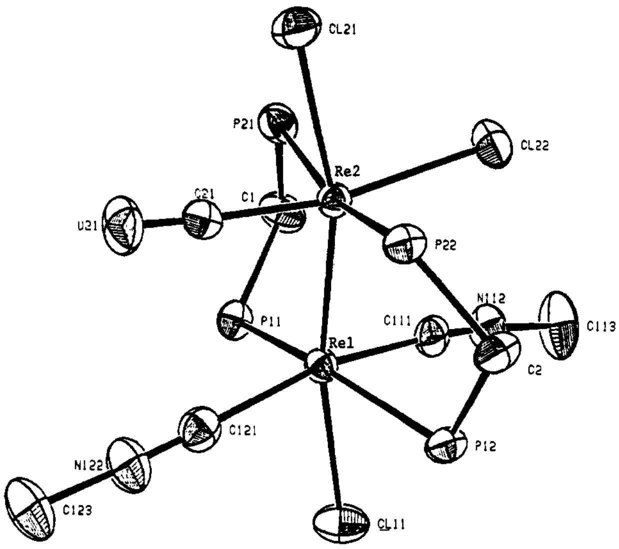

Figure 1. ORTEP view of the structure of the $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CN\text{-}t\text{-}Bu)_2]^+$ cation with methyl groups and phenyl rings omitted. The thermal ellipsoids are drawn at the 50% probability level. Important bond lengths (Å) and angles (deg) are as follows: Re–Re = 2.379 (1), $Re_1–Cl_{11}$ = 2.496 (2), $Re_2–Cl_{21}$ = 2.538 (2), $Re_2–Cl_{22}$ = 2.404 (3), $Re_1–P_{11}$ = 2.485 (3), $Re_1–P_{12}$ = 2.493 (3), $Re_2–P_{21}$ = 2.494 (3), $Re_2–P_{22}$ = 2.468 (3), $Re_2–C_{21}$ = 1.922 (9), $Re_1–C_{121}$ = 2.09 (1), $Re_1–C_{111}$ = 2.05 (1); $Re_1–Re_2–Cl_{21}$ = 161.9 (1), $Re_2–Re_1–Cl_{11}$ = 168.3 (1), $Re_1–Re_2–Cl_{22}$ = 107.9 (1), $Re_1–C_{111}–N_{112}$ = 174 (1), $Re_1–C_{121}–N_{122}$ = 175 (1).

$(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2Cl_3(CO)$,[3] $Re_2(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2Cl_3(CNxyl)$,[4] $[Re_2(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2Cl_2(CO)(NCEt)]PF_6$,[13] and $[Re_2(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2Cl_2(CO)(CN\text{-}t\text{-}Bu]PF_6$.[5] This Re–Re bond shortening in **3b**, compared to the bond length in the Re(μ-CO)Re species, is in accord with the presence of an electron-rich Re≡Re bond, although it is weakened (and lengthened) through back-bonding involving the π components of the metal–metal bond and the π^* orbitals on the terminal CO and *t*-BuNC ligands. The change to an edge-sharing bioctahedral structure leads to a lengthening in this bond of ca. 0.2 Å; the effect is tantamount to the change in Re–Re distance that occurs upon forming a doubly bonded dirhenium(III) complex such as $Re_2(\mu\text{-Cl})_2(\mu\text{-dppm})_2Cl_4$.[14] Thus, the formation of a μ-CO unit in these dirhenium complexes gives the same effect as a net two-electron oxidation from Re_2^{4+} to Re_2^{6+}. This is a consequence of treating the CO ligand as forming a divalent bridge.[4]

The structure of **2b** most likely resembles that of **3b** in possessing terminally bound CO and *t*-BuNC ligands, i.e. $(CO)Cl_2Re(\mu\text{-dppm})_2ReCl_2(CN\text{-}t\text{-}Bu)$. We also find that CH_2Cl_2 solutions of **2b** react with nitriles and with xylyl isocyanide at room temperature in the presence of $TlPF_6$ to yield complexes of stoichiometry $[Re_2Cl_3(dppm)_2(CO)(CN\text{-}t\text{-}Bu)(L)]PF_6$, where L = MeCN, EtCN, and xylNC (70–75% yield). These complexes possess electrochemical properties that resemble those of **3b** (see ref 5) and IR spectral properties that accord with a structure very similar to that of **3b**, i.e. a terminal CO ligand and the *t*-BuNC ligand trans to L.[15] The lability of the nitrile ligands L in these complexes is demonstrated by the conversion of $[Re_2Cl_3(dppm)_2(CO)(CN\text{-}t\text{-}Bu)(NCMe)]PF_6$ into **3b** (70% yield) upon its reaction with *t*-BuNC in dichloromethane. Accordingly, **3b** is a new structural prototype for dirhenium complexes that contain π-acceptor ligands, and studies are under way to examine the scope of this chemistry.

Acknowledgment. Support from the National Science Foundation (Grant No. CHE85-06702) is gratefully acknowledged.

Supplementary Material Available: A table of atomic coordinates and an ORTEP view of the cation $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CN\text{-}t\text{-}Bu)_2]^+$ showing the full atomic numbering scheme (5 pages). Ordering information is given on any current masthead page.

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(15) For example, $[Re_2Cl_3(dppm)_2(CO)(CN\text{-}t\text{-}Bu)(CNxyl)]PF_6$ has ν(CO) = 1927 cm^{-1} and ν(C≡N) = 2161 and 2134 cm^{-1} for a Nujol mull.

Phosphinecarboxylate Ligands Formed by the Insertion of Carbon Dioxide into Metal–Phosphido Bonds. Preparation and Structural Characterization of Tetrakis(di-*tert*-butylphosphinecarboxylato)dimolybdenum

Sir:

We recently demonstrated that amido (NR_2) ligands are stronger π donors than phosphido (PR_2) ligands in structural and spectroscopic studies of $1,2\text{-}M_2[P(t\text{-}Bu)_2]_2(NMe_2)_4$ (M = Mo (**1**) and W),[1] and next sought to compare NR_2 and PR_2 ligands on the basis of chemical reactivity. The conversion of NR_2 ligands to carbamate (O_2CNR_2) ligands by reaction with CO_2 is well-known,[2] and we and others[3] suspected that PR_2 groups might also undergo formal CO_2 insertion to give phosphinecarboxylate (O_2CPR_2) ligands. We now report the preparation of the mixed-ligand complex $Mo_2[O_2CP(t\text{-}Bu)_2]_2(O_2CNMe_2)_2(NMe_2)_2$ (M≡M) (**2**) from **1**, and its unexpected decomposition to give $Mo_2[O_2CP(t\text{-}Bu)_2]_4$ ($M\overset{4}{—}M$) (**3**). To our knowledge **3** is the first homoleptic O_2CPR_2 complex and the first O_2CPR_2 complex to be structurally characterized. The structure of **3** reveals important differences in the bonding capabilities of O_2CPR_2 and O_2CNR_2 ligands.

Phosphido–amido complex **1** and excess CO_2 react rapidly to give **2** as a yellow precipitate (54%) according to eq 1. Complex

$$\underset{\mathbf{1}}{1,2\text{-}Mo_2[P(t\text{-}Bu)_2]_2(NMe_2)_4} + 4CO_2 \xrightarrow{\text{hexane}} \underset{\mathbf{2}}{Mo_2[O_2CP(t\text{-}Bu)_2]_2(O_2CNMe_2)_2(NMe_2)_2} \quad (1)$$

2 has been characterized by spectroscopic and elemental analyses.[4] The lack of any $\nu_{C=O}$ in the IR spectrum indicates that $O_2CP(t\text{-}Bu)_2$ and O_2CNMe_2 ligands are bound in a η^2 fashion. NMR data show that the two $O_2CP(t\text{-}Bu)_2$ ligands, the two O_2CNMe_2 ligands, and the two NMe_2 ligands are chemically equivalent, respectively, and that each bears diastereotopic alkyl groups. Various geometries are consistent with these data, and the structure of **2** is likely to be similar to known structures of related carbamate complexes.[5]

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(1) Buhro, W. E.; Chisholm, M. H.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 905.

(2) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*; Wiley: New York, 1980; p 577.

(3) (a) Baker's studies of CO_2 insertion into metal–phosphido bonds preceded our own.[3b] (b) Baker, R. T. *Abstracts of Papers*, 192nd National Meeting of the American Chemical Society, Anaheim, CA; American Chemical Society: Washington, DC, 1986; INOR-96. (c) Insertion of CS_2 into the Zr–P bonds of $Zr(\eta^5\text{-}C_5H_5)_2[P(SiMe_3)_2](X)$ (X = Cl, Me) was recently reported; similar reactions with CO_2 were attempted.[3d] (d) Hey, E.; Lappert, M. F.; Atwood, J. L.; Bott, S. G. *J. Chem. Soc., Chem. Commun.* **1987**, 421.

(4) Data for **2**: $^{31}P\{^1H\}$ NMR (ppm, C_6D_6) 43.0 (s); ^1H NMR (δ, C_6D_6) 4.85 (s, 6 H, NMe_2), 3.10 (s, 6 H, NMe_2), 2.83 (s, 6 H, O_2CNMe_2), 2.63 (s, 6 H, O_2CNMe_2), 1.48 (d, $^3J_{HP}$ = 11.1 Hz, 18 H, *t*-Bu), 1.46 (d, $^3J_{HP}$ = 11.2 Hz, 18 H, *t*-Bu); $^{13}C\{^1H\}$ NMR (ppm, C_6D_6) 189.0 (d, $^1J_{CP}$ = 24.7 Hz, O_2CP), 174.8 (s, O_2CN); IR (cm^{-1}, KBr) ν_{O_2CN} 1575 s; 1480 m, 1455 m; mp 169–176 °C dec. Anal. Calcd for $C_{28}H_{60}Mo_2N_4O_8P_2$: C, 40.29; H, 7.25. Found: C, 40.18; H, 7.11.

(5) (a) Chisholm, M. H.; Extine, M.; Cotton, F. A.; Stults, B. R. *J. Am. Chem. Soc.* **1976**, *98*, 4683. (b) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Stults, B. R. *Inorg. Chem.* **1977**, *16*, 603. (c) Chisholm, M. H.; Reichert, W. W. *Inorg. Chem.* **1978**, *17*, 767. (d) See also: Chisholm, M. H.; Heppert, J. A.; Hoffman, D. M.; Huffman, J. C. *Inorg. Chem.* **1985**, *24*, 3214.

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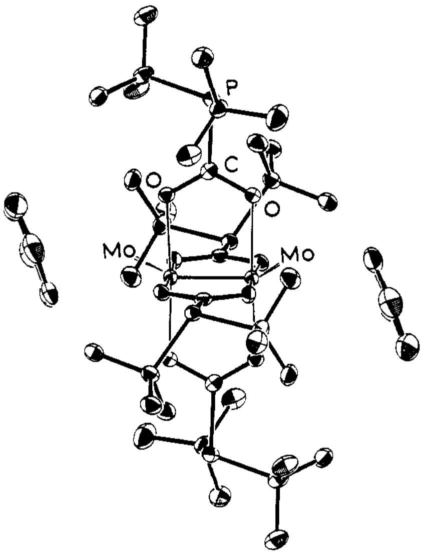

Figure 1. ORTEP view of $Mo_2[O_2CP(t\text{-}Bu)_2]_4 \cdot 2C_6H_6$ ($3 \cdot 2C_6H_6$). Selected distances (Å): Mo–Mo = 2.092 (3), Mo–O(av) = 2.107 (9), O–C(av) = 1.27 (1), and O_2C–P(av) = 1.860 (5).

Our attempts to crystallize **2** have been frustrated by its slow decomposition in solution at ambient temperature, giving several new species (by NMR monitoring). We initially considered the instability might result from reversible CO_2 insertion and deinsertion, but **2** does not undergo exchange with $^{13}CO_2$ over the course of several weeks. One decomposition product readily crystallizes in small amounts (0.08–0.10 molar equiv based on **2**) from C_6H_6, and has been identified as $Mo_2[O_2CP(t\text{-}Bu)_2]_4 \cdot 2C_6H_6$ ($\mathbf{3} \cdot 2C_6H_6$) by spectroscopic analyses,[6] and X-ray crystallography.[7] Thus, the decomposition of **2** involves both ligand exchange and redox chemistry. Complex **3** can be prepared directly from $Mo_2[P(t\text{-}Bu)_2]_2[\mu\text{-}P(t\text{-}Bu)_2]_2$,[8] and CO_2 (in ca. 25% yield based on $MoCl_3$).[9]

The molecular structure of $\mathbf{3} \cdot 2C_6H_6$ is shown in Figure 1, and important distances are listed in the caption. The compound adopts the familiar paddlewheel geometry for $Mo_2(O_2CX)_4$ species,[10] with benzene solvate molecules in axial positions at distances precluding significant bonding interactions (the closest solvate Mo–C distance is 3.11 Å).[11] Of special interest are parameters for the $\mu,\eta^2\text{-}O_2CP(t\text{-}Bu)_2$ ligands. Configurations at P are grossly pyramidal, as shown by the sums of angles about P atoms, 310.2–313.4 (6)°. The P–CO_2 distances of 1.86 (1) Å are normal P–C single-bond lengths.[12] This contrasts with typical parameters for $\mu,\eta^2\text{-}O_2CNR_2$ ligands, which describe planar configurations at N and short N–CO_2 distances, resulting from effective delocalization of N lone pairs into CO_2 π^* frameworks.[5b,13] The net effect is stronger metal–ligand bonding via O-to-M π donation in O_2CNR_2 complexes. The lack of this effect in **3** is presumably a reflection of inherently poor P–C π overlap.[14] Further studies are in progress.[15]

Registry No. **1**, 106651-37-0; **3**, 109801-37-8; $\mathbf{3} \cdot 2C_6H_6$, 109801-38-9; $Mo_2[P(t\text{-}Bu)_2]_2[\mu\text{-}P(t\text{-}Bu)_2]_2$, 86802-71-3; CO_2, 124-38-9; $HP(t\text{-}Bu)_2$, 819-19-2; Mo, 7439-98-7.

Supplementary Material Available: Tables of fractional coordinates and isotropic thermal parameters, anisotropic thermal parameters, and complete listings of bond distances and angles and atom-numbering diagrams (11 pages); a listing of calculated and observed structure factors (8 pages). Ordering information is given on any current masthead page.

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(6) Data for **3**: $^{31}P\{^1H\}$ NMR (ppm, C_6D_6) 51.0 (s); ^1H NMR (δ, C_6D_6) 1.47 (d, $^3J_{HP}$ = 11.6 Hz, 72 H); $^{13}C\{^1H\}$ NMR (ppm, C_6D_6) 192.5 (d, $^1J_{CP}$ = 31.3 Hz, O_2CP); IR (cm^{-1}, KBr) 1469 m, 1438 m; dec pt 213–245 °C.

(7) Crystal data for $\mathbf{3} \cdot 2C_6H_6$ at −155 °C: yellow hexagonal prism (0.25 × 0.25 × 0.30 mm), a = 13.731 (21) Å, b = 12.789 (17) Å, c = 15.835 (23) Å, β = 94.86 (8)°, space group $P2_1/n$, $Z = 2$, d_{calcd} = 1.324 g cm^{-3}. Using Mo Kα (graphite monochromated), $6° \leq 2\theta \leq 45°$, 4401 total reflections with 2943 having $F > 3\sigma(F)$ ($+h,+k,\pm l$) yielded final residuals $R(F)$ = 0.032 and $R_w(F)$ = 0.035. The diffractometer has been described previously: Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1984**, *23*, 1021.

(8) Jones, R. A.; Lasch, J. G.; Norman, N. C.; Whittlesey, B. R.; Wright, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 6184.

(9) (a) We generate $Mo_2[P(t\text{-}Bu)_2]_2[\mu\text{-}P(t\text{-}Bu)_2]_2$ in situ from $2MoCl_3$ + $6LiP(t\text{-}Bu)_2$ in THF at −78 °C. Reduction of Mo(III) to Mo(II) is accompanied by the formation of $(t\text{-}Bu)_2P\text{–}P(t\text{-}Bu)_2$.[9b] (b) Data for $Mo_2[P(t\text{-}Bu)_2]_2[\mu\text{-}P(t\text{-}Bu)_2]_2$ in situ: $^{31}P\{^1H\}$ NMR (ppm, THF, −35 °C) 279.9 (t, $^2J_{PP}$ = 64.8 Hz), 231.7 (t, $^2J_{PP}$ = 64.8 Hz).

(10) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982; p 84.

(11) (a) We note the structural similarity of $\mathbf{3} \cdot 2C_6H_6$ to $Hb_2(O_2CCF_3)_4(\eta^2\text{-}C_6Me_6)_2$, in which the C_6Me_6 ligands occupy axial positions with much shorter M–C distances (2.56–2.58 Å).[11b] (b) Lau, W.; Huffman, J. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 5515.

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(15) We thank the National Science Foundation and the Wrubel Computing Center at Indiana University for support. W.E.B. thanks Indiana University for a Chester Davis Fellowship (1985–1986) and W. G. Van Der Sluys for important suggestions and discussions.

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