of interstitial nitrides to a lower coordination (5) and their preference for unusual and less regular cavities. Thus the chemistry of large nitrido clusters might reveal a novel variety of geometries, stabilized by these interstitial atoms. Further work on large species of this class is in progress,[11] and preliminary structural results seem to confirm our suggestions.

Acknowledgment. We thank the Italian C.N.R. for financial support.

Supplementary Material Available: A listing of positional and thermal parameters and of interatomic distances and angles (13 pages). Ordering information is given on any current masthead page.

---

(10) Jackson, P. F.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1980**, 224.

(11) Martinengo, S.; Ciani, G.; Sironi, A., unpublished results.

Geometric and Electronic Structure of $C_2H_6^{2+}$ (Dimer of Methyl Cation)

George A. Olah

Hydrocarbon Research Institute and
Department of Chemistry
University of Southern California
Los Angeles, California 90007

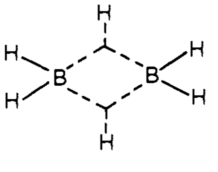
Massimo Simonetta*

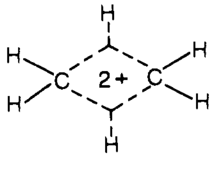
Institute of Physical Chemistry and C.N.R. Center
University of Milan, 20133 Milan, Italy

Received August 3, 1981

Diborane has two fewer valence electrons than ethane, but it took a long time before the non-ethane-like bridged structure for B_2H_6 was established. Neither the discarded ethane-like nor the bridged structure can be represented satisfactorily by a single Lewis structure. Such molecules are termed "electron deficient". The nature of the multicenter bonding in B_2H_6 was first described by Longuet-Higgins. Basically, four electrons hold the two boron atoms and the two bridging hydrogens together (the remaining four B-H bonds can be described by conventional 2c-2e bonds). B_2H_6 can be thus regarded as possessing two three-center-two electron bonds.

When considering the relationship of diborane, an electron-deficient boron compound, with its possible carbocationic analogue, the corresponding compound would be $C_2H_6^{2+}$, the dimer of the methyl cation, i.e., $(CH_3^+)_2$.





There was no evidence so far for $(CH_3^+)_2$ even in the gas phase in mass spectrometric studies (i.e.). Charge-charge repulsion seems mainly responsible for the inability to observe $(CH_3^+)_2$.

In a theoretical study Peyerimhoff and Buenker[1] investigated by SCF-MO and CI calculations ammonia borane ($NH_3 \cdot BH_3$) and positive ions of ethane, including $C_2H_6^{2+}$. Their calculations found the open-shell configuration of $(CH_3^+)_2$ the more stable in the D_{3d} geometry.

Due to our interest in higher coordinate carbon compounds and their relationship to boron analogues, we have restudied the problem of the methyl cation dimer and, in sharp contrast to Peyerimhoff and Buenker, found the bridged, diborane-like structure to be stable.

Table I. Energy, Bond Lengths, Bond Angles, and Charges in $C_2H_6^{2+}$ (D_{2h} Symmetry)[a]

	4-31G	6-31**G
energy, a.u.	−78.09449	−78.24919
C-C, Å	1.548	1.536
CH_b, Å	1.288	1.285
CH_t, Å	1.088	1.101
H_bCH_b, deg	106.2	106.6
H_tCH_t, deg	120.2	119.3
q(C), e	−0.403	−0.242
$q(H_b)$, e	+0.461	+0.398
$q(H_t)$, e	+0.471	+0.422

[a] The energy of optimized CH_3^+ (planar, C-H = 1.086 Å) is −39.23621 a.u. at the 6-31**G level.

Table II. Force Constants of $C_2H_6^{2+}$[a]

symmetry	i,j	$F(i,j)$	description	symmetry	i,j	$F(i,j)$	description
A_g	1,1	5.630	s–s	B_{1g}	11,11	5.694	s–s
	2,2	2.758	s–s		12,12	1.327	b–b
	3,3	2.917	b–b		11,12	−0.035	s–b
	4,4	1.936	b–b	B_{1u}	13,13	1.809	s–s
	1,2	+0.041	s–s		14,14	0.881	b–b
	1,4	+0.025	s–b		13,14	+0.130	s–b
	2,4	−1.420	s–b	B_{3g}	15,15	0.692	b–b
	3,4	−0.836	b–b	B_{3u}	16,16	5.718	s–s
A_u	5,5	0.289	b–b		17,17	2.386	s–s
					18,18	2.601	b–b
B_{2g}	6,6	1.639	s–s		16,17	−0.010	s–s
	7,7	0.679	b–b		16,18	−0.059	s–b
	6,7	−0.432	s–b		17,18	−0.004	s–b
B_{2u}	8,8	5.760	s–s				
	9,9	1.068	b–b				
	10,10	0.666	b–b				
	8.9	+0.040	s–b				
	8,10	+0.066	s–b				
	9,10	+0.386	b–b				

[a] Symmetry coordinates and force constants defined as in ref 6. Units are mdyn $Å^{-1}$, mdyn, and mdyn Å for stretching (s–s), stretch/bend (s–b), and bending (b–b) force constants, respectively.

We performed a geometry optimization of $C_2H_6^{2+}$ by means of MO calculations of the 4-31G type[2] imposing D_{3d} or D_{2h} symmetry. In the former case the system in the closed-shell configuration dissociates without barrier to $2CH_3^+$, while in the latter case we found a minimum for the geometry reported in Table I. Since in isoelectronic diborane boron d orbitals have a significant influence on the electron density,[3] the geometry optimization has been repeated, for the D_{2h} species, using a 6-31**G basis set.[4] These results are also reported in Table I. It can be noticed that while the total energy and charge densities are substantially changed, the geometry is almost unaffected by the inclusion of polarization functions. To obtain further evidence that a true energy minimum had been found we carried on a complete vibrational analysis of ethane dication. The method given by Blom and Altona[5] was shown to perform successfully in the case of diborane[6] using 4-31G wave functions and energies. For this reason and taking account of the results in Table I, force constants have been evaluated at the 4-31G level by the same procedure. They are reported in Table II. Since we could not calibrate scale factors on experimental frequencies, a direct comparison with diborane is not appropriate. It is worth noting, however, that our values are in general somewhat higher than the

---

(1) Peyerimhoff, S. D.; Buenker, R. J. *J. Chem. Phys.* **1968**, *49*, 312-325.

(2) Ditchfield, R.; Here, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724-728.

(3) Bianchi, R.; Morosi, G.; Simonetta, M. *Chem. Phys. Lett.* **1981**, *81*, 406-408.

(4) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213-222.

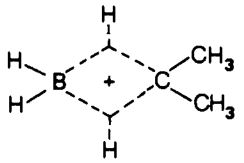
(5) Blom, C. E.; Altona, C. *Mol. Phys.* **1976**, *31*, 1377-1391.

(6) Blom, C. E.; Muller, A. *J. Chem. Phys.* **1978**, *69*, 3397-3402.

0002-7863/82/1504-0330$01.25/0

corresponding ones for diborane, but scale factors in this case range between 0.961 and 0.717. The existence of a true energy minimum is, however, well founded. One reason for missing the minimum in the previous calculations was the fact that a complete geometrical optimization was not carried out. In particular the maximum C–C distance included was 1.51 Å, well below our optimized value of 1.54 Å. The idea that the C–C distance in the dication should be shorter than in neutral ethane was mainly supported by considerations of the electron density for $C_2H_6^{2+}$ and B_2H_6, but we already pointed out the dependence of electron distribution on the participation of d orbitals.[3]

The demonstration by our calculations of the preferred hydrogen bridged, i.e., diborane-like structure of $C_2H_6^{2+}$ is of substantial significance as it further demonstrates the close relationship between electron-deficient boron and carbon compounds, even in the case of parent systems. The obvious charge–charge repulsion makes the difference in energy between $C_2H_6^{2+}$ and $2CH_3^+$ so large (0.44 a.u. according to ref 1; 0.22 a.u. in the present work) that it must be seen whether any experimental conditions may be found to directly observe the $C_2H_6^{2+}$. A "mixed" borane–carbocation dimer, lacking such charge repulsion, is, however, indicated in NMR spectroscopic studies of a system comprised of the isopropyl cation and borane.[7]



---

(7) Olah, G. A.; Field, L.; Prakash, G. K. S., unpublished results.

Phosphinyl Radicals as Ligands. Preparation of Novel Paramagnetic Organometallic Compounds

A. H. Cowley,* R. A. Kemp, and J. C. Wilburn[1]

Department of Chemistry
The University of Texas at Austin
Austin, Texas 78712

Received May 4, 1981

Interesting work by Lappert, Goldwhite, and co-workers[2] has established that phosphinyl radicals can be stabilized by means of sterically demanding substituents such as $(Me_3Si)_2CH$ and $(Me_3Si)_2N$. We have now found that stabilized phosphinyl radicals constitute a new class of ligand, intermediate in character between phosphenium cations and phosphide anions.[3,4] Furthermore, the reactivity of persistent $R_2P\cdot$ species toward metal carbonyls represents a useful source of novel organometallic radicals.

Upon treatment of $[\{(Me_3Si)_2CH\}_2P]\cdot$ (**1**)[2] with $Fe_2(CO)_9$ in *n*-hexane at room temperature, the initial blood-red color of the solution darkened very rapidly. Removal of solvent and $Fe(CO)_5$ in vacuo afforded the purple-black solid radical of composition $[\{(Me_3Si)_2CH\}_2PFe(CO)_4]\cdot$ (**2**)[5] for which $\mu_{eff} = 0.88\ \mu_B$ at 300 K. The 70-eV mass spectrum of **2** exhibited a parent peak at *m/e* 517 and a high intensity peak (30%) at *m/e* 405 which is attributable to $[\{(Me_3Si)_2CH\}_2PFe]^+$. A cryoscopic molecular weight indicated that **2** is monomeric in benzene solution (calcd 518; found 494).

It is interesting to note that, despite the presence of an unpaired electron in **1** and **2**, it is possible to record limited NMR data for both radicals. **1**: $^{31}P\{^1H\}$ NMR (36.43 MHz) δ +404 (s).[6] **2**: ^1H NMR (90.0 MHz) δ 0.28 (s, Me_3Si); $^{13}C\{^1H\}$ NMR (20.0 MHz, Me_4Si) δ 3.0 (br s, Me_3Si); $^{31}P\{^1H\}$ NMR (36.43 MHz) +300 ppm (s).[6] The fact that ^1H and ^{13}C NMR spectra are detectable for **2** but not for **1** suggests that the unpaired electron resides in the $Fe(CO)_4$ moiety of **2**. Two additional lines of spectroscopic evidence are consistent with this view: (i) In contrast to that of **1** (for which $a_P = 9.63$ and $a_H = 0.64$ mT, and $g = 2.009$),[2] the ESR of **2** consists of a narrow singlet ($g = 2.004$) with no perceptible hyperfine coupling to ^{31}P or ^1H; (ii) the Mössbauer spectrum of **2** (Figure 1) provides evidence for unresolved hyperfine coupling; moreover, in contrast to phosphenium–$Fe(CO)_4$ complexes,[7] the isomer shift (IS = –0.03 mm/s) and quadrupole splitting (QS = 0.52 mm/s) for the two intense lines of **2** are significantly removed from the linear (Collins–Pettit)[8] plot of isomer shifts vs. quadrupole splittings typical of diamagnetic $LFe(CO)_4$ complexes. Assuming that the phosphinyl ligand occupies an axial site of a locally trigonal bipyramidal geometry at iron,[9] the P–Fe σ bond in **2** can be formed by interaction of the phosphorus lone pair with the a_1 MO of the C_{3v} $Fe(CO)_4$ fragment,[11,12] and delocalization of the unpaired electron can occur via interaction of the singly occupied P(3p) orbital with the Fe($3d_{xz}$) component of the le MO.[13] If the latter interaction is sufficiently strong, the SOMO would be a π^*(CO) orbital. Consistent with the postulate of one-electron increase to the $Fe(CO)_4$ moiety, we have found that the CO stretching frequencies

---

[1] Present address: Allied Chemical, Buffalo Research Laboratory, Buffalo, NY 14210.

[2] Gynane, M. J. S.; Hudson, A.; Lappert, M. F.; Power, P. P.; Goldwhite, H. *J. Chem. Soc., Chem. Commun.* **1976**, 623–624. Gynane, M. J. S.; Hudson, A.; Lappert, M. F.; Power, P. P.; Goldwhite, H. *J. Chem. Soc., Dalton Trans.* **1980**, 2428–2433.

[3] Two-coordinate phosphorus (phosphenium) cations, R_2P^+, can be regarded as carbenoids in the sense that their bonding involves a lone pair of electrons in an approximately sp^2 hybrid orbital and a vacant 3p orbital at phosphorus (Cowley, A. H.; Cushner, M. C.; Lattman, M.; McKee, M. L.; Szobota, J. S.; Wilburn, J. C. *Pure Appl. Chem.* **1980**, *52*, 789–797). One- and two-electron addition to the vacant orbital produces phosphinyl radicals and phosphide anions, respectively.

[4] Interesting parallels exist between R_2M^n species of groups 4A and 5A. Thus, R_2P^+ and R_2P^- are isoelectronic with R_2Si and R_2Si^{2-}, and phosphinyl radicals are isoelectronic with unknown silicon anion radicals, $R_2Si^{-}\cdot$. At present the group 4A chemistry is limited to carbene radical complexes (Krusic, P. J.; Klabunde, V.; Casey, C. P.; Block, T. F. *J. Am. Chem. Soc.* **1976**, *98*, 2015–2017) and complexes of the heavier congeners such as $[R_2Sn\{base\}Fe(CO)_4]$, $[R_2SnFe(CO)_4]^{2-}$, and several $[(Me_3Si)_2CH]_2M$ (M = Ge, Sn, Pb) complexes. See: Marks, T. J. *Ibid.* **1971**, *93*, 7090–7091. Marks, T. J.; Newman, A. R. *Ibid.* **1973**, *95*, 769–773. Lappert, M. F.; Miles, S. J.; Power, P. P.; Carty, A. J.; Taylor, N. J. *J. Chem. Soc., Chem. Commun.* **1977**, 458–495. Sosinsky, B. A.; Shelly, J.; Shong, R. *Inorg. Chem.* **1981**, *20*, 1370–1374 and references therein.

[5] A satisfactory elemental analysis was obtained for **2**.

[6] ^{31}P chemical shifts measured with respect to 85% H_3PO_4 as external standard. + means downfield (deshielded).

[7] Baxter, S. G.; Collins, R. L.; Cowley, A. H.; Sena, S. F. *J. Am. Chem. Soc.* **1981**, *103*, 714–715.

[8] Collins, R. L.; Pettit, R. *J. Chem. Phys.* **1963**, *39*, 3433–3436. This relationship, which is phenomenological, may be limited to simple, diamagnetic $LFe(CO)_4$ systems. Like **2**, mixed-metal $MFe(CO)_4$ complexes have been found to deviate from the linear plot; e.g., for $(NH_3)ZnFe(CO)_4$, IS = –0.08 mm/s; QS = 0.8 mm/s (Sosinsky, B. A., private communication, 1981). The theoretical reasons for the linear plot, and deviations therefrom, remain to be elucidated.

[9] This geometry is anticipated on theoretical grounds (Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365–374). Moreover, it has been established that, with the exception of the triphosphine ligand $PhP(PPh_2)_2$,[10] phosphorus donors prefer axial sites in (phosphine)$Fe(CO)_4$ complexes. See: Jarvis, J. A. J.; Mais, R. H. B.; Owston, P. G.; Thompson, D. T. *J. Chem. Soc. A* **1963**, 622–628. Einstein, F. W. B.; Jones, R. D. G. *J. Chem. Soc., Dalton Trans.* **1972**, 442–446. Pickardt, J.; Rösch, L.; Schumann, H. *J. Organomet. Chem.* **1976**, *107*, 241–248. Bennett, D. W.; Neustadt, R. J.; Parry, R. W.; Cagle, F. W., Jr. *Acta Crystallogr., Sect. B.* **1978**, *34*, 3362–3364. Cowley, A. H.; Davis, R. E.; Remadna, K. *Inorg. Chem.* **1981**, *20*, 2146–2152.

[10] Sheldrick, W. S.; Morton, S.; Stelzer, O. *Z. Anorg. Allg. Chem.* **1981**, *475*, 232–240.

[11] The MO's of an $Fe(CO)_4$ fragment of C_{3v} symmetry are well-known[12] and comprise filled 1e (principally $3d_{xz}$ and $3d_{yz}$ on Fe) and 2e (principally $3d_{x^2-y^2}$ and $3d_{xy}$ on Fe) and vacant a_1 (principally $3d_{z^2}$ on Fe) and a_2 (CO π^*) levels in order of increasing energy.

[12] Hoffmann; R.; Chen, M. M. L.; Elian, M.; Rossi, A. R.; Mingos, D. M. P. *Inorg. Chem.* **1974**, *13*, 2666–2675. Burdett, J. K. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 1599–1613. Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058–1076. Böhn, M. C.; Daub, J.; Gleiter, R.; Hofmann, P.; Lappert, M. F.; Öfele, K. *Chem. Ber.* **1980**, *113*, 3629–3646.

[13] A rather similar argument has been advanced to explain the physical properties of and bonding in $[R_2SnFe(CO)_4]^{2-}$. Silvestre, J.; Albright, T. A.; Sosinsky, B. A. *Inorg. Chem.* **1981**, *20*, 3937–3940. We are grateful to Professors Albright and Sosinsky for preprints of their work and for valuable discussion.

0002-7863/82/1504-0331$01.25/0