approximately as $Li_3ThH_7{\cdot}0.6TMEDA$.[16b] Studies of $Th(CH_3)_7^{3-}$ reactivity are continuing.

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Registry No. 1, 92366-20-6.

Supplementary Material Available: Tables of fractional atomic coordinates and anisotropic thermal parameters (7 pages). Ordering information is given on any current masthead page.

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(16) (a) Nujol mulls and KBr pellets exhibit only very weak TMEDA-associated features and a strong, broad ($\nu_{1/2} \approx 700$ cm^{-1}) transition centered at ca. 900 cm^{-1}, which shifts to ca. 630 cm^{-1} ($\nu_{Th-H}/\nu_{Th-D} \approx 1.43$) in the analogue prepared with D_2. (b) Anal. Calcd for $Li_3C_{3.60}H_{16.6}N_{1.20}Th$: Li, 6.32; C, 13.11; H, 5.09; N, 5.10. Found: Li, 6.76; C, 12.69; H, 4.38; N, 5.63.

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Photoinduced Electron Transfer between Cytochrome *c* and Ruthenium/Osmium Bipyridine and Phenanthroline Complexes

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Recently there has been considerable interest in elucidating the mechanism of electron transfer in biological molecules.[2-8] Important information pertaining to this problem is the dependence of the transfer rate on the driving force ΔE for the reaction. Existing data have been obtained mostly from reactions between metalloproteins and inorganic reagents.[5,7] Unfortunately, these are available only within a limited ΔE range around 0.25 V.

An attractive method for measuring electron-transfer rates over a wide ΔE range has been developed in the past few years. Excited inorganic complexes were used as oxidants or reductants[9-11] and the transfer rate was determined by studying the luminescence quenching of the complexes. In such experiments, complications often arise as a result of the presence of other competing processes, such as quenching by energy transfer. To avoid this difficulty, we have employed the transient absorption method to measure directly the kinetics of electron transfer between cytochrome *c* (Cyt-*c*) and several inorganic complexes $X^{2+/3+}$ where X corresponds to $Ru(bpy)_3$ (bpy = 2,2′-bipyridine), $Ru(phen)_3$ (phen = 1,10-phenanthroline), $Os(bpy)_3$, and $Os(phen)_3$. After being photoexcited, a small amount of the complex X^{2+} is converted into X^{3+} while simultaneously Cyt-c^{3+} is reduced to Cyt-c^{2+}. Subsequently, by monitoring the back reaction, the electron-transfer rate between Cyt-c^{2+} and X^{3+} can be directly determined. The results are interesting in that there are very few data in the high driving force regime ($E°$ for $X^{3+}/X^{2+} \simeq 1$ V vs. NHE).

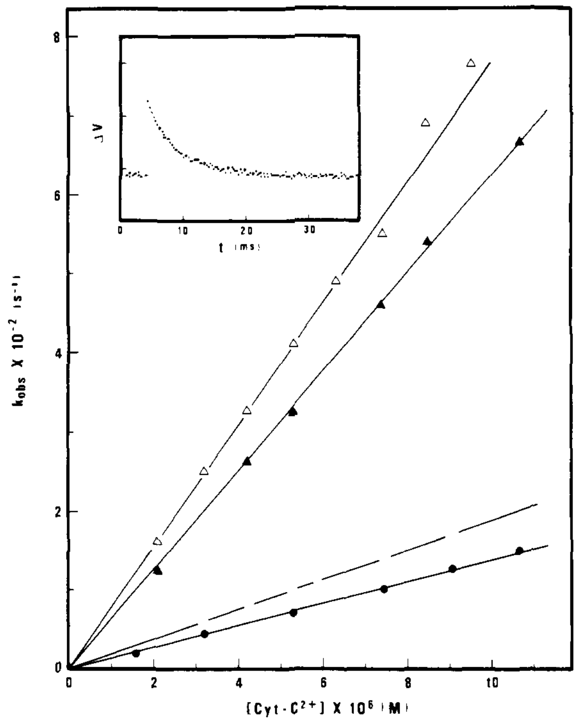

Figure 1. Plot of k_{obsd} vs. Cyt-c^{2+} for the oxidation of ferrocytochrome *c* by $Ru(bpy)_3^{3+}$ (▲), $Ru(phen)_3^{3+}$ (△), $Os(bpy)_3^{3+}$ (●), and $Os(phen)_3^{3+}$ (○) in 5 mM (pH 7) phosphate buffer. The complex concentration was 50 μM, and the reaction was followed at 550 nm. Inset: Typical transient observed for a deoxygenated sample containing 50 μM (oxidized + reduced) cytochrome *c* and 50 μM $Os(bpy)_3^{2+}$ in 50 mM NaCl and 5 mM (pH 7) phosphate buffer. The signal was averaged for 100 laser shots and the laser power was 15 mJ/pulse.

Horse heart cytochrome c (type VI), purchased from Sigma, was used without further purification. The protein as received contained (10.6 ± 0.5)% ferrocytochrome *c* as determined by the addition of a slight excess of $K_3Fe(CN)_6$ to several concentrations of protein while monitoring its optical change at 550 nm. The kinetics was studied by a typical transient absorption setup in which the excitation source was the 355-nm output of a Quanta-Ray DCR-2 Nd:YAG laser. The reaction was initiated by flashing a deoxygenated sample containing cytochrome *c* (concentration varying from 10 to 100 μM, 10.6% reduced) and a complex (X^{2+}) in pH 7 phosphate buffer. The signals were typically averaged for 100 laser shots. The rate of the back reaction was determined by monitoring the transient absorption decay at 550 nm (which reflects changes in Cyt-c^{3+}/Cyt-c^{2+} concentration since the complexes absorb weakly at this wavelength) and 434/504 nm (which reflects changes in X^{3+}/X^{2+} concentration since they correspond to Cyt-c^{3+}/Cyt-c^{2+} isosbestic points).

Following excitation we observe a prompt signal which decays in a millisecond time scale (Figure 1 inset). When the magnitude of the prompt signal is examined at constant laser power as a function of wavelength, the spectrum obtained agrees very well with that predicted from a superposition of the difference spectra of Cyt-c^{3+}/Cyt-c^{2+} and X^{2+}/X^{3+}, indicating that the prompt signal

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Table I. Electron-Transfer Rate between Ferrocytochrome *c* and Oxidized (+3) Complex

complex	ΔE,[a] V	k_{12}, $M^{-1}\ s^{-1}$ $\mu = 0.01$ M	 $\mu = 0.1$ M	k_{12}^{∞}, $M^{-1}\ s^{-1}$ [b]	k_{12}^{calcd}, $M^{-1}\ s^{-1}$ [c]
$Ru(bpy)_3^{2+/3+}$	1.0	6.2×10^7	1.2×10^8	2.5×10^8	8.3×10^{10}
$Os(bpy)_3^{2+/3+}$	0.56	1.5×10^7	6.5×10^7	1.4×10^8	5.4×10^9
Ru-$(phen)_3^{2+/3+}$	1.0	7.9×10^7	1.2×10^8	2.5×10^8	8.3×10^{10}
$Os(phen)_3^{2+/3+}$	0.56	1.9×10^7	7.6×10^7	1.6×10^8	5.4×10^9

[a] Overall potential for the reaction Cyt-c^{2+} + X^{3+} → Cyt-c^{3+} + X^{2+}.[5,12] [b] The charge and radius of the protein are taken to be +6.5 and 16.6 Å, and those for the complex are taken to be +3 and 7 Å.[5] [c] The self-exchange rate for the protein and the complex are taken to be $1.0 \times 10^3\ M^{-1}\ s^{-1}$ [5] and $2.0 \times 10^9\ M^{-1}\ s^{-1}$,[13] respectively.

corresponds to photoinduced reduction of the protein. Such a case of quenching of the excited complex by electron transfer has previously been demonstrated in $Ru(bpy)_3^{2+}$/Cyt-c^{3+} [6] and Ru-$(bpy)_3^{2+}$/blue copper protein[9] systems. From the magnitude of the prompt signal and the reported lifetime of the excited complex,[10] the lower limit of the bimolecular electron-transfer rates between the excited complex $*X^{2+}$ and Cyt-c^{3+} are estimated to be $2 \times 10^8\ M^{-1}\ s^{-1}$, $8 \times 10^7\ M^{-1}\ s^{-1}$, $5 \times 10^9\ M^{-1}\ s^{-1}$, and $7 \times 10^8\ M^{-1}\ s^{-1}$, for X being $Ru(bpy)_3$, $Ru(phen)_3$, $Os(bpy)_3$, and $Os(phen)_3$, respectively.

The decay can be well fitted to a single exponential, and the rate constant obtained is independent of the signal amplitude. The rates at 550 and 434/504 nm were found to be identical, indicating that the decay corresponds to the back-electron-transfer reaction from Cyt-c^{2+} to X^{3+}:

$$\text{Cyt-}c^{2+} + X^{3+} \xrightarrow{k_{12}} \text{Cyt-}c^{3+} + X^{2+}$$

The exponential behavior results from the pseudo-first-order condition since the Cyt-c^{2+} concentration (>1 μM) was much larger than that of X^{3+}, which was estimated to be no more than 0.1 μM. No evidence of rate saturation is discerned for the four complexes (Figure 1) for Cyt-c^{2+} concentration in the range of 1–10 μM. The rate constant increases with increasing ionic strength as would be expected for a reaction between two positively charged species. The bimolecular rates are summarized in Table I.

At low ionic strength (0.01 M), the rate constants k_{12} obtained for the ruthenium complex are about a factor of 4 higher than those of the osmium complexes. A large part of this difference may originate from electrostatic interactions as the factor becomes smaller at an ionic strength of 0.11 M. To further correct for such nonspecific electrostatic effects, the rate constants at infinite ionic strength k_{12}^{∞} were calculated according to the scheme of Gray and co-workers[5] (see Table I).

It is seen that k_{12}^{∞} for the ruthenium and osmium complexes differ by less than a factor of 2 even though the driving forces of the ruthenium complexes are substantially higher. This indicates that the transfer rates are insensitive to ΔE in the range 0.56–1.0 eV. According to the theories proposed by Marcus[3] and Hopfield,[2] the electron-transfer rate increases rapidly at low driving force, reaches a maximum at $\Delta E_{max} = \lambda$ (molecular reorganization energy), and then drops with further increase in ΔE. Therefore, our results imply that the observed transfer rates correspond to values near the maximum and $\lambda \simeq 0.8$ eV for the cytochrome *c*/complex systems.

To gain more insight into the nature of the protein/complex interactions, we attempted to calculate the transfer rate from Marcus relation[4,5] assuming the reactions are adiabatic. The calculated values k_{12}^{calcd}, shown in Table I, are about 2 orders of magnitude higher than k_{12}^{∞}. A plausible explanation for this discrepancy is that the protein self-exchange reaction and/or the protein/complex reaction are in fact nonadiabatic.[13]

In conclusion, we have measured directly the electron-transfer rate between a metalloprotein and inorganic complexes in the high driving force regime where there are scarcely any data. This work is being extended to cover a variety of protein/complex systems having different ΔE values, with the aim of searching for the "inverted region" which was recently observed by Miller et al.[14] in intramolecular electron transfer between two redox groups separated by a steroid spacer.

Registry No. $Ru(bpy)_3$, 15158-62-0; $Ru(phen)_3$, 22873-66-1; $Os(bpy)_3$, 23648-06-8; $Os(phen)_3$, 31067-98-8; Cyt-*c*, 9007-43-6.

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A "Closed" Bridging Stibinidene Complex

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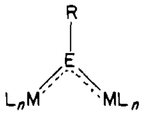
Several complexes are known in which an "inidene" moiety (RE, E = P,[1] As,[2] Sb,[3] Bi[4]) bridges two transition metals. Without exception, these complexes adopt the "open" structure **1**, which features an sp^2 σ-bonding framework and π-delocalization of the E lone pair electrons between the two metals. It is, however, also possible to write a "closed" structure, **2**, for these "inidene" complexes. We report the first example of such a complex.[5]



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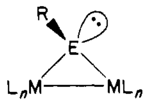
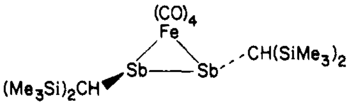


2

A mixture of $(Me_3Si)_2CHSbCl_2$[6] (1.06 g, 3.0 mmol) and $Na_2[Fe(CO)_4]$ (1.04 g, 3.0 mmol) in 25 mL of THF was stirred for 2 h at 25 °C. The crude product was separated by column chromatography (silica gel, *n*-hexane) to afford a 20% yield of **3** (mp 111–113 °C): HRMS for **3** calcd 727.9271, found



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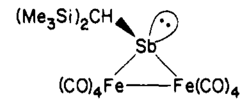

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