Synthesis, Structure, and Properties of an Intramolecularly Coordinated Diindacycle: 9,10-Dihydro-9,10-bis[2,6-bis((dimethylamino)methyl)-phenyl]-9,10-diindaanthracene

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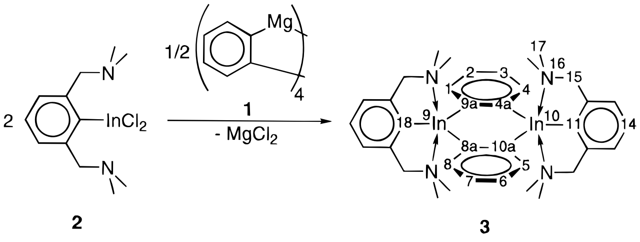
*Summary: o-Phenylenemagnesium (**1**) was used to prepare the first structurally characterized intramolecularly coordinated diindacycle: 9,10-dihydro-9,10-bis[2,6-bis((dimethylamino)methyl)phenyl]-9,10-diindaanthracene (**3**).*

For many years we have been engaged in the investigation of bifunctional organomagnesium compounds with short interlinking carbon chains.[1] Efforts are now being made to expand the chemistry of these compounds toward other main-group metals. For example, *o*-phenylenemagnesium[1d] (**1**) can be used in a novel synthetic approach which makes new 9,10-dimetallatriptycenes of group 14 readily accessible.[2]

In our initial attempts to prepare 1,2-bifunctional organometallic compounds from **1** and alkylmetal dichlorides of group 13, we observed oligomerization, disproportionation, and solvent/ligand exchange. To prevent these complicating phenomena, which are frequently encountered in group 13 chemistry, we used the *o*-bis((dialkylamino)methyl)aryl ligand system.[3] In this paper we report the synthesis, structure, and properties of the first structurally characterized, intramolecularly coordinated diindacycle: 9,10-dihydro-9,10-bis[2,6-bis((dimethylamino)methyl)phenyl]-9,10-diindaanthracene (**3**).

Treatment of 2,6-bis((dimethylamino)methyl)phenylindium dichloride (**2**)[4] with **1** at −15 °C afforded **3**[5] (Scheme 1), which after workup could be isolated as colorless crystals.

Scheme 1. Synthesis and IUPAC Numbering[6] of 3



The ^{1}H NMR spectrum (400 MHz, Tol-d_8, 295 K) of **3** consists of an aromatic AA′BB′ system, an aromatic triplet and doublet, and two aliphatic singlets. This pattern stays virtually unchanged over a broad temperature range (185−380 K); only in the lower temperature range is line broadening observed. Interestingly, the addition of 1 equiv of pyridine (based on **3**) to the NMR sample does not affect the spectrum of **3** at any temperature. These findings suggest that, in toluene, the intramolecular coordination of the (dimethylamino)-methyl groups in **3** is not replaced by intermolecular coordination of pyridine. This may be explained by a combination of strong intramolecular coordination of the (dimethylamino)methyl groups, together with the steric crowding around the In atoms in **3**, which both prevent the coordination of pyridine.

The X-ray crystal structure of **3**[7] (Figure 1) revealed a 9,10-dihydro-9,10-diindaanthracene structure in which the central six-membered ring has a slightly puckered conformation[8] with In(1) and In(1)a positioned 0.114-(1) Å on opposite sides of the plane defined by C(5), C(6), C(5)a, and C(6)a. The geometry of both indium atoms

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(5) Procedure for **3** (for general methods, see ref 2): At −15 °C, **1** (prepared from *o*-phenylenemercury and magnesium metal in THF according to ref 1d; 1.92 mmol of the formal unit C_6H_4Mg) in THF (40.0 mL) was added over 1 h to **2** (0.660 g, 1.75 mmol) in Et_2O (10 mL), after which the mixture was stirred for 4 h; it was subsequently stirred overnight at 5 °C and warmed to room temperature. The solvent was evaporated, and the residue was extracted with toluene (3 × 20 mL). Recrystallization from toluene (2×) gave a 55% yield (0.378 g) of **3** (in a sealed capillary: sublimation at 256 °C, decomposition at 315 °C). ^{1}H NMR (400 MHz, Tol-d_8): δ 7.38 (m, ^3J(H,H) = 7.1 Hz, ^4J(H,H) = 1.5 Hz, ^4J(H,H) = 1.3 Hz, ^5J(H,H) = 0.7 Hz, 4H; H(1,4,5,8)), 7.22 (t, ^3J(H,H) = 7.4 Hz, 2H; H(14,20)), 7.07 (m, ^3J(H,H) = 7.4 Hz, ^3J(H,H) = 7.1 Hz, ^4J(H,H) = 1.5 Hz, 4H; H(2,3,6,7)), 6.98 (d, ^3J(H,H) = 7.4 Hz, 4H; H(13,19)), 3.32 (s, 8H; H(15,21)), 1.92 (s, 24H; H(16,22)). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 170.6 (bs; C(4a,8a,9a,10a)), 155.8 (bs; C(11,-17)), 146.9 (s; C(12,18)), 138.9 (dd, ^1J(C,H) = 152.0 Hz, ^2J(C,H) = 3.5 Hz; C(1,4,5,8)), 127.5 (d, ^1J(C,H) = 155.6 Hz; C(14,20)), 126.4 (dd, ^1J(C,H) = 154.4 Hz, ^2J(C,H) = 7.0 Hz; C(2,3,6,7)), 124.8 (d, ^1J(C,H) = 158.0 Hz; C(13,19)), 66.6 (t, ^1J(C,H) = 130.2 Hz; C(15,21)), 46.0 (t, ^1J(C,H) = 129.7 Hz; C(16,22)). Anal. Calcd for $C_{36}H_{46}N_4In_2$: C, 56.6; H, 6.1. Found: C, 57.1; H, 6.2.

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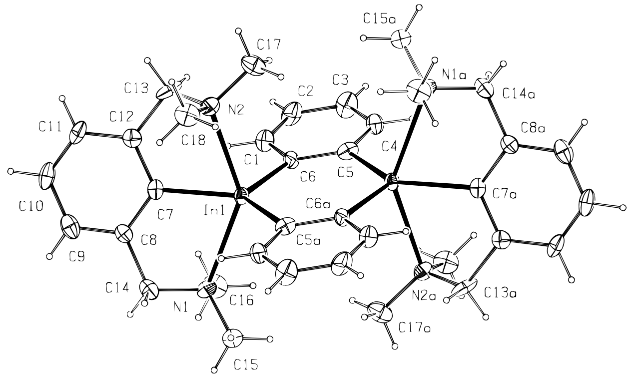

Figure 1. ORTEP plot of **3** drawn at the 50% probability level (note that the numbering in Figure 1 is different from the IUPAC numbering in Scheme 1, because of the crystallographic inversion symmetry of the molecule). Selected bond lengths (Å) and bond angles (deg): In(1)−C(5)a, 2.161(8); In(1)−C(6), 2.191(8); In(1)−C(7), 2.160(8); In(1)−N(1), 2.657(7); In(1)−N(2), 2.540(7); C(5)−C(6), 1.410(11); C(6)−In(1)−C(5)a, 115.7(3); C(6)−In(1)−C(7), 112.8(3); C(7)−In(1)−C(5)a, 131.4(3); N(1)−In(1)−N(2), 143.5(2); In(1)−C(6)−C(5), 124.0(5); In(1)−C(6)−C(1), 118.0(6); In(1)a−C(5)−C(6), 120.0(6); In(1)a−C(5)−C(4), 121.0(5).

can be described as strongly distorted trigonal bipyramidal: two coordinating nitrogen atoms occupy the axial positions (N−In−N = 143.5(2)°), and the equatorial plane is formed by indium and its three covalently bonded carbon atoms (sum of angles at indium 359.9(3)°). The observed In−N distances (2.540(7)−2.657(7) Å) and the N−In−N angle (143.5(2)°) are in accordance with those found for the *o*-bis((dialkylamino)methyl)phenylindium system.[9] However, the observed In−C(phenylene) bonds (2.160(8) and 2.161(8) Å), and especially the In−C(aryl) bonds (2.191(8) Å), are longer than those in $(C_6H_5)_3In$ (2.111(14)−2.155(14) Å).[10] The chairlike puckering of **3** is unusual, as most 9,10-dihydro-9,10-dimetallaanthracenes (M = Zn,[11] B,[12] Si,[13] Ge,[14] As,[15] Te[16]) are planar or have a boat conformation; to our knowledge, there is only one other example of a sterically hindered 9,10-dihydro-9,10-dimetallaanthracene with a chairlike puckering of the central six-membered ring (M = Si).[17] In **3**, deviations from planarity are small and can be explained by the fact that, in a puckered chairlike conformation, the nonbonding interactions between two opposing (dimethylamino)methyl groups on the same side of the plane containing the central six-membered ring are relieved. Even in the actually observed conformation of **3**, the methyl groups are within van der Waals contact distance (H(151)−H(171)a = 2.34(1) Å; H(151)−H(173)a = 2.51(1) Å); in the usually encountered boat or planar conformation, severe repulsion would occur.

Just after we had finished our investigations on **3**, the synthesis and structure of $(o\text{-}C_6H_4(InBr(THF)_2)_2$ (**4**) was published.[18] The environment of the indium atoms in both compounds is trigonal bipyramidal, and also the In−C bond distances of the central 9,10-dihydro-9,10-diindaanthracene ring in both compounds are comparable (**3**, 2.160(8)−2.261(8) Å; **4**, 2.153(4)−2.162(5) Å). However, in contrast to **3**, the central six-membered ring in **4** is practically planar.

In conclusion, it has been demonstrated once again that *o*-phenylenemagnesium (**1**) is a powerful and versatile reagent for the synthesis of new cyclic organometallic compounds.

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Supporting Information Available: Tables giving atomic coordinates, thermal parameters, bond distances and angles, and torsion angles for **3** (10 pages). Ordering information is given on any current masthead page.

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(7) Crystal data for **3**: $C_{36}H_{46}N_4In_2$, $M_r = 764.43$, colorless block-shaped crystal (0.05 × 0.15 × 0.20 mm), monoclinic, space group $C2/c$, with $a = 19.216(8)$ Å, $b = 9.689(8)$ Å, $c = 18.681(3)$ Å, $\beta = 102.92(2)°$, $V = 3390(3)$ Å^3, $Z = 4$, $D_{\mathrm{calcd}} = 1.498$ g cm^{-3}, $F(000) = 1552$, μ(Mo Kα) = 13.9 cm^{-1}; 6157 reflections ($1.12 < \theta < 25.00°$; ω scan; $T = 150$ K) were measured on an Enraf-Nonius CAD-4T diffractometer (rotating anode; graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). The crystal was found to be twinned; data were collected on one of the twin lattices. Data were corrected for Lp effects, for a linear decay (10%) of the intensity control reflections, and for absorption (DIFABS; correction range 0.771−1.205) and merged into a data set of 2982 unique reflections ($R_i = 0.0620$). The structure was solved with Patterson methods (DIRDIF) and difference Fourier techniques. Hydrogen atoms were introduced at calculated positions and refined riding on their carrier atoms. All non-H atoms were refined on F^2 (SHELXL-96) using 2971 unique reflections, with anisotropic thermal parameters. Convergence was reached at R1 = 0.0548 for 2234 reflections with $I > 2.0\sigma(I)$ and 194 parameters; wR2 = 0.1325, $S = 1.090$ for all 2971 reflections, $w = 1/[\sigma^2(F_o^2) + (0.0473P)^2 + 56.93P]$. A final difference Fourier map shows some residual densities between −0.96 and +2.29 e/Å^3, which are probably residual twinning effects. Geometrical details of the structure are provided as Supporting Information.

(8) Average torsion angle of adjacent bonds in the central six-membered ring 6.8(3)°.

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