initiated by decarbonylation, which occurs at a significant rate at 80 °C. The product **2** was the first of several that were formed. It was formed by decarbonylation and the activation of one of the CH bonds on the *C*-methyl group. The ynamine ligand was transformed into a μ-η^3-aminoallenyl ligand and a bridging hydride ligand. A triply bridging aminoallenyl ligand was formed by a decarbonylation and CH activation at the *C*-methyl group of the ynamine ligand in the osmium complex $Os_3(CO)_{10}(\mu\text{-}MeC_2NMe_2)$ to yield the complex $Os_3(CO)_{10}(\mu\text{-}H_2CCNMe_2)(\mu\text{-}H)$ (eq 2).[2c] Compound **2** was found to add CO at room temperature to form compound **4** by converting the μ-η^3-aminoallenyl ligand to a μ-η^2-aminoallenyl ligand. At 75 °C, **4** lost CO to re-form **2**. However, at 75 °C in a closed system, compound **4** was slowly converted to **3**. This is believed to occur by decarbonylation to **2** and a slow readdition of CO to yield **3**, which is simply a more stable isomer of **4**. With prolonged heating **3** was converted to the even more stable isomer **5**, which can be decarbonylated to yield **6**. However, we also found that substantial amounts of **6** were formed by heating **2** to 100 °C for 10 min in the absence of CO. Since compound **5** was not significantly converted to **6** and **6** does not add CO to yield **5** under these conditions, we believe that **2** can probably also be converted to **6** without the intermediacy of **5**.

We have shown previously that the manganese complex $Mn_2(CO)_8(\mu\text{-}MeC_2NEt_2)$, which is structurally very similar to **1**, also undergoes a series of hydrogen-shift transformations to yield an isomer containing a bridging aminoallene ligand, an isomer similar to **5** that contains a bridging η^2-metalated aminoallyl ligand, and a decarbonylated complex containing a bridging η^4-metalated aminoallyl ligand similar to that proposed for **6**.[12] In the present study, we have characterized yet another isomeric form of the ynamine ligand, namely, the vinyl(amino)carbene as found in compound **3**. In contrast to the manganese study, we have also demonstrated that hydride-containing intermediates are involved in the hydrogen-shift processes.

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Supplementary Material Available: Tables of hydrogen atom positional parameters and anisotropic thermal parameters for **2**–**4** (11 pages); listings of structure factor amplitudes (47 pages). Ordering information is given on any current masthead page.

Chemistry of Organoindium Hydrides. Synthesis, Characterization, and Crystal Structure of $K\{H[In(CH_2CMe_3)_3]_2\}$

O. T. Beachley, Jr.,* Sun-Hua L. Chao, Melvyn Rowen Churchill,* and Ronald F. See

Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214

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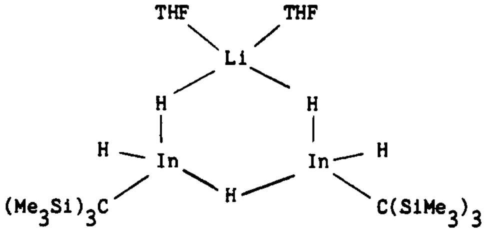
Two new organoindium hydrides $K\{H[In(CH_2CMe_3)_3]_2\}$ and $K[HIn(CH_2CMe_3)_3]$ have been prepared and fully characterized according to their physical properties, partial elemental analyses, molecular weight studies, and IR and ^1H and ^{13}C NMR spectral studies. The unique hydrogen atoms bonded to indium in the two compounds provide characteristic infrared bands and ^1H NMR resonances, which have been identified by comparative studies with the corresponding deuterium derivatives. The indium hydride $K\{H[In(CH_2CMe_3)_3]_2\}$ crystallizes in the monoclinic space group *C*2/*c* (No. 15) with cell parameters of a = 22.243 (5) Å, b = 17.021 (3) Å, c = 21.290 (3) Å, β = 110.350 (10)°, V = 7557 (2) Å^3, and Z = 8. Final discrepancy indicies were R = 6.32% and R_w = 4.97% for all 4947 independent data and R = 2.96% and R_w = 3.67% for those 2924 reflections with $|F_o| > 6\sigma(F_o)$. The crystal is composed of K^+ cations and $(Me_3CCH_2)_3In\text{-}H\text{-}In(CH_2CMe_3)_3^-$ anions, each of which lie on 2-fold axes. In–C(neopentyl) distances range from 2.199 (6) to 2.231 (6) Å (averaging 2.213 Å), while In–(μ-H) distances are 1.933 (15) and 1.950 (23) Å. In–H–In angles are 151 (5) and 161 (5)°.

Introduction

Compounds which contain indium–hydrogen bonds are difficult to prepare, isolate, and fully characterize. Thus, no indium hydride has been fully characterized previously by elemental analyses, molecular weight studies, diagnostic spectroscopic data, and X-ray structural studies. The only compound with indium–hydrogen bonds for which an X-ray structural study has been reported is $[(Me_3Si)_3C]In(H)(\mu\text{-}H)Li(THF)_2(\mu\text{-}H)In(\mu\text{-}H)(H)[C(SiMe_3)_3]$.[1]



However, the unique hydrogen atoms were not located. The presence of indium–hydrogen bonds was inferred from infrared and $^6Li\{^1H\}$ NMR spectral data. This compound was too unstable to permit satisfactory carbon and hydrogen analyses. The closely related compounds $M[InR_3H]$ (M = Na, K; R = Me[2], Et[2], CH_2SiMe_3[3]) are also unstable and decompose to $MInR_4$, MH, indium metal, and hydrogen. Thus, when $In(CH_2SiMe_3)_3$ and KH were combined in the absence of solvent, $KIn(CH_2SiMe_3)_4$ was isolated and was fully characterized.[3]

In this paper, the syntheses and characterizations of two novel compounds with indium–hydrogen bonds, K{H[In-

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$(CH_2CMe_3)_3]_2\}$ and $K[HIn(CH_2CMe_3)_3]$, are reported. Both compounds appear to be stable at room temperature and have been fully characterized.

Experimental Section

All compounds described in this investigation were extremely sensitive to oxygen and moisture and were manipulated in a standard vacuum line or under a purified argon atmosphere. The starting compound $In(CH_2CMe_3)_3$ was prepared and purified by the literature method.[4] The reagents KH and KD were obtained from Aldrich Chemical Co. and were washed with pentane to remove oil prior to use. Solvents were dried by conventional procedures. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY, or by E + R Microanalytical Laboratory, Inc., Corona, NY. Infrared spectra of Nujol mulls between CsI plates were recorded by means of a Perkin-Elmer 683 spectrometer. The ^1H NMR spectra were recorded at 400 MHz by means of a Varian VXR-400 S spectrometer, or at 300 MHz with a Varian Gemini-300 spectrometer. Proton chemical shifts are reported in δ units (ppm) and are referenced to C_6H_6 at δ 7.15 ppm. The $^{13}C\{^1H\}$ NMR spectra were recorded at 75 MHz by means of a Varian Gemini-300 spectrometer or at 101 MHz by means of a Varian VXR-400 S spectrometer. The proton-decoupled ^{13}C spectra are reported relative to benzene at δ 128.0 ppm. All samples for NMR spectra were contained in sealed NMR tubes. Melting points were observed in sealed capillaries. Molecular weights were measured cryoscopically in benzene solution by using an instrument similar to that described by Shriver and Drezdzon.[5]

Synthesis of $K[HIn(CH_2CMe_3)_3]$. The reagents $In(CH_2CMe_3)_3$ (1.923 g, 5.858 mmol) and excess KH (0.583 g, 14.5 mmol) were combined in 20 mL of pentane, and the resulting mixture was stirred for 8 h at room temperature. The product was then separated from excess KH by extraction with pentane. Recrystallization of the crude product from pentane solution at -20 °C yielded $K[HIn(CH_2CMe_3)_3]$ (1.354 g, 3.676 mmol, 62.8% yield based on $In(CH_2CMe_3)_3$). Recrystallization at -20 °C of the concentrated mother liquor from the first recrystallization yielded additional $K[HIn(CH_2CMe_3)_3]$ (0.641 g, 1.74 mmol, 29.7% yield based on $In(CH_2CMe_3)_3$). The two batches of crystals were identical. The total yield of purified $K[HIn(CH_2CMe_3)_3]$ was 92%.

$K[HIn(CH_2CMe_3)_3]$: mp 112–120 °C dec. Anal. Calcd for $C_{15}H_{34}InK$: C, 48.91; H, 9.30. Found: C, 48.83; H, 9.28. ^1H NMR (C_6D_6): δ 0.59 (s, 6 H, $InCH_2$), 1.30 (s, 27 H, $InCCCH_3$), 3.41 (br, 1 H, InH). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 33.0 (CMe_3), 35.2 (CH_3). IR (Nujol mull): 1350 (w), ~1250 (vs, br spans region 1400–1000), 1215 (w), 1096 (m), 1002 (m, sh), 923 (w), 904 (w), 736 (vw), ~700 (vs, br spans region 900–500), 656 (vw), 595 (vw), 553 (w), 446 (m), 371 (w), 340 (vw), 241 (m) cm^{-1}. Cryoscopic molecular weight, formula weight 368.35 (obsd molality, obsd mol wt, association): 0.0724, 660.3, 1.79; 0.0497, 664.0, 1.80; 0.0315, 689.7, 1.87; 0.0218, 721.2, 1.96; 0.0160, 749.5, 2.03; 0.00994, 856.0, 2.26. Hydrolysis with excess HCl (3 M, 30 mL) yielded 0.947 mmol of H_2/mmol of $K[HIn(CH_2CMe_3)_3]$ and 2.83 mmol of CMe_4/mmol of $K[HIn(CH_2CMe_3)_3]$.

Synthesis of $K[DIn(CH_2CMe_3)_3]$. The deuteride $K[DIn(CH_2CMe_3)_3]$ was synthesized by using KD and the procedure previously described. Recrystallizations from pentane yielded crystals of $K[DIn(CH_2CMe_3)_3]$.

$K[DIn(CH_2CMe_3)_3]$: mp 117–120 °C dec. ^1H NMR (C_6D_6): δ 0.63 (s, 6 H, $InCH_2$), 1.29 (s, 27 H, $InCCCH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 32.9 (CMe_3), 35.2 (CH_3). IR (Nujol mull): 1354 (s), 1228 (s), 1210 (s), 1101 (m, sh), 1076 (w), ~990 (s, br spans region 1200–820), 922 (w), 904 (w), 736 (m), 699 (w, sh), 659 (vs), 649 (vs), 561 (s, sh), 448 (m, sh), ~405 (w, br spans region 500–300), 372 (w), 343 (m, sh), 246 (m, sh), 240 (m, sh) cm^{-1}.

Synthesis of $K\{H[In(CH_2CMe_3)_3]_3\}$. Stoichiometric amounts of $K[HIn(CH_2CMe_3)_3]$ (0.431 g, 1.17 mmol) and $In(CH_2CMe_3)_3$ (0.385 g, 1.17 mmol) were combined in 30 mL of pentane. Initially, the mixture was a clear colorless solution, but after approximately 5 min a fine, colorless precipitate formed. The product was isolated after 10 min of stirring by cooling the mixture to -30 °C and filtering. Removal of the pentane left $K\{H[In(CH_2CMe_3)_3]_2\}$ (0.793 g, 1.14 mmol, 97.2% yield). X-ray-quality crystals were obtained by slow recrystallization of a pentane solution.

$K\{H[In(CH_2CMe_3)_3]_2\}$: mp 137–143 °C dec. Anal. Calcd for $C_{30}H_{67}InK$: C, 51.73; H, 9.55. Found: C, 51.51; H, 9.60. ^1H NMR (C_6D_6): δ 0.81 (s, 12 H, $InCH_2$), 1.25 (s, 54 H, $InCCCH_3$), 3.09 (br, 1 H, InH). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 33.2 (CMe_3), 35.4 (CH_3). IR (Nujol mull): ~1800–1100 (m, br), 1356 (s), 1348 (m), 1300 (vw, br), 1260 (w), 1228 (s), 1211 (m), ~1130–900 (w, br), 1106 (m), 1092 (m), 1079 (w), 999 (w, sh), 981 (vw), 805 (w, br), ~760–630 (m, br), 734 (vw), 704 (vw), 679 (w), 645 (w), 563 (m), 449 (w), 373 (w) cm^{-1}. Cryoscopic molecular weight, formula weight 696.60 (obsd molality, obsd mol wt, association): 0.0449, 729.9, 1.05; 0.0283, 746.4, 1.07; 0.0185, 783.0, 1.12.

Synthesis of $K\{D[In(CH_2CMe_3)_3]_2\}$. The deuteride $K\{D[In(CH_2CMe_3)_3]_2\}$ was synthesized by using $K[DIn(CH_2CMe_3)_3]$ and the procedure previously described.

$K\{D[In(CH_2CMe_3)_3]_2\}$: mp 140–145 °C dec. ^1H NMR (C_6D_6): δ 0.78 (s, 2 H, $InCH_2$), 1.26 (s, 9 H, $InCCCH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 32.8 (CMe_3), 35.0 (CH_3). IR (Nujol mull): 1355 (s), 1349 (vw), 1229 (s), 1213 (s), 1103 (m), 1078 (w), ~1250–770 (s, br), 999 (m), 992 (m), 922 (w), 906 (w), ~750–600 (m, br), 735 (s), 700 (m), 661 (m), 650 (m), 600 (vw), 565 (vs, sh), ~500–350 (m, br), 470 (vw), 448 (m, sh), 406 (w), 374 (m), 343 (vw), 243 (m, sh) cm^{-1}.

Product Formed from $In(CH_2CMe_3)_3$ and KH after 2 h, $K\{H[In(CH_2CMe_3)_3]_2\}$. The reagents $In(CH_2CMe_3)_3$ (1.692 g, 5.153 mmol) and excess KH (0.703 g, 17.5 mmol) were combined in 20 mL of pentane. After the resulting mixture was stirred for 2 h at room temperature, the crude product (0.547 g) was isolated by pentane extraction (×6). The ^1H NMR spectrum identified the product as $K\{H[In(CH_2CMe_3)_3]_2\}$. ^1H NMR (C_6D_6): δ 0.78 (s, 2 H, $InCH_2$), 1.26 (s, 9 H, $InCCCH_3$), 3.05 (br, InH).

NMR Spectra of Mixtures of Components. The following experiments were performed in order to gain an understanding of the reactions occurring between KH, $In(CH_2CMe_3)_3$, $K[HIn(CH_2CMe_3)_3]$, and/or $K\{H[In(CH_2CMe_3)_3]_2\}$.

(A) $In(CH_2CMe_3)_3$ and Excess $K[HIn(CH_2CMe_3)_3]$. Solvent (0.8 mL of C_6D_6) was added to a mixture of $In(CH_2CMe_3)_3$ (0.0146 g, 0.0445 mmol) and excess $K[HIn(CH_2CMe_3)_3]$ (0.0386 g, 0.105 mmol). ^1H NMR (C_6D_6): δ 0.71 (s, $InCH_2$), 1.28 (s, $InCCCH_3$), 3.22 (s, InH).

(B) $In(CH_2CMe_3)_3$ and Excess $K\{H[In(CH_2CMe_3)_3]_2\}$. Solvent (0.8 mL of C_6D_6) was added to a mixture of $In(CH_2CMe_3)_3$ (0.0158 g, 0.0481 mmol) and excess $K\{H[In(CH_2CMe_3)_3]_2\}$ (0.0450 g, 0.0646 mmol). ^1H NMR (C_6D_6): δ 0.85 (s, $InCH_2$), 1.21 (s, $InCCCH_3$), 2.97 (s, InH).

(C) $In(CH_2CMe_3)_3$ and Excess $K[HIn(CH_2CMe_3)_3]$. C_6D_6 (0.8 mL) was added to a mixture of $In(CH_2CMe_3)_3$ (0.0123 g, 0.0375 mmol) and excess $K[HIn(CH_2CMe_3)_3]$ (0.0368 g, 0.0999 mmol). ^1H NMR (C_6D_6): δ 0.70 (s, $InCH_2$), 1.28 (s, $InCCCH_3$), 3.24 (s, InH). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 32.9 (CMe_3), 35.1 (CH_3).

Collection of the X-ray Diffraction Data for $K\{H[In(CH_2CMe_3)_3]_2\}$. A clear crystal having the dimensions 0.25 × 0.30 × 0.40 mm was aligned on a Siemens-upgraded Syntex $P2_1/R3$ diffractometer. Data for $\pm h,k,\pm l$ were collected by the coupled θ(crystal)–2θ(counter) scan technique and were merged to a set of unique reflections. Details of data collection appear in Table I.

Axial photographs indicated that the crystal belonged to the C-centered subset of the monoclinic system. The systematic absences of hkl for $h + k = 2n + 1$ and $h0l$ for $l = 2n + 1$ indicate the possible space groups as Cc or $C2/c$. Intensity statistics clearly favored the centrosymmetric case. The space group $C2/c$ [C_{2h}^6; No. 15] was assumed and confirmed by the successful solution and refinement of the structure in this higher symmetry space group.

Solution and Refinement of the Crystal Structure. All crystallographic calculations were carried out on a VAX3100 workstation with the use of the Siemens SHELXTL PLUS program set.[6] The analytical scattering factors for neutral atoms were

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[6] *Siemens SHELXTL PLUS Manual*; 2nd ed.; Siemens Analytical Instruments: Madison, WI, 1990.

Table I. Experimental Data for the X-ray Diffraction Study on K{H[In(CH$_2$CMe$_3$)$_3$]$_2$}

Crystal Data	
emprical formula	$C_{30}H_{67}In_2K$
color; habit	clear crystal
crystal size, mm	0.40 × 0.30 × 0.25
cryst syst	monoclinic
space group	*C*2/*c*
unit cell dimsn	
a, Å	22.243 (5)
b, Å	17.021 (3)
c, Å	21.290 (3)
β, deg	110.350 (10)
volume, Å^3	7557 (2)
Z	8
fw	696.6
dens(calcd), Mg m^{-3}	1.224
abs coeff, mm^{-1}	1.326
F(000)	2912
Data Collection	
diffractometer used	Siemens R3m/V
λ(Mo Kα radiation), Å	0.710 73
temp, K	295
monochromator	highly oriented graphite crystal
2*θ* range, deg	8.0–45.0
scan type	2*θ*–*θ*
scan speed, deg min^{-1}	constant; 1.75 in *ω*
scan range (*ω*), deg	0.80 plus Kα separation
bckgd measurement	stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time
std reflns	3 measured every 97 reflns
index ranges	$-24 \le h \le 24$, $0 \le k \le 18$, $-22 \le l \le 22$
no. of reflns collcd	10 270
no. of ind reflns	4947 (R_{int} = 2.74%)
no. of obsd reflns	4947 ($F > 0.5\sigma(F)$)
abs corrn	semiempirical
min/max transm	0.3912/0.4473
Solution and Refinement	
system used	Siemens SHELXTL PLUS (VMS)
soln	direct methods
refinement method	full-matrix least-squares
quantity minimized	$\sum w(F_o - F_c)^2$
absolute structure	N/A
extinction corr	N/A
hydrogen atoms	riding model, fixed isotropic *U*
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0008F^2$
no. of params refined	327
final *R* indices (obs data), %	*R* = 6.32, R_w = 4.97
R indices (all data), %	*R* = 6.32, R_w = 4.97
goodness-of-fit	0.95
largest and mean Δ/*σ*	0.003, 0.001
data-to-param ratio	15.1:1
largest diff peak, e Å^{-3}	0.83
largest diff hole, e Å^{-3}	−0.61

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3)

	x	*y*	*z*	*U*(eq)^a
In(1)	−874 (1)	11624 (1)	1949 (1)	40 (1)
In(2)	222 (1)	16625 (1)	1712 (1)	45 (1)
K(1)	0	9745 (2)	2500	83 (1)
H(1)	0	11340 (51)	2500	79 (27)
K(2)	0	14748 (2)	2500	80 (1)
H(2)	0	16434 (46)	2500	69 (26)
C(11)	−818 (3)	12884 (3)	1747 (3)	48 (2)
C(12)	−1354 (3)	13248 (3)	1150 (3)	53 (3)
C(13)	−1320 (5)	12929 (5)	497 (3)	97 (4)
C(14)	−2014 (3)	13061 (5)	1181 (4)	86 (4)
C(15)	−1302 (4)	14145 (4)	1156 (4)	90 (4)
C(21)	−1433 (4)	11233 (5)	2567 (3)	73 (3)
C(22)	−1409 (3)	11662 (3)	3210 (3)	52 (3)
C(23)	−746 (5)	11656 (9)	3694 (4)	181 (8)
C(24)	−1834 (6)	11263 (6)	3537 (5)	135 (6)
C(25)	−1620 (6)	12475 (6)	3071 (5)	152 (8)
C(31)	−900 (3)	10810 (4)	1119 (3)	54 (3)
C(32)	−1465 (3)	10240 (4)	812 (3)	53 (2)
C(33)	−1458 (3)	9590 (4)	1302 (4)	77 (3)
C(34)	−2094 (3)	10677 (4)	642 (4)	81 (3)
C(35)	−1415 (5)	9858 (5)	174 (4)	105 (4)
C(41)	442 (3)	17901 (3)	1829 (3)	53 (3)
C(42)	882 (4)	18253 (4)	1501 (4)	71 (4)
C(43)	655 (7)	18047 (6)	771 (6)	163 (8)
C(44)	898 (5)	19139 (5)	1560 (5)	109 (5)
C(45)	1544 (5)	17963 (7)	1822 (8)	174 (9)
C(51)	−657 (3)	16242 (5)	910 (4)	87 (4)
C(52)	−1273 (3)	16724 (4)	695 (3)	60 (3)
C(53)	−1457 (5)	16934 (10)	1264 (5)	213 (10)
C(54)	−1160 (5)	17476 (7)	386 (6)	168 (7)
C(55)	−1814 (4)	16315 (6)	168 (6)	160 (6)
C(61)	1047 (3)	15802 (4)	1962 (3)	58 (3)
C(62)	1144 (3)	15210 (4)	1458 (3)	61 (3)
C(63)	620 (4)	14592 (4)	1267 (4)	83 (4)
C(64)	1105 (4)	15653 (5)	826 (4)	98 (5)
C(65)	1798 (4)	14800 (5)	1746 (4)	96 (4)

^{a} Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

corrected for the $\Delta f'$ and $i\Delta f''$ components of anomalous dispersion. The structure was solved by a combination of direct-methods and difference-Fourier techniques. Refinement led to convergence with *R* = 6.32%, *R* = 4.97%, and GOF = 0.95 for all 4947 reflections and 327 variables (*R* = 2.96% and R_w = 3.67% for those 2924 reflections with $F_o > 6.0\sigma(F_o)$).

All non-hydrogen atoms were refined anisotropically. The positions and isotropic thermal parameters of the bridging hydride ions were refined. All hydrogen atoms of the neopentyl groups were included in calculated staggered positions with *d*(C–H) = 0.96 Å.[7] A final difference-Fourier synthesis showed features only in the range −0.61 to +0.83 e Å^{-3}. Final atomic coordinates are collected in Table II.

Results and Discussion

Our studies of the reaction between In(CH$_2$CMe$_3$)$_3$ and KH suggest that K[HIn(CH$_2$CMe$_3$)$_3$], a simple Lewis acid–base adduct, is formed initially. However, this compound reacts rapidly with more In(CH$_2$CMe$_3$)$_3$ to form K{H[In(CH$_2$CMe$_3$)$_3$]$_2$}, the initial isolable product. If excess KH is available, then K{H[In(CH$_2$CMe$_3$)$_3$]$_2$} reacts to form K[HIn(CH$_2$CMe$_3$)$_3$] as the final product. The observation that K{H[In(CH$_2$CMe$_3$)$_3$]$_2$} can be isolated after In(CH$_2$CMe$_3$)$_3$ and excess KH are stirred in pentane for 2 h must be related to the limited solubility of K{H[In(CH$_2$CMe$_3$)$_3$]$_2$} and the insolubility of KH. When K[HIn(CH$_2$CMe$_3$)$_3$] and In(CH$_2$CMe$_3$)$_3$ were combined in pentane, a solution was formed initially. However, after approximately 5 min, a fine, colorless precipitate of K{H[In(CH$_2$CMe$_3$)$_3$]$_2$} was observed and a quantitative yield was isolated after 10 min. A reaction mixture prepared from In(CH$_2$CMe$_3$)$_3$ and excess KH must be stirred for 8 h in order to ensure the formation of K[HIn(CH$_2$CMe$_3$)$_3$]. Both new compounds have been characterized according to their physical properties, elemental analyses for carbon and hydrogen, cryoscopic molecular weight data, infrared spectra, and ^{1}H and ^{13}C NMR spectra. The structure of K{H[In(CH$_2$CMe$_3$)$_3$]$_2$} in the solid state has also been elucidated by an X-ray structural study. Crystals of K[HIn(CH$_2$CMe$_3$)$_3$] were isolated also, but the diffraction data were too poor to be used in structure determination.

The crystal of K{H[In(CH$_2$CMe$_3$)$_3$]$_2$} is best viewed as an ordered array of K$^+$ cations and (Me$_3$CCH$_2$)$_3$In–H–In(CH$_2$CMe$_3$)$_3^-$ anions in a 1:1 ratio, all of which are bisected by a crystallographic 2-fold axis. The crystallographic asymmetric unit consists of half of two potassium cations (K(1) and K(2)) and half of two [In(CH$_2$CMe$_3$)$_3$]$_2$H$^-$ anions (centered about H(1) and H(2)). Figure 1 shows the mu-

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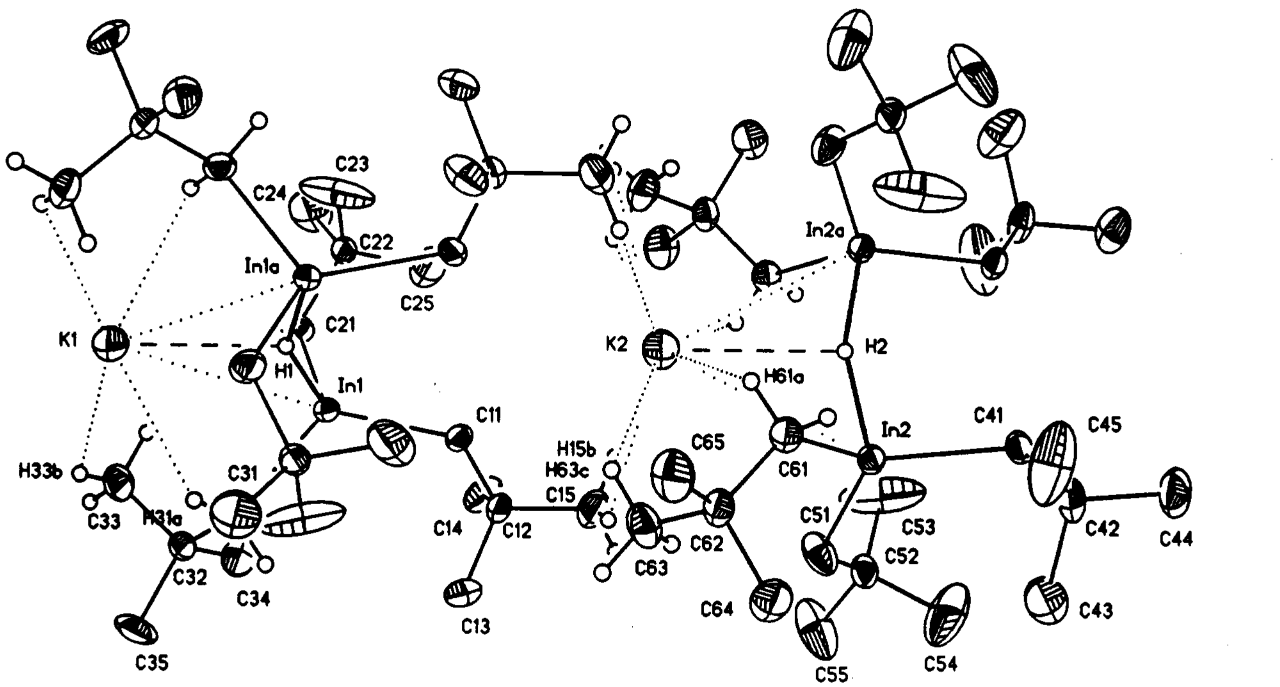

Figure 1. Structure of K{H[In(CH_2CMe_3)$_3$]$_2$}. Hydrogen atoms of the neopentyl groups are omitted unless they interact with K^+ ions. Note that a crystallographic 2-fold axis passes through K(1)···H(1)···K(2)···H(2).

Table III. Interatomic Distances (Å) for K{H[In(CH_2CMe_3)$_3$]$_2$}

In(1)–K(1)	3.715 (2)	In(1)–C(11)	2.199 (6)
In(1)–C(21)	2.204 (9)	In(1)–C(31)	2.231 (6)
In(1)–H(1)	1.950 (23)	In(2)–K(2)	3.721 (2)
In(2)–C(41)	2.221 (6)	In(2)–C(51)	2.200 (7)
In(2)–C(61)	2.222 (6)	In(2)–H(2)	1.933 (15)
K(1)–H(31A)	2.757	K(1)–H(33B)	2.780
K(1)–H(1)	2.714 (87)	K(1)–In(1A)	3.715 (2)
K(1)–H(31C)	2.757	K(1)–H(33D)	2.780
K(1)–H(44D)	3.050	K(1)–H(44E)	3.050
K(1)–H(44F)	2.965	K(1)–H(44G)	2.965
K(2)–H(15B)	3.007	K(2)–H(15C)	3.024
K(2)–H(61A)	2.761	K(2)–H(63C)	2.751
K(2)–H(2)	2.869 (79)	K(2)–In(2A)	3.721 (2)
K(2)–H(15D)	3.007	K(2)–H(15E)	3.024
K(2)–H(61C)	2.761	K(2)–H(63D)	2.751
C(11)–C(12)	1.539 (7)	C(12)–C(13)	1.519 (11)
C(12)–C(14)	1.525 (11)	C(12)–C(15)	1.531 (9)
C(21)–C(22)	1.535 (10)	C(22)–C(23)	1.475 (10)
C(22)–C(24)	1.518 (15)	C(22)–C(25)	1.459 (12)
C(31)–C(32)	1.542 (8)	C(32)–C(33)	1.515 (10)
C(32)–C(34)	1.513 (9)	C(32)–C(35)	1.544 (11)
C(41)–C(42)	1.509 (12)	C(42)–C(43)	1.501 (14)
C(42)–C(44)	1.512 (10)	C(42)–C(45)	1.476 (13)
C(51)–C(52)	1.524 (10)	C(52)–C(53)	1.452 (14)
C(52)–C(54)	1.498 (14)	C(52)–C(55)	1.503 (11)
C(61)–C(62)	1.541 (10)	C(62)–C(63)	1.517 (10)
C(62)–C(64)	1.518 (11)	C(62)–C(65)	1.535 (10)
H(1)–In(1A)	1.950 (23)	H(2)–In(2A)	1.933 (15)

Table IV. Interatomic Angles (deg) for K{H[In(CH_2CMe_3)$_3$]$_2$}

K(1)–In(1)–C(11)	147.4 (2)	K(1)–In(1)–C(21)	83.9 (2)
C(11)–In(1)–C(21)	119.5 (3)	K(1)–In(1)–C(31)	65.3 (1)
C(11)–In(1)–C(31)	116.0 (2)	C(21)–In(1)–C(31)	114.9 (3)
K(1)–In(1)–H(1)	45.1 (24)	C(11)–In(1)–H(1)	104.3 (24)
C(21)–In(1)–H(1)	102.6 (9)	C(31)–In(1)–H(1)	93.9 (16)
K(2)–In(2)–C(41)	148.0 (2)	K(2)–In(2)–C(51)	82.8 (2)
C(41)–In(2)–C(51)	118.6 (3)	K(2)–In(2)–C(61)	65.0 (2)
C(41)–In(2)–C(61)	117.3 (2)	C(51)–In(2)–C(61)	115.8 (3)
K(2)–In(2)–H(2)	49.5 (23)	C(41)–In(2)–H(2)	100.4 (22)
C(51)–In(2)–H(2)	101.4 (8)	C(61)–In(2)–H(2)	97.1 (15)
In(1)–C(11)–C(12)	118.3 (4)	C(11)–C(12)–C(13)	110.0 (6)
C(11)–C(12)–C(14)	111.1 (6)	C(13)–C(12)–C(14)	108.6 (6)
C(11)–C(12)–C(15)	111.1 (5)	C(13)–C(12)–C(15)	109.7 (6)
C(14)–C(12)–C(15)	106.2 (6)	In(1)–C(21)–C(22)	122.4 (5)
C(21)–C(22)–C(23)	109.7 (7)	C(21)–C(22)–C(24)	111.2 (6)
C(23)–C(22)–C(24)	107.9 (7)	C(21)–C(22)–C(25)	111.2 (6)
C(23)–C(22)–C(25)	108.8 (8)	C(24)–C(22)–C(25)	108.0 (9)
In(1)–C(31)–C(32)	121.3 (5)	C(31)–C(32)–C(33)	110.8 (4)
C(31)–C(32)–C(34)	110.0 (5)	C(33)–C(32)–C(34)	108.2 (6)
C(31)–C(32)–C(35)	109.8 (6)	C(33)–C(32)–C(35)	108.2 (6)
C(34)–C(32)–C(35)	109.9 (5)	In(2)–C(41)–C(42)	119.3 (5)
C(41)–C(42)–C(43)	110.3 (7)	C(41)–C(42)–C(44)	111.0 (7)
C(43)–C(42)–C(44)	108.0 (7)	C(41)–C(42)–C(45)	110.9 (8)
C(43)–C(42)–C(45)	108.9 (10)	C(44)–C(42)–C(45)	107.7 (7)
In(2)–C(51)–C(52)	122.4 (5)	C(51)–C(52)–C(53)	111.5 (7)
C(51)–C(52)–C(54)	108.8 (7)	C(53)–C(52)–C(54)	107.2 (9)
C(51)–C(52)–C(55)	112.2 (7)	C(53)–C(52)–C(55)	110.6 (8)
C(54)–C(52)–C(55)	106.3 (7)	In(2)–C(61)–C(62)	123.4 (4)
C(61)–C(62)–C(63)	111.0 (7)	C(61)–C(62)–C(64)	108.3 (6)
C(63)–C(62)–C(64)	107.7 (6)	C(61)–C(62)–C(65)	111.3 (5)
C(63)–C(62)–C(65)	108.9 (6)	C(64)–C(62)–C(65)	109.6 (7)
In(1)–H(1)–K(1)	104.4 (24)	In(1)–H(1)–In(1A)	151.3 (49)
K(1)–H(1)–In(1A)	104.4 (24)	In(2)–H(2)–K(2)	99.7 (23)
In(2)–H(2)–In(2A)	160.6 (46)	K(2)–H(2)–In(2A)	99.7 (23)

tual juxtaposition of two such crystallographic asymmetric units and the atomic labeling scheme. Interatomic distances (with eds's) are listed in Table III, and interatomic angles are collected in Table IV.

The (Me_3CCH_2)$_3$In-H-In(CH_2CCMe_3)$_3^-$ anions have precise C_2 symmetry. The bridging hydride ligands are involved in 2-electron 3-center bonds. Observed indium-hydrogen distances are In(1)-H(1) = In(1A)-H(1) = 1.950 (23) Å, with In(1)-H(1)-In(1A) = 151 (5)°, and In(2)-H(2) = In(2A)-H(2) = 1.933 (15) Å, with In(2)-H(2)-In(2A) = 161 (5)°. The indium-(μ-hydride) distance is, as expected, substantially longer (by ~0.2 Å) than the predicted terminal In-H distance of about 1.75 Å (based on r(In) = 1.44 Å, from In-C(av) = 2.21 Å in the present structure less $r(C_{sp^3})$ = 0.77 Å,[8a] and r(H) = 0.31 Å from d(C-H) = 1.08 Å,[8b] less $r(C_{sp^3})$ = 0.77 Å).

The geometry about each indium atom is that of a slightly flattened tetrahedron formed by the three α-carbon atoms of the neopentyl groups and the bridging hydride

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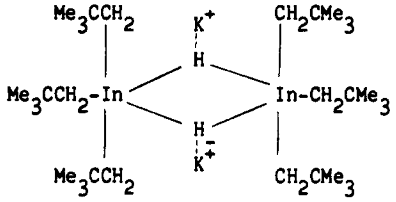
(8) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1960; (a) Table 7-2, p 224, (b) Table 7-4, p 226.

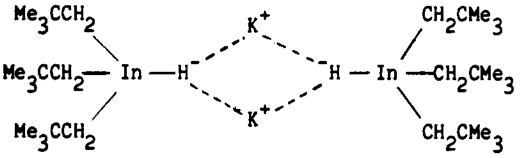
ligand. The In–C bonds are equivalent within the limits of experimental error with In(1)–C(11) = 2.199 (6), In(1)–C(21) = 2.204 (9), and In(1)–C(31) = 2.231 (6) Å (average = 2.211 Å about In(1)) and In(2)–C(41) = 2.221 (6), In(2)–C(51) = 2.200 (7), and In(2)–C(61) = 2.222 (6) Å (average = 2.214 Å about In(2)). These In–C distances in $(Me_3CCH_2)_3In\text{–}H\text{–}In(CH_2CMe_3)_3^-$ are similar to the corresponding distances in other organoindium anions. For example, $KIn(CH_2SiMe_3)_4$[3] has an average In–C distance of 2.239 [8] Å whereas that in $LiIn[C(SiMe_3)_3]_2H_5{\cdot}2THF$ is 2.20 (3) Å; that in $KInMe_4$[9] is 2.239 (3) Å, that in $CsInMe_4$[9] is 2.26 (2) Å, and that in $NaInPh_4$[10] is 2.230 (3) Å. The In–C distances in these anionic species are longer than the In–C distances in most neutral, four-coordinate indium compounds. Representative In–C distances in neutral species are 2.125 (12) and 2.140 (13) Å for $[In(CH_2CMe_3)(CH_2SiMe_3)Cl]_2$,[11] 2.146 (9) and 2.174 (10) Å for $[In(C_6Me_3H_2)_2Cl]_2$,[12] and 2.182 (6) and 2.210 (7) Å for $[(Me_3CCH_2)_2InPPh_2]_3$.[13] One exception is the neutral organoindium compound $[(Me_3CCH_2)_2InCH_2PPh_2]_2$[14] whose In–C distances are comparable to those in $K\{H[In(CH_2CMe_3)_3]_2\}$; the In–$CH_2$ distance is 2.258 Å, and the average In–C(neopentyl) distance is 2.222 Å.

The C–In–C angles about the In(1) atom in $K\{H[In(CH_2CMe_3)_3]_2\}$ are C(21)–In(1)–C(31) = 114.9 (3), C(11)–In(1)–C(31) = 116.0 (2), and C(11)–In(1)–C(21) = 119.5 (3)° (average = 116.8°). The C–In–C angles observed about In(2) are C(51)–In(2)–C(61) = 115.8 (3), C(41)–In(2)–C(61) = 117.3 (2), and C(41)–In(2)–C(51) = 118.6 (3)° (average = 117.2°). The C–In–H bond angles show values that are significantly smaller than the C–In–C angles. The values about In(1) are C(11)–In(1)–H(1) = 104.3 (24), C(21)–In(1)–H(1) = 102.6 (9), and C(31)–In(1)–H(1) = 93.9 (16)° (average = 100.3°). About In(2) the observed bond angles are C(41)–In(2)–H(2) = 100.4 (22), C(51)–In(2)–H(2) = 101.4 (8), and C(61)–In(2)–H(2) = 97.1 (15)° (average = 99.6°). This flattening of the tetrahedron, resulting in larger values for the C–In–C bond angles as compared to the C–In–H bond angles, is to be expected, since the neopentyl groups are substantially more bulky than the bridging hydride ligand (which is also electron deficient).

The potassium ions also lie on the crystallographic 2-fold axis. They have their closest interactions with the hydride ligands (K(1)···H(1) = 2.71 (9) and K(2)···H(2) = 2.87 (8) Å). The K···In distances are K(1)···In(1) = K(1)···In(1A) = 3.715 (2) and K(2)···In(2) = K(2)···In(2A) = 3.721 (2) Å. There are also some interactions between the potassium ions and hydrogen atoms on the neopentyl groups; these interactions are shown as dotted lines in Figure 1.

The two new indium hydrides are soluble in benzene and have been characterized by cryoscopic molecular weight data. The calculated molecular weights of the solutes in solutions prepared from $K\{H[In(CH_2CMe_3)_3]_2\}$ reveal the presence of ion pairs with the simplest formula of the compound. In contrast, solutions of $K[HIn(CH_2CMe_3)_3]$ are composed of dimeric units, $\{K[HIn(CH_2CMe_3)_3]\}_2$. Because the calculated molecular weights of either compound do not vary significantly with concentration, neither associative nor dissociative equilibria are significant. Thus, $K\{H[In(CH_2CMe_3)_3]_2\}$ can be envisioned to exist in solution as species related to the units identified in the solid state and to have a hydride ion serving as a Lewis base to two $In(CH_2CMe_3)_3$ molecules as Lewis acids. Two alternative structures can be suggested for $\{K[HIn(CH_2CMe_3)_3]\}_2$:





One structure involves a five-coordinate indium species with bridging hydride ions whereas the alternative structure has tetrahedral $HIn(CH_2CMe_3)_3^-$ anions with bridging potassium ions. The neopentyl group hydrogen atoms probably serve to coordinate with the potassium ions, as observed in the structural study. Available data do not permit us to distinguish between the two structures.

The ^1H NMR spectra of $K\{H[In(CH_2CMe_3)_3]_2\}$ and of $K[HIn(CH_2CMe_3)_3]$ have features which are directly related to hydride ions bonded to indium. The ^1H NMR spectra of $K\{H[In(CH_2CMe_3)_3]_2\}$ and $K[HIn(CH_2CMe_3)_3]$ have broad lines at 3.09 and 3.41 ppm, respectively, which are not present in the spectra of the corresponding deuterium derivatives. Thus, these lines must be due to the unique hydrogen atoms bonded to indium. In contrast, the resonances of the methylene and methyl protons for the two indium hydride derivatives remain unchanged when the spectra of the respective protium and deuterium complexes are compared. It is also noteworthy that mixtures of $K\{H[In(CH_2CMe_3)_3]_2\}$ and $K[HIn(CH_2CMe_3)_3]$ exhibit only one set of resonances at chemical shifts which are intermediate between the two compounds. Thus, the neopentyl and hydride ligands exchange rapidly between the two compounds. Similarly, mixtures of $K\{H[In(CH_2CMe_3)_3]_2\}$ and $In(CH_2CMe_3)_3$ undergo rapid exchange of ligands, as only one set of resonances is observed.

The infrared spectra of the two compounds are also consistent with the presence of indium–hydrogen bonds. The compound $K\{H[In(CH_2CMe_3)_3]_2\}$ has broad bands at ~1800–1100, ~1130–980, and ~760–630 cm^{-1}, which are partially obscured by Nujol and by other bands of the compound. These bands can be assigned to asymmetric stretching, symmetric stretching, and bending modes for an In–H–In moiety which is bent rather than linear. These bands shift to ~1250–770, 750–600, and 500–300 cm^{-1} upon deuterium substitution and are consistent with the results of reduced mass calculations. In comparison, $K[HIn(CH_2CMe_3)_3]$ has broad, partially obscured bands at 1400–1000 and 900–500 cm^{-1} which shift to 1200–820 and 500–300 cm^{-1}, respectively, upon deuterium substitution. The bands centered about 1250 and 990 cm^{-1} are assigned to In–H and In–D stretching modes whereas the lower frequency bands are due to bending modes. The shifts of the bands upon deuterium substitution are less than that expected by calculations based on reduced masses. Thus, the bands in $K[HIn(CH_2CMe_3)_3]$ probably are due to combinations of various modes and are not pure In–H vibrations.

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The two new indium hydrides K{H[In(CH$_2$CMe$_3$)$_3$]$_2$} and K[HIn(CH$_2$CMe$_3$)$_3$] are inert to decomposition reactions in benzene solution over long periods of time. Neopentane (CMe$_4$) was not observed to be present in benzene solutions of the compounds, even after 3 months of standing at room temperature. In contrast, the closely related compound K[HIn(CH$_2$SiMe$_3$)$_3$][3] was observed to decompose in benzene solution to form indium metal, SiMe$_4$, biphenyl, and varying amounts of H$_2$. All CH$_2$SiMe$_3$ groups were converted to SiMe$_4$ within 2 months at room temperature.[3] These decomposition reactions of K[HIn(CH$_2$SiMe$_3$)$_3$] were proposed to be related to the formation of KCH$_2$SiMe$_3$ by the dissociation of CH$_2$SiMe$_3^-$. Thus, the stability of the neopentyl derivatives suggests increased inertness to dissociative reactions, a property which might be related to the Lewis acidity of trineopentylindium.[4] It is noteworthy that the reagents, 1 mmol of InMe$_3$ and excess KH, formed 0.159 mmol of CH$_4$ and indium metal in 12 h at 25 °C.[15]

Acknowledgment. This work was supported in part by the Office of Naval Research and by a grant from Eastman Kodak Co. We thank the National Science Foundation for providing funds for the upgrade of the P2$_1$ diffractometer to a Siemens P2$_1$/R3m through a grant from the Chemical Instrumentation Program (89-13733).

Registry No. K[HIn(CH$_2$CMe$_3$)$_3$], 139408-74-5; In(CH$_2$CMe$_3$)$_3$, 106136-98-5; K[DIn(CH$_2$CMe$_3$)$_3$], 139408-76-7; K{H[In(CH$_2$CMe$_3$)$_3$]$_2$}, 139408-75-6; K{D[In(CH$_2$CMe$_3$)$_3$]$_2$}, 139408-77-8.

Supplementary Material Available: Tables of bond distances and angles, anisotropic thermal parameters, and calculated positions of hydrogen atoms for K{H[In(CH$_2$CMe$_3$)$_3$]$_2$} (10 pages); F_o/F_c list (18 pages). Ordering information is given on any current masthead page.

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Conformations of Heteroferrocenes. Synthesis and Crystal and Dynamic Solution Behavior of 2,2′,5,5′-Tetrakis(trimethylsilyl)-3,3′,4,4′-tetramethyl-1,1′-distibaferrocene

Arthur J. Ashe, III,* and Jeff W. Kampf
Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109-1055
Samir M. Al-Taweel
Chemistry Department, Mu'tah University, Al Karak, Jordan

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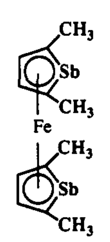
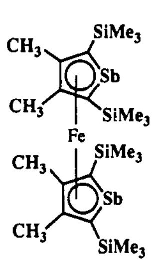
2,2′,5,5′-Tetrakis(trimethylsilyl)-3,3′,4,4′-tetramethyl-1,1′-distibaferrocene (2) as been obtained from the reaction of 1-phenyl-2,5-bis(trimethylsilyl)-3,4-dimethylstibole with lithium followed by FeCl$_2$. In a similar manner 2,2′,5,5′-tetrakis(trimethylsilyl)-3,3′,4,4′-tetramethyl-1,1′-dibismaferrocene (3) was obtained from 1-phenyl-2,5-bis(trimethylsilyl)-3,4-dimethylbismole. Dark red crystals of 2 form in the $P\bar{1}$ (No. 2) space group with $Z = 2$, $a = 9.243$ (2) Å, $b = 11.310$ (2) Å, $c = 17.345$ (3) Å, $\alpha = 76.51$ (1)°, $\beta = 79.23$ (2)°, and $\gamma = 73.18$ (1)°. A full structure has been determined and shows a ferrocene-like arrangement in which the trimethylsilyl groups are arranged in a staggered fashion. In solution a barrier to ring rotation for both 2 and 3 of $\Delta G^* = 13$ kcal/mol can be estimated from variable-temperature ^{1}H-NMR spectroscopy.

We recently reported the crystal structure of 2,2′,5,5′-tetramethyl-1,1′-distibaferrocene (1), which adopts a totally eclipsed ferrocene-like conformation with a short separation between the Sb atoms in each ring.[1] The inter-ring Sb···Sb contact (3.68 Å) is 0.72 Å shorter than the van der Waals radius separation (4.4 Å), which seems indicative of secondary bonding between the Sb atoms. Formally similar secondary bonding has been found for a number of compounds of antimony and other heavy main group elements.[2,3] In order to examine this phenomenon further, we have prepared the highly substituted distibaferrocene and the analogous dibismaferrocene 3. We report here on the X-ray structure of 2 and dynamic behavior of 2 and 3 in solution.



1



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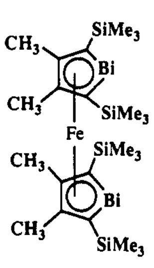

3

Results and Discussion

Synthesis. Distibaferrocene 2 was prepared by a route similar to that which we have recently reported for bismaferrocenes.[4] See Scheme I. 1-(Trimethylsilyl)-1-propyne (4) reacts with zirconocene dichloride and magnesium amalgam to give 1,1-bis(η^5-cyclopentadienyl)zirconacyclopentadiene (5).[4] The direct exchange of 5 with

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