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Photochemistry of $(Me_3P)_4Mo(\eta^2\text{-}CO_2)_2$: deoxygenation of coordinated carbon dioxide and phosphine oxidation

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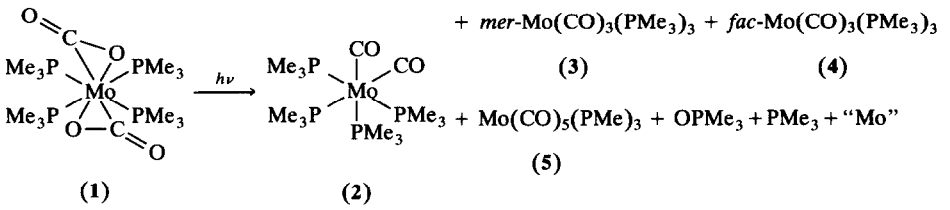
Abstract

Irradiation of the title compound **1** through quartz in toluene solution at −20°C produces *cis*-$Mo(CO)_2(PMe_3)_4$ and $OPMe_3$ as the major products along with lesser amounts of *mer*- and *fac*-$Mo(CO)_3(PMe_3)_3$ and $Mo(CO)(PMe_3)_5$. Irradiation of **1** through Pyrex produces in addition substantial amounts of an unstable species formulated as *trans*-$Mo(CO)_2(PMe_3)_4$.

Interest in the thermal and photochemical reactions of transition metal-carbon dioxide complexes has been sparked by their potential role in catalytic schemes for CO_2 reduction, splitting, and incorporation into organic compounds [1]. Recent studies in this laboratory have provided the first examples of photochemically induced transformations of carbon dioxide complexes including reductive disproportionation [2] and decarbonylation [3]. The complex $(Me_3P)_4Mo(\eta^2\text{-}CO_2)_2$ (**1**) is a representative of the only known series of bis-CO_2-monometallic adducts [4] and, as such, appeared to offer new pathways for photoinduced CO_2 transformations. Herein we report preliminary observations on the photolysis of **1** which results in oxygen transfer from CO_2 to phosphine.

The UV-Vis spectrum of yellow **1** in toluene features broad tailing absorptions at ca. 290 and 320 nm. Although such solutions are stable in the dark for weeks at −20°C, irradiation at this temperature [5*] (400W Hg-vapor lamp, quartz vessel) of a 10 m*M* solution of **1** in toluene under a CO_2 atmosphere results in virtually complete disappearance of **1** over 4–5 h. IR monitoring indicates the appearance of a major new species **2** with absorptions at 1848 and 1786 cm^{-1}, minor products with additional bands at 1917, 1824 and 1763 cm^{-1}, as well as a quantity (8% by weight) of an uncharacterized brown precipitate [6*]. ^1H and ^{31}P NMR spectra of the hexane-soluble fraction of the reaction residue [7*] combined with literature data [8] lead to the conclusion that the major Mo-containing product **2** is *cis*-$Mo(CO)_2(PMe_3)_4$ (29% yield) and that the minor components are *mer*-

* Reference number with asterisk indicates a note in the list of references.



Scheme 1

$Mo(CO)_3(PMe_3)_4$ (**3**, ca. 5%), *fac*-$Mo(CO)_3(PMe_3)_3$ (**4**, ca. 1%) and $Mo(CO)(PMe_3)_5$ (**5**, trace). Crystallizing from the hexane extract was $OPMe_3$ (ca. 35% yield) identified by IR, ^1H and ^{31}P NMR analysis. Also formed was a substantial quantity of free PMe_3 [9*] (detected by ^1H NMR monitoring of the irradiated solution in benzene-d_6) (Scheme 1).

Photolysis of **1** through Pyrex (> 300 nm) proceeded at a similar rate but IR monitoring revealed a second major component **6** (IR: 1824 cm^{-1}) in addition to **2** which gradually decayed over a few hours [10]. The instability of **6** and the position and singular "multiplicity" of its M–CO absorption leads us to formulate it as the previously unreported *trans*-$Mo(CO)_2(PMe_3)_4$. *Trans*-**6** may thus be an intermediate in the photoconversion of **1** to *cis*-**2**.

Although formation of phosphine oxides has been observed previously in *thermal* reactions of metal phosphine complexes with CO_2 [11], this study provides the first example of a *photoinduced* phosphine oxidation by a metal–CO_2 complex. Whether this process is initiated by photoinduced phosphine expulsion and subsequent thermal O-transfer from coordinated CO_2 or by photochemical M–CO_2 charge transfer followed by phosphine oxidation awaits the results of detailed mechanistic and photochemical studies.

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References and notes

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5 Temperature was measured in the reaction solution. The separate reaction vessel was cooled by a thermostated bath at ca. −30°C and was secured externally to the lamp well (also cooled externally). The lamp was insulated from the reaction solution by circulating cold water and vacuum jackets.

6 The precipitate was largely insoluble in common solvents and non-volatile hence satisfactory NMR or mass spectra could not be obtained; IR analysis (KBr) revealed only trace amounts of **2**–**4** but significant absorptions at 3400 (br), 1630, and 953 cm^{-1}. These physical properties suggest the presence of Mo or Mo_xO_y; this would account for approximately 1/3–1/4 of the original Mo.

7 For *cis*-$Mo(CO)_2(PMe_3)_4$: IR (hexane) 1860, 1802 cm^{-1}; ^1H NMR (C_6D_6, δ) 1.38 (apparent q, $J = 2$ Hz, 18H), 1.04 (apparent q, $J = 2$ Hz, 18H); $^{31}P\{^1H\}$ NMR (C_6D_6, δ vs. ext. 85% H_3PO_4), −8 (t, $J = 26$ Hz, 2P), −17 (t, $J = 26$ Hz, 2P); MS (70 eV, DIP) M^+ 458 m/e (^{98}Mo); lit. IR (hexadecane, ref. 8a): 1861, 1801 cm^{-1}; For *mer*-$Mo(CO)_3(PMe_3)_4$: IR (hexane) 1960 (w), 1856 (s) cm^{-1}; ^{31}P NMR (C_6D_6, δ vs. ext. 85% H_3PO_4), −6 (d, $J = 24$ Hz, 2P), −16 (t, $J = 23$ Hz, 1P); lit. IR (ref. 7a); 1961, 1854 cm^{-1}; for *fac*-$Mo(CO)_3(PMe_3)_4$: IR (hexane) 1945 (w), 1856 (s) cm^{-1}; ^{31}P NMR (C_6D_6, δ vs. ext. 85% H_3PO_4), −18 (s); lit. IR (ref. 8b): 1944, 1854 cm^{-1} for $Mo(CO)(PMe_3)_5$: IR (hexane) 1775 cm^{-1}; lit (hexadecane, ref. 8c) 1773 cm^{-1}.

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9 The apparent excess of free and coordinated PMe_3 presumably reflects the production of the unphosphinated Mo-containing precipitate (note 6).

10 Complex **6** converts to **2** both thermally and (faster) photochemically.

11 See e.g.: T. Ito and A. Yamamoto, J. Chem. Soc., Dalton, (1975) 1398; M. Aresta and L.F. Nobile, Inorg. Chim. Acta, 24 (1977) L49; K.M. Nicholas, J. Organomet. Chem., 188 (1980) C10; and ref. 4.