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Comparing the asymmetric dppf-type ligands with their semi-homologous counterparts☆

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ABSTRACT

Two series of asymmetric ferrocene diphosphines, namely the dppf-type ligands $R_2PfcPPh_2$ (protected as BH_3 adducts; fc = ferrocene-1,1′-diyl) and their semi-homologous counterparts $R_2PfcCH_2PPh_2$ (both in free and BH_3-protected form), with diverse PR_2 groups (R = cyclohexyl, isopropyl and *tert*-butyl), were prepared and further converted into the respective phosphine selenides, $R_2P(Se)fcP(Se)Ph_2$ and $R_2P(Se)fcCH_2P(Se)Ph_2$, which were in turn used to evaluate the electronic properties of these diphosphines through $^1J_{SeP}$ coupling constants. When reacted with $[PdCl_2(MeCN)_2]$ or $[PdCl_2(cod)]$ (cod = cycloocta-1,5-diene), the dppf-type ligands exclusively afforded the chelate complexes $[PdCl_2(R_2PfcPPh_2\text{-}\kappa^2P,P')]$, whereas the more flexible, homologous ligands produced mixtures mainly containing the similar chelate complexes $[PdCl_2(R_2PfcCH_2PPh_2\text{-}\kappa^2P,P')]$ and the *P,P′*-bridged dimers $[PdCl_2(\mu(P,P')\text{-}R_2PfcCH_2PPh_2)]2$.

1. Introduction

1,1′-Bis(diphenylphosphino)ferrocene (**1**; dppf) has become a truly iconic ferrocene ligand thanks to its unique coordination properties and numerous successful catalytic applications [1,2], which also triggered the search for analogous donors. Thus far, most attempts to modify the dppf structure have followed three main directions, namely (1) altering phosphine substituents, (2) replacing one of the phosphine groups by another functional moiety, and (3) introducing an additional substituent to the ferrocene core to provide planar-chiral ferrocene ligands. These approaches have already generated a vast family of ferrocene phosphines applicable as supporting ligands in coordination compounds and in a range of simple and enantioselective metal-catalyzed transformations [3].

Recently, we introduced an alternative approach to the design of ferrocene phosphines based on ligand desymmetrization by inserting a spacer group between the ferrocene scaffold and a directly bonded donor substituent. In the case of dppf, this approach using a simple methylene spacer led to its congener **2** [4] (Scheme 1). Coordination studies with this ligand and other, similarly modified phosphinoferrocene donors [5] revealed considerable changes in coordination properties associated with increased molecular flexibility. These results and our recent findings demonstrating that even simple variations of substituents at the phosphine groups can markedly affect the coordination and catalytic behavior of phosphinoferrocene donors [6] have led us to investigate parallel series of dppf and type-**2** ligands with different phosphine substituents (Scheme 1). The properties of these diphosphines were compared by preparing and structurally characterizing Pd(II) complexes with these ligands and by analyzing the $^1J_{SeP}$ scalar coupling constants of the corresponding phosphine diselenides [7].

2. Results and discussion

2.1. Synthesis and characterization of dppf-type diphosphines and their derivatives

Asymmetric, dppf-like diphosphines with one PPh_2 substituent replaced by a dicyclohexylphosphino, diisopropylphosphino or di-*tert*-butylphosphino moiety were prepared by lithiation/phosphinylation of 1′-(diphenylphosphino)-1-bromoferrocene [8,9] and were isolated as air-stable borane adducts **3a-c** (Scheme 2) rather than the corresponding, oxidation-sensitive phosphines **1a-c** [10]. This procedure typically afforded minor amounts of $FcPPh_2{\cdot}BH_3$ (Fc = ferrocenyl) resulting from unwanted protonolysis of the

☆ dppf = 1,1′-bis(diphenylphosphino)ferrocene.

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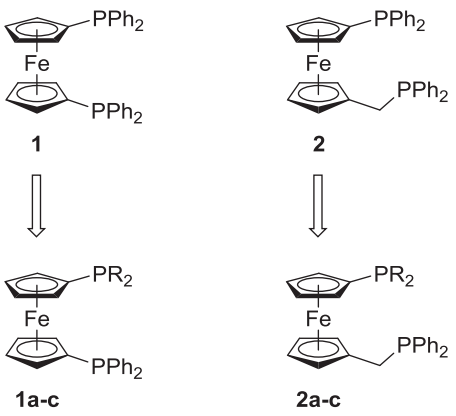
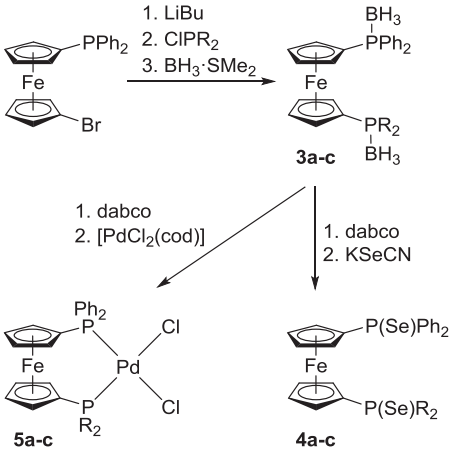


R = cyclohexyl (Cy; **a**), *i*-Pr (**b**), *t*-Bu (**c**).

Scheme 1.

lithiated intermediate. Fortunately, this side product could be separated by chromatography.

In the subsequent reactions, the borane protecting groups [11] in **3a-c** were removed by treatment with 1,4-diazabicyclo[2.2.2] octane (dabco) [12] in toluene (at elevated temperature). The resulting free phosphines **1a-c** were separated by flash chromatography and, after evaporation, converted into the respective phosphine selenides **4a-c** by reacting with KSeCN [13] in dichloromethane-methanol. In the complexation reactions, the eluate containing the free diphosphine was directly added to $[PdCl_2(cod)]$ ($cod = \eta^2{:}\eta^2$-cycloocta-1,5-diene) dissolved in dichloromethane, producing the corresponding *P,P'*-chelate complexes **5a-c** as the sole products (Scheme 2). Notably, these simplified procedures avoiding the isolation of the air-sensitive diphosphines **1** provided the target compounds at generally good yields. For instance, the selenides **4** were isolated at 79% (**4a**), 53% (**4b**) and 40% (**4c**) yields after column chromatography and crystallization (Note: the relatively lower yield of **4c** can be explained by the higher solubility of this compound). Even the complexation reactions were accomplished with very good isolated yields, namely 74% for **5a**, and 49% for the remaining members of the series, **5b** and **5c**.



Scheme 2. Synthesis of adducts **3** and their conversion into selenides **4** and Pd(II) complexes **5** (R = cyclohexyl (**a**), isopropyl (**b**), and *tert*-butyl (**c**); dabco = 1,4-diazabicyclo[2.2.2]octane, $cod = \eta^2{:}\eta^2$-cycloocta-1,5-diene).

Compounds **3**–**5** were characterized by multinuclear NMR spectroscopy, electrospray ionization mass spectrometry (ESI MS) and elemental analysis. The ^1H and ^{13}C NMR spectra of **3**–**5** comprise the characteristic signals of the asymmetrically 1,1′-disubstituted ferrocene moiety and of the phosphine moieties. The presence of the protecting BH_3 groups in compounds **3a-c** is indicated by very broad, structured resonances due to six BH protons in the ^1H NMR spectra and broad, doublet-like signals in the $^{31}P\{^1H\}$ NMR spectra. The signals of the $PPh_2{\cdot}BH_3$ moieties are found at $\delta_P \approx 16.3$, whereas those of the other phosphine substituents appear at lower fields (**3a**: δ_P 24.4, **3b**: δ_P 31.8, and **3c**: δ_P 45.4). Upon conversion to the selenides **4**, the ^{31}P NMR signals shift to lower fields, becoming sharp singlets associated with ^{77}Se satellites ($I = ½$, natural abundance 7.6%; Note: for further discussion of the ^{31}P NMR parameters, see below). Finally, the ^{31}P NMR resonances of complexes **5a-c** are consistently shifted to even lower fields and split into doublets due to interactions between the non-equivalent phosphorus atoms, with $^2J_{PP} = 22$ Hz (in all compounds).

In addition to the conventional characterization, the solid-state structures of adducts **3b** and **3c** [14] and, mainly, the complete series of selenides **4a-c** and Pd(II) complexes **5a-c** were determined by single-crystal X-ray diffraction analysis. The molecular structures of adducts **3b** and **3c** are shown in Fig. 1. In the case of **3b**, the ferrocene substituents are rotated to an intermediate conformation between eclipsed anticlinal and staggered antiperiplanar [2a] with the torsion angle C1-Cg1-Cg2-C6 (τ), where Cg1 and Cg2 denote the centroids of the cyclopentadienyl rings C(1–5) and C(6–10), at −158.06(9)°. The cyclopentadienyl rings are mutually tilted by 7.06(8)°, which corresponds to individual Fe-C distances ranging from 2.019(1) to 2.072(2) Å. The lengths of the pivotal C-P bonds (C1-P1 1.793(1) Å and C6-P2 1.794(1) Å), as well as the P-B distances (P1-B1 1.927(2) Å and P2-B2 1.920(2) Å) in **3b** are similar to those observed in dppf·2BH$_3$ (1.790(3) Å and 1.922(4) Å, respectively)

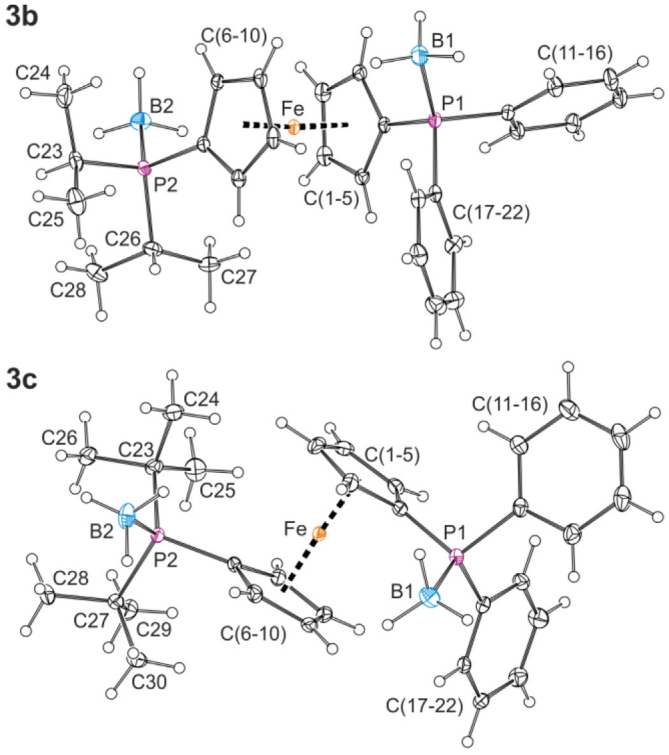


Fig. 1. PLATON plots of the molecular structures of **3b** (top) and **3c** (bottom) showing the displacement ellipsoids at 30% probability level.

[15]. In contrast, the ferrocene unit in **3c** is tilted by only 3.8(1)° (Fe-C distances in the range 2.041(2)-2.064(2) Å) and adopts a similar, albeit slightly more opened, conformation with τ = 163.5(1)°. The P-C(Ph) distance (C1-P1) in **3c** (1.792(2) Å) compares well with that in **3b**, whereas the P-C(*t*-Bu) distance (C6-P2; 1.812(2) Å) is somewhat elongated. Similarly, the Ph_2P-B bond in **3c** (P1-B1; 1.913(2) Å) is slightly but statistically significantly shorter than the $(t\text{-Bu})_2$P-B bond (P2-B2; 1.932(3) Å).

The solid-state structures of the phosphine selenides **4a-c** are presented in Fig. 2. Their geometric parameters outlined in Table 1 indicate that the 1,1′-disubstituted ferrocene units in the molecules of **4a-c** have similar conformations near-eclipsed anticlinal (optimal value: τ = 144°) and are negligibly tilted (<3°). The variation of P=Se bond lengths in the entire series is small (ca. 0.014 Å), and the individual parameters do not differ much from those reported for analogous dppf-type compounds fc[P(Se)R_2]$_2$ (R/P=Se [Å]: Ph/2.103(6) [16], Cy/2.113 and 2.126 [17], *i*-Pr/2.118 and 2.123 [18], and *t*-Bu/2.1194(5) and 2.1200(5) [19]), and for R_2P(Se) fcCONHMe (R = Cy, *i*-Pr, *t*-Bu and Ph) [6]. Similarly, only small variations in the pivotal C-P bonds were observed, even when using diverse phosphine substituents (e.g., the C6-P2 bond lengths vary by only 0.013 Å).

As mentioned above, the whole series of the Pd(II) complexes **5a-c** was structurally characterized (compound **5c** in the solvated form **5c**·CH_2Cl_2). The structures are shown in Fig. 3, and the pertinent structural data are given in Table 2. The compounds are *P,P′*-chelate complexes similar to those formed by dppf and its symmetrical analogues with other substituents at the phosphorus atoms (i.e., fc(PR_2)$_2$). The chelate coordination reduces the twisting of the ferrocene scaffold (cf. the τ angles: 15–26°), albeit without substantial tilting of the ferrocene cyclopentadienyls (the largest tilt angle is 5.4(1)° in **5b**).

Remarkably, the variation of the Pd-donor distances and even the interligand angles in the structures of **5a-c** are relatively small and with no clear-cut trends (N.B. some similarities can be observed between **5a** and **5b**, particularly in Pd-PR_2 bond lengths and in the P-Pd-Cl and Cl1-Pd-Cl2 angles). For instance, the Pd-P1 distances in the molecule of **5a** are slightly shorter than those in the two remaining compounds, whereas the Pd-P2 distance in **5c**·CH_2Cl_2 in a similar degree exceeds those in **5a** and **5b** (by ca. 0.03–0.04 Å). The variation in the non-equivalent Pd-Cl bonds is practically marginal (<0.01 Å for an individual compound). In all structures, the P1-Pd-P2 angle associated with the chelating ligand is the most opened of the interligand angles, which is compensated by closing adjacent angles, particularly P1-Pd-Cl2. Notably, the value of the bite angle P1-Pd-P2 lies between those reported for the analogous complexes featuring the parent dppf (≈98–99° for $CHCl_3$ and CH_2Cl_2 solvates [20,10d]) and those of the respective congener fc(PR_2)$_2$ (R = Cy: 102.5° [21], R = *i*-Pr: 103.4° [22], and R = *t*-Bu: 104.2° [23]). The dihedral angle subtended by the {Pd,Cl1,Cl2} and {Pd,P1,P2} "half-planes", which can serve as a measure of coordination sphere distortion, increase from 1.02(3)° in **5c**·CH_2Cl_2, and 2.07(2)° in **5a** to 5.45(3)° in **5b**. Again, this increase is apparently unrelated to the steric demands of the phosphine substituents.

Table 1
Selected distances and angle for **4a-c** (in Å and deg).[a]

Parameter	4a	4b	4c
Fe-C[b]	2.029(2)-2.058(2)	2.024(2)-2.063(2)	2.032(2)-2.058(2)
φ	2.3(1)	1.3(1)	2.79(9)
τ	141.9(2)	−145.0(1)	147.9(1)
C1-P1	1.789(2)	1.793(2)	1.793(2)
P1-Se1	2.1084(7)	2.1157(5)	2.1124(5)
C6-P2	1.805(2)	1.796(2)	1.814(2)
P2-Se2	2.1220(8)	2.1090(6)	2.1179(4)

[a] Definition of the parameters: τ is the torsion angle C1-Cg1-Cg2-C6 (τ), where Cg1 and Cg2 stand for the centroids of the cyclopentadienyl rings C(1–5) and C(6–10), respectively, and φ is the dihedral angle of the cyclopentadienyl least-square planes (tilt angle).
[b] The range of the individual Fe-C bond distances.

2.2. Synthesis of type-*2* donors, their phosphine selenides and Pd(II) complexes

In an initial attempt, the asymmetric, semi-homologous diphosphines **2** were synthesized by introducing the different phosphine moiety first (in BH_3-protected form). The synthesis was performed in parallel for the derivatives with the PCy_2 and P(*i*-Pr)$_2$ substituents, as shown in Scheme 3 (route A). Thus, stepwise lithiation and functionalization of 1,1′-dibromoferrocene [8,9] was used to prepare the known *P*-protected bromides **6a** and **6b** [6],

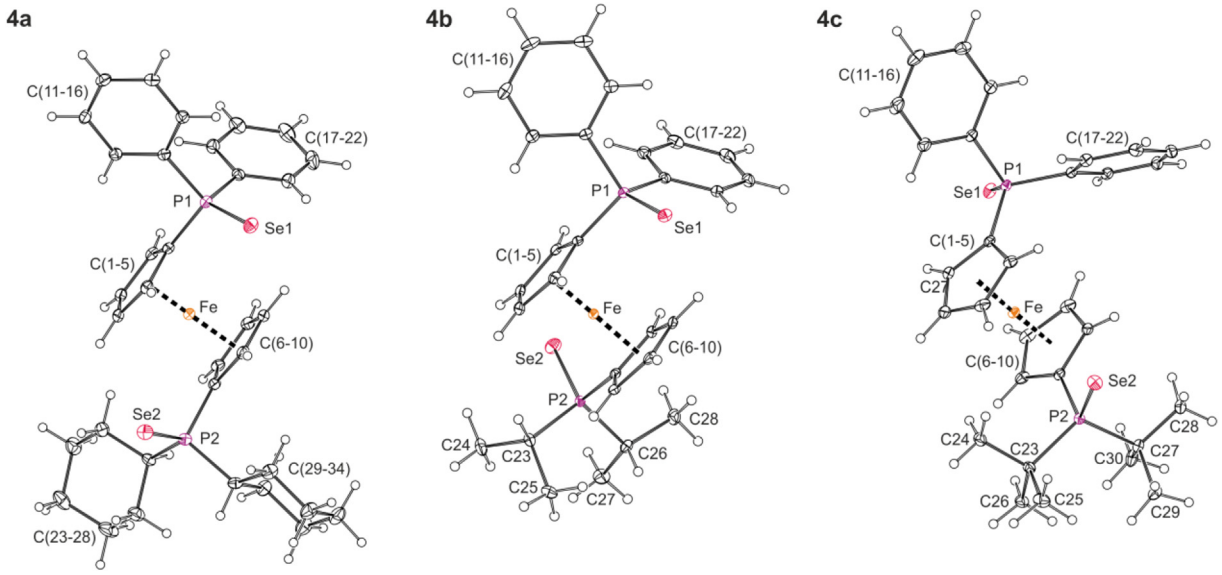


Fig. 2. PLATON plots of the molecular structures of **4a-c** showing the displacement ellipsoids at 30% probability level.

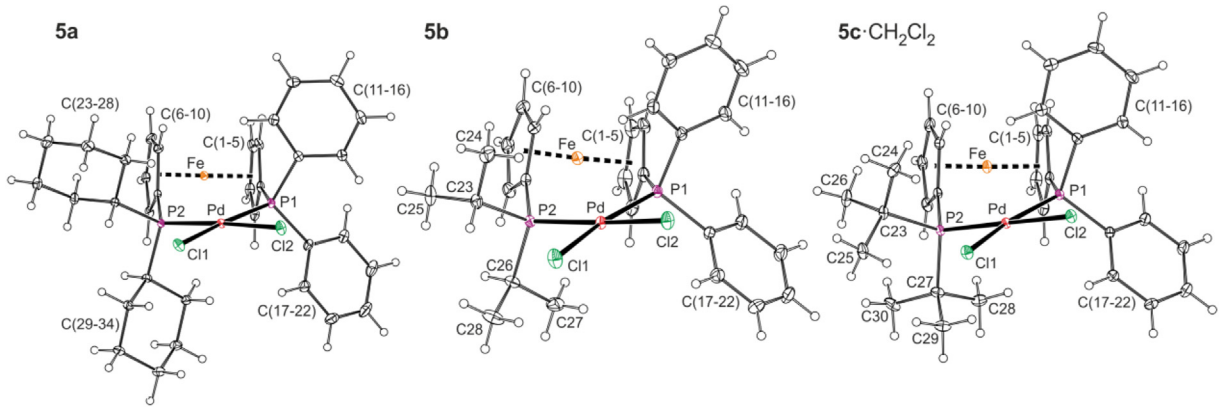


Fig. 3. PLATON plots of the complex molecules in the structures of **5a**, **5b** and **5c**·CH_2Cl_2. The displacement ellipsoids are shown at 30% probability level.

Table 2
Selected distances and angle for **5a**, **5b** and **5c**·CH_2Cl_2 (in Å and deg).[a]

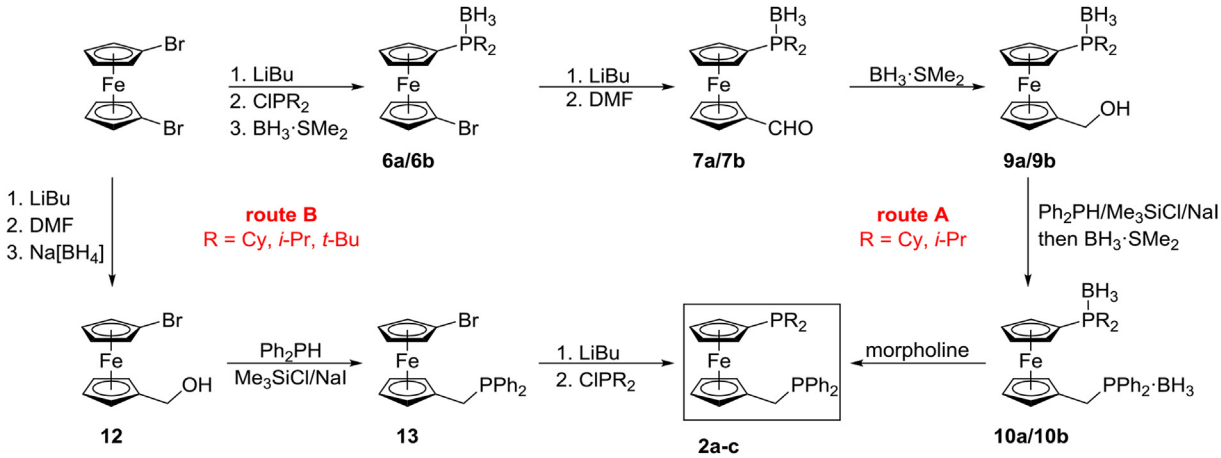
Parameter	5a	5b	5c·CH_2Cl_2
Pd-P1	2.2643(4)	2.2900(4)	2.2844(5)
Pd-P2	2.2841(4)	2.2816(5)	2.3222(6)
Pd-Cl1	2.3458(4)	2.3427(5)	2.3537(5)
Pd-Cl2	2.3560(4)	2.3378(5)	2.3550(6)
P1-Pd-P2	101.28(1)	102.49(2)	101.97(2)
Cl1-Pd-Cl2	88.08(1)	87.65(2)	85.70(2)
P1-Pd-Cl2	82.83(2)	83.09(2)	80.12(2)
P2-Pd-Cl1	87.81(1)	87.00(2)	92.22(2)
Fe-C	2.017(2)-2.056(2)	2.003(2)-2.060(2)	2.008(2)-2.059(2)
φ	1.94(9)	5.4(1)	3.2(1)
τ	−15.2(1)	−26.4(1)	−23.5(2)

[a] The parameters are defined as for compounds **4a-c**, see footnotes to Table 1.

which were then converted into the respective protected aldehydes **7a** and **7b** by similar lithium/halogen exchange and formylation with *N*,*N*-dimethylformamide (DMF). The aldehydes were obtained at good yields (72 and 77% after chromatography) together with minor amounts of the respective adducts $FcPR_2 \cdot BH_3$ (**8a-b**; 14% in both cases) resulting from decomposition of the lithiated intermediates. The introduction of the formyl substituent was clearly identified in the NMR spectra through distinct CHO resonances at δ_H 10.0 and δ_C 194.

A subsequent reduction of aldehydes **7** with borane (namely with $BH_3 \cdot SMe_2$) [5f] afforded the corresponding alcohols $R_2PfcCH_2OH \cdot BH_3$ (**9a-b**; fc = ferrocene-1,1′-diyl) at isolated yields exceeding 90% (95 and 92% after chromatographic purification). The reduction is accompanied by a change in color from an initial deep red to an orange yellow associated with the replacement of the conjugated ferrocene substituent (CHO) by a non-conjugated one (CH_2OH) and can be thus easily followed visually. After the reduction, the NMR resonances of aldehyde substituent are replaced by those of the hydroxymethyl group, namely a doublet at δ_H 4.4 ($^3J_{HH} \approx 5.5$ Hz) and a singlet at δ_C 60.4 (Note: similar parameters were reported for $Ph_2PfcCH_2OH \cdot BH_3$ [5f]).

In the following step, the alcohols **9a** and **9b** were reacted with diphenylphosphine in the presence of Me_3SiCl and NaI (in excess) in dry acetonitrile [4,24] to provide the respective diphosphines, which were isolated as the corresponding adducts **10a** and **10b** following $BH_3 \cdot SMe_2$ addition and column chromatography. The yields of the BH_3-protected diphosphines were approximately 30%. The reaction also produced the deoxygenated products $R_2PfcMe \cdot BH_3$ (**11a-b**) (typically at 20% isolated yields) which, however, corresponds to the ability of the Me_3SiCl-NaI-MeCN reagent to promote the reductive removal of reactive OH groups [25]. Compounds **10a-b** are characterized by a pair of broad, doublet-like resonances in the $^{31}P\{^1H\}$ NMR spectra and signals due to the methylene group in the newly installed CH_2PPh_2 pendant (δ_H 3.5, doublet with $^2J_{PH} = 10.4$ Hz; δ_C 28.5, doublet with $^1J_{PC} = 34$ Hz). The methyl group in the byproducts **11a** and **11b** also has a characteristic signature, consisting of singlets at δ_H 1.99 and δ_C 14.6, approximately.



Scheme 3. Alternative synthetic routes to the semi-homologous diphosphines **2a-c** (R = cyclohexyl (**a**), isopropyl (**b**), and *tert*-butyl (**c**); DMF = *N*,*N*-dimethylformamide).

The deprotection of adducts **10a-b** was effected by heating to 70 °C in neat morpholine [26] overnight (dabco proved less efficient in this reaction). In the case of **10b**, the reaction produced the target diphosphine **2b** at a good yield (76%, after column chromatography). By contrast, a similar reaction with **10a** was less efficient (the yield of **2a** was 57%), and the isolated product was typically contaminated with minor amounts (5–10%) of the partly deprotected compound $Ph_2PCH_2fcPCy_2 \cdot BH_3$.

Rather than optimizing the last two reaction steps, which substantially reduced the overall yield of the target diphosphines **2** (the yields of **2a** and **2b** over the five steps were 9 and 14%, respectively), we sought an alternative, more efficient procedure. Specifically, we decided to introduce the most oxidation-sensitive dialkylphosphino moiety at a late stage of the synthesis towards eliminating the additional protection/deprotection steps. In the modified synthesis, represented by route B in Scheme 3, we used the recently reported phosphinoferrocene bromide **13**, which is accessible in three steps from 1,1′-dibromoferrocene (via alcohol **12**) [5h]. Gratifyingly, the lithiation of **13** with butyllithium in anhydrous tetrahydrofurane (THF), followed by addition of the respective chlorophosphine $ClPR_2$, produced the unprotected diphosphines **2a-c** at 52, 71 and 72% yields, respectively (N.B. the overall yields of **2a** and **2b** were 28% and 39% from the same starting material, which were considerably higher than those of route A). In addition, minor amounts of the monophosphine $FcCH_2PPh_2$ were isolated analogously to other reactions involving lithioferrocene intermediates.

The presence of the (diphenylphosphino)methyl groups in **2a-c** is indicated by the signals of the methylene linker (^{1}H NMR: $\delta_H \approx 3.16$, ^{13}C NMR: δ_C 30.0, doublet with $^1J_{PC} = 15$ Hz) and by the ^{31}P NMR resonances at $\delta_P \approx -11.5$. The ^{31}P NMR signals of the other phosphine substituents directly bound to the ferrocene unit are observed at δ_P −7.1, 0.9 and 28.3 for **2a**, **2b** and **2c**, respectively.

The formulation of compounds **7a** and **9b** was corroborated by single-crystal X-ray diffraction analysis. The molecular structure of **7a** (Fig. 4) is unexceptional considering the data reported for the analogous compound $Ph_2PfcCHO$ [27]. The ferrocene cyclopentadienyls are tilted by 4.4(1)° and their substituents assume a synclinal eclipsed conformation with $\tau = 76.5(1)°$. The formyl substituent (C11 = O = 1.207(2) Å) is slightly rotated from the plane of its bonding cyclopentadienyl ring C(1–5), and the torsion angle C2-C1-C11-O is 11.5(3)°.

Compound **9b** crystallizes (Fig. 5) with two structurally independent molecules primarily differing in the mutual orientation of the substituents at the ferrocene unit (space group $P2_1/c$). In both molecules, the cyclopentadienyls adopt a similar, approximately synclinal eclipsed conformation ($\tau = 73.2(2)°$ and $-74.1(2)°$ for molecules 1 and 2). Considering the conformation of the ferrocene unit, the molecules are formally pseudoenantiomers because the rotation of the cyclopentadienyls is prevented in the solid state, and the CH_2OH groups are positioned in roughly mirror-image positions with respect to the phosphine substituent (see the overlap in Fig. 5). In addition, the CH_2OH moiety is directed away from the ferrocene moiety in molecule 1 (C102-C101-C111-O1 = 82.4(3)°),

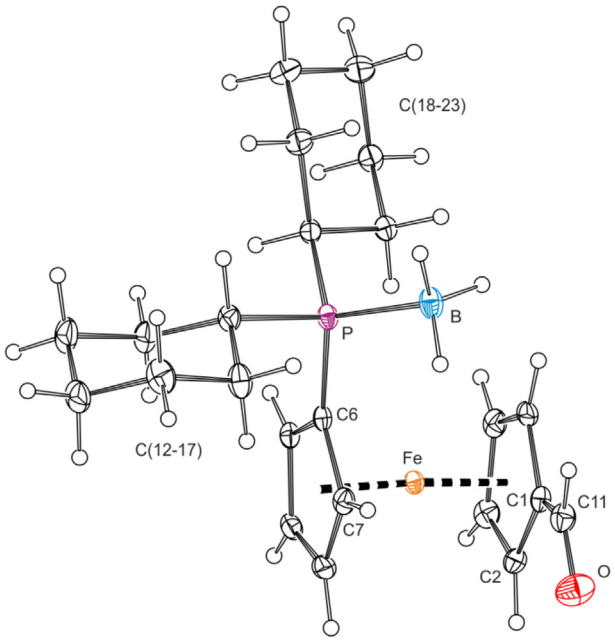


Fig. 4. PLATON plots of the molecular structure of **7a**. The displacement ellipsoids enclose the 30% probability level.

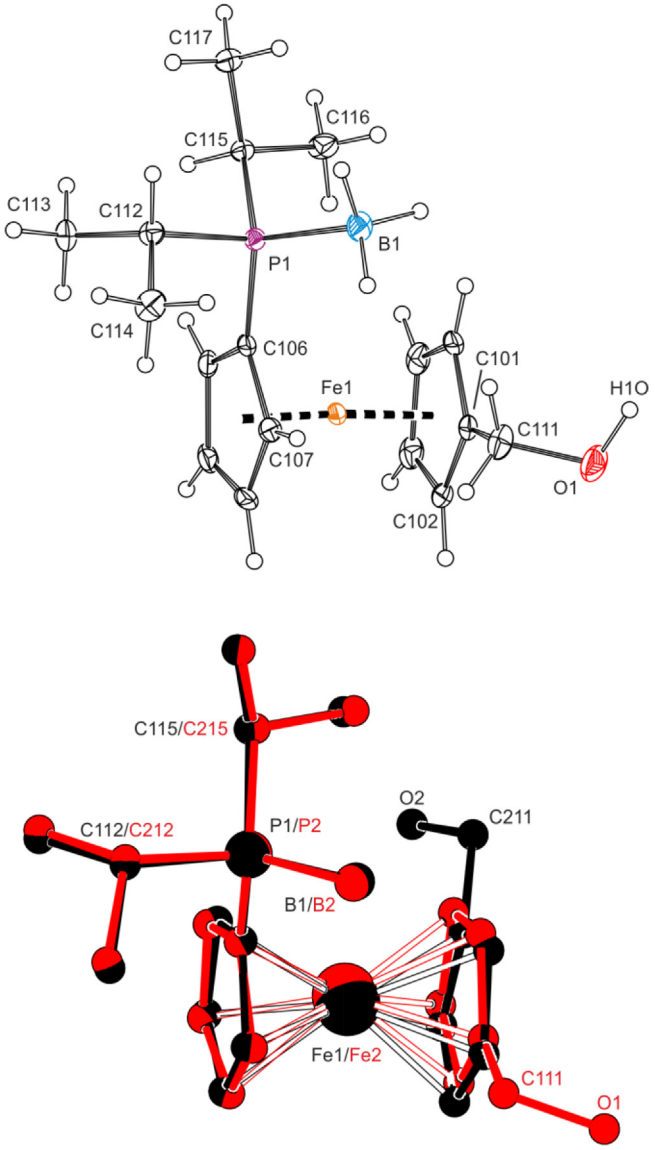
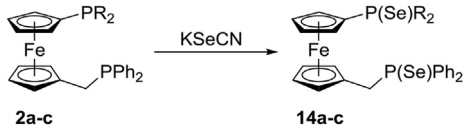


Fig. 5. (top) PLATON plot of molecule 1 in the structure of **9b** with displacement ellipsoids at 30% probability level. Note: the labelling scheme in molecule 2 is strictly analogous, and the first digit is replaced by 2. (bottom) Overlap of the two independent molecules. The hydrogen atoms are omitted for clarity.

whereas this moiety is rotated toward the iron atom in molecule 2 (C202-C201-C211-O2 = −158.3(2)°). In the solid state, the independent molecules interact via O-H···O hydrogen bonds to form dimers, which further assemble into infinite helical chains along the crystallographic 2_1 screw axis (O1-H1O···O2: O1···O2 = 2.696(2) Å, angle at H1O = 163°; O2-H2O···O1^{i}: O2···O1^{i} = 2.649(3) Å, angle at H2O = 170°, i = x, 1/2−y, 1/2 + z). Similar interactions resulting in the multiplication of the structurally independent molecules were also noted in the crystal structures of $FcCH_2OH$ [28], Ph_2PfcCH_2OH [27], and $Ph_2PfcCH_2OH{\cdot}BH_3$ [5f].

Similarly to their dppf-like counterparts, the free phosphines **2a-c** were converted into the respective selenides **14a-c** by reaction with potassium selenocyanate in dichloromethane-methanol (Scheme 4; Note: the polar solvent is required to dissolve the inorganic reagent) and were isolated at 84, 82 and 58% yields, respectively, by column chromatography and subsequent crystallization. The selenation of the phosphine moieties results in a shift of the ^{31}P NMR signals to lower fields and in the emergence of the



Scheme 4. Synthesis of phosphine selenides **14a-c** (R = cyclohexyl (**a**), isopropyl (**b**), and *tert*-butyl (**c**)).

Table 3
^{31}P NMR shifts (in ppm) and $^{1}J_{SeP}$ coupling constants (in Hz; values in parentheses) of phosphine selenides **4a-c** and **14a-c**.[a]

Compound	R	δ_P ($^{1}J_{SeP}$)	
		$P(Se)Ph_2$	$P(Se)R_2$
4a	Cy	31.7 (736)	50.0 (704)
4b	*i*-Pr	31.8 (737)	58.2 (710)
4c	*t*-Bu	31.8 (736)	74.6 (705)
14a	Cy	34.0 (729)	50.4 (696)
14b	*i*-Pr	34.0 (729)	58.8 (702)
14c	*t*-Bu	33.8 (728)	75.3 (699)

[a] The spectra were recorded in $CDCl_3$. Chemical shifts are given relative to 85% H_3PO_4.

^{77}Se satellites. In the case of the CH_2PPh_2 substituents, this is also manifested as a shift of the methylene resonances to a lower field ($\delta_H \approx 4.14$; $\Delta\delta_H \approx +1.0$ ppm) and their splitting into doublets ($^{2}J_{PH} \approx 12$ Hz; Note: the methylene signals in the free phosphines are observed as singlets). Similar changes are noted also in the ^{13}C NMR spectra, wherein the methylene resonances appear shifted to a lower field ($\Delta\delta_C \approx +6$ ppm), and the $^{1}J_{PC}$ coupling constants increase (from 15 to 44 Hz).

The comparison of the ^{31}P NMR parameters of **4a-c** and **14a-c** outlined in Table 3 shows that, although the chemical shifts (δ_P) and the $^{1}J_{SeP}$ coupling constants of the invariant $P(Se)Ph_2$ moieties in both *separated* series remain largely unchanged, those of the other phosphinoselenoyl substituents $P(Se)R_2$ expectedly vary. In the dppf-type compounds, the chemical shifts increase in the series **4a** < **4b** < **4c**, whereas the $^{1}J_{SeP}$ coupling constants rise in the following sequence of the phosphine substituents, Cy ≈ *t*-Bu < *i*-Pr ≪ Ph, suggesting a decrease in donor ability of the phosphorus atoms in the same order. Overall, the observed coupling constants are quite similar to those determined for the symmetric compounds $fc[P(Se)R_2]_2$ (R/$^{1}J_{SeP}$ [Hz]: Ph/737 [16], Cy/710 [17], *i*-Pr/716 [18], and *t*-Bu/700 [19]).

The $^{1}J_{SeP}$ coupling constants determined for the $P(Se)Ph_2$ substituents in **14a-c** are 7−8 Hz lower than the respective values in **4a-c**, and a similar trend is observed even for the varied $P(Se)R_2$ substituents, which in turn allows us to classify the homologous diphosphines **14** as better donors than their dppf-type analogues **4**. However, it should be noted that the $^{1}J_{SeP}$ coupling constants are not a simple measure of either electronic or steric properties. Indeed, the $^{1}J_{SeP}$ coupling constants (in absolute values) were shown to increase with the increasing electron-withdrawing character of the phosphine substituents (due to the higher s-character of the phosphorus lone pair) [7] and also correlate with the basicity (pK_b) of the phosphine ligands [29]. However, they are also affected by steric factors. In particular, closing the C-P-C angles in phosphines with bulky substituents reduces the s-character of the phosphorus lone pair and, consequently, decreases the $^{1}J_{SeP}$ coupling constants [30].

In addition to spectroscopic characterization, the solid-state structures of the phosphine selenides **14a-c** were determined by single-crystal X-ray diffraction analysis. The structures are presented in Fig. 6, and the selected geometric parameters are outlined in Table 4. The substituents at the central ferrocene units in the

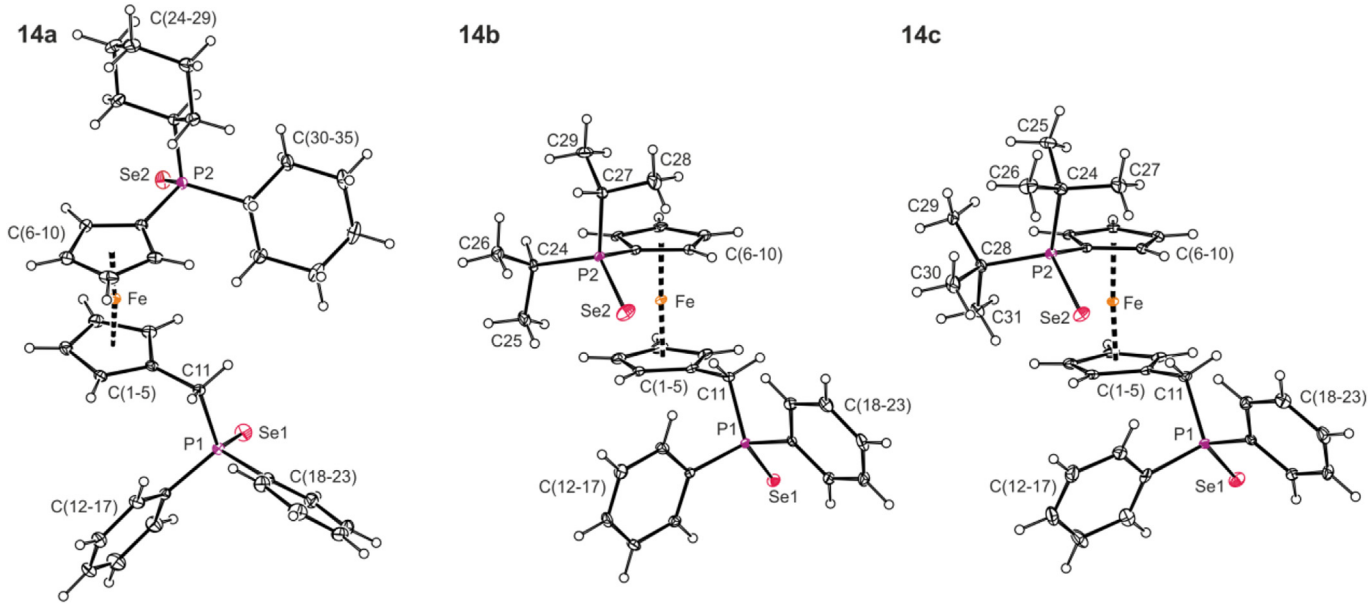
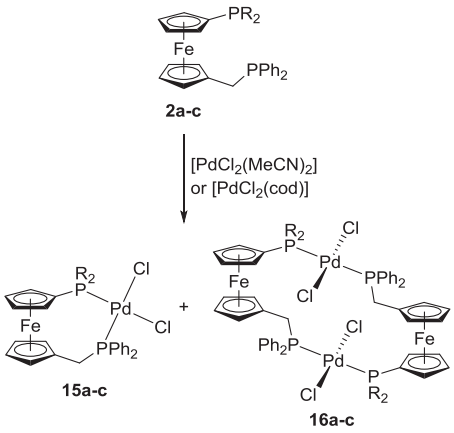


Fig. 6. PLATON plots of the molecular structures of **14a-c** with the displacement ellipsoids scaled to the 30% probability level.

Table 4
Selected distances and angle for **14a-c** (in Å and deg).[a]

Parameter	14a	14b	14c
Fe-C	2.036(3)-2.067(3)	2.038(3)-2.056(3)	2.030(3)-2.062(3)
φ	5.9(2)	1.9(2)	4.2(2)
τ	84.2(2)	−74.0(2)	−76.7(2)
C11-P1	1.834(3)	1.829(3)	1.834(3)
P1-Se1	2.1105(7)	2.1086(8)	2.111(1)
C6-P2	1.792(3)	1.790(3)	1.800(3)
P2-Se2	2.1249(7)	2.1117(9)	2.1284(9)
C1-C11-P1	112.0(2)	114.4(2)	113.7(2)

[a] The parameters are defined as for **4a-c**. See footnotes to Table 1.



Scheme 5. Synthesis of Pd(II) complexes from diphosphines **2a-c** (R = cyclohexyl (**a**), isopropyl (**b**), and *tert*-butyl (**c**); cod = cyclocta-1,5-diene).

molecules of **14a-c** are rotated to closer positions than those in **4a-c**, assuming near-synclinal eclipsed conformations in all cases (ideal value: τ = 72°). This can be associated with decreased steric crowding due to the presence of the methylene spacer, which allows placing the P(Se)Ph_2 groups away from the ferrocene moiety. The orientation of the terminal P(Se)Ph_2 moieties in the three compounds is rather similar, as shown by the torsion angles Se1-P1-C11-C1 of 66.3(2)°, 54.3(2)° and 57.0(3)° for **14a-c**, and even the terminal P(Se)R_2 substituents are similarly positioned, with the P2=Se2 bond roughly parallel to the bonding cyclopentadienyl ring. Other parameters, including the P=Se distances, are similar to those determined for **4a-c**.

In contrast to complexation reactions with dppf-type ligands **1a-c**, which afforded the complexes **5a-c** as the sole products (see above), the addition of phosphines **2a-c** to $PdCl_2$ equivalents (viz., [$PdCl_2$(MeCN)$_2$] or [$PdCl_2$(cod)]) produced mixtures of several Pd(II) complexes, whose relative amounts partly depended on how the reaction was performed (e.g., whether a ligand solution was added to a solid Pd precursor or to its solution) and changed over time [31]. In the case of diphosphines **2a** and **2b** (Scheme 5), the reaction mixtures were markedly dominated by the *cis*-chelate complexes **15a-b** (85–90%) analogous to **5** and also contained minor amounts of the symmetrical dinuclear complexes **16a-b** (10–15%) as well as some other unidentified compounds (most likely the plausible asymmetric dimer also). Upon prolonged standing at room temperature or after heating to 50 °C for several hours, the unknown minor species nearly disappeared, and the compounds **15a-b** and **16a-b** became the dominant products (>95%), whilst their ratio remained practically unchanged (around 85:15; see Fig. 7). Notably, a similar reaction with ligand **2c**

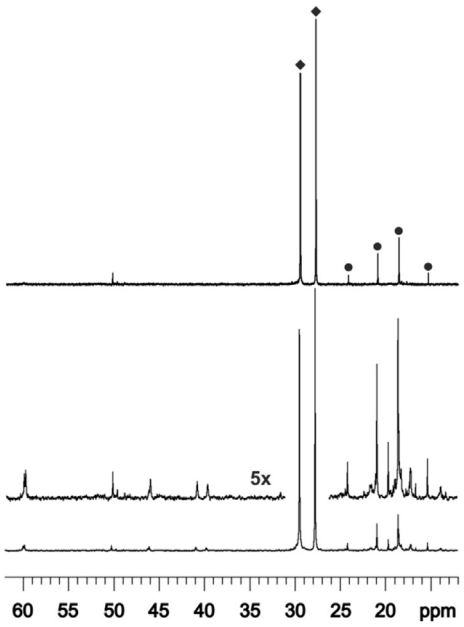


Fig. 7. $^{31}P\{^1H\}$ NMR spectra of the mixture obtained upon reacting stoichiometric amounts of **2a** and [$PdCl_2$(MeCN)$_2$] in $CDCl_3$ (bottom) and after heating this mixture to 50 °C overnight (top). The signals due to **15a** (◆) and **16a** (•) are indicated in the spectra.

featuring the bulky di-*tert*-butylphosphino substituent proved less selective and, after equilibration (50 °C/overnight), led to a mixture of **15c** and **16c** with a modest preference for the dinuclear complex (**15c**:**16c** ≈ 40:60).

Compounds **15** and **16** could be clearly distinguished based on their NMR parameters. Thus, complexes **15a-c** give rise to a pair of singlets in the ^{31}P NMR spectra, and the signals of the PPh_2 donor occur at $\delta_P \approx 29$. This is consistent with the NMR data of the *cis*-chelate complexes [$PdCl_2$(dppf-κ^2*P,P′*)] (δ_P 34.0 [32]) and [$PdCl_2$($Ph_2PfcCH_2PPh_2$-κ^2*P,P′*)] (δ_P 18.2 and 24.6, both singlets [4]). Conversely, a pair of doublets with $^2J_{PP}$ coupling constants in the range 528–541 Hz [33] are observed in the spectra of **16a-c,** and the signals of the PPh_2 moieties are found at $\delta_P \approx 16.5$, which corresponds to the position of the ^{31}P NMR signals of the bis-phosphine complexes *trans*-[$PdCl_2$(Ph_2PfcY-κ*P*)$_2$] (Y = CH=CH_2 [34], $(CH_2)_n$OMe [35,5f], $(CH_2)_n$SMe [36,5i], $(CH_2)_nC_5H_4N$ [5a], CO_2H [37], PO_3Et_2 [38], etc.; n = 0 and 1 in all cases).

Our attempts to isolate pure compounds by crystallization of the reaction mixtures failed. Nevertheless, the crystallization, which is apparently governed by the relative solubility of the components (**15** vs. **16**), provided small amounts of crystalline **15a**·CH_2Cl_2, **16b** and **16c,** which were structurally characterized. The molecular structure of **15a**·CH_2Cl_2 is shown in Fig. 8, and the relevant structural parameters are outlined in Table 5. Comparison with the parameters determined for **5a** (see Table 2) reveals that the more flexible ligand **2a** coordinates with a slightly larger bite angle (P1-Pd-P2, by ca. 1.7°). This finding contrasts with the changes observed when replacing dppf by $Ph_2PfcCH_2PPh_2$ in a similar complex, decreasing the bite angle by 2–3°. Nonetheless, this can be attributed to steric effects, namely to the presence of the bulky cyclohexyl groups that occupy a larger volume than flat phenyl rings. The same effects may explain the significant distortion of the coordination sphere around palladium, where the two half planes, {Pd, P1, P2} and {Pd, Cl1, Cl2}, are twisted by as much as 13.00(3)°. However, the individual geometric parameters match well those

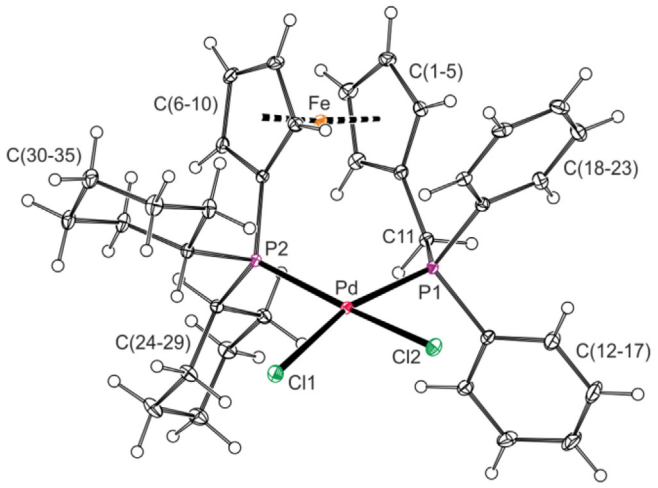


Fig. 8. PLATON plot of the complex molecule in the structure of **15a**·CH_2Cl_2. The displacement ellipsoids enclose the 30% probability level.

Table 5
Selected distances and angles for **15a**·CH_2Cl_2 (in Å and deg).[a]

Pd-P1	2.2901(5)	P1-Pd-P2	102.99(2)
Pd-P2	2.2883(5)	Cl1-Pd-Cl2	87.11(2)
Pd-Cl1	2.3435(5)	P1-Pd-Cl2	82.95(2)
Pd-Cl2	2.3606(5)	P2-Pd-Cl1	88.54(2)
Fe-C	2.030(2)-2.047(2)	φ	3.80(9)
Fe···Pd	4.7156(5)	τ	−16.7(1)
C11-P1	1.853(2)	C1-C11-P1	122.6 (1)

[a] The parameters are defined as for compounds **4a-c**, see footnotes to Table 1.

determined for **5a**. Even the ferrocene cyclopentadienyls in the structure of **15a**·CH_2Cl_2 are rotated similarly to those in **5a**, assuming an intermediate conformation between eclipsed synperiplanar ($\tau = 0°$) and staggered synclinal ($\tau = 36°$), and are tilted by approximately 4°. Because of the chelate coordination, the CH_2PPh_2 group is inclined toward the ferrocene unit at an angle between the C11-P1 bond and the C(1–5) plane of 34.18(8)°.

Complexes **16b** and **16c** (Fig. 9 and Table 6) crystallize distributed around the crystallographic inversion centers. Therefore, only half of their molecules are structurally independent, which

Table 6
Selected distances and angles for **15b** and **15c** (in Å and deg).[a]

Parameter	15b	15c
Pd-P1	2.3203(8)	2.3255(8)
Pd-P2′	2.3615(8)	2.4214(8)
Pd-Cl1	2.2946(9)	2.3349(8)
Pd-Cl2	2.2989(8)	2.2788(8)
P1-Pd-Cl1	84.41(3)	83.68(3)
P1-Pd-Cl2	91.13(3)	89.82(3)
P2′-Pd-Cl1	93.51(3)	97.66(3)
P2′-Pd-Cl2	91.28(3)	89.82(3)
Fe-C	2.042(3)-2.061(3)	2.038(3)-2.083(3)
φ	4.1(2)	8.0(2)
τ	81.3(2)	149.5(2)
C11-P1	1.853(3)	1.844(3)
C1-C11-P1	114.8(2)	116.3(2)

[a] The parameters are defined as for compounds **4a-c**, see footnotes to Table 1. The prime-labeled atoms are generated by crystallographic inversion.

underlines the symmetric (head-to-tail) character of these dimeric compounds. Notably, the coordination spheres around the palladium atoms in **16b** and **16c** are considerably less angularly distorted than those in **5a-c** and **15a**, presumably because the bulky phosphine moieties are more distant, occupying *trans* positions. In both structures, the Pd-Cl1 arms are diverted from the bulky PR_2 groups so that the P1-Pd-Cl1 angles are the most acute and the P2′-Pd-Cl1 angles the most opened of the interligand angles, and this departure from the ideal 90° is more pronounced in **16c** featuring the bulkier P(*t*-Bu)$_2$ moiety. The changed disposition of the donor atoms also affects the Pd-P and the Pd-Cl distances due to different *trans* influence [39] of the donor atoms (P > Cl): the Pd-Cl distances are shorter than those in the *cis*-chelate complexes, whereas the Pd-P bonds are longer. For steric reasons, the Pd-P2′ distance in **16c** is 0.06 Å longer than that in **16b** (Note: the difference between the Pd-P2 distances in **5b** and **5c** is much smaller, 0.04 Å). In addition, the molecules of **16b** and **16b** differ by mutual orientation of their substituted ferrocene moieties. The less opened conformation of the ferrocene scaffold in **16b** ($\tau \approx 80°$) than in **16c** ($\tau \approx 150°$) results in a more compact structure with a shorter Pd···Pd' distance (6.8777(5) Å vs. 8.3827(6) Å). Furthermore, the bridging conformation also allows the reorientation of the CH_2PPh_2 arm to a sterically more relaxed position, away from the ferrocene unit (cf. the angles between the C11-P1 bonds and the C(1–5) planes of 65.3(2)° and 57.0(2)° for **16b** and **16c**, respectively).

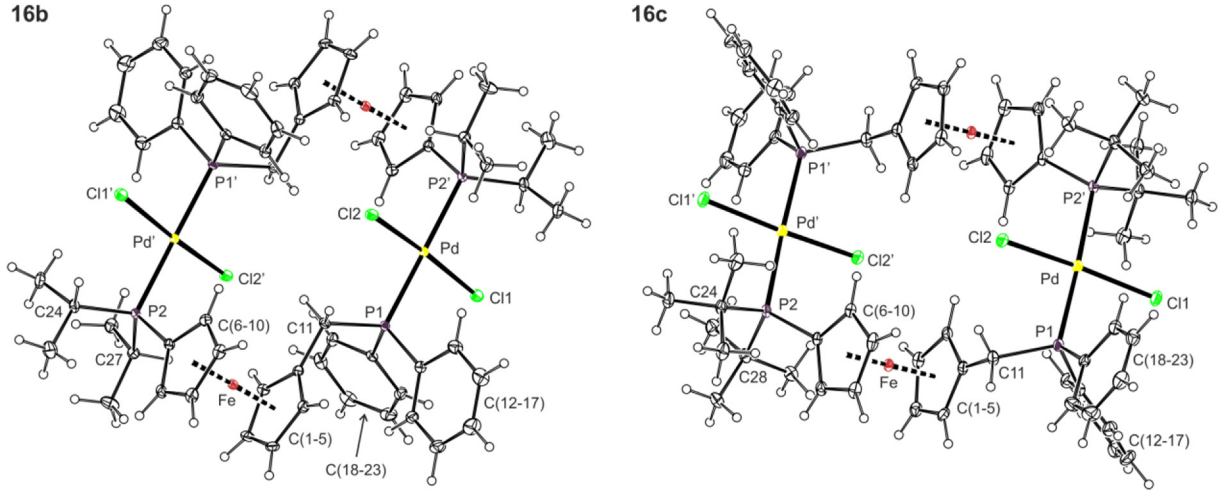


Fig. 9. PLATON plot of the molecular structure of dimeric complexes **16b** and **16c** showing 30% displacement ellipsoids.

3. Conclusion

Several asymmetric, dppf-type diphosphines with diverse phosphine substituents were prepared by bromine/lithium exchange and phosphinylation from 1′-(diphenylphosphino)-1-bromoferrocene and isolated in the form of air-stable borane adducts. These compounds were smoothly deprotected with dabco, and the resulting free diphosphines (requiring no tedious isolation) were converted into the respective phosphine selenides and *P,P′*-chelate palladium(II) complexes. The corresponding homologous ligands containing a methylene spacer between the PPh_2 moiety were prepared via BH_3-protected intermediates (with the varied PR_2 group introduced first) and also directly in the free phosphine form with the PR_2 introduced in the last step. The latter synthesis proved to be more practical, allowing an easier variation of the varied phosphine substituents and affording substantially higher yields. The coordination tests with $R_2PfcCH_2PPh_2$ revealed the concurrent formation of monopalladium chelate complexes (dominant) and ligand-bridged dimers. Thus, although the $^1J_{SeP}$ coupling constants suggest that the homologous diphosphines are better (stronger) donors than their non-spaced, dppf-type counterparts, the former coordinate less selectively, presumably because they form larger and less rigid chelate rings.

4. Experimental

4.1. General considerations

All reactions were performed in an argon atmosphere using standard Schlenk techniques. 1′-(Diphenylphosphino)-1-bromoferrocene [9], **6a-b** [6], **12** and **13** [5h] were prepared according to literature methods. Other chemicals were purchased from commercial suppliers (Alfa-Aesar, Sigma-Aldrich; solvents from Lach-Ner, Czech Republic) and were used without additional purification. Tetrahydrofuran (THF), methanol and dichloromethane were dried using a PureSolv MD5 solvent purification system (Innovative Technology, Amesbury, USA). Acetonitrile was dried over CaH_2 and distilled under an argon atmosphere. Toluene and triethylamine were dried over sodium metal and distilled similarly. Morpholine was distilled under argon.

NMR spectra were recorded at 25 °C using a Varian UNITY Inova 400 spectrometer operating at 399.95, 100.58, and 161.90 MHz for ^1H, ^{13}C, and ^{31}P, respectively. Chemical shifts (δ in ppm) are expressed relative to the internal $SiMe_4$ standard (^1H and ^{13}C) or to the external 85% aqueous H_3PO_4 (^{31}P), all set to 0 ppm. In addition to the usual notation of signal multiplicity [40], vt and vq are used to denote virtual triplets and quartets in the ^1H NMR spectra arising from the AA'BB′ and AA'BB′X (A, B = ^1H; X = ^{31}P) spin systems constituted by the protons at the ferrocene cyclopentadienyls. IR spectra were measured using an FTIR Nicolet 760 instrument in the range 400–4000 cm^{-1}. Conventional low-resolution electrospray ionization mass spectra (ESI MS) were obtained on a Bruker Esquire 3000 spectrometer using samples dissolved in HPLC-grade methanol. High-resolution (HR) ESI MS measurements were performed using a Q-tof Micro (Waters) spectrometer. Elemental analyses were performed in a PE 2400 Series II CHNS/O elemental analyzer (Perkin Elmer).

4.2. Synthesis of 1′-(dicyclohexylphosphino)-1-(diphenylphosphino)ferrocene–borane (1/2), adduct ***3a***

A two-neck, oven-dried reaction flask was charged with 1′-(diphenylphosphino)-1-bromoferrocene (2.24 g, 5.0 mmol) and a stirring bar. The solid educt was dissolved by adding anhydrous THF (25 mL), and the solution was cooled to −78 °C in a dry ice/ethanol bath while stirring. *n*-Butyllithium (2.2 mL 2.5 M in hexanes, 5.5 mmol) was added continuously stirring at −78 °C for 15 min to afford an orange suspension. Subsequently, neat chlorodicyclohexylphosphine (1.4 mL, 6.0 mmol) was introduced, and the reaction mixture was stirred with cooling for 30 min, and then at room temperature for 90 min. The resulting red solution was treated with an excess of borane-dimethyl sulfide (7.5 mL of 2 M solution in diethyl ether, 15 mmol) and stirred for another 30 min before quenching by adding saturated aqueous $NaHCO_3$ (a vigorous effervescence was observed due to decomposition of an excess $BH_3{\cdot}SMe_2$). Then, the mixture was diluted with chloroform (ca. 15 mL) and brine (ca. 10 mL). The organic phase was separated, washed with brine, dried over anhydrous magnesium sulfate and evaporated with chromatographic silica gel (40–63 μm, ca. 10–15 mL). The pre-adsorbed product was transferred onto a silica gel column packed in hexane-toluene (1:3). Elution with the same solvent provided a minor yellow band containing mostly $FcPPh_2{\cdot}BH_3$, and then a major orange red band due to **3a**, which was isolated as an orange microcrystalline solid after evaporation. Yield: 2.44 g (82%). The product could be crystallized from hot heptane.

^1H NMR (399.95 MHz, $CDCl_3$): δ 0.20–1.50 (br m, 6 H, BH_3), 1.05–1.35 (m, 10 H, Cy), 1.60–1.90 (m, 12 H, Cy), 4.19 (vq, J' = 1.8 Hz, 2 H, fc), 4.42 (d of vt, J = 0.9, 1.8 Hz, 2 H, fc), 4.45 (vq, J' = 1.9 Hz, 2 H, fc), 4.77 (d of vt, J = 1.2, 1.8 Hz, 2 H, fc), 7.39–7.51 (m, 6 H, Ph), 7.54–7.60 (m, 4 H, Ph). $^{13}C\{^1H\}$ NMR (100.58 MHz, $CDCl_3$): δ 25.87 (d, J_{PC} = 1 Hz, 2 C, CH_2 of Cy), 26.79 (s, 2 C, CH_2 of Cy), 26.89 (s, 4 C, CH_2 of Cy), 27.17 (d, J_{PC} = 2 Hz, 2 C, CH_2 of Cy), 32.44 (d, $^1J_{PC}$ = 34 Hz, 2 C, CH of Cy), 70.12 (d, $^1J_{PC}$ = 67 Hz, 1 C, C_{ipso}–P of fc), 70.26 (d, $^1J_{PC}$ = 55 Hz, 1 C, C_{ipso}–P of fc), 72.95 (d, J_{PC} = 7 Hz, 2 C, CH of fc), 73.15 (d, J_{PC} = 6 Hz, 2 C, CH of fc), 73.93 (d, J_{PC} = 10 Hz, 2 C, CH of fc), 74.82 (d, J_{PC} = 7 Hz, 2 C, CH of fc), 128.50 (d, J_{PC} = 10 Hz, 4 C, CH of Ph), 130.85 (d, $^1J_{PC}$ = 59 Hz, 2 C, C_{ipso}–P of Ph), 131.05 (d, $^4J_{PC}$ = 2 Hz, 2 C, CH of Ph), 132.58 (d, J_{PC} = 10 Hz, 4 C, CH of Ph). $^{31}P\{^1H\}$ NMR (161.90 MHz, $CDCl_3$): δ 16.3 (br d, PPh_2), 24.4 (br d, PCy_2). ESI + MS: *m/z* 617 ($[M+Na]^+$). Anal. Calc. for $C_{34}H_{46}B_2FeP_2$ (594.14): C 68.73, H 7.80%. Found: C 68.47, H 7.63%.

4.3. Synthesis of 1′-(diisopropylphosphino)-1-(diphenylphosphino) ferrocene–borane (1/2), adduct ***3b***

The same procedure exploiting chlorodiisopropylphosphine (1.0 mL, 6.0 mmol) provided adduct **3b** as an orange-red crystalline solid. Yield: 2.21 g (86%). Compound **3b** can be recrystallized from hot heptane.

^1H NMR (399.95 MHz, $CDCl_3$): δ 0.10–0.95 (br m, 6 H, BH_3), 1.06 (dd, $^3J_{HH}$ = 7.1 Hz, $^3J_{PH}$ = 14.2 Hz, 6 H, CH*Me*$_2$), 1.11 (dd, $^3J_{HH}$ = 7.1 Hz, $^3J_{PH}$ = 14.9 Hz, 6 H, CH*Me*$_2$), 2.04 (d of sept, $^2J_{PH}$ = 10.1 Hz, $^3J_{HH}$ = 7.1 Hz, 2 H, C*H*Me$_2$), 4.22 (vq, J' = 1.8 Hz, 2 H, fc), 4.44 (d of vt, J = 0.9, 1.8 Hz, 2 H, fc), 4.48 (vq, J' = 1.9 Hz, 2 H, fc), 4.79 (d of vt, J = 1.2, 1.9 Hz, 2 H, fc), 7.39–7.61 (m, 10 H, Ph). $^{13}C\{^1H\}$ NMR (100.58 MHz, $CDCl_3$): δ 17.22 (s, 2 C, CH*Me*$_2$), 17.47 (d, $^2J_{PC}$ = 2 Hz, 2 C, CH*Me*$_2$), 22.62 (d, $^1J_{PC}$ = 35 Hz, 2 C, *C*HMe$_2$), 69.75 (d, $^1J_{PC}$ = 55 Hz, 1 C, C_{ipso}–P of fc), 70.19 (d, $^1J_{PC}$ = 67 Hz, 1 C, C_{ipso}–P of fc), 72.83 (d, J_{PC} = 7 Hz, 2 C, CH of fc), 73.18 (d, J_{PC} = 6 Hz, 2 C, CH of fc), 73.94 (d, J_{PC} = 10 Hz, 2 C, CH of fc), 74.80 (d, J_{PC} = 7 Hz, 2 C, CH of fc), 128.52 (d, J_{PC} = 10 Hz, 4 C, CH of Ph), 130.84 (d, $^1J_{PC}$ = 59 Hz, 2 C, C_{ipso}–P of Ph), 131.06 (d, $^4J_{PC}$ = 3 Hz, 2 C, CH of Ph), 132.59 (d, J_{PC} = 10 Hz, 4 C, CH of Ph). $^{31}P\{^1H\}$ NMR (161.90 MHz, $CDCl_3$): δ 16.2 (br d, PPh_2), 31.8 (br d, P*i*Pr$_2$). ESI + MS: *m/z* 537 ($[M+Na]^+$), 553 ($[M+K]^+$). Anal. Calc. for $C_{28}H_{38}B_2FeP_2$ (513.99): C 65.42, H 7.45%. Found: C 65.11, H 7.58%.

4.4. Synthesis of 1′-(di-tert-butylphosphino)-1-(diphenylphosphino)ferrocene–borane (1/2), adduct **3c**

Compound **3c** was synthesized and isolated similarly to **3a** using chloro-di-*tert*-butylphosphine (1.2 mL, 6.0 mmol) as the phosphinylating agent (Note: during the chromatographic purification, the product followed two minor, faster travelling bands, which were discarded). Yield of **3c**: 1.17 g (43%), orange solid. The compound was crystallized from hot heptane.

^{1}H NMR (399.95 MHz, $CDCl_3$): δ 0.20–1.00 (br m, 6 H, BH_3), 1.19 (d, $^3J_{PH}$ = 12.9 Hz, 18 H, CMe_3), 4.29 (vq, J' = 1.7 Hz, 2 H, fc), 4.44 (vq, J' = 1.9 Hz, 2 H, fc), 4.51 (d of vt, J = 0.9, 1.9 Hz, 2 H, fc), 4.80 (d of vt, J = 1.2, 1.9 Hz, 2 H, fc), 7.39–7.61 (m, 10 H, Ph). ^{13}C{^{1}H} NMR (100.58 MHz, $CDCl_3$): δ 28.55 (d, $^2J_{PC}$ = 2 Hz, 6 C, C*Me*$_3$), 33.32 (d, $^1J_{PC}$ = 28 Hz, 2 C, *C*Me$_3$), 70.18 (d, $^1J_{PC}$ = 67 Hz, 1 C, C_{ipso}–P of fc), 71.78 (d, $^1J_{PC}$ = 49 Hz, 1 C, C_{ipso}–P of fc), 73.03 (d, J_{PC} = 6 Hz, 2 C, CH of fc), 74.24 (d, J_{PC} = 10 Hz, 2 C, CH of fc), 74.43 (d, J_{PC} = 7 Hz, 2 C, CH of fc), 75.15 (d, J_{PC} = 7 Hz, 2 C, CH of fc), 128.52 (d, J_{PC} = 10 Hz, 4 C, CH of Ph), 130.88 (d, $^1J_{PC}$ = 59 Hz, 2 C, C_{ipso}–P of Ph), 131.05 (d, $^4J_{PC}$ = 2 Hz, 2 C, CH of Ph), 132.61 (d, J_{PC} = 10 Hz, 4 C, CH of Ph). ^{31}P{^{1}H} NMR (161.90 MHz, $CDCl_3$): δ 16.3 (br d, PPh_2), 45.4 (br d, P*t*Bu$_2$). ESI + MS: *m/z* 565 ([M+Na]$^+$), 581 ([M+K]$^+$). Anal. Calc. for $C_{30}H_{42}B_2FeP_2$ (542.05): C 66.47, H 7.81%. Found: C 66.22, H 7.72%.

4.5. Synthesis of 1′-(dicyclohexylphosphinoselenoyl)-1-(diphenylphosphinoselenoyl)ferrocene, compound **4a**

A Schlenk tube equipped with a stirring bar was charged with borane adduct **1a** (297 mg, 0.50 mmol), dabco (229 mg, 2.0 mmol) and anhydrous toluene (5 mL), flushed with argon and sealed with a glass stopper. After heating to 80 °C overnight, the mixture was cooled to room temperature and transferred to a chromatographic column (silica gel, hexane-ethyl acetate 3:1; the mobile phase was deoxygenated by degassing in an ultrasound bath and then by bubbling with argon). Elution with the same solvent afforded a single orange band, which was evaporated. The residue was dissolved in anhydrous dichloromethane (5 mL) and methanol (15 mL) and added onto solid potassium selenocyanate (159 mg, 1.1 mmol). After stirring at room temperature for 24 h, the reaction mixture was evaporated with chromatographic silica gel. The pre-adsorbed product was purified by column chromatography over silica gel using toluene as the eluent. The first yellow band was discarded and the following, major orange red band, eluted by toluene-ethyl acetate (20:1) to avoid tailing, was collected and evaporated to afford the crude product, which was subsequently dissolved in a boiling mixture of toluene (5 mL) and heptane (15 mL). The solution was treated with little charcoal, filtered and slowly cooled down to 4 °C to afford compound **4a** as an orange crystalline solid, which was isolated by suction and dried under vacuum. Yield: 286 mg (79%).

^{1}H NMR (399.95 MHz, $CDCl_3$): δ 1.08–1.38 (m, 10 H, Cy), 1.62–1.98 (m, 12 H, Cy), 4.30 (vq, J' = 1.8 Hz, 2 H, fc), 4.50 (vq, J' = 2.1 Hz, 2 H, fc), 4.59 (vq, J' = 1.7 Hz, 2 H, fc), 4.90 (vq, J' = 1.8 Hz, 2 H, fc), 7.40–7.51 (m, 6 H, Ph), 7.66–7.73 (m, 4 H, Ph). ^{13}C{^{1}H} NMR (100.58 MHz, $CDCl_3$): δ 25.73 (d, J_{PC} = 2 Hz, 2 C, CH_2 of Cy), 26.35 (s, 2 C, CH_2 of Cy), 26.37 (d, J_{PC} = 8 Hz, 2 C, CH_2 of Cy), 26.52 (d, J_{PC} = 6 Hz, 2 C, CH_2 of Cy), 27.22 (d, J_{PC} = 4 Hz, 2 C, CH_2 of Cy), 37.18 (d, $^1J_{PC}$ = 45 Hz, 2 C, CH of Cy), 73.22 (d, J_{PC} = 10 Hz, 2 C, CH of fc), 73.85 (d, J_{PC} = 9 Hz, 2 C, CH of fc), 74.35 (d, $^1J_{PC}$ = 69 Hz, 1 C, C_{ipso}–P of fc), 74.63 (d, J_{PC} = 12 Hz, 2 C, CH of fc), 75.28 (d, $^1J_{PC}$ = 88 Hz, 1 C, C_{ipso}–P of fc), 75.95 (d, J_{PC} = 9 Hz, 2 C, CH of fc), 128.30 (d, J_{PC} = 13 Hz, 4 C, CH of Ph), 131.43 (d, $^4J_{PC}$ = 3 Hz, 2 C, CH of Ph), 132.00 (d, J_{PC} = 11 Hz, 4 C, CH of Ph), 133.07 (d, $^1J_{PC}$ = 78 Hz, 2 C, C_{ipso}–P of Ph). ^{31}P{^{1}H} NMR (161.90 MHz, $CDCl_3$): δ 31.7 (s with ^{77}Se satellites, $^1J_{SeP}$ = 736 Hz, PPh_2), 50.0 (s with ^{77}Se satellites, $^1J_{SeP}$ = 704 Hz, PCy_2). IR (Nujol): ν_{max} 1483 *m*, 1437 s, 1417 w, 1386 *m*, 1367 *m*, 1344 w, 1308 *m*, 1296 w, 1268 w, 1198 *m*, 1193 *m*, 1175 s, 1169 *m*, 1101 *m*, 1079 w, 1072 w, 1059 *m*, 1038 *m*, 1024 *m*, 1000 w, 975 w, 923 w, 906 w, 891 w, 885 w, 862 w, 849 *m*, 841 *m*, 836 *m*, 827 w, 819 w, 813 w, 748 *m*, 740 s, 712 *m*, 704 *m*, 694 s, 675 w, 632 *m*, 620 w, 595 w, 575 s, 551 *m*, 536 *m*, 530 *m*, 526 *m*, 502 s, 480 s, 469 *m*, 454 *m*, 446 *m*, 432 *m*, 414 w cm^{-1}. ESI + MS: *m/z* 749 ([M+Na]$^+$). Anal. Calc. for $C_{34}H_{40}FeP_2Se_2$ (724.37): C 56.37, H 5.57%. Found: C 56.32, H 5.49%.

4.6. Synthesis of 1′-(diisopropylphosphinoselenoyl)-1-(diphenylphosphinoselenoyl)ferrocene, compound **4b**

Compound **4b** was prepared similarly, starting from **1b** (103 mg, 0.2 mmol) and dabco (183 mg, 1.2 mmol) in 3 mL of toluene, and using KSeCN (55 mg, 0.38 mmol) in dry methanol (15 mL) and dichloromethane (5 mL) for the subsequent selenation. The product was crystallized from a mixture of toluene (2 mL) and heptane (13 mL). Yield of **4b**: 193 mg (53%), orange crystalline solid.

^{1}H NMR (399.95 MHz, $CDCl_3$): δ 1.10 (dd, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 19.7 Hz, 6 H, CH*Me*$_2$), 1.14 (dd, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 20.0 Hz, 6 H, CH*Me*$_2$), 2.21 (d of sept, $^2J_{PH}$ = 8.6 Hz, $^3J_{HH}$ = 7.0 Hz, 2 H, *CH*Me$_2$), 4.35 (vq, J' = 1.8 Hz, 2 H, fc), 4.53 (vq, J' = 2.1 Hz, 2 H, fc), 4.59 (vq, J' = 1.7 Hz, 2 H, fc), 4.91 (vq, J' = 1.8 Hz, 2 H, fc), 7.40–7.51 (m, 6 H, Ph), 7.66–7.74 (m, 4 H, Ph). ^{13}C{^{1}H} NMR (100.58 MHz, $CDCl_3$): δ 16.86 (d, $^2J_{PC}$ = 1 Hz, 2 C, CH*Me*$_2$), 17.53 (d, $^2J_{PC}$ = 2 Hz, 2 C, CH*Me*$_2$), 27.72 (d, $^1J_{PC}$ = 45 Hz, 2 C, *C*HMe$_2$), 73.16 (d, J_{PC} = 10 Hz, 2 C, CH of fc), 73.85 (d, J_{PC} = 9 Hz, 2 C, CH of fc), 73.91 (d, $^1J_{PC}$ = 69 Hz, 1 C, C_{ipso}–P of fc), 74.61 (d, J_{PC} = 12 Hz, 2 C, CH of fc), 75.38 (d, $^1J_{PC}$ = 88 Hz, 1 C, C_{ipso}–P of fc), 75.93 (d, J_{PC} = 10 Hz, 2 C, CH of fc), 128.31 (d, J_{PC} = 13 Hz, 4 C, CH of Ph), 131.44 (d, $^4J_{PC}$ = 3 Hz, 2 C, CH of Ph), 132.02 (d, J_{PC} = 11 Hz, 4 C, CH of Ph), 133.04 (d, $^1J_{PC}$ = 78 Hz, 2 C, C_{ipso}–P of Ph). ^{31}P{^{1}H} NMR (161.90 MHz, $CDCl_3$): δ 31.8 (s with ^{77}Se satellites, $^1J_{SeP}$ = 737 Hz, PPh_2), 58.2 (s with ^{77}Se satellites, $^1J_{SeP}$ = 710 Hz, P*i*Pr$_2$). IR (Nujol): ν_{max} 1435 s, 1415 w, 1405 w, 1387 *m*, 1368 *m*, 1333 w, 1308 *m*, 1244 w, 1188 *m*, 1172 s, 1099 s, 1071 w, 1063 w, 1057 w, 1043 *m*, 1026 *m*, 998 w, 965 w, 931 w, 880 *m*, 869 w, 850 w, 834 s, 816 w, 760 *m*, 742 *m*, 699 s, 691 *m*, 678 *m*, 646 *m*, 633 *m*, 619 w, 592 w, 571 s, 536 *m*, 513 *m*, 505 *m*, 489 s, 478 s, 459 w, 449 w, 438 w, 419 *m*, 414 w cm^{-1}. ESI + MS: *m/z* 669 ([M+Na]$^+$). Anal. Calc. for $C_{28}H_{32}FeP_2Se_2$ (644.25): C 52.20, H 5.01%. Found: C 52.18, H 4.74%.

4.7. Synthesis of 1′-(di-tert-butylphosphinoselenoyl)-1-(diphenylphosphinoselenoyl)ferrocene, compound **4c**

The synthesis of phosphine selenide **4c** was performed as described for **4a**, starting from **1c** (108 mg, 0.20 mmol) and dabco (183 mg, 1.6 mmol) in 3 mL of toluene. The selenation was performed with KSeCN (46 mg, 0.32 mmol) in a mixture of dry methanol (10 mL) and dichloromethane (5 mL). Isolation, performed as described above (2 mL of toluene and 10 mL of heptane were used for crystallization), provided compound **4c** as an orange crystalline solid. Yield: 54 mg (40%).

^{1}H NMR (399.95 MHz, $CDCl_3$): δ 1.28 (d, $^3J_{PH}$ = 15.6 Hz, 18 H, CMe_3), 4.45 (vq, J' = 1.8 Hz, 2 H, fc), 4.49 (vq, J' = 2.1 Hz, 2 H, fc), 4.69 (vq, J' = 1.7 Hz, 2 H, fc), 4.91 (vq, J' = 1.8 Hz, 2 H, fc), 7.40–7.51 (m, 6 H, Ph), 7.67–7.74 (m, 4 H, Ph). ^{13}C{^{1}H} NMR (100.58 MHz, $CDCl_3$): δ 28.60 (d, $^2J_{PC}$ = 2 Hz, 6 C, C*Me*$_3$), 38.14 (d, $^1J_{PC}$ = 36 Hz, 2 C, *C*Me$_3$), 73.68 (d, J_{PC} = 8 Hz, 2 C, CH of fc), 74.79 (d, J_{PC} = 2 Hz, 2 C, CH of fc), 74.90 (d, J_{PC} = 5 Hz, CH of fc), 75.16 (d, $^1J_{PC}$ = 88 Hz, 1 C, C_{ipso}–P of fc), 76.03 (d, $^1J_{PC}$ = 61 Hz, 1 C, C_{ipso}–P of fc), 76.18 (d, J_{PC} = 10 Hz, 2 C, CH of fc), 128.31 (d, J_{PC} = 13 Hz, 4 C, CH of Ph), 131.42 (d, $^4J_{PC}$ = 3 Hz, 2 C, CH of Ph), 132.04 (d, J_{PC} = 11 Hz, 4 C, CH of Ph), 133.12 (d, $^1J_{PC}$ = 78 Hz, 2 C, C_{ipso}–P of Ph). ^{31}P{^{1}H} NMR (161.90 MHz, $CDCl_3$):

δ 31.8 (s with ^{77}Se satellites, $^{1}J_{SeP}$ = 736 Hz, PPh_2), 74.6 (s with ^{77}Se satellites, $^{1}J_{SeP}$ = 705 Hz, P*t*Bu$_2$). IR (Nujol): ν_{max} 1477 *m*, 1436 s, 1409 w, 1366 *m*, 1361 *m*, 1332 w, 1310 *m*, 1195 w, 1173 *m*, 1158 *m*, 1099 *m*, 1072 w, 1053 w, 1037 *m*, 1030 *m*, 998 w, 946 w, 939 w, 894 w, 864 w, 848 w, 833 *m*, 823 *m*, 807 *m*, 759 *m*, 740 *m*, 712 *m*, 700 *m*, 689 *m*, 636 *m*, 613 w, 591 w, 595 w, 569 s, 536 *m*, 513 *m*, 492 *m*, 482 s, 461 w, 446 *m*, 418 w cm^{-1}. ESI + MS: *m/z* 675 ([M+H]$^+$), 697 ([M+Na]$^+$). Anal. Calc. for $C_{30}H_{36}FeP_2Se_2$ (672.30): C 53.59, H 5.40%. Found: C 53.47, H 5.17%.

4.8. Synthesis of dichlorido{1′-(dicyclohexylphosphino-κP)-1-(diphenylphosphino-κP)ferrocene}palladium, complex **5a**

Adduct **1a** (119 mg, 0.20 mmol) and dabco (92 mg, 0.80 mmol) were dissolved in anhydrous toluene (2 mL) in a dry Schlenk tube equipped with a stirring bar, and the resultant mixture was stirred at 85 °C overnight. After cooling to room temperature, the reaction mixture was transferred to a chromatographic column (silica gel, hexane-ethyl acetate 3:1). The first orange band eluted with the same solvent was directly added to a dichloromethane solution of [$PdCl_2$(cod)] (57 mg, 0.20 mmol in 1–2 mL of the solvent), immediately generating an orange-red precipitate. After the addition was completed, the mixture was stirred for 30 min and evaporated. The residue was dissolved in dichloromethane, filtered through a Celite pad, and the filtrate was precipitated by adding diethyl ether. The formed solid was redissolved in dichloromethane, and the solution was layered with diethyl ether and then set aside for crystallization by liquid phase diffusion. Deep red crystals of **5a**, which formed during several days, were isolated by suction and dried under vacuum. Yield: 109 mg (74%). Crystals for structure determination were obtained from chloroform-hexane.

^{1}H NMR (399.95 MHz, CD_2Cl_2): δ 1.20–1.44 (m, 8 H, Cy), 1.65–2.06 (m, 10 H, Cy), 2.38–2.48 (m, 2 H, Cy), 2.64–2.76 (m, 2 H, Cy), 4.11 (vq, J' = 1.9 Hz, 2 H, fc), 4.35 (br m, 2 H, fc), 4.44 (br m, 2 H, fc), 4.70 (vq, J' = 1.7 Hz, 2 H, fc), 7.45–7.54 (m, 6 H, Ph), 7.94–8.01 (m, 4 H, Ph). ^{13}C{^{1}H} NMR (100.58 MHz, CD_2Cl_2): δ 26.39 (s, 2 C, CH_2 of Cy), 27.15 (d, J_{PC} = 12 Hz, 2 C, CH_2 of Cy), 27.54 (d, J_{PC} = 13 Hz, 2 C, CH_2 of Cy), 29.90 (s, 2 C, CH_2 of Cy), 30.58 (s, 2 C, CH_2 of Cy), 37.34 (d, $^{1}J_{PC}$ = 29 Hz, 2 C, CH of Cy), 72.77 (d, J_{PC} = 6 Hz, 2 C, CH of fc), 72.89 (d, J_{PC} = 6 Hz, 2 C, CH of fc), 74.79 (d, J_{PC} = 8 Hz, 2 C, CH of fc), 76.94 (d, J_{PC} = 9 Hz, 2 C, CH of fc), 128.42 (d, J_{PC} = 11 Hz, 4 C, CH of Ph), 131.32 (d, $^{4}J_{PC}$ = 2 Hz, 2 C, CH of Ph), 133.09 (d, $^{1}J_{PC}$ = 58 Hz, 2 C, C_{ipso}–P of Ph), 135.21 (d, J_{PC} = 12 Hz, 4 C, CH of Ph). The signals due to the ferrocene C_{ipso}–P were not found. ^{31}P{^{1}H} NMR (161.90 MHz, CD_2Cl_2): δ 39.9 (d, $^{2}J_{PP}$ = 22 Hz, PPh_2), 57.8 (d, $^{2}J_{PP}$ = 22 Hz, PCy_2). ESI + MS: *m/z* 673 ([M−2Cl+H]$^+$), 707 ([M−Cl]$^+$). Anal. Calc. for $C_{34}H_{40}Cl_2FeP_2Pd$ (743.75): C 54.90, H 5.42%. Found: C 54.53, H 5.31%.

4.9. Synthesis of dichlorido{1′-(diisopropylphosphino-κP)-1-(diphenylphosphino-κP)ferrocene}palladium, complex **5b**

Complex **5b** was obtained similarly to **1b** (103 mg, 0.20 mmol) and was isolated as a burgundy red crystalline solid. Yield: 64.5 mg (49%). The crystals used for structure determination were grown from dichloromethane-diethyl ether.

^{1}H NMR (399.95 MHz, CD_2Cl_2): δ 1.20 (dd, $^{3}J_{HH}$ = 7.0 Hz, $^{3}J_{PH}$ = 16.4 Hz, 6 H, CH*Me*$_2$), 1.59 (dd, $^{3}J_{HH}$ = 7.0 Hz, $^{3}J_{PH}$ = 17.5 Hz, 6 H, CH*Me*$_2$), 2.93 (d of sept, $^{2}J_{PH}$ = 9.9 Hz, $^{3}J_{HH}$ = 7.0 Hz, 2 H, C*H*Me$_2$), 4.13 (vq, J' = 1.9 Hz, 2 H, fc), 4.36 (br m, 2 H, fc), 4.46 (br m, 2 H, fc), 4.73 (vq, J' = 1.7 Hz, 2 H, fc), 7.45–7.55 (m, 6 H, Ph), 7.94–8.01 (m, 4 H, Ph). ^{13}C{^{1}H} NMR (100.58 MHz, CD_2Cl_2): δ 19.91 (s, 2 C, CH*Me*$_2$), 20.15 (d, $^{2}J_{PC}$ = 2 Hz, 2 C, CH*Me*$_2$), 27.65 (d, $^{1}J_{PC}$ = 30 Hz, 2 C, *C*HMe$_2$), 72.80 (d, J_{PC} = 6 Hz, 2 C, CH of fc), 72.97 (d, J_{PC} = 6 Hz, 2 C, CH of fc), 74.66 (dd, $^{2}J_{PC}$ = 7 Hz, $^{4}J_{PC}$ = 1 Hz, 2 C, CH of fc), 76.85 (dd, $^{2}J_{PC}$ = 9 Hz, $^{4}J_{PC}$ = 3 Hz, 2 C, CH of fc), 78.58 (dd, $^{1}J_{PC}$ = 43 Hz, $^{3}J_{PC}$ = 9 Hz, 1 C, C_{ipso}–P of fc), 79.33 (dd, $^{1}J_{PC}$ = 54 Hz, $^{3}J_{PC}$ = 6 Hz, 1 C, C_{ipso}–P of fc), 128.45 (d, J_{PC} = 11 Hz, 4 C, CH of Ph), 131.34 (d, $^{4}J_{PC}$ = 3 Hz, 2 C, CH of Ph), 133.06 (d, $^{1}J_{PC}$ = 58 Hz, 2 C, C_{ipso}–P of Ph), 135.17 (d, J_{PC} = 12 Hz, 4 C, CH of Ph). ^{31}P{^{1}H} NMR (161.90 MHz, CD_2Cl_2): δ 40.1 (d, $^{2}J_{PP}$ = 22 Hz, PPh_2), 66.81 (br s, P*i*Pr$_2$). ESI + MS: *m/z* 627 ([M−Cl]$^+$). Anal. Calc. For $C_{28}H_{32}FeP_2PdCl_2$ (663.67): C 50.67, H 4.86%. Found: C 50.64, H 4.86%.

4.10. Synthesis of dichlorido{1′-(di-tert-butylphosphino-κP)-1-(diphenylphosphino-κP)ferrocene}palladium, complex **5c**

Compound **5c** was prepared as described above from **1c** (108 mg, 0.20 mmol), resulting in a deep red crystalline solid. Yield: 77 mg (49%). Single crystals were obtained by recrystallization from dichloromethane-diethyl ether.

^{1}H NMR (399.95 MHz, CD_2Cl_2): δ 1.61 (d, $^{3}J_{PH}$ = 14.7 Hz, 18 H, C*Me*$_3$), 3.96 (vq, J' = 1.8 Hz, 2 H, fc), 4.30 (br m, 2 H, fc), 4.52 (br m, 2 H, fc), 4.88 (vq, J' = 1.7 Hz, 2 H, fc), 7.46–7.53 (m, 6 H, Ph), 7.98–8.06 (m, 4 H, Ph). ^{13}C{^{1}H} NMR (100.58 MHz, CD_2Cl_2): δ 31.89 (d, $^{2}J_{PC}$ = 3 Hz, 6 C, C*Me*$_3$), 41.45 (d, $^{1}J_{PC}$ = 19 Hz, 2 C, *C*Me$_3$), 72.67 (d, $^{3}J_{PC}$ = 5 Hz, 2 C, CH of fc), 72.93 (d, $^{3}J_{PC}$ = 5 Hz, 2 C, CH of fc), 76.02 (br m, 2 C, CH of fc), 76.90 (dd, $^{1}J_{PC}$ = 51 Hz, $^{3}J_{PC}$ = 4 Hz, 1 C, C_{ipso}–P of fc), 77.86 (dd, $^{2}J_{PC}$ = 9 Hz, $^{4}J_{PC}$ = 3 Hz, 2 C, CH of fc), 84.65 (dd, $^{1}J_{PC}$ = 35 Hz, $^{3}J_{PC}$ = 10 Hz, 1 C, C_{ipso}–P of fc), 128.41 (d, J_{PC} = 12 Hz, 4 C, CH of Ph), 131.11 (d, $^{4}J_{PC}$ = 2 Hz, 2 C, CH of Ph), 134.06 (d, $^{1}J_{PC}$ = 58 Hz, 2 C, C_{ipso}–P of Ph), 135.14 (d, J_{PC} = 12 Hz, 4 C, CH of Ph). ^{31}P{^{1}H} NMR (161.90 MHz, CD_2Cl_2): δ 38.8 (d, $^{2}J_{PP}$ = 22 Hz, PPh_2), 81.6 (d, $^{2}J_{PP}$ = 22 Hz, P*t*Bu$_2$). ESI + MS: *m/z* 621 ([M−2Cl+H]$^+$). Anal. Calc. for $C_{30}H_{36}Cl_2FeP_2Pd \cdot 0.25CH_2Cl_2$ (712.91): C 50.96, H 5.16%. Found: C 50.86, H 5.15%.

4.11. Synthesis of 1′-(dicyclohexylphosphino)ferrocene-1-carbaldehyde–borane (1/1), compound **7a**

Bromide **6a** (1.43 g, 3.0 mmol) was dissolved in anhydrous THF (30 mL) in a dry, two-necked reaction flask equipped with a stirring bar, septum and an argon inlet. The solution was cooled in a dry ice/ethanol bath to ca. −78 °C and then treated with *n*-butyllithium (1.4 mL 2.5 M, 3.5 mmol). After stirring at −78 °C for 20 min, dry *N*,*N*-dimethylformamide (1.2 mL, 15 mmol) was added, changing the color of the reaction mixture from orange red to orange yellow. The mixture was continuously stirred and cooled for 30 min, and then left stirring at room temperature for 90 min before quenching by adding brine and 3 M HCl (ca. 5 mL each), subsequently diluting with ethyl acetate. The red organic layer was separated, washed with brine and dried over $MgSO_4$. The crude product was pre-adsorbed by evaporation with chromatographic silica gel and transferred to silica gel column. Eluting with hexane-ethyl acetate (3:1) firstly resulted in a yellow band containing $FcPCy_2 \cdot BH_3$ (**8a**) and then in a red band due to the aldehyde **7a**. Both compounds were isolated by evaporation, resulting in an orange solid (**8a**; 169 mg, 14%) and a red microcrystalline solid (**7a**; 913 mg, 72%), respectively. Single crystals of the aldehyde were obtained from hot heptane.

Characterization data for **7a**: ^{1}H NMR (399.95 MHz, $CDCl_3$): δ 0.18–1.06 (br m, 3 H, BH_3), 1.12–1.38 (m, 10 H, Cy), 1.66–1.74 (m, 2 H, Cy), 1.78–1.98 (m, 10 H, Cy), 4.41 (vq, J' = 1.8 Hz, 2 H, fc), 4.54 (d of vt, J = 0.8, 1.8 Hz, 2 H, fc), 4.74 (vt, J' = 1.9 Hz, 2 H, fc), 4.90 (vt, J' = 2.0 Hz, 2 H, fc), 10.02 (s, 1 H, CHO). ^{13}C{^{1}H} NMR (100.58 MHz, $CDCl_3$): δ 22.87 (d, J_{PC} = 1 Hz, 2 C, CH_2 of Cy), 26.78 (d, J_{PC} = 1 Hz, 2 C, CH_2 of Cy), 26.87 (s, 2 C, CH_2 of Cy), 26.88 (d, J_{PC} = 2 Hz, 2 C, CH_2 of Cy), 27.19 (d, J_{PC} = 2 Hz, 2 C, CH_2 of Cy), 32.25 (d, $^{1}J_{PC}$ = 34 Hz, 2 C, CH of Cy), 70.81 (d, $^{1}J_{PC}$ = 54 Hz, 1 C, C_{ipso}–P of fc), 71.14 (s, 2 C, CH of fc), 72.00 (d, J_{PC} = 6 Hz, 2 C, CH of fc), 73.12 (d, J_{PC} = 7 Hz, 2 C, CH of fc),

75.21 (s, 2 C, CH of fc), 79.97 (s, 1 C, C_{ipso}–CHO of fc), 193.87 (s, 1 C, CHO). $^{31}P\{^1H\}$ NMR (161.90 MHz, $CDCl_3$): δ 24.2 (br d, PCy_2). IR (Nujol): ν_{max} 2378 *m*, 2361 *m*, 2334 *m*, 1683 s, 1667 s, 1408 w, 1342 w, 1335 w, 1309 w, 1291 w, 1267 w, 1248 *m*, 1199 w, 1168 *m*, 1132 w, 1118 w, 1067 *m*, 1059 *m*, 1042 *m*, 1034 *m*, 1006 w, 922 w, 915 w, 889 w, 878 w, 849 *m*, 822 *m*, 766 w, 757 w, 744 *m*, 635 w, 603 w, 523 *m*, 506 w, 496 w, 463 w, 443 w, 434 w cm^{-1}. ESI + MS: *m/z* 447 ($[M+Na]^+$), 463 ($[M+K]^+$). Anal. Calc. for $C_{23}H_{34}BFeOP$ (424.13): C 65.13, H 8.08%. Found: C 65.14, H 7.88%.

Compound **8a**: ^1H NMR (399.95 MHz, $CDCl_3$): δ 0.16–1.04 (br m, 3 H, BH_3), 1.10–1.40 (m, 10 H, Cy), 1.64–1.72 (m, 2 H, Cy), 1.76–2.02 (m, 10 H, Cy), 4.27 (s, 5 H, C_5H_5), 4.33 (vq, $J' = 1.8$ Hz, 2 H, C_5H_4), 4.42 (d of vt, $J = 0.9$, 1.8 Hz, 2 H, C_5H_4). $^{13}C\{^1H\}$ NMR (100.58 MHz, $CDCl_3$): δ 25.95 (d, $J_{PC} = 1$ Hz, 2 C, CH_2 of Cy), 26.87 (s, 2 C, CH_2 of Cy), 26.88 (d, $J_{PC} = 3$ Hz, 2 C, CH_2 of Cy), 26.99 (d, $J_{PC} = 5$ Hz, 2 C, CH_2 of Cy), 27.14 (d, $J_{PC} = 2$ Hz, 2 C, CH_2 of Cy), 32.44 (d, $^1J_{PC} = 34$ Hz, 2 C, CH of Cy), 68.17 (d, $^1J_{PC} = 57$ Hz, 1 C, C_{ipso}–P of C_5H_4), 69.87 (s, 5 C, C_5H_5), 70.41 (d, $J_{PC} = 6$ Hz, 2 C, CH of C_5H_4), 71.87 (d, $J_{PC} = 8$ Hz, 2 C, CH of C_5H_4). $^{31}P\{^1H\}$ NMR (161.90 MHz, $CDCl_3$): δ 24.2 (br d, PCy_2). ESI + MS: *m/z* 419 ($[M+Na]^+$), 435 ($[M+K]^+$). Anal. Calc. for $C_{22}H_{34}BFeP$ (396.14): C 66.70, H 8.65%. Found: C 66.64, H 8.68%.

4.12. Synthesis of 1′-(diisopropylphosphino)ferrocene-1-carbaldehyde–borane (1/1), compound **7b**

Using bromide **6b** (1.04 g, 2.6 mmol in 25 mL of THF), 1.3 mL 2.5 M *n*-butyllithium and *N*,*N*-dimethylformamide (1.0 mL, 13 mmol), the procedure described in the previous section afforded $FcP(iPr)_2 \cdot BH_3$ (**8b**; 117 mg, 14%) as an orange solid, and the desired aldehyde **7b** (698 mg, 77%) as a deep red microcrystalline solid. Crystals of **7b** suitable for X-ray diffraction analysis were grown from hot heptane.

Characterization data for **7b**: ^1H NMR (399.95 MHz, $CDCl_3$): δ 0.18–1.04 (br m, 3 H, BH_3), 1.15 (dd, $^3J_{HH} = 7.1$ Hz, $^3J_{PH} = 2.9$ Hz, 6 H, $CHMe_2$), 1.18 (dd, $^3J_{HH} = 7.1$ Hz, $^3J_{PH} = 3.9$ Hz, 6 H, $CHMe_2$), 2.14 (d of sept, $^2J_{PH} = 10.1$ Hz, $^3J_{HH} = 7.1$ Hz, 2 H, $CHMe_2$), 4.43 (vq, $J' = 1.8$ Hz, 2 H, fc), 4.55 (d of vt, $J = 0.9$, 1.9 Hz, 2 H, fc), 4.76 (vt, $J' = 1.8$ Hz, 2 H, fc), 4.92 (vt, $J' = 1.9$ Hz, 2 H, fc), 10.04 (s, 1 H, CHO). $^{13}C\{^1H\}$ NMR (100.58 MHz, $CDCl_3$): δ 17.12 (s, 2 C, $CHMe_2$), 17.41 (d, $^2J_{PC} = 2$ Hz, 2 C, $CHMe_2$), 22.49 (d, $^1J_{PC} = 34$ Hz, 2 C, $CHMe_2$), 70.13 (d, $^1J_{PC} = 53$ Hz, 1 C, C_{ipso}–P of fc), 71.16 (s, 2 C, CH of fc), 72.12 (d, $J_{PC} = 6$ Hz, 2 C, CH of fc), 73.02 (d, $J_{PC} = 7$ Hz, 2 C, CH of fc), 72.21 (s, 2 C, CH of fc), 79.97 (s, 1 C, C_{ipso}–CHO of fc), 193.92 (s, 1 C, CHO). $^{31}P\{^1H\}$ NMR (161.90 MHz, $CDCl_3$): δ 31.9 (br d, $PiPr_2$). IR (Nujol): ν_{max} 2371 *m*, 2364 *m*, 2329 *m*, 1686 s, 1671 *m*, 1414 w, 1338 w, 1315 w, 1247 *m*, 1205 w, 1169 *m*, 1135 w, 1068 *m*, 1037 *m*, 932 w, 888 w, 844 *m*, 828 *m*, 741 *m*, 693 *m*, 633 *m*, 589 w, 523 *m*, 506 *m*, 489 w, 463 w, 436 w cm^{-1}. ESI + MS: *m/z* 367 ($[M+Na]^+$), 383 ($[M+K]^+$). Anal. Calc. for $C_{17}H_{26}BFeOP$ (344.01): C 59.35, H 7.62%. Found: C 59.29, H 7.48%.

Compound **8b**: ^1H NMR (399.95 MHz, $CDCl_3$): δ 0.17–1.02 (br m, 3 H, BH_3), 1.14 (dd, $^3J_{HH} = 7.1$ Hz, $^3J_{PH} = 1.8$ Hz, 6 H, $CHMe_2$), 1.18 (dd, $^3J_{HH} = 7.1$ Hz, $^3J_{PH} = 2.8$ Hz, 6 H, $CHMe_2$), 2.13 (d of sept, $^2J_{PH} = 10.1$ Hz, $^3J_{HH} = 7.1$ Hz, 2 H, $CHMe_2$), 4.29 (s, 5 H, C_5H_5), 4.35 (vq, $J' = 1.7$ Hz, 2 H, CH of C_5H_4), 4.43 (d of vt, $J = 0.9$, 1.9 Hz, 2 H, CH of C_5H_4). $^{13}C\{^1H\}$ NMR (100.58 MHz, $CDCl_3$): δ 17.16 (s, 2 C, $CHMe_2$), 17.41 (d, $^2J_{PC} = 2$ Hz, 2 C, $CHMe_2$), 22.57 (d, $^1J_{PC} = 35$ Hz, 2 C, $CHMe_2$), 67.45 (d, $^1J_{PC} = 56$ Hz, 1 C, C_{ipso}–P of C_5H_4), 69.89 (s, 5 C, C_5H_5), 70.51 (d, $J_{PC} = 6$ Hz, 2 C, CH of C_5H_4), 71.77 (d, $J_{PC} = 7$ Hz, 2 C, CH of C_5H_4). $^{31}P\{^1H\}$ NMR (161.90 MHz, $CDCl_3$): δ 31.8 (br m, $PiPr_2$). ESI + MS: *m/z* 315 ($[M-H]^+$), 339 ($[M+Na]^+$), 355 ($[M+K]^+$). Anal. Calc. for $C_{16}H_{26}BFeP$ (316.01): C 60.81, H 8.29%. Found: C 60.79, H 8.19%.

4.13. Synthesis of 1-(dicyclohexylphosphino)-1′-(hydroxymethyl) ferrocene–borane (1/1), compound **9a**

A solution of $BH_3 \cdot SMe_2$ (1.3 mL of 2 M in diethyl ether, 2.6 mmol) was added to a solution aldehyde **7a** (0.85 g, 2.0 mmol) in anhydrous THF (15 mL) while stirring and cooling on ice. The reaction was allowed to proceed at 0 °C for 90 min whereupon the color of the reaction mixture changed from red to deep orange, and then terminated by adding saturated aqueous $NaHCO_3$ (1 mL). The mixture was partitioned between dichloromethane and water, and the organic layer was separated, washed with brine, dried over $MgSO_4$, and evaporated under vacuum. The crude product was dissolved in little dichloromethane and evaporated with chromatographic silica gel. The pre-adsorbed material was transferred to silica gel column and eluted with hexane-ethyl acetate (1:1). The single orange band eluted was collected and evaporated to afford alcohol **9a** as an orange microcrystalline solid. Yield: 813 mg (95%).

^1H NMR (399.95 MHz, $CDCl_3$): δ 0.15–1.16 (br m, 3 H, BH_3), 1.08–1.36 (m, 10 H, Cy), 1.64–1.72 (m, 2 H, Cy), 1.76–2.03 (m, 10 H, Cy), 4.25 (vt, $J' = 1.9$ Hz, 2 H, fc), 4.31 (vq, $J' = 1.8$ Hz, 2 H, fc), 4.35 (vt, $J' = 1.9$ Hz, 2 H, fc), 4.41 (br d, $^3J_{HH} = 5.4$ Hz, 2 H, CH_2OH), 4.43 (d of vt, $J = 0.9$, 1.8 Hz, 2 H, fc). The signal due to OH proton was not found. $^{31}P\{^1H\}$ NMR (161.90 MHz, $CDCl_3$): δ 24.0 (br d, PCy_2). The NMR data are in accordance with the literature [5f].

4.14. Synthesis of 1-(diisopropylphosphino)-1′-(hydroxymethyl) ferrocene–borane (1/1), compound **9b**

Using the aforementioned procedure, aldehyde **7b** (0.69 g, 2.0 mmol) was converted into alcohol **9b**. Yield: 650 mg (92%), orange microcrystalline solid. Single crystals used for structure determination were obtained from hot heptane.

^1H NMR (399.95 MHz, $CDCl_3$): δ 0.20–1.06 (br m, 3 H, BH_3), 1.14 (dd, $^3J_{HH} = 7.1$ Hz, $^3J_{PH} = 2.4$ Hz, 6 H, $CHMe_2$), 1.17 (dd, $^3J_{HH} = 7.1$ Hz, $^3J_{PH} = 3.5$ Hz, 6 H, $CHMe_2$), 1.97 (t, $^3J_{HH} = 5.8$ Hz, 1 H, CH_2OH), 2.13 (d of sept, $^2J_{PH} = 10.1$ Hz, $^3J_{HH} = 7.1$ Hz, 2 H, $CHMe_2$), 4.28 (vt, $J' = 1.9$ Hz, 2 H, fc), 4.34 (vq, $J' = 1.8$ Hz, 2 H, fc), 4.36 (vt, $J' = 1.9$ Hz, 2 H, fc), 4.42 (d, $^3J_{HH} = 5.6$ Hz, 2 H, CH_2OH), 4.45 (d of vt, $J = 0.9$, 1.9 Hz, 2 H, fc). $^{13}C\{^1H\}$ NMR (100.58 MHz, $CDCl_3$): δ 17.12 (s, 2 C, $CHMe_2$), 17.36 (d, $^2J_{PC} = 2$ Hz, 2 C, $CHMe_2$), 22.46 (d, $^1J_{PC} = 35$ Hz, 2 C, $CHMe_2$), 60.43 (s, 1 C, CH_2OH), 67.87 (d, $^1J_{PC} = 56$ Hz, 1 C, C_{ipso}–P of fc), 69.28 (s, 2 C, CH of fc), 70.04 (s, 2 C, CH of fc), 70.91 (d, $J_{PC} = 6$ Hz, 2 C, CH of fc), 72.22 (d, $J_{PC} = 7$ Hz, 2 C, CH of fc), 89.79 (s, 1 C, C_{ipso}–CH_2OH of fc). $^{31}P\{^1H\}$ NMR (161.90 MHz, $CDCl_3$): δ 31.6 (br m, $PiPr_2$). IR (Nujol): ν_{max} 3242 br m, 3098 *m*, 3078 *m*, 2378 s, 2352 s, 2327 s, 2251 *m*, 1713 w, 1652 w, 1313 w, 1250 *m*, 1239 *m*, 1230 w, 1202 w, 1167 s, 1134 w, 1105 w, 1068 s, 1037 s, 1022 *m*, 983 *m*, 954 w, 926 w, 916 w, 888 *m*, 867 w, 842 *m*, 835 w, 813 *m*, 750 *m*, 691 *m*, 638 *m*, 631 *m*, 586 *m*, 521 *m*, 515 *m*, 492 *m*, 483 w, 466 *m*, 450 w, 420 w cm^{-1}. ESI + MS: *m/z* 369 ($[M+Na]^+$), 385 ($[M+K]^+$). Anal. Calc. for $C_{17}H_{28}BFeOP$ (346.03): C 59.00, H 8.16%. Found: C 59.03, H 8.01%.

4.15. Synthesis of 1′-(dicyclohexylphosphino)-1-[(diphenylphosphino)methyl]ferrocene–borane (1/2), compound **10a**

Alcohol **9a** (0.77 g, 1.8 mmol) and NaI (0.82 g, 5.5 mmol) were dissolved in dry acetonitrile (60 mL). Neat chloro-trimethylsilane (0.56 mL, 4.4 mmol) was added to a stirring mixture, causing an immediate separation of a fine white precipitate (NaCl). After stirring for 5 min, diphenylphosphine (0.84 mL, 4.8 mmol) was introduced, and the reaction mixture was stirred at room temperature for 18 h. Then, $BH_3 \cdot SMe_2$ (2.7 mL of a 2 M ethereal solution, 5.3 mmol) was added, continuously stirring for another 5 min. The reaction mixture was quenched by saturated aqueous $NaHCO_3$

(5 mL) and diluted with diethyl ether (60 mL) and brine (20 mL). The organic layer was separated, washed with brine, dried over $MgSO_4$, and evaporated. The solid residue was dissolved in dichloromethane and evaporated with chromatographic silica gel, and the pre-adsorbed crude product was transferred to a chromatographic column. After elution with hexane removed some colorless $HPPh_2 \cdot BH_3$, the mobile phase was changed to hexane-toluene (1:3), which afforded a minor band containing compound **11a** (150 mg, 20%; yellow-orange solid). Subsequent elution removed a minor band containing some impurities and, finally, an orange band due to **10a**. This band was collected and evaporated under reduced pressure to afford adduct **10a** as an orange microcrystalline product. Yield: 300 mg (27%).

Characterization data for **10a**. ^{1}H NMR (399.95 MHz, $CDCl_3$): δ 0.20–1.05 (br m, 6 H, BH_3), 1.08–1.36 (m, 10 H, Cy), 1.52–1.95 (m, 12 H, Cy), 3.50 (d, $^2J_{PH} = 10.4$ Hz, 2 H, CH_2PPh$_2$), 4.05 (s, 4 H, fc), 4.18 (vq, $J' = 1.7$ Hz, 2 H, fc), 4.38 (d of vt, $J = 0.9$, 1.8 Hz, 2 H, fc), 7.38–7.49 (m, 6 H, Ph), 7.61–7.67 (m, 4 H, Ph). ^{13}C{^{1}H} NMR (100.58 MHz, $CDCl_3$): δ 25.91 (d, $J_{PC} = 1$ Hz, 2 C, CH_2 of Cy), 26.79 (s, 2 C, CH_2 of Cy), 26.82 (d, $J_{PC} = 6$ Hz, 2 C, CH_2 of Cy), 26.93 (d, $J_{PC} = 8$ Hz, 2 C, CH_2 of Cy), 27.06 (d, $J_{PC} = 2$ Hz, 2 C, CH_2 of Cy), 28.49 (d, $^1J_{PC} = 34$ Hz, 1 C, CH_2PPh$_2$), 32.29 (d, $^1J_{PC} = 34$ Hz, 2 C, CH of Cy), 68.38 (d, $^1J_{PC} = 56$ Hz, 1 C, C_{ipso}–P of fc), 69.56 (s, 2 C, CH of fc), 71.25 (d, $J_{PC} = 7$ Hz, 2 C, CH of fc), 71.94 (d, $J_{PC} = 2$ Hz, 2 C, CH of fc), 73.00 (d, $J_{PC} = 8$ Hz, 2 C, CH of fc), 80.34 (d, $^2J_{PC} = 2$ Hz, 1 C, C_{ipso}–CH_2 of fc), 128.59 (d, $J_{PC} = 10$ Hz, 4 C, CH of Ph), 128.79 (d, $^1J_{PC} = 53$ Hz, 2 C, C_{ipso}–P of Ph), 131.14 (d, $^4J_{PC} = 2$ Hz, 2 C, CH of Ph), 132.66 (d, $J_{PC} = 9$ Hz, 4 C, CH of Ph). ^{31}P{^{1}H} NMR (161.90 MHz, $CDCl_3$): δ 17.3 (br d, PPh_2), 23.9 (br d, PCy_2). ESI + MS: *m/z* 609 ([M+H]$^+$), 631 ([M+Na]$^+$), ESI– MS: *m/z* 607 ([M–H]$^-$). Anal. Calc. for $C_{35}H_{48}B_2FeP_2$ (608.17): C 69.12, H 7.96%. Found: C 68.89, H 7.90%.

Compound **11a**. ^{1}H NMR (399.95 MHz, $CDCl_3$): δ 0.16–1.04 (br m, 3 H, BH_3), 1.10–1.40 (m, 10 H, Cy), 1.64–1.99 (m, 12 H, Cy), 1.99 (s, 3 H, Me), 4.14 (vt, $J' = 1.8$ Hz, 2 H, fc), 4.17 (vt, $J' = 1.8$ Hz, 2 H, CH of fc), 4.23 (vt, $J' = 1.7$ Hz, 2 H, CH of fc), 4.32 (d of vt, $J = 0.9$, 1.8 Hz, 2 H, fc). ^{13}C{^{1}H} NMR (100.58 MHz, $CDCl_3$): δ 14.50 (s, 1 C, Me), 25.97 (d, $J_{PC} = 2$ Hz, 2 C, CH_2 of Cy), 26.89 (d, $J_{PC} = 3$ Hz, 2 C, CH_2 of Cy), 26.92 (s, 2 C, CH_2 of Cy), 27.00 (d, $J_{PC} = 4$ Hz, 2 C, CH_2 of Cy), 27.17 (d, $J_{PC} = 2$ Hz, 2 C, CH_2 of Cy), 32.49 (d, $^1J_{PC} = 35$ Hz, 2 C, CH of Cy), 67.99 (d, $^1J_{PC} = 57$ Hz, 1 C, C_{ipso}–P of fc), 69.39 (s, 2 C, CH of fc), 70.79 (s, 2 C, CH of fc), 71.57 (d, $J_{PC} = 7$ Hz, 2 C, CH of fc), 72.48 (d, $J_{PC} = 8$ Hz, 2 C, CH of fc), 85.45 (s, 1 C, C_{ipso}–CH_3 of fc). ^{31}P{^{1}H} NMR (161.90 MHz, $CDCl_3$): δ 24.1 (br d, PCy_2). ESI + MS: *m/z* 433 ([M+Na]$^+$), 449 ([M+K]$^+$). Anal. Calc. for $C_{23}H_{36}BFeP$ (410.16): C 67.35, H 8.85%. Found: C 67.22, H 8.55%.

4.16. Synthesis of 1′-(diisopropylphosphino)-1-[(diphenylphosphino)methyl]ferrocene–borane (1/2), compound ***10b***

Reacting alcohol **9b** (0.65 g, 1.9 mmol) and NaI (0.82 g, 5.5 mmol) in 40 mL of acetonitrile with $ClSiMe_3$ (0.58 mL, 4.5 mmol), $HPPh_2$ (0.88 mL, 5.0 mmol) and, finally, $BH_3 \cdot SMe_2$ (2.7 ml 2 M, 5.3 mmol) as described above provided **11b** (first yellow band; 136 mg, 22%) and adduct **10b** (third orange band; 325 mg, 33%).

Characterization data for **10b**: yellow-orange microcrystalline solid. ^{1}H NMR (399.95 MHz, $CDCl_3$): δ 0.26–0.98 (br m, 6 H, BH_3), 1.11 (dd, $^3J_{HH} = 7.1$ Hz, $^3J_{PH} = 15.4$ Hz, 6 H, CHMe_2), 1.15 (dd, $^3J_{HH} = 7.1$ Hz, $^3J_{PH} = 16.5$ Hz, 6 H, CHMe_2), 2.11 (d of sept, $^2J_{PH} = 10.0$ Hz, $^3J_{HH} = 7.1$ Hz, 2 H, CHMe$_2$), 3.53 (d, $^2J_{PH} = 10.4$ Hz, 2 H, CH_2PPh$_2$), 4.08 (s, 4 H, fc), 4.21 (vq, $J' = 1.7$ Hz, 2 H, fc), 4.40 (d of vt, $J = 0.9$, 1.8 Hz, 2 H, fc), 7.39–7.50 (m, 6 H, Ph), 7.62–7.68 (m, 4 H, Ph). ^{13}C{^{1}H} NMR (100.58 MHz, $CDCl_3$): δ 17.10 (s, 2 C, CHMe_2), 17.33 (d, $^2J_{PC} = 2$ Hz, 2 C, CHMe_2), 22.42 (d, $^1J_{PC} = 35$ Hz, 2 C, CHMe$_2$), 28.47 (d, $^1J_{PC} = 34$ Hz, 1 C, CH_2PPh$_2$), 67.61 (d, $^1J_{PC} = 56$ Hz, 1 C, C_{ipso}–P of fc), 69.54 (s, 2 C, CH of fc), 71.34 (d, $J_{PC} = 6$ Hz, 2 C, CH of fc), 71.99 (d, $J_{PC} = 2$ Hz, 2 C, CH of fc), 72.90 (d, $J_{PC} = 7$ Hz, 2 C, CH of fc), 80.39 (d, $^2J_{PC} = 2$ Hz, 1 C, C_{ipso}–CH_2 of fc), 128.59 (d, $J_{PC} = 10$ Hz, 4 C, CH of Ph), 128.77 (d, $^1J_{PC} = 54$ Hz, 2 C, C_{ipso}–P of Ph), 131.14 (d, $^4J_{PC} = 2$ Hz, 2 C, CH of Ph), 132.67 (d, $J_{PC} = 9$ Hz, 4 C, CH of Ph). ^{31}P{^{1}H} NMR (161.90 MHz, $CDCl_3$): δ 17.2 (br d, PPh_2), 31.6 (br d, PiPr$_2$). ESI + MS: *m/z* 551 ([M+Na]$^+$), 567 ([M+K]$^+$); ESI– MS: *m/z* 527 ([M–H]$^-$). Anal. Calc. for $C_{29}H_{40}B_2FeP_2$ (528.04): C 65.96, H 7.64%. Found: C 65.82, H 7.63%.

Compound **11b**: yellow-orange solid. ^{1}H NMR (399.95 MHz, $CDCl_3$): δ 0.18–1.03 (br m, 3 H, BH_3), 1.14 (dd, $^3J_{HH} = 7.1$ Hz, $^3J_{PH} = 3.5$ Hz, 6 H, CHMe_2), 1.18 (dd, $^3J_{HH} = 7.1$ Hz, $^3J_{PH} = 4.5$ Hz, 6 H, CHMe_2), 1.99 (s, 3 H, Me), 2.13 (d of sept, $^2J_{PH} = 10.1$ Hz, $^3J_{HH} = 7.1$ Hz, 2 H, CHMe$_2$), 4.16 (vt, $J' = 1.8$ Hz, 2 H, fc), 4.19 (vt, $J' = 1.8$ Hz, 2 H, fc), 4.25 (vq, $J' = 1.7$ Hz, 2 H, fc), 4.33 (d of vt, $J = 0.9$, 1.8 Hz, 2 H, fc). ^{13}C{^{1}H} NMR (100.58 MHz, $CDCl_3$): δ 14.76 (s, 1 C, Me), 17.44 (s, 2 C, CHMe_2), 17.69 (d, $^2J_{PC} = 2$ Hz, 2 C, CHMe_2), 22.85 (d, $^1J_{PC} = 35$ Hz, 2 C, CHMe$_2$), 67.47 (d, $^1J_{PC} = 57$ Hz, 1 C, C_{ipso}–P of fc), 69.69 (s, 2 C, CH of fc), 71.07 (s, 2 C, CH of fc), 71.98 (d, $J_{PC} = 7$ Hz, 2 C, CH of fc), 72.63 (d, $J_{PC} = 8$ Hz, 2 C, CH of fc), 85.76 (s, 1 C, C_{ipso}–CH_3 of fc). ^{31}P{^{1}H} NMR (161.90 MHz, $CDCl_3$): δ 31.7 (br m, PiPr$_2$). ESI + MS: *m/z* 329 ([M–H]$^+$), 353 ([M+Na]$^+$), 369 ([M+K]$^+$). Anal. Calc. for $C_{17}H_{28}BFeP$ (330.03): C 61.87, H 8.55%. Found: C 62.10, H 8.47%.

4.17. Synthesis of 1′-(dicyclohexylphosphino)-1-[(diphenylphosphino)methyl]ferrocene (***2a***) from ***10a***

An oven-dried Schlenk tube was charged with adduct **10a** (122 mg, 0.20 mmol), filled with argon (by three vacuum-argon cycles) and sealed with a septum. Freshly distilled morpholine (2.0 mL) was added, and the mixture was cooled in dry ice/ethanol bath until solidification, evacuated and then allowed to thaw at room temperature. This cooling-warming procedure was repeated three or four times until no gas evolution was observed upon thawing. Then, the reaction mixture was heated to 70 °C overnight and evaporated, leaving an orange residue, which was purified by column chromatography (silica gel, hexane-ethyl acetate 3:1). The single orange band was collected and evaporated to afford compound **2a** as a gummy orange-red solid. Yield 66 mg (57%). The product typically contained minor amounts of $Ph_2PCH_2fcPCy_2 \cdot BH_3$ [5–10%; ^{31}P{^{1}H} NMR ($CDCl_3$): –11.0 (s, PPh_2), 24.1 (br m, PCy_2)]. For analytical data of **2a**, see section 4.19.

4.18. Synthesis of 1′-(diisopropylphosphino)-1-[(diphenylphosphino)methyl]ferrocene (***2b***) from ***10b***

Applying a similar deprotection procedure, compound **10b** (106 mg, 0.20 mmol) was converted to pure **2b** as a red-orange oil. Yield: 76 mg (76%). For analytical data of **2b**, see section 4.20.

4.19. Synthesis of ***2a*** from ***13***

Bromide **13** (0.463 g, 1.0 mmol) was dissolved in THF (10 mL) in an oven-dried flask equipped with a stirring bar, a rubber septum and a gas inlet. The solution was cooled in a dry ice/ethanol bath to ca. –78 °C before adding a solution of *n*-butyllithium (0.44 mL 2.5 M, 1.1 mmol) dropwise. After the mixture was stirred, continuously cooling for 30 min, neat chlorodicyclohexylphosphine (0.25 mL, 1.2 mmol) was introduced continuously stirring at –78 °C for 30 min and then at room temperature for 90 min. Subsequently, the reaction was terminated by adding brine (3 mL) and diethyl ether (15 mL), both carefully degassed to avoid oxidation. The aqueous layer was removed using a syringe, and the remaining organic residue was dried by adding anhydrous magnesium sulfate, filtered and evaporated under reduced pressure. The residue was

purified by flash chromatography over silica gel using deoxygenated toluene as the eluent. The first orange band containing mostly $FcCH_2PPh_2$ [41] was discarded, and the following band due to the diphosphine **2a** was collected and evaporated, affording the product as an orange red gummy solid (300 mg, 52%).

^{1}H NMR (399.95 MHz, $CDCl_3$): δ 0.98–1.34 (m, 10 H, Cy), 1.60–1.92 (m, 12 H, Cy), 3.16 (s, 2 H, C*H*$_2$PPh$_2$), 3.87 (vt, $J' = 1.8$ Hz, 2 H, fc), 3.95 (vt, $J' = 1.8$ Hz, 2 H, fc), 4.07 (vq, $J' = 1.7$ Hz, 2 H, fc), 4.20 (vt, $J' = 1.7$ Hz, 2 H, fc), 7.29–7.33 (m, 6 H, Ph), 7.36–7.42 (m, 4 H, Ph). ^{13}C{^{1}H} NMR (100.58 MHz, $CDCl_3$): δ 26.45 (s, 2 C, CH_2 of Cy), 27.34 (d, $J_{PC} = 9$ Hz, 2 C, CH_2 of Cy), 27.41 (d, $J_{PC} = 11$ Hz, 2 C, CH_2 of Cy), 30.00 (d, $^1J_{PC} = 15$ Hz, 1 C, *C*H$_2$PPh$_2$), 30.30 (d, $J_{PC} = 13$ Hz, 2 C, CH_2 of Cy), 30.40 (d, $J_{PC} = 11$ Hz, 2 C, CH_2 of Cy), 33.56 (d, $^1J_{PC} = 11$ Hz, 2 C, CH of Cy), 69.00 (s, 2 C, CH of fc), 70.13 (d, $J_{PC} = 4$ Hz, 2 C, CH of fc), 70.60 (d, $J_{PC} = 3$ Hz, 2 C, CH of fc), 72.25 (d, $J_{PC} = 11$ Hz, 2 C, CH of fc), 76.38 (d, $^1J_{PC} = 16$ Hz, 1 C, C_{ipso}–P of fc), 84.62 (d, $^2J_{PC} = 16$ Hz, 1 C, C_{ipso}–CH_2 of fc), 128.27 (d, $J_{PC} = 6$ Hz, 4 C, CH of Ph), 128.56 (s, 2 C, CH of Ph), 132.87 (d, $J_{PC} = 19$ Hz, 4 C, CH of Ph), 138.62 (d, $^1J_{PC} = 15$ Hz, 2 C, C_{ipso}–P of Ph). ^{31}P{^{1}H} NMR (161.90 MHz, $CDCl_3$): δ −11.5 (s, PPh_2), −7.1 (s, PCy_2). HR MS (ESI+) calc. for $C_{35}H_{43}^{56}FeP_2$ ([M+H]$^+$): 581.2184, found 581.2183.

4.20. Synthesis of **2b** from **13**

A similar reaction with chlorodiisopropylphosphine (0.20 mL, 1.2 mmol) furnished diphosphine **2b** as an orange-red oil (354 mg, 71%).

^{1}H NMR (399.95 MHz, $CDCl_3$): δ 1.05 (dd, $^3J_{HH} = 7.0$ Hz, $^3J_{PH} = 12.1$ Hz, 6 H, CH*Me*$_2$), 1.08 (dd, $^3J_{HH} = 7.1$ Hz, $^3J_{PH} = 13.8$ Hz, 6 H, CH*Me*$_2$), 1.90 (d of sept, $^2J_{PH} = 2.7$ Hz, $^3J_{HH} = 7.0$ Hz, 2 H, C*H*Me$_2$), 3.17 (s, 2 H, C*H*$_2$PPh$_2$), 3.89 (vt, $J' = 1.8$ Hz, 2 H, fc), 3.96 (vt, $J' = 1.8$ Hz, 2 H, fc), 4.10 (vq, $J' = 1.8$ Hz, 2 H, fc), 4.21 (vt, $J' = 1.8$ Hz, 2 H, fc), 7.30–7.42 (m, 10 H, Ph). ^{13}C{^{1}H} NMR (100.58 MHz, $CDCl_3$): δ 19.98 (d, $^2J_{PC} = 11$ Hz, 2 C, CH*Me*$_2$), 20.14 (d, $^2J_{PC} = 15$ Hz, 2 C, CH*Me*$_2$), 23.44 (d, $^1J_{PC} = 11$ Hz, 2 C, *C*HMe$_2$), 29.99 (d, $^1J_{PC} = 15$ Hz, 1 C, *C*H$_2$PPh$_2$), 69.08 (s, 2 C, CH of fc), 70.14 (d, $J_{PC} = 4$ Hz, 2 C, CH of fc), 70.69 (d, $J_{PC} = 2$ Hz, 2 C, CH of fc), 71.98 (d, $J_{PC} = 11$ Hz, 2 C, CH of fc), 76.01 (d, $^1J_{PC} = 17$ Hz, 1 C, C_{ipso}–P of fc), 84.61 (d, $^2J_{PC} = 16$ Hz, 1 C, C_{ipso}–CH_2 of fc), 128.28 (d, $J_{PC} = 6$ Hz, 4 C, CH of Ph), 128.56 (s, 2 C, CH of Ph), 132.88 (d, $J_{PC} = 19$ Hz, 4 C, CH of Ph), 138.60 (d, $^1J_{PC} = 15$ Hz, 2 C, C_{ipso}–P of Ph). ^{31}P{^{1}H} NMR (161.90 MHz, $CDCl_3$): δ −11.5 (s, PPh_2), 0.9 (s, P*i*Pr$_2$). HR MS (ESI+) calc. for $C_{29}H_{35}^{56}FeP_2$ ([M+H]$^+$): 501.1558, found 501.1555.

4.21. Synthesis of 1′-(di-tert-butylphosphino)-1-[(diphenylphosphino)methyl]ferrocene (**2c**)

Compound **2c** was similarly prepared using chloro-di-*tert*-butylphosphine (0.24 mL, 1.2 mmol), resulting in a red-orange oil (380 mg, 72%).

^{1}H NMR (399.95 MHz, $CDCl_3$): δ 1.17 (d, $^3J_{PH} = 11.2$ Hz, 18 H, CMe_3), 3.16 (s, 2 H, C*H*$_2$PPh$_2$), 3.90 (vt, $J' = 1.7$ Hz, 2 H, fc), 3.98 (vt, $J' = 1.8$ Hz, 2 H, fc), 4.18 (vq, $J' = 1.7$ Hz, 2 H, fc), 4.26 (vt, $J' = 1.8$ Hz, 2 H, fc), 7.29–7.42 (m, 10 H, Ph). ^{13}C{^{1}H} NMR (100.58 MHz, $CDCl_3$): δ 30.02 (d, $^1J_{PC} = 15$ Hz, 1 C, *C*H$_2$PPh$_2$), 30.80 (d, $^2J_{PC} = 13$ Hz, 6 C, C*Me*$_3$), 32.62 (d, $^1J_{PC} = 20$ Hz, 2 C, *C*Me$_3$), 69.63 (s, 2 C, CH of fc), 70.34 (d, $J_{PC} = 4$ Hz, 2 C, CH of fc), 70.55 (d, $J_{PC} = 3$ Hz, 2 C, CH of fc), 73.70 (d, $J_{PC} = 13$ Hz, 2 C, CH of fc), 77.86 (d, $^1J_{PC} = 27$ Hz, 1 C, C_{ipso}–P of fc), 84.53 (d, $^2J_{PC} = 16$ Hz, 1 C, C_{ipso}–CH_2 of fc), 128.29 (d, $J_{PC} = 6$ Hz, 4 C, CH of Ph), 128.59 (s, 2 C, CH of Ph), 132.87 (d, $J_{PC} = 19$ Hz, 4 C, CH of Ph), 138.56 (d, $^1J_{PC} = 15$ Hz, 2 C, C_{ipso}–P of Ph). ^{31}P{^{1}H} NMR (161.90 MHz, $CDCl_3$): δ −11.6 (s, PPh_2), 28.3 (s, P*t*Bu$_2$). HR MS (ESI+) calc. for $C_{31}H_{39}^{56}FeP_2$ ([M+H]$^+$): 529.1871, found 529.1862.

4.22. Synthesis of 1′-(dicyclohexylphosphinoselenoyl)-1-[(diphenylphosphinoselenoyl)methyl]ferrocene (**14a**)

Diphosphine **2a** (29 mg, 50 μmol) and KSeCN (16 mg, 0.11 mmol) were reacted in anhydrous dichloromethane and methanol (2 mL each) overnight. The resulting mixture was evaporated under vacuum, and the residue was dissolved in a minimum of dichloromethane and purified by column chromatography on silica gel using hexane-toluene-ethyl acetate (1:1:1) as the eluent. A single orange band was collected and evaporated to afford the phosphine selenide as an orange solid (35 mg, 95%). Additional purification was achieved by recrystallization from hot toluene-heptane (ca. 1:4). Yield of crystalline **14a**: 31 mg (84%).

^{1}H NMR (399.95 MHz, $CDCl_3$): δ 1.10–1.42 (m, 10 H, Cy), 1.63–2.04 (m, 12 H, Cy), 4.07 (vt, $J' = 1.9$ Hz, 2 H, fc), 4.14 (d, $^2J_{PH} = 11.7$ Hz, 2 H, C*H*$_2$P(Se)Ph$_2$), 4.19 (d of vt, $J = 1.1$, 1.8 Hz, 2 H, fc), 4.25 (vq, $J' = 1.8$ Hz, 2 H, fc), 4.42 (vq, $J' = 1.7$ Hz, 2 H, fc), 7.40–7.49 (m, 6 H, Ph), 7.83–7.90 (m, 4 H, Ph). ^{13}C{^{1}H} NMR (100.58 MHz, $CDCl_3$): δ 25.76 (d, $J_{PC} = 2$ Hz, 2 C, CH_2 of Cy), 26.32 (d, $J_{PC} = 2$ Hz, 2 C, CH_2 of Cy), 26.40 (d, $J_{PC} = 2$ Hz, 2 C, CH_2 of Cy), 26.53 (d, $J_{PC} = 1$ Hz, 2 C, CH_2 of Cy), 27.21 (d, $J_{PC} = 3$ Hz, 2 C, CH_2 of Cy), 36.18 (d, $^1J_{PC} = 44$ Hz, 1 C, *C*H$_2$P(Se)Ph$_2$), 37.15 (d, $^1J_{PC} = 45$ Hz, 2 C, CH of Cy), 69.74 (s, 2 C, CH of fc), 70.96 (d, $J_{PC} = 9$ Hz, 2 C, CH of fc), 72.75 (d, $^1J_{PC} = 71$ Hz, 1 C, C_{ipso}–P of fc), 72.93 (d, $J_{PC} = 2$ Hz, 2 C, CH of fc), 73.26 (d, $J_{PC} = 10$ Hz, 2 C, CH of fc), 79.97 (s, 1 C, C_{ipso}–CH_2 of fc), 128.41 (d, $J_{PC} = 12$ Hz, 4 C, CH of Ph), 130.99 (d, $^1J_{PC} = 71$ Hz, 2 C, C_{ipso}–P of Ph), 131.41 (d, $J_{PC} = 3$ Hz, 2 C, CH of Ph), 132.23 (d, $J_{PC} = 10$ Hz, 4 C, CH of Ph). ^{31}P{^{1}H} NMR (161.90 MHz, $CDCl_3$): δ 34.0 (s with ^{77}Se satellites, $^1J_{SeP} = 729$ Hz, PPh_2), 50.4 (s with ^{77}Se satellites, $^1J_{SeP} = 696$ Hz, PCy_2). IR (Nujol): ν_{max} 1587 w, 1574 w, 1437 *m*, 1414 w, 1400 w, 1344 w, 1310 w, 1291 w, 1264 w, 1239 w, 1195 *m*, 1180 *m*, 1168 *m*, 1114 w, 1099 *m*, 1069 w, 1041 *m*, 1033 *m*, 1003 *m*, 924 *m*, 903 w, 886 w, 863 w, 849 *m*, 836 s, 830 *m*, 823 *m*, 756 *m*, 747 *m*, 738 s, 693 s, 628 *m*, 619 w, 606 *m*, 551 *m*, 531 *m*, 524 s, 509 w, 500 *m*, 490 *m*, 479 s, 456 *m*, 432 w, 418 w cm^{-1}. ESI + MS: *m/z* 741 ([M+H]$^+$), 763 ([M+Na]$^+$). Anal. Calc. for $C_{35}H_{42}FeP_2Se_2$ (738.42): C 56.93, H 5.73%. Found: C 56.50, H 5.57%.

4.23. Synthesis of 1′-(diisopropylphosphinoselenoyl)-1-[(diphenylphosphinoselenoyl)methyl]ferrocene (**14b**)

Starting with diphosphine **2b** (25 mg, 50 μmol), the same procedure afforded compound **14b** as orange crystalline solid (27 mg, 82%).

^{1}H NMR (399.95 MHz, $CDCl_3$): δ 1.14 (dd, $^3J_{HH} = 7.0$ Hz, $^3J_{PH} = 17.5$ Hz, 6 H, CH*Me*$_2$), 1.19 (dd, $^3J_{HH} = 7.0$ Hz, $^3J_{PH} = 17.8$ Hz, 6 H, CH*Me*$_2$), 2.26 (d of sept, $^2J_{PH} = 8.3$ Hz, $^3J_{HH} = 7.0$ Hz, 2 H, C*H*Me$_2$), 4.09 (vt, $J' = 1.9$ Hz, 2 H, fc), 4.14 (d, $^2J_{PH} = 11.7$ Hz, 2 H, C*H*$_2$P(Se)Ph$_2$), 4.19 (d of vt, $J = 1.0$, 1.8 Hz, 2 H, fc), 4.27 (vq, $J' = 1.7$ Hz, 2 H, fc), 4.43 (vq, $J' = 1.7$ Hz, 2 H, fc), 7.40–7.47 (m, 6 H, Ph), 7.83–7.90 (m, 4 H, Ph). ^{13}C{^{1}H} NMR (100.58 MHz, $CDCl_3$): δ 16.80 (s, 2 C, CH*Me*$_2$), 17.45 (d, $^2J_{PC} = 2$ Hz, 2 C, CH*Me*$_2$), 27.63 (d, $^1J_{PC} = 45$ Hz, 2 C, *C*HMe$_2$), 36.17 (d, $^1J_{PC} = 44$ Hz, 1 C, *C*H$_2$P(Se)Ph$_2$), 69.73 (s, 2 C, CH of fc), 71.03 (d, $J_{PC} = 9$ Hz, 2 C, CH of fc), 72.04 (d, $^1J_{PC} = 71$ Hz, 1 C, C_{ipso}–P of fc), 72.99 (d, $J_{PC} = 2$ Hz, 2 C, CH of fc), 73.18 (d, $J_{PC} = 10$ Hz, 2 C, CH of fc), 79.98 (s, 1 C, C_{ipso}–CH_2 of fc), 128.40 (d, $J_{PC} = 12$ Hz, 4 C, CH of Ph), 130.94 (d, $^1J_{PC} = 71$ Hz, 2 C, C_{ipso}–P of Ph), 131.43 (d, $J_{PC} = 3$ Hz, 2 C, CH of Ph), 132.24 (d, $J_{PC} = 10$ Hz, 4 C, CH of Ph). ^{31}P{^{1}H} NMR (161.90 MHz, $CDCl_3$): δ 34.0 (s with ^{77}Se satellites, $^1J_{SeP} = 729$ Hz, PPh_2), 58.8 (s with ^{77}Se satellites, $^1J_{SeP} = 702$ Hz, P*i*Pr$_2$). IR (Nujol): ν_{max} 1483 *m*, 1435 s, 1415 w, 1400 *m*, 1310 w, 1291 w, 1242 *m*, 1213 w, 1197 w, 1178 *m*, 1169 *m*, 1158 w, 1114 w, 1094 s, 1065 w, 1042 *m*, 1028 s, 997 w, 973 w, 929 *m*, 891 w, 885 w, 875 w, 842 *m*, 836 *m*, 827 *m*, 820 *m*, 806 *m*, 759 *m*, 749 *m*, 697 s, 675 *m*, 656 *m*, 627 w, 603 *m*, 563 *m*, 527 s, 513 *m*,

505 *m*, 494 *m*, 483 *m*, 476 *m*, 441 w, 429 w, 418 w cm^{-1}. ESI + MS: *m/z* 683 ($[M+Na]^+$). Anal. Calc. for $C_{29}H_{34}FeP_2Se_2$ (658.29): C 52.91, H 5.21%. Found: C 52.67, H 5.05%.

4.24. Synthesis of 1′-(di-tert-butylphosphinoselenoyl)-1-[(diphenylphosphinoselenoyl)methyl]ferrocene (**14c**)

Diphosphine **2c** (53 mg, 0.10 mmol), KSeCN (32 mg, 0.22 mmol) were reacted in a mixture of methanol (5 mL) and dichloromethane (4 mL), as described above. Chromatography and crystallization from hot heptane produced the target diselenide **14c** as an orange crystalline solid. Yield: 40 mg (58%).

^{1}H NMR (399.95 MHz, $CDCl_3$): δ 1.36 (d, $^3J_{PH} = 15.5$ Hz, 18 H, CMe_3), 4.08 (vt, $J' = 1.9$ Hz, 2 H, fc), 4.13 (d, $^2J_{PH} = 11.6$ Hz, 2 H, $CH_2P(Se)Ph_2$), 4.16 (d of vt, $J = 1.1$, 1.9 Hz, 2 H, fc), 4.42 (vq, $J' = 1.7$ Hz, 2 H, fc), 4.45 (vq, $J' = 1.7$ Hz, 2 H, fc), 7.40–7.48 (m, 6 H, Ph), 7.83–7.89 (m, 4 H, Ph). ^{13}C{^{1}H} NMR (100.58 MHz, $CDCl_3$): δ 28.77 (d, $^2J_{PC} = 2$ Hz, 6 C, CMe_3), 36.31 (d, $^1J_{PC} = 44$ Hz, 1 C, $CH_2P(Se)Ph_2$), 38.17 (d, $^1J_{PC} = 36$ Hz, 2 C, CMe_3), 70.03 (s, 2 C, CH of fc), 70.71 (d, $J_{PC} = 8$ Hz, 2 C, CH of fc), 73.33 (d, $J_{PC} = 2$ Hz, 2 C, CH of fc), 74.77 (d, $J_{PC} = 9$ Hz, 2 C, CH of fc), 75.00 (d, $^1J_{PC} = 63$ Hz, 1 C, C_{ipso}–P of fc), 79.90 (s, 1 C, C_{ipso}–CH_2 of fc), 128.40 (d, $J_{PC} = 12$ Hz, 4 C, CH of Ph), 130.95 (d, $^1J_{PC} = 71$ Hz, 2 C, C_{ipso}–P of Ph), 131.43 (d, $J_{PC} = 3$ Hz, 2 C, CH of Ph), 132.24 (d, $J_{PC} = 10$ Hz, 4 C, CH of Ph). ^{31}P{^{1}H} NMR (161.90 MHz, $CDCl_3$): δ 33.8 (s with ^{77}Se satellites, $^1J_{SeP} = 728$ Hz, PPh_2), 75.3 (s with ^{77}Se satellites, $^1J_{SeP} = 699$ Hz, $PtBu_2$). IR (Nujol): ν_{max} 1435 s, 1398 *m*, 1311 w, 1242 w, 1181 *m*, 1160 *m*, 1112 w, 1095 s, 1066 w, 1043 w, 1029 *m*, 996 w, 972 w, 950 w, 931 *m*, 888 w, 869 w, 863 w, 849 w, 839 *m*, 828 *m*, 810 *m*, 758 *m*, 745 *m*, 697 s, 687 *m*, 631 w, 618 *m*, 603 *m*, 587 w, 567 *m*, 542 w, 527 s, 512 *m*, 494 *m*, 480 s, 474 *m*, 450 w, 436 w, 423 w cm^{-1}. ESI + MS: *m/z* 711 ($[M+Na]^+$). Anal. Calc. for $C_{31}H_{38}FeP_2Se_2$ (686.35): C 54.25, H 5.58%. Found: C 54.21, H 5.53%.

4.25. Synthesis of palladium complexes from diphosphine **2a**

A solution of diphosphine **2a** (29 mg, 50 μmol) in chloroform (1.5 mL) was added to a reaction vial containing solid $[PdCl_2(MeCN)_2]$ (13 mg, 50 μmol). The resulting mixture was stirred for 10 min to dissolve the solid educt and then heated to 55 °C under argon for 12 h. Addition of methyl *tert*-butyl ether (ca. 8 mL) and crystallization by liquid-phase diffusion over several days afforded the product, which is a mixture of monopalladium chelate complex **15a** and of the dimeric complex **16a**. Combined yield: 19.5 mg. Single crystals of **15a** were obtained by crystallization from dichloromethane-diethyl ether. Anal. Calc. for $C_{35}H_{42}Cl_2FeP_2Pd \cdot 0.15CH_2Cl_2$ (770.56): C 54.79, H 5.53%. Found: C 54.68, H 5.40%. ESI + MS: *m/z* 685 ($[M-Cl-HCl]^+$), 721 ($[M-Cl]^+$).

Compound **15a**. ^{1}H NMR (399.95 MHz, $CDCl_3$): δ 1.12–1.56 (m, 10 H, Cy), 1.70–1.92 (m, 6 H, Cy), 2.14–2.22 (m, 2 H, Cy), 2.38–2.45 (m, 2 H, Cy), 2.83–2.94 (m, 2 H, Cy), 3.23 (br s, 2 H, fc), 3.38 (d, $^2J_{PH} = 10.7$ Hz, 2 H, CH_2PPh_2), 4.05 (vt, $J' = 1.9$ Hz, 2 H, fc), 4.27 (vq, $J' = 1.7$ Hz, 2 H, fc), 4.40 (vq, $J' = 1.6$ Hz, 2 H, fc), 7.46–7.54 (m, 6 H, Ph), 7.94–8.02 (m, 4 H, Ph). ^{31}P{^{1}H} NMR (161.90 MHz, $CDCl_3$): δ 27.7 (s, PPh_2), 29.5 (s, PCy_2).

Compound **16a**. ^{1}H NMR (399.95 MHz, CD_2Cl_2): δ 1.10–1.80 (m, 16 H, Cy), 2.04–2.18 (m, 4 H, Cy), 2.44–2.58 (m, 2 H, Cy), 4.07 (br s, 2 H, fc), 4.10 (vt, $J' = 1.8$ Hz, 2 H, fc), 4.12 (d, $^2J_{PH} = 7.0$ Hz, 2 H, CH_2PPh_2), 4.36 (vt, $J' = 1.6$ Hz, 2 H, fc), 4.61 (br s, 2 H, fc), 7.35–7.50 (m, 6 H, Ph), 7.65–7.72 (m, 4 H, Ph). ^{31}P{^{1}H} NMR (161.90 MHz, CD_2Cl_2): δ 16.6 (d, $^2J_{PP} = 528$ Hz, PPh_2), 22.9 (d, $^2J_{PP} = 528$ Hz, PCy_2).

4.26. Synthesis of palladium complexes from diphosphine **2b**

Using diphosphine **2b** (25 mg, 50 μmol), the procedure described above furnished red crystalline product (22 mg) containing the chelate complex **15b** and dimer **16b**. Single crystals of **16b** were obtained from dichloromethane-diethyl ether. ESI + MS: *m/z* 605 ($[M-Cl-HCl]^+$), 641 ($[M-Cl]^+$). Anal. Calc. for $C_{29}H_{34}Cl_2FeP_2Pd \cdot 0.25CHCl_3$ (701.57): C 49.99, H 4.91%. Found: C 49.86, H 4.75%.

Compound **15b**. ^{1}H NMR (399.95 MHz, $CDCl_3$): δ 1.29 (dd, $^3J_{HH} = 7.0$ Hz, $^3J_{PH} = 16.3$ Hz, 6 H, $CHMe_2$), 1.46 (dd, $^3J_{HH} = 6.9$ Hz, $^3J_{PH} = 17.4$ Hz, 6 H, $CHMe_2$), 3.05–3.16 (m, 2 H, $CHMe_2$), 3.28 (br s, 2 H, fc), 3.40 (d, $^2J_{PH} = 10.7$ Hz, 2 H, CH_2PPh_2), 4.06 (vt, $J' = 1.9$ Hz, 2 H, fc), 4.30 (vq, $J' = 1.7$ Hz, 2 H, fc), 4.42 (vq, $J' = 1.8$ Hz, 2 H, fc), 7.46–7.56 (m, 6 H, Ph), 7.94–8.02 (m, 4 H, Ph). ^{31}P{^{1}H} NMR (161.90 MHz, $CDCl_3$): δ 29.6 (s, PPh_2), 35.7 (s, $PiPr_2$).

Compound **16b**. ^{1}H NMR (399.95 MHz, CD_2Cl_2): δ 1.27 (dd, $^3J_{HH} = 7.2$ Hz, $^3J_{PH} = 14.0$ Hz, 6 H, $CHMe_2$), 1.42 (dd, $^3J_{HH} = 7.2$ Hz, $^3J_{PH} = 15.7$ Hz, 6 H, $CHMe_2$), 2.61–2.74 (m, 2 H, $CHMe_2$), 3.98 (dd, $^2J_{PH} = 8.9$ Hz, $^4J_{PH} = 2.1$ Hz, 2 H, CH_2PPh_2), 4.24 (br s, 2 H, fc), 4.27 (vt, $J' = 1.8$ Hz, 2 H, fc), 4.34 (d of vt, $J = 0.7$, 1.7 Hz, 2 H, fc), 4.73 (vq, $J' = 1.6$ Hz, 2 H, fc), 7.33–7.48 (m, 6 H, Ph), 7.59–7.65 (m, 4 H, Ph). ^{31}P{^{1}H} NMR (161.90 MHz, CD_2Cl_2): δ 16.5 (d, $^2J_{PP} = 541$ Hz, PPh_2), 30.0 (d, $^2J_{PP} = 541$ Hz, $PiPr_2$).

4.27. Synthesis of palladium complexes from diphosphine **2c**

The same procedure using diphosphine **2c** (26 mg, 50 μmol) led to a mixture of the analogous products **15c** and **16c**. The mixture was recrystallized as described above. ESI– MS: *m/z* 529 ($[M-PdCl_2+H]^-$). Anal. Calc. for $C_{31}H_{38}Cl_2FeP_2Pd \cdot 0.6CH_2Cl_2$ (756.71): C 50.16, H 5.22%. Found: C 50.14, H 5.07%.

Compound **15c**. ^{31}P{^{1}H} NMR (161.90 MHz, $CDCl_3$): δ 28.6 (d, $^2J_{PP} = 7$ Hz, PPh_2), 50.6 (d, $^2J_{PP} = 7$ Hz, $PtBu_2$). Compound **16c**: ^{31}P{^{1}H} NMR (161.90 MHz, $CDCl_3$): δ 16.9 (d, $^2J_{PP} = 538$ Hz, PPh_2), 51.6 (d, $^2J_{PP} = 538$ Hz, $PtBu_2$). The ^{1}H NMR spectra could not be unambiguously interpreted due to the poor solubility of the compounds and to extensive signal broadening.

4.28. X-ray crystallography

Full-set diffraction data ($\pm h \pm k \pm l$, $\theta_{max} \approx 26.0$ or 27.5°, completeness ≥ 99.6%) were collected with a Nonius KappaCCD diffractometer equipped with a Bruker ApexII detector and a Cryostream Cooler (Oxford Cryosystems) or, alternatively, with a Bruker D8 Venture Kappa Duo diffractometer equipped with a PHOTON 100 detector, a IμS 3.0 microfocus source (only for **14a**, **14c**, **16b** and **16c**) at 120(2) or 150(2) K. Mo Kα radiation (λ = 0.71073 Å) was used throughout. The data were corrected for absorption using routines incorporated in the diffractometer software.

The structures was solved by direct methods using SHELXS-97 [42] or SHELXT-2014 [43] and refined by full-matrix least-squares routine based on F^2 (SHELXL-97 [42] or SHELXL-2014 [44]). All non-hydrogen atoms were refined with anisotropic displacement parameters. The OH hydrogens in the structure of **9b** were identified on the difference density maps and refined as riding atoms with U_{iso}(H) assigned to 1.5U_{eq}(O) of its bonding oxygen atom. The hydrogen atoms in the CH_n groups were all placed in their theoretical positions and similarly refined with U_{iso}(H) = 1.5U_{eq}(C) (methyl groups) or with 1.2U_{eq}(C) (all other hydrogen atoms). Relevant crystallographic data and refinement parameters are presented in the Supporting Information (Table S1).

Geometric calculations were performed using a recent version of the PLATON program [45], which was also used to prepare the structural drawings. All geometric parameters of atoms in refined positions are indicated with their estimated standard deviations (ESDs) rounded to one decimal place. The parameters involving

atoms in constrained positions (hydrogen atoms) are given without ESDs.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.jorganchem.2018.01.009.

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