Carborane-Functionalized Polyaza Aromatic Ligands: Synthesis, Crystal Structure, and a Copper(II) Complex

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A consecutive aromatic nucleophilic substitutions of hydrogen in 1,2,4-triazine 4-oxides and an aza Diels−Alder reaction is a versatile route to carborane-functionalized bi- and terpyridines and their 1,2,4-triazine analogues. The heterocycles facilitate deboronation of the substituted carboranes, and the carborane moiety has a significant influence on the coordination properties of the ligands as well.

Polypyridines (i.e. 2,2′-bipyridines, 2,2′:6′,2″-terpyridines, phenanthrolines, and their aza analogues) are undoubtedly among the most widely used ligands in coordination and supramolecular chemistry.[1] It has been shown in numerous studies that transition-metal polypyridine complexes have various applications: from catalysis[2] and photocatalysis[3] to analytical reagents[4] and selective extracting agents in the separation of lanthanides and actinides in the management of nuclear wastes.[5] We have been developing strategies for the synthesis of functionalized aza aromatic ligands and their metallo complexes.[6] Our approach combines two general features of the 1,2,4-triazines: (1) a susceptibility to nucleophilic aromatic substitution reactions[7] and (2) the relatively easy transformation of 1,2,4-triazines to pyridines via an aza Diels−Alder reaction.[8] In particular, we decided to obtain carborane-functionalized ligands of the pyridine and 1,2,4-triazine series, since they are expected to exhibit properties different from "typical" polypyridines due to the steric and electronic influence of a carborane moiety.[9] However, one of the most appropriate methods for the synthesis of *C*-heteroaryl carboranes (i.e. condensation of haloheteroarenes with *C*-copper[10] or *C*-lithium[9,11] carboranes) is limited by the starting materials. In this paper we describe some of our studies in ligand design and initial studies of coordination properties of new carborane-functionalized polypyridines.

We chose to use the available 3-pyridyl-1,2,4-triazine 4-oxides[6a] as precursors to the cluster-functionalized ligands. The triazine **1** is expected to react with nucleophiles at the 5-site with concomitant loss of the *N*-oxygen in the presence of acylating agents.[7]

Lithiation of 1-phenyl-1,2-dicarba-*closo*-dodecaborane generated 2-lithium-1-phenyl-1,2-dicarba-*closo*-dodecaborane in situ, and this was reacted with the 1,2,4-triazine 4-oxide **1** in THF. Treatment of the reaction mixture with *N*,*N*-dimethylcarbamyl chloride resulted in the formation of 1-(1,2,4-triazin-5-yl)-1,2-dicarba-*closo*-dodecaborane (**2a**) as an air-stable yellow solid in 56% yield (Scheme 1). The reaction is expected to proceed by addition of the nucleophile at the 5-site of the 1,2,4-triazine ring followed by aromatization of the intermediate σ adducts.[12] To provide the latter step, an O-acylation of the σ adduct is usually used to eliminate an acid molecule instead of water. Only smoothly acylating agents can be used in the reaction described: dimethylcarbamyl chloride or acetic anhydride (the former gave better yields). Acetyl chloride has to be avoided

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(1) (a) Lehn, J.-M. *Supramolecular Chemistry-Concepts and Perspectives*; VCH: Weinheim, Germany, 1995. (b) Ward, M. D. *Chem. Soc. Rev.* **1995**, 121. (c) Constable, E. C. *Prog. Inorg. Chem.* **1994**, *42*, 67.

(2) Chelucci, G.; Thummel, R. P. *Chem. Rev.* **2002**, *102*, 3129.

(3) Ziessel, R. In *Photosensitization and Photocatalysis Using Inorganic and Organic Compounds*; Kalyanasundaram, K., Grätzel, M., Eds.; Kluwer Academic: Dordrecht, The Netherlands, 1993; p 217.

(4) Croot, P. L.; Hunter, K. A. *Anal. Chim. Acta* **2000**, *406*, 289−295.

(5) Kolarik, Z.; Mullich, U.; Gassner, F. *Solvent Extr. Ion Exch.* **1999**, *17*, 23.

(6) (a) Kozhevnikov, V. N.; Kozhevnikov, D. N.; Nikitina, T. V.; Rusinov, V. L.; Chupakhin, O. N.; Zabel, M.; Koenig., B. *J. Org. Chem.* **2003**, *68*, 2882. (b) Kozhevnikov, V. N.; Kozhevnikov, D. N.; Rusinov, V. L.; Chupakhin, O. N.; Koenig, B. *Synthesis* **2003**, 2400. (c) Kozhevnikov, V. N.; Kozhevnikov, D. N.; Shabunina, O. V.; Rusinov, V. L.; Chupakhin, O. N. *Tetrahedron Lett.* **2005**, *46*, 1791. (d) Kozhevnikov, V. N.; Kozhevnikov, D. N.; Prokhorov, A. M.; Ustinova, M. M.; Rusinov, V. L.; Chupakhin, O. N. *Tetrahedron Lett.* **2006**, *47*, 869.

(7) (a) Neunhoeffer, H. In *Comprehensive Heterocyclic Chemistry II*; Katrizky, A. R., Rees, C. W., Scriven, E. F. V., Eds.; Pergamon Press: Oxford, U.K., 1996; Vol. 6, p 50. (b) Kozhevnikov, D. N.; Rusinov, V. L.; Chupakhin, O. N. *Adv. Heterocycl. Chem.* **2002**, *82*, 261.

(8) (a) Pabst, G. R.; Pfüller, O. C.; Sauer, J. *Tetrahedron* **1999**, *55*, 8045. (b) Stanforth, S. P.; Tarbit, B.; Watson, M. D. *Tetrahedron* **2004**, *60*, 8893. (c) Kozhevnikov, V. N.; Kozhevnikov, D. N.; Shabunina, O. V.; Rusinov, V. L.; Chupakhin, O. N. *Tetrahedron Lett.* **2005**, *46*, 1791. (d) Branowska, D.; Rykowski, A.; Wysocki, W. *Tetrahedron Lett.* **2005**, *46*, 6223.

(9) (a) Armspach, D.; Constable, E. C.; Housecroft, C. E.; Neuburger, M.; Zehnder, M. *New J. Chem.* **1996**, *20*, 331. (b) Armspach, D.; Constable, E. C.; Housecroft, C. E.; Neuburger, M.; Zehnder, M. *Supramol. Chem.* **1996**, *7*, 97. (c) Armspach, D.; Constable, E. C.; Housecroft, C. E.; Neuburger, M.; Zehnder, M. *J. Organomet. Chem.* **1998**, *550*, 193.

(10) Coult, R.; Fox, M. A.; Gill, W. R.; Herbertson, P. L.; MacBride, J. A. H.; Wade, K. *J. Organomet. Chem.* **1993**, *462*, 19.

(11) Hawthorne, M. F.; Maderma, A. *Chem. Rev.* **1999**, *99*, 3421.

(12) Chupakhin, O. N.; Prokhorov, A. M.; Kozhevnikov, D. N.; Rusinov, V. L.; Glukhov, I. A.; Starikova, Z. A.; Olshevskaya, V. A.; Kalinin, V. N.; Antipin, M. Yu. *Russ. Chem. Bull. (Engl. Transl.)* **2004**, *53*, 1223.

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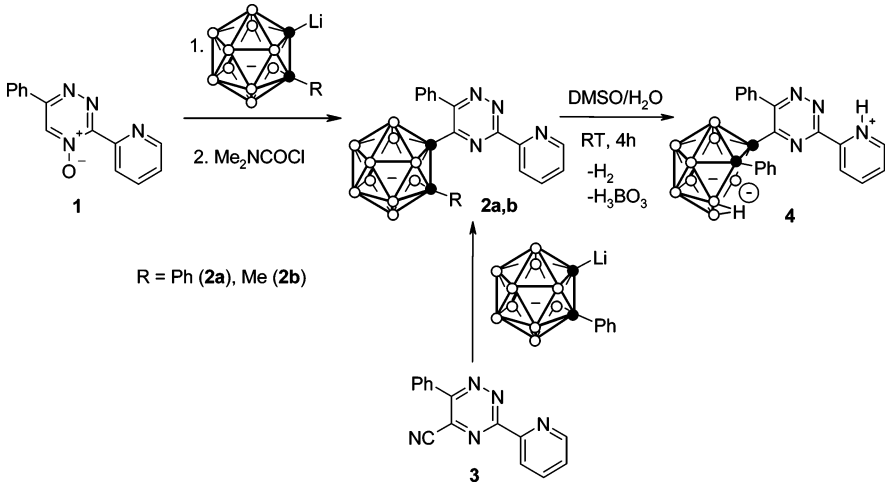
Scheme 1



because it induces 1,2,4-triazine ring contraction to give carboranyltriazolines.[12] The ^{1}H and ^{13}C NMR spectra of **2a** and elemental analysis confirmed the proposed structure. The ^{1}H NMR spectrum of **2a** showed typical signals for the two phenyls and the 2-pyridyl moiety and a broad multiplet for the B−H protons as well. The absence of a low-field singlet indicated the H-5 substitution. Elemental analysis confirmed loss of the *N*-oxygen atom. Both the ^{11}B and ^{13}C NMR spectra of **2a** were in accord with a 1,2-disubstituted *closo*-dodecaborane. In particular, the ^{11}B NMR spectrum exhibited two signals indicative of the most deshielded atoms, B-3 and B-6 (δ −3.5 and −1.4), and broad signal for the remaining boron atoms. The ^{13}C NMR spectrum of **2a** was fully consistent with the presence of two phenyl groups, pyridyl, 1,2,4-triazine, and *closo*-carborane.

Single crystals of compound **2a** suitable for X-ray diffraction were grown from acetonitrile. The molecular structure of **2a** is shown in Figure 1, and selected bond distances are given in the figure caption. The structural parameters for the ordered *closo*-dodecaborane cage are unexceptional.[13] The pyridyltriazine fragment is approximately planar, while the torsion angle between the 1,2,4-triazine ring and the aromatic substituent is 56.28°. 1,2,4-Triazine ring and phenyl binding to the cluster

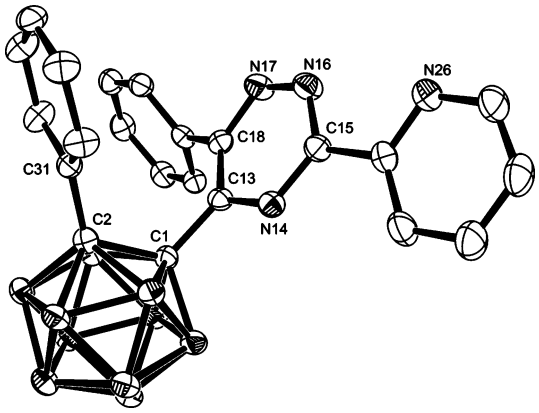


Figure 1. Molecular structure of **2a**. Hydrogens are omitted. Selected bond lengths (Å): C(1)−C(13) = 1.522(3), C(1)−C(2) = 1.725(3), C(1)−B(3) = 1.724(3), C(1)−B(4) = 1.701(4), C(1)−B(5) = 1.706(3), C(1)−B(6) = 1.737(3), C(2)−B(3) = 1.733(4), C(2)−B(6) = 1.733(3), C(2)−B(7) = 1.714(3), C(2)−B(11) = 1.707(3), C(2)−C(31) = 1.498(3). Selected torsion angles (deg): C(2)−C(1)−C(13)−N(14) = 97.4(2), C(1)−C(2)−C(31)−C(36) = 89.3(2).

are almost perpendicular to the C−C bond of the carborane (the torsion angles are 78.92 and 89.32°, respectively).

As an additional confirmation, we carried out the straightforward synthesis of **2a** via the well-studied reaction of nucleophilic substitution of the cyano group in 5-cyano-1,2,4-triazines with carbanions.[14] All spectroscopic data for the product of the reaction of 1-lithio-2-phenyl-1,2-dicarba-*closo*-dodecaborane with 5-cyano-6-phenyl-3-(pyridyl-2)-1,2,4-triazine (**3**) were identical with those of triazinylcarborane **2a**.

The reaction of triazine **1** with lithiated 1-methyl-1,2-dicarba-*closo*-dodecaborane under the conditions mentioned above yielded the methylcarboranyltriazine **2b** (Scheme 1). Spectroscopic data and elemental analysis were consistent with the formulation of **2b**.

We found that the triazinylcarborane **2a** very easily underwent a decapping process in polar solvents in the presence of water under neutral conditions. The zwitterionic 1,2,4-triazinyl-*nido*-carborane **4** was obtained in quantitative yield at room temperature by dissolving **2a** in DMSO containing 5−10% of water. The structure of **4** was defined by ^{1}H and ^{11}B NMR spectroscopy. The ^{1}H NMR spectrum of **4** showed signals typical of phenyl groups and 2-pyridyl. The most diagnostic feature is the observation of a bridging hydrogen (highest field broad signal, δ −2.75) and an acid proton (lowest field broad signal, δ 10.2 ppm) of the deboronated *nido*-carborane. All signals of the ^{11}B NMR spectrum of **4** are shifted to higher field (highest field resonance δ −33.6) in comparison with **2a**, which provides additional evidence for the formation of an anionic nido cluster.[9]

Single-crystal X-ray diffraction studies of compound **4** revealed the molecular structure shown in Figure 2. The bridging hydrogen atom binds to boron atoms next to the carbon bound to phenyl. The geometry of the phenylpyridyltriazine moiety of **4** is very similar to that of **2a**, except for N-protonation of the pyridyl group. The 1,2,4-triazine ring is perpendicular to, while phenyl is nearly coplanar with, the open face of the cluster.

A similar zwitterion formation was found to occur in the deboronation of terpyridylcarborane.[9] However, we were lucky to observe the decapping process *live* with ^{1}H NMR spectroscopy. Thus, the appearance and rise of three new signals in the ^{1}H NMR spectra of **2a** solution in wet DMSO-d_6 (1% of water) were clearly observed in 5 min after dissolving **2a** at room

(13) Beaudet, R. A. In *Advances in Boron and the Boranes*; Liebman, J. F.., Greenberg, A., Williams, R. E., Eds.; VCH: New York, 1988; p 417.

(14) Konno, S.; Ohba, S.; Agata, M.; Aizawa, V.; Sagi, M.; Yamanaka, H. *Heterocycles* **1987**, *26*, 3259.

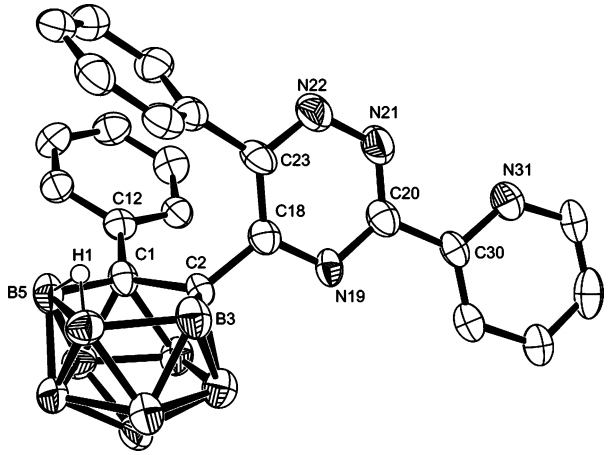
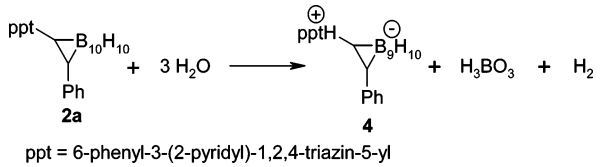


Figure 2. Molecular structure of **4**. Hydrogens are omitted. Selected bond lengths (Å): C(1)−C(12) = 1.513(4), C(1)−C(2) = 1.596(4), C(1)−B(5) = 1.655(4), C(2)−B(3) = 1.614(5), C(2)−C(18) = 1.497(4). Selected torsion angles (deg): C(1)−C(2)−C(18)−C(23) = 58.4(4), C(2)−C(1)−C(12)−C(17) = 35.6(4).

Scheme 2



ppt = 6-phenyl-3-(2-pyridyl)-1,2,4-triazin-5-yl

temperature. Full conversion of **2a** to **4** under the conditions discussed occurred in 30 h. Resonances for a bridging hydrogen (highest field broad signal, δ −2.75) and an acid proton (lowest field broad signal, δ 10.2 ppm) indicated formation of the zwitterion **4**. The third signal (sharp singlet, δ 4.61) was a puzzle; it could not be explained in terms of structures **2** and **4**. However, the full equation of the decapping reaction shows that formation of the zwitterion **4** in the presence of water is accompanied by elaboration of boric acid and molecular hydrogen (Scheme 2). The resonance of the latter could be the signal observed. However, we were surprised that it was not easy to find literature data on the chemical shift for such a simple molecule. Only in a recent issue of *J. Am. Chem. Soc.* did we find a resonance for *o*-hydrogen (*o*-H_2) in polar solvents observed around δ 4.6.[15] To remove all doubt, we bubbled gaseous hydrogen through DMSO-d_6 in an NMR tube and observed the same signal (δ 4.61).

Increasing the water concentration significantly increases the rate of the decapping reaction. Full conversion of **2a** to **4** occurred in 3−4 h at room temperature in a DMSO−water mixture (5:1).

The triazines **2** are potential N,N-chelating ligands; nitrogen atoms of the 1,2,4-triazine and pyridine moieties can act as donor atoms in transition-metal coordination. However, the N-4 atom of the 1,2,4-triazine is obviously hindered by the bulk carborane moiety. Thus, reaction of **2b** with copper(II) chloride resulted in the complex $[Cu_2(\mathbf{2b})_2Cl_4]$, where N-2 but not N-4 is coordinated to the metal. Single-crystal X-ray diffraction studies of the complex revealed the molecular structure shown in Figure 3. Complex $[Cu_2(\mathbf{2b})_2Cl_4]$ is a dinuclear centrosymmetric dimer. Each Cu atom is chelated by bidentate **2b**. In addition, two bridging and one exocyclic chloride anion complete the five-coordinated square-pyramidal structure of each copper(II) center.

(15) Matsumoto, M.; Espenson, J. H. *J. Am. Chem. Soc.* **2005**, *127*, 11447.

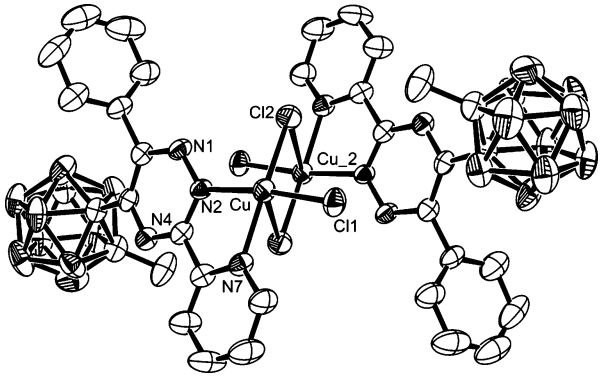


Figure 3. Molecular structure of $[Cu_2(\mathbf{2b})_2Cl_4]$. Selected bond lengths (Å): N(2)−Cu = 2.029(2), N(7)−Cu = 2.054(3), Cu−Cl(1) = 2.2523(11), Cu−Cl(2) = 3.4131(14),

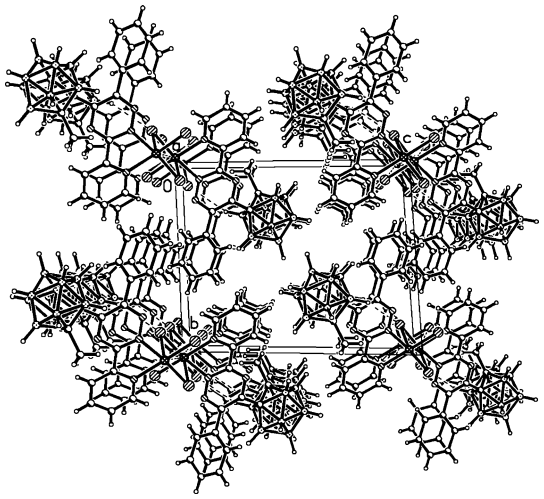


Figure 4. Crystal structure of $[Cu_2(\mathbf{2b})_2Cl_4]$.

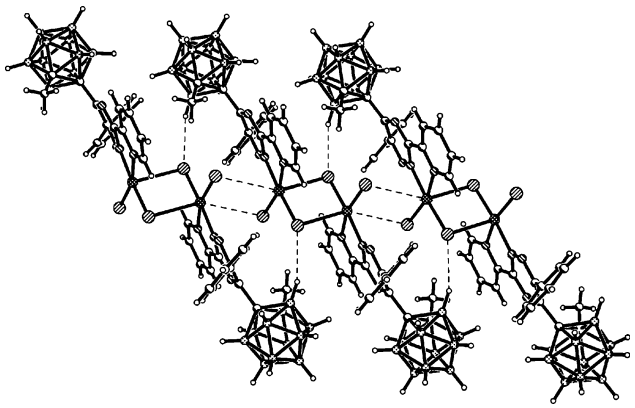
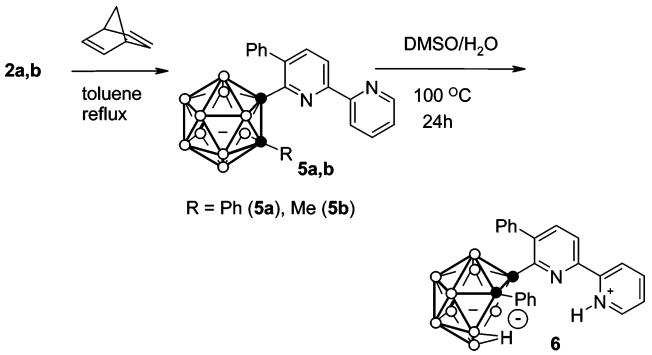


Figure 5. Chains of $[Cu_2(\mathbf{2b})_2Cl_4]$ along the *a* axis.

In the crystal state the complex $[Cu_2(\mathbf{2b})_2Cl_4]$ forms chains along the *a* axis due to intermolecular interactions Cu···Cl(2*) of length 3.413(1) Å, less than the sum of the van der Waals radii of Cu and Cl (3.7 Å) (Figures 4 and 5). The structure of the ligand **2b** in the complex is very similar to that of **2a**.

The electron-withdrawing *closo*-carborane moiety had to facilitate transformation of the 1,2,4-triazine ring to pyridine via an inverse electron-accepting aza Diels−Alder reaction. Indeed, refluxing the triazines **2a**,**b** with 2,5-norbornadiene in toluene yielded the 6-(*closo*-carboranyl)-2,2′-bipyridines **5a**,**b** (Scheme 3). The structures of the latter were defined by ^{1}H, ^{13}C, and ^{11}B NMR spectroscopy. The most indicative feature is the observation of H-4 and H-3 protons of the new pyridine

Scheme 3



ring as two doublets at δ 7.5 and 8.3 (J = 8.0 Hz) and two additional signals in the ^{13}C NMR spectra of **5a**,**b** in comparison with those of **2a**,**b**. Transformation of the triazine ring to pyridine did not actually change the ^{11}B NMR spectra.

The carboranylbipyridine **5a** underwent a deboronation reaction similar to that of carboranyltriazine **2a**, but at a significantly decreased rate: just prolonged heating (not less than 24 h) of **5a** at 90 °C in DMSO/water (5:1) gave the *nido*-carboranyl-2,2′-bipyridine **6** (Scheme 3). The observation of the ^{11}B resonance of **6** shifting to higher field (highest field resonance, δ −33.5) in comparison with **5a** provided evidence for the formation of an anionic nido cluster. Moreover, the ^{11}B NMR spectrum of **6** became more complicated: for **5a,** chemical shifts of all boron atoms except B-3 and B-6 are very close and are represented by one broad singlet, whereas for **6**, the shifts are more different because of deboronation and carborane cage symmetry breakdown.[9] X-ray diffraction studies revealed the structure of the zwitterion **6**, shown in Figure 6. The molecular structure of bipyridine **6** is very similar to that of triazine **4**. The approximately planar bipyridinium cation adopts a cis conformation of the two pyridine rings about the interannular bond. Molecules of **6** form stacks with alternation of the anionic carborane moiety of one molecule and the cationic bipyridine residue of the next molecule.

The deboronation reactions of **2a** and **5a** can be considered as a process facilitated by the basicity of pyridine or triazine groups. The heterocycles can serve as intramolecular bases, generating hydroxides as deboronating agents. From this point of view, the rates of the decapping of both compounds have to be approximately equal. Moreover, taking into consideration that pyridine is more basic than 1,2,4-triazine, the easiest deboronation can be expected for carboranylbipyridine **5a**, but experimental data do not confirm this consideration. On the other hand, a significant difference in the electron-withdrawing properties of these heterocyclic systems is a more plausible argument. It is known[16] that introduction of an electron-withdrawing substituent renders the carborane cage susceptible to removal of a boron vertex. The influence of the heterocycle attached to the carborane may be directly quantified by a comparison of the carborane carbon C-1′ resonances in compounds **2a** and **5a**. In the triazine **2a** C-1′ is observed at δ 86.6, whereas in the pyridine **5a** C-1′ is observed at δ 69.5. This indicates a stronger deshielding effect of the more π-deficient 1,2,4-triazine in comparison with pyridine. Obviously, a nucleophilic attack on the carborane binding to 1,2,4-triazine has to be more facilitated. Indeed, the decapping of the triazine **2a** proceeds in a DMSO−water mixture (5:1) at room temperature in 4 h, while the same reaction of the pyridine **5a** was observed only after 24 h of heating at 100 °C.

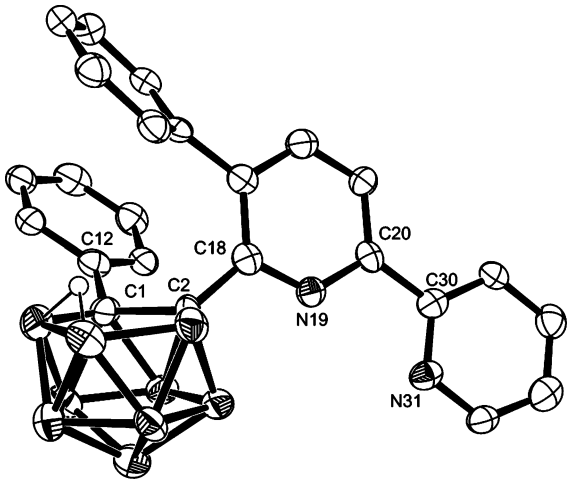


Figure 6. Molecular structure of **6**. Hydrogens are omitted. Selected bond lengths (Å): C(1)−C(12) = 1.503(4), C(1)−C(2) = 1.579(4), C(2)−C(18) = 1.486(4), C(1)−B(5) = 1.623(5), C(2)−B(3) = 1.614(4). Selected torsion angles (deg): C(1)−C(2)−C(18)−C(23) = 61.5(4), C(2)−C(1)−C(12)−C(17) = 46.2(4).

The suggested approach is appropriate for the synthesis of tricyclic azines bearing two carborane cages. The reaction of the bis(1,2,4-triazinyl)pyridine *N*,*N*′-dioxide **7** with *o*-carboranes under the conditions mentioned above resulted in the bis[5-carboranyl-1,2,4-triazinyl]pyridines **8a**,**b**. The dicarboranyltriazine **8b** was transformed to the 6,6″-bis(2-methyl-*o*-carboran-1-yl)-2,2′:6′,2″-terpyridine **9** through the aza Diels−Alder reaction of **8** with 2,5-norbornadiene in a way similar to that for the monocarboranyltriazines **2** (Scheme 4). Compounds **8a**,**b** and **9** exhibited the expected spectroscopic properties. The ^{1}H NMR spectra of **8a**,**b** and **9** are in accord with the presence of two carborane moieties in the molecules. The ^{1}H NMR spectrum of **9** showed signals typical for the terpyridine moiety, indicating that both triazine rings transformed to pyridine rings via the reaction with norbornadiene. Elemental analysis confirmed the proposed structures.

Conclusions

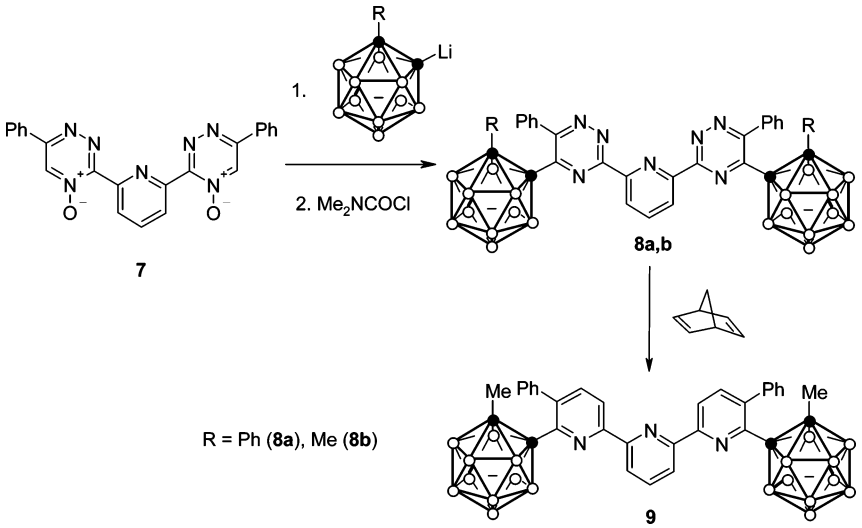
In conclusion, we have shown that carboranyl-functionalized aza aromatic ligands may be obtained using a consecutive nucleophilic aromatic substitution and aza Diels−Alder reaction. The method is limited by aryl substituents in 1,2,4-triazine/pyridine rings because of limitations of the method for the synthesis of the starting 6-(hetero)aryl-3-pyridyl-1,2,4-triazine 4-oxides.[6a] Carborane-functionalized pyridyl-1,2,4-triazines are interesting ligands for transition metals due to the electronic and steric influence of the carborane cage. The easy deboronation reaction extends this approach to new compounds.

Experimental Section

General Remarks. The manipulations were performed under an atmosphere of dry argon using vacuum-line and standard Schlenk techniques. All reagents were obtained from commercial suppliers and used without further purification. Solvents were dried by standard methods and distilled under nitrogen before use. The starting compounds **1**, **3**, and **7** were prepared according to methods reported in the literature.[6a] The C, H, and N analyses were carried out with a Perkin-Elmer PE 2400 microanalyzer. Mass spectra were determined with a Varian CH-5 mass spectrometer. NMR spectra were recorded on a Bruker DPX-300 instrument at 300 MHz (^{1}H),

(16) Schaeck, J. J.; Kahl, S. B. *Inorg. Chem.* **1999**, *38*, 204.

Scheme 4



75.4 MHz (^{13}C), or 128.4 MHz (^{11}B), using $SiMe_4$ (^{1}H and ^{13}C NMR) and $BF_3 \cdot Et_2O$ (^{11}B NMR) as standards.

Preparation of 1-(3,6-Disubstituted 1,2,4-triazin-5-yl)-1,2-dicarba-*closo*-dodecaboranes (2). *tert*-Butyllithium (1.6 M pentane solution, 2.5 mL) was added to a solution of the carborane (4 mmol) in 20 mL of THF at room temperature. The resulting solution of carboranyllithium was added dropwise to a suspension of the 1,2,4-triazine 4-oxide **1** (1.0 g, 4 mmol) in THF (10 mL) at −50 °C, and the mixture was stirred for 20 min. When the mixture had become clear, dimethylcarbamyl chloride (0.37 mL, 4 mmol) was added. The solvent was removed, and the residue was treated with toluene (20 mL). The toluene solution was separated from the solids, and the solvent was removed. The residue was treated with acetonitrile (1 mL), and pale yellow crystals were filtered off. All of the products were recrystallized from acetonitrile.

1-[6-Phenyl-3-(2-pyridyl)-1,2,4-triazin-5-yl]-2-phenyl-1,2-dicarba-*closo*-dodecaborane (2a). Yield: 1.03 g, 56%. Mp: 227 °C. ^{1}H NMR ($CDCl_3$; δ): 1.20−3.20 (m, 10H, B−H), 7.10−7.30 (m, 7H), 7.40−7.60 (m, 4H), 7.97 (m, 1H, Py), 8.42 (m, 1H, Py), 8.92 (m, 1H, Py). ^{13}C NMR ($CDCl_3$; δ): 81.6 (carborane C-2′), 86.6 (carborane C-1′), 124.4 (Py), 126.1 (Py), 128.3, 128.5, 129.6, 129.9, 130.4, 130.5, 130.8, 134.7, 137.3 (Py), 145.0, 150.8 (Py), 151.3 (Py), 158.1, 159.00. ^{11}B{^{1}H} NMR ($CDCl_3$): −10.3 (8B), −3.5 (1B), −1.4 (1B). Anal. Calcd for $C_{22}H_{24}B_{10}N_4$: C, 58.39; H, 5.35; N, 12.38. Found: C, 58.33; H, 5.37; N, 12.26.

1-[6-Phenyl-3-(2-pyridyl)-1,2,4-triazine-5-yl]-2-methyl-1,2-dicarba-*closo*-dodecaborane (2b). Yield: 900 mg, 48%. Mp: 183 °C. ^{1}H NMR ($CDCl_3$; δ): 1.86 (s, 3?, CH_3), 1.20−3.20 (m, 10H, B−H), 7.46 (m, 2H), 7.50−7.65 (m, 4H), 7.98 (m, 1H), 8.58 (m, 1H), 8.95 (m, 1H). Anal. Calcd for $C_{17}H_{22}B_{10}N_4$: C, 52.29; H, 5.68; N, 14.35. Found: C, 52.33; H, 5.48; N, 14.36.

Reaction of 5-Cyano-1,2,4-triazine (3) with Carborane. *tert*-Butyllithium (1.6 M pentane solution, 2.5 mL) was added to a solution of the phenylcarborane (880 mg, 4 mmol) in 20 mL of THF at room temperature. The resulting solution of carboranyllithium was added dropwise to a solution of the cyanotriazine **3** (1036 mg, 4 mmol) in THF (10 mL) at −50 °C; the mixture was stirred for 25 min, and acetic acid (0.24 mL, 4 mmol) was added. The solvent was removed, and the residue was treated with toluene (20 mL). The toluene solution was separated from the solids, and the solvent was removed. The residue was treated with acetonitrile (1 mL), and pale yellow crystals were filtered off and recrystallized from acetonitrile to give the carboranyltriazine **2a**. Yield: 864 mg, 47%.

1-[6-Phenyl-3-(2-pyridyl)-1,2,4-triazin-5-yl]-2-phenyl-1,2-dicarba-*nido*-undecaborane (4). The triazinyl-*closo*-carborane **2a** (452 mg, 1 mmol) was dissolved in DMSO (5 mL); then water (1 mL) was added, and the resulting solution was kept at room temperature for 4 h. Next, 10 mL of water was added, and the yellow precipitate was filtered off and recrystallized from acetonitrile. Yield: 380 mg, 85%. Mp: >300 °C dec. ^{1}H NMR (δ): −2.85 (br s, 1H, carborane bridge H), 0.20−3.00 (m, 9H, B−H), 6.47−6.91 (m, 5H, Ph), 7.30−7.49 (m, 5H, Ph), 8.05 (m, 1H, Py), 8.59 (m, 1H, Py), 8.74 (m, 1H, Py), 8.92 (m, 1H, Py), 10.21 (br s, 1H). ^{11}B{^{1}H} NMR ($CDCl_3$; δ): −33.6 (2B), −31.6 (1B), −21.8 (2B), −11.8 (2B), −7.4 (1B), −2.4 (1B). Anal. Calcd for $C_{22}H_{25}B_9N_4 \cdot CH_3CN$: C, 59.58; H, 5.83; N, 14.48. Found: C, 59.49; H, 5.81; N, 14.60. MS (EI-MS): *m*/*z* 442 [M^+].

Preparation of Carboranylbipyridines 5a,b. The carboranyltriazines **2a**,**b** (1 mmol) and 2,5-norbornadiene (0.54 mL, 5 mmol) were dissolved in toluene (20 mL) and heated at reflux for 5 h. The solvent was removed under reduced pressure, the residue was treated with acetonitrile, and the resulting solids were filtered off.

1-(5-Phenyl-2,2′-bipyridin-6-yl)-2-phenyl-1,2-dicarba-*closo*-dodecaborane (5a). Yield: 410 mg, 90%. Mp: 183 °C. ^{1}H NMR (δ): 1.20−3.50 (m, 10H, B−H), 6.91 (m, 2H), 7.18−7.38 (m, 5H), 7.41−7.52 (m, 4H), 7.55 (d, 2H, J = 8.0 Hz), 8.08 (m, 1H, Py), 8.27 (d, 1H, J = 8.0 Hz), 8.33 (m, 1H, Py), 8.69 (m, 1H, Py). ^{13}C NMR ($CDCl_3$; δ): 47.4 (carborane C2′), 69.5 (carborane C1′), 122.3, 123.1, 123.6, 123.9, 124.0, 124.6, 125.3, 128.2, 128.6, 129.2, 157.1, 160.6, 164.0. ^{11}B{^{1}H} NMR ($CDCl_3$): −10.4 (8B), −3.5 (1B), −1.4 (1B). Anal. Calcd for $C_{24}H_{26}B_{10}N_2$: C, 63.97; H, 5.82; N, 6.22. Found: C, 63.83; H, 5.87; N, 6.26.

1-(5-Phenyl-2,2′-bipyridin-6-yl)-2-methyl-1,2-dicarba-*closo*-dodecaborane (5b). Yield: 398 mg, 90%. Mp: >300 °C. ^{1}H NMR (DMSO-d_6; δ): 1.88 (s, 3H, CH_3), 1.20−3.20 (m, 10H, B−H), 7.3−7.5 (m, 6H), 7.77 (d, 1H, J = 8 Hz), 8.03 (m, 1H, H-4′), 8.38 (m, 1H, H-3′), 8.50 (d, 1H, J = 8 Hz), 8.72 (m, 1H, H-6′). ^{13}C NMR ($CDCl_3$; δ): 47.4 (carborane C2′), 69.5 (carborane C1′), 122.3, 123.1, 123.6, 123.9, 124.0, 124.6, 125.3, 128.2, 128.6, 129.2, 157.1, 160.6, 164.0. ^{11}B{^{1}H} NMR ($CDCl_3$; δ): −10.05 (8B), −3.59 (1B), −1.39 (1B). Anal. Calcd for $C_{19}H_{24}B_{10}N_2$: C, 58.74; H, 6.23; N, 7.21. Found: C, 58.73; H, 6.27; N, 7.33.

Preparation of 1-(5-Phenyl-2,2′-bipyridin-6-yl)-2-phenyl-1,2-dicarba-*nido*-undecaborane (6). The bipyridylcarborane **5a** (450 mg, 1 mmol) was dissolved in 5 mL of DMSO; then 1 mL of water was added, and the resulting solution was kept at 90 °C for 24 h. Next, 10 mL of water was added, and the precipitate was filtered off and recrystallized from acetonitrile. Yield: 380 mg, 86%. Mp: > 300 °C dec. ^{1}H NMR (δ): −2.75 (br s, 1H), 0.00−3.00 (m, 9H, B−H), 6.65−6.90 (m, 5H, Ph), 6.97 (m, 2H), 7.20−7.35 (m, 3H), 7.53 (d, 1H, J = 8.0 Hz, H-4), 7.72 (m, 1H, H-5′), 8.22 (d, 1H, J = 8.0 Hz, H-3), 8.29 (m, 1H, H-4′), 8.65 (d, 1H, H-3′), 8.82 (m, 1H, H-6′), 11.00 (br s, 1H). ^{11}B{^{1}H} NMR ($CDCl_3$): −33.52 (2B),

Table 1. Crystal Data and Structure Refinement Details for 2a, 4, 6, and $[Cu_2(2b)_2Cl_4]$

	2a	4	6	$[Cu_2(\mathbf{2b})_2Cl_4]$
chem formula	$C_{22}H_{24}B_{10}N_4$	$C_{24}H_{28}B_9N_5$	$C_{24}H_{27}B_9N_2$	$C_{34}H_{44}B_{20}Cl_4Cu_2N_8$
fw	452.55	483.80	440.77	1049.85
T, K	120(2)	120(2)	120(2)	293
wavelength, Å	0.710 73	0.710 73	0.710 73	0.710 73
cryst syst	tetragonal	monoclinic	monoclinic	triclinic
space group	$P4_3$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a (Å)	11.231(1)	10.885(3)	10.574(2)	7.341(2)
b (Å)	11.231(1)	17.343(6)	15.120(2)	12.045(2)
c (Å)	19.104(2)	14.540(5)	14.707(2)	14.775(3)
α (deg)	90	90	90	84.33(2)
β (deg)	90	105.938(10)	96.781(4)	76.13(2)
γ (deg)	90	90	90	79.00(2)
V (Å^3)	2409.8(5)	2639.5(2)	2335.0(7)	1243.1(5)
Z	4	4	4	1
d_{calcd} (g cm^{-3})	1.247	1.217	1.254	1.40
μ (mm^{-1})	6.8	6.8	6.7	1.108
F(000)	936	1008	920	530
no. of rflns collected	9659	12 971	12 163	3467
no. of indep rflns	4609	4926	4510	3173
no. of params	365	384	360	367
R ($I > 2\sigma(I)$)				
R1	0.0487	0.0487	0.0629	0.035
wR2	0.0940	0.0940	0.0995	0.070

−31.94 (1B), −21.72 (2B), −12.60 (2B), −8.77 (1B), −2.76 (1B). Anal. Calcd for $C_{24}H_{27}B_9N_2$ (440.78): C, 65.40; H, 6.17; N, 6.36. Found: C, 65.49; H, 6.11; N, 6.49. MS (EI-MS): *m*/*z* 440 [M^+].

2,6-Bis[6-phenyl-5-(2-phenyl-1,2-dicarba-*closo*-dodecaboran-1-yl)-1,2,4-triazin-3-yl]pyridine (8a). *tert*-Butyllithium (1.6 M pentane solution. 2.5 mL, 4 mmol) was added to a solution of phenylcarborane (880 mg, 4 mmol) in 20 mL of THF at room temperature. The resulting solution of carboranyllithium was added dropwise to a suspension of the 1,2,4-triazine 4-oxide **7** (842 mg, 2 mmol) in THF (10 mL) at −50 °C, and the mixture was stirred for 20 min. When the mixture had become clear, dimethylcarbamyl chloride (0.37 mL, 4 mmol) was added. The solvent was removed, and the residue was treated with toluene (30 mL). The toluene solution was separated from the solids, and the solvent was removed. The residue was treated with acetonitrile (1 mL), and pale yellow crystals were filtered off and recrystallized from acetonitrile. Yield: 332 mg, 20%. Mp: 262 °C. ^{1}H NMR ($CDCl_3$; *δ*): 1.20−3.20 (m, 20H, B−H), 7.13−7.65 (m, 20H, Ph), 8.35 (t, 1H, $J = 8.0$ Hz, Py), 8.62 (d, 2H, $J = 8.0$ Hz, Py). Anal. Calcd for $C_{39}H_{43}B_{20}N_7$: C, 56.71; H, 5.25; N, 11.87. Found: C, 56.83; H, 5.39; N, 11.96.

2,6-Bis[5-(2-methyl-1,2-dicarba-*closo*-dodecaboran-1-yl)-6-phenyl-1,2,4-triazin-3-yl]pyridine (8b). *tert*-Butyllithium (1.6 M pentane solution, 5 mL, 8 mmol) was added to a solution of methylcarborane (1264 mg, 8 mmol) in 30 mL of THF at room temperature. The resulting solution of carboranyllithium was added dropwise to a suspension of the 1,2,4-triazine 4-oxide **7** (1684 mg, 4 mmol) in THF (20 mL) at −50 °C, and the mixture was stirred for 20 min. When the mixture became clear, dimethylcarbamyl chloride (0.74 mL, 8 mmol) was added. The solvent was removed, and the residue was treated with toluene (30 mL). The toluene solution was separated from the solids, and the solvent was removed. The residue was treated with acetonitrile (1 mL), and pale yellow crystals were filtered off and recrystallized from acetonitrile. Yield: 1.48 g, 53%. Mp: >300 °C. ^{1}H NMR ($CDCl_3$; *δ*): 1.93 (s, 6H, carborane CH_3), 1.20−3.20 (m, 20H, B−H), 7.49−7.65 (m, 10H, Ph), 8.29 (t, 1H, $J = 7.9$ Hz, Py), 8.85 (d, 2H, $J = 7.9$ Hz, Py). Anal. Calcd for $C_{29}H_{39}B_{20}N_7$: C, 49.62; H, 5.60; N, 13.97. Found: C, 49.46; H, 5.76; N, 13.82.

Preparation of 6,6″-Bis(2-methyl-1,2-dicarba-*closo*-dodecaboran-1-yl)-5,5″-diphenyl-2,2′:6′,2″-terpyridine (9). The carboranyltriazine **8b** (702 mg, 1 mmol) and 2,5-norbornadiene (1.08 mL, 10 mmol) were dissolved in toluene (30 mL) and heated to reflux over 6 h. The solvent was removed under reduced pressure, the residue was treated with acetonitrile, and the resulting solids were filtered off. Yield: 630 mg, 91%. Mp: >300 °C. ^{1}H NMR ($CDCl_3$; *δ*): 1.20−3.20 (m, 20H, B−H), 1.82 (s, 6H), 7.25 (m, 4H), 7.47 (m, 6H), 7.69 (d, 2H, $J = 7.8$ Hz), 8.14 (t, 1H, $J = 8.0$ Hz), 8.60 (d, 2H, $J = 7.8$ Hz), 8.64 (d, 2H, $J = 8.0$ Hz). Anal. Calcd for $C_{33}H_{43}B_{20}N_3$: C, 56.79; H, 6.21; N, 6.02. Found: C, 56.70; H, 6.37; N, 6.16.

Complex $[Cu_2(2b)_2Cl_4]$. A solution of $CuCl_2 \cdot 2H_2O$ (34 mg, 0.20 mmol) in acetonitrile (20 mL) was added to a solution of the ligand (78 mg, 0.20 mmol) in acetonitrile (30 mL). The mixture was slowly concentrated over a few days to about 20 mL. Dark green crystals (50 mg, 47%) were filtered off. Anal. Calcd for $C_{34}H_{44}B_{20}Cl_4Cu_2N_8$: C, 38.90; H, 4.22; N, 10.67. Found: C, 39.06; H, 4.35; N, 10.91.

X-ray Structure Determinations of 2a, 4, 6, and $[Cu_2(2b)_2Cl_4]$. Crystals suitable for X-ray diffraction analysis were obtained by slow solvent (MeCN) evaporation from saturated solutions of **2a**, **4**, **6**, and $[Cu_2(\mathbf{2b})_2Cl_4]$ in acetonitrile. Data collection, crystal, and refinement parameters are collected in Table 1. Diffraction data for **2a**, **4**, and **6** were recorded on a Bruker Smart 1000 diffractometer and for complex $[Cu_2(\mathbf{2b})_2Cl_4]$ on an Enraf-Nonius CAD-4 diffractometer (in all cases $\omega/2\theta$ scans, Mo Kα radiation). The structures were solved by direct methods. Isotropic least-squares refinement on F^2 was performed. During the final stages of the refinements, all positional parameters and the anisotropic temperature factors of all non-H atoms were refined. The H atoms were geometrically placed, and their coordinates were refined riding on their parent atoms with common isotropic thermal parameters. All calculations were performed using SHELXTL 5.1 (for **2a**, **4**, and **6**) and SHELXL97 (for the complex $[Cu_2(\mathbf{2b})_2Cl_4]$).[17]

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Supporting Information Available: Crystallographic data for the structures of **2a**, **4**, **6** and the complex $[Cu_2(\mathbf{2b})_2Cl_4]$ as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org. These data have also been deposited with the Cambridge Crystallographic Data Center as Supplementary Nos. CCDC 210343−210345 and 284092. Copies of the data can be obtained free of charge on application to the CCDC (e-mail: deposit@ccdc.cam.ac.uk).

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(17) (a) Sheldrick, G. M. SHELXTL 5.1; University of Göttingen, Göttingen, Germany, 1998. (b) Sheldrick, G. M. SHELXL-97; University of Göttingen, Göttingen, Germany, 1997.