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.

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-fluorenide ions, 9-R_2N-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
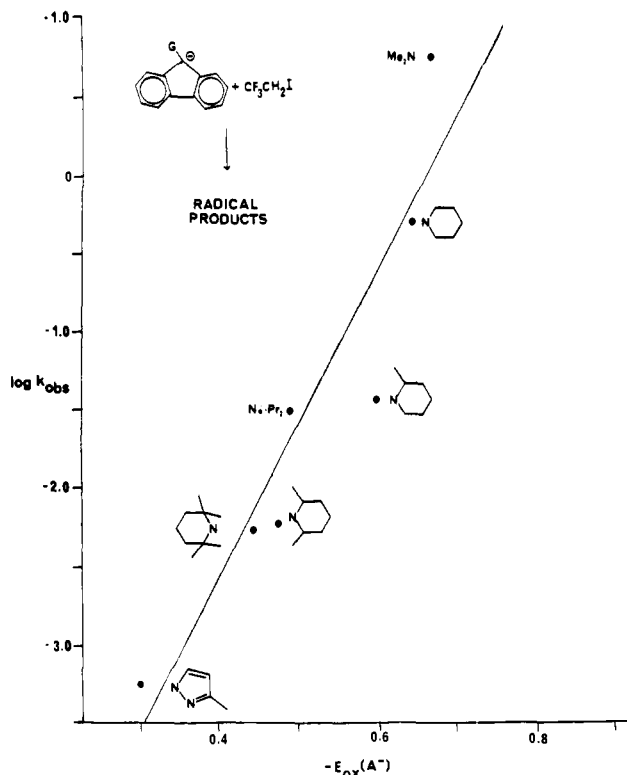
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Figure 1. Plot of log k_{obsd} for single-electron-transfer reactions of 9-dialkylaminofluorenide ions with 1,1,1-trifluoro-2-iodoethane in Me_2SO solution at 25 °C vs their oxidation potentials, $E_{ox}(A^-)$, in Me_2SO.
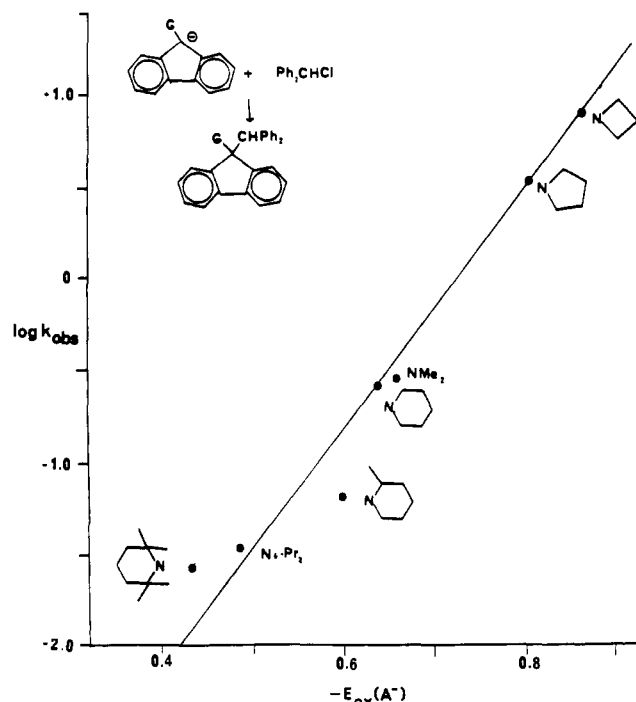

Figure 2. Plot of log k_{obsd} for substitution reactions of 9-dialkylaminofluorenide ions with benzhydryl chloride in Me_2SO solution at 25 °C vs their oxidation potentials, $E_{ox}(A^-)$, in Me_2SO.

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-Ts-1-NO_2-*c*-C_6H_{10}.[6] A linear Marcus-type plot[7] has now been observed for

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Table I. Comparison of Rates (log k_{obsd}) with Expected Rates of Single-Electron Transfer (log k_{SET}) for Reactions of 9-Dialkylaminofluorenide Ions, 9-R$_2$N-Fl$^-$, with F$_3$CCH$_2$I, Ph$_2$CHCl, and PhCH$_2$Cl

NR$_2$[a]	E_{ox}(A$^-$)[b]	F$_3$CCH$_2$I[c]		Ph$_2$CHCl[f]		PhCH$_2$Cl[g]	
		log k_{obsd}[d]	log k_{SET}[e]	log k_{obsd}[d]	log k_{SET}[e]	log k_{obsd}[d]	log k_{SET}[e]
N⟨⟩	−0.865	fast	+1.57	+0.91	+1.37	+1.35	−0.50
N⟨⟩	−0.805	fast	+1.11	+0.54	+0.92	+0.46	−0.99
NMe$_2$	−0.660	+0.75	−0.03	−0.57	−0.17	+0.27	−2.2
N⟨⟩	−0.643	−0.28	−0.17	−0.57	−0.31	+0.11	−2.4
N⟨⟩	−0.598	−1.43	−0.56	−1.21	−0.66	−1.14	−2.8
N(*i*-Pr)$_2$	−0.485	−1.50	−1.53	−1.45	−1.61	−1.00	−3.8
N⟨⟩	−0.438	−2.25	−1.91	−1.55	−1.99	−2.49	−4.2

[a] The 9-R$_2$N-FlH compounds were prepared by the reaction of 9-BrFlH with the appropriate amine; pK_a data and physical properties will be reported separately. [b] Measured by cyclic voltammetry in Me$_2$SO with Ag/AgI reference electrode;[9] referenced to the aqueous standard hydrogen electrode (SHE) by subtracting 0.125 V. [c] E_{rd} = 0.4 × (−1.425) = −0.57; λ = 60.[10] [d] Measured spectrophotometrically by monitoring the disappearance of 9-R$_2$N-Fl$^-$ ion absorbance.[5] [e] Calculated by using an equation derived from the Marcus equation by Eberson:[3] log k_{SET} = log k_d − log $\{1 + 0.2 \exp [^{\lambda}/_4(1 + (\Delta G°/4))^2/RT]\}$, where k_d is the diffusion rate in Me$_2$SO (3.3 × 10^9);[11] λ is the intrinsic barrier chosen from literature values[3b,4] to give the best fit, and $\Delta G°$ is estimated from the redox potentials.[3b] [f] E_{rd} = 0.4 × (−1.185) = −0.474 (vs SHE);[10] λ = 65; Eberson[3b] reports λ = 63 for the reaction of Ph$_2$CH$^-$ with PhCH$_2$Cl. [g] E_{rd} = −0.72 (Eberson[12]); λ = 65.

the reactions of members of the 9-R$_2$N-Fl$^-$ ion family with F$_3$C-CH$_2$I, a known electron acceptor[6] (Figure 1; Table I).

The kinetics with F$_3$CCH$_2$I were first order in each reactant but remained so for only about 1 half-life, which is typical of the nonchain SET reactions that we have studied earlier.[6] Reaction of the 9-R$_2$N-Fl$^-$ ion family with Ph$_2$CHCl, which has a slightly more positive reduction potential (E_{rd}) than F$_3$CCH$_2$I (−1.2 vs −1.4), also gave a linear Marcus-type plot (Figure 2), but here the kinetics remained second order for several half-lives, and substitution products were formed in high yield with no indication of the presence of radical products.[13] Comparison of log k_{obsd} with log k_{SET}, calculated according to the method of Eberson (Table I), shows a close correspondence of values for reactions of both F$_3$CCH$_2$I and Ph$_2$CHCl. This evidence suggests that both are reacting by SET mechanisms, F$_3$CCH$_2$I giving radical-type products[6] and Ph$_2$CHCl giving S$_N$2-type products.

Surprisingly, PhCH$_2$Cl, which has a 0.8 V less positive E_{rd} (E_p) than does Ph$_2$CHCl, also gave a linear Marcus-type plot for reactions with 9-R$_2$N-Fl$^-$ ions, and the correspondence between k_{obsd} and k_{SET} (Table I) is close enough to fall in the range that Eberson designates as "SET feasible".[3b] A similar appearing Marcus-type plot was obtained with *n*-BuBr (E_{rd} = −2.1[3b]) and the log k_{obsd} − log k_{SET} values were 3–4, which is still in the "SET feasible" range.[3b]

We conclude that the reactions of 9-R$_2$N-Fl$^-$ ions with Ph$_2$CHCl are occurring by SET involving rapid coupling of radical pair

intermediates, whereas those with PhCH$_2$Cl and *n*-BuBr are probably in the hybrid[2a] or merged[2b] region of a SET–S$_N$2 spectrum. Application of this test to other electrophiles is in progress.

Molecular Hydrogen Complexes. 5. Electronic Control of η^2-H$_2$ versus Dihydride Coordination. Dihydride Structure of MoH$_2$(CO)(R$_2$PC$_2$H$_4$PR$_2$)$_2$ for R = Et, *i*-Bu versus η^2-H$_2$ for R = Ph

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Since their discovery,[1] new examples of transition-metal molecular-hydrogen (M-η^2-H$_2$) complexes have been established at an increasingly rapid pace,[2] including several complexes previously formulated as classical hydrides (e.g., FeH$_4$(PEtPh$_2$)$_3$).[3] Equilibrium between dihydrogen and dihydride ligands has been observed in solution,[2a,2d] emphasizing that η^2-H$_2$ complexes can be considered *tautomers* of hydrides and not merely arrested

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(7) Marcus plots log k_{obsd} vs $\Delta G°'$; Figure 1 is a Marcus-type plot in the sense that, since E_{rd} is constant, changes in E_{ox}(A$^-$) are proportional to changes in $\Delta G°'$. Over large ranges of $\Delta G°'$ the Marcus equation predicts curvature, but over relatively small ranges in the endergonic region the curve is flat and essentially linear.[8]

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(12) Eberson[3a] reports E_{rd} = −0.52 V vs SHE$_{Me2SO}$. By applying −$\Delta G°_{tr}$(H$_2$O → Me$_2$SO) for the proton, we converted this value to E_{rd} vs SHE$_{aq}$ to be consistent with our E_{ox} values. The resulting value is ∼40% of our measured E_{rd}.

(13) In the reaction of 9-(I-Pr)$_2$N-Fl$^-$ ion with Ph$_2$CHCl, the presence of the persistent 9-(I-Pr)$_2$N-Fl· radical (λ_{max} = 450 nm)[6] was not observed.

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