complex or partially overlapped spectra by use of 2-D NMR spectroscopy.

Acknowledgment. We are grateful to the UAB Chemistry Department NMR Facility for use of the Nicolet NMC-300 NMR. M.A.K. thanks Drs. C. L. Krumdieck and C. E. Butterworth for their encouragement in this work and acknowledges research support from NIH Grants NS-18350 and CA-Z8103.

Registry No. Valinomycin, 2001-95-8.

Reaction of *cis*-[$\mathrm{Mo(N_2)_2(PMe_3)_4}$] with CO_2. Synthesis and Characterization of Products of Disproportionation and the X-ray Structure of a Tetrametallic Mixed-Valence $\mathrm{Mo^{II}}$–$\mathrm{Mo^{V}}$ Carbonate with a Novel Mode of Carbonate Binding

Ernesto Carmona,* Francisco González, Manuel L. Poveda, and José M. Marin

Departamento de Quimica Inorgânica, Facultad de Quimica
Universidad de Sevilla, Sevilla, Spain

Jerry L. Atwood*

Department of Chemistry, University of Alabama
University, Alabama 35486

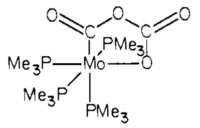
Robin D. Rogers*

Department of Chemistry, Northern Illinois University
Dekalb, Illinois 60115

Received January 31, 1983

Although most of the emphasis in C_1 chemistry has so far relied on carbon monoxide, the potential application of carbon dioxide as starting material for organic synthesis has been appreciated in recent years.[1] The current interest in CO_2 chemistry and the existence of only a brief report on the reactions of this molecule with dinitrogen complexes of molybdenum[2] prompted us to investigate its interaction with the recently prepared[3] *cis*-[$\mathrm{M(N_2)_2(PMe_3)_4}$] and [$\mathrm{M(N_2)(PMe_3)_5}$] (M = Mo, W) complexes. Here we report preliminary results based on reactions with *cis*-[$\mathrm{Mo(N_2)_2(PMe_3)_4}$] that lead to the formation of a bis-CO_2 complex, [$\mathrm{Mo(CO_2)_2(PMe_3)_4}$] (**1**), two related compounds resulting from the metal-induced disproportionation of CO_2, [$\mathrm{Mo(CO_3)(CO)(PMe_3)_4}$] (**2**), and [$\mathrm{Mo(CO_3)(CO)(PMe_3)_3}$]$_2$ (**3**), and an unusual mixed-valence $\mathrm{Mo^{II}}$–$\mathrm{Mo^{V}}$ complex, [$\mathrm{Mo_4(\mu_4\text{-}CO_3)(CO)_2(O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}OH)_4(PMe_3)_6}$] (**4**).

Treatment of petroleum ether solutions of *cis*-[$\mathrm{Mo(N_2)_2(PMe_3)_4}$] (1.1 g, ca. 2.4 mmol, 50 mL) with 50–60 psi of CO_2 at room temperature results in the formation[4] of the pale-yellow **1** and the red-orange **3** in ca. equivalent amounts, together with minor amounts of the dark-blue **2**. Complex **1** can be extracted with toluene from the above mixtures and has a structure still undetermined. Two possibilities can be envisaged: a bis-CO_2 adduct and a head-to-tail dimer [$\mathrm{Mo(C_2O_4)(PMe_3)_4}$]. Although efforts to grow crystals suitable for X-ray analysis have so far proved unsuccessful, chemical evidence, particularly the stability of the complex toward loss of CO_2 and the failure to observe CO_2 displacement by N_2, C_2H_4, or phosphine ligands (PMe_3 and PMe_2Ph), seems more in favor of formulation as a head-to-tail dimer A, similar to [$\mathrm{IrCl(C_2O_4)(PMe_3)_3}$].[5]

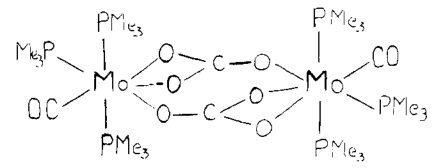


A

Further chemical and spectroscopic studies now in progress may clarify these points. It should be recalled here that although head-to-tail dimers are considered to be intermediates in the metal-induced disproportionation of CO_2, in those instances where they have been isolated, they are stable and do not rearrange.[1a] We have similarly been unable to observe conversion of **1** into the disproportionation products **2** or **3**.

For **2**, formulation as a carbonyl–carbonate complex with a bidentate CO_3 group [$\mathrm{Mo(O_2CO)(CO)(PMe_3)_4}$] comes from both spectroscopic and chemical evidence.[6] Upon attempted dissolution, **2** loses one of the coordinated PMe_3 molecules to afford **3**, which has been characterized by X-ray[7] analysis as a dimeric species with tridentate bridging CO_3 groups, B. Conversely, interaction of **3** with neat PMe_3 yields **2** (eq 1).

$$\underset{\mathbf{2}}{2[\mathrm{Mo(CO_3)(CO)(PMe_3)_4}]} \underset{\mathrm{PMe_3}}{\overset{\mathrm{THF}}{\rightleftharpoons}} \underset{\mathbf{3}}{[\mathrm{Mo(CO_3)(CO)(PMe_3)_3}]_2} \tag{1}$$



B

It is pertinent to note here that the partially characterized complex of composition [$\mathrm{Mo(CO_2)_2(PMe_2Ph)_4}$], formed in the reaction of *cis*-[$\mathrm{Mo(N_2)_2(PMe_2Ph)_4}$] with CO_2 and formulated[2] as a Mo–CO_2 complex, behaves similarly to **2**, dissociating in solution one of the PMe_2Ph ligands to yield [$\mathrm{Mo(CO_3)(CO)(PMe_2Ph)_3}$]$_2$, which is structurally analogous to **3**. Furthermore, the IR data reported for [$\mathrm{Mo(CO_2)_2(PMe_2Ph)_4}$] may also be interpreted[8] by assuming the presence of a carbonyl and a monodentate carbonate ligands, i.e., [$\mathrm{Mo(OCO_2)(CO)(PMe_2Ph)_4}$].

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(4) **1**: IR (Nujol) 1685 sh, 1670 vs, 1635 sh, 1155 s, 1135 w, 1100 s (CO_2 groups). Anal. Calcd for $\mathrm{MoC_{14}H_{36}O_4P_4}$: C, 34.43; H, 7.38; O, 13.12. Found: C, 34.68; H, 7.57; O, 13.1. **2**: IR 1810 vs (CO), 1600 vs, 1235 m, 1015 w, 840 m (CO_3). Anal. Calcd for $\mathrm{MoC_{14}H_{36}O_4P_4}$: C, 34.43; H, 7.38. Found: C, 34.20; H, 7.43. **3**: IR 1765 vs (CO), 1500 vs, 840 m (CO_3). Anal. Calcd for $\mathrm{MoC_{11}H_{27}O_4P_3}$: C, 32.04; H, 6.55. Found: C, 32.25; H, 6.75.

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(6) For $\mathrm{Fe(O_2CO)(CO)(PMe_3)_3}$ IR bands at 1898, 1604, 1239, 1013. and 832 $\mathrm{cm^{-1}}$ have been reported: Karsch, H. H. *Chem. Ber.* **1977**, *210*, 2213–2221.

(7) Complex **3** crystallizes in the triclinic space group $P\bar{1}$ with unit cell dimensions $a = 9.320$ (3) Å, $b = 9.570$ (3) Å, c 12.010 (4) Å. $\alpha = 77.32$ (2)°, $\beta = 70.64$ (2)°, $\gamma = 64.23$ (2), and $D_{\mathrm{calcd}} = 1.46$ g cm^{-3} for $Z = 1$.

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(8) Bands at 1760 (νCO), 1510, and 1335 $\mathrm{cm^{-1}}$ ($\nu_{\mathrm{CO_t}}$ (B_2) and ($\nu_{\mathrm{CO_t}} + \nu_{\mathrm{CO_c}}$) ($A_1$), respectively, for monodentate carbonate $\mathrm{(O_t)_2C\text{–}O_c\text{–}M}$, assuming linear $\mathrm{CO_cM}$ group and C_{2v} symmetry). See: Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed.; Wiley: New York, 1978; pp 243–245.

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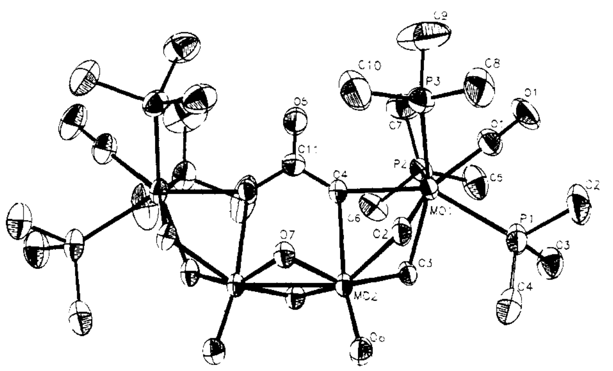
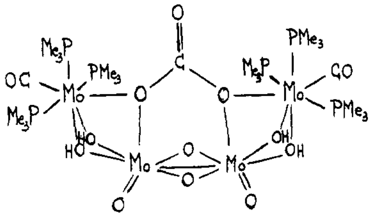


Figure 1. Molecular structure of the carbonate complex **4** $[Mo_4(\mu_4\text{-}CO_3)(CO)_2(O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}OH)_4(PMe_3)_6]$.

If *cis*-$[Mo(N_2)_2(PMe_3)_4]$ and CO_2 are reacted at room temperature and pressure, in a 2:1 acetone:toluene mixture, complex **2** crystallizes upon standing for a period of 1–3 days. If the mixture is allowed to stand at 20–25 °C for 15–20 days, small amounts of red-orange crystals[9] of a complex characterized by X-ray crystallography as an unusual mixed-valence Mo^{II}–Mo^{V} species of composition $[Mo_4(\mu_4\text{-}CO_3)(CO)_2(O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}OH)_4(PMe_3)_6]$ (**4**) are also obtained. Complex **4** contains a bidentate, quadruply bridging CO_3 group, engaged in a novel mode of binding. The molecular structure and atom labeling scheme for **4** are presented in Figure 1.[10] The molecule resides on a crystallographic 2-fold axis that contains C11 and O5 of the carbonate ligand. The carbonate ligand bridges all four molybdenum atoms, with two molybdenum atoms bonded to each carbonate oxygen off the symmetry axis (Mo1–O4 = 2.221 (3) Å, Mo2–O4 = 2.419 (4) Å). The outer Mo^{II} atoms are seven coordinate, bonded to one oxygen of the carbonate ligand, two bridging hydroxy ligands, three trimethylphosphine groups, and a carbonyl moiety. The overall coordination about these Mo^{II} atoms is similar to that found for $[Mo(\mu\text{-}CO_3)(CO)(PMe_3)_3]_2$[7] (**3**) and $[Mo(\mu\text{-}CO_3)(CO)(PMe_2Ph)_3]_2$.[2]



4

The two inner Mo^{V} atoms show bonding characteristics similar to other $Mo_2O_4^{2+}$ moieties that have been structurally characterized;[11] these include a Mo–Mo single bond (2.5522 (9) Å), a bent bridging arrangement of oxygen atoms to form a distorted octahedral coordination about the Mo^{V} atoms, and a terminal oxo group (Mo2–O6 = 1.672 (4) Å) that weakens the bond trans to it (Mo2–O4 = 2.419 (4) Å). Although it is not easy to rationalize the formation of this complex, it is evident that small amounts of water present in the acetone used must play an important role. Data available so far suggest the implication of **3** at some stages of the reaction.

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[9] **4**: IR (Nujol) 3570, 3400 (OH), 1760 (CO), 1560, 1280, 1080 (CO_3^{2-}), 975 (Mo═O), and 945 cm; (PMe_3). Anal. Calcd for $Mo_4C_{21}H_{58}O_{13}P_6$: C, 23.17; H, 5.33; O, 19.1. Found: C, 24.32; H, 5.63; O, 18.7. In addition to **2** and **4**, *cis*-$[Mo(CO)_2(PMe_3)_4]$ was crystallized from the mother liquor.

[10] **4** crystallizes in the orthorhombic space group *Pbcn* with lattice constants $a = 26.866$ (9) Å, $b = 12.934$ (4) Å, $c = 11.965$ (2) Å, and $D_{calc} = 1.74$ g cm^{-3} for four tetrametallic units in the cell. Least-squares refinement based on 1638 observed reflections led to a final R value of 0.018.

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Acknowledgment. We are grateful to the Spanish CAICYT (E.C.) and Ministerio de Educaciôn y Ciencia (J.M.M. and M.L.P.) and to the U.S. National Science Foundation (J.L.A.) for support of this work.

Registry No. 1, 85405-72-7; **2**, 85405-73-8; **3**, 85405-74-9; **4**, 85405-75-0; *cis*-$[Mo(N_2)_2(PMe_3)_4]$, 82044-78-8; CO_2, 124-38-9.

Supplementary Material Available: Tables of final fractional coordinates, thermal parameters, bond distances and angles, and observed and calculated structure factors for **4** (13 pages). Ordering information is given on any current masthead page.

Anion Ordering in Mixed-Valence Cs_2SbCl_6 and Related Salts

Kosmas Prassides and Peter Day*

Inorganic Chemistry Laboratory
Oxford University, Oxford OXI 3QR, United Kingdom

Anthony K. Cheetham

Chemical Crystallography Laboratory
Oxford University, Oxford OXI 3QR, United Kingdom

Received January 21, 1983

Cs_2SbCl_6, first prepared in 1901,[1] was originally described as an Sb^{IV} salt. However, a great deal of spectroscopic evidence (e.g., Mössbauer,[2] far infrared,[3] Raman,[4] ultraviolet,[5] and photoelectron spectra[6]) points to the existence of distinguishable $Sb^{III}Cl_6^{3-}$ and $Sb^{V}Cl_6^{-}$ in the structure, and its semiconductivity[7] and visible absorption[5,8] show that Cs_2SbCl_6 is a classical Robin–Day[9] class II mixed-valency compound. Additional recent measurements[10] of the far infrared and Raman spectra have also been interpreted in terms of increased localization of the Sb oxidation states at low temperature. Nevertheless, there remains a puzzle about its crystal structure. Wells[1] showed that Cs_2SbCl_6 forms mixed crystals with salts like Cs_2SnCl_6 and Cs_2PtCl_6, and early X-ray powder diffraction patterns[11,12] were indexed by using the space group *Fm*3*m*. X-ray powder photographs of mixed-metal compounds $Cs_2M^{III}{}_{0.5}Sb^{V}{}_{0.5}Cl_6$[8] were also indexed as *Fm*3*m*, implying that the MCl_6^{3-} and $SbCl_6^{-}$ groups were randomly distributed. Given the difference in charge between the two anions, this seems inherently unlikely, and given that the X-ray scattering is dominated by the Cs and Sb, we have recorded neutron powder diffraction profiles of Cs_2SbCl_6 itself and a number of mixed-metal analogues. We find that there is indeed a superlattice ordering of Sb^{III} (and other M^{III}) and Sb^{V} at low temperature in several salts of this type, while others remain disordered. The presence or absence

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