tmtacn, tacn, and Triammine Complexes of (η^6-arene)Os^{II}: Syntheses, Characterizations, and Photosubstitution Reactions (tmtacn = 1,4,7-Trimethyl-1,4,7-triazacyclononane; tacn = 1,4,7-Triazacyclononane)

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A series of (η^6-arene)Os^{II} complexes containing the saturated nitrogen donor ligands tmtacn, tacn, and NH$_3$ are prepared and characterized. The electrochemical properties and photochemical reactions of these complexes are studied, and the solid-state structures for [(η^6-p-cymene)Os(tacn)](PF$_6$)$_2$ (**1**) and [(η^6-p-cymene)Os(tmtacn)](PF$_6$)$_2$ (**2**) are determined. Single-crystal X-ray data: **1**, orthorhombic, space group $Pbca$-D_{2h}^{15} (No. 61), with $a = 14.716(3)$ Å, $b = 17.844(3)$ Å, $c = 18.350(4)$ Å, $V = 4819(2)$ Å^3, and $Z = 8$; **2**, monoclinic, space group $C2$-C_2^3 (No. 5), with $a = 17.322(4)$ Å, $b = 10.481(3)$ Å, $c = 15.049(4)$ Å, $\beta = 98.72°$, $V = 2701(1)$ Å^3, and $Z = 4$.

Introduction

The chemistry of η^6-arene complexes of osmium and ruthenium has advanced significantly during the past 10−15 years.[1] Of recent interest are coordinatively unsaturated metal(0) species for carbon−hydrogen bond activation,[2] dinuclear metal−metal-bonded species,[3] and (arene)metal imides which show novel reactivities.[4] (Arene)metal complexes containing ligands commonly used in traditional coordination chemistry are rare, although the preparation of a limited number of (π-arene)Os^{II} complexes containing oxygen and/or nitrogen σ-donor ligands has been reported.[5] Recently, we observed that reduction of Os-(tacn)Cl$_3$ in acidic aqueous solutions of amino acids bearing aromatic side chains, such as phenylalanine, results in robust complexes where the Os^{II}(tacn) entity is coordinated to the aromatic ring in an η^6 fashion.[6]

The reduction of [Os(NH$_3$)$_4$(CF$_3$SO$_3$)$_2$]$^+$(CF$_3$SO$_3$)$^-$ by Zn/Hg amalgam in the presence of arene ligands such as benzene, naphthalene, and phenol results in the formation of [(η^6-arene)-Os(NH$_3$)$_3$]$^{2+}$.[5] The kinetics of solvent exchange[7] for [(η^6-arene)M(CH$_3$CN)$_3$]$^{2+}$ (M = Ru, Os) and photosubstitution reactions[8] of [(η^6-arene)Ru(NH$_3$)$_3$]$^{2+}$ have been reported. For osmium, little is known about the electrochemical and photochemical properties of its arene complexes.

In the course of our efforts to extend the chemistry of osmium triamines and enhance their potential for use as reagents in metallopeptide chemistry, we decided to investigate a series of η^6-arene complexes with the saturated nitrogen donor ligands NH$_3$, tacn, and tmtacn (tacn = 1,4,7-triazacyclononane; tmtacn = 1,4,7-trimethyl-1,4,7-triazacyclononane). These species bridge the gap between traditional Werner and typical organometallic complexes. While considerable work has been reported on the Fe and Ru complexes of tacn and tmtacn,[9] only three reports on the osmium complexes of these ligands have appeared.[10,11] It was of special interest to learn whether the coordinated arene can be removed to provide a convenient entry to the chemistry of osmium triam(m)ines.

In this contribution we report the systematic syntheses and characterizations of (η^6-arene)Os^{II} complexes (arene = p-cymene, benzene) with NH$_3$, tacn, and tmtacn as supporting ligands, and the photochemical properties of these species (Figure 1).

Experimental Section

Reagents, Solvents, and General Procedures. All operations were conducted in a nitrogen-filled drybox or under an argon atmosphere using standard Schlenk-line techniques unless otherwise noted. A Hanovia 450 W medium-pressure mercury arc lamp was used as the light source for the photolysis reactions. Oxygen-free solutions for

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(1) For a review of (η^6-arene)Os^{II} or -Ru^{II} chemistry, see: Le Bozec, H.; Touchard, D.; Dixneuf, Ph. H. *Adv. Organomet. Chem.* **1989**, *29*, 163.
(2) (a) Werner, H.; Roder, K. *J. Organomet. Chem.* **1985**, *281*, C38. (b) Benneth, M. A.; Weerasuria, A. M. M. *J. Organomet. Chem.* **1990**, *394*, 481. (c) Hung, Y.; Kung, W.-J.; Taube, H. *Inorg. Chem.* **1981**, *20*, 457.
(3) Hoyano, J. K.; Grahan, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 3723.
(4) (a) Michelman, R. I.; Anderson, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 5100. (b) Michelman, R. I.; Bergman, R. G.; Andersen, R. A. *Organometallics* **1993**, *12*, 2741.
(5) Li, X.-W.; Taube, H. *Inorg. Chem.* **1994**, *33*, 3635.
(6) Wang, R.; Taube, H. Unpublished results.
(7) Luginbühl, W.; Zbinden, P.; Pittet, P. A.; Armbruster, T.; Bürgi, H.-B.; Merbach, A. E.; Ludi, A. *Inorg. Chem.* **1991**, *30*, 2350.
(8) Weber, W.; Ford, P. *Inorg. Chem.* **1986**, *25*, 1088.
(9) (a) Chaudhuri, P.; Wieghardt, K. *Prog. Inorg. Chem.* **1987**, *35*, 329. (b) Wieghardt, K.; Herrmam, W.; Köppen, M.; Jibril, I.; Huttner, G. *Naturforsch.* **1984**, *39B*, 1335. (c) Hotzelmann, R.; Wieghardt, K.; Ensling, J.; Romstedt, H.; Gütlich, P.; Bill, E.; Flörke, U.; Haupt, H.-J. *J. Am. Chem. Soc.* **1992**, *114*, 9470. (d) Neubold, P.; Della Vedova, B. S. P. C.; Wieghardt, K.; Nuber, B.; Weiss, J. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 763. (e) Neubold, P.; Della Vedova, B. S. P. C.; Wieghardt, K.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1990**, *29*, 3355. (f) Schneider, R.; Weyhermüller, T.; Wieghardt, K.; Nuber, B. *Inorg. Chem.* **1993**, *32*, 4925.
(10) (a) Schröder, M. *Pure Appl. Chem.* **1988**, *60*, 517. (b) Bell, M. N.; Blake, A. J.; Schröder, M.; Stephenson, T. A. *J. Chem. Soc., Chem. Commun.* **1986**, 471.
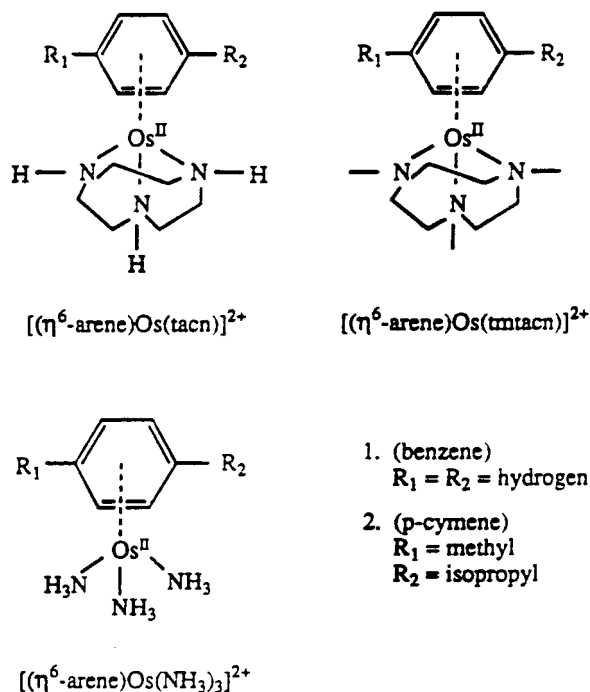(11) Ware, D.; Olmstead, M. M.; Wang, R.; Taube, H. *Inorg. Chem.* **1996**, *35*, 2576.

Figure 1. tmtacn, tacn, and triammine complexes of (η^6-arene)Os^{II}.

photolysis were sealed in J. Young valved cylindrical quartz tubes and subjected to several freeze−pump−thaw cycles prior to photolysis. The photolysis tube containing the reaction mixture was placed 10 cm from the UV lamp and irradiated for the specified time. The following were purchased from commercial sources and used without further purification: tetrabutylammonium hexafluorophosphate (Fluka); (R)-(−)-D-phellandrene (99%, Fluka); thallium triflate (Strem); Na$_2$OsCl$_6$·xH$_2$O, tacn, tmtacn, 1,3-cyclohexadiene, and triflic acid (Aldrich). Acetonitrile (Aldrich, Sureseal) used for electrochemical measurements was purged with argon immediately prior to use. All other solvents were of reagent grade and were used without purification. [(η^6-C$_6$H$_6$)OsCl$_2$]$_2$ and [(η^6-p-cymene)OsCl$_2$]$_2$ were prepared according to literature methods.[12]

Analytical Procedures. ^{1}H NMR spectra were recorded on a 400 MHz Varian VXR-400 spectrometer and referenced internally to tetramethylsilane.

Elemental analyses were performed by Desert Analytical, Co., Tucson, AZ. Samples containing osmium were analyzed using vanadium oxide as a combustion aid.

All electrochemical measurements were made in an argon-purged cell with an EG&G model 173 potentiostat/galvanostat driven by an EG&G model 175 universal programmer. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile. A glassy carbon electrode was used as the working electrode, platinum gauze as the counter electrode, and Ag/AgCl as the reference electrode. All potentials are reported versus the Ag/AgCl couple.

Preparation of [(η^6-p-cymene)Os(tacn)](PF$_6$)$_2$ (1). A degassed solution of tacn (25 mg, 0.2 mmol) in absolute methanol (5 mL) was added to a degassed solution of [(η^6-p-cymene)OsCl$_2$]$_2$ (66 mg, 0.08 mmol) in absolute methanol (5 mL) with stirring. The resulting solution was heated at 60 °C for 15 h, followed by heating at gentle reflux an additional 2 h. After cooling to room temperature, the light yellow solution was filtered in air and the filtrate treated with 0.5 mL of saturated aqueous NaPF$_6$. The volume was reduced to 2 mL in vacuo, the precipitated product was collected by filtration, washed with cold H$_2$O (3 × 4 mL) and then ether (10 mL), and dried in vacuo. Yield: 90%. Anal. Calcd for C$_{16}$H$_{29}$F$_{12}$N$_3$OsP$_2$: C, 25.85; H, 3.93; N, 5.65. Found: C, 25.94; H, 3.76; N, 6.10. ^{1}H NMR (CD$_3$CN): δ 7.08 (br s, 3H, N**H**), 5.85 (d, 2H, p-cymene ring), 5.77 (d, 2H, p-cymene ring), 2.97 (m, 6H, tacn), 2.80 (m, 1H, C**H**), 2.75 (m, 6H, tacn), 2.29 (s, 3H, ArC**H**$_3$), 1.23 (d, 6H, CH(C**H**$_3$)$_2$).

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

Preparation of [(η^6-p-cymene)Os(tmtacn)](PF$_6$)$_2$ (2). A degassed solution of tmtacn (25 mg, 0.15 mmol) in 2-methoxyethanol (1 mL) was added dropwise to a stirred suspension of [(η^6-p-cymene)OsCl$_2$]$_2$ (50 mg, 0.06 mmol) in 2-methoxyethanol (1 mL). The resulting solution was heated in an oil bath at 85 °C under a continuous argon purge for 12 h. The orange solution was cooled to room temperature and then filtered through a plug of glass wool, and the filtrate was added to ether (100 mL). Cooling the mixture to 0 °C yielded a precipitate, which was collected by filtration and washed with ether (2 × 10 mL). The product was dissolved in methanol (10 mL), and saturated aqueous NaPF$_6$ (1 mL) was added. The volume was reduced to 2 mL in vacuo, and the crystallized product was collected by filtration, washed with cold H$_2$O (3 × 2 mL) and then ether (2 mL), and dried in vacuo. Yield: 40%. Anal. Calcd for C$_{19}$H$_{35}$F$_{12}$N$_3$OsP$_2$: C, 29.05; H, 4.49; N, 5.35. Found: C, 29.08; H, 4.36; N, 5.36. ^{1}H NMR (CD$_3$CN): δ 5.93 (dd, 4H, p-cymene ring), 3.58 (s, 9H, NC**H**$_3$), 3.01−2.90 (m, 13H, tmtacn and C**H**(CH$_3$)$_2$), 2.31 (s, 3H, ArC**H**$_3$), 1.25 (d, 6H, CH(C**H**$_3$)$_2$).

Preparation of [(η^6-C$_6$H$_6$)Os(tacn)](PF$_6$)$_2$ (3). Compound **3** was prepared using a modification of the reported procedure[11] that results in a pure product without need for chromatography. A solution of tacn (25 mg, 0.2 mmol) in methanol (1 mL) was added dropwise to a suspension of [(η^6-C$_6$H$_6$)OsCl$_2$]$_2$ (57 mg, 0.08 mmol) in methanol (17 mL). After the mixture was stirred for 5 min, argon-sparged H$_2$O (2 mL) was added, followed by refluxing for 2 h, cooling to room temperature, and stirring for 12 h. The resulting mixture was filtered to remove a brown precipitate, and 1 mL of a saturated solution of NH$_4$PF$_6$ (methanol) was added to the yellow filtrate. After removal of the methanol by rotary evaporation, the colorless crystals were collected by filtration, washed with cold H$_2$O (4 × 2 mL) and then ether (5 mL), and dried in vacuo. Yield: 40%. ^{1}H NMR (CD$_3$CN): δ 7.43 (br s, 3H, N**H**), 5.89 (s, 6H, C$_6$**H**$_6$), 3.00 (m, 6H, tacn), 2.72 (m, 6H, tacn).

Preparation of [(η^6-C$_6$H$_6$)Os(tmtacn)](PF$_6$)$_2$ (4). This material was prepared by the reaction of [(η^6-C$_6$H$_6$)OsCl$_2$]$_2$ with 1.1 equiv of tmtacn, conducted as described for **3**. Yield: 40%. Anal. Calcd for C$_{15}$H$_{27}$F$_6$-OsP$_6$: C, 24.70; H, 3.73; N, 5.76. Found: C, 24.72; H, 3.64; N, 5.61. ^{1}H NMR (CD$_3$CN): δ 6.01 (s, 6H, C$_6$**H**$_6$), 3.63 (s, 9H, NC**H**$_3$), 3.10−2.90 (m, 12H, tacn).

Preparation of [(η^6-p-cymene)Os(NH$_3$)$_3$](PF$_6$)$_2$ (5). Concentrated aqueous NH$_4$OH (1 mL) was added dropwise to a rapidly stirred solution of [(η^6-p-cymene)OsCl$_2$]$_2$ (50 mg, 63 mmol) in methanol (10 mL). The resulting solution was purged with argon for 15 min, brought to 85 °C for 15 min, and then heated to reflux for 15 min. Following the addition of an additional 0.5 mL of NH$_4$OH (concentrated), the solution was heated at 60 °C for 1 h. The resulting faint yellow solution was cooled to room temperature and filtered, and concentrated NH$_4$-PF$_6$ (1.0 mL) was added to the filtrate. The methanol was removed by rotary evaporation, and the resulting white crystalline solid was collected by filtration. The product was washed with H$_2$O (2 mL) and dried in vacuo. Yield: 40%. Anal. Calcd for C$_{10}$H$_{23}$F$_{12}$N$_3$OsP$_2$: C, 18.05; H, 3.48; N, 6.31. ^{1}H NMR (CD$_3$CN): δ 5.94 (d, 2H, p-cymene ring), 5.69 (d, 2H, p-cymene ring), 3.57 (br s, 9H, N**H**$_3$), 2.69 (quint, 1H, C**H**(CH$_3$)$_3$), 2.19 (s, 3H, ArC**H**$_3$), 1.23 (d, 6H, CH(C**H**$_3$)$_3$).

Preparation of [(η^6-C$_6$H$_6$)Os(NH$_3$)$_3$](PF$_6$)$_2$ (6). Compound **6** was prepared using a higher yielding modification of the procedure we previously reported.[2c] Concentrated NH$_4$OH (1.5 mL) was added dropwise to a suspension of [(η^6-C$_6$H$_6$)OsCl$_2$]$_2$ (100 mg, 147 mmol) in methanol (15 mL), followed by purging with argon for 15 min. The reaction mixture was then stirred rapidly at 60 °C for 2 h, cooled to room temperature, and filtered. The filtrate was treated with saturated aqueous NH$_4$PF$_6$ solution (2 mL), and the volume was reduced to 3 mL. The concentrated solution was stored at ~5 °C for 5 h, and the white microcrystalline solid that formed was collected by filtration, washed with cold water (1 mL), and dried in vacuo. Yield: 60%. Anal. Calcd for C$_6$H$_{15}$F$_{12}$N$_3$OsP$_2$: C, 11.83; H, 2.48; N, 6.90. ^{1}H NMR (CD$_3$-CN): δ 5.93 (s, 6H, C$_6$**H**$_6$), 3.71 (br s, 9H, N**H**$_3$).

Preparation of the Tetraphenylborate Salts of the Cations of 1−6. The tetraphenylborate salts were synthesized as described above for the hexafluorophosphate salts with the following modifications. Upon completion of the reflux period, the reaction mixture was evaporated to dryness on a rotary evaporator at 30 °C, the residue was dissolved in a minimum amount of H$_2$O, and saturated aqueous NaBPh$_4$ solution

was added to precipitate the desired product, which was collected by filtration, washed with H_2O, and dried in vacuo.

Preparation of the Triflate Salts of the Cations of 1−6. The triflate salts were obtained by metathesis of the tetraphenylborate salts using thallium triflate (1 M in methanol). After filtration to remove the white TlBPh$_4$, each solution was concentrated on a rotary evaporator and the product was precipitated by the addition of ether. The solid was collected, washed with ether, and dried in vacuo.

Crystal Structure Determinations for [(η^6-*p*-cymene)Os(tacn)]-(PF$_6$)$_2$ (1) and [(η^6-*p*-cymene)Os(tmtacn)](PF$_6$)$_2$ (2). Single crystals of the PF$_6^-$ salt of [(*p*-cymene)Os(1,4,7-triazacyclononane)]$^{2+}$ are, at 20 ± 1 °C, orthorhombic, of space group *Pbca*-D_{2h}^{15} (No. 61), with $a =$ 14.716(3) Å, $b = 17.844(3)$ Å, $c = 18.350(4)$ Å, $V = 4819(2)$ Å^3, and $Z = 8$ [$d_{calcd} = 2.050$ g cm^{-3}; μ_a(Mo Kα) $= 5.53$ mm^{-1}]. Single crystals of the PF$_6^-$ salt of [((CH$_3$)$_2$CHC$_6$H$_4$CH$_3$)Os(1,4,7-trimethyl-1,4,7-triazacyclononane)]$^{2+}$ are, at 20 ± 1 °C, monoclinic, of space group *C*2-C_2^3 (No. 5), with $a = 17.322(4)$ Å, $b = 10.481(3)$ Å, $c = 15.049(4)$ Å, $\beta = 98.72°$, $V = 2701(1)$ Å^3, and $Z = 4$ [$d_{calcd} = 1.932$ g cm^{-3}; μ_a(Mo Kα) $= 4.94$ mm^{-1}]. Totals of 3307 (1) and 3089 (2) independent absorption-corrected reflections having 2θ (Mo Kα) $< 45.8°$ (1) and 55.0° (2) [the equivalent of 0.60 (1) and 1.00 (2) limiting Cu Kα spheres] were collected on a computer-controlled Nicolet autodiffractometer using ω scans and graphite-monochromated Mo Kα radiation. Both structures were solved using "heavy-atom" Patterson techniques with the Siemens SHELXTL-PC software package. The resulting structural parameters were refined to convergence [R1 (unweighted, based of F) $= 0.034$ (1) and 0.044 (2) for 1368 (1) and 2340 (2) independent absorption-corrected reflections having 2θ(Mo Kα) $< 45.8°$ (1) and 55.0° (2) and $I > 3\sigma(I)$] using counter-weighted full-matrix least-squares techniques and structural models which incorporated anisotropic thermal parameters for all full-occupancy non-hydrogen atoms. Isotropic thermal parameters were used for four disordered (minor occupancy) fluorine atoms in 1.

The first PF$_6^-$ anion in the salt of 1 is disordered with two preferred nonstatistical orientations about the linear F$_{11}$−P$_1$−F$_{16}$ linkage in the lattice. The major orientation is occupied 77% of the time and the minor is occupied 23% of the time. The four disordered fluorines are specified as F$_{12}$, F$_{13}$, F$_{14}$, and F$_{15}$ in the major orientation and as F$_{12'}$, F$_{13'}$, F$_{14'}$, and F$_{15'}$ in the minor orientation.

The structure of [(η^6-*p*-cymene)Os(tmtacn)](PF$_6$)$_2$ (2) (Figure 2) is sterically crowded as compared with that of the nonmethylated congener, Figure 3. The addition of the three methyl groups completely blocks the equatorial girdle sterically, and it drastically reduces the photolability of the coordinated arene; *vide infra*. We propose that this steric bulk is responsible for some of the differences in reactivity observed between the tacn and tmtacn derivatives.
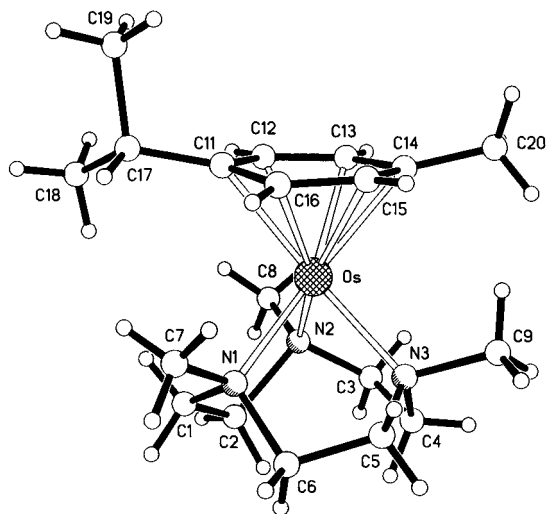

Figure 2. Perspective drawing of [(η^6-*p*-cymene)Os(tmtacn)](PF$_6$)$_2$ (2) in the solid state.
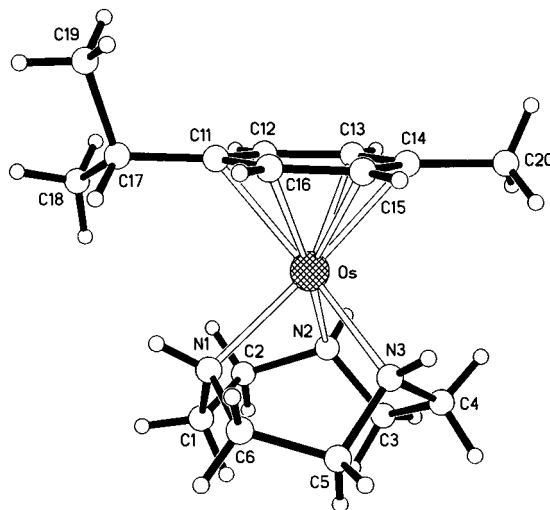
Figure 3. Perspective drawing of [(η^6-*p*-cymene)Os(tacn)](PF$_6$)$_2$ (1) in the solid state.
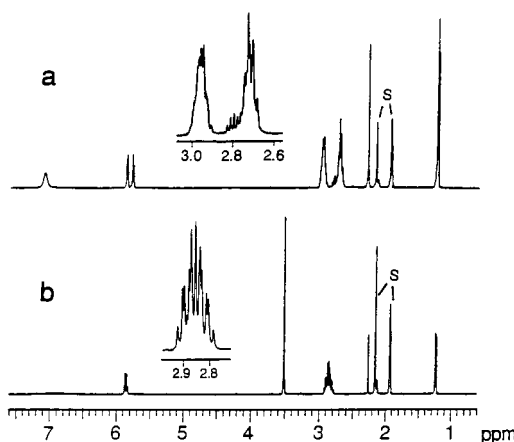
Figure 4. ^{1}H NMR spectra (CD$_3$CN, 400 MHz) for (a) [(η^6-*p*-cymene)-Os(tacn)](PF$_6$)$_2$ and (b) [(η^6-*p*-cymene)Os(tmtacn)](PF$_6$)$_2$.

Results and Discussion

Syntheses. The first preparation of [(η^6-C$_6$H$_6$)Os(NH$_3$)$_3$]$^{2+}$ was performed in our laboratory by the reaction of [(η^6-arene)-Os(L)$_n$]$^{2+}$ with aqueous ammonia.[2c] We extended this method to the preparation of complexes of the general formula [(η^6-arene)Os(L)$_n$]$^{2+}$ where L represents a nitrogen donor, using a modification of this procedure,[5] which results in improved yield and purity. The optimal reaction temperature was found to be between 50 and 60 °C, with the total reaction time being no more than 3 h. Higher temperatures or longer reaction times resulted in intractable dark precipitates. A similar procedure was used for synthesizing [(η^6-*p*-cymene)Os(NH$_3$)$_3$]$^{2+}$ (cation of 5) from [(η^6-*p*-cymene)OsCl$_2$]$_2$ as the starting material. Reaction of [(η^6-*p*-cymene)OsCl$_2$]$_2$ that was prepared according to the method reported by Arthur and Stephenson[12] with aqueous ammonia resulted in a clean conversion to [(η^6-*p*-cymene)Os-(NH$_3$)$_3$]$^{2+}$ in good yield. By contrast, when [(η^6-*p*-cymene)-OsCl$_2$]$_2$ prepared according to the procedure of Cabeza and Maitlis[14] was treated with aqueous ammonia under identical conditions, the cation of 5 could not be detected. The isolated product displayed a clean ^{1}H NMR spectrum in CD$_3$CN, but

(13) Freedman, D. A.; Magneson, D. J.; Mann, K. R. *Inorg. Chem.* **1995**, *34*, 2617.
(14) Cabeza, X. A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1985**, 5473.

Table 1. ^{1}H NMR (400 MHz) Data for [(η^6-*p*-cymene)Os(tacn)](Otf)$_2$ and [(η^6-C$_6$H$_6$)Os(tacn)](Otf)$_2$

compound	solvent	chemical shift,[a] (ppm)				
		tacn		arene		
		NH	CH$_2$CH$_2$	*i*-Pr	CH$_3$	ring
[(η^6-*p*-cymene)Os(tacn)](Otf)$_2$	CD$_3$CN	7.30 (s)	2.75−3.05 (m)	1.23 (d, 6H)	2.29 (s)	5.88 (d, 2H)
			2.65−2.75 (m)	2.85 (m, 1H)		5.79 (d, 2H)
	py-*d*$_5$	9.33 (s)	3.28−3.34 (m)	1.17 (d, 6H)	2.40 (s)	6.21 (d, 2H)
			3.05−3.20 (m)	3.05 (m, 1H)		6.13 (d, 2H)
	acetone-*d*$_6$	8.00 (s)	3.15−3.30 (m)	1.21 (d, 6H)	2.36 (s)	6.08 (d, 2H)
			2.90−3.15 (m)	2.95 (m, 1H)		5.96 (d, 2H)
	CD$_3$OD	8.28 (s)	2.95−2.30 (m)	1.29 (d, 6H)	2.37 (s)	5.90 (d, 2H)
			2.80−2.95 (m)	2.90 (h, 1H)		5.80 (d, 2H)
	D$_2$O	7.94 (s)	2.75−2.85 (m)	1.04 (d, 6H)	2.11 (s)	5.69 (d, 2H)
			2.55−2.78 (m)	2.60 (h, 1H)		5.59 (d, 2H)
[(η^6-*p*-cymene)Os(tacn)](Otf)$_2$	CD$_3$CN	7.59 (s)	2.95−3.05 (m)			5.91 (s, 6H)
			2.65−2.80 (m)			
	py-*d*$_5$	10.50 (s)	3.40−3.60 (m)			6.07 (s, 6H)
			3.25−3.40 (m)			
	acetone-*d*$_6$	8.45 (s)	3.15−3.35 (m)			6.06 (s, 6H)
			2.95−3.05 (m)			
	CD$_3$OD	8.83 (s)	3.00−3.10 (m)			5.71 (s, 6H)
			2.85−2.95 (m)			
	D$_2$O	8.49 (s)	2.75−2.95 (m)			5.72 (s, 6H)
			2.60−2.75 (m)			

[a] m = multiplet; d = doublet; s = singlet; h = hidden.

no coordinated NH$_3$ was observed, and the ring protons of the coordinated *p*-cymene ring were observed as a sharp singlet at δ 6.94 (both the starting material and product exhibited two doublets in same solvent). In our hands, the procedure described by Cabeza and Maitlis failed to produce the desired intermediate.

We have also followed up on the report[11,12] that while refluxing a solution of [(η^6-arene)Os^{II}Cl$_2$]$_2$ and tacn in methanol leads to the formation of [(η^6-arene)Os^{II}(tacn)]$^{2-}$, this procedure fails when the procedure is applied to tmtacn,[12] a somewhat unexpected result because the methylated derivative is expected to be the stronger base. In examining the reaction with tmtacn, we found that refluxing [(η^6-C$_6$H$_6$)OsCl$_2$]$_2$ with tmtacn in methanol for 15 h does indeed result in binding of the tmtacn ligand to the (η^6-C$_6$H$_6$)Os^{II} moiety. The ^{1}H NMR spectrum of the isolated product suggests that tmtacn is attached to the Os^{II} center in an η^2 fashion, the sixth coordination site being occupied by methanol. The product, [(η^6-C$_6$H$_6$)Os(η^2-tmtacn)(CH$_3$OH)]$^{2+}$, decomposes in the presence of H$_2$O, resulting in a dark precipitate. This is in accord with the observation that refluxing [(η^6-(arene)OsCl$_2$]$_2$ complexes with tmtacn in 10:1 methanol/H$_2$O results in intractable dark brown mixtures. We infer that because tmtacn is a stronger base than tacn, it facilitates the oxidation of Os^{II}, the Os^{III} product decomposing in the presence of H$_2$O. Steric hindrance by the N-bound methyl groups may also play a role in the outcome. Complete ligation of tmtacn to (η^6-arene)Os^{II} was achieved by using higher-boiling solvents such as 2-methoxyethanol and elevated reaction temperatures.

^{1}H NMR Spectroscopy. The methylene protons of free tacn, in CD$_3$CN, appear as a singlet at δ 2.36. Upon ligation, the NH protons of the tacn ligand appear as a broad singlet at δ 7.08 and 7.43 for **1** and **3** respectively; see Figure 4a. This indicates that the Os^{II} center is more electron rich in (η^6-*p*-cymene)Os^{II} than in (η^6-C$_6$H$_6$)Os^{II}. This is caused by the weaker π-accepting and stronger π-donating capability of *p*-cymene compared to benzene. For [(η^6-*p*-cymene)Os(tacn)](PF$_6$)$_2$, the methylene proton resonances of the tacn ligand split into two sets of complicated multiplets, as observed earlier for [(η^6-C$_6$H$_6$)Os-(tacn)]$^{2+}$.[10,11] The splitting is attributed to the chemically different environments for the endo and exo protons. No significant differences are found for the arene resonances of

[(η^6-*p*-cymene)Os(tacn)]$^{2+}$ compared to the ^{1}H NMR spectrum of [(η^6-*p*-cymene)OsCl$_2$]$_2$ in CD$_3$CN. The ^{1}H NMR spectra of [(η^6-*p*-cymene)Os(tacn)](OTf)$_2$ and [(η^6-C$_6$H$_6$)Os(tacn)](OTf)$_2$ were recorded in a variety of solvents (see Table 1). In all the solvents examined, the NH proton resonances of coordinated the tacn for [(η^6-*p*-cymene)Os(tacn)]$^{2+}$ lie upfield of those for [(η^6-C$_6$H$_6$)Os(tacn)]$^{2+}$. Also evident is that the coupling patterns of the methylene proton resonances are insensitive to the nature of the solvents, unlike those of their tmtacn analogues, [(η^6-arene)Os(tmtacn)]$^{2+}$ (vide infra).

The NH protons of the tacn ligand in [(η^6-*p*-cymene)Os-(tacn)]$^{2+}$ do not undergo rapid H/D exchange in acetone-*d*$_6$, or even in protic solvents. In D$_2$O or methanol-*d*$_4$, no detectable H/D exchange was detected even after 24 h. Catalytic H/D exchange does occur in certain cases, however. In D$_2$O, with D-phenylalanine (D-phe) present, H/D exchange of the NH protons was complete within several minutes. It is difficult to see how protons alone might catalyze the exchange, and we infer that a special property of −COOH, which can act as both a proton donor and a proton acceptor, renders it more effective than protons alone. In acetone-*d*$_6$ containing pyridine (1.0 × 10^{-3} M), the signal for the NH protons of the tacn ligand in [(η^6-*p*-cymene)Os(tacn)]$^{2+}$ disappear in about 10 h, suggesting that deprotonation provides a path for proton exchange to occur. Since the rest of the tacn resonances (C−H) remain unchanged, the extent of deprotonation is small.

The ^{1}H NMR spectrum of [(η^6-*p*-cymene)Os(tmtacn)](PF$_6$)$_2$ in CD$_3$CN is shown in Figure 2b. A notable feature of the spectrum is the inversion of the positions of the methyl and methylene proton resonances of the coordinated tmtacn as compared to that of the free ligand. (The methyl protons appear at δ 2.43 and the methylene protons at δ 2.70.)

The methyl proton resonances of coordinated tmtacn are shifted downfield by about 1 ppm, indicating significant electron donation by tmtacn to the Os^{II} center, its d electron density having been reduced due to π back-bonding into the π* orbitals of the *p*-cymene. The methylene protons are observed as a multiplet, with the endo and exo protons virtually indistinguishable. For [(η^6-C$_6$H$_6$)Os(tmtacn)]$^{2+}$, the methyl proton resonances also appear at lower field (3.63 ppm) than the methylene proton

Table 2. ^{1}H NMR Data (400 MHz) for [(η^6-*p*-cymene)Os(tmtacn)](Otf)$_2$ and [(η^6-C$_6$H$_6$)Os(tmtacn)](Otf)$_2$

| | | chemical shift,[a] (ppm) | | | | |
| | | tmtacn | | arene | | |
compound	solvent	CH$_3$	CH$_2$CH$_2$	*i*-Pr	CH$_3$	ring
[(η^6-*p*-cymene)Os(tmtacn)](Otf)$_2$	CD$_3$CN	3.60 (s)	2.90−3.04 (m)	1.25 (d, 6H) 3.00 (h, 1H)	2.32 (s)	5.93 (m, 4H)
	acetone-d_6	3.89 (s)	3.31 (s)	1.36 (d, 6H) 3.15 (m, 1H)	2.52 (s)	6.40 (d, 2H) 6.34 (d, 2H)
	CD$_3$OD	3.73 (s)	3.12 (m)	1.33 (d, 6H) 3.00 (m, 1H)	2.41 (s)	6.17 (d, 2H) 6.12 (d, 2H)
	D$_2$O	3.49 (s)	2.90 (m)	1.10 (d, 6H)	2.15 (s) 2.75 (h, 1H)	5.95 (d, 2H) 5.85 (d, 2H)
[(η^6-*p*-C$_6$H$_5$)Os(tmtacn)](Otf)$_2$	CD$_3$CN	3.63 (s)	2.90−3.03 (m) 3.03−3.12 (m)			6.01 (s, 6H)
	CD$_3$OD	3.79 (s)	3.12−3.30 (m)			6.22 (s, 6H)
	DMSO	3.63 (s)	3.05 (m)			6.14 (s, 6H)

[a] m = multiplet; d = doublet; s = singlet; h = hidden.
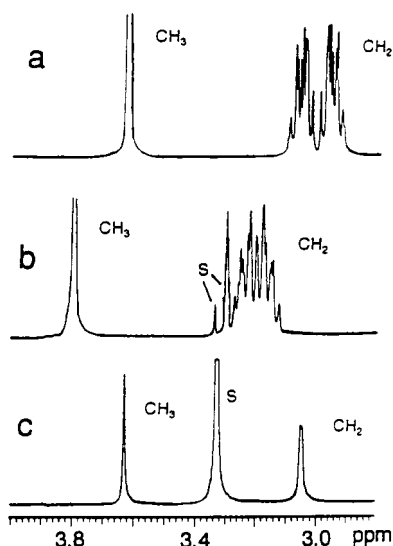
Figure 5. ^{1}H NMR spectra (400 MHz) for [(η^6-C$_6$H$_6$)Os(tmtacn)](Otf)$_2$ in (a) CD$_3$CN, (b) CD$_3$OD, and (c) DMSO-d_6.

resonances (2.90−3.10 ppm). The endo and exo proton resonances of the methylene groups are two closely spaced sets of multiplets.

The coupling of the endo and exo methylene proton resonances of the coordinated tmtacn ligands is strongly solvent dependent. The ^{1}H NMR spectra of [(η^6-C$_6$H$_6$)Os(tmtacn)](Otf)$_2$, recorded in different solvents are shown in Figure 5. In CD$_3$-CN, the methylene groups give rise to two sets of multiplets. In a more polar solvent, CD$_3$OD, only one set of multiplets is observed. In an even more polar solvent, DMSO-d_6, the methylene protons appear as two very closely spaced singlets, and the coupling between endo and exo proton resonances disappears. A similar solvent dependence is observed for the methylene protons of coordinated tmtacn in **2**. In CD$_3$CN, the methylene protons appear as a set of multiplets. In acetone-d_6, CD$_3$OD, and D$_2$O, only a sharp singlet is observed (Table 2), behavior which is not observed for the analogous complexes [(η^6-arene)Os(tacn)]$^{2+}$.

For [(η^6-*p*-cymene)Os(NH$_3$)$_3$](PF$_6$)$_2$ and [(η^6-C$_6$H$_6$)Os(NH$_3$)$_3$]-(PF$_6$)$_2$, the NH$_3$ protons appear as a broad singlet. The NH$_3$ proton resonances of [(η^6-*p*-cymene)Os(NH$_3$)$_3$]$^{2+}$ appear at higher field (3.60 ppm) compared to those of [(η^6-C$_6$H$_6$)Os-(NH$_3$)$_3$]$^{2+}$ (3.71 ppm). This is again a reflection of the difference in the electron density at the Os^{II} centers and is consistent with the results obtained for the analogous tacn-containing complexes.

Table 3. Electrochemical Data[a]

compound	E_{oxidn}[b]	E_{redn}[b]
1	1.79	0.55,[d] −2.20
2	1.75[c]	−1.64
3	1.82	0.50,[d] −2.08
4	2.00	−1.72
5	1.65	0.40,[d] −1.94, −2.18
6	1.70	0.33,[d] −1.99
p-cymene	2.20	not detected
benzene	>2.40	not detected
tacn	0.95	−1.80[d]
tmtacn	0.70, 1.56	1.20, −1.70[d]

[a] Measured in 0.1 M TBAP/CH$_3$CN. Potentials are in volts vs the Ag/AgCl couple. The sweep rate for all experiments was 100 mV/s. [b] All potentials reported are for irreversible processes and indicate the peak potential at which the process occurred. [c] This process was reversible, and the reported value is $E_{1/2}$. [d] Present only if the oxidative scan was carried out first.

Electrochemistry. The electrochemical data for the (η^6-arene)Os^{II} complexes of tacn, tmtacn, and NH$_3$ and for the free ligands, in CH$_3$CN as solvent, are listed in Table 3. Irreversible oxidation was observed for free *p*-cymene and benzene at 2.2 and 2.4 V, respectively, but no reduction was detected at potentials as low as −2.4 V. *p*-Cymene is slightly easier to oxidize than benzene, an effect attributed to the electron-donating groups (methyl and isopropyl) on the aromatic ring. Free tacn is oxidized at 0.95 V and reduced at −1.8 V. For tmtacn, two successive oxidations were observed at 0.7 and 1.56 V and reductions were observed at −1.2 and −1.7 V. Because reductive current was only observed when the oxidative scans were carried out first, they must be attributed to an oxidation product of tmtacn.

Oxidations of **1**−**4** occur at peak potentials of 1.79, 1.79, 1.82, and 2.00 V, respectively. Direct comparison of the π^* energy level for the benzene and *p*-cymene ligands cannot be made from electrochemical data because no reduction peaks are observed for the free ligands. However, the oxidation potentials suggest that *p*-cymene is more electron rich than benzene. It is reasonable to suppose that benzene is a slightly better "π-acid" than *p*-cymene, in harmony with compounds **3** and **4** being somewhat more difficult to oxidize than their *p*-cymene analogues **1** and **2**. This is also consistent with the argument made in the interpretation of the ^{1}H NMR spectra, where the resonances of the NH protons of the tacn ligand appear at lower field for [(η^6-C$_6$H$_6$)Os(tacn)]$^{2+}$ than for [(η^6-*p*-cymene)Os-(tacn)]$^{2+}$. What is more difficult to understand is why **3** is easier to oxidize than **4**. In the simplest view, tmtacn as a stronger base than tacn would be expected to stabilize Os^{III} relative to
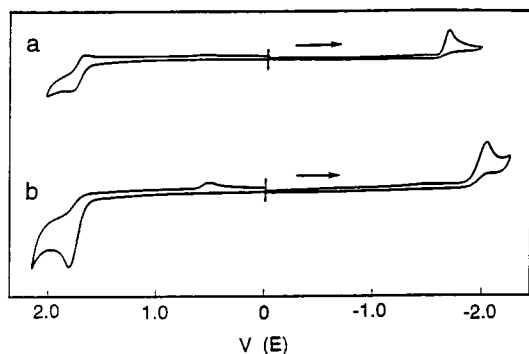
Figure 6. Cyclic voltammograms for (a) [(η^6-*p*-cymene)Os(tmtacn)]-(PF$_6$)$_2$ and (b) [(η^6-C$_6$H$_6$)Os(tacn)](PF$_6$)$_2$ (scan rate 200 mV/s; potential vs Ag/AgCl).

Os^{II}. However, electrochemical data tend to suggest that tacn is in fact a better σ donor. That base strength, as measured by proton affinity, is not the only factor affecting the oxidation potentials becomes evident when the oxidation potentials for [(η^6-arene)Os(NH$_3$)$_3$]$^{2+}$ are considered. The peak potentials, 1.65 V for **5** and 1.70 V for **6**, are the lowest values in the series examined (Table 3). Other factors must be considered: the chelating effect of the macrocyclic triamine ligands may stabilize Os^{II} slightly better than in the case of monodentate NH$_3$ ligands, and the steric effect may also adjust the σ-donating capability of the ligands.

All the oxidation processes are irreversible up to scan rate 500 mV/s except for the case of **2**, which shows a quasi-reversible oxidation peak (Figure 6a). This suggests that (tmtacn)Os^{III}(*p*-cymene) remains intact on the time scale of cyclic voltammetry (100 mV/s).

For [(η^6-arene)Os(tacn)]$^{2+}$, in **1** and **3**, and [(η^6-arene)Os-(NH$_3$)$_3$]$^{2+}$, in **5** and **6**, a small reductive peak is observed in the range 0.33−0.55 V (see Table 3). An example is depicted in the cyclic voltammogram of **3** (Figure 6b). This peak is absent if the oxidative scan is reversed at a potential too low for oxidation of the Os^{II} center to occur, and the peak is attributed to the reduction of the oxidation products. After oxidation of Os^{II} to Os^{III}, a number of processes may occur, such as arene dissociation, solvent substitution, and oxidation of Os^{III} to Os^{IV} by trace O$_2$ in the electrochemical cell. In the case of [(η^6-arene)Os(tmtacn)]$^{2+}$, in **2** and **4**, however, no peaks were detected corresponding to reduction of such products.

A reduction peak (Figure 6) is observed for each of **1**−**4** and **6** at potentials more negative than −1.6 V, and for **5**, two closely spaced reductive peaks are observed. In all cases, they are independent of the oxidative scan, and successive oxidative scans up to +2.2 V did not change either the shape or the magnitude of the reductive peaks. The irreversibility of the waves shows that, in each case, a chemical change takes place upon the addition of an electron, and because the signal remains irreversible even at a scan rate of 500 mV/s, the change is rapid. It is remarkable that no oxidation signals assignable to the products of the reaction are observed. A possibility is that the immediate product of 1 e$^-$ reduction reacts with the solvent to yield a species that is not oxidizable in the potential range applied. To conform to our observations, such a product cannot be reducible in the same potential range. High reactivity of an intermediate of this kind requires that the arene be lost. Oxidative addition of solvent to such a species would yield an Os^{III} species with a carbon fragment attached which conceivably would fulfill the experimental requirements. The second reduction wave observed for **5** may correspond to a reduction of this kind.

Table 4. UV−vis Absorption Data^a

compound	λ_{max}, nm (ϵ, cm^{-1} M^{-1})
1	230 (1190), 252 (848), 304 (300)
2	230 (1090), 254 (870), 304 (348)
3	<198, 246 (969), 316 (440)
4	<198, 274 (862), 322 (545)
5	228 (898), 252 (735), 304 (378)
6	226 (1085), 252 (929), 302 (423)

^{a} Measured in acetonitrile.

Electronic Spectra. The UV−vis absorption data are listed in Table 4. The UV−vis absorption spectra recorded in acetonitrile for each of the η^6-arene complexes studied exhibit a band with an absorption maximum between 302 and 322 nm (ϵ = 300−545 cm^{-1} M^{-1}). This band is assigned to a metal-centered ligand field transition. The energy of this band is sensitive to the nature of the ligands and insensitive to solvents. For both arene complexes, the energies follow the trend (NH$_3$)$_3$ $\approx$ tacn > tmtacn. As in the case of the electrochemical data, this energy order is contrary to that expected on the basis of relative basicity, which would lead to the expectation that 10*Dq* would be larger for the ligand having the greater proton affinity.

A second band (shoulder) is found between 252 and 274 nm, and in the case of [(η^6-C$_6$H$_6$)Os(NH$_3$)$_3$]$^{2+}$, this band has been assigned as a metal-to-ligand charge transfer (MLCT) transition, d(M) $\rightarrow$ π*(arene).[2c] The energies follow the same order as their d−d transitions, (NH$_3$)$_3$ $\geq$ tacn > tmtacn, as is expected for transitions from the πd level to a common π* state of the ligand. The transition energies for the *p*-cymene complexes are higher than that for those of benzene, in line with the expectation that adding electron-donating substituents to the aromatic ring will raise the π* level.

The highest energy band (also a shoulder), with absorption maxima between 198 and 226 nm, is assigned as the arene π $\rightarrow$ π* transition.

Photochemistry. Electrochemical data obtained from cyclic voltammetry indicate all of the above arene complexes containing macrocyclic ligands are very resistant to oxidation. The compounds also show remarkable thermal stability. For instance, heating [(η^6-*p*-cymene)Os(tmtacn)]$^{2+}$ in neat triflic acid (CF$_3$-SO$_3$H) at 130 °C for 7 days results in no appreciable changes.

It is of interest for preparative purposes to be able to replace the arene ligand in the triamine complexes. Due to the high oxidation potentials observed for this class of compounds, removal of the ligated arene by oxidation of Os(II) to Os(III) is not an attractive approach. Instead, we turned to photochemistry for an alternative method. It had been reported that photolysis of [(η^6-C$_6$H$_6$)OsCl$_2$] in D$_2$O/DCl leads to labilization of the coordinated benzene.[2c] Photochemical cleavage of benzene from [(Cp)Os(η^6-C$_6$H$_6$)]$^+$ by UV irradiation in acetonitrile was also reported with the photolysis product [(Cp)Os(CH$_3$CN)$_3$]$^+$, displaying useful reactivity patterns with olefins as well as arenes.[15] More recently, similar success in the photolysis of arene complexes of the general formula [(η^6-C$_6$H$_6$)Os(NCCH$_3$)$_{3-x}$-Cl$_x$]$^{(2-x)+}$ was reported.[13]

Photolysis of [(η^6-arene)Os(tacn)]$^{2+}$. Photolysis of [(η^6-*p*-cymene)Os(tacn)](PF$_6$)$_2$ in acetonitrile results in the formation of [(CH$_3$CN)$_3$Os(tacn)](PF$_6$)$_2$. Prolonged photolysis leads to products which exhibit no resonances in the ^{1}H NMR spectra and are believed to be photooxidized (Os^{III}) species. No less than three compounds were isolated by chromatography on

(15) Freedman, D. A.; Matachek, J. R.; Mann, K. *Inorg. Chem.* **1993**, *32*, 1078.

neutral alumina. No attempt was made to characterize the resulting complexes.

Clean conversion of $[(\eta^6\text{-}p\text{-cymene})Os(tacn)](PF_6)_2$ to the tris-(acetonitrile) complex was achieved by adding biphenyl (5×10^{-2} M) to the photolysis solution. (Biphenyl has an intense absorption near 254 nm.) The product $[(CH_3CN)_3Os(tacn)](PF_6)_2$ can be easily isolated from the photolysis solution in yields exceeding 90%. The coordinated acetonitrile ligands appear as a singlet at δ 2.69, and the signals corresponding to the methylene groups of the coordinated tacn ligand show little change as compared to those of its π-arene precursor. The amine protons of the tacn ligand yield a broad singlet at δ 5.65 which is shifted upfield ~2.5 ppm from the resonances of corresponding protons in $[(\eta^6\text{-}p\text{-cymene})Os(tacn)](PF_6)_2$. Exchange of solvent CH$_3$CN with coordinated CH$_3$CN was not observed, in contrast to the behavior of $[(tmtacn)Ru(CH_3CN)_3]^{2+}$ and $[Ru(CH_3CN)_6]^{2+}$.[9e] We attribute this to the stronger π back-bonding of the Os^{II} center.

Though $[(CH_3CN)_3Os(tacn)](PF_6)_2$ has a relatively low redox potential ($E_{1/2} = 0.59$ V, in acetonitrile), it is air stable. Oxidation of $[(CH_3CN)_3Os^{III}(tacn)]^{3+}$ was not observed on scanning up to 2.3 V, nor was reduction of the complex observed, down to -2.3 V.

Photolysis of $[(\eta^6\text{-}C_6H_6)Os(tacn)](PF_6)_2$ in acetonitrile in the presence of biphenyl also cleanly yields $[(CH_3CN)_3Os(tacn)](PF_6)_2$. The rate for this reaction is found to be similar to that for the photolysis of $[(\eta^6\text{-}p\text{-cymene})Os(tacn)](PF_6)_2$.

Photolysis of $[(\eta^6\text{-arene})Os(tmtacn)]^{2+}$. Because the electronic spectra and molecular extinction coefficients for $[(\eta^6\text{-arene})Os(tacn)]^{2+}$ and $[(\eta^6\text{-arene})Os(tmtacn)]^{2+}$ complexes are very similar, similar photochemical behaviors were expected. To our surprise, photolysis of $[(\eta^6\text{-}p\text{-cymene})Os(tmtacn)]^{2+}$ in acetonitrile for 2 days, with or without biphenyl, showed no detectable free p-cymene. For $[(\eta^6\text{-}C_6H_6)Os(tmtacn)]^{2+}$, photosubstitution does occur, but the reaction rate is very slow. Prolonged photolysis (12 h) leads to about 10% conversion, as calculated from the integration of the free and coordinated benzene resonances in ^{1}H NMR spectra.

We suggest two possibilities to account for the difference in photoreactivities between the tacn- and tmtacn-containing osmium π-arene complexes. First, although the ground-state electronic transitions for the first two types of compounds are almost identical, the excited-state lifetimes could differ. It is possible that the excited-state lifetime of the tmtacn-containing complexes are too short to allow photolabilization of the coordinated arene to occur. Since none of the compounds studied here are emissive at room temperature, determination of the excited-state lifetimes is not feasible. Also, it is expected that the steric bulk of tmtacn will reduce the reactivity of its derivative by hampering ring slippage and the approach of the entering nucleophile CH$_3$CN. In $[(\eta^6\text{-}C_6H_6)Os(tmtacn)](PF_6)_2$, where the Os^{II} center is slightly less crowded, photosubstitution of coordinated benzene does proceed, but kinetically the process is very slow.

Photolysis of $[(\eta^6\text{-arene})Os(NH_3)_3]^{2+}$. If steric effects play an important role, we would expect the photolysis of $[(\eta^6\text{-}C_6H_6)Os(NH_3)_3](PF_6)_2$ and $[(\eta^6\text{-}p\text{-cymene})Os(NH_3)_3](PF_6)_2$ to be more facile than that of their tacn analogues. The photolysis of the analogous Ru^{II} compounds $[(\eta^6\text{-}C_6H_6)Ru(NH_3)_3](PF_6)_2$ and $[(\eta^6\text{-}p\text{-cymene})Ru(NH_3)_3](PF_6)_2$ in aqueous solution has been shown to result in dissociation of the arene but not of the ammine.[8] In the present case, irradiation of both $[(\eta^6\text{-}C_6H_6)Os(NH_3)_3](PF_6)_2$ and $[(\eta^6\text{-}p\text{-cymene})Os(NH_3)_3](PF_6)_2$ in acetonitrile, in the presence of biphenyl, resulted in $[(CH_3CN)_3Os(NH_3)_3](PF_6)_2$ as the
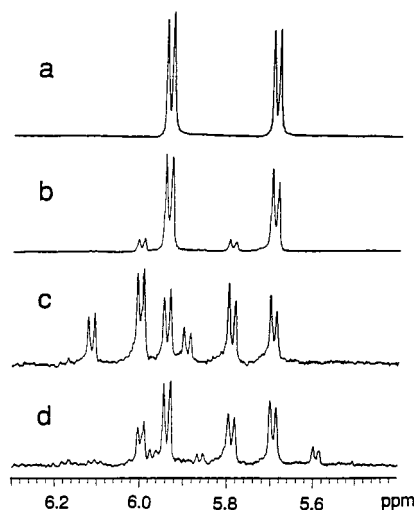

Figure 7. Photolysis of $[(\eta^6\text{-}p\text{-cymene})Os(NH_3)_3](PF_6)_2$ in CD$_3$CN monitored by ^{1}H NMR spectroscopy (For clarity, only the aromatic region for coordinated p-cymene is shown.) Conditions: (a) before photolysis; (b) after photolysis for 2 h; (c) after photolysis for 3 h and 10 min; (d) same as (c) except for storage in the dark for 2 h after photolysis.

final product (yield >95% from ^{1}H NMR). The photosubstitution rates for **5** and **6** were similar and were about a factor of 3 faster than that observed for $[(\eta^6\text{-}p\text{-cymene})Os(tacn)](PF_6)_2$.

Only during the photolysis of $[(\eta^6\text{-}p\text{-cymene})Os(NH_3)_3](PF_6)_2$ were intermediates observed by ^{1}H NMR spectroscopy. After photolysis in acetonitrile-d_3 for 2 h, apart from the coordinated and free p-cymene peaks, another set of small peaks, adjacent to those of η^6-coordinated p-cymene, was detected (Figure 7a,b). The new peaks remained unchanged for about 2–3 h, but after longer periods of time, even in the absence of light, they slowly decreased. Continuing photolysis resulted in another set of new p-cymene resonances (Figure 7c). We postulate that the first observed intermediate is $[(\eta^4\text{-}p\text{-cymene})(CH_3CN)Os(NH_3)_3]^{2+}$ while the later observed intermediate is $[(\eta^2\text{-}p\text{-cymene})(CH_3CN)_2Os(NH_3)_3]^{2+}$. The peaks assigned to $[(\eta^2\text{-}p\text{-cymene})(CH_3CN)_2Os(NH_3)_3]^{2+}$ diminished on storing the sample in the dark for several hours, while another set of resonances at higher field appeared, which might be due to isomerization of $[(\eta^2\text{-}p\text{-cymene})(CH_3CN)_2Os(NH_3)_3]^{2+}$ (Figure 7d). The isomeric possibilities include rearrangement of the ligands and migration of the Os^{II} center to an alternative double bond on the p-cymene. In the dark, the intermediate that is postulated as η^4 coordinated seems to survive slightly longer than the others. The thermal instability of the intermediates may result from the competition between the coordinated acetonitrile and the η^2- and η^4-coordinated p-cymene molecules in withdrawing the electron density from the Os^{II} center. An alternative interpretation may be that the observed intermediates result from photoejection of coordinated NH$_3$ from $[(\eta^6\text{-}p\text{-cymene})Os(NH_3)_3]^{2+}$. In other words, the observed intermediates would be $[(\eta^6\text{-}p\text{-cymene})Os(NH_3)_{3-x}(CH_3CN)_x]$ ($x = 1, 2$). However, the η^6-coordinated p-cymene is not expected to be thermally labile, and therefore, the decrease in the intensity of the ^{1}H NMR signals corresponding to the intermediates in the absence of light seems contrary to this assignment. Moreover, no ^{1}H NMR signal corresponding to free NH$_3$ was observed. Due to the small quantities of the intermediates that are present in the photolysis solution and their instability, attempts to isolate such intermediates for further characterization have not yet proven successful. The photostability of the arene complexes of Os^{II} triamines in acetonitrile follows the order $[(\eta^6\text{-arene})Os(tmtacn)]^{2+} \gg [(\eta^6\text{-arene})Os\text{-}$

$(tacn)]^{2+} > [(\eta^6\text{-arene})Os(NH_3)_3]^{2+}$, in line with the suggestion that steric effects play an important role. Even so, the complete absence of photosubstitution reactions for the $[(\eta^6\text{-arene})Os\text{-}(tmtacn)](PF_6)_2$ complexes, is surprising.

Photolysis in Other Solvents. The photolysis of $[(\eta^6\text{-arene})\text{-}Os(tacn)]^{2+}$ and $[(\eta^6\text{-arene})Os(tmtacn)]^{2+}$ was also examined in acetone-d_6, CD_3OD, and pyridine-d_5. In all cases, photocleavage of the Os^{II}−arene bond, if any, was very slow.

In acetone-d_6, photolysis for 25 h resulted in <15% release of benzene from $[(\eta^6\text{-}C_6H_6)Os(tacn)]^{2+}$, with similar results for $[(\eta^6\text{-}p\text{-cymene})Os(tacn)]^{2+}$. The reduced reactivity can be attributed to the fact that acetone is a much weaker π-acid than CH_3CN, so that it cannot induce the formation of the intermediate $[(\eta^4\text{-arene})Os(tacn)(acetone)]^{2+}$. Acetone has a strong absorption in the UV region up to 340 nm, which, if energy transfer is inefficient, will hinder the reaction.

Although pyridine is both a σ-donor and a π-acceptor, photocleavage of the Os^{II}−arene bond in pyridine-d_5 is very slow. Photolysis of $[(\eta^6\text{-}C_6H_6)Os(tacn)](PF_6)_2$ for 48 h leads to only ca. 30% release of benzene. One possibility is that the size of the pyridine prevents effective access to the Os^{II} center. The strong absorption by pyridine (cutoff wavelength 305 nm) may also be a factor. The photolysis product shows a single NH peak at 7.98 ppm. According to the integration of NH and free benzene peaks, the photoconversion is clean. The reaction product has been identified as $[(tacn)Os(py)_3]^{2+}$.

Photolysis of $[(\eta^6\text{-}p\text{-cymene})Os(tacn)](OTf)_2$ in CD_3OD for 20 h results in only a 5% release of p-cymene, while, for the tmtacn analogue, no free arene is detected. In the case of the p-cymene derivatives, the only reagent-related signals observed are for starting material and released ligand, suggesting that the osmium-containing product is paramagnetic. The fact that CH_3-OH, though a good donor ligand and less sterically demanding than pyridine, is less effective in promoting photodissociation suggests that π-acidity of the entering ligand is a factor affecting the efficiency of the exchange.

Summary

A series of $(\eta^6\text{-arene})Os^{II}$ complexes containing the saturated nitrogen donor ligands tmtacn, tacn, and NH_3 have been prepared and characterized. Electrochemical measurements reveal that these compounds are all resistant toward oxidation and reduction. The photosubstitution reactions show a very strong dependence on the steric size of the N-donor ligands. Facile arene dissociation is observed for less sterically hindered complexes in coordinating solvents such as acetonitrile. The photosubstitution reactions can be completely shut off if the $(\eta^6\text{-arene})Os^{II}$ moiety is coordinated to the more sterically demanding ligand tmtacn. These results are relevant to the reactivity studies of the η^6-amino acid complexes of Os^{II} triamines now in progress.

Supporting Information Available: Crystal structure reports, tables of complete atomic coordinates and anisotropic thermal parameters and complete bond lengths and angles for non-hydrogen atoms, and ORTEP plots for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org. Complete structural data, in CIF format, for **1** (CCDC 136719) and **2** (CCDC 136720) have been deposited with the Cambridge Crystallographic Data Centre.

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