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.

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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
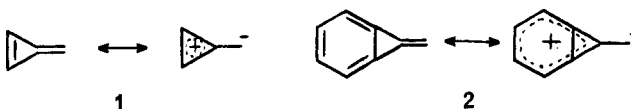
been prepared and characterized.[5]   By comparison the highly

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

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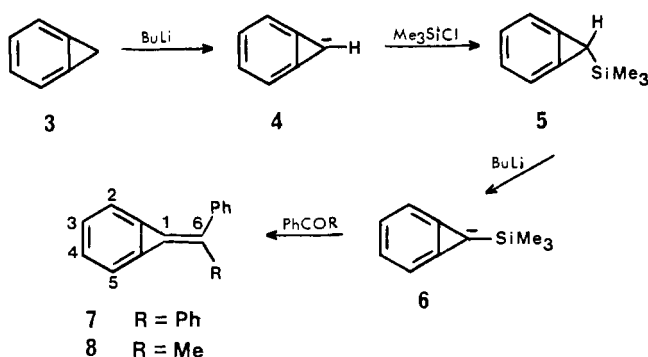
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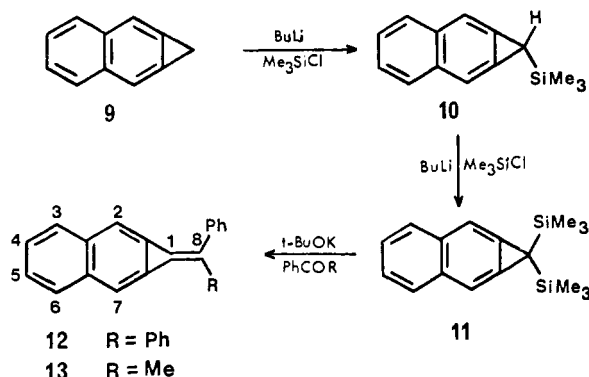
(9) Li, T. T.-T.; Weaver, M. J., manuscript in preparation.

(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}.

Communications to the Editor

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Scheme I

7 R = Ph
8 R = Me

Scheme II

12 R = Ph
13 R = Me

strained methylenecycloproparenes, e.g., **2**, are unknown. We now report the successful synthesis[6] of the methylenecyclopropabenzenes **7** and **8** and their cyclopropa[*b*]naphthalene analogues **12** and **13**.

The acidity of the benzylic protons of cyclopropabenzene (**3**) is greater than that of toluene making the cyclopropabenzenyl anion (**4**) readily available.[7] Metalation (BuLi) of **3** and quenching with chlorotrimethylsilane is known[7] to deliver **5**, and, to our knowledge, this is the only example of the use of a cyclopropabenzenyl anion in synthesis.[8] The facility of silicon to stabilize an α-anion[9] and the synthetic utility of the Peterson olefination[9,10] suggested that alkylidenecycloproparenes, e.g., **7**, may be available by the route depicted in Scheme I. We have found this to be the case, but in practice it is more efficient to convert **3** into the alkylidenecyclopropabenzenes **7**[11] and **8**[12] in a "one-pot" procedure without isolating **5**. Thus, sequential treatment of **3** with molar equivalents of the reagents indicated in Scheme I delivers **7** as a stable, yellow, crystalline solid[11] and

8 as a less stable oil[12] in yields of 41% and 10%, respectively. The meager yield of **8** is thought to be due to effective competition from enolate formation and regeneration of **5**; with benzophenone as substrate such competition is avoided.

Quenching of the anion derived from cyclopropa[*b*]naphthalene (**9**) with chlorotrimethylsilane delivers the bis(silyl) derivative **11** (40%)[13] and not the anticipated **10** (Scheme II). Compound **9** is also recovered (49%) from the reaction, and it seems likely that **10** is deprotonated immediately upon formation[14] by the anion of **9**. Treatment of **11** with potassium *tert*-butoxide[15] in the presence of benzophenone in dry tetrahydrofuran results in an almost quantitative conversion to the methylenecyclopropa[*b*]-naphthalene **12** as a stable, yellow, crystalline solid.[16] With acetophenone **11** provides the derivative **13**[17] also as a stable yellow solid, but as with the conversion **3** → **8**, the yield is significantly reduced (41%).

The assignment of alkylidenecycloproparene structure of **7, 8, 12**, and **13** is fully consistent with their spectral data.[11,12,16,17] The ^{13}C NMR spectra are particularly informative and reveal that the aromatic methine carbons adjacent to the three-membered ring are more shielded than in their precursors or other cycloproparenes.[8] Thus C2(5) of **7** and **8** appear at ~110.5 ppm (cf. 114.7 ppm in **3**[18]) while C2(7) of **12** and **13** resonate at ~106.9 ppm (cf. 112.3 ppm in **9**[19]). Moreover, the non-equivalence of these centres in **8**[12] and **13**[17] is apparent. The presence of the exocyclic double bond is shown by the appearance of two low-intensity quaternary sp^2-carbon resonances for each compound with C1 at ~111 ppm, and extended conjugation is evident from their color. The electronic spectra (in cyclohexane) display absorption maxima approaching 380 nm for the methylenecyclopropabenzenes[11,12] and 430 nm for the naphthalene analogues.[16,17] More importantly the long-wavelength band, of, for example, **7**, suffers a blue shift of 5 nm when recorded in acetonitrile. Although this shift is not great,[3] when taken in conjuction with moderate infrared absorption at ~1780 cm^{-1} some contribution to the structure of the methylenecycloproparenes from charge separated forms (cf. **2**) could be implied.[3-5] More definitive data could stem from structural parameters and from the provision of less heavily substituted derivatives; appropriate studies are under way.

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(11) Compound **7** may be named as 1-(diphenylmethylene)bicyclo-[4.1.0]hepta-1,3,5-triene since fusion nomenclature requires that cyclopropabenzene (**3**) be named as bicyclo[4.1.0]hepta-1,3,5-triene: mp 89.5–91 °C. Anal. (C$_{20}$H$_{14}$) C, H. ^{1}H NMR δ 7.0–7.8 (m); ^{13}C NMR δ 110.7 (C2/C5), 111.3 (C6), 113.3 (C1), 126.3 (C10), 127.6 (C9/C9′, C11/C11′), 128.4 (C8/C8′, C12/C12′), 132.7 (C1a/C5a), 133.2 (C3/C4), 140.1 (C7/C7′); λ$_{max}$ (C$_6$H$_{12}$) 249 (4.34), 265 (sh, 4.25), 385 (4.41), 405 nm (sh, log ε 4.32); λ$_{max}$ (CH$_3$CN) 380 nm (4.49); ν̄$_{max}$ (KBr) 3055, 1775, 1595, 1530, 1495, 1440, 1350, 1150, 775, 738, 695 cm^{-1}.

(12) Compound **8** may be named as 1-(1-phenylethylidene)bicyclo-[4.1.0]hepta-1,3,5-triene: Anal. (C$_{15}$H$_{12}$) C, H. ^{1}H NMR δ 2.37 (s, CH$_3$), 7.0–7.5 (m, 7 H), 7.74 (d of d, *J* = 1.3 and 8.0 Hz, 2 H); ^{13}C NMR δ 18.3 (CH$_3$), 103.9 (C6), 110.2 and 110.5 (C2/C5), 111.4 (C1), 124.3 (C9/C11), 125.6 (C10), 128.4 (C8/C12), 132.0 and 132.7 (C3/C4), 134.1 (C1a or C5a), 140.3 (C7); λ$_{max}$ (C$_6$H$_{12}$) 242 (4.04), 249 (4.09), 256 (sh, 3.95), 357 (sh, 4.15), 371 (4.26), 394 nm (log ε 4.12); ν̄$_{max}$ (film) 3085, 2940, 1797, 1595, 1495, 1460, 1455, 1365, 1343, 1115, 765, 748, 700 cm^{-1}.

(13) Compound **11** may be named as 1,1-bis(trimethylsilyl)-1*H*-cyclopropa[*b*]naphthalene: mp 95–96 °C. Anal. (C$_{17}$H$_{24}$Si$_2$) C, H. ^{1}H NMR δ 0.01 (s, 18 H), 7.05 (s, 2 H), 7.30 (m, 2 H), 7.65 (m, 2 H); ^{13}C NMR δ −1.3 (CH$_3$), 29.3 (C1), 107.9 (C2/C7), 124.7 (C4/C5), 127.4 (C3/C6), 131.3 (C1a/C7a), 136.2 (C2a/C6a).

(14) It has not proved possible to isolate **10** despite many variations in the experimental procedures. The yield of **11** has been increased to 76% from a complex series of manipulations, details of which will be provided in the full paper.

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(16) Compound **12** may be named as 1-(diphenylmethylene)cyclopropa-[*b*]naphthalene: mp 110–111 °C. Anal. (C$_{24}$H$_{16}$) C, H. ^{1}H NMR δ 7.1–7.4 (m, 10 H), 7.5–7.8 (m, 6 H); ^{13}C NMR δ 107.3 (C2/C7), 112.0 (C1), 120.0 (C8), 126.7 and 127.4 (C4/C5, C12/C12′), 128.2 and 128.5 (C10/C10′, C11/C11′, C13/C13′, C14/C14′), 128.8 (C3/C6), 138.9 and 139.6 (C2a/C6a, C9/C9′); λ$_{max}$ (C$_6$H$_{12}$) 230 (4.61), 251 (4.34), 260 (sh, 4.32), 270 (sh, 4.28), 291 (4.13), 412 (4.48), 438 nm (log ε = 4.52). ν̄$_{max}$ (KBr) 3050, 1765, 1590, 1485, 1440, 1410, 1340, 1130, 843, 838, 760, 750, 740, 690 cm^{-1}.

(17) Compound **13** may be named as 1-(1-phenylethylidene)cyclopropa-[*b*]naphthalene: mp 94–95 °C. Anal. (C$_{19}$H$_{14}$) C, H. ^{1}H NMR δ 2.52 (s, CH$_3$), 7.2–7.6 (m, 7 H), 7.7–8.0 (m, 4 H); ^{13}C NMR δ 18.9 (CH$_3$), 106.6 and 106.9 (C2/C7), 110.3 (C1), 113.8 (C8), 125.1 and 126.4 (C4/C5, C11/C13), 126.8 (C12), 128.4 (C10/C14), 128.6 and 128.7 (C3/C6), 129.0 (C1a or 7a), 138.1, 138.7, and 139.6 (C2a/6a/9); λ$_{max}$ (C$_6$H$_{12}$) 230 (4.70), 242 (sh, 4.38), 253 (sh, 4.24), 289 (4.38), 377 (sh, 4.32), 294 (4.62), 412 (sh, 4.49), 422 nm (log ε 4.72). ν̄$_{max}$ (KBr) 3050, 2980, 1775 (w), 1590, 1505, 1490, 1440, 1415, 1245, 1175, 1155, 1145, 845, 760, 745, 690 cm^{-1}.

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Scheme I

Synthesis of Dialkylruthenium Nitrosyls and Thermal Conversion to Ruthenium Oximate, Carboxamide, and Cyano Complexes

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Several years ago, in search of homogeneous models for the metal-catalyzed oxidation of propylene to acrylonitrile, a group at Du Pont[1] uncovered a reaction in which an allyl group and a nitric oxide ligand underwent conversion to an oxime π-complexed to nickel. This discovery presaged a growing number of processes in which coordinated nitric oxide can be used to form new carbon–nitrogen bonds in organic molecules.[2] We wish to report here some unusual ruthenium chemistry germane to the understanding of such processes, which includes the observation of (1) the transformation of coordinated nitric oxide into oxime functionality σ-bound to the metal, (2) in one system, the rearrangement to an isomeric amide structure, and (3) in another system, dehydration of the oxime, leading to coordinated cyanide.

Our results are summarized in Scheme I. Nitric oxide was introduced into the coordination sphere of ruthenium by treating Cp*Ru(CO)$_2$Cl (Cp* = η^5-C$_5$Me$_5$)[3] with NOCl[4] in methylene chloride at room temperature. After chromatography on silica gel and recrystallization from boiling toluene, air-stable dark green crystals of Cp*(NO)RuCl$_2$ (1) were obtained in 53% yield.[5] After experimenting with a variety of alkylating agents, the transformation of 1 to the dialkyl complexes 2 was found to be most cleanly achieved with trialkylaluminum compounds. Thus treatment of a slurry of 1 in toluene with a dilute solution of AlMe$_3$ gave red-orange crystalline 2a in 67% yield. The diethyl complex 2b was prepared in a similar manner from AlEt$_3$ in 56% yield and also forms red-orange crystals. Both 2a and 2b are slightly air sensitive, in solution and as solids, and were purified by sublimation at 60 and 50 °C, respectively, at 10^{-4} torr.

In contrast to the closely related complex[6] CpFe(NO)Me$_2$, which slowly decomposes at room temperature, complexes 2 are remarkably thermally stable. In the absence of phosphine, dimethyl complex 2a decomposes slowly at 120 °C over 24 h, leading to intractable products. However, thermolysis in benzene at 150 °C for 20 h in the presence of trimethylphosphine produces a new material having an intense IR absorption at 2060 cm^{-1} and resonances in the ^{1}H NMR spectrum at δ 1.66 (t, 15 H, J = 1.4 Hz) and 1.16 (virtual triplet, 18 H, $J + J$ = 8.4 Hz). This, as well as other spectral evidence, is consistent with the formulation of this material as the metal cyanide Cp*Ru(PMe$_3$)$_2$(CN) (3, Scheme I). Compound 3 is isolated as yellow crystals in 51% yield. Water and methane are also produced in this reaction (identified by GC/MS and quantified by GC and ^{1}H NMR). Complex 3 may be prepared independently by treatment of Cp*Ru(PMe$_3$)$_2$Cl[7]
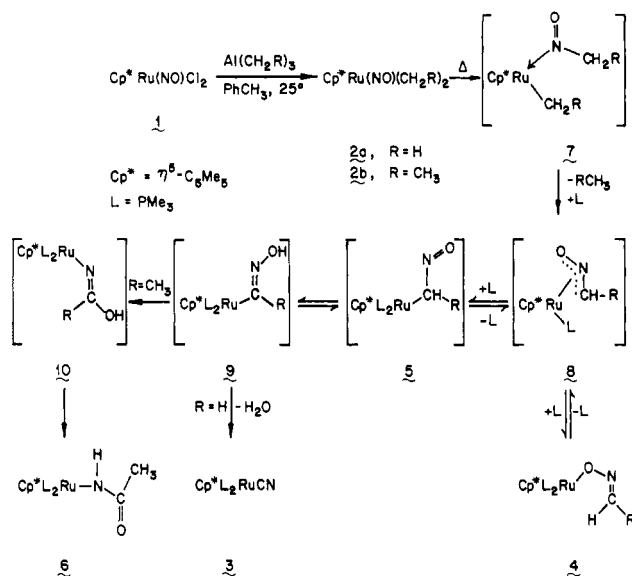
with potassium cyanide in methanol.[8]

Additional insight as to how this cyanide complex may be formed is provided by thermolysis of the corresponding diethyl complex 2b in the presence of trimethylphosphine. This reaction proceeds, under somewhat milder conditions (85 °C in benzene), with extrusion of 0.82 equiv of ethane (as determined by GC/MS and quantified by GC; 0.09 equiv of ethylene is also formed); it gives as the organometallic product a yellow crystalline material analyzing correctly for the formula C$_{18}$H$_{37}$NOP$_2$Ru in 76% isolated yield. In addition to resonances for one Cp* and two trimethylphosphine ligands in the ^{1}H NMR (δ 1.55 (t, 15 H, J = 1.4 Hz), 1.28 (virtual triplet, 18 H, $J + J$ = 8.2 Hz)), it exhibits resonances characteristic of one vinylic hydrogen and methyl group (δ 6.43 (q, 1 H), 2.17 (d, 3 H)) weakly coupled to one another (J = 5.2 Hz). We therefore propose a ruthenium oximate (aza enolate) (Cp*L$_2$Ru(ONCHCH$_3$)) formulation for this complex. That the carbon attached to nitrogen is in fact sp^2 hybridized is confirmed by the ^{13}C–H coupling constant of 172.7 Hz measured in the gated carbon spectrum. This requires that the ruthenium oximate has the unusual[9] (at least for a late-transition-metal complex) oxygen–metal bound structure 4 rather than the analogous carbon–metal bound structure 5. Thermolysis of 4 at 75 °C for 4.5 h in benzene leads (35%) to an isomeric crystalline yellow material containing an exchangeable, rather than vinylic, hydrogen, which spectral data demonstrate to be the N-ruthenium amide complex 6. Confirmation of this assignment was obtained by independent synthesis of 6 from Cp*Ru(PMe$_3$)$_2$Cl and CH$_3$CONHLi in Me$_2$SO. The transformation of 4 to 6 is strongly inhibited by added phosphine. This explains why 6 is not formed at the higher temperature at which 4 is prepared. Furthermore, if dimethylphenylphosphine is added instead of trimethylphosphine, phosphine substitution is observed before isomerization.[10]

We propose the pathways outlined in Scheme I to explain these observations. The process is presumably initiated by migratory insertion of NO into one of the metal alkyl bonds,[6,11] leading to nitrosoalkane intermediate 7. Transfer of a hydrogen to the metal center from the carbon adjacent to nitrogen (this can be viewed either as β-elimination cyclometallation), reductive elimination

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