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 co-workers[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).

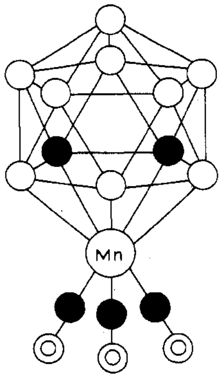

Figure 1. (π-(3)-1,2-Dicarbollyl)tricarbonylmanganese anion where ○ = boron, ● = carbon, and ◎ = oxygen.

as well as in complexes without carbonyl groups. Thus, one may regard the dangling orbitals of the dicarbollide dianion as essentially σ orbitals with respect to any 12th atom of a cluster.

Registry No. $CpMn(CO)_3$, 12079-65-1; $[CbMn(CO)_3]^-$, 73333-88-7.

Department of Chemistry
University College
Belfield, Dublin 4, Ireland

David A. Brown*
Matthew O. Fanning
Noel J. Fitzpatrick

Received October 19, 1979

Electron Transfer in Metal–Dioxygen Adducts

Sir:

The conventional delineation of metal–dioxygen adducts into "superoxides" and "peroxides" is a convenient formalism which conveys no information concerning the actual negative charge residing on the dioxygen unit. "Superoxides" are characterized by having an ν(O–O)stretching frequency in the range 1075–1195 cm^{-1}.[1] X-ray studies reveal a (O–O) bond length of about 133 pm, and, so far, all structures show the dioxygen bound end-on to a metal atom. Thus the observation of a ν(O–O) frequency in this range in an oxygen adduct conveys a bond order of about 1.5 and almost certainly end-on binding.

The "peroxides" are closed shell and are characterized by an ν(O–O) frequency in the range 790–932 cm^{-1}.[1] X-ray studies show an (O–O) bond length of about 146 pm and sideways bonding for 1:1 complexes. Thus an infrared frequency in the range indicated implies a bond order of about 1.0 and, for 1:1 complexes, probably sideways bonding.

Neither of these descriptions in themselves provides any information about net electronic charge on oxygen.[2] Molecular orbital and valence-bond descriptions have inferred that the net charge in superoxides may be quite small.[3,4] Drago[5] has shown that the ESR spectra of some cobalt–dioxygen adducts may be interpreted in terms of 0.1–0.8 electron net transfer to dioxygen. Several oxygen-17 ESR studies[6,7] may be similarly, and perhaps more directly, interpreted. With the exception of such ESR studies, direct experimental evidence for net-electron transfer is sparse.

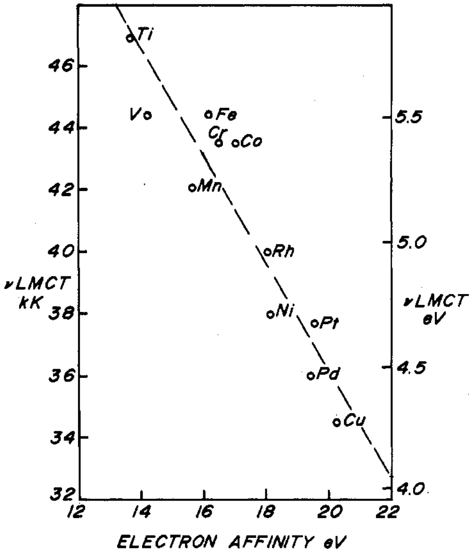

Figure 1. A plot of the more intense oxygen to metal LMCT band (maximum) energy vs. the electron affinity of M(II) for a series of $M(O_2)_2$ species. Most of the $M(O_2)_2$ species included here have been reported by Ozin and co-workers.[8] Ogden[17] has reported $Cr(O_2)_2$ and $Cu(O_2)_2$. The Ti, V, Fe, and Mn species were prepared in pure oxygen[18] and are presumed, though not as yet proven, to be $M(O_2)_2$ moieties. The best line through these data is (LMCT) = 8.88 − 0.22(EA) (11 points) with both (LMCT) and (EA) in eV.

We now report additional experimental information and show that infrared spectra in combination with electronic spectra can be interpreted in terms of net negative charge residing on oxygen. Ozin and co-workers[8] have synthesized two series of binary metal dioxygen complexes, $M(O_2)$ and $M(O_2)_2$, by using cryogenic matrix techniques.[9] In the absence of any other ligands any electron density, $\delta-$, transferred to (O_2) must leave $\delta+$ on the metal. It should therefore be possible to correlate charge properties on the metal with those on dioxygen. These species all exhibit an electronic spectrum consisting of one strong band and one weak band usually seen as a lower energy shoulder on the principal peak. In most cases these two bands are the only absorption noted in the 200–800-nm region. A simple group theoretical treatment[10] predicts one strong LMCT (σ–σ^*) transition[10] and one weaker LMCT (π–σ^*) transition irrespective of whether end-on or sideways bound dioxygen is assumed.[11] The spectrum is assigned accordingly. As inferred above, there is no evidence, in most of these species, for any band assignable to an internal π–π^* transition within the oxygen ligand. Studies on 1:1 "superoxo" cobalt(III) complexes reveal that this band, observed near 250 nm in free superoxide ion, blue shifts at least to 215 nm in the terminally bound 1:1 superoxides.[12,13] It will clearly be absent from the peroxy derivatives.

---

(1) L. Vaska, *Acc. Chem. Res.*, **9**, 175 (1976).
(2) R. S. Drago, *Inorg. Chem.*, **18**, 1408 (1979).
(3) R. F. Kirchner and G. H. Loew, *J. Am. Chem. Soc.*, **99**, 4639 (1977).
(4) B. D. Olafson and W. A. Goddard, III, *Proc. Natl. Acad. Sci. U.S.A.*, **74**, 1315 (1977).
(5) B. S. Tovrog, D. J. Kitko, and R. S. Drago, *J. Am. Chem. Soc.*, **98**, 5144 (1976).
(6) R. K. Gupta, A. S. Mildvan, T. Yonetani, and T. S. Srivastava, *Biochem. Biophys. Res. Commun.*, **67**, 1005 (1975).
(7) B. M. Hoffman, T. Szymanski, T. G. Brown, and F. Basolo, *J. Am. Chem. Soc.*, **100**, 7253 (1978).
(8) H. Huber, W. Klotzbucher, G. A. Ozin, and A. Vander Voet, *Can. J. Chem.*, **51**, 2722 (1973); D. McIntosh and G. A. Ozin, *Inorg. Chem.*, **15**, 2869 (1976); **16**, 59 (1977); A. J. Lee Hanlan and G. A. Ozin, *ibid.*, **16**, 2848 (1977); A. J. Lee Hanlan, G. A. Ozin, and W. J. Power, *ibid.*, **18**, 2390 (1979); D. McIntosh, Ph.D. Thesis, University of Toronto, 1979, and unpublished observations.
(9) The $M(O_2)_x$ binary complexes of the present study are to be regarded as the kinetically stable primary products formed and trapped under cryochemical conditions in pure dioxygen or dioxygen/inert gas mixtures. Under higher temperature reaction conditions the likely M/O_2 products are the thermodynamically stable metal oxides. The dioxygen complexes represent reactive intermediates which may be regarded as precursors to molecular or bulk oxide generation.
(10) A. B. P. Lever, G. A. Ozin, and H. B. Gray, to be submitted for publication.
(11) A. B. P. Lever and H. B. Gray, *Acc. Chem.* Res., **11**, 348 (1978).
(12) S. R. Pickens, A. E. Martell, G. McLendon, A. B. P. Lever, and H. B. Gray, *Inorg. Chem.*, **17**, 2190 (1978).

0020-1669/80/1319-1823$01.00/0