polymers, prebaked at 120 °C, and then irradiated with a 500-W Xe–Hg lamp for 2 min.

Stoichiometry of Diorganotin Dihalide Adducts in Solution

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The formation of Lewis acid–base adducts of diorganotin dihalides of the type R$_2$SnX$_2$, where R = CH$_3$, C$_2$H$_5$, C$_3$H$_7$, n-C$_4$H$_9$, t-C$_4$H$_9$, or C$_6$H$_5$ and X = Cl or Br, with a variety of bases (triphenylphosphine oxide [TPPO], Me$_2$SO, DMA, diphenyl sulfoxide, dibenzyl sulfoxide, pyridine N-oxide, and acetonitrile) was studied by both NMR spectroscopy and calorimetry. The ^{31}P chemical shift of TPPO and the ^{119}Sn shift of the acid were monitored as a function of concentration. The effects of different equilibria including formation of the 1:1 adduct, the 1:2 adduct, simultaneous formation of the 1:1 and 1:2 adducts, and simultaneous formation of the 1:1 adduct and either associated acid, associated base, or associated adduct on the NMR shifts as a function of concentration were determined by computer simulation. The experimentally observed plots can be attributed to predominant formation of the 1:1 adduct along with the associated adduct. The formation of the 1:2 adduct also occurs in solution as demonstrated by isolation of 1:2 adducts and the curvature obtained in the chemical shift plots for weak acids and bases. Calorimetric data were analyzed by schematic mapping and show that the only model that successfully reproduces the data is predominant formaton of the 1:1 adduct. The size of the substituents on the acid was found to have a significant effect on the equilibrium constants; the constants for di-tert-butyltin dichloride were a factor of 100 lower than those of dimethyltin dichloride. Base strengths toward dimethyltin dichloride vary in the order TPPO > pyridine N-oxide > Me$_2$SO ≥ DMA ≥ dibenzyl sulfoxide ≥ diphenyl sulfoxide > acetonitrile. Previous reports that the 1:2 adducts are favored for the dihalotins are most likely a result of the use of excess base to precipitate the 1:2 adduct and the generally greater insolubility of the 1:2 adduct.

Introduction

Organotin halides comprise one of the most convenient systems for the investigation of Lewis acid–base interactions. The acids are stable and not extremely sensitive to moisture and have no lone pair electrons on the central atom. Moreover, the heats of interaction are in a range accessible for study by calorimetry, there are two spin $^1/_2$ isotopes of moderate abundance that provide coupling constant and chemical shift data, and the nucleus can also be studied by Mössbauer spectroscopy. In the majority of the studies of complexation of these acids, the complexes have been isolated in the solid state and then studied by a variety of techniques such as IR, NMR, and, occasionally, X-ray diffraction. The results of these studies indicate that with monodendate bases the triorganotin halides form 1:1 complexes with trigonal-bipyramidal geometry, and the diorganotin dihalides and organotin trihalides form 1:2 complexes with octahedral geometry. Most studies of the complexes in solution have reported the same stoichiometries.[1,2]

That the triorganotin halides form 1:1 complexes in solution and in the solid state has been firmly established, but there is a small body of literature that suggests that 1:1 stoichiometry is also favored for the diorganotin di-

halides and possibly even the trihalides in solution. Both 1:1 and 1:2 complexes of (CH$_3$)$_2$SnCl$_2$ with DMF,[3] 1:1 complexes of (CH$_3$)$_2$SnCl$_2$ with aromatic carbonyls,[3] 1:1 and 1:2 complexes of (CH$_3$)$_2$SnCl$_2$ with alkyl sulfoxides (but only 1:1 for dibenzyl sulfoxide),[4,5] only 1:1 complexes for (CH$_3$)$_2$SnCl$_2$ and (C$_6$H$_5$)$_2$SnCl$_2$ with tribulylphosphine,[6] and both 1:1 and 1:2 complexes of (CH$_3$)$_2$SnCl$_2$ and (C-H$_3$)$_2$SnBr$_2$ with Me$_2$SO, DMF, and HMPT[7] have been reported. Recently, Fujiwara, Sakai, and Sasaki have used NMR to determine equilibrium constants for the reaction of (CH$_3$)$_2$SnCl$_2$ with Me$_2$SO, DMF, HMPT,[8] pyridine,[9] and picolines[10] in solution and have found that the 1:1 complex is favored in all cases.

As part of our continuing investigation[11,12] of the Lewis acidities of the organometallic group 14 halides, we report

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here our study, by calorimetry and both ^{31}P and ^{119}Sn NMR spectrometry, of the interaction of dialkyl- and diphenyltin dihalides with a variety of bases. Our principal objective has been to determine the thermodynamic parameters and equilibrium constants for the equilibria that exist in solution.

Experimental Section

Reagents. All organotin reagents were obtained commercially, and solids were purified by sublimation, while liquids were fractionally distilled under nitrogen. Purity was checked by ^{1}H, ^{13}C, and ^{119}Sn NMR spectra and melting points and in all cases was greater than 98%. Pyridine N-oxide and triphenylphosphine oxide were sublimed in vacuo and stored in a vacuum dessicator. Acetonitrile, dimethyl sulfoxide, and dimethylacetamide were refluxed over CaH$_2$ for 12 h and then distilled. Solvents were dried over CaSO$_4$, distilled from P$_2$O$_5$, and stored over molecular sieves. All operations were performed under argon in a glovebag or drybox using oven-dried glassware.

NMR Studies. Solutions for NMR analysis were prepared with volumetric glassware and then placed in 10-mm tubes containing an inner coaxial tube with acetone-d_6 and a reference. For observation of ^{119}Sn the reference was 0.80 M tetraethyltin in acetone-d_6 but all shifts were determined relative to tetramethyltin by using 1.40 ppm as the shift of tetraethyltin); for observation of ^{31}P the reference was trimethyl phosphate, 1:50 v/v in acetone-d_6. ^{31}P and ^{119}Sn NMR spectra were obtained on a JEOL FX-90Q spectrometer operating at 36.19 (frequency width = 3000 Hz, pulse width = 90°, pulse delay = 1 s, points = 16k) and 33.34 MHz (frequency width = 16000 Hz, pulse width = 22°, pulse delay = 0.2 s, points = 16k), respectively. In both cases gated proton decoupling with no nuclear Overhauser effect was employed.

Calorimetric Analyses. The calorimeter and calorimetric data acquisition have been previously described.[11,12] Pure acids were crushed in ampules in the base–benzene mixture so as to have an acid concentration of 0.01–0.03 M; base concentrations ranged from 0.05 to 0.3 M.

Data analysis for 1:1 adducts has been described previously.[11,12] These methods have been extended by making use of schematic mapping techniques to allow analysis of simultaneous 1:1 and 1:2 adduct formation, simultaneous 1:1 and associated adduct, associated base, or associated acid, and formation of only 1:2 and only 2:1 (acid–base) adducts. For these models it is necessary to determine simultaneously the enthalpies and equilibrium constants for two equilibria. Thus, four parameters—ΔH_1, ΔH_2, K_1, and K_2—must be determined. The analysis is carried out by assuming values for K_1 and K_2, from which the best values of ΔH_1 and ΔH_2 are found by least-squares techniques. The error square sum is used as a measure of how well these four parameters describe the experimental data. The values of the parameters are varied until a minimum error square sum is found.

Combined NMR–Calorimetric Analyses. Equilibrium constants determined by NMR and heats determined calorimetrically may be combined to give enthalpy and entropy changes for the formation of the 1:1 adduct. The heat of interaction, Q, is determined calorimetrically by injection of acid into a dilute solution of the base in the solvent of interest. Q is related to the enthalpy of adduct formation by $Q = \Delta H C_c V$, where V is the volume of the reaction mixture and C_c is the equilibrium concentration of the adduct. C_c can be calculated from the equilibrium constant determined by NMR, and ΔH is calculated directly from Q, C_c, and V. For the systems studied, the authors feel that the most reliable thermodynamic data are obtained from this combination of data.

Preparation of Adducts. Solid adducts were isolated by mixing the appropriate stoichiometric amounts of acid and base in concentrations of acid of about 1 M. The precipitate was suction filtered in an argon atmosphere and washed several times with cyclohexane. The precipitate was finally vacuum dried for 4–6 h. The stoichiometry of the compounds were determined by integration of the proton spectrum. Melting points, except that of the pyridine N-oxide adduct, were in excellent agreement with those reported in the literature. The following are melting points for adducts of dimethyldichlorostannane. 1:1 Adducts: TPPO, 126–128 °C, pyridine N-oxide, 101–102 °C (lit.[5] 114–116 °C);

dibenzyl sulfoxide, 118.5–119.5 °C (lit.[4] 117–119 °C). 1:2 Adducts: TPPO, 137–138 °C (lit.[13] 135–136 °C); pyridine N-oxide, 134–135 °C (lit.[13] 132–133 °C); dibenzyl sulfoxide, 101–102.5 °C; diphenyl sulfoxide, 98–99 °C (lit.[5] 93–95 °C); dimethyl sulfoxide, 110–111 °C (lit.[5] 108–110 °C). The 1:1 adducts of diphenyl sulfoxide and dimethyl sulfoxide could not be prepared, presumably due to the insolubility of the 1:2 adduct.

Results and Discussion

NMR Studies. Two sets of studies were performed by NMR. In the first set, adduct formation of a series of acids, R$_2$SnX$_2$, with triphenylphosphine oxide (TPPO) was studied. In the second, adduct formation of a variety of bases—TPPO, DMA, Me$_2$SO, diphenyl sulfoxide, dibenzyl sulfoxide, pyridine N-oxide, and acetonitrile—with dimethyldichlorostannane was explored. In all cases, only one peak was observed for the ^{31}P and ^{119}Sn nuclei because of the rapid exchange of base between adduct molecules. Although the observed resonance did broaden at lower concentrations and lower temperature, it remained a singlet even at -100 °C.

Formation of a 1:1 adduct from equimolar concentrations of acid and base should result in a linear plot of Δ vs. the $(\Delta/c)^{1/2}$,[11,12] where Δ is the difference between the chemical shift observed and the chemical shift of the pure acid or base, depending upon which contains the nucleus being observed, and c is the original concentration of the acid (and base). Computer simulations reveal that formation of the 1:2 adduct, on the other hand, produces Δ vs. $(\Delta/c)^{1/2}$ plots with very pronounced curvature as shown in Figure 1c. Simultaneous formation of 1:1 and 1:2 adducts produces plots whose curvature depends upon the relative values of the equilibrium constants for the first and second steps

$$A + B \rightarrow AB \ (K_1)$$

$$AB + B \rightarrow AB_2 \ (K_2)$$
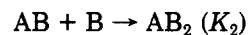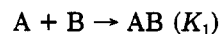
as well as the values of chemical shifts of the species containing the nuclei being observed.

All of the systems studied (except one, vide infra) resulted in plots with curvature as shown in Figure 2. Generally, the stronger the base, the more pronounced the curvature (compare the plot for TPPO with that for acetonitrile in Figure 2). The curvature was also greater when a range of higher concentrations was used. For di-*tert*-butyltin dichloride, the slope of the curve was opposite in direction and the curvature was very pronounced as shown in Figure 3.
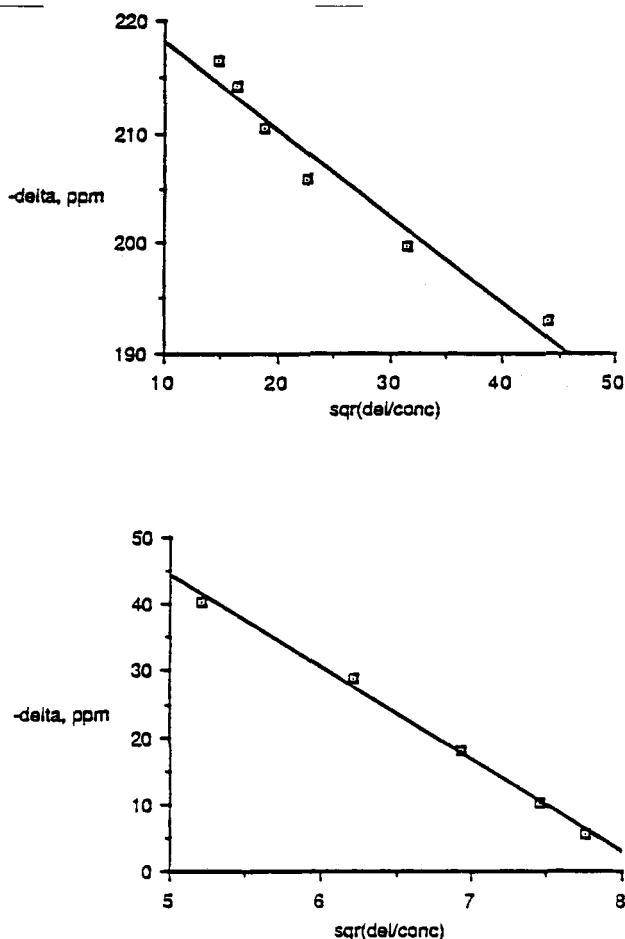
It is clear from computer simulations of the formation of adducts of 1:1 stoichiometry, adducts of 1:2 stoichiometry, and simultaneous formation of 1:1 and 1:2 adducts that none of these three equilibria can produce the curvature observed. In order to explain the curvature observed in the experimental plots, four additional equilibria were considered: (a) hydrolysis of the tin halide which would produce HCl or HBr, which in turn would deplete some base by protonation, (b) self-association of the acid, in its most simple form expressed as 2A = A$_2$, (c) self-association of the base, expressed as 2B = B$_2$, and (d) self-association of the adduct, expressed as 2AB = (AB)$_2$. Each of these cases was then explored by simulation.

The first, hydrolysis, results in curvature in the correct direction when the base TPPO is observed through ^{31}P NMR but produces curvature in the opposite direction to that observed when the acid is monitored through ^{119}Sn NMR. Moreover, the rigorous purification of reagents and preparation of solutions makes this explanation unlikely.

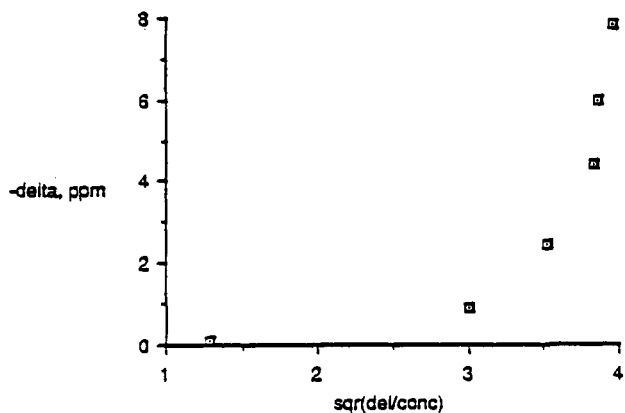(13) Das, V. G. K.; Kitching, W. *J. Organomet. Chem.* 1986, *13*, 523.
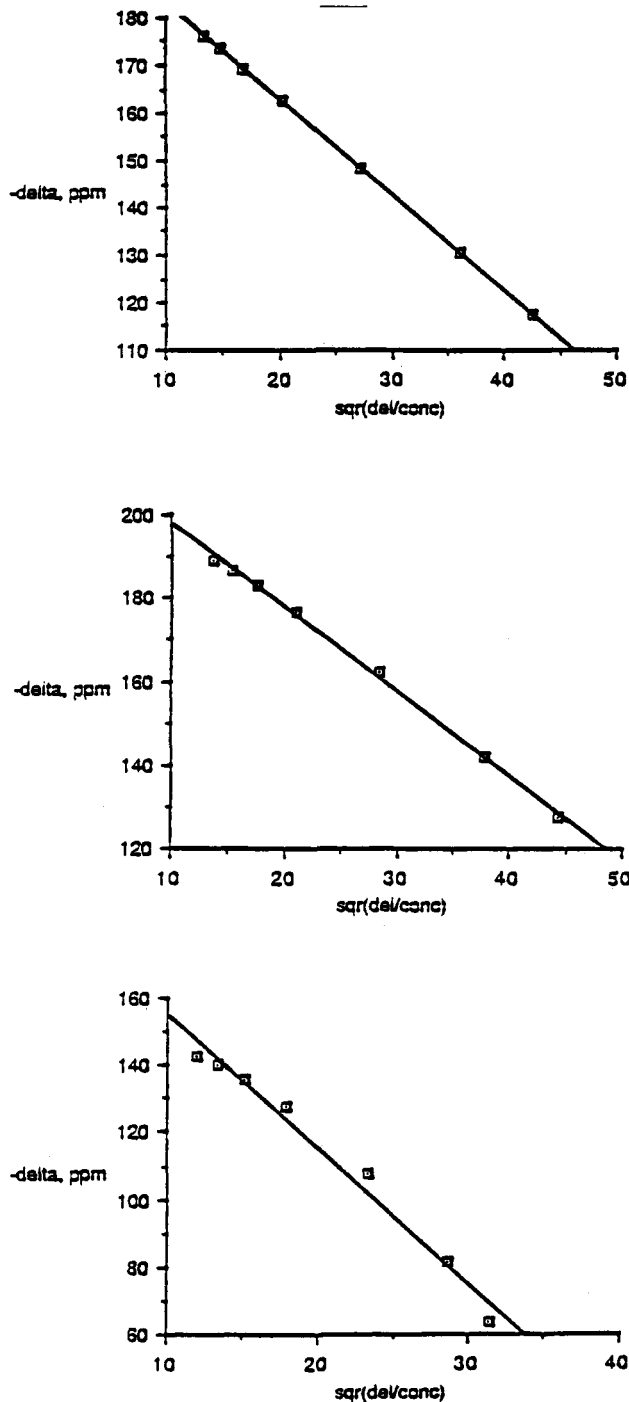
Figure 1. Computer simulations of plots of ^{119}Sn chemical shift (Δ) vs. $(\Delta/c)^{1/2}$ for simultaneous formation of 1:1 and 1:2 adducts [^{119}Sn chemical shifts: acid (138 ppm), 1:1 adduct (−65 ppm), 1:2 adduct (−250 ppm)]: (a) $K_1 = 50$, $K_2 = 0.001$; (b) $K_1 = 50$, $K_2 = 5$; (c) $K_1 = 5$, $K_2 = 20$.

Figure 2. Experimental plots for $(CH_3)_2SnCl_2$ in chlorobenzene: (a) TPPO; (b) acetonitrile.

Figure 3. Experimental plot for $[(CH_3)_3C]_2SnCl_2$ in chlorobenzene with TPPO.

Simulations of the three association equilibria show that all three produce curvature of the type observed, although the concentration of associated adduct cannot exceed approximately 30% of the initial concentration of acid. In order to determine whether association of acid or base was a viable explanation of the observed curvature, the concentration dependence of the ^{31}P shift of TPPO in benzene and the ^{119}Sn shift of $(CH_3)_2SnCl_2$ in chlorobenzene were determined. The ^{31}P shift of TPPO varied by less than 0.03 ppm over a 20-fold dilution range, while the ^{119}Sn shift of $(CH_3)_2SnCl_2$ varied by about 1 ppm over a 10-fold

change in concentration (the same was true for $(CH_3)_2SnBr_2$). This is consistent with previous observations.[14] Since these variations are just barely outside experimental error, the shifts can be assumed to be concentration independent. It does not seem likely, therefore, that either TPPO or $(CH_3)_2SnCl_2$ are significantly associated at these concentrations.

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The most likely explanation of the observed curvature appears, then, to be association of the 1:1 adduct. The following structure can be proposed for the associated adduct
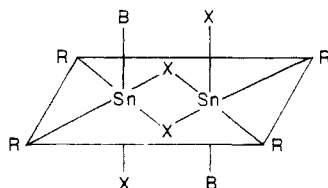
and has the virtue of 1:1 stoichiometry and 6-coordination about each tin. Similar association was proposed by Ulich et al.[15] for the benzonitrile complex of $SnCl_4$ and by Seyferth and Grim for complexes of the type $(CH_3)_2SnX_3^-$.[16] The following observations are consistent with the presence of associated adduct: (a) The curvature observed for the dibromo derivative is somewhat less pronounced than that of the dichloro derivatives. The ability of halogens to associate with tin is generally believed to decrease down the group.[17] (b) The curvature for the formation of the $(CH_3)_2SnCl_2$·TPPO complex in THF is less than in benzene. Presumably, coordination of THF to the acid decreases the concentration of associated adduct. (c) The molecular weights determined by cryoscopy in benzene for several 1:1 adducts were consistently higher than indicated by a monomeric formula. For example, the calculated molecular weight for the dibenzyl sulfoxide–dimethyldichlorostannane adduct is 450, while the molecular weight in benzene at 0.1 M was found to be 590. Similarly, the calculated molecular weight for the 1:1 TPPO·$(CH_3)_2SnCl_2$ adduct is 498, whereas molecular weights of 640, 630, and 670 were obtained in three separate determinations (in the range 0.1–0.2 M) with three different samples.

Although the plots of Δ vs. $(\Delta/c)^{1/2}$ for most of the systems studied do not reveal the presence of 1:2 adduct, the fact that solid compounds of this stoichiometry can be prepared by adding excess base to the acid indicates that some 1:2 adduct is probably present in solution. The plot of one system did reveal, however, the presence of the 1:2 adduct. The plot for the $[(CH_3)_3C]_2SnCl_2$–TPPO system was a dramatic reversal of the usual plot. This plot was approximately reproduced by solving the three simultaneous equations for formation of 1:1, 1:2, and associated adducts with the program TK Solver. The best fit was obtained with the following parameters: $K_1 = 0.3$, $K_2 = 1$, and $K_{assoc} = 1$. The $(CH_3)_2SnCl_2$–acetonitrile system also exhibits a slightly upward deviation from a straight line which can also be attributed to formation of the 1:2 adduct. In these cases, the equilibrium constant for the formation of the 1:1 adduct is small $(K < 1)$ and the presence of a small amount of 1:2 adduct is more influential. In all systems studied, however, the equilibrium constant for the second step in the formation of the 1:2 adduct did not exceed a value of 1.

The $(CH_3)_2SnCl_2$–TPPO system was investigated in both benzene and chlorobenzene, and the equilibrium constants obtained were within experimental error. Methylene chloride was used as the solvent for the Me_2SO system because of the greater solubility of the adducts in this solvent.

Fortunately, in all but one system the curvature was sufficiently small to conclude that the predominant

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Table I. Equilibrium Constants for Formation of 1:1 Adducts Determined by NMR[a]

R_2SnX_2		base	K_1
CH_3	Cl	TPPO	460
		pyridine N-oxide	366
		Me_2SO	100
		DMA	57
		Bz_2SO	49
		Ph_2SO	42
		acetonitrile	0.7
CH_3	Br	TPPO	108
C_2H_5	Cl	TPPO	173
n-C_3H_7	Cl	TPPO	103
n-C_4H_9	Cl	TPPO	122
n-C_4H_9	Br	TPPO	33
C_6H_5	Cl	TPPO	295
t-C_4H_9	Cl	TPPO	0.7

[a] All TPPO runs observed by ^{31}P in benzene over concentrations ranges of 0.1–0.006. All other systems observed by [119]Sn in chlorobenzene (except for Me_2SO which was done in CH_2Cl_2) over concentrations of 1–0.06 M. In most cases the K was determined from six data points and the error is estimated at ca. 10%.

Table II. Enthalpies of Solution in Benzene at 298 K

R_2SnX_2		ΔH_s, kcal/mol
CH_3	Cl	5.66 ± 0.36
CH_3	Br	5.15 ± 0.45
C_2H_5	Cl	6.64 ± 0.07
n-C_3H_7	Cl	8.24 ± 0.14
n-C_4H_9	Cl	7.61 ± 0.09
n-C_4H_9	Br	0.74 ± 0.03
t-C_4H_9	Cl	3.94 ± 0.03
C_6H_5	Cl	5.43 ± 0.35
$(CH_3)_2SnCl_2$[a]		−10.5 ± 0.1
$(CH_3)_2SnCl_2$[b]		6.15 ± 0.08
$(CH_3)_2GeCl_2$[a]		−5.6 ± 0.3
$(CH_3)_2GeCl_2$[b]		0.39 ± 0.03

[a] Me_2SO solvent. [b] CCl_4 solvent.

Table III. Schematic Mapping Analysis of Heat Data for Di-n-butyltin Dichloride–TPPO Interaction in Benzene (15 points)[a]

model	K	ΔH, kcal/mol	error sum of squares
1. 1:1 adduct	118 ± 13	−9.2 ± 0.1	0.029
2. 1:1 and 1:2 adducts	$K_1 = 242$	$\Delta H_1 = -8.1 \pm 0.04$	
	$K_2 = 2$	$\Delta H_2 = -3.6 \pm 0.2$	0.00497
3. 1:1 and associated adduct	$K_1 = 113$	$\Delta H_1 = -9.4 \pm 0.15$	
	$K_a = 1$	$\Delta H_a = 1.6 \pm 13$	0.024
4. 1:1 and associated acid	$K_1 = 120$	$\Delta H_1 = -9.4 \pm 0.1$	
	$K_a = 0.001$	$\Delta H_a = -13265$	0.024
5. 1:1 and associated base	$K_1 = 275$	$\Delta H_1 = -7.9 \pm 0.05$	
	$K_b = 0.6$	$\Delta H_b = +8.6 \pm 0.5$	0.0048

[a] Other models had error square sums of greater than 0.1.

equilibrium in solution is formation of the 1:1 adduct. The least-squares lines (in most cases $r > 0.98$) were then used to approximate the equilibrium constant for formation of the 1:1 adduct. These constants are presented in Table I. The error in the equilibrium constant as determined from the errors in slope and intercept of the least-squares line did not exceed 15% in any system studied.

Calorimetric Studies. The heats of solution of the acids are given in Table II. The calorimetric data were analyzed by schematic mapping using seven models: formation of the 1:1 adduct, formation of the 1:2 adduct, simultaneous formation of 1:1 and 1:2 adducts, simultaneous formation of 1:1 adduct and associated acid, si-

Table IV. Equilibrium Constants and Enthalpies for the Formation of 1:1 TPPO Adducts in Benzene at 298 K Determined by Calorimetry[a]

R_2SnX_2		K	$-\Delta H$, kcal/mol
CH_3	Cl	126 ± 19	9.3 ± 0.1
CH_3	Br	40 ± 2	11.0 ± 0.1
C_2H_5	Cl	98 ± 14	9.4 ± 0.1
$n\text{-}C_3H_7$	Cl	93 ± 10	9.0 ± 0.1
$n\text{-}C_4H_9$	Cl	118 ± 13	9.2 ± 0.1
$n\text{-}C_4H_9$	Br	40 ± 7	8.6 ± 0.3
$t\text{-}C_4H_9$	Cl	0	0
C_6H_5	Cl	96 ± 23	11.4 ± 0.3

[a] 9–15 points used in analyses.

Table V. Comparison of Thermodynamic Parameters for R_3SnX and R_2SnX_2 Adducts with TPPO in Benzene[a]

	$-\Delta H$, kcal/mol	K	$-\Delta S°$, cal K^{-1} mol^{-1}
$(CH_3)_3SnCl$	8.1 ± 0.1	21.4 ± 0.5	21
$(CH_3)_2SnCl_2$	8.8 ± 0.4	460	17
$(C_2H_5)_3SnCl$	8.3 ± 0.2	9.1 ± 0.4	23
$(C_2H_5)_2SnCl_2$	9.0 ± 0.3	173	20
$(C_3H_7)_3SnCl$	7.3 ± 0.2	5.0 ± 0.2	21
$(C_3H_7)_2SnCl_2$	8.7 ± 0.4	103	20
$(C_4H_9)_3SnCl$	7.6 ± 0.4	5.5 ± 0.6	22
$(C_4H_9)_2SnCl_2$	9.2 ± 0.2	122	21
$(C_6H_5)_3SnCl$	8.3 ± 0.1	12.6 ± 0.3	23
$(C_6H_5)_2SnCl_2$	10.7 ± 0.4	295	25
$(CH_3)_3SnBr$	8.3 ± 0.1	19 ± 1	22
$(CH_3)_2SnBr_2$	9.9 ± 0.5	108	24

[a] Equilibrium constants, enthalpies, and entropies for the monohalo compounds determined by calorimetric analyses. Equilibrium constants ($\pm 10\%$) for the dihalo compounds were determined by NMR and enthalpies by a combination of NMR and calorimetric analyses.

multaneous formation of 1:1 and associated base, simultaneous formation of 1:1 adduct and associated acid, and formation of a 2:1 (acid–base) adduct.[18] For most systems, either the heats or equilibrium constants for one or more steps were unrealistic for all models except formation of the 1:1 adduct. The results of a typical analysis are shown in Table III for the dibutyltin dichloride–TPPO system. The fit of the model to the experimental data, in this case 15 points, is measured by the sum of the squares of the deviations of the experimental points from the points calculated by the model. For these data, five models produce error square terms of less than 0.03. For the formation of the 1:1 adduct the equilibrium constant (118 $\pm$ 13) is in good agreement with that determined by NMR (122 $\pm$ 13) and the enthalpy change is reasonable when compared with the enthalpies found for the trialkyltin halides.[12] For the trialkyltin chlorides, the enthalpies vary from −7.3 to −8.1 kcal/mol, with a value of −7.6 $\pm$ 0.4 kcal/mol for tributyltin chloride. The increase in acidity due to the addition of another chlorine[1,2] would be expected to increase the heat of complexation, and therefore enthalpies for the formation of 1:1 adducts of the dichlorides of 8 kcal/mol or below were deemed unreasonable. Thus, the fit of the second model in Table III, simultaneous formation of 1:1 and 1:2 adducts, is unsatisfactory for two reasons: first, $-\Delta H_1$ is too small and, second, $-\Delta H_2$ (the enthalpy change for attachment of the second mole of base) is unreasonably small (3.6 kcal/mol). Because of the large error associated with the enthalpy of association in model three, simultaneous formation of the 1:1 adduct and the associated adduct, it is difficult to determine its validity. The fourth model, simultaneous formation of 1:1 adduct and associated acid, is unsatisfactory because of the unreasonably exothermic enthalpy of association. The fifth model, formation of 1:1 adduct and associated base, gives a positive enthalpy change for base self-association and can, therefore, be eliminated.

In all systems studied by calorimetry, only the formation of the 1:1 adduct consistently gave chemically reasonable results. Fujiwara et. al. found only the 1:1 complex for the interaction of $(CH_3)_2SnCl_2$ with Me_2SO in 1,2-dichloroethane. Our analysis of $(C_4H_9)_2SnCl_2\cdot Me_2SO$ in benzene also revealed only a 1:1 adduct with $K = 50 \pm 5$ and $\Delta H = -10.4 \pm 0.2$ kcal/mol as determined calorimetrically. The enthalpy for the $(CH_3)_2SnCl_2\cdot Me_2SO$ adduct was also determined by the pure base techniques[11] in pure Me_2SO solvent. The model compound used for the calculation of the enthalpy was $(CH_3)_2GeCl_2$, for which no complex formation has been found with a variety of bases by both

calorimetric and NMR techniques. The enthalpy calculated by the pure base method is −10.7 kcal/mol which is so similar to that for the 1:1 complex of $(C_4H_9)_2SnCl_2$ with Me_2SO that it appears that even in pure Me_2SO only the 1:1 adduct is formed with $(CH_3)_2SnCl_2$.

Trends. When the equilibrium constants obtained by NMR are used for comparative purposes, it is apparent that for the interaction of the acids with TPPO there is a fairly regular decline in equilibrium constant with an increase in size of alkyl group. In fact, if the CH_3 group is omitted, the constants for the alkyl and phenyl chlorides correlate moderately well ($r = 0.92$) with E_s values (E_s(min) used for C_6H_5).[19] The effect of size is most dramatic with CH_3 and $(CH_3)_3C$ groups, which have constants of 460 and 0.7 for complexation with TPPO. Replacement of chlorine with bromine also leads to a decrease in equilibrium constant, probably a result of both an increase in size and a decrease in electronegativity. The phenyl group results in an increase in equilibrium constant relative to alkyl groups of similar size.

While the size dependence of the enthalpies and equilibrium constants determined by calorimetry are not as dramatic, the effect can be seen in the zero enthalpy change for the di-*tert*-butyl derivative. The enthalpy changes and equilibrium constants reported previously[12] for R_3SnX adduct formation with TPPO in benzene are given in Table V along with the corresponding thermodynamic parameters for R_2SnX_2. The data of Table V were calculated from combined NMR and calorimetric data and represent what the authors believe to be the best values for these thermodynamic parameters. In all cases the enthalpy changes and equilibrium constants are larger for the dihalo derivatives.

The basicities toward dimethyltin dichloride vary as expected: TPPO > pyridine N-oxide > Me_2SO $\geq$ DMA $\geq$ dibenzyl sulfoxide $\geq$ diphenyl sulfoxide > acetonitrile. Those bases whose structures can be represented with a formal negative change on oxygen—e.g. $(C_6H_5)_3P^+O^-$—produce the strongest interactions.

Conclusions. The most significant conclusion of the present work is that formation of the 1:1 adduct is the predominant equilibrium in the interaction of diorganotin dihalides with monodentate bases. Previous conclusions that adducts of 1:2 stoichiometry are favored with these acids are very likely a reflection of the mode of preparation

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(the use of excess base) and the generally greater insolubility of the 1:2 adducts. Preliminary work in our laboratory indicates that the 1:1 adducts also predominate for trihaloorganotin compounds, and thus it can be stated that *in general organotin halides form predominantly 1:1 adducts in solution.* We believe that it is also significant that in addition to the formation of small concentrations of 1:2 adduct (depending of course upon the ratio of acid to base), a third equilibrium is very likely present. The most reasonable candidate for this equilibrium at present is the formation of the associated 1:1 adduct. Finally, it is significant that the equilibrium constants for the formation of the 1:1 adduct are rather severely dependent upon the size of the substituent.

Bridging Hydrides vs. Polyhydrogen Units: The Importance of Electron Count

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The electronic structure of $(ML_x)_yH_{n-y}$ complexes are explored where the metal and hydrogen atoms form a polynuclear cluster with n vertices. A special case of this type of molecule is the recently characterized class of dihydrogen complexes such as $Cr(CO)_5(H_2)$ with $n = 3$ and $y = 1$, based on the triangle. Fragments typified by $V(CO)_5^-$ and $Co(CO)_3^-$, which each contain an empty frontier orbital, are isoelectronic with H^+ and may be built into clusters which have a total of two skeletal electrons. The triangle, tetrahedron, square, trigonal bipyramid and octahedron are investigated. There is a class of complexes predicted with n vertices with good HOMO–LUMO gaps of the type *trans*-$(ML_x)_2H_{n-2}$ for deltahedra with $n = 5$–7, which have a total of 34 valence electrons and a planar $(n - 2)$ gon of cyclically bound hydrogen atoms. These structures are linked geometrically to a set of analogous 30-electron complexes with $(n - 2)$ bridging hydrides of which several examples have been characterized. A model that uses only one empty frontier orbital on each of the transition-metal-containing fragments, while successful in understanding the structures of many of these species, is restrictive in that it does not allow access to other geometries for the coordinated hydrogen oligomer. Inclusion of other fragment orbitals shows low-energy pathways between closed and open H_n geometries and the stability of the square over the tetrahedron for the hypothetical species $Co_2(CO)_6H_2^{2-}$.

Introduction

Recently, several examples of a new class of species, namely, metal–dihydrogen complexes **1** and **2**, have been synthesized.[1-15] We will write such species as $ML_n(H_2)$

$W(CO)_5(H_2)$
$W(CO)_3(PR_3)_2(H_2)$*
*H-H=0.84Å

1

$Co(CO)_2(NO)(H_2)$
$Fe(CO)(NO)_2(H_2)$

2
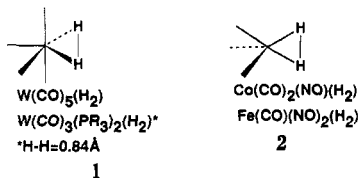
to distinguish them from the conventional hydride ML_nH_2. Such (H_2) complexes have received some theoretical attention.[16-24] All of these are isoelectronic (in the broad

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