Easy formation of indium–silicon bonds: reaction of decamethylsilicocene with trimethylindium

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The reaction of decamethylsilicocene **1** with trimethyl-indium yields the disilyl indium compound [Cp*₂Si-(Me)]₂InMe (**2**) in nearly quantitative yield; **2** is characterised by ¹H, ¹³C and ²⁹Si NMR and microanalytical data and by X-ray crystallography.

For the majority of main group elements a variety of silyl derivatives have been previously described in the literature. It is therefore somewhat surprising that silyl indium compounds are rarely known. Although $(Me_3Si)_3In$[1] has previously been synthesised by Bürger and Götze in 1969 it took nearly 20 years before a second representative of this class of compound, namely $[(Me_3Si)_3Si]_2InCl_2Li\cdot2THF$, was reported by Cowley *et al.* in 1986.[2] It was not until the late 1990's that further silyl indium compounds were reported in the literature. Besides the silyl indium halides $(Bu^t_3Si)_nInHal_{3-n}$ ($n = 1$ and 2) prepared by Wiberg,[3] these were mainly examples of low valent indium compounds like the sterically crowded diindanes $\{[(Me_3Si)_3-Si]_2In\}_2$ described by Weidlein *et al.*[4] and $[(Bu^t_3Si)_2In]_2$ synthesized by Wiberg.[5] The most recent examples are the indium cluster compounds $(Bu^t_3Si)_6In_8$[6] and $(Bu^t_3Si)_8In_{12}$[7] which were again prepared by Wiberg *et al.* Of the afore-mentioned compounds only the diindanes, the cluster compounds and the lithium indanate have been structurally characterised. It is of great interest to find new preparations for silyl–indium compounds and to structurally identify them.

In the course of our investigations on the reactivity of decamethylsilicocene[8] **1** we have already reported on the reactions of **1** with halides and organo halides of group 13 compounds.[9] Here we present the result of the reaction of **1** with trimethylindium (Scheme 1) where the disilyl indium compound **2** is formed by insertion of **1** into two of the three indium–carbon bonds.

When an excess of trimethylindium was added to **1** in pentane at low temperature a colourless solution was formed which turned yellow on warming to room temperature. Evaporation of all volatiles *in vacuo* gave **2** as a bright yellow, air and moisture sensitive solid in nearly quantitative yield.† Recrystallisation from pentane gave single crystals of **2** that were suitable for X-ray structure analysis. Fig. 1 shows the molecular structure of **2** in the solid state.‡

The indium atom is surrounded by the methyl group and the two silyl substituents in a trigonal planar fashion. The sum of the bond angles at the indium centre is 360°. The indium–silicon distances are 2.642(2) Å for In(1)–Si(1) and 2.640(3) Å for In(1)–S(2) and thus slightly longer than the sum of the covalent radii of 2.61 Å. However, they are decidedly shorter than the mean Si–In distances of 2.78 Å in the sterically crowded diindane $(Bu^t_3Si)_4In_2$[5] and of 2.68 Å in the somewhat less demandingly substituted conjuncto cluster $(Bu^t_3Si)_8In_{12}$.[7] Only in the indanate anion $[(Me_3Si)_3Si]_2InCl_2^-$ are shorter Si–In distances of 2.605(7) and 2.591(7) Å observed.[2] The widening of the C_{Cp}–Si–C_{Cp} angle (116° as compared to 109.5° for a perfect tetrahedral coordination) is due to the steric bulk of the Cp* groups. The Cp* moieties are in van der Waals contact with those on the other silicon centre as well as with the methyl groups on the silicon and indium atoms (for details see Fig. 1). This provides a tight organic wrapping of the inorganic core of the molecule.

This rigid structure of **2** is not retained in solution as is shown by the NMR spectra where conformational changes and sigmatropic rearrangements of the Cp* substituents are observed. In the room temperature ¹H NMR spectrum (500 MHz) of **2** in C_6D_6 the resonances for the methyl groups at indium and silicon are detected as singlets at δ 0.45 and 0.82, respectively. For the 60 methyl protons of the Cp* moieties the spectrum shows one broad signal of low intensity at δ 1.17 and a higher intensity broad signal at δ 1.82; only one broad signal at δ 1.66 is detected for the Cp* methyl protons in toluene-d₈ at 100 °C. The room-temperature ¹³C NMR spectrum shows five signals for the ring carbon atoms of the Cp* groups and four broad signals for the Cp* methyl carbon atoms.[10] Owing to the prochiral character of the silicon centers five signals each would be expected. The observations described above are in accordance with the assumption that the Cp* groups perform rather slow sigmatropic shifts due to the steric interference of the Cp* groups as deduced from the molecular structure. In the ²⁹Si NMR spectrum one resonance at δ 20.6 can be detected for the two equivalent silicon centres. The mass spectrum (CI) of **2** shows no M⁺ peak; however the $[M - Cp*_2SiMe]^+$ ion is observed in low intensity at $m/z = 443$.

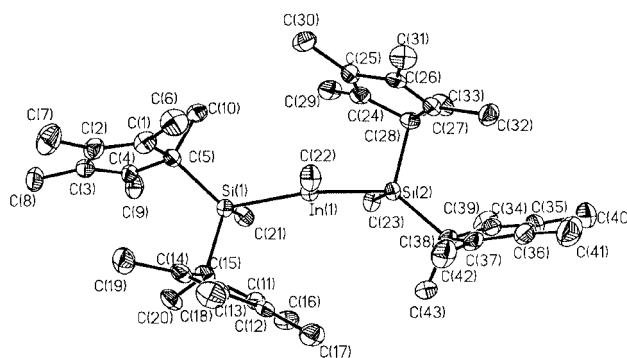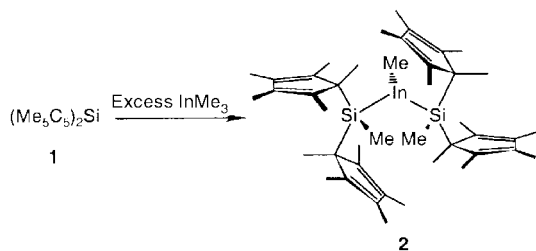Scheme 1 Reaction of **1** with trimethylindium. *Reagents and conditions*: −90 °C → RT, pentane.

Fig. 1 Molecular structure of **2**. Selected interatomic distances (Å) and angles (°): In(1)–Si(1) 2.642(2), In(1)–Si(2) 2.640(3), In(1)–C(22) 2.172(6), C(10)–C(29) 3.7428(115), C(17)–C(42) 3.8451(119), C(22)–C(30) 3.9836(115), C(16)–C(21) 3.43, C(22)–In–(1)–Si(2) 120.40(18), C(22)–In(1)–Si(1) 120.87(18), Si(2)–In(1)–Si(1) 118.73(7), C(15)–Si(1)–C(5) 116.7(3), C(38)–Si(2)–C(28) 116.4(3).

The thermal stability of **2** in solution and in the gas phase is limited. Thermal decomposition is observed to result in the formation of Cp*In. Evidence for this process can be found in the ^{1}H NMR spectrum of **2** at 100 °C which in addition to the aforementioned resonances shows a signal at δ 2.01 for the methyl groups of Cp*In[11] which grows on prolonged heating. No further defined decomposition products can be identified. As far as the stability of **2** in the gas phase is concerned the CI mass spectrum of **2** is very instructive. Here a very strong signal (rel. int. 94%) for the [Cp*In]$^+$ ion is observed. This can also be explained as the result of thermal decomposition of **2** in the spectrometer. The thermolability of silyl indium compounds has been previously described.[4]

Concerning the mechanistic aspects of the formation of **2** we assume that the reaction is started by a nucleophilic attack of **1** on the Lewis acidic indium centre *via* the silicon lone pair. This attack is followed by a migration of one methyl group from indium to silicon accompanied by a rearrangement of the Cp* moieties from $\eta^{2/3}$ to η^1 thus forming an intermediate monosilyl substituted indium compound. This intermediate is again attacked by a silylene molecule in the way described above leading to the final product. The formation of **2** is one of the very few examples for the insertion of a silylene into a metal–carbon bond.[12]

Notes and references

† To a solution of **1** (298 mg, 1.0 mmol) in pentane (20 ml) was added a solution of InMe$_3$ in pentane (2.2 molar, 1.5 ml) at −100 °C. On warming to room temperature the solution changed to a light yellow. After 2 h all volatiles were removed *in vaco* to yield **2** (388 mg) as a yellow solid that can be recrystallized from pentane. Yield (after recrystallization): 302 mg (0.4 mmol, 80%). ^{1}H NMR (C$_6$D$_6$): 0.45 (s, 3 H, InMe), 0.82 (s, 6 H, SiMe), 1.17, 1.82 (br, 60 H, C$_5$Me$_5$). ^{1}H NMR (toluene-d$_8$, 100 °C): 0.38 (s, 3 H, InMe), 0.69 (s, 6 H, SiMe), 1.66 (brs, 60 H, C$_5$Me$_5$), 2.01 (s, Cp*In). ^{13}C NMR (C$_6$D$_6$): 10.32 (SiMe), 10.46 (InMe), 11.71, 12.97, 13.20, 18.63 (br, C$_5$*Me*$_5$), 57.66 (br, allyl-*C*$_5$Me$_5$), 134.15, 134.71, 140.68, 141.90 (br, vinyl-

C$_5$Me$_5$). ^{29}Si NMR (C$_6$D$_6$): 20.6. MS (CI, NH$_3$: 137 (100%) Me$_5$C$_5$H$_2$$^+$, 251 (94) Me$_5C_5In^+$, 443 (2) (Me$_5C_5$)$_2$SiInMe$_2$$^+$. C$_{43}H_{69}$InSi$_2$, M_r = 757.00 g mol^{-1}; calc.: C 68.23, H 9.19; found: C 68.10, H 9.18%.

‡ *Crystal data for* **2**: C$_{43}$H$_{69}$InSi$_2$; M = 756.98; T = 173(2) K; λ(Mo-Kα) = 0.71073 Å; triclinic, $P\bar{1}$; a = 10.808(7), b = 12.425(9), c = 16.592(11) Å, α = 71.99(5)°, β = 77.40(6)°, γ = 81.18(6)°; V = 2059(2) Å^3; Z = 2; D_c = 1.221 Mg m^{-3}; μ = 0.659 mm^{-1}; reflections collected/unique: 7680/7249 [R(int) = 0.1046]; final R indices [$I > 2\sigma(I)$]: R_1 = 0.0614, wR_2 = 0.1462 [5534]; R indices (all data): R_1 = 0.0903, wR_2 = 0.1628. Data collected on a Siemens P2(1) diffractometer. CCDC 154849. See http://www.rsc.org/suppdata/cc/b0/b009839f/ for crystallographic data in .cif or other electronic format.

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