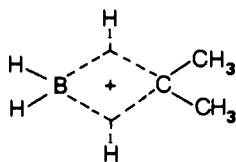


corresponding ones for diborane, but scale factors in this case range between 0.961 and 0.717. The existence of a true energy minimum is, however, well founded. One reason for missing the minimum in the previous calculations was the fact that a complete geometrical optimization was not carried out. In 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(7) Olah, G. A.; Field, L.; Prakash, G. K. S., unpublished results.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

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Interesting work by Lappert, Goldwhite, and co-workers² 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 phosphonium cations and phosphide anions.^{3,4} Furthermore, the reactivity of persistent $R_2P\cdot$ species toward metal

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(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 (phosphonium) 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^- . 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.

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 $[(Me_3Si)_2CH]_2PFe(CO)_4$ (**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) δ 0.28 (s, Me_3Si); $^{13}C\{^1H\}$ NMR (20.0 MHz, Me_3Si) 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 phosphonium- $Fe(CO)_4$ 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 $1e$ 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

(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 $Ph(PPh_2)_3$,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-known¹² and comprise filled $1e$ (principally $3d_{xz}$ and $3d_{yz}$ on Fe) and $2e$ (principally $3d_{z^2}$ 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.

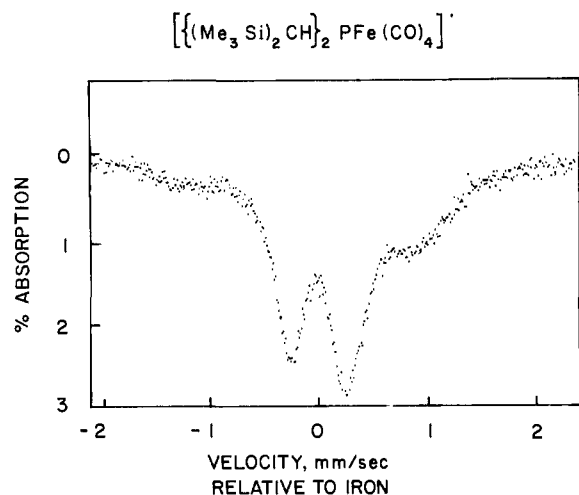
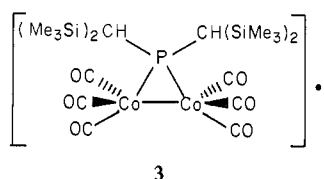


Figure 1. ^{57}Fe Mössbauer spectrum of $\{[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{PFe}(\text{CO})_4\}^-$ (**2**) at 25 K.

of **2** (2040, 1930, 1920, and 1880 cm^{-1}) are $\sim 100 \text{ cm}^{-1}$ lower¹⁴ than those of phosphonium complexes such as $[(\text{Me}_2\text{N})_2\text{PFe}(\text{CO})_4]^+$ (2123, 2063, 2014, and 1972 cm^{-1}).¹⁵

The reaction of **1** with $\text{Co}_2(\text{CO})_8$ 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 $\{[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{PCo}_2(\text{CO})_6\}^-$ (**3**) for which $\mu_{\text{eff}} = 1.82 \mu_{\text{B}}$ 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 $\{[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{PCo}_2(\text{CO})\}^+$ and $\{[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{PCo}(\text{CO})_2\}^+$, 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 $g = 2.001$; $a_{\text{Co}} = 3.4 \text{ mT}$, thus indicating delocalization of the unpaired electron into the $\text{Co}_2(\text{CO})_6$ 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

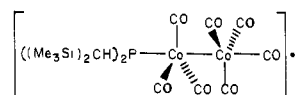


(14) ν_{CO} shifts of $\sim 100 \text{ cm}^{-1}$ are indicative of one-electron increase at iron. See: Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds"; Wiley: New York, 1978; pp 279-294.

(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.

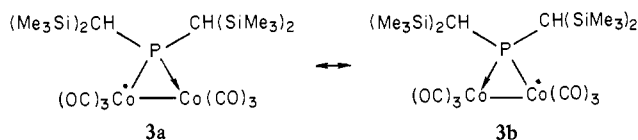
(16) Very similar ESR spectra have been observed for bridged $\text{Co}_2(\text{CO})_6$ anion radicals. See: Peake, B. M.; Rieger, P. H.; Robinson, B. H.; Simpson, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 156-163. *Inorg. Chem.* **1981**, *20*, 2540-2543.

(17) The analytical data for the cobalt product agree best with the formulation $\{[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{PCo}_2(\text{CO})_6\}^-$. Anal. Calcd for $\text{C}_{20}\text{H}_{36}\text{Co}_2\text{P}_2\text{O}_6\text{Si}_4$: C, 37.79; H, 6.02. Found: C, 37.8; H, 6.3. However, these analytical data are also close to those for $\{[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{PCo}_2(\text{CO})_7\}^-$. Anal. Calcd for $\text{C}_{21}\text{H}_{38}\text{Co}_2\text{P}_2\text{O}_7\text{Si}_4$: C, 38.00; H, 5.77. Since there are no bridging CO's (see text), the most likely structure for $\{[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{PCo}_2(\text{CO})_7\}^-$ would be



However, two arguments render the $\{[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{PCo}_2(\text{CO})_7\}^-$ 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.

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



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

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Registry No. **1**, 63429-86-7; **2**, 80049-76-9; **3**, 80145-58-0; $\text{Fe}_2(\text{CO})_9$, 15321-51-4; $\text{Co}_2(\text{CO})_8$, 10210-68-1.

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

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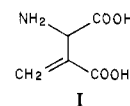
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Received March 30, 1981

β -Methylene-DL-aspartic acid (**I**) has recently been synthesized¹ for use in the study of the β -methyl-L-aspartate \rightleftharpoons L-glutamate carbon skeleton rearrangement, a reaction catalyzed by the vitamin B₁₂ dependent enzyme, methylaspartate mutase.² It occurred



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" inhibitors³ of pyridoxal 5'-phosphate dependent and flavin dependent enzymes.^{4,5} Active suicide inhibitors include propargylglycine⁴ and vinylglycine.^{5,6} DL-Vinylglycine irreversibly inactivates soluble pig heart glutamate-aspartate transaminase⁶ 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

(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.

(5) Reviews: Rando, R. R. *Science (Washington, D.C.)* **1974**, *185*, 320. Rando, R. R. *Acc. Chem. Res.* **1975**, *8*, 281. Abeles, R. H.; Maycock, A. L. *Acc. Chem. Res.* **1976**, *9*, 313. Walsh, C. T. *Horiz. Biochem. Biophys.* **1977**, *3*, 36.

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

(7) King, S.; Phillips, A. T. *J. Neurochem.* **1978**, *30*, 1399.