Table II. Maximum Absorbance Wavelengths (λ_{max}) and Corresponding Molar Absorptivities ($\epsilon \times 10^{-3}$) of Neutral and Singly Reduced (TpTP)MFe(CO)$_4$ Complexes in PhCN with 0.1 M TBA(PF$_6$)

compd	λ_{max}, nm ($\epsilon \times 10^{-3}$, cm^{-1} M^{-1})				
(TpTP)GeFe(CO)$_4$	364 (11)	456 (165)	585 (10)	629 (13)	
[(TpTP)GeFe(CO)$_4$]$^-$	366 (11)	472 (54)	710 (3)	776 (5)	829 (4)
(TpTP)SnFe(CO)$_4$	369 (34)	454 (302)	588 (17)	634 (21)	
[(TpTP)SnFe(CO)$_4$]$^-$	369 (34)	468 (77)	790 (17)	849 (12)	

that the most positive reduction potentials are found for (P)M^{II} complexes having the highest electronegativity. The differences in reduction potentials between (TpTP)SnFe(CO)$_4$ and (TpTP)GeFe(CO)$_4$ amounts to 50 mV with the former complex being the most easy to reduce. This is consistent with the slightly higher electronegativity of Ge(II) (2.01) with respect to Sn(II) (1.96) and also suggests that the site of electroreduction occurs at the porphyrin π ring system.

The above conclusions regarding the site of reduction were verified by controlled-potential electrolysis coupled with ESR and thin-layer spectroelectrochemistry. Time-resolved thin-layer spectra were recorded after each reduction and are represented in Figure 2 for the case of (TpTP)GeFe(CO)$_4$. After reduction by one electron, the Soret band, which is initially at 456 nm, is shifted to 472 nm and there is a significant decrease in intensity of this peak. The two peaks at 585 and 629 nm also decrease while new peaks appear at 710, 776, and 829 nm. A further one-electron reduction of [(TpTP)GeFe(CO)$_4$]$^-$ yields the species whose spectrum is shown in Figure 2b. Only two broad absorptions are detected at 468 and 587 nm. No bands are observed at wavelengths higher than 600 nm. After back-electrolysis, the initial spectrum is totally recovered. The two reduced forms are characteristic of anion radicals and dianions resulting from ring-centered reductions.[6] Similar spectral changes are also observed upon electroreduction of (TpTP)SnFe(CO)$_4$ and [(TpTP)SnFe(CO)$_4$]$^-$. This is illustrated in Table II, where wavelength maxima of the neutral and the singly reduced species are summarized.

The ESR spectrum of the species generated after bulk electrolysis of (TpTP)GeFe(CO)$_4$ at -1.35 V has an absorbance at $g = 2.00$ and is typical of porphyrin anion radicals.[6] This reaction is reversible, and if one switches to a positive potential, the original diamagnetic species can be regenerated. Similar behavior is observed for (TpTP)SnFe(CO)$_4$, and it appears that the addition of both the first and the second electron is at the π ring system of the metalloporphyrin. This is in contrast to LFe(CO)$_4$ and (P)InM(CO)$_3$Cp where the initial reduction occurs at the Fe(0) atom[7] and at the axial ligand,[4] respectively. The former reductions occur in a range of potentials between -1.6 and -2.1 V and depend upon the donor character of the bound L group.[7] While one might expect (P)M^{II}Fe(CO)$_4$ to exhibit these same electrode reactions, the addition of two electrons to the porphyrin ring of (P)M^{II} will change the donor character of the metalloporphyrin such that extremely negative potentials should be needed for reduction of the iron carbonyl unit.

The differences in stability between reduced (P)InM(CO)$_3$Cp (M = W or Mo) and (P)MFe(CO)$_4$ (M = Sn or Ge) seem to be clearly related to differences in the site of reduction between the two complexes. The σ-bonded complexes are extremely unstable after electroreduction, which occurs at a site localized at the metal-metal bond.[3] In contrast, the (P)MFe(CO)$_4$ complexes are extremely stable, and in these cases, the site of electroreduction is at the porphyrin π ring system. The Sn atom is removed by 0.81 Å from the plane of the porphyrin ring, and this may account for the high stability of these reduced complexes. It does not, however, account for the differences in the reduction site between (P)MFe(CO)$_4$ and (P)InM(CO)$_3$Cp complexes, which may be related to the different donor properties of the M(CO)$_3$Cp and Fe(CO)$_4$ units. Studies of other (P)MM′L complexes are now in progress and should help to clarify these differences.

Acknowledgment. The support of the National Science Foundation (Grants 8215507 and INT-8413696) and the CNRS (Grant 142) is gratefully acknowledged.

Registry No. TBA(PF$_6$), 3109-63-5; (TpTP)SnFe(CO)$_4$, 92479-19-1; (TpTP)GeFe(CO)$_4$, 92479-20-4; [(TpTP)GeFe(CO)$_4$]$^-$, 99595-05-8; [(TpTP)SnFe(CO)$_4$]$^-$, 99604-83-8; Ge, 7440-56-4; Sn, 7440-31-5; Fe, 7439-89-6.

Department of Chemistry
The University of Houston
Houston, Texas 77004

K. M. Kadish*
B. Boisselier-Cocolios
C. Swistak

Laboratoire de Synthese et d'Electrosynthese Organometallique associe au CNRS (UA 33)
Faculte des Sciences "Gabriel"
21100 Dijon, France

J. M. Barbe
R. Guilard*

Received July 11, 1985

---

(6) Clack, D. W.; Hush, N. S. *J. Am. Chem. Soc.* **1965**, *87*, 4238.
(7) Connelly, N. G.; Geiger, W. E. *Adv. Organomet. Chem.* **1984**, *23*, 24.

Synthesis of Tris(3,5-di-*tert*-butylcatecholato)molybdenum(VI) and Its Reaction with Molecular Oxygen

Sir:

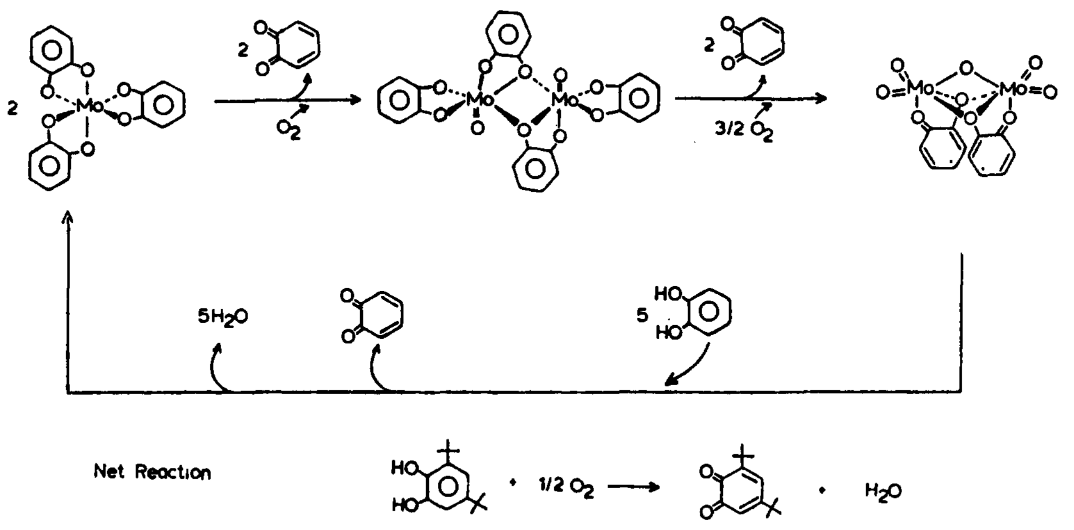
Reactions between Mo(CO)$_6$ and *o*-benzoquinones carried out under nitrogen, but not under scrupulously oxygen-free conditions, produced dramatically different products. With use of tetrachloro-1,2-benzoquinone the dimeric Mo(VI) product Mo$_2$(Cl$_4$Cat)$_6$ was obtained.[1] Starting with 3,5-di-*tert*-butyl-1,2-benzoquinone or 9,10-phenanthrenequinone the binuclear oxomolybdenum(VI) products Mo$_2$O$_2$(DBCat)$_4$ and Mo$_2$O$_5$(PhenSQ)$_2$ were obtained.[2,3] The 9,10-phenanthrenequinone reaction was found to be photochemical. Soxhlet extraction of crude Mo$_2$O$_5$(PhenSQ)$_2$ with CH$_2$Cl$_2$ gave Mo(PhenCat)$_2$(PhenSQ).[4] In this report we present the results of more recent studies carried out to provide information that might place these apparently divergent and puzzling results in better chemical perspective.

Reactions carried out between vanadium hexacarbonyl and the quinones used in studies with molybdenum indicated a parallel chemistry.[5] Under conditions similar to those that lead to Mo$_2$O$_2$(DBCat)$_4$ the complex V$_2$O$_2$(DBSQ)$_2$(DBCat)$_2$ could be formed. Rigorous exclusion of oxygen revealed that the initial product of the reaction between V(CO), and 3,5-di-*tert*-butylbenzoquinone was V(DBSQ)$_3$; the oxovanadium(V) product resulted from subsequent reaction of V(DBSQ)$_3$ with oxygen. Due to the paramagnetism of these products EPR was found to be a useful means of monitoring reactions. If observations made on vanadium complexes are extended to the Mo reactions described

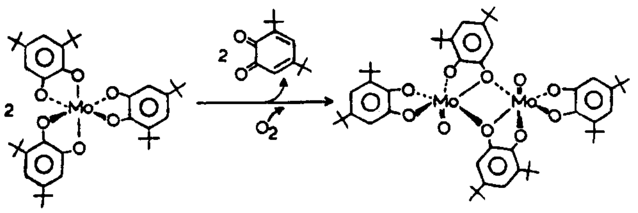
---

(1) Pierpont, C. G.; Downs, H. H. *J. Am. Chem. Soc.* **1975**, *97*, 2123.
(2) Pierpont, C. G.; Buchanan, R. M. *J. Am. Chem. Soc.* **1975**, *97*, 6450.
(3) Buchanan, R. M.; Pierpont, C. G. *Inorg. Chem.* **1979**, *18*, 1616.
(4) Pierpont, C. G.; Buchanan, R. M. *J. Am. Chem. Soc.* **1975**, *97*, 4912.
(5) Cass, M. E.; Greene, D. L.; Buchanan, R. M.; Pierpont, C. G. *J. Am. Chem. Soc.* **1983**, *105*, 2680.

Scheme I



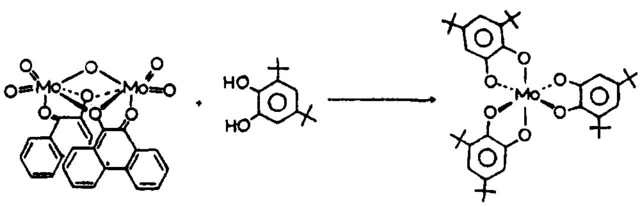
above, a scheme can be constructed, which relates the observed products by reactions with oxygen (Scheme I). Tertrachloro-1,2-benzoquinone, with a positive reduction potential, forms complexes with both V and Mo which are free of oxo ligands and are relatively inert to further oxidation by O_2. The reaction between $Mo(CO)_6$ and 3,5-di-*tert*-butyl-1,2-benzoquinone carried out in toluene with careful exclusion of oxygen gave $Mo(DBCat)_3$. This product showed two sharp *tert*-butyl resonances in the proton NMR spectrum at 1.27 and 1.11 ppm, indicating symmetrical equivalence of the three ligands, and a parent ion peak at $m/e = 758$ in the mass spectrum, indicating a monomeric structure similar to that of $Os(DBCat)_3$.[6] The infrared spectrum of the complex is quite similar to that of $Mo_2O_2(DBCat)_4$ with the Mo=O stretching band at 966 cm^{-1} missing. Upon exposure to trace quantities of oxygen the oxomolybdenum dimer is formed with free benzoquinone:



This reaction can be observed by appearance of the four *tert*-butyl resonances of the dimer at 1.717, 1.097, 1.056, and 1.020 ppm and signals for the benzoquinone at 1.128 and 0.769 ppm. This process is the first step in the reaction sequence described in Scheme I and is quite similar to the chemistry of the related vanadium complex.

The second reaction in the scheme, addition of oxygen to $Mo_2O_2(DBCat)_4$, has not been observed. The expected product of this step by analogy with the 9,10-phenanthrenequinone reaction would be $Mo_2O_5(DBSQ)_2$. Oxidation of $Mo_2O_5(DBCat)_2^{2-}$ led to dissociation of the quinone ligands,[7] suggesting that the strong interaction between π orbitals of the semiquinones in $Mo_2O_5(PhenSQ)_2$ is an important stabilizing effect for the complex. Further air oxidation of $V_2O_2(DBCat)_2(DBSQ)_2$ led to V_2O_5.

To study the third step in the reaction scheme, $Mo_2O_5(PhenSQ)_2$ was treated with 9,10-phenanthrenediol. The products formed were $Mo(PhenCat)_2(PhenSQ)$ and presumably water, although this was not observed directly. In a second reaction $Mo_2O_5(PhenSQ)_2$ was treated with 3,5-di-*tert*-butylcatechol in the hope of forming a mixed-quinone-ligand complex. The reaction produced $Mo(DBCat)_3$ exclusively, which was stable in the presence of water but immediately formed $Mo_2O_2(DBCat)_4$ upon exposure to oxygen:



These reactions show that $Mo(DBCat)_3$ can be formed either by treating Mo(0) with benzoquinone or by using a Mo(VI) complex and the catecholate form of the ligand. They also illustrate steps in the series of reactions shown in Scheme I whereby oxygen and catechol are converted to water and benzoquinone through a series of well-characterized Mo complex intermediates.

Acknowledgment. This research was supported by Grant GM-23386 from the National Institutes of Health.

Registry No. $Mo(CO)_6$, 13939-06-5; $Mo(DBCat)_3$, 64020-85-5; $Mo_2O_2(DBCat)_4$, 69847-07-0; $Mo_2O_5(PhenSQ)_2$, 57473-26-4; $Mo(PhenCat)_2(PhenSQ)$, 56637-35-5; 3,5-di-*tert*-butyl-1,2-benzoquinone, 3383-21-9; 9,10-phenanthrenediol, 604-84-2; 3,5-di-*tert*-butylcatechol, 1020-31-1.

Department of Chemistry
University of Colorado
Boulder, Colorado 80309

Marion E. Cass
Cortlandt G. Pierpont*

Received April 29, 1985

Electrochemical Generation of an Iron(IV) Porphyrin

Sir:

A variety of recent investigations has revealed a rich redox chemistry present in iron porphyrin systems. The oxidation of simple iron(III) porphyrins by one or two electrons is known to occur, and examples of Fe^{IV},[1] $Fe^{III}P^{+\cdot}$,[2] and $Fe^{IV}P^{+\cdot}$[3] (where $P^{+\cdot}$

---

(6) Hursthouse, M. B.; Fram, T.; New, L.; Griffith, W. P.; Nielson, A. J. *Transition Met. Chem. (Weinheim, Ger.)* **1978**, *3*, 255.

(7) Pierpont, C. G.; Buchanan, R. M. *Inorg. Chem.* **1982**, *21*, 652.

(1) (a) Groves, J. T.; Quinn, R.; McMurry, T. J.; Nakamura, M.; Lang, G.; Boso, B. *J. Am. Chem. Soc.* **1985**, *107*, 354–360. (b) Chin, D.-H.; Balch, A. L.; La Mar, G. N. *J. Am. Chem. Soc.* **1980**, *102*, 1446–1447. (c) Balch, A. L.; Chan, Y.-W.; Cheng, R.-J.; La Mar, G. N.; Latos-Grazynski, L.; Renner, M. W. *J. Am. Chem. Soc.* **1984**, *106*, 7779–7785.