

significant extent and (b) the enhanced rate of oxidation with electron-rich arenes is consistent with an electrophilic displacement pathway as shown in eq 2 and 3.

By using toluene- d_0 and toluene- d_8 , a primary isotope effect (k_H/k_D) of 5.0 (5) was observed for the oxidation reaction. The magnitude of the isotope effect clearly indicates that the rate-determining step involves C-H bond breaking rather than a simple π -coordination of the arene or the formation of a Wheland intermediate.¹⁶ The formation of the latter species has been proposed as the slow step in the electrophilic metalation of arenes by Pt(IV).¹⁷

Finally, preliminary results indicate that the Pd(II)-mediated monotrifluoroacetoxylation of *p*-dimethoxybenzene can be made catalytic in Pd(II) by using $K_2S_2O_8$ as the cooxidant. For example, quantitative conversion of *p*-dimethoxybenzene was observed in 1 h at 80 °C in CF_3CO_2H , starting with the following concentrations: *p*-dimethoxybenzene (0.43 M), $Pd(O_2CMe)_2$ (0.09 M), and $K_2S_2O_8$ (1.1 M).

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Registry No. $Pd(O_2CMe)_2$, 301-04-2; CH_4 , 74-82-8; CF_3CO_2Me , 431-47-0; adamantane, 281-23-2; 1-adamantyl trifluoroacetate, 58652-54-3; *p*-dimethoxybenzene, 150-78-7; *p*-xylene, 106-42-3.

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Synthesis and Structure of $Os_4(CO)_{16}$, a Metal Carbonyl Analogue of Cyclobutane

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We have recently described the synthesis of $Os_4(CO)_{15}$ (from $Os_3(CO)_{10}(C_8H_{14})_2$ and $Os(CO)_5$) along with the determination of its structure.¹ This was believed to be the first report of a tetranuclear binary carbonyl of osmium. At that time we remarked that, given the stability of $Os_3(CO)_{12}$, one might expect $Os_4(CO)_{16}$ would be stable. We now find that this intriguing cluster can be readily prepared from $Os_4(CO)_{15}$ but that, contrary to arguments based on simple bonding theory, the cluster is not particularly stable.

Treatment of $Os_4(CO)_{15}$ in CH_2Cl_2 at 0 °C with an atmosphere of CO caused essentially quantitative conversion to $Os_4(CO)_{16}$ (**1**) after 4 h; the compound was isolated (86% yield) as air-stable, yellow-orange crystals.² The structure of **1**³ (Figure

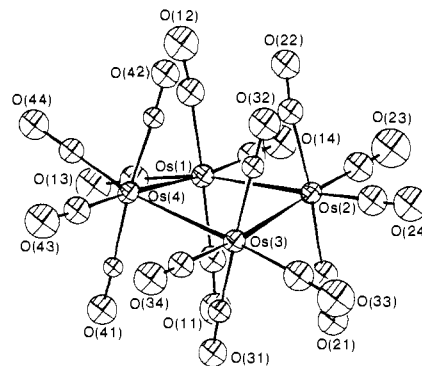


Figure 1. Molecular structure of $Os_4(CO)_{16}$ (**1**). Selected bond distances (Å) and angles (deg) not mentioned in the text: Os-C_{eq} range 1.84 (3)–1.91 (3), Os-C_{ax} range 1.92 (2)–1.97 (2), Os–Os–Os range 88.73 (3)–89.27 (3).

1) shows a puckerd Os_4 framework (the dihedral angle between the planes $Os(1)-Os(2)-Os(3)$ and $Os(1)-Os(3)-Os(4)$ is 158.9°, i.e., the compound is a metal carbonyl analogue of cyclobutane. The puckerd configuration allows shorter, potentially bonding interactions between diagonally related osmium atoms and relieves the steric interactions between carbonyls syn to each other.⁴ Unlike **1**, the syn carbonyls in $Os_3(CO)_{12}$ are eclipsed, an observation that has been taken to indicate that electronic considerations are more important than steric factors in determining the conformation of $Os_3(CO)_{12}$.⁵

The metal-metal bonds in **1** are remarkably long for Os–Os single bonds: $Os(1)-Os(2) = 2.997$ (1) Å, $Os(1)-Os(4) = 2.985$ (1) Å, $Os(2)-Os(3) = 2.979$ (1) Å, $Os(3)-Os(4) = 3.000$ (1) Å. In $Os_3(CO)_{12}$, the average Os–Os bond length is 2.877 (3) Å. This indicates the metal-metal bonds in **1** are weak. In agreement with this view, **1** decomposes when stirred in hexane solution (under N_2) to give mainly $Os_3(CO)_{12}$ ⁷ plus traces of $Os_4(CO)_{15}$ ⁸ after 30 h, i.e., $Os_4(CO)_{16}$ is thermodynamically unstable with respect to $Os_3(CO)_{12}$. The metal-metal bonds in $Os_3(CO)_{12}$ are often regarded as two-center-two-electron bonds.⁹ If this were the case then it might be expected that, even allowing for the increase in the steric interactions of the equatorial carbonyls, **1** would be more stable than $Os_3(CO)_{12}$. This is because in the former cluster the angles about the osmium atoms more closely approach the 90° required for octahedral coordination. That **1** is less stable than $Os_3(CO)_{12}$ suggests that the most important component of the metal-metal bonding in $Os_3(CO)_{12}$ is the occupancy of a molecular orbital that can be considered the result of the overlap of an atomic

(2) Anal. Calcd for $C_{16}O_{16}Os_4$: C, 15.90; H, 0.0. Found: C, 15.89; H, 0.0. $Ir \nu(CO)$ (hexane) 2075.5 (vs), 2054 (m), 2036.5 (s), 2018.5 (w), 2000 (w), 1993 (sh) cm^{-1} ; ^{13}C NMR (CH_2Cl_2/CD_2Cl_2 , 5/1, ambient temperature) δ 168.8 and 176.6. A satisfactory mass spectrum (EI, FAB) could not be obtained; peaks due to $[Os_3(CO)_{12}]^+$, $[Os_6(CO)_{18}]^+$, etc. observed in EI spectrum.

(3) X-ray diffraction data for $Os_4(CO)_{16}$: $M_r = 1208$; triclinic; space group $P\bar{1}$; $a = 9.436$ (1) Å, $b = 9.482$ (1) Å, $c = 14.082$ (2) Å, $\alpha = 87.67$ (1)°, $\beta = 79.09$ (1)°, $\gamma = 69.69$ (1)°; $V = 1159.93$ Å³; $D_c = 3.462$ g cm^{-3} (an empirical absorption correction was applied); diffractometer, Enraf-Nonius CAD4F; radiation, Mo $K\alpha$, graphite monochromator ($\lambda(K\alpha_1)$ 0.709 30 Å); scan range = 0° ≤ 2 θ ≤ 50°; reflections = 3019 with $I_o \geq 2.5\sigma(I_o)$; (no. of variables = 166) $R_f = 0.0448$, $R_w = 0.0538$.

(4) Torsion angles around Os–Os bonds are similar for opposite bond pairs: $C(11)-Os(1)-Os(2)-C(21) = 6.4$ (9)°, $C(31)-Os(3)-Os(4)-C(41) = 8.4$ (10)°; $C(11)-Os(1)-Os(4)-C(41) = 25.6$ (9)°, $C(21)-Os(2)-Os(3)-C(31) = 25.4$ (9)°.

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(7) It is most probable that **1** is the unidentified intermediate observed in the decomposition of $Os_2(CO)_9$ in heptane: Moss, J. R.; Graham, W. A. G. *J. Chem. Soc., Dalton Trans.* **1977**, 95.

(8) That the cluster $Os_4(CO)_{15}$ is stable in hexane solution at room temperature indicates **1** decomposes by different pathways to give $Os_3(CO)_{12}$ and $Os_4(CO)_{15}$.

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orbital on each osmium atom directed to the center of the cluster, as proposed previously.¹⁰

In hexane, **1** exhibits six infrared active CO stretches² which indicates it has a puckered (D_{2d}) rather than planar (D_{4h}) configuration in solution as well as in the solid state. The ¹³C NMR spectrum of **1** (¹³CO-enriched) in CH₂Cl₂/CD₂Cl₂ consists of two signals² even at -95 °C. This suggests that there is rapid exchange between the various puckered configurations of **1** such that the inner and outer axial carbonyls in the molecule are rendered equivalent on the NMR time scale.

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Supplementary Material Available: Stereoview of **1** and tables of atomic coordinates, temperature factors, and bond lengths and angles for **1** (5 pages). Ordering information is given on any current masthead page.

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Hybrid Single-Electron-Transfer-S_N2 Reactions

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Substitution reactions of a family of seven 9-dialkylamino-fluorene ions, 9-R₂N-Fl⁻, with Ph₂CHCl, PhCH₂Cl, and *n*-BuBr have been found to exhibit some of the characteristics of both single electron transfer (SET) and S_N2 reactions.

Evidence that nucleophilic substitution with alkyl halides occurs, at least in some instances, by a SET mechanism has been accumulating for over 20 years.¹ Several authors have suggested that SET and S_N2 are extremes of a hybrid model for substitution reactions.² Ebersson has used the Marcus equation to estimate, from rates of reactions and redox potentials of donors and acceptors, whether or not SET for substitution (and other) reactions is feasible.³ This approach has been used recently to provide supporting evidence for SET character in the S_N2-type substitution reactions of *t*-BuBr with the carbanion derived from 1-*N*-methyl-4(methoxycarbonyl)-1,4-dihydropyridine and with anion radicals.⁴ In our laboratory the rates for S_N2 reactions of remotely substituted 9-G-fluorene ions with alkyl halides have usually been found to be linearly correlated by the Brønsted equation (log *k* vs p*K*_{HA}).⁵ When the size and/or electronic nature of G was

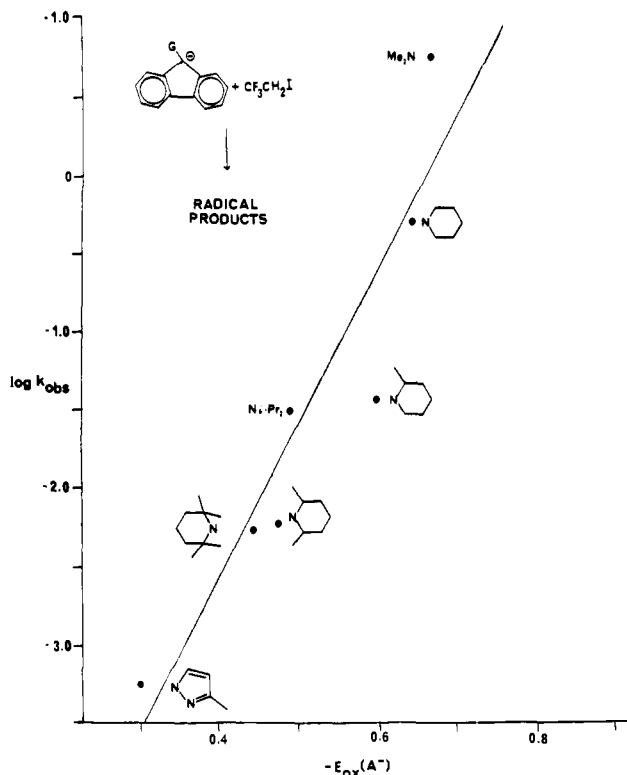


Figure 1. Plot of log *k*_{obs} for single-electron-transfer reactions of 9-dialkylamino-fluorene ions with 1,1,1-trifluoro-2-iodoethane in Me₂SO solution at 25 °C vs their oxidation potentials, *E*_{ox}(A⁻), in Me₂SO.

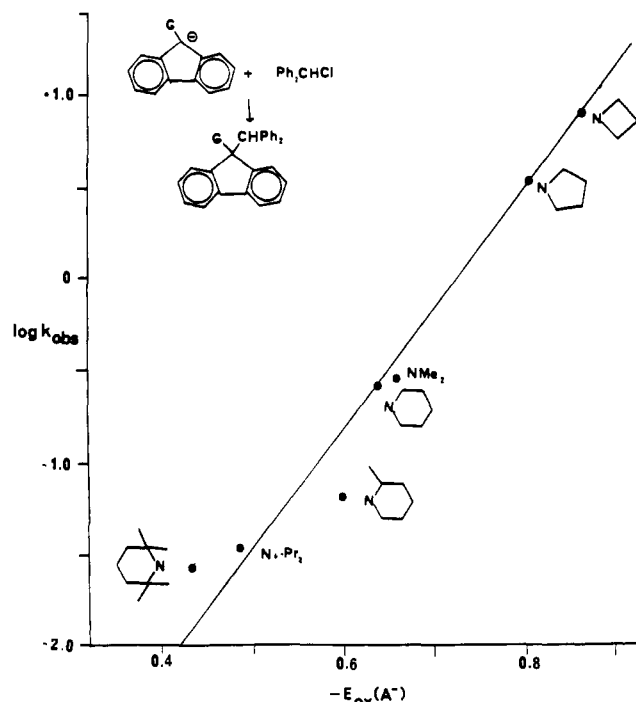


Figure 2. Plot of log *k*_{obs} for substitution reactions of 9-dialkylamino-fluorene ions with benzhydryl chloride in Me₂SO solution at 25 °C vs their oxidation potentials, *E*_{ox}(A⁻), in Me₂SO.

varied, however, a scattered Brønsted plot was obtained for an S_N2 reaction with an alkyl halide, but a Marcus-type plot of log *k* vs *E*_{ox}(A⁻) was linear with a SET acceptor, 1-Ts-1-NO₂-c-C₆H₁₀.⁶ A linear Marcus-type plot⁷ has now been observed for

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