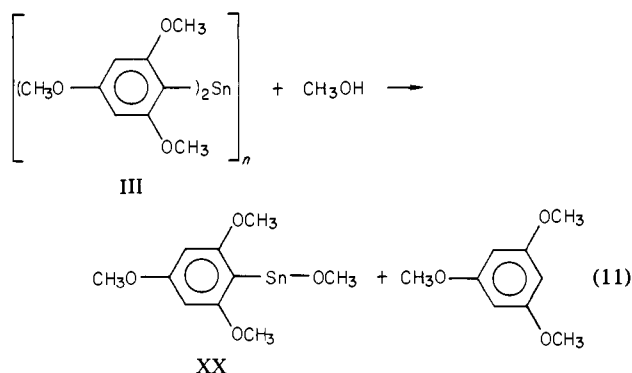aryllithiation by 2,4,6-trimethoxybenzene also reacts exothermically with methanol to give XX

III

    (11)

XX

whose doublet Mössbauer and infrared spectra are similar to those of the [2,6-bis(trifluoromethyl)phenyl]tin(II) methoxide. An attempt to prepare the chloride derivative by an exchange reaction of (2,4,6-trimethoxyphenyl)trimethyltin(IV)[36] with tin(II) chloride gave the expected trimethyltin chloride

    + Me₃SnCl (12)
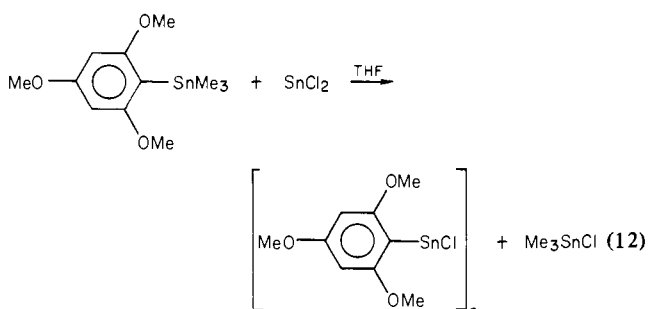
but the brown waxy nature of the precipitate indicated that the product had oligomerized. Similar attempts by other workers also failed.[23] By contrast VI–VIII resist oligomerization and disproportionation but are converted by air and moisture into the aryltin(IV) chloride oxides XV–XVII.

Finally, the tin product V from the reaction of (2,4,6-tri-*tert*-butyl-phenyl)lithium, could not be completely separated from the nontin-containing byproducts, but the Mössbauer and mass spectrometric data suggest that V is a stable tin(II) monomer in the solid.[37,38]

Our results can be rationalized in terms of the inhibition to further reaction provided by the substituted phenyl ligands. Both the pentafluoro- and 2,4,6-trimethyloxyphenyl ligands give oligomeric products, despite their strong and opposite electronic effects. The bulky CF₃ and *tert*-butyl groups inhibit oligomerization of their 2,6-disubstituted derivatives, presumably by preventing the approach of the tin(II) atoms within interaction distance. Coordination by one or two oxygen atoms in the methoxymethyl derivatives stops the synthesis at the monoaryltin(II) chloride stage. However, the analogous nitrogen derivatives apparently exist only as lithium chloride complexes and react further to produce tetraaryltin(IV) products when one nitrogen is available and presumably complexed by lithium chloride[39] or various aryltin(IV) chlorides when two nitrogens are present.[40]

(36) Kroth, H.-J.; Schumann, H.; Kuivila, H. G.; Schaeffer, C. D., Jr.; Zuckerman, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 1754.

(37) Reference to the recently solved structure of the sterically congested bis(2,4,6-tri-*tert*-butylphenyl)mercury(II), in which the two phenyl rings are perpendicular to one another in contrast to the coplanar diphenylmercury(II), is relevant here.[38]

(38) Huffman, J. C.; Nugent, W. A.; Kochi, J. K. *Inorg. Chem.* **1980**, *19*, 2740.

(39) The lithium chloride may also be complexed by the tin(II) atom using its lone pair.

(40) Ruddick, J. N. R. *Rev. Silicon, Germanium, Tin, Lead Compnds.* **1976**, *2*, 115.

(41) The reaction of (2,4,6-tri-*tert*-butylphenyl)lithium with phosphorus-(III) trichloride gives the corresponding arylphosphorus(III) dichloride. Treatment with magnesium metal gives bis(2,4,6-tri-*tert*-butylphenyl)diphosphene, whose crystal structure was reported, and not the monomeric arylphosphine species [Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 4587]. Bis(2,4,6-tri-*tert*-butylphenyl)phosphinic chloride is also known, and its X-ray crystal structure has been reported [Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 399].

Models for the Coordination Site of Iron in Cytochrome P-450. Synthesis and Spectroscopic Properties of a Dioxygen Adduct of [(2,3,5,6-Fluorophenyl)thiolato]iron(II) Tetraphenylpivaloylporphyrin

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The reaction cycle of cytochrome P-450 now commonly accepted[1] includes four states: low-spin ferric resting state A, substrate-bound high-spin ferric state B, high-spin ferrous (deoxy state) state C, and the diamagnetic ferrous oxy state D. Past efforts in many laboratories have produced well-defined iron porphyrin thiolato complexes that represent models for states B and C.[2–4] We now describe the synthesis and properties of a potential model for state D.

Previous studies in our laboratory have shown that pentacoordinate thiolato anions of the type FeTPP(SR)⁻ react with oxygen or carbon monoxide in the solid state to yield well-defined, reversibly exchangeable complexes.[5] The oxygenation reaction, however, had to be carried out at −30 °C to avoid side reactions.

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‡ Physik, Medizinische Hochschule.

(1) (a) Gunsalus, I. C.; Meeks, J. R.; Lipscomb, J. D.; Debrunner, P.; Münck, E. In "Molecular Mechanisms of Molecular Oxygen Activation"; Academic Press: New York, 1974; p 559. (b) Debrunner, P. G.; Gunsalus, I. C.; Sligar, S. G.; Wagner, G. C. In "Metal Ions in Biological Systems"; Marcel Dekker: Bâle, 1978; Vol. 7, p 241. (c) Ullrich, V. *Top. Curr. Chem.* **1979**, *83*, 67. (d) Ullrich, V. *J. Mol. Catal.* **1980**, *7*, 159.

(2) Koch, S.; Tang, S. C.; Holm, R. H.; Frankel, R. B.; Ibers, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 916.

(3) Caron, C.; Rivière, G.; Mitschler, A.; Ricard, L.; Schappacher, M.; Weiss, R. *J. Am. Chem. Soc.* **1979**, *101*, 7401.

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(5) Ricard, L.; Schappacher, M.; Fischer, J.; Weiss, R.; Montiel-Montoya, R.; Bill, E.; Gonser, U.; Trautwein, A., submitted for publication.

Table I. UV–Visible Spectra of the Complexes

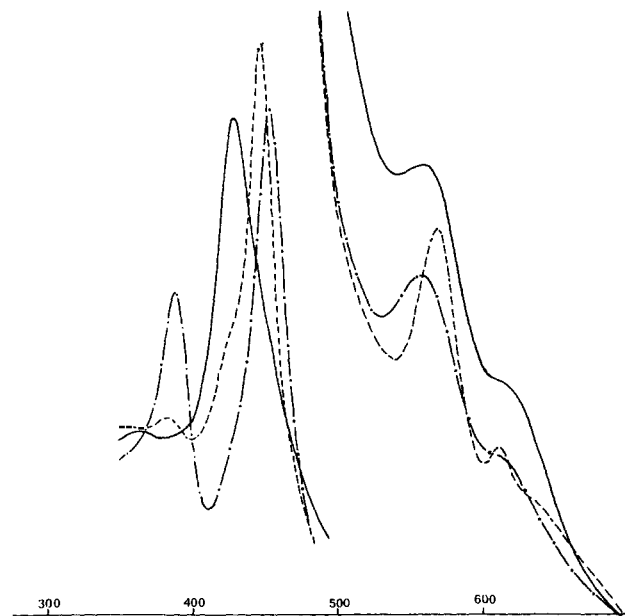| complex	absorption, nm			
[FeTPpivP(SC$_6$HF$_4$)][K-222]	381	446	568	610
[Fe(CO)TPpivP(SC$_6$HF$_4$)][K-222]	387	452	558	610
[Fe(O$_2$)TPpivP(SC$_6$HF$_4$)][K-222]	364	427	562	610
FeTPpivP(SC$_6$HF$_4$)		419	505	
[FeTPpivP(OH)][K-222]		446	538	569	609

Figure 1. UV–visible spectra of the [Fe(L)TPpivP(SC$_6$HF$_4$)]⁻[K-2.2.2.]⁺ complexes: full line, O$_2$ complex; dash–dot line, CO complex; dashed line, five-coordinate material.

The products also undergo rapid thermal degradation above −10 °C to yield, in most cases, a hydroxy derivative with a characteristic Soret absorption at 446 nm.[6,7] It quickly became apparent that the cause of this instability was the absence of a protecting cavity around oxygen and the large charge transferred to iron by the presence of the anionic sulfur donor. Collman's work on hemoglobin models has shown the excellent kinetic stabilization attainable through the use of the picket fence porphyrin. Preliminary work with picket fence porphyrins, however, yielded no appreciable or only nonreproducible gains in stability.

These observations were rationalized when the crystal structures of three compounds of the type [FeTPpivP(SR)]⁻[Na-2.2.2.]⁺ (R = Et, C$_6$H$_5$, 2,4,5-C$_6$H$_2$Cl$_3$) were obtained.[8] In all three cases, the thiolate lies within the cavity formed by the pivaloyl arms; thus, oxygen can only bind outside and the benefit of a protecting pocket is lost. These observations led to the choice of a bulkier, less reducing thiolate, 2,3,5,6-C$_6$HF$_4$S⁻, in the hope that the picket fence cavity would remain empty and would improve the stability of the oxy adduct.

The synthesis of the five-coordinate ferrous derivative **1** [Fe^{II}TPpivP(SC$_6$HF$_4$)]⁻[K-2.2.2.]⁺ can be conducted in two fashions. Derivative **1** can be obtained by reducing the iron(III) starting material, FeBrTPpivP, with a threefold excess of the cryptated potassium thiolate. However, the preferred preparation involves reduction by zinc amalgam prior to addition of a twofold excess of the cryptated potassium thiolate.[9] The product is only

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(6) The exact nature of the precursor is still under investigation. All thiolates used so far present Soret absorption near 424 nm and three low-intensity bands in the α,β region.[3] A similar spectrum has been observed at low temperatue when CO is pumped off from crushed single crystals of **2** or upon cooling C$_6$H$_5$F solutions of **1**.

The OH⁻ complex has been synthesized by reacting cryptated KOH with iron(II) porphyrins and displays identical spectroscopic properties. A previous report on the OEP analogues can be found in ref 7.

(7) Mincey, T.; Taylor, T. G. *J. Am. Chem. Soc.* **1979**, *101*, 765.

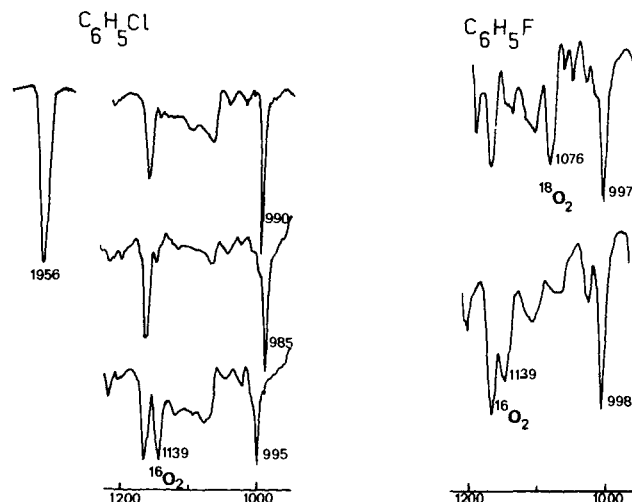(8) Ricard, L.; Schappacher, M.; Weiss, R., in preparation.

C_6H_5Cl $\qquad\qquad\qquad\qquad$ C_6H_5F

Figure 2. IR spectra of the complexes in the 1200–1000-cm⁻¹ range: top, CO adduct; middle, five-coordinate material; bottom, oxygen complex. Notice the shift of the porphyrin band at 985 cm⁻¹ toward 1000 cm⁻¹ upon coordination of a sixth ligand.

soluble in chlorobenzene or fluorobenzene and precipitates in other aromatics. The UV–visible spectra of the complexes are assembled in Table I and reproduced in Figure 1.

Quite surprisingly, the SC$_6$HF$_4$⁻ adduct displays a UV spectrum nearly identical with that of the OH⁻ complex.[6] One essential difference is the behavior of the thiolato adduct under CO and O$_2$: the characteristic splitting of the Soret band appears (Figure 1) when the CO adduct [Fe(CO)TPpivP(SC$_6$HF$_4$)][K-2.2.2.] (**2**) is formed whereas the hydroxo species gives rise to a single absorption at 428 nm. Under oxygen, the OH⁻ complex gives an absorption at 438 nm while the thiolato adduct gives two absorptions, one at 427 nm and a minor band at 364 nm. This spectrum is similar to that reported by Dolphin and James for oxy-P-450;[10] the reaction is reversible and oxygen can either be pumped off or exchanged by CO according to the equilibrium reaction

$$[Fe(O_2)TPpivP(SC_6HF_4)]^- \underset{O_2}{\overset{CO}{\rightleftharpoons}} [Fe(CO)TPpivP(SC_6HF_4)]^-$$
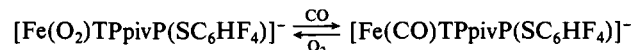
The thermal stability of the oxy adduct is dramatically improved: concentrated solutions can be manipulated at room temperature and can be kept for days at 4 °C.[11] Similarly, all products are less sensitive to traces of water. These effects are not perfectly understood at present but it seems reasonable to assume that the oxy adduct, in particular, is stabilized by the electron-withdrawing effect of the ring substituents. A similar electronic effect would explain the observed shift of the UV spectrum of **1**.

Further evidence supporting the formation of the oxy anion **3**, [Fe(O$_2$)TPpivP(SC$_6$HF$_4$)]⁻, comes from infrared and Mössbauer studies. Initially, IR experiments were conducted in chlorobenzene solutions. The sample and reference cells were filled with identical solutions of [K-2.2.2.(SC$_6$HF$_4$)] and the porphyrin was added to the sample cell. When ^{16}O$_2$ was admitted, an absorption appeared

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(9) FeBrTPpivP is prepared according to: Collman, J. P.; Gagné, R. G.; Reed, C. A.; Halbert, T. H.; Lang, G.; Robinson, W. T. *J. Am. Chem. Soc.* **1975**, *97*, 1427. One hundred milligrams of the complex, dissolved in 30 mL of freshly distilled and deaerated C$_6$H$_5$Cl, is mixed with solutions containing cryptand 222 and KSC$_6$HF$_4$. The potassium thiolate is prepared by reacting the thiol and KOH in dry ethanol and precipitating with ether. The thiol is available from Aldrich Chemical Co.

UV–visible spectra were measured on a Cary 210 spectrometer and IR spectra on a Perkin-Elmer Model 398 apparatus. Mössbauer spectra were accumulated in Saarbrücken with a standard apparatus in the constant-acceleration mode with a ^{57}Co/Rh (ca. 50 mCi) source. Isomer shifts are given with respect to α-Fe at room temperature.

Oxygen-18 (98.5%) was obtained from "Service des isotopes stables", Saclay, France.

(10) Dolphin, D.; James, B. R.; Curtis Welborn, H. *J. Mol. Catal.* **1980**, *7*, 201.

(11) The solutions must, however, be kept in the dark. Daylight and UV accelerate the decomposition.
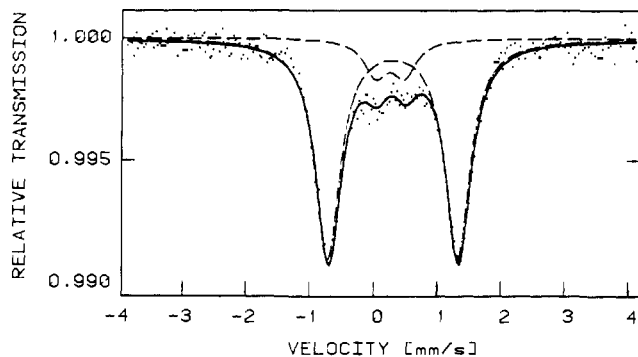
Figure 3. Mössbauer spectrum of $[Fe(O_2)TPpivP(SC_6HF_4)]^-[K-2.2.2.]^+$ at 77 K. The sample is 85 ± 5% pure and may contain 15 ± 5% iron-(III).

at 1139 cm^{-1}. This band is not present in the CO adduct or in the five-coordinate material (Figure 2). Substituting $^{18}O_2$ for natural oxygen would shift this absorption to the 1073-cm^{-1} region. Unfortunately, this part of the spectrum is obscured by a near total absorption of chlorobenzene so the initial experiments could only indirectly confirm the attribution of the O–O stretching vibration: when $^{18}O_2$ was used, there was indeed no absorption at this wavelength but we could not detect the oxygen-18 stretching vibration. A careful search for a different good solvent led to the use of fluorobenzene (Figure 2). The experiments carried out in this solvent revealed the appearance of the $^{18}O_2$ stretch at 1076 cm^{-1}, in good agreement with the calculated value of 1073 cm^{-1} for a pure harmonic oscillator.

Finally, Mössbauer spectroscopy confirms the formulation of **3** as an O_2 adduct. The studies carried out on the anion [FeTPP(SC$_6$H$_5$)]$^-$ at low temperature have shown that a species displaying the Mössbauer features of an oxy adduct are indeed observed when oxygen is admitted to the solid sample: a quadrupole doublet with IS = 0.312 mm·s^{-1}, ΔE_q = 2.015 mm·s$^-$, and Γ_{expt} = 0.272 mm·s^{-1} was observed at 77 K. These values are similar to those reported for oxy-P-450.[12] They are quite insensitive to the nature of the sixth ligand and have the same magnitude for oxyhemoglobin[13] and the oxyhemoglobin model compounds reported by Collman et al.[14] However, despite repeated attempts under various conditions of pressure and temperature, we could not obtain more than about 40% oxygenation on bulk samples of 100 mg.[5]

The sample used in the present study, [Fe(O$_2$)TPpivP-(SC$_6$HF$_4$)]$^-$, was obtained by exchanging CO in the carbonyl adduct **2**. A solution of **2** was purged with oxygen for 30 min, pentane was added, and the resulting oil was frozen and transferred to the sample holder. The Mössbauer spectrum, reproduced in Figure 3, shows that 85 ± 5% exchange has taken place. There is about 15% of a second species, probably iron(III) (vide infra). The parameters obtained at 77 K are nearly the same as for the TPP adduct, namely, IS = 0.30, ΔE_q = 2.04, and Γ_{expt} = 0.48 mm·s^{-1} (±0.02 mm·s^{-1}). Present efforts are directed at obtaining a pure sample. A complete Mössbauer study of all three complexes will be reported later.

Prolonged exposure of **3** to an oxygen atmosphere or UV irradiation at 190 nm results in the formation of a new species with absorptions at 419 and 505 nm. This spectrum is typical of five-coordinate iron(III), and Mössbauer spectroscopy indeed confirms that an iron(III) species is formed under these circumstances (≈30% in 6 h). A material with an identical UV–visible spectrum, FeTPpivP(SC$_6$HF$_4$), **4**, can be synthesized in a manner similar to Holm's preparation.[2] The above-mentioned observations suggest that the oxy complex **3** is degraded following the reaction $[Fe^{II}(O_2)TPpivP(SC_6HF_4P)]^- \rightleftharpoons Fe^{III}TPpivP(SC_6HF_4) + O_2^-$.[20]

Interestingly, solutions of **3** can be reduced to the iron(II) complex **1** upon slight warming when the oxygen atmosphere is pumped off, even though there seems to be no excess thiolate left. In a separate experiment, solutions of **4** were reacted under argon at –30 °C with solutions of $[K^+-2.2.2.]O_2^-$, resulting in the immediate formation of **3**, as shown by the identity of UV–visible spectra. This parallels the results of Valentine et al.[15]

That superoxide ions are formed upon degradation of the oxy complex **3** constitutes a further similarity with the behavior of cytochrome P-450.[16] Current ESR experiments should further confirm this point.

The evidence presented above shows that an oxy adduct mimicking the properties of oxy-P-450 can be obtained. The reversibility of the oxygenation–carbonylation reaction demonstrates the presence of sulfur bonding to iron.[17] The decreased frequency of the O–O stretching vibration relative to that reported for oxyhemoglobin models[18] (1163 cm^{-1}) would similarly indicate the presence of a larger charge on iron.[19] This complex undoubtedly constitutes a model for the oxy state of cytochrome P-450. Its good thermal stability will facilitate further studies on other putative intermediates in the P-450 cycle.

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(17) X-ray structure determinations of the CO and O$_2$ complex are under way and will be reported in a future communication.
(18) Collman, J. P.; Brauman, J. I.; Halbert, T. R.; Suslick, K. S. *Proc. Natl. Acad. Sci. U.S.A.* **1976**, *73*, 3333.
(19) A similar effect is observed in the CO complex, where a shift of 14 cm^{-1} is observed relative to the value of 1970 cm^{-1} reported in the imidazole complexes.[18]
(20) As suggested by one referee, an outer-sphere autoxidation mechanism cannot be excluded. See: Billecke, J.; Kokisch, W.; Buchler, J. W. *J. Am. Chem. Soc.* **1980**, *102*, 3622.

Synthesis and Structure of [FeCo$_3$(CO)$_{12}$AuPPh$_3$]: A Trimetallic Trigonal-Bipyramidal Cluster. Gold Derivatives as Structural Analogues of Hydrides

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The stereochemical influence of the hydride ligand and the structures of transition-metal hydrides have been topics of considerable controversy and discussion.[1,2] Overlooked has been a close structural relationship between certain hydrido–metal complexes and AuPPh$_3$ derivatives exemplified by such pairs of compounds as the complexes [Co(CO)$_4$AuPPh$_3$] and [Co(CO)$_4$H] with capped tetrahedral geometries,[3,4] the complex [Fe(CO)$_4${AuPPh$_3$}$_2$], which we have shown to have the same bicapped tetrahedral geometry as the hydride [Fe(CO)$_4$H$_2$],[4,5] and the double-bridged Os$_3$ clusters [Os$_3$(CO)$_{10}$(μ-X)(μ-L)] with X = Cl or Br and L = H or AuPPh$_3$.[6,7,8]

The structural similarities may seem to be surprising at first because it would seem that a gold phosphine group and a hydride

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