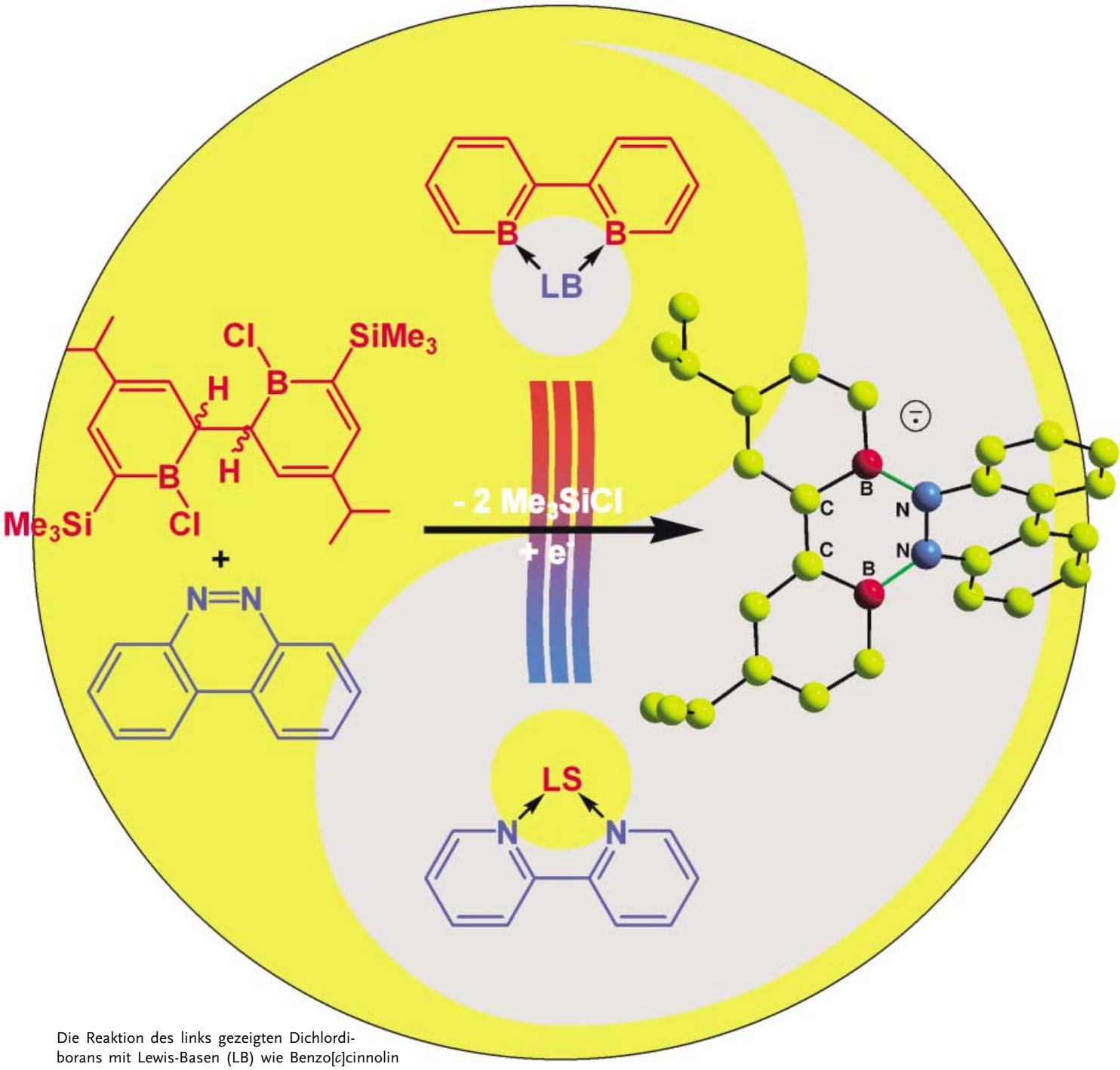
Zuschriften



Die Reaktion des links gezeigten Dichlordiborans mit Lewis-Basen (LB) wie Benzo[*c*]cinnolin liefert Lewis-Säure/Lewis-Base-Addukte des ersten Mitglieds einer neuartigen Familie chelatbildender Lewis-Säuren (LS), 2,2′-Diborabiphenyl. Diese Addukte, Analoga von 2,2′-Bipyridin-Komplexen, können zu Radikalanionensalzen reduziert werden, die strukturell charakterisiert wurden. Lesen Sie mehr in der Zuschrift von Piers et al. auf den folgenden Seiten.

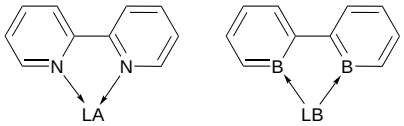
  0044-8249/03/11511-1289 $ 20.00+.50/0

Lewis Acid Analogues of Bipyridine

2,2′-Diborabiphenyl: A Lewis Acid Analogue of 2,2′-Bipyridine**

David J. H. Emslie, Warren E. Piers, and Masood Parvez*

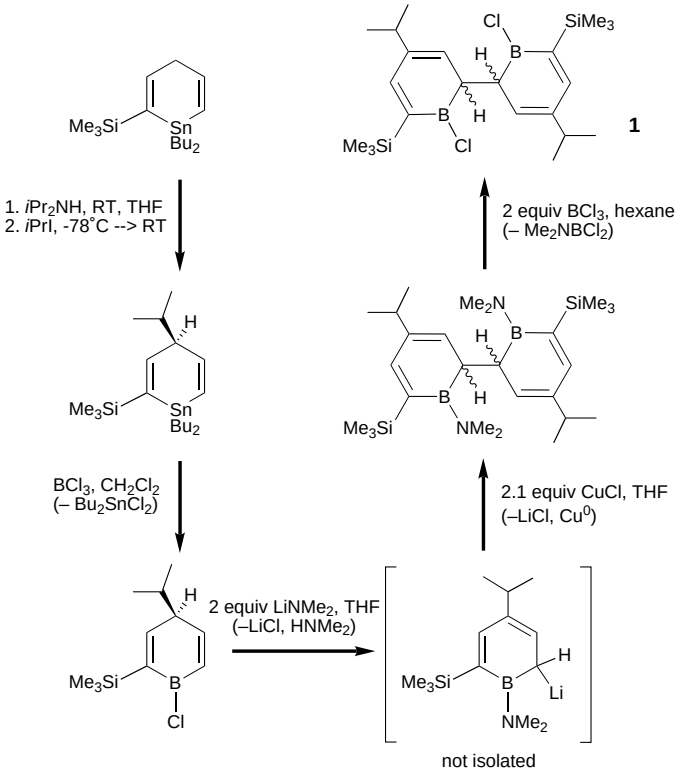
Chelating Lewis bases are indispensable chemical tools as ligands for Lewis acidic transition metals, and the 2,2′-bipyridine family of ligands (**I**) is among the most important.[1] Conversely, chelating Lewis acids that act as reverse ligands



I **II**

for anionic centers or bifunctional Lewis bases are less common.[2] Given the success of **I** as a bidentate ligand, we became interested in its boron analogue **II** as a potential chelating Lewis acid towards anionic and neutral Lewis bases. While the former holds promise for preparing novel anionic heterocycles and boratabiphenyl ligands for transition metals,[3] use of neutral bifunctional nitrogen Lewis bases could lead to B_2N_2 diboraarene adducts which are isoelectronic with all-carbon polycyclic aromatic hydrocarbons (PAHs).[4] Although PAHs are of fundamental interest for probing aromaticity,[5] recent interest in PAHs stems from potential applications in materials chemistry.[6] B_2N_2 analogues would, in all likelihood, exhibit optical and redox properties that are markedly different from their parent hydrocarbons, because of the polarization inherent to such structures. Herein we report the synthesis of some Lewis base adducts of a derivative of **II** that includes bifunctional pyridazine donors, which lead to novel heterocyclic analogues of polycyclic aromatic hydrocarbons that contain a $\{C_2B_2N_2\}$ core.

Synthesis of the precursor to the Lewis base adducts of the title molecule, the silated chlorodiborane compound **1**, was accomplished according to the chemistry shown in Scheme 1.



Scheme 1.

The route involves the construction and deprotonation of a six-membered boron heterocycle, followed by a C–C bond-forming coupling reaction to give the desired molecular framework. Building on methodology first used by Maier et al.[7] and then developed by Fu and co-workers,[8] the silated stannacycle shown was used as the precursor to the desired boracycle. To direct the crucial C–C bond-forming step to the position *ortho* to the boron atom, it was necessary to first block the *para* position. This was executed by quenching the lithium salt of the stannacycle with isopropyl iodide.[7b,9] This reaction proceeded with high regioselectivity (in 81% yield), and transmetalation of the resulting isopropyl substituted stannacycle with excess BCl_3 proceeded smoothly to give the *para*-substituted chloroboracyclohexadiene in excellent yield (98%). This material was then deprotonated to generate the organolithium species that was to be coupled in situ; treatment with two equivalents of $LiNMe_2$ is necessary to deprotonate the boracycle since one equivalent only leads to the nucleophilic displacement of the chloro group on the boron center. Although this lithium salt was not isolated, its ^{1}H NMR spectrum was very clean and consistent with the formulation given in the Scheme. Treatment with a slight excess of CuCl[10] leads to coupling in the position *ortho* to boron, and gives the diamido diborane in an 89% overall yield (for the two steps) as a mixture of the *meso* and *rac* diastereomers. This material is readily converted back to a dichloro diborane by treatment with BCl_3, to give precursor compound **1** in 93% yield as a dark-red oil, again consisting of a diastereomeric mixture of isomers. This oil was stable for long periods at room temperature under dry, inert atmos-

[*] Prof. W. E. Piers, Dr. D. J. H. Emslie, Dr. M. Parvez
Department of Chemistry
University of Calgary, 2500 University Drive N.W.
Calgary, Alberta, T2N 1N4 (Canada)
Fax: (+1) 403-289-9488
E-mail: wpiers@ucalgary.ca

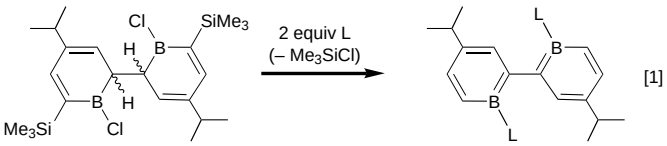
[**] Funding for this work came from the Natural Sciences and Engineering Research Council of Canada in the form of a Discovery Grant (to W.E.P.), and an E.W.R. Steacie Fellowship (2001–2003; to W.E.P.). D.J.H.E. thanks the Alberta Ingenuity Fund for a Postdoctoral Fellowship (2002–2004). W.E.P. is the S. Robert Blair Professor of Chemistry.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

  0044-8249/03/11511-1290 $ 20.00+.50/0

pheric conditions and proved a convenient starting material for subsequent transformations. Although synthetically intensive, the reactions of Scheme 1 are generally high yielding and we were able to prepare and store quantities of **1** on the gram scale. Each compound, with the exception of the lithium salts generated in situ, was isolated and fully characterized; full details can be found in the Supporting Information.

In chemistry analogous to that reported by Fu and coworkers for the preparation of borabenzenes,[4d,8] treatment of dichlorodiborane **1** with Lewis bases such as PMe_3 or pyridine leads to elimination of Me_3SiCl and a 1,3-shift of the 1,1′ hydrogen atom to give adducts **2** and **3** [Eq. (1)]. The



1 L = PMe_3, **2**; L = C_5H_5N, **3** [1]

bistrimethylphosphane adduct **2** is a crystalline solid and crystals suitable for X-ray analysis were obtained, which allowed us to firmly establish that the desired heterocyclic framework had been constructed. The molecular structure of **2**, along with selected metrical parameters, is given in Figure 1.[11] There are three independent molecules in the unit cell, which differ mainly in the torsion angles about the C–C bond linking the two borabenzene rings; other metrical parameters are essentially identical, so only values from one of the molecules are presented. The phosphane ligands are bonded to the trigonal-planar boron nuclei through bonds

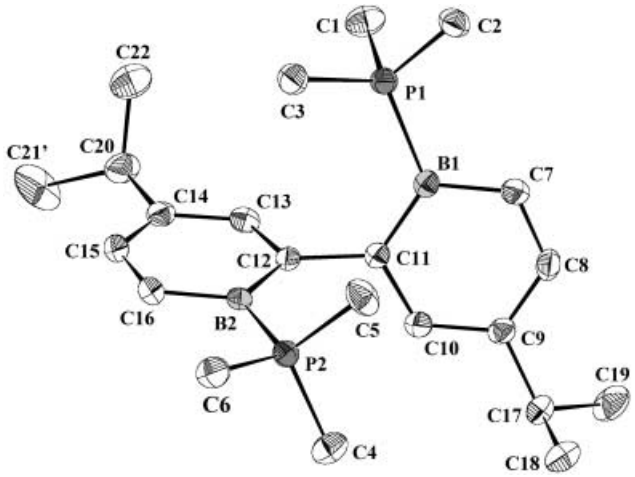
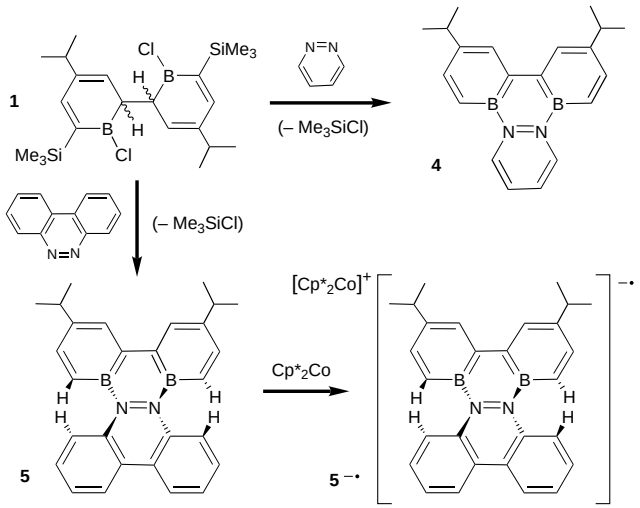


Figure 1. Molecular structure of **2**. Selected bond lengths [Å]: P1-B1 1.925(3), C7-C8 1.396(4), C7-B1 1.491(4), C8-C9 1.393(4), C9-C10 1.404(4), C10-C11 1.393(4), C11-B1 1.494(4), C11-C12 1.505(4); selected bond angles [°]: C8-C7-B1 118.6(3), C9-C8-C7 122.8(3), C8-C9-C10 118.9(3), C11-C10-C9 124.7(3), C10-C11-B1 116.6(2), C10-C11-C12 118.1(2), B1-C11-C12 125.3(2), C7-B1-C11 118.4(3), C7-B1-P1 117.0(2), C11-B1-P1 124.6(2); selected torsion angles [°]: B1-C11-C12-C13 70.5(4), B1-C11-C12-B2 −107.0(3).

which are slightly longer (1.925(4) Å) than that found in the trimethylphosphane adduct of borabenzene (1.900(8) Å).[4] The two borabenzene rings are joined at C11 and C12, which places the boron atoms in the 2 and 2′ positions as desired. The rings are twisted by about 107° such that the boron atoms are pointing in opposite directions, which is the most sensible steric arrangement for the monodentate phosphane base.

The pyridine adduct **3** is also easily prepared and is a B_2N_2 analogue of the aromatic hydrocarbon *ortho*-quaterphenyl. In contrast to yellow **2**, bispyridine adduct **3** is strongly purple in color ($\lambda_{max}(CH_2Cl_2) = 504$ nm, $\varepsilon = 2 \times 10^3\ mol^{-1}\,dm^3\,cm^{-1}$), which suggests extended conjugation throughout the four contiguous aromatic rings. The synthesis of other B_2N_2 congeners of aromatic hydrocarbons can be realized by making use of the chelating ability of the 2,2′-diborabiphenyl framework. Reaction of **1** with bifunctional nitrogen bases such as pyridazine or benzo[*c*]cinnoline similarly leads to the loss of Me_3SiCl and the generation of the novel heterocyclic compounds **4** and **5**, which contain a $\{C_2B_2N_2\}$ molecular core, in good yields (Scheme 2). These compounds are analogues of the polycyclic aromatic hydrocarbons triphenylene and dibenzo[*g*,*p*]chrysene, respectively, and are intensely colored with strong charge-transfer absorptions (**4**: deep red, $\lambda_{max}(CH_2Cl_2) = 509$ and 545 nm, $\varepsilon = 1.6 \times 10^4$ and $2.0 \times 10^4\ mol^{-1}\,dm^3\,cm^{-1}$; **5**: deep red, $\lambda_{max}(CH_2Cl_2) = 501$ nm, $\varepsilon = 1.8 \times 10^4\ mol^{-1}\,dm^3\,cm^{-1}$). Ab initio molecular-orbital computations carried out using MacSpartan Plus at the 6-31G* level on the unsubstituted parent of triphenylene analogue **4** indicate that the HOMO is associated with the pyridazine part of the molecule, while the LUMO is localized largely on the 2,2′-diborabiphenyl moiety. These absorptions thus presumably arise through charge transfer of an electron from the HOMO to the LUMO, a notion supported by the observed shift in the value of λ_{max} to higher energies when the spectrum of **5** was acquired in less polar solvents ($\lambda_{max} = 499$ and 493 nm in THF and hexane, respectively).

The synthesis of compounds **4** and **5** demonstrates the ability of **1** to act as a precursor for a potentially wide variety of PAH analogues with novel optical[12] and redox[13] proper-



Scheme 2.

ties. For example, cyclic voltammetry experiments on these compounds (1 mM **4** (or **5**); 0.1M NBu_4PF_6, THF, 20 $mV s^{-1}$, potentials relative to a saturated calomel electrode (SCE) using Cp^*_2Fe as an internal standard ($Cp^* = \eta^5$-C_5Me_5)) show two reversible one-electron reductions for each compound (**4**: $E_{1/2} = -1.25$ V, -1.85 V; **5**: $E_{1/2} = -1.03$ V, -1.45 V). The former compound is harder to reduce than the dibenzo[*g,p*]-chrysene analogue as it most likely has a planar geometry, whereas **5** probably assumes a less aromatic, twisted geometry resulting from steric interactions between the 3,3′ protons of the diborabenzene moiety and the opposing 3,3′ protons of the benzo[*c*]cinnoline fragment, in analogy to the structure of the parent hydrocarbon.[14] Since addition of electrons disrupts the aromaticity of the molecules, reduction of **5** is inherently more facile than for the (presumably) planar triphenylene analogue **4**.

Indeed, compound **5** can be chemically reduced by the one-electron source Cp^*_2Co, to selectively form the radical anion of **5**, as shown in Scheme 2. The ESR spectrum of this paramagnetic species exhibits a broad signal with a g_{iso} value of 2.003 and little discernable hyperfine structure at either room temperature or 100 K. Its structure was confirmed crystallographically, and is shown in Figure 2.[15] As expected, the framework is twisted considerably about the $\{C_2B_2N_2\}$ core (note the torsion angles associated with this part of the molecule) to alleviate steric interactions between the C–H groups of C22/C33 and C31/C42. The B–N bond lengths of 1.466(4) and 1.482(4) Å are shorter than that found for the pyridine adduct of borabenzene (1.56 Å)[4e] but similar to those found for amide derivatives of boratabenzene (for example, 1.45 Å for NMe_2 derivatives of boratabenzenes[16]). This suggests that some of the aromatic character of the $\{C_2B_2N_2\}$ core of the molecule is retained when an electron populates the LUMO. However, the N1–N2 bond length of 1.430(4) Å is considerably longer than this bond in free benzo[*c*]cinnoline (1.292(3) Å). While some lengthening of this bond should be expected upon coordination to a Lewis acid,[17] we note that the LUMO in the neutral complexes is slightly N–N antibonding in character. More meaningful analysis of this data will follow with structural characterization of **5** and $[\mathbf{5}]^{2-}$.

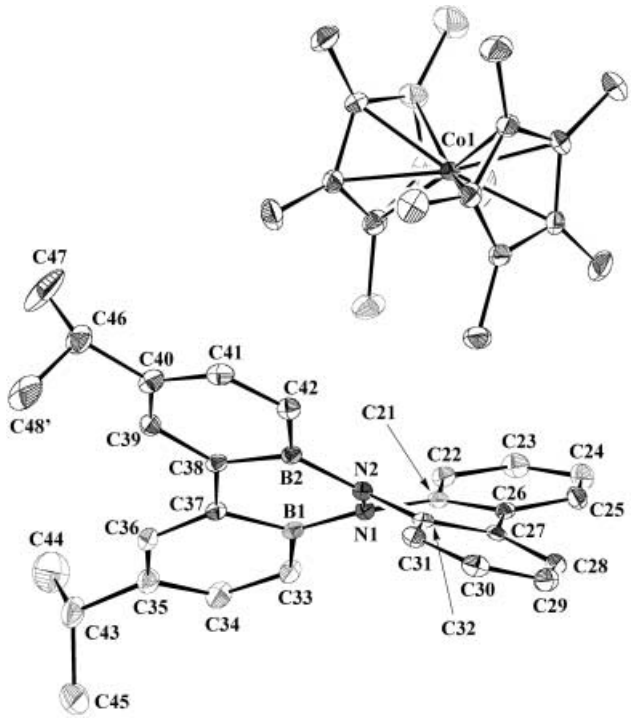


Figure 2. Molecular structure of radical anion $[\mathbf{5}]^{\cdot-}$. Selected bond lengths [Å]: B1-N1 1.466(4), B1-C33 1.519(5), B1-C37 1.527(5), B2-N2 1.482(4), B2-C38 1.511(5), B2-C42 1.513(5), N1-C21 1.413(4), N1-N2 1.430(3), N2-C32 1.402(4), C21-C26 1.405(4), C26-C27 1.460(4), C27-C32 1.412(4), C37-C38 1.444(4); selected bond angles [°]: N1-B1-C33 123.8(3), N1-B1-C37 119.2(3), C33-B1-C37 116.9(3), N2-B2-C38 119.3(3), N2-B2-C42 123.6(3), C38-B2-C42 117.1(3), C21-N1-N2 114.1(2), C21-N1-B1 126.4(3), N2-N1-B1 119.1(2), C32-N2-N1 114.8(2), C32-N2-B2 126.0(3), N1-N2-B2 118.2(2); selected torsion angles [°]: B1-C37-C38-B2 −19.3(4), B1-N1-N2-B2 −29.5(4), C21-N1-N2-C32 −46.9(3), C21-C26-C27-C32 −18.5(4), C33-B1-N1-C21 24.5(5), C42-B2-N2-C32 32.5(4).

In conclusion, we have developed a reliable synthetic route to a precursor of the novel chelating Lewis acid 2,2′-diborabiphenyl and examined its complexation chemistry with simple monodentate Lewis bases, and the bifunctional dinitrogen bases pyridazine and benzo[*c*]cinnoline. Adducts of the latter are isoelectronic with polycyclic aromatic hydrocarbons, which have many applications in materials chemistry.[18] In addition to further development of this theme of research, the propensity of 2,2′-diborabiphenyl to chelate anionic Lewis bases, and the coordination chemistry of the resulting 2,2′-diboratabiphenyl derivatives is being developed.

Complete experimental details including synthesis and characterization of all new compounds can be found in the Supporting Information.

Received: November 14, 2002 [Z50555]

Keywords: boraarenes · boron · chelates · Lewis acids · radical ions

[1] C. Kaes, A. Katz, M. W. Hosseini, *Chem. Rev.* **2000**, *100*, 3553.
[2] a) W. E. Piers, G. J. Irvine, V. C. Williams, *Eur. J. Inorg. Chem.* **2000**, 2131; b) J. D. Wuest, *Acc. Chem. Res.* **1999**, *32*, 81; c) J. Vaugeois, M. Simard, J. D. Wuest, *Coord. Chem. Rev.* **1995**, *145*, 55; d) M. F. Hawthorne, Z. Zheng, *Acc. Chem. Res.* **1997**, *30*, 267; e) J. D. Hoefelmeyer, M. Schult, M. Tschinkl, F. P. Gabbai, *Coord. Chem. Rev.* **2002**, *235*, 93.
[3] a) G. E. Herberich, H. Ohst, *Adv. Organomet. Chem.* **1986**, *25*, 199; b) G. C. Fu, *Adv. Organomet. Chem.* **2001**, *47*, 101.
[4] a) P. I. Paetzold, G. Stohr, H. Maisch, H. Lenz, *Chem. Ber.* **1968**, *101*, 2881; b) A. J. Ashe III, H. Yang, X. Fang, J. W. Kampf, *Organometallics* **2002**, *21*, 4578; c) S.-Y. Liu, M. M.-C. Lo, G. C. Fu, *Angew. Chem.* **2002**, *114*, 182; *Angew. Chem. Int. Ed.* **2002**, *41*, 174; d) S. Qiao, D. A. Hoic, G. C. Fu, *Organometallics* **1997**, *16*, 1501; e) R. Boese, N. Finke, J. Henkelmann, G. Maier, P. Paetzold, H. P. Reisenauer, G. Schmid, *Chem. Ber.* **1985**, *118*, 1644.
[5] P. von R. Schleyer (Guest Editor), *Chem. Rev.* **2001**, *101*, 1115.
[6] a) M. D. Watson, A. Fechtenkötter, K. Müllen, *Chem. Rev.* **2001**, *101*, 1267; b) A. J. Berresheim, M. Müller, K. Müllen, *Chem. Rev.* **1999**, *99*, 1747.

  0044-8249/03/11511-1292 $ 20.00+.50/0

[7] a) G. Maier, H. P. Reisenauer, J. Henkelmann, C. Kliche, *Angew. Chem.* **1988**, *100*, 303; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 295; b) G. Maier, H. Wolf, R. Boese, *Chem. Ber.* **1990**, *123*, 505.
[8] D. A. Hoic, J. Robbins-Wolf, W. M. Davis, G. C. Fu, *Organometallics* **1996**, *15*, 1315.
[9] a) J. Tweddell, D. A. Hoic, G. C. Fu, *J. Org. Chem.* **1997**, *62*, 8286; b) A. J. Ashe III, S. Al-Ahmad, X. Fang, J. W. Kampf, *Organometallics*, **1998**, *17*, 3883, and references therein.
[10] a) J. Hassan, M. Sevignon, C. Gozzi, E, Schulz, M. Lemaire, *Chem. Rev.* **2002**, *102*, 1359; b) G. E. Herberich, U. Engert, B. Ganter, M. Pons, R. Wang, *Organometallics* **1999**, *18*, 3406.
[11] Crystal data for **2**: $C_{22}H_{38}B_2P_2$, $M_r = 386.08$, monoclinic, space group $P2_1/c$, $a = 16.6747(2)$, $b = 14.1980(2)$, $c = 30.4768(4)$ Å, $\beta = 91.7737(10)°$, $V = 7211.85(16)$ Å^3, $Z = 12$, $\rho_{calcd} = 1.067$ g cm^{-3}, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = 173(2)$ K, 23909 measured reflections, 12615 unique, $R_{int} = 0.065$, 7222 reflections with $I_{net} > 2\sigma(I_{net})$, $\mu = 0.18$ mm^{-1}, min./max. transmission = 0.973 and 0.985, $R1$ $(I > 2\sigma) = 0.053$, $wR2 = 0.117$, GOF = 1.00, No. of parameters = 713, final difference map within +0.24 and −0.30 e Å^3. CCDC-197380 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).
[12] a) B. Y. Lee, S. Wang, M. Putzer, G. P. Bartholomew, X. Bu, G. C. Bazan, *J. Am. Chem. Soc.* **2000**, *122*, 3969; b) J. Abe, Y. Shirai, *J. Am. Chem. Soc.* **1996**, *118*, 4705.
[13] a) K. Meerholz, J. Heinze, *Electrochim. Acta* **1996**, *41*, 1839; b) V. D. Parker, *J. Am. Chem. Soc.* **1976**, *98*, 98.
[14] a) F. H. Herbstein, *Acta Crystallogr. Sect. B* **1979**, *35*, 1661; b) D. A. Klumpp, D. N. Back, G. K. S. Prakash, G. A. Olah, *J. Org. Chem.* **1997**, *62*, 6666.
[15] Crystal data for $[\mathbf{5}]^{-}$: $C_{50}H_{62}B_2Cl_4CoN_2$, $M_r = 913.37$, monoclinic, space group $P2_1/c$, $a = 16.562(3)$, $b = 12.371(2)$, $c = 23.779(6)$ Å, $\beta = 101.927(7)°$, $V = 4766.9(17)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.273$ g cm^{-3}, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = 173(2)$ K, 31354 measured reflections, 8807 unique, $R_{int} = 0.0951$, $\mu = 0.620$ mm^{-1}, min./max. transmission = 0.7721 and 0.9406, $R1$ $(I > 2\sigma) = 0.0626$, $wR2 = 0.1256$, GOF = 1.058, No. of parameters = 554, final difference map within +0.661 and −0.613 e Å^3. CCDC-197381 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).
[16] a) G. E. Herberich, B. Schmidt, U. Englert, T. Wagner, *Organometallics* **1993**, *12*, 2891; b) G. E. Herberich, U. Englert, M. U. Schmidt, R. Standt, *Organometallics* **1996**, *15*, 2707.
[17] Y. Nakayama, A. Nakamura, K. Mashima, *Chem. Lett.* **1997**, 803.
[18] A. M. van de Craats, J. M. Warman, *Adv. Mater.* **2001**, *13*, 130, and references therein.