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Synthesis of (Transition metal carbonyl)zinc Alkoxides and the Crystal Structure of Tetrameric (Dicarbonyl(η^5-cyclopentadienyl)iron)zinc Methoxide

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Bis(transition metal carbonyl)zinc compounds react with methanol giving tetrameric (transition metal carbonyl)zinc methoxides, $[CH_3OZn(ML_n)]_4$ (where ML_n is one of the following: $Co(CO)_4$, $Mn(CO)_5$, $Mo(CO)_3Cp$, and $Fe(CO)_2Cp$; Cp = η^5-C_5H_5), and the corresponding metal carbonyl hydride, HML_n. Ethyl analogues for all but the first of these were also synthesized from ethanol. The formation reactions are favored by elimination of undissociated metal carbonyl hydride and are inhibited by basic, aprotic solvents. The degree of conversion to alkoxide in neat methanol is in the order $Zn[Fe(CO)_2Cp]_2 > Zn[Mo(CO)_3Cp]_2 > Zn[Mn(CO)_5]_2 \gg Zn[Co(CO)_4]_2$ and qualitatively follows the pK_a of the hydride formed. Ethanol was always less reactive than methanol. The methoxide $[CH_3OZnFe(CO)_2Cp]_4$ was characterized by single-crystal X-ray structure analysis. This compound crystallizes in space group $P2_1/n$ with $Z = 4$ and monoclinic unit-cell dimensions $a = 14.340$ (3) Å, $b = 12.819$ (5) Å, $c = 21.493$ (9) Å, and $\beta = 96.82$ (3)°. The structure has been refined to an R index on F^2 of 0.045. The tetramer possesses C_1 symmetry with a distorted cubic Zn_4O_4 core made up of interpenetrating tetrahedra of zinc and oxygen atoms with Zn–O distances in the range 2.099 (4)–2.048 (5) Å. Each oxygen atom of the core is bonded to a methyl group, and each zinc is bonded to the iron atom of a normal $Fe(CO)_2Cp$ group; the Zn–Fe bond lengths range from 2.344 (2) to 2.354 (2) Å (2.350-Å average). The tetrameric nature of the other alkoxides has been deduced from mass spectroscopy. Two analogous hydroxo derivatives, $[HOZnFe(CO)_2Cp]_x$ and $[HOZnCo(CO)_4]_x$, were prepared similarly.

Introduction

The formation of (transition metal carbonyl)zinc alkoxides, from the reaction of lower alcohols with transition metal carbonyl derivatives of zinc[1] was unexpected since alcohols had been used in previous studies of bis(metal carbonyl)zinc compounds without apparent reaction.[2,3] The analogous transformations of dialkylzinc and dialkylcadmium compounds into organozinc and organocadmium alkoxides are well known.[4-6] The alkylzinc alkoxides are predominately tetrameric in solution[4] and in the gas phase.[6] For $[MeZnOMe]_4$[7] and $[EtZnO\text{-}t\text{-}Bu]_4$ a tetrameric structure was observed in the crystalline state.[8]

In this paper we describe the syntheses of several (transition metal carbonyl)zinc alkoxides and of two analogous hydroxides. We examine the factors bearing on the diverse conditions required for their formation. Finally we present the crystal and molecular structure of $[CH_3OZnFe(CO)_2Cp]_4$ (Cp = η^5-C_5H_5) as determined by X-ray diffraction analysis.

Experimental Section

All manipulations were carried out under a purified argon atmosphere in Schlenk reaction vessels (SRV)[9] that had been flame dried under vacuum. Solvents (reagent grade) were distilled from suitable drying agents[10] directly into the reaction vessels. All melting and decomposition points were determined under argon in sealed capillaries. All IR spectra were obtained by using a Perkin-Elmer Model 337 spectrophotometer calibrated with polystyrene. Solution spectra were obtained as described previously[10] and are given in Table I. KBr pellets of solid samples were prepared by using a Mini press (Wilks Scientific Corp.) in a Vacuum/Atmospheres Co. nitrogen-filled drybox and were recorded within 2 min after exposure to air. Mass spectra were obtained at 70 eV at a source temperature in the range 160–220 °C using an AEI MS902 instrument calibrated with PFK and equipped with a direct insertion probe; the listed value of m/z corresponds to that of the isotope combination of highest abundance in the cluster of peaks due to the given ion. ^1H NMR spectra of samples in $CHCl_3$ or CH_2Cl_2 solutions in evacuated, sealed tubes were obtained with a Varian A-60A spectrometer and were calibrated by using the resonance of the solvent referenced to Me_4Si. Microanalyses were performed by Pascher Mikroanalytiches Laboratorium, Bonn, Germany; results are given in Table I.

The following compounds were prepared by methods described in the literature: $Zn[Co(CO)_4]_2$,[11] $Zn[Mn(CO)_5]_2$,[12] $Zn[Mo(CO)_3Cp]_2$,[11] $HMn(CO)_5$,[13] and $HCo(CO)_4$ (in toluene).[14] Methanol and ethanol were distilled under argon from magnesium alkoxides formed in situ from magnesium turnings. Distilled water was deaerated with argon while being boiled.

Preparation of $Zn[Fe(CO)_2Cp]_2$. A 400-mL SRV was charged with 15.6 g (90 mmol) of zinc powder (Cerac, Inc.), 8.48 g (9.00 mmol) of $[Fe(CO)_2Cp]_2$ (Strem Chemical Co., resublimed), and 240 mL of diglyme (distilled from sodium) and then was equipped with a cold-finger condenser. The mixture was heated in an oil bath at 120 °C and stirred magnetically to keep the zinc suspended. After 67.5 h, when the meniscus of the deep red solution appeared yellow, the solution was allowed to cool and filtered through a "medium" frit and evaporated to dryness under vacuum. The residue was dissolved in toluene (70 mL) at 60 °C, and the resulting red solution was filtered and cooled slowly to −22 °C.

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Table I. Analytical and IR Spectroscopic Data for $ROZnML_n$ Compounds

compd	% C calcd	% C obsd	% H calcd	% H obsd	ν_{CO},[b] cm^{-1}	solvent
$[CH_3OZnFe(CO)_2C_5H_5]_4$	35.37	35.14	2.77	2.96	1966 sh (6), 1956 (10), 1905 sh (6), 1895 (9)	toluene
$[CH_3OZnMn(CO)_5]_4$	24.65	24.66	0.89	1.04	2077 (3), 1978 (10)	dichloromethane
$[CH_3OZnMo(CO)_3C_5H_5]_x$	31.36	31.67	2.46	2.36	1976 (10), 1908 sh (2), 1885 (7), 1868 (7), 1857 (6), 1843 (8)	toluene
$[C_2H_5OZnFe(CO)_2C_5H_5]_4$	36.49	37.64	3.29	3.51	1964 (8), 1958 (9), 1909 (7), 1895 (10)	toluene
$[C_2H_5OZnMn(CO)_5]_4$	26.56	27.53	1.70	1.65	2084 (4), 1990 sh (8), 1977 (10)	dichloromethane
$[C_2H_5OZnMo(CO)_3C_5H_5]_x$	33.49	33.78	2.92	2.83	1990 sh (4), 1979 (9), 1963 (6), 1893 (8), 1865 (10), 1832 (7)	dichloromethane
$[HOZnCo(CO)_4]_x$	20.55	18.96	0.51	0.40	2074 (4), 2009 (2), 1979 (10)	toluene
$[HOZnFe(CO)_2C_5H_5]_x$	32.25	32.41	2.48	2.34	[c]	
$[C_6H_5OZnFe(CO)_2C_5H_5]_x$	46.89	46.66	3.00	3.00	[c]	
$[CH_3OZnCo(CO)_4]_4$	22.26	22.44	1.06	1.13[a]	2081 (5), 2017 (3), 1982 (10)	hexane

[a] Anal. Calcd: Co, 22.03; Zn, 24.44 Obsd: Co, 22.02; Zn, 24.62. [b] Relative intensities based on absorbance are given in parentheses. [c] Compound was unstable in solution; see Experimental Section for solid-state spectrum.

This afforded large, red prismatic crystals of $Zn[Fe(CO)_2Cp]_2$ which were dried under vacuum. The yield was 8.5 g (93%) of crystals, mp 158.5–160 °C (lit.[11] mp 158–159.5 °C).

Reaction of $Zn[Co(CO)_4]_2$ with Methanol. To a filtered solution of $Zn[Co(CO)_4]_2$ prepared in situ from $Hg[Co(CO)_4]_2$ (1.19 g, 2.20 mmol) in hexane (38 mL) was added methanol (64.8 μL, 1.60 mmol) with a microsyringe. The SRV was equipped with an oil bubbler. After being left standing in the dark for 1 h, the solution had darkened and slow gas evolution was observed. After 19.5 h the brown supernatant liquid was removed with a syringe, and the clear, colorless cubic crystals were washed with hexane and dried under vacuum. This gave 0.271 g (63%) of white, crystalline $[CH_3OZnCo(CO)_4]_4$: mp 193–200 °C dec; NMR δ −3.99 (s, OCH_3); mass spectrum, m/z 1070 (M^+), 930 ($M^+ - 5CO$), 899 ($M^+ - 5CO$, CH_3O), 790 ($M^+ - 10CO$), 759 ($M^+ - 10CO$, CH_3O); IR (CH_3OH) ν_{CO} 2061 (m), 2052 (w, sh), 1971 (s, sh), 1958 (vs), 1908 (s) cm^{-1}.

Reaction of $[CH_3OZnCo(CO)_4]_4$ with $HCo(CO)_4$. Bubbling CO through a solution of $HCo(CO)_4$ (prepared from $Co_2(CO)_8$ (1.04 g) in toluene (20 mL)[14]) and thence into a solution of $[CH_3OZnCo(CO)_4]_4$ (0.40 g, 1.57 mmol) in methanol (20 mL) caused a steady increase in the ν_{CO} at 2067, 2050, and 1962 cm^{-1}, attributed to $Zn[Co(CO)_4]_2$, and a concomitant decrease in the intensities of the ν_{CO} of $[CH_3OZnCo(CO)_4]_4$. After 30 min the ν_{CO} of $HCo(CO)_4$ and its decomposition products obscured the spectrum; no attempt was made to isolate the $Zn[Co(CO)_4]_2$ formed. In a control reaction without $[CH_3OZnCo(CO)_4]_4$, the ν_{CO} of $HCo(CO)_4$ and its decomposition products appeared after 3 min; an IR spectrum taken immediately after introduction of $HCo(CO)_4$ had ν_{CO} at 2075 (vw), 2030 (w), and 1908 (s) cm^{-1}, and subsequent spectra showed increasing intensities of the first two bands relative to the third.

Attempted Reaction of $Zn[Co(CO)_4]_2$ with Ethanol. A solution of $Zn[Co(CO)_4]_2$ (0.092 g, 0.226 mmol) and ethanol (13.0 μL, 0.226 mmol) in hexane (10 mL) turned orange after being left standing in the dark for 12 h, but no changes were seen in the IR spectrum. After 4.6 days a weak absorption at 1860 cm^{-1} was the only new feature. A similar experiment employing a tenfold excess of EtOH gave the same result.

Reaction of $Zn[Co(CO)_4]_2$ with Water. With use of a microsyringe, water (18.7 μL, 1.04 mmol) was added to a solution of $Zn[CO(CO)_4]_2$ (0.424 g, 1.04 mmol) in toluene. After the solution was stirred for several minutes, the water dissolved, giving a clear yellow solution. A weak band at 2123 cm^{-1} in the IR spectrum of the solution taken after 40 min indicated that some $HCo(CO)_4$ had formed.[15] After 1.7 h the brown supernatant liquid was decanted from the light colored precipitate. The latter was washed with hexane (2 mL) and dried under vacuum giving 0.097 g of a white powder. A second crop precipitated from the supernatant liquid upon standing for 12 h. The combined crops were recrystallized from toluene (30 mL, +60 to −65 °C) and afforded 0.109 g (41%) of white, microcrystalline $[HOZnCo(CO)_4]_x$, mp slow decomposition above 157 °C. The ion with the largest m/z in the mass spectrum corresponded to $Zn[Co(CO)_4]_2^+$. No resonance was observed in the NMR spectra of saturated solutions of the product in toluene or dichloromethane in the range −17 to +8.5 ppm relative to Me_4Si. IR (KBr): 3591 (m), 2940 (vw), 2910 (vw), 2837 (vw), 2073 (s), 2018 (m), 1966 (s, sh), 1941 (s), 1630 (vw), 752 (w), 740 (w), 550 (m), and 495 (w) cm^{-1}.

Reaction of $Zn[Fe(CO)_2Cp]_2$ with Methanol in Toluene. To a solution of $Zn[Fe(CO)_2Cp]_2$ (0.923 g, 2.20 mmol) in toluene (30 mL) was added methanol (90.2 μL, 2.20 mmol). After the solution was stirred for 2 h, an IR spectrum showed that essentially all of the starting zinc compound had reacted (disappearance of ν_{CO} at 1982 cm^{-1}) and that $HFe(CO)_2Cp$ (ν_{CO} at 2016 cm^{-1}[16]) had formed. The solution was refrigerated at −8 °C for 2 days, but no solid formed and the IR spectrum was unchanged. Hexane (10 mL) was distilled in, and after filtration, the solution was slowly cooled to −22 °C. The resulting crystals were collected, were washed with hexane (which caused them to become opaque) and toluene, then dried under vacuum, and gave straw-colored crystals (0.274 g, 47%). A second crop of yellow crystals (0.097 g, 17%) was obtained by addition of hexane (20 mL) to the supernatant liquid followed by cooling to −22 °C; drying caused the crystals to become opaque. The first crop of crystals was recrystallized from methylene chloride–hexane (1:1) and dried under vacuum to give an analytical sample (0.090 g) of clear, yellow-orange prismatic crystals of $[CH_3OZnFe(CO)_2Cp]_4$: mp 300 °C dec; NMR ($CHCl_3$) δ −4.80 (s, 5 H, C_5H_5), −3.75 (s, 3 H, CH_3O); mass spectrum (source, 160 °C), m/z 917 ($M^+ - C_5H_5$, 4CO).

Preparation of $[CH_3OZnFe(CO)_2Cp]_4$ in Methanol. A mixture of $Zn[Fe(CO)_2Cp]_2$ (0.258 g, 0.651 mmol) and methanol (10 mL) was stirred for 8 min during which all the starting material dissolved and a yellow solid precipitated. The IR spectrum of the supernatant liquid contained only ν_{CO} due to $HFe(CO)_2Cp$. After 10 min the supernatant liquid was removed with a syringe, and the orange residue was washed with methanol (2 × 10 mL) via a syringe then dried under vacuum. Thus 0.157 g (88%) of $[CH_3OZnFe(CO)_2Cp]_4$ was obtained as a yellow-orange powder, mp 300–303 °C dec.

Reaction of $Zn[Fe(CO)_2Cp]_2$ with Ethanol. Stirring a mixture of $Zn[Fe(CO)_2Cp]_2$ (0.400 g, 1.00 mmol) and ethanol (10 mL) gave a cloudy solution. After 30 min an orange solid had formed, and the IR spectrum of the supernatant liquid showed only bands at 2013 and 1954 cm^{-1} due to $HFe(CO)_2Cp$.[16] The supernatant liquid was removed with a syringe, and the orange, powdery product was washed with ethanol (3 mL) and then dried under vacuum. The product was redissolved in 7 mL of dichloromethane and 3 mL of ethanol. After being filtered through a "medium" frit, the solution was cooled slowly to −22 °C. The resulting crystals were washed with ethanol (2 mL) and then dried under vacuum. The yield was 0.161 g (59%) of orange, prismatic crystals of $[C_2H_5OZnFe(CO)_2Cp]_4$: mp 245–250 °C; NMR (CH_2Cl_2) δ −1.47 (t, J = 7 Hz, CH_3), −4.09 (q, J = 7 Hz, OCH_2) and −4.99 (s, C_5H_5); mass spectrum (source at 170 °C), m/z 418 from $Zn[Fe(CO)_2Cp]_2^+$.

Reaction of $Zn[Fe(CO)_2Cp]_2$ with Water. To a solution of $Zn[Fe(CO)_2Cp]_2$ (0.671 g, 1.60 mmol) in toluene (25 mL) was added

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water (28.8 μL, 1.60 mmol). The mixture was stirred vigorously to disperse the water into fine droplets. After 24 h, when IR spectroscopy indicated that formation of $HFe(CO)_2Cp$ had ceased, the orange supernatant liquid was decanted off and the yellow, powdery precipitate was washed with toluene (2 × 2 mL) and then dried under vacuum to afford 0.232 g (57%) of yellow, powder-like $[HOZnFe(CO)_2Cp]_x$, mp 148–152 °C dec. The product was insoluble in toluene, hexane, and water and decomposed in water. IR (KBr): 3615 (m), 3010 (vw), 2925 (w), 2860 (w), 2010 (w, sh), 1957 (vs, sh), 1946 (vs), 1890 (vs, sh), 1870 (vs, br), 1647 (vw), 1516 (vw), 1405 (w), 1010 (vw), 998 (vw), 839 (w), 825 (w), 744 (w), 653 (m), 593 (m), and 512 (vw) cm^{-1}.

Reaction of $Zn[Fe(CO)_2Cp]_2$ with Phenol. A solution of $Zn[Fe(CO)_2Cp]_2$ (0.264 g, 0.630 mmol) and phenol (0.0593 g, 0.630 mmol; Mallinckrodt, recrystallized from hexane) in toluene (15 mL) was stirred for 2 h and then filtered through a "fine" frit. The clear yellow filtrate was slowly cooled to −22 °C. After 2 days the resulting crystals were collected, washed with toluene (2 × 2 mL), and then dried under vacuum. This afforded 0.107 g (51%) of irregular yellow-orange crystals of $[C_6H_5OZnFe(CO)_2Cp]_x$, mp decomposition above 175 °C. The product was too unstable in solution (e.g., toluene) in the absence of $HFe(CO)_2Cp$, for reliable spectra to be obtained: IR (KBr) 3075 (w, br), 3020 (w, br), 1955 (vs), 1926 (s, sh), 1899 (vs), 1865 (m, sh), 1584 (m), 1478 (m), 1402 (w), 1198 (s), 1167 (m), 1110 (vw), 1060 (w, br), 1015 (w), 997 (vw), 895 (w), 835 (m), 816 (ms), 760 (ms), 697 (ms), 648 (ms), 591 (s), 565 (mw), 500 (ms) cm^{-1}.

Preparation of $Zn[Mn(CO)_5]_2$. A mixture of powdered zinc (0.65 g, 10 mmol, Cerac, Inc.) and $Mn_2(CO)_{10}$ (0.389 g, 1.0 mmol[17]), in diglyme (20 mL, Ansul Chemical Co., No. 141, triply distilled from sodium) was stirred at 120 °C for 10 h during which time the yellow solution gradually turned light salmon in color. Filtration and evaporation of the solvent under vacuum gave a light orange residue (5.3 g). This powder-like solid was transferred under argon to a sublimator with a sidearm Schlenk tube receiver (similar to Ace Glass Co., Cat. No. 7775), covered with a loose pad of glass wool, and sublimed at 115–120 °C and 0.001 torr. The cream white sublimate afforded $Zn[Mn(CO)_5]_2$: 3.8 g (84%) as a microcrystalline solid; mp 210–211.5 °C; mass spectrum *m/z* 453.75434 (calcd for $^{64}Zn^{55}Mn_2{}^{12}C_{10}{}^{16}O_{10}$, 453.75439); IR ν_{CO} (THF) 2075 (w), 2052 (wm), 2014 (mw), 1965 (vs) cm^{-1}; ν_{CO} (KBr) 2065 (m), 1985 (ms, sh), 1945 (vs), 645 (m). Anal. Calcd for $C_{10}O_{10}Mn_2Zn$: C, 26.35; H, 0.00. Found: C, 26.21; H, 0.04; 0.10. The extreme sensitivity of this compound to water may have produced a small amount of $HMn(CO)_5$ in the THF solution responsible for the band at 2014 cm^{-1}.

Attempted Preparation of $Zn[Re(CO)_5]_2$ from $Re_2(CO)_{10}$. A mixture of powdered zinc (2.0 g, 30 mmol, Cerac, Inc.), $Re_2(CO)_{10}$ (1.96 g, 3.0 mmol, Strem Chemical Co.), and diglyme (30 mL) was stirred at 120 °C for 40.8 h, then at 150 °C for 16 h, and finally at 165 °C for 76.1 h. IR spectroscopic analysis of the red-brown solution showed that ~90% of the starting material remained. The solvent was removed from the filtered mixture, and most of the $Re_2(CO)_{10}$ was removed from the residue by vacuum sublimation (175 °C). No ions other than those attributable to $Re_2(CO)_{10}$ were seen in the mass spectra of the residue.

Several variations on the above procedure were tried. A stirred mixture of zinc powder and $Re_2(CO)_{10}$ was heated at 165 °C in diglyme in the dark for 60 h. Also zinc dust (Baker and Adamson, 90–95% Zn) was substituted for zinc powder in another experiment carried out at 165 °C in the dark for 86.5 h. IR spectroscopic analysis of the reaction solution showed only ν_{CO} due to $Re_2(CO)_{10}$.

Attempted Preparation of $Zn[Re(CO)_5]_2$ from $Hg[Re(CO)_5]_2$. A mixture of $Hg[Re(CO)_5]_2$ (0.941 g, 1.10 mmol; this was prepared by a modification of the published procedure[2] whereby a THF solution of $NaRe(CO)_5$ was added to a THF solution of $Hg(CN)_2$[1b]) and zinc powder (0.72 g, 11 mmol) in diglyme (100 mL) was stirred at 165 °C in the dark for 5 days). IR spectra taken during and at the end of this period showed that only $Re_2(CO)_{10}$ had formed (ν_{CO} 2073 (m), 2013 (s), and 1974 (m) cm^{-1}). The same procedure was tried (1) with zinc powder (0.262 g) which had been amalgamated by prior reaction with mercuric chloride (0.271 g) in THF and (2) with a zinc–copper couple[18] formed from copper citrate (0.38 g) and zinc powder (0.20 g); no evidence for $Zn[Re(CO)_5]_2$ was found.

Reaction of $Zn[Mn(CO)_5]_2$ with Methanol. With use of a microsyringe, methanol (70 μL, 1.70 mmol) was added to a suspension of $Zn[Mn(CO)_5]_2$ (0.835 g, 1.84 mmol) in dichloromethane (20 mL). The mixture was stirred for 10 h during which time the solid partly dissolved. Additional methanol (212 μL, 5.17 mmol) was added slowly with a syringe while the mixture was stirred until all of the solid dissolved. The solvent was removed by trap-to-trap distillation leaving a white powder (0.536 g, 100%). The IR spectrum of the distillate contained only ν_{CO} for $HMn(CO)_5$ at 2010 cm^{-1}, identified by comparison with the spectrum of an authentic sample. The crude product was recrystallized from dichloromethane (10 mL) by cooling to −22 °C and gave 0.403 g (75%) of colorless, prismatic crystals of $[CH_3OZnMn(CO)_5]_4$: mp 195–196.5 °C; NMR (CH_2Cl_2) δ −3.99 (s, OCH_3); mass spectrum, *m/z* 971 ($M^+ - Mn(CO)_5$).

When $Zn[Mn(CO)_5]_2$ (0.454 g, 0.997 mmol) and methanol (82 μL, 2.01 mmol) were mixed in tetrahydrofuran (10 mL), IR spectroscopic analysis showed no change in the spectrum during 47 h compared to that taken before methanol was added. No absorption due to $HMn(CO)_5$ was observed.

When $Zn[Mn(CO)_5]_2$ (0.345 g, 0.759 mmol) was dissolved in methanol (10 mL) and stirred for 3 h, IR spectroscopic analysis, using the absorbance of 2010-cm^{-1} band of $HMn(CO)_5$, indicated that only 40 ± 5% of the expected quantity of $HMn(CO)_5$ had formed; no change in the absorbance was seen after 30 min.

Reaction of $Zn[Mn(CO)_5]_2$ with Ethanol. Sufficient ethanol (5 mL) to dissolve $Zn[Mn(CO)_5]_2$ (0.454 g, 0.99 mmol) was distilled onto the solid. The yellow solution was stirred for 0.5 h, and then the solvent was removed under vacuum. The residue was dissolved in the minimum amount of ethanol (20 mL), giving a clear yellow solution. After 0.5 h the solvent was removed under vacuum; the clear, colorless distillate turned yellow on exposure to air. The residue was dissolved in ethanol (10 mL) at 70 °C and was cooled rapidly to −60 °C; no precipitate formed over 15 min. The yellow solution was distilled to dryness giving an orange residue (0.303 g). This was dissolved in CH_2Cl_2 (5 mL), filtered, and cooled slowly to −22 °C. The resulting crystals were washed with cold CH_2Cl_2 (2 × 2 mL) and dried under vacuum for 1 h. This afforded 0.239 g (79%) of opaque, off-white crystals of $[C_2H_5OZnMn(CO)_5]_4$: mp 153–154.5 °C; NMR (CH_2Cl_2) δ −1.55 (q, *J* = 7 Hz, CH_3), 4.25 (t, *J* = 7 Hz, CH_2O); mass spectrum (source, 200 °C), *m/z* 997 (M^+ − Mn, 6CO).

Reaction of $[CH_3OZnMn(CO)_5]_4$ with $HMn(CO)_5$. To a solution of $[CH_3OZnMn(CO)_5]_4$ (0.072 g, 0.24 mmol) in CH_2Cl_2 (10 mL) was added a solution of $HMn(CO)_5$ (0.37 mmol) in CH_2Cl_2 (0.5 mL). After being stirred for 3.3 h, the IR spectrum of the solution showed that no reaction had occurred. Additional $HMn(CO)_5$ (4.7 mL, 3.11 mmol) was added, and when IR spectroscopic analysis showed no reaction, the SRV was equipped with a cold-finger condenser and the solution was heated at reflux for 1.5 h. The IR spectrum of the orange supernatant liquid showed that ~40% of the $HMn(CO)_5$ had been consumed. The white precipitate was collected and washed with CH_2Cl_2 (1 mL) and then dried under vacuum to give 0.027 g of $Zn[Mn(CO)_5]_2$: mp 208 °C dec (lit.[12] mp 209–210 °C); IR ν_{CO} (KBr) 2063 (m), 2050 (m, br), 1996 (s), 1948 (vs) cm^{-1}.

Reaction of $[C_2H_5OZnMn(CO)_5]_4$ with Methanol. Into an NMR tube was placed a solution containing 0.0235 mmol of $[C_2H_5OZnMn(CO)_5]_4$ and 0.73 mmol of methanol in CH_2Cl_2 (0.65 mL); the tube was sealed under vacuum: ^1H NMR δ −0.9–1.4 (br), −1.62 (t, *J* = 7 Hz, CH_3CH_2OZn), −3.98 (s, CH_3OZn) −3.5–4.0 (br), 4.30 (q, *J* = 7 Hz, CH_3CH_2OZn); integration by planimetry gave the area ratio $t/s = 0.55$.

Preparation of $Zn[Mo(CO)_3Cp]_2$ from $[Mo(CO)_3Cp]_2$. A solution of $[Mo(CO)_3Cp]_2$ (1.96 g, 4.0 mmol) in THF (60 mL) was stirred with zinc powder (2.61 g, 40 mmol) in a 90-mL SRV equipped with a water condenser at 60 °C (oil bath). After 15.5 h the light brown mixture was filtered and the solvent was removed by trap-to-trap distillation under vacuum. The resulting light gray crystalline residue was recrystallized from toluene (30 mL; +60 °C to −35 °C). The first crop of crystals was washed

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with cold toluene (5 mL) and gave Zn[Mo(CO)$_3$Cp]$_2$ as light yellow flakes, mp 194.4–195.8 °C (lit.[11] mp 194–196 °C). A second crop (0.27 g) of light brown crystals, mp 192.5–194.5 °C, was obtained by concentrating and cooling the mother liquor.

Reaction of Zn[Mo(CO)$_3$Cp]$_2$ with Methanol. Stirring a solution of Zn[Mo(CO)$_3$Cp]$_2$ (0.423 g, 0.763 mmol) in methanol (5 mL) for 5 min caused a white precipitate to form. IR spectroscopic analysis of the supernatant liquid showed it to contain HMo(CO)$_3$Cp (ν_{CO} 2021 (s) and 1932 (s) cm^{-1}; lit.[13] ν_{CO} (CS$_2$) 2030 (s) and 1949 (s) cm^{-1}). The precipitate was washed with methanol (5 mL) and then was dissolved in a mixture of CH$_2$Cl$_2$ (7.5 mL) and methanol (1 mL). This was slowly reduced to half volume by trap-to-trap distillation, and the resulting crystals were collected, washed with methanol, and dried under vacuum. The yield was 0.158 g (66%) of nearly white crystals of [CH$_3$OZnMo(CO)$_3$Cp]$_x$: mp decomposition slowly above 210 °C; NMR δ –5.39 (s, C$_5$H$_5$), –3.78 (s, CH$_3$).

Reaction of Zn[Mo(CO)$_3$Cp]$_2$ with Ethanol. After being stirred for several min a solution of Zn[Mo(CO)$_3$Cp]$_2$ (0.293 g, 0.474 mmol) in ethanol (10 mL) became cloudy. The mixture was left standing for 12 h, then the pink supernatant liquid was decanted, and the light pink precipitate was washed with ethanol and dried under vacuum. This gave 0.051 g (30%) of [C$_2$H$_5$OZnMo(CO)$_3$Cp]$_x$ as a white powder, mp 280 °C dec. The supernatant liquid stood for 7 days without further formation of any solid. The solvent was removed by trap-to-trap distillation, and after the residue was washed with hexane, ethanol (5 mL) was added. Stirring the solution for 5 min at 40 °C caused a white precipitate to form. The process was repeated, and a third quantity of light colored solid was obtained. The product was not sufficiently soluble in hexane, toluene, or dichloromethane to give an NMR spectrum.

Collection of X-ray Diffraction Data. In the drybox a yellow-orange crystal of [CH$_3$OZnFe(CO)$_2$Cp]$_4$, prepared as described above, was mounted on the tip of a 0.2-mm Lindemann glass capillary which was sealed into a 0.5-mm capillary. The crystal was mounted on a Syntex $P2_1$ automated four-circle diffractometer equipped with a graphite monochromator and was centered with 15 reflections having $2\theta > 20°$. Details of the crystal data, the data collection experiment, data reduction, and the structure solution and subsequent refinement are presented in Table II. The final positional parameters with estimated errors are given in Table III. Anisotropic thermal parameters are given in Table VIII. Hydrogen atom positions (with $B_H = 7.35$) were calculated for each of the last five cycles at 0.95 Å from Cp carbon atoms and are listed in Table IX.

Results and Discussion

Formally, the syntheses of alkoxides described in this work (eq 1) consist of the replacement of a transition metal

$$\mathrm{ROH} + \mathrm{Zn[M(CO)_xL]_2} \rightleftharpoons {}^1/_4\mathrm{[ROZnM(CO)_xL]_4} + \mathrm{HM(CO)_xL} \quad (1)$$

carbonyl anion ([M(CO)$_x$L]$^-$ = Co(CO)$_4^-$, Mn(CO)$_5^-$, Mo(CO)$_3$Cp$^-$, or Fe(CO)$_2$Cp$^-$) by an alkoxide anion (OCH$_3^-$ or OC$_2$H$_5^-$) with concomitant formation of a metal carbonyl hydride. In essence this involves transfer of a proton from the hydroxo species ROH to the metal hydride, HM(CO)$_x$L. In all cases the hydride was identified by IR spectroscopy whereas the alkoxides were isolated and characterized by analyses and spectroscopic methods.

Reactions of Zn[Fe(CO)$_2$Cp]$_2$. When the compound Zn[Fe(CO)$_2$Cp]$_2$ was dissolved in methyl alcohol, a rapid reaction occurred with precipitation of [CH$_3$OZnFe(CO)$_2$Cp]$_4$ as a light orange solid in high yield; the supernatant liquid contained only HFe(CO)$_2$Cp (IR spectroscopy). In toluene with added methyl alcohol the same reaction occurred somewhat more slowly but without formation of a precipitate. The orange crystalline product from both reactions was identified as [CH$_3$OZnFe(CO)$_2$Cp]$_x$ by elemental analysis and ^{1}H NMR spectroscopy. The first indication of its tetrameric nature came from its mass spectrum, the highest mass ion of which had the expected isotopic distribution and nominal m/z values for [(CH$_3$OZn)$_4$Fe$_4$(CO)$_4$Cp$_3$]$^+$. Subsequently, formulation as a tetramer in the solid state was confirmed by the results of a single-crystal X-ray diffraction study described below.

Table II. Experimental Conditions and Data from the X-ray Structure Analysis of [CH$_3$OZnFe(CO)$_2$Cp]$_4$

Crystal Data	
cryst shape	rectangular block
cryst dimens, mm	0.20 × 0.20 × 0.10
cell parameters	
a, Å	14.340 (3)
b, Å	12.819 (5)
c, Å	21.493 (9)
$\alpha = \gamma$, deg	90
β, deg	96.82 (3)
cell vol, Å^3	3923.1 (23)
Z	4
ρ_{calcd}, g/cm^3	1.99
ρ_{obsd}, g/cm^3 (flotation CCl$_4$/CBr$_4$)	1.89
Laue symmetry	monoclinic
space group	$P2_1/n$ (alternate $P2_1/c$; C_{2h}^5; no. 14)
systematic absences	OkO, k = 2n + 1; hOl, $h + l = 2n + 1$
mol formula	[CH$_3$OZnFe(CO)$_2$C$_5$H$_5$]$_4$
Data Collection and Reduction	
radiatn	Mo Kα
μ, cm^{-1}	36.30
mounting axis	$\sim a$
take off angle, deg	6.2
scan type	ω
scan speed, deg/min	2.0–29.3
scan width, deg	1.0
bkgd(total):scan ratio	1:1
std reflctns and freq	3/50
variatn of I_{std}	<6%
2θ limits	0.0–43.0°
criterion for observ	$3\sigma(F)$
total data/obsd data	4275/3826
Structure Solution and Refinement	
solutn	direct methods and difference fourier
refinement	full-matrix least squares
isotropic convergence[b]	R_1 = 14.9%; R_2 = 15.9%
anisotropic convergence[b]	R_1 = 4.5%; R_2 = 5.0%
max shifts in parameters (Δ/σ) in final cycle	positional, 0.16; thermal, 0.14
error of fit	2.85
data/parameters	8.15
estimated variation in I's due to absorptn	<2% (spherical model)
max residual electron density in final difference map	1.02 (e/Å) at $\sim$1.1 Å from center of Zn(4)–Fe(4) bond

[a] All crystallographic calculations were done on a Prime 400 computer operated by the Materials Science Center and the Department of Chemistry, Cornell University. The principal programs used were as follows: REDUCE and UNIQUE, data reduction programs, M. E. Leonowicz, Cornell University, 1978; BLS, block-diagonal least-squares refinement, K. Hirotsu, Cornell University, 1978; ORFLS (modified), full-matrix least squares, W. R. Busing, K. O. Martin, and H. S. Levy, Oak Ridge, ORNL-TM-305; ORTEP, crystallographic illustration program, C. Johnson, Oak Ridge, ORNL-3794; BOND, Structural parameters and errors, K. Hirotsu, Cornell University, 1978; MULTAN-76, direct methods and fast fourier transform, G. Germain, P. Main, and M. Woolfson, University of York. [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|E_o|^2)^{1/2}$.

The reaction of Zn[Fe(CO)$_2$Cp]$_2$ with neat ethyl alcohol also occurred readily, giving an orange precipitate of [C$_2$H$_5$OZnFe(CO)$_2$Cp]$_x$. In this case no evidence for the degree of aggregation of the product was obtained; its mass

Table III. Fractional Coordinates for $[CH_3OZnFe(CO)_2Cp]_4$[a]

atom	x	y	z
Zn(1)	0.6098 (1)	0.2753 (1)	0.3732 (1)
Zn(2)	0.5056 (1)	0.1003 (1)	0.3113 (1)
Zn (3)	0.4943 (1)	0.3281 (1)	0.2671 (1)
Zn(4)	0.3921 (1)	0.2610 (1)	0.3957 (1)
Fe(1)	0.7390 (1)	0.3143 (1)	0.4264 (1)
Fe(2)	0.5098 (1)	0.0761 (1)	0.2811 (1)
Fe(3)	0.4805 (1)	0.4386 (1)	0.1815 (1)
Fe(4)	0.2534 (1)	0.2740 (1)	0.4657 (1)
O(1)	0.4038 (3)	0.2112 (3)	0.3020 (2)
O(2)	0.4928 (3)	0.3657 (3)	0.3604 (2)
O(3)	0.5074 (3)	0.1628 (4)	0.3989 (2)
O(4)	0.5967 (3)	0.2232 (3)	0.2838 (2)
C(1)	0.3212 (6)	0.1836 (7)	0.2718 (4)
C(2)	0.4849 (6)	0.4728 (6)	0.3845 (4)
C(3)	0.5167 (6)	0.0958 (6)	0.4529 (4)
C(4)	0.6806 (6)	0.2090 (6)	0.2392 (4)
C(11)	0.7333 (6)	0.4352 (8)	0.3891 (5)
O(11)	0.7331 (5)	0.5141 (6)	0.3642 (4)
C(12)	0.6516 (8)	0.3388 (7)	0.4836 (4)
O(12)	0.5913 (6)	0.3516 (6)	0.5254 (3)
C(13)	0.8524 (7)	0.2456 (9)	0.3713 (5)
C(14)	0.7910 (7)	0.1677 (8)	0.3990 (7)
C(15)	0.7863 (7)	0.1777 (8)	0.4648 (5)
C(16)	0.8460 (8)	0.2620 (9)	0.4762 (5)
C(17)	0.8853 (7)	0.3030 (8)	0.4199 (6)
C(21)	0.5253 (7)	0.0168 (7)	0.2093 (4)
O(21)	0.5341 (6)	0.0244 (6)	0.1607 (3)
C(22)	0.6241 (7)	0.0635 (7)	0.2974 (5)
O(22)	0.6991 (6)	0.0567 (6)	0.3100 (5)
C(23)	0.3761 (7)	0.1301 (9)	0.2753 (6)
C(24)	0.3809 (8)	0.0930 (8)	0.3366 (6)
C(25)	0.4505 (9)	0.1543 (9)	0.3602 (5)
C(26)	0.4829 (8)	0.2266 (7)	0.3149 (6)
C(27)	0.4374 (8)	0.2119 (7)	0.2627 (5)
C(31)	0.5595 (6)	0.5124 (7)	0.2177 (4)
O(31)	0.6097 (5)	0.5651 (6)	0.2414 (3)
C(32)	0.3874 (7)	0.4809 (7)	0.2299 (5)
O(32)	0.3225 (5)	0.5107 (6)	0.2648 (4)
C(33)	0.5291 (12)	0.4597 (11)	0.0862 (5)
C(34)	0.4335 (12)	0.4451 (12)	0.0934 (6)
C(35)	0.4127 (11)	0.3477 (12)	0.1209 (5)
C(36)	0.4976 (13)	0.3022 (9)	0.1295 (5)
C(37)	0.5683 (9)	0.3713 (14)	0.1093 (5)
C(41)	0.2630 (7)	0.1410 (9)	0.4641 (5)
O(41)	0.2671 (6)	0.0508 (6)	0.4640 (5)
C(42)	0.3277 (7)	0.2849 (9)	0.5223 (5)
O(42)	0.3752 (6)	0.2908 (8)	0.5612 (4)
C(43)	0.1081 (6)	0.2936 (9)	0.4721 (5)
C(44)	0.1476 (7)	0.2960 (9)	0.4094 (5)
C(45)	0.2109 (7)	0.3801 (9)	0.4007 (5)
C(46)	0.2100 (8)	0.4274 (8)	0.4580 (6)
C(47)	0.1450 (8)	0.3737 (11)	0.5018 (5)

[a] Numbers in parentheses are estimated standard deviations in the last significant figure.

spectrum was essentially that of $Zn[Fe(CO)_2Cp]_2$, which may have resulted from synproportionation during the analysis.

The infrared spectra of toluene solutions of the methoxy and ethoxy derivatives in the C–O stretching region are similar (Table I); each consists of two doublets with the component of lower intensity appearing about 10 cm^{-1} higher in energy. The number of bands is greater than predicted by local symmetry of the $Fe(CO)_2Cp$ group but fewer than expected on the basis of the observed molecular symmetry in the crystal (C_1).

Water also reacted with $Zn[Fe(CO)_2Cp]_2$ when equimolar amounts were vigorously mixed in toluene for 24 h. The yellow product, (cyclopentadienyldicarbonyliron)zinc hydroxide was found to be insoluble in all common solvents. The solid-state infrared spectrum is similar in the carbonyl region to those of the alkoxides $[ROZnFe(CO)_2Cp]_4$ ($R = CH_3$ or $R = C_2H_5$) but also shows an O–H stretching vibration at 3615 cm^{-1}. The degree of association of $[HOZnFe(CO)_2Cp]_x$ is not known, but its insolubility suggests a polymeric form.

Phenol was also found to react readily with $Zn[Fe(CO)_2Cp]_2$, but in contrast to the reaction with ethanol and methanol, an excess of phenol gave more than the expected amount of $HFe(CO)_2Cp$ (determined by IR spectroscopy) and a solid tentatively identified as zinc phenoxide (eq 2).

$$Zn[Fe(CO)_2Cp]_2 + 2C_6H_5OH \rightarrow 2HFe(CO)_2Cp + Zn(OC_6H_5)_2 \quad (2)$$

When equal amounts of $Zn[Fe(CO)_2Cp]_2$ and phenol were combined in toluene, $[C_6H_5OZnFe(CO)_2Cp]_x$ was obtained as irregular orange crystals. However, recrystallization of the product was thwarted by the persistent formation of $Zn(OC_6H_5)_2$. The product gave a satisfactory elemental analysis and a solid-state infrared spectrum similar to those of the analogous alkoxides.

Crystal Structure of $[CH_3OZnFe(CO)_2Cp]_4$. The crystal structure of $[CH_3OZnFe(CO)_2Cp]_4$ is composed of discrete tetrameric molecules located in general positions of space group $P2_1/n$. The tetramer possesses C_1 symmetry and adopts a pseudo-cubic structure as shown in Figure 1. The distorted cubic Zn_4O_4 core is made up of interpenetrating tetrahedra of zinc and oxygen atoms. Each oxygen atom is bonded to a methyl group while each zinc is bonded to the iron atom of an (η^5-cyclopentadienyl)dicarbonyliron ligand. As observed in other M_4X_4 systems[19] the Zn_4 and O_4 units deviate substantially from idealized tetrahedral geometry; the Zn–Zn distances range from 3.106 (2) to 3.049 (2) Å (3.081-Å average), the O–O distances range from 2.771 (6) to 2.739 (6) Å (2.755-Å average), and the Zn–O distances (Table IV) range from 2.099 (4) to 2.048 (5) Å. The Zn–Zn interactions are considered to be nonbonding as the observed separation is substantially longer than the Zn–Zn distance of 2.665 Å in zinc metal.[20a] Likewise the O–O distances are considerably longer than the value of 1.32 Å computed from the covalent single-bond radius.[20b]

The average Zn–O distance of 2.07 Å compares favorably with the value of 2.09 Å determined for $[CH_3OZnCH_3]_4$.[21] The Zn–O–Zn angles (Table V) range from 97.6 (2) to 94.8 (2)° (96.2° average), and the O–Zn–O angles vary between 84.7 (2) and 82.3 (2)° (83.4° average). The best planes calculated from the six sets of four facial atoms of the core are within 1° of being parallel to opposite planes and within 1° of being perpendicular to adjacent planes (Table VII); the component atoms of these planes are all found to lie within 0.07 Å of the calculated planes. The tetrahedral coordination of each core atom is completed by the methyl groups on oxygen with Zn–O–C angles between 123.6 (4) and 117.5 (4)° (120.8° average) and the $Fe(CO)_2Cp$ group on zinc with O–Zn–Fe angles between 134.0 (1) to 126.2 (1)° (129.6° average). The core atom to substituent atom distances vary in a nonsystematic fashion. The $O-CH_3$ distances range from 1.468 (9) to 1.458 (9) Å with an average distance of 1.462 Å that is similar to the value of 1.44 Å in $[CH_3OZnCH_3]_4$.[21] The Zn–Fe bond lengths range from 2.354 (2) to 2.344 (2) Å. These are significantly shorter than the previously reported Zn–Fe bond lengths of 2.532 and 2.585 Å in the cyclic complex $[(bpy)ZnFe(CO)_4]_2$.[22] The observed bond lengths (2.350-Å

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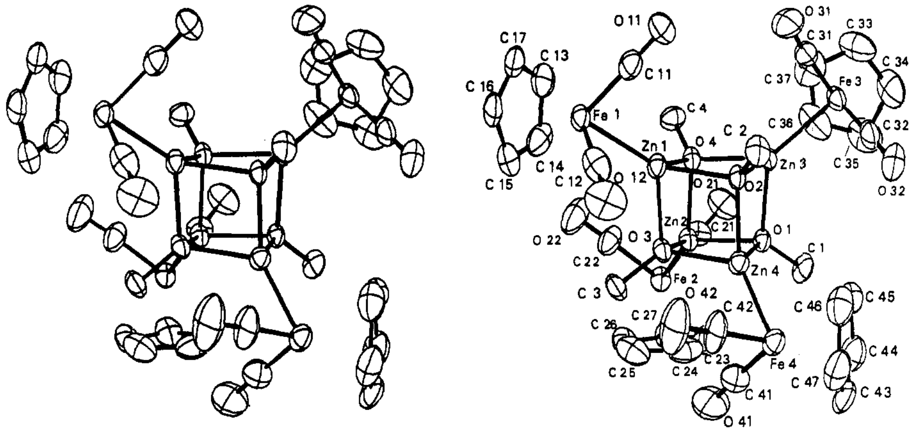

Figure 1. A stereoscopic ORTEP drawing of $[CH_3OZnFe(CO)_2Cp]_4$ with 35% probability thermal ellipsoids.

Table IV. Bond Distances[a] (Å) in $[CH_3OZnFe(CO)_2Cp]_4$

Zn(1)-O(2)	2.083 (5)	Zn(3)-O(1)	2.065 (4)
Zn(1)-O(3)	2.085 (5)	Zn(3)-O(2)	2.059 (4)
Zn(1)-O(4)	2.063 (4)	Zn(3)-O(4)	2.054 (4)
Zn(2)-O(2)	2.064 (4)	Zn(4)-O(1)	2.099 (4)
Zn(2)-O(3)	2.048 (5)	Zn(4)-O(2)	2.049 (4)
Zn(2)-O(4)	2.086 (4)	Zn(4)-O(3)	2.085 (5)
	Zn-O(av) = 2.070		
O(1)-C(1)	1.460 (10)	O(3)-C(3)	1.463 (10)
O(2)-C(2)	1.468 (9)	O(4)-C(4)	1.458 (9)
	$O-CH_3$(av) = 1.462		
Zn(1)-Fe(1)	2.344 (2)	Zn(3)-Fe(3)	2.348 (2)
Zn(2)-Fe(2)	2.352 (2)	Zn(4)-Fe(4)	2.354 (2)
	Zn-Fe(av) = 2.350		
Fe(1)-C(11)	1.752 (11)	Fe(3)-C(31)	1.729 (9)
Fe(1)-C(12)	1.677 (10)	Fe(3)-C(32)	1.682 (10)
Fe(2)-C(21)	1.711 (9)	Fe(4)-C(41)	1.710 (12)
Fe(2)-C(22)	1.724 (11)	Fe(4)-C(42)	1.714 (11)
	Fe-CO(av) = 1.712		
C(11)-O(11)	1.143 (13)	C(31)-O(31)	1.150 (12)
C(12)-O(12)	1.181 (12)	C(32)-O(32)	1.185 (12)
C(21)-O(21)	1.165 (11)	C(41)-O(41)	1.158 (14)
C(22)-O(22)	1.143 (14)	C(42)-O(42)	1.141 (14)
	C-O(av) = 1.158		
Fe(1)-C(13)	2.090 (10)	Fe(3)-C(33)	2.102 (11)
Fe(1)-C(14)	2.081 (11)	Fe(3)-C(34)	2.086 (14)
Fe(1)-C(15)	2.083 (11)	Fe(3)-C(35)	2.075 (14)
Fe(1)-C(16)	2.083 (12)	Fe(3)-C(36)	2.075 (11)
Fe(1)-C(17)	2.090 (10)	Fe(3)-C(37)	2.069 (13)
Fe(1)-CTR(1)[b]	1.709 (10)	Fe(3)-CTR(3)	1.717 (12)
Fe(2)-C(23)	2.056 (11)	Fe(4)-C(43)	2.088 (9)
Fe(2)-C(24)	2.089 (11)	Fe(4)-C(44)	2.070 (11)
Fe(2)-C(25)	2.067 (11)	Fe(4)-C(45)	2.093 (11)
Fe(2)-C(26)	2.081 (10)	Fe(4)-C(46)	2.077 (11)
Fe(2)-C(27)	2.089 (10)	Fe(4)-C(47)	2.089 (11)
Fe(2)-CTR(2)	1.706 (11)	Fe(4)-CTR(4)	1.715 (11)
	Fe-CTR(av) = 1.712		
	Fe-C(av) = 2.082		
C(13)-C(14)	1.415 (15)	C(33)-C(34)	1.374 (24)
C(14)-C(15)	1.412 (18)	C(34)-C(35)	1.398 (21)
C(15)-C(16)	1.419 (16)	C(35)-C(36)	1.383 (24)
C(16)-C(17)	1.375 (16)	C(36)-C(37)	1.379 (21)
C(17)-C(13)	1.405 (17)	C(37)-C(33)	1.383 (22)
C(23)-C(24)	1.410 (18)	C(43)-C(44)	1.399 (14)
C(24)-C(25)	1.410 (17)	C(44)-C(45)	1.407 (15)
C(25)-C(26)	1.384 (15)	C(45)-C(46)	1.371 (17)
C(26)-C(27)	1.376 (17)	C(46)-C(47)	1.423 (16)
C(27)-C(23)	1.374 (15)	C(47)-C(43)	1.350 (17)
	C-C(av) = 1.392		

[a] The uncertainty of the least significant figure(s) is given in parentheses. [b] CTR is the center of the Cp ring calculated as the average of the carbon atom positions in the ring.

average) are close to the value of 2.36 Å estimated from the sum of the covalent radii derived from similar molecules.[23] The Zn-Fe bond length is also dependent on the hybridization of the iron atoms which in turn is dependent on the geometry of the $CpFe(CO)_2$ moiety which varies in a nonsystematic way in this case.

Teo and Calabrese considered nonsystematic distortion in M_4X_4 clusters in terms of steric effects and hybridization.[19] In the present example the observed trend of increasing M-Y bond length (i.e., Zn-Fe or O-C) with increasing X-M-Y bond angle (i.e., O-Zn-Fe or Zn-O-C) is not seen in the Zn-Fe distances and may or may not be present in the O-C bond lengths; the esd's of the O-C bond lengths are larger than the variations observed.

The shapes of the $Fe(CO)_2Cp$ moieties are very similar to those previously reported except for the Fe-C distances in the carbonyls on Fe(1), viz., 1.677 (10) and 1.752 (11) Å, which deviate considerably from the mean distance (1.712 Å) found in this compound and in others (1.72-Å average.[24-29] The average Zn-Fe-CO angle of 81.7° is smaller than the X-Fe-CO angle in similar $XFe(CO)_2Cp$ compounds (90° average[24-29]) but is very similar to the average Zn-Co-C angle of 81.1° observed in $Zn[Co(CO)_4]_2$.[30] This may be the result of a bonding interaction between the carbonyl carbon and the zinc atom similar to that postulated for carbonyl carbon-silicon interactions in $X_3SiCo(CO)_4$ compounds.[31]

The $CpFe(CO)_2$ groups assume a gauche rotational conformation (about the Zn-Fe bond) relative to the three core oxygen atoms adjacent to that bond as shown by the torsional angles found for O-Zn-Fe-CO and for O-Zn-Fe-CTR linkages (see Table VI).

Reactions of $Zn[Co(CO)_4]_2$. In contrast to the chemistry of $Zn[Fe(CO)_2Cp]_2$ described above, the reaction of $Zn[Co(CO)_4]_2$ in pure methyl alcohol predominantly consists of the partial ionic dissociation of the metal-metal bonds into $Co(CO)_4^-$ and (presumably) the cation

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(23) By subtracting the covalent radius of oxygen[21] from the average Zn-O bond length in $[CH_3OZnCH_3]_4$[22], we obtain a value of 1.17 Å for the covalent radius of zinc. Similarly by subtracting the appropriate covalent radius[21] of the atom X from the reported Fe-X distance in six compounds containing the $Fe(CO)_2Cp$ moiety,[24-29] we obtain an average value of 1.19 Å for the covalent radius of iron with a range of 1.13-1.31 Å.

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Table V. Selected Interatomic Angles[a] (Deg) for [$CH_3OZnFe(CO)_2Cp$]$_4$

O(2)-Zn(1)-O(3)	82.3 (2)	O(1)-Zn(3)-O(2)	83.2 (2)
O(2)-Zn(1)-O(4)	83.9 (2)	O(1)-Zn(3)-O(4)	83.8 (2)
O(3)-Zn(1)-O(4)	83.3 (2)	O(2)-Zn(3)-O(4)	84.7 (2)
O-Zn(1)-O(av)	83.2	O-Zn(3)-O(av)	83.9
O(1)-Zn(2)-O(3)	84.6 (3)	O(1)-Zn(4)-O(2)	82.7 (2)
O(1)-Zn(2)-O(4)	83.0 (2)	O(1)-Zn(4)-O(3)	82.8 (2)
O(3)-Zn(2)-O(4)	83.7 (3)	O(2)-Zn(4)-O(3)	83.2 (2)
O-Zn(2)-O(av)	83.8	O-Zn(4)-O(av)	82.9
O-Zn-O(av) = 83.4			
Fe(1)-Zn(1)-O(2)	129.9 (1)	Fe(3)-Zn(3)-O(1)	127.9 (1)
Fe(1)-Zn(1)-O(3)	126.2 (1)	Fe(3)-Zn(3)-O(2)	129.0 (1)
Fe(1)-Zn(1)-O(4)	133.5 (1)	Fe(3)-Zn(3)-O(4)	131.3 (1)
Fe(1)-Zn(1)-O(av)	129.9	Fe(3)-Zn(3)-O(av)	129.4
Fe(2)-Zn(2)-O(1)	129.1 (1)	Fe(4)-Zn(4)-O(1)	126.9 (1)
Fe(2)-Zn(2)-O(3)	128.8 (2)	Fe(4)-Zn(4)-O(2)	134.0 (1)
Fe(2)-Zn(2)-O(4)	130.8 (1)	Fe(4)-Zn(4)-O(3)	129.3 (1)
Fe(2)-Zn(2)-O(av)	129.6	Fe(4)-Zn(4)-O(av)	130.3
Fe-Zn-O(av) = 129.6			
Zn(2)-O(1)-Zn(3)	96.5 (2)	Zn(1)-O(3)-Zn(2)	96.4 (2)
Zn(2)-O(1)-Zn(4)	95.3 (2)	Zn(1)-O(3)-Zn(4)	96.3 (2)
Zn(3)-O(1)-Zn(4)	95.9 (2)	Zn(2)-O(3)-Zn(4)	96.3 (2)
Zn-O(1)-Zn(av)	95.9	Zn-O(3)-Zn(av)	96.3
Zn(1)-O(2)-Zn(3)	94.8 (2)	Zn(1)-O(4)-Zn(2)	95.9 (2)
Zn(1)-O(2)-Zn(4)	97.5 (2)	Zn(1)-O(4)-Zn(3)	95.6 (2)
Zn(3)-O(2)-Zn(4)	97.6 (2)	Zn(2)-O(4)-Zn(3)	96.2 (2)
Zn-O(2)-Zn(av)	96.6	Zn-O(4)-Zn(av)	95.9
Zn-O-Zn(av) = 96.2			
C(1)-O(1)-Zn(2)	119.8 (4)	C(3)-O(3)-Zn(1)	119.2 (4)
C(1)-O(1)-Zn(3)	121.5 (4)	C(3)-O(3)-Zn(2)	120.8 (4)
C(1)-O(1)-Zn(4)	121.6 (4)	C(3)-O(3)-Zn(4)	121.9 (4)
C(1)-O(1)-Zn(av)	121.0	C(3)-O(3)-Zn(av)	120.6
C(2)-O(2)-Zn(1)	120.2 (4)	C(4)-O(4)-Zn(1)	119.6 (4)
C(2)-O(2)-Zn(3)	123.6 (4)	C(4)-O(4)-Zn(2)	122.1 (4)
C(2)-O(2)-Zn(4)	117.5 (4)	C(4)-O(4)-Zn(3)	121.2 (4)
C(2)-O(2)-Zn(av)	120.4	C(4)-O(4)-Zn(av)	121.0
C-O-Zn(av) = 120.8			
Zn(1)-Fe(1)-C(11)	83.2 (3)	Zn(3)-Fe(3)-C(31)	81.8 (3)
Zn(1)-Fe(1)-C(12)	80.4 (4)	Zn(3)-Fe(3)-C(32)	81.0 (4)
Zn(1)-Fe(1)-CTR(1)[b]	122.0 (4)	Zn(3)-Fe(3)-CTR(3)	118.7 (5)
Zn(1)-Fe(1)-CO(av)	81.8	Zn(3)-Fe(3)-CO(av)	81.4
Zn(2)-Fe(2)-C(21)	79.5 (3)	Zn(4)-Fe(4)-C(41)	81.8 (3)
Zn(2)-Fe(2)-C(22)	81.2 (3)	Zn(4)-Fe(4)-C(42)	84.9 (3)
Zn(2)-Fe(2)-CTR(2)	122.3 (4)	Zn(4)-Fe(4)-CTR(4)	119.9 (4)
Zn(2)-Fe(2)-CO(av)	80.4	Zn(4)-Fe(4)-CO(av)	83.4
Zn-Fe-CO(av) = 81.7			
Zn-Fe-CTR(av) = 120.7			
Fe(1)-C(11)-O(11)	177.4 (8)	Fe(3)-C(31)-O(31)	177.1 (8)
Fe(1)-C(12)-O(12)	176.7 (9)	Fe(3)-C(32)-O(32)	179.0 (10)
Fe(2)-C(21)-O(21)	178.7 (9)	Fe(4)-C(41)-O(41)	178.1 (9)
Fe(2)-C(22)-O(22)	177.8 (10)	Fe(4)-C(42)-O(42)	178.0 (9)
Fe-C-O(av) = 177.7			
C(11)-Fe(1)-C(12)	95.6 (4)	C(31)-Fe(3)-C(32)	93.5 (5)
C(11)-Fe(1)-CTR(1)	129.0 (5)	C(31)-Fe(3)-CTR(3)	131.2 (6)
C(12)-Fe(1)-CTR(1)	129.4 (5)	C(32)-Fe(3)-CTR(3)	131.2 (7)
C(21)-Fe(2)-C(22)	96.7 (5)	C(41)-Fe(4)-C(42)	92.3 (5)
C(21)-Fe(2)-CTR(2)	129.0 (6)	C(41)-Fe(4)-CTR(4)	130.8 (5)
C(22)-Fe(2)-CTR(2)	129.6 (5)	C(42)-Fe(4)-CTR(4)	130.3 (5)
OC-Fe-CO(av) = 94.5			
OC-Fe-CTR(av) = 130.1			

[a] The uncertainty of the least significant figure(s) is given in parentheses. [b] CTR is the center of the Cp ring.

$(CH_3OH)_xZnCo(CO)_4^+$. Evidence for dissociation comes from the conductivity and IR spectrum of a 0.01 M solution of $Zn[Co(CO)_4]_2$ in methyl alcohol; the molar conductivity, measured at room temperature at 1000 Hz, was 116 (Ω cm)$^{-1}$, and the ν_{CO} were observed at 2060 (vw), 1962 (m), and 1911 (s) cm^{-1}.[32] The last band listed is assigned to the anion, $Co(CO)_4^-$. No evidence for decomposition products characteristic of $HCo(CO)_4$ in methyl alcohol was seen by IR spectroscopy, and we conclude that it does not form to a significant extent under these conditions. Yet when a hexane solution of nearly equimolar amounts of methyl alcohol and $Zn[Co(CO)_4]_2$ stood in the dark, [$CH_3OZnCo(CO)_4$]$_4$ formed as clear, colorless, cubic crystals in 63% yield. The expected coproduct $HCo(CO)_4$ was detected by its characteristic pungent odor and by IR spectroscopy.[33] The elemental analytical and spectroscopic data for the crystalline methoxide are all consistent with a highly symmetrical, tetrameric structure similar to

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(32) Burlitch, J. M.; Blackmore, T., unpublished observations.

(33) Ungváry, F.; Markó, L. *J. Organomet. Chem.* **1969**, *20*, 205.

Table VI. Selected Torsional Angles (Deg) $[CH_3OZnFe(CO)_2Cp]_4$

O(3)-Zn(1)-Fe(1)-C(11)	156.2
O(4)-Zn(1)-Fe(1)-C(12)	179.0
O(2)-Zn(1)-Fe(1)-CTR(1)	175.1
O(3)-Zn(2)-Fe(2)-C(21)	170.1
O(1)-Zn(2)-Fe(2)-C(22)	168.5
O(4)-Zn(2)-Fe(2)-CTR(2)	179.4
O(1)-Zn(3)-Fe(3)-C(31)	161.1
O(4)-Zn(3)-Fe(3)-C(32)	173.5
O(2)-Zn(3)-Fe(3)-CTR(3)	177.8
O(2)-Zn(4)-Fe(4)-C(41)	167.0
O(1)-Zn(4)-Fe(4)-C(42)	165.9
O(3)-Zn(4)-Fe(4)-CTR(4)	174.3

the $Fe(CO)_2Cp$ analogue. The highest mass ion in the mass spectrum at *m*/*z* 1064–1076 showed a distribution of isotopic abundances which corresponds to that calculated for four zinc atoms. Other ions corresponding to the loss of CO or CH_3O groups were observed. Three IR-active C–O stretching modes are predicted (and observed) for $[CH_3OZnCo(CO)_4]_4$, viz., $3T_2$ or $2A_1 + E$ assuming overall T_d symmetry or C_{3v} local symmetry for equivalent $Co(CO)_4$ groups, respectively. In methanol, this alkoxide partially dissociates; the ν_{CO} observed at 2061 (m), 2052 (w, sh), 1971 (s, sh), 1958 (vs), and 1908 (s) cm^{-1} include the characteristic absorption for the anion $Co(CO)_4^-$.[34] The degree of aggregation is not known.

Under conditions similar to those used for the reaction with methanol, $Zn[Co(CO)_4]_2$ did not react with ethanol. Infrared spectra of reaction mixtures in hexane indicated the formation of the Lewis base adduct $[Co(CO)_4]_2Zn\cdot(C_2H_5OH)_2$. Addition of a tenfold excess of ethanol caused the spectrum's complexity to increase from the three terminal carbonyl peaks of $Zn[Co(CO)_4]_2$[11] to five terminal carbonyl peaks (ν_{CO} 2068 (1), 2051 (6), 1983 (9), 1976 sh (8), and 1959 (10) cm^{-1}). Coordination of ethanol apparently decreases the symmetry of the molecule from D_{3d} to C_{2v} or lower; seven terminal bands are predicted for C_{2v} symmetry. A similar increase in the complexity of the infrared spectrum in the carbonyl region of the adduct $Cd[Mn(CO)_5]_2\cdot$(diglyme) as compared with spectra of $Cd[Mn(CO)_5]_2$ has been reported by Hsieh and Mays.[2a]

Equimolar amounts of water and $Zn[Co(CO)_4]_2$ in toluene reacted in several hours, giving $HCo(CO)_4$ and a white, crystalline compound, the elemental analysis of which was consistent with the formula $[HOZnCo(CO)_4]_x$. IR spectra of the compound in toluene (ν_{CO} 2074 (4), 2009 (2), and 1979 (10) cm^{-1}) and in potassium bromide pellets are very similar to those of $[CH_3OZnCo(CO)_4]_4$. In the O–H stretching region the toluene solution shows a broad single peak at 3497 cm^{-1}, while the spectrum of the compound in the potassium bromide pellet contains a sharper single peak at 3591 cm^{-1}; both indicate the presence of OH groups. This assignment was confirmed by the solid state infrared spectrum of $[DOZnCo(CO)_4]_x$ (synthesized from D_2O and $Zn[Co(CO)_4]_2$), which displayed a band at 2660 cm^{-1} assigned to ν_{O-D}.

Since the highest mass ion in the mass spectrum of $[HOZnCo(CO)_4]_x$ was $Zn[Co(CO)_4]_2^+$ and since no peaks appeared in the ^1H NMR spectrum, the structure of $[HOZnCo(CO)_4]_x$ is uncertain. The shift in the position of the O–H stretching band on going from the solid state to solution suggests a change in structure, while the broadness of the O–H stretching band in the solution IR spectrum and the lack of an observable ^1H NMR spectrum suggest dissociation of the molecule or hydrogen bonding in solution.

When the foregoing reaction was carried out in hexane, an unstable adduct tentatively identified as $[Co(CO)_4]_2Zn(H_2O)_x$ precipitated from the reaction mixture.[1b]

Reactions of $Zn[Mo(CO)_3Cp]_2$. Both ethanol and methanol reacted readily with the complex $Zn[Mo(CO)_3Cp]_2$; methanol as the solvent gave $[CH_3OZnMo(CO)_3Cp]_x$ as a cream colored solid in high yield. The product gave the expected ^1H NMR spectrum, with two sharp resonances at δ –5.39 (C_5H_5) and δ –3.78 (OCH_3). The IR spectrum of a sample in KBr had four bands in the carbonyl stretching region while the spectrum in dichloromethane solution showed six bands. Although some of the bands fall at relatively low frequencies (Table I), all are characteristic of terminal carbonyls in compounds containing the cyclopentadienyl ligand. The degree of aggregation of the product is unknown in the absence of mass spectroscopic or molecular weight data.

The reaction of $Zn[Mo(CO)_3Cp]_2$ with neat ethanol gave a 30% yield of $[C_2H_5OZnMo(CO)_3Cp]_x$. No more ethoxide formed when the reaction stood longer. When the supernatant liquid was decanted, evaporated to dryness, washed with hexane to remove the hydride $HMo(CO)_3Cp$, and then retreated with ethanol, more product was obtained. The significance of this behavior is considered in a subsequent section.

As observed for the methoxy analogue, the spectrum of a solution contained six terminal C–O stretching bands while that from the solid state contained four. The general appearance of these spectra suggest that the $A_1 + E$ pattern expected on the basis of the C_{2v} local symmetry of the $-Mo(CO)_3Cp$ group is perturbed by considerable splitting of the E mode especially in the solid state.

Reactions of $Zn[Mn(CO)_5]_2$. Bis(pentacarbonylmanganese)zinc is quite insoluble in solvents which are not Lewis bases. Thus when equimolar amounts of $Zn[Mn(CO)_5]_2$ and methanol were mixed in dichloromethane, most of the $Zn[Mn(CO)_5]_2$ remained undissolved and unreacted after 12 h. A 3.5-fold excess of methanol dissolved the starting material, but the reaction (eq 3) was not

$$CH_3OH + Zn[Mn(CO)_5]_2 \rightarrow HMn(CO)_5 + {}^1/_4[CH_3OZnMn(CO)_5]_4 \quad (3)$$

complete until the volatile product, $HMn(CO)_5$, was removed by trap-to-trap distillation. The concentration of $HMn(CO)_5$ which was determined from the infrared spectra of the reaction solution and of the distillate indicated that before distillation the reaction was only 60% complete.

The white, crystalline product had the expected singlet in a ^1H NMR spectrum. The highest mass ion in the mass spectrum has the isotopic distribution expected for four zinc atoms and is attributed to $(CH_3OZn)_4(Mn(CO)_5)_3^+$. Thus the mass spectrum establishes the tetrameric nature of $[CH_3OZnMn(CO)_5]_4$ in the vapor phase.

When a suspension of $Zn[Mn(CO)_5]_2$ in dichloromethane was treated with a 13-fold excess of ethanol, the solid dissolved, but very little pentacarbonylmanganese hydride or $[C_2H_5OZnMn(CO)_5]_4$ formed. Appreciable yields of ethoxide were obtained only when the reaction mixture was repeatedly vacuum distilled to remove the volatile $HMn(CO)_5$ and the residue redissolved in pure ethanol. No reaction was observed in THF.

The isotopic distribution of the highest mass ion in the mass spectrum of the white product was identified as $(C_2H_5OZn)_4Mn_3(CO)_{14}^+$ and suggests that $[C_2H_5OZnMn(CO)_5]_4$ is also tetrameric in the vapor phase. The infrared spectrum of $[CH_3OZnMn(CO)_5]_4$ contained two bands in

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[34] Burlitch, J. M. *J. Am. Chem. Soc.* **1969**, *91*, 4563.

the carbonyl stretching region, while that of $[C_2H_5OZnMn(CO)_5]_4$ shows three bands (Table I); the solid-state spectra of both compounds show three bands in agreement with expectations based on the local symmetry the $(CO)_5Mn$ group.

The necessity of removing $HMn(CO)_5$ in order to drive to completion the reactions of $Zn[Mn(CO)_5]_2$ with ethanol and methanol strongly suggests the equilibria shown in eq 4. The presence of these equilibria was established by

$$ROH + Zn[Mn(CO)_5]_2 \rightleftharpoons HMn(CO)_5 + {}^1/_4[ROZnMn(CO)_5]_4 \quad (4)$$

$$R = CH_3, C_2H_5$$

treating $[C_2H_5OZnMn(CO)_5]_4$ with $HMn(CO)_5$ from which $Zn[Mn(CO)_5]_2$ (and presumably ethanol) was obtained.

As noted previously methanol was found to be more reactive than ethanol in every case. Additional evidence for this order of reactivity was gleaned from the observation that $[C_2H_5OZnMn(CO)_5]_4$ was largely converted to $[CH_3OZnMn(CO)_5]_4$ on treatment of the former with methanol. One and one-tenth equivalents of the ethoxide were used per equivalent of methanol, so that both the methoxide and the ethoxide were present in sufficient quantities to be seen easily in an ^1H NMR spectrum of the reaction mixture. From signal intensities the K_{eq} for the process of eq 5 was estimated to be 8.

$$4CH_3OH + [C_2H_5OZnMn(CO)_5]_4 \rightleftharpoons 4C_2H_5OH + [CH_3OZnMn(CO)_5]_4 \quad (5)$$

We were unable to extend the above chemistry to the analogous rhenium compound $Zn[Re(CO)_5]_2$ because of our inability to synthesize it. Neither the reported insertion reaction (eq 6)[1b] analogous to that used for the synthesis of $Zn[Mn(CO)_5]_2$[12] nor the reported metal–metal exchange reaction (eq 7)[1b] worked in our hands.

$$Zn + Re_2(CO)_{10} \rightarrow Zn[Re(CO)_5]_2 \quad (6)$$

$$Zn + Hg[Re(CO)_5]_2 \rightarrow Zn[Re(CO)_5]_2 \quad (7)$$

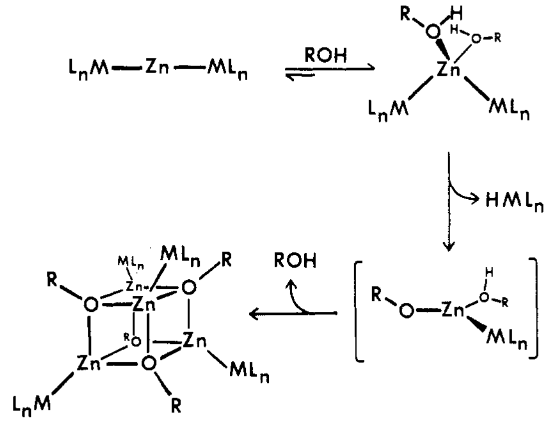
Reactivity Patterns. From the degree of conversion of the trimetallic species $Zn(ML_n)_2$ to alkoxides $MeOZn(ML_n)$ estimated by IR spectroscopy, the order of reactivity in methanol is the following: $Zn[Fe(CO)_2Cp]_2 > Zn[Mo(CO)_3Cp]_2 > Zn[Mn(CO)_5]_2 \gg Zn[Co(CO)_4]_2$.

The Lewis base property of the solvent has a marked influence on the rates and equilibrium positions of these reactions. The clearest example of this was seen in the reactions of $Zn[Mn(CO)_5]_2$. The reaction of a 3.7-fold excess of methanol with $Zn[Mn(CO)_5]_2$ in dichloromethane reached equilibrium when 60% of the theoretical amount of $HMn(CO)_5$ was produced (IR). In contrast, when $Zn[Mn(CO)_5]_2$ was treated with a 3.7-fold excess of methanol in tetrahydrofuran, no $HMn(CO)_5$ formed.

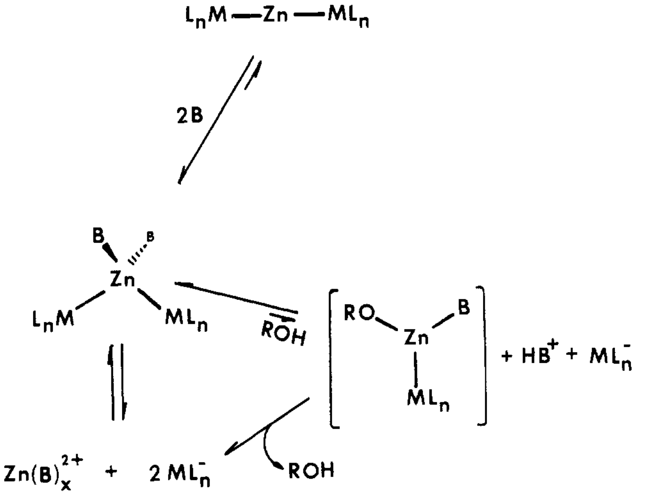
The formation of Lewis base adducts of $Zn[Mn(CO)_5]_2$ by the basic solvent, THF, appears to give the most plausible explanation of this inhibition. Considerable precedent exists for the formation of such adducts especially for cadmium analogues such as $\{Cd[Mn(CO)_5]_2\cdot(diglyme)\}$.[2a,35] Two coordination sites on zinc in $Zn[Mn(CO)_5]_2$ are occupied by THF molecules so that coordination by methanol is blocked and little or no reaction occurs (Scheme I). This line of reasoning leads us to postulate that coordination of the alcohol at zinc is the first step toward alkoxide formation.

The order of reactivity noted above and the consistently lower reactivity of ethanol suggest that one of the major driving forces for these reactions is the formation of an *undissociated* metal hydride. The K_a's of the product hydrides decrease as $HCo(CO)_4 \gg HMn(CO)_5 \geq HMo(CO)_3Cp > HFe(CO)_2Cp$[36] and correlate inversely with the order of reactivity. Thus any process which either reduces the K_a of the hydride relative to that of the alcohol or which removes the hydride entirely will enhance transfer of protons from the alcohol and formation of the alkoxide. Some metal carbonyl hydrides, especially $HCo(CO)_4$ and $HFe(CO)_2Cp$, are unstable toward formation of hydrogen and metal dimer.[33,37] This process and that of volatilization, by sublimation, as used for $HMn(CO)_5$ and $HMo(CO)_3Cp$, remove hydride. These processes are shown in Scheme II.

Scheme I. Promotion of Alkoxide Formation by Elimination of Undissociated Transition Metal Carbonyl Hydride



Scheme II. Behavior of Lewis Bases as Inhibitors for (Transition metal)zinc Alkoxide Formation



The facile reaction of $Zn[Co(CO)_4]_2$ with methanol in hexane to form the methoxide $[CH_3OZnCo(CO)_4]_4$, in contrast to the heterolytic dissociation seen with methanol as solvent, is attributed to a combination of the above effects. In hexane solvent the K_a's of $HCo(CO)_4$ and of methanol would be expected to be considerably smaller than they are in methanol solvent. In hexane the $HCo(CO)_4$ formed will exist mainly as the undissociated hydride and will decompose to H_2 and $Co_2(CO)_8$[33] or be lost through volatilization. In methanol, however, small amounts of $HCo(CO)_4$ will exist in the dissociated form, viz., as

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[35] Clegg, W.; Wheatley, P. J. *J. Chem. Soc., Dalton Trans.* **1974**, 511.

[36] (a) Shriver, D. F. *Acc. Chem. Res.* **1970**, *3*, 231. (b) Fischer, E. O.; Hafner, W.; Stahl, H. O. *Z. Anorg. Allg. Chem.* **1955**, *282*, 46.

[37] Green, M. L. H.; Street, C. N.; Wilkinson, G. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1959**, *14B*, 738.

$CH_3OH_2^+$ and $Co(CO)_4^-$, and effectively inhibit formation of significant amounts of alkoxide.

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Registry No. $Zn[Fe(CO)_2Cp]_2$, 82246-68-2; $[Fe(CO)_2Cp]_2$, 12154-95-9; $Zn[Co(CO)_4]_2$, 16985-99-2; $[CH_3OZnCo(CO)_4]_4$, 38999-00-7; $HCo(CO)_4$, 16842-03-8; $[HOZnCo(CO)_4]_x$, 82246-70-6; $HFe(CO)_2Cp$, 35913-82-7; $[CH_3OZnFe(CO)_2Cp]_4$, 37328-46-4; $[C_2H_5OZnFe(CO)_2Cp]_4$, 37328-48-6; $[HOZnFe(CO)_2Cp]_x$, 82246-72-8; $[C_6H_5OZnFe(CO)Cp]_x$, 82246-74-0; $Zn[Mn(CO)_5]_2$, 21686-75-9; $Mn_2(CO)_{10}$, 10170-69-1; $Zn[Re(CO)_5]_2$, 33728-44-8; $Re_2(CO)_{10}$, 14285-68-8; $Hg[Re(CO)_5]_2$, 33728-46-0; $[CH_3OZnMn(CO)_5]_4$, 38999-01-8; $[C_2H_5OZnMn(CO)_5]_4$, 38999-02-9; $HMn(CO)_5$, 16972-33-1; $Zn[Mo(CO)_3Cp]_2$, 54244-98-3; $[Mo(CO)_3Cp]_2$, 12091-64-4; $[CH_3OZnMn(CO)_3Cp]_x$, 82246-76-2; $[C_2H_5OZnMo(CO)_3Cp]_x$, 82264-85-5.

Supplementary Material Available: Table VII (calculated planes), Table VIII (thermal parameters), Table XI (calculated H atom positions), and a listing of structure factor amplitudes (32 pages). Ordering information is given on any current masthead page.

Acetal and Ketal Derivatives Related to Metal Formyl and Metal Acyl Complexes

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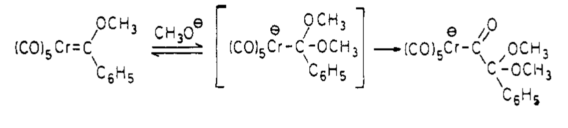
Addition of $NaOCH_3$ to $(C_5H_5)(CO)_2Fe{=}CH(OCH_3)^+PF_6^-$, **4**, and to $(C_5H_5)(CO)[P(C_6H_5)_3]Fe{=}CH(OCH_3)^+PF_6^-$, **6** led to the isolation of the stable acetals $(C_5H_5)(CO)_2FeCH(OCH_3)_2$, **5**, and $(C_5H_5)(CO)[P(C_6H_5)_3]FeCH(OCH_3)_2$, **7**. Similarly addition of $NaOCH_3$ to $(C_5H_5)(CO)_2Fe{=}C(OCH_3)C_6H_5{}^+BF_4^-$, **8**, led to the isolation of the stable ketal $(C_5H_5)(CO)_2FeC(OCH_3)_2C_6H_5$, **9**.

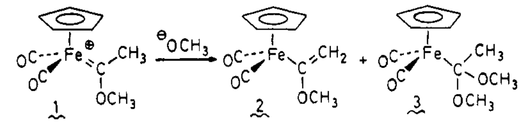
Introduction

Anionic ketal derivatives of metal acyl compounds have previously been suggested as unstable intermediates in the exchange of alkoxy groups of alkylalkoxycarbene complexes[1-3] and in the conversion of alkylalkoxycarbene complexes into (2,2-dialkoxyacyl)metal complexes.[2,3] Here we report the synthesis and isolation of stable neutral acetal and ketal derivatives related to metal formyl and metal acyl complexes. A dithioacetal complex, $(C_5H_5)(CO)_2Fe[C(H)S(CH_2)_3S]$, and ortho ester complexes such as $(C_5H_5)(CO)_2FeC(SCH_3)_3$ have recently been reported.[4]



Results and Discussion

In the course of studying the reactions of $[(C_5H_5)(CO)_2Fe{=}C(OCH_3)CH_3]^+BF_4^-$, **1**, with methyl organometallic reagents, we found that deprotonation to give the vinyl ether $(C_5H_5)(CO)_2Fe{-}C(OCH_3){=}CH_2$, **2**, was a major product of the reaction with methyllithium.[5] In an attempt to prepare a pure sample of vinyl ether **2**, we examined the reaction of **1**[6] with $NaOCH_3$ in CH_2Cl_2 at −78 °C. In addition to vinyl ether **2**, this reaction also produced $(C_5H_5)(CO)_2FeCOCH_3$ and the dimethyl ketal $(C_5H_5)(CO)_2FeC(OCH_3)_2CH_3$, **3**, in a 55:6:39 ratio. Dimethyl ketal **3** was tentatively identified by the ^1H NMR ($CDCl_3$) spectrum of the mixture which had resonances at δ 4.84, 3.20, and 1.80 in an area ratio of 5:6:3 in addition to peaks due to **2**. Attempted purification of **3** by both vacuum sublimation and alumina chromatography failed. Similar treatment of **1** with the more hindered base potassium *tert*-butoxide led to the isolation of vinyl ether **2** in 87% yield. The related conversion of $(C_5H_5)(CO)[P(C_6H_5)_3]Fe{=}C(OCH_2CH_3)CH_3^+$ to $(C_5H_5)(CO)[P(C_6H_5)_3]FeC(OCH_2CH_3){=}CH_2$ has been reported by Davison and Reger.[9]



This observation of a mixture of compounds containing a stable ketal of a metal acyl complex led us to attempt the synthesis of pure compounds containing this new functional group by studying the reactions of methoxide with cationic iron methoxycarbene complexes which cannot be deprotonated to vinyl ether complexes.

The preparation of an acetal complex related to a metal formyl complex was achieved by addition of methoxide to $(C_5H_5)(CO)_2Fe{=}CH(OCH_3)^+PF_6^-$ (**4**).[10] The acetal complex $(C_5H_5)(CO)_2FeCH(OCH_3)_2$ (**5**) was isolated as a yellow oil in 77% yield and was characterized by ^1H and ^{13}C NMR and by IR spectroscopy. Similarly, addition of methoxide to $(C_5H_5)(CO)[P(C_6H_5)_3]Fe{=}CH(OCH_3)^+PF_6^-$ (**6**)[10] gave the acetal complex $(C_5H_5)(CO)[P(C_6H_5)_3]FeCH(OCH_3)_2$ (**7**) in 99% yield as a yellow solid. In the ^1H and ^{13}C NMR

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