New Bimetallic, Phosphido-bridged Iron Complexes derived from $[Fe_2(\mu\text{-}CO)(\mu\text{-}PPh_2)(CO)_5(PPh_2)]^{2-}$

Yuan-Fu Yu, Judith Gallucci, and Andrew Wojcicki*

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, U.S.A.

The title dianion, obtained by deprotonation of $[Fe_2(\mu\text{-}CO)(\mu\text{-}PPh_2)(CO)_5(PPh_2H)]^-$ at low temperature, affords various phosphido-bridged di-iron complexes upon reaction with iodohydrocarbons; new complexes include $[Fe_2(\mu\text{-}CO)(\mu\text{-}PPh_2)(CO)_5(PPh_2R)]^-$ (R = Me, Et, Pr^n, Pr^i, allyl), $Fe_2(\mu\text{-}PPh_2)[\mu\text{-}C(R)O](CO)_5(PPh_2R)$ (R = Pr^n, Pr^i), $Fe_2(\mu\text{-}PPh_2)(CO)_5(\eta^3\text{-}C_3H_5)(PPh_2C_3H_5)$, the structure of which was determined by *X*-ray diffraction, and $Fe_2(\mu\text{-}PPh_2)(\mu\text{-}CH_2PPh_2)(CO)_6$.

We have recently shown[1] that reduction of $Fe_2(\mu\text{-}PPh_2)_2(CO)_6$ with MBR_3H (M = Li, Na, or K; R = Et or Bu^s proceeds to $[Fe_2(\mu\text{-}CO)(\mu\text{-}PPh_2)(CO)_5(PPh_2H)]^-$, (**1**). Herein we report the preparation of the related dianion, $[Fe_2(\mu\text{-}CO)(\mu\text{-}PPh_2)(CO)_5(PPh_2)]^{2-}$, (**2**), and demonstrate its usefulness in the synthesis of a variety of new phosphido-bridged di-iron complexes.

A freshly prepared tetrahydrofuran (THF) solution of (**1**) from equimolar amounts of $Fe_2(\mu\text{-}PPh_2)_2(CO)_6$ and $LiBEt_3H$ at 25 °C was cooled to −78 °C and then treated slowly with one equivalent of Bu^{n}Li. Immediately the solution changed colour from red to purple, and its ^{31}P n.m.r. spectrum indicated deprotonation of the PPh_2H ligand. The resulting (**2**)† is stable in solution under N_2 below −40 °C; however, at higher temperatures it completely and irreversibly isomerizes to the known[2] $[Fe_2(\mu\text{-}PPh_2)_2(CO)_6]^{2-}$, (**3**). The dianion (**2**) displays high reactivity, even at −78 °C, toward a number of iodohydrocarbons (Scheme 1).

Upon treatment with MeI (1 equiv. or an excess) in THF at −78 °C, (**2**) was rapidly and quantitatively methylated at the terminal PPh_2 to yield $[Fe_2(\mu\text{-}CO)(\mu\text{-}PPh_2)(CO)_5(PPh_2Me)]^-$, (**4a**),‡ which was not isolated. Red solutions of (**4a**) are stable at 25 °C under N_2 and in the absence of excess of MeI. With an excess of MeI, (**4a**) underwent further methylation on warming from −78 to 25 °C to afford the previously reported[1] $Fe_2(\mu\text{-}PPh_2)[\mu\text{-}C(Me)O](CO)_5(PPh_2Me)$, (**5a**), in 90% isolated yield. The methylation with a second equivalent of MeI was found by $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ n.m.r. spectroscopy to proceed *via* two detectable intermediates. Although available data do not allow complete characterization of these species, they appear to be iron–methyl and iron–acetyl complexes. This suggests that the reaction proceeds by methylation at Fe(2) followed by migratory insertion of CO into the Fe(2)–Me bond and closure of the acetyl bridge. Complexes (**4b**—**d**) and (**5b**—**d**),§ analogous to (**4a**) and (**5a**) respectively, were prepared from (**2**) and each of EtI, Pr^{n}I, and Pr^{i}I; the former were characterized in solution while the latter were characterized after isolation in 53—65% yields.

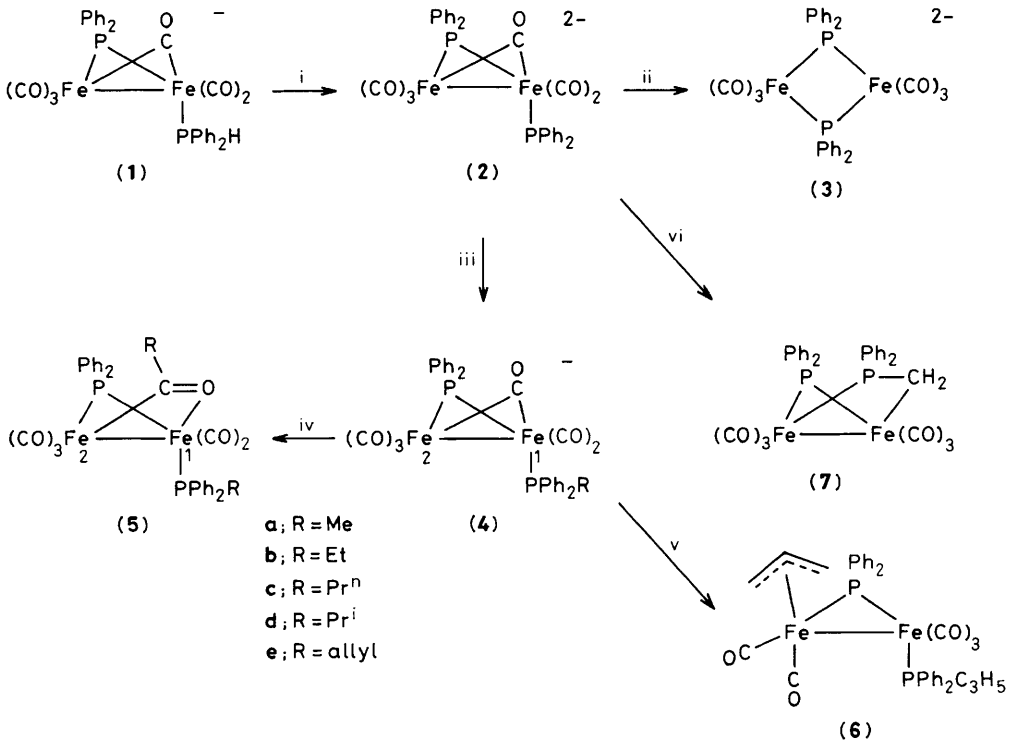
Reaction of (**2**) with allyl iodide in THF also proceeded at −78 °C to give a red solution containing (**4e**).§ Excess of allyl iodide with warming to 25 °C converted (**4e**) into the red complex $Fe_2(\mu\text{-}PPh_2)(CO)_5(\eta^3\text{-}C_3H_5)(PPh_2C_3H_5)$, (**6**), in 72% isolated yield. The molecular structure of (**6**) was

---

† Selected spectroscopic data for (**2**): $^{31}P\{^1H\}$ n.m.r. (THF, −73 °C) δ 136.8 (d, J_{PP} 7 Hz, bridging *P*Ph$_2$), 20.7 p.p.m. (d, terminal *P*Ph$_2$); no one-bond P–H coupling observed in ^{31}P n.m.r. spectrum; $^{13}C\{^1H\}$ n.m.r., CO signals (THF, −83 °C) δ 254.5 (br., bridging *C*O), 225.1 p.p.m. (br., terminal *C*O).

‡ Selected spectroscopic data for (**4a**): ν(CO) (THF) 1989m, 1938s, 1895s br., 1840sh, 1625m cm^{-1}; $^{31}P\{^1H\}$ n.m.r. (THF, 25 °C) δ 128.2 (d, J_{PP} 37 Hz, *P*Ph$_2$), 59.2 p.p.m. (d, *P*Ph$_2$Me); $^{13}C\{^1H\}$ n.m.r., CO signals (THF, −83 °C) δ 257.7 (br., bridging *C*O), 219.9 p.p.m. (br., terminal *C*O).

§ Complexes (**4b**—**d**) showed ν(CO) absorptions at frequencies similar to those for (**4a**) and $^{31}P\{^1H\}$ n.m.r. signals (THF) at δ 128—129 (d, J_{PP} 29—36 Hz, *P*Ph$_2$) and 67—80 p.p.m. (d, *P*Ph$_2$R). Complexes (**5b**—**d**) showed ν(CO) absorptions at frequencies similar to those for (**5a**); satisfactory ^1H and $^{13}C\{^1H\}$ n.m.r. (CDCl$_3$), including a ^{13}C signal at δ 300—305 p.p.m. [d, J_{PC} 17—21 Hz, *C*(O)R]; $^{31}P\{^1H\}$ n.m.r. signals (THF) at δ 168—172 (d, J_{PP} 36—49 Hz, *P*Ph$_2$) and 49—62 p.p.m. (d, *P*Ph$_2$R); and the parent ion in its mass spectrum (fast atom bombardment). The spectroscopic properties of (**4e**) (i.r. and $^{31}P\{^1H\}$ n.m.r.) are similar to those of (**4a**—**d**).



Scheme 1. i, Bu^{n}Li at −78 °C; ii, warming to *ca.* −40 °C; iii, 1 equiv. RI; iv (**a**—**d** only), RI and warming to *ca.* 25 °C; v (**e** only), allyl iodide and warming to *ca.* 25 °C; vi, excess of CH_2I_2.

established by *X*-ray diffraction;¶ suitable crystals were obtained from CH_2Cl_2–hexane at *ca.* 5 °C.

The structure of complex (**6**) is shown in Figure 1 together with some important bond parameters. The molecular framework consists of $Fe(CO)_3(PPh_2C_3H_5)$ and $Fe(CO)_2(\eta^3\text{-}C_3H_5)$ moieties joined by an Fe–Fe bond and an unsymmetrically bridging PPh_2, the distance Fe(1)–P(1) being 0.045 Å longer than the distance Fe(2)–P(1). The Fe–Fe bond distance of 2.802(2) Å in (**6**) is longer than the Fe–Fe bond distance in related, but doubly-bridged, di-iron complexes of general formula $[Fe_2(\mu\text{-}PPh_2)(\mu\text{-}X)(CO)_5L]^{0\text{ or }-}$ [X = PPh_2, Cl, C(Me)O, C≡CPh, *inter alia*; L = CO, PR_3, or C(Me)O], which are in the range of 2.548—2.718 Å.[3—5] As a consequence, the Fe(1)–P(1)–Fe(2) angle of 79.0(1)° in (**6**) is larger than that in the aforementioned complexes. The geometry of the η^3-allyl group is normal, and the dihedral angle between the planes C(6)C(7)C(8) and C(6)Fe(2)C(8) is 73.1(14)°, which is in the 70—80° range found for other η^3-allyl complexes.[6]

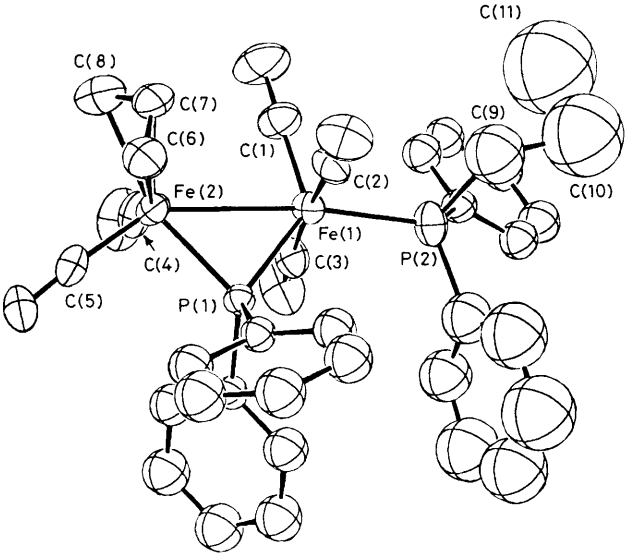


Figure 1. ORTEP Drawing of (**6**). Non-hydrogen atoms are drawn at the 50% probability level, and the hydrogen atoms are omitted for clarity. Selected structural parameters: Fe–Fe 2.802(2), Fe(1)–P(1) 2.225(2), Fe(2)–P(1) 2.180(3), Fe(1)–P(2) 2.232(3), Fe(2)–C(6) 2.153(10), Fe(2)–C(7) 2.097(10), Fe(2)–C(8) 2.175(12) Å; Fe(1)–P(1)–Fe(2) 79.0(1), P(2)–Fe(1)–Fe(2) 170.9(1), Fe(1)–Fe(2)–C(5) 146.3(3), Fe(1)–Fe(2)–C(6) 103.9(3), Fe(1)–Fe(2)–C(7) 94.8(3), Fe(1)–Fe(2)–C(8) 113.4(3)°.

¶ *Crystal data:* (**6**), $C_{35}H_{30}Fe_2O_5P_2$, M_r = 704.27, monoclinic, space group $P2_1$, a = 9.137(3), b = 16.997(4), c = 11.300(3) Å; β = 108.23(3)°, U = 1667 Å^3, D_c = 1.403 g/cm^3, Z = 2. Intensities were measured at 20(1) °C by the ω scan method up to 2θ = 55° by using a Syntex P$\bar{1}$ diffractometer with graphite-monochromated Mo-K_α radiation [λ(Mo-$K_{\bar{\alpha}}$) = 0.71069 Å]. The structure was solved by a combination of direct, Patterson, and Fourier methods. The data were corrected for absorption (μ = 10.02 cm^{-1}) by the Gaussian grid method. Hydrogen atoms were included in calculated positions (C–H = 0.95 Å), except for the σ-bonded allyl group to which no hydrogens were added. This σ-bonded allyl group appears to be disordered and it was necessary to constrain the P(2)–C(9) bond length during least-squares refinement. The final refinement used rigid body constraints for the phenyl rings, isotropic thermal parameters for the σ-bonded allyl group, and anisotropic thermal parameters for the remaining non-hydrogen atoms and converged to $R(F)$ = 0.065 and $R_w(F)$ = 0.082 for 3250 intensities with $F_o^2 > 3\sigma(F_o^2)$ and 213 variables with the weighting scheme $w = 1/\sigma^2(F)$. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

Reaction of (**2**) with an excess of CH_2I_2 in THF proceeded rapidly at *ca.* −78 °C to yield, after chromatography on Florisil, $Fe_2(\mu\text{-}PPh_2)_2(CO)_6$ (42%) and olive green $Fe_2(\mu\text{-}PPh_2)(\mu\text{-}CH_2PPh_2)(CO)_6$ (25%), (**7**).** Complex (**7**) was characterized by comparison of its spectroscopic properties with those of $Fe_2(\mu\text{-}PPh_2)(\mu\text{-}CH_2PPh_2)(NO)_4$, the structure of which was recently determined by *X*-ray diffraction.[7] Bimetallic complexes containing $\mu\text{-}CH_2PR_2$ ligands are rare,[8] and reactions of dianionic species such as (**2**) with CH_2X_2 represent a potential general route to these compounds. The formation of (**7**) indicates that Fe(2) and P(2) in (**2**) are the sites for attack by CH_2I_2. It also suggests that other di-iodo species, *i.e.*, ML_nI_2, may react analogously to CH_2I_2 with the dianion (**2**).

The support of this research by the National Science Foundation is gratefully acknowledged.

Received, 30th December 1983; Com. 1699

** Selected spectroscopic data for (**7**): ν(CO) (C_6H_{12}) 2046s, 2004s, 1991s, 1963s, 1952s cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ 1.6 (d, J_{PH} 33 Hz, CH_2); $^{13}C\{^1H\}$ n.m.r. ($CDCl_3$) δ 213.3 (m, *C*O), −18.8 p.p.m. (t or dd, J_{PC} 7 Hz, CH_2); $^{31}P\{^1H\}$ n.m.r. (THF) δ 181.0 (d, J_{PP} 31 Hz, *P*Ph_2), 20.4 p.p.m. (d, CH_2*P*Ph_2); parent ion (*m/z* 664) in mass spectrum (fast atom bombardment). Satisfactory C and H microanalyses were obtained.

References

1 Y.-F. Yu, J. Gallucci, and A. Wojcicki, *J. Am. Chem. Soc.*, 1983, **105**, 4826.
2 J. P. Collman, R. K. Rothrock, R. G. Finke, E. J. Moore, and F. Rose-Munch, *Inorg. Chem.*, 1982, **21**, 146.
3 A. J. Carty, *Adv. Chem. Ser.*, 1982, **196**, 163.
4 J. R. Huntsman, Ph.D. Thesis, University of Wisconsin-Madison, 1973.
5 R. E. Ginsburg, J. M. Berg, R. K. Rothrock, J. P. Collman, K. O. Hodgson, and L. F. Dahl, *J. Am. Chem. Soc.*, 1979, **101**, 7218.
6 U. Franke and E. Weiss, *J. Organomet. Chem.*, 1977, **139**, 305.
7 M. Calligaris, G. Nardin, Y.-F. Yu, and A. Wojcicki, Abstracts, XI International Conference on Organometallic Chemistry, Pine Mountain, Georgia, U.S.A., October 10—14, 1983, p. 86.
8 H.-F. Klein, J. Wenninger, and V. Schubert, *Z. Naturforsch., Teil B*, 1979, **34**, 1391; P. Braunstein, D. Matt, and Y. Dusausoy, *Inorg. Chem.*, 1983, **22**, 2043; G. L. Geoffroy, S. Rosenberg, P. M. Shulman, and R. R. Whittle, *J. Am. Chem. Soc.*, 1984, **106**, 1519.