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Self-Assembly of Trinuclear Half-Sandwich Metal (Co and Ru) Complexes Containing Ancillary *ortho*-Carborane-1,2-dithiolato Ligands

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One-step syntheses of cobalt- and ruthenium-based trinuclear complexes have been accomplished in high yields by a self-assembly strategy. Reaction of 16-electron "pseudoaromatic" half-sandwich cobalt complex [Cp*Co{$S_2C_2(B_{10}H_{10})$}] (**1**) (Cp* = η^5-pentamethylcyclopentadienyl) and ruthenium complex [(*p*-cymene)Ru{$S_2C_2(B_{10}H_{10})$}] (**2**) with 2,4,6-tri-4-pyridyl-1,3,5-triazine (tpt) and 2,4,6-tri[(4-pyridyl) sulfanylmethyl]-1,3,5-triazine (tpst) in dichloromethane gave the corresponding multicluster complexes [Cp*Co{$S_2C_2(B_{10}H_{10})$}]$_3$(tpt) (**3**), [(*p*-cymene)Ru{$S_2C_2(B_{10}H_{10})$}]$_3$(tpt) (**4**), and [Cp*Co{$S_2C_2(B_{10}H_{10})$}]$_3$(tpst) (**5**), respectively. The X-ray structures of complexes **3** and **4** reveal that each tpt unit bridges three [Cp*Co{$S_2C_2(B_{10}H_{10})$}] and [(*p*-cymene)Ru{$S_2C_2(B_{10}H_{10})$}] fragments in a *cis*-conformation, respectively. However, three [Cp*Co{$S_2C_2(B_{10}H_{10})$}] units in complex **5** are arranged in a *trans*-conformation. Single-crystal X-ray diffraction analyses also show that there are different packing patterns in complexes **3**–**5**. Complexes **3** and **4** form two different channels by pairing up molecules, while complex **5** forms one-dimensional infinite chains through π–π stacking interactions.

Introduction

The use of multidentate organic ligands and suitable transition metal complexes to construct specific supramolecular architectures has been demonstrated to be a major strategy.[1,2] Supramolecular architectures have attracted much attention, not only because of their novel structures but also because of potential applications, such as ion and molecular recognition and ion-exchange.[1e,3] In the synthesis of supramolecular materials with interesting properties, there is an increasing interest in designing transition metal complexes as well as suitable multidentate ligands, since the potential uses of such architectures, which include molecular cages, two- and three-dimensional synthetic receptors, and extended porous frameworks, largely depend on their cavity size and type, which are mainly controlled by the liangds and appropriate metal ions.[4]

Meanwhile, carboranyl cluster-based complexes have been proved to be versatile precursors to novel structures.[5] The 16-electron half-sandwich complexes [Cp*M{$E_2C_2(B_{10}H_{10})$}] (M = Co, Rh, Ir; E = S, Se)[6] and [(*p*-cymene)Ru{$S_2C_2(B_{10}H_{10})$}],[7] which contain the "pseudoaromatic" metalladichalcogenolene five-membered ring, have exhibited a rich coordination chemistry due to both their unsaturation at the metal atom[8] and the bridging properties of the sulfur or selenium atoms.[9] The use of cyclopentadienyl or arene ligands can control the accessibility of coordination sites of an octahedral metal center, these η^5 or η^6 ligands occupy three of the six coordination sites at the metal

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(1) (a) Moulton, B.; Zaworotko, M. *J. Chem. Rev.* **2001**, *101*, 1629–1658. (b) Saha, B. K.; Nangia, A. *Cryst. Growth Des.* **2007**, *7*, 393–401. (c) Adams, C. J.; Colquhoun, H. M.; Crawford, P. C.; Lusi, M.; Orpen, A. G. *Angew. Chem., Int. Ed.* **2007**, *46*, 1124–1128. (d) Glaser, R. *Acc. Chem. Res.* **2007**, *40*, 9–17. (e) Sieklucka, B.; Podgajny, R.; Przychodzeń, P.; Korzeniak, T. *Coord. Chem. Rev.* **2005**, *249*, 2203–2221. (f) Braga, D.; Maini, L.; Polito, M.; Tagliavini, E.; Grepioni, F. *Coord. Chem. Rev.* **2003**, *246*, 53–71.

(2) (a) Dong, Y.-B.; Geng, Y.; Ma, J.-P.; Huang, R.-Q. *Organometallics* **2006**, *25*, 447–462. (b) Stang, P. J.; Olenyuk, B. *Acc. Chem. Res.* **1997**, *30*, 502–518. (c) Ye, B.-H.; Tong, M.-L.; Chem, X.-M. *Coord. Chem. Chem.* **2005**, *249*, 545–565. (d) Fujita, M.; Fujita, N.; Ogura, K.; Yamaguchi, K. *Nature* **1999**, *400*, 52–55. (e) Solntsev, P. V.; Sieler, J.; Krautscheid, H.; Domasevitch, K. V. *Dalton Trans.* **2004**, 1153–1158.

(3) (a) Fiedler, D.; Leung, D. H.; Bergman, R. G.; Raymond, K. N. *J. Am. Chem. Soc.* **2004**, *126*, 3674–3675. (b) Yaghi, O. M.; Li, H.; Davis, C.; Richardson, D.; Groy, T. L. *Acc. Chem. Res.* **1998**, *31*, 474–484. (c) Trans, D. T.; Zavalij, P. Y.; Oliver, S. R. J. *J. Am. Chem. Soc.* **2002**, *124*, 3966–3969. (d) Luo, T.-T.; Tsai, H.-L.; Yang, S.-L.; Liu, Y.-H.; Yadav, R. D.; Su, C.-C.; Ueng, C.-H.; Lin, L.-G.; Lu, K.-L. *Angew. Chem., Int. Ed.* **2005**, *44*, 6063–6067. (e) Liu, Y.-H.; Wu, H.-C.; Lin, H.-M.; Hou, W.-H.; Lu, K.-L. *Chem. Commun.* **2003**, 60–61.

(4) (a) Abrahams, B. F.; Jackson, P. A.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 2656–2659. (b) Ghadiri, M. R.; Granja, J. R.; Milligan, R. A.; McRee, D. E.; Khazanovich, N. *Nature* **1993**, *366*, 324–327. (c) Scherer, M.; Gaulder, D. L.; Johnson, D. W.; Raymond, K. N. *Angew. Chem., Int. Ed.* **1999**, *38*, 1588–1592.

(5) (a) Wedge, T. J.; Hawthorne, M. F. *Coord. Chem. Rev.* **2003**, *240*, 111–128. (b) Xie, Z. *Coord. Chem. Rev.* **2002**, *231*, 23–46. (c) Xie, Z. *Coord. Chem. Rev.* **2006**, *250*, 259–272. (d) Jin, G.-X. *Coord. Chem. Rev.* **2004**, *248*, 587–602.

(6) (a) Herberhold, M.; Jin, G.-X.; Yan, H.; Milius, W.; Wrackmeyer, B. *Eur. J. Inorg. Chem.* **1999**, 873–875. (b) Herberhold, M.; Jin, G.-X.; Yan, H.; Milius, W.; Wrackmeyer, B. *J. Organomet. Chem.* **1999**, *587*, 252–257. (c) Kim, D.-H.; Ko, J.; Park, K.; Cho, S.; Kang, S. K. *Organometallics* **1999**, *18*, 2738–2740. (d) Won, J.-H.; Kim, D.-H.; Kim, B. Y.; Kim, S.-J.; Lee, C.; Cho, S.; Ko, J.; Kang, S. O. *Organometallics* **2002**, *21*, 1443–1453.

(7) Herberhold, M.; Yan, H.; Milius, W.; Wrackmeyer, B. *J. Organomet. Chem.* **2000**, *598*, 142–149.

(8) (a) Chen, Y.-Q.; Zhang, J.-S.; Cai, S.; Hou, X.-F.; Schumann, H.; Jin, G.-X. *Dalton Trans.* **2007**, 749–758. (b) Wang, J.-Q.; Herberhold, M.; Jin, G.-X. *Organometallics* **2006**, *25*, 3508–3514.

(9) (a) Lu, S.-X.; Jin, G.-X.; Hu, N.-H.; Jia, H.-Q. *Chem. Res. Chin. Univ.* **2002**, *18*, 405–408. (b) Lu, S.-X.; Jin, G.-X.; Eibl, S.; Herberhold, M.; Xin, Y. *Organometallics* **2002**, *21*, 2533–2535. (c) Yu, X.-Y.; Jin, G.-X.; Hu, N.-H.; Weng, L.-H. *Organometallics* **2002**, *21*, 5540–5548. (d) Herberhold, M.; Yan, H.; Milius, W.; Wrackmeyer, B. *Organometallics* **2000**, *19*, 4289–4294.

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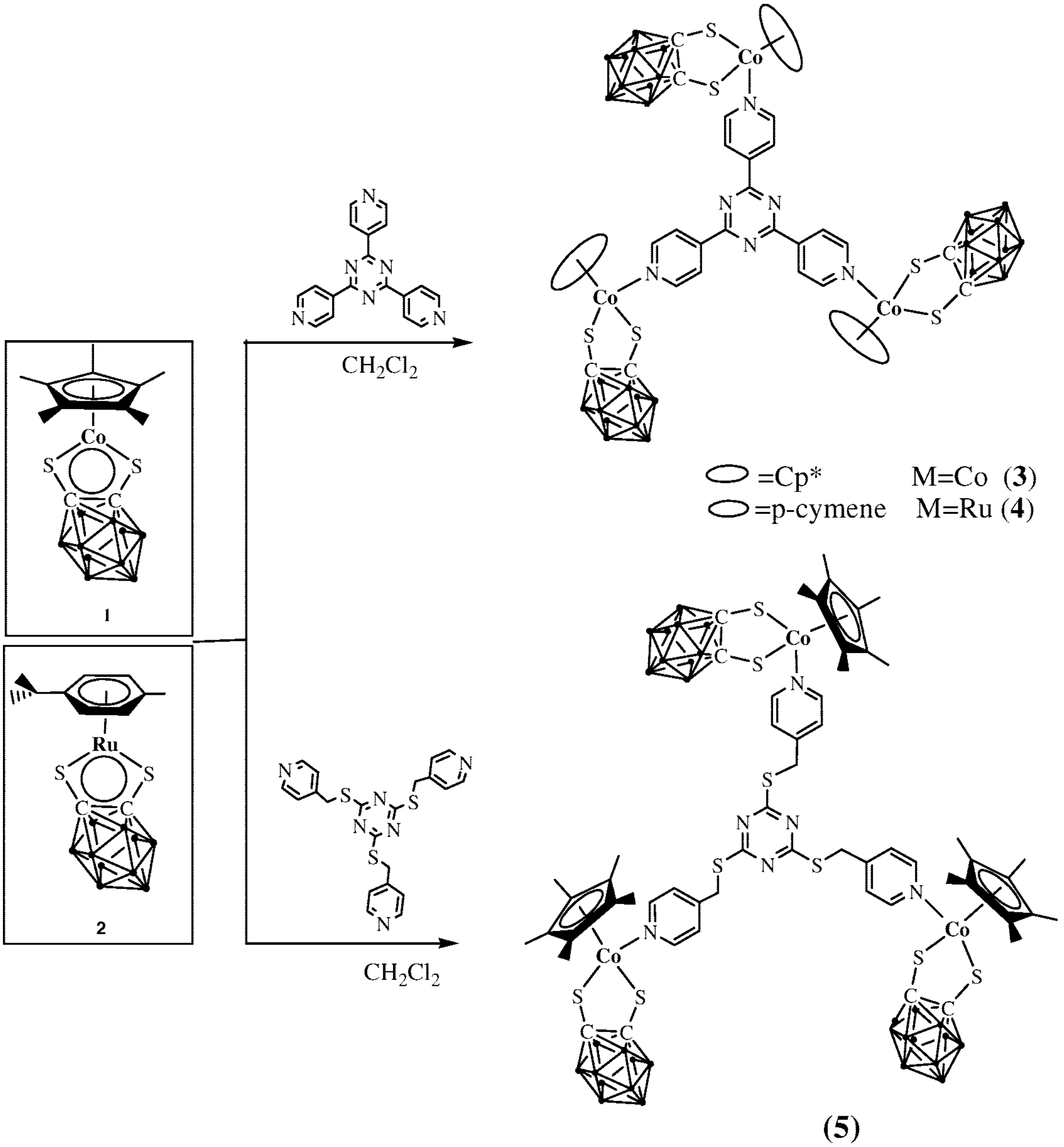
Scheme 1. Reactions with Pyridyl-Based Ligands to Give Complexes 3–5



center, and the resulting coordination geometry is pseudotetrahedral, allowing a better control of the specific geometry.[10] More important, the solubility of these complexes can be greatly enhanced by using the carborane dichalcogenolato ligands.[11] We have been working on the formation of a metal−metal bond using 16-electron complexes as starting materials[12] and decided to use them as building blocks in supramolecular assemblies.

Herein, we synthesize the rigid ligand-2,4,6-tri-4-pyridyl-1,3,5-triazine (tpt) and the flexible ligand-2,4,6-tri[(4-pyridyl) sulfanylmethyl]-1,3,5-triazine (tpst) and describe the assembly of soluble, air-stable, supramolecular structures based on the metal-containing moieties [Cp*Co{$S_2C_2(B_{10}H_{10})$}] and [(*p*-cymene)Ru{$S_2C_2(B_{10}H_{10})$}], bridged by tridentate organic spacers tpt and tpst (Scheme 1).

Results and Discussion

In the past several years, we have synthesized a series of cobalt-, rhodium-, and iridium-containing multicluster complexes based on *ortho*-carborane-1,2-dichalcogenolato ligands.[13] These highly symmetrical supramolecules not only exhibited novel structures but also supplied us a template for more novel topology of other late transition metal complexes. In addition, compared to the supramolecules with rigid ligands, the corresponding species with flexible ligands have not been sufficiently studied. Aiming at this target, we chose the mononuclear 16-electron half-sandwich complexes of Co and Ru as building blocks to react with tpt and tpst. Scheme 1 shows the formation of dendritic molecules **3**−**5**, which were characterized by elemental analyses, ^{1}H NMR, ^{11}B NMR, IR spectroscopy, and single-crystal X-ray analyses.

Reaction of 1 with tpt Ligand. The reaction between the *mono*nuclear 16-electron cobalt complex [Cp*Co{$S_2C_2(B_{10}H_{10})$}] and tpt in dichloromethane at room temperature for 24 h

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[10] (a) Govindaswamy, P.; Süss-Fink, G.; Therrien, B. *Organometallics* **2007**, *26*, 915–924. (b) Han, W. S.; Lee, S. W. *Dalton Trans.* **2004**, 1656–1663.

[11] (a) Wang, J.-Q.; Ren, C.-X.; Jin, G.-X. *Organometallics* **2006**, *25*, 74–81. (b) Liu, S.; Zhang, J.-S.; Wang, X.; Jin, G.-X. *Dalton Trans.* **2006**, 5225–5230.

[12] (a) Cai, S.; Hou, X.-F.; Chen, Y.-Q.; Jin, G.-X. *Dalton Trans.* **2006**, 3736–3741. (b) Jin, G.-X.; Wang, J.-Q.; Zhang, C.; Weng, L.-H.; Herberhold, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 259–262. (c) Cai, S.; Wang, J.-Q.; Jin, G.-X. *Organeometallics* **2005**, *24*, 4226–4231.

[13] (a) Wang, J.-Q.; Ren, C.-X.; Jin, G.-X. *Eur. J. Inorg. Chem.* **2006**, 3274–3282. (b) Wang, J.-Q.; Ren, C.-X.; Jin, G.-X. *Chem. Commun.* **2005**, 4738–4740. (c) Wang, J.-Q.; Ren, C.-X.; Jin, G.-X. *Chem. Commun.* **2006**, 162–164.

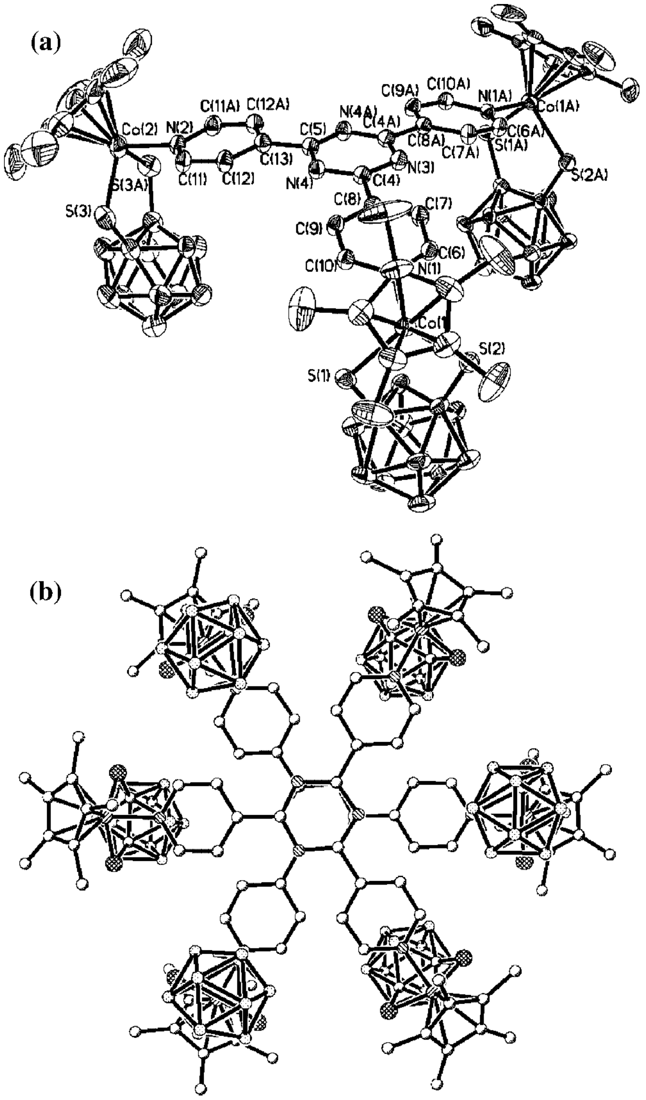

Figure 1. (a) Molecular structure of compound **3**. Thermal ellipsoids are drawn at the 30% probability level. (b) Two units of **3** in a staggered disposition. The hydrogen atoms are omitted for clarity. Symmetry transformation for the generation of equivalent atoms A: $-x + 1/2$, $-y + 1/2$, z. Selected bond lengths (Å) and angles (deg): Co(1)−N(1) 1.990(4), Co(1)−S(1) 2.2617(16), Co(1)−S(2) 2.2585(18), S(1)−C(1) 1.780(6), S(1)−C(2) 1.777(5), C(1)−C(2) 1.651(8), Co(2)−N(2) 2.002(7), Co(2)−S(3) 2.257(2), S(3)−C(3) 1.763(7), C(3)-C(3A) 1.664(13); S(1)−Co(1)−S(2) 93.89(6), S(3)−Co(2)−S(3A) 93.22, N(1)−Co(1)−S(1) 93.06(13), N(1)−Co(1)−S(2) 93.78(13), N(2)−Co(2)−S(3) 93.27(15), C(1)−S(1)−Co(1) 105.35 (19), C(2)−S(2)−Co(1) 105.22(19), C(3)−S(3)−Co(2) 105.9(2).

leads to formation of the trinuclear complex [Cp*Co{$S_2C_2(B_{10}H_{10})$}]$_3$($C_{18}H_{12}N_6$) (**3**) in high yield (85%). The color of the solution gradually changed from yellow-green to green during the reaction.

In addition to a strong band for the B−H vibration at approximately 2582 cm^{-1} in the infrared spectrum, there are absorptions of the coordinated tpt ligand, which are only slightly shifted as compared to those of the free ligand (1517 (s), 1374 (s), 795 (s), 642 (s) cm^{-1}). The formation of **3** is also confirmed by the appearance of the ^{1}H NMR signals at 1.63, 8.55, and 9.06 ppm, which can be ascribed to the methyl of Cp* and the pyridyl of tpt. The ^{11}B NMR spectrum exhibits resonances at −7.22, −8.20, −9.71, and −11.11 ppm, and the elemental analysis also proves the components of the complex.

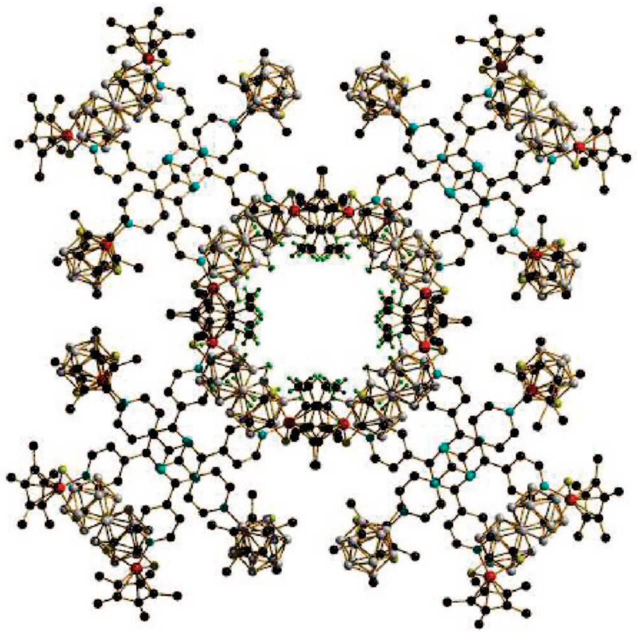

Figure 2. Crystal structure of **3** viewed down the *c* axis (red: Co, white: B, black: C, yellow: S, turquoise: N, bright green: H).

Suitable single crystals of [Cp*Co{$S_2C_2(B_{10}H_{10})$}]$_3$($C_{18}H_{12}N_6$) (**3**) were obtained by slow diffusion of hexane into a dichloromethane or chloroform solution. An X-ray diffraction study on **3** confirmed that the complex has the expected trigonal geometry. The molecular structure of **3** is shown in Figure 1a. Three [Cp*Co{$S_2C_2(B_{10}H_{10})$}] units are symmetrically arranged around the periphery of one tpt core, just like a triangular prism. All of the cobalt centers adopt a three-legged piano-stool conformation to form a pseudotetrahedron coordination sphere. The Co−N bond distances range from 1.991 to 2.002 Å, which are comparable to those of binuclear half-sandwich cobalt complexes.[11b]

It is interesting that there are strong parallel $\pi-\pi$ stacking interactions between the triazine rings of two neighboring independent tpt units in the crystal packing of **3** (Figure 1b). The centroid$\cdots$centroid distance observed between corresponding aromatic rings of the $\pi-\pi$ interacting systems (3.44 Å) is slightly shorter than the 3.46 Å separation reported in the crystal packing of [Cp*Ir{$S_2C_2(B_{10}H_{10})$}]$_3$($C_{18}H_{12}N_6$) and [Cp*Rh{$S_2C_2(B_{10}H_{10})$}]$_3$($C_{18}H_{12}N_6$).[13a,b] The two neighboring molecules within the stack are rotated by about 60° with respect to each other because of steric hindrance. In addition, the two triazines in a staggered fashion made the $\pi\cdots\pi$ interactions between them stronger due to the overlapping of the carbon atoms and nitrogen atoms, whose electric charges are opposite, which made them serve as an independent pseudohexanuclear coordination unit.

Another interesting feature of **3** is the packing pattern along the *c* axis. As shown in Figure 2, every eight molecules of **3** pair up to form one channel. In other words, each molecule of **3** is locked into position by pairing up with neighboring molecules in the crystal lattice. The packing in the crystal creates infinite tunnels, just like wells, and the diameter of each well is about 3.74 Å, considering van der Waals interactions.

Reaction of 2 with tpt Ligand. As previously described, the 16-electron "pseudoaromatic" ruthenium complex [(*p*-cymene)Ru{$S_2C_2(B_{10}H_{10})$}] acts as a Lewis acid and forms 1:1 adducts with pyridine derivatives.[11b] When a solution of **2** and

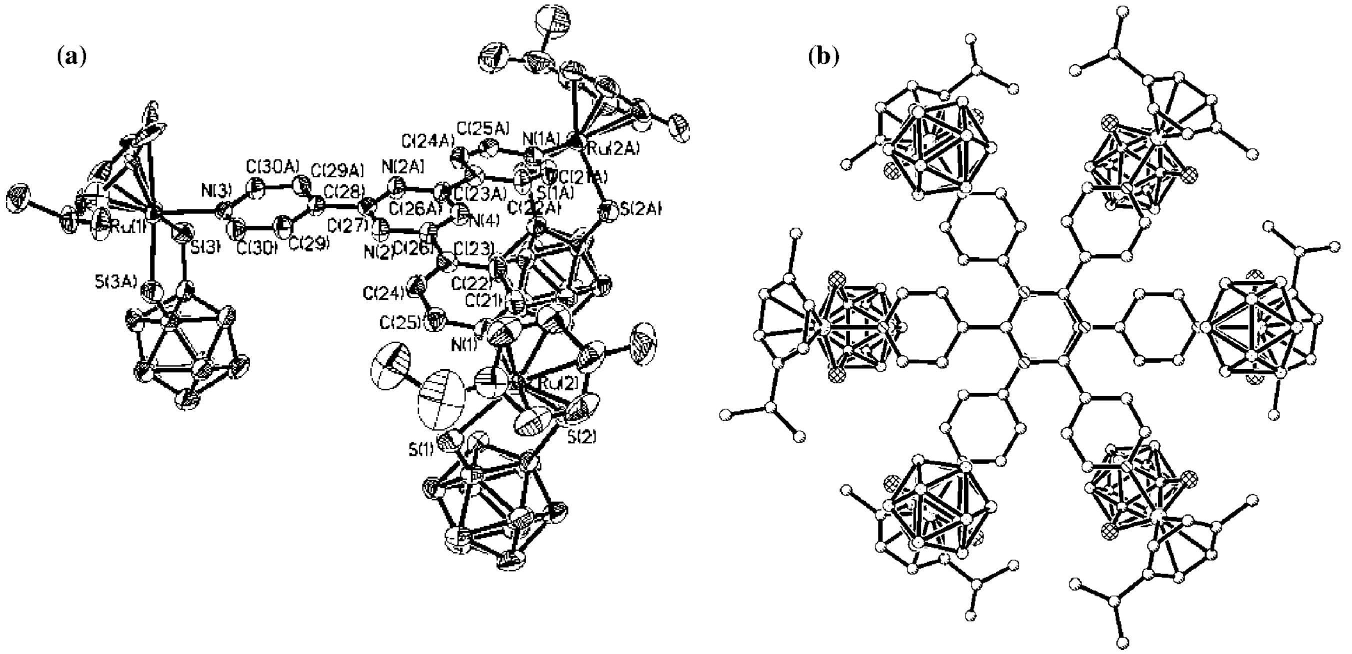

Figure 3. (a) Molecular structure of compound **4**. Thermal ellipsoids are drawn at the 30% probability level. (b) Two units of **4** in a staggered disposition. Symmetry transformation for the generation of equivalent atoms A: *x*, *y*, −*z*. The hydrogen atoms and solvent molecule are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)−N(3) 2.147(5), Ru(1)−S(3) 2.379(2), S(3)−C(33) 1.777(5), C(33)−C(33A) 1.681(10), Ru(2)−N(1) 2.126(4), Ru(2)−S(1) 2.3755(16), Ru(2)−S(2) 2.3865(17), S(1)−C(31) 1.800(5), S(2)−C(32) 1.773(5), C(31)−C(32) 1.670(7); S(3)−Ru(1)−S(3A) 89.569(16), Ru(1)−S(3)−C(33) 107.13(17), N(3)−Ru(1)−S(3) 88.30(11), S(1)−Ru(2)−S(2) 89.54(5), N(1)−Ru(2)−S(1) 88.82(13), N(1)−Ru(2)−S(2) 87.93(13), Ru(2)−S(2)−C(32) 107.10(18), Ru(2)−S(1)−C(31) 107.13(17).

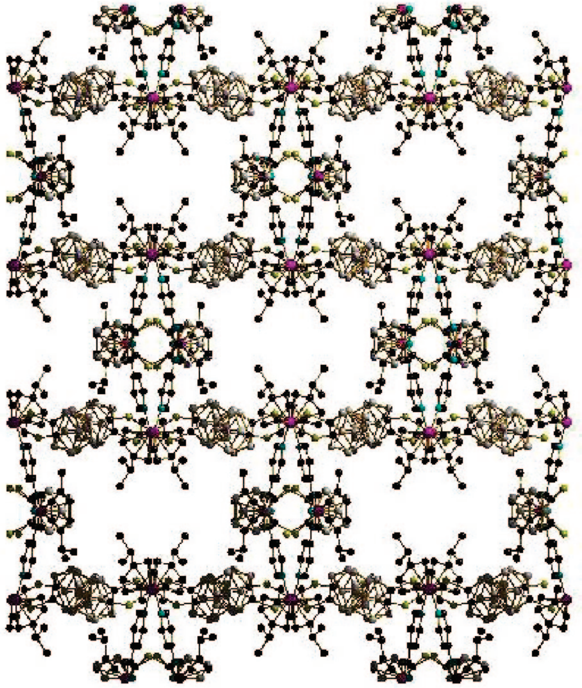

Figure 4. Illustration of channels in complex **4** viewed down the *b* axis (pink: Ru, white: B, black: C, yellow: S, and turquoise: N). All hydrogen atoms and solvent molecules have been omitted for clarity.

tpt in a 3:1 ratio was stirred under similar experimental conditions, the trinuclear complex **4** can be generated as a violet solid.

Similarly, the B−H vibration at 2581(s) cm^{-1} and absorptions of coordinated tpt at 1517 (s), 1372 (m), and 802 (m) cm^{-1} were observed in the infrared spectrum. In the ^{1}H NMR spectrum the resonance signals at 1.27, 2.42, 2.67, 5.39, 7.95, and 9.64 ppm demonstrate the coexistence of *p*-cymene and the tpt ligand, and the ^{11}B NMR spectra also prove the maintenance of carborane cages.

The structure of complex **4** has also been determined by X-ray analysis using single crystals grown from CHCl$_3$/hexane. One of the three *p*-cymene ligands that bonds with ruthenium was strongly disordered, and it was refined to two idealized orientation, with 50% probability of each orientation. The molecular structure, together with selected bond distances and angles, is depicted in Figure 3. Complexes **4** and **3** have similar trinuclear structure, with the tpt ligand as a trigonal 3-connecting linker. Similar to that of complex **3**, the *p*-cymene and the carboranyl ligands also adopt a *cis*-conformation. The three ruthenium atoms are separated by 13.304 Å (Ru1−Ru2, Ru1−Ru2A) and 13.077 Å (Ru2−Ru2A), respectively, which form an isoceles triangle. The three pyridyl groups are distorted from the triazine plane by about 7.7°.

Through the packing image, it can be seen clearly that every two neighboring molecules of **4** are paired and staggered in a face-to-face fashion along the two triazine centroids. The distance between two centroid is about 3.41 Å, comparable to that of complex **3**. Meanwhile, we note that *p*-cymene ligands have two different orientations; that is to say, there are both head-to-tail and head-to-head orientations.

Compared to the building block of 16-electron cobalt complex [Cp*Co{S$_2$C$_2$(B$_{10}$H$_{10}$)}], the [(*p*-cymene)Ru{S$_2$C$_2$(B$_{10}$H$_{10}$)}] has

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(14) (a) Hong, M.-C.; Zhao, Y.-J.; Su, W.-P.; Cao, R.; Fujita, M.; Zhou, Z.-Y.; Chan, A. S. C. *Angew. Chem., Int. Ed.* **2000**, *39*, 2468–2470. (b) Hong, M.-C.; Zhao, Y.-J.; Su, W.-P.; Cao, R.; Fujita, M.; Zhou, Z.-Y.; Chan, A. S. C. *J. Am. Chem. Soc.* **2000**, *122*, 4819–4820.

(15) Anderson, H. L.; Anderson, S.; Sanders, J. K. M. *J. Chem. Soc., Perkin Trans.* **1995**, 2231–2246.

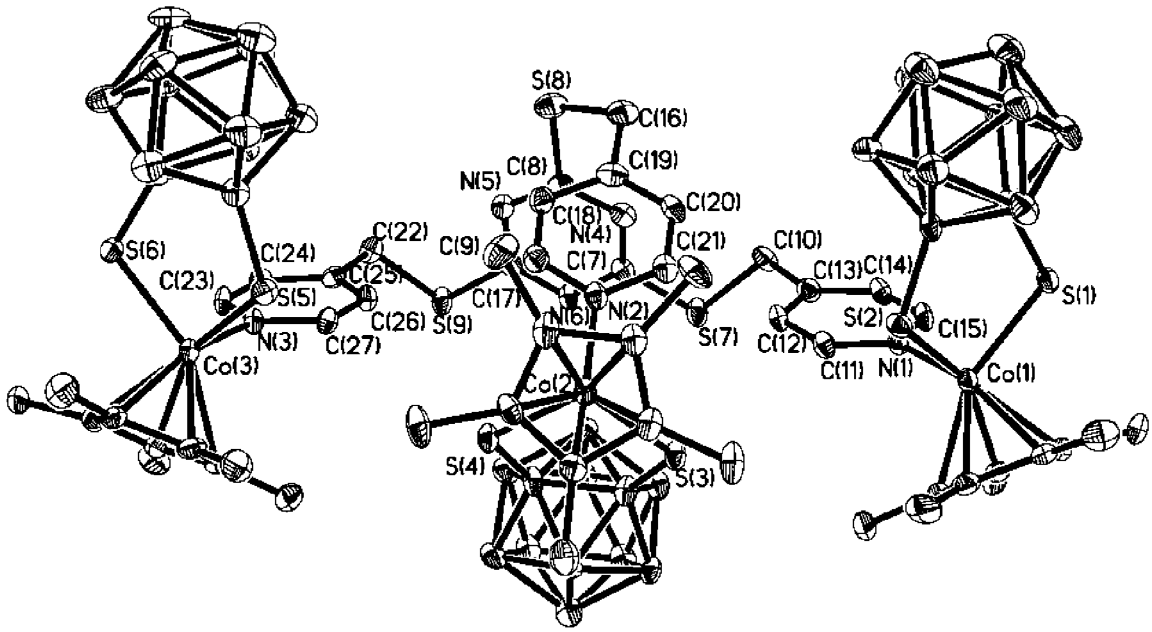

Figure 5. Molecular structure of compound **5**. Thermal ellipsoids are drawn at the 30% probability level. The hydrogen atoms and solvent molecule are omitted for clarity. Selected bond lengths (Å) and angles (deg): Co(1)−N(1) 1.9967(6), Co(2)−N(2) 2.0032(9), Co(3)−N(3) 1.9977(6), Co(1)−S(1) 2.2641(7), Co(1)−S(2) 2.2656(8), Co(2)−S(3) 2.2632(7), Co(2)−S(4) 2.2670(8), Co(3)−S(5) 2.2605(8), Co(3)−S(6) 2.2674(8), S(7)−C(10) 1.8006(6), S(7)−C(7) 1.7446(7), S(8)−C(16) 1.8108(6), S(8)−C(8) 1.7436(6), S(9)−C(22) 1.8135(6), S(9)−C(9) 1.7381(6); S(1)−Co(1)−S(2) 93.17(3), S(3)−Co(2)−S(4) 93.01(4), S(5)−Co(3)−S(6) 93.12(3), C(7)−S(7)−C(10) 103.72(3), C(8)−S(8)−C(16) 100.67(3), C(9)−S(9)−C(22) 102.74(4).

Figure 6. One-dimensional chain in the crystal of complex **5** (red: Co, gray: B, black: C, yellow: S, and blue: N).

distinctly different symmetry and orientation. In contrast with the channels constructed with a double-stranded helix along the *c* axis in complex **3**, the remarkable feature of **4** is the packing pattern along the *b* axis (Figure 4). Each of the eight molecules **4** is paired up to form a pseudotetragonal channel when considering the van der Waals interactions. A small modification in the building block led to great change in the packing pattern, which gave us a strategy to synthesize more supramolecules with novel structures.

Reaction of 1 with tpst Ligand. Compared to the rigid tpt ligand, the flexible ligand tpst has a distinctly different symmetry and orientation and may serve as a template for architectures with novel topology that are not achievable by types of rigid ligands.[14] The preparation procedure of complex **5** is almost the same as for complexes **3** and **4**, and the blue solid [Cp*Co{$S_2C_2(B_{10}H_{10})$}]$_3$(tpst) (**5**) can be prepared in ca. 80% yield through stirring a CH_2Cl_2 solution of a mixture of [Cp*Co{$S_2C_2(B_{10}H_{10})$}] and tpst at room temperature for 24 h.

The infrared spectrum of complex **5** is dominated by absorptions of the carboranes at 2580 cm^{-1} and the coordinated tpst ligand, which are only slightly shifted as compared to those of the free ligand (1602 (s), 1479 (s), 1419 (m), 1243(s) cm^{-1}). The ^{1}H NMR spectrum displays signals at 1.48, 4.20, 7.26, and 8.77, which can be ascribed to the Cp*, sulfanylmethyl, and pyridyl ligand, repectively. The ^{11}B NMR spectrum of **5** consists of signals around −7.4, −8.3, −10.3, and −11.2 ppm.

The structure of complex **5** has been determined by X-ray analysis using single crystals grown from $CHCl_3$/toluene. Compared to complexes **3** and **4**, the solubility of complex **5** is excellent in common organic solvents, but the crystals are easily efflorescent. Hence the structure was determined at 173 K. The molecular structure of **5** is shown in Figure 5.

The structure of complex **5** is obviously different from those of complexes **3** and **4**. Three [Cp*Co{$S_2C_2(B_{10}H_{10})$}] units are arranged on one side of the triazine plane and staggered in a *trans*-conformation to minimize steric repulsion. The dihedral angles along the S···S vector in the metallocycle (CoS_2C_2) range from 168° to 170°, which demonstrates the coordination addition reaction has destroyed the aromacity of the previously planar CoS_2C_2.

In addition, a supramolecular structure is observed in the crystal of complex **5**. One of six guest toluene molecules

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(16) Sheldrick, G. M. *SADABS, A Program for Empirical Absorption Correction*; University of Göttingen: Göttingen, Germany, 1998.

Table 1. Crystallographic Data for Complexes 3–5

	3	4	5
formula	$C_{54}H_{87}B_{30}Co_3N_6S_6$	$C_{55}H_{85}B_{30}Cl_3N_6Ru_3S_6$	$C_{99}H_{141}B_{30}Co_3N_6S_9$
M	1513.75	1756.51	2204.81
cryst syst	tetragonal	orthorhombic	orthorhombic
space group	*P*4(2)/*ncm*	*Pnnm*	*Pca*2(1)
a [Å]	34.927(6)	20.384(6)	26.785(13)
b [Å]	34.927(6)	22.015(7)	11.490(6)
c [Å]	16.073(4)	24.629(8)	37.643(18)
α [deg]	90	90	90
β [deg]	90	90	90
γ [deg]	90	90	90
V [Å^3]	19 607(6)	11 052(6)	11 585(10)
Z	8	4	4
density [g cm^{-3}]	1.026	1.056	1.264
μ(Mo Kα) [mm^{-1}]	0.662	0.621	0.634
T [K]	293(2)	293(2)	173(2)
R1 ($I > 2\sigma(I)$)[a]	0.0748	0.0452	0.0746
wR2 (all data)	0.2483	0.1166	0.1543

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o^2| - |F_c^2|)^2/\sum w|F_o^2|^2]^{1/2}$.

interacts with the two adjacent Cp* groups through strong $\pi-\pi$ stacking interaction. The distances between Cp* and toluene range from 3.04 to 3.63 Å. In this crystal, we found only this toluene has the strong interactions with Cp*, the other five toluene molecules have no obvious interactions with Cp* and other groups. We concluded that the other five toluenes may easily be removed from the crystal under certain conditions. In fact, the elemental analysis proves the existene of [Cp*Co{$S_2C_2(B_{10}H_{10})$}]$_3$(tpst) and toluene in a 1:1 ratio, which also proves our expectation. Through this toluene bridge, the neighboring two-layer molecules form one-dimensional infinite zigzag chains (Figure 6). Furthermore, enantiomorphs of complex **5** are arranged alternately in this chain to form a racemate.

Conclusion

In summary, we have successfully synthesized and characterized three new coordination complexes by introducing carboranyl dichalcogenolates into pyridyl-functionalized organic building blocks. We anticipate this is a noteworthy approach for the design of a variety of more complex coordination motifs with novel patterns.

Experimental Section

General Procedures. All manipulations were carried out under dry nitrogen. The organic solvents used were dried and purified according to standard procedures and stored under dry nitrogen. Elemental analyses were performed on an Elementar III Vario EI analyzer. IR spectra were recorded on a Nicolet AVATAR-360IR spectrometer. ^{1}H NMR (500 MHz) and ^{11}B NMR (160 MHz) spectra were obtained on a Bruker DMX-500 spectrometer. [Cp*Co{$S_2C_2(B_{10}H_{10})$}],[6d] [(*p*-cymene)Ru$S_2C_2(B_{10}H_{10})$)],[7] tpt,[15] and tpst[14b] were prepared according to literature methods.

Synthesis of [Cp*Co{$S_2C_2(B_{10}H_{10})$}]$_3$($C_{18}H_{12}N_6$) (3). A solution of **1** (120 mg, 0.3 mmol) in CH_2Cl_2 (20 mL) was added to tpt (31 mg, 0.1 mmol) in CH_2Cl_2 (20 mL). The yellow-green solution was stirred for 24 h, whereupon it gradually changed to green. The solvent was then evaporated under vacuum. The residue was washed with toluene to give a green solid of **3**. Yield: 128 mg (85%). Fine green crystals can be obtained through recrystallization from $CHCl_3$/hexane or CH_2Cl_2/hexane at −18 °C. Anal. Calcd for $C_{54}H_{87}B_{30}N_6Co_3S_6$: C, 42.85; H, 5.79; N, 5.55. Found: C, 42.78; H, 5.79; N, 5.77. IR (KBr pellet): ν 2581 (s) ($\acute{\nu}_{B-H}$), 1516 (s), 1374 (s), 804 (m), 640 (m) cm^{-1}. ^{1} H NMR ($CDCl_3$, ppm): δ 1.63 (s, 45 H, C_5Me_5), 8.55 (br, 6H, 3,5-pyridyl), 9.06 (br, 6H, 2,6-pyridyl). ^{11}B NMR ($CDCl_3$, ppm): δ −7.22, −8.20, −9.71, −11.11.

Synthesis of [(*p*-cymene)Ru{$S_2C_2(B_{10}H_{10})$}]$_3$($C_{18}H_{12}N_6$) (4). A mixture of **2** (125 mg, 0.3 mmol) and tpt (31 mg, 0.1 mmol) was dissolved in CH_2Cl_2 (40 mL). The blue-colored mixture was stirred for 24 h, whereupon it gradually changed to violet. The solvent was then evaporated under vacuum. The residue was washed with toluene to give a violet solid. Yield: 137 mg (88%). Fine purple crystals can be obtained through recrystallization from $CHCl_3$/hexane at −18 °C, and compound **4** crystallized in the form of $C_{54}H_{84}B_{30}Ru_3S_6N_6 \cdot CHCl_3$. Anal. Calcd for $C_{54}H_{84}B_{30}Ru_3S_6N_6 \cdot CHCl_3$: C, 37.45; H, 4.86; N, 4.77. Found: C, 38.10; H, 4.95; N, 4.73. IR (KBr pellet): ν 2581 (s) (ν_{B-H}), 1517 (s), 1372 (m), 802 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$, ppm): δ 1.27 (d, 18H, CH_3); 2.42(m, 9H, CH_3); 2.67 (m, 3H, CH); 5.39 (m, 12 H, C_6H_4); 7.95 (d, 6H, 3,5-pyridyl), 9.64(d, 6H, 2,6-pyridyl). ^{11}B NMR ($CDCl_3$, ppm): δ −4.00, −9.96, −14.24.

Synthesis of [Cp*Co{$S_2C_2(B_{10}H_{10})$}]$_3$(tpst) (5). A solution of **1** (120 mg, 0.3 mmol) in CH_2Cl_2 (20 mL) was added to tpst (45 mg, 0.1 mmol) in CH_2Cl_2 (20 mL). The solution gradually turned blue from yellow-green during the reaction. After reaction, the solvent was then evaporated under vacuum. The residue was washed with toluene to give a blue solid. Yield: 132 mg (80%). Fine crystals can be obtained through recrystallization from $CHCl_3$/toluene at −18 °C, and compound **5** crystallized in the form of $C_{57}H_{93}Co_3N_6S_9B_{30} \cdot C_7H_8$. As described before, five toluenes that have no interactions with Cp* are easily removed from the crystal. Anal. Calcd for $C_{57}H_{93}Co_3N_6S_9B_{30} \cdot C_7H_8$: C, 44.07; H, 5.84; N, 4.82. Found: C, 43.50; H, 6.21; N, 4.45. IR (KBr pellet): ν 2580 (s) (ν_{B-H}), 1611 (m), 1480 (s), 1420 (m), 1244 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, ppm): δ 1.48 (s, 45H, CH_3); 4.20 (m, 6H, SCH_2); 7.26 (br, 6H, 3,5-pyridyl); 8.77 (br, 6 H, 2,6-pyridyl). ^{11}B NMR ($CDCl_3$, ppm): δ −7.43, −8.28, −10.34, −11.18.

Crystal Structure Determination of Complexes 3–5. Suitable single crystals of complexes were sealed under nitrogen in Lindemann glass capillaries for X-ray structural analysis. Diffraction data were collected on a Bruker SMART Apex CCD diffractometer using graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. During the intensity data collection, no significant decay was observed. The intensities were corrected for Lorentz−polarization effects and empirical absorption with the SADABS program.[16] The structures were solved by direct methods using the SHELXL-97 program.[17] All non-hydrogen atoms were found from the difference

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(17) Sheldrick, G. M. *SHELXL-97*, *Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

(18) *SMART*, *SAINT*, and *SADABS* Packages, Version 5.1; Bruker AXS: Madison, WI, 1997–1999.

Fourier syntheses. All calculation were performed using the Bruker Smart program.[18] A summary of the crystallographic data is given in Table 1.

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Supporting Information Available: The crystallographic data for **3**, **4**, and **5** are available free of charge via the Internet at http//pubs.acs.org.

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