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Different coordination modes of a 1,1′,2,2′-ferrocenyltetraphosphine: bi- and tri-dentate behaviour with group 6 and 7 transition metals

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The behaviour of 1,1′,2,2′-tetrakis(diphenylphosphino)-4,4′-di(*tert*-butyl)ferrocene (**1**), acting as a homoannular or heteroannular ligand, has been studied. Due to the *cisoid* disposition of the phosphino groups of each ring, different coordination modes are observed. With group 6 metal carbonyls, $M(CO)_6$, the tetraphosphine acts exclusively as a tridentate ligand. In contrast, the reaction with $MnCp(CO)_3$ leads to complexes showing 1,1′ and 1,2 bidentate coordination modes. All these complexes have been characterised by ^1H and ^{31}P NMR spectroscopy. The molecular structures of the molybdenum complex [(**1**)$Mo(CO)_3$] (**2b**) and the 1,1′ manganese complex [(**1**)MnCp(CO)] (**3**) have been established by X-ray diffraction.

Introduction

Ferrocenyl polyphosphines have been extensively used in transition metal coordination chemistry and their ability to be powerful auxiliaries has been demonstrated.[1] Their steric and electronic properties have been examined by studing different substitutions on the cyclopentadienyl rings, the most classical being the 1,1′ disubstitution. Over the past five years, access to ferrocenes with potential 1,2, 1,3, 1,1′,2, 1,1′,2,3 and 1,1′,2,2′ coordination properties have been reported.[2] The substitutions on the cyclopentadienyl rings of dppf derivatives (where dppf is the diphenylphosphinoferrocene), inducing different ring twists and tilts, lead to particular constraint geometries for the entire ligand. From the resulting conformations of the polyphosphine, various modes of coordination have been observed, which depend mainly on the availability of the phosphorus donors.

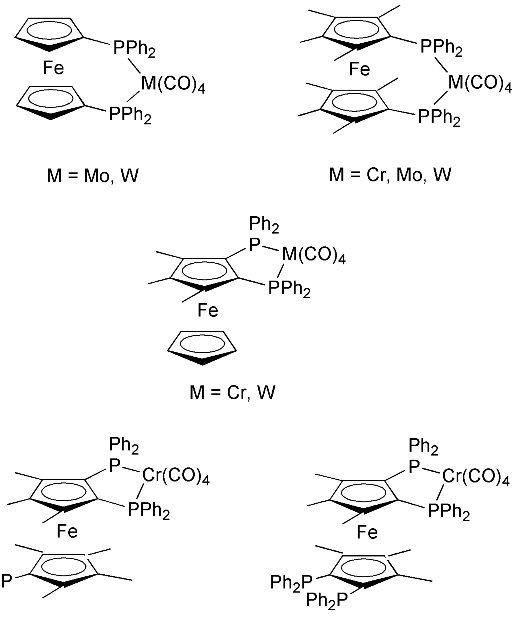
Recently, we have described the synthesis of a new tetraphosphine, 1,1′,2,2′-tetrakis(diphenylphosphino)-4,4′-di(*tert*-butyl)ferrocene (**1**), which displays a hindered rotation of the cyclopentadienyl rings about the Fe–Cp vectors, and presents, in the solid state, a *cisoid* disposition of its phosphino groups.[2d] This ligand can be viewed as a combination of various chelating units: (a) 1,1′ or (b) 1,2 diphosphine, (c) 1,1′,2 triphosphine and (d) 1,1′,2,2′ bisdiphosphine. We have reported the reaction of **1** with palladium(II), rhodium(I) and iridium(I) salts, and a series of complexes in which all the coordination modes (a)–(d) are exhibited have been obtained.[2d] It was of interest to extend the available examples of complexes containing **1** to other metal species usually exhibiting a tetrahedral or octahedral environment instead of a planar geometry.

We herein describe the preparation and the characterisation of complexes obtained by thermal or photochemical substitution reactions of $MnCp(CO)_3$ and $M(CO)_6$ (where M = Cr, Mo, W) with ligand **1**.

Results and discussion

Syntheses and structures

Several studies regarding the behaviour of group 6 metal carbonyls with various ferrocenic polyphosphines: 1,1′ or 1,2 diphosphines,[2a,3,4] 1,1′,2 triphosphine and 1,1′,2,2′ tetraphosphine have been previously reported (see Scheme 1).[2a] The complexes shown in Scheme 1 have a common chelation number. Each ferrocenyl ligand is bidentate and leads to a single compound; thus, both the 1,1′ and the 1,2 diphosphine ligand allow the selective preparation of bimetallic complexes. It is worth noting the exclusive 1,2 coordination obtained with the tri- or tetra-dentate ligands, which are actually potentially 1,2 or 1,1′ chelating. The most likely cause is that these 1,1′,2 and 1,1′,2,2′ polyphosphines adopt a *transoid* disposition for the phosphino groups of each ring.



Scheme 1

As a consequence of the potential versatility of the tetraphosphine **1**, bimetallic species of the previous bidentate types might be expected, as well as new tridentate ones. Thus, the chemical behaviour of **1** with $M(CO)_6$ (M = Cr, Mo, W) has been investigated. **1** best reacts with $Cr(CO)_6$ or $Mo(CO)_6$ at

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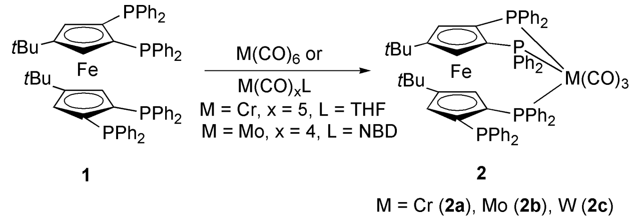
Table 1 Optimized J_{12}, $J_{11'}$ and $J_{1'2}$ coupling constants (Hz)

	2a	**2b**	**2c**
J_{12}	30	18	16
$J_{11'}$	28	8.5	3
$J_{1'2}$	35	21	14

Table 2 Bond lengths (Å) and angles (°) for **2b**

Fe–CNT(1)	1.676	Mo–C(69)	1.961(4)
Fe–CNT(2)	1.675	Mo–P(1)	2.535(1)
Mo–C(67)	1.963(5)	Mo–P(2)	2.530(1)
Mo–C(68)	1.971(4)	Mo–P(3)	2.583(1)
CNT(1)–Fe–CNT(2)	176.8	C(68)–Mo–P(2)	170.5(2)
C(69)–Mo–C(67)	81.9(2)	C(69)–Mo–P(2)	93.5(2)
C(69)–Mo–C(68)	92.6(2)	C(67)–Mo–P(3)	169.6(2)
C(67)–Mo–C(68)	84.2(2)	C(68)–Mo–P(3)	88.3(2)
C(67)–Mo–P(1)	100.3(2)	C(69)–Mo–P(3)	91.3(2)
C(68)–Mo–P(1)	98.4(2)	P(1)–Mo–P(2)	75.68(3)
C(69)–Mo–P(1)	168.9(2)	P(1)–Mo–P(3)	87.85(3)
C(67)–Mo–P(2)	89.5(2)	P(2)–Mo–P(3)	98.84(4)

elevated temperatures in toluene, and with $W(CO)_6$ under photochemical conditions. Only one major compound is obtained in each case. The bimetallic, air-stable species **2a**–**c**, in which the metal carbonyl centres coordinate three phosphorus atoms, were synthesised (see Scheme 2). The ferrocenic tetraphosphine displays tridentate facial coordination to a single metal centre, structurally similar to a tripodal phosphine.[5–9] The tricoordination of polyphosphines is the highest coordination mode which has been encountered with group 6 metal carbonyls, even in the case of penta or hexaphosphine ligands.[10,11] In order to obtain other modes of coordination, $Mo(CO)_4$-(NBD) and $Cr(CO)_5(THF)$ were allowed to react with **1**. No evidence for the formation of bimetallic complexes containing mono- or bi-dentate polyphosphine ligands could be found. The complexes **2** were obtained from both precursors, even under non-stoichiometric conditions.



Scheme 2

For all the complexes **2**, the ^1H NMR spectra are clearly consistent with an unsymmetrical structure. The *tert*-butyl groups appear as two distinct singlets and the four protons on the cyclopentadienyl rings as four singlets. The ^{31}P NMR spectra may be the result of an ABMX system. We observed a singlet at −27.3 ppm, which can be assigned to the free phosphorus donor atom of the tetraphosphine ligand. More complex resonances are detected for the coordinated phosphorus atoms due to the couplings between the phosphorus nuclei in the 1, 1′ and 2 positions. Experimental and simulated spectra are presented in Fig. 1–3. Due to the different coupling constants between the 1, 1′ and 2 atoms, small differences in the spectra of **2a**–**c** were found. In order to optimize these different *J* values, iterative calculations were performed and the results are reported in Table 1.[12]

The ν(CO) regions in the infrared spectra of **2a**–**c** are similar, with two major absorptions: **2a** (1834, 1925 cm^{-1}), **2b** (1844, 1938 cm^{-1}), **2c** (1838, 1933 cm^{-1}).

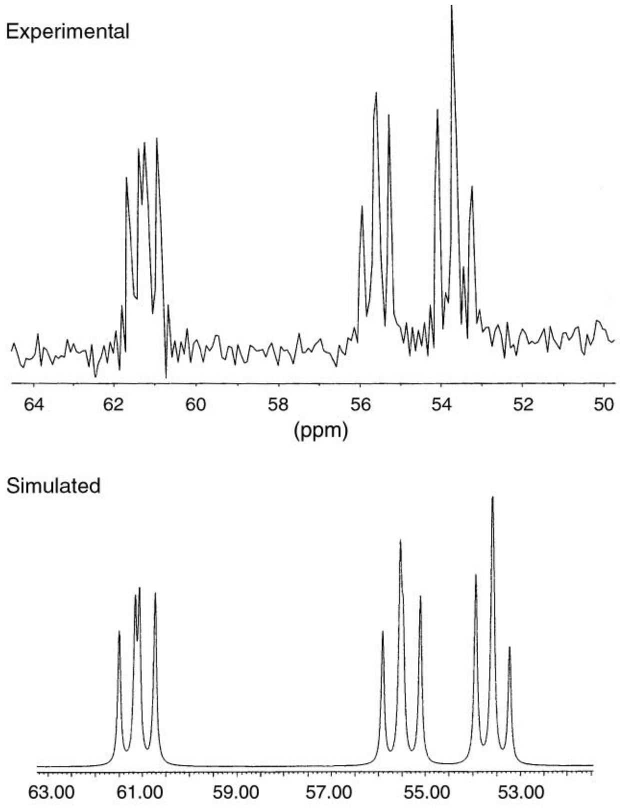


Fig. 1 ^{31}P NMR signals of coordinated phosphorus atoms of **2a** (experimental and simulated spectra).

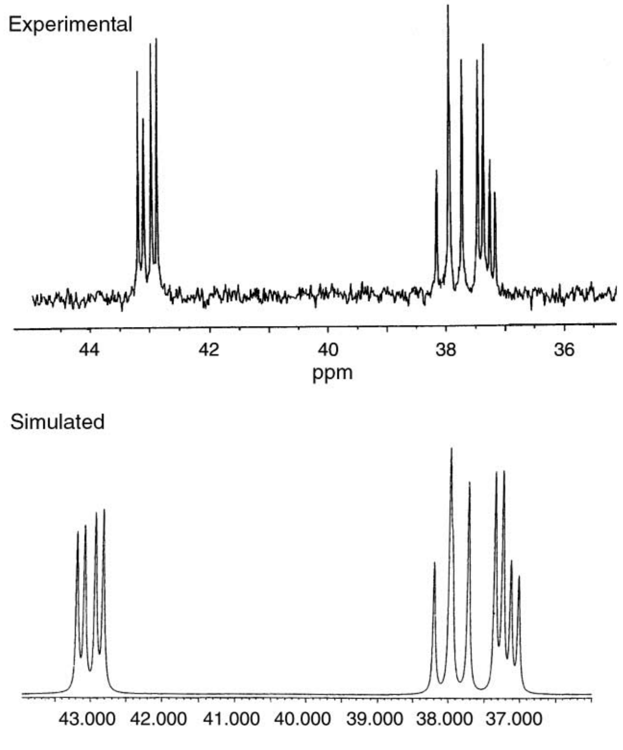


Fig. 2 ^{31}P NMR signals of coordinated phosphorus atoms of **2b** (experimental and simulated spectra).

The solid-state structure of **2b** (shown in Fig. 4) confirms the NMR observations. Relevant bond distances and angles are listed in Table 2. The bond lengths and angles values for the ferrocenyl part of the complexes **2** are close to those reported for the free tetraphosphine **1**.[2d] In contrast, the distortion from octahedral coordination around the Mo centre is evident: the P–Mo–P angles are far from the ideal value of 90°. The P(1)–Mo–P(2) angle of 75.68(3)° is a result of the constraint induced by the 1,2 substitution on the cyclopentadienyl rings. The steric hindrance due to the *tert*-butyl groups does not allow a sym-

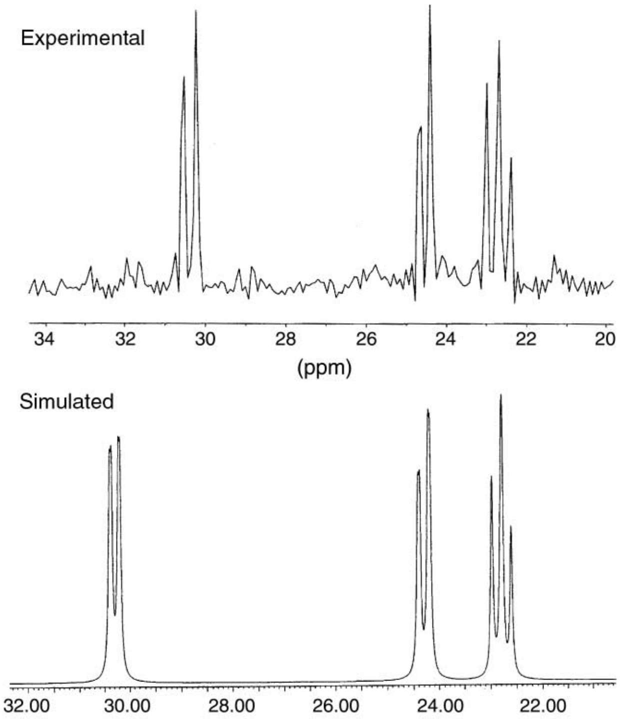


Fig. 3 ^{31}P NMR signals of coordinated phosphorus atoms of **2c** (experimental and simulated spectra).

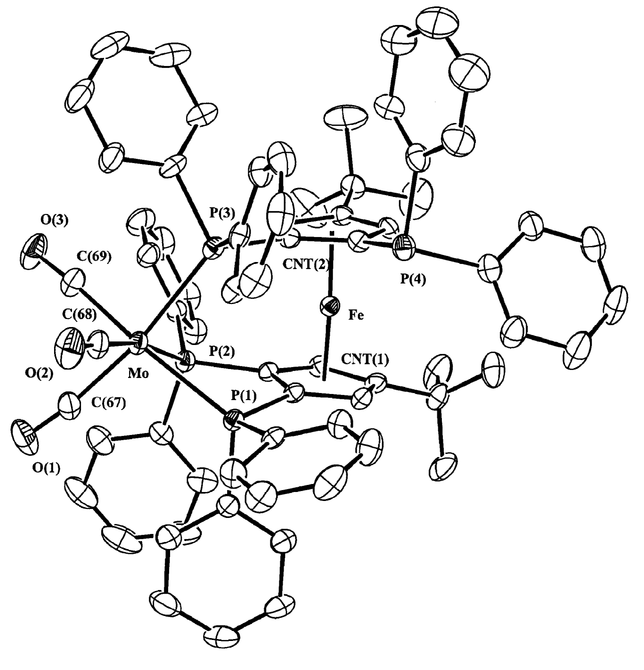


Fig. 4 ORTEP view of **2b**.[15] Thermal ellipsoids are drawn at the 30% probability level. The hydrogen atoms and the toluene solvate molecule are omitted for clarity.

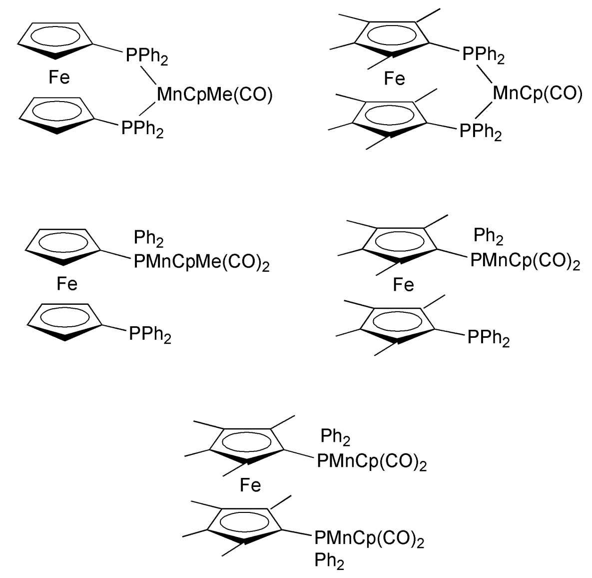
metric position for P(3) with regard to P(1) and P(2). As a consequence, two different P–Mo–P(3) angles are observed [P(1)–Mo–P(3) 87.85(3); P(2)–Mo–P(3), 98.84(4)°]. The Mo–P(3) distance of 2.583(1) Å is slightly longer than the Mo–P(1) and Mo–P(2) distances [2.535 (1) and 2.530 (1) Å, respectively].

The coordination chemistry of dppf,[13] and octamethyldppf,[4] with manganese carbonyl species, and especially cyclopentadienyl or methylcyclopentadienylcarbonyl manganese, has been well established.[14] Several complexes displaying monodentate and bridging or chelating bidentate coordination have been prepared (see Scheme 3 for examples). Upon complexation with MnCp(CO)$_3$, our related tetraphosphine **1** appears to be both a heteroannular bidentate ligand (like a 1,1′ ferrocenyldiphosphine) and a homoannular bidentate ligand (like a 1,2 ferrocenyldiphosphine). Indeed, two components, **3** and **4**, were isolated from the photolysis of **1** with MnCp(CO)$_3$ (see Scheme 4). Interestingly, a final 1 : 1 ratio of **3** and **4** was observed, whatever the different reaction conditions (reaction time) employed. This observation could suggest that after the coordination of the first phosphorus atom to the manganese nucleus,[13] no decisive preference for 1,1′ or 1,2 bidentate coordination occurs. The complexes **3** and **4** are easily separated from the mixture using their solubility properties: **3** is soluble in hexane, while, in contrast, **4** is only sparingly soluble. Recrystallisation of **3** from toluene–pentane yields crystals suitable for single crystal X-ray diffraction analysis. A view of the molecular structure of **3** is shown in Fig. 5 and selected bond distances and angles are given in Table 3. Unfortunately, the low solubility of **4** prevented satisfactory growth of single crystals.

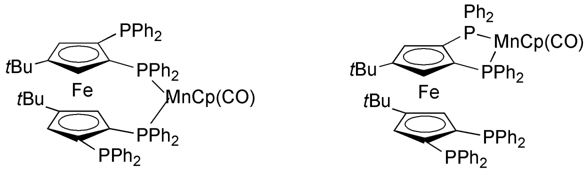
A closely related complex, Mn(CO)(MeCp)dppf, obtained from the reaction of dppf with methylcymantrene, has been described by Onaka *et al.*[13] The comparison of crystallographic structural data between the complex **3** and Mn(CO)(MeCp)-dppf attests to the similar features of the compounds. In the ferrocenyl part, the two cyclopentadienyl rings are approximately eclipsed, with a deviation from an ideal eclipsed conformation of

Table 3 Bond lengths (Å) and angles (°) for **3**

Fe–CNT(1)	1.671	Mn–C(77)	1.769(9)
Fe–CNT(2)	1.668	Mn–P(2)	2.244(3)
Mn–CNT(3)	1.782	Mn–P(3)	2.241(3)
CNT(1)–Fe–CNT(2)	178.1	C(77)–Mn–P(2)	97.8(3)
CNT(3)–Mn–P(2)	118.8	C(77)–Mn–P(3)	88.2(3)
CNT(3)–Mn–P(3)	124.4	P(2)–Mn–P(3)	98.86(9)
CNT(3)–Mn–C(77)	121.8		



Scheme 3



3 **4**

Scheme 4

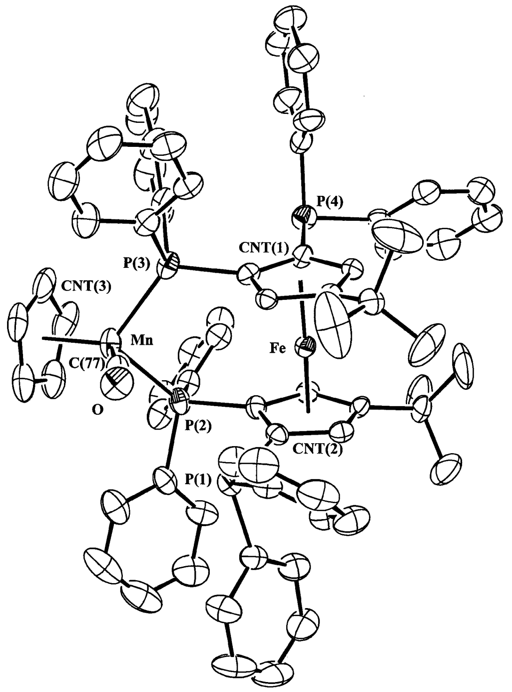


Fig. 5 ORTEP view of **3**.[15] Thermal ellipsoids are drawn at the 30% probability level. The hydrogen atoms and the pentane solvate molecule are omitted for clarity.

3.5(3)° for **3**, and 3.1(9)° for Mn(CO)(MeCp)dppf. These same cyclopentadienyl rings deviate slightly from being parallel, the tilt angles being 4.5(5)° for **3** and 4.3(6)° for Mn(CO)(MeCp)-dppf. Concerning complex **3**, all the phosphorus atoms are displaced from the mean plane of the cyclopentadienyl rings (*exo* type: P(1), 0.52; P(2), 0.07; P(3), 0.20; P(4), 0.17 Å), the greater deviation is due to the steric hindrance existing between the CO group and the P(1) phosphino group. In contrast, for Mn(CO)(MeCp)dppf, one of the phosphorus atoms is displaced toward the iron atom (*endo* type), while the other is displaced outside the iron atom (*exo* type).

The other spectroscopic observations support the formulation of **3** as a [3]-ferrocenophane. At room temperature, the well-resolved ^{1}H NMR spectrum displays two singlets for the *tert*-butyl protons, two singlets for the ferrocenyl protons, and one singlet for the CpMn protons. The ^{31}P NMR spectrum shows two broad peaks at 98.0 and *ca.* −21 ppm. However, at 0 °C, the ^{31}P NMR spectrum exhibits the expected pattern of two sharp singlets (−24.2 and −18.1 ppm) and a doublet at 98.8 ppm for the free and coordinated phosphorus donor atoms, respectively. This observation probably indicates an exchange of conformers in solution. Because of the hindered rotation of the ferrocenyl ligand, the likely explanation is that the spectrum at room temperature depicts a reversal bridging process around the Mn atom.

Concerning **4**, the elemental analysis and the mass spectrum are very similar to those of complex **3**, unquestionably pointing to the bidentate ligation of the tetraphosphine to the manganese centre. Moreover, other data support the structure depicted in Scheme 4. Indeed, the IR spectrum of **4** shows a CO stretching frequency at 1851 cm^{-1}, characteristic of a terminal CO, and the ^{1}H NMR spectrum exhibits two signals for the *tert*-butyl groups and three for the ferrocenyl protons, integrating for 2, 1 and 1 protons, respectively. These patterns are consistent with the proposed unsymmetrical structure (see Scheme 4). It is noteworthy that the ^{31}P NMR data (see Experimental) indicate the existence of two diastereoisomeric species, as suggested by the non-rotatability of the *tert*-butyl-substituted cyclopentadienyl rings. Similar results have also been described concerning the analogous complex with palladium.[2d]

Conclusion

Different coordination modes of the ferrocenyltetraphosphine **1** with group 6 and 7 transition metals have been evidenced. The present study shows different behaviours of this novel polyphosphine ligand in relation to the nature of the metal. With tricarbonyl (η^5-cyclopentadienyl)manganese, the tetraphosphine acts as a bidendate ligand (1,1′ or 1,2 chelating mode). With chromium, molybdenum or tungsten hexacarbonyl, the 1,1′,2 ligation of the phosphine was observed. To our knowledge, this represents unprecedented behaviour in ferrocenic polyphosphine chemistry. We are currently investigating the possibility of using this coordination property in the synthesis of new polynuclear heterometallic species and in catalytic processes.

Experimental

General considerations

Reactions were carried out under an atmosphere of argon by means of conventional Schlenk techniques and a vacuum line. Solvents were dried and deoxygenated before distillation from sodium benzophenone ketyl or Na–K alloy. Elemental analyses were performed by the analytical service of the L.S.E.O. of the Université de Bourgogne (Eager 200). Mass spectra were recorded on a Kratos Concept IS instrument. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker AC200 spectrometer. The synthesis of the starting compound **1** has been recently reported.[2d]

Syntheses of the complexes

2a. A mixture of 60 mg (0.058 mmol) of **1** and 13 mg (0.059 mmol) of $Cr(CO)_6$ in 20 ml of toluene was refluxed for 15 h. The red solution was concentrated and the resulting oil was chromatographed on a silica gel column with toluene. Two fractions were obtained and evaporated to dryness: the first one being unreacted $Cr(CO)_6$, and the second an orange solid identified as **2a**. Recrystallisation from hot toluene yielded orange crystals of **2a** (51 mg, 0.043 mmol, 75%); m.p. >260 °C. Found: C, 72.60; H, 5.72; $C_{69}H_{62}Fe\ O_3P_4Cr{\cdot}C_7H_8$ requires: C, 72.31; H, 5.60%. ^{1}H NMR ($CDCl_3$): δ 0.80 (s, 9H, *t*Bu), 0.85 (s, 9H, *t*Bu), 3.84 (s, 1H, CH), 4.53 (s, 1H, CH), 4.82 (s, 1H, CH), 4.99 (s, 1H, CH), 7.00–8.30 (m, 40H, Ph). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −27.3 (s), 53.6, 55.5, 61.2 (three m, $J_{12} = 30$, $J_{11'} = 28$, $J_{1'2} = 35$ Hz). MS (EI), *m*/*z* (%): 1170 (5) [M]$^+$, 1086 (100) [M − 3CO]$^+$, 1034 (15) [M − 3CO − Cr]$^+$. IR (CH_2Cl_2, cm^{-1}): ν_{CO} 1925 and 1834.

2b. A mixture of 80 mg (0.08 mmol) of **1** and 12 mg (0.09 mmol) of $Mo(CO)_6$ in 25 ml of toluene was refluxed for 6 h. The red solution was concentrated and the resulting oil was chromatographed on a silica gel column with toluene. Two fractions were obtained and evaporated to dryness: the first one being unreacted $Mo(CO)_6$, and the second an orange solid identified as **2b**. Recrystallisation by slow diffusion of hexane into a toluene solution of **2b** afforded bright orange crystals (84 mg, 0.069 mmol, 86%); m.p. >260 °C. Found: C, 69.16; H, 5.30; $C_{69}H_{62}Fe\ O_3P_4Mo,\ C_7H_8$ requires: C, 69.82; H, 5.40%. ^{1}H NMR (C_6D_6): δ 0.80 (s, 9H, *t*Bu), 0.86 (s, 9H, *t*Bu), 4.03 (s, 1H, CH), 4.40 (s, 1H, CH), 4.65 (s, 1H, CH), 5.00 (s, 1H, CH), 6.30–8.40 (m, 40H, Ph). ^{31}P{^{1}H} NMR (C_6D_6): δ −27.3 (s), 37.3, 37.9, 43.0 (three m, $J_{12} = 18$, $J_{11'} = 8.5$, $J_{1'2} = 21$ Hz). MS (EI), *m*/*z* (%): 1216 (15) [M]$^+$, 1188 (20) [M − CO]$^+$, 1160 (50) [M − 2CO]$^+$, 1132 (100) [M − 3CO]$^+$, 947 (10) [M − 3CO − PPh_2]$^+$. IR (CH_2Cl_2, cm^{-1}): ν_{CO} 1938 and 1844.

2c. A mixture of 70 mg (0.068 mmol) of **1** and 25 mg (0.071 mmol) of $W(CO)_6$ in 15 ml of toluene was stirred at room temperature under irradiation for 15 h (UV mercury

Table 4 Crystal data and structure refinement for **2b** and **3**

Compound	**2b**	**3**
Formula	$C_{69}H_{58}P_4O_3FeMo{\cdot}C_7H_8$	$C_{72}H_{67}P_4OFeMn{\cdot}C_5H_{12}$
Formula weight	1306.99	1255.07
Temperature/K	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	15.045(3)	11.390(3)
b/Å	17.246(3)	24.300(8)
c/Å	25.762(4)	24.760(13)
β/°	97.899(14)	102.91(3)
V/Å^3	6621(2)	6680(4)
Z	4	4
F(000)	2712	2640
D_{calc}/g cm^{-3}	1.311	1.248
Scan type	ω	ω
λ/Å	0.71073	0.71073
μ/mm^{-1}	0.553	0.546
Index ranges	$-18 \le h \le 18$	$-12 \le h \le 0$
	$-21 \le k \le 0$	$-26 \le k \le 0$
	$0 \le l \le 32$	$-26 \le l \le -26$
RC (reflections collected)	13744	9146
IRC (independent RC) [R_{int}]	13430 [0.0419]	8664 [0.0645]
IRCGT {IRC with [$I > 2\sigma(I)$]}	7422	4126
Data/parameters	13430/720	8664/732
R_1[a], wR_2[b] for IRCGT	0.0456, 0.1067	0.0650, 0.1549
R_1[a], wR_2[b] for IRC	0.1645, 0.1315	0.2058, 0.1979
Goodness-of-fit[c]	1.011	1.005
Largest diff. peak and hole/e Å^{-3}	0.633 and −0.681	0.732 and −0.319

[a] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)]^2/\Sigma[w(F_o^2)]^2\}^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.0614P)^2]$ for **2b** and $w = 1/[\sigma^2(F_o^2) + (0.0929P)^2]$ for **3**; $P = [\mathrm{Max}(F_o^2, 0) + 2{*}Fc^2]/3$. [c] Goodness-of-fit $= \{\Sigma[w(F_o^2 - F_c^2)]^2/(N_o - N_v)\}^{1/2}$.

lamp, $\lambda > 300$ nm). The solution was concentrated and the resulting oil was chromatographed on a silica gel column with toluene. Two fractions were obtained and evaporated to dryness: the first being unreacted $W(CO)_6$, and the second an orange solid identified as **2c** (68 mg, 0.052 mmol, 76%); m.p. >260 °C. Found: C, 66.01; H, 5.09; $C_{69}H_{62}Fe\ O_3P_4W$, C_7H_8 requires: C, 65.43; H, 5.06%. ^1H NMR (C_6D_6): δ 0.81 (s, 9H, *t*Bu), 0.87 (s, 9H, *t*Bu), 4.02 (s, 1H, CH), 4.64 (s, 1H, CH), 5.06 (s, 1H, CH), 5.10 (s, 1H, CH), 6.36–8.50 (m, 40H, Ph). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −27.3 (s), 22.7, 24.5, 30.3 (three m, $J_{12} = 16$, $J_{11'} = 3$, $J_{1'2} = 14$, $J_{P-W} = 221$ Hz). MS (EI), *m*/*z* (%): 1302 (100) $[M]^+$, 1274 (35) $[M - CO]^+$, 1246 (25) $[M - 2CO]^+$, 1218 (60) $[M - 3CO]^+$, 1034 (15) $[M - 3CO - W]^+$. IR (CH_2Cl_2, cm^{-1}): ν_{CO} 1933 and 1838.

3 and 4. A mixture of 156 mg (0.15 mmol) of **1** and 31 mg (0.15 mmol) of $MnCp(CO)_3$ in 20 ml of toluene was stirred at room temperature under irradiation for 15 h (UV mercury lamp, $\lambda > 300$ nm). The toluene was evaporated and replaced by 10 ml of hexane. The mixture was filtered in order to separate the precipitate and the solution. (a) The solution was evaporated to dryness and the product, identified as **3**, was recrystallised in a mixture of toluene–pentane to give well-formed red crystals (49 mg, 0.041 mmol, 27%). Found: C, 74.15; H, 6.83; $C_{72}H_{67}FeOP_4Mn$, $2(C_5H_{12})$ requires: C, 74.19; H, 6.92%. ^1H NMR (C_6D_6): δ 0.68 (s, 9H, *t*Bu), 0.98 (s, 9H, *t*Bu), 4.33 (s, 2H, CH), 4.52 (s, 2H, CH), 4.71 (s, 5H, CpMn), 6.70–8.40 (m, 40H, Ph). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −21.5 (m), 98.0 (m). MS (EI), *m*/*z* (%): 1182 (5) $[M]^+$, 1154 (30) $[M - CO]^+$, 1090 (5) $[M - CO - Cp]^+$, 1034 (100) $[M - CO - Cp - Mn]^+$. IR (diethyl ether, cm^{-1}): ν_{CO} 1873.(b) The solid identified as **4** was recrystallised in toluene–hexane, yielding a red–orange powder (37 mg, 0.031 mmol, 21%). Found: C, 72.99; H, 5.69; $C_{72}H_{67}FeOP_4Mn$ requires: C, 73.15; H, 5.72%. ^1H NMR (C_6D_6): δ 0.69 (s, 9H, *t*Bu), 0.75 (s, 9H, *t*Bu), 3.95 (s, 5H, CpMn), 4.31 (s, 2H, CH), 5.15 (s, 1H, CH), 5.39 (s, 1H, CH), 6.50–8.10 (m, 40H, Ph). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −30.9 (s), −30.7 (s), −26.8 (s, one singlet resonance obscured), 89.2 (d, $J_{PP} = 33$ Hz), 89.4 (d, $J_{PP} = 36$ Hz), 92.9 (d, $J_{PP} = 36$ Hz, one doublet resonance obscured). MS (EI), *m*/*z* (%): 1182 (5) $[M]^+$, 1154 (60) $[M - CO]^+$, 1090 (5) $[M - CO - Cp]^+$, 1034 (100) $[M - CO - Cp - Mn]^+$. IR (diethyl ether, cm^{-1}): ν_{CO} 1851.

X-Ray diffraction analyses of complexes 2b and 3

2b. Single crystals for the X-ray structure analysis were obtained by recrystallisation in a toluene–hexane mixture. An orange crystal of dimensions 0.32 × 0.28 × 0.25 mm^3 was mounted on an Enraf-Nonius CAD4 diffractometer. A total of 13744 reflections (13430 unique) were collected at room temperature up to $\sin(\theta)/\lambda = 0.623$ Å^{-1}. The data were corrected for Lorentz and polarisation effects,[16] and for absorption (psi-scan method).[17] A 3% decay was linearly corrected. The structure was solved *via* a Patterson search program and refined in the monoclinic $P2_1/c$ space group with full-matrix least squares methods[18] based on $|F^2|$. All non-hydrogen atoms, except for the carbon atoms of the toluene solvate molecule, were refined with anisotropic thermal parameters. Hydrogen atoms were included in their calculated positions and refined with a riding model. Crystal data and refinement parameters are reported in Table 4.

3. Single crystals for the structure analysis were obtained by recrystallisation in a toluene–pentane mixture. An orange crystal of 0.35 × 0.30 × 0.22 mm^3 was mounted on an Enraf-Nonius CAD4 diffractometer. A total of 9146 reflections (8664 unique) were collected at room temperature up to $\sin(\theta)/\lambda = 0.545$ Å^{-1}. The data were corrected for Lorentz and polarisation effects,[16] and for absorption (psi-scan method).[17] The structure was solved *via* a Patterson search program and refined in the monoclinic $P2_1/c$ space group with full-matrix least squares methods[18] based on $|F^2|$. All non-hydrogen atoms, except for the carbon atoms of the pentane solvate molecule, were refined with anisotropic thermal parameters. Except for the poorly defined pentane molecule, hydrogen atoms were included in their calculated positions, and refined with a riding model. Crystal data and refinement parameters are reported in Table 4.

CCDC reference numbers 163669 and 163670.

See http://www.rsc.org/suppdata/dt/b1/b108833p/ for crystallographic data in CIF or other electronic format.

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