hydrazine complex (**2c**) during the controlled-potential electrolysis in a thin-layer cell. During oxidation at 0.05 V (vs. Ag wire) an isosbestic spectral change was observed, which we believe corresponds to the change from Ru(II)Ru(II) to Ru(II)Ru(III) (Figure 4A). The Soret band decreases in intensity slightly and shifts toward the blue. The visible bands, which are partly obscured by an interference pattern of the thin-layer cell, also change position (λ_{max}) and decrease in intensity. When the applied potential was changed to 0.5 V, a similar isosbestic behavior corresponding to the change from Ru(II)Ru(III) to Ru(III)Ru(III) was observed (Figure 4B). The small change in intensity of the Soret peak and the lack of strong absorption above 550 nm in both oxidations support the assignment of metal-centered oxidation.[29] When the applied potential is switched to −0.2 V, these spectral changes are reversed to restore the original spectrum of **2c**. The reversibility of this electrochemical process leads us to believe that the bridging hydrazine remains intact during these metal-centered electrooxidations. A continuous decrease in intensity of the Soret band upon electrolysis above 1.2 V indicates irreversible degradation of the reduction product. The original spectrum of **2c** is not restored when the potential is switched to −0.2 V.

Oxidation of the hydrazine complex **1c** with $AgBF_4$ gave a product showing a UV-vis spectrum identical with that of the Ru(III)Ru(III) species generated by controlled-potential electrolysis of **1c**.

Osmium Complexes. Dicarbonylosmium complexes of DPA and FTF4 analogous to **2a** and **3a′** were synthesized. Photolysis of the $Os_2FTF4(CO)_2$ complex gave a mixture of two isomeric monocarbonyl complexes analogously to **3d**. Attempts to make pure bis(triphenylphosphine)osmium complexes by the same procedure used for the ruthenium analogues failed, apparently because of the much slower substitution kinetics of osmium with respect to those of ruthenium.

Oxidation of the $Os_2DPA(CO)_2$ complex with MCPBA (*m*-chloroperoxybenzoic acid) gave a product that shows a UV–vis spectrum similar to that of $Os(OEP)(O)_2$.[30] The oxidation product, which has not been fully characterized, reacts with hydrazine hydrate to give a compound that has been formulated as $Os_2DPA(NH_3)_4$.[31] An analogous transformation leading to $Os(OEP)(NH_3)_2$ has been reported.[32] Further work on osmium complexes is in progress.

Summary and Conclusion

Novel diruthenium cofacial porphyrin dimers have been synthesized and characterized. Some of these complexes are analogous to known monomeric ruthenium porphyrins (i.e the dicarbonyl and the tetrakis(pyridine) complexes). In addition, we have prepared coordinatively unsaturated bis(triphenylphosphine) complexes in which a bulky phosphine binds each metal on the outside of the cavity, leaving a vacant coordination site on each metal inside. Such structures may serve as catalysts for the electrochemical reduction of dinitrogen. Although the bis(triphenylphosphine) complexes do not bind dinitrogen, they do bind hydrazine, a possible reduction product of dinitrogen, inside the cavity. Electrochemistry reveals strong interaction between two metal centers in these complexes except $Ru_2DPA(PPh_3)_2$ (**1b**), as indicated by well-separated metal-centered oxidation waves in cyclic voltammograms. Vacuum pyrolysis of the tetrakis(pyridine) complex of DPB yields a paramagnetic complex containing an intramolecular Ru–Ru bond, which reacts with triphenylphosphine to give $Ru_2DPB(PPh_3)_2$ (**2b**). This suggests a general route to five-coordinate diruthenium DPB complexes, $Ru_2DPB(L)_2$, where L is a bulky ligand that cannot enter the diporphyrin cavity. With the proper choice of L this type of compound may bind dinitrogen or other small molecules between the two metal centers and serve as a catalyst for subsequent electrochemical transformations.

Acknowledgment. We thank G. T. Yee and M. G. Finn for helpful discussion. The support of the National Science Foundation is gratefully acknowledged (Grant NSFCHE83-18512). We also thank the Bio-organic, Biomedical Mass Spectrometry Resource (A. L. Burlingame, Director) supported by NIH Division of Research Resources Grant RR01614.

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(29) Kadish, K. M.; Davis, D. G.; Führhop, J.-H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 1014.

(30) Buchler, J. W.; Smith, P. D. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 341.

(31) ^1H NMR (C_6D_6, 300 MHz): δ 8.81 (s, 1 H, anth), 8.63 (s, 1 H, anth), 8.19 (d, 2 H, anth), 7.85 (s, 2 H, meso), 7.80 (d, 2 H, anth), 7.54 (dd, 2 H, anth), 3.64 (q, 8 H, Et), 3.10 (q, 8 H, Et), 3.04 (s, 12 H, Me), 2.15 (s, 12 H, Me), 1.78 (t, 12 H, Et), 1.17 (t, 12 H, Et), −9.42 (s, 6 H, NH_3), −9.70 (s, 6 H, NH_3). UV–vis (THF): λ_{max} 349, 392 (Soret), 474, 484 (sh), 505 nm. MS (SIM): *m/e* 1575 ($[M - 2H]^+$), 1558, 1541, 1524, 1506.

(32) Antipas, A.; Buchler, J. W.; Gouterman, M.; Smith, P. D. *J. Am. Chem. Soc.* **1980**, *102*, 198.

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Electrochemical Studies of Reactive Polyanionic Chelating Ligand Complexes in Liquid Sulfur Dioxide. Formation of Highly Oxidizing Inorganic Complexes

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Liquid SO_2 has been used as a medium for testing the limits of oxidative stability of osmium complexes of the polyanionic chelating (PAC) ligand $[\eta^4\text{-CHBA-DCB}]^{4-}$ (**1**) (H_4CHBA-DCB = 1,2-bis(3,5-dichloro-2-hydroxybenzamido)-4,5-dichlorobenzene). The production of potent solution-stable oxidants has resulted. Liquid SO_2 is a very useful solvent for obtaining electrochemical information on highly reactive, oxidizing inorganic complexes that decompose in conventional media.

Introduction

Stable potent one-electron oxidants are rare. The development of new compounds with very positive formal potentials poses several problems. First, new oxidation-resistant ligand complements must be found. Second, the solution media in which powerful oxidants are studied must also be resistant to oxidation. In the process of developing new polyanionic chelating (PAC) ligands (e.g. **1**) that are compatible with highly oxidizing metal centers,[2-7] we have developed a series of stable oxidants (e.g. **2**)

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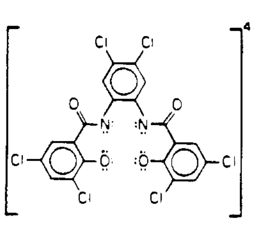

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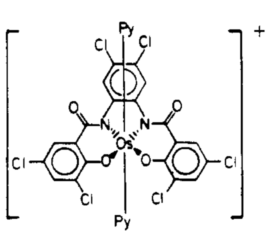

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with positive formal potentials (ca. 1.0–1.4 V vs. SCE).[2a] We were interested in learning if these compounds would afford stable materials upon further oxidation. Liquid sulfur dioxide, which is stable at very positive potentials, has proven to be a useful solvent for these studies.

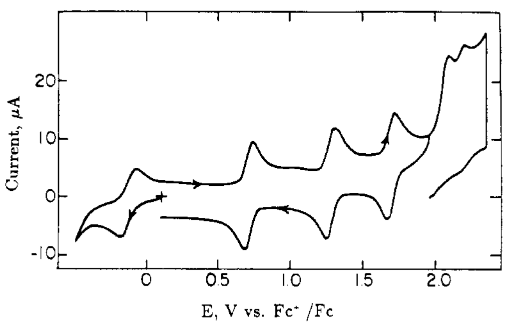

Figure 1. Cyclic voltammogram of 1 mM *trans*-Os(η^4-CHBA-DCB)-$(PPh_3)_2$ in SO_2 containing 0.1 M tetrabutylammonium tetrafluoroborate at −60 °C at a 0.03 cm^2 Pt electrode. Scan rate = 200 mV/s.

Table I. Formal Potentials of Osmium Complexes Os(η^4-**1**)L_2

	formal potential, V				
L	Os(IV/III)	1^+/Os(IV)	$2^+/1^+$	$3^+/2^+$	$4^+/3^{+\,b}$
py[a,c]	−0.15	+0.82	+1.29	+1.69	(+2.12)
py[d]	−0.44	+0.72			
PPh_3[a,c]	−0.15	+0.72	+1.29	+1.71	(+2.16)
PPh_3[d]	−0.46	+0.59			
t-BuNC[a,e]	−0.30	+0.98	(+1.48)	(+1.70)	(+2.20)
t-BuNC[d]	−0.57	+0.92			

[a] Formal potential measured in liquid SO_2/0.1 M (TBA)BF_4 and referenced to Fc^+/Fc internal standard. [b] Peak potential of irreversible oxidation enclosed in parentheses. [c] Trans isomer. [d] Measured in CH_2Cl_2/0.1 M TBAP and referenced to Fc^+/Fc internal standard. [e] Cis-α isomer.[17]

Liquid sulfur dioxide was seldom used as a solvent for electrochemical studies until the 1970's.[8] Early work was hampered by the lack of a good supporting electrolyte and a stable reference electrode.[9] In 1970, Miller and Mayeda reported that the use of tetraalkylammonium salts as supporting electrolytes in SO_2 gave reasonable conductivities and that 9,10-diphenylanthracene could be oxidized reversibly in SO_2 to a stable cation radical.[10] Launay and Castellonese have performed anodic halogenations with trityl and tetraalkylammonium halides in SO_2.[11] Lacaze et. al. have used $AlCl_3$ both as a drying agent and as a supporting electrolyte in SO_2 and have studied the oxidation of aromatics.[12] The oxidation of mercury in SO_2 to produce Hg_3AsF_6 and Hg_3SbF_6 has also been studied.[13] The considerable anodic range accessible in liquid SO_2 has been exploited by Bard and co-workers, who have shown that liquid SO_2 is stable at remarkably oxidizing potentials (up to ca. 4.0 V vs. SCE).[14] In 1979 this group first reported the oxidation of thianthrene, phenothiazine, and 9,10-diphenylanthracene in SO_2.[14a] The oxidation of thianthrene in the presence of water and anisole was also examined.[14b] Later, the highly oxidizing complexes $[Ru(by)_3]^{2+}$ and $[Fe(bpy)_3]^{2+}$ were studied.[14c] The use of tetrabutylammonium BF_4^- or PF_6^- as supporting electrolytes in place of tetrabutylammonium perchlorate extended the anodic range from ca. +3.4 to ca. +4 V (vs. SCE). Highly oxidized forms of ferrocene, decamethylferrocene, iron bis[tris(1-pyrazolyl)borate],[14d] bipyridine and phenanthroline complexes of osmium, ruthenium, and iron,[14e] and copper(II) tetrakis(pyridine *N*-oxide)[14f] were produced in liquid SO_2. Complexes with formal potentials as high as ca. 2.40 V (vs. SCE) were obtainable. The more oxidizing complexes slowly oxidized the liquid SO_2 medium.[14e] Recently, the oxidation of anthracene and 9,9′-bianthryl to the respective dication and tetracation was studied in liquid SO_2.[15]

Here we report the electrochemical studies of **2** and related species in liquid SO_2. These experiments have alllowed us to probe the limits of oxidative stability of complexes of **1** and related ligands.

Experimental Section

All complexes were synthesized as previously described.[2]

Electrochemistry in Liquid Sulfur Dioxide. Anhydrous sulfur dioxide (Matheson, 99.99%) was further purified by washing with concentrated sulfuric acid to remove SO_3 and some water and passed through two 45-cm columns packed with P_2O_5 on glass wool for final drying. The sulfur dioxide was then condensed at −78 °C into an electrochemical cell attached to a vacuum line. The three-compartment cell used for controlled-potential electrolyses was of the same design as one reported by Smith and Bard.[16] A small two-compartment cell was used for experiments involving CV only. Working electrodes for CV were a platinum disk (0.03 cm^2) or a glassy-carbon disk (0.32 cm^2), both prepared by polishing with 0.3-μm alumina polishing powder (Linde) followed by sonication, rinsing with water, acetone, and methylene chloride, and vacuum drying. The behavior and formal potentials of the osmium compounds were not dependent upon the working electrode used. The silver-wire quasi-reference electrode was prepared in the same manner and was isolated in a separate compartment containing only supporting electrolyte. The counter electrode and working electrode for controlled-potential electrolyses were made of platinum gauze. The supporting electrolyte was tetrabutylammonium tetrafluoroborate (Southwestern Analytical Chemicals) and was recrystallized three times from ethyl acetate/ether and vacuum dried. Before adding sulfur dioxide, the cell was loaded with the electrodes, supporting electrolyte, and the compound to be examined and dried for at least 12 h under vacuum. Ex-

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(2) (a) Anson, F. C.; Christie, J. A.; Collins, T. J.; Coots, R. J.; Furutani, T. T.; Gipson, S. L.; Keech, J. T.; Krafft, T. E.; Santarsiero, B. D.; Spies, G. H. *J. Am. Chem. Soc.* **1984**, *106*, 4460–4472. (b) Anson, F. C.; Collins, T. J.; Coots, R. J.; Gipson, S. L.; Keech, J. T.; Krafft, T. E.; Santarsiero, B. D.; Spies, G. H. *Inorg. Chem.* **1987**, *26*, 1161–1168.

(3) Christie, J. A.; Collins, T. J.; Krafft, T. E.; Santarsiero, B. D.; Spies, G. H. *J. Chem. Soc., Chem. Commun.* **1984**, 198–199.

(4) Collins, T. J.; Santarsiero, B. D.; Spies, G. H. *J. Chem. Soc., Chem. Commun.* **1983**, 681–682.

(5) Anson, F. C.; Collins, T. J.; Coots, R. J.; Gipson, S. L.; Richmond, T. G. *J. Am. Chem. Soc.* **1984**, *106*, 5037–5038.

(6) Collins, T. J.; Richmond, T. G.; Santarsiero, B. D.; Treco, B. G. R. T. *J. Am. Chem. Soc.* **1986**, *108*, 2088–2090.

(7) (a) Collins, T. J.; Coots, R. J.; Furutani, T. T.; Keech, J. T.; Peake, G. T.; Santarsiero, B. D. *J. Am. Chem. Soc.* **1986**, *108*, 5333–5339. (b) Anson, F. C.; Collins, T. J.; Gipson, S. L.; Keech, J. T.; Krafft, T. E.; Peake, G. T. *J. Am. Chem. Soc.* **1986**, *108*, 6593–6605.

(8) For a review of the chemistry and electrochemistry of liquid SO_2 to 1970 see: Burrow, D. F. In *Chemistry of Non-*Aqueous *Solvents*; Lagowski, J. J., Ed.; Academic: New York, Vol. 3, pp 137–185.

(9) (a) Elving, P. J.; Markowitz, J. M.; Rosenthal, I. *J. Phys. Chem.* **1961**, *65*, 680–686. (b) Elving, P. J.; Markowitz, J. M.; Rosenthal, I. *Ibid.* **1961**, *65*, 686–690. (c) Elving, P. J.; Markowitz, J. M. *J. Chem. Educ.* **1960**, *37*, 75–81. (d) See reference 15a.

(10) Miller, L. L.; Mayeda, E. A. *J. Am. Chem. Soc.* **1970**, *92*, 5818–5819.

(11) (a) Launay, G.; Castellonese, P. *Bull. Soc. Chim. Fr.*, **1978**, I-226–I-230. (b) Castellonese, P.; Launay, G. *Bull. Soc. Chim. Fr.* **1978**, I-317–I-322.

(12) (a) Lacaze, P. C.; Dubois, J. E.; Delamar, M. *J. Electroanal. Chem. Interfacial Electrochem.* **1979**, *102*, 135–137. (b) Dubois, J. E.; Delamer, M.; Lacaze, P. C. *Electrochim. Acta* **1980**, *25*, 429–433. (c) Delamar, M.; Lacaze, P. C.; Dumousseau, J. Y.; Dubois, J. E. *Electrochim. Acta* **1982**, *27*, 61–65.

(13) Whitwell, G. E., II; Miller, D. C.; Burlitch, J. M. *Inorg. Chem.* **1982**, *21*, 1692–1693.

(14) (a) Tinker, L. A.; Bard, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 2316–2319. (b) Tinker, L. A.; Bard, A. J. *J. Electroanal. Chem. Interfacial Electrochem.* **1982**, *133*, 275–285. (c) Gaudiello, J. G.; Sharp, P. R.; Bard A. J. *J. Am. Chem. Soc.* **1982**, *104*, 6373–6377. (d) Sharp, P. R.; Bard A. J. *Inorg. Chem.* **1983**, *22*, 2689–2693. (e) Gaudiello, J. G.; Bradley, P. G.; Norton, K. A.; Woodruff, W. H.; Bard, A. J. *Inorg. Chem.* **1984**, *23*, 3–10. (f) Sharp, P. R.; Bard A. J. *Inorg. Chem.* **1983**, *22*, 3462–3464.

(15) Dietrich, M.; Mortensen, J.; Heinze, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 508–509.

(16) Smith, W. H.; Bard, A. J. *J. Am. Chem. Soc.* **1975**, *97*, 5203–5210.

periments were performed at −40 ± 3 °C, or at −60 ± 3 °C where noted, with the temperature controlled by slow addition of dry ice to a 2-propanol bath. Formal potentials of reversible couples were taken as the average of the anodic and cathodic peak potentials. For each compound studied at least one experiment was performed in the presence of ferrocene as an internal potential standard, and all potentials are quoted with respect to the formal potential of the ferrocenium/ferrocene (Fc^+/Fc) couple.

Results and Discussion

Before electrochemical studies were attempted, the solubility properties in SO_2 of complexes of **1** were investigated. The osmium(IV) complexes *trans*-$Os(\eta^4$-**1**$)(py)_2$[2] and *trans*-$Os(\eta^4$-**1**$)(PPh_3)_2$[2] are reasonably soluble, but *trans*-$Os(\eta^4$-**1**$)(t\text{-}Bupy)_2$[2] is insoluble. These solubility properties are consistent with reports that aromatic compounds are more soluble in liquid SO_2 than aliphatic compounds. During the work, unexpected complex precipitation was occasionally observed. An osmium(IV) complex would dissolve, but would later suddenly precipitate and not redissolve on stirring or warming. These incidents were unpredictable and indicate that low-temperature SO_2 solutions can be metastable with respect to precipitation. Where neutral complexes could not be dissolved, the first oxidation products were produced in acetonitrile or dichloromethane, isolated, and then dissolved in liquid SO_2.

Production of Potent Solution-Stable Oxidants. The cyclic voltammogram of *trans*-$Os(\eta^4$-**1**$)(PPh_3)_2$ in liquid SO_2 at −60 °C is shown in Figure 1. The osmium(IV/III) couple is found at $E_f = -0.14$ V (Fc^+/Fc), and three reversible oxidations are seen at +0.72, +1.29, and +1.71 V. Following the third reversible oxidation, nonreversible anodic activity begins. An almost identical CV was obtained with *trans*-$Os(\eta^4$-**1**$)(py)_2$. However, the CV of *cis*-α-$Os(\eta^4$-**1**$)(t\text{-}BuNC)_2$[17] showed second and third oxidations that were not completely reversible. This information is summarized in Table I. It is interesting to compare the formal potentials measured in sulfur dioxide with those measured in dichloromethane, although interpretations of such comparisons are limited by the shift of the internal standard reference potential in different solvents. In SO_2 the osmium(IV/III) couples are shifted about 300 mV positive, while the monocation/osmium(IV) couples are shifted about 100 mV positive. The large shift of the osmium(IV/III) couples may arise from strong solvation of the anionic osmium(III) species by SO_2. It has been reported that SO_2 does not solvate cations well, but interacts strongly with nucleophiles and donor molecules.[11,12,14b]

The large variation in monocation/osmium(IV) formal potentials for the complexes of **1** in dichloromethane with changes in the monodentate ligands was cited as evidence that the first oxidation occurs at the metal center.[2] We have studied a smaller number of compounds in liquid SO_2, but some tentative conclusions can be drawn from the available data. The monocation/osmium(IV) formal potentials in SO_2 vary in the same direction and with the same magnitude as those in CH_2Cl_2 (Table I). However, the other oxidations show very little variation with monodentate ligand. Note, in particular, that the second, third, and fourth oxidations of *trans*-$Os(\eta^4$-**1**$)(py)_2$ and *trans*-$Os(\eta^4$-**1**$)(PPh_3)_2$ occur at essentially identical potentials, suggesting that these higher oxidations are ligand-localized.

The first oxidation products of both *trans*-$Os(\eta^4$-**1**$)(py)_2$ and *trans*-$Os(\eta^4$-**1**$)(PPh_3)_2$ are stable in dichloromethane[2,8] and can be isolated as crystalline species. These compounds are also stable when produced in liquid SO_2 by bulk electrolysis (1 faraday/mol of osmium is consumed). The stability of the second and third oxidation products was investigated by controlled-potential electrolysis experiments. For *trans*-$Os(\eta^4$-**1**$)(py)_2$, the second oxidation product (produced by oxidation by 1 faraday/mole of osmium) is stable in solution or as a solid under vacuum at −40 °C, but when the solid is warmed to room temperature, decomposition occurs to give a brown product that exhibits no reversible electrochemistry upon redissolution. The third oxidation product can be produced by oxidation by slightly more than 1 faraday/mol of osmium (1.1–1.2) and decomposes slowly in solution at −40 °C. The second and third oxidation products of *trans*-$Os(\eta^4$-**1**$)(PPh_3)_2$ are less stable than those of *trans*-$Os(\eta^4$-**1**$)(py)$, each being produced by transfer of slightly more than 1 faraday/mol of osmium (1.1–1.3). At room temperature in CH_2Cl_2, *trans*-$[Os(\eta^4$-**1**$)(py)_2]^+$ undergoes isomerization to produce an equilibrium mixture of the trans and cis-α isomers.[7b] This isomerization is not observed in liquid SO_2, presumably because of the low temperature.

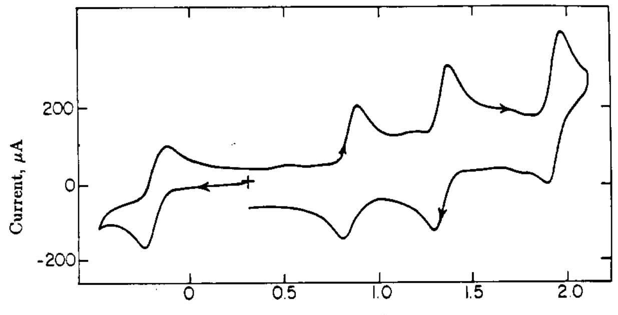


Figure 2. Cyclic voltammogram of 3 mM **3** in SO_2 containing 0.1 M tetrabutylammonium tetrafluoroborate at −60 °C at a 0.32 cm² glassy-carbon electrode. Scan rate = 200 mV/s.

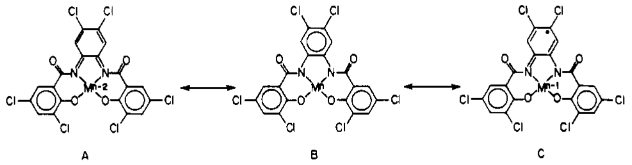
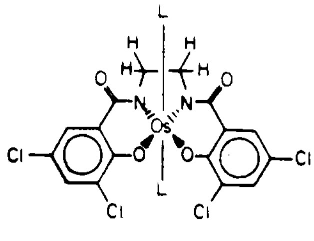


Figure 3. Alternative electronic structures for aromatic chelating ligands.

Electrochemical Investigation in SO_2 of Highly Reactive Oxidants That Decompose in Conventional Media. The oxidation of **3** in dichloromethane is nonreversible because the ethylene unit undergoes oxidative degradation.[2] In liquid SO_2 not only is the first oxidation reversible, but a second reversible oxidation can be seen on the CV time scale (Figure 2).



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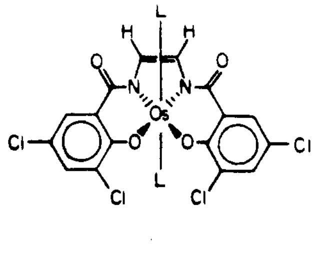

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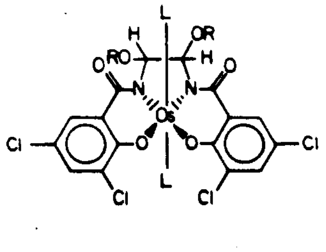
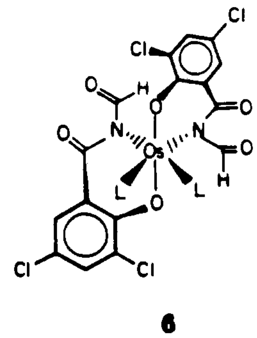


5(R = Et)



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A third oxidation is nonreversible as is further anodic activity. The oxidized forms are not stable on the bulk electrolysis time

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[17] The nomenclature for octahedral complexes of tetradentate ligands such as **1** has been defined previously. The cis-β isomer is obtained by interchanging one phenolate and one monodentate ligand in the trans isomer, and the cis-α isomer is obtained by interchanging two phenolate and two monodentate ligands: Sargeson, A. M.; Searle, G. H. *Nature* (*London*) **1963**, *200*, 356–357.

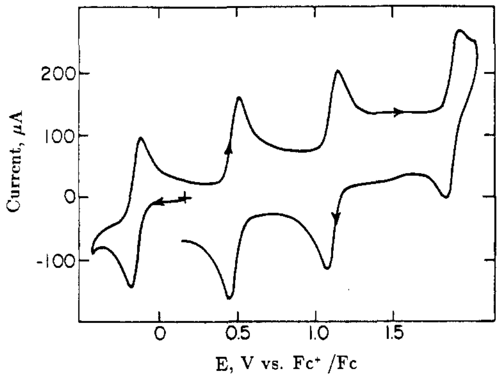

Figure 4. Cyclic voltammogram of 2.4 mM **4** in SO_2 containing 0.1 M tetrabutylammonium tetrafluoroborate at −40 °C at a 0.32 cm^2 glassy-carbon electrode. Scan rate = 200 mV/s.

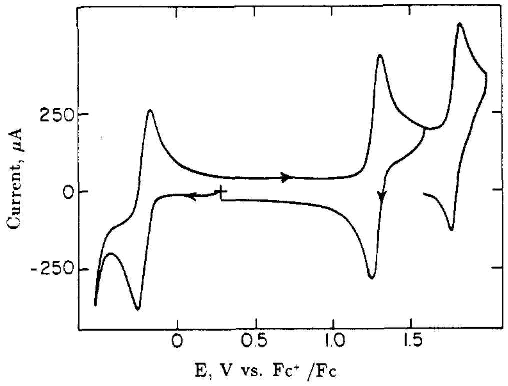

Figure 5. Cyclic voltammogram of 4.4 mM **6** in SO_2 containing 0.1 M tetrabutylammonium tetrafluoroborate at −40 °C at a 0.32 cm^2 glassy-carbon electrode. Scan rate = 200 mV/s.

scale. The formal potentials for the two reversible oxidations are +0.86 and +1.37 V. Note that the formal potential of the monocation/osmium(IV) couple is only 40 mV more positive than that of the monocation/osmium(IV) couple of *trans*-Os(η^4-**1**)(py)$_2$ (Table I). This similarity of formal potentials suggest that alternate electronic structures for complexes of **1** (Figure 3C), which cannot exist for **3**, do not contribute significantly to the structure of *trans*-Os(η^4-**1**)(py)$_2$ or its monocation.[18]

Complex **4** is derived from **3** by dehydrogenation of the ethylene unit linking the two amido nitrogen atoms.[2] The CV in liquid SO_2 of **4** is shown in Figure 4. In dichloromethane this complex displayed one reversible oxidation at +0.37 V and one nonreversible oxidation at +0.92 V.[2] In liquid SO_2 three reversible oxidations at +0.48, +1.11, and +1.89 V and nonreversible anodic activity, starting at +2.17 V, can be observed. Compound **5** is produced by oxidation of the bis(*N*-amido)-substituted alkene group of **4** to the trans diether. More information can also be derived from electrochemical studies of compound **5** (R = Et)[2] in liquid SO_2 than in dichloromethane. Two reversible oxidations at +1.03 and +1.46 V are found in liquid SO_2, but only one nonreversible oxidation (ca. +0.90 V) is observed in dichloromethane. One of the final products of the oxidative degradation of **3**, compound **6**,[2] did not show any anodic activity in dichloromethane. In liquid SO_2, **6** exhibited one reversible oxidation, at +1.28 V, and one nonreversible oxidation, at +1.79 V (Figure 5). Note that replacement of the amido ligands of **3** with the imido ligands of **6** increases the formal potential of the monocation/osmium(IV) couple by more than 400 mV. This observation serves to highlight further the considerable donor ability of the N-coordinated organic amido ligand.[2,8,19] The formal potentials for these complexes are summarized in Table II.

Table II. Formal Potentials of **3** and Oxidized Derivatives in Liquid SO_2

	formal potential,[a] V			
compd	Os(IV/III)	monocation/ Os(IV)	2+/1+	3+/2+
3	−0.19	+0.86	+1.37	(+2.01)
4	−0.13	+0.48	+1.11	+1.89
5 (R=Et)	−0.20	+1.03	+1.46	
6	−0.22	+1.28	(+1.79)	

[a] Formal potentials measured in liquid SO_2/0.1 M (TBA)BF_4 and referenced to Fc^+/Fc internal standard. [b] Peak potential of irreversible oxidation enclosed in parentheses.

Conclusion

As has been shown in prior work,[8-15] liquid sulfur dioxide is a valuable solvent for electrochemical studies. Advantages are associated with the high purity and large anodic range of the liquid SO_2 medium, which has proven to be ideal for testing the limits of oxidative stability of the PAC ligand complexes reported here. Moderately solution-stable PAC ligand complexes with formal potentials in the neighborhood of 2.00 V (vs. SCE) are accessible. An interesting question for oxidation chemistry is "How oxidizing can a solution-stable oxidant be?" Since liquid sulfur dioxide is stable at anodic potentials as high as +4.00 V, the limiting feature in approaching this boundary would appear to be the stability of the ligand complements of complexes explored to date. However, it should be noted that strongly oxidizing complexes have been observed to react with liquid sulfur dioxide.[14e] We have modified the PAC ligands described herein by replacing all aromatic groups with aliphatic substituents and are currently studying the resistance to oxidation of the derivative complexes.

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(18) New aliphatic ligands, free of aromatic functionalities, and derivative osmium complexes have been recently produced and are being studied electrochemically in liquid SO_2.

(19) See for example (a) Margerum, D. W. *Pure Appl. Chem.* **1983**, *55*, 23–34. (b) Margerum, D. W. *Oxidases Relat. Redox Syst., Proc. Int. Symp, 3rd., 1979*, **1982**, 193–206. (c) Diaddario, L. L.; Robinson, W. R.; Margerum, D. W. *Inorg. Chem.* **1983**, *22*, 1021–1025. (d) Sigel, H.; Martin, R. B. *Chem. Rev.* **1982**, *82*, 385–426. (e) Kimura, E.; Sakonaka, A.; Machila, R.; Kodama, M. *J. Am. Chem. Soc.* **1982**, *104*, 4255. (f) Buttafava, A.; Fabbrizzi, L.; Perotti, A.; Seghi, B. *J. Chem. Soc., Chem. Commun.* **1982**, 1166–1167. (g) Fabbrizzi, L.; Perotti, A.; Poggi, A. *Inorg. Chem.* **1983**, *22*, 1411–1412. (h) Buttafava, A.; Fabbrizzi, L.; Perotti, A.; Poggi, A.; Seghi, B. *Inorg. Chem.* **1984**, *23*, 3917–3922.