3 gives torsion angles for the complex. Fig. 1 shows a view of the compound.

Related literature. The crystal structure of the tetrahedral cation [Li($OPPh_3$)$_4$]$^+$ has been reported previously (Yasin, Hodder & Powell, 1966), although the Li-atom position was not well defined and Li—O bond lengths were inferred to be approximately 1.97 Å, considerably longer than the 1.90 Å reported here. Other phosphine oxide complexes of Li include complexes of $Ph_2P(O)PP(O)Ph_2$ (Schmidpeter, Burget, von Schnering & Weber, 1984) and of $N[CH_2CH_2P(O)Ph_2]_3$ (Ghilardi, Innocenti, Midollini & Orlandini, 1986). The P—O distance in Ph_3PO is 1.483 Å (Ruban & Zabel, 1976), slightly longer than the one reported here (1.469 Å). [$CuBr_2$]$^-$ anions have also been reported previously (Asplund, Jagner & Nilsson, 1983; Cecconi, Ghilardi, Midollini & Orlandini, 1983). Iodide has also been reported as a counterion (Issleib & Krech, 1964).

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Structure of (4-Pentynoato-*O,O′*){tris[2-(diphenylphosphino)ethyl]phosphine}iron(II) Tetraphenylborate

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Abstract. [Fe($C_5H_5O_2$)($C_{42}H_{42}P_4$)][B(C_6H_5)$_4$], M_r = 1142.9, monoclinic, $P2_1/a$, a = 26.296 (3), b = 12.304 (4), c = 19.061 (2) Å, β = 103.63 (2)°, V = 5993.4 (22) Å^3, Z = 4, λ(Cu $K\alpha$) = 1.5418 Å, μ = 33.9 cm^{-1}, F(000) = 2404, room temperature, final R = 0.086 for 4321 significant reflections. The molecular structure consists of tetraphenylborate anions and discrete complex cations in which an Fe^{II} metal is pseudo-octahedrally coordinated by the ligand pp$_3$ [pp$_3$ = $P(CH_2CH_2PPh_2)_3$] and by a 4-pentynoate group. The latter ligand is bonded in a chelating mode through the two O atoms.

Introduction. As part of our ongoing studies into the factors that control the oxidative cleavage of C—H bonds as opposed to O—H bonds at metal centers (Bianchini, Masi, Meli, Peruzzini, Ramirez, Vacca & Zanobini, 1989), we have reacted the hydride dinitrogen complex [(pp$_3$)Fe(H)(η^1-N_2)]BPh_4 (Bianchini, Peruzzini & Zanobini, 1988) with a stoichiometric amount of 4-pentynoic acid, $HCCCH_2CH_2COOH$. As a result the novel carboxylate complex [(pp$_3$)Fe($O_2CCH_2CH_2CCH$)]BPh_4 has been synthesized as cherry red crystals. The product has also been characterized by spectroscopic techniques.

Experimental. Selected spectroscopic data for the title compound are: $^{31}P[^1H]$ NMR (CD_2Cl_2, 121.42 MHz, 173 K); *ABCD* spin system, δ_A 164.92, δ_B 90.2, δ_C 68.06, δ_D 57.22; J_{AB} 10.0, J_{AC} 21.2, J_{AD} 21.0, J_{BC} 32.5, J_{BD} 33.1, J_{CD} 148.0 Hz. ^1H NMR (CD_2Cl_2, 299.94 MHz, 294 K) δ 1.79 (*t*, 1H, C≡CH, $^4J_{HH}$ 2.30 Hz), δ 1.33 (*td*, 2H, $CH_2C{\equiv}C$, $^3J_{HH}$ 7.70 Hz), δ 0.92 (*t*, 2H, CH_2CH_2). $^{13}C[^1H]$ NMR (CD_2Cl_2, 50.32 MHz, 294 K), δ 186.05 (*s*, OOC), δ 83.23 (*s*, C≡CH), δ 36.70 (*s*, $OOCCH_2$), δ 13.07 (*s*, CH_2CH_2); the assignment of the ^{13}C resonances was confirmed by a DEPT 135° experiment; the quaternary C atom of the acetylene was not detected as it is obscured by the resonances of the aromatic C atoms in the 138–122 p.p.m. region of the spectrum. IR: ν(C≡CH) 3276 cm^{-1} (*m*), ν(C≡C) 2118 cm^{-1} (*vw*),

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Table 1. *Coordinates* (× 10^4) *and thermal parameters* ($\text{Å}^2 \times 10^3$) *of the complex cation atoms in the title structure*

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{iso} or U_{eq}*
Fe(1)	1302 (1)	3017 (1)	2720 (1)	38 (1)
P(1)	1993 (1)	2952 (3)	2206 (2)	45 (2)
P(2)	536 (1)	3601 (2)	2976 (2)	45 (2)
P(3)	1176 (1)	1233 (2)	2765 (2)	44 (2)
P(4)	821 (1)	2914 (3)	1641 (2)	49 (2)
O(1)	1784 (3)	3474 (6)	3706 (4)	48 (4)
O(2)	1438 (3)	4654 (6)	2883 (4)	44 (4)
C(1)	1759 (4)	2625 (10)	1245 (6)	57 (3)
C(2)	1204 (4)	3053 (11)	959 (6)	64 (3)
C(3)	262 (5)	4464 (10)	2208 (6)	65 (3)
C(4)	318 (4)	3981 (10)	1484 (6)	61 (3)
C(5)	552 (4)	887 (10)	2141 (6)	57 (3)
C(6)	475 (5)	1600 (10)	1452 (7)	63 (3)
C(7)	1723 (4)	4458 (10)	3505 (7)	51 (7)
C(8)	1983 (4)	5357 (9)	4006 (7)	57 (7)
C(9)	1869 (6)	6472 (11)	3736 (8)	82 (9)
C(10)	2143 (7)	7243 (13)	4267 (9)	103 (10)
C(11)	2366 (9)	7795 (15)	4686 (11)	139 (15)
C(1′1)	2551 (3)	2070 (6)	2548 (3)	47 (3)
C(2′1)	2735 (3)	1983 (6)	3295 (3)	54 (3)
C(3′1)	3202 (3)	1434 (6)	3583 (3)	62 (3)
C(4′1)	3485 (3)	973 (6)	3124 (3)	71 (4)
C(5′1)	3301 (3)	1061 (6)	2378 (3)	69 (4)
C(6′1)	2835 (3)	1609 (6)	2090 (3)	61 (3)
C(1′2)	2333 (3)	4257 (7)	2226 (4)	51 (3)
C(2′2)	2174 (3)	4989 (7)	1657 (4)	76 (4)
C(3′2)	2427 (3)	5987 (7)	1670 (4)	95 (5)
C(4′2)	2839 (3)	6255 (7)	2251 (4)	75 (4)
C(5′2)	2999 (3)	5523 (7)	2820 (4)	72 (4)
C(6′2)	2745 (3)	4525 (7)	2807 (4)	69 (4)
C(1′3)	582 (3)	4495 (7)	3766 (3)	51 (3)
C(2′3)	307 (3)	5473 (7)	3703 (3)	68 (4)
C(3′3)	326 (3)	6114 (7)	4312 (3)	83 (4)
C(4′3)	620 (3)	5778 (7)	4984 (3)	80 (4)
C(5′3)	896 (3)	4800 (7)	5047 (3)	70 (4)
C(6′3)	876 (3)	4158 (7)	4438 (3)	60 (3)
C(1′4)	−4 (3)	2720 (7)	3077 (4)	58 (3)
C(2′4)	−441 (3)	2541 (7)	2512 (4)	76 (4)
C(3′4)	−834 (3)	1834 (7)	2605 (3)	86 (4)
C(4′4)	−790 (3)	1304 (7)	3264 (4)	94 (5)
C(5′4)	−354 (3)	1482 (7)	3829 (4)	93 (5)
C(6′4)	40 (3)	2190 (7)	3736 (4)	71 (4)
C(1′5)	1142 (3)	675 (7)	3630 (4)	52 (3)
C(2′5)	875 (3)	−291 (7)	3683 (4)	89 (4)
C(3′5)	896 (3)	−749 (7)	4359 (4)	118 (6)
C(4′5)	1182 (3)	−240 (7)	4981 (4)	107 (5)
C(5′5)	1448 (3)	726 (7)	4928 (4)	84 (4)
C(6′5)	1428 (3)	1183 (7)	4253 (4)	60 (3)
C(1′6)	1619 (3)	242 (7)	2495 (3)	52 (3)
C(2′6)	2034 (3)	−201 (7)	3011 (3)	63 (3)
C(3′6)	2397 (3)	−872 (7)	2797 (3)	81 (4)
C(4′6)	2346 (3)	−1100 (7)	2066 (3)	86 (4)
C(5′6)	1932 (3)	−657 (7)	1550 (3)	82 (4)
C(6′6)	1568 (3)	14 (7)	1765 (3)	61 (3)

* U_{eq} for Fe, P, O and carboxylate C atoms; U_{iso} for residual C atoms.

Table 2. *Selected bond distances* (Å) *and angles* (°) *of the title complex with e.s.d.'s in parentheses*

Fe(1)—P(1)	2.259 (4)	Fe(1)—P(4)	2.151 (3)
Fe(1)—P(2)	2.297 (3)	Fe(1)—O(1)	2.080 (7)
Fe(1)—P(3)	2.224 (3)	Fe(1)—O(2)	2.057 (7)
P(1)—Fe(1)—O(1)	91.1 (2)	P(1)—Fe(1)—P(3)	97.1 (1)
P(2)—Fe(1)—O(1)	95.8 (2)	P(1)—Fe(1)—P(4)	86.3 (1)
P(3)—Fe(1)—O(1)	107.3 (2)	P(2)—Fe(1)—P(3)	98.9 (1)
P(4)—Fe(1)—O(1)	167.4 (2)	P(2)—Fe(1)—P(4)	82.7 (1)
O(1)—Fe(1)—O(2)	63.4 (3)	P(3)—Fe(1)—P(4)	85.3 (1)
P(1)—Fe(1)—P(2)	159.7 (2)	O(1)—C(7)—O(2)	118 (1)

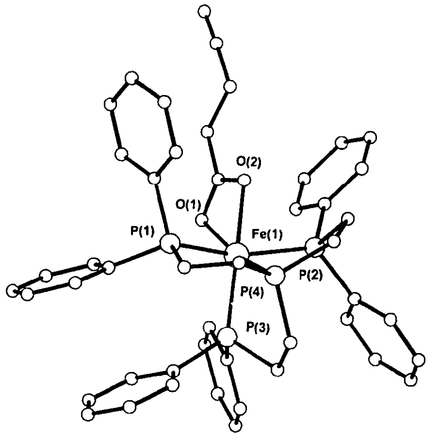

Fig. 1. A drawing of the complex cation with the atom-numbering scheme.

ν(COO) 1518 cm^{-1} (*ms*). Philips PW1100 diffractometer, lattice parameters determined using 25 reflections in the θ range 12–16°, scan mode $\omega/2\theta$, scan rate $0.05°\ \text{s}^{-1}$, scan width $0.7 + 0.15(\tan\theta)°$, 5304 unique reflections, of which 4321 had $I \geq 3\sigma(I)$; $5 \leq 2\theta \leq 110°$, $-25 \leq h \leq 25$, $0 \leq k \leq 12$, $0 \leq l \leq 20$; three standard reflections, no appreciable variation of their intensities; Lp correction, crystal size 0.45 × 0.25 × 0.10 mm, empirical correction for the absorption effect with the program *DIFABS* (Walker & Stuart, 1983) with coefficients ranging between 0.71 and 1.59; scattering factors for non-H atoms from *International Tables for X-ray Crystallography* (1974, Vol. IV) and for H atoms from Stewart, Davidson & Simpson (1965). Patterson and Fourier methods, full-matrix least-squares refinement on F values, $\sum w(|F_o| - |F_c|)^2$ minimized, anisotropic thermal parameters for Fe, P, B and the non-H atoms of the carboxylate group, all the phenyl rings were treated as rigid bodies with D_{6h} symmetry (C—C = 1.39 Å); the H atoms were introduced at calculated positions (C—H = 0.95 Å). Final $R = 0.086$, $wR = 0.088$, $w = 1/\sigma(F_o)^2$, the poor crystalline quality of the sample being responsible for the relatively large values of R. The shift/e.s.d. ratio was < 1.0; maximum height in final ΔF map $0.68\ \text{e}\ \text{Å}^{-3}$. *SHELX76* (Sheldrick, 1976) and *PLUTO* (Motherwell & Clegg, 1978) programs adapted for the Digital Dec 5000/200 workstation.

Discussion. Atomic parameters for the compound $[(pp_3)(C_5H_5O_2)Fe][B(C_6H_5)_4]$ are given in Table 1* with selected bond distances and angles in Table 2. A perspective view of the cation is shown in Fig. 1. The compound has a pseudo-octahedral structure with a (pp_3)Fe fragment having an approximate butterfly

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* Lists of structure factors, anisotropic thermal parameters, coordinates of BPh_4 and all H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55404 (29 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1002]

shape (C_{2v} symmetry). One of the angles at the metal, involving the terminal phosphine groups of pp_3, P(1)—Fe—P(2), is opened to 159.7 (2)°. Such a $(pp_3)M$ conformation has been observed for metals of the second and third rows of the transition-element series, but is unprecedented for Fe. The carboxylate ligand lies in the equatorial plane. The two O atoms are almost symmetrically coordinated to the Fe^{II} ion in a chelating fashion [the Fe—O(1) and Fe—O(2) distances being 2.080 (7) and 2.057 (7) Å, respectively]. As expected, the O-atom donors have a weaker *trans* influence than the phosphine ligands. In fact, both Fe—P bonds *trans* to the O atoms are slightly shorter than those *trans* to a second P-atom donor. To our knowledge no other structure of an octahedral Fe^{II} complex containing a chelating carboxylate ligand has been reported.

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cis-1,1-Dimethyl-2,6-diphenyl-1-silacyclohexan-4-one

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Abstract. $C_{19}H_{22}OSi$, $M_r = 294.5$, orthorhombic, $P2_12_12_1$, $a = 8.896\ (3)$, $b = 11.006\ (3)$, $c = 17.310\ (6)$ Å, $V = 1695\ (2)$ Å^3, $Z = 4$, $D_m = 1.150$, $D_x = 1.154$ g cm^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0.71073$ Å, $\mu = 1.00$ cm^{-1}, $F(000) = 632$, $T = 298$ K, $R = 0.058$ for 1263 observed reflections. The molecule assumes a somewhat distorted chair conformation to accommodate the longer Si—C bonds and sp^2 C(4) bond angle.

Experimental. Crystals were grown by slow evaporation from ethanol. A colorless plate, 0.15 × 0.30 × 0.25 mm (density determined by flotation in KI solution), was used for data collection on an Enraf–Nonius CAD-4 diffractometer with Mo $K\alpha$ radiation, using ω–2θ scans of width $(0.9 + 0.35\tan\theta)°$ and speed 1.4 to 16.5° min^{-1}. 24 reflections with $12 \leq \theta \leq 16°$ were used to refine cell constants; systematic absences: $h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$. No absorption correction was applied. Data were collected to $2\theta_{\max} = 53°$ for $0 \leq h \leq 11$, $0 \leq k \leq 13$, $0 \leq l \leq 21$. Three standard reflections measured after every 3600 s of X-ray exposure showed no deterioration. Of 2007 unique reflections (no redundant reflections measured), 1263 were observed $[F \geq 4\sigma(F)]$. The structure was solved by direct methods with *SHELX76* (Sheldrick, 1976). Refinement was based on F, minimizing $\sum w(F_o - F_c)^2$, where $w = 4F_o^2[\sigma^2(I) + (0.04F_o^2)^2]^{-1}$. H atoms were placed at calculated positions with fixed isotropic thermal parameters, updated after each cycle of refinement but not refined. Non-H atoms were refined with anisotropic thermal parameters. The polarity of the structure was not clearly established, the reported configuration giving only slightly better agreement than the inverted structure. $R = 0.058$, $wR = 0.057$, $S = 2.00$; $(\Delta/\sigma)_{\max}$ in the final cycle was less than 1%; the final difference map maxima were ±0.25 e Å^{-3}. Atomic scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV); all calculations were performed with *SHELX76* (Sheldrick, 1976).

A perspective drawing of the molecule with the numbering scheme is given in Fig. 1 (Johnson, 1976). Final positional parameters for the non-H atoms are

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