enzymes[19,20] or the small molecular weight Mo cofactor which they have in common.[9]

Acknowledgment. Support from NSF Grants CHE 75-08188-A01 (to R.A.D.W.) and CHE 76-07026 (to E.I.S.) is gratefully acknowledged. We are also grateful to Drs. W. E. Newton, E. I. Stiefel, and J. W. McDonald for helpful discussions and to J. W. McDonald for providing us with his unpublished method of obtaining high levels of enrichment.

Registry No. $Mo_2O_3(Etcys)_4$, 24228-97-5; $Mo_2O_4(Etcys)_2$, 22775-76-4; $Mo_2O_3(Et_2dtc)_4$, 20023-86-3; $MoO(Et_2dtc)_2$, 25395-92-0; $Mo_2O_3(Et_2dtp)_4$, 60384-05-6; $MoO(Et_2dtp)_2$, 25395-91-9.

---

(19) S. P. Cramer, H. B. Gray, and K. V. Rajagopalan, *J. Am. Chem. Soc.*, **101**, 2772 (1979).

(20) T. D. Tullius, D. M. Kurtz, S. D. Conradson, and K. O. Hodgson, *J. Am. Chem. Soc.*, **101**, 2776 (1979).

(21) A. D. English, J. P. Jesson, W. G. Klemperer, T. Mamouneas, L. Messerle, W. Shum, and A. Tramontano, *J. Am. Chem. Soc.*, **97**, 4785 (1975).

(22) L. R. Melby, *Inorg. Chem.*, **8**, 349 (1969).

(23) L. Ricard, J. Estienne, P. Karagiaanidis, P. Toledano, J. Fischer, A. Mitschler, and R. Weiss, *J. Coord. Chem.*, **3**, 277 (1974).

(24) J. R. Knox and C. K. Prout, *Acta Crystallogr., Sect. B*, **25**, 2281 (1969).

Contribution from the Department of Chemistry,
The Pennsylvania State University,
University Park, Pennsylvania 16802

Photoinduced Elimination of H_2 from $[MoH_4(diphos)_2]$ and $[MoH_4(PPh_2Me)_4]$

Ronald Pierantozzi and Gregory L. Geoffroy*

Received October 16, 1979

Photolysis of a number of di- and trihydride complexes has been shown to lead to loss of H_2.[1-7] This appears to be a general reaction pathway for this class of compounds and in several cases has led to the formation of highly reactive complexes, many of which are not easily obtained thermally.[4-7] Photolysis of *poly*hydride complexes possessing four or more hydride ligands can, in principle, lead to *multiple* H_2 *loss* and hence to extremely reactive, coordinatively unsaturated species. To test this notion, we have examined the photochemical properties of a series of polyhydride complexes of Re[7] and the molybdenum tetrahydrides $[MoH_4(diphos)_2]$ (diphos = $Ph_2PCH_2CH_2PPh_2$) and $[MoH_4(PPh_2Me)_4]$. The results of this latter study are of relevance to recent reports[8-10] that describe the photoluminescent and photochemical properties of *trans*-$[W(L)_2(diphos)_2]$ (L = CO, N_2) complexes and are described herein.

Experimental Section

The $[MoH_4(diphos)_2]$ and $[MoH_4(PPh_2Me)_4]$ complexes were prepared by published procedures.[11] Solvents employed in these studies were dried by standard methods and were rigorously degassed prior to use. All manipulations of the compounds were carried out under prepurified Ar, N_2, or CO as appropriate.

Irradiations were conducted at 366 nm by using a 450-W Hanovia medium-pressure Hg lamp equipped with Corning Glass 0-52 and 7-37 filters, with a 100-W Blak-Ray B100A lamp equipped with a 366-nm narrow band-pass filter, or in a 350-nm Rayonet photoreactor. The complex to be studied was placed in an evacuable quartz UV cell or a Schlenk tube attached to the vacuum line, and after being degassed, the appropriate solvent was distilled onto the sample. Solutions were irradiated with the appropriate lamp, and IR, NMR, and electronic absorption spectra were periodically recorded.

Results and Discussion

We initially irradiated the $[MoH_4L_4]$ complexes under an N_2 atmosphere, expecting to form the known bis(dinitrogen) complexes if photoinduced loss of all four hydride ligands were to occur. This expectation was realized, and high yields of *trans*-$[Mo(N_2)_2(diphos)_2]$ and *trans*-$[Mo(N_2)_2(PPh_2Me)_4]$ were obtained. For example, photolysis of a benzene solution of $[MoH_4(diphos)_2]$ at 25 °C for 12 h with 366-nm light under a continuous N_2 purge gave a 93% yield of *trans*-$[Mo(N_2)_2(diphos)_2]$, eq 1. The nondescript spectral changes which

$$[MoH_4(diphos)_2] + 2N_2 \xrightarrow{h\nu} 2H_2 + trans\text{-}[Mo(N_2)_2(diphos)_2] \quad (1)$$

obtain upon photolysis and the necessity of the N_2 purge in order to drive the reactions have precluded accurate quantum yield measurements, although the time scale of the photolysis indicates that the quantum yields are low. The conversion shown in eq 1 has been observed to occur thermally[12] but at a rate much slower than that which obtains under photochemical conditions. We also found that photolysis of $[MoH_4(diphos)_2]$ under a CO atmosphere gives a mixture of *cis*- and *trans*-$[Mo(CO)_2(diphos)_2]$. Irradiation under C_2H_4, C_2H_2, and CO_2 atmospheres leads to complex arrays of products which have proven difficult to separate and characterize.

An important question is what happens in the absence of a suitable substrate that can trap the photogenerated intermediate(s): Are reactive species such as $[Mo(diphos)_2]$ and $[Mo(PPh_2Me)_4]$ photogenerated and do they persist in solution? Photolysis of rigorously degassed benzene solutions of $[MoH_4(diphos)_2]$ with 366-nm light gives a color change from yellow to bright orange over a period of several hours. This color change is accompanied by a steady decrease in intensity of the 1714-cm^{-1} ν_{Mo-H} vibration and the $\delta = -3.6$ ppm hydride resonance characteristic of $[MoH_4(diphos)_2]$. No new hydride resonances or metal hydride vibrations appear in either spectrum. The singlet at 83.5 ppm initially present in the ^{31}P NMR spectrum of $[MoH_4(diphos)_2]$ in benzene-d_6 solution also decreases in intensity as the photolysis proceeds, and a new singlet at 80.2 ppm appears and grows in.

Mass spectral, gas chromatographic, and Toepler pump analyses of the gases above irradiated benzene solutions show the formation of H_2 with an average of 1.9 mol of H_2 released per mole of $[MoH_4(diphos)_2]$ irradiated. Evaporation of solvent from these irradiated solutions gives an extremely air-sensitive orange solid which shows no metal hydride vibrations in its infrared spectrum and no hydride resonances in its ^1H NMR spectrum. The ^{31}P NMR spectrum of this compound is complex, showing 12 separate resonances, including an intense peak at 13.2 ppm attributable to free diphos. Repeated attempts at recrystallization and purification of this

---

(1) Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979.

(2) Geoffroy, G. L. *Prog. Inorg. Chem.*, in press.

(3) Geoffroy, G. L.; Bradley, M. G.; Pierantozzi, R. *Adv. Chem. Ser.* **1978**, *No. 167*, 181.

(4) Geoffroy, G. L.; Bradley, M. G. *Inorg. Chem.* **1978**, *17*, 2410.

(5) Geoffroy, G. L.; Pierantozzi, R. *J. Am. Chem. Soc.* **1976**, *98*, 8054.

(6) (a) Elmitt, K.; Green, M. L. H; Forder, R. A.; Jefferson, I.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1974**, 747. (b) Farrugia, L.; Green, M. L. H. *Ibid.* **1975**, 416. (c) Giannotti, C.; Green, M. L. H. *Ibid.*, **1972**, 1114. (d) Green, M. L. H.; Berry, M.; Couldwell, C.; Prout, K. *Nouv. J. Chim.* **1977**, *1*, 187. (e) Samat, A.; Sala-Pala, J.; Guglielmetti, R.; Guerchais, J. *Ibid.*, **1978**, *2*, 13.

(7) Bradley, M. G.; Roberts, D. A.; Geoffroy, G. L., to be submitted for publication.

(8) Thomas, R. J. W.; Laurence, G. S.; Diamantis, A. A. *Inorg. Chim. Acta* **1978**, *30*, L353.

(9) Caruana, A.; Kisch, H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 328.

(10) Caruana, A.; Kisch, H. *Int. Conf. Organomet. Chem. 9th* **1979**, Abstract D10.

(11) Penella, F. *Inorg. Synth.* **1976**, *15*, 42.

(12) Archer, L. J.; George, T. A. *Inorg. Chem.* **1979**, *18*, 2079.

compound failed to give a pure product. Elemental analyses of compounds obtained from several different experiments did not agree well with each other nor with any obvious formulation.

The observation of loss of 1.9 mol of H_2 per mole of [MoH_4(diphos)$_2$] irradiated and the accompanying infrared, ^1H, and ^{31}P NMR spectral changes are not inconsistent with the formation of [Mo(diphos)$_2$] upon irradiation of [MoH_4(diphos)$_2$] in degassed solution. However, the ^{31}P NMR spectrum of the solid material isolated from these experiments clearly indicates that this species, if formed, is not sufficiently stable for isolation. We suspect that [Mo(diphos)$_2$], possibly solvated, may initially be photogenerated but that it subsequently decomposes or reacts with solvent when no other suitable substrate is available. Loss of H_2 from [MoH_4(diphos)$_2$] presumably proceeds in a stepwise fashion via initial generation of [MoH_2(diphos)$_2$].

In regard to the question of whether or not [Mo(diphos)$_2$] is photogenerated from [MoH_4(diphos)$_2$], Diamantis[8] and Kisch[10] and their co-workers have concluded from a series of flash photolysis studies that irradiation of *trans*-[W(N_2)$_2$(diphos)$_2$] does give transient formation of the analogous [W(diphos)$_2$] complex, possibly as a solvated species. This latter complex subsequently reacts with N_2 to regenerate *trans*-[W(N_2)$_2$(diphos)$_2$] and with CO and H_2 to give [W(CO)$_2$(diphos)$_2$] and [WH_4(diphos)$_2$], respectively. The formation of [W(diphos)$_2$] in these reported studies clearly makes [Mo(diphos)$_2$] a reasonable intermediate in our experiments.

Acknowledgment. We thank the National Science Foundation for support of this research. G.L.G. gratefully acknowledges the Camille and Henry Dreyfus Foundation for a Teacher-Scholar grant and the Alfred P. Sloan Foundation for a Research Fellowship.

Registry No. MoH_4(diphos)$_2$, 32109-09-4; MoH_4(PPh_2Me)$_4$, 32109-07-2; *trans*-[Mo(N_2)$_2$(diphos)$_2$], 25145-64-6; *trans*-[Mo(N_2)$_2$(PPh_2Me)$_4$], 33248-03-2; *cis*-[Mo(CO)$_2$(diphos)$_2$], 17523-42-1; *trans*-[Mo(CO)$_2$(diphos)$_2$], 40219-77-0; WH_4(diphos)$_2$, 36352-27-9.

Correspondence

Bonding in the (π-(3)-1,2-Dicarbollyl)tricarbonylmanganese Anion

Sir:

On the basis of SCCC MO calculations,[1] we have suggested recently that the intuitive view of bonding[2] in metallocarborane complexes of the dicarbollyl type, e.g., [CpFeCb]$^-$, as being very similar to that in the analogous cyclopentadienyl complex $FeCp_2$ (Cb = $C_2B_9H_{11}$; Cp = C_5H_5), requires an important qualification, namely, that, while in Cp$^-$, the a_2'' (π) and e_1'' (π) are genuine frontier orbitals, their counterparts in Cb^{2-} lie much lower in energy than the HOMO, and in fact the predominant interaction between the iron atom and the dicarbollide dianion (Cb^{2-}) involves the σ orbitals of the latter.

We have now extended our calculations to the "half-sandwich" title compound [CbMn(CO)$_3$]$^-$ and compare the results with those of CpMn(CO)$_3$. The SCCC MO method was identical with that reported previously.[1] However, the program used previously had a slight error, and the present results are based on new calculations. For CpMn(CO)$_3$, the geometry was as used previously,[3] and for Cp$^-$ and Cb^{2-} the geometry was as in the corresponding complexes. In [CbMn(CO)$_3$]$^-$, the structural parameters of Zalkin and coworkers[4] for the analogous rhenium complex were used with suitable modification. Within the dicarbollide cage, the following parameters were taken: r(B–B) = 1.78 Å, r(C–B) = 1.72 Å, r(C–C) = 1.61 Å, r(C–H) = 1.11 Å, and r(B–H) = 1.02 Å. The geometry was idealized so that one carbonyl group was taken in the symmetry plane of the molecule (r(Mn–CO) = 1.79 Å, r(C–O) = 1.16 Å, Mn–C–O = 180° in the tricarbonyl moiety). The perpendicular distance of the dicarbollide cage from the manganese atom was then 0.256 Å shorter than the corresponding value reported for the rhenium complex. Table I gives a comparison of the metal charge, ligand (A) charge, carbonyl charge, and carbonyl overlap population for the two compounds. It is immediately obvious that whereas in CpMn(CO)$_3$ the Cp$^-$ anion donates 0.905 electron, the Cb^{2-} dianion donates more electrons (1.436) to the Mn(CO)$_3$ group. In both complexes, the metal atom carries similar positive charges supporting earlier qualitative ideas of one of us that the metal atom in organometallic systems tends to "conduct" charge from one part of the molecule to another.[5] Charge transfer from the C_2B_3 face involves nearly twice as much donation of σ density (0.327 electron) as π density (0.187 electron), but, interestingly, the complexation of the dicarbollide dianion does not simply involve the C_2B_3 face but also leads to a considerable decrease in σ density (0.479 electron) and a small increase in π density (0.065 electron) of the B_5 ring.

Table I. Metal, Ligand, and Carbonyl Charges and C–O Overlap Populations

	CpMn(CO)$_3$	[CbMn(CO)$_3$]$^-$
q_M	0.524	0.584
q_A	−0.095	−0.564
q_{CO}	−0.143	−0.340
OP(C–O)	0.714	0.678

The C–O bond order in both complexes is lower than that calculated for free CO (0.759) suggesting that charge donated to the metal is largely transferred (by the above "conduction" mechanism) to the (CO)$_3$ group. The greater donation and electron transfer in [CbMn(CO)$_3$]$^-$ compared to CpMn(CO)$_3$ is demonstrated by the calculated C–O overlap populations (OP, Table I) and is nicely reflected in the lower carbonyl stretching frequencies of [CbMn(CO)$_3$]$^-$ (2020 and 1908 cm^{-1})[2] compared to those of CpMn(CO)$_3$ (2035 and 1949 cm^{-1}).[6]

Our calculations suggest that while the bonding in metal–dicarbollyl complexes and analogous metal–cyclopentadienyl complexes is formally similar, the dicarbollide dianion should be regarded primarily as a σ-electron donor and only in a secondary manner as a π-electron donor in carbonyl complexes,

---

(1) D. A. Brown, M. O. Fanning, and N. J. Fitzpatrick, *Inorg. Chem.*, **17**, 1620 (1978).

(2) M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, Jr., and P. A. Wegner, *J. Am. Chem. Soc.*, **90**, 879 (1968).

(3) D. A. Brown, J. P. Chester, N. J. Fitzpatrick, and I. J. King, *Inorg. Chem.*, **16**, 2497 (1977).

(4) A. Zalkin, T. E. Hopkins, and D. H. Templeton, *Inorg. Chem.*, **5**, 1189 (1966).

(5) D. A. Brown, *Transition Met. Chem.*, **3**, 1 (1966).

(6) R. D. Fischer, *Spectrochim. Acta*, **19**, 842 (1963).

0020-1669/80/1319-1822$01.00/0