Osmium Complexes of 1,4,7-Triazacyclononane (tacn) and 1,4,7-Trimethyl-1,4,7-triazacyclononane (Me_3tacn) and the X-ray Crystal Structure of [(Me_3tacn)Os(η^6-$C_6H_5BPh_3$)]$BPh_4\cdot CH_3CN$

David C. Ware,[†] Marilyn M. Olmstead,[§] Renyi Wang,[‡] and Henry Taube*,[‡]

Departments of Chemistry, Stanford University, Stanford, California 94305, University of Auckland, Private Bag 92019, Auckland, New Zealand, and University of California, Davis, California 95616

Received October 9, 1995[⊗]

The complexes of osmium with tacn (1,4,7-triazacyclononane) and Me_3tacn (1,4,7-trimethyl-1,4,7-triazacyclononane), [LOs (η^6-C_6H_6)]$(PF_6)_2$ (L = tacn) and $LOsCl_3$ (L = tacn, Me_3tacn), have been prepared by substitution of L on $[Os(\eta^6\text{-}C_6H_6)Cl_2]_2$ or $[Os_2Cl_8]^{2-}$, respectively. Reaction of $LOsCl_3$ with neat triflic acid leads to partial replacement of chloride and formation of the binuclear Os(III)−Os(III) complexes $[LOs(\mu\text{-}Cl_3)OsL](PF_6)_3$ (L = tacn, Me_3tacn). The binuclear nature was established by NMR spectroscopy and elemental analysis and, for L = tacn, a partially refined X-ray crystal structure which shows the Os−Os separation to be 2.667 Å, indicative of significant metal−metal bonding. Reduction of $[LOs(\mu\text{-}Cl_3)OsL]^{3+}$ over zinc amalgam in either aqueous or nonaqueous solution yields the intensely colored Os(II)−Os(III) mixed-valence ions $[LOs(\mu\text{-}Cl_3)OsL]^{2+}$. Electrochemical measurements on $[LOs(\mu\text{-}Cl_3)OsL]^{3+}$ in CH_3CN reveal the reversible formation of the mixed valence ions. These are further reduced at lower potential to the Os(II)−Os(II) binuclear species, reversibly for L = Me_3tacn. (Me_3tacn)$OsCl_3$ is oxidized by persulfate ion to give $[(Me_3tacn)OsCl_3]^+$; zinc amalgam reduction in an aqueous solution at high concentration produces the binuclear complex $[(Me_3tacn)Os(\mu\text{-}Cl_3)Os(Me_3tacn)]^{3+}$ or, at low concentration, a solution containing an air sensitive osmium(II) species. Addition of BPh_4^- results in the η^6-arene zwitterion $[(Me_3tacn)Os(\eta^6\text{-}C_6H_5BPh_3)]^+$, which was characterized by X-ray diffraction on the BPh_4^- salt. The compound crystallizes in the triclinic space group $P1$ with $a = 11.829(2)$ Å, $b = 12.480(3)$ Å, $c = 17.155(4)$ Å, $\alpha = 84.42(2)°$, $\beta = 83.52(2)°$, $\gamma = 71.45(2)°$, $V = 2380(2)$ Å^3, $Z = 2$, and $R = 7.62\%$, and $R_w = 7.39\%$.

Introduction

The chemistry of low-valence osmium has made notable advances in recent years and led to the merging of two previously distinct areas of osmium(II) chemistry, namely classical coordination chemistry, which is based mainly on saturated ligands, particularly ammonia and amines and the organometallic chemistry of π-acid ligands such as alkenes, alkynes, and arenes.[1] Several general classes of such compounds can be identified, according to the number of saturated ligands in the coordination sphere. The pentaammine osmium(II) fragment $[Os(NH_3)_5]^{2+}$ will coordinate one additional two-electron donor unsaturated ligand, such as $H_2C{=}CH_2$, $HC{\equiv}CH$, η^2-arene, η^2-$Me_2C{=}O$ or η^2-$CH_3CH{=}NH$, etc.[1−5] The tetraammine or tetraamine fragments $[Os(NH_3)_4]^{3+}$ or $[Os(en)_2]^{2+}$ will coordinate two such two-electron donor ligands or one four-electron donor ligand such as η^4-arene.[1,4−7] *Cis/trans* isomerism is possible and has been observed in these compounds. In contrast to these two classes of compounds, the chemistry of the next class in the series containing the triammine or triamine osmium(II) moiety, $[Os(NH_3)_3]^{2+}$ or $[Os(amine)_3]^{2+}$, is much less well developed. The only prior examples are triammines, $[(\eta^6\text{-}C_6H_6)Os(NH_3)_3]^{2+}$ [8] and a number of trihalospecies,[9] among them $Os(NH_3)_3Cl_3$. When the goal of the research requires the blocking (ammine) ligands to be constrained to the facial coverage, NH_3 is not the best choice because of isomer possibilities. The ligands tacn and Me_3tacn chosen for our studies offer an obvious advantage in this regard and a further advantage in that the chelating triamine unit is much more resistant to replacement than are ammonias.

Transition metal tacn and Me_3tacn complexes, which show diverse structural and chemical properties, have received widespread recent attention,[10] and applications to bioinorganic model systems have provided some of the impetus for the development of this area.[11] In particular, the chemistry of tacn and Me_3tacn complexes of ruthenium is well established. Convenient access to this chemistry is provided via the labile Ru(II) to yield Ru(tacn)Cl_3 or Ru(Me_3tacn)Cl_3, which have been used as precursors to a range of both mono- and binuclear complexes in a number of oxidation states.[12−16] In contrast to

---

[†] University of Auckland.

[‡] Stanford University.

[§] University of California.

[⊗] Abstract published in *Advance ACS Abstracts*, March 15, 1996.

(1) Taube, H. *Pure Appl. Chem.* **1991**, *63*, 651−664.

(2) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1987**, *109*, 1883−1885.

(3) Hasegawa, T.; Kwan, K. S.; Taube, H. *Inorg. Chem.* **1992**, *31*, 1598−1600.

(4) Nunes, F. S.; Taube, H. *Inorg. Chem.* **1994**, *33*, 3111−3115.

(5) Lay, P. A.; Harmon, W. D. *Adv. Inorg. Chem.* **1991**, *37*, 219−379.

(6) Li, Z.-W.; Harman, D.; Lay, P. A.; Taube, H. *Inorg. Chem.* **1994**, *33*, 3635−3638.

(7) Pu, L.; Hasegawa, T.; Parkin, S.; Taube, H. *J. Am. Chem. Soc.* **1993**, *115*, 2545−2546.

(8) Hung, Y.; Kung, W.-J.; Taube, H. *Inorg. Chem.* **1981**, *20*, 457−463.

(9) Buhr, J. D.; Winkler, J. R.; Taube, H. *Inorg. Chem.* **1980**, *19*, 2416−2425.

(10) Chaudhuri, P.; Wieghardt, K. *Prog. Inorg. Chem.* **1987**, *35*, 329−436.

(11) McKee, V. *Adv. Inorg. Chem.* **1994**, *40*, 323−410.

(12) Wieghardt, K.; Herrmann, W.; Köppen, M.; Jibril, I.; Huttner, G. *Z. Naturforsch.* **1984**, *39B*, 1335−1343.

(13) Neubold, P.; Della Vedova, B. S. P. C.; Wieghardt, K.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1990**, *29*, 3355−3363.

(14) Neubold, P.; Wieghardt, K.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1989**, *28*, 459−467.

(15) Schneider, R.; Weyhermüller, T.; Wieghardt, K.; Nuber, B. *Inorg. Chem.* **1993**, *32*, 4925−4934.

(16) Schneider, R.; Wieghardt, K.; Nuber, B. *Inorg. Chem.* **1993**, *32*, 4935−4939.

0020-1669/96/1335-2576$12.00/0

the ruthenium analog, the osmium halide, $OsCl_3$, is insoluble, inert and has demonstrated little synthetic utility. As a result, the synthetic scheme used for the ruthenium chemistry would not be expected to have a direct parallel in osmium chemistry.

A general method for the preparation of $[Os(\eta^6\text{-arene})(tacn)]^{2+}$ complexes has appeared in a review article, although details of the synthesis and characterization were not given.[17] By following this method we have prepared $[(tacn)Os(\eta^6\text{-}C_6H_6)](PF_6)_2$ but have devoted most of our efforts to following the lead provided by the ruthenium chemistry, choosing $(tacn)OsCl_3$ and $(Me_3tacn)OsCl_3$ as the preparative intermediates to the desired chemistry.

In contrast to $OsCl_3$, the Os(III)−Os(III) metal−metal bonded dimer, $Os_2Cl_8{}^{2-}$ proves to be labile to substitution and serves as a convenient entry into osmium tacn and Me_3tacn chemistry. We report here the results of these studies, which include the preparation of $Os(tacn)Cl_3$ and $Os(Me_3tacn)Cl_3$, and our observations on the substitution and redox chemistry of these complexes. Derivatives include binuclear complexes such as $[LOs(\mu\text{-}Cl)_3OsL]^{3+}$ (L = tacn, Me_3tacn) and a salt containing the π-arene complex, $[(Me_3tacn)Os\{(\eta^6\text{-}C_6H_5)BPh_3\}]BPh_4$, which has been structurally characterized.

Experimental Section

Reagents. OsO_4 (Nat. Colonial Metal) and tacn, Me_3tacn, 1,3-cyclohexadiene, and triflic acid (CF_3SO_3H, Aldrich) were used as received. $(NH_4)_2[OsCl_6]$,[18] $[Os(C_6H_6)Cl_2]_2$,[8] $Os_2(\mu\text{-}O_2CMe)_4Cl_2$,[19] $[PPN]_2[Os_2Cl_8]$ (PPN ≡ bis(triphenylphosphoranylidine)(ammonium), and $[n\text{-}Bu_4N]_2[Os_2Cl_8]$[20] were prepared by literature methods.

Instrumentation and Techniques. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian XL-400 spectrophotometer. Measurements were made in CD_3CN (referenced to TMS using residual solvent signal at δ = 1.93 ppm) or D_2O (referenced to internal DSS, sodium 3-(trimethylsilyl)-1-propanesulfonate). UV−vis spectra were recorded on a Hewlett-Packard 8452A diode-array spectrophotometer. Microanalyses were performed by Desert Analytics, Inc., Tucson, AZ. Reductions with zinc amalgam were carried out in a VAC Atmospheres inert atmosphere box under nitrogen.

Preparation of $[(tacn)Os(\eta^6\text{-}C_6H_6)](PF_6)_2$. $[Os(\eta^6\text{-}C_6H_6)Cl_2]_2$ (310 mg, 0.46 mmol) was suspended in MeOH (35 mL), and tacn (130 mg, 1.01 mmol) dissolved in MeOH (1 mL) was added. The solution was refluxed under N_2 for 1 h, during which time the initial yellow suspension became cream-colored. The mixture was evaporated to dryness *in vacuo* and the residue dissolved in H_2O (*ca.* 100 mL) and filtered. The filtrate was adsorbed onto a Sephadex SP-C25 cation exchange column and washed with H_2O. Elution was begun with 0.1 M HCl and continued with 0.2 M HCl. A diffuse yellow band eluted first, followed by a larger pale yellow band that was collected over a large volume (*ca.* 150 mL). This was concentrated to *ca.* 15 mL in vacuo, and an excess of NH_4PF_6 in H_2O (1.5 mL) was added dropwise. The solution was cooled at 5 °C and the white crystals that formed were filtered, washed twice with H_2O and extensively with Et_2O, and dried over $CaCl_2$ (281 mg, 45%). ^1H NMR (CD_3CN): δ 7.45 (br s, 3H, NH), 5.90 (s, 6H, CH), 3.00 (mult, 6H, CH_2), 2.72 (mult, 6H, CH_2). Anal. Calcd for $C_{12}H_{21}N_3F_{12}OsP_2$: C, 20.96; H, 3.08; N, 6.11. Found: C, 20.77; H, 2.87; N, 6.00.

Preparation of $(tacn)OsCl_3$. $(PPN)_2[Os_2Cl_8]$ (900 mg, 0.52 mmol) was suspended in MeOH (25 mL) and a solution of tacn (0.16 g, 1.21 mmol) in MeOH (1.25 mL) was added with stirring. The suspension was refluxed under N_2 for 2 h, cooled, filtered and washed with MeOH and diethyl ether. The product was dried in a desiccator over $CaCl_2$ (0.36 g, 82%). Anal. Calcd for $C_6H_{15}N_3Cl_3Os$: C, 16.93; H, 3.55; N, 9.87. Found: C, 17.35; H, 3.59; N, 9.16.

Preparation of $(Me_3tacn)OsCl_3$. $(Bu_4N)_2[Os_2Cl_8]$ (743 mg, 0.65 mmol) was dissolved in dry DMF (10 mL) in an inert atmosphere glovebox. Me_3tacn (0.33 g, 1.90 mmol) dissolved in DMF (2.6 mL) was added and the solution heated at 90−100 °C for 6 h under argon. The solution was cooled to room temperature and the yellow-brown microcrystalline solid filtered off and washed with MeOH−Et_2O (35:65) and then Et_2O. The product was dried in a desiccator over $CaCl_2$ (281 mg, 46.5%). ^1H NMR (CD_3CN): δ 21.7 (br, 6H, CH_2), −11.3 (br, 9H, CH_3), −11.8 (br, 6H, CH_2). Anal. Calcd for $C_9H_{21}N_3Cl_3Os$: C, 23.10; H, 4.52; N, 8.98; Cl, 22.74. Found: C, 23.42; H, 4.23; N, 8.69; Cl, 22.29.

Preparation of $[(Me_3tacn)OsCl_3]PF_6$. $(Me_3tacn)OsCl_3$ (40 mg, .086 mmol) was suspended in H_2O (5 mL). $Na_2S_2O_8$ (80 mg, 0.34 mmol) dissolved in H_2O (5 mL) was added and the solution stirred for 1 h. The suspended powder was slowly replaced by yellow-red crystals during this time. The crystals were dissolved by warming at *ca.* 50 °C and solid $NaPF_6$ (0.05 g) was added. Immediately a yellow-orange solid formed, which after the solution had cooled, was filtered off, washed with cold H_2O and then Et_2O, and dried over $CaCl_2$ (47 mg, 90%). ^1H NMR (CD_3CN): δ 4.60 (br, 6H, CH_2), 1.90 (br, 9H, CH_3), −0.78 (br, 6H, CH_2). ^1H NMR (d_6-DMSO): d 5.19 (br, 6H, CH_2), 1.89 (br, 9H, CH_3), −0.86 (br, 6H, CH_2). Anal. Calcd for $C_9H_{21}N_3Cl_3F_6OsP$: C, 17.64; H, 3.45; N, 6.86; Cl, 17.36. Found: C, 17.73; H, 3.14; N, 6.86; Cl, 17.21.

Preparation of $[(tacn)Os(\mu\text{-}Cl_3)Os(tacn)](PF_6)_3$. $(tacn)OsCl_3$ (140 mg; 0.33 mmol) was dissolved in neat CF_3SO_3H (2 mL). The solution was heated at *ca.* 100 °C for 4 h while N_2 was bubbling through. After the solution cooled, Et_2O (*ca.* 50 mL) was added slowly with efficient stirring. The flocculent ppt that formed was filtered and washed with Et_2O, and dried *in vacuo* (184 mg, 94%). This material, formulated as $[(tacn)Os(\mu\text{-}Cl_3)Os(tacn)](CF_3SO_3)_3$ (117 mg, 0.098 mmol), was dissolved in 0.1 M CF_3SO_3H (10 mL). The red solution was stirred for 5 min then filtered to remove a small amount of black precipitate and $NaPF_6$ (1.1 g) in H_2O (5 mL) was added to the filtrate. After the solution was kept at 5 °C overnight, light brown shiny plates appeared which were filtered, washed with a small amount of ice-cold H_2O and then with Et_2O, and dried over $CaCl_2$ (86 mg, 74%). UV−vis (H_3O^+): λ_{max} 520, 312 nm. UV−vis (OH^-): λ_{max} 610, 434, 286(sh) nm. ^1H NMR (CD_3CN): δ 10.03 (br s, 3H, NH), 3.93 (mult, 6H, CH_2), 3.38 (mult, 6H, CH_2).^1H NMR (D_2O): δ 3.98 (mult, 6H, CH_2), 3.47 (mult, 6H, CH_2). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 63.3 (CH_2). Anal. Calcd for $C_{12}H_{30}N_6Cl_3F_{18}Os_2P_3$: C, 12.21; H, 2.56; N, 7.12; Cl, 9.01. Found: C, 12.20; H, 2.36; N, 6.90; Cl, 8.91.

Preparation of $[(Me_3tacn)Os(\mu\text{-}Cl_3)Os(Me_3tacn)](PF_6)_3$. $(Me_3tacn)OsCl_3$ (100 mg, 0.21 mmol) was added to neat CF_3SO_3H (1.5 mL) cooled in an ice bath. The solution was bubbled with argon and then heated at 50 °C for 2 h. The green solution was cooled to room temperature and then in an ice bath and Et_2O (*ca.* 30 mL) was slowly added with rapid stirring. The solid that formed was filtered, washed extensively with Et_2O, and dried *in vacuo* (135 mg, 99%). A portion of this material, $[(Me_3tacn)Os(\mu\text{-}Cl_3)Os(Me_3tacn)](CF_3SO_3)_3$ (100 mg, 0.078 mmol), was dissolved in 0.1 M CF_3SO_3H (10 mL) and the solution filtered. $NaPF_6$ (10 mg) in H_2O (5 mL) was added, and the fine precipitate that formed was redissolved by warming. The solution was then slowly cooled to room temperature and then at 5 °C for a few hours. The pale green solid that formed was filtered, washed with ice-cold H_2O and then Et_2O, and dried over $CaCl_2$ (60 mg, 61%). UV−vis (H_2O): λ_{max} 638, 332 nm. ^1H NMR (CD_3CN): δ 5.78 (mult, 6H, CH_2), 3.47 (mult, 6H, CH_2), 1.42 (s, 9H, CH_3). $^{13}C\{^1H\}$ (CD_3CN): δ 86.4 (CH_2), 72.4 (CH_3). Anal. Calcd for $C_{18}H_{42}N_6Cl_3F_{18}Os_2P_3$: C, 17.10; H, 3.35; N, 6.65; Cl, 8.41. Found: C, 16.94; H, 3.07; N, 6.43; Cl, 7.68.

Preparation of $[(Me_3tacn)Os(\eta^6\text{-}C_6H_5BPh_3)]BPh_4$. $(Me_3tacn)OsCl_3$ (60 mg, 0.013 mmol) was suspended in deoxygenated H_2O (*ca.* 15 mL), 3 drops of 1.0 M CF_3SO_3H were added, followed by Zn/Hg in excess, and the mixture was stirred for 1 h. The Zn/Hg was removed and an excess of $NaBPh_4$ was added, producing an off-white precipitate which was filtered, washed with H_2O, D_2O, and Et_2O, and dried *in vacuo*. Crystallization from CH_3CN produced pale yellow crystals suitable for X-ray structure determination. ^1H NMR (CD_3CN): δ 7.26 (mult, 8H, H_o), 7.20 (d, 6H, H_o', ^3J = 6.9 Hz), 7.10 (t, 6H, H_m', ^3J =

---

[17] (a) Schröder, M. *Pure Appl. Chem.* **1988**, *60*, 517−524. (b) Bell, M. N.; Blake, A. J.; Schröder, M.;Stephenson, T. A. *J. Chem. Soc., Chem Commun.* **1986**, 471−472.

[18] Dwyer, F. P.; Hogarth, J. W. *Inorg. Synth.* **1957**, *5*, 206−207.

[19] Behling, T.; Wilkinson, G.; Stephenson, T. A.; Tocher, D. A.; Walkinshaw, M. D. *J. Chem. Soc., Dalton Trans.* **1983**, 2109−2116.

[20] Fanwick, P. E.; Tetrick, S. M.; Walton, R. A. *Inorg. Chem.* **1986**, *25*, 4546−4552.

Table 1. Crystallographic Data for $[(Me_3tacn)Os(\eta^6\text{-}C_6H_5BPh_3)]BPh_4{\cdot}CH_3CN$

formula: $C_{59}H_{64}B_2N_4Os$	fw = 1041.0
crystal system: triclinic	$V = 2380(2)$ Å^3
space group: $P\bar{1}$	$Z = 2$
$a = 11.829(2)$ Å	$T = 130$ K
$b = 12.480(3)$ Å	$\lambda = 1.541\ 78$ Å
$c = 17.155(4)$ Å	$\rho_{calc} = 1.453$ mg/m^3
$\alpha = 84.42(2)°$	$R = 7.62\%$
$\beta = 83.52(2)°$	$R_w = 7.39\%$
$\gamma = 71.45(2)°$	GOF = 0.99

7.5 Hz), 6.98 (t, 8H + 3H, $H_m + H_p'$), 6.83 (t, 4H, H_p, $^3J = 7.2$ Hz), 6.07 (t, 1H, H_p''), 6.00 (d, 2H, H_o'', $^3J = 5.8$ Hz), 5.70 (t, 2H, H_m''), 3.24 (s, 9H, CH_3), 2.83 (mult, 6H, CH_2), 2.72 (mult, 6H, CH_2).

Electrochemistry. Cyclic voltammetry was carried out in 0.1 M TBAP/CH_3CN (TBAP = tetrabutylammonium hexafluorophosphate), using an EG&G Model 173 potentiostat/galvanostat driven by an EG&G Model 175 universal programmer. Cyclic voltammograms were recorded using a 7045A HP X-Y recorder. The working electrode was a glassy carbon disk (ϕ 2.5 mm), the counter elecrode was a platinum gauze, and the reference electrode was Ag/AgCl. Prior to each measurement, the solution was degassed with a stream of argon for 20 min and then argon blanket was maintained throughout the measurements. All the cited potentials are vs Ag/AgCl.

Determination of the Structure of $[(Me_3tacn)Os(\eta^6\text{-}C_6H_5BPh_3)]BPh_4{\cdot}CH_3CN$. The crystal selected for data collection was mounted in a cold stream (130 K) of a Siemens P4 diffractometer equipped with a LT-2 low temperature apparatus. The radiation employed was Ni-filtered Cu Kα from a Siemens rotating anode source operating at 15 kW. A linear decay of 2.6% in the intensities of three related standard reflections was observed during data collection, and the data were scaled to adjust for this decay. The structure was solved in the space group *P*1 using direct and difference Fourier methods. Hydrogens were added geometrically and refined by the use of a riding model and fixed isotropic thermal parameters. An absorption correction (XABS) was applied. Refinement was by full least-squares methods, with anisotropic thermal parameters for Os. The final difference map showed four peaks ranging from 1.5 to 1.9 e Å^{-3} in magnitude that were *ca.* 1 Å from Os. There are no short intermolecular contacts in the structure. Crystallographic data are given in Table 1, and atomic coordinates and equivalent isotropic displacement coordinates for the cation are given in Table 2.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å$^2 \times 10^3$) for the Cation in $[(Me_3tacn)Os(\eta^6\text{-}C_6H_5BPh_3)]BPh_4{\cdot}CH_3CN$

	x	*y*	*z*	*U*(eq)
Os	500(1)	1424(1)	2563(1)	13(1)
N(1)	1412(11)	1954(10)	1471(7)	14(3)
N(2)	343(12)	3163(11)	2808(7)	18(3)
N(3)	−1039(11)	2379(10)	1931(7)	14(3)
C(1)	1927(14)	2786(13)	1702(9)	18(4)
C(2)	1048(15)	3681(14)	2167(9)	23(4)
C(3)	−953(15)	3785(14)	2818(9)	23(4)
C(4)	−1455(15)	3630(13)	2086(9)	20(4)
C(5)	−644(15)	2183(14)	1084(9)	24(4)
C(6)	506(14)	2486(13)	867(9)	18(4)
C(7)	2347(16)	1023(15)	1080(10)	33(5)
C(8)	731(14)	3284(13)	3569(8)	18(4)
C(9)	−2127(16)	2006(15)	2098(10)	30(4)
C(10)	1643(14)	410(12)	3597(9)	14(3)
C(11)	2012(14)	−153(12)	2863(8)	15(4)
C(12)	1192(14)	−403(12)	2434(9)	15(4)
C(13)	−29(16)	−140(14)	2711(10)	26(4)
C(14)	−458(15)	485(13)	3387(9)	17(4)
C(15)	352(14)	773(13)	3780(9)	17(4)
C(16)	2302(15)	1344(14)	4808(9)	22(4)
C(17)	1248(14)	1482(13)	5365(9)	18(4)
C(18)	874(17)	2322(15)	5885(10)	31(4)
C(19)	1494(17)	3120(15)	5859(10)	33(5)
C(20)	2474(16)	3021(15)	5336(10)	30(4)
C(21)	2902(15)	2150(13)	4834(9)	19(4)
C(22)	2762(14)	−866(13)	4754(9)	18(4)
C(23)	3530(15)	−1146(14)	5361(9)	20(4)
C(24)	3727(17)	−2169(15)	5806(10)	33(5)
C(25)	3174(15)	−2951(14)	5691(9)	21(4)
C(26)	2368(17)	−2669(15)	5130(10)	32(5)
C(27)	2184(14)	−1657(13)	4641(9)	18(4)
C(28)	3946(14)	236(12)	3684(8)	13(3)
C(29)	4048(14)	1109(13)	3125(8)	16(4)
C(30)	5053(16)	1049(15)	2607(10)	30(4)
C(31)	6029(15)	98(13)	2658(9)	23(4)
C(32)	6011(16)	−769(15)	3226(9)	27(4)
C(33)	4983(16)	−711(15)	3731(10)	28(4)
B(1)	2666(16)	332(14)	4213(10)	11(4)

Results and Discussion

Preparation of $[(tacn)Os(\eta^6\text{-}C_6H_6)](PF_6)_2$. A complex containing both $\eta^6\text{-}C_6H_6$ and tacn ligands can conceptually be prepared either by addition of tacn to an osmium $\eta^6\text{-}C_6H_6$ precursor, or by the reverse route, namely additon of C_6H_6 to a preformed osmium tacn complex. While the development of the latter route, which would have general utility for the preparation of other low-valence osmium triamine complexes, was the primary goal of this work, we also prepared one example of a complex containing $\eta^6\text{-}C_6H_6$ and tacn by the former method.

The cleavage of the binuclear Os^{II} complex $[(\eta^6\text{-}C_6H_6)OsCl(\mu\text{-}Cl)_2OsCl(\eta^6\text{-}C_6H_6)]$ by donor ligands to give substituted mononuclear complexes has been described,[21−23] and aspects of the chemistry of the complexes containing the $[(\eta^6\text{-}C_6H_6)Os]^{2+}$ fragment in aqueous solutions have been investigated.[24] Our experimental results on the reaction of tacn with $[(\eta^6\text{-}C_6H_6)OsCl(\mu\text{-}Cl)_2OsCl(\eta^6\text{-}C_6H_6)]$ shows that this also leads to cleavage, a major product being a salt containing the complex $[(tacn)Os(\eta^6\text{-}C_6H_6)]^{2+}$. The characterization of the complex rests on the elemental analysis and on ^1H NMR spectroscopy. The spectrum in CD_3CN shows a singlet at 5.90 ppm corresponding to the benzene protons, and multiplets at 2.72 and 3.00 ppm arising from the chemically different *endo* and *exo* protons of the tacn CH_2CH_2 groups. These protons are equivalent in the free ligand due to rapid inversion at nitrogen: upon coordination to a metal they become chemically differentiated because inversion at nitrogen is supressed so that the two faces of the ligand become inequivalent. The multiplets are nonidentical, reflecting the different coupling constants between the *endo* and *exo* protons and the NH protons. In D_2O the NH protons are no longer observed due to rapid H/D exchange with the solvent. In this case the multiplets arising from the CH_2CH_2 protons simplify and become identical.

Preparation of $LOsCl_3$ (L = tacn, Me_3tacn). The entry into the chemistry of osmium complexes of tacn and Me_3tacn described here is through the octachloro Os(III)−Os(III) dimer $[Os_2Cl_8]^{2-}$.[20,25−27] While, as mentioned earlier, $OsCl_3$ is quite inert (and indications are that this is true also of $OsBr_3$),[27a] rendering $OsCl_3$ of limited utility as a precursor to osmium(III) complexes,[5] the dimer $[Os_2Cl_8]^{2-}$ is quite reactive. This reactivity has been attributed to the perturbation produced by metal−metal interaction which greatly modifies the electronic

---

(21) Bennett, M. A.; Matheson, T. W.;Robertson, G. B.; Smith, A. K.; Tucker, P. A. *Inorg. Chem.* **1980**, *19*, 1014−1021.

(22) Arthur, T.; Stephenson, T. A. *J. Organomet. Chem.* **1981**, *208*, 369−387.

(23) Cabeza, J. A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1985**, 573.

(24) Stebler-Röthlisberger, M.; Hummel, W.; Pittet, P.-A.;Bürgi, H.-B.; Ludi, A.; Merbach, A. E. *Inorg. Chem.* **1988**, *27*, 1358−1363.

(25) Fanwick, P. E.; King, M. K.; Tetrick, S. M.; Walton, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 5009−5011.

(26) Agaskar, P. A., Cotton, F. A.; Dunbar, K. R.; Falvello, L. R.; Tetrick, S. M.; Walton, R. A. *J. Am. Chem. Soc.* **1986**, *108*, 4850−4855.

(27) (a) Fanwick, P. E.; Fraser, I. F.; Tetrick, S. M.; Walton, R. A. *Inorg. Chem.* **1987**, *26*, 3786−3791. (b) Schukarev, S. A.; Kolbin, N. E.; Semonov, I. N., *Russ. J. Inorg. Chem.* **1961**, *6*, 638.

structure, giving rise to vacant axial coordination sites which provide access to nucleophiles. In particular, coordination of an axial ligand results in population of orbitals which are σ-antibonding with respect to the Os−Os bond, and leads to rapid cleavage of the Os−Os bond and further substitution of the complex. A limited use has been made of the dimer as a precursor to other osmium(III) complexes.[27] For example, the very rapid reaction of the dimer with pyridine gives *trans*-$[OsCl_4(py)_2]^-$ as the initial product under very mild conditions. This complex can then be further substituted to give, for example, *mer*-$OsCl_3(py)_3$. Other attributes of $[Os_2Cl_8]^{2-}$, which enhance its synthetic utility, are its ready preparation as a range of stable salts soluble in non-aqueous solvents and its reactivity toward a range of donor molecules.[20,25−27] The homoleptic bromo and iodo analogs are also known.[28,29]

We have shown that tacn in CH_3OH or Me$_3$tacn in DMF, on heating, reacts with a salt containing $[Os_2Cl_8]^{2-}$ to produce (tacn)OsCl$_3$ and (Me$_3$tacn)OsCl$_3$ respectively in good yield. The neutral products are readily isolated and the sparingly soluble (tacn)OsCl$_3$ has been characterized by elemental analysis, as has the more soluble Me$_3$tacn analog which has also been characterized by ^{1}H NMR. The spectrum shows three broadened, paramagnetically shifted peaks corresponding to the methyl protons and the *endo* and *exo* protons of the CH_2CH_2 groups. Further characterization of both complexes derives from their reactions, for both L = tacn and Me$_3$tacn the preparation of the binuclear complexes $[LOs(\mu\text{-}Cl_3)OsL]^{3+}$ and, for L = Me$_3$tacn, persulfate oxidation to the osmium(IV) complex [(Me$_3$tacn)OsCl$_3$]$^+$ (*vide infra*).

Preparation and General Chemistry of $[LOs(\mu\text{-}Cl)_3OsL]^{3+}$ (L = tacn, Me$_3$tacn). Reaction of transition metal halide complexes with neat triflic acid to produce HCl(g) and the corresponding labile metal triflato ($CF_3SO_3^-$) complexes has been established as a general route for derivatizing metal halide precursors.[30] In particular, for the penta- and tetraammineosmium complexes, the preparation of $[Os^{III}(NH_3)_5(CF_3SO_3)](CF_3SO_3)_2$ and $[Os^{III}(NH_3)_4(CF_3SO_3)_2](CF_3SO_3)$ from the corresponding halide complexes, followed by reduction, has proved useful as an entry to osmium(II) chemistry.[2,6,31] The reaction of LOsCl$_3$ (L = tacn, Me$_3$tacn) with neat triflic acid (CF_3SO_3H) did not, however, result in substitution of all the chloride ligands, giving instead, after precipitation with ether as the triflate salt and subsequent isolation and purification as the PF_6^- salt, the binuclear species $[LOs(\mu\text{-}Cl)_3OsL]^{3+}$ (L = tacn, Me$_3$tacn). $[LOs(\mu\text{-}Cl)_3OsL](PF_6)_3$ were characterized by elemental analysis and by ^{1}H and ^{13}C NMR. Initially, the binuclear nature was established for L = tacn by integration of the ligand protons relative to the phenyl protons of the counterion in the BPh_4^- salt, indicating an L:BPh$_4$ ratio of 2:3. This was confirmed by a partially refined X-ray crystal structure determination of $[(tacn)Os(\mu\text{-}Cl)_3Os(tacn)](PF_6)_3$.

The failure of triflate (neat HO_3SCF_3) to substitute for all the chloride ligands in LOsCl$_3$ (L = tacn, Me$_3$tacn) illustrates the strength and inertness typical of the Os(III)−Cl bond.[9] The formation of the triply-bridged μ-chloro binuclear species also illustrates a common structural motif for binuclear tacn and Me$_3$tacn complexes, where triply-bridged complexes containing not only halide but also oxo, hydroxo, hydrido, and other bridging ligands have been observed.[10] Presumably, once the Os(μ-Cl)$_3$-Os fragment forms after partial substitution of chloride in the precursor by triflate, the complex is greatly stabilized and further substitution by triflate is difficult even with prolonged heating in neat triflic acid.

The ^{1}H NMR spectra of $[LOs(\mu\text{-}Cl)_3OsL](PF_6)_3$ has resonances close to the expected diamagnetic positions for L = tacn, but distinct paramagnetic shifts are observed for L = Me$_3$tacn. Despite the paramagnetic shifts, both complexes give spectra with narrow line widths. A preliminary determination of the magnetic moment in solution (Evans method) for L = Me$_3$tacn indicates a value for μ_{eff} of approximately 0.4 μ_B per osmium. The ^{1}H NMR spectrum of $[(tacn)Os(\mu\text{-}Cl)_3Os(tacn)](PF_6)_3$ in CD_3CN shows two different multiplets for the *endo* and *exo* protons of the CH_2CH_2 groups in the tacn ligand, while in D_2O the NH protons are no longer observed and the mutiplets arising from the CH_2CH_2 protons simplify and become identical. The ^{1}H NMR spectra of the Me$_3$tacn analog shows identical resonances for the *endo* and *exo* protons in both CD_3CN and D_2O, reflecting the lack of NH protons in the complex.

An attempt was made to determine the structure of $[(tacn)Os(\mu\text{-}Cl)_3Os(tacn)(PF_6)_3]$ by X-ray diffraction of a crystal.[32] The structure was found to be severely disordered, consisting of the superposition of two molecules rotated about the Os−Os axis at an angle of 60°, and could not be fully refined. However the partially refined structure (R = 7.1%) did confirm the binuclear nature of the complex and the connectivity of the atoms, showing the coordination of one tacn ligand to each osmium and the presence of three bridging chloro ligands. The Os−Os bond length of 2.667 Å is unaffected by the disorder problem.[32]

The binuclear complexes $[LOs(\mu\text{-}Cl)_3OsL]^{3+}$ (L = tacn, Me$_3$tacn) belong to the general class of transition metal complexes with confacial bioctahedal geometry containing three bridging ligands, typically halides although hydroxo, oxo, etc. are also known. A point of interest of such compounds is the degree of metal−metal bonding. It is affected not only by the electron count but is heavily influenced also by steric and electrostatic factors associated with the bridging ligands. As a result combination of structural, spectroscopic and magnetic data are usually required to evaluate the degree of metal−metal bonding.[33] In D_{3h} symmetry the metal frontier orbitals comprise σ (a_1') and two π (e') bonding orbitals, and two σ^* (a_2'') and π^* (e'') antibonding orbitals.[33] For example, ruthenium complexes containing the $[Ru(\mu\text{-}X)_3Ru]^{n+}$ (X = Cl, Br) core range from $Ru^{II}Ru^{II}$ (12 electrons, formal bond order 0), through $Ru^{II}Ru^{III}$, $Ru^{III}Ru^{III}$, and $Ru^{III}Ru^{IV}$ to $Ru^{IV}Ru^{IV}$ (8 electrons, bond order 2). The II/II, II/III, and III/III complexes are exemplified by the tacn or Me$_3$tacn complexes $[LRu(\mu\text{-}Cl)_3RuL]^{n+}$.[12,13] The binuclear species $[Br_3Ru(\mu\text{-}Br)_3RuBr_3]^{n+}$ can access the III/III, III/IV, and IV/IV oxidation states;[34,35] and has been structurally characterized in the III/III state.[36] Structurally characterized examples containing osmium are rarer, and are limited to $[(PEt_3)_3Os(\mu\text{-}Cl)_3Os(PEt_3)_3]PF_6$ ($Os^{II}Os^{II}$),[27] and $[Br_3Os(\mu\text{-}Br)_3OsBr_3]^{3-}$ ($Os^{III}Os^{III}$).[37] Only for the ennea bromo composition have osmium and ruthenium complexes of analagous composition been structurally characterized. The III/III oxidation state gives an electron count of 10, which corresponds to a $\sigma^2\pi^4\pi^{*4}$ configuration, spin pairing, and a net bond order of 1. However magnetic data for the $Ru^{III}Ru^{III}$ complex indicate

---

[28] Cotton, F. A.; Vidyasagar, K. *Inorg. Chem.* **1990**, *29*, 3197−3199.

[29] Preetz, W.; Hollmann, P.; Thiele, G.; Hillbrecht, H. *Z. Naturforsch.* **1990**, *45B*, 1416−1424.

[30] Lawrance, G. A. *Chem. Rev.* **1986**, *86*, 17−33.

[31] Harman, W. D.; Fairlie, D. P.; Taube, H. *J. Am. Chem. Soc.* **1986**, *108*, 82338237.

[32] Parkin, S.; Olmstead, M. Private communication.

[33] Cotton, F. A.; Ucko, D. A. *Inorg. Chim. Acta* **1972**, *6*, 161−172.

[34] Coombe, V. T.; Heath, G. A.; Stephenson, T. A.; Vattis, D. K. *J. Chem. Soc., Dalton Trans.* **1983**, 2307−2309.

[35] Kennedy, B. J.; Heath, G. A.; Khoo, T. J. *Inorg. Chim. Acta* **1991**, *190*, 265−269.

[36] Appleby, D.; Hitchcock, P. B.; Seddon, K. R.; Turp, J. E.; Zora, J. A.; Hussey, C. L.; Sanders, J. R.; Ryan, T. A. *J. Chem. Soc., Dalton Trans.* **1990**, 1879−1887.

[37] Gheller, S. F.; Heath, G. A.; Hockless, D. C. R.; Humphrey, D. G.; McGrady, J. E. *Inorg. Chem.* **1994**, *33*, 3986−3989.

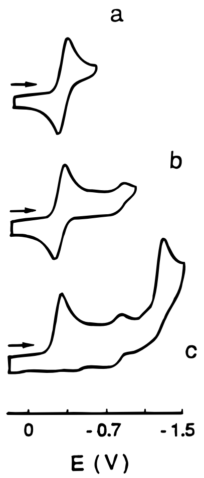

Figure 1. Cyclic voltammograms of $[(tacn)_2(\mu\text{-}Cl_3)Os_2](PF_6)_3$. Scan rate: 200 mV/s. Potential vs Ag/AgCl.

reduced metal−metal bonding and appreciable paramagnetism ($\mu_{eff} = 1.1$ per Ru), proposed to arise from a thermally accessible triplet state.[37] The osmium analog is much closer to diamagnetic ($\mu_{eff} = 0.25$/Os), and this is consistent with a short Os−Os bond of 2.779(1) Å, relative to the Ru−Ru bond of 2.880(3) Å.[36,37] The Os−Os bond length of 2.667 Å in $[(tacn)Os(\mu\text{-}Cl)_3Os(tacn)](PF_6)_3$ is shorter still, suggesting that the metal−metal interaction is even stronger in this complex, and contrasts with the nonbonded Os−Os distance of 3.47 Å in $[(PEt_3)_3Os(\mu\text{-}Cl)_3Os(PEt_3)_3]PF_6$.[27]

Redox Chemistry of $[LOs(\mu\text{-}Cl)_3OsL]^{3+}$. The mixed valence binuclear complexes, $[LRu(\mu\text{-}Cl)_3RuL]^{2+}$ (L = tacn, Me$_3$tacn) have been isolated and are formed by spontaneous reduction of the Ru(III) precursors.[12,13] The isolation of the osmium complexes as the oxidised Os(III)−Os(III) form is consistent with the greater stability of osmium relative to ruthenium in higher oxidation states. The binuclear osmium complexes $[LOs(\mu\text{-}Cl)_3OsL]^{3+}$ can be reduced by stirring over zinc amalgam in aqueous solution. During the course of the reaction the pale yellow (L = tacn) or green (L = Me$_3$tacn) color of the Os(III)−Os(III) complex turns to deep red or purple, respectively. The intense colors and increased extinction coefficients are indicative of the formation of an Os(II)−Os(III) mixed valence species.[38] The reduction to the mixed valence species can also be accomplished in non-aqueous solution. Stirring the pale-colored solution containing $[(tacn)Os(\mu\text{-}Cl)_3Os(tacn)]^{3+}$ and Zn/Hg in MeCN or pyridine again leads to very rapid formation of the deep red color characteristic of the Os(II)−Os(III) mixed-valence species. Prolonged reaction (*ca.* 1.5 h) leads to a further color change, to pale yellow (in MeCN-d_3) or dichroic red/green (in d$_5$-pyridine). The ^{1}H NMR spectrum of these solutions show diamagnetically shifted resonances expected for Os(II) species. The formation of a number of MeCN−Os(II) species indicates cleavage of the Os(II)−Os(II) binuclear species to mononuclear Os(II) products.

Attempts to exchange the PF_6^- counterion in $[(Me_3tacn)Os(\mu\text{-}Cl_3)Os(Me_3tacn)](PF_6)_3$ for BPh_4^- in aqueous solution led to spontaneous reduction, presumably by BPh_4^- , to the mixed valence Os(II)−Os(III) complex, as evidenced by formation of the deep purple color and significantly paramagnetically shifted and broadened resonances in the NMR spectrum of the product.

The electrochemistry of the two μ-trichloro species was studied by cyclicvoltammetry, and in CH_3CN the voltammograms obtained at a scan rate of 100 mV/s for the tacn and Me$_3$tacn derivatives are shown in Figures 1 and 2 respectively.

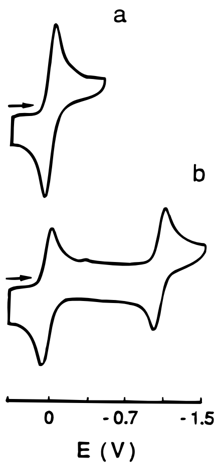

Figure 2. Cyclic voltammograms of $[(Me_3tacn)_2(\mu\text{-}Cl_3)Os_2](PF_6)_3$. Scan rate 200 mV/s. Potential vs Ag/AgCl.

For the former, when the scan to lower potentials, begun at 0.2 V, is reversed at −0.6 V, a reversible le couple ($E_{1/2} = -0.28$ V) is observed (Figure 1a). When the scan is extended to −1.0 V (Figure 1b) another redox couple at $E_{1/2} = -0.87$ V is registered but the waves corresponding to this couple have a much smaller amplitude than those associated with $E_{1/2} = -0.28$ V. When the scan is continued to −1.5 V before reversal (Figure 1c) an additional le reductive peak is observed ($E_{1/2} = -1.32$ V). While for neither major reductive peak does a corresponding oxidation peak now appear, the minor electrochemical action at intermediate potential remains reversible. We have recorded cyclic voltammograms also at scan rates ranging from 50 to 500 mV/s over the potential range +0.2 to −1.5 V and find no alteration in the general features described. On scanning (100 mV/s) to higher potentials from 0.2 V, a small amplitude wave is observed at 0.80 V which however is not accompanied by a complementary reduction signal. At still higher potentials, very high oxidative currents are registered but appear at *ca.* 0.3 V lower than the potential where background currents begin to be observed for CH_3CN containing only supporting electrolyte.

The amplitude of the minor peak at $E_{1/2} = -0.87$ V is not changed by first scanning to positive potentials, nor by holding the starting potential (0.20 V) for several seconds before beginning the scan. We conclude therefore that it does not arise from electrochemical action on the major species, and assign it to a contaminant. Because the ^{1}H NMR spectrum is very clean, we believe that the impurity is paramagnetic, and it presumably is an Os(III) complex. We attribute the small amplitude wave at $E_{pa} = 0.80$ V to the same impurity.

The assignments for the major species in the tacn system are summarized below

$$\mathrm{Os^{III}Os^{IV}} \leftarrow \mathrm{Os^{III}Os^{III}} \rightleftharpoons \mathrm{Os^{III}Os^{II}} \rightarrow \mathrm{Os^{II}Os^{II}}$$

$$E_{pa} > 1.5\ \mathrm{V} \quad E_{1/2} = -0.28\ \mathrm{V} \quad E_{pc} = -1.32\ \mathrm{V}$$

The Os^{II}Os^{II} species is very labile and the changes which ensue after it is generated take place within 4 s (even at a scan rate of 500 mV/s, there is no hint of reversibility). The most reasonable reaction mode for the Os^{II}Os^{II} species is far reaching disruption of the bridging bonds. This would lead to entry of CH_3CN into the coordination sphere, and entry of three solvent molecules per osmium could raise the Os(III)/Os(II) potential to the point that it would lie in the range above 1.5 V.

Typical voltammograms for the Me$_3$tacn derivative (scan rate 100 m V/s) are depicted in Figure 2. They follow the behavior outlined for the tacn derivative but lack the complication of an

---

(38) Ludi, A. *Mixed Valence Compounds*; Brown, D. B., Ed.; Reidel Publishing Co.: Dordrecht, The Netherlands, 1980; p25.

Table 3. Electrochemical Data[a]

	E, V[b]			
	$Os^{III} \rightarrow Os^{IV}$	$Os^{III} \rightarrow Os^{II}$	$Os^{III}Os^{III} \rightarrow Os^{III}Os^{II}$	$Os^{III}Os^{II} \rightarrow Os^{II}Os^{II}$
[Os(tacn)Cl$_3$]	0.72[c]	−0.80[c]		
[Os(Me$_3$tacn)Cl$_3$]	0.64 (0.58)	−0.57[c]		
[(tacn)Os(μ-Cl$_3$)Os(tacn)](PF$_6$)$_3$			−0.32 (−0.28)	−1.32[c]
[(Me$_3$tacn)Os(μ-Cl$_3$)Os(Me$_3$tacn)](PF$_6$)$_3$			0.00 (0.04)	−1.12 (−1.08)

[a] 0.1 M TBAP/CH$_3$CN. Scan rate 100 mV/s. Potentials vs Ag/AgCl. [b] Data in parentheses are $E_{1/2}$ values. [c] Irreversible.

impurity peak either in the reduction mode or oxidation mode. As to the latter, break-through currents are observed at potentials more positive than that observed for the tacn derivative, but short of that shown by CH$_3$CN containing only electrolyte (1.8 V). A major difference from the behavior of the tacn derivative is that the le reduction of Os^{III}Os^{II} is now reversible.

The results of the electrochemical measurements on the two binuclear species are summarized in Table 3. One point of difference is that $E_{1/2}$ for the 3+/2+ potential is higher for the methylated derivative than it is for the tacn analog, a difference in the same sense was observed in the corresponding ruthenium case.[12,13] A second is the greater lability to disruption of the II/II species derived from tacn as compared to Me$_3$tacn. This is also observed for the ruthenium analogs.[12,13]

For the Me$_3$tacn derivative, we have values of $E_{1/2}$ for the two stages of reduction of the Os^{III}Os^{III} species enabling comparison of the comproportionation constant for the reactions

$$\mathrm{III/III} + \mathrm{II/II} \rightleftharpoons 2\mathrm{III/II}$$

with that for the ruthenium case.[12,13] The values of $\Delta E_{1/2}$ governing the equilibria are 8.9×10^{18} and 20×10^{20} respectively. A major difference between the two systems is the degree of metal−metal bonding, which is expected to be greater for osmium than for ruthenium. It is greatest in the III/III state and on this account the mixed valence species is expected to be relatively less stable for the osmium analog than for ruthenium.

Redox Chemistry of (Me$_3$tacn)OsCl$_3$. (Me$_3$tacn)OsCl$_3$ can be oxidized by persulfate ion in aqueous solution to the osmium(IV) complex [(Me$_3$tacn)OsCl$_3$]$^+$, isolated and characterized as the PF$_6^-$ salt. The salt is soluble in water, and the cation can be chromatographed on Sephadex cation exchange resin where its behavior is that expected for a unipositive ion. The ^{1}H NMR spectrum shows paramagnetically shifted resonances but with smaller shifts than those of the Os(III) precursor. Again, the accessibility of a stable Os(IV) complex illustrates the greater stability of osmium in higher oxidation states, relative to ruthenium for which the Ru(IV) analog has not been reported.

Reduction of (Me$_3$tacn)OsCl$_3$ over zinc amalgam in a nonaqueous solvent such as CD$_3$CN gives a diamagnetic Os(II) species, identified by ^{1}H NMR spectroscopy. However the result of reduction by zinc amalgam in aqueous solution is dependent on concentration. At high concentration (greater than *ca.* 0.50 mM) a reduction product is the mixed-valence binuclear species [(Me$_3$tacn)Os(μ-Cl)$_3$Os(Me$_3$tacn)]$^{2+}$, identified by comparison of the characteristic deep purple color with that of the authentic complex prepared directly by reduction of the Os(III)−Os(III) binuclear complex. In aqueous solution at low concentration (*ca.* 0.50 mM) zinc amalgam reduction gives an air-sensitive, pale yellow solution indicative of an osmium(II) species. However the known greater lability of chloride on osmium(II)[39] and the subsequent substitution chemistry suggests that the complex has retained the Me$_3$tacn ligand and also contains other labile ligands. Upon addition of NaBPh$_4$ to this solution a pale yellow solid precipitates. Recrystallization from CH$_3$CN gave crystals suitable for X-ray crystallography, which, together with the NMR data showed the complex to contain one BPh$_4$ ligand η^6-coordinated through one C$_6$H$_5$ group, and a second BPh$_4^-$ ion as a counterion, with overall formula [(Me$_3$tacn)Os{(η^6-C$_6$H$_5$)BPh$_3$}]BPh$_4$. The ^{1}H NMR spectrum showed clearly the resonances for the η^6-C$_6$H$_5$ group, the remaining phenyl resonances of the coordinated BPh$_4$ group, and the equivalent resonances of the BPh$_4^-$ counterion. If benzene was added to the pale yellow osmium(II) solution prior to the addition of BPh$_4$, then the major product was the complex containing the (η^6-C$_6$H$_5$)BPh$_3$ ligand, but a second, minor product could be identified by NMR as [(Me$_3$tacn)Os(η^6-C$_6$H$_6$)]$^{2+}$. The formation of only a small amount of this product can be attributed to the low solubility of benzene in water. The η^6-C$_6$H$_6$ ligand gives a singlet at 5.95 ppm, which compares with the peak at 5.90 ppm for the same ligand in [(tacn)Os(η^6-C$_6$H$_6$)]$^{2+}$.

The electrochemical results obtained for the mononuclear complexes (at 100 m V/s) also appear in Table 3. Reduction of Os(tacn)Cl$_3$ and of Os(Me$_3$tacn)Cl$_3$ are both irreversible, with $E_{pc} = -0.80$ and -0.57 V respectively. Oxidation of Os(Me$_3$tacn)Cl$_3$ proves to be reversible ($E_{1/2} = 0.64$ V) while that of Os(tacn)Cl$_3$ is irreversible ($E_{pa} = 0.72$ V). The irreversibility of the reduction is ascribable to rapid replacement of Cl$^-$ by CH$_3$CN in the Os(II) complexes. In view of difference in behavior registered on oxidation of the two complexes, it seems likely that the process responsible for the irreversibility of the case of the tacn derivative is ascribable to ligand oxidation (net dehydrogenation).

Quite unexpected is the large difference in the potentials for the reduction of the 3+ state to the 2+ in the two cases, and an explanation for this behavior is not immediately obvious. A difference in the same sense, but much smaller is retained on the reduction of the binuclear species. The most striking difference between the mono and binuclear complexes is the much greater difficulty of generating the 4+ oxidation state for the latter complexes. Oxidation is expected to increase the Os−Os bond order but a countervailing influence is that the d orbitals would tend to shrink on raising the oxidation state. If this is in fact the reason for the difference in the potential required to remove an electron, it emerges as a powerful effect.

Crystal Structure of [(Me$_3$tacn)Os{(η^6-C$_6$H$_5$)BPh$_3$}]BPh$_4$·CH$_3$CN. A number of complexes containing the BPh$_4^-$ ligand η^6-coordinated through one of the phenyl rings have been reported and recently reviewed.[40] Although structural data indicate that an η^6-coordinated BPh$_4^-$ ligand is no more strongly bonded to a given metal ion than a neutral η^6-arene ligand, electrostatic interactions are probably important as NMR data for zirconium complexes indicate that neutral arene ligands do not displace the η^6-coordinated BPh$_4^-$ ligand.[41] The low yield of [(Me$_3$tacn)Os(η^6-C$_6$H$_6$)]$^{2+}$ formed from an aqueous reaction mixture containing both BPh$_4^-$ and benzene probably results

---

(39) Gulens, J.; Page, J. A. *J. Electroanal. Chem. Interfacial Electrochem.* **1976**, *67*, 215−230.

(40) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927−942.

(41) Bochmann, M.; Karger, G.; Jaggar, A. *J. Chem. Soc., Chem Commun.* **1986**, 1038−1039.

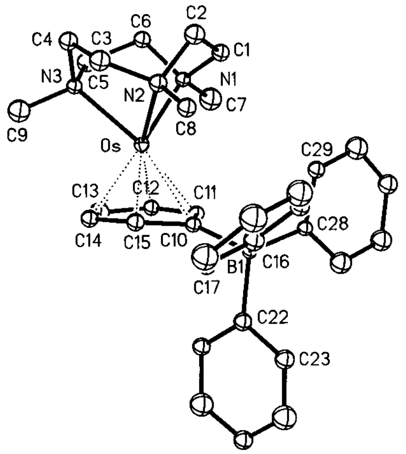

Figure 3. Ortep drawing of the cation $[(Me_3tacn)Os\{(\eta^6\text{-}C_6H_5)BPh_3\}]^+$.

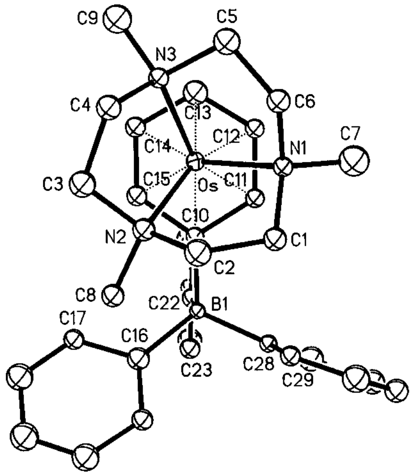

Figure 4. Ortep drawing of the cation $[(Me_3tacn)Os\{(\eta^6\text{-}C_6H_5)BPh_3\}]^+$. (View down plane of nitrogen atoms.)

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) for $[(Me_3tacn)Os(\eta^6\text{-}C_6H_5BPh_3)]BPh_4{\cdot}CH_3CN$

Bond Lengths			
Os−N(1)	2.208(12)	Os−N(2)	2.197(14)
Os−N(3)	2.172(12)	Os−C(10)	2.365(14)
Os−C(11)	2.260(13)	Os−C(12)	2.188(15)
Os−C(13)	2.215(19)	Os−C(14)	2.194(17)
Os−C(15)	2.173(15)	C(10)−C(11)	1.456(21)
C(11)−C(12)	1.407(25)	C(12)−C(13)	1.411(23)
C(13)−C(14)	1.415(22)	C(14)−C(15)	1.383(26)
B(1)−C(10)	1.669(25)	B(1)−C(16)	1.621(24)
B(1)−C(22)	1.659(23)	B(1)−C(28)	1.651(23)
Bond Angles			
N(1)−Os−N(2)	79.6(5)	N(1)−Os−N(3)	79.8(5)
N(2)−Os−N(3)	79.1(5)	Os−C(10)−B(1)	148.4(11)
C(10)−B(1)−C(16)	115.0(12)	C(10)−B(1)−C(22)	103.8(14)
C(10)−B(1)−C(28)	107.9(12)	C(16)−B(1)−C(22)	107.4(12)
C(16)−B(1)−C(28)	112.2(15)		

both from electrostatic factors and from the low solubility of benzene relative to BPh_4^- in water.

Selected bond lengths and angles are given in Table 4; drawings of the cation are shown in Figures 3 and 4. The complex is a pseudosandwich structure, with the Me_3tacn ligand occupying three facial coordination sites and the approximately coplanar η^6-C_6H_5 group of the coordinated BPh_4 ligand occupying the other three coordination sites in the $[(Me_3tacn)Os\{(\eta^6\text{-}C_6H_5)BPh_3\}]^+$ cation. The normals to the plane through the three nitrogen atoms and the mean plane through the carbon atoms in the η^6-C_6H_5 group are at an angle of 4.6°. The structure contains a BPh_4 counterion and one CH_3CN solvent molecule. The average Os−N bond length is 2.192 Å, with the shortest bond, Os−N(3) = 2.172(12) Å, occurring on the side of the molecule opposite to the BPh_3 group. The projections of the Os−N bonds approximately bisect C−C bonds of the η^6-arene group. The N−Os−N bond angles are all very close to the average value of 79.5°. The Os−C bond lengths range from 2.173(15) to 2.365(14) Å, averaging 2.23 Å, with the longest bond, Os−C(10), to the arene carbon attached to B(1), presumably for steric reasons. The C−C bonds in the η^6-group are longest (1.45 Å) for the two bonds to the substituted carbon C(10), and the other C−C bonds are at least 0.04 Å shorter. The C(10)−B(1) bond length of 1.669(25) Å is not significantly different from the other B−C bond lengths in either the coordinated BPh_4 group or the BPh_4 counterion, with B(1)−C(av) and B(2)−C(av) both close to 1.65 Å. The angles at boron (C−B−C) show more distortion in the coordinated BPh_4 group, ranging from 103.8(14) to 115.0(12)°, with the largest angle, C(10)−B(1)−C(16) between the coordinated η^6-C_6H_5 group and the C_6H_5 group containing C(16) which projects toward a methyl group, C(8), of the Me_3tacn ligand. The C−B(2)−C angles of the BPh_4 counterion lie in a much narrower range, 108.0(14)−112.3(13) Å, centered around the idealized tetrahedral angle.

Few structures of (η^6-arene)osmium complexes are available for comparison. The most closely related complex, which contains the sulfur analog of tacn, is $[(1\text{-Me-4-iPr-}C_6H_4)OsL][BPh_4]_2$ (L = 1,4,7-trithiacyclononane).[42] The average Os−C bond length of 2.24 Å is almost the same, and similarly the longest Os−C bonds involve the Me- or iPr-substituted carbon atoms. Like the Me_3tacn structure, the sulfur donor atoms are staggered with respect to three of the arene C−C bonds.

Several other structures of transition metal complexes containing the $(\eta^6\text{-}C_6H_5)BPh_3^-$ ligand have been reported,[40] and both planar and distorted η^6-coordinated phenyl rings have been observed. The most common distortion from planarity involves displacement of the *ipso* and *para* carbon atoms from the mean plane through the ring, which can be either towards or away from the metal atom.[40] In $[(Me_3tacn)Os\{(\eta^6\text{-}C_6H_5)BPh_3\}]^+$ the C(10) (*ipso*) and C(13) (*para*) carbon atoms are displaced from the mean plane by 0.051 and 0.041 Å, respectively, away from the osmium atom. As discussed above, the Os−C(10) bond is relatively long (2.365(14) Å) whereas the Os−C(13) bond (2.215(19) Å) is very close to the average Os−C bond length of 2.23 Å.

Acknowledgment. Support of this work by National Institutes of Health Grant GM13638-29 and National Science Foundation Grant CHE-9505379 is gratefully acknowledged.

Supporting Information Available: Tables giving details of crystal data, data collection, structure solution and refinement, atomic coordinates, bond lengths and angles, and equivalent isotropic displacement coefficients and figures showing the BPh_4^- group and a stereoview of the unit cell. (12 pages). Ordering information is given on any current masthead page.

IC951296Q

---

(42) Bell, M. N.; Blake, A. J.; Christie, R. M.; Gould, R. O.; Holder, A. J.; Hyde, T. I.; Schröder, M.; Yellowlees, L. J. *J. Chem. Soc., Dalton Trans.* **1992**, 2977−2986.