class of monometallic acyl hydrides[15,16] and is unusual even among this group. Most other known examples have been prepared by oxidative addition of aldehydes to late-transition-metal centers, and none are as electron-deficient as this cationic Nb(V) derivative. In spite of this, **4** shows no tendency (at 25 °C) to eliminate aldehyde, presumably because this is precluded by the O-inside geometry. If **4** is treated with 2 equiv of sodium, it reverts to the ketene hydride complex **3**; mechanistic studies are in progress.

In summary, then, we have utilized metal-ketene precursors to prepare and characterize the first acylniobocene compounds. These highly substituted derivatives show a tendency to degrade via $\beta$-H elimination, giving ketene-hydride complexes. Studies of the chemistry of these and related compounds are ongoing.

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**Supplementary Material Available:** Tables of spectral and analytical data for **2** and **4**, synthetic procedures, and listings of unit cell data, bond lengths and angles, atomic coordinates, and thermal parameters for **2** (11 pages); listing of observed and calculated structure factors for **2** (20 pages). Ordering information is given on any current masthead page.

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# Correlating Temperature Dependence to Free Energy Dependence of Intramolecular Long-Range Electron Transfers[†]

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Recent experiments have demonstrated a simple relationship between the rates and energetics for electron-transfer (ET) reactions.[1-6] The dependence of long-range intramolecular ET rate constants on the free-energy change ($\Delta G°$) remarkably confirmed predictions of theory.[7] Those data together with a fit to theory could be used to predict the activation energies for the ET reactions with the knowledge of temperature dependence of $\Delta G°$ and the solvent reorganization energy. Therefore the measurement of temperature-dependence, reported in Figure 1, provides a critical test of the internal consistency of electron-transfer theory and its implementation in describing ET rate as a function of $\Delta G°$.

The reaction studied is the charge-shift ET from biphenylyl$^-$ ($B^-$) to naphthyl (N) group in the rigid molecule BSN shown in the inset to Figure 1. ET rates were measured in the temperature range −94 to 100 °C[8] by pulse radiolysis, which is used to add an electron to the bifunctional molecule. Time-dependent concentrations of the radical anions were followed by their optical absorption. Sample preparation and data analysis have been described elsewhere.[1] Solutions in 2-methyltetrahydrofuran (MTHF) in silica cells were held in an insulated metal block which was cooled by cold nitrogen gas and regulated to ±0.5 °C by a temperature controller (Love Control 585).

**$\Delta G°$ and $T$ Dependence.** Earlier measurements[1] at room temperature of ET rates in the molecule shown in Figure 1 and seven others in which different acceptor groups replaced the naphthyl provided a range of $\Delta G°$ from −0.06 to −2.5 eV. Those data were well-described by nonadiabatic ET theory of eq 1, in which the ET reaction is considered coupled to reorganization of both low-frequency ($h\nu \leq kT$) motions of the solvent and high-frequency ($h\nu \gg kT$) skeletal vibrations of the donor and acceptor groups. The solvent reorganization energy ($\lambda_s = 0.75$ eV), the

$$k_{el} = (\pi/\hbar^2\lambda_s k_B T)^{1/2}|V_2|\sum_{w=0}^{\infty}(e^{-S}S^w/w!)\exp\{-[(\lambda_s + \Delta G° + wh\nu)^2/4\lambda_s k_B T]\} \qquad S = \lambda_v/h\nu \quad (1)$$

reorganization energy ($\lambda_v = 0.45$ eV) of high frequency modes, represented by a single average frequency ($h\nu = 1500$ cm$^{-1}$), and electronic coupling matrix element ($V$) were determined from dependence of $k_{et}$ on $\Delta G°$. The ET rate predicted by eq 1 with use of these reorganization parameters is plotted along with the measured ET rates as a function of temperature in Figure 1. This comparison must consider the temperature dependence of $\Delta G°$ and $\lambda_s$.

**Thermodynamics.** The temperature dependence of $\Delta G°$ was determined from direct measurement of the reaction equilibrium constant, $K_{eq}$ ($B^-SN \rightleftharpoons BSN^-$).[9] Over the temperature range 100 to −94 °C $\Delta G°$ can be described as $\Delta H° - T\Delta S°$ with $\Delta H° = -1.5 \pm 0.1$ kcal/mol and $\Delta S° = -0.49 \pm 0.37$ cal/mol·K. This standard entropy change is very small: $T\Delta S° = -0.15 \pm 0.11$ kcal/mol at 25 °C, which is only one tenth of $\Delta H°$ or one fourth of $kT$. This observation is consistent with an early report.[10] It is also consistent with the expectation that little entropy change

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(9) To accurately determine $K_{eq}$ at temperatures below −20 °C, mixtures of BC and NC, in which the spacer is cyclohexane were used. At room temperature and above $K_{eq}$ measured with BC/NC or BS/NS mixtures agree with each other and those obtained with the bifunctional molecule BSN.

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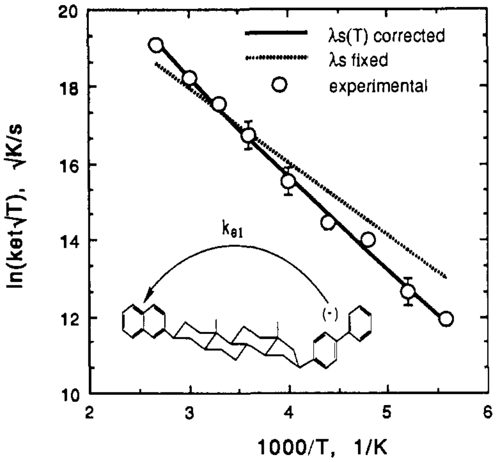

**Figure 1.** Temperature dependence of the electron-transfer rate constant $k_{et}$. The experimental data are matched well by the solid line which is the prediction of eq 1 with parameters determined from $\Delta G°$ dependence with inclusion of the temperature dependence of the solvent reorganization energy $\lambda_s(T)$. The dotted line represents the predicted $k_{et}$ evaluated in the same procedure except that $\lambda_s$ 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 $|\Delta S°|$ 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 $\lambda_s$ 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 ($\epsilon_{op}$)[13] and static ($\epsilon_s$)[14] dielectric constants. $\lambda_s$ increased by 20% as $T$ decreased from 100 to −94 °C. Considering only the change in $\epsilon_s$ (or only $\epsilon_{op}$) $\lambda_s$ increased by 43% (or decreased by 23%). While there is reason to doubt the accuracy of the dielectric continuum result, the correction to $\Delta H^*$ is small, so that only a large error in the correction would seriously affect the calculated $\Delta H^*$.

**Activation Energy, $\Delta H^*$.** The solid line in Figure 1 is $k_{et}$ calculated by eq 1 with the temperature-dependent values of $\lambda_s$. The calculated $k_{et}$ almost perfectly matches the measured $k_{et}$ without any adjustable parameters. In accordance with eq 1 the activation enthalpy $\Delta H^*$ is evaluated as $R\mathrm{d}\{\ln (k_{et}\sqrt{T})\}/\mathrm{d}(1/T)$, where $R$ is the gas constant. The directly measured $\Delta H^*$ is 0.215 ± 0.005 eV (4.96 kcal/mol), the calculated $\Delta H^*$ is 0.216 eV with experimentally determined $\lambda_s(T)$. This excellent agreement (0.5%) is certainly fortuitous because the calculated $\Delta H^*$ is much more uncertain. If the temperature dependence of $\lambda_s$ 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 $\Delta G°$ 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, $NaRe(O)(RC{\equiv}CR)_2$[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 >d², oxo ligands usually bridge two or more metal centers.[4] Octahedral d⁴ 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 d⁴ rhenium(III) oxo bis(acetylene) compounds $Re(O)X(RC{\equiv}CR)_2$ that are stable and relatively unreactive because in their tetrahedral structure no Re–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, $NaRe(O)(RC{\equiv}CR)_2$, in which the metal is formally rhenium(I), d⁶.

Reduction of $Re(O)I(RC{\equiv}CR)_2$ (R = Me, **1a**; Et, **1b**; Ph, **1c**)[7,8] with 1 equiv of sodium or sodium naphthalenide ($NaC_{10}H_8$) in THF gives NaI and the rhenium dimers $Re_2O_2(RC{\equiv}CR)_4$.[9] The use of 2 equiv of reducing agent at −78 °C yields rhenium oxo bis(acetylene) anions: orange $NaRe(O)(RC{\equiv}CR)_2$ (R = Me, **2a**; Et, **2b**) or red-purple $NaRe(O)(PhC{\equiv}CPh)_2$ (**2c**).[10]

Complex **2c** crystallizes from acetonitrile as $NaRe(O)(PhC{\equiv}CPh)_2{\cdot}2MeCN$, with pairs of $[Re(O)(PhC{\equiv}CPh)_2]^-$ anions linked through the oxo ligands to $Na(MeCN)_2^+$ 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 Å out of the plane defined by the oxo and the acetylene midpoints). The structure is similar to those of the rhenium(III) complexes $Re(O)X(RC{\equiv}CR)_2$,[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 Re–O axis and are not parallel but splayed. In

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(10) Selected NMR ($CD_3CN$) and IR (Nujol) data are as follows. **2a**: $^1H$ 2.74 (s); $^{13}C\{^1H\}$ ($C_6D_6$) 166.3, 19.9; IR 835, 805 (ReO). **2b**: $^1H$ 3.04, 2.98 (each m, 4 H, $CH_3C\mathit{HH'}$), 1.23 (12 H, t, 7 Hz, $C\mathit{H}_3CH_2$); $^{13}C\{^1H\}$ 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); $^{13}C\{^1H\}$ 172.2 ($Ph\mathit{CC}Ph$).

(11) Crystal data for **2c**·$2CD_3CN$: 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) Å³, $Z$ = 4; 7179 reflections to $2\theta$ = 55° were collected by using a CAD4 diffractometer (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 GOF = 1.28; Re–O, 1.756 (3) Å; Re–C1, 2.019 (5); Re–C2, 1.994 (5); Re–C3, 1.995 (6); Re–C4, 2.017 (6); C1–C2, 1.312 (7); C3–C4, 1.319 (7); O–Na, 2.274 (4); O–Na′, 2.301 (4); O–Re–C1, 123.4 (2)°; O–Re–C2, 114.8 (2); O–Re–C3, 114.8 (2); O–Re–C4, 125.8 (2), C1–Re–C4, 91.7 (2); C2–Re–C3, 123.9 (2); Re–O–Na, 157.7 (2); Re–O–Na′, 112.8 (2); Na–O–Na′, 89.5 (1); O–Na–O′, 90.5 (1).

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