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A Linked Diphosphido Ironcarbonyl Complex, μ-*P*,*P'*-Diphenyltrimethylenebis(phosphido)-μ-*P*:μ-*P'*-bis(tricarbonyliron)(*Fe–Fe*), $[Fe_2(C_{15}H_{16}P_2)(CO)_6]$

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Abstract. $M_r = 537\cdot99$, monoclinic, $P2_1/n$, $a = 11\cdot551\,(3)$, $b = 13\cdot254\,(3)$, $c = 15\cdot655\,(5)$ Å, $\beta = 106\cdot28\,(2)^\circ$, $U = 2300\cdot6\,(9)$ Å^3, $Z = 4$, $D_x = 1\cdot55$ g cm^{-3}, $\lambda(\text{Mo }K\alpha) = 0\cdot71073$ Å, $\mu = 14\cdot7$ cm^{-1}, $F(000) = 1088$, $T = 292$ K, $R = 0\cdot035$ for 2576 observed reflections. The tetragonal-pyramidal metal-atom coordination geometries are joined along a basal edge formed by the mutually bridging phosphorus termini of the $PhP(CH_2)_3PPh$ group. The 'non-bonding' P(1)$\cdots$P(2) distance is short, $2\cdot742\,(1)$ Å, suggesting some interaction.

Introduction. Diphosphido-bridged diiron carbonyl complexes, $[Fe_2(CO)_6(\mu\text{-}R_2P)_2]$, have recently been extensively studied as potential dinuclear, homogeneous catalysts (Ginsburg, Rothrock, Finke, Collman & Dahl, 1979; MacLaughlin, Carty & Taylor, 1982; Fultz, Rheingold, Kreter & Meek, 1983). We have recently reported the structures of two members of this class of compounds containing phosphido groups linked by an all-phosphorus bridge $[Fe_2(CO)_6(PR)_4]$, $R = CH_3$ (4) or C_6H_5 (5) (Rheingold & Fountain, 1984). We now report the structure of an all-carbon-linked diphosphido complex $[Fe_2(CO)_6\{C_6H_5P(CH_2)_3PC_6H_5\}]$, (1).

Experimental. Crystals (Flood, DiSanti & Campbell, 1978) obtained from acetone recrystallization. Yellow-orange, $0\cdot26 \times 0\cdot30 \times 0\cdot35$ mm, mounted on glass fiber. Nicolet *R*3, graphite monochromator, unit cell from least-squares fit of angular settings of 25 reflections ($19 \leq 2\theta \leq 24^\circ$). 3306 reflections, $2\theta \leq 45^\circ$, collected for $-11 \leq h \leq 11$, $0 \leq k \leq 14$, $0 \leq l \leq 16$ at 3° min^{-1} using $\theta/2\theta$ scans. No decay in three standard reflections, semi-empirical absorption correction (transmission $0\cdot67$ to $0\cdot83$) based on ψ-scan measurements of six reflections at different azimuthal angles (10° increments). 2576 unique observed reflections $[F_o \geq 3\sigma(F_o)]$, $R_{\text{int}} = 0\cdot021$. Multisolution direct methods (*SOLV*), blocked-cascade least squares on *F*, $w^{-1} = \sigma^2(F) + 0\cdot0001\,F^2$, complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974). Non-hydrogen atoms anisotropic, hydrogen atoms fixed, idealized contributions, $C-H = 0\cdot96$ Å, $U(H) = 1\cdot2U_{\text{eq}}(C)$, extinction correction necessary, $F = F_o/[1\cdot0 + (2\cdot1 \times 10^{-5})F^2/\sin(2\theta)]^{0\cdot25}$. 281 parameters, $R = 0\cdot035$, $wR = 0\cdot032$, slope of normal probability plot = $1\cdot30$, max. final $\Delta/\sigma = 0\cdot09$, largest peak in final difference map = $0\cdot23$ e Å^{-3}, deepest trough = $0\cdot25$ e Å^{-3}. *SHELXTL* program system (Sheldrick, 1984).

Discussion. Atomic coordinates are given in Table 1, bond lengths and angles in Table 2.* The molecular

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* Lists of structure factors, anisotropic thermal parameters and hydrogen-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42153 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atom coordinates* (×10⁴) *and temperature factors* (Å² × 10³)

	x	*y*	*z*	U_{eq}*
Fe(1)	6330 (1)	1236 (1)	8987 (1)	45 (1)
Fe(2)	6137 (1)	3161 (1)	8563 (1)	45 (1)
P(1)	5068 (1)	1914 (1)	7794 (1)	46 (1)
P(2)	7529 (1)	2101 (1)	8376 (1)	41 (1)
C(1)	5158 (4)	1212 (3)	9524 (3)	66 (2)
C(2)	6352 (3)	−25 (3)	8620 (2)	52 (1)
C(3)	7485 (4)	1174 (3)	10019 (2)	65 (2)
C(4)	4938 (3)	3532 (3)	9013 (3)	65 (2)
C(5)	6048 (3)	4006 (3)	7672 (2)	55 (1)
C(6)	7195 (3)	3774 (3)	9468 (3)	62 (2)
C(7)	5264 (3)	1606 (3)	6696 (2)	59 (2)
C(8)	6482 (3)	1172 (3)	6723 (2)	62 (2)
C(9)	7539 (3)	1803 (3)	7234 (2)	48 (1)
C(11)	3442 (3)	1831 (3)	7571 (2)	59 (2)
C(12)	2735 (3)	2652 (4)	7301 (3)	84 (2)
C(13)	1492 (4)	2566 (5)	7050 (3)	116 (3)
C(14)	973 (5)	1660 (7)	7082 (4)	138 (4)
C(15)	1671 (5)	867 (5)	7359 (5)	162 (4)
C(16)	2896 (4)	928 (4)	7609 (4)	115 (3)
C(21)	9127 (3)	2305 (3)	8900 (2)	45 (1)
C(22)	9654 (3)	3229 (3)	8853 (3)	63 (2)
C(23)	10882 (3)	3358 (3)	9189 (3)	75 (2)
C(24)	11596 (4)	2574 (4)	9593 (3)	82 (2)
C(25)	11092 (3)	1654 (4)	9643 (3)	83 (2)
C(26)	9864 (3)	1514 (3)	9299 (3)	65 (2)
O(1)	4409 (3)	1216 (2)	9873 (2)	106 (2)
O(2)	6339 (3)	−838 (2)	8381 (2)	79 (1)
O(3)	8221 (3)	1098 (3)	10675 (2)	107 (2)
O(4)	4206 (3)	3791 (2)	9326 (2)	105 (2)
O(5)	5988 (3)	4508 (2)	7071 (2)	90 (1)
O(6)	7851 (3)	4195 (2)	10039 (2)	104 (1)

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

structure shown in Fig. 1 is that typically encountered for η^2,μ_2-diorganodiphosphido-bridged diironhexacarbonyl structures, *i.e.* tetragonal-pyramidal metal-atom coordination geometries joined along a basal edge formed by the mutually iron-bridging phosphorus atoms. The Fe—Fe distance, 2·630 (1) Å, is similar to those found in the unlinked complexes $[Fe_2(CO)_6(\mu\text{-}PPh_2)_2]$, (2), 2·665 (4) Å, and $[Fe_2(CO)_6(\mu\text{-}PMe_2)_2]$, (3) 2·623 (3) Å (Huntsman, 1973; Ginsburg *et al.*, 1979), and to those in the all-phosphorus-linked compounds $[Fe_2(CO)_6(PCH_3)_4]$, (4), 2·634 (2) Å, and $[Fe_2(CO)_6(PC_6H_5)_4]$, (5), 2·633 (1) Å (Rheingold & Fountain, 1984). The Fe—P—Fe′ to Fe—P′—Fe′ 'butterfly' dihedral angle, 100·9 (1)°, is between the larger values found for the unlinked complexes (2), 112·3 (2)°, and (3), 105·0 (2)°,[*] and the smaller values found for the all-phosphorus-linked complexes (4), 99·0 (1)°, and (5), 97·6 (1)°, in which the less flexible P_2, rather than C_3 linkage in (1), restricts 'wing' opening. The presence of the linkage in (1) causes a decrease in the P···P distance, to 2·742 (1) Å, in comparison to (2), 2·924 (4) Å, and (3), 2·866 (3) Å, but this distance is similar to those of the P_2-linked complexes (4), 2·715 (2) Å, and (5), 2·689 (3) Å. P···P distances in the range of 2·6 to 2·7 Å (*cf.* normal P—P ~ 2·2 to 2·3 Å) are short enough to suggest that an attractive, fractional bond-order interaction may exist, as has been suggested by molecular-orbital calculations (Teo, Hall, Fenske & Dahl, 1978).

The crystals of (1) were generously provided by T. C. Flood.

Table 2. *Bond lengths* (Å) *and angles* (deg)

Fe(1)—Fe(2)	2·630 (1)	Fe(1)—P(1)	2·212 (1)
Fe(1)—P(2)	2·212 (1)	Fe(1)—C(1)	1·782 (5)
Fe(1)—C(2)	1·770 (4)	Fe(1)—C(3)	1·785 (3)
Fe(2)—P(1)	2·207 (1)	Fe(2)—P(2)	2·215 (1)
Fe(2)—C(4)	1·789 (4)	Fe(2)—C(5)	1·770 (4)
Fe(2)—C(6)	1·786 (3)	P(1)—C(7)	1·842 (4)
P(1)—C(11)	1·815 (4)	P(2)—C(9)	1·835 (3)
P(2)—C(21)	1·818 (3)	C(1)—O(1)	1·146 (6)
C(2)—O(2)	1·139 (4)	C(3)—O(3)	1·140 (4)
C(4)—O(4)	1·143 (6)	C(5)—O(5)	1·138 (5)
C(6)—O(6)	1·142 (4)	C(7)—C(8)	1·510 (5)
C(8)—C(9)	1·510 (5)	C(11)—C(12)	1·356 (6)
C(11)—C(16)	1·361 (6)	C(12)—C(13)	1·383 (6)
C(13)—C(14)	1·350 (11)	C(14)—C(15)	1·321 (10)
C(15)—C(16)	1·362 (7)	C(21)—C(22)	1·379 (5)
C(21)—C(26)	1·383 (5)	C(22)—C(23)	1·378 (5)
C(23)—C(24)	1·366 (6)	C(24)—C(25)	1·363 (7)
C(25)—C(26)	1·382 (5)		
Fe(2)—Fe(1)—P(1)	53·4 (0)	Fe(2)—Fe(1)—P(2)	53·6 (0)
P(1)—Fe(1)—P(2)	76·6 (0)	Fe(2)—Fe(1)—C(1)	96·6 (1)
P(1)—Fe(1)—C(1)	89·9 (1)	P(2) Fe(1) C(1)	149·7 (1)
Fe(2)—Fe(1)—C(2)	147·4 (1)	P(1)—Fe(1)—C(2)	100·1 (1)
P(2)—Fe(1)—C(2)	106·3 (1)	C(1)—Fe(1)—C(2)	102·6 (2)
Fe(2)—Fe(1)—C(3)	105·2 (1)	P(1)—Fe(1)—C(3)	158·6 (1)
P(2)—Fe(1)—C(3)	90·9 (1)	C(1)—Fe(1)—C(3)	92·7 (2)
C(2)—Fe(1)—C(3)	100·1 (2)	Fe(1)—Fe(2)—P(1)	53·6 (0)
Fe(1)—Fe(2)—P(2)	53·5 (0)	P(1)—Fe(2)—P(2)	76·6 (0)
Fe(1)—Fe(2)—C(4)	100·8 (1)	P(1)—Fe(2)—C(4)	92·5 (1)
P(2)—Fe(2)—C(4)	153·7 (1)	Fe(1)—Fe(2)—C(5)	142·7 (1)
P(1)—Fe(2)—C(5)	98·3 (1)	P(2)—Fe(2)—C(5)	100·4 (1)
C(4)—Fe(2)—C(5)	104·8 (2)	Fe(1)—Fe(2)—C(6)	104·5 (1)
P(1)—Fe(2)—C(6)	158·0 (1)	P(2)—Fe(2)—C(6)	91·9 (1)
C(4)—Fe(2)—C(6)	89·8 (2)	C(5)—Fe(2)—C(6)	102·3 (2)
Fe(1)—P(1)—Fe(2)	73·0 (0)	Fe(1)—P(1)—C(7)	118·3 (1)
Fe(2)—P(1)—C(7)	118·6 (1)	Fe(1)—P(1)—C(11)	122·6 (1)
Fe(2)—P(1)—C(11)	122·8 (1)	C(7)—P(1)—C(11)	101·4 (2)
Fe(1)—P(2)—Fe(2)	72·9 (0)	Fe(1)—P(2)—C(9)	119·0 (1)
Fe(2)—P(2)—C(9)	118·0 (1)	Fe(1)—P(2)—C(21)	124·2 (1)
Fe(2)—P(2)—C(21)	122·0 (1)	C(9)—P(2)—C(21)	100·9 (2)
Fe(1)—C(1)—O(1)	178·6 (3)	Fe(1)—C(2)—O(2)	178·5 (3)
Fe(1)—C(3)—O(3)	177·6 (4)	Fe(2)—C(4)—O(4)	177·2 (3)
Fe(2)—C(5)—O(5)	176·5 (3)	Fe(2)—C(6)—O(6)	177·7 (3)
P(1)—C(7)—C(8)	114·5 (2)	C(7)—C(8)—C(9)	114·3 (3)
P(2)—C(9)—C(8)	114·2 (3)	P(1)—C(11)—C(12)	120·8 (3)
P(1)—C(11)—C(16)	120·8 (3)	C(12)—C(11)—C(16)	118·3 (4)
C(11)—C(12)—C(13)	120·6 (5)	C(12)—C(13)—C(14)	119·9 (6)
C(13)—C(14)—C(15)	119·0 (5)	C(14)—C(15)—C(16)	122·4 (6)
C(11)—C(16)—C(15)	119·7 (5)	P(2)—C(21)—C(22)	121·0 (2)
P(2)—C(21)—C(26)	120·6 (3)	C(22)—C(21)—C(26)	118·2 (3)
C(21)—C(22)—C(23)	120·8 (3)	C(22)—C(23)—C(24)	120·3 (4)
C(23)—C(24)—C(25)	119·7 (4)	C(24)—C(25)—C(26)	120·4 (4)
C(21)—C(26)—C(25)	120·6 (4)		

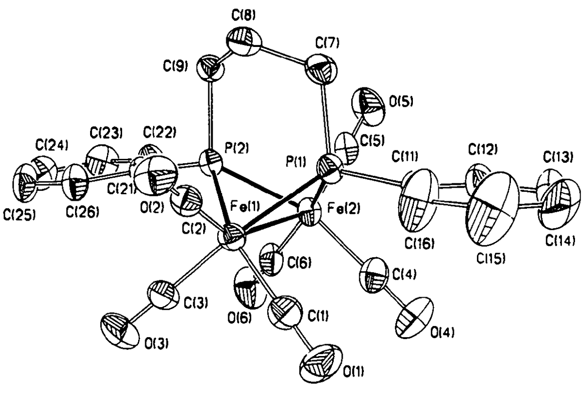

Fig. 1. Structure and labeling scheme for $[(CO)_3Fe\{\mu\text{-}PPh(CH_2)_3\text{-}\mu\text{-}PPh\}Fe(CO)_3]$, (1), with 50% probability thermal ellipsoids.

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[*] The angles for (2) and (3) are calculated from the atomic coordinates (Huntsman, 1973).

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Dichlorobis(η^5-isopropylcyclopentadienyl)titanium(IV), $[TiCl_2(C_8H_{11})_2]$

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Abstract. $M_r = 333{\cdot}2$, orthorhombic, *Ccmm*, $a = 6{\cdot}808\,(4)$, $b = 11{\cdot}618\,(11)$, $c = 20{\cdot}495\,(21)$ Å, $V = 1621{\cdot}1$ Å^3, $Z = 4$, $D_x = 1{\cdot}365$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 8{\cdot}6$ cm^{-1}, $F(000) = 696$, $T = 295$ K, $R_{\rm final} = 0{\cdot}047$ for 725 independent observed reflections. The molecules have pseudotetrahedral symmetry at the metal atom, with the isopropylcyclopentadienyl rings eclipsed in projection on the $TiCl_2$ plane. The Ti–ring-carbon-atom distances vary from 2·350 (3) to 2·444 (4) Å, the longest distance being to the carbon atom carrying the substituent alkyl group.

Introduction. The rather limited data presently available suggest that the molecular geometries of bis(η^5-alkylcyclopentadienyl)metal dihalides are determined primarily by the steric requirements of the substituent alkyl groups. Thus in dichlorobis(η^5-methylcyclopentadienyl)titanium(IV), $(MeCp)_2TiCl_2$, the methyl groups eclipse each other directly above and below the $TiCl_2$ group (Peterson & Dahl, 1975), but the corresponding *tert*-butyl compound, $(t\rm BuCp)_2TiCl_2$, has a less symmetrical structure with the more bulky alkyl groups directed away from each other on opposite sides of the molecule (Howie, McQuillan & Thompson, 1984). As these structural features may well affect the reactivity of titanium–aluminium reagent systems derived from these molecules, we were interested to determine the structure of dichlorobis(η^5-isopropylcyclopentadienyl)titanium(IV), $(i\rm PrCp)_2TiCl_2$, in which the steric effect of the alkyl group is intermediate between those of methyl and *tert*-butyl.

Experimental. $(i\rm PrCp)_2TiCl_2$ prepared using the method of Sullivan & Little (1967), deep-red elongated rhombohedral crystals from slowly evaporating dichloromethane.

Single crystal approx. 1·0 × 0·4 × 0·4 mm, Nicolet *P*3 four-circle diffractometer (Mo $K\alpha$), cell parameters from 14 high-angle reflections. Space group *Ccmm* (non-standard setting of *Cmcm*, No. 63). θ–2θ scan technique, variable scan speed, $0 < 2\theta < 50°$, 725 independent reflections, $I > 3\sigma(I)$, measured in one octant of reciprocal space, $h\,0\rightarrow8$, $k\,0\rightarrow13$, $l\,0\rightarrow24$. Four standard reflections showed no sign of deterioration or crystal movement. No absorption correction. Non-hydrogen-atom positions from Patterson and Fourier syntheses, block-diagonal least-squares refinement, all atoms anisotropic, to $R = 0{\cdot}052$. Ring hydrogen atoms from difference map, included in refinement with isotropic temperature factors, $R_{\rm final} = 0{\cdot}047$. Second difference map showed diffuse areas of electron density ($<0{\cdot}3$ e Å^{-3}) in areas of methyl hydrogen atoms, but no clear indication of hydrogen-atom positions. Temperature factors indicate high thermal vibrational amplitude for methyl carbon atoms. Weighting scheme $w = \{1 + [(|F_o| - 13)/24]^2\}^{-1}$. No reflections discarded. $(\Delta/\sigma)_{\rm max} = 0{\cdot}15$. $\Delta\rho$ in final difference map within +0·3 and −0·3 e Å. Computer programs based on those of Ahmed, Hall, Pippy & Huber (1966), atomic scattering factors from

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