poration, **1985** and **1992**). Crystal data for *cis-trans*-**2a**: $C_{16}H_{12}S_4Se_8$, $M = 964.19$, red columnar crystal ($0.25 \times 0.13 \times 0.06$ mm^3), monoclinic, space group $P2_1/n$, $a = 8.304(3)$, $b = 22.611(3)$, $c = 13.678(2)$ Å, $\beta = 103.71(2)^\circ$, $V = 2494.9(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.567$ g cm^{-3}, $\mu = 168.70$ cm^{-1}, $R = 0.060$, $R_w = 0.051$, 4214 measured reflections, 3903 independent reflections, 2459 observed reflections [$I > 3.0\sigma(I)$], 253 refined parameters. Crystal data for *cis-cis*-**2b**: $C_{18}H_{16}S_4Se_8$, $M = 992.24$, red prismatic crystal ($0.42 \times 0.42 \times 0.30$ mm^3), monoclinic, space group $P2_1/a$, $a = 10.378(2)$, $b = 13.198(2)$, $c = 10.683(2)$ Å, $\beta = 113.78(1)^\circ$, $V = 1339.1(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.461$ g cm^{-3}, $\mu = 157.43$ cm^{-1}, $R = 0.059$, $R_w = 0.070$, 4197 measured reflections, 2671 independent reflections, 2300 observed reflections [$I > 3.0\sigma(I)$], 136 refined parameters. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-100683. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ (fax: int. code + (44) 1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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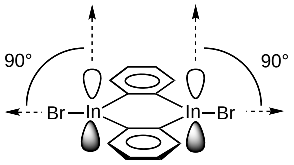
A Bifunctional Lewis Acidic Spacer in Self-Assembled Molecular Stairs and Ladders[**]

François P. Gabbaï,[*] Annette Schier, and Jürgen Riede

Neutral polyfunctional Lewis acids are becoming a well-established class of compounds which serve as anion receptors[1] and catalysts.[2] An emerging field of application concerns their use as electrophilic spacers in molecular self-assembly. Whereas a great number of self-assembled coordination macromolecules have been obtained by linking metallic centers with polyfunctional Lewis bases,[3] the use of organometallic polyfunctional Lewis acids as linker unit between nucleophiles has been only scarcely examined. For example, bis(stannyl)methanes[4a] and mercury crown compounds[4b, c] can form polymers or oligomers. More recently, palladium- and platinum-based cationic linkers were used as building blocks for the synthesis of coordination dendrimers[5a] and molecular hexagons.[5b] Considering the growing interest in coordination macromolecules[6] as microporous solids[7] and catalysts,[8] Lewis acidic spacers constitute an appealing novelty which greatly broadens the scope of the possible assembly sets. Here we report our findings on the use of a neutral bifunctional Lewis acidic spacer in the synthesis of self-assembled molecular stairs and ladders.

The synthesis and structure of the first *ortho*-phenyleneindium complexes were reported in 1996 and 1997.[9] *ortho*-Phenyleneindium bromide is dimeric (**1**) and was isolated as the tetrakis(THF) adduct **2**.[9a] This simple molecule contains two electrophilic indium centers positioned at the opposite apexes of a flat six-membered ring. Since the vacant indium p orbitals are oriented orthogonal to the plane containing the diindacycle, **1** appears to be well suited for the formation of coordination macromolecules with building blocks assembled at 90° angles.[10]



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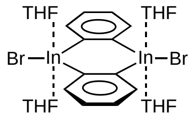
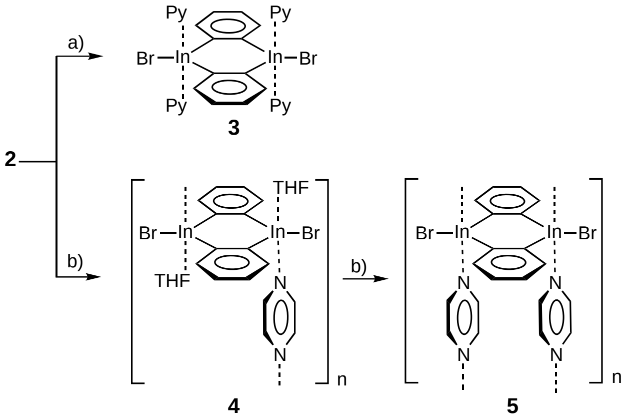


2

To assess the lability of the coordinated THF molecules, a solution of **2** in THF was treated with an excess of pyridine. Crystals of **3** formed instantaneously at 25 °C (Scheme 1). The solid-state structure of **3**[11] is very similar to that of **2**, however, the axial positions of the indium coordination sphere in **3** are occupied with pyridine instead of THF ligands.



Scheme 1. Reaction of 2 with pyridine (py) and pyrazine in THF at 25 °C. a) Excess pyridine; b) 2 equiv of pyrazine.

The isolation of **3** gave us a clue as to which type of nucleophile to combine with **1** for synthesizing a coordination polymer. Addition of one or two equivalents of pyrazine to a solution of **2** in [D$_8$]THF did not result in the formation of a precipitate. Moreover, as suggested by the fact that the chemical shifts of the aromatic proton of **2** and pyrazine are the same,[12] there is no strong association in solution. Pyrazine remains essentially unligated, and **1** still exists as its tetrakis(THF) adduct **2**. However, upon slow cooling of a solution of **2** in THF with one or two equivalents of pyrazine, crystals of a new compound (**4** · 2 THF) formed (Scheme 1). The ^{1}H NMR spectrum indicated the presence of one molecule of pyrazine and four molecules of THF per molecule of **1**.[12] Upon exposure to a dry, inert atmosphere, crystals of **4** become brittle through partial loss of THF, as indicated by elemental analysis. Compound **4** crystallizes with two inter-

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stitial THF molecules and consists of polymeric [**1**-$(THF)_2$-pyrazine]$_n$.[11] Figure 1 shows a portion of a polymeric chain. The diindacycle is planar within experimental error, and the bromine atoms are displaced by 0.274 Å out of the plane containing the phenylene rings and the indium atoms. Each indium atom is in a trigonal-bipyramidal coordination geometry which does not exhibit any noteworthy angular distortion. The two phenylene rings and the bromine atom are at the equatorial sites. The axial positions are unsymmetrically occupied by one THF and one pyrazine molecule. The In–C, In–Br, and In–O(1) bond lengths fall within the expected range and are similar to those in **2**.[9a] The In–N distance of 2.478(5) Å is almost equal to the mean In–N distance in **3** (2.477 Å).

Examination of the cell-packing diagram reveals the polymeric nature of **4**. The "infinite chains" run parallel to one another and do not form any short interchain contacts. The monomeric units **1**-$(THF)_2$-pyrazine are linked through a single In–N linkage. All diindacycles are parallel to one another, and the In''-In-In' angle of 94.8° approaches normality (Figure 1). Thus, chains of **4** are reminiscent of stairs in which the diindacycles constitute the steps. The solvate THF molecules occupy the void space between the chains and are not involved in intermolecular contacts.

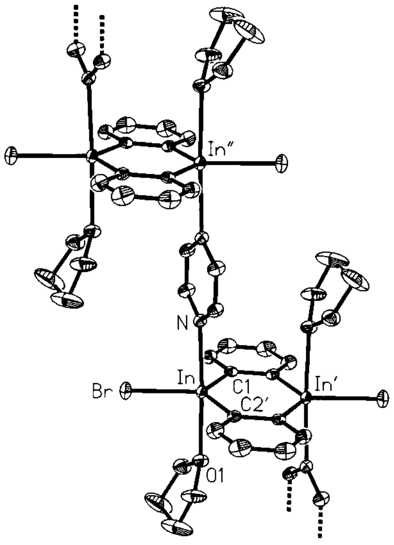

Figure 1. View of two monomeric units of polymer **4**; ORTEP drawing at the 30% probability level. Selected bond lengths [Å] and angles [°]: In–C(1) 2.156(3), In–C(2)' 2.151(3), In–Br 2.542(1), In–O(1) 2.463(4), In–N 2.478(3); C(1)-In-C(2)' 124.0(1), C(1)-In-Br 113.1(1), C(2)'-In-Br 122.7(1), N-In-O(1) 177.6(1).

Stoichiometric control of the assembly of **1** with pyrazine was our next aim. When the ratio of pyrazine to **1** in THF was increased to four, crystals of a novel compound (**5**·2THF) precipitated spontaneously (Scheme 1). The pale yellow needles obtained have strongly anisotropic mechanical properties and are easily cleaved along the direction of growth axis. The ^1H NMR spectrum revealed the presence of two molecules of pyrazine and two molecule of THF per molecule of **1**.[12] However, as observed for **4**·2THF, loss of THF occurs rapidly at 25°C when the crystals are exposed to a dry, inert atmosphere. Definitive structural insights were gained from an X-ray study.[11] Compound **5** crystallizes with two interstitial THF molecules and consists of polymeric [**1**-(pyrazine)$_2$]$_n$. The structure of the monomeric unit can be derived from that of **3** by replacing the four axial pyridine ligands by two bridging pyrazine ligands (Figure 2).

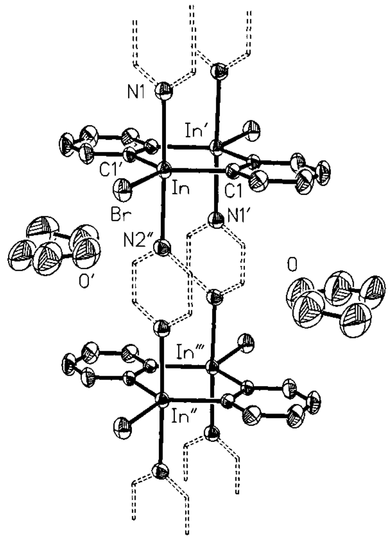

Figure 2. View of two monomeric units of polymer **5** with the interstitial THF molecules; ORTEP drawing at the 30% probability level. The disordered pyrazine molecules are represented by dotted lines in their average positions. Selected bond lengths [Å] and angles [°]: In–C(1) 2.159(3), In–Br 2.523(1), In–N(1) 2.528(4), In–N(2)'' 2.540(4); C(1)-In-C(1)' 122.4(2), C(1)-In-Br 118.8(1), N(1)-In-N(2)'' 176.5(1).

All distances and angles in **5** are similar to those in **3** and **4** with the exception of the appreciably longer In–N distances (2.528(4)–2.540(4) Å). As in **4**, the infinite chains run parallel to one another and do not form any short interchain contacts. In contrast to **4**, the monomeric units of **5** are assembled through two In–N linkages. Thus, chains of **5** ressemble a ladder in which the diindacycles constitute the rungs, and the [In-pyrazine]$_n$ sequences the legs. With In'-In-In'' and In-In'–In''' angles of 88.6 and 91.4°, respectively, the cavity generated between the indiviual rungs of the ladder approximately resembles a rectangular space of 7.8 × 3.6 Å (In–In' × N1'–N2''). The THF molecules are position halfway between the rungs and do not penetrate the cavity deeply enough to be involved in short intermolecular contacts.

Polymers **4** and **5** are insoluble in nonpolar sovents. However, upon being heated in their THF mother liquors for a short time at reflux, the polymers dissolve completely. This process is reversible, and both polymers spontaneously reform upon cooling. When heated in the solid state, **4** and **5** first become brittle (0–50°C) and then decompose at 380 and 300°C, respectively.

The present results demonstrate that bifunctional Lewis acids are useful building blocks for coordination macromolecules, and that they can be regarded as electrophilic spacers. The system **1**/pyrazine/THF is versatile, and the stoichiometry and composition of the assembly can be controlled.

Experimental Section

3: Compound **3** spontaneously crystallized from a solution of **1**-(THF)$_2$ (40 mg, 58 μmol) in THF (0.5 mL) upon addition of pyridine (25 μL, 310 μmol). Yield: 79% (40 mg); m.p. 235 °C (decomp); elemental analysis calcd for $C_{32}H_{28}Br_2In_2N_4$: C 44.7, H 3.3, N 6.5; found: C 44.3, H 3.3, N 6.2.

4·2THF and **5**·2THF: **1**-(THF)$_2$ (69 mg, 100 μmol) and pyrazine (16 mg, 200 μmol for **4**·2THF and 32 mg, 400 μmol for **5**·2THF) were mixed in Schlenck tubes, and THF (2 mL) was added. The resulting solutions were slowly concentrated until crystalline material started to appear on the sides of the tubes. All solids were then redissolved by heating the solutions at reflux for a short time. Upon slow cooling of the solutions from 60 to −15 °C, **4**·2THF and **5**·2THF were obtained as crystals in 67% (80 mg) and 60% yields (50 mg), respectively. Compounds **4**·2THF and **5**·2THF spontaneously loose THF at 25 °C. Elemental analysis carried out on "withered" samples indicated a THF depletion of 78% for **4**·2THF and 34% for **5**·2THF after one week at 25 °C under atmospheric pressure.

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[11] Crystal structure analyses: Enraf Nonius CAD4 diffractometer, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The data were corrected for Lorentzian and polarization effects and for absorption [psi scans]. The structure were solved with direct methods (SHELXS-86), and refined against F^2 (SHELXL-93).[13] Hydrogen atoms were calculated in idealized geometry and allowed to ride on their corresponding C atom with isotropic contributions ($U_{iso(fix)} = 1.5\,U_{eq}$ of the attached C); non-hydrogen atoms were refined with anisotropic displacement parameters with the exception of those of one pyridine ring in **3** [N22–C225], which was treated isotropically as a rigid group. The pyrazine rings in **5**·2THF are disordered and were refined in split positions. The function minimized was $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, $w = [\sigma^2(F_o^2) + (ap)^2 + bp]^{-1}$, $p = (F_o^2 + 2F_c^2)/3$. Structure data: **3**: $C_{32}H_{28}Br_2In_2N_4$, $M_r = 858.04$, triclinic, $a = 9.489(1)$, $b = 9.915(1)$, $c = 16.846(2)$ Å, $\alpha = 88.21(1)$, $\beta = 87.47(1)$, $\gamma = 86.72(1)^\circ$, space group $P\bar{1}$, $Z = 2$, $V = 1580.1(3)$ Å^3, $\rho_{calcd} = 1.803\,g\,cm^{-3}$, $F(000) = 832$, $T = -80\,^\circ C$, $\mu(Mo_{K\alpha}) = 40.15\,cm^{-1}$, $T_{min}/T_{max} = 0.731/0.999$; of 9904 measured reflections [$(\sin\theta/\lambda)_{max} = 0.64$ Å^{-1}], 6780 were used for the refinement of 319 refined, R_1 (wR_2) = 0.0404 (0.1000), $a = 0.0437$, $b = 5.39$, residual electron densities: $+1.91/-0.94\,e\,Å^{-3}$. **4**·2THF: $C_{32}H_{44}Br_2In_2N_2O_4$, $M_r = 904.15$, monoclinic, $a = 8.716(1)$, $b = 10.609(1)$, $c = 19.359(2)$ Å, $\beta = 91.46(1)^\circ$, space group $P2_1/c$, $Z = 2$, $V = 1789.5(3)$ Å^3, $\rho_{calcd} = 1.689\,g\,cm^{-3}$, $F(000) = 900$, $T = -74\,^\circ C$, $\mu(Mo_{K\alpha}) = 35.57\,cm^{-1}$, $T_{min}/T_{max} = 0.757/0.999$; of 3688 measured reflections [$(\sin\theta/\lambda)_{max} = 0.64$ Å^{-1}], 3583 were used for the refinement of 190 parameters, R_1 (wR_2) = 0.0277 (0.0641), $a = 0.0318$, $b = 1.10$, residual electron densities: $+1.02/-0.93\,e\,Å^{-3}$. **5**·2THF: $C_{28}H_{32}Br_2In_2N_4O_2$, $M_r = 864.04$, monoclinic, $a = 12.365(1)$, $b = 16.231(1)$, $c = 7.830(1)$ Å, $\beta = 93.88(1)^\circ$, space group $C2/m$, $Z = 2$, $V = 1567.9(3)$ Å^3, $\rho_{calcd} = 1.792\,g\,cm^{-3}$, $F(000) = 824$, $T = +20\,^\circ C$, $\mu(Mo_{K\alpha}) = 40.50\,cm^{-1}$, $T_{min}/T_{max} = 0.834/0.999$; of 2896 measured reflections [$(\sin\theta/\lambda)_{max} = 0.64$ Å^{-1}], 1432 were used for the refinement of 111 parameters, R_1 (wR_2) = 0.0292 (0.0626), $a = 0.0769$, $b = 0.20$, residual electron densities: $+0.62/-0.67\,e\,Å^{-3}$. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666 (Frau S. Höhler-Schlimm); e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD 407782, CSD 407781, and CSD 407780.

[12] Incremental addition of pyrazine (2 × 4 mg, 2 × 50 μmol) to **2** (34 mg of **1**-(THF)$_2$,[9a] 50 μmol) in [D$_8$]THF (0.5 mL) did not result in any change in the chemical shift of the aromatic protons of **2** and pyrazine. For **3**–**5**, heating the samples for a short time to 65 °C was necessary to obtain solutions. For **4** and **5**, the ^1H and ^{13}C chemical shifts of the diindacycle phenylene atoms are the same as those measured for **2**.[9a] The ^1H and ^{13}C chemical shifts of the pyrazine atoms in **4** and **5** correspond exactly to those measured for the free bases in [D$_8$]THF. **3:** ^1H NMR (400 MHz, [D$_8$]THF): $\delta = 7.13$ (m, 4H; H(2, 3,6, 7)), 7.33 (m, 8H; H(3, 5), py), 7.57 (m, 4H; H(1, 4, 5, 8)), 7.75 (m, 4H; H(4), py), 8.54 (m, 8H; H(2, 6), py); ^{13}C NMR (400 MHz, [D$_8$]THF): $\delta = 125.0$ (s, C(3, 5), py), 127.7 (s, C(2, 3, 6, 7)), 137.7 (s, C(1, 4, 5, 8), 137.8 (s, C(4), py), 150.4 (s, C(2, 6)) 170.2 (s, *C*In).

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