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Hydrophosphination reactions with transition metal ferrocenylphosphine complexes†

Julian Rodger Frederic Pritzwald-Stegmann, Peter Lönnecke and Evamarie Hey-Hawkins*

The group 6 metal mono-, bis- and tris-ferrocenylphosphine complexes $[M(CO)_5(PH_2Fc)]$ (**1a**, M = Cr; **1b**, M = Mo; **1c**, M = W), cis- $[M(CO)_4(PH_2Fc)_2]$ (**2a**, M = Cr; **2b**, M = Mo; **2c**, M = W) and fac- $[M(CO)_3(PH_2Fc)_3]$ (**3a**, M = Cr; **3b**, M = Mo; **3c**, M = W) [Fc = Fe(η^5 -C₅H₄)(η^5 -C₅H₅)] were prepared and fully characterised. IR and NMR spectroscopy and single-crystal X-ray diffraction analysis indicate that FcPH₂ is as good a σ donor as PhPH₂ but is easier to handle and furthermore has a redox-active ferrocenyl group. Complex **1c** was employed in the hydrophosphination of acrylonitrile and methyl acrylate in the presence of catalytic amounts of KOtBu giving the secondary phosphine complexes $[W(CO)_5\{PH(Fc)(CH_2CH_2CN)\}]$ (**4a**) and $[W(CO)_5\{PH(Fc)(CH_2CH_2C(O)OMe)\}]$ (**4b**). In addition, FcP(CH₂CH₂CN)₂ (**5**) was prepared by a similar method from FcPH₂ and acrylonitrile. These hydrophosphination products represent a convenient method for the modification of phosphines.

Introduction

The majority of organometallic phosphine complexes involve mono-, bi- or polydentate tertiary phosphines, while primary and secondary phosphines have received much less attention, due to their toxicity and high reactivity (some are even pyrophoric). However, these phosphines are very interesting, as they facilitate post-coordination modification of the P–H bond, allowing for chemical flexibility in the synthesis of new and intriguing transition metal phosphine complexes. Several air-stable primary and secondary phosphines have been reported; developments in this area include the use of bulky aryl groups or aminoalkyl substituents. A recent review by Higham *et al.* gives an excellent overview on primary phosphine chemistry, including air-stable phosphines.

Due to the redox properties of the ferrocenyl unit and the possibility to readily obtain chiral compounds, 11 ferrocenyl-phosphines are an important class of ligands in transition metal chemistry. Henderson *et al.* 4-6 used the methyl-ferrocenyl fragment to stabilise primary phosphines. FcCH₂PH₂ [Fc = Fe(η^5 -C₅H₄)(η^5 -C₅H₅)] proved to be indefinitely air-stable, probably due to electronic rather than steric effects,

Institute of Inorganic Chemistry, Faculty of Chemistry and Mineralogy, Universität Leipzig, Johannisallee 29, 04103 Leipzig, Germany. E-mail: hey@uni-leipzig.de † Electronic supplementary information (ESI) available: Experimental and simulated ¹H and ³¹P NMR spectra of 2a and 3a (only PH₂ region); summary of data collection, structure solution and refinement details for 1a,c, 2a-c, 3a,b and 4a. CCDC 1420127–1420134. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt03374h

as well as having the ability to coordinate to molybdenum carbonyls or $[\{RuCl_2(p\text{-cymene})\}_2]$ (p-cymene = 1-Me-4-iPrC₆H₄) without alteration of the PH2 group, whereas P-H activation occurred in the reaction with [Ru₃(CO)₁₂] to give two products with capping phosphinidene ligands.⁵ Ferrocenylphosphine, FcPH2, was first published by Roesky et al. in 1989 as an airsensitive yellow oil prepared by reduction of FcPCl2 with LiAlH₄.¹³ Henderson et al. have obtained FcPH₂ from the reduction of FcP(O)(OEt)2 with a mixture of LiAlH4 and Me₃SiCl as a brown oil that crystallises upon standing.⁴ They reported that a solution of FcPH2 is slowly oxidised in 5 d to the corresponding primary phosphine oxide and phosphinic acid.4 We have previously extended this chemistry to the sterically demanding air-stable secondary and tertiary ferrocenylphosphines PH(CH₂Fc)₂ and P(CH₂Fc)₃ ¹⁴ and transition metal complexes thereof. 14,15-19

FcPH₂ is a remarkably convenient starting material considering its easy synthesis and stability compared with related compounds, but has mostly been neglected. In contrast, the highly reactive PhPH₂ has been used extensively.²⁰ We have previously reported the synthesis of [MI₂(CO)₃(PH₂Fc)₂] (M = Mo, W),¹⁹ [Cp*TaCl₄(PH₂Fc)]¹⁵ (Cp* = C₅Me₅) and [RuCl₂(*p*-cymene)(PH₂Fc)].¹⁷ Presented below is the synthesis and characterisation of the ferrocenylphosphine transition metal carbonyl complexes [M(CO)₅(PH₂Fc)] (1a, M = Cr; 1b, M = Mo; 1c, M = W), *cis*-[M(CO)₄(PH₂Fc)₂] (2a, M = Cr; 2b, M = Mo; 2c, M = W) and *fac*-[M(CO)₃(PH₂Fc)₃] (3a, M = Cr; 3b, M = Mo; 3c, M = W). Furthermore, the reactivity of the P-H bond of the coordinated and free ligand in the hydrophosphination of alkenes was investigated, and the hydrophosphination

products $[W(CO)_5{PH(Fc)(CH_2CH_2CN)}]$ (4a), $[W(CO)_5{PH(Fc)-(CH_2CH_2C(O)OMe)}]$ (4b) and $FcP(CH_2CH_2CN)_2$ (5) were obtained.

Results and discussion

Synthesis

Freshly prepared [M(CO)₅(thf)] (M = Cr, Mo, W)²¹ was added to a solution of FcPH₂ ³ in THF at room temperature and the mixture was stirred for 30 min (Scheme 1). All volatile materials including unconsumed M(CO)₆ and FcPH₂ were removed under high vacuum (10^{-3} mbar) at elevated temperature to leave a pale orange powder of crude [M(CO)₅(PH₂Fc)] (1a, M = Cr; 1b, M = Mo; 1c, M = W), which was purified by column chromatography. Small amounts of *cis*-[M(CO)₄(PH₂Fc)₂] (2a, M = Cr; 2b, M = Mo; 2c, M = W) were also obtained by this method, since *cis*-[M(CO)₄(thf)₂] is a side product in the preparation of [M(CO)₅(thf)].²¹ The three complexes 1a–c are air- and moisture-stable and highly soluble in common organic solvents.

The bis-ferrocenylphosphine complexes cis-[M(CO)₄(PH₂Fc)₂] (2a, M = Cr; 2b, M = Mo) were obtained from two equivalents of FcPH₂ and [M(CO)₄(nbd)]²² (M = Cr, Mo, nbd = norbornadiene) in toluene after stirring at room temperature for 24 h (Scheme 2). In the case of cis-[W(CO)₄(PH₂Fc)₂] (2c), a mixture of FcPH₂ and cis-[W(CO)₄(tmpa)]²² (tmpa = N,N,N',N'-tetramethyl-1,3-propanediamine) in toluene was heated to 60 °C for 1 d. Complexes 2a–c crystallise from dichloromethane/n-hexane as pale orange powders.

Scheme 1 Synthesis of $[M(CO)_5(PH_2Fc)]$ (1a, M = Cr; 1b, M = Mo; 1c, M = W).

Scheme 2 Synthesis of cis-[M(CO)₄(PH₂Fc)₂] (2a, M = Cr; 2b, M = Mo; 2c, M = W).

Scheme 3 Synthesis of fac-[M(CO)₃(PH₂Fc)₃] (3a, M = Cr; 3b, M = Mo; 3c, M = W).

The tris-ferrocenylphosphine complexes fac-[M(CO)₃(PH₂Fc)₃] (3**a**, M = Cr; 3**b**, M = Mo; 3**c**, M = W) were obtained from three equivalents of FcPH₂ and fac-[M(CO)₃(NCR)₃] (M = Cr, Mo, R = Me; M = W, R = Et)²¹ in dichloromethane overnight at room temperature (Scheme 3). The air- and moisture-stable products were purified by column chromatography.

Spectroscopic data

The $^{31}P\{^1H\}$ NMR spectra show a remarkable difference between the three complexes with $\delta(^{31}P)$ observed at progressively lower ppm in the order Cr > Mo > W (1a: -47.6, 1b: -81.5 and 1c: -101.8 ppm). In the proton-coupled ^{31}P NMR spectra these singlets split into triplets $[^1J_{\rm PH}\approx 334$ Hz (Table 1)]. In addition, the spectrum of 1c shows $^{31}P^{-183}W$ coupling of 221 Hz.

In the 1 H NMR spectra, the signals of the hydrogen atoms of the primary phosphine are shifted downfield from 3.81 ppm in FcPH₂ to 5.27 ppm in **1a**, 5.31 ppm in **1b** and 5.65 ppm in **1c** (1 J_{HP} increases from 203.6 Hz in FcPH₂ to 333.9 Hz in **1a**, 328 Hz in **1b** and 341.5 Hz in **1c**).

In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, two doublets are observed for the carbonyl carbon atoms (1a: 220.4 ppm, $^2J_{\text{CP}} = 7.3$ Hz, 216.1 ppm, $^2J_{\text{CP}} = 13.7$ Hz; 1b: 208.8 ppm, $^2J_{\text{CP}} = 23.7$ Hz,

Table 1 Selected spectroscopic data for FcPH₂, 1a-c, 2a-c, 3a-c, 4a,b and 5

Compound	δ^{31} P (ppm)	$^{1}J_{\mathrm{PH}}\left(\mathrm{Hz}\right)$	ν(CO) (cm ⁻¹)
FcPH ₂	-144.2	203.6	_
1a	-47.5	333.9	2066, 1946, 1931, 1917
1b	-81.5	328.0	2074, 1950, 1933, 1921
1c	-101.8	341.5	2073, 1935, 1916, 1898
2a	-36.3	333.1	2018, 1922, 1901, 1870
2b	-72.4	326.4	2024, 1901, 1879
2c	-94.2	328.0	2025, 1922, 1898, 1865
3a	-25.9	306.0	1922, 1837
3 b	-63.8	307.0	1932, 1842
3c	-82.3	315.0	1938, 1840
4a	-45.4	345.1	2073, 1980, 1916
4b	-42.6	343.0	2071, 1978, 1914, 1738
5	-74.4	_	_

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205.0 ppm, $^2J_{\rm CP}$ = 9.2 Hz; **1c**: 198.1 ppm, $^2J_{\rm CP}$ = 22.2 Hz, 195.9 ppm, $^2J_{\rm CP}$ = 7.1 Hz). The doublet with the larger coupling constant is assigned to the single *trans* carbonyl group, since $^{31}{\rm P}^{-13}{\rm C}$ coupling through multiple bonds is usually greatest when the bonds are linear. 23

The same trends as seen for 1a-c are also observed for 2a-c in the ¹H, ¹³C(¹H), ³¹P(¹H) and ³¹P NMR spectra, but the spectra exhibit a higher spin system due to coupling with the second magnetically inequivalent phosphorus atom (the ¹H and ³¹P NMR spectra of 2a (experimental and simulated) are shown in Fig. S1 and S2, ESI†). The signals in the ³¹P NMR spectra of 2a-c show downfield shifts of roughly 10 ppm compared to 1a-c (Table 1). The only significant change in the ¹H NMR spectra of 2a-c compared to 1a-c is the increased complexity of the signal of the hydrogen atoms attached to the phosphorus atoms due to the apparent AA'X₂X'₂ (2a,b) or AA' MX₂X'₂ (2c) spin system. These signals are observed at 5.23 in **2a**, 5.22 in **2b** and 5.53 ppm in **2c**. Accordingly, the ${}^{13}C{}^{1}H$ NMR spectra of 2a-c show increased complexity due to the second phosphorus atom, but the same downfield shift trend is observed from chromium to tungsten. The greatest change is seen in the carbonyl carbon signals, which become more deshielded (downfield shifts of 3.9 to 6.2 ppm). This deshielding of the carbonyl carbon atoms is accompanied by a decrease in ν (CO) of the A₁ carbonyl mode (2018–2025 cm⁻¹, Table 1) in the IR spectra of 2a-c by about 50 cm⁻¹ due to increased backbonding between the d_M and π^* orbitals of the M-CO bond, which is due to the presence of the second FcPH₂ ligand.²⁴

Introduction of a third ferrocenylphosphine ligand further increases the complexity of the ¹H, ¹³C{¹H}, ³¹P{¹H} and ³¹P NMR spectra (AA'A"X₂X'₂X"₂ (3a,b) or AA'A"MX₂X'₂X"₂ (3c) spin system; the ¹H and ³¹P NMR spectra of 3a (experimental and simulated) are shown in Fig. S3 and S4, ESI†). However, the trends seen in the spectra of 2a-c are also observed in those of 3a-c. $\delta(^{31}P)$ of 3a-c is shifted further downfield by about 10 ppm (Table 1). This suggests increasing deshielding of the phosphine with increased substitution. This same deshielding trend is seen between cis-[M(CO)₄(PH₂Ph)₂] and fac- $[M(CO)_3(PH_2Ph)_3]$ (M = Mo, W; M = Mo, $\delta(^{31}P)$ is -60.5 and -53.5 ppm; M = W, $\delta(^{31}P)$ is -80.9 and -72.0 ppm). ²⁵ In addition, the ³¹P{¹H} NMR spectra of the tungsten complexes (1c, 2c and 3c) show ³¹P-¹⁸³W coupling which decreases from 221.0 Hz in $[W(CO)_5(PH_2Fc)]$ (1c) to 209.0 Hz in fac- $[W(CO)_3(PH_2Fc)_3]$ (3c). Coupling to the two NMR active (I = 5/2) molybdenum isotopes, 95Mo and 97Mo, is only observed for fac-[Mo(CO)₃(PH₂Fc)₃] (3**b**). In the ¹³C{¹H} NMR spectra of 3**a-c** the signals of the carbonyl carbon atoms are also shifted by about 4 ppm compared to 2a-c.

Molecular structures

Single-crystal X-ray structure determinations were carried out for 1a, 1c, 2a-c, 3a and 3b. Complexes 1a and 1c are isostructural, as are complexes 2a-c and complexes 3a,b. Therefore, only one representative structure is shown here in each case (1a (Fig. 1, Table 2), 2a (Fig. 2, Table 3), and 3a (Fig. 3, Table 4). Furthermore, in 2a-c two symmetry-independent

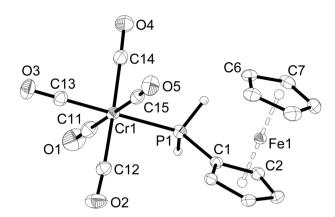


Fig. 1 Molecular structure of $[Cr(CO)_5(PH_2Fc)]$ (1a). The hydrogen atoms of the ferrocenyl moiety are omitted for clarity. Ellipsoids drawn at 50% probability.

Table 2 Selected bond lengths (pm) and bond angles (°) for 1a and 1c

Compound	1a (M = Cr)	1c (M = W)	
M(1)-P(1)	236.30(3)	251.12(8)	
M(1)-C(13)	186.4(1)	201.0(3)	
M(1)-C(14)	189.3(1)	204.3(3)	
M(1)-C(15)	189.7(1)	203.5(3)	
M(1)-C(11)	189.7(1)	204.3(3)	
M(1)-C(12)	190.4(1)	205.1(3)	
P(1)-C(1)	179.9(1)	180.0(3)	
O(1)-C(11)	113.8(2)	113.6(4)	
O(2)-C(12)	113.8(2)	113.4(4)	
O(3)-C(13)	114.8(2)	114.3(4)	
O(4)-C(14)	113.9(2)	113.6(4)	
O(5)-C(15)	113.9(2)	113.9(4)	
C(13)-M(1)-P(1)	179.06(4)	179.5(1)	
C(14)-M(1)-P(1)	90.09(4)	90.6(1)	
C(15)-M(1)-P(1)	90.80(4)	90.30(9)	
C(11)-M(1)-P(1)	89.17(4)	88.9(1)	
C(12)-M(1)-P(1)	91.83(4)	92.13(9)	
C(1)-P(1)-M(1)	122.49(4)	121.69(9)	

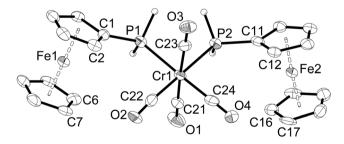


Fig. 2 Molecular structure of cis-[Cr(CO)₄(PH₂Fc)₂] (2a). The hydrogen atoms of the ferrocenyl moieties are omitted for clarity. Ellipsoids drawn at 50% probability. Only one of the symmetry-independent molecules is shown.

molecules are present in the asymmetric unit. As these molecules have very similar structures, only one of the two molecules is shown and discussed. Complexes 3a and 3b crystallise

Table 3 Selected bond lengths (pm) and bond angles (°) for 2a–2c. Values of the second symmetry-independent molecule are given in parentheses II

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Compound	2a (M = Cr)	$2\mathbf{b}$ (M = Mo)	$2c (M = W)^a$
M(1)-P(1)	234.4(3)	250.4(1)	249.3(2)
[M(2)-P(3)]	[234.8(3)]	[250.3(1)]	[249.6(3)]
M(1)-P(2)	235.0(3)	250.2(1)	249.1(2)
[M(2)-P(4)]	[234.4(3)]	[250.3(1)]	[249.2(2)]
M(1)-C(24)	185(1)	198.1(6)	197(1)
[M(2)-C(48)]	[182.7(9)]	[198.1(6)]	[197(1)]
M(1)-C(22)	187(1)	198.8(6)	199(1)
[M(2)-C(46)]	[185(1)]	[199.5(5)]	[198(1)]
M(1)-C(21)	187(1)	204.0(6)	204(1)
[M(2)-C(47)]	[188(1)]	[203.5(5)]	[204(1)]
M(1)-C(23)	189(1)	201.9(5)	198(1)
[M(2)-C(45)]	[188.9(9)]	[204.1(6)]	[201(1)]
P(1)-C(1)	180(1)	180.3(5)	182(1)
[P(3)-C(25)]	[181(1)]	[180.5(5)]	[178.5(9)]
P(2)-C(11)	180(1)	179.7(5)	180(1)
[P(4)-C(35)]	[181(1)]	[181.3(5)]	[180(1)]
C(24)-M(1)-P(1)	178.4(3)	176.9(2)	176.9(3)
[C(48)-M(2)-P(3)]	[178.5(3)]	[178.5(2)]	[178.2(3)]
C(22)-M(1)-P(1)	93.7(3)	94.0(2)	93.9(3)
[C(46)-M(2)-P(3)]	[92.8(3)]	[93.3(1)]	[93.2(3)]
C(21)-M(1)-P(1)	93.1(3)	93.6(2)	93.3(3)
[C(47)-M(2)-P(3)]	[87.1(3)]	[86.5(1)]	[85.8(3)]
C(23)-M(1)-P(1)	87.0(3)	86.7(1)	86.4(3)
[C(45)-M(2)-P(3)]	[88.8(3)]	[89.1(2)]	[88.9(3)]
C(24)-M(1)-P(2)	93.1(3)	92.8(2)	92.8(3)
[C(48)-M(2)-P(4)]	[94.1(3)]	[94.2(2)]	[94.0(3)]
C(22)-M(1)-P(2)	178.8(3)	178.6(2)	178.2(3)
[C(46)-M(2)-P(4)]	[178.4(3)]	[177.6(1)]	[177.5(3)]
C(21)-M(1)-P(2)	89.3(3)	89.0(2)	88.7(3)
[C(47)-M(2)-P(4)]	[87.3(3)]	[86.6(2)]	[86.5(3)]
C(23)-M(1)-P(2)	86.7(3)	86.7(2)	86.6(3)
[C(45)-M(2)-P(4)]	[91.5(3)]	[93.7(2)]	[93.0(3)]
P(1)-M(1)-P(2)	85.7(1)	84.85(4)	84.52(8)
[P(4)-M(2)-P(3)]	[85.7(9)]	[84.88(4)]	[84.69(8)]
C(1)-P(1)-M(1)	122.8(3)	122.6(2)	122.6(3)
[C(25)-P(3)-M(2)]	[124.5(3)]	[124.2(2)]	[123.9(3)]
C(11)-P(2)-M(1)	124.8(3)	124.5(2)	123.9(3)
[C(35)-P(4)-M(2)]	[124.2(3)]	[122.9(2)]	[122.6(3)]

^a As a result of the extremely small and moderately diffracting crystal (small needle), the carbon atoms of **2c** were refined isotropically.

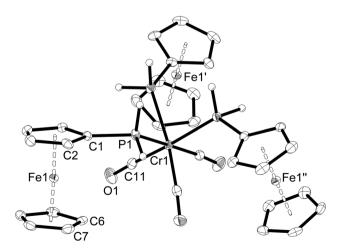


Fig. 3 Molecular structure of fac-[Cr(CO)₃(PH₂Fc)₃] (3a). The hydrogen atoms of the ferrocenyl moieties are omitted for clarity. Ellipsoids drawn at 50% probability. Symmetry operators: Fe1': 1-y, 2+x-y, z; Fe1'': -1-x+y, 1-x, z.

Table 4 Selected bond lengths (pm) and bond angles (°) for 3a and 3b

Compound	3a (M = Cr)	3b (M = Mo)
M(1)-P(1)	235.15(6)	250.57(7)
P(1)-C(1)	180.5(2)	180.6(2)
M(1)-C(11)	184.9(2)	198.0(3)
C(11)-M(1)-C(11)'	88.0(1)	87.8(1)
C(11)-M(1)-P(1)	172.70(7)	173.64(7)
C(11)'-M(1)-P(1)	87.55(7)	88.50(7)
C(11)''-M(1)-P(1)	97.62(7)	97.22(7)
P(1)-M(1)-P(1)'	87.26(3)	86.83(2)
C(1)-P(1)-M(1)	125.87(7)	125.34(8)
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in the trigonal space group R3 with three molecules in the unit cell. The chirality arises from the lack of rotoinversion symmetry elements in the molecule. The molecules are located on a crystallographic C_3 axis.

All complexes retain the octahedral geometry of the parent metal carbonyl complexes with bond angles at the metal centre ranging from 88.0(1) to 92.13(9)° in 1a and 1c, but become more distorted with bond angles ranging from 84.5(1)-94.3(4)° in 2a-c. The most acute angle in 2a-c is the P-M-P angle, which suggests that there is less steric hindrance between the ferrocenylphosphine ligands than between the carbonyl ligands. The P-Cr-P bond angles increase from 85.7(1)° in 2a to 87.26(3)° in 3a. The Cr-P-C bond angles also become more obtuse, increasing from 122.49(4)° in 1a to 123.8(3)° (average) in 2a and finally to 125.87(7)° in 3a. Likewise, the P-Mo-P (86.83(2)° (3b), 84.85(4)° (2b)) and Mo-P-C (125.34(8)° (3b), 123.5(2)° (2b)) (average) bond angles in 3b increase compared to 2b. The P-Mo-P bond angle in cis- $[Mo(CO)_4(PH_2Ph)_2]^{25}$ is 87.9(1)°, as opposed to the more acute angle of 84.85(4)° in 2b. The M-P-C_{Fc} bond angles are large and very similar for all complexes (122.49(4) and 121.69(9)° in **1a** and **1c** and slightly larger in **2a-c** (122.6(3) to 124.8(3)°) and 3a,c (125.87(7) and 125.34(8)°). In comparison, the Mo-P-C bond angles in cis-[Mo(CO)₄(PH₂Ph)₂] are more acute (120.6(1)°) compared to 2b. The P-C_{Fc} bond lengths of 1a-c and 2a-c are also very similar (ca. 180 pm) as are the ferrocenyl moieties in these complexes.

However, the bond lengths around the metal atom differ greatly between the complexes, as expected from the larger differences in atomic radii. For example, the Cr-P bond length of **1a** is 236.30(3) pm, and the W-P bond length of **1c** is 251.12(8) pm. The Cr-P and W-P bond lengths of **2a** and **2c** are shorter than those of **1a** and **1c**. This is again due the second FcPH₂ ligand. The Cr-P bond lengths remain relatively constant at 236.30(3) pm in **1a**, 234.4(3) and 235.0(3) pm in **2a** and 235.15(6) pm in **3a**. The Mo-P bond in **3b** increases insignificantly to 250.57(7) pm from 250.3(1) pm in **2b**. Likewise, the Mo-P bond lengths of *cis*-[Mo(CO)₄(PH₂Ph)₂] and *fac*-[Mo(CO)₃(PH₂Ph)₃] do not change at 250.8(3) and 249.8(3) pm, respectively.²⁵

The average Cr–C bond length of **1a** is 189.1(1) pm with the shortest bond (186.4(1) pm) *trans* to phosphorus. Bond lengths of **1c** follow the same trend but are longer (average W–C bond

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length is 203.6(3) pm with the shortest bond (201.0(3) pm) trans to phosphorus). The bond lengths around the Cr and W atoms of 2a and 2c are shorter than those of 1a and 1c (2a: average Cr-C 186.9(1) pm; 2c: W-C average 199.7(1) pm). The same trend is observed in 2b which has an average Mo-C bond length of 200.7(6) pm (Mo-C 202.0(1) pm in $[M(CO)_4(PH_2Ph)_2]^{25}$) and for 3a,b (3a: Cr-C 184.9(2) pm; 3b: Mo-C 198.0(3) pm). This shortening can be attributed to increased back-bonding between the metal centre and carbonyl ligands and is supported by a decrease in the A1 mode of the CO stretching vibration (Table 1). This correlation was also observed for the phenylphosphine complexes $[M(CO)_4(PH_2Ph)_2]$ and $[M(CO)_3(PH_2Ph)_3]$ (M = Cr, Mo, W).²⁵

Hydrophosphination

The addition of P-H bonds to C-C double or triple bonds (hydrophosphination reaction) is a very versatile way of synthesising new phosphines.^{3,26} After seminal work on catalytic hydrophosphination, ^{26g,h} renewed activity in this area was observed recently. 26i-k Therefore, the ability of the coordinated ferrocenylphosphine to undergo hydrophosphination reactions was tested by screening 1c with a number of alkene substrates. KOtBu (10 mol%) was used to catalyse the hydrophosphination reactions, and dry THF was employed as the reaction medium to allow for sufficient solubility of all reaction components. The general procedure involved mixing 1c with KOtBu in THF followed by addition of one equivalent of one of the alkene substrates, all of which are liquids, after which the mixture was heated to reflux for several hours. Subsequent analysis of the reaction mixture by ³¹P{¹H} NMR spectroscopy showed that alkenes bearing an electron-donating group (EDG), that is, styrene and cyclopentene, did not undergo hydrophosphination even when refluxing was continued for 24 h. However, alkenes with an electron-withdrawing group (EWG) did undergo hydrophosphination, and the stronger the EWG effect the faster the reaction. Thus, hydrophosphination of acrylonitrile, which bears a strong EWG, was complete after 5 h, while that of methyl acrylate, containing a weak EWG, took 20 h. The products [W(CO)₅{PH(Fc)(CH₂CH₂CN)}] (4a) and [W(CO)₅{PH(Fc)(CH₂CH₂C(O)OMe)}] (4b) were purified by column chromatography (they are eluted considerably more slowly than 1c) and fully characterised (Scheme 4).

The ¹H, ³¹P{¹H} and ³¹P NMR spectra confirm the anti-Markovnikov addition of the P-H bond across the C-C double

Scheme 4 Synthesis of [W(CO)₅{PH(Fc)(CH₂CH₂CN)}] $[W(CO)_5\{PH(Fc)(CH_2CH_2C(O)OMe)\}]$ (4b).

bond of the alkene substrate. In the ¹H NMR spectrum, the signal of the P-H protons of 4a and 4b is shifted downfield (5.87 or 5.76 ppm, respectively) compared to 1c (5.65 ppm) with a large ³¹P-¹H coupling of 344 Hz, a slight increase from 342 Hz in 1c, but appears as a doublet of triplets due to the $^{3}J_{\rm HH}$ coupling of 4 or 5.4 Hz with the two methylene protons of the new cyanoethyl or methoxycarbonylethyl substituent. Likewise, a doublet with a large downfield shift to -45.4 ppm (4a, ${}^{1}J_{PH}$ = 345 Hz) or -42.6 ppm (4b, ${}^{1}J_{PH}$ = 343 Hz) from -101.8 ppm in 1c is observed in the ³¹P NMR spectrum. The IR spectra of 4a,b show some similarity to that of 1c. The carbonyl stretching frequencies are unchanged at 2073 and 2071 cm⁻¹, respectively. The carbonyl stretching band of the carboxylate moiety of 4b was observed at 1738 cm⁻¹, but no nitrile stretching band was observed for 4a.

The distorted octahedral environment (87.8(1)° to 94.2(1)°) and the bond lengths around the tungsten atom in 4a (Fig. 4) change only slightly compared to 1c (W-P 252.0(8) vs. 251.1(8) pm in 1c). The average W-C bond length is 202.4(4) pm (cf. 203.6(3) pm in 1c). The shortest W-C bond (197.9(4) pm) is again that trans to phosphorus, which is 3.1 pm shorter than that in 1c. These very small changes in bond lengths indicate that there is no significant change in the coordination properties, which would otherwise be expected when moving from a primary to secondary phosphine. The phosphorus atom exhibits a distorted tetrahedral environment with large W-P-CFc and W-P-C_{Et} bond angles (121.7(1)° and 110.7(1)°, respectively) and a small C_{Fc} -P- C_{Et} bond angle (104.0(2)°).

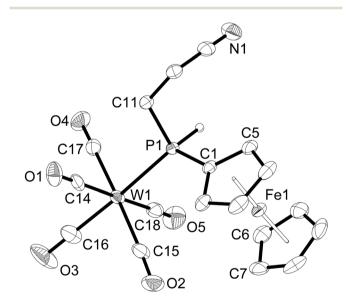


Fig. 4 Molecular structure of [W(CO)₅{PH(Fc)(CH₂CH₂CN)}] (4a). Hydrogen atoms other than P-H are omitted for clarity. Ellipsoids drawn at 50% probability. Selected bond lengths (pm) and bond angles (°): W(1)-C(16) 197.9(4), W(1)-C(18) 202.1(5), W(1)-C(15) 203.7(4), W(1)-C(14)203.8(5), W(1)-C(17) 204.5(4), W(1)-P(1) 252.04(8), P(1)-C(1) 178.4(3), P(1)-C(11) 183.2(3), C(16)-W(1)-P(1) 175.8(2), C(18)-W(1)-P(1) 93.2(1), C(15)-W(1)-P(1) 94.2(1), C(14)-W(1)-P(1) 87.8(1), C(17)-W(1)-P(1) 90.6(1), C(1)-P(1)-C(11) 104.0(2), C(1)-P(1)-W(1) 121.7(1), C(11)-P(1)-W(1) 110.7(1), C(12)-C(11)-P(1) 118.3(2)

Scheme 5 Synthesis of FcP(CH₂CH₂CN)₂ (5).

FcPH₂ undergoes a similar hydrophosphination reaction as 1c; however, the di-hydrophosphination product, the tertiary phosphine FcP(CH₂CH₂CN)₂ (5), is observed even with only one equivalent of acrylonitrile in refluxing THF and a catalytic amount of KOtBu (Scheme 5). 5 is obtained in a better yield when two equivalents of acrylonitrile are empoloyed. 5 was isolated as a viscous orange oil by column chromatography under an inert atmosphere, since it is rapidly oxidised upon exposure

In the ³¹P NMR spectrum, the signal of the phosphorus atom of 5 is shifted downfield to -74.4 ppm compared to FcPH₂ (-144.2 ppm). This signal is still significantly upfield from those of the related compounds FcCH2P(CH2CH2CN)2 $(-22.1 \text{ ppm})^{27}$ and PhP(CH₂CH₂CN)₂ (-23.8 ppm).²⁸ The ¹³C{¹H} NMR spectrum of 5 reveals an increase in the ¹³C-³¹P coupling constants compared with FcPH2. The signal of the ipso carbon atom shifts downfield to 68.1 ppm from 64.1 ppm in FcPH₂ with similar ¹J_{CP} values (5.0 Hz in FcPH₂, 5.1 Hz in 5). Likewise, the signal of the meta carbon atom is shifted downfield to 71.2 ppm with an increased ¹³C-³¹P coupling constant of 10.1 Hz compared with 4.0 Hz in FcPH₂.

Conclusions

The mono-, bis- and tris-ferrocenylphosphine complexes $[M(CO)_5(PH_2Fc)]$ (1a-c), $[M(CO)_4(PH_2Fc)_2]$ (2a-c) $[M(CO)_3(PH_2Fc)_3]$ (3a-c) with M = Cr, Mo, W are readily available from FcPH₂ and suitable metal carbonyl complexes. The molecular structures of 1a,c, 2a-c and 3a,b and a comparison of the X-ray structural and spectroscopic data of 2b and 3b with those of the known phenylphosphine complexes cis- $[Mo(CO)_4(PH_2Ph)_2]$ and $fac-[Mo(CO)_3(PH_2Ph)_3]$ reveal that FcPH2 exerts similar steric effects on the complex as PhPH2, but its electronic behaviour is significantly different. By comparing the carbonyl stretching frequencies of the complexes, it can be concluded that FcPH₂ is as good a σ donor as PhPH₂.

The coordinated FcPH2 ligand of 1c undergoes hydrophosphination in the presence of catalytic amounts of KOtBu with alkene substrates bearing EWGs, such as acrylonitrile and methyl acrylate, yielding the secondary phosphine complexes $[W(CO)_5{PH(Fc)(CH_2CH_2CN)}]$ (4a) and $[W(CO)_5{PH(Fc)}]$ (CH₂CH₂C(O)OMe)}] (4b). Extending this method to the free ferrocenylphosphine yielded FcP(CH₂CH₂CN)₂ (5).

The findings presented above show that FcPH2 is a versatile ligand that behaves and interacts much like the far more difficult to handle PhPH2, and it also contains a useful redoxactive ferrocenyl moiety.

Experimental

General methods

Preparation of all compounds was carried out under an N2 atmosphere using standard vacuum-line and Schlenk techniques. All reactions were performed at ambient temperature and pressure unless otherwise stated. Where necessary, solvents were degassed using the standard freeze-pump-thaw method.29 The drying and distillation of solvents was conducted according to literature methods29 or solvents were dried with an MB SPS-800 Solvent Purification System. $[M(CO)_5(thf)]$ (M = Cr, Mo, W), ²¹ $[M(CO)_4(L)]$ (M = Cr, Mo, L = nbd; M = W, L = tmpa) (nbd = 2,5-norbornadiene; tmpa = *N,N,N',N'*-tetramethyl-1,3-propanediamine),²² $[M(CO)_3(L)_3]$ (M = Mo, Cr, L = MeCN; M = W, L = EtCN), and CPH_2 were prepared according to literature methods. Cr(CO)₆ (Roth), Mo(CO)₆ and W(CO)₆ (Acros) were used as supplied without further purification. Silica gel 60A (Acros) was used as the stationary phase for column chromatography. Mass spectra were obtained in ESI mode with a BRUKER Daltonics FT-ICR-MS spectrometer (Type APEX II, 7 Tesla). Elemental analysis was performed with a Heraeus VARIO EL Analyser. IR spectra (4000-400 cm⁻¹) were recorded as Nujol mulls with a PerkinElmer Spectrum 2000 FT-IR spectrometer. ¹H, ¹³C{¹H}, ³¹P{¹H} and ³¹P NMR spectra were recorded with a Bruker AVANCE DRX 400 MHz instrument at 25 °C. Chemical shifts δ of 1 H, 13 C, 31 P are reported in parts per million (ppm) at 400.12, 100.63 and 162.02 MHz, respectively. ¹H NMR spectra were referenced to TMS (0.00 ppm) or the protic impurity solvent signals in the solvent CDCl₃ (7.26 ppm). ¹³C NMR spectra were referenced to the solvent signal, CDCl₃ (77.16 ppm). ¹³C{¹H} and ³¹P{¹H} experiments were referenced to TMS on the E scale. 30 31P NMR experiments were referenced to 85% H₃PO₄ as external standard. Coupling constants of higher spin systems were determined by using the NMR software MestReNova 8 (Mestrelab Research).31

Synthesis and characterisation

 $Fe(\eta^5-C_5H_4PH_2)(\eta^5-C_5H_5)$ (FcPH₂). This is a modification of the method reported previously.¹² A solution of FcP(O)(OEt)₂ (5.0 g, 15.5 mmol) in diethyl ether (ca. 10 mL) was added to LiAlH₄ (0.59 g, 15.5 mmol) in diethyl ether (ca. 20 mL) with stirring at ca. -70 °C. This mixture was warmed to room temperature and left to stir overnight (14-20 h). Unconsumed LiAlH₄ was carefully hydrolysed with distilled water while the mixture was cooled over ice. The orange organic phase was separated and dried over anhydrous MgSO₄. After reducing the volume to ca. 2-3 mL the crude product was purified by column chromatography on silica gel with CH2Cl2 as eluent.

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The resulting viscous orange oil was still contaminated with ferrocene, which was removed by sublimation (36 °C, 10^{-3} mbar) over several hours. Additional purification can be achieved by sublimation of the product, FcPH₂, at 30 °C under high vacuum (10^{-6} mbar). Yield = 3.22 g, 55%. FcPH₂ has already been described in the literature. However, the NMR data are presented here for easy reference. ¹H NMR (CDCl₃): δ = 3.81 (d, 2H, $^1J_{HP}$ = 203.6 Hz, PH₂), 4.16 (s, 5H, C_5H_5), 4.25 (s, 2H, C_5H_4), 4.27 (s, 2H, C_5H_4); $^{13}C\{^1H\}$ NMR (CDCl₃): δ = 64.1 (d, $^1J_{CP}$ = 5.0 Hz, *ipso*-C in C_5H_4), 69.3 (s, C_5H_5), 70.7 (d, $^3J_{CP}$ = 4.0 Hz, *m*-C in C_5H_4), 75.7 (d, $^2J_{CP}$ = 13.8 Hz, *o*-C in C_5H_4); ^{13}P NMR (CDCl₃): δ = -144.2 (t, $^1J_{PH}$ = 203.6 Hz, PH₂).

 $[M(CO)_5(PH_2Fc)]$ (1a, M = Cr; 1b, M = Mo; 1c, M = W). A solution of M(CO)₆ in THF (ca. 50 mL) was irradiated with a Hg vapour lamp for 3 h at room temperature to generate $[M(CO)_5(thf)]$ (M = Cr, Mo, W). This solution was then added immediately to an equimolar amount of FcPH2 in THF (ca. 10 mL) and the mixture was stirred overnight at room temperature. An orange residue containing the product was obtained after all solvent and volatiles were evaporated under reduced pressure. This residue was dissolved in a minimal volume of CH₂Cl₂ (ca. 2 mL) and passed through a silica gel column with CH₂Cl₂/n-hexane (30:70) as eluent. The orange band corresponding to the product was collected and the solvent evaporated under reduced pressure to obtain [M(CO)₅(PH₂Fc)] as an orange powder of high purity. Any remaining FcPH2 and/or M(CO)₆ in the product was removed by sublimation under high vacuum (10^{-3} mbar). Yields: **1a** 30%, **1b** 44%, **1c** 52%.

1a: 1 H NMR (CDCl₃): δ = 4.16 (s, 5H, Fe-C₅ H_5), 4.35 (s, 4H, Fe-C₅ H_4), 5.27 (d, 1 $_{HP}$ = 333.9 Hz, 2H, P H_2); 13 C{ 1 H} NMR (CDCl₃): δ = 64.5 (d, 1 $_{CP}$ = 45.7 Hz, *ipso*-C in C_5 H₄), 69.8 (s, C_5 H₅), 71.5 (d, 3 $_{CP}$ = 7.7 Hz, m-C in C_5 H₄), 73.9 (d, 2 $_{CP}$ = 12.2 Hz, o-C in C_5 H₄), 216.1 (d, 2 $_{CP}$ = 13.7 Hz, CO eq), 220.4 (d, 2 $_{CP}$ = 7.3 Hz, CO ex); 31 P NMR (CDCl₃): δ = -47.5 (t, 1 $_{PH}$ = 333.9 Hz, PH₂); IR (Nujol, cm $^{-1}$): 2066w (CO), 1946m (CO), 1931s (CO), 1917vs (CO); MS ESI pos., CH₂Cl₂/MeOH, m/z = 431.89 [M + Na] $^{+}$; elemental analysis calcd (%) for C_{15} H₁₁CrFeO₅P: C 43.94, H 2.70; found: C 44.05, H 2.68.

1b: ¹H NMR (CDCl₃): δ = 4.24 (s, 5H, Fe-C₅H₅), 4.40 (m, 2H, Fe-C₅H₄) 4.42 (m, 2H, Fe-C₅H₄), 5.31 (d, ¹J_{HP} = 328.0 Hz, 2H, PH₂); ¹³C{¹H} NMR (CDCl₃): δ = 63.7 (d, ¹J_{CP} = 45.9 Hz, *ipso*-C in C₅H₄), 69.9 (s, C₅H₅), 71.8 (d, ³J_{CP} = 7.7 Hz, *m*-C in C₅H₄), 74.7 (d, ²J_{CP} = 13.2 Hz, *o*-C in C₅H₄), 205.0 (d, ²J_{CP} = 9.2 Hz, CO eq), 208.8 (d, ²J_{CP} = 23.7 Hz, CO ax); ³¹P NMR (CDCl₃): δ = -81.5 (t, ¹J_{PH} = 328.0 Hz, PH₂); IR (Nujol, cm⁻¹): 2074w (CO), 1950s (CO), 1933s (CO), 1921vs (CO); MS ESI pos., CH₂Cl₂/MeOH, *m*/z = 477.86 [M + Na]⁺; elemental analysis calcd (%) for C₁₅H₁₁FeMoO₅P: C 39.68, H 2.44; found: C 39.59, H 2.40.

1c: ¹H NMR (CDCl₃): δ = 4.25 (s, 5H, Fe-C₅ H_5), 4.42 (m, 2H, Fe-C₅ H_4), 4.46 (m, 2H, Fe-C₅ H_4), 5.65 (d, ¹ $J_{\rm HP}$ = 341.5 Hz, 2H, P H_2); ¹³C{¹H} NMR (CDCl₃): δ = 63.5 (d, ¹ $J_{\rm CP}$ = 51.9 Hz, *ipso*-C in C_5 H₄), 70.0 (s, C_5 H₅), 71.9 (d, ³ $J_{\rm CP}$ = 8.1 Hz, m-C in C_5 H₄), 74.6 (d, ² $J_{\rm CP}$ = 13.2 Hz, o-C in C_5 H₄), 195.9 (d, ² $J_{\rm CP}$ = 7.1 Hz, CO eq), 198.1 (d, ² $J_{\rm CP}$ = 22.2 Hz, CO ax); ³¹P NMR (CDCl₃): δ = -101.8 (t with ¹⁸³W satellites, ¹ $J_{\rm PH}$ = 341.5 Hz, ¹ $J_{\rm PW}$ = 221.0 Hz, PH₂); IR (Nujol, cm⁻¹): 2073w (CO), 1935vs (CO), 1916vs (CO),

1898s (CO); MS ESI pos., $CH_2Cl_2/MeOH$, m/z = 563.90 [M + Na]⁺; elemental analysis calcd (%) for $C_{15}H_{11}FeO_5PW$: C 33.25; H 2.05; found: C 33.30; H 1.99.

 $cis-[M(CO)_4(PH_2Fc)_2]$ (2a, M = Cr; 2b, M = Mo; 2c, M = W). A solution containing two equivalents of FcPH2 in toluene (5.0 mL) was added to a solution of $[M(CO)_4(L)]$ (M = Cr or Mo, L = nbd; M = W, L = tmpa) in toluene (ca. 10 mL) at room temperature. The mixture was stirred overnight at room temperature or, in the case of 2c, heated to 60 °C. The solvent and volatiles were then removed under high vacuum (10⁻³ mbar). The remaining orange residue was dissolved in a minimal volume of CH₂Cl₂ (ca. 2 mL) and passed through a silica gel column with CH2Cl2/n-hexane (1:1) as eluent. The orange band corresponding to the product was collected and the solvent evaporated under reduced pressure until pale orange crystals of pure cis-[M(CO)₄(PH₂Fc)₂] formed. The crystals were isolated by filtration, washed with *n*-hexane (3 \times 10 mL) and dried under vacuum. Yields: 2a 59%, 2b 58%, 2c 69%.

2a: 1 H NMR (CDCl₃): δ = 4.22 (s, 10H, Fe-C₅ H_5), 4.38 (br s, 4H, Fe-C₅ H_4), 4.41 (br s, 4H, Fe-C₅ H_4), 5.23 (m, $^{1}J_{\rm HP}$ = 333.1 Hz, $^{3}J_{\rm HP}$ = 13.0 Hz, 4H, P H_2 , AA'X₂X'₂ spin system, simulated³¹ (see ESI†)); 13 C(1 H} NMR (CDCl₃): δ = 65.9 (t, $^{1}J_{\rm CP}$ = 49.5 Hz, $^{3}J_{\rm CP}$ = 25.3 Hz, i pso-C in C_5 H₄), 69.9 (s, C_5 H₅), 71.3 (t, $^{3}J_{\rm CP}$ = 7.1 Hz, $^{5}J_{\rm CP}$ = 3.3 Hz, i m-C in C_5 H₄), 74.0 (t, $^{2}J_{\rm CP}$ = 11.1 Hz, $^{4}J_{\rm CP}$ = 5.6 Hz, i 0-C in C_5 H₄), 220.1 (t, $^{2}J_{\rm CP}$ = 14.4 Hz, i CO cis), 226.0 (d, $^{2}J_{\rm CP}$ = 9.3 Hz, CO trans); 31 P NMR (CDCl₃): δ = -36.3 (m, $^{1}J_{\rm PH}$ = 333.1 Hz, $^{2}J_{\rm PP}$ = -29.0 Hz, i PH₂, AA'X₂X'₂ spin system, simulated³¹ (see ESI†)); IR (Nujol, cm⁻¹): 2018w (CO), 1922s (CO), 1901s (CO), 1870vs (CO); MS ESI pos., CH₂Cl₂/MeOH, i M= 622.9 [M + Na][†]; elemental analysis calcd (%) for i C₂₄H₂₂CrFe₂O₄P₂: C 48.04, H, 3.70; found: C 47.93, H, 3.61.

2b: 1 H NMR (CDCl₃): δ = 4.24 (s, 10H, Fe-C₅ H_5), 4.40 (br s, 4H, Fe-C₅ H_4), 4.42 (br s, 4H, Fe-C₅ H_4), 5.22 (m, $^{1}J_{HP}$ = 327.0 Hz, $^{3}J_{HP}$ = 11.0 Hz, 4H, P H_2 , AA'X₂X'₂ spin system); 13 C{ 1 H} NMR (CDCl₃): δ = 64.8 (t, $^{1}J_{CP}$ = 48.5 Hz, $^{3}J_{CP}$ = 24.2 Hz, *ipso*-C in C_5 H₄), 69.9 (s, C_5 H₅), 71.5 (t, $^{3}J_{CP}$ = 7.1 Hz, $^{5}J_{CP}$ = 3.5 Hz, m-C in C_5 H₄), 74.7 (t, $^{2}J_{CP}$ = 12.1 Hz, $^{4}J_{CP}$ = 6.1 Hz, o-C in C_5 H₄), 208.1 (t, $^{2}J_{CP}$ = 9.5 Hz, CO cis), 214.1 (d, $^{2}J_{CP}$ = 9.3 Hz, CO trans); 31 P NMR (CDCl₃): δ = -72.4 (m, $^{1}J_{PH}$ = 326.4 Hz, $^{2}J_{PP}$ = -17.0 Hz, $^{2}J_{PH}$ AA'X₂X'₂ spin system); IR (Nujol, cm⁻¹): 2024w (CO), 1901vs (CO), 1879s (CO); MS ESI pos., CH₂Cl₂/MeOH, $^{2}M_2$ = 668.8 [M + Na][†]; elemental analysis calcd (%) for $C_{24}H_{22}$ Fe₂MoO₄P₂: C 44.76, H 3.44; found: C 44.74, H 3.50.

2c: 1 H NMR (CDCl₃): δ = 4.25 (s, 10H, Fe-C₅ H_5), 4.46 (s, 8H, Fe-C₅ H_4), 5.53 (m, ${}^{1}J_{HP}$ = 328.0 Hz, ${}^{3}J_{HP}$ = 12.0 Hz, 4H, P H_2 , AA'X₂X'₂ spin system); 13 C{ 1 H} NMR (CDCl₃): δ = 64.6 (m, ${}^{1}J_{CP}$ = 50.6 Hz, ${}^{3}J_{CP}$ = 26.3 Hz, ipso-C in C_5 H₄), 69.9 (s, C_5 H₅), 71.6 (p, ${}^{3}J_{CP}$ = 8.1 Hz, ${}^{5}J_{CP}$ = 4.0 Hz, m-C in C_5 H₄), 74.6 (t, ${}^{2}J_{CP}$ = 12.1 Hz, ${}^{4}J_{CP}$ = 6.1 Hz, o-C in C_5 H₄), 200.0 (t, ${}^{2}J_{CP}$ = 7.3 Hz, CO cis), 204.3 (m, cis) (m, cis) NMR (CDCl₃): δ = -94.2 (m, ${}^{1}J_{PH}$ = 328.0 Hz, ${}^{2}J_{PP}$ = -11.0 Hz, ${}^{1}J_{WP}$ = 214.9 Hz, PH₂ AA'MX₂X'₂ spin system); IR (Nujol, cm⁻¹): 2025w (CO), 1922s (CO), 1898s (CO), 1865vs (CO); MS ESI pos., CH₂Cl₂/MeOH, m/z = 754.9 [M + Na]⁺; elemental analysis calcd (%) for C₂₄H₂₂Fe₂O₄P₂W: C 39.38, H 3.03; found: C 39.35, H 2.86.

 $fac-[M(CO)_3(PH_2Fc)_3]$ (3a, M = Cr; 3b, M = Mo; 3c, M = W). A solution of three equivalents of FcPH2 in CH2Cl2 (5.0 mL) was added to a solution of fac- $[M(CO)_3(L)_3]$ (M = Mo, Cr, L = MeCN; M = W, L = EtCN) in CH_2Cl_2 (ca. 10 mL) at room temperature. The mixture was stirred overnight before the solvent and volatiles were removed under high vacuum (10^{-3} mbar) . The orange residue was dissolved in a minimal volume of CH₂Cl₂ (ca. 2 mL) and passed through a silica gel column, first with a 1:1 mixture of CH₂Cl₂ and n-hexane to elute any cis-[M(CO)₄(PH₂Fc)₂], followed by a 3:1 mixture to elute the product. The orange band corresponding to the product was collected and the solvent evaporated under reduced pressure until pale orange crystals of pure fac-[M(CO)₃(PH₂Fc)₃] formed. The crystals where isolated by filtration, washed with *n*-hexane $(3 \times 10 \text{ mL})$ and dried under vacuum. Yields: 3a 43%, 3b 31%, 3c 52%.

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3a: 1 H NMR (CDCl₃): δ = 4.16 (s, 15H, Fe-C₅ H_5), 4.35 (s, 6H, Fe-C₅ H_4), 4.42 (s, 6H, Fe-C₅ H_4), 5.10 (m, ${}^{1}J_{HP}$ = 306.3 Hz, ${}^{3}J_{HP}$ = 15.0 Hz, 6H, P H_2 , AA'A"X₂X'₂X"₂ spin system, simulated³¹ (see ESI†)); 13 C{ 1 H} NMR (CDCl₃): δ = 67.1 (m, *ipso*-C in C_5 H₄), 69.8 (s, C_5 H₅), 70.9 (m, m-C in C_5 H₄), 73.9 (m, o-C in C_5 H₄), 230.3 (m, cCO); 31 P NMR (CDCl₃): δ = -25.9 (m, ${}^{1}J_{PH}$ = 306.0 Hz, ${}^{2}J_{PP}$ = -11.0 Hz, pH₂, AA'A"X₂X'₂X"₂ spin system, simulated³¹ (see ESI†)); IR (Nujol, cm⁻¹): 1922s (CO), 1837vs (CO); MS ESI pos., CH₂Cl₂/MeCN, m/z = 812.9 [M + Na]⁺, 789.9 [M]⁺; elemental analysis calcd (%) for $C_{33}H_{33}$ CrFe₃O₃P₃: C 50.17, H 4.21; found: C 50.02, H 4.17.

3b: 1 H NMR (CDCl₃): $\delta = 4.25$ (s, 15H, Fe-C₅ H_5), 4.36 (s, 6H, Fe-C₅ H_4), 4.44 (s, 6H, Fe-C₅ H_4), 5.08 (m, $^{1}J_{HP} = 307.0$ Hz, $^{3}J_{HP} = 8.0$ Hz, 6H, P H_2 , AA'A"X₂X'₂X"₂ spin system); 13 C{ 1 H} NMR (CDCl₃): $\delta = 66.1$ (m, *ipso*-C in C_5 H₄), 69.9 (s, C_5 H₅), 71.2 (m, *m*-C in C_5 H₄), 74.7 (m, *o*-C in C_5 H₄), 218.8 (m, CO); 31 P NMR (CDCl₃): $\delta = -63.8$ (m, $^{1}J_{PH} = 307.0$ Hz, $^{2}J_{PP} = -17$ Hz, $^{1}J_{95\text{MOP}} = 121.5$ Hz, $^{1}J_{97\text{MOP}} = 166.9$ Hz, $^{1}J_{94}$, AA'A"MX₂X'₂X"₂ spin system); IR (Nujol, cm⁻¹): 1932s (CO), 1842vs (CO); MS ESI pos., CH₂Cl₂/MeOH, m/z = 858.8 [M + Na][†]; elemental analysis calcd (%) for C₃₃H₃₃Fe₃MoO₃P₃: C 47.52; H 3.99; found: C 47.26, H 3.93.

3c: ¹H NMR (CDCl₃): δ = 4.25 (s, 15H, Fe-C₅ H_5), 4.38 (s, 6H, Fe-C₅ H_4), 4.45 (s, 6H, Fe-C₅ H_4), 5.41 (m, ¹ $J_{\rm HP}$ = 315.0 Hz, ³ $J_{\rm HP}$ = 9.0 Hz, 6H, P H_2 , AA'A"MX₂X'₂X"₂ spin system); ¹³C{¹H} NMR (CDCl₃): δ = 65.9 (d, ¹ $J_{\rm CP}$ = 57.6 Hz, *ipso*-C in C_5H_4), 70.0 (s, C_5H_5), 71.3 (m, m-C in C_5H_4), 74.6 (m, o-C in C_5H_4), 209.9 (m, CO); ³¹P NMR (CDCl₃): δ = -82.3 (m, ¹ $J_{\rm PH}$ = 315.0 Hz, ² $J_{\rm PP}$ = -9.0 Hz, ¹ $J_{\rm PW}$ = 209.0 Hz, PH₂, AA'A"MX₂X'₂X"₂ spin system); IR (Nujol, cm⁻¹): 1938s (CO), 1840vs (CO); MS ESI pos., CH₂Cl₂/MeOH, m/z = 944.9 [M + Na]⁺; elemental analysis calcd (%) for C₃₃H₃₃Fe₃O₃P₃W: C 42.99; H 3.61; found: C 42.85, H 3.63.

[W(CO)₅{PH(Fc)(CH₂CH₂CN)}] (4a). 1c (0.5 g, 0.923 mmol) and KOtBu (0.001 g, 0.092 mmol) were dissolved in THF (10 mL). Acrylonitrile (91 μ L, 1.38 mmol) was added *via* syringe. The mixture was heated to reflux for 4 hours. All volatiles were removed under reduced pressure, and the orange residue was redissolved in Et₂O and washed with HCl (1.0 mol L⁻¹, *ca.* 20 mL). The organic layer was separated and washed

three times with distilled water and then dried over anhydrous MgSO₄. After filtration, all solvent was removed under reduced pressure. The orange residue was redissolved in a minimum volume of CH_2Cl_2 and passed through a silica gel column with $\text{CH}_2\text{Cl}_2/n$ -hexane (70:30) as eluent. The product was collected in the second orange band (the first band contained unconsumed $\mathbf{1c}$, which was pure enough to be recycled). The solvent was removed to give pure $\mathbf{4a}$ as an orange powder. Yield: 0.40 g, 72%. Crystals of $\mathbf{4a}$ were obtained from $\text{CH}_2\text{Cl}_2/n$ -hexane.

¹H NMR (CDCl₃): δ = 2.2–2.5 (m, 4H, CH₂CH₂CN), 4.22 (s, 5H, Fe–C₅H₅), 4.32 (s, 1H, Fe–C₅H₄), 4.35 (s, 1H, Fe–C₅H₄), 4.45 (s, 1H, Fe–C₅H₄), 4.50 (s, 1H, Fe–C₅H₄), 5.81 (dt, ${}^{1}J_{\text{HP}}$ = 346.0 Hz, ${}^{3}J_{\text{HH}}$ = 5.4 Hz, 1H, PH); ${}^{13}\text{C}\{{}^{1}\text{H}\}$ NMR (CDCl₃): δ = 15.5 (CH₂CN), 28.1 (d, ${}^{1}J_{\text{CP}}$ = 26.3 Hz, PCH₂) 68.8 (d, ${}^{1}J_{\text{CP}}$ = 48.5 Hz, *ipso*-C in C₅H₄), 69.9 (s, C₅H₅), 72.0 (d, ${}^{3}J_{\text{CP}}$ = 10.1 Hz, *m*-C in C₅H₄), 75.0 (d, ${}^{2}J_{\text{CP}}$ = 21.2 Hz, *o*-C in C₅H₄), 118.4 (s, CH₂CN), 196.1 (d, ${}^{2}J_{\text{CP}}$ = 7.1 Hz, CO *eq*), 197.6 (d, ${}^{2}J_{\text{CP}}$ = 23.2 Hz, CO *ax*); ${}^{31}\text{P}$ NMR (CDCl₃): δ = −45.4 (d with ¹⁸³W satellites, ${}^{1}J_{\text{PH}}$ = 345.1 Hz, ${}^{1}J_{\text{PW}}$ = 235.1 Hz, *P*H); IR (Nujol, cm⁻¹): 2073w (CO), 1980m (CO), 1916vs (CO); MS ESI pos., CH₂Cl₂/MeOH, *m*/*z* = 618.0 [M + Na][†]; elemental analysis calcd (%) for C₁₈H₁₄NFeO₅PW: C 36.34, H 2.37; found: C 36.18, H 2.35.

[W(CO)₅{PH(Fc)(CH₂CH₂C(O)OMe)}] (4b). The same procedure was used as for 4a. 1c (0.134 g, 0.248 mmol) and methyl acrylate (22 μ L, 0.248 mmol) were mixed and reflux was maintained for 8 h. Purification involved column chromatography through silica gel with CH₂Cl₂ as eluent. The product was eluted from the column as the second band. Yield: 0.09 g, 58%.

¹H NMR (CDCl₃): $\delta = 2.3$ –2.6 (m, 4H, C H_2 C H_2 C(O)OMe), 3.69 (s, 3H, C(O)OMe), 4.27 (s, 5H, Fe–C₅ H_5), 4.39 (d, J = 13.2 Hz, 2H, Fe–C₅ H_4), 4.49 (d, J = 13.2 Hz, 2H, Fe–C₅ H_4), 5.76 (dt, $^1J_{\rm HP} = 344$ Hz, $^3J_{\rm HH} = 5.6$ Hz, 1H, PH); 13 C(1 H) NMR (CDCl₃): $\delta = 26.5$ (d, $^1J_{\rm CP} = 29.7$ Hz, PCH₂), 31.0 (s, CH₂C(O)OMe), 52.2 (s, OMe), 69.8 (s, C_5 H₅), 70.7 (d, $^1J_{\rm CP} = 47.7$ Hz, ipso-C in C_5 H₄), 71.6 (d, $^3J_{\rm CP} = 9.1$ Hz, m-C in C_5 H₄), 74.5 (d, $^2J_{\rm CP} = 19.2$ Hz, o-C in C_5 H₄), 172.4 (d, $^3J_{\rm CP} = 12.1$ Hz, C(O) OMe), 196.5 (d, $^2J_{\rm CP} = 7.1$ Hz, CO eq), 198.3 (d, $^2J_{\rm CP} = 21.1$ Hz, CO ax); 31 P NMR (CDCl₃): $\delta = -42.6$ (d with 183 W satellites, $^1J_{\rm PH} = 343.0$ Hz, $^1J_{\rm PW} = 231.7$ Hz, PH); IR (Nujol, cm⁻¹): 2071m (CO), 1978w (CO), 1914vs (CO), 1738m (C=O); MS ESI neg., CH₂Cl₂/MeOH, m/z = 626.8 [M - H]⁻; elemental analysis calcd (%) for C₁₉H₁₇FeO₇PW: C 36.34, H 2.73; found: C 36.40, H 2.75.

FcP(CH₂CH₂CN)₂ (5). FcPH₂ (0.5 g, 2.293 mmol) and KOtBu (0.026 g, 0.229 mmol) were dissolved in THF (10 mL). Acrylonitrile (0.30 μ L, 4.587 mmol) was added *via* syringe and the mixture was heated to reflux for 15 h. After cooling the reaction mixture to room temperature, all volatiles were removed under reduced pressure. The orange residue was dissolved in a minimum of CH₂Cl₂ and the product isolated by column chromatography through a silica gel column under an inert atmosphere with CH₂Cl₂ as eluent. After collecting the second band (the first was pure FcPH₂) all solvent was removed to

leave pure $FcP(CH_2CH_2CN)_2$ as an oily orange solid. Yield: 0.52 g, 70%.

¹H NMR (CDCl₃,): δ = 1.78 (m, 4H, CH₂CH₂CN), 2.36 (br, 4H, CH₂CH₂CN), 4.13 (s, 5H, Fe-C₅H₅), 4.18 (br, 2H, Fe-C₅H₄), 4.27 (s, 2H, Fe-C₅H₄); ¹³C{¹H} NMR (CDCl₃): δ = 16.5 (d, ² $J_{\rm CP}$ = 7.4 Hz, CH₂CN), 20.5 (d, ¹ $J_{\rm CP}$ = 15.1 Hz, PCH₂), 68.1 (d, ¹ $J_{\rm CP}$ = 5.1 Hz, *ipso*-C in C_5 H₄), 69.0 (s, C_5 H₅), 71.2 (s, *m*-C in C_5 H₄), 74.6 (d, ² $J_{\rm CP}$ = 13.4 Hz, *o*-C in C_5 H₄), 119.3 (s, CH₂CN); ³¹P NMR (CDCl₃): δ = -74.4 (s); MS ESI pos., CH₂Cl₂/MeOH, m/z = 325.06 [M + H]⁺.

Crystal structure determinations

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The data were collected on a Gemini area detector diffractometer (Rigaku Inc.) using Mo-K α radiation ($\lambda = 71.073$ pm) and ω -scan rotation. Data reduction was performed with CrysAlis-Pro³² including the program SCALE3 ABSPACK for empirical absorption correction. The structures of 1a,c, 2a-c and 3a,b were solved by direct methods and that of 4a was solved with Patterson methods with SHELXS-97³³ or SIR92.³⁴ The refinement was performed with SHELXL-97.³³ As a result of the extremely small and moderately diffracting crystal (small needle), the carbon atoms of 2c were refined isotropically. The non-hydrogen atoms of all other structures were refined with anisotropic thermal parameters. A difference-density Fourier map was used to locate all hydrogen atoms of 1a and 1c, whereas H atoms of all other structures were calculated on idealised positions by using the riding model. The structures 1a and 1c are isostructural. This is also the case for the series 2a-c and 3a,b (see Table S1, ESI†). Structure figures were generated with ORTEP35 and DIAMOND-3.36 CCDC 1420127 (1a), 1420128 (1c), 1420129 (2a), 1420130 (2b), 1420131 (2c), 1420132 (3a), 1420133 (3b) and 1420134 (4a) contain the supplementary crystallographic data for this paper.

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References

- 1 (a) T. B. Rauchfuss, in *Homogeneous Catalysis with Metal Phosphine Complexes*, ed. L. H. Pignolet, Plenum Press, New York, 1993, ch. 7; (b) *Phosphorus(III) Ligands in Homogeneous Catalysis: Design and Synthesis*, ed. P. C. Kamer and P. W. N. M. van Leeuven, John Wiley & Sons Ltd., UK, 2012; (c) A. Behr and P. Neubert, *Applied Homogeneous Catalysis*, Wiley-VCH Verlag & Co. KGaA, 2012.
- 2 D. E. C. Corbridge, Phosphorus: Chemistry, Biochemistry and Technology, CRC Press, Taylor & Francis Group, Boca Raton, FL, 6th edn, 2013.

- 3 J. T. Fleming and L. J. Higham, Coord. Chem. Rev., 2015, 297-298, 127.
- 4 W. Henderson and S. R. Alley, *J. Organomet. Chem.*, 2002, 656, 120.
- 5 N. J. Goodwin, W. Henderson, B. K. Nicholson, J. Fawcett and D. R. Russell, *J. Chem. Soc., Dalton Trans.*, 1999, 1785.
- 6 N. J. Goodwin, W. Henderson and B. K. Nicholson, *Chem. Commun.*, 1997, 31.
- 7 P. P. Power, R. A. Bartlett, M. M. Olmstead and G. A. Sigel, Inorg. Chem., 1987, 26, 1941.
- 8 P. P. Power, B. Twamley, C. Hwang and N. J. Hardman, J. Organomet. Chem., 2000, 609, 152.
- 9 K. V. Katti, K. R. Prabhu, N. Pillarsetty and H. Gali, *J. Am. Chem. Soc.*, 2000, **122**, 1554.
- 10 R. M. Hiney, L. J. Higham, H. Müller-Bunz and D. G. Gilheany, *Angew. Chem.*, 2006, **118**, 7406, (*Angew. Chem. Int. Ed.*, 2006, **45**, 7248).
- 11 (a) P. Štěpnička, Ferrocenes. Ligands, Materials and Biomolecules, John Wiley & Sons Ltd., West Sussex, 2008; (b) A. Togni and T. Hayashi, Ferrocenes. Homogeneous Catalysis. Organic Synthesis. Material Science, VCH, New York, Weinheim, 1995.
- 12 S. Tschirschwitz, P. Lönnecke and E. Hey-Hawkins, J. Chem. Soc., Dalton Trans., 2007, 1377.
- 13 C. Spang, F. T. Edelmann, M. Noltemeyer and H. W. Roesky, *Chem. Ber.*, 1989, **122**, 1247.
- 14 R. Kalio, P. Lönnecke and E. Hey-Hawkins, *J. Organomet. Chem.*, 2008, **693**, 590.
- 15 R. Kalio, P. Lönnecke, A. Cinquantini, P. Zanello and E. Hey-Hawkins, *Z. Anorg. Allg. Chem.*, 2007, **633**, 2470.
- 16 S. I. M. Paris, F. R. Lemke, R. Sommer, P. Lönnecke and E. Hey-Hawkins, *J. Organomet. Chem.*, 2005, **690**, 1807.
- 17 S. I. M. Paris, J. L. Petersen, E. Hey-Hawkins and M. P. Jensen, *Inorg. Chem.*, 2006, **45**, 5561.
- 18 R. Sommer, P. Lönnecke, P. K. Baker and E. Hey-Hawkins, *Inorg. Chem. Commun.*, 2002, **5**, 115.
- 19 R. Sommer, P. Lönnecke, J. Reinhold, P. K. Baker and E. Hey-Hawkins, *Organometallics*, 2005, **24**, 5256.
- 20 J. Svara, N. Weferling and T. Hofmann, Phosphorus Compounds, Organic, in *Ullmann's Encyclopedia of Industrial Chemistry*, John Wiley & Sons, Inc, 2008.
- 21 W. A. Herrmann and A. Salzer, Synthetic Methods of Organometallic and Inorganic Chemistry, Thieme, New York, 1996, vol. 1.
- 22 J. C. Kotz, C. L. Nivert, J. M. Lieber and R. C. Reed, J. Organomet. Chem., 1975, 84, 255.
- 23 O. Kühl, Phosphorus-31 NMR Spectroscopy: A Concise Introduction for the Synthetic Organic and Organometallic Chemist, Springer, 2008.
- 24 R. H. Crabtree, *The Organometallic Chemistry of the Tran*sition Metals, John Wiley & Sons, Inc., New Jersey, 5th edn, 2009.
- 25 T. Campbell, A. M. Gibson, R. Hart, S. D. Orchard, S. J. A. Pope and G. Reid, J. Organomet. Chem., 1999, 592, 296

Dalton Transactions

Rosenberg, ACSCatal., (b) S. A. Pullarkat and P.-H. Leung, Top. Organomet. Chem., 2013, 43, 145; (c) Science of Synthesis, Stereoselective Synthesis, ed. A. L. Reznichenko and K. C. Hultzsch, J. G. De Vries, G. A. Molander and P. A. Evans, 2011, vol. 1, p. 689; (d) D. S. Glueck, Top. Organomet. Chem., 2010, 31, 65; (e) O. Delacroix and A. C. Gaumont, Curr. Org. Chem., 2005, 9, 1851; (f) W. Malisch, B. Klupfel, D. Schumacher and M. Nieger, J. Organomet. Chem., 2002, 661, 95; (g) D. K. Wicht and D. S. Glueck, in Catalytic Heterofunctionalization, ed. A. Togni and H. Grützmacher, Wiley-VCH Verlag GmbH, 2001, ch. 5; (h) I. P. Beletskaya, V. P. Ananikov and L. L. Khemchyan, in Phosphorus Chemistry: Catalysis and Material Science Applications, ed. M. Peruzzini and L. Gonsalvi, Springer, 2011, ch. 8, vol. 37; (i) M. B. Ghebreab, C. A. Bange and R. Waterman, J. Am. Chem. Soc., 2014, 136, 9240; (j) I. V. Basalov, V. Dorcet, G. K. Fukin, J.-F. Carpentier, Y. Sarazin and A. A. Trifonov, Chem. - Eur. J., 2015, 21, 6033; (k) C. A. Bange, M. B. Ghebreab, A. Ficks, N. T. Mucha, L. Higham and Waterman, Dalton Trans., 2015, DOI: 10.1039/ C5DT03544A.

- 27 A. J. Downard, N. J. Goodwin and W. Henderson, *J. Organomet. Chem.*, 2003, **676**, 62.
- 28 J. Tong, S. Liu, S. Zhang and S. Z. Li, Spectrochim. Acta, Part A, 2007, 67, 837.
- 29 W. L. F. Armarego and C. L. L. Chai, *Purification of Laboratory Chemicals*, Butterworth-Heinemann, Burlington, 5th edn, 2003.
- 30 R. K. Harris, E. D. Becker, S. M. Cabral De Menezes, R. Goodfellow and P. Granger, *Concepts Magn. Reson.*, 2002, 14, 326.
- 31 Spectra have been simulated with the software MestReNova Version: 8.0.2-11021, 2012 Mestrelab Research S. L.
- 32 CrysAlis-Pro: Data collection and data reduction software package, Rigaku Inc.
- 33 SHELX includes SHELXS-97, SHELXL-97: G. M. Sheldrick, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 2008, **64**, 112.
- 34 A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi, J. Appl. Crystallogr., 1994, 27, 435.
- 35 ORTEP3 for Windows: L. J. Farrugia, J. Appl. Crystallogr., 1997, 30, 565.
- 36 K. Brandenburg, *DIAMOND 3*, Crystal Impact GbR, Bonn, Germany.