

Figure 1. Temperature dependence of the electron-transfer rate constant k_{et} . The experimental data are matched well by the solid line which is the prediction of eq 1 with parameters determined from ΔG° dependence with inclusion of the temperature dependence of the solvent reorganization energy $\lambda_s(T)$. The dotted line represents the predicted k_{et} evaluated in the same procedure except that λ_s was fixed to the room temperature value.

will occur in the solvent for this simple charge shift reaction, which destroys a solvation environment around the reactant, B^- , but creates a similar one around the product, N^- . The finding that $|\Delta S^\circ|$ is small is different from the observation on the triplet energy transfer study,¹¹ where a substantial entropy change appears to arise from changes in the inter-ring torsional mode of biphenyl.

$\lambda_s(T)$. The temperature dependence of λ_s was estimated by the dielectric continuum model ($\lambda_s \propto (1/\epsilon_{op} - 1/\epsilon_s)$)¹² and measurements of the temperature dependence of the optical (ϵ_{op})¹³ and static (ϵ_s)¹⁴ dielectric constants. λ_s increased by 20% as T decreased from 100 to -94°C . Considering only the change in ϵ_s (or only ϵ_{op}) λ_s increased by 43% (or decreased by 23%). While there is reason to doubt the accuracy of the dielectric continuum result, the correction to ΔH^* is small, so that only a large error in the correction would seriously affect the calculated ΔH^* .

Activation Energy, ΔH^* . The solid line in Figure 1 is k_{et} calculated by eq 1 with the temperature-dependent values of λ_s . The calculated k_{et} almost perfectly matches the measured k_{et} without any adjustable parameters. In accordance with eq 1 the activation enthalpy ΔH^* is evaluated as $Rd[\ln(k_{et}\sqrt{T})]/d(1/T)$, where R is the gas constant. The directly measured ΔH^* is 0.215 ± 0.005 eV (4.96 kcal/mol), the calculated ΔH^* is 0.216 eV with experimentally determined $\lambda_s(T)$. This excellent agreement (0.5%) is certainly fortuitous because the calculated ΔH^* is much more uncertain. If the temperature dependence of λ_s is not taken into account, the calculated $\Delta H^* = 0.166$ eV (the dashed line in Figure 1), which is 23% less than the experimental value.

In conclusion we have studied an ET reaction which is well-suited to quantitative tests of ET theory because the rate and the thermodynamics are precisely measurable as a function of temperature. An excellent correlation between temperature dependence and ΔG° dependence of the long-range intramolecular electron transfers of organic anions at normal region was found. In contrast recent work on photosynthetic reaction centers will require a more sophisticated model.¹⁵ Work in the inverted region is in progress which will help to further reveal the important aspects of nuclear tunneling and electron-transfer dynamics.

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Synthesis, Characterization, and Reactivity of a Formally Rhenium(I) Terminal Oxo Complex, $\text{NaRe}(\text{O})(\text{RC}\equiv\text{CR})_2^1$

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The terminal oxo ligand is most commonly found in high oxidation state transition metal complexes; with oxidation states $<+4$ or electron configurations $>d^2$, oxo ligands usually bridge two or more metal centers.⁴ Octahedral d^4 terminal oxo complexes, such as the FeO^{2+} unit implicated in catalysis by cytochrome P-450 enzymes,⁵ are highly reactive species in part because metal-oxygen antibonding orbitals are populated.^{4,6} We have been studying d^4 rhenium(III) oxo bis(acetylene) compounds $\text{Re}(\text{O})\text{X}(\text{RC}\equiv\text{CR})_2$ that are stable and relatively unreactive because in their tetrahedral structure no $\text{Re}-\text{O}$ antibonding orbitals are occupied.⁷ This report describes the addition of two more electrons to the rhenium(III) compounds to give remarkable rhenium terminal oxo compounds, $\text{NaRe}(\text{O})(\text{RC}\equiv\text{CR})_2$, in which the metal is formally rhenium(I), d^6 .

Reduction of $\text{Re}(\text{O})\text{I}(\text{RC}\equiv\text{CR})_2$ ($\text{R} = \text{Me}$, **1a**; Et , **1b**; Ph , **1c**)^{7,8} with 1 equiv of sodium or sodium naphthalenide ($\text{NaC}_{10}\text{H}_8$) in THF gives NaI and the rhenium dimers $\text{Re}_2\text{O}_2(\text{RC}\equiv\text{CR})_4$.⁹ The use of 2 equiv of reducing agent at -78°C yields rhenium oxo bis(acetylene) anions: orange $\text{NaRe}(\text{O})(\text{RC}\equiv\text{CR})_2$ ($\text{R} = \text{Me}$, **2a**; Et , **2b**) or red-purple $\text{NaRe}(\text{O})(\text{PhC}\equiv\text{CPh})_2$ (**2c**).¹⁰

Complex **2c** crystallizes from acetonitrile as $\text{NaRe}(\text{O})(\text{PhC}\equiv\text{CPh})_2 \cdot 2\text{MeCN}$, with pairs of $[\text{Re}(\text{O})(\text{PhC}\equiv\text{CPh})_2]^-$ anions linked through the oxo ligands to $\text{Na}(\text{MeCN})_2^+$ cations (Scheme I).¹¹ The rhenium center is coordinated only to an oxo and two acetylene ligands, in a roughly trigonal planar arrangement (the Re is 0.12 \AA out of the plane defined by the oxo and the acetylene midpoints). The structure is similar to those of the rhenium(III) complexes $\text{Re}(\text{O})\text{X}(\text{RC}\equiv\text{CR})_2$,^{7,12} except that the fourth ligand (X) is missing. These structures all have approximate mirror symmetry, and the acetylene ligands lie in a plane roughly perpendicular to the $\text{Re}-\text{O}$ axis and are not parallel but splayed. In

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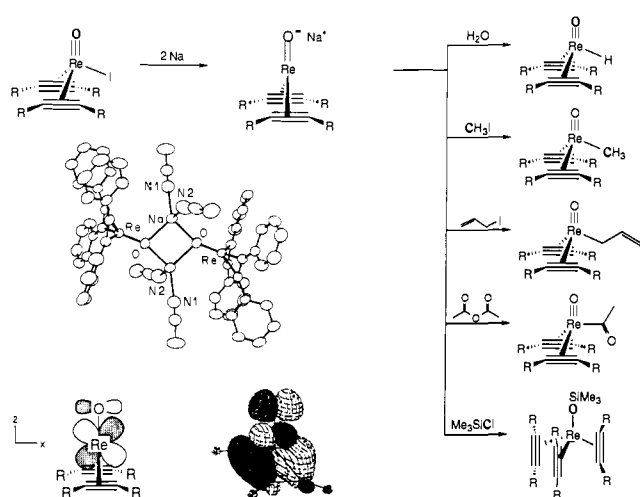
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(10) Selected NMR (CD_3CN) and IR (Nujol) data are as follows. **2a**: ^1H 2.74 (s); $^{13}\text{C}\{^1\text{H}\}$ (C_6D_6) 166.3, 19.9; IR 835, 805 (ReO). **2b**: ^1H 3.04, 2.98 (each m, 4 H, CH_2CHH), 1.23 (12 H, t, 7 Hz, CH_2CH_2); $^{13}\text{C}\{^1\text{H}\}$ 171.2, 27.9, 16.1; IR 830, 804 (ReO). **2c**: ^1H 7.67 (8 H, d, 8 Hz), 7.29 (8 H, t, 8 Hz), 7.14 (4 H, t, 8 Hz); $^{13}\text{C}\{^1\text{H}\}$ 172.2 ($\text{PhC}\equiv\text{CPh}$).

(11) Crystal data for **2c**: $2\text{CD}_3\text{CN}$: monoclinic, $P2_1/c$, $a = 11.640$ (2) Å , $b = 12.648$ (2) Å , $c = 19.668$ (4) Å , $\beta = 99.19$ (2)°, $V = 2858$ (2) Å^3 , $Z = 4$; 7179 reflections to $2\theta = 55^\circ$ were collected by using a CAD4 diffractometer ($\text{Mo K}\alpha$). Refinement^{12c} of 334 parameters based on 4325 independent observed reflections converged to $R_F = 0.032$, $R_{wF} = 0.035$, and $\text{GOF} = 1.28$; $\text{Re}-\text{O}$, 1.756 (3) Å ; $\text{Re}-\text{C}1$, 2.019 (5); $\text{Re}-\text{C}2$, 1.994 (5); $\text{Re}-\text{C}3$, 1.995 (6); $\text{Re}-\text{C}4$, 2.017 (6); $\text{C}1-\text{C}2$, 1.312 (7); $\text{C}3-\text{C}4$, 1.319 (7); $\text{O}-\text{Na}$, 2.274 (4); $\text{O}-\text{Na}'$, 2.301 (4); $\text{O}-\text{Re}-\text{C}1$, 123.4 (2)°; $\text{O}-\text{Re}-\text{C}2$, 114.8 (2); $\text{O}-\text{Re}-\text{C}3$, 114.8 (2); $\text{O}-\text{Re}-\text{C}4$, 125.8 (2); $\text{C}1-\text{Re}-\text{C}4$, 91.7 (2); $\text{C}2-\text{Re}-\text{C}3$, 123.9 (2); $\text{Re}-\text{O}-\text{Na}$, 157.7 (2); $\text{Re}-\text{O}-\text{Na}'$, 112.8 (2); $\text{Na}-\text{O}-\text{Na}'$, 89.5 (1); $\text{O}-\text{Na}-\text{O}'$, 90.5 (1).

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Scheme I



solution, NMR spectra of complexes **2**¹⁰ indicate a more symmetrical C_{2v} structure and suggest that acetylene rotation is not facile (the methylene hydrogens in **2b** are diastereotopic).

The rhenium-oxo distance of 1.756 (3) Å is indicative of substantial multiple bonding, but it is one of the longest reported for rhenium monooxo complexes^{13,14} (compare 1.70 ± 0.02 Å in six $\text{Re}(\text{O})\text{X}(\text{MeC}\equiv\text{CMe})_2$ structures^{7,12}). The Re-O distance in **2c**-2MeCN is more comparable to an Re-O double bond distance (average 1.76 Å in *trans*- ReO_2 species) than the Re-O triple bond present in most rhenium monooxo compounds (average 1.69 Å).¹⁴ The Re-O stretching frequencies in **2a-c** are much lower than in the Re(III) analogues, for instance, 824 cm^{-1} in **2c** ($\nu(\text{Re}-^{18}\text{O}) = 763 \text{ cm}^{-1}$) vs 972 cm^{-1} in **1c**. In the presence of 15-crown-5, $\nu(\text{Re}-\text{O})$ is 885 cm^{-1} , indicating that only part of the large shift is due to the Na-O interaction.

The bond length and low stretching frequencies suggest that Re-O bonding in **2** is weaker than that in **1**. Preliminary calculations¹⁵ indicate that this is due to the population of a Re-O antibonding orbital: the two added electrons occupy the d_{xz} orbital in the mirror plane of the molecule (see drawings in Scheme I) which is Re-O π^* and rhenium-acetylene π backbonding. High electron density in this orbital is consistent with the location of the Na^+ ions in the xz plane in the crystal structure. Strong backbonding to the acetylenes is indicated by the short Re-C distances (average 2.006 (5) Å compared to 2.051 (5) Å for the Re-2-butyne distances in **1a**), the long C=C distances (average 1.316 (7) Å),¹⁶ and the low C=C stretching frequencies (1685 cm^{-1} in **2a** vs 1800 cm^{-1} in **1a**). The presence of significant backbonding complicates the oxidation state assignment: **2a-c** can also be considered as Re(III) if the added electrons are taken to be on the acetylenes rather than the metal, although **2a-c** are nucleophilic at the metal, not at the acetylene ligands.

Compounds **2** are readily protonated (with water), alkylated (with methyl or allyl iodide), and acylated (with acetic anhydride) to form rhenium hydride, methyl, allyl,^{12c} and acyl complexes^{12d} (Scheme I). The high nucleophilicity of the rhenium center is unprecedented for metal-oxo complexes.¹⁷ Reaction with Me_3SiCl , however, forms a siloxide complex; in the presence of added acetylene, $\text{Re}(\text{OSiMe}_3)(\text{RC}\equiv\text{CR})_3$ is obtained in 30-40% yield. Compounds **2** are rapidly oxidized by atmospheric oxygen

or Cp_2FeBF_4 to give $\text{Re}_2\text{O}_2(\text{RC}\equiv\text{CR})_4$ dimers.⁹ Further studies are in progress to explore the properties and reactivity of compounds **2**, rare examples of terminal oxo complexes in which metal-oxygen antibonding orbitals are populated.

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Registry No. **1a**, 90623-35-1; **1b**, 98778-24-6; **1c**, 123170-29-6; **2a**, 123170-30-9; **2b**, 123170-31-0; **2c**, 123170-32-1; **2c**-2CD₃CN, 123170-35-4; **12a**, 123170-36-5; $\text{Re}(\text{OSiMe}_3)(\text{EtC}\equiv\text{CEt})_3$, 123170-37-6; $\text{EtC}\equiv\text{CEt}$, 928-49-4.

Supplementary Material Available: Preparations and spectroscopic and analytical data for **2a-c**, $\text{Re}(\text{O})[\text{C}(\text{O})\text{Me}](\text{MeC}\equiv\text{CMe})_2$, and $\text{Re}(\text{OSiMe}_3)(\text{EtC}\equiv\text{CEt})_3$ and tables of the data collection and refinement details, atom parameters, bond distances, bond angles, and least-squares planes for **2c**-2CD₃CN (13 pages); listing of observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

Chelate-Assisted, Pd-Catalyzed Efficient Carbonylation of Aryl Chlorides

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Palladium-catalyzed carbonylation of aryl halides under mild pressure forms the basis for a number of synthetically useful reactions, including the syntheses of carboxylic acids,^{1,2} esters,^{1,3} lactones,^{1,4} amides^{1,5} lactams,^{1,6} keto esters, and keto amides,^{7,8} and considerable effort has been devoted to the study of the scope and mechanisms of these reactions. One serious limitation common to all of these reactions, which hinders industrial utilization, is the fact that aryl chlorides, which are obviously more attractive as starting materials than the aryl bromides and iodides, are generally unreactive.⁹ Recently, activation of aryl chlorides

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