[1] H. Nishiyama in *Comprehensive Asymmetric Catalysis* (Eds.: E. N. Jacobsen, A. Pfaltz, H. Yamamoto), Springer, New York, **1999**, chap. 6.3.
[2] H. Nishiyama, H. Sakaguchi, T. Nakamura, M. Horihata, M. Kondo, K. Itoh, *Organometallics* **1989**, *8*, 846 – 848.
[3] For a review of applications of C_2-symmetric bis(oxazolines) in asymmetric catalysis, see: A. K. Ghosh, P. Mathivanan, J. Cappiello, *Tetrahedron: Asymmetry* **1998**, *9*, 1 – 45.
[4] For our initial study, see: S. Qiao, G. C. Fu, *J. Org. Chem.* **1998**, *63*, 4168 – 4169.
[5] For example, see: a) Asymmetric isomerization of allylic alcohols: K. Tanaka, S. Qiao, M. Tobisu, M. M.-C. Lo, G. C. Fu, *J. Am. Chem. Soc.* **2000**, *122*, 9870 – 9871; K. Tanaka, G. C. Fu, *J. Org. Chem.* **2001**, *66*, 8177 – 8186; b) asymmetric synthesis of β-lactams from alkynes and nitrones: M. M.-C. Lo, G. C. Fu, *J. Am. Chem. Soc.* **2002**, *124*, 4572 – 4573.
[6] For a review of the use of phosphanyl–pyridyl ligands, see: P. Espinet, K. Soulantica, *Coord. Chem. Rev.* **1999**, *193*–195, 499 – 556.
[7] R. Rios, J. Liang, M. M.-C. Lo, G. C. Fu, *Chem. Commun.* **2000**, 377 – 378.
[8] $MesPhSiH_2$ can be synthesized in one step by treating Ph_2SiH_2 with TfOH and MesMgBr.
[9] Notes: a) Comparable enantioselectivity is observed in THF, Et_2O, toluene, and CCl_4; b) a small enhancement in enantioselectivity is obtained at lower temperature; c) the stereoselectivity does not appear to be dependent on the concentration.
[10] In the case of isopropyl phenyl ketone, we observe good enantioselectivity (86 % *ee*), but a very slow reaction rate (14 % conversion after 5 days with a 5 % catalyst loading).
[11] The modest yield is due to the volatility of the product.
[12] For leading references to uses of enantiopure [α-D]benzyl alcohol, see: a) I. Sato, D. Omiya, T. Saito, K. Soai, *J. Am. Chem. Soc.* **2000**, *122*, 11739 – 11740; b) I. Yamada, R. Noyori, *Org. Lett.* **2000**, *2*, 3425 – 3427.
[13] For an unsymmetrical disubstituted silane such as $MesPhSiH_2$, there is the potential for differentiation by the chiral catalyst of the two enantiotopic Si–H bonds. We have established that Rh/**1** can in fact efficiently distinguish between the two; thus, for the reaction of $MesPhSiH_2$ with acetone, $MesPhSiH(OCHMe_2)$ is generated in 97 % *ee*. For leading references to the synthesis and applications of "Si-chiral" silanes, see: T. H. Chan, D. Wang, *Chem. Rev.* **1992**, *92*, 995 – 1006.
[14] For examples of asymmetric hydrosilylation catalysts that are effective for aryl alkyl ketones but relatively ineffective for dialkyl ketones, see: a) H. Mimoun, J. Yves de Saint Laumer, L. Giannini, R. Scopelliti, C. Floriani, *J. Am. Chem. Soc.* **1999**, *121*, 6158 – 6166; b) J. Yun, S. L. Buchwald, *J. Am. Chem. Soc.* **1999**, *121*, 5640 – 5644.
[15] Until now, taking into account both scope and enantioselectivity, the best catalysts for asymmetric hydrosilylations of dialkyl ketones were rhodium complexes of Ito's TRAP family of ligands: a) R. Kuwano, T. Uemura, M. Saitoh, Y. Ito, *Tetrahedron Lett.* **1999**, *40*, 1327 – 1330; b) R. Kuwano, M. Sawamura, J. Shirai, M. Takahashi, Y. Ito, *Bull. Chem. Soc. Jpn.* **2000**, *73*, 485 – 496. The Rh/TRAP catalysts provide good, but not exceptionally high, enantioselectivities for hydrosilylations of aryl alkyl ketones. See also: D. K. Heldmann, D. Seebach, *Helv. Chim. Acta* **1999**, *82*, 1096 – 1110; Y. Nishibayashi, K. Segawa, K. Ohe, S. Uemura, *Organometallics* **1995**, *14*, 5486 – 5487.
[16] *o*-Tol_2SiH_2 can be synthesized in one step by treating $HSiCl_3$ with *o*-TolMgBr and $LiAlH_4$.
[17] Dialkyl ketones have proved to be very challenging substrates for asymmetric hydrogenation catalysts. a) For overviews, see: T. Ohkuma, R. Noyori in *Comprehensive Asymmetric Catalysis* (Eds.: E. N. Jacobsen, A. Pfaltz, H. Yamamoto), Springer, New York, **1999**, chap. 6.1; V. Fehring, R. Selke, *Angew. Chem.* **1998**, *110*, 1927 – 1930; *Angew. Chem. Int. Ed.* **1998**, *37*, 1827 – 1830; b) Q. Jiang, Y. Jiang, D. Xiao, P. Cao, X. Zhang, *Angew. Chem.* **1998**, *110*, 1203 – 1207; *Angew. Chem. Int. Ed.* **1998**, *37*, 1100 – 1103.

Design Optimization of 1,3-Diphospha-2,4-diboretane Diradicals**

Mark Seierstad, Christopher R. Kinsinger, and Christopher J. Cramer*

Diradicals may be defined as molecules having an even number of electrons and a narrow separation between their highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO, respectively).[1–4] Degeneracy of these orbitals is also a possibility. Diradicals share a number of characteristic features associated with having frontier MO energies that are similar. They tend, for instance, to exhibit relatively small energy splittings between their lowest energy singlet and triplet states (ΔE_{S-T}) and between their lowest energy and first excited singlet states, where the latter splitting is associated with a long-wavelength absorption in the ultraviolet/visible (UV/Vis) spectrum of the lower energy state.

A large number of organic diradicals are known, although they are almost exclusively characterized as reactive intermediates. Typical single-center diradicals include carbenes,[5–9] nitrenes,[5,10–13] and nitrenium ions,[14–16] and well known multicenter diradicals include didehydroarenes[5,17–20] (e.g., benzynes) and non-Kekulé hydrocarbons like trimethylenemethane[21–24] and tetramethyleneethane.[21,25–27] An example of a diradical system that has been known since the pioneering work of Huckel in the 1930s is a high-symmetry "antiaromatic" cycloarene having $4n$ electrons and $4n$ ring atoms. All-carbon examples such as cyclobutadiene and cyclooctatetraene, however, are well known to lift the degeneracy of their frontier orbitals by distorting from D_{nh} structures to geometries belonging to lower symmetry point groups (although this by no means precludes their possible continuing description as diradicals).[1,28,29] A key to success, then, in the design of any diradical, is to engineer the molecular and electronic structure in such a way that the frontier orbital separation remains as small as possible.[30–32]

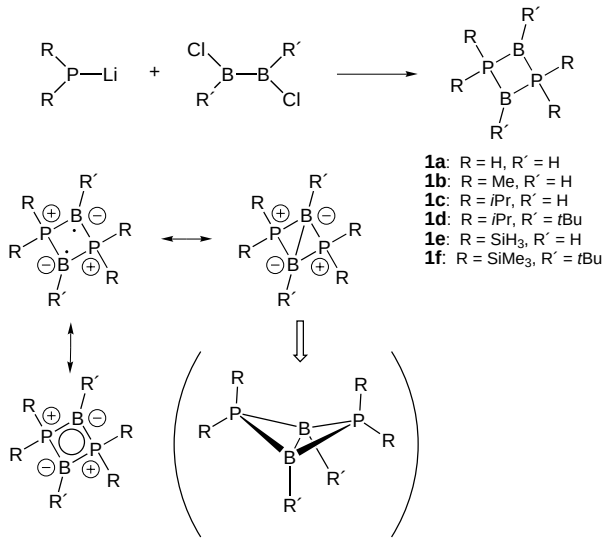
Recently, Scheschkewitz et al.[33] reported that the reaction of lithium diisopropylphosphide with 1,2-di-*tert*-butyl-1,2-dichlorodiborane provided an isolable 1,3-diphospha-2,4-diboretane product **1d** (Scheme 1) having a long-wavelength UV absorption (446 nm) consistent with it having substantial diradical character, in spite of its thermal stability. Such character is easily inferred from consideration of the simplest resonance structure that may be drawn for **1d**, which places positive charges on the P atoms and a negative charge and one formally unpaired electron on each of the B atoms (Scheme 1).

[*] Prof. Dr. C. J. Cramer, M. Seierstad, C. R. Kinsinger
Department of Chemistry and Supercomputing Institute
University of Minnesota
207 Pleasant St. SE
Minneapolis, MN 55455-0431 (USA)
Fax: (+1) 612-626-2006
E-mail: cramer@chem.umn.edu

[**] Support from the National Science Foundation (CHE-9876792) is gratefully acknowledged.

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

  0044-8249/02/4120-3894 $ 20.00+.50/0



Scheme 1. Synthesis and resonance structures of 1,3-diphospha-2,4-diboretanes **1a–f**.

However, other resonance structures, also illustrated in Scheme 1, might also be reasonably expected to contribute strongly to the overall character of **1**. Clearly, if σ bonding between the B atoms can be achieved, the resulting diphosphadiborabicyclo[1.1.0]butane structure would not be expected to deviate much from normal closed-shell character. However, the ring puckering required in such a bicyclo structure is strongly disfavored when the ring is substituted with large substituents, and an X-ray crystal structure analysis of **1d** indicates the four-membered ring to be perfectly planar. Another alternative, however, is that mixing of the out-of-plane boron p orbitals with appropriate σ_{PR} and σ^*_{PR} orbitals may create the equivalent of an aromatic π system, and that spin-pairing in such delocalized hybrid orbitals will contribute to closed-shell character. This orbital picture is illustrated in Figure 1 where, in D_{2h} symmetry, the 1,3-diphospha-2,4-diborete ring contributes four electrons and four π orbitals and the P substituents contribute two electrons and two symmetry-adapted orbitals of π-like symmetry (two other symmetry-adapted combinations carrying the remaining two substituent electrons are not shown as they belong to *a*-type irreducible representations that do not mix with the π system). Note that the HOMO is dominated by a cross-ring B–B π bonding interaction, while the LUMO, which by symmetry cannot mix with the σ_{PR} and σ^*_{PR} combination orbitals, is B–B π* antibonding.

This frontier orbital picture receives support from calculations reported by Scheschkewitz et al.,[33] who reported a HOMO for **1d** from density functional theory (DFT) that was in perfect agreement with that illustrated in Figure 1. These same calculations predicted ΔE_{S-T} for **1a** to be −17.2 kcal mol^{-1}. This value is fairly close to the known S–T splitting of *m*-benzyne,[34] suggesting that the appellation diradical may be as warranted for **1d** as it is for the *meta* aryne.

With Figure 1 as a guide, however, one may ask how one might engineer still more diradical character into the 1,3-diphospha-2,4-diboretane framework, to optimize its utility as a component in molecular electronic or magnetic devices, for

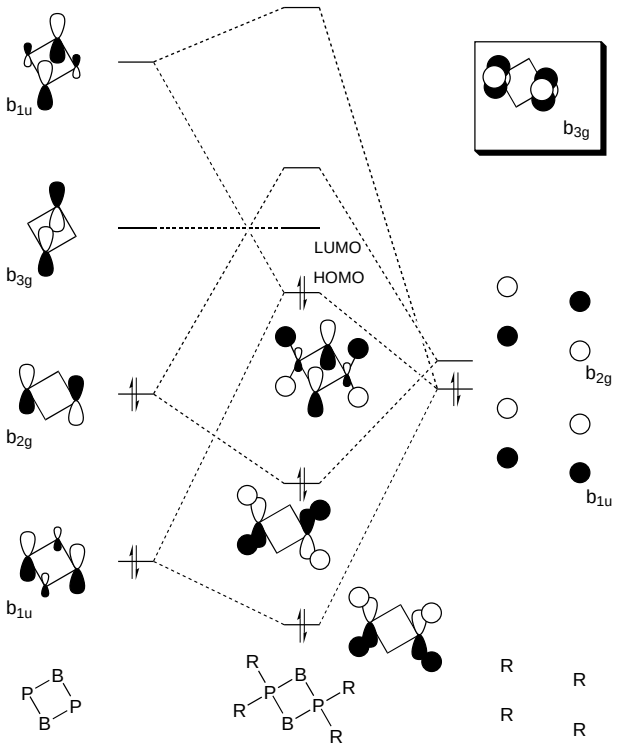


Figure 1. MO diagram of the mixing of diphosphadiborete π orbitals with symmetry-adapted substituent orbitals on P (e.g., 1s orbitals for R = H or sp^3 orbitals for R = alkyl or silyl). Inset at upper right is a b_{3g} combination of d orbitals that could hybridize with and lower the energy of the LUMO if P were to be replaced by an early transition metal.

instance. Clearly, accomplishing this goal requires that either the HOMO energy be raised relative to the LUMO or that the LUMO energy be lowered relative to the HOMO. With respect to the latter option, Figure 1 shows as an inset an orbital of appropriate symmetry to mix with the LUMO and reduce the frontier gap were the phosphorus atoms to be replaced by early transition metals so that the necessary empty d orbitals would be available for hybridization. While this option would appear to merit future consideration, we focus our attention here on what would appear to be a simpler endeavor from a synthetic perspective, namely raising the HOMO energy by employing phosphorus substituents having more electropositive character than alkyl groups; the most obvious alternative is a silyl group.

To predict whether such an approach has merit, we have carried out calculations at several levels of electronic structure theory for **1a–f** (Table 1).[35] In addition to ΔE_{S-T}, we evaluate as a diagnostic HOMO and LUMO occupation numbers from two-electron-in-two-orbital generalized valence bond (GVB(2,2)) calculations[36]—perfect diradicals are characterized by occupation numbers of 1.0 in each orbital, while perfectly closed-shell systems have HOMO and LUMO occupation numbers of 2.0 and 0.0, respectively.[2] Molecular geometries for all species were optimized at the DFT level using the B3LYP functional[37,38] and the 6-31G* basis set.[39] Energetic and geometric results with this relatively small basis set were found to be very close to those from calculations employing the much larger 6-311 + G(d,p) basis set for **1a**, **1b**, and **1e**, validating the use of the more efficient

  0044-8249/02/4120-3895 $ 20.00+.50/0

Table 1. Computed properties of ground-state singlet diphosphadiboretanes **1** at DFT-optimized planar geometries.

Compound[a]	*r*PB [Å]	ΔE_{S-T}[b] [kcal mol^{-1}]	HOMO occ. no.[c]	LUMO occ. no.[c]
1a	1.888	−18.7 (−20.0) [−19.8][d]	1.79	0.21
1b	1.887	−20.1 (−22.0)	1.79	0.21
1c	1.892	−20.7	1.80	0.20
1d	1.907	−23.4	1.81	0.19
1e	1.905	−5.8 (−5.1)	1.61	0.39
1f	1.932	−8.7	1.70	0.30

[a] Based on analytic frequency analysis, **1d** and **1f** are true minima; all other compounds are transition-state structures for inversion of puckered minima. [b] Computed as 0 K enthalpy at the B3LYP/6-31G(d) and CASPT2/GVB(2,2)/6-31G(d)//B3LYP/6-31G(d) levels (the latter in parentheses, where computed). [c] From GVB(2,2)/6-31G(d) wave functions. [d] From calculations at the CCSD(T)/6-311 + G(d,p)//B3LYP/6-311 + G(d,p) level.

level for the larger structures. As for the functional, we note that time-dependent B3LYP/6-311 + G(d,p) calculations for **1b** predict a UV/Vis absorption of 451 nm, in excellent agreement with experiment for **1d**, and moreover that ΔE_{S-T} values from all DFT calculations are in excellent agreement with predictions from multireference second-order perturbation theory (CASPT2) using as reference either the GVB(2,2) wave functions or multiconfiguration wave functions spanning the full (6,6) active space illustrated in Figure 1, as well as CCSD(T)/6-311 + G(d,p) calculations for **1a** (Table 1).

As expected, replacement of alkyl groups on P with silyl groups substantially increases the diradical character of **1** by raising the energy of the hybrid HOMO relative to the LUMO. The predicted ΔE_{S-T} value of −8.7 for **1f** is closer to that of *p*-benzyne than *m*-benzyne,[34,40] the former being an extremely reactive diradical. Its orbital occupation numbers of 1.70 and 0.30, on the other hand, are less close than the values of 1.23 and 0.77 for *p*-benzyne;[34,40] nevertheless, the **1f** values represent a substantial increase in diradical character compared to **1d**. In addition, time-dependent B3LYP/6-311 + G(d,p) calculations for **1e** predict a UV/Vis absorption of 704 nm, that is, at much longer wavelength than measured for **1d**. As a final point of interest, we note that the ring geometry changes substantially upon silyl substitution; in particular, the P–B bonds lengthen. This derives from two phenomena. As the HOMO is net P–B bonding while the LUMO is not, enhanced occupation of the latter at the expense of the former increases P–B distances. As well, however, P devotes more s character to its bonds with Si than to those with C, thus placing more p character in its bonds to B, and this too extends P–B bond lengths.[41] Interestingly, it also reduces B-P-B bond angles,[41] so that the B–B distances are actually shorter in **1e** and **1f** than in any of the other compounds considered (by from 0.01 to 0.05 Å). This offers the mildly amusing paradox of increased diradical character for the species with minimum separation between the centers formally assigned as carrying the unpaired spins in the simple resonance picture of Scheme 1.

Realization of the synthesis of **1f** from the appropriate lithium bis(trimethylsilyl)phosphide would be expected to be straightforward (at least to a blithe theorist). Irrespective of that point, the design principles implicit in Figure 1 should prove useful in future synthetic efforts founded on this exciting heterocyclic system and its analogues.

Received: June 18, 2002 [Z19550]

[1] W. T. Borden, E. R. Davidson, *Acc. Chem. Res.* **1981**, *14*, 69.
[2] V. Bonacic-Koutecky, J. Koutecky, J. Michl, *Angew. Chem.* **1987**, *99*, 216; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 170.
[3] A. Rajca, *Chem. Rev.* **1994**, *94*, 871.
[4] C. J. Cramer, *J. Chem. Soc. Perkin Trans. 2* **1998**, 1007.
[5] T. L. Gilchrist, C. W. Rees, *Carbenes, Nitrenes, and Arynes*, Nelson, London, **1969**.
[6] M. Jones, R. A. Moss, *Carbenes, Vol. I*, Wiley, New York, **1973**.
[7] M. S. Platz, *Kinetics and Spectroscopy of Carbenes and Diradicals*, Plenum, New York, **1990**.
[8] A. Nickon, *Acc. Chem. Res.* **1993**, *26*, 84.
[9] H. Tomioka, E. Iwamoto, H. Itakura, K. Hirai, *Nature* **2001**, *412*, 626.
[10] M. S. Platz, *Acc. Chem. Res.* **1995**, *28*, 487.
[11] W. T. Borden, N. P. Gritsan, C. M. Hadad, W. L. Karney, C. R. Kemnitz, M. S. Platz, *Acc. Chem. Res.* **2000**, *33*, 765.
[12] N. P. Gritsan, M. S. Platz, *Adv. Phys. Org. Chem.* **2001**, *36*, 255.
[13] W. T. G. Johnson, C. J. Cramer, *Int. J. Quantum Chem.* **2001**, *85*, 492.
[14] R. A. Abramovitch, R. Jeyaraman in *Azides and Nitrenes: Reactivity and Utility* (Ed.: E. F. V. Scriven) Academic, New York, **1984**, p. 297.
[15] C. J. Cramer, F. J. Dulles, D. E. Falvey, *J. Am. Chem. Soc.* **1994**, *116*, 9787.
[16] M. Novak, S. Rajagopal, *Adv. Phys. Org. Chem.* **2001**, *36*, 167.
[17] R. Hoffmann, A. Imamura, W. J. Hehre, *J. Am. Chem. Soc.* **1968**, *90*, 1499.
[18] C. J. Cramer, J. J. Nash, R. R. Squires, *Chem. Phys. Lett.* **1997**, *277*, 311.
[19] R. R. Squires, C. J. Cramer, *J. Phys. Chem. A* **1998**, *102*, 9072.
[20] W. Sander, *Acc. Chem. Res.* **1999**, *32*, 669.
[21] H. C. Longuet-Higgins, *J. Chem. Phys.* **1950**, *18*, 265.
[22] P. Dowd, *J. Am. Chem. Soc.* **1966**, *88*, 2587.
[23] W. T. Borden, L. S. Salem, *J. Am. Chem. Soc.* **1973**, *95*, 932.
[24] C. J. Cramer, B. A. Smith, *J. Phys. Chem.* **1996**, *100*, 9664.
[25] P. Dowd, *J. Am. Chem. Soc.* **1970**, *92*, 1066.
[26] W. T. Borden, H. Iwamura, J. A. Berson, *Acc. Chem. Res.* **1994**, *27*, 109.
[27] M. Filatov, S. Shaik, *J. Phys. Chem. A* **1999**, *103*, 8885.
[28] P. G. Wenthold, D. A. Hrovat, W. T. Borden, W. C. Lineberger, *Science* **1996**, *272*, 1456.
[29] P. G. Wenthold, W. C. Lineberger, *Acc. Chem. Res.* **1999**, *32*, 597.
[30] J. A. Berson, *Acc. Chem. Res.* **1997**, *30*, 238.
[31] S. L. Debbert, C. J. Cramer, *Int. J. Mass. Spectrom.* **2000**, *201*, 1.
[32] W. W. Schoeller, C. Begemann, E. Niecke, D. Gudat, *J. Phys. Chem. A* **2001**, *105*, 10731.
[33] D. Scheschkewitz, H. Amii, H. Gornitzka, W. W. Schoeller, D. Bourissou, G. Bertrand, *Science* **2002**, *295*, 1880.
[34] P. G. Wenthold, R. R. Squires, W. C. Lineberger, *J. Am. Chem. Soc.* **1998**, *120*, 5279.
[35] Gaussian 98 (Revision A.7), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **2001**.
[36] W. A. Goddard, L. B. Harding, *Annu. Rev. Phys. Chem.* **1978**, *29*, 363.
[37] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.
[38] P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623.
[39] W. J. Hehre, L. Radom, P. von R. Schleyer, J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, **1986**.
[40] C. J. Cramer, *J. Am. Chem. Soc.* **1998**, *120*, 6261.
[41] H. A. Bent, *Chem. Rev.* **1961**, *61*, 275.

  0044-8249/02/4120-3896 $ 20.00+.50/0