Toward a Hexagonal Grid Polymer: Synthesis, Coupling, and Chemically Reversible Surface-Pinning of the Star Connectors, 1,3,5-$C_6H_3(CB_{10}H_{10}CX)_3$

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Abstract: A synthetic approach to a two-dimensional grid polymer is proposed and the execution of initial steps is described. Pd-catalyzed coupling of (1,12-dicarba-*closo*-dodecaboran-1-yl)copper (**10**) with iodobenzene, *m*-diiodobenzene, and 1,3,5-triiodobenzene yielded the known 1,12-dicarba-*closo*-dodecaboran-1-ylbenzene (**3**) and the new *m*-bis(1,12-dicarba-*closo*-dodecaboran-1-yl)benzene (**4**) and 1,3,5-tris(1,12-dicarba-*closo*-dodecaboran-1-yl)benzene (**1**), respectively. Each arm of the trigonal connector **1** was provided with one or two sticky tentacles by conversion to 1,3,5-tris[12-((3-(ethylthio)propyl)dimethylsilyl)-1,12-dicarba-*closo*-dodecaboran-1-yl]benzene (**7**) and 1,3,5-tris[12-(bis(3-(ethylthio)propyl)methylsilyl)-1,12-dicarba-*closo*-dodecaboran-1-yl]benzene (**8**). Linear coupling of carboranyl CH terminals through a mercury atom produced very stable dimeric structures from **3** and **4**. The carborane **3**, its mercury-linked dimer **13**, the 1:1 complex of **13** with 2,2′-bipyridyl, and the 2:1 complex of **13** with 2,2′-bipyrimidyl have been structurally characterized by single-crystal X-ray crystallography, but crystals of **1** showed an intriguing disorder and could not be used for molecular structure determination. Grazing incidence IR spectra show that the tentacled species **7** and **8** adsorb firmly on the surface of gold, apparently without a strong preference for a particular orientation. At room temperature, the tritentacled species **7** can be removed readily and the hexatentacled species **8** more slowly by treatment with a THF solution containing fluoride, which severs the tentacles.

Introduction

We are developing a molecular-size construction kit analogous to the children's Tinkertoy[2] play set for use in modular construction.[3−6] Nanotechnology has seen much speculation,[7] and great progress in the experimental design of two- and three-dimensionally networked three-dimensional crystal structures[8,9] and in supramolecular architecture[10] has been reported.

Our long-range plan[5,6] is to use molecular modules for the construction of firmly connected regular two-dimensional grid-shaped polymers with a trigonal, square, or hexagonal lattice, with openings of a controlled size.[11] Subsequently, we hope to attach covalently additional regular grid layers on top of the first, one at a time, to construct ultimately thin layers of materials whose structure is periodic in two wide dimensions and controlled in an aperiodic fashion in the third thin dimension. Desired active groups are to be incorporated into the building elements.

The elementary modules are inert rods and connectors, chosen to permit controlled cross-linking polymerization constrained to two dimensions. The elementary modules are to be combined into "complex monomeric modules", in which they are mounted in a desired orientation on flat molecular pedestals equipped with detachable tentacles carrying functionalities with affinity for a liquid surface. Initially, we use the tentacled bottom deck of a metal sandwich complex as a pedestal and the top deck as

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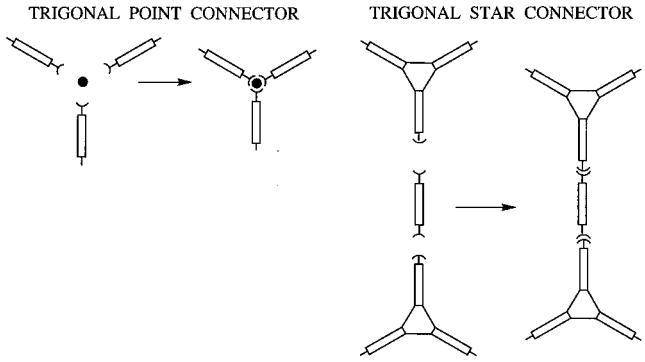

Figure 1. "Point" and "star" connectors (schematic).

a connector. Grid formation is to involve linking of neighboring modules by sturdy bonds under reversible conditions and subsequent annealing. Langmuir−Blodgett techniques offer control over surface concentrations and product transfer to other substrates. Our initial choice of interface is mercury plus either a gas or a solvent phase. Hg surface is readily cleaned, has high affinity for various functional groups, is atomically well defined, and is favorable for electrochemistry and grazing incidence reflection spectroscopy.

The synthesis of a two-dimensional regular grid polymer therefore requires the following: (1) A complex monomeric module built from (i) rods, (ii) a plain connector, and (iii) a tentacled connector. (2) Reagent solutions or vapors for (i) two-dimensional polymerization by coupling of the surface-mounted complex monomeric modules, (ii) annealing into larger single-crystal domains by controlled temporary partial reversal of the coupling process, and (iii) detachment of the tentacles. (3) Analytical techniques for monitoring the concentration and orientation of the complex monomeric modules on a surface and for following their local structural transformations. (4) Analytical techniques for monitoring long-range order in the polymer grid. (5) Techniques for transfer of the grid to other substrates and for its further manipulation.

1. Synthesis. (i) Rods. Many classes of axially end-functionalized straight and relatively rigid rods are now available,[3,5,12−16] permitting the rod length to be controlled to the nearest Å.[17]

(ii) Connectors. Few of the connectors used in crystal engineering[8] are suitable for truly sturdy linear coupling. We envisage two kinds,[6] "point" and "star" (Figure 1). In star connectors, the coupling bonds emanate from the termini of preattached rigid arms radiating from a common origin, as in 1,3,5-tris(ethynyl)benzene[18] and some organometallic complexes.[4,19] In point connectors, the coupling bonds are geminal at the connector, as in the well-studied[20] complexes of Rh_2^{4+}, to which four [*n*]staffane rods have been attached equatorially[21] and two axially.[22]

We report the details of the synthesis[1] of the trigonal star connector **1**[23] with three acidic hydrogens at the termini of 1,12-dicarba-*closo*-dodecaboran-1-yl (**2**) arms, suitable for oxidative C−C coupling[15,16] similar to the Glaser coupling of terminal acetylenes. It resembles 1,3,5-tris(ethynyl)benzene, but is far more stable. The synthesis yields **3** and **4** as byproducts.

(iii) Tentacled Pedestals and Their Reversible Pinning. We plan to use **1** both as a connector and as a tentacled pedestal. For the latter, we attached one (**5**) or two (**6**) thioether-carrying aliphatic chains through Si atoms at each arm end, equipping the tentacled pedestals **7** and **8** for adhesion to a metal surface, with the benzene ring parallel to the surface if all the tentacles make contact, and in less well-defined orientations if only some do. We used a more easily handled gold substrate instead of mercury, expecting similar adsorption properties for both.

(iv) Complex Module Assembly. We anticipate three principal options. The arms on the upper deck can be identical with the tentacles of the lower deck (e.g., *meso* pyridine termini in a double-decker metalloporphyrin[6b]). The two decks can be distinct, permitting selective introduction of arms and tentacles (e.g., derivatives of cyclobutadienecyclopentadienylcobalt[4]). The decks can be identical, and the arms and tentacles alone distinct. Stepwise assembly of triple-decker metallocenes has been reported[24] and inspired the present work, in which the third option was chosen. This offers access to a two-ply grid by a second coupling reaction after tentacle removal.

2. Two-Dimensional Polymerization. (i) Arm Coupling. Oxidative C−C coupling yields strong bonds but is irreversible. Searching for a reversible linear coupling of the acidic *p*-carboranyl termini on the model systems **3** and **4**, to avoid the uncontrolled cross-linking expected for **1**, we tried linking through Hg atoms. Coupling of *p*-carborane carbons through mercury[25] is sturdy and resembles the long-known[26] and recently much exploited[27] mercury coupling of *o*-carboranes.

(ii) Annealing. For annealing, the coupling, irreversible under conditions of intended grid use, must be performed reversibly. We have looked for conditions that sever the C−Hg−C link.

(iii) Tentacle Detachment. The removal of the pinned tentacles was tested by treatment with the fluoride anion.[28] Without thioether groups, the connectors should desorb from the surface.

3. Analytical Techniques for Local Structure. Grazing-incidence IR, with which we have had encouraging experience,[29] detects the B−H stretch of **1** easily, but the IR signature of the

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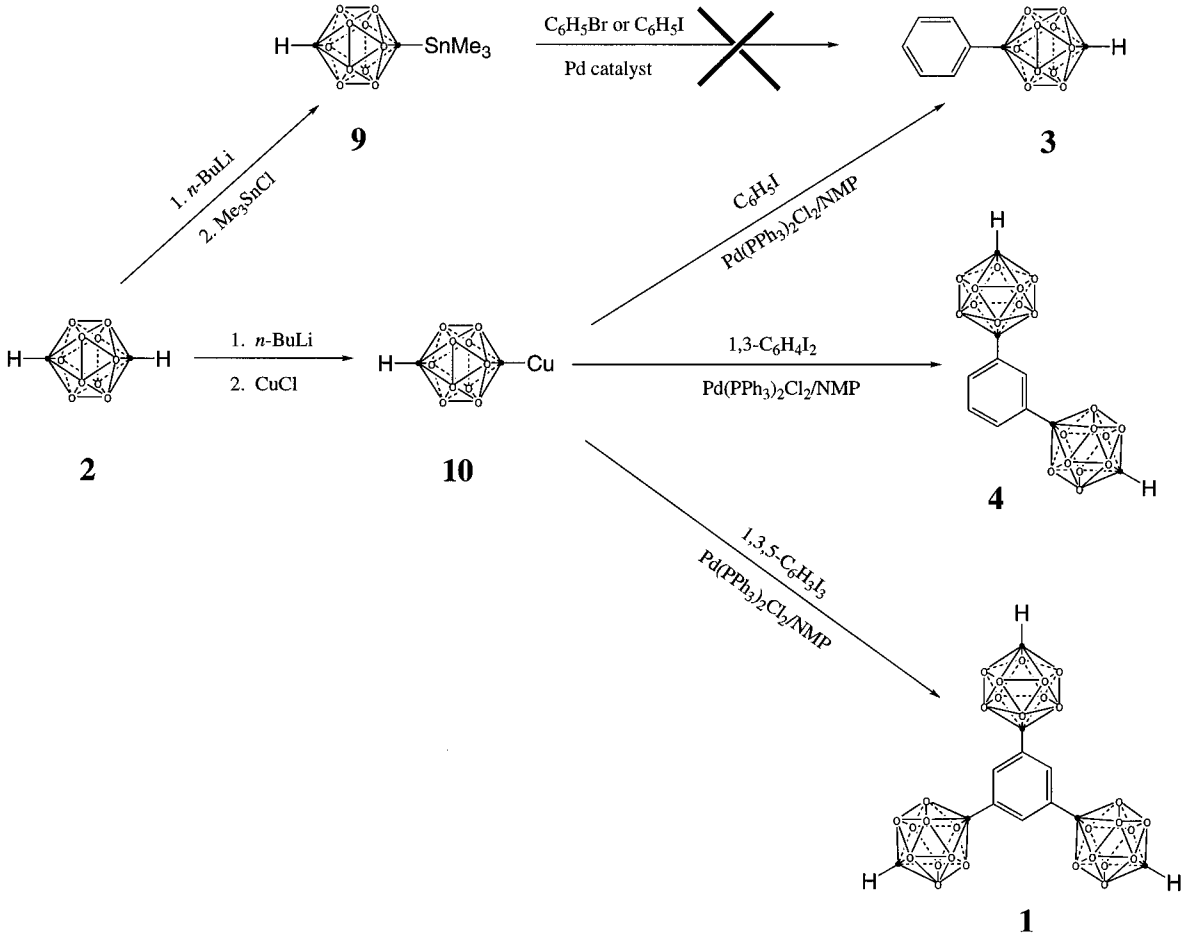
Scheme 1



carborane−Hg−carborane link is indistinct and useless for monitoring the progress of the coupling reaction. Hoping to find a spectroscopic marker for these links, we have investigated the formation of their complexes with 2,2′-bipyridyl and 2,2′-bipyrimidyl and have characterized two of them structurally.

Requirements 4 and 5 are not addressed presently. Since issue 1(i) is largely settled, we address issues 1(ii), 1(iii), 2(i), 2(iii), and 3.

Results and Discussion

Connector Synthesis. A palladium-catalyzed cross-coupling[30] of three 1,12-dicarba-*closo*-dodecaborane (**2**) units to a 1,3,5-trihalobenzene (Scheme 1) offered the simplest route. The initial reagent choice,[31] l-(trimethylstannyl)-1,12-dicarba-*closo*-dodecaborane (**9**),[32] failed to react with aryl bromides and iodides, despite variation of the solvent (THF, DMF, *N*-methylpyrrolidinone), temperature, and catalyst [$Pd(CH_2Ph)Cl(PPh_3)_2$, $Pd(PPh_3)_2Cl_2$].

In contrast to the reported[33] preparation of 1-aryl-1,12-dicarba-*closo*-dodecaboranes by uncatalyzed coupling of (1,-12-dicarba-*closo*-dodecaboran-l-yl)copper (**10**) with iodobenzene, all uncatalyzed coupling reactions of the organocopper compound **10**, obtained by reaction of the *p*-carborane **2** with *n*-BuLi in Et_2O followed by metal exchange with CuCl in THF, gave very low yields at best. The Pd-catalyzed reaction with 1,3,5-tribromobenzene yielded mainly the known[33] (1,12-dicarba-*closo*-dodecaboran-1-yl)benzene (**3**), 1,3-bis(1,12-dicarba-*closo*-dodecaboran-1-yl)benzene (**4**), and only a small amount of the desired 1,3,5-tris(1,12-dicarba-*closo*-dodecaboran-1-yl)benzene (**1**). However, a reaction with 1,3,5-triiodobenzene afforded **1** in 56% yield. The compounds **3** and **4** can be prepared in a similar way by Pd-catalyzed coupling of **10** with iodobenzene (68% yield) and 1,3-diiodobenzene (61% yield), respectively. Coupling reactions of carboranylcopper derivatives with aryl halides were developed concurrently by others.[1,34]

The requisite 1,3,5-triiodobenzene can be prepared in 20% overall yield by the classical multistep procedure from 2,6-diiodo-4-nitroaniline.[35] We find that it can be obtained in 75% yield in a single step from the commercial 1,3,5-tribromobenzene and KI with nickel catalysis, in analogy to the known[36] similar reactions of other aryl bromides.

Connector Structure. We were not able to grow a high-quality single crystal of **1**, and X-ray diffraction data were collected on disordered twinned crystals. The diffraction data are compatible with an arrangement of carborane icosahedra approximately in a cubic closest packed array, with the benzene rings occupying triangular faces of this array. In a two-dimensional layer, each icosahedron is a vertex of six different triangular faces. Only one of these is actually occupied, in a random fashion. The disorder thus is a result of the closeness

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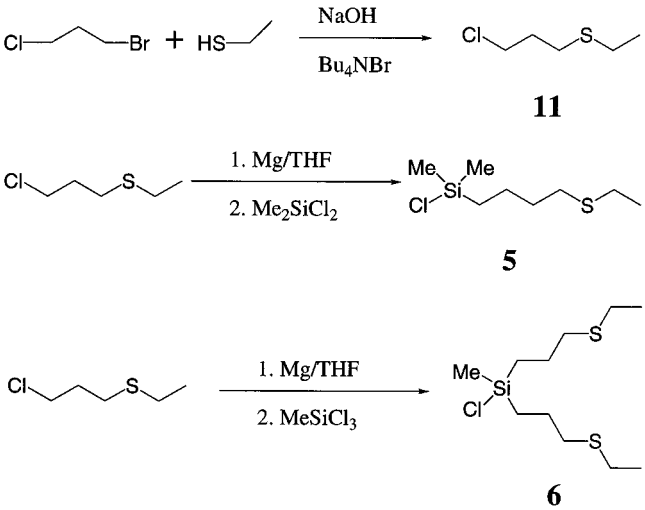
Scheme 2



of the distance between the two carborane icosahedra in **1** to their van der Waals distance. An example of a molecule in one of the possible orientations is shown in Figure 2 of the Supporting Information. It must be emphasized that the *R* factor is very poor (24.6%) and the analysis (Supporting Information), although compatible with the structure **1**, cannot be viewed as an independent structural determination for **1**.

A successful X-ray structure analysis was performed for **3** (Figure 3 of the Supporting Information). For our purposes, the important features are the 1.502 Å C−C bond length between the phenyl substituent and the carborane ring and the 3.101 Å transannular C−C separation in the 12-vertex *p*-carborane cage. Combined with the 1.395 Å distance from the center of the benzene ring to its carbons, this produces a distance of 6.0 Å from the benzene ring center to the outer carbon, and this is our best estimate of the length of the arms of the connector **1**. Their thickness (diameter), obtained from the estimated positions of the hydrogen atoms in **3** and standard van der Waals radii for hydrogen (1.2 Å), amounts to 7.3 Å.

Tentacle Attachment and Removal. The (3-(ethylthio)-propyl)dimethylsilyl and bis(3-(ethylthio)propyl)methylsilyl groups appeared to offer reasonable adhesive groups and sufficient mechanical flexibility. The reaction of sodium ethanethiolate with 1-bromo-3-chloropropane is known to yield 3-(ethylthio)-propyl chloride[37] (**11**), and we have performed it under phase transfer conditions. (3-(Ethylthio)propyl)dimethylsilyl chloride (**5**) was obtained by a subsequent reaction of the Grignard compound derived from **11** with Me_2SiCl_2, and bis(3-(ethylthio)-propyl)methylsilyl chloride (**6**) resulted from a similar reaction of the Grignard compound with $MeSiCl_3$ (Scheme 2).

Reactions of **5** and **6** with the trilithium salt of the trigonal connector **1** yielded the desired tentacled pedestals, 1,3,5-tris-[12-((3-(ethylthio)propyl)dimethylsilyl)-1,12-dicarba-*closo*-dodeca-boran-1-yl]benzene (**7**) and 1,3,5-tris[12-(bis(3-(ethylthio)-propyl)methylsilyl)-1,12-dicarba-*closo*-dodecaboran-1-yl]-benzene (**8**), respectively (Scheme 3). These reactions are slower than the model reaction, the silylation of **4** with *tert*-butyldimethylsilyl chloride to yield **12**, and proceed in only about 25−30% yield. The tentacles are removed with a solution of Bu_4NF in THF.

Connector Arm Linking. In initial tests of linear coupling (Scheme 4), we used **3** and **4**, in which the extent of coupling can be controlled easier than in **1**. Bulk coupling of **3** to yield **13** is accomplished readily by treatment with LDA in THF at −78 °C followed by metal exchange with $HgCl_2$. Although this is a perfectly acceptable synthetic procedure, it does not offer suitable conditions for the two-dimensional coupling that we ultimately need to perform on a metal surface, as this will require a one-step treatment with a homogeneous solution.

We find that the coupling of **3** to the mercury-coupled dimer **13** proceeds in 97% yield (79% isolated yield) upon treatment with *t*-BuOK, a Hg(II) salt, and excess NaBr, in DMF (dimethylformamide), TMU (tetramethylurea), or DMPU ("dimethylpropyleneurea"), but not in *tert*-butyl alcohol or propylene carbonate. These reaction conditions were inspired by a report[38] of mercuration of an *o*-carborane with a Hg(II) salt and excess bromide in a basic aqueous medium. While the less forcing aqueous reaction conditions are sufficient for the more reactive *o*-carborane, they are not adequate for the *p*-carborane derivative **3**, reflecting the generally lower acidity of *p*-carboranes.

In a similar fashion, **4** was converted smoothly into its mercury-coupled dimer **14** in a homogeneous solution of *t*-BuOK, $HgBr_2$, and NaBr in DMF. When the reaction was stopped before all **4** was consumed, the formation of higher oligomers did not interfere significantly, and **14** was formed in 61% yield. After correction for recovered **4**, the yield was 75%. Thus, these reaction conditions are likely to be general for the coupling of *p*-carboranes under homogeneous conditions.

The mercury coupling link is thermally very stable. No decomposition occurs when **13** melts at 266 °C, and little occurs when **14** melts at 354 °C (after cooling it remelts at 330−350 °C).

Under these strongly basic single-step conditions, the coupling reaction appears to be reversible. In DMF, **14** is not affected by a 5 h treatment with an 8-fold excess of 0.02 M NaBr, but about half of it is converted to **4** after a 5-h treatment with a similar excess of 0.02 M *t*-BuOK. Unfortunately, the strongly basic conditions also cause a loss of the silyl substituents from the carborane cages. Thus, *t*-$BuMe_2Si$ protecting groups are stable in DMF and DMPU, but when *t*-BuOK is added, they are removed rapidly. Also, the action of *t*-BuOK in DMF on **7** removes its tentacles. Even though the attack of *t*-BuOK on the silicon atom may be hindered in the adsorbed state, this result makes it unlikely that we shall be able to use these reaction conditions in the surface-confined coupling of complex monomeric modules containing a connector with carborane arms in the upper deck and the tentacled pedestals **7** and **8** in the lower deck, since the tentacles would be lost in the process. It is conceivable that bulkier substituents on the silicon atom would slow down tentacle removal sufficiently for our purposes, but the attachment of such modified tentacles to **1** would then probably be even harder than it is with the present tentacles.

Short of changing the nature of the coupler or the nature of the attachment of the tentacles to the central unit, there seem to be two ways out of the dilemma. First, one could reduce the affinity of the coupling solution for the silicon atom, perhaps by use of a sterically hindered base. Second, one could enhance the reactivity of the carborane center toward mercury by replacing the hydrogen by a suitable leaving group, such as trimethylstannyl in **15**, and by using a strong mercurating agent, such as mercury(II) triflate in propylene carbonate. These possibilities are currently under examination.

Structure of Mercury-Linked Connector Arms. An X-ray structure analysis of **13** revealed a molecule with rotational disorder in the phenyl rings (Figure 4, Table 1). The C−Hg−C angle is approximately linear at 174°. The Hg−C bond distance of 2.075 Å is comparable to that in bis(*p*-carboran-1-yl)-mercury[25] at 2.084 Å, and this makes the separation of benzene

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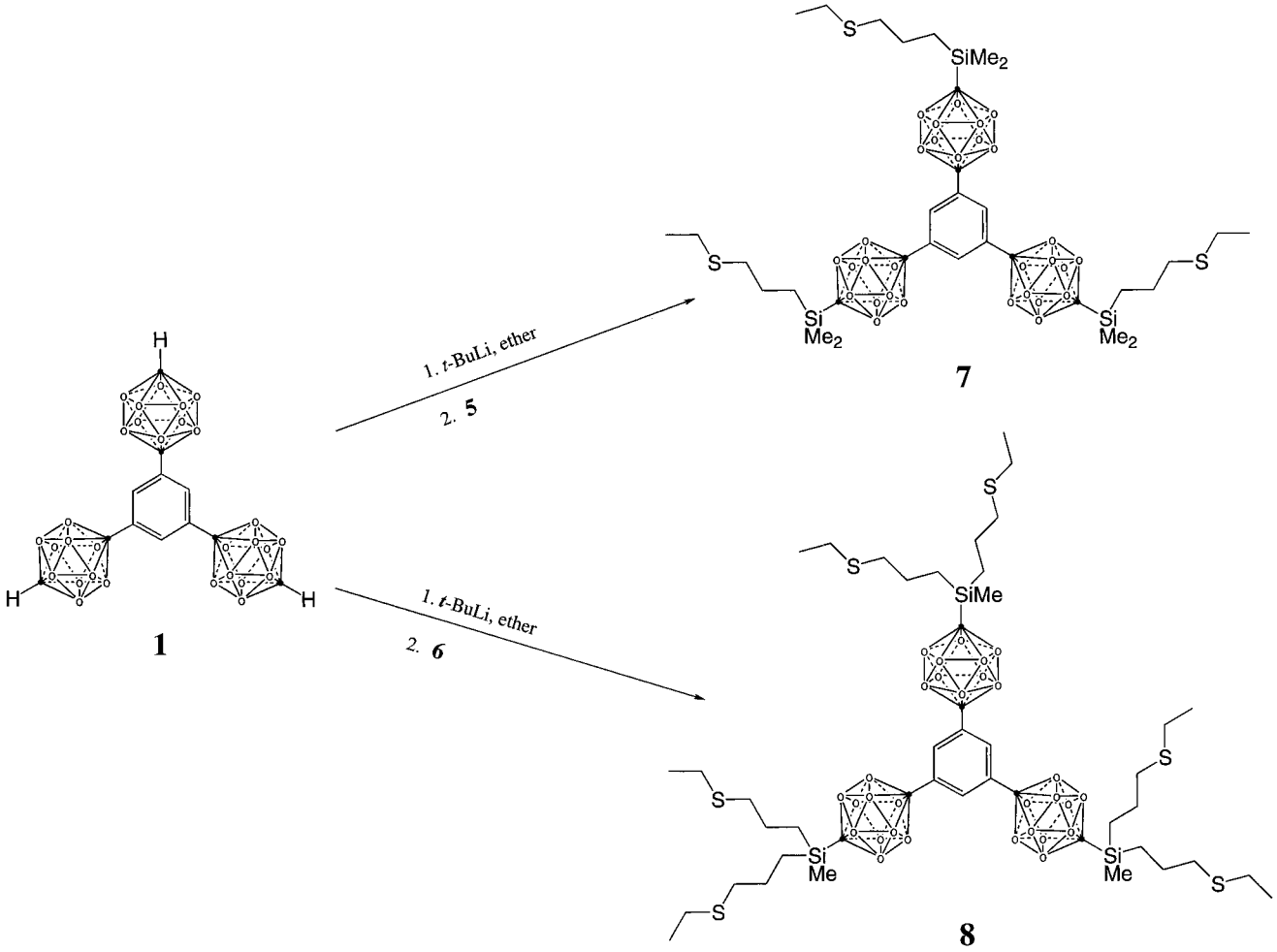
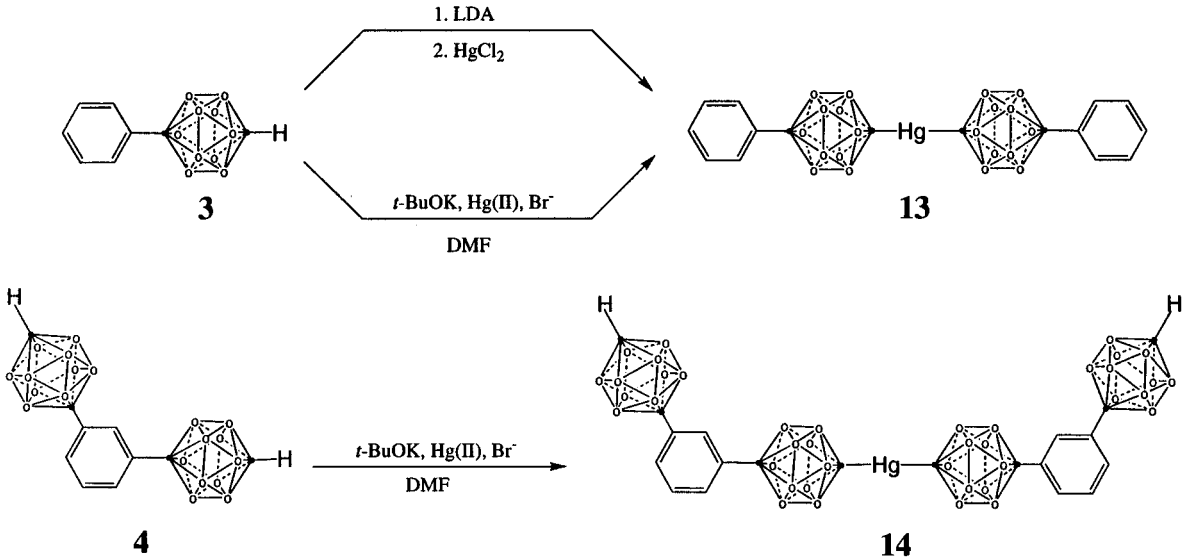
Scheme 3



Scheme 4



centroids in the crystal equal to 16.195 Å. This corresponds to two arms plus a linker and would be the length of the side of the repeated hexagons that we hope to produce ultimately in the surface-controlled coupling reaction. If the sides of the hexagon are linear, the diameter of a circle passing through the benzene centers would be a little over 32 Å. The smallest diameter of the resulting hexagonal opening then would be on the order of 22 ± 2 Å. Since the van der Waals radius of the rod varies along its length and is smallest at the mercury atom in the center, it is difficult to provide an exact value. In realistic situations, the instantaneous value of the diameter will be subject to modulation by vibrations.

In the crystal, the molecules of **13** are packed in crossed pairs, with their central mercury atoms 4.904 Å apart. Chloroform occupies the spaces between the arms of the cross. There is a 3.102 Å contact between the Hg atom of one member of the pair and the hydrogen atoms H(2), and its 2-fold equivalent, that belongs to the other member of the pair. The H(2)−Hg−

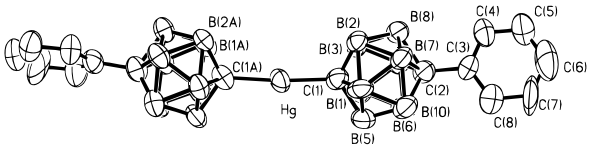


Figure 4. Single-crystal X-ray structure of **13**.

Table 1. Selected Bond Lengths (Å) and Angles (deg) in **13** and Its Complexes

	13	**13**·bipyridyl	2(**13**)·bipyrimidyl	**3**-Hg−Cl·bipyridyl
Hg−C	2.075	2.102	2.098	2.088 (2.383)[a]
Hg−N		2.631	2.696	2.468
C−Hg−C	174	165	168	(151)[b]
N−Hg−N		62.2	60.9	66.3

[a] Hg−Cl bond. [b] C−Hg−Cl angle.

H(2) angle is 86.3°. This crossed arrangement is similar to that described below for the 2,2′-bipyridyl and 2,2′-bipyrimidyl complexes, with the BH hydrogens of one molecule of **13** acting as "ligands" for the other molecule of **13**, except that in the present case, the long axis of each rod is slightly bent with its ends toward its partner, not away from it.

Structure of Complexed Connector Arm Links. In order to permit connector coupling on a metal surface to be followed by grazing-incidence absorption spectroscopy, we examined whether the carborane−Hg−carborane link associates in a structurally well defined way with an intensely absorbing UV and/or IR chromophore with well-characterized transition moment directions, which does not by itself strongly adsorb to mercury in the same geometry. In spite of the less strongly electron-withdrawing character of *p*-carborane, we found that the complexation of **13** with aromatic nitrogen heterocycles resembles that known[39] to occur with bis(*o*-carboranyl)mercury derivatives. Complexes of **13** with 2,2′-bipyridyl and 2,2′-bipyrimidyl form readily upon mixing of the components in solution and crystallize well.

There were two additional reasons for this investigation. It may be useful to find a template for the formation of these very large rings, and complexation to the mercury atoms may provide the requisite means of attachment to the templating species. Also, in future attempts to bind constituents of an additional layer to the polymer grid, heterocycles with two opposed complexing sites, one of them bound to a mercury atom in the bottom layer, may provide the necessary sites for epitaxial attachment of constituents of a top layer. For all three purposes, it would be best if the complexation did not affect the linear geometry of the carborane−Hg−carborane link at all.

The complex with 2,2′-bipyridyl has a 1:1 stoichiometry. There are two crystallographically and chemically distinct molecules in the asymmetric unit (A and B) shown in Figure 5 (Table 1). In form A, both bipyridyl nitrogens are well coordinated to the mercury atom, and in form B, only one of the bipyridyl nitrogens is, while the other is more distant. The Hg−C bond length is similar in both species, with an average value of 2.104 Å. In the fully coordinated form A, one of the Hg−N dative bonds is 2.613(4) Å long and the other 2.656(5) Å. The corresponding values for the "half-coordinated" form B are 2.624(4) and 2.726(6) Å. The presence of the bipyridyl ligand perturbs the geometry of **13** detectably, but not excessively, to give a C−Hg−C bond angle of 165°, with the carborane rod ends tilted slightly away from the bipyridyl. The

(39) Bregadze, V. I.; Okhlobystin, O. Yu. *Dokl. Akad. Nauk SSSR* **1967**, *177*, 347 *Usp. Khim.* **1968**, *37*, 353. Zakharkin, L. I.; Podvisotskaya, L. S. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1968**, *3*, 681.

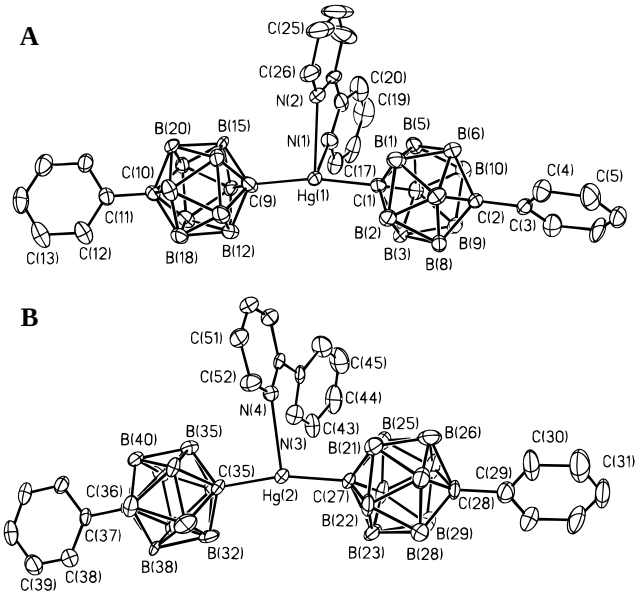


Figure 5. Single-crystal X-ray structure of the 1:1 complex of **13** with 2,2′-bipyridyl: (A) the fully coordinated molecule; (B) the half-coordinated molecule.

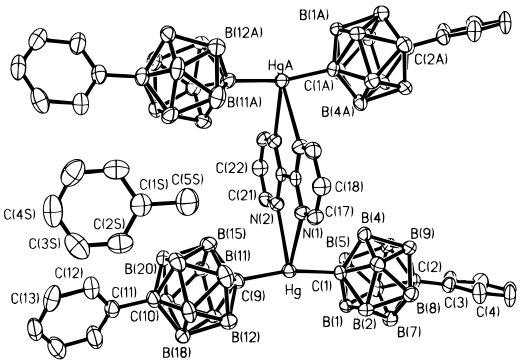


Figure 6. Single-crystal X-ray structure of the 2:1 complex of **13** with 2,2′-bipyrimidyl.

pyridine rings are coplanar in form A and twisted 22° with respect to each other in form B.

2,2′-Bipyrimidyl binds two molecules of **13** to form a centrosymmetric 2:1 complex (Figure 6, Table 1). The two mercury atoms are bound to opposite sides of the bipyrimidyl molecule and lie in the same plane as the four carbon atoms bound to them. This plane is nearly perpendicular (86.6°) to the plane defined by the two pyrimidine rings. The average Hg−C bond length is 2.098 Å, slightly longer than in free **13**. The rest of the structure of **13** is not perturbed. The average Hg−N bond length is 2.696 Å, longer than in the bipyridyl complex. The C−Hg−C bond angle is 168.3°, intermediate between **13** and its bipyridyl complex. We also analyzed a complex of (12-phenyl-1,12-dicarba-*closo*-dodecaboran-1-yl)-mercury chloride (**3-Hg−Cl**) with 2,2′-bipyridyl, presumably formed from an impurity present in initial crude samples of **13** (Table 1 and Supporting Information).

In none of the isolated crystals did we observe a single mercury with more than one nitrogen heterocycle ligand. The limitation may be steric but is more likely electronic in nature, since more electronegative substituents on a divalent mercury generally promote the formation of stronger complexes. The *p*-carborane substituents may withdraw insufficient electron density to favor the binding of more than one ligand. Using the C−Hg−C bond angle and the Hg−N bond lengths as a measure of the strength of the complexes, the complex of

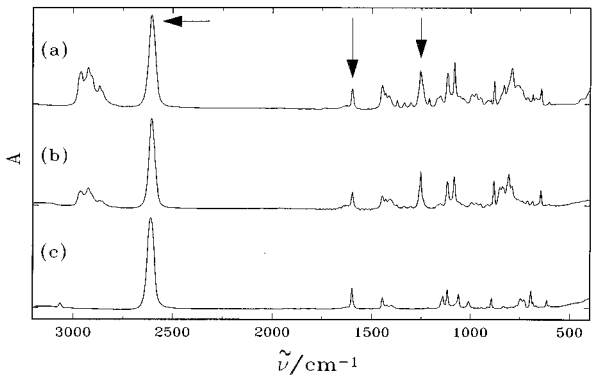


Figure 7. IR absorption spectra of **7** (a), **8** (b), and **1** (c) in KBr pellet.

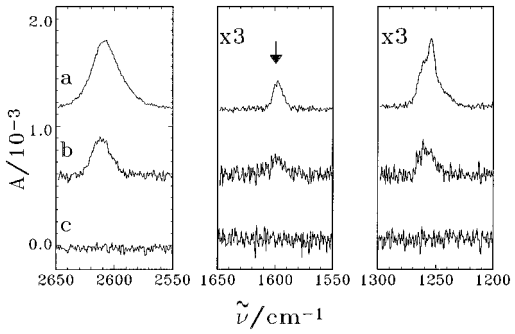


Figure 8. Grazing-incidence IR absorption spectrum of a layer of **7** on a gold surface. The B−H stretching (left), benzene ring deformation (center), and $SiCH_3$ deformation (right) spectral regions are shown. As adsorbed from hexane (a); after 1 h of reflux in hexane (b); and after subsequent treatment with Bu_4NF in THF (c).

phenylcarboranylmercury chloride with 2,2′-bipyridyl would appear to be the strongest and that of **13** with 2,2′-bipyrimidyl the weakest.

The results obtained so far are quite encouraging from all three points of view listed above. The structural modification induced in **13** by complex formation is minor, the structures of the complexes are regular and symmetrical, and binding on the opposite sides of 2,2′-bipyrimidine is possible. The inability of the mercury atom of **13** to bind to two nitrogen heterocycles simultaneously imposes some limitations on the concept of using 2,2′-bipyrimidyl as a pillar between hexagonal grid layers, in that half of the mercury atoms would have to carry such pillars on one side of the grid plane and the other half on the other side.

Infrared Spectra of the Connectors. We have chosen IR spectroscopy for monitoring the adsorption of the tentacled connectors on metal surfaces. The isotropic IR spectra of **1, 7,** and **8** in a KBr pellet are shown in Figure 7. The assignments of the three peaks to be used in the surface studies are based on their positions and on the differences between the spectra of **1, 7,** and **8**. The intense peaks at 1598 and 2609 cm^{-1} are attributed to a benzene ring deformation vibration and an unresolved sum of all the BH stretching vibrations, respectively. Their peak intensity ratio is about 1:5. The intense peak at 1254 cm^{-1} in the spectra of **7** and **8**, absent in the spectrum of **1**, is assigned to the deformation vibration of the $SiMe_2$ or SiMe groups. It is much broader for **7** than for **8**. Its integrated relative intensity is about 2 times higher in **7**, which has twice the number of methyl groups.

Adsorption of the Connectors on a Gold Surface and Their Removal. A thin layer of gold sputtered on glass was immersed in a 10^{-7} M solution of **7** or **8** in hexane for 10 h, rinsed carefully with hexane, and dried. The grazing-incidence IR spectra of the surface (Figure 8a, and Figure 9a of the Supporting Information) contained the characteristic peaks of the connectors, showing the presence of an adsorbed layer: the BH stretching vibration, the in-plane benzene ring vibration, and the deformation vibration of methyl groups on silicon. Subsequent 1 h boiling of the sample in hexane removed about half of the adsorbed molecules of **7**, as judged by the intensity of the BH stretching vibration (Figure 8b), whereas **8** appears not to be removed by this treatment at all (Figure 9b of the Supporting Information).

The ratio of the peak heights of the ring vibration to the BH stretching vibration was 1:7 for **7** (1:6 after boiling in hexane, Figure 8b) and 1:5 for **8** (unchanged after boiling in hexane, Figure 9b of the Supporting Information), and thus was not significantly different from the 1:5 value observed in the isotropic spectrum (Figure 7). Since the ring vibration is polarized in the plane of the benzene ring, while the sum of the BH stretching vibrations is likely to be more isotropic, ratios lower than 1:5 would be expected if the benzene rings of the adsorbed molecules were oriented parallel to the conducting surface.[40] The observed result suggests that the adsorbed layer may be quite disordered. Since we ultimately plan to use a mercury surface, on which surface concentration can be adjusted easily by use of a Langmuir trough, we did not consider it important to optimize the conditions for adsorption on the gold surface and to achieve the proper orientation of the tentacled pedestal.

In the spectra of the adsorbed layers, the methyl deformation peak is doubled. This appears clearly in the spectrum of **7** (Figure 8a) and only vaguely in that of **8**, where this peak has only about half of the relative intensity (Figure 9a of the Supporting Information). The lower-frequency component appears very close to the position it has in the spectrum measured in the KBr pellet, whereas the other component is shifted by about 5 cm^{-1} higher to the vicinity of 1260 cm^{-1}. After the adsorbed layer is treated with boiling hexane, the lower-frequency component is significantly reduced in intensity. The peak shifted to higher frequencies is probably due to methyl groups perturbed by the proximity of the metal surface, and the likely effect of the boiling is to reduce the number of tentacles in the adsorbed layer that are unattached to the surface. Keeping the samples with an adsorbed layer of **7** or **8** in hexane over the weekend or in CH_2Cl_2 for over an hour did not remove the adsorbate. The effect of refluxing in THF or *t*-BuOH was similar to that of refluxing in hexane.

The removal of the tentacles with a solution of fluoride is facile. Treatment of the gold surface with an adsorbed layer of **7** with a 10^{-3} M solution of Bu_4NF in tetrahydrofuran at 40 °C for 20 min removed all of it (Figure 8c). A similar treatment of the adsorbed layer of **8** for 1 h reduced the intensity of the BH stretching peak by 80%, that of the ring vibration down into the noise level, and that of the silicon methyl deformation peak by 25%. At the same time, this last peak lost its doubled character and was shifted to lower frequencies, appearing at about 1250 cm^{-1}. Tentatively, we take these results to mean that most of the tentacles have been severed and 80% of the trigonal connectors removed, but that the bulk of the detached tentacles still adhere to the gold surface, albeit in an orientation different from the one they had while still attached to the connector. After 36 h of treatment with Bu_4NF, none of the IR signals persist and the gold surface is clean (Figure 9c of the Supporting Information). Clearly, the hexatentacled molecule **8** adheres better to the gold surface, but can be removed if desired.

(40) Michl, J.; Thulstrup, E. W. *Spectroscopy with Polarized Light. Solute Alignment by Photoselection, in Liquid Crystals, Polymers, and Membranes*; VCH Publishers: Deerfield Beach, FL 1986.

Table 2. Summary of Crystallographic Parameters

compound number	**1**	**3**	**13**	**13**·bipyridyl	2(**13**)·bipyrimidyl	**3**-Hg−Cl·bipyridyl
empirical formula	$C_{12}H_{36}B_{30}$	$C_8H_{16}B_{10}$	$C_{17}H_{31}B_{20}Cl_3Hg$	$C_{26}H_{38}B_{20}HgN_2$	$C_{23.5}H_{37}B_{20}HgN_2$	$C_{18}H_{23}B_{10}ClHgN_2$
formula mass	504.75	220.30	758.56	795.37	764.34	611.52
crystal system	rhombohedral	orthorhombic	tetragonal	triclinic	orthorhombic	monoclinic
space group	$R\bar{3}$	*Pbca*	$I4_1/a$	$P\bar{1}$	*Pnma*	$P2_1/n$
a, Å	7.11	7.6170(10)	15.162(2)	13.4313(2)	14.7396(3)	7.1620(14)
b, Å	7.11	15.377(2)	15.162(2)	16.4607(2)	27.3694(6)	21.480(4)
c, Å	17.42	22.715(3)	27.256(6)	17.11950(10)	17.5151(3)	15.318(3)
α, deg	90	90	90	89.5360(10)	90	90
β, deg	90	90	90	89.9270(10)	90	99.39(3)
γ, deg	120	90	90	70.8180(10)	90	90
volume, Å^3	762.64	2660.5(6)	6265(2)	3574.67(7)	7065.8(2)	2324.9(8)
Z	1	8	8	4	8	4
ρ_{calcd}, mg m^{-3}	1.099	1.100	1.608	1.478	1.437	1.747
μ, mm^{-1}	0.05	0.047	5.182	4.330	4.378	6.745
trans. coeff.	0.83 and 0.76	0.99 and 0.96	0.39 and 0.27	0.80 and 0.73	0.90 and 0.68	0.48 and 0.24
T (K)	ambient	ambient	178(2)	156(2)	146(2)	178(2)
λ, Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
reflections collected	7657	6782	3701	10227	35815	7212
unique reflections	71, $R_{int} = 0.052$	3067, $R_{int} = 0.0343$	2755, $R_{int} = 0.0680$	10220, $R_{int} = 0.0047$	6369, $R_{int} = 0.0692$	5335, $R_{int} = 0.0535$
reflections observed	71	961 ($F > 6.0\sigma(F)$)	1660 ($I > 2.0\sigma(I)$)	9858 ($I > 2.0\sigma(I)$)	4385 ($I > 2.0\sigma(I)$)	4043 ($I > 2.0\sigma(I)$)
R indices[a] [obsd data]		$R_1 = 0.0599$; wR = 0.0766	$R_1 = 0.0561$; $wR_2 = 0.1221$	$R_1 = 0.0321$; $wR_2 = 0.0837$	$R_1 = 0.0428$; $wR_2 = 0.0653$	$R_1 = 0.0435$; $wR_2 = 0.0994$
R indices[a] (all data)	$R_1 = 0.2459$; $wR_2 = 0.5680$	$R = 0.1652$; wR = 0.1131	$R_1 = 0.1045$; $wR_2 = 0.1423$	$R_1 = 0.0342$; $wR_2 = 0.0932$	$R_1 = 0.0768$; $wR_2 = 0.0797$	$R_1 = 0.0617$; $wR_2 = 0.1068$
weighting coeffs.		$a = 0.0010$[b]	$a = 0.0700$, $b = 0$[c]	$a = 0.0360$, $b = 15.4586$[c]	$a = 0.0074$, $b = 30.3038$[c]	$a = 0.0600$, $b = 0$[c]
goodness-of-fit[d] on F^2		1.71	0.969	1.166	1.136	0.981

[a] $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$; $wR = \{\sum(w|F_o|^2 - |F_c|^2)/\sum[w(F_o)^2]\}^{1/2}$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o2)^2]\}^{1/2}$. [b] $w^{-1} = [\sigma^2(F_o) + aF^2]$. [c] $w^{-1} = [\sigma^2(F_o2) + (aP)^2 + bP]$, $P = (F_o2 + 2F_c2)/3$. [d] Goodness-of-fit $= \{\sum[w(F_o2 - F_c2)^2]/(M - N)\}^{1/2}$, M = number of reflections and N = number of parameters refined.

Conclusions

We have taken several steps toward the ultimate goal, the synthesis of two-dimensional grid polymers: (i) a new type of trigonal connector of the star type has been prepared and characterized, (ii) it has been converted to a tentacled pedestal by attachment of three or six tentacles whose affinity for gold is sufficient for firm pinning to an Au surface, (iii) chemical removal of the pedestal from the surface has been shown to be facile under conditions that sever the arms, (iv) two sets of homogeneous single-step reaction conditions suitable for symmetric linear coupling of its arms have been found, one of them apparently reversible, and (v) complexation of the links with IR and UV spectroscopic markers has been demonstrated and structurally characterized.

Three major and several minor steps remain before the crucial concept, regular grid formation by two-dimensional cross-linking polymerization, can be tested for connector **1**. The major steps are (i) to find a compatible choice of coupling conditions and tentacle attachment mode, (ii) to show that the reversible pinning works on mercury and orients the tentacled pedestal properly, and if not, to modify the adhesive functionalities in the tentacles until it does, and (iii) to join the connector and the tentacled pedestal into an asymmetric metal sandwich complex.

Experimental Section

All reactions were carried out under nitrogen atmosphere with dry solvent, freshly distilled under anhydrous conditions unless otherwise noted. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials, unless otherwise stated. Melting points were determined on a Boëtius micro heating stage with PHMK 05 viewing device. ^{1}H NMR spectra (299.949 MHz) and ^{11}B NMR spectra were measured on a Varian VXR-300 S spectrometer and referenced to external TMS and $(MeO)_3B$, respectively. IR spectra were recorded on a Nicolet 800 FT-IR Spectrometer. Flat gold surface for adsorption studies was prepared by sputtering gold on a microscope slide until it was opaque and was used immediately. Before use, the glass surface was cleaned with a detergent and absolute alcohol and sputter-etched with argon ions. The solvents were dried by distillation over sodium metal. Grazing-incidence spectra used a Harrick RGA single-reflection grazing-incidence attachment. GC MS spectra were measured on an HP GC/MS 5988A instrument with a fused silica capillary column (cross linked 5% phenyl methyl silicone). MS spectra were measured on a VG 7070 EQ-HF Hybrid Tandem Mass spectrometer in EI$^+$ mode. 1,12-Dicarba-*closo*-dodecaborane was purchased from Katchem, Prague, Czech Republic. Elemental analyses were performed by Desert Analytics, Tucson, AZ, and Microanalytical Laboratory, University of California, Berkeley, CA. Details of X-ray structure determinations are provided in the Supporting Information and a summary is available in Table 2.

1,3,5-Triiodobenzene. 1,3,5-Tribromobenzene (2.20 g, 7.0 mmol), KI (7.00 g, 42 mmol), Ni powder (4.00 g), I_2 (10.20 g), and DMF (25 mL) were charged into a 100 mL round-bottomed Schlenk flask. The flask was evacuated on the vacuum line at 0 °C for 15 min. The mixture was refluxed under N_2 at 185−190 °C for 3 h. After cooling, the solution was poured into a 500 mL separation funnel. The flask was washed with 3% aqueous HCl (100 mL) and CH_2Cl_2 (100 mL) until all material, except for Ni powder, was transferred into the separation funnel. The CH_2Cl_2 layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 20 mL). The combined CH_2Cl_2 phase was washed with distilled water (3 × 50 mL) and dried over $MgSO_4$. The solvent was evaporated, leaving a light-brown crude product (2.8 g). This was further purified by sublimation at 60 °C overnight to remove most $C_6H_3I_2Br$ (ca. 6%) and other impurities (ca. 6%). The residue was sublimed at 120 to 140 °C. Yield, 2.38 g (75%), purity 98% by NMR.

1-(Trimethylstannyl)-1,12-dicarba-*closo*-dodecaborane (9). Further spectral data obtained for this known[32] compound: ^{1}H NMR ($CDCl_3$) δ −0.01 (s, 6 H, CH_3), 0.07 (s, 3 H, CH_3), 1.20−3.20 (br m, 10 H, BH), 2.72 (s, 1 H, CH); ^{11}B{^{1}H} NMR ($CDCl_3$) δ −13.74; IR (KBr) 2928 (w), 2603 (s), 1399(s), 1093 (s), 767 cm^{-1}.

1,3,5-Tris(1,12-dicarba-*closo*-dodecaboran-1-yl)benzene (1). 1,12-Dicarba-*closo*-dodecaborane (**2**,[41] 808 mg, 5.6 mmol) and CuCl (554 mg, 5.6 mmol) were charged into a 250 mL three-neck round-bottomed flask and into a tip tube attached to the flask, respectively. After the

(41) Papetti, S.; Obenland, C.; Heying, T. L. *Ind. Eng. Chem. Prod. Res. Dev.* **1966**, *5*, 334. Our material was purchased from Katchem, Ltd., El. Krásnohorské 6, 11000 Praha 1, Czech Republic.

(42) *International Tables for Crystallography*; D. Reidel Publishing Co.: Boston, 1991, Vol. C.

flask was evacuated, THF (50 mL) was added under nitrogen. *n*-BuLi (3.5 mL, 1.6 M in hexane, 5.6 mmol) was added at −30 °C. After 2 h of stirring at room temperature, the CuCl was added from the tip tube to the solution at −30 °C and the reaction was allowed to proceed for 1 h at room temperature (rt) and then for 2 h at reflux. The solvent was removed under reduced pressure. A clean tip tube was charged with 1,3,5-triiodobenzene (640 mg, 1.4 mmol) and attached to the flask. After evacuation, $Pd(PPh_3)_2Cl_2$ in *N*-methylpyrrolidinone (30 mL), made from 100 mg of PPh_3 and 40 mg of $PdC1_2$, was added through a syringe needle under nitrogen atmosphere. 1,3,5-Triiodobenzene was added from the tip tube. The reaction mixture was stirred for 16 h at 100 °C and then poured into H_2O (20 mL) and extracted with toluene (4 × 30 mL). The combined organic phases were washed with brine and dried with $MgSO_4$. After the solvent was removed, product **1** (342 mg, 56%) was obtained by crystallization from a hexane−toluene mixture, leaving mostly *p*-carboranylbenzene **(3)** and 1,3-bis(*p*-carboranyl)benzene **(4)** in the mother liquor: mp > 320 °C; ^{1}H NMR ($CDCl_3$) δ 1.20−3.20 (br m, 30 H, BH), 2.76 (s, 3 H, CH), 6.87 (s, 3 H, aromatic); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 60.09 ($C_{carborane}H$), 84.91 ($C_{carborane}C_{ar}$), 125.83 (C_{ar}), 136.44 ($C_{ar}C_{carborane}$); ^{11}B NMR ($CDCl_3$) δ −13.51 (d, J = 165 Hz, 15 B), −15.89 (d, J = 168 Hz, 15 B); MS *m/z* (rel intensity) 505 (boron cluster center, isotope pattern fits the calculated cluster for M, 100), 355 (10), 248 (50); IR (KBr) 3100 (CH_{Ar}), 3063 (BCH), 2611 (BH), 1599 (C═C), 1447, 1140, 1117, 1059, 1009, 893, 747, 731, 695, 617 cm^{-1}. HRMS calcd 505.5790, found 505.5804. Anal. Calcd for $C_{12}H_{36}B_{30}$: C, 28.56; H, 7.19. Found: C, 28.77; H, 7.01.

(1,12-Dicarba-*closo*-dodecaboran-1-yl)benzene[33] (3). To a solution of 1,12-dicarba-*closo*-dodecaborane[41] (**2**, 1.0 g, 6.9 mmol) in diethyl ether (25 mL) was added *n*-BuLi (1.6 M in hexane, 4.3 mL, 6.9 mmol) at 0 °C. After 1.5 h of stirring at rt, CuCl (0.69 g, 6.9 mmol) and THF (20 mL) were added at −30 °C under nitrogen. The mixture was stirred at room temperature for 1 h and refluxed for 0.5 h. After solvent was removed under reduced pressure, *N*-methylpyrrolidinone (25 mL), iodobenzene (1.59 g, 7.8 mmol), and $Pd(PPh_3)_2Cl_2$ (276 mg, 0.39 mmol) were added. The mixture was stirred at 100 °C for 18 h, poured into water (30 mL), and extracted with diethyl ether (5 × 25 mL). The combined organic phases were washed with water and dried over $MgSO_4$. After the solvent was removed, the product was purified by thick-layer chromatography (silica, hexane) to give a white solid: 1.03 g (68%), mp 99.5−100.5 °C (lit.[33] 99−100 °C); ^{1}H NMR ($CDCl_3$) δ 1.20−3.40 (br m, 10 H, BH), 2.77 (s, 1 H, CH), 7.12−7.24 (m, 5 H, aromatic); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 59.74 ($C_{carborane}H$), 86.37 ($C_{carborane}C_{ar}$), 127.01 (C_{ar}), 128.05 (C_{ar}), 128.31 (C_{ar}), 136.78 ($C_{ar}C_{carborane}$); ^{11}B NMR ($CDCl_3$) δ −13.38 (d, J = 167 Hz), −16.02 (d, J = 168 Hz); MS *m/z* (rel intensity) 220 (boron cluster center, isotope pattern fits the calculated cluster for M, 100), 191 (10), 139 (10), 108 (20); IR (KBr) 3058 (BCH), 2604 (BH), 1583, 1476, 1211, 1147, 1144, 1023, 1007, 831, 583 cm^{-1}; HRMS calcd 222.2183, found 222.2185.

1-Phenyl-12-(trimethylstannyl)-1,12-dicarba-*closo*-dodecaborane (15). Compound **3** (100 mg, 0.454 mmol) was dissolved in THF (20 mL) under Ar and cooled to −78 °C. LDA (0.33 mL, 1.5 M in cyclohexane) was added dropwise, and the solution was allowed to stir for 2 h at −78 °C. Solid Me_3SnCl (120 mg, 0.601 mmol) was added from a tip tube. The mixture was kept at −78 °C for 5 h and allowed to warm slowly to room temperature. The reaction mixture was poured into water (100 mL) and extracted with diethyl ether (3 × 50 mL). After drying the solution over $MgSO_4$ and removing the solvent, the product was purified by column chromatography (silica, hexanes) to yield 126 mg (72%) of a white solid (98% pure by NMR). An analytical sample was produced by gradient sublimation: mp 88−91 °C; ^{1}H NMR ($CDCl_3$) δ 7.17 (m, 5 H, aromatic), 1.0−3.5 (br m, 10 H, BH), 0.11 (s, J_{SnH} = 27 Hz, 9 H, $SnCH_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ −8.49 (CH_3), 64.15 ($C_{carborane}Sn$), 89.15 ($C_{carborane}C_{ar}$), 127.01 (C_{ar}), 127.94 (C_{ar}), 128.05 (C_{ar}), 137.21 ($C_{ar}C_{carborane}$); ^{11}B NMR ($CDCl_3$) δ −11.34 (d, J = 175 Hz), −13.89 (d, J = 170 Hz); MS *m/z* (rel intensity) 383 (boron cluster center, isotope pattern fits the calculated cluster for M, 5), 368 (cluster center, M − CH_3, 100), 338 (cluster center, M − $2CH_3$, 20), 217 (10), 184 (10), 135 (10), 120 (10); IR (KBr) 2924, 2856, 2596, 1459, 1381, 1088, 1023, 777, 691, 539 cm^{-1}. Anal. Calcd for $C_{11}H_{24}B_{10}Sn$: C, 34.48; H, 6.31. Found: C, 34.65; H, 6.40.

***m*-Bis(1,12-dicarba-*closo*-dodecaboran-1-yl)benzene (4).** To a solution of 1,12-dicarba-*closo*-dodecaborane[41] (**2**, 935 mg, 6.49 mmol) in diethyl ether (25 mL) was added *n*-BuLi (1.6 M in hexane, 4.10 mL, 6.56 mmol). After 1.5 h of stirring at room temperature, CuCl (700 mg, 7.08 mmol) and THF (25 mL) were added at −30 °C under N_2. The mixture was stirred at room temperature for 1 h and refluxed for 0.5 h. After the solvent was removed under reduced pressure, *N*-methylpyrrolidinone (20 mL), 1,3-diiodobenzene (1.07 g, 3.24 mmol), and $Pd(PPh_3)_2Cl_2$ (190 mg, 0.27 mmol) were added under N_2. The mixture was stirred at 100 °C for 18 h, poured into water (30 mL), and extracted with methylene chloride (5 × 25 mL). The aqueous layer was saturated with NaCl, and the combined organic phases were washed with H_2O and dried over $MgSO_4$. After the solvent was removed, the product was purified by thick-layer chromatography (silica, hexane) to give a white solid (714 mg, 61%): mp 239−240 °C; ^{1}H NMR ($CDCl_3$) δ 1.20−3.20 (br m, 20 H, BH), 2.76 (s, 2 H, BCH), 6.95−7.06 (m, 4 H, aromatic); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 59.94 ($C_{carborane}H$), 85.67 ($C_{carborane}C_{ar}$), 126.25 (C_{ar}), 126.83 (C_{ar}), 127.77 (C_{ar}), 136.65 ($C_{ar}C_{carborane}$); ^{11}B NMR ($CDCl_3$) δ −13.46 (d, J = 172 Hz), −15.96 (d, J = 175 Hz); MS *m/z* (rel intensity) 362 (boron cluster center, isotope pattern fits the calculated cluster for M, 100), 220 (cluster center, M $-C_2B_{10}H_{11}$, 20), 177 (20), 143 (cluster center, $C_2B_{10}H_{11}$, 40); IR (KBr) 3061 (BCH), 2606 (BH), 1604, 1579, 1418, 1091, 1053, 1008, 828, 742, 733 cm^{-1}; HRMS calcd 366.3896, found 366.3900.

***m*-Bis(12-(*tert*-butyldimethylsilyl)-1,12-dicarba-*closo*-dodecaboran-1-yl)benzene (12).** To a solution of *m*-bis(1,12-dicarba-*closo*-dodecaboran-1-yl)benzene **(4)** (31 mg, 0.08 mmol) in THF (5 mL) was added *t*-BuLi (0.12 mL, 1.7 M in pentane, 0.2 mmol) at −78 °C under N_2. After 2 min, *tert*-butyldimethylsilyl chloride (40 mg, 0.27 mmol) was added (*t*-BuLi deprotonates much faster than *n*-BuLi). The reaction mixture slowly warmed to room temperature. After 16 h of stirring, it was poured into H_2O (20 mL) and extracted with methylene chloride (3 × 20 mL). After drying the solution with $MgSO_4$, the product was purified by thick-layer chromatography (silica, hexanes) to give 43 mg (85%) of a white solid: mp 255 °C; ^{1}H NMR ($CDCl_3$) δ −0.01 (s, 12 H, $SiCH_3$), 0.88 (s, 18 H, *t*-Bu), 1.20−3.40 (br m, 20 H, BH), 6.95−7.06 (m, 4 H, aromatic); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ −4.39 ($SiCH_3$), 19.18 ($SiC(CH)_3$), 26.88 [$SiC(CH)_3$], 69.43 ($C_{carborane}Si$), 89.74 ($C_{carborane}C_{ar}$), 125.99 (C_{ar}), 126.59 (C_{ar}), 127.62 (C_{ar}), 136.84 ($C_{carborane}C_{ar}$); ^{11}B NMR ($CDCl_3$) δ −12.16 (d, J = 164 Hz, 10 B), −13.53 (d, J = 166 Hz, 10 B); MS *m/z* (rel intensity) 591 (boron cluster center, isotope pattern fits the calculated cluster for M, 5) 535 (cluster center, M − C_4H_9, 20), 277 (cluster center, M − $C_8H_{25}B_{10}Si$, 100); IR (KBr) 2958, 2933 (CH), 2610 (BH), 1254, 1099, 874, 819, 794, 637 cm^{-1}. Anal. Calcd for $C_{22}H_{54}B_{20}Si_2$: C, 44.71; H, 9.21. Found: C, 44.79; H, 9.25.

(3-(Ethylthio)propyl)dimethylsilyl Chloride (5). To a mixture of 1-bromo-3-chloropropane (126 g, 0.80 mol), 50% aqueous NaOH (40 g, 0.50 mol), and Bu_4NBr (483 mg, 1.5 mmol) was slowly dropped ethanethiol (24.8 g, 0.40 mol) under vigorous stirring at 0 °C. After 2 h stirring at room temperature, the organic layer was separated, washed twice with water (50 mL), dried over Na_2SO_4, and fractionally distilled. After a fraction of 1-bromo-3-chloropropane (35−60 °C/15 Torr), 36.7 g (264 mmol, 66%) of 3-(ethylthio)propyl chloride **(11)** (65−75 °C/15 Torr, lit.[37] 71.5 °C/15 Torr) was collected as a pale yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.24 (t, J = 7.3 Hz, 3 H, CH_3), 2.01 (m, 2 H, CH_2), 2.52 (q, J = 7.4 Hz, 2 H, SCH_2), 2.65 (t, J = 7.0 Hz, 2 H, SCH_2), 3.63 (t, J = 6.4 Hz, 2 H, $ClCH_2$). 3-(Ethylthio)propyl chloride (**11**, 7.00 g, 50 mmol) was dropped slowly to Mg turnings (1.22 g, 50 mmol) activated with 2 drops of Br_2 in Et_2O (70 mL). After 12 h of reflux, the Grignard reagent was added to Me_2SiCl_2 (25.8 g, 200 mmol) in diethyl ether (100 mL). After 18 h of refluxing under mechanical stirring, the Mg salts were filtered, and washed with Et_2O (2 × 25 mL), and the solvent was evaporated from the combined filtrates. The residue was fractionally distilled to yield **5** (45 °C/0.01 Torr, 4.20 g, 42%): ^{1}H NMR ($CDCl_3$) δ 0.41 (s, 6 H, $SiCH_3$), 0.91−0.95 (m, 2 H, $SiCH_2$), 1.24 (t, J = 3 Hz, 3 H, CH_3), 1.64−1.74 (m, 2 H, CH_2), 2.49−2.58 (m, 4 H, CH_2SCH_2); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 1.87 ($SiCH_3$), 15.07 ($SiCH_2$), 18.58 (CH_3), 23.50 (CH_2), 26.00 (SCH_2CH_2), 34.85 (CH_3CH_2S); MS *m/z* (rel intensity) 196 (M, 14), 181 (M − CH_3, 20), 93 (M − $C_5H_{11}S$, 100), 75 (C_3H_7S, 49); IR (neat) 2944 (CH), 1254 (SiMe), 1057 (br), 801, 473. Anal. Calcd for $C_7H_{17}ClSSi$: C, 42.72; H, 8.71. Found: C, 43.02; H, 8.91.

1,3,5-Tris[12-((3-(ethylthio)propyl)dimethylsilyl)-1,12-dicarba-*closo*-dodecaboran-1-yl]benzene (7). A solution of 1,3,5-tris(1,12-

dicarba-*closo*-dodecaboran-1-yl)benzene (**1**, 100 mg, 0.2 mmol) in ether (40 mL) was cooled to −40 °C. *tert*-Butyllithium (1.7 M in pentanes, 0.2 mL) was added over 5 min, and the solution was stirred for 1.5 h while the temperature rose to about −5 °C. It was cooled again to −25 °C, and **5** (67 mg, 0.34 mmol) was added. The solution was stirred at −25 °C for 15 min and then heated under reflux for 20 h. The sequence of cooling, adding *tert*-butyllithium and **5**, and refluxing was repeated four times. The reaction mixture was then poured into sulfuric acid (50 mL, 5 M). The organic layer was separated, and the acid layer was extracted twice with ether (2 × 25 mL). The combined ether fractions were washed with potassium carbonate solution (10%, 2 × 50 mL) and dried over sodium sulfate. The solvent was removed, giving a clear oil, which was chromatographed on silica gel (60−200 mesh, 30 × 1.2 cm) with benzene−hexane (20:80). The product **7** was separated from a siloxane impurity by preparative TLC. Methanol removed the siloxane and left **7** at the start, and extraction with dichloromethane gave 54 mg (28%) of a white crystalline solid of approximately 98% purity. Analytically pure material was obtained by column chromatography on silica gel (60−200 mesh, hexane−dichloromethane 1:1): mp 92 °C; ^{1}H NMR ($CDCl_3$) δ −0.03 (s, 18 H, CH_3), 0.56 (m, 6 H, $SiCH_2$), 1.23 (t, J = 7.3 Hz, 9 H, CH_3), 1.46 (m, 6 H, CH_2), 2.48 (m, 12 H, CH_2SCH_2), 1.20−3.20 (br m, 30 H, BH), 6.82 (s, 3 H, aromatic); ^{13}C{^{1}H} NMR ($CDCl_3$) δ −3.00 ($SiCH_3$), 14.58 ($SiCH_2$), 14.79 (CH_3), 23.89 (CH_2), 25.87 (SCH_2CH_2), 35.01 (CH_3CH_2S), 69.36 ($C_{carborane}Si$), 87.94 ($C_{carborane}C_{ar}$), 125.62 (C_{ar}), 136.62 ($C_{ar}C_{carborane}$); ^{11}B NMR ($CDCl_3$) δ −12.3 (d, J = 165 Hz, 15 B), −14.1 (d, J = 165 Hz, 15 B); MS *m/z* (rel intensity) 986 (boron cluster center, isotope pattern fits the calculated cluster for M, 5), 971 (cluster center, isotope pattern fits the calculated cluster for M − CH_3, 19), 883 (cluster center, M − $C_5H_{11}S$, 27), 763 (cluster center, M − $C_9H_{22}S_2Si$, 16), 722 (cluster center, M − $C_{12}H_{26}S_2Si$, 18), 161 ($C_7H_{17}SSi$, 100); IR (KBr) 3140 (CH_{Ar}), 2963, 2926 (CH), 2866, 2608 (BH), 1598 (C═C), 1448, 1432, 1410, 1254 (SiMe), 1117, 1083, 882, 852, 840, 808, 792, 646 cm^{-1}. Anal. Calcd for $C_{33}H_{84}B_{30}S_3Si_3$: C, 40.21; H, 8.59. Found: C, 40.06; H, 8.67.

Bis(3-(ethylthio)propyl)methylsilyl Chloride (6). Mg turnings (10.4 g, 0.433 mol) were placed in a three-neck 500 mL round-bottomed flask fitted with a pressure equalizing dropping funnel, reflux condenser, and nitrogen inlet. 3-(Ethylthio)propyl chloride (**11**, 41.5 g, 0.3 mol) and THF (250 mL) were charged to the dropping funnel, and several drops of the solution were added to the main flask. The reaction was initiated with a few crystals of iodine and gentle heating. The chloride solution was added slowly over 2 h resulting in a gray solution of the Grignard reagent. Trichloromethylsilane (22.4 g, 0.15 mol) was then added to the Grignard reagent, and the mixture was heated under reflux for 16 h. Mg salts were filtered and washed with THF (3 × 100 mL). The organic fractions were combined, and the solvent was removed under reduced pressure to give a light-brown oil. The product was fractionally distilled at reduced pressure (65 °C/0.1 Torr, 18.8 g, 44%) to afford **6**: ^{1}H NMR ($CDCl_3$) δ 0.39 (s, 3 H, $SiCH_3$), 0.90−0.96 (m, 4 H, $SiCH_2$), 1.25 (t, J = 6 Hz, 6 H, CH_3), 1.64−1.74 (m, 4 H, CH_2), 2.49−2.58 (m, 8 H, CH_2SCH_2); ^{13}C{^{1}H} NMR ($CDCl_3$) δ −0.29 ($SiCH_3$), 14.63 ($SiCH_2$), 16.70 (CH_3), 22.97 (CH_2), 25.53 (SCH_2CH_2), 34.41 (CH_3CH_2S); MS *m/z* (rel intensity) 284 (M, 2), 249 (M − Cl, 4), 181 (M − $C_5H_{11}S$, 100); IR (neat) 2926 (CH), 1418, 1255 (SiMe), 791, 477 cm^{-1}. Anal. Calcd for $C_{11}H_{25}ClS_2Si$: C, 46.36; H, 8.84. Found: C, 46.37; H, 8.81.

1,3,5-Tris[12-(bis(3-(ethylthio)propyl)methylsilyl)-1,12-dicarba-*closo*-dodecaboran-1-yl]benzene (8). A solution of 1,3,5-tris(1,12-dicarba-*closo*-dodecaboran-1-yl)benzene (**1**, 425 mg, 0.85 mmol) in ether (100 mL) was cooled to −40 °C. *tert*-Butyllithium (1.7 M in pentanes, 0.7 mL) was added over 5 min, and the solution was stirred for 1.5 h, while it warmed to about −5 °C. It was cooled again to −25 °C, **6** (340 mg, 1.2 mmol) was added, the stirring was continued at −25 °C for 15 min, and the solution was then heated under reflux for 20 h. The sequence of cooling, adding *tert*-butyllithium and **6**, and heating under reflux was repeated six times. The reaction mixture was then poured into 5 M sulfuric acid (70 mL). The acidic layer was extracted twice with ether (2 × 50 mL) and added to the organic layer, and the combined ether fractions were washed with potassium carbonate solution (10%, 2 × 50 mL) and dried over sodium sulfate. The solvent was removed to give a clear oil, which was chromatographed (silica gel 60−200 mesh, 40 × 2.5 cm column) with benzene−hexane (1:4, then 1:2, and finally 1:1). The desired product eluted together with a siloxane impurity, from which it was separated by preparative TLC. Methanol left **8** at the start and removed the siloxane. Subsequent elution with dichloromethane gave 262 mg (25%) of a clear viscous oil of about 98% purity. Analytically pure material was obtained by column chromatography on silica gel (60−200 mesh) with hexane−dichloromethane (1:1). For **8**: ^{1}H NMR ($CDCl_3$) δ −0.01 (s, 3 H, $SiCH_3$), 0.59 (m, 4 H, $SiCH_2$), 1.26 (t, J = 7 Hz, 6H, CH_3), 1.5−3.2 (br, 10H, BH), 1.49 (m 4H, $CH_2CH_2CH_2$,), 2.50 (t, J = 7 Hz, 4H, SCH_2CH_2), 2.52 (q, J = 8 Hz, 4H, CH_3CH_2S), 6.83 (s, 1H, aromatic); ^{13}C{^{1}H} NMR ($CDCl_3$) δ −4.63 ($SiCH_3$), 13.26 ($SiCH_2$), 14.74 (CH_3), 23.78 (CH_2), 25.85 (SCH_2CH_2), 35.01 (CH_3CH_2S), 69.01 ($C_{carborane}Si$), 88.24 ($C_{carborane}C_{ar}$), 125.55 (C_{ar}), 136.55 ($C_{ar}C_{carborane}$); IR (KBr) 2962, 2925, 2869 (CH), 2607 (BH), 1598 (BH), 1448, 1256 (SiMe), 1115, 1081, 879, 790, 644 cm^{-1}; MS *m/z* (rel intensity) 1250 (M$^+$, <1%), 1147 (boron cluster center, isotope pattern fits the calculated cluster for the ion [M − $C_5H_{11}S$]$^+$, 100), 1086 (cluster center, [M − $C_7H_{16}S_2$]$^+$, 37), 1026 (cluster center, [M − $C_9H_{21}S_3$]$^+$, 20), 899 (cluster center, 62), 651 (cluster center, 21). Anal. Calcd for $C_{45}H_{108}B_{30}S_6Si_3$: C, 43.23; H, 8.71. Found: C, 43.19; H, 8.68.

Desilylation of 1,3,5-Tris[12-((3-(ethylthio)propyl)dimethylsilyl)-1,12-dicarba-*closo*-dodecaboran-1-yl]benzene (7) with Fluoride Anion. A solution of **7** (1.8 mg, 0.0018 mmol) and tetra-*n*-butylammonium fluoride (21 mg, 0.065 mmol, 12 equiv) in THF (1 mL) was stirred at room temperature for 62 h. THF was evaporated, the residue was extracted with toluene (5 mL), the solvent was evaporated, and the residue was dissolved in $CDCl_3$. ^{1}H NMR spectrum showed only the signals of 1,3,5-tris(1,12-dicarba-*closo*-dodecaboran-1-yl)benzene (**1**) and no signals of **7**.

Desilylation of 1,3,5-Tris[12-(bis(3-(ethylthio)propyl)methylsilyl)-1,12-dicarba-*closo*-dodecaboran-1-yl]benzene (8) with Fluoride Anion. The above procedure was applied to **8** (2.1 mg, 0.0017 mmol), using tetra-*n*-butylammonium fluoride (25 mg, 0.078 mmol, 8 equiv) in THF (1 mL). At the end, the ^{1}H NMR spectrum again showed only the presence of **1** and no **8**.

Stability of *m*-Bis(12-(*tert*-butyldimethylsilyl)-1,12-dicarba-*closo*-dodecaboran-1-yl)benzene (12) toward DMF and *t*-BuOK. Compound **12** (5 mg, 0.0085 mmol) was dissolved in dry DMF and stirred for 1 h at room temperature and then 1 h at 100 °C. No changes were observed by ^{1}H NMR. Then, *t*-BuOK (4 mg, 0.035 mmol, 4 equiv) was added, and the mixture was stirred at room temperature for 1 h. ^{1}H NMR showed complete desilylation of **12**. The reaction mixture was poured into water and extracted with diethyl ether. After the solvent was removed under reduced pressure, the ^{1}H NMR spectrum showed only the signals of **4**.

Stability of 1,3,5-Tris[12-((3-(ethylthio)propyl)dimethylsilyl)-1,12-dicarba-*closo*-dodecaboran-1-yl]benzene (7) toward DMF and *t*-BuOK. **7** (2.5 mg, 0.0026 mmol) was dissolved in DMF-d_6 and heated to 100 °C for 1 h. ^{1}H NMR showed no signs of desilylation. *t*-BuOK (2 mg, 0.018 mmol, 6 equiv) was added, and the NMR tube was shaken vigorously. An ^{1}H NMR spectrum taken immediately thereafter showed no signals of the starting material. The mixture was poured into water and extracted with diethyl ether. After the solvent was removed under reduced pressure, the ^{1}H NMR spectrum in $CDCl_3$ was identical with the spectrum for **1**.

Bis(12-phenyl-1,12-dicarba-*closo*-dodecaboran-1-yl)mercury (13). Two-Step Procedure. To a solution of *p*-carboranylbenzene (**3**) (120 mg, 0.54 mmol) in THF (15 mL) was added lithium diisopropylamide (2 M, 0.4 mL, 0.8 mmol) at −78 °C. After 1 h of stirring, $HgCl_2$ (70 mg, 0.26 mmol) was added and the reaction mixture was slowly warmed to room temperature. After 4 h of stirring, the yellow solution was poured into aqueous NH_4Cl and extracted with Et_2O (3 × 10 mL). The combined organic phases were washed with H_2O (10 mL) and dried with $MgSO_4$. After the solvent was removed under reduced pressure, the beige residue (160 mg) was dissolved in CH_2Cl_2 and purified by chromatography (silica, $CHCl_3$) to give a white solid (120 mg, 72%): mp 239−240 °C; ^{1}H NMR ($CDCl_3$) δ 1.20−3.40 (br m, 20 H, BH), 7.14−7.17 (m, 10 H, phenyl); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 89.1 ($C_{carborane}C_{ar}$), 90.5 ($C_{carborane}Hg$), 126.9 (C_{ar}), 128.0 (C_{ar}), 128.3 (C_{ar}), 136.3 ($C_{ar}C_{carborane}$); ^{11}B NMR ($CDCl_3$) δ −11.80 (d, J = 180 Hz, 10 B), −13.98 (d, J = 175 Hz, 10 B); ^{199}Hg NMR (acetone-d_6, against

Me_2Hg; internal standard, PhHgCl in DMSO-d_6 δ −1187.00) δ −720.4; MS *m/z* (rel intensity) 639 (boron cluster center, isotope pattern fits the calculated cluster for M, 100), 439 (10), 296 (50), 218 (80); IR (KBr) 3063 (BCH), 2605 (BH), 1598 (C═C), 1499, 1450, 1400, 1090, 1027, 1006, 915, 844, 780, 738, 690, 625 cm^{-1}; HRMS calcd (rel intensity) 639.4001 (34.8), 639.4057 (33.1), 639.4097 (32.1), found 639.4055 (unresolved). Anal. Calcd for $C_{16}H_{30}B_{20}Hg$: C, 30.06; H, 4.73. Found: C, 29.64; H, 4.65.

One-Step Procedure. To a solution of $HgBr_2$ (8.2 mg, 0.023 mmol), NaBr (4.3 mg, 0.042 mmol), and *p*-carboranylbenzene (**3**, 5.0 mg, 0.023 mmol) in DMF (2.5 mL, freshly distilled) was added *t*-BuOK (10.0 mg, 0.089 mmol) at −10 °C under N_2. The reaction mixture was stirred at rt for 3 h. The mixture was poured into water and extracted with diethyl ether (3 × 10 mL). The combined organic phases were washed with brine and dried over $MgSO_4$. The yield was 97% on the basis of GC. After the solvent was removed, the product was purified by thick-layer chromatography (silica, $CHCl_3$) and subsequent sublimation (200 °C/10^{-4} Torr) and isolated in 79% yield. The reaction was performed in a similar fashion in TMU, DMPU, propylene carbonate, and *tert*-butyl alcohol, and followed by NMR. In TMU and DMPU, it proceeded similarly as in DMF.

Complex of 13 with 2,2′-Bipyridyl (1:1). 2,2′-Bipyridyl (2.7 mg, 0.017 mmol) and **13** (4.4 mg, 0.007 mmol) were dissolved in chloroform (0.5 mL). Slow room temperature evaporation of the solvent yielded small colorless crystals.

Complex of 13 with 2,2′-Bipyrimidyl (2:1). 2,2′-Bipyrimidyl (5.0 mg, 0.032 mmol) and **13** (3.5 mg, 0.0055 mmol) were dissolved in toluene (1.0 mL). Slow room temperature evaporation of the solvent yielded small colorless crystals.

Bis{12′-[*m*-(1′,12′-dicarba-*closo*-dodecaboran-1′-yl)phenyl]-1,12-dicarba-*closo*-dodecaboran-1-yl}mercury (14). Under argon atmosphere, *m*-bis(1,12-dicarba-*closo*-dodecaboran-1-yl)benzene (**4**, 58 mg, 0.16 mmol), NaBr (24 mg, 0.23 mmol), and $HgBr_2$ (28 mg, 0.077 mmol) were dissolved in freshly distilled DMF (40 mL) and cooled to 0 °C. Potassium *tert*-butoxide (35 mg, 0.31 mmol) was then added from a tip tube, and the mixture was stirred for 2.5 h at 0 °C. The mixture was poured in water (50 mL) and extracted with ether (3 × 30 mL). After the solution was dried over Na_2SO_4 the solvent was removed under reduced pressure, column chromatography (silica, hexanes) yielded 11 mg of the starting material and 44 mg (60%, after correction for recovered **4**, 74%) of **14** as a white solid: mp 354 °C; ^1H NMR ($CDCl_3$) δ 1.20−3.40 (br m, 40 H, BH), 2.78 (s, 2 H, BCH), 6.88−7.05 (m, 8 H, aromatic); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 59.9 ($C_{carborane}H$), 85.6 ($C_{carborane}Hg$), 89.3 ($C_{carborane}C_{ar}$), 89.7 ($C_{carborane}C_{ar}$), 126.1 (C_{ar}), 126.7 (C_{ar}), 126.8 (C_{ar}), 127.7 (C_{ar}), 136.1 ($C_{ar}C_{carborane}$), 136.6 ($C_{ar}C_{carborane}$); ^{11}B NMR ($CDCl_3$) δ −11.85 (d, J = 151 Hz, 10 B), −13.57 (br d, J = 154 Hz, 20 B), −15.96 (d, J = 166 Hz, 10 B); MS *m/z* (rel intensity) 925 (boron cluster center, isotope pattern fits the calculated cluster for M, 50), 782 (cluster center, M − $C_2B_{10}H_{11}$, 40), 706 (30), 365 (100); IR (KBr) 3063 (BCH), 3056 (CH_{Ar}), 2605 (BH), 1604 (aromatic), 1488, 1097, 1089, 793, 734, 687 cm^{-1}; HRMS calcd 924.7632, found 924.7623. Anal. Calcd for $C_{20}H_{50}B_{40}Hg$: C, 26.01; H, 5.46. Found: C, 25.93; H, 5.66.

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Supporting Information Available: Figures 2, 3, and 9, discussion of X-ray diffraction, and crystallographic data (81 pages). See any current masthead page for ordering and Internet access instructions.

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