clear brown solution was added K[Bu_2acac] (0.22 g, 1.0 mmol), and stirring was continued for 10 min. Dropwise addition of H_2O (5 mL) and filtration initiated the precipitation of brown-green crystals of **4** within 5 h; yield 0.31 g (52 %).

Physical data of complexes: UV/Vis (CH_2Cl_2): λ_{max} nm (ε[L mol^{-1} cm^{-1}]): **2**: 252 (8.1×10^3), 315 (5.3×10^3), 532 (1.2×10^3); **3**: 254 (2.71×10^4), 334 (1.67×10^4), 358 (1.60×10^4); **4**: 256 (1.6×10^4), 293 (1.8×10^4), 451(500). $[\mathbf{2}]^{\bullet+}$: 236 (4.5×10^3), 308 (1.4×10^4), 413 (5.1×10^3), 431 (5.2×10^3), 485 (2.4×10^3); $[\mathbf{3}]^{\bullet+}$: 270 (2.6×10^4), 304 (2.4×10^4), 352 (2.2×10^4), 412 (6.1×10^3); $[\mathbf{4}]^{\bullet+}$: 259 (1.9×10^4), 303 (2.5×10^4), 347sh (6.4×10^3), 391 (3.2×10^3), 411 (4.0×10^3), 477(990).

The radical complexes $[\mathbf{2}]^{\bullet+}$, $[\mathbf{3}]^{\bullet+}$, and $[\mathbf{4}]^{\bullet+}$ were generated in CH_2Cl_2 solution (0.10 M [$(n\mathrm{Bu})_4$N]PF_6) by coulometry. X-Band EPR spectra (CH_2Cl_2, 10 K, 9.45 GHz): g_x, g_y, g_z ($A_x = A_y$, A_z [10^{-4} cm^{-1}]): **2**: 2.05, 2.05, 2.24 (20, 180); **3**: 2.05, 2.06, 2.26 (21.7, 176); **4**: 2.06, 2.07, 2.25 (0, 175).

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[7] The complex described in ref. [6a] is an exception. It has the phenoxyl radical in apical position of the Cu^{II} square pyramid. An (S=1) ground state has been proposed.

[8] X-ray structure analysis of **3**: Brown-green crystal ($0.42 \times 0.60 \times 0.49$ nm); $C_{35}H_{45}CuN_3O_4$, $M_r = 635.3$, monoclinic, space group $P2_1/c$, $a = 15.407(3)$, $b = 11.490(2)$, $c = 18.438(4)$ Å, $\beta = 101.69(3)^\circ$, $V = 3196(1)$ Å^3, $Z = 4$ at 293(2) K; $\rho_{calcd} = 1.32$ g cm^{-3}; $\mu_{Mo} = 0.726$ mm^{-1}, semiempirical absorption correction. Full-matrix least-squares refinement based on F with 6083 reflections with [$I > 2\sigma(I)$] and 388 variables, final R values: $R(F) = 0.037$ and $wR(F) = 0.091$. Intensities were measured on an Enraf-Nonius CAD-4 diffractometer. The crystallographic data were deposited as supplementary publication no. CCDC-100759 at the Cambridge Crystallographic Data Centre. Copies of the data are available from CCDC, 12 Union Road, GB-Cambridge CB2 1EZ (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[11] In the first-derivative representation (dX″/dB) of the EPR spectrum (Figure 6) an apparently dominant signal of a Cu^{II} compound ($S = {}^1/_2$) is detected; its intensity, however, represents only 10 % of the doubly integrated total signal. In a broad field range the oxidation product $[\mathbf{3}]^{\bullet+}$ displays typical resonances of a triplet spectrum with small zero-field splitting ($D < h\nu$) as is observed for spin pairs ($S_1 = S_2 = {}^1/_2$). $\Delta m = 1$ signals at $g < 2$ (350–430 mT) are clearly detected, as well as the typical half-field transitions with $\Delta m = 2$ at $g = 4$, which display a clearly resolved Cu hyperfine splitting ($I = {}^3/_2$). The spectrum was simulated with a spin Hamiltonian for an effective spin $S = 1$ (strong coupling case) and parameters $D = 0.086$ cm^{-1}, $E/D = 0.13$, $g = (2.034, 2.021, 2.10)$ and $\mathbf{A} = (20, 20, 100) \times 10^{-4}$ cm^{-1}. For the local spin of the Cu^{II} ion ($S = {}^1/_2$) we obtained $\boldsymbol{a}_{\mathbf{Cu}} = (40, 40, 200) \times 10^{-4}$ cm^{-1}, $\boldsymbol{g}_{\mathbf{Cu}} = (2.07, 2.04, 2.20)$ by using the usual spin projection technique. These values are similar to those obtained for the Cu^{II} ion in **3**. Since the signals are observed down to 4 K, the spin triplet is the ground state of $[\mathbf{3}]^{\bullet+}$, owing to an intramolecular ferromagnetic coupling. The splitting energy $2J$ between the triplet and (EPR-silent) singlet has been determined from the temperature dependence of the intensities(IT vs. T) by a fitting procedure to the Boltzmann function IT = const.$(1 + \exp(2J/kT)^{-1})$ in the temperature range 4–60 K. For I the peak-to-peak amplitudes of the measured derivative spectra at $g = 4$ were used, because the resonances are not perturbed by signals of the Cu^{II} impurity.

Synthesis and Characterization of the First Double-Bridged Tetraselenafulvalenophanes[**]

Kazuo Takimiya, Akinobu Oharuda,
Atsushi Morikami, Yoshio Aso, and Tetsuo Otsubo[*]

Since the discovery of the tetrathiafulvalene/tetracyano-*p*-quinodimethane complex (TTF–TCNQ) as the first low-dimensional organic metal,[1] TTF derivatives with modified frameworks have been examined in order to develop yet more superior organic conductors.[2] One of the basic modifications is dimerization of TTF, which makes it possible to prepare charge-transfer complexes of given stoichiometry.[3] To date, a variety of dimeric TTFs have been thus synthesized and characterized.[4] Among them, tetrathiafulvalenophanes (TTF phanes) are of current interest, because in such sophisticated systems the two TTF units can adopt a unique sandwich structure and interact strongly with each other.[5, 6] We have recently found that the double-layered TTF phanes **1** are especially good electron donors, forming highly conductive radical cation salts. The high conductivities are induced by strong intra- and intermolecular nonbonding interactions between the sulfur atoms incorporated in the TTF moieties.[6] Since nonbonding interactions between selenium atoms are generally more effective than those of sulfur, tetraselenaful-

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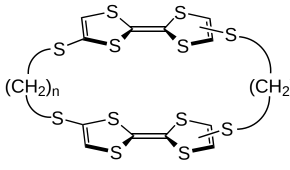
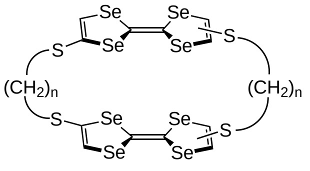
valenophanes (TSF phanes) should be even better electron donors. To our knowledge, however, TSF phanes have not yet been described. We report here on the synthesis and properties of the first examples, double-bridged TSF phanes **2**.

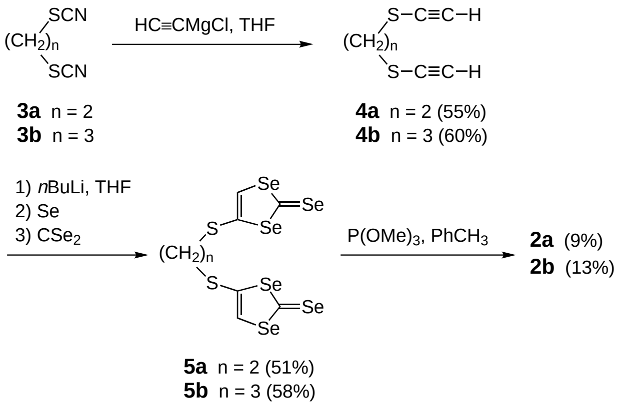


1a n = 2
1b n = 3

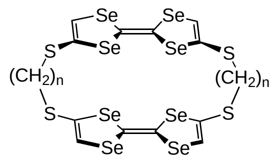


2a n = 2
2b n = 3

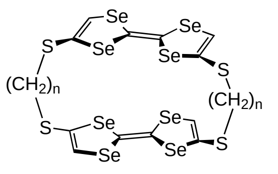
TSF phanes **2** were synthesized according to the three-stage route shown in Scheme 1. The key step is the ready preparation of the bridged precursors, bis(1,3-diselenole-2-selones) **5**. Our recent improved synthetic method for 1,3-diselenole-2-selone derivatives[7] was successfully applied to the preparation of **5**: bis(ethynylthio)alkanes **4**, obtained from dithiocyanatoalkanes **3** and ethynylmagnesium chloride, were metalated with butyllithium in tetrahydrofuran, and then treated consecutively with selenium powder and carbon diselenide to give **5a** and **5b** in moderate yields (51 and 58%, respectively). The subsequent double-coupling reaction of **5** induced by trimethyl phosphite in refluxing toluene gave the desired TSF phanes **2a** and **2b** in 9 and 13% yield, respectively.



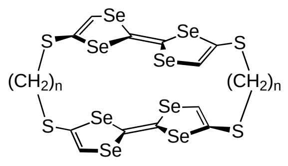
Scheme 1. Synthesis of TSF phanes **2a** and **2b**.



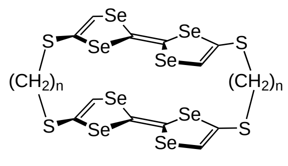
*cis–cis–***2**



*cis–trans–***2**



*trans–trans–***2** (*twist*)



*trans–trans–***2** (*eclipse*)

In analogy to the TTF phanes **1**, the TSF phanes **2** are expected to exist as a mixture of four diasteromers: *cis-cis*-**2**, *cis-trans*-**2**, and *twist* and *eclipse trans-trans*-**2**. Indeed, the ^{1}H NMR spectra of the crude products display five singlets for the fulvalenic protons, of which a pair of singlets corresponds to the *cis-trans* isomer and the remaining singlets to the other isomers. Recrystallization of a mixture of **2a** isomers from hot carbon disulfide/benzene gave a red columnar material, which was assigned on the basis of its NMR analysis to be the *cis-trans* isomer. In addition, during the NMR measurement in solution the compound slowly isomerized into the other isomers, an observation previously made for the TTF phanes **1**. The precise molecular structure of the *cis-trans* isomer was determined by an X-ray crystallographic analysis (Figure 1).[8] The two TSF units are almost planar and stacked with partial overlap. The shortest distance between Se atoms in the stacked TSF units is 3.92 Å, which is slightly longer than the normal van der Waals contact (3.8 Å). In the crystal structure the TSF phane **2a** is stacked with other molecules to make a stacking column, but there are no intermolecular Se ··· Se contacts between the stacked molecules.

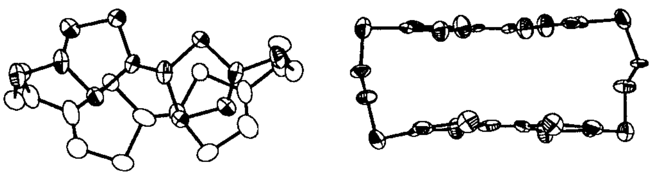


Figure 1. X-ray crystal structure of *cis-trans*-**2a** (ORTEP plots): top view (left) and side view (right).

Recrystallization of **2b** from carbon disulfide gave orange prisms, which were shown by X-ray crystallographic analysis to be the *cis-cis* isomer (Figure 2). In contrast to the almost planar TSF in *cis-trans*-**2a**, the TSF frameworks of *cis-cis*-**2b** are strongly bent, with dihedral angles of 24.3 and 42.9° between the central and the outer ethylene units. The molecule as a whole assumes an *anti* conformation. The two TSF units do not overlap and there is no close, nonbonding Se ··· Se contact. The crystal structure of **2b** unlike **2a** contains no intermolecular stacking, and instead some face-to-edge interactions through very short Se ··· Se contacts existing between the neighboring TSF phanes.

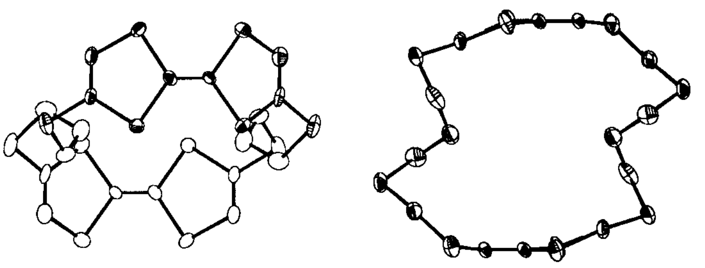
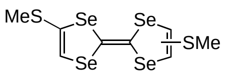


Figure 2. X-ray crystal structure of *cis-cis*-**2b** (ORTEP plots): top view (left) and side view (right).

The cyclic voltammogram of the TSF phane **2a** shows two reversible one-electron redox waves ($E_{1/2} = 0.47$ and 0.62 V) and one quasi-reversible two-electron redox wave ($E_{1/2} = 0.96$ V), and the pattern is very similar to that of the TTF phane **1a**. The splitting of the first and second redox processes is ascribed to a marked through-space interaction between the two TSF units. When compared with the first half-wave oxidation potential of 4,4′(5′)-bis(methylthio)tetraselenafulvalene (BMT-TSF) ($E_{1/2} = 0.57$ V), the low potential shift of the first oxidation of **2a** indicates that the resulting monocationic state is stabilized by transannular charge delocalization. The high potential shift of the second oxidation reflects destabilization of the dicationic state due to transannular coulombic repulsion. The finding that the combined third and fourth oxidation wave is higher than the second oxidation potential of BMT-TSF ($E_{1/2} = 0.86$ V) also supports large coulombic repulsion in the tri- and tetracationic states. The cyclic voltammogram of **2b**, which has longer methylene bridges, shows only two broad two-electron redox waves at $E_{1/2} = 0.51$ and 0.93 V. The two TSF units do not interact strongly enough to split the first and second redox processes.



BMT-TSF

Preliminary attempts to electrocrystallize **2a** from a chlorobenzene solution containing a small amount of 2-propanol and with tetrabutylammonium perchlorate as supporting electrolyte gave thin black needles of the radical cation salt $\mathbf{2a} \cdot ClO_4$. Its conductivity at room temperature is 3.5 S cm^{-1}, which is one order of magnitude higher than that of its sulfur counterpart, $\mathbf{1a} \cdot ClO_4$ (0.16 S cm^{-1}).[6] This suggests interaction of the selenium atoms incorporated in the TSF phane.

Experimental Section

All reactions were performed in a nitrogen atmosphere. Cyclic voltammetry was conducted in benzonitrile containing 0.1 M [nBu$_4$N]ClO$_4$ with an Ag/AgCl standard electrode and Pt working and counter electrodes. Electrical conductivity was measured on a single crystal with a four-probe technique.

4a: To a stirred solution of ethynylmagnesium chloride[9] (0.61 mol) in anhydrous THF (450 mL) was added **3a**[10] (21.5 g, 149 mmol) at 0°C, and the mixture was stirred for 12 h at room temperature. The reaction mixture was then poured into ice water (1 L) and extracted with CH_2Cl_2 (3 × 300 mL). The extract was washed with water and dried ($MgSO_4$). After evaporation of the solvent, the residue was purified by column chromatography (silica gel, hexane) and recrystallized from hexane to give colorless plates of **4a** (11.6 g, 55 %). M.p. 40–40.5°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.84$ (s, 2H; CH), 3.08 (s, 4H; CH$_2$); IR (KBr): $\tilde{\nu} = 2035$ cm^{-1} (C≡C); Elemental analysis calcd for $C_6H_6S_2$ (142.23): C 50.67, H 4.25; found: C 50.62, H 4.21.

4b: Yield 60 %; colorless oil; b.p. 74°C/1.5 mmHg; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.24$ (quintet, $J = 6.8$ Hz, 2H; CH$_2$), 2.78 (s, 2H; CH), 2.89 (t, $J = 6.8$ Hz, 4H; SCH$_2$); IR (neat): $\tilde{\nu} = 2041$ cm^{-1} (C≡C); Elemental analysis calcd for $C_7H_8S_2$ (156.26): C 53.81, H 5.16; found: C 53.76, H 5.16.

5a: According to the recently reported procedure,[7] a solution of **4a** (142 mg, 1 mmol) and TMEDA (0.61 mL, 4 mmol) in anhydrous THF (10 mL) was treated successively with 1.6 N nBuLi in hexane (1.25 mL, 2 mmol), selenium powder (158 mg, 2 mmol), carbon diselenide (0.14 mL, 2.2 mmol), and water/THF (1/1 v/v, 20 mL). Water (30 mL) was added to the reaction mixture, and the insoluble materials were removed by filtration and washed with MeOH (30 mL). The filtrate and washings were combined and concentrated, and the residue was recrystallized from chlorobenzene to give purple plates of **5a** (324 mg, 51 %). M.p. 142–143°C; ^{1}H NMR (400 MHz, CS$_2$/CDCl$_3$): $\delta = 3.11$ (s, 4H; CH$_2$), 7.98 (s, 2H; CH); IR (KBr): $\tilde{\nu} = 899$ cm^{-1} (C=Se); Elemental analysis calcd for $C_8H_6S_2Se_6$ (640.02): C 15.01, H 0.94; found: C 15.23, H 0.95.

5b: Yield 58 %; purple plates from chloroform; m.p. 100–101°C; ^{1}H NMR (400 MHz, CS$_2$/CDCl$_3$): $\delta = 2.07$ (quintet, $J = 7.1$ Hz, 2H; CH$_2$), 2.97 (t, $J = 7.1$ Hz, 4H; SCH$_2$), 7.91 (s, 2H; CH); IR (KBr): $\tilde{\nu} = 920$ cm^{-1} (C=Se); Elemental analysis calcd for $C_9H_8S_2Se_6$ (654.02): C 16.53, H 1.23; found: C 16.53, H 1.14.

2a: A mixture of **5a** (319 mg, 0.5 mmol) and trimethyl phosphite (2.4 mL, 20 mmol) in toluene (40 mL) was refluxed for 10 min. After evaporation of the solvent, the residual solid was extracted with CS$_2$ (50 mL) and purified by column chromatography (silica gel, CS$_2$, $R_f = 0.2$) to give a reddish purple solid as an isomeric mixture of **2a** (21 mg, 9 %). M.p. 194°C (decomp); ^{1}H NMR (400 MHz, CS$_2$/[D$_6$]acetone): $\delta = 2.94$–3.09 (m; CH$_2$), 7.288, 7.304, 7.345, 7.371, 7.375 (each s; fulvalenyl H); MS (positive-ion FAB): $m/z = 965$ [M^+] with an isotopic pattern for eight selenium atoms; Elemental analysis calcd for $C_{16}H_{12}S_4Se_8$ (964.19): C 19.93, H 1.25; found: C 19.96, H 1.19. Recrystallization from benzene/CS$_2$ afforded red columnar crystals of *cis-trans*-**2a**: m.p. 184°C (decomp); ^{1}H NMR (400 MHz, CS$_2$/[D$_6$]acetone): $\delta = 2.94$–2.98 (m, AA′BB′, 4H; CH$_2$), 3.05–3.09 (m, AA′BB′, 4H; CH$_2$), 7.304 (s, 2H; fulvalenyl H), 7.375 (s, 2H; fulvalenyl H).

2b (isomeric mixture): Yield 13 %; m.p. 159°C (decomp); ^{1}H NMR (400 MHz, CS$_2$/[D$_6$]acetone): $\delta = 2.03$–2.15 (m; CH$_2$), 2.76–2.88 (m; CH$_2$), 7.285. 7.287, 7.310, 7.321, 7.368 (each s; fulvalenyl H); MS (positive-ion FAB): $m/z = 993$ [M^+] with an isotopic pattern for eight selenium atoms; Elemental analysis calcd for $C_{18}H_{16}S_4Se_8$ (992.24): C 21.79, H 1.63; found: C 21.81, H 1.53. Recrystallization from CS$_2$ gave orange prisms of *cis-cis*-**2b**: m.p. 198°C (decomp); ^{1}H NMR (400 MHz, CS$_2$/[D$_6$]acetone): $\delta = 2.046$ (quintet, $J = 7.6$ Hz, 4H; CH$_2$), 2.830 (t, $J = 7.6$ Hz, 8H; CH$_2$), 7.310 (s, 4H; fulvalenyl H).

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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 CB21EZ (fax: int. code + (44)1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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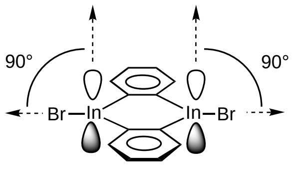
A Bifunctional Lewis Acidic Spacer in Self-Assembled Molecular Stairs and Ladders**

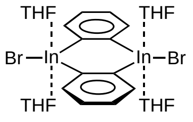
François P. Gabbaï,* Annette Schier, and Jürgen Riede

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]

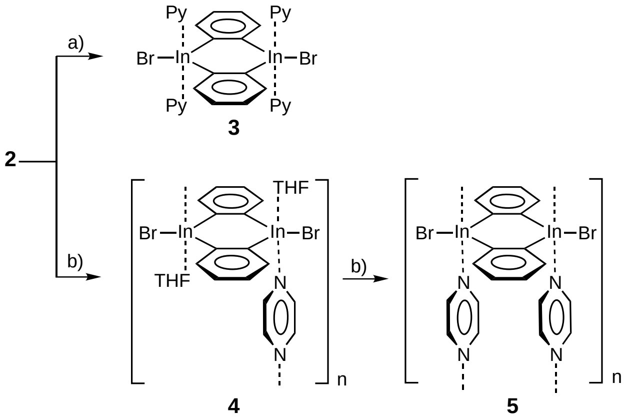


1



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**·2THF) 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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