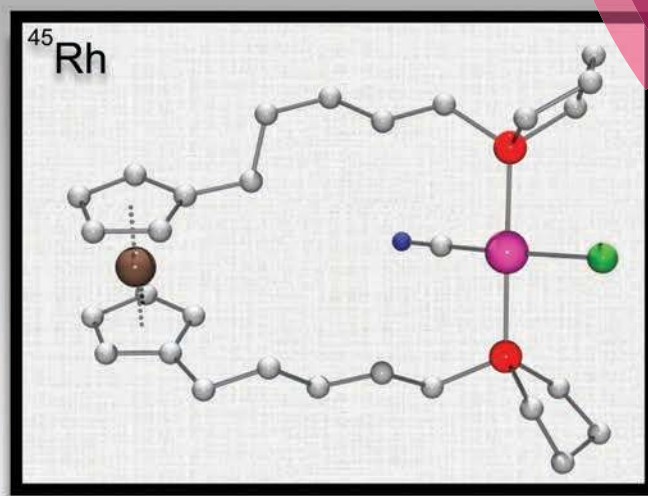
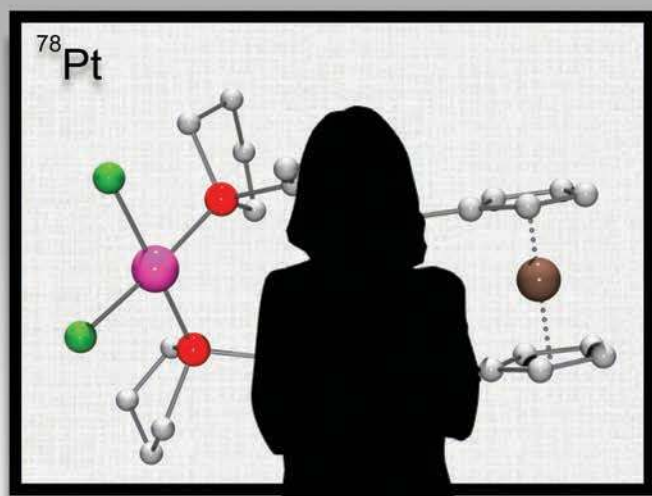


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## Heterobimetallic complexes with highly flexible 1,1'-bis(phospholanoalkyl)ferrocene ligands†‡

Andy Schmied, Axel Straube, Toni Grell, Sascha Jähnigen and Evamarie Hey-Hawkins\*

The two highly flexible ligands 1,1'-bis(4-phospholanobutyl)ferrocene (**5a**) and 1,1'-bis(5-phospholano-pentyl)ferrocene (**5b**) reacted with [PtCl<sub>2</sub>(cod)] (cod = 1,5-cyclooctadiene), [AuCl(tht)] (tht = tetrahydrothiophene) and [RhCl(CO)<sub>2</sub>]<sub>2</sub> to give the respective chelate complexes *cis*-[PtCl<sub>2</sub>(**5a,b**-κ<sup>2</sup>P,P')] (**7a,b**), [AuCl(**5a,b**-κ<sup>2</sup>P,P')] (**8a,b**) and *trans*-[RhCl(CO)(**5b**-κ<sup>2</sup>P,P')] (**9b**). Treatment of **5a,b** with selenium gave the corresponding selenides **6a,b**. All compounds have been fully characterised by NMR (<sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P) and IR spectroscopy and mass spectrometry. In addition, crystal structures of **6a**, **7b**, **8a,b** and **9b** were determined by X-ray crystallography. Furthermore, the rhodium-catalysed hydroformylation of 1-octene has been studied with ligand **5b**.

### Introduction

Bis(phosphino)ferrocenes are commonly used ligands in a variety of homogeneously catalysed reactions.<sup>1</sup> Enormous progress has been made in the chemistry of 1,1'-bis(diphenylphosphino)ferrocene (dppf)<sup>2</sup> and its achiral<sup>3</sup> and chiral<sup>4,5</sup> derivatives. However, less rigid ligands in which the ferrocene moiety and the phosphine are separated by a flexible carbon-based spacer are rare,<sup>6</sup> and the preparation of the corresponding metal complexes often suffers from low selectivity. Usually, complex product mixtures resulting from intra- and intermolecular reactions are obtained due to insufficient differentiation caused by the high conformational flexibility of 1,1'-substituted ferrocene derivatives. Thus, no metal complexes of the type [Fe{C<sub>5</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>n</sub>PR<sub>2</sub>}<sub>2</sub>] (*n* = 2, R = Ph, *t*Bu; *n* = 3, R = Ph) could be isolated.<sup>7</sup> However, flexibility of a bidentate ligand may be important for the acceleration of specific transitions within a catalytic cycle and, therefore, may have a significant effect on the catalyst's efficiency.<sup>8</sup>

Recently, we have shown that highly flexible bis-phospholane ligands based on solely aliphatic backbones react selectively with [AuCl(tht)] (tht = tetrahydrothiophene) to give macrocyclic complexes [Au<sub>2</sub>Cl<sub>2</sub>{μ-(C<sub>4</sub>H<sub>8</sub>P)(CH<sub>2</sub>)<sub>n</sub>(PC<sub>4</sub>H<sub>8</sub>)-κ<sup>2</sup>P, P'}<sub>2</sub>] (*n* = 5, 7, 9, 11),<sup>9</sup> without using high-dilution techniques or templates to avoid polymerisation.<sup>10</sup>

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†Dedicated to Professor Christian Robl on the occasion of his 60<sup>th</sup> birthday.

‡Electronic supplementary information (ESI) available: Crystal structures of **1b** and **6a**, crystallographic data, and cyclic voltammograms of **5ab**, **7ab**, **8ab** and **9b**. CCDC 1410618–1410623. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt02567b

As the phospholane moiety apparently increases the selectivity of metal complex formation and bisphospholanes proved to be privileged structures in catalysis,<sup>11</sup> we have prepared the ferrocene-based bis-phospholanes [Fe{C<sub>5</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>n</sub>P(C<sub>4</sub>H<sub>8</sub>)<sub>2</sub>}<sub>2</sub>] [*n* = 4 (**5a**), 5 (**5b**)] and studied their coordination behaviour in platinum(II), gold(I) and rhodium(I) complexes.

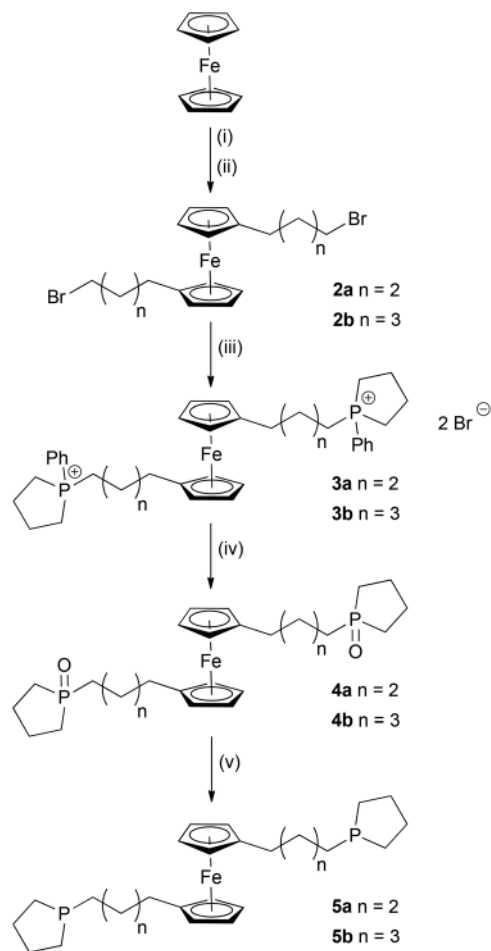
### Results and discussion

#### Synthesis of bis-phospholane ligands and selenides

Two bis-phospholane ligands having highly flexible alkylene spacers with four or five methylene groups between the ferrocene moiety and the phospholane were synthesised by a modification of a strategy published by Haddow *et al.* in 2009 (Scheme 1).<sup>12</sup> The starting materials, 1,1'-bis(ω-bromoalkyl)ferrocenes, were prepared by Friedel–Crafts acylation of ferrocene with ω-bromoacyl chlorides and subsequent reduction of the obtained 1,1'-acylferrocenes **1a,b**.<sup>13</sup> The crystal structure of 1,1'-bis(5-bromopentanoyl)ferrocene (**1b**) shows no unusual features and can be found in the ESI.† Treatment of two equivalents of 1-phenylphospholane with 1,1'-bis(ω-bromoalkyl)ferrocenes **2a,b** gave the corresponding phosphonium salts **3a** and **3b** in quantitative yield as orange solids. Basic hydrolysis of the P–C(phenyl) bond by aqueous sodium hydroxide solution led to the formation of the phosphine oxides **4a** and **4b**. From these, the bis-phospholane ligands **5a** and **5b** were obtained as viscous, orange oils by reduction with a mixture of lithium aluminium hydride and trimethylsilyl chloride.

The corresponding selenides **6a** and **6b** were prepared by treating **5a** and **5b** with two equivalents of grey selenium. Crystals of **6a** suitable for X-ray diffraction (crystal structure shown



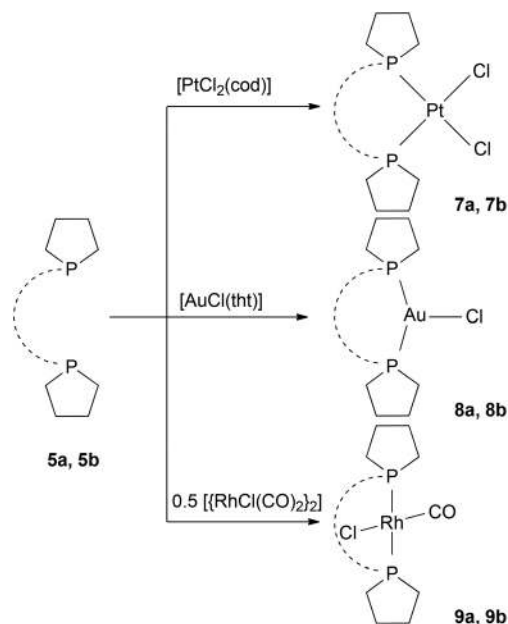


**Scheme 1** Synthesis of bis-phospholane ligands **5a** and **5b**. (i)  $\text{AlCl}_3$ , 2 equiv.  $\text{Br}(\text{CH}_2)_n\text{COCl}$ ,  $\text{CHCl}_3$  ( $n = 3, 4$ ); (ii)  $\text{AlCl}_3$ ,  $\text{LiAlH}_4$ ,  $\text{Et}_2\text{O}$ ; (iii) 2 equiv. 1-phenylphospholane,  $\text{CH}_3\text{CN}$ ,  $80^\circ\text{C}$ ; (iv)  $\text{NaOH}_{\text{aq}}$ ,  $95^\circ\text{C}$ ; (v)  $\text{LiAlH}_4$ ,  $\text{SiMe}_3\text{Cl}$ , THF.

in the  $\text{ESI}^{\ddagger}$ ) could be obtained from ethyl acetate/*n*-hexane. In contrast, **6b** is a yellow oil at room temperature. In the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of both compounds, a sharp singlet at  $\delta = 45.6$  ppm is observed ( $^1J_{\text{P-Se}} = 693$  Hz, determined from the  $^{77}\text{Se}$  satellites). Since  $^1J_{\text{P-Se}}$  is directly related to the *s* character of the lone pair of electrons,<sup>14</sup> **6a** and **6b** appear to be stronger  $\sigma$  donors in comparison with FerroLANE (FerroLANE = 1,1'-bis-(phospholano)ferrocene) ligands (*cf.*  $J_{\text{P-Se}} = 738$  Hz in (*S*)-1,1'-bis(2,5-dimethylphospholanoselenide)ferrocene).<sup>5</sup>

### Metal complexes

Treatment of  $[\text{PtCl}_2(\text{cod})]$  (*cod* = 1,5-cyclooctadiene) with one equivalent of the bis-phospholanes **5a** and **5b** in dichloromethane afforded the corresponding complexes  $[\text{PtCl}_2(\mathbf{5a}\text{-}\kappa^2\text{P}, \text{P}')] (\mathbf{7a})$  and  $[\text{PtCl}_2(\mathbf{5b}\text{-}\kappa^2\text{P}, \text{P}')] (\mathbf{7b})$  (Scheme 2). While **7a** is formed selectively, the reaction of **5b** with  $[\text{PtCl}_2(\text{cod})]$  gave a mixture containing **7b** and another platinum complex (two singlets,  $^1J_{\text{P-Pt}} \approx 3450$  Hz, determined from the  $^{195}\text{Pt}$  satellites, consistent with *cis*-coordinated phosphines, are observed in the  $^1\text{P}\{^1\text{H}\}$  NMR spectrum of the reaction mixture). In analogy to



**Scheme 2** Synthesis of metal complexes.

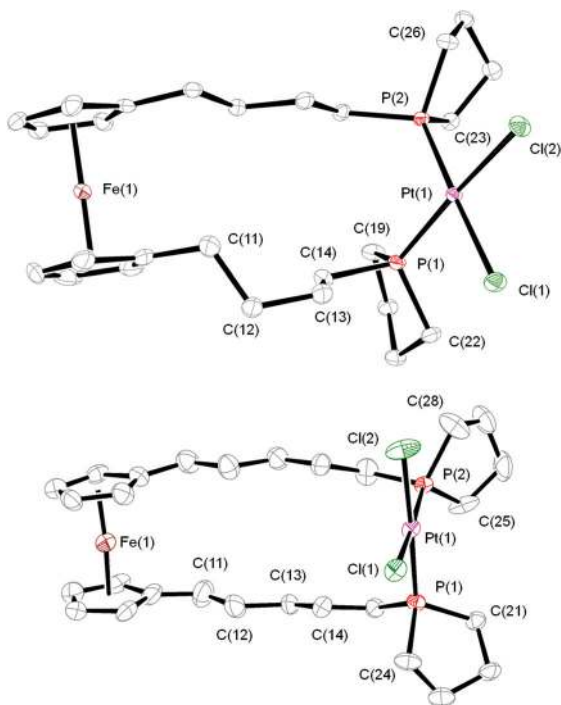
observations made by Guino-o *et al.* on the formation of platinum complexes with FerroLANE ligands, the minor side product may contain **5b** in a bridging binding mode.<sup>15</sup> Compounds **7a** and **7b**, the latter isolated from the product mixture by crystallisation, were obtained as slightly hygroscopic orange solids and were fully characterised by NMR and IR spectroscopy, mass spectrometry, cyclic voltammetry and elemental analysis. In the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra, a downfield shift is observed on coordination, from  $\delta \approx -26.8$  ppm (free ligand) to sharp signals at 17.4 (**7a**) and 15.7 ppm (**7b**). Crystal structures of both complexes were obtained (Fig. 1). **7a** crystallises in the space group  $P\bar{1}$  from  $\text{CH}_2\text{Cl}_2/n$ -hexane, while **7b** crystallises in space group  $P2_1/n$ . The platinum atoms in **7a** and **7b** are coordinated in a square-planar fashion by two phospholane moieties and two chlorido ligands in *cis* configuration, as expected from the  $^1J_{\text{P-Pt}}$  values of 3426 and 3452 Hz, respectively. The Pt–P and Pt–Cl bond lengths as well as the P–Pt–P and Cl–Pt–Cl bond angles are in agreement with those of related bis-phospholane platinum(*n*) complexes (*e.g.*, *cis*- $[\text{PtCl}_2(\text{PPh}(\text{C}_4\text{H}_8))_2]$ : Pt–P 223.9(1) pm, Pt–Cl 236.7(1) pm, P–Pt–P  $92.60(6)^\circ$  Cl–Pt–Cl  $88.30(7)^\circ$ ).<sup>16</sup>

While the environment of the platinum atoms in **7a** and **7b** is very similar, differences are observed in the structural parameters of the ferrocene moieties and the aliphatic spacers (Table 1).

Although the cyclopentadienyl rings in both complexes adopt a synperiplanar conformation, the dihedral angle between the mean planes through the cyclopentadienyl rings is significantly larger in **7b** ( $5.54$  vs.  $2.10^\circ$ ).

A *gauche* conformation ( $\theta = 71.2(3)^\circ$ ) is observed in one of the two alkylene spacers of **7a**. In contrast, all methylene groups in the aliphatic backbone of **7b** have an almost perfect antiperiplanar conformation.





**Fig. 1** Molecular structures of **7a** (top) and **7b** (bottom). Ellipsoids are drawn at the 50 and 30% probability level, respectively. Hydrogen atoms are omitted for clarity. Selected bond lengths (in pm) and angles (in °): **7a**: Pt1–Cl1 234.9(1), Pt1–Cl2 237.1(2), Pt1–P1 223.2(1), Pt1–P2 223.8(1), P1–C19 184.7(3), P1–C22 182.0(3), P2–C23 182.4(4), P2–C26 184.0(4); P1–Pt1–P2 94.27(4), Cl2–Pt1–Cl1 87.71(4), C22–P1–C19 95.1(2), C23–P2–C26 94.1(2); dihedral angle C11–C12–C13–C14 71.2(3). **7b**: Pt1–Cl1 234.7(2), Pt1–P1 223.8(2), Pt1–P2 222.7(2), P1–C21 182.5(8), Pt1–Cl2 234.3(3), P1–C24 184.7(8), P2–C25 180(1), P2–C28 183(1); P1–Pt1–P2 94.52(8), Cl2–Pt1–Cl1 87.62(9), C21–P1–C24 93.9(4), C25–P2–C28 94.2(5); dihedral angle C11–C12–C13–C14 167.5(8).

**Table 1** Structural parameters of the ferrocene moiety

Compound	$\theta^a$ (°)	$\tau^b$ (°)	Cp <sup>R</sup> ring conformation
<b>1b</b>	1.40	142.12	Anticlinical
<b>6a</b>	1.55	146.83	Anticlinical
<b>7a</b>	2.10	10.50	Synperiplanar
<b>7b</b>	5.54	11.41	Synperiplanar
<b>8b</b>	2.81	4.32	Synperiplanar
<b>9b</b>	0.54	72.30	Synclinal

<sup>a</sup> Dihedral angle between mean planes through cyclopentadienyl (Cp<sup>R</sup>) rings. <sup>b</sup> Torsional twist about Cp<sup>R</sup>(centroid)–Fe–Cp<sup>R</sup>(centroid) axis.

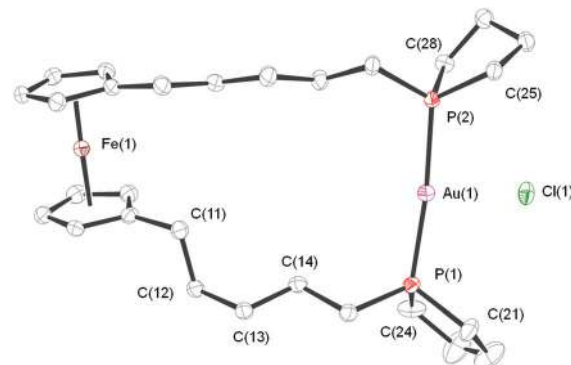
Addition of [AuCl(tht)] to a solution of one equivalent of **5a** or **5b** led to the selective formation of the corresponding complexes [AuCl(**5a**-κ<sup>2</sup>P,P')] (**8a**) and [AuCl(**5b**-κ<sup>2</sup>P,P')] (**8b**) (Scheme 2). The formation of polymeric products, known for the dppf ligand and several dppf derivatives, was not observed.<sup>17</sup> The <sup>31</sup>P{<sup>1</sup>H} NMR spectra of **8a** and **8b** exhibit sharp singlets at  $\delta = 34.3$  and 37.4 ppm, respectively. In the mass spectra (ESI+ mode), [M – Cl]<sup>+</sup> peaks are observed. All

attempts to obtain single crystals of **8a** suitable for structure determination were unsuccessful. The molecular structure of **8b**, which crystallises in the orthorhombic space group *P*<sub>2</sub><sub>1</sub><sub>2</sub><sub>1</sub>, is shown in Fig. 2. In **8b**, the gold atom is almost linearly coordinated by the two phospholane moieties (P1–Au1–P2 173.06(5)°). The distortion occurs due to an additional, weak coordination of a terminal chlorido ligand. The Au–Cl bond (287.1(1) pm vs. 250.0(4) pm in [AuCl(PPh<sub>3</sub>)<sub>2</sub>]<sup>18</sup>) is conspicuously long, but is in line with non-ferrocene-based analogues, as are the Au–P bond lengths (cf. [Au<sub>2</sub>Cl<sub>2</sub>{μ-(C<sub>4</sub>H<sub>8</sub>P)(CH<sub>2</sub>)<sub>7</sub>(PC<sub>4</sub>H<sub>8</sub>)}]<sub>2</sub>): Au–Cl 290.3(1) pm, Au–P 229.7(1) and 229.4(1) pm).<sup>9</sup> The cyclopentadienyl rings adopt a synperiplanar arrangement, and a *gauche* conformation is observed in analogy to **7a** in one of the two alkylene spacers.

Treatment of [{RhCl(CO)<sub>2</sub>}] with two equivalents of **5b** in dichloromethane gave the corresponding complex [RhCl(CO)-(**5b**-κ<sup>2</sup>P,P')] (**9b**). All attempts to isolate pure [RhCl(CO)(**5a**-κ<sup>2</sup>P,P')] (**9a**) from the obtained product mixture were unsuccessful. However, the appearance of an [M]<sup>+</sup> peak in the mass spectrum (ESI+ mode) supports the formation of **9a**.

A sharp doublet is observed at  $\delta = 26.5$  ppm in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **9b**. The coupling constant of <sup>1</sup>J<sub>P–Rh</sub> = 115.4 Hz indicates a *trans* configuration. The IR spectrum shows one absorption for  $\nu_{\text{CO}}$  at 1952 cm<sup>-1</sup> (cf. 1968 cm<sup>-1</sup> in [Rh<sub>2</sub>Cl<sub>2</sub>(CO)<sub>2</sub>{μ-(C<sub>4</sub>H<sub>8</sub>P)(CH<sub>2</sub>)<sub>3</sub>(PC<sub>4</sub>H<sub>8</sub>)}]<sub>2</sub>).<sup>12</sup> Compound **9b** crystallises from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O in the monoclinic space group *P*<sub>2</sub><sub>1</sub>/*n* (Fig. 3). The rhodium atom is coordinated in a square-planar fashion by the *trans*-coordinated bis-phospholane, a carbonyl and a chlorido ligand. Bond lengths and angles are in agreement with those of structurally related bis-phospholane rhodium complexes.<sup>12</sup>

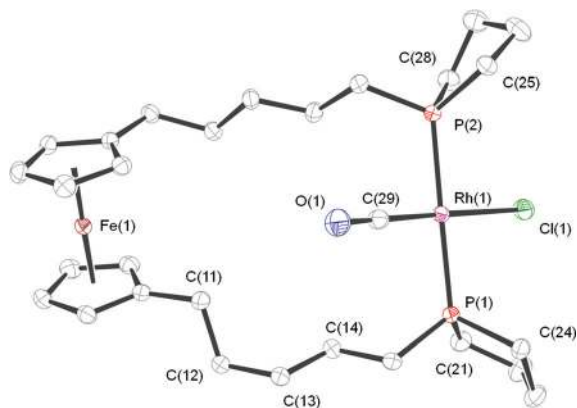
The cyclopentadienyl rings in **9b** adopt a synclinal conformation, in contrast to the obtained platinum and gold complexes. Similar to **7a** and **8b**, a *gauche* conformation is observed in one of the two alkylene spacers.



**Fig. 2** Molecular structure of **8b**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (in pm) and angles (in °): Au1–P1 229.1(1), Au1–P2 229.5(1), Au–Cl1 287.1(1), P1–C21 183.6(6), P1–C24 181.9(6), P2–C25 183.3(5), P2–C28 183.1(5); P1–Au1–P2 173.06(5), P1–Au1–Cl1 96.20(5), P2–Au1–Cl1 90.66(5), C21–P1–C24 95.5(3), C25–P2–C28 95.2(2); dihedral angle C11–C12–C13–C14 70.10(3).







**Fig. 3** Molecular structure of **9b**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (in pm) and angles (in °): Rh1–P1 231.10(8), Rh1–P2 230.42(8), Rh1–Cl1 236.38(6), Rh1–C29 180.1(2), P1–C21 184.5(2), P1–C24 183.7(2), P2–C25 184.0(2), P2–C28 184.7(2), C29–O1 114.9(2); P1–Rh1–P1 176.66(1), C21–P1–C24 94.43(7), Cl1–Rh1–C29 175.27(5), C25–P2–C28 94.36(8), Rh1–C29–O1 177.9(2); dihedral angle C11–C12–C13–C14 70.58(1).

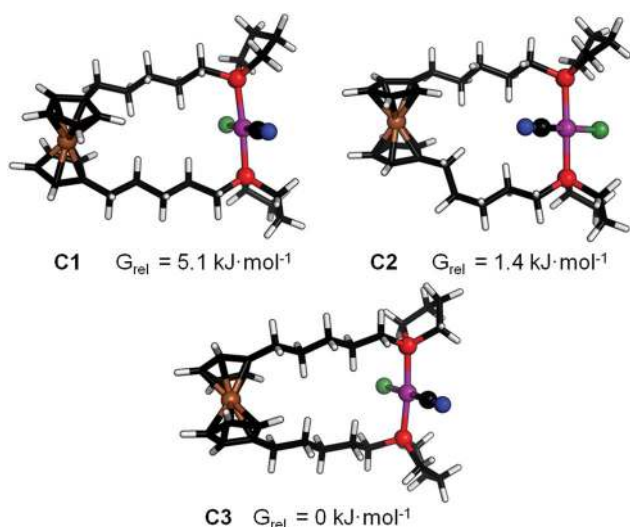
### Cyclovoltammetry

In the cyclic voltammograms (see ESI<sup>†</sup>), a single, reversible oxidation occurs in all isolated complexes (**6a,b**, **7a,b**, **8a,b** and **9b**) at  $E_{1/2} = -0.06$ , 0.10 or  $-0.13$  V versus  $\text{Fc}^+/\text{FcH}$ , attributed to the  $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$  redox couple.

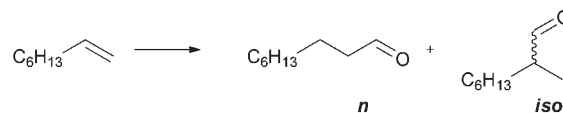
### Theoretical considerations

DFT calculations were conducted to comprehend the *gauche* conformation observed in **7a**, **8b** and **9b**.

Three conformers of **9b** in which the ferrocene moieties adopt a synclinal conformation were optimised (Fig. 4). One of the two alkylene chains exhibits a *gauche* conformation in **C1**



**Fig. 4** Optimised structures of the most stable conformers of **9b**.



**Scheme 3** Hydroformylation of 1-octene. Reaction conditions: 50 °C, 40 bar  $\text{CO}/\text{H}_2$  (1 : 1) for 18 h, 0.05 mol%  $[\{\text{RhCl}(\text{CO})_2\}_2]$ , **5b**: Rh = 5 : 2. See Experimental part for details. Conversion 100%,  $n$  :  $iso$  = 1.8.

and **C2**, the latter similar to that in the crystal structure. In contrast, all methylene groups in **C3** are antiperiplanar to each other. Furthermore, the ferrocene moiety in **C3** exhibits a stronger tilt towards the plane that contains the chloride and the metal atoms (angle of slope  $54^\circ$  vs.  $60^\circ$  in **C1**). However, energy differences between the three conformers ( $G_{\text{rel}}$ ) are negligible (see Fig. 4). Therefore, we suggest that the *gauche* conformation arises from effects of crystal packing. The appearance of **C2** instead of the energetically favoured conformer **C3** supports this suggestion.

### Hydroformylation catalysis

Bis-phospholanes with a flexible aliphatic backbone are interesting ligands for the rhodium-catalysed hydroformylation of alkenes.<sup>12</sup> Total conversion of 1-octene is observed with **5b**/ $[\{\text{RhCl}(\text{CO})_2\}_2]$  as catalyst over 18 h at 40 bar  $\text{CO}/\text{H}_2$  (1 : 1) pressure and 50 °C (Scheme 3). The regioselectivity ( $n$  :  $iso$  = 1.8) is similar to those of non-ferrocene-based bis-phospholane systems.<sup>12</sup>

## Conclusions

A new class of highly flexible 1,1'-bis(phosphino)ferrocene ligands was prepared. Their selective reaction with  $[\text{PtCl}_2(\text{cod})]$ ,  $[\{\text{RhCl}(\text{CO})_2\}_2]$  and  $[\text{AuCl}(\text{tht})]$ , independent of the number of methylene groups in the spacer molecule, was shown. Chelate complexes from intramolecular reactions were obtained exclusively. Furthermore, all complexes show a reversible  $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$  redox process. To the best of our knowledge, the reported metal complexes are the first 1,1'-bis(phosphino)ferrocene-based heterobimetallic complexes with highly flexible alkylene backbones that could be isolated and structurally characterised by X-ray diffraction.

The reported results are essential for a deeper understanding of the influence of the substituent at the phosphorus atom on the metal complex formation of flexible bis(phosphino)ferrocenes.

## Experimental

### General methods

All reactions were carried out in a nitrogen atmosphere by using standard Schlenk techniques<sup>19</sup> and anhydrous solvents, which were purified with an MB SPS-800 solvent purification system from MBRAUN or as mentioned in the literature.<sup>20</sup>



1-Phenylphospholane,<sup>21</sup> [AuCl(tht)],<sup>22</sup> [PtCl<sub>2</sub>(cod)]<sup>23</sup> and **2a,b**<sup>13</sup> were prepared according to the literature. All other chemicals were used as purchased. NMR spectra were recorded at 298 K on a Bruker AVANCE DRX 400 spectrometer or a Bruker VARIAN 300 spectrometer. The chemical shifts  $\delta$  of <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P are reported in parts per million (ppm) at 400.12 (300.23), 100.63 (75.49) and 162.02 MHz, respectively, with tetramethylsilane as an internal standard and referencing to the unified scale.<sup>24</sup> Coupling constants *J* are given in Hz. FTIR spectra were recorded on a Perkin-Elmer Spectrum 2000 FTIR spectrometer, scanning between 400 and 4000 cm<sup>-1</sup>, using KBr pellets. Wavenumbers  $\tilde{\nu}$  are reported in cm<sup>-1</sup>. Mass spectra were recorded on an ESQUIRE 3000 plus spectrometer. Elemental analyses were carried out with a Heraeus VARIO EL oven. Melting and decomposition points were measured in sealed capillaries by using a variable heater from Gallenkamp. Cyclic voltammetry experiments were conducted at ambient temperature with an SP-50 potentiostat from BioLogic Science Instruments. All scans were performed with 0.1 M tetrabutylammonium tetrafluoroborate as supporting electrolyte in CH<sub>2</sub>Cl<sub>2</sub> and a standard three-electrode cell (glassy carbon working electrode, platinum counter electrode, silver wire reference electrode). Ferrocene was used as internal reference.

### Synthesis and characterisation

**Preparation of phosphonium salts.** Phenylphospholane (0.66 g, 4.0 mmol) was added to a stirred solution of the respective 1,1'-bis( $\omega$ -bromoalkyl)ferrocene (2.0 mmol) in acetonitrile (20 mL). The mixture was stirred for 2 days at 80 °C. Then volatile compounds were removed under reduced pressure. The resulting orange solids (**3a,b**) were used without further purification.

**1,1'-Bis(4-(phenylphospholanium)butyl)ferrocene dibromide (3a).** Yield 1.56 g (99%). Decomp. >156 °C. Found C, 58.4; H, 6.6. Calc. for C<sub>38</sub>H<sub>50</sub>Br<sub>2</sub>FeP<sub>2</sub>: C, 58.2; H, 6.4. IR  $\tilde{\nu}$  3054w, 2935s, 2359w, 1636m, 1438s, 1404m, 1264m, 1165w, 1120s, 1020m, 879m, 805m, 751m, 692m, 516m. <sup>1</sup>H NMR (CD<sub>3</sub>OD, 400 MHz):  $\delta$  7.93 (m, 4H), 7.83 (m, 2H), 7.74 (m, 4H), 3.95 (m, 4H), 3.93 (m, 4H), 2.74–2.58 (m, 12H), 2.35 (t, *J* = 7.2, 4H), 2.30–2.08 (m, 8H), 1.66–1.47 (m, 8H). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>3</sub>OD, 100 MHz):  $\delta$  135.5 (d, *J*<sub>C,P</sub> = 3.2), 133.2 (d, *J*<sub>C,P</sub> = 9.5), 131.2 (d, *J*<sub>C,P</sub> = 12.3), 121.0 (d, *J*<sub>C,P</sub> = 77.1), 89.3 (s), 69.8 (s), 69.0 (s), 33.1 (d, *J*<sub>C,P</sub> = 15.6), 29.6 (s), 27.2 (d, *J*<sub>C,P</sub> = 5.9), 23.5 (d, *J*<sub>C,P</sub> = 45.3), 23.3 (d, *J*<sub>C,P</sub> = 52.3), 22.9 (d, *J*<sub>C,P</sub> = 4.6). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>3</sub>OD, 162 MHz):  $\delta$  50.1 (s). MS (ESI(+), CH<sub>3</sub>OH) *m/z* 703.2 [M – Br]<sup>+</sup>, 312.1 [M – 2Br]<sup>+</sup>.

**1,1'-Bis(5-(phenylphospholanium)pentyl)ferrocene dibromide (3b).** Yield 1.61 g (99%). Decomp. >220 °C. Found C, 59.1; H, 6.7. Calc. for C<sub>40</sub>H<sub>54</sub>Br<sub>2</sub>FeP<sub>2</sub>: C, 59.3; H 6.8. IR  $\tilde{\nu}$  2964m, 2932m, 2854w, 1456m, 1438m, 1404w, 1262m, 1097m, 1024m, 803m, 749w, 693w, 518w. <sup>1</sup>H NMR (CD<sub>3</sub>OD, 400 MHz):  $\delta$  7.96 (m, 4H), 7.80 (m, 2H), 7.71 (m, 4H), 3.93 (m, 4H), 3.92 (m, 4H), 2.75–2.61 (m, 12H), 2.3 (t, *J* = 6.8, 4H), 2.27–2.08 (m, 8H), 1.60–1.40 ppm (m, 12H). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>3</sub>OD, 100 MHz):  $\delta$  135.5 (d, *J*<sub>C,P</sub> = 2.9), 133.1 (d, *J*<sub>C,P</sub> = 9.5), 131.2 (d, *J*<sub>C,P</sub> = 12.1), 121.1 (d, *J*<sub>C,P</sub> = 77.1), 89.8 (s), 69.8 (s),

69.0 (s), 31.7 (s), 31.2 (d, *J*<sub>C,P</sub> = 15.5), 30.2 (s), 27.2 (d, *J*<sub>C,P</sub> = 5.8), 23.6 (d, *J*<sub>C,P</sub> = 45.3), 23.3 (d, *J*<sub>C,P</sub> = 52.3), 23.3 (d, *J*<sub>C,P</sub> = 4.5). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>3</sub>OD, 162 MHz):  $\delta$  50.0 (s). MS (ESI(+), CH<sub>3</sub>OH) *m/z* 733.2 [M – Br]<sup>+</sup>, 326.1 [M – 2Br]<sup>+</sup>.

**Preparation of phosphine oxides.** 2.0 mmol of the respective phosphonium salt was dissolved in aqueous sodium hydroxide solution (20 wt%, 20 mL) and the mixture was stirred at 95 °C overnight. The reaction mixture was extracted with CHCl<sub>3</sub> (3 × 20 mL). The combined organic layers were washed with distilled water and brine and dried over MgSO<sub>4</sub>. Removal of the solvent under reduced pressure gave the bis-phospholane oxides **4a,b** as orange oils.

**1,1'-Bis(4-(phospholano oxide)butyl)ferrocene (4a).** Yield 1.28 g (96%). Found C, 62.3; H, 8.1. Calc. for C<sub>26</sub>H<sub>40</sub>FeO<sub>2</sub>P<sub>2</sub>: C, 62.2; H, 8.0. IR  $\tilde{\nu}$  3092w, 2935s, 2864m, 1635m, 1451m, 1407m, 1266s, 1162s, 1111m, 1056m, 1023m, 862m, 803m, 729m, 518m. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  3.91 (d, *J* = 1.6, 4H), 3.88 (d, *J* = 1.6, 4H), 2.29 (t, *J* = 7.2, 4H), 1.94 (m, 4H), 1.81–1.46 (m, 24H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  88.3 (s), 68.7 (s), 67.9 (s), 32.7 (d, *J*<sub>C,P</sub> = 13.5), 30.8 (d, *J*<sub>C,P</sub> = 61.6), 29.1 (s), 26.9 (d, *J*<sub>C,P</sub> = 64.8), 24.5 (d, *J*<sub>C,P</sub> = 7.8), 22.0 (d, *J*<sub>C,P</sub> = 4.0). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 162 MHz):  $\delta$  71.2 (s). MS (ESI(+), CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>CN) *m/z* 503.5 [M + H]<sup>+</sup>.

**1,1'-Bis(5-(phospholano oxide)pentyl)ferrocene (4b).** Yield 1.38 g (99%). Found C, 63.4; H, 8.2. Calc. for C<sub>28</sub>H<sub>44</sub>FeO<sub>2</sub>P<sub>2</sub>: C, 63.4; H, 8.4. IR  $\tilde{\nu}$  3094w, 2925s, 2860m, 1464m, 1405m, 1264s, 1169s, 1110s, 1053s, 1042s, 1021s, 858m, 816s, 803s, 752w, 728m, 514m, 498m. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  3.96 (m, 4H), 3.94 (m, 4H), 2.32 (t, *J* = 7.2, 4H), 2.01 (m, 4H), 1.88–1.58 (m, 20H), 1.58–1.34 (m, 8H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  88.6 (s), 68.4 (s), 67.6 (s), 30.8 (s), 30.7 (d, *J*<sub>C,P</sub> = 61.5), 30.7 (d, *J*<sub>C,P</sub> = 14.0), 29.0 (s), 26.8 (d, *J*<sub>C,P</sub> = 64.7), 24.3 (d, *J*<sub>C,P</sub> = 7.8), 21.9 (d, *J*<sub>C,P</sub> = 4.0). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 162 MHz):  $\delta$  70.9 (s). MS (ESI(+), CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>CN) *m/z* 530.2 [M]<sup>+</sup>.

**Preparation of bis-phospholanes.** Chlorotrimethylsilane (1.30 g, 12.0 mmol) was added to a stirred suspension of lithium aluminium hydride (0.46 g, 12.0 mmol) in THF (10 mL) at 0 °C. The mixture was stirred for 2 h at rt and a solution of the respective bis-phospholane oxide (3.0 mmol) in THF (10 mL) was added at 0 °C *via* cannula. The reaction mixture was stirred overnight at rt and quenched carefully with CH<sub>3</sub>OH. All volatile compounds were removed under reduced pressure, and the residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> and filtered over vacuum-dried silica. Removal of the solvent under reduced pressure gave the bis-phospholanes **5a–b** as orange oils.

**1,1'-Bis(4-(phospholano)butyl)ferrocene (5a).** Yield 0.97 g (69%). Found C, 66.1; H, 8.25. Calc. for C<sub>26</sub>H<sub>40</sub>FeP<sub>2</sub>: C, 66.4; H, 8.6. IR  $\tilde{\nu}$  3081w, 2930s, 2852m, 1458w, 1447w, 1262s, 1106s, 1040s, 1021s, 872m, 802s, 709w, 485m. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  3.89 (m, 4H), 3.88 (m, 4H), 2.24 (t, *J* = 6.0, 4H), 1.77–1.56 (m, 12H), 1.55–1.23 (m, 16H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  89.0 (s), 68.6 (s), 67.7 (s), 33.9 (d, *J*<sub>C,P</sub> = 10.8), 29.2 (s), 28.8 (d, *J*<sub>C,P</sub> = 14.8), 27.8 (s), 26.8 (d, *J*<sub>C,P</sub> = 14.7), 25.9 (d, *J*<sub>C,P</sub> = 10.4). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 162 MHz):  $\delta$  –26.7 (s). MS (ESI(+), CHCl<sub>3</sub>, CH<sub>3</sub>CN) *m/z* 471.2 [M + H]<sup>+</sup>.



*1,1'-Bis(5-(phospholano)pentyl)ferrocene (5b)*. Yield 0.97 g (65%). Found C, 67.45; H, 8.5. Calc. for  $C_{28}H_{44}FeP_2$ : C, 67.5; H, 8.9. IR  $\tilde{\nu}$  3087m, 2925s, 2855s, 1447m, 1262s, 1095s, 1022s, 803s, 743w, 705m, 668m, 488m.  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  3.88 (m, 4H), 3.87 (m, 4H), 2.22 (t,  $J = 7.4$ , 4H), 1.77–1.53 (m, 12H), 1.45–1.27 (m, 16H), 1.21 (m, 4H).  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 75 MHz):  $\delta$  89.2 (s), 68.2 (s), 67.7 (s), 31.3 (d,  $J_{C,P} = 9.1$ ), 31.2 (s), 29.4 (s), 29.0 (d,  $J_{C,P} = 13.0$ ), 27.9 (s), 26.8 (d,  $J_{C,P} = 13.0$ ), 26.0 (d,  $J_{C,P} = 8.8$ ).  $^{31}P\{^1H\}$  NMR ( $CDCl_3$ , 162 MHz):  $\delta$  -26.8 (s). MS (ESI(+),  $CHCl_3$ ,  $CH_3CN$ )  $m/z$  499.4  $[M + H]^+$ .

**Preparation of selenides.** Grey selenium (31.6 mg 0.4 mmol) was added to a solution of the respective bis-phospholane (0.2 mmol) in  $CHCl_3$  (6 mL). The mixture was heated to reflux for 2 h and stirred overnight at rt. Unconsumed selenium was removed by filtration and the solvent was removed under reduced pressure to afford the selenides as yellow (**6a**) crystalline solid and viscous oil (**6b**), respectively.

*1,1'-Bis(4-(phospholanoselenide)butyl)ferrocene (6a)*. Yield 94.2 mg (75%). mp 107 °C (*n*-hexane/ethyl acetate) Found C, 49.6; H, 6.6. Calc. for  $C_{26}H_{40}FeP_2Se_2$ : C, 49.7; H, 6.4. IR  $\tilde{\nu}$  3084w, 2928s, 2861m, 1656w, 1649w, 1460m, 1401m, 1336w, 1301w, 1256w, 1178w, 1114m, 1101m, 1067m, 1040w, 1017m, 881m, 860m, 820m, 766w, 750w, 728m, 704m, 675m, 528m.  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  3.92 (m, 4H), 3.89 (m, 4H), 2.30 (t,  $J = 7.6$ , 4H), 2.25–1.89 (m, 16H), 1.83–1.61 (m, 8H), 1.55 (m, 4H).  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  88.3 (s), 68.1 (s), 67.8 (s), 33.8 (d,  $J_{C,P} = 45.3$ ), 33.3 (d,  $J_{C,P} = 39.2$ ), 32.1 (d,  $J_{C,P} = 14.8$ ), 29.1 (s), 26.5 (d,  $J_{C,P} = 5.1$ ), 23.7 (d,  $J_{C,P} = 3.2$ ).  $^{31}P\{^1H\}$  NMR ( $CDCl_3$ , 162 MHz):  $\delta$  45.6 (s,  $^{77}Se$  satellites d,  $J_{P,Se} = 693$ ). MS (ESI(+),  $CH_2Cl_2$ ,  $CH_3CN$ ) 630.0  $[M]^+$ .

*1,1'-Bis(5-(phospholanoselenide)pentyl)ferrocene (6b)*. Yield 99.8 mg (76%). Found C, 51.1; H, 6.65. Calc. for  $C_{28}H_{44}FeP_2Se_2$ : C, 51.2; H, 6.8. IR  $\tilde{\nu}$  3085w, 2929s, 2856m, 1656w, 1631w, 1446m, 1409m, 1262s, 1108s, 1068s, 1023s, 919w, 860m, 802s, 699w, 661w, 527m.  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  3.91 (m, 4H), 3.89 (m, 4H), 2.26 (t,  $J = 7.4$ ), 2.22–1.88 (m, 16H), 1.83–1.57 (m, 8H), 1.51–1.31 (m, 8H).  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  88.9 (s), 68.8 (s), 67.9 (s), 33.9 (d,  $J_{C,P} = 45.4$ ), 33.3 (d,  $J_{C,P} = 39.2$ ), 30.8 (s), 30.2 (d,  $J_{C,P} = 15.0$ ), 29.2 (s), 26.5 (d,  $J_{C,P} = 5.1$ ), 23.7 (d,  $J_{C,P} = 3.4$ ).  $^{31}P\{^1H\}$  NMR ( $CDCl_3$ , 162 MHz):  $\delta$  45.6 (s,  $^{77}Se$  satellites d,  $J_{P,Se} = 693$ ). MS (ESI(+),  $CH_2Cl_2$ ,  $CH_3CN$ ) 658.1  $[M]^+$ .

**Preparation of platinum complexes.**  $[PtCl_2(cod)]$  (74.8 mg, 0.2 mmol) was added to a solution of the respective bis-phospholane (0.2 mmol) in  $CH_2Cl_2$  (6 mL) and the mixture was stirred for 18 h at rt. All volatile compounds were removed under reduced pressure. Crystallisation from diethyl ether/ $CH_2Cl_2$  afforded the platinum complexes **7a,b** as yellow, crystalline solids. Crystals suitable for X-ray diffraction were grown by liquid-phase diffusion from  $CH_2Cl_2/n$ -hexane (**7a**) or vapour diffusion of diethyl ether into a solution of **7b** in  $CH_2Cl_2$  over two weeks at rt.

*cis-Dichlorido-[1,1'-bis(4-(phospholano)butyl)ferrocene- $\kappa^2P,P'$ ]-platinum(II) (7a)*. Yield 123.7 mg (84%). Decomp. >180 °C. Found C, 42.55; H, 5.4. Calc. for  $C_{26}H_{40}Cl_2FeP_2Pt$ : C, 42.4; H, 5.5. IR  $\tilde{\nu}$  3078w, 2932s, 2858m, 1697w, 1636m, 1448m,

1262m, 1111s, 1074s, 1024s, 882m, 808s, 714w, 685w, 514m, 498m, 418m.  $^1H$  NMR ( $CD_2Cl_2$ , 400 MHz):  $\delta$  4.08 (m, 8H), 2.40 (m, 4H), 2.33–2.08 (m, 8H), 2.05–1.77 (m, 12H), 1.78–1.55 (m, 8H).  $^{13}C\{^1H\}$  NMR ( $CD_2Cl_2$ , 75 MHz): 88.9 (s), 69.1 (s), 68.2 (s), 32.4 (m), 29.5–28.5 (m), 27.9–26.0 (m), 25.4 (s).  $^{31}P\{^1H\}$  NMR ( $CD_2Cl_2$ , 162 MHz):  $\delta$  17.4 (s,  $^{195}Pt$  satellites d,  $J_{P,Pt} = 3426$ ). MS (ESI(-),  $CH_2Cl_2$ ,  $CH_3OH$ )  $m/z$  771.0  $[M + Cl]^-$ .

*cis-Dichlorido-[1,1'-bis(5-(phospholano)pentyl)ferrocene- $\kappa^2P,P'$ ]-platinum(II) (7b)*. Yield 85.6 mg (56%). Decomp. >160 °C. Found C, 43.6; H, 6.1. Calc. for  $C_{28}H_{44}Cl_2FeP_2Pt$ : C, 44.0; H, 5.8. IR  $\tilde{\nu}$  3084w, 2964m, 2828m, 2854m, 1456m, 1419w, 1263s, 1096s, 1024s, 804s, 689w, 661w, 498m.  $^1H$  NMR ( $CD_2Cl_2$ , 400 MHz):  $\delta$  4.04 (m, 4H), 3.96 (m, 4H), 2.31 (m, 4H), 2.12–1.96 (m, 8H), 1.93–1.76 (m, 12H), 1.68 (m, 4H), 1.47–1.58 (m, 8H).  $^{13}C\{^1H\}$  NMR ( $CD_2Cl_2$ , 75 MHz):  $\delta$  90.4 (s), 69.8 (s), 68.8 (s), 31.4–30.8 (m), 29.8 (s), 29.7–29.0 (m), 28.1–27.5 (m), 27.2–26.5 (m), 26.3–25.6 (m).  $^{31}P\{^1H\}$  NMR ( $CD_2Cl_2$ , 162 MHz):  $\delta$  15.7 (s,  $^{195}Pt$  satellites d,  $J_{P,Pt} = 3452$ ). MS (ESI(-),  $CH_2Cl_2$ ,  $CH_3CN$ )  $m/z$  800.1  $[M + Cl]^-$ . MS (ESI(+),  $CH_2Cl_2$ ,  $CH_3CN$ )  $m/z$  764.2  $[M - Cl]^+$ .

**Preparation of gold complexes.**  $[AuCl(tht)]$  (64.1 mg, 0.2 mmol) was added to a solution of the respective bis-phospholane (0.2 mmol) in  $CH_2Cl_2$  (6 mL) and the mixture was stirred for 18 h at rt. Volatile compounds were removed under reduced pressure to afford the gold complexes **8a,b** as yellow solids.

Crystals suitable for X-ray diffraction could be obtained through vapour diffusion of diethyl ether into a solution of **8b** in dichloromethane over two weeks at 4 °C.

*[1,1'-Bis(4-(phospholano)butyl)ferrocene- $\kappa^2P,P'$ ]-gold(I) chloride (8a)*. Yield 136.3 mg (97%). Decomp. >170 °C. Found C, 44.2; H, 5.4. Calc. for  $C_{28}H_{44}AuClFeP_2$ : C, 44.4; H, 5.7. IR  $\tilde{\nu}$  2928m, 2865m, 1653m, 1631s, 1456m, 1262s, 803m, 694w, 516m, 490m, 417w.  $^1H$  NMR ( $CD_2Cl_2$ , 400 MHz):  $\delta$  3.99 (m, 8H), 2.44–2.22 (m, 8H), 2.10–1.75 (m, 16H), 1.75–1.56 (m, 8H).  $^{13}C\{^1H\}$  NMR ( $CD_2Cl_2$ , 75 MHz):  $\delta$  88.9 (s), 68.9 (s), 68.0 (s), 32.2 (bs), 29.1 (s), 28.5 (m), 27.1 (s), 27.0–26.2 (m).  $^{31}P\{^1H\}$  NMR ( $CD_2Cl_2$ , 162 MHz):  $\delta$  34.3 (s). MS (ESI(+),  $CH_2Cl_2$ ,  $CH_3CN$ )  $m/z$  667.1  $[M - Cl]^+$ .

*[1,1'-Bis(5-(phospholano)pentyl)ferrocene- $\kappa^2P,P'$ ]-gold(I) chloride (8b)*. Yield 143.3 mg (98%). Decomp. >175 °C. Found C, 45.7; H, 6.1. Calc. for  $C_{28}H_{44}AuClFeP_2$ : C, 46.0; H, 6.1. IR  $\tilde{\nu}$  3084w, 2963m, 2927m, 2854m, 1437w, 1419w, 1263s, 1099s, 1023s, 803s, 701w, 668m, 488m.  $^1H$  NMR ( $CD_2Cl_2$ , 400 MHz):  $\delta$  4.02 (m, 4H), 3.92 (m, 4H), 2.42 (m, 4H), 2.31 (m, 4H), 2.05 (m, 4H), 1.96–1.77 (m, 12H), 1.70 (m, 4H), 1.60 (m, 4H), 1.50 (m, 4H).  $^{13}C\{^1H\}$  NMR ( $CD_2Cl_2$ , 75 MHz):  $\delta$  90.0 (s), 69.1 (s), 67.5 (s), 31.7–31.4 (m), 31.4 (s), 29.5–28.9 (m), 28.8 (s), 27.4 (bs), 27.2 (m).  $^{31}P\{^1H\}$  NMR ( $CD_2Cl_2$ , 162 MHz):  $\delta$  37.4 (s). MS (ESI(+),  $CH_2Cl_2$ ,  $CH_3CN$ )  $m/z$  695.2  $[M - Cl]^+$ . MS (ESI(-),  $CH_2Cl_2$ ,  $CH_3CN$ )  $m/z$  765.4  $[M + Cl]^+$ .

**Preparation of rhodium complexes.**  $[\{RhCl(CO)_2\}_2]$  (38.9 mg, 0.1 mmol) was added to a solution of the respective bis-phospholane (0.2 mmol) in  $CH_2Cl_2$  (6 mL) and the mixture was stirred for 18 h at rt. The solution was concentrated and





filtered. Diethyl ether was slowly added. The resulting precipitate was filtered and washed with diethyl ether. Crystallisation from diethyl ether/CH<sub>2</sub>Cl<sub>2</sub> afforded **9b** as orange, crystalline solid. Crystals suitable for X-ray diffraction were obtained by vapour diffusion of diethyl ether into a saturated solution of **9b** in dichloromethane over 4 days at rt.

*trans*-Carbonylchlorido-[1,1'-bis(5-(phospholano)butyl)ferrocene-κ<sup>2</sup>P,P']rhodium(i) (**9a**). **9a** could not be isolated in pure form and was therefore only characterised by <sup>31</sup>P{<sup>1</sup>H} NMR and ESI-MS. <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 162 MHz): 26.9 (d, <sup>1</sup>J<sub>P,Rh</sub> = 115.6). MS (ESI(+), CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>CN) *m/z* 636.2 [M]<sup>+</sup>.

*trans*-Carbonylchlorido-[1,1'-bis(5-(phospholano)pentyl)ferrocene-κ<sup>2</sup>P,P']rhodium(i) (**9b**). Yield 109.2 mg (82%). Decomp. >125 °C. Found C, 52.6; H, 6.4. Calc. for C<sub>29</sub>H<sub>44</sub>ClFeOP<sub>2</sub>Rh: C, 52.4; H, 6.7. IR  $\tilde{\nu}$  3079w, 2928s, 2854m, 1952w (CO), 1656m, 1627m, 1558w, 1506m, 1498w, 1405m, 1263m, 1111m, 1053m, 1022m, 853w, 802m, 658w, 517w. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz):  $\delta$  3.91(m, 4H), 3.87 (m, 4H), 2.30 (m, 4H), 2.20 (m, 4H), 1.96–1.66 (m, 20H), 1.62–1.41 (m, 8H). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 75 MHz):  $\delta$  188.9–187.3 (m, CO), 89.7 (s), 68.6 (s), 66.8 (s), 31.5–30.8 (m), 29.5–29.0 (m), 28.0 (s), 27.0 (bs), 26.3–25.5 (m). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 162 MHz): 26.5 (d, <sup>1</sup>J<sub>P,Rh</sub> = 115.4). MS (ESI(+), CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>CN) *m/z* 629.2 [M – Cl]<sup>+</sup>.

### Crystal structure determinations

Data for compounds **1b**, **6a**, **7a**, **7b**, **8b** and **9b** were collected on an Oxford Diffraction CCD Xcalibur-S diffractometer (data reduction with CrysAlis Pro,<sup>25</sup> including the program SCALE 3

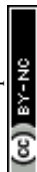
ABSPACK<sup>26</sup> for empirical absorption correction) by using MoK $\alpha$  irradiation ( $\lambda$  = 71.073 pm) and  $\omega$ -scan rotation. Structures were solved with the SIR tool.<sup>27</sup> Refinement was performed with SHELXL97.<sup>28</sup> Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined by constrained methods using the riding model. The refinement was carried out with the least-squares method on  $F^2$ . Final  $R$  indices were calculated as follows:  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$  and  $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2 \}^{1/2}$ . Figures were drawn with ORTEP.<sup>29</sup> CCDC 1410621 (**1b**), 1410623 (**6a**), 1410618 (**7a**), 1410619 (**7b**), 1410620 (**8b**), 1410622 (**9b**) contain the supplementary crystallographic data for this paper. Table 2 summarises the details of the data collection, structure solution and refinement for **7a**, **8b**, and **9b**.

### Hydroformylation catalysis

Catalytic reactions were performed with an AMTEC SPR16 generation 2 slurry-phase reactor system and stock solutions in toluene. Typical procedure: 15 mL steel autoclaves were purged with argon. 0.25  $\mu$ mol [RhCl(CO)<sub>2</sub>]<sub>2</sub> and 1.25  $\mu$ mol **5b** were transferred into the reactor and stirred for 30 min at rt. Toluene (to achieve a bulk volume of 3 mL) and 0.5 mmol 1-octene were added. The autoclave was then pressurised with 40 bar of CO/H<sub>2</sub> (1 : 1) and heated to 50 °C. The mixture was stirred vigorously for 18 h. Analysis of the reaction products was performed by GC-MS with a GCMS-QP2010 spectrometer from Shimadzu.

**Table 2** Summary of data collection, structure solution and refinement details for **7a**, **8b**, **9b**

Compound	<b>7a</b>	<b>7b</b>	<b>8b</b>	<b>9b</b>
Formula	C <sub>26</sub> H <sub>40</sub> Cl <sub>2</sub> FeP <sub>2</sub> Pt	C <sub>28</sub> H <sub>44</sub> Cl <sub>2</sub> FeP <sub>2</sub> Pt	C <sub>28</sub> H <sub>44</sub> AuClFeP <sub>2</sub>	C <sub>29</sub> H <sub>44</sub> ClFeOP <sub>2</sub> Rh
Formula weight	736.36	764.41	730.84	664.79
Temperature [K]	130(2)	130(2)	130(2)	130(2)
Crystal system	Triclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
Unit cell				
<i>a</i> [pm]	885.8(5)	1986.9(5)	1229.6(5)	1077.3(5)
<i>b</i> [pm]	1049.0(5)	777.4(5)	1352.6(5)	1218.3(5)
<i>c</i> [pm]	1540.0(5)	2021.6(5)	1697.4(5)	2216.6(5)
$\alpha$ [°]	72.024(5)	90	90	90
$\beta$ [°]	85.158(5)	112.348(5)	90	97.477(5)
$\gamma$ [°]	76.207(5)	90	90	90
<i>V</i> [Å <sup>3</sup> ]	1322(1)	2888(2)	2823(2)	2885(2)
<i>Z</i>	2	4	4	4
$\rho$ <sub>calcd.</sub> [g cm <sup>-3</sup> ]	1.850	1.758	1.720	1.531
$\mu$ [mm <sup>-1</sup> ]	6.172	5.653	5.928	1.300
<i>F</i> (000)	728	1520	1456	1376
Crystal size [mm]	0.15 × 0.10 × 0.10	0.10 × 0.10 × 0.02	0.25 × 0.15 × 0.04	0.30 × 0.30 × 0.30
$\theta$ <sub>Min</sub> – $\theta$ <sub>Max</sub> [°]	2.09–26.37	2.45–25.35	2.54–26.37	2.54–36.32
Collected reflections	10 398	13 600	24 262	64 818
Indep. reflections ( <i>R</i> <sub>int</sub> )	5383 (0.0287)	5292 (0.0510)	5759 (0.0386)	13 973 (0.0359)
Completeness to $\theta$ <sub>Max</sub>	100.0%	99.9%	99.9%	100.0%
Restraints/parameters	0/289	0/307	0/298	0/492
Goof ( <i>F</i> <sup>2</sup> )	0.917	1.045	1.050	1.041
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0229, 0.0452	0.0520, 0.0931	0.0268, 0.0603	0.0315, 0.0668
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.0319, 0.0478	0.0795, 0.1027	0.0301, 0.0615	0.0427, 0.0714
Residual electron density [e Å <sup>-3</sup> ]	0.768/–1.375	1.063/–0.679	0.866/–0.366	1.632/–0.725
Absolute structure parameter	—	—	–0.010(5)	—





## Computational studies

For all quantum chemical calculations, geometry optimisations as well as vibrational analysis, the programme suite ORCA<sup>30</sup> version 3.0.2 was used. DFT calculations were performed using the B3LYP functional<sup>31</sup> with the basis set Def2-TZVP.<sup>32</sup> The convergence criterion was set to  $10^{-8}$  Hartree in all calculations. The vibrational analyses were carried out numerically. All structures were verified as local energy minima by only positive eigenvalues of the Hessian matrix. The simulation of the solvent environment was performed using the COSMO model<sup>33</sup> for which the dielectric constant  $\epsilon$  was set to 8.93 (CH<sub>2</sub>Cl<sub>2</sub>). The picture was generated with PYMOL.<sup>34</sup>

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