Table I. Decomposition of Endoperoxide 8

decomposition conditions	yields, %			
	9	15[a]	16	17[b]
1. thermal: 400 °C vapor phase	40	21	5	
2. photochemical: direct irradiation,[c] $CFCl_3$, −20 °C				100
3. photochemical: Ph_2CO sensitized,[c] $CFCl_3$, −20 °C	100			
4. $TiCl_4$, CH_2Cl_2, 0 °C		95		
5. $AlCl_3$, $CDCl_3$, 43 °C		45		
6. TsOH, THF, reflux	5	5	50	
7. $FeCl_3$, THF, H_2O, reflux	9	5	34	

[a] Under acidic conditions 15 undergoes aldol condensations to afford 2,3-dimethylcyclohex-2-enone and 3-ethylcyclohex-2-enone. The yields of these cyclohexenones are included in the yields of 15. [b] The epoxide 17 is readily transformed into frontalin (9) by acid or heat. Therefore it was usually impossible to determine whether 9 was a primary product or derived from 17. [c] The ultraviolet output (3 W) of an argon ion laser was used: 363.8, 351.4, 351.1, 335.8, 334.5, and 333.6 nm.

10 via photosensitized decomposition of the azoalkane **11**,[8] using monochromatic laser light, and trapping this species with oxygen under high pressure[1d] (Scheme III). In this sequence evidence for a stepwise biradical trapping has been obtained for the first time. The observation of the three possible olefinic hydroperoxides **12a–c** indicates the intermediacy of the hydroperoxy biradical **13** which can undergo either intramolecular hydrogen abstraction to form the hydroperoxides **12a–c** or closure to form the endoperoxide **8**. Unfortunately, these hydroperoxides complicate the isolation of the desired endoperoxide **8**. Therefore, we were most pleased to observe that the same ketone (**14**)[8] used in the azo route (Scheme II) could be converted directly to **8** in much higher yields via a unique acid-mediated cyclization with hydrogen peroxide.[9]

With endoperoxide **8** available in quantity,[10] it has become possible to study its decomposition under a variety of conditions (see Table I). The rapid thermal decomposition of **8** proceeds at about 400 °C in the vapor phase. Preferential one-carbon bridge cleavage is observed, with frontalin (**9**) being the major product along with diketone **15** (Scheme IV). A small amount of the three-carbon bridge cleavage product **16** is also formed thermally. Conditions have been found which lead to preferential formation of each of the products listed in Table I: **9**, **15**, **16**, and **17**. Thus, direct photodecomposition with all of the ultraviolet lines of an argon ion laser leads to the quantitative formation of the epoxide **17**.[11] In contrast benzophenone-sensitized photodecomposition leads to quantitative formation of frontalin (**9**). Lewis acid mediated decomposition of **8** leads to the exclusive formation of the diketone **15**, whereas protic acid favors cleavage of the larger bridge and formation of **16**. The structures of all decomposition products were confirmed by synthesis.[10,12]

Epoxide **17** arising from direct excitation of the peroxide could be produced via homolytic extrusion and collapse of a singlet species (Scheme IV, **18**, * = ↑,↓). The ketal **9** arising from photosensitization could be produced via a homolytic extrusion to a triplet species (Scheme IV, **18**, * = ↑,↑) from which bond rotation and stepwise addition to the carbonyl could occur before spin inversion would make possible collapse to the epoxide **17**. The formation of the diketone **15** (Scheme IV) and the keto aldehyde **5** (Scheme I) implies the intermediacy of an ionic species with a substantial amount of positive charge on the bridge carbon fragments (Scheme IV, **18**, * = +,−; Scheme I, **6**, * = +,−). Such species would be expected to undergo 1,2-methyl and -hydride shifts to form the dicarbonyl compounds observed. The formation of the three-carbon bridge cleavage product **16** might be rationalized as outlined in Scheme IV (* = +,−) but it is felt that this pathway is inconsistent with the dihedral angle considerations outlined earlier. Since this product is characteristic of decompositions in protic medium, we suspect that a basic change in mechanism has occurred to one involving the protic solvent or acid[13] and are currently investigating this point.

Finally, the route to the pine beetle pheromone frontalin (**9**) via **11** and **8** constitutes an isomorphous synthesis, since the molecular skeleton of these three substances does not change but only the locations of the heteroatoms within that molecular skeleton are altered. This isomorphism with respect to the natural pheromone frontalin (**9**) probably accounts for the strong electroantennagram signals observed when antenna of the western pine beetle *Dendroctonus brevicomis* are exposed to either the azoalkane **11** or the peroxide **8**.[14] We are continuing to investigate the role of **8** and other peroxides in natural products chemistry.

Acknowledgment. We thank the NSF for financial support (Grant No. CHE 76-15343) and M. C. Birch and D. M. Light for conducting the electroantennagram studies.

---

(8) Wilson, R. M.; Rekers, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 4005. Wilson, R. M.; Elder, R. C.; Packard, A. B.; Rekers, J. W. *Ibid.* **1980**, *102*, 1633.

(9) The mechanistic aspects of this unique cyclization are uncertain at present.

(10) All new compounds described here had satisfactory elemental analysis and spectral properties in accord with their proposed structures. **8**: IR (neat) 2840–3000, 1448, 1370, 1343, 1301, 1235, 1164, 1028, 854 cm^{-1}; NMR (60 MHz, $CDCl_3$) δ 1.30 (6 H, s), 1.5–2.0 (6 H, complex), 2.16 (2 H, br s); *m/e* 142 (M^+).

(11) The nature of the electronic transition(s) which gives rise to this process is not at all clear. Apparently there are very weak and broad bands associated with the peroxide linkage at wavelengths greater than about 333 nm. The spectroscopy of the peroxide linkage is being investigated further.

(12) Epoxidation of **14** with MCPBA under buffered conditions afforded **17** followed by conversion to frontalin (**9**) under acidic conditions. Ozonolysis of 1-methyl-2-ethylcyclopentene afforded diketone **15**. The tetrahydrofuran **16** was prepared in a multistep sequence starting with the THP derivative of 5-hydroxypentan-2-one. Horner–Emmons chain extension with the sodium salt of triethyl phosphonoacetate gives the THP derivative of ethyl 6-hydroxy-3-methyl-2-hexenoate. Saponification of this ester followed by treatment with methyllithium yields the methyl ketone which upon removal of the THP blocking group with acid yields **16**: IR (neat) 1706 cm^{-1}; NMR (60 MHz, $CDCl_3$) δ 1.24 (3 H, s), 1.75–2.05 (4 H, br m), 2.19 (3 H, s), 2.63 (2 H, s), 3.83 (2 H, br t, *J* = 6 Hz); *m/e* 142 (M^+).

(13) The greatly diminished stability of bicyclo[2.2.1] endoperoxides in protic solvents has been observed before: Nugteren, D. H.; Hazelhof, E. *Biochim. Biophys. Acta* **1973**, *326*, 448. Hamberg, M.; Svensson, J.; Wakabayashi, T.; Samuelsson, B. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 345 and ref 2g and 2k. However, the formation of new products in the presence of protic species has not been observed until now.

(14) Electroantennagram signals of the following intensity relative to that observed for the same quantity of frontalin (**9**) were observed: azoalkane **11**, male (53–81%), female (43–105%); peroxide **8**, male (20–39%), female (62–90%). Competitive receptor-site studies indicated that **8**, **11**, frontalin (**9**), and *exo*-brevicomin all compete for the same antenna receptor sites. Light, D. M.; Birch, M. C. *J. Insect. Physiol.* **1979**, *25*, 161. Dickens, J. C.; Payne, T. L. *J. Ibid.* **1977**, *23*, 481. The biochemical and biological significance of these most intriguing findings must await further studies with the intact insects.

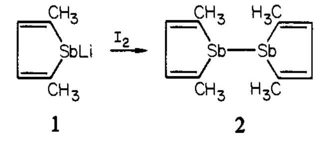
2,2′,5,5′-Tetramethyldistibolyl. A Thermochromic Distibine

Arthur J. Ashe, III,* William Butler, and
Timothy R. Diephouse

Department of Chemistry
The University of Michigan
Ann Arbor, Michigan 48109

Received September 16, 1980

In the course of our investigation of aromatic antimony compounds[1] we have found that lithium 2,5-dimethylstibacyclopentadienide (**1**) will undergo coupling on treatment with iodine to give 2,2′,5,5′-tetramethyldistibolyl (**2**).



1 2

---

(1) Ashe, A. J., III; Diephouse, T. R. *J. Organomet. Chem.*, in press.

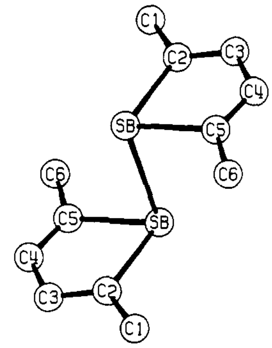


Figure 1. Molecular structure of 2,2′,5,5′-tetramethyldistibolyl (**2**). Hydrogen atoms are omitted for clarity.

Table I

	Bond Distances (Å)		
Sb–C_2	2.140 (5)	C_2–C_3	1.319 (7)
Sb–C_5	2.135 (4)	C_3–C_4	1.459 (7)
Sb–Sb′	2.835 (1)	C_4–C_5	1.321 (7)
C_1–C_2	1.501 (5)	C_5–C_6	1.495 (6)
	Bond Angles (Deg)		
C_2SbC_5	81.5 (2)	$C_2C_3C_4$	120.2 (5)
C_2SbSb'	91.4 (1)	$C_3C_4C_5$	120.3 (4)
C_5SbSb'	92.2 (1)	$C_4C_5C_6$	124.8 (5)
C_1C_2Sb	124.7 (4)	C_4C_5Sb	109.0 (4)
$C_1C_2C_3$	126.3 (5)	SbC_5C_6	126.2 (4)
SbC_2C_3	109.0 (3)		

This distibine has rather remarkable properties. Unlike all other reported distibines,[2] **2** is air stable. It crystallizes as intensely colored plates which are iridescent purple-blue in reflected light but appear red to transmitted light. A thin film of crystals of **2** shows a broad absorption maximum centered at 520 nm. Most strikingly these crystals melt reversibly at 99 °C to a pale yellow oil. Similarly, solutions of **2** in toluene or carbon tetrachloride are pale yellow (UV shoulder at 346 nm (ϵ 1900); only weak end absorption to 420 nm). Since these data indicate that the color of **2** is a solid-phase effect, we have obtained an X-ray crystal structure for **2**.

A 0.086 × 0.363 × 0.129 mm crystal obtained by slow vacuum sublimation was used for data collection. The space group and cell data are as follows: triclinic, space group $P\bar{1}$ with $a = 6.963$ (2) Å, $b = 6.450$ (3) Å, $c = 7.557$ (3) Å, $\alpha = 90.83$ (4)°, $\beta = 99.84$ (3)°, $\gamma = 89.88$ (3)°, $V = 334.3$ Å^3, $d = 2.00$ g/cm^3, and $Z = 1$. Three-dimensional diffraction data (a total of 1644 independent reflections having $2\theta(\text{Mo K}\bar{\alpha}) < 55°$) were collected on a computer-controlled Syntex $P2_1$ auto diffractometer, using graphite-monochromated Mo K$\bar{\alpha}$ radiation. The data were reduced by procedures previously described.[3] The Sb atoms were found by Patterson synthesis and the nonhydrogen atoms by difference Fourier analysis. Least-squares refinement using anisotropic thermal parameters for all nonhydrogen atoms gave $R_1 = 0.034$ and $R_2 = 0.049$.[4] Difference Fourier maps revealed the hydrogen atoms. Refinement to convergence gave $R_1 = 0.032$ and $R_2 = 0.041$.

The molecular structure of 2,2′,5,5′-tetramethyldistibolyl is illustrated in Figure 1 while the intramolecular bond distances and angles (for nonhydrogen atoms) are listed in Table I. These parameters do not appear to be unusual and in particular both Sb–Sb and Sb–C bond lengths are similar to those recently reported for tetraphenyldistibine.[5] The molecule adopts a staggered trans conformation about the Sb–Sb axis with the dimethylstibacyclopentadienyl rings in approximately parallel planes perpendicular to this axis.

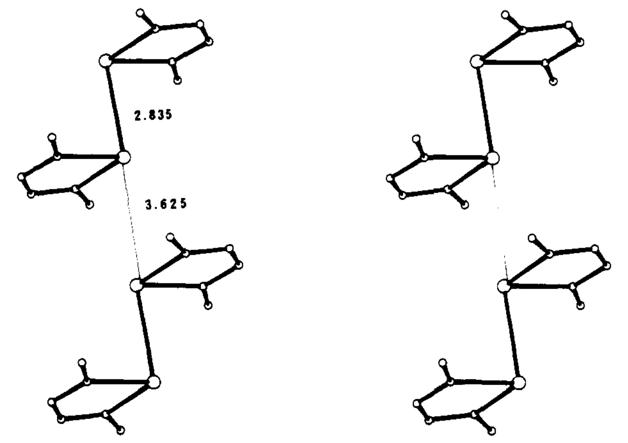


Figure 2. Stereoview of the solid-state structure of **2**. Sb–Sb distances along the *b* axis are indicated.

However, the crystal packing structure of **2** (Figure 2) reveals several unusual features. All of the antimony atoms are aligned in a collinear chain along the *b* crystal axis. This 010 face is normal to the longest morphological axis of the crystal. There is a very short "intermolecular" Sb–Sb separation of 3.625 (2) Å. The expected van der Waals radius separation is 4.4 Å but the closest intermolecular Sb–Sb approach in tetraphenyldistibine is 4.28 Å. Presumably there is an extended bonding along the Sb–Sb···Sb–Sb chain, and the solid-phase color is probably due to electronic excitation along this chain.

The bond angles C_5SbC_2, C_5SbSb', and C_2SbSb' of 81.5, 92.2, and 91.4°, respectively, indicate that antimony uses primarily p orbitals in bonding and the lone pair is essentially s hybridized. Since the antimony 5p_z orbitals must be aligned along the chain of antimony atoms, a simple model involving partial bonding via p orbitals seems indicated. This bonding scheme is very similar to that proposed for the extended bonding in solid molecular iodine,[6] which also shows short "intermolecular" distances.[7]

While the thermochromic properties of crystals of **2** are fascinating, they are not unique. In 1934, Paneth reported that tetramethyldistibine (**3**) (red to pale yellow) and tetraethyldistibine (**4**) (deep yellow to pale yellow) showed similar color changes on melting.[8] Although this phenomenon has been frequently noted in review articles,[2,9] it seemed particularly mysterious since other reported distibines [Ar_4Sb_2,[10] $(C_4H_9)_4Sb_2$,[11] $(C_6H_{11})_4Sb_2$,[12] etc.] did not show thermochromic behavior. We propose that **3** and **4** show a solid-phase association similar to that of **2**. However, the more bulky substituents of nonthermochromic distibines must prevent the close approach of the metal atoms.

Acknowledgment. We are grateful to the National Science Foundation for support of this work under Grant CHE-77-0940 and for a grant for the purchase of the Syntex $P2_1$ diffractometer. We also thank The University of Michigan Computing Center for a grant of computer time.

---

[2] For a short summary of the properties of distibines see: Doak, G. O.; Freedman, L. D. "Organometallic Compounds of Arsenic, Antimony and Bismuth"; Wiley: New York, 1970; pp 404–6.

[3] Computations were carried out on an Amdahl 470-V8 computer. Computer programs used during the structural analysis were SNCOP (data reduction, by W. Schmonsees), FORDAP (Fourier refinement, by A. Zalkin), ORFLS (full-matrix least-squares refinement, by Busing, Martin, and Levy), ORFFE (distances, angles, and their esd's, by Busing, Martin, and Levy), ORTEP (thermal ellipsoid drawings, by S. K. Johnson), HATOMS (hydrogen atom positions, by A. Zalkin), and PLANES (least-squares planes, by D. M. Blow).

[4] $R_1 = \sum[|F_o| - |F_c|]/\sum|F_o|$. $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

[5] von Deuten, K.; Rehder, D. *Cryst. Struct. Commun.* **1980**, *9*, 167.

[6] Pimentel, G. C. *J. Chem. Phys.* **1951**, *19*, 446. Hach, R. J.; Rundle, R. E. *J. Am. Chem. Soc.* **1951**, *73*, 4321.

[7] van Bolhuis, F.; Koster, P. B.; Migchelsen, J. *Acta Crystallogr.* **1967**, *23*, 90.

[8] Paneth, F. A. *Trans. Faraday Soc.* **1934**, *30*, 179. Paneth, F. A.; Loleit, H. *J. Chem. Soc.* **1935**, 366.

[9] Coates, G. E.; Wade, K. "Organometallic Compounds"; Meuthen and Co.: London, 1969; Vol. 1, pp 533–5.

[10] Blicke, F. F.; Oakdale, U. O.; Smith, F. D. *J. Am. Chem. Soc.* **1931**, *53*, 1025. Blicke, F. F.; Oakdale, U. O. *Ibid.* **1933**, *55*, 1198.

[11] Issleib, K.; Hamann, B.; Schmidt, L. *Z. Anorg. Allg. Chem.* **1965**, *339*, 298.

[12] Issleib, K.; Hamann, B. *Z. Anorg. Allg. Chem.* **1964**, *332*, 179.

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

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

Bruno Longato and Jack R. Norton*†

Department of Chemistry
Colorado State University
Fort Collins, Colorado 80523

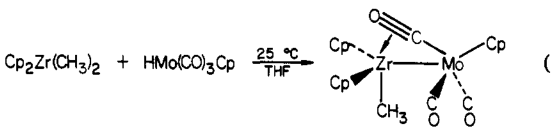
John C. Huffman, John A. Marsella, and
Kenneth G. Caulton*

Contribution No. 3550
Department of Chemistry and Molecular Structure Center
Indiana University
Bloomington, Indiana 47405

Received July 30, 1980

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

The coordinatively unsaturated alkyl Cp_2ZrMe_2 and the hydride $HMo(CO)_3Cp$ fulfill the requirements for dinuclear elimination[5a] and it is therefore not suprising that a mixture of these compounds in THF (reaction 1) eliminates methane to form **1**. Although the original report[4] proposed no structure and gave only ^1H NMR spectroscopic data, IR and ^{13}C NMR[6] (the latter obtained on **1** prepared from 32% ^{13}C-enriched $HMo(CO)_3Cp$) imply that **1** has the structure illustrated.[7,8] It seems likely that the reaction of metal carbonyl hydrides with $Cp_2Zr(CH_3)_2$ will be a general route to dinuclear complexes with carbonyls π-bonded to zirconium.



(1)

1

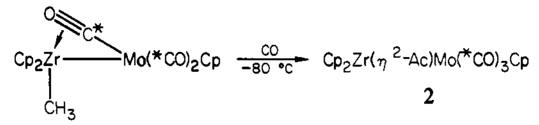
Although at room temperature **1** has a single carbonyl peak in the ^{13}C NMR at δ 236.1, two peaks at δ 245.4 and 232.5 (relative intensity 1:2) are observed on cooling to −80 °C. The barrier $\Delta G^{\ddagger}$ for migration of the π-bonded carbonyl to one of the two equivalent terminal carbonyl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

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

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

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

Labeling experiments establish unambiguously that the carbon in the acyl carbonyl in **2** arises from the added carbon monoxide in reaction 2. A sample of **1** which was 32% ^{13}CO-enriched was treated with 1 atm of ^{12}CO[14] at −80 °C (reaction 4) but the reaction was quenched by freezing at −196 °C before it was complete. Removal of the unreacted CO left a mixture which contained **2** with (NMR analysis[15] at −50 °C) ^{13}CO only in its



(4)

2

1-^{13}*C*

---

† Alfred P. Sloan Fellow, 1977–1981.

[1] Wojcicki, A. *Adv. Organomet. Chem.* **1973**, *11*, 87–145.

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

[3] Bergman, R. G. *Acc. Chem. Res.* **1980**, *13*, 113–20.

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

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

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

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

[8] (a) Colton, R.; Commons, C. J.; Hoskins, B. F. *J. Chem. Soc., Chem. Commun.* **1975**, 363–4. (b) Manassero, M.; Sansoni, M.; Longoni, G. *J. Chem. Soc., Chem. Commun.* **1976**, 919–20. (c) Pasynskii, A. A.; Skripkin, Yu. V.; Eremenko, I. L.; Kalinnikov, V. T.; Aleksandrov, G. G.; Adrianov, V. G.; Struchkov, Yu. T. *J. Organomet. Chem.* **1979**, *164*, 49–56. (d) Herrmann, W. A.; Ziegler, M. I.; Weidenhammer, K.; Biersack, H. *Angew. Chem., Int. Ed. Engl.* **1979**, 960–2. (e) Barger, Paul T.; Bercaw, John E. *J. Organomet. Chem.*, in press.

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

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

[11] IR (toluene): ν(CO) 2020 (w), 1930 (s), 1835 (m), 1590 (s) cm^{-1}. ^1H NMR (C_6D_6): δ 5.55 (s, 10 H, Cp_2Zr), 5.39 (s, 5 H, CpMo), 2.19 (s, 3 H, CH_3). ^{13}C NMR (toluene-d_8): δ 316.5 (1, acyl CO), 248.4 (1, CO), 232.6 (2, CO), 110.3(10, Cp_2Zr), 89.1 (5, CpMo), 33.0 (1, acyl CH_3).

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

[13] (a) Fachinetti, G.; Fochi, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1977**, 1946–50. (b) Erker, G.; Rosenfeldt, F. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 605–6. *J. Organomet. Chem.* **1980**, *188*, C1–C4. (c) Lappert, M. F.; Luong-thi, N. T.; Milne, C. R. C. *Ibid.* **1979**, *174*, C35–C37. (d) Marsella, J. A.; Moloy, K. G.; Caulton, K. G. *Ibid.*, in press.

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

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

0002-7863/81/1503-209$01.00/0