Communications

Electrochemistry of Porphyrins Containing a Metal–Metal Bond. Reactions of "Carbenoid" (TpTP)GeFe(CO)₄ and (TpTP)SnFe(CO)₄

Sir:

The synthesis and characterization of several metal–metal-bonded tin and germanium metalloporphyrins has recently been reported.[1,2] These donor–acceptor complexes have been identified by various physicochemical techniques, and X-ray structures of (OEP)SnFe(CO)₄[1] and (TPP)SnMn(CO)₄HgMn(CO)₅[2] have been published. The former compound has also been examined by IR and Mössbauer data, and on the basis of these data, a Sn(II) oxidation state has been assigned.[1]

In view of our earlier electrochemical studies[3] on the σ-bonded metalloporphyrins such as (TPP)InM(CO)₃Cp (M = Mo or W),[4] we were interested in similar electrochemical characterization of the (TpTP)MFe(CO)₄ complexes, where M = Ge or Sn and (TpTP) = the *meso*-tetra-*p*-tolylporphyrin dianion. These carbenoid complexes were prepared by the reaction of $Na_2Fe(CO)_4$ and $(P)M^{IV}Cl_2$ according to the method described in a previous publication.[1] Characterization was achieved by IR, NMR, and UV–visible spectroscopy and gave results in good agreement with published values. Cyclic voltammetric measurements were carried out in dichloromethane (CH_2Cl_2) or benzonitrile (PhCN) containing 0.1 M tetrabutylammonium hexafluorophosphate (TBA-(PF_6)) as supporting electrolyte. Spectroelectrochemical measurements are reported in PhCN (due to its lower vapor pressure) and gave results similar to those in CH_2Cl_2.

Both (TpTP)SnFe(CO)₄ and (TpTP)GeFe(CO)₄ are reversibly reduced in two single-electron-transfer steps, which occur in a range of potentials between −1.00 and −1.45 V. The exact potentials of each electrode reaction are given in Table I, and a representative cyclic voltammogram of (TpTP)GeFe(CO)₄ is shown in Figure 1.

The two reduction waves are reversible and diffusion-controlled as ascertained by experimentally measured values of $i_{pa}/i_{pc} = 1.0$, $i_p/v^{1/2}$ = a constant, and $E_{pa} - E_{pc}$ = 60 mV. This was true at scan rates between 0.05 V/s and 3 V/s. The potential difference between the first and second reduction is 0.39 V for (TpTP)-SnFe(CO)₄ and 0.40 V for (TpTP)GeFe(CO)₄. These values are in agreement with an average separation of 0.44 ± 0.05 V for various metalloporphyrins in which reduction occurs at the porphyrin π ring system.[5] Fuhrhop, Kadish, and Davis[5] have also

Table I. Potentials (V vs. SCE) for Reduction of (TpTP)MFe(CO)₄ in CH_2Cl_2 with 0.1 M TBA(PF_6)

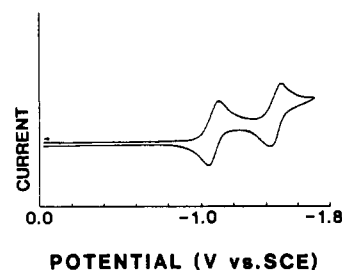| compd	$E_{1/2}(1)$	$E_{1/2}(2)$
(TpTP)SnFe(CO)₄	−1.00	−1.39
(TpTP)GeFe(CO)₄	−1.05	−1.45

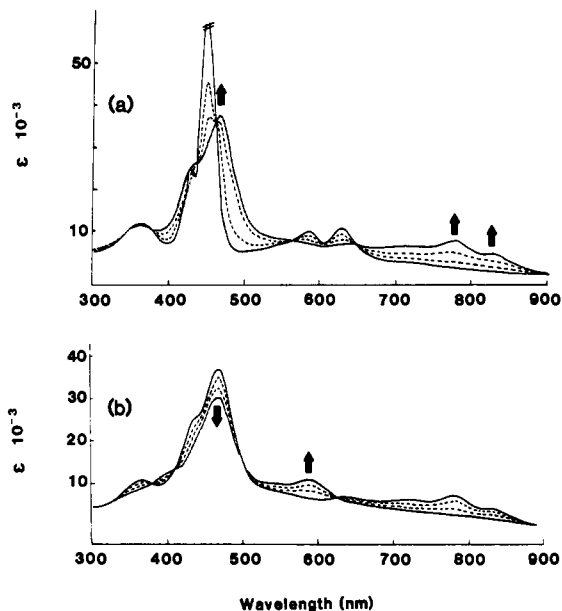**Figure 1.** Cyclic voltammogram of (TpTP)GeFe(CO)₄ in CH_2Cl_2, 0.1 M TBA(PF_6).

Figure 2. Time-resolved electronic absorption spectra of (TpTP)GeFe-(CO)₄ in PhCN with 0.1 M TBA(PF_6). The solid line represents the initial and final spectrum during controlled-potential reduction at (a) −1.30 and (b) −1.75 V. The total electrolysis time varied as a function of the applied potential. For the above compounds the final spectrum was obtained after approximately 2.0 min.

shown that the potentials for porphyrin π anion radical formation are linearly related to the electronegativity of the M(II) ion and

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(3) Concolios, P.; Chang, D.; Vittori, O.; Guilard, R.; Moise, C.; Kadish, K. M. *J. Am. Chem. Soc.* **1984**, *106*, 5724.

(4) Cocolios, P.; Moise, C.; Guilard, R. *J. Organomet. Chem.* **1982**, *228*, C43.

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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.

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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)$_6$ and 3,5-di-*tert*-butyl-benzoquinone 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

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