Dalton Transactions

PAPER

CrossMark

Cite this: *Dalton Trans.*, 2016, **45**, 2208

Received 31st August 2015, Accepted 3rd November 2015 DOI: 10.1039/c5dt03374h

www.rsc.org/dalton

Introduction

The majority of organometallic phosphine complexes involve mono-, bi- or polydentate tertiary phosphines,¹ 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.^{2,3} Several air-stable primary and secondary phosphines have been reported;^{4–10} developments in this area include the use of bulky aryl groups^{7,8} or aminoalkyl substituents.⁹ A recent review by Higham *et al.* gives an excellent overview on primary phosphine chemistry, including air-stable phosphines.³

Due to the redox properties of the ferrocenyl unit and the possibility to readily obtain chiral compounds,¹¹ ferrocenylphosphines are an important class of ligands in transition metal chemistry.^{11,12} Henderson *et al.*^{4–6} used the methylferrocenyl fragment to stabilise primary phosphines. FcCH₂PH₂ [Fc = Fe(η^{5} -C₅H₄)(η^{5} -C₅H₅)] proved to be indefinitely air-stable,⁶ probably due to electronic rather than steric effects,

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) $[Fc = Fe(\eta^5-C_5H_4)(\eta^5-C_5H_5)]$ 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.

as well as having the ability to coordinate to molybdenum carbonyls or $[{RuCl_2(p-cymene)}_2]$ (p-cymene = 1-Me-4-*i*PrC₆H₄,) 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)₃¹⁴ 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 $[MI_2(CO)_3(PH_2Fc)_2]$ (M = Mo, W),¹⁹ $[Cp^*TaCl_4(PH_2Fc)]^{15}$ (Cp* = C₅Me₅) and $[RuCl_2(p-cymene)(PH_2Fc)]$.¹⁷ Presented below is the synthesis and characterisation of the ferrocenylphosphine transition metal carbonyl 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; 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

ROYAL SOCIETY OF CHEMISTRY

View Article Online

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

products [W(CO)₅{PH(Fc)(CH₂CH₂CN)}] (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 FcPH2³ 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 $(CO)_4(PH_2Fc)_2$] (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 $cis-[M(CO)_4(PH_2Fc)_2]$ (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(PH₂Fc)] (1a, M = Cr; 1b, M = Mo; 1c, 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] (3a, M = Cr; 3b, M = Mo; 3c, M = W) were obtained from three equivalents of FcPH₂ and fac-[M(CO)₃(NCR)₃] (M = Cr, Mo, R = Me; M = W, R = Et²¹ in dichloromethane overnight at room temperature (Scheme 3). The air- and moisture-stable products were purified by column chromatography.

Spectroscopic data

The $^{31}\text{P}\{^{1}\text{H}\}$ 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 ³¹P NMR spectra these singlets split into triplets $[{}^{1}J_{PH} \approx 334$ Hz (Table 1)]. In addition, the spectrum of 1c shows ³¹P-¹⁸³W coupling of 221 Hz.

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

b



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

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

Compound	δ^{31} P (ppm)	$^{1}J_{\rm PH}$ (Hz)	ν (CO) (cm ⁻¹)
FcPH ₂	-144.2	203.6	_
1a ²	-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
3b	-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	_	_

205.0 ppm, ${}^{2}J_{CP}$ = 9.2 Hz; 1c: 198.1 ppm, ${}^{2}J_{CP}$ = 22.2 Hz, 195.9 ppm, ${}^{2}J_{CP}$ = 7.1 Hz). The doublet with the larger coupling constant is assigned to the single trans carbonyl group, since ³¹P-¹³C 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 $AA'X_2X'_2$ (2a,b) or AA' $MX_2X'_2$ (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 $\{^{1}H\}$, ³¹P $\{^{1}H\}$ and ³¹P NMR spectra (AA'A" $X_2X'_2X''_2$ (3a,b) or AA'A" $MX_2X'_2X''_2$ (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.** δ ⁽³¹P) 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 $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the tungsten complexes (1c, 2c and 3c) show ${}^{31}P-{}^{183}W$ 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*- $[Mo(CO)_3(PH_2Fc)_3]$ (3b). In the ¹³C{¹H} NMR spectra of 3a-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(PH₂Fc)] (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 3Selected bond lengths (pm) and bond angles (°) for 2a-2c.Values of the second symmetry-independent molecule are given in par-
entheses []

Compound	2a (M = Cr)	2 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 $2\mathbf{c}$ 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)	3 b (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)
$\mathcal{O}(1) = \mathcal{P}(1) = \mathcal{M}(1)$	123.8/(/)	125.34(8)

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 $84.85(4)^{\circ}$ 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 $(120.6(1)^{\circ})$ 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

Paper

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 ${}^{31}P{}^{1}H$ 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 $[W(CO)_5{PH(Fc)(CH_2CH_2CN)}]$ (4a) and $[W(CO)_5{PH(Fc)(CH_2CH_2C(O)OMe)}]$ (4b) were purified by column chromatography (they are eluted considerably more slowly than 1c) and fully characterised (Scheme 4).

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



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 $J_{\rm PH}$ = 345 Hz) or -42.6 ppm (**4b**, ¹ $J_{\rm PH}$ = 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 $(87.8(1)^{\circ} \text{ to } 94.2(1)^{\circ})$ 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–C_{Fc} 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 $[W(CO)_5{PH(Fc)(CH_2CH_2CN)}]$ (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).



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 to air.

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 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) and $[M(CO)_3(PH_2Fc)_3]$ (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 $[W(CO)_5{PH(Fc)-(CH_2CH_2CO)}]$ (**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),²¹ and $FcPH_2^{3}$ 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 $\{^{1}H\}$, ³¹P $\{^{1}H\}$ and ³¹P NMR spectra were recorded with a Bruker AVANCE DRX 400 MHz instrument at 25 °C. Chemical shifts δ of ¹H, ¹³C, ³¹P 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 Ξ 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(**η**⁵-**C**₅**H**₄**PH**₂)(**η**⁵-**C**₅**H**₅) (**FcPH**₂). 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.

Paper

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, ¹*J*_{HP} = 203.6 Hz, PH₂), 4.16 (s, 5H, C₅H₅), 4.25 (s, 2H, C₅H₄), 4.27 (s, 2H, C₅H₄); ¹³C{¹H} NMR (CDCl₃): δ = 64.1 (d, ¹*J*_{CP} = 5.0 Hz, *ipso*-C in C₅H₄), 69.3 (s, C₅H₅), 70.7 (d, ³*J*_{CP} = 4.0 Hz, *m*-C in C₅H₄), 75.7 (d, ²*J*_{CP} = 13.8 Hz, *o*-C in C₅H₄); ³¹P NMR (CDCl₃): δ = -144.2 (t, ¹*J*_{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 CH_2Cl_2/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: ¹H NMR (CDCl₃): δ = 4.16 (s, 5H, Fe–C₅H₅), 4.35 (s, 4H, Fe–C₅H₄), 5.27 (d, ¹J_{HP} = 333.9 Hz, 2H, PH₂); ¹³C{¹H} NMR (CDCl₃): δ = 64.5 (d, ¹J_{CP} = 45.7 Hz, *ipso*-C in C₅H₄), 69.8 (s, C₅H₅), 71.5 (d, ³J_{CP} = 7.7 Hz, *m*-C in C₅H₄), 73.9 (d, ²J_{CP} = 12.2 Hz, *o*-C in C₅H₄), 216.1 (d, ²J_{CP} = 13.7 Hz, CO *eq*), 220.4 (d, ²J_{CP} = 7.3 Hz, *CO ax*); ³¹P NMR (CDCl₃): δ = -47.5 (t, ¹J_{PH} = 333.9 Hz, *P*H₂); 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 C₁₅H₁₁CrFeO₅P: 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–C₅H₅), 4.42 (m, 2H, Fe–C₅H₄), 4.46 (m, 2H, Fe–C₅H₄), 5.65 (d, ¹J_{HP} = 341.5 Hz, 2H, PH₂); ¹³C{¹H} NMR (CDCl₃): δ = 63.5 (d, ¹J_{CP} = 51.9 Hz, *ipso*-C in C₅H₄), 70.0 (s, C₅H₅), 71.9 (d, ³J_{CP} = 8.1 Hz, *m*-C in C₅H₄), 74.6 (d, ²J_{CP} = 13.2 Hz, *o*-C in C₅H₄), 195.9 (d, ²J_{CP} = 7.1 Hz, CO eq), 198.1 (d, ²J_{CP} = 22.2 Hz, CO ax); ³¹P NMR (CDCl₃): δ = -101.8 (t with ¹⁸³W satellites, ¹J_{PH} = 341.5 Hz, ¹J_{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 CH_2Cl_2/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: ¹H NMR (CDCl₃): δ = 4.22 (s, 10H, Fe-C₅H₅), 4.38 (br s, 4H, Fe-C₅H₄), 4.41 (br s, 4H, Fe-C₅H₄), 5.23 (m, ¹J_{HP} = 333.1 Hz, ³J_{HP} = 13.0 Hz, 4H, PH₂, AA'X₂X'₂ spin system, simulated³¹ (see ESI[†])); ¹³C{¹H} NMR (CDCl₃): δ = 65.9 (t, ¹J_{CP} = 49.5 Hz, ³J_{CP} = 25.3 Hz, *ipso*-C in C₅H₄), 69.9 (s, C₅H₅), 71.3 (t, ³J_{CP} = 7.1 Hz, ⁵J_{CP} = 3.3 Hz, *m*-C in C₅H₄), 74.0 (t, ²J_{CP} = 11.1 Hz, ⁴J_{CP} = 5.6 Hz, *o*-C in C₅H₄), 220.1 (t, ²J_{CP} = 14.4 Hz, CO cis), 226.0 (d, ²J_{CP} = 9.3 Hz, CO trans); ³¹P NMR (CDCl₃): δ = -36.3 (m, ¹J_{PH} = 333.1 Hz, ²J_{PP} = -29.0 Hz, 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, *m*/*z* = 622.9 [M + Na]⁺; elemental analysis calcd (%) for C₂₄H₂₂CrFe₂O₄P₂: C 48.04, H, 3.70; found: C 47.93, H, 3.61.

2b: ¹H 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); ¹³C{¹H} NMR (CDCl₃): δ = 64.8 (t, ¹*J*_{CP} = 48.5 Hz, ³*J*_{CP} = 24.2 Hz, *ipso*-C in *C*₅*H*₄), 69.9 (s, *C*₅*H*₅), 71.5 (t, ³*J*_{CP} = 7.1 Hz, ⁵*J*_{CP} = 3.5 Hz, *m*-C in *C*₅*H*₄), 74.7 (t, ²*J*_{CP} = 12.1 Hz, ⁴*J*_{CP} = 6.1 Hz, *o*-C in *C*₅*H*₄), 208.1 (t, ²*J*_{CP} = 9.5 Hz, *CO cis*), 214.1 (d, ²*J*_{CP} = 9.3 Hz, *CO trans*); ³¹P NMR (CDCl₃): δ = -72.4 (m, ¹*J*_{PH} = 326.4 Hz, ²*J*_{PP} = -17.0 Hz, *P*H₂ AA'X₂X'₂ spin system); IR (Nujol, cm⁻¹): 2024w (CO), 1901vs (CO), 1879s (CO); MS ESI pos., CH₂Cl₂/ MeOH, *m*/*z* = 668.8 [M + Na]⁺; elemental analysis calcd (%) for C₂₄H₂₂Fe₂MoO₄P₂: C 44.76, H 3.44; found: C 44.74, H 3.50.

2c: ¹H NMR (CDCl₃): $\delta = 4.25$ (s, 10H, Fe–C₅ H_5), 4.46 (s, 8H, Fe–C₅ H_4), 5.53 (m, ¹ $J_{\rm HP} = 328.0$ Hz, ³ $J_{\rm HP} = 12.0$ Hz, 4H, P H_2 , AA'X₂X'₂ spin system); ¹³C{¹H} NMR (CDCl₃): $\delta = 64.6$ (m, ¹ $J_{\rm CP} = 50.6$ Hz, ³ $J_{\rm CP} = 26.3$ Hz, *ipso*-C in C_5H_4), 69.9 (s, C_5H_5), 71.6 (p, ³ $J_{\rm CP} = 8.1$ Hz, ⁵ $J_{\rm CP} = 4.0$ Hz, *m*-C in C_5H_4), 74.6 (t, ² $J_{\rm CP} = 12.1$ Hz, ⁴ $J_{\rm CP} = 6.1$ Hz, *o*-C in C_5H_4), 200.0 (t, ² $J_{\rm CP} = 7.3$ Hz, CO *cis*), 204.3 (m, *CO trans*); ³¹P NMR (CDCl₃): $\delta = -94.2$ (m, ¹ $J_{\rm PH} = 328.0$ Hz, ² $J_{\rm PP} = -11.0$ Hz, ¹ $J_{\rm WP} = 214.9$ Hz, *P*H₂ 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 CH_2Cl_2 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%.

3a: ¹H NMR (CDCl₃): δ = 4.16 (s, 15H, Fe–C₅H₅), 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, ${}^{3}J_{\rm HP}$ = 15.0 Hz, 6H, PH₂, AA'A"X₂X'₂X"₂ spin system, simulated³¹ (see ESI[†])); ¹³C{¹H} NMR (CDCl₃): δ = 67.1 (m, *ipso*-C in C₅H₄), 69.8 (s, C₅H₅), 70.9 (m, m-C in C₅H₄), 73.9 (m, o-C in C_5H_4), 230.3 (m, CO); ³¹P NMR (CDCl₃): $\delta = -25.9$ (m, ¹ $J_{PH} =$ 306.0 Hz, ${}^{2}J_{PP} = -11.0$ Hz, PH_2 , $AA'A''X_2X'_2X''_2$ spin system, simulated³¹ (see ESI⁺)); IR (Nujol, cm⁻¹): 1922s (CO), 1837vs (CO); MS ESI pos., $CH_2Cl_2/MeCN$, m/z = 812.9 $[M + Na]^+$, 789.9 $[M]^+$; elemental analysis calcd (%) for C₃₃H₃₃CrFe₃O₃P₃: C 50.17, H 4.21; found: C 50.02, H 4.17.

3b: ¹H NMR (CDCl₃): δ = 4.25 (s, 15H, Fe–C₅H₅), 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, ${}^{3}J_{\rm HP}$ = 8.0 Hz, 6H, PH₂, AA'A"X₂X'₂X"₂ spin system); ${}^{13}C{}^{1}H{}$ NMR (CDCl₃): δ = 66.1 (m, *ipso*-C in C₅H₄), 69.9 (s, C₅H₅), 71.2 (m, m-C in C_5H_4), 74.7 (m, o-C in C_5H_4), 218.8 (m, CO); ³¹P NMR (CDCl₃): δ = -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, *P*H₂, AA'A"MX₂X'₂X"₂ spin system); IR (Nujol, cm⁻¹): 1932s (CO), 1842vs (CO); MS ESI pos., $CH_2Cl_2/MeOH$, $m/z = 858.8 [M + Na]^+$; 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, PH₂, AA'A"MX₂X'₂X"₂ spin system); ${}^{13}C{}^{1}H{}$ NMR (CDCl₃): δ = 65.9 (d, ¹*J*_{CP} = 57.6 Hz, *ipso*-C in *C*₅H₄), 70.0 (s, C₅H₅), 71.3 (m, m-C in C₅H₄), 74.6 (m, o-C in C₅H₄), 209.9 (m, CO); ³¹P NMR (CDCl₃): $\delta = -82.3$ (m, ¹ $J_{PH} = 315.0$ Hz, ² $J_{PP} =$ -9.0 Hz, ${}^{1}J_{PW} = 209.0$ Hz, PH_2 , $AA'A''MX_2X'_2X''_2$ spin system); IR (Nujol, cm⁻¹): 1938s (CO), 1840vs (CO); MS ESI pos., $CH_2Cl_2/MeOH$, $m/z = 944.9 [M + Na]^+$; 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 µL, 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 Et_2O 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 CH₂Cl₂ and passed through a silica gel column with CH_2Cl_2/n -hexane (70:30) as eluent. The product was collected in the second orange band (the first band contained unconsumed 1c, which was pure enough to be recycled). The solvent was removed to give pure 4a as an orange powder. Yield: 0.40 g, 72%. Crystals of 4a were obtained from CH₂Cl₂/ *n*-hexane.

¹H NMR (CDCl₃): δ = 2.2–2.5 (m, 4H, CH₂CH₂CN), 4.22 (s, 5H, Fe-C₅ H_5), 4.32 (s, 1H, Fe-C₅ H_4), 4.35 (s, 1H, Fe-C₅ H_4), 4.45 (s, 1H, Fe-C₅ H_4), 4.50 (s, 1H, Fe-C₅ H_4), 5.81 (dt, ${}^{1}J_{\text{HP}}$ = 346.0 Hz, ${}^{3}J_{HH} = 5.4$ Hz, 1H, PH); ${}^{13}C{}^{1}H$ NMR (CDCl₃): δ = 15.5 (*C*H₂CN), 28.1 (d, ¹*J*_{CP} = 26.3 Hz, P*C*H₂) 68.8 (d, ¹*J*_{CP} = 48.5 Hz, *ipso*-C in C_5H_4), 69.9 (s, C_5H_5), 72.0 (d, ${}^{3}J_{CP}$ = 10.1 Hz, *m*-C in C_5H_4), 75.0 (d, ${}^2J_{CP}$ = 21.2 Hz, *o*-C in C_5H_4), 118.4 (s, CH₂*C*N), 196.1 (d, ${}^{2}J_{CP}$ = 7.1 Hz, *CO eq*), 197.6 (d, ${}^{2}J_{CP}$ = 23.2 Hz, CO ax); ³¹P NMR (CDCl₃): $\delta = -45.4$ (d with ¹⁸³W satellites, ${}^{1}J_{PH} = 345.1$ Hz, ${}^{1}J_{PW} = 235.1$ Hz, *P*H); IR (Nujol, cm⁻¹): 2073w (CO), 1980m (CO), 1916vs (CO); MS ESI pos., $CH_2Cl_2/MeOH$, $m/z = 618.0 [M + Na]^+$; elemental analysis calcd (%) for C18H14NFeO5PW: C 36.34, H 2.37; found: C 36.18, H 2.35.

 $[W(CO)_5 \{PH(Fc)(CH_2CH_2C(O)OMe)\}]$ (4b). The same procedure was used as for 4a. 1c (0.134 g, 0.248 mmol) and methyl acrylate (22 µL, 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): δ = 2.3–2.6 (m, 4H, CH₂CH₂C(O)OMe), 3.69 (s, 3H, C(O)OMe), 4.27 (s, 5H, Fe- C_5H_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 $(dt, {}^{1}J_{HP} = 344 \text{ Hz}, {}^{3}J_{HH} = 5.6 \text{ Hz}, 1H, PH); {}^{13}C{}^{1}H$ NMR (CDCl₃): δ = 26.5 (d, ¹J_{CP} = 29.7 Hz, PCH₂), 31.0 (s, CH₂C(O)-OMe), 52.2 (s, OMe), 69.8 (s, C_5H_5), 70.7 (d, ${}^{1}J_{CP}$ = 47.7 Hz, *ipso*-C in C_5H_4), 71.6 (d, ${}^{3}J_{CP}$ = 9.1 Hz, *m*-C in C_5H_4), 74.5 (d, ${}^{2}J_{CP}$ = 19.2 Hz, o-C in $C_{5}H_{4}$), 172.4 (d, ${}^{3}J_{CP}$ = 12.1 Hz, C(O)OMe), 196.5 (d, ${}^{2}J_{CP}$ = 7.1 Hz, CO eq), 198.3 (d, ${}^{2}J_{CP}$ = 21.1 Hz, CO ax); ³¹P NMR (CDCl₃): $\delta = -42.6$ (d with ¹⁸³W satellites, ¹J_{PH} = 343.0 Hz, ${}^{1}J_{PW}$ = 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 µL, 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, ²J_{CP} = 7.4 Hz, CH₂CN), 20.5 (d, ¹J_{CP} = 15.1 Hz, PCH₂), 68.1 (d, ¹J_{CP} = 5.1 Hz, *ipso*-C in C₅H₄), 69.0 (s, C₅H₅), 71.2 (s, *m*-C in C₅H₄), 74.6 (d, ²J_{CP} = 13.4 Hz, *o*-C in C₅H₄), 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

The data were collected on a Gemini area detector diffractometer (Rigaku Inc.) using Mo-K α radiation (λ = 71.073 pm) and w-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.

Acknowledgements

We gratefully acknowledge financial support from by the European Union and the Free State of Saxony (Landesinnovationspromotion for J. P. S.) and the Graduate School Leipzig School of Natural Sciences – Building with Molecules and Nanoobjects (BuildMoNa).

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 Transition 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.

- Rosenberg, ACS Catal., 2013, 2845; 26 (a) L. 3. (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/ R. 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.