the X-Pd-X bond angle is slightly acute, 86-89°, and the Pd-X-Pd bond angle slightly obtuse, 91-94°; the corresponding angles in 1 are within these ranges. The coordination geometry about Pd(II) is clearly square planar: the maximum deviation (0.008 Å) from perfect planarity is slight and occurs at C(37). The interplanar angle relating the central rhombus to the Pd coordination plane is 2.4°. The five-membered chelate ring is folded along the P···C(37) vector at a dihedral angle of 40.6°.

As indicated in the Introduction, steric congestion in the precursor is a prerequisite for cyclopalladation. The effect of this congestion is to force the placement of a C-H bond in an axial coordination site where activation can occur. Empirical evidence has been cited for the repulsive nature of distal, axial CH···Pd interactions;[23] this conclusion has very recently been supported for d^8 square-planar coordination by a theoretical study of C-H bond activation.[24] Therefore, in the absence of steric constraint, axial CH···Pd interactions are avoided. The structure of 1 provides evidence for the axial placement of one of the C(27) bonded hydrogen atoms at 2.84 (3) Å and 89 (2)° to the Pd(II) coordination plane. (In one form of $(Me_2PhP)_2PdI_2$, two phenyl hydrogen atoms are similarly positioned at 2.84 and 2.85 Å.[25]) Additionally, all structurally characterized products of cyclopalladation reactions of *o*-alkylphenyl substituents show the formation of five-membered chelate rings[9,11,13,26] In the cyclopalladation of $P(t\text{-}Bu)_2(o\text{-}EtC_6H_4)$, the α side chain carbon is preferentially metalated.[27] The unique preference for five-membered ring formation provides strong circumstantial evidence for a specific steric constraint in cyclopalladation reactions.

Acknowledgment. The National Science Foundation provided funds supporting the purchase of the diffractometer. Crystals of 1 were kindly supplied by Prof. R. Heck.

Registry No. 1, 89510-88-3.

Supplementary Material Available: Tables of bond distances, bond angles, anisotropic temperature factors, hydrogen atom coordinates, and observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

---

[22] Holden, J. R.; Baenziger, N. C. *J. Am. Chem. Soc.* **1955,** *77,* 4987.

[23] Deeming, A. J.; Rothwell, I. P. *Pure Appl. Chem.* **1980,** *52,* 649.

[24] Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984,** *106,* 2006.

[25] Bailey, N. A.; Mason, R. *J. Chem. Soc. A* **1968,** 2594.

[26] Gill, D. F.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1972,** 65.

[27] Gill, D. F.; Mann, B. E.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1973,** 270.

Coordinated Homoatomic Polyorganophosphorus Catenates. The Crystal Structure and Molecular Geometry of $Fe_2(CO)_6(PCH_3)_4$ and $Fe_2(CO)_6(PC_6H_5)_4$

Arnold L. Rheingold* and Mark E. Fountain

Department of Chemistry, University of Delaware, Newark, Delaware 19716

Received March 20, 1984

The crystal structure and molecular geometry of $Fe_2(CO)_6(PCH_3)_4$ (I) and $Fe_2(CO)_6(PC_6H_5)_4$ (II) have been determined. I: $P2_1/c$, monoclinic, $a = 7.906$ (4) Å, $b = 17.139$ (6) Å, $c = 13.849$ (6) Å, $\beta = 101.41$ (3)°, $V = 1839.5$ (12) Å^3, $Z = 4$, $R_F = 6.4\%$. II: $P2_1/c$, monoclinic, $a = 16.988$ (6) Å, $b = 11.492$ (2) Å, $c = 16.336$ (4) Å, $\beta = 101.09$ (2)°, $V = 3129.5$ (16) Å^3, $Z = 4$, $R_F = 3.6\%$. Both I and II possess similar distorted tetragonal-pyramidal metal atom coordination geometries joined along a basal edge formed by the mutually bridging termini of tetraphosphorus atom catenates. The structure of I is crystallographically isomorphous with its arsenic analogue. Both I and II possess single Fe-Fe bonds [I, 2.634 (2) Å; II, 2.633 (1) Å]. The only significant structural accommodation for the greater steric demands of phenyl vs. methyl substitution is the P-P-P-P dihedral angle [I, -10.5 (2)°; II, -23.6 (1)°]. The formally nonbonded phosphorus chain termini are separated by a distance only 0.5 Å longer than a normal P-P single bond [d(P···P): I, 2.715 (3) Å, II, 2.689 (1) Å]. The $^{31}P\{^1H\}$ NMR data for II reveals a rather large $^2J_{P\text{-}P}$, 125.4 Hz, possibly indicative of an attractive P···P interaction.

Introduction

Homoatomic polyorganophosphorus and arsenic rings, *cyclo*-$(RE)_n$, E = P or As, readily undergo ring-opening reactions when combined with metal carbonyls to yield a variety of coordinated homoatomic catenates.[1,2] One class of products is binuclear and contains a chain of RE units with usually four or five but occasionally as many as eight units. Each chain terminus bridges both metal atoms. Examples both with and without metal-metal bonds are known. If each chain terminus is considered a three-electron donor, then metal-metal bonds are expected for 14-electron metal groups, and no metal-metal bond for 15-electron groups. No exceptions to these expectations are known for this class of compound.

Of the compounds believed to possess this structure, only three have been structurally characterized: $[Fe(CO)_3]_2(AsCH_3)_4$, III,[3] $[\eta^5\text{-}C_5H_5Mo(CO)_2]_2(AsCH_3)_5$,[2] and $[Mo(CO)_3]_2(AsC_3H_7)_8$.[4] No polyorganophosphorus structures of this kind have been previously determined. West et al. originally reported the preparation of a series

---

[1] West, B. O. In "Homoatomic Rings, Chains and Macromolecules of Main-Group Elements"; Rheingold, A. L., Ed.; Elsevier: Amsterdam, 1977; p 409.

[2] Rheingold, A. L.; Churchill, M. R. *J. Organomet. Chem.* **1983,** *243,* 165.

[3] (a) Gatehouse, B. M. *J. Chem. Soc., Chem. Commun.* **1969,** 948. (b) Foust, A. Ph.D. Dissertation, University of Wisconsin-Madison, 1970.

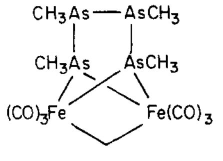
[4] Elmes, P. S.; Gatehouse, B. M.; Lloyd, D. J.; West, B. O. *J. Chem. Soc., Chem. Commun.* **1974,** 953. The As_8 chain, in addition to terminal bonding, is further bonded through the As atoms in the 4- and 5-positions.

0276-7333/84/2303-1417$01.50/0

Table I. Crystal and Data Collection Parameters

	$(CO)_6Fe_2(PMe)_4$ (I)	$(CO)_6Fe_2(PPh)_4$ (II)
formula	$C_{10}H_{12}Fe_2P_4O_6$	$C_{30}H_{20}Fe_2P_4O_6$
crystal system	monoclinic	
space group	$P2_1/c$	
a, Å	7.906 (4)	16.988 (6)
b, Å	17.139 (6)	11.492 (2)
c, Å	13.849 (6)	16.336 (4)
β, deg	101.41 (3)	101.09 (2)
V, Å^3	1839.5 (12)	3129.5 (16)
Z	4	4
ρ(calcd), g cm^{-3}	1.67	1.51
temp, °C	22	23
cryst dimens, mm	0.12 × 0.22 × 0.32	0.37 × 0.40 × 0.42
radiation	graphite monochromated Mo Kα (λ = 0.710 73 Å)	
diffractometer	Nicolet R3	
abs coeff, cm^{-1}	19.4	11.6
scan speed, deg min^{-1}	var 2.5–10	
2θ scan range, deg	4–48	
scan technique	$\theta/2\theta$	ω
data collected	$\pm h,+k,+l$	$\pm h,+k,+l$
unique data	2393 (2640 collected)	4518 (4897 collected)
unique data $F_o \geqslant 3\sigma(F_o)$	1876	3919
std reflctns	3/97 (no decay)	3/97 (no decay)
R_F, R_{wF}, GOF	0.0642, 0.0668, 1.767	0.0364, 0.0408, 1.148
highest peak, final diff map, e Å^{-3}	0.70	0.26

of compounds $Fe_2(CO)_6(PR)_4$ (R = CH_3 (I), C_2H_5, and C_6H_5 (II) from the reaction of $Fe(CO)_5$ and the cyclocatenates $(PCH_3)_5$, $(PC_2H_5)_5$, and $(PC_6H_5)_6$.[1,5,6] On the basis of mass spectral data, they proposed structures analogous to that determined crystallographically for III.[3]



III

Due to the variety of possible structures for the polyphosphorus series, definite structural characterizations seemed a necessity. Additional interest in these structures arises from the recent discovery that *o*-benzo, P-to-P linking of μ-phosphido groups to form a chelating ligand produces important differences in the behavior of the complex on two-electron reduction.[7] Whereas the two-electron reduction of the unlinked compound $[Fe(CO)_3(\mu\text{-}PPh_2)]_2$ (V) leads to Fe–Fe bond cleavage,[8] the linked complex apparently undergoes Fe–P bond cleavage. Electrochemical studies of I and II, both P-to-P linked complexes, reveal that both undergo completely reversible two-electron reductions at room temperature.[9]

Experimental Section

$^{31}P\{^1H\}$ NMR data were obtained by using a Bruker WM 250 spectrometer at 101.1 MHz and are referred to 85% H_3PO_4 (external); negative chemical shifts are upfield from the reference.

Samples of I and II were prepared by West's procedures.[5] The course of the reaction and product analytical data were similar to those described earlier. Crystals suitable for diffraction studies were obtained by recrystallization from acetone at −20 °C. The data collection crystals were affixed to fine glass fibers with urethane varnish.

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Temperature Factors (×10^3) for I

atom	x	y	z	U,^{a} Å^2
Fe(1)	3140 (2)	3926 (1)	2277 (1)	40 (1)
Fe(2)	417 (2)	4003 (1)	3103 (1)	38 (1)
P(1)	739 (3)	3234 (2)	1865 (2)	40 (1)
P(2)	1115 (3)	1975 (2)	2140 (2)	53 (1)
P(3)	2455 (3)	2076 (2)	3682 (2)	50 (1)
P(4)	2833 (3)	3347 (1)	3667 (2)	38 (1)
O(1)	5578 (10)	2978 (5)	1479 (6)	85 (4)
O(2)	5473 (13)	5087 (6)	3397 (7)	99 (4)
O(3)	2045 (13)	4985 (7)	624 (7)	120 (5)
O(4)	1609 (11)	5250 (5)	4522 (5)	79 (3)
O(5)	−1996 (12)	4980 (6)	1747 (6)	85 (4)
O(6)	−2034 (10)	3210 (5)	4063 (6)	70 (3)
C(1)	4658 (12)	3349 (7)	1811 (8)	57 (4)
C(2)	4591 (14)	4639 (6)	2963 (8)	59 (4)
C(3)	2466 (15)	4577 (7)	1261 (10)	69 (5)
C(4)	1140 (13)	4788 (6)	3965 (7)	51 (4)
C(5)	−1047 (14)	4607 (7)	2256 (8)	52 (4)
C(6)	−1071 (13)	3526 (6)	3706 (8)	51 (4)
C(7)	−654 (14)	3269 (7)	648 (7)	64 (4)
C(8)	−1049 (14)	1672 (7)	2312 (9)	71 (5)
C(9)	4608 (13)	1697 (7)	3634 (8)	68 (5)
C(10)	4200 (13)	3548 (7)	4872 (7)	63 (4)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Crystal data as well as data collection and refinement procedures and parameters are collected in Table I. The unit-cell parameters were obtained from the angular settings of 25 well-centered reflections (25° ≤ 2θ ≤ 30°). Systematic absences uniquely defined the monoclinic space group $P2_1/c$ in both cases. All computer programs used are contained in the P3 or SHELXTL (prerelease version 4.0) packages of programs distributed by the Nicolet Corp. The data for both I and II were corrected for absorption by an empirical ψ-scan technique.

The structure of I was solved by using the heavy atom (Fe and As) coordinates from the isomorphous complex $Fe_2(CO)_6(AsMe)_4$;[3b] the C and O atom coordinates were obtained from a subsequent difference Fourier synthesis.

The structure of II was solved by the direct-method routine SOLV. The E map with the highest combined figures of merit yielded the positions of the Fe and P atoms, and the remaining non-hydrogen atoms were found on subsequent difference maps.

In both cases final refinement by blocked-cascade methods used a model containing ellipsoidal thermal parameters for all non-

---

(5) Ang. H. G.; West, B. O. *Aust. J. Chem.* **1967**, *20*, 1133.

(6) Elmes, P. S.; West, B. O. *J. Organomet. Chem.* **1971**, *32*, 365.

(7) McKennis, J. S.; Kyba, E. P. *Organometallics* **1983**, *2*, 1249. Other examples of linked phosphido groups are known: Flood, T. C.; DiSanti, F. J.; Campbell, K. D. *Inorg. Chem.* **1978**, *17*, 1643. Charrier, C.; Guihem, J.; Mathey, F. *J. Org. Chem.* **1981**, *46*, 3.

(8) (a) Huntsman, J. R. Ph.D. Dissertation, University of Wisconsin—Madison 1973. (b) Ginsburg, R. E.; Rothrock, R. K.; Finke, R. G.; Collman, J. P.; Dahl, L. F. *J. Am. Chem. Soc.* **1979**, *101*, 6550.

(9) Dessy, R. E.; Rheingold, A. L., unpublished results.

(10) Clegg, W. *Inorg. Chem.* **1976**, *15*, 1609.

Table III. Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Temperature Factors ($\times10^3$) for I

atom	*x*	*y*	*z*	U,[a] Å^2
Fe(1)	2320 (1)	4664 (1)	1413 (1)	49 (1)
Fe(2)	2448 (1)	2495 (1)	1942 (1)	45 (1)
P(1)	1851 (1)	3937 (1)	2488 (1)	48 (1)
P(2)	2476 (1)	4206 (1)	3798 (1)	51 (1)
P(3)	3610 (1)	4768 (1)	3462 (1)	46 (1)
P(4)	3371 (1)	3879 (1)	2242 (1)	42 (1)
C(1)	2871 (2)	4643 (4)	583 (2)	62 (1)
C(2)	2370 (2)	6178 (3)	1618 (2)	62 (1)
C(3)	1377 (3)	4528 (4)	706 (3)	78 (2)
C(4)	3029 (2)	1741 (3)	1301 (2)	56 (1)
C(5)	2525 (2)	1495 (3)	2771 (2)	53 (1)
C(6)	1518 (2)	2025 (4)	1322 (3)	66 (2)
C(11)	5162 (2)	4228 (4)	4118 (2)	56 (1)
C(12)	5804 (2)	3572 (4)	4504 (3)	68 (2)
C(13)	5674 (3)	2507 (4)	4844 (3)	72 (2)
C(14)	4905 (2)	2105 (4)	4793 (2)	69 (2)
C(15)	4257 (2)	2756 (3)	4399 (2)	54 (1)
C(16)	4383 (2)	3827 (3)	4050 (2)	46 (1)
C(21)	4740 (2)	4822 (3)	1790 (2)	49 (1)
C(22)	5538 (2)	4809 (3)	1733 (2)	57 (1)
C(23)	5987 (2)	3816 (4)	1923 (3)	61 (2)
C(24)	5634 (2)	2815 (3)	2148 (2)	61 (1)
C(25)	4835 (2)	2823 (3)	2201 (2)	51 (1)
C(26)	4381 (2)	3824 (3)	2032 (2)	42 (1)
C(31)	542 (3)	3050 (4)	3073 (3)	88 (2)
C(32)	−248 (4)	3069 (5)	3181 (4)	109 (3)
C(33)	−752 (3)	3917 (5)	2836 (4)	107 (2)
C(34)	−488 (3)	4758 (5)	2414 (5)	142 (3)
C(35)	290 (3)	4758 (4)	2286 (4)	101 (2)
C(36)	807 (2)	3908 (3)	2596 (2)	54 (1)
C(41)	1421 (3)	5444 (5)	4514 (3)	85 (2)
C(42)	1019 (3)	6423 (6)	4721 (4)	112 (3)
C(43)	1249 (4)	7504 (6)	4525 (4)	121 (3)
C(44)	1853 (4)	7646 (5)	4098 (4)	105 (3)
C(45)	2252 (3)	6677 (4)	3875 (3)	76 (2)
C(46)	2027 (2)	5570 (4)	4069 (2)	58 (1)
O(1)	3237 (2)	4642 (3)	73 (2)	93 (1)
O(2)	2403 (2)	7157 (3)	1748 (2)	93 (1)
O(3)	791 (2)	4418 (4)	234 (3)	131 (2)
O(4)	3389 (2)	1234 (3)	903 (2)	84 (1)
O(5)	2534 (2)	827 (3)	3302 (2)	81 (1)
O(6)	932 (2)	1725 (3)	926 (2)	108 (2)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

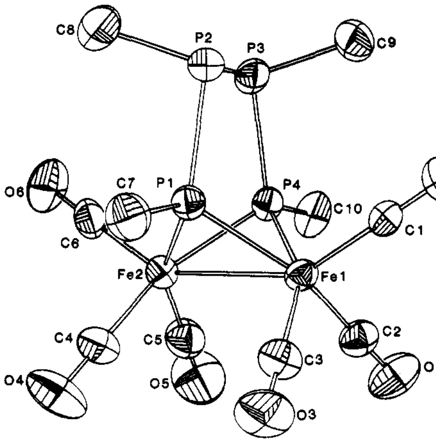


Figure 1. Molecular structure and labeling scheme for $Fe_2(CO)_6(PCH_3)_4$, I.

hydrogen atoms and isotropic hydrogen atoms in idealized, fixed locations. Neither structure showed any unusual trends with regard to Miller index, parity group, or sin θ.

Tables II and III provide the atomic coordinates for I and II, respectively, and Table IV contains selected bond distances and angles. Complete listings of structure factors, bond parameters, anisotropic temperature factors, and hydrogen atom coordinates are available as supplementary material.

Table IV. Bond Distances (Å) and Angles (deg) for $Fe_2(CO)_6(PMe)_4$ (I) and $Fe_2(CO)_6(PPh)_4$ (II)

	I	II
	(a) Bond Distances	
Fe(1)-Fe(2)	2.634 (2)	2.633 (1)
Fe(1)-P(1)	2.215 (3)	2.218 (1)
Fe(1)-P(4)	2.220 (3)	2.221 (1)
Fe(2)-P(1)	2.218 (3)	2.226 (1)
Fe(2)-P(4)	2.221 (3)	2.214 (1)
P(1)-P(2)	2.201 (4)	2.220 (1)
P(2)-P(3)	2.194 (4)	2.198 (1)
P(3)-P(4)	2.200 (4)	2.207 (1)
P(1)···P(4)	2.715 (3)	2.689 (1)
Fe(1)-C(1)	1.773 (1)	1.762 (4)
Fe(1)-C(2)	1.812 (10)	1.794 (4)
Fe(1)-C(3)	1.794 (13)	1.788 (4)
Fe(2)-C(4)	1.813 (10)	1.789 (4)
Fe(2)-C(5)	1.802 (10)	1.793 (4)
Fe(2)-C(6)	1.776 (11)	1.771 (4)
C(1)-O(1)	1.13 (1)	1.156 (5)
C(2)-O(2)	1.13 (1)	1.135 (5)
C(3)-O(3)	1.12 (1)	1.131 (5)
C(4)-O(4)	1.12 (1)	1.132 (5)
C(5)-O(5)	1.12 (1)	1.143 (5)
C(6)-O(6)	1.13 (1)	1.145 (5)
C-O(av)	1.125 (15)	1.140 (6)
	(b) Bond Angles	
Fe(1)-P(1)-Fe(2)	72.9 (1)	72.7 (0)
Fe(1)-P(4)-Fe(2)	72.8 (1)	72.8 (0)
P(1)-Fe(1)-P(4)	75.5 (1)	74.6 (0)
P(1)-Fe(2)-P(4)	75.4 (1)	74.5 (0)
Fe(1)-Fe(2)-P(1)	53.5 (1)	53.5 (0)
Fe(1)-Fe(2)-P(4)	53.6 (1)	53.7 (0)
Fe(2)-Fe(1)-P(1)	53.6 (1)	53.8 (0)
Fe(2)-Fe(1)-P(4)	53.6 (1)	53.5 (0)
Fe(1)-P(1)-P(2)	113.6 (1)	108.7 (0)
Fe(2)-P(1)-P(2)	118.7 (1)	122.1 (0)
Fe(1)-P(4)-P(3)	119.3 (1)	122.0 (1)
Fe(2)-P(4)-P(3)	113.3 (1)	110.5 (0)
P(1)-P(2)-P(3)	96.5 (1)	94.6 (1)
P(2)-P(3)-P(4)	96.3 (1)	94.1 (0)
P(1)-Fe(1)-C(1)	102.4 (3)	98.6 (1)
P(1)-Fe(1)-C(2)	156.6 (4)	160.2 (1)
P(1)-Fe(1)-C(3)	91.4 (4)	91.8 (1)
P(4)-Fe(1)-C(1)	105.3 (4)	110.6 (1)
P(4)-Fe(1)-C(2)	90.8 (4)	91.7 (1)
P(4)-Fe(1)-C(3)	153.1 (4)	148.3 (1)
Fe(2)-Fe(1)-C(1)	149.0 (4)	149.2 (1)
Fe(2)-Fe(1)-C(2)	103.0 (4)	106.6 (1)
Fe(2)-Fe(1)-C(3)	99.7 (4)	95.3 (1)
C(1)-Fe(1)-C(2)	99.4 (5)	99.6 (2)
C(1)-Fe(1)-C(3)	100.3 (6)	99.5 (2)
C(2)-Fe(1)-C(3)	92.9 (5)	92.8 (2)
P(1)-Fe(2)-C(4)	151.7 (4)	155.7 (1)
P(1)-Fe(2)-C(5)	89.7 (4)	93.7 (2)
P(1)-Fe(2)-C(6)	106.2 (4)	103.3 (1)
P(4)-Fe(2)-C(4)	90.4 (3)	88.9 (1)
P(4)-Fe(2)-C(5)	156.4 (4)	150.9 (1)
P(4)-Fe(2)-C(6)	101.9 (3)	106.3 (1)
Fe(1)-Fe(2)-C(4)	98.3 (3)	97.8 (1)
Fe(1)-Fe(2)-C(5)	102.8 (4)	102.4 (1)
Fe(1)-Fe(2)-C(6)	149.0 (3)	105.5 (1)
C(4)-Fe(2)-C(5)	94.6 (5)	92.5 (2)
C(4)-Fe(2)-C(6)	100.6 (5)	102.2 (2)
C(5)-Fe(2)-C(6)	99.8 (5)	98.3 (2)
Fe(1)-C(1)-O(1)	177.2 (8)	176.5 (3)
Fe(1)-C(2)-O(2)	178.8 (12)	178.0 (4)
Fe(1)-C(3)-O(3)	180.0 (17)	179.5 (4)
Fe(2)-C(4)-O(4)	177.3 (9)	178.0 (3)
Fe(2)-C(5)-O(5)	177.8 (11)	177.2 (4)
Fe(2)-C(6)-O(6)	177.9 (9)	179.8 (4)

Results and Discussion

Both compounds I and II crystallize as discrete, well-separated molecules. The molecular structure and labeling schemes for I and II are shown in Figures 1 and 2, respectively. The molecules are similar in their metal atom

Table V. A Comparison of the Fe-P and Fe-As Frameworks of Selected $[Fe(CO)_3]_2X$ Complexes

X =	$(PCH_3)_4$, I[b]	$(PC_6H_5)_4$, II[b]	$(AsCH_3)_4$, III[3b]	$[P(CH_3)_2]_2$, IV[8]	$[P(C_6H_5)_2]_2$, V[8]
Fe-Fe, Å	2.634 (2)	2.633 (1)	2.664 (5)	2.665 (4)	2.623 (3)
Fe-E(av), Å	2.219 (3)	2.220 (5)	2.309 (10)	2.208 (8)	2.233 (3)
E···E, Å	2.715 (2)	2.689 (3)	2.895 (4)	2.924 (4)	2.866 (3)
E-E(av), Å	2.198 (4)	2.208 (11)	2.422 (10)		
Fe-E-Fe, deg	72.9 (1) 72.8 (1)	72.8 (0) 72.7 (0)	70.5 (2) 70.4 (2)	74.2 (2)	72.0 (1) 71.9 (1)
E-Fe-E, deg	75.5 (1) 75.4 (1)	74.5 (0) 74.6 (0)	77.5 (2) 77.8 (2)	82.9 (2)	79.9 (1) 79.6 (1)
"butterfly" dihedral Fe-E-Fe′ to Fe-E′-Fe′, deg	99.0 (1)	97.6 (1)	100.3 (2)[a]	67.7 (2)	75.0 (1)
E(1)-E(2)-E(3)-E(4), deg	−10.5 (2)	−23.6 (1)	9.1 (3)[a]		

[a] Calculated from the atomic coordinates in ref 3b. [b] This work.

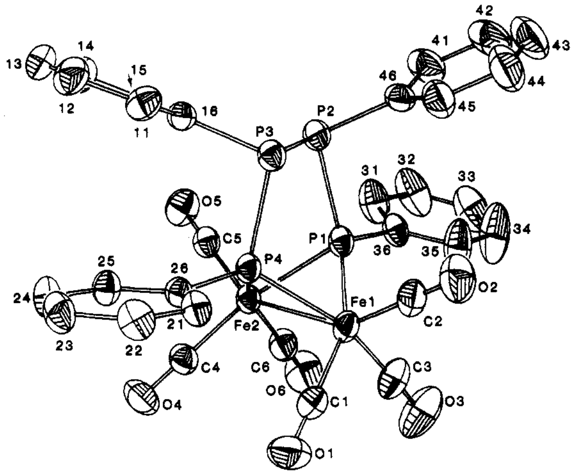


Figure 2. Molecular structure and labeling scheme for $Fe_2(CO)_6(PC_6H_5)_4$, II. Phenyl ring carbon atoms are numerically designated.

coordination geometry and in the arrangement of the P_4 chain. I is crystallographically isomorphous with its arsenic analogue III.[3] Table V provides comparisons between the structures of I and II and further compares these to $[Fe(CO)_3]_2(AsCH_3)_4$, III, and to the unlinked bis(μ-diorganophosphido) complexes $[Fe(CO)_3]_2(\mu\text{-}PMe_2)_2$, IV, and $[Fe(CO)_3]_2(\mu\text{-}PPh_2)_2$, V.[8]

In all cases the geometry about Fe is formally comprised of two distorted tetragonal pyramids that share a common basal edge, the P···P vector. If a bent Fe–Fe bond is included, the geometry is distorted octahedral; the existence and bent nature of the Fe–Fe bond is supported by MO calculations.[22] The bonded Fe–Fe distance in complexes I (2.634 (2) Å) and II (2.633 (1) Å) are within the range (2.62–2.67 Å) previously reported for bis(μ-phosphido)-diiron hexacarbonyl complexes.[8,11] The distances are, however, somewhat longer than those found in the bis(μ-carbonyl)-bridged complexes $[(C_5Me_5)Fe(CO)_2]_2$,[12] 2.560 (1) Å, and $[(C_5H_5)Fe(CO)_2]_2$, 2.531 (2) Å.[13]

The average Fe–P bond distances in I (2.219 (3) Å) and II (2.220 (5) Å) are identical; the unbridged complexes IV (2.208 (8) Å) and V (2.233 (3) Å) have similar Fe–P bond distances. The average P–P bond distances in I (2.198 (4) Å) and II (2.208 (11) Å) are also identical; individual P–P bond distances are also insensitive to whether the bond is internal or terminal in the P_4 chain. The observed distances compare closely to the average found in the uncoordinated homonuclear ring structures *cyclo*-$(PPh)_5$, 2.217 (6) Å,[14] and *cyclo*-$(PPh)_6$, 2.233 (9) Å.[15]

The P–P–P bond angles in I and II are similar: 96.5 (1) and 96.3 (1)° in I and 94.6 (1) and 94.1 (0)° in II. These values may be compared to the P–P–P bond angle averages for the cyclotetramers $(PCF_3)_4$, 84.7°,[16] $(PC_6H_{11})_4$, 85.47 (6)°,[17] and $(PC_6F_5)_4$, 85.24 (21)°,[18] the cyclopentamers $(PCF_3)_5$, 102.2°,[19] $(PC_6H_5)_5$, 100.01°,[14] and $(PC_6H_5)_4CH_2$, 102.3°,[20] and the cyclohexamer $(PC_6H_5)_6$, 95.52°.[15] The range of values found in $(PC_6H_5)_6$, 94.3 (2)–96.7 (2)°, is much smaller than found in $(PC_6H_5)_5$, 94.1 (2)–107.1 (2)°. It would appear that the P–P–P bond angles in I and II are most similar in their average values and range to that of $(PC_6H_5)_6$ that as a cyclohexamer, would be least likely to show ring-strain effects in the determination of its P–P–P bond angles. The P(1)–P(2)–P(3)–P(4) dihedral angles in I (−10.5 (2)°) and II (−23.6 (1)°) indicate the presence of significant deviations from planarity in the P_4 structural unit. The larger deviation from planarity for the phenyl derivative II reflects the accommodation made for the greater steric demands of the phenyl groups. This is, in fact, the only significant difference in the two complexes; the "butterfly" dihedral angle relating the two Fe–P–Fe planes in I, 99.0 (1)°, and in II, 97.6 (1)°, are similar, and the four values for the Fe–P–Fe and P–Fe–P bond angles in both I and II all are in the narrow range of 73–75°. While the Fe–P–Fe bond angles in the bridged (I and II) and unbridged complexes (IV and V) are not significantly different, the P–Fe–P bond angles are substantially larger for the unbridged complexes and allow for a closer approach of the formally non-bonded, metal-bound phosphorus atoms in I and II as compared to IV and V.[8]

If a "normal" P–P single bond distance is taken to be ~2.22 Å, the nonbonded P(1)···P(4) distances in I, 2.715 (2) Å, and in II, 2.689 (3) Å, are short enough to suggest that an attractive, fractional bond order interaction may exist, as has been suggested by molecular orbital calculations.[8b,21-23] Short, nonbonded P···P contacts are fairly common among complexes containing μ_3-P, μ_4-PR, and μ-PR_2 structural bridges and are sometimes accompanied by pronounced structural distortions to achieve short P···P distances, e.g., $[Co_4(\eta^5\text{-}C_5H_5)_4(\mu_3\text{-}P)_4]$, 2.568 Å (av),[24]

---

(11) The Fe–Fe distance in $\{Fe_2(CO)_6[\mu\text{-}P(CF_3)_2]_2\}$[10] is outside this range, 2.819 (1) Å, as are other parameters in this somewhat anomalous structure.

(12) Teller, R. G.; Williams, J. M. *Inorg. Chem.* **1980**, *19*, 2770.

(13) Bryan, R. F.; Green, P. T.; Newlands, M. J.; Field, D. S. *J. Chem. Soc. A* **1970**, 3068.

(14) Daly, J. J. *J. Chem. Soc.* **1964**, 6147.

(15) Daly, J. J *J. Chem. Soc. A* **1966**, 428.

(16) Palenik, G. J.; Donohue, J. *Acta Crystallogr.* **1962**, *15*, 564.

(17) Bart, J. C. *Acta Crystallogr. Sect. B* **1969**, *B25*, 762.

(18) Sanz, F.; Daly, J. J. *J. Chem. Soc. A* **1971**, 1083.

(19) Spenser, C. J.; Lipscomb, W. N. *Acta Crystallogr.* **1961**, *14*, 250.

(20) Lex, J.; Baudler, M. *Z. Anorg. Allg. Chem.* **1977**, *431*, 49.

(21) Cowley, A. J.; Dewar, M. J. S.; Lattman, M.; Mills, J. L.; McKee, M. *J. Am. Chem. Soc.* **1978**, *100*, 3349.

(22) Teo, B. K.; Hall, M. B.; Fenske, R. F.; Dahl, L. F. *Inorg. Chem.* **1975**, *14*, 3103.

(23) Burdett, J. K. *J. Chem. Soc., Dalton Trans.* **1977**, 610.

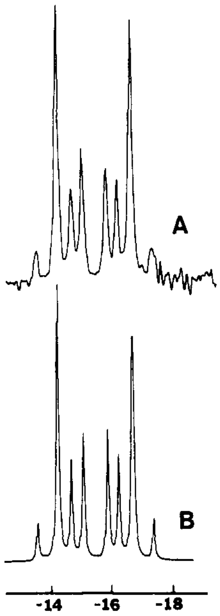


Figure 3. Half of the $^{31}P\{H\}$ NMR spectrum of II: (a) experimental and (b) calculated AA′XX′ spectrum. Best fit parameters are as follows: ν (ppm) (1) 162.4 and (2) −15.5; J (Hz) (1,2) 273.9, (1,3) 2.2, (1,4) 123.4, and (2,3) 250.9. (For I: ν(ppm) (1) 148.8 and (2) −12.3.)

$[Co_4(CO)_8(\mu\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2]$, 2.544 (3) Å,[25] $[Fe_4(CO)_{10}(\mu_4\text{-}P\text{-}p\text{-}tol)_2P(OMe)_3]$, 2.646 (8) Å,[26] $[Fe_4(CO)_{11}(\mu_4\text{-}P\text{-}p\text{-}tol)_2P(OMe)_3]$, 2.598 (3) Å,[26] and $[Rh_4(\mu_4\text{-}PC_6H_5)_2(COD)_4]$, 2.679 (4) Å.[27] Somewhat longer P···P distances are seen in the unlinked $[Fe_2(CO)_6(\mu\text{-}PR_2)_2]$ complexes: R = C_6H_5 (IV), 2.866 (3) Å; R = CH_3, 2.925 (4) Å, R = CF_3, 2.921 (2) Å.[1,8] Related As structures also commonly contain "short", formally nonbonded As···As interactions, e.g., III, 2.895 (4) Å,[3] and $\{[CpMo(CO)_2]_2[\mu\text{-}(CH_3As)_5]\}$, 2.835 (2) Å[2] (compared to a normal As–As distance of ~2.4 Å).

The $^{31}P\{^1H\}$ NMR spectrum and data for II are given in Figure 3 and its caption. (The low solubility of I in suitable solvents precluded a similar study of it.) $^2J_{P\cdots P}$ is large, 125.4 Hz, for a neutral Fe–Fe bonded complex and may be compared to $^2J_{P\cdots P}$ in $Fe_2(CO)_6(\mu\text{-}PCH_3)_2$, 80 Hz.[28] Although several investigators have shown a correlation between $^2J_{P\cdots P}$ values and d(P···P) in complexes of this type,[28,29] "through-bond" spin polarization effects may be comparable to, or greater than, "through-space" effects.[22] Only very limited data exist to examine such correlations, although a comparison of $^2J_{PP}$ values for neutral and dianion states for $[Fe_2(CO)_6(\mu\text{-}PMe_2)_2]$ (addition of two electrons leads to Fe–Fe bond cleavage and a decrease in the P···P distance) shows an increase in $^2J_{PP}$ from 85 ± 10 (neutral) to >500 Hz (dianion).[28] For IV, on conversion to IV^{2-}, the P···P distance decreases from 2.866 (3) to 2.759 (5) Å,[8b] but NMR data are lacking. Additional NMR and crystallographic studies will be required to demonstrate the extent and nature of correlations between d(P···P) and $^2J_{P\cdots P}$.[30]

Acknowledgment. The National Science Foundation provided funds to purchase the diffractometer. Dr. Roger Crecely provided assistance in the collection and simulation of the NMR data.

Registry No. I, 90900-69-9; II, 80962-84-1.

Supplementary Material Available: Tables of structure factor amplitudes, bond distances and angles, anisotropic temperature factors and hydrogen atom coordinates for I and II (41 pages). Ordering information is given on any current masthead page.

---

(24) Simon, G. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1973**, 95, 2175.

(25) Ryan, R. C.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6904.

(26) Vahrenkamp, H.; Wolters, D. *Organometallics* **1982**, *1*, 874.

(27) Burkhardt, E. W.; Mercer, W. C.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. C. *J. Chem. Soc., Chem. Commun.* **1983**, 1251.

(28) Dessy, R. E.; Rheingold, A. L.; Howard, G. D. *J. Am. Chem. Soc.* **1972**, *95* 738.

(29) Carty, A. J. *Adv. Chem. Ser.* **1982**, *No. 196*, 163.

(30) The inadvisability of comparing J_{PP} values between dissimilar metal is well documented and thus severely limits the range of useful data. Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.