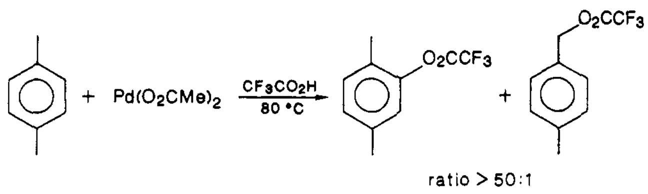

(7)

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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(16) Reviews on isotope effects in aromatic electrophilic substitutions: (a) Zollinger, H. *Adv. Phys. Org. Chem.* **1964**, *2*, 163. (b) Berliner, E. *Prog. Phys. Org. Chem.* **1964**, *2*, 253.

(17) Shul'pin, G. B.; Nizova, G. V.; Nikitaev, A. T. *J. Organomet. Chem.* **1984**, *276*, 115. However, the mercuration of arenes is usually accompanied by large isotope effects: Lau, W.; Kochi, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 6720.

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

Victor J. Johnston, Frederick W. B. Einstein,* and
Roland K. Pomeroy*

Department of Chemistry, Simon Fraser University
Burnaby, British Columbia, Canada V5A 1S6

Received September 1, 1987

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 $Os_4(CO)_{15}$[1] 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 1) shows a puckered 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 puckered 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]

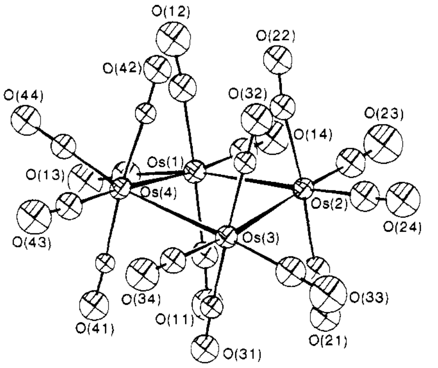

Figure 1. Molecular structure of $Os_4(CO)_{16}$ (**1**). Selected bond distances (Å) and angles (deg) not mentioned in the text: Os–C_{eq} range 1.84 (3)–1.91 (3), Os–C_{ax} range 1.92 (2)–1.97 (2), Os–Os–Os range 88.73 (3)–89.27 (3).

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

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(1) Johnston, V. J.; Einstein, F. W. B.; Pomeroy, R. K. *J. Am. Chem. Soc.* **1987**, *109*, 7220–7222.

(2) Anal. Calcd for $C_{16}O_{16}Os_4$: C, 15.90; H, 0.0. Found: C, 15.89; H, 0.0. Ir ν(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)°; $V = 1159.93$ Å^3; $D_c = 3.462$ g cm^{-3} (an empirical absorption correction was applied); diffractometer, Enraf-Nonius CAD4F; radiation, Mo Kα, graphite monochromator (λ(Kα_1) 0.709 30 Å); scan range = $0° \leq 2\theta \leq 50°$; 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)°.

(5) Lauher, J. W. *J. Am. Chem. Soc.* **1986**, *108*, 1521.

(6) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878.

(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 $Os_4(CO)_{15}$.

(9) For example: (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980; p 1083. (b) Wade, K. In *Transition Metal Clusters*; Johnson, B. F. G., Ed.; Wiley: Chicester, England, 1980; p 211.

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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 stretches[2] which indicates it has a puckered (D_{2d}) rather than planar (D_{4h}) configuration in solution as well as in the solid state. The ^{13}C NMR spectrum of **1** (^{13}CO-enriched) in CH_2Cl_2/CD_2Cl_2 consists of two signals[2] 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.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and Simon Fraser University for financial support.

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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[10] (a) Lauher, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 5305. (b) Delley, B.; Manning, M. C.; Ellis, D. E.; Berkowitz, J.; Trogler, W. C. *Inorg. Chem.* **1982**, *21*, 2247 and references therein.

Hybrid Single-Electron-Transfer-S_N2 Reactions

F. G. Bordwell* and John A. Harrelson, Jr.

Department of Chemistry, Northwestern University
Evanston, Illinois 60208

Received June 15, 1987

Substitution reactions of a family of seven 9-dialkylaminofluorenide ions, $9\text{-}R_2N\text{-}Fl^-$, with Ph_2CHCl, $PhCH_2Cl$, 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] Eberson 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-fluorenide ions with alkyl halides have usually been found to be linearly correlated by the Brønsted equation (log *k* vs pK_{HA}).[5] When the size and/or electronic nature of G was 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 an SET acceptor, $1\text{-Ts-1-NO}_2\text{-}c\text{-}C_6H_{10}$.[6] A linear Marcus-type plot[7] has now been observed for

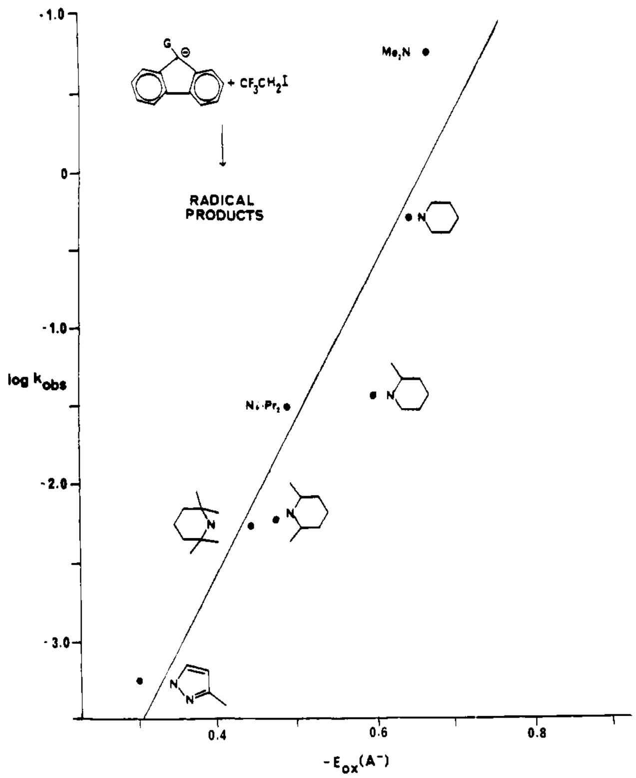

Figure 1. Plot of log k_{obsd} for single-electron-transfer reactions of 9-dialkylaminofluorenide ions with 1,1,1-trifluoro-2-iodoethane in Me_2SO solution at 25 °C vs their oxidation potentials, $E_{ox}(A^-)$, in Me_2SO.

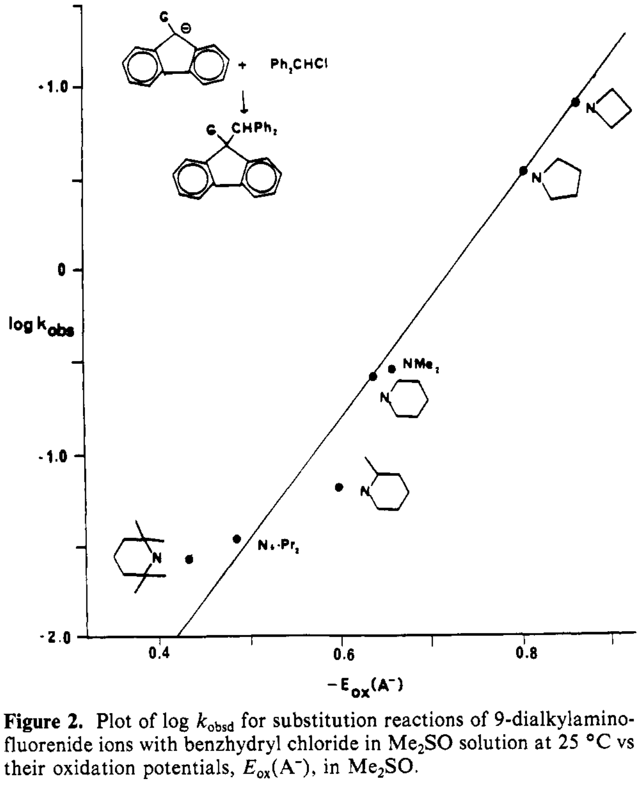

Figure 2. Plot of log k_{obsd} for substitution reactions of 9-dialkylaminofluorenide ions with benzhydryl chloride in Me_2SO solution at 25 °C vs their oxidation potentials, $E_{ox}(A^-)$, in Me_2SO.

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[1] (a) Dessy, R. E.; Pohl, R. L.; King, R. B. *J. Am. Chem. Soc.* **1966**, *88*, 5121–5124. (b) Dessy, R. E.; Weisman, P. H. *Ibid.* **1966**, *88*, 5124–5129. (c) Bilevitch, K. A.; Pubnov, N. N.; Okhlobystin, O. Yu. *Tetrahedron Lett.* **1968**, 3465–3468. (d) Kormer, G. S.; Hall, M. L.; Traylor, T. J. *J. Am. Chem. Soc.* **1972**, *94*, 7205–7206. (e) Bank, S.; Noyd, D. A. *J. Am. Chem. Soc.* **1973**, *95*, 8203–8205. (f) Garst, J. F.; Barbas, J. T. *J. Am. Chem. Soc.* **1974**, *96*, 3239–3249. (g) Zieger, H. E.; Angres, I.; Mathisen, D. *J. Am. Chem. Soc.* **1976**, *98*, 2580–2585. (h) Russell, G. C.; Jawdosiuk, M.; Makosza, M. *J. Am. Chem. Soc.* **1979**, *101*, 2355–2359. (i) Smith, G. F.; Kuivila, H. G.; Simon, R.; Sultan, L. *J. Am. Chem. Soc.* **1981**, *103*, 833–839. Kuivila, H. G.; Alnajjah, M. S. *J. Am. Chem. Soc.* **1982**, *104*, 6146–6147. (j) Ashby, E. C.; DePriest, R. *J. Am. Chem. Soc.* **1982**, *104*, 6144–6146.

[2] (a) Lund, H.; Kristensen, L. H. *Acta Chem. Scand.* **1979**, *B33*, 495–498. (b) Pross, A. *Acc. Chem. Res.* **1985**, *18*, 212–219. (c) Pross, A.; Shaik, S. S. *Acc. Chem. Res.* **1983**, *16*, 363–370.

[3] (a) Eberson, L. *Acta Chem. Scand.* **1982**, *B36*, 533–543. (b) Eberson, L. *Ibid.* **1984**, *B38*, 439–459.

[4] Lund, T.; Lund, H. *Acta Chem. Scand.* **1986**, *B40*, 470–485.

[5] Bordwell, F. G.; Hughes, D. L. *J. Org. Chem.* **1980**, *45*, 3314–3320; **1983**, *48*, 2206–2215. Bordwell, F. G.; Hughes, D. L. *J. Am Chem. Soc.* **1986**, *108*, 7300–7309. Bordwell, F. G.; Clemens, A. H.; Cheng, J.-P. *J. Am. Chem. Soc.* **1987**, *109*, 1773–1782.