

mmol) and methyl iodide (1.0 mL, 2.3 g, 15 mmol) were added. The mixture was heated to reflux for 4 h and the reaction was monitored by HPLC. Additional methyl iodide was added until no starting material remained. Water was added and the solution was extracted with ethyl acetate. The organic layer was washed with brine, dried over $MgSO_4$, and filtered. After the solvent was removed under reduced pressure, the residue was chromatographed on a dry column of silica gel using methylene chloride/methanol (97/3) as solvent. The resulting viscous oil was heated to 35 °C under vacuum (0.05 Torr) for 72 h to remove residual solvent, yielding a viscous oil (3.3 g, 90% yield, mixture of erythro and threo isomers, very hygroscopic). 1H NMR ($CDCl_3$): [a mixture of threo and erythro isomers] δ 2.75 (m, 1 H, CH_2OH), 3.4-3.7 (m, 2 H, CH_2), 3.7 (d, 1 H, $CHOH$), 3.85-3.95 (m, 9 H, OCH_3), 4.0-4.2 (m, 1 H, OCH), 5.0 (m, 1 H, $CHOH$), 6.8-7.2 (m, 7 H, Ar). ^{13}C NMR: [threo isomer] δ 55.7 (OCH_3), 60.9 (CH_2OH), 73.6 (ArCH), 88.7 (HCOAr); [erythro isomer] δ 55.7 (OCH_3), 60.7 (CH_2OH), 72.5 (ArCH), 86.7 (HCOAr). Anal. Calcd for $C_{18}H_{22}O_6$: C, 64.66; H, 6.63. Found: C, 65.19; H, 6.90.

Stoichiometric Oxidation of Lignin Model Compounds with Cobalt(III) Acetate. In a typical procedure, a solution of DMMP (6.8 mg, 0.018 mmol) and cobalt(III) acetate (84.3%, 10.5 mg, 0.037 mmol) in 18 mL of glacial acetic acid was heated to reflux in 20 min with stirring. One hour later, the color turned from greenish black to pink. The solution was cooled to room temperature and veratrole (10.2 mg, 0.074 mmol) was added as an internal standard for HPLC analysis. A 67% selectivity to DMB at 99% conversion of DMMP was obtained. For reactions where cobalt(III) acetate still remained, an aqueous solution of ferrous sulfate was added dropwise until the color of the solution turned from green to pink; then veratrole was added as internal standard.

Regeneration of Co(III) for the Oxidation of DMMP by the Addition of Peracetic Acid. To a solution of DMMP (23.9 mg, 0.072 mmol) and cobalt(II) acetate (3.4 mg 0.019 mmol) in 60 mL of glacial acetic acid with stirring was added peracetic acid (35%, 4.2 μ L, 0.25 mmol). This solution turned from pink to

greenish black. After 2 h, the color turned back to pink and another aliquot of peracetic acid (4.2 μ L) was added. Two more aliquots of peracetic acid were added each time the greenish black color disappeared. Finally the color stayed yellow. Veratrole (42.5 mg, 0.31 mmol) was added as an HPLC internal standard. The mixture was analyzed by HPLC to give 48% selectivity to DMB and 15% to DBA at 90% conversion.

Catalytic Oxidation of Lignin Model Compounds. In a typical procedure, a Pyrex glass liner containing a Teflon-coated magnetic stirring bar, DMMP (8.4 mg, 0.025 mmol), manganese(II) acetate (4.3 mg, 0.025 mmol), cobalt(II) acetate (39.8 mg, 0.23 mmol), and acetaldehyde (14 μ L, 0.25 mmol) in 2.5 mL of 80% acetic acid was placed in a 71-mL Parr Hastalloy C high pressure reaction vessel (Model 4740). The reactor was sealed, purged three times by pressurizing to 320 psi of N_2 and then venting to atmospheric pressure, and then charged with 336 psi of 4% O_2 in N_2 . The reactor was put in a heating block preheated at 170 °C and the reaction mixture stirred for 3 h; at 170 °C, the reactor pressure increased to 500 psi. The reactor was then rapidly cooled to room temperature by placing it in an ice/water bath and the vessel subsequently vented to atmospheric pressure. Veratrole (11.2 mg, 0.081 mmol) was added to the reaction mixture as an HPLC internal standard and the mixture was analyzed to yield DMB (37%), DBA (25%), and guaiacol (2.4%) at 87% conversion.

Registry No. BMPD, 85272-48-6; DHA, 4464-76-0; DMPD, 35863-57-1; DHMA, 113303-19-8; HMMP, 7382-59-4; DMMP, 10535-17-8; DMB, 120-14-9; DBA, 93-07-2; Co(III) acetate, 917-69-1; Mn(II) acetate, 638-38-0; 4- $H_3COC_6H_4CH(OH)CH_2OH$, 13603-63-9; 4- $H_3COC_6H_4CHO$, 123-11-5; 2- $H_3COC_6H_4OH$, 90-05-1; β -hydroxy- α -(2-methoxyphenoxy)-4-hydroxy-3-methoxypropio-phenone, 22317-34-6; lignin, 9005-53-2.

Supplementary Material Available: Table containing the results of the stoichiometric oxidation of lignin model compounds by cobalt(III) acetate (2 pages). Ordering information is given on any current masthead page.

Direct Osmylation of Benzenoid Hydrocarbons. Charge-Transfer Photochemistry of Osmium Tetraoxide

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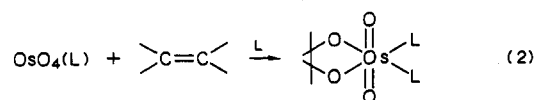
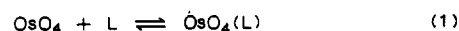
Received August 7, 1987

Benzene and related arenes are well-known to be inert to osmium tetraoxide and are often employed as solvents for alkene osmylations. However, when these mixtures are deliberately exposed even to roomlight, a facile addition of OsO_4 occurs to arenes such as benzene, mesitylene, and hexamethylbenzene to afford 2:1 adducts. This photoactivated osmylation is shown to derive from the charge-transfer (CT) excitation of the electron-donor-acceptor (EDA) complex of OsO_4 with the aromatic donor (ArH). The spectral properties of the EDA complexes vary with the ionization potentials of the arenes in accord with the expectations of Mulliken theory. Indeed the limited magnitudes of the association constants of $K < 1 M^{-1}$ for the formation of $[ArH, OsO_4]$, as measured by the Benesi-Hildebrand procedure, classify these as contact charge transfer in which the photochemical excitation of the CT band leads to the ion pair $[ArH^{+} OsO_4^{-}]$. The collapse of the ion pair to the 1:1 osmylated cycloadduct is discussed, together with the eventual formation of the ternary adduct that is routinely isolated as the pyridine complex with the stoichiometry $(ArH)(OsO_4)_2(py)_4$. The common role of EDA complexes as intermediates in both the CT osmylation of arenes as well as the ubiquitous thermal osmylation of alkenes is considered in the context of a unifying activation process.

Introduction

Osmium(VIII) tetraoxide is an effective reagent for the cis hydroxylation of alkenes under stoichiometric conditions¹ as well as in a variety of catalytic systems.^{2,3} In both, the critical step depends on the formation of an

osmium(VI) cycloadduct⁴ which is promoted by bases L, typically pyridine, i.e.^{1,5}



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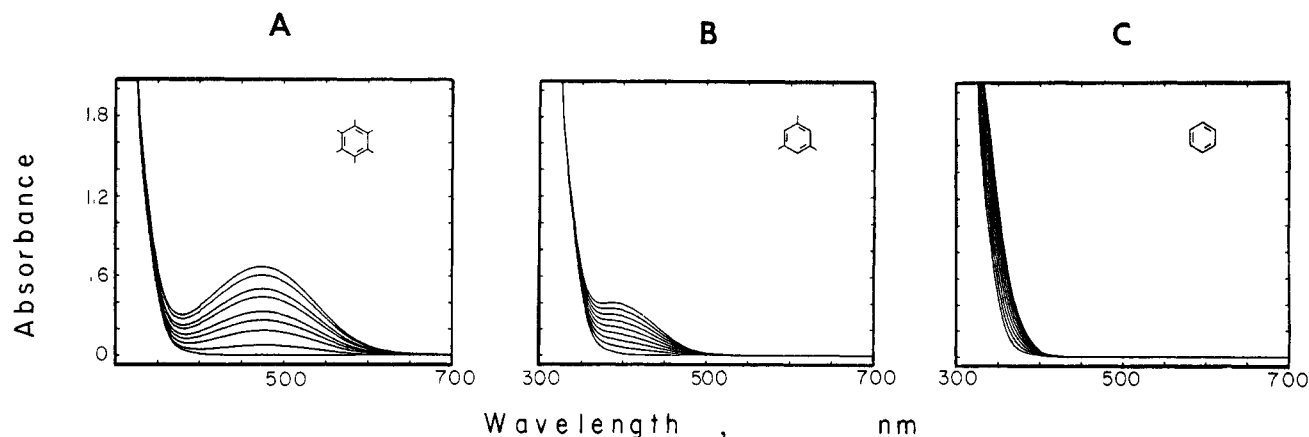


Figure 1. Charge-transfer absorption bands in CCl_4 containing 8.1×10^{-3} M OsO_4 and bottom to top: (A) 0, 0.02, 0.05, 0.07, 0.09, 0.12, 0.14, 0.17, 0.19 M hexamethylbenzene; (B) 0, 0.02, 0.05, 0.07, 0.10, 0.12, 0.14, 0.17, and 0.19 M mesitylene; (C) 0, 0.06, 0.11, 0.17, 0.23, 0.28, 0.34, 0.39, and 0.45 M benzene.

The cis diol can be liberated from the osmate(VI) ester by either reductive or oxidative cleavage. The regeneration of OsO_4 in the latter leads to a catalytic cycle.³

Aromatic substrates are by and large unaffected by osmium tetroxide, benzene actually being a desirable solvent for hydroxylation.⁶ The notable exceptions are some extended polynuclear hydrocarbons such as benzopyrene, dibenzanthracene, and cholanthrene which slowly generate polyalcohols, in some cases accompanied by the degradation of the cyclic framework.⁷

Common to both alkenes and arenes is the immediate appearance of various colors when they are exposed to osmium tetroxide. Owing to the rapid rates of OsO_4 addition to most alkenes, the appearances of the different colors are not readily distinguished from those of the ultimate osmate(VI) ester.⁸ However, in one case, that of the highly encumbered diadamantylidene which undergoes addition only slowly, a pale red-orange color (with an absorption band centered at $\lambda_{\text{max}} = 415$ nm) was formed immediately upon mixing.⁹ Moreover, the intensity of this band did not increase further but slowly diminished as the reactants were consumed. With aromatic hydrocarbons, the immediate colors produced by OsO_4 persist indefinitely, especially in the case of simple benzenoid hydrocarbons.¹⁰ The change in these colors from yellow to orange to red upon the variation of the aromatic component from benzene to xylene to naphthalene, respectively, is diagnostic of charge-transfer absorptions arising from electron-donor-acceptor or EDA complexes.¹¹

Aromatic hydrocarbons (ArH) like alkenes are known to function as electron donors with a wide variety of electron acceptors (A) such as tetracyanoethylene,¹² halogens,¹³ nitroalkanes,¹⁴ polyhalocarbons,¹⁵ as well as various inorganic complexes in high oxidation states.¹⁶ According

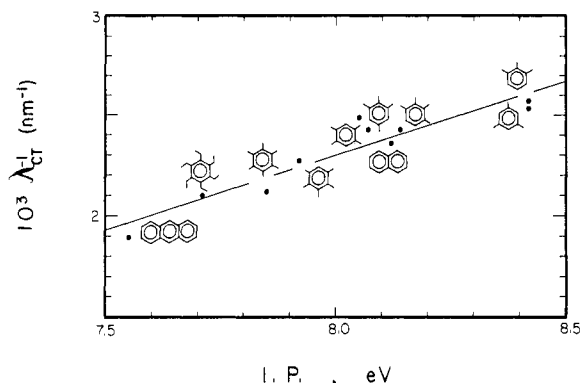


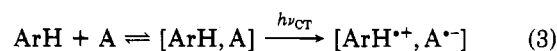
Figure 2. Correlation of the CT transition energy ($\lambda_{\text{max}}^{-1}$) of the $[\text{OsO}_4, \text{ArH}]$ complex with the ionization potential of the arene donor.

Table I. Charge-Transfer Absorption Spectra of the EDA Complexes of OsO_4 with Aromatic Donors^a

aromatic donor	IP (eV) ^b	λ_{max} (nm)
1,2,3-trimethylbenzene	8.42	389
1,3,5-trimethylbenzene	8.42	395
1,2,3,4-tetramethylbenzene	8.14	412
1,2,3,5-tetramethylbenzene	8.07	412
1,2,4,5-tetramethylbenzene	8.05	402
pentamethylbenzene	7.92	440
hexamethylbenzene	7.85	472
hexaethylbenzene	7.71	476
naphthalene	8.12	424
anthracene	7.55	528

^a In carbon tetrachloride at 25 °C. ^b From ref 18.

to Mulliken,¹⁷ the charge-transfer (CT) absorption band ($h\nu_{\text{CT}}$) is associated in these EDA complexes with the electronic excitation to the ion-pair state, i.e. eq 3. Aro-



matic activation via such a CT ion pair represents a potentially useful method to induce processes that are otherwise inaccessible by the usual thermal means. Accordingly in this report we examine the CT photochemistry associated with the EDA complexes of OsO_4 with some representative aromatic donors.

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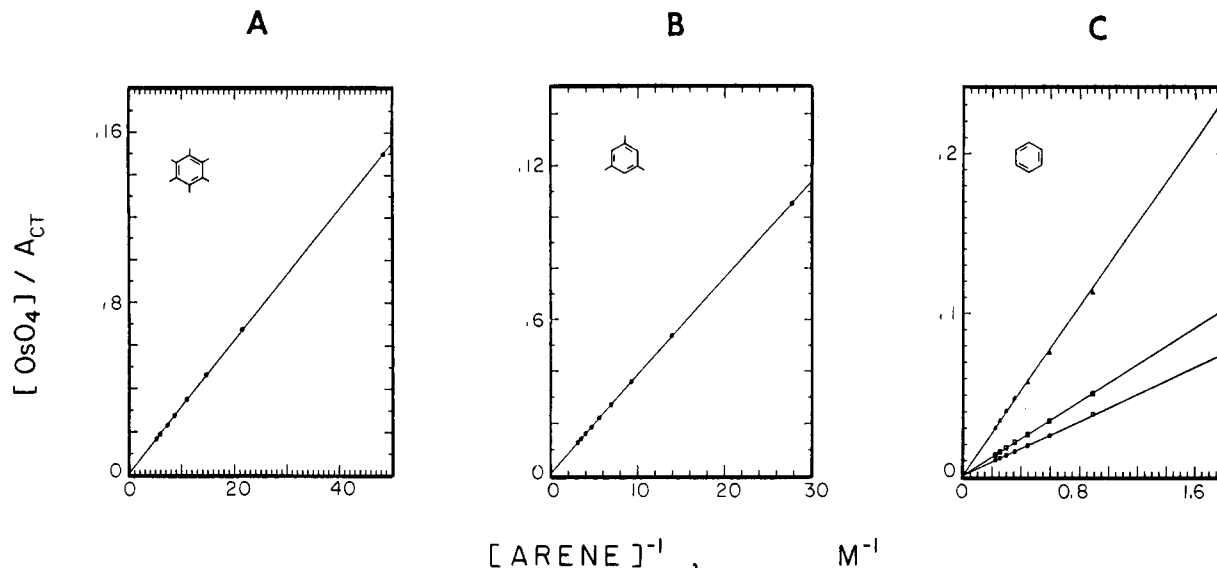


Figure 3. Typical Benesi-Hildebrand plots for the formation of $[\text{ArH}, \text{OsO}_4]$ in CCl_4 containing $8.1 \times 10^{-3} \text{ M OsO}_4$ and various amounts of (A) hexamethylbenzene, (B) mesitylene, and (C) benzene monitored at $\lambda = 472, 395,$ and 340 (○), 360 (■) or 380 (△) nm, respectively.

Results

I. Electron-Donor-Acceptor Complexes of OsO_4 with Aromatic Donors. The addition of benzene to a colorless solution of OsO_4 dissolved in *n*-hexane or carbon tetrachloride, caused a rapid change to yellow. With mesitylene an orange coloration developed immediately, and a clear, bright red solution resulted from hexamethylbenzene. Examination of the UV-vis absorption spectrum of the solution of hexamethylbenzene and OsO_4 revealed the presence of a distinct new band centered at $\lambda_{\text{max}} = 472 \text{ nm}$, as shown in Figure 1A. Other polymethylbenzenes also exhibited similar behavior (Figure 1B), and the positions (λ_{max}) of the new absorption bands are listed in Table I. With benzene (Figure 1C), toluene, and xylene, the new band was not clearly resolved from the low energy tail of the OsO_4 absorption (cutoff $< 380 \text{ nm}$), and they merely appeared as shoulders with a progressive red-shift of $\lambda(\text{onset})$ at 410, 450, and 490 nm, respectively.

The CT bands in Table I follow a monotonic trend with the vertical ionization potentials (IP) of the aromatic donors.¹⁸ Indeed the plot of ionization potentials as a function of the transition energies ($\lambda_{\text{max}}^{-1}$) in Figure 2 is consistent with CT origin of these absorption bands according to Mulliken theory.¹⁷ As such, we evaluated the formation constants of the EDA complexes between OsO_4 and various aromatic donors by the Benesi-Hildebrand spectrophotometric method.^{19,20} For the formation of the 1:1 complex in eq 4, the concentration dependence of the



intensity of the CT band is given by

$$\frac{[\text{OsO}_4]}{A_{\text{CT}}} = \frac{1}{K\epsilon_{\text{CT}}[\text{ArH}]} + \frac{1}{\epsilon_{\text{CT}}} \quad (5)$$

where A_{CT} and ϵ_{CT} are the molar absorbance and extinction coefficient, respectively, of the EDA complex at the monitoring CT wavelength, under conditions in which one component is present in excess, i.e., $[\text{ArH}] \gg [\text{OsO}_4]$. Typical Benesi-Hildebrand (B-H) plots of $[\text{OsO}_4]/A_{\text{CT}}$

Table II. Temperature Dependence of the Charge-Transfer Absorption of OsO_4 Complexes^a

temp (K)	$K\epsilon_{\text{CT}}$ (cm^{-1})	K^b (M^{-1})	ϵ_{CT}^b ($\text{M}^{-1} \text{cm}^{-1}$)	K^c (M^{-1})
278	284	0.13	2200	0.23
288	281	0.45	630	0.23
296	262	0.29	890	0.21
303	254	0.16	1600	0.21
318	233	0.28	830	0.19

^a With 1,3,5-trimethylbenzene in carbon tetrachloride. ^b From the Benesi-Hildebrand treatment using eq 5. ^c From the slope in column 2 and an average $\bar{\epsilon}_{\text{CT}} = 1200 \text{ M}^{-1} \text{cm}^{-1}$.

Table III. Formation Constants and Extinction Coefficients of Charge-Transfer Complexes of OsO_4 and Aromatic Donors^a

ArH	(M) ^b	λ_{mon}^c (nm)	K (M^{-1})	ϵ_{CT}^d ($\text{M}^{-1} \text{cm}^{-1}$)
benzene	0.45	360	0.23 ^d	770
toluene	0.47	380	0.32 ^e	610
<i>p</i> -xylene	0.37	380	0.25 ^f	820
hemimellitene	0.50	389	0.19 ^g	870
mesitylene	0.32	395	0.32	830
durene	0.26	410	0.47 ^h	490
pentamethylbenzene	0.21	460	0.37 ⁱ	750
hexamethylbenzene	0.19	472	0.38	850

^a In carbon tetrachloride solutions containing $8.1 \times 10^{-3} \text{ M OsO}_4$. ^b $[\text{ArH}]_{\text{max}}$ with seven other concentrations. ^c Monitoring wavelength. ^d 0.32 at 340 nm. ^e 0.34 at 360 nm. ^f 0.23 at 360 nm. ^g 0.14 at 380 nm. ^h 0.43 at 402 nm. ⁱ 0.27 at 440 nm.

versus $1/[\text{ArH}]$ are shown in Figure 3 for some representative aromatic donors. In all cases, precise values of the product $K\epsilon_{\text{CT}}$ were obtained from the well-defined slopes in Figure 3 (linearity with $r > 0.9999$), but the accurate determination of ϵ_{CT} was hampered by the limited values of the intercepts.²⁰ Accordingly, we turned to the temperature dependence of the CT bands over the range 278–318 K. For the EDA complex of OsO_4 and mesitylene, Table II shows that $K\epsilon_{\text{CT}}$ decreases monotonically with increasing temperature. If for the moment we ascribe this change solely to the diminution of the formation constant K , we can assign a constant value to the extinction coefficient $\bar{\epsilon}_{\text{CT}} = 1200 \text{ M}^{-1} \text{cm}^{-1}$ from the B-H plots over the limited range of temperatures studied. The formation constants estimated in this manner are listed in the last column of Table II. The thermodynamic parameters for the EDA complex of OsO_4 and mesitylene obtained from

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the Eyring relationship were $\Delta H = -4 \text{ kJ mol}^{-1}$ and $\Delta S = -24 \text{ J K}^{-1} \text{ mol}^{-1}$.²¹ The limited magnitudes of the intercepts in Figure 3 prevented the formation constants of the other OsO_4 complexes with different aromatic donors to be determined reliably. However, the similarity of the Benesi-Hildebrand data in Table III with that of the mesitylene complex indicates $K \leq 0.5 \text{ M}^{-1}$ for all the aromatic donors examined in this study. Indeed these EDA complexes are so weak that all attempts at isolation, including the freezing of various mixtures of OsO_4 in neat aromatic donors, merely led to phase separation.¹⁰ Thus the absorption bands are properly ascribed to contact charge transfer.²²

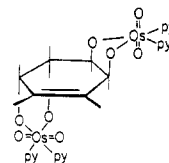
Solutions of OsO_4 and aromatic donors exhibited new CT absorption bands only in solvents such as hexane, dichloromethane, and carbon tetrachloride. In more polar solvents such as acetone and acetonitrile, no new absorption bands could be discerned. Similarly, upon the addition of small amounts of pyridine to a hexane solution of OsO_4 and arene, the colors were immediately discharged, undoubtedly due to the preferential coordination of the Lewis base with the acceptor.²³

II. Charge-Transfer Photochemistry of the EDA Complexes of OsO_4 with Aromatic Donors. The CT absorption bands of the aromatic donors listed in Table III were persistent, but upon prolonged standing those of the more electron-rich ones were altered slightly. For example, the yellow color of the benzene complex remained unchanged for several days if the solution was protected from light. Similarly, we could detect no alteration of the orange color from the mesitylene complex for several hours. After an hour, the solutions of OsO_4 in carbon tetrachloride containing either hexamethylbenzene or anthracene showed slight increases (<5%) in the absorbances at the monitoring wavelengths of 472 and 530 nm, respectively, together with a corresponding elevation of the base line owing to the formation of highly colored adducts (vide supra).

The absence of a thermal reaction between simple benzenoid hydrocarbons with OsO_4 was in strong contrast to the facile photochemical activation which is described below for some representative systems.

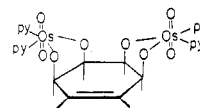
Hexamethylbenzene. Solutions of OsO_4 in *n*-hexane containing hexamethylbenzene were bright red and showed only slight changes over several days when left in the dark at room temperature. However, when these solutions were exposed to actinic radiation, the clear red solution immediately became turbid followed by the precipitation of a brown powder.²⁴ For these experiments, the focussed beam from a Hg-Xe lamp was passed through a sharp cutoff filter to insure that only light with wavelengths $\lambda > 480 \text{ nm}$ impinged on the photochemical cell. An inspection of Figure 1A shows that such irradiation could only excite the charge-transfer band of the complex $[\text{ArH}, \text{OsO}_4]$. Thus there was no ambiguity about either the adventitious local excitation of the complexed (or uncomplexed) chromophores or the generation of intermediates that did not arise from the CT excitation of the EDA complex. It was thus clear that the appearance of

the brown precipitate was a direct consequence of the population of the CT excited state. Owing to the instability of this material, it was dissolved in dichloromethane and immediately converted to the pyridine adduct, with the stoichiometry $\text{C}_6(\text{CH}_3)_6(\text{OsO}_4)_2(\text{py})_4$ established by elemental analysis.²⁵ The IR spectrum of the 2:1 adduct I revealed a strong band at 828 cm^{-1} , diagnostic of the *trans*-dioxosmium moiety $\text{O}=\text{Os}=\text{O}$.^{26,27} The pyridine ligands appeared in the ^1H NMR spectrum of I as three resonances at δ 8.89, 7.81, and 7.43 in a characteristic 8:4:8 intensity ratio for the α , γ , and β protons, respectively.²⁸ These diagnostic resonances were used to calibrate the remaining ^1H resonances arising from the methyl groups associated with hexamethylbenzene. Thus the ^1H NMR spectrum of I included three high-field singlets at δ 1.73 (6 H), 1.65 (6 H), and 1.58 (6 H), from which we deduced the presence of three equivalent pairs of methyl groups that exhibited their distinctive resonances in the ^{13}C NMR spectrum at δ 23.3, 18.0, and 13.2. The ^{13}C NMR spectrum also included resonances at δ 131.4, 92.5, and 91.6 assignable to a pair of olefin (sp^2) carbons and two pairs of saturated (sp^3) carbons bearing oxygen atoms from the osmate ester. These results coupled with the analogy to olefin osmylations^{26,27} (compare eq 2) led to the structure of the pyridine adduct shown below.



I

Although the spectroscopic results were completely consistent with this structural assignment, we made varied but unsuccessful attempts to grow a single crystal suitable for X-ray crystallography (see Experimental Section). Especially problematic was anti stereochemistry of the bulky osmate moieties, which we based largely on an inspection of molecular models. In the alternative syn adduct, i.e.



we considered the residual olefinic linkage to be significantly more exposed than that in I and thus subject to further addition of a third osmyl group, particularly from the anti face. Accordingly, the 2:1 adduct I was redissolved in dichloromethane and treated with 1 equiv of OsO_4 at room temperature for 3 days. The solution showed no spectral changes, and the starting material was recovered intact (>80%). That the reaction of I with OsO_4 did not proceed to the eventual formation of a tris-osmylated adduct was attributed to steric hindrance from the pair of $\text{OsO}_4(\text{py})_2$ moieties located on either side of the six-membered ring. Indeed, Harman and Taube²⁹ suggested that similar steric interactions between octahedral osmium centers led to an anti configuration in the bridged benzene dimer $[[\text{Os}(\text{NH}_3)_5]_2(\mu\text{:}\eta^2, \eta^2\text{-C}_6\text{H}_6)]^{4+}$, which prevented the addition of a third $\text{Os}(\text{NH}_3)_5^{2+}$ moiety.

(21) Compare with $\Delta H = -400, -500 \pm 200$, and $-770 \pm 110 \text{ cal mol}^{-1}$ for the naphthalene, benzene, and mesitylene complexes with OsO_4 .¹⁰

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(24) Product separation from the reaction mixture limited the photochemical conversion to <40%. Since the reactants were not destroyed, the yields for CT osmylation based on OsO_4 were usually high.

(25) Elemental analysis by Atlantic Microlab, Inc., Atlanta, GA.

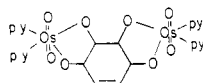
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(29) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* 1987, 109, 1883.

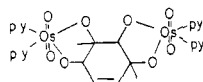
Benzene. The exposure of a pale yellow solution of benzene and OsO_4 in *n*-hexane to filtered light with $\lambda > 380$ nm corresponded to the excitation of the low energy tail of the CT band (see Figure 1C). Nonetheless, a rapid discharge of the color occurred, and a deep brown solid separated from the reaction mixture. Similarly, a clear yellow solution of OsO_4 dissolved in neat benzene rapidly became turbid and deposited a brown powder upon irradiation with the same filtered light. The brown amorphous-looking solid was insoluble in chlorinated hydrocarbons, acetone, and water. However, it dissolved readily in pyridine to give a deep red-brown solution, which deposited red-brown microcrystals II upon standing. Elemental analysis of II was consistent with the formulation $(\text{C}_6\text{H}_6)(\text{OsO}_4)_2(\text{py})_4$ (see Experimental Section). The infrared spectrum of the 2:1 adduct II closely resembled that of the corresponding hexamethylbenzene adduct I (vide supra), especially with regard to the strong absorption at 834 cm^{-1} characteristic of the trans $\text{O}=\text{Os}=\text{O}$ moiety and a band at 618 cm^{-1} for the $\text{Os}-\text{O}(\text{ester})$ vibration. The ^1H NMR spectrum of II was also akin to that of the hexamethylbenzene adduct I with regard to the diagnostic triad of pyridine resonances at δ 8.92, 7.83, and 7.44. The protons associated with benzene appeared at δ 6.12 (d, 2 H) and 5.17 (m, 4 H) for the unique pair of olefinic protons and the pairs of inequivalent hydrogens bound to carbon atoms bearing the two osmate groups, respectively, in the structure shown below.



II

All attempts to grow single crystals of II suitable for X-ray crystallography were unfruitful. However, we presumed that the osmate groups result from the addition of two OsO_4 to opposite faces of the benzene ring, by analogy with the structure proposed for the hexamethylbenzene adduct I.

Mesitylene. Bright yellow solutions of mesitylene and OsO_4 in either *n*-hexane or the neat arene rapidly discolored to brown upon exposure to filtered light with $\lambda > 425$ nm (see Figure 1B). This brown precipitate was washed with *n*-hexane and isolated as a pale brown powder. Although it was somewhat soluble in dichloromethane, all attempts at crystallization were unsuccessful owing to its gradual decomposition to a black, insoluble material. However, it afforded a stable, red-brown solution with pyridine from which clusters of deep brown crystals could be isolated by the slow vapor-phase diffusion of diethyl ether. Elemental analysis was consistent with the composition $[\text{C}_6(\text{CH}_3)_3\text{H}_3](\text{OsO}_4)_2(\text{py})_4$ (III). X-ray analysis indicated the tetrapyridine adduct III to be microcrystalline. The corresponding methyl analogue obtained from the crystallization of the brown powder from 4-picoline was also unsuitable for X-ray crystallography. The infrared spectrum of III was similar to those of the hexamethylbenzene and benzene adducts—showing the prominent trans-dioxosmium band at 829 cm^{-1} . The pyridine ligands appeared in the ^1H NMR spectrum of III as the usual triad of low-field resonances at δ 8.86, 7.81, and 7.42. The singlet at δ 5.49 (1 H) was assigned to the unique olefinic hydrogen in the structure shown below.



III

Since the chemical shift of the multiplet at δ 4.65 (2 H) was analogous to that observed in the benzene adduct at δ 5.17, it was assigned to the pair of hydrogens bound to the carbon atoms bearing oxygens from the osmate groups. The partially resolved high-field resonances at δ 1.82 (6 H) and 1.79 (3 H) were akin to those observed in the hexamethylbenzene adduct, and they were assigned to the three chemically inequivalent methyl groups in the structure shown above. Although there is no spectral indication of the stereochemical disposition of the two osmate groups, we presume they occupy anti positions, as in I.

III. Quantum Yield for the Charge-Transfer Osmylation of Hexamethylbenzene. In order to determine the photoefficiency of the aromatic osmylation, we determined the quantum yield for the hexamethylbenzene donor owing to its well-resolved CT band in Figure 1A. In order to ensure the specific excitation of the charge-transfer absorption band, we employed monochromatic light at $\lambda = 505$ nm by passing the output from the Hg-Xe source through a narrow band pass (± 5 nm) interference filter. The overall photochemical conversion was determined by iodometric titration of OsO_4 in conjunction with Reinecke salt actinometry.^{1,30} The measured quantum yield $\Phi = 0.7$ was considered to be a minimum value owing to unavoidable losses of the light scattered by the insoluble adduct.

Discussion

Osmium tetroxide is a versatile electron acceptor that is capable of forming electron-donor-acceptor (EDA) complexes with both alkenes and arenes. With alkene donors, the EDA complexes are transient and readily undergo a thermal reaction that can be considered formally as an overall [2 + 3] cycloaddition.³¹ On the other hand, simple benzenoid hydrocarbons require photochemical activation via the charge-transfer absorption band to induce an equivalent [2 + 3] cycloaddition. The difference in reactivity is not due to electronic factors alone since the arenes are generally better donors than alkenes—as evaluated by their ionization potentials (e.g., IP of hexamethylbenzene, mesitylene, tetramethylethylene, cyclohexene, and 1-octene are 7.85, 8.42, 8.27, 8.95, and 9.43 eV, respectively).^{18,33} Indeed this dichotomy is reminiscent of that previously noted with alkene and arene donors toward bromine (Br_2) as the electron acceptor.³⁴ In the latter we found that the charge-transfer transition energy ($h\nu_{\text{CT}}$) associated with the excitation of the EDA complex to be a unifying factor. Accordingly let us initially consider alkenes and arenes in their capacity as electron donors toward osmium tetroxide as the electron acceptor—particularly with regard to their CT absorption bands.

The facility with which alkenes undergo addition to OsO_4 can be examined at low temperatures. For example, a colorless solution of OsO_4 in *n*-hexane at -78°C immediately takes on a yellow coloration upon the addition of tetramethylethylene. In the electronic spectrum a new absorption band appears which partially overlaps with the

(30) Wegner, E. E.; Adamson, A. W. *J. Am. Chem. Soc.* 1966, 88, 394.
 (31) It could proceed by either a concerted mechanism or stepwise via a [2 + 2] cycloaddition followed by a sigmatropic rearrangement.³²

(32) Cf. Sharpless, K. B.; Teranishi, A. Y.; Bäckvall, J. E. *J. Am. Chem. Soc.* 1977, 99, 3120.

(33) Masclat, P.; Grosjean, D.; Moivier, G.; DuBois, J. E. *J. Electron Spectrosc. Relat. Phenom.* 1973, 2, 225. Remane, H. Graefe, J.; Herzschuh, P. *Z. Chem.* 1972, 12, 194. Demeo, D. A.; El-Sayed, M. A. *J. Chem. Phys.* 1970, 52, 2622. Kobayashi, T.; Yokota, K.; Nagakura, S. *J. Electron Spectrosc. Relat. Phenom.* 1973, 3, 449.

(34) Fukuzumi, S.; Kochi, J. K. *J. Am. Chem. Soc.* 1982, 104, 7599.

OsO₄ absorption and it tails to 540 nm. Even at this temperature, the thermal reaction cannot be quenched, and broad, intense absorption bands of the adduct with $\lambda_{\text{max}} = 480$ and 590 nm swamp out the CT band within 20 min. Strained alkenes such as norbornene and hexamethyl(Dewar benzene) that are even better electron donors³⁵ unfortunately react too rapidly with OsO₄ to observe the transient CT band even at -78 °C. By way of comparison, the EDA complex of cyclohexene and OsO₄ persists as a pale yellow adduct in *n*-hexane at -78 °C. The CT band is manifested in the electronic spectrum as a shoulder on the OsO₄ absorption, and it tails to 440 nm. Moreover the absorbance of the new band increases with incremental additions of cyclohexene, as expected for complex formation. The hindered *tert*-butylethylene is inert, and it shows no new bands in the absorption spectrum upon its addition to a hexane solution of OsO₄ at -78 °C. The sterically hindered but better electron donor diadamantylidene³⁶ forms a weak EDA complex with OsO₄ ($\lambda_{\text{CT}} = 415$ nm) which is slowly converted to the cycloadduct.⁹ These spectral observations suggest that a right combination of steric hindrance and electron-donor property (i.e., ionization potential) in the alkene is required for the effective formation of the EDA complex showing CT absorption bands.

All of the arene donors examined in this study show pronounced CT absorption bands (Table I) associated with the formation of EDA complexes in eq 4. The limited magnitudes of the formation constants *K* in Table III evaluated by the Benesi-Hildebrand procedure (eq 5) indicate that the EDA complexes are best classified as weak. Nonetheless we made extensive but fruitless efforts to isolate these as 1:1 complexes (see Experimental Section), analogous to our recent successful efforts with the similarly weak tetrabromomethane complexes.^{37,38} Indeed both electron acceptors exhibit a tetrahedral configuration about the central core atom. As such, the orbital overlap of the donor HOMO with the LUMO of the acceptor may be related.³⁹ For arene donors with tetrabromomethane, X-ray crystallography has established the HOMO-LUMO interaction to involve a delocalized bromine "bond", i.e.⁴⁰



An analogous structure for the OsO₄ complex would find the oxygen atom of the osmyl moiety lying directly on the 6-fold symmetry axis as opposed to a π - π interaction involving the oxo-osmium bond, i.e.^{41,42}



(35) Jones, G., II; Becker, W. G. *J. Am. Chem. Soc.* 1983, 105, 1276. Bieri, G.; Heilbronner, E.; Kobayashi, T.; Schmelzer, A.; Goldstein, M. J.; Leight, R. S.; Lipton, M. S. *Helv. Chim. Acta* 1976, 59, 2657.

(36) Nelsen, S. F.; Kapp, D. L.; Akaba, R.; Evans, D. H. *J. Am. Chem. Soc.* 1986, 108, 6863.

(37) Blackstock, S. C.; Kochi, J. K. *J. Am. Chem. Soc.* 1987, 109, 2484. Blackstock, S. C.; Lorand, J. P.; Kochi, J. K. *J. Org. Chem.* 1987, 52, 1451.

(38) Note however the weak complexes isolated were derived from rather localized σ -donors rather than the delocalized π -donors typical of arenes. For the structural distinction, see Foster.¹¹

(39) Cf. Gur'yanova, E. N.; Gol'dshtein, I. P.; Romm, I. P. *Donor-Acceptor Bond*; Wiley: New York, 1975.

(40) See: Streiter, F. J.; Templeton, D. H., in ref 15.

(41) Cf. Lindqvist, I. *Inorganic Adduct Molecules of Oxo Compounds*; Springer: Berlin, 1963.

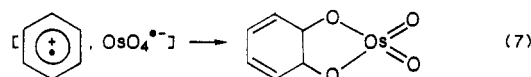
(42) Although the arene donors are presented as η^6 -ligands, it is also possible for them to act as η^2 -ligands⁴⁵ in CT photochemistry.

(43) See: Lau, W.; Kochi, J. K., in ref 16.

Be that as it may, the direct irradiation of the charge-transfer absorption band of such an EDA complex corresponds to charge separation leading to the ion pair in eq 6. This formulation is based on Mulliken's theory of

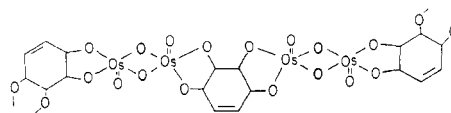


charge-transfer,^{15,16} and it derives experimental verification from the direct observation of various transient ion pairs by time-resolved spectroscopic studies on the picosecond timescale.^{44,45} Arene cation radicals such as that in eq 6 are known to be highly susceptible to nucleophilic attack.⁴⁶ Accordingly, the collapse of the ion pair represents the most direct pathway to cycloaddition,⁴⁷ i.e.



Such a condensation process must compete with back electron transfer to regenerate the EDA complex. The latter is likely to be highly exergonic.⁴⁹ Thus the measured quantum yield of $\Phi \sim 0.7$ is somewhat surprising since it indicates that the collapse of the ion pair to the cycloadduct occurs at a rate comparable to that of a simple back electron transfer.⁵⁰ Indeed the lifetime of such an ion pair must be <10 ns since preliminary studies failed to detect arene cation radicals on this timescale.

The formation of the 1:1 adduct of the arene and OsO₄ in eq 7 occurs with the concomitant loss of aromaticity and produces a diene which is now highly susceptible to a facile thermal osmylation.³ The isolated product of CT osmylation always consisted of the 2:1 adduct, irrespective of the molar ratio of OsO₄/arene, including the use of neat benzene. The persistence of the 2:1 stoichiometry accords with a fast addition of a second mole of OsO₄.⁵¹ The precipitation of the brown solid associated with the latter can be attributed to the ready formation of polymeric structures, e.g.



resulting from the mutual association of the coordinatively unsaturated osmium(VI) centers.^{27,52} These extended structures are converted to monomeric units such as I-III

(44) (a) Hilinski, E. F.; Masnovi, J. M.; Kochi, J. K.; Rentzepis, P. M. *J. Am. Chem. Soc.* 1984, 106, 8071. (b) Masnovi, J. M.; Kochi, J. K.; Hilinski, E. F.; Rentzepis, P. M. *J. Phys. Chem.* 1985, 89, 5387. (c) Masnovi, J. M.; Kochi, J. K.; Hilinski, E. F.; Rentzepis, P. M. *J. Am. Chem. Soc.* 1986, 108, 1126.

(45) Mataga, N. *Pure Appl. Chem.* 1984, 56, 1255.

(46) See: Yoshida, K. *Electrooxidation in Organic Chemistry*; Wiley: New York, 1984.

(47) By either a concerted or stepwise process, compare footnote 31 and ref 48.

(48) For an analogous ion-pair process in the Diels-Alder reaction, see: Dern, M.; Korth, H. G.; Kopp, G.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* 1985, 24, 337. Takahashi, Y.; Kochi, J. K. *Chem. Ber.* 1988, 121, 253.

(49) Preliminary electrochemical studies indicate that OsO₄ undergoes a reversible one-electron reduction at $E_{1/2} = -0.05$ V vs SCE in CH₂Cl₂. The corresponding values for aromatic cation radicals are ~ 2 V.³³

(50) The reorganization energy for OsO₄ \rightarrow OsO₄⁻ is unknown, but it is likely to be small. Thus the rate of back electron transfer of the ion pair in eq 7 will be fast. See: Klingner, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* 1981, 103, 5839.

(51) According to this mechanism, the measured quantum yield of 0.66 corresponds to $\Phi = 0.33$ for eq 6.

(52) Although five-coordinate oxo-osmium(VI) complexes are known, the μ_2 -oxo dimers are more common. See: (a) Collin, R. J.; Jones, J.; Griffith, W. P., in ref 4. (b) Phillips, F. L.; Skapski, A. C. *J. Chem. Soc., Dalton Trans* 1975, 2586. (c) Collin, R. J.; Griffith, W. P.; Phillips, F. L.; Skapski, A. C. *Biochim. Biophys.* 1973, 320, 745.

in the presence of coordinating ligands such as pyridine.⁵³

In closing, we compare briefly the thermal osmylation of alkenes and the CT osmylation of arenes. We believe that both share EDA complexes as common precursors along their reaction pathways.⁵⁴ If so, the thermal osmylation of alkene donors could proceed via a thermally pumped CT activation which is akin to the photochemically pumped process described in this study of arene donors.⁵⁶ According to this unifying formulation, it is possible to account for the reactivity difference between alkene and arene donors in terms of the magnitudes of the solvation energy of their cation radicals. We hope that further studies of osmylation will elucidate this mechanistic commonality.

Experimental Section

Materials. Osmium tetroxide (Aldrich, Platina) was used as received. Hexamethylbenzene (Aldrich) was recrystallized from ethanol and sublimed. Mesitylene (J. T. Baker) was distilled from sodium. Benzene (Mallinckrodt) was stirred with concentrated sulfuric acid overnight, washed with dilute, aqueous NaOH, and distilled from sodiobenzophenone. Pyridine (Matheson, Coleman and Bell) was stirred with KOH pellets and fractionally distilled. *n*-Hexane (Mallinckrodt) was treated with concentrated sulfuric acid, washed with aqueous NaHCO₃, dried over anhydrous CaCl₂, and distilled from sodium. Dichloromethane (Mallinckrodt) was stirred with concentrated sulfuric acid, washed with aqueous NaHCO₃ and then water, dried over anhydrous CaCl₂, and distilled from calcium hydride. Carbon tetrachloride (Matheson, Coleman and Bell), glass distilled, was used as supplied.

Instrumentation. UV-vis absorption spectra were recorded on a Hewlett-Packard 8450A diode-array spectrometer (2-nm resolution) with a HP 89100A temperature-control assembly (accuracy: ± 0.2 between -10 to 105 °C) and interfaced to a Compaq PC. All measurements were carried out with 1.0-cm quartz cells equipped with greaseless Teflon stopcocks. ¹H and ¹³C{¹H} NMR spectra were measured in solution on a JEOL FX90Q NMR spectrometer. Chemical shifts are given in ppm relative to an internal Me₄Si standard. Infrared spectra were obtained with KBr disks on a Nicolet 10DX FTIR spectrometer (4 cm⁻¹ resolution). Actinic irradiations were carried out with a focussed beam from either a Hanovia 977B0010 1-kW high-pressure mercury-xenon lamp or an Osram HBO-2L2 500-W high-pressure mercury lamp. Corning sharp cutoff filters were used to absorb high energy radiation at wavelengths less than those of the charge-transfer bands. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, GA.

Determination of the Formation Constants of the EDA Complexes. In a typical experiment, a 2.0-mL aliquot of a standard solution of OsO₄ (ca. 8 mM) in carbon tetrachloride was transferred to a quartz cuvette (1-cm pathlength) equipped with a stirrer bar. The UV-vis spectrum was measured with a sample of pure solvent as reference. A known volume (or weight) of arene was then added with stirring, and the absorbance was measured at three wavelengths close to λ_{\max} of the CT band. This procedure was repeated to give a total of at least 8 data points under conditions where the concentration of arene was always much greater than the concentration of osmium tetroxide. The change in volume that accompanied the incremental addition of arene was assumed to be negligible. After the final addition of arene, the spectrum was remeasured after 30 min and 1 h to check for the occurrence of a thermal reaction. The change in the absorbance due to any thermal reaction was negligible over the course of the measurements. In order to assess the temperature dependence of the CT spectra, a standard solution of osmium tetroxide in

CCl₄ (7.92 mM) was prepared at 23.0 °C. A 3.0-mL aliquot was transferred to a 1.0-cm quartz cell, and the spectrum was measured at three wavelengths with pure CCl₄ as the reference at the appropriate temperature (5.0, 15.0, 23.0, 30.0 or 45.0 °C). A 10- μ L aliquot of mesitylene was added, and the spectrum was remeasured after allowing 5 min for the temperature to equilibrate. This procedure was repeated until a total of 80 μ L of mesitylene and had been added. For measurements taken below room temperature, a flow of argon was maintained through the variable temperature unit in order to minimize the condensation of water vapor. Reference spectra were remeasured at each temperature, and the concentrations were compensated for solvent expansion, coefficient of expansion for CCl₄ being taken as $\alpha = 0.001229$ °C⁻¹.

Preparation of [OsO₄(C₆H₅N)₂]₂[C₆Me₆]. A mixture of osmium tetroxide (0.24 g, 0.94 mmol) and hexamethylbenzene (0.17 g, 1.05 mmol) was dissolved in hexane (5.0 mL) to give a clear, deep-red solution. The solution was photolyzed with light at wavelengths greater than 480 nm for 8 h, using a 500-W mercury lamp and Corning glass sharp cutoff filter. The sample was centrifuged from time to time to precipitate the solid material formed. The resulting pale red solution was decanted from the solid material. The latter was washed with hexane (3 \times 10 mL) and dried in high vacuum. The pale brown solid was dissolved in pyridine, the solution filtered, and the solvent evaporated to give a pale brown powder. The solid could be crystallized as deep brown plates by the slow diffusion of diethyl ether into a concentrated dichloromethane solution; yield 0.17 g, 36%. IR (KBr): 1606 (m), 1481 (m), 1450 (s), 1359 (m), 1212 (m), 1097 (m), 1069 (s), 1041 (s), 1016 (m), 925 (m), 894 (m), 866 (s), 828 (vs), 787 (s), 766 (s), 719 (s), 694 (s), 656 (s), 634 (s), 581 (m), 559 (w), 528 (w), 456 (w) cm⁻¹. ¹H NMR (CDCl₃): δ 8.89 (d, 8 H, H-2,6(py), $J = 4$ Hz), 7.81 (t, 4 H, H-4(py), $J = 8$ Hz), 7.43 (t, 8 H, H-3,5(py), $J = 7$ Hz), 1.73, 1.65, 1.58 (3 \times 6 H, 6 Me). ¹³C{¹H}NMR (CDCl₃): δ 149.3, 139.5, 124.7 (py), 131.4 (C-5, C-6), 92.5, 91.6 (C-1, C-2, C-3, C-4), 23.3, 18.0, 13.2 (3 \times 2 Me). Anal. Calcd for C₃₂H₃₈N₄O₈Os₂: C, 38.94; H, 3.88; N, 5.68. Found: C, 38.82; H, 3.91; N, 5.60. Among the osmylated arenes, the hexamethylbenzene (HMB) adduct evinced the most readily formed crystals. Accordingly a number of varied attempts were made to grow single crystals of sufficient quality for X-ray analysis. For example, when 20 mg of the CT product of OsO₄ and hexamethylbenzene was shaken vigorously with pyridine (3 mL), it slowly dissolved to give a deep red-brown solution. On standing at room temperature, brown microcrystals separated. A sample of the above pyridine adduct (ca. 10 mg) was also redissolved in dichloromethane (2 mL) and exposed to diethyl ether vapor for several days, whereupon dark brown microcrystals separated. The pyridine adduct [C₆Me₆][2OsO₄][4py] (10 mg) was dissolved in dichloromethane (3 mL) and carefully layered with hexane (10 mL). Over several days brown microcrystals separated out as the two phases mixed. Dissolution of the pyridine adduct (ca. 10 mg) in 1,2-dichloroethane (2 mL) gave a deep red-brown solution. Careful layering with hexane gave brown microcrystals after several days. In all these cases, the material was microcrystalline and did not diffract the X-rays sufficiently well for crystallographic analysis. Alternatively, the brown powder, (ca. 20 mg) isolated from the photolysis of solutions of osmium tetroxide and hexamethylbenzene was dissolved in γ -picoline (2 mL), and the resultant red-brown solution was exposed to diethyl ether vapor. Small brown microcrystals slowly separated. [Anal. Calcd for C₃₆H₄₆N₄O₈Os₂: C, 41.45; H, 4.45. Found: C, 41.29, 41.45; H, 4.38, 4.44.]²⁵ The [C₆Me₆][2OsO₄] adduct (ca. 20 mg) was also dissolved in γ -picoline (2 mL) and exposed to hexane vapor for several days. A dark brown powder was deposited. A dichloromethane (3 mL) solution of [HMB][2OsO₄][4(γ -pic)] (ca. 20 mg) was carefully layered with hexane (8 mL), and over several days dark brown shiny microcrystals were deposited in clusters. Additionally, [HMB][2OsO₄][4(γ -pic)] (10 mg) was dissolved in 1,2-dichloroethane (2 mL), giving a dark red-brown solution. Exposure of this solution to an atmosphere saturated with diethyl ether vapor gave clusters of microcrystals over several days. Similar exposure to hexane vapor gave analogous results. Finally, the dissolution of [HMB][2OsO₄] in dichloromethane gave a deep red-brown solution. Addition of a dichloromethane solution containing, α,α' -dipyridine caused the immediate formation of a brown precipitate, which was insoluble in common organic

(53) For a review of dioxoosmium(VI) bispyridine and related complexes, see ref 3.

(54) The spectral observation of EDA complexes of both alkene and arene donors with OsO₄ is necessary but not sufficient to formulate them as obligatory intermediates.⁵⁵

(55) Colter, A. K.; Dack, M. R. J. In *Molecular Complexes*; Foster, R., Ed.; Crane Russak: New York, 1974, Vol. 2, p 2f.

(56) For a thorough discussion of this point, see: Fukuzumi, S.; Kochi, J. K. *J. Am. Chem. Soc.* 1982, 104, 7599 and ref 34.

solvents. Addition of *o*-phenanthroline to a dichloromethane solution of [HMB][2OsO₄] caused the slow precipitation of a brown, microcrystalline, insoluble material. All the samples were polycrystalline as judged by their X-ray diffraction characteristics.

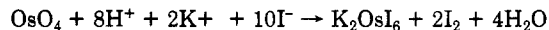
Reaction of [OsO₄(C₅H₅N)₂]₂[C₆Me₆] with OsO₄. [OsO₄(C₅H₅N)₂]₂[C₆Me₆] (0.17 g, 0.17 mmol) was dissolved in dichloromethane (15 mL), and osmium tetroxide (0.043 g, 0.17 mmol) was added to the deep red-brown solution. The mixture was stirred at room temperature for 3 days, whereupon the solvent was removed in high vacuum. The dark residual solid was reextracted into dichloromethane and the solution filtered. Removal of the solvent under reduced pressure gave a pale brown solid (0.134 g), which was shown to be identical with the starting material by ¹H NMR analysis; 79% recovery.

Preparation of [OsO₄(C₅H₅N)₂]₂[C₆H₆]. Osmium tetroxide (0.212 g, 0.834 mmol) was dissolved in benzene (4.0 mL) to give a bright orange solution. This solution was irradiated for 3.5 h at room temperature (water bath) with light from a 1-kW Osram Hg-Xe lamp which was passed through a Corning 380-nm sharp cutoff filter. A dark brown precipitate formed rapidly. It was separated by periodic centrifugation in order to maintain a clear path for the light beam. The volatile components were removed in vacuo, and the remaining brown powder was dissolved in pyridine (4 mL) with vigorous shaking. When the intensely colored, red-brown solution was allowed to stand at room temperature it slowly produced a mass of red-brown crystals, which were isolated and dried in vacuo: yield 0.038 g, 10%. IR (KBr): 1451 (m), 1212 (w), 1070 (w), 1017 (m), 989 (w), 936 (w), 900 (w), 870 (w), 834 (s), 766 (m), 694 (m), 618 (m), cm⁻¹. ¹H NMR (CDCl₃): δ 8.92 (d, 8 H, H-2,6(py), *J* = 5 Hz), 7.83 (t, 4 H, H-4(py), *J* = 8 Hz), 7.44 (t, 8 H, H-3,5(py), *J* = 7 Hz), 6.12 (d, 2 H, H-5,6, *J* ~ 1 Hz), 5.32, 5.02 (m, 4 H, H-1,2,3,4). Anal. Calcd for C₂₆H₂₆N₄O₈Os₂: C, 34.58; H, 2.90. Found: C, 34.45; H, 3.04.

Preparation of [OsO₄(C₅H₅N)₂]₂C₆H₃Me₃. Mesitylene (55 μL, 0.048 g, 4.0 × 10⁻⁴ mol) was added to a solution of osmium tetroxide (0.099 g, 3.9 × 10⁻⁴ mol) in hexane (5.0 mL) to afford a bright yellow solution. Photolysis of this solution using a 1000-W lamp and a 425-nm glass cutoff filter for 6 h afforded a brown precipitate and a pale yellow solution. The mixture was centrifuged, and the clear solution was removed by decantation. The residual brown solid was washed with hexane (2 × 5 mL) and dried in vacuo: yield 0.019 g, 15%. Dissolution in pyridine (4 mL) with shaking led to a deposit of red-brown crystals over several days at room temperature. IR (KBr): 1609 (m), 1450 (s), 1357 (w), 1212 (m), 1070 (m), 1010 (m), 982 (m), 930 (w), 873 (w), 829 (s), 764 (m), 728 (w), 695 (s), 635 (m), 621 (m) cm⁻¹. ¹H NMR (CDCl₃): δ 8.86 (d, 8 H, H-2,6(py), *J* = 5 Hz), 7.81 [m, 4 H, H-4(py)], 7.42 [m, 8 H, H-3,5(py)], 5.49 (s, 1 H, H-6), 4.80, 4.50 (m, 2 H, H-2, H-4), 1.82, 1.79 (m, 9 H, 3 Me). Anal. Calcd for C₂₉H₃₂N₄O₈Os₂: C, 36.86; H, 3.41. Found C, 34.07; H, 3.21. Attempts were made to grow single crystals suitable for X-ray crystallography. For example, a solution of [C₆H₆][2OsO₄][4py] (20 mg) in dichloromethane (3 mL) was carefully layered with hexane and left to stand at room temperature for several days. Upon mixing, a microcrystalline cluster was produced. Similarly, layering with diethyl ether gave brown microcrystals. Slow, vapor phase diffusion of diethyl ether into a dichloromethane solution of [C₆H₆][2OsO₄][4py] produced an amorphous brown precipitate. Dissolution of [C₆H₆][2OsO₄] (20 mg) in *γ*-picoline (3 mL) gave a red-brown solution. Exposure of this solution to an atmosphere of diethyl ether vapor produced a dark brown powder. Furthermore, the photolysis of a solution of naphthalene and osmium tetroxide gave a dark brown powder, which was converted to the *γ*-picoline adduct, [C₁₀H₈][2OsO₄][4(*γ*-pic)]. Dissolution of this

dark brown powder in 1,2-dichloromethane gave a deep brown solution, which upon exposure to a saturated hexane atmosphere generated a brown powder. Photolysis of 1,3-di-*tert*-butylbenzene and osmium tetroxide gave a brown solid. This was dissolved in *γ*-picoline to give a clear, deep red brown solution. Exposure of this solution to diethyl ether vapor produced a dark brown powder.

Determination of the Quantum Yield for CT Osmylation. Osmium tetroxide was estimated by Criegee's iodometric method based on the stoichiometry¹



An aliquot of OsO₄ solution (0.20 mL of ca. 8 mM) was added to a mixture of aqueous KI (10.0 mL of 0.40 M) and dilute sulfuric acid (5.0 mL of 2 M) containing 3 mL of chloroform in a 100-mL separatory funnel. The pink color of the liberated iodine in the chloroform layer was titrated with aqueous sodium thiosulfate (5.506 mM, standardized against potassium iodate). The 1000-W Hg-Xe lamp was equipped with a 505-nm narrow band-pass interference filter, and the number of einsteins emitted at this wavelength was determined with the aid of the Reinecke salt actinometer.³⁰ Excess K[Cr(NCS)₄(NH₃)₂] was shaken well with distilled water (5 mL) and the aqueous solution filtered. One 2.0-mL aliquot served as a blank to monitor the dark, thermal reaction. The second 2.0-mL aliquot was photolyzed for 20.0 min with continuous stirring. Both the blank and photolyzed samples were then treated similarly in the dark. A 1.0-mL aliquot of each solution was diluted to 5.0 mL with an aqueous solution of iron(III) nitrate (0.1 M) and perchloric acid (0.5 M), which was then left to develop for 30 min. The difference in measured absorbance at 450 nm between the photolyzed and blank solutions yielded *n* = 4.92 × 10¹⁵ quanta s⁻¹. The absorbance of a hexane (2.20 mL) solution of osmium tetroxide and hexamethylbenzene (2:1 molar ratio) was measured at 506 nm to ensure that all incident radiation was absorbed (absorbance >> 2). A 0.20-mL aliquot was withdrawn and titrated as described above. The remaining 2.00 mL was photolyzed at 505 nm for a total of 10320 s with stirring. A second 0.20-mL aliquot was withdrawn and again titrated iodometrically. From the difference in titres, the quantum yield was calculated to be Φ_{OsO₄} = 0.66.

Electronic Spectra of OsO₄ and Olefins at Low Temperature. A solution of osmium tetroxide in purified hexane (25.0 mL) of known concentration was prepared. A 2.0-mL aliquot was transferred to a 1.0-cm UV-vis quartz cell equipped with a greaseless stopcock and a magnetic stirrer bar. The cell was cooled to -78 °C by immersion in a dry ice-acetone slush bath. The electronic spectrum was measured, and then an aliquot of the pure olefin (10 μL) was added with stirring, and the spectrum remeasured. In the cases where a fast thermal reaction occurred (e.g., norbornene) at this temperature, the investigation was terminated here. Otherwise, four-five aliquots (10 μL) of alkene were added, and the spectrum remeasured after each addition. The solutions were left stirring at -78 °C for 20 min and the spectrum remeasured to determine the degree of thermal reaction at -78 °C.

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