crowding.[22] The $(\eta^5\text{-}C_5Ph_5)Mo(CO)_3(L_2\text{-}P)$ complex is even more sterically crowded than its C_5Ph_4H analogue, and the reaction to give $(\eta^5\text{-}C_5Ph_5)Mo(CO)_2(L_2\text{-}P,P')$ should therefore be even more facile. Hence, it is unlikely that the $(\eta^5\text{-}C_5Ph_5)Mo(CO)_3(L_2\text{-}P)$ complex will be long-lived enough to be spectroscopically observable, and therefore, the quartet ESR spectrum cannot be assigned to the $(\eta^5\text{-}C_5Ph_5)Mo(CO)_3(L_2\text{-}P)$ complex.

We suggest assignment of the quartet spectrum to the 17-electron $(\eta^5\text{-}C_5Ph_5)Mo(CO)_2(L_2\text{-}P)$ complex. This species has two inequivalent phosphorus atoms, and therefore, a quartet spectrum is predicted. The variable-temperature ESR spectra in Figure 2, which show a reversible conversion between the triplet and quartet signals, are consistent with this proposed assignment. The conversion between the two was cycled numerous times by raising and lowering the temperature, and the conversion is completely reversible. Assignment of the quartet spectrum to the 17-electron $(\eta^5\text{-}C_5Ph_5)Mo(CO)_2(L_2\text{-}P)$ complex is logical because of the simple equilibrium that can be written between the two species:

$$\underset{19e^-}{(\eta^5\text{-}C_5Ph_5)Mo(CO)_2(L_2\text{-}P,P')} \overset{K_{eq}}{\rightleftharpoons} \underset{17e^-}{(\eta^5\text{-}C_5Ph_5)Mo(CO)_2(L_2\text{-}P)} \quad (3)$$

Note that the temperature dependence of the proposed equilibrium is correct: higher temperature will favor the dissociation of the Mo-P bond, giving rise to more of the $(\eta^5\text{-}C_5Ph_5)Mo(CO)_2(L_2\text{-}P)$ complex (the quartet).[23] Assignment of the infrared bands at 2013 and 1939 cm^{-1} to this 17-electron species is suggested.

The behavior of the $(\eta^5\text{-}C_5Ph_5)Mo(CO)_2(L_2\text{-}P,P')$ complex in solution is different from that of the $(\eta^5\text{-}C_5Ph_4H)Mo(CO)_2(L_2\text{-}P,P')$ complex. We found no evidence for dissociation of a Mo-P bond in the latter complex.[3] The lack of dissociation is probably attributable to the fact that the $(\eta^5\text{-}C_5Ph_4H)Mo(CO)_2(L_2\text{-}P,P')$ molecule is less sterically crowded than the $(\eta^5\text{-}C_5Ph_5)Mo(CO)_2(L_2\text{-}P,P')$ molecule.

The ESR data lend further support to the proposed assignment of the 4-line spectrum to the 17-electron $(\eta^5\text{-}C_5Ph_5)Mo(CO)_2(L_2\text{-}P)$ species rather than to the 19-electrn $(\eta^5\text{-}C_5Ph_5)Mo(CO)_3(L_2\text{-}P)$ complex. The phosphorus coupling constants of this latter complex would be similar to the coupling constants of the related 19-electron $(\eta^5\text{-}C_5Ph_4H)Mo(CO)_3(L_2\text{-}P)$ and $(\eta^5\text{-}C_5H_4Me)Mo(CO)_3(L_2\text{-}P)$ complexes. Note, however, that while the a_{P_2} values of these two 19-electron complexes are similar to each other, they are quite different from the a_{P_2} value of the complex we assign as $(\eta^5\text{-}C_5Ph_5)Mo(CO)_2(L_2\text{-}P)$ (Table III).

Acknowledgment is made to the National Science Foundation for support of this research. D.R.T. acknowledges the Alfred P. Sloan Foundation for a fellowship.

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[22] Langford, C. H.; Gray, H. B. *Ligand Substitution Processes*; W. A. Benjamin: New York, 1966.

[23] Also observed in Figure 2 is a weak 1:2:1 triplet. We assign this weak triplet to the $(\eta^5\text{-}C_5Ph_5)Mo(CO)(L_2\text{-}P,P')$ 17-electron radical, formed by CO loss from the $(\eta^5\text{-}C_5Ph_5)Mo(CO)_2(L_2\text{-}P,P')$ complex.

Synthesis and Chemistry of Novel 2,2′-Binaphthyl-Substituted Organotin Lewis Acids

Ramesh Krishnamurti, Henry G. Kuivila,* Naseem S. Shaik, and Jon Zubieta

Department of Chemistry, State University of New York at Albany, Albany, New York 12222

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The synthesis and chemistry of novel Lewis acids containing neutral tin-centered Lewis acidic groups at the 2- and 2′-positions of 1,1′-binaphthyl are described. (±)-2,2′-Dibromo-1,1′-binaphthyl (**3**) was converted to the dilithio derivative, which was treated with trimethyltin chloride to yield 2,2′-bis(trimethylstannyl)-1,1′-binaphthyl (**4**) in excellent yield. Compound **4** then underwent highly selective methyl–Sn cleavage in the redistribution reactions with methyltin trichloride and tin tetrachloride to afford 2,2′-bis(monochlorodimethylstannyl)- and 2,2′-bis(dichloromethylstannyl)-1,1′-binaphthyl, **2a** and **2b**, respectively. The chlorotins were then converted into the organotin triflates, **2c** and **2d**, by metathetic reactions with silver triflate. Interaction of the bis(dichlorotin) **2b** and DMSO afforded a mono-DMSO (**12**) whose X-ray crystal structure revealed that coordination of DMSO occurred to one tin center and a chloride ligand from this tin had bridging interaction with the other tin moiety. An estimation of the equilibrium constant for the formation of **12** was obtained by ^{119}Sn NMR spectroscopy.

Introduction

Chiral ligands containing the 2,2′-disubstituted binaphthyl group have achieved remarkable success in the areas of chiral recognition of host molecules[1-3] and in certain asymmetric syntheses, such as the rhodium-catalyzed hydrogenation of aminoacrylic acid derivatives[4,5] and the alkylation and arylation of aldehydes.[6] On the other hand, very little is known about Lewis acids containing the 1,1′-binaphthyl group,[7] and we are not aware of any report of a Lewis acid, chiral or achiral, in which the Lewis acidic center is *directly* attached to the 1,1′-binaphthyl group in

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[1] Kyba, E. P.; Gokel, G. W.; Feike, de Jong; Koga, K.: Sousa, L. R.; Siegel, M. G.; Kaplan, L.; Cram, D. J. *J. Org. Chem.* **1977**, *42*, 4173.

[2] Tamao, K.; Yamamoto, H.; Matsumoto, H.; Miyake, N.; Hayashi, T.; Kumada, M. *Tetrahedron Lett.* **1977**, 1389.

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[6] Mazeleyrat, J. P.; Cram, D. J. *J. Am. Chem. Soc.* **1981**, *103*, 4585.

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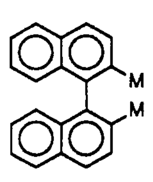
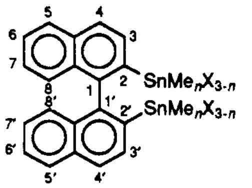
the literature. Bis organometallic derivatives of the general type 1 should be particularly interesting Lewis acids because the two metal centers might interact with ligands of varying size through appropriate rotation about the C(1)–C(1′) pivot. In the case of the organotin analogue **2**, one can also alter the "X" groups so as to vary the strength of the Lewis acids over a wide range. The present work describes the synthesis and chemistry of the novel didentate organotin Lewis acids **2a**–**2d**. A thorough understanding of the properties of these racemic Lewis acids can then lead the way to a rational study of their chiral counterparts.



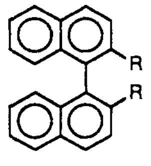
1
M = R_3Sn, R_2B, R_2Al



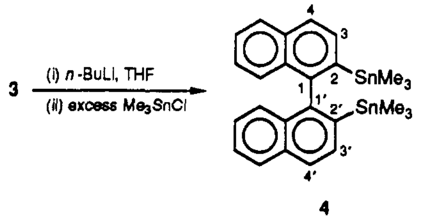
2
2a: X = Cl, $n = 2$
b: X = Cl, $n = 1$
c: X = OSO_2CF_3, $n = 2$
d: X = OSO_2CF_3, $n = 1$

Results and Discussion

Metalation of (±)-2,2′-dibromo-1,1′-binaphthyl (**3**)[4,8] with *n*-butyllithium at −45 °C provided 2,2′-dilithio-1,1′-binaphthyl.[4,9] Reaction of this dilithio species with excess trimethyltin chloride at −78 °C provided an 87% yield of (±)-2,2′-bis(trimethylstannyl)-1,1′-binaphthyl (**4**) (eq 1).



3: R = Br
4: R = $SnMe_3$
5: R = OH
6: R = OSO_2CF_3

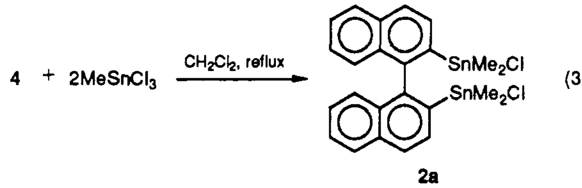


4

$$4 \xrightarrow[\text{CDCl}_3\ 0\ ^\circ\text{C}]{2\text{Br}_2} 3 \qquad (2)$$

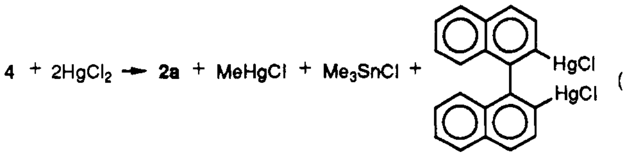
Attempts were also made to prepare **4** from the more readily accessible binaphthol **5** by applying the recently discovered palladium(0)-catalyzed coupling of enol triflate with hexamethyldistannane.[10] However, treatment of the ditriflate **6**[11] with hexamethyldistannane did not afford **4** even after prolonged heating (60 °C, 10 days). The identity of **4** was confirmed by its brominolysis, which afforded 2,2′-dibromo-1,1′-binaphthyl quantitatively (eq 2). Several interesting observations were made in the NMR spectra of **4**. The ^{1}H NMR spectrum showed the tin–methyls at −0.34 ppm with a two-bond coupling to the ^{119}Sn of 55.3 Hz. The normal values for these two parameters in aryltrimethyltins are about 0.28 ppm and 56.6 Hz, respectively.[12] This unusually high field absorption of these protons is presumably due to shielding by the ring current generated by the naphthyl ring, with one ring shielding the methyl protons on the tin bonded to the other naphthyl ring. The aromatic protons ortho to the trimethyltin groups were seen as a doublet with a proton–proton coupling constant of 8.6 Hz and a three-bond coupling to the tin of 42.8 Hz, which is consistent with the cis-1,2-arrangement of the ortho protons and the tin. The ^{13}C NMR spectrum (see Table I) showed a signal at 147.2 ppm for the quaternary aromatic carbons, which showed two different couplings to the tin: one of 23.2 Hz and the other of 31.5 Hz. As C(1) is cis to the tin group that is bonded to C(2′), it is reasonable to assign the value of 31.5 Hz to the three-bond coupling to the tin. The two-bond coupling constant for C(1) (and C(1′)) would then be 23.2 Hz. Carbon C(3) had a two-bond coupling to the tin of 39.5 Hz and was virtually identical with the three-bond value for C(4). One would expect the three-bond value to be higher due to the dihedral angle approaching 180°. The three-bond coupling constants between C and Sn in a variety of substituted benzenes are normally in the range 40–50 Hz.[13]

2,2′-Bis(chlorostannyl)-1,1′-binaphthyls. The reaction of 2,2′-bis(trimethylstannyl)-1,1′-binaphthyl with electrophilic reagents such as tin tetrachloride or mercuric chloride can in principle give rise to products derived from either tin–aryl cleavage or tin–methyl cleavage. These exchange reactions could be conveniently followed by ^{119}Sn NMR spectroscopy. The observations indicated that they proceed predominantly with cleavage of the tin–methyl bond. Thus, treatment of **4** with 2 equiv of methyltin trichloride afforded the bis(monochlorotin) **2a** (eq 3).



2a

When mercuric chloride was employed, **2a** was formed to the extent of about 60%. A substantial amount (approximately 35%) of trimethyltin chloride was also seen, which is indicative of tin–aryl cleavage (eq 4). Reaction with 4 equiv of tin tetrachloride afforded the bis(dichlorotin) derivative **2b** (eq 5).



$$4 + 4\text{SnCl}_4 \xrightarrow{\text{CH}_2\text{Cl}_2,\ -78\ ^\circ\text{C, room temp}} \mathbf{2b} \qquad (5)$$

The tin–methyl protons of the bis(monochlorotin) **2a** appeared as two broad singlets at 0.028 and 0.042 ppm, each with a two-bond coupling to the tin of 61.4 Hz. The two methyls on each tin are diastereotopic, hence, the two methyl signals. The protons ortho to the tin were seen as

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(8) Pichat, L.; Clement, J. *Bull. Soc. Chim. Fr.* **1961**, 525.

(9) Brown, K. J.; Berry, M. S.; Waterman, K. C.; Lingenfelter, D.; Murdoch, J. R. *J. Am. Chem. Soc.* **1984**, *106*, 4717.

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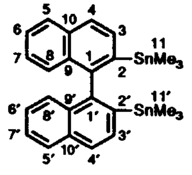
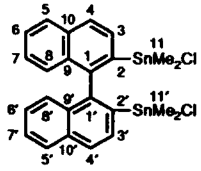
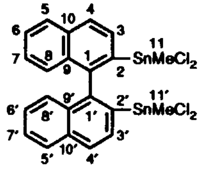
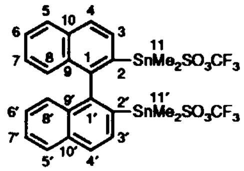
(13) Schaeffer, C. D.; Zuckerman, J. J. *J. Organomet. Chem.* **1975**, *99*, 407.

Table I. ^{13}C Chemical Shifts and ^{119}Sn–^{13}C Coupling Constants

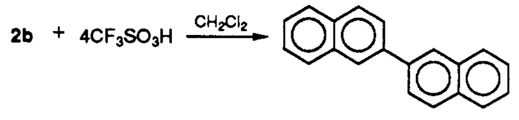
compound	carbons, δ (^{n}J, Hz) of carbon							
	1	2	3	4	5–8	9	10	11
 **4**	147.5 (21.6, 31.4)	142.5 (480.3)	132.0 (39.3)	126.9 (40.9)	127.8, 126.8, 125.9, 125.8	133.3 (42.7)	133.6 (9.9)[b]	−8.7 (349.2)
 **2a**	145.5 (29.9, 50.4)	142.6 (576.8)	131.0 (40.2)	128.8 (54.2)	128.3, 127.4, 127.1,[c] 126.5[c]	132.9 (54.7)	134.3 (10.4)[b]	−0.8 (410.9)
 **2b**	144.1[d]	142.9 (779.3)	129.5 (40.9)	130.6 (69.6)	128.8, 128.6, 128.4,[c] 125.7[c]	132.7 (78.3)	134.8 (13.5)[b]	5.5 (547.2)
 **2c**	145.7[e] (29.0, 43.4)	142.4 (678.5)	f	131.1 (48.9)	128.8, 128.3, 127.7, 127.3	133.4 (58.4)	134.6 (10.5)[b]	−0.7 (508.2)

[a] In $CDCl_3$ unless otherwise mentioned. [b] Four-bond coupling. [c] Long-range couplings. [d] Weak signal. Satellites could not be observed. [e] In CD_3CN. [f] Signal was not apparent.

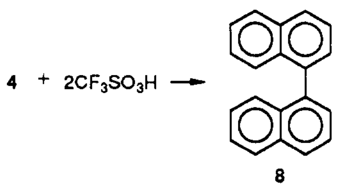
a doublet with a proton–proton coupling constant of 8.4 Hz and a three-bond coupling to the tin of 50.0 Hz. In the case of the bis(dichlorotin) **2b**, the tin–methyl protons appeared at 0.077 ppm with a two-bond coupling to the tin of 79.2 Hz. The normal chemical shifts for the tin–methyl protons in mono- and dichlorotin derivatives are around 0.6 and 1.2 ppm, respectively. The abnormally upfield chemical shifts of the tin–methyl protons are attributable to strong shielding by the naphthyl rings. The ^{13}C NMR spectrum of **2a** showed the characteristic two- and three-bond couplings to the tin of 29.9 and 50.4 Hz, respectively, for the quaternary carbons C(1) and C(1′) at 145.5 ppm. Carbon C(3) showed a two-bond coupling to the tin of only 40.2 Hz, which is about the same as that seen in the bis(trimethylstannyl) derivative 4. The three-bond coupling constants for the carbons C(4) and C(9), however, increase in the expected manner. One can find an alternating feature in the chemical shifts of the carbons C(3), C(4), and C(9). Upon going from 4 to **2a** to **2b**, the chemical shifts of C(3) decrease and those of C(4) and C(9) increase (Table I). With the tin-bearing carbon, however, there is virtually no change in chemical shift as the tin–methyls are replaced with chlorine. A number of long-range (greater than three-bond) tin–carbon couplings were also observed. It is also interesting to note that while the proton chemical shifts are moved considerably upfield, the carbon and tin chemical shifts appear normal.

2,2′-Bis[[[(trifluoromethyl)sulfonyl]oxy]stannyl]-1,1′-binaphthyls. On the basis of the observed course of reaction with tin tetrachloride, one might expect the reaction of the bis(dichlorotin) **2b** with 4 mol of triflic acid in dichloromethane to give the cleavage product **2d** (eq 6). In practice, however, the reaction afforded a 50% isolated yield of the hydrocarbon 2,2′-binaphthyl (**7**) (eq 7)! The fate of the tin-containing product(s) was not determined. Only one tin species was seen in the ^{1}H NMR spectrum (δ 1.69, $^2J(^{119}\text{Sn}-\text{C}H_3)$ = 98 Hz) and the ^{119}Sn NMR spectrum (δ 20.9) of the reaction mixture. The tin chemical shift is very close to that reported for methyltin trichloride (δ 21.0).[14] Perhaps dichloromethyltin triflate, the cleavage product, is in equilibrium with methyltin trichloride by fast chloride–triflate exchange, and a time-averaged ^{119}Sn signal is observed. No other peak was apparent in the tin spectrum in the range of +400 to −400 ppm. When only 2 molar equiv of triflic acid was used, unreacted **2b** (15%) and 1,1′-binaphthyl (**8**) (40%, based on recovered **2b**) were isolated. The identity of the latter was confirmed by comparing its spectral (UV, ^{1}H, ^{13}C) and melting point data with those of an authentic sample prepared by protonolysis of 4 with 2 molar equiv of triflic acid (eq 8). Finally, when 8 was treated with 2 molar equiv of triflic acid, 2,2′-binaphthyl (**7**) was obtained in quantitative yield (eq 9). These results show that initially triflic acid cleaves the tin–aryl bonds of **2b** to produce 8, which subsequently isomerizes to 7 in a clean reaction. The isomerization presumably involves initial protonation of C(1) followed by migration of the other naphthyl group to C(2) and deprotonation of C(2). The sequence is then repeated with initial protonation of the original C(1′), migration to C(2′), and deprotonation, resulting in the formation of the thermodynamically more stable 2,2′-binaphthyl.[15] The rearrangement of 1,1′-binaphthyl to 2,2′-binaphthyl was previously studied by Kovacic and Koch[16] in the course of examining the Scholl reaction[17] products of the coupling of naphthalene by Lewis acids. Use of triflic acid, therefore, enables one to obtain, selectively, 2,2′-binaphthyl in almost quantitative yield under mild conditions. The results of the electrophilic cleavage reactions of 2 are noteworthy in that the course of the reactions seems to depend on the bulk of the electrophile. The proton and bromine yield aryl–tin cleavage, mercuric chloride reacts by competing aryl– and methyl–tin cleavage, and the bulky tin tetrachloride and methyltin trichloride yield only tin–alkyl cleavage. Presumably the steric bulk around the tins in the binaphthyls is a major contributor to this trend.

$$\mathbf{2b} + 4\mathrm{CF_3SO_3H} \not\longrightarrow \mathbf{2d} \qquad (6)$$



7 (7)



8 (8)

$$\mathbf{8} \xrightarrow{2\mathrm{CF_3SO_3H}} \mathbf{7} \qquad (9)$$

The preparation of the organotin triflates **2c** and **2d** was readily accomplished by employing silver triflate in the metathetic reaction with the corresponding organotin chlorides (eqs 10 and 11) in a nitromethane–dichloromethane solvent mixture. Attempts to prepare the bis(ditriflate) **2d** in solvents other than nitromethane were also made. Acetone and benzaldehyde were chosen as solvents in the hope that a stable complex of the type **2d**·*x*(solvent) could be isolated. No report of an aldehyde or a ketone complex of an organotin Lewis acid is found in the literature. Addition of 4 molar equiv of silver triflate to **2b** in these solvents resulted in gradual coloration of the reaction mixture. Silver chloride was formed quantitatively in each case, indicating formation of the triflate. However, removal of the solvent after 2 h yielded deep red oily materials with complex ^{1}H NMR spectra from which the presence of stoichiometric complexes could not inferred. It is, therefore, reasonable to conclude that **2d** is indeed formed; however, the solvents enter into reactions with the strongly Lewis acidic product.

$$\mathbf{2a} + 2\mathrm{AgSO_3CF_3} \xrightarrow{\mathrm{CH_3NO_2-CH_2Cl_2}} \mathbf{2c} \qquad (10)$$

$$\mathbf{2b} + 4\mathrm{AgSO_3CF_3} \xrightarrow{\mathrm{CH_3NO_2-CH_2Cl_2}} \mathbf{2d} \qquad (11)$$

The tin-119 NMR spectrum of the bis(monotriflate) **2c** in CD$_3$CN showed a peak at −1.90 ppm. Evidently coordination with the solvent moves the chemical shift upfield. On the other hand, the ^{119}Sn NMR spectrum of the bis(ditriflate) **2d** in donor solvents such as acetone-d_6 and CD$_3$CN showed a multitude of peaks between −193.9 and −364.4 ppm, indicating that it was undergoing extensive decomposition. In CD$_3$NO$_2$, however, only one sharp peak at −298.1 ppm was seen. This value indicates either pentacoordination or, less probably, hexacoordination at the tin. This strikingly different observation suggests that a poorly donating solvent such as nitromethane can coor-

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[14] Harris, R. K.; Mann, B. E. *NMR and the Periodic Table*; Academic Press: New York, 1978; p 352.

[15] Friedel, R. A.; Orchin, M.; Reggel, L. *J. Am. Chem. Soc.* **1948**, *70*, 199.

[16] Kovacic, P.; Koch, F. W. *J. Org. Chem.* **1965**, *30*, 3176.

[17] Balaban, A. T.; Nenitzescu, C. D. In *Friedel Crafts and Related Reactions*; Olah, G. A., Ed.; Interscience: New York, 1964; Vol. II, p 979.

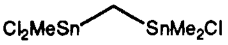
Table II. Complexation of DMSO and 2b[a]

DMSO/**2b** mole ratio	$\delta(^{119}Sn)^a$	$\delta(^1H)^b$	$^2J(^{119}Sn-CH_3)$, Hz
0.00	+22.6	0.076	78.6
0.75	−52.9	0.064	87.0
0.90	−63.0	0.040	90.0
1.50	−97.8	0.040	90.0
3.00	−106.7	0.040	90.0
4.00	−107.4	0.040	90.0
5.00	−107.8	0.04	92.7

[a] Measured at 23.5 °C with **2b** = 0.076 M in dichloromethane. Benzene-d_6 was the external lock. Chemical shifts are referenced to external tetramethylstannane. Values in ppm (±0.1). An exponential line broadening factor of 30 Hz was applied to improve the signal-to-noise ratio of the ^{119}Sn signals. [b] Values in ppm (±0.01).

dinate with **2d** and resists decomposition as well.

Studies on the Complexation Behavior of 2,2′-Bis(dichloromethylstannyl)-1,1′-binaphthyl (2b) with DMSO. A unique aspect of the 2,2′-binaphthyl-substituted Lewis acids such as **2a** and **2b** is that the distance between the two tins can be varied over a moderate range by proper rotation about the C(1)–C(1′) pivot. So, in principle, ligands of varying size could be accommodated between the two tins so as to produce chelate complexes. The bis(dichlorotin) **2b** can be regarded as a rough analogue of the known bis(dichloromethylstannyl)methane (**9**).[18] Whereas the Sn–C–Sn bond angle in **9** is fixed for tetrahedral geometry, the dihedral angle between the two tin–carbon bonds in **2b** can approach 90°, or might even exceed this value. The two tins are therefore in a position to interact cooperatively in processes such as bidentate coordination with Lewis bases. Karol et al. have prepared novel chelate complexes of **9** and other analogues with DMSO. The chelate complex **10** was studied by single-crystal X-ray diffractometry.[18] The tin coordination in organotin halides can also be expanded through interactions with halogens. For example, Jurkschat et al. have observed such a long bridging interaction in the monodentate complex **11** (HMPA = $(Me_2N)_3P{=}O$).[19] This was indicated by the longer Sn(2)–Cl(1) bond distance of 3.02 Å than the Sn(2)–Cl(2) distance of 2.43 Å. The two tin environments are not equivalent because HMPA is not a bridging ligand. A study of the complexation behavior of 2,2′-binaphthyl-substituted Lewis acids was made so as to anticipate how they might function in catalysis.



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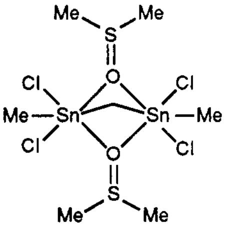

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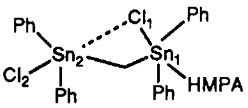

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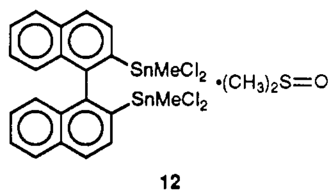

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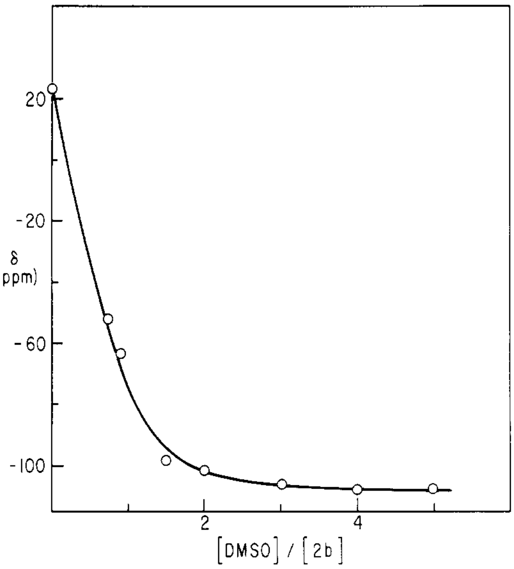

Figure 1. Effect of DMSO on the tin-119 chemical shift of (±)-2,2′-bis(dichloromethylstannyl)-1,1′-binaphthyl (**2b**) with increasing DMSO concentrations. DMSO/**2b** represents the mole ratio of DMSO to the bis(dichlorotin) **2b**. Points are experimental; the curve was generated in the computer solution with K = 123 M^{-1}.

The complexation behavior of **2b** with DMSO in methylene chloride was examined by ^1H and ^{119}Sn NMR with the results shown in Table II. The proton parameters showed relatively small changes upon addition of DMSO as has been observed earlier with compounds such as **9**. However, the ^{119}Sn chemical shifts moved upfield by more than 100 ppm upon addition of 1.5 molar equiv of DMSO. The presence of only one signal indicated the expected rapid exchange in equilibria such as those of eqs 12 and 13.

$$\mathbf{2b} + \mathrm{DMSO} \rightleftharpoons \mathbf{12} \tag{12}$$

$$\mathbf{12} + \mathrm{DMSO} \rightleftharpoons \mathbf{12}\cdot\mathrm{DMSO, etc.} \tag{13}$$

The data were analyzed by nonlinear least-squares regression using the Marquardt algorithm[28] assuming formation of the 1:1 complex (**2b**·DMSO) only. Figure 1 shows a plot of the experimental points and the curve generated with K_1 = 123 M^{-1} and chemical shift values of 24.4 ppm for **2b** and −112 ppm for **2b**·DMSO. The excellent fit indicates that **2b**·DMSO is the only complex formed in significant amount under the conditions of the experiments. It may be worth noting that the chemical shift for **2b** is at a higher field than the typical values of about 160 ppm for chlorotrialkylstannanes.[14] About 40 ppm of the upfield shift in **2b** may be attributed to the substitution of the naphthyl ring for an alkyl group; the remaining 100 ppm is most probably due to chlorine bridging, which results in one tetracoordinate and one

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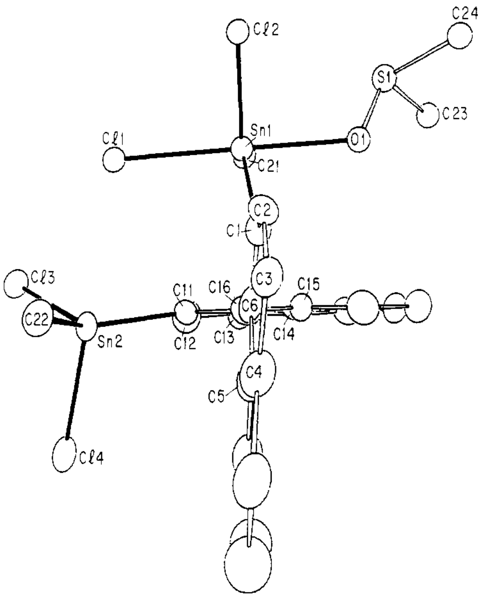

Figure 2. ORTEP drawing of the complex moiety of $Sn_2(C_{10}H_6)_2(CH_3)_2Cl_4\cdot(CH_3)_2SO\cdot CCl_4$ (**2b**·DMSO) displaying all of the atoms in the molecule. The thermal ellipsoids enclose 50% of the electron density. Hydrogen atoms and carbon tetrachloride have been omitted for clarity.

Table III. Selected Bond Lengths (Å) and Bond Angles (deg) for $Sn_2(C_{10}H_6)_2(CH_3)_2Cl_4\bullet(CH_3)_2SO\bullet CCl_4$

Sn(1)–Cl(1)	2.503 (8)	Sn(1)–Cl(2)	2.337 (8)
Sn(1)–O(1)	2.295 (25)	Sn(1)–C(1)	2.109 (25)
Sn(1)–C(21)	2.071 (30)	Sn(2)–Cl(3)	2.320 (10)
Sn(2)–Cl(4)	2.381 (9)	Sn(2)–C(11)	2.111 (27)
Sn(2)–C(22)	2.134 (27)	S(1)–O(1)	1.629 (27)
Sn(2)–Cl(1)	3.221 (9)		
Cl(1)–Sn(1)–Cl(2)	91.8 (3)	Cl(1)–Sn(1)–O(1)	175.2 (6)
Cl(2)-Sn(1)–O(1)	87.1 (6)	Cl(1)–Sn(1)–C(1)	92.2 (7)
Cl(2)–Sn(1)–C(1)	109.6 (7)	O(1)–Sn(1)–C(1)	83.8 (9)
Cl(1)–Sn(1)–C(21)	93.2 (9)	Cl(2)–Sn(1)–C(21)	114.0 (9)
O(1)–Sn(1)–C(21)	91.4 (11)	C(1)–Sn(1)–C(21)	135.9 (11)
Cl(3)–Sn(2)–Cl(4)	98.3 (3)	Cl(3)–Sn(2)–C(11)	109.2 (8)
Cl(4)–Sn(2)–C(11)	100.4 (8)	Cl(3)–Sn(2)–C(22)	112.0 (8)
Cl(4)–Sn(2)–C(22)	103.2 (8)	C(11)–Sn(2)–C(22)	128.2 (10)
O(1)–S(1)–C(23)	95.9 (22)	O(1)–S(1)–C(24)	92.9 (21)
C(23)–S(1)–C(24)	97.1 (28)	Sn(1)–O(1)–S(1)	110.9 (14)
Sn(1)–C(1)–C(2)	123.2 (18)	Sn(1)–C(1)–C(6)	120.0 (18)
Sn(2)–C(11)–C(12)	116.5 (19)	Sn(2)–C(11)–C(16)	126.5 (20)
Cl(1)–Sn(2)–Cl(4)	177.1 (3)		

pentacoordinate tin. Then, upon further coordination with DMSO, both tins become pentacoordinate, producing the additional upfield shifts of about 130 ppm.

The complex **2b**·DMSO was isolated by treating a solution of **2b** with excess DMSO in carbon tetrachloride. Its IR spectrum showed no free S–O stretching frequency at 1050 cm^{-1}; a split band due to the coordinated oxygen–tin interaction appeared at 993 and 943 cm^{-1} instead.

The structure of the complex was determined by single-crystal X-ray diffraction. Its showed a molecule of CCl_4 per molecule of the complex. ORTEP diagrams of the complex are shown in Figures 2 and 3; selected bond lengths are given in Table III and bonds angles in Table IV.

The structure consists of a discrete binuclear tin compound with the two centers separated by 4.505 (3) Å. The geometry of Sn(2) is approximately trigonal bipyramidal with the two carbon atoms and the chlorine, C(11), C(22), and Cl(3), respectively, forming the basal plane and with Cl(4) in the apical position. The tin coordination is expanded through a long apical interaction, 3.221 (9) Å, to Cl(1), which is directly bonded to Sn(1). The bond angle Cl(1)–Sn(2)–Cl(4) is 177.1°. This pattern is consistent with the general rule that more electronegative groups occupy apical positions of the trigonal bipyramid. The geometry at Sn(1) is also trigonal bipyramidal with Cl(1), C(21), and

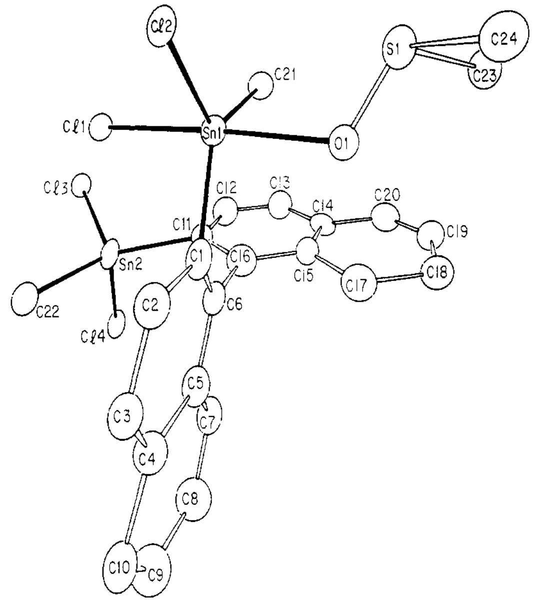

Figure 3. ORTEP drawing of the complex moiety of $Sn_2(C_{10}H_6)_2(CH_3)_2Cl_4\cdot(CH_{32}SO\cdot CCl_4$ (**2b**·DMSO) showing the dihedral angle between the two naphthalene rings. The molecule is viewed along the planes of the naphthalene rings bearing the dichlorotin groups. The thermal ellipsoids enclose 50% of the electron density. Hydrogen atoms and carbon tetrachloride have been omitted for clarity.

Table IV. Atomic Positional Parameters ($\times10^4$) for $Sn_2(C_{10}H_6)_2(CH_3)_2Cl_4\bullet(CH_3)_2SO\bullet CCl_4$

atom	*x*	*y*	*z*
Sn(1)	1442 (1)	9501 (2)	7525 (1)
Sn(2)	1466 (1)	8045 (2)	9043 (1)
Cl(1)	1774 (4)	7602 (7)	7950 (3)
Cl(2)	1237 (4)	8540 (8)	6772 (3)
Cl(3)	2371 (4)	6946 (10)	9196 (3)
Cl(4)	1295 (5)	8370 (10)	9866 (3)
S(1)	1382 (6)	11440 (13)	6649 (5)
O(1)	1053 (11)	11190 (24)	7135 (7)
C(1)	626 (11)	9576 (23)	7858 (8)
C(2)	59 (11)	9141 (22)	7639 (9)
C(3)	−437 (11)	9095 (22)	7859 (9)
C(4)	−415 (11)	9485 (26)	8353 (9)
C(5)	142 (11)	101059 (23)	8601 (9)
C(6)	644 (11)	10025 (22)	8319 (8)
C(7)	177 (12)	10443 (24)	9092 (8)
C(8)	−332 (12)	10403 (27)	9334 (10)
C(9)	−843 (15)	9889 (28)	9124 (11)
C(10)	−919 (14)	9471 (29)	8648 (11)
C(11)	1683 (12)	9784 (24)	8839 (9)
C(12)	2273 (15)	10284 (31)	9080 (11)
C(13)	2402 (13)	11463 (26)	8965 (10)
C(14)	2029 (14)	12178 (29)	8721 (10)
C(15)	1424 (12)	11769 (25)	8469 (9)
C(16)	1295 (12)	10560 (24)	8574 (8)
C(17)	1009 (15)	12455 (29)	8204 (11)
C(18)	1160 (7)	13691 (34)	8110 (13)
C(19)	1728 (16)	14049 (34)	8339 (12)
C(20)	2129 (15)	13423 (31)	8604 (11)
C(21)	2319 (14)	10237 (30)	7658 (11)
C(22)	694 (12)	6976 (26)	8756 (10)
C(23)	683 (27)	11636 (62)	6247 (20)
C(24)	1513 (22)	12962 (50)	6798 (18)
C(25)	1073 (27)	3588 (58)	34 (23)
Cl(5)	1531 (10)	2259 (22)	−113 (6)
Cl(6)	865 (12)	3783 (26)	−550 (7)
Cl(7)	715 (18)	3136 (32)	382 (13)
Cl(8)	1537 (14)	4855 (27)	185 (11)

Cl(2) occupying the equatorial plane and Cl(1) and O(1) in the apical positions. The Sn(1)–Cl(1) bond distance of 2.505 (9) Å is considerably longer than the Sn(2)–Cl(4) distance of 2.378 (1) Å. Austin et al. have observed a correlation between the Sn–X and Sn–Y bond distances, where "X" and "Y" groups occupy the apical positions of a trigonal bipyramid: as the nonbonded Sn–Y distance becomes shorter, the bonding Sn–X distance tends to become longer.[21] This correlation has been discussed in terms of the mapping of the S_N2 pathway with inversion of configuration between four- and five-coordinate tin.[22] An interesting feature of the structure of complex **12** is that the dihedral angle between the two naphthalene rings (Figure 3) is close to 90°. A molecular model of 2,2′-dihydroxy-1,1′-binaphthyl shows that, with a dihedral angle of 75°, the two oxygens are located with respect to one another about the same as they are in gauche ethylene glycol.[1] The dihedral angle increases to 90° in **12** presumably to accommodate the bulky dichloromethylstannyl groups. The chelation of DMSO to the two tins does not occur probably due to severe steric interactions in such a structure.

In summary, we have described the synthesis and some properties of the first example of a 1,1′-binaphthyl bearing neutral metal-centered Lewis acidic groups in the 2- and 2′-positions. In complexation of the 2,2′-bis(dichloromethylstannyl) analogue with DMSO, a 1:1 complex has been isolated and its structure obtained by single-crystal X-ray diffraction. It shows that cooperative binding occurs through coordination of the DMSO to one tin and bridging of the chlorine from that tin to the other tin. It remains to be determined whether complexes in which the donor is bound by chelation to both tins can be obtained by appropriate choice of substituents on the binaphthyl and the tins and of the structure of the donor.

Experimental Section

Proton nuclear magnetic resonance spectra were obtained at 60 MHz by using a Varian EM-360 A spectrometer or at 300 MHz by using a Varian XL-300 spectrometer. Chemical shifts are reported in parts per million downfield from internal tetramethylsilane followed in parentheses by the multiplicity, number of protons, coupling constants, and assignments. Proton–tin-119 coupling constants are reported as $^nJ(^{119}\text{Sn–H})$ with the first superscript denoting the number of bonds intervening between nuclei. Carbon-13 nuclear magnetic resonance spectra were obtained at 75.43 MHz by using the Varian XL-300 spectrometer. The spectra were recorded by using chloroform-*d* as both a lock and solvent unless otherwise specified. Chemical shifts (δ) are reported in parts per million downfield from tetramethylsilane followed by $^nJ(^{119}\text{Sn–}^{13}\text{C})$ where "n" denotes the number of bonds intervening between nuclei and "J" the coupling constant. Tin-119 nuclear magnetic resonance spectra were obtained at 111.86 MHz by using the Varian XL-300 spectrometer. Chemical shifts are reported in parts per million with respect to tetramethylstannane. In those cases where tetramethylstannane might react with the material under examination, a sealed capillary tube containing a solution of the reference in chloroform-*d* was used as the external reference. Otherwise, internal tetramethylstannane was used. Infrared spectra were obtained on a Perkin-Elmer 283-B infrared spectrophotometer and are reported in cm^{-1}. Gas chromatographic analyses were performed on a Hewlett-Packard Model 5750 instrument or an F & M 720 instrument using a thermal conductivity detector. All analyses were performed by using a 9.5 ft or 17 ft × 0.25 in. stainless steel column packed with 15% SE-30 on Chromosorb-W, 60–80 mesh, unless otherwise noted. Ultraviolet spectra were recorded on a Shimadzu UV-160 UV–visible spectrophotometer. Flash chromatography was performed on silica gel, Davisil 200–425 mesh (Aldrich). Thin-layer chromatography (TLC) was performed on E. Merck precoated silica gel plates (60F-254). Anhydrous tetrahydrofuran was obtained by distillation from lithium aluminum hydride. Racemic 2,2′-dihydroxy-1,1′-binaphthyl[23] and 2,2′-dibromo-1,1′-binaphthyl[4] were prepared according to published procedures.

(±)-2,2′-Bis(trimethylstannyl)-1,1′-binaphthyl (4). Into a three-necked 100-mL flask was placed 0.89 g (2.17 mmol) of the dibromide **3** dissolved in 14 mL of dry THF. The solution was cooled to −45 °C (acetonitrile–dry ice bath), and 2.25 mL of 2.1 M (4.73 mmol, 2.2 molar equiv) of *n*-butyllithium was added dropwise over 10 min. After being stirred for 0.5 h at this temperature, the yellow-green slurry was cooled to −78 °C, and a solution of 1.80 g (9.03 mmol) of trimethyltin chloride in 5 mL of THF was added. The bath was then allowed to warm up to room temperature. The yellow-green color of the solution was discharged at a temperature of about −50 °C. After the solution was stirred overnight (12 h), 2 mL of water was added, and the reaction mixture was extracted with 30 mL of hexanes. The organic layer was washed with 25 mL of saturated aqueous ammonium chloride solution, dried with $MgSO_4$, and concentrated. The residual oil was purified by flash column chromatography using 98/2 hexanes–ether to afford 1.1 g (87%) of **4** as a white viscous oil. ^{1}H NMR ($CDCl_3$) δ −0.34 (s, 18 H, $^2J(^{119}\text{Sn–C}H_3)$ = 55.3 Hz, Sn(CH_3)$_3$), 7.53 (m, 4 H), 7.72 (m, 2 H), 8.05 (d, 2 H, J = 8.6 Hz, $^3J(^{119}\text{Sn–C=CH})$ = 42.8 Hz, 2 ortho H), 8.22 (m, 4 H); ^{119}Sn NMR ($CDCl_3$) δ −32.7. Satisfactory carbon, hydrogen analyses for the material were not obtained.

Anal. Calcd for $C_{26}H_{30}Sn_2$: C, 53.87; H, 5.19. Found: C, 55.10; H, 5.70.

(±)-2,2′-Bis(chlorodimethylstannyl)-1,1′-binaphthyl (2a). To a solution of 4.00 g (6.90 mmol) of **4** in 15 mL of dichloromethane, cooled to 0 °C, was added a solution of 3.48 g (14.5 mmol) of methyltin trichloride in 15 mL of dichloromethane. After the addition, the ice bath was removed, and the solution was heated under reflux for 18 h. The solvents were then removed, and the residual solid was stirred at 0.05 Torr and 80 °C for 1 h to remove dimethyltin dichlorode and other volatiles. The residual solid was dissolved in a CCl_4–CH_2Cl_2 mixture, treated with decolorizing carbon, and gravity filtered. The filtrate was concentrated, and the residual solid was crystallized from hexanes–CCl_4 mixed solvent to afford 2.8 g (65%) of the product as shiny pale yellow crystals: mp 166–168 °C. Recrystallization of the product from hexanes–CCl_4 mixed solvent afforded the analytical sample: mp 169–170 °C. ^{1}H NMR ($CDCl_3$) δ 0.028, 0.042 (two br s, 12 H, $^2J(^{119}\text{Sn–C}H_3)$ = 61.4, 2 Sn(CH_3)$_2$), 7.25 (d, 2 H, J = 8.1 Hz), 7.33 (m, 2 H), 7.53 (m, 2 H), 7.97 (d, 2 H, J = 8.9 Hz), 8.00 (d, 2 H, J = 8.4 Hz, $^3J(^{119}\text{Sn–C=C}H)$ = 50.0 Hz, 2 ortho H), 8.71 (d, 2 H, J = 8.8 Hz); ^{119}Sn NMR ($CDCl_3$) δ +82.3.

Anal. Calcd for $C_{24}H_{24}Sn_2Cl_2$: C, 46.44; H, 3.90. Found: C, 46.12; H, 3.98.

(±)-2,2′-Bis(dichloromethylstannyl)-1,1′-binaphthyl (2b). To a solution of 3.31 g (5.69 mmol) of **4** in 25 mL of dichloromethane, cooled to −78 °C, was added a solution of 5.33 g (20.5 mmol) of tin tetrachloride in 15 mL of dichloromethane. After the addition, the dry ice bath was allowed to warm up to room temperature. After the solution was stirred for 26 h, the solvent was evaporated, and the residue was stirred at 0.025 Torr and 65 °C for 1.5 h to remove methyltin trichloride and other volatiles. The solid residue was dissolved in 100 mL of dichloromethane, treated with decolorizing carbon, and gravity filtered. Concentration of the filtrate afforded a solid that was crystallized from hexanes–dichloromethane mixed solvent to provide 2.44 g (65%) of the product as colorless crystals, mp 241–243 °C. Recrystallization of the crude sample from the same solvent mixture afforded the analytically pure sample: mp 246–247 °C. ^{1}H NMR ($CDCl_3$) δ 0.069 (s, 6 H, $^2J(^{119}\text{Sn–C}H_3)$ = 78.6 Hz, Sn(CH_3)$_3$), 7.31 (d, 2 H, J = 9.0 Hz), 7.47 (m, 2 H), 8.06 (d, 2 H, J = 7.7 Hz), 8.16 (d, 2 H, J = 8.2 Hz), 8.24 (d, 2 H, J = 8.3 Hz); IR (KBr) 3045, 1308, 812, 780, 740, 685, 342 cm^{-1}; ^{119}Sn NMR ($CDCl_3$) δ +24.3.

Anal. Calcd for $C_{22}H_{18}Sn_2Cl_4$: C, 39.94; H, 2.74. Found: C, 39.91; H, 2.76.

(±)-2,2′-Bis{dimethyl[[(trifluoromethyl)sulfonyl]oxy]stannyl}-1,1′-binaphthyl (2c). A solution of 0.62 g (0.99 mmol) of the bis(monochlorotin) compound **2a** in 5 mL of dichloromethane was added to a solution of 0.51 g (1.98 mmol) of silver tiflate in 60 mL of nitromethane. After being stirred for 2 h, the solution was filtered and the solvents were removed by using an aspirator at room temperature (25 °C). The resulting solid residue was then dried at 0.025 Torr for 11 h to afford 0.79 g (94%) of the product as a white powder: mp 150 °C (dec, sealed tube). ^{1}H NMR (CD_3CN) δ 0.13 (s, 12 H, $^2J(^{119}Sn{-}CH_3)$ = 69.3 Hz, 2 $Sn(CH_3)_2$), 7.27 (d, 2 H, J = 8.5 Hz), 7.38 (m, 2 H), 7.60 (m, 2 H), 7.95 (d, 2 H, J = 8.4 Hz), 8.07 (d, 2 H, J = 8.3 Hz), 8.19 (d, 2 H, J = 7.8 Hz); ^{119}Sn (CD_3CN): δ −1.90; IR (KBr) 1310–1160, 1020, 800–760, 630, 520 cm^{-1}.

Anal. Calcd for $C_{26}H_{24}Sn_2S_2O_6F_6$: C, 36.83; H, 2.85. Found: C, 36.88; H, 3.17.

(±)-2,2′-Bis{methyl[[(trifluoromethyl)sulfonyl]oxy]stannyl}-1,1′-binaphthyl (2d). A solution of 0.306 g (1.22 mmol) of silver triflate in 15 mL of nitromethane was treated with a solution of 0.202 g (0.306 mmol) of **2b** in 6 mL of dichloromethane. After being stirring for 2.5 h, the solution was filtered, and the solvents were removed by using an aspirator at room temperature. The white solid was stirred at 0.025 Torr and room temperature for 5 h to afford 0.3 g (89%) of a dry powder whose ^{1}H NMR spectrum suggested that the desired product had been formed, mp 90 °C (dec, sealed tube). The product was stored at −10 °C immediately. ^{1}H NMR (CD_3NO_2) δ 0.29 (s, 6 H, $^2J(^{119}Sn{-}CH_3)$ = 90.7 Hz, 2 $Sn(CH_3)$), 7.20–8.60 (m, 12 H); ^{119}Sn NMR (CD_3NO_2) δ −298.1; ^{119}Sn NMR (CD_3CN) δ −197.1, −199.9, −230.4, −257.6, −314.8, −325.0, −341.3, −364.3.

Anal. Calcd for $C_{26}H_{18}Sn_2O_{12}F_{12}S_4$: C, 27.99; H, 1.63. Found: C, 28.82; H, 2.13.

Preparation of the DMSO Complex 12. To a solution of 0.16 g (0.24 mmol) of **2b** in 6 mL of dichloromethane was added 0.05 mL (0.63 mmol, 2.6 molar equiv) of dry DMSO. After the solution was stirred for 5 min, the solvent was rotary evaporated, and the gummy solid was dissolved in CCl_4 and gravity filtered. The filtrate was concentrated, and the residue was treated with 20 mL of CCl_4 followed by dichloromethane in drops with warming until a clear solution resulted. The solution on standing at room temperature for 1 h followed by cooling afforded 0.16 g (88%) of the complex **12** as colorless crystals, which were of suitable quality for X-ray crystal structure determination: mp 213–215 °C (sealed tube). ^{1}H NMR ($CDCl_3$) δ 0.083 (s, 12 H, $^2J(^{119}Sn{-}CH_3)$ = 86.8 Hz, $Sn(CH_3)_2$), 2.55 (s, 6 H, $(CH_3)_2SO$), 7.33 (dd, 2 H, J = 8.5 Hz), 8.14 (d, 2 H, J = 8.3 Hz), 8.19 (d, 2 H, J = 7.5 Hz); ^{119}Sn NMR ($CDCl_3$) δ −70.0; IR (KBr) 1016, 985, 935, 814, 781–745, 335 cm^{-1}.

Anal. Calcd for $C_{24}H_{24}Sn_2Cl_4SO$: C, 38.97; H, 3.27. Anal. Calcd for $C_{24}H_{24}Sn_2Cl_4SO{\cdot}CCl_4$: C, 33.61; H, 2.71. Found: C, 33.88; H, 2.63.

^{1}H NMR and ^{119}Sn NMR Study of the Complexation Behavior of 2,2′-Bis(dichloromethylstannyl)-1,1′-binaphthyl (2b) with Dimethyl Sulfoxide. Into an NMR tube was placed 0.02 g (0.03 mmol) of **2b** dissolved in 0.4 mL of dichloromethane. DMSO was then added in incremental quantity, and for each addition, the ^{119}Sn and proton chemical shifts were recorded. The spectra were obtained by using benzene-d_6 as the external lock and external tetramethylstannane as the reference for tin-119 spectra. The ^{119}Sn chemical shifts were utilized to determine the mole fractions of the free and complexed **2b**. These values were then employed to arrive at the equilibrium constant for the formation of the mono-DMSO complex **12** (see Table II). The changes in the ^{1}H NMR parameters were much smaller than those observed in the ^{119}Sn NMR spectra and were therefore not utilized for the calculation. The equilibrium constant data are shown in Table II.

Reaction of (±)-2,2′-Bis(dichloromethylstannyl)-1,1′-binaphthyl (2b) with 4 mol of Triflic Acid. To a solution of 0.19 g (0.28 mmol) of **2b** in 8 mL of dichloromethane was added 0.1 mL (1.15 mmol) of triflic acid via syringe. The solution immediately became blue. After being stirred at room temperature for 24 h, the solution was filtered, and the filtrate was concentrated. The residual solid was dissolved in 15 mL of ethanol with heating and cooled to give 0.03 g (50%) of 2,2′-binaphthyl (**7**) as shiny pale green plates: mp 187–188 °C (lit.[24] mp 187–188 °C). ^{1}H NMR ($CDCl_3$) δ 7.51 (m, 4 H), 7.93 (m, 8 H), 8.18 (br s, 2 H); UV (CH_3OH) (λ_{max} (ϵ)) 305 (30 183), 252.4 (85 500, 214.0 (17 728) (lit.[25] UV (CH_3OH) (λ_{mas} (ϵ)) 305 (17 900), 253 (98 000), 212 (42 300)); ^{13}C NMR ($CDCl_3$) δ 125.7, 126.0, 126.1, 126.4, 127.7, 128.2, 128.5, 132.7, 133.8, 138.4.

Reaction of (±)-2,2′-Bis(dichloromethylstannyl)-1,1′-binaphthyl (2b) with 2 mol of Triflic Acid. To a solution of 0.161 g (0.243 mmol) of **2b** in 8 mL of dichloromethane, cooled to −60 °C, was added 0.045 mL (0.486 mmol) of triflic acid via syringe. The bath was allowed to warm up to room temperature, and the reaction mixture was stirred for 20 h. The solution was only turbid and colorless and not deep blue as in the previous case. The reaction mixture was filtered, and the filtrate was concentrated. The residue was stirred at 0.05 Torr and 70 °C for 0.5 h to remove volatiles. The solid residue was dissolved in dichloromethane and gravity filtered. The filtrate was concentrated, and the residue was dissolved in hexanes–dichloromethane mixed solvent with heating and cooled to afford 0.025 g (15%) of unreacted **2b**. The filtrate was concentrated, and the residue was recrystallized from hot ethanol to afford 0.02 g (40%, based on recovered **2b**) of 1,1′-binaphthyl (**8**) as pale yellow crystals: mp 144–145 °C (lit.[26] mp 144–145 °C). The ^{1}H NMR and ^{13}C NMR spectra of the material were superimposable on those of authentic **8**, which was prepared from (±)-2,2′-bis(trimethylstannyl)-1,1′-binaphthyl (**4**) as described below.

Table V. Summary of Experimental Details for the X-ray Diffraction Studies of $Sn_2(C_{10}H_6)_2(CH_3)_2Cl_4 \bullet (CH_3)_2SO \bullet CCl_4$ at 296 K[a]

formula	$Sn_2Cl_8OSC_{25}H_{24}$
MW	893.54
cryst class	monoclinic
cryst color, habit	rectangular, transparent
space group	$A2/a$
a, Å	21.790 (4)
b, Å	11.270 (3)
c, Å	27.670 (9)
β, deg	97.6 (5)
V, Å^3	6736.32 (11)
Z	8
ρ_{calcd}, g cm^{-3}	1.76
$F(000)$	2880
μ(Mo Kα), cm^{-1}	18.82
cryst size, mm	0.23 × 0.35 × 0.24
T_{max}/T_{min}	1.02
radiation	graphite monochromated (λ = 0.710 73 Å), Mo Kα
octants data	$h,k,\pm l$
ω scan speed, deg min^{-1}	2–10
scan range, deg	0–45
ω scan width, deg	1.2
reflns measd	4869 (unique)
reflns obsd, $[F_o \geq 6\sigma(F_o)]$	1677
final R	0.073
R_w	0.075

[a] Unit cell parameters based on least-squares fitting of the setting angles of 25 reflections with 23° < 2θ < 30°.

A solution of 0.312 g (0.539 mmol) of **4** in 5 mL of dichloromethane, cooled to 0 °C, was treated with 0.095 mL (1.077 mmol) of triflic acid. After being stirred for 0.5 min, a homogeneous solution resulted. The ice bath was removed, and a spectral examination of the reaction mixture showed complete formation of trimethyltin triflate (^{1}H NMR (CH_2Cl_2, C_6D_6 as external lock) δ 0.82 ($^2J(^{119}Sn{-}CH_3)$ = 65.5 Hz); ^{119}Sn NMR (CH_2Cl_2) δ +194.3). The reaction mixture was treated with 5 mL of water, and the layers were separated. The organic layer was washed with water, dried ($MgSO_4$), and concentrated. The residue was dissolved in 20 mL of hot ethanol, and the hot solution was gravity filtered. The filtrate was briefly boiled and cooled to afford 0.088 g (64%) of **8** as pale yellow plates: mp 145–146 °C. ^{1}H NMR ($CDCl_3$) δ 7.26 (m, 2 H), 7.34 (m, 2 H), 7.46 (m, 4 H), 7.59 (m, 2 H), 7.94 (m, 4 H); UV (CH_3OH) (λ_{max} (ϵ) 292.6 (18 439), 283.2 (19 287), 223 (107 401) (lit.[2]17 UV (CH_3OH) (λ_{max} (ϵ)) 292.5 (18 500), 282.5 (19 000), 220.5 (100 900)); ^{13}C NMR ($CDCl_3$) δ 125.4, 125.8, 126.0, 126.6, 127.8, 127.9, 128.1, 132.9, 133.5, 138.5.

Rearrangement of 1,1′-Binaphthyl (8) to 2,2′-Binaphthyl (7) by Use of Triflic Acid. To a solution of 0.02 g (0.083 mmol) of **8** in 0.3 mL of dichloromethane was added 0.014 mL (0.165 mmol) of triflic acid. A deep blue solution resulted, which was stirred for 2.5 h. The reaction mixture was then treated with 5 mL of water and extracted with 10 mL of dichloromethane. The organic layer was separated, dried ($MgSO_4$), and concentrated. The solid residue was crystallized from hot ethanol to afford 0.02 g (95%) of 2,2′-binaphthyl (**7**) as pale yellow shiny plates: mp

187–188 °C. The spectral parameters were found to be identical with that reported above.

X-ray Diffraction Study of $Sn_2(C_{10}H_6)_2(CH_3)_2Cl_4\cdot(CH_3)_2SO\cdot CCl_4$. Single crystals of this compound were grown by slow cooling of warm CCl_4 solution. One rectangular crystal, of approximate dimensions 0.23 × 0.35 × 0.24 mm, was mounted on a glass fiber for data collection on a Nicolet P3m diffractometer. The unit cell parameters were determined from 25 centered reflections. The details of the crystal data, data collection methods, and refinement procedures are given in Table V. Full details of the crystallographic methodologies may be found in ref 28. Atomic positional parameters, selected bond lengths, and bond angles are given in Tables III and IV, respectively. The intensities of three standard reflections were periodically measured and indicated 20% decay in intensity at the end of data collection. No empirical absorption correlation was applied. In addition to the decay problem, the sulfur and C(23) atom of DMSO as well as the solvent of crystallization (CCl_4) were disordered. In the initial stages, refinement of all atoms excluding biphenyl rings and hydrogens gave an R value of 0.108. At this point, it was evident that sulfur, C(23) of DMSO, as well as CCl_4 are disordered. After changing the population density of sulfur, C(23) and C(15), C(16) and C(18), and C(17) to 70%; 60%, and 50% and including all hydrogen atoms at their fixed positions, the R factor converged to 0.0811 with R_w to 0.858. Although this refinement produced a perfectly satisfactory molecular geometry, C–C bond distances of the biphenyl rings displayed considerable spread. Also, around the sulfur and C(23) of DMSO and C(16), C(17) of CCl_4, peaks and troughs of considerable electron density were located due to disorder that could not be adequately modeled (1.3 e/Å^3).

As a final recourse, the population density of C(23) was fixed at 70% and for C′ at 30%; the CCl_4 molecule was fixed at 50% and Cl′ and Cl″ as 20%. The R factor converged to 0.0735 and R_w to 0.0752. This model resulted in some exaggerated thermal parameters but appeared to be adequate. The disorder problems associated with this structure containing the solvent of crystallization posed some considerable difficulty. However, since the Sn complex was well-behaved, no further attempts were made to resolve the disorder.

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Supplementary Material Available: Tables containing bond lengths, bond angles, anisotropic temperature factors, and hydrogen atom coordinates (5 pages); tables of calculated and observed structure factors (20 pages). Ordering information is given on any current masthead page.

AM1 Parameters for Tin

Michael J. S. Dewar,*,[†] Eamonn F. Healy,[‡] Daniel R. Kuhn,[§] and Andrew J. Holder[⊥]

Department of Chemistry, The University of Florida, Gainesville, Florida 32611, St. Edwards University, Austin, Texas 78704, C_Graph Software, P.O. Box 5641, Austin, Texas 78763, and Department of Chemistry, The University of Missouri—Kansas City, Kansas City, Missouri 64110

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The AM1 semiempirical method has been successfully extended to tin. AM1 heats of formation are slightly better than those obtained by using MNDO, but ionization potential and geometric results have been significantly improved. The AM1 results for organometallic species are especially promising. The correct prediction of the bent sandwich structure for stannocene is indicative of this.

Introduction

The MNDO[1] semiempirical method has been successfully applied to a wide range of tin chemistry. MNDO has been used to study multiple bonding in tin,[2] reactions of stannylene,[3] tin radical cations,[4] and S_N2 reaction of tetramethyltin with Br_2,[5] as well as the cation and radical of trithiatristannaadamantane.[6] Despite these successes, some deficiencies have become apparent. The failure of MNDO to predict the bent C_{2v} structure of stannocene as a minimum on the potential energy surface probably results from its well-documented tendency to overestimate core–core repulsions for extended nonbonded distances. In addition, there is a systematic underestimation of bond lengths.

To correct these failures and to continue our extension of the very successful[7] AM1[8] procedure, we now report AM1 parameters for Sn and calculations for a number of compounds containing tin.

Procedure

Determination of parameters was accomplished by minimizing the sum of the squares (SSQ) of the weighted errors in the heat of formation (ΔH_f), the ionization potential (IP), the dipole moment (μ), and the geometries of a parameterization set of molecules representing the important chemistry of tin. The

Table I. AM1 and MNDO Parameters for Tin

parameter	AM1	MNDO[a]
	Optimized	
U_{ss}/eV	−35.496 741	−40.851 802
U_{pp}/eV	−28.097 636	−28.560 249
ζ_s/au	2.599 376	2.080 380
ζ_p/au	1.695 962	1.937 106
β_s/eV	−3.235 000	−3.235 147
β_p/eV	−2.577 890	−4.290 416
α/Å^{-1}	1.836 936	1.800 814
g_{ss}/eV	9.80	9.80
g_{pp}/eV	8.30	8.30
g_{sp}/eV	7.30	7.30
g_{p2}/eV	6.50	6.50
h_{sp}/eV	1.30	1.30
	Derived	
E_{ht}/kcal mol^{-1}	72.20	72.20
E_{el}/eV	−80.688 754	−92.324 102
D_1/au	1.152 823	1.569 777
D_2/au	1.514 802	1.326 230
AM/au	0.360 162	0.360 162
AD/au	0.382 378	0.321 999
AQ/au	0.340 076	0.371 383

[a] See ref 8.

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* To whom correspondence should be addressed.

[†] The University of Florida.

[‡] St. Edwards University.

[§] C_Graph Software.

[⊥] The University of Missouri—Kansas City.

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