result is consistent with the most recent study of (arene)$Cr(CO)_3$ electrochemistry[35] that suggests the radical species interacts with the supporting anion in CH_2Cl_2 solutions, and another study[34] that makes a similar observation for the less sterically hindered $(C_6Me_6)W(CO)_3$ system. The 100-cm^{-1} shift to higher energy for the A and E symmetry ν(CO) spectral bands of the oxidized (mes)$Cr(CO)_3^+$ was expected; however, the overall decrease in the integrated intensity exhibited by these bands is of additional interest and is perhaps indicative of a decrease in the transition dipole for these transitions in the (mes)$Cr(CO)_3^+$ complex.

In summary, we have demonstrated that the application of the IR–OTTLE technique can significantly aid in the structural characterization of electrochemically generated species that may be difficult to isolate. Homogeneous reactions of the electrogenerated species may also be conveniently studied by the technique. Future work we plan includes the improvement of the cell design to further decrease the electrolysis times and to obtain more accurate control of the working electrode potential.

Acknowledgment. We thank Professors John Evans, Harold Swofford, Lawrence Potts, and Peter Carr for several stimulating discussions, Johnson Matthey, Inc., for a generous loan of rhodium trichloride, and the NSF (Grant No. CHE 8509325) for the funds used to purchase the FT-IR spectrometer.

Registry No. $[Rh_2(dimen)_2(dppm)_2](PF_6)_2$, 103731-85-7; $[Rh_2(dimen)_2(dppm)_2]^{3+}$, 103731-86-8; (mes)$Cr(CO)_3$, 12129-67-8; (mes)$Cr(CO)_3^+$, 52826-61-6; Au, 7440-57-5; ferrocene, 102-54-5; ferrocenium, 12125-80-3.

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A Multiply Bonded Dimetal Complex of the M_2L_{10} Type That Contains π-Acceptor Ligands and Does Not Possess an Edge-Shared Bioctahedral Structure. The $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CN\text{-}t\text{-Bu})_2]^+$ Cation

Sir:

The reactivity of the triply bonded dirhenium(II) complex $Re_2Cl_4(\mu\text{-dppm})_2$ (**1**) toward carbon monoxide, isocyanides, and nitriles is currently under investigation.[1] The facile M–M bond-cleavage reactions that can occur upon reacting multiply bonded dimetal species with CO and RNC ligands[2] can be prevented through the use of μ-$R_2PCH_2PR_2$ ligands. A structural feature common to the resultant complexes is that those which contain carbonyl ligand(s) seem to prefer edge-sharing bioctahedral structures, within which there is a $[Re_2(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2]$ unit. Thus, **1** can be converted by CO into the A-frame-like complex $Re_2(\mu\text{-Cl})(\mu\text{-dppm})_2Cl_3(CO)$,[3,4] which in turn reacts with 1 equiv of xylNC (xyl = 2,6-$Me_2C_6H_3$) and with xylNC (2 equiv)/$TlPF_6$ mixtures to give $Re_2(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2Cl_3(CNxyl)$ (**2a**)[4] and $[Re_2(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2Cl_2(CNxyl)_2]PF_6$ (two isomers); (**3a**),[5] respectively.

We have reported previously the synthesis of the *t*-BuNC analogue of **2a**, viz., a complex of stoichiometry $Re_2Cl_4(dppm)_2(CO)(CN\text{-}t\text{-Bu})$ (**2b**), and noted that unlike **2a** it does not contain a bridging CO ligand (IR-active $\nu(CO)_t$ mode at 1968 cm^{-1}).[4] Further reaction of **2b** with *t*-BuNC in acetone in the presence of $TlPF_6$ gives the complex $[Re_2Cl_3(dppm)_2(CO)(CN\text{-}t\text{-Bu})_2]PF_6$ (**3b**), in which a terminal Re–CO bond is retained (ν(CO) at 1960 cm^{-1} for a Nujol mull).[5] The possibility that **3b** and, by implication, **2b** are of a structural type different from that encountered previously (i.e. different from an edge-shared bioctahedral geometry) has been examined. Herein we report the preliminary results of this investigation.

A batch of red-brown crystals of **3b** were grown from a CH_2Cl_2–CH_3OH solvent mixture, and a suitable single crystal was selected and subjected to an X-ray structure analysis. Subsequent analysis of the data indicated that the crystal was that of the salt $[Re_2Cl_3(dppm)_2(CO)(CN\text{-}t\text{-Bu})_2](PF_6)_{0.5}(OMe)_{0.5}$.[6-10] The structure of the cation (Figure 1) is closely akin to that of a molecule of the M_2L_8 type,[11] with two additional ligands (chlorides) in axial positions. The *t*-BuNC ligands are trans to one another and their stereochemical disposition thereby resembles that of the nitrile ligands in the complexes $[(RCN)_2ClRe(\mu\text{-dppm})_2ReCl_2]PF_6$.[12] The Re–Re distance of 2.379 (1) Å is longer than that in $[(PhCN)_2ClRe(\mu\text{-dppm})_2ReCl_2]PF_6$ (2.270 (1) Å) but much shorter than the comparable distances (2.58–2.61 Å) found for formally dirhenium(II) complexes that are edge-sharing bioctahedra with $[Re_2(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2]$ units, i.e. Re_2-

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(6) Crystals of $[Re_2Cl_3(dppm)_2(CO)(CN\text{-}t\text{-Bu})_2](PF_6)_{0.5}(OCH_3)_{0.5}$ are triclinic, space group $P\bar{1}$, with a = 12.125 (2) Å, b = 23.877 (4) Å, c = 11.694 (2) Å, α = 100.74 (1)°, β = 90.38 (1)°, γ = 76.34 (1) °, V = 3230 (2) $Å^3$, Z = 2, d_{calcd} = 1.574 g/cm^3, and μ = 40.90 cm^{-1}. X-ray diffraction data were collected at 22 °C on a 0.17 × 0.14 × 0.05 mm crystal for 8394 independent reflections having $4 < 2\theta < 45°$ on an Enraf-Nonius CAD4 diffractometer using graphite-crystal-monochromated Mo Kα radiation (λ = 0.710 73 Å). Details of the crystal data collection and reduction methods are the same as those described elsewhere.[7] An empirical absorption correction was applied,[8] but no correction for extinction was made. During the course of the structure analysis it became apparent that there was only one PF_6^- anion for the two dirhenium cations in the unit cell. This did not satisfy the charge requirements for this complex. The largest peak in the difference Fourier map at this stage was less than 2.5 e/$Å^3$. Subsequent refinement of this residual electron density suggested the presence of a small molecule, which we concluded could be a methoxide anion. This lies on a general position and is disordered within the unit cell. Refinement was carried out on this assumption.[9] Accordingly, there is a total of two anions per unit cell, each occupying sites of half-occupancy. All atoms except the C and O atoms of the methoxide anion were refined anisotropically, and corrections for anomalous scattering were applied to these atoms.[10] Hydrogen atoms were not included in the least-squares refinement. The final residuals were R = 0.038 and R_w = 0.063 for 6512 data with $I > 3\sigma(I)$. The IR spectrum (Nujol mull) and cyclic voltammogram of the crystals were found to be the same as those of the bulk synthetic batches of the complex **3b**. This sample was also, as expected, ESR-silent (1:1 CH_2Cl_2/toluene at −150 °C) in accord with the expected diamagnetism of the cation. The ^1H NMR spectrum of these crystals (recorded in $(CD_3)_2CO$) showed a resonance at δ +3.33 that we attribute to methanol (CH_3); this could form through the reaction of methoxide anion with trace amounts of water present in the solvent.

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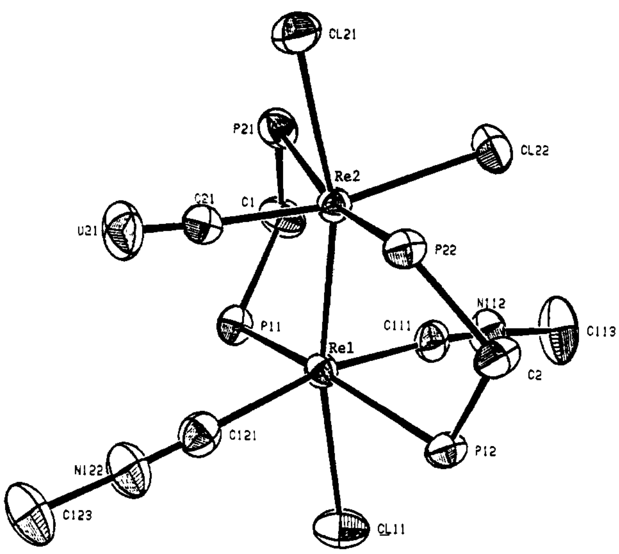

Figure 1. ORTEP view of the structure of the $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CN\text{-}t\text{-}Bu)_2]^+$ cation with methyl groups and phenyl rings omitted. The thermal ellipsoids are drawn at the 50% probability level. Important bond lengths (Å) and angles (deg) are as follows: Re–Re = 2.379 (1), 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.

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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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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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(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.

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