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Synthesis and characterization of novel σ-alkynyl cyclopentadienyl iron(II) complexes $[Fe(C{\equiv}CR)L_2(\eta\text{-}C_5H_5)]$ $[L = CO;\ L_2 =$ bis(diphenylphosphino)methane (dppm)$]$. Crystal structure of $[Fe(C{\equiv}CC_6H_5)(dppm)(\eta\text{-}C_5H_5)]$

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Abstract

The synthesis of novel σ-alkynyl cyclopentadienyl iron(II) complexes of the type $[Fe(C{\equiv}CR)L_2(\eta\text{-}C_5H_5)]$ $[L = CO$; $R = SiMe_3$, ${}^tBu$, CO_2Me; $L_2 =$ bis(diphenylphosphino)methane (dppm), $R = SiMe_3$, ${}^tBu$, CCO_2Me, H, $C_6H_5]$ is described. IR and ^1H, $^{31}P\{^1H\}$ and ^{13}C NMR data are discussed. The structure of $[Fe(C{\equiv}CPh)(dppm)(\eta\text{-}C_5H_5)]$ has been determined by an X-ray diffraction study. The coordination around the Fe atom of the cyclopentadienyl ring (considered as bonded at its centroid), the two P atoms of the dppm molecule acting as a chelating ligand, and the terminal carbon of the phenylacetylide ligand, can be described as a three-legged piano stool. The stabilities of the dppm chelate rings in the complexes have been studied, and their reactions with CO under atmospheric or higher pressure examined.

Introduction

The chemistry of metal alkynyl complexes has undergone important development in recent years [1–4]. The ability of the acetylide anions $RC{\equiv}C^-$ to bond to transition metals as terminal, bridging or multisite ligands [3,4] has no equivalent among unsaturated hydrocarbyls. The ability of the coordinated ligands to react with both nucleophilic and electrophilic agents is well established [5], and they have been shown to be excellent precursors for the generation of other hydrocarbyl ligands in polynuclear coordinated ligands systems [6].

We have recently reported a new method of synthesis of tetra- and tri-nuclear copper(I) acetylide complexes of the types $[Cu(\mu_3\text{-}\eta^1\text{-}C{\equiv}CR)(dppm\text{-}P)]_4$ [4a], $[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CR)]^{2+}$ [4b] and $[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-Cl})(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)]^+$

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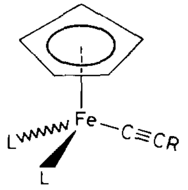
[4c] starting from dinuclear systems containing the "$Cu_2(\mu\text{-dppm})_2$" moiety (dppm = bis(diphenylphosphino)methane) and taking advantage of the well known ability of dppm to act mainly as a bridging ligand [7].

In continuation of our studies of the chemistry of acetylide complexes and of the ability of dppm to form polynuclear complexes, we report here the preparation of a series of novel cyclopentadienyl iron(II) alkynyl complexes $Fe(C{\equiv}CR)L_2(\eta\text{-}C_5H_5)$ [L = CO (**6–9**) and L_2 = dppm (**1–5**)] in which dppm acts as a chelating bidentate ligand.



R	*L_2 = dppm*	*L = CO*
$SiMe_3$	1	6
CO_2Me	2	7
^tBu	3	8
H	4	-
C_6H_5	5	9

The structure of complex **5**, determined by a single-crystal X-ray diffraction study, has a piano stool arrangement of the phenylacetylide and dppm ligands around the metal atom, with a small bite angle P–M–P (ca. 74°) characteristic of the chelated dppm complexes. The chelation shift values Δ_R for the corresponding phosphorus resonances in the NMR spectra (ca. −28) reflect the typical upfield shifting of the strained four membered metal-dppm rings [8]. With the aim of exploring the behavior of these complexes as metal-containing bifunctional ligands, we have studied their reactions with CO to bring about ring opening by displacement of one of the two coordinated phosphorus atoms. However, in contrast with the ability of other dppm complexes to undergo ring opening reactions (i.e. MX_2(dppm) [9], $[M(dppm)_2]Cl_2$ M = Pd, Pt [10], $Fe(CO)_4$(dppm) [11], $RuH_2(dppm)_2$ [12] used as precursors of homo and heterodinuclear compounds), complexes **1–5** seem to be resistant towards opening processes of the chelate ring. $^{31}P\{^1H\}$ NMR studies show that significant ring opening takes place only in the presence of CO under high pressures (ca. 30 atm), the equilibrium

$$Fe(C{\equiv}CR)(dppm)(\eta\text{-}C_5H_5) + CO \rightleftharpoons Fe(C{\equiv}CR)(CO)(dppm\text{-}P)(\eta\text{-}C_5H_5)$$

lying over to the left at lower pressures.

We also present ^{13}C NMR data which extend the limited information available for alkynyl cyclopentadienyl complexes of iron. A new cyclopentadienyl monocarbonyl derivative containing a monodentate dppm ligand, $FeBr(CO)(dppm\text{-}P)(\eta\text{-}C_5H_5)$, is also described.

Results and discussion

Although a variety of methods of preparing σ-alkynyl cyclopentadienyl transition metal complexes have been described [1a] the most useful approach involves the reaction of halide derivatives with an acetylide reagent, which is generally prepared *in situ* (as a lithium derivative or from the terminal alkyne in the presence of a base) [1b]. However the enhanced reactivity of the alkynyl group C≡CR upon coordination, even when only a σ-bond is formed, limits the synthetic utility of organolithium reagents and leads to rather low yields after work up of the reaction mixtures.

Table 1

Infrared [a] and analytical data

Complex	Yield (%)	ν (cm^{-1}) [b] (C≡C)	(CO)	Analysis (%) [c] C	H	M^+ [d]
(1) $[\mathrm{Fe(C{\equiv}CSiMe_3)(dppm)(\eta\text{-}C_5H_5)}]$	96	1995m	–	69.1 (69.8)	6.3 (6.1)	602
(2) $[\mathrm{Fe(C{\equiv}CCO_2Me)(dppm)(\eta\text{-}C_5H_5)}]$	65	2054m	–	69.3 (69.4)	5.0 (5.1)	588
(3) $[\mathrm{Fe(C{\equiv}C^tBu)(dppm)(\eta\text{-}C_5H_5)}]$	78	2081m	–	72.9 (73.7)	6.2 (6.2)	586
(4) $[\mathrm{Fe(C{\equiv}CH)(dppm)(\eta\text{-}C_5H_5)}]$	75	1930w	–	71.4 (72.5)	5.5 (5.3)	530
(5) $[\mathrm{Fe(C{\equiv}CC_6H_5)(dppm)(\eta\text{-}C_5H_5)}]$	81	2071m	–	74.3 (75.3)	5.3 (5.3)	606
(6) $[\mathrm{Fe(C{\equiv}CSiMe_3)(CO)_2(\eta\text{-}C_5H_5)}]$	75	1989w	2053s 2025s	53.1 (52.6)	5.0 (5.1)	274
(7) $[\mathrm{Fe(C{\equiv}CCO_2Me)(CO)_2(\eta\text{-}C_5H_5)}]$	45	2110w [e]	2046s 2004s	49.9 (50.8)	3.0 (2.9)	260
(8) $[\mathrm{Fe(C{\equiv}C^tBu)(CO)_2(\eta\text{-}C_5H_5)}]$	70	2115w	2034s 1984s	59.9 (60.5)	5.6 (5.5)	258
(10) $[\mathrm{FeBr(CO)(dppm\text{-}}P\mathrm{)(\eta\text{-}C_5H_5)}]$	70	–	1954s	61.0 (60.7)	4.5 (4.4)	

[a] In THF. [b] ν(C≡C) (KBr) cm^{-1}: 1992s (1), 2036s (2), 2082s (3), 1924 (4), 2065 (5). [c] Calculated values are given in parenthesis. [d] By electron impact mass spectrometry. [e] $\nu(\mathrm{CO_2Me})$ cm^{-1} = 1728 m.

Table 2

Proton and phosphorus NMR data [a]

Complex	^{1}H	^{31}P{^{1}H} [a]
(1) $[\mathrm{Fe({\equiv}CSiMe_3)(dppm)(\eta\text{-}C_5H_5)}]$	7.67–7.25 (m, 20H, $\mathrm{Ph_2P}$), 4.40 (s, 5H, $\mathrm{C_5H_5}$), 4.38, 3.85 (m, 2H, $\mathrm{CH_aH_b}$), –0.58 (s, 9H, $\mathrm{SiMe_3}$)	44.7
(2) $[\mathrm{Fe(C{\equiv}CCO_2Me)(dppm)(\eta\text{-}C_5H_5)}]$	7.61–7.26 (m, 20H, $\mathrm{Ph_2P}$), 4.49 (s, 5H, $\mathrm{C_5H_5}$), 4.20–4.00 (m, 2H, $\mathrm{CH_aH_b}$), 3.30 (s, 3H, $\mathrm{CO_2Me}$)	43.1
(3) $[\mathrm{Fe(C{\equiv}C^tBu)(dppm)(\eta\text{-}C_5H_5)}]$	7.80–7.16 (m, 20H, $\mathrm{Ph_2P}$), 4.42 (s, 5H $\mathrm{C_5H_5}$), 4.14–3.85 (m, 2H, $\mathrm{CH_aH_b}$) 0.86 (s, 9H, ^{t}Bu)	45.1
(4) $[\mathrm{Fe(C{\equiv}CH)(dppm)(\eta\text{-}C_5H_5)}]$	7.90–6.95 (m, 20H, $\mathrm{Ph_2P}$), 4.53 (s, 5H, $\mathrm{C_5H_5}$), 4.20 (m, 2H, $\mathrm{CH_2}$), 1.84 (t, 1H, ≡CH, J(P–H) 3.2)	45.5
(5) $[\mathrm{Fe(C{\equiv}CC_6H_5)(dppm)(\eta\text{-}C_5H_5)}]$	7.69–7.21 (m, 20H, $\mathrm{Ph_2P}$), 6.85–6.22 (m, 5H, C≡CPh), 4.46 (s, 5H, $\mathrm{C_5H_5}$), 4.27, 3.86 (m, 2H, $\mathrm{CH_aH_b}$)	44.6
(6) $[\mathrm{Fe(C{\equiv}CSiMe_3)(CO)_2(\eta\text{-}C_5H_5)}]$	4.89(s, 5H, $\mathrm{C_5H_5}$), –0.07 (s, 9H, $\mathrm{SiMe_3}$)	
(7) $[\mathrm{Fe(C{\equiv}CCO_2Me)(CO)_2(\eta\text{-}C_5H_5)}]$	5.08(s, 5H, $\mathrm{C_5H_5}$), 3.67 (s, 3H, $\mathrm{CO_2Me}$)	
(8) $[\mathrm{Fe(C{\equiv}C^tBu)(CO)_2(\eta\text{-}C_5H_5)}]$	4.94 (s, 5H, $\mathrm{C_5H_5}$), 1.17 (s, 9H, ^{t}Bu)	
(10) $[\mathrm{FeBr(CO)(dppm\text{-}}P\mathrm{)(\eta\text{-}C_5H_5)}]$	7.14–7.80 (m, 20H, $\mathrm{Ph_2P}$), 4.35 (s, 5H, $\mathrm{C_5H_5}$), 3.38, 3.19 (m, 2H, $\mathrm{CH_aH_b}$)	61.7d, –25.0d [c]

[a] Chemical shifts (δ) in ppm to high frequency (downfield) of $\mathrm{SiMe_4}$ or $\mathrm{H_3PO_4}$. Measured in $\mathrm{CDCl_3}$ at ca. 20 °C, 300 MHz spectra (J values in Hz). [b] Δ_R (chelation shifts) (see text): –26.7 (1); –28.3 (2); –26.3 (3); –25.9 (4), –26.8 (5). [c] J(P–P) 54.

Bruce and his colleagues found [13] that terminal alkynes can be readily deprotonated by NEt_3 or $HNEt_2$ as solvents in the presence of catalytic amounts of copper(I) halides. This provides an efficient alternative synthesis in certain cases, although the nucleophilic nature of the solvents can lead to potentially competitive displacement of soft ligands, e.g. of carbonyl ligands.

We have studied the experimental conditions suitable for application of both methods to the synthesis of the new σ-alkynylcyclopentadienyl iron(II) complexes, $Fe(C{\equiv}CR)L_2(\eta\text{-}C_5H_5)$ (**1**–**8**). To the best of our knowledge complexes **1** and **6** are the first σ-alkynyl transition metal derivatives containing the $C{\equiv}CSiMe_3$ group. Table 1 lists analytical data and infrared spectral data and Table 2 ^1H and $^{31}P\{^1H\}$ NMR data for the novel complexes.

*(a) Carbonyl derivatives (**6**–**9**)*

Treatment of a solution in tetrahydrofuran of $FeBr(CO)_2(\eta\text{-}C_5H_5)$ with the lithium derivatives of $HC{\equiv}CR$ ($R = SiMe_3$, ^tBu, prepared *in situ* from the corresponding alkyne and Li^nBu in THF at −20 °C) gives a yellow solution from which after filtration through Alox IV, complexes **6**–**8** can be isolated, (eq. 1)

$$FeBr(CO)_2(\eta\text{-}C_5H_5) + LiC{\equiv}CR \xrightarrow{THF,\ -20\,^\circ C} Fe(C{\equiv}CR)(CO)_2(\eta\text{-}C_5H_5) + LiBr \quad (1)$$

$$\left(R = SiMe_3\ (\mathbf{6}),\ CO_2Me\ (\mathbf{7}),\ {}^tBu\ (\mathbf{8})\right)$$

However the method is not suitable for the synthesis of complex **7** (yield 5%) probably because the lithium reagent attacks the ester carbonyl group. Complex **7** is obtained in higher yield (45%) by a route similar to that used for the previously known complex **9** [13], dissolving the reactants in NEt_3 in the presence of CuI. For the other alkynes this method gave a mixture of starting materials and unidentified products.

Complexes **6**–**9** are air-stable yellow crystalline solids which are soluble in chlorinated solvents and slightly soluble in hydrocarbons. The IR spectra show the expected weak $\nu(C{\equiv}C)$ and two strong $\nu(CO)$ absorption. The wavenumber depens on R in the opposite way for $\nu(CO)$ and $\nu(C{\equiv}C)$ viz. $^tBu < CO_2Me \approx Ph < SiMe_3$ and $SiMe_3 < CO_2Me \approx Ph < {}^tBu$, respectively, and the sequences appear to reflect the electron releasing ability of R. A similar sequence for $\nu(C{\equiv}C)$ is found for the analogous dppm alkynyl complexes (see below). Proton NMR spectra (Table 2) show the expected resonances for the R and C_5H_5 groups.

*(b) Dppm complexes (**1**–**5**)*

Photolysis with UV light of solutions of alkynyl dicarbonyl derivatives $Fe(C{\equiv}CR)(CO)_2(\eta\text{-}C_5H_5)$ in THF containing an equimolar amount of dppm at −20 °C proceeds smoothly with evolution of CO, and leads to the corresponding dppm complexes (eq. 2):

$$Fe(C{\equiv}CR)(CO)_2(\eta\text{-}C_5H_5) + dppm \xrightarrow{h\nu\ (THF,\ -20\,^\circ C)} Fe(C{\equiv}CR)(dppm)(\eta\text{-}C_5H_5) + 2CO \quad (2)$$

$$\left(R = SiMe_3\ (\mathbf{1}),\ CO_2Me\ (\mathbf{2}),\ {}^tBu\ (\mathbf{3}),\ C_6H_5\ (\mathbf{5})\right)$$

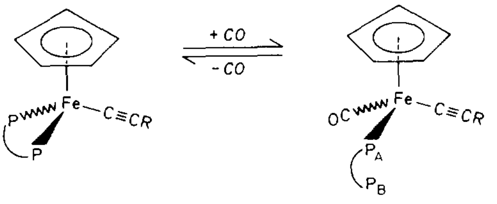
Other approaches to the synthesis of complexes were tried unsucessfully. Thus, no reaction was observed upon treatment of a solution of $Fe(C{\equiv}CC_6H_5)(CO)_2(\eta\text{-}C_5H_5)$ with dppm in toluene under reflux. The presence of an equimolar amount of Me_3NO or $[Fe(\eta\text{-}C_5H_5)(CO)_2]_2$ (catalytic amount) did not lead to better results. Complex **4** R = H was obtained by deprotonation of the corresponding vinylidene derivative $[Fe(C{=}CH_2)(dppm)(\eta\text{-}C_5H_5)]^+$ [14] with bases such as KO^tBu or $LiN(SiMe_3)_2$ in THF.

The synthesis of $FeBr(dppm)(\eta\text{-}C_5H_5)$, a potential precursor for the alkynyl derivatives, was also attempted, but the UV irradiation of a solution in THF of $FeBr(CO)_2(\eta\text{-}C_5H_5)$ and dppm in fact gave $FeBr(dppm\text{-}P)(CO)(\eta\text{-}C_5H_5)$ (**10**). When the reaction was carried out in refluxing toluene, the previously known cationic complex $[Fe(\eta C_5H_5)(dppm)(CO)]Br$ [15] was isolated.

Complexes **1**–**5** are air-stable red-orange solids soluble in chlorinated and hydrocarbon solvents. They were characterized by chemical analysis and spectroscopic methods. The structure of **5** was determined by an X-ray diffraction study (see below). The infrared spectra exhibit the expected $\nu(C{\equiv}C)$ absorption band between 1925 and 2081 cm^{-1} (Table 1) and show a similar dependence on R to that shown by the carbonyl analogues (see above). ^1H and $^{31}P\{^1H\}$ NMR spectra in $CDCl_3$ exhibit aromatic, cyclopentadienyl, methyl, methylene (CH_2P_2) and phosphorus signals in accord with the proposed structures. Thus, the methylene resonances in the proton NMR spectra appear as one or two unresolved multiplets showing the (ABX_2) spin system, consistent with the chemical inequivalence of the protons $CH_aH_bP_2$ in the chelated coordination of the phosphine. This is confirmed by the appearance of a single resonance in the ^{31}P NMR spectra, in the range $\delta = 43$ to 45 ppm (Table 2), showing the chemical equivalence of the phosphorus atoms. The ^{13}C NMR spectra also exhibit the expected resonances. We have tentatively assigned the signals arising from C_α and C_β of the acetylide groups on the basis of the observed phosphorus coupling $J(C_\alpha\text{–}P)$ of C_α which appears at lower field than C_β (113–150 and 83–122 ppm, respectively). The alkynyl carbon chemical shifts can be compared with those reported for $Fe(C{\equiv}CMe)(dppe)(\eta\text{-}C_5H_5)$ [16] (112.6 C_α; 97.5 C_β).

The values of the chelation shift Δ_R, given by $\delta_{chel} - \delta_{coord}$ ($\delta_{coord} = 71.4$ ppm for $Fe(C{\equiv}CC_6H_5))(CO)(dppm\text{-}P)(\eta\text{-}C_5H_5)$, see below), are in the range -25.9 to -28.3 (Table 2), and reflect the upfield shift typical of the strained four-membered metal-dppm ring [8]. From the phosphorus chemical shifts reported for $[Fe(\eta\text{-}C_5H_5)(dppm)(dppm\text{-}P)]^+$, $[Fe(\eta\text{-}C_5H_5)(dppm)(CO)]^+$ and $[Fe(\eta\text{-}C_5H_5)(dppm)(MeCN)]^+$ [17], the corresponding values of Δ_R can be calculated as -35, -31.5 and -22.7, respectively. The angle P–Fe–P of ca. 74° found in complex **5** (see below) reflects the small bite of the chelate dppm ligand.

The formation of the complexes **1**–**5**, by the reactions shown in eq. 2, proceeds through the monocarbonyl derivatives as intermediates, as was shown by periodic scans of the IR spectra in the 2200–1800 cm^{-1} range. New $\nu(C{\equiv}C)$ and one $\nu(CO)$ absorption bands appear during the course of each reaction and can be attributed to the presence of an intermediate monocarbonyl derivative along with the simultaneously formed chelated dppm complex. In order to confirm the formation of the monocarbonyl derivatives, metal-dppm ring opening processes with CO were investigated. A systematic study has not been carried out, but the phosphorus NMR spectra of the reaction mixtures after bubbling of CO for 2 h indicate the existence of an equilibrium of the type



R = C_6H_5 (11), ${}^tBu$ (12)

Thus, for $R = C_6H_5$ the spectrum shows two doublets at $\delta = -25.0$ and 71.4 ppm (${}^2J(P-P) = 55$ Hz), typical of an AB system, along with the single phosphorus resonance of the chelated complex **5** at $\delta = 44.6$ ppm, consistent with a mixture of complexes **5** and **11** in a molar ratio of ca. 1 : 1. Similar behaviour is observed for $R = {}^tBu$ ($\delta = 45.1$ s and -24.7 d, 73.6 d ppm; (${}^2J(P-P) = 58$ Hz). At higher pressures of CO (30–40 atm) both equilibria can be displaced progressively to the right, as shown by the phosphorus NMR spectra of the solutions. For R = Ph, only the doublet resonances of the P_A and P_B atoms can be observed after 48 h, whilst for $R = {}^tBu$ the corresponding phosphorus resonances indicate a molar ratio of ca. 1 : 3. However, the monocarbonyl derivatives **11** and **12** are unstable at atmospheric pressure, losing carbon monoxide, especially in solution, to reform the chelated precursor complexes.

Attempts to use the transient monocarbonyl species as bifunctional metallic ligands to prepare polynuclear complexes have been unsucessful. Thus, the reaction of a mixture of complex **11** and $Fe_2(CO)_9$ or $Co_2(CO)_8$, in THF or toluene with CO (1 atm) at room temperature or heating under reflux, gave a complex mixture of compounds from which the very stable alkynyl derivative Fe(C≡CPh)(dppm)(η-C_5H_5) was separated as the major component.

(c) Description of the crystal structure of [Fe(C≡CC$_6$H$_5$)(dppm)(η-C$_5$H$_5$)] (5)

The unit cell of complex **5** contains two crystallographically independent but essentially identical complexes. The structure of one of them is depicted in Fig. 1 together with the atomic numbering scheme; selected bond distances and angles are listed in Table 3. The complex **5** consists of discrete monomeric molecules in which the cyclopentadienyl ring is bound to the Fe atom in a η^5-fashion (with Fe–C distances ranging from 2.070(7) [2.063(9)] to 2.086(8) [2.106(8)] Å; here and below values in squares brackets refer to the second independent molecule), the phenylethynyl ligand is almost linearly bonded to the metal (the Fe–C(1)–C(2) angle is 177.4(7)° [179.3(6)°]). The coordination around the Fe atom is completed by two P atoms from a dppm molecule acting as a chelating ligand (Fe–P bonds: 2.162(2) and 2.167(2) Å [2.164(2) and 2.176(2) Å]). The coordination around the Fe atom of the cyclopentadienyl ring (taken as bonded at its centroid M(1)), the two P atoms of the chelating dppm molecule, and the terminal carbon C(1) of the phenylethynyl ligand, can be described as a three-legged piano stool. The values of the M(1)–Fe–P(1), M(1)–Fe–C(1) and M(1)–Fe–C(2) angles are 125.7(4) [123.6(4)], 133.7(3) [133.5(3)], and 134.4(3)° [136.9(2)°], whereas the values of the P(1)–Fe–P(2), P(1)–Fe–C(1) and P(2)–Fe–C(1) angles involving the legs are 74.8(2) [74.4(2)], 84.0(3) [86.8(3)] and 85.2(3)° [83.0(2)°]. These two sets of values of angles are consistent with a "pseudo-octahedral" structure for this complex [18]. The distance

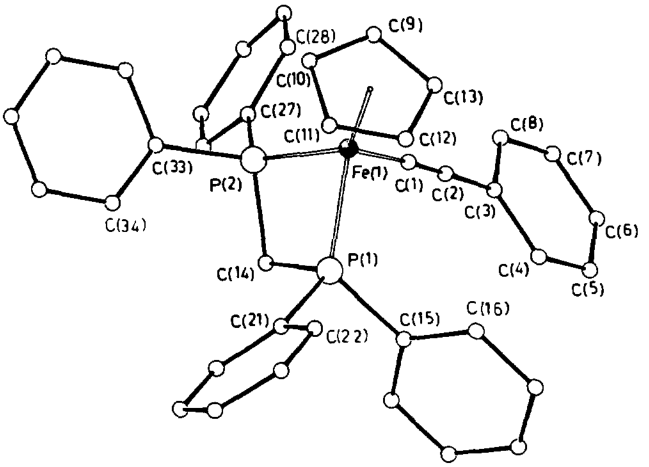


Fig. 1. View of the molecular structure of the complex [Fe(C≡CPh)(dppm)(η-C_5H_5)] (5) with the atomic numbering scheme.

between the metal and the centroid of the cyclopentadienyl ring, Fe–M(1), is 1.707(8) Å [1.709(9) Å]. The structure of the complex 5 is comparable to that of [Fe(C≡CPh)$(CO)_2$(η-C_5H_5)], where two carbonyl groups replace the dppm chelating ligand [19]; in particular the Fe–C and C–C bond lenghts and the Fe–C–C angle, involving the phenylethynyl ligand, are 1.920(6), 1.201(9) Å and 174.4(4)° respectively, and the interleg angles are 86.4(3), 89.3(3) and 94.8(2)°.

As regards the bonding of the phenylethynyl ligand it is noteworthy that the Fe, C(1), C(2) and the C(3)–C(8) atoms are practically coplanar, the C(1)–C(2) bond length (1.206(10) Å [1.201(10) Å]) is practically that expected for a triple bond, and finally the Fe–C(1) bond length, 1.900(7) Å [1.909(7) Å], is close to that of a single bond. These structural features are consistent with the alkynyl ligands in complexes of this type behaving as essentially pure σ-donors as was indicated by theoretical studies [20], which also indicated that, in contrast, strong π bonds are to be expected for the vinylidene ligands. The results of the structure determination of the cationic complex, comparable to 5, [Fe(C=C{(Me)Ph}(dppm)(η-C_5H_5)]$^+$, in which the Fe–C bond length is 1.748(4) Å [14], are in agreement with these theoretical studies.

The dppm molecule in the complex 5, acting as a chelating ligand, forms a strained four-membered ring with a narrow "bite" P(1)–Fe–P(2) angle (74.8(2)° [74.4(2)°]) and a very narrow P(1)–C(14)–P(2) angle (90.6(3)° [90.5(3)°]). Similar values for the "bite" P–Fe–P angle, 74.6(1) and 75.2(1)°, have been found in the cationic complexes [Fe(dppm)(MeCN)(η-C_5H_5)]$^+$ and [Fe(dppm)(CO)(η-C_5H_5)]$^+$, in which, however, the Fe–P bond lengths are slightly longer, 2.198(1), 2.208(1) and 2.214(1), 2.210(1) Å [17], than those in the complex 5.

Experimental

The reactions were carried out under dry nitrogen by Schlenk techniques. All solvents were dried by standard methods and distilled under nitrogen before use. The complexes FeBr$(CO)_2$(η-C_5H_5) [18] and Fe(C≡CPh)$(CO)_2$(η-C_5H_5) [13] were

Table 3

Selected bond distances (Å) and angles (°) for **5** [a]

	Molecule 1	Molecule 2
Fe(1)–P(1)	2.167(2)	2.164(2)
Fe(1)–P(2)	2.162(2)	2.176(2)
Fe(1)–C(1)	1.900(7)	1.909(7)
Fe(1)–C(9)	2.086(8)	2.106(8)
Fe(1)–C(10)	2.070(7)	2.080(8)
Fe(1)–C(11)	2.079(7)	2.063(9)
Fe(1)–C(12)	2.073(8)	2.074(9)
Fe(1)–C(13)	2.083(8)	2.086(9)
Fe(1)–M(1)	1.707(8)	1.709(9)
P(1)–C(14)	1.849(6)	1.846(6)
P(1)–C(15)	1.819(6)	1.821(6)
P(1)–C(21)	1.826(7)	1.820(7)
P(2)–C(14)	1.851(6)	1.847(6)
P(2)–C(27)	1.824(7)	1.823(7)
P(2)–C(33)	1.824(7)	1.822(7)
C(1)–C(2)	1.206(10)	1.201(10)
C(2)–C(3)	1.438(10)	1.430(10)
P(1)–Fe(1)–P(2)	74.8(2)	74.4(2)
P(1)–Fe(1)–C(1)	84.0(3)	86.8(3)
P(1)–Fe(1)–M(1)	133.7(3)	133.5(3)
P(2)–Fe(1)–C(1)	85.2(3)	83.0(2)
P(2)–Fe(1)–M(1)	134.4(3)	136.9(2)
C(1)–Fe(1)–M(1)	125.7(4)	123.6(4)
Fe(1)–P(1)–C(14)	95.4(3)	95.1(3)
Fe(1)–P(1)–C(15)	123.4(3)	124.1(3)
Fe(1)–P(1)–C(21)	122.3(3)	120.6(3)
Fe(1)–P(2)–C(14)	95.5(3)	94.7(3)
Fe(1)–P(2)–C(27)	124.0(3)	123.3(3)
Fe(1)–P(2)–C(33)	121.4(3)	122.7(3)
Fe(1)–C(1)–C(2)	177.4(7)	179.3(6)
C(1)–C(2)–C(3)	175.9(8)	177.4(8)
P(1)–C(14)–P(2)	90.6(3)	90.5(3)

[a] M(1) is the centroid of the cyclopentadienyl ring.

prepared by published procedures. Alkynes $HC\equiv CPh$, $HC\equiv C^tBu$, $HC\equiv CCO_2Me$ and $HC\equiv CSiMe_3$ were used as received from Aldrich Chemical Co.

Photolysis experiments were performed with external irradiation using an UV lamp (400 W, Applied Photophysics). Infrared spectra were recorded on a Perkin–Elmer 1720-X FT spectrometer and electron impact mass spectra were obtained with an Hewlet–Packard 58971 instrument. The C and H analyses were carried out with a Perkin–Elmer 240-B microanalyzer. NMR spectra were recorded on a Bruker AC300 at 300 MHz (^1H), 121.5 MHz (^{31}P) or 75.4 MHz (^{13}C) using $SiMe_4$ or 85% H_3PO_4 as standards.

Preparation of $Fe(C\equiv CCO_2Me)(CO)_2(\eta\text{-}C_5H_5)$ *(7)*

(a) A mixture of $FeBr(CO)_2(\eta\text{-}C_5H_5)$ (1.07 g, 4.17 mmol) and CuI (5 mg) suspended in deoxygenated NEt_3 (70 cm^3) was treated at 0 °C with $HC\equiv CCO_2Me$ (0.445 cm^3, 5 mmol) and stirred for 12 h in the dark. After removal of solvent the solid residue was extracted with diethyl ether (75 cm^3) and the solution filtered through an Alox IV column. The filtrate was reduced in volume and cooled to give the desired product as yellow crystals. Analytically pure samples were obtained from an Alox IV/n-hexane chromatography column by elution with n-hexane and cooling of the concentrated eluate at −20 °C. Yield: 45%. Mass spectrum: 121 $[M - 2CO - C_2CO_2Me]$; 146 $[M - 2CO - CO_2CH_2]$; 204 $[M - 2CO]$; M^+ (parent ion) 260.

(b) Treatment of $FeBr(CO)_2(\eta\text{-}C_5H_5)$ with a mixture in THF of $HC{\equiv}CCO_2Me$ and Li^nBu in stoicheiometric amounts in THF and work-up as described below for the preparation of **6** and **8** also gave **7**. Yield: 5%.

Preparation of $Fe(C{\equiv}CR)(CO)_2(\eta\text{-}C_5H_5)$ *(R =* $SiMe_3$ *(6),* ^tBu *(8))*

To a solution of $FeBr(CO)_2(\eta\text{-}C_5H_5)$ (1 g, 3.9 mmol) in 35 cm^3 of THF were added 4 mmol of $LiC{\equiv}CR$ (prepared *in situ* by treating the corresponding alkyne with Li^nBu 1.6 *M* in 15 cm^3 of THF at −20 °C). After warming to room temperature the solution was evaporated. The resulting solid residue was extracted with diethyl ether (3 × 25 cm^3) and purified by filtration through an Alox IV plug. The filtrate was concentrated and cooled at −20 °C to give yellow crystals of the products. Yields (%): **6** (75); **8** (70). Mass spectra: **6**: 121 $[M - 2CO - C_2SiMe_3]$; 218 $[M^+ - 2CO]$; 246 $[M - CO]$; M^+ (parent ion) 274. **8**: 121 $[M - 2CO - C_2{}^tBu]$; 202 $[M - 2CO]$; 230 $[M - CO]$; M^+ (parent ion) 258. $^{13}C\{^1H\}$ NMR: $\delta(CDCl_3)$ (**8**): 30.05, CMe_3; 32.8s, Me_3; 85.05s, Cp; 125.4s, FeC_α; 88.05s, $\equiv C_\beta$; 213.2s, CO ppm.

Preparation of $Fe(C{\equiv}CR)(dppm)(\eta\text{-}C_5H_5)$ *(R =* $SiMe_3$ *(1),* CO_2Me *(2),* ^tBu *(3),* C_6H_5 *(5))*

General procedure. A mixture of $Fe(C{\equiv}CR)(CO)_2(\eta\text{-}C_5H_5)$ (1 mmol) and dppm (0.384 g, 1 mmol) in 40 cm^3 of THF at −20 °C was irradiated with a UV lamp (400 W, Applied Photophysics). The reaction was monitored by IR spectroscopy in the $\nu(CO)$ region, and the irradiation discontinued when the carbonyl absorptions had completely disappeared. (The reaction times are indicated below.) The resulting solution was evaporated to dryness to give a residue solid which was dissolved in CH_2Cl_2 (5 cm^3). The solution was transferred to an Alox IV n-hexane chromatography column. Elution with n-hexane–dichloromethane (3/1) gave an orange-red band which was collected, reduced in volume and cooled at −20 °C to give the desired product as a crystalline solid. Reaction times, yields (%) and colours: **1**, 4 h, 96, red; **2**, 6 h, 65, orange; **3**, 4 h, 78, red; **5**, 4 h, 81, dark red.

Mass spectra: **1**: 121 $[M - dppm - C_2SiMe_3]$, 440 $[M - C_2SiMe_3 - C_5H_5]$, M^+ (parent ion) 602; **2**: 121 $[M - dppm - C_2CO_2Me]$; 440 $[M - C_2CO_2Me - C_5H_5]$, M^+ (parent ion) 588; **3**: 121 $[M - dppm - C_2{}^tBu]$, 440 $[M - C_2{}^tBu - C_5H_5]$, 505 $[M - C_2{}^tBu]$, M^+ (parent ion) 586, **5**: 121 $[M - dppm - C_2Ph]$, 440 $[M - C_2Ph - C_5H_5]$, 505 $[M - C_2Ph]$, M^+ (parent ion) 606.

$^{13}C\{^1H\}$ NMR ($CDCl_3$) **1**: δ 0.15 (s, Me); 42.9 (t, CH_2P, $J(C\text{-}P)$ 21 Hz); 75.5 (s, C_5H_5); 126–138 (C_6H_5); 103.1 (s, FeC_β); 138 (m, FeC_α). **2**: δ 42.7 (t, CH_2P, $J(C\text{-}P)$ 21 Hz); 50.1 (s, Me); 74.8 (s, C_5H_5); 126–140 (m, C_6H_5); 112.4 (s, $\equiv C_\beta$); 150.9 (t, FeC_α, $J(C\text{-}P)$ 37 Hz). **3**: δ 25.6 (s, CMe_3); 31.9 (s, Me); 44.5 (t, CH_2P, $J(C\text{-}P)$ 20 Hz); 75.8 (s, C_5H_5); 127–140 (m, C_6H_5); 83.9 (s, $\equiv C_\beta$); 138.7 (m, FeC_α). **5**: δ 44.5 (t, CH_2P, $J(C\text{-}P)$ 21 Hz); 76.3 (s, C_5H_5); 122.8 (s, $\equiv C_\beta$); 129.8 (m, FeC_α).

Preparation of $Fe(C{\equiv}CH)(dppm)(\eta\text{-}C_5H_5)$ *(4)*

A solution of $[Fe(C{=}CH_2)(dppm)(\eta\text{-}C_5H_5)]BF_4$ (0.1 g, 0.16 mmol) in 10 cm^3 of THF was treated with KO^tBu (0.075 g; 0.67 mmol) and the mixture stirred at room temperature for 0.5 h. The solution was evaporated to dryness and the resulting solid extracted with diethyl ether (2 × 10 cm^3). **4** was obtained as a red crystalline solid after cooling at $-20\,^\circ C$. Yield: 75%. Mass spectrum: 121 $[M - dppm - C_2H]$; 440 $[M - C_2H - C_5H_5]$; 505 $[M - C_2H]$; M^+ (parent ion) 530. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 44.25 (t, CH_2P, J(C–P) 20 Hz); 76.8 (s, C_5H_5); 127–131 (m, C_6H_5); 83.2 (s, $\equiv C_\beta$); 113.8 (t, FeC_α, J(C–P) 39.5 Hz).

Preparation of $FeBr(CO)(dppm\text{-}P)(\eta\text{-}C_5H_5)$ *(9)*

A mixture of $FeBr(CO)_2(\eta\text{-}C_5H_5)$ (0.23 g, 1 mmol) and dppm (0.384 g, 1 mmol) in 40 cm^3 of THF at $-20\,^\circ C$ was irradiated externaly with a UV lamp for 4 h. The resulting green solution was evaporated to dryness to leave a solid residue, which was extracted with dichloromethane. Addition of hexane followed by concentration and cooling gave green microcrystals of **9**. Yield: 90%.

$FeI(CO)(dppm\text{-}P)(\eta\text{-}C_5H_5)$ was made in the way described for **9**. Yield: 80%. (This compound has been previously prepared by refluxing $FeI(CO)_2(\eta\text{-}C_5H_5)$ with dppm in benzene [19].) $\nu(CO)$ cm^{-1} (CH_2Cl_2) = 1952. ^1H NMR ($CDCl_3$): δ ppm 7.85–7.83 (m, Ph); 4.37 (s, C_5H_5); 3.16 m, 3.58 (m, CH_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 63 d, -25 d (J(P–H) 51 Hz).

Reactions of $Fe(C{\equiv}CR)(dppm)(\eta\text{-}C_5H_5)$ *with CO*

(a) at atmospheric pressure. Carbon monoxide was bubbled through a solution of $Fe(C{\equiv}CC_6H_5)(dppm)(\eta\text{-}C_5H_5)$ (0.1 mmol) in toluene. After 2 h the phosphorus NMR spectrum of a sample of the solution showed resonances which were assigned to the presence of a ca. 1 : 1 mixture of $Fe(C{\equiv}CC_6H_5)(dppm)(\eta\text{-}C_5H_5)$ and $Fe(C{\equiv}CC_6H_5)(CO)(dppm\text{-}P)(\eta\text{-}C_5H_5)$. ($\delta$ ppm: 71.4 d, 44.6 s, -2.5 d (^2J(P–P) = 55 Hz)).

(b) at 30–40 atm. In an autoclave, a solution of $Fe(C{\equiv}CR)(dppm)(\eta\text{-}C_5H_5)$ (0.2 mmol) (R = C_6H_5, ^tBu) in toluene (10 cm^3) was kept under CO (30–40 atm) for 48 h. The resulting solution was partially evaporated and hexane was added. Cooling at $0\,^\circ C$ gave a crystalline solid identified by ^{31}P NMR spectroscopy as $Fe(C{\equiv}CC_6H_5)(CO)(dppm\text{-}P)(\eta\text{-}C_5H_5)$ (δ ppm: 71.4 d, -2.5 d (^2J(P–P) = 55 Hz)) or a mixture, in ca. 1 : 3 molar ratio, of $Fe(C{\equiv}C^tBu)(dppm)(\eta\text{-}C_5H_5)$ and $Fe(C{\equiv}C^tBu)(CO)(dppm\text{-}P)(\eta\text{-}C_5H_5)$($\delta$ ppm: 73.6 d, 45.1 s, -24.7 d (^2J(P–P) = 58 Hz)).

Determination of the crystal structure of $[Fe(C{\equiv}CPh)(dppm)(\eta\text{-}C_5H_5)]$ *(5)*

A crystal of approximate dimensions 0.12 × 0.20 × 0.45 mm was selected for the X-ray analysis.

Crystal data. $C_{38}H_{32}FeP_2$, $M = 606.46$, monoclinic, space group $P2_1/n$, $a = 26.754(8)$, $b = 9.334(7)$, $c = 24.739(8)$ Å, $\beta = 94.53(2)^\circ$, $V = 6159$ Å^3 (by least-squares refinement from the θ values of 30 accurately measured reflections, $\lambda = 0.71073$ Å), $Z = 8$, $D_c = 1.308$ g cm^{-3}, $F(000) = 2528$, $\mu(Mo\text{-}K_\alpha) = 6.15$ cm^{-1}.

Data collection, structure solution and refinement. Siemens AED single-crystal diffractometer ($\theta/2\theta$ scan mode, niobium-filtered Mo-K_α radiation) was employed. All reflections with θ in the range 3–24° were measured; of 9705 independent

Table 4

Fractional atomic coordinates ($\times 10^4$) for **5**

Atom	x	y	z
Fe(11)	1801(1)	1783(1)	211(1)
P(11)	2389(1)	517(2)	633(1)
P(21)	1435(1)	593(2)	817(1)
C(11)	1959(2)	3127(7)	775(3)
C(21)	2070(3)	3938(8)	1145(3)
C(31)	2236(3)	4920(7)	1569(3)
C(41)	2745(3)	5057(9)	1733(3)
C(51)	2905(4)	6063(11)	2120(4)
C(61)	2568(5)	6934(10)	2343(4)
C(71)	2071(4)	6797(11)	2199(4)
C(81)	1895(4)	5793(8)	1812(3)
C(91)	1317(3)	2936(9)	−329(3)
C(101)	1288(3)	1473(9)	−450(3)
C(111)	1760(3)	1009(10)	−580(3)
C(121)	2080(3)	2178(11)	−533(3)
C(131)	1821(4)	3355(9)	−384(3)
C(141)	2020(2)	29(7)	1207(2)
C(151)	2980(2)	1268(7)	918(2)
C(161)	3224(3)	2263(8)	609(3)
C(171)	3703(3)	2782(9)	800(3)
C(181)	3908(3)	2304(9)	1296(3)
C(191)	3669(3)	1380(9)	1604(3)
C(201)	3200(3)	850(8)	1413(3)
C(211)	2622(2)	−1142(7)	352(2)
C(221)	2841(3)	−1029(8)	−139(3)
C(231)	3032(3)	−2247(9)	−375(3)
C(241)	3004(3)	−3558(10)	−120(3)
C(251)	2789(3)	−3685(9)	365(3)
C(261)	2614(2)	−2443(8)	602(3)
C(271)	1047(2)	1410(7)	1306(3)
C(281)	807(3)	2679(10)	1178(4)
C(291)	515(3)	3330(12)	1581(4)
C(301)	494(3)	2694(10)	2063(4)
C(311)	718(3)	1414(10)	2187(4)
C(321)	997(3)	773(9)	1797(3)
C(331)	1074(2)	−1023(7)	641(2)
C(341)	1285(3)	−2361(8)	655(3)
C(351)	1003(3)	−3578(10)	501(3)
C(361)	509(3)	−3426(10)	327(3)
C(371)	292(3)	−2107(9)	299(3)
C(381)	572(3)	−892(9)	463(3)
Fe(12)	1229(1)	7631(1)	6641(1)
P(12)	543(1)	8865(2)	6540(1)
P(22)	1210(1)	8903(2)	7376(1)
C(12)	863(2)	6291(7)	7039(3)
C(22)	636(3)	5454(7)	7295(3)
C(32)	386(2)	4440(7)	7613(3)
C(42)	−56(3)	3768(8)	7411(3)
C(52)	−285(3)	2766(9)	7714(3)
C(62)	−100(3)	2417(9)	8227(3)
C(72)	331(3)	3071(10)	8440(3)
C(82)	571(3)	4081(9)	8134(3)
C(92)	1929(3)	6642(10)	6577(3)

Table 4 (continued)

Atom	x	y	z
C(102)	1937(3)	8069(9)	6391(4)
C(112)	1571(3)	8210(11)	5955(4)
C(122)	1343(3)	6858(13)	5874(3)
C(132)	1560(3)	5932(9)	6252(4)
C(142)	536(2)	9340(7)	7264(2)
C(152)	−67(2)	8113(7)	6317(3)
C(162)	−94(3)	6749(8)	6115(3)
C(172)	−562(3)	6149(10)	5934(3)
C(182)	−983(3)	6936(9)	5970(3)
C(192)	−968(3)	8294(10)	6166(3)
C(202)	−504(3)	8892(8)	6341(3)
C(212)	521(2)	10536(7)	6160(3)
C(222)	488(3)	10432(8)	5596(3)
C(232)	478(3)	11663(9)	5280(3)
C(242)	506(3)	12999(10)	5525(4)
C(252)	549(3)	13099(9)	6079(3)
C(262)	556(3)	11870(8)	6395(3)
C(272)	1303(3)	8144(8)	8056(3)
C(282)	948(3)	8286(9)	8435(3)
C(292)	1058(3)	7684(9)	8959(4)
C(302)	1491(3)	6988(10)	9073(4)
C(312)	1839(4)	6815(10)	8707(4)
C(322)	1740(3)	7387(9)	8181(3)
C(332)	1522(2)	10632(7)	7463(3)
C(342)	1709(3)	11289(8)	7020(3)
C(352)	1925(3)	12663(9)	7079(3)
C(362)	1949(3)	13376(10)	7565(3)
C(372)	1771(3)	12708(9)	8005(3)
C(382)	1562(3)	11342(8)	7965(3)

reflections, 4855, having $I > 2\sigma(I)$, were considered observed and used in the analyses. The individual profiles were analyzed as described by Lehmann and Larsen [23]. No absorption correction was applied.

The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares with anisotropic thermal parameters in the last cycles for all the non hydrogen atoms, excepting for the carbon atoms of the phenyl rings. All the hydrogen atoms were placed at their calculated positions (C–H = 1.00 Å) and refined riding on the corresponding carbon atoms. A weighting scheme $w = K[s^2(F_o) + gF_o^2]^{-1}$ was used in the last cycles of refinement, with $K = 0.660$ and $g = 0.0015$. Final R and R' values were 0.0543 and 0.0606 respectively. The SHELX-76 and SHELXS-86 programs were used [24]. Atomic scattering factors, corrected for anomalous dispersion, were taken from Ref. 25. Final atomic coordinates for the non hydrogen atoms are given in Table 4. All calculations were carried out on the Cray X-MP/12 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna and on the Gould Powernode 6040 of the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Parma. Additional data (H-atom coordinates, thermal parameters) are available from the the authors.

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References

1 (a) For a review see: R. Nast, Coord. Chem. Rev., 47 (1982) 89; (b) For a recent contribution on $Cp^{\star}$Fe derivatives see: M. Akita, M. Terada, S. Oyama and Y. Moro-oka, Organometallics, 9 (1990) 816.

2 A.J. Carty, Pure Appl. Chem., 54 (1982) 113.

3 P.R. Raithby and M.J. Rosales, Adv. Inorg. Chem. Radiochem., 29 (1985) 169; E. Sappa, A. Tiripicchio and P. Braunstein, Coord. Chem. Rev., 65 (1985) 219.

4 (a) M.P. Gamasa, J. Gimeno, E. Lastra and X. Solans, J. Organomet. Chem., 346 (1988) 277 and references therein; (b) M.P. Gamasa, J. Gimeno, E. Lastra, A. Aguirre and S. García-Granda, J. Organomet. Chem., 378 (1989) C11; (c) M.P. Gamasa, J. Gimeno and J. Diez, Organometallics, in press.

5 P.S. Braterman (Ed.), Reactions of Coordinated Ligands, Vol. 1, Plenum Press, 1986.

6 For reactivity on polynuclear acetylide complexes see: A.A. Cherkas, L.H. Randall, S.A. MacLaughlin, G.N. Mott, N.J. Taylor and A.J. Carty, Organometallics, 7 (1988) 969; idem, ibid., 7 (1988) 1115 and references therein; J. Holton, M.F. Lappert, R. Pearce and P.I.W. Yarrow, Chem. Rev., 83 (1983) 135.

7 R.J. Puddephatt, Chem. Soc. Rev., (1983) 99; B. Chaudret, B. Delavaux and R. Poilblanc, Coord. Chem. Rev., 86 (1988) 191.

8 P.E. Garrou, Chem. Rev., (1981) 229.

9 F.S.M. Hassan, D.P. Markham, P.G.Pringle and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1985) 279.

10 B. Chaudret, F. Dahan and S. Sato, Organometallics, 4 (1985) 1490; C.R. Langrick, P.G. Pringle and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1984) 1233.

11 G.B. Jacobsen, B.L. Shaw and M. Thorton-Pett, J. Chem. Soc., Chem. Commun., (1986) 13.

12 B. Delavaux, B. Chaudret, J. Dellivers, F. Dahan, G. Commenges and R. Poilblanc, J. Am. Chem. Soc., 108 (1986) 3703; B. Delavaux, T. Arliguie, B. Chaudret and R. Poilblanc, Nouv. J. Chim., 10 (1986) 619; B. Chaudret, F. Dahan and S. Sabo, Organometallics, 4 (1985) 1490.

13 M.I. Bruce, M.G. Humphrey, J.G. Matisons, S.K. Roty and A.G. Swincer, Aust. J. Chem., 37 (1984) 1955.

14 M.P. Gamasa, J. Gimeno, E. Lastra, A. Anillo and A. Tiripicchio, in preparation.

15 E.E. Isaacs and W.A.G. Graham, J. Organomet. Chem., 120 (1976) 407.

16 A. Davison and J.P. Selegue, J. Am. Chem. Soc., 100 (1978) 7763.

17 J. Ruiz, M.T. Garland, E. Román and D. Astruc, J. Organomet. Chem., 377 (1989) 309.

18 (a) S.G. Davies and J.I. Seeman, Tetrahedron Lett., (1984) 1845; (b) J.I. Seeman and S.G. Davies, J. Am. Chem. Soc., 107 (1985) 6522.

19 R. Goddard, J. Howard and P. Woodward, J. Chem. Soc., Dalton Trans., (1974) 2025.

20 N.M. Kostic and R.F. Fenske, Organometallics, 1 (1982) 974.

21 T.S. Piper, F.A. Cotton and G. Wilkinson, J. Inorg. Nucl. Chem., 1 (1955) 165.

22 R.J. Haines and A.L. du Preez, Inorg. Chem., 11 (1972) 330.

23 M.S. Lehmann and F.K. Larsen, Acta Crystallogr., Sect. A, 30 (1974) 580.

24 G.M. Sheldrick, SHELX-76 Program for crystal structure determination, University of Cambridge, 1976; SHELXS-86 Program for the solution of crystal structures, University of Göttingen, 1986.

25 International Tables for X-Ray Crystallography, Vol. 4, Kynoch Press, Birmingham, 1974.