Journal of Organometallic Chemistry, 423 (1992) C35–C37
Elsevier Sequoia S.A., Lausanne
JOM 22377PC

Preliminary communication

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

Wolfram Ziegler and Kenneth M. Nicholas *
Department of Chemistry and Biochemistry, University of Oklahoma, Norman, OK 73019 (USA)

(Received June 26, 1991; in revised form September 4, 1991)

Abstract

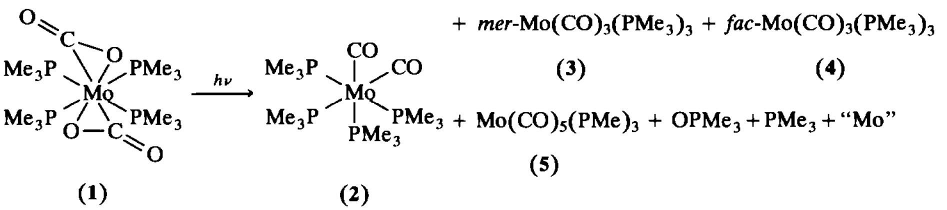
Irradiation of the title compound **1** through quartz in toluene solution at −20°C produces *cis*-$Mo(CO)_2(PMe_3)_4$ and $OPMe_3$ as the major products along with lesser amounts of *mer*- and *fac*-$Mo(CO)_3(PMe_3)_3$ and $Mo(CO)(PMe_3)_5$. Irradiation of **1** through Pyrex produces in addition substantial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

Acknowledgement. We are grateful for support provided by the U.S. Department of Energy, Office of Basic Energy Sciences (89ER 13997).

References and notes

1 Reviews: (a) A. Behr, Carbon Dioxide Activation by Metal Complexes, VCH Germany, 1988; (b) W.M. Ayers (Ed.), Catalytic Activation of Carbon Dioxide, ACS Symposium Series #363, ACS Publ., Washington, D.C., 1988; (c) T. Ito and A. Yamamoto, in S. Inoue and N. Yamazaki (Ed.), Organic and Bioorganic Chemistry of Carbon Dioxide, Halstead Press, New York, 1982, Chap. 3, pp. 79–151; (d) D. Darensbourg and R.A. Kudaroski, Adv. Organomet. Chem., 22 (1983) 129.

2 K.A. Belmore, R.A. Vanderpool, J.-C. Tsai, M.A. Khan and K.M. Nicholas, J. Am. Chem. Soc., 110 (1988) 2004.

3 P.-F. Fu, M.A. Khan and K.M. Nicholas, Organometallics, 10 (1991) 382.

4 E. Carmona, M.A. Munoz, P.J. Perez and M.L. Poveda, Organometallics, 9 (1990) 1337; R. Alvarez, E. Carmona, J.M. Marin, M.L. Poveda, E. Gutierrez-Puebla and A. Monge, J. Am. Chem. Soc., 108 (1986) 2286.

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}.

8 (a) R. Mathieu, M. Lenzi and R. Poilblanc, Inorg. Chem., 9 (1970) 2030; (b) R. Poilblanc and M. Bigorgne, Bull. Chem. Soc. Fr., (1962) 1301; (c) R. Mathieu and R. Poilblanc, Inorg. Chem., 11 (1972) 1858.

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.