carbon distance is >3.5 Å from all of the published X-ray structural data on I–VI. The trial correlations involving the isotropic shieldings (δ_{iso}), the tensor components δ_{11} and δ_{22}, and the asymmetry parameters (η), are not good, but excellent correlations are obtained between δ_{33} and $\Delta\delta$ with R (Figures 1 and 2) and between δ_{33} and $\Delta\delta$ with D (Figures 3 and 4). In each of these correlations the horizontal bars that correspond to IV arise because of the uncertainty in the choice of the particular structural isomer and hence the appropriate values for r_1 and r_2. In each of these four cases (Figures 1–4) we made a least-squares fit of the data to a hyperbolic curve and the quality of the fits is such that we suggest that these curves may be used to find D and R and hence r_1 and r_2 (via eqs 6 and 7) for asymmetric bridging groups. It should be borne in mind that these carbonyl chemical shifts, while reflecting the degree of asymmetry of the bridge also include contributions from the nature and number of other substituents in the molecule and both intra- and intermolecular solid-state effects. However these additional contributions are likely to be relatively small, probably smaller than the spread in shielding values shown by the terminal ligands.

Conclusion

The slow MAS solid-state ^{13}C spectra of symmetrical double-bridging CO groups have the lowest frequency component of the chemical shift tensor in the region δ_{33} = 155–185 ppm and the chemical shift anisotropy in the region $\Delta\delta$ = 120–140 ppm. *Asymmetric* double-bridging and *terminal* CO groups have significantly lower frequency values for δ_{33} and much greater values for $\Delta\delta$. It has previously been reported[30] that the δ_{33} component for CO is quite invariant to the metal in the complexes $Ni(CO)_4$ and $Fe(CO)_5$ and in free CO. In contrast to this our results show that δ_{33} is the one component to give good correlation with the degree of bridging of the CO group. Furthermore, it is interesting to note that the value of δ_{33} is the least sensitive to errors in our application of the analysis of experimental data. This makes δ_{33} an even more valuable parameter. Similarly, $\Delta\delta$ (but not the asymmetry parameter, η) is a good indicator of the asymmetry in the CO group bridging. If our results are substantiated by further work, it may be possible to use derived δ_{33} and $\Delta\delta$ values to estimate the distances between the carbonyl carbon of an asymmetric bridging CO group and the iron atoms to which it is coordinated. This is an empirical correlation for which, as yet, we have no theoretical explanation. We are, however, investigating the quality of this type of correlation for the carbonyl complexes of the second- and third-row transition metals ruthenium and osmium.

Acknowledgment. The spectra of *cis*- and *trans*-I, II, IV, and V were measured by the University of London Intercollegiate Solid-State NMR Service (Bruker MSL-300) managed by Dr. C. J. Groombridge at Royal Holloway and Bedford New College.

Registry No. *cis*-I, 33221-55-5; *trans*-I, 32757-46-3; II, 76216-28-9; III, 57556-83-9; IV, 12101-59-6; V, 15321-51-4; VI, 17685-52-8.

---

(30) Mahnke, H.; Sheline, R. K.; Spiess, H. W. *J. Chem. Phys.* **1974**, *61*, 55–60.

Contribution from the Departamento de Quîmica Inorgânica—Instituto de Ciencia de Materiales,
Facultad de Quîmica, Universidad de Sevilla—CSIC, 41071 Sevilla, Spain, Department of Chemistry,
University of Alabama, University, Alabama 35486, and Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115

Formation of Carbonyl–Carbonate Complexes of Molybdenum by Reductive Disproportionation of Carbon Dioxide. X-ray Structure of $Mo_4(\mu_4\text{-}CO_3)(CO)_2(O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}OH)_4(PMe_3)_6$

Rafael Alvarez,[1a] Jerry L. Atwood,*[,1b] Ernesto Carmona,*[,1a] Pedro J. Pêrez,[1a] Manuel L. Poveda,[1a] and Robin D. Rogers*[,1c]

Received April 16, 1990

The reaction of carbon dioxide with the bis(dinitrogen) complex *cis*-$Mo(N_2)_2(PMe_3)_4$, in coordinating solvents, gives the carbonyl–carbonate complexes $[Mo(\mu_2\text{-}\eta^1,\eta^2\text{-}CO_3)(CO)(PMe_3)_3]_2$ (**2**) and $Mo(CO_3)(CO)(PMe_3)_4$ (**3**) derived from the metal-induced reductive disproportionation of CO_2. The use of Et_2O or THF as the reaction solvent leads to the preferential formation of binuclear **2** whereas in acetone monomeric **3** is the preferred product. Compounds **2** and **3** interconvert readily by association or dissociation of PMe_3, and their solution stabilities have been found to be strongly solvent dependent. Interaction of **3** with the chelating phosphines dmpe or dmpm (dmpe = $Me_2PCH_2CH_2PMe_2$; dmpm = $Me_2PCH_2PMe_2$), under appropriate conditions, affords the related complexes $Mo(CO_3)(CO)(P\text{-}P)(PMe_3)_2$ (P-P = dmpe, **4**; P-P = dmpm, **5**) and $Mo(CO_3)(CO)(dmpe)_2$ (**6**). Compounds **2** and **3** react with H_2O with formation of an unusual tetrametallic, mixed-valence Mo(II)–Mo(V) complex $Mo_4(\mu_4\text{-}CO_3)(CO)_2(O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}OH)_4(PMe_3)_6$ (**7**) that contains a unique carbonate ligand engaged in a novel type of bonding. The structure of **7** has been determined by X-ray crystallography. Crystals of **7** are orthorhombic, *Pbcn*, with unit cell constants a = 26.866 (9) Å, b = 12.934 (4) Å, c = 11.965 (2) Å, and D(calcd) = 1.74 g cm^{-3} for Z = 4.

Introduction

Studies on the chemical reactivity of electron-rich metal complexes have shown they are able to promote a number of interesting transformations of carbon dioxide.[2] A commonly observed reaction is oxygen transfer from CO_2 to another substrate. The latter could be for example an oxophilic metal center[3,4] or a readily oxidized ligand, frequently a phosphine ligand.[5] In some other cases, oxygen transfer from one molecule of CO_2 to another is observed, and in fact, a common reaction experienced by CO_2, when exposed to strongly reducing metal systems, is its reductive disproportionation[6a] to CO_3^{2-} and CO (eq 1). This transformation,

---

(1) (a) Universidad de Sevilla—CSIC. (b) University of Alabama. (c) Northern Illinois University.

(2) For recents reviews on CO_2 chemistry see: (a) Walter, D. *Coord. Chem. Rev.* **1987**, *79*, 135. (b) Braunstein, P.; Matt, D.; Nobel, D. *Chem. Rev.* **1988**, *88*, 747. (c) Behr, A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 661. (d) Behr, A. *Carbon Dioxide Activation by Metal Complexes*; VCH Publishers: Weinheim, FRG, 1988.

(3) Fachinetti, G.; Floriani, C.; Chiesei-Villa.; Gaustini, C. *J. Am. Chem. Soc.* **1979**, *101*, 1767.

(4) Bryan, J. C.; Geib, S. J.; Rheingold, A. L.; Mayer, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 2826.

(5) (a) Bianchini, C.; Mealli, C.; Melli, A.; Sabat, M. *Inorg. Chem.* **1984**, *23*, 2731. (b) Bianchini, C.; Melli, A. *J. Am. Chem. Soc.* **1984**, *106*, 2698. (c) Ito, T.; Yamamoto, A. *J. Chem. Soc., Dalton Trans.* **1975**, 1398. (d) Aresta, M.; Nobile, C. F. *Inorg. Chim. Acta* **1977**, *24*, L49.

0020-1669/91/1330-1493$02.50/0 © 1991 American Chemical Society

$$2CO_2 + 2e^- \rightarrow CO_3^{2-} + CO \qquad (1)$$

first observed by Chatt and co-workers[7] in the reaction of *cis*-$Mo(N_2)_2(PMe_2Ph)_4$ with CO_2, was later investigated by Floriani in titanium based systems,[3] e.g. $Cp_2Ti(CO)_2$. Often, the usually irreversible formation of CO_3^{2-} and CO is an unwanted feature when one is pursuing more interesting metal-induced transformations of carbon dioxide. Recently, however, we have reported[8] the first examples of the reverse reaction of eq 1, namely the oxidative conproportionation of CO_3^{2-} and CO to two molecules of CO_2, a reaction subsequently observed by others in an iridium system.[9]

Several years ago, we carried out the reaction of CO_2 with the dinitrogen complex *cis*-$Mo(N_2)_2(PMe_3)_4$ and found out that, depending upon the reactions conditions, products resulting from adduct formation or from the reductive disproportionation of CO_2 can be formed. Although a few mononuclear transition-metal–carbon dioxide complexes are already known, complex formation is still a rare process in CO_2 chemistry.[10] On the other hand, reductive disproportionation can be induced either by thermal methods[3,7,11] or by photochemical methods.[12] Observation of both type of products, i.e. CO_2 adduct and disproportionation products, is however remarkable and hence this unusual molybdenum system is amenable to a detailed study of the conditions that favour the formation of one or the other type of products. The synthesis and characterization of bis-carbon dioxide adducts of molybdenum have been described in a previous publication.[10a] In this contribution we wish to report in full detail[13] the formation of carbonyl-carbonate complexes resulting from the metal-promoted reductive disproportionation of carbon dioxide.

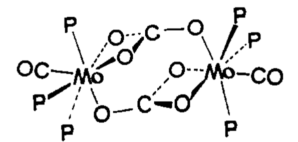
Results

Formation of $[Mo(\mu_2\text{-}\eta^1,\eta^2\text{-}CO_3)(CO)(PMe_3)_3]_2$ (2) and $Mo(\eta^2\text{-}CO_3)(CO)(PMe_3)_4$ (3). As already reported,[10a] exposure of dilute petroleum ether solutions (ca. 0.01 M) of the dinitrogen complex *cis*-$Mo(N_2)_2(PMe_3)_4$ to an atmosphere of carbon dioxide (3–4 atm total pressure) results in the formation of the yellow, microcrystalline adduct *trans*-$Mo(CO_2)_2(PMe_3)_4$ (**1**) in ca. 80% yield. This transformation is very sensitive to the reaction conditions, in particular to the nature of the solvent used. Thus if the reaction is carried out in weakly coordinating solvents, the main products are either the red dimeric, carbonate-bridged $[Mo(\mu_2\text{-}\eta^1,\eta^2\text{-}CO_3)(CO)(PMe_3)_3]_2$ (**2**) or the monomeric, dark-blue $Mo(CO_3)(CO)(PMe_3)_4$ (**3**). For example, upon leaving undisturbed at room temperature the reaction mixture resulting from the exposure of a ca. 0.04 M diethyl ether solution of *cis*-$Mo(N_2)_2(PMe_3)_4$ to 3 atm of CO_2, the originally yellow solution slowly becomes red in color, and after several hours well-formed red crystals of **3** are obtained. After the mixture is allowed to stand at room temperature for ca. 12 h, the reaction is essentially complete and the resulting crystalline product can be separated by filtration. When obtained in this way, **2** is contaminated by yellow **1** (ca. 30%) from which it can be separated either by a manual method, taking advantage of the stability of both complexes in air for short periods of time, or preferably by successive washings with toluene or THF (THF = tetrahydrofuran), which bring into solution the more soluble bis(carbon dioxide) adduct **1**. An alternative, higher yield route to **2**, which is devoid of the above inconveniences, has been developed and will be discussed at a later stage.

As already indicated, red, binuclear $[Mo(CO_3)(CO)(PMe_3)_3)]_2$ can be manipulated in air for short periods of time when in a crystalline form, although in solution it becomes much more sensitive to the atmosphere. In addition to characteristic bands associated with the PMe_3 ligands, its IR spectrum shows two strong absorptions centered at 1765 and 1500 cm^{-1}. Despite its low wavenumber, the first can be attributed to ν(C–O) of a terminal carbonyl group (1760 cm^{-1} in the analogous $[Mo(CO_3)(CO)(PMe_2Ph)_3]_2$[7]) whereas the latter indicates the presence of a carbonate ligand. Formation of **2** can be represented as shown in eq 2.

$$cis\text{-}Mo(N_2)_2(PMe_3)_4 + 2CO_2 \rightarrow \tfrac{1}{2}[Mo(CO_3)(CO)(PMe_3)_3]_2 + 2N_2 + 2PMe_3 \qquad (2)$$

The dimeric nature of this compound has been demonstrated by X-ray studies. The structural features found are similar to those reported for the closely related[7] $[Mo(CO_3)(CO)(PMe_2Ph)_3]_2$, but the quality of the X-ray data does not warrant a useful discussion. A schematic representation of **2** is given and will not be further discussed.



2

Compound **2** is sparingly soluble in common organic solvents. Of the solvents tested, the only one in which **2** has appreciable solubility is hot THF, and in this respect, it should be pointed out that, once in solution, recrystallization at lower temperatures is a very slow process. Compound **2** also dissolves in acetone–water mixtures, from which it can be recrystallized, but the manipulation time at room temperature must be short since other chemical transformations could otherwise occur. The $^{31}P\{^1H\}$ NMR spectrum of **2**, recorded after dissolution in THF at 40 °C, shows two AX_2 spin systems in a ca. 2:1 ratio (δ_A 40.9, δ_X 44.0 ppm, $^2J_{AX}$ = 29.3 Hz; δ_A 39.4, δ_X 43.2 ppm, $^2J_{AX}$ = 29.6 Hz, respectively). Since prolonged heating at 40 °C does not alter the above ratio, it is clear that solutions of **2** contain two isomeric species that are under thermodynamic equilibrium. The similarity of the ^{31}P NMR data for these two species further suggests that both complexes have closely related structures.

One of these isomers could be that found in the solid state, since an AX_2 pattern would be expected in the $^{31}P\{^1H\}$ NMR spectrum for such a species. At this respect, it should be recalled that the halves of the molecule are related by a center of inversion and, moreover, that each of the carbonyl groups in the dimeric molecules of **2** caps the triangular face formed by the phosphine ligands in the pseudo-capped-octahedral geometry around the molybdenum atoms. As for the second isomer, a related structure in which one of the phosphine ligands has exchanged its position with the carbonyl group would be consistent with the available spectroscopic data. We note, however, that other structures are also conceivable, and hence, in the absence of sufficient spec-

---

[6] (a) Inoue, S.; Yamazaki, N. *Organic and Bio-organic Chemistry of Carbon Dioxide*; Halsted Press: Tokyo, Japan, 1982. (b) Palmer, D. A.; Van Eldik, R. *Chem. Rev.* **1983**, *83*, 651.

[7] Chatt, J.; Kubota, M.; Leigh, G. J.; March, T. C.; Mason, R.; Yarrow, D. J. *J. Chem. Soc., Chem. Commun.* **1974**, 1033.

[8] (a) Carmona, E.; Palma, P.; Paneque, M.; Poveda, M. L.; Gutiérrez-Puebla, E.; Monge, A. *J. Am. Chem. Soc.* **1986**, *108*, 6424. (b) Carmona, E.; Gutiérrez-Puebla, E.; Marín, J. M.; Monge, A.; Paneque, M.; Poveda, M. L.; Ruiz, C. *J. Am. Chem. Soc.* **1989**, *111*, 2883. (c) Carmona, E.; Marín, J. M.; Palma, P.; Paneque, M.; Poveda, M. L. *Inorg. Chem.* **1989**, *28*, 1895.

[9] Reinking, M. K.; Ni, J.; Fanwick, P. E.; Kubiak, C. P. *J. Am. Chem. Soc.* **1989**, *111*, 6454.

[10] For mononuclear, structurally characterized M–CO_2 complexes see: (a) Alvarez, R.; Carmona, E.; Marín, J. M.; Poveda, M. L.; Gutiérrez-Puebla, E.; Monge, A. *J. Am. Chem. Soc.* **1986**, *108*, 2286. (b) Aresta, M.; Nobile, C. F.; Albano, V. G.; Forni, E.; Manassero, M. *J. Chem. Soc., Chem. Commun.* **1975**, 36. (c) Bristow, G. S.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1981**, 1145. (d) Gambarotta, S.; Arena, F.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* **1982**, *104*, 5082. (e) Calabrese, J. C.; Herskovitz, T.; Kinney, J. B. *J. Am. Chem. Soc.* **1983**, *105*, 5914. (f) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Gaustini, C. *J. Am. Chem. Soc.* **1985**, *107*, 2985.

[11] (a) Karsch, H. H. *Chem. Ber.* **1977**, *110*, 2213. (b) Lee, G. R.; Maher, J. M.; Cooper, N. J. *J. Am. Chem. Soc.* **1987**, *109*, 2956. (c) Fong, L. K.; Fox, J. R.; Cooper, N. J. *Organometallics* **1987**, *6*, 223. (d) Dahlenburg, L.; Pietsch, B. *Chem. Ber.* **1989**, *122*, 2085. (e) Dahlenburg, L.; Pietsch, B. *J. Organomet. Chem.* **1989**, *378*, 199. (f) Allen, D. L.; Green, M. L. H.; Bandy, J. A. *J. Chem. Soc., Dalton Trans.* **1990**, 541.

[12] Belmore, K. A.; Vanderpool, R. A.; Tsai, J.-C.; Khan, M. A.; Nicholas, K. M. *J. Am. Chem. Soc.* **1988**, *110*, 2004.

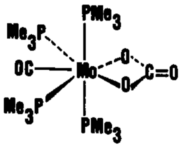
[13] For a preliminary communication of this work, see: Carmona, E.; González, F.; Poveda, M. L.; Marín, J. M. *J. Am. Chem. Soc.* **1983**, *105*, 3365.

troscopic data, further speculation on the nature of these species seems unwarranted.

When the reaction of *cis*-$Mo(N_2)_2(PMe_3)_4$ and CO_2 is carried out in acetone, in the presence of free, added PMe_3, a new, dark-blue highly crystalline solid of composition $Mo(CO_3)(CO)(PMe_3)_4$ (**3**) is formed in ca. 80% yield. Again, the existence in the molecules of this complex of carbonyl and carbonate ligands can be inferred from the appearance of characteristic, strong IR absorptions at 1810 and 1600 cm^{-1}. The frequency of the latter suggests bidentate coordination of the CO_3 ligand.[14] The formation of complex **3** can be represented as depicted in eq 3.

$$cis\text{-}Mo(N_2)_2(PMe_3)_4 + 2CO_2 \rightarrow Mo(CO_3)(CO)(PMe_3)_4 + 2N_2 \quad (3)$$

Compound **3** is very soluble in CH_3OH and CH_2Cl_2, in which solvents it forms red solutions from which it can be recovered unaltered by evaporation of the solvent under vacuum.[15] Its $^{31}P\{^1H\}$ NMR spectrum consists of an A_2X_2 spin system with δ_A 28.9, δ_X 0.0 ppm and $^2J_{AX}$ = 28.2 Hz. From these data, structure A can be proposed for this complex.



A

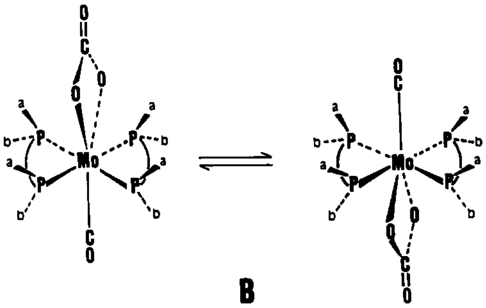
Reactions of 3 with Chelating Phosphines. The facility with which THF solutions of complex **3** dissociate one of the PMe_3 ligands (see Discussion) can be successfully exploited for the preparation of related carbonyl–carbonate complexes containing chelating phosphine ligands. Thus, addition of the bidentate phosphines dmpe or dmpm (dmpe = $Me_2PCH_2CH_2PMe_2$; dmpm = $Me_2PCH_2PMe_2$) to solutions of **3** yields orange-red crystalline materials of composition $Mo(CO_3)(CO)(P\text{-}P)(PMe_3)_2$ (P-P = dmpe, **4**; P-P = dmpm, **5**), eq 4. Both complexes show IR spectral

$$Mo(CO_3)(CO)(PMe_3)_4 + P\text{-}P \rightarrow \underset{\mathbf{4,5}}{Mo(CO_3)(CO)(P\text{-}P)(PMe_3)_2} + 2PMe_3 \quad (4)$$

features similar to those of **3**, with characteristic IR absorptions at around 1790 (CO) and 1600 cm^{-1} (CO_3). Substitution of the PMe_3 ligands in **5** by a second molecule of dmpm does not take place at room temperature, and upon heating at 40–50 °C decomposition is observed. In contrast, complex **4** undergoes a smooth reaction with dmpe (eq 5) with formation of the $(dmpe)_2$

$$Mo(CO_3)(CO)(dmpe)(PMe_3)_2 + dmpe \rightarrow Mo(CO_3)(CO)(dmpe)_2 + 2PMe_3 \quad (5)$$

derivative **6** (IR bands at 1793 and 1604 for the CO and CO_3 ligands, respectively). Compounds **4**–**6** display dynamic behavior in solution. The $^{31}P\{^1H\}$ NMR spectrum of **4** exhibits at −85 °C an AMNX pattern, which converts into two very broad signals at 20 °C. As for **5**, two very broad ^{31}P doublets are observed at low temperatures, whereas in the fast-exchange limit (60 °C) an A_2X_2 system is obtained (δ_A 7.5, δ_X 24.4 ppm; $^2J_{AX}$ = 22.8 Hz). The seven-coordinate nature of these species, which allows three idealized geometries (pentagonal bipiramid, monocapped octahedron and monocapped trigonal prism), along with the complexity of the spectra obtained, does not allow a unique structural proposal to be made. For **6** the situation is somewhat simpler. At −45 °C (CD_3CN), the four ^{31}P nuclei are equivalent and give rise to a singlet at 52.7 ppm, which broadens upon raising the temperature ($\Delta\nu_{1/2}$ = 40 Hz at 20 °C) but becomes sharper again at higher temperatures (50–60 °C). On the other hand, the methyl protons of the chelating diphosphine give two well-defined resonances of equal intensity at −40 °C, but become equivalent at higher temperatures and yield a pseudoquintet at temperatures close to 75 °C. These data are consistent with a ground structure of type B, for which two degenerate representations can be drawn. The equilibration of these degenerate structures could involve exchange of the CO_3 and CO sites through the intermediacy of an η^1-CO_3.



B

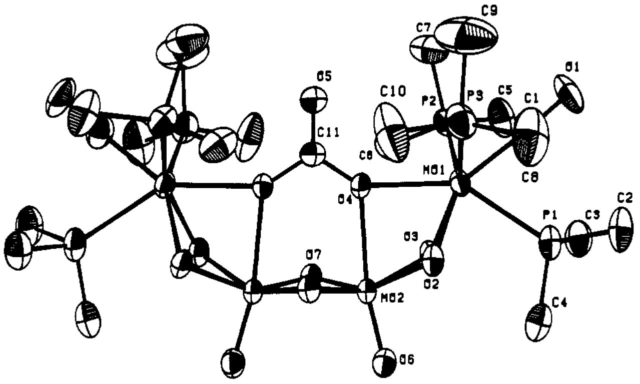


Figure 1. ORTEP illustration of $[Mo_4(\mu_4\text{-}CO_3)(CO)_2(O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}OH)_4(PMe_3)_6]$ with 50% probability ellipsoids for thermal motion. Hydrogen atoms have been omitted.

Synthesis and X-ray Structure of $Mo_4(\mu_4\text{-}CO_3)(CO)_2(O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}OH)_4(PMe_3)_6$ (7). As reported in preliminary form,[13] the reaction of *cis*-$Mo(N_2)_2(PMe_3)_4$ with CO_2 in a 2:1 acetone–toluene mixture gives, in addition to **3**, small amounts of a highly crystalline red-orange complex **7**. Since this transformation provides very low yields of **7** and requires 15–20 days for completion, an alternative route has been sought. The nature of compound **7**, which as discussed below contains coordinated oxo and hydroxo groups, indicates the participation of water in the reaction leading to its formation. Indeed heating a THF solution of **2** at 50 °C for several hours, in the presence of water, produces complex **7**, although yields are very low (~10%). In spite of our efforts, we have not succeeded in devising a better route to **7**. This complex is obtained upon heating solutions of either **2** or **3** for several hours at ~50 °C in THF, acetone, or CH_3OH as the solvent, but yields remain low (10–15%) under a variety of experimental conditions.

The IR spectrum of this material shows characteristic absorptions indicating the presence of hydroxo (3750 and 3400 cm^{-1}), carbonyl (1760 cm^{-1}), carbonate (1560 and 1280 cm^{-1}), oxo (975 cm^{-1}), and PMe_3 (945 cm^{-1}) ligands, but its insolubility in common organic solvents has precluded its characterization by NMR methods. Its molecular complexity has been determined by X-ray studies. An ORTEP illustration of the tetrametallic molecules of **7** is presented in Figure 1, bond distances and angles are given in Table I, and a summary of the crystallographic data is given in Table II.

Discussion

The formation of the compound $[Mo(CO_3)(CO)(PMe_2Ph)_3]_2$, i.e. the dimethylphenylphosphine analogue of complex **2**, in the reaction of *cis*-$Mo(N_2)_2(PMe_2Ph)_4$ and CO_2 led Chatt and coworkers to assume that a disproportionation reaction had occurred, although other possible routes could not be discarded.[7] Later work

---

(14) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley: New York, 1986.

(15) Complex **3** slowly converts in CH_2Cl_2 into a compound of composition $[PMe_4][MoCl_3(CO)(PMe_3)_3]$: Carmona, E.; Muñoz, M. A.; Rogers, R. D. *Inorg. Chem.* **1988**, *27*, 1598.

Table I. Bond Distances (Å) and Angles (deg) for 7

Bond Distances			
Mo(1)—Mo(2)	3.2014 (6)	Mo(1)—P(1)	2.442 (2)
Mo(1)—P(2)	2.451 (2)	Mo(1)—P(3)	2.428 (2)
Mo(1)—O(2)	2.211 (4)	Mo(1)—O(3)	2.222 (3)
Mo(1)—O(4)	2.221 (3)	Mo(1)—C(1)	1.918 (6)
Mo(2)—O(2)	2.092 (3)	Mo(2)—O(3)	2.078 (3)
Mo(2)—O(4)	2.419 (3)	Mo(2)-O(6)	1.671 (3)
Mo(2)—O(7)	1.948 (3)	Mo(2)—O(7)[a]	1.943 (3)
Mo(2)—Mo(2)[a]	2.552 (1)	P(1)—C(2)	1.822 (6)
P(1)—C(3)	1.819 (6)	P(1)—C(4)	1.817 (7)
P(2)—C(5)	1.830 (6)	P(2)—C(6)	1.828 (6)
P(2)—C(7)	1.804 (7)	P(3)—C(8)	1.810 (7)
P(3)—C(9)	1.796 (9)	P(3)—C(10)	1.802 (7)
O(1)—C(1)	1.183 (7)	O(4)—C(11)	1.316 (5)
O(5)—C(11)	1.210 (9)		
Bond Angles			
Mo(2)—Mo(1)—P(1)	95.63 (4)	Mo(2)—Mo(1)—P(2)	112.24 (4)
P(1)—Mo(1)—P(2)	113.73 (6)	Mo(2)—Mo(1)—P(3)	112.65 (5)
P(1)—Mo(1)—P(3)	110.66 (6)	P(2)—Mo(1)—P(3)	111.12 (6)
Mo(2)—Mo(1)—O(2)	40.53 (8)	P(1)—Mo(1)—O(2)	79.39 (9)
P(2)—Mo(1)—O(2)	152.49 (9)	P(3)—Mo(1)—O(2)	84.1 (1)
Mo(2)—Mo(1)—O(3)	40.18 (9)	P(1)—Mo(1)—O(3)	77.88 (9)
P(2)—Mo(1)—O(3)	86.9 (1)	P(3)—Mo(1)—O(3)	152.8 (1)
O(2)—Mo(1)—O(3)	71.9 (1)	Mo(2)—Mo(1)—O(4)	48.99 (9)
P(1)—Mo(1)—O(4)	144.6 (1)	P(2)—Mo(1)—O(4)	85.2 (1)
P(3)—Mo(1)—O(4)	87.4 (1)	O(2)—Mo(1)—O(4)	72.3 (1)
O(3)—Mo(1)—O(4)	73.5 (1)	Mo(2)—Mo(1)—C(1)	168.7 (2)
P(1)—Mo(1)—C(1)	73.1 (2)	P(2)—Mo(1)—C(1)	72.7 (2)
P(3)—Mo(1)—C(1)	73.3 (2)	O(2)—Mo(1)—C(1)	134.7 (2)
O(3)—Mo(1)—C(1)	133.1 (2)	O(4)—Mo(1)—C(1)	142.3 (2)
Mo(1)—Mo(2)—O(2)	43.4 (1)	Mo(1)—Mo(2)—O(3)	43.64 (9)
O(2)—Mo(2)—O(3)	77.2 (1)	Mo(1)—Mo(2)—O(4)	43.87 (8)
O(2)—Mo(2)—O(4)	70.5 (1)	O(3)—Mo(2)—O(4)	72.0 (1)
Mo(1)—Mo(2)—O(6)	125.6 (1)	O(2)—Mo(2)—O(6)	101.5 (2)
O(3)—Mo(2)—O(6)	100.0 (2)	O(4)—Mo(2)—O(6)	169.5 (1)
Mo(1)—Mo(2)—O(7)	108.8 (1)	O(2)—Mo(2)—O(7)	84.2 (1)
O(3)—Mo(2)—O(7)	151.5 (1)	O(4)—Mo(2)—O(7)	81.5 (1)
O(6)—Mo(2)—O(7)	104.9 (2)	O(2)—Mo(2)—O(7)[a]	151.1 (1)
O(3)—Mo(2)—O(7)[a]	89.5 (1)	O(4)—Mo(2)—O(7)[a]	81.1 (1)
O(6)—Mo(2)—O(7)[a]	106.1 (2)	O(7)—Mo(2)—O(7)[a]	96.8 (2)
Mo(2)—O(7)—Mo(2)[a]	82.0 (2)	Mo(1)—P(1)—C(2)	120.4 (2)
Mo(1)—P(1)—C(3)	113.6 (2)	C(2)—P(1)—C(3)	102.1 (3)
Mo(1)—P(1)—C(4)	115.2 (2)	C(2)—P(1)—C(4)	100.6 (3)
C(3)—P(1)—C(4)	102.5 (3)	Mo(1)—P(2)—C(5)	118.3 (2)
Mo(1)—P(2)—C(6)	114.6 (2)	C(5)—P(2)—C(6)	101.0 (3)
Mo(1)—P(2)—C(7)	114.8 (3)	C(5)—P(2)—C(7)	103.6 (3)
C(6)—P(2)—C(7)	102.4 (3)	Mo(1)—P(3)—C(8)	113.5 (3)
Mo(1)—P(3)—C(9)	119.7 (3)	C(8)—P(3)—C(9)	101.5 (5)
Mo(1)—P(3)—C(10)	116.8 (2)	C(8)—P(3)—C(10)	100.8 (4)
C(9)—P(3)—C(10)	101.8 (4)	Mo(1)—O(2)—Mo(2)	96.1 (1)
Mo(1)—O(3)—Mo(2)	96.2 (1)	Mo(1)—O(4)—Mo(2)	87.1 (1)
Mo(1)—O(4)—C(11)	145.4 (4)	Mo(2)—O(4)—C(11)	127.4 (4)
Mo(1)—C(1)—O(1)	178.3 (6)	O(4)—C(11)—O(5)	123.2 (3)
O(4)—C(11)—O(4)[a]	113.5 (7)		

[a] Atoms related by $-x, y, {}^{3}/_{2} - z$.

Table II. Crystallographic data for 7[b]

chem formula: $C_{21}H_{58}Mo_4O_{13}P_6$	$Z = 4$
fw = 1088.3	$T = 22$ °C
space group: *Pbcn*	$\lambda = 0.71073$ Å
$a = 26.866$ (9) Å[a]	$\rho_{calc} = 1.74$ g cm^{-3}
$b = 12.934$ (4) Å[a]	$\mu_{calc} = 14.36$ cm^{-1}
$c = 11.965$ (2) Å[a]	$R = \sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\sum\lvert F_o\rvert = 0.018$
$V = 4157.7$ Å^3	$R_w = 0.022$

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections $\theta > 20°$. [b] Computer programs: SHELX.[26] Neutral scattering factors and anomalous dispersion corrections were taken from ref 27.

by Floriani, based on the reaction of $Cp_2Ti(CO)_2$ with $^{13}CO_2$ (eq 6), conclusively demonstrated this assumption.

$$4Cp_2Ti(CO)_2 + 4\,^{13}CO_2 \rightarrow [(Cp_2Ti)_2(^{13}CO_3)]_2 + 8CO + 2\,^{13}CO \quad (6)$$

Since at variance with Floriani's transformation both disproportionation products (i.e. CO_3^{2-} and CO) remain coordinated to the metal center in our molybdenum system, we have sought to demonstrate, with the aid of isotopic labeling experiments, that these groups form in a metal-promoted reductive disproportionation of CO_2. A sample of **2*** (enriched in ^{13}C in the CO and CO_3 ligands) was obtained by carrying out the reaction of *cis*-$Mo(N_2)_2(PMe_3)_4$ with $^{13}CO_2$, as shown in eq 7. The CO stretch

$$cis\text{-}Mo(N_2)_2(PMe_3)_4 + 2\,^{13}CO_2 \rightarrow \tfrac{1}{2}[Mo(^{13}CO_3)(^{13}CO)(PMe_3)_3]_2 + PMe_3 + 2N_2 \quad (7)$$

of **2*** appears at 1715 cm^{-1} (1765 cm^{-1} in **2**) whereas the band at 1500 cm^{-1}, assigned to the bridging CO_3 group in **2**, is also shifted to lower frequency in the IR spectrum of **2*** (1450 cm^{-1}). Other weaker bands that are associated with the CO_3 ligands in **2** and **2*** compare as follows: 1345, 835, and 560 cm^{-1} (data for **2**) vs 1310, 815, and 540 cm^{-1} in **2***. For **3***, the characteristic IR bands are at 1770 (CO) and 1550 cm^{-1} (CO_3). Similar IR absorptions have been reported for other carbonate complexes.[11,14]

When a suspension of **3** in THF is heated at 40-50 °C, in a closed vessel, the dark blue crystals dissolve slowly to yield a red solution that can be shown by $^{31}P\{^1H\}$ NMR to contain only the red dimer **2** (isomer ratio 5:1) and free PMe_3. Prolonged heating at 50 °C equilibrates this kinetically controlled mixture of isomers to a final ratio of ca. 2:1. On the other hand, when the mixture is cooled to room temperature or below, blue crystals of **3** deposit. These experiments demonstrate that compound **2** and **3** are closely related and interconvert readily in the way represented in eq 8.

$$\tfrac{1}{2}[Mo(CO_3)(CO)(PMe_3)_3]_2 + PMe_3 \rightleftharpoons Mo(CO_3)(CO)(PMe_3)_4 \quad (8)$$

Also in accord with the above is the fact that **3** is obtained in high yields (ca. 80%) upon exposure to CO_2 (3 atm) of a ca. 0.25 M THF solution of the dinitrogen complex *cis*-$Mo(N_2)_2(PMe_3)_4$, in the presence of ca. 1 equiv of added PMe_3 (under these conditions the bis(carbon dioxide) adduct is obtained in ca. 20% yield). The above observations highlight a convenient, high-yield synthesis of the binuclear carbonate **2**: this compound is quantitatively formed upon dissolution of **3** in THF at 50 °C, followed by evaporation of the solvent at this temperature.

At this time, some comments can be devoted to the different solution stabilities exhibited by complexes **2** and **3**. In THF solutions, only **2** can be detected, even in the presence of PMe_3, while, by contrast, monomeric $Mo(CO_3)(CO)(PMe_3)_4$ (**3**) is favored in CH_3OH to such an extent that solutions of **2** in this solvent rapidly disproportionate with formation of **3** and other unidentified products (eq 9). The course of this transformation

$$[Mo(CO_3)(CO)(PMe_3)_3]_2 \xrightarrow{CH_3OH} Mo(CO_3)(CO)(PMe_3)_4 + \text{other products} \quad (9)$$

can be monitored by $^{31}P\{^1H\}$ NMR spectroscopy: the spectrum of a recently prepared solution of **2** in MeOH at −40 °C (solubility reasons prevent solubilization at lower temperatures) reveals the presence of **2** and **3** in ca. 2:1 ratio, along with that of an unknown species, which gives a broad hump centered at ca. 19 ppm. Upon warming at 0 °C, only the latter signal and resonances associated to **3** can be detected, the latter gaining rapidly in intensity at the expense of the former signal. After 10 min at room temperature, only signals due to **3** are discernible. Obviously, some other unknown compounds that do not contain PMe_3 must be formed to account for the stoichiometry of the above transformation.

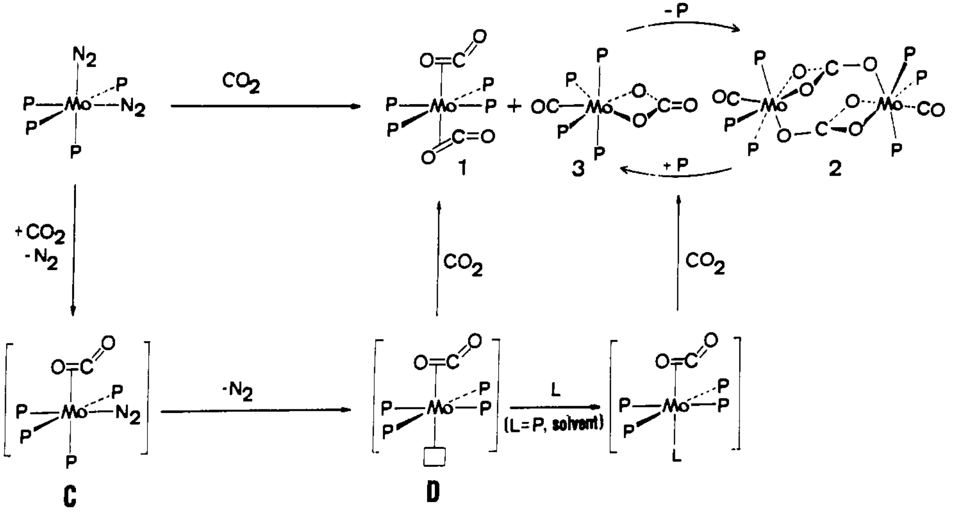
As already mentioned, the structure of complex **7** has been determined by X-ray crystallography. The compound is a mixed-valence Mo(II)-Mo(V) species of composition $Mo_4(\mu_4\text{-}CO_3)(CO)_2(O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}OH)_4(PMe_3)_6$. The molecules consist of two seven-coordinate Mo(II) and two six-coordinate (ignoring the Mo–Mo interaction) Mo(V) atoms bridged by a μ_4-carbonate ion and four μ_2-hydroxide ions. Furthermore, the two Mo(V) centers are bridged by two μ_2-oxide ions and form a Mo–Mo single bond. The carbonate ion resides on a crystallographic 2-fold axis containing C(11) and O(5).

The most interesting feature of this structure is the unique bridging mode of the carbonate ion. To the seemingly endless varieties of metal–carbonate coordination (a–i)[6b,16] we can now

---

(16) Einstein, F. W. B.; Willis, A. C. *Inorg. Chem.* **1981**, *20*, 609.

Scheme I. Formation of Compounds 1-3



add type j (Chart I). The two carbonate oxygen atoms off the 2-fold axis both bridge a Mo(II) (Mo(1)) atom and a Mo(V) (Mo(2)) atom. The Mo(II)-O(4) separation is 2.221 (3) Å while the Mo(V)-O(4) distance is 2.419 (4) Å. The latter bonds are probably longer than expected by virtue of the trans relationship to the molybdenum oxygen double bonds.

As expected with this type of bonding, the C-O bond without any metal interactions is significantly shorter (C(11)-O(5) = 1.210 (9) Å) than the other two such bonds (C(11)-O(4) = 1.316 (5) Å). In addition the O(4)-C(11)-O(4)′ angle is a compressed 113.5 (7)° versus 123.2 (3)° for O(4)-C(11)-O(5). The Mo(1)-O(4)-Mo(2) angle is nearly perpendicular at 87.1 (1)°. The molybdenum atoms are not bonded symmetrically to the carbonate ion, Mo(1)-O(4)-C(11) is a wide 145.4 (4)° compared to the Mo(2)-O(4)-C(11) angle of only 127.4 (4)°. The four metal atoms and the carbonate ligand are all planar to within 0.03 Å.

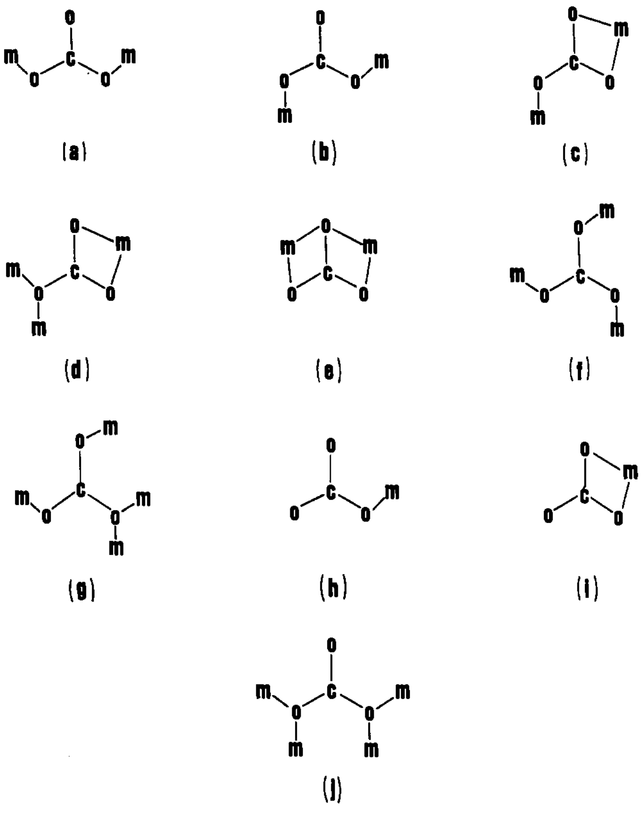
Mo(1) and Mo(2) are also bridged by two hydroxy ligands. The Mo(1)-OH distances average 2.216 (6) Å, nearly identical with the Mo(1)-OCO_2 separation. The Mo(2)-OH bonds are slightly shorter, averaging 2.085 (7) Å. Mo(1) is capped octahedral with the carbonyl capping the triangular face formed by the phosphine ligands. The Mo-CO and average Mo-P distances are 1.918 (6) and 2.440 (9) Å, respectively.

The $Mo_2O_4^{2+}$ moiety containing both Mo(2) atoms is characteristic of crystallographically studied units of this type.[17] The two Mo atoms have a distorted octahedral geometry, and there is a Mo-Mo single bond (2.552 (1) Å). The two μ_2-oxides form a bent bridge between the octahedron. The dihedral angle between Mo(2), O(7), and O(7)′ and Mo(2)′, O(7), and O(7)′ is 18.1°. The oxide bridges are nearly identical at 1.948 (3) and 1.943 (3) Å. The Mo(2)-O(6) double bond is a short 1.671 (3) Å.

Some Comments on the Competitive Reactions Leading to the CO_2 Adduct 1 and to the Disproportionation Products 2 and 3. The reaction of *cis*-$Mo(N_2)_2(PMe_3)_4$ with CO_2 can produce the $(CO_2)_2$ adduct **1** or the disproportionation products **2** and **3** either as the main reaction products or as mixtures in different proportions. For example, when CO_2 is bubbled through a petroleum ether solution of *cis*-$Mo(N_2)_2(PMe_3)_4$, a mixture of **1**, **2**, and **3** is obtained. If the reaction is carried out in the same solvent, but at relatively high dilution (ca. 0.01 M) and in the presence of a large excess of CO_2 (3-4 atm), **1** is obtained as the main reaction product. The use of Et_2O or THF as the solvent produces a mixture of **1** and **2** in variable amounts, whereas in acetone or toluene **3** is obtained as the main product. The presence of free, added PMe_3 favors the disproportionation of CO_2, and for instance, if the reaction is carried out in THF, in the presence of PMe_3, the yield of carbonate **3** rises to 80-85%.

As the CO_2 adduct **1** and the disproportionation products **2** and **3** cannot be interconverted, two different competitive pathways must lead to their respective formation. Consequently, any reasonable mechanistic proposal should take this fact into account. Since substitution of the N_2 ligands of *cis*-$Mo(N_2)_2(PMe_3)_4$ can be readily accomplished,[18] it is reasonable to assume that the first step in the above transformation is the formation of a common intermediate C, which can be formulated as a CO_2 adduct (arbitrarily proposed in Scheme I as having cis N_2 and CO_2 ligands) resulting from the substitution of one of the N_2 ligands by CO_2. Loss of N_2 from this intermediate could lead to a coordinatively and electronically unsaturated species, D. The proposed structure for D finds precedent in the unsaturated molecule Mo(CO)-$(Ph_2CH_2CH_2PPh_2)_2$, which has been structurally characterized by X-ray crystallography.[19] Incorporation of a second molecule

Chart I. Coordination Modes of the Carbonate Ligand



---

[17] Stiefel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 1 and references therein.

[18] Carmona, E.; Marín, J. M.; Poveda, M. L.; Atwood, J. L.; Rogers, R. D. *J. Am. Chem. Soc.* **1983**, *105*, 3014.

[19] Sato, M.; Tatsumi, T.; Kodama, T.; Hidai, M.; Uchida, T.; Uchida, Y. *J. Am. Chem. Soc.* **1978**, *100*, 4447.

of CO_2 into the vacant coordination site at D could lead to the bis(carbon dioxide) adduct **1**. Alternatively, incorporation of PMe_3 or of a solvent molecule would block the available coordination position and activate the coordinated CO_2, making it susceptible to electrophilic attack at the exo oxygen atom by the carbon atom of a second molecule of CO_2. Generation of the carbonate and carbonyl ligands, i.e. the products of the reductive disproportionation of CO_2, could involve a Herskovitz-type intermediate,[20] but while this seems to be a reasonable proposal, no evidence has ever been found for the intermediacy of such a species.[21]

The above arguments provide reasonable explanations for the results of the reactions of CO_2 with other dinitrogen complexes of molybdenum. The mono(dinitrogen) complexes $Mo(N_2)(dmpe)(PMe_3)_3$[22] and $Mo(N_2)(PP_2)(PMe_3)_2$ (PP_2 = $MeP(CH_2CH_2CH_2PMe_2)_2$[11d]), which contain five basic phosphorus donors bonded to molybdenum, react with CO_2 with exclusive formation of the disproportionation products $Mo(CO_3)(CO)(dmpe)(PMe_3)_2$ and $Mo(CO_3)(CO)(PP_2)(PMe_3)$. The latter compound is also the product of the reaction of the related complex $MoH(CH_2PMe_2)(PP_2)(PMe_3)$ with CO_2,[11e] whereas the bis(dinitrogen) complex $Mo(N_2)_2(PP_2)(PMe_3)$ gives, under appropriate conditions, the carbonyl–carbonate $Mo(CO_3)(CO)(PP_2)(PMe_3)$, together with minor amounts of a complex formulated as a $(CO_2)_2$ adduct, $Mo(CO_2)_2(PP_2)(PMe_3)$.[11d] The low yield obtained for this CO_2 adduct is probably a reflection of the higher electron density in the mixed PP_2–PMe_3 dinitrogen complex as compared to our system.

On the other hand, the reaction of the PMe_2Ph derivative *cis*-$Mo(N_2)_2(PMe_2Ph)_4$, originally thought to provide a CO_2 complex,[7] has been shown to give in fact only the compound $[Mo(CO_3)(CO)(PMe_2Ph)_3]_2$ resulting from the reductive disproportionation of CO_2.[10a,23] The lack of formation of the corresponding $(CO_2)_2$ adduct in this reaction cannot be easily rationalized. It seems however plausible that in this case CO_2 reductive disproportionation is as favorable as in the analogous PMe_3 system while the coordination of a second molecule of CO_2 to give the expected adduct may be hindered by the bulkier PMe_2Ph ligands and/or by the solvent used (aromatic hydrocarbons, THF, or THF–Et_2O mixtures). This argumentation seems to be at variance with the formation of *trans*-$Mo(CO_2)_2(dppe)_2$ (dppe = $Ph_2PCH_2CH_2PPh_2$) in the reaction of *trans*-$Mo(N_2)_2(dppe)_2$ with CO_2.[24] We note, however that in the latter case the disproportionation reaction may be much less favorable, as compared to the previous system due to (i) the much lower basicity of the phosphine ligands and (ii) their bidentate nature, which could prevent formation of the purported head-to-tail CO_2 dimer intermediate. In addition, it is worth mentioning that *trans*-$Mo(CO_2)_2(dppe)_2$ is a very insoluble species, which decomposes very easily in common organic solvents.[25]

Experimental Section

Microanalyses were by Butterworth Microanalytical Consultancy, Ltd., Middlesex, England, Pascher Microanalytical Laboratories, Remagen, Germany, and the Microanalytical Service of the University of Sevilla. Infrared spectra were recorded on Perkin-Elmer spectrophotometers, Models 577 and 684. ^1H and ^{31}P NMR spectra were run on a Varian XL-200 spectrometer. ^{31}P NMR shifts were measured with respect to external 85% H_3PO_4. All preparations and other operations were carried out under oxygen-free nitrogen following conventional Schlenk techniques. Solvents were dried before use. The petroleum ether used had a boiling point of 40–60 °C. The compound *cis*-$Mo(N_2)_2(PMe_3)_4$ was prepared according to the literature[18] and its purity checked by $^{31}P\{^1H\}$ NMR spectroscopy.

Table III. Final Fractional Coordinates for **7**

atom	x/a	y/b	z/c	B(eqv),[a] Å^2
Mo(1)	0.11614 (2)	0.17786 (4)	0.65494 (4)	1.96
Mo(2)	0.04426 (2)	−0.01255 (4)	0.71132 (4)	1.71
P(1)	0.18733 (6)	0.0721 (1)	0.6000 (1)	2.54
P(2)	0.08340 (6)	0.2861 (1)	0.5037 (1)	2.54
P(3)	0.13598 (6)	0.2810 (1)	0.8186 (1)	3.00
O(1)	0.1993 (2)	0.3305 (4)	0.5838 (4)	3.98
O(2)	0.1100 (1)	0.0498 (3)	0.7765 (3)	2.14
O(3)	0.0796 (1)	0.0452 (3)	0.5701 (3)	1.89
O(4)	0.0381 (1)	0.1740 (3)	0.7158 (3)	2.00
O(5)	0.0000	0.3233 (5)	0.7500	3.87
O(6)	0.0592 (1)	−0.1376 (3)	0.7004 (3)	2.27
O(7)	0.0195 (1)	0.0032 (3)	0.8634 (3)	1.95
C(1)	0.1682 (2)	0.2711 (5)	0.6115 (5)	2.78
C(2)	0.2491 (2)	0.0998 (6)	0.6551 (6)	3.87
C(3)	0.1985 (2)	0.0707 (5)	0.4500 (5)	3.22
C(4)	0.1821 (2)	−0.0647 (5)	0.6328 (6)	3.47
C(5)	0.1195 (2)	0.2964 (6)	0.3745 (5)	3.83
C(6)	0.0230 (2)	0.2450 (5)	0.4492 (6)	3.35
C(7)	0.0718 (3)	0.4189 (5)	0.5418 (6)	4.15
C(8)	0.1969 (3)	0.2540 (7)	0.8762 (7)	5.15
C(9)	0.1375 (4)	0.4195 (6)	0.8078 (7)	6.95
C(10)	0.0974 (3)	0.2622 (7)	0.9401 (6)	5.40
C(11)	0.0000	0.2297 (6)	0.7500	2.18
H(1)	0.058	0.045	0.504	
H(2)	0.104	0.076	0.855	
H(3)	0.259	0.179	0.639	
H(4)	0.253	0.083	0.725	
H(5)	0.274	0.065	0.627	
H(6)	0.219	0.020	0.429	
H(7)	0.166	0.045	0.405	
H(8)	0.202	0.146	0.421	
H(9)	0.217	−0.103	0.617	
H(10)	0.179	−0.075	0.707	
H(11)	0.155	−0.093	0.606	
H(12)	0.122	0.219	0.345	
H(13)	0.103	0.340	0.323	
H(14)	0.157	0.334	0.394	
H(15)	0.023	0.187	0.406	
H(16)	0.003	0.209	0.507	
H(17)	0.011	0.316	0.396	
H(18)	0.101	0.458	0.558	
H(19)	0.056	0.454	0.481	
H(20)	0.055	0.424	0.609	
H(21)	0.201	0.285	0.958	
H(22)	0.229	0.273	0.814	
H(23)	0.200	0.173	0.889	
H(24)	0.153	0.450	0.874	
H(25)	0.098	0.426	0.800	
H(26)	0.153	0.456	0.728	
H(27)	0.115	0.305	1.002	
H(28)	0.083	0.180	0.945	
H(29)	0.062	0.297	0.924	

[a] $B(\mathrm{eqv}) = {}^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Synthesis of $[Mo(CO_3)(CO)(PMe_3)_3]_2$ (2). (a) A solution of *cis*-$Mo(N_2)_2(PMe_3)_4$ (0.52 g, ca. 1.14 mmol) in 50 mL of Et_2O was transferred into a thick-glass pressure vessel via cannula. After the contents were degassed with CO_2, the bottle was pressurized with CO_2 (2–3 atm) and left undisturbed overnight. The resulting mixture of red and yellow crystals (**2** and **1**, respectively) was decanted off, washed with 20 mL of Et_2O, and dried in vacuo. Complex **2** was separated manually from this mixture, or preferably, the mixture was washed with THF until the yellow crystals of **1** had completely dissolved. Yield: 30–40%.

(b) A suspension of complex **3** (0.15 g, ca. 0.3 mmol) in THF (20 mL) was stirred at 50 °C until complete dissolution of the violet crystals was achieved. The solvent was then evaporated at this temperature by careful application of vacuum, and the resulting red solid was washed with petroleum ether. The yield of **2** was quantitative. Selected analytical and spectroscopical data for **2** are as follows. IR (Nujol mull, cm^{-1}): 1765 s (CO), 1500 s, 1345 m, 835 m (CO_3). IR for **2*** (99% $^{13}CO_2$ enriched (Nujol mull, cm^{-1}): 1715 s, 1450 s, 1310 m, 815 m. $^{31}P\{^1H\}$ NMR (THF–C_6D_6), two AX_2 spin systems: δ_A 40.9, δ_X 44.0, J_{AX} = 29.3 Hz (major isomer); δ_A 39.4, δ_X 43.2, J_{AX} = 29.6 Hz (minor isomer).

---

(20) Herzskovitz, T.; Guggenberger, L. *J. Am. Chem. Soc.* **1976**, *98*, 1615.

(21) Ibers, J. A. *Chem. Soc. Rev.* **1982**, *11*, 57.

(22) Carmona, E.; Pérez, P. J. Unpublished results.

(23) Leigh, G. J.; Richards, R. L. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Guillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, England, 1987; Vol. 3, Chapter 36.2.

(24) Chatt, J.; Hussain, W.; Leigh, G. J. *Transition Met. Chem. (Weinheim, Ger.)* **1983**, *8*, 383.

(25) The analogous, and possibly more soluble, *trans*-$Mo(CO_2)_2(PMe_2Ph)_4$ could transiently form and decompose in solution. In fact we believe that failure to isolate this compound is not due to its intrinsic instability but is rather due to the lack of a suitable synthetic methodology.

Anal. Calcd for $[Mo(CO_3)(CO)(PMe_3)_3]_2$: C, 32.0; H, 6.5. Found: C, 32.2; H, 6.7.

Synthesis of $Mo(CO_3)(CO)(PMe_3)_4$ (3). Although details of the experimental procedure used for the synthesis of this complex have been given in a prior, though unrelated publication,[15] full details are given here for the sake of completeness. The compound *cis*-$Mo(N_2)_2(PMe_3)_4$ (0.72 g, ca. 1.58 mmol) was dissolved in 25 mL of acetone. The solution was then transferred into a pressure bottle, neat PMe_3 was added (0.2 mL, ca. 2 mmol), and the resulting mixture was exposed, without stirring, to 2 atm of CO_2 overnight. The violet crystalline product that formed was filtered, washed with Et_2O (2 × 20 mL) and dried in vacuo. Yield: 80%. Selected analytical and spectroscopic data for **3** are as follows. IR (Nujol mull, cm^{-1}): 1810 s (CO), 1600 s, 1240 m (CO_3). IR for **3*** (99% $^{13}CO_2$ enriched) (Nujol mull, cm^{-1}): 1770 s, 1550 s, 1205 m. $^{31}P\{^1H\}$ NMR (CD_3OD), A_2X_2 spin system: δ_A 28.9, δ_X 0.0, J_{AX} = 28.2 Hz. Anal. Calcd for $Mo(CO_3)(CO)(PMe_3)_4$: C, 34.4; H, 7.4. Found: C, 34.2; H, 7.4.

Synthesis of $Mo(CO_3)(CO)(PMe_3)_2(dmpe)$ (4). Complex **3** (0.3 g, ca. 0.6 mmol) dissolved in CH_3OH (10 mL) was treated with 1 equiv of dmpe (0.6 mL of a ca. 1 M solution in THF). After 30 min of stirring, the resulting mixture was taken to dryness and the orange residue was washed with Et_2O (3 × 40 mL) and dried in vacuo. Yield: 80%. Selected analytical and spectroscopical data for **4** are as follows. IR (Nujol mull, cm^{-1}): 1795 s (CO), 1590 s (CO_3). $^{31}P\{^1H\}$ NMR (CD_3OD, −85 °C), AMNX spin system: δ_A (PMe_3) 8.4, δ_M (PMe_3) 43.1, δ_N (dmpe) 47.1, δ_X (dmpe) 67.8 ppm, J_{AM} = 15 Hz, J_{AN} = 169.5 Hz, J_{AX} = 15 Hz, J_{MN} = 57.5 Hz, J_{MX} = 26 Hz, J_{NX} = 20.5 Hz. Anal. Calcd for $Mo(CO_3)(CO)(PMe_3)_2(dmpe)$: C, 34.6; H, 7.0. Found: C, 33.5; H, 7.1.

Synthesis of $Mo(CO_3)(CO)(PMe_3)_2(dmpm)$ (5). To a stirred suspension of complex **3** (0.25 g, ca. 0.51 mmol) in THF (20 mL) was added 1.2 equiv of dmpm via syringe (1.2 mL of a ca. 0.5 M solution in THF). This mixture was heated at 40 °C, and after 30 min the resulting yellow-orange precipitate was filtered off, washed with Et_2O (2 × 20 mL), and dried in vacuo. Yield: 80%. Selected spectroscopic and analytical data are as follows. IR (Nujol mull, cm^{-1}): 1790 s (CO), 1591 s (CO_3). $^{31}P\{^1H\}$ NMR (CD_3OD, 55 °C), A_2X_2 spin system: δ_A 7.48, δ_X 24.4, J_{AX} = 22.8 Hz. Anal. Calcd for $Mo(CO_3)(CO)(PMe_3)_2(dmpm)$: C, 33.0; H, 6.8. Found: C, 32.8; H, 6.8.

Synthesis of $Mo(CO_3)(CO)(dmpe)_2$ (6). This compound was prepared by following a procedure analogous to that discussed above for the synthesis of **4** but employing 2 equiv of dmpe instead of 1 equiv. Red, microcrystalline **6** was isolated in ca. 70% yield. Selected spectroscopic and analytical data are as follows. IR (Nujol mull, cm^{-1}): 1774 s (CO), 1580 s (CO_3). ^1H NMR (CD_3CN, 75 °C): δ 1.45 (pseudoquintet, P-Me, $J(HP)_{app}$ = 2.2 Hz). $^{31}P\{^1H\}$ NMR (CD_3CN, −45 °C): δ 52.7 s. Anal. Calcd. for $Mo(CO_3)(CO)(dmpe)_2$: C, 34.7, H, 6.6. Found: C, 34.4; H, 6.6.

Synthesis of 7. (a) *cis*-$Mo(N_2)_2(PMe_3)_4$ (0.46 g, ca. 1 mmol) was dissolved in a 2:1 acetone–toluene mixture (30 mL) and exposed to 1 atm of CO_2. The closed system was left aside for 15–20 days and the resulting crystalline precipitate isolated by decantation. A small amount of red-orange crystals of compound **7** could be easily separated by hand.

(b) Complex **3** (0.50 g, ca. 1 mmol) was dissolved in 50 mL of THF, with stirring at 50 °C, and the resulting solution was stirred for several hours at this temperature. The formation of a very fine divided solid was noted, and it was filtered off and washed with THF. Compound **7** was obtained in the form of a yellow powder in ca. 10% yield. IR (Nujol mull, cm^{-1}): 3570 m, 3400 s (OH), 1760 s (CO), 1560 m, 1280 m (CO_3), 975 s (Mo=O). Anal. Calcd for $Mo_4C_{21}H_{58}O_{13}P_6$: C, 23.2; H, 5.3; O, 19.1. Found: C, 24.3; H, 5.6; O, 18.7.

Single-Crystal X-ray Diffraction Study of 7. Single crystals of the slightly air-sensitive compound **7** were sealed under N_2 in thin-walled glass capillaries. The space group was uniquely determined as *Pbcn* from the systematic absences. A summary of data collection parameters is given in Table II.

Least-squares refinement with isotropic thermal parameters led to R = 0.068. The methyl and hydroxy hydrogen atoms were located with the aid of a difference Fourier map and included with fixed (B = 5.5 Å^2) parameters. The 110 reflection was omitted because of severe secondary extinction. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to the final values of R = 0.018 and R_w = 0.022. The final values of the positional parameters are given in Table III.

Acknowledgment. We thank the Dirección General de Investigación Científica y Técnica (Grants No. PB860653 and PB020101) and the U.S. National Science Foundation for support this research. E.C. also thanks the Commission of the European Communities for financial support of this work (Project No. SC1000227).

Supplementary Material Available: Table SI, listing thermal parameters, Table SII, listing least-squares-planes results, Table SIV, listing crystallographic data for **7**, and Figure SFI, showing the cell packing diagram for **7** (5 pages); Table SIII, listing observed and calculated structure factors for **7** (7 pages). Ordering information is given on any current masthead page.

---

(26) Sheldrick, G. M. SHELX76, A system of computer programs for X-ray structure determination as locally modified. University of Cambridge, England, 1976.

(27) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 72, 99, 149 (Present distributor: Kluwer Academic Publishers, Dordrecht, The Netherlands).