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Synthesis and Solution Properties of the Heterobimetallic Complexes $Cp_2ZrMe(\mu\text{-}OC)M(CO)_2Cp$ (M = Cr, Mo, W) and of Their Carbonylation Derivatives. Structure of $Cp_2ZrMe(\mu\text{-}OC)Mo(CO)_2Cp$

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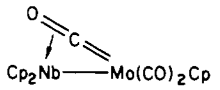
The crystal structure of $Cp_2ZrMe(\mu\text{-}OC)Mo(CO)_2Cp$ (**1b**) has been determined by single-crystal X-ray diffraction methods and refined to an R (R_w) value of 0.0380 (0.0332) for 3618 reflections with $F_o^2 > 2.5\sigma(F_o^2)$. The space group is $P2_1/n$, $Z = 8$, and the cell dimensions are a = 18.451 (4) Å, b = 10.713 (2) Å, c = 19.675 (3) Å, and β = 105.23 (1)°. There are two discrete, chemically identical, molecules in the asymmetric unit. The Cp_2ZrMe moiety is bound to the $CpMo(CO)_3$ moiety only through the interaction of one carbonyl oxygen with Zr. Various bond distances indicate a larger contribution from an oxycarbyne resonance structure than has been observed for any previous structure of this type. Important average distances are as follows: Zr–O, 2.107 (3) Å; bridge O–C, 1.236 (5) Å; bridge C–Mo, 1.847 (5) Å. There is no bonding interaction between Zr and Mo or the bridging carbonyl carbon. The Cr and W analogues (**1a** and **1c**) of **1b** react with CO to form $Cp_2Zr[C(O)Me](\mu\text{-}OC)M(CO)_2Cp$ (**2a**, M = Cr; **2c**, M = W). **2c** loses CO to form $Cp_2Zr(\mu\text{-}\eta^2,\eta^1\text{-}CO)(\mu\text{-}OCMe)W(CO)Cp$. Conductivities, determined in CH_3CN, show that **1** and **2** dissociate extensively in that solvent and that the relative Lewis basicities toward Zr of the $CpM(CO)_3^-$ anions agree with their relative proton basicities. The Zr in **1** is a more powerful Lewis acid than the Zr in **2**, in agreement with the structural importance of an oxycarbyne resonance structure for **1b**.

Recent interest in the heterobimetallic activation of carbon monoxide[1,2] prompted us to investigate[2k,3] the structure and properties of the compound reported by Renaut, Tainturier, and Gautheron[4] as a product of reaction 1. The original report[4]

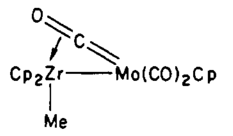
$$Cp_2ZrMe_2 + HMo(CO)_3Cp \xrightarrow{THF} CH_4 + \underset{\mathbf{1b}}{Cp_2ZrMeMo(CO)_3Cp} \quad (1)$$

series **a**, Cr; series **b**, Mo; series **c**, W

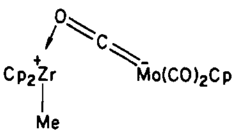
included only ^1H NMR and microanalytical data and proposed no structure for **1b**. We found[3] a carbonyl band at 1545 cm^{-1}, very close to that (1560 cm^{-1}) reported for the η^2,η^1-bridging carbonyl that had been observed crystallographically in the isoelectronic $Cp_2Nb(\mu\text{-}\eta^2,\eta^1\text{-}CO)Mo(CO)_2Cp$:[2d]



We therefore suggested[3] that **1b** had an η^2,η^1-bridging carbonyl and a Zr–Mo bond (structure I). However, in 1981 Stucky and

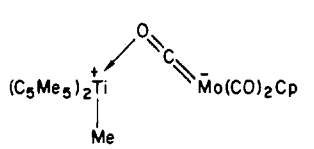


I



II

co-workers found that $(C_5Me_5)_2TiMeMo(CO)_3Cp$ had a carbonyl-*O,C* bridged structure



and suggested[2h] that **1b** might have a similar structure (II). We therefore attempted to determine the structure of **1b**, but repeated recrystallizations from toluene/hexane under a variety of experimental conditions gave aggregates of crystals too small for satisfactory X-ray analysis. Now, however, reaction of solid Cp_2ZrMe_2 and $HMo(CO)_3Cp$ in the presence of a trace of THF has given suitable crystals and has permitted us to determine and report the X-ray structure of **1b**.

In order to determine the generality of this approach to heterobimetallic chemistry, we have also investigated the extent to

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(1) Shriver, D. F. *ACS Symp. Ser.* **1981**, *No. 152*, 1 and references therein.

(2) Many structures have been reported in which the C–O bond of carbon monoxide is lengthened by the formation of M–C–O–M′ linkages of all sorts, including η^2,η^1-bridging carbonyls and bridging acyls. Examples (with M and M′ two different transition metals or one transition metal and a lanthanide or actinide) can be found in: (a) Blickensderfer, J. R.; Kaesz, H. D. *J. Am. Chem. Soc.* **1975**, *97*, 2681. (b) Schmid, G.; Stutte, B.; Boese, R. *Chem. Ber.* **1978**, *111*, 1239–1245. Stutte, B.; Bätzel, V.; Boese, R.; Schmid, G. *Chem. Ber.* **1978**, *111*, 1603. (c) Stutte, B.; Schmid, G. *J. Organomet. Chem.* **1978**, *155*, 203. (d) Pasynskii, A. A.; Skripkin, Yu, V.; Eremenko, I. L.; Kalinnikov, V. T.; Aleksandrov, G. G.; Andrianov, V. G.; Struchkov, Yu. *J. Organomet. Chem.* **1979**, *165*, 49. (e) Wolczanski, P. T.; Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 218–220. (f) Barger, P. T.; Bercaw, J. E. *J. Organomet. Chem.* **1980**, *201*, C39. (g) Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 1747–1748. (h) Hamilton, D. M., Jr.; Willis, W. S.; Stucky, G. D. *J. Am. Chem. Soc.* **1981**, *103*, 4255. (i) Abys, J.; Risen, W. M., Jr. *J. Organomet. Chem.* **1981**, *204*, C5–C9. (j) Tilley, T. D.; Andersen, R. A. *J. Chem. Soc., Chem. Commun.* **1981**, 985. (k) Marsella, J. A.; Huffman, J. C.; Caulton, K. G.; Longato, B.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 6360. (l) LaCroce, S.; Cutler, A. R. *J. Am. Chem. Soc.* **1982**, *104*, 2312–2314. (m) Berry, D. H.; Bercaw, J. E.; Jircitano, A. J.; Mertes, K. G. *J. Am. Chem. Soc.* **1982**, *104*, 4712–4715. (n) Brun, P.; Dawkins, G. M.; Green, M.; Miles, A. D.; Orpen, A. G.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1982**, 926. (o) Merola, J. S.; Gentile, R. A.; Ansell, G. B.; Modrick, M. A.; Zentz, S. *Organometallics* **1982**, *1*, 1731. (p) Tilley, T. D.; Andersen, R. A. *J. Am. Chem. Soc.* **1982**, *104*, 1772. (q) Barr, R. D.; Green, M.; Howard, J. A. K.; Marder, T. B.; Moore, I.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1983**, 746. (r) Cramer, R. E.; Higa, K. T.; Pruskin, S. L.; Gilje, J. W. *J. Am. Chem. Soc.* **1983**, *105*, 6749. (s) Dawkins, G. M.; Green, M.; Mead, K. A.; Salaün, J.-Y.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1983**, 527. (t) Park, J. T.; Shapley, J. R.; Churchill, M. R.; Bueno, C. *Inorg. Chem.* **1983**, *22*, 1579. Shapley, J. R.; Park, J. T.; Churchill. M. R.; Ziller, J. W.; Beanan, L. R. *J. Am. Chem. Soc.* **1984**, *106*, 1144–1145. (u) Sünkel, K.; Nagel, U.; Beck, W. *J. Organomet. Chem.* **1983**, *251*, 227–243. (v) Barger, P. T.; Bercaw, J. E. *Organometallics* **1984**, *3*, 278–284. (w) Merola, J. S.; Campo, K. S.; Gentile, R. A.; Modrick, M. A.; Zentz, S. *Organometallics* **1984**, *3*, 334–337. (x) Boncella, J. M.; Andersen, R. A. *Inorg. Chem.* **1984**, *23*, 432. (y) Jeffery, J. C.; Orpen, A. G.; Robinson, W. T.; Stone, F. G. A.; Went, M. J. *J. Chem. Soc., Chem. Commun.* **1984**, 396. (z) Rosen, R. P.; Hoke, J. B.; Whittle, R. R.; Geoffroy, G. L.; Hutchison, J. P.; Zubieta, J. A. *Organometallics* **1984**, *3*, 846. (aa) Carriedo, G. A.; Hodgson, D.; Howard, J. A. K.; Marsden, K.; Stone, F. G. A.; Went, M. J.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1982**, 1006–1008.

(3) A preliminary communication of part of this work has appeared: Longato, B.; Norton, J. R.; Huffman, J. C.; Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 209.

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

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Table I. Crystallographic Details for $Cp_2ZrMe(CO)_3MoCp$ (**1b**)

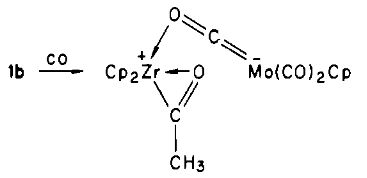
empirical formula	$C_{19}H_{18}O_3MoZr$
cryst dimens, mm	0.35 × 0.15 × 0.14
space group	$P2_1/n$
cell dimens (20 (1) °C, 24 reflcns)	
a, Å	18.451 (4)
b, Å	10.713 (2)
c, Å	19.675 (3)
β, deg	105.23 (1)
molecules per unit cell, *Z*	8
F(000)	1904
cell vol, Å^3	3752 (1)
calcd density, g/cm^3	1.71
mol wt	481.51
μ, linear abs coeff, cm^{-1}	12.11
diffractometer	Nicolet R3m/E
monochromator	graphite
radiation	Mo Kα (λ = 0.710 73 Å)
2θ limits, deg	3.0–50.0
scan speed, deg/min	variable (2–30)
scan width, deg	$(2\theta(K\alpha_1) - 1.0)$–$(2\theta(K\alpha_2) + 1.2)$
reflcns measd	$h \geqslant 0, k \geqslant 0, l$
scan type	$\theta/2\theta$
diffraction geometry	bisecting
Lorentz, polarizn factors	cor applied
abs cor	none applied
no. of reflcns collected	5728
no. of unique reflcns used ($F_o^2 > 2.5\sigma(F_o^2)$)	3618
R	0.0380
R_w	0.0332
GOF	1.307
no. of least squares parameters	439
max. shift/esd (last cycle)	0.10

Table II. Atom Coordinates (×10^4) and Temperature Factors (Å^2 ×10^3)[a] for Compound **1b**

atom	*x*	*y*	*z*	U^b
Mo(a)	1676 (1)	11119 (1)	−39 (1)	53 (1)
Mo(b)	5670 (1)	11683 (1)	1140 (1)	67 (1)
Zr(a)	1711 (1)	7199 (1)	1298 (1)	51 (1)
Zr(b)	5955 (1)	7715 (1)	2480 (1)	54 (1)
C(1a)	1560 (4)	9512 (6)	248 (3)	62 (3)
O(1a)	1488 (3)	8437 (4)	438 (2)	79 (2)
C(2a)	722 (5)	10862 (6)	−737 (4)	77 (4)
O(2a)	160 (3)	10690 (5)	−1151 (3)	117 (3)
C(3a)	1092 (4)	11654 (5)	616 (3)	65 (3)
O(3a)	756 (3)	11965 (4)	1000 (3)	94 (2)
C(1b)	5948 (3)	10098 (5)	1485 (3)	57 (3)
O(1b)	6102 (2)	9031 (4)	1729 (2)	67 (2)
C(3b)	6329 (6)	12292 (7)	2005 (4)	140 (5)
O(3b)	6724 (5)	12653 (6)	2534 (3)	225 (5)
C(2b)	4917 (6)	11547 (10)	1624 (4)	136 (6)
O(2b)	4419 (5)	11414 (10)	1886 (4)	243 (6)
C(7a)	2728 (4)	6304 (7)	1076 (4)	97 (4)
C(7b)	4705 (4)	7964 (10)	2208 (5)	126 (5)
C(11a)	475 (4)	6360 (7)	594 (4)	87 (4)
C(12a)	1004 (4)	5521 (7)	504 (4)	81 (4)
C(13a)	1317 (4)	4962 (6)	1140 (4)	76 (3)
C(14a)	999 (4)	5457 (6)	1635 (4)	72 (3)
C(15a)	477 (4)	6332 (6)	1293 (4)	78 (3)
C(21a)	1833 (6)	9189 (7)	1974 (4)	88 (4)
C(22a)	2552 (5)	8845 (7)	1971 (4)	95 (4)
C(23a)	2709 (4)	7764 (8)	2377 (3)	86 (3)
C(24a)	2098 (5)	7447 (7)	2599 (3)	74 (3)
C(25a)	1553 (4)	8338 (6)	2352 (3)	80 (3)
C(31a)	2733 (5)	11108 (8)	−488 (5)	142 (6)
C(32a)	2319 (5)	12108 (10)	−792 (4)	141 (5)
C(33a)	2305 (5)	12938 (8)	−264 (6)	108 (5)
C(34a)	2717 (5)	12433 (9)	345 (4)	107 (4)
C(35a)	2977 (5)	11309 (9)	201 (6)	124 (5)
C(11b)	6853 (7)	7852 (12)	3641 (5)	116 (5)
C(12b)	6849 (4)	9037 (9)	3352 (4)	120 (4)
C(13b)	6149 (8)	9518 (8)	3312 (4)	111 (6)
C(14b)	5757 (5)	8680 (8)	3574 (4)	95 (4)
C(15b)	6184 (5)	7672 (7)	3772 (3)	95 (4)
C(21b)	5588 (10)	6079 (9)	1569 (5)	154 (8)
C(22b)	5431 (7)	5575 (8)	2146 (5)	131 (6)
C(23b)	6141 (9)	5473 (8)	2635 (6)	133 (7)
C(24b)	6732 (7)	5914 (9)	2360 (7)	129 (6)
C(25b)	6398 (7)	6285 (7)	1691 (6)	148 (7)
C(31b)	5902 (7)	13341 (8)	439 (4)	109 (5)
C(32b)	5142 (7)	13296 (8)	336 (4)	101 (5)
C(33b)	4912 (5)	12119 (8)	11 (4)	82 (4)
C(34b)	5532 (5)	11537 (7)	−78 (3)	70 (3)
C(35b)	6142 (5)	12289 (9)	172 (4)	87 (4)

[a] Estimated standard deviations in the least significant digits are given in parentheses. [b] Equivalent isotropic *U*, defined as one-third of the trace of the orthogonalized U_{ij} tensor.

which other metals can be used in place of molybdenum in reaction 1 and in the formation of carbonylated derivatives such as **2b**.[2k]



(2)

2b

Finally, as the μ-OC carbonyl bridges in **1** and **2** suggest that these compounds can be viewed as ion pairs, we have investigated the extent of dissociation of these compounds in solution.[5]

Experimenal Section

All manipulations involving these highly air- and moisture-sensitive compounds were performed in a Vacuum Atmospheres inert-atmosphere glovebox unless otherwise stated. THF, toluene, and diethyl ether were distilled under nitrogen from Na/benzophenone and hexanes similarly from K/benzophenone. Reagent grade acetonitrile (Fischer) was predried over molecular sieves and distilled from P_2O_5 and then from CaH_2 under nitrogen. Literature methods were used for the preparation of $CpM(CO)_3H$ (M = Cr, Mo, W)[6] and Cp_2ZrMe_2.[7] NMR spectra were recorded on a JEOL FX-100Q spectrometer with the residual solvent proton peak as an internal reference (chemical shifts generally varied with concentration for **1** and **2**, as previously discussed for **2b**[2k]). IR spectra were recorded on a Perkin-Elmer 983 spectrometer with a Model 3600 data station for spectral storage and subtraction or on a Beckman 4240. Elemental analyses were performed by Analytische Laboratorien of Engelskirchen, West Germany, or by Galbraith Laboratories, Inc., of Knoxville, TN.

[Bis(η^5-cyclopentadienyl)methylzirconium(IV)](μ-carbonyl-*O*,*C*)dicarbonyl(η^5-cyclopentadienyl)chromium(0) (1a). A solution of Cp_2ZrMe_2 (718 mg, 2.85 mmol) in 2 mL of THF was added to a THF (2 mL) solution of $HCr(CO)_3Cp$ (577 mg, 2.85 mmol), and the reaction mixture was stirred at room temperature overnight. The solvent was removed and the residue dried under high vacuum for 3 h. The resulting solid was stirred with hexanes (25 mL) for several hours at room temperature, collected by filtration, and dried under vacuum. The yield of powdery, mustard-colored product was 1.05 g (84%). ^{1}H NMR: in C_6D_6, δ 5.74 (s, 10 H), 4.75 (s, 5 H), 0.44 (s, 3 H); in CD_3CN, δ 6.04 (s, 10 H), 4.42 (s, 5 H), 0.03 (s, 3 H). IR (cm^{-1}): in toluene, 1939 (s), 1855 (s), 1551 (s, broad); in Nujol, 1915 (s), 1825 (s), 1540 (s, broad); in CH_3CN, 1920 (m), 1891 (vs), 1841 (w), 1772 (vs), 1586 (w).

X-ray Crystallographic Study of $Cp_2ZrMe(\mu\text{-}OC)Mo(CO)_2Cp$ (1b). Crystals of **1b** were obtained from an equimolar (4.18 mmol of each) mixture of solid $CpMo(CO)_3H$ and Cp_2ZrMe_2. After 1 day 3 mL of THF was vacuum transferred onto the solid mixture. The solvent was removed from the stirred solution after 0.5 h, leaving an orange oil. After several cycles of freezing, degassing, and thawing of this oil over a 1-h

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(5) Some of these results have been quoted as unpublished work in a short review: Edidin, R. T.; Longato, B.; Martin, B. D.; Matchett, S. A.; Norton, J. R. In "Organometallic Compounds: Synthesis, Structure and Theory"; Shapiro, B. L., Ed.; Texas A & M University Press: College Station, TX, 1983; pp 260–280. A complete account of kinetic studies establishing the proton-transfer nature of reactions 1, 3, and 4 will be published separately.

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(7) Wailes, P. C.; Weigold, H.; Bell, A. P. *J. Organomet. Chem.* **1972**, *34*, 155.

Table III. Important Bond Lengths (Å) and Angles (deg) for $Cp_2ZrMe(CO)_3MoCp$ (**1b**)[a]

atoms	molecule A	molecule B
Mo–C1	1.842 (7)	1.851 (6)
Mo–C2	1.947 (7)	1.886 (12)
Mo–C3	1.969 (7)	1.927 (8)
Zr–O1	2.103 (4)	2.111 (4)
Zr–C7	2.251 (8)	2.243 (7)
C1–O1	1.229 (8)	1.243 (7)
C2–O2	1.153 (9)	1.176 (16)
C3–O3	1.146 (9)	1.168 (10)
Mo···Zr[b]	4.948 (1)	4.956 (1)
Mo···O1[b]	3.191 (6)	3.214 (6)
Zr–O1–C1	145.3 (4)	145.6 (4)
O1–C1–Mo	179.5 (6)	176.8 (6)
C7–Zr–O1	96.3 (3)	93.8 (3)
O2–C2–Mo	178.9 (7)	175.2 (8)
O3–C3–Mo	179.6 (5)	179.2 (7)
Cp1 ring		
Zr–C11	2.504 (7)	2.448 (9)
Zr–C12	2.511 (7)	2.486 (12)
Zr–C13	2.500 (6)	2.496 (9)
Zr–C14	2.470 (7)	2.498 (10)
Zr–C15	2.456 (7)	2.466 (7)
Cp2 ring		
Zr–C21	2.491 (7)	2.471 (10)
Zr–C22	2.488 (9)	2.508 (9)
Zr–C23	2.491 (7)	2.435 (9)
Zr–C24	2.484 (6)	2.452 (12)
Zr–C25	2.488 (8)	2.469 (16)
Cp3 ring		
Mo–C31	2.343 (13)	2.356 (9)
Mo–C32	2.377 (13)	2.373 (8)
Mo–C33	2.369 (10)	2.341 (7)
Mo–C34	2.341 (9)	2.347 (6)
Mo–C35	2.330 (8)	2.383 (9)

[a] Entries in parentheses are estimated standard deviations in the least significant digits. [b] Nonbonding distance.

period, brown crystals of the moisture- and air-sensitive complex **1b** were serendipitously obtained.

One of the larger crystals (sealed under N_2 in a thin-walled glass capillary tube) was employed for data collection on a Nicolet R3m/E diffractometer. Crystallographic details are reported in Table I. Heavy-atom positions were obtained from the Patterson map, and subsequent Fourier maps revealed the positions of carbon and oxygen atoms. Standard atomic scattering factors were used.[8,9] All non-hydrogen atoms were refined with use of anisotropic thermal parameters, while all hydrogen atoms were placed in idealized positions. Hydrogen atoms were assigned isotropic thermal parameters set at 1.2 times the isotropic equivalent of the thermal parameters for the carbon atoms to which they were bound.

The final atomic coordinates are in Table II. Tables of anisotropic thermal parameters, all bond lengths and angles, and observed and calculated structure factors are available as supplementary material. Important bond lengths and angles are given in Table III.

Barrier to Exchange of Bridging and Terminal Carbonyls in 1b. Labeled **1b**, prepared from 32% ^{13}CO-enriched $CpMo(CO)_3H$ as previously reported,[2k] was dissolved in toluene-d_8 (0.43 M) and sealed in an NMR tube. The ^{13}C NMR spectrum (25.05 MHz, JEOL FX-100Q) showed one peak in the carbonyl region at ambient temperature, a sharp singlet at δ 236.2. At −86 °C there were two singlets, of relative intensity 1:2, at δ 245.5 and 232.5, respectively. The coalescence temperature was −60 ± 5 °C. The exchange barriers were calculated by the method of Shanan-Atidi and Bar-Eli,[10] assuming Δ = 325.0 Hz at coalescence.

[Bis(η^5-cyclopentadienyl)methylzirconium(IV)](μ-carbonyl-*O*,*C*)dicarbonyl(η^5-cyclopentadienyl)tungsten(0) (1c). A solution of $CpW(CO)_3H$ (1.39 g, 4.17 mmol) and Cp_2ZrMe_2 (0.94 g, 3.7 mmol) in 4.5 mL of THF was refluxed for 10 h. ^1H NMR showed the reaction to be about 80% complete. The solvent was removed under vacuum, and the reaction was allowed to go to completion as the resulting orange oil was dried under high vacuum (about 10^{-3} torr) for 2 h at room temperature. The oil was dissolved in 2 mL of THF and reprecipitated by the addition of 40 mL of hexanes to the red-brown solution. Upon freezing at 77 K and warming to room temperature three times, the oil formed a powdered yellow-orange product, which was collected by filtration, washed with hexanes, and dried under vacuum (yield 1.8 g, 84%). ^1H NMR: in C_6D_6, δ 5.76 (s, 10 H), 5.15 (s, 5 H), 0.44 (s, 3 H); in CD_3CN, δ 6.10 (s, 10 H), 5.18 (s, 5 H), 0.085 (s, 3 H). IR (cm^{-1}): in toluene, 1938 (vs), 1855 (vs), 1544 (vs); in Nujol, 1925 (sh), 1915 (s), 1825 (s, broad), 1540 (s, broad); in CH_3CN, 1890 (vs), 1834 (s), 1765 (vs), 1580 (s).

[(η^2-Acetyl)bis(η^5-cyclopentadienyl)zirconium(IV)](μ-carbonyl-*O*,*C*)dicarbonyl(η^5-cyclopentadienyl)chromium(0) (2a). A solution of **1a** (650 mg, 1.4 mmol) in toluene (10 mL) was treated at 25 °C with CO (about 1 atm) for 0.5 h. When the mixture was allowed to stand at room temperature for a few minutes, olive green crystals were formed. These were collected by filtration and dried under vacuum. The yield was 399 mg. By addition of a few milliliters of hexanes to the mother liquor, a second crop was obtained (222 mg), which was collected by filtration, washed with hexanes, and dried under vacuum. The total yield was 90%. IR (cm^{-1}): in Nujol, 1920 (s), 1825 (s), 1600 (s, broad); in toluene, 1925 (s), 1840 (s), 1595 (s); in CH_3CN, 1892 (vs), 1773 (vs). ^1H NMR: in C_6D_6, δ 5.50 (s, 10 H), 4.86 (s, 5 H), 2.05 (s, 3 H); in CD_3CN, δ 5.97 (s, 10 H), 4.44 (s, 5 H), 3.03 (s, 3 H). Anal. Calcd for $C_{20}H_{18}O_4CrZr$: C, 51.59; H, 3.89. Found: C, 51.25; H, 3.87.

[(η^2-Acetyl)bis(η^5-cyclopentadienyl)zirconium(IV)](μ-carbonyl-*O*,*C*)dicarbonyl(η^5-cyclopentadienyl)tungsten(0) (2c). A solution of Cp_2ZrMe_2 (0.84 g, 3.35 mmol) and $HW(CO)_3Cp$ (1.12 g, 3.35 mmol) in 5 mL of THF was refluxed for 8 h to form **1c**. The solvent was then removed under vacuum and the residue dried under high vacuum for 3 h at room temperature. The resulting red-orange oil was dissolved in about 10 mL of toluene and treated with 1 atm of CO for 1 h at room temperature. The unreacted CO was evacuated, and a yellow precipitate formed from the solution on standing overnight. Filtration and drying under vacuum gave 0.95 g (48%) of **2c** (with 0.057 equiv of toluene of crystallization as determined by ^1H NMR). Additional product was obtained by addition of hexanes to the filtrate. ^1H NMR: in C_6D_6, δ 5.55 (s, 10 H), 5.28 (s, 5 H), 2.10 (s, 3 H); in CD_3CN, δ 6.01 (s, 10 H), 5.09 (s, 5 H), 3.08 (s, 3 H). IR (cm^{-1}): in toluene, 1925 (vs), 1834 (vs), 1593 (s); in CH_3CN, 1890 (vs), 1770 (vs). Anal. Calcd for $C_{20.4}H_{18.5}O_4WZr$: C, 40.68; H, 3.09. Found: C, 40.75; H, 3.06.

$(\eta^5\text{-}C_5H_5)_2Zr(\mu\text{-}\eta^2,\eta^1\text{-}CO)[\mu\text{-}OC(CH_3)]W(CO)(\eta^5\text{-}C_5H_5)$ (3c). A solution of **2c** (300 mg) in benzene (20 mL) was stirred at 38 °C for 12 days. The reaction mixture was filtered, and the filtrate was concentrated to about 10 mL. Upon addition of hexanes (10 mL), a beige, powdery precipitate formed, which was removed by filtration. After the filtrate was concentrated under vacuum, a yellow microcrystalline precipitate formed and was collected by filtration. Recrystallization from benzene/hexanes gave 105 mg (36%) of pure **3c**. IR (cm^{-1}): in Nujol, 1856 (vs), 1536 (s), 1314 (m); in CH_3CN, 1890 (s), 1772 (s); in toluene, 1879 (vs), 1544 (s), 1309 (m). ^1H NMR: in C_6D_6, δ 6.01 (s, 5 H), 5.71 (s, 5 H), 5.20 (s, 5 H), 2.16 (s, 3 H); in CD_3CN, δ 6.14 (s, 5 H), 6.04 (s, 5 H), 5.64 (s, 5 H), 2.20 (s, 3 H). Anal. Calcd for $C_{19}H_{18}O_3WZr$: C, 40.08; H, 3.18. Found: C, 39.80; H, 3.34.

Conductivity Studies. Electrical resistivities (in CH_3CN) were determined with a YSI 31 conductivity meter with a glass/Pt electrode cell (cell constant 1.0 cm^{-1}). All solutions were 1.00 (4) × 10^{-3} M, including $N(n\text{-}Bu)_4Br$, which was measured to have a molar conductivity of 159 ± 2 $M^{-1}\ \Omega^{-1}\ cm^{-1}$, consistent with average literature values.[11] The conductivity reported herein for **2b**, measured with this instrument, is much more accurate than the approximate one reported previously.[2k]

Results and Discussion

Structure of 1b. There are two discrete molecules in the asymmetric unit of crystals of **1b**. For the most part these molecules are structurally equivalent, with some small differences due to imperfect modeling of thermal motion; this is most pronounced in the C2–O2 terminal carbonyl in molecule B. (Distances and angles quoted in the text are averages of the values in Table III for the crystallographically independent molecules A and B.) The only significant difference between these molecules is in the rotational conformation about the Zr–O1 bond: the Zr–O1–Mo–Cp(centroid) dihedral angle is 104.4° in molecule A and 30.5° in molecule B. The difference is similar to that observed between the two independent molecules of $Cp_2(C(O)CH_3)ZrOCMo(CO)_2Cp$ (**2b**).[2k] The shortest intermolecular

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(8) All crystallographic computations were carried out with the SHELXTL program package written by G. M. Sheldrick and supplied by Nicolet XRD Corp. for the Data General Eclipse S/140 computer in the crystallography laboratory at Colorado State University.

(9) Ibers, J. A., Hamilton, W. C., Eds. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(10) Shanan-Atidi, H.; Bar-Eli, K. H. *J. Phys. Chem.* **1970**, *74*, 961–963.

(11) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81–122.

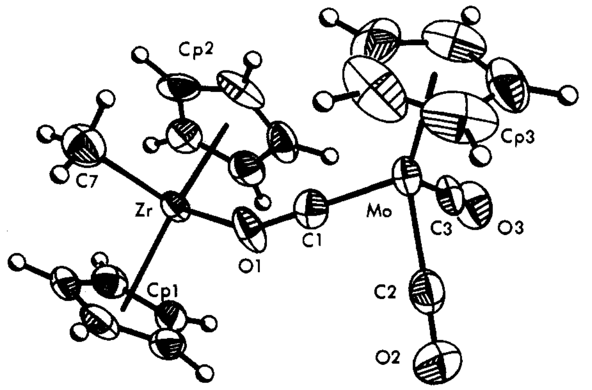


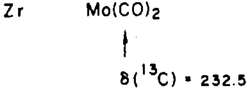
Figure 1. One conformer (molecule A) of [bis(η^5-cyclopentadienyl)methylzirconium(IV)](μ-carbonyl-*O*,*C*)dicarbonyl(η^5-cyclopentadienyl)molybdenum(0) (**1b**). Hydrogen atoms are shown with fixed arbitrary radii; non-hydrogen atoms are represented by 50% probability ellipsoids.

distance is 2.25 Å, between an O3 and an H32; the shortest intermolecular distance involving a metal atom is 3.54 Å, between an Mo atom and H34. There is thus no intermolecular bonding.

A perspective view of molecule A, showing the atom-numbering scheme, is given in Figure 1. It is clear that (certainly in the solid state and probably in solution[12]) complex **1b** has the μ-OC carbonyl-bridged structure II. There is no direct interaction between the metals; the Zr and the Mo are almost 5 Å apart. The geometry about the oxygen of the bridging carbonyl is nonlinear (145°), as found in $(C_5Me_5)_2TiMe(\mu\text{-}OC)Mo(CO)_2Cp$ (144°)[2h] and in $(C_5H_5)_2Zr(\eta^2\text{-}Ac)(\mu\text{-}OC)Mo(CO)_2Cp$ (**2b**) (136°).[2k] The Zr in **1b**, like the Ti in $(C_5Me_5)_2TiMe(\mu\text{-}OC)Mo(CO)_2Cp$ but in contrast with the Zr in **2b**, is coordinatively unsaturated.

The ν_{CO} (1545 cm^{-1}) of the μ-OC carbonyl bridge in **1b**[12] is thus close to that (1560 cm^{-1}) observed[2d] for an η^2,η^1-bridging carbonyl in a near-isoelectronic molecule $(Cp_2Nb(\mu\text{-}\eta^2,\eta^1\text{-}CO)\text{-}Mo(CO)_2Cp)$ of structure I and is much further from that (1623 cm^{-}1) observed[2h] for another μ-OC carbonyl bridge in the isostructural $(C_5Me_5)_2TiMe(\mu\text{-}OC)Mo(CO)_3Cp$. It seems clear that the IR range characteristic of the carbonyl in structure I overlaps with that characteristic of the carbonyl in structure II and makes IR useless for distinguishing between them.

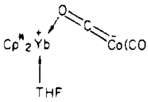
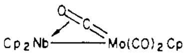
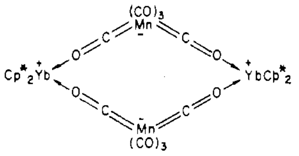
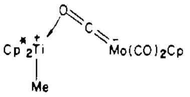
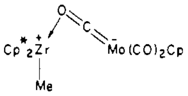
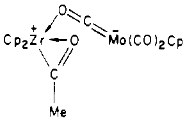
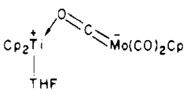
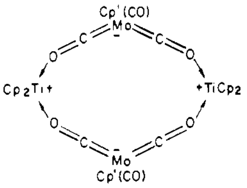
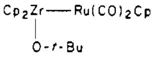
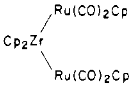
A similar situation arises with ^{13}C NMR. Marsella and Caulton[13] have noted that the ^{13}C chemical shift of the η^2,η^1-bridging carbonyl in (bis(diphenylphosphino)methane)pentacarbonyldimanganese lies within the Mn terminal carbonyl region. Furthermore, the η^2,η^1-bridging carbonyl in $Cp_2Zr(\mu\text{-}\eta^2,\eta^1\text{-}CO)(\mu\text{-}Ac)Mo(CO)Cp$ (**3b**) has a ^{13}C NMR chemical shift within 2 ppm of that of the terminal carbonyl on Mo,[2k] and the η^2,η^1-bridging carbonyls in $Cp_2M(\mu\text{-}\eta^2,\eta^1\text{-}CO)(\mu\text{-}CC_6H_4Me)W(CO)Cp$ (M = Ti, Zr) have ^{13}C chemical shifts within 5 ppm of those of the terminal carbonyls on Mo.[2s] The ^{13}C chemical shift range of η^2,η^1-bridging carbonyls thus overlaps with the ^{13}C chemical shift range of terminal carbonyls[13] on the metal to which the η^2,η^1-bridging carbonyl is linearly bonded. The ^{13}C chemical shift range of μ-OC bridging carbonyls also overlaps with that of terminal carbonyls: at −86 °C in toluene-d_8 the ^{13}C NMR of **1b** shows a peak at δ 245.5 due to the μ-OC bridge and one at δ 232.5 due to the terminal carbonyls



(If one assumes that the crystallographically observed structure persists in solution,[12] the observed 1:2 relative intensity can only be explained by assigning the less intense peak to the μ-OC bridge and the more intense one to the two terminal carbonyls, rendered equivalent by rapid rotation about the Zr–O bond.) The ^{13}C chemical shift ranges of μ-OC carbonyl bridges and η^2,η^1-bridging carbonyls thus overlap with each other[14] and ^{13}C NMR cannot be used to distinguish between structures I and II.

Both structural types (I and II) are common in binuclear complexes containing an electropositive early transition metal (or a lanthanide) along with a carbonyl coordinated to a low-valent metal. Heterobimetallic compounds for which ion-paired resonance structures can be drawn, and for which type I and type II structures are therefore both conceivable, are listed in Table IV. As we have noted previously,[2k] the situation parallels that observed with main-group metals and transition-metal carbonyl anions, where the main-group metals show roughly equal Lewis acidity

Table IV. Structures Adopted by Heterobimetallic Complexes with Available Ion-Paired Resonance Structures

structure of compd[a,b]	structure type	bridging C–O dist, Å[b]	ν_{CO}, cm^{-1}	ref
	II	1.188 (3)	1761	2j
	I	1.22 (1)	1560	2d
	II	1.186 (4)	1775	2x
	II	1.212 (5)	1623	2h
	II	1.236 (5)	1545	this work
	II	1.209 (4)	1600	2k
	II	1.201 (8)	1650	2o
	II	1.208 (7)	1710	2w
	neither			16a
	neither			16b

[a] Key: Cp* = η^5-C_5Me_5; Cp′ = η^5-C_5H_4Me. [b] As determined by X-ray crystallography.

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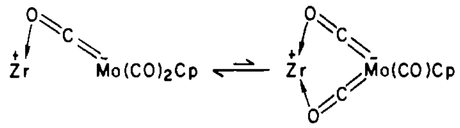
[12] There is no reason to believe that the structure of **1b** in noncoordinating solvents differs from that in the solid state. The solid-state IR spectrum (Nujol, 1945 (s), 1860 (s), 1550 (s) cm^{-1}) agrees with that in toluene,[2k] including a weak band of variable intensity at 2020 cm^{-1} due to traces of $CpMo(CO)_3H$ formed during sample preparation.

[13] Marsella, J. A.; Caulton, K. G. *Organometallics* **1982**, *1*, 274.

[14] The observation of broad carbonyl resonances at δ 298 and 215 for $(C_5Me_5)_2Zr(\mu\text{-}CO)(\mu\text{-}\eta^2,\eta^1\text{-}CO)RhCp$ at low temperature[2v] suggests that the ^{13}C chemical shift ranges for η^2,η^1-bridging carbonyls and for conventional (η^1) bridging carbonyls may differ substantially.

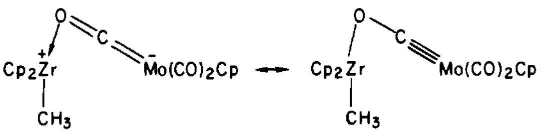
Scheme I



toward the carbonyl oxygens and the transition-metal atoms and different structures are observed in closely related compounds (e.g., a Ga–W bond in $Me_2GaW(CO)_3Cp$[15a] and O-to-Al coordination in $Me_2AlW(CO)_3Cp$[15b]). The factors that determine the structures adopted in the cases in Table IV are not entirely clear, although some trends are apparent: structure II is more likely in the presence of more electropositive and oxophilic metals (e.g., Ti, Zr, and Yb rather than Nb) and in the presence of $CpMo(CO)_3^-$ rather than $CpRu(CO)_2^-$. The failure of the Zr atoms in $Cp_2Zr(O\text{-}t\text{-}Bu)Ru(CO)_2Cp$[16a] and $Cp_2Zr[Ru(CO)_2Cp]_2$[16b]—which both contain Zr–Ru bonds—to complete the formation of structure I by acquiring η^2,η^1-bridging carbonyls is puzzling, as these Zr atoms are coordinatively unsaturated.[17]

The μ-OC bridging carbonyl in **1b** exchanges readily with the terminal carbonyls on Mo. Low-temperature ^{13}C NMR studies (on ^{13}CO-enriched material in toluene-d_8) show a barrier $\Delta G^{\ddagger}$ of 9.9 ± 0.2 kcal/mol to migration of a terminal carbonyl into the μ-OC bridging position and a corresponding barrier of 9.6 ± 0.2 kcal/mol to migration of the μ-OC bridging carbonyl into a terminal position. This exchange probably proceeds via the transient coordination of a second carbonyl oxygen—an "associative" mechanism on Zr (Scheme I). The importance of coordinative unsaturation is illustrated by the fact that complex **2b**, also with a μ-OC bridging carbonyl but with a coordinatively saturated Zr, shows no evidence of carbonyl exchange on the NMR time scale under ambient conditions.[2k]

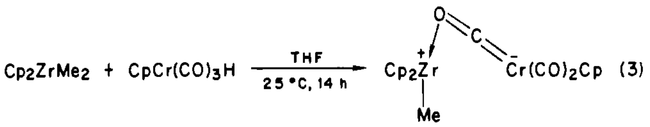
The structural results on the μ-OC bridging carbonyl in **1b** show, in addition to a contribution from the resonance structure drawn as II, a significant contribution from an oxycarbyne resonance structure:



The Mo–C distance, 1.847 (5) Å, is much shorter than that in molybdenum carbene complexes (e.g., 2.06 (1) Å in $Cp(CO)_2(Ph_3Ge)Mo{=}C(OEt)Ph$[18a] and 1.98 (1) Å in $Cp(OC)_3MoMo(CR_2)(N_2CR_2)Cp$, R = *p*-tolyl[18b]); it approaches that in comparable carbyne complexes (e.g., 1.84 (3) Å in $(OC)_5ReMo(CPh)(CO)_4$,[19a] 1.81 (1) Å in $Cp(OC)(Ph_3P)W{\equiv}CSPh$,[19b] 1.789 (2) Å in $[Cp(P(OMe)_3)_2HMo{\equiv}CCH_2CMe_3]^+[BF_4]^-$ and its unprotonated analogue $Cp[P(OMe)_3]_2Mo{\equiv}CCH_2CMe_3$,[19c] 1.82 (2) Å in $(\mu\text{-}OCN)_2[(CO)_3MoCNEt_2]_2$,[19d] and 1.80 (2) Å in $(\mu\text{-}I)_2[(CO)_3MoCNEt_2]_2$[19d]). The C–O distance in the μ-OC bridge of **1b**, 1.236 (5) Å, shows a bond order less than 2; if one takes 1.36 Å as characteristic of a single bond between oxygen and sp^2 carbon[2k] and corrects by 0.05 Å for sp carbon,[19b] one obtains a C–O distance of 1.31 Å in a pure oxycarbyne. Comparison of these structural results for **1b** with the corresponding ones for the other compounds of structural type II in Table IV shows that **1b** has the greatest participation by the oxycarbyne resonance form and therefore the greatest heterobimetallic CO activation.

Behavior of Heterobimetallic Complexes in Polar Solvents. Synthesis of Cr and W Analogues of 1b and 2b. A structure of type II can be viewed as a contact ion pair, although the solubility of **1b** in nonpolar solvents and the structurally significant contribution of the oxycarbyne resonance structure suggest that the association between $CpMo(CO)_3^-$ and the Lewis acid "Cp_2ZrMe^+" is quite strong. We therefore decided to investigate the extent of ionization of **1b** in polar solvents. In order to take advantage of our knowledge[20] of the relative base strengths of all three anions $CpM(CO)_3^-$ (M = Cr, Mo, W), we also undertook the preparation of Cr and W analogues of **1b** and the other Mo/Zr heterobimetallics.

The Cr and W analogues of **1b** were readily prepared from Cp_2ZrMe_2 and the appropriate $CpM(CO)_3H$ in THF—the same method used for the preparation of **1b** (eq 3 and 4). The tungsten reaction is much slower, reflecting its slower rate of proton transfer.[5,20]

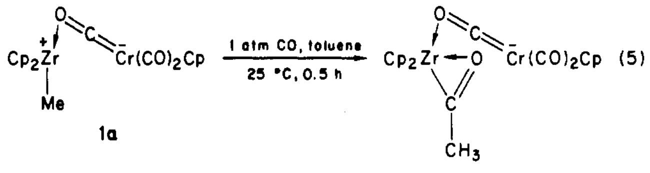


1a

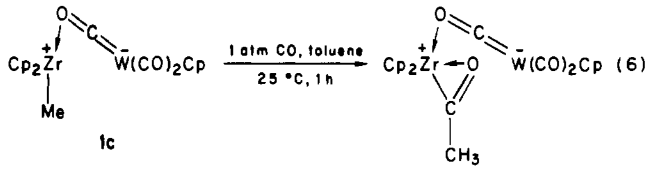
1c

For the reasons given above, it is impossible to demonstrate rigorously by spectroscopic means that **1a** and **1c** have the same structure (type II) as that observed crystallographically for **1b**. However, all three compounds have very similar NMR spectra and IR spectra, strongly implying that they are isostructural.[21] For reasons like those given previously for **1b**,[12] their solid-state structures are probably preserved in solution.

The Zr–Me bonds in **1a** and **1c**, like that in **1b**, take up CO readily to form the η^2-acetyl derivatives **2a** and **2c**. As in the



1a **2a**



1c **2c**

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(15) (a) St. Denis, J. N.; Butler, W.; Glick, M. D.; Oliver, J. P. *J. Organomet. Chem.* **1977**, *129*, 1. (b) Conway, A. J.; Gainsford, G. J.; Schrieke, R. R.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **1975**, 2499.

(16) (a) Casey, C. P.; Jordan, R. F.; Rheingold, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 665. (b) Casey, C. P.; Jordan, R. F.; Rheingold, A. L. *Organometallics* **1984**, *3*, 504.

(17) The stability of the coordinately unsaturated $Cp_2Zr(O\text{-}t\text{-}Bu)Ru(CO)_2Cp$[16a] is plausibly rationalized as the result of π donation from the *tert*-butoxy ligand, but such an explanation is impossible for $Cp_2Zr(CH_3)Ru(CO)_2Cp$ (which appears spectroscopically to be isostructural).[16a]

(18) (a) Chan, L. Y. Y.; Dean, W. K.; Graham, W. A. G. *Inorg. Chem.* **1977**, *16*, 1067. (b) Messerle, L.; Curtis, M. D. *J. Am. Chem. Soc.* **1982**, *104*, 889.

(19) (a) Hüttner, G.; Frank, A.; Fischer, E. O. *Isr. J. Chem.* **1977**, *15*, 133. (b) Greaves, W. W.; Angelici, R. J.; Helland, B. J.; Klima, R.; Jacobson, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 7618. (c) Green, M.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Chem. Commun.* **1982**, 493–495. (d) Fischer, E. O.; Wittmann, D.; Himmelreich, D.; Cai, R.; Ackermann, K.; Neugebauer, D. *Chem. Ber.* **1982**, *115*, 3152–3166.

(20) Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1255.

(21) In the main-group case mentioned in the text, where the structure of $Me_2GaW(CO)_3Cp$ (Ga–W bond, no Ga–O interaction)[15a] differs from that of its Al analogue (μ-OC carbonyl bridges),[15b] the IR spectra are readily distinguishable. While in principle the ν_{CO} of an η^2,η^1-bridging carbonyl in a type I structure cannot be distinguished from the ν_{CO} of a μ-OC bridging carbonyl in a type II structure, there is no known case where a periodic analogue changes from a type I to a type II structure and retains a similar IR spectrum throughout the entire carbonyl region; for example, the IR spectra of **1b**[2k] and $Cp_2Nb(\mu\text{-}\eta^2,\eta^1\text{-}CO)Mo(CO)Cp$[2d] are quite different above 1600 cm^{-1}. It seems unlikely that compounds as closely related as **1a–c** would have such similar spectra throughout the entire carbonyl region without being isostructural.

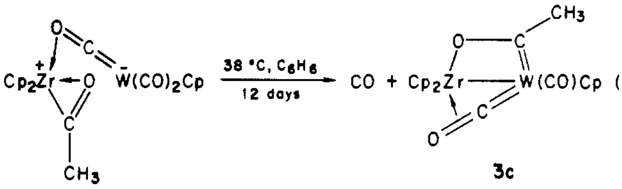
Table V. Molar Conductivities (cm^2 Ω^{-1} mol^{-1}) of Zr/M Heterobimetallic Complexes in $CH_3CN^{a,b}$

structure of complex	a, M = Cr	b, M = Mo	c, M = W
$Cp_2ZrMe(\mu\text{-}OC)M(CO)_2Cp$ (1)	65 (3)	10 (2)	7 (2)
$Cp_2Zr[C(O)Me](\mu\text{-}OC)M(CO)_2Cp$ (2)	120 (5)	114 (5)	80 (3)

[a] For 1.0×10^{-3} M solutions under ambient conditions.
[b] Numbers in parentheses are estimated maximum errors in the least significant digit.

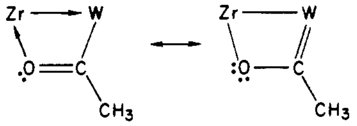
case of **1**, the similarities in the IR and NMR spectra of **2a–c** suggest that they are isostructural; in this case there is also no plausible alternative to the μ-OC carbonyl-bridged structure observed crystallographically for **2b**.[2k]

The η^2-acetyl tungsten complex **2c** undergoes loss of CO and formation of the acetyl/oxycarbene-bridged heterobimetallic **3c** much more slowly than does its Mo analogue **2b**,[22] in somewhat lower yield (attempts to increase the rate by running reaction 7 at higher temperatures have resulted in a substantial increase in the amount of byproduct formation and a decrease in the yield of **3c**). The ν_{CO} associated with the acetyl/oxycarbene bridge in **3c** is even lower (1314 cm^{-1}) than that (1339 cm^{-1}) in **3b**,[2k] implying a lower C–O bond order and greater heterobimetallic CO activation in **3c** than in **3b**:



(7)

2c **3c**



Attempts to carry out a similar reaction with Cr (**2a**) have failed; presumably the smaller covalent radius of Cr is inconsistent with the geometry—particularly the metal–metal bond—of **3**.

As expected, solutions of $Cp_2Zr(\mu\text{-}\eta^2,\eta^1\text{-}CO)[\mu\text{-}OC(CH_3)]\text{-}Mo(CO)Cp$ (**3b**) and its W analogue **3c**, which do not have ion-paired resonance structures, give specific conductivities within experimental error ($\pm 2 \times 10^{-6}$ Ω^{-1} cm^{-1}) of the specific conductivity observed for acetonitrile alone. However, substantial conductivity is observed (Table V) for **1** and **2**, although generally less than that expected for a fully dissociated 1:1 electrolyte (>120 cm^2 Ω^{-1} mol^{-1}).[11] These measurements demonstrate the importance of the ion-paired resonance structures of **1** and **2**.

The IR spectra of **2a**, **2b**,[23] and **2c** in CH_3CN show only free, symmetrically solvated $CpM(CO)_3^-$ anions[20,24] in their carbonyl regions. The ^{1}H NMR spectra of **2a**, **2b**,[2k] and **2c** in CD_3CN show Mo cyclopentadienyl resonances with chemical shifts almost identical with those reported[20] for the free anions. Both observations confirm the substantial dissociation of **2** in acetonitrile implied by the conductivities measured in that solvent.

The increase of the conductivities in the order **2c** < **2b** < **2a** shows that the Lewis basicity of the $CpM(CO)_3^-$ anions toward the Zr cation from **2** (presumably $[Cp_2Zr(Ac)(NCCH_3)]^+$) decreases in the order W > Mo > Cr. This order parallels the relative Brønsted basicities of the $CpM(CO)_3^-$ anions toward protons in the same solvent, despite the fact that the thermodynamically preferred site for Zr binding is oxygen while that for H^+ binding is the metal. The relative basicity of these anions thus appears to be independent of the donor site involved.

The conductivities of the complexes **1** also increase in the order W (**1c**) < Mo (**1b**) < Cr (**1a**); the $CpM(CO)_3^-$ anions of **1** thus show the same relative Lewis basicities toward Zr, at their carbonyl oxygens, as the $CpM(CO)_3^-$ anions of **2**. However, for all three metals the conductivity of **1** is substantially less than that of **2**, implying that **1** is less extensively dissociated in acetonitrile than is **2**. This decrease in the extent of dissociation is also reflected in the IR spectra of **1a**, **1b**, and **1c** in CH_3CN, which contain peaks apparently due to intact **1** as well as those of the $CpM(CO)_3^-$ anion. (The ^{1}H NMR chemical shifts of the cyclopentadienyls of **1a**, **1b**,[23] and **1c** in CD_3CN are still approximately those of the $CpM(CO)_3^-$ anions.)

These results show that the Zr cation from **1**, presumably $[Cp_2Zr(CH_3)(NCCH_3)_x]^+$, is a better Lewis acid in solution than is $[Cp_2Zr(Ac)(NCCH_3)]^+$, the Zr cation from **2**. "Cp_2ZrMe^+" is also a better Lewis acid than "Cp_2ZrAc^+" in the solid state, as shown by the greater oxycarbyne character in **1b** than in **2b**:[2k] the Zr–O distance in **1b** is 2.107 (3) Å, appreciably shorter than that (2.224 (2) Å) in **2b**; the O–C distance in **1b** is 1.236 (5) Å, longer than that (1.209 (4) Å) in **2b**; the C–Mo distance in **1b** is 1.847 (5) Å, shorter than that (1.881 (3) Å) in **2b**. The Zr in the "Cp_2ZrMe^+" group of **1b** is both coordinatively unsaturated and devoid of any other oxygen ligands—unlike the Zr in the "Cp_2ZrAc^+" group of **2b**—and is thus extremely effective at coordinating an oxygen of the comparatively weak[20] Lewis base $CpMo(CO)_3^-$ and reducing the carbonyl bond order.

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Registry No. **1a**, 95344-40-4; **1b**, 95344-41-5; **1c**, 95344-42-6; **2a**, 95344-43-7; **2b**, 95344-46-0; **2c**, 95344-44-8; **3c**, 95344-45-9; Cp_2ZrMe_2, 12636-72-5; $HCr(CO)_3Cp$, 36495-37-1; $CpMo(CO)_3H$, 12176-06-6; $CpW(CO)_3H$, 12128-26-6.

Supplementary Material Available: Tables of all bond lengths and angles, anisotropic thermal parameters of non-hydrogen atoms, positional parameters of hydrogen atoms, and observed and calculated structure factors (28 pages). Ordering information is given on any current masthead page.

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(22) The X-ray structure of **3b** has already been reported,[2k] and the IR and the NMR spectra of **3c** make it clear that the latter is isostructural with **3b**.

(23) The IR spectra for the Mo series in CH_3CN are as follows (cm^{-1}): **1b**, 1956 (s), 1897 (s), 1776 (s); **2b**, 1896 (s), 1776 (s); **3b**, 1870 (s), 1546 (m), 1331 (m). The ^{1}H NMR spectrum of **1b** in CD_3CN is as follows: δ 6.08 (s, 10 H), 5.07 (s, 5 H), 0.06 (s, 3 H).

(24) Darensbourg, M.; Jimenez, P.; Sackett, J. R.; Hanckel, J. M.; Kump, R. L. *J. Am. Chem. Soc.* **1982**, *104*, 1521.