

**Selective borane reduction of phosphinoferrocene carbaldehydes to the corresponding phosphinoalcohol-borane adducts. The coordination behaviour of 1-(diphenylphosphino)-1'-(methoxymethyl)ferrocene, a new ferrocene O,P-hybrid donor prepared from such an adduct.**

Petr Štěpnička\* and Ivana Císařová

## Supporting Information

### Contents

The synthesis and crystal structures of compounds <b>3</b> and <b>9</b> .....	S-2
Description of the crystal packing of adduct <b>5</b> .....	S-6
The crystal structure of <i>trans</i> - <b>17</b> .....	S-7
A view of the coordination geometry and crystal packing diagram for <b>18</b> .....	S-8
Summary of crystallographic data (Tables S1 and S2) .....	S-9
References .....	S-12

## The synthesis and crystal structures of **3** and **9**

**1'-(Dicyclohexylphosphino)-1-bromoferrocene (9).** *n*-Butyllithium (4 mL 2.5 M in hexanes, 10 mmol) was added drop-wise to a solution of 1,1'-dibromoferrocene<sup>1</sup> (3.44 g, 10 mmol) in dry THF (35 mL) with stirring and cooling in a dry ice/ethanol bath (ca. -75°C). Stirring was continued at -75°C for 15 min, whereupon the reaction mixture deposited an orange precipitate. Then, chlorodicyclohexylphosphine (2.4 mL, 11 mmol) was introduced, causing an immediate dissolution of the precipitate, and the resulting mixture was stirred at the same temperature for 15 min and at room temperature for 90 min. The reaction was terminated by the addition of saturated aqueous NaHCO<sub>3</sub> and diethyl ether. The organic layer was separated, washed with saturated aqueous NaHCO<sub>3</sub>, dried over MgSO<sub>4</sub> and filtered through a silica gel pad, eluting with hexane-diethyl ether (1:1). The eluate was evaporated under vacuum and the residue was dissolved in hot heptane (ca. 60 mL). The solution was treated with charcoal, filtered and the filtrate was slowly cooled down to 4°C to afford a crystalline solid, which was filtered off, washed with cold pentane and dried under vacuum. Yield of **9**: 3.25 g (70%), orange crystals. According to the NMR spectra, the phosphine contained some impurities (ca. 5%), most likely the corresponding phosphine oxide. Crystallisation of the residuum from the first crystallisation afforded another batch (ca. 0.3 g) of a less pure product.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.98-2.03 (m, 22 H, Cy), 4.07, 4.20, 4.33 and 4.37 (4× br s, 2 H, C<sub>5</sub>H<sub>4</sub>).  
<sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 26.40 (br s), 27.29 (br virtual t) and 30.31 (br virtual t) (3× CH<sub>2</sub> of Cy); 33.39 (br d, *J*<sub>PC</sub> ≈ 11 Hz, CH of Cy), 68.77 (br s), 71.11 (br s), 72.83 (br s) and 73.83 (br d, *J* ≈ 10 Hz) (4× CH of C<sub>5</sub>H<sub>4</sub>); 78.06 (C<sub>ipso</sub> of C<sub>5</sub>H<sub>4</sub>Br). Note: The signal due to C<sub>ipso</sub> of C<sub>5</sub>H<sub>4</sub>PCy<sub>2</sub> was not identified. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ -7.4 (s). HR MS (EI) calc. for C<sub>22</sub>H<sub>30</sub><sup>79</sup>Br<sup>56</sup>FeP (M<sup>+</sup>) 460.0618; found 460.0629.

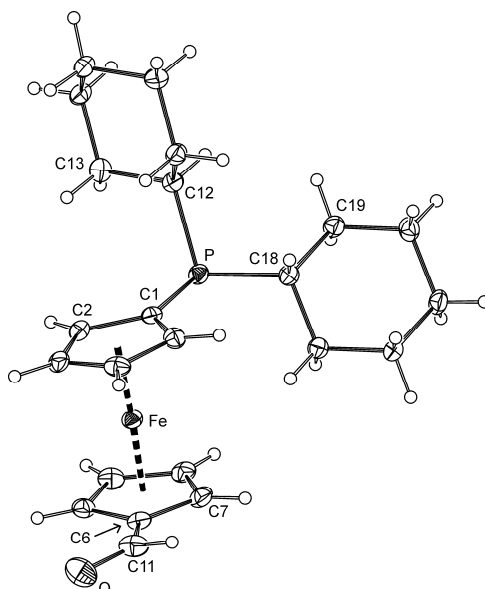
**1'-(Dicyclohexylphosphino)ferrocene-1-carbaldehyde (3).** *n*-Butyllithium (2.8 mL 2.5 M in hexanes, 7 mmol) was added to a solution of **9** (2.77 g, 6 mmol) in dry THF (30 mL) with stirring and cooling to ca. -75°C. The stirring was continued at this temperature for 15 min, during which time the reaction mixture turned from orange-brown to orange-red. Dry *N,N*-dimethylformamide (1.5 ml, ca. 20 mmol) was introduced, causing the colour of the reaction mixture to return to the initial amber-orange, and stirring was continued at ca. -75°C for 15 min and then at room temperature for 90 min. The reaction mixture was quenched by the addition of water, saturated aqueous NaCl and 3 M HCl (5 mL each, in this order) and stirring for 15 min. The resulting mixture was diluted with THF and the red organic layer was separated, washed with brine and dried over MgSO<sub>4</sub>. Then, it was passed through a

silica gel column and the column was washed with THF. The orange-red eluate was evaporated and the residue was dissolved in warm ethyl acetate (30 mL). The solution was filtered, diluted with hexane (30 mL) and allowed to crystallise at  $-18^{\circ}\text{C}$  overnight. The separated crystalline solid was filtered off, washed with pentane and dried under vacuum. Yield of **3**: 1.31 g (53%), red crystals. The product typically contained ca. 5% of P=O impurities.

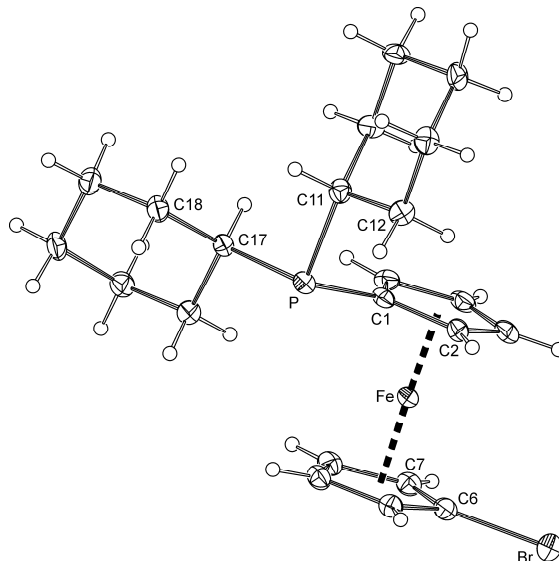
$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.99-2.03 (m, 22 H, Cy), 4.26, 4.43, 4.58 and 4.76 (4 $\times$  br s, 2 H,  $\text{C}_5\text{H}_4$ ); 9.97 (s, 1 H, CHO).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  26.33 (s), 27.25 (virtual t,  $J' \approx 9$  Hz) and 30.18 (virtual t,  $J' \approx 11$  Hz) (3 $\times$   $\text{CH}_2$  of Cy); 33.34 (br d,  $J_{\text{PC}} \approx 11$  Hz, CH of Cy); 70.55 (s), 71.04 (br s), 72.75 (br d,  $J_{\text{PC}} \approx 10$  Hz) and 73.97 (s) (4 $\times$  CH of  $\text{C}_5\text{H}_4$ ); 79.54 ( $\text{C}_{\text{ipso}}$  of  $\text{C}_5\text{H}_4\text{CHO}$ ), 193.69 (CHO). Note: The signal due to  $\text{C}_{\text{ipso}}$  of  $\text{C}_5\text{H}_4\text{PCy}_2$  was not found.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$   $-7.5$  (s). IR (Nujol):  $\nu/\text{cm}^{-1}$   $\nu_{\text{C=O}}$  1685 vs, 16667 s. HR MS (EI) calc. for  $\text{C}_{23}\text{H}_{31}^{56}\text{FeOP}$  ( $\text{M}^+$ ) 410.1465; found 410.1462. Anal. calc. for  $\text{C}_{23}\text{H}_{31}\text{FeOP}$  (410.3): C 67.32, H 7.62%. Found: C 67.45, H 7.67%.

Compounds **3** and **9** crystallise both with the symmetry of the space group  $P2_12_12_1$  as racemic twins. The compounds are practically isostructural, which in turn indicates that their crystal structures are determined mainly by solid-state packing of the bulky phosphinoferrocenyl groups when strong and directional intermolecular contacts (e.g., classical hydrogen bonds) are absent.

Views of the molecular structures of **3** and **9** are shown in Figures S1 and S2. The structural data are unexceptional when compared with those reported earlier for  $\text{Ph}_2\text{PfcBr}$ ,  $\text{Ph}_2\text{P(S)fcCHO}$ ,<sup>2</sup>  $\text{Ph}_2\text{PfcCHO}$ ,<sup>3</sup> and  $\text{fc(CHO)}_2$ <sup>4</sup> (fc = ferrocene-1,1'-diyl). Ferrocene moieties in both molecules assume eclipsed anticlinal conformations with the angles of the bond vectors C1-P/C6-C11 for **3** and C1-P/C6-Br for **9** being  $152.7(3)$  and  $133.2(3)^{\circ}$ , respectively. The formyl group in **3** is slightly rotated from the plane of its bonding cyclopentadienyl ring. The angle subtended by the C11-O bond and the C(6-10) plane is  $7.1(3)^{\circ}$ .



**Figure S1.** PLATON<sup>5</sup> plot of the molecular structure of **3** showing the atom labelling scheme and displacement ellipsoids at the 30 % probability level. Selected distances and angles (in Å and deg): Fe-Cg<sup>P</sup> 1.651(2), Fe-Cg<sup>Br</sup> 1.648(2), ∠Cp<sup>P</sup>,Cp<sup>Br</sup> 4.3(2); P-C1 1.831(3), P-C12 1.875(3), P-C18 1.861(3), C11-C6 1.448(5), C11-O 1.228(5); C6-C11-O 123.1(4). The ring planes are defined as follows: Cp<sup>P</sup> = C(1-5), Cp<sup>C</sup> = C(6-10); Cg<sup>P/C</sup> are the respective centroids.



**Figure S2.** PLATON<sup>5</sup> plot of the molecular structure of **9** showing the atom labelling scheme and displacement ellipsoids at the 30 % probability level. Selected distances and angles (in Å and deg): Fe-Cg<sup>P</sup> 1.651(2), Fe-Cg<sup>Br</sup> 1.647(2), ∠Cp<sup>P</sup>,Cp<sup>Br</sup> 3.4(3); P-C1 1.834(5), P-C11 1.876(5), P-C17 1.853(5), Br-C6 1.890(5). The ring planes are defined as follows: Cp<sup>P</sup> = C(1-5), Cp<sup>Br</sup> = C(6-10); Cg<sup>P/Br</sup> are the respective centroids

*Crystallographic data and structure refinement parameters for 3:* C<sub>23</sub>H<sub>31</sub>FeOP, *M* = 410.3, red prism from ethyl acetate, 0.25 × 0.25 × 0.30 mm<sup>3</sup>; orthorhombic, space group *P2*<sub>1</sub>*2*<sub>1</sub>*2*<sub>1</sub> (no. 19), *T* = 150(2) K, *a* = 6.4488(3), *b* = 7.7891(4), *c* = 39.978(2) Å; *V* = 2008.1(2) Å<sup>3</sup>, *Z* = 4, *D*<sub>calc</sub> = 1.357 g mL<sup>-1</sup>. Full-set diffraction data ( $\pm h\pm k\pm l$ ,  $\theta_{\max} = 27.5^\circ$ , completeness 99.2%) were recorded with a Nonius Kappa CCD diffractometer (Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å); absorption was neglected ( $\mu = 0.840$  mm<sup>-1</sup>). A total of 12140 was measured, from which 4545 were unique (*R*<sub>int</sub> = 6.5%), and 3362 observed (*I* > 2 $\sigma$ (*I*) criterion).

The structure was solved by direct methods (SIR97<sup>6</sup>) and refined by full-matrix least squares on *F*<sup>2</sup> (SHELXL97<sup>7</sup>). Non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in their calculated positions and refined as riding atoms with *U*<sub>iso</sub>(H) assigned to a multiple of *U*<sub>eq</sub> of their bonding atom. The refinement converged ( $\Delta/\sigma_{\max} = 0.000$ , 236 parameters) to *R* = 4.46% for the observed, and *R* = 7.88%, *wR* = 10.52%, GOF = 1.005 for all diffractions. The final difference map displayed no peaks of chemical significance ( $\Delta\rho_{\max} = 0.36$ ,  $\Delta\rho_{\min} = -0.67$  e Å<sup>-3</sup>). CCDC deposition no. 906417.

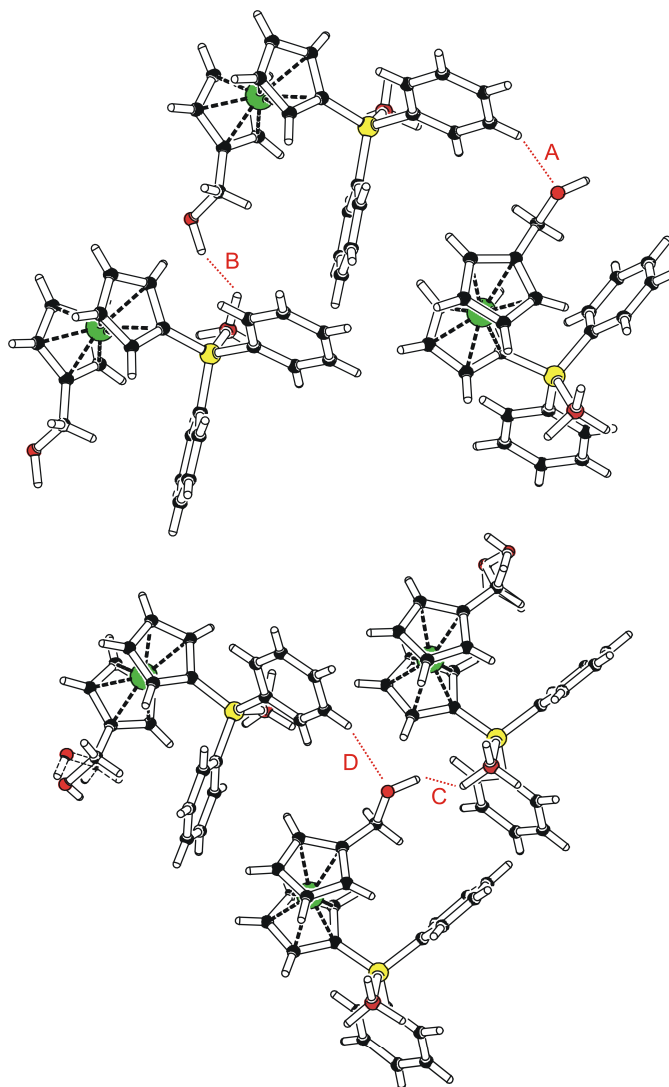
*Crystallographic data and structure refinement parameters for 9:* C<sub>22</sub>H<sub>31</sub>BrFeP, *M* = 461.2, orange-yellow prism from heptane, 0.25 × 0.28 × 0.35 mm<sup>3</sup>; orthorhombic, space group *P2*<sub>1</sub>*2*<sub>1</sub>*2*<sub>1</sub> (no. 19), *T* = 150(2) K, *a* = 6.3769(1), *b* = 7.9364(2), *c* = 39.9711(8) Å; *V* = 2022.92(7) Å<sup>3</sup>, *Z* = 4, *D*<sub>calc</sub> = 1.514 g mL<sup>-1</sup>. Full-set diffraction data ( $\pm h\pm k\pm l$ ,  $\theta_{\max} = 27.5^\circ$ , completeness 99.7%) were recorded with a Nonius Kappa CCD diffractometer (graphite-monochromatised Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å); an absorption correction was applied ( $\mu = 2.802$  mm<sup>-1</sup>; transmission factors: 0.376-0.535). A total of 16709 was measured, from which 4616 were unique (*R*<sub>int</sub> = 6.4%), and 4070 observed according to the *I* > 2 $\sigma$ (*I*) criterion.

The structure was solved by direct methods (SIR97<sup>6</sup>) and refined by full-matrix least squares based on *F*<sup>2</sup> (SHELXL97<sup>7</sup>). Non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in their calculated positions and refined as riding atoms with *U*<sub>iso</sub>(H) assigned to a multiple of *U*<sub>eq</sub> of their bonding atom. The refinement converged ( $\Delta/\sigma_{\max} = 0.001$ , 228 parameters) to *R* = 4.40% for the observed, and *R* = 5.30%, *wR* = 11.60%, GOF = 1.116 for all diffractions. The final difference map displayed no peaks of chemical significance ( $\Delta\rho_{\max} = 1.56$ ,  $\Delta\rho_{\min} = -0.60$  e Å<sup>-3</sup>). CCDC deposition no. 906418.

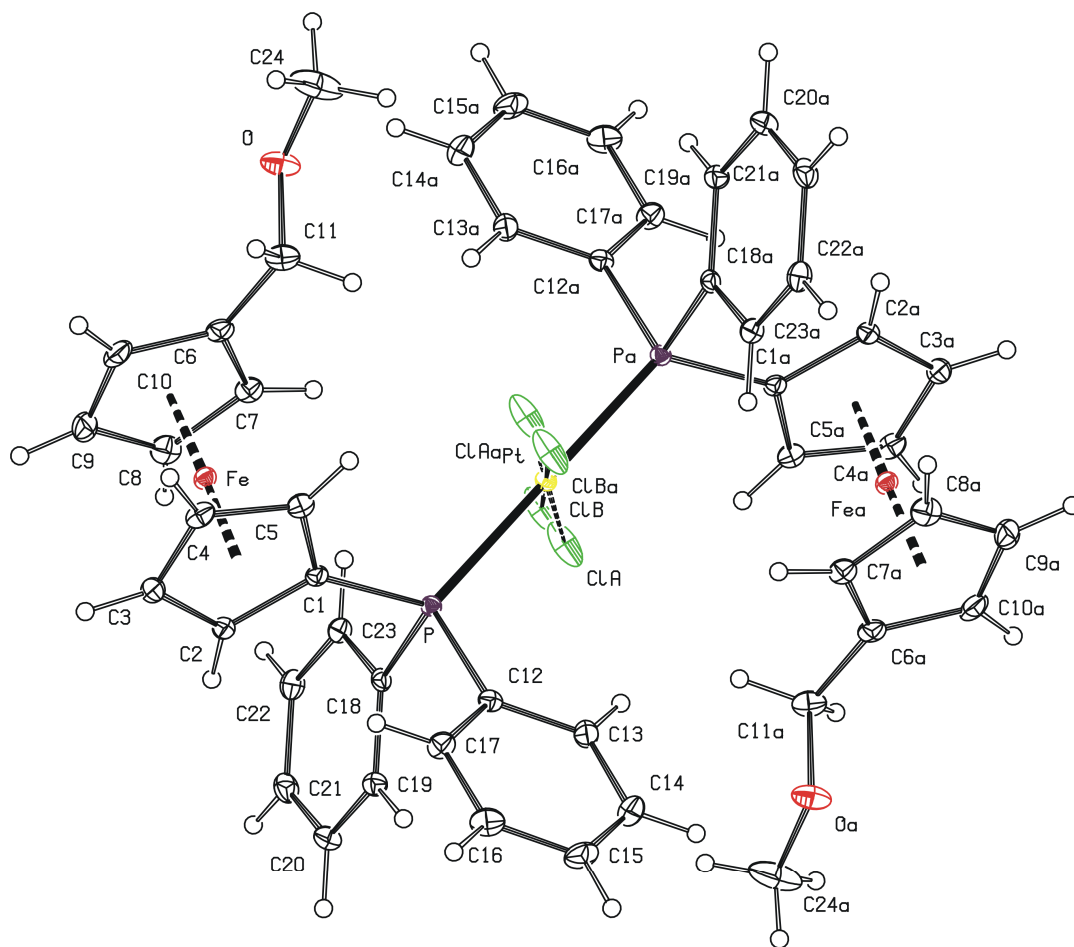
## Description of the crystal packing of adduct **5**

The crystal packing of **5** is difficult to interpret in full because of the high number of structurally independent molecules and the disorder of the CH<sub>2</sub>OH moieties. Nonetheless, even in this case, a fine interplay of C–H...O and dihydrogen interactions (O–H...HB and C–H...HB) and  $\pi$ - $\pi$  stacking seem to determine the crystal assembly. No O–H...O interactions were not detected in the structure.

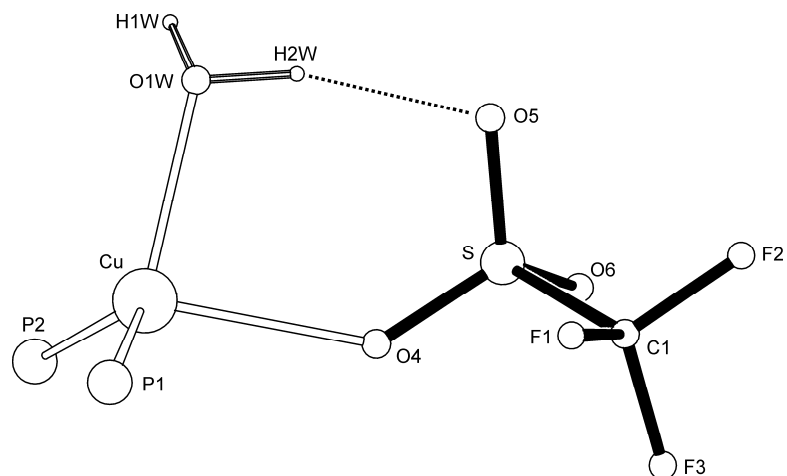
Molecules **1** in the structure of adduct **5** associate into helical arrays via C120–H120...O1 contacts between a molecule and its image related by the crystallographic screw axis (**A**: C120...O1 = 3.343(4) Å, angle at H120 = 143°). Each molecule **1** further forms a dihydrogen bond towards one BH hydrogen, H10B located in a proximal molecule **4** (**B**: O1–H91...H10B<sup>i</sup>: H91...H10B = 2.03 Å, O1...H10B = 2.95 Å, angle at H91 = 150°; *i.* 2–*x*, –½+*y*, ½–*z*). Molecule **4** further acts as a dihydrogen bond acceptor for H8B in a neighbouring molecule **3** (**C**: O4–H94...H8B<sup>ii</sup>: H94...H8B = 1.93 Å, O4...H8B = 2.85 Å, angle at H94 = 145°; *ii.* *x*, ½–*y*, –½+*z*) and forms an additional O4...H222<sup>iii</sup>–C222<sup>iii</sup> contact with molecule **2** (**D**: C222...O4 = 3.396(4) Å, angle at H222 = 146°; *iii.* 1–*x*, 1–*y*, –*z*).



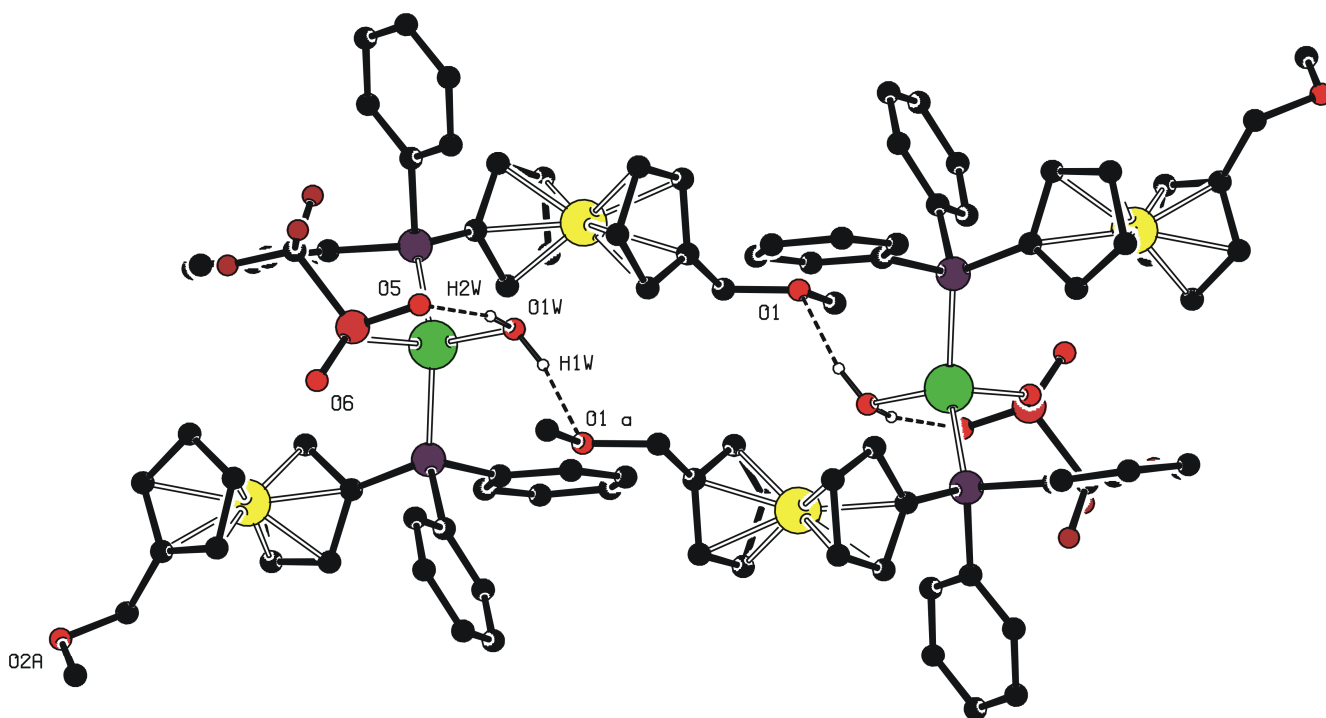
In addition, there are a number of other intermolecular C–H...O (some with unfavourably acute angles at the H atoms) and C–H...HB contacts detectable in the crystal structure with no clear cut-off. These interactions and interactions of the  $\pi$ -systems further complicate the crystal assembly.



**Figure S3.** PLATON<sup>5</sup> plot of the molecular structure of *trans*-17 showing full atom labelling scheme and displacement ellipsoids at the 30% probability level.



**Figure S4.** A detailed view of the coordination environment of Cu(I) in complex **18** showing the intramolecular O–H···O hydrogen bond (a projection perpendicular to the Cu–O1W bond is shown).



**Figure S5.** Partial packing diagram for **18** showing O···H–O hydrogen bonds as dashed lines. Hydrogen bond parameters: O5···H2W–O1W; O5···O1W = 2.807(1) Å, angle at H2W = 162°; O1<sub>a</sub>···H1W–O1W; O1<sub>a</sub>···O1W = 2.802(3) Å, angle at H1W = 162° (a = 2–x, 2–y, 2–z).



**Note:** Single crystals suitable for X-ray diffraction measurements were obtained from hot heptane (**5**: yellow plate,  $0.10 \times 0.15 \times 0.53 \text{ mm}^3$ ; ( $S_p$ )-**7**: orange bar,  $0.03 \times 0.05 \times 0.23 \text{ mm}^3$ ; **8**: orange prism,  $0.11 \times 0.24 \times 0.27 \text{ mm}^3$ ; **9**: yellow-orange prism,  $0.25 \times 0.28 \times 0.35 \text{ mm}^3$ ; **10**: orange prism,  $0.25 \times 0.40 \times 0.45 \text{ mm}^3$ ; **11**: orange block,  $0.25 \times 0.30 \times 0.53 \text{ mm}^3$ ) and ethyl acetate (**3**: red prism,  $0.25 \times 0.25 \times 0.30 \text{ mm}^3$ ). Crystals of the complexes were grown by liquid-phase diffusion from  $\text{CHCl}_3$ /hexane (**12**: red plate,  $0.06 \times 0.14 \times 0.22 \text{ mm}^3$ ),  $\text{CH}_2\text{Cl}_2$ /ethanol (**16**· $\text{CH}_2\text{Cl}_2$ : red bar,  $0.15 \times 0.30 \times 0.55 \text{ mm}^3$ ),  $\text{CH}_2\text{Cl}_2$ /THF+pentane (*trans*-**15**: red prism,  $0.08 \times 0.10 \times 0.25 \text{ mm}^3$ ) and  $\text{CDCl}_3$ /diethyl ether (**18**: orange prism,  $0.31 \times 0.31 \times 0.57 \text{ mm}^3$ ).

**Table S1** Summary of crystallographic data and structure refinement parameters for compounds **5**, ( $S_p$ )-**7**, **8**, **10** and **11**.<sup>a</sup>

Compound	<b>5</b>	( $S_p$ )- <b>7</b>	<b>8</b>	<b>10</b>	<b>11</b>
Formula	$\text{C}_{23}\text{H}_{24}\text{BFeOP}$	$\text{C}_{23}\text{H}_{24}\text{BFeOP}$	$\text{C}_{23}\text{H}_{24}\text{BFeP}$	$\text{C}_{24}\text{H}_{26}\text{BFeOP}$	$\text{C}_{24}\text{H}_{23}\text{FeOP}$
<i>M</i>	414.05	414.05	398.05	428.08	414.24
Crystal system	monoclinic	orthorhombic	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$ (no. 14)	$P2_12_12_1$ (no. 19) <sup>g</sup>	$P2_1/c$ (no. 14)	$P-1$ (no. 2)	$P2_1/n$ (no. 14)
<i>a</i> /Å	13.4231(2)	8.7423(2)	13.3300(8)	9.4573(2)	10.8960(2)
<i>b</i> /Å	17.6047(2)	9.3366(3)	17.528(1)	13.4113(3)	17.2531(3)
<i>c</i> /Å	34.0211(4)	24.9336(8)	34.422(2)	17.4666(4)	10.9826(2)
$\alpha$ /°				88.596(1)	
$\beta$ /°	99.6903(6)		100.118(2)	81.764(1)	106.343(1)
$\gamma$ /°				75.498(1)	
<i>V</i> /Å <sup>3</sup>	7924.8(2)	2035.2(1)	7917.7(8)	2122.52(8)	1981.19(6)
<i>Z</i>	16	4	16	4	4
<i>D<sub>c</sub></i> /g mL <sup>-1</sup>	1.388	1.351	1.336	1.340	1.389
$\mu$ (Mo K $\alpha$ )/mm <sup>-1</sup>	0.852	0.829	0.846	0.797	0.853
Diffractions collected	118977	19003	49847	40793	31152
Independent/obsd <sup>b</sup> diffns	17472/11375	4010/3619	17266/10336	9711/8219	4529/3926
<i>R</i> <sub>int</sub> <sup>c</sup> /%	6.6	2.6	3.8	3.5	1.3
<i>R</i> <sup>c</sup> observed diffns/%	5.06	3.44	4.22	4.16	2.80
<i>R</i> , <i>wR</i> <sup>c</sup> all data/%	8.85, 14.1	4.29, 7.29	8.74, 10.4	5.20, 10.9	3.50, 7.26
$\Delta\rho$ /e Å <sup>-3</sup>	1.71, -0.48 <sup>f</sup>	0.40, -0.20	0.43, -0.32	0.46, -0.50	-0.27, 0.38
CCDC reference no.	906406	906407	906408	906409	906410

<sup>a</sup> Common details: *T* = 150(2) K. <sup>b</sup> *I* > 2σ(*I*). <sup>c</sup> Definitions:  $R_{\text{int}} = \frac{\sum |F_o^2 - F_c^2(\text{mean})|}{\sum F_o^2}$ , where  $F_o^2(\text{mean})$  is the average intensity of symmetry-equivalent diffractions.  $R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$ ,  $wR = [\frac{\sum \{w(F_o^2 - F_c^2)^2\}}{\sum w(F_o^2)^2}]^{1/2}$ . <sup>e</sup> Not corrected. <sup>f</sup> Residual electron density in the space accommodating the disordered hydromethyl moieties. <sup>g</sup> Flack's enantiomorph parameter was determined to be -0.01(2).

**Table S2** Summary of crystallographic data and structure refinement parameters for complexes **12**, **13**·½CHCl<sub>3</sub>, *trans*-**15**, **16**·CH<sub>2</sub>Cl<sub>2</sub>, *trans*-**17** and **18**.<sup>a</sup>

Compound	<b>12</b>	<b>13</b> ·½CHCl <sub>3</sub>	<i>trans</i> - <b>15</b>
Formula	C <sub>34</sub> H <sub>37</sub> Cl <sub>2</sub> FeOPRu	C <sub>36.5</sub> H <sub>40.5</sub> Cl <sub>2.5</sub> F <sub>6</sub> FeNOPRuSb	C <sub>48</sub> H <sub>46</sub> Cl <sub>2</sub> Fe <sub>2</sub> O <sub>2</sub> P <sub>2</sub> Pd
<i>M</i>	722.27	1021.46	1005.79
Crystal system	monoclinic	triclinic	monoclinic
Space group	<i>P2</i> <sub>1</sub> / <i>n</i> (no. 14)	<i>P</i> -1 (no. 2)	<i>P2</i> <sub>1</sub> / <i>n</i> (no. 14)
<i>a</i> /Å	9.7055(8)	10.5750(7)	13.4772(3)
<i>b</i> /Å	10.241(1)	13.9675(8)	9.1167(2)
<i>c</i> /Å	30.665(2)	14.6000(8)	17.3793(4)
α/°		96.764(4)	
β/°	98.795(8)	97.044(5)	98.485(1)
γ/°		111.478(6)	
<i>V</i> /Å <sup>3</sup>	3012.2(5)	1960.5(2)	2111.98(8)
<i>Z</i>	4	2	2
<i>D</i> <sub>c</sub> /g mL <sup>-1</sup>	1.593	1.730	1.582
μ(Mo Kα)/mm <sup>-1</sup>	1.287	1.700	1.341
<i>T</i> <sup>b</sup>	0.861-0.938	0.553-0.669	0.756-0.905
Diffractions collected	33228	43999	29903
Independent/obsd <sup>c</sup> diffns	5871/4416	8948/7819	4854/3943
<i>R</i> <sub>int</sub> <sup>d</sup> /%	9.5	3.1	4.6
<i>R</i> <sup>d</sup> observed diffns/%	5.67	2.74	3.06
<i>R</i> , <i>wR</i> <sup>d</sup> all data/%	8.57, 11.2	3.71, 6.98	4.46, 7.72
Δρ/e Å <sup>-3</sup>	0.91, -0.90	1.43, -1.62 <sup>e</sup>	1.02, -0.75
CCDC reference no.	906411	906412	906413

<sup>a</sup> Common details: *T* = 150(2) K. <sup>b</sup> The range of transmission factors. <sup>c</sup> *I* > 2σ(*I*). <sup>d</sup>  $R_{\text{int}} = \frac{\sum |F_o^2 - F_o^2(\text{mean})|}{\sum F_o^2}$ , where  $F_o^2(\text{mean})$  is the average intensity of symmetry-equivalent diffractions.  $R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$ ,  $wR = [\sum \{w(F_o^2 - 5 F_c^2)^2\} / \sum w(F_o^2)^2]^{1/2}$ . <sup>e</sup> Residual electron density in areas accommodating disordered moieties or close to metal atoms.

**Table S2** (continued)

Compound	<b>16</b> -CH <sub>2</sub> Cl <sub>2</sub>	<i>trans</i> - <b>17</b>	<b>18</b>
Formula	C <sub>49</sub> H <sub>48</sub> Cl <sub>6</sub> Fe <sub>2</sub> O <sub>2</sub> P <sub>2</sub> Pd <sub>2</sub>	C <sub>48</sub> H <sub>46</sub> Cl <sub>2</sub> Fe <sub>2</sub> O <sub>2</sub> P <sub>2</sub> Pt	C <sub>49</sub> H <sub>48</sub> CuF <sub>3</sub> Fe <sub>2</sub> O <sub>6</sub> P <sub>2</sub> S
<i>M</i>	1268.01	1094.48	1057.10
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>C2/c</i> (no. 15)	<i>P2<sub>1</sub>/n</i> (no. 14)	<i>P2<sub>1</sub>/n</i> (no. 14)
<i>a</i> /Å	22.7193(3)	13.4348(4)	13.1234(3)
<i>b</i> /Å	18.7832(3)	9.1071(3)	26.0560(6)
<i>c</i> /Å	15.3334(2)	17.4178(7)	13.6517(3)
$\alpha$ /°			
$\beta$ /°	131.4336(6)	98.860(1)	102.489(1)
$\gamma$ /°			
<i>V</i> /Å <sup>3</sup>	4905.7(1)	2105.7(1)	4557.7(2)
<i>Z</i>	4	2	4
<i>D<sub>c</sub></i> /g mL <sup>-1</sup>	1.717	1.726	1.544
$\mu$ (Mo K $\alpha$ )/mm <sup>-1</sup>	1.732	4.236	1.270
<i>T</i> <sup>b</sup>	0.600-0.810	0.236-0.756	0.502-0.697
Diffractions collected	53794	32707	67700
Independent/obsd <sup>c</sup> diffns	5622/5069	4846/4301	10455/9231
<i>R</i> <sub>int</sub> <sup>d</sup> /%	4.8	3.1	1.9
<i>R</i> <sup>d</sup> observed diffns/%	4.27	1.68	5.83
<i>R</i> , <i>wR</i> <sup>d</sup> all data/%	4.65, 11.1	2.18, 3.82	6.58, 16.0
$\Delta\rho$ /e Å <sup>-3</sup>	1.59, -1.58 <sup>e</sup>	0.56, -0.58	2.97, -2.00 <sup>e</sup>
CCDC reference no.	906414	906415	906416

((for footnotes see the first part of this Table))

## References

1. T.-Y. Dong and L.-L. Lai, *J. Organomet. Chem.*, 1996, **509**, 131.
2. P. Štěpnička and I. Císařová, *J. Organomet. Chem.*, 2006, **691**, 2863.
3. P. Štěpnička and T. Baše, *Inorg. Chem. Commun.*, 2001, **4**, 682.
4. D. Braga, F. Paganelli, E. Tagliavini, S. Casolari, G. Cojazzi and F. Grepioni, *Organometallics*, 1999, **18**, 4191.
5. A. L. Spek, *Platon—a multipurpose crystallographic tool*, Utrecht University, Utrecht, The Netherlands, 2007. For a reference, see: A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.
6. A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 1999, **32**, 115.
7. G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **64**, 112.