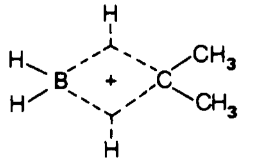
corresponding ones for diborane, but scale factors in this case range between 0.961 and 0.717. The existence of a true energy minimum is, however, well founded. One reason for missing the minimum in the previous calculations was the fact that a complete geometrical optimization was not carried out. In 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]



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(7) Olah, G. A.; Field, L.; Prakash, G. K. S., unpublished results.

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# Phosphinyl Radicals as Ligands. Preparation of Novel Paramagnetic Organometallic Compounds

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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) $\delta$ +404 (s).[6] **2**: ${}^1H$ NMR (90.0 MHz) $\delta$ 0.28 (s, $Me_3Si$); ${}^{13}C\{{}^1H\}$ NMR (20.0 MHz, $Me_4Si$) $\delta$ 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 $\sigma$ 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 1e MO.[13] If the latter interaction is sufficiently strong, the SOMO would be a $\pi^*$(CO) orbital. Consistent with the postulate of one-electron increase to the $Fe(CO)_4$ moiety, we have found that the CO stretching frequencies

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[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 $\pi^*$) 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.

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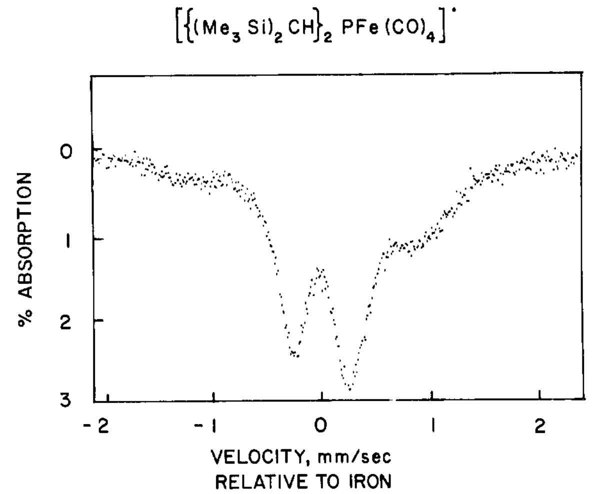
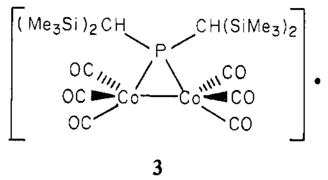


**Figure 1.** $^{57}$Fe Mössbauer spectrum of $[\{(Me_3Si)_2CH\}_2PFe(CO)_4]\cdot$ (**2**) at 25 K.

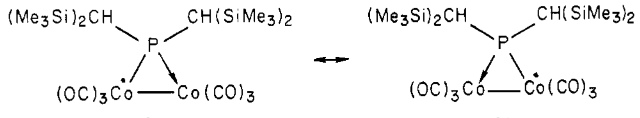
of **2** (2040, 1930, 1920, and 1880 cm$^{-1}$) are ~100 cm$^{-1}$ lower[14] than those of phosphenium complexes such as $[(Me_2N)_2PFe(CO)_4]^+$ (2123, 2063, 2014, and 1972 cm$^{-1}$).[15]

The reaction of **1** with $Co_2(CO)_8$ in toluene solution resulted in the rapid evolution of CO and the production of a dark purple solution, evaporation of which produced a purple solid radical of composition $[\{(Me_3Si)_2CH\}_2PCo_2(CO)_6]\cdot$ (**3**) for which $\mu_{eff} = 1.82$ $\mu_B$ at 300 K. The 70-eV mass spectrum of **3** does not exhibit a parent peak; the highest *m/e* peaks appear at 495 and 464 and are attributable to $[\{(Me_3Si)_2CH\}_2PCo_2(CO)]^+$ and $[\{(Me_3Si)_2CH\}_2PCo(CO)_2]^+$, respectively. It is not possible to record satisfactory NMR spectra for **3**. The ESR spectrum of **3** in toluene solution consists of a 15-line pattern at $g = 2.001$; $a_{Co} = 3.4$ mT, thus indicating delocalization of the unpaired electron into the $Co_2(CO)_6$ moiety ($^{59}$Co, $I = {}^7/_2$, natural abundance = 100%).[16] The IR spectrum of **3** (cyclohexane solution) exhibits CO stretching frequencies at 2070, 2035, 2010, 1990, and 1975 cm$^{-1}$. There is no evidence for the presence of bridging CO ligands. The molecular weight determination was rendered inaccurate by slow decomposition in benzene solution; however, the observed value of 485 is indicative of the monomeric nature of **3** (calcd 636). The equivalence of the $^{59}$Co nuclei in the ESR experiment and the absence of bridging CO's in the IR spectrum imply the following structure for **3**:[17]



**3**

The above delocalized structure can be regarded as arising from canonical forms **3a** and **3b**.



**3a** **3b**

The reaction of stabilized phosphinyl radicals with other organometallic substrates is under active investigation.

**Acknowledgment.** We thank the National Science Foundation (Grant CHE79-10155) and the Robert A. Welch Foundation for generous financial support. We are also grateful to Professor R. L. Collins for the Mössbauer spectrum and Professor W. H. Woodruff for the resonance Raman spectrum.

**Registry No. 1**, 63429-86-7; **2**, 80049-76-9; **3**, 80145-58-0; $Fe_2(CO)_9$, 15321-51-4; $Co_2(CO)_8$, 10210-68-1.

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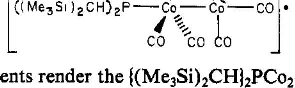
(14) $\nu_{CO}$ shifts of ~100 cm$^{-1}$ are indicative of one-electron increase at iron. See: Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds"; Wiley: New York, 1978; pp 279-294.

(15) Montemayer, R. G.; Sauer, D. T.; Fleming, S., Sr.; Bennett, D. W.; Thomas, M. G.; Parry, R. W. *J. Am. Chem. Soc.* **1978**, *100*, 2231-2233.

(16) Very similar ESR spectra have been observed for bridged $Co_2(CO)_6$ anion radicals. See: Peake, B. M.; Rieger, P. H.; Robinson, B. H.; Simpson, J. *J. Am. Chem. Soc.* **1980**, *102*, 156-163. *Inorg. Chem.* **1981**, *20*, 2540-2543.

(17) The analytical data for the cobalt product agree best with the formulation $\{(Me_3Si)_2CH\}_2PCo_2(CO)_6$. Anal. Calcd for $C_{20}H_{38}Co_2PO_6Si_4$: C, 37.79; H, 6.02. Found: C, 37.8; H, 6.3. However, these analytical data are also close to those for $\{(Me_3Si)_2CH\}_2PCo_2(CO)_7$. Anal. Calcd for $C_{21}H_{38}Co_2PO_7Si_4$: C, 38.00; H, 5.77. Since there are no bridging CO's (see text), the most likely structure for $\{(Me_3Si)_2CH\}_2PCo_2(CO)_7$ would be



However, two arguments render the $\{(Me_3Si)_2CH\}_2PCo_2(CO)_7$ structure unlikely: (i) the Co's are equivalent on the ESR time scale and (ii) no Co-Co stretch is detectable in resonance Raman experiments.

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## β-Methylene-DL-aspartic Acid: A Selective Inhibitor of Glutamate-Aspartate Transaminase

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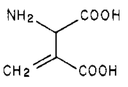
*Received March 30, 1981*

β-Methylene-DL-aspartic acid (I) has recently been synthesized[1] for use in the study of the β-methyl-L-aspartate ⇄ L-glutamate carbon skeleton rearrangement, a reaction catalyzed by the vitamin $B_{12}$ dependent enzyme, methylaspartate mutase.[2] It occurred



I

to us that β-methylene-DL-aspartate (I) might have wider biological application.

The β,γ-unsaturated amino acids have been intensely studied as "suicide" inhibitors[3] of pyridoxal 5′-phosphate dependent and flavin dependent enzymes.[4,5] Active suicide inhibitors include propargylglycine[4] and vinylglycine.[5,6] DL-Vinylglycine irreversibly inactivates soluble pig heart glutamate-aspartate transaminase[6] and highly purified forms of mitochondrial and soluble rat brain glutamate-aspartate transaminase.[7] Glutamate-aspartate transaminase plays a central role in intermediary metabolism.[8] It

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(1) Dowd, P.; Kaufman, C. *J. Org. Chem.* **1979**, *44*, 3956.

(2) Barker, H. A.; Weissbach, H.; Smyth, R. D. *Proc. Natl. Acad. Sci. U.S.A.* **1958**, *44*, 1093.

(3) Suicide ($k_{cat}$ or mechanism based) inhibition was first described by: Helmkamp, G. M.; Rando, R. R.; Brock, D. J. H.; Bloch, K. *J. Biol. Chem.* **1968**, *243*, 3229. Bloch, K. *Acc. Chem. Res.* **1969**, *2*, 193. Bloch, K. *Enzymes, 3rd Ed.* **1971**, *5*, 441.

(4) Abeles, R. H.; Walsh, C. T. *J. Am. Chem. Soc.* **1973**, *95*, 6124.

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(6) Rando, R. R. *Biochemistry* **1974**, *13*, 3859.

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