Supplementary Material Available: Tables of atomic positional parameters, thermal parameters, and structure factors for **2** (8 pages). Ordering information is given on any current masthead page.

A Bridging Acetyl Group from the Reaction of a Dinuclear Methyl Complex with Carbon Monoxide

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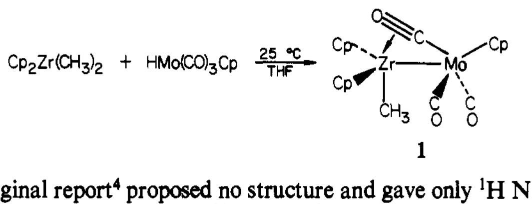
Although much is known about the reactions of mononuclear alkyl complexes with carbon monoxide,[1,2] attention is only beginning to be paid to the corresponding reactions of polynuclear alkyls.[3] Our attention was thus attracted by the report[4] of the formation of the heterometallic dinuclear alkyl $Cp_2Zr(CH_3)$-$Mo(CO)_3Cp$ (**1**) from Cp_2ZrMe_2 and $HMo(CO)_3Cp$. The reaction itself represents an interesting synthetic application of dinuclear elimination[5a] and contrasts to the selectivity observed[5b] for hydride transfer from Cp_2MH_n to the *acetyl* group of $Cp_2Zr(Ac)CH_3$. We now report that (1) one of the carbonyl ligands in **1** appears to be a four-electron-donor μ-η^1,η^2-CO bridge, (2) ^{13}C NMR indicates that interconversion of the four-electron-donor carbonyl with the other carbonyl ligands occurs with an activation energy of 9.6 kcal/mol, (3) the methyl ligand on zirconium in **1** does not react with the four-electron-donor carbonyl but rather with an external CO to give a dinuclear η^2-acetyl complex, and (4) the carbon end of that η^2-acetyl ligand migrates from Zr to Mo, yielding an acetyl-bridged dimer containing CO bonds of three different orders.

The coordinatively unsaturated alkyl Cp_2ZrMe_2 and the hydride $HMo(CO)_3Cp$ fulfill the requirements for dinuclear elimination[5a] and it is therefore not suprising that a mixture of these compounds in THF (reaction 1) eliminates methane to form **1**. Although



(1)

1

the original report[4] proposed no structure and gave only ^1H NMR spectroscopic data, IR and ^{13}C NMR[6] (the latter obtained on **1** prepared from 32% ^{13}C-enriched $HMo(CO)_3Cp$) imply that **1** has the structure illustrated.[7,8] It seems likely that the reaction of metal carbonyl hydrides with $Cp_2Zr(CH_3)_2$ will be a general route to dinuclear complexes with carbonyls π-bonded to zirconium.

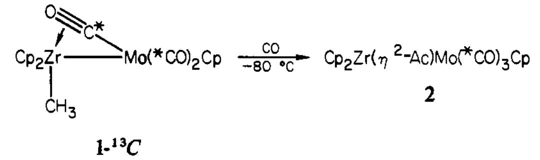
Although at room temperature **1** has a single carbonyl peak in the ^{13}C NMR at δ 236.1, two peaks at δ 245.4 and 232.5 (relative intensity 1:2) are observed on cooling to −80 °C. The barrier $\Delta G^{\ddagger}$ for migration of the π-bonded carbonyl to one of the two equivalent terminal carbonyl sites in **1** is 9.6 kcal/mol. This measurement is the first direct (i.e., by ^{13}C NMR) observation of mobility of a π-bonded four-electron-donor carbonyl ligand.[9,10]

Carbonylation of **1** proceeds rapidly and quantitatively at room temperature (reaction 2). The η^2-acetyl dimer **2**[11-13] can also be obtained directly by dinuclear elimination from $Cp_2Zr(Ac)CH_3$ (reaction 3).

$$\mathbf{1} \xrightarrow[25\ ^\circ\mathrm{C,\ toluene}]{\mathrm{CO}} \underset{\mathbf{2}}{Cp_2Zr(\eta^2\text{-}Ac)Mo(CO)_3Cp} \qquad (2)$$

$$Cp_2Zr(\eta^2\text{-}Ac)CH_3 + HMo(CO)_3Cp \xrightarrow[C_6H_6]{25\ ^\circ\mathrm{C}} \underset{\mathbf{2}}{Cp_2Zr(\eta^2\text{-}Ac)Mo(CO)_3Cp} \qquad (3)$$

Labeling experiments establish unambiguously that the carbon in the acyl carbonyl in **2** arises from the added carbon monoxide in reaction 2. A sample of **1** which was 32% ^{13}CO-enriched was treated with 1 atm of ^{12}CO[14] at −80 °C (reaction 4) but the reaction was quenched by freezing at −196 °C before it was complete. Removal of the unreacted CO left a mixture which



(4)

1-^{13}*C*

contained **2** with (NMR analysis[15] at −50 °C) ^{13}CO only in its

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† Alfred P. Sloan Fellow, 1977–1981.

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(2) Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299–311.

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(4) Renaut, P.; Tainturier, G.; Gautheron, B. *J. Organomet. Chem.* **1978**, *150*, C9.

(5) (a) Norton, J. R. *Acc. Chem. Res.* **1979**, *12*, 139–45. (b) Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 1747–8.

(6) IR (toluene): ν(CO) 2025 (w), 1948 (s), 1863 (s), 1545 (vs) cm^{-1}. The weak peak at 2025 cm^{-1} increases in intensity in more polar solvents and probably belongs to a small amount of another conformer. ^{13}C NMR (toluene-d_8): δ 35.1 (3, CH_3), 113.5 (10, CpZr), 89.9 (5, CpMo), 236.1 (3, CO).

(7) The intense IR band at 1545 cm^{-1} is in the region where such features have been observed for known four-electron-donor π-bonded carbonyls;[8] the agreement is particularly good with the band at 1560 cm^{-1} assigned to a carbonyl π-bonded to Nb in the closely related dimer $Cp_2NbMo(CO)_3Cp$.[8c]

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(9) Mobility of a μ_3-η^2-CO ligand in $Cp_3Nb_3(CO)_7$ has been demonstrated indirectly by a study of the ^1H NMR of a methylcyclopentadienyl ligand: Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 3201–3.

(10) The rearrangement of the carbonyls within **1** can be seen as a variant of the cis–trans interconversions of $CpMo(CO)_2LR$ examined by: Faller, J. W.; Anderson, A. S. *J. Am. Chem. Soc.* **1970**, *92*, 5852–60.

(11) IR (toluene): ν(CO) 2020 (w), 1930 (s), 1835 (m), 1590 (s) cm^{-1}. ^1H NMR (C_6D_6): δ 5.55 (s, 10 H, Cp_2Zr), 5.39 (s, 5 H, CpMo), 2.19 (s, 3 H, CH_3). ^{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).

(12) The ν(CO) at 1590 cm^{-1} and methyl ^1H resonance at δ 2.19 suggest that the acetyl ligand in **2** is η^2, a structural feature which is a typical result of the carbonylation of 16-electron Zr alkyl complexes.[13] The ^{13}C NMR resonance of the acyl carbon (δ 316.5) is quite close to the values (δ 317–323) recently reported[13c] for several η^2-acyls of Zr. Although it has recently been shown[13b] that such Zr η^2-acyls can exist in two isomeric forms, it is not possible to say which form is correct for **2** on the basis of the present data.

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(14) The use of ^{13}C-labeled **1** and isotopically normal CO rather than the reverse combination permits the insertion 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.

(15) In addition to ^{13}C NMR spectra, the fraction of ^{13}C in the carbonyl group of the acetyl ligand is conveniently determined from the relative intensity of the ^{13}C satellites (J = 5.6 Hz) of the methyl resonance in the ^1H spectrum.

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terminal carbonyls; the acetyl carbonyl must therefore have arisen from the external ^{12}CO. After the sample was warmed at 40 °C for 1 h, NMR analysis showed ^{13}CO randomly distributed among the terminal and acetyl positions in **2**, reflecting the operation of a carbonyl scrambling process after the insertion reaction.

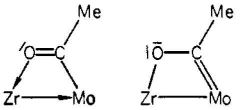
In solution, complex **2** slowly loses 1 equiv of CO (reaction 5)

$$\underset{\mathbf{2}}{Cp_2Zr(\eta^2\text{-Ac})Mo(CO)_3Cp} \xrightarrow[\text{40 °C, 3 days; toluene}]{-CO} \underset{\mathbf{3}}{Cp_2Zr(Ac)Mo(CO)_2Cp} \quad (5)$$

to form **3**,[16] which may be isolated as air-stable yellow crystals. An X-ray study[17] reveals a structure (Figure 1) based on Cp_2Zr and Mo(CO)Cp units bridged by a nearly planar (±0.11 Å) array composed of a four-electron-donor bridging carbonyl and a bridging η^2-OCMe moiety. The carbon part of the η^2-acetyl has thus migrated away from the oxophilic Zr. In view of the carbenoid character established[18] for the carbon in η^2-acetyl complexes of zirconium and the oxycarbenoid character (see below) of the OCMe ligand toward Mo in **3**, the migration can be viewed as a formal carbene transfer from Zr to Mo.

The three CO bonds in **3** reveal increasing degrees of bond-order reduction: the CO bond in the four-electron-donor bridge is significantly (17σ) longer than in the terminal CO, but is significantly (9σ) shorter than in the η^2-OCMe group. This four-electron-donor carbonyl is the first in which the carbonyl oxygen is closer to the metal (Zr–O(7) = 2.271 (2) Å) than is the carbon (Zr–C(6) = 2.343 (3) Å). It is also noteworthy that the distance from Mo to the carbon of the π-bonded carbonyl (Mo–C(6) = 1.876 (3) Å) is shorter than that to the terminal carbonyl carbon (Mo–C(8) = 1.957 (3) Å).

Although **3** is unambiguously a 34-electron dimer with a Zr–Mo bond, two resonance forms (A, acetyl, and B, oxycarbene) can



A B

be drawn for the bridging η^2-OCMe moiety. The C(4)–O(3) and Mo–C(4) distances, long and short, respectively, in comparison to those in reference compounds,[19] indicate significant participation by both forms. The C–O bond length in the bridging η^2-OCMe moiety in **3** exceeds that in all known monometallic η^2-C(O)R complexes.[13a,20] It also exceeds that in several cases where an η^2-OCR unit spans middle- and late-transition elements (Mn/Ir,[21] Fe/Fe,[22] and Ru/Ru[23]). However, the Zr–O binding in **3** is not as effective in C–O bond-order reduction as is the Al–O coordination in $(OC)_4Mn(\mu\text{-Br})[\mu\text{-C}(CH_3)O]AlBr_2$.[24] Both the C(4)–O(3) distance and the stretching frequency (1339 cm^{-1} [25]) in **3** agree quite well with those reported (1.30 Å and 1330 cm^{-1}) for the μ_3-η^2-CO ligand in $Cp_3Nb_3(CO)_7$.[8d]

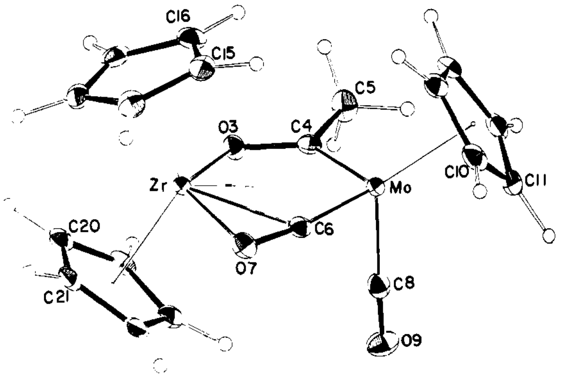
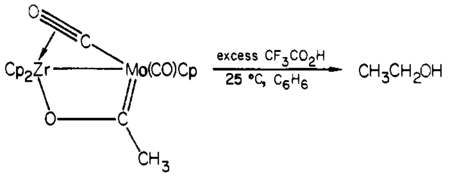


Figure 1. Molecular structure of $(\eta^5\text{-}C_5H_5)(CO)Mo(\mu\text{-}\eta^1,\eta^2\text{-}CO)[\mu\text{-}C(CH_3)O]Zr(\eta^5\text{-}C_5H_5)_2$ (**3**). Structural parameters (see also text) are as follows. Distances: Mo–Zr = 3.297 (1), C(8)–O(9) = 1.147 (4), C(6)–O(7) = 1.241 (4), C(4)–O(3) = 1.285 (3), Mo–C(4) = 2.078 (3), $(Mo\text{–}C(Cp))_{av}$ = 2.378 (3), $(Zr\text{–}C(Cp))_{av}$ = 2.522 (3) Å. Angles: Zr–O(3)–C(4) = 111.2 (2), O(3)–C(4)–Mo = 125.4 (2), O(3)–C(4)–C(5) = 110.5 (2), C(5)–C(4)–Mo = 124.1 (2), Mo–C(8)–O(9) = 178.3 (3), Mo–C(6)–O(7) = 172.3 (2)°.

Compound **3** is quite unreactive toward most donor ligands, e.g, pyridine and tertiary phosphines. However, in further reflection of the oxycarbene nature of the bridging OCMe ligand,[26] it does react with excess CF_3CO_2H to give ethanol (reaction 6).



(6)

3

The intermediate stages in this reaction and the nature of the inorganic products are under investigation. The sequence of reactions 2, 5, and 6 is thus a stoichiometric reduction of carbon monoxide to ethanol.

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Supplementary Material Available: A list of atomic coordinates and thermal parameters for $Cp_2Zr(OCMe)(OC)MoCOCp$ (1 page). Ordering information is given on any current masthead page.

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(16) IR (Nujol): ν(CO) 1856 (vs), 1534 (s), 1339 (s) cm^{-1}. ^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). An acceptable C, H analysis was obtained.

(17) Crystallographic data (−172 °C): a = 15.237 (3) Å, b = 13.353 (2) Å, c = 8.787 (1) Å, V = 1709.82 Å^3, Z = 4 in space group $P2_1/n$; $R(F)$ = 0.0299, $R_w(F)$ = 0.0360 for 3570 observed ($F_o^2 > 2.33\sigma(F_o^2)$) reflections using anisotropic thermal parameters for all nonhydrogen atoms; all hydrogen atoms were refined isotropically.

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(23) Merlino, S.; Montagnoli, G.; Braca, S.; Sbrana, G. *Inorg. Chim. Acta* **1978**, *27*, 233.

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(25) The assignment of this band has been confirmed by determining that it shifts to 1309 cm^{-1} in ^{13}CO-enriched **3**.

(26) The acid cleavage of $M{=}CR_1R_2$ to $H_2CR_1R_2$ is common; for an example see: Schrock, R. R.; Fellmann, J. D. *J. Am. Chem. Soc.* **1979**, *100*, 3359–70.