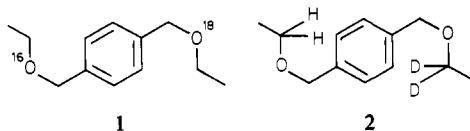


Calculations<sup>12</sup> indicate that a  $^{16}\text{O}/^{18}\text{O}$  isotope effect would be significant if the decomposition were concerted (or stepwise with the second-step rate determining). The intramolecular isotope effect on loss of  $\text{CH}_3\text{CH}^{16}\text{O}$  and  $\text{CH}_3\text{CH}^{18}\text{O}$  from the molecular ion of **1** has been measured as  $1.15 \pm 0.04$ .<sup>13</sup> Metastable ions



were measured;<sup>7,13</sup> the mass difference allowed the peaks for loss of  $\text{CH}_3\text{CH}^{16}\text{O}$  and  $\text{CH}_3\text{CH}^{18}\text{O}$  to be resolved clearly. The deuterium isotope effect measured for **2** was 3.2.

The  $^{16}\text{O}/^{18}\text{O}$  isotope effect rules out the possibility of a stepwise mechanism in which the first step is rate determining.<sup>12</sup> The  $^{16}\text{O}/^{18}\text{O}$  and H/D isotope effects taken together, considering also the substituent effects, leave only one possibility, namely, that the elimination of acetaldehyde from the benzyl ethyl ether molecular ion is concerted and that the reaction occurs through the six-centered transition-state I.<sup>14</sup> The benzyl ethyl ether molecular ion provides a clear example of the concerted rupture and formation of a number of bonds under conditions of low energy, since metastable ions were studied. We conclude that the concerted reaction possesses a low critical energy relative to that of a stepwise reaction, i.e., syncoordinated movement of the atoms is the lowest energy pathway for this decomposition.

**Acknowledgment.** The support of the Australian Research Grants Committee is acknowledged.

(13) The electric sector was swept under computer control, and the peaks were signal averaged. Abundances were determined from both peak heights and peak areas, giving isotope effects  $^{16}\text{O}/^{18}\text{O}$  of  $1.19 \pm 0.005$  and  $1.12 \pm 0.005$ , respectively. The figure  $1.15 \pm 0.04$  represents the maximum uncertainty. A small correction was necessary for loss of  $\text{C}_2\text{H}_5^{16}\text{OH}$ —a process observed with **1** but not with benzyl ethyl ether.

(14) A referee has suggested that the intervention of an ion-molecule complex  $\text{C}_6\text{H}_5\text{CH}_2\text{---}^+\text{OCH}_2\text{CH}_3$  might provide an alternative explanation of the results. See T. H. Morton, *J. Am. Chem. Soc.*, **102**, 1596 (1982) and references therein. The crucial objection to this mechanism is that if the rearrangement of the complex to give the products is rate determining as suggested by the referee, the  $^{16}\text{O}/^{18}\text{O}$  isotope effect is unexplained.

## Highly Reduced Organometallics. 13.<sup>1</sup> Synthesis and Chemistry of the Tricarbonylnitrosylmanganate(2-) Ion, $\text{Mn}(\text{CO})_3\text{NO}^{2-}$

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Reductions of compounds of the general formula  $\text{M}(\text{CO})_x\text{L}_y$ , where L is a better acceptor group than CO, should result in the preferential loss of coordinated CO or a reduced form thereof and the formation of the substituted dianions  $\text{M}(\text{CO})_{x-1}\text{L}_y^{2-}$ , provided coordinated L is not reduced.<sup>2</sup> In this paper we report on the first successful reaction of this type, which provides the initial example of a previously unknown class of substituted carbonylmetallate dianions of the general formula  $\text{M}(\text{CO})_{x-1}(\text{NO})_y^{2-}$ .<sup>3</sup>

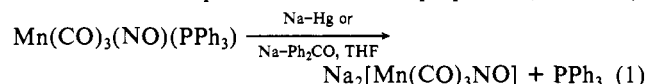
(1) Part 12: Rochfort, G. L.; Ellis, J. E. *J. Organomet. Chem.*, in press.

(2) Reductions of  $\text{M}(\text{CO})_x\text{L}_y$ , where L is a poorer  $\pi$ -acceptor group than CO, usually result in the loss of L if it is a good leaving group. For example,  $\text{Cr}(\text{CO})_4(\text{TMED})$  (TMED = tetramethylethylenediamine) undergoes reduction to give  $\text{Na}_2\text{Cr}(\text{CO})_4$ ; Ellis, J. E.; Parnell, C. P.; Hagen, G. P. *J. Am. Chem. Soc.* **1978**, *100*, 3605.

(3) It is noteworthy that only two examples of carbonylnitrosylmetallate monoanions presently exist,  $\text{Fe}(\text{CO})_3\text{NO}^-$  and the recently prepared  $\text{Mn}(\text{CO})_3(\text{NO})_2^-$ ; Stevens, R. E.; Yanta, T. J.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1981**, *103*, 4981.

Ten equivalents of potassium tri-*sec*-butylborohydride (1.0 M solution in THF) react at reflux with  $\text{Mn}(\text{CO})_4\text{NO}^4$  or at room temperature with  $\text{Mn}(\text{CO})_3(\text{NO})(\text{PPh}_3)^5$  to provide, after about 3 h, 60% or 80% yields, respectively, of the same nearly insoluble microcrystalline yellow solid. This material gives satisfactory analyses for the composition  $\text{K}_2[\text{Mn}(\text{CO})_3\text{NO}]$ .<sup>6</sup> Formally analogous reductions of  $\text{Fe}(\text{CO})_4\text{L}$  (L = CO<sup>7</sup> or  $\text{PPh}_3$ <sup>8</sup>) by  $\text{K}[\text{HBR}_3]$  have been shown previously to provide high yields of the isoelectronic species  $\text{K}_2[\text{Fe}(\text{CO})_4]$ .

Sodium amalgam reductions of  $\text{Mn}(\text{CO})_4(\text{NO})$  and  $\text{Mn}(\text{CO})_3(\text{NO})(\text{PPh}_3)$  were also examined and provide remarkable contrasts. Reduction of  $\text{Mn}(\text{CO})_4\text{NO}$  by Na-Hg proceeds slowly (>12 h) at room temperature to provide  $\text{Mn}(\text{CO})_5^-$  as the only carbonyl-containing product in low yields (10–15%), a result similar to those reported previously for reductions of  $\text{Fe}(\text{CO})_2(\text{NO})_2^9$  and  $\text{Co}(\text{CO})_3\text{NO}$ .<sup>10</sup> However, Na-Hg or Na- $\text{Ph}_2\text{CO}$  reductions of  $\text{Mn}(\text{CO})_3(\text{NO})(\text{PPh}_3)$  in THF at room temperature (eq 1) provide within 2 h essentially quantitative yields of a soluble orange-yellow substance that is formulated as  $\text{Na}_2[\text{Mn}(\text{CO})_3\text{NO}]$  on the basis of its spectral and chemical properties (vide infra).



Fluorolube mull infrared spectra of  $\text{K}_2[\text{Mn}(\text{CO})_3\text{NO}]$  in the  $\nu(\text{CO}, \text{NO})$  region show three principal bands at 1900 (m), 1755 (vs), and 1420 (s)  $\text{cm}^{-1}$ . In the same region, THF solution spectra of  $\text{Na}_2[\text{Mn}(\text{CO})_3\text{NO}]$  show principal bands at 1918 (s), 1815 (vs, br), 1380 (m, br), and 1345 (m, br)  $\text{cm}^{-1}$ . The two very low-energy bands for the disodium salt are undoubtedly caused by significant interactions between sodium cations and nitrosyl oxygens. These interactions appear to be destroyed by adding 2 equiv of cryptand(2.2.2)<sup>11</sup> to a THF solution of  $\text{Na}_2[\text{Mn}(\text{CO})_3\text{NO}]$ . The resulting light yellow precipitate,  $[\text{Na}(\text{crypt}(2.2.2))]_2[\text{Mn}(\text{CO})_3\text{NO}]$ ,<sup>12</sup> has a mull spectrum in the  $\nu(\text{CO}, \text{NO})$  region consisting of three relatively sharp bands: 1840 (s), 1720 (vs), and 1480 (m)  $\text{cm}^{-1}$ , where the  $\nu(\text{CO})$  values are significantly lower and the  $\nu(\text{NO})$  value is higher than corresponding bands of  $\text{K}_2[\text{Mn}(\text{CO})_3\text{NO}]$  and  $\text{Na}_2[\text{Mn}(\text{CO})_3\text{NO}]$ . These  $\nu(\text{NO})$  values are among the lowest ever observed for compounds containing only terminal NO groups.<sup>13</sup> By comparison, infrared spectra in the  $\nu(\text{CO}, \text{NO})$  region of  $\text{Na}[\text{Fe}(\text{CO})_3\text{NO}]$  in  $\text{Et}_2\text{O}$ , where the NO group is believed to be tightly ion paired with  $\text{Na}^+$  (2001, 1900, 1599  $\text{cm}^{-1}$ ) and  $[(\text{Ph}_3\text{P})_2\text{N}][\text{Fe}(\text{CO})_3\text{NO}]$  in THF, where no such interaction is possible (1978, 1876, 1645  $\text{cm}^{-1}$ ), show trends similar to those observed above, but the corresponding bands are at considerably higher energies.<sup>14</sup>

Further confirmation of the natures of  $\text{Na}_2[\text{Mn}(\text{CO})_3\text{NO}]$  and  $\text{K}_2[\text{Mn}(\text{CO})_3\text{NO}]$  has been obtained from an examination of their chemical properties, which are essentially identical. Equimolar

(4) Treichel, P. M.; Pitcher, E.; King, R. B.; Stone, F. G. A. *J. Am. Chem. Soc.* **1961**, *83*, 2593.

(5) Hieber, W.; Tengler, H. *Z. Anorg. Allg. Chem.* **1962**, *318*, 136. Wawersik, H.; Basolo, F. *J. Am. Chem. Soc.* **1967**, *89*, 4526.

(6) Anal. Calcd for  $\text{C}_3\text{K}_2\text{MnNO}_4$ : C, 14.58; K, 31.64; Mn, 22.23; N, 5.66; H, 0.00. Found: C, 13.80; K, 31.79; Mn, 22.00; N, 5.50; H, 0.24. All of the above analyses were obtained for one sample. Other attempts to obtain a better carbon analysis were not more successful.

(7) Gladysz, J. A.; Tam, W. J. *J. Org. Chem.* **1978**, *43*, 2279.

(8) Chen, Y.-S.; Ellis, J. E. *J. Am. Chem. Soc.* **1982**, *104*, 1141.

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(10) Hieber, W.; Ellermann, J. *Chem. Ber.* **1963**, *96*, 1667. Piazza, G.; Foffani, A.; Paliani, G. *Z. Phys. Chem. Neue Folge* **1968**, *60*, 167.

(11) 4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane or Kryptofix-222.

(12) The chemical properties of this product are identical with those of  $\text{K}_2[\text{Mn}(\text{CO})_3\text{NO}]$ . The crystal structure of the related  $[\text{Na}(\text{crypt}(2.2.2))]_2[\text{Fe}(\text{CO})_4]$  shows the presence of an essentially undistorted tetrahedral  $\text{Fe}(\text{CO})_4^{2-}$  unit, free of ion pairing. Teller, R. G.; Finke, R. G.; Collman, J. P.; Chin, H. B.; Bau, R. *J. Am. Chem. Soc.* **1977**, *99*, 1104.

(13) The related  $\text{K}_3[\text{Mn}(\text{NO})_2(\text{CN})_2]$ , presumably containing linear nitrosyls, also has very low  $\nu(\text{NO})$  values: 1455, 1425  $\text{cm}^{-1}$ . Behrens, H.; Lindner, E.; Schindler, H. *Z. Anorg. Allg. Chem.* **1969**, *365*, 119.

(14) Pannell, K. H.; Chen, Y.-S.; Belknap, K. L. *J. Chem. Soc., Chem. Commun.* **1977**, 363. Chen, Y.-S. M.S. Thesis, University of Texas, El Paso, TX, 1976.

amounts of  $\text{Ph}_3\text{SnCl}$  and  $\text{K}_2[\text{Mn}(\text{CO})_3\text{NO}]$  react in THF to provide, after cation exchange, a 43% isolated yield of orange, crystalline  $[\text{Et}_4\text{N}][\text{Mn}(\text{CO})_3(\text{NO})(\text{SnPh}_3)]$ .<sup>15</sup> Other derivatives of  $\text{Mn}(\text{CO})_3\text{NO}^{2-}$  have been obtained by the reactions of  $\text{K}_2[\text{Mn}(\text{CO})_3\text{NO}]$  with equivalent amounts of  $\text{Mn}(\text{CO})_4\text{NO}$  and  $\text{Fe}(\text{CO})_5$  in THF. From these reactions, air-stable, crystalline, bright orange  $[\text{PNP}]_2[\text{Mn}_2(\text{CO})_6(\text{NO})_2]$ <sup>16</sup> and golden  $[\text{PNP}]_2[\text{FeMn}(\text{CO})_7(\text{NO})]$ <sup>17</sup> were obtained in 40% and 30% isolated yields, respectively. Equimolar amounts of  $\text{Na}_2\text{Fe}(\text{CO})_4 \cdot 1.5\text{dioxane}$  and  $\text{Mn}(\text{CO})_4\text{NO}$  in THF, followed by cation exchange, also provided the identical heterobimetallic dianion in 40% yield as the  $\text{PNP}^+$  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  $\text{Co}(\text{CO})_3\text{NO}$ ,  $\text{Fe}(\text{CO})_3\text{NO}^-$ , and  $\text{Mn}(\text{CO})_3\text{NO}^{2-}$  to corresponding chromium and vanadium anions that would be analogous to  $\text{Mn}(\text{CO})_4^{3-}$  and  $\text{Cr}(\text{CO})_4^{4-}$ .<sup>18</sup> Further, since NO appears to be a stronger  $\pi$ -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.

**Acknowledgment.** We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (CHE82-10496) for continuing support of this research.

(15) Anal. Calcd for  $\text{C}_{29}\text{H}_{35}\text{MnN}_2\text{O}_4\text{Sn}$ : C, 53.65; H, 5.40; N, 4.32. Found: C, 53.62; H, 5.53; N, 4.25. <sup>1</sup>H NMR ( $\text{CD}_3\text{CN}$ )  $\delta$  7.74-7.24 (m, 15 H,  $\text{C}_6\text{H}_5$  of  $\text{Ph}_3\text{Sn}$ ), 3.14 (q, 8 H,  $\text{CH}_2$  of  $\text{Et}_4\text{N}^+$ ), 1.20 (tt, 12 H,  $\text{CH}_3$  of  $\text{Et}_4\text{N}^+$ ). IR ( $\nu(\text{CO}, \text{NO})$ ,  $\text{CH}_3\text{CN}$ ) 1975 (s), 1895 (m), 1860 (s), 1640 (m)  $\text{cm}^{-1}$ .

(16) Anal. Calcd for  $\text{C}_{78}\text{H}_{60}\text{Mn}_2\text{N}_4\text{O}_8\text{P}_4$ : 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 ( $\nu(\text{CO}, \text{NO})$ , THF) 1970 (m), 1890 (s), 1860 (s), 1650 (m), 1610 (s)  $\text{cm}^{-1}$ . <sup>1</sup>H NMR (acetone- $d_6$ )  $\delta$  7.77-7.30 (m,  $\text{C}_6\text{H}_5$  of  $(\text{Ph}_3\text{P})_2\text{N}^+$ ); no M-H signals were present.

(17) Anal. Calcd for  $\text{C}_{79}\text{H}_{60}\text{FeMnN}_3\text{O}_8\text{P}_4$ : C, 67.10; H, 4.29; N, 2.97. Found: C, 67.03; H, 4.41; N, 2.79. IR ( $\nu(\text{CO}, \text{NO})$ , THF) 1985 (m), 1940 (w), 1870 (s), 1645 (m)  $\text{cm}^{-1}$ . <sup>1</sup>H NMR (acetone- $d_6$ )  $\delta$  7.80-7.30 (m,  $\text{C}_6\text{H}_5$  of  $(\text{Ph}_3\text{P})_2\text{N}^+$ ); no M-H signals were present.

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

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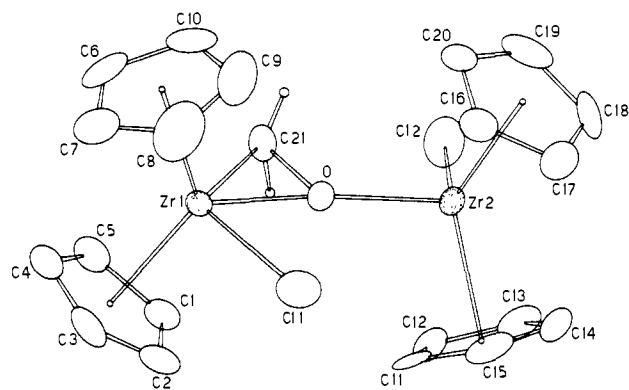
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All chemists interested in carbon monoxide activation are familiar with Bercaw's modeling studies based on zirconium hydrides, which detail the promotion of the stoichiometric reduction of CO to methanol and to  $\text{C}_2$ -unit precursors.<sup>1</sup> Many of the Bercaw's observations have been interpreted in a sequence involving, as a key intermediate, the oxymethylene ligand bridging

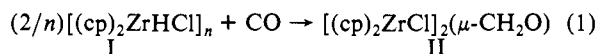
(1) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* 1980, 13, 121-127 and references cited therein.



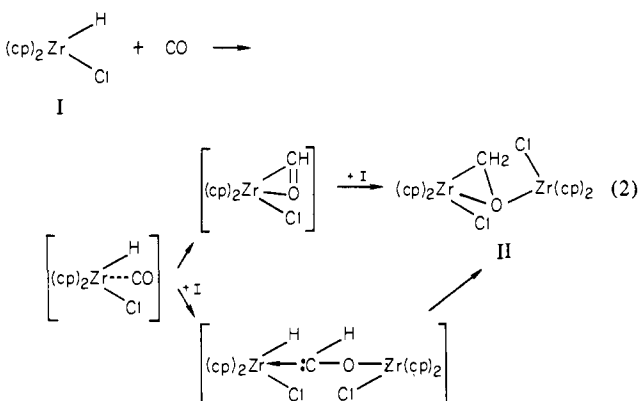
**Figure 1.** ORTEP view of II. Selected bond lengths (Å) and angles (deg) are as follows: Zr1-C21, 2.19 (1); Zr1-O, 2.13 (1); Zr1-Cl1, 2.522 (5); Zr2-Cl2, 2.344 (4); Zr2-O, 2.10 (1); O-C21, 1.43 (2); Zr1-O-Zr2, 166.9 (4); cp1-Zr1-cp2, 126.6(5); cp3-Zr-cp4, 129.1 (4). cp1, cp2, cp3, and cp4 are the centroids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

two zirconium atoms ( $\text{Zr}-\text{O}-\text{CH}_2\text{Zr}$ ), whose reactivity with carbon monoxide was viewed as the reaction leading to  $\text{C}_2$  units.<sup>1,2</sup> The intermediacy of such a unit is partially supported by our isolation of a complex<sup>3</sup> coming from the reaction of CO with  $[(\text{cp})_2\text{Zr}(\text{H})\text{Cl}]_n$ .<sup>4</sup> The choice of  $[(\text{cp})_2\text{Zr}(\text{H})\text{Cl}]_n$  was mainly dictated by the fact that it contains only one potential migrating ligand rather than two as in  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2]$ .<sup>1</sup>

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



zirconium, allowing the isolation of complex II.<sup>5</sup> 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,<sup>1</sup> 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.<sup>1</sup> The

(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.; Moley, 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 exposed 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  $\text{CHCl}_3$  (50 mL). Undissolved NaCl was filtered out. The resulting solution was concentrated, and 30 mL of  $\text{Et}_2\text{O}$  was added. The solution upon standing for 12 h at room temperature gave a light yellow crystalline solid (1.05 g). Anal. Calcd for  $[(\text{cp})_2\text{ZrCl}]_2(\mu\text{-CH}_2\text{O})$  ( $\text{C}_{21}\text{H}_{22}\text{Cl}_2\text{OZr}$ ): C, 46.41; H, 4.05; Cl, 13.08. Found: C, 46.00; H, 4.04; Cl, 13.36.  $\nu_{\text{CO}}(\text{Nujol})$  1015  $\text{cm}^{-1}$  (s). <sup>1</sup>H NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , room temperature) 7.17 (2 H, s,  $\text{CH}_2$ ), 3.87 (20 H, s, cp).