

Protonation of Metal–Metal Bonds in $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PR}_3)$ and $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{PR}_3)_2^\dagger$

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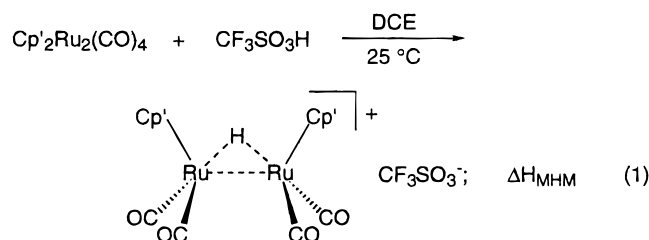
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Despite the much higher basicity expected for the Ru bearing the PR_3 ligand in $\text{Cp}(\text{PR}_3)\text{Ru}(\mu\text{-CO})_2\text{Ru}(\text{CO})\text{Cp}$, NMR studies demonstrate that protonation of this complex with $\text{CF}_3\text{SO}_3\text{H}$ occurs at the Ru–Ru bond, rather than at the more basic Ru. As determined by calorimetric titration at 25.0 °C in 1,2-dichloroethane solvent, the enthalpy of protonation (ΔH_{MHM}) of the Ru–Ru bond is higher in $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PMe}_3)$ (–30.0(4) kcal/mol) than in its carbonyl analogue $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ (–18.4(1) kcal/mol). Enthalpies (ΔH_{MHM}) for protonation of the Mo–Mo bond in the dinuclear Mo complexes $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{PR}_3)_2$ show that the PMe_3 complex (–27.4(2) kcal/mol) is dramatically more basic than its PMe_2Ph analogue (–18.9(5) kcal/mol). Considering the ΔH_{MHM} values as measures of the basicities of the complexes, these results show that the basicities of metal–metal bonds are highly sensitive to the nature of their associated ligands. In addition, evidence indicates that Ru–Ru bonds are more basic than Ru in comparable mononuclear complexes. The structures, as determined by X-ray crystallographic studies, of $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PMe}_3)$ and its protonated derivative $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PMe}_3)(\mu\text{-H})^+\text{CF}_3\text{SO}_3^-$ are also discussed.

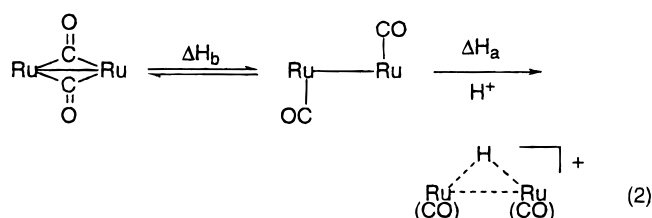
Introduction

The tendency of a transition metal complex to undergo acid protonation at the metal is defined as its basicity. Quantitative measures of the basicity of a metal complex are $\text{p}K_{\text{a}}$ and ΔH_{MHM} .¹ Most basicities have been reported^{2–9} for mononuclear complexes although there are a 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 study¹⁰ of the heats of protonation (ΔH_{MHM}) of a series of dinuclear $\text{Cp}'_2\text{Ru}_2(\text{CO})_4$ complexes (eq 1). The $-\Delta H_{\text{MHM}}$ values, measured in 1,2-



dichloroethane(DCE) solvent, increased with variations in the Cp'_2 ligands in the following order ($-\Delta H_{\text{MHM}}$ values given in kcal/mol; the CO-bridged (b) or nonbridged (nb) structure of

each $\text{Cp}'_2\text{Ru}_2(\text{CO})_4$ complex is given in parentheses): ($\text{C}_5\text{Me}_4\text{-CF}_3$)₂ (12.0, b) < (indenyl)₂ (14.1, b) < fulvalene (16.1, nb) < $\text{Cp}_2(\text{CH}_2)_2$ (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 the 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) a CO-bridged isomer to its nonbridged isomer.

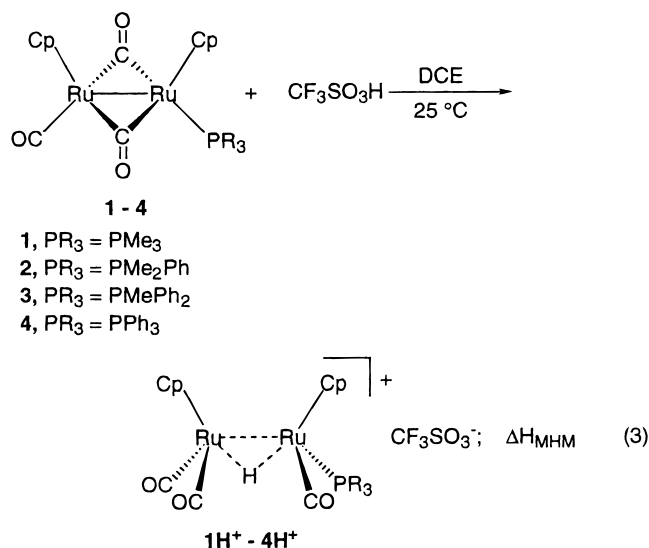


For bridged $\text{Cp}'_2\text{Ru}_2(\text{CO})_4$ complexes, the overall ΔH_{MHM} value may be considered as the sum of ΔH_{b} and ΔH_{a} . For two complexes that have Cp'_2 ligands with similar donor abilities, ΔH_{a} will be similar, but if one of the complexes is CO-bridged, an endothermic ΔH_{b} term will cause its $-\Delta H_{\text{MHM}}$ to be less positive than that of the other $\text{Cp}'_2\text{Ru}_2(\text{CO})_4$ complex with no bridging CO groups. Thus, bridging CO groups reduce the basicity of the Ru–Ru bond as compared with those of analogous complexes that are nonbridged.

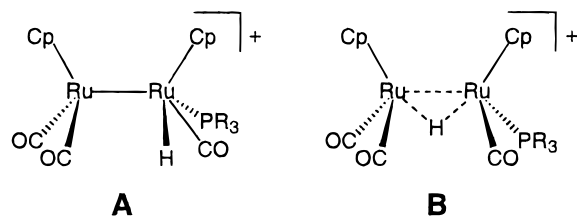
In the present study, we sought to determine the basicity ($-\Delta H_{\text{MHM}}$) of the phosphine-substituted CO-bridged complexes $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PR}_3)$ by the reaction in eq 3. These complexes were of particular interest because the Ru atom bonded to the PR_3 ligand is expected to be much more basic than the Ru coordinated to a terminal CO.^{1–9} The magnitude of this expected difference is suggested by the $-\Delta H_{\text{MHM}}$ values for $\text{Cp}^*\text{Ir}(\text{CO})(\text{PMe}_3)$ (38.0(2) kcal/mol) and $\text{Cp}^*\text{Ir}(\text{CO})(\text{PPh}_3)$ (37.1(2) kcal/mol) as compared with that of $\text{Cp}^*\text{Ir}(\text{CO})_2$ (21.4(1) kcal/mol).¹¹ If the PR_3 -substituted Ru in $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PR}_3)$ were 15.7–16.6 kcal/mol more basic than the CO-substituted

[†] Dedicated to Professor Warren R. Roper on the occasion of his 60th birthday.

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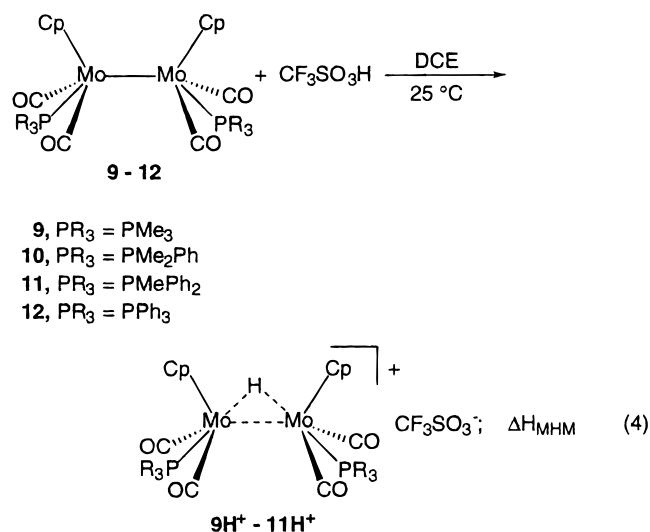


Ru, one would expect protonation to occur at the PR_3 -substituted Ru as in **A**. On the other hand, if the electron density provided



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 $1\text{H}^+\text{CF}_3\text{SO}_3^-$ and $4\text{H}^+\text{CF}_3\text{SO}_3^-$. In addition, ΔH_{MHM} for $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PMe}_3)$ has been measured and compared with those for $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ and related complexes.

Protonation reactions (eq 4) of four $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{PR}_3)_2$ complexes have also been examined. NMR studies indicate



that the proton bridges the Mo–Mo bond in the product, as expected for these symmetric structures. Measured basicities

($-\Delta H_{\text{MHM}}$) of $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{PR}_3)_2$ ($\text{PR}_3 = \text{PMe}_3$, PMe_2Ph) are compared with those of 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 methods¹² as described below. Hexanes, heptanes, 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 ($\text{CF}_3\text{SO}_3\text{H}$) 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 N_2 -saturated water (3% w/w for ruthenium compounds and 5% w/w for molybdenum compounds), and stored under N_2 .

The compounds $\text{Cp}_2\text{Ru}_2(\text{CO})_4$,¹³ $\text{Cp}_2\text{Ru}_2(\text{CO})_2(\text{COC}_2\text{Ph}_2)$,^{14,15} $\text{Cp}_2\text{Mo}_2(\text{CO})_6$,¹⁶ and $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ ¹⁶ were prepared by literature methods. Diphenylacetylene was purchased from Eastman-Kodak, and $\text{Ru}_3(\text{CO})_{12}$ was purchased from Strem. Dicyclopentadiene was purchased from Aldrich and cracked over iron filings prior to use.¹³ The phosphines PPh_3 , PMePh_2 , PMe_2Ph , and PMe_3 (1.0 M in toluene) were purchased from Aldrich. The ^{13}C (^{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. $^{31}\text{P}\{\text{H}\}$ 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 100.6 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.

$\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PR}_3)$. In a typical reaction, approximately 0.1 g (0.2 mmol) of $\text{Cp}_2\text{Ru}_2(\text{CO})_2(\text{COC}_2\text{Ph}_2)$ and 1 equiv 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 within 30 min. Upon cooling and vacuum removal of solvent, the compounds were chromatographed on an alumina column (1.5 × 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.¹⁷

$\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PMe}_3)$ (1). ^1H NMR (CD_2Cl_2): δ 5.23 (s, 5H, Cp), 5.00 (s, 5H, Cp), 1.23 ($d^2 J_{\text{P-H}}$ 10.0 Hz, 9H, Me). ^{31}P NMR (CD_2Cl_2): δ 9.95 (s). IR (toluene): $\nu(\text{CO})$ (cm^{-1}) 1929 (m), 1742 (s). Anal.

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Table 1. IR Data for $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PR}_3)$ and $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PR}_3)(\mu\text{-H})^+$ in CH_2Cl_2 Solvent

complex	$\nu(\text{CO}), \text{cm}^{-1}$		
	terminal		bridging
1 ^a	1929 (s)		1728 (s)
1H ⁺ ^a	2043 (s)	1995 (s)	1964 (m)
2 ^b	1932 (s)		1727 (s)
2H ⁺ ^b	2045 (s)	1996 (s)	1965 (m)
3 ^c	1937 (s)		1727 (s)
3H ⁺ ^c	2045 (s)	1998 (s)	1966 (m)
4 ^d	1947 (s)		1725 (s)
4H ⁺ ^d	2046 (s)	2000 (s)	1969 (m)

^a $\text{PR}_3 = \text{PMe}_3$. ^b $\text{PR}_3 = \text{PMe}_2\text{Ph}$. ^c $\text{PR}_3 = \text{PMePh}_2$. ^d $\text{PR}_3 = \text{PPh}_3$.**Table 2.** IR Data for $\text{Cp}_2\text{Ru}_2(\text{CO})_4$, $\text{Cp}_2\text{Ru}_2(\text{CO})_2(\text{COC}_2\text{Ph}_2)$, $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PMe}_3)$, $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PPh}_3)$, and Their ^{13}CO -Labeled Analogues in CH_2Cl_2 Solvent

complex	$\nu(\text{CO}), \text{cm}^{-1}$				
$\text{Cp}_2\text{Ru}_2(\text{CO})_4$	2003	1966	1934	1771	
$\text{Cp}_2\text{Ru}_2(\text{CO})_3(^{13}\text{CO})$, 5	1999	1956	1927	1897	1742
calcd (^{13}CO) ^a		1958	1921	1891	1731
$\text{Cp}_2\text{Ru}_2(\text{CO})_2(\text{COC}_2\text{Ph}_2)$	1980		1803	1733	
$\text{Cp}_2\text{Ru}_2(\text{CO})_2(^{13}\text{CO})(\text{COC}_2\text{Ph}_2)$, 6	1979	1934	1802	1772	1700
calcd (^{13}CO) ^a			1935	1762	1694
$\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PMe}_3)$, 1	1929		1728		
$\text{Cp}_2\text{Ru}_2(\text{CO})_2(^{13}\text{CO})(\text{PMe}_3)$, 7	1929	1884	1729	1701	
calcd (^{13}CO) ^a		1886		1689	
$\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PPh}_3)$, 4	1947		1725		
$\text{Cp}_2\text{Ru}_2(\text{CO})_2(^{13}\text{CO})(\text{PPh}_3)$, 8	1947	1925	1725	1699	
calcd (^{13}CO) ^a		1903		1686	
$\text{Ru}_3(\text{CO})_{12}$	2060	2028	2010		
$\text{Ru}_3(^{13}\text{CO})_{12}$	2048	2021	1982	1938	
calcd (^{13}CO) ^a		2014	1982	1965	
$\text{CpRu}(\text{CO})(\text{PPh}_3)\text{H}^b$	1937				
$\text{CpRu}(^{13}\text{CO})(\text{PPh}_3)\text{H}$	1920	1876			
calcd (^{13}CO) ^a		1877			

^a See text. ^b In hexanes, see ref 19.

Calcd for $\text{C}_{16}\text{H}_{19}\text{O}_3\text{PRu}_2$: C, 39.03; H, 3.89. Found: C, 39.13; H, 4.03. Orange crystals of **1** were obtained by cooling an ether solution of **1** to -20°C for 3 days.

$\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PMe}_2\text{Ph})$ (2). ^1H NMR (CD_2Cl_2): δ 7.44 (m, 5H, Ph), 5.25 (s, 5H, Cp), 4.75 (s, 5H, Cp), 1.40 (d, $^2J_{\text{P-H}}$ 10.0 Hz, 6H, Me). ^{31}P NMR (CD_2Cl_2): δ 24.3 (s). IR (toluene): $\nu(\text{CO})$ (cm^{-1}) 1933 (s), 1739 (s).

$\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PMePh}_2)$ (3). ^1H NMR (CD_2Cl_2): δ 7.41 (m, 10H, Ph), 5.20 (s, 5H, Cp), 4.80 (s, 5H, Cp), 1.64 (d, $^2J_{\text{P-H}}$ 8.0 Hz, 3H, Me). ^{31}P NMR (CD_2Cl_2): δ 39.6 (s). IR (toluene): $\nu(\text{CO})$ (cm^{-1}) 1936 (m), 1739 (s).

$\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PPh}_3)$ (4). ^1H NMR (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): $\nu(\text{CO})$ (cm^{-1}) 1939 (m), 1737 (s).

$\text{Cp}_2\text{Ru}_2(\text{CO})_3(^{13}\text{CO})$ (5). $\text{Cp}_2\text{Ru}_2(\text{CO})_2(\text{COC}_2\text{Ph}_2)$ (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 mixture was heated to 90°C for 20 min, during which 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 10-fold excess of ether and allowing the solvents to slowly mix at room temperature. Yield: 0.218 g (93%). ^1H NMR (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 ($\text{M}^+ - \text{CO}$), 390 ($\text{M}^+ - 2\text{CO}$), 361 ($\text{M}^+ - 2\text{CO} - ^{13}\text{CO}$).

$\text{Cp}_2\text{Ru}_2(\text{CO})_2(^{13}\text{CO})(\text{COC}_2\text{Ph}_2)$ (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 h 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%).

$\text{Cp}_2\text{Ru}_2(\text{CO})_2(^{13}\text{CO})(\text{PMe}_3)$ (7). With **6** as the starting material, **7** was prepared using the same methods as in the preparation of **1**. ^1H NMR (CD_2Cl_2): δ 5.24 (s, 5H, Cp), 5.01 (s, 5H, Cp), 1.23 (d, $^2J_{\text{P-H}}$ 10.0 Hz, 9H, Me). ^{13}C NMR (CD_2Cl_2): δ 89.1 (s), 88.7 (s), 19.8 (d, $^1J_{\text{P-C}}$ 31.6 Hz). ^{13}C NMR (CD_2Cl_2 , -78°C): δ 246.3 (d, $^2J_{\text{P-C}}$ 11.0 Hz), 205.2 (s), 89.1 (s), 88.7 (s), 19.8 (d, $^1J_{\text{P-C}}$ 31.6 Hz).

$\text{Cp}_2\text{Ru}_2(\text{CO})_2(^{13}\text{CO})(\text{PPh}_3)$ (8). With **6** as the starting material, **8** was prepared using the same methods as in the preparation of **4**. ^1H NMR (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, $J_{\text{P-C}}$ 45.2 Hz), 132.8 (d, $J_{\text{P-C}}$ 10.0 Hz), 128.7 (d, $J_{\text{P-C}}$ 2.5 Hz), 126.8 (d, $J_{\text{P-C}}$ 10.0 Hz), 89.0 (s), 88.0 (s). ^{13}C NMR (CD_2Cl_2 , -78°C): δ 245.6 (d, $^2J_{\text{P-C}}$ 10.0 Hz), 200.7 (s), 134.3 (d, $J_{\text{P-C}}$ 45.2 Hz), 132.8 (d, $J_{\text{P-C}}$ 10.0 Hz), 128.7 (d, $J_{\text{P-C}}$ 2.5 Hz), 126.8 (d, $J_{\text{P-C}}$ 10.0 Hz), 89.0 (s), 88.0 (s).

$\text{CpRu}(^{13}\text{CO})(\text{PPh}_3)\text{H}$. The ^{13}CO enrichment (45–65%) of $\text{Ru}_3(\text{CO})_{12}$ was performed as described in the literature.¹⁸ The $\text{Ru}_3(^{13}\text{CO})_{12}$ was used to prepare $\text{CpRu}(^{13}\text{CO})(\text{PPh}_3)\text{H}$ by a modification of a previously reported procedure.¹⁹ $\text{Ru}_3(^{13}\text{CO})_{12}$ (0.0443 g, 0.0687 mmol), cyclopentadiene (0.45 mL), and heptanes (67 mL) were heated to reflux for 1 h, during which the solution changed color from orange-red to pale yellow. Then, PPh_3 (0.0544 g, 0.207 mmol) was added and the solution was refluxed an additional 20 min, during which the color changed to bright yellow. Solvent was removed, and the residue was recrystallized from a 10:1 (v/v) mixture of hexanes/ CH_2Cl_2 to give 0.0075 g (72%) of the product. IR data for $\text{Ru}_3(^{13}\text{CO})_{12}$ and $\text{CpRu}(^{13}\text{CO})(\text{PPh}_3)\text{H}$ are presented in Table 2. ^1H NMR (CD_2Cl_2) for $\text{CpRu}(^{13}\text{CO})(\text{PPh}_3)\text{H}$: δ 7.46 (m, 15H, Ph), 4.93 (s, 5H, Cp), -11.67 (d, $^2J_{\text{P-H}}$ 32.0 Hz, 1H, Ru–H). ^{31}P NMR (CD_2Cl_2): δ 69.8 (s). ^{13}C NMR (CD_2Cl_2 at 100.6 MHz): δ 206.6 (dd, $^2J_{\text{P-C}}$ 23.1 Hz, $^2J_{\text{H-C}}$ 9.1 Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 at 400 MHz): δ 206.6 (d, $^2J_{\text{P-C}}$ 23.1 Hz), 133.7 (d, $J_{\text{P-C}}$ 11.1 Hz), 129.9 (s), 128.3 (d, $J_{\text{P-C}}$ 9.0 Hz), 84.4 (s).

$\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{PR}_3)_2$. The synthesis of these compounds follows the method developed by Riera^{20–22} for $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{dppm})$. Approximately 0.2 g (0.4 mmol) of $\text{Cp}_2\text{Mo}_2(\text{CO})_6$ and 5 mL of diglyme were used to prepare $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ in situ according to the literature procedure.¹⁶ In a separate flask, 2 equiv of the desired phosphine were dissolved in 5 mL of CH_2Cl_2 . The phosphine solution was added to the solution of $\text{Cp}_2\text{Mo}_2(\text{CO})_4$, and the reaction mixture was allowed to stir at room temperature for 1 h. The resulting precipitate was filtered from the reaction solution, and the collected product was washed with 3×5 mL of hexanes. Upon drying, no further purification of the compounds was necessary. The compounds all have a very deep, brick-red color. Because 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.

$\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{PMe}_3)_2$ (9). From 0.222 g (0.453 mmol) of $\text{Cp}_2\text{Mo}_2(\text{CO})_6$ in the above synthesis was collected 0.212 g (0.402 mmol) of **9** (80% yield). ^1H NMR (CD_2Cl_2): δ 4.87 (s, 10H, Cp), 1.57 (d, $^2J_{\text{P-H}}$

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Table 3. IR Data for $\text{Cp}_2\text{Ru}_2(\text{CO})_4(\text{PR}_3)_2$ and $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{PR}_3)_2(\mu\text{-H})^+$ in CH_2Cl_2 Solvent

complex	$\nu(\text{CO}), \text{cm}^{-1}$		
9^a	1839 (sh)	1818 (s)	
9H⁺ ^a	1979 (m)	1954 (m)	1894 (s)
10^b	1842 (sh)	1820 (s)	
10H⁺ ^b	1980 (m)	1966 (m)	1896 (s)
11^c	1844 (sh)	1826 (s)	
11H⁺ ^c	1982 (m)	1966 (m)	1898 (s)
12^d	1851 (sh)	1832 (s)	

^a $\text{PR}_3 = \text{PMe}_3$. ^b $\text{PR}_3 = \text{PMe}_2\text{Ph}$. ^c $\text{PR}_3 = \text{PMePh}_2$. ^d $\text{PR}_3 = \text{PPh}_3$.

Table 4. IR Data for $\text{Cp}_2\text{Ru}_2(\text{CO})_4(\mu\text{-H})^+$, $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PMe}_3)(\mu\text{-H})^+$, $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PPh}_3)(\mu\text{-H})^+$, and Their ^{13}CO -Labeled Analogues in CH_2Cl_2 Solvent

complex	$\nu(\text{CO}), \text{cm}^{-1}$				
$\text{Cp}_2\text{Ru}_2(\text{CO})_4(\mu\text{-H})^+$	2073	2049	2017		
$\text{Cp}_2\text{Ru}_2(\text{CO})_3(^{13}\text{CO})(\mu\text{-H})^+, 5\text{H}^+$	2064	2036	2011	1981	1960
calcd (^{13}CO) ^a			2026	2003	1972
$\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PMe}_3)(\mu\text{-H})^+, 1\text{H}^+$	2043	1995	1964		
$\text{Cp}_2\text{Ru}_2(\text{CO})_2(^{13}\text{CO})(\text{PMe}_3)(\mu\text{-H})^+, 7\text{H}^+$	2043	1996	1966	1921	
calcd (^{13}CO) ^a		1997	1950	1920	
$\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PPh}_3)(\mu\text{-H})^+, 4\text{H}^+$	2046	2000	1969		
$\text{Cp}_2\text{Ru}_2(\text{CO})_2(^{13}\text{CO})(\text{PPh}_3)(\mu\text{-H})^+, 8\text{H}^+$	2045	2000	1972	1925	
calcd (^{13}CO) ^a		2000	1955	1925	

^a See text.

8.9 Hz, 18H, Me). ^{31}P NMR (CD_2Cl_2): δ 32.9 (s). Anal. Calcd for $\text{C}_{20}\text{H}_{28}\text{Mo}_2\text{O}_4\text{P}_2$: C, 40.97; H, 4.81. Found: C, 40.63; H, 4.80.

$\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{PMe}_2\text{Ph})_2$ (10). From 0.223 g (0.454 mmol) of $\text{Cp}_2\text{Mo}_2(\text{CO})_6$ in the above preparation was obtained 0.289 g (0.409 mmol) of **10** (90% yield). ^1H NMR (CD_2Cl_2): δ 7.58 (m, 10H, Ph), 4.68 (d, $^3J_{\text{P-H}} = 1.8$ Hz, 10H, Cp), 1.88 (d, $^2J_{\text{P-H}} = 8.5$ Hz, 12H, Me). ^{31}P NMR (CD_2Cl_2): δ 42.6 (s).

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

$\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{PPh}_3)_2$ (12). From 0.239 g (0.488 mmol) of $\text{Cp}_2\text{Mo}_2(\text{CO})_6$ was obtained 0.400 g (0.449 mmol) of **12** (92% yield). ^1H NMR (CD_2Cl_2): δ 7.48 (m, 30H, Ph), 4.56 (d, $^3J_{\text{P-H}} = 1.6$ Hz, 10H, Cp). ^{31}P NMR (CD_2Cl_2): δ 79.1 (s).

Protonation Reactions. Compounds **1–5** and **7–12** were protonated for characterization of either the $[\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{L})(\mu\text{-H})]^+\text{CF}_3\text{SO}_3^-$ ($\text{L} = \text{CO}, \text{PR}_3$) or the $[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{PR}_3)_2(\mu\text{-H})]^+\text{CF}_3\text{SO}_3^-$ 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 $\text{CF}_3\text{SO}_3\text{H}$ 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 $12\text{H}^+\text{CF}_3\text{SO}_3^-$ was not formed. The molybdenum complexes **9–11** also protonated quantitatively. NMR (^1H and ^{31}P) spectral data for 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.

$[\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PMe}_3)(\mu\text{-H})]^+\text{CF}_3\text{SO}_3^-$ (1H⁺CF₃SO₃[−]**).** ^1H NMR (CD_2Cl_2): δ 5.67 (s, 5H, Cp), 5.35 (s, 5H, Cp), 1.81 (d, $^2J_{\text{P-H}} = 10.0$ Hz, 9H, Me), -18.51 (d, $^2J_{\text{P-H}} = 20.0$ Hz, 1H, $\mu\text{-H}$). ^{31}P NMR (CD_2Cl_2): δ 14.7 (s). Orange crystals of **1H⁺CF₃SO₃[−]** were obtained by slowly cooling an NMR sample to -78°C .

$[\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PMe}_2\text{Ph})(\mu\text{-H})]^+\text{CF}_3\text{SO}_3^-$ (2H⁺CF₃SO₃[−]**).** ^1H NMR (CD_2Cl_2): δ 7.57 (m, 5H, Ph), 5.51 (s, 5H, Cp), 5.19 (s, 5H, Cp), 2.1 (d, $^2J_{\text{P-H}} = 10.0$ Hz, 6H, Me), -18.57 (d, $^2J_{\text{P-H}} = 20.0$ Hz, 1H, $\mu\text{-H}$). ^{31}P NMR (CD_2Cl_2): δ 28.4 (s).

$[\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PMePh}_2)(\mu\text{-H})]^+\text{CF}_3\text{SO}_3^-$ (3H⁺CF₃SO₃[−]**).** ^1H NMR (CD_2Cl_2): δ 7.37 (m, 10H, Ph), 5.40 (s, 5H, Cp), 5.24 (s, 5H, Cp), 2.30 (d, $^2J_{\text{P-H}} = 10.0$ Hz, 3H, Me), -18.68 (d, $^2J_{\text{P-H}} = 22.0$ Hz, 1H, $\mu\text{-H}$). ^{31}P NMR (CD_2Cl_2): δ 42.9 (s).

$[\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PPh}_3)(\mu\text{-H})]^+\text{CF}_3\text{SO}_3^-$ (4H⁺CF₃SO₃[−]**).** ^1H NMR (CD_2Cl_2): δ 7.59 (m, 15H, Ph), 5.64 (s, 5H, Cp), 5.52 (s, 5H, Cp), -18.75 (d, $^2J_{\text{P-H}} = 21.6$ Hz, 1H, $\mu\text{-H}$). ^{31}P NMR (CD_2Cl_2): δ 51.3 (s).

$[\text{Ru}_2\text{Cp}_2(\text{CO})_3(^{13}\text{CO})(\mu\text{-H})]^+\text{CF}_3\text{SO}_3^-$ (5H⁺CF₃SO₃[−]**).** ^1H NMR (CD_2Cl_2): δ 5.60 (s, 10H, Cp), -19.12 (d, $^2J_{\text{C-H}} = 4.0$ Hz, 1H, $\mu\text{-H}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 195.4 (s), 87.6 (s).

$[\text{Cp}_2\text{Ru}_2(\text{CO})_2(^{13}\text{CO})(\text{PMe}_3)(\mu\text{-H})]^+\text{CF}_3\text{SO}_3^-$ (7H⁺CF₃SO₃[−]**).** ^1H NMR (CD_2Cl_2): δ 5.61 (s, 5H, Cp), 5.33 (s, 5H, Cp), 1.79 (d, $^2J_{\text{P-H}} = 10.0$ Hz, 9H, Me), -18.41 (dd, $^2J_{\text{P-H}} = 20.0$ Hz, $^2J_{\text{C-H}} = 4.0$ Hz, 1H, $\mu\text{-H}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 at 50.33 MHz): δ 200.0 (d, $^2J_{\text{P-C}} = 19.1$ Hz), 197.3 (s), 196.6 (s), 86.7 (s), 85.5 (s), 21.8 (d, $^2J_{\text{P-C}} = 37.2$ Hz). ^{13}C NMR (CD_2Cl_2 at 100.6 MHz): δ 200.6 (dd, $^2J_{\text{P-C}} = 19.3$ Hz, $^2J_{\text{H-C}} = 3.1$ Hz), 197.7 (dd, $^3J_{\text{P-C}} = 8.2$ Hz, $^2J_{\text{H-C}} = 3.5$ Hz), 196.9 (dd, $^3J_{\text{P-C}} = 8.1$ Hz, $^2J_{\text{H-C}} = 3.5$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 at 400 MHz): δ 200.6 (d, $^2J_{\text{P-C}} = 19.3$ Hz), 197.7 (d, $^3J_{\text{P-C}} = 8.2$ Hz), 196.9 (d, $^3J_{\text{P-C}} = 8.1$ Hz), 86.7 (s), 85.5 (s), 21.8 (d, $^2J_{\text{P-C}} = 37.2$ Hz).

$[\text{Cp}_2\text{Ru}_2(\text{CO})_2(^{13}\text{CO})(\text{PPh}_3)(\mu\text{-H})]^+\text{CF}_3\text{SO}_3^-$ (8H⁺CF₃SO₃[−]**).** ^1H NMR (CD_2Cl_2): δ 7.37 (m, 15H, Ph), 5.35 (s, 5H, Cp), 5.15 (s, 5H, Cp), -18.75 (dd, $^2J_{\text{P-H}} = 20.0$ Hz, $^2J_{\text{C-H}} = 4.0$ Hz, 1H, $\mu\text{-H}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 at 50.33 MHz): δ 200.7 (d, $^2J_{\text{P-C}} = 17.6$ Hz), 196.6 (s), 196.1 (s), 134.3 (d, $J_{\text{P-C}} = 50.2$ Hz), 132.8 (d, $J_{\text{P-C}} = 10.0$ Hz), 131.0 (d, $J_{\text{P-C}} = 2.5$ Hz), 128.7 (d, $J_{\text{P-C}} = 10.0$ Hz), 86.9 (s), 85.8 (s). ^{13}C NMR (CD_2Cl_2 at 100.6 MHz): δ 201.1 (dd, $^2J_{\text{P-C}} = 18.4$ Hz, $^2J_{\text{H-C}} = 2.9$ Hz), 197.0 (dd, $^3J_{\text{P-C}} = 6.9$ Hz, $^2J_{\text{H-C}} = 3.8$ Hz), 196.4 (dd, $^3J_{\text{P-C}} = 6.7$ Hz, $^2J_{\text{H-C}} = 3.1$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 at 400 MHz): δ 201.1 (d, $^2J_{\text{P-C}} = 18.4$ Hz), 197.0 (d, $^3J_{\text{P-C}} = 6.9$ Hz), δ 196.4 (d, $^3J_{\text{P-C}} = 6.7$ Hz), 134.3 (d, $J_{\text{P-C}} = 50.2$ Hz), 132.8 (d, $J_{\text{P-C}} = 10.0$ Hz), 131.0 (d, $J_{\text{P-C}} = 2.5$ Hz), 128.7 (d, $J_{\text{P-C}} = 10.0$ Hz), 86.9 (s), 85.8 (s).

$[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{PMe}_3)_2(\mu\text{-H})]^+\text{CF}_3\text{SO}_3^-$ (9H⁺CF₃SO₃[−]**).** ^1H NMR (CD_2Cl_2): δ 5.27 (s, 10H, Cp), 1.71 (d, $^2J_{\text{P-H}} = 9.8$ Hz, 18H, Me), -19.75 (t, $^2J_{\text{P-H}} = 11.9$ Hz, 1H, $\mu\text{-H}$). ^{31}P NMR (CD_2Cl_2): δ 21.7 (s).

$[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{PMe}_2\text{Ph})_2(\mu\text{-H})]^+\text{CF}_3\text{SO}_3^-$ (10H⁺CF₃SO₃[−]**).** ^1H NMR (CD_2Cl_2): δ 7.60 (m, 10 H, Ph), 5.21 (s, 10H, Cp), 2.04 (d, $^2J_{\text{P-H}} = 9.8$ Hz, 12H, Me), -20.23 (t, $^2J_{\text{P-H}} = 9.7$ Hz, 1H, $\mu\text{-H}$). ^{31}P NMR (CD_2Cl_2): δ 27.9 (s).

$[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{PMePh}_2)_2(\mu\text{-H})]^+\text{CF}_3\text{SO}_3^-$ (11H⁺CF₃SO₃[−]**).** ^1H NMR (CD_2Cl_2): δ 7.52 (m, 20H, Ph), 5.09 (s, 10H, Cp), 2.28 (d, $^2J_{\text{P-H}} = 9.9$ Hz, 6H, Me), -20.86 (t, $^2J_{\text{P-H}} = 9.1$ Hz, 1H, $\mu\text{-H}$). ^{31}P NMR (CD_2Cl_2): δ 45.4 (s).

Calorimetric Studies. Heats of protonation (ΔH_{MHM}) of the $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PR}_3)$ and $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{PR}_3)_2$ complexes were measured using a Tronac model 458 isoperibol titration calorimeter as originally described²³ and then modified.²⁴ A typical calorimetric run consisted of three sections:²⁵ 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 $\text{CF}_3\text{SO}_3\text{H}$ 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 exhibited $\nu(\text{CO})$ bands for the $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PR}_3)(\mu\text{-H})^+$ or $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{PR}_3)_2(\mu\text{-H})^+$ 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).²⁴ The reported error in ΔH_{MHM} is the average deviation from the mean of all of the

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Table 5. Crystal and Data Collection Parameters for $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PMe}_3)$ (**1**) and $[\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PMe}_3)(\mu\text{-H})]^+\text{CF}_3\text{SO}_3^-$ ($1\text{H}^+\text{CF}_3\text{SO}_3^-$)

	1	$1\text{H}^+\text{CF}_3\text{SO}_3^-$
empirical formula	$\text{C}_{16}\text{H}_{19}\text{O}_3\text{PRu}_2$	$\text{C}_{17}\text{H}_{20}\text{F}_3\text{O}_6\text{PRu}_2\text{S}$
space group	$P2_1/c$	$P2_1/c$
<i>a</i> , Å	7.997(5)	12.760(1)
<i>b</i> , Å	14.40(1)	11.288(1)
<i>c</i> , Å	15.46(1)	16.691(2)
β , deg	101.18(6)	111.93(1)
<i>V</i> , Å ³	1746(2)	2230.1(4)
<i>Z</i>	4	4
<i>d</i> _{calc} , g/cm ³	1.873	1.914
μ , cm ⁻¹	18.28	130.41
radiation (monochromated in incident beam)	Mo K α (λ = 0.710 73 Å)	Cu K α (λ = 1.541 78 Å)
temp, °C	20(1)	-60(2)
<i>R</i> ^a	0.0558	0.0410
<i>R</i> _w ^b	0.1956	0.0439

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

Table 6. Selected Bond Distances (Å) and Angles (deg)^a for $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PMe}_3)$ (**1**)

Distances					
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)

Angles					
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.

determinations. Titrations of 1,3-diphenylguanidine (GFS Chemicals) with $\text{CF}_3\text{SO}_3\text{H}$ in DCE (-37.0 ± 0.3 kcal/mol; literature value -37.2 ± 0.4 kcal/mol²³) were used to monitor the accuracy of the calorimeter before each set of determinations. Titrations of complexes **2–4** and **11** failed to give reproducible ΔH_{MHM} values for reasons that are not known at this time.

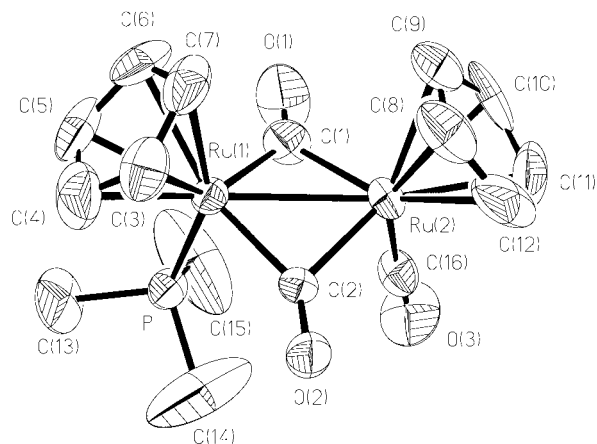
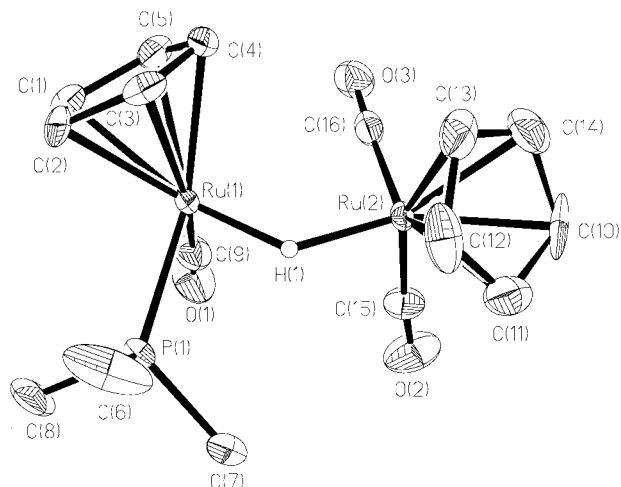
X-ray Diffraction Studies. The crystals were mounted on glass fibers and transferred to a Siemens P4RA diffractometer. Data were collected at 20 ± 1 °C for **1** and at -60 ± 2 °C for $1\text{H}^+\text{CF}_3\text{SO}_3^-$. Cell constants for **1** and $1\text{H}^+\text{CF}_3\text{SO}_3^-$ were determined from reflections in 360° rotation photographs. Pertinent data collection and reduction details 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 $1\text{H}^+\text{CF}_3\text{SO}_3^-$. Series of azimuthal reflections were also collected for both. No absorption correction was applied to **1**. A semiempirical absorption correction based on the azimuthal scan was applied to $1\text{H}^+\text{CF}_3\text{SO}_3^-$. The space groups were determined by systematic absences and intensity statistics, and the structures were solved by direct methods.²⁶ 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 $1\text{H}^+\text{CF}_3\text{SO}_3^-$. 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 and angles are listed in Table 6 for **1** and in Table 7 for 1H^+ . The ORTEP drawing of **1** is shown in Figure 1 and that of 1H^+ in Figure 2.

Table 7. Selected Bond Distances (Å) and Angles (deg)^a for $[\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PMe}_3)(\mu\text{-H})]^+\text{CF}_3\text{SO}_3^-$ ($1\text{H}^+\text{CF}_3\text{SO}_3^-$)

Distances					
Ru(1)–Ru(2)	3.0271(6)	Ru(1)–H(1)	1.67(3)	Ru(2)–H(1)	1.75(3)
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)

Angles					
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		
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.

**Figure 1.** Thermal ellipsoid drawing of $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PMe}_3)$ (**1**) showing the atom numbering scheme (50% probability ellipsoids). Hydrogen atoms have been omitted for clarity.**Figure 2.** Thermal ellipsoid drawing of $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PMe}_3)(\mu\text{-H})^+$ (1H^+) showing the atom numbering scheme (50% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

Results

$\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PR}_3)$ Syntheses. Refluxing $\text{Cp}_2\text{Ru}_2(\text{CO})_2(\text{COC}_2\text{Ph}_2)$ and the desired phosphine in toluene for approximately 30 min results in nearly quantitative formation of the phosphine-substituted complexes $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PR}_3)$. Knox reported¹⁴ that the reaction of $\text{Cp}_2\text{Ru}_2(\text{CO})_2(\text{COC}_2\text{Ph}_2)$ with $\text{P}(\text{OMe})_3$ in refluxing toluene occurs quickly to give $\text{Cp}_2\text{Ru}_2(\text{CO})_3[\text{P}(\text{OMe})_3]$ 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 $\nu(\text{CO})$ bands at 1953(s) and 1733(s) cm^{-1} .¹⁴ 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 $\text{Cp}_2\text{Ru}_2(\text{CO})_2(\text{COC}_2\text{Ph}_2)$ with $\text{H}_2\text{C}=\text{PPh}_3$.¹⁷ The analogous iron complexes, $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{PR}_3)$, have also been prepared; they exist in only the CO-bridged form in solution.²⁷ However, it was not determined whether the Cp ligands are cis or trans to each other. IR data for compounds **1–4** compare favorably with those of the related iron complexes in number of bands and relative intensities, indicating that compounds **1–4** also exist solely as bridged isomers 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 $\text{Cp}_{\text{cent}}\text{—Ru—Ru—Cp}_{\text{cent}}$ 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 $\text{Ru}(1)\text{—C}(1)\text{—Ru}(2)$ and $\text{Ru}(1)\text{—C}(2)\text{—Ru}(2)$ 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 $\text{Cp}_2\text{Fe}_2(\text{CO})_4$.²⁸ The Ru—Ru bond distance is 2.722(2) Å, which is slightly shorter than that in $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ (2.735(2) Å).²⁹

By the reaction of $\text{Cp}_2\text{Ru}_2(\text{CO})_2(\text{COC}_2\text{Ph}_2)$ with ^{13}CO (1 atm) in toluene at 90°C , diphenylacetylene was displaced to give $\text{Cp}_2\text{Ru}_2(\text{CO})_3(^{13}\text{CO})$ (**5**) in 93% yield. The mass spectrum of **5** showed that there was only one ^{13}CO group in the complex. Complex **6**, $\text{Cp}_2\text{Ru}_2(\text{CO})(^{13}\text{CO})(\text{COC}_2\text{Ph}_2)$, easily prepared from **5**, reacted with phosphines to give $\text{Cp}_2\text{Ru}_2(\text{CO})_2(^{13}\text{CO})(\text{PMe}_3)$ (**7**) and $\text{Cp}_2\text{Ru}_2(\text{CO})_2(^{13}\text{CO})(\text{PPh}_3)$ (**8**). The IR spectrum (Table 2) of compound **5** consists of six $\nu(\text{CO})$ bands, four in the terminal carbonyl region and two in the bridging region. The unlabeled complex, $\text{Cp}_2\text{Ru}_2(\text{CO})_4$, has four carbonyl bands, three terminal and one bridging.¹⁰ To understand the spectrum of the ^{13}CO -labeled compound **5**, the positions of its $\nu(\text{CO})$ bands were estimated by assuming that each of the four bands of $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ could be approximated by calculating the ^{13}CO isotope effect using a diatomic vibrational model: $[\nu(^{13}\text{C})]^2/[\nu(^{12}\text{C})]^2 = \{m(^{12}\text{C})[m(^{13}\text{C}) + m(\text{O})]\}/\{m(^{13}\text{C})[m(^{12}\text{C}) + m(\text{O})]\}$, 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 four bands in $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ 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 $\nu(\text{CO})$ 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 $\nu(\text{CO})$ values for **5**. Compounds **6–8** also give IR spectra (Table 2) that have $\nu(\text{CO})$ bands that can be satisfactorily explained by this method of estimating the $\nu(\text{CO})$ values for 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. Gansow³⁰ had previously studied the low-temperature ^{13}C NMR spectrum of $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ and observed separate singlet signals for the terminal and bridging CO groups at -118°C in 95% $\text{CH}_2\text{Cl}_2/5\%$ CS_2 .

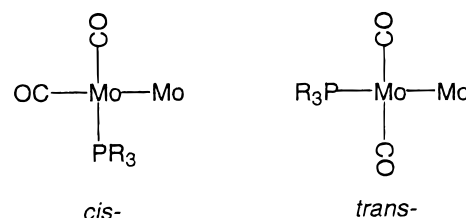


Figure 3. Top-down views (Cp excluded for clarity) of cis and trans CO ligand arrangements in $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{PR}_3)_2$.

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 ($\sim\delta$ 246 ppm) for the bridging CO groups is split into a doublet by the phosphorus; however the peak ($\sim\delta$ 203 ppm) for the terminal CO's is not split by phosphorus.

$\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{PR}_3)_2$ Syntheses. Compounds **9–12** were prepared in greater than 75% yields by reacting phosphine (2 molar equiv) with $\text{Cp}_2\text{Mo}_2(\text{CO})_4$. Compound **12** was prepared previously by two very different routes. By stirring $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ and PPh_3 together in toluene, Curtis and Klingler³¹ obtained **12** in 41% yield. Bruce et al. prepared **12** in 89% yield by reaction of $\text{Mo}(\text{CO})_3(\text{PPh}_3)_3$ with CpH in refluxing dibutyl ether.³² The relatively high $\nu(\text{CO})$ values (Table 3) suggest that all of the $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{PR}_3)_2$ complexes have only terminal CO ligands. IR studies of $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{PR}_3)_2$ ($\text{R} = \text{Ph}, \text{OMe}$)³¹ 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 $\nu(\text{CO})$ bands for the symmetric and asymmetric vibrational modes.

Protonation Reactions. Quantitative formation of the hydride-bridged dinuclear Ru complexes $1\text{H}^+\text{CF}_3\text{SO}_3^-$ – $5\text{H}^+\text{CF}_3\text{SO}_3^-$, $7\text{H}^+\text{CF}_3\text{SO}_3^-$, and $8\text{H}^+\text{CF}_3\text{SO}_3^-$ occurs (eq 3) upon addition of 1 equiv of triflic acid to complexes **1–5**, **7**, and **8**. The CO-bridged structure of the reactants is converted to the nonbridged 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 δ –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 ligand. The ^1H NMR signals for the Cp groups in the protonated dimers are approximately 0.7 ppm downfield of those for **1–4**.

The $\nu(\text{CO})$ bands of the protonated dimers are higher than those of **1–4**, and there are no $\nu(\text{CO})$ bands below 1850 cm^{-1} , which indicates that there are no bridging CO groups (Table 1). Complex 5H^+ , $\text{Cp}_2\text{Ru}_2(\text{CO})_3(^{13}\text{CO})(\mu\text{-H})^+$, exhibits five $\nu(\text{CO})$ bands (Table 4) while the analogous unlabeled compound $\text{Cp}_2\text{Ru}_2(\text{CO})_4(\mu\text{-H})^+$ displays only three $\nu(\text{CO})$ bands.¹⁰ Table 4 lists IR data for both of these compounds as well as estimated wavenumbers for $\nu(\text{CO})$ 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 for the unlabeled complex. The remaining two calculated bands (2003 and 1972 cm^{-1}) are in reasonable

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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 equivalent terminal carbonyl groups. For compounds 7H^+ and 8H^+ , there are three peaks in the terminal carbonyl region as expected for a structure (Figure 2) 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 $J_{\text{P-C}}$ 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 $\text{Ru}(\text{CO})_2\text{Cp}$ end of the dimers. The doublet with the large $J_{\text{P-C}}$ coupling constant (19.3 Hz for 7H^+ ; 18.4 Hz for 8H^+) is assigned to the CO on the $\text{Ru}(\text{CO})(\text{PR}_3)\text{Cp}$ end of the dimers. When the ^{13}C NMR spectrum was taken with ^1H coupling, each of the three ^{13}C signals became a doublet of doublets, and the $^2J_{\text{H-C}}$ coupling constants (3.1, 3.5, 3.5 Hz for 7H^+ ; 2.9, 3.8, 3.1 Hz for 8H^+) involving all three 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, $\text{Cp}_2\text{Ru}_2(\text{CO})_4(\mu\text{-H})^+$, is longer (3.037 Å)³ than that of $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ (2.735(2) Å).²⁹ 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 (average 1.868 Å in 1H^+ vs 1.855(9) Å in **1**). This small change in the Ru–C distance to the terminal carbonyl groups is also observed in the protonation of $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ (average 1.88 Å in $\text{Cp}_2\text{Ru}_2(\text{CO})_4(\mu\text{-H})^+$ vs 1.86 Å in $\text{Cp}_2\text{Ru}_2(\text{CO})_4$).^{10,29} The bridging hydride in 1H^+ was located, and it appears to be closer to the ruthenium atom with the phosphine (Ru(1)–H 1.67(3) Å vs 1.75(3) Å for Ru(2)–H).

Quantitative formation of the hydride-bridged dinuclear Mo complexes $9\text{H}^+\text{CF}_3\text{SO}_3^-$ – $11\text{H}^+\text{CF}_3\text{SO}_3^-$ occurs (eq 4) upon addition of 1 equiv of triflic acid to complexes **9**–**11**. The products were characterized by IR and ^1H and ^{31}P NMR spectroscopy. A triplet is observed for the hydride ligand at approximately δ –20 ppm in the ^1H 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 $\nu(\text{CO})$ 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**, $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{dppm})$ is known²⁰ to react with $\text{HBF}_4\cdot\text{Et}_2\text{O}$ to give $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{dppm})(\mu\text{-H})^+\text{BF}_4^-$, which contains a bridging hydride. This complex, whose structure was established by X-ray diffraction studies, has IR and ^1H NMR spectra^{21,22} 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 $\text{CF}_3\text{SO}_3\text{H}$ in DCE solvent at 25.0 °C according to eqs 3 and 4, are presented in Table 8. Plots of temperature vs amount of acid added were linear, indicating that the protonations occurred rapidly and stoichiometrically.²⁵ 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 1 equiv of the

Table 8. Heats of Protonation (ΔH_{MHM}) of $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PR}_3)$ and $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{PR}_3)_2$

metal complex	$-\Delta H_{\text{MHM}},^{a,b}$ kcal/mol
$\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PMe}_3)$ (1)	30.0(4)
$\text{Cp}_2\text{Ru}_2(\text{CO})_4$	18.4(1) ^c
$\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{PMe}_3)_2$ (9)	27.4(2)
$\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{PMe}_2\text{Ph})_2$ (10)	18.9(5)

^a For protonation with 0.1 M $\text{CF}_3\text{SO}_3\text{H}$ in DCE solvent at 25.0 °C.

^b Numbers in parentheses are average deviations from the mean of at least four titrations. ^c Reference 10.

base diphenylguanidine. The resulting solution was passed through an alumina column (1.5 × 30 cm) eluting with $\text{CH}_2\text{-Cl}_2$. Isolation of the pure, unprotonated complexes (**1**, **8**, **9**) was achieved by recrystallization of the complexes from $\text{CH}_2\text{-Cl}_2$ by layering with hexanes.

Discussion

Protonation of $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PR}_3)$. Reactions of the CO-bridged $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PR}_3)$ complexes (**1**–**4**) with $\text{CF}_3\text{SO}_3\text{H}$ proceed according to eq 3 to give products $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PR}_3)(\text{H})^+$ in which all of the CO ligands are nonbridging. An X-ray diffraction study of $1\text{H}^+\text{CF}_3\text{SO}_3^-$ supports this structural assignment (Figure 2). The site of protonation in the $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PR}_3)(\text{H})^+$ 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 $\text{Cp}^*\text{Ir}(\text{CO})(\text{PR}_3)$ complexes is 15.7–16.6 kcal/mol more basic than that in $\text{Cp}^*\text{Ir}(\text{CO})_2$.^{11,33} Assuming that ΔS is the same for the protonation of all of these complexes, the equilibrium constant (K) for protonation of the $\text{Cp}^*\text{Ir}(\text{CO})(\text{PR}_3)$ complexes is estimated ($\Delta G = \Delta H_{\text{HM}} = -RT \ln K$) to be 5×10^{11} times greater than that for protonation of $\text{Cp}^*\text{Ir}(\text{CO})_2$.^{11,33} In a variety of other metal carbonyl complexes, the basicities of the metals as measured by the equilibrium constant (K) for protonation also increase many orders of magnitude when a CO ligand in the complex is replaced by a phosphine.⁴ Thus, in the $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PR}_3)(\text{H})^+$ complexes, one might expect the H ligand to be bonded to the Ru in the relatively basic $\text{Cp}(\text{CO})(\text{PR}_3)\text{Ru}$ unit as in **A** (see Introduction). The other likely 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}C -labeled $\text{Cp}_2\text{Ru}_2(\text{CO})_2(^{13}\text{CO})(\text{PR}_3)(\text{H})^+$ complexes, where $\text{PR}_3 = \text{PMe}_3$ (7H^+) or PPh_3 (8H^+), were performed. The ^{13}C CO ligand was distributed among the three 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 $J_{\text{C-P}}$ coupling constant for the ^{13}C CO group in the $\text{Cp}(\text{CO})(\text{PR}_3)\text{Ru}$ unit than for the ^{13}C CO's in the $\text{Cp}(\text{CO})_2\text{Ru}$ moiety, each of the three ^{13}C signals were assigned to the three different ^{13}C CO ligands. With these assignments, it was possible to determine, from a proton-coupled ^{13}C NMR spectrum, $J_{\text{C-H}}$ coupling constants between each CO and the hydride. In 7H^+ , $J_{\text{C-H}}$ for hydride coupling to the CO in $\text{Cp}(\text{CO})(\text{PMe}_3)\text{Ru}$ was 3.1 Hz; $J_{\text{C-H}}$ values for hydride coupling to the two inequivalent CO's in $\text{Cp}(\text{CO})_2\text{Ru}$ were both 3.5 Hz. In 8H^+ , $J_{\text{C-H}}$ for the CO in $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}$ was 2.9 Hz; $J_{\text{C-H}}$ values for the two CO groups in $\text{Cp}(\text{CO})_2\text{Ru}$ 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-H} values are reasonable for bridging hydride-to- ^{13}CO coupling is supported by a J_{C-H} value of 4.0 Hz for hydride coupling to the four equivalent ^{13}CO ligands in $\text{Cp}_2\text{Ru}_2(\text{CO})_3(^{13}\text{CO})(\mu\text{-H})^+$, 5H^+ . If the proton were on the Ru at the $\text{Cp}(\text{CO})(\text{PR}_3)\text{Ru}$ end of the molecule (structure **A**), a significantly larger J_{C-H} value for coupling between the ^{13}CO and H on the same Ru would be expected. Such a configuration of ligands is present in $\text{CpRu}(^{13}\text{CO})(\text{PPh}_3)\text{H}$, and the J_{C-H} coupling constant (9.1 Hz) is indeed larger than that for the bridging hydride complex $\text{Cp}_2\text{Ru}_2(\text{CO})_3(^{13}\text{CO})(\mu\text{-H})^+$, 5H^+ , and it is larger than those for 7H^+ and 8H^+ . Thus, the NMR evidence, as well as the X-ray diffraction study, strongly supports structure **B** for the $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PR}_3)(\mu\text{-H})^+$ 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 ($-\Delta H_{\text{MHM}}$) of $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PMe}_3)$ (**1**) according to eq 3 is 30.0(4) kcal/mol (Table 8) as compared with only 18.4(1) kcal/mol for the carbonyl analogue $\text{Cp}_2\text{Ru}_2(\text{CO})_4$.¹⁰ 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 nonbridged isomer and ΔH_a for protonation of the nonbridged isomer. The ΔH_b for $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ is known^{30,34} to be approximately +2 kcal/mol; since $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ is approximately 50% in the CO-bridged form, about +1 kcal is required to convert the bridged isomer to the nonbridged form. The ΔH_a value for $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ is then –19.4 kcal/mol, roughly +1 kcal/mol more exothermic than ΔH_{MHM} .

For $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PMe}_3)$ (**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 $\text{Cp}_2\text{Ru}_2(\text{CO})_4$. Thus, the energy required to convert **1** from the bridged to the nonbridged form would make the overall ΔH_{MHM} value less exothermic than it would be if its ΔH_b were comparable to that of $\text{Cp}_2\text{Ru}_2(\text{CO})_4$. Therefore, if $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ and $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PMe}_3)$ (**1**) had the same ΔH_b values, **1** would be even more basic than $\text{Cp}_2\text{Ru}_2(\text{CO})_4$; that is, there would be more than the observed 11.6 kcal/mol difference in their ΔH_{MHM} values.

Previously,¹⁰ we compared the basicity of the Ru–Ru bond in the dinuclear $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ with that of the single Ru atom in mononuclear $\text{CpRu}(\text{CO})_2\text{H}$. Although this comparison relied on an estimate of $-\Delta H_{\text{HM}}$ for $\text{CpRu}(\text{CO})_2\text{H}$, it was nevertheless possible to state that the Ru–Ru bond in $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ was substantially more basic than the Ru in $\text{CpRu}(\text{CO})_2\text{H}$. In the present studies, it would be desirable to compare $-\Delta H_{\text{MHM}}$ for **1** with $-\Delta H_{\text{HM}}$ for $\text{CpRu}(\text{CO})(\text{PMe}_3)\text{H}$. While the latter complex is known,³⁵ its basicity is not. However, it can be estimated from $-\Delta H_{\text{HM}}$ (21.2(4) kcal/mol) for $\text{CpRu}(\text{PMe}_3)_2\text{Cl}$ 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.^{36,37} Thus, the overall estimated basicity ($-\Delta H_{\text{HM}}$) of $\text{CpRu}(\text{CO})(\text{PMe}_3)\text{H}$ is 22 kcal/mol. Therefore, the basicity ($-\Delta H_{\text{MHM}}$) of the Ru–Ru bond in $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PMe}_3)$ (30.0 kcal/mol) is greater than that of the Ru in $\text{CpRu}(\text{CO})(\text{PMe}_3)\text{H}$ (22 kcal/mol). Of course, such comparisons of di- and mononuclear complex basicities depend on the choice of the compared

mononuclear complex. If $\text{CpRu}(\text{CO})(\text{PMe}_3)\text{Cl}$ or $\text{CpRu}(\text{CO})_2\text{H}$ had been selected instead of $\text{CpRu}(\text{CO})(\text{PMe}_3)\text{H}$, the Ru–Ru bond in $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PMe}_3)$ would have been relatively even more basic than the Ru in these mononuclear complexes, because $\text{CpRu}(\text{CO})(\text{PMe}_3)\text{Cl}$ and $\text{CpRu}(\text{CO})_2\text{H}$ are substantially less basic than $\text{CpRu}(\text{CO})(\text{PMe}_3)\text{H}$.

Infrared spectra (Table 1) of the $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PR}_3)$ complexes in CH_2Cl_2 solvent show the expected decrease in $\nu(\text{CO})$ as the $\text{PMe}_x\text{Ph}_{3-x}$ ligand donor strength increases. For example, $\nu(\text{CO})$ for the PPh_3 complex is 1947 cm^{-1} while that for the PMe_3 complex is 1929 cm^{-1} . In contrast, the $\nu(\text{C}=\text{O})$ value for the bridging CO groups increases slightly as the $\text{PMe}_x\text{Ph}_{3-x}$ donor strength increases. Thus, $\nu(\text{C}=\text{O})$ is 1725 cm^{-1} for the PPh_3 complex, 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 Section). Although the same trend is observed in the analogous $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{PR}_3)$ complexes,²⁷ a convincing explanation for these data is not apparent.

Protonation of $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{PR}_3)_2$ Complexes. These complexes have only terminal CO ligands both before and after protonation (eq 4). The basicity ($-\Delta H_{\text{MHM}}$) of $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{PMe}_3)_2$ (27.4(2) kcal/mol) is substantially higher than that of the closely related $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{PMe}_2\text{Ph})_2$ (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 ligands in $\text{Fe}(\text{CO})_3(\text{PR}_3)_2$ (2.1 kcal/mol) and in $\text{CpOs}(\text{PR}_3)_2\text{Br}$ (3.2 kcal/mol).^{36,37} It is even larger than that observed in *fac*- $\text{W}(\text{CO})_3(\text{PR}_3)_3$ (2.0 kcal/mol), where three PR_3 ligands are replaced.³⁸ Thus, the Mo–Mo bond basicity in these $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{PR}_3)_2$ 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 and co-workers³⁹ studied the protonation in ethanol of the series of $\text{Fe}_2(\text{CO})_4(\mu\text{-SMe})_2\text{L}_2$ ($\text{L} = \text{PMe}_3, \text{PMe}_2\text{Ph}, \text{PMePh}_2, \text{PPh}_3$) complexes where the phosphine ligands are trans to the Fe–Fe bond. When $\text{L} = \text{PMe}_3$ or PMe_2Ph , the compounds could be completely protonated with an excess of aqueous HCl. However, when $\text{L} = \text{PMePh}_2$ and PPh_3 , excess HCl would give only partial protonation of the Fe–Fe bond and the protonated complexes could not be isolated. Poilblanc attributes this drastic difference in basicity to the trans disposition of the phosphines.

The $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{PR}_3)_2$ complexes are clearly more basic than $\text{Cp}_2\text{Mo}_2(\text{CO})_6$, which requires 3 equiv of $\text{CF}_3\text{SO}_3\text{H}$ in $\text{CD}_2\text{-Cl}_2$ solvent for complete protonation. The $\text{Cp}_2\text{Mo}_2(\text{CO})_6(\mu\text{-H})^+$ 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 .⁴⁰ It has also been prepared from the reaction of $\text{CpMo}(\text{CO})_3\text{H}$ with $\text{CpMo}(\text{CO})_3(\text{BF}_4)$.⁴¹

When compared with the $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{L})$ complexes, $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{PMe}_3)_2$ has an intermediate basicity ($-\Delta H_{\text{MHM}}$) in the series $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PMe}_3)$ (30.0 kcal/mol) > $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{PMe}_3)_2$ (27.4 kcal/mol) > $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ (18.4 kcal/mol). Because of the differences in metals, ligands, and structures, many factors may contribute to this trend.

Summary

NMR studies lead to the interesting conclusion that the site of protonation in the unsymmetrically substituted $\text{Cp}(\text{PMe}_3)\text{Ru}(\mu\text{-H})$

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$\text{CO})_2\text{Ru}(\text{CO})\text{Cp}$ (**1**) is the Ru–Ru bond rather than the Ru bearing the strongly donating PMe_3 ligand. The Ru–Ru bond in $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PMe}_3)$ is 11.6 kcal/mol more basic than that in $\text{Cp}_2\text{Ru}_2(\text{CO})_4$, as expected for the replacement of a CO ligand by PMe_3 . The Ru–Ru bonds in $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PMe}_3)$ and $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ are substantially more basic than the Ru in related mononuclear complexes such as $\text{CpRu}(\text{CO})(\text{PMe}_3)\text{H}$ and $\text{CpRu}(\text{CO})_2\text{H}$. The effect of changing the PR_3 ligand in $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{PR}_3)_2$ on the basicity of the Mo–Mo bond is much larger than comparable effects on the basicities of mononuclear complexes.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for the structures of **1** and $\text{1H}^+\text{CF}_3\text{SO}_3^-$ are available on the Internet only. Access information is given on any current masthead page.

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