Inorg. Chem. **2008**, *47*, 2940−2942

Inorganic Chemistry

Communication

Helical Supramolecular Assemblies of {2,4,6-[Cp∗Rh(E_2-1,2-$C_2B_{10}H_{10}$)-($NC_5H_4CH_2S$)]$_3$(triazine)} (E = S, Se) Shaped by Cp∗−Toluene−Cp∗ π-Stacking Forces and BH−Pyridine Hydrogen Bonding

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Received January 21, 2008

Polycarborane-substituted molecules [Cp∗Rh{$E_2C_2(B_{10}H_{10})$}]$_3$(tpst) [E = S (**2a**), Se (**2b**)] were synthesized and characterized. **2a** and **2b** form toluene solvates in the solid state showing infinitely connected [(**2a**,**b**)-(toluene)]$_\infty$ helices. The chains of these supramolecules are held together by Cp∗−toluene−Cp∗ π-stacking interactions of two of the three Cp∗ ligands of the bell-shaped **2a** and **2b** molecules. Unconventional BH$^{\delta-}$−pyridyl$^{\delta+}$ aromatic hydrogen bonding enforces the bell-shapes of the molecular units, and the Cp∗ conformations are expected to induce the supramolecular structures.

Boron-rich macromolecules were recently intensively studied for their potential applications in diagnostic tumor imaging and as analytical supports of boron neutron capture therapy (BNCT).[1] Derivatives of 1,2-dicarba-*closo*-dodecaborane ($C_2B_{10}H_{12}$) are promising candidates as advanced pharmaceutical materials because of their high boron content and their facile derivatization for a wider range of specialized applications.[2]

Our and Herberhold et al.'s laboratories have previously reported the synthesis of the 16-electron "pseudoaromatic" complexes [Cp∗M{$E_2C_2(B_{10}H_{10})$}] (M = Co, Rh, Ir; E = S, Se) and suggested that these species have a vacant site at the metal center to be used as an extra valency for building up multimetallic supramolecules containing three or even four carborane clusters.[3] Various topologies of such polynuclear structures with [Cp∗M{$E_2C_2(B_{10}H_{10})$}] (M = Co, Rh, Ir; E = S, Se) could be governed by structural motives of mostly rigid nitrogen-based organic ligands, such as bpy, tpt, and TPyP (bpy = 4,4′-bipyridine; tpt = 2,4,6-tri-4-pyridyl-1,3,5-triazine; TPyP = tetrakis(4-pyridylporphyrin).[4] In this context, we were intrigued by the possibility of building polynuclear carborane molecules bearing a flexible organic ligand to be arranged in manifold conformations[5] through various topology-dependent secondary-type interactions. By application of the tpst [tpst = 2,4,6-tris(4-sulfanylmethylpyridyl)triazine] ligand, flexibility would be provided mainly by the sulfanylmethyl spacer groups.[6]

Herein, polycarborane-substituted molecules [Cp∗Rh{E_2C_2($B_{10}H_{10}$)}]$_3$(tpst) [E = S (**2a**), Se (**2b**)] were prepared by stirring a mixture of [Cp∗Rh{$E_2C_2(B_{10}H_{10})$}] [E = S (**1a**), Se (**1b**)] and tpst in CH_2Cl_2 at room temperature for 12 h, allowing one to isolate the assemblies of [Cp∗Rh{E_2C_2-($B_{10}H_{10}$)}]$_3$(L) [L = tpst; E = S (**2a**), Se (**2b**)] complexes as orange crystals in high yields (Scheme 1). They were characterized by ^{1}H NMR and IR spectroscopy and elemental analysis. Apparently, all three pyridyl groups of the tpst ligand are involved in metal coordination. Complexes **2a** and **2b** are both well-soluble in common organic solvents, but when crystallized

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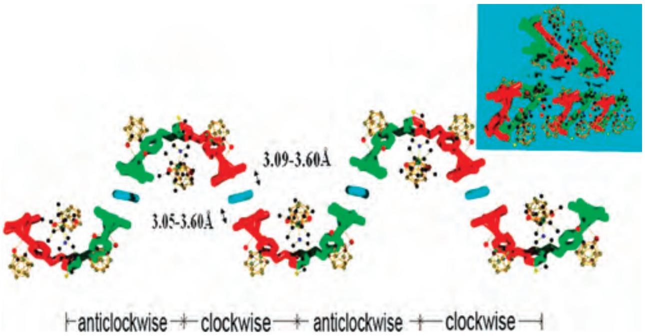
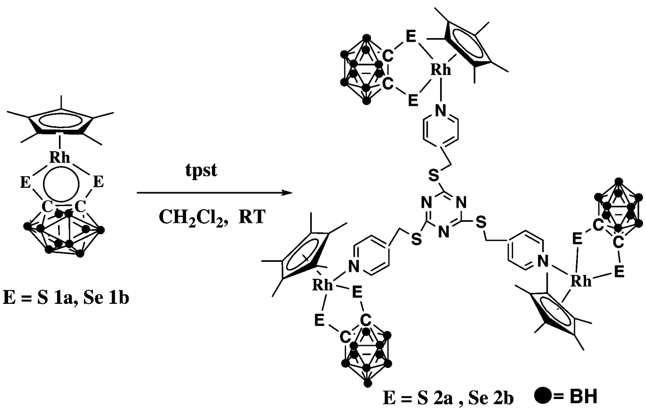


Figure 1. Structure of [(**2b**)-(toluene)]$_\infty$. Toluene is represented by blue. Red and green parts show clockwise and anticlockwise tropisms, respectively. Carborane groups and the middle branches are represented by a ball−stick model for clarity. Hydrogen atoms and other nonchain toluene molecules have been omitted for clarity also.

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



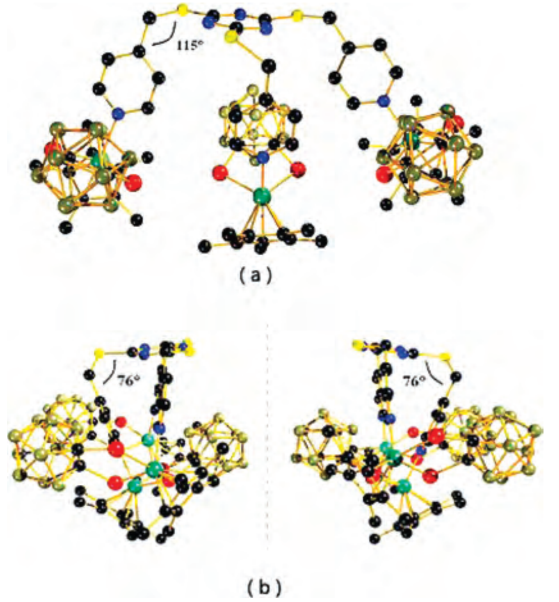


Figure 2. (a) Molecular structure of **2b**. (b) Side view of molecular structure (*R*)- and (*S*)-**2b**. Rhodium, selenium, sulfur, nitrogen, carbon, and boron atoms are represented by sea green, red, yellow, blue, black, and brown spheres, respectively. Hydrogen atoms have been omitted for clarity.

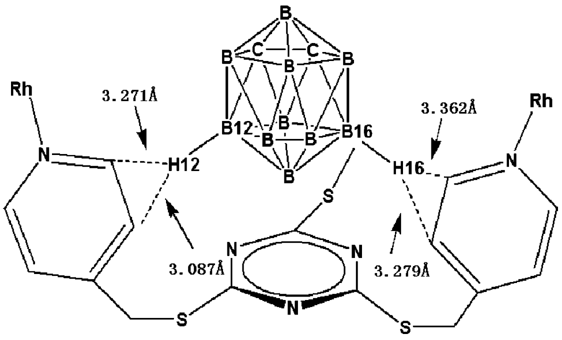


Figure 3. Schematic sketch of BH$^{\delta-}\cdots$pyridyl$^{\delta+}$ hydrogen bonding of **2b**.

from CH$_2$Cl$_2$, THF, or MeOH, they form microcrystalline solvated powders, losing the solvent especially when exposed to air. However, slow diffusion of toluene into a ClCH$_2$CH$_2$Cl solution of **2a** and **2b** leads to the stable solvate derivatives **2a**,**b**·toluene. These toluene solvates exhibit in the solid state infinitely connected [(**2a**,**b**)-(toluene)]$_\infty$ supramolecular helices. Also, on the basis of spectroscopic grounds, both complexes have closely related structures. The single-crystal X-ray diffraction study (173 K) on [(**2a**,**b**)-(toluene)]$_\infty$ is exemplarily discussed in greater detail. It indeed revealed infinite helical chains (Figure 1) held together by Cp∗−toluene−Cp∗ π-stacking interactions of two of the three Cp∗ ligands (Figure 2). The proximal orientation of these two “intrachain” Cp∗ rings is supposed to originate from the overall bell shape of the molecular unit of **2b**, with the rhodium fragments all on one side of the pyrazine ring. Lattice enforcement of the π interactions could also be anticipated. The bell shape is apparently caused by two attractive BH$^{\delta-}\cdots$pyridyl$^{\delta+}$ aromatic hydrogen bonds pulling the two “intrachain” rhodium−pyridyl units and the unique “extrachain” carborane unit to one side of the triazine plane (Figure 3). This aromatic hydrogen bonding is denoted as “unconventional” because of the inverse polarization of the partners with respect to conventional aromatic hydrogen-bonding XH$^{\delta+}\cdots$Ar$^{\delta-}$.[9] It is estimated to be in the energy range of 2–3 kcal/mol and is quite often observed in respective solid-state structures containing substituted dodecacarboranes and pyridines to interact inter-[7] as well as intramolecularly.[4b,c,7b,c,8] The BH$\cdots$C$_{\text{pyridyl}}$ distances of **2b** fall well into the typical range of 2.8–3.4 Å. Negatively polarized (hydridic) −H$^{\delta-}$ atoms of boranes and of transition-metal hydrides are known to also get involved in other forms of unconventional hydrogen bonding, such as, for instance, in dihydrogen bonding of the XH$^{\delta-}\cdots{}^{\delta+}$HY type (X = L$_n$M, B; Y = O, N),[10] where the XH$^{\delta-}$ moieties indeed play the role of hydrogen-bond acceptors.

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The S−CH$_2$−pyridyl angles around the pyrazine ring of **2b** differ significantly because of its asymmetric environment. As shown in Figure 2, the "intrachain" S−CH$_2$−pyridyl angles are about 115°, but the "extrachain" pyridyl branch is only about 76° with the triazine plane. Another important observation is that there are two enantiomers of **2b** in the unit cell, which we assign as (*R*)- and (*S*)-**2b** configurations based on their pseudotetrahedral symmetry. In Figure 1, the red parts show clockwise tropism and the green parts are anticlockwise.

It is interesting to note at this point that **2a**·toluene was shown to possess a molecular structure related to **2b**·toluene.[11] The solvate toluenes of both complexes are apparently so strongly bound that they survive recrystallizations from various nonaromatic solvents. The same crystal structures were obtained as indicated by the determination of the cell parameters of single-crystal X-ray diffraction studies. We concluded from these observations that the Cp∗−toluene−Cp∗ π-stacking interactions must be substantial, even though the distances between the planes of the Cp∗ and toluene rings ranging from 3.05–3.60 Å are quite long $\pi-\pi$-stacking contacts.[12] Some enhancement of these interactions was anticipated to originate from the fact that the "sandwiched" toluene is in a bridging contact with the two Cp∗ units.[13] Density functional theory calculations were carried out on simplified dithiolene models, circumventing the computations of the large carborane moieties.[14] Applying two Cp∗Rh(NC$_5$H$_5$)(S$_2$C$_2$H$_2$) and one "sandwiched" benzene revealed a stabilization energy of 2.2 kcal/mol for the Cp∗−C$_6$H$_6$−Cp∗ $\pi-\pi$-stacking interaction relative to the sum of the total energies of the free species. When unsubstituted C$_5$H$_5$ ligands were used instead of Cp∗, the relative energy dropped to 1.3 kcal/mol. Even though the values of these model calculations on cutouts of the total structures seem to be small, one should take into consideration that similar to hydrogen bonding of these $\pi-\pi$-stacking interactions such values are significant because they behave additively in the crystal lattice and sum up to large total values.

In summary, polycarborane-substituted molecules [Cp∗Rh{E$_2$C$_2$(B$_{10}$H$_{10}$)}]$_3$(tpst) [E = S (**2a**), Se (**2b**)] are reported in this paper. **2a** and **2b** form toluene solvates in the solid state, showing infinitely connected [(**2a**,**b**)-toluene)]$_\infty$ helices. Cp∗−toluene−Cp∗ π-stacking interactions and unconventional BH$^{\delta-}$−pyridyl$^{\delta+}$ aromatic hydrogen bonding are expected to induce the supramolecular structures.[15] In further studies, we will explore the possibilities of **2a** and **2b** to accept other "flat" guest molecules, as well as the potential of these types of complexes for variations in the supramolecular motifs.

Acknowledgment. This work was supported by the National Science Foundation of China (20531020, 20721063, and 20771028), by Shanghai Leading Academic Discipline project (B108), and by Shanghai Science and Technology Committee (06XD14002). H.B. received a grant from the Key Foreign Experts Program of Ministry of Education during his stay at Fudan University, which is gratefully acknowledged.

Supporting Information Available: Listings of experimental details, crystal-structure determination, and X-ray crystallographic files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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