to W.C.T.), and W.C.T. thanks the Alfred P. Sloan Foundation for a research fellowship. Funds supporting the purchase of the University of Delaware diffractometer were provided by NSF.

Supplementary Material Available: Tables of observed and calculated structure factors, bond distances and angles, anisotropic temperature factors, hydrogen atom coordinates, and a charge analysis for all valence molecular orbitals from SCF-Xα-DV calculations (25 pages). Ordering information is given on any current masthead page.

Nucleophilic Attack on η^2-Acetyl Ligands. Structure of a Bridging η^2-Acetone Complex

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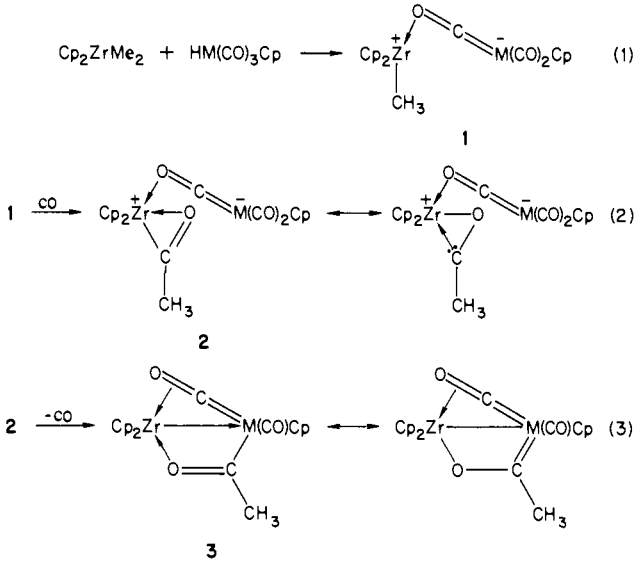
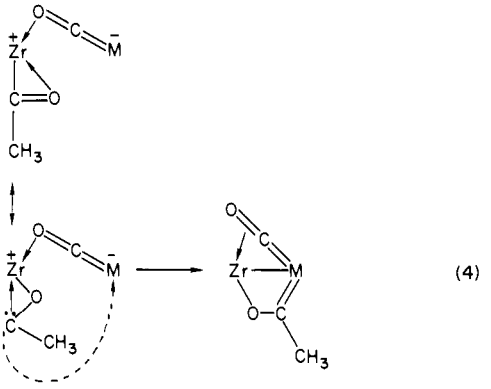
Abstract: The formation of the acetyl/oxycarbene bridge in **3** from the η^2-acetyl complex **2** occurs by nucleophilic attack on the η^2-acetyl carbon by the Mo of the $(\mu\text{-}OC)Mo(CO)_2Cp$ ligand of **2**. Nucleophilic attack on the same carbon by the Zr–Me bond of Cp_2ZrMe_2 gives a trinuclear complex **4** with a bridging η^2-acetone. The crystal structure of **4c**, with η^5-C_5H_4Me ligands on Zr, has been determined by single-crystal X-ray diffraction methods and refined to an R (R_w) value of 0.037 (0.039) for 4429 reflections with $F_o > 5\sigma(F_o)$. The space group is $P2_1/c$, $Z = 4$, and the cell dimensions are $a = 8.683$ (2) Å, $b = 17.814$ (3) Å, $c = 21.852$ (6) Å, and $\beta = 93.53$ (2)°. The acetone of **4c** is η^2-*C,O* toward one Zr atom, and η^1-*O* toward the other Zr atom, with a C–O distance of 1.469 (5) Å.

In previous papers,[1] we have reported the characterization of the heterobimetallic complex **1**, its carbonylation to the η^2-acetyl complex **2**, and the decarbonylation of **2** to the acetyl/oxycarbene bridged **3**, an isomer of **1**. One possible mechanism for the



series a. CpM = $(\eta^5\text{-}C_5H_5)Mo$, $Cp_2Zr = (\eta^5\text{-}C_5H_5)_2Zr$
series b. CpM = $(\eta^5\text{-}C_5H_4Me)Mo$, $Cp_2Zr = (\eta^5\text{-}C_5H_4Me)_2Zr$
series c. CpM = $(\eta^5\text{-}C_5H_5)Mo$, $Cp_2Zr = (\eta^5\text{-}C_5H_4Me)_2Zr$
series d. CpM = $(\eta^5\text{-}C_5H_5)W$, $Cp_2Zr = (\eta^5\text{-}C_5H_5)_2Zr$

formation of **3** from **2** involved a carbene migration from the oxophilic zirconium onto the low-valent molybdenum. This mechanism, reaction 4, found precedent in the oxycarbene resonance structure invoked to explain other reactions of η^2-acetyl ligands, e.g., their dimerization through carbon.[2] We therefore



investigated the ability of η^2-acetyl ligands on $Cp_2Zr(IV)$ to serve as oxycarbene ligands toward other metals with accessible coordination sites. However, reactions 5–8 did not lead to the formation of an oxycarbene-bridged heterobimetallic; the reaction most commonly observed instead (e.g., reactions 5 and 6) was coordination of the carbon monoxide made available by slow decarbonylation of the η^2-acetyl.

We then hypothesized that reaction 3 might be better described as a *nucleophilic* attack by the molybdenum of the $CpMo(CO)_3^-$ fragment of **2** on the η^2-acetyl ligand carbon of **2**. We have therefore investigated the kinetics and mechanism of the conversion of **2** to **3** (reaction 3) and have discovered that the η^2-acetyl ligand of **2** is indeed subject to nucleophilic attack at carbon.

Results

Between 37.2 and 60.8 °C in toluene, reaction 3 proved first-order in [**2**] and independent of the CO pressure (up to 6.8 atm) and of the presence of added **3**. The reaction was roughly twice as fast in toluene as in THF. The temperature dependence

(1) (a) Longato, B.; Norton, J. R.; Huffman, J. C.; Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 209. (b) Marsella, J. A.; Huffman, J. C.; Caulton, K. G.; Longato, B.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 6360. (c) 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. (d) Longato, B.; Martin, B. D.; Norton, J. R.; Anderson, O. P. *Inorg. Chem.* **1985**, *24*, 1389.

(2) (a) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121 and references therein. (b) Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 2650.

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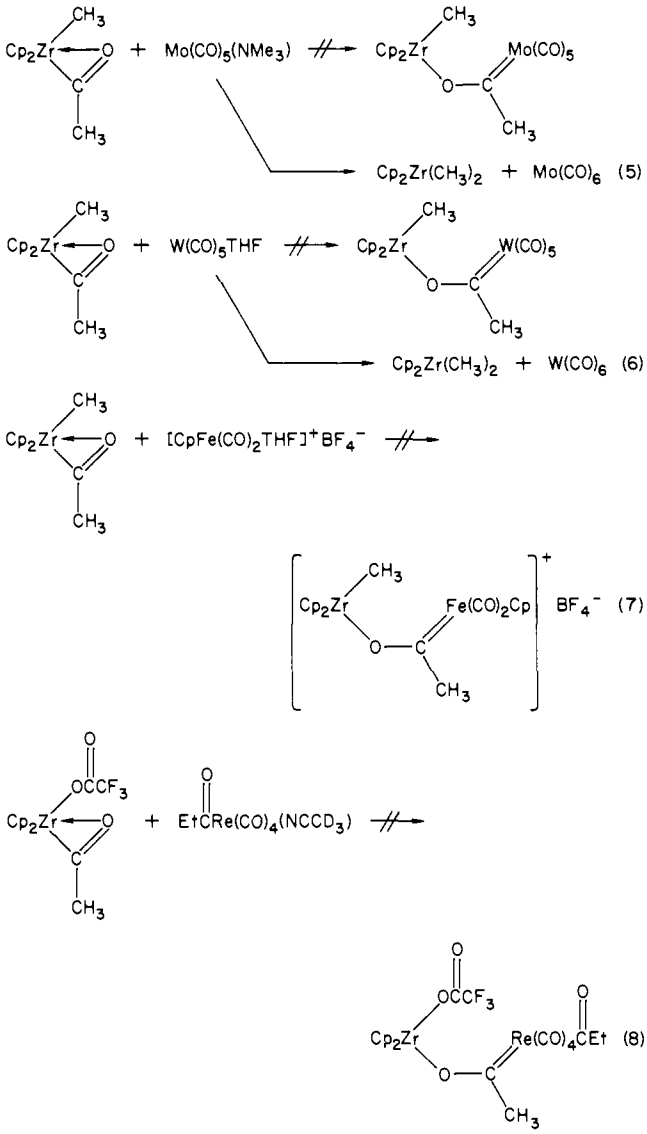
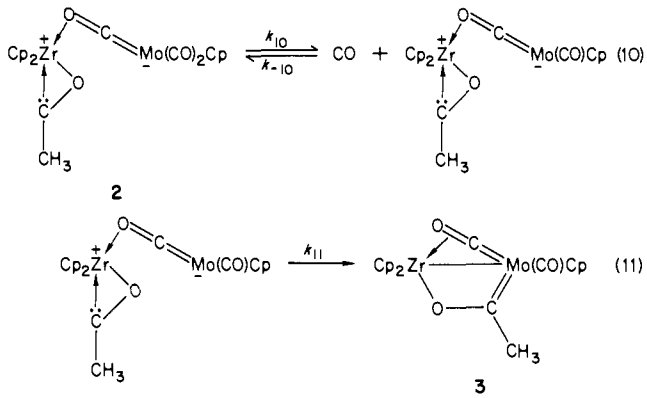


$$\frac{d[3]}{dt} = -\frac{d[2]}{dt} = k_{obsd}\,[2] \qquad (9)$$

of k_{obsd}, shown in Table I, indicated that $\Delta H^{\ddagger}$ was 17.7 (7) kcal/mol and that $\Delta S^{\ddagger}$ was −21 (2) eu; k_{obsd} extrapolated to 25 °C was 2.0 (2) × 10^{-5} s^{-1}.

These results argued against a mechanism like that in eq 10 and 11, with k_{11} being the rate constant for nucleophilic attack on the coordinatively unsaturated molybdenum by the oxycarbene carbon of the η^2-acetyl ligand.



$$\frac{-d[2]}{dt} = \frac{k_{10}k_{11}[2]}{k_{-10}[CO] + k_{11}} \qquad (12)$$

Table I. Observed First-Order Rate Constants for Reaction 3 in Toluene

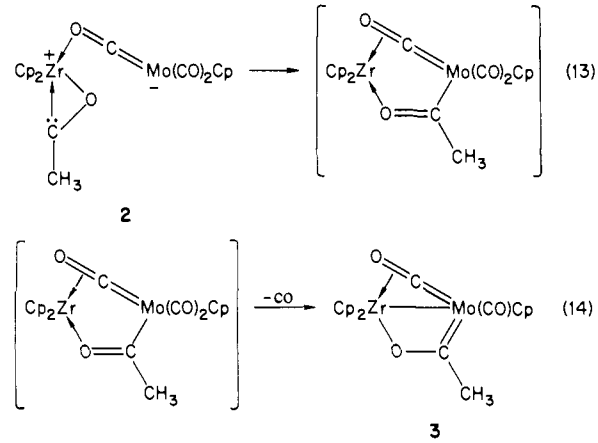
$[2]_0$, mM	temp, °C	CO pressure, atm[a]	$10^4 k_{obsd}$, s^{-1} [b]
11.68	48.5		2.17 (4)
3.37	48.4		1.63 (1)
7.16	48.4		1.87 (2)
14.62	48.5		2.20 (2)
7.90	48.5		1.73 (2)
2.74	48.5		2.29 (5)
3.18	48.5		1.78 (5)[c]
1.38	48.5	1.0	2.07 (5)
6.23	48.5	5.1	2.10 (11)
8.11	48.5	6.8	1.79 (5)
4.47	37.2		0.68 (1)
2.48	43.2		1.23 (3)
9.42	55.8		4.03 (5)
5.65	60.8		5.29 (5)

[a] If blank, the reaction was run under 1 atm of argon. [b] Figure in parentheses is estimated standard deviation in the least significant digit. [c] **3** added to starting material to make initial solution 8.12 mM in total Mo.

It seemed likely, however, that the terminal carbonyl ligands on the Mo of **2** would be labile under the reaction conditions. Darensbourg and co-workers[3] had demonstrated that ion pairing of $CpMo(CO)_3^-$ with Li^+ labilized the carbonyl ligands not coordinated to the cation. As $Cp_2Zr(Ac)^+$ is a much stronger Lewis acid toward $CpMo(CO)_3^-$ than is Li^+ (the *μ-OC* bridging carbonyl of **2** has a stretching frequency of 1607 cm^{-1}, whereas that of $Li^+CpMo(CO)_3^-$ has a stretching frequency of 1717 cm^{-1} [3]), the rate of dissociation of the terminal carbonyls on the Mo of **2** should exceed that (6.6×10^{-4} s^{-1} at 22 °C) reported[3] for the terminal carbonyls of $Li^+CpMo(CO)_3^-$ and should easily exceed k_{obsd} at the temperatures in Table I.

Indeed, the terminal carbonyls on the Mo of **2a** exchanged with external CO much more rapidly than the **2a** changed into **3a**,[1b] implying that decarbonylation and carbonylation, rate constants k_{10} and k_{-10}[CO], were both fast under the conditions of reaction 3. The CO pressure independence of k_{obsd} could thus not be explained by a value of k_{-10}[CO] less than that of k_{11} (i.e., by $k_{obsd} = k_{10}$ in eq 12), and the mechanism of eq 10 and 11 was clearly incorrect.

We therefore concluded that reaction 3 occurred by a sequence like reactions 13 and 14 (illustrated for **2a** and **3a**), with nucleophilic attack on the carbon of the η^2-acetyl ligand by the molybdenum of the $CpMo(CO)_3^-$ and decided to investigate the reaction of **2** with other nucleophilic reagents. Treatment of **2**



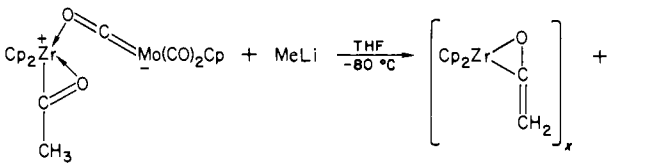
with MeLi at −80 °C gave deprotonation to the known[4] ketene

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

Table II. Crystallographic Details for 4c

empirical formula	$C_{36}H_{42}O_4MoZr_2$
cryst dimensions, mm	0.49 (100–$\bar{1}$00) × 0.34 (010–0$\bar{1}$0) × 0.18 (001–00$\bar{1}$)
space group	$P2_1/c$
cell dimensions	
a, Å	8.683 (2)
b, Å	17.814 (3)
c, Å	21.852 (6)
β, deg	93.53 (2)
molecules per unit cell, Z	4
$F(000)$	1648
cell volume, Å^3	3374 (1)
M_r, g mol^{-1}	817.11
calcd density, g cm^{-3}	1.61
μ, linear abs. coeff, cm^{-1}	9.82
diffractometer	Nicolet $R3m/E$
monochromator	graphite
radiation	Mo Kα (λ = 0.71073 Å)
2θ limits, deg	3.5–50
scan speed, deg min^{-1}	variable, 2–29
scan width, deg	0.9 below Kα_1 to 1.1 above Kα_2
reflections measd	$+h,\pm k,\pm l$
R(merge)	0.0171
scan type	$\theta/2\theta$
diffraction geometry	bisecting
Lorentz, polarization factors	corrections applied
no. of reflections collected	9779
no. of unique reflections collected	5993
used ($F_o > 5\sigma(F_o)$)	4429
R	0.037
R_w	0.039
GOF	1.131
g	5.6 × 10^{-4}
slope of normal probability plot	1.16
no. of least-squares parameters	412
max. shift/esd (last five cycles)	0.103
final difference Fourier	
max electron density, e Å^{-3}	0.99
min electron density, e Å^{-3}	−0.64

5, as did deliberate deprotonation of **2** by the less nucleophilic base lithium diisopropylamide.



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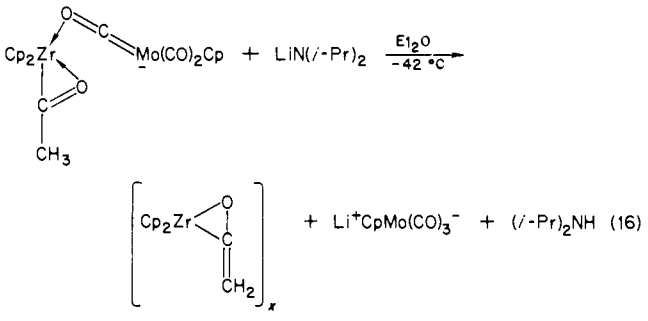
$$Li^+CpMo(CO)_3^- + CH_4 \quad (15)$$



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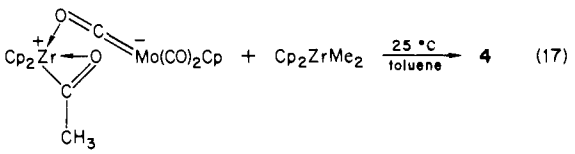
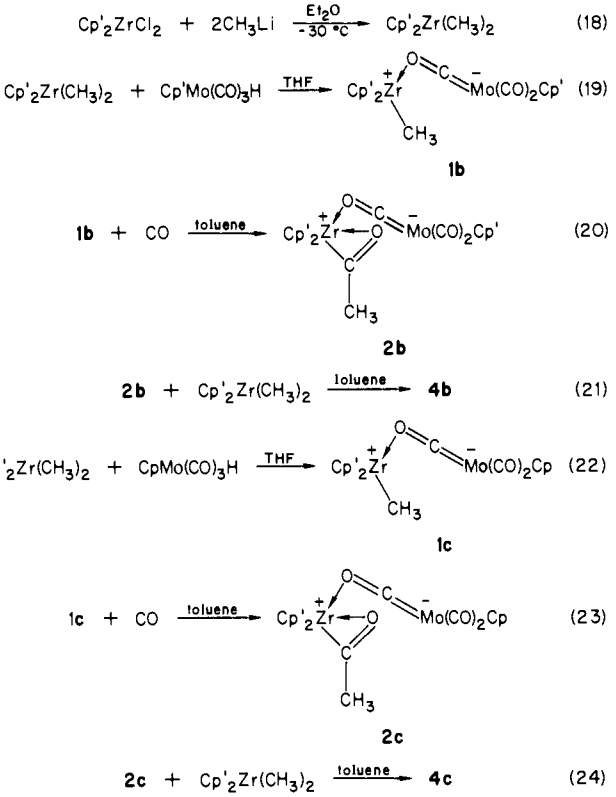
Nucleophilic attack at the carbon of the η^2-acetyl ligand was only observed with Cp_2ZrMe_2. The product, **4a**, had an IR spectrum (1935, 1849, and 1587 cm^{-1}) that suggested that a μ-*OC*-bound $CpMo(CO)_3^-$ was still present. No IR band due



2

to a carbonyl arising from the η^2-acetyl ligand was immediately apparent; however, isotope difference IR spectroscopy showed a ^{12}C ν_{CO} at 1163.5 cm^{-1}, and a corresponding ^{13}C ν_{CO} at 1147 cm^{-1}. The ^1H NMR spectrum of **4a**, however, showed three methyl groups in two different environments (intensity ratio 6:3) and five cyclopentadienyl ligands in three different environments (intensity ratio 10:10:5). As this information was insufficient to permit the unambiguous assignment of a structure, a single-crystal X-ray structure determination was undertaken.

Structure of 4. X-ray studies on two different crystals of **4a** yielded data which did not refine well (R factors of 0.13 and 0.09). As it seemed likely that some sort of disorder was present in crystalline **4a**, we attempted the synthesis of more conformationally rigid analogues of **4a**. Replacement of all five cyclopentadienyl ligands (Cp) by monomethylcyclopentadienyl ligands (Cp′) gave an analogue (**4b**) which was much more soluble in hydrocarbon solvents than **4a**; repeated attempts to grow suitable crystals of **4b** gave only oils and powders. A less soluble analogue, **4c**, was made with a normal cyclopentadienyl ligand on Mo and monomethylated cyclopentadienyl ligands (Cp′) on zirconium. Crystal



growth from toluene/pentene was straightforward for **4c** and yielded crystals suitable for X-ray analysis. Crystallographic details are given in Table II, while the atomic coordinates are given in Table III.

A perspective view of a molecule of **4c**, giving the atom-numbering scheme, is given in Figure 1. The Zr–CH_3 bond has added across the carbon–oxygen bond of the η^2-acetyl ligand of **2**, forming an acetone ligand which is coordinated through oxygen to one Zr atom and through both carbon and oxygen to the other. The C–O bond length of the acetone ligand is a long 1.469 (5) Å (Figure

(4) (a) Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 5499. (b) Moore, E. J.; Straus, D. A.; Armantrout, J.; Santarsiero, B. D.; Grubbs, R. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *105*, 2068. (c) $[Cp_2Zr(C,O\text{-}\eta^2\text{-}H_2CCO)]_x$ was originally prepared by treating $Cp_2Zr(COCH_3)Cl$ with $LiN(CHMe_2)_2$ in THF, following similar procedures: ^1H NMR (C_6D_6, concentration dependent) δ 5.80 (s, 10 H, Cp_2Zr), 5.16 (s, 1 H, vinylic), 4.31 (s, 1 H, vinylic); ($CDCl_3$) δ 6.03 (s, 10 H, Cp_2Zr), 4.84 (s, 1 H, vinylic), 4.00 (s, 1 H, vinylic). Ho, S.; Grubbs, R. H., personal communication.

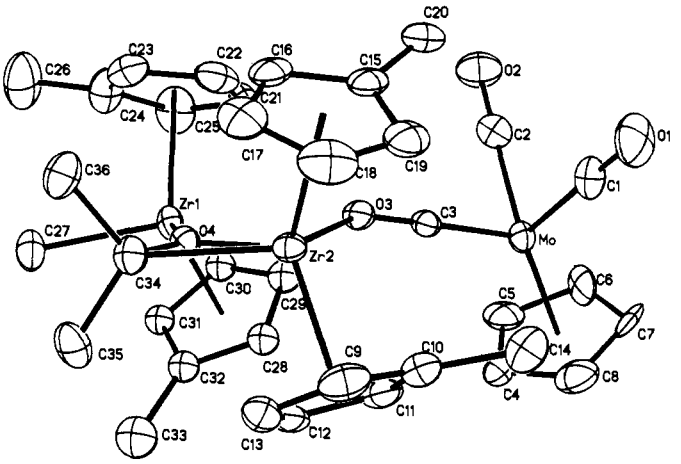


Figure 1. View of complex 4c showing complete atom-number scheme. Ellipsoids are scaled to the 30% probability level for additional clarity.

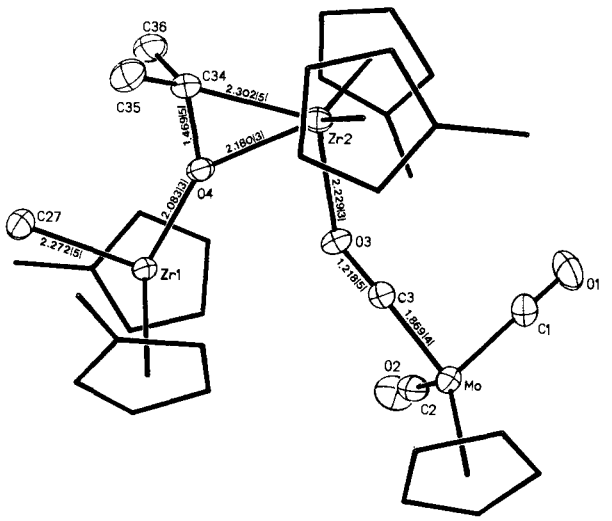
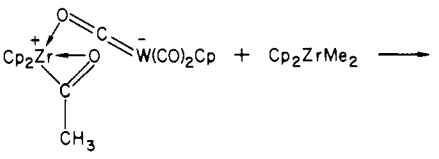


Figure 2. View of complex 4c in the plane of the acetone bridge. The Cp rings have been reduced to outline form and the ellipsoids shown have been scaled to the 30% probability level for additional clarity. Additional bond lengths (Å): Mo–C1, 1.947 (5); Mo–C2, 1.943 (5); C1–O1, 1.148 (7); C2–O2, 1.156 (7); C34–C35, 1.540 (7); C34–C36, 1.509 (7). Relevant bond angles (deg): Mo–C1–O1, 180.0 (7); Mo–C2–O2, 179.6 (5); Mo–C3–O3, 177.7 (4); Zr1–O4–C34, 141.2 (3); Zr1–O4–Zr2, 143.2 (1); Zr2–C34–C36, 123.4 (3); Zr2–O3–C3, 142.6 (3); C1–Mo–C2, 86.9 (2); C1–Mo–C3, 86.9 (2); C2–Mo–C3, 86.1 (2); C27–Zr1–O4, 96.6 (2); C34–O4–Zr2, 75.4 (2); C34–Zr2–O4, 38.1 (1); C35–C34–C36, 108.9 (4); O4–C34–C35, 110.5 (4); O4–C34–Zr2, 66.4 (2).

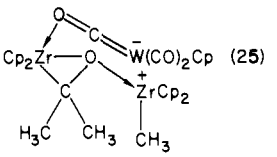
2), as expected in view of its low carbonyl stretching frequency. A μ-*OC* bridged $CpMo(CO)_3^-$ unit, as predicted above, is coordinated to the Zr atom bearing the η^2-acetone, and the unique methyl group is coordinated to the other Zr atom.

The carbonyl, acetone, and methyl ligands are shown more clearly in Figure 2, which also contains important bond lengths and angles.

Related Ketone Complexes. The tungsten analogue of **4a**, **4d**, was formed in good yield by treating **2d**,[1d] the tungsten analogue of **2a**, with Cp_2ZrMe_2 (reaction 25). However, a number of other η^2-acetyl complexes (e.g., $Cp_2Zr(\eta^2\text{-Ac})CH_3$[5] and $Cp_2Zr(\eta^2\text{-Ac})Cl$[6]) failed to react with Cp_2ZrMe_2, and the failure of $Cp_2Zr(\eta^2\text{-Ac})OEt$ to react with Cp_2ZrMe_2 was inferred from the results of carbonyl-transfer experiments of Caulton.[6] The (μ-*OC*)$Mo(CO)_2Cp$ ligand in **2** thus appeared to be essential for its



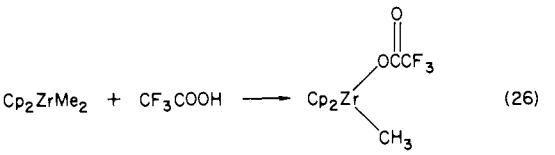
2d



(25)

4d

reactivity toward Cp_2ZrMe_2. The effect of other ligands on the electrophilicity of η^2-acetyls (OR, Cl, Me ≪ (μ-*OC*)$Mo(CO)_2Cp$) thus paralleled the previously reported[1b,6] effect of the same ligands on the resistance of η^2-acetyls to decarbonylation (OR < Cl < Me ≪ (μ-*OC*)$Mo(CO)_2Cp$). As the second series reflects the strong σ-donor ability of (μ-*OC*)$Mo(CO)_2Cp$,[1b] we decided to see if other strong σ-donor oxygen ligands also encouraged nucleophilic attack on η^2-acetyls. Preliminary experiments (reactions 26–28)



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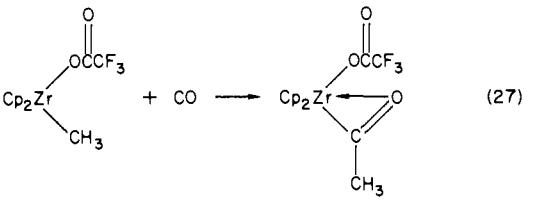

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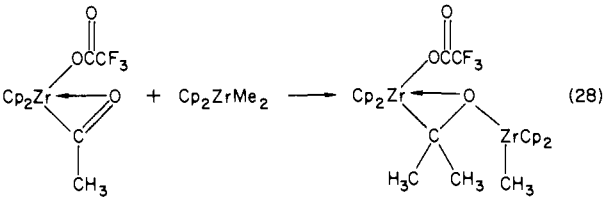

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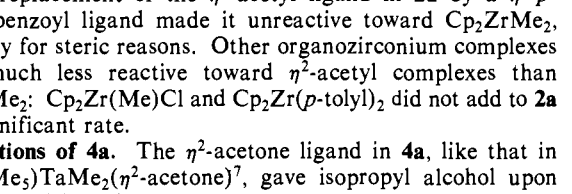
showed that the replacement of (μ-*OC*)$Mo(CO)_2Cp$ by trifluoroacetate in **2** also gave a η^2-acetyl complex susceptible to nucleophilic attack at the acetyl carbon by Cp_2ZrMe_2.

The replacement of the η^2-acetyl ligand in **2d** by a η^2-*p*-methylbenzoyl ligand made it unreactive toward Cp_2ZrMe_2, probably for steric reasons. Other organozirconium complexes were much less reactive toward η^2-acetyl complexes than Cp_2ZrMe_2: $Cp_2Zr(Me)Cl$ and $Cp_2Zr(p\text{-tolyl})_2$ did not add to **2a** at a significant rate.

Reactions of 4a. The η^2-acetone ligand in **4a**, like that in $(\eta^5\text{-}C_5Me_5)TaMe_2(\eta^2\text{-acetone})$[7], gave isopropyl alcohol upon treatment with acid. Upon exposure to excess CO, **4a** took up



(29)

4a

(5) Fachinetti, G.; Floriani, C.; Marchetti, F.; Merlino, S. *J. Chem. Soc., Chem. Commun.* **1976**, 522.

(6) Marsella, J.; Moloy, K. G.; Caulton, K. G. *J. Organomet. Chem.* **1980**, *201*, 389.

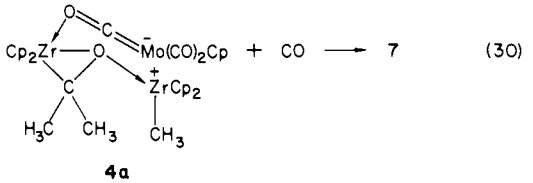
(7) Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5421.

Table III. Atomic Coordinates ($\times 10^4$) and Thermal Parameters ($Å^2 \times 10^3$)[a] for $C_{36}H_{42}O_4MoZr_2$

atom	x	y	z	U_{iso}[b]
Mo	1500 (1)	5613 (1)	6073 (1)	39 (1)
Zr(1)	1783 (1)	6206 (1)	8609 (1)	40 (1)
Zr(2)	3248 (1)	7778 (1)	7442 (1)	35 (1)
C(1)	929 (7)	6451 (3)	5533 (2)	57 (2)
C(2)	-649 (6)	5579 (3)	6270 (2)	51 (2)
C(3)	1764 (5)	6319 (2)	6704 (2)	35 (1)
C(4)	3681 (8)	4816 (5)	6314 (3)	51 (4)
C(5)	2319 (8)	4375 (5)	6311 (3)	59 (4)
C(6)	1628 (8)	4373 (5)	5705 (3)	64 (4)
C(7)	2563 (8)	4814 (5)	5333 (3)	58 (4)
C(8)	3832 (8)	5088 (5)	5710 (3)	77 (5)
C(4′)	3239 (13)	5025 (6)	5381 (4)	146 (11)
C(5′)	1956 (13)	4544 (6)	5450 (4)	96 (6)
C(6′)	1981 (13)	4316 (6)	6074 (4)	105 (8)
C(7′)	3279 (13)	4656 (6)	6389 (4)	80 (5)
C(8′)	4056 (13)	5094 (6)	5961 (4)	75 (5)
C(9)	5709 (6)	8214 (3)	7002 (3)	62 (2)
C(10)	5172 (6)	7658 (3)	6590 (3)	57 (2)
C(11)	5257 (5)	6984 (3)	6921 (3)	53 (2)
C(12)	5809 (5)	7125 (3)	7519 (2)	47 (2)
C(13)	6107 (5)	7887 (3)	7575 (2)	52 (2)
C(14)	4828 (8)	7741 (6)	5915 (3)	105 (4)
C(15)	661 (5)	8250 (3)	6883 (2)	47 (2)
C(16)	729 (6)	8525 (3)	7478 (2)	52 (2)
C(17)	1961 (7)	9030 (3)	7556 (3)	62 (2)
C(18)	2690 (7)	9056 (3)	7010 (3)	72 (2)
C(19)	1903 (6)	8561 (3)	6594 (3)	62 (2)
C(20)	-564 (6)	7790 (3)	6572 (3)	63 (2)
C(21)	-826 (7)	6008 (4)	8133 (3)	70 (2)
C(22)	-680 (6)	6778 (4)	8195 (3)	68 (2)
C(23)	-634 (6)	6960 (3)	8816 (3)	59 (2)
C(24)	-802 (7)	6296 (4)	9143 (3)	69 (2)
C(25)	-910 (8)	5713 (3)	8727 (3)	77 (2)
C(26)	-1039 (10)	6246 (5)	9820 (3)	111 (4)
C(27)	2526 (7)	6389 (3)	9613 (2)	59 (2)
C(28)	3543 (6)	5457 (3)	8016 (2)	46 (2)
C(29)	2080 (6)	5104 (3)	7931 (2)	52 (2)
C(30)	1714 (6)	4786 (3)	8500 (2)	46 (2)
C(31)	2951 (6)	4943 (3)	8937 (2)	43 (2)
C(32)	4081 (6)	5358 (3)	8637 (2)	46 (2)
C(33)	5602 (13)	5609 (6)	8916 (5)	78 (3)
C(28′)	4618 (7)	5586 (4)	8456 (3)	33 (2)
C(29′)	3716 (7)	5543 (4)	7893 (3)	46 (3)
C(30′)	2436 (7)	5068 (4)	7981 (3)	45 (3)
C(31′)	2548 (7)	4817 (4)	8599 (3)	42 (3)
C(32′)	3896 (7)	5137 (4)	8893 (3)	34 (3)
C(33′)	4587 (19)	4926 (10)	9506 (7)	78 (5)
C(34)	3526 (6)	7877 (3)	8493 (2)	44 (2)
C(35)	5022 (6)	7714 (3)	8886 (3)	61 (2)
C(36)	2469 (7)	8341 (3)	8866 (3)	62 (2)
O(1)	593 (6)	6945 (3)	5215 (2)	88 (2)
O(2)	-1931 (5)	5560 (2)	6384 (2)	77 (2)
O(3)	1937 (3)	6758 (2)	7129 (1)	40 (1)
O(4)	2791 (3)	7174 (2)	8280 (1)	37 (1)

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

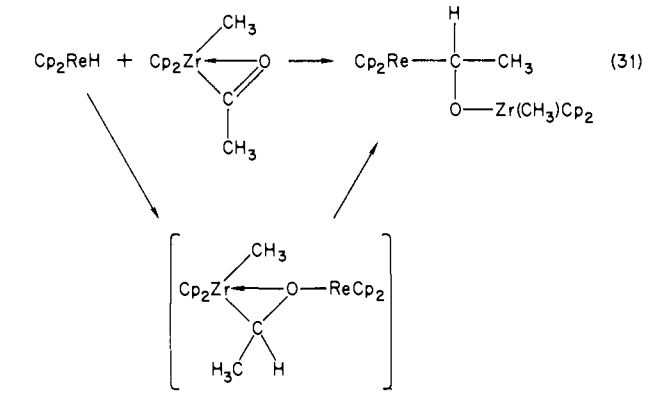
1 equiv to form **7**, the structure of which is presently under investigation.



4a (30)

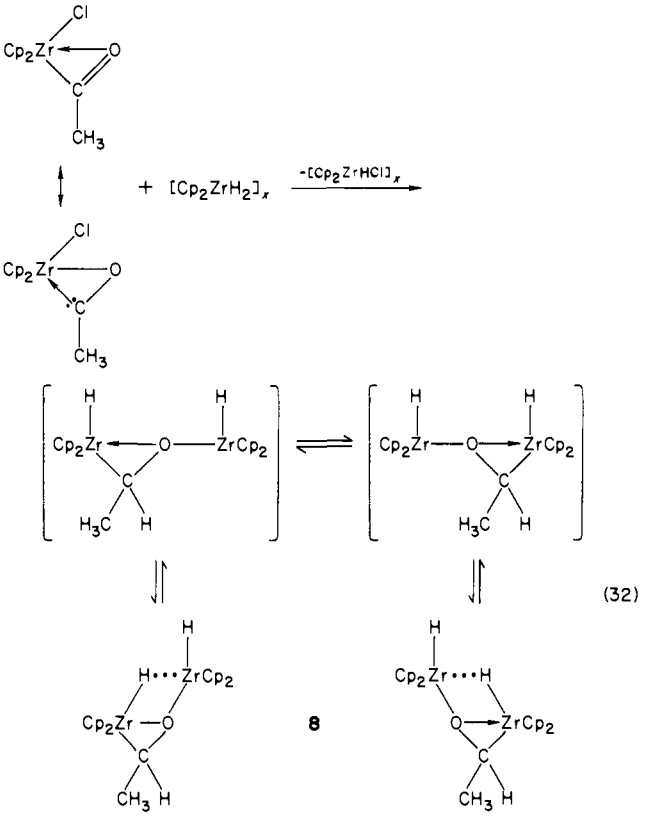
Discussion

It appears that the conversion of **2** to **3** (reaction 3), and the reaction of **2** with Cp_2ZrMe_2 (reactions 17, 21, 24, and 25), both occur by nucleophilic attack on the carbonyl carbon of the η^2-acetyl ligand. Caulton[8] has stated that such carbons are, as a result of the importance of the oxycarbene resonance structure of η^2-acyl ligands, highly electrophilic and has suggested that their reaction with certain transition-metal hydrides (reaction 31) involves some form of nucleophilic attack at carbon by the M–H bond. A



(31)

number of apparent 1,2-additions of metal hydrides across the carbonyls of η^2-acyl ligands, forming coordinated aldehydes, have been reported,[9-11] although the nature of the products is complicated by "dyotropic" shifts such as that illustrated in reaction 32.[9b,10b,11,12] Interestingly, the NMR of **4** shows no evidence (i.e.,



(32)

(8) Marsella, J. A.; Huffman, J. C.; Folting, K.; Caulton, K. G. *Inorg. Chim. Acta* **1985**, *96*, 161. Recent theoretical work[13b] has deemphasized the importance of an oxycarbene description of the bonding in η^2-acyl complexes in favor of a "carbenium-type" description.

(9) (a) Fachinetti, G.; Floriani, A. R.; Pucci, S. *J. Chem. Soc., Chem. Commun.* **1978**, 269. (b) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1983**, *105*, 1690.

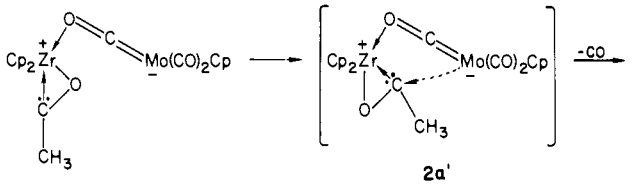
(10) (a) Gell, K. I.; Schwartz, J. *J. Organomet. Chem.* **1978**, *162*, C11. (b) Gell, K. I.; Williams, G. M.; Schwartz, J. *J. Chem. Soc., Chem. Commun.* **1980**, 550.

(11) (a) Erker, G.; Kropp, K.; Krüger, C.; Chiang, A.-P. *Chem. Ber.* **1982**, *115*, 2447. (b) Erker, G.; Kropp, K. *Chem. Ber.* **1982**, *115*, 2437. (c) Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103.

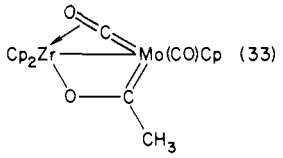
(12) Caulton and co-workers[8] have pointed out that the apparent 1,1-addition of a Re–H bond to an η^2-acetyl carbon in reaction 31 may actually be (as illustrated in brackets under reaction 31) a straightfoward 1,2-addition followed by a dyotropic rearrangement.

the two sets of Cp_2Zr resonances remain inequivalent) that such shifts occur when the bridging ligand is a ketone rather than an aldehyde.

In the formation of **3** from **2**, nucleophilic attack by $M(CO)_3Cp^-$ at the η^2-acetyl carbon is sterically unlikely when the two ligands have the geometry found in the X-ray structure of **2a**.[1b] The reaction may well proceed through an O-outside intermediate such as **2a'**, which calculations[13] suggest should be accessible over a barrier of 18.5 kcal/mol.



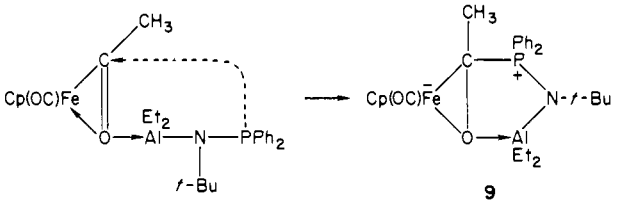
2a **2a'**



(33)

3a

There are other reported examples[14,15] of nucleophilic attack on the carbonyl carbon of a η^2-acyl ligand. Nucleophilic attack on carbon by phosphorus is the kinetically preferred fate of the η^2-acyl intermediate in reaction 34, forming a ketone complex (**9**) like **4**.[15] (The formation of other, thermodynamically favored,



9

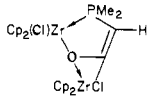
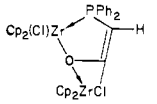
(34)

products eventually occurs.) The formation of **4** from **2** and Cp_2ZrMe_2 is, however, the first reported case where the attacking nucleophile is a metal alkyl and the product has a bridging ketone. The acetone bridge in **4** is the first crystallographically characterized ketone bridge (other than aldehyde and ketene bridges) between two transition metals.

Structure of 4c. The C–O bond in **4c** is quite long (1.469 (5) Å), and it is clear that the coordinated ketone is best described as a metallaoxirane.[16] The C–O bond length in Erker's related acetaldehyde complex **8** is appreciably shorter (1.404 (4) and 1.420 (4) Å in two independent molecules),[11a] as is that (1.401 (3) Å) in the related ketone complex **9**.[15] Comparison with the C–O distances of the other crystallographically characterized aldehyde and ketone complexes in Table IV shows that the C–O bond length in **4c** is longer than that in any other known aldehyde or ketone complex except the 1.584 (11) Å in $Os(PPh_3)_2(CO)_2(\eta^2\text{-}H_2CO)$.[17]

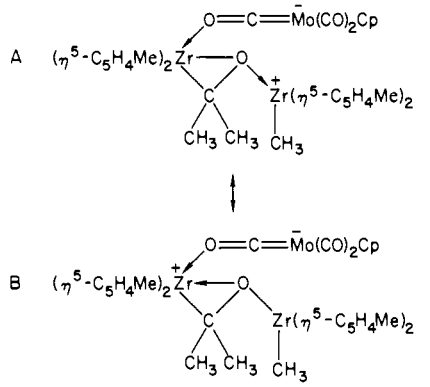
The bridging aldehydes and ketenes in Table IV show the same bonding mode (η^2-*C,O* toward one Zr and η^1-*O* toward the other) as the bridging acetone in **4c**. Two resonance structures, A and

Table IV. Ketone (Including Ketene and Aldehyde) Complexes with C–O Bond Lengths ≥ 1.32 Å, in Order of Decreasing Length

complex	length, Å	ref
$Os(CO)_2(PPh_3)_2(\eta^2\text{-}CH_2O)$	1.584 (11)	*a*
4	1.469 (5)	this work
$(Cp_2ZrCl)_2(\mu\text{-}\eta^2\text{-}CH_2O)$	1.43 (2)	*b*
$Cp_2Zr(\mu\text{-}\eta^2\text{-}CH_3CHO)(\mu\text{-}H)ZrHCp_2$ (**8**)	1.412 (4)	*c*
9	1.401 (3)	*d*
$[Cp_2Zr(Ph_2C{=}C{=}O)]_2$	1.371 (4)	*e*
$Cp_2Mo(\eta^2\text{-}CH_2O)$	1.360 (9)	*f*
$Mo_2(CO)_4(\mu\text{-}\eta^2\text{-}CH_3CHO)Cp_2$	1.354 (8)	*g*
$Cp_2V(CH_2O)$	1.353 (10)	*h*
	1.35 (2)	*i*
$Ni(PEt_3)_2(Ph_2CO)$	1.335 (4)	*j*
$CpMo(CO)(\eta^2\text{-}Ar_2CNHMe)(\eta^2\text{-}PhCHO)$	1.333 (12)	*k*
$Ni(cy_3P)_2(PhCHO)$	1.325 (7)	*l*
$Ni(PPh_3)_2(\eta^2\text{-}(CF_3)_2CO)$	1.32 (2)	*m*
	1.319 (10)	*n*

[a] Reference 17. [b] Reference 9b. [c] Reference 11a. [d] Reference 15. [e] Lappert, M. F. *J. Chem. Soc., Chem. Commun.* 1982, 462. [f] Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* 1985, *107*, 2985. [g] Adams, H.; Bailey, N. A.; Guantlett, J. T.; Winter, M. J. *J. Chem. Soc., Chem. Commun.* 1984, 1360. [h] Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* 1982, *104*, 2019. [i] Engelhardt, L. M.; Jacobsen, G. E.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* 1984, 220. [j] Tsou, T. T.; Huffman, J. C.; Kochi, J. K. *Inorg. Chem.* 1979, *18*, 2311. [k] Brunner, H.; Wachter, J.; Bernal, I.; Creswick, M. *Angew. Chem., Int. Ed. Engl.* 1979, *11*, 861. [l] Kaiser, J.; Sieler, J.; Walther, D.; Dingus, E.; Golic, L. *Acta Crystallogr., Sect. B* 1982, *B38*, 1584. [m] Countryman, R.; Penfold, B. R. *J. Cryst. Mol. Struct.* 1972, *2*, 281. [n] Choukroun, R.; Dahan, F.; Gervais, D. *J. Organomet. Chem.* 1984, *266*, C33.

B, can be written for **4c**, just as they can be written for the aldehyde- and ketene-bridged structures (e.g., **8**) in Table IV. In



resonance structure A, the right-hand Zr serves as a Lewis acid toward the oxygen atom of the acetone in **4c** and thus converts that acetone into an excellent π-acceptor ligand for the left-hand Zr—forming the metallaoxirane ring. In resonance structure B, the Lewis acid interaction with the right-hand Zr has become so powerful that the acetone oxygen is merely a neutral σ donor toward the left-hand Zr. The observed distance between the acetone oxygen and the left-hand Zr (Zr(2)–O(4) = 2.180 (3) Å) is longer than the observed distance between the acetone oxygen and the right-hand Zr (Zr(1)–O(4) = 2.083 (3) Å), implying that resonance structure B is more important than A. In any case, the structure of **4c** makes it clear that a Lewis acid-complexed ketone can serve as a powerful π acceptor for an early transition metal.

Experimental Section

General. All operations were performed under a nitrogen or argon atmosphere or under vacuum by Schlenk, inert atmosphere box, and

(13) (a) Hofmann, P.; Stauffert, P.; Tatsumi, K.; Nakamura, A.; Hoffmann, R. *Organometallics* **1985**, *4*, 404. (b) Tatsumi, K.; Nakamara, A.; Hoffmann, P.; Stauffert, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 4440.

(14) Borohydride reduction of an η^2-C(S)SMe ligand has been reported by: Touchard, D.; Dixneuf, P. H.; Adams, R. D.; Segmuller, B. E. *Organometallics* **1984**, *3*, 640.

(15) Labinger, J. A.; Bonfiglio, J. N.; Grimmett, D. L.; Masuo, S. T.; Shearin, E.; Miller, J. S. *Organometallics* **1983**, *2*, 733.

(16) Erker, G.; Rosenfeldt, F. *J. Organomet. Chem.* **1982**, *224*, 29–42.

(17) Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *J. Organomet. Chem.* **1982**, *231*, 335.

vacuum line techniques. The solvents employed were distilled under N_2 from sodium benzophenone ketyl and vacuum-transferred from titanocene. The C_6D_6 was dried by vacuum transfer from P_4O_{10}. The known compounds $Mo(CO)_5NMe_3$,[18] $W(CO)_5(THF)$,[19] $[CpFe(CO)_2(THF)]BF_4$,[20] and $EtC(O)Re(CO)_4(NCCD_3)$[21] were prepared by literature methods. The ^1H NMR data were collected on a JEOL FX-100 and an IBM WP-270SY spectrometer; residual solvent proton shifts were used as secondary internal standards. IR data were collected on a Perkin-Elmer 983 spectrometer and processed on its data station. Gas chromatography was performed on a Perkin-Elmer 3920.

Kinetic Analysis of Reaction 3. In a typical kinetics run, a vacuum line bulb with a Teflon stopcock was charged in an inert atmosphere box with $Cp_2Zr(C(O)Me)(\mu\text{-}OC)Mo(CO)_2Cp$, **2a** (48.4 mg, 0.0950 mmol). Toluene (10.42 g, 12.02 mL) was vacuum-transferred from titanocene into the bulb containing **2a**, producing a clear, golden 7.90 mM solution. The vacuum line bulb was closed and placed in a constant temperature bath. At appropriate intervals ($^1/_4$ half-life), the vacuum line bulb was removed and cooled to 0 °C, while a 0.1-mm CaF_2 septum-capped IR cell was purged 3 times with argon through a needle in the upper septum. Solution was syringed from the bulb (under argon flow) into the cell, and the appearance of **3a** was monitored through its IR absorption[22] at 1883 cm^{-1}. The results agreed well with those from monitoring the loss of the absorption due to **2a** at 1837 cm^{-1}. A reference spectrum of toluene was subtracted from each spectrum. Under these conditions, the product solution of **3a** did not decompose for at least 15 half-lives. For runs done under CO (filtered through CaO) pressure, a Fischer-Porter apparatus was used instead of a vacuum line bulb, and solvent was added by syringe instead of by vacuum transfer. Runs under a CO atmosphere (or in THF) failed to yield good infinity points at 1883 cm^{-1} because of decomposition, so the rate was determined by monitoring the disappearance of the IR absorption of **2a** at 1837 cm^{-1} (1838 cm^{-1} in THF). Experimental and theoretical (i.e., zero absorbance) infinity points yielded similar results.

Acetone Complex 4a. Complex **2a** (0.506 g, 0.1 mmol) and Cp_2ZrMe_2 (0.251 g, 0.1 mmol) in toluene (10 mL) were allowed to react for 1 h at room temperature, turning from yellow to light orange. The reaction mixture was then reduced in volume by $^2/_3$, and 20 mL of hexane was added. After standing for 0.5 h at room temperature, the product precipitated from solution as bright-yellow crystals in 81% yield: ^1H NMR (C_6D_6) δ 5.94 (s, 10 H, Cp_2Zr), 5.82 (s, 10 H, Cp_2Zr), 5.36 (s, 5 H, CpMo), 1.36 (s, 6 H, acetone methyls), 0.36 (s, 3 H, ZrMe); IR (toluene) 1935, 1849, 1587, 1163.5 (C–O of acetone, weak, see below) cm^{-1}.

Acetone Complex 4a-^{13}C (Ketone Carbon). Complex **2a** was prepared from isotopically normal 1 and ^{13}CO by the method already reported.[1b] By keeping the reaction time to 15 min and using a ^{13}CO pressure of <1 atm in order to minimize scrambling into other positions, the **2** obtained had 78% ^{13}CO in the acetyl carbonyl. Freshly prepared **2-^{13}C** (0.060 g, 0.12 mmol) was reacted with 1 equiv of Cp_2ZrMe_2 in 10 mL of toluene. After 25 min, the solution was concentrated, and the product was precipitated with hexane as a light tan solid in 61% yield: ^1H NMR (C_6D_6) δ 5.95 (s, 10 H, Cp_2Zr), 5.83 (s, 10 H, Cp_2Zr), 5.37 (s, 5 H, CpMo), 1.36 (d, 3 H, $^2J_{C\text{-}H}$ = 4.4 Hz, acetone methyls), 0.36 (s, 3 H, ZrMe); IR (toluene) identical with that of **4a** except for the labeled ketone stretch seen at 1147 cm^{-1} (instead of at 1164 cm^{-1}), as determined by isotope difference spectroscopy.

Isotope Difference Spectrum of Ketone Complex 4a and 4a-^{13}C. Preliminary experiments with KBr pellets suggested a scanning range of 1250–1100 cm^{-1}, making C_6D_6 the solvent of choice. A solution of isotopically normal **4a** (0.0117 g, 0.015 mmol) in C_6D_6 (0.5 mL) was loaded into a 0.0984-mm NaCl IR cell. The instrument was then programmed to scan the 1250–1100-cm^{-1} range 16 times and to average the spectra. Total acquisition time was 1 h 8 min. Identical parameters were then employed on a solution of **4a-^{13}C** (0.0126 g, 0.016 mmol) in C_6D_6 (0.5 mL). Finally, under the same conditions, the same cell containing only C_6D_6 was scanned 16 times, and the spectra were averaged. This solvent spectrum was used for spectral subtraction with each of the previously stored spectra to generate spectra of solvent-free **4a** and **4a-^{13}C**. The averaged spectrum of **4a** was subtracted from the averaged **4a-^{13}C** spectrum. The resulting isotope difference spectrum gave a negative peak at 1163.5 cm^{-1} ($\nu^{12}CO$ of bridging acetone) and a positive peak at 1147 cm^{-1} ($\nu^{13}CO$ of bridging acetone) after concentration differences were removed by a scaling factor of 0.8783 applied to the absorbance spectrum of **4a**.

Protolysis of Complex 4a: Identification of Resulting Organic Fragment. Through a suspension of **4a** (0.615 g, 0.8 mmol) in Et_2O (2 mL), dry HCl was bubbled for 5 min. The major product volatile at room temperature was identified as isopropyl alcohol by coinjection on a Poropak column at 120 °C and by preparative GLC on a Carbowax column at 90 °C.

Complex 4c: Derivative of 4a with Cp′ on Both Zr Atoms (Cp′ = C_5H_4Me). In a synthesis analogous to that for the normal Cp analogues, **1c** was made from an equimolar mixture of Cp'_2ZrMe_2[23] and $HMo(CO)_3Cp$ in THF. The **1c** was treated with CO in toluene to yield **2c** as a tan solid upon isolation: ^1H NMR (C_6D_6) δ 6–5 (complex multiplets with s at 5.38, ring protons), 2.18 (s, 3 H, acetyl methyl), 1.71 (s, 6 H, Cp'_2Zr Me groups).

The isolated **2c** (0.119 g, 0.211 mmol) was combined with Cp'_2ZrMe_2 (0.059 g, 0.211 mmol) as a toluene solution. The resulting solution was allowed to stir for 1 h at room temperature, becoming gold in color. Concentration and addition of pentane yielded orange-yellow single crystals in 12 h: ^1H NMR (C_6D_6) δ 6.4–5.2 (complex multiplets with a s at 5.38, ring protons), 2.206 (s, 6 H, Cp'_2Zr Me), 1.83 (s, 6 H, Cp'_2Zr Me), 1.37 (s, 6 H, acetone methyls), 0.29 (s, 3 H, ZrMe).

Crystal Data for Complex 4c. Orange crystals of **4c** were grown straightforwardly from toluene/pentane and sealed in a capillary under N_2 to prevent decomposition during data collection. All crystallographic data were collected at −40 °C. At temperatures below −50 °C, the crystals shattered; this behavior had not been noted with **4a**. Crystallographic details are reported in Table II.[24] The structure was solved by interpretation of the Patterson map (for Mo and Zr atom positions); carbon and oxygen atoms were found in subsequent difference Fourier maps. Standard atomic scattering factors, with anomalous dispersion corrections, were used.[25]

The rings containing C4–C8 (Cp) and C28–C33 (Cp′) exhibited disorder. The best model of this disorder was achieved by assigning half atoms to the electron densities of the disordered rings. The disordered rings were then refined as rigid regular pentagons (C–C 1.42 Å, ring H's omitted). Atoms in the C4–C8 rings were given anisotropic thermal parameters, while atoms in the C28–C33 rings were given isotropic thermal parameters. Site occupancy factors were refined for both pairs of rings; final values were 50.8% and 49.2% for C4–C8/C4′–C8′, and 59.4% and 40.6% for C28–C33/C28′–C33′. The hydrogen atoms of the nondisordered rings (C9–C14, C15–C20, and C21–C26) were included in idealized positions (C–H = 0.96 Å). The methyl groups (C14, C20, C26, and C27) were modeled as rigid groups, with hydrogen atoms placed at idealized tetrahedral positions. These rigid methyl groups were allowed to rotate during refinement. The thermal parameters of all hydrogen atoms were fixed at 1.2 times the equivalent isotropic thermal parameters of the carbon atoms to which they were attached. No absorption correction was performed. The final atomic coordinates are given in Table III. Tables of all bond lengths and angles, anisotropic thermal parameters for non-hydrogen atoms, calculated hydrogen atom positions, and observed and calculated structure factors are available as supplementary material. Important bond lengths and angles are shown in Figure 2.

Acetone Complex 4d: The $W(CO)_3Cp^-$ Analogue of 4a. Cp_2ZrMe_2 (0.152 g, 0.60 mmol) was combined with 2d[1d] (0.336 g, 0.56 mmol, 0.93 equiv) in a minimum of toluene. After 1 h at room temperature, the solution was reduced in volume and the product precipitated with hexanes as a yellow powder in 70% yield: ^1H NMR (C_6D_6) δ 5.94 (s, 10 H, Cp_2Zr), 5.82 (s, 10 H, Cp_2Zr), 5.26 (s, 5 H, CpW), 1.37 (s, 6 H, acetone methyls), 0.37 (s, 3 H, ZrMe). Anal. Calcd for $C_{32}H_{34}O_4WZr_2$: C, 45.27; H, 4.01. Found: C, 45.11; H, 3.96.

$Cp_2ZrMe(O_2CCF_3)$. To a solution of Cp_2ZrMe_2 (0.338 g, 1.34 mmol) in toluene (8 mL) was added dry, degassed CF_3COOH (1 equiv). Gas evolution was observed for 5 min. The solution was allowed to stir for 1 h, as the color changed from clear to pale yellow. The solvent was removed in vacuo to give the product as a white solid in 92% yield: ^1H NMR (C_6D_6) δ 5.63 (s, 10 H, Cp_2Zr), 0.424 (s, 3 H, ZrMe); IR (toluene) 1730, 1624, 1441, 1396, 1212, 1184, 1165 cm^{-1}.

$Cp_2Zr(\eta^2\text{-}COMe)(O_2CCF_3)$. The product of the above reaction was dissolved in toluene (15 mL), degassed, and then pressurized with >1 atm of CO for 1 h. The solvent was then stripped away to yield a bright-

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yellow oil. Trituration of this oil with hexanes for 0.5 h gave the product as a pale-yellow solid in >80% yield: ^{1}H NMR (C_6D_6) δ 5.48 (s, 10 H, Cp_2Zr), 2.22 (s, 3 H, acetyl methyl); IR (toluene) 1718, 1401, 1209, 1147, 1017, 812 cm^{-1}.

Complex 6: The $O_2CCF_3^-$ Analogue of 4a. Cp_2ZrMe_2 (0.030 g, 0.12 mmol) and $Cp_2Zr(\eta^2$-COMe)(O_2CCF_3) (0.055 g, 0.14 mmol) were sealed in an NMR tube as a C_6D_6 solution. The solution turned yellow, and a pale-yellow crystalline precipitate was isolated by filtration after 1 h. The compound was thermally unstable, decomposing at room temperature in about a day: ^{1}H NMR (C_6D_6) δ 5.84 (s, 10 H, Cp_2Zr), 5.74 (s, 10 H, Cp_2Zr), 1.48 (s, 6 H, acetone methyls), 0.49 (s, 3 H, ZrMe); IR (toluene) 1709, 1205, 1181, 1138, 810 cm^{-1}.

Deprotonation of 2a with LDA at Low Temperature. A double male (14/20) glass filtration frit, connected to a vacuum line with a horizontal 14/20 joint permitting the inversion of the frit, was fitted with a round-bottom flask on each end. A suspension of **2a** (0.100 g, 0.196 mmol) and LDA (0.021 g, 0.196 mmol) in Et_2O (10 mL) was stirred at −42 °C in one flask for 1 h. The suspension was then stripped of solvent and extracted with benzene and the benzene filtered to yield a tan precipitate and a yellow solution. The precipitate was found to be Li^+-$CpMo(CO)_3^-$ by comparison of its IR to that of an authentic sample independently synthesized from LDA and $HMo(CO)_3Cp$. The solvent was removed to yield a pale-yellow oil, which upon tituration with hexanes gave the product as a white powder. The product was shown by NMR to be the ketene complex **5** previously reported[4] from the deprotonations of η^2-acetyls.

Reaction of 2a with MeLi at −80 °C. Using the filtration apparatus described above, a yellow solution of **2a** (0.100 g, 0.19 mmol) in THF (5 mL) was cooled to −80 °C and allowed to stir for 0.5 h. To the cold stirring solution 1 equiv of MeLi was added dropwise. After 10 min, the flask was allowed to warm (0.5 h) to room temperature. The mixture was then stirred for an additional 0.5 h. The solution was reduced in volume, and addition of hexanes and filtration yielded a pale-yellow solid ($Li^+CpMo(CO)_3^-$, identified by its IR). The filtrate was pumped to dryness, yielding an orange–yellow residue, shown by ^{1}H NMR (C_6D_6 and $CDCl_3$) to be mostly the known[4] Zr ketene complex **5**.

Complex 7: Reaction of 4a with CO. A degassed solution of **4a** (0.102 g, 0.13 mmol) in toluene (3 mL) was pressurized with >1 atm of CO. The solution was then cooled in an ice bath and allowed to stir at 0 °C for 4.5 h. The solvent was then removed in vacuo to yield a light-yellow powder. The powder was washed with 2 mL of a 80:20 mixture of hexanes and benzene to give the product in 55% yield: ^{1}H NMR (C_6D_6) δ 5.76 (s, 10 H, Cp_2Zr), 5.74 (s, 10 H, Cp_2Zr), 5.39 (s, 5 H, CpMo), 1.01 (s, 6 H, acetone methyls), 0.25 (s, 3 H, ZrMe); IR (toluene) 1931, 1840, 1591, 1180.6, 1017, 804 cm^{-1}. Anal. Calcd for $C_{32}H_{34}O_5MoZr_2$: C, 50.23; H, 4.30. Found: C, 50.08; H, 4.40.

In a separate experiment, a calibrated vacuum bulb with **4a** (0.104 g, 0.137 mmol) in toluene (20 mL) was observed manometrically to take up CO (0.124 mmol, 0.91 equiv) at 20 °C over the course of 3.25 h.

Acknowledgment. This research was partially supported by NSF Grant CHE82-07597. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. We thank Prof. S. H. Strauss for assistance in the manometric measurements. The Nicolet *R3m/E* diffractometer and computing system at Colorado State University was purchased with funds provided by the National Science Foundation (Grant CHE-8103011).

Supplementary Material Available: Tables of all bond lengths and angles, anisotropic thermal parameters for non-hydrogen atoms, positional parameters of hydrogen atoms, and observed and calculated structure factors (31 pages). Ordering information is given on any current masthead page.

Association Phenomena. 6. NMR Studies of the Mixed Chelates of Triethylenetetramine, Phosphate, and Metal Ions

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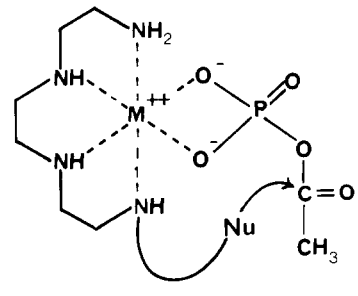
Abstract: Experiments reported in earlier papers in this series described the synthesis of several polyamines and polyamides carrying pendant arms terminating in nucleophilic groups. These compounds were designed as catalysts for the decomposition of acetyl phosphate on the premise that the polyamines or polyamides would form mixed chelates with metal ions and acetyl phosphate and that the forced proximity of the nucleophile and acetyl moieties would lead to pseudointramolecular acyl transfer. The observed rates of catalyzed decomposition of acetyl phosphate, however, were far lower than anticipated. The reasons for this failure to observe catalysis are probed in the present work by using a model system consisting of triethylenetetramine, phosphate, and metal ions. By means of ^{31}P NMR measurements of longitudinal and transverse relaxation rates, we show that mixed chelates containing the polyamine, metal ion, and phosphate do, indeed, form to a finite extent and that the entry and exit of the phosphate into and out of the complex occur sufficiently rapidly to preclude them as rate-determining steps in the acetyl phosphate decomposition reaction.

Two earlier papers of this series[1,2] described studies of the hydrolysis of acetyl phosphate. Lau and Gutsche[2] attempted to detect polyfunctional catalysis of the process by using various polyamines or polyamides and metal ions, the premise being that a mixed chelate (**1**) would form from the metal ion, the amine or amide, and acetyl phosphate and that its geometry would promote intramolecular displacement of the acetyl group by the nucleophilic moiety of the polyamine or polyamide. However, only modest rate enhancements were observed, and the purpose of the present paper is to explore some of the possible reasons for this behavior. In particular, the questions of the extent of mixed-chelate formation and the rate at which a phosphate moiety enters and leaves the mixed chelate are addressed.



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The system chosen for study included triethylenetetramine (**2**)

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