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Articles

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A Reexamination of the Reactions of $Ga(CH_2SiMe_3)_3$ and $In(CH_2SiMe_3)_3$ with Alkali-Metal Hydrides. The Search for a Reductive-Elimination Reaction

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The nature of the reactions that occur between $Ga(CH_2SiMe_3)_3$ and $In(CH_2SiMe_3)_3$ with alkali-metal hydrides has been reinvestigated. The previously reported results[2,3] suggesting reductive elimination reactions have not been reproduced. The product from the reaction between $Ga(CH_2SiMe_3)_3$ and KH in benzene at 45 °C has been identified as $KGa(CH_2SiMe_3)_3H$ by an X-ray structural study, infrared and ^1H NMR spectral data, and reaction chemistry. Thermal decomposition has not been observed until the temperature is above 200 °C. The compound $KGa(CH_2SiMe_3)_3H$ crystallizes in the monoclinic space group $P2_1/c$ with unit cell dimensions $a = 14.560$ (7) Å, $b = 13.316$ (6) Å, $c = 23.592$ (8) Å, $\beta = 104.42$ (5)°, and $Z = 8$ for $d_{calcd} = 1.11$ g cm^{-3}. Full-matrix least-squares refinement led to a final R value of 0.076 for 3834 observed reflections. The geometry about each of the two gallium atoms is distorted tetrahedral with gallium–hydrogen distances of 1.49 and 1.36 Å and Ga–C(av) lengths of 2.04 (1) and 2.02 (1) Å, respectively. The infrared spectra of $KGa(CH_2SiMe_3)_3H$ and $KGa(CH_2SiMe_3)_3D$ have been compared in order to identify the bands associated with the gallium–hydrogen bond. The observed frequency for ν(Ga–D) at 1075 cm^{-1} suggests that ν(Ga–H) should be around 1500 cm^{-1}, an unusually low frequency. The reaction chemistry of $KGa(CH_2SiMe_3)_3H$ also confirms the presence of a typical nucleophilic hydride. The reactions between $In(CH_2SiMe_3)_3$ and KH or NaH have been reexamined under a great variety of experimental conditions. The primary products of reactions in pentane at room temperature are $KIn(CH_2SiMe_3)_3H$ and mixtures of $NaIn(CH_2SiMe_3)_3H$ and $NaIn(CH_2SiMe_3)_4$. In one reaction between $In(CH_2SiMe_3)_3$ and KH, colorless crystals were isolated and identified by an X-ray structural study as $KIn(CH_2SiMe_3)_4$. The complex $KIn(CH_2SiMe_3)_4$ crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ with $a = 11.106$ (4) Å, $b = 19.712$ (6) Å, $c = 12.882$ (3) Å, $\beta = 91.65$ (2)°, $V = 2819$ (1) Å^3, and $Z = 4$. Diffraction data (Mo Kα, $2\theta = 4.5$–45.0°) were collected with a Syntex $P2_1$ automated four-circle diffractometer. All atoms were located, and the structure was refined to $R = 3.6\%$ and $R_w = 3.2\%$ for all 3520 independent reflections (none rejected). The complex is composed of discrete K^+ cations and $In(CH_2SiMe_3)_4^-$ anions; In–C distances range from 2.234 (4) through 2.251 (4) Å, averaging 2.239 [8] Å. The thermal decomposition reactions of $KIn(CH_2SiMe_3)_3H$, $KIn(CH_2SiMe_3)_4$, and mixtures of $NaIn(CH_2SiMe_3)_3H$ and $NaIn(CH_2SiMe_3)_4$ have been investigated in detail under a variety of conditions by using benzene and saturated hydrocarbon solvents. The products of decomposition of the indium hydride derivatives, which include indium metal, $SiMe_4$, biphenyl, and varying amounts of H_2 depending on the reactant, solvent, and conditions, are indicative of reactions more complicated than a simple stoichiometric reductive-elimination reaction. All experimental observations including the formation of $SiMe_4$ are consistent with the dissociation and reactions of alkali-metal alkyls, presumably KCH_2SiMe_3 and $NaCH_2SiMe_3$.

Introduction

The recent literature describes the preparation and characterization of the first examples of anionic, σ-bonded organometallic gallium(I)[2] and indium(I)[3] derivatives. The gallium(I) compounds[2] $KGa(CH_2SiMe_3)_2$, $NaGa(CH_2SiMe_3)_2$, and $LiGa(CH_2SiMe_3)_2{\cdot}MeOC_2H_4OMe$ were reported to be easily prepared from $Ga(CH_2SiMe_3)_3$ and the alkali-metal hydride in benzene at 45 °C or in dimethoxyethane at 25 °C. Similarly, the indium(I) compound[3] $NaIn(CH_2SiMe_3)_2$ was reportedly synthesized from $In(CH_2SiMe_3)_3$ and NaH in refluxing hexane or benzene. The observed stoichiometries of these preparative reactions including the formation of 1 mol of $SiMe_4$/mol of $M(CH_2SiMe_3)_3$ (M = Ga, In) and alkali-metal hydride consumed, as well as elemental analyses and infrared spectral data, were used as evidence for the formation of the low oxidation state products.[2,3] The organometallic hydride derivatives, $KGa(CH_2SiMe_3)_3H$ and $NaIn(CH_2SiMe_3)_3H$, were believed to be the necessary intermediates for the very facile but quantitative reductive-elimination reactions.[2,3] Since the proposed low oxidation state compounds were so unusual and novel in main-group organometallic chemistry, an X-ray structural study was considered necessary to verify their identity. The product from the $Ga(CH_2SiMe_3)_3$–KH reaction at 45 °C was chosen for the initial study and is herein identified as $KGa(CH_2SiMe_3)_3H$, the originally proposed intermediate[2] for reductive elimination. We also report the infrared and ^1H NMR spectra, thermal stability, and reaction chemistry of $KGa(CH_2SiMe_3)_3H$. Since the preparation of the low oxidation state gallium compound could not be repeated, the reactions of $In(CH_2SiMe_3)_3$ with NaH and KH were then reinvestigated. The indium(III) hydrides should be more readily reduced than the corresponding gallium(III) compounds. Our current observations of the $In(CH_2SiMe_3)_3$–alkali-metal hydride systems support this hypothesis, but the product of the reduction of indium(III) is indium metal, not an organoindium(I) compound. Therefore, the major goal of this aspect of the research was to isolate and identify the primary products of the $In(CH_2SiMe_3)_3$–MH (M = Na, K) reactions and then investigate the nature of the decomposition and/or reduction reactions.

Experimental Section

General Comments. All compounds described in this investigation were extremely oxygen and moisture sensitive and were manipulated in a vacuum line or under a purified argon atmosphere. All solvents were rigorously dried and vacuum distilled just prior to use. Infrared spectra were obtained by using a Perkin-Elmer 683 infrared spectrometer. The spectra were recorded as Nujol mulls using CsI plates. (Bands due to Nujol have been omitted from data). Proton NMR

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(2) Beachley, O. T., Jr.; Simmons, R. G. *Inorg. Chem.* **1980**, *19*, 3042.

(3) Beachley, O. T., Jr.; Rusinko, R. N. *Inorg. Chem.* **1981**, *20*, 1367.

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spectra were recorded by using a Varian EM-390 spectrometer. Proton chemical shifts are reported in δ units, downfield from tetramethylsilane, with benzene as an internal reference (δ 7.13). The solvent was vacuum distilled onto samples at −196 °C. Spectra of indium compounds were recorded immediately upon warming samples to room temperature unless stated otherwise.

Standard Grignard reactions in diethyl ether were used to prepare $Ga(CH_2SiMe_3)_3$[4] and $In(CH_2SiMe)_3$.[5] The alkali-metal hydrides and deuterides were purchased from Alfa Inorganics as oil dispersions. The oil was removed by repeated extractions with dry pentane.

$SiMe_4$ formed during synthetic, hydrolysis, and thermal decomposition reactions was separated by vacuum distillation with passage through two −78 °C traps and into a −196 °C trap and was measured by *PVT* or mass measurements. The purity of the $SiMe_4$ was determined by its ^1H NMR spectrum. Hydrogen was isolated and measured with a Toepler pump-gas buret assembly.

Synthesis and Characterization of $KGa(CH_2SiMe_3)_3H$. The compound $KGa(CH_2SiMe_3)_3H$ was prepared from $Ga(CH_2SiMe_3)_3$ (3.98 g, 12.0 mmol) and excess KH (1.4 g, 35 mmol) in benzene at 45 °C in a sealed tube apparatus. After 4 days, the resulting mixture was filtered to remove unreacted KH and then the volatile components in the soluble portion of the reaction mixture were removed by vacuum distillation and fractionated. Only 0.15 mmol of $SiMe_4$ was observed to be formed in this preparative reaction. The product, $KGa(CH_2SiMe_3)_3H$, is typically isolated in greater than 90% yield as a colorless microcrystalline solid. The deuterium analogue, $KGa(CH_2SiMe_3)_3D$, was prepared and isolated by the same experimental procedure using KD.

Crystals suitable for the X-ray structural study were grown at room temperature in the drybox. A sample of the microcrystalline solid was dissolved in benzene and then sufficient methylcyclohexane was added to reduce the solubility so that crystals of the solute would form. The resulting crystals were isolated by decantation and then solvent was removed by vacuum distillation.

A 0.112-g (0.302 mmol) sample of the microcrystalline $KGa(CH_2SiMe_3)_3H$ powder was hydrolyzed in 6 M HCl in a sealed evacuated tube at a bath temperature of 110 °C in order to verify the composition of the material. After 3 days of hydrolysis, 0.313 mmol of H_2 and 0.863 mmol of $SiMe_4$ were formed. The tube was resealed and subjected to further heating at 110 °C for 5 days longer. During this time an additional 0.044 mmol of $SiMe_4$ was formed but no more H_2 was observed. Thus, 0.302 mmol of $KGa(CH_2SiMe_3)_3H$ produced 0.313 mmol of H_2 and 0.907 mmol of $SiMe_4$.

Elemental analysis of $KGa(CH_2SiMe_3)_3H$ was performed by commerical laboratories in the USA and Germany, but the results were always inconsistent with the formula. An analysis of a crystal selected from the same batch used for the X-ray structural study gave the following results: Anal. Calcd: K, 10.52; Ga, 18.76; C, 38.79; H, 9.24. Found: K, 9.85; Ga, 17.3; C, 33.78; H, 8.08.

$KGa(CH_2SiMe_3)_3H$. Mp: 142–144 °C (single crystal); 98–125 °C (microcrystalline solid), 220 °C (bubbles and turns brown). ^1H NMR (benzene solution): δ 0.30 (s, 4.9, SiMe), −0.91 (s, 1, CH_2). (The hydrogen bound to gallium is not observed.) IR (cm^{-1}): 1915 (vw), 1840 (vw), 1250 (sh), 1243 (s), 1235 (sh), 956 (s), 920 (s), 852 (s, br), 825 (s, br), 753 (s), 730 (sh), 712 (sh), 675 (s), 604 (m), 598 (sh), 585 (sh), 564 (w), 502 (s), 480 (m). A prominent feature of the spectrum is a broad, medium-intensity band spanning the region, approximately 1700–1400 cm^{-1}, that is overlapped with Nujol bands.

$KGa(CH_2SiMe_3)_3D$. IR (cm^{-1}): 1915 (vw), 1845 (vw), 1285 (w), 1250 (sh), 1240 (s), 1230 (sh), 1075, (m, br), 950 (s), 914 (s), 850 (s, br), 820 (s, br), 748 (s), 720 (sh), 710 (sh), 672 (s), 601 (m), 593 (sh), 575 (sh), 560 (w), 499 (s), 429 (m).

Thermal Stability of $KGa(CH_2SiMe_3)_3H$. A 0.352-g (0.949 mmol) sample of $KGa(CH_2SiMe_3)_3H$ was dissolved in benzene and contained in a tube sealed under vacuum. The resulting solution was heated in an oil bath at 80 °C for 1 day. Upon fractionation of the volatile components, only a trace of $SiMe_4$ was observed. All fractions contained a total of less than 0.01 mmol of $SiMe_4$. The benzene was then readded to the $KGa(CH_2SiMe_3)_3H$, and the solution was heated at a bath temperature of 105–110 °C for 5 days. No $SiMe_4$ or H_2 was formed under these conditions. The infrared and ^1H NMR spectra of the solid remaining in the tube after the benzene was removed were identical with that recorded before heating.

Table I. Crystal Data for $KGa(CH_2SiMe_3)_3H$

compd	$KGaSi_3C_{12}H_{34}$
mol wt	371.45
space group	$P2_1/c$
cell constants	
a, Å	14.560 (7)
b, Å	13.316 (6)
c, Å	23.592 (8)
β, deg	104.42 (5)
V, Å^3	4429.9
molecules/unit cell (Z)	8
d_{calcd}, g cm^{-3}	1.11
μ_{calcd}, cm^{-1}	16.35
radiation	Mo Kα
max crystal dimens, mm	0.6 × 0.5 × 0.2
scan width, deg	0.8 + 0.20 tan θ
std reflcns	400, 040
decay of stds	<3%
reflcns measd	4991
2θ range, deg	1–42
obsd reflcns	3834
no. of parameters varied	307
GOF	3.40
R	0.076
R_w	0.075

Collection of X-ray Diffraction Data and Solution of Structure for $KGa(CH_2SiMe_3)_3H$. Single crystals of the air-sensitive compound were sealed under N_2 in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of $((\sin \theta)/\lambda)^2$ values for 15 reflections ($\theta > 20°$) accurately centered on the diffractometer are given in Table I.

Data were collected on an Enraf-Nonius CAD-4 diffractometer by the θ–2θ scan technique. This method has been previously described.[6] A summary of data collection parameters is given in Table I. The intensities were corrected for Lorentz and polarization effects.

Calculations were carried out with SHELX system of computer programs.[7] Neutral-atom scattering factors for K and Ga were taken from Cromer and Waber.[8] Scattering factors stored within the SHELX program were used for the other atoms. The scattering of K and Ga was corrected for the real and imaginary components of anomalous dispersion by using the table of Cromer and Liberman.[9] The positions of the K and Ga atoms were located with use of the MULTAN80 system of programs.[10] Difference Fourier maps phased on these atoms readily revealed the positions of the remaining non-hydrogen atoms. Full-matrix least-squares refinement with isotropic thermal parameters led to $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.091$. Further refinement with anisotropic thermal parameters led to $R = 0.079$. At this point a difference Fourier map was computed, and the hydrogen atoms on the gallium atoms were located. The hydrogen atoms on the alkyl groups were not included in the refinement, and the hydride on each gallium atom was held fixed with an isotropic thermal parameter of 6.31 Å^2. Further cycles of refinement led to final values of $R = 0.076$ and $R_w = 0.075$.

A final difference Fourier showed no feature greater than 0.6 e/Å^3. The weighting scheme was based on unit weights; no systematic variation of $w(|F_o| - |F_c|)^2$ vs. $|F_o|$ or $(\sin \theta)/\lambda$ was noted. The final values of the positional parameters are given in Table II. Anisotropic thermal parameters, Table VII-S-Ga, are deposited as supplementary material.

Reactions of $KGa(CH_2SiMe_3)_3H$ with CO_2. In a typical reaction, 1.00 g (2.69 mmol) of $KGa(CH_2SiMe_3)_3H$ and an excess (5.39 mmol) of CO_2 were combined in a bulb equipped with a Teflon valve. After the solvent, 20 mL of pentane, was added by vacuum distillation, the mixture was warmed to room temperature and was stirred overnight. A colorless pentane-insoluble solid (0.23 g) was isolated by filtration and was characterized after recrystallization from water. The infrared spectrum and melting point (glass formed at 165–170 °C) were identical with those of an authentic sample of potassium formate.

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(4) Beachley, O. T., Jr.; Simmons, R. G. *Inorg. Chem.* **1980**, *19*, 1021.

(5) Beachley, O. T., Jr.; Rusinko, R. N. *Inorg. Chem.* **1979**, *18*, 1966.

(6) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 46.

(7) SHELX, a system of computer programs by G. Sheldrick.

(8) Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104.

(9) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(10) MULTAN80, a system of computer programs for the application of direct methods by G. Germain, P. Main, and M. M. Woolfson.

Table II. Final Fractional Coordinates for $KGa(CH_2SiMe_3)_3H$

atom	*x/a*	*y/b*	*z/c*
K(1)A	0.1928 (2)	−0.0021 (2)	0.1604 (1)
Ga(1)A	0.51846 (7)	0.01731 (7)	0.75183 (5)
C(1)A	0.5268 (7)	−0.0679 (7)	0.6819 (4)
Si(1)A	0.6071 (2)	−0.0263 (2)	0.6369 (1)
C(2)A	0.7346 (9)	−0.038 (1)	0.6801 (7)
C(3)A	0.590 (1)	−0.101 (1)	0.5678 (6)
C(4)A	0.585 (1)	0.1114 (9)	0.6148 (7)
C(5)A	0.4435 (6)	0.1472 (6)	0.7277 (4)
Si(2)A	0.3216 (2)	0.1442 (2)	0.6849 (2)
C(6)A	0.2697 (8)	0.2764 (8)	0.6801 (6)
C(7)A	0.2435 (9)	0.061 (1)	0.7149 (8)
C(8)A	0.317 (1)	0.107 (1)	0.6068 (6)
C(9)A	0.4637 (7)	−0.0658 (7)	0.8077 (4)
Si(3)A	0.4848 (2)	−0.0249 (2)	0.8843 (1)
C(10)A	0.613 (1)	−0.033 (1)	0.9205 (6)
C(11)A	0.4494 (9)	0.1122 (9)	0.8897 (6)
C(12)A	0.415 (1)	−0.102 (1)	0.9258 (6)
K(1)B	0.3695 (2)	−0.2677 (2)	0.2079 (1)
Ga(1)B	−0.10243 (7)	0.24739 (7)	0.36564 (5)
C(1)B	−0.0199 (6)	0.3645 (7)	0.4028 (4)
Si(1)B	0.1018 (2)	0.3352 (3)	0.4460 (2)
C(2)B	0.126 (1)	0.391 (1)	0.5213 (7)
C(3)B	0.185 (1)	0.372 (3)	0.407 (1)
C(4)B	0.124 (1)	0.194 (1)	0.4601 (9)
C(5)B	−0.0437 (8)	0.1700 (8)	0.3109 (5)
Si(2)B	−0.0604 (2)	0.2096 (2)	0.2353 (1)
C(6)B	0.0155 (9)	0.131 (1)	0.1970 (5)
C(7)B	−0.1871 (9)	0.193 (1)	0.1926 (6)
C(8)B	−0.026 (1)	0.3449 (9)	0.2307 (7)
C(9)B	−0.134 (1)	0.1489 (9)	0.4235 (7)
Si(3)B	−0.1890 (3)	0.1883 (3)	0.4814 (2)
C(10)B	−0.186 (2)	0.085 (1)	0.538 (1)
C(11)B	−0.133 (2)	0.291 (2)	0.525 (1)
C(12)B	−0.319 (2)	0.220 (2)	0.447 (1)
H(1)A	0.61798 (7)	0.03999 (7)	0.78471 (5)
H(1)B	−0.19198 (7)	0.27079 (7)	0.33461 (5)

Distillation of pentane from the filtrate at room temperature left a colorless liquid. Distillation of this liquid at 110 °C produced pure $Ga(CH_2SiMe_3)_3$ and a small amount of residue, a light yellow viscous liquid. The $Ga(CH_2SiMe_3)_3$ was converted to $Ga(CH_2SiMe_3)_3 \cdot NMe_3$, a colorless solid, and identified by its ^1H NMR spectrum and melting point.

Reactions of $KGa(CH_2SiMe_3)_3H$ with Me_3SnCl and Me_3SiCl. In a typical reaction 0.500 g (1.35 mmol) of $KGa(CH_2SiMe_3)_3H$ was combined with 0.268 g (1.35 mmol) of Me_3SnCl in a tube equipped with a Teflon valve and then 25 mL of benzene was added by vacuum distillation. The mixture was stirred overnight at 45 °C. The volatile components were fractionated by using two −78 °C traps and a −196 °C trap. The product collected in the −196 °C trap was identified as Me_3SnH by its ^1H NMR spectrum.[11] The $Ga(CH_2SiMe_3)_3$ was isolated by vacuum distillation at 110 °C and identified by its ^1H NMR spectrum. A white solid (KCl) and a small amount of yellow paste remained in the tube. A similar reaction of $KGa(CH_2SiMe_3)_3H$ with Me_3SiCl in dimethoxyethane produced Me_3SiH, $Ga(CH_2SiMe_3)_3$, KCl, and a yellow paste. The Me_3SiH was identified by its ^1H NMR spectrum.[12]

Synthesis and Characterization of $KIn(CH_2SiMe_3)_3H$. To 0.640 g (16.0 mmol) of KH in a reaction tube equipped with a high-vacuum Kontes lo-hold-up Teflon valve was added 20 mL of pentane. After the KH had settled to the bottom of the tube, 2.00 g (5.32 mmol) of $In(CH_2SiMe_3)_3$ was added. The reaction tube was removed from the drybox, frozen to −196 °C and evacuated. The tube was allowed to warm to room temperature, and the contents were stirred for 3 days. When the tube was opened, no H_2 or $SiMe_4$ was observed. The mixture was then filtered through a medium glass frit and washed twice with pentane. After removal of the pentane, a very small quantity of an unidentified yellow viscous liquid remained. Benzene (20 mL) was then added to the pentane-insoluble solid by vacuum distillation. When the mixture was allowed to warm to room temperature, the solid immediately turned black in color. The resulting mixture was filtered through a glass frit, and a colorless solution was obtained. After removal of the benzene by vacuum distillation, 1.79 g (4.30 mmol, 80.9% yield based on $In(CH_2SiMe_3)_3$) of $KIn(CH_2SiMe_3)_3H$ remained.

Table III. Experimental Data for the X-ray Diffraction Study of $KIn(CH_2SiMe_3)_4$

(A) Crystal Parameters[a] at 24 °C

cryst system: monoclinic
space group: $P2_1/n$[b]
$a = 11.106$ (4) Å
$b = 19.712$ (6) Å
$c = 12.882$ (3) Å
$\beta = 91.65$ (2)°
$V = 2819.1$ (14) Å^3
$Z = 4$
mol wt = 502.88
ρ(calcd) = 1.18 g cm^{-3}

(B) Measurement of Data

radiation: Mo Kα ($\lambda = 0.710\,730$ Å)
monochromator: highly oriented graphite, equatorial
reflcns measd: $+h,+k,\pm l$
2θ range: 4.5–45.0°
scan type: θ(crystal)–2θ(counter)
scan speed: 4.0/min
scan range: $[2.0 + \Delta(\alpha_1 - \alpha_2)]°$
reflcns collected: 3739 total, yielding 3520 indep
stds: 3 every 97 reflcns (10,4,−9), (1,12,−3), (6,8,−1); no significant changes in intensity obsd
abs coeff: 11.4 cm^{-1}

[a] Unit cell parameters were derived from a least-squares fit to the setting angles of the unresolved Mo K$\bar{\alpha}$ component of the 24 reflections of the forms (0,4,9), (1,8,−8), (1,12,−3), (5,1,−6), (6,8,−1), and and (5,6,6), all with 2θ = 27–32°. [b] Nonstandard setting of space group $P2_1/c$ [C_{2h}^5, No. 14] having the equipoints $\pm(x, y, z)$ and $\pm(^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z)$.

A 0.415-g (0.997 mmol) sample of $KIn(CH_2SiMe_3)_3H$ was hydrolyzed in 6 M HCl. The reaction mixture was heated at a bath temperature of 105–110 °C for 30 days. The noncondensable gas (0.993 mmol of H_2) was measured by means of a Toepler pump-gas buret assembly. $SiMe_4$ (2.90 mmol) was purified and isolated by vacuum distillation.

$KIn(CH_2SiMe_3)_3H$. Mp: 109 °C dec (turns black), 125 °C (liquid). ^1H NMR (benzene solution): δ 0.33 (s, 4.9, SiMe), −0.83 (s, 1, CH_2). IR (cm^{-1}): 1915 (vw), 1835 (vw), 1700–1300 (s, vbr), 1280 (w), 1240 (vs), 905 (vs, br), 850 (vs, br), 820 (vs, br), 742 (vs), 719 (s), 706 (s, sh), 672 (s), 612 (m), 595 (m, sh), 578 (m), 511 (w), 453 (s), 435 (m, sh), 381 (w), 252 (m).

$KIn(CH_2SiMe_3)_3D$. ^1H NMR (benzene solution): δ 0.33 (s, 4.8, SiMe), −0.82 (s, 1, CH_2). IR (cm^{-1}): 1280 (w), 1251 (m, sh), 1240 (s), 1025 (m, br), 913 (s), 892 (m, sh), 850 (s), 820 (s), 743 (s), 720 (m), 710 (m, sh), 674 (m), 576 (m), 562 (w, sh), 454 (m), 395 (w, sh), 381 (m), 252 (w).

Synthesis and Characterization of $KIn(CH_2SiMe_3)_4$. One reaction of $In(CH_2SiMe_3)_3$ (2.66 mmol) and KH (7.98 mmol) produced $KIn(CH_2SiMe_3)_4$. (Attempts to synthesize only $KIn(CH_2SiMe_3)_4$ were unsuccessful.) The two reagents were combined in the drybox, and significant heat was generated. Pentane was then added by vacuum distillation. The mixture was warmed to room temperature and allowed to stand for 2 days without stirring. The colorless crystals growing out of the black reaction mixture were isolated mechanically and identified as $KIn(CH_2SiMe_3)_4$. Mp: 85 °C (glass), 107 °C (melts to clear liquid). ^1H NMR (benzene solution): δ 0.30 (s, 4.7, SiMe), −1.05 (s, 1, CH_2). IR (cm^{-1}): 1250 (m), 1240 (m), 1220 (m, sh), 1012 (vw), 930 (m), 917 (m), 900 (m, sh), 875 (m, sh), 850 (vs), 818 (vs), 744 (m), 720 (m), 673 (w), 662 (w), 600 (vw), 552 (vw), 530 (vw), 453 (m), 436 (w, sh), 387 (w).

Collection of X-ray Diffraction Data and Solution of the Structure for $KIn(CH_2SiMe_3)_4$. A translucent white crystal of approximate dimensions 0.5 × 0.5 × 0.2 mm was inserted into a thin-walled glass capillary in an inert atmosphere (Ar) drybox. The capillary was flame sealed and mounted onto a eucentric goniometer on a Syntex P2$_1$ automated four-circle diffractometer. The crystal was accurately centered, the orientation matrix and unit cell parameters were determined, and data were collected as described previously.[13] Details specific to the present analysis appear in Table III. All data were

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(11) Clark, H. C.; Kwon, J. T.; Reeves, L. W.; Wells, E. J. *Inorg. Chem.* **1964**, *3*, 907.

(12) Webster, D. E. *J. Chem. Soc.* **1960**, 5132.

(13) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265.

Table IV. Positional parameters (with Esd's) for $KIn(CH_2SiMe_3)_4$

atom	*x*	*y*	*z*
In	−0.01113 (2)	0.20932 (1)	−0.29583 (2)
C(1)	0.0077 (3)	0.12369 (20)	−0.4080 (3)
Si(1)	0.14776 (10)	0.10998 (6)	−0.47813 (9)
C(11)	0.2116 (6)	0.0268 (3)	−0.4528 (7)
C(12)	0.1179 (6)	0.1133 (4)	−0.6184 (5)
C(13)	0.2654 (4)	0.1731 (3)	−0.4509 (5)
C(2)	0.1167 (3)	0.19379 (18)	−0.1608 (3)
Si(2)	0.08553 (10)	0.12550 (6)	−0.06804 (9)
C(21)	0.2124 (5)	0.11099 (25)	0.0279 (4)
C(22)	−0.0478 (5)	0.1473 (3)	0.0074 (4)
C(23)	0.0628 (4)	0.04338 (22)	−0.1354 (4)
C(3)	−0.2011 (3)	0.22099 (20)	−0.2460 (3)
Si(3)	−0.31921 (10)	0.15794 (6)	−0.27262 (9)
C(31)	−0.4624 (4)	0.1819 (3)	−0.2082 (3)
C(32)	−0.2793 (4)	0.0715 (3)	−0.2271 (4)
C(33)	−0.3556 (4)	0.1526 (3)	−0.4143 (3)
C(4)	0.0310 (3)	0.30769 (18)	−0.3758 (3)
Si(4)	0.09059 (9)	0.37824 (5)	−0.29651 (8)
C(41)	0.1008 (4)	0.45840 (23)	−0.3722 (4)
C(42)	−0.0101 (4)	0.39463 (25)	−0.1866 (4)
C(43)	0.2443 (3)	0.35828 (22)	−0.2419 (3)
K	0.35965 (10)	0.25739 (6)	0.95518 (8)

converted to $|F_o|$ values following correction for absorption and for Lorentz and polarization factors. Any reflection with $I(\text{net}) < 0$ was assigned a value of $|F_o| = 0$. No datum was rejected.

During structure factor calculations, the analytical scattering factors of the neutral atoms were corrected for both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion.[14] The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, with $w = [(\sigma(|F_o|))^2 + 0.015|F_o|^2]^{-1}$. All calculations were performed on our in-house NOVA 1200 computer using the SUNY-Buffalo modified version of the Syntex XTL interactive crystallographic program package.

The structure was solved by a combination of Patterson, difference Fourier, and full-matrix least-squares refinement techniques. All 44 hydrogen atoms were located directly but were included in their idealized positions (with $B = 6.0$ Å^2) based upon d(C–H) = 0.95 Å[15] and idealized staggered tetrahedral geometry. Refinement of positional and anisotropic thermal parameters for all 22 non-hydrogen atoms led smoothly to convergence ($(\Delta/\sigma)_{\max} < 0.1$) with $R = 3.6\%$, $R_w = 3.2\%$, and GOF = 1.818 for 199 parameters refined against all 3520 reflections.[16]

A final difference Fourier map showed no significant features; the structure is thus both correct and complete. Final positional parameters for non-hydrogen atoms appear in Table IV. Positional parameters for hydrogen atoms (Table IV-S-In) and anisotropic thermal parameters (Table VIII-S-In) are deposited as supplementary material.

Reactions of $In(CH_2SiMe_3)_3$ with NaH. The reactions of $In(CH_2SiMe_3)_3$ with NaH were investigated in refluxing hexane and at room temperature in pentane. The reaction products included $NaIn(CH_2SiMe_3)_3H$, $NaIn(CH_2SiMe_3)_4$, and smaller amounts of unidentified impurities. However, neither product could be isolated as a pure compound.

To 0.20 g (8.3 mmol) of NaH in 20 mL of pentane contained in a reaction tube equipped with a Teflon high-vacuum valve was added 1.00 g (2.66 mmol) of $In(CH_2SiMe_3)_3$ in the drybox. The tube was then evacuated and sealed, and the reaction mixture was stirred overnight. A precipitate formed. Repeated extraction (20 times) of the reaction mixture with the reaction solvent yielded 0.70 g of a colorless solid. The ^1H NMR spectrum of a benzene solution of this solid exhibited three lines: 0.25 (30, $SiMe_3$), −0.80 (6, CH_2 of $NaIn(CH_2SiMe_3)_3H$), −1.01 (1, unassigned). IR (cm^{-1}) for $NaIn(CH_2SiMe_3)_3H$ (impure—see discussion): 1700–1320 (m, vbr), 1285 (w), 1239 (vs), 950 (m, sh), 930 (m, sh), 915 (s), 845 (vs), 822 (vs), 742 (s), 708 (s), 677 (m), 600 (w), 552 (m), 475 (m), 434 (m). Hydrolysis of 0.679 g of this solid (6 M HCl, 110 °C bath temperature, 25 days) produced 1.27 mmol of H_2 and 4.57 mmol of $SiMe_4$. If the sample had been pure $NaIn(CH_2SiMe_3)_3H$, 1.70 mmol of H_2 and 5.09 mmol of $SiMe_4$ would have been formed. These data suggest that the pentane-soluble solid contains 80–85% $NaIn(CH_2SiMe_3)_3H$ and an unidentified impurity.

The pentane-insoluble material remaining from the above reaction was then extracted once with 10 mL of benzene to yield 0.10 g of a colorless solid. The solid is probably impure $NaIn(CH_2SiMe_3)_4$, according to ^1H NMR (benzene solution) [δ 0.25 (4.8, $SiMe_3$), −1.11 (1, CH_2), −1.00 (0.16, impurity)], the absence of infrared bands in the 1500–1300- and 475-cm^{-1} regions indicative of In–H modes and its decomposition chemistry in benzene solution. IR (cm^{-1}) for $NaIn(CH_2SiMe_3)_4$ (impure—see discussion): 1283 (w), 1239 (vs), 950 (w, sh), 914 (m), 843 (vs), 820 (vs), 741 (m), 730 (m, sh), 708 (m), 675 (m), 600 (vw), 551 (m), 460 (vw, sh), 435 (m). This material, which is suggested to be $NaIn(CH_2SiMe_3)_4$, is more stable in benzene solution than $NaIn(CH_2SiMe_3)_3H$. However, $SiMe_4$, a colorless precipitate, but no indium metal is formed after heating samples in benzene.

Thermal Decomposition Reactions of $MIn(CH_2SiMe_3)_3H$ and $MIn(CH_2SiMe_3)_4$. The decomposition reactions of all isolated compounds were investigated under a great variety of temperature, time, and solvent conditions. The specific conditions and results are given in the Results and Discussion. The biphenyl isolated as a benzene-soluble product after some decompositions of $KIn(CH_2SiMe_3)_3H$ was identified by comparisons of ^1H NMR and IR spectra and melting points (66–68 °C) with those of authentic samples.

Results and Discussion

The reactions of $Ga(CH_2SiMe_3)_3$ and $In(CH_2SiMe_3)_3$ with alkali-metal hydrides have been reinvestigated, but there is no evidence to support the original conclusion of the occurrence of a stoichiometric reductive-elimination reaction with the formation of low oxidation state organogallium(I)[2] or -indium(I)[3] compounds. The current data suggests that the initial products are $KGa(CH_2SiMe_3)_3H$, $KIn(CH_2SiMe_3)_3H$, or $NaIn(CH_2SiMe_3)_3H$ depending on the specific reagents and reaction conditions. The gallium hydride derivative has been identified by an X-ray structural study and then fully characterized by hydrolysis studies, infrared and ^1H NMR spectral data, thermal stability studies, and reaction chemistry. For the case of the indium(III) hydride derivatives, crystals suitable for an X-ray structural study have not been obtained due to the instability of the compounds. Consequently, the indium hydride derivatives have been characterized by only spectroscopic and chemical means. During the course of extensive thermal decomposition studies of the indium derivatives, $KIn(CH_2SiMe_3)_4$ was isolated, identified by an X-ray structural study, and characterized. Other products of the decompositon of $KIn(CH_2SiMe_3)_3H$ include $SiMe_4$, indium metal, biphenyl, and H_2 depending on conditions. All aspects of these studies are discussed in appropriate sections.

X-ray Structural Study of $KGa(CH_2SiMe_3)_3H$. The X-ray structural study of the product from the $Ga(CH_2SiMe_3)_3$–KH reaction in benzene at 45 °C identifies the compound as a hydridotrialkylgallium(III) species, $KGa(CH_2SiMe_3)_3H$, rather than the expected dialkylgallium(I) complex, $KGa(CH_2SiMe_3)_2$. Hydrolysis experiments, infrared spectral studies, and ^1H NMR data indicate that the compound identified in the crystal and the initial bulk reaction product were the same, $KGa(CH_2SiMe_3)_3H$. The crystals isolated for the X-ray structural study had not been altered by the recrystallization process.

The crystal of $KGa(CH_2SiMe_3)_3H$ consists of discrete K^+ and $Ga(CH_2SiMe_3)_3H^-$ ions. The crystallographic asymmetric unit contains two K^+ cations and two $Ga(CH_2SiMe_3)_3H^-$ anions. The stereochemistry of the anion is illustrated in Figure 1. Selected interatomic distances and angles are presented in Table V. Each gallium(III) atom is in a tetrahedral coordination environment. The gallium(III)–carbon (sp^3) bond lengths range from 2.003 (9) through 2.048 (8) Å,

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(14) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4, pp 99–101, 149–150.

(15) Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

(16) Discrepancy indices are defined as follows: $R = [\sum ||F_o| - |F_c|| / \sum |F_o|] \times 100$ (%); $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} \times 100$ (%); GOF = $[\sum w(|F_o| - |F_c|)^2/(\text{NO} - \text{NV})]^{1/2}$, where NO = number of observations and NV = number of variables.

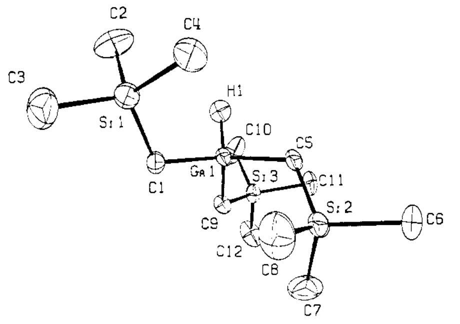

Figure 1. ORTEP-II diagram of the $Ga(CH_2SiMe_3)_3H^-$ ion (molecule A), showing the 30% probability contours of the thermal vibration ellipsoids of non-hydrogen atoms. Hydrogen atoms on carbon are omitted.

the average value being 2.029 [14] Å; C–Ga–C angles range from 107.8 (5) through 114.6 (5)°. The two independent Ga–H distances of 1.36 and 1.49 Å (as determined from a difference Fourier map) are somewhat shorter than the predicted value[17-19] of 1.61 Å. The Ga–C(α)–Si angles range from 117.3 (5) through 122.2 (6)°; all are substantially greater than the ideal tetrahedral angle of 109.47°. All other distances and angles are normal.

Infrared Spectral Study of $KGa(CH_2SiMe_3)_3H$. The infrared spectra of $KGa(CH_2SiMe_3)_3H$ and $KGa(CH_2SiMe_3)_3D$ were studied in order to identify the infrared-active bands associated with the gallium–hydrogen bond and to specify a band diagnostic of the $Ga(CH_2SiMe_3)_3H^-$ anion. A comparison of the spectra of $KGa(CH_2SiMe_3)_3H$ and $KGa(CH_2SiMe_3)_3D$ reveal only two major changes. The spectrum in the 1400–1700-cm^{-1} region has changed in appearance and a new broad band, centered at 1075 cm^{-1}, has appeared in the spectrum of $KGa(CH_2SiMe_3)_3D$. The position of this band suggests that it is due to the gallium–deuterium stretching mode. A back-calculation using this Ga–D frequency and the reduced mass ratio suggests that the gallium–hydrogen stretching mode would be centered at 1509 cm^{-1}. The position of this band would be overlapping, coincident with or masked by the Nujol bands (1400–1600 cm^{-1}), and is consistent with the observed spectrum of $KGa(CH_2SiMe_3)_3H$. A Ga–H stretching band centered in the 1500-cm^{-1} region would be at the lowest frequency observed for any gallium hydride. For comparison, the following infrared data for Ga–H stretch (cm^{-1}) have been reported: $NaGaH_4$, 1760;[20] $(HGaCl_2)_2$, 2047;[21] $HGaCl_2NMe_3$, 1968, 1949;[22] $H_2GaClNMe_3$, 1905, 1899;[22] H_3GaNMe_3, 1853;[23] H_3GaPMe_3, 1832.[24] In an attempt to better define the Ga–H stretching frequency, a sample of $KGa(CH_2SiMe_3)_3H$ was mixed with Kel-F. However, an apparent reaction prevented an infrared spectrum of the compound from being observed. The remaining gallium–hydrogen mode, which should be infrared active, would be due to a gallium–hydrogen bending motion. The comparison of the two spectra show that the Ga–H bend occurs at 480 cm^{-1} as a medium-intensity band and the Ga–D bend is at 429 cm^{-1}. Since the gallium–hydrogen stretching band is masked by Nujol, the band at 480 cm^{-1} due to the gallium–hydrogen bending motion is clearly visible and is diagnostic of the $Ga(CH_2SiMe_3)_3H^-$ anion. The infrared spectra[4] of $Ga(CH_2SiMe_3)_3$, $Ga(CH_2SiMe_3)_2Cl$, $Ga(CH_2SiMe_3)_2Cl{\cdot}N(CH_3)_3$, $Ga(CH_2SiMe_3)Cl_2$, $Ga(CH_2SiMe_3)_2Br$, and $Ga(CH_2SiMe_3)Br_2$ do not have bands around 480 cm^{-1}. Therefore, the 480-cm^{-1} band is not related to a motion associated with CH_2SiMe_3 ligands. The reported use of the absence of an infrared band in the 2100–1800-cm^{-1} region[2] to suggest that $KGa(CH_2SiMe_3)_3H$ was readily and quantitatively converted to the gallium(I) product was inappropriate. It is also important to realize that the similarity of the infrared spectra of $KGa(CH_2SiMe_3)_3H$ and of the compound[2] reported to be $KGa(CH_2SiMe_3)_2$ suggest that the two materials are one and the same compound, $KGa(CH_2SiMe_3)_3H$. The other materials reported in the low oxidation state organogallium(I) paper[2] were also probably misidentified. Since the spectra[2] reported for $NaGa(CH_2SiMe_3)_2$, $NaGa(CH_2SiMe_3)_2{\cdot}MeOC_2H_4OMe$, and $LiGa(CH_2SiMe_3)_2{\cdot}MeOC_2H_4OMe$ have bands at 480, 481, and 475 cm^{-1}, respectively, and the diagnostic gallium–hydrogen bending band occurs at 480 cm^{-1}, the above compounds should probably be reformulated as $NaGa(CH_2SiMe_3)_3H$, $NaGa(CH_2SiMe_3)_3H{\cdot}MeOC_2H_4OMe$, and $LiGa(CH_2SiMe_3)_3H{\cdot}MeOC_2H_4OMe$, respectively.

Table V. Bond Lengths (Å) and Bond Angles (deg) for $KGa(CH_2SiMe_3)_3H$

atoms	distance	
	molecule A	molecule B
Ga(1)-C(1)	2.030 (9)	2.030 (9)
Ga(1)-C(5)	2.048 (8)	2.003 (9)
Ga(1)-C(9)	2.030 (9)	2.03 (1)
Ga(1)-H(1)	1.494	1.363
Si(1)-C(1)	1.850 (9)	1.852 (9)
Si(1)-C(2)	1.89 (1)	1.88 (1)
Si(1)-C(3)	1.87 (1)	1.77 (2)
Si(1)-C(4)	1.91 (1)	1.93 (2)
Si(2)-C(5)	1.811 (9)	1.82 (1)
Si(2)-C(6)	1.91 (1)	1.90 (1)
Si(2)-C(7)	1.85 (1)	1.88 (1)
Si(2)-C(8)	1.89 (1)	1.88 (1)
Si(3)-C(9)	1.838 (9)	1.82 (1)
Si(3)-C(10)	1.85 (1)	1.91 (2)
Si(3)-C(11)	1.91 (1)	1.78 (2)
Si(3)-C(12)	1.89 (1)	1.92 (2)

atoms	angle	
	molecule A	molecule B
C(1)-Ga(1)-C(5)	112.4 (4)	111.9 (4)
C(1)-Ga(1)-C(9)	109.6 (4)	114.6 (5)
C(5)-Ga(1)-C(9)	111.9 (4)	107.8 (5)
C(1)-Ga(1)-H(1)	106.7 (3)	116.1 (3)
C(5)-Ga(1)-H(1)	110.7 (2)	106.0 (3)
C(9)-Ga(1)-H(1)	105.1 (3)	99.3 (5)
C(1)-Si(1)-C(2)	109.9 (6)	111.4 (6)
C(1)-Si(1)-C(3)	111.9 (5)	110.0 (8)
C(2)-Si(1)-C(3)	109.1 (7)	113 (1)
C(1)-Si(1)-C(4)	111.0 (5)	113.4 (6)
C(2)-Si(1)-C(4)	107.5 (7)	103.7 (9)
C(3)-Si(1)-C(4)	107.3 (7)	105 (1)
C(5)-Si(2)-C(6)	109.4 (5)	110.7 (5)
C(5)-Si(2)-C(7)	114.2 (6)	111.4 (6)
C(6)-Si(2)-C(7)	107.7 (6)	106.9 (6)
C(5)-Si(2)-C(8)	109.9 (6)	111.2 (6)
C(6)-Si(2)-C(8)	105.5 (6)	107.7 (6)
C(7)-Si(2)-C(8)	109.8 (8)	108.8 (8)
C(9)-Si(3)-C(10)	109.7 (5)	112.4 (7)
C(9)-Si(3)-C(11)	111.5 (5)	115.6 (8)
C(10)-Si(3)-C(11)	106.5 (7)	103 (1)
C(9)-Si(3)-C(12)	111.6 (5)	108.3 (9)
C(10)-Si(3)-C(12)	110.0 (8)	108 (1)
C(11)-Si(3)-C(12)	107.3 (6)	110 (1)
Ga(1)-C(1)-Si(1)	118.3 (5)	117.3 (5)
Ga(1)-C(5)-Si(2)	121.1 (4)	120.6 (5)
Ga(1)-C(9)-Si(3)	118.7 (5)	122.2 (6)

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(17) Atwood, J. L.; Hrncir, D. C.; Rogers, R. D.; Howard, J. A. K. *J. Am. Chem. Soc.* **1981**, *103*, 6787.

(18) Almenningen, A.; Anderson, G. A.; Forgaard, F. R.; Haaland, A. *Acta Chem. Scand.* **1972**, *26*, 2315.

(19) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Interscience: New York, 1980; p 326.

(20) Shirk, A. E.; Shriver, D. F. *J. Am. Chem. Soc.* **1973**, *95*, 5904.

(21) Beachley, O. T., Jr.; Simmons, R. G. *Inorg. Chem.* **1980**, *19*, 783.

(22) Greenwood, N. N.; Storr, A. *J. Chem. Soc.* **1965**, 3426.

(23) Greenwood, N. N.; Storr, A.; Wallbridge, M. G. H. *Inorg. Chem.* **1963**, *2*, 1036.

(24) Odom, J. D.; Chatterjee, K. K.; Durig, J. R. *J. Phys. Chem.* **1980**, *84*, 1843.

Chemical Reactivity of $KGa(CH_2SiMe_3)_3H$. The reactions of $KGa(CH_2SiMe_3)_3H$ with the reagents Me_3SiCl, Me_3SnCl, and CO_2 in solvents such as benzene, tetrahydrofuran, and/or dimethoxyethane were investigated in order to confirm the hydridic nature of the anion and to define its reactivity. Equations 1–3 summarize the observed reactions. Appropriate

$$KGa(CH_2SiMe_3)_3H + Me_3SiCl \rightarrow KCl + Ga(CH_2SiMe_3)_3 + Me_3SiH \quad (1)$$

$$KGa(CH_2SiMe_3)_3H + Me_3SnCl \rightarrow KCl + Ga(CH_2SiMe_3)_3 + Me_3SnH \quad (2)$$

$$KGa(CH_2SiMe_3)_3H + CO_2 \rightarrow KCO_2H + Ga(CH_2SiMe_3)_3 \quad (3)$$

products were identified by their ^1H NMR spectra. The silicon and tin hydrides are volatile at room temperature and are easily separated from $Ga(CH_2SiMe_3)_3$ or an ether adduct on the vacuum line. The ^1H NMR spectra of Me_3SiH[12] and Me_3SnH[11] are very distinctive as the resonances of the Si–H or Sn–H are multiline patterns, those of the methyl groups are doublets and the integrated intensities are in a ratio of 1 to 9. The identity of the gallium product was confirmed directly from the reaction without purification (Si,Sn reaction) by its ^1H NMR spectrum or the $Ga(CH_2SiMe_3)_3$ was purified and/or isolated by vacuum distillation (CO_2 reaction). Only one resonance at +0.13 is observed for pure $Ga(CH_2SiMe_3)_3$ in benzene solution. The methylene proton resonance is probably coincident with that for Me–Si. For several reactions of CO_2, the soluble gallium product (which was not purified) exhibited an NMR spectrum in benzene that had two or sometimes three very closely spaced lines around 0.13 signifying that the product was impure. A vacuum distillation of the impure material gave pure $Ga(CH_2SiMe_3)_3$. The identity of the potassium formate (KCO_2H) was confirmed by its infrared spectrum and melting point. The products of all three reactions were formed in high yields (greater than 70%), but no attempt was made to measure the precise quantities of products by overcoming the experimental problems generated by liquids spread over flasks, solids isolated on frits, or volatile compounds mixed with solvents. The observed reactions that produce well-known compounds are not novel, but they serve to confirm the presence of a reactive and nucleophilic hydride ion.

Reactions of $In(CH_2SiMe_3)_3$ with Alkali-Metal Hydrides and Characterization of $KIn(CH_2SiMe_3)_3H$ and $KIn(CH_2SiMe_3)_4$. The reactions of $In(CH_2SiMe_3)_3$ with alkali-metal hydrides (NaH, KH) have been investigated, but there is no evidence to support the occurrence of reductive-elimination reactions of organoindium(III) hydrides. When excess KH was added to a pentane solution of $In(CH_2SiMe_3)_3$ and the resultant solution stirred for 2 days at room temperature, a heavy precipitate but no $SiMe_4$ or noncondensable gas were formed. Extraction of the reaction mixture with the reaction solvent produced only a very small amount of an unidentified yellow viscous liquid. Further extraction with benzene led to the isolation of $KIn(CH_2SiMe_3)_3H$ in approximately 80% yield based on $In(CH_2SiMe_3)_3$. The product was identified by its analysis (hydrolysis studies with resultant formation of H_2 and $SiMe_4$), its infrared spectrum and comparison with that of $KIn(CH_2SiMe_3)_3D$, and its ^1H NMR spectrum. The compound when initially isolated is a colorless solid, but it decomposes at room temperature, as indicated by a color change from colorless to black, within several days. All attempts to grow crystals of $KIn(CH_2SiMe_3)_3H$ from a benzene solution were frustrated by decomposition as shown by formation of an indium mirror.

The infrared spectra of $KIn(CH_2SiMe_3)_3H$ and $KIn(CH_2SiMe_3)_3D$ have been compared in order to identify the bands associated with the indium–hydrogen bond. The band associated with the In–H stretching mode occurs as a broad, strong band in the 1300–1500-cm^{-1} region and overlaps with the bands of the Nujol mulling agent as was observed for $KGa(CH_2SiMe_3)_3H$. (An apparent reaction between Kel-F and $KIn(CH_2SiMe_3)_3H$ prevents the infrared spectrum from being observed). Upon deuterium substitution, the broad band in the 1300–1500-cm^{-1} region disappears and the new broad band at 1025 cm^{-1} can be assigned to the In–D stretching mode. A further comparison of the spectra suggest that the bending modes occur as bands at 440 (In–H) and 390 cm^{-1} (In–D).

The new compound $KIn(CH_2SiMe_3)_4$ has been isolated from a reaction mixture of $In(CH_2SiMe_3)_3$, KH, and pentane at room temperature. In contrast to the previous experiment, $In(CH_2SiMe_3)_3$ and KH were combined in the absence of solvent at room temperature in the drybox but significant heat, indicative of an exothermic reaction, was generated. Finally, pentane was added but the reaction mixture was not stirred. Large colorless crystals were observed to have grown out of a black insoluble reaction solid after 2 days. These crystals were mechanically isolated, were identified as $KIn(CH_2SiMe_3)_4$ by an X-ray structural study (see following section), and were characterized by their melting point, infrared and ^1H NMR spectra, and solubility properties. It is of interest to note that $KIn(CH_2SiMe_3)_4$ and $KIn(CH_2SiMe_3)_3H$ are readily distinguishable by their ^1H NMR spectra in benzene solution. The compound $KIn(CH_2SiMe_3)_4$ has lines at 0.30 (SiMe) and −1.05 (CH_2), whereas the lines for $KIn(CH_2SiMe_3)_3H$ occur at 0.33 (SiMe) and −0.83 (CH_2). Both compounds are insoluble in saturated hydrocarbon solvents such as pentane and cyclohexane but soluble in benzene.

When 5.28 mmol of $In(CH_2SiMe_3)_3$, excess NaH, and hexane were heated in a previously evacuated sealed tube at a bath temperature of 68 °C for 18 h (experimental conditions for the reported synthesis[3] of $NaIn(CH_2SiMe_3)_2$), a heavy precipitate but only a trace of noncondensable gas and $SiMe_4$ (~0.02 mmol) were formed. The indium-containing products from this reaction were also isolated by benzene extraction and were identified as a mixture of $NaIn(CH_2SiMe_3)_3H$ and another closely related material, probably $NaIn(CH_2SiMe_3)_4$. The repeated extraction of the product mixture with pentane, in which $NaIn(CH_2SiMe_3)_3H$ is more soluble than $NaIn(CH_2SiMe_3)_4$, leads to a partial separation of the compounds. Good analytical data indicative of pure $NaIn(CH_2SiMe_3)_3H$ or $NaIn(CH_2SiMe_3)_4$ have not been obtained. However, the comparison of analytical data with ^1H NMR integration and infrared spectral data supports the hypothesis of a product mixture. The infrared-active In–H stretching mode for $NaIn(CH_2SiMe_3)_3H$ occurs as a broad band in the 1300–1500-cm^{-1} region, but it is coincident with the bands of Nujol. The In–H bending mode occurs at 475 cm^{-1}. These assignments have been confirmed with spectra of products from NaD reactions. The comparison of these data and that for the material identified[3] as $NaIn(CH_2SiMe_3)_2$ suggest that the original product was probably a mixture of $NaIn(CH_2SiMe_3)_3H$ with small amounts of $NaIn(CH_2SiMe_3)_4$ and another unidentified impurity. The similarity of the diagnostic indium–hydrogen rocking mode at 475 cm^{-1} and the observation of a medium-strength band at 480 cm^{-1} for the compound[3] previously reported to be $NaIn(CH_2SiMe_3)_2$ support the hypothesis. However, we have not been able to reproduce the ^1H NMR spectrum previously reported.[3] It is of interest to note that solid samples containing $NaIn(CH_2SiMe_3)_3H$ turned black within a few days at room temperature and those in sealed melting point tubes turned brown at 107 °C and black at 115 °C and began to melt at 160 °C. Bubbling was noticed at about 190 °C. Samples of $NaIn(CH_2SiMe_3)_4$ started to darken at about 160 °C and melted to a gray liquid

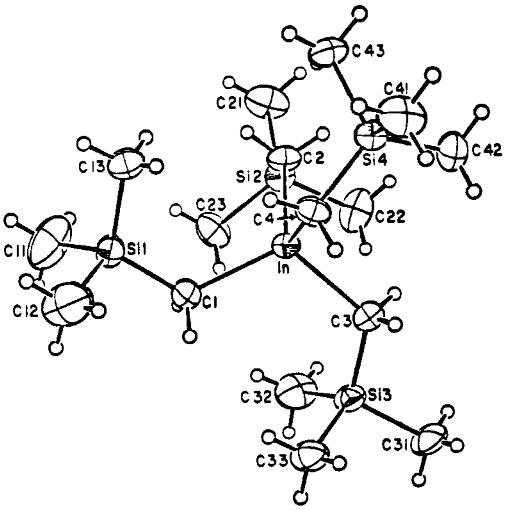

Figure 2. ORTEP-II diagram of the $In(CH_2SiMe_3)_4^-$ ion, showing the 30% probability contours of the thermal vibration ellipsoids of nonhydrogen atoms. Hydrogen atoms are shown, artifically reduced, in their idealized positions.

at 220–223 °C. The material[3] $NaIn(CH_2SiMe_3)_2$ was reported to undergo a series of color changes from 125 to 200 °C and then turn black at 235–245 °C.

The observed products from reactions of $In(CH_2SiMe_3)_3$ with alkali-metal hydrides were different when benzene was used as the reaction medium. Tetramethylsilane was observed as a major product, but the amount was dependent on the temperature and reaction time. For example, when 5.32 mmol of $In(CH_2SiMe_3)_3$ and excess NaH were heated at a bath temperature of 110 °C for 2 months, 14.69 mmol of $SiMe_4$ (2.76 mol of $SiMe_4$/mol of In) and an indium mirror but no noncondensable gas were observed. When a mixture of $NaIn(CH_2SiMe_3)_3H$ and $NaIn(CH_2SiMe_3)_4$ in benzene, contained in a sealed NMR tube, was kept at room temperature for 9 weeks, only about 10% of the CH_2SiMe_3 groups were converted to $SiMe_4$ but an indium mirror was formed. However, heating of this tube at a bath temperature of 110 °C for 3 h converted approximately half of the CH_2SiMe_3 groups to $SiMe_4$. In addition four separated pairs of $SiCH_3/CH_2$ lines were observed by ^1H NMR. After an additional 24 h at 110 °C, all CH_2SiMe_3 groups were converted to $SiMe_4$. The potassium compound $KIn(CH_2SiMe_3)_3H$ also decomposed in benzene to form $SiMe_4$, but the reactions were faster. The decomposition reactions of the indium(III) hydrides in benzene are discussed in detail in another section.

X-ray Structural Study of $KIn(CH_2SiMe_3)_4$. The tetraalkylindium(III) species, $KIn(CH_2SiMe_3)_4$, was isolated from a reaction in which liquid $In(CH_2SiMe_3)_3$ and KH were combined in the drybox and then pentane was added by vacuum distillation. The crystal consists of discrete K^+ and $In(CH_2SiMe_3)_4^-$ ions between which there are no abnormally short contacts. Selected interatomic distances and interatomic angles are presented in Table VI. The labeling of atoms within the $In(CH_2SiMe_3)_4^-$ anion is shown in Figure 2. The $In(CH_2SiMe_3)_4^-$ anion consists of an indium(III) center, which is surrounded tetrahedrally by four (trimethylsilyl)methyl ligands. The individual indium(III)–carbon (sp^3) bond lengths are In–C(1) = 2.236 (4), In–C(2) = 2.234 (4), In–C(3) = 2.235 (4), and In–C(4) = 2.251 (4) Å; the average value is 2.239 [8] Å.[25] This may be compared with In–C(sp^3) distances of 2.239 (3) Å in $KInMe_4$[26] and 2.26 (2) Å in $CsInMe_4$,[26] and with the In–C(sp^2) distance of 2.230 (3) Å in $NaInPh_4$.[27] There are slight distortions from regular tetrahedral symmetry about the indium(III) center, with individual C–In–C angles ranging from C(3)–In–C(4) = 104.67 (14) through C(2)–In–C(3) = 112.00 (14)°; in the absence of any electronic cause, these distortions are assigned to steric effects.

Table VI. Bond Lengths (Å) and Bond Angles (deg) for $KIn(CH_2SiMe_3)_4$

(A) Metal-Carbon (Methylene) Distances			
In–C(1)	2.236 (4)	In–C(3)	2.235 (4)
In–C(2)	2.234 (4)	In–C(4)	2.251 (4)
(B) Carbon (Methylene)–Silicon Distances			
C(1)–Si(1)	1.840 (4)	C(3)–Si(3)	1.832 (4)
C(2)–Si(2)	1.840 (4)	C(4)–Si(4)	1.837 (4)
(C) Silicon–Carbon (Methyl) Distances			
Si(1)–C(11)	1.812 (7)	Si(3)–C(31)	1.876 (5)
Si(1)–C(12)	1.829 (6)	Si(3)–C(32)	1.852 (5)
Si(1)–C(13)	1.830 (6)	Si(3)–C(33)	1.861 (5)
Si(2)–C(21)	1.869 (5)	Si(4)–C(41)	1.862 (5)
Si(2)–C(22)	1.846 (5)	Si(4)–C(42)	1.858 (5)
Si(2)–C(23)	1.850 (5)	Si(4)–C(43)	1.869 (4)
(D) Interactions Involving the Potassium Ion[a,b]			
K···C(2)	3.294 (4)	K···C(31)	3.284 (5)
K···C(4)	3.126 (4)	K···In	3.537 (1)
K···H(1A)	2.65	K···H(31B)	2.85
K···H(2A)	2.86	K···H(33C)	2.88
K···H(2B)	2.94	K···H(4A)	2.58
K···H(21C)	2.95	K···H(43B)	2.65
(E) Carbon–Indium–Carbon Angles			
C(1)–In–C(2)	109.28 (14)	C(2)–In–C(3)	112.00 (14)
C(1)–In–C(3)	111.74 (14)	C(2)–In–C(4)	109.78 (13)
C(1)–In–C(4)	109.26 (14)	C(3)–In–C(4)	104.67 (14)
(F) Indium–Carbon–Silicon Angles			
In–C(1)–Si(1)	121.64 (20)	In–C(3)–Si(3)	123.59 (20)
In–C(2)–Si(2)	118.60 (18)	In–C(4)–Si(4)	118.29 (18)
(G) Carbon–Silicon–Carbon Angles			
C(1)–Si(1)–C(11)	112.09 (27)	C(11)–Si(1)–C(12)	105.61 (33)
C(1)–Si(1)–C(12)	110.37 (26)	C(12)–Si(1)–C(13)	105.83 (29)
C(1)–Si(1)–C(13)	114.49 (23)	C(13)–Si(1)–C(11)	107.88 (31)
C(2)–Si(2)–C(21)	112.89 (20)	C(21)–Si(2)–C(22)	106.75 (23)
C(2)–Si(2)–C(22)	109.95 (20)	C(22)–Si(2)–C(23)	110.49 (22)
C(2)–Si(2)–C(23)	111.18 (19)	C(23)–Si(2)–C(21)	105.42 (22)
C(3)–Si(3)–C(31)	110.97 (21)	C(31)–Si(3)–C(32)	106.86 (23)
C(3)–Si(3)–C(32)	113.65 (21)	C(32)–Si(3)–C(33)	107.56 (22)
C(3)–Si(3)–C(33)	110.86 (20)	C(33)–Si(3)–C(31)	106.59 (22)
C(4)–Si(4)–C(41)	112.18 (19)	C(41)–Si(4)–C(42)	107.37 (22)
C(4)–Si(4)–C(42)	109.88 (19)	C(42)–Si(4)–C(43)	108.23 (20)
C(4)–Si(4)–C(43)	111.12 (18)	C(43)–Si(4)–C(41)	107.90 (20)

[a] K···C < 3.3 Å, and K···H < 3.0 Å. [b] All K···H distances involve hydrogen atoms in calculated positions based upon the X-ray-determined value of C–H = 0.95 Å.

The In–C(α)–Si angles are all substantially increased from the regular tetrahedral value of 109.47°; individual values are In–C(1)–Si(1) = 121.64 (20), In–C(2)–Si(2) = 118.60 (18), In–C(3)–Si(3) = 123.59 (20), and In–C(4)–Si(4) = 118.29 (18)°; the average such value is 120.5 [25]°. Such increases are normal in transition-metal alkyls,[28] but here may well result from intramolecular ligand···ligand repulsions.

All other distances and angles are normal. C(α)–Si distances range from 1.832 (4) through 1.840 (4) Å (average 1.837 [4] Å) and Si–Me distances are 1.812 (7)–1.876 (5) Å (average 1.850 [18] Å); C(α)–Si–C(Me) angles are all slightly greater than the ideal tetrahedral value (range 109.95 (20)–114.49 (23)°, average 111.6 [15]°), while nearly all C(Me)–Si–C(Me) angles are less than 109.47° (range 105.42 (22)–110.49 (22)°, average 107.2 [14]°).

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(25) Esd's of average values, calculated by the "scatter formula" below, are enclosed in square brackets.

$$[\sigma] = [\sum_{i=1}^{i=N}(\bar{d} - d_i)^2/(N-1)]^{1/2}$$

(26) Hoffman, K.; Weiss, E. *J. Organomet. Chem.* **1973**, *50*, 17.

(27) Hoffman, K.; Weiss, E. *J. Organomet. Chem.* **1973**, *50*, 25.

(28) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 2454.

Thermal Decomposition Studies. The nature of the thermal stability and the subsequent decomposition reactions of KGa(CH$_2$SiMe$_3$)$_3$H and KIn(CH$_2$SiMe$_3$)$_3$H have been studied in order to answer questions concerning the origin of the decomposition products and the occurrence of the proposed reductive-elimination reactions. The pure compound KGa(CH$_2$SiMe$_3$)$_3$H does not show any signs of thermal decomposition until a temperature of 200 °C is exceeded. Samples of KGa(CH$_2$SiMe$_3$)$_3$H can be recovered unchanged from benzene solution after refluxing for 5 days in a previously evacuated tube at a bath temperature of 105–110 °C. In contrast, KIn(CH$_2$SiMe$_3$)$_3$H and, apparently, NaIn(CH$_2$SiMe$_3$)$_3$H decompose readily at room temperature and in benzene solution. The products of the indium hydride decompositions in benzene solution include SiMe$_4$, KIn(CH$_2$SiMe$_3$)$_4$, indium metal, biphenyl, and hydrogen. Since SiMe$_4$ was a product of both the thermal decomposition and the original proposed reductive-elimination reaction, a goal of our work was to define the nature of the reaction path that led to the formation of SiMe$_4$.

The nature of the products from the decomposition of KIn(CH$_2$SiMe$_3$)$_3$H in benzene and cyclohexane in the presence or absence of excess KH provide the data to define the reactions that produce SiMe$_4$. The extent of decomposition and the specific products depend on all of the reaction conditions including the quantities of KIn(CH$_2$SiMe$_3$)$_3$H and KH, temperature, and time of reaction. Heating a 0.428-mmol sample of KIn(CH$_2$SiMe$_3$)$_3$H in benzene for 16 h at 85 °C produced an indium mirror, 0.092 mmol of H$_2$, and 0.225 mmol of SiMe$_4$(0.526 mol of SiMe$_4$/mol of In). In comparison, a 1.057-mmol sample in benzene was heated for 27 days at a bath temperature of 110 °C and an indium mirror, 0.402 mmol of H$_2$, 0.929 mmol of SiMe$_4$ (0.879 mol of SiMe$_4$/mol of In), and 0.71 mmol of biphenyl were formed. The biphenyl was identified by melting point, infrared, and ^{1}H NMR data. When excess KH (2.49 mmol) was added to KIn(CH$_2$SiMe$_3$)$_3$H (0.589 mmol) in benzene and the sample was heated at 85 °C for 3 days, only 0.053 mmol of H$_2$ but 0.815 mmol of SiMe$_4$ (1.38 mol of SiMe$_4$/mol of In), biphenyl, and an indium mirror were formed. More extensive heating of a different sample in benzene containing 1.146 mmol of KIn(CH$_2$SiMe$_3$)$_3$H and 2.10 mmol of KH for 30 days at 110 °C produced 0.918 mmol of H$_2$, 3.412 mmol of SiMe$_4$ (2.98 mol of SiMe$_4$/mol of In), and 1.03 mmol of biphenyl. In addition, a black, extremely pyrophoric solid was formed. A decomposition study of KIn(CH$_2$SiMe$_3$)$_3$H (2.08 mmol) in cyclohexane yielded only 0.063 mmol of H$_2$ and 0.084 mmol of SiMe$_4$ after the sample was heated for 3 days at a bath temperature of 110 °C. However, all KIn(CH$_2$SiMe$_3$)$_3$H had decomposed into an uncharacterized cyclohexane and benzene-insoluble brown solid.

The data for the decomposition studies indicate that KIn(CH$_2$SiMe$_3$)$_3$H decomposes in benzene solution to form indium metal, SiMe$_4$, biphenyl, and varying amounts of H$_2$. The presence of KH accelerates the decomposition reaction and enhances the formation of SiMe$_4$. However, even in the absence of KH all CH$_2$SiMe$_3$ groups can be converted to SiMe$_4$ within 2 months at room temperature in benzene. However, it is important to remember the observation that the decomposition of KIn(CH$_2$SiM$_3$)$_3$H in cyclohexane did not produce significant amounts of SiMe$_4$, only 0.04 mmol of SiMe$_4$/mol of KIn(CH$_2$SiMe$_3$)$_3$H. The data suggest (1) a simple reductive elimination of SiMe$_4$ from MIn(CH$_2$SiMe$_3$)$_3$H is not a viable pathway to SiMe$_4$ formation, (2) KIn(CH$_2$SiMe$_3$)$_3$H decomposes to form SiMe$_4$ significantly faster in benzene than cyclohexane, (3) KIn(CH$_2$SiMe$_3$)$_3$H decomposes faster than NaIn(CH$_2$SiMe$_3$)$_3$H, and (4) biphenyl is observed as a product from the decomposition of KIn(CH$_2$SiMe$_3$)$_3$H in benzene.

All of our available data including the formation of MIn(CH$_2$SiMe$_3$)$_4$, SiMe$_4$, biphenyl, and varying amounts of H$_2$ can be explained by the existence of and the occurrence of known reactions of alkali-metal alkyls,[29-31] presumably KCH$_2$SiMe$_3$ and NaCH$_2$SiMe$_3$. These compounds can be formed by the dissociation of CH$_2$SiMe$_3^-$ from MIn(CH$_2$SiMe$_3$)$_3$H (eq 4). The dissociation of H$^-$ from In(CH$_2$SiMe$_3$)$_3$H$^-$ (eq 4) and subsequent recombination of In(CH$_2$SiMe$_3$)$_3$ with CH$_2$SiMe$_3^-$ would yield In(CH$_2$SiMe$_3$)$_4^-$, an observed product (eq 5). If CH$_2$SiMe$_3^-$ is present in solution, the formation of SiMe$_4$ can then arise from the reactions of MCH$_2$SiMe$_3$ with benzene or H$_2$, typical reactions of sodium and potassium alkyls.[29-31] The hydrogen is believed to result from a very rapid decomposition reaction of InH$_3$, a product from a rapid disproportionation or ligand-exchange reaction of In(CH$_2$SiMe$_3$)$_2$H (eq 8). Our data suggest that In(CH$_2$SiMe$_3$)$_2$H does not decompose directly to indium metal, SiMe$_4$, and possibly other products by a reductive-elimination reaction, but it cannot be ruled out completely. Similarly, we cannot discard the possibility that H$_2$ arises from the decomposition of InH$_4^-$. However, the apparent stability of In(CH$_2$SiMe$_3$)$_3$H$^-$ suggests that InH$_4^-$ might not decompose without prior dissociation of H$^-$. Thus, the varying amounts of H$_2$ would result from a competition[30,31] of MCH$_2$SiMe$_3$ for H$_2$ and C$_6$H$_6$. When decomposition reactions occurred in saturated hydrocarbon solvents, minimum amounts of SiMe$_4$ and H$_2$ were formed. The compound NaIn(CH$_2$SiMe$_3$)$_4$ does not decompose or form SiMe$_4$ in refluxing cyclohexane. The observed formation of biphenyl from KIn(CH$_2$SiMe$_3$)$_3$H but not NaIn(CH$_2$SiMe$_3$)$_3$H further supports the hypothesis of the reaction of MCH$_2$SiMe$_3$ with benzene and formation of MC$_6$H$_5$ (eq 6). Biphenyl is an observed product[32] from the reaction of KC$_6$H$_5$ with benzene after subsequent pyrolysis at 150 °C. The other product, potassium metal,[32] is consistent with our observation of a black pyrophoric solid from KIn(CH$_2$SiMe$_3$)$_3$H decompositions in benzene. Sodium alkyls also metalate benzene[33] to form NaC$_6$H$_5$ but do not react further to form biphenyl,[32] a report consistent with our observations. Further support for the existence of indium–phenyl compounds comes from our observations of products from decompositions of NaIn(CH$_2$SiMe$_3$)$_3$H/NaIn(CH$_2$SiMe$_3$)$_4$ in benzene. The four sets of SiMe/CH$_2$ line pairs observed in the ^{1}H NMR spectrum suggest the presence of species of the type In(CH$_2$SiMe$_3$)$_{4-x}$(C$_6$H$_5$)$_x^-$.

$$\mathrm{MH} + \mathrm{In(CH_2SiMe_3)_3} \rightleftarrows \mathrm{MIn(CH_2SiMe_3)_3H} \rightleftarrows \mathrm{MCH_2SiMe_3} + \mathrm{In(CH_2SiMe_3)_2H} \quad (4)$$

$$\mathrm{In(CH_2SiMe_3)_3} + \mathrm{MCH_2SiMe_3} \rightleftarrows \mathrm{MIn(CH_2SiMe_3)_4} \quad (5)$$

$$\mathrm{MCH_2SiMe_3} + \mathrm{C_6H_6} \rightarrow \mathrm{SiMe_4} + \mathrm{MC_6H_5} \quad (6)$$

$$\mathrm{MCH_2SiMe_3} + \mathrm{H_2} \rightarrow \mathrm{SiMe_4} + \mathrm{MH} \quad (7)$$

$$3\mathrm{In(CH_2SiMe_3)_2H} \rightleftarrows 2\mathrm{In(CH_2SiMe_3)_3} + \mathrm{InH_3} \quad (8)$$

$$\mathrm{InH_3} \rightarrow \mathrm{In} + {}^3/_2\mathrm{H_2} \quad (9)$$

Our hypothesis to explain the experimental observations in the In(CH$_2$SiMe$_3$)$_3$/MH systems can also be used to account for observations in the InMe$_3$/MH systems.[34,35] The reaction of 1 mmol of InMe$_3$ with KH in benzene at 25 °C for 12 h

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(29) Coates, G. E.; Green, M. L. H.; Wade, K. "Organometallic Compounds", 3rd ed.; Methuen: London, 1967; Vol. 1, pp 46–47.

(30) Schlosser, M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 287.

(31) Gilman, H.; Jacoby, A. L.; Ludeman, H. *J. Am. Chem. Soc.* **1938**, *60*, 2336.

(32) Morton, A. A.; Lanpher, E. J. *J. Org. Chem.* **1958**, *23*, 1639.

(33) Bryce-Smith, D.; Turner, E. E. *J. Chem. Soc.* **1953**, 861.

(34) Beachley, O. T., Jr.; Tessier-Youngs, C.; Simmons, R. G.; Hallock, R. B. *Inorg. Chem.* **1982**, *21*, 1970.

(35) Gavrilenko, V. V.; Kolesove, V. S.; Zakharin, L. I. *J. Gen. Chem. USSR* (*Engl. Transl.*) **1979**, *49*, 1623; **1977**, *47*, 881.

produced 0.159 mmol of CH_4 and indium metal.[34] Similarly, heating 1 mmol of $InMe_3$ and NaH in dimethoxyethane at 130 °C for 12 h gave only 0.120 mmol of CH_4 and indium metal.[34] The indium hydride $MInMe_3H$ was most likely formed but was not isolated. Dissociation of $MInMe_3H$ to form $InMe_2H$ and MMe followed by subsequent reaction with solvent or possibly H_2 would yield CH_4. Benzene is probably more reactive with KMe than dimethoxyethane is with NaMe. Russian workers[35] have reported that $KInMe_3H$ can be prepared in refluxing THF after a reaction time of 5 h. Decomposition products were observed but were not identified. Percentage yields of $KInMe_3H$ were not reported either. Similar observations were reported for $NaInMe_3H$. Heating $NaInMe_3H$ at 100 °C produced $NaInMe_4$, indium metal, and H_2. The previously suggested pathway[35] involved a disproportionation reaction of $NaInMe_3H$ to form $NaInMe_4$ and $NaInH_4$. Decomposition of $NaInH_4$ would give the other observed products, indium metal and hydrogen. However, an alternative and simpler route for the formation of $NaInMe_4$ would involve dissociation of NaMe from $NaInMe_3H$ to form $InMe_2H$. Rapid disproportionation of $InMe_2H$ would give $InMe_3$ and InH_3, or indium metal and hydrogen after rapid decomposition. Subsequent reaction of NaMe with $InMe_3$, from $InMe_2H$ or from $NaInMe_3H$ after dissociation of NaH, would give the observed product, $NaInMe_4$.

Conclusions

The previous literature[2,3] suggested that alkali-metal hydrides reacted with $Ga(CH_2SiMe_3)_3$ and $In(CH_2SiMe_3)_3$ to form compounds such as $KGa(CH_2SiMe_3)_2$ and $NaIn(CH_2SiMe_3)_2$ and $SiMe_4$ by stoichiometric reductive-elimination reactions. These experimental observations have not been reproduced. Instead, the types of compounds suggested to be the intermediates in the proposed reductive-elimination reactions,[2,3] $KGa(CH_2SiMe_3)_3H$ and $KIn(CH_2SiMe_3)_3H$, were isolated. The gallium hydride derivative has been observed to be thermally stable under the normal synthetic conditions and does not convert to $KGa(CH_2SiMe_3)_2$ and $SiMe_4$ as originally proposed.[2] In contrast, $KIn(CH_2SiMe_3)_3H$ decomposes at room temperature but $SiMe_4$ is only a significant product when this indium hydride is dissolved in benzene. These differences in thermal stability between $KGa(CH_2SiMe_3)_3H$ and $KIn(CH_2SiMe_3)_3H$ can be related to the ease of the dissociative reactions of the four coordinate anions and their relative metal–carbon bond strengths. Reductive elimination does not appear to be an important reaction path for these organo group 3 derivatives. It is even doubtful that group 3 compounds of the type MR_2H (M = Ga, In) are transformed by reductive-elimination reactions. The current data suggest that ligand-exchange reactions will occur instead. These ideas are being investigated further, and our results will be the subject of a future communication.

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Registry No. $KGa(CH_2SiMe_3)_3H$, 87461-80-1; $KGa(CH_2SiMe_3)_3D$, 87461-81-2; $Ga(CH_2SiMe_3)_3 \cdot NMe_3$, 72709-15-0; $KIn(CH_2SiMe_3)_3H$, 87461-82-3; $KIn(CH_2SiMe_3)_3D$, 87461-83-4; $KIn(CH_2SiMe_3)_4$, 87461-84-5; $NaIn(CH_2SiMe_3)_3H$, 87461-85-6; $NaIn(CH_2SiMe_3)_4$, 87461-86-7; $Ga(CH_2SiMe_3)_3$, 72708-53-3; $In(CH_2SiMe_3)_3$, 69833-15-4; KH, 7693-26-7; KD, 13886-67-4; $SiMe_4$, 75-76-3; CO_2, 124-38-9; Me_3SnCl, 1066-45-1; Me_3SiCl, 75-77-4; Me_3SiH, 993-07-7; NaH, 7646-69-7; biphenyl, 92-52-4.

Supplementary Material Available: Listings of calculated positions for hydrogen atoms (Table IV-S-In), anisotropic thermal parameters (Tables VII-S-Ga and VIII-S-In) for $KGa(CH_2SiMe_3)_3H$ and $KIn(CH_2SiMe_3)_4$, and observed and calculated structure factor amplitudes (23 pages). Ordering information is given on any current masthead page.