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An indium(II)-indium(II) compound with intramolecular donor-acceptor bonds[1]

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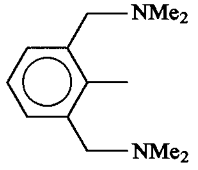
Abstract

The diindium compound $\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}(Cl)In{-}In(Cl)\{(2,6\text{-}Me_2NCH_2)_2C_6H_3\}$(**2**) has been prepared via the reaction of $[(2,6\text{-}Me_2NCH_2)_2C_6H_4]InCl_2$ with $Li_2[(C_4H_4BN(^iPr)_2]$. By means of X-ray crystallography, it was established that four N → In donor-acceptor bonds are made to the unsuspended In–In moiety: monoclinic, space group C_2/c, with $a = 21.913$ (6), $b = 8.364$ (1), $c = 17.877$ (3) Å, $\alpha = 90$, $\beta = 117.21$ (2), $\gamma = 90°$, $V = 2914$ (1) Å^3 and $Z = 4$.

Keywords: Diindium; Intramolecular coordination; X-ray structure

Despite the heightened interest in the lower oxidation states of the heavier group 13 elements, structurally characterized examples of compounds with indium–indium bonds are relatively rare (For reviews, see [1]). In the particular case of indium(II), the organometallic examples comprise $\{(Me_3Si)_2CH\}_2InIn\{CH(SiMe_3)_2\}_2$ [2], $(^tBuN)_2\{MeSi(^tBu)N\}_2InIn\{N(^tBu)SiMe\}_2(N^tBu)_2$ [3], $\{2,4,6\text{-}(CF_3)_3C_6H_2\}_2InIn\{C_6H_2\text{-}2,4,6\text{-}(CF_3)_3\}_2$ [4], $(^tBu_3Si)_2InIn(Si^tBu_3)_2$ [5], and $(2,4,6\text{-}^iPr_3C_6H_2)_2InIn(2,4,6\text{-}^iPr_3C_6H_2)_2$ [6] for which the In–In bond lengths are 2.828 (1), 2.768 (1), 2.744 (2), 2.922 (1), and 2.775 (2) Å, respectively. In other work, it has been demonstrated that the 'two-arm' ligand **1** [7] is very useful for stabilizing a number of unusual group 13 species such as intermetallics, terminal hydrides, and azides (for a review, see [8]).



1

We were therefore curious to determine whether ligand **1** is capable of supporting an indium–indium bond.

The dilithium salt of diisopropylaminoborole [9] (639 mg, 3.6 mmol) was dissolved in 50 ml of THF and added dropwise to $[(2,6\text{-}Me_2NCH_2)_2C_6H_4]InCl_2$ [10] (1.35g, 3.6 mmol) in 20 ml of THF at − 78°C. The reaction mixture was allowed to warm slowly to ambient temperature and stirred for an additional 12 h period. The solvent and volatiles were removed under reduced pressure and the grayish residue was extracted with 30 ml of toluene. Removal of the toluene in vacuo from the filtrate left a yellow powder from which colorless crystals were grown by layering a THF solution with pentane. The yield of product (**2**) was 24.9%, m.p.: 178°C (dec). Elemental analysis for $C_{24}H_{38}Cl_2In_2N_4$: calculated C 42.2%, H 5.61%, N 8.2%;

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[1] Dedicated to Professor R. Bruce King on the occasion of his 60th birthday.

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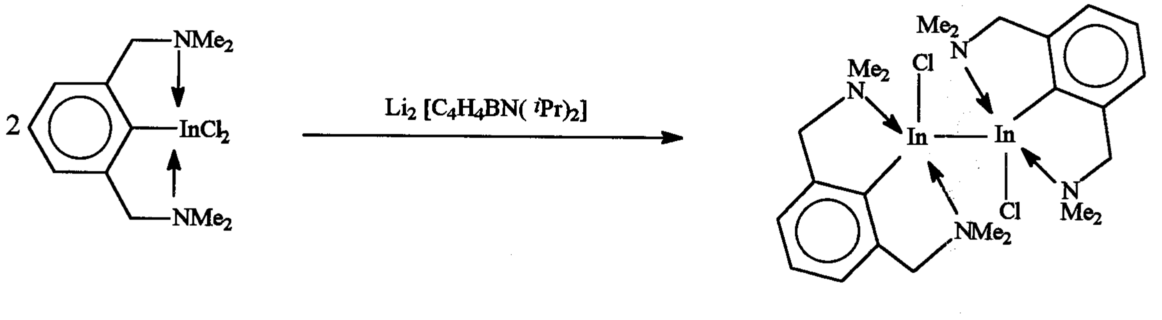
found C 41.87%, H 5.42%, N 7.93%. HRMS (CI+): calculated for $C_{24}H_{38}Cl_2{}^{115}In_2N_4$ (M^+), 682.055103; found, 682.053511.



2

Preliminary information on the structure of **2** was derived from ^1H- and ^{13}C-NMR data [11], which showed the presence of the 'two-arm' ligand **1**. The equivalence of the resonances for the two amine arms implied that they were linked to indium atoms in a symmetrical fashion or that some fluxional process was taking place. In order to gain more insights into the connectivity of the amine arms, it was necessary to undertake an X-ray crystal structure determination.

Crystal data: $C_{24}H_{38}Cl_2In_2N_4$, $M = 683.12$, monoclinic, space group C_2/c, $a = 21.913$ (6), $b = 8.364$ (1), $c = 17.877(3)$ Å, $\alpha = 90$, $\beta = 117.21$ (2), $\gamma = 90°$, $V = 2914$ (1) Å^3, $D_{calc} = 1.557$ g cm^{-3}, $Z = 4$, λ(Mo–K$_\alpha$) = 0.71073 Å, μ(Mo–K$_\alpha$) = 17.84 cm^{-1}. A total of 2547 independent reflections was collected on an Enraf Nonius CAD 4 diffractometer at 298 K with 2θ between 5.3 and 50.0° using the θ–2θ scan mode and a graphite monochrometer. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 to R_1 and wR^2 values of 0.0246 and 0.0557, respectively.

The X-ray analysis demonstrated that the solid state consists of individual molecules of **2** which reside on a center of symmetry (Fig. 1). There are no conspicuously short intermolecular contacts. An unsupported indium–indium bond is present and both indium centers are five coordinate, each being connected to two amine arm nitrogens, a chloride, an aryl carbon, and an indium atom. In the sense that the sum of the C(1)–In(1)–Cl(2), C(1)–In(1)–In(1A), and Cl(2)–In(1)–In(1A) bond angles is 360.99 (9)°, the geometry at indium can be regarded as trigonal bipyramidal. Note, however, that if this view is adopted that the angle between the axial ligands (N(1)–In(1)–N(2)) is markedly less than the ideal value (145.6 (1)°) due to the constraints of the two-armed ligand system. Alternatively, the molecular geometry of **2** can be thought of as comprising two distorted square pyramids, the axial sites of which are connected by an indium–indium bond. The observation that, despite the higher coordination number in **2**, the indium–indium bond length (2.7162 (8) Å) is shorter than those cited in the Introduction is presumably a consequence of the fact that the ligation is pulled back from the diindium moiety. Steric interactions are also minimized by the adoption of a staggered arrangement for the two closest (chlorides) ligands the Cl(1)–In(1)–In(1A)–Cl(1A) dihedral angle is 79.7°. Overall, the metrical parameters for the $(2,6\text{-}Me_2NCH_2)_2C_6H_2In$ moiety resemble those in $2,6\text{-}(Me_2NCH_2)_2C_6H_2In(Me)Cl$ (**3**) [10] quite closely, the major difference being that the In–Cl bond length in **2** (2.4505(9) Å) is somewhat longer than that in **3**. Finally, we note that **2** is a rare example of a diindium compound that features both organo and halo substituents. To our knowledge, this is also the first example of an In_2X_4 derivative that involves the attachment of four Lewis base moieties.

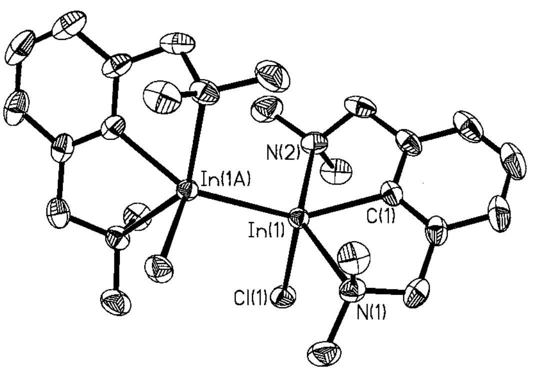


Fig. 1. View of the molecular structure of **2**. Important bond lengths (Å) and angles (°): In(1)–In(1A) 2.7162(8), In(1)–C(1) 2.139(3), In(1)–N(1) 2.554(3), In(1)–N(2) 2.601(3), C(1)–In(1)–N(1) 73.5(1), C(1)–In(1)–N(2) 72.5(1), N(1)–In(1)–N(2) 145.7(1), Cl(1)–In(1)–N(1) 92.75(7), Cl(1)–In(1)–N(2) 95.16(7).

Acknowledgements

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[11] ^{1}H-NMR (C_6D_6): δ (CH_3N): 2.13 (s, 12H); δ ($NCH_2C_6H_3$): 3.03 (s, 4H); δ (C_6H_3): 7.129–6.735 (m, 3H). ^{13}C-NMR ($CDCl_3$): δ (CH_3N): 46.1 (s); δ ($NCH_2C_6H_3$): 65.9 (s); δ (C2,C6): 144.99; δ (C3,C5): 126.37; δ (C4): 129.38; *ipso* C not detected.