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Dinuclear Elimination as a Route to Unusual Bridging Carbonyls and Acetyls in Heterobimetallic Complexes

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Abstract: Reaction of Cp_2ZrMe_2 with $CpMo(CO)_3H$ yields methane and $Cp_2ZrMeMo(CO)_3Cp$ (**1**), which has two terminal carbonyl ligands and a third carbonyl with a low (1545 cm^{-1}) stretching frequency. Added gaseous CO inserts into the Zr–Me bond in **1** to form the η^2-acetyl ligand in **2**, $Cp_2Zr[C(O)Me](OC)Mo(CO)_2Cp$, which is shown by X-ray crystallography to lack a Zr–Mo bond but to be held together by a carbonyl-*OC* bridge. Complex **2**, which is also formed from $Cp_2Zr[C(O)Me]Me$ and $CpMo(CO)_3H$, reacts rapidly with proton sources to form $CpMo(CO)_3H$ and CH_3CHO. Complex **2** slowly loses CO in solution to form $Cp_2Zr(OCMe)(OC)MoCOCp$ (**3**), which contains a Zr–Mo bond, a bridging oxycarbene/acetyl, and a four-electron-donor carbonyl.

Introduction

In seeking means to effect the reduction of carbon monoxide, we have been examining bimetallic hydrogen transfer to carbon of the η^2-acyl group; the latter is readily formed by insertion of CO into the bond from an early transition metal to an alkyl. Both Cp_2MoH_2 and Cp_2ReH are effective reagents for hydrogen transfer to $Cp_2Zr[\eta^2\text{-}C(O)Me]Me$.[1,2] In seeking to broaden the range of useful hydrides, we attempted to employ $CpMo(CO)_3H$ in this reaction. In contrast to our results with other hydrides, we observed selective elimination of methane on treatment of $Cp_2Zr[\eta^2\text{-}C(O)Me]Me$ with $CpMo(CO)_3H$.

A related methane elimination, from Cp_2ZrMe_2 and $CpMo(CO)_3H$, had been reported by Renaut et al. in 1978.[3] Both reactions appeared to represent extensions of dinuclear alkane elimination (which we had established as a general reaction pattern for organoosmium complexes and had suggested as a general synthesis of heterobimetallic compounds)[4] to organozirconium complexes. However, although both reactions involved the same transition-metal hydride ($CpMo(CO)_3H$), the first involved the coordinatively saturated $Cp_2Zr[\eta^2\text{-}C(O)Me]Me$ whereas the second involved the coordinatively unsaturated Cp_2ZrMe_2. As we had found that a vacant coordination site was required for the dinuclear eliminations previously studied,[4] a comparative study of the two methane elimination reactions was indicated. We therefore undertook a complete spectroscopic and structural investigation of both systems and of their interconversion by the addition and loss of carbon monoxide.[5]

Experimental Section

All manipulations were performed in a Vacuum Atmospheres inert-atmosphere box or on a Schlenk or high-vacuum line unless otherwise stated. THF, toluene, and hexane were distilled from Na/benzophenone under nitrogen. Literature methods were used for the preparation of $CpMo(CO)_3H$,[6] Cp_2ZrMe_2,[7] $Cp_2Zr[C(O)Me]Me$,[8] and $(Cp_2ZrO)_3$.[9] Variable-temperature ^1H and ^{13}C NMR spectra were recorded on JEOL FX-100Q and Varian HR-220 spectrometers with Me_4Si or the residual solvent proton peak or a solvent carbon peak as an internal reference. Electron impact mass spectra were obtained on a VG-Micromass MM-16F at 70 eV.

$Cp_2ZrMeMo(CO)_3Cp$ (1). A solution of $CpMo(CO)_3H$ (246 mg, 1 mmol) and Cp_2ZrMe_2 (251 mg, 1 mmol) in 20 mL of THF was stirred for 1 h at room temperature under N_2 in a standard Schlenk apparatus; the solvent was then removed under vacuum. (This second-order reaction, although incomplete in solution at this point, goes to completion rapidly as the solvent is removed, and the concentration of both reactants is thereby increased). The resulting orange oil was dissolved in 5 mL of toluene. The addition of 30 mL of hexane and cooling to −20 °C gave a yellow-orange precipitate, which was filtered at that temperature by standard Schlenk techniques. Recrystallization at room temperature in an inert-atmosphere box from toluene/hexane gave 303 mg (63%) of orange-yellow microcrystalline **1**: ^1H NMR (C_6D_6) δ 5.72 (s, 10 H), 5.2 (s, 5 H), 0.45 (s, 3 H), in agreement with the spectrum reported by Renaut et al.;[3] ^{13}C NMR (toluene-d_8) δ 35.1 (3, CH_3), 113.5 (10, Cp_2Zr), 89.9 (5, CpMo), 236.1 (3, CO); IR (toluene) 1948 (s), 1863 (s), 1545 (vs) cm^{-1}. The weak band at 2025 cm^{-1} reported in our preliminary communication[5] is of variable intensity and is apparently due to traces of $CpMo(CO)_3H$ formed during sample preparation for infrared spectroscopy.

(μ-Carbonyl-*OC*)[(η^2-acetyl)bis(η^5-cyclopentadienyl)zirconium(IV)]-dicarbonyl(η^5-cyclopentadienyl)molybdenum(0) (2). A solution of Cp_2ZrMe_2 (503 mg, 2.0 mmol) and $CpMo(CO)_3H$ (492 mg, 2.0 mmol) in 5 mL of THF was stirred at room temperature for 2 h and the solvent then removed under vacuum. The resulting orange oil, **1**, was dissolved in 10 mL of toluene and treated with 1 atm of CO for 30 min. Yellow crystals separated after the solution was left at room temperature for several additional minutes. These were collected by filtration and dried under vacuum. The yield of pure **2** was 0.685 g (67%). Additional **2** can be obtained by the addition of hexane to the filtrate; ^1H NMR (C_6D_6) δ 5.55 (s, 10 H), 5.37 (s, 5 H), 2.20 (variable, see text; s, 3 H); ^1H NMR (CD_3CN) δ 6.02 (s, 10 H), 5.07 (s, 5 H), 3.08 (s, 3 H); ^{13}C NMR (toluene-d_8) δ 316.5 (1, acyl CO), 248.4 (1, CO), 232.6 (2, CO), 110.3 (10, Cp_2Zr), 89.1 (5, CpMo), 33.0 (1, acyl CH_3); IR (toluene) 1932 (s), 1839 (s), 1590 (s, br) cm^{-1}; IR (CH_2Cl_2) 1935 (s), 1831 (s), 1600 (s, br) cm^{-1}. The weak band at 2020 cm^{-1} reported in our preliminary communication[5] is of variable intensity and is apparently due to traces of $CpMo(CO)_3H$ formed during sample preparation for infrared spectroscopy. Attempts to obtain a mass spectrum of **2** give only the spectrum of the decarbonylation and rearrangement product **3**. Electrical conductivity (in CH_3CN): $\Lambda = 115$ M^{-1} Ω^{-1} cm^{-1} at 1.9×10^{-3} M, 96 M^{-1} Ω^{-1} cm^{-1} at 6.9×10^{-3} M. At these concentrations in CH_3CN, $N(n\text{-}Bu)_4Br$ was measured to have conductivities of 144 and 130 M^{-1} Ω^{-1} cm^{-1}, respectively.

Reaction of $Cp_2Zr[\eta^2\text{-}C(O)Me]Me$ with $CpMo(CO)_3H$. A THF solution of 150 mg (0.6 mmol) of Cp_2ZrMe_2 was treated with 1 atm of CO to give $Cp_2Zr[\eta^2\text{-}C(O)Me]Me$. This stirred solution was then treated with 150 mg (0.6 mmol) of $CpMo(CO)_3H$. Stirring was continued for 10 min, at which point the solvent was removed under vacuum to leave

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a fluffy yellow powder. The ^1H NMR showed mainly **2**, with additional resonances in the region δ 5.3–6.0 and a singlet at δ 1.70. Recrystallization of this solid from toluene/hexane gave 160 mg (ca. 50% yield) of a yellow solid, which retained ca. 10% of the above impurities. It was shown in an independent experiment that **2** reacts with $Cp_2Zr[C(O)Me]Me$ to yield some of these same impurities.

Isotope Labeling Studies of the Conversion of 1 into 2. $CpMo(CO)_3H$ (250 mg, 1 mmol) was dissolved in 10 mL of toluene and stirred under 1.68 mmol of ^{13}CO (isotopic purity 90%) for 3 days. The CO and solvent were removed under vacuum, and the solid residue was sublimed in vacuo at 50 °C to give 150 mg of ^{13}CO-enriched $CpMo(CO)_3H$. The intensities of the ^{13}C satellites of the hydride ^1H NMR resonance (δ −5.48 in C_6D_6; $J(^{13}C{-}^1H)$, averaged over cis and trans carbonyls at ambient temperature, is 6.6 Hz) showed 32% ^{13}C enrichment in the carbonyl ligands. Stirring 85 mg (0.34 mmol) of this material with 86 mg (0.34 mmol) of Cp_2ZrMe_2 in 3 mL of THF for 2 h, followed by removal of the solvent in vacuo, gave **1** with 32% ^{13}C enrichment in its carbonyl ligands.

This labeled **1** was dissolved in 0.8 mL of toluene-d_8 and the resulting solution divided into two portions. The first portion was placed in an NMR tube attached to the vacuum line, cooled to −78 °C, and exposed to 1 atm of isotopically normal CO for a few seconds. After removal of the CO, the tube was sealed and its ^{13}C NMR spectrum obtained at −50 °C. In addition to the resonances of unreacted **1** (about 90%), the spectrum showed carbonyl resonances at δ 248.3 and 232.9 (relative intensity 1:2) corresponding to the carbonyl-*OC* bridge and the terminal carbonyls of **2**. The tube was then warmed to 30 °C and held at that temperature for 1 h, and its ^{13}C NMR spectrum was obtained at −50 °C under the conditions previously employed. This spectrum showed a new carbonyl resonance at δ 316.3, corresponding to the η^2-acetyl carbonyl of **2**; its intensity relative to those of the other carbonyl resonances of **2** was 1:1:2, indicating that the distribution of ^{13}CO within **2** was now random.

The second portion of the toluene-d_8 solution of labeled **1** was similarly placed in an NMR tube attached to the vacuum line and exposed to 1 atm of isotopically normal CO for a few minutes *at room temperature*. After removal of the CO the tube was sealed and its ^1H NMR spectrum obtained immediately at 30 °C. The spectrum (δ 5.55 (10 H), 5.25 (5 H), 2.44 (3 H)) showed the quantitative formation of **2**; the toluene of observable ^{13}C satellites on the methyl resonance of the η^2-acetyl ligand showed that there had been no significant ^{13}CO incorporation into that ligand. (Such satellites, J = 5.6 Hz, were observed in samples of ^{13}CO-enriched **2** which had developed ^{13}CO-labeled η^2-acetyl ligands after prolonged standing). After some time at room temperature this tube gave a ^{13}C NMR spectrum that indicated the random distribution of ^{13}C among the carbonyl resonances of **2**.

Reaction of 2 with CF_3CO_2H. CF_3CO_2H (10 mg, 0.087 mmol) was condensed on the vacuum line into an NMR tube containing **2** (20 mg, 0.039 mmol) in 0.4 mL of C_6D_6. The tube was then frozen at −196 °C and sealed; after thawing at room temperature it contained a yellow solution. ^1H NMR allowed identification of the principal products of the reaction, formed in approximately equal amounts, as $CpMo(CO)_3H$ (δ 4.56 (5 H), −5.47 (1 H)), CH_3CHO (δ 9.14 (q, 1 H), 1.40 (d, 3 H)), and $Cp_2Zr(O_2CCF_3)_2$ (δ 5.72 (10 H)). After the tube was opened and the solvent removed under vacuum, the IR spectrum of the residue showed peaks due to $CpMo(CO)_3H$ and to $Cp_2Zr(O_2CCF_3)_2$.[10] The ^1H NMR chemical shift assigned to $Cp_2Zr(O_2CCF_3)_2$ agreed with that of an authentic sample (which gave the reported[10] IR spectrum) prepared by reacting a benzene solution of $Cp_2Zr(\eta^2\text{-Ac})Me$ with an excess of CF_3CO_2H. The mass spectrum of $Cp_2Zr(O_2CCF_3)_2$ showed a molecular ion at *m/e* 446 (^{90}Zr) with an isotopic distribution agreeing with that calculated for the empirical formula.

$(\eta^5\text{-}C_5H_5)_2Zr(\mu\text{-}\eta^2,\eta^1\text{-}CO)[\mu\text{-}OC(CH_3)]Mo(CO)(\eta^5\text{-}C_5H_5)$ (3). A solution of Cp_2ZrMe_2 (1.00 g, 4.0 mmol) and $CpMo(CO)_3H$ (0.98 g, 4.0 mmol) in 5 mL of THF was stirred at room temperature for 3 h. The solvent was then vacuum evaporated and the residue left under high vacuum for 4 h. The **1** thus formed was taken up in ca. 10 mL of toluene and exposed to 1 atm of CO for 20 min. The resulting solution of **2** was placed in a flask that was briefly evacuated, closed, and warmed at 48 °C for 10 h. The flask was then frozen at −196 °C, evacuated, and warmed to room temperature. The yellow crystalline precipitate that had formed was collected by filtration, washed with hexane, and dried under vacuum. The yield of pure **3** was 1.31 g (68%): ^1H NMR (C_6D_6) δ 5.98 (s, 5 H, Cp), 5.70 (s, 5 H, Cp), 5.30 (s, 5 H, Cp), 2.32 (s, 3 H, CH_3); ^{13}C NMR (toluene-d_8) δ 317.3 (1, acyl CO), 229.9 (1, CO), 227.8 (1, CO), 113.7 (5, Cp), 111.1 (5, Cp), 92.7 (5, Cp), 48.3 (1, CH_3); IR (Nujol) 1858 (vs), 1536 (s), 1339 (s) cm^{-1}. The mass spectrum showed a molecular ion at *m/e* 482 (^{90}Zr, ^{98}Mo) with an isotopic distribution agreeing with that calculated for the empirical formula.

Table I. Crystal Data

	$Cp_2Zr[C(O)Me]$-$(OC)_3MoCp$ (2)	$Cp_2Zr(OCMe)$-$(OC)MoCOCp$ (3)
formula	$C_{20}O_4H_{18}MoZr$	$C_{19}H_{18}O_3MoZr$
color	yellow	yellow
cryst dimens, mm	0.16 × 0.15 × 0.29	0.15 × 0.18 × 0.15
space group	$P\bar{1}$	$P2_1/n$
cell dimens	at −168°, 38 rflctns	at −172°, 48 rflctns
a, Å	14.548 (3)	15.237 (3)
b, Å	12.800 (3)	13.353 (2)
c, Å	10.432 (2)	8.787 (1)
α, deg	85.24 (1)	(90)
β, deg	90.06 (1)	106.98 (1)°
γ, deg	73.87 (1)	(90)
molecules/cell	4	4
cell vol, Å^3	1859.02	1709.8
calcd density, g/cm^3	1.81	1.93
wavelength, Å	0.710 69	0.710 69
mol wt	509.50	481.51
linear abs coeff, cm^{-1}	12.310	13.36
no. of unique intensities colltd	8581	3956
no. with $F > 0.0$	7980	3818
no. with $F > \sigma(F)$	7619	3726
no. with $F > 2.33\sigma(F)$	7129	3570
final residuals		
R_F	0.0381	0.0299
R_{wF}	0.0406	0.0360
GOF[a] for the last cycle	0.965	0.950
max Δ/σ for last cycle	0.05	0.05

[a] Goodness of fit.

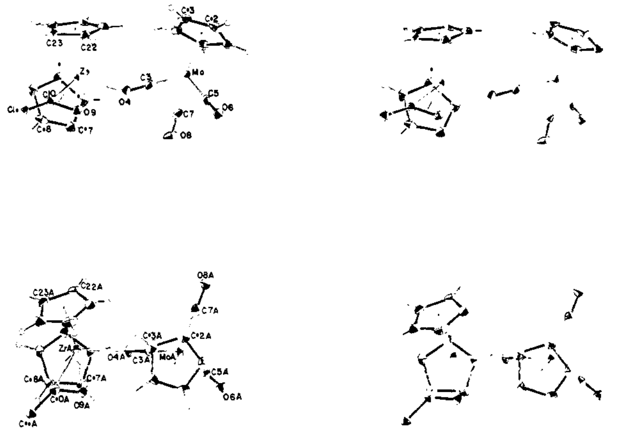

Figure 1. Stereo ORTEP drawings of the two conformers of $Cp_2Zr[C(O)Me](OC)_3MoCp$. Each conformer is drawn with the Zr moiety in approximately the same orientation in order to display the difference at the Mo end, caused by rotation about the Zr–O4 bond.

X-ray Diffraction Study of 2. Crystal data and parameters of the data collection (at −168 °C, 5° ≤ 2θ ≤ 45°) are shown in Table I. Crystal handling prior to and during data collection was carried out under a nitrogen atmosphere; data collection and processing techniques have been described.[11] The structure was solved by a combination of direct methods and Fourier techniques. All non-hydrogen atoms were located and refined anisotropically. Cyclopentadienyl hydrogen atoms were included in idealized positions with a thermal parameter 1 unit larger than that of the attached carbon. The crystal contains two independent molecules in the asymmetric unit; these display essentially identical bond lengths (differences are all less than 5σ) but differ in rotational conformation about the bond Zr–O4. The relationship between the two conformers is shown in Figures 1 and 2.

The results of the X-ray study are shown in Tables II–IV. Anisotropic *U*'s and a table of observed and calculated structure factors are available as supplementary material. Molybdenum is 2.057 and 2.052 Å from the ring least-squares planes, while for zirconium the distances are 2.200, 2.190, 2.193, and 2.206 Å. Normals to the Cp rings on Zr intersect at an angle of 129.5°.

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[10] Wailes, P. C.; Weigold, H. *J. Organomet. Chem.* **1970**, *24*, 413.

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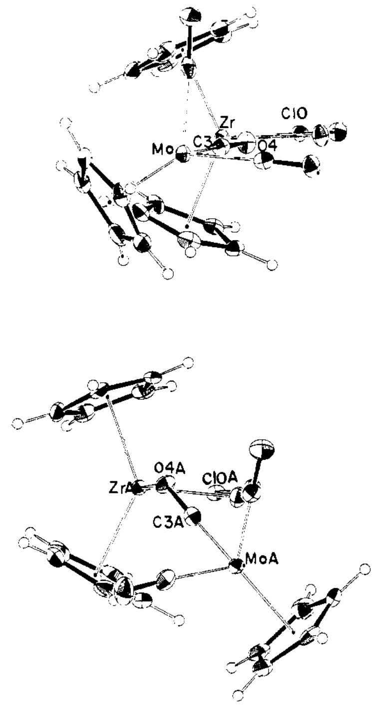


Figure 2. ORTEP drawings of both conformers of $Cp_2Zr[C(O)Me](OC)_3MoCp$, viewed nearly down the Zr–O4 bond.

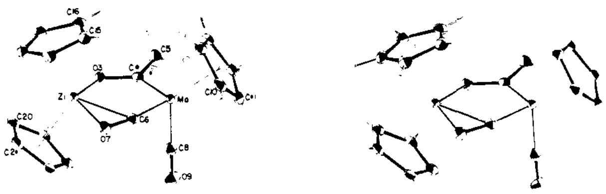


Figure 3. Stereoscopic view of $Cp_2Zr(OCMe)(OC)MoCOCp$. Numbering of ring carbons follows sequentially from those shown.

X-ray Diffraction Study of 3. Crystal data and parameters of the data collection (at −172 °C, 5° ≤ 2θ ≤ 55°) are given in Table I. No absorption correction was applied to the data. The structure was solved by using both direct (LSAM) and Fourier methods. Full-matrix least-squares refinement was carried out for all atoms; hydrogen atoms were refined independently by using isotropic temperature factors. Fractional coordinates and thermal parameters for non-hydrogen atoms are presented in Table V. Bond lengths and angles are presented in Tables VI and VII. Anisotropic U's, hydrogen atom parameters, and calculated and observed structure factors are available as supplementary material. The molecular structure is shown in Figures 3–5. Molybdenum is 2.05 Å from its Cp ring plane, while zirconium is 2.22 Å from each of its attached ring planes.

Results

Reaction of $CpMo(CO)_3H$ with $Cp_2Zr[\eta^2\text{-}C(O)Me]Me$ in THF occurs not with hydrogen transfer to the η^2-acetyl ligand but instead with elimination of methane (observed by ^1H NMR of the reaction mixture) to form as the principal product (Scheme I) a heterobimetallic complex $Cp_2Zr(Ac)Mo(CO)_3Cp$, **2**, which will be described more fully below in connection with another reaction in which it is formed.

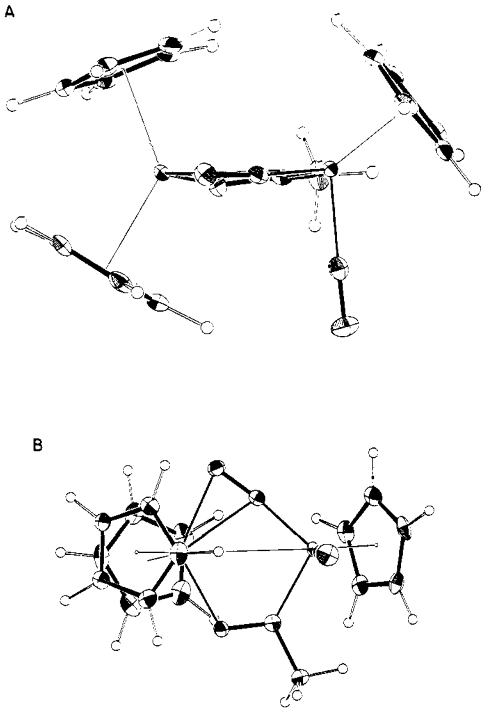


Figure 4. View along (A) and perpendicular to (B) the plane of the bridging ligands in $Cp_2Zr(OCMe)(OC)MoCOCp$.

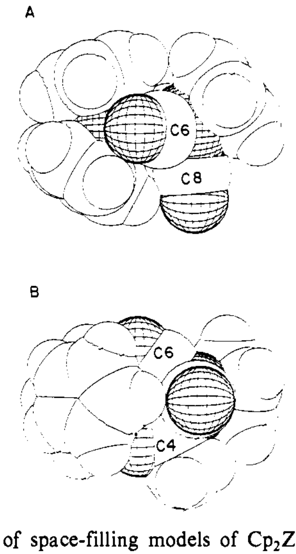
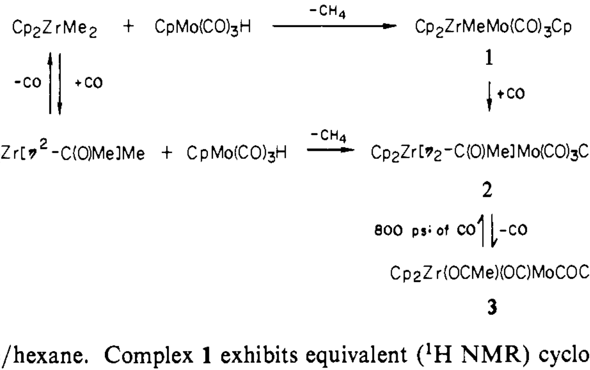


Figure 5. Views of space-filling models of $Cp_2Zr(OCMe)(OC)MoCOCp$: (A) side view, from same perspective as Figure 4A, showing end-to-end H···H and H···CO contacts: (B) viewed 90° from Figure 5A, as in Figure 4B. Hydrogen atoms have been positioned by assuming a C–H distance of 1.08 Å.

Scheme I



Methane elimination is also observed, as previously reported by Renaut et al.,[3] in the reaction (Scheme I) of $CpMo(CO)_3H$ with Cp_2ZrMe_2 in THF to form $Cp_2ZrMeMo(CO)_3Cp$, **1**.[12] This extremely air-sensitive heterobimetallic methyl complex is quite soluble in aromatic solvents as well as in THF. It forms aggregates of orange-yellow microcrystals upon crystallization from toluene/hexane. Complex **1** exhibits equivalent (^1H NMR) cyclopentadienyl rings on zirconium and terminal carbonyl stretching bands at 1948 and 1863 cm^{-1}; it also displays an additional

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[12] A study of the kinetics of this reaction and of the analogous reactions of Cp_2ZrMe_2 with $CpCr(CO)_3H$ and $CpW(CO)_3H$ will be reported separately: Edidin, R. R.; Longato, B.; Norton, J. R., manuscript in preparation. The rates of all three reactions vary appreciably with solvent (CH_3CN > THF > C_6H_6), and they appear to proceed by a proton-transfer mechanism.

Table II. Fractional Coordinates and Thermal Parameters for $Cp_2Zr[C(O)Me](OC)_3MoCp$[a, b]

	10^4x	10^4y	10^4z	$10B_{iso}$
Mo(1)	5784.9 (3)	2783.6 (3)	6762.5 (3)	10
Zr(2)	4730.7 (3)	2091.4 (3)	11200.3 (4)	10
C(3)	5165 (3)	2312 (3)	8186 (4)	13
O(4)	4755 (2)	2005 (3)	9084 (3)	16
C(5)	5134 (3)	1934 (3)	5806 (4)	13
O(6)	4766 (2)	1398 (3)	5279 (3)	18
C(7)	4642 (3)	4039 (4)	6561 (4)	15
O(8)	3980 (2)	4785 (3)	6490 (4)	24
O(9)	3705 (2)	1093 (2)	10929 (3)	15
C(10)	3775 (3)	1208 (3)	12092 (4)	13
C(11)	3265 (3)	709 (3)	13089 (4)	16
C(12)	7391 (3)	1979 (4)	6172 (5)	22
C(13)	7407 (3)	2202 (4)	7477 (5)	22
C(14)	7089 (3)	3353 (4)	7540 (4)	18
C(15)	6893 (3)	3823 (4)	6278 (4)	17
C(16)	7072 (3)	2991 (4)	5427 (4)	18
C(17)	3404 (3)	3801 (4)	10621 (5)	19
C(18)	3335 (3)	3549 (4)	11952 (5)	19
C(19)	4168 (4)	3643 (4)	12573 (4)	18
C(20)	4740 (3)	3986 (3)	11632 (4)	17
C(21)	4283 (4)	4071 (4)	10427 (4)	19
C(22)	5977 (3)	281 (3)	11506 (4)	14
C(23)	5790 (3)	683 (3)	12737 (4)	13
C(24)	6099 (3)	1627 (4)	12743 (4)	16
C(25)	6482 (3)	1812 (4)	11527 (5)	18
C(26)	6419 (3)	969 (4)	10784 (4)	20
Mo(1A)	48.3 (2)	2477.3 (3)	1579.8 (3)	11
Zr(2A)	1164.4 (3)	2596.1 (3)	6013.6 (4)	10
C(3A)	808 (3)	2616 (3)	2978 (4)	13
O(4A)	1289 (2)	2721 (2)	3882 (3)	15
C(5A)	683 (3)	3441 (3)	589 (4)	14
O(6A)	1052 (2)	4028 (3)	45 (3)	20
C(7A)	1052 (3)	1205 (4)	1104 (4)	18
O(8A)	1610 (2)	427 (3)	821 (3)	25
O(9A)	−222 (2)	3860 (2)	5441 (3)	16
C(10A)	−127 (3)	3747 (3)	6644 (4)	15
C(11A)	−831 (3)	4434 (4)	7481 (5)	20
C(12A)	−1184 (3)	1635 (4)	1241 (5)	19
C(13A)	−1267 (3)	1942 (4)	2504 (4)	19
C(14A)	−1503 (3)	3099 (4)	2434 (5)	22
C(15A)	8438 (3)	3500 (4)	1140 (5)	18
C(16A)	−1383 (3)	2590 (4)	390 (4)	17
C(17A)	1991 (3)	4070 (3)	5874 (4)	15
C(18A)	1720 (3)	3953 (4)	7166 (4)	17
C(19A)	2241 (3)	2912 (4)	7703 (4)	15
C(20A)	2849 (3)	2392 (3)	6751 (4)	15
C(21A)	2694 (3)	3102 (4)	5624 (4)	14
C(22A)	1710 (3)	567 (4)	6191 (5)	21
C(23A)	1428 (4)	875 (4)	7426 (4)	21
C(24A)	440 (4)	1351 (4)	7383 (5)	26
C(25A)	95 (3)	1324 (4)	6110 (5)	24
C(26A)	876 (4)	832 (4)	5399 (4)	20

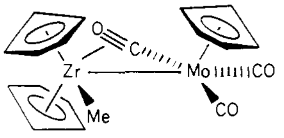
[a] The isotropic thermal parameter listed is the isotropic equivalent: *Acta Crystallogr.* 1959, *12*, 609. [b] Numbers in parentheses in this and all following tables refer to the estimated standard deviation (esd) in the least significant digits.

Table III. Bond Distances (Å) for $Cp_2Zr[C(O)Me](OC)_3MoCp$

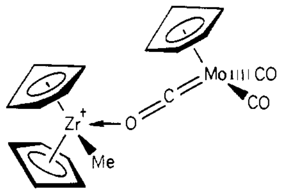
		conformer 1	conformer 2 ("A")
Mo(1)	C(3)	1.882 (4)	1.879 (4)
Mo(1)	C(5)	1.956 (4)	1.966 (4)
Mo(1)	C(7)	1.961 (5)	1.961 (5)
Mo(1)	C(12)	2.382 (5)	2.375 (4)
Mo(1)	C(13)	2.368 (4)	2.383 (4)
Mo(1)	C(14)	2.378 (4)	2.375 (5)
Mo(1)	C(15)	2.388 (4)	2.368 (4)
Mo(1)	C(16)	2.396 (4)	2.386 (4)
Zr(2)	O(4)	2.220 (3)	2.228 (3)
Zr(2)	O(9)	2.249 (3)	2.251 (3)
Zr(2)	C(10)	2.186 (4)	2.181 (4)
Zr(2)	C(17)	2.512 (4)	2.498 (4)
Zr(2)	C(18)	2.522 (4)	2.498 (4)
Zr(2)	C(19)	2.497 (4)	2.487 (4)
Zr(2)	C(20)	2.506 (4)	2.505 (4)
Zr(2)	C(21)	2.498 (4)	2.509 (4)
Zr(2)	C(22)	2.510 (4)	2.486 (4)
Zr(2)	C(23)	2.483 (4)	2.483 (4)
Zr(2)	C(24)	2.466 (4)	2.500 (5)
Zr(2)	C(25)	2.492 (4)	2.542 (5)
Zr(2)	C(26)	2.536 (5)	2.540 (4)
O(4)	C(3)	1.207 (5)	1.211 (5)
O(6)	C(5)	1.151 (5)	1.153 (5)
O(8)	C(7)	1.150 (5)	1.157 (5)
O(9)	C(10)	1.241 (5)	1.254 (5)
C(10)	C(11)	1.481 (6)	1.488 (6)
C(12)	C(13)	1.416 (7)	1.402 (6)
C(12)	C(16)	1.413 (7)	1.411 (6)
C(13)	C(14)	1.423 (7)	1.420 (7)
C(14)	C(15)	1.397 (6)	1.397 (7)
C(15)	C(16)	1.412 (6)	1.421 (6)
	av[a]	1.412 (11)	1.410 (11)
C(17)	C(18)	1.409 (7)	1.412 (6)
C(17)	C(21)	1.425 (7)	1.415 (6)
C(18)	C(19)	1.413 (7)	1.406 (6)
C(19)	C(20)	1.408 (7)	1.413 (6)
C(20)	C(21)	1.403 (6)	1.403 (6)
	av	1.412 (9)	1.410 (5)
C(22)	C(23)	1.423 (6)	1.406 (7)
C(22)	C(26)	1.401 (7)	1.412 (6)
C(23)	C(24)	1.401 (6)	1.396 (7)
C(24)	C(25)	1.415 (6)	1.425 (8)
C(25)	C(26)	1.402 (7)	1.385 (7)
	av	1.408 (10)	1.405 (15)

[a] Esd's on average values are calculated by using the scatter formula $\sigma(\text{av}) = [\Sigma(d_i - \bar{d})^2/(N-1)]^{1/2}$, where d_i is one of N individual values and $\bar{d}$ is their average.

carbonyl stretching band at 1545 cm^{-1}. Although, in view of the close resemblance between the latter band and that (1560 cm^{-1}) of the π-bonded carbonyl in the isoelectronic $Cp_2NbMo(CO)_3Cp$[13] we had originally[5] assigned **1** a structure (**1A**) with a π-bonded carbonyl and an Mo–Zr bond, preliminary X-ray results[14] suggest that **1** has no Mo–Zr bond and a carbonyl-*OC* bridged structure **1B** like that found by Stucky[15] for $(C_5Me_5)_2Ti(Me)Mo(CO)_3Cp$ (ν_{CO} 1623 cm^{-1}); a similar structure is reported herein for **2**.



1A



1B

The initial zirconium complexes Cp_2ZrMe_2 and $Cp_2Zr[\eta^2\text{-}C(O)Me]Me$ are linked by a CO insertion equilibrium,[8,16] and **1**, the heterobimetallic derivative of Cp_2ZrMe_2, can be quantitatively carbonylated at 1 atm to **2**, the heterobimetallic derivative of $Cp_2Zr[\eta^2\text{-}C(O)Me]Me$ (Scheme I). Attempts to reverse this carbonylation gave only 4% conversion of **2** into **1** after 20 freeze/pump/thaw cycles.

When dissolved in acetonitrile, **2** gives free (i.e., symmetrically solvated) $CpMo(CO)_3^-$, as shown by the carbonyl IR bands (1890 and 1777 cm^{-1}) and ^1H NMR chemical shift (δ 5.07) characteristic of that anion in that solvent.[17a] The electrical conductivity of

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(17) (a) Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1255. (b) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81. Roberts, D. A.; Mercer, W. C.; Zahurak, S. H.; Geoffroy, G. L.; DeBrosse, C. W.; Cass, M. E.; Pierpont, C. G. *J. Am. Chem. Soc.* **1982**, *104*, 910.

Table IV. Bond Angles (deg) for $Cp_2Zr[C(O)Me](OC)_3MoCp$

			conformer 1	conformer 2 ("A")
C(3)	Mo	C(5)	84.1 (2)	85.5 (2)
C(3)	Mo	C(7)	85.3 (2)	90.6 (2)
C(5)	Mo	C(7)	90.0 (2)	89.6 (2)
O(4)	Zr	O(9)	78.7 (1)	79.7 (1)
O(4)	Zr	C(10)	111.2 (1)	112.3 (1)
O(9)	Zr	C(10)	32.5 (1)	32.8 (1)
Zr	O(4)	C(3)	137.4 (3)	135.4 (3)
Zr	O(9)	C(10)	71.0 (2)	70.5 (2)
Mo	C(3)	O(4)	178.9 (3)	179.1 (3)
Mo	C(5)	O(6)	177.2 (4)	177.5 (4)
Mo	C(7)	O(8)	177.3 (4)	176.6 (4)
Zr	C(10)	O(9)	76.6 (2)	76.7 (2)
Zr	C(10)	C(11)	160.7 (3)	161.2 (3)
O(9)	C(10)	C(11)	122.7 (4)	121.8 (4)
C(13)	C(12)	C(16)	107.4 (4)	108.3 (4)
C(12)	C(13)	C(14)	108.6 (4)	107.5 (4)
C(13)	C(14)	C(15)	106.9 (4)	108.7 (4)
C(14)	C(15)	C(16)	109.4 (4)	107.6 (4)
C(12)	C(16)	C(15)	107.7 (4)	107.9 (4)
av			108.0	108.0
C(18)	C(17)	C(21)	107.4 (4)	107.9 (4)
C(17)	C(18)	C(19)	108.2 (4)	108.0 (4)
C(18)	C(19)	C(20)	108.0 (4)	108.0 (4)
C(19)	C(20)	C(21)	108.2 (4)	108.2 (4)
C(17)	C(21)	C(20)	108.1 (4)	108.0 (4)
av			108.0	108.0
C(23)	C(22)	C(26)	107.6 (4)	107.4 (4)
C(22)	C(23)	C(24)	107.8 (4)	108.1 (4)
C(23)	C(24)	C(25)	108.2 (4)	108.1 (4)
C(24)	C(25)	C(26)	107.6 (4)	107.3 (4)
C(22)	C(26)	C(25)	108.7 (4)	109.1 (4)
av			108.0	108.0

Table V. Fractional Coordinates and Thermal Parameters for $Cp_2Zr(OCMe)(OC)MoCOCp$

atom	10^4x	10^4y	10^4z	$10B_{iso}$
Zr(1)	7331.2 (2)	4315.6 (2)	8830.7 (3)	9
Mo(2)	6601.4 (2)	2392.4 (2)	10478.2 (3)	9
O(3)	7614 (1)	4341 (1)	11382 (2)	14
C(4)	7231 (2)	3598 (2)	11867 (3)	12
C(5)	7316 (2)	3709 (3)	13615 (4)	19
C(6)	6727 (2)	2690 (2)	8466 (3)	12
O(7)	6791 (1)	3005 (2)	7174 (2)	15
C(8)	7817 (2)	1770 (2)	11148 (3)	14
O(9)	8521 (1)	1386 (2)	11554 (3)	21
C(10)	5255 (2)	1389 (2)	9626 (4)	18
C(11)	5816 (2)	992 (2)	11068 (4)	18
C(12)	5869 (2)	1706 (2)	12282 (4)	17
C(13)	5351 (2)	2550 (2)	11579 (4)	16
C(14)	4970 (2)	2359 (2)	9953 (4)	17
C(15)	5643 (2)	4789 (2)	7862 (4)	20
C(16)	6014 (2)	5300 (3)	9298 (4)	21
C(17)	6660 (2)	5990 (2)	9092 (4)	19
C(18)	6681 (2)	5927 (2)	7503 (4)	19
C(19)	6060 (2)	5177 (3)	6746 (4)	18
C(20)	8740 (2)	5295 (2)	8828 (4)	14
C(21)	8475 (2)	4742 (2)	7386 (4)	14
C(22)	8625 (2)	3719 (2)	7773 (4)	16
C(23)	8945 (2)	3632 (9)	9444 (4)	18
C(24)	9031 (2)	4609 (2)	10085 (4)	16

Table VI. Bond Distances (Å) for $Cp_2Zr(OCMe)(OC)MoCOCp$

Mo	Zr	3.297 (1)	Zr	O(3)	2.156 (2)
Mo	C(4)	2.078 (3)	Zr	O(7)	2.271 (2)
Mo	C(6)	1.875 (3)	Zr	C(6)	2.343 (3)
Mo	C(8)	1.957 (3)	Zr	C(15)	2.542 (3)
Mo	C(10)	2.381 (3)	Zr	C(16)	2.531 (3)
Mo	C(11)	2.358 (3)	Zr	C(17)	2.497 (3)
Mo	C(12)	2.373 (3)	Zr	C(18)	2.509 (3)
Mo	C(13)	2.385 (3)	Zr	C(19)	2.521 (3)
Mo	C(14)	2.392 (3)	Zr	C(20)	2.515 (3)
O(3)	C(4)	1.285 (3)	Zr	C(21)	2.503 (3)
O(7)	C(6)	1.241 (4)	Zr	C(22)	2.541 (3)
C(9)	C(8)	1.147 (4)	Zr	C(23)	2.529 (3)
C(4)	C(5)	1.510 (4)	Zr	C(24)	2.531 (3)
C(10)	C(11)	1.409 (4)	C(15)	C(16)	1.400 (5)
C(10)	C(14)	1.421 (5)	C(15)	C(19)	1.414 (5)
C(11)	C(12)	1.416 (5)	C(16)	C(17)	1.398 (5)
C(12)	C(13)	1.411 (4)	C(17)	C(18)	1.408 (5)
C(13)	C(14)	1.399 (5)	C(18)	C(19)	1.405 (5)
	av	1.411 (8)		av	1.405 (9)
			C(20)	C(21)	1.420 (4)
			C(20)	C(24)	1.403 (4)
			C(21)	C(22)	1.410 (4)
			C(22)	C(23)	1.410 (4)
			C(23)	C(24)	1.412 (5)
				av	1.411 (6)

Table VII. Bond Angles (deg) for $Cp_2Zr(OCMe)(OC)MoCOCp$

Zr	Mo	C(4)	59.8 (1)	Zr	O(7)	C(6)	77.6 (2)
Zr	Mo	C(6)	44.0 (1)	Mo	C(4)	O(3)	125.4 (2)
Zr	Mo	C(8)	93.0 (1)	Mo	C(4)	C(5)	124.1 (2)
C(4)	Mo	C(6)	103.5 (1)	O(3)	C(4)	C(5)	110.5 (2)
C(4)	Mo	C(8)	85.3 (1)	Mo	C(6)	Zr	102.2 (1)
C(6)	Mo	C(8)	91.4 (1)	Mo	C(6)	O(7)	172.3 (2)
Mo	Zr	O(3)	63.0 (1)	Mo	C(8)	O(9)	178.3 (3)
Mo	Zr	O(7)	64.9 (1)	C(16)	C(15)	C(19)	107.6 (3)
Mo	Zr	C(6)	33.8 (1)	C(15)	C(16)	C(17)	108.6 (3)
O(3)	Zr	O(7)	127.1 (1)	C(16)	C(17)	C(18)	108.0 (3)
C(11)	C(10)	C(14)	107.6 (3)	C(17)	C(18)	C(19)	107.8 (3)
C(10)	C(11)	C(12)	108.0 (3)	C(15)	C(19)	C(18)	108.0 (3)
C(11)	C(12)	C(13)	107.9 (3)	C(21)	C(20)	C(24)	107.7 (3)
C(12)	C(13)	C(14)	108.2 (3)	C(20)	C(21)	C(22)	107.7 (3)
C(10)	C(14)	C(13)	108.2 (3)	C(21)	C(22)	C(23)	108.3 (3)
O(3)	Zr	C(6)	96.2 (1)	C(22)	C(23)	C(24)	107.6 (3)
O(7)	Zr	C(6)	31.2 (1)	C(20)	C(24)	C(23)	108.5 (3)
Zr	O(3)	C(4)	111.2 (2)				

such a solution is in the range appropriate to a 1:1 electrolyte,[17b] with evidence for decreasing conductivity with increasing concentration. The companion cation is presumably $Cp_2Zr(Ac)(NCMe)^+$.

Compound **2** dissolves in noncoordinating solvents such as benzene, toluene,[18] and halocarbons to give infrared spectra (carbonyl bands around 1935, 1835, and 1590 cm^{-1}) considerably different from that observed in acetonitrile and similar to those observed in the solid state (Nujol, KBr). Although the strong absorption at 1590 cm^{-1} and the downfield (δ 316.5) ^{13}C NMR resonance (observed in toluene) indicate the presence of an η^2-acetyl ligand on Zr[8,19] in **2**, they offer no evidence as to the way in which the $CpMo(CO)_3$ unit is linked to the $Cp_2Zr(\eta^2\text{-Ac})$ unit in these solvents. The structure of **2** has therefore been established by X-ray crystallography.

Complex **2** exists in the solid state as a molecular species devoid of any metal–metal bond, with the $CpMo(CO)_3$ unit linked to the $Cp_2Zr(\eta^2\text{-Ac})$ unit only by the oxygen of a carbonyl ligand (Figure 1). Curiously, two conformers are present in the lattice, differing in the rotational orientation about the Mo–C3–O4–Zr unit (Figure 2).

The IR data presented above show that the principal features of the solid-state structure of **2** are preserved in solution in noncoordinating solvents. The extremely broad band ($\Delta\nu_{1/2}$ = 34 cm^{-1} in THF) around 1600 cm^{-1} must contain components due to the CO stretches of both the η^2-acetyl carbonyl and the carbonyl-*OC* bridge. However, other evidence shows that the detailed structural picture in solution is complex. The chemical shifts of **2** in aromatic solvents vary appreciably with concentration. The chemical shift of the acetyl methyl group varies from δ 2.05 in dilute (0.01 M)

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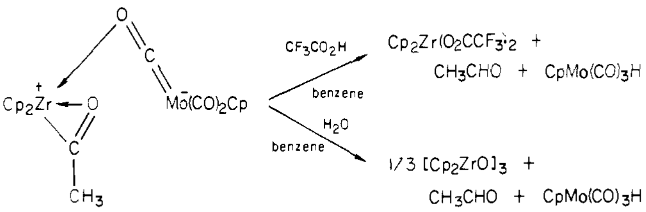
(18) Although quite concentrated (0.3 M) solutions of **2** in toluene can be made by the carbonylation of **1** in that solvent, crystalline **2** dissolves only sparingly in toluene. This difference may be related to the aggregation of **2** in concentrated solution.

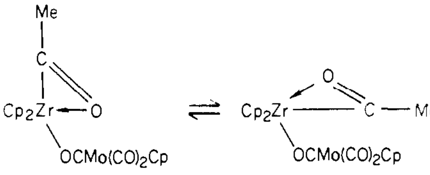
(19) Erker, G.; Rosenfeldt, F. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 605; *J. Organomet. Chem.* **1980**, *188*, C1. Lappert, M. F.; Luong-thi, N. T.; Milne, C. R. C. *Ibid.* **1979**, *174*, C35.

Scheme II



solution to δ 2.35 in supersaturated solution (achieved by in situ carbonylation of **1** in C_6D_6).[20] Over this same 16-fold concentration range, the Cp protons on Zr vary by less than 0.1 ppm while the CpMo protons are invariant within experimental error.

The most likely explanation for these concentration-dependent chemical shifts is association of the highly polar molecules of **2** at high concentrations in nonpolar solvents. Such association may affect the relative solution population of the two conformers observed in the solid state and therefore the average chemical shift. An alternative explanation based upon changes in the relative solution population of the acetyl isomers **2A** and **2B**[19] is much less likely, as there is no evidence for even fractional population of isomer **2B** in the solid-state structure of either conformer. The averaging process involved must be rapid. Only one ^1H NMR signal is observed for each type of proton in **2** even at high field (360 MHz). Although the chemical shifts of **2** in toluene-d_8 are influenced by temperature (most in the methyl resonance and least in the CpZr resonance), only one signal of each type is evident down to −45 °C (220 MHz).



2A 2B

Origin of the η^2-Acetyl Carbonyl in the Formation of 2 from 1. Alkyl ligands and CO can react by a variety of mechanisms.[21] In the case at hand, it was necessary to determine whether the carbonyl group in the η^2-acetyl ligand of **2** arose from the external CO or from one of the carbonyl ligands of **1**. Labeling experiments encountered unexpected complications. Complex **1**, prepared 32% ^{13}CO-enriched from enriched $CpMo(CO)_3H$, was reacted with 1 atm of isotopically normal CO at room temperature to form **2**. When examined later by ^{13}C NMR under ambient conditions this **2** had a random distribution of ^{13}CO among the η^2-acetyl carbonyl resonance and the other carbonyl resonances, suggesting that **2** exhibits some carbonyl-scrambling process. However, the ^1H NMR of this **2**, taken immediately after its synthesis, showed no ^{13}C satellites on the methyl resonance of the η^2-acetyl ligand, suggesting that this ligand had initially been formed from external unlabeled CO.

This implication was confirmed when the same carbonylation reaction was performed carefully at low temperature.[22] Treatment of the 32% ^{13}CO-enriched **1** with isotopically normal CO at −78 °C for a few seconds gave partial conversion to **2**. ^{13}C NMR at −50 °C showed significant ^{13}CO in **2** only in the resonances corresponding to its carbonyl-*OC* bridge and its terminal carbonyls, not in the resonance corresponding to its η^2-acetyl ligand carbonyl. After the sample had been warmed at 30 °C for 1 h, however, ^{13}C NMR showed that the distribution of ^{13}CO within **2** was random. The details of the carbonyl-scrambling process responsible for redistribution of CO within **2** are under investigation and will be reported separately.

Table VIII. Distances from Least-Squares Plane of $MoZr(\mu\text{-}CO)(OCMe)$

atom	dist from plane, Å	atom	dist from plane, Å
Zr	−0.11	C6	0.05
Mo	−0.05	O7	0.02
O3	0.11	M1[a]	−1.25
C4	0.01	M2[b]	−2.23
C5	−0.35	M3[c]	1.75

[a] M1 is the midpoint of the ring attached to Mo. [b] M2 is the midpoint of the ring containing C15–C19. [c] M3 is the midpoint of the ring containing C20–C24.

The formation of **2** from **1** is thus a carbonyl insertion reaction involving external CO and not a methyl migration involving one of the carbonyl ligands already present in **1**.

Reaction of 2 with Proton Sources. Complex **2** (see Discussion) can be viewed as an intimate ion pair involving the Zr(IV) cation $Cp_2Zr(\eta^2\text{-}Ac)^+$ and the Mo(0) anion $CpMo(CO)_3^-$. It thus reacts readily with protic materials. For example, it reacts (Scheme II) with CF_3CO_2H to form $Cp_2Zr(O_2CCF_3)_2$,[10] acetaldehyde, and $CpMo(CO)_3H$; it reacts with water to form acetaldehyde, $CpMo(CO)_3H$, and $[Cp_2ZrO]_3$ (identified by comparison of its ^1H NMR chemical shifts in C_6D_6 (δ 6.22) and in $CDCl_3$ (δ 6.34) with those of an authentic sample).[9]

Formation of 3 from 2. On standing under an inert atmosphere, **2** slowly (1–2 days in toluene) decarbonylates, but *not* to reform **1**. Rather, **3**, an isomer of **1**, is formed (Scheme I). Finally, **3** reverts to **2** under 800 psi of carbon monoxide (Scheme I), although the yield is low because of the inherent difficulties of carrying out a high-pressure reaction on small quantities of material under completely anhydrous conditions.

Compound **3**, the least air- and moisture-sensitive compound of these three, shows inequivalent Cp rings on zirconium and also an acetyl methyl. The IR spectrum of **3** shows a single (and low) terminal carbonyl frequency (1858 cm^{-1}), one stretch at 1536 cm^{-1}, and a third band (1339 cm^{-1}) identified as a carbon–oxygen stretch by labeling with ^{13}CO.[23,24] The structural ambiguities implicit in these data prompted an X-ray structural determination of **3**. This revealed that **3** exists in the solid state as isolated molecules (Figures 3–5). Individual molecules are asymmetric and therefore chiral, but the crystal is composed of a racemic mixture. The inequivalence of all three Cp rings in this structure is consistent with the ^1H and ^{13}C NMR data. The molecules are comprised of Cp_2Zr and CpMoCO units held together by a μ-OCMe bridge, a metal–metal bond, and one carbonyl bridge. As shown in Table VIII, the μ-OCMe bridge, the metal–metal bond, and the π-bonded carbonyl are approximately coplanar. This plane is approximately perpendicular to the plane containing the two metal atoms, the terminal carbonyl (C8, O9), and M1.

Discussion

Dinuclear Methane Elimination. We have shown (Scheme I) that $CpMo(CO)_3H$ reacts with both coordinatively saturated $Cp_2Zr[\eta^2\text{-}C(O)Me]Me$ and coordinatively unsaturated Cp_2ZrMe_2. Since this pair of zirconium complexes is related by a facile carbonylation/decarbonylation equilibrium, the question arises as to whether *both* reactions proceed via the single zirconium species Cp_2ZrMe_2. This mechanistic proposal is untenable, however, since **2** is formed faster from $Cp_2Zr[\eta^2\text{-}C(O)Me]Me$

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(20) This concentration dependence is graphically illustrated during the decarbonylation of **2** to **3**. As the concentration of unreacted **2** decreases, the chemical shift of the **2** methyl group varies smoothly from δ 2.23 to 2.08.

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(22) The use of ^{13}C-labeled **1** and isotopically normal CO rather than the reverse combination permitted the carbonylation reaction to be carried out at higher pressure (e.g., 1 atm) and therefore at a faster rate relative to the subsequent carbonyl-scrambling reaction.

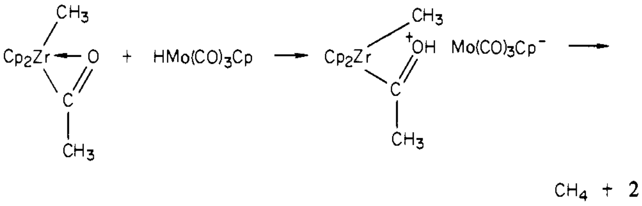
(23) When the ^{13}CO-enriched **2** from the above labeling experiments is allowed to decarbonylate and form **3**, ^{13}CO bands are observed at 1817, 1498, and 1310 cm^{-1}, in good agreement with calculated[24] values.

(24) Braterman, P. S. "Metal Carbonyl Spectra"; Academic Press: New York, 1975; p 36.

than **1** is from Cp_2ZrMe_2 when they are reacted with $CpMo(CO)_3H$ under the same conditions.

The origin of these relative rates of methane elimination with $CpMo(CO)_3H$ is not immediately obvious. The fact that the coordinatively unsaturated Cp_2ZrMe_2 reacts more slowly than $Cp_2Zr[\eta^2\text{-}C(O)Me]Me$ suggests that these reactions do not require coordinative unsaturation. Although $Cp_2Zr[\eta^2\text{-}C(O)Me]Me$ may react via an intermediate η^1-acyl form, the need for such isomerization prior to reaction with $CpMo(CO)_3H$ would presumably decrease the net methane elimination rate.

An explanation of these relative rates can be based on our conclusion that the reaction of Cp_2ZrMe_2 and $CpMo(CO)_3H$ proceeds by a proton-transfer mechanism.[12] If the reaction of $Cp_2Zr[\eta^2\text{-}C(O)Me]Me$ and $CpMo(CO)_3H$ also proceeds by such a mechanism, it is reasonable for it to proceed more rapidly because it can begin with a fast proton transfer onto the acyl oxygen instead of a slow proton transfer onto a Zr–C bond. (A proton transfer onto an oxygen lone pair requires less electronic and structural reorganization than one onto a metal or carbon site of the same thermodynamic base strength and is therefore much faster.[17a]) Intramolecular methane elimination and coordination of an oxygen of $CpMo(CO)_3^-$ to Zr can then give **2**.

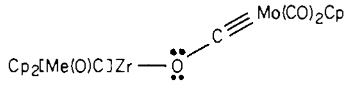


It is noteworthy that this reaction of an acetyl complex with a transition-metal hydride gives methane instead of acetaldehyde. Dinuclear eliminations involving hydrides and coordinated unsaturated acyls of the later transition metals (e.g., Mo,[25] Mn,[26] and Co[4,27]) frequently give aldehydes, although alkane and aldehyde elimination are both seen with alkyl carbonyls of some metals (e.g., Os[4]). Such reactions may prove quite different mechanistically from the early-transition-metal ones discussed in this paper. Regardless of mechanism, however, it is not surprising that a metal as oxophilic as zirconium shows considerable reluctance to lose the oxygen of a η^2-acyl ligand.

Structure of $Cp_2Zr[\eta^2\text{-}C(O)Me](OC)_3MoCp$ (2). Distances and angles within the Cp_2Zr unit are unexceptional,[2] as are those of the CpMo unit.[28] The structure of $Cp_2Zr[\eta^2\text{-}C(O)Me]Me$[8,29] offers a useful standard for comparison of the η^2-acetyl binding in **2**. In these two compounds the Zr–C and C–CH_3 distances are identical within the (small) experimental error. In **2**, the C10–O9 distance is longer (by 0.030 and 0.043 Å or 3–5σ) and the Zr–O distance is shorter (by 0.04 Å or 13σ) than in the η^2-acetyl ligand of $Cp_2Zr[\eta^2\text{-}C(O)Me]Me$. We suggest that this is indicative of weak bonding of Zr to O4 in compound **2**. At 2.22 Å, this bond is considerably longer than the Zr–O bond in $Cp_2ZrMe(OCHMe)ReCp_2$ (1.95 Å)[2] and the Zr–O bond in $(C_5Me_5)_2Zr(H)OCH{=}WCp_2$ (1.97 Å).[30]

The $CpMo(CO)_3$ end of the molecule exhibits identical bond lengths and angles for the two terminal carbonyls, but these are distinctly different from those of the carbonyl bridge, C3–O4. While all carbonyls are linear at carbon, Mo–C is longer and C–O is shorter in the terminal carbonyls. The distance C3–O4 (1.21 Å) lies between the terminal CO distance (1.15 Å) and the acetyl CO distance (1.25 Å). The bridge and terminal Mo–C distances, at 1.88 and 1.96 Å, bracket the value (1.93 Å)[28] in $CpMo(CO)_3^-$.

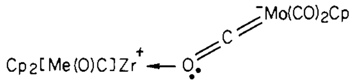
Some contribution from the oxycarbyne resonance structure **2C** may be invoked to account for the short Mo–C3 and long C3–O4 distances, as well as the nonlinearity (136°) at O4.



2C

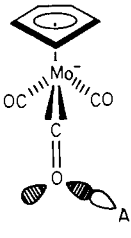
However, this resonance form must be quantitatively minor, since the C3–O4 distance (1.21 Å) is much shorter than that of a C–O single bond, and the Mo–C3 distance (1.88 Å) has decreased only half-way to the 1.82- and 1.81-Å distances in $Cp(OC)_2W{\equiv}C{-}R$ (R = *p*-tolyl[31] and $SiPh_3$[32]).

A more acceptable picture is that of the intimate ion pair or zwitterion **2D**. This resonance structure accounts for the linearity at C3, the nonlinearity at O4, the lengthened C3–O4 bond, and the weak bond from O4 to Zr (ethers and ketones are known to form longer bonds to group 4 metals than do alkoxides).[2,33]



2D

A contributing factor in the short Mo–C3 distance may be the dominance by the C3–O4 unit of the backbonding from molybdenum. Such dominance could arise if Zr(IV) induces rehybridization at O4 to sp^2 and thereby leaves an empty p orbital on C3, which then dominates the backbonding from molybdenum. It is known[34,35] that the HOMO of a "pyramidal" d^6 $CpM(CO)_2$ fragment lies perpendicular to the mirror plane of that fragment as in E. This fact leads to the prediction that the Zr(IV) Lewis acid should be found out of the mirror plane of the $CpMo(CO)_2$ fragment. Figure 2 shows that this prediction of bonding mode E is qualitatively confirmed in both conformers.



E

The intimate ion pairing of transition-metal carbonyl anions and alkali metal cations[36,37] is not strongly directional, is not exclusively directed toward oxygen, and does not perturb the M–C and C–O bond lengths to the extent that we observe in **2**. In contrast, intimate ion pairing of group 2A and Group 3A cations to $CpM(CO)_3^-$ (M = Mo, W) has been shown to effect structural modifications similar to those in **2**. In $Mg(py)_4[CpMo(CO)_3]_2$[38] (py = pyridine) and $Al(THF)_3[CpW(CO)_3]_3$[39] M–C distances are short, bridging C–O distances are long, and the angles at oxygen are nonlinear but variable (140–163°). In [CpW-

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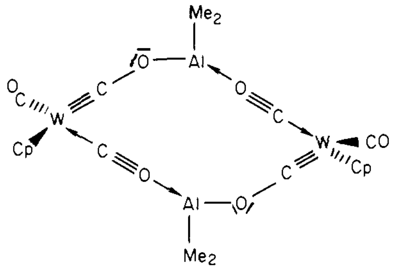
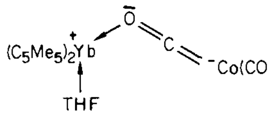
$(CO)_3AlMe_2]_2$[40] each Me_2Al is bound to two carbonyl oxygens, one linear and one bent, reflecting a significant contribution from the resonance structure shown in I.

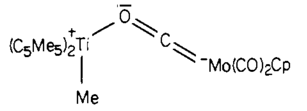


I

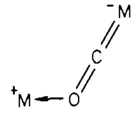
Relationship between Carbonyl-*OC*-Bridged and Metal–Metal-Bonded Structures. Few examples of carbonyl-*OC* bridges between two transition elements as in **2** were known until recently. $V(THF)_4[V(CO)_6]_2$ is linear about the carbonyl oxygen,[41] $(C_5Me_5)_2(THF)YbCo(CO)_4$ (II) has a somewhat bent geometry about oxygen (163°),[42] and $(C_5Me_5)_2TiMeMo(CO)_3Cp$ (III) has a significantly bent geometry about oxygen (144°)[15] like that (136°) in **2**. The relative stability of the zwitterionic form F and of the corresponding metal–metal-bonded isomer G is clearly a complex matter and one that may well depend upon environment (e.g., crystalline lattice, solvent polarity). For the pair of complexes $Me_2EW(CO)_3Cp$ (E = Ga and Al) in the solid state, a monomer with a metal–metal bond is found for E = Ga[43] while a carbonyl-*OC*-bridged dimer (vide supra) is found for E = Al.[40] The significance of solvent is evident from the description of $Cp_2HfFe(CO)_4$,[44] where structural isomers appear to have been detected. The case of $Cp_2TiMo(CO)_3Cp$ warrants reexamination.[45]



II



III



F

M — M′(CO)

G

Bonds between early and late transition metals are not inherently unstable. $CpTi[Co(CO)_4][OCCo_3(CO)_9]_2$[46] contains an unbridged Co–Ti bond, $Cp_2OCNbCo(CO)_4$[47] contains a Nb–Co bond with a CO semibridge, and $(C_5Me_5)_2Zr(OC)_2Co(C_5H_5)$[48] contains a Zr–Co bond (although bridging by a four-electron donor CO and a normal CO bridge is a major factor).

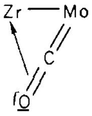
Burlitch et al.[49] studied the interaction of Ph_3E acids (E = Al, Ga, In) with the bases $CpFe(CO)_2^-$, $CpW(CO)_3^-$, $Co(CO)_4^-$, and $Mn(CO)_5^-$, in weakly basic solvents and in the solid state, in order to compare the metal and the carbonyl oxygen as sites of Lewis basicity. Of all the pairs they studied, the transition metal is the site of Lewis basicity in every case except $CpW(CO)_3^-$ with Ph_3Al; for Ph_3Ga and $CpW(CO)_3^-$, solutions exhibit an equilibrium between coordination at W and at O. Even the hardest acid, Ph_3Al, binds to iron, not oxygen, in $CpFe(CO)_2AlPh_3^-$. Since $CpW(CO)_3^-$ has the strongest "oxygen base strength" (as judged by the lowest average ν_{CO} value) of the anion employed, it appears that oxygen is the favored site of Lewis basicity only when a hard Lewis acid is confronted by an anion with maximum O basicity and modest metal basicity.

The weak *metal* basicity of the $CpM(CO)_3^-$ unit is shown by the substantial acidity of $CpM(CO)_3H$ (relative to other monomeric metal hydrides).[17a] The structure of complex **2** thus appears to be determined by three factors. First, the $Cp_2Zr[C(O)Me]^+$ center is a hard Lewis acid. Second, the potential anionic center, $CpMo(CO)_3^-$, has modest nucleophilic character at the metal and maximum basicity at oxygen. Finally, steric effects play a major role. There is good evidence that $[CpMo(CO)_3]_2$ itself is crowded,[50] and the formal replacement of one $CpMo(CO)_3$ unit in $[CpMo(CO)_3]_2$ by the bulkier $Cp_2Zr[\eta^2\text{-}C(O)Me]$ fragment to make a Zr–Mo-bonded dimer would only enhance such crowding.

Solid-State Structure of $Cp_2Zr(OCMe)(OC)MoCOCp$ (3). Mo–Zr separation in compound **3**, while long (3.3 Å), is comparable to the metal–metal distances in the closely related species $Cp_2NbMo(CO)_3Cp$ (3.07 Å)[13] and $Cp_3Nb_3(CO)_7$ (3.04–3.32 Å).[51]

Bimetallic compounds with cyclopentadienyl ligands on each metal may suffer significant end-to-end nonbonded repulsions. This is evident in the space-filling models (Figure 5) and is responsible for the fact that the ring containing C20–C24 is bent away further from the Zr–Mo bond than the C15–C19 ring. Even so, incipient van der Waals contacts are evident in the structure.

This study provides the first accurate comparison of the dimensions of terminal and four-electron-donor carbonyl ligands in the same complex, and the results are surprising. Donation of electron density from one π orbital of the carbonyl bridge to Zr predictably lengthens this CO bond in comparison to that in the terminal carbonyl. However, the four-electron donor carbonyl carbon (C6) is closer to Mo than is the terminal carbonyl carbon (C8). This is just the reverse of what is found in $Cp_2MoRe(CO)_3Cp$,[52] which contains two carbonyl semibridges; semibridges are of course functionally distinct from the four-electron-donor bridging carbonyl in **3**.[53] We must conclude that electron withdrawal by Zr on the carbonyl bridge in **3** enhances backbonding to this ligand by lowering the energy of its π* orbital. The valence bond equivalent of this argument is shown in H; this simultaneously explains the CO lengthening and the Mo–C shortening. It is worth noting that this mechanism is more effective at lengthening (weakening) the CO bond than is the carbonyl-*OC* bridge in compound **2**. The C–O distance in the four-electron-donor carbonyl of **3** (ν_{CO} 1536 cm^{-1}) is actually as long as the η^2-acetyl CO bond in **2** (1.25 Å).



H

The units Cp_2Zr and CpMoCO are short of 18-electron configurations by a total of 9 electrons; these must be sought from the bridging CO and acyl ligands, as well as from metal–metal bonding. If a Zr–Mo bond of unit order is postulated, it follows that the acyl and CO ligands must contribute three and four electrons respectively to the pool of valence electrons. The resultant bridging framework closely approaches coplanarity (Table VIII), but it must be emphasized that this plane does not precisely bisect the M2–Zr–M3 angle.

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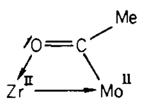
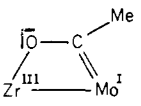
However, the ambiguous nature of the bonding in the three-electron-donor η^2-OCMe unit permits the following two resonance structures to be drawn. Form J is a μ_2:η^2 acetyl, while K is a μ_2:η^2-oxycarbene. Three bond lengths, Zr–O, O–C, and C–Mo are useful in assessing the relative importance of these two resonance forms. The observed O3–C4 separation, 1.285 (3) Å, significantly exceeds the C–O distance (1.25 Å) in the η^2-acetyl ligand in **2**. It is halfway between the 1.21 Å characteristic of a double bond between oxygen and sp^2 carbon (as found in various ketones[54,55]) and the 1.36 Å characteristic of a single bond between oxygen and sp^2 carbon (as found in furan and in various phenols, esters, and carboxylic acids[56]). The C–O stretching frequency associated with the μ-acetyl group is very low (1339 cm^{-1}).



J

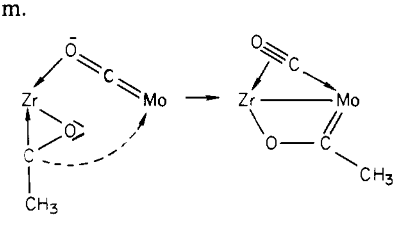


K

The Mo–C4 distance, 2.078 (3) Å, is much shorter than the Mo–acyl distance (2.264 (14) Å) in CpMo(CO)$_2$PPh$_3$[C(O)Me].[57] The Mo–C4 distance is only 0.12 Å longer than that to the terminal carbonyl carbon, C8, of compound **3**, and it is shorter than the tungsten–carbene distance (2.14 Å) in Ph$_2$CW(CO)$_5$.[58] The observed Zr–O3 separation in **3**, 2.156 (2) Å, approximates that (2.198 Å) in Zr(acac)$_4$,[59] which contains equal weights of the two Zr–O bond types drawn in J and K. This distance is 0.1 Å shorter than the Zr–O(acetyl) distance in **2**. Taken together, the structural data on **3** indicate nearly equal participation by both resonance forms. The presence of what is formally the potent reductant Zr(II) in J of course favors structure K.

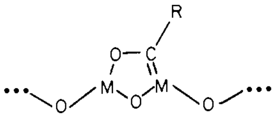
Reactivity of Heterobimetallic Acetyl Complexes. It was noted above that **2**, unlike Cp$_2$Zr[C(O)Me]X (X = Me and Cl[8,16]), shows a great reluctance to decarbonylate *at the acetyl group.* It is this stability that allows the alternative decarbonylation pathway (to **3**) to occur. We have previously drawn a correlation of η^2-acetyl stability (i.e., resistance to decarbonylation) with the π-donor capacity of the group X in the sequence Me > Cl ≫ OR; the complex Cp$_2$ZrMe(OR) shows no tendency to insert CO, due apparently to competitive π donation by alkoxide lone pairs.[16] Since Cp$_2$Zr[C(O)Me]Mo(CO)$_3$Cp is even more resistant than Cp$_2$Zr[C(O)Me]Me to decarbonylation of the acetyl group, this provides further support for the (dative) purely σ bonding of the carbonyl-*OC* bridge in this compound.

As η^2-acyl ligands in mononuclear complexes of early transition metals display oxycarbene character in their reactions,[60,61] one may expect such behavior on the part of the η^2-acetyl ligand in **2**. The conversion of **2** to **3** may thus be seen as a formal carbene migration away from the oxophilic zirconium onto the electron-rich molybdenum.



Bifunctional Reduction of C–O Bond Order in Heterobimetallic Complexes. Simple coordination of a strong Lewis acid (AlCl$_3$) to ketones does not significantly lengthen the C=O bond.[62] Effective lengthening requires a bifunctional approach;[63a] the partial Mo–C double bond in **3** is crucial to the reduction in C–O bond order. The results of such bifunctional CO activation are illustrated by the sequence of CO bond lengths in **2** and **3**: terminal CO (1.15 Å) < carbonyl-*OC* bridge (1.21) < η^2-acetyl (1.25) ≈ π-bonded CO (1.24) < μ:η^2-acetyl/oxycarbene (1.29). The total bond stretching is 0.14 Å. The acetyl C–O bond lengthening (bond order reduction) in complex **3** exceeds that in all known monometallic η^2-C(O)R complexes.[5] It also exceeds that in several cases where a μ_2:η^2-OCR unit spans middle- and late-transition elements (Mn/Ir,[63b] Fe/Fe,[64] Os/Os,[65] and Ru/Ru[66]). However, the Zr–O binding in **3** is not as effective in C–O bond order reduction as are (a) the Al–O coordination in (OC)$_4$Mn(μ_2-Br)(μ_2:η^2-MeCO)AlBr$_2$ (C–O distance 1.30 Å and ν_{CO} 1450 cm^{-1}),[67] (b) the B–O coordination in Cp(OC)Fe[C(O)Me][C(O)-*i*-Pr]BF$_2$ (C–O distance 1.30 Å),[68] (c) the coordination to all three atoms of an Fe$_3$ triangle in [Fe$_3$(CO)$_9$Ac]$^-$ (CO distance 1.31 (2) Å),[69] and (d) the coordination of O and C to a WOs$_2$ triangle in CpWOs$_3$(CO)$_{11}$(OCCH$_2$Ph)[70] (C–O = 1.394 (27) Å). The C–O distance (1.29 Å) in the acetyl/oxycarbene ligand in **3** and the associated ν_{CO} agree quite well with those reported (1.30 Å, 1330 cm^{-1}) for the η^2(μ_3-C, μ_2-O) carbonyl ligand in Cp$_3$Nb$_3$(CO)$_7$.[51]

The μ_2:η^2-OCMe group is an exceedingly flexible structural unit, spanning metal–metal separations of from 2.57[64] to 3.54 Å.[63b] Surface-bound μ_2-oxycarbenes may be important, not only on pure metals of varying sizes but also on metal oxides devoid of metal–metal bonding:



Heterobimetallic complexes containing early and late transition metals are ideally suited for the synthesis of such μ_2:η^2-OCMe units and should be generally useful for the bifunctional activation of carbon monoxide.

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Registry No. **1**, 67202-09-9; **2**, 83291-31-0; **3**, 83269-55-0; CpMo(CO)$_3$H, 12176-06-6; Cp$_2$ZrMe$_2$, 12636-72-5; Cp$_2$Zr[η^2-C(O)Me]Me, 60970-97-0; CF$_3$CO$_2$H, 76-05-1; CH$_3$CHO, 75-07-0; Cp$_2$Zr(O$_2$CCF$_3$)$_2$, 37205-20-2.

Supplementary Material Available: For compounds **2** and **3**, a list of anisotropic *U*'s, hydrogen positions (for **3** only), and observed and calculated structure factors (82 pages). Ordering information is given on any current masthead page.

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