Lewis Acidities of Trimethylchlorosilane, -germane, and -stannane

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The Lewis acidities of $(CH_3)_3MCl$ (M = C, Si, Ge, Sn) relative to triphenylphosphine oxide, Me_2SO, and pyridine in benzene solvent were determined calorimetrically. Enthalpies and equilibrium constants for adduct formation show that the tin derivative is a stronger Lewis acid than the germanium derivative which has essentially no Lewis acidity. Heats of reaction for the silane were not initially reproducible, presumably due to hydrolysis of the silane. After the application of rigorously anhydrous conditions, the chlorosilane exhibited Lewis behavior similar to the germane. Thus, the previously reported acidity of trimethylchlorosilane can be attributed to hydrolysis and the conventional acidity order Sn > Ge > Si is retained. These results were confirmed by concentration analysis of the ^{31}P chemical shift of triphenylphosphine oxide in mixtures with each Lewis acid.

Introduction

Although the Lewis acidities of the group 14 tetrahalides have been the subject of study by a variety of techniques,[1,11] the simplest group 14 Lewis acids, the monochloride system, have received little attention because of their weak Lewis acidity. Recent investigations[2,3] have concluded that trimethylchlorosilane is a stronger acid than trimethylchlorostannane, a conclusion that is in opposition to the order Sn > Ge > Si obtained in studies of most other systems.[1] Graddon and Rana[2,3] reported the formation of 1:1 adducts between trimethylchlorosilane and several bases in acetonitrile with equilibrium constants greater than 10^6 and enthalpy changes about 13 kcal/mol of complex. Zeldin et al.[4] calculated an equilibrium constant of 60 ± 5 for the 1:1 complex formed between trimethylchlorosilane and triphenylphosphine oxide. On the other hand, an early study by Beattie and Leigh[5] indicated no evidence for adduct formation between trimethylchlorosilane and pyridine or trimethylamine. We have reexamined the trimethylchloro derivatives using two independent techniques—calorimetry and ^{31}P NMR—under strictly anhydrous conditions with three bases and three solvents.

Experimental Section

ACS reagent grade benzene and cyclohexane were refluxed over P_2O_5 and then distilled over nitrogen or argon and stored over activated Linde type 4A molecular sieves. ACS reagent grade Me_2SO was dried over $CaCl_2$ for 24 h and then fractionally distilled under reduced pressure and collected over activated molecular sieves. Fisher Scientific gold label pyridine was refluxed over KOH for several hours, distilled under nitrogen, and collected over activated molecular sieves. Aldrich reagent grade quinuclidine was sublimed under reduced pressure and stored in vacuo. Aldrich reagent grade TPPO was dried at 110 °C for 24 h and stored in vacuo (mp 156–157 °C). Petrarch trimethylchlorosilane was used as received and was also purified by fractional distillation, by stirring over anhydrous sodium carbonate under reduced pressure followed by fractional distillation, and by stirring over sodium carbonate/drierite under argon followed by fractional distillation under argon. Trimethylchlorogermane was prepared by the method of Mironov and Kravchenko[6] and fractionally distilled (bp 98–100 °C), $n_D^{25} = 1.4288$. Alfa Products trimethylchlorostannane was sublimed under reduced pressure and stored in vacuo. Petrarch triphenylchlorosilane (91–92 °C) was dried in vacuo.

Table I. Enthalpies and Equilibrium Constants for Adduct Formation (298 K) by $(CH_3)_3SnCl$

solv	base	$-\Delta H$, kcal mol^{-1}	K
C_6H_6	Me_2SO	7.7[b]	8.1[b]
		7.7 ± 0.4[a]	8.1 ± 0.9[a]
C_6H_6	quinuclidine	9.5[b]	15[b]
		9.4 ± 0.6[a]	15 ± 3[a]
C_6H_6	$(Ph)_3PO$	8.0[b]	21[b]
		8.0 ± 0.3[a]	21 ± 3[a]
C_6H_{12}	pyridine	11.0[b]	1.4[b]
		11.0 ± 1.0[a]	1.3 ± 0.1[a]
PB[e]	Me_2SO	9.3[c]	
PB	pyridine	9.7[c]	
PB	pyridine	9.8[d]	

[a] Determined by the Bolles–Drago method. [b] Determined by least-squares analysis. [c] Model compound is $(CH_3)_3CCl$. [d] Model compound is $(CH_3)_3GeCl$. [e] Pure base.

All reagents and solvents were handled in a glovebag or drybox under argon. Glassware was oven-dried at 110 °C and cooled either in a vacuum desiccator or in a glovebag.

All calorimetric analysis was done with a Model 450 Tronac calorimeter with ampule assembly and 25-mL reaction vessel. Ampules were oven-dried for at least 24 h, filled and capped in a glovebag, and then heat sealed.

The base concentrations varied from 0.1 to 0.9 M while the acid concentrations ranged from 0.004 to 0.04 M.

Three methods of analysis of the calorimetric data for complex formation were used. The Bolles–Drago method[7] uses the heat change, Q, corrected for the heat of solution of the acid, the initial concentrations of acid and base, C_0^A and C_0^B, and the volume, V, of the solvent in eq 1. Q is obtained for several different acid

$$K^{-1} = \frac{Q}{\Delta H V} + \frac{C_0^A C_0^B \Delta H V}{Q} - (C_0^A - C_0^B) \qquad (1)$$

and base concentrations. Arbitrary values of ΔH are chosen, and K^{-1} is plotted vs. the assumed ΔH, and a curve is obtained for each set on concentrations; the intersections of these curves give graphical solutions to the simultaneous equations.

The second method uses a least-squares technique for data anlaysis.[8] In general, the heat change for n reactions in the reaction vessel can be given by

$$Q = \sum_{i=1}^{h} n_{i},p \Delta H_i \qquad (2)$$

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Table II. Enthalpies of Solution (kcal mol^{-1}, 298 K)

	C_6H_{12}	pyridine	Me_2SO	C_6H_6
$(CH_3)_3SnCl$	5.94 ± 0.42	−4.40 ± 0.05	−2.83 ± 0.08	4.42 ± 0.20
$(CH_3)_3GeCl$	1.15 ± 0.06	−0.96 ± 0.22		0.30 ± 0.02
$(CH_3)_3SiCl$	0.63 ± 0.02			0.38 ± 0.03
$(CH_3)_3CCl$	0.61 ± 0.12	0.28 ± 0.05	1.09 ± 0.07	0.21 ± 0.08

Table III. Transfer Enthalpies (kcal mol^{-1}, 298 K)

	$C_6H_{12} \rightarrow C_6H_6$	$C_6H_{12} \rightarrow$ pyridine
$(CH_3)_3CCl$	−0.40 ± 0.14	−0.33 ± 0.13
$(CH_3)_3SiCl$	−0.25 ± 0.04	
$(CH_3)_3GeCl$	−0.85 ± 0.06	−2.11 ± 0.22
$(CH_3)_3SnCl$	−1.52 ± 0.21	−9.98 ± 0.42

where n_i,p is the number of moles of product i and is a function of the equilibrium constant for reaction i. The best values of K and ΔH are calculated by a least-squares analysis of eq 2. The error square sum over the m data *points* is given by

$$U(K_i,\Delta H_i) = \sum_{p=1}^{m} (Q_p - \sum_{i=1}^{n} (n_i,p\Delta H_i))^2$$

where the subscript p is over all data points and i is over all reactions. The best values for K and ΔH for a given determination are those which minimize $U(K_i,\Delta H_i)$.

The third method follows the pure base calorimetric procedure.[9] For this method a model compound, as similar as possible to the acid but incapable of the heat-producing acid–base interaction, must be used. The method then requires the determination of the enthalpies of solution of the compound of interest and its model in a pure base and a reference solvent. The enthalpy change for complex formation, ΔH is calculated from

$$\Delta H = (\bar{\Delta}H_{s_{acid}} - \bar{\Delta}H_{s_{model}})_{base} - (\bar{\Delta}H_{s_{acid}} - \bar{\Delta}H_{s_{model}})_{ref}$$

where ΔH_s is the enthalpy of solution.

Phosphorus-31 spectra were obtained on a Bruker WP-250 at 25 °C in 10-mm tubes. Stock solutions of acid and base, both 0.2 M in benzene containing about 10% deuteriobenzene, were prepared and then mixed equally by volume in a 10-mL volumetric flask. A 5-mL aliquot was in turn diluted to 10 mL, and this was repeated until six solutions, ranging in concentrations from 0.1 to 0.001 M were prepared. The equilibrium constant for formation of a 1:1 adduct can be obtained from the exchange-averaged chemical shift of some nucleus using the equation[4]

$$K = \Delta/(\Delta_c - \Delta)[C_0^B] - \Delta[C_0^A]/\Delta_c$$

where Δ is the difference between the chemical shift of the solution and that of the base, Δ_c is the difference between the chemical shift of the adduct and the free base, and $[C_0^A]$ and $[C_0^B]$ are the initial concentration of the acid and base. When the initial concentrations are the same the equation becomes

$$\Delta = \Delta_c - (\Delta_c/K)^{1/2}(\Delta_c/C_0)^{1/2}$$

where $[C_0^A] = [C_0^B] = [C_0]$. The equilibrium constant is obtained from the slope of a plot of Δ vs. $(\Delta/C_0)^{1/2}$.

Results and Discussion

Calorimetric Data. Enthalpies and equilibrium constants for the formation of adducts with trimethylchlorostannane are given in Table I. Enthalpies of solutions for all the group 14 halides appear in Table II; transfer enthalpies are given in Table III. The transfer from cyclohexane to benzene becomes more exothermic as the group is descended, a trend that is most likely due to an increasingly strong acid–base interaction between the group 14 atom and benzene. The same trend occurs for transfer to pyridine. The large transfer enthalpy for trimethylchlorostannane is principally due to adduct formation with pyridine. It was not possible to determine the enthalpy of solution of trimethylchlorosilane in pyridine due to the formation of a precipitate.

The enthalpy of solution of trimethylchlorogermane in solutions of triphenylphosphine oxide (TPPO) in benzene (0.22 ± 0.02 kcal mol^{-1}) was nearly the same as the enthalpy of solution in neat benzene (0.30 ± 0.03 kcal mol^{-1}). Likewise, no appreciable heat was detected when trimethylchlorogermane was injected into solutions of Me_2SO in cyclohexane solvent. The interaction of trimethylchlorogermane with pyridine and dimethylacetamide in benzene and cyclohexane solvents produced small quantities of heat, but no matter what the system it appears that the enthalpy change and equilibrium constant for the germanium derivative are very small. Graddon and Rana report that they find no Lewis acidity for chlorogermane[1]0,11 triphenylchlorogermane.[10]

Also given in Table I are enthalpies for the formation of adducts between trimethylchlorostannane and Me_2SO and pyridine as determined by the pure base method.[9] A suitable model compound for trimethylchlorostannane should be trimethylchloromethane. In pyridine solvent the pure base enthalpy for the $(CH_3)_3SnCl$–pyridine adduct is −9.7 kcal mol when $(CH_3)_3CCl$ is the model compound. If $(CH_3)_3GeCl$ interacts only weakly with pyridine, $(CH_3)_3GeCl$ should also be an appropriate model compound for trimethylchlorostannane. The pure base enthalpy value of −9.8 kcal/mol for the $(CH_3)_3SnCl$–pyridine adduct using $(CH_3)_3GeCl$ as the model compound is further evidence that the germanium derivative is a very weak Lewis acid.

When unpurified trimethylchlorosilane was used as the Lewis acid, the heats of reaction were very large and not reproducible. When the chlorosilane was treated with anhydrous sodium carbonate and calcium sulfate and then distilled over nitrogen, the heat decreased but varied somewhat from run to run. With pyridine as the base, the smallest amount of heat was observed with fresh trimethylchlorosilane (99%, distilled and stored over argon, Petrarch Chemical Co.) but still varied from one run to another. With the assumption that adduct formation is essentially complete, the enthalpy change ranged from 3 to a few tenths of a kilocalorie per mole of adduct.

It is likely that the erratic behavior of trimethylchlorosilane is due to hydrolysis, a reaction both thermodynamically and kinetically favorable for chlorosilanes. This reaction with atmospheric moisture produces hexamethyldisiloxane and HCl, some of which remains dissolved in the silane. Very careful distillation under nitrogen or argon using only a center fraction suffices to produce pure compound. The amount of HCl actually in the calorimeter at the time of the experiment depends upon purification of the silane, the base, and the solvent, the care taken in preparing the solutions, loading the calorimeter, etc. The major factor, however, seems to be the initial purity of the chlorosilane.

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(11) The group notation is being changed in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is being eliminated because of wide confusion. Group I becomes groups 1 and 11, group II becomes groups 2 and 12, group III becomes groups 3 and 13, etc.

Because of the hydrolytic instability of trimethylchlorosilane, triphenylchlorosilane was used in a series of experiments. This compound is less sensitive to hydrolysis than trimethylchlorosilane and is reported[2,3] to be a slightly stronger acid. When triphenylchlorosilane was injected into a TPPO–benzene solution, very little heat was detected. If the equilibrium constant for the complex is as large as that reported by Graddon and Rana[2,3] for similar systems, the enthalpy change for complexation may be calculated to be about 0.3 kcal/mol.

The reproducible results obtained for triphenylchlorosilane suggests that there may be some interaction which generates heat for both the silicon and germanium derivatives. However, the quantiy of heat suggests that either the equilibrium constants are very small and/or that the complexation enthalpy is very small.

Thus, the large heats reported by Graddon and Rana, and attributed by them to interaction of the base at the chlorine of the chlorosilane, are almost certainly due to hydrolysis. If, as Graddon and Rana report, the equilibrium constant for the reaction of trimethylchlorosilane with pyridine in acetonitrile is greater than 10^6, the enthalpy change must be much less than the 13.3 kcal/mol reported (the equilibrium constant in cyclohexane should be even greater than in acetonitrile). Likewise, if the enthalpy of Graddon and Rana is correct, the equilibrium constant must be small (<20). On the basis of the present results it appears that there is little or no interaction between trimethylchlorosilane and bases such as pyridine.

NMR Spectroscopy. Complexation frequently alters the chemical shifts of NMR-active nuclei at the active sites of the acid and base. Zeldin, Mehta, and Vernon[4] have used the change in ^{31}P chemical shift of triphenylphosphine oxide to monitor the Lewis acidity of some group 14 halides. In our laboratory this procedure allowed the calculation of a value of 20 for the equilibrium constant for the interaction of trimethylchlorostannane with triphenylphosphine oxide in benzene. This value is in excellent agreement with that obtained calorimetrically (Table I) but different from the value of 100 ± 5 obtained by Zeldin, et al.[4] Trimethylchlorogermane produced no change in the ^{31}P shift of TPPO, in agreement with the calorimetric data that indicated a small or zero enthalpy change. The values obtained for trimethylchlorosilane were not reproducible (HCl should protonate TPPO and lead to a change in the ^{31}P shift).

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Registry No. $(CH_3)_3SnCl$, 1066-45-1; $(CH_3)_3GeCl$, 1529-47-1; $(CH_3)_3SiCl$, 75-77-4; $(CH_3)_3CCl$, 507-20-0.

Tricarbonylbis(trichlorosilyl)nickel. An Unusual Carbonyl Complex of Nickel(II)

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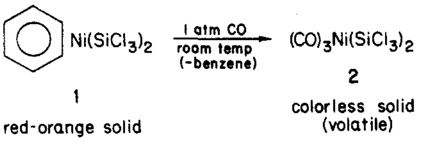
Displacement of η^6-arene by carbon monoxide in (η^6-benzene)bis(trichlorosilyl)nickel yields an unusual tricarbonyl derivative of nickel(II). The compound crystallizes with four molecules of $(SiCl_3)_2Ni(CO)_3$ per unit cell in space group $P2_1/c$ with lattice constants of a = 9.709 (8) Å, b = 22.65 (2) Å, c = 6.731 (5) Å, and β = 75.76 (5)°. The structure was determined from 1219 diffractometer data and refined to an R value of 5.9%. The molecular geometry is a slightly distorted trigonal bipyramid with three CO ligands in the equatorial plane and two trichlorosilyl ligands in the axial positions.

Introduction

Recently we reported that the facile displacement of η^6-arene by CO in $(\eta^6\text{-}C_6H_6)Ni(SiCl_3)_2$ (1) yielded an unusual carbonyl derivative of Ni(II).[2] The product 2 possesses very labile CO ligands and can be converted quantitatively back to 1 in excess benzene. This appears to be the first example of such reversible CO ⇄ arene complexation under such mild conditions.



Complete characterization of 2 has been difficult due to its reactivity, and some confusion as to whether two or three carbonyl groups were attached in the solid state persisted until we were able to grow suitable crystals for X-ray structural elucidation. The unusual nature of 2 and the need to clarify its structure and bonding prompted us to determining the structure of this compound.

Experimental Section

Crystals were obtained by subliming the compound at room temperature in a vacuum sealed Pyrex tube. A colorless crystal of the compound with dimensions 1.00 × 0.40 × 0.33 mm was wedged in a thin-walled glass capillary under an argon atmosphere in a specially modified inert-atmosphere chamber. Preliminary Weisenberg and precession photographs led to the determination

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