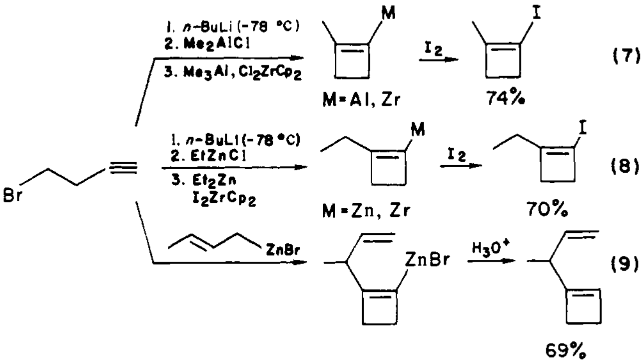
Although unclear, the role of Si in the π-type process might be mainly to increase the nucleophilicity of the alkene group through σ donation. If so, it should, in principle, be possible to replace Si with other metals. The results shown in eq 7–9 demonstrate that Si may indeed be replaced with Zn as well as with Al and/or Zr. All of these reactions appear to require two metals and involve the π-process. Unlike cycloalkenylsilanes, cycloalkenylmetals containing Al, Zn, or Zr are readily convertible into the corresponding halides and other demetalated derivatives by known methods, thereby significantly augmenting the synthetic utility of the alkenylmetal cyclization methodology.



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Supplementary Material Available: IR, MS, and ^{1}H and ^{13}C NMR of compounds mentioned (3 pages). Ordering information is given on any current masthead page.

Intramolecular Electron Transfer at Metal Surfaces. 4. Dependence of Tunneling Probability upon Donor–Acceptor Separation Distance

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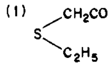
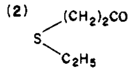
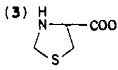
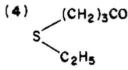
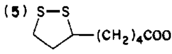
There is currently much interest in elucidating the manner in which electron transfer occurs for large separations between the donor and acceptor sites.[1-5] Activity in this area has been heightened recently with the examination of a number of binuclear transition metal and related systems in which the redox centers are separated by a variety of saturated, relatively rigid organic linkages.[1-3] These data indicate that reasonably facile electron transfer can occur over substantial distances (10–20 Å), probably via highly nonadiabatic pathways.

Table I. Rate Data for Reduction of $\mathrm{Co^{III}(NH_3)_5X}$ with Surface-Attaching Ligands X

X	surface	k_{et}^{-300},[a] s^{-1}	α_{et}[b]	k_{Ru},[c] $M^{-1}\,s^{-1}$
(1) 	Au	9.5×10^3	0.57	0.022
	Hg	4.5×10^3	0.56	
(2) 	Au	3.0×10^3	0.61	0.025
	Hg	4.0×10^3	0.60	
(3) 	Au	1.0×10^3	0.60	0.023
	Hg	5.5×10^3	0.80	
(4) 	Au	1.4×10^2	0.60	0.024
	Hg	3.0×10^3	0.60	
(5) 	Au	2.0	0.60	0.016
	Hg	5.5×10^3	0.62	

[a] Unimolecular rate constant for reduction of surface-attached complex in 0.1 M $NaClO_4$ + 5 mM $HClO_4$ at −300 mV vs. SCE, determined by using rapid linear sweep voltammetry as described in ref 6c. [b] Transfer coefficient of electron-transfer step, from $\alpha_{et} = -(RT/F)(\mathrm{d}\ln k_{et}/\mathrm{d}E)$. [c] Second-order rate constant for homogeneous reduction of Co(III) complex by $\mathrm{Ru(NH_3)_6^{2+}}$ in 0.05 M sodium trifluoracetate–trifluoroacetic acid evaluated as described in ref 6c.

A key question concerns the dependence of the electron-tunneling probability on the donor–acceptor separation distance. We have recently been examining the kinetics of a number of "surface intramolecular" processes, i.e., where one of the redox centers is replaced by a metal surface.[6] Included are surface attachment groups consisting of extended organic bridges.[6c] Here we report measurements on a series of such systems containing saturated surface anchoring groups. The results provide the first direct information on electron-tunneling–distance relationships for heterogeneous systems.

Table I contains rate data for the reduction of pentaamminecobalt(III) anchored to gold or mercury surfaces by means of a series of thioalkylcarboxylate ligands. Each ligand contains one or two strongly adsorbing sulfur atoms, being separated from the coordinated carboxylate group by means of a variable-length alkyl chain. The synthesis of these complexes followed the general procedures described in ref 6c. Each reactant is sufficiently strongly adsorbed at gold so to yield a close-packed monolayer (surface concentration, Γ, ca. $(1.5\text{–}2) \times 10^{-10}$ mol cm^{-2}) even for very low (10–50 μM) bulk concentrations. Both rate and adsorption data were obtained by using rapid linear sweep voltammetry as described in ref 6c. The rate constants, k_{et}^{-300} (s^{-1}), refer to the reduction of surface-attached Co(III) at −300 mV vs. saturated calomel electrode (SCE). [Other choices of the common potential yielded essentially the same relative values of k_{et} since the transfer coefficients, α_{et} ($=-(RT/E)(\mathrm{d}\ln k_{et}/\mathrm{d}E)$), are approximately invariant, 0.58 ± 0.02 (Table I).]

Inspection of Table I reveals that the values of k_{et}^{-300} at gold decrease substantially (ca. 10^4-fold) as the number, n, of alkyl carbons increase from one to five. Lengthening the pendant thiol

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(1) (a) Winkler, J. R.; Nocera, D. G.; Yocum, K. M.; Bordignon, E.; Gray, H. B. *J. Am. Chem. Soc.* **1982**, *104*, 5798. (b) Yocum, K. M.; Winkler, J. R.; Nocera, D. G.; Bordignon, E.; Gray, H. B. *Chem. Scr.* **1983**, *21*, 29. (c) Kostic, N. M.; Margalit, R.; Che, C.-M.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 7765.

(2) (a) Isied, S. S.; Worosila, G.; Atherton, S. J. *J. Am. Chem. Soc.* **1982**, *104*, 7659. (b) Isied, S. S.; Kuehn, C.; Worosila, G. *J. Am. Chem. Soc.* **1984**, *106*, 1722. (c) Isied, S. S.; Vassihan, A. *J. Am. Chem. Soc.* **1984**, *106*, 1726, 1732.

(3) (a) Stein, C. A.; Lewis, N. A.; Seitz, G. *J. Am. Chem. Soc.* **1982**, *104*, 2596. (b) Richardson, D. W.; Taube, H. *J. Am. Chem. Soc.* **1983**, *105*, 40.

(4) (a) Calcaterra, L. T.; Closs, G. L.; Miller, J. R. *J. Am. Chem. Soc.* **1983**, *105*, 670. (b) Huddleston, R. K.; Miller, J. R. *J. Chem. Phys.* **1983**, *79*, 5337. (c) Miller, J. R.; Calcaterra, L. T.; Closs, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 3047.

(5) (a) Larsson, S. *J. Am. Chem. Soc.* **1981**, *103*, 4034. (b) Larsson, S. *J. Chem. Soc., Faraday Trans. 2* **1983**, *79*, 1375. (c) Beretan, D. N.; Hopfield, J. J. *J. Am. Chem. Soc.* **1984**, *106*, 1585. (d) Logan, J.; Newton, M. D. *J. Chem. Phys.* **1983**, *78*(2), 4086.

(6) (a) Part 1: Barr, S. W.; Weaver, M. J. *Inorg. Chem.* **1984**, *23*, 1657. (b) Part 2: Guyer, K. L.; Weaver, M. J. *Inorg. Chem.* **1984**, *23*, 1664. (c) Part 3: Li, T. T.-T.; Liu, H. Y.; Weaver, M. J. *J. Am. Chem. Soc.* **1984**, *106*, 1233. (d) Barr, S. W.; Guyer, K. L.; Li, T. T.-T.; Liu, H. Y.; Weaver, M. J. *J. Electrochem. Soc.* **1984**, *131*, 1626.

(7) Bond distances: C–C, 1.54; C–O, 1.36; O–Co(III), 2.3; C–S, 1.8; S–Au, ca. 2.3 Å. Values taken from: Gordon, A. J., Ford, R. A., Eds. "The Chemist's Companion"; Wiley: New York, 1972; p 108.

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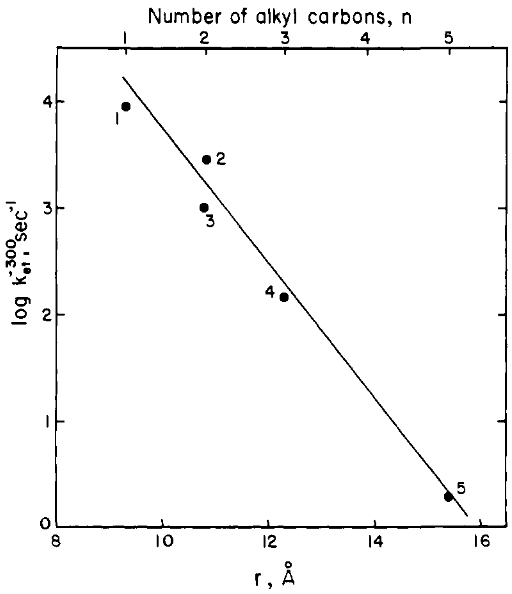

Figure 1. Plot of unimolecular rate constants for electroreduction of surface-attached $Co^{III}(NH_3)_5X$ complexes at gold electrodes at -300 mV, k_{et}^{-300}, vs. the estimated through-bond surface–Co(III) distance, r, and number of alkyl carbons, n. Data from Table I; identifying numbers as listed in Table I.

group, however, yielded only minor rate variations. These rate decreases contrast the virtually invariant second-order rate constants, k_{Ru} ($M^{-1}\ s^{-1}$), observed for the homogeneous outer-sphere reduction of these complexes by $Ru(NH_3)_6^{2+}$ (Table I). The unimolecular reduction of each complex at mercury also yielded approximately constant rates, the values of k_{et}^{-300} approximating those observed at gold for the shortest alkyl group reactants (Table I).

The tenacious adsorption at gold presumably yields a rigidly packed matrix, constraining the Co(III) redox center to lie progressively further from the metal surface as the number of bridging alkyl carbons increases. The reactant bound to mercury, on the other hand, should be markedly more flexible since submonolayer adsorption ($\Gamma \sim 5 \times 10^{-11}$ mol cm^{-2}) is involved, presumably enabling Co(III) to closely approach the metal surface in each case. Although there is evidence[8,9] that the values of k_{et} seen at mercury for these, as for similarly nonconjugated reactants,[6c] reflect moderately nonadiabatic pathways (where the transmission coefficient $\kappa_{el} \sim 0.05$[8]), this flexibility therefore appears to provide an alternative "through-space" mechanism irrespective of the alkyl chain length (cf. homogeneous systems[2c]). Consequently, the striking decrease in k_{et} seen at gold is attributed to the progressive diminution of κ_{el} as the surface–Co(III) separation distance increases. The rigid impervious nature of the adsorbed layers at gold is also evidenced by comparable (up to ca. 10^4-fold) rate decreases observed for the *outer-sphere* reduction of $Co(NH_3)_5OAc^{2+}$ (OAc = acetate) upon coating the gold surface with these films.

Figure 1 is a plot of log k_{et}^{-300} at gold for the five reactants against the estimated bond distances, r, between the metal surface and the Co(III) redox centers[7] (or similarly, against n). The approximately linear plot observed is consistent with the relation[10]

$$\kappa_{el}^{r_2} = \kappa_{el}^{r_1} \exp[-\beta(r_2 - r_1)] \qquad (1)$$

for a pair of donor–acceptor distances r_1 and r_2. The slope of the straight line shown in Figure 1 yields $\beta = 1.45$ Å^{-1}. This value is very close to that predicted, 1.4 Å^{-1}, for electron tunneling in a medium via a square 2-eV barrier.[11] Similar values of β have also been obtained from ab initio calculations for outer-sphere electron transfer.[5d] A comparable value, ca. 1.3 Å^{-1}, is obtained from rate data[2c] for electron tunneling through oligoproline bridging ligands, although the distance dependence of k_{et} was attributed[2c] partly to changes in the solvent reorganization barrier ΔG^*_{os}. This latter factor is less likely to influence the $k_{et} - r$ dependence for electrochemical reactions since ΔG^*_{os} should be almost independent of r for $r \gtrsim 6$ Å.[12]

The present data can also be utilized to roughly estimate *absolute* values of κ_{el}, assuming that the observed rates at mercury, $k_{et}^{-300} \approx 5 \times 10^3\ s^{-1}$, correspond to $\kappa_{el} \sim 0.05$ (vide supra). From this we deduce that $\kappa_{el} \sim 2 \times 10^{-5}$ for $n = 5$ at gold, for which $r \sim 15$ Å (Figure 1) (cf. ref 1). Of course, the actual surface–Co(III) distances may be shorter than the estimates in Figure 1 if the carbon linkages are somewhat staggered. Assuming 120° bond angles diminishes the effective r values about 15%. Even though a distribution in the surface–Co(III) distances will result from variations in the film structure, the measured k_{et} values will tend to reflect the smaller distances since k_{et} increases with decreasing r.

The present results are compatible with our recent deduction for some related outer-sphere electrochemical reactions that $\kappa_{el} < 1$ for $r \gtrsim 6$ Å[13] (cf. homogeneous reactions[5d]). These results apparently refute the claim[14] that heterogeneous electron transfer will be adiabatic even at large (10–20 Å) separations due to the continuum of electronic states at metal surfaces. Rather they reveal striking behavioral similarities for electron tunneling in heterogeneous and homogeneous environments.

Acknowledgments. This work is supported by the Air Force Office of Scientific Research and the Office of Naval Research. M.J.W. acknowledges a fellowship from the Alfred P. Sloan Foundation.

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(8) Li, T. T.-T.; Guyer, K. L.; Barr, S. W.; Weaver, M. J. *J. Electroanal. Chem. Intefacial Electrochem.* **1984**, *164*, 27.

(9) Li, T. T.-T.; Weaver, M. J., manuscript in preparation.

(10) Note that the coefficient β (Å^{-1}) in eq 1 will be *twice* the corresponding value obtained from relations where the electronic coupling matrix element is employed instead of κ_{el}.

(11) Hopfield, J. J. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 3640. Also see: Marcus, R. A.; Siders, P. *J. Phys. Chem.* **1982**, *86*, 622.

(12) For example, see: Weaver, M. J. *J. Phys. Chem.* **1980**, *84*, 568.

(13) Hupp, J. T.; Weaver, M. J. *J. Phys. Chem.* **1984**, *88*, 1463.

(14) (a) Hale, J. M. *J. Electroanal. Chem. Interfacial Electrochem.* **1968**, *19*, 315. (b) Hale, J. M. "Reactions of Molecules at Electrodes"; Hush, N. S., Ed.; Interscience: New York, 1971; Chapter 4. (c) Doganadze, R. R.; Kuznetsov, A. M.; Vorotyntsev, M. A. *J. Electroanal. Chem. Interfacial Electrochem.* **1970**, *25*, Appendix 17.

Synthesis and Spectral Characterization of Methylenecycloproparene Derivatives[1]

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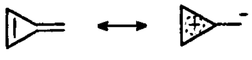
While the first derivatives of methylenecyclopropene were isolated over 20 years ago,[3] the resonance-stabilized parent hydrocarbon **1** eluded detection[4] unitl 1976 and has only recently been prepared and characterized.[5] By comparison the highly



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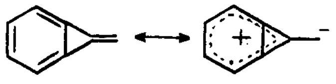

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(1) Studies in the Cycloproparene Series. For the previous part, see: Halton, B.; Randall, C. J. *J. Am. Chem. Soc.* **1983**, *105*, 6310–6311.

(2) (a) Victoria. (b) Fulbright scholar and visiting Professor University of Utah 1981–1982. (c) Utah.

(3) Kende, A. S. *J. Am. Chem. Soc.* **1963**, *85*, 1882–1884. Battiste, M. A. *Ibid.* **1964**, *86*, 942–944. Review: Eicher, T.; Weber, J. L. *Top. Curr. Chem.* **1975**, *57*, 1.

(4) Billups, W. E.; Blackeney, A. J.; Chamberlain, W. T. *J. Org. Chem.* **1976**, *41*, 3771–3772. Billups, W. E.; Blakeney, A. J.; Rao, N. A.; Buynak, J. D. *Tetrahedron* **1981**, *37*, 3215–3220.

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