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Cyclopentadienyl Ligand Effects on Enthalpies of Protonation of the Ru−Ru Bond in $Cp'_2Ru_2(CO)_4$ Complexes[†]

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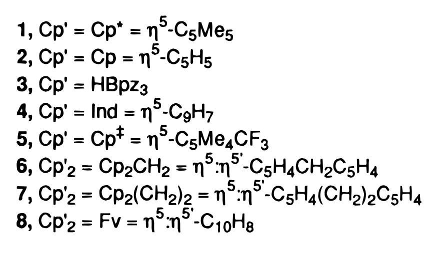
Basicities of a series of $Cp'_2Ru_2(CO)_4$ complexes were established by measuring the heats evolved (ΔH_{MHM}) when the complexes were protonated by CF_3SO_3H in 1,2-dichloroethane at 25.0 °C. Spectroscopic studies show that the protonation occurs at the metal−metal bond to form $[Cp'_2Ru_2(CO)_4(\mu\text{-}H)]^+CF_3SO_3^-$, in which all of the CO ligands are terminal. The basicities ($-\Delta H_{MHM}$) increase with the Cp'_2 ligands in the following order: $(C_5Me_4CF_3)_2 < (C_9H_7)_2 < C_5H_4C_5H_4 < C_5H_4CH_2CH_2C_5H_4 < (C_5H_5)_2 < (C_5Me_5)_2 < C_5H_4CH_2C_5H_4$. 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 nonbridging 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, determined by titration calorimetry, 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). Of course, the term basicity refers not only to the enthalpy change associated with the transfer of H^+ from CF_3SO_3H to the Ru−Ru bond but also to the enthalpy change accompanying any structural rearrangement of the dimer that occurs upon protonation.



(1)

1 - 8

1H+ - 8H+

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

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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) complexes.[8a] In this series, $-\Delta H_{HM}$

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

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 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 4.8−7.7 kcal/mol more basic than the analogous Cp compounds.

More directly relevant to the dinuclear ruthenium complexes reported in this paper are the $Cp'Ru(PR_3)_2X$ complexes.[8h] For $Cp'Ru(PPh_3)_2H$, the Cp* complex is 5.5 kcal/mol more basic than the Cp derivative. For $Cp'Ru(PMe_3)_2Cl$, 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 $Cp'_2Ru_2(CO)_4$ 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 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 bis(cyclopentadienyl)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 (δ = 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(HB(pz)$_3$)] were prepared by literature methods.

Dimer Syntheses. The dimers $Cp^*_2Ru_2(CO)_4$ (**1**),[16] $Cp_2Ru_2(CO)_4$ (**2**),[11] $(HB(pz)_3)_2Ru_2(CO)_4$ (**3**),[17] $Ind_2Ru_2(CO)_4$ (**4**),[18] $(Cp_2CH_2)Ru_2(CO)_4$ (**6**),[19] and $(Fv)Ru_2(CO)_4$ (**8**)[13] were prepared by literature methods. $Cp^{\ddagger}_2Ru_2(CO)_4$ (**5**) was generously provided by J. H. Nelson at the University of Nevada−Reno.[20]

$(Ind)_2Ru_2(CO)_4$ (4). Although some spectroscopic data were reported[18,21] previously for this compound, ^1H NMR and IR data in CD_2Cl_2 and CH_2Cl_2 are given below. Proton assignments in the ^1H NMR spectrum of **4** are based on those of Ind_2Ru.[18,22] ^1H (CD_2Cl_2): δ 7.29 (m, 8H, H4−H7), 5.69 (d, $^3J_{H-H}$ = 3.0 Hz, 4H, H1, H3), 5.58 (d, $^3J_{H-H}$ = 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 $Cp_2Ru_2(CO)_4$ synthesis,[11] was presumed to be a hydride intermediate, $(Cp_2(CH_2)_2)(Ru(CO)_2H)_2$. 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 × 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 10-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 (AA′BB′ system, J = 2.08 Hz, 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 10-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 equiv of CF_3SO_3H through the rubber septum using a gas-tight microliter syringe. The solutions immediately

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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)	
$Cp^*_2Ru_2(CO)_4H^+$, **1**H$^+$	2049 (s)	2020 (m)	1989 (s)		2019
$Cp_2Ru_2(CO)_4$, **2**	2008 (s)	1967 (s)	1936 (m)	1770 (s)	
$Cp_2Ru_2(CO)_4H^+$, **2**H$^+$	2073 (s)	2049 (m)	2017 (s)		2046
$(HB(pz)_3)_2Ru_2(CO)_4$, **3**	2024 (s)	1976 (m)	1940 (s)		
$(HB(pz)_3)_2Ru_2(CO)_4H^+$, **3**H$^+$	2076 (s)	2029 (s)	2012 (m)		2039
$Ind_2Ru_2(CO)_4$, **4**	2001 (s)	1956 (m)		1763 (s)	
$Ind_2Ru_2(CO)_4H^+$, **4**H$^+$	2084 (m)	2044 (s)	2011 (m)		2046
$Cp^{\ddagger}_2Ru_2(CO)_4$, **5**	1956 (s)			1772 (s)	
$Cp^{\ddagger}_2Ru_2(CO)_4H^+$, **5**H$^+$	2068 (m)	2045 (s)	2015 (s)		2042
$(Cp_2CH_2)Ru_2(CO)_4$, **6**	2012 (s)	1960 (s)	1940 (s)	1780 (w)	
$(Cp_2CH_2)Ru_2(CO)_4H^+$, **6**H$^+$	2075 (s)	2048 (m)	2021 (s)		2048
$(Cp_2(CH_2)_2)Ru_2(CO)_4$, **7**	1998 (s)	1956 (m)		1770 (s)	
$(Cp_2(CH_2)_2)Ru_2(CO)_4H^+$, **7**H$^+$	2073 (s)	2045 (m)	2018 (s)		2045
$FvRu_2(CO)_4$, **8**	2020 (s)	1952 (s)			
$FvRu_2(CO)_4H^+$, **8**H$^+$	2082 (s)	2056 (m)	2028 (s)		2055

changed color from bright yellow, to faint 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 ^{1}H NMR spectroscopy. Compound **1**H$^+$BF$_4^-$ was previously reported;[23] its IR and ^{1}H NMR data compare favorably with that of **1**H$^+$CF$_3$SO$_3^-$ in these studies. Compound **2**H$^+$ has been characterized by ^{1}H NMR in H_2SO_4[24] and by IR and ^{1}H NMR in acetic acid.[25]

Crystals of **2**H$^+$CF$_3$SO$_3^-$ were obtained by layering the protonation reaction solution with a 10-fold excess of ether. The solvents were allowed to mix slowly at room temperature. Crystals of **6**H$^+$CF$_3$SO$_3^-$ were formed by slow evaporation of CD_2Cl_2 from its solution at room temperature. ^{1}H NMR data for **1**H$^+$−**8**H$^+$ are given below; IR data are presented in Table 1.

[Cp*$_2$Ru$_2$(CO)$_4$(μ-H)]$^+$CF$_3$SO$_3^-$ (1H$^+$CF$_3$SO$_3^-$). ^{1}H NMR (CD_2Cl_2): δ 2.07 (s, 30H, Me), −17.71 (s, 1H, μ-H).

[Cp$_2$Ru$_2$(CO)$_4$(μ-H)]$^+$CF$_3$SO$_3^-$ (2H$^+$CF$_3$SO$_3^-$). ^{1}H NMR (CD_2Cl_2): δ 5.74 (s, 10H, Cp), −19.27 (s, 1H, μ-H).

[(HB(pz)$_3$)$_2$Ru$_2$(CO)$_4$(μ-H)]$^+$CF$_3$SO$_3^-$ (3H$^+$CF$_3$SO$_3^-$). Assignments of the ^{1}H NMR peaks for **3**H$^+$CF$_3$SO$_3^-$ are based upon those for (HB(pz)$_3$)W(CO)$_2$[C(H)SMe]$^+$ CF$_3$SO$_3^-$,[26a] which undergoes slow rotation on the ^{1}H NMR time scale around the H−B−W axis.[26b] ^{1}H NMR (CD_2Cl_2): δ 8.22 (d, $^3J_{H-H}$ = 2.35 Hz, 4H, H3 of pz), 8.02 (d, $^3J_{H-H}$ = 2.02 Hz, 2H, H3 of pz), 7.86 (d, $^3J_{H-H}$ = 2.56 Hz, 4H, H5 of pz), 7.56 (d, $^3J_{H-H}$ = 2.23 Hz, 2H, H5 of pz), 6.86 (t, $^3J_{H-H}$ = 2.52 Hz, 4H, H4 of pz), 6.53 (t, $^3J_{H-H}$ = 2.14 Hz, 2H, H4 of pz), −25.53 (s, 1H, μ-H). IR (CH_2Cl_2): ν(BH) (cm^{-1}) 2087 (m).

[Ind$_2$Ru$_2$(CO)$_4$(μ-H)]$^+$CF$_3$SO$_3^-$ (4H$^+$CF$_3$SO$_3^-$). ^{1}H 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$^‡_2$Ru$_2$(CO)$_4$(μ-H)]$^+$CF$_3$SO$_3^-$ (5H$^+$CF$_3$SO$_3^-$). ^{1}H NMR (CD_2Cl_2): δ 2.26 (s, 12H, 2,5-Me$_2$), 2.12 (s, 12H, 3,4-Me$_2$), −18.44 (s, 1H, μ-H).

[(Cp$_2$CH$_2$)Ru$_2$(CO)$_4$(μ-H)]$^+$CF$_3$SO$_3^-$ (6H$^+$CF$_3$SO$_3^-$). ^{1}H NMR (CD_2Cl_2): δ 5.73 (m, 4H, C$_5$H$_4$), 5.22 (m, 4H, C$_5$H$_4$), 4.02 (s, 2H, CH$_2$), −17.95 (s, 1H, μ-H).

[(Cp$_2$(CH$_2$)$_2$)Ru$_2$(CO)$_4$(μ-H)]$^+$CF$_3$SO$_3^-$ (7H$^+$CF$_3$SO$_3^-$). ^{1}H NMR (CD_2Cl_2): δ 5.68 (m, 4H, C$_5$H$_4$), 5.63 (m, 4H, C$_5$H$_4$), 2.65 (s, 4H, CH$_2$), −17.79 (s, 1H, μ-H).

[FvRu$_2$(CO)$_4$(μ-H)]$^+$CF$_3$SO$_3^-$ (8H$^+$CF$_3$SO$_3^-$). ^{1}H NMR (CD_2Cl_2): δ 6.10 (m, 4H, C$_5$H$_4$), 4.99 (m, 4H, C$_5$H$_4$), −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 base-line 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 (**6**H$^+$CF$_3$SO$_3^-$) or an Enraf-Nonius CAD4 diffractometer (**2**H$^+$CF$_3$SO$_3^-$ and **7**). Data was collected at 20 ± 2 °C for **2**H$^+$CF$_3$SO$_3^-$ and **7** and at 25 ± 1 °C for **6**H$^+$CF$_3$SO$_3^-$. The cell constants for **6**H$^+$CF$_3$SO$_3^-$ were determined from reflections found from a random search routine, while those for **2**H$^+$CF$_3$SO$_3^-$ 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 **2**H$^+$CF$_3$SO$_3^-$ and **7**. A series of azimuthal reflections was collected, and a semiempirical absorption correction based on the azimuthal scan was applied. For **2**H$^+$CF$_3$SO$_3^-$, 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 **6**H$^+$CF$_3$SO$_3^-$ was located and refined anisotropically. The bridging hydrides of the two crystallographically independent molecules of **2**H$^+$CF$_3$SO$_3^-$ were placed from the *E*-map, and their coordinates were refined. Selected bond distances and angles are listed in Table 4 for **2**H$^+$, Table 5 for **6**H$^+$, and Table 3 for **7**. The ORTEP drawing of **2**H$^+$ is shown in Figure 3, that of **6**H$^+$ is in Figure 4, and that of **7** is in Figure 2.

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

	$\mathbf{2}H^+CF_3SO_3^-$	$\mathbf{6}H^+CF_3SO_3^-$	**7**
formula	$C_{15}H_{11}F_3O_7Ru_2S$	$C_{16}H_{11}F_3O_7Ru_2S$	$C_{16}H_{12}O_4Ru_2$
formula wt	594.443	606.454	470.409
space group	$P2_1/n$	$C2/c$	$P2_1/c$
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
μ, mm^{-1}	14.852 (Cu Kα)	1.797 (Mo Kα)	2.021 (Mo Kα)
radiation (monochromated in incident beam)	Cu Kα (λ = 1.541 78 Å)	Mo Kα (λ = 0.710 73 Å)	Mo Kα (λ = 0.710 73 Å)
temp, °C	20(2)	25(1)	20(2)
R^a	0.0758	0.0389	0.0503
R_w	0.0869^b	0.0651^c	0.1185^b

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] $R_w = [\sum[w(F_o^2 - F_c^2)^2/\sum[w(F_o^2)^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

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

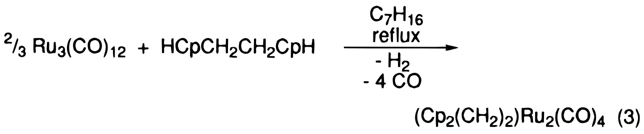
Bond Angles (deg)

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.

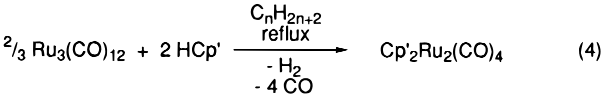
Results

$Cp'_2Ru_2(CO)_4$ 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 3 h (eq 3). This



$$\tfrac{2}{3}\,Ru_3(CO)_{12} + HCpCH_2CH_2CpH \xrightarrow[\substack{-\,H_2\\ -\,4\,CO}]{\substack{C_7H_{16}\\ \text{reflux}}} (Cp_2(CH_2)_2)Ru_2(CO)_4 \quad (3)$$

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



$$\tfrac{2}{3}\,Ru_3(CO)_{12} + 2\,HCp' \xrightarrow[\substack{-\,H_2\\ -\,4\,CO}]{\substack{C_nH_{2n+2}\\ \text{reflux}}} Cp'_2Ru_2(CO)_4 \quad (4)$$

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*, nonbridged 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 nonbridged 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 (Figure 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 nonbridged 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**−**8** can only be *cis* due to the linking of the Cp rings. In compound **6**, both bridged and nonbridged forms are observed in CH_2Cl_2 at room temperature, with the nonbridged being the dominant (≥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 nonbridged isomer in CH_2Cl_2 at room temperature as determined by IR spectroscopy.[30]

Upon protonation with 1 equiv of triflic acid, complexes **1**−**8** are converted to the hydride-bridged complexes $\mathbf{1}H^+CF_3SO_3^-$−$\mathbf{8}H^+CF_3SO_3^-$ in which all of the CO ligands are nonbridging. A singlet resonance in the ^1H NMR spectrum of these compounds in the range δ −17.71 to −25.53 is assigned to the bridging hydride ligand. Protonation of **2**, **4**, and **6**−**8** causes the Cp′ resonances to shift downfield by approximately 0.7 ppm.

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Table 4. Selected Bond Distances (Å) and Angles (deg)[a] for $[Cp_2Ru_2(CO)_4(\mu\text{-}H)^+][CF_3SO_3^-]$ (**2**$H^+CF_3SO_3^-$)

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)	115.8	Ru(1b)−H(b)−Ru(2b)	117.5
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

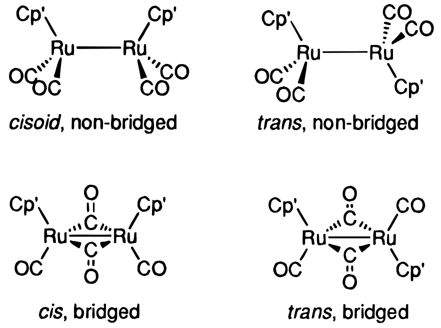
[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Cp$_c$ = centroid of Cp ring.

Table 5. Selected Bond Distances (Å) and Angles (deg)[a] for $[(Cp_2CH_2)Ru_2(CO)_4(\mu\text{-}H)^+][CF_3SO_3^-]$ (**6**$H^+CF_3SO_3^-$)

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.



cisoid, non-bridged

trans, non-bridged

cis, bridged

trans, bridged

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

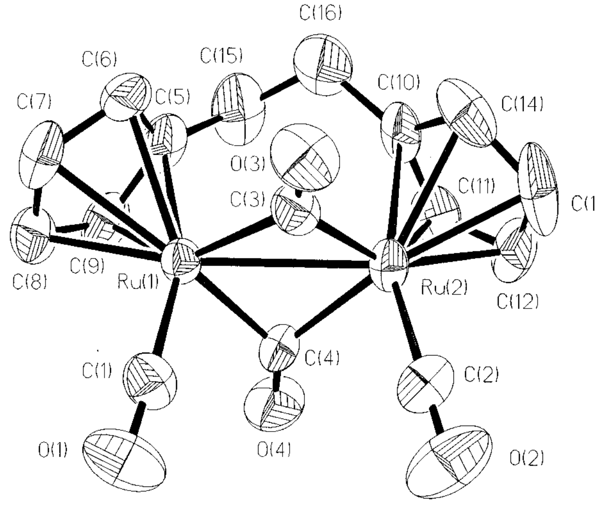


Figure 2. Thermal ellipsoid drawing of $(Cp_2(CH_2)_2)Ru_2(CO)_4$ (**7**) showing the atom-numbering scheme (50% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

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 **2**$H^+CF_3SO_3^-$ (Figure 3) shows two crystallographically independent molecules of **2**H^+. In both, the Cp ligands are *trans* and all of the CO ligands are terminal. The average Ru−Ru distance in **2**H^+ (3.037 Å) is considerably longer than in **2** (2.735(2) Å).[32] The structure of **6**$H^+CF_3SO_3^-$ (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 **6**H^+ (3.019(1) Å) than in **6** (2.767(1) Å).[19] The Cp$_{cent}$−Ru−Ru−Cp$_{cent}$ torsion angle in **6**H^+ (11.6°) is smaller than that (39.9°) in **6**.[19] The hydride in **6**H^+ is not equidistant from the two Ru atoms (Ru−H, 1.49(8) Å; Ru′−H, 2.0(1) Å). This

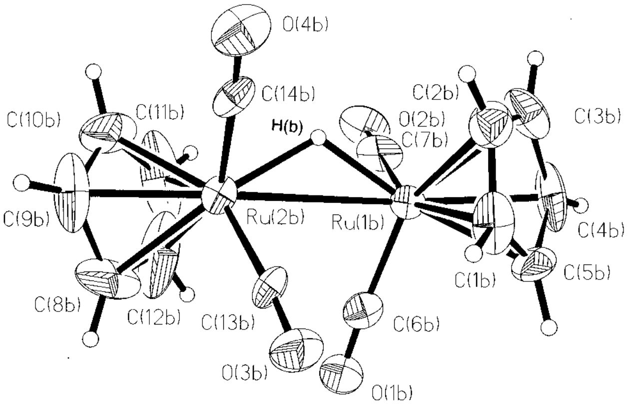


Figure 3. Thermal ellipsoid drawing of $Cp_2Ru_2(CO)_4(\mu\text{-}H)^+$ ($\mathbf{2H^+}$) showing the atom-numbering scheme (50% probability ellipsoids).

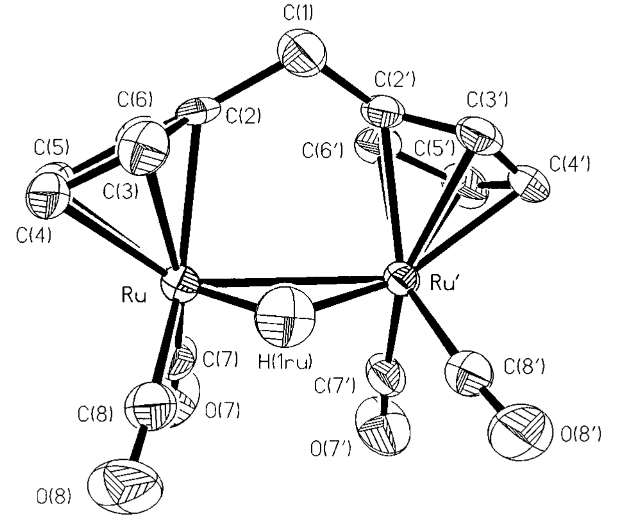


Figure 4. Thermal ellipsoid drawing of $(Cp_2CH_2)Ru_2(CO)_4(\mu\text{-}H)^+$ ($\mathbf{6H^+}$) showing the atom-numbering scheme (50% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

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; 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; Pd_b-H_b, 1.73(4) Å).[35b]

Calorimetry Studies. Table 6 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 ^1H NMR studies. Normal pre- and posttitration 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.

As discussed previously,[5,8h] the products of the protonation reactions in the calorimetric studies are likely to exist as ion pairs in the relatively nonpolar DCE solvent. In order to determine whether or not the enthalpies of protonation depend on the concentration of the base, ΔH_{HP} values for the reaction of PPh_3 with CF_3SO_3H were determined using PPh_3 concentrations ranging from 2.5 to 8.4 mM. In all cases, the ΔH_{HP} values were 21.1(2) kcal/mol, which are the same as that (21.2(1) kcal/mol) originally measured.[7a] Thus, the ΔH_{MHM} values are unlikely to depend on reactant concentrations at least within this concentration range.

Table 6. 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)
$(HB(pz)_3)_2Ru_2(CO)_4$, **3**	16.6(1)
$Ind_2Ru_2(CO)_4$, **4**	14.1(2)
$Cp^‡Ru_2(CO)_4$, **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 parentheses are average deviations from the mean of at least four titrations.

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 $(HB(pz)_3)_2Ru_2(CO)_4$, increase (Table 6) with the Cp′ ligand in the following order ($-\Delta H_{MHM}$, kcal/mol, in parentheses): Cp‡ (12.0) < Ind (14.1) < $HB(pz)_3$ (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 average 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) < $HB(pz)_3$ (2039) << Cp* (2019). The similar donor abilities of Cp, Ind, and Cp‡ are consistent with previous comparisons of these ligands.[8c,37,38] The $HB(pz)_3$ 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 from the basicity trend

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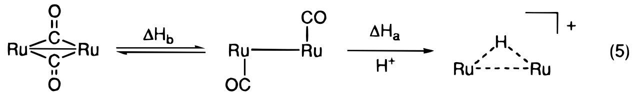
($-\Delta H_{MHM}$) for the complexes. Another feature of the basicity ($-\Delta H_{MHM}$) trend that is not understandable in terms of the Cp′ ligand donor ability is the small difference between the $-\Delta H_{MHM}$ values for the Cp (18.4 kcal/mol) and Cp* (19.2 kcal/mol) complexes (**2** and **1**).

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 groups, no bridging CO groups, or an equilibrium mixture of bridged and nonbridged forms. In solution, the Cp* (**1**), Ind (**4**), and Cp‡ (**5**) complexes are present only as the bridged isomers; the $HB(pz)_3$ complex (**3**) is all nonbridged; and the Cp (**2**) analog is an equilibrium mixture of bridged and nonbridged forms. One might consider the protonation of bridged isomers as being composed of two steps (eq 5): (i) opening of the bridge to give the nonbridged form, a step which requires energy (ΔH_b); and (ii) protonation of the nonbridged isomer, which is exothermic (ΔH_a). The overall measured ΔH_{MHM} is then the sum of ΔH_b and ΔH_a. If one 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 nonbridged form. Thus, the ΔH_{MHM} values of the Ind (**4**) and Cp‡ (**5**) dimers are expected to be less exothermic than that for Cp (**2**), which is the observed trend.



(5)

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 6), 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 nonbridged 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‡ < Ind < Cp < Cp*. Only the relative ordering of the Cp‡ and Ind dimers cannot be predicted because ΔH_b values (or estimates) are not available for their bridged to nonbridged conversions.

The relative basicity of the $HB(pz)_3$ dimer (**3**) is a somewhat special case compared with the Cp′ dimers. Since **3** exists in the nonbridged form only, there is no bridge to nonbridge reaction (ΔH_b) to reduce its basicity ($-\Delta H_{MHM}$). Therefore, the stronger donor ability of $HB(pz)_3$ 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 $HB(pz)_3$ complex 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 $HB(pz)_3$). For example, $CpMo(CO)_3H$ ($pK_a = 13.9$ in CH_3CN) is less acidic than $(HB(pz)_3)Mo(CO)_3H$ ($pK_a = 10.7$). The authors rationalize this trend by suggesting that the $(HB(pz)_3)Mo(CO)_3^-$ ion resists formation of the seven-coordinate $(HB(pz)_3)Mo(CO)_3H$ due to a combination of steric and stereoelectronic effects. Although the precise nature of the effects that lead to a lower basicity for $(HB(pz)_3)Mo(CO)_3^-$ 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 $CpRu(PPh_3)_2H$ ($\Delta H_{HM} = -29.7$ 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 × 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 $Cp_2Ru_2(CO)_4$ ($\Delta H_{MHM} = -18.4$ kcal/mol). Subtracting the ΔH_b (~1 kcal/mol) for the conversion of the bridged to the nonbridged form (eq 5) gives a basicity for the nonbridged 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−

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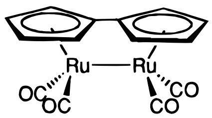
Ru bond would have been relatively even more basic than Ru in a mononuclear complex.

Basicities of $\mathbf{Cp'_2Ru_2(CO)_4}$ Complexes with Linked Cp′ Ligands. Because of the *cisoid* geometry imposed on the complexes with $-\text{CH}_2-$ or $-\text{CH}_2\text{CH}_2-$ linking groups, it seemed possible that the basicities of compounds **6** and **7** would not follow trends observed for the unlinked $\text{Cp}'_2\text{Ru}_2(\text{CO})_4$ complexes. The values (Table 6) of $-\Delta H_{\text{MHM}}$ for **6**, **7**, and $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ (**2**) increase in the order ($-\Delta H_{\text{MHM}}$, kcal/mol, in parentheses): $\text{Cp}_2(\text{CH}_2)_2$ (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 nonbridging forms of the complexes. The Cp_2 complex (**2**) is approximately 50% each of the bridged and nonbridged isomers in CH_2Cl_2 solution.[34] On the other hand, the $\text{Cp}_2(\text{CH}_2)_2$ 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 $\Delta H_a + \Delta H_b = \Delta H_{\text{MHM}}$ should be less exothermic for **7** than **2**, as observed.

The higher basicity ($-\Delta H_{\text{MHM}}$) 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 nonbridged 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 **6**H^+. 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 $\text{Cp}_{\text{cent}}-\text{Ru}-\text{Ru}-\text{Cp}_{\text{cent}}$ torsion angle (39.9°)[19] in the solid state structures of the nonbridged 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 nonbridged form in solution. Thus, three factors could contribute to the larger $-\Delta H_{\text{MHM}}$ 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 $\text{Cp}_2(\text{CH}_2)_2$ < Cp_2 < Cp_2CH_2.

The fulvalene complex $\text{FvRu}_2(\text{CO})_4$ (**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 $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ 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 $\text{FvRu}_2(\text{CO})_4(\mu\text{-H})^+$, 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 6). 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 nonbridged 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) $-\Delta H_{\text{MHM}}$ value. It might be noted that while the cyclopentadienyl complex $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ (**2**) is more basic than fulvalene $\text{FvRu}_2(\text{CO})_4$ (**8**) in the present studies, qualitative investigations[44] of $\text{Cp}_2\text{W}_2(\text{CO})_6$ and $\text{FvW}_2(\text{CO})_6$ (both nonbridged) show that the Fv complex is protonated by $\text{HBF}_4{\cdot}\text{Et}_2\text{O}$ 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 $\text{Cp}'_2\text{Ru}_2(\text{CO})_4$ complexes in this study, the $-\Delta H_{\text{MHM}}$ values increase in the following order, where the compound number, $-\Delta H_{\text{MHM}}$ value, and bridging (b) or nonbridging (nb) form present in solution are indicated in parentheses: $\text{Cp}^{\ddagger}_2$ (**5**, 12.0, b) < Ind_2 (**4**, 14.1, b) < Fv (**8**, 16.1, nb) < $\text{Cp}_2(\text{CH}_2)_2$ (**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 nonbridged form of the $\text{Cp}'_2\text{Ru}_2(\text{CO})_4$ becomes more predominant. *Thus, in general, one expects 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 nonbridging, 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 nonbridged complex; this is due to the weakly donating nature of the Fv ligand.

Although one can understand how the existence of bridging and nonbridging isomers affects the $-\Delta H_{\text{MHM}}$ values, it is not so clear why some of the $\text{Cp}'_2\text{Ru}_2(\text{CO})_4$ dimers are bridged while others are nonbridged. 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, $\text{Cp}^{\ddagger}$ and Cp have similar donor abilities,[38] but **5** with the bulky $\text{Cp}^{\ddagger}$ 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 nonbridging isomer distribution is less direct. While $\text{Cp}^*_2\text{Ru}_2(\text{CO})_4$ (**1**) is completely bridged and $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ (**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 its being 50% bridged whereas **8** is completely nonbridged. 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

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

variety of factors probably contribute to the bridging vs nonbridging 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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Supporting Information Available: X-ray crystallographic files in CIF format for the structures of **2**$H^+CF_3SO_3^-$, **6**$H^+CF_3SO_3^-$, and **7** are available on the Internet only. Access information is given on any current masthead page.

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