

Reaction of Indium Bromide with 1,4-Dilithiotetraphenylbutadiene. Synthesis and Molecular Structure of $(\text{Et}_2\text{O})_2\text{Li}(\text{Br})_2\text{In}\{(\text{C}_6\text{H}_4)\}_2\text{In}(\text{Br})_2\text{Li}(\text{OEt}_2)_2$: A Novel Ten-Membered-Ring Organometallic Complex

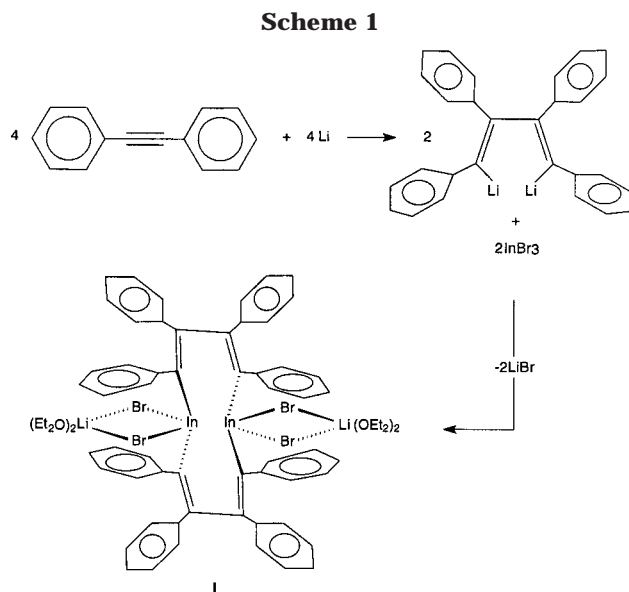
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Summary: Reaction of 1,4-dilithiotetraphenylbutadiene with indium bromide affords the organometallic complex $(\text{Et}_2\text{O})_2\text{Li}(\text{Br})_2\text{In}\{(\text{C}_6\text{H}_4)\}_2\text{In}(\text{Br})_2\text{Li}(\text{OEt}_2)_2$ as yellow monoclinic crystals. The two 1,4-tetraphenylbutadienylene units are bridged by two indium atoms, affording a severely twisted In_2C_8 ten-membered ring.

The present renaissance of organometallic chemistry involving the group 13 metals is due, inter alia, to the stabilization of the M–M (M = Al, Ga, In) bond.¹ Critical in the development of this chemistry is the judicious choice of organic ligand. The utilization of sterically demanding ligands such as substituted *m*-terphenyls has proven particularly fruitful in this regard. The general synthetic procedure which affords compounds containing the M–M bond involves reaction of a sterically demanding lithium alkyl or aryl with MCl_3 followed by alkali-metal reduction of the resulting RMCl_2 (R = alkyl, aryl). Recently, we reported the synthesis and molecular structure of a spirogallane anion, $[(\text{Ph}_4\text{C}_4)\text{Ga}(\text{C}_6\text{H}_4)]^-$, isolated from the reaction of gallium trichloride with 1,4-dilithiotetraphenylbutadiene in the presence of 12-crown-4.² As an extension of this work, we have investigated the organoindium chemistry of 1,4-dilithiotetraphenylbutadiene and report herein the synthesis³ and molecular structure⁴ of $(\text{Et}_2\text{O})_2\text{Li}(\text{Br})_2\text{In}\{(\text{C}_6\text{H}_4)\}_2\text{In}(\text{Br})_2\text{Li}(\text{OEt}_2)_2$ (**1**) isolated from the reaction of 1,4-dilithiotetraphenylbutadiene with indium tribro-



mide in diethyl ether (Scheme 1). The title compound, characterized by ^1H and ^{13}C NMR spectroscopy, elemental analyses, and single-crystal X-ray diffraction, is significant, as it represents the first organometallic compound of indium involving the tetraphenylbutadienylene ligand. Moreover, **1** is interesting, as it crystallizes as a severely twisted, and quite rare, In_2C_8 ten-membered ring (Figure 1).

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(3) (a) 1,4-Dilithiotetraphenylbutadiene^{3b} was prepared by charging a reaction vessel with diphenylacetylene (1.73 g, 10 mmol) and lithium powder (0.070 g, 10 mmol) in diethyl ether (30 mL). The resulting orange-red slurry was slowly added (over a period of 30 min) to InBr_3 (1.77 g, 5.0 mmol) in diethyl ether (25 mL) and cooled to -78°C . The resulting mixture was kept at -78°C for 3 h and warmed slowly to room temperature, where it was stirred for an additional 24 h. After filtration, the solution was concentrated in vacuo and stored at -25°C . This afforded bright yellow, diamond-shaped crystals (4.21 g, 54% yield). Mp: 222°C dec. Anal. (E+R Microanalytical Laboratories, Parsippany, NJ) Calcd (found) for $\text{C}_{68}\text{H}_{70}\text{In}_2\text{Br}_4\text{Li}_2\text{O}_3$: C, 54.50 (54.62); H, 4.70 (4.24) (perhaps owing to the lability of the diethyl ether moieties under combustion conditions, elemental analyses suggest the presence of only three OEt_2 units). ^1H NMR (250 MHz, 298 K, $\text{THF}-d_6$; δ): 1.11 (m, 24H), $-\text{OCH}_2\text{CH}_3$; 3.38 (m, 16H), $-\text{OCH}_2\text{CH}_3$; 6.67–7.46 (br, m, 40H), C_6H_5 . ^{13}C NMR (250 MHz, 298 K, $\text{THF}-d_6$) proved largely uninformative, as several signals overlapped in the 125–140 ppm region. (b) Eisch, J. J. Ed. *Organometallic Syntheses*; Academic Press: New York, 1981; Vol. 2 (Nontransition-Metal Compounds), p 98.

(4) A number of crystals of the title compound were mounted in glass capillaries under an atmosphere of nitrogen inside the drybox. The X-ray intensity data were measured at room temperature on a Bruker SMART TM CCD-based X-ray diffractometer system with graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) using the ω -scan technique to a maximum 2θ value of 48.36° . The structure was solved by direct methods using the SHELXTL 5.1 software package. The non-hydrogen atoms, except for carbon atoms C19, C20, C26, and C27, the oxygen atom O3, and all carbon atoms of the three diethyl ether molecules, were refined anisotropically, while hydrogen atoms were placed in ideal positions with their coordinates and thermal parameters riding on the attached carbon atoms. The carbon atoms C35, C36, C35', C36' of one diethyl ether were found disordered with site occupancy of 0.55 for C35 and C36, and site occupancy of 0.45 for C35' and C36'. The monoclinic space group is C2/c (No. 15) with unit cell parameters $a = 23.188(3) \text{ \AA}$, $b = 14.567(2) \text{ \AA}$, $c = 24.921(4) \text{ \AA}$, $\beta = 103.296(3)^\circ$, $D_{\text{calcd}} = 1.395 \text{ g cm}^{-3}$, and $V = 8192(2) \text{ \AA}^3$ for $Z = 4$. Full-matrix F^2 refinement, based upon 3945 observed reflections, converged at $R1 = 0.0574$ and $wR2 = 0.136$. The asymmetric unit for the compound contains a half-molecule of $(\text{Ph}_4\text{C}_4\text{In}_2\text{Li}_2\text{Br}_4(\text{Et}_2\text{O})_4)$ and one discrete diethyl ether solvent unit which is not associated with the title compound.

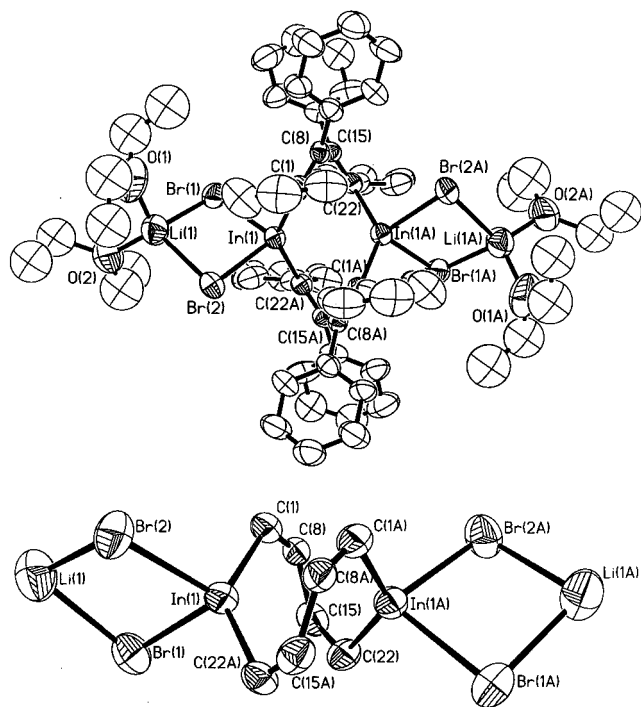
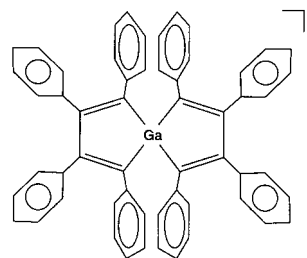


Figure 1. (a, top) Molecular structure of **I**. Hydrogen atoms have been omitted for clarity. Ellipsoids are shown at the 30% probability level. Bond distances (Å) and angles (deg): In(1)–C(1), 2.206(7); In(1)–C(22a), 2.200(7); In(1)–Br(1), 2.6589(10); In(1)–Br(2), 2.6610(10); Li(1)–O(1), 1.96(2); Li(1)–O(2), 1.90(2); Li(1)–Br(1), 2.585(18); Li(1)–Br(2), 2.598(17). C(1)–In(1)–C(22a), 137.0(3); C(1)–In(1)–Br(1), 101.67(18); C(1)–In(1)–Br(2), 109.99(19); C(22a)–In(1)–Br(1), 108.43(18); C(22a)–In(1)–Br(2), 100.58(19); Br(1)–In(1)–Br(2), 89.08(3); Br(1)–Li(1)–Br(2), 92.1(6); Li(1)–Br(1)–In(1), 88.3(4); Li(1)–Br(2)–In(1), 88.0(4); O(1)–Li(1)–O(2), 110.0(10); O(1)–Li(1)–Br(1), 104.8(8); O(1)–Li(1)–Br(2), 119.9(9); O(2)–Li(1)–Br(1), 116.3(9); O(2)–Li(1)–Br(2), 112.6(8). (b, bottom) View of the core of **I** with phenyl groups and diethyl ether units omitted.

Organometallic compounds of group 13 containing small four-membered rings, M_2E_2 ($M = Al, Ga, In; E = N, P, As$), are rather commonplace, while there are very few examples of compounds containing larger ring systems (*i.e.*, beyond 6). Relative to the butadienylene moiety and group 13 elements, one notable compound is 1,2-bis(tetramethylene)diborane(6), prepared by the hydroboration of 1,3-butadiene in ether.⁵ This is a tricyclic compound consisting of two $H_2CH_2CB-H-BCH_2CH_2$ seven-membered rings bridged by a B_2H_2 four-membered ring. It is also noteworthy that boron and aluminum have been shown to form five-membered rings with the butadienylene moiety.^{6,7} Thus, the fact that the title compound adopts a rare, if not unprecedented, In_2C_8 ten-membered-ring structure is significant—particularly considering the fact that gallium has recently been shown by this laboratory² to interact with

two tetraphenylbutadienylene units to afford the spirogallane anion (consisting of two five-membered rings sharing one gallium atom):



There are several interesting aspects concerning the structure and bonding of the title compound. **I** resides about a 2-fold axis passing through the center of the molecule. Moreover, the angles about the indium atoms range from 89.08(3)° to 137.0(3)° for Br(1)–In(1)–Br(2) and C(1)–In(1)–C(22a), respectively. This span of near 50° is quite large for a four-coordinate indium atom and results in the coordination of the indium atoms being severely distorted tetrahedral. The average In–Br and Li–Br bond distances are 2.660 and 2.592 Å, respectively. These values compare well to the average bond lengths of In–Br (2.654 Å) and Li–Br (2.54 Å) for a similarly anionic compound of TMEDA, lithium bis-(μ -bromo)bis[bis(trimethylsilyl)methyl]indanate.⁸ The In–Br bond distance in the T-shaped $(Mes_2C_6H_5)_2InBr$ molecule is considerably shorter than that observed in **I** at 2.505(4) Å.⁹ Moreover, the In–Br distance in $[Bu'_3C_6H_2]_2InBr$ ¹⁰ was shown to be 2.597(1) Å. The Li–Br bond distance of 2.592 Å in **I** is easily compared to the values of 2.52(2), 2.67(3), and 2.80(3) Å recently reported for the Li_2Br_4 octahedrally stabilized organoaluminum bromide dimer $[(Mes_2C_6H_3)AlBr_3Li]_2$.¹¹

Unlike the case for the spirogallane, the four carbon atoms of the butadienylene units of **I** (C(1), C(8), C(15), C(22)) are not coplanar with a torsion angle of 50.7°. Indeed, as evidenced by Figure 1b (wherein all phenyl groups and diethyl ether units have been omitted), the two butadienylene backbones are severely twisted. It is interesting that such diverse compounds as the spirogallane anion and the title compound may be obtained with elements as similar as gallium and indium.

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Supporting Information Available: A textual summary of data collection and refinement and tables of crystal data, bond distances and angles, final fractional coordinates, and thermal parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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