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PHOSPHORUS-BASED 1,3-DIPOLES AS THREE-ELECTRON ONE-CARBON LIGANDS: X-RAY STRUCTURE OF μ-[PHENYL(DICYCLOHEXYLPHOSPHONIO)ETHENIDYL]-μ-(DIPHENYLPHOSPHIDO)HEXACARBONYLDIIRON, $Fe_2(CO)_6[CC(PCy_2H)Ph](PPh_2)$

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Summary

The synthesis of μ-[phenyl(dicyclohexylphosphonio)ethenidyl]-μ-(diphenylphosphido)hexacarbonyldiiron, $Fe_2(CO)_6[CC(PCy_2H)Ph](PPh_2)$ via nucleophilic attack by dicyclohexylphosphine at the β-carbon atom of the σ—π-acetylide in $Fe_2(CO)_6(C{\equiv}CPh)(PPh_2)$ is described. This complex, which contains a one-carbon 3-electron bridging ligand has been characterised by microanalysis, infrared, mass, Mössbauer and ^{31}P NMR spectroscopy and by a single crystal X-ray structure determination. Crystals are monoclinic, space group $P2_1/c$ with a 10.932(3), b 8.983(2), c 38.644(6) Å, β 94.48(2)°. With four molecules per unit cell and a formula weight of 764.4, the calculated density of 1.342 g cm^{-3} agrees with the measured value of 1.34 g cm^{-3}. The structure was solved by heavy atom methods and refined by least squares techniques with iron and phosphorus atoms having anisotropic thermal parameters, to R and R_w values of 0.068 and 0.075 respectively. In the binuclear molecule an iron—iron bond of length 2.550(2) Å is bridged by a diphenylphosphido group and the carbon atom of an unusual dipolar ligand $Cy_2(H)P^+$—$C(Ph){=}C^-$. In the bridging one-carbon-3-electron ligand the coordinated carbon atom is trigonal and the atoms P(1), C(8), C(31), C(7) are virtually coplanar. Structural parameters are compared with those of other complexes containing bridging one-carbon, 3-electron and two-carbon, 3-electron ligands. Nucleophilic attack by phosphorus and nitrogen nucleophiles on σ—π-acetylides appears to be a general route to these ligands.

Introduction

We have recently shown [1—3] that σ—π-acetylides, as exemplified by the binuclear complex $Fe_2(CO)_6(C{\equiv}CPh)(PPh_2)$ (I) possess an unusual pattern of chemical reactivity being readily attacked at carbon by neutral phosphorus [1,3] and nitrogen [2,3] nucleophiles to generate zwitterionic complexes containing one- and two-carbon-3-electron ligands. Subsequent reports from the laboratories of Deeming [4] and Shapley [5] have established that σ—π-vinyl [4,5] and σ—π-acetylide [4] groups in triosmium clusters also undergo similar nucleophilic additions with phosphorus ligands. Clearly the coordinated carbon atoms in these σ—π species are highly electrophilic exhibiting reactivity reminiscent of electrophilic carbene complexes. The products of these reactions are of interest not only because of the unusual structural features of the derived, bridging 3-electron ligands, but also because the dipolar nature of the elaborated acetylide or vinylide can be exploited in subsequent reactions. Two types of phosphonium-based 1,3-dipolar complexes have been structurally characterised by X-ray diffraction, these being the dinuclear iron complex $Fe_2(CO)_6(C[P(OEt)_3]CPh)(PPh_2)$ where a two-carbon bridge is present [1] and $Os_3(CO)_{10}(H)(CHCH_2PMe_2Ph)$ where a single tetrahedral carbon atom bridges two osmium atoms [5]. In this paper, we describe the synthesis and structural characterisation of a third type of three-electron carbon ligand in the complex $Fe_2(CO)_6[CC(PCy_2H)Ph](PPh_2)$ (Cy = cyclohexyl) (II). In this molecule formed via attack by dicyclohexylphosphine at the β-carbon atom of the acetylide in $Fe_2(CO)_6(C{\equiv}CPh)(PPh_2)$ a single, trigonal carbon atom bridges two iron atoms.

Experimental

General procedures

Manipulations under nitrogen were carried out using standard Schlenk type apparatus with a double manifold and stainless steel transfer tubes. Solvents were stored over $LiAlH_4$ under N_2. Mass, infrared and Mössbauer spectra were obtained as described previously [6]. ^{31}P NMR spectra were measured on a Bruker WP60 instrument; the ^{31}P probe operates at 24.29 MHz and an external 85% H_3PO_4 reference was used.

Synthesis

Dicyclohexylphosphine (0.25 g) was added to a solution of $Fe_2(CO)_6(C_2Ph)(PPh_2)$ [6] (0.5 g) in petroleum ether (50 ml) under a nitrogen atmosphere. After ca. 5 minutes a heavy yellow precipitate had formed. Stirring was continued for 30 min to ensure that the reaction was complete. The solvent was removed by transfer tube and the precipitate dissolved in toluene (50 ml). After filtration the bright yellow solution was concentrated to ca. 10 ml in vacuo and left overnight at −10°C. Bright yellow crystals of $Fe_2(CO)_6[CC(PCy_2H)Ph](PPh_2)$ (90%, m.p. 165°C) were obtained. Anal. Found: C, 59.79; H, 5.01; P, 8.05. Calcd.: C, 59.71; H, 5.01; P, 8.10%. Mass spectrum (70 eV) *m/e* 764(5) M^+, 736(5), 708(10), 680(42), 652(29), 624(35), 596(76)(Fe_2L^+), 584(40), 578(36), 558(36), 542(29), 522(100), 514(100), 494(79). IR (cm^{-1}; THF; ν(CO)): 2033s, 1989vs, 1961s, 1939s, 1918m. ^{31}P NMR (C_6D_6; ppm with respect to 85% H_3PO_4)

32.07, 32.77(d) (PCy_2H); 122.73, 123.44(d) (PPh_2); J(P—P) 17 Hz. Mössbauer (77 K, shifts in mm s^{-1} with respect to sodium nitroprusside) δ 0.17 ppm, Δ 0.80 mm s^{-1}.

TABLE 1

FINAL COORDINATES (fractional, X 10^5 for Fe, X 10^4 others) WITH STANDARD DEVIATIONS IN PARENTHESES

	x/a	*y/b*	*z/c*		*x/a*	*y/b*	*z/c*
Fe(1)	19672(11)	15349(14)	12318(3)	C(51)	3062(7)	—1192(10)	1847(2)
Fe(2)	14337(11)	—10952(14)	10228(3)	C(52)	3028(9)	—2667(11)	1939(2)
				C(53)	4008(9)	—3283(12)	2139(3)
P(1)	—1342(2)	2805(3)	1040(1)	C(54)	4985(9)	—2431(11)	2247(2)
P(2)	1769(2)	—431(3)	1568(1)	C(55)	5053(9)	—982(12)	2158(3)
				C(56)	4051(9)	—325(12)	1955(2)
C(1)	3558(9)	1455(11)	1231(2)				
O(1)	4642(8)	1403(10)	1223(2)	H(11)	—3129(7)	2371(9)	1345(2)
C(2)	1732(9)	2914(12)	1534(3)	H(12A)	—928(8)	3422(11)	1786(2)
O(2)	1576(7)	3809(10)	1745(2)	H(12B)	—1375(8)	1548(11)	1726(2)
C(3)	1911(9)	2597(13)	854(3)	H(13A)	—2080(9)	2523(12)	2273(3)
O(3)	1898(8)	3315(11)	602(2)	H(13B)	—3323(9)	2118(12)	1979(3)
C(4)	1411(9)	—645(11)	583(3)	H(14A)	—2305(10)	5208(12)	2083(3)
O(4)	1363(7)	—267(9)	293(2)	H(14B)	—3704(10)	4582(12)	2229(3)
C(5)	2791(9)	—2217(11)	1033(2)	H(15A)	—3989(9)	6045(12)	1691(2)
O(5)	3633(7)	—2994(9)	1048(2)	H(15B)	—4468(9)	4183(12)	1629(2)
C(6)	391(8)	—2574(11)	1005(2)	H(16A)	—3331(8)	4937(10)	1146(2)
O(6)	—278(7)	—3585(9)	996(2)	H(16B)	—2062(8)	5487(10)	1426(2)
				H(21)	—2231(7)	4731(10)	668(2)
C(7)	382(7)	644(9)	1067(2)	H(22A)	—3928(8)	3090(11)	760(2)
C(8)	—800(7)	938(8)	1005(2)	H(22B)	—3285(8)	1734(11)	499(2)
				H(23A)	—4049(9)	4837(12)	271(3)
C(11)	—2343(7)	3097(9)	1385(2)	H(23B)	—4835(9)	3182(12)	149(3)
C(12)	—1699(8)	2682(11)	1735(2)	H(24A)	—3535(9)	4084(14)	—307(3)
C(13)	—2561(9)	2875(12)	2026(3)	H(24B)	—3068(9)	2329(14)	—140(3)
C(14)	—3073(10)	4465(12)	2029(3)	H(25A)	—1912(9)	5249(13)	49(3)
C(15)	—3684(9)	4904(12)	1679(2)	H(25B)	—1296(9)	3856(13)	—208(3)
C(16)	—2817(8)	4713(10)	1390(2)	H(26A)	—1121(8)	2182(11)	295(2)
				H(26B)	—376(8)	3879(11)	403(2)
C(21)	—2087(7)	3552(10)	637(2)	H(32)	—2620(8)	—130(10)	1354(2)
C(22)	—3367(8)	2913(11)	546(2)	H(33)	—4272(10)	—1896(12)	1146(3)
C(23)	—3946(9)	3664(12)	220(3)	H(34)	—4314(11)	—2892(13)	555(3)
C(24)	—3132(9)	3501(14)	—82(3)	H(35)	—2770(10)	—2168(12)	168(3)
C(25)	—1849(9)	4064(13)	7(3)	H(36)	—1077(8)	—461(10)	379(2)
C(26)	—1254(8)	3357(11)	337(2)	H(42)	—620(8)	—1949(10)	1557(2)
				H(43)	—2212(9)	—2053(12)	1990(3)
C(31)	—1766(7)	—172(9)	876(2)	H(44)	—1867(9)	—761(11)	2540(3)
C(32)	—2647(8)	—581(10)	1094(2)	H(45)	—57(10)	741(12)	2669(3)
C(33)	—3580(10)	—1570(12)	976(3)	H(46)	1530(9)	909(11)	2245(3)
C(34)	—3596(11)	—2129(13)	646(3)	H(52)	2234(9)	—3333(11)	1858(2)
C(35)	—2732(10)	—1733(12)	429(3)	H(53)	3989(9)	—4447(12)	2208(3)
C(36)	—1787(8)	—756(10)	546(2)	H(54)	5730(9)	—2928(11)	2407(2)
				H(55)	5863(9)	—342(12)	2237(3)
C(41)	567(7)	—524(9)	1871(2)	H(56)	4075(9)	845(12)	1982(2)
C(42)	—495(8)	—1347(10)	1799(2)				
C(43)	—1376(9)	—1428(12)	2045(3)	H(P1)	—381	3805	1071
C(44)	—1198(9)	—683(11)	2349(3)				
C(45)	—181(10)	163(12)	2424(3)				
C(46)	711(9)	256(11)	2185(3)				

TABLE 2

BOND LENGTHS (Å) WITH STANDARD DEVIATIONS IN PARENTHESES

Fe(1)—Fe(2)	2.550(2)	C(11)—C(12)	1.52(1)
Fe(1)—P(2)	2.214(2)	C(11)—C(16)	1.54(1)
Fe(1)—C(1)	1.741(9)	C(12)—C(13)	1.53(1)
Fe(1)—C(2)	1.735(10)	C(13)—C(14)	1.53(1)
Fe(1)—C(3)	1.741(10)	C(14)—C(15)	1.51(1)
Fe(1)—C(7)	1.969(7)	C(15)—C(16)	1.53(1)
Fe(2)—P(2)	2.193(2)	C(21)—C(22)	1.53(1)
Fe(2)—C(4)	1.747(9)	C(21)—C(26)	1.45(1)
Fe(2)—C(5)	1.791(9)	C(22)—C(23)	1.52(1)
Fe(2)—C(6)	1.749(9)	C(23)—C(24)	1.53(1)
Fe(2)—C(7)	1.956(7)	C(24)—C(25)	1.50(1)
		C(25)—C(26)	1.53(1)
P(1)—C(8)	1.787(7)		
P(1)—C(11)	1.811(7)	C(31)—C(32)	1.38(1)
P(1)—C(21)	1.829(7)	C(31)—C(36)	1.38(1)
P(2)—C(41)	1.829(7)	C(32)—C(33)	1.40(1)
P(2)—C(51)	1.841(7)	C(33)—C(34)	1.37(1)
		C(34)—C(35)	1.36(1)
C(1)—O(1)	1.189(9)	C(35)—C(36)	1.40(1)
C(2)—O(2)	1.168(10)		
C(3)—O(3)	1.167(10)	C(41)—C(42)	1.39(1)
C(4)—O(4)	1.168(10)	C(41)—C(46)	1.40(1)
C(5)—O(5)	1.153(9)	C(42)—C(43)	1.14(1)
C(6)—O(6)	1.165(9)	C(43)—C(44)	1.35(1)
		C(44)—C(45)	1.36(1)
C(7)—C(8)	1.322(9)	C(45)—C(46)	1.40(1)
C(8)—C(31)	1.509(10)		
		C(51)—C(52)	1.37(1)
		C(51)—C(56)	1.38(1)
		C(52)—C(53)	1.39(1)
		C(53)—C(54)	1.35(1)
		C(54)—C(55)	1.35(1)
		C(55)—C(56)	1.41(1)
		P(1)—H(P1)	1.38

X-ray structure analysis

Crystal data: $C_{38}H_{38}Fe_2O_6P_2$, $M = 764.4$. Monoclinic, a 10.932(3), b 8.983(2), c 38.644(6) Å, β 94.48(2)°, U 3783.3 Å^3, $Z = 4$, D_m 1.34 g cm^{-3}, $F(000) = 1584$. Space group $P2_1/c$ (C^5_{2h}, No. 14) from systematic absences ($h0l$ when $l = 2n + 1$, $0k0$ when $k = 2n + 1$). Mo-K_α radiation, λ 0.71069 Å, μ 8.3 cm^{-1}; D_c = 1.342 g cm^{-3}.

Collection and reduction of intensity data

Unit cell dimensions and space group information were obtained from Weissenberg and precession photographs. The lattice parameters were refined by the least-squares treatment of the diffractometer coordinates of 12 reflections for which θ(Mo-K_α) was between 10 and 20°. The crystal was a prism of dimensions 0.18 mm × 0.20 mm × 0.20 mm. Three-dimensional intensity data for all reflections with $\theta \leqslant 22°$ were collected on a computer-controlled four-circle Hilger and Watts diffractometer using graphite monochromated Mo-K_α radiation and the θ/ω step scan technique. Despite the length of the c axis, peaks were very well resolved and no serious overlapping was apparent. For each reflection,

TABLE 3

VALENCE ANGLES (deg.) WITH STANDARD DEVIATIONS IN PARENTHESES

Fe(2)—Fe(1)—P(2)	54.3(1)	P(1)—C(8)—C(7)	119.9(6)
Fe(2)—Fe(1)—C(1)	99.5(3)	P(1)—C(8)—C(31)	114.7(5)
Fe(2)—Fe(1)—C(2)	146.3(3)	C(7)—C(8)—C(31)	125.2(7)
Fe(2)—Fe(1)—C(3)	104.5(3)		
Fe(2)—Fe(1)—C(7)	49.3(2)	P(1)—C(11)—C(12)	110.8(5)
P(2)—Fe(1)—C(1)	96.4(3)	P(1)—C(11)—C(16)	111.6(5)
P(2)—Fe(1)—C(2)	98.5(3)	C(12)—C(11)—C(16)	110.7(7)
P(2)—Fe(1)—C(3)	158.6(3)	C(11)—C(12)—C(13)	110.8(6)
P(2)—Fe(1)—C(7)	75.0(2)	C(12)—C(13)—C(14)	111.0(8)
C(1)—Fe(1)—C(2)	103.3(4)	C(13)—C(14)—C(15)	111.7(8)
C(1)—Fe(1)—C(3)	89.5(4)	C(14)—C(15)—C(16)	111.6(7)
C(1)—Fe(1)—C(7)	146.9(4)	C(11)—C(16)—C(15)	110.0(7)
C(2)—Fe(1)—C(3)	100.1(4)		
C(2)—Fe(1)—C(7)	109.5(4)	P(1)—C(21)—C(22)	113.4(5)
C(3)—Fe(1)—C(7)	88.8(3)	P(1)—C(21)—C(26)	110.4(5)
		C(22)—C(21)—C(26)	111.8(6)
Fe(1)—Fe(2)—P(2)	55.0(1)	C(21)—C(22)—C(23)	109.7(7)
Fe(1)—Fe(2)—C(4)	94.6(3)	C(22)—C(23)—C(24)	111.1(7)
Fe(1)—Fe(2)—C(5)	110.2(3)	C(23)—C(24)—C(25)	112.5(8)
Fe(1)—Fe(2)—C(6)	148.0(3)	C(24)—C(25)—C(26)	112.2(8)
Fe(1)—Fe(2)—C(7)	49.7(2)	C(21)—C(26)—C(25)	110.1(7)
P(2)—Fe(2)—C(4)	149.5(3)		
P(2)—Fe(2)—C(5)	93.2(3)	C(8)—C(31)—C(32)	118.5(7)
P(2)—Fe(2)—C(6)	107.6(3)	C(8)—C(31)—C(36)	121.2(7)
P(2)—Fe(2)—C(7)	75.7(2)	C(32)—C(31)—C(36)	120.2(7)
C(4)—Fe(2)—C(5)	95.8(4)	C(31)—C(32)—C(33)	119.6(8)
C(4)—Fe(2)—C(6)	100.3(5)	C(32)—C(33)—C(34)	119.5(9)
C(4)—Fe(2)—C(7)	86.4(4)	C(33)—C(34)—C(35)	121.3(10)
C(5)—Fe(2)—C(6)	96.3(4)	C(34)—C(35)—C(36)	119.7(9)
C(5)—Fe(2)—C(7)	159.9(3)	C(31)—C(36)—C(35)	119.6(8)
C(6)—Fe(2)—C(7)	103.0(3)		
		P(2)—C(41)—C(42)	121.8(6)
C(8)—P(1)—C(11)	114.5(3)	P(2)—C(41)—C(46)	119.7(6)
C(8)—P(1)—C(21)	114.0(3)	C(42)—C(41)—C(46)	118.5(7)
C(11)—P(1)—C(21)	108.7(3)	C(41)—C(42)—C(43)	119.9(8)
		C(42)—C(43)—C(44)	120.1(9)
Fe(1)—P(2)—Fe(2)	70.7(1)	C(43)—C(44)—C(45)	121.5(9)
Fe(1)—P(2)—C(41)	121.4(3)	C(44)—C(45)—C(46)	119.6(9)
Fe(1)—P(2)—C(51)	122.3(3)	C(41)—C(46)—C(45)	120.4(8)
Fe(2)—P(2)—C(41)	121.9(3)		
Fe(2)—P(2)—C(51)	121.6(2)	P(2)—C(51)—C(52)	118.3(6)
C(41)—P(2)—C(51)	99.5(3)	P(2)—C(51)—C(56)	121.4(6)
		C(52)—C(51)—C(56)	120.2(8)
Fe(1)—C(1)—O(1)	178.6(8)	C(51)—C(52)—C(53)	119.6(8)
Fe(1)—C(2)—O(2)	177.9(9)	C(52)—C(53)—C(54)	120.2(9)
Fe(1)—C(3)—O(3)	178.6(9)	C(53)—C(54)—C(55)	121.7(9)
Fe(2)—C(4)—O(4)	176.0(8)	C(54)—C(55)—C(56)	119.2(9)
Fe(2)—C(5)—O(5)	176.5(8)	C(51)—C(56)—C(55)	119.1(8)
Fe(2)—C(6)—O(6)	178.1(7)		
Fe(1)—C(7)—Fe(2)	81.0(3)	H(P1)—P(1)—C(8)	111.3
Fe(1)—C(7)—C(8)	143.2(6)	H(P1)—P(1)—C(11)	110.0
Fe(2)—C(7)—C(8)	135.7(6)	H(P1)—P(1)—C(21)	96.9

60 steps of 0.01°(θ) and 1 s duration were taken through the diffracting position and backgrounds of 15 s were measured at each end of the scan. The standard deviation in intensity was calculated using $\sigma^2(I) = S + 4B + (0.03S)^2$ where S is the scan count, B is the sum of the two backgrounds and $I = S - 2B$. After

corrections for Lorentz, polarization and absorption effects, 3156 reflections were found to have $I \geqslant 3\sigma(I)$ and were retained as the observed data.

Solution and refinement

The structure was solved by Patterson and Fourier [7] methods and refined by least-squares minimization of $\Sigma[F_o - F_c)/\sigma(F_o)]^2$. The hydrogen atoms were refined using the scattering factors of ref. 8. Except for H(P1) they were constrained to ride (in idealized positions) on the carbon atoms to which they are attached and were given a single overall isotropic temperature factor U which refined to 0.077(5) Å^2. The hydrogen atom on P(1) was located on a subsequent difference map and was included in the final calculation of structure factors. The remaining atoms were given the scattering factors of ref. 9 and corrections [10] for anomalous dispersion were made for iron and phosphorus. Final values of R and R_w ($R = \Sigma|\Delta F|/\Sigma|F_o|$; $R_w = [\Sigma w\Delta F^2/\Sigma_w F_o]^{1/2}$ were 0.068 and 0.075 respectively.

Atomic coordinates and their standard deviations are given in Table 1. Tables 2 and 3 contain bond lengths and valency angles and their standard deviations calculated using the covariance matrix. A list of calculated and observed structure factors, thermal parameters and an analysis of variance calculated after the final refinement cycle have been deposited *.

Results and discussion

Reaction of the secondary amines R_2NH (R = Me, Et, n-Pr) with $Fe_2(CO)_6(C\equiv CPh)(PPh_2)$ at −20°C yields yellow precipitates of 1/1 adducts which on warming to 50°C in benzene convert smoothly to dipolar iminium complexes $Fe_2(CO)_6[CHC(NR_2)Ph](PPh_2)$ formed via addition of N—H across the triple bond of the acetylide followed by a valence isomerisation [2,3]. It was of interest therefore to attempt the reactions of secondary phosphines, containing active P—H bonds, with the same σ—π-acetylide $Fe_2(CO)_6(C\equiv CPh)(PPh_2)$. Recent work has shown that secondary phosphines R_2PH undergo rapid P—H addition to the uncoordinated triple bond in phosphinoacetylene complexes *cis*-$MCl_2(Ph_2PC\equiv CR')_2$ (M = Pd, Pt) generating stereospecifically the diphosphine complexes *cis*-$MCl_2(Ph_2PCH{=}C(R')PR_2)$ [11]. Dicyclohexylphosphine and $Fe_2(CO)_6(C\equiv CPh)(PPh_2)$ react rapidly in petroleum ether at room temperature giving a complex shown by microanalysis to be a 1/1 adduct. A mass spectrum showed a parent ion (*m/e* 764) and successive loss of six carbonyl groups giving an ion of *m/e* 596 corresponding to $Fe_2(C_2Ph)(PPh_2)(PCy_2H)^+$. An IR spectrum showed a ν(P—H) absorption at 2454 cm^{-1} (vw) and five ν(CO) bands at frequencies somewhat lower than in the parent molecule [6]. The highest frequency ν(CO) band (2033 cm^{-1}) compares with corresponding bands at 2072 cm^{-1} in $Fe_2(CO)_6(C\equiv CPh)(PPh_2)$ [6], 2045 cm^{-1} in $Fe_2(CO)_6\{CP(OEt)_3CPh\}(PPh_2)$ [1] and 2033

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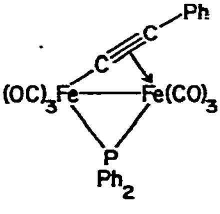
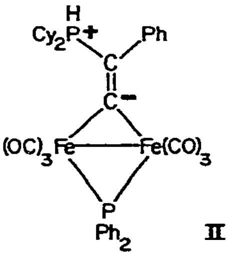
* A list of calculated and observed structure factors, thermal parameters and an analysis of variance have been deposited as NAPS Document No. 03216 (21 pages). Order from ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513 Grand Central Station, New York, N.Y. 10017. A copy may be secured by citing the document number, remitting $5 for photocopies or $3 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications.

cm^{-1} in $Fe_2(CO)_6[CHC(NEt_2)Ph](PPh_2)$ [2,3]. Analysis of IR spectra for a wide variety of diiron complexes with bridging 1C-3e and 2C-3e* ligands derived from $Fe_2(CO)_6(C{\equiv}CPh)(PPh_2)$ via nucleophilic attack by amines has revealed [3] that for isomeric pairs $Fe_2(CO)_6[CHC(NRR')Ph](PPh_2)$ and $Fe_2(CO)_6[C(NRR')CHPh]PPh_2$ the 1C-3e ligand in the former gives lower $\nu(CO)$ frequencies. In particular, the frequency of the highest $\nu(CO)$ band can be used as an empirical test of ligand type. Apparently for these dipolar ligands greater charge transfer from the formally carbanionic carbon atom to the iron tricarbonyl groups occurs with a single bridging carbon atom. Thus IR data for $Fe_2(CO)_6(C_2Ph)(PPh_2)(PCy_2H)$ suggested attack by the secondary phosphine at the β-carbon atom of the acetylide in $Fe_2(CO)_6(C{\equiv}CPh)(PPh_2)$ generating a ligand with a single trigonal, bridging carbon atom. This result was totally unexpected when compared to the quantitiative formation of P—C bonds at the acetylenic α-carbon atom with phosphites [1].

The molecular structure of the dicyclohexylphosphine adduct (Fig. 1) was revealed by a single crystal X-ray structural analysis. In the binuclear molecule an iron—iron bond is bridged by a diphenylphosphido group and a single trigonal carbon atom of a dipolar betaine ligand $Cy_2(H)P^+{-}C(Ph){=}C^-{<}$. The Fe(1)—Fe(2) distance (2.550(2) Å) is very similar to the corresponding bond lengths in $Fe_2(CO)_6[CHC(NEt_2)Ph](PPh_2)$ (2.548(1) Å) [2] and $Fe_2(CO)_6[CHC(NHCy)Ph](PPh_2)$ (2.576(1) Å) [3] where tetrahedral bridging 1C-3e ligands are present but quite distinct from the longer Fe—Fe distances in $Fe_2(CO)_6[CP(OEt)_3CPh](PPh_2)$ (2.671(2) Å) [1] and $Fe_2(CO)_6[C(NHCy)CHPh](PPh_2) \cdot \frac{1}{2}C_6H_6$ (2.628(1) Å) [3] which contain 2C-3e donors. The acute Fe(1)—P(2)—Fe(2) angle (70.7(1)°) reflects the shortness of the iron—iron bond. The principal structural feature of interest is the unusual bridging betaine ligand. The bridging atom C(7) is planar; indeed P(1), C(31), C(8), C(7), Fe(1) and Fe(2) deviate by only —0.066, 0.032, 0.038, 0.020, 0.043, —0.067 Å, respectively, from a least squares plane defined by these atoms. The C(7)—C(8) distance (1.322(9) Å) is close to the standard value for a $C_{(sp^2)}{-}C_{(sp^2)}$ bond length (1.337(6) Å) [12] confirming that the acetylenic triple bond of the original acetylide has been reduced to an olefinic linkage. The bulky cyclohexyl groups attached to the phosphonium phosphorus atom P(1) are oriented away from the Fe(1) tricarbonyl group, presumably to minimise intramolecular steric contacts, with the result that the hydrogen atom on P(1) is suitably placed to interact with one metal atom although insufficiently close (Fe(1)···H(P) 3.30 Å) for chemical bonding. Comparison of P(1)—C(8)



I



II

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* The abbreviations 1C-3e and 2C-3e are used for one-carbon three-electron and two-carbon three-electron ligands respectively.

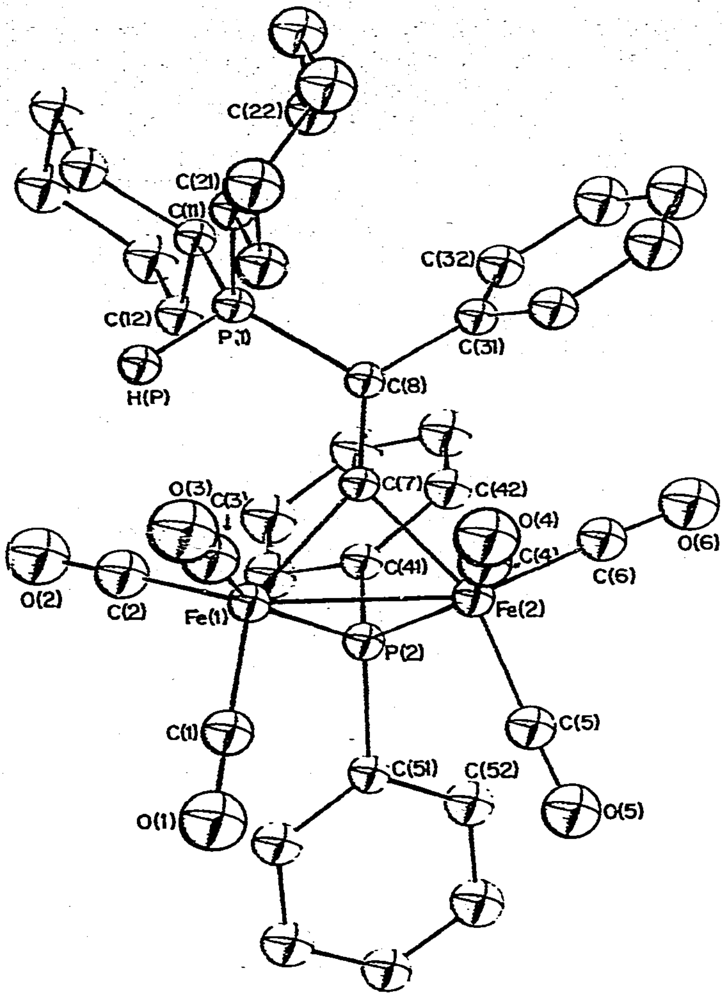

Fig. 1. A perspective view of the molecular structure of $Fe_2(CO)_6[CC(PCy_2H)Ph](PPh_2)$ showing the atomic numbering scheme used.

(1.787(7) Å) and P—C (cyclohexyl) (av. 1.820 Å) reveals the difference expected (~0.04 Å) on the basis of $C_{(sp^2)}$ and $C_{(sp^3)}$ covalent radii.

If the ligand in $Fe_2(CO)_6[CC(PCy_2H)Ph]PPh_2$ (II) is formulated as the phosphonium betaine $Cy_2(H)P^+—C(Ph)=\ddot{C}^-$, the carbanionic carbon atom (C(7)) should contribute 3 electrons to the binuclear framework. There is some interest in the nature of the interaction with the two iron atoms since structural comparisons can be made with a number of systems containing single bridging carbon atoms of the 2e or 3e types. There is for example a structural similarity between the angle Fe(1)—C(7)—Fe(2) (81.0(2) Å) and the angle subtended at the bridging carbonyl carbon atom by the iron atoms in $Fe_2(CO)_9$ (77.6(1)°) [13]. Similarly acute angles are generally found in binuclear complexes with μ-bonded isocyanide [14], alkylidene [15], phenylvinylidene [16] and dicyanovinylidene [17] groups all of which are formal 2e ligands. However C(7) appears to be even more tightly bound to Fe(1) and Fe(2) in $Fe_2(CO)_6[CC(PCy_2H)Ph]$-

(PPh_2) (Fe—C(7) av. 1.960 Å) than the bridging carbonyl groups to the iron atoms in $Fe_2(CO)_9$ (Fe—C_{br} 2.013(3) Å). It is also notable that while the Fe(1)—C—Fe(2) bridge angles to tetrahedral carbon atom bridges in $Fe_2(CO)_6$-$[CHC(NEt_2)Ph](PPh_2)$ (76.2(0)°) [2] and $Fe_2(CO)_6[CHC(NHCy)Ph](PPh_2)$ (77.4(0)°) [3] are somewhat smaller than in the present case, the Fe—C_{br} distances (av. 2.064 Å in $Fe_2(CO)_6[CHC(NEt_2)Ph](PPh_2)$ [2] and 2.061 Å in $Fe_2(CO)_6[CHC(NHCy)Ph](PPh_2)$ [3]) are significantly longer.

Apart from the carbyne metal complexes [18], 1C-3e ligands are rare. It appears that nucleophilic attack by phosphorus nucleophiles on diiron [1,3] or triosmium [4,5] σ—π-acetylides and vinylides as well as reactions of diiron σ—π-acetylides with primary, secondary and tertiary amines [3] offers a general route to such ligands. A few other isolated examples have recently been described including $HRu_3(CO)_{10}(C{=}NMe_2)$ [19] where the ligand $C{=}NMe_2$ is obtained via fission of (dimethylaminomethyl)trimethyltin by $Ru_3(CO)_{12}$ and $HOs_3[CNMe(R)](CO)_{10}$ (R = Me, CH_2Ph) prepared from $Os_3(CO)_{12}$ and NMe_3 or NMe_2CH_2Ph [20]. Nucleophilic attack by trimethylphosphine at a carbyne carbon atom has also afforded a 1C-3e ligand in the complex $ReW(CO)_9[C(Ph)PMe_3]$ [21]. We are currently exploring other routes to these highly dipolar complexes.

The Mössbauer spectrum shows only one quadrupole doublet albeit with rather broad lines (Γ_{av} 0.29 mm s^{-1}). Although the two iron sites are structurally non-equivalent (vide infra) it is clear that the difference, in electronic and stereochemical terms is sufficiently small that the Mössbauer experiment is insufficiently sensitive to resolve the difference. The isomer shift is characteristic of 18-electron iron(0) derivatives [22] and as would be expected from the distorted octahedral stereochemistry of each iron atom (Fig. 1) the value of Δ is below 1.00 mm s^{-1}. The quadrupole splitting (Δ 0.80 mm s^{-1}) for $Fe_2(CO)_6[CC(PCy_2H)$-$Ph](PPh_2)$ is larger than in the 2C-3e complexes $Fe_2(CO)_6[CP(OEt)_3CPh]$-(PPh_2) (Δ 0.26 mm s^{-1}) [1] and $Fe_2(CO)_6[C(NHCy)CHPh](PPh_2)$ (Δ 0.39 mm s^{-1}) [3] and closer to the value in $Fe_2(CO)_6[CHC(NHCy)Ph](PPh_2)$ (Δ 0.65 mm s^{-1}) [3]. Thus Δ can be used as a guide to the type of 3e ligand present.

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