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

complex	ΔE,[a] V	k_{12}, M^{-1} s^{-1}: μ = 0.01 M	μ = 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 1.0×10^3 M^{-1} s^{-1} [5] and 2.0×10^9 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 2×10^8 M^{-1} s^{-1}, 8×10^7 M^{-1} s^{-1}, 5×10^9 M^{-1} s^{-1}, and 7×10^8 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]

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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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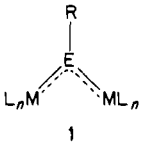
Received July 18, 1984

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



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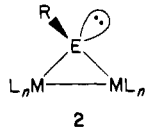

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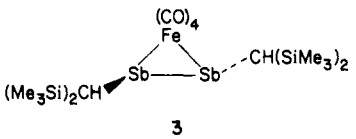
features an sp^2 σ-bonding framework and π-delocalization of the E lone pair electrons between the two metals. It is, however, also possible to write a "closed" structure, **2**, for these "inidene" complexes. We report the first example of such a complex.[5]

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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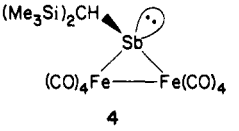

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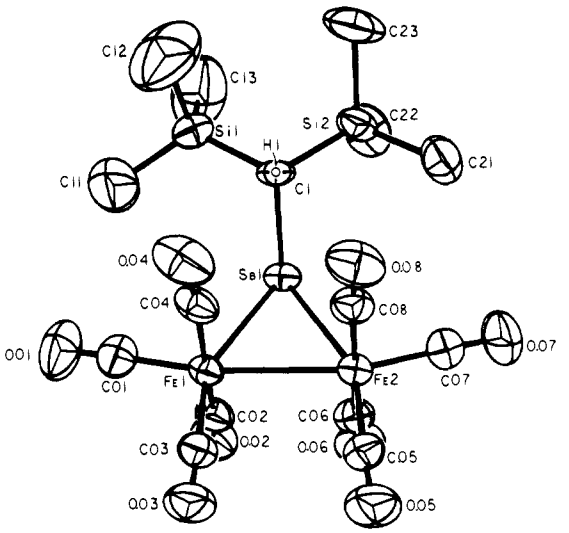

Figure 1. ORTEP view of $[Fe_2(\mu\text{-}SbCH(SiMe_3)_2)(CO)_8]$. Pertinent metric parameters: Fe(1)–Sb(1) = 2.663 (1), Fe(2)–Sb(1) = 2.641 (1), Fe(1)–Fe(2) = 2.801 (1) Å, Fe(1)–Sb(1)–C(1) = 110.81 (9)°, Fe(2)–Sb(1)–C(1) = 112.1 (1)°, Fe(1)–Sb(1)–Fe(2) = 64.15 (2)°.

727.9246. The structure of **3** was established by X-ray crystallography.[7] The Sb–Sb bond length (2.774 (1) Å) indicates that, as in the case of other η^2-bonded trans RE=ER complexes,[8] the bond order is ~1.5. Treatment of **3** (1.61 g, 2.1 mmol) with $Fe_2(CO)_9$ (0.80 g, 2.1 mmol) in 20 mL of *n*-hexane at 25 °C, followed by chromatography (silica gel, *n*-hexane), resulted in a 26% yield of **4** (mp 84–86 °C): HRMS calcd 615.8354, found 615.8333. The structure of **4** was determined by X-ray crystallography (Figure 1).[7] The existence of a "closed" structure is established by the pyramidality at the Sb atom (sum of bond angles = 287.1 (1)°), since in the "open" form the Sb geometry would be trigonal planar. Although the Fe–Fe distance (2.801 (1) Å) exceeds the usual single-bond range of 2.50–2.65 Å, it is clear that the Fe atoms are weakly bonded. Significant differences in the reactivities of the "open" and "closed" complexes are observed. Thus while complexes of type **1** are Lewis acidic at the E center, we find that **4** acts as a Lewis base. For example, **4** reacts readily with $HBF_4{\cdot}OEt_2$ to afford the (unstable) cation, $[(Me_3Si)_2CHSb(H)\{Fe(CO)_4\}_2]^+$.

Interestingly, a minor (labile) fraction is eluted from the column prior to **4**. However, the crystals that are deposited from this solution are identical with **4** in all respects. We speculate that this solution initially contains the "open" form of **4**. The reason for M–M bond formation in **4** is not completely clear. When compared to previous "inidene" complexes, $RE(ML_n)_2$ (ML_n = $Cr(CO)_5$, $Mo(CO)_5$, $W(CO)_5$, $(C_5H_5)Mn(CO)_2$),[1-4] the iron system is less sterically congested when the Fe–Fe bond is present. However, Fe–Fe bonding is also expected on electronic grounds.

The isolobal relationships RSb ↔ CH_2 ↔ $Fe(CO)_4$ reveal parallels between **3**, **4**, cyclopropane, and $Fe_3(CO)_{12}$. (Note, however, that the "open" form of **4** is analogous to the allyl anion.) There is also an interesting analogy between **4** and bridging methylene compounds.[9]

Acknowledgment. We are grateful to the National Science Foundation and the Robert A. Welch Foundation for financial support.

Registry No. 3, 92315-34-9; **4**, 92345-49-8; $(Me_3Si)_2CHSbCl_2$, 86509-03-7; $Na_2[Fe(CO)_4]$, 14878-31-0; $Fe_2(CO)_9$, 15321-51-4; Sb, 7440-36-0.

Supplementary Material Available: Tables of bond lengths, bond angles, atomic coordinates, thermal parameters, and structure factors for **3** and **4** (53 pages). Ordering information is given on any current masthead page.

A Synthetic Amphiphilic β-Strand Tridecapeptide: A Model for Apolipoprotein B

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Received May 29, 1984

The biological activity of many proteins and peptides acting in amphiphilic environments depends on the ability of the polypeptide to assume amphiphilic secondary structures. Previous studies have mainly concerned model amphiphilic α-helices, but it is probable that any possible secondary structure would occur in the amphiphilic form.[1,2] Indeed, indirect evidence suggests that apolipoprotein B, the major protein component of plasma low-density lipoproteins, exists in a predominant β-strand at the surface of the lipoprotein.[3] In order to explore the general properties of amphiphilic β-strands, and to have at our disposal an apolipoprotein B (apoB) model, we designed peptide I, a tridecapeptide with the following amino acid sequence:

NH_2-Val-Glu-Val-Orn-Val-Glu-Val-Orn-Val-Glu-Val-Orn-Val-COOH

We decided upon a tridecapeptide in order to assure that the peptide would be long enough to assume a stable secondary structure and yet short enough to be water soluble. Peptide I contains three different amino acids, valine, glutamate, and ornithine, arranged so that alternating amino acids are hydrophilic and lipophilic and so that alternating hydrophilic amino acids have acidic and basic side chains, conducive to staggering the electric charges upon self-association. Valine is the amino acid with the highest β-forming potential[4] and forms soluble β-sheets in copolymers such as poly(Val-Lys).[5a,b] Although glutamic acid has a low β-forming potential, poly(Glu) and copolymers such as poly(Glu-Val) and poly(Glu-Ala) may under certain conditions be induced to form β-structures.[6,7] We chose ornithine to maximize side chain interactions, and we chose ornithine over lysine because the former can serve as a chemical marker since apoB does not contain ornithine. Thus the use of this amino acid assures that the peptide will have little chemical homology with natural apoB. Peptide I was synthesized by the solid-phase method

(7) Complex **3**: $C_{18}H_{38}FeO_4Sb_2Si_4$, M_r 730.18; monoclinic, $P2_1/n$; a = 19.958 (4) Å, b = 6.635 (1) Å, c = 24.408 (6) Å, β = 103.51 (2)°; V = 3143 (2) Å^3; Z = 4; D(calcd) = 1.543 g cm^{-3}. Complex **4**: $C_{15}H_{19}Fe_2O_8SbSi_2$; M_r 616.92; triclinic, $P\bar{1}$; a = 7.065 (5) Å, b = 9.179 (2) Å, c = 19.814 (7) Å, α = 86.86 (3)°, β = 85.23 (5)°, γ = 70.04 (4)°; V = 1203 (1) Å^3, Z = 2; D(calcd) = 1.702 g cm^{-3}. Intensity data: Enraf-Nonius CAD4-F diffractometer, ω–2θ scan mode in the range $2.0 \le 2\theta \le 50.0$; 5844 and 3859 unique reflections for **3** and **4**, respectively. The structures of **3** and **4** were solved (Patterson and difference Fourier) and refined (full matrix, least squares) by use of 3884 and 3283 data, respectively. Final residuals were as follows: **3**, R = 0.036, R_w = 0.060; **4**, R = 0.031, R_w = 0.039.

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