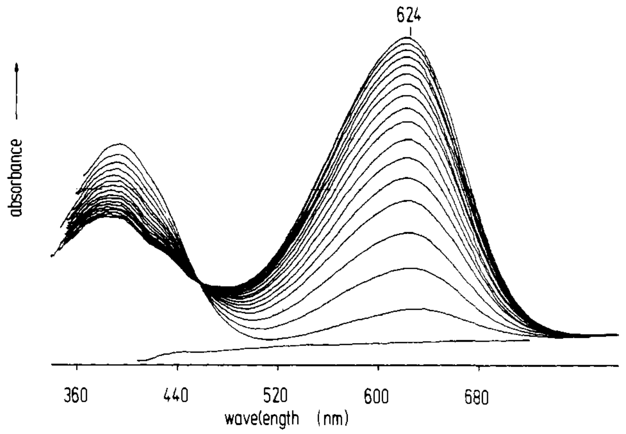

Figure 1. Reconstitution of 13-(trifluoromethyl)retinal-BR. Spectra were recorded continuously on an Aminco DW-2 spectrophotometer.

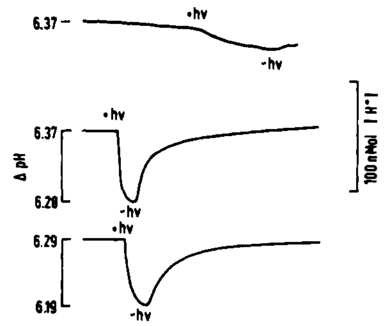

Figure 2. pH response of a 13-(trifluoromethyl)retinal-containing cell vesicle preparation: top, control with retinal-free BO; middle, BR containing (trifluoromethyl)retinal; bottom, BR containing retinal. The ratio of 13-(trifluoromethyl)retinal-BR to retinal-BR, as determined spectroscopically, was about 1:0.7; in both cases the retinals were added in amounts slightly less than stoichiometric.

NMR spectrum, supporting the all-trans configuration of **7**, are also given in Scheme I.[11] All chemicals used for the synthesis were of analytical grade.

When **7** (λ_{max} 390 nm, ethanol) is converted to the SBH^+ with *n*-butylamine, a bathochromic shift to 460 nm is measured. Upon addition of **7** to an aqueous suspension of BO at 15 °C which had been isolated from retinal (–) *H. halobium* mutants (JW 5) the absorption at 390 nm disappeared, and immediate formation of a blue species with an absorption at 624 nm took place with a half-time of formation of approximately 5 min (Figure 1). This λ_{max} constitutes the largest red shift so far observed for a pentaene retinal-containing chromoprotein.

To test the proton-pumping facilities of this new artificial BR, we incorporated **7** into BO-containing vesicles, which were obtained by sonication of *H. halobium* mutant cells deficient in retinal biosynthesis as described in ref 12. Upon reconstitution the same 624-nm chromophore was formed. After being placed in a thermostated (15 °C) cuvette, the vesicle suspension was left in darkness to stabilize the pH. Then the cuvette was illuminated with light from a slide projector, filtered through a cutoff filter (GG 495 nm, Schott), and the pH response monitored (Figure 2). Compared to retinal-containing vesicles, the extent of acidification was about 70%, indicating a proton-pumping activity of 13-(trifluoromethyl)retinal comparable to that of retinal.

The dramatic influence of the trifluoromethyl group on the bathochromic shift ("opsin shift"; cf. ref 9) demonstrates that the electronic properties of the C-13 substituent of retinal do have a pronounced effect on the absorption characteristics of retinals in BO.

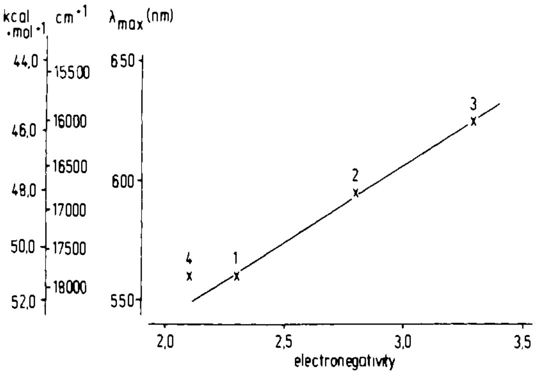

Figure 3. Relationship between the λ_{max} of BR's and the electronegativity of the C-13 substituent of the incorporated retinals (1, CH_3; 2, Br; 3, CF_3; 4, H). The λ_{max} value for 2 (Br) was taken from ref 10.

We note an interesting linear relationship between the electronegativity of the C-13 substituents methyl, bromine, and trifluoromethyl, which possess similar van der Waals radii of about 220 pm, and the absorption shifts of the corresponding BR's, (Figure 3).

The importance of steric identity of the retinal analogues is demonstrated by 13-demethylretinal (H as the C-13 substituent, van der Waals radius of 120 pm), which does not fit into the correlation in Figure 3.

Obviously, the energy difference between the ground and the excited states of retinal in BR strikingly depends on the electron-withdrawing effect of the substituent at position 13. It will be of interest to show by comparison with, for example, 9-(trifluoromethyl)retinal, whether the 13-position of the polyene chain plays a special role in the absorption properties in BR. Furthermore, theoretical analysis of the absorption spectra of these BR analogues will be helpful to check on the charge distribution models already suggested.

Acknowledgment. We thank Ms. R. Schoeningh for preparation of cell vesicles, Dr. J. Weber for making available a retinal (–) *H. halobium* mutant (JW 5), and the Deutsche Forschungsgemeinschaft and the Fonds der Chemischene Industrie for financial support.

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[12] Lanyi, J. K.; MacDonald, R. E. *Methods Enzymol.* **1979**, *56*, 398-407.

Synthesis of Stabilized Phenyltin(II) Compounds: Inhibition of the Conversion to Tin(IV) by Ortho Substitution[1]

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Norman, Oklahoma 73019

Received April 6, 1981

We have synthesized the first example of an organotin(II) compound with phenyltin(II) σ bonds.

During the past century many reports appeared describing what were believed to be diorganostannylenes.[3-5] Diphenyltin, I, was

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[1] Some of these results have been preliminarily communicated: Bigwood, M. P.; Corvan, P. J.; Meese, M. R.; Zuckerman, J. J. *Abstr. 2nd Conf. N. Am. Continent*, Las Vegas, NV, Aug 1980. Zuckerman, J. J. *Abstr. Xth Int. Conf. Organomet. Chem.*, Toronto, Ont., Aug 1981.

[2] Present address: Research Laboratories, Eastman Kodak Co., Rochester, NY 14650.

[3] Donaldson, J. D. *Prog. Inorg. Chem.* **1967**, *8*, 287.

[4] Neumann, W. P. In "The Organometallic and Coordination Chemistry of Germanium, Tin and Lead", Gielen, M., Harrison, P. G., Eds.; Freund Publishing Co.: Tel-Aviv, Israel, 1978.

[5] Neumann, W. P. "The Organic Chemistry of Tin"; Wiley: New York, 1970; Chapter 14, p 128 ff.

first prepared as a bright yellow solid in the 1920s by a Grignard route[6]

$$2C_6H_5MgBr + SnCl_2 \xrightarrow{Et_2O} [(C_6H_5)_2Sn]_n + 2MgBrCl \qquad (1)$$

or from a liquid ammonia/ether solution of diphenyltin(IV) hydride which is allowed to warm to room temperature[7]

$$(C_6H_5)_2SnH_2 \xrightarrow[Et_2O]{NH_3} [(C_6H_5)_2Sn]_n + H_2 \qquad (2)$$

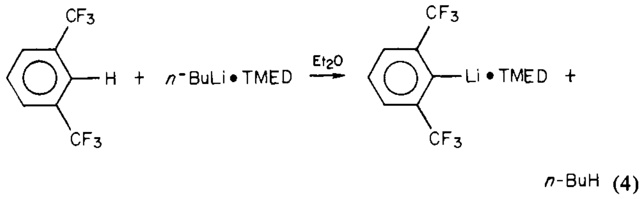
Four modifications of I were elucidated in the 1960s, including a product from phenyllithium[8,9]

$$2C_6H_5Li + SnCl_2 \rightarrow [(C_6H_5)_2Sn]_n + 2LiCl \qquad (3)$$

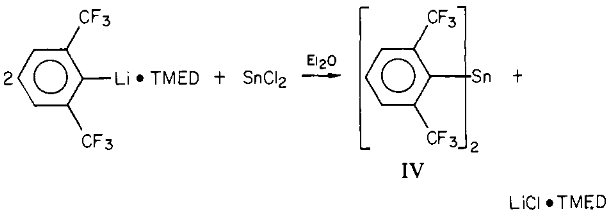
But these supposed diorganotin materials are the result of rapid polymerization of the stannylene intermediates.[4,5] In particular, an X-ray diffraction study reveals that tetrahedral diphenyltin moieties form a hexameric chair-conformation ring in diphenyltin.[10,11]

The synthesis of phenyltin(II) compounds, stabilized by inhibition to further reaction through steric and electronic effects as well as by coordination of the tin(II) atom by heteroatom-containing substituents on the phenyl rings, is the subject of this Communication.

An ether solution of [2,6-bis(trifluoromethyl)phenyl]lithium prepared from aryllithiation of 1,3-bis(trifluoromethyl)benzene by tetramethylethylenediamine–*n*-butyllithium complex (*n*-BuLi·TMED) was added to tin(II) chloride to precipitate a light brown solid (IV):



(4)



IV

(5)

The tin-119m Mössbauer spectrum of IV is a doublet with a high isomer shift (IS) (see Table I for the structural formulas and Mössbauer parameters of compounds I–XX), confirming that the tin atom is in the divalent state[12,13] and that the solid is the first genuine example of a stable phenyltin(II) species.

The Mössbauer spectra of freshly precipitated I–III are, on the other hand, singlets in the IS region typical of $(R_2Sn^{IV})_n$ species.[12] Such species readily react with elemental oxygen, sulfur, and halogens to give R_2SnE (E = O, S, and X_2)[14] and undergo insertion into the S–S bond in dibenzyl disulfide.[15] The yellow colors of various reported modification of I have been attributed to branching of the tin chains,[16] and treatment with elemental iodine in benzene gives appreciable quantities of triphenyl- and phenyltin(IV) iodides in addition to the expected diphenyltin(IV) iodide.[17] Other known hexameric diaryltin derivatives include the *p*-tolyl-, *p*-ethoxyphenyl-, *p*-biphenylyl-, and 2-naphthyl compounds.[4] The properties of the 1-naphthyl species are anomalous, and Russian workers have claimed that the 9-phenanthryl derivative[18] is monomeric, but their Mössbauer IS value (1.8 mm/s)[19] is indicative of an oligomeric structure.[12,13]

Table I. ^{119m}Sn Mössbauer Parameters for the Substituted Aryltin Derivatives at 77K[a]

compound	IS,[b] mm/s	QS,[c] mm/s
$[(C_6H_5)_2Sn]_n$ (I)	1.56[d]	
$[(C_6F_5)_2Sn]_n$ (II)	1.69	1.39
$\{[2,4,6\text{-}(OCH_3)_3C_6H_2]_2Sn\}_n$ (III)	1.60	
$[2,6\text{-}(CF_3)_2C_6H_3]_2Sn$ (IV)	3.37	1.93
$[2,4,6\text{-}(t\text{-}C_4H_9)_3C_6H_2]_2Sn$ (V)[e]	3.28	1.90
$2\text{-}OCH_3C_6H_4SnCl$ (VI)	3.29	1.99
$2\text{-}O\text{-}i\text{-}C_3H_7C_6H_4SnCl$ (Vii)	3.19	2.12
$2,4,6\text{-}(OCH_3)_3C_6H_2SnCl$ (VIII)	3.25	2.27
$2,6\text{-}[N(CH_3)_2]C_6H_3SnCl\cdot LiCl$ (IX)[e]	3.31	1.72
$2,4,6\text{-}[N(CH_3)_2]C_6H_2SnCl\cdot LiCl$ (X)[e]	3.43	2.10
$(C_6H_5)_4Sn$	1.15–1.40[d]	
$[2\text{-}[N(CH_3)_2]C_6H_4]_4Sn$ (XI)	1.23	
$[2\text{-}[N(i\text{-}C_3H_7)_2]C_6H_4]_4Sn$ (XII)	1.39	
$2,6\text{-}[N(CH_3)_2]_2C_6H_3SnCl_2C_4H_9\text{-}n$ (XIII)	0.69	2.12
$2,4,6\text{-}[N(CH_3)_2]_3C_6H_2SnCl$ (XIV)	0.80	1.73
$[2\text{-}OCH_3C_6H_4SnClO]_n$ (XV)	0.00	
$[2\text{-}O\text{-}i\text{-}C_3H_7C_6H_4SnClO]_n$ (XVI)	0.02	
$[2,4,6\text{-}(OCH_3)_3C_6H_2SnClO]_n$ (XVII)	0.26	
$2,6\text{-}(CF_3)_2C_6H_3SnOCH_3$ (XVIII)	2.88	2.31
$(4\text{-}CH_3C_6H_4S)_2Sn$ (XIX)	3.48	1.79
$2,4,6\text{-}(OCH_3)_3C_6H_2SnOCH_3$ (XX)	2.76	2.41

[a] Recorded vs. a $Ca^{119m}SnO_3$ source (New England Nuclear Corp.) at ambient temperature. [b] ±0.03 mm s^{-1}. [c] ±0.06 mm s^{-1}. [d] References 12 and 41. [e] Could not be isolated in a pure form.

Arylation of tin(II) chloride by the pentafluorophenyl Grignard reagent

$$2C_6F_5MgBr + SnCl_2 \xrightarrow{Et_2O} [(C_6F_5)_2Sn]_n + 2MgBrCl \qquad (6)$$

gives II as a yellow solid which quickly converts on drying in vacuo into a dark brown paste. Mössbauer data confirm that this paste is a tin(IV) oligomer. The initial precipitate may be an etherate which polymerizes when the ether is removed. Attempted synthesis of II by the decarboxylation of bis(pentafluorophenyl benzoate)tin(II) failed.[20] The nonzero QS value derives from the inductive pull of this electronegative group, and the same effect is seen in the trialkyltin(IV) perfluoro organics.[12]

Lithioarylations using phenyl groups with oxygen- and nitrogen-bearing substituents capable of internal coordination with the tin atom give different results. Ortho- or 2,6-substituted [(alkoxymethyl)phenyl]lithiums give the aryltin(II) chloride products VI–VIII only. Coordination by oxygen is confirmed by the decrease of the infrared stretching frequencies of the CH_2OR linkage compared with the parent (alkoxymethyl)benzene ligands.

The behavior of the dialkylamino analogues is more complex. The action of [2-[(dialkylamino)methyl]phenyl]lithium[21] on $SnCl_2$ gives the tetraphenyltin(IV) derivatives XI and XII[22] whose Mössbauer spectrum contains a very broad singlet absorption in the tin(IV) region, results in accord with recent findings.[23] It

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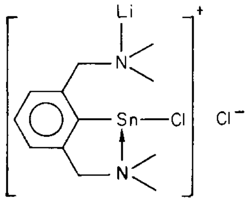
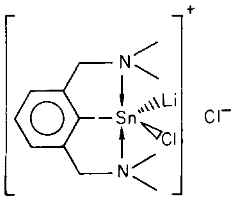
(22) Reaction of [2-[(dimethylamino)methyl]phenyl]lithium with tin(II) chloride has been reported to give dark colored and partly tarry products whose Mössbauer spectra showed the presence of a mixture of tin derivatives.[23]

(23) Bos, K. "Organic and Organometallic Chemistry of Divalent Tin", Drukkerig Elinkwijk Bv: Utrecht, 1976; p 32.

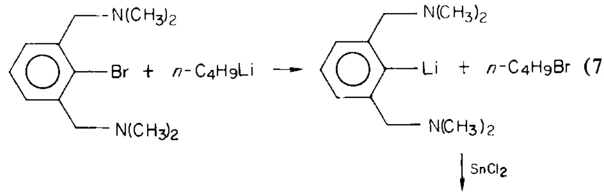
has been well-established by variable-temperature NMR[24-26] and X-ray studies[27,28] that there is a strong nitrogen → tin coordination where there are one or two *o*-[(dimethylamino)methyl] groups substituting phenyltin(IV) systems. However, this coordinating effect is apparently insufficient to stabilize a tin(II) product in the presence of lithium chloride (vide infra).

Yet another behavior is seen with [2,6-bis- and 2,4,6-tris-[(dimethylamino)methyl]phenyl]lithium which give mixtures of the monoaryltin(II) chloride product complexed by lithium chloride, IX and X, respectively. By analogy with the result obtained in the tin(IV) series using the same ligand,[25] we formulate these complexes as ionic materials in which lithium is coordinated either to one of the amine nitrogen atoms (A) and/or to the tin(II) lone pair (B).


A


B

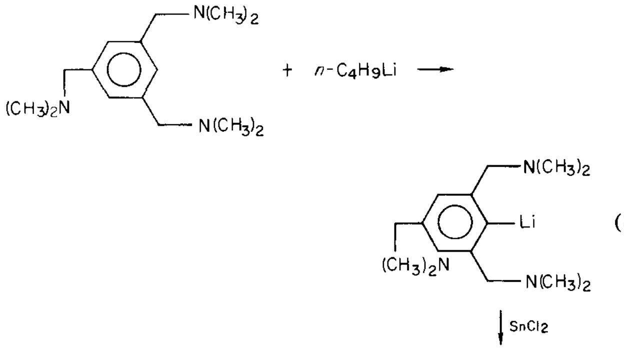
When butyl bromide is a byproduct of syntheses such as eq 7, the initially formed complex IX reacts with the butyl bromide to yield XIII:


(7)

IX + XIII

Prolonged reaction time yields pure XIII.

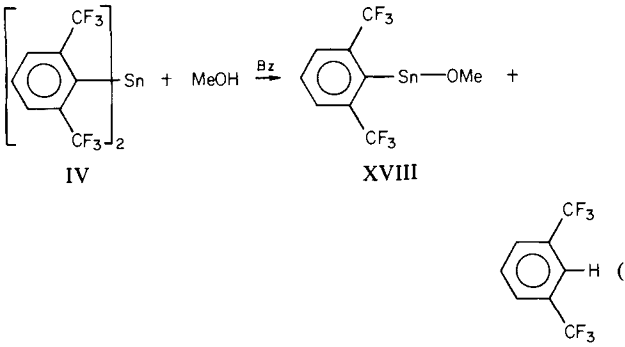
Eliminating the butyl bromide by starting from the 1,3,5-tris derivative gave a triaryltin(IV) chloride, XIV, instead:


(8)

X + XIV

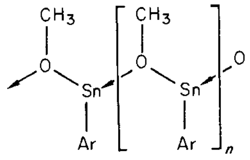
The formation of a complex involving the single nitrogen atom available when only one (dimethylamino)methyl group is present on the phenyl ring rationalizes the lack of stability of the corresponding aryltin(II) chlorides which undergo further reaction to tin(IV) products. Oxidative additions to such complexes by organic halide and lithium compounds present in the reaction mixture explain the production of XI–XIV. Nitrogen coordination of the tin atom in XIII and XIV is apparent from their low IS values compared with analogous diorgano- and triphenyltin(IV) chlorides.

In the 2,6-bis(trifluoromethyl)phenyl derivative, IV, the infrared absorption pattern of the product is identical with that of the parent *m*-bis(trifluoromethyl)benzene ligand in the trifluoromethyl region, 1355-1070 cm^{-1}, from which we are forced to conclude that little direct across-space interaction of the trifluoromethyl groups with the tin(II) atom occurs. The tin(II) Mössbauer spectrum of IV does not alter on aging. This derivative undergoes methanolysis in an exothermic reaction

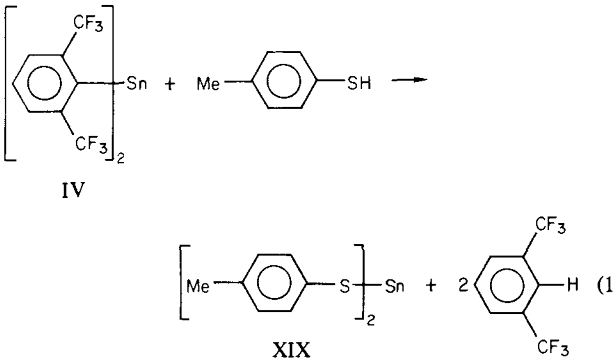

IV XVIII

(9)

which contrasts with the inert nature of I which is recrystallized from methanol/benzene.[8] The doublet Mössbauer spectrum of XVIII is similar to that of dimethoxytin(II).[29-31] The infrared spectrum shows absorptions arising from ν(Sn–O) modes at 740 cm^{-1}, the latter occurring in tin(II) di-*tert*-butoxide[32] and diorganotin(IV) oxides,[33] and is characteristic of a three-coordinated, associated structure with bridging methoxide and terminal aryl groups:



However, an alternative ladder structure such as that found in (η^5-cyclopentadienyl)tin(II) chloride[34] cannot be ruled out. Both aryl groups are cleaved by the more acidic *p*-toluenethiol:


IV

XIX

(10)

The doublet Mössbauer spectrum of bis(*p*-toluenethiolato)tin(II), XIX, resembles that of tin(II) dithiophenoxide (IS = 3.51; QS = 1.60 mm/s).[35] The freshly precipitated (etherate) product of

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(24) van Koten, G.; Noltes, J. G. *J. Am. Chem. Soc.* **1976**, *98*, 5393.

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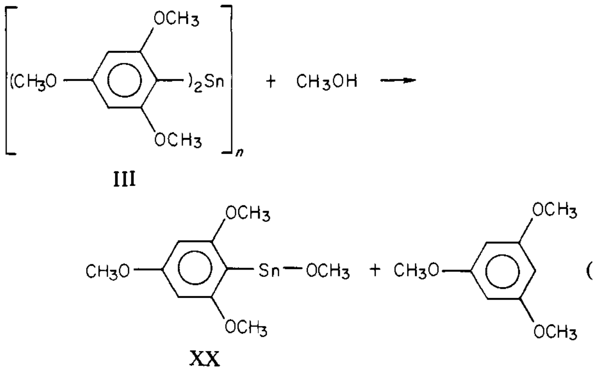
(35) Harrison, P. G. *J. Chem. Soc., Chem. Commun.* **1972**, 544.

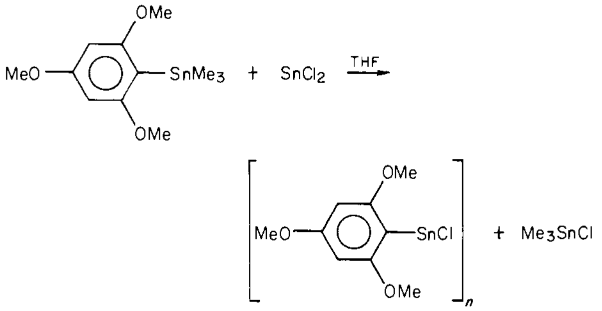
aryllithiation by 2,4,6-trimethoxybenzene also reacts exothermically with methanol to give XX


III

XX

(11)

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


(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 CF_3 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]

Acknowledgment. Our work is supported by the Office of Naval Research and by the National Science Foundation through Grant CHE-78-26548. We thank Mr. M. R. Meese for carrying out the preparations of some of the substituted phenyl ligands.

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(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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