amounts of Ph_3SnCl and $K_2[Mn(CO)_3NO]$ react in THF to provide, after cation exchange, a 43% isolated yield of orange, crystalline $[Et_4N][Mn(CO)_3(NO)(SnPh_3)]$.[15] Other derivatives of $Mn(CO)_3NO^{2-}$ have been obtained by the reactions of $K_2[Mn(CO)_3NO]$ with equivalent amounts of $Mn(CO)_4NO$ and $Fe(CO)_5$ in THF. From these reactions, air-stable, crystalline, bright orange $[PNP]_2[Mn_2(CO)_6(NO)_2]$[16] and golden $[PNP]_2[FeMn(CO)_7(NO)]$[17] were obtained in 40% and 30% isolated yields, respectively. Equimolar amounts of $Na_2Fe(CO)_4\cdot 1.5$dioxane and $Mn(CO)_4NO$ in THF, followed by cation exchange, also provided the identical heterobimetallic dianion in 40% yield as the PNP^+ salt.

The most significant result of the above work is the demonstration that carbonylnitrosylmetallate dianions are viable species. In principle, an entire series of such highly reduced anions, isoelectronic with known binary carbonyl anions, is possible. For example, it may be possible to extend the isoelectronic series $Co(CO)_3NO$, $Fe(CO)_3NO^-$, and $Mn(CO)_3NO^{2-}$ to corresponding chromium and vanadium anions that would be analogous to $Mn(CO)_4^{3-}$ and $Cr(CO)_4^{4-}$.[18] Further, since NO appears to be a stronger π-acceptor group than CO, the corresponding NO substituted anions may well be more stable and less reactive than their purely carbonyl analogues. These possibilities are presently under investigation.

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[15] Anal. Calcd for $C_{29}H_{35}MnN_2O_4Sn$: C, 53.65; H, 5.40; N, 4.32. Found: C, 53.62; H, 5.53; N, 4.25. ^1H NMR (CD_3CN) δ 7.74–7.24 (m, 15 H, C_6H_5 of Ph_3Sn), 3.14 (q, 8 H, CH_2 of Et_4N^+), 1.20 (tt, 12 H, CH_3 of Et_4N^+). IR (ν(CO,NO), CH_3CN) 1975 (s), 1895 (m), 1860 (s), 1640 (m) cm^{-1}.

[16] Anal. Calcd for $C_{78}H_{60}Mn_2N_4O_8P_4$: C, 66.20; H, 4.27; P, 8.75; N, 3.96. Found: C, 66.07; H, 4.15; P, 8.79; N, 3.80. IR (ν(CO,NO), THF) 1970 (m), 1890 (s), 1860 (s), 1650 (m), 1610 (s) cm^{-1}. ^1H NMR (acetone-d_6) δ 7.77–7.30 (m, C_6H_5 of $(Ph_3P)_2N^+$); no M–H signals were present.

[17] Anal. Calcd for $C_{79}H_{60}FeMnN_3O_8P_4$: C, 67.10; H, 4.29; N, 2.97. Found: C, 67.03; H, 4.41; N, 2.79. IR (ν(CO,NO), THF) 1985 (m), 1940 (w), 1870 (s), 1645 (m) cm^{-1}. ^1H NMR (acetone-d_6) δ 7.80–7.30 (m, C_6H_5 of $(Ph_3P)_2N^+$); no M–H signals were present.

[18] Lin, J. T.; Hagen, G. P.; Ellis, J. E. *J. Am. Chem. Soc.*, in press (and references cited therein).

Genesis, Bonding Mode and Reaction with Carbon Monoxide of an Oxymethylene Unit Bridging Two Metal Atoms

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All chemists interested in carbon monoxide activation are familiar with Bercaw's modeling studies based on zirconium hydrides, which detail the promotion of the stoichiometric reduction of CO to methanol and to C_2-unit precursors.[1] Many of the Bercaw's observations have been interpreted in a sequence involving, as a key intermediate, the oxymethylene ligand bridging two zirconium atoms ($Zr-O-CH_2Zr$), whose reactivity with carbon monoxide was viewed as the reaction leading to C_2 units.[1,2] The intermediacy of such a unit is partially supported by our isolation of a complex[3] coming from the reaction of CO with $[(cp)_2Zr(H)Cl]_n$.[4] The choice of $[(cp)_2Zr(H)Cl]_n$ was mainly dictated by the fact that it contains only one potential migrating ligand rather than two as in $[(\eta^5\text{-}C_5Me_5)_2ZrH_2]$.[1]

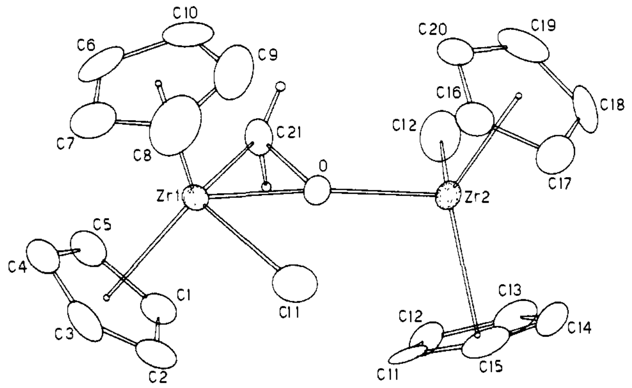
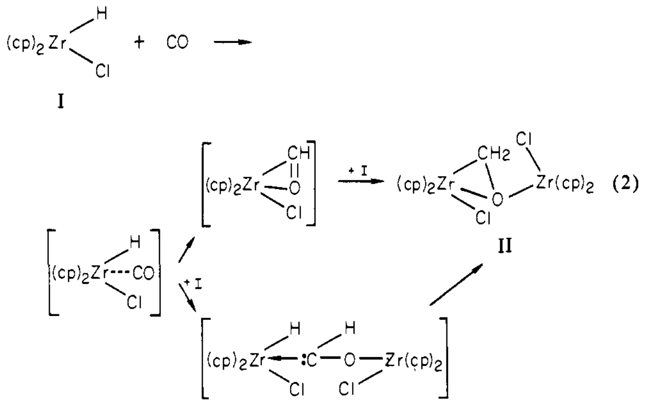


Figure 1. ORTEP view of II. Selected bond lengths (Å) and angles (deg) are as follows: Zr1–C21, 2.19 (1); Zr1–O, 2.13 (1); Zr1–Cl1, 2.522 (5); Zr2–Cl2, 2.344 (4); Zr2–O, 2.10 (1); O–C21, 1.43 (2); Zr1–O–Zr2, 166.9 (4); cp1–Zr1–cp2, 126.6(5); cp3–Zr–cp4, 129.1 (4). cp1, cp2, cp3, and cp4 are the centroids of the rings C1⋯C5, C6⋯C10, C11⋯C15, and C16⋯C20, respectively.

We found that complex I in THF absorbs 0.5 mol of CO per

$$\underset{\text{I}}{(2/n)[(cp)_2ZrHCl]_n} + CO \rightarrow \underset{\text{II}}{[(cp)_2ZrCl]_2(\mu\text{-}CH_2O)} \quad (1)$$

zirconium, allowing the isolation of complex II.[5] We further describe the solid-state structure of this species, some unexpected peculiarities, and its reaction with CO. According to the scheme proposed by Bercaw,[1] complex II may be formed (eq 2) either by intramolecular insertion of CO into a Zr–H bond or by a bimolecular hydride transfer from I to a Zr-bonded CO.[1] The



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[1] Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121–127 and references cited therein.

[2] Formation of related units was ascertained in carbon monoxide activation by organo actinides: Maatta, E. A.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 3576–3578. Fagan, P. J.; Moloy, K. G.; Marks, T. J. *Ibid.* **1981**, *103*, 6959–6962 and references therein.

[3] Fachinetti, G.; Floriani, C.; Roselli, A.; Pucci, S. *J. Chem. Soc., Chem. Commun.* **1978**, 269–270.

[4] Hart, D. W.; Schwartz, J. *J. Am. Chem. Soc.* **1974**, *96*, 8115–8116 and references therein.

[5] A THF (50 mL) suspension of I (2.84 g) containing NaCl was explosed to a carbon monoxide atmosphere under stirring in the dark. The absorption of CO stopped after 30 min, and a light yellow solution with a small amount of white crystals was obtained. The solution, after evaporation to dryness, gave a residue which was dissolved in boiling $CHCl_3$ (50 mL). Undissolved NaCl was filtered out. The resulting solution was concentrated, and 30 mL of Et_2O was added. The solution upon standing for 12 h at room temperature gave a light yellow crystalline solid (1.05 g). Anal. Calcd for $[(cp)_2ZrCl]_2(\mu\text{-}CH_2O)$ ($C_{21}H_{22}Cl_2OZr$): C, 46.41; H, 4.05, Cl, 13.08. Found: C, 46.00; H, 4.04; Cl, 13.36. ν_{CO}(Nujol) 1015 cm^{-1} (s). ^1H NMR ($CDCl_3$, Me_4Si, room temperature) 7.17 (2 H, s, CH_2), 3.87 (20 H, s, cp).

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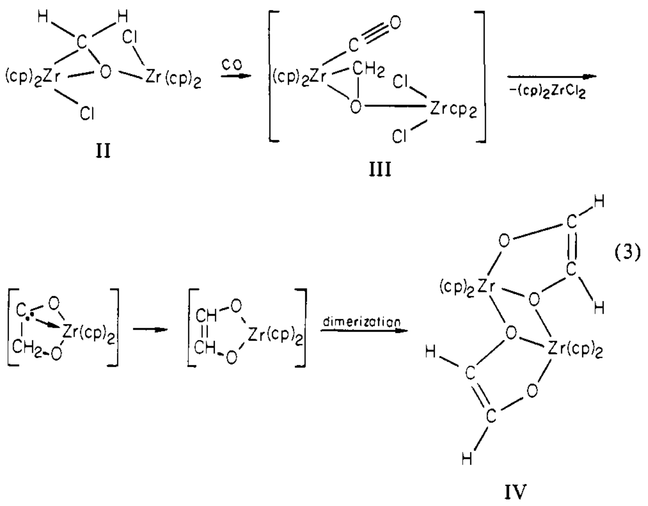
structure of II (Figure 1) was confirmed by X-ray diffraction methods.[6] All cyclopentadienyl ligands are coordinated in a conventional η^5 mode. [Zr–cp distances (Å) are as follows: cp1–Zr1, 2.24 (1); cp2–Zr1, 2.21 (1); cp3–Zr2, 2.21 (1); cp4–Zr2, 2.20 (1) (Figure 1)], the oxymethylene bridge is η^2-C,O bonded to Zr1 [Zr1–C21, 2.19 (1); Zr1–O, 2.13 (1) Å] with a Zr1–O–Zr2 angle of 166.9 (4)°. The distance Zr2···C21 = 3.07 (1) Å rules out any possible interaction of C21 with both zirconium atoms. The C–O bond distance [1.43 (2) Å] and the C–O stretching vibration (1015 cm^{-1}) are to be compared with the corresponding ones found in $(cp)_2V(\eta^2\text{-}CH_2O)$ [1.353 (10) Å, 1160 cm^{-1}],[7] $Os(CO)_2(PPh_3)_2(\eta^2\text{-}CH_2O)$[1.59 (1) Å, 1017 cm^{-1}],[8] and $Fe(CO)_2\{P(OMe)_3\}_2(\eta^2\text{-}CH_2O)$ [1.32 (2) Å, 1220 cm^{-1}].[9] The oxymethylene ligand in complex II displays a bonding mode that strongly resembles that of formaldehyde bonded to vanadium in $(cp)_2V(\eta^2\text{-}CH_2O)$.[7] Zr1, Cl1, C21, O, Zr2, and Cl2 atoms are close to being coplanar, the dihedral angle between Zr1, Cl1, C21, O, and Zr2, Cl2, O planes being 10.5 (8)°. Zr1, Cl1, C21, and O are nearly coplanar with a maximum deviation from the plane of 0.07 (1) Å. The two chloride ligands having trans configuration [the torsional angle Cl1–Zr1–Zr2–Cl2 is 169.5 (2)°], are bonded at unexpected different distances. Zr1–Cl1, 2.522 (4) Å, is significantly weaker than the corresponding Zr2–Cl2, 2.344 (3) Å. The ^{1}H NMR spectrum shows only one singlet for all cp ligands, suggesting an easy exchange in the roles of the two zirconium atoms in the equatorial plane.[5,10]

Complex II can be formally viewed as a η^2-formaldehydo complex $[Zr(\eta^2\text{-}CH_2O)]$ with the oxygen interacting with a Lewis acid center, Zr2 in Figure 1.[7,9] Lewis acids have been employed for converting a formaldehydo into an oxymethylene ligand, which is more appropriate for inserting carbon monoxide, as complex II does.[7,9,11] Carbonylation of II is a slow reaction in THF solution at atmospheric pressure of CO and at room temperature.[12,13] A simplified picture of how this reaction may occur is given in eq 3. The IR spectrum of the THF solution of II exposed to a carbon monoxide atmosphere showed a weak band at 1970 cm^{-1} and a band at 1605 cm^{-1}, whose intensity increased during the carbonylation. Carbon monoxide caused the loss of $(cp)_2ZrCl_2$ from complex II. Analytical data and IR and mass spectra agree with the proposed formula for complex IV.[12]



(3)

Acknowledgment. We thank Dr. A. Stefani (ETH Zürich) for mass spectra and the Italian National Research Council for financial support.

Registry No. I, 37342-97-5; II, 83385-36-8; IV, 84750-99-2; CO, 630-08-0.

Supplementary Material Available: Tables of positional (SI) and thermal parameters (SII) for complex II and a listing of structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

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[6] Crystals of $[(cp)_2ZrCl]_2(\mu\text{-}CH_2O)$ are monoclinic with a = 10.775 (2) Å b = 15.166 (4) Å, c = 13.687 (3) Å, β = 115.85 (2)°, U = 2012.8 (9) Å^3, space group $P2_1/n$, Z = 4, Mo Kα 13.0 cm^{-1}. Of the 4052 independent reflections ($5 < 2\theta < 52°$) measured on a Philips PW 1100 diffractometer using Mo Kα radiation, 2065 were considered observed [$I > 3\sigma(I)$]. No absorption correction was applied. The structure was solved by heavy-atom methods and refined anisotropically to give a current R = 0.058. During the refinement all the cp rings were treated as rigid groups. All the hydrogen atoms were found from a difference Fourier synthesis and introduced in the refinement as fixed contributors with B_{iso} = 6.3 Å^2.

[7] Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1982**, *104*, 2019–2020.

[8] Brown, K. L.; Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *J. Am. Chem. Soc.* **1979**, *101*, 503–505.

[9] Berke, H.; Bankhardt, W.; Huttner, G.; v. Seyerl, J.; Zsolnai, L. *Chem Ber.* **1981**, *114*, 2754–2768. Berke, H.; Huttner, G.; Weiler, G.; Zsolnai, L. *J. Organomet. Chem.* **1981**, *219*, 353–362.

[10] This was recently confirmed by a detailed study: Erker, G.; Kropp, K. *Chem. Ber.* **1982**, *115*, 2437–2446.

[11] Dombek, B. D. *J. Am. Chem. Soc.* **1980**, *102*, 6855–6857; **1979**, *101*, 6466–6468.

[12] A THF (50 mL) solution of complex II (0.97 g) was exposed to a carbon monoxide atmosphere in the dark. After 1 day the IR spectrum of the solution showed two weak bands at 1970 and 1605 cm^{-1}. Five days later the band at 1970 cm^{-1} remained constant, while the intensity of the band at 1605 cm^{-1} had increased. The IR spectrum did not change further. Faster carbonylation can be carried out under 100 atm of carbon monoxide. The THF solution, concentrated and cooled at 0 °C, gave beautiful crystals of complex IV (0.30 g), $[((cp)_2Zr)_2(C_2H_2O_2)_2]$. Anal. Calcd for $C_{24}H_{24}O_4Zr_2$: C, 51.61; H, 4.30. Found: C, 51.60; H, 4.37. The IR spectrum shows two sharp and strong bands (Nujol) at 1600 and 1225 cm^{-1} for the C═C and C–O bond vibrations. Complex IV showed mass spectral peaks at *556*, *557*, *558*, 559, *560*, 561, 562, 564 $[(cp_2Zr)_2(\mu\text{-}CHO{=}CHO)_2]$, 278, 279, 280, 282 $[cp_2Zr(CHO{=}CHO)]$ whose positions and relative intensity are in agreement with the natural isotopic mixture of zirconium.

[13] Carbonylation of a related proposed (η^2-formaldehyde)zirconocene complex is reported: Erker, G.; Kropp, K.; Krüger, C.; Chiang, A. P. *Chem, Ber.* **1982**, *115*, 2447–2460.

Evidence for a Perepoxide Intermediate in the 1,2-Cycloaddition of Singlet Oxygen to Adamantylideneadamantane: Nucleophilic Oxygen Atom Transfer to Sulfoxides

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Singlet oxygen ($^1O_2$) reacts with adamantylideneadamantane (**1**, Scheme I) to afford the unusually stable 1,2-dioxetane **3**.[1,2] Under certain conditions the photooxidation of **1** can yield the corresponding epoxide **4** in addition to **3**.[3] The mechanism for the formation of **3**, and in particular **4**, has been a subject of considerable controversy.[4] Dewar[5] and Bartlett[3c] have suggested that epoxide **4** may be produced by reaction of an intermediate perepoxide **2** with $^1O_2$ with concomitant generation of ozone. On the other hand, free-radical processes have also been proposed for the formation of **4**.[3d]

We now provide evidence for a trappable intermediate in the reaction of $^1O_2$ with **1**. This species, which we suggest is perep-

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[1] (a) Wieringa, J. H.; Strating, J.; Wynberg, H.; Adam, W. *Tetrahedron Lett.* **1972**, 169. (b) Schuster, G. B.; Turro, N. J.; Steinmetzer, H.-C.; Schaap, A. P.; Faler, G. R.; Adam, W.; Liu, J. C. *J. Am. Chem. Soc.* **1975**, *97*, 7110. (c) Numan, H.; Wieringa, J. H.; Wynberg, H.; Hess, J.; Voss, A. *J. Chem. Soc., Chem. Commun.* **1977**, 591.

[2] For reviews of 1,2-dioxetanes, see: (a) Bartlett, P. D.; Landis, M. E. In "Singlet Oxygen", Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979; Chapter 7. (b) Adam, W. *Pure Appl. Chem.* **1980**, *52*, 2591.

[3] (a) Schaap, A. P.; Faler, G. R. *J. Am. Chem. Soc.* **1973**, *95*, 3381. (b) Bartlett, P. D.; Ho, M. S. *Ibid.* **1974**, *96*, 627. (c) Bartlett, P. D. *Chem. Soc. Rev.* **1976**, 149. (d) Jefford, C. W.; Boschung, A. F. *Helv. Chim. Acta* **1977**, *60*, 2673.

[4] For reviews of the 1,2-cycloaddition of $^1O_2$ to olefins, see: (a) Schaap, A. P.; Zaklika, K. A. In "Singlet Oxygen"; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979; Chapter 6. (b) Frimer, A. A. *Chem. Rev.* **1979**, *79*, 359.

[5] Dewar, M. J. S.; Griffin, A. C.; Thiel, W.; Turchi, I. J. *J. Am. Chem. Soc.* **1975**, *97*, 4439.

0002-7863/83/1505-1691$01.50/0 © 1983 American Chemical Society