Table II. Coalescence Temperatures (T_c) and Free Energies of Activation ($\Delta G^{\ddagger}_{Tc}$) of **5**

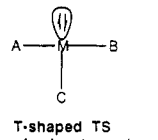
	solvents				
	toluene-d_8[a]	nitrobenzene	2,6-lutidine	DMSO-d_6	pyridine
T_c (°C)	125	170	170	55	40
$\Delta G^{\ddagger}_{Tc}$ (kcal mol^{-1})	20.5 ± 0.1	20.6 ± 0.1	20.6 ± 0.1	15.4 ± 0.1	14.6 ± 0.1

[a] Coalescence could be observed only for CH_2 group.

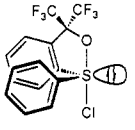
methylamino group and the central bismuth atom is 2.63 Å, which is very much shorter than the sum of van der Waals radii (ca. 3.74 Å).[13] Thus, the coordination of the NMe_2 group effectively forms a hypervalent 10-Bi-4[14] compound. The geometry about the bismuth atom is a distorted pseudotrigonal bipyramid, where the carbon atoms bound to bismuth occupy the equatorial plane with a C-Bi-C angle of 93.1°. The apical positions are occupied by the oxygen and the nitrogen atoms with an O-Bi-N angle of 160.2°. The apical Bi-O bond length is 2.19 Å. The lone pair of electrons can be considered to occupy one equatorial position.

The ^{19}F NMR peaks (acetone-d_6) of **4** and **5** appear as a pair of quartets [δ -72.6, -75.9 (**4**) (J = 8.6 Hz, $\Delta\nu$ 279 Hz), -73.1, -76.5 (**5**) (J = 8.3 Hz, $\Delta\nu$ 288 Hz)] at room temperature, showing that these compounds also possess stable configurations. At elevated temperatures, these pairs of quartets of **1**, **4**, and **5** coalesce at different temperatures in DMSO-d_6 (Table I). The lowered coalescence temperatures and activation energies ($\Delta G^{\ddagger}_{Tc}$) of compounds **4** and **5** clearly show the distinct effect of intramolecularly coordinating groups (OMe, NMe_2) as compared to noncoordinated **1**.

Solvent effects on the barriers of **5** have been investigated (Table II).[4d,15] The dramatic difference between pyridine and 2,6-lutidine strongly indicates that nucleophilic solvents stabilize the transition state **A** in addition to the NMe_2 substituent as shown in Scheme I. The fact that the inversion of **1** cannot be observed without nucleophilic solvents such as DMSO-d_6 (T_c = 175 °C) and pyridine (T_c = 110 °C) also supports nucleophilic assistance. The barrier of 20.5 kcal mol^{-1} (125 °C) for **5** in toluene-d_8 should be that of an intramolecular edge inversion of **5** without solvent participation since a concentration effect could not be observed at all between 0.14 and 0.017 M. It is thus estimated that the T-shaped transition state is stabilized by at least 5.8 kcal mol^{-1} from intramolecular coordination of the NMe_2 group and by 5.9 kcal mol^{-1} from additional coordination with the solvent pyridine. It should be noted here that the inversion cannot be rationalized by Berry pseudorotation because the lone pair electrons must be placed at an apical position in the inevitable intermediate during the pseudorotation process. The high energy required for such a pseudorotation has been previously demonstrated by the isolation of the chiral 10-S-4 sulfurane **6**.[16]



T-shaped TS
of edge inversion



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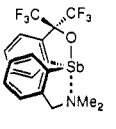

7

We have also prepared the corresponding antimony compound **7**.[17] The coalescence of the two CF_3 groups could not be observed, and the inversion barrier was measured to be higher than 20 kcal mol^{-1} (at 150 °C in DMSO-d_6). This is consistent with the prediction by edge inversion.

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Supplementary Material Available: Listings of synthetic procedures of **1**, **3**, **4**, and **5**, tables including activation entropies and activation enthalpies, and a list of the X-ray crystallographic data (intramolecular bond lengths, bond angles, selected intermolecular bond lengths, and positional and thermal parameters) of **4** and **5** (24 pages). Ordering information is given on any current masthead page.

(12) The crystal data for **5** are as follows: $C_{18}H_{16}F_6NOBi$, monoclinic, space group $P2_1/a$, a = 11.050 (2) Å, b = 18.572 (3) Å, c = 9.856 (2) Å, β = 108.21 (1)°, Z = 4. With 3588 reflections of intensity greater than 3σ, the structure was solved by direct methods (Multan 78) and standard difference Fourier techniques. The final R factors were R = 0.062 and R_w = 0.085. The crystal data and the selected bond lengths and bond angles of **4** are as follows: $C_{19}H_{17}F_6O_2Bi$, monoclinic, space group $P2_1/n$, a = 17.807 (4) Å, b = 11.002 (3) Å, c = 10.423 (2) Å, β = 106.68 (2)°, Z = 4, R = 0.059, R_w = 0.074, Bi-O(Me) 2.527 (8) Å, Bi-O(ring) 2.195 (7) Å, ∠O-Bi-O 155.4 (3)°, equatorial ∠C-Bi-C 94.4 (4)°.

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(18) This paper is dedicated to celebrate the 70th birthday of Professor Harold Hart of Michigan State University.

Ferricytochrome *c* Binding Induces Detectable Proton NMR Shift Changes in Cytochrome *c* Peroxidase-CN

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The formation of protein-protein docking complexes involved in electron transfer is currently an intense area of interest that has raised questions about molecular recognition, communication between partner proteins, and association of conformational changes (i.e., conformational gating) with electron-transfer dynamics. One paradigm for studying complex formation between heme redox proteins is the noncovalent complex formed between yeast cytochrome *c* peroxidase (EC 1.1.11.5; CcP) and cytochromes *c* from various species.[1-9]

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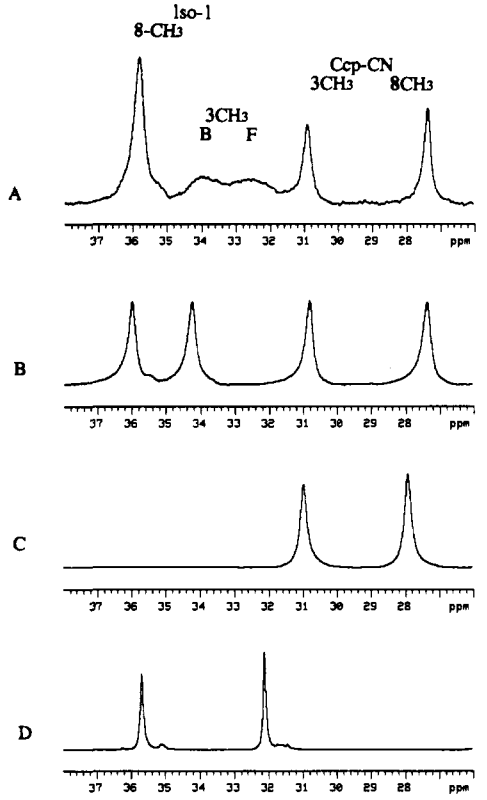

Figure 1. Downfield proton hyperfine shift region (at 500 MHz) of the following mixtures of CcPCN and yeast iso-1 ferricytochrome *c*: (A) 1:2 mole ratio; (B) 1:1 mole ratio; (C) CcPCN alone; and (D) yeast iso-1 ferricytochrome *c* alone. In A, letter B denotes the heme 3-methyl resonance of iso-1 bound to CcPCN in the 1:1 complex, whereas letter F denotes the same resonance for iso-1 molecules free in solution. All solution conditions were identical, with CcPCN concentrations in each approximately 1.0 mM; in D_2O, 10 mM KNO_3, pH′ (meter reading) 6.5, 19.7 °C, with observed shifts referenced to residual water, assigned 4.70 ppm.

We have been performing NMR studies of these complexes as a result of the singular ability of proton NMR spectroscopy to directly report on complex formation between native CcP, the high-spin ferriheme-containing resting-state enzyme, and ferricytochromes *c* from several species.[8,9] The latter are low-spin, paramagnetic ferriheme proteins with easily observed heme hyperfine resonances. Noncovalent complex formation between these proteins under low ionic strength conditions has been found to induce shift changes in the proton NMR spectrum of each of the ferricytochromes *c* studied to date (horse, tuna, and yeast isozymes 1 and 2).[8,9] Indeed, those shifts are diagnostic of a complex's formation and its disruption. However, until now we have found no evidence that noncovalent complex formation with either ferricytochromes *c* or ferrocytochromes *c* induces any NMR spectroscopic changes for CcP, suggesting that cytochrome *c* binding at the CcP surface does not noticeably affect the CcP active site.

Recently, we initiated studies of the noncovalent CcP-CN/ferricytochrome *c* complexes. In these cases the cyanide-ligated form of CcP is low-spin, analogous to the oxidized enzyme intermediates, CcP compound I and CcP compound II. Both of these enzyme intermediates are low-spin ferryl compounds whose heme electronic structure has so far stymied meaningful NMR studies.[4,10] The results of initial experiments are shown in Figure 1. This figure shows hyperfine shifted proton NMR spectra of the heme methyl region for (A) a 1:2 [CcPCN]/[yeast iso-1 ferricytochrome *c*] mixture; (B) a 1:1 CcP-CN/yeast iso-1 ferricytochrome *c* mixture; (C) the analogous spectral region of CcP-CN alone; and (D) the analogous spectral region of yeast iso-1 ferricytochrome *c* alone. Identical solution and NMR conditions were used for each of these samples.

It is obvious from these spectra that both CcP-CN and iso-1 ferricytochrome *c* heme methyl resonances exhibit comparatively large shifts as a result of complex formation, which occurs in situ under these solution conditions.[1-9] The CcP-CN heme 8-methyl resonance shifts 0.547 ppm to lower frequency (upfield by 273 Hz at 500 MHz), while the heme 3-methyl resonance shifts 0.166 ppm to lower frequency (upfield by 83 Hz at 500 MHz). Smaller complex-induced shifts in the CcP-CN resonances are found in the similarly formed noncovalent complex of CcP-CN with horse ferricytochrome *c* (CcP-CN 8-methyl = 0.039 ppm to lower frequency or 19.5 Hz at 500 MHz; 3-methyl = 0.029 ppm to lower frequency or 14.5 Hz at 500 MHz). As expected, these mixtures of two low-spin, paramagnetic heme proteins produce a complicated pattern of overlapping hyperfine resonances elsewhere in the proton NMR spectrum that we are currently attempting to unravel and assign.

The significance of the observations presented here is that these are the first examples of cytochrome *c* binding causing changes in the CcP NMR spectrum. In view of the buried nature of the CcP heme and the sensitivity of the proton hyperfine shifts to their magnetic environment, one can conclude that ferricytochrome *c* binding is communicated to the CcP heme via structural changes. It is possible that a structure-based rationalization of the observed complex-induced shifts will be possible as additional, comprehensive proton resonance assignments emerge from the complicated pattern of overlapping hyperfine resonances. Also, the results presented here reinforce our recent work[9] with complexes of the native enzyme, which showed that the complex-induced proton NMR shifts of both CcP-CN and the ferricytochromes *c* are much larger for the physiological complex (CcP with yeast iso-1 ferricytochrome *c*) than for nonphysiological complexes (such as CcP with horse ferricytochromes *c*).

Similar effects have not been detected for the proton resonances of native cytochrome *c* peroxidase in noncovalent complexes with ferricytochromes *c*, which may be due to the larger hyperfine resonance line widths in the high-spin form of the enzyme and this may make detection of such shifts more difficult. However, it is also conceivable that the low-spin form of the peroxidase is more sensitive to ferricytochrome *c* binding than is the native enzyme. Work is currently underway to resolve this ambiguity.

In regard to the effects on the spectrum of yeast iso-1 ferricytochrome *c*, Figure 1 confirms that in situ complex formation does occur at 0.01 M salt from the previously established criteria of shifts and line width changes that occur in the presence of the peroxidase (compare spectra B and D).[9] Furthermore, similar to results found for the yeast iso-1 ferricytochrome *c* complex with unligated, native CcP, Figure 1A displays individual resonances of approximately equal integrated intensity for both the free and bound forms of the iso-1 heme 3-methyl resonance in the 1:2 complex. This result and titration data (not shown) reveal the 1:1 stoichiometry of the noncovalent complex by the fact that above concentration ratios of 1:1 the free heme 3-CH_3 (iso-1) resonance is observed. Figure 1A also demonstrates that, qualitatively, the exchange rate between free and bound forms of iso-1 ferricytochrome *c* is similar for complexes with CcPCN and CcP.[9] Quantitation of this exchange rate for both types of complexes is in progress.

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Novel Radical Chain Reactions Based on *O*-Alkyl Tin Dithiocarbonates

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Most of the recent applications of radical reactions to organic synthesis are based on tin hydride chemistry.[1] One of the limitations of such a system is that the last propagation step involves a fast, irreversible, hydrogen atom transfer.[2a,c] Not only is a potential means of introducing an extra functionality lost but the intervening steps (cyclizations, additions etc.) have to be fast in order to compete with premature hydrogen abstraction. In practice, either high dilution conditions are employed or the tin hydride is added very slowly to keep its concentration low. Another approach has involved the use of the rather expensive germanium hydrides[2b,c] or tris(trimethylsilyl)silane,[3] both of which are less efficient hydrogen donors. An important variant involves the use of allyltin derivatives to introduce an allyl group.[4] In this communication, we wish to introduce *O*-alkyl tin dithiocarbonates (xanthates) as reagents which circumvent both of these limitations.

Our conception, outlined in Scheme I, is based on the fact that addition of tin radicals onto the thiocarbonyl group of a xanthate is reversible.[5] Thus, starting from tin xanthate **1** as the source of stannyl radicals, it should be possible to generate a radical R• from a substrate RX. This radical can of course react with the tin xanthate reagent to give xanthate **3** by a series of reversible steps (path A) or it can be converted through cyclization, fragmentation, etc. (summarized as step B) into another radical R*•, which in turn reacts to give xanthate **4**. Both pathways propagate the chain by regenerating the stannyl radical. One can, therefore, not only carry out the common radical reactions traditionally based on tin hydride chemistry but also introduce a very useful xanthate group into the end product **4**.[6] Moreover, as all of the steps involving transfer of the xanthate group are reversible, it should not be necessary to worry about high dilution, etc. in cases where one or more of the desired reactions of the intermediate carbon radical ("step B") are relatively slow, since one can always go back to the carbon radical through the action of stannyl radicals on xanthate **3** (reverse of path A).

Scheme I

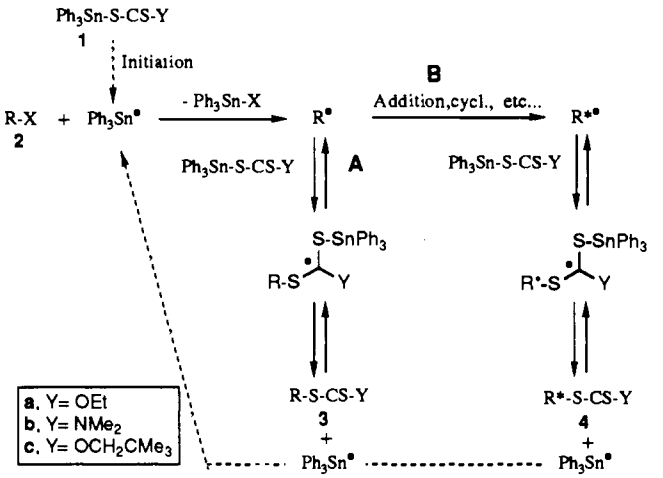

Table I. Reaction of Various RX Derivatives with Tin Dithiocarbonates

entry	RX	tin xanthate	additive	reaction time (initiator)[a]	product (yield, %)
1	**5**	**1a**	none	3 h, A	**6** (88)[b]
2	**7**	**1a**	none	4 h, A	**8** (67)[c]
3	**5**	**1a**	none	6 h, B	**6** (84)[b]
4	**7**	**1a**	none	6 h, B	**8** (55)[c]
5	**5**	**1b**	none	7 h, A	**9** (55)[b]
6	**5**	**1b**	none	10 h, B	**10** (24)[b]
7	**5**	**1c**	none	8 h, B	**11** (56)[b]
8	**5**	**1c**	$(Ph_3Sn)_2$	1 h, B	**11** (96)[b]
9	**5**	**1c**	$(Bu_3Sn)_2$	3 h, B	**11** (82)[b]
10	**12**	**1c**	none	10 h, B	**13** (55, 68[d])
11	**14**	**1c**	none	18 h, B	**15** (65)[e]
12	**16**	**1c**	$(Ph_3Sn)_2$	5 h, B	**17** (65)
13	**18**	**1c**	$(Ph_3Sn)_2$	2 h, B	**19** (80)
14	**20**	**1c**	$(Ph_3Sn)_2$	4 h, B	**19** (27, 48[d])
15	**21**	**1c**	$(Ph_3Sn)_2$	8 h, B	**22** (63)
16	**23**	**1c**	$(Ph_3Sn)_2$	3 h, B	**24** (25, 65[d])
17	**25**	**1c**	$(Ph_3Sn)_2$	15 h, B	**26** (79)
18	**27**	**1c**	$(Ph_3Sn)_2$	8 h, B	**28** (64, 80[d])

[a] A = initiation with 10 mol % (with respect to substrate) each of Bu_3SnH and AIBN; B = initiation with a 500-W tungsten halogen lamp. [b] 7:3 mixture of isomers. [c] 8:2 mixture of isomers. [d] Yield was based on recovered starting material. [e] 9:1 mixture of isomers.

These expectations were borne out in practice as shown by the following examples. Refluxing a solution of bromide **5** with *O*-ethyl triphenyltin xanthate **1a** in cyclohexane in the presence of a small amount of tributyltin hydride and AIBN as initiator resulted in the formation of bicyclic xanthate **6** in 88% yield. In a similar way, **8** was produced in 67% yield from **7**. Initiation of these reactions could be accomplished using visible light in comparable yields (Table I). The tin xanthate reagent **1a** is easily prepared[7a] from commercially available triphenyltin chloride and

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