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# Systematic Experimental and Quantum Chemical Investigation into the Structures, the Stability, and the Spectroscopic Properties of Alkylindium(I) Compounds: Tetrameric $In_4[C(SiMeRR')_3]_4$ versus Monomeric $InC(SiMeRR')_3$ Derivatives[†]

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The reaction of indium monobromide (InBr) with $LiC(SiMeRR')_3 \cdot x$THF gives in a high yield alkylindium(I) derivatives with the indium atoms in the unusual low oxidation state of +1. The properties of these products are investigated by the systematic variation of the steric demand of the $C(SiMeRR')_3$ substitutents (R = Me, Et; R′ = Me, Et, $^n$Bu, $^i$Pr, Ph). Tetrahedral $In_4$ clusters are observed in the solid state and in solution for smaller substituents such as $C(SiMe_3)_3$, $C(SiMe_2Et)_3$ (**1**), and $C(SiMe_2{}^nBu)_3$ (**2**). As shown by two crystal structure determinations, those clusters exhibit undistorted tetrahedra of four indium atoms and short In−In distances of 3.00 Å on average. In contrast, owing to the larger steric stress, complete dissociation into the monomeric formula units InR is observed in solution with the more voluminous $C(SiMe_2{}^iPr)_3$ group (**3**), while in the solid state once more an almost undistorted tetrahedron of the tetramer is found, showing, however, much elongated In−In distances of 3.155 Å on average. Single crystals could not be obtained for the compounds with $C(SiMe_2Ph)_3$ (**4**) and $C(SiEt_2Me)_3$ groups (**5**); **4** is monomeric in benzene, while **5** gives the formula mass of the dimer, and complete dissociation into the monomer is observed only in very dilute solutions. All compounds show unusual downfield shifts of the resonances of the carbon atoms bound to indium up to $\delta = 76$ ppm, which are very characteristic of the alkylindium(I) compounds. Quantum chemical NMR chemical shift calculations using density functional theory indicate that the large shifts are related to the presence of low-lying magnetically allowed excited states, and they are further enhanced by unusually large spin−orbit effects. Optimized structure parameters for $InCH_3$, $In_4(CH_3)_4$, InH, and $In_4H_4$ are compared with the experimental results. Our best estimate for the tetramerization energy of $InCH_3$ is ca. 290 kJ/mol at the MP2 level.

## Introduction

The synthesis of compounds containing the elements of the third main group in low oxidation states is of particular interest in current organoelement chemistry. An oxidation state of +1 has long been known in cyclopentadienyl derivatives of the heavier elements indium and thallium,[1−4] but corresponding aluminum(I) and gallium(I) derivatives have been described only recently.[5,6] The cyclopentadienyl ligands are bound in a pentahapto fashion, and mostly, the compounds form

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[†] Dedicated to Prof. Dr. B. Krebs on the occasion of his 60th birthday.

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chain polymers in the solid state.[1,3] With sterically demanding substituents such as pentamethyl or pentabenzyl cyclopentadienyl pseudohexamers or dimers[2,4] are detected with weak element−element bonds. Only the Al($C_5Me_5$) derivative deviates in its structure and shows a tetrahedral arrangement of four aluminum atoms with short bonding Al−Al distances.[6] All cyclopentadienyl compounds are readily volatile on heating and monomerize in the gas phase.[7] Alkyl derivatives of the univalent elements have been obtained only recently, and only a few examples are described in the literature: $B_4(CMe_3)_4$,[8] $Ga_4[C(SiMe_3)_3]_4$,[9] and $In_4[C(SiMe_3)_3]_4$[10,11] as well as the silyl derivative $Ga_4[Si(SiMe_3)_3]_4$.[12] The similar compounds $Al_4[Si(CMe_3)_3]_4$,[13] $Al_4(CH_2CMe_3)_4$, and $(GaCH_2CMe_3)_x$[14] were up to now not characterized by a crystal structure determination. All these compounds need bulky substituents in order to prevent a disproportionation reaction, and as far as crystal structures are available they form almost undistorted tetrahedral molecules with strong element−element bonding interactions. In contrast, the alkylthallium(I) compound $Tl_4[C(SiMe_3)_3]_4$ shows a severely distorted $Tl_4$ molecular center with long Tl−Tl distances and dissociates to monomers completely upon dissolution in benzene.[15] The $In_4$ analogue remains a tetramer in solution, while the Ga derivative dissociates to monomers slowly with increasing dilution. The difference between the In and Ga compounds may be caused by the shorter Ga−Ga and Ga−C distances, which lead to a larger steric strain in the molecule and favor the dissociation. The monomeric Ga compound could even be characterized by electron diffraction in the gas phase above 200 °C.[16] These monomeric alkylelement(I) fragments have highly coordinatively and electronically unsaturated central atoms and may be important intermediates in the intensively investigated chemical reactions of those tetraelement compounds. We now have tried to generate monomeric organo In(I) compounds by the systematic enlargement of the substituents, to intensively study their singular chemical and physical properties. Monomeric pyrazolyl compounds with univalent gallium, indium, and thallium atoms have been described, but their central atoms are saturated by coordination to three nitrogen atoms, and they do not tend to form stable oligomers.[17] A monomeric indium(I) aryl derivative sterically highly shielded by a tris(triisopropylphenyl)phenyl group recently has been synthesized by the group of Power.[18]

## Results and Discussion

**Syntheses of the Alkylindium(I) Compounds.** The $C(SiMeRR')_3$ substituents and the corresponding lithium derivatives were synthesized according to literature procedures.[19−22] Details are given in the Experimental Section. The syntheses of the alkylindium(I) compounds followed the simple route recently published by our group[10] and the group of Cowley[11] for the preparation of $In_4[C(SiMe_3)_3]_4$: A suspension of an excess of freshly sublimed indium monobromide in toluene was treated at low temperature with the corresponding trisilylmethyllithium derivatives (eq 1). The mixtures were warmed slowly to room temperature, and the color of the orange InBr disappeared. After the filtration deep violet solutions of the indium compounds were obtained. Only the phenyl derivative **4** yielded an orange solution. The reaction mixtures were stirred at room temperature for different periods depending on the stability of the compounds in solution. The $SiMe_2Et$ derivative (**1**) is stable at room temperature, similar to the $SiMe_3$ compound.[10] Slow decomposition was observed with $SiMe_2{}^nBu$ (**2**) and $SiEt_2Me$ (**5**) derivatives, while the $SiMe_2{}^iPr$ and $SiMe_2Ph$ derivatives (**3** and **4**) rapidly decomposed in solution at room temperature to give gray elemental indium and the corresponding methanes in several hours. After concentration of their solutions and cooling to −50 °C the products **1**, **3**, and **5** were isolated as deep violet, almost black, crystals. **4** ($SiMe_2Ph$) precipitated as an orange-brown, amorphous solid, **2** ($SiMe_2{}^nBu$) could not be recrystallized and was

$$4\,InBr + 4\,LiC(SiMeRR')_3 \cdot xTHF \longrightarrow 4/n\,[In\text{-}C(SiMeRR')_3]_n + 4\,LiBr + x\,THF \qquad (1)$$

R = Me, R′ = Et: **1**
R = Me, R′ = *n*-Bu: **2**
R = Me, R′ = *i*-Pr: **3**
R = Me, R′ = Ph: **4**
R = Et, R′ = Et: **5**

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**Table 1. Properties of the Known Alkylindium(I) Compounds $[InC(SiMeRR')_3]_n$**

| R,R′ | UV/vis (nm)[a] | $\delta(^{13}C)$ InC[b] | solution[c] | solid state | In−In (Å) | IR $\nu(In_4C_4)$ ($cm^{-1}$)[d] |
|---|---|---|---|---|---|---|
| Me,Me[10] | 490 | 72.0 | tetrameric | tetrameric | 3.002 | 567 |
| Me,Et **1** | 490 | 73.3 | tetrameric | tetrameric | 3.004 | 600; 561 |
| Me,$^n$Bu **2** | 490 | 73.5 | tetrameric | | | 569 |
| Me,$^i$Pr **3** | 390 | 60.1 | monomeric | tetrameric | 3.152 | 604; 521 |
| Me,Ph **4** | 365 | 43.0 | monomeric | | | 554 |
| Et,Et **5** | 495 | 76.3 | dimeric − monomeric | tetrameric | | 606; 554 |

[a] *n*-Hexane. [b] $C_6D_6$. [c] Benzene. [d] Paraffin.

isolated as a dark violet oil. All crystalline compounds are air-stable. Their decomposition points correlate with steric strain and decrease from $In_4[C(SiMe_3)_3]_4$ (180 °C)[10] to 147 °C (**1**), 120 °C (**5**), and 65 °C (**3**). $LiC(SiMe_2c\text{-}Hex)_3$ did not react with InBr at low temperature, and even after 10 min at room temperature no reaction was detected by NMR spectroscopy. After 1 h the reaction mixture became black due to precipitating elemental indium, and the hydrogen compound $HC(SiMe_2c\text{-}Hex)_3$ was formed in quantitative yield.

$In_4[C(SiMe_3)_3]_4$ is tetrameric in the solid state and in dilute solutions, as shown by the cryoscopically determined molar mass in benzene. Similarly, compounds **1** ($SiMe_2Et$) and **2** ($SiMe_2{}^nBu$) are tetrameric independent of their concentration in benzene. As expected, the larger steric demand of the substituents in the $SiMe_2{}^iPr$ (**3**) or the $SiMe_2Ph$ derivatives (**4**) led to their complete dissociation in benzene at all concentrations, and only the mass of the monomer was observed cryoscopically. This is the first time that monomeric alkylindium(I) species could be detected unambiguously. These species are possible intermediates in many reactions of $In_4[C(SiMe_3)_3]_4$ and could up to now only be trapped by their reaction with heterobutadiene derivatives such as benzil;[23] they are unique in their extreme coordinative and electronic unsaturation. The structure of the analogous monomeric compound $GaC(SiMe_3)_3$, which is stable in the gas phase up to 250 °C, has been determined recently in collaboration with the group of Haaland by gas-phase electron diffraction.[16] The $SiEt_2Me$ compound **5** shows an intermediate behavior and remarkably gives a dimeric formula mass at a normal concentration (see Experimental Section) and dissociates to monomers gradually with increasing dilution. **5** is thus quite similar to the gallium analogue $Ga_4[C(SiMe_3)_3]_4$.[9] **1** and **3** are tetrameric in the solid state (see below). In view of its orange-brown color, the $SiMe_2Ph$ derivative **4** seems to have another structure. But dark violet crystals were isolated on very slow crystallization from dilute solution in *n*-pentane, cyclopentane, or diisopropyl ether, which were, however, not suitable for a crystal structure determination. Their tetrameric form can be deduced only from the very characteristic color. **5** typically crystallizes as red-violet needles, which were not suitable for X-ray diffraction. Octahedral crystals could, however, be obtained from mixtures of some solvents (*n*-pentane, cyclopentane, diisopropyl ether, xylene) with acetone. However, X-ray data collections gave only insufficient data sets, and only the $In_4$ molecular center could be refined satisfactorily. The results concerning the aggregation are summarized in Table 1.

The most interesting result of the NMR spectroscopic characterization of the In(I) compounds is the strong downfield chemical shift in the $^{13}C$ NMR spectra of the carbon atoms bound to the univalent indium atom (Table 1). A chemical shift of about 73 ppm is observed for those compounds, which are tetrameric or oligomeric in solution. This is more than 40 ppm downfield to the region where alkyl derivatives of trivalent indium atoms usually are observed.[24] A less dramatic shift to 60.1 and 43.0 ppm was observed for the monomeric compounds **3** and **4**, respectively.

The tetrameric or oligomeric derivatives **1**, **2**, and **5** as well as $In_4[C(SiMe_3)_3]_4$ show a very characteristic UV/vis spectrum with the most bathochromatically shifted absorption at about 490 nm. This can be assigned to the $In_4$ cluster in the molecular center (Table 1). Those compounds that dissociate completely and are monomeric in solution show the most bathochromically shifted absorptions at 390 (**3**) or 365 nm (**4**). This is in good agreement with the color observed for the corresponding solutions, which is violet for the tetrameric species and orange for **3** ($SiMe_2{}^iPr$) or orange-brown to yellow for **4** ($SiMe_2Ph$) depending on the concentration.

**Crystal Structures of the Compounds 1 and 3.** Single crystals of **1** were obtained by recrystallization from diisopropyl ether at 0 °C. The $SiMe_2{}^iPr$ compound **3** normally crystallizes as multiple-twinned octahedral crystals from all solvents that were tried, and after many unsuccessful attempts, we succeeded in growing small hexagonal prisms, suitable for a crystal structure determination, by storing a very dilute solution in diisopropyl ether for several weeks at −30 °C. The lattice parameters were subsequently determined also for the twinned crystals. **1** has the acentric rhombohedral space group *R*3; **3** the centrosymmetric trigonal space group $P\bar{3}$. Both molecules are located on crystallographic 3-fold rotation axes through the atoms In2 and C2.

Figure 1 shows the molecular structure of compound **1**; an identical numbering scheme for the displayed atoms was used for **3**. Both compounds exhibit almost undistorted tetrahedra of four In atoms, with a very small deviation of the In−In distances from the average value in the order of the standard deviations for **1** (Table 2) and somewhat larger with ±0.01 Å in the $SiMe_2{}^iPr$ derivative **3** (Table 2). All inner cluster angles approach the ideal value of 60°. A comparison of both structures should give important insight into the reason for the differing behavior in solution and should help to verify the hypothesis that the easy dissociation of **3** is mainly

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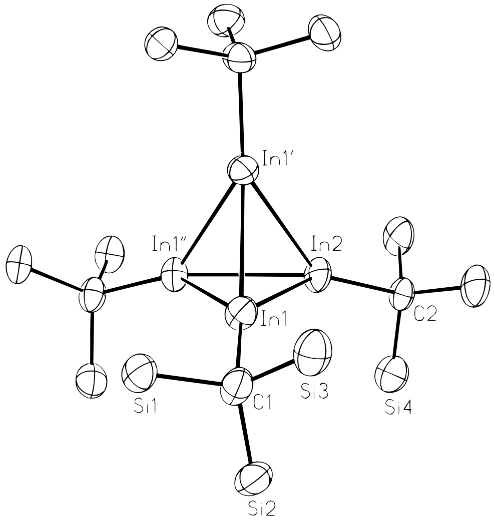

**Figure 1.** Molecular structure of **1**. An identical numbering scheme is used for **3**. The ellipsoids are drawn at the 50% probability level. Methyl groups are omitted for clarity. the atom In1′ was generated by the symmetry operation $-y$, $x - y$, $z$; In1″ by $-x + y$, $-x$, $z$.

**Table 2. Important Bond Lengths (Å) and Angles (deg) of the Tetraindium Compounds 1 and 3**[a]

| | **1** | **3** |
|---|---|---|
| In1−In2 | 3.004(1) | 3.145(1) |
| In1−In1′ | 3.005(1) | 3.165(2) |
| In1−C1 | 2.27(1) | 2.299(8) |
| In2−C2 | 2.24(1) | 2.28(1) |
| In1′−In1−In2 | 59.99(2) | 59.80(2) |
| In1′−In1−In1″ | 60.00 | 60.00 |
| In1−In2−In1′ | 60.02(3) | 60.41(4) |
| In2−In1−C1 | 145.8(2) | 145.5(2) |
| In1′−In1−C1 | 143.4(3) | 145.2(2) |
| In1″−In1−C1 | 145.0(3) | 143.8(2) |
| In1−In2−C2 | 144.72(2) | 144.49(2) |

[a] The atom In1′ was generated by the symmetry operation $-y$, $x - y$, $z$ (**1**) and $-y + 1$, $x - y$, $z$ (**3**) and the atom In1″ by $-x + y$, $-x$, $z$ (**1**) and $-x + y + 1$, $-x + 1$, $z$ (**3**).

a consequence of a strong intramolecular steric repulsion between the bulky substituents. The In−In distances in the less shielded $SiMe_2Et$ derivative **1** are 3.004 Å on average, which is almost identical to the value found in $In_4[C(SiMe_3)_3]_4$ (3.002(1) Å),[10] so that the transition from $SiMe_3$ to $SiMe_2Et$ groups apparently has no influence on the steric repulsion in the molecule. As expected for the delocalized electronic system in the cluster with eight bonding electrons, the In−In distance is slightly longer than the In−In single bond length in organoelement derivatives of the type $R_2In{-}InR_2$, in which values below 2.82 Å were observed.[13,25] The In−C bond lengths in both cluster molecules are quite similar 2.26(1) Å in **1** and 2.25(1) Å in **3**, which, as expected, is lengthened compared to the standard value of 2.18 Å for compounds with trivalent indium atoms. In contrast, the In−In distances in **3**, with the bulkier $SiMe_2{}^iPr$ substituents, show a strong effect of steric overloading and are increased by 0.15 Å to 3.155 Å on average. This clearly indicates a significant weakening of the In−In bonding interactions in the cluster and may be responsible for the easy dissociation in solution. A comparison of the In−In distances of all known $In_4$ clusters is given in Table 1. The In−C bond lengths in **3** are also lengthened to 2.29 Å on average, but since the standard deviation for the In−C bond lengths is about 0.01 Å, the lengthening should not be further discussed.

**Table 3. Calculated Structural Parameters for the Compounds InX, $(InX)_4$, and $InX_3$ (X = H, $CH_3$)**[a]

| | $r$(In−In) | $r$(In-X) | $r$(C−H) | ∠(H−C−In) | $\Delta E_{\text{tetr}}$[b] |
|---|---|---|---|---|---|
| InH | | 1.853 | | | |
| | | (1.823) | | | |
| $(InH)_4$ | 2.935 | 1.753 | | | −266 (−337) |
| | (2.932) | (1.731) | | | |
| $InH_3$ | | 1.726 | | | |
| | | (1.712) | | | |
| $InCH_3$ | | 2.261 | 1.100 | 111.8 | |
| | | (2.247) | (1.100) | (111.7) | |
| $(InCH_3)_4$ | 2.950 | 2.198 | 1.096 | 110.3 | −261 (−351) |
| | (2.946) | (2.189) | (1.097) | (110.2) | |
| $In(CH_3)_3$ | | 2.179 | 1.097 | 110.9 | |
| | | (2.178) | (1.097)[c] | (111.0)[c] | |

[a] Distances in Å, angles in deg, energies in kJ/mol. B3PW91 results with MP2 results in parentheses. [b] Energy for the reaction: $4InX \rightarrow (InX)_4$. [c] Average values. At B3PW91 level, one hydrogen atom acts as an (axial) hyperconjugative donor to the empty $p_z$-type orbital at the metal (with correspondingly longer C−H bond and smaller H−C−In angle). At the MP2 level, the orientation of the methyl groups is such that two C−H bonds act as hyperconjugative donors, with the third one in the $InC_3$ plane.

**Quantum Chemical Calculations on InX, $InX_3$, and $(InX)_4$ (X = H, $CH_3$). Structures and Binding Energies.** Optimized structural parameters for $InCH_3$, $In(CH_3)_3$, and $(InCH_3)_4$ are summarized in Table 3. Results for InH, $InH_3$, and $(InH)_4$ are also included for comparison. In all cases, the MP2 results (values in parentheses) agree well with the B3PW91 density-functional data. For $(InCH_3)_4$, we obtain In−In and In−C distances of ca. 2.95 and 2.19 Å, respectively. This is shorter than the measured values for compound **1** (cf. above), as one might expect in view of the reduced bulk of the unsubstituted methyl groups. An only very slightly shorter In−In distance is computed for $(InH)_4$. This suggests that the steric repulsion between the methyl groups in $(InCH_3)_4$ is insignificant.

For the monomer $InCH_3$, an In−C distance of ca. 2.26 Å is computed. This is significantly longer than that in the tetramer. This might be surprising at first sight. However, natural population analyses (NPA[26]) show that a) the In−C bond becomes considerably more covalent upon tetramerization (B3PW91 charges $Q$(In) = +0.699 and +0.506 in the monomer and in the tetramer, respectively) and (b) while in the monomer the In 5p character is essentially concentrated in the In−C bond (the lone pair being largely an In 5s orbital), the rehybridization upon tetramerization is considerable, such that the In−C bond obtains predominant 5s character (the hybridization analysis of the corresponding natural localized molecular orbital gives an $sp^{0.43}$ ratio, compared to $sp^{11.99}$ for the monomer). By this dramatic rehybridization, the In−C bond is actually strenghtened and thus shortened upon tetramerization of $InCH_3$. Similar arguments hold for the even more pronounced contraction of the In−H bond in going from InH to $(InH)_4$, and a similar contraction has previously been noted in calculations on various AlX and $(AlX)_4$

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**Table 4. Computed $^{13}$C Chemical Shifts (in ppm with Respect to TMS)[a]**

| | $\delta_{AE}$ ($\delta_{ECP}$)[b] | SO correction[c] | $\delta_{AE+SO}$[d] | expt[e] |
|---|---|---|---|---|
| $InCH_3$ | +38.4 (+39.1) | +33.1 | +71.4 | ca. 45−60 |
| $(InCH_3)_4$ | +27.1 (+35.0) | +15.0 | +42.1 | ca. 70−75 |
| $In(CH_3)_3$ | −5.7 (−0.1) | +5.1 | −0.6 | ca. 25−30 |

[a] SOS-DFPT results, see experimental section. [b] All-electron results (results with ECP on In in parentheses). [c] Spin−orbit correction with all-electron basis set. [d] With spin−orbit correction added. [e] Range of typical data in benzene solution for silyl-substituted derivatives, see above.

species.[27] It is expected that steric effects may partially compensate for this contraction in the bulkier, experimentally studied derivatives (see above; also see ref 27b). This is significant in the context of comparing computed and experimental NMR chemical shifts (see below). For the trigonal planar $InX_3$ species, still shorter In−X distances are computed, consistent with the larger metal charge in the In(III) compounds and with experimental comparisons between In(I) and In(III) species (see discussion of the crystal structures above).

The calculations also provide rough estimates for the tetramerization energy of $InCH_3$, 260.8 and 351.0 kJ/mol at the B3PW91/ECP-DZP and MP2/ECP-DZP levels, respectively (note the very similar results for InH). A counterpoise correction[28] for basis-set superposition errors (BSSE) reduces these values to 250.4 and 289.7 kJ/mol, respectively. This indicates (a) that the MP2 calculations have larger BSSE, as expected, and (b) that the cluster bonding may involve some dispersion-type bonding contributions, which are not recovered at the DFT level. The MP2 results may be compared to an MP2/TZVP tetramerization energy of 571 kJ/mol for AlH, computed by Ahlrichs et al.[27] This is consistent with the expected weaker aggregation of indium(I) compared to aluminum(I) compounds (the $(AlX)_4$ tetramers in turn are bound more weakly than the corresponding boron compounds[27,29]).

**NMR Chemical Shifts.** Table 4 gives $^{13}C(CH_3)$ shifts computed at the SOS-DFPT (sum-over-states density-functional perturbation theory) level, with and without spin−orbit (SO) corrections. First of all, we note that the SO contributions due to the presence of the heavy indium neighbor increase the $^{13}$C shift in $InCH_3$ by more than 30 ppm. This is a very large SO effect. Recent computations for methyl mercury compounds $CH_3HgX$ give $^{13}$C SO shifts in the same direction,[30] but only of ca. 3−20 ppm (depending on the substituent X), despite the larger nuclear charge of mercury (80) compared to indium (49). A canonical MO analysis shows that, analogous to the situation for the mercury compounds,[30] the interaction between a $\sigma_u$-type occupied MO and empty $\pi^*$-type metal orbitals accounts for the deshielding SO contributions. However, in contrast to $CH_3HgX$, the $\sigma_u$-type MO is nonbonding and of very high energy in $InCH_3$ (it corresponds essentially to the indium lone pair). Moreover, the $\pi^*$-type MOs (essentially indium $5p_x$ and $5p_y$ AOs) are rather low in energy. The combination of these facts accounts for the very large $^{13}$C SO shifts in $InCH_3$ (cf. ref 31 for a detailed discussion of the mechanisms underlying such SO contributions to NMR chemical shifts). Paramagnetic contributions involving the same MOs dominate the relatively large $^{13}$C shifts already at the nonrelativistic level.

Table 4 also shows that the shifts computed for both $InCH_3$ and $(InCH_3)_4$ are considerably larger than that found for $In(CH_3)_3$, in agreement with the experimental comparison between $In^I$ and $In^{III}$ alkyl compounds (see above and ref 24). The shifts for both $(InCH_3)_4$ and $In(CH_3)_3$ appear to be underestimated in the calculations by ca. 25−30 ppm. This is a somewhat larger deviation than one might expect from systematic errors in the calculations, and it is larger than the pure electronic effect of the silyl substituents present experimentally (for example, the $^{13}$C shift of $CH_4$ is only −7 ppm relative to $Si(CH_3)_4$). The largest part of the discrepancy does appear to be due to the structural changes induced by the sterically demanding silyl substituents. Thus, for example, the In−In distances in **1** are larger by ca. 0.05 Å and the In−C distances by ca. 0.07 Å than those computed for $(InCH_3)_4$. Moreover, the average Si−C−In angles are only ca. 105° compared to the optimized 110° for the H−C−In angles in the methyl compound. If we use the experimental structure of **1** but replace the silyl substituents by hydrogen atoms at 1.100 Å (keeping the 105° angles), we compute a ca. 10 ppm larger $^{13}$C shift for $(InCH_3)_4$.

In contrast to the observed decrease of the shift upon dissociation of the tetramers in solution (see above), the computed $^{13}$C shift for the $(InCH_3)_4$ tetramer is even somewhat lower than that of the $InCH_3$ monomer, already without SO corrections. This difference is further increased by the SO contributions. It is notable in this context that HF-GIAO and MP2-GIAO calculations by Gauss et al.[32] on the $^{27}$Al shifts in AlH, $AlSiR_3$, and the corresponding tetramers also gave a decrease of the shift (in that case of the metal shift) upon aggregation (also in disagreement with experimental evidence in solution). In the present case, the aggregation reduces both the uncorrected $^{13}$C shifts and the spin−orbit corrections (both depend on the presence of specific high-lying occupied as well as of low-lying unoccupied $\pi^*$ MOs).

Note that experimentally the UV spectra in solution are blue-shifted for the monomeric compared to the tetrameric compounds (see Table 1). This is compatible with our calculations on the isolated InX and $(InX)_4$ (X = H, $CH_3$) systems, where the monomer exhibits a ca. 0.5 eV larger energy gap between the highest occupied and lowest unoccupied MOs (the experimentally observed blue shift would correspond to an energy difference of ca. 0.65 eV). However, the smaller HOMO−LUMO gap in the tetramer is not reflected in a larger $^{13}$C shift, as occupied−virtual MO couplings other than those involving just the HOMO and LUMO are involved.

Two major points may be considered as the source of the discrepancy between theory and experiment: (i) the above-mentioned structural changes (bond expansion, low Si−C−In angles) in the tetramer due to the bulky

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silyl substituents (this accounts at least for ca. 10 ppm, see above); (ii) solvent effects. The experimental NMR spectra have been taken in benzene solution, and it appears reasonable to assume the formation of $\pi$ complexes of the aromatic solvent with the monomeric alkylindium(I) species. At least one $\pi$-arene complex of an indium(I) compound, $[(MesH)_2In]^+[InBr_4]^-$, has been structurally characterized.[33] The solvent donor interactions may be expected to shift unoccupied MOs in the monomer to higher energies (see also discussion in ref 32) and thus to reduce both paramagnetic and SO contributions to the shifts. However, our calculations (MP2 optimizations) on the model compound $InCH_3(\eta^6\text{-}C_6H_6)$ gave only very weak coordination of the benzene ligand. Correspondingly, the benzene coordination gave much too small corrections to the $^{13}C$ shifts to account for the observations.

## Conclusion

Alkylindium(I) compounds bearing large substituents to prevent a disproportionation reaction show a high tendency toward the formation of tetrahedral $In_4$ cluster compounds in the solid state. In solution, however, a complete dissociation into the monomers InR occurs with the largest substituents, probably because the thermal motion of the most bulky groups and the larger steric interactions compensate for the tetramerization energy (for which our ab initio calculations on $[InCH_3]_4$ give ca. −290 kJ/mol). The indium atoms of the monomeric fragments are coordinatively and electronically highly unsaturated, which may cause the reactivity of alkylindium(I) compounds observed in former studies. The similar thallium(I) compounds are exclusively monomer in solution owing to only weak Tl−Tl interactions even in the solid state, and all known alkylgallium(I) compounds dissociate slowly with increasing dilution owing to the smaller Ga−Ga and Ga−C distances and a stronger steric interaction between the substituents. The most characteristic spectroscopic property of the monomeric, and even more so of the tetrameric alkylindium(I) compounds, is the downfield shift of the $^{13}C$ NMR resonances of the carbon atoms bound to indium (or gallium) in comparison with alkylindium(III) derivatives. The large shifts are related to the presence of low-lying magnetically allowed excited states and to unusually large spin−orbit effects. We could not reproduce in our model calculations the lower shifts found for the monomeric species. We suspect solvent coordination to the monomers to account for this discrepancy, which will require further investigation.

## Experimental Section

All procedures were carried out under purified argon in dried solvents (*n*-pentane and *n*-hexane with $LiAlH_4$, toluene, diisopropyl ether and THF with Na/benzophenone). $HC(SiMe_2Et)_3$,[21] $HC(SiMe_2{}^iPr)_3$,[20] $HC(SiMe_2Ph)_3$,[19] and $LiC(SiMe_2Et)_3\cdot 1.5THF$[21] were synthesized according to literature procedures. $LiC(SiMe_2Ph)_3\cdot 2THF$ was obtained according to the literature,[19,22] but the reaction time was reduced to 3.5 h in boiling THF to avoid decomposition by ether cleavage (yield: 85%). The synthesis of $LiC(SiMe_2{}^iPr)_3\cdot 1.5THF$[20] has been reported before; the product was, however, only characterized by reactions and not isolated in a pure form. Detailed information on the improved synthesis and the characterization is given below. $BrSiMeEt_2$[34] was synthesized by a modified procedure (see below). Commercially available bromoform is stabilized by ethanol, which was removed by the repeated extraction with water. The organic layer was separated, dried with anhydrous calcium chloride, and distilled in vacuo. The pure bromoform was stored under argon at 4 °C. $ClSi(^nBu)Me_2$, $HSiEt_2Me$, $ClSi(c\text{-}Hex)Me_2$, and $ClSiHMe_2$, solutions of methyllithium in diethyl ether and *n*-butyllithium in *n*-hexane, all from Aldrich, were used without further purification. $In^IBr$ was synthesized by the reaction of $InBr_3$ with elemental indium in a melt at 320 °C[35] and sublimed in vacuo at $10^{-3}$ Torr and a bath temperature of 230 °C before use.

**$BrSiMeEt_2$.** $HSiMeEt_2$ (49.38 g, 0.484 mol) was dissolved in 500 mL of *n*-hexane and cooled to −30 °C. Bromine (77.36 g, 0.484 mol) was added dropwise under vigorous stirring. Subsequently, the light brown-orange solution was further stirred for 1 h at −30 °C and slowly warmed to room temperature. After removal of the solvent the residue was fractionated under reduced pressure to give the colorless product, bp 90 °C (165 Torr). Yield: 77.88 g (89%). Anal. Calcd for $C_5H_{13}SiBr$ (181.1): C, 33.2; H, 7.2. Found: C, 32.9; H, 7.2. $^1H$ NMR (300 MHz, $C_6D_6$): $\delta = 0.88$ (pseudo-t, 6 H, $CH_3$ of Et), 0.66 (m, 4 H, diastereotopic methylene protons of Et), 0.27 (s, 3 H, $SiCH_3$). $^{13}C$ NMR (75 MHz, $C_6D_6$): $\delta = 9.8$ ($CH_2$ of Et), 7.1 ($CH_3$ of Et), −0.5 ($SiCH_3$).

**Syntheses of the Trisilylmethane Derivatives: General Procedure.** The starting compounds $ClSiRMe_2$ or $BrSiMeEt_2$, respectively, and purified bromoform in a molar ratio of 3:1 were dissolved in 100 mL of THF and cooled to −78 °C. A cooled (−78 °C) solution of *n*-butyllithium in *n*-hexane was added dropwise under vigorous stirring. The mixtures were slowly warmed to room temperature overnight. After filtration the solvent was removed in vacuo, and the colorless, highly viscous products were purified by fractional distillation in vacuo. For R = cyclohexyl, the residue was heated to 150 °C at $10^{-3}$ Torr and recrystallized from *n*-pentane (20/−50 °C).

**$HC(SiMe_2{}^nBu)_3$.** Yield: 55%. Bp: 86−91 °C ($10^{-3}$ Torr). Anal. Calcd for $C_{19}H_{46}Si_3$ (358.8): C, 63.6; H, 12.9. Found: C, 63.1; H, 13.0; mol wt 334 (cryoscopically in benzene). $^1H$ NMR (300 MHz, $C_6D_6$): $\delta = 1.35$ (m, 12 H, $CH_2CH_2CH_3$ of $^nBu$), 0.93 (t, $^3J_{HH} = 6.9$ Hz, 9 H, $CH_3$ of $^nBu$), 0.68 (pseudo-t, 6 H, $SiCH_2$ of $^nBu$), 0.19 (s, 18 H, $SiCH_3$), −0.61 (s, 1 H, $HCSi_3$). $^{13}C$ NMR (75 MHz, $C_6D_6$): $\delta = 27.1$ and 26.9 ($CH_2CH_2CH_3$ of $^nBu$), 19.1 ($SiCH_2$), 14.0 ($CH_3$ of $^nBu$), 1.6 ($SiMe_2$), 0.1 ($HCSi_3$).

**$HC(SiMe_2c\text{-}Hex)_3$.** Yield: 42%. Mp (argon, closed capillary): 105 °C. Anal. Calcd for $C_{25}H_{52}Si_3$ (436.9): C, 68.7; H, 12.0. Found: C, 68.6; H, 12.0. $^1H$ NMR (300 MHz, $C_6D_6$): $\delta =$ 1.76 and 1.26 (each: m, 12 H, $CH_2$ of C2 and C3 of *c*-Hex), 1.10 (m, 6 H, $CH_2$ of C4 of *c*-Hex), 0.86 (m, 3 H, CH of C1 of *c*-Hex), 0.17 (s, 18 H, $SiCH_3$), −0.29 (s, 1 H, $HCSi_3$). $^{13}C$ NMR (75 MHz, $C_6D_6$): $\delta = 28.8$ and 28.1 (C2 and C3 of *c*-Hex), 27.8 and 27.4 (C1 and C4 of *c*-Hex), −0.6 (SiMe), −2.9 ($HCSi_3$).

**$HC(SiEt_2Me)_3$.** Yield: 68%. Bp: 82−92 °C (0.03 Torr). Anal. Calcd for $C_{16}H_{40}Si_3$ (316.8): C, 60.7; H, 12.7. Found: C, 60.1; H, 12.6. MS: *m/z* (%) (CI, isobutane) 301.6 (8) $[M^+ - CH_3]$, 287.5 (100) $[M^+ - CH_2CH_3]$. $^1H$ NMR (300 MHz, $C_6D_6$): $\delta =$ 0.97 (t, $^3J_{HH} = 7.9$ Hz, 18 H, $CH_3$ of Et), 0.66 (q, $^3J_{HH} = 7.9$ Hz, 12 H, $CH_2$ of Et), 0.14 (s, 9 H, $SiCH_3$), −0.39 (s, 1 H, $HCSi_3$). $^{13}C$ NMR (75 MHz, $C_6D_6$): $\delta = 8.9$ ($CH_2$ of Et), 8.1 ($CH_3$ of Et), −1.7 (SiMe), −6.7 ($HCSi_3$).

**Syntheses of the Compounds $LiC(SiMeRR')_3\cdot xTHF$: General Procedure.** Solutions of methyllithium in diethyl ether (10% excess) were added to the trisilylmethane derivatives dissolved in THF. The mixtures were stirred up to 22 h

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at room temperature. With R = Me and R′ = isopropyl or cyclohexyl the diethyl ether was subsequently distilled off under normal pressure, and the brown THF solutions were refluxed for 14 and 15 h, respectively. An additional amount of the methyllithium solution was added ($\mathrm{SiMe_2{}^{n}Bu}$, $\mathrm{SiMe_2{}^{i}Pr}$: same quantity as above. $\mathrm{SiMe_2}$*c*-Hex: double quantity. $\mathrm{SiEt_2Me}$: half the original quantity). In each case, diethyl ether was distilled off under normal pressure, and the brown THF solutions were refluxed for 4 h ($\mathrm{SiMe_2{}^{n}Bu}$), 10 h ($\mathrm{SiEt_2Me}$), 14 h ($\mathrm{SiMe_2{}^{i}Pr}$), 8 h ($\mathrm{SiMe_2}$*c*-Hex). The solvents were removed in vacuo, and the brown, highly viscous residues were evacuated overnight, treated with *n*-pentane, and filtered. $\mathrm{LiC(SiMe_2{}^{n}Bu)_3{\cdot}2THF}$ could not be obtained as a solid and was used without further purification. $\mathrm{LiC(SiMe_2{}^{i}Pr)_3{\cdot}THF}$ crystallized from the filtrate after concentration and cooling to −50 °C. After evaporation of the filtrate, $\mathrm{LiC(SiEt_2Me)_3{\cdot}1.5THF}$ was recrystallized from diisopropyl ether. The excess of the methane derivative $\mathrm{HC(SiMe_2}$*c*-Hex$)_3$ was isolated upon recrystallization of the cyclohexyl compound from diisopropyl ether; $\mathrm{LiC(SiMe_2}$*c*-Hex$)_3{\cdot}1.5\mathrm{THF}$ was obtained subsequently after evaporation and recrystallization from pentane. The THF content was determined by $^1$H NMR spectroscopy.

**$\mathrm{LiC(SiMe_2{}^{n}Bu)_3{\cdot}2THF}$.** Yield: 82%; brown, highly viscous liquid. $^1$H NMR (300 MHz, $C_6D_6$): $\delta = 3.38$ (m, 8 H, $OCH_2$ of THF), 1.53 (m, 12 H, $C\mathit{H}_2C\mathit{H}_2CH_3$ of $^n$Bu), 1.24 (m, 8 H, $CH_2CH_2$ of THF), 1.04 (m, 9 H, $CH_3$ of $^n$Bu), 0.88 (pseudo-t, 6 H, $SiCH_2$ of $^n$Bu), 0.40 (18 H, $SiCH_3$). $^{13}$C NMR (75 MHz, $C_6D_6$): $\delta = 68.5$ (CO of THF), 28.7 and 27.5 ($\mathit{C}H_2\mathit{C}H_2CH_3$ of $^n$Bu), 25.2 (CC of THF), 23.9 ($SiCH_2$ of $^n$Bu, 23.1 ($CSi_3$?), 14.3 ($CH_3$ of $^n$Bu), 5.6 (SiMe).

**$\mathrm{LiC(SiEt_2Me)_3{\cdot}1.5THF}$.** Yield: 62%, colorless solid, which partially melted on warming to room temperature. $^1$H NMR (300 MHz, $C_6D_6$): $\delta = 3.32$ (m, 6 H, $OCH_2$ of THF), 1.23 (m, 6 H, $CH_2CH_2$ of THF), 1.17 (t, $^3J_{HH} = 7.9$ Hz, 18 H, $CH_3$ of Et), 0.86 (m, 12 H, diastereotopic protons of $CH_2$ of Et), 0.33 (s, 9 H, $SiCH_3$). $^{13}$C NMR (75 MHz, $C_6D_6$): $\delta = 68.4$ (CO of THF), 25.3 (CC of THF), 13.0 ($SiCH_2$ of Et), 9.7 ($CH_3$ of Et), 8.9 (LiC?), 2.0 (SiMe).

**$\mathrm{LiC(SiMe_2{}^{i}Pr)_3{\cdot}THF}$.** Yield: 47%, colorless crystals, which partially melted on warming to room temperature and contained about 15% of the methane derivative after repeated recrystallization from diisopropyl ether. $^1$H NMR (300 MHz, $C_6D_6$): $\delta = 3.19$ (m, 4 H, $OCH_2$ of THF), 1.16 (s, 18 H, $CH_3$ of $^i$Pr), 1.10 (m, 4 H, $CH_2CH_2$ of THF), 0.97 (s, 3 H, CH of $^i$Pr), 0.29 (s, 18 H, $SiCH_3$). $^{13}$C NMR (75 MHz, $C_6D_6$): $\delta = 68.7$ (CO of THF), 25.1 (CC of THF), 19.7 ($CH_3$ of $^i$Pr), 18.2 (CH of $^i$Pr), 17.7 (LiC?), 3.1 (SiMe).

**$\mathrm{LiC(SiMe_2}$*c*-Hex$)_3{\cdot}1.5\mathrm{THF}$.** Yield: 33%, colorless crystals, which include a minimum of 20% of the methane derivative. $^1$H NMR (300 MHz, $C_6D_6$): $\delta = 3.39$ (m, 6 H, $OCH_2$ of THF), 1.82 and 1.25 (each: m, THF and cyclohexyl), 0.31 (s, 18 H, $SiCH_3$). $^{13}$C NMR (75 MHz, $C_6D_6$): $\delta = 68.7$ (CO of THF), 31.0, 29.8, 29.3 27.8 (cyclohexyl), 25.2 (CC of THF), 3.6 (SiMe).

**Synthesis of the Alkylindium(I) Compounds: General Procedure.** A suspension of about 1.2 g freshly sublimed $\mathrm{In^{I}Br}$ (30−50% excess) in 25 mL of toluene was cooled to −40 °C and treated with the corresponding trisilylmethyllithium derivative dissolved in 30 mL of the same solvent with vigorous stirring. The mixture was slowly warmed to +10 °C, and the color changed from orange-red of InBr to dark red-brown or deep violet; only the $\mathrm{SiMe_2Ph}$ derivative **4** gave a yellow-brown mixture. Depending on the stability of the products, the suspensions thus obtained subsequently were stirred at room temperature for different periods: **1** ($\mathrm{SiMe_2Et}$) 30 min, **2** ($\mathrm{SiMe_2{}^{n}Bu}$) 2.5 h, **3** ($\mathrm{SiMe_2{}^{i}Pr}$) 5 min, **4** ($\mathrm{SiMe_2Ph}$) 10 min, and **5** ($\mathrm{SiEt_2Me}$) 1.5 h. The suspensions were rapidly filtered under exclusion of light, and the deeply colored filtrates were concentrated in vacuo and cooled to −50 °C to crystallize the products. With the $\mathrm{SiEt_2Me}$ derivative **5** and the $\mathrm{SiMe_2Ph}$ derivative **4** the solvent was completely removed and the residue treated with *n*-pentane. The suspension was filtered and cooled to −50 °C to crystallize the product. The $\mathrm{SiMe_2{}^{n}Bu}$ derivative **2** could not be isolated as a solid, although several solvents (*n*-pentane, toluene, diisopropyl ether, diethyl ether, THF) were tried. However, it was obtained sufficiently pure for the usual characterizations.

**$\mathrm{In_4[C(SiMe_2Et)_3]_4}$ (1).** Yield: 47%; dark violet, air-stable crystals; stable in solution at room temperature. Dec (argon, sealed capillary): 146−147 °C. Anal. Calcd for $C_{52}H_{132}Si_{12}In_4$ (1553.9): C, 40.2; H, 8.6; Si, 21.7; In, 29.6. Found: C, 39.8; H, 8.4; Si, 20.8; In, 29.0; mol wt 1467 (cryoscopically in benzene). $^1$H NMR (300 MHz, $C_6D_6$): $\delta = 1.08$ (t, $^3J_{HH} = 6.5$ Hz, 36 H, $CH_3$ of Et), 0.98 (q, $^3J_{HH} = 6.5$ Hz, 24 H, $CH_2$ of Et), 0.44 (s, 72 H, $SiCH_3$). $^{13}$C NMR (75 MHz, $C_6D_6$): $\delta = 73.3$ (InC), 15.2 ($CH_2$ of Et), 8.4 ($CH_3$ of Et), 3.7 (SiMe). IR (paraffin, CsBr plates, cm$^{-1}$): 1254 vs $\delta CH_3$; 1003 vs, 957 s $\nu CC$; 843 vs, 766 vs, 741 s $\rho CH_3(Si)$; 677 vs $\nu_{as}SiC$; 623 s $\nu_sSiC$; 600 m, 561 vs $\nu In_4C_4$; 465 vw, 415 vw, 357 m $\delta CC$, $\delta SiC$. UV/vis (*n*-hexane) $\lambda_{max}$ (lg $\epsilon$): 200 (5), 230 (5.3), 320 (5.2), 490 (4.1).

**$\mathrm{In_4[C(SiMe_2{}^{n}Bu)_3]_4}$ (2).** Yield: 57%; dark red-violet, highly viscous liquid; slow decomposition in solution at room temperature. Mol wt (cryoscopically in benzene): found 1790; calcd 1890.6 of the tetramer. $^1$H NMR (300 MHz, $C_6D_6$): $\delta = 1.49$ (m, 48 H, $C\mathit{H}_2C\mathit{H}_2CH_3$ of $^n$Bu), 0.99 (m, 60 H, $C\mathit{H}_2CH_2CH_2C\mathit{H}_3$ of $^n$Bu), 0.59 (s, 72 H, $SiCH_3$). $^{13}$C NMR (75 MHz, $C_6D_6$): $\delta = 73.5$ (InC), 27.1 and 26.9 ($\mathit{C}H_2\mathit{C}H_2CH_3$ of $^n$Bu), 23.0 ($SiCH_2$), 14.2 ($CH_3$ of $^n$Bu), 5.2 (SiMe). IR (paraffin, CsBr plates, cm$^{-1}$): 1252 vs $\delta CH_3$; 1188 m, 1127 w, 1109 w, 1078 m, 1047 w, 1017 w, 997 w, 963 w $\nu CC$; 885 s, 843 vs, 731 m $\rho CH_3(Si)$; 675 m, 648 m $\nu_{as}SiC$; 619 vw $\nu_sSiC$; 598 w, 569 s $\nu In_4C_4$; 498 vw, 463 vw, 436 vw, 397 vw, 355 vw, 346 vw, 336 vw $\delta CC$, $\delta SiC$. UV/vis (*n*-hexane) $\lambda_{max}$ (lg $\epsilon$): 210 (4.7), 250 (4.9), 320 (4.8), 490 (3.7).

**$\mathrm{[InC(SiMe_2{}^{i}Pr)_3]_{\mathit{x}}}$ (3).** Yield: 64%; dark red-violet, air-stable crystals, slow decomposition in solution at room temperature. Dec (argon, sealed capillary): 64−65 °C. Anal. Calcd for $C_{16}H_{39}Si_3In$ (430.6): C, 49.1; H, 9.1; Si, 17,7; In, 24.1 (for $\mathrm{InR{\cdot}0.5toluene}$ as determined by NMR spectroscopy). Anal. Found: C, 49.6; H, 9.8; Si, 18.1; In, 23.6; mol wt 410 (cryoscopically in benzene). $^1$H NMR (300 MHz, $C_6D_6$): $\delta = 1.14$ (septet, $^3J_{HH} = 6.1$ Hz, 3 H, CH of $^i$Pr), 1.04 (d, $^3J_{HH} = 6.1$ Hz, 18 H, $CH_3$ of $^i$Pr), 0.17 (s, 18 H, $SiCH_3$). $^{13}$C NMR (75 MHz, $C_6D_6$): $\delta = 60.1$ (InC), 19.8 ($CH_3$ of $^i$Pr), 16.3 (CH of $^i$Pr), 2.3 (SiMe). IR (paraffin, CsBr plates, cm$^{-1}$): 1293 w, 1256 vs $\delta CH_3$; 1155 w, 1061 m, 997 s, 970 m, 922 m $\nu CC$; 878 s, 833 vs, 820 vs, 785 vs, 719 s $\rho CH_3(Si)$; 675 s, 664 m $\nu_{as}SiC$; 629 vw $\nu_sSiC$; 604 vs, 521 s $\nu In_4C_4$; 463 w, 444 m, 432 m, 397 vw, 363 w, 328 w $\delta CC$, $\delta SiC$. UV/vis (*n*-hexane) $\lambda_{max}$ (lg $\epsilon$): 210 (3.8), 240 (3.8), 290 (3.2), 390 (3.3).

**$\mathrm{[InC(SiMe_2Ph)_3]_{\mathit{x}}}$ (4).** Yield: 66%; orange-brown, amorphous solid, decomposition in solution at room temperature. Dec (argon, sealed capillary): 103−106 °C. Anal. Calcd for $C_{25}H_{33}Si_3In$ (532.6): C, 56.4; H, 6.2; Si, 15.8; In, 21.6. Found: C, 55.5; H, 6.2; Si, 15.5; In, 21.6; mol wt 495 (cryoscopically in benzene). $^1$H NMR (300 MHz, $C_6D_6$): $\delta = 7.41$ (m, 6 H, phenyl), 7.14 (m, 9 H, phenyl), 0.47 (s, 18 H, $SiCH_3$). $^{13}$C NMR (75 MHz, $C_6D_6$): $\delta = 143.0$, 134.5, and 128.9 (phenyl); 43.0 (InC), 5.5 (SiMe). IR (paraffin, CsBr plates, cm$^{-1}$): 1956 vw, 1885 vw, 1811 vw, 1645 vw, 1588 w, 1564 w phenyl; 1485 m, 1462 s, 1425 s, 1377 s, 1317 w, 1298 m, 1254 vs $\delta CH_3$, paraffin; 1192 w, 1155 w, 1103 vs, 1069 w, 999 m, 964 w $\nu CC$; 909 w, 837 vs, 804 vs, 783 vs, 770 vs, 733 vs, 702 vs, 689 vs $\rho CH_3(Si)$; 675 m, 662 vs $\nu_{as}SiC$; 635 m, 619 w $\nu_sSiC$; 554 vs $\nu In_4C_4$; 475 s, 434 w, 403 m, 376 w, 316 vw $\delta CC$, $\delta SiC$. UV/vis (*n*-hexane) $\lambda_{max}$ (lg $\epsilon$): 220 (4.3), 290 (3.9), 365 (3.3).

**$\mathrm{[InC(SiEt_2Me)_3]_{\mathit{x}}}$ (5).** Yield: 56%; dark violet, air-stable needles, slow decomposition in solution at room temperature. Dec (argon, sealed capillary): 120 °C. Anal. Calcd for $C_{16}H_{39}Si_3In$ (monomer 430.6; dimer 861.2; tetramer 1722.3): C, 44.6; H, 9.1; Si, 19.6; In, 26.7. Found: C, 44.9; H, 9.2; Si, 18.7; In, 26.8; mol wt 869 (0.0139 mol L$^{-1}$, violet solution), 819 (0.0028 mol L$^{-1}$, light violet), 695 (0.0017 mol L$^{-1}$, light violet), 436

**Table 5. Crystal Data, Data Collection Parameters, and Structure Refinement of 1 and 3**

| | **1** | **3** |
|---|---|---|
| formula | $C_{52}H_{132}In_4Si_{12}$ | $C_{64}H_{156}In_4Si_{12}$ |
| crystal system | rhombohedral | trigonal |
| space group | $R3$; No. 146[36] | $P\bar{3}$; No. 147[36] |
| $Z$ | 3 | 2 |
| $a$ (Å) | 22.094(3) | 19.483(2) |
| $b$ (Å) | 22.094(3) | 19.483(2) |
| $c$ (Å) | 14.000(1) | 14.762(2) |
| α (deg) | 90 | 90 |
| $\beta$ (deg) | 90 | 90 |
| $\gamma$ (deg) | 120 | 120 |
| $V$ ($10^{-30}$ m$^3$) | 5918(1) | 4853(1) |
| $d_{calc}$ (g·cm$^{-3}$) | 1.308 | 1.179 |
| temp (K) | 293(2) | 300(2) |
| $\mu$ (mm$^{-1}$) | 1.365 | 1.116 |
| cryst dimens (mm) | 0.42 × 0.49 × 0.91 | 0.30 × 0.30 × 0.13 |
| diffractometer | Siemens AED 2 | STOE IPDS |
| radiation | Mo Kα graphite monochromated | |
| range | $3.6 \leq 2\theta \leq 50°$ | $3.6 \leq 2\theta \leq 48.4°$ |
| index range | $-26 \leq h \leq 12$ | $-21 \leq h \leq 20$ |
| | $0 \leq k \leq 26$ | $-22 \leq k \leq 22$ |
| | $0 \leq l \leq 16$ | $-16 \leq l \leq 16$ |
| scan technique | $\omega-2\theta$ | 155 imaging plates; $\Delta\varphi = 1.1°$ |
| independent reflns | 2302 | 5091 |
| no. of reflns $F > 4\sigma(F)$ | 2203 | 2852 |
| program | SHELXTL, SHELXL-93;[37] solutions by direct methods; full-matrix refinement with all independent structure factors | |
| params | 216 | 265 |
| $R$, $wR^{2a}$ | 0.0455; 0.0889 | 0.0898; 0.1287 |
| max. residual ($10^{30}$ e/m$^3$) | 1.094 | 1.618$^b$ |
| min. residual ($10^{30}$ e/m$^3$) | −0.509 | −1.388 |

$^a$ $R = \sum||F_o| - |F_c||/\sum|F_o|$ ($F > 4\ \sigma(F)$); $wR^2 = \{\sum w(|F_o|^2 - |F_c|^2)^2/\sum w(F_o2)^2\}^{1/2}$ (all data). $^b$ Near the indium atoms.

(0.00083 mol L$^{-1}$, red) (cryoscopically in benzene). $^1$H NMR (300 MHz, $C_6D_6$): $\delta = 1.20$ (t, $^3J_{HH} = 7.5$ Hz, 72 H, $CH_3$ of Et), 1.05 (q, $^3J_{HH} = 7.5$ Hz, 48 H, $CH_2$ of Et), 0.47 (s, 36 H, $SiCH_3$). $^{13}$C NMR (75 MHz, $C_6D_6$): $\delta = 76.3$ (InC), 15.1 ($CH_2$ of Et), 9.8 ($CH_3$ of Et), 0.3 (SiMe). IR (paraffin, CsBr plates, cm$^{-1}$): 1306 vw, 1252 s $\delta CH_3$; 1167 vw, 1109 w, 1080 w, 1042 w, 1011 vs, 964 w, 945 w, 918 vw $\nu$CC; 826 vs, 791 s, 770 m, 735 m $\rho CH_3$(Si); 685 w, 669 m $\nu_{as}$SiC; 606 m, 579 w, 554 m, 521 vw $\nu In_4C_4$; 463 w, 394 vw $\delta$CC, $\delta$SiC. UV/vis ($n$-hexane) $\lambda_{max}$ (lg $\epsilon$): 250 (5.0), 325 (4.8), 495 (3.8).

**Crystal Structure Determinations of 1 and 3.** Details of the crystal data, data collection parameters, and structure determinations are given in Table 5. The crystals of **3** include diisopropyl ether, as shown by NMR spectroscopy. Part of an ether molecule (5 atoms) with low occupancy factors can be taken from an electron density map, but it could not be refined satisfactorily nor could the missing atoms be found. Therefore, we finally ignored the ether molecule completely in refining the structure.

**Quantum Chemical Calculations.** The structures of the InX, $InX_3$, $(InX)_4$ (X = H, $CH_3$), and $InCH_3(\eta^6\text{-}C_6H_6)$ model systems have been optimized at the hybrid-DFT level, using the B3PW91 exchange−correlation functional[38,39] and the Gaussian94 program.[40] For comparison, the structures have also been optimized at the MP2 level. Point group symmetry was enforced for $InCH_3$ ($C_{3v}$), $In(CH_3)_3$ ($C_3$), $(InX)_4$ ($T_d$), and $InH_3$ ($D_{3h}$). The optimizations employed a quasirelativistic small-core effective-core potential (ECP) for indium (keeping 21 electrons in the valence space),[41] as well as an ECP for carbon.[42] The size of the valence basis sets was (9s9p5d)/[6s5p3d] for In[43] and (4s4p1d)/[2s2p1d] for C.[42] A (4s)/[2s] basis was used on hydrogen[44] (for calculations on indium hydride species, one polarization p-function with exponent 1.0 was added).

$^{13}$C NMR chemical shifts were calculated at the SOS-DFPT level,[45] with an IGLO choice of gauge origin,[46] using the deMon-KS[47] and deMon-NMR[45] programs. If not stated otherwise, the B3PW91-optimized structures were employed. These calculations employed either the same quasirelativistic ECP and valence basis for In described above or an all-electron atomic natural orbital (28s23p17d)/[5s4p2d] basis[48] with the most diffuse s-, p-, and d-functions of the ECP-valence basis[43] added in an uncontracted fashion, leading to an overall basis-set size of 9s8p4d (for the tetramer, only the indium atom neighboring the methyl group of interest was treated at an all-electron level, whereas the ECPs were kept for the other metal atoms). IGLO-II basis sets[46] were used for C and H. We will denote these basis sets as either ECP or AE, depending on the treatment of the indium atoms. Auxiliary charge-density and exchange−correlation potential fitting basis sets were of the sizes 5,1 (H), 5,2 (C), 5,5 (In all-electron), and 3,4 (In ECP) ($n$,$m$ denotes $n$ s-functions and $m$ spd-shells with shared exponents).[47] The PW91 functional[39] was used in these calculations, as well as a FINE angular integration grid with 32 points of radial quadrature.[47]

Spin−orbit corrections to the chemical shifts were calculated separately with a recently developed triple-perturbation ansatz,[49] using the AE basis, the P86 exchange−correlation functional,[50] and 64 points of radial quadrature. In these calculations, a common gauge origin was placed at the indium nucleus (the one treated at an all-electron level in the tetramer, cf. above; the validity of this approximation has been tested using different ECP combinations).

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Computed absolute carbon shieldings $\sigma$ were converted to relative $^{13}$C shifts $\delta$ using an absolute shielding value $\sigma$ of 187.5 ppm computed for TMS.

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**Supporting Information Available:** Tables of atomic coordinates, isotropic and anisotropic displacement parameters, and all bond lengths and angles for **1** and **3** (11 pages). Ordering information is given on any current masthead page. Further details of the crystal structure determinations are also available from the Fachinformationzentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-408174 (**1**) and -408173 (**3**). IR spectra of the methane and lithium methanide derivatives are available from the author (3 pages).

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