the bromide complex was dissolved in hexane (60 mL) and crystallized (from ca. 20 mL of solvent, −25 °C). The orange plates (mp >280 °C) were collected and dried under vacuum: IR (Nujol) 1410 (w), 1289 (m), 1271 (m), 1060 (w), 1016 (m), 929 (s), 840 (m), 708 (m), 660 (m) cm^{-1}. Anal. Calcd for $BrC_{16}H_{33}P_2Ru$: Br, 17.1; C, 41.0; H, 7.10; P, 13.2. Found: Br, 17.1; C, 41.0; H, 7.07; P, 13.3.

[(η^5-C_5Me_5)Ru(PMe_3)$_2$(CO)][PF_6]. Carbon monoxide was bubbled through a refluxing methanol solution (25 mL) of (η^5-C_5Me_5)Ru(PMe_3)$_2$Cl (0.18 g, 0.42 mmol) and KPF_6 (0.08 g, 0.43 mmol). After 6 h, the volatile components were removed under vacuum, and the residue was extracted with methylene chloride (20 mL). This solution was concentrated to ca. 6 mL and diethyl ether (35 mL) was added, depositing white microcrystals. Cooling to −70 °C caused further crystallization. The yield of isolated material (mp >280 °C) was 0.20 g (85%): IR (Nujol) 1935 (s), 1281 (w), 949 (s), 820 (s), 721 (w), 666 (w) cm^{-1}. Anal. Calcd for $C_{17}F_6H_{33}OP_3Ru$: C, 36.4; H, 5.99; P, 16.5. Found: C, 36.5; H, 6.04; P, 16.4.

[(η^5-C_5Me_5)Ru(PMe_3)$_2$HCl][PF_6]. A flask was charged with (η^5-C_5Me_5)Ru(PMe_3)$_2$Cl (0.24 g, 0.57 mmol), NH_4PF_6 (0.10 g, 0.61 mmol), and tetrahydrofuran (20 mL). The solution was refluxed for 17 h, after which the solvent was evaporated and methylene chloride (20 mL) added. After filtration, this solution was evaporated to ca. 12 mL and diethyl ether (10 mL) was added. Cooling (−25 °C) afforded yellow crystals (mp 208–213 °C dec). Further crystallization from the mother liquors resulted in an overall yield of 54%: IR (Nujol) 2012 (w), 1300 (w), 1284 (m), 1274 (w sh), 1069 (w), 1013 (w), 940 (s), 830 (s), 734 (m), 705 (m), 672 (m), 673 (m), 550 (m), 356 cm^{-1}. Anal. Calcd for $C_{16}ClF_6H_{34}P_3Ru$: C, 33.7; H, 6.01. Found: C, 33.8; H, 6.05.

Acknowledgment. Financial support from the National Science Foundation (INT-8106810) and the Department of Energy (DE-AT03-79ER10491) is gratefully acknowledged. We also wish to acknowledge Professors L. M. Venanzi and P. Pino for stimulating discussions and laboratory space and equipment at ETH, Zurich, Switzerland, where a portion of this work was conducted by T.D.T. Dr. G. Consiglio is also thanked for valuable discussions.

Registry No. (η^5-C_5Me_5)Ru(NBD)Cl, 87640-46-8; (η^5-C_5Me_5)$_2$Ru, 84821-53-4; (η^5-C_5Me_5)Ru(PMe_3)$_2$Cl, 87640-47-9; (η^5-C_5Me_5)Ru(PMe_3)$_2$Br, 87640-48-0; (η^5-C_5Me_5)Ru(PMe_3)$_2$Me, 87640-49-1; (η^5-C_5Me_5)Ru(PMe_3)$_2$Et, 87640-50-4; (η^5-C_5Me_5)Ru(PMe_3)$_2$$CH_2CMe_3$, 87640-51-5; ($\eta^5$-$C_5Me_5$)Ru($PMe_3$)$_2$$CH_2SiMe_3$, 87640-52-6; ($\eta^5$-$C_5Me_5$)Ru($PMe_3$)$_2$H, 87640-53-7; [$\eta^5$-$C_5Me_5$)Ru($PMe_3$)$_2$Co][$PF_6$], 87640-55-9; [$\eta^5$-$C_5Me_5$)Ru($PMe_3$)$_2$HCl][$PF_6$], 87640-57-1; (Ru(NBD)$Cl_2$)$_x$, 42740-82-9; *trans*-$RuCl_2(PMe_3)_4$, 71936-64-6.

Reactivity of Bis(pentamethylcyclopentadienyl)zirconium Hydrides with Group 8 Transition-Metal Carbonyls[†]

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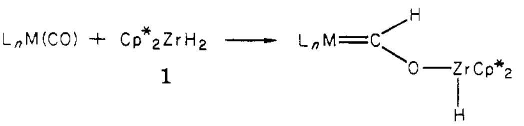
The reactions of $Cp^*_2ZrH_2$ ($Cp^* \equiv \eta^5$-C_5Me_5) with cyclopentadienyl carbonyl complexes of Co, Rh, Fe, and Ru have been carried out in order to explore the generality of Zr–H addition across the C–O bond of transition-metal carbonyls to form the corresponding zirconoxycarbene complexes. These reactions have been observed to follow two different reaction pathways. The first proceeds by interaction of a carbonyl group with the zirconium center, reductive elimination of H_2, and rearrangement to afford carbonyl-bridged "early" and "late" mixed-metal dimers. Thus CpM(μ-CO)(μ-η^1,η^2-CO)ZrCp^*_2 ($Cp \equiv \eta^5$-C_5H_5; M = Co, Rh) and Cp(H)Ru(μ-CO)(μ-η^1,η^2-CO)ZrCp^*_2 are obtained by treatment of CpM$(CO)_2$ (M = Co, Rh) or CpRu$(CO)_2$(H) with $Cp^*_2ZrH_2$. The second reaction pathway involves CO reduction by Zr–H, giving the corresponding group 8 metal zirconoxycarbene complex, or products arising from zirconoxycarbene intermediates. Thus Cp(CO)M=CHOZr(X)Cp^*_2 (M = Co, Rh; X = Cl, F) are obtained by treatment of CpM$(CO)_2$ with Cp^*_2Zr(H)(X) (X = Cl, F). The reaction between CpM(CO)(PMe_3)(H) (M = Fe, Ru), $Cp^*_2ZrH_2$, and PMe_3 yields Cp$(PMe_3)_2$M–CH_2O–Zr(H)Cp^*_2, whereas CpM$(CO)_2$(CH_3) (M = Fe, Ru), $Cp^*_2ZrH_2$, and PMe_3 afford Cp^*_2Zr(H)(OCH=CH_2) and CpM(CO)(PMe_3)H.

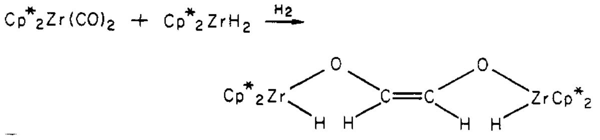
Introduction

In view of the ease with which $Cp^*_2ZrH_2$ (1) ($Cp^* \equiv \eta^5$-C_5Me_5) reduces group 5 and 6 transition-metal carbonyls to the corresponding oxycarbene complexes,[1] the reactions of 1 and related hydrides with other metal carbonyls have been investigated to explore the generality of Zr–H reduction of coordinated CO. Prior to this work $Cp^*_2Zr(CO)_2$ was the only transition-metal dicarbonyl complex observed to give a clean product, *cis*-(Cp^*_2ZrH)$_2$(μ-OCH=CHO–),[1b,2] upon treatment with $Cp^*_2ZrH_2$ (eq 2). Unfortunately, no intermediates could be identified during the course of this reaction to provide information as to the mechanism of this unique transformation. The reactivity of 1 with other



(1)

L_nM = Cp_2Cr, Cp_2Mo, Cp_2W, Cp_2NbR; $Cp \equiv \eta^5$-C_5H_5



(2)

[†] Contribution No. 6874.

(1) (a) Wolczanski, P. T.; Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* 1979, *101*, 218. (b) Threlkel, R. S.; Bercaw, J. E. *Ibid.* 1981, *103*, 2650.

(2) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* 1978, *100*, 2716.

Table I. NMR[a] and IR[b] Data

compound	IR	¹H NMR	
$CpCo(CO)_2ZrCp*_2$ (**3a**)	ν(CO) 1737, 1683	C_5H_5	4.91 (s)
		$C_5(CH_3)_5$	1.71 (s)
$CpRh(CO)_2ZrCp*_2$ (**3b**)	ν(CO) 1752, 1696	C_5H_5	5.40 (s)
		$C_5(CH_3)_5$	1.76 (s)
$Cp(CO)Co{=}CHO{-}Zr(Cl)Cp*_2$ (**5a**)	ν(CO) 1947	Co=C*H*O—Zr	12.6 (s)
		C_5H_5	5.48 (s)
		$C_5(CH_3)_5$	1.82 (s)
$Cp(CO)Rh{=}CHO{-}Zr(Cl)Cp*_2$ (**5b**)	ν(CO) 1952	Rh=CHO—Zr	13.1 (s)
		C_5H_5	4.94 (s)
		$C_5(CH_3)_5$	1.87 (s)
$Cp(CO)Co{=}CHO{-}Zr(F)Cp*_2$ (**7a**)	ν(CO) 1948	Co=CHO—Zr	12.6 (s)
		C_5H_5	4.87 (s)
		$C_5(CH_3)_5$	1.80 (s)
$Cp(CO)Rh{=}CHO{-}Zr(F)Cp*_2$ (**7b**)[c]	ν(CO) 1956	Rh=CHO—Zr	13.1 (s)
		C_5H_5	5.41 (s)
		$C_5(CH_3)_5$	1.80 (s)
$Cp(H)Ru(CO)_2ZrCp*_2$ (**9**)	ν(CO) 1706, 1671	C_5H_5	5.17 (s)
		$C_5(CH_3)_5$	1.67 (s)
		$C_5(CH_3)_5$	1.74 (s)
		RuH	−15.7 (s)
$Cp(PMe_3)_2Fe{-}CH_2O{-}Zr(H)Cp*_2$ (**11a**)		$Fe{-}CH_2O{-}Zr$	5.07 (t, $^3J_{P-H} = 7$)
		C_5H_5	3.87 (t, $^3J_{P-H} = 2$)
		$C_5(CH_3)_5$	2.07 (s)
		$P(CH_3)_3$	1.04 (t, $^3J_{P-H} = 3$)
		ZrH	5.25 (s)
$Cp(PMe_3)_2Ru{-}CH_2O{-}Zr(H)Cp*_2$ (**11b**)		$Ru{-}CH_2O{-}Zr$	5.32 (dd, $^3J_{P-H} = 7, 9$)
		C_5H_5	4.99 (s)
		$C_5(CH_3)$	2.09 (s)
		$P(CH_3)_3$	1.11 (m)
		ZrH	5.22 (s)

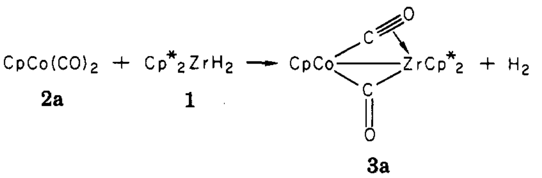
[a] NMR spectra in benzene-d_6 or toluene-d_8 at 34 °C at 90 MHz. Chemical shifts in δ measured from internal Me_4Si, coupling constants in hertz. [b] IR spectra recorded as Nujol mulls. Values given in cm⁻¹. Additional bands are listed in the Experimental Section. [c] IR spectrum in C_6H_6.

transition-metal dicarbonyl complexes has been examined in order to gain some understanding of reaction pathways available to compounds of this type. The preparation of some carbene hydride and carbene alkyl complexes of iron and ruthenium has also been attempted to gain further insight about the mechanism of the migratory insertion, previously reported for zirconoxycarbene hydride and alkyls of niobocene.[1b,3]

We report herein our investigations of the reactions of $Cp*_2ZrHX$ (X = H, F, Cl) with some group 8 transition-metal mono- and dicarbonyl complexes. These reactions have been observed to follow two different reaction pathways. The first proceeds by an interaction of a carbonyl group with the zirconium center, reductive elimination of H_2 (for X = H), and rearrangement to afford an "early" and "late" mixed-metal dimer. The second class involves CO reduction by the zirconium hydride, giving group 8 metal zirconoxycarbene complexes or products arising from zirconoxycarbene intermediates.

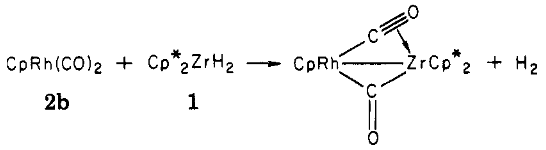
Results

1. Reactivity of Zirconium Hydrides with Cobalt and Rhodium Carbonyls. We have previously reported that the reaction of $Cp*_2ZrH_2$ (**1**) and $CpCo(CO)_2$ (**2a**) affords $CpCo(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CO)ZrCp*_2$ (**3a**).[4] A single-crystal X-ray diffraction study has confirmed the structure of **3a** as containing a cobalt–zirconium single bond, bridged by two carbonyls with distinctly different bonding modes. Treatment of $CpRh(CO)_2$ (**2b**) with $Cp*_2ZrH_2$ (**1**) at 25 °C for 30 min affords a new complex, $CpRh(CO)_2ZrCp*_2$ (**3b**),



(3)

2a 1 3a



(4)

2b 1 3b

that can be isolated in 44% yield. The similarity of the ¹H NMR and IR (ν_{CO} = 1752 and 1696 cm⁻¹ for **3b** compared to ν_{CO} = 1737 and 1683 cm⁻¹ for **3a**) spectra (Table I) of **3b** to those of **3a** indicates that the rhodium–zirconium dimer is isostructural with **3a**, containing a conventional bridging CO and a $\mu\text{-}\eta^1,\eta^2$-bridging CO. However, in contrast to the preparation of $CpCo(CO)_2ZrCp*_2$ in which no intermediates are seen, a mixture of $CpRh(CO)_2$ and **1** in a sealed NMR tube shows the initial formation of an intermediate with a downfield resonance in the ¹H NMR spectrum, suggesting the presence of a zirconoxycarbene ligand. Over several minutes at 25 °C this complex converts to **3b**, which is the only product that can be isolated from solution. Treatment of **2b** with $\{Cp*_2ZrN_2\}_2N_2$ shows no evidence of the transient species, giving **3b** directly.

The ¹³C NMR spectrum of $CpRh(CO)_2ZrCp*_2$ enriched with ¹³CO has only one resonance for the carbonyls at room

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[3] (a) Mango, F. D.; Dvoretzky, I. *J. Am. Chem. Soc.* **1966**, *88*, 2654. (b) Empsall, H. D.; Hyde, E. M.; Markham, M.; McDonald, W. S.; Norton, M. C.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Chem. Commun.* **1977**, 589.

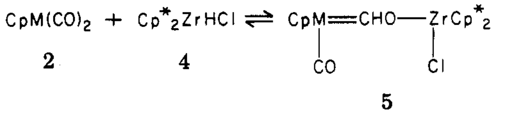
[4] Barger, P. T.; Bercaw, J. E. *J. Organomet. Chem.* **1980**, *201*, C39.

[5] (a) Connor, J. A.; Fischer, E. O. *J. Chem. Soc. A* **1969**, 578. (b) Fischer, E. O.; Kollmeier, H.-J. *Chem. Ber.* 1971, *104*, 1339. (c) Klabunde, U.; Fischer, E. O. *J. Am. Chem. Soc.* **1967**, *89*, 7141.

$$\underset{\mathbf{2b}}{2CpRh(CO)_2} + \{Cp^*_2ZrN_2\}_2N_2 \rightarrow \underset{\mathbf{3b}}{2CpRh(CO)_2ZrCp^*_2} + 3N_2 \quad (5)$$

temperature (δ 254 ($^1J_{C-Rh}$ = 59 Hz)), indicating that the two carbonyls are rapidly interchanging bonding modes. Variable-temperature 22.5-MHz ^{13}C NMR spectra show collapse of this resonance at ca. −60 °C, but attempts to observe the low-temperature limit, where the carbonyls are inequivalent, were unsuccessful at this field strength. However, the 125.8-MHz spectrum at −70 °C shows two broad resonances at δ 298 and 215, due to the carbonyls in the two different bonding modes. This chemical shift difference and the coalescence temperature give an upper limit of 8 kcal/mol for the activation barrier of the fluxional process.

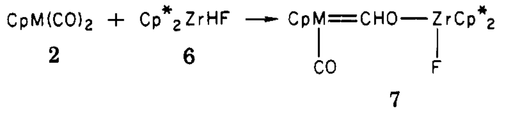
The reductive elimination of H_2 from **1** that leads to the formation of the mixed-metal dimers can be prevented by replacement of one of the zirconium hydrides by a halide. Thus, treatment of an excess of **2** with Cp^*_2ZrHCl (**4**) in



$$\underset{\mathbf{2}}{CpM(CO)_2} + \underset{\mathbf{4}}{Cp^*_2ZrHCl} \rightleftharpoons \underset{\mathbf{5}}{\underset{CO}{\underset{|}{CpM}}{=}CHO{-}\underset{Cl}{\underset{|}{ZrCp^*_2}}} \quad (6)$$

M = Co, Rh

toluene affords the cobalt or rhodium zirconoxycarbene complexes, Cp(CO)M=CHO—Zr(Cl)Cp^*_2 (M = Co (**5a**), Rh (**5b**)), in good yield after 2 h at room temperature. The zirconoxycarbene complexes can be isolated free of dicarbonyl by precipitation with petroleum ether at −78 °C. The corresponding zirconoxycarbene fluoride complexes (**7**) can be prepared in an analogous manner by using Cp^*_2ZrHF (**6**) in place of Cp^*_2ZrHCl.



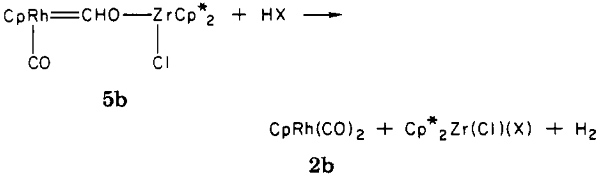
$$\underset{\mathbf{2}}{CpM(CO)_2} + \underset{\mathbf{6}}{Cp^*_2ZrHF} \rightarrow \underset{\mathbf{7}}{\underset{CO}{\underset{|}{CpM}}{=}CHO{-}\underset{F}{\underset{|}{ZrCp^*_2}}} \quad (7)$$

M = Co, Rh

The ^1H NMR spectra of **5** (Table I) show resonances attributable to the Cp and Cp* ligands as well as a downfield peak (**5a**, δ 12.6; **5b**, δ 13.1) attributable to the carbene hydrogen. The IR spectra of Nujol mulls of **5** show one strong band in the CO stretching region at 1947 cm^{-1} for **5a** and 1952 cm^{-1} for **5b**. The ^1H NMR and IR spectra for **7** (Table I) are similar.

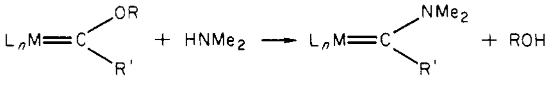
The equilibrium depicted in eq 6, between the zirconoxycarbene complex and the group 8 dicarbonyl and Cp^*_2ZrHCl, can be attained from either direction. Thus the reaction between **2** and **4** is incomplete even after many hours, and both starting materials can be observed in the reaction mixture. Likewise, over several days resonances due to **2** and **4** slowly grow into the ^1H NMR spectra of isolated **5**. In the case of **5a** the equilibrium (at ~0.1 M) consists of approximately 70% Cp(CO)Co=CHO—Zr(Cl)Cp^*_2 to 30% $CpCo(CO)_2$ and Cp^*_2ZrHCl; for **5b** the observed ratio is about 90:10, **5b** to **2b** and **4**.

In the presence of protic acids, HX (X = Cl$^-$, PhCOO$^-$), **5b** is rapidly converted to $CpRh(CO)_2$ and $Cp^*_2Zr(Cl)(X)$



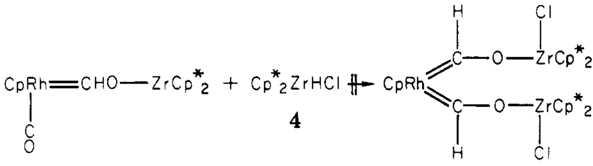
$$\underset{\mathbf{5b}}{\underset{CO}{\underset{|}{CpRh}}{=}CHO{-}\underset{Cl}{\underset{|}{ZrCp^*_2}}} + HX \rightarrow \underset{\mathbf{2b}}{CpRh(CO)_2} + Cp^*_2Zr(Cl)(X) + H_2 \quad (8)$$

at 25 °C with the evolution of H_2. Attempts to prepare an amine-substituted rhodium carbene complex by aminolysis of **5b** with $HNMe_2$, a reaction pathway that is common for Fischer-type carbenes,[15] have been unsuccessful.



(9)

Cp(CO)Rh=CHO—Zr(Cl)Cp^*_2 is unaffected by an excess of Cp^*_2ZrHCl, indicating that the remaining carbonyl is inert toward reduction to give a bis(carbene) complex.



5b **4** (10)

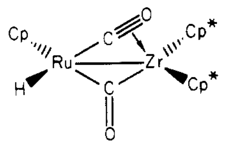
2. Reactivity of Zirconium Hydrides with Iron and Ruthenium Carbonyls. Addition of $Cp^*_2ZrH_2$ to heptane solution of $CpRu(CO)_2H$ (**8**) affords the dark red Cp(H)-$Ru(CO)_2ZrCp^*_2$ (**9**) in 59% isolated yield after 1 h at room temperature. Like $CpM(CO)_2ZrCp^*_2$ (M = Co, Rh), **9** can

$$\underset{\mathbf{8}}{CpRu(CO)_2H} + \underset{\mathbf{1}}{Cp^*_2ZrH_2} \rightarrow \underset{\mathbf{9}}{Cp(H)Ru(CO)_2ZrCp^*_2} + H_2 \quad (11)$$

also be prepared from **8** and $\{Cp^*_2ZrN_2\}_2N_2$ with the liberation of N_2. The IR spectrum of a Nujol mull of **9** is

$$\underset{\mathbf{8}}{2CpRu(CO)_2H} + \{Cp^*_2ZrN_2\}_2N_2 \rightarrow \underset{\mathbf{9}}{2Cp(H)Ru(CO)_2ZrCp^*_2} + 3N_2 \quad (12)$$

similar to those of **3a** and **3b**, exhibiting two intense bands in the carbonyl stretching region as 1706 and 1671 cm^{-1}. The ^1H NMR spectrum of **9** (Table I) shows a peak at δ 5.17 for the Cp ring on Ru and two resonances for the Cp* rings at δ 1.67 and 1.74. A peak, integrating as one proton, appears at δ −15.7 and is assigned to the ruthenium hydride. These results suggest the structure of **9** is similar to those of **3a** and **3b** with Cp and hydride ligands on opposite sides of the metal–carbonyl plane, making the Cp* rings inequivalent. Analogously to the reactions of **3a** and **3b** with carbon monoxide, treatment of **9** with an excess of CO gives a mixture of $CpRu(CO)_2H$ and $Cp^*_2Zr(CO)_2$ after 24 h at room temperature.

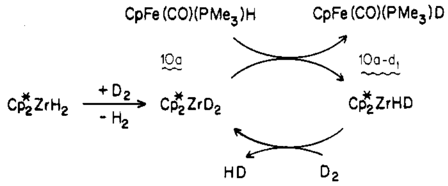


9

When $CpM(CO)(PMe_3)H$ (M = Fe (**10a**), Ru (**10b**)) are treated with $Cp^*_2ZrH_2$, no (net) reaction is observed by ^1H NMR spectroscopy, even after 7 weeks at 25 °C. On the other hand, addition of 4 equiv of PMe_3 to a benzene solution of **10a** and **1** affords $Cp(PMe_3)_2Fe–CH_2O–Zr$-(H)Cp^*_2 (**11a**) after 10 min at room temperature. The ^1H NMR spectrum of **11a** (Table I) is consistent with its

$$\underset{\mathbf{10a}}{CpFe(CO)(PMe_3)H} + \underset{\mathbf{1}}{Cp^*_2ZrH_2} \xrightarrow{PMe_3} \underset{\mathbf{11a}}{Cp(PMe_3)_2Fe–CH_2O–Zr(H)Cp^*_2} \quad (13)$$

Scheme I



formulation as a CH_2O-bridged dimer. The presence of two phosphine ligands on the iron center is clearly indicated by the pseudotriplet (AA′XX′) pattern of the resonance due to the methyl groups on phorphorus and the triplet splitting ($^2J_{PH}$ = 2 Hz) of the Cp resonance at δ 3.87. A broad peak at δ 5.26, integrating to one proton, is assigned as the resonance of the remaining zirconium hydride. The signal for the methylene group appears as a pseudotriplet (AA′XX′) pattern at δ 5.07. The reaction of $CpRu(PMe_3)(CO)H$ (**10b**), 1 equiv of PMe_3, and $Cp*_2ZrH_2$ (1 equiv) proceeds analogously, although much more slowly, to yield a compound identified as $Cp(PMe_3)_2Ru–CH_2O–Zr(H)Cp*_2$ (**11b**) by the close similarity of its ^1H NMR spectrum to that for **11a** (Table I).

In the absence of PMe_3 the hydride ligands of **10a** and **1** readily exchange between the two metal centers. Treatment of a mixture of **10a** and **1** with a large excess

$$\underset{\mathbf{10a}}{CpFe(CO)(PMe_3)H} + \underset{\mathbf{1}}{Cp*_2ZrH_2} \xrightarrow{\text{excess } D_2} \underset{\mathbf{10a}\text{-}d_1}{CpFe(CO)(PMe_3)D} + \underset{\mathbf{1}\text{-}d_2}{Cp*_2ZrD_2} \quad (14)$$

of D_2 at 0 °C for 1 h places deuterium into both iron and zirconium hydride sites. The hydrides of $Cp*_2ZrH_2$ are known to rapidly exchange with D_2;[6] however, $CpFe(CO)(PMe_3)H$ alone is inert to D_2 under these conditions, indicating that the exchange between D_2 and the iron hydride is catalyzed by **1** (Scheme I).

The reactions between $Cp*_2ZrH_2$ and $CpM(CO)_2CH_3$ (M = Fe (**12a**), Ru (**12b**)) also proceed by a pathway which appears to involve hydride transfer to CO. Thus, a mixture of **12b** and **1** with 2 equiv of PMe_3 in a sealed NMR tube

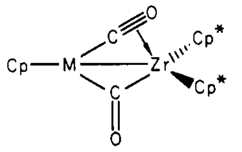
$$\underset{\mathbf{12b}}{CpRu(CO)_2CH_3} + \underset{\mathbf{1}}{Cp*_2ZrH_2} \xrightarrow{PMe_3} \underset{\mathbf{13}}{Cp*_2Zr(OCH{=}CH_2)(H)} + \underset{\mathbf{10b}}{CpRu(CO)(PMe_3)H} \quad (15)$$

affords the previously reported $Cp*_2Zr(OCH{=}CH_2)(H)$[1b] (**13**) and $CpRu(CO)(PMe_3)H$ quantitatively after 2 h at 25 °C. In the case of **12a** the major zirconium-containing product is again **13**, but $CpFe(CO)(PMe_3)H$ is only a minor component of the resulting myriad of iron complexes. A plausible mechanism for this transformation will be discussed in the following section.

Discussion

The reaction of bis(pentamethylcyclopentadienyl)zirconium hydrides with group 8 transition-metal carbonyls have been observed to follow two distinct pathways depending upon the natures of the reactants. Mixed-metal dimers are prepared by treating the dicarbonyls, $CpM(CO)_2$ (M = Co, Rh, RuH), with $Cp*_2ZrH_2$. These molecules represent some of the first examples of metal–metal bonding between Zr and a group 8 metal.[7]

The zirconium–group 8 metal dimers, $CpM(CO)_2ZrCp*_2$ (M = Co, Rh, RuH), have similar structures consisting of a metal–metal single bond bridged by one conventional μ-carbonyl ligand and a CO that is bound in a linear, terminal fashion to the group 8 metal and via a C–O π donation to the zirconium (a μ-η^1,η^2-bonding mode). This formulation has been confirmed by the single-crystal X-ray diffraction structure determination of $CpCo(CO)_2ZrCp*_2$.[4] The μ-η^1,η^2 mode of bonding for a carbonyl bridging two or more metal centers has been previously seen in six molecules. The first such bridge was reported by Colton et al. in 1975 in the structure of $Mn_2(CO)_5(Ph_2P(CH_2)_3PPh_2)_2$.[8] Since that time η^1,η^2-carbonyls have been observed in $Fe_4(CO)_{13}H^-$,[9] $Cp_2Nb(CO)_3MoCp$,[10] $Cp_2(CH_3)Zr(CO)Mo(CO)_2Cp$,[11] $Cp_2Zr(CO)(COCH_3)Mo(CO)Cp$,[11] and $Cp_3Nb_3(CO)_7$,[12] the last being unique in that the CO has a π interaction with two niobiums of the triangular cluster. In each of these compounds, as well as in $CpM(\mu\text{-}\eta^1,\eta^2\text{-}CO)ZrCp*_2$ (M = Co, Rh) and $Cp(H)Ru(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CO)ZrCp*_2$, a π bond is needed to complete the valence electron shells for both metals. All of these molecules are also characterized by a low carbonyl stretching frequency in the IR spectrum due to the η^1,η^2-CO. These three new compounds join this class as the first examples of an η^1,η^2-carbonyl bridging two significantly different metal centers.



M = Co, Rh

That $CpM(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CO)ZrCp*_2$ (M = Co, Rh) and $Cp(H)Ru(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CO)ZrCp*_2$ can also be made from the metal dicarbonyls and $\{Cp*_2ZrN_2\}_2N_2$, a ready source of the coordinatively unsaturated species ($Cp*_2Zr^{II}$), due to the lability of the N_2 ligands, suggests that permethylzirconocene, formed by reductive elimination of H_2 from $Cp*_2ZrH_2$, could be a feasible intermediate in the reaction of $Cp*_2ZrH_2$ with $CpM(CO)_2$ (M = Co, Rh) or $CpRu(CO)_2H$. Since $Cp*_2ZrH_2$ is quite stable to H_2 loss in the absence of $CpM(CO)_2$ (M = Co, Rh) or $CpRu(CO)_2H$ under the reaction conditions, it appears that the dicarbonyl induces the H_2 elimination, possibly by an interaction between the empty zirconium $1a_1$ orbital and the oxygen lone pair or filled C–O π orbital of a carbonyl. Interestingly, simply substituting the second carbonyl of the group 8 complex with PMe_3 effectively arrests reductive elimination of H_2 from $Cp*_2ZrH_2$.

It is conceivable that an alternative mechanism is operating in the reaction between $Cp*_2ZrH_2$ and $CpRu(CO)_2H$. Since the pK_a difference for these two metal "hydrides" is undoubtedly very large, protonation of the Zr–H bond may be expected (eq 16). Such an acid–base reaction has been observed between $Cp*_2ZrH_2$ and

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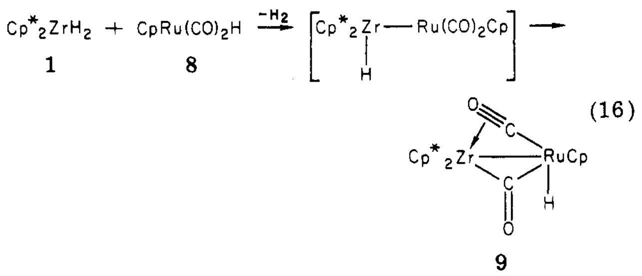
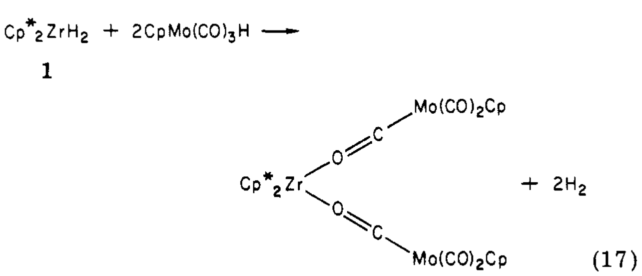


(16)

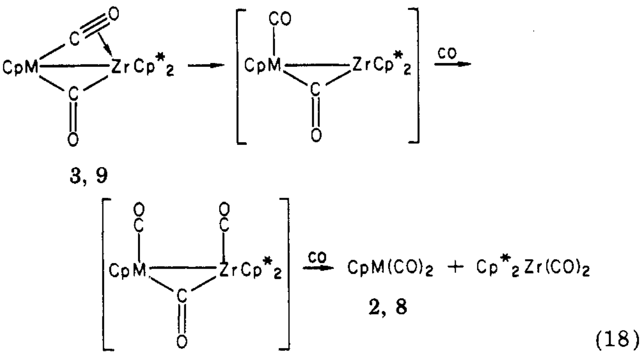
$CpMo(CO)_3H$ to yield $Cp^*_2Zr[OCMo(CO)_2Cp]_2$ (eq 17).[13]



(17)

Indeed, the intermediate shown in eq 16 is closely related to the recently reported complexes $Cp(CO)_2Ru\text{-}Zr(X)Cp_2$ (X = Cl, CH_3, $OCMe_3$),[7] although the Zr-to-Ru transfer needed to afford **9** was not observed for chloride, methyl, or *tert*-butoxide substituents.

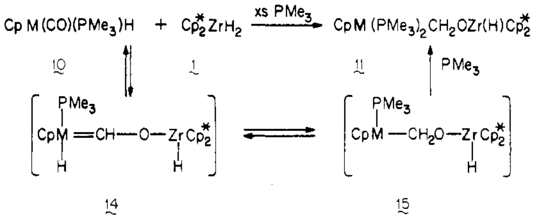
The low activation barrier (less than 8 kcal/mol) for interchange of the carbonyls of $CpRh(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CO)ZrCp^*_2$ is smaller than the barriers observed for $Cp_3Nb_3(CO)_7$[14] and $Mn_2(CO)_5(Ph_2P(CH_2)_3PPh_2)_2$[15] and suggests that the zirconium-carbonyl π interaction is fairly weak. This is supported by the reactions of all three compounds with CO to give $Cp^*_2Zr(CO)_2$ and $CpM(CO)_2$ (M = Co, Rh, RuH), which is presumably initiated by the opening of a coordination site on zirconium by the breaking of the zirconium-carbonyl π bond, (eq 18).



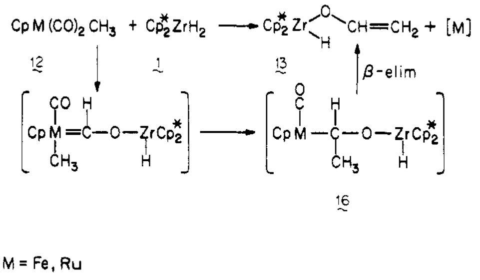
(18)

The observation of a transient species, immediately upon mixing of $CpRh(CO)_2$ and $Cp^*_2ZrH_2$, with the spectral characteristics of a rhodium zirconoxycarbene complex suggests that addition of a zirconium hydride of **1** across the C-O bond of a carbonyl of $CpM(CO)_2$ (M = Co, Rh) is facile, but reversible. Treatment of $CpM(CO)_2$ (M = Co, Rh) with Cp^*_2ZrHX (X = Cl, F), where reductive elimination of HX is thermodynamically prohibitive, affords only the zirconoxycarbene (eq 6 and 7). The reversible nature of the zirconium hydride addition to cobalt and rhodium carbonyls is clearly demonstrated by the equilibrium observed between $CpM(CO)_2$, Cp^*_2ZrHCl, and $Cp(CO)M{=}CHO\text{—}Zr(Cl)Cp^*_2$ (M = Co, Rh) (eq 6).

Scheme II



Scheme III



The lower CO stretching frequencies of the oxycarbene carbonyl complexes (ν_{CO} = 1947 (**5a**) and 1952 cm^{-1} (**5b**)) relative to the dicarbonyls (ν_{CO} = 2028, 1967 (**2a**)[16] and 2051, 1987 cm^{-1} (**2b**))[17] indicates that the zirconoxycarbene is a poorer π-accepting ligand than carbonyl in this system. This conclusion is consistent with the nature of other heteroatom-substituted carbenes.[18] The increased electron density at the carbonyl of **5** and the steric bulk of the permethylzirconocene substituent on the oxycarbene should make the remaining CO less susceptible to hydridic attack. It is not surprising, therefore, that $Cp(CO)Rh{=}CHOZr(Cl)Cp^*_2$ does not react with excess $Cp^*_2Zr(H)(Cl)$ to give a bis(carbene) complex.

Attempts to isolate or spectroscopically observe iron or ruthenium oxycarbene hydride or alkyl complexes have been thwarted by the apparent ease with which the carbene ligand reverts to the metal carbonyl and zirconium hydride or inserts into the group 8 metal-hydride or -alkyl bond. The mechanism for the formation of $Cp(PMe_3)_2M\text{-}CH_2O\text{-}Zr(H)Cp^*_2$ (M = Fe, Ru) (Scheme II) is presumably similar to that of $Cp_2(CO)Nb\text{-}CH_2O\text{-}Zr(H)Cp^*_2$,[1b] proceeding through the initial formation of a transient oxycarbene complex, **14**, which is in equilibrium with **15**, where the carbene ligand has inserted into the M-H bond. Trapping of the coordinatively unsaturated **15** by free PMe_3 to give **11** is expected. That only **10** and **1** are observed in solution in the absence of PMe_3 indicates that the equilibria between the starting complexes, **14** and **15** lie far toward the metal carbonyl and zirconium hydride. These equilibria also provide a mechanism for hydride exchange between iron and zirconium that is required to explain deuterium incorporation into the hydride site of **10a** from D_2 in the presence of **1** (Scheme I).

In the case of the reaction of **1** with the iron and ruthenium methyl complexes **12** an intramolecular pathway, via β-H elimination, is available to the coordinatively unsaturated intermediate **16**, formed upon carbene insertion into the $M\text{-}CH_3$ bond (Scheme III). This step affords the zirconium-containing product $Cp^*_2Zr(OCH{=}CH_2)H$ and $[CpM(CO)H]$ which may be trapped by free PMe_3 to give the observed ruthenium product **10b** or react further to

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give the myriad of iron products seen. As in the reaction of **10** and **1** neither the zirconoxycarbene complex nor inserted intermediates have been observed by spectroscopic methods.

The results discussed above have shown that bis(pentamethylcyclopentadienyl)zirconium hydrides readily add to the C–O bond of group 8 transition-metal carbonyls. The zirconoxycarbene complexes so formed are often present in only low concentrations due to the reversibility of the hydride addition and the rapid migratory insertion of the carbene ligand into a metal–hydride or –alkyl bond.

Experimental Section

General Considerations. All manipulations were performed under an inert atmosphere by employing a nitrogen-filled glovebox and vacuum line techniques. Hydrogen, deuterium, nitrogen and argon were purified by passing through MnO on vermiculate[19] and activated 4-Å molecular sieves. Benzene, toluene, and petroleum ether (30–60 °C) and NMR solvents were vacuum transferred from $LiAlH_4$ or molecular sieves then from "titanocene"[20] prior to use. Carbon monoxide (MCB), ^{13}C carbon monoxide (Monsanto-Mound), and PMe_3 (Strem) were used as received; $NHMe_2$ was vacuum transferred from 4-Å molecular sieves.

$CpCo(CO)_2$,[14] $CpRh(CO)_2$,[15] $CpFe(CO)_2CH_3$,[21] $CpRu(CO)_2CH_3$,[22] $CpRu(CO)_2H$,[23] $CpFe(CO)(PMe_3)H$[24] were prepared by literature methods. $CpFe(CO)(PMe_3)CH_3$ was prepared by treatment of $CpFe(CO)(PMe_3)H$ with CCl_4 followed by CH_3MgBr and isolated by sublimation. $CpRu(CO)(PMe_3)H$ was made by a variation of the reported synthesis of $CpRu(CO)(PPh_3)H$.[23] ^{13}CO enrichment of the carbonyls of $CpRh(CO)_2$ was done by photolysis under a ^{13}CO atmosphere. $Cp^*{}_2ZrH_2$[2] and $\{Cp^*{}_2ZrN_2\}_2N_2$[25] were prepared by literature methods. Conproportionation of $Cp^*{}_2ZrH_2$ and $Cp^*{}_2ZrX_2$ (X = F, Cl) at 150 °C for 2 weeks under an H_2 atmosphere affords $Cp^*{}_2ZrHX$.

^1H NMR spectra were recorded in C_6D_6 or C_7D_8 with Me_4Si as an internal reference using Varian EM-390, JEOL FX90Q, and Bruker WM-500 spectrometers. ^{13}C NMR spectra were recorded on the JEOL and Bruker instruments. IR spectra were recorded as Nujol mulls or benzene solutions on a Beckmann IR 4240 spectrophotometer. Elemental analyses were performed by Alfred Bernhardt Analytical Laboratory and Dornis and Kolbe Microanalytical Laboratory.

$CpRh(CO)_2ZrCp_2$ (3b). Petroleum ether solutions of $Cp^*{}_2ZrH_2$ (500 mg, 1.38 mmol) and $CpRh(CO)_2$ (200 μL, 375 mg, 1.67 mmol) were combined at −78 °C, warmed, and stirred at room temperature for 20 min. All solvent and excess $CpRh(CO)_2$ were removed in vacuo. $CpRh(CO)_2ZrCp^*{}_2$ (510 mg, 44%) was recrystallized from toluene: IR (Nujol mull) 1752 (vs), 1696 (vs), 1027 (w), 780 (s), 650 (m) cm^{-1}. Anal. Calcd for $C_{27}H_{35}O_2RhZr$: C, 55.37; H, 6.02. Found: C, 55.94, 55.87; H, 6.03, 6.06.

Addition of $CpRh(CO)_2$ (ca. 10 μL, ca. 0.08 mmol)) to a C_6D_6 solution of $\{Cp^*{}_2ZrN_2\}_2N_2$ (30 mg, 0.04 mmol) in an NMR tube gives an ^1H NMR spectrum identical with that of **3b** prepared from $Cp^*{}_2ZrH_2$. The IR spectrum of a C_6D_6 solution was also the same as that of **3b** prepared by the above procedure.

Variable-Temperature ^{13}C NMR of $CpRu(CO)_2ZrCp^*{}_2$. Substitution of $CpRh(^{13}CO)_2$ for $CpRh(CO)_2$ in the above procedure allowed the preparation of **3b** enriched with ^{13}C at the carbonyl carbons. Variable-temperature ^{13}C NMR spectra at 22.5 MHz yielded the coalescence temperature, and a spectrum at −70 °C at 125.8 MHz provided an approximate chemical shift difference of the resonances of the inequivalent carbonyl carbons in the low-temperature limit. Use of the Gutowsky-Holm approximation[26] allowed the calculation of an upper limit for the barrier to carbonyl interchange.

$Cp(CO)Co{=}CHO{-}Zr(Cl)Cp^*{}_2$ (5a). Toluene solutions of $Cp^*{}_2ZrHCl$ (400 mg, 1.01 mmol) and $CpCo(CO)_2$ (150 μL 220 mg, 1.20 mmol) were mixed at −78 °C and then warmed to 25 °C with stirring for 2 h to effect reaction. Concentration to ca. 2 mL and addition of 10 mL of petroleum ether afforded red crystals that were isolated by filtration, washed with cold petroleum ether, and dried to give $Cp(CO)Co{=}CHO{-}Zr(Cl)Cp^*{}_2$ (260 mg, 45%): IR (Nujol mull) 1947 (vs), 1350 (m), 1308 (m), 1295 (vs), 1165 (w), 1110 (w), 1020 (w), 802 (m), 670 (w), 532 (w), 495 (m) cm^{-1}. Anal. Calcd for $C_{27}H_{36}ClCoO_2Zr$: C, 56.09; H, 6.28; Found: C, 56.59, 56.47; H, 6.30, 6.31.

$Cp(CO)Rh{=}CHO{-}Zr(Cl)Cp^*{}_2$ (5b). Treatment of $CpRh(CO)_2$ (200 μL, 1.67 mmol) with $Cp^*{}_2ZrHCl$ (600 mg, 1.51 mmol) by the above procedure afforded **5b** (720 mg, 78%) as golden crystals: IR (Nujol mull) 1952 (vs), 1353 (s), 1308 (m), 1015 (w), 783 (m), 712 (w), 650 (w) cm^{-1}. Anal. Calcd for $C_{27}H_{36}ClO_2RhZr$: C, 52.12; H, 5.83; Cl, 5.70. Found: C, 51.95; H, 6.04; Cl, 5.78.

$Cp(CO)Co{=}CHO{-}Zr(F)Cp^*{}_2$ (7a). Treatment of $CpCo(CO)_2$ (165 mg, 120 μL, 0.94 mmol) with $Cp^*{}_2ZrHF$ (300 mg, 0.83 mmol) by the method used for **5a** afforded **7a** (260 mg, 57%) as orange crystals: IR (Nujol mull) 1948 (vs), 1350 (m), 1300 (vs), 1167 (w), 1111 (w), 1021 (w), 801 (m), 670 (w), 614 (w), 538 (m), 498 (m) cm^{-1}.

$Cp(CO)Rh{=}CHO{-}Zr(F)Cp^*{}_2$ (7b). $CpRh(CO)_2$ (15 μL, 0.12 mmol) was added to a C_6D_6 solution of $Cp^*{}_2ZrHF$ (30 mg, 0.08 mmol) in a NMR tube at 25 °C. $Cp(CO)Rh{=}CHO{-}Zr(F)Cp^*{}_2$ was identified by its ^1H NMR and IR spectra: IR (C_6H_6 solution) 1953 (vs), 1382 (m), 1304 (s), 1166 (w), 1008 (w), 792 (w) cm^{-1}.

$Cp(CO)Rh{=}CHO{-}Zr(Cl)Cp^*{}_2$ + HCl. HCl (0.05 mmol) was condensed onto a C_7D_8 solution of **5b** (25 mg, 0.05 mmol) at −196 °C in an NMR tube, which was then sealed and warmed to room temperature. The products were identified by ^1H NMR spectroscopy.

$Cp(H)Ru(CO)_2ZrCp^*{}_2$ (9). $CpRu(CO)_2H$ was prepared by using the procedure of Humphries and Knox[23] by reflux of $Ru_3(CO)_{12}$ (250 mg, 0.39 mmol) and cyclopentadiene (ca. 3 mL, ca. 36 mmol) in 60 mL of heptane for 1$^1/_2$ h. $Cp^*{}_2ZrH_2$ (405 mg, 1.12 mmol) was added to this reaction mixture at 25 °C causing the solution to turn red over a period 10 min. Concentration to ca. 5 mL and cooling to −78 °C precipitated the product which was isolated by filtration and washed with cold petroleum ether giving $Cp(H)Ru(CO)_2ZrCp^*{}_2$ (380 mg, 59%) as brick red crystals.

Alternatively, **9** was prepared from $Ru_3(CO)_{12}$ (170 mg, 0.27 mmol) and CpH (ca. 3 mL, ca. 36 mmol), followed by addition of $\{Cp^*{}_2ZrN_2\}_2N_2$ (290 mg, 0.36 mmol), using a similar procedure. In this case the non LN_2 condensable gas liberated during the course of the reaction (2.56 mmol of N_2/mmol of $\{Cp^*{}_2ZrN_2\}_2N_2$) was collected with a Toepler pump. The ^1H NMR and IR spectra of **9** prepared from $\{Cp^*{}_2ZrN_2\}_2N_2$ were identical with those of **9** made from $Cp^*{}_2ZrH_2$: IR (Nujol mull) 1706 (vs), 1671 (vs), 1021 (m), 831 (w), 794 (m), 718 (m), 668 (m) cm^{-1}. Anal. Calcd for $C_{27}H_{36}O_2RuZr$: C, 55.45; H, 6.20; Ru, 17.28. Found: C, 55.09; H, 6.03; Ru, 17.50.

$Cp(H)Ru(CO)_2ZrCp^*{}_2$ + CO. A C_6D_6 solution of **9** (27 mg, 0.05 mmol) was placed under 700 torr CO at −78 °C in an NMR tube and the tube sealed and warmed at room temperature. The products were identified as pure $CpRu(CO)_2H$ and $Cp^*{}_2Zr(CO)_2$ by ^1H NMR spectroscopy.

$Cp(PMe_3)_2Fe{-}CH_2O{-}Zr(H)Cp^*{}_2$ (11a). Toluene (15 mL) and PMe_3 (0.49 mmol) were added to a mixture of $CpFe(CO)(PMe_3)H$ (90 mg, 0.40 mmol) and $Cp^*{}_2ZrH_2$ (135 mg, 0.37 mmol) at −196 °C. When the mixture was warmed to room temperature over a period of 2 h, red crystals formed. Concentration to ca. 2 mL, filtration, and washing with cold petroleum ether afforded $Cp(PMe_3)_2Fe{-}CH_2O{-}Zr(H)Cp^*{}_2$ (125 mg, 51%). Anal. Calcd for $C_{32}H_{56}FeOP_2Zr$: C, 57.73; H, 8.48; P, 9.30. Found: C, 57.88; H, 8.10; P, 9.30.

$Cp(PMe_3)_2Ru{-}CH_2O{-}Ru(H)Cp^*{}_2$ (11b). C_6D_6 and PMe_3 (0.08 mmol) were added to a mixture of $CpRu(CO)(PMe_3)H$ (20 mg,

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0.07 mmol) and $Cp^*{}_2ZrH_2$ (25 mg, 0.07 mmol) at −196 °C in an NMR tube. The tube was sealed and warmed to room temperature and the reaction monitored by NMR spectroscopy. The product was identified as $Cp(PMe_3)_2Ru–CH_2O–Zr(H)Cp^*{}_2$ by the similarity of its ^1H NMR spectrum to that of **11a**.

$CpFe(CO)_2CH_3 + Cp^*{}_2ZrH_2$. NMR samples of **1** (50 mg, 0.14 mmol) and **12a** (30 mg, 0.15 mmol) were prepared in C_7D_8 with and without PMe_3 (0.25 mmol) at −196 °C. After being sealed, the samples were warmed to −78 °C to liquify the solvent and then to 25 °C. The reactions were monitored by ^1H NMR spectroscopy, the products being identified by comparison to previously reported spectra.[1b,24] A similar procedure to that above was employed by using **1** (30 mg, 0.08 mmol), **12b** (20 mg, 0.08 mmol), and PMe_3 (0.10 mmol).

Acknowledgment. This work was supported by the National Science Foundation (Grant No. CHE 8024869). Use of the Bruker WM500 at the Southern California Regional NMR Facility, supported by National Science Foundation Grant No. CHE 7916324, is acknowledged.

Registry No. **1**, 61396-34-7; **1**-d_2, 83708-61-6; **2a**, 12078-25-0; **2b**, 12192-97-1; **2b** (^{13}C enriched), 87985-74-8; **3a**, 76545-15-8; **3b**, 87985-75-9; **3b** (^{13}C enriched), 87985-76-0; **4**, 77299-72-0; **5a**, 87985-77-1; **5b**, 87985-78-2; **6**, 87985-79-3; **7a**, 87985-80-6; **7b**, 87985-81-7; **8**, 57349-59-4; **9**, 87985-82-8; **10a**, 35796-54-4; **10a**-d_1, 87985-83-9; **10b**, 87985-84-0; **11a**, 87999-37-9; **11b**, 87999-38-0; **12a**, 12080-06-7; **12b**, 53449-90-4; **13**, 77309-18-3; $\{Cp^*{}_2ZrN_2\}_2N_2$, 54387-50-7.

Comparison of Isolobal Fragments: Bonding of Tricarbonyliron and Cyclopentadienylcobalt to Cyclobutadiene and Cyclopentadienone

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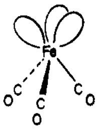
Generalized molecular orbital and configuration interaction calculations are reported for $(\eta^4\text{-}C_4H_4)Fe(CO)_3$, $(\eta^4\text{-}C_4H_4)Co(\eta^5\text{-}C_5H_5)$, $(\eta^4\text{-}C_4H_4CO)Fe(CO)_3$, and $(\eta^4\text{-}C_4H_4CO)Co(\eta^5\text{-}C_5H_5)$. The results suggest that $Co(C_5H_5)$ bonds more strongly to the C_4H_4 ligand than to the C_4H_4CO ligand, while the opposite behavior is seen for $Fe(CO)_3$. Both Co complexes have a more covalent diene–M bond than the Fe complexes. Deformation density plots suggest that previous conclusions concerning how the two isolobal fragments $Fe(CO)_3$ and $Co(C_5H_5)$ perturb the C–C bonds in a 1,3-diene may be inacccurate.

Introduction

Part of the challenge in synthetic chemistry is to find reaction schemes that have general applicability. In organometallic chemistry, the interest focuses on the similarities and differences in the chemical and physical behavior of organic ligands complexed to similar transition-metal fragments. One simple way of investigating such effects is to gradually change the nature of the transition-metal moiety, while keeping its theoretically equivalent bonding ability the same. This theoretical equivalence is termed isolobal. Two metal fragments are isolobal if they afford the same number of bonding electrons and orbitals to the complexed organic ligand.[1] In this sense, $Fe(CO)_3$ and $Co(C_5H_5)$ are isolobal fragments, even though they are composed of quite different atoms. Hoffmann and co-workers have already examined the structure and bonding of the $M(CO)_3$, $M(C_6H_6)$, and $M(C_5H_5)$ fragments with extended Hückel calculations and concluded that $M(CO)_3$ is a better π-bonding group than M(Bz) or M(Cpd), whereas the latter two have stronger σ interactions.[2] From our work on (polyene)ML_n complexes,[3] it is a logical extension to consider a comparison of the effects of isolobal fragments on the same polyenes.

We are primarily interested in examining the bonding effects of two different, but isolobal, fragments [$Fe(CO)_3$, **1**, and $Co(\eta^5\text{-}C_5H_5)$, **2**] on the same polyene. On the basis of a number of X-ray diffraction studies performed on complexes of **1** and **2** containing 1,3-butadienes and butadiene-like ligands (which we will collectively refer to as dienes), Churchill, Mason, and co-workers concluded that dienes have three approximately equal C–C bond lengths when bound to **1**, as in **3**, but one short and two long C–C bond lengths when complexed to **2**, as in **4**.[4] Though this principle has been repeated in at least one textbook for a number of years,[5] it is of questionable validity in light



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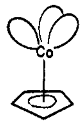

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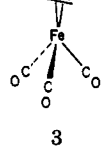

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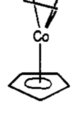

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(1) See, for example: (a) Albright, T. A.; Hofmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546. (b) Albright, T. A.; Hoffmann, R.; Tse, Y.; D'Ottavio, T. *Ibid.* **1979**, *101*, 3812. (c) Hoffmann, R. *Science (Washington, D.C.)* **1981**, *211*, 995.

(2) Elian, M.; Chen, M. M. L.; Mingos, D. M. P.; Hoffmann, R. *Inorg. Chem.* **1976**, *15*, 1148.

(3) Chinn, J. W., Jr.; Hall, M. B. *J. Am. Chem. Soc.* **1983**, *105*, 4930.

(4) Churchill, M. R.; Mason, R. *Proc. R. Soc. London, Ser. A* **1967**, *301*, 433 and references therein.

(5) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 3rd ed.; Wiley: New York, 1972; p 731.

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