Nagy, A; Kakkar, A. K.; Marder, T. B. *Organometallics* **1993**, *12*, 3688. (b) O'Hare, D.; Green, J. C.; Marder, T.; Collins,

S.; Stringer, G.; Kakkar, A. K.; Kaltsoyannis, N.; Kuhn, A.; Lewis, R.; Mehnert, C.; Scott, P.; Kurmoo, M.; Pug, S. *Organometallics* **1992**, *11*, 48.

[38] (a) Gassman, P. G.; Mickelson, J. W.; Sowa, J. R. Jr. *J. Am. Chem. Soc.* **1992**, *114*, 6942. (b) Marken, F.; Marx, H. W.; Englert, V. *Struct. Chem.* **1994**, *5*, 177. (c) Gassman, P. G.; Sowa, J. R., Jr.; Hill, M. G.; Mann, K. R. *Organometallics* **1995**, *14*, 4879.

[39] (a) Trofimenko, S. J. *J. Am. Chem. Soc.* **1969**, *91*, 588. (b) Trofimenko, S. *Prog. Inorg. Chem.* **1986**, *34*, 115. (c) Doyle, R. A.; Angelici, R. J. *Organometallics* **1989**, *8*, 2213.

[40] Novak, K. *J. Organomet. Chem.* **1967**, *7*, 151.

[41] Skagestad, V.; Tilset, M. *J. Am. Chem. Soc.* **1993**, *115*, 5077.

[42] Chinn, M. S.; Heinekey, D. M.; Payne, N. G.; Sofield, C. D. *Organometallics* **1989**, *8*, 1824.

[43] McGovern, P. A.; Vollhardt, K. P. C. *Synlett* **1990**, 493.

[44] Tilset, M.; Vollhardt, K. P. C.; Boese, R. *Organometallics* **1994**, *13*, 3146.

Table 1. IR Data (CH_2Cl_2) for $Cp'_2Ru_2(CO)_4$ and $Cp'_2Ru_2(CO)_4(\mu\text{-}H)^+$ Complexes.

	(ν CO), cm^{-1}				
Complex	terminal			bridging	Av
$Cp^*_2Ru_2(CO)_4$, **1**	1928 (s)			1743 (s)	
$Cp^*_2Ru_2(CO)_4H^+$, **1H$^+$**	2049 (s)	2020 (m)	1989 (s)		2019
$Cp_2Ru_2(CO)_4$, **2**	2008 (s)	1967 (s)	1936 (m)	1770 (s)	
$Cp_2Ru_2(CO)_4H^+$, **2H$^+$**	2073 (s)	2049 (m)	2017 (s)		2046
$(HBpz_3)_2Ru_2(CO)_4$, **3**	2024 (s)	1976 (m)	1940 (s)		
$(HBpz_3)_2Ru_2(CO)_4H^+$, **3H$^+$**	2076 (s)	2029 (s)	2012 (m)		2039
$Ind_2Ru_2(CO)_4$, **4**	2001 (s)	1956 (m)		1763 (s)	
$Ind_2Ru_2(CO)_4H^+$, **4H$^+$**	2084 (m)	2044 (s)	2011 (m)		2046
$Cp^‡_2Ru_2(CO)_4$, **5**	1956 (s)			1772 (s)	
$Cp^‡_2Ru_2(CO)_4H^+$, **5H$^+$**	2068 (m)	2045 (s)	2015 (s)		2042
$(Cp_2CH_2)Ru_2(CO)_4$, **6**	2012 (s)	1960 (s)	1940 (s)	1780 (w)	
$(Cp_2CH_2)Ru_2(CO)_4H^+$, **6H$^+$**	2075 (s)	2048 (m)	2021 (s)		2048
$(Cp_2(CH_2)_2)Ru_2(CO)_4$, **7**	1998 (s)	1956 (m)		1770 (s)	
$(Cp_2(CH_2)_2)Ru_2(CO)_4H^+$, **7H$^+$**	2073 (s)	2045 (m)	2018 (s)		2045
$FvRu_2(CO)_4$, **8**	2020 (s)	1952 (s)			
$FvRu_2(CO)_4H^+$, **8H$^+$**	2082 (s)	2056 (m)	2028 (s)		2055

Table 2. Crystallographic Data for $Cp_2Ru_2(CO)_4(\mu\text{-}H)^+ CF_3SO_3^-$ (**$2H^+ CF_3SO_3^-$**), $(Cp_2CH_2)Ru_2(CO)_4(\mu\text{-}H)^+ CF_3SO_3^-$ (**$6H^+ CF_3SO_3^-$**) and $(Cp_2(CH_2)_2)Ru_2(CO)_4$ (**7**).

	$2H^+ CF_3SO_3^-$	**$6H^+ CF_3SO_3^-$**	**7**
formula	$C_{15}H_{11}F_3O_7Ru_2S$	$C_{16}H_{11}F_3O_7Ru_2S$	$C_{16}H_{12}O_4Ru_2$
space group	$P2_1/n$	$C\,2/c$	$P\,2_1/c$
a, Å	14.399(3)	30.709(4)	8.097(2)
b, Å	16.128(3)	10.374(1)	13.376(3)
c, Å	16.045(3)	12.696(2)	13.925(3)
β, deg	94.62(3)	112.62(1)	94.17(3)
V, Å^3	3714.0(12)	3733.6(9)	1504.2(6)
Z	8	8	4
d_{calc}, g/cm^3	2.126	2.158	2.077
crystal size, mm	0.2 x 0.15 x 0.1	0.41 x 0.19 x 0.04	0.3 x 0.15 x 0.03
μ, mm^{-1}	14.852 (Cu Kα)	1.797 (Mo Kα)	2.021 (Mo Kα)
data collection instrument	Siemens P4RA	Enraf-Nonius, CAD4	Enraf-Nonius, CAD4
radiation (monochromated in incident beam)	Cu Kα (λ=1.54178 Å)	Mo Kα (λ=0.71073 Å)	Mo Kα (λ=0.71073 Å)
no. of orientation reflections; range (2θ)	25; 19.353< θ <28.128	25; 8.72< θ <14.37	25; 7.45< θ <17.40
temp, °C	20(2)	25(1)	20(2)

Table 2. (continued)

	$2H^+ CF_3SO_3^-$	$6H^+ CF_3SO_3^-$	7
scan method	ω	2θ-θ	ω
data collection range, 2θ, deg	7.00-113.5	4.0-50.0	4.00-55.00
no. of data collected	6319	6886	4522
no. of unique data total	4976	3286	3447
with $I \geq 2\sigma$ (I)	4339	2192	2115
no. of parameters refined	494	276	199
trans factors; max; min	1.000/0.393	0.9942/0.8163	0.623/0.560
R^a	0.0758	0.0389	0.0503
R_w	0.0869[b]	0.0651[c]	0.1185[b]
quality of fit indicator[d]	1.180	1.12	1.039
largest shift/esd, final cycle	0.000	0.038	0.000
largest peak, e/Å^{-3}	2.598	0.92	0.885

[a] $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [b] $R_w = [\Sigma[w(F_o^2-F_c^2)^2/\Sigma[w(F_o^2)^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [d] Quality-of-fit = $[\Sigma w(|F_o|-|F_c|)^2/(N_{obs}-N_{parameters})]^{1/2}$.

Table 3. Selected Bond Distances (Å) and Angles (deg)[a] for $(Cp_2(CH_2)_2)Ru_2(CO)_4$ (**7**).

Distances (Å)					
Ru(1)-Ru(2)	2.7037(10)	Ru(1)-C(1)	1.875(9)	Ru(1)-C(3)	2.041(8)
Ru(1)-C(4)	2.053(8)	Ru(2)-C(2)	1.864(9)	Ru(2)-C(3)	2.035(9)
Ru(2)-C(4)	2.037(8)	C(1)-O(1)	1.128(10)	C(2)-O(2)	1.141(10)
C(3)-O(3)	1.175(9)	C(4)-O(4)	1.165(9)	C(5)-C(15)	1.529(13)
C(15)-C(16)	1.46(2)	C(10)-C(16)	1.517(13)	Ru(1)-Cp_c[b]	1.913
				Ru(2)-Cp_c[b]	1.920

Bond Angles (deg)			
Ru(2)-Ru(1)-C(1)	101.2(3)	Ru(1)-Ru(2)-C(2)	100.5(3)
C(1)-Ru(1)-C(3)	88.8(3)	C(1)-Ru(1)-C(4)	89.0(3)
C(2)-Ru(2)-C(3)	87.7(4)	C(2)-Ru(2)-C(4)	88.9(4)
Ru(1)-C(1)-O(1)	176.8(8)	Ru(2)-C(2)-O(2)	178.3(9)
Ru(1)-C(3)-O(3)	138.8(7)	Ru(1)-C(4)-O(4)	138.7(7)
Ru(2)-C(3)-O(3)	137.8(7)	Ru(2)-C(4)-O(4)	138.2(7)
Ru(1)-Ru(2)-Cp_c[b]	129.7	C(10)-C(16)-C(15)	116.5(10)
C(5)-C(15)-C(16)	116.5(10)	C(5)-C(15)-C(16)-C(10)	78.3
Ru(2)-Ru(1)-Cp_c[b]	127.9	Cp_c-Ru(1)-Ru(2)-Cp_c[b]	0.9

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

[b] Cp_c = centroid of Cp ring.

Table 4. Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Coefficients ($Å^2$ x 10^3) for $(Cp_2(CH_2)_2)Ru_2(CO)_4$ **(7).**

Atom	x	y	z	U_{eq}
Ru(1)	6881(1)	1885(1)	3938(1)	33(1)
Ru(2)	6682(1)	3884(1)	3466(1)	38(1)
O(1)	3812(8)	1578(6)	4988(5)	78(2)
O(2)	3444(8)	4372(6)	4264(6)	86(2)
O(3)	4615(7)	2434(5)	2194(4)	59(2)
O(4)	7951(9)	3374(5)	5499(5)	71(2)
C(1)	4944(11)	1717(6)	4581(6)	47(2)
C(2)	4685(12)	4182(7)	3970(7)	55(2)
C(3)	5515(10)	2622(6)	2870(6)	40(2)
C(4)	7391(10)	3155(6)	4733(6)	43(2)
C(5)	9466(11)	1623(7)	3456(8)	58(3)
C(6)	8350(11)	1054(7)	2848(6)	51(2)
C(7)	7580(10)	364(6)	3412(7)	55(2)
C(8)	8231(11)	511(7)	4379(7)	55(2)
C(9)	9414(11)	1260(7)	4393(7)	55(2)
C(10)	9060(10)	3945(6)	2674(7)	52(2)
C(11)	9198(11)	4625(7)	3456(7)	58(2)
C(12)	7952(12)	5312(6)	3335(8)	64(3)
C(13)	7026(12)	5117(9)	2476(10)	84(4)
C(14)	7682(13)	4290(9)	2061(7)	70(3)
C(15)	10721(12)	2412(9)	3193(10)	84(4)
C(16)	10190(14)	3096(8)	2418(9)	82(4)

Table 5. Selected Bond Distances (Å) and Angles (deg)[a] for $[Cp_2Ru_2(CO)_4(\mu\text{-}H)^+]$ $[CF_3SO_3^-]$ ($\mathbf{2H^+CF_3SO_3^-}$).

Distances (Å)					
Ru(1a)-Ru(2a)	3.040(2)	Ru(1a)-C(6a)	1.88(2)	Ru(1a)-C(7a)	1.90(2)
C(6a)-O(1a)	1.16(2)	C(7a)-O(2a)	1.13(2)	Ru(2a)-C(13a)	1.85(2)
Ru(2a)-C(14a)	1.88(2)	C(13a)-O(3a)	1.18(2)	C(14a)-O(4a)	1.14(2)
Ru(1b)-Ru(2b)	3.034(2)	Ru(1b)-C(6b)	1.90(2)	Ru(1b)-C(7b)	1.86(2)
C(6b)-O(1b)	1.14(2)	C(7b)-O(2b)	1.15(2)	Ru(2b)-C(13b)	1.89(2)
Ru(2b)-C(14b)	1.86(2)	C(13b)-O(3b)	1.13(2)	C(14b)-O(4b)	1.16(2)
Ru(1a)-H(a)	1.79(17)	Ru(2a)-H(a)	1.80(17)	Ru(1b)-H(b)	1.74(17)
Ru(2b)-H(b)	1.81(17)	Ru(1a)-Cp_c[b]	1.870	Ru(2a)-Cp_c[b]	1.878
Ru(1b)-Cp_c[b]	1.886	Ru(2b)-Cp_c[b]	1.886		

Bond Angles (deg)			
Ru(2a)-Ru(1a)-C(6a)	80.6(5)	Ru(2a)-Ru(1a)-C(7a)	97.3(4)
Ru(1a)-Ru(2a)-C(13a)	78.4(5)	Ru(1a)-Ru(2a)-C(14a)	96.6(5)
C(6a)-Ru(1a)-C(7a)	90.3(7)	C(13a)-Ru(2a)-C(14a)	91.1(8)
Ru(1a)-C(6a)-O(1a)	174.2(14)	Ru(1a)-C(7a)-O(2a)	178.9(14)
Ru(2a)-C(13a)-O(3a)	176.0(14)	Ru(2a)-C(14a)-O(4a)	175(2)
Ru(2b)-Ru(1b)-C(6b)	79.6(5)	Ru(2b)-Ru(1b)-C(7b)	96.9(5)
Ru(1b)-Ru(2b)-C(13b)	79.0(5)	Ru(1b)-Ru(2b)-C(14b)	97.6(5)
C(6b)-Ru(1b)-C(7b)	92.4(7)	C(13b)-Ru(2b)-C(14b)	91.7(6)
Ru(1b)-C(6b)-O(1b)	177(2)	Ru(1b)-C(7b)-O(2b)	179(2)
Ru(2b)-C(13b)-O(3b)	175(2)	Ru(2b)-C(14b)-O(4b)	178.2(14)
Ru(1a)-H(a)-Ru(2a)	116(1)	Ru(1b)-H(b)-Ru(2b)	117(1)

Table 5. (continued)

Bond Angles (deg)			
Ru(1a)-Ru(2a)-Cp_c[b]	126.8	Ru(2a)-Ru(1a)-Cp_c[b]	126.2
Ru(1b)-Ru(2b)-Cp_c[b]	123.8	Ru(2b)-Ru(1b)-Cp_c[b]	126.0
Cp_c-Ru(1a)-Ru(2a)-Cp_c[b]	177.5	Cp_c-Ru(1b)-Ru(2b)-Cp_c[b]	176.8

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

[b] Cp_c = centroid of Cp ring.

Table 6. Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Coefficients ($Å^2$ x 10^3) for $[Cp_2Ru_2(CO)_4(\mu\text{-}H)^+][CF_3SO_3^-]$ (**$2H^+CF_3SO_3^-$**).

Atom	x	y	z	U_{eq}
Ru(1a)	576(1)	2703(1)	6614(1)	25(1)
Ru(2a)	-472(1)	2532(1)	8176(1)	27(1)
H(a)	-82(118)	3196(109)	7375(104)	0.050
C(1a)	-673(13)	2457(13)	5720(9)	47(4)
C(2a)	-38(15)	1864(13)	5615(11)	55(4)
C(3a)	790(14)	2250(15)	5355(11)	58(4)
C(4a)	603(14)	3123(14)	5315(9)	52(4)
C(5a)	-328(14)	3218(13)	5546(10)	50(4)
C(6a)	1324(11)	1900(11)	7188(9)	33(4)
O(1a)	1819(9)	1396(8)	7479(8)	51(3)
C(7a)	1412(11)	3548(11)	7017(9)	31(4)
O(2a)	1908(8)	4050(8)	7246(7)	43(3)
C(8a)	607(15)	2110(14)	9161(10)	57(6)
C(9a)	704(12)	2961(14)	9078(10)	47(5)
C(10a)	-109(15)	3335(13)	9292(11)	54(5)
C(11a)	-764(13)	2705(19)	9492(10)	69(8)
C(12a)	-278(17)	1942(15)	9427(10)	64(7)
C(13a)	-781(11)	1549(11)	7623(10)	36(4)
O(3a)	-977(10)	901(9)	7318(8)	59(4)
C(14a)	-1584(12)	3029(11)	7733(10)	37(4)
O(4a)	-2271(9)	3340(9)	7523(9σ)	56(3)
Ru(1b)	669(1)	8131(1)	7201(1)	25(1)

Table 6. (continued)

Atom	x	y	z	U_{eq}
Ru(2b)	-356(1)	6496(1)	7309(1)	28(1)
H(b)	26(120)	7343(106)	6684(108)	0.050
C(1b)	-431(13)	8975(11)	6748(12)	48(5)
C(2b)	-533(13)	8961(11)	6755(12)	46(5)
C(3b)	227(14)	9264(12)	6457(12)	50(5)
C(4b)	891(12)	9468(11)	7132(16)	57(6)
C(5b)	457(17)	9303(12)	7871(12)	66(7)
C(6b)	1340(11)	7652(10)	8146(10)	34(4)
O(1b)	1761(8)	7403(7)	8725(8)	42(3)
C(7b)	1540(11)	7772(12)	6484(10)	38(4)
O(2b)	2083(8)	7556(9)	6042(8)	52(3)
C(8b)	124(24)	5380(15)	7998(13)	86(10)
C(9b)	-528(12)	5152(11)	7294(18)	64(7)
C(10b)	-100(22)	5345(14)	6609(13)	75(8)
C(11b)	735(20)	5690(16)	6870(28)	99(12)
C(12b)	900(20)	5682(17)	7630(31)	109(15)
C(13b)	-755(11)	7058(9)	8254(10)	31(4)
O(3b)	-986(10)	7341(8)	8844(8)	55(3)
C(14b)	-1433(11)	6792(10)	6663(9)	31(4)
O(4b)	-2113(8)	6956(8)	6261(8)	51(3)

Table 7. Selected Bond Distances (Å) and Angles (deg)[a] for $[(Cp_2CH_2)Ru_2(CO)_4(\mu\text{-}H)^+][CF_3SO_3^-]$ (**$6H^+CF_3SO_3^-$**).

Distances (Å)					
Ru-H	1.498(84)	Ru'-H	2.000(98)	C(7)-O(7)	1.145(11)
Ru-C(7)	1.887(8)	Ru-C(8)	1.870(11)	Ru'-C(8')	1.872(10)
C(8)-O(8)	1.152(14)	Ru'-C(7')	1.866(9)	C(1)-C(2)	1.534(14)
C(7')-O(7')	1.145(12)	C(8')-O(8')	1.136(12)	Ru-Cp_c[b]	1.88
C(1)-C(2')	1.490(10)	Ru-Ru'	3.019(1)	Ru'-Cp'_c[b]	1.88
Bond Angles (deg)					
Ru'-Ru-C(7)	83.5(3)	Ru-Ru'-C(7')	94.0(3)	Ru'-Ru-C(8)	107.5(3)
Ru-Ru'-C(8')	104.4(4)	C(7)-Ru-C(8)	90.3(4)	C(7')-Ru'-C(8')	89.4(4)
Ru-C(7)-O(7)	177.3(7)	Ru-C(8)-O(8)	176.4(7)	Ru'-C(7')-O(7')	174.5(9)
C(2)-C(1)-C(2')	114.1(8)	H-Ru-C(7)	98.7(34)	H-Ru-C(8)	75.4(40)
Ru-H-Ru'	118.6(57)	H-Ru'-C(8')	79.1(25)	Cp_c-Ru-Ru-Cp_c[b]	11.6
H-Ru'-C(7')	98.6(27)	Ru'-Ru-Cp_c[b]	116.2	Ru-Ru'-Cp_c[b]	113.2

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

[b] Cp_c = centroid of Cp ring.

Table 8. Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Coefficients ($Å^2$ x 10^3) for $[(Cp_2CH_2)Ru_2(CO)_4(\mu\text{-}H)^+][CF_3SO_3^-]$ (**$6H^+CF_3SO_3^-$**).

Atom	x	y	z	U_{eq}
Ru	1911(1)	2385(1)	1811(1)	26(1)
Ru'	855(1)	2612(1)	1080(1)	26(1)
H	1488(31)	3196(91)	1165(72)	63(27)
C(1)	1503(3)	3110(10)	3867(8)	45(4)
C(2)	1927(3)	2691(8)	3591(6)	35(3)
C(3)	2236(3)	3604(8)	3366(7)	39(3)
C(4)	2585(3)	2896(9)	3181(7)	40(3)
C(5)	2498(3)	1590(9)	3286(7)	44(4)
C(6)	2092(3)	1462(9)	3531(7)	38(3)
C(7)	1754(3)	912(8)	867(7)	39(3)
O(7)	1676(2)	-2(7)	320(6)	63(3)
C(8)	2077(3)	3263(10)	735(8)	46(4)
O(8)	2204(3)	3799(7)	110(6)	70(3)
C(2')	1037(3)	2737(8)	2986(6)	32(3)
C(3')	674(3)	3606(8)	2422(7)	37(4)
C(4')	280(3)	2896(10)	1681(7)	46(4)
C(5')	401(3)	1585(9)	1801(8)	43(4)
C(6')	876(3)	1478(8)	2604(7)	36(3)
C(7')	724(3)	1414(9)	-99(8)	41(4)
O(7')	609(3)	667(8)	-817(7)	71(3)
C(8')	683(3)	3941(10)	0(8)	50(4)
O(8')	555(3)	4766(8)	-633(7)	86(4)

Table 9. Heats of Protonation (ΔH_{MHM}) of $Cp'_2Ru_2(CO)_4$ Complexes.

Unlinked-Cp' Complexes	$-\Delta H_{MHM}$,[a,b] kcal/mol
$Cp^*_2Ru_2(CO)_4$, **1**	19.2 (4)
$Cp_2Ru_2(CO)_4$, **2**	18.4 (1)
$(HBpz_3)_2Ru_2(CO)_4$, **3**	16.6 (1)
$Ind_2Ru_2(CO)_4$, **4**	14.1 (2)
$Cp^{\ddagger}_2Ru_2(CO)_4$, **5**	12.0 (1)

Linked-Cp' Complexes	$-\Delta H_{MHM}$,[a,b] kcal/mol
$(Cp_2CH_2)Ru_2(CO)_4$, **6**	21.0 (3)
$(Cp_2(CH_2)_2)Ru_2(CO)_4$, **7**	16.9 (2)
$FvRu_2(CO)_4$, **8**	16.1 (4)

[a] For protonation with 0.1 M CF_3SO_3H in DCE solvent at 25.0 °C. [b] Numbers in parenthesis are average deviations from the mean of at least four titrations.

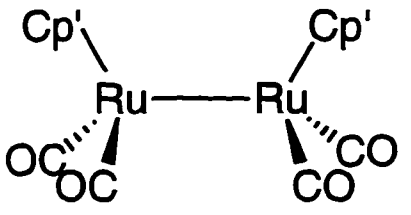
Figure 1. Possible isomeric forms of $Cp'_2Ru_2(CO)_4$ complexes.

Figure 2. Thermal ellipsoid drawing of $(Cp_2(CH_2)_2)Ru_2(CO)_4$ (**7**) showing the atom numbering scheme (50% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

Figure 3. Thermal ellipsoid drawing of $Cp_2Ru_2(CO)_4(\mu\text{-}H)^+$ (**2H$^+$**) showing the atom numbering scheme (50% probability ellipsoids).

Figure 4. Thermal ellipsoid drawing of $(Cp_2CH_2)Ru_2(CO)_4(\mu\text{-}H)^+$ (**6H$^+$**) showing the atom numbering scheme (50% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

Figure 1.



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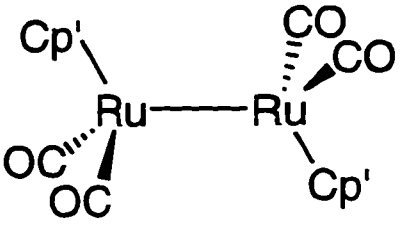

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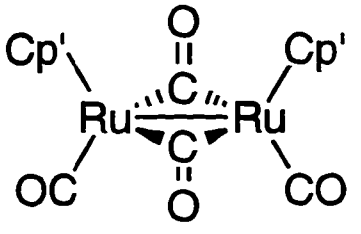
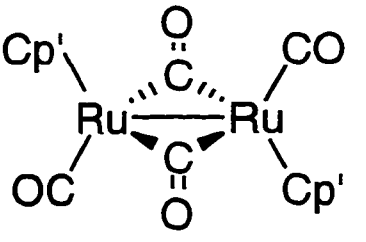


cis, bridged



trans, bridged

Figure 2.

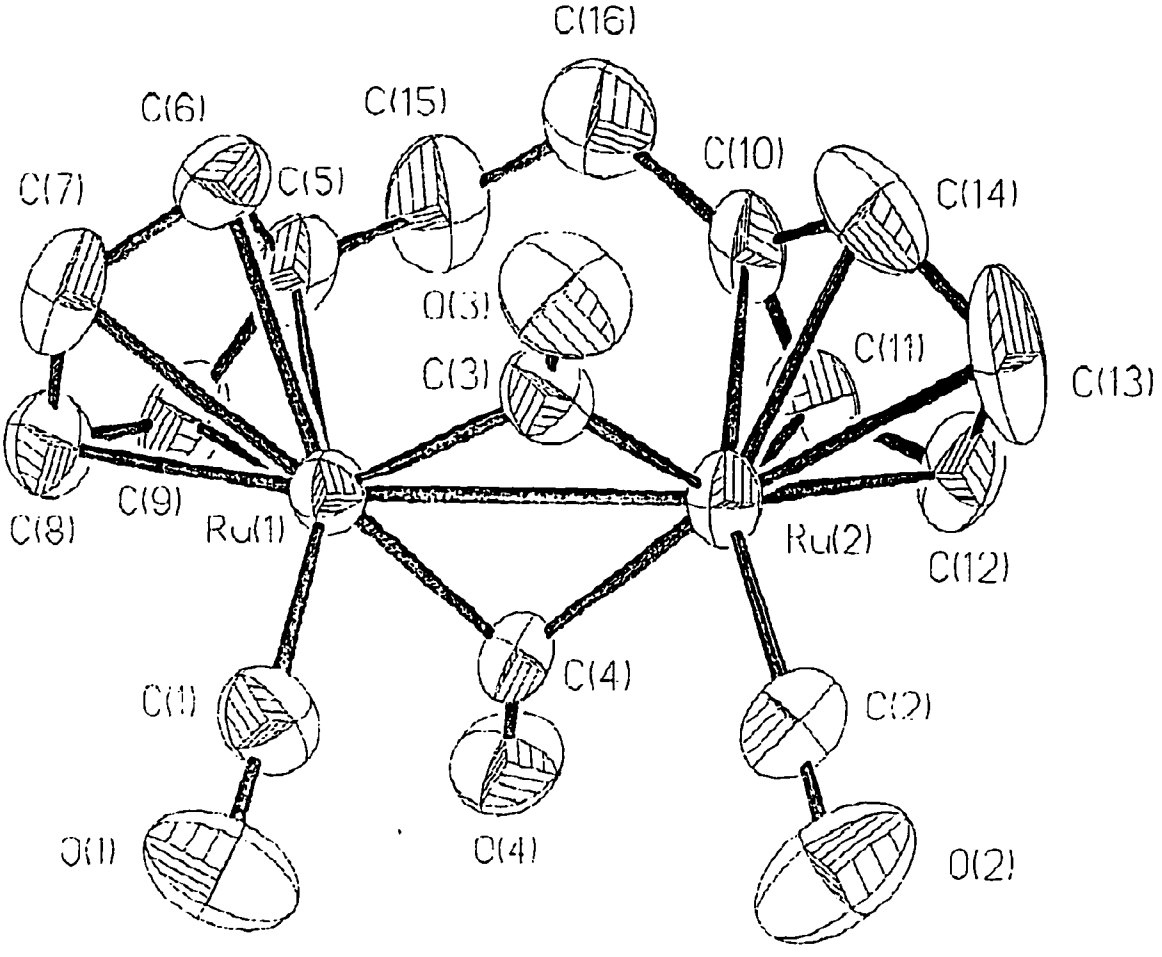

C(16)
C(6)
C(15)
C(10)
C(7)
C(5)
C(14)
O(3)
C(11)
C(3)
C(13)
C(9)
C(8)
Ru(1)
Ru(2)
C(12)
C(4)
C(1)
C(2)
O(1)
C(4)
O(2)

Figure 3.

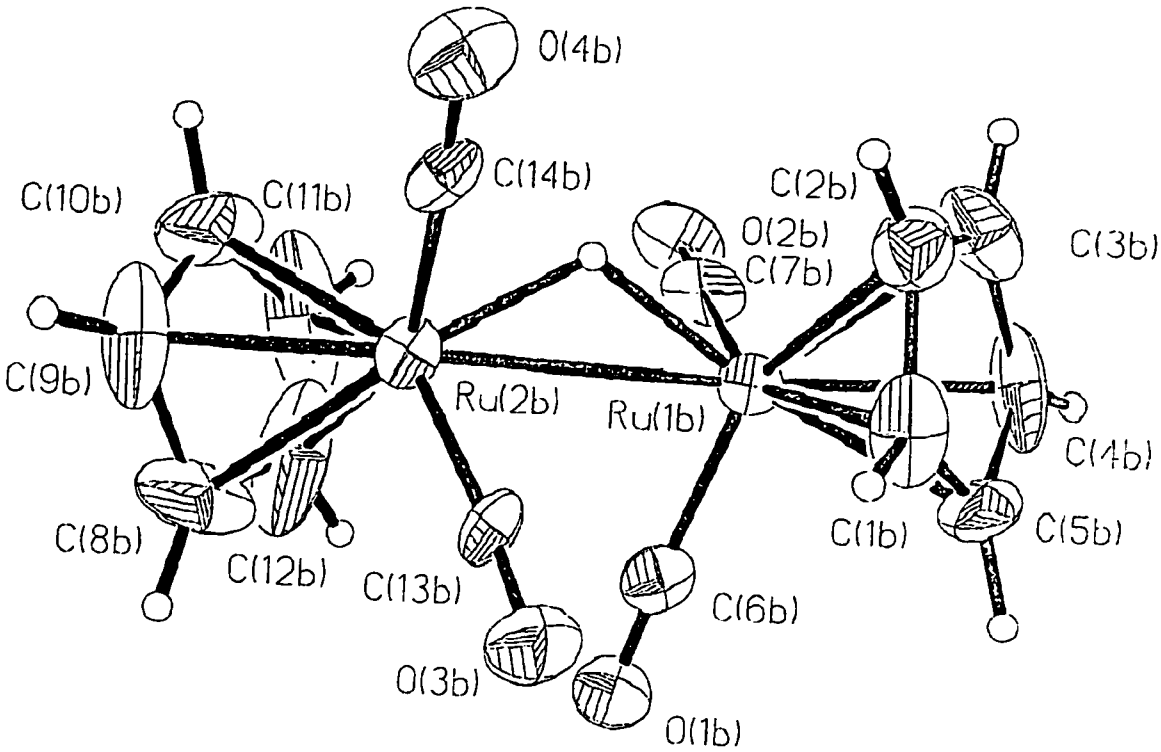
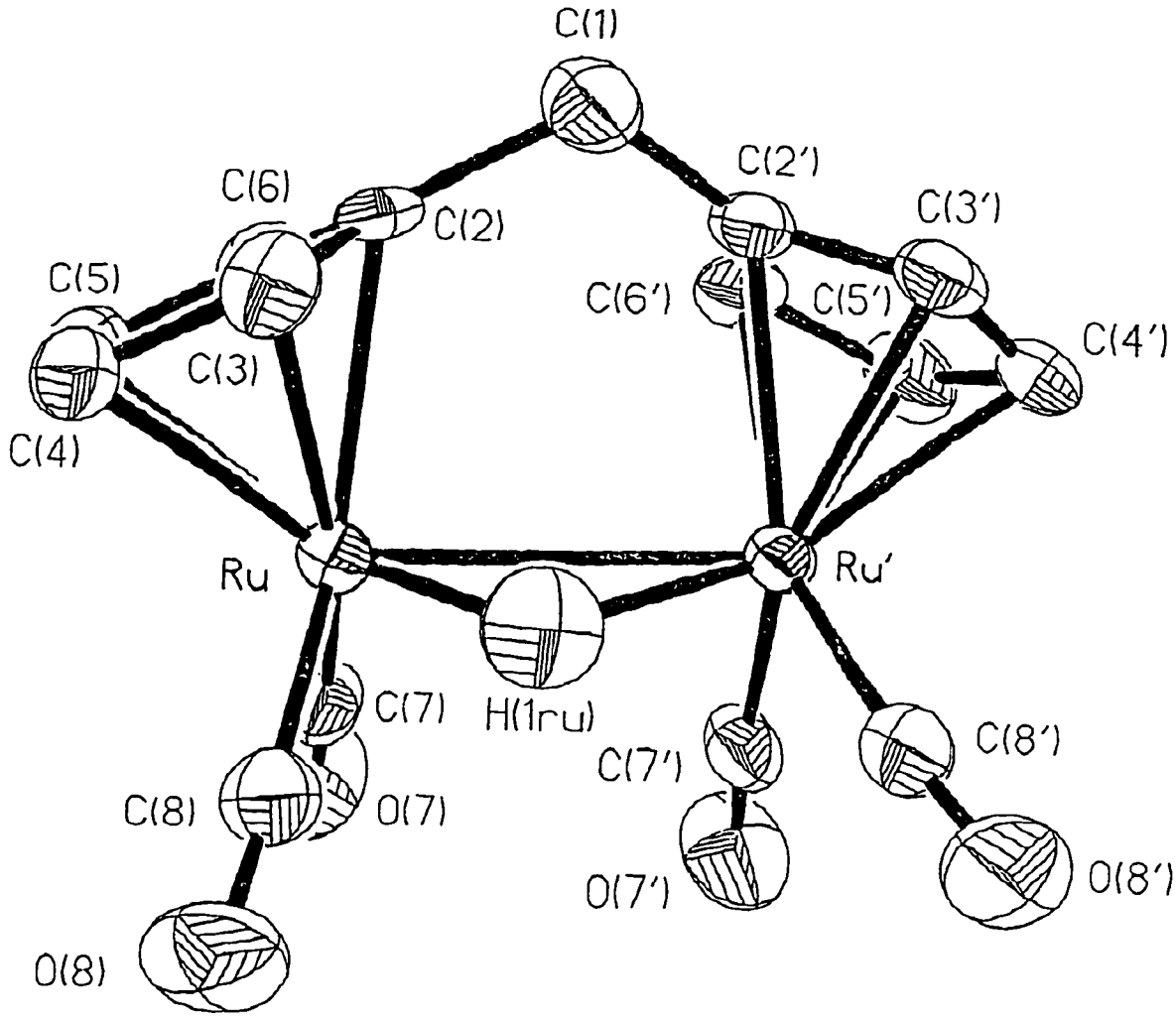

O(4b)
C(14b)
C(10b)
C(11b)
C(2b)
O(2b)
C(7b)
C(3b)
C(9b)
Ru(2b)
Ru(1b)
C(4b)
C(8b)
C(12b)
C(13b)
C(1b)
C(5b)
C(6b)
O(3b)
O(1b)

Figure 4.



STUDIES OF THE PROTONATION OF METAL-METAL BONDS IN $Cp_2Ru_2(CO)_3(PR_3)$ AND $Cp_2Mo_2(CO)_4(PR_3)_2$

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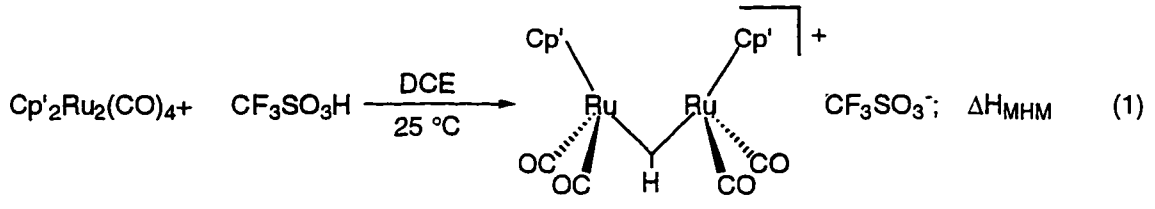
Abstract

Basicities for the series of the complexes $Cp_2Ru_2(CO)_3(PMe_3)$, $Cp_2Mo_2(CO)_4(PMe_2Ph)_2$ and $Cp_2Mo_2(CO)_4(PMe_3)_2$ have been determined by the heat evolved (ΔH_{MHM}) when the complex is protonated by CF_3SO_3H in 1,2-dichloroethane at 25.0 °C. In the ruthenium system, ^{13}C labeling was used to aid in the determination of the protonation site. Spectroscopic studies show that the protonation occurs at the metal-metal bond to form $[Cp_2Ru_2(CO)_3(PMe_3)(\mu\text{-}H)]^+$ $CF_3SO_3^-$. The $Cp_2Ru_2(CO)_3(PMe_3)$ has a basicity of 30.0(4) kcal/mol, which is significantly more basic than the carbonyl analog, $Cp_2Ru_2(CO)_4$ (18.4(1) kcal/mol). In the molybdenum system, spectroscopic studies also show that the protonation occurs at the metal-metal bond to form $[Cp_2Mo_2(CO)_4(PMe_3)_2(\mu\text{-}H)]^+$ $CF_3SO_3^-$. By replacing the PMe_2Ph ligands with the more electron donating PMe_3 ligands the basicity of the Mo-Mo bond is significantly increased (from 18.9(5) to 27.4(2) kcal/mol). In addition, the structures of $Cp_2Ru_2(CO)_3(PMe_3)$ and $[Cp_2Ru_2(CO)_3(PMe_3)(\mu\text{-}H)]^+$ $CF_3SO_3^-$ are presented.

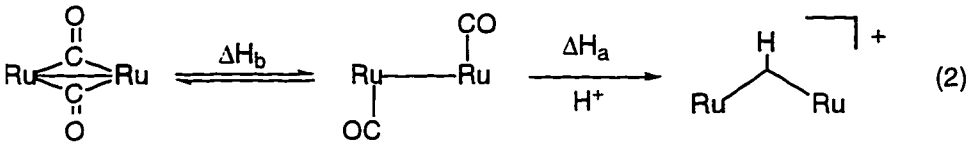
Introduction

The tendency of a transition metal complex to undergo acid protonation at the metal is defined as its basicity. Quantitative measures of complex basicity are pK_a and ΔH_{HM}, which are determined calorimetrically.[1] Most of these basicities have been reported for mononuclear complexes; there are very few quantitative studies of di- or polynuclear compounds in which protonation occurs at a metal-metal bond to give a bridging hydride product. Recently, we reported results of a titration calorimetry study[2] of the heats of protonation (ΔH_{MHM}) of a series of dinuclear $Cp'_2Ru_2(CO)_4$ complexes (eq 1). The $-\Delta H_{MHM}$ values, measured in



(1)

1,2-dichloroethane(DCE) solvent, increased with variations in the Cp'_2 ligands in the order ($-\Delta H_{MHM}$ values in kcal/mol; the CO-bridged(b) or non-bridged(nb) structure of each $Cp'_2Ru_2(CO)_4$ complex is given in parentheses): $(C_5Me_4CF_3)_2$ (12.0, b) < $Indenyl_2$ (14.1, b) < fulvalene (16.1, nb) < $Cp_2(CH_2)_2$ (16.9, b) < Cp_2 (18.4, 50% nb) < $(C_5Me_5)_2$ (19.2, b) < Cp_2CH_2 (21.0, 90%nb). An analysis of these data suggested that two factors were primarily responsible for this trend. The first is the donor ability of the Cp'_2 ligands; the more strongly donating the Cp'_2 ligands, the more basic the Ru-Ru bond. The second factor is the energy (ΔH_b) required to convert (eq 2)

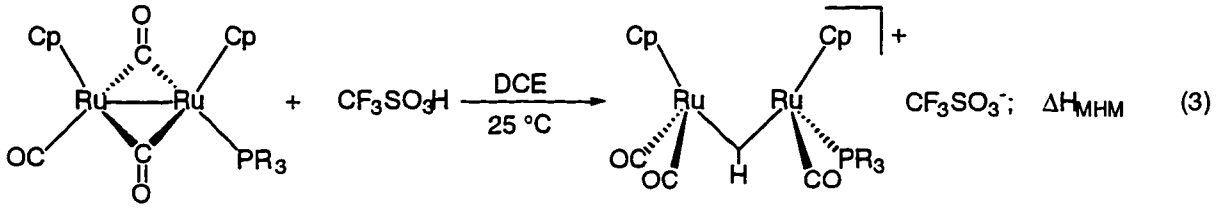


(2)

a CO-bridged isomer to its non-bridged isomer. For bridged $Cp'_2Ru_2(CO)_4$ complexes, the overall ΔH_{MHM} value may be considered as the sum of ΔH_b and ΔH_a. For two complexes that

have Cp'_2 ligands with similar donor abilities, ΔH_a will be similar, but if one of the complexes is CO-bridged an endothermic ΔH_b term will cause its $-\Delta H_{MHM}$ to be less positive than the other $Cp'_2Ru_2(CO)_4$ complex with no bridging CO groups. Thus, bridging CO groups reduce the basicity of the Ru-Ru bond as compared with analogous complexes that are non-bridged.

In the present study, we sought to determine the basicity ($-\Delta H_{MHM}$) of the phosphine-substituted CO-bridged complexes $Cp_2Ru_2(CO)_3(PR_3)$ by the reaction in eq 3. These



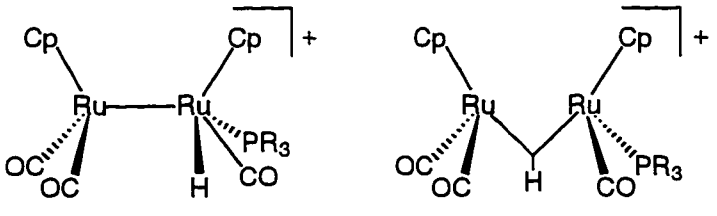
(3)

1 - 4

1, $PR_3 = PMe_3$
2, $PR_3 = PMe_2Ph$
3, $PR_3 = PMePh_2$
4, $PR_3 = PPh_3$

1H⁺ - 4H⁺

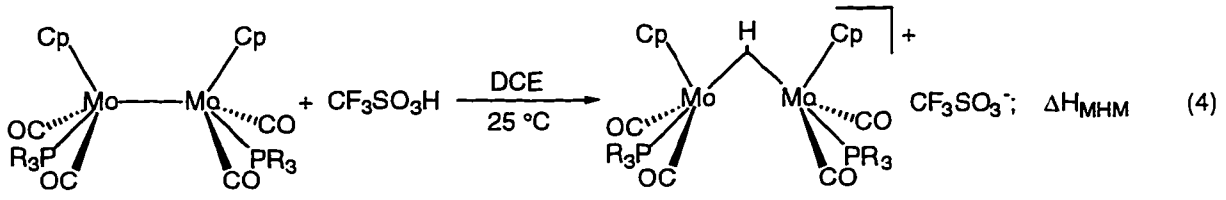
complexes were of particular interest because the Ru atom bonded to the PR_3 ligand is expected to be much more basic than the Ru coordinated to a terminal CO.[1,3] The magnitude of this expected difference is suggested by the $-\Delta H_{HM}$ values for $Cp^*Ir(CO)(PMe_3)$ (38.0(2) kcal/mol) and $Cp^*Ir(CO)(PPh_3)$ (37.1(2) kcal/mol) as compared with $Cp^*Ir(CO)_2$ (21.4(1) kcal/mol).[4] If the PR_3-substituted Ru in $Cp_2Ru_2(CO)_3(PR_3)$ were 15.7-16.6 kcal/mol more basic than the CO-substituted Ru, one would expect protonation to occur at the PR_3-substituted



A **B**

Ru as in **A**. On the other hand, if the electron density provided by the phosphine were distributed into the Ru-Ru bond, the proton might bridge the two Ru atoms as in **B**. NMR and X-ray diffraction studies provide evidence for the location of the hydrogen in $\mathbf{1H^+CF_3SO_3^-}$ and $\mathbf{4H^+CF_3SO_3^-}$. In addition, ΔH_{MHM} for $Cp_2Ru_2(CO)_3(PMe_3)$ has been measured and compared with that for $Cp_2Ru_2(CO)_4$ and related complexes.

Protonation reactions (eq 4) of four $Cp_2Mo_2(CO)_4(PR_3)_2$ complexes have also been



9 - 12 **9H⁺ - 12H⁺**

9, $PR_3 = PMe_3$
10, $PR_3 = PMe_2Ph$
11, $PR_3 = PMePh_2$
12, $PR_3 = PPh_3$

examined. NMR studies indicate that the proton bridges the Mo-Mo bond in the product, as expected for these symmetric structures. Measured basicities ($-\Delta H_{MHM}$) of $Cp_2Mo_2(CO)_4(PR_3)_2$, where PR_3 is PMe_3 or PMe_2Ph, are compared with related dinuclear complexes.

Experimental Section

General Procedures. All preparative reactions, chromatography and manipulations were carried out under an atmosphere of nitrogen or argon using standard Schlenk techniques. Solvents were purified under nitrogen using standard methods[5] as described below. Hexanes, toluene and methylene chloride were refluxed over CaH_2 and then distilled. Diglyme was refluxed over CaH_2 and vacuum distilled. Diethyl ether was distilled from sodium benzophenone. CD_2Cl_2 was stored over molecular sieves under nitrogen. 1,2-Dichloroethane

(DCE) was purified by washing successively with concentrated sulfuric acid, distilled deionized water, 5% NaOH, and again with water. The solvent was then predried over anhydrous $MgSO_4$ and stored in amber bottles over molecular sieves (4 Å). The DCE was distilled from P_4O_{10} under argon immediately before use. Triflic acid (CF_3SO_3H) was purchased from 3M Co. and purified by fractional distillation under argon prior to use. Neutral Al_2O_3 (Brockmann, activity I) used for chromatography was deoxygenated at room temperature under vacuum for 12 h, deactivated with either 3% (w/w) N_2-saturated water (for ruthenium compounds) or 5% (w/w) N_2-saturated water (for molybdenum compounds), and stored under N_2.

The compounds $Cp_2Ru_2(CO)_4$,[6] $Cp_2Ru_2(CO)_2(COC_2Ph_2)$,[7] $Cp_2Mo_2(CO)_6$[8] and $Cp_2Mo_2(CO)_4$[9] were prepared by literature methods. Diphenylacetylene was purchased from Eastman. The phosphines, PPh_3, $PMePh_2$, PMe_2Ph and PMe_3 (1.0 M in toluene), were purchased from Aldrich. The ^{13}CO (^{13}C, 99%) was purchased from Cambridge Isotopes. The ^1H NMR spectra were obtained at ambient temperature unless indicated otherwise on samples dissolved in CD_2Cl_2 on a Nicolet NT 300-MHz or a Bruker AC 200 MHz spectrometer with TMS ($\delta = 0.00$ ppm) as the internal reference. ^{31}P NMR spectra were obtained in CD_2Cl_2 on a Bruker AC 200 MHz spectrometer with H_3PO_4 ($\delta = 0.00$ ppm) as the reference. The ^{13}C NMR spectra were obtained at room temperature in CD_2Cl_2 on a Bruker AC 200 MHz spectrometer with the solvent ($\delta = 53.8$ ppm) as the internal reference. The ^{13}C NMR spectra at 400 MHz were obtained on a Bruker DRX 400-MHz spectrometer. Solution infrared spectra were recorded on a Nicolet 710 FT-IR spectrometer using sodium chloride cells with 0.1 mm

spacers. Electron Ionization Mass Spectra (EIMS) were run on a Finnigan 4000 spectrometer. Elemental microanalyses were performed on a Perkin Elmer 2400 Series II CHNS/O analyzer.

$Cp_2Ru_2(CO)_3(PR_3)$. In a typical reaction, approximately 0.1 g (0.2 mmol) of $Cp_2Ru_2(CO)_2(COC_2Ph_2)$ and 1 equivalent of the desired phosphine were heated to reflux in 20 mL of toluene. The solution changed from orange-red to bright yellow. Monitoring by IR spectroscopy indicated that the reaction was complete after 30 min. Upon cooling and vacuum removal of solvent, the compounds were chromatographed on an alumina column (1.5 x 30 cm); the yellow product band was eluted with a 3:2 (v/v) mixture of CH_2Cl_2 and hexanes. Solvent was removed and the compounds were crystallized at -20 °C from ether. Isolated yields of the complexes were greater than 90% in all cases. IR data for compounds **1-4** and **5-8** are presented in Tables 1 and 2, respectively. ^1H NMR and IR data for compound **4** are essentially the same as those reported previously for this compound.[10]

$Cp_2Ru_2(CO)_3(PMe_3)$ (1). ^1H (CD_2Cl_2): δ 5.23 (s, 5H, Cp), 5.00 (s, 5H, Cp), 1.23 (d $^2J_{P-H}$ 10.0 Hz, 9H, Me). ^{31}P (CD_2Cl_2): δ 9.95 (s). IR (toluene): ν(CO) (cm^{-1}) 1929 (m), 1742 (s). Orange crystals of **1** were obtained by cooling an ether solution of **1** to -20 °C for three days.

$Cp_2Ru_2(CO)_3(PMe_2Ph)$ (2). ^1H (CD_2Cl_2): δ 7.44 (m, 5H, Ph), 5.25 (s, 5H, Cp), 4.75 (s, 5H, Cp), 1.40 (d $^2J_{P-H}$ 10.0 Hz, 6H, Me). ^{31}P (CD_2Cl_2): δ 24.3 (s). IR (toluene): ν(CO) (cm^{-1}) 1933 (s), 1739 (s).

$Cp_2Ru_2(CO)_3(PMePh_2)$ (3). ^1H (CD_2Cl_2): δ 7.41 (m, 10H, Ph), 5.20 (s, 5H, Cp), 4.80 (s, 5H, Cp), 1.64 (d $^2J_{P-H}$ 8.0 Hz, 3H, Me). ^{31}P (CD_2Cl_2): δ 39.6 (s). IR (toluene): ν(CO) (cm^{-1}) 1936 (m), 1739 (s).

$Cp_2Ru_2(CO)_3(PPh_3)$ (4). ^1H (CD_2Cl_2): δ 7.37 (m, 15H, Ph), 4.94 (s, 5H, Cp), 4.80 (s, 5H, Cp). ^{31}P (CD_2Cl_2): δ 48.6 (s). IR (toluene): ν(CO) (cm^{-1}) 1939 (m), 1737 (s).

$Cp_2Ru_2(CO)_3(^{13}CO)$ (5). $Cp_2Ru_2(CO)_2(COC_2Ph_2)$ (0.3134 g, 0.5271 mmol) was placed in a Fischer-Porter bottle and dissolved in 20 mL of toluene. After two freeze-pump-thaw cycles, the solution was cooled to -100 °C and degassed under vacuum. Gaseous ^{13}CO was then introduced into the reaction vessel, which was allowed to warm to room temperature. The reaction was heated to 90 °C for 20 min, over which time it changed from red-orange to bright yellow. After cooling, the solution was transferred to a Schlenk flask and solvent was removed under vacuum. The residue was chromatographed on alumina, and the yellow product band was eluted with 1:1 (v/v) hexanes/CH_2Cl_2. Solvent was removed and the product was recrystallized by layering a CH_2Cl_2 solution of the product with a ten-fold excess of ether and allowing the solvents to slowly mix at room temperature. Yield 0.218 g (93%). ^1H (CD_2Cl_2): δ 5.30 (s, 5H, Cp). ^{13}C NMR (CD_2Cl_2): δ 217.7 (s), 89.8 (s). ^{13}C NMR (CD_2Cl_2, -78 °C): δ 89.8 (s). MS: *m/e* 446 (M^+), 418 (M^+ - CO), 390 (M^+ - 2 CO), 361 (M^+ - 2 CO - ^{13}CO).

$Cp_2Ru_2(CO)(^{13}CO)(COC_2Ph_2)$ (6). In a quartz photolysis vessel, 121.6 mg (0.2042 mmol) of **5** and 152.3 mg (0.8545 mmol) of diphenylacetylene were dissolved in 10 mL of toluene. The solution was irradiated with 366 nm light under a slow N_2 purge and monitored by IR spectroscopy. The reaction was complete after 40 hours of photolysis. Solvent was removed and the solid was chromatographed on alumina. The red-orange product band was eluted with a 20:1 (v/v) mixture of CH_2Cl_2/acetone. Solvent was removed under vacuum, and the product was used without further purification. Yield 55.9 mg (34%).

$Cp_2Ru_2(CO)_2(^{13}CO)(PMe_3)$ (7). Using **6** as the starting material, **7** was prepared using the same methods as in the preparation of **1**. ^1H (CD_2Cl_2): δ 5.24 (s, 5H, Cp), 5.01 (s, 5H, Cp), 1.23 (d $^2J_{P-H}$ 10.0 Hz, 9H, Me). ^{13}C NMR (CD_2Cl_2): δ 89.1 (s), 88.7 (s), 19.8 (d $^1J_{P-C}$ 31.6 Hz). ^{13}C NMR (CD_2Cl_2, -78 °C): δ 246.3 (d $^2J_{P-C}$ 11.0 Hz), 205.2 (s), 89.1 (s), 88.7 (s), 19.8 (d $^1J_{P-C}$ 31.6 Hz).

$Cp_2Ru_2(CO)_2(^{13}CO)(PPh_3)$ (8). Using **6** as the starting material, **8** was prepared using the same methods as in the preparation of **4**. ^1H (CD_2Cl_2): δ 7.40 (m, 15H, Ph), 4.94 (s, 5H, Cp), 4.71 (s, 5H, Cp). ^{13}C NMR (CD_2Cl_2): δ 134.3 (d J_{P-C} 45.2 Hz), 132.8 (d J_{P-C} 10.0 Hz), 128.7 (d J_{P-C} 2.5 Hz), 126.8 (d J_{P-C} 10.0 Hz), 89.0 (s), 88.0 (s). ^{13}C NMR (CD_2Cl_2, -78 °C): δ 245.6 (d $^2J_{P-C}$ 10.0 Hz), 200.7 (s), 134.3 (d J_{P-C} 45.2 Hz), 132.8 (d J_{P-C} 10.0 Hz), 128.7 (d J_{P-C} 2.5 Hz), 126.8 (d J_{P-C} 10.0 Hz), 89.0 (s), 88.0 (s).

$Cp_2Mo_2(CO)_4(PR_3)_2$. The synthesis of these compounds follows the method developed by Riera[11a] for $Cp_2Mo_2(CO)_4$(dppm). Approximately 0.2 g (0.4 mmol) of $Cp_2Mo_2(CO)_6$ and 5 mL of diglyme were used to prepare $Cp_2Mo_2(CO)_4$ *in situ* according to the literature procedure.[9] In a separate flask, 2 equivalents of the desired phosphine were dissolved in 5 mL of CH_2Cl_2. The phosphine solution was added to the solution of $Cp_2Mo_2(CO)_4$, and the reaction was allowed to stir at room temperature for one hour. The resulting precipitate was filtered from the reaction solution, and the collected product was washed with 3 x 5 mL of hexanes. Upon drying, no further purification of the compounds was necessary. The compounds all have a very deep, brick-red color. As halocarbon

solutions of these compounds decompose rapidly upon exposure to light, care was taken to limit the exposure of all solutions to light. IR data for compounds **9-12** are presented in Table 3.

$Cp_2Mo_2(CO)_4(PMe_3)_2$ (9). Starting from 0.222 g (0.453 mmol) of $Cp_2Mo_2(CO)_6$ in the above synthesis, 0.212 g (0.402 mmol) of **9** were collected (80% yield). ^1H (CD_2Cl_2): δ 4.87 (s, 10H, Cp), 1.57 (d $^2J_{P-H}$ 8.9 Hz, 18 H, Me). ^{31}P (CD_2Cl_2): δ 32.9 (s).

$Cp_2Mo_2(CO)_4(PMe_2Ph)_2$ (10). Beginning with 0.223 g (0.454 mmol) of $Cp_2Mo_2(CO)_6$, 0.289 g (0.409 mmol) of **10** were obtained from the above preparation (90% yield). ^1H (CD_2Cl_2): δ 7.58 (m, 10H, Ph), 4.68 (d $^3J_{P-H}$ 1.8 Hz, 10H, Cp), 1.88 (d $^2J_{P-H}$ 8.5 Hz, 12 H, Me). ^{31}P (CD_2Cl_2): δ 42.6 (s).

$Cp_2Mo_2(CO)_4(PMePh_2)_2$ (11). Using 0.223 g (0.454 mmol) of $Cp_2Mo_2(CO)_6$ in the above procedure resulted in the formation of 0.289 g (0.345 mmol) of **11** (76% yield). ^1H (CD_2Cl_2): δ 7.51 (m, 20H, Ph), 4.64 (d $^3J_{P-H}$ 1.5 Hz, 10H, Cp), 2.17 (d $^2J_{P-H}$ 8.1 Hz, 6H, Me). ^{31}P (CD_2Cl_2): δ 61.2 (s).

$Cp_2Mo_2(CO)_4(PPh_3)_2$ (12). From 0.239 g (0.488 mmol) of $Cp_2Mo_2(CO)_6$, 0.400 g (0.449 mmol) of **12** were obtained (92% yield). ^1H (CD_2Cl_2): δ 7.48 (m, 30H, Ph), 4.56 (d $^3J_{P-H}$ 1.6 Hz, 10H, Cp). ^{31}P (CD_2Cl_2): δ 79.1 (s).

Protonation Reactions. Compounds **1-5** and **7-12** were protonated for characterization of either the $[Cp_2Ru_2(CO)_3(L)(\mu\text{-}H)]^+ CF_3SO_3^-$ (L = CO or PR_3) or the $[Cp_2Mo_2(CO)_4(PR_3)_2(\mu\text{-}H)]^+ CF_3SO_3^-$ products by dissolving approximately 10 mg of the

complex in 0.50 mL of either CD_2Cl_2 (for NMR) or CH_2Cl_2 (for IR) in an NMR tube under nitrogen. To the solution was added 1 equivalent of CF_3SO_3H with a gastight microliter syringe through the rubber septum. Solutions of the ruthenium compounds turned from yellow to yellow-orange. Yields of the protonated ruthenium compounds were determined to be quantitative by IR and NMR spectroscopy of the solutions. The molybdenum complex solutions turned from a deep red to dark orange with the exception of **12**, which produced a precipitate, and an IR spectrum of the solution showed that **12H$^+$CF$_3$SO$_3^-$** was not formed. The molybdenum complexes **9-11** also protonated quantitatively. NMR (^{1}H and ^{31}P) spectra of the protonated dinuclear complexes are given below. IR data for compounds **1H$^+$-4H$^+$** are presented in Table 1, for compounds **5H$^+$**, **7H$^+$** and **8H$^+$** in Table 4 and for compounds **9H$^+$-11H$^+$** in Table 3.

[Cp$_2$Ru$_2$(CO)$_3$(PMe$_3$)(μ-H)]$^+$ CF$_3$SO$_3^-$ (1H$^+$ CF$_3$SO$_3^-$). ^{1}H (CD_2Cl_2): δ 5.67 (s, 5H, Cp), 5.35 (s, 5H, Cp), 1.81 (d $^2J_{P-H}$ 10.0 Hz, 9H, Me), -18.51 (d $^2J_{P-H}$ 20.0 Hz, 1H, μ-H). ^{31}P (CD_2Cl_2): δ 14.7 (s). Orange crystals of **1H$^+$ CF$_3$SO$_3^-$** were obtained by slowly cooling an NMR sample to -78 °C.

[Cp$_2$Ru$_2$(CO)$_3$(PMe$_2$Ph)(μ-H)]$^+$ CF$_3$SO$_3^-$ (2H$^+$ CF$_3$SO$_3^-$). ^{1}H (CD_2Cl_2): δ 7.57 (m, 5H, Ph), 5.51 (s, 5H, Cp), 5.19 (s, 5H, Cp), 2.1 (d $^2J_{P-H}$ 10.0 Hz, 6H, Me), -18.57 (d $^2J_{P-H}$ 20.0 Hz, 1H, μ-H). ^{31}P (CD_2Cl_2): δ 28.4 (s).

[Cp$_2$Ru$_2$(CO)$_3$(PMePh$_2$)(μ-H)]$^+$ CF$_3$SO$_3^-$ (3H$^+$ CF$_3$SO$_3^-$). ^{1}H (CD_2Cl_2): δ 7.37 (m, 10H, Ph), 5.40 (s, 5H, Cp), 5.24 (s, 5H, Cp), 2.30 (d $^2J_{P-H}$ 10.0 Hz, 3H, Me), -18.68 (d $^2J_{P-H}$ 22.0 Hz, 1H, μ-H). ^{31}P (CD_2Cl_2): δ 42.9 (s).

$[Cp_2Ru_2(CO)_3(PPh_3)(\mu\text{-}H)]^+ CF_3SO_3^-$ ($4H^+ CF_3SO_3^-$). ^1H (CD_2Cl_2): δ 7.59 (m, 15H, Ph), 5.64 (s, 5H, Cp), 5.52 (s, 5H, Cp), -18.75 (d $^2J_{P\text{-}H}$ 12.6 Hz, 1H, μ-H). ^{31}P (CD_2Cl_2): δ 51.3 (s).

$[Ru_2Cp_2(CO)_3(^{13}CO)(\mu\text{-}H)]^+ CF_3SO_3^-$ ($5H^+ CF_3SO_3^-$). ^1H (CD_2Cl_2): δ 5.60 (s, 5H, Cp), -19.12 (d $^2J_{C\text{-}H}$ 4.0 Hz, 1H, μ-H). ^{13}C (CD_2Cl_2): δ 195.4 (s), 87.6 (s).

$[Cp_2Ru_2(CO)_2(^{13}CO)(PMe_3)(\mu\text{-}H)]^+ CF_3SO_3^-$ ($7H^+ CF_3SO_3^-$). ^1H (CD_2Cl_2): δ 5.61 (s, 5H, Cp), 5.33 (s, 5H, Cp), 1.79 (d $^2J_{P\text{-}H}$ 10.0 Hz, 9H, Me), -18.41 (dd $^2J_{P\text{-}H}$ 20.0 Hz $^2J_{C\text{-}H}$ 4.0 Hz, 1H, μ-H). ^{13}C (CD_2Cl_2 at 200 MHz): δ 200.0 (d $^2J_{P\text{-}C}$ 19.1 Hz), 197.3 (s), 196.6 (s), 86.7 (s), 85.5 (s), 21.8 (d $^2J_{P\text{-}C}$ 37.2 Hz). ^{13}C (CD_2Cl_2 at 400 MHz): δ 200.6 (dd $^2J_{P\text{-}C}$ 19.3 Hz, $^2J_{H\text{-}C}$ 3.1 Hz), 197.7 (dd $^3J_{P\text{-}C}$ 8.2 Hz, $^2J_{H\text{-}C}$ 3.5 Hz), 196.9 (dd $^3J_{P\text{-}C}$ 8.1 Hz, $^2J_{H\text{-}C}$ 3.5 Hz), 86.7 (s), 85.5 (s), 21.8 (d $^2J_{P\text{-}C}$ 37.2 Hz). $^{13}C\{^1H\}$ (CD_2Cl_2 at 400 MHz): δ 200.6 (d $^2J_{P\text{-}C}$ 19.3 Hz), 197.7 (d $^3J_{P\text{-}C}$ 8.2 Hz), 196.9 (d $^3J_{P\text{-}C}$ 8.1 Hz), 86.7 (s), 85.5 (s), 21.8 (d $^2J_{P\text{-}C}$ 37.2 Hz).

$[Cp_2Ru_2(CO)_2(^{13}CO)(PPh_3)(\mu\text{-}H)]^+ CF_3SO_3^-$ ($8H^+ CF_3SO_3^-$). ^1H (CD_2Cl_2): δ 7.37 (m, 15H, Ph), 5.35 (s, 5H, Cp), 5.15 (s, 5H, Cp), -18.75 (dd $^2J_{P\text{-}H}$ 20.0 Hz $^2J_{C\text{-}H}$ 4.0 Hz, 1H, μ-H). ^{13}C (CD_2Cl_2 at 200 MHz): δ 200.7 (d $^2J_{P\text{-}C}$ 17.6 Hz), 196.6 (s), 196.1 (s), 134.3 (d $J_{P\text{-}C}$ 50.2 Hz), 132.8 (d $J_{P\text{-}C}$ 10.0 Hz), 131.0 (d $J_{P\text{-}C}$ 2.5 Hz), 128.7 (d $J_{P\text{-}C}$ 10.0 Hz), 86.9 (s), 85.8 (s). ^{13}C (CD_2Cl_2 at 400 MHz): δ 201.1 (dd $^2J_{P\text{-}C}$ 18.4 Hz, $^2J_{H\text{-}C}$ 2.9 Hz), 197.0 (dd $^3J_{P\text{-}C}$ 6.9 Hz, $^2J_{H\text{-}C}$ 3.8 Hz), 196.4 (dd $^3J_{P\text{-}C}$ 6.7 Hz, $^2J_{H\text{-}C}$ 3.1 Hz), 134.3 (d $J_{P\text{-}C}$ 50.2 Hz), 132.8 (d $J_{P\text{-}C}$ 10.0 Hz), 131.0 (d $J_{P\text{-}C}$ 2.5 Hz), 128.7 (d $J_{P\text{-}C}$ 10.0 Hz), 86.9 (s),

85.8 (s). $^{13}C\{^1H\}$ (CD_2Cl_2 at 400 MHz): δ 201.1 (d $^2J_{P-C}$ 18.4 Hz), 197.0 (d $^3J_{P-C}$ 6.9 Hz), δ 196.4 (d $^3J_{P-C}$ 6.7 Hz), 134.3 (d J_{P-C} 50.2 Hz), 132.8 (d J_{P-C} 10.0 Hz), 131.0 (d J_{P-C} 2.5 Hz), 128.7 (d J_{P-C} 10.0 Hz), 86.9 (s), 85.8 (s).

$[Cp_2Mo_2(CO)_4(PMe_3)_2(\mu\text{-}H)]^+ CF_3SO_3^-$ ($9H^+ CF_3SO_3^-$). ^1H (CD_2Cl_2): δ 5.27 (s, 10H, Cp), 1.71 (d $^2J_{P-H}$ 9.8 Hz, 18H, Me), -19.75 (t $^2J_{P-H}$ 11.9 Hz, 1H, μ-H). ^{31}P (CD_2Cl_2): δ 21.7 (s). Anal. Calcd. for $C_{20}H_{28}Mo_2O_4P_2$: C, 40.97; H, 4.81. Found: C, 40.63; H, 4.80.

$[Cp_2Mo_2(CO)_4(PMe_2Ph)_2(\mu\text{-}H)]^+ CF_3SO_3^-$ ($10H^+ CF_3SO_3^-$). ^1H (CD_2Cl_2): δ 7.60 (m, 10 H, Ph), 5.21 (s, 10H, Cp), 2.04 (d $^2J_{P-H}$ 9.8 Hz, 12H, Me), -20.23 (t $^2J_{P-H}$ 9.7 Hz, 1H, μ-H). ^{31}P (CD_2Cl_2): δ 27.9 (s).

$[Cp_2Mo_2(CO)_4(PMePh_2)_2(\mu\text{-}H)]^+ CF_3SO_3^-$ ($11H^+ CF_3SO_3^-$). ^1H (CD_2Cl_2): δ 7.52 (m, 20H, Ph), 5.09 (s, 10H, Cp), 2.28 (d $^2J_{P-H}$ 9.9 Hz, 6H, Me), -20.86 (t $^2J_{P-H}$ 9.1 Hz, 1H, μ-H). ^{31}P (CD_2Cl_2): δ 45.4 (s).

Calorimetric Studies. Heats of protonation (ΔH_{MHM}) of the $Cp_2Ru_2(CO)_3(PR_3)$ and $Cp_2Mo_2(CO)_4(PR_3)_2$ complexes were performed using a Tronac Model 458 isoperibol, titration calorimeter as originally described[12] and then modified.[13] A typical calorimetric run consisted of three sections:[14] initial heat capacity calibration, titration and final heat capacity calibration. Each section was preceded by a baseline acquisition period. During the titration, 1.2 mL of a 0.1 M CF_3SO_3H solution (standardized to a precision of ±0.0002 M) in DCE was added at a rate of 0.3962 mL/min to 50 mL of a 2.6 M solution of the complex (5-10% excess) in DCE at 25.0 °C. Infrared spectra of the titrated solutions exhibited ν(CO) bands for the

$Cp_2Ru_2(CO)_3(PR_3)(\mu\text{-}H)^+$ or $Cp_2Mo_2(CO)_4(PR_3)_2(\mu\text{-}H)^+$ products, as well as small bands for the excess starting complexes.

Two different standardized acid solutions were used for determining the (ΔH_{MHM}) of each complex. The reported values are an average of at least four titrations and as many as five. The reaction enthalpies were corrected for the heat of dilution (ΔH_{dil}) of the acid in DCE (-0.2 kcal/mol).[13] The reported error in ΔH_{MHM} is the average deviation from the mean of all of the determinations. Titrations of 1,3-diphenylguanidine (GFS Chemicals) with CF_3SO_3H in DCE (-37.0 $\pm$ 0.3 kcal/mol; literature value, -37.2 $\pm$ 0.4 kcal/mol[12]) were used to monitor the accuracy of the calorimeter before each set of determinations. Titrations of complexes **2**, **3**, **4** and **11** failed to give reproducible ΔH_{MHM} values for reasons that are not known at this time.

X-ray Diffraction Studies. The crystals were mounted on glass fibers and transferred to a Siemens P4RA diffractometer. Data were collected at 20 $\pm$ 1 °C for **1**, and at -60 $\pm$ 2 °C for $\mathbf{1H^+CF_3SO_3^-}$. Cell constants for **1** and $\mathbf{1H^+CF_3SO_3^-}$ were determined from reflections in 360° rotation photographs. Pertinent data collection and reduction information are given in Table 5. Lorentz and polarization corrections were applied. Nonlinear corrections based on decay in the standard reflections were applied to the data for both **1** and $\mathbf{1H^+CF_3SO_3^-}$. Series of azimuthal reflections were also collected for both. No absorption correction was applied to **1**. A semi-empirical absorption correction based on the azimuthal scan was applied to $\mathbf{1H^+CF_3SO_3^-}$. The space groups were determined by systematic absences and intensity statistics, and the structures were solved by direct methods.[15] All non-hydrogen atoms were placed directly from the E-map and refined with anisotropic displacement parameters. Hydrogen atoms were treated as riding-atoms with individual isotropic displacement parameters, except for atom H in $\mathbf{1H^+CF_3SO_3^-}$. Atom H is the bridging hydrogen between Ru(1) and Ru(2) and was found from the difference map; its coordinates

were refined. Selected bond distances, angles and atomic coordinates are listed in Tables 6 and 7 for **1** and in Tables 8 and 9 for $\mathbf{1H^+}$. The ORTEP drawing of **1** is shown in Figure 1 and that of $\mathbf{1H^+}$ is in Figure 2.

Results

$Cp_2Ru_2(CO)_3(PR_3)$ Syntheses. Refluxing $Cp_2Ru_2(CO)_2(COC_2Ph_2)$ and the desired phosphine in toluene for approximately 30 min results in nearly quantitative formation of the phosphine substituted complexes $Cp_2Ru_2(CO)_3(PR_3)$. Knox reported[7] that the reaction of $Cp_2Ru_2(CO)_2(COC_2Ph_2)$ with $P(OMe)_3$ in refluxing toluene occurs quickly to give $Cp_2Ru_2(CO)_3[P(OMe)_3]$, in very high yield; however, details of the reaction conditions and product isolation were not provided. The IR spectrum of the complex in CH_2Cl_2 shows ν(CO) bands at 1953(s), 1733(s) cm^{-1}.[7] Knox also reported ^1H NMR, IR and elemental analysis data for compound **4**,[10] which was isolated as a side product from the reaction of $Cp_2Ru_2(CO)_2(COC_2Ph_2)$ with $H_2C{=}PPh_3$.[10] The analogous iron complexes, $Cp_2Fe_2(CO)_3(PR_3)$, have also been studied; they exist in only the CO-bridged form in solution.[16] However, it was not determined whether the Cp ligands are *cis-* or *trans-* to each other. IR data for compounds **1-4** compare favorably to those of the related iron complexes in number of bands and relative intensities, indicating that compounds **1-4** also exist solely as the bridged isomer in solution. Although the *cis-/trans-* relationship of the Cp ligands in **1** is not known in solution, the compound adopts the *cis-* geometry in the solid state (Figure 1). The Cp ligands are eclipsed as indicated by the Cp_{cent}-Ru-Ru-Cp_{cent} torsion angle of only 2.4°. The bridging CO groups and ruthenium atoms are not planar as indicated by the 155.5° dihedral angle between the Ru(1)-C(1)-Ru(2) and Ru(1)-C(2)-Ru(2) planes. This angle presumably results from the bridging CO groups adopting positions that maximize the overlap with the

metal orbitals in the π^* HOMO, as proposed for $Cp_2Fe_2(CO)_4$.[17] The Ru-Ru bond distance is 2.722(2) Å, which is slightly shorter than that in $Cp_2Ru_2(CO)_4$ (2.735(2) Å).[18]

Treating $Cp_2Ru_2(CO)_2(COC_2Ph_2)$ with ^{13}CO (1 atm) in toluene at 90 °C, diphenylacetylene was displaced to give $Cp_2Ru_2(CO)_3(^{13}CO)$ (**5**) in 93% yield. The mass spectrum of **5**, showed that there was only one ^{13}CO group in the complex. Complex **6**, $Cp_2Ru_2(CO)(^{13}CO)(COC_2Ph_2)$, easily prepared from **5**, reacted with phosphines to give $Cp_2Ru_2(CO)_2(^{13}CO)(PMe_3)$ (**7**) and $Cp_2Ru_2(CO)_2(^{13}CO)(PPh_3)$ (**8**). The IR spectrum (Table 2) of compound **5** consists of six ν(CO) bands, four in the terminal carbonyl region and two in the bridging region. The unlabeled complex, $Cp_2Ru_2(CO)_4$, has four carbonyl bands, three terminal and one bridging.[2] In order to understand the spectrum of the ^{13}CO-labeled compound **5**, the positions of its ν(CO) bands were estimated by assuming that each of the 4 bands in $Cp_2Ru_2(CO)_4$ could be approximated by calculating the ^{13}CO isotope effect using a diatomic vibrational model: $\nu(^{13}C)^2/\nu(^{12}C)^2 = \{m(^{12}C)[m(^{13}C) + m(O)]\}/\{m(^{13}C)[m(^{12}C) + m(O)]\}$, where m values are masses of the indicated isotopes. The overall result (Table 2) of this calculation is that the positions of each of the 4 bands in $Cp_2Ru_2(CO)_4$ shift 40-45 cm^{-1} to lower values when the ^{13}CO group is located in a terminal or bridging position that directly affects the ν(CO) value. Two of these calculated bands (1958 and 1921 cm^{-1}) overlap bands from unlabeled CO groups of **4**. The two other calculated bands (1891 and 1731 cm^{-1}) have wavenumber values similar to those observed in **5**, which supports this simplified method of estimating ν(CO) values in **5**. Compounds **6-8** also give IR spectra (Table 2) that have ν(CO) bands that can be satisfactorily explained by this method of estimating the ν(CO) values in the ^{13}CO-labeled complexes. These estimates also suggest that the ^{13}CO occupies both bridging and terminal positions in compounds **5-8**.

At room temperature in the ^{13}C NMR spectrum of **5**, there is only one singlet in the ^{13}CO region. Gansow[19] had previously studied the low temperature ^{13}C NMR spectrum of $Cp_2Ru_2(CO)_4$ and observed separate singlet signals for the terminal and bridging CO groups at -118 °C in 95% $CHFCl_2$/5% CS_2. When a CD_2Cl_2 solution of **5** was cooled to -78 °C, no ^{13}C signals were observed in the carbonyl region, due to fluxionality of the CO ligands. The ^{13}C NMR spectra of **7** and **8** at room temperature also show no signals in the carbonyl region. Upon cooling to -78 °C, two signals are observed. The peak (~δ 246 ppm) for the bridging CO groups is split into a doublet by the phosphorus; however the peak (~δ 203 ppm) for the terminal CO's is not split by phosphorus.

$Cp_2Mo_2(CO)_4(PR_3)_2$ Syntheses. Compounds **9-12** were prepared in greater than 75% yields by treating $Cp_2Mo_2(CO)_4$ with phosphine (two molar equivalents). Compound **12** was prepared previously by two very different routes. By stirring $Cp_2Mo_2(CO)_4$ and PPh_3 together in toluene, Curtis and Klingler[20] obtained **12** in 41% yield. Bruce, *et. al* prepared **12** in 89% yield by reaction of $Mo(CO)_3(PPh_3)_3$ with CpH in refluxing dibutyl ether.[21] The relatively high ν(CO) values (Table 3) suggest that all of the $Cp_2Mo_2(CO)_4(PR_3)_2$ complexes have only terminal CO ligands. IR studies of $Cp_2Mo_2(CO)_4(PR_3)_2$ (R = Ph or OMe)[20] established that these complexes exist only as the isomer in which the two CO groups are *trans-* to each other (Figure 3); this assignment was based on the relative intensities of the ν(CO) bands for the symmetric and asymmetric vibrational modes.

Protonation Reactions. Quantitative formation of the hydride-bridged dinuclear Ru complexes **$1H^+CF_3SO_3^-$-$5H^+CF_3SO_3^-$** and **$7H^+CF_3SO_3^-$-$8H^+CF_3SO_3^-$** occurs (eq 3) upon addition of 1 equivalent of triflic acid to complexes **1-5**, **7** and **8**. The CO-bridged structure of the reactants is converted to the all terminal CO structure of the products, which were characterized by IR and ^1H, ^{13}C and ^{31}P NMR spectroscopy. The Ru-H-Ru resonances

in the ^1H NMR spectra occur as doublets between -18.51 and -18.75 for compounds **1H$^+$-4H$^+$** due to coupling with the phosphorus of the PR_3 ligand. For compound **5H$^+$**, the hydride signal is a doublet, due to coupling with the single labeled ^{13}CO group. The hydride signals for compounds **7H$^+$** and **8H$^+$** are doublets of doublets, due to splitting by the phosphorus and labeled carbonyl. The ^1H NMR signals for the Cp groups in the protonated dimers are approximately 0.7 ppm downfield of those in **1-4**.

The ν(CO) bands of the protonated dimers are higher than those of **1-4**, and there are no ν(CO) bands below 1850 cm^{-1} which indicates that there are no bridging CO groups (Table 1). Compound **5H$^+$**, $Cp_2Ru_2(CO)_3(^{13}CO)(\mu\text{-}H)^+$, exhibits 5 ν(CO) bands (Table 4) while the analogous unlabeled compound $Cp_2Ru_2(CO)_4(\mu\text{-}H)^+$ displays only three ν(CO) bands.[2] Table 4 lists the IR data for both of these compounds as well as estimated wavenumbers for ν(CO) modes that involve the ^{13}CO group; these estimations were performed as described for **5** above. One of the calculated bands (2026 cm^{-1}) overlaps one of the bands observed in the unlabeled complex. The remaining two calculated bands (2003 and 1972 cm^{-1}) are in reasonable agreement with the lowest wavenumber, isotopically shifted bands observed for **5H$^+$**. Compounds **7H$^+$** and **8H$^+$** display similar features in their IR spectra (Table 4).

The ^{13}C NMR spectrum of compound **5H$^+$** exhibits one peak (δ 195.4) for the four terminal carbonyl groups. For compounds **7H$^+$** and **8H$^+$**, there are three peaks in the terminal carbonyl region as expected for a structure (Figure 1) with only terminal CO groups. When collected on the 200 MHz instrument, these peaks were broad singlets. On the 400 MHz instrument, the signals appeared as doublets due to coupling with the phosphorus atom of the PR_3 ligand. Two of the doublets exhibited relatively small $J_{P\text{-}C}$ coupling constants (8.2 and 8.1 Hz for **7H$^+$**; 6.9 and 6.7 Hz for **8H$^+$**); these are assigned to the two CO groups on the $Ru(CO)_2Cp$ end of the dimers. The doublet with the large $J_{P\text{-}C}$ coupling constant (19.3 Hz for **7H$^+$**; 18.4 Hz for **8H$^+$**) is assigned to the CO on the $Ru(CO)(PR_3)Cp$ end of the dimers. When the ^{13}C NMR spectrum was taken with ^1H coupling, each of the three ^{13}CO signals

became a doublet of doublets, and the $^2J_{H-C}$ coupling constants (3.1, 3.5, 3.5 for **7H$^+$**; 2.9, 3.8, 3.1 for **8H$^+$**) to all 3 CO ligands in each complex are about the same. This suggests that the hydride ligand is not associated with one Ru substantially more strongly than the other.

A comparison of the structures of **1** (Figure 1) and **1H$^+$** (Figure 2) as determined by X-ray diffraction studies shows that the Ru-Ru bond distance is longer in **1H$^+$** (3.0271(6) Å) than in **1** (2.722(2) Å). Similarly the Ru-Ru bond in the protonated dimer, $Cp_2Ru_2(CO)_4(\mu\text{-}H)^+$, is longer (3.037 Å)[2] than that of $Cp_2Ru_2(CO)_4$ (2.735(2) Å).[18] The Ru-P bond length does not change significantly upon protonation (2.299(2)Å in **1H$^+$** *vs.* 2.291(3)Å in **1**). and neither does the Ru-C distance to the terminal carbonyl groups (avg. 1.868Å in **1H$^+$** *vs* 1.855(9) in **1**). This small change in the Ru-C distance to the terminal carbonyl groups is also observed in the protonation of $Cp_2Ru_2(CO)_4$ (avg. 1.88Å in $Cp_2Ru_2(CO)_4(\mu\text{-}H)^+$ *vs.* 1.86 in $Cp_2Ru_2(CO)_4$).[2, 18] The bridging hydride in **1H$^+$** was located and it appears to be closer to the ruthenium atom with the phosphine (Ru(1)-H 1.669(6) Å *vs.* 1.746(6) Å for Ru(2)-H).

Quantitative formation of the hydride-bridged dinuclear Mo complexes **9H$^+$CF$_3$SO$_3^-$**-**11H$^+$CF$_3$SO$_3^-$** occurs (eq 4) upon addition of 1 equivalent of triflic acid to complexes **9-11**. The products were characterized by IR and ^{1}H and ^{31}P NMR spectroscopy. A triplet is observed for the hydride ligand at approximately δ -20 ppm in the ^{1}H NMR spectra of complexes **9H$^+$-11H$^+$**. The chemical shift and equal coupling to both phosphorus atoms is consistent with a bridging hydride in these protonated dimers. The average positions of the ν(CO) bands of the dimers **9-11** increase approximately 100 cm^{-1} upon protonation. While there are no previous reports of the protonation of **9-11** $Cp_2Mo_2(CO)_4(dppm)$ is known[11a] to react with $HBF_4{\bullet}Et_2O$ to give $Cp_2Mo_2(CO)_4(dppm)(\mu\text{-}H)^+ BF_4^-$; which contains a bridging hydride. This complex, whose structure was established by X-ray diffraction studies, has IR and ^{1}H NMR spectra[11b, c] that are similar to those of **9H$^+$-11H$^+$**.

Calorimetry Studies. Heats of protonation (ΔH_{MHM}), determined by calorimetric titration of complexes **1**, **8** and **9** with CF_3SO_3H in DCE solvent at 25.0 °C according to eq 3 and 4 are presented in Table 10. Plots of temperature *vs.* amount of acid added were linear, indicating that the protonations occurred rapidly and stoichiometrically.[14] Normal pre- and post-titration traces were evidence that no decomposition of the neutral or protonated species occurred. The unprotonated dimers were recovered from the titration solutions by adding one equivalent of the base diphenylguanidine. The resulting solution was passed through an alumina column (1.5 x 30 cm) eluting with CH_2Cl_2. Isolation of the pure, unprotonated complexes, (**1**, **8**, **9**) was achieved by recrystallization of the complexes from CH_2Cl_2 by layering with hexanes.

Discussion

Protonation of $Cp_2Ru_2(CO)_3(PR_3)$. Reactions of the CO-bridged $Cp_2Ru_2(CO)_3(PR_3)$ complexes (**1-4**) with CF_3SO_3H proceed according to equation (3) to give products $Cp_2Ru_2(CO)_3(PR_3)(H)^+$ in which all of the CO ligands are non-bridging. An X-ray diffraction study of $\mathbf{1H^+CF_3SO_3^-}$ supports this structural assignment (Figure 2). The site of protonation in the $Cp_2Ru_2(CO)_3(PR_3)(H)^+$ complexes was of particular interest because the Ru bearing the PR_3 ligand should be much more basic than the other Ru with only CO ligands. As detailed in the Introduction, the metal in $Cp^*Ir(CO)(PR_3)$ complexes are 15.7-16.6 kcal/mol more basic than in $Cp^*Ir(CO)_2$.[4] Assuming that ΔS is the same for the protonation of all of these complexes, the equilibrium constant (K) for protonation of the $Cp^*Ir(CO)(PR_3)$ complexes is estimated ($\Delta G = \Delta H_{HM} = -RTlnK$) to be 5×10^{11} times greater than for protonation of $Cp^*Ir(CO)_2$.[4] In a variety of other metal carbonyl complexes, the basicities of the metals as measured by the equilibrium constant(K) for protonation increase many orders of

magnitude when a CO ligand in the complex is replaced by a phosphine.[3c] Thus, in the $Cp_2Ru_2(CO)_3(PR_3)(H)^+$ complexes, one might expect the H ligand to be bonded to the Ru in the relatively basic $Cp(CO)(PR_3)Ru$ unit as in **A** (see Introduction). The other possible location of the hydride is bridging the Ru-Ru bond as in **B**. With the goal of ascertaining the binding site of the H ligand, ^1H and ^{13}C NMR studies of the mono-^{13}CO-labeled $Cp_2Ru_2(CO)_2(^{13}CO)(PR_3)(H)^+$ complexes, where $PR_3 = PMe_3$(**7H$^+$**) or PPh_3(**8H$^+$**), were performed. The ^{13}CO ligand was distributed among the 3 possible sites in the complex, which gave rise to three ^{13}C NMR signals; each was a doublet due to coupling with the phosphorus (see Results for details). On the basis of the larger $J_{C\text{-}P}$ coupling constant for the ^{13}CO group in the $Cp(CO)(PR_3)Ru$ unit than for the ^{13}CO's in the $Cp(CO)_2Ru$ moiety, each of the three ^{13}CO signals were assigned to the three different ^{13}CO ligands. With these assignments, it was possible to determine, from a proton-coupled ^{13}C NMR spectrum, $J_{C\text{-}H}$ coupling constants between each CO and the hydride. In **7H$^+$**, $J_{C\text{-}H}$ for hydride coupling to the CO in $Cp(CO)(PMe_3)Ru$ was 3.1 Hz; $J_{C\text{-}H}$ values for hydride coupling to the two inequivalent CO's in $Cp(CO)_2Ru$ were both 3.5 Hz. In **8H$^+$**, $J_{C\text{-}H}$ for the CO in $Cp(CO)(PPh_3)Ru$ was 2.9 Hz; $J_{C\text{-}H}$ values for the two CO groups in $Cp(CO)_2Ru$ were 3.8 and 3.1 Hz. The fact that coupling constants between the hydride and CO groups on both Ru atoms all fall within the narrow range 2.9-3.8 Hz suggests that the hydride ligand bridges the Ru-Ru bond and couples nearly equally with CO groups on both Ru atoms. That the $J_{C\text{-}H}$ values are reasonable for bridging hydride-to-^{13}CO coupling is supported by a $J_{C\text{-}H}$ value of 4.0 Hz for hydride coupling to the 4 equivalent ^{13}CO ligands in $Cp_2Ru_2(CO)_3(^{13}CO)(\mu\text{-}H)^+$, **5H$^+$**. The NMR evidence, as well as the X-ray diffraction study, therefore strongly supports a structure for the $Cp_2Ru_2(CO)_3(PR_3)(\mu\text{-}H)^+$ complexes in which the hydride ligand bridges the Ru-Ru bond, despite the presence of a strongly donating phosphine ligand on one of the Ru atoms.

The heat of protonation ($-\Delta H_{MHM}$) of $Cp_2Ru_2(CO)_3(PMe_3)$ (**1**) according to eq 3 is 30.0(4) kcal/mol (Table 10) as compared with only 18.4(1) kcal/mol for the carbonyl analog $Cp_2Ru_2(CO)_4$.[2] The 11.6 kcal/mol higher basicity of **1** is easily understandable in terms of the stronger electron donor ability of PMe_3 as compared with CO. However, as noted in the Introduction, the overall ΔH_{MHM} value for this protonation may be considered (eq 2) as the sum of ΔH_b for converting the CO-bridged isomer to the non-bridged isomer and ΔH_a for protonation of the non-bridged isomer. The ΔH_b for $Cp_2Ru_2(CO)_4$ is known[19, 22] to be approximately +2 kcal/mol; since $Cp_2Ru_2(CO)_4$ is approximately 50% in the CO-bridged form, about +1 kcal is required to convert the bridged isomer to the non-bridged form. The ΔH_a value for $Cp_2Ru_2(CO)_4$ is then -19.4 kcal/mol, roughly +1 kcal/mol more exothermic than ΔH_{MHM}.

For $Cp_2Ru_2(CO)_3(PMe_3)$ (**1**), the ΔH_b value is not known, but since **1** exists completely in the bridged form, ΔH_b is likely to be more endothermic for **1** than for $Cp_2Ru_2(CO)_4$. Thus, the energy required to convert **1** from the bridged to the non-bridged form would make the overall ΔH_{MHM} value less exothermic than it would be if its ΔH_b were comparable to that of $Cp_2Ru_2(CO)_4$. Therefore, if $Cp_2Ru_2(CO)_4$ and $Cp_2Ru_2(CO)_3(PMe_3)$ (**1**) had the same ΔH_b values, **1** would be even more basic than $Cp_2Ru_2(CO)_4$, that is, more than the observed 11.6 kcal/mol.

As noted earlier, a comparison of $-\Delta H_{HM}$ values for $Cp^*Ir(CO)_2$ and its PMe_3-substituted analog $Cp^*Ir(CO)(PMe_3)$ shows that replacement of CO by PMe_3 increases the basicity of the iridium by 16.6 kcal/mol.[4] The same replacement in $Cp_2Ru_2(CO)_4$ leads to an increase of 11.6 kcal/mol. However, as discussed in the preceding paragraph the electronic effect of the PMe_3 ligand on ΔH_{MHM} is reduced by a more positive value of ΔH_b for **1**. Nevertheless, it is evident that substitution of a CO ligand in $Cp_2Ru_2(CO)_4$ by PMe_3

substantially increases the basicity ($-\Delta H_{MHM}$) of the Ru-Ru bond. Studies[23,24] of the acidities of the $H_4Ru_4(CO)_{12-x}[P(OMe)_3]_x$ complexes (x = 0, 1, 2) show that replacement of a CO ligand by a $P(OMe)_3$ decreases the acidity of the complex by 3 pK_a units. Although this is a smaller effect than observed in the present $Cp_2Ru_2(CO)_{4-x}(PMe_3)_x$ (x = 0, 1) studies, $P(OMe)_3$ is a weaker donor ligand than PMe_3 and would be expected to have a smaller effect on the basicities of metal-metal bonds.

Previously,[2] we compared the basicity of the Ru-Ru bond in the dinuclear $Cp_2Ru_2(CO)_4$ with that of the single Ru atom in mononuclear $CpRu(CO)_2H$. Although this comparison relied on an estimate of $-\Delta H_{HM}$ for $CpRu(CO)_2H$, it was nevertheless possible to state that the Ru-Ru bond in $Cp_2Ru_2(CO)_4$ was substantially more basic than the Ru in $CpRu(CO)_2H$. In the present studies, it would be desirable to compare $-\Delta H_{MHM}$ for **1** with $-\Delta H_{HM}$ for $CpRu(CO)(PMe_3)H$. While the latter complex is known,[25] its basicity is not. However, it can be estimated from $-\Delta H_{HM}$ (21.2(4) kcal/mol) for $CpRu(PMe_3)_2Cl$ by replacing one PMe_3 with a CO, which decreases the basicity by approximately 16.6 kcal/mol (see above),[1] and by replacing Cl by H, which increases the basicity by approximately 17.6 kcal/mol.[26] Thus, the overall estimated basicity ($-\Delta H_{HM}$) of $CpRu(CO)(PMe_3)H$ is 22 kcal/mol. Therefore, the basicity ($-\Delta H_{MHM}$) of the Ru-Ru bond in $Cp_2Ru_2(CO)_3(PMe_3)$ (30.0 kcal/mol) is greater than that of the Ru in $CpRu(CO)(PMe_3)H$ (22 kcal/mol). Of course, such comparisons of di- and mononuclear complex basicities depend on the choice of the comparison mononuclear complex. If $CpRu(CO)(PMe_3)Cl$ or $CpRu(CO)_2H$ had been selected instead of $CpRu(CO)(PMe_3)H$, the Ru-Ru bond in $Cp_2Ru_2(CO)_3(PMe_3)$ would have been relatively even more basic than the Ru in these mononuclear complexes, because $CpRu(CO)(PMe_3)Cl$ and $CpRu(CO)_2H$ are substantially less basic than $CpRu(CO)(PMe_3)H$.

Infrared spectra (Table 1) of the $Cp_2Ru_2(CO)_3(PR_3)$ complexes in CH_2Cl_2 solvent show the expected decrease in ν(CO) as the PMe_x-Ph_{3-x} ligand donor strength increases. For

example, ν(CO) for the PPh_3 complex is 1947 cm^{-1} while that for the PMe_3 complex is 1929 cm^{-1}. In contrast, the ν(C=O) value for the bridging CO groups *increases* slightly as the PMe_xPh_{3-x} donor strength increases. Thus, ν(C=O) for the PPh_3 complex is 1725 cm^{-1} but it increases to 1728 cm^{-1} for the PMe_3 complex. A similar trend is seen when the spectra are taken in toluene solvent (see Experimental). Although the same trend is observed in the analogous $Cp_2Fe_2(CO)_3(PR_3)$ complexes,[16] a convincing explanation for these data is not apparent.

Protonation of $Cp_2Mo_2(CO)_4(PR_3)_2$ Complexes. These complexes have only terminal CO ligands both before and after protonation (eq 4). The basicity ($-\Delta H_{MHM}$) of $Cp_2Mo_2(CO)_4(PMe_3)_2$ (27.4(2) kcal/mol) is substantially higher than that of the closely related $Cp_2Mo_2(CO)_4(PMe_2Ph)_2$ (18.9(5) kcal/mol). The 8.5 kcal/mol difference is much larger than that observed for the replacement of two PMe_2Ph ligands by two PMe_3 in $Fe(CO)_3(PR_3)_2$ (2.1 kcal/mol) and in $CpOs(PR_3)_2Br$ (3.2 kcal/mol).[26] It is even larger than that observed in *fac*-$W(CO)_3(PR_3)_3$ (2.0 kcal/mol), where three PR_3 ligands are replaced.[27] Thus, the Mo-Mo bond basicity in these $Cp_2Mo_2(CO)_4(PR_3)_2$ complexes is very sensitive to the donor ability of the PR_3 ligands, much more so than in mononuclear complexes. The position of the phosphine ligand *trans*- to the Mo-Mo bond (Figure 3) may account for the large effect of the PR_3 ligands on the Mo-Mo bond basicity. Poilblanc, *et. al.*[28] studied the protonation in ethanol of the series of $Fe_2(CO)_4(\mu\text{-}SMe)_2L_2$ (L = PMe_3, PMe_2Ph, $PMePh_2$ and PPh_3) complexes where the phosphine ligands are *trans*- to the Fe-Fe bond. When L = PMe_3 or PMe_2Ph, the compounds could be completely protonated with an excess of aqueous HCl. However, when L = $PMePh_2$ or PPh_3 excess HCl would only give partial protonation of the Fe-Fe bond and the protonated complex could not be isolated. Poilblanc attributes this drastic difference in basicity to the *trans*- disposition of the phosphines.

The $Cp_2Mo_2(CO)_4(PR_3)_2$ complexes are clearly more basic than $Cp_2Mo_2(CO)_6$ which requires three equivalents of CF_3SO_3H in CD_2Cl_2 solvent for complete protonation. The $Cp_2Mo_2(CO)_6(\mu\text{-}H)^+$ product, which exhibits Cp and hydride signals at δ 5.88 and -20.55 ppm, respectively, in the ^1H NMR spectrum, was previously identified in 98% H_2SO_4.[29] It has also been prepared from the reaction of $CpMo(CO)_3H$ with $CpMo(CO)_3(BF_4)$.[30]

The $Cp'_2Ru_2(CO)_4$ complexes are the only other dinuclear complexes whose basicities have been determined.[2] Thus, one might compare $-\Delta H_{MHM}$ values for $Cp_2Mo_2(CO)_4(PMe_3)_2$ (27.4(2) kcal/mol) and $Cp_2Ru_2(CO)_4$ (18.4(1) kcal/mol). In a thought experiment, the Mo dimer may be converted to the Ru dimer by adding 2 protons(p) and 2 electrons(e) to each Mo and removing a PMe_3 ligand from each Mo (eq 5). If the additions of equal numbers of protons and electrons cancel each others' effects on the basicities of the metals, the removal of the electron donating PMe_3 ligands should decrease the overall basicity of the metals,

$$Cp_2Mo_2(CO)_4(PMe_3)_2 + 4\,p + 4\,e \xrightarrow{-2\ PMe_3} Cp_2Ru_2(CO)_4 \qquad (5)$$

which is the observed result. Whether or not such a simplified approach is useful for understanding metal-metal bond basicities more broadly requires further study.

Summary

NMR studies lead to the surprising conclusion that the site of protonation in the unsymmetrically substituted $Cp(PMe_3)Ru(\mu\text{-}CO)_2Ru(CO)Cp$ (1) is the Ru-Ru bond rather than the Ru bearing the strongly donating PMe_3 ligand. The Ru-Ru bond in $Cp_2Ru_2(CO)_3(PMe_3)$ is 11.6 kcal/mol more basic than that in $Cp_2Ru_2(CO)_4$, as expected for the replacement of a CO ligand by PMe_3. The Ru-Ru bonds in $Cp_2Ru_2(CO)_3(PMe_3)$ and $Cp_2Ru_2(CO)_4$ are substantially more basic than the Ru in related mononuclear complexes such as $CpRu(CO)(PMe_3)H$ or $CpRu(CO)_2H$. The effect of changing the PR_3 ligand in

$Cp_2Mo_2(CO)_4(PR_3)_2$ on the basicity of the Mo-Mo bond is much larger than comparable changes on the basicities of mononuclear complexes.

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References

[1] Angelici, R. J. *Acc. Chem. Res.* **1995**, *28*, 51.

[2] Nataro, C.; Thomas, L. M.; Angelici, R. J. *submitted to Inorganic Chemistry.*

[3] (a) Pearson, R. G. *Chem. Rev.* **1985**, *85*, 41. (b) Martinho Simões, J. A.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629. (c) Kristjánsdóttir, S. S.; Norton, J. R. in *Transition Metal Hydrides: Recent Advances in Theory and Experiment*; Dedieu, A., *ed.*; VCH: New York, 1991; Chap 10. (d) Bullock, R. M. *Comments Inorg. Chem.* **1991**, *12*, 1. (e) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (f) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155. (g) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913. (h) Kramarz, K.; Norton, J. R. *Prog. Inorg. Chem.* **1994**, *42*, 1.

[4] (a) Sowa, J. R., Jr.; Zanotti, V.; Facchin, G.; Angelici, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 9185. (b) Wang, D.; Angelici, R. J. *Inorg. Chem.* **1996**, *35*, 1321.

[5] Perrin, D. D.; Armarego, W. L. F.; Rerrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon: New York, 1980.

[6] Doherty, N.M.; Knox, S. A. R.; Morris, M. J. *Inorg. Synth.* **1990**, *28*, 189.

[7] Davies, D. L.; Dyke, A. F.; Knox, S. A. R.; Morris, M. J. *J. Organomet. Chem.* **1981**, *215*, C30.

[8] Curtis, M. D.; Hay, M. S. *Inorg. Synth.* **1990**, *28*, 150.

[9] *ibid.* 152.

[10] Davies, D. L.; Knox, S. A. R.; Mead, K. A.; Morris, M. J.; Woodward, P. *J. Chem. Soc.: Dalton Trans.* **1984**, 2293.

[11] (a) Riera, V.; Ruiz, M. A.; Villafañe, F. *Organometallics* **1992**, *11*, 2854. (b) Riera, V.; Ruiz, M. A.; Villiafañe, F.; Bois, C.; Jeannin, Y. *J. Organomet. Chem.* **1990**, *382*, 407. (c) Riera, V.; Ruiz, M. A.; Villiafañe, F.; Jeannin, Y.; Bois, C. *J. Organomet. Chem.* **1988**, *345*, C4.

[12] Bush, R. C.; Angelici, R. J. *Inorg. Chem.* **1988**, *27*, 681.

[13] Sowa, J. R., Jr.; Angelici, R. J. *J Am. Chem. Soc.* **1991**, *113*, 2537.

[14] Eatough, D. J., Christiensen, J. J., Izatt, R. M. *Experiments in Thermometric and Titration Calorimetry*; Brigham Young University: Provo, UT, 1974.

[15] SHELXTL-PLUS, Siemens Analytical Xray, Inc., Madison, WI.

[16] Haines, R. J.; du Preez, A. L. *Inorg. Chem.* **1969**, *8*, 1459.

[17] Jemmis, E. D.; Pinhas, A. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 2576 and references therein.

[18] Mills, D. S.; Nice, J. P. *J. Organomet. Chem.* **1967**, *9*, 339.

[19] Gansow, O. A.; Burke, A. R.; Vernon, W. D. *J. Am. Chem. Soc.* **1976**, *98*, 5817.

[20] Curtis, M. D.; Klingler, R. J. *J. Organomet. Chem.* **1978**, *161*, 23.

[21] Bruce, M. I.; Goodall, B. L.; Sharrocks, D. N.; Stone, F. G. A. *J. Organomet. Chem.* **1972**, *39*, 139.

[22] Novak, K. *J. Organomet. Chem.* **1967**, *7*, 151.

[23] Walker, H. W.; Pearson, R. G.; Ford, P. C. *J. Am. Chem. Soc.* **1983**, *105*, 1179.

[24] Kristjánsdóttir, S. S.; Moody, A. E.; Weberg, R. T.; Norton, J. R. *Organometallics* **1988**,*7*, 1983.

[25] Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5166.

[26] (a) Rottink, M. K.; Angelici, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 8296. (b) Rottink, M. K.; Angelici, R. J. *J. Am. Chem. Soc.* **1993**, *115*, 7267.

[27] Sowa, J. R., Jr.; Zanotti, V.; Angelici, R. *Inorg. Chem.* **1993**, *32*, 848.

[28] Fauvel, K.; Mathieu, R.; Poilblanc, R. *Inorg. Chem.* **1976**, *15*, 976.

[29] Davison, A.; McFarlane, W.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1962**, 3653.

[30] Beck, W.; Schloter, K. *Z. Naturforsch.* **1978**, *33B*, 1214.

Table 1. IR Data for $Cp_2Ru_2(CO)_3(PR_3)$ and $Cp_2Ru_2(CO)_3(PR_3)(\mu\text{-}H)^+$ in CH_2Cl_2 Solvent.

	ν(CO), cm^{-1}			
Complex	terminal			bridging
$Cp_2Ru_2(CO)_3(PMe_3)$, **1**	1929 (s)			1728 (s)
$Cp_2Ru_2(CO)_3(PMe_3)(\mu\text{-}H)^+$, **1H$^+$**	2043 (s)	1995 (s)	1964 (m)	
$Cp_2Ru_2(CO)_3(PMe_2Ph)$, **2**	1932 (s)			1727 (s)
$Cp_2Ru_2(CO)_3(PMe_2Ph)(\mu\text{-}H)^+$, **1H$^+$**	2045 (s)	1996 (s)	1965 (m)	
$Cp_2Ru_2(CO)_3(PMePh_2)$, **3**	1937 (s)			1727 (s)
$Cp_2Ru_2(CO)_3(PMePh_2)(\mu\text{-}H)^+$, **3H$^+$**	2045 (s)	1998 (s)	1966 (m)	
$Cp_2Ru_2(CO)_3(PPh_3)$, **4**	1947 (s)			1725 (s)
$Cp_2Ru_2(CO)_3(PPh_3)(\mu\text{-}H)^+$, **4H$^+$**	2046 (s)	2000 (s)	1969 (m)	

Table 2. IR Data for $Cp_2Ru_2(CO)_4$, $Cp_2Ru_2(CO)_2(COC_2Ph_2)$, $Cp_2Ru_2(CO)_3(PMe_3)$, $Cp_2Ru_2(CO)_3(PPh_3)$ and their ^{13}CO-labeled Analogs in CH_2Cl_2 Solvent.

Complex	ν(CO), cm^{-1}					
$Cp_2Ru_2(CO)_4$	2003	1966	1934		1771	
$Cp_2Ru_2(CO)_3(^{13}CO)$, **5**	1999	1956	1927	1897	1772	1742
Calculated (^{13}CO)[a]		1958	1921	1891		1731
$Cp_2Ru_2(CO)_2(COC_2Ph_2)$	1980		1803		1733	
$Cp_2Ru_2(CO)(^{13}CO)(COC_2Ph_2)$, **6**	1979	1934	1802	1772	1730	1700
Calculated (^{13}CO)[a]		1935		1762		1694
$Cp_2Ru_2(CO)_3(PMe_3)$, **1**	1929		1728			
$Cp_2Ru_2(CO)_2(^{13}CO)(PMe_3)$, **7**	1929	1884	1729	1701		
Calculated (^{13}CO)[a]		1886		1689		
$Cp_2Ru_2(CO)_3(PPh_3)$, **4**	1947		1725			
$Cp_2Ru_2(CO)_2(^{13}CO)(PPh_3)$, **8**	1947	1925	1725	1699		
Calculated (^{13}CO)[a]		1903		1686		

[a] See text.

Table 3. IR Data for $Cp_2Mo_2(CO)_4(PR_3)_2$ and $Cp_2Mo_2(CO)_4(PR_3)_2(\mu\text{-}H)^+$ in CH_2Cl_2 Solvent.

Complex	ν(CO), cm^{-1}		
$Cp_2Mo_2(CO)_4(PMe_3)_2$, **9**	1839 (sh)	1818 (s)	
$Cp_2Mo_2(CO)_4(PMe_3)_2(\mu\text{-}H)^+$, **9H$^+$**	1979 (m)	1954 (m)	1894 (s)
$Cp_2Mo_2(CO)_4(PMe_2Ph)_2$, **10**	1842 (sh)	1820 (s)	
$Cp_2Mo_2(CO)_4(PMe_2Ph)_2(\mu\text{-}H)^+$, **10H$^+$**	1980 (m)	1966 (m)	1896 (s)
$Cp_2Mo_2(CO)_4(PMePh_2)_2$, **11**	1844 (sh)	1826 (s)	
$Cp_2Mo_2(CO)_4(PMePh_2)_2(\mu\text{-}H)^+$, **11H$^+$**	1982 (m)	1966 (m)	1898 (s)
$Cp_2Mo_2(CO)_4(PPh_3)_2$, **12**	1851 (sh)	1832 (s)	

Table 4. IR Data for $Cp_2Ru_2(CO)_4(\mu\text{-}H)^+$, $Cp_2Ru_2(CO)_3(PMe_3)(\mu\text{-}H)^+$, $Cp_2Ru_2(CO)_3(PPh_3)(\mu\text{-}H)^+$ and their ^{13}CO-labeled Analogs in CH_2Cl_2 Solvent.

Complex	ν(CO), cm^{-1}				
$Cp_2Ru_2(CO)_4(\mu\text{-}H)^+$	2073	2049	2017		
$Cp_2Ru_2(CO)_3(^{13}CO)(\mu\text{-}H)^+$, **5H⁺**	2064	2036	2011	1981	1960
Calculated (^{13}CO)[a]			2026	2003	1972
$Cp_2Ru_2(CO)_3(PMe_3)(\mu\text{-}H)^+$, **1H⁺**	2043	1995	1964		
$Cp_2Ru_2(CO)_2(^{13}CO)(PMe_3)(\mu\text{-}H)^+$, **7H⁺**	2043	1996	1966	1921	
Calculated (^{13}CO)[a]		1997	1950	1920	
$Cp_2Ru_2(CO)_3(PPh_3)(\mu\text{-}H)^+$, **4H⁺**	2046	2000	1969		
$Cp_2Ru_2(CO)_2(^{13}CO)(PPh_3)(\mu\text{-}H)^+$, **8H⁺**	2045	2000	1972	1925	
Calculated (^{13}CO)[a]		2000	1955	1925	

[a] See text.

Table 5. Crystal and Data Collection Parameters for $Cp_2Ru_2(CO)_3(PMe_3)$ (**1**) and $[Cp_2Ru_2(CO)_3(PMe_3)(\mu\text{-}H)]^+ CF_3SO_3^-$ (**$1H^+ CF_3SO_3^-$**).

	1	**$1H^+ CF_3SO_3^-$**
formula	$C_{16}H_{19}O_3PRu_2$	$C_{17}H_{20}F_3O_6PRu_2S$
space group	$P2_1/c$	$P\ 2_1/c$
a, Å	7.997(5)	12.7600(10)
b, Å	14.401(10)	11.2880(10)
c, Å	15.460(12)	16.691(2)
β, deg	101.18(6)	111.930(10)
V, Å^3	1746.7(21)	2230.1(4)
Z	4	4
d_{calc}, g/cm^3	1.873	1.914
crystal size, mm	0.2 x 0.1 x 0.08	0.4 x 0.2 x 0.12
μ, mm^{-1}	1.828	13.041
data collection instrument	Siemens P4RA	Siemens P4RA
radiation (monochromated in incident beam)	Mo Kα (λ=0.71073 Å)	Cu Kα (λ=1.54178 Å)
no. of orientation reflections; range (2θ)	25; 7.2< θ <17.6	25; 19< θ <33
temp, °C	20(1)	-60(2)
scan method	2θ-θ	2θ-$\sigma\theta$
data collection range, 2θ, deg	2.60-30.06	2.11-27.47
no. of data collected	6577	3877

Table 5. (continued)

	1	$1H^+ CF_3SO_3^-$
no. of unique data total	5130	2984
with $I \geq 2\sigma$ (I)	1632	2730
no. of parameters refined	200	275
trans factors; max; min	0.987/0.692	1.00/0.411
R^a	0.0558	0.0410
R_w^b	0.1956	0.0439
quality of fit indicator[c]	0.987	1.071
largest shift/esd, final cycle	0.02	-0.001
largest peak, e/Å^{-3}	0.865	1.219

[a] $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality -of-fit = $[\Sigma w(|F_o|-|F_c|)^2/(N_{obs}-N_{parameters})]^{1/2}$.

Table 6. Selected Bond Distances (Å) and Angles (deg)[a] for $Cp_2Ru_2(CO)_3(PMe_3)$ (**1**).

Distance (Å)					
Ru(1)-Ru(2)	2.722(2)	Ru(1)-Cp_c[b]	1.924	Ru(1)-P	2.291(3)
P-C(13)	1.793(10)	P-C(14)	1.745(12)	P-C(15)	1.781(12)
Ru(1)-C(1)	1.994(10)	C(1)-O(1)	1.173(10)	Ru(1)-C(2)	1.985(9)
C(2)-O(2)	1.184(8)	Ru(2) -Cp_c[b]	1.930	Ru(2)-C(1)	2.071(1)
Ru(2)-C(2)	2.089(8)	Ru(2)-C(16)	1.855(9)	C(16)-O(3)	1.130(9)

Bond Angles (deg)			
Ru(1)-C(1)-Ru(2)	84.1(4)	Ru(1)-C(2)-Ru(2)	83.8(3)
Ru(1)-Ru(2)-C(16)	103.9(3)	Ru(2)-Ru(1)-P	104.04(8)
Ru(1)-P-C(13)	115.8(4)	Ru(1)-P-C(14)	119.1(4)
Ru(1)-P-C(15)	117.5(4)	C(1)-Ru(1)-P	90.8(3)
C(2)-Ru(1)-P	89.7(2)	C(1)-Ru(2)-C(16)	90.9(4)
C(2)-Ru(2)-C(16)	91.3(3)	O(1)-C(1)-Ru(1)	140.4(9)
O(2)-C(2)-Ru(1)	143.4(6)	O(3)-C(16)-Ru(2)	175.4(9)
Cp_c-Ru(1)-Ru(2)-Cp_c[b]	2.4		

[a]Numbers in parentheses are estimated standard deviations in the least significant digits.

[b]Cp_c = centroid of Cp ring.

Table 7. Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Coefficients ($Å^2$ x 10^3) for $Cp_2Ru_2(CO)_3(PMe_3)$ (**1**).

Atom	x	y	z	U_{eq}
Ru(1)	3271(1)	3848(1)	1948(1)	35(1)
Ru(2)	904(1)	2470(1)	1818(1)	40(1)
C(1)	1095(12)	3775(7)	2393(6)	55(3)
C(2)	3497(10)	2492(6)	1770(4)	31(2)
C(3)	4243(15)	4222(7)	687(6)	60(3)
C(4)	5213(15)	4663(9)	1397(8)	82(4)
C(5)	4138(17)	5289(7)	1758(6)	72(4)
C(6)	2510(16)	5210(7)	1245(6)	68(3)
C(7)	2552(16)	4525(7)	590(6)	68(3)
C(8)	-15(16)	2332(12)	338(7)	74(4)
C(9)	-1144(17)	2903(9)	645(8)	80(4)
C(10)	-1847(12)	2350(13)	1190(8)	80(4)
C(11)	-1170(23)	1488(11)	1261(10)	115(7)
C(12)	45(19)	1477(13)	679(11)	114(7)
C(13)	6490(14)	4534(8)	3671(7)	106(5)
C(14)	5906(21)	2669(8)	3662(8)	242(12)
C(15)	3718(17)	3880(13)	4239(6)	203(10)
C(16)	1354(11)	1911(7)	2919(6)	51(3)
O(1)	215(10)	4237(6)	2742(5)	99(3)
O(2)	4441(8)	1911(4)	1611(4)	54(2)

Table 7. (continued)

Atom	x	y	z	U_{eq}
O(3)	1539(11)	1528(6)	3577(5)	100(3)
P	4814(3)	3703(2)	3354(1)	40(1)

Table 8. Selected Bond Distances (Å) and Angles (deg)[a] for $[Cp_2Ru_2(CO)_3(PMe_3)(\mu\text{-}H)]^+$ $CF_3SO_3^-$ (**1H$^+$ CF$_3$SO$_3^-$**).

Distance (Å)					
Ru(1)-Ru(2)	3.0271(6)	Ru(1)-H(1)	1.669(6)	Ru(2)-H(1)	1.746(6)
Ru(1)-P(1)	2.299(2)	Ru(1)-C(9)	1.866(7)	Ru(1)-Cp_c[b]	1.891
P(1)-C(6)	1.801(7)	P-C(7)	1.805(7)	P-C(8)	1.794(6)
C(9)-O(1)	1.139(8)	Ru(2)-C(15)	1.854(6)	Ru(2)-C(16)	1.885(7)
Ru(2)-Cp_c[b]	1.880	C(15)-O(2)	1.162(7)	C(16)-O(3)	1.146(7)

Bond Angles (deg)			
Ru(2)-Ru(1)-C(9)	88.5(2)	Ru(2)-Ru(1)-P(1)	101.15(4)
Ru(1)-Ru(2)-C(15)	96.7(2)	Ru(1)-Ru(2)-C(16)	74.8(2)
Ru(1)-C(9)-O(1)	176.8(6)	Ru(2)-C(15)-O(2)	174.8(6)
Ru(2)-C(16)-O(3)	176.4(5)	P-Ru(1)-C(9)	88.2(2)
C(15)-Ru(2)-C(16)	90.2(3)	Ru(1)-H(1)-Ru(2)	124.8(3)
Cp_c-Ru(1)-Ru(2)-Cp_c[b]	62.9		

[a]Numbers in parentheses are estimated standard deviations in the least significant digits. [b]Cp_c = centroid of Cp ring.

Table 9. Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Coefficients ($Å^2$ x 10^3) for $[Cp_2Ru_2(CO)_3(PMe_3)(\mu\text{-}H)]^+ CF_3SO_3^-$ (**$1H^+$ $CF_3SO_3^-$**).

Atom	x	y	z	U_{eq}
Ru(1)	7838(1)	3242(1)	2739(1)	18(1)
Ru(2)	7553(1)	944(1)	1746(1)	17(1)
C(1)	8123(6)	4004(6)	4032(4)	35(2)
C(2)	7029(6)	4315(6)	3458(4)	34(2)
C(3)	6382(6)	3261(6)	3191(4)	33(2)
C(4)	7089(6)	2300(5)	3604(4)	33(2)
C(5)	8153(6)	2738(6)	4113(4)	34(2)
C(6)	5899(6)	5057(9)	1220(6)	69(3)
C(7)	7609(9)	4167(6)	684(5)	65(3)
C(8)	8085(6)	5996(6)	1908(5)	41(2)
C(9)	9322(6)	3313(5)	2789(4)	32(2)
C(10)	6756(6)	-547(6)	874(5)	45(2)
C(11)	6281(6)	529(7)	451(4)	43(2)
C(12)	5704(5)	1051(6)	929(5)	44(2)
C(13)	5844(5)	329(7)	1631(5)	41(2)
C(14)	6473(6)	-644(7)	1599(5)	46(2)
C(15)	8748(5)	1168(6)	1385(4)	31(1)
C(16)	8576(5)	593(5)	2870(4)	25(1)
H(1)	7280(59)	2443(68)	1838(45)	.050
O(1)	10241(4)	3381(4)	2856(4)	50(1)

Table 9. (continued)

Atom	x	y	z	U_{eq}
O(2)	9484(4)	1220(6)	1135(3)	55(1)
O(3)	9217(4)	330(4)	3536(3)	38(1)
P(1)	10190(14)	3096(8)	2418(9)	82(4)

Table 10. Heats of Protonation (ΔH_{MHM}) of $Cp_2Ru_2(CO)_3(PR_3)$ and $Cp_2Mo_2(CO)_4(PR_3)_2$.

Metal Complex	$-\Delta H_{MHM}$,[a,b] kcal/mol
$Cp_2Ru_2(CO)_3(PMe_3)$	30.0(4)
$Cp_2Ru_2(CO)_4$	18.4(1)[c]
$Cp_2Mo_2(CO)_4(PMe_3)_2$	27.4(2)
$Cp_2Mo_2(CO)_4(PMe_2Ph)_2$	18.9(5)

[a]For protonation with 0.1 M CF_3SO_3H in DCE solvent at 25.0 °C. [b]Numbers in parentheses are average deviations from the mean of at least four titrations. [c]Reference 2.

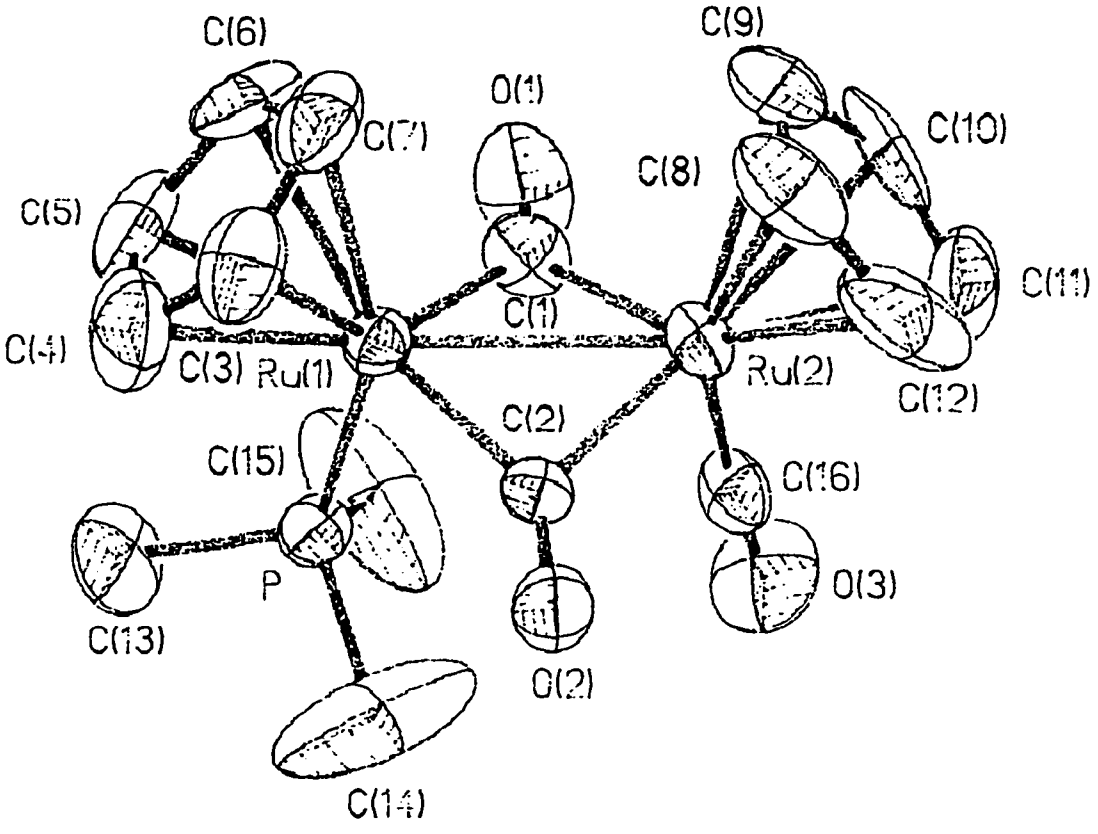
Figure Captions

Figure 1. Thermal ellipsoid drawing of $Cp_2Ru_2(CO)_3(PMe_3)$ (**1**) showing the atom numbering scheme (50% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

Figure 2. Thermal ellipsoid drawing of $Cp_2Ru_2(CO)_3(PMe_3)(\mu\text{-}H)^+$ (**1H$^+$**) showing the atom numbering scheme (50% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

Figure 3. Top down views (Cp excluded for clarity) of *cis-* and *trans--* CO ligand arrangements in $Cp_2Mo_2(CO)_4(PR_3)_2$.

Figure 1.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O(1)
C(9)
C(10)
C(5)
C(8)
C(11)
C(4)
C(3)
Ru(1)
C(1)
Ru(2)
C(12)
C(2)
C(15)
C(16)
P
O(3)
C(13)
O(2)
C(14)

Figure 2.

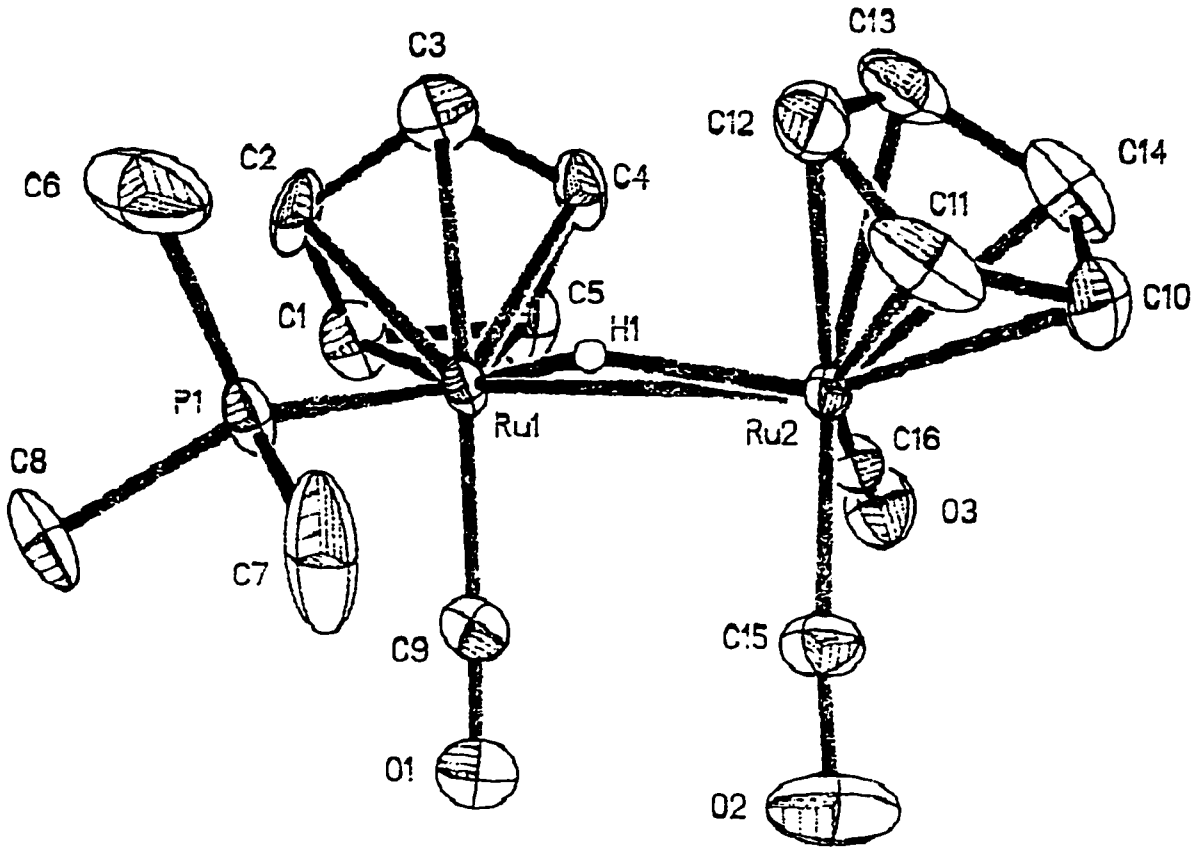
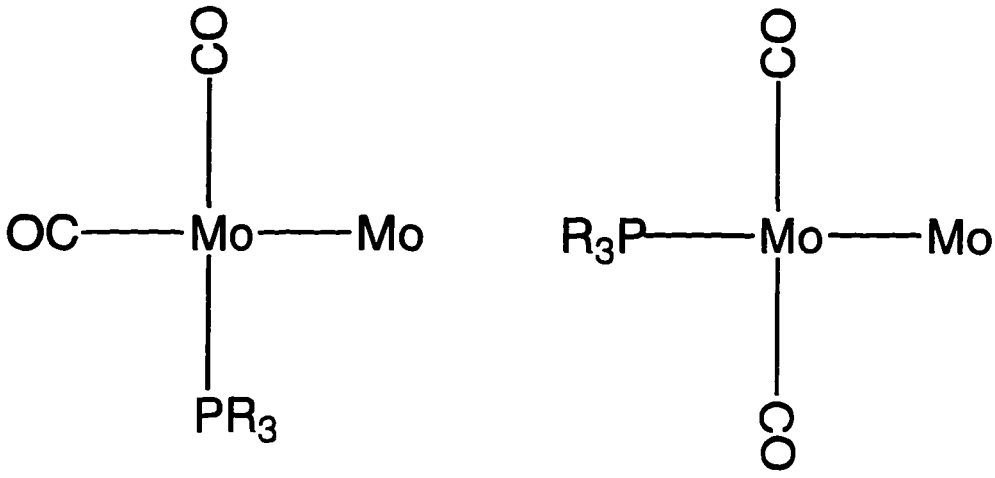

C3
C13
C12
C2
C14
C6
C4
C11
C10
C1
C5
H1
P1
Ru1
Ru2
C16
C8
O3
C7
C9
C15
O1
O2

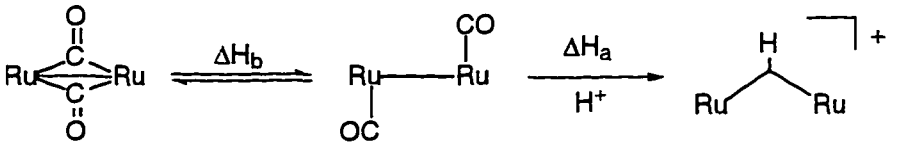
Figure 3.



cis- *trans-*

GENERAL SUMMARY

Heats of protonation for the series of complexes $Ru_2Cp'_2(CO)_3L$ [Cp' = Cp, Cp*, fv, Ind, $Cp^‡$, $HBpz_3$, $Cp_2(CH_2)$ or $Cp_2(CH_2)_2$; L = CO or PMe_3] have been measured by the heat evolved (ΔH_{MHM}) when the complex is protonated by CF_3SO_3H in 1,2-dichloroethane (DCE) at 25.0 °C. The $-\Delta H_{MHM}$ values ranged from 12.0 kcal/mol for $Ru_2Cp^‡_2(CO)_4$ to 30.0 kcal/mol for $Ru_2Cp_2(CO)_3(PMe_3)$. Two major factors appear to contribute significantly to the Ru-Ru bond basicity in these complexes, the relative amounts of the bridging and non-bridging carbonyl isomers and the electron donating ability of the Cp' and L ligands. The overall measured ΔH_{MHM} can be considered to be the sum of the heats contributed by these processes ($\Delta H_b + \Delta H_a$) (Equation 1). In this series, the dominant factor was ΔH_a, and this value was negative. The ΔH_b was considered to be significantly smaller than ΔH_a and positive, thereby lowering the observed ΔH_{MHM}.



(1)

The Cp, Ind and $Cp^‡$ ligands are similar in electron donating ability, but the complexes have different basicities due to differing amounts of the bridging and non-bridging carbonyl isomers. In general, one expects that M-M bonds in complexes with bridging CO ligands should be less basic than M-M bonds in similar compounds lacking bridging CO ligands. The Cp* complex is more basic than the Cp analog as expected by electron donor ability. However, the relatively small difference in basicity (0.8 kcal/mol) was surprising. This small difference can be attributed to the Cp* complex existing predominantly as the carbonyl bridged isomer. The phosphine complex, $Ru_2Cp_2(CO)_3(PMe_3)$, is 11.6 kcal/mol more basic than

$Ru_2Cp_2(CO)_4$. While an increase in basicity was anticipated, the difference that was measured was lower than expected due to the phosphine complex existing entirely as the bridged isomer.

Three factors contribute most significantly to stabilization of the carbonyl bridged dimer in this system. First, greater electron density on ruthenium favors the formation of bridging carbonyls. Second, bulky groups on ruthenium also appear to favor the formation of bridging carbonyls. Finally, by linking the Cp' ligands some steric strain is exerted on the Ru-Ru bond. The strain can either cause the relative amount of the bridging isomer to increase, as in $Ru_2(Cp_2(CH_2))(CO)_4$, or decrease, as seen in $Ru_2fv(CO)_4$.

An attempt to compare the basicity of the metal-metal bond in $Cp_2Ru_2(CO)_4$ with that of the metal in a related mononuclear complex $CpRu(CO)_2H$ was made by estimating the heat of protonation of $CpRu(CO)_2H$. The Ru-Ru bond is estimated to be much more basic than the single metal site in $CpRu(CO)_2H$. This conclusion may depend, of course, on the particular complexes that are compared.

The compounds $Cp_2Mo_2(CO)_4(PR_3)_2$ are more basic than $Cp_2Mo_2(CO)_6$ as expected due to phosphine ligands being better electron donors than carbonyl ligands. Changing the PR_3 ligand in $Cp_2Mo_2(CO)_4(PR_3)_2$ has a much greater effect on the basicity of the Mo-Mo bond than comparable changes on the basicities of mononuclear complexes. This may in part be due to the phosphine ligands being *trans-* to the Mo-Mo bond.

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