Synthesis and Characterization of Neopentylindium Compounds: X-ray Crystal Structures of $[(Me_3CCH_2)_2InAs(SiMe_3)_2]_2$ and $(Me_3CCH_2)_2InAs(SiMe_3)_2In(CH_2CMe_3)_2Cl$

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The 1:1 and 2:1 mole ratio reactions of $(Me_3CCH_2)_2InCl$ with $As(SiMe_3)_3$ yield the dimeric and mixed-bridging compounds $[(Me_3CCH_2)_2InAs(SiMe_3)_2]_2$ (**1**) and $(Me_3CCH_2)_2InAs(SiMe_3)_2$-$In(CH_2CMe_3)_2Cl$ (**2**), respectively. **1** and **2** were characterized by melting point, ^1H and ^{13}C NMR spectra, partial elemental analyses (C and H), and single-crystal X-ray analyses. Dimer **1** crystallizes in the monoclinic system, space group $C2/m$ (C_{2h}^3), with a = 19.789(2) Å, b = 12.878(1) Å, c = 12.282(1) Å, β = 127.49(1)°, V = 2484(1) Å^3, and Z = 2. Crystals of **2** belong to the monoclinic system, space group $C2/c$ (C_{2h}^6), with a = 20.191(2) Å, b = 9.967(1) Å, c = 19.758(2) Å, β = 99.67(1)°, V = 3920(1) Å^3, and Z = 4. The facile interconversions of **1** and **2** are reported.

Introduction

A major impetus for main group chemists lies in the desire for new precursors to ceramic and electronic materials.[1] As investigators of group 13–15 compounds, our interest can be attributed to the quest for new precursors to semiconducting materials such as GaAs and InP.[2–4] An important aspect of this research is ascertaining the fundamental chemistry of these systems in order to synthesize the most efficient precursors for a specific method of deposition. Research in our laboratory has primarily focused on the use of dehalosilylation and salt elimination reactions to form the group 13–15 bond.[5] These methods have allowed us to prepare compounds containing M–E–M–E (M = Ga, E = As[6–8] or P;[2,9] M = In, E = As[10,11] or P;[11,12] M = Al, E = As[13,14] or P[15]) and M–E–M–Cl (M = Ga, E = As[6–8] or P;[16] M = In, E = As[10] or P[12]) rings. It has been found that most compounds containing one of the above ring systems can readily be converted to the similar compound containing the other ring system. Herein we report the synthesis and characterization of $[(Me_3CCH_2)_2InAs(SiMe_3)_2]_2$ (**1**) and $(Me_3CCH_2)_2InAs(SiMe_3)_2$-$In(CH_2CMe_3)_2Cl$ (**2**) as well as the interconversion of these compounds.

Experimental Section

General Considerations. All manipulations were performed using general Schlenk, drybox, and/or high vacuum techniques. Solvents (including C_6D_6) were appropriately dried, distilled under nitrogen, and degassed prior to use. Literature methods were used to prepare $(Me_3CCH_2)_2InCl$,[17] $As(SiMe_3)_3$,[18] and $LiAs(SiMe_3)_2$.[18] ^1H and $^{13}C\{^1H\}$ NMR spectra were obtained on a Varian XL-300 spectrometer at 300.0 or 75.4 MHz, respectively. ^1H and ^{13}C spectra were referenced to TMS *via* the residual protons or carbons of C_6D_6. Melting points (uncorrected) were obtained in sealed capillaries with a Thomas-Hoover Uni-melt apparatus. Crystals used in the X-ray analyses were mounted inside thin-walled glass capillaries which were flame-sealed under an argon atmosphere. Elemental analyses were performed by E + R Microanalytical Laboratory, Inc., Corona, NY.

Synthesis of $[(Me_3CCH_2)_2InAs(SiMe_3)_2]_2$ (1). In a round-bottom flask fitted with a Teflon screw-cap and a side arm, a benzene solution of $As(SiMe_3)_3$ (0.561 g, 1.90 mmol) was added to a benzene solution containing 0.585 g (2.00 mmol) of $(Me_3CCH_2)_2InCl$. The resulting yellow solution was stirred at room temperature for 96 h, at which time the volatiles were removed

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in vacuo. The orange solid residue was recrystallized in pentane at −15 °C, producing colorless X-ray diffraction quality crystals of **1** (0.354 g, 37% yield); mp, crystals became orange upon heating above 126 °C and began melting to a red liquid above 189 °C. The red liquid gradually became black as the temperature was raised to 238 °C, and some solid was still present up to this temperature. Anal. Calcd (found) for $C_{32}H_{80}As_2In_2Si_4$: C, 40.17 (40.07); H, 8.43 (8.15). ^{1}H NMR: δ 0.58 (s, 36 H, Si*Me*$_3$), 1.36 (s, 36 H, C*Me*$_3$), 1.63 (s, 8 H, C*H*$_2$). $^{13}C\{^1H\}$ NMR: δ 5.77 (Si*Me*$_3$), 33.33 (CMe$_3$), 35.33 (C*Me*$_3$), 41.36 (CH$_2$).

Alternate Preparation of $[(Me_3CCH_2)_2InAs(SiMe_3)_2]_2$ (1). In an NMR tube, $(Me_3CCH_2)_2InCl$ (0.060 g, 0.205 mmol) and $LiAs(SiMe_3)_2$ (0.047 g, 0.206 mmol) were combined and the tube was evacuated. Benzene-d_6 was distilled onto the reagents and the tube flame sealed under vacuum. The sample was allowed to thaw for 5 min at which time a fine white powder was suspended throughout the solution. This powder, presumably LiCl, prevented locking the NMR instrument, and the ^{1}H NMR spectrum was taken with the lock off. The spectrum showed three peaks at δ 0.52, 1.30, and 1.56 ppm corresponding to the peaks assigned to dimer **1** minus 0.06 ppm. After standing for 50 min, the LiCl had settled to the bottom of the tube and the ^{1}H and ^{13}C NMR spectra were run. The resulting properly-locked spectra were identical to that for an authentic sample of **1**. The NMR tube was opened in the drybox, and the solvent was removed so as not to disturb the precipitated LiCl. After the benzene-d_6 was evaporated, the resulting light yellow solid was dissolved in pentane and the solution cooled to −15 °C. After 2 days, colorless crystals exhibiting a melting point range similar to pure **1** were obtained from the pentane solution.

Synthesis of $(Me_3CCH_2)_2\overline{InAs(SiMe_3)_2In(CH_2CMe_3)_2Cl}$ (2). A round-bottom flask equipped with a Teflon screw-cap and a side arm was charged with $(Me_3CCH_2)_2InCl$ (0.762 g, 2.60 mmol) dissolved in benzene. To this was added 0.383 g (1.30 mmol) of $As(SiMe_3)_3$. The solution was stirred and within 0.5 h had become light orange. The solution was stirred for 96 h at room temperature. The volatiles were removed *in vacuo*, leaving an orange film inside the flask. This residue was dissolved in <2 mL of pentane and the resulting solution cooled to −15 °C. Colorless crystals suitable for an X-ray diffraction study were recovered (0.206 g, 21% yield), mp 120–129 °C with decomposition to an orange liquid. Anal. Calcd (found) for $C_{26}H_{62}AsClIn_2Si_2$: C, 40.51 (40.37); H, 8.11 (8.14). ^{1}H NMR: δ 0.43 (s, 18 H, Si*Me*$_3$), 1.24 (s, 36 H, C*Me*$_3$), 1.54 (s, 8 H, C*H*$_2$). $^{13}C\{^1H\}$ NMR: δ 5.25 (Si*Me*$_3$), 33.28 (CMe$_3$), 35.02 (C*Me*$_3$), 44.20 (CH$_2$).

Reaction of 1 with $(Me_3CCH_2)_2InCl$. An NMR tube was charged with 0.0254 g (0.0868 mmol) of $(Me_3CCH_2)_2InCl$ and 0.0410 g (0.0429 mmol) of **1**. The NMR tube was evacuated and 0.75 mL of benzene-d_6 vacuum distilled onto the solids. The ^{1}H NMR spectrum taken 1 min after thawing the solvent showed peaks at δ 0.43, 1.24, and 1.54 corresponding to the mixed-bridged **2** and a peak at δ 1.09 from the methyl protons of $(Me_3CCH_2)_2InCl$. No peaks assignable to the original dimer were observed. After 8 min, the ^{1}H NMR spectrum was identical to that of an authentic sample of **2**. The NMR tube was opened and the benzene-d_6 allowed to evaporate. The resulting solid was dissolved in pentane and cooled to −15 °C. After 48 h, colorless crystals were obtained which had a melting point range identical to that of pure **2**.

Reaction of 2 with $LiAs(SiMe_3)_2$. Mixed-bridge **2** (0.0460 g, 0.060 mmol) and $LiAs(SiMe_3)_2$ (0.0136 g, 0.060 mmol) were combined in a 5-mm NMR tube. The tube was evacuated and benzene-d_6 vacuum distilled onto the mixture. Immediately upon thawing, a white powder formed throughout the solution. The ^{1}H NMR spectrum taken 5 min after thawing showed **2** to be the predominant species in solution, with **1** being present to a smaller extent. No peak for $LiAs(SiMe_3)_2$ was evident. The spectra run after 10 and 15 min showed an increasing 1:2 ratio, and the spectrum taken after 20 min showed only those peaks corresponding to **1**. The ^{13}C NMR spectrum taken after approximately 20 min also showed only peaks assignable to **1**. The NMR tube was taken into the drybox, where it was opened and the solvent allowed to evaporate. The resulting white powder was dissolved in pentane and the pentane-insoluble powder allowed to settle. The liquor was decanted from the powder and cooled to −15 °C. After 12 h, colorless crystals had grown and were found to have the same melting point range as an authentic sample of **1**.

Table 1. Crystallographic Data for $[(Me_3CCH_2)_2InAs(SiMe_3)_2]_2$ (1) and $(Me_3CCH_2)_2\overline{InAs(SiMe_3)_2In(CH_2CMe_3)_2Cl}$ (2)

	1	2
mol formula	$C_{32}H_{80}As_2In_2Si_4$	$C_{26}H_{62}AsClIn_2Si_2$
fw	956.82	770.97
cryst syst	monoclinic	monoclinic
space group	$C2/m$ (C_{2h}^3), No. 12	$C2/c$ (C_{2h}^6), No. 15
a, Å	19.789(2)	20.191(2)
b, Å	12.878(1)	9.967(1)
c, Å	12.282(1)	19.758(2)
β, deg	127.49(1)	99.67(1)
V, Å^3	2484(1)	3920(1)
Z	2	4
D_{calcd}, g cm^{-3}	1.279	1.306
temp, °C	23	23
radiation (λ, Å)	Cu Kα (1.5418)	Cu Kα (1.5418)
cryst dimens, mm	0.08 × 0.34 × 0.50	0.08 × 0.20 × 0.20
μ, cm^{-1}	101.5	118.8
T_{max}:T_{min}, relative	1.00:0.24	1.00:0.40
scan type	$\omega-2\theta$	$\omega-2\theta$
scan width, deg	0.90 + 0.14 tan θ	0.50 + 0.14 tan θ
θ_{max}, deg	75	65
intensity control rflns	512, 332, 42$\bar{3}$, 51$\bar{2}$	115, $\bar{1}\bar{1}\bar{5}$, 42$\bar{2}$, 62$\bar{2}$
variation, %; repeat time, h	<2; 2	<2; 2
no. of rflns recorded	2751 (+h,+k,±l)	3414 (+h,+k,±l)
no. of nonequiv rflns	2671	3306
R_{merge} (on I)	0.033	0.054
no. of reflns retained	2089, $I > 3.0\sigma(I)$	901, $I > 3.0\sigma(I)$
no. of params refined	102	151
extinction correction	1.6(2) × 10^{-6}	3(1) × 10^{-7}
R (R_w)[b]	0.059 (0.088)	0.071 (0.090)
goodness-of-fit[c]	2.02	1.96
max shift/esd in final least-squares cycle	0.03	0.01
final max, min $\Delta\varrho$, e Å^{-3}	1.1; −1.2	1.00; −0.60

[a] An Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator was used for all measurements. Crystallographic calculations were performed on PDP11/44 and MicroVAX computers by use of the Enraf-Nonius Structure Determination Package (SDP). [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $\sum w\Delta^2[w = 1/\sigma^2(|F_o|), \Delta = (|F_o| - |F_c|)]$ was minimized. [c] Goodness-of-fit = $[\sum w\Delta^2/(N_{observns} - N_{params})]^{1/2}$.

X-ray Crystal Structure Analysis of 1 and 2. Crystallographic data and a summary of data collection and refinement parameters are presented in Table 1. Intensity data were corrected for the usual Lorentz and polarization effects; empirical absorption corrections, based in each case on the ϕ dependency of the intensities of several reflections with ψ ca. 90°, were also applied. The crystal structure of **1** was solved by the heavy-atom approach. Initial In and As coordinates were derived from a Patterson map. Weighted F_0 and difference Fourier syntheses yielded Si and C atom positions. For **2**, coordinates for the non-hydrogen atoms of the isomorphous phosphorus analog[19] were used as initial input to the structure-factor calculations. Positional and thermal parameters of the non-hydrogen atoms of **1** and **2** (at first isotropic, then anisotropic) were adjusted by means of several rounds of full-matrix least-squares calculations. The resulting extremely large anisotropic displacement parameter of the Cl atom perpendicular to the ring plane as well as the orientations and

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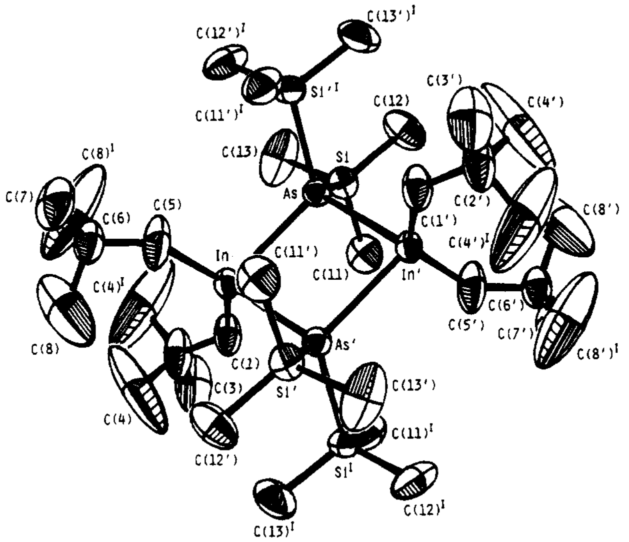

Figure 1. ORTEP diagram (30% probability ellipsoids) showing the solid-state structure of $[(Me_3CCH_2)_2InAs(SiMe_3)_2]_2$ (**1**). Hydrogen atoms have been omitted. Primed atoms are related to the unprimed atoms by a crystallographic center of symmetry. Roman numeral superscript I indicates atoms related by a mirror plane of symmetry passing through the In atoms and perpendicular to the In—As—In'—As' ring plane.

magnitudes of the thermal ellipsoids of the neopentyl carbon atoms in **2** indicated that the crystal sites were occupied by pairs of rings puckered in the opposite sense, resulting in an averaged apparently planar geometry. The Cl atom was moved off of the 2-fold axis and refined with 50% occupancy in the subsequent iterations. Attempts to derive pairs of positions for the disordered neopentyl carbon atoms by Fourier methods proved unsuccessful due to the very diffuse nature of the electron density distributions. In the later iterations, hydrogen atoms, other than those of the neopentyl groups of **2**, were incorporated at their calculated positions (C—H = 1.05 Å). An extinction correction was included as a variable in the final cycles. Final difference Fourier syntheses for **1** and **2** contained no unusual features. For all structure-factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from ref 20.

Results and Discussion

The dehalosilylation reaction between $(Me_3CCH_2)_2InCl$ and $As(SiMe_3)_3$ in a 1:1 mole ratio at room temperature in benzene affords the dimeric compound $[(Me_3CCH_2)_2InAs(SiMe_3)_2]_2$ (**1**). This dimer has been characterized by melting point, ^1H and ^{13}C NMR spectroscopy, a partial elemental analysis (C and H), and an X-ray crystal structure determination. The net reaction is shown in eq 1. Compound **1** has also been

$$2(Me_3CCH_2)_2InCl + 2As(SiMe_3)_3 \rightarrow [(Me_3CCH_2)_2InAs(SiMe_3)_2]_2 + 2Me_3SiCl \quad (1)$$

prepared from the 1:1 mole ratio reaction of $(Me_3CCH_2)_2InCl$ with $LiAs(SiMe_3)_2$. This salt elimination reaction, although only run on an NMR tube scale, appears to be more efficient than the dehalosilylation method.

Crystals of **1** suitable for an X-ray diffraction study were grown from pentane. An ORTEP diagram showing the atom-numbering scheme and solid-state conformation of **1** is presented in Figure 1. Non-hydrogen atom fractional coordinates and equivalent isotropic thermal parameters are listed in Table 2; selected distances and angles are provided in Table 3.

Table 2. Non-Hydrogen Atom Fractional Coordinates and Equivalent Isotropic Thermal Parameters for $[(Me_3CCH_2)_2InAs(SiMe_3)_2]_2$ (1), with Estimated Standard Deviations in Parentheses

atom	x	y	z	B_{eq}, Å^2
In	0.11325(3)	0.00000(−)[a]	0.19472(5)	4.86(1)
As	0.00000(−)[a]	0.14224(8)	0.00000(−)[a]	4.65(2)
Si	−0.0566(1)	0.2533(2)	0.0779(2)	6.03(5)
C(1)	0.0937(6)	0.0000(−)[a]	0.3504(9)	7.7(4)
C(2)	0.1581(7)	0.0000(−)[a]	0.4983(10)	10.6(6)
C(3)	0.1247(9)	0.0000(−)[a]	0.5786(13)	14.8(9)
C(4)	0.2153(9)	−0.0834(23)	0.5399(13)	35.0(8)
C(5)	0.2204(6)	0.0000(−)[a]	0.1885(14)	10.9(6)
C(6)	0.3098(6)	0.0000(−)[a]	0.2928(10)	7.7(4)
C(7)	0.3596(7)	0.0000(−)[a]	0.2346(14)	11.5(6)
C(8)	0.3319(8)	−0.0928(23)	0.3751(14)	29.8(8)
C(11)	−0.1056(5)	0.1767(9)	0.1396(8)	8.7(3)
C(12)	−0.1398(6)	0.3395(9)	−0.0621(9)	10.1(3)
C(13)	0.0306(6)	0.3341(11)	0.2239(9)	12.8(3)

[a] Fixed by symmetry.

Table 3. Selected Bond Lengths (Å) and Angles (deg), for $[(Me_3CCH_2)_2InAs(SiMe_3)_2]_2$ (1), with Estimated Standard Deviations in Parentheses

(a) Bond Lengths			
In—As	2.752(1)	In—C(1)	2.17(1)
As—Si	2.350(3)	In—C(5)	2.17(2)
(b) Bond Angles			
As—In—As'	83.46(2)	In—As—In'	96.54(3)
As—In—C(1)	106.2(1)	In—As—Si	112.91(5)
As—In—C(5)	105.4(2)	In—As—Si'[I]	114.91(2)
C(1)—In—C(5)	137.2(4)	Si—As—Si'[I]	105.0(1)
In—C(1)—C(2)	128(1)	In—C(5)—C(6)	133(1)

Molecules of **1** lie on a crystallographic center of symmetry and thus the In—As—In—As ring is strictly planar in the solid state as are the core rings in crystals of $[(Me_3CCH_2)_2GaAs(SiMe_3)_2]_2$ (**3**),[21] $[(Me_3SiCH_2)_2InAs(SiMe_3)_2]_2$ (**4**),[10] and $[(Me_3SiCH_2)_2GaAs(SiMe_3)_2]_2$ (**5**),[7] where the molecules lie on C_2 symmetry axes. That the In—As bond length of 2.752(1) Å in **1** is longer than the mean of 2.728 Å in **4** (Δ 0.024 Å) is a reflection of the greater steric demands of neopentyl versus (trimethylsilyl)methyl substituents; a like difference (0.020 Å) occurs between the Ga—As bonds in **3** and **5**. Moreover, the C—In—C bond angle of 137.2(4)° in **1** is similar to the C—Ga—C angle in **3** [135.2(3)°] whereas both are significantly smaller than the C—In—C angle in **4** [125.0(5)°] and the mean C—Ga—C angle in **5** [123.9°]. Although the Si—As—Si angles at 105.0(1)° in **1**, 102.32(1)° in **3**, 105.4(2)° in **4**, and 103.66(6)° in **5** show much less variation, those in the In dimers are consistently smaller than those in the corresponding Ga analogs. The In—As—In and As—In—As bond angles in **1** are in accord with the usually observed pattern for group 13−15 dimers wherein the endocyclic bond angle at the group 15 center is larger than that at the group 13 center,[1,5] In—As—In [96.54(3)°] ≫ As—In—As [83.46(2)°] in **1**. Corresponding values in **3**−**5** are 94.98° (mean)/85.02(3)°, 94.57(5)°/85.43° (mean), and 93.91(2)°/86.09° (mean), respectively.

The reaction of $(Me_3CCH_2)_2InCl$ and $As(SiMe_3)_3$ in a 2:1 mole ratio yields the mixed-bridging compound (Me3-

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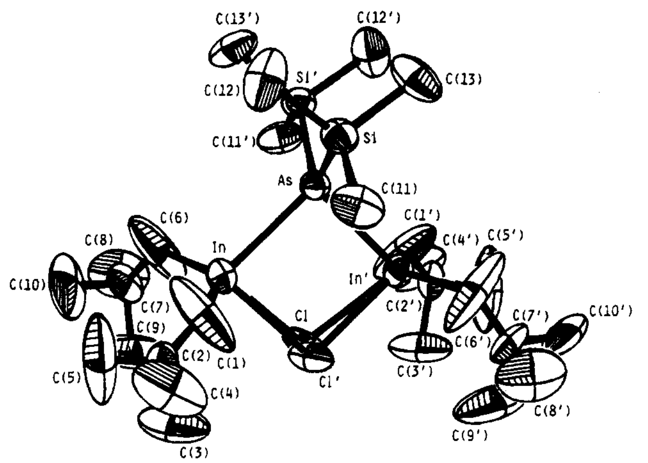

Figure 2. ORTEP diagram (20% probability ellipsoids) showing the solid-state structure of $(Me_3CCH_2)_2InAs(SiMe_3)_2In(CH_2CMe_3)_2Cl$ (**2**). Hydrogen atoms have been omitted. Primed atoms are related to the unprimed atoms by a crystallographic C_2 axis of symmetry passing through As and the midpoint of the disordered Cl atom positions.

Table 4. Non-Hydrogen Atom Fractional Coordinates and Equivalent Isotropic Thermal Parameters for $(Me_3CCH_2)_2InAs(SiMe_3)_2In(CH_2CMe_3)_2Cl$ (2), with Estimated Standard Deviations in Parentheses

atom	*x*	*y*	*z*	B_{eq}, Å^2
In	0.0910(1)	0.2797(2)	0.2313(1)	8.39(5)
As	0.0000(−)[a]	0.0916(4)	0.2500(−)[a]	7.3(1)
Cl[b]	−0.0103(6)	0.4486(11)	0.2268(9)	13.6(7)
Si	0.0367(4)	−0.0494(8)	0.3439(4)	9.5(2)
C(1)	0.168(2)	0.297(4)	0.331(2)	28(1)
C(2)	0.216(1)	0.377(3)	0.345(1)	10(1)
C(3)	0.191(2)	0.521(3)	0.323(2)	23(2)
C(4)	0.247(2)	0.382(4)	0.414(2)	23(2)
C(5)	0.259(2)	0.385(8)	0.303(2)	33(3)
C(6)	0.101(2)	0.272(5)	0.118(2)	35(2)
C(7)	0.118(1)	0.364(3)	0.081(1)	12(1)
C(8)	0.088(2)	0.383(5)	0.008(2)	23(2)
C(9)	0.122(3)	0.508(4)	0.105(2)	30(3)
C(10)	0.185(2)	0.360(4)	0.082(2)	34(2)
C(11)	0.064(2)	0.056(3)	0.421(1)	13(1)
C(12)	0.107(1)	−0.157(4)	0.325(1)	16(1)
C(13)	−0.033(2)	−0.162(3)	0.360(2)	15(1)

[a] Fixed by symmetry. [b] Occupancy factor = 0.5.

Table 5. Selected Bond Lengths (Å) and Angles (deg), for $(Me_3CCH_2)_2InAs(SiMe_3)_2In(CH_2CMe_3)_2Cl$ (2), with Estimated Standard Deviations in Parentheses

(a) Bond Lengths			
In—As	2.694(3)	In—C(1)	2.30(4)
In—Cl	2.639(12)	In—C(6)	2.28(4)
In—Cl′	2.574(14)	As—Si	2.346(8)
(b) Bond Angles			
As—In—Cl	84.6(3)	In—As—In′	91.8(1)
As—In—Cl′	85.9(3)	In—As—Si′	116.1(2)
As—In—C(1)	108(1)	Si—As—Si′	106.4(3)
As—In—C(6)	107(1)	In—Cl—In′	95.8(4)
Cl—In—Cl(1)	113(1)	As—Si—C(11)	109(1)
Cl—In—C(6)	101(1)	As—Si—C(12)	110(1)
Cl′—In—C(1)	93(1)	As—Si—C(13)	110(1)
Cl′—In—C(6)	120(1)	In—C(1)—C(2)	129(3)
C(1)—In—C(6)	133(1)	In—C(6)—C(7)	129(3)
In—As—Si	113.2(2)		

$CCH_2)_2InAs(SiMe_3)_2In(CH_2CMe_3)_2Cl$ (**2**). It is extremely soluble in benzene, toluene, pentane, ligroin, and chlorobenzene, a property that makes it difficult to separate from the orange byproduct(s) by recrystallization, even at −78 °C. Attempts to sublime **2** failed, as the crude reaction products decomposed to a nonvolatile black material after prolonged heating. The net reaction is shown in eq 2.

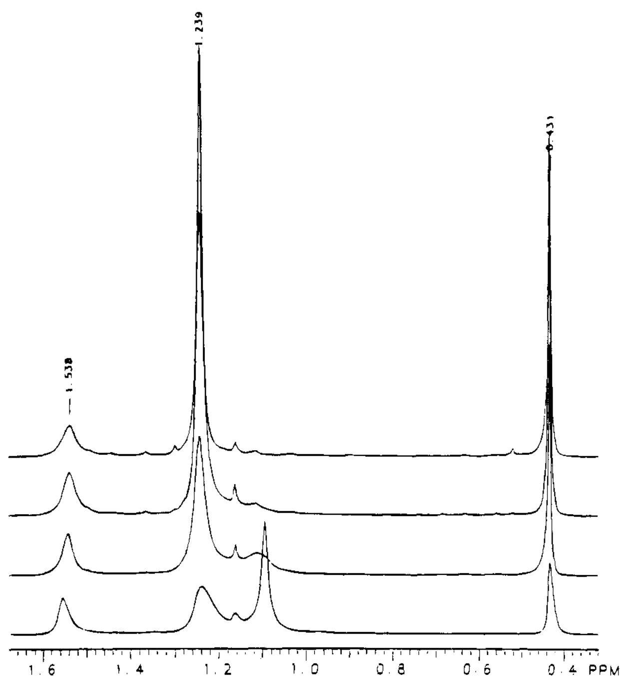

Figure 3. ^1H NMR spectra showing the reaction of $[(Me_3CCH_2)_2InAs(SiMe_3)_2]_2$ (**1**) with 2 mol equiv of $(Me_3CCH_2)_2InCl$ to produce the mixed-bridge $(Me_3CCH_2)_2InAs(SiMe_3)_2In(CH_2CMe_3)_2Cl$ (**2**). From bottom to top, spectra recorded 1, 4, 8, and 20 min after the solvent (C_6D_6) was allowed to thaw.

$$2(Me_3CCH_2)_2InCl + As(SiMe_3)_3 \rightarrow (Me_3CCH_2)_2InAs(SiMe_3)_2In(CH_2CMe_3)_2Cl + Me_3SiCl \quad (2)$$

The stoichiometry of $(Me_3CCH_2)_2InCl$ and $As(SiMe_3)_3$ determines whether the reaction product is dimeric or mixed-bridging. This is analogous to the 1:1 and 2:1 mole ratio reactions between $(Me_3SiCH_2)_2InCl$ and $As(SiMe_3)_3$;[10] however, the 1:1 reaction is in marked contrast to the 1:1 reactions of $(Me_3CCH_2)_2GaCl$[21] or $(Me_3SiCH_2)_2GaCl$[7] with $As(SiMe_3)_3$. The 1:1 mole ratio reaction of $(Me_3CCH_2)_2GaCl$ with $As(SiMe_3)_3$ yields the adduct $(Me_3CCH_2)_2(Cl)Ga{\cdot}As(SiMe_3)_3$. This adduct does not react with an additional equivalent of $(Me_3CCH_2)_2GaCl$, nor does it eliminate Me_3SiCl upon prolonged heating to produce the dimer $[(Me_3CCH_2)_2GaAs(SiMe_3)_2]_2$. When equimolar amounts of $(Me_3SiCH_2)_2GaCl$ and $As(SiMe_3)_3$ are allowed to react, the mixed-bridge $(Me_3SiCH_2)_2GaAs(SiMe_3)_2Ga(CH_2SiMe_3)_2Cl$ is the only product isolated.

Recrystallization of **2** from pentane furnished crystals suitable for an X-ray structure analysis. An ORTEP diagram of **2**, with the atom-numbering scheme, is shown in Figure 2. Non-hydrogen atom fractional coordinates and equivalent isotropic thermal parameters are listed in Table 4; selected distances and angles are provided in Table 5. Unlike its (trimethylsilyl)methyl analog $(Me_3SiCH_2)_2InAs(SiMe_3)_2In(CH_2SiMe_3)_2Cl$

(**6**),[10] which contains a crystallographically-imposed planar In—As—In—Cl ring with a C_2 symmetry axis passing through the As and Cl atoms, the corresponding ring in **2** is slightly puckered (mean endocyclic torsion angle about ring bonds = 10.5°). The In—As bond length in **2** [2.694(3) Å] is longer than that in **6** [2.677(1) Å], whereas the In—Cl distances [2.61 Å (mean) in **2**; 2.619(2) Å in **6**] are essentially equal as are the As—Si lengths [2.346(8) Å in **2**; 2.356(2) Å in **6**]. The mean As—In—Cl bond angle at 85.3° in **2** is slightly smaller than that of 86.59(6)° in **6**, while the exocyclic C—In—C angle at 133(1)° in **2** is considerably enlarged over that at 126.3(3)° in **6**. Increased steric demands of the neopentyl group versus the (trimethylsilyl)methyl group account for these variations.

Compound **1** can be readily converted to mixed-bridging compound **2** by reaction with 2 mol equiv of $(Me_3CCH_2)_2InCl$. Figure 3 shows the ^1H NMR spectra for this reaction approximately 1, 4, 8, and 20 min (from bottom to top) after the solvent had been allowed to thaw. The first spectrum shows peaks corresponding to compound **2** and the methyl protons of $(Me_3CCH_2)_2InCl$. The methylene protons of **2** and $(Me_3CCH_2)_2InCl$ occur at very similar chemical shifts, and the unsymmetric peak at δ 1.56 ppm is mainly due to the latter. After 8 min, the predominant species in solution is **2**, and after an additional 12 min, the spectrum has not changed. No peaks corresponding to **1** were observed in any of the spectra. Apparently, the more soluble $(Me_3CCH_2)_2InCl$ reacts with **1** as soon as the dimer goes into solution. On the basis of the low yield of **2** obtained *via* the dehalosilylation method, this equilibration reaction is a much better means for preparing the mixed-bridge compound.

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Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom coordinates and isotropic thermal parameters, and complete lists of bond lengths and angles for **1** and **2** (6 pages). Ordering information is given on any current masthead page.

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