It was not expected that such similar radical chain mechanisms would selectively yield thexyl products for tin and germanium vs. the dimethylsilyl products in the case of molybdenum hydrides. However, analysis employing the steady-state approximation for the radical species in (2)-(5) predicts that, irrespective of initiation,

$$CpMo(CO)_3SiMe_2CMe_2CMe_2^{\bullet} + CpMo(CO)_3H \xrightarrow{k_3} CpMo(CO)_3SiMe_2CMe_2CMe_2H + CpMo(CO)_3^{\bullet} \quad (5)$$

3a

the product ratio for this mechanism is given by [**3a**]/[**2a**] = k_3[**1a**]/k_e, where **3a** is the thexylsilyl product in analogy to the group 14 derivatives.[25] In other words, formation of the thexyl product should be favored by high concentrations of **1a**.

As no substantial quantity of any other product was observed at hydride concentrations up to ca. 0.9 M in benzene, a finely ground sample of **1a** was treated with neat HMS. Analysis of this reaction mixture by ^{1}H NMR showed the formation of **2a** and ca. 13% of **3a**, the thexyldimethylsilyl molybdenum complex,[26] as predicted by the proposed radical chain mechanism.

The trace amounts of molybdenum dimers $[CpMo(CO)_2(L)]_2$ formed in eq 1 are consistent with chain termination during the reaction.

A ca. 10-fold increase in the initial rate is observed upon addition of a few mole percent of triphenylmethyl radical (as the dimer).[27] In a separate experiment, stoichiometric reaction of trityl dimer with **1a** in the absence of HMS produced triphenylmethane and $[CpMo(CO)_3]_2$, presumably from the coupling of $CpMo(CO)_3$ radicals.

Attempts to establish the intermolecularity of (1) by means of a cross-over experiment using $CpMo(CO)_3D$ and $(MeCp)Mo(CO)_3H$ were thwarted by the extremely rapid isotopic scrambling observed between these complexes in the absence of HMS.

Comparison of initial rates measured by using a single batch of **1a** shows no effect on eq 1 by carbon monoxide (1.5 atm) or tetramethylethylene (0.317 M).[19] These facts, in conjunction with a negative activation entropy ($\Delta S^{\ddagger} = -25 \pm 3$ eu),[28] preclude reversible dissociation of these species in the rate-controlling step. Changing solvent from benzene to THF also leaves the rate unchanged.

In summary, silylene transfer from HMS to molybdenum hydrides is quantitative, and appears to proceed by radical chain ring opening and olefin elimination to yield a transient silyl radical. The apparent stabilization of the silyl radical by metal substitution suggests that radical paths may be more common with metal complexes of silicon ligands than is generally observed in organosilicon chemistry.[29]

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Registry No. 1a, 12176-06-6; **1b**, 78392-89-9; **2a**, 55177-91-8; **2b**, 108083-21-2; **3a**, 108083-22-3; HMS, 55644-09-2; $[CpMo(CO)_3]_2$, 12091-64-4; $[CpMo(CO)_2(PMe_3)]_2$, 69364-22-3; 2,3-dimethyl-2-butene, 563-79-1; 3-(diphenylmethylene)-6-(triphenylmethyl)-1,4-cyclohexadiene, 18909-18-7; triphenylmethane, 519-73-3.

(25) The product ratio is determined from the following rate expressions for formation of products: $d[\mathbf{2a}]/dt = k_1k_e[Mp^{\bullet}][HMS]/(k_3[\mathbf{1a}] + k_e)$ and $d[\mathbf{3a}]/dt = k_1k_3[Mp^{\bullet}][HMS][\mathbf{1a}]/(k_3[\mathbf{1a}] + k_e)$, where Mp designates the $CpMo(CO)_3$ group.

(26) The residue from a subsequent fractional sublimation was enriched in this product (60%), although we have been unable to isolate **3a** completely free of **1a** and **2a**. Compound **3a**: ^{1}H NMR δ 4.59 (s, Cp), 1.98 (septet, J = 6.7 Hz, CMe_2H), 1.07 (s, $SiCMe_2$), 0.94 (d, J = 6.7 Hz, CMe_2H), 0.63 (s, $SiMe_2$); mass spectrum, m/z calcd 390.0549; found 390.0604.

(27) The trityl dimer 3-(diphenylmethylene)-6-(triphenylmethyl)-1,4-cyclohexadiene is in equilibrium with the trityl radical: March, J. *Organic Chemistry*; Wiley: New York; p 164 and references therein.

(28) Activation parameters were determined from an Eyring plot of rates at four temperatures (16.7-50.5 °C): $\Delta H^{\ddagger} = 13.3 \pm 0.5$ kcal/mol and $\Delta S^{\ddagger} = -25 \pm 3$ eu.

(29) The facile radical chain halogenation of silicon hydrides in $M(R_2SiH)$ complexes also appears to be a result of the stability of $M(R_2Si^{\bullet})$.[13]

Reversible Long-Range Electron Transfer in Ruthenium-Modified Sperm Whale Myoglobin

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The kinetics and thermodynamics of long-range (>10 Å) electron transfer (ET) for several ruthenium-modified metalloproteins have been reported recently.[1-5] Electron transfer in these systems has been measured from a reduced surface ruthenium(II) (a_5Ru, a = NH_3) to an oxidized-protein center (either Fe^{III} or Cu^{II}). Measurement of ET in the reverse direction, however, requires formation of a mixed-valence ruthenium(III)-reduced-protein complex, a species that was inaccessible by methods previously employed.[2-4] We have now developed a technique utilizing flash photolysis to generate this key intermediate, thereby enabling us to measure ET rates from the iron(II)-heme to different ruthenium(III) histidine-48 acceptors in sperm whale myoglobin (Mb). In this system the closest donor-acceptor edge-edge distance is 13 Å.[1,2]

Our methodology for studying ET from a reduced-protein center to a covalently bound ruthenium acceptor is summarized in Scheme I; the kinetics are followed using flash spectroscopic techniques. Flash photolysis generates electronically excited tris(2,2′-bipyridine)ruthenium(II) ($Ru(bpy)_3^{2+*}$), a powerful oxidant, which is quenched via electron transfer from the reduced (Ru^{II}) metalloprotein complex (Ru^{II}-PFe^{II}, Fe^{II} = iron(II)-heme or other reduced-protein center) in a rapid bimolecular step to yield Ru^{III}-PFe^{II}. In order to observe the desired intramolecular ET process, Ru^{III}-$PFe^{II} \rightarrow Ru^{II}$-$PFe^{III}$, it is essential that $Ru(bpy)_3^{+}$ be efficiently removed from the system; otherwise, the exergonic ($\Delta E^{\circ} = 1.1$ V) back reaction (k_b, Scheme I) will rapidly regenerate Ru^{II}-PFe^{II}. We have found that a suitable scavenger system for aqueous solution experiments consists of nickel(II) hexamethyltetraazacyclodecane ($Ni^{II}Me_6ane$) and 3-bromopropionic acid (RBr). In this system $Ni^{II}Me_6ane$ is reduced by $Ru(bpy)_3^{+}$ to the Ni^{I} species, which then reacts irreversibly with RBr.[6]

With this technique, we have measured the Fe^{II} to Ru^{III} ET kinetics in a_5Ru(histidine-48)-modified myoglobin ($a_5Ru(48)$-MbFe), a system in which the reduction potentials of the heme and the pentaammineruthenium are closely matched ($\Delta E^{\circ} = 20$ mV).[1,2] The change in the heme absorption at 556 nm following flash photolysis of a solution containing $a_5Ru^{II}(48)MbFe^{II}$ is shown in Figure 1. Immediately after the flash, a small net bleaching is observed (the direct oxidation of the heme by $Ru(bpy)_3^{2+*}$), followed by a relatively slow further oxidation that can be assigned

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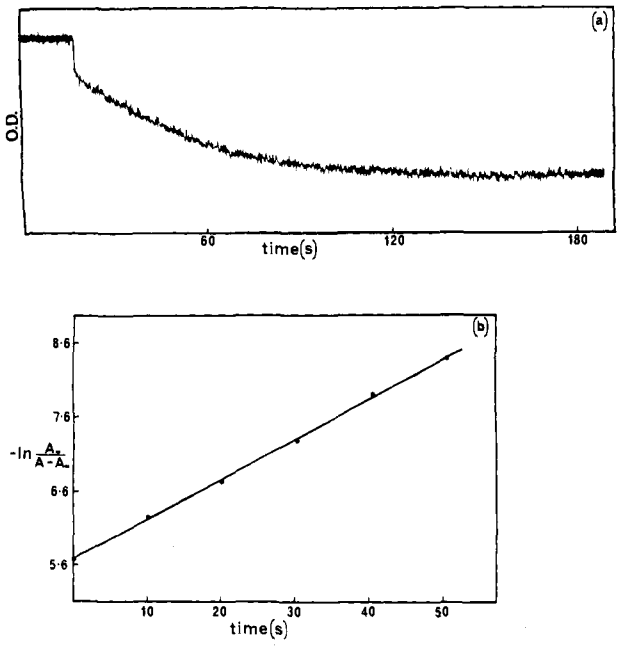
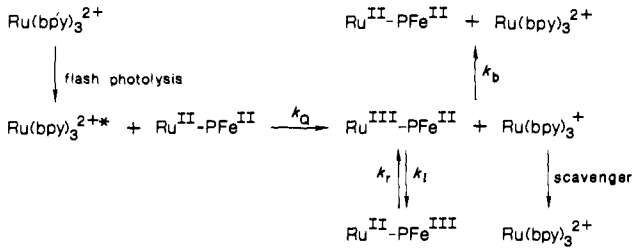


Figure 1. (a) Change in optical density of the heme absorption at 556 nm following flash photolysis of a 0.1 M, pH 7 phosphate solution containing $a_5Ru^{II}(48)MbFe^{II}$ (5 μM), $Ru(bpy)_3^{2+}$ (65 μM), $Ni^{II}Me_6ane$ (5 mM), and RBr (20 mM); 25 °C. (b) First-order plot of the experimental data (●). The line is a least-squares fit for these points.

Scheme I



to intramolecular ET: $a_5Ru^{III}(48)MbFe^{II} \rightarrow a_5Ru^{II}(48)MbFe^{III}$. This oxidation of the Fe^{II}–heme follows first-order kinetics for at least three half-lives with an observed rate constant of 0.058 s^{-1}. The kinetics were found to be independent of protein concentration (5–50 μM), thereby establishing that bimolecular ET processes are not significant.

The rate of Fe^{II} to Ru^{III} Et for $a_5Ru(48)MbFe$(k_{obsd} = 0.058 ± 0.004 s^{-1}) is within experimental error of that previously determined for the reverse ET (k_{obsd} = 0.060 ± 0.004 s^{-1}).[2] Kinetic analysis[7] of a reversible unimolecular process yields an observed first-order rate constant that is equal to the sum of the forward (k_f) and reverse (k_r) rates:

$$a_5Ru^{III}(48)MbFe^{II} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} a_5Ru^{II}(48)MbFe^{III}; \quad k_{obsd} = k_f + k_r$$

Our finding that the observed rate constant is independent of the initial [Ru^{III}–PFe^{II}]:[Ru^{II}–PFe^{III}] ratio demonstrates unequivocally that long-range ET in $a_5Ru(48)MbFe$ is reversible.

We have also employed the new methodology to measure the long-range ET rate in myoglobin modified at histidine-48 with a_4pyRu (py = pyridine). This derivative of myoglobin was prepared and characterized by procedures analogous to those employed for $a_5Ru(48)MbFe$.[2,8] The overall driving force for Fe^{II} to Ru^{III} ET in $a_4pyRu^{III}(48)MbFe^{II}$ is 220 mV larger than in $a_5Ru^{III}(48)MbFe^{II}$. The general features of the kinetics are similar to those previously discussed for the a_5Ru-modified protein except that the overall reaction is considerably faster. The measured Fe^{II} to Ru^{III} long-range ET rate of 2.5 s^{-1} indicates that Ru(48)MbFe follows Marcus theory with a reorganization energy (λ)[9] similar to those reported for related protein[10,11] and steroid-spacer[12] ET reactions. In terms of the Hoffman–Ratner treatment of gated ET reactions,[13] our findings are of particular relevance because they show that the rates of long-range ET in ruthenium-modified myoglobins are not controlled by conformational interconversions.[14]

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Novel Synthesis of a Polyketone via Radical Ring-Opening Polymerization of 2,2-Diphenyl-4-methylene-1,3-dioxolane

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Although the ionic ring-opening polymerization has been widely investigated, few papers have reported on the free radical ring-opening polymerization. Recent examples of the free radical ring-opening polymerization involve the vinylcyclopropanes,[1] unsaturated spiro orthocarbonates,[2] unsaturated spiro ortho esters,[3] 2-phenyl-3-vinyloxylanes,[4] cyclic ketene acetals such as 2-methylene-1,3-dioxolane,[5] and 2-methylene-4-phenyl-1,3-dioxolane.[6] In the course of researching the radical ring-opening polymerization of 2-substituted-4-methylene-1,3-dioxolanes, it was found that a polyketone was obtained in good yield by the polymerization of 2,2-diphenyl-4-methylene-1,3-dioxolane (**1**) accompanying the quantitative elimination of benzophenone without any side reactions. Although some ways of synthesizing a polyketone, such as the copolymerization of ethylene with carbon monoxide under high pressure,[7] the oxidation of poly(vinyl alcohol),[8] the cationic polymerization of a ketene or diketene,[9] and

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