Journal of Organometallic Chemistry, 256 (1983) 111–124
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

PHOTOLYTIC PREPARATION OF (BENZYLIDENEACETONE)-CARBONYLPHOSPHINEIRON(0) COMPLEXES. THE MOLECULAR STRUCTURES OF $Fe(CO)_2(PEt_3)(bda)$ AND $Fe(CO)_2(PPhMe_2)(bda)$ (bda = benzylideneacetone)

EDUARDO J.S. VICHI *,

Instituto de Quimica, Universidade Estadual de Campinas, C. Postal 6154, 13100-Campinas-SP (Brasil)

PAUL R. RAITHBY,

University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW (Great Britain)

and MARY McPARTLIN

Department of Chemistry, Polytechnic of North London Holloway, London N7 8DB (Great Britain)

(Received March 29th, 1983)

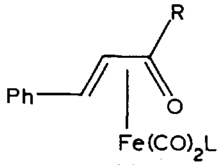
Summary

The (benzylideneacetone) carbonylphosphine iron(0) complexes, $Fe(CO)_2L(bda)$, $Fe(CO)L'_2(bda)$ and Fe(CO)(dpe)(bda) (L = PEt_3, $PPhMe_2$, PPh_2Me; L′ = $PPhMe_2$, PPh_2Me; dpe = $[Ph_2P(CH_2)]_2$) have been prepared by irradiating the corresponding tetracarbonylmonophosphine iron(0), tricarbonyldiphosphine iron(0) or tricarbonyl-1,2-bis(diphenylphosphine)ethane iron(0) complexes in benzene in the presence of benzylideneacetone. The X-ray crystal structures of the complexes with L = PEt_3 (A) and $PPhMe_2$ (B) have been determined, and show that the Fe atom adopts a distorted octahedral coordinated geometry in which three of the sites are occupied by the bda ligand. The bond parameters in the bda ligand suggest that this coordinated group is intermediate between its ground and first excited states. The complex $Fe(CO)_2(PEt_3)(bda)$ crystallises in the monoclinic space group $P2_1/c$ with a 10.203(3), b 12.964(4), c 16.960(6) Å, β 120.00(2)°, and $Z = 4$. The structure was solved by a combination of Patterson and Fourier difference techniques and refined by blocked full matrix least squares to $R = 0.035$ for 3351 unique observed diffractometer data. The complex $Fe(CO)_2(PPhMe_2)(bda)$ also crystallises in space group $P2_1/c$, with a 8.134(3), b 21.394(8), c 11.658(5) Å, β 108.18(2)° and $Z = 4$. The structure was solved and refined as above to $R = 0.036$ for 3498 diffractometer data. The IR and ^1H NMR data for all the complexes studied agree with the observed structures.

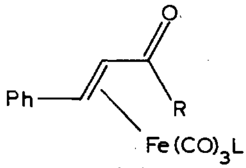
0022-328X/83/$03.00

Introduction

The ability of heterodiene molecules containing either $-C{=}C{-}C{=}O$ or $-C{=}C{-}C{=}N$ units to coordinate to the iron tricarbonyl moiety has been demonstrated in a series of papers [1–4]. Substitution of one or more CO ligands by Group V ligands is of interest because the electronic and steric properties of such ligands could help in understanding the nature of the irondiene bonds. However, reactions of the tricarbonyl complexes with phosphines and phosphites generally lead to the monoolefin complex or to the replacement of the heterodiene ligand. For example, reaction of I (L = CO; R = H, CH_3 or C_6H_6) with PMe_2Ph at room temperature



(I)



(II)

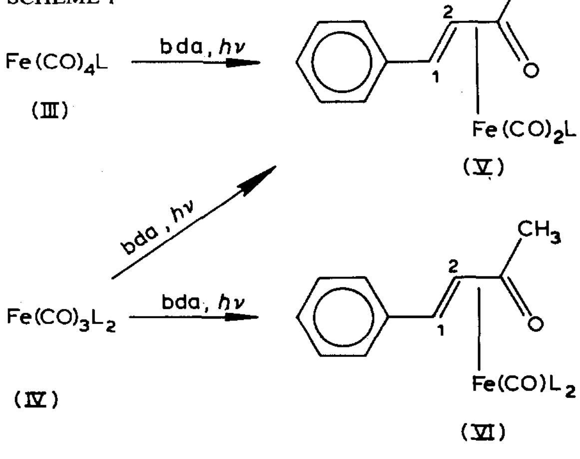
produced the monoolefin complex II (L = PMe_2Ph), which is stable in refluxing benzene [5].

The conversion of II into I can be brought about satisfactorily when L = $P(OPh)_3$ [6] but only slowly when L = $P(OMe)_3$ and is in competition with thermal decomposition [5]. The thermal stabilities of the monoolefin complexes II, formed in the first stage of the reaction seems to increase as the basicities of the Group V ligands increase. Heating I (L = CO), in benzene, in the presence of PPh_3 leads to the replacement of the ketone to produce $Fe(CO)_3(PPh_3)_2$ [7], but irradiation of $Fe(CO)_4PPh_3$ or $Fe(CO)_3(PPh_3)_2$, in benzene, in the presence of benzylideneacetone, produced I (R = CH_3, L = PPh_3) in very good yields [8]. In this paper, extension of this photolytic route to other tertiary phosphines is described.

Results and discussion

Irradiation of benzene solutions of tetracarbonylphosphines (III) or tricarbonyldiphosphines (IV) in the presence of benzylideneacetone (bda) produced the complexes V and VI, according to Scheme 1.

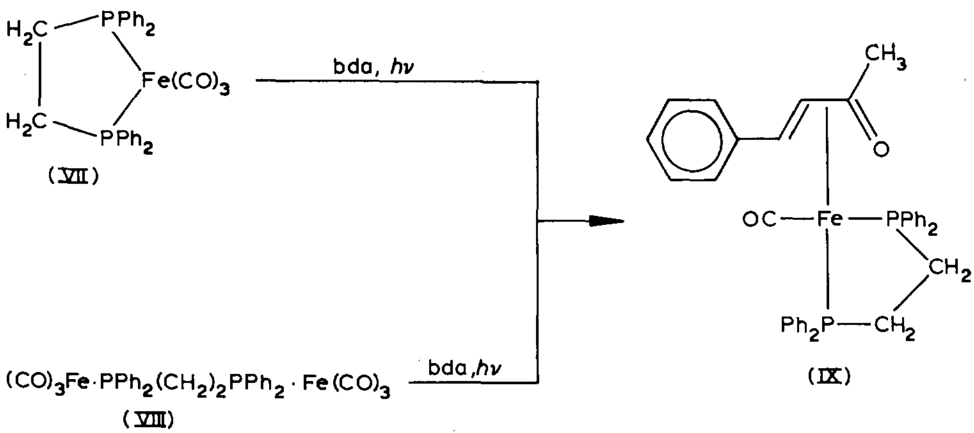
SCHEME 1



When L = PEt_3, two CO ligands in III or one CO and one PEt_3 ligand in IV are displaced by bda to give exclusively the monophosphine complex V. The same result was observed previously in the preparation of V (L = PPh_3) [8]. When L = PPh_2Me or $PPhMe_2$, irradiation under the same conditions produced a mixture of mono and diphosphine derivatives with V/VI ratios of ca. 9/1 and 3/1, respectively. From these results and the trends in the basicities [9] and cone angle [10] of the phosphines, it is reasonable to suppose that the replacement of one CO and one phosphine by bda in compounds IV is probably due to steric rather than electronic factors. It was shown that the stabilities of carbonylphosphine nickel(0) complexes are primarily determined by the size of the phosphine ligands [10].

Irradiation of $Fe(CO)_3dpe$ (VII) or $Fe_2(CO)_6dpe$ (VIII) with bda, in benzene for 24 h gave only IX (Scheme 2). The IR spectrum of the reaction medium with VIII as starting material, recorded at various times showed that several intermediates were involved and that IX was the final product. An analysis of the ν(CO) bands suggests

SCHEME 2



the presence of $Fe(CO)_2$ moieties, possibly present in $(bda)_2Fe_2(CO)_4(dpe)$ bridging species. All attempts to isolate these intermediates failed.

The molecular weights and precise molecular formulae of the complexes were obtained by mass spectrometry and confirmed by microanalysis. The complexes V (L = PEt_3 and $PPhMe_2$) were fully characterized by X-ray diffraction.

Molecular structures of $Fe(CO)_2(PEt_3)(bda)$ (A) and $Fe(CO)_2(PPhMe_2)(bda)$ (B)

The molecular structure of A is illustrated in Fig. 1 and that of B in Fig. 2; in both cases the hydrogen atoms have been omitted for clarity. The associated bond lengths and interbond angles for the two complexes are listed in Table 1.

In the solid state, both complexes exist as discrete, neutral, monomeric molecules separated by normal Van der Waals' distances.

Although the coordination geometry around the iron atom in A and B may be regarded as tetrahedral, with the bda ligand occupying a single coordination site, it is better to regard it as octahedral. A pseudo-octahedral symmetry was previously suggested for $Fe(CO)_2L$(diene) (L = CO or Group V ligands) [11] on the basis of available X-ray data [11,12]. The iron atom is then formally d^2sp^3 hybridized. The bond angles between the carbonyls and the phosphines at iron are close to the idealized octahedral angle. The two carbonyl groups are *cis* to each other while the

(Continued on p. 116)

TABLE 1

BOND DISTANCES AND ANGLES IN THE COMPOUNDS $Fe(CO)_2(PEt_3)(bda)$ (A) AND $Fe(CO)_2(PPhMe_2)(bda)$ (B) (C–H distances fixed at 1.08 Å)

Compound A

Distances (Å)					
Fe(1)–O(1)	2.027(2)	P(1)–C(111)	1.831(3)	C(4)–C(3)	1.422(3)
Fe(1)–C(2)	2.065(2)	P(1)–C(121)	1.833(3)	C(4))–C(5)	1.475(4)
Fe(1)–C(3)	2.060(2)	P(1)–C(131)	1.829(4)	C(6)–C(5)	1.401(5)
Fe(1)–C(4)	2.133(3)	C(111)–C(112)	1.535(5)	C(6)–C(7)	1.383(5)
Fe(1)–C(11)	1.739(3)	C(121)–C(122)	1.539(4)	C(7)–C(8)	1.379(5)
Fe(1)–C(12)	1.786(3)	C(131)–C(132)	1.522(5)	C(8)–C(9)	1.369(6)
Fe(1)–P(1)	2.235(1)	O(1)–C(2)	1.310(4)	C(9)–C(10)	1.404(5)
C(11)–O(11)	1.156(4)	C(1)–C(2)	1.513(3)	C(10)–C(5)	1.395(4)
C(12)–O(12)	1.144(4)	C(3)–C(2)	1.413(4)		
Angles (deg.)					
C(2)–Fe(1)–O(1)	37.3(1)	P(1)–Fe(1)–C(3)	134.8(1)	C(3)–C(2)–C(1)	124.2(3)
C(3)–Fe(1)–O(1)	68.5(1)	P(1)–Fe(1)–C(4)	96.6(1)	C(2)–C(3)–Fe(1)	70.2(2)
C(4)–Fe(1)–O(1)	77.9(1)	P(1)–Fe(1)–C(11)	94.7(1)	C(4)–C(3)–Fe(1)	73.2(2)
C(3)–Fe(1)–C(2)	40.1(1)	P(1)–Fe(1)–C(12)	99.6(1)	C(4)–C(3)–C(2)	116.8(3)
C(4)–Fe(1)–C(3)	39.6(1)	Fe(1)–P(1)–C(111)	118.3(1)	C(3)–C(4)–Fe(1)	67.4(2)
C(11)–Fe(1)–O(1)	167.8(1)	Fe(1)–P(1)–C(121)	113.6(1)	C(5)–C(4)–Fe(1)	128.1(2)
C(11)–Fe(1)–C(2)	130.5(1)	Fe(1)–P(1)–C(131)	112.2(1)	C(5)–C(4)–C(3)	122.1(3)
C(11)–Fe(1)–C(3)	100.6(1)	C(111)–P(1)–C(121)	104.2(1)	C(6)–C(5)–C(4)	122.6(2)
C(12)–Fe(1)–O(1)	91.6(1)	C(111)–P(1)–C(131)	102.7(1)	C(10)–C(5)–C(4)	119.3(3)
C(12)–Fe(1)–C(2)	92.3(1)	C(121)–P(1)–C(131)	105.0(2)	C(10)–C(5)–C(6)	118.1(3)
C(12)–Fe(1)–C(3)	122.6(1)	Fe(1)–C(2)–O(1)	69.7(1)	O(11)–C(11)–Fe(1)	178.3(3)
C(12)–Fe(1)–C(4)	161.7(1)	C(1)–C(2)–Fe(1)	131.4(2)	O(12)–C(12)–Fe(1)	179.6(2)
C(12)–Fe(1)–C(11)	89.9(1)	C(1)–C(2)–O(1)	120.6(3)	P(1)–C(111)–C(112)	113.8(2)
P(1)–Fe(1)–O(1)	97.0(1)	C(3)–C(2)–Fe(1)	69.8(1)	P(1)–C(121)–C(122)	117.0(2)
P(1)–Fe(1)–C(2)	133.4(1)	C(3)–C(2)–O(1)	115.2(2)	P(1)–C(131)–C(132)	113.6(2)

Compound B

Distances (Å)					
Fe(1)–P(1)	2.228(1)	C(1)–C(2)	1.497(4)	C(113)–C(114)	1.373(6)
Fe(1)–O(1)	2.023(2)	C(2)–C(3)	1.415(4)	C(114)–C(115)	1.378(6)
Fe(1)–C(2)	2.069(2)	C(3)–C(4)	1.423(4)	C(115)–C(116)	1.399(5)
Fe(1)–C(3)	2.065(2)	C(4)–C(5)	1.475(4)	C(5)–C(6)	1.399(4)
Fe(1)–C(4)	2.134(3)	P(1)–C(101)	1.827(3)	C(5)–C(10)	1.404(4)
Fe(1)–C(11)	1.740(2)	P(1)–O(102)	1.824(3)	C(6)–C(7)	1.381(5)
Fe(1)–C(12)	1.791(3)	P(1)–P(111)	1.822(3)	C(7)–C(8)	1.380(6)
C(11)–O(11)	1.149(3)	C(111)–C(112)	1.400(3)	C(8)–C(9)	1.390(5)
C(12)–O(12)	1.147(4)	C(111)–C(116)	1.390(4)	C(9)–C(10)	1.388(5)
O(1)–C(2)	1.312(3)	C(!12)–C(113)	1.385(5)		
Angles (deg.)					
O(1)–Fe(1)–P(1)	96.3(1)	C(11)–Fe(1)–C(4)	94.5(1)	O(1)–C(2)–Fe(1)	69.4(1)
C(2)–Fe(1)–P(1)	132.2(1)	C(12)–Fe(1)–P(1)	101.4(1)	C(1)–C(2)–Fe(1)	132.4(2)
C(3)–Fe(1)–P(1)	132.6(1)	C(12)–Fe(1)–O(1)	95.0(1)	C(1)–C(2)–O(1)	120.1(2)
C(4)–Fe(1)–P(1)	94.5(1)	C(12)–Fe(1)–C(3)	123.8(1)	C(3)–C(2)–Fe(1)	69.8(1)
C(2)–Fe(1)–O(1)	37.4(1)	C(12)–Fe(1)–C(4)	163.4(1)	C(3)–C(2)–O(1)	115.7(2)
C(3)–Fe(1)–O(1)	68.8(1)	C(12)–Fe(1)–C(11)	89.3(1)	C(3)–C(2)–C(1)	124.1(2)
C(4)–Fe(1)–O(1)	78.3(1)	Fe(1)–P(1)–C(101)	113.3(1)	C(2)–C(3)–Fe(1)	70.1(1)
C(3)–Fe(1)–C(2)	40.0(1)	Fe(1)–P(1)–C(102)	115.7(1)	C(4)–C(3)–Fe(1)	72.8(1)
C(4)–Fe(1)–C(2)	70.1(1)	Fe(1)–P(1)–C(111)	116.0(1)	C(4)–C(3)–C(2)	116.6(2)
C(4)–Fe(1)–C(3)	39.6(1)	C(101)–P(1)–C(102)	103.7(2)	C(3)–C(4)–Fe(1)	67.6(1)
C(11)–Fe(1)–P(1)	93.8(1)	C(101)–P(1)–C(111)	105.1(1)	C(5)–C(4)–Fe(1)	123.8(1)
C(11)–Fe(1)–O(1)	168.1(1)	C(102)–P(1)–C(111)	101.6(1)	C(11)–Fe(1)–C(2)	131.1(1)
Fe(1)–C(11)–O(11)	179.0(2)	C(11)–Fe(1)–C(3)	99.6(1)	Fe(1)–C(12)–O(12)	177.6(2)

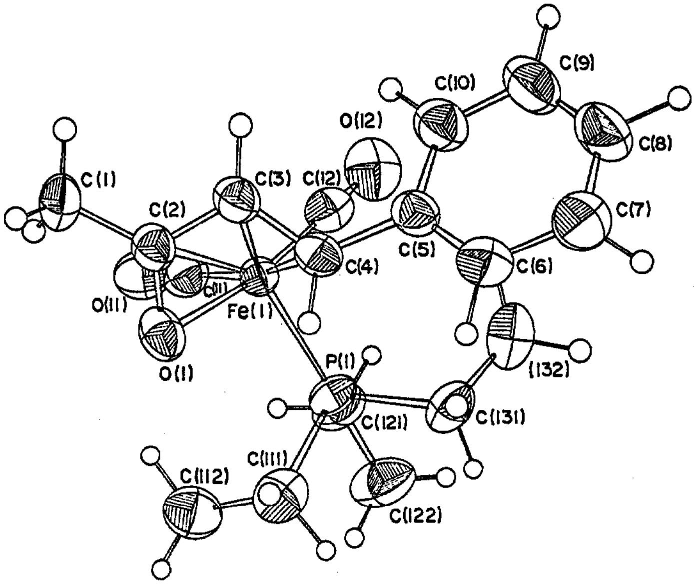


Fig. 1. Structural view of the complex $Fe(CO)_2(PEt_3)(bda)$ (A).

phosphine is approximately *trans* to the midpoint of the central C(2)–C(3) bond of the bda ligand. The other two sites are occupied by the O(1) atom and the C(4) atom of this ligand. This suggests that the C(2)–C(3) bond should exhibit multiple bond

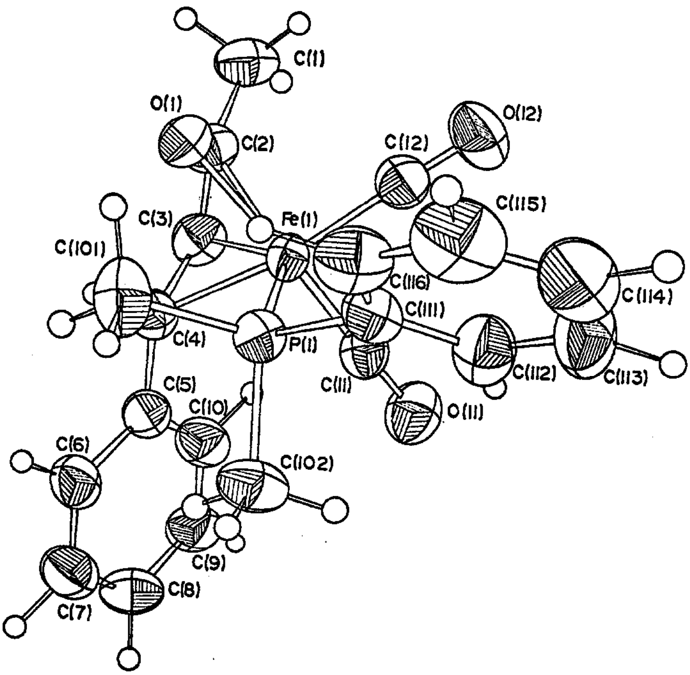


Fig. 2. Structural view of the complex $Fe(CO)_2(PPhMe_2)(bda)$ (B).

character since the higher donor capacity of the *trans* P atom should increase the flow of metal electron density into the antibonding "diene" orbitals. This enhances the promotion of the "diene" to the first excited state. The C(2)–C(3) bond lengths in both complexes are slightly shorter than the C(1)–C(2) and C(3)–C(4) bonds, in keeping with this suggestion. The Fe(1)–O(1) bonds are shorter than the Fe(1)–C(4) bonds and the Fe–C(carbonyl) bonds *trans* to O(1) are shorter than the Fe–C(carbonyl) bonds *trans* to C(4). This is as expected on the basis of the higher donor capacity of oxygen, which enhances back-donation from the iron atom to the *trans* carbonyl. The geometries of the PEt_3 and $PPhMe_2$ groups in the two complexes do not deviate significantly from the expected values.

Spectral data

Infrared and ^1H NMR data are summarized in Table 2.

The infrared spectra of the dicarbonyl derivatives V showed two strong ν(CO) bands of same intensity in the region 1928–2000 cm^{-1}, typical of $Fe(CO)_2L$ (diene) derivatives [8,13,14]. The monocarbonyl derivatives VI and IX showed a single ν(CO) band in the region 1890–1900 cm^{-1}. As expected, in complexes V the frequencies decrease as the basicities of L increase, viz CO(7) > $P(OPh)_3$ [8] > PPh_3[8] ~ PPh_2Me > $PPhMe_2$ > PEt_3. The shifts to lower frequencies of ν(CO) when compared with $Fe(CO)_2L$(diene) complexes [8] can be understood on the basis of the molecular structures observed in the solid state – the O-donor atom increases the electron density at the iron atom, lowering the order of the C–O bond. The strong ν(CO) band at 1680 cm^{-1} found in the spectrum of free bda disappears on coordination. This is also consistent with the molecular structures observed, in which

TABLE 2

^1H NMR [a] AND IR [b] DATA FOR $Fe(CO)_2(L)(bda)$ (V), $Fe(CO)L_2(bda)$ (VI) AND Fe(CO)dpe(bda) (IX) (τ in ppm, J in Hz; ν in cm^{-1})

Complex	τ(H(1))	τ(H(2))	$\tau(CH_3)$	Other	ν(C≡O)
V, L = PEt_3	7.74 t	4.61 dd	7.66 d	CH_3 9.20 dt; CH_2 8.36	1990,1928
	J(HH) = J(PH) = 8.5	J(HH) 8.5; J(PH) 2.0	J(PH) 2.5	J(HH) 7.5; J(H) 15.0 J(PH) = J(HH) = 7.0	
V, L = $PPhMe_2$	7.91 dd	4.57 dd	7.69 d	$P(CH_3)_2$ 8.53 d	1994,1938
	J(HH) 8.5; J(PH) 10.0	J(HH) 8.5; J(PH) 2.5	J(PH) 2.5	J(PH) 8.5	
V, L = PPh_2Me	7.85 dd	4.53 dd	7.69 d	PCH_3 8.24 d	2000, 1940
	J(HH) 8.5; J(PH) 9.5	J(HH) 8.5; J(PH) 2.5	J(PH) 2.5	J(PH)7.5	
VI, L = $PPhMe_2$	8.04	4.92	8.30		1891
	J(HH) 8.0; J(PH) 3.0	J(HH) 8.0; J(PH) 3.0	J(PH) 2.5		
VI, L = PPh_2Me	8.00	4.66	8.05		1890
		J(HH) 8.0; J(PH) 3.0	J(PH) 2.5		
IX	7.60	4.37	7.97		1898
		J(HH) 8.5; J(PH) 3.0	J(PH) 2.5		

[a] In C_6D_6 solution, [b] In cyclohexane solution.

the carbonyl group of the ketone loses most of its double bond character.

The ^1H NMR spectra are typical of (hetero-1,3-diene) iron carbonyl systems [7,8]. The "inner" olefin protons are located in the region τ 4.5–5.0 ppm, the "outer" protons in the region τ 7.6–8.0 and the methyl protons of bda in the region τ 7.7–8.3 ppm. The olefinic protons in the coordinated bda are shifted to higher field compared to free bda (H(1), τ 2.52; H(2), τ 3.30 ppm). This is expected as a result of shielding due to coordination. However the "outer" protons are shifted by 5.0–5.5 ppm, whereas the "inner" protons are shifted by only 1.0–1.5 ppm. This could be an indication that upon coordination the "outer" carbon atom increases its sp^3 character whereas the "inner" one retains most of its sp^2 character. The fact that the resonances of the methyl protons appear at similar values in both free and coordinated bda suggests that the shieldings at the carbonyl carbons are very similar. The coupling constants J(H(1)H(2)) falls from 17 Hz in the free bda to 8–10 Hz in the coordinated bda. Both protons are coupled to phosphorus, the coupling constant being bigger for the "outer" protons (8.5 Hz) than for the "inner" ones (2.5 Hz). On the basis of the above discussion the ^1H NMR data are fully consistent with the molecular structures observed in the solid state.

Mass spectral data are presented in the experimental section. All the complexes lose the carbonyls before the phosphines and bda. A intense peak assignable to the bdaFe$^+$ fragment is observed in the spectra of all the complexes, pointing to the stability of the iron–heterodiene bond in this fragment. The m/e values assignable to FeL$^+$ fragments were found only in the spectra of V ($L = PEt_3$) and IX.

Experimental

The photolyses were carried out under dry nitrogen in a quartz annular reactor, using a 125-W medium-pressure mercury lamp. Infrared spectra were recorded on a Perkin–Elmer 257 spectrometer, ^1H NMR spectra on a Varian Associates HA100 spectrometer and mass spectra on a Finnigan Instruments 1015S/L spectrometer equipped with a 6100 MS data System. Elemental analysis was by the microanalytical laboratories of University Chemical Laboratory in Cambridge and the Research Center of Rhodia in Campinas.

Preparations

(Benzylideneacetone) dicarbonyl(triethylphosphine) iron(0) (V, $L = PEt_3$)

A solution of triethylphosphine (830 mg, 7.0 mmol) and dodecacarbonyltriiron (1000 mg, 2.0 mmol) in tetrahydrofuran (THF) (100 cm^3) was stirred for 1 h at 70°C. The resulting red solution was filtered and the solvent removed under vacuum. The dark-red solid residue was a mixture of $Fe(CO)_4PEt_3$ (ν(CO) 2047, 1967, 1933 cm^{-1}) and $Fe(CO)_3(PEt_3)_2$ (ν(CO) 1867 cm^{-1}). This mixture (600 mg) and benzylideneacetone (bda) (230 mg, 1.55 mmol) were dissolved in benzene (200 cm^3) and the solution was irradiated for 16 h. The resulting red-brown solution was chromatographed on silica. Elution with benzene gave a small amount of unchanged $Fe(CO)_3(PEt_3)_2$ and a second elution with 10% ethyl acetate/benzene gave the product as orange-red crystals (370 mg (63% based on bda)), after two washings with n-pentane (2 cm^3) (Found: C, 57,7; H, 6.7; P, 7.8. $C_{18}H_{25}FeO_3P$ calcd.: C, 57.5, H, 6.7; P, 8.2%. Mass spectrum: M, 376 (calcd. 376.22); $M - CO$ 348; $M - 2CO$ 320; $C_{10}H_{10}OFe$, 202; $Fe[P(C_2H_5)_3]_3$ 174).

The unreacted $Fe(CO)_3(PEt_3)_2$ was further irradiated in the presence of bda, to give little more $Fe(CO)_2(PEt_3)$(bda).

(Benzylideneacetone) dicarbonyl(dimethylphenylphosphine) iron(0) (V, L = $PPhMe_2$) and (benzylideneacetone) carbonyl-bis(dimethylphenylphosphine) iron(0) (VI, L = $PPhMe_2$)

A solution of dimethylphenylphosphine (1000 mg, 7.0 mmol) and dodecacarbonyltriiron (1000 mg, 2.0 mmol) in THF (100 cm^3) was stirred for 6 h, at 70°C then filtered. The solvent was removed under vacuum to leave a green mixture of $Fe(CO)_4PPhMe_2$ (ν(CO) 2055, 1975, 1939 cm^{-1}) and $Fe(CO)_3(PPhMe_2)_2$ (ν(CO) 1867 cm^{-1}). This mixture was dissolved in benzene (200 cm^3) and the solution was irradiated for 24 h after addition of bda (1000 mg, 6.8 mmol). The resulting red solution was chromatographed on silica. Elution with benzene gave some unchanged $Fe(CO)_3(PPhMe_2)_2$ (557 mg), and a second elution with 10% ethyl acetate/benzene gave two orange bands. The faster-moving band gave $Fe(CO)_2(PPhMe_2)$(bda) as orange crystals (820 mg (30% based on bda)) after two washings with n-pentane (3 cm^3) (Found: C, 59.5; H, 5.6; P, 7.8. $C_{20}H_{21}FeO_3P$ calcd.: C, 60.6; H, 5.3; P, 7.8%. Mass spectra; *M*, 396 (calcd. 396.21); $M-$ CO, 368; $M-$ 2CO, 340; $C_{10}H_{10}Fe$, 202). The slower-moving band gave $Fe(CO)(PPhMe_2)_2$(bda) as brown crystals (330 mg (8.6% based on bda)) after two washings with n-pentane (2 cm^3) (Found: C, 64.0; H, 6.5; P, 12.9 $C_{27}H_{32}FeO_2P_2$ calcd.: C, 64.0; H, 6.4; P, 12.2%. Mass spectrum; *M*, 506 (Calcd. 506. 38); $M-$ CO, 478; $C_{10}H_{10}OFe$, 202). The unreacted $Fe(CO)_3(PPhMe_2)_2$ (557 mg, 1.34 mmol) was further irradiated in benzene (200 cm^3) with bda (300 mg, 2.05 mmol). A mixture of $Fe(CO)_2(PPhMe_2)$(bda) (237 mg; 45% based on $Fe(CO)_3(PPhMe_2)_2$) and $Fe(CO)(PPhMe_2)_2$(bda) (102 mg; 20% based on $Fe(CO)_3(PPhMe_2)_2$), was obtained after chromatography on silica and elution with 10% ethyl acetate/benzene.

(Benzylidenacetone) dicarbonyl(methyldiphenylphosphine) iron(0) (V, L = PPh_2Me) and (benzylideneacetone) carbonyl-bis(methyldiphenylphosphine) iron(0) (VI, L = PPh_2Me)

A solution of methyldiphenylphosphine (1410 mg, 7.0 mmol) and dodecacarbonyltriiron (1000 mg, 2.0 mmol) in THF (100 cm^3) was stirred for 2 h, at 70°C then filtered. The solvent was removed under vacuum to leave a mixture of $Fe(CO)_4PPh_2Me$ (ν(CO) 2051, 1975, 1937 cm^{-1}) and $Fe(CO)_3(PPh_2Me)_2$ (ν(CO) 1879 cm^{-1}) as a brown oil. This oil was dissolved in benzene (200 cm^3) and the solution was irradiated for 24 h after addition of bda (1000 mg, 6.8 mmol). The resulting red-brown solution was chromatographed on silica. Elution with benzene gave a mixture of unchanged $Fe(CO)_3(PPh_2Me)_2$ and $Fe(CO)_4PPh_2Me$ enriched with the bisphosphine derivative. A second elution with 10% ethyl acetate/benzene gave a red oil, identified by its infrared spectrum as $Fe(CO)_2$ (PPh_2Me)(bda) (ν(CO) 2000, 1940 cm^{-1}) containing a small amount of $Fe(CO)(PPh_2Me)_2$(bda) (ν(CO) 1897 cm^{-1}). This mixture was again chromatographed as described above, to give $Fe(CO)_2(PPh_2Me)$(bda) as orange-red crystals (2070 mg (66% based on bda) after washing with n-pentane (4 cm^3) (Found: C, 65.2; H, 5.5; P, 6.8. $C_{25}H_{23}FeO_3P$ calcd.: C, 65.5; H, 5.1; P, 6.8%. Mass spectrum: $M-$ 458 (Calcd. 458.30); $M-$ CO, 430; $M-$ 2CO, 402, $C_{10}H_{10}OFe$, 202).

A second irradiation of the unreacted iron carbonylphosphines (410 mg) in benzene (200 cm^3), in the presence of bda (150 mg, 1.03 mmol) gave $Fe(CO)_2(PPh_2Me)(bda)$ (240 mg (51% based on bda) and $Fe(CO)(PPh_2Me)_2(bda)$ (38 mg (6% based on bda)).

(Benzylideneacetone) carbonyl-bis(diphenylphosphine)ethane iron(0) (IX)

A solution of tricarbonyl-bis(diphenylphosphine)ethane (VII) (830 mg, 1.55 mmol) and bda (226 mg, 1.55 mmol) in benzene (200 cm^3) was irradiated for 24 h then chromatographed on silica. Elution with benzene gave small amounts of unchanged $Fe(CO)_3$dpe, and a second elution with 10% ethyl acetate/benzene gave the product as a red-brown powder (620 mg (64%)) after two washings with n-pentane (3 cm^3) (Found: C, 70.8; H, 5.5; P, 10.0. $C_{37}H_{34}FeO_2P_2$ calcd.: C, 70.7; H, 5.4; P, 9.9%. Mass spectrum: M 629 (calcd., 628.50); $M-CO$, 601; $Fe[(C_6H_5)_4(CH_2)_2P_2]$, 455; $C_{10}H_{10}OFe$, 202).

X-ray structural analysis of $Fe(CO)_2(PEt_3)(bda)$

Crystal data: $C_{18}H_{25}FeO_3P$, Mol wt. 376.2, monoclinic, a 10.203(3), b 12.964(4), c 16.960(6) Å, β 120.00(2)°, U 1943.5 Å^3, d_c 1.285 g cm^3, $Z = 4$, $F(000) = 792$. Space group $P2_1/c$ from systematic absences, graphite-monochromated Mo-K_α radiation; λ 0.71069 Å, μ(Mo-K_α) 8.11 cm^{-1}. Intensity data was recorded from a crystal of dimensions 0.35 × 0.29 × 0.15 mm.

A single crystal of $Fe(CO)_2(PEt_3)(bda)$ was mounted on a glass fibre and placed on a Phillips PW1100 four-circle diffractometer. Cell parameters were determined from the accurate angular measurement of 25 strong reflections in the range

TABLE 3

ATOMIC COORDINATES ($\times 10^4$) FOR $Fe(CO)_2(PEt_3)(dba)$

Atom	x/a	y/b	z/c
Fe	−348(1)	964(1)	1543(1)
O(1)	−1928(2)	2058(1)	1290(1)
C(1)	−3553(3)	1501(3)	−293(2)
C(2)	−2043(3)	1818(2)	508(2)
C(3)	−689(3)	1902(2)	476(2)
C(4)	601(3)	2288(2)	1270(2)
C(5)	2090(3)	2386(2)	1333(2)
C(6)	2550(3)	1740(2)	854(2)
C(7)	3939(4)	1881(3)	911(2)
C(8)	4897(3)	2660(3)	1440(2)
C(9)	4478(3)	3303(3)	1915(2)
C(10)	3068(3)	3174(2)	1860(2)
C(11)	883(3)	56(2)	1514(2)
O(11)	1682(2)	−567(2)	1501(2)
C(12)	−1630(3)	−43(2)	1421(2)
O(12)	−2459(3)	−685(2)	1339(2)
P	918(1)	116(1)	3058(1)
C(111)	2853(3)	1621(2)	3610(2)
C(112)	3957(3)	944(3)	3472(3)
C(121)	1091(3)	−107(2)	3645(2)
C(122)	1898(5)	−75(3)	4692(2)
C(131)	−21(3)	1992(2)	3465(2)
C(132)	−1534(4)	1591(3)	3310(2)

$15° < 2\theta < 25°$. Intensities in the range $3° < 2\theta < 50°$ were measured using graphite monochromated Mo-K_α radiation and an ω-2θ scan technique. The scan speed was set at 0.5° s^{-1} and the scan width at 0.8°. The variance of the intensity (I) was calculated as $\{[c(I)^2] + (0.04I)^2\}^{1/2}$, where $[c(I)]$ is the variance due to counting statistics, and the term in I^2 was introduced to allow for other sources of error. Three standard reflections were monitored periodically throughout the course of data collection but shows no significant variation in intensity. Lorentz polarisation corrections were applied, and equivalent reflections averaged to give 3351 unique observed intensities $[F > 6\sigma(F)]$.

The position of the Fe atom was derived from a Patterson synthesis, and the remaining non-hydrogen atoms from subsequent electron-density difference syntheses. Hydrogen atoms were placed in idealised positions (C–H 1.08 Å) and constrained to ride on the relevant C atom; methyl groups were refined as rigid bodies. Each type of hydrogen atom was assigned a common isotropic thermal parameter. The structure was refined by blocked full-matrix least squares with all the non-hydrogen atoms assigned anisotropic thermal parameters. A weighting scheme of the form $w = 2.4417\sigma/^2F$ was introduced and refinement continued until convergence was reached. The final residuals were $R = 0.035$ and $R_w = [\Sigma w^{1/2}\Delta/\Sigma w^{1/2}|F_0|] =$ 0.039. An electron density difference map computed at this stage revealed no regions of significant electron density. Final atomic coordinates for the non-hydrogen atoms and associated anisotropic thermal parameters are presented in Tables 3 and 4, respectively, while details of the hydrogen atom parameters are given in Table 5.

TABLE 4

ANISOTROPIC THERMAL PARAMETERS (Å × 10^3) FOR $Fe(CO)_2(PEt_3)(dba)$ (The temperature factor exponent takes the form: $-2\pi^2(U_{11}h^2a^{\star 2} + \ldots + 2U_{12}hk\,a^{\star}b^{\star})$)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe	41(1)	38(1)	36(1)	−1(1)	20(1)	2(1)
O(1)	49(1)	59(1)	58(1)	6(1)	32(1)	13(1)
C(1)	42(1)	112(3)	56(2)	11(2)	16(1)	1(2)
C(2)	47(1)	60(2)	49(1)	14(1)	24(1)	13(1)
C(3)	48(1)	58(1)	44(1)	14(1)	25(1)	10(1)
C(4)	50(1)	41(1)	51(1)	6(1)	30(1)	4(1)
C(5)	49(1)	51(1)	51(1)	11(1)	28(1)	2(1)
C(6)	56(2)	77(2)	55(2)	8(1)	34(1)	8(1)
C(7)	66(2)	109(3)	72(2)	15(2)	47(2)	18(2)
C(8)	53(2)	134(3)	78(2)	30(2)	40(2)	6(2)
C(9)	58(2)	106(3)	75(2)	14(2)	29(2)	−21(2)
C(10)	64(2)	67(2)	63(2)	5(1)	35(2)	−10(1)
C(11)	57(2)	44(1)	51(1)	−6(1)	27(1)	0(1)
O(11)	81(1)	59(1)	95(2)	−10(1)	48(1)	17(1)
C(12)	54(2)	55(2)	46(1)	−4(1)	23(1)	−6(1)
O(12)	88(2)	78(2)	93(2)	−5(1)	42(1)	−37(1)
P	52(1)	37(1)	38(1)	−2(1)	19(1)	−1(1)
C(111)	56(2)	54(2)	52(2)	−8(1)	15(1)	−11(1)
C(112)	51(2)	76(2)	89(2)	−4(2)	16(2)	7(2)
C(121)	76(2)	52(2)	51(2)	14(1)	20(1)	−5(1)
C(122)	121(3)	97(3)	52(2)	25(2)	23(2)	−3(2)
C(131)	74(2)	69(2)	56(2)	−16(1)	33(2)	7(2)
C(132)	83(2)	104(3)	70(2)	−4(2)	50(2)	8(2)

TABLE 5

HYDROGEN ATOM COORDINATES ($\times 10^4$) AND ISOTROPIC TEMPERATURE FACTORS ($Å^2 \times 10^3$) FOR $Fe(CO)_2(PEt_3)(bda)$

Atom	x/a	y/b	z/c	U
H(11)	−3499(3)	1162(3)	−858(2)	130(4)
H(12)	−4177(3)	2217(3)	−508(2)	130(4)
H(13)	−4116(3)	976(3)	−65(2)	130(4)
H(31)	−635(3)	1683(2)	−121(2)	74(3)
H(41)	410(30)	2862(15)	1662(16)	74(3)
H(61)	1813(3)	1128(2)	435(2)	94(5)
H(71)	4279(4)	1375(3)	540(2)	94(5)
H(81)	5977(3)	2763(3)	1478(2)	94(5)
H(91)	5231(3)	3909(3)	2334(2)	94(5)
H(101)	2735(3)	3690(2)	2228(2)	94(5)
H(11A)	3265(3)	1683(2)	4331(2)	74(3)
H(11B)	2825(3)	2377(2)	3335(2)	74(3)
H(12A)	5080(3)	1266(3)	3857(3)	130(4)
H(12B)	3641(3)	892(3)	2763(3)	130(4)
H(12C)	3943(3)	184(3)	3728(3)	130(4)
H(21A)	1706(3)	−637(2)	3458(2)	74(3)
H(21B)	−39(3)	−397(2)	3404(2)	74(3)
H(22A)	1998(5)	−813(3)	5012(2)	130(4)
H(22B)	1338(5)	464(3)	4912(2)	130(4)
H(22C)	3012(5)	211(3)	4883(2)	130(4)
H(31A)	−209(3)	2719(2)	3114(2)	74(3)
H(31B)	716(3)	2108(2)	4186(2)	74(3)
H(32A)	−2051(4)	2224(3)	3468(2)	130(4)
H(32B)	−1392(4)	946(3)	3749(2)	130(4)
H(32C)	−2250(4)	1365(3)	2609(2)	130(4)

X-ray structural analysis of $Fe(CO)_2(PPhMe_2)(bda)$

Crystal data: $C_{19}H_{21}FeO_3P$, mol, wt. 384.18, monoclinic, a 8.134(3), b 21.394(8), c 11.658(5) Å, β 108.18(2)°, U 1927.4 Å^3, d_c 1.324 g cm^{-2}, $Z = 4$, $F(000) = 800$. Space group $P2_1/c$ from systematic absences. Graphite-monochromated Mo-K_α radiation, λ 0.71069 Å, μ(Mo-K_α) 8.25 cm^{-1}. Intensity data was recorded from a crystal of dimensions 0.41 × 0.27 × 0.23 mm.

The crystal was mounted and data collected as described for $Fe(CO)_2(PEt_3)(bda)$. Lorentz polarisation corrections were again applied and equivalent reflections averaged to give 3498 unique observed intensities [$F > 6\sigma(F)$].

The structure was solved and refined in the same way as for $Fe(CO)_2(PEt_3)(bda)$, and the hydrogen atoms treated in a similar manner. In this case the weighting scheme was $w = 12.1326/[\sigma^2(F) + 0.0008|F_0|]$, and the converged residuals were $R = 0.036$ and $R_w = [\Sigma w^{1/2}\Delta/\Sigma w^{1/2}|F_0|] = 0.041$. Final atomic coordinates for the non-hydrogen atoms, anisotropic thermal parameters, and hydrogen atom parameters are presented in Tables 6, 7, and 8 respectively.

For both structures complex neutral-atom scattering factors were employed [15]. Calculations were performed on the University of Cambridge IBM 370/165 computer using SHELX 76 [16]. The molecular plats were drawn using ORTEP. Copies of observed and calculated structure factor tables may be obtained from the authors.

TABLE 6. ATOMIC COORDINATES ($\times 10^4$) FOR $Fe(CO)_2(PPhMe_2)(bda)$

Atom	x/a	y/b	z/c
Fe	1314(1)	1341(1)	686(1)
P	1671(1)	2267(1)	−79(1)
O(1)	3104(2)	1471(1)	2319(1)
C(1)	2224(4)	548(1)	3205(3)
C(2)	2733(3)	872(1)	2229(2)
C(3)	2902(3)	569(1)	1192(2)
C(4)	3562(3)	935(1)	415(2)
C(5)	3632(3)	705(1)	−762(2)
C(6)	2669(4)	194(1)	−1362(2)
C(7)	2742(4)	2(2)	−2477(3)
C(8)	3763(5)	317(2)	−3036(3)
C(9)	4766(4)	817(2)	−2449(3)
C(10)	4711(3)	1006(1)	−1323(3)
C(11)	−92(3)	1067(1)	−672(2)
O(11)	−1018(3)	895(1)	−1577(2)
C(12)	−504(3)	1492(1)	1200(2)
O(12)	−1706(3)	1588(1)	1488(2)
C(101)	3731(3)	2639(1)	724(3)
C(102)	1652(4)	2261(1)	−1647(2)
C(111)	31(3)	2854(1)	−121(2)
C(112)	−1684(4)	2723(2)	−799(3)
C(113)	−2986(4)	3151(2)	−858(3)
C(114)	−2613(5)	3708(2)	−249(4)
C(115)	−935(6)	3847(2)	424(4)
C(116)	394(4)	3420(1)	492(3)

TABLE 7

ANISOTROPIC THERMAL PARAMETERS ($Å^2 \times 10^3$) FOR $Fe(CO)_2(PPhMe_2)(bda)$ (The temperature facture exponent takes the form: $-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^*)$)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe	39(1)	34(1)	40(1)	0(1)	11(1)	−2(1)
P	43(1)	36(1)	46(1)	2(1)	15(1)	−1(1)
O(1)	50(1)	49(1)	46(1)	−3(1)	6(1)	−4(1)
C(1)	82(2)	65(2)	49(1)	8(1)	22(1)	2(1)
C(2)	52(1)	47(1)	43(1)	4(1)	10(1)	3(1)
C(3)	54(1)	41(1)	49(1)	3(1)	13(1)	8(1)
C(4)	43(1)	45(1)	49(1)	2(1)	13(1)	6(1)
C(5)	47(1)	50(1)	50(1)	8(1)	16(1)	14(1)
C(6)	67(2)	58(2)	57(2)	−5(1)	22(1)	9(1)
C(7)	77(2)	81(2)	58(1)	−10(2)	18(2)	18(2)
C(8)	75(2)	95(2)	54(2)	1(2)	22(2)	32(2)
C(9)	63(2)	93(2)	71(2)	28(2)	34(2)	35(2)
C(10)	48(1)	66(2)	61(2)	12(1)	21(1)	16(1)
C(11)	43(1)	42(1)	55(1)	−3(1)	15(1)	−4(1)
O(11)	58(1)	82(1)	62(1)	−21(1)	4(1)	−13(1)
C(12)	51(1)	51(1)	53(1)	−5(1)	18(1)	−7(1)
O(12)	64(1)	112(2)	92(2)	−15(1)	46(1)	−5(1)
C(101)	43(1)	51(2)	91(2)	0(1)	17(1)	−11(1)
C(102)	86(2)	53(1)	55(2)	11(1)	37(1)	13(1)
C(111)	51(1)	43(1)	48(1)	9(1)	19(1)	6(1)
C(112)	50(1)	68(2)	72(2)	6(1)	11(1)	8(1)
C(113)	56(2)	95(3)	94(2)	31(2)	21(2)	25(2)
C(114)	89(3)	84(2)	103(3)	33(2)	49(2)	45(2)
C(115)	117(3)	57(2)	88(2)	5(2)	44(2)	32(2)
C(116)	72(2)	46(1)	60(2)	2(1)	22(1)	10(1)

TABLE 8

HYDROGEN ATOM COORDINATES ($\times 10^4$) AND ISOTROPIC TEMPERATURE FACTORS ($Å^2 \times 10^2$) FOR $Fe(CO)_2(PPhMe_2)(bda)$

Atom	x/a	y/b	z/c	U
H(11)	1616(4)	101(1)	2926(3)	92(4)
H(12)	1330(4)	854(1)	3450(3)	92(4)
H(13)	3367(4)	485(1)	3974(3)	92(4)
H(31)	2544(3)	85(1)	1000(2)	85(3)
H(41)	4532(32)	1273(12)	869(27)	85(3)
H(61)	1849(4)	−55(1)	−947(2)	85(3)
H(71)	1995(4)	−397(2)	−2913(3)	85(3)
H(81)	3784(5)	174(2)	−3920(3)	85(3)
H(91)	5590(4)	1061(2)	−2871(3)	85(3)
H(101)	5513(3)	1390(1)	−870(3)	85(3)
H(O1A)	3924(3)	2709(1)	1675(3)	92(4)
H(O1B)	3824(3)	3083(1)	307(3)	92(4)
H(O1C)	4710(3)	2325(1)	612(3)	92(4)
H(O2A)	2548(4)	1919(1)	−1787(2)	92(4)
H(O2B)	1975(4)	2717(1)	−1913(2)	92(4)
H(O2C)	352(4)	2140(1)	−2185(2)	92(4)
H(112)	−1992(4)	2285(2)	−1277(3)	85(3)
H(113)	−4303(4)	3046(2)	−1388(3)	85(3)
H(114)	−3635(5)	4039(2)	−297(4)	85(3)
H(115)	−647(6)	4286(2)	900(4)	85(3)
H(116)	1707(4)	3530(1)	1023(3)	85(3)

Acknowledgements

We thank CNPq and FAPESP for financial support.

References

1 S. Otsuka, T. Yoshida and A. Nakanima, Inorg. Chem., 6 (1967) 20.
2 H. tom Dieck and H. Bock, J. Chem. Soc., Chem. Commun., (1968) 678.
3 A.M. Brodie, B.F.G. Johnson, P.L. Josty and J. Lewis, J. Chem. Soc., Dalton Trans., (1972) 2031.
4 D. Liebfritz and H. tom Dieck, J. Organomet. Chem., 105 (1976) 255.
5 A. Vessieres and P. Dixneuf, Tetrahedron Lett., (1974) 1499.
6 A. Vessieres and P. Dixneuf, J. Organomet. Chem., 108 (1976) C5.
7 J.A.S. Howell, B.F.G. Johnson and J. Lewis, J. Organomet. Chem., 39 (1972) 326.
8 B.F.G. Johnson, J. Lewis, G.R. Stephenson and E.J.S. Vichi, J. Chem. Soc., Dalton Trans., (1978) 369.
9 W.A. Henderson and C.A. Streuli, J. Amer. Chem. Soc., 82 (1960) 5791.
10 C.A. Tolman, Chem. Revs., 77 (1977) 313.
11 A.J. Pearson and P.R. Raithby, J. Chem. Soc., Dalton Trans., (1981) 884.
12 (a) C. Kruger, B.L. Barnett and O. Brauer in E.A. Koerner von Gustorf, F.W. Grevels and I. Fischler (Eds.), The Organic Chemistry of Iron, Academic Press, New York, 1978, ch. 1 and refs. therein; (b) A.J. Pearson and P.R. Raithby, J. Chem. Soc., Perkin Trans. I, (1980) 395; (c) M.R. Churchill and S.W.Y. Chang, Inorg. Chem., 129 (1977) 105; (d) O.S. Mills and G. Robinson, Proc. Chem. Soc., (1960) 421 and Acta Crystallogr., 16 (1963) 758.
13 F.M. Chaudari and P.L. Pauson, J. Organomet. Chem., 5 (1966) 73.
14 R. Edwards, J.A.S. Howell, B.F.G. Johnson and J. Lewis, J. Chem. Soc., Dalton Trans., (1974) 2107.
15 International Tables for X-ray Crystallography, Vol. IV, Kynoch Press, Birmingham, 1974.
16 SHELX 76, G M Sheldrick, A molecular structure determination program package, Cambridge, 1976.