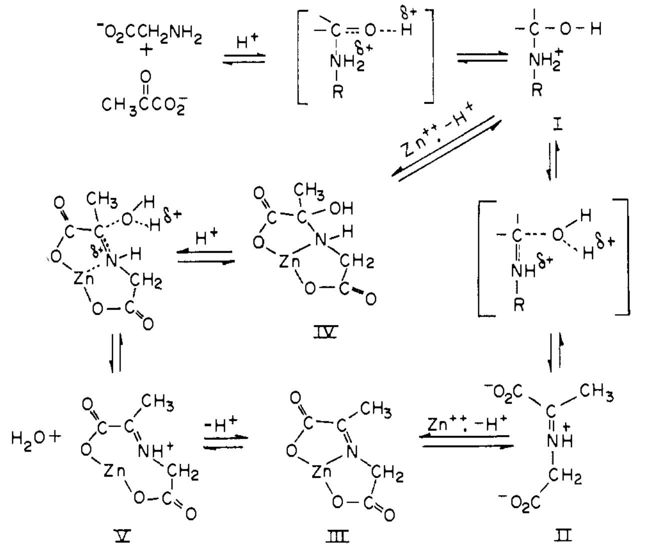
of k'_{spec} and those calculated for k'_{pH} with the exception of the pH 6.0 experiments. It appears from this discrepancy and also from the tendency for the pH 6.0 points in Figure 2 to lie at high values that an additional path becomes important as neutrality is approached.

The zinc ion most reasonably enters into reaction as shown in the following microscopic scheme which is based on the present rate data, the currently accepted mechanism for carbonyl addition reactions,[3,15] and the coordination behavior of Zn(II).



The protonated carbinolamine I first formed may undergo dehydration in the manner normally observed in the absence of metal ions to give the unstable immonium ion II. II readily undergoes a proton displacement reaction with Zn^{2+} and is trapped as the stable product III. Alternately I may react with Zn^{2+} by losing a proton giving the carbinolamine complex IV. IV then undergoes dehydration through a proton-catalyzed sequence ultimately yielding III. Proton catalysis in this alternate path requires the breaking of a metal ion–nitrogen bond. However, the bicoordinated intermediate V can undergo a rapid deprotonation to yield tricoordinated III. Owing to the high lability of zinc complexes, any deleterious effect from metal–ligand bond breaking is likely to be small compared to the beneficial effect accrued by increasing the total carbinolamine concentration available for reaction.

At least under the somewhat acidic conditions prevailing in this study, Zn^{2+} ions do not act as a "kinetic template"[6] in the sense that the free ligands are first gathered independently by the metal ion to form a mixed complex and held in close proximity until condensation occurs. Rather the proton is the effective catalyst in both reaction steps, addition and dehydration. The role of the metal ion is to provide a stabilizing influence for the easily dissociated intermediate carbinolamine and imine product. The metal ion appears to serve a function in the pyruvate–glycinate reaction system similar to the role played in converting the bisbenzthiazolines to the Schiff base form,[16] through its influence on the free energy of reaction.

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(15) T. C. Bruice and S. Benkovic, "Biorganic Mechanisms," Vol. 2, W. A. Benjamin, Inc., New York, N. Y., 1966.

(16) H. Jadamus, Q. Fernando, and H. Freiser, *J. Am. Chem. Soc.*, **86**, 3056 (1964).

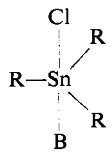
Evidence for a Linear Relation between $J_{Sn^{119}-CH_3}$ and the ΔH_f of Trimethyltin Chloride Complexes[1]

Theodore F. Bolles and Russell S. Drago

Contribution from the William A. Noyes Laboratory, University of Illinois, Urbana, Illinois. *Received July 11, 1966*

Abstract: The tin–proton coupling constants of trimethyltin chloride adducts have been measured and are linearly related to the enthalpies of formation of the complexes. Having established the relationship, it was then employed to obtain enthalpies of systems that are difficult to measure directly. Trimethyltin chloride is found to react more strongly with oxygen or nitrogen donors than with sulfur or phosphorus donors. A model describing the structure of the complexes is proposed which is based on an interpretation of the tin–proton coupling constant in terms of the Fermi contact mechanism and evidence of steric interactions in the adducts. The heat of formation of the trimethyltin iodide–DMA complex was also measured.

Triorganotin halides show a marked tendency to form 1:1 addition compounds with Lewis bases. These adducts appear to be approximately trigonal bipyramidal in solution[2] as well as in the solid state[3] with the basic structure



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(1) Abstracted in part from the Ph.D. thesis of T. F. Bolles, University of Illinois, Urbana, Ill.

(2) N. A. Matwiyoff and R. S. Drago, *Inorg. Chem.*, **3**, 337 (1964). There are also many other examples which support an analogous five-coordinate structure for triorganotin compounds; *e.g.*, see R. C. Poller, *J. Organometal. Chem.* (London), **3**, 321 (1965), and references therein.

(3) R. Hulme, *J. Chem. Soc.*, 1524 (1963); I. R. Beattie, G. P. McQuillan, and R. Hulme, *Chem. Ind.* (London), 1429 (1962).

in which B represents a Lewis base. In these adducts, distortions from the trigonal bipyramidal structure could arise if the hybridization of the tin atom is dependent on the nature of the B–Sn–Cl bonding. It has been proposed[2] that the tin orbital utilized in the axial bonds of the adduct is p_z or $(d_{z^2} + p_z)$, but it is also possible that there may be some s character in these bonds. Certainly, the hybridization of this orbital, as well as the extent of rehybridization in the tin–carbon orbitals, will be related to the electropositive nature of the base.

It has been shown that the $Sn^{117,119}$–CH_3 coupling constants change when trimethyltin chloride is dissolved in various Lewis bases.[2] If the Fermi contact term makes the dominant contribution to the Sn–CH_3 coupling constant,[4,5] J_{Sn-CH_3} should give an indication of the hybridization the tin atom employs in the tin–carbon bond. Therefore, it was of interest to explore a possible relationship between the strength of the B–Sn bond and the Sn–CH_3 coupling constant in adducts of trimethyltin chloride.

Experimental Section

A. Preparation and Purification of Chemicals. Hexamethylthiophosphoramide was prepared by the procedure of Better[6] and purified by distillation. *Anal.* Calcd for $C_6H_{18}N_3PS$: C, 36.89; H, 9.29; N, 21.31. Found: C, 36.66; H, 9.39; N, 21.12. The solvents and the other bases used were distilled and purified prior to use as previously described[7] with the exception of 2,6-dimethylpyridine, which was first distilled from a BF_3–$(C_2H_5)_2O$ solution. The following abbreviations have been employed for the various bases: HMPA for hexamethylphosphoramide, DMSO for dimethyl sulfoxide, DMA for N,N-dimethylacetamide, DMCA for N,N-dimethylcyanamide, DMTA for N,N-dimethylthioacetamide, THMPA for hexamethylthiophosphoramide, and 2,6-lutidine for 2,6-dimethylpyridine.

Trimethyltin iodide was prepared from tetramethyltin and iodine,[8] distilled, and repeatedly recrystallized until a sharp-melting fraction was obtained, mp 3.4°, lit.[8] 3.4°. Trimethyltin chloride was sublimed before use, mp 37.5°, lit.[9] 37.0°.

B. Nuclear Magnetic Resonance Spectra. The Sn^{119}–CH_3 coupling constant values were determined from nmr spectra obtained on a Varian Model A-60 high-resolution nuclear magnetic resonance spectrometer equipped with a Varian temperature regulator. The probe temperature was measured with an iron–constantan thermocouple to ±0.5°. The spectra were traced three times and found to be reproducible to ±0.2 cps. The spectrometer sweep was calibrated with a standard $(CH_3)_4Sn$ sample before and after the measurements, and all coupling constant values are reported relative to $J_{Sn^{119}-CH_3} = 54.0$ cps for $(CH_3)_4Sn$.

C. Calorimetric Measurements. The calorimetric measurements were performed as previously described.[10]

Results

The coupling constants, $J_{Sn^{119}-CH_3}$, for the complexes of trimethyltin chloride were measured by using the pure bases as solvents and are reported in Table I. In order to test for complete complexation of the trimethyltin chloride, each system was observed at a series of successively lower temperatures until a further decrease in temperature produced no change in the J_c value observed. The temperatures corresponding to complete complexation are also included in Table I.

Table I. Sn^{119}–CH_3 Coupling Constants for the Systems Lewis Base–$(CH_3)_3SnCl$

Donor	[A], moles $l.^{-1}$ at 26°	[B], moles $l.^{-1}$ at 26°	Temp, C°	$J_{Sn^{119}-CH_3}$, cps
HMPA[c]	0.49	5.4	35	71.6
DMSO[c]	0.47	13.3	35	69.2
DMA[c]	0.53	10.1	35	68.8
Pyridine[c]	0.51	12.3	35	67.0
DMCA[a]	0.60	12.1	35	66.8
Acetone[c]	0.52	12.7	−20	66.1
DMTA[c]	...	...	...	65.7
THF	0.50	11.4	−56	64.5
$CH_3C{\equiv}N$[c]	0.45	17.9	−20	64.2
THMPA[a]	0.50	...	35	63.9
$(n\text{-}C_4H_9)_3P$[a]	0.50	4.0	35	63.0
$(C_2H_5)_2O$[b]	0.49	8.91	−56	60.6
$(C_2H_5)_2S$	0.51	8.7	−56	60.4
2,6-Lutidine[a]	0.58	8.80	35	58.6
Toluene	0.44	9.4	−56	57.6
(CCl_4)	0.51	...	−20	57.6

[a] Measured only at temperature given. [b] Coupling constant still increasing at lowest temperature listed. [c] Ref 7.

The equilibrium constant and enthalpy of formation for the adduct of $(CH_3)_3SnI$ with DMA were evaluated simultaneously by use of eq 1. A_0 and B_0 represent the

$$K^{-1} = \frac{1000H^1}{V\Delta H^\circ} + \frac{A_0B_0V\Delta H^\circ}{1000H^1} - (A_0 + B_0) \quad (1)$$

initial concentrations of the acid and base, V represents the total volume of the solution in ml, H^1 is the experimentally measured enthalpy of reaction, and ΔH° is the calculated molar enthalpy of formation of the complex. The data were evaluated by a previously proposed procedure[10] and are presented in Table II.

Table II. $(CH_3)_3SnI$–DMA at 26°

A_0, moles $l.^{-1}$	B_0, moles $l.^{-1}$	CCl_4, ml	H^1, cal	K^{-1}, mole $l.^{-1}$
0.03358	0.2789	100.2	−9.44	0.64
0.03598	0.4095	100.3	−12.98	0.64
0.02965	0.6358	100.2	−13.85	0.64

$K^{-1} = 0.64 \pm 0.03$ mole $l.^{-1}$

$\Delta H^\circ = -9.4 \pm 0.3$ kcal $mole^{-1}$ at sharpness $\gtrsim 20$

The equilibrium constant and the coupling constant for the $(CH_3)_3SnI$–DMA adduct were evaluated by use of eq 2 which had been derived for the simultaneous evaluation of K and J_c in conditions of rapid exchange.[7]

$$K^{-1} = \frac{(J_{obsd} - J_f)A_0}{(J_c - J_f)} + \frac{B_0(J_c - J_f)}{(J_{obsd} - J_f)} - (A_0 + B_0) \quad (2)$$

In this equation, J_{obsd}, J_f, and J_c represent the observed coupling constant, the coupling constant of the free acid, and the coupling constant of the complex, respectively, and A_0 and B_0 represent the initial acid and base concentrations. Equation 2 is of the same form

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(4) J. R. Holmes and H. D Kaesz, *J. Am. Chem. Soc.*, **83**, 3903 (1961); N. Flitcroft and H. D. Kaesz, *ibid.*, **85**, 1377 (1963).

(5) G. Klose, *Arch. Sci.* (Geneva), **14**, 427 (1961).

(6) H. J. Better and H. Nöth, *Ber.*, **96**, 1308 (1963).

(7) T. F. Bolles and R. S. Drago, *J. Am. Chem. Soc.*, **88**, 3921 (1966).

(8) G. Grutter and E. Krause, *Ber.*, **50**, 1802 (1917).

(9) C. A. Kraus and C. C. Callis, *J. Am. Chem. Soc.*, **45**, 2628 (1923).

(10) T. F. Bolles and R. S. Drago, *ibid.*, **87**, 5015 (1965).

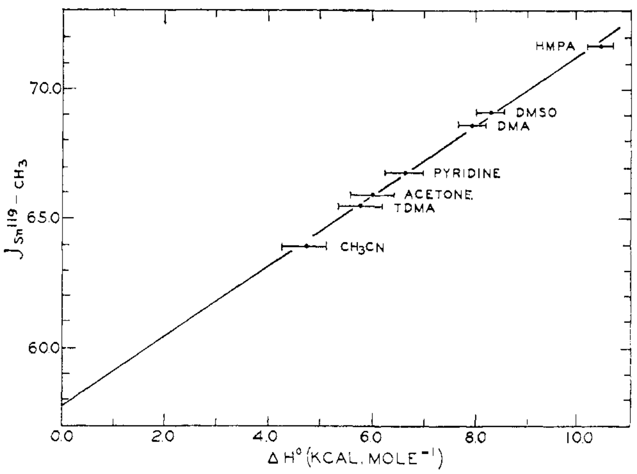

Figure 1. Relationship of $J_{SN^{119}-CH_3}$ to the enthalpy of adduct formation (J in units of cps).

as eq 1 and was solved for the unknowns J_c and K^{-1} by the same procedure. The data for the calculation of the equilibrium constant for the trimethyltin iodide–DMA system are given in Table III.

Table III. $(CH_3)_3SnI$–DMA in CCl_4, at 31°

A_0, moles l.$^{-1}$	B_0, moles l.$^{-1}$	$(J_{obsd} - J_f)A_0$, cps moles l.$^{-1}$	K^{-1}, moles l.$^{-1}$
0.05140	0.6212	0.2878	0.59
0.05038	0.4341	0.2368	0.56
0.05023	0.3103	0.1858	0.59
0.04964	0.1898	0.1291	0.58

K^{-1} (31°) = 0.57 ± 0.10 mole l.$^{-1}$
$(J_c - J_f) = 11.1 \pm 1.0$ cps; measured value of $J_f = 57.6$; J_c = 68.7 cps at sharpness ≥20

Discussion

$J_{Sn^{119}-CH_3}$–$\Delta H°$ Relationship. A linear relationship between J_{Sn-H} or J_{Sn-CH_3} and the per cent s character in the Sn–H or Sn–C bond has been proposed.[4] For methyltin compounds the relationship is

$$J_{Sn^{119}-CH_3} = 2.16\rho \qquad (3)$$

The constant 2.16 was evaluated from the measured $J_{Sn^{119}-CH_3}$ for $(CH_3)_4Sn$ and the assumption that ρ, the per cent s character in the tin–carbon bond, is equal to 25% in this compound.[11] This relationship assumes that the Fermi contact term makes the dominant contribution to the nuclear spin interaction and that the carbon–hydrogen bonding does not change appreciably.[5] If this is the case in the adducts reported here, $J_{Sn^{119}-CH_3}$ provides a measure of the hybridization the tin atom employs in the tin–carbon bond. Although there is some evidence in the literature to support a relationship between $J_{Sn^{119}-CH_3}$ and per cent s character, this has been by no means rigorously established. It should be pointed out that there may be changes in $J_{Sn^{119}-CH_3}$ due to a change in the effective nuclear charge on the tin atom upon complex formation or from several other effects. If the three methyl carbons were coplanar with the tin, and if all of the tin s orbital used in bonding in the addition compound were used to bond to the carbon, the upper limit of per cent s character in the tin–carbon bond would theoretically correspond to 33%. It is interesting that the coupling constant for the adduct of the strongest base studied, HMPA, corresponds to 33% s character in the Sn–C bond, and no reported examples exist where $J_{Sn^{119}-CH_3}$ is greater than this value for any trimethyltin compound. Since $(CH_3)_4Sn$ was used to establish the relationship in eq 3, this indicates that the total amount of tin s orbital participation in the bonding in the adduct and free $(CH_3)_3SnCl$ is constant (*i.e.*, to the extent that $(CH_3)_4Sn$ can be approximated as an sp^3 hybrid, the tin–carbon bonds in the adduct are sp^2). At least in this series of compounds, the changes in $J_{Sn^{119}-CH_3}$ are thought to be due primarily to changes in the Fermi contact term.

The increase in $J_{Sn^{119}-CH_3}$ with increasing donor strength is clearly contradictory to the simple application of the model explaining coupling constant changes on the basis of changes in formal charge.[12] Application of this model to the present system would predict that as the donor strength increased, the formal positive charge on tin would decrease and the tin–proton coupling constant would decrease. Effects other than formal charge must be operative. If one proposes that hybridization changes cause the formal charge tin manifests toward the methyl groups to increase as a result of the increasing s character in the tin–carbon bond while the total charge on tin decreases, the argument becomes equivalent to the hybridization arguments[13] and the problem becomes one of semantics.

In the adducts reported here, the trimethyltin halide must undergo extensive rehybridization upon coordination. In addition, the energy of the Sn–X bond may decrease as suggested by a lower tin–halide stretching frequency in the complex.[2] The measured enthalpy change, then, must be the sum of the following terms.

$$\Delta H° = \Delta H_{B-Sn} + H_{rehybrid} + \Delta H_{Sn-X} \qquad (4)$$

It is not unreasonable to expect a relationship between these terms. As the B–Sn interaction increases, a larger decrease in the tin–halogen bond energy and more extensive rehybridization would result. If this is a linear relationship, the measured enthalpy change should be related to the extent of reorganization about the tin atom, which may be evaluated by use of the dependence of $J_{Sn^{119}-CH_3}$ on the per cent s character in the tin–carbon bond. A plot of the value of $J_{Sn^{119}-CH_3}$ for the complex *vs.* $\Delta H°$ is given in Figure 1 and shows that indeed such a relationship exists. It is significant that the line drawn through the experimental points extrapolates to the $J_{Sn^{119}-CH_3}$ value measured for free trimethyltin chloride at $\Delta H° = 0$. This indicates that this linear relationship also exists for donors which are

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[11] It will be seen that this assumption does not affect the conclusions to be drawn. It is possible that some of the orbitals are used in bonding and part of the s orbital is empty. It is only necessary that the total amount of s orbital involved in bonding in the free $(CH_3)_3SnCl$ and the adducts remain approximately the same so the constant does not vary. These results give no measure of the amount of d-orbital participation, but, as will be seen, indicate it is constant in the carbon bonds in this series of compounds.

[12] D. M. Grant and W. M. Litchman, *J. Am. Chem. Soc.*, 87, 3994 (1965).

[13] (a) C. Juan and H. S. Gutowsky, *J. Chem. Phys.*, 30, 6 (1959); (b) R. S. Drago and N. A. Matwiyoff, *J. Organometal. Chem.* (Amsterdam), 3, 62 (1965).

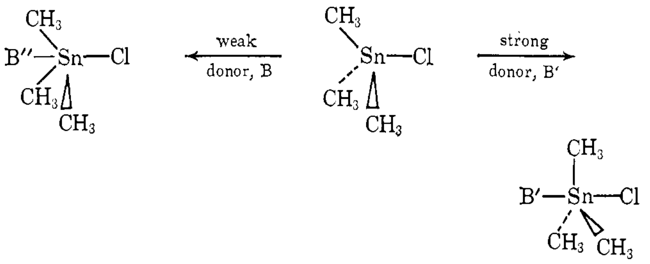
weaker than $CH_3C{\equiv}N$, the poorest donor for which the enthalpy of adduct formation has been measured.

The values listed for $J_{Sn^{119}\text{-}CH_3}$ in Table I therefore give a quantitative measure of the magnitude of the interaction between the base and trimethyltin chloride. It is evident that trimethyltin chloride interacts more strongly with oxygen or nitrogen donors than with sulfur or phosphorus donors, *e.g.*, $(C_2H_5)_2S < (C_2H_5)_2O$; DMTA < DMA; THMPA < HMPA; $(n\text{-}C_4H_9)_3P <$ pyridine. This result is in agreement with the conclusions previously drawn concerning the nature of the acidity of $(CH_3)_3SnCl$ on the basis of thermochemical measurements[7] and substantiates the interpretation of the trimethyltin chloride E_A and C_A parameters previously evaluated from the double-scale enthalpy equation. In this treatment,[14] the equation

$$-\Delta H_c = C_A C_B + E_A E_B \qquad (5)$$

indicates that the enthalpy of formation of the adduct will be equal to the empirically calculated enthalpy of formation, ΔH_c, within experimental error. In eq 5, C_A and E_A represent constants assigned to trimethyltin chloride and C_B and E_B represent constants assigned to the base. The C_A/E_A ratio for trimethyltin chloride is comparatively small (approximately the same as phenol). This indicates that trimethyltin chloride is a type A or relatively hard Lewis acid and therefore will react most strongly with oxygen or nitrogen donors.

A Proposed Model for Coordination. The relationship between $J_{Sn^{119}\text{-}CH_3}$ of the complex and the enthalpy of formation of the complex suggests the following model.



In this model, the magnitude of the distortion of the structure of $(CH_3)_3SnCl$ is dependent upon the strength of the B–Sn coordinate bond. A weak donor would give an adduct in which the CH_3-Sn-Cl angle is close to 109°. A strong donor would induce more extensive rehybridization of the tin and the structure of the adduct would be approximately trigonal bipyramidal. Consequently, it would be expected that, especially for weak complexes, a steric interaction between the methyl groups bonded to tin and the donor may exist. A steric interaction between the 2,6-pyridine protons and the tin methyl groups has been proposed[7] in this adduct on the basis of an anomaly in the *E* and *C* correlation. If steric interactions are present, the observed enthalpy of formation of the adduct should be much less than that calculated from eq 5 since the correlation is not valid for systems in which steric effects are present. The extension of this treatment to the adducts observed here is demonstrated in Table IV. The low $J_{Sn^{119}\text{-}CH_3}$ values measured for the adducts of $(C_2H_5)_2O$, $(C_2H_5)_2S$, and THF indicate that these bases are unexpectedly poor donors and/or have very low equilibrium constants. Consequently, the value of $\Delta H°$ evaluated from Figure 1 is much smaller than ΔH_c calculated from eq 5.

Table IV

Acid	*C*	*E*		
$(CH_3)_3$ SnCl	0.60	6.25		
Base	*C*	*E*	ΔH_c	$\Delta H°$
DMSO[a]	3.42	0.969	8.1	8.2
DMA[a]	3.00	1.00	8.0	7.9
Pyridine[a]	6.92	0.88	9.6	6.5
Acetone[a]	3.22	0.61	5.7	5.7, 6.0
DMTA[a]	9.06	0.064	5.8	5.7
$CH_3C{\equiv}N$[a]	1.77	0.533	4.4	4.8
THF	4.69	0.61	6.6	5.1[b]
$(C_2H_5)_2O$	3.55	0.654	6.2	2.2[b]
$(C_2H_5)_2S$	7.78	0.041	4.9	2.0[b]

[a] Reference 7. [b] Estimated from Figure 1.

These results are exactly those which would be predicted on the basis of this model since these adducts are the most likely to contain steric effects. If the methyl groups bonded to tin are completely planar in the $(C_2H_5)_2O$ and $(C_2H_5)_2S$ adducts, Shulman molecular models show very little chance of steric repulsion. However, if the methyl groups are bent toward the base to the degree indicated by the values of $J_{Sn^{119}\text{-}CH_3}$, serious steric problems arise and a reduced interaction would be expected. The steric interactions would be much smaller in the THF complex and, as a result, ΔH_c is in closer agreement with $\Delta H°$ in this case.

A model of the pyridine adduct suggests that steric repulsion is expected in the adduct, especially if the Cl–Sn–CH_3 angle is >90°. This effect would be enhanced if the protons were replaced by larger groups. From the low $J_{Sn^{119}\text{-}CH_3}$ value measured for $(CH_3)_3SnCl$ dissolved in 2,6-dimethylpyridine, it can be concluded that steric effects are indeed important. If steric interactions were not present, 2,6-dimethylpyridine should be a stronger, or at least as strong, a donor toward $(CH_3)_3$-SnCl as pyridine. However, an extremely low value of $J_{Sn^{119}\text{-}CH_3}$ and no change in the Sn–Cl stretching frequency is observed for solutions of trimethyltin chloride in 2,6-dimethylpyridine. These results indicate that very little, if any, interaction occurs and lend strong support to the proposed model. It may be concluded that both the steric requirements of the adduct and the nature of the basicity of the donor determine the magnitude of interaction between trimethyltin chloride and a Lewis base.

Finally, it should be pointed out that these studies further substantiate the interpretations of changes in the M–CH_3 coupling constant with solvent basicity which have been reported for several organothallium salts[15] as well as for a series of organolead compounds.[16] In both cases, it was proposed that an increasing $J_{M\text{-}CH_3}$ was indicative of an increasing solvent interaction with

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(14) R. S. Drago and B. B. Wayland, *J. Am. Chem. Soc.*, 87, 3571 (1965).

(15) G. D. Shier and R. S. Drago, *J. Organometal. Chem.* (Amsterdam), 5, 330 (1966).

(16) G. D. Shier and R. S. Drago, *ibid.*, in press.

the metal ion. The order of donor strength which was proposed toward the organothallium and organolead compounds is observed in these studies of the similar acid trimethyltin chloride, *i.e.*, HMPA > DMA = DMSO > $(CH_3)_2CO$ > CH_3CN. It should be very interesting if it were shown that a quantitative relationship exists between the enthalpy of formation of these adducts and the spin-spin coupling constant. It is possible that coupling constant changes may be a very valuable tool for the evaluation of the enthalpy of adduct formation of a large number of heavy metal adducts.

$(CH_3)_3SnI \cdot DMA$. Trimethyltin iodide is a better acid toward DMA than is trimethyltin chloride. Since $J_{Sn^{119}-CH_3}$ is approximately the same for both of these adducts, it is reasonable that the rehybridization energy is similar in both cases. The larger observed enthalpy of formation of the iodide adduct may arise from differences in the magnitude of the ΔH_{Sn-X} term in eq 4. This may be due to a reduced sensitivity of the tin-halogen bond energy to changes in hybridization of the tin as the size of the halogen increases or to the fact that the Sn–I bond is originally much weaker than the Sn–Cl bond.

Acknowledgment. The authors acknowledge the generous support of the National Science Foundation through Grant GP −5498.

Nucleophilic Reactivity in Substitution Reactions of Square-Planar Metal Complexes. I. Effect of the Total Charge of the Substrate in Platinum(II) Complexes

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Abstract: The behavior of a series of platinum(II) complexes in their displacement reactions with a range of nucleophiles is discussed. The relative index of nucleophilicity, n_{Pt}, defined for the standard substrate *trans*-$[Pt(py)_2Cl_2]$, can also apply to the other compounds examined, except for the reactions with NO_2^-, $SeCN^-$, and thiourea. These reagents have decided biphilic behavior and their relative reactivity is markedly affected by the charge and nature of the substrate.

The rates of bimolecular nucleophilic substitution reactions are determined by several factors, relative to the nature of the substrate and reagent and to the conditions (solvent, temperature, etc.).[1] By measuring, under the same experimental conditions, the rate of displacement of the ligand X from a substrate M–X by various reagents Y, a quantitative sequence of relative reactivity can be obtained. In view of the number of variables that can affect the nucleophilicity it is desirable to limit the range of nucleophiles studied in order to eliminate certain structural factors such as steric hindrance and α effects. Following Pearson's classification of soft and hard acids and bases,[2] it appears that, in substitution reactions at soft reaction centers, the micropolarizability or "softness" of Y is the most important factor in determining nucleophilicity, whereas the basicity of Y plays only a minor role. Unfortunately, from a practical point of view, "softness" is not a property that can be quantitatively measured by a direct physical experiment. In fact, the polarizability of Y in a strong directional field (such as encountered in a transition state) is different, in principle, from its polarizability in a homogeneous weak field, which is the quantity that is usually determined experimentally. In kinetic studies, the word "softness" can be interpreted as the factor, or combination of factors, that is responsible for departures from a simple relationship between the nucleophilicity and the basicity of the entering reagent. In addition, when the substrate M–X is a transition metal complex, one must also consider the possible influence of π interactions between the substrate and the entering group in either the ground or transition states upon the nucleophilicity.

Platinum(II) square-planar complexes are typical soft reaction centers in which it is now generally accepted that nucleophilic displacement reactions occur with an associative mechanism.[3] An extensive study of the kinetic behavior of substrates of the type *trans*-$[PtL_2Cl_2]$ have been recently made[4] and, by selecting as a standard the complex with L = pyridine, an index of nucleophilicity, "n_{Pt}," has been defined for each nucleophile Y. The reactions of these reagents toward the other platinum(II) complexes studied, followed the equation

$$\log k_Y = s(n_{Pt}) + \log k_S \qquad (1)$$

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[1] J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, **84**, 16 (1962).

[2] R. G. Pearson, *ibid.*, **85**, 3533 (1963).

[3] C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1965, pp 19–54.

[4] U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *J. Am. Chem. Soc.*, **87**, 241 (1965).