

- (12) T. Matsubara and P. C. Ford, *Inorg. Chem.*, **15**, 1107 (1976).
 (13) R. E. Connick, "Advances in the Chemistry of Coordination Compounds", Macmillan, New York, 1961, p 15.
 (14) J. A. Broomhead, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, **3**, 826 (1964).
 (15) J. A. Broomhead and L. Kane-Maguire, *Inorg. Chem.*, **7**, 2519 (1968).
 (16) P. C. Ford, *Coord. Chem. Rev.*, **5**, 75 (1970).
 (17) J. A. Broomhead and L. Kane-Maguire, *Inorg. Chem.*, **10**, 85 (1971).
 (18) H. Taube, *Surv. Progr. Chem.*, **6**, 1 (1973).
 (19) C.-K. Poon and D. A. Isabirye, *J. Chem. Soc.*, 2115 (1977).
 (20) N. Sutin and J. K. Yandell, *J. Biol. Chem.*, **247**, 6932 (1972).
 (21) B. S. Brunshwig and N. Sutin, *Inorg. Chem.*, **15**, 631 (1976).
 (22) G. M. Brown and W. D. K. Clark, personal communication.
 (23) Data for L = acetonitrile, pyrazine, and isonicotinamide are presented in Table SI (supplementary material).
 (24) F. L. Garvan in "Chelating Agents and Metal Chelates", F. P. Dwyer and D. P. Mellor, Eds., Academic Press, New York, 1964, p 283.
 (25) R. N. F. Thorneley and A. G. Sykes, *J. Chem. Soc. A*, 742 (1969).
 (26) R. N. F. Thorneley, A. G. Sykes, and P. Gauss, *J. Chem. Soc. A*, 1494 (1971).
 (27) R. E. Hamm, *J. Am. Chem. Soc.*, **75**, 5670 (1953).
 (28) F. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.*, **82**, 4823 (1960).
 (29) H. A. Weakliem and J. L. Hoard, *J. Am. Chem. Soc.*, **81**, 549 (1959).
 (30) J. L. Hoard, M. Lind, and J. V. Silverton, *J. Am. Chem. Soc.*, **83**, 2770 (1961).
 (31) G. Navon and N. Sutin, *Inorg. Chem.*, **13**, 2159 (1974).
 (32) T. W. Kallen and J. E. Earley, *Inorg. Chem.*, **10**, 1149 (1971).
 (33) E. E. Mercer and R. R. Buckley, *Inorg. Chem.*, **4**, 1692 (1965).
 (34) (a) T. R. Bhat, D. Radhamma, and J. Shankar, *J. Inorg. Nucl. Chem.*, **25**, 1147 (1963); (b) *ibid.*, **27**, 2641 (1965).
 (35) H. E. Toma and J. M. Malin, *J. Am. Chem. Soc.*, **94**, 4039 (1972).
 (36) H. E. Toma and J. M. Malin, *Inorg. Chem.*, **12**, 1039 (1973).
 (37) H. E. Toma and C. Creutz, *Inorg. Chem.*, **16**, 545 (1977).
 (38) R. Magnuson and H. Taube, *J. Am. Chem. Soc.*, **97**, 5129 (1975).
 (39) J. A. Broomhead, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, **3**, 826 (1964).
 (40) T. Matsubara, unpublished results.
 (41) An exception is provided by the reaction of $\text{Ru}(\text{NH}_3)_6^{3+}$ with nitric oxide, for which a rate constant of $2 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$ has been reported at 25 °C: J. N. Armor, H. A. Scheidegger, and H. Taube, *J. Am. Chem. Soc.*, **90**, 5928 (1968). This substitution reaction appears, however, to be electrophilic, rather than nucleophilic, in character.
 (42) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2nd ed., Wiley, New York, 1967, p 124 ff.
 (43) T. W. Swaddle, *Coord. Chem. Rev.*, **14**, 217 (1974).
 (44) H. Ogino, T. Watanabe, and N. Tanaka, *Inorg. Chem.*, **44**, 2093 (1975).
 (45) Y. Sulfab, R. S. Taylor, and A. G. Sykes, *Inorg. Chem.*, **15**, 2388 (1976).
 (46) The exception is provided by the work of D. W. Franco and H. Taube, *Inorg. Chem.*, **17**, 571 (1978).
 (47) C. Creutz and H. Taube, *Inorg. Chem.*, **10**, 2664 (1971).
 (48) R. E. Shepherd and H. Taube, *Inorg. Chem.*, **12**, 1392 (1973).
 (49) S. S. Isied and H. Taube, *Inorg. Chem.*, **15**, 3070 (1976).

Contribution from the Department of Chemistry,
 State University of New York at Buffalo, Buffalo, New York 14214

Preparation and Properties of ((Trimethylsilyl)methyl)indium(III) Compounds

O. T. BEACHLEY, JR.,* and R. N. RUSINKO

Received December 8, 1978

A series of organoindium compounds which incorporate the (trimethylsilyl)methyl ligand, $\text{In}(\text{CH}_2\text{SiMe}_3)_x\text{Cl}_{3-x}$ ($x = 1, 2, 3$), have been prepared and fully characterized by elemental analyses, NMR and IR spectroscopy, molecular weight data, solubility properties, Lewis acid-base studies, and hydrolysis experiments. The parent compound $\text{In}(\text{CH}_2\text{SiMe}_3)_3$ was prepared from InCl_3 by a standard Grignard reaction in diethyl ether solution. All data confirm that $\text{In}(\text{CH}_2\text{SiMe}_3)_3$, a liquid at room temperature, exists as a monomeric three-coordinate species. The ((trimethylsilyl)methyl)indium-chlorine compounds were prepared from $\text{In}(\text{CH}_2\text{SiMe}_3)_3$ by means of an exchange reaction with InCl_3 or an elimination reaction with HCl. All properties of $[\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}]_2$ and $[\text{In}(\text{CH}_2\text{SiMe}_3)\text{Cl}_2]_2$, crystalline solids at room temperature, are consistent with chlorine-bridged dimeric structures. The available data suggest that the chlorine-bridged dimer of $[\text{In}(\text{CH}_2\text{SiMe}_3)\text{Cl}_2]_2$ probably has extensive association in the solid state. The Lewis acid-base and hydrolysis studies suggest that the bulky (trimethylsilyl)methyl ligand does not substantially alter the behavior of the indium derivatives when compared to other analogous organoindium compounds.

Introduction

Organometallic compounds which incorporate the (trimethylsilyl)methyl ligand are of interest because of their unusual chemical properties.¹ A characteristic property of this class of compounds is their enhanced thermal stability when compared with methyl or ethyl analogues. Even though this bulky ligand has produced some transition-metal derivatives with unusual coordination numbers, many compounds are normal. Tris((trimethylsilyl)methyl)aluminum,² $\text{Al}(\text{CH}_2\text{SiMe}_3)_3$, exists as the expected mixture of monomeric and dimeric species in benzene solution. All attempts to prepare the corresponding gallium compound² were surprisingly unsuccessful. Some compounds of the group 4 elements, germanium, tin, and lead, with the bis(trimethylsilyl)methylene ligand, $-\text{CH}(\text{SiMe}_3)_2$, have been investigated.^{3,4} The tin(II) compound exists as a dimer in the crystalline state³ and has an extensive chemistry,⁴ (i) behaving as a Lewis base, (ii) behaving as a Lewis acid, and (iii) undergoing oxidative addition reactions. Unusual radicals of the general formula, $\cdot\text{M}[\text{CH}(\text{SiMe}_3)_2]_3$ ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}$), have also been prepared and characterized.⁵

In this paper we report the syntheses and complete characterization of some (trimethylsilyl)methyl derivatives of indium(III) including $\text{In}(\text{CH}_2\text{SiMe}_3)_3$, $\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}$, and

$\text{In}(\text{CH}_2\text{SiMe}_3)\text{Cl}_2$. The goal of this research was to determine whether the CH_2SiMe_3 ligand introduced any unusual or unexpected chemical properties in indium(III) chemistry.

Experimental Section

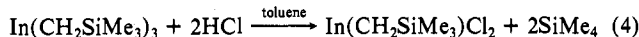
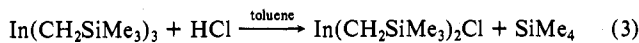
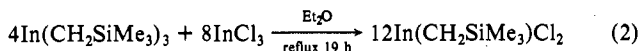
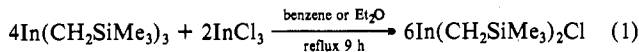
All compounds described in this investigation were manipulated in a vacuum line or a purified nitrogen or argon atmosphere. The solvents and reagents were purified by conventional means. New compounds were analyzed for indium by EDTA titration.⁶ Chlorine was determined by standard gravimetric procedures.

Preparation of $\text{In}(\text{CH}_2\text{SiMe}_3)_3$. The compound $\text{In}(\text{CH}_2\text{SiMe}_3)_3$ was prepared from InCl_3 and the Grignard reagent $\text{Me}_3\text{SiCH}_2\text{MgCl}$ in diethyl ether solution.⁷ An argon-purged flask, charged with 5.62 g (25.4 mmol) of InCl_3 and 50 mL of ether, was equipped with a mechanical stirrer, condenser, dropping funnel, and inert-gas bubbler. Then, the previously prepared and standardized Grignard reagent (65 mL, 1.24 M) in ether solution was slowly added to the InCl_3 over a period of 1 h. After addition was complete, the white pasty mixture was refluxed for 3 h. Diethyl ether was removed by vacuum distillation. The product, $\text{In}(\text{CH}_2\text{SiMe}_3)_3$, a liquid at room temperature, was then distilled from the reaction flask at 110 °C under high vacuum. The yield of $\text{In}(\text{CH}_2\text{SiMe}_3)_3$ was 7.78 g (81.5%) based on InCl_3 . Anal. Calcd for $\text{In}(\text{CH}_2\text{SiMe}_3)_3$: In, 30.5. Found: In, 30.4.

Preparative reactions for $\text{In}(\text{CH}_2\text{SiMe}_3)_3$ with InBr_3 in diethyl ether or tetrahydrofuran lead to impure products or an adduct, $\text{In}(\text{CH}_2\text{SiMe}_3)_3 \cdot \text{THF}$. It was not possible to remove the THF from $\text{In}(\text{CH}_2\text{SiMe}_3)_3$ quantitatively. Typical solvents for $\text{In}(\text{CH}_2\text{SiMe}_3)_3$

include *n*-pentane, benzene, methylene chloride, acetonitrile, and diethyl ether.

Preparation of $\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}$ and $\text{In}(\text{CH}_2\text{SiMe}_3)\text{Cl}_2$. The chloro derivatives were prepared by either an exchange reaction between $\text{In}(\text{CH}_2\text{SiMe}_3)_3$ and InCl_3 (eq 1 and 2) or an elimination reaction between $\text{In}(\text{CH}_2\text{SiMe}_3)_3$ and HCl (eq 3 and 4). Different stoi-



chiometries were required for the different products. All four reactions went to completion and were apparently quantitative. The product, $\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}$, a white crystalline solid, was purified by vacuum sublimation at 90 °C and had a melting point of 88–91 °C. Typical solvents for $\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}$ include *n*-pentane, benzene, methylene chloride, acetonitrile, and diethyl ether. Anal. Calcd for $\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}$: In, 35.4; Cl, 10.9. Found: In, 35.5; Cl, 11.2.

The compound $\text{In}(\text{CH}_2\text{SiMe}_3)\text{Cl}_2$, a white crystalline solid, was purified by vacuum sublimation at 150 °C and had a melting point of 167–170 °C. Solvents include diethyl ether and acetonitrile. The compound has very limited solubility in benzene and methylene chloride. Anal. Calcd for $\text{In}(\text{CH}_2\text{SiMe}_3)\text{Cl}_2$: In, 42.1; Cl, 26.0. Found: In, 42.6; Cl, 25.9.

Molecular Weight Studies. Molecular weight measurements were obtained cryoscopically in benzene with an instrument similar to that described by Shriver.⁸ The following molecular weight data were observed. $\text{In}(\text{CH}_2\text{SiMe}_3)_3$ (mol wt 376) calcd molality of monomer (obsd mol wt): 0.0836 (417), 0.0612 (410), 0.0454 (400). $\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}$ (mol wt 325): 0.0780 (659), 0.0605 (647). $\text{In}(\text{CH}_2\text{SiMe}_3)\text{Cl}_2$: insufficient solubility in benzene for molecular weight measurements.

Infrared Spectra. The infrared spectra were recorded in the range 4000–250 cm^{-1} by means of a Perkin-Elmer Model 457 spectrometer. The spectra were recorded as neat liquids or as Nujol mulls by using CsI plates. Absorption intensities were measured by using the method of Durkin, Glone, and DeHayes.⁹

The following are the spectral data [frequency, cm^{-1} (intensity: s, strong; m, medium; w, weak; sh, shoulder)]. Bands due to the mulling agents have been omitted.

$\text{In}(\text{CH}_2\text{SiMe}_3)_3$ (neat liquid): 2935 (vs), 2885 (s, sh), 1440 (w), 1400 (w), 1350 (w), 1291 (w, sh), 1244 (vs), 920 (s), 825 (vs), 757 (vs), 720 (vs), 692 (s, sh), 580 (m), 490 (m).

$\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}$ (Nujol mull): 1248 (vs), 946 (s), 825 (vs), 757 (vs), 720 (s), 693 (m, sh), 573 (m), 518 (w, sh), 477 (m), 360 (w).

$\text{In}(\text{CH}_2\text{SiMe}_3)\text{Cl}_2$ (Nujol mull): 1305 (w, sh), 1255 (vs), 1008 (s), 825 (vs), 775 (s), 763 (s, sh), 725 (s), 697 (m, sh), 595 (m), 512 (m), 308 (m, sh), 265 (m).

Nuclear Magnetic Resonance Spectra. The ^1H NMR spectra were recorded at 100 MHz and ambient temperature with a Jeolco Model MH-100 spectrometer. All chemical shifts are given in ppm and are referenced to tetramethylsilane as 10.00 ppm. The following chemical shifts (τ) were observed in CH_2Cl_2 solution: $\text{In}(\text{CH}_2\text{SiMe}_3)_3$ 9.98 (CH_2), 9.88 (Me_3); $\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}$ 9.67 (CH_2), 9.82 (Me_3); $\text{In}(\text{CH}_2\text{SiMe}_3)\text{Cl}_2$ 9.77 (CH_2), 9.84 (Me_3).

Lewis Acidity Studies. The Lewis acidity of the ((trimethylsilyl)methyl)indium compounds was determined by reacting a stoichiometric quantity of the desired acid with excess base ($\text{N}(\text{CH}_3)_3$, CH_3CN , diethyl ether, tetrahydrofuran, and dimethoxyethane). After the reaction mixture was warmed to room temperature, the volatile components were removed by pumping on the sample for 4 h. If a stoichiometric quantity of base was retained by the acid, the stable adduct was characterized by its melting point and NMR spectrum. In those cases in which a nonstoichiometric quantity of base remained, the product was not further characterized. The only stable 1:1 adduct isolated was $(\text{Me}_3\text{SiCH}_2)_3\text{InN}(\text{CH}_3)_3$, mp 78–81 °C. NMR spectrum (benzene solution): τ 10.31 (CH_2), 9.54 (SiMe), 8.06 (NCH_3). Dissociation pressures of base from an adduct were observed at room temperature for the following acid–base pairs: $\text{In}(\text{CH}_2\text{SiMe}_3)_3$ –THF and –dimethoxyethane; $\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}$ – $\text{N}(\text{CH}_3)_3$; $\text{In}(\text{CH}_2\text{SiMe}_3)\text{Cl}_2$ – $\text{N}(\text{CH}_3)_3$, –THF, –dimethoxyethane, and –diethyl ether. No acid–base interaction was observed for any other pair.

Hydrolysis Studies. The extent and relative rate of hydrolysis of the three organoindium compounds was studied. The hydrolysis of $\text{In}(\text{CH}_2\text{SiMe}_3)_3$ with water was followed quantitatively over a period of 12 days. Degassed water (5.0 mL) was vacuum distilled onto 0.171 g (0.456 mmol) of $\text{In}(\text{CH}_2\text{SiMe}_3)_3$. When the mixture was warmed to room temperature, two immiscible liquids were initially observed. Gradually a white solid formed, which persisted throughout the experiment. The tetramethylsilane (Me_4Si) generated during hydrolysis was removed on the vacuum line by fractional distillation and was measured. The following amounts of Me_4Si were observed (time, mol of Me_4Si /mol of $\text{In}(\text{CH}_2\text{SiMe}_3)_3$): 1 h, 0.570; 3 days, 1.38; 5 days, 1.83; 9 days, 2.02; 12 days, 2.04. The organoindium product from the 12-day hydrolysis had the following ^1H NMR spectrum in CDCl_3 solution: τ 2.65 (OH), 8.42 (SiMe_3), 8.69 (SiCH_2). The stoichiometry and NMR integration data suggest that the product of the 12-day hydrolysis has the simplest formula, $\text{In}(\text{CH}_2\text{SiMe}_3)(\text{OH})_2$.

The extent of reaction of $\text{In}(\text{CH}_2\text{SiMe}_3)_3$, $\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}$, and $\text{In}(\text{CH}_2\text{SiMe}_3)\text{Cl}_2$ in 95% ethanol was determined by following the ^1H NMR spectra as a function of time. All initial samples were clear solutions. The following is a list of the pertinent data (compound, time for initial appearance of Me_4Si , time for half of the organo groups to be converted to Me_4Si): $\text{In}(\text{CH}_2\text{SiMe}_3)_3$, 1 h, less than 1 day; $\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}$, 10 days, greater than 60 days; $\text{In}(\text{CH}_2\text{SiMe}_3)\text{Cl}_2$, 18 days, greater than 6 months.

An attempt was also made to follow the hydrolysis of the three organoindium compounds in water by ^1H NMR. Even though Me_4Si was observed to be formed, the limited solubilities of initial samples and products limit interpretation of the data.

Results and Discussion

A series of organoindium compounds with the (trimethylsilyl)methyl ligand, $\text{In}(\text{CH}_2\text{SiMe}_3)_x\text{Cl}_{3-x}$ ($x = 1, 2, 3$), have been prepared and fully characterized. The elemental analyses, NMR and IR spectroscopy, molecular weight data, solubility properties, and the acid–base chemistry suggest the following molecular formulas: $\text{In}(\text{CH}_2\text{SiMe}_3)_3$, $[\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}]_2$, $[\text{In}(\text{CH}_2\text{SiMe}_3)\text{Cl}_2]_2$. It is noteworthy that the bulky (trimethylsilyl)methyl ligand does not introduce any novel structures or alter substantially the Lewis acidic behavior of any of these compounds when compared to other analogous organoindium compounds. These new compounds exhibit the high thermal stability expected for (trimethylsilyl)methyl derivatives.

The simplest compound of the series, $\text{In}(\text{CH}_2\text{SiMe}_3)_3$, is readily prepared in 80% yield by a standard Grignard reaction in diethyl ether solution. The best synthetic conditions involved adding a 13% excess of the Grignard reagent to the InCl_3 in ether. After the addition of reagents was complete, a 3-h reflux period was observed to maximize the yield of $\text{In}(\text{CH}_2\text{SiMe}_3)_3$. It is critical that all of the Grignard reagent is added before heating is initiated. Otherwise, the principal product is $[\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}]_2$. These data suggest that reaction occurs stepwise. If the dimer of $\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}$ is permitted to form, further reaction with more Grignard to yield $\text{In}(\text{CH}_2\text{SiMe}_3)_3$ does not occur. This hypothesis was confirmed when the mixture $[\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}]_2$ and $\text{Me}_3\text{SiCH}_2\text{MgCl}$ in ether was observed not to react at reflux temperature.

A variety of reaction conditions were changed in order to possibly maximize the yield of $\text{In}(\text{CH}_2\text{SiMe}_3)_3$. When InBr_3 was substituted for InCl_3 in the preparative reaction, very poor yields of $\text{In}(\text{CH}_2\text{SiMe}_3)_3$ were obtained. The product was a mixture of $[\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Br}]_2$ and smaller amounts of $\text{In}(\text{CH}_2\text{SiMe}_3)_3$. In another attempt to increase the yield, the ether was replaced with tetrahydrofuran. This change in the synthetic conditions lead to the isolation of solvent-adducted product, $\text{In}(\text{CH}_2\text{SiMe}_3)_3 \cdot \text{THF}$. It was not possible for us to remove the THF quantitatively.

The chemical properties of $\text{In}(\text{CH}_2\text{SiMe}_3)_3$, a mobile liquid at room temperature, are indicative of a simple three-coordinate indium compound. A monomeric species was shown to be present in benzene solution by cryoscopic molecular

weight data. The ^1H NMR and IR data are also consistent with this formulation. The bulkiness of the CH_2SiMe_3 ligand apparently only slightly reduces the Lewis acidity of the indium in $\text{In}(\text{CH}_2\text{SiMe}_3)_3$ when compared to other organoindium compounds of similar formulation. The acid-base studies clearly show that diethyl ether and acetonitrile do not form adducts at room temperature with $\text{In}(\text{CH}_2\text{SiMe}_3)_3$. However, $\text{In}(\text{CH}_2\text{SiMe}_3)_3$ can still function as a moderately strong Lewis acid toward other bases. A 1:1 adduct stable at room temperature was observed for $\text{N}(\text{CH}_3)_3$ whereas less stable adducts were observed for tetrahydrofuran and dimethoxyethane.

The chloro-substituted derivatives are readily prepared from $\text{In}(\text{CH}_2\text{SiMe}_3)_3$ by using appropriate stoichiometric quantities of InCl_3 in an exchange reaction or anhydrous HCl in an elimination reaction. When InCl_3 is used as a reagent, refluxing solvent (benzene or diethyl ether) is necessary for complete reaction. Reactions with HCl occur at room temperature or below. These reactions have the advantage of forming either one product or two easily separable compounds. Both chloro species are solids at room temperature and are readily purified by vacuum sublimation at temperatures close to their respective melting points.

Our available data suggest that both chloroindium compounds exist as chlorine-bridged dimers, but $[\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}]_2$ probably has more extensive association in the solid state. This association probably also accounts for the higher melting point, higher sublimation temperature, and limited solubility of $[\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}]_2$. Structures which involve ion pairs such as $[\text{In}(\text{CH}_2\text{SiMe}_3)_2]^+\text{InCl}_4^-$ are ruled out by spectral and chemical properties. Cryoscopic molecular weight measurements confirm the dimeric nature of $[\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}]_2$ in benzene solution. It is regrettable that $[\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}]_2$ is not sufficiently soluble in benzene for molecular weight measurements. Therefore, our structural hypothesis for $[\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}]_2$ is based on chemical, physical, and spectral properties and their comparisons with other organoindium-halogen compounds. Structures based on ion pair formulations have been discarded because metathesis reactions gave negative results. If the structure of $\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}$ were based on ions such as $[\text{In}(\text{CH}_2\text{SiMe}_3)_2]^+$ and InCl_4^- , reaction with $\text{N}(\text{C}_2\text{H}_5)_4\text{Cl}$ should have formed $\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}$ and $\text{N}(\text{C}_2\text{H}_5)_4\text{InCl}_4$, known compounds. Our experimental results indicate that these reactants could be recovered unchanged. The infrared spectrum of $\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}$ does not have bands consistent with these or other ions either.¹⁰ It is of interest that $\text{In}(\text{CH}_3)_2\text{Cl}$ has properties¹¹ very similar to those of $\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}$, melting points of 165 vs. 167–170 °C, respectively, and both compounds are only soluble in hot benzene. The structure¹² of $\text{In}(\text{CH}_3)_2\text{Cl}$ in the solid state has associated dimeric units. The indium has a strongly distorted trigonal-bipyramidal coordination of one methyl group and four chlorines. The compounds $\text{In}(\text{C}_6\text{H}_5)_2\text{Cl}$ ¹³ and InRBr_2 ($\text{R} = \text{CH}_3$,¹⁴ C_2H_5 ,¹⁴ $n\text{-C}_3\text{H}_7$,¹⁴ $n\text{-C}_4\text{H}_9$,¹⁴ and C_6H_5 ¹³) are also believed to have a polymeric lattice with multiply associated halogen atoms. In contrast, $\text{In}(\text{CH}_3)_2\text{I}$ has the ion pair formulation¹⁵ $[\text{In}(\text{CH}_3)_2]^+\text{InI}_4^-$.

The studies of the interactions of the two chloroindium compounds with Lewis bases gave interesting results. Neither indium compound formed a stable adduct with any base tried ($\text{N}(\text{CH}_3)_3$, CH_3CN , diethyl ether, tetrahydrofuran, or dimethoxyethane). However, the oxygen bases did distinguish the relative acidities of the two chloroindium compounds. The compound $[\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}]_2$ did not exhibit any acidic properties whereas $[\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}]_2$ formed weak adducts with appreciable dissociation pressures. These data might suggest that the dimer molecules remain intact in the presence of the various bases used. However, we have no specific data which can confirm the hypothesis.

The relative rates of hydrolysis of the series of ((trimethylsilyl)methyl)indium compounds are $\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl} < \text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl} < \text{In}(\text{CH}_2\text{SiMe}_3)_3$. Similar observations have been made in ethanol and water, but it should be noted that all compounds were soluble in ethanol but insoluble in water. It is noteworthy that the half-life for hydrolysis of $[\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}]_2$ in ethanol is about 60 days and for $\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}$ it is about 6 months, whereas $\text{In}(\text{CH}_2\text{SiMe}_3)_3$ is hydrolyzed in 12 days to a product with one CH_2SiMe_3 ligand per indium atom. These data suggest that the organoindium chlorine compounds probably persist in ethanol solution. The bridging chlorine atoms in the dimer could prevent the ethanol from forming the necessary intermediate for hydrolysis. If the hydrolysis reactions of $\text{In}(\text{CH}_2\text{SiMe}_3)_3$ and the dissolution of the chloroindium compounds had formed identical species, similar rates of hydrolysis would have been observed. It is noteworthy that the steric effects of the three CH_2SiMe_3 groups in $\text{In}(\text{CH}_2\text{SiMe}_3)_3$ are insufficient to hinder hydrolysis or prevent adduct formation.

Acknowledgment. We thank The Indium Corp. of America, Utica, NY, for a generous gift of indium trichloride.

Registry No. $\text{In}(\text{CH}_2\text{SiMe}_3)_3$, 69833-15-4; $[\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}]_2$, 69847-03-6; $[\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}]_2$, 69847-04-7; InCl_3 , 10025-82-8; $\text{Me}_3\text{SiCH}_2\text{MgCl}$, 13170-43-9; $\text{In}(\text{CH}_2\text{SiMe}_3)(\text{OH})_2$, 69833-16-5.

References and Notes

- (1) (a) Cundy, C. S.; Kingston, B. M.; Lappert, M. F. *Adv. Organomet. Chem.* **1973**, *11*, 253. (b) Davidson, P. J.; Lappert, M. F.; Pearce, R. *Acc. Chem. Res.* **1974**, *7*, 209.
- (2) Nyathi, J. Z.; Ressler, J. M.; Smith, J. D. *J. Organomet. Chem.* **1974**, *70*, 35.
- (3) Davidson, P. J.; Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2268.
- (4) Cotton, J. D.; Davidson, P. J.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2275.
- (5) Hudson, A.; Lappert, M. F.; Lednor, P. W. *J. Chem. Soc., Dalton Trans.* **1976**, 2369.
- (6) Coates, G. E.; Graham, J. *J. Chem. Soc.* **1963**, 233.
- (7) Sommer, L. H.; Whitmore, F. C. *J. Am. Chem. Soc.* **1946**, *68*, 481.
- (8) Shriver, D. F. "The Manipulation of Air-Sensitive Compounds", McGraw-Hill, New York, 1969, p 159.
- (9) Durkin, T.; Glone, J.; DeHayes, L. *J. Chem. Educ.* **1971**, *48*, 452.
- (10) Atkinson, A. W.; Field, B. O. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2615.
- (11) Clark, H. C.; Packard, A. L. *J. Organomet. Chem.* **1968**, *13*, 61.
- (12) Mertz, K.; Schwarz, W.; Zettler, F.; Hansen, H. D. *Z. Naturforsch., B* **1975**, *30*, 159.
- (13) Miller, S. B.; Jelus, B. L.; Brill, T. B. *J. Organomet. Chem.* **1975**, *96*, 1.
- (14) Gynane, M. J. S.; Waterworth, L. G.; Worrall, I. J. *J. Organomet. Chem.* **1972**, *43*, 257.
- (15) Poland, J. S.; Tuck, D. G. *J. Organomet. Chem.* **1972**, *42*, 315.