(c = 1.16, H₂O): ¹H NMR (400 MHz, 389 K, CD₃SOCD₃): δ = 2.42 (br., 12H), 2.65 (br., 24H), 3.09 (t, *J* = 8.0 Hz, 36H), 3.21 (br., 72H), 3.23 (br., 36H), 3.54 (br., 72H), 3.72 (d, *J* = 11.5 Hz, 36H), 3.87 (d, 36H), 4.08 (d, 48H), 4.25 (d, *J* = 7.6 Hz, 36H), 6.84, 7.59, 8.46 (br., 18H), 8.49 (s, 3H); ¹³C NMR (100.6 MHz, 304 K, CD₃SOCD₃): δ = 33.5-44.9, 59.7, 60.9, 67.4, 69.9, 73.4, 76.5, 76.7, 105.8, 128.8, 137.7, 168.8-173.6.

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- [7] The hexamethyl ester of 2, obtained as a colorless oil by the reaction of 3,3'-iminobis(methyl propionate) [5] with benzenetricarbonyl chloride in CH_2Cl_2 in the presence of Et₃N, was hydrolyzed with aqueous 2M NaOH and MeOH to afford 2 (72%) as a foamy solid.
- [8] A solution of 1 [5] (300 mg, 0.125 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a stirred solution of 2 (9 mg, 0.014 mmol), DCC (23 mg, 0.112 mmol), and HOBT (15 mg, 0.112 mmol) in CH_2Cl_2/DMF (1/1, 10 mL) at 0°C under an N₂ atmosphere. The reaction mixture was stirred at room temperature for 5 days, filtered, and worked up as described for 5 (see *Experimental Section*).
- [9] GPC of the fully protected dendrimers was performed on Phenogel (500 and 1000 Å, Phenomenex, Cheshire, UK) semi-preparative columns (300×7.80 mm) attached to a Gilson 714 high-performance liquid chromatography system fitted with a UV-detector. Detection was carried out at 260 nm, and GPC grade THF (Fisons) was used for the elutions. The fully deprotected dendrimers were purified on a Fractogel ($25-40 \ \mu m$, Merck) column ($100 \times 0.25 \ cm$) fitted with a differential refractometer (Waters) with deionized and degassed H₂O as eluant.
- [10] MALDI-TOF mass spectra were obtained with either 2.5-dihydroxy benzoic acid (gentistic acid) or *trans*-3-indoleacrylic acid and an average of 50 laser shots per sample.
- [11] In line with our previous experience, ref [5], ¹H NMR spectra were recorded at high temperatures to reduce their complexity by ensuring that torsion around the tertiary amide bonds was fast on the ¹H NMR timescale.
- [12] In addition to the expected signals, there are quite a few resonances that could not be assigned in both the ¹H NMR and ¹³C NMR spectra. At present these peaks are presumed to arise from an impurity.
- [13] To gain insight into the nature of substitution around the core, the 24-mer was allowed to react with Gly-OtBu to obtain the corresponding Gly-OtBu extended amide after purification by GPC. The ¹HNMR spectrum of the Gly-OtBu extended amide, recorded in CD₃SOCD₃ at 389 K, revealed the presence of four resonances (major $\delta = 1.424$ and 1.418, minor $\delta = 1.412$ and 1.405) arising from the tert-butyl groups. This observation not only suggests

that there are constitutional isomers as a result of disposition of the wedge around the core in the 24-mer, but also that the *tert*-butyl groups in the 24-mer residue are in two different environments. This is perhaps due to increased restriction of rotation about the tertiary amide bonds at its highly hindered core.

- [14] The tetracarboxylic acid wedge 3 was obtained by coupling one equivalent of N-[N³-(benzyloxycarbonyl)glycinamido]-3,3'-bis(propionic acid) [5] with two equivalents of the amine 3,3'-iminobis(methylpropionate) followed by hydrolysis of the methyl ester functions.
- [15] The MALDI-TOF mass spectroscopic analysis of the fully deprotected dendrimers 8 and the 24-mer requires Ag⁺ ion assisted laser desorption: Z. Xu, M. Kahr, K. L. Walker, C. L. Wilkins, J. S. Moore, J. Am. Chem. Soc. 1994, 116, 4537-4550. Although peaks were observed in the molecular ion regions for the free saccharide-containing dendrimers named above, the spectra were complex, presumably due to the use of silver salts.
- [16] Molecular simulations were carried out as described previously [5], with the exception that the molecular volume calculations were performed with Biosym's Insight and Discover software (Biosym Technologies, San Diego, CA) on a Silicon graphics Indy workstation.
- [17] Since the system is in slow exchange at room temperature, average values are only quoted for the ¹H NMR chemical shifts.

Supramolecular Weaving**

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The logical design of organized, organic, solid-state superstructures-namely, crystal engineering^[1]-continues to be a formidable challenge, even though the number of identifiable design elements that can be exploited for noncovalent synthesis (supramolecular synthons)^[1b] is expanding rapidly. Due to its high selectivity and directionality, the hydrogen bond^[2] has become one of the most widely used implements in the crystal engineer's toolbox; it has permitted the noncovalent synthesis of a comprehensive range of solid-state systems, traversing the whole superstructural kingdom from oligomeric supramolecular macrocycles^[3] and cages^[4] to polymeric supramolecular arrays.^[5] Nevertheless, only recently have scientists utilized the potential of the hydrogen bond for the rational synthesis of interwoven systems,^[6] involving noncovalent association of pseudorotaxanes--supramolecular complexes in which a thread-like molecule or ion is encircled by a macrocyclic species without the presence of a mechanical bond-in the solid state.

We reasoned that by combining two recognition motifs that employ hydrogen bonding as their principal noncovalent "adhesive", namely, the carboxyl dimer^[3c, 7] supramolecular synthon (A in Scheme 1) and the self-assembly^[8] of [3]pseudorotaxanes by double threading^[9] of two secondary dialkylammonium strands through the cavity of the ditopic macrocyclic polyether bis-*p*-phenylene[34]crown-10 (BPP34C10), we could synthesize

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Scheme 1. Schematic representation of the supramolecular synthesis of a doubly encircled, six-component organic supermolecule and an interwoven supramolecular cross-linked polymer. The building blocks are BPP34C10 (red) and carboxyl (green) containing secondary dialkylammonium cations (blue) that utilize the carboxyl dimer supramolecular synthon. A and the double threading of pairs of ammonium cations through the crown ethers' cavities.

noncovalently a whole new range of encircled and interwoven superstructures. The construction of these self-assembled superstructures would be tantamount to supramolecular weaving, that is, [3]pseudorotaxanes with pendant carboxyl groups for noncovalent association could interlace with one another using the carboxyl dimer to generate novel multiply encircled supermolecules and interwoven supramolecular arrays.

Here we describe 1) the synthesis of the carboxyl-substituted ammonium salts $3-H \cdot PF_6$ and $4-H \cdot PF_6$, 2) the noncovalent dimerization of the [BPP34C10· $(3-H)_2$]²⁺ [3]pseudorotaxane in the solid state to form a doubly encircled, six-component organic supermolecule (Scheme 1), and 3) the noncovalent synthesis of an interwoven supramolecular cross-linked polymer in the solid state by the noncovalent polymerization of [BPP34C10· $(4-H)_2$]²⁺ (Scheme 1). The ammonium salts $3-H \cdot PF_6$ and $4-H \cdot PF_6$, which possess the requisite carboxyl groups for noncovalent association, were prepared in reasonable yields from the aminoesters $1^{[9d]}$ and $2^{[10]}$ by boiling with concentrated



hydrochloric acid, to effect hydrolysis with concomitant protonation, followed by counterion exchange from chloride to hexafluorophosphate.

The X-ray crystallographic analysis^[13, 14] of the 1:2 complex^[15] formed between BPP34C10 and 3-H⁺ reveals that both of the cations are threaded codirectionally through the center of the macrocycle (Figure 1). This arrangement is stabilized by a total of six $[N^+-H\cdots O]$ hydrogen bonds between the NH_2^+ centers and three oxygen atoms from each polyether linkage $(N \cdots O)$ 2.86-3.18 Å). Secondary stabilization is conferred upon the [3]pseudorotaxane superstructure by an edge-to-face $[C-H\cdots\pi]$ contact between one of the methylene hydrogen atoms of the 4-carboxybenzyl group and one of the hydroquinone rings of BPP34C10 (the associated $[H \cdots \pi]$ distance and $[C - H \cdots \pi]$ angle are 2.88 Å and 143°). The centroid--centroid separation between the benzoic acid rings of distinct 3-H⁺ cations is about 4.6 Å, the rings being inclined by 28°, thus ruling out any significant aryl-aryl stacking interactions. Both of the independent cations have conventional "gull wing" conformations, in which each of their aromatic rings is oriented approximately orthogonally with respect to their associated planar all-anti CCH2NH2+CH2C backbones. Furthermore, a fluorine atom from one of the $PF_6^$ anions is directed into the cleft between the two dialkylammonium cations and lies about 2.5 Å away from one cation's benzylic

hydrogen atoms.^[16] An approach of about 2.5 Å was also discovered between one of this anion's equatorial fluorine atoms and one of the hydroquinone ring's hydrogen atoms. We hypothesize that this PF_6^- anion assists the macrocyclic polyether by helping to enforce the codirectionality of the [3]pseudorotaxane's two carboxyl groups. This leads to the noncovalent association of pairs of C_i symmetrically related [3]pseudorotaxane-like complexes and the generation of doubly encircled, six-component organic supermolecules that are linked by the carboxyl dimer supramolecular synthon through pairs of strong $[O-H\cdots O]$ hydrogen bonds $(O\cdots O 2.61 \text{ and } 2.68 \text{ Å}, Fig$ ure 1). In many respects, this structure is similar to the 2:2 complex formed between α, α' -bis(benzylammonium)-p-xylene bis(hexafluorophosphate) and BPP34C10, $\{9a-c\}$ an observation that is not surprising since the carboxyl dimer may be consid-



Figure 1. View of the $[{BPP34C10 \cdot (3-H)_2}^{2+}]_2$ supermolecule; left: ball-and-stick representation, right: space-filling representation; red: BPP34C10, green: carboxyl groups of 3-H⁺ (remainder in blue). For clarity, only the PF₆⁻ counterion associated with the benzylic methylene groups is shown.

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ered to behave [1b] as a surrogate for a *p*-disubstituted benzene ring.

In contrast with the solid-state structure of $[BPP34C10 \cdot (3-H)_2]^{2+}$ (vide supra), the X-ray crystal structure^[13, 14] of the 1:2 complex^[15] formed between the BPP34C10 macrocycle and the 4-H⁺ secondary dialkylammonium strand reveals that the cations are threaded centrosymmetrically with respect to each



Figure 2. Ball-and-stick representation of the $[BPP34C10\cdot(4-H)_2]^{2+}$ pseudorotaxane; red: BPP34C10, green: carboxyl groups of $4-H^+$ (remainder in blue).

5. other, that is, in an antiparallel orientation (Figure 2). Once again, stabilization of the [3]pseudorotaxane superstructure is achieved by $[N^+ - H \cdots O]$ hydrogen bonds (N···O 2.87 and 2.88 Å) between the NH_2^+ centers and pairs of oxygen atoms in each of the macrocycle's polyether arcs. Furthermore, the cations also maintain a gull wing conformation with a planar allanti CCH, NH⁺₂CH, C backbone, though the isophtha-

late ring is noticeably skewed from an orthogonal relationship. Noncovalent association utilizing the carboxyl dimer supramolecular synthon occurs between the pairs of carboxyl groups of each cation and their nonequivalent counterparts in symmetry-related complexes. The [O-H···O] hydrogen bonds are strong, and the O...O distances range from 2.57 to 2.69 Å. In this case, the effect of combining multiple carboxyl dimer and double threading motifs is the creation of a novel type of supramolecular polymer,^[17] specifically, an interwoven supramolecular cross-linked polymer (Figure 3). Cross-linking of isophthalic acid tapes^[18] is induced by the macrocyclic polyether, since it directs two isophthalic acid units from separate 4-H⁺ cations in opposing directions, that is, the tapes are interlinked by the [3]pseudorotaxane unit to form two-dimensional pseudopolyrotaxane^[19] sheets. The sheets are fairly thick (about 12.5 Å) since the planes of the $[O-H\cdots O]$ hydrogen bonds are approximately orthogonal to the planes of BPP34C10. Included benzene solvent molecules and disordered PF_{6}^{-} counterions are located in the interstices between the polymeric layers. Neither of these species play any significant role in determining the pseudopolyrotaxane sheet superstructure.

The solid-state superstructures discussed here illustrate two powerful concepts which can be utilized for the logical synthesis of interwoven systems in the crystalline phase. Firstly, the ditopic crown ether BPP34C10, possibly with assistance from attendant anions, may be used as a scaffold that orients functional groups--in this case, carboxyl groups--in space to form multiply encircled supermolecules and interwoven supramolecular arrays, that is, the macroring enforces supramolecular preorganization of the benzoic or isophthalic acid units for noncovalent association. Indeed, the $[{BPP34C10 \cdot (3-H)_2}^{2+}]_2$ and $[{BPP34C10 (4-H)_2}^{2+}]_n$ superstructures have analogies in the covalent kingdom, where molecular preorganization^[20] dictates the spatial orientation of benzoate or isophthalate subunits leading to a particular superstructure. Molecular dicarboxylic acids with codirectionally oriented carboxyl groups located within the same covalent skeleton^[21], like the supramolecular dicarboxylic acid [BPP34C10 (3-H)2]2+, form dimeric supermolecules in the solid state. Similarly, molecular bisisophthalic acids, in which two isophthalic acid moieties are located at the extremities of a covalent framework, have crystal structures that



Figure 3. View of the interwoven supramolecular cross-linked polymer generated by the noncovalent polymerization of $[BPP34C10 \cdot (4-H)_2]^{2+}$; top: ball-and-stick representation, bottom: space-filling representation; red: BPP34C10, green: carboxyl groups of 4-H⁺ (remainder in blue).

exhibit, $[^{7a, 22}]$ like the corresponding supramolecular bisisophthalic acid [BPP34C10·(4-H)₂]²⁺, the formation of supramolecular cross-linked polymers.

Secondly, the system described here illustrates the concurrent operation of two distinct hydrogen-bonding algorithms—namely, the self-recognition of the secondary dialkylammonium ions' carboxyl groups and the interaction of these cation's NH_2^+ centers with the polyether linkages of BPP34C10—for generating novel supramolecular aggregates and arrays. As both of these algorithms operate independently of one another, there is no crossover between the hydrogen-bonding motifs, that is, noncovalent association is observed only between the carboxyl groups of the dialkylammonium cations as well as between the cations'

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 NH_2^+ centers and the crown ethers' polyether arcs. Research is currently underway to test whether the paradigms presented here can be utilized in other supramolecular systems, in which the ditopic crown ether BPP34C10 could be used as a scaffold to direct other functional groups in space, thereby permitting the solid-state synthesis of novel multiply encircled and interwoven supramolecular architectures utilizing combinations of different recognition motifs.^[23]

Experimental Section

3-H·PF₆: Aminoester 1 (1.03 g, 4.0 mmol) was boiled with 12 N HCl (40 mL) for 19 h. Upon cooling, the residual white solid was collected and washed with EtOH (25 mL), CHCl₃ (25 mL), and Et₂O (25 mL). The solid was taken up in boiling H₂O (300 mL) and treated with a solution of NH₄PF₆ (0.86 g, 5.3 mmol) in H₂O (8 mL). The cooled solution was extracted with MeNO₂ (3 × 200 mL). The combined MeNO₂ fractions were washed with H₂O (200 mL) and dried under reduced pressure to give 3-H·PF₆ as a white solid (0.97 g, 62%): m.p. =176-179 °C; ¹H NMR (300 MHz, CD₃CN, 20 °C): δ = 4.25 (s, 2H), 4.29 (s, 2H), 7.46 (s, 5H), 7.57 (d, J = 8 Hz, 2H), 8.06 (d, J = 8 Hz, 2H); ¹³C NMR (75.5 MHz, CD₃CN, 20 °C): δ = 51.9, 52.8, 128.9, 130.2, 130.9, 131.25, 131.28, 131.32, 132.0, 136.6, 168.5. Elemental analysis calcd for C_{1.5}H₁₆F₆NO₂P: C 46.52, H 4.16, N 3.62; found: C 46.41, H 4.16, N 3.53; MS (LSI): m/z = 242 [M - PF₆]⁺.

4-H·PF₆: This salt was obtained as a white solid in 61 % yield from the aminodiester **2** by an procedure analogous to the one described above: m.p. =194–195 °C (decomp.); ¹H NMR (300 MHz, CD₃CN, 20 °C): δ = 4.25 (s, 2H), 4.38 (s, 2H), 7.46 (s, 5H), 8.35 (s, 2H), 8.58 (s, 1H); ¹³C NMR (75.5 MHz, CD₃CN, 20 °C): δ = 51.4, 52.5, 130.0, 130.5, 130.7, 131.0, 131.8, 132.2, 132.4, 136.7, 166.3. Elemental analysis calcdfor C₁₆H₁₆F₆NO₄P: C 44.56, H 3.74, N 3.25; found: C 44.49, H 3.95, N 3.17; MS (LS1): m/z = 286 [M - PF₆]⁺.

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- [14] Crystal data for $[BPP34C10 \cdot (3-H)_2][PF_6]_2$: C58H72N2O14 2PF6 1.5 MeOH \cdot 2H₂O, M_r = 1395.21, triclinic, space group $P\overline{1}$, a = 10.619(1), $b = 17.292(1), c = 22.109(2) \text{ Å}, \alpha = 79.64(1), \beta = 79.54(1), \gamma = 76.94(1)^{\circ}, V = 3848.2(4) \text{ Å}, Z = 2, \rho_{calcd} = 1.204 \text{ g cm}^{-3}, \mu = 1.289 \text{ mm}^{-1}, F(000) = 1.204 \text{ g cm}^{-3}, \mu = 1.204 \text{ g cm}^{-3}, \mu = 1.288 \text{ mm}^{-3}, \mu = 1.288 \text{$ 1462. Of 7886 independent reflections collected on a Siemens P4/PC RA diffractometer (graphite-monochromated Cu_{K2} radiation, ω scans, $2\theta < 110^{\circ}$) 3168 reflections had $|F_0| > 4\sigma(|F_0|)$ and were considered to be observed. The data were corrected for Lorentz and polarization effects, but not for absorption. The structure was solved by direct methods. Due to the severe shortage of observed data, all aromatic rings and PF_6^- counterions were refined as rigid bodies. Only the latter and the polyether chains were refined anisotropically, the remainder of the structure remained isotropic. Hydrogen atoms on the [3] pseudorotaxane complex were assigned idealized positions with U(H) = 1.2 $U_{eq}(C)$, while those of the MeOH and H₂O solvent molecules could not be located. Full-matrix least-squares refinement on F^2 gave $R_1 = 0.1567$ and $wR_2 = 0.4087$ for 795 refined parameters. Crystal data for [BPP34C10·(4-H)₂][PF₆]₂: $C_{60}H_{68}N_2O_{18} \cdot 2PF_6 \cdot C_6H_6$, $M_r = 1473.21$, monoclinic, space group $P2_1/c$, a = 12.513(1), b = 16.555(1), c = 18.592(1) Å, $\beta = 96.10(1)^c$, V = 3829.7(5) Å³, Z = 2 (the [3]pseudorotaxane supermolecule has C_i symmetry), $\rho_{calcd} = 1.278 \text{ g cm}^{-3}$, $\mu = 1.334 \text{ mm}^{-1}$, F(000) = 1532. Of 5661 independent reflections collected on a Siemens P4/RA diffractometer (graphitemonochromated Cu_{Ka} radiation, ω scans, $2\theta < 120^{\circ}$), 3507 reflections had $|F_0| > 4\sigma(|F_0|)$ and were considered to be observed. The data were corrected for Lorentz and polarization effects, but not for absorption. The structure was solved by direct methods, and all non-hydrogen atoms, with the exception of the partial occupancy C₆H₆ molecules, were refined anisotropically using fullmatrix least squares based on F^2 . Disorder was observed in the PF_6^- anions, part of the crown ether macrocycle, and the terminal N-benzyl group. In each case, this was resolved by refining two half-occupied orientations. Hydrogen atoms were assigned idealized positions with $U(H) = 1.2 U_{ee}(C)$ and allowed to ride on their parent atoms. $R_1 = 0.1101$ and $wR_2 = 0.3232$ for 607 refined parameters. Computations for both of the structures were carried out on a SGI station with the SHELXTL package, version 5.03. The crystallographic data (excluding structure factors) for both of the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100088 Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: Int. code +(1223)336-033; e-mail: deposit@chemcrys.cam.ac.uk).
- [15] Formation of pseudorotaxane-like inclusion complexes between BPP34C10 and the secondary dialkylammonium cations was indicated in solution and "gas" phases from ¹HNMR and liquid secondary ion mass spectroscopies (LSIMS, obtained from a VG Zabspec mass spectrometer equipped with a cesium ion source and utilizing a m-nitrobenzyl alcohol matrix), respectively. The ¹H NMR spectrum (300 MHz, CD₂Cl₂/MeCN 2/1, 20 °C) of a solution of BPP34C10 and 3-H PF₆ (1:2) shows reasonable ($\Delta \delta \ge 0.05$) chemical shift changes of $\Delta \delta = -0.10, -0.15, -0.08$, and -0.06 for the signals of the *o*-carboxy, m-carboxy, connected 4-carboxybenzyl, and benzylic protons, respectively, on the 3-H⁺ cation; a $\Delta\delta$ of -0.08 was observed for the resonance corresponding to the γ/δ -protons on the BPP34C10 macroring. Reasonable changes in the δ value (≥ 0.05) were also seen in the ¹H NMR spectrum (300 MHz, CD₂Cl₂/MeCN 2/1, 20 °C) of a 1:2 mixture of BPP34C10 and 4-H·PF₆. Relatively large shifts were uncovered for the proton resonances associated with the isophthalic acid portion of the secondary dialkylammonium cation: $\Delta\delta$ values of -0.09 and -0.20 were observed for the resonances of the proton at the 4-position and the equivalent protons at the 2,6-positions of this subunit, while the neighboring 3,5-dicarboxybenzyl protons were also

shifted to higher field by -0.10. The resonances for the hydroquinone ring protons and the α -protons of the macrocyclic polyether are at $\Delta \delta = -0.11$ and -0.05, respectively. The LSIMS of a 1:2 solution of BPP34C10 and 3-H PF₆ displayed a peak at m/z = 1165, which corresponds to a [BPP34C10 and 3-H PF₆ (1·2) exhibited a peak at m/z = 1254, which can be attributed to [BPP34C10·(4-H)₂][PF₆]₂ with loss of one counterion.

- [16] Following this discovery, we reexamined the crystal structure [9b,9c] of the 2:2 complex formed between α,α'-bis(benzylammonium)-p-xylene bis(hexafluorophosphate) and BPP34C10. There we found that one of the principal F-P-F axes of a PF₀⁻ anion was directed into the complex's central cleft between two NH[±]₂ cationic centers. The contact distances from the hydrogen atoms of the 2:2 complex to either of these "axial" fluorine atoms are all greater than 2.8 Å. Nevertheless, a contact of about 2.5 Å was identified between one of the complex's benzylic hydrogen atoms and one of the "equatorial" fluorine atoms of PF₀⁻.
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- [23] While this article was in press, we became aware of the research of Whang and Kim (D. Whang, K. Kim, J. Am. Chem. Soc. 1997, 119, 451-452), who have combined hydrogen bonding and dative bonding interactions to generate interwoven supramolecular arrays.

The Reactivity of the Unbridged Co-Sn Bond in $[(\eta^5-C_5H_5)(\eta^2-C_2H_4)Co-Sn\{CH[Si(CH_3)_3]_2\}_2]$ — The First Organometallic Complexes with direct Co-Sn-Chalcogen Bonding (Chalcogen = Se, Te)**

Jörg J. Schneider,* Jörg Hagen, Dieter Bläser, Roland Boese, and Carl Krüger

Dedicated to Professor Günter Schmid on the occasion of his 60th birthday

Unbridged metal-metal bonds offer ideal prerequisites for the linkage of novel metal-element bonds by insertion or addition reactions. Metal-metal bonds in heterodimetallic complexes are particularly promising, since these bonds can be strongly polarized by the appropriate combination of metals and thus exhibit a high reactivity.^[1] Our interest in this area has focused on heterodinuclear organometallic complexes containing a reactive M-M' bond (M = transition metal; M' = metal from group 12, 13, or 14), particularly those with an unbridged M-Sn bond. These can form low molecular weight complexes with direct Sn-chalcogen-M bonds either by insertion or addition. It is our aim to use such compounds as precursors for the depo-

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sition of ternary magnetically doped group 14/16 semiconductors, which show very promising potential for magnetooptical applications.^[2] To date examples are known for the deposition of binary metal chalcogenide films such as $M'/E^{[3]}$ (M = Fe, Mn; E = S, Se, Te), $M/E^{[4]}$ ((M' = metals from group 12, 13, or 14), and $M''/E^{[5]}$ (M'' = Eu, Sm, Yb) from precursor complexes of the appropriate composition.

The reaction of $[(\eta^5 - C_5 R_5)Co(\eta^2 - C_2 H_4)_2]$ ($\mathbf{R} = \mathbf{H}^{[6]}$ 1a, $\mathbf{R} = \mathbf{M}e^{[7]}$ 1b) with $[:Sn^{II}{CH[Si(CH_3)_3]_2}_2]$ (2)^[8] leads to the formation of brown and black crystals of 3a and 3b, respectively, in up to 60% yield (Scheme 1).



According to IR and NMR spectra the Co/Sn ratio is 1:1, and the ethene ligand is π -bound. The signals of the ethene protons of **3a** and **3b** appear as very broad signals in the ¹H NMR spectrum, which is an indication of a possible temperature dependency of the spectra due to hindered olefin rotation. Surprisingly, however, neither decreasing the measuring temperature to -80 °C nor increasing it to +80 °C resulted in a significant change in the form of the signal present at room temperature. Similar broadening of the ¹H NMR signals of a π -complexed ethene molecule was reported for $[(\eta^5-C_5H_5)(\eta^2-C_2H_4)Co-Sn(C_6H_4CH_2o-NMe_2)_2]$.^[9]

The crystal structure analysis^[10] of **3a** (Figure 1) revealed a very short Co–Sn distance (2.396(1) Å), which is significantly shorter than the sum of the covalent radii of Co and Sn (2.55 Å) and also significantly shorter than that in $[(\eta^5-C_5H_5)(\eta^2-C_2H_4)Co-Sn(C_6H_4CH_2o-NMe_2)_2]$ (2.44 Å),^[9] the (apart from **3a,b**) only known Co–stannylene complex. The Co–Sn bond is also significantly shorter than other M–Sn bonds in similar complexes of the stannylene **2**,^[11] which indicates possible



Figure 1. Crystal structure of **3a**. Selected bond lengths [Å] and angles [°]: D1-Co 1.707, Co-Sn 2.396(1), D2-Co 1.891, Sn-C1 2.206(5), Sn-C2 2.202(7), C1-Si1 1.863(6), Si2-C1 1.876(5), Si3-C2 1.871(5), Si4-C2 1.882(6); C1-Sn-C2 97.4(2), Sn-C1-Si1 112.3(3), Sn-C1-Si2 117.2(2), Sn-C2-Si3 117.1(3), Sn-C2-Si4 110.7(2). Sn-Co-D1 129.0, Sn-Co-D2 98.2; D1 and D2 are the centers of the cyclopentadienyl ring and the C=C bond in ethene, respectively.

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