



Figure 3. Cyclic voltammogram of $\text{Ru}(\text{TAP})_3(\text{PF}_6)_2$ (10^{-3} M) in CH_3CN (0.1 M) in $n\text{-Bu}_4\text{ClO}_4$ (scan rate 180 mV/s).

Electrochemistry

The electrochemical measurements were performed on the chloride and the hexafluorophosphate salt of the complex. This latter was obtained from the chloride as described for the corresponding bipyrazine complex.⁶ Table I gives the oxidation and reduction potentials vs. SCE of the free ligand and the complex in DMF and CH_3CN . The reduction potentials in DMF (0.1 M Bu_4NI) are measured at a dropping-mercury electrode by polarography or by cyclic voltammetry with scan rates ranging from 0.5 to 1.5 V s^{-1} , with a mercury pool as reference and counterelectrode (-0.55 V vs. SCE). In acetonitrile (0.1 M Bu_4NClO_4), a platinum wire is used and the SCE is connected through a double bridge. The scan rate is 0.2 or 0.25 V s^{-1} .

As shown in Table I, the free ligand is reduced only at -1.5 V, with a one-electron reversible wave, followed by an irreversible wave at -2.1 V, whereas the first reduction of the complex occurs already at -0.76 V. $\text{Ru}(\text{TAP})_3^{2+}$ shows actually three successive one-electron reversible reduction waves, followed by a fourth quasi-reversible one in cyclic voltammetry ($\Delta E_p \approx 100$ mV) (Figure 3), this fourth wave being irreversible in polarography. The three first-reduction waves are slightly better defined in CH_3CN than in DMF.

The oxidation potential of $\text{Ru}(\text{TAP})_3^{2+}$ in CH_3CN was difficult to measure because it occurs ($\sim +1.93$ V) at the limit of the potential region that can be examined with the Pt/ CH_3CN system.

As could be expected for the complexes, the two additional nitrogen atoms in TAP induce a fairly strong anodic shift of the first-reduction wave compared to those of bipyridine or 1,10-phenanthroline and make it very similar to the case of $\text{Ru}(\text{bpz})_3^{2+}$ (Table I).

Conclusions

The data collected here lead to the conclusion that the $\text{Ru}(\text{TAP})_3^{2+}$ and $\text{Ru}(\text{bpz})_3^{2+}$ complexes have similar properties, with one exception for the excited-state lifetime, and both differ from the corresponding $\text{bpy}^{15,19,20,22}$ and $\text{phen}^{15,19}$ complexes. The MLCT excited state of $\text{Ru}(\text{TAP})_3^{2+}$ should thus behave as a weak reducing reagent (~ -0.2 V vs. SCE) but as a strong oxidant ($\sim +1.4$ V), and analogously to what was shown by Crutchley and Lever for the bipyrazine complex,

it should be thermodynamically able to oxidize water. The good photostability of $\text{Ru}(\text{TAP})_3^{2+}$ in aqueous acid would allow us to use it for the water-splitting reaction in acid medium; its moderate photostability in neutral water, as compared to the case of $\text{Ru}(\text{bpy})_3^{2+}$, precludes its use, however, as an ideal photosensitizer in neutral aqueous medium.

Registry No. $\text{Ru}(\text{TAP})_3\text{Cl}_2$, 88181-59-3; $\text{Ru}(\text{TAP})_3(\text{PF}_6)_2$, 88181-61-7; $\text{Ru}(\text{Me}_2\text{SO})_4\text{Cl}_2$, 11070-19-2; D, 7782-39-0.

Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

Mixed Isocyanide-Halide Complexes of Osmium(II) and Osmium(III)

Stephen M. Tetrick and Richard A. Walton*

Received June 21, 1983

We have been engaged in a systematic study of the synthetic, structural, and reaction chemistry of homoleptic isocyanide complexes of the early transition series, especially those of chromium, molybdenum, tungsten, and rhenium.¹ In view of the tremendous stability and ease of preparation of the 18-electron rhenium(I) cations $[\text{Re}(\text{CNR})_6]^+$ (with both alkyl and aryl isocyanide ligands), we wondered whether a similar chemistry might not exist for the isoelectronic osmium(II) cations $[\text{Os}(\text{CNR})_6]^{2+}$. The hexakis(alkyl isocyanide)- and hexakis(aryl isocyanide)iron(II) and -ruthenium(II) compounds are uncommon and their chemistry has been little explored,²⁻⁵ while for osmium there is but a single report describing the syntheses of $[\text{Os}(\text{CNMe})_6](\text{ClO}_4)_2$ and $\text{trans-Os}(\text{CNMe})_4\text{Br}_2$.⁸

Following our recent isolation of several osmium(VI) complexes of the type $\text{trans-OsO}_2\text{X}_2(\text{PR}_3)_2$,^{9,10} we have been investigating their chemical reactivity toward a variety of bridging ligands.¹⁰⁻¹² In the course of this work, we discovered that these osmyl derivatives could be converted into the dismium(IV) complexes $\text{Os}_2(\mu\text{-O})(\mu\text{-O}_2\text{CR})_2\text{X}_4(\text{PR}_3)_2$ ^{11,12} upon reaction with carboxylic acid-anhydride mixtures. We have now found that the reactions of alkyl isocyanide ligands with $\text{trans-OsO}_2\text{X}_2(\text{PPh}_3)_2$ and $\text{Os}_2(\mu\text{-O})(\mu\text{-O}_2\text{CCH}_3)_2\text{X}_4(\text{PPh}_3)_2$

(18) Gillard, R. D.; Knight, D. W.; Williams, P. *Transition Met. Chem. (Weinheim, Ger.)* 1979, 4, 375-381.

(19) Tokel-Takvoryan, N. E.; Hemingway, R. E.; Bard, A. J. *J. Am. Chem. Soc.* 1973, 95, 6582-6589.

(20) Saji, T.; Ao-yagui, S. *J. Electroanal. Chem. Interfacial Electrochem.* 1975, 58, 401-410.

(21) Lin, C. P.; Sutin, N. *J. Phys. Chem.* 1976, 80, 97-105.

(22) Demas, J. N.; Adamson, A. W. *J. Am. Chem. Soc.* 1971, 93, 1800-1801.

- (1) For representative studies see: (a) Cameron, C. J.; Wigley, D. E.; Wild, R. E.; Wood, T. E.; Walton, R. A. *J. Organomet. Chem.* 1983, 255, 345. (b) Allison, J. D.; Wood, T. E.; Wild, R. E.; Walton, R. A. *Inorg. Chem.* 1982, 21, 3540. (c) Klendworth, D. D.; Welters, W. W., III; Walton, R. A. *Organometallics* 1982, 1, 336. (d) Walton, R. A. "Reactivity of Metal-Metal Bonds"; Chisholm, M. H., Ed.; American Chemical Society: Washington, DC, 1981; ACS Symp. Ser. No. 155, p 207. (e) Mialki, W. S.; Wild, R. E.; Walton, R. A. *Inorg. Chem.* 1981, 20, 1380. (f) Wood, T. E.; Deaton, J. C.; Corning, J.; Wild, R. E.; Walton, R. A. *Ibid.* 1980, 19, 2614. (g) Brant, P.; Cotton, F. A.; Sekutowski, J. C.; Wood, T. E.; Walton, R. A. *J. Am. Chem. Soc.* 1979, 101, 6588.
- (2) Bonati, F.; Minghetti, G. *J. Organomet. Chem.* 1970, 22, 195.
- (3) Albertin, G.; Bordignon, E.; Orio, A.; Pelizzi, G.; Tarasconi, P. *Inorg. Chem.* 1981, 20, 2862.
- (4) Note that homoleptic iron(0) and ruthenium(0) isocyanide compounds of the types $\text{M}(\text{CNR})_6$ and $\text{M}_2(\text{CNR})_6$ have been successfully prepared and structurally characterized,^{5,6} and the existence of the mixed halide-isocyanide complexes $\text{M}(\text{CNR})_4\text{Cl}_2$ is well documented.⁵⁻⁷
- (5) Bassett, J. M.; Berry, D. E.; Barker, G. K.; Green, M.; Howard, J. A. K.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* 1979, 1003.
- (6) Bassett, J. M.; Barker, G. K.; Green, M.; Howard, J. A. K.; Stone, F. G. A.; Wolsey, W. C. *J. Chem. Soc., Dalton Trans.* 1981, 219.
- (7) Kargol, J. A.; Angelici, R. J. *Inorg. Chim. Acta* 1983, 68, 127 and references cited therein.
- (8) Chatt, J.; Richards, R. L.; Royston, G. H. D. *J. Chem. Soc., Dalton Trans.* 1973, 1433.
- (9) Salmon, D. J.; Walton, R. A. *Inorg. Chem.* 1978, 17, 2379.
- (10) Armstrong, J. E.; Walton, R. A. *Inorg. Chem.* 1983, 22, 1545.
- (11) Armstrong, J. E.; Robinson, W. R.; Walton, R. A. *J. Chem. Soc., Chem. Commun.* 1981, 1120.
- (12) Armstrong, J. E.; Robinson, W. R.; Walton, R. A. *Inorg. Chem.* 1983, 22, 1301.

(X = Cl or Br) provide a convenient entry into complexes of the type *trans*-Os(CNR)₄X₂, and this has permitted us an opportunity to examine the properties of this class of complexes (for R = isopropyl, *tert*-butyl, and cyclohexyl). Of special note is their chemical oxidation to the intensely colored 17-electron [Os(CNR)₄X₂]⁺ cations. Herein we describe the synthesis of these complexes along with their spectroscopic and electrochemical properties.

Experimental Section

Starting Materials. The alkyl isocyanide ligands, *trans*-OsO₂Cl₂(PPh₃)₂, *trans*-OsO₂Br₂(PPh₃)₂, and Os₂(μ-O)(μ-O₂CCH₃)₂X₄(PPh₃)₂ (X = Cl or Br) were prepared as described in the literature.^{10,12,13} Other reagents and solvents were obtained from commercial sources and used as received.

Reaction Procedures. All reactions were carried out under a dinitrogen atmosphere. Toluene and acetonitrile were distilled under an N₂(g) atmosphere over sodium-benzophenone ketyl and calcium hydride, respectively, and were stored over molecular sieves.

A. Preparation of *trans*-Os(CNR)₄X₂ Complexes. (i) *trans*-Os(CNMe₃)₄Cl₂. A sample of Os₂(μ-O)(μ-O₂CCH₃)₂Cl₄(PPh₃)₂ (218 mg, 0.185 mmol) was dissolved in 30 mL of toluene. An excess of *tert*-butyl isocyanide (2.0 mL, 19 mmol) was added, and the solution was refluxed for 19¹/₂ h. The mixture was cooled to room temperature and filtered. The yellow-brown filtrate was evaporated to dryness, and dichloromethane was added to dissolve the residue. Diethyl ether was then added, and the resulting solution was refrigerated overnight. The yellow crystals were filtered off, washed with cold diethyl ether, and air-dried; yield 67 mg (31%). Anal. Calcd for C₂₀H₃₆Cl₂N₄Os: C, 40.47; H, 6.11; Cl, 11.94. Found: C, 40.75; H, 6.08; Cl, 12.20.

(ii) *trans*-Os(CNCHMe₂)₄Cl₂. A quantity of OsO₂Cl₂(PPh₃)₂ (249 mg, 0.305 mmol) was added to 25 mL of toluene. An excess of isopropyl isocyanide (1.0 mL, 11 mmol) was added, and the solution was refluxed for 18 h. The solution was cooled to room temperature and filtered. The yellow-brown filtrate was evaporated to dryness, and dichloromethane was added to dissolve the residue. Diethyl ether was then added and the solution refrigerated overnight. The yellow crystals were filtered off, washed with diethyl ether, and air-dried; yield 80 mg (49%). Anal. Calcd for C₁₆H₂₈Cl₂N₄Os: C, 35.75; H, 5.25. Found: C, 35.71; H, 5.45.

(iii) *trans*-Os(CNC₆H₁₁)₄Cl₂¹/₅CH₂Cl₂. This complex was prepared as its dichloromethane solvate in a manner similar to that described for *trans*-Os(CNMe₃)₄Cl₂ (see A(i)) with the following modification. Following the evaporation of the toluene reaction solution, the residue was dissolved in dichloromethane and chromatographed on 60–200 mesh silica gel. Elution with dichloromethane yielded a yellow fraction that was evaporated to dryness under a stream of nitrogen gas. The residue was redissolved in dichloromethane-diethyl ether and the solution refrigerated overnight. The resulting yellow crystals that formed were filtered off, washed with diethyl ether, and air-dried; yield 52%. The presence of lattice CH₂Cl₂ was confirmed by ¹H NMR spectroscopy (δ 5.25) and the amount ascertained by peak integration relative to the cyclohexyl peak at δ 4.07. Anal. Calcd for C₂₈H₄₄Cl₂N₄Os: C, 47.39; H, 6.26. Found: C, 47.40; H, 6.60.

(iv) *trans*-Os(CNMe₃)₄Br₂. This complex was prepared as described for *trans*-Os(CNCHMe₂)₄Cl₂ (see A(ii)), except that OsO₂Br₂(PPh₃)₂ (278 mg, 0.307 mmol) was used as starting material; yield 112 mg (54%). Anal. Calcd for C₂₀H₃₆Br₂N₄Os: C, 35.19; H, 5.32. Found: C, 35.97; H, 6.00.

(v) *trans*-Os(CNCHMe₂)₄Br₂. Yellow crystals of this complex were prepared by a method analogous to that used for *trans*-Os(CNCHMe₂)₄Cl₂, except for the use of OsO₂Br₂(PPh₃)₂ (188 mg, 0.207 mmol) in place of OsO₂Cl₂(PPh₃)₂; yield 56 mg (43%). Anal. Calcd for C₁₆H₂₈Br₂N₄Os: C, 30.68; H, 4.51. Found: C, 31.54; H, 4.60.

(vi) *trans*-Os(CNC₆H₁₁)₄Br₂. The reaction between OsO₂Br₂(PPh₃)₂ and cyclohexyl isocyanide afforded this complex as yellow crystals; yield 61%. Anal. Calcd for C₂₈H₄₄Br₂N₄Os: C, 42.75; H, 5.64. Found: C, 43.07; H, 5.83.

B. Preparation of *trans*-[Os(CNR)₄X₂]BF₄ Complexes. (i) *trans*-[Os(CNMe₃)₄Cl₂]BF₄. A 2-mL volume of acetonitrile was added to *trans*-Os(CNMe₃)₄Cl₂ (60.0 mg, 0.101 mmol). The re-

sulting bright yellow solution was transferred by cannula to a flask containing a stir bar and a slight excess of NOBF₄ (12.8 mg, 0.110 mmol). A gas was evolved, and the solution changed in color to dark yellow. After the reaction mixture was stirred for 30 min at room temperature, it was filtered and the filtrate evaporated to dryness. The residue was redissolved in 1:1 (v/v) dichloromethane-diethyl ether (10 mL) and refrigerated. A brown solid was filtered off, washed with diethyl ether, and air-dried; yield 48 mg (70%). Anal. Calcd for C₂₀H₃₆BCl₂F₄N₄Os: C, 35.30; H, 5.33. Found: C, 35.71; H, 5.53.

The above procedure was representative of the one used in the preparation of all other osmium(III) complexes of this type.

(ii) *trans*-[Os(CNCHMe₂)₄Cl₂]BF₄. This complex was prepared as a brown powder with use of a method similar to that described in B(i) from *trans*-Os(CNCHMe₂)₄Cl₂ (92.4 mg, 0.172 mmol) and NOBF₄ (28.7 mg, 0.246 mmol); yield 35 mg (33%). Anal. Calcd for C₁₆H₂₈BCl₂F₄N₄Os: C, 30.78; H, 4.52. Found: C, 31.03; H, 4.80.

(iii) *trans*-[Os(CNC₆H₁₁)₄Cl₂]BF₄¹/₂Et₂O. This brown complex was prepared from *trans*-Os(CNC₆H₁₁)₄Cl₂¹/₅CH₂Cl₂ (65.7 mg, 0.092 mmol) and NOBF₄ (12.9 mg, 0.110 mmol); yield 55 mg (76%). Anal. Calcd for C₃₀H₄₉BCl₂F₄N₄O_{0.5}Os: C, 43.86; H, 6.01. Found: C, 44.17; H, 6.18. The stoichiometric amount of lattice Et₂O in this paramagnetic complex was confirmed by ¹H NMR spectroscopy in the following fashion. A small piece of clean Li metal was added to a CDCl₃ solution of the complex, thereby reducing it to osmium(II). The ¹H NMR spectrum of this solution showed diethyl ether resonances at δ 1.24 (triplet) and δ 3.52 (quartet) whose integrated intensities were in accord with a C₆H₁₁NC:Et₂O ratio close to 8:1.

(iv) *trans*-[Os(CNMe₃)₄Br₂]BF₄. This dark blue complex was prepared from *trans*-Os(CNMe₃)₄Br₂ (101.2 mg, 0.148 mmol) and NOBF₄ (22.2 mg, 0.190 mmol); yield 84 mg (74%). Anal. Calcd for C₂₀H₃₆BBBr₂F₄N₄Os: C, 31.22; H, 4.72. Found: C, 31.73; H, 5.01.

(v) *trans*-[Os(CNCHMe₂)₄Br₂]BF₄. This complex was prepared from *trans*-Os(CNCHMe₂)₄Br₂ (79.9 mg, 0.128 mmol) and NOBF₄ (21.1 mg, 0.181 mmol); yield 36 mg (40%). Anal. Calcd for C₁₆H₂₈BBBr₂F₄N₄Os: C, 26.94; H, 3.96. Found: C, 27.43; H, 4.08.

(vi) *trans*-[Os(CNC₆H₁₁)₄Br₂]BF₄. This complex was prepared from *trans*-Os(CNC₆H₁₁)₄Br₂ (119.8 mg, 0.152 mmol) and NOBF₄ (25.2 mg, 0.216 mmol); yield 123 mg (92%). Anal. Calcd for C₂₈H₄₄BBBr₂F₄N₄Os: C, 38.50; H, 5.08. Found: C, 39.23; H, 5.05.

Physical Measurements. Infrared spectra of these complexes were obtained as Nujol mulls on a Beckman IR-12 or Acculab 6 spectrophotometer. A Perkin-Elmer R32 spectrometer was used to obtain the ¹H NMR spectra. Samples were dissolved in deuterated solvents and resonances were referenced internally to Me₄Si. A Varian XL-200 spectrometer was used to obtain magnetic moments by the Evans method.^{14,15} Cyclic voltammetry experiments were carried out on solutions in 0.2 M (*n*-Bu₄N)PF₆-CH₂Cl₂ and were performed as described previously.¹⁶ Electronic absorption spectra were recorded on dichloromethane solutions with a Varian Series 634 spectrophotometer. X-Band ESR spectral measurements were attempted at room temperature and at -160 °C on 5:2(v/v) toluene-dichloromethane glasses and on diluted samples of the solid complexes with a Varian E-109 spectrometer. Far-infrared spectra were obtained as Nujol mulls on polyethylene disks with a Digilab FTS-20B spectrometer. Elemental microanalyses were performed by Dr. H. D. Lee of the Purdue University microanalytical laboratory.

Results and Discussion

The reactions of OsO₂X₂(PPh₃)₂ or Os₂(μ-O)(μ-O₂CCH₃)₂X₄(PPh₃)₂ with alkyl isocyanides did not lead to the homoleptic alkyl isocyanide complexes of osmium, viz., [Os(CNR)₆]ⁿ⁺, but instead yielded the crystalline complexes *trans*-Os(CNR)₄X₂, where R = CMe₃, CHMe₂, C₆H₁₁, and X = Cl, Br. This constitutes a useful and, to date, the only general route to this class of osmium complexes. The only complex of this type reported previously was *trans*-Os(CNMe₃)₄Br₂, which was prepared (albeit in a low yield of 15%) by refluxing (NH₄)₂OsBr₆ with methyl isocyanide in ethanol.⁸ Although either OsO₂X₂(PPh₃)₂ or Os₂(μ-O)(μ-

(14) Evans, D. F. *J. Chem. Soc.* 1959, 2003.

(15) Deutsch, J. L.; Poling, S. M. *J. Chem. Educ.* 1969, 46, 167.

(16) Brisdon, B. J.; Conner, K. A.; Walton, R. A. *Organometallics* 1983, 2, 1159.

(13) Weber, W. D.; Gokel, G. W.; Ugi, I. K. *Angew. Chem., Int. Ed. Engl.* 1972, 11, 530.

$\text{Os}_2\text{CCH}_3)_2\text{X}_4(\text{PPh}_3)_2$ can be used as the starting material in our procedure, the former is usually preferred since the diosmium(IV) complexes are themselves prepared from $\text{OsO}_2\text{X}_2(\text{PPh}_3)_2$.¹² However, in some instances the reactions of $\text{OsO}_2\text{X}_2(\text{PPh}_3)_2$ with isocyanides proceed sufficiently slowly that $\text{Os}_2(\mu\text{-O})(\mu\text{-O}_2\text{CCH}_3)_2\text{X}_4(\text{PPh}_3)_2$ complexes do indeed constitute the starting materials of choice.¹⁷

The yellow, diamagnetic complexes each possess a single $\nu(\text{C}\equiv\text{N})$ and a single $\nu(\text{Os}-\text{X})$ mode in their IR spectra (Table I), in accord with a trans geometry, as was proposed previously in the case of $\text{Os}(\text{CNMe})_4\text{Br}_2$.⁸ These complexes form nonconducting solutions in acetonitrile and possess ¹H NMR spectra (Table I) that are characteristic of coordinated RNC ligands. Their electronic absorption spectra are dominated by halogen(π) \rightarrow Os transitions below 350 nm (Table I), although these complexes also display a weak shoulder at ca. 400 nm ($\epsilon_{\text{max}} < 100 \text{ L mol}^{-1} \text{ cm}^{-1}$) that may owe its origin to a $d \leftrightarrow d$ transition.

The most noteworthy feature of these complexes is their ready oxidation to the osmium(III) analogues $[\text{Os}(\text{CNR})_4\text{X}_2]^+$. This was first demonstrated electrochemically with use of the cyclic voltammetric technique, which showed that solutions of these complexes in 0.2 M tetra-*n*-butylammonium hexafluorophosphate-dichloromethane possess a couple at +0.70 (± 0.01) V, corresponding to a one-electron oxidation. The peak current ratio $i_{\text{p,a}}/i_{\text{p,c}}$ was in all instances equal to unity, and the values of $i_{\text{p,c}}/\nu^{1/2}$ were constant for scan rates (ν) from 50 to 400 mV/s. The values of $E_{\text{p,a}} - E_{\text{p,c}}$ (of between 60 and 120 mV at $\nu = 200 \text{ mV/s}$) increased with increasing scan rate. These properties are consistent with a quasi-reversible electron-transfer process.

Bulk electrolysis at +0.80 V ($n = 1.0 \pm 0.1$) converted the yellow solutions of $\text{Os}(\text{CNR})_4\text{X}_2$ to a dark yellow-brown ($\text{X} = \text{Cl}$) or intense blue ($\text{X} = \text{Br}$) that was characteristic of the corresponding monocations. This oxidation could be achieved chemically with NOBF_4 as the oxidant and resulted in the isolation of $[\text{Os}(\text{CNR})_4\text{X}_2]\text{BF}_4$. The retention of the trans geometry is suggested by the electrochemical reversibility of the $[\text{Os}(\text{CNR})_4\text{X}_2]^{0,+}$ couple¹⁸ and the persistence of a single $\nu(\text{C}\equiv\text{N})$ and $\nu(\text{Os}-\text{X})$ mode in the IR spectra of these complexes (Table I). The difference in the $\nu(\text{C}\equiv\text{N})$ and $\nu(\text{Os}-\text{X})$ frequencies of the pairs of osmium(II) and osmium(III) complexes, i.e. the modes occur at higher frequencies for $[\text{Os}(\text{CNR})_4\text{X}_2]^+$, is entirely expected on the basis of the oxidation-state change.¹⁹ Acetonitrile solutions of all six complexes of the type $[\text{Os}(\text{CNR})_4\text{X}_2]\text{BF}_4$ possess conductivities typical of 1:1 electrolytes,²⁰ viz., $\Lambda_m = 115\text{--}126 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$ for $c \approx 10^{-3} \text{ M}$. While the paramagnetic nature of these complexes was confirmed by the Evans method^{14,15} ($\mu_{\text{eff}} = 1.8\text{--}2.1 \mu_B$, see Table I), we were unable to obtain ESR signals under any of the following conditions: (1) electrochemically generated dichloromethane solutions of the monocations at ambient or low (-160°C) temperatures; (2) dichloromethane-toluene glasses of the complexes at ambient or low (-160°C) temperatures; (3) powdered samples of the complexes.

The dramatic color changes that occur upon oxidizing $\text{Os}(\text{CNR})_4\text{X}_2$ to $[\text{Os}(\text{CNR})_4\text{X}_2]^+$ are reflected by changes in the electronic absorption spectra of these species. Specifically,

- (17) Workup of the reaction solutions following the isolation of *trans*- $\text{Os}(\text{CNR})_4\text{X}_2$ yielded oils that were shown by IR spectroscopy to contain triphenylphosphine oxide and oligomers derived from the alkyl isocyanides. We found no evidence for the formation of RNCO as organic byproducts of these reactions.
- (18) This is true provided a very fast isomerization does not occur, with the two isomeric forms possessing very nearly the same redox potential. We feel that this is unlikely to be the case.
- (19) See, for example: Adams, D. M. "Metal-Ligand and Related Vibrations"; Edward Arnold: London, 1967; p 48.
- (20) Geary, W. J. *Coord. Chem. Rev.* **1971**, 7, 81.

Table I. Spectroscopic and Magnetic Properties of $[\text{Os}(\text{CNR})_4\text{X}_2]^{n+}$ ($n = 0, 1$)

complex	IR abs, cm^{-1}		¹ H chem shifts, δ^d			electronic abs spectra, nm ^e	μ_{eff} , μ_B^f
	$\nu(\text{C}\equiv\text{N})^a$	$\nu(\text{Os}-\text{X})^b$	CH_3	$-\text{CH}_2-$	$-\text{CH}$		
$\text{Os}(\text{CNCMe}_3)_4\text{Cl}_2$	2125 ^c	301	1.55 s			330 (3.4)	295 (5.8)
$\text{Os}(\text{CNCHMe}_2)_4\text{Cl}_2$	2136	295	1.47 d		4.28 h	330 (2.0)	295 (3.75)
$\text{Os}(\text{CNC}_6\text{H}_{11})_4\text{Cl}_2 \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$	2138	300		1.38 m, 1.81 m	4.07 m	330 (3.4)	292 (6.1)
$\text{Os}(\text{CNCMe}_3)_4\text{Br}_2$	2130 ^c	218	1.54 s			330 (2.5)	295 (4.6)
$\text{Os}(\text{CNCHMe}_2)_4\text{Br}_2$	2140	218	1.50 d		4.28 h	325 (2.2)	290 (4.4)
$\text{Os}(\text{CNC}_6\text{H}_{11})_4\text{Br}_2$	2138 ^c	218		1.41 m, 1.84 m	4.05 m	325 (3.1)	290 (6.3)
$[\text{Os}(\text{CNCMe}_3)_4\text{Cl}_2]\text{BF}_4$	2220	328				375 (11.2)	
$[\text{Os}(\text{CNCHMe}_2)_4\text{Cl}_2]\text{BF}_4$	2222	334				375 (1.2)	295 sh
$[\text{Os}(\text{CNC}_6\text{H}_{11})_4\text{Cl}_2]\text{BF}_4 \cdot \frac{1}{2}\text{Et}_2\text{O}$	2220	330				377 (1.4)	~305 sh
$[\text{Os}(\text{CNCMe}_3)_4\text{Br}_2]\text{BF}_4$	2218	239				430 (0.9)	325 (0.25)
$[\text{Os}(\text{CNCHMe}_2)_4\text{Br}_2]\text{BF}_4$	2218	237				590 (11.0)	427 (0.3)
$[\text{Os}(\text{CNC}_6\text{H}_{11})_4\text{Br}_2]\text{BF}_4$	2215	238				587 (10.5)	325 (0.3)
						430 (1.05)	320 (sh)

^a Recorded as Nujol mulls on KBr plates. ^b Recorded as Nujol mulls on polyethylene plates. ^c Weak shoulder at $\sim 2080 \text{ cm}^{-1}$. ^d All spectra were recorded in CDCl_3 , except for the use of acetone- d_6 in the case of $\text{Os}(\text{CNCMe}_3)_4\text{Cl}_2$. Abbreviations are as follows: d = doublet, h = heptet, m = multiplet, s = singlet. ^e All spectra were recorded in CH_2Cl_2 . Extinction coefficients ($\times 10^{-3}$) are given in parentheses. ^f Recorded at ambient temperature in CH_2Cl_2 by the Evans method ($\pm 0.1 \mu_B$).

we observe the encroachment of intense halogen(π) \rightarrow Os charge-transfer transitions into the visible region in the case of osmium(III) (Table I), the most dominant spectral feature being an intense band ($\epsilon_{\max} \approx 1 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) at 455 nm in the case of X = Cl and ~ 590 nm for X = Br. Qualitatively at least, these spectral features seem in reasonable accord with those expected on the basis of a comparison with the spectra of *trans*-[Os(NH₃)₄X₂]⁺ species,²¹⁻²³ for which the corresponding charge-transfer bands are located at much higher energies (270 nm for X = Cl and 320 nm for X = Br). In the case of [Os(CNR)₄X₂]⁺, the π -accepting RNC ligands should lead to a lowering in the energies of the t_{2g} -type metal orbitals (split, of course, into an orbital doublet and singlet in a field of D_{4h} symmetry) and hence to a decrease in the energy separation between them and the halogen π -type orbitals. The consequence of this is that the X(π) \rightarrow Os(t_{2g}) transitions shift well into the visible region and impart an intense coloration to these complexes.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We also thank John E. Armstrong for carrying out some preliminary studies. The Varian XL-200 spectrometer was purchased with funds from the National Science Foundation (Grant No. CHE80-04246).

Registry No. *trans*-Os(CNCMe₃)₄Cl₂, 88272-01-9; *trans*-Os(CNCHMe₂)₄Cl₂, 88272-02-0; *trans*-Os(CNC₆H₁₁)₄Cl₂, 88272-03-1; *trans*-Os(CNCMe₃)₄Br₂, 88272-04-2; *trans*-Os(CNCHMe₂)₄Br₂, 88272-05-3; *trans*-Os(CNC₆H₁₁)₄Br₂, 88272-06-4; *trans*-[Os(CNCMe₃)₄Cl₂]BF₄, 88272-08-6; *trans*-[Os(CNCHMe₂)₄Cl₂]BF₄, 88272-10-0; *trans*-[Os(CNC₆H₁₁)₄Cl₂]BF₄, 88272-12-2; *trans*-[Os(CNCMe₃)₄Br₂]BF₄, 88272-14-4; *trans*-[Os(CNCHMe₂)₄Br₂]BF₄, 88272-16-6; *trans*-[Os(CNC₆H₁₁)₄Br₂]BF₄, 88272-18-8; Os₂(μ -O)(μ -O₂CCH₃)₂Cl₄(PPh₃)₂, 81282-98-6; OsO₂Cl₂(PPh₃)₂, 66984-36-9.

(21) Allen, A. D.; Stevens, J. R. *Can. J. Chem.* 1973, 51, 92.

(22) Verdonck, E.; Vanquickenborne, L. G. *Inorg. Chem.* 1974, 13, 762.

(23) Buhr, J. D.; Winkler, J. R.; Taube, H. *Inorg. Chem.* 1980, 19, 2416.

Contribution from the Department of Chemistry,
The University of Western Ontario,
London, Ontario, Canada N6A 5B7

One-Electron, Visible-Light Photooxidation of Porphyrins in Alkyl Chloride Solutions

Zbigniew Gasyna,[†] William R. Browett, and Martin J. Stillman*

Received April 22, 1983

It has been well documented that porphyrin and metalloporphyrin compounds can undergo reversible one-electron oxidation¹⁻³ to form porphyrin π -cation-radical complexes. These oxidation products have been implicated as intermediates in a number of biological reactions, including heme enzymes,^{4,5} photosynthetic reaction centers,^{6,7} and photosynthetic model systems,⁸ as well as in artificial photocatalytic systems.^{9,10} Because of their unusual electronic properties and their novel reactivities, there is great interest in the preparation of these oxidized compounds by chemical, electrochemical, and photochemical methods.^{11,12} In particular, the photooxidation of the parent porphyrin by an electron acceptor to give π -cation-radical species has been the subject of many studies.¹²⁻¹⁵

In previous work,¹⁶ we have shown that the diagnostic spectral features that identify specifically whether the porphyrin ring or the metal has been oxidized can be obtained using magnetic circular dichroism (MCD) spectroscopy. Prior to this work, identification of the porphyrin π -cation-radical species in solution was based primarily upon the analysis of optical absorption and ESR spectra.^{5,6} In the present paper we report results of the direct photooxidation of porphyrin and metalloporphyrin compounds in alkyl chloride solutions monitored with use of optical absorption and MCD spectra. In these reactions the photooxidation involves a charge-transfer interaction between the photoexcited porphyrin and the alkyl chloride that leads to the formation of a porphyrin π cation radical.

Experimental Section

The 5,10,15,20-tetraphenylporphine (H₂TPP) and metal complexes of the tetraphenylporphine were prepared by literature methods.¹⁷ Reagent grade 1,1,2,2-tetrachloroethane (TCE) obtained from Fisher Chemical Inc. was extracted with several changes of concentrated sulfuric acid followed by alternate washings with water and aqueous sodium hydroxide and then distilled under a nitrogen atmosphere. All other solvents were ACS Certified Spectroanalyzed grade obtained from Fisher Chemical Inc.

Photooxidations of tetraphenylporphine and the magnesium, zinc, cobalt, and copper complexes of tetraphenylporphine were carried out either in dichloromethane solutions containing TCE or CCl₄ or in neat TCE. Nitrogen-saturated solutions were irradiated in a water-cooled cell with visible light (wavelength >400 nm). The light source was a 300-W tungsten-halogen projector lamp, controlled by variable transformer. Quantum yield measurements employing standard ferrioxalate actinometry were carried out with a Jasco CRM-FA spectroirradiator. The porphyrins were dissolved in nitrogen-purged TCE and irradiated in a 1-cm cell at 20 °C with an excitation wavelength of 417 nm. The absorption spectra before and after irradiation were recorded. Initial rates of the photolytic product formation and the quantum yields were determined by monitoring absorption bands in spectral regions where the absorption by the parent porphyrin was negligible (typically about 650 nm). Published molar extinction coefficients were used to determine the concentrations of the porphyrins in solution as follows: H₂TPP, $\lambda = 515$ nm, $\epsilon = 18\,700$;¹⁸ MgTPP, $\lambda = 424$ nm, $\epsilon = 666\,000$;¹⁹ ZnTPP, $\lambda = 419$ nm, $\epsilon = 560\,000$;²⁰ CoTPP, $\lambda = 527$ nm, $\epsilon = 16\,000$;²¹ CuTPP, $\lambda = 540$ nm, $\epsilon = 20\,000$.²¹ The degree of photooxidation was easily determined by using the spectrum of a completely oxidized sample. In the case

- (1) Fuhrhop J. H. In "Porphyrins and Metalloporphyrins"; Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; pp 593-623.
- (2) Wolberg, A.; Manassen J. *J. Am. Chem. Soc.* 1970, 92, 2982.
- (3) Fajer, J.; Borg, D. C.; Forman, A.; Dolphin, D.; Felton, R. H. *J. Am. Chem. Soc.* 1970, 92, 3451.
- (4) Hewson, W. D.; Hager, L. P. In "Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. 7, pp 295-332.
- (5) Dolphin, D.; Felton, R. H. *Acc. Chem. Res.* 1974, 7, 26.
- (6) Fajer, J.; Davies, H. S. In "Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. 4, pp 197-256.
- (7) Davies, H. S.; Forman, A.; Fajer, J. *Proc. Natl. Acad. Sci. U.S.A.* 1979, 76, 4170.
- (8) McIntosh, A. R.; Siemiarczuk, A.; Bolton, J. R.; Stillman, M. J.; Ho, Te-Fe; Weedon, A. C. *J. Am. Chem. Soc.*, in press.
- (9) Whitten, D. G. *Acc. Chem. Res.* 1980, 13, 83.
- (10) Darvent, J. R.; Douglas, P.; Harriman, A.; Porter, G.; Richoux, M.-C. *Coord. Chem. Rev.* 1982, 44, 83.
- (11) Felton, R. H. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. 5, pp 53-115.
- (12) Seely, G. R. *Photochem. Photobiol.* 1978, 27, 639.
- (13) Mauzerall, D. *Coord. Chem. Rev.* 1982, 44, 29.
- (14) Potter, W.; Levin, G. *Photochem. Photobiol.* 1979, 30, 225.
- (15) Harriman, A.; Porter, G.; Searle, N. *J. Chem. Soc., Faraday Trans. 2*, 1979, 75, 1515.
- (16) Browett, W. R.; Stillman, M. J. *Inorg. Chim. Acta* 1981, 49, 69.
- (17) Fuhrhop, J. H. In ref 1, pp 757-869.
- (18) Badger, G. M.; Jones, R. A.; Laslett, R. L. *Aust. J. Chem.* 1964, 17, 1028.
- (19) Dolphin, D.; Muljiani, Z.; Rousseau, K.; Borg, D. C.; Fajer, J.; Felton, R. M. *Ann. N.Y. Acad. Sci.* 1973, 202, 177.
- (20) Pekkarinen, L.; Linnschitz, H. *J. Am. Chem. Soc.* 1960, 82, 2407.
- (21) Dorough, G. D.; Miller, J. R.; Huennekens, F. M. *J. Am. Chem. Soc.* 1951, 73, 4315.

[†] Permanent address: Institute of Radiation Chemistry, Lodz, Poland.