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Metallocenes

Palladium(II) Complexes of Homologated Ferrocene Phosphanylether and Thioether Ligands

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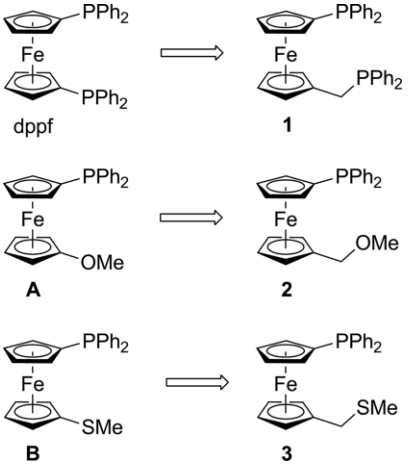
Abstract: The reaction of [1′-(diphenylphosphanyl)ferrocenyl]methanol/borane (1:1) with in situ formed *N*,*N*,*N*′,*N*′,*S*-pentamethylisothiouronium iodide and sodium hydride, followed by removal of the borane protecting group with 1,4-diazabicyclo[2.2.2]octane, afforded 1-(diphenylphosphanyl)-1′-[(methylthio)methyl]ferrocene (**3**) as a new, homologated, hybrid phosphanylferrocene ligand. Compound **3** and the congeneric phosphanyl ether **2** were studied as ligands in Pd^{II} complexes. When treated with $[PdCl_2(MeCN)_2]$ in a Pd/ligand ratio of 1:1, compound **3** furnished a mixture of two Pd complexes, including the ligand-bridged dimer $[\{\mu(P,S)\text{-}\mathbf{3}\}PdCl_2]_2$ (**6**), which was structurally characterized. Upon increasing the amount of ligand to 2 equiv., a similar reaction produced the bis(phosphane) complex $[PdCl_2(\mathbf{3}\text{-}\kappa P)_2]$ (**7**). Bridge-cleavage reactions of the dipalladium complex $[(L^{NC})Pd(\mu\text{-}Cl)]_2$ {L^{NC} = 2-[(dimethylamino-κ*N*)methyl]phenyl-κC^1} with donors **3** and **2** proceeded in a uniform manner to give the corresponding phosphane complexes $[(L^{NC})PdCl(\mathbf{3}\text{-}\kappa P)]$ (**8**) and $[(L^{NC})PdCl(\mathbf{2}\text{-}\kappa P)]$ (**9**). Conversely, removing the Pd-bonded chloride from these complexes with $AgClO_4$ generated the bis(chelate) complex $[(L^{NC})Pd(\mathbf{3}\text{-}\kappa^2 P,S)]$ (**10**) and the aqua complex $[(L^{NC})Pd(H_2O)(\mathbf{2}\text{-}\kappa P)]$ (**11**), respectively, both of which could be converted back into their precursors by adding Bu_4NCl. The structures of the complexes **6**–**11** (some in solvated form) were determined by single-crystal X-ray diffraction analysis.

Introduction

First reported in 1965,[1] 1,1′-bis(diphenylphosphanyl)ferrocene (dppf) has been extensively used as a versatile donor for coordination chemistry and as an efficient supporting ligand for a plethora of transition-metal-catalyzed organic transformations.[2] The practical success of dppf has naturally led to the search for analogues with different substituents on the phosphorus atoms[3] or with one of the two phosphane moieties replaced by another functional group.[4] Recently, we used an alternative approach to modify the archetypal dppf structure by inserting a spacer group between one of the functional substituents and the ferrocene unit, thereby preparing the semi-homologous dppf congener **1** (see Scheme 1).[5] More recently, we described the analogous O,P donor **2**,[6] related to the known phosphanyl ether **A**,[7] and several other compounds of this type.[8]

A recent serendipitous discovery led us to pursue the synthesis of phosphanyl thioether **3**, which also has a directly functionalized ferrocene counterpart, namely compound **B**[9] (Scheme 1), and is structurally related to planar-chiral phosphanylferrocene donors with CH_2SR groups at the 2-position of the ferrocene moiety. These phosphanylferrocene donors have been studied as ligands in coordination compounds and catalysts.[10] In this contribution, we describe the synthesis and structural characterization of the new ferrocene-based phosphanyl thioether ligand **3** and its Pd^{II} complexes and compare these with the complexes resulting from the analogous phosphanyl ether **2**.



Scheme 1. Homologation route to new phosphanylferrocene ligands.

Results and Discussion

Synthesis of Ligand 3

The borane adduct of phosphanylferrocene thioether **3**, compound **4**, was initially detected in varying minor amounts

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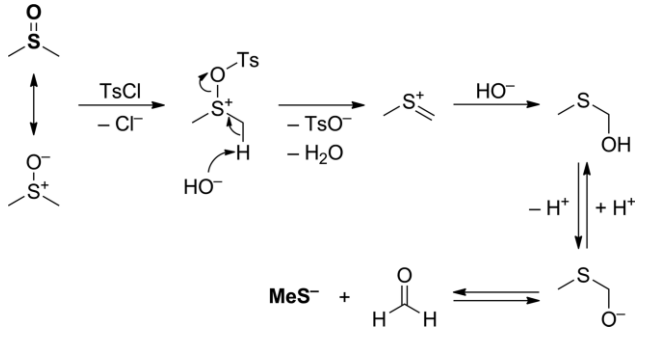
among the products of the reactions of adduct [1′-(diphenylphosphanyl)ferrocenyl]methanol/borane (1:1; **5**)[6] with KOH and 4-toluenesulfonyl (tosyl) chloride in dry dimethyl sulfoxide, which were originally aimed at the synthesis of the tosyl derivative $Ph_2PfcCH_2OTs{\cdot}BH_3$ (fc = ferrocene-1,1′-diyl). The rather unexpected formation of $Ph_2PfcCH_2SMe{\cdot}BH_3$ (**4**) suggested that the methylthiolate anion derives from the solvent during the reaction and also indicated intermediate formation of the mentioned tosylate. However, this tosylate could not be isolated.

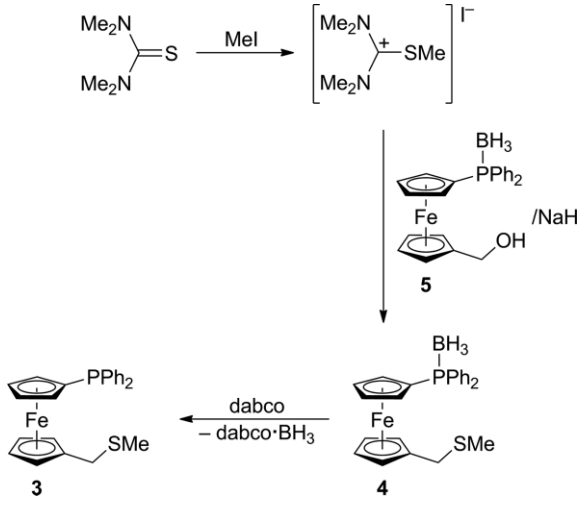
A plausible mechanism for the formation of the methylthiolate is formulated in Scheme 2 and involves a Pummerer rearrangement[11] as its key step. Initially, dimethyl sulfoxide is activated with tosyl chloride[12] and the species formed undergoes elimination upon the action of a base (KOH) to afford a thionium cation. Addition of OH^- to this cation provides an intermediate hemithioacetal, which eventually degrades to formaldehyde and the methylthiolate anion under basic conditions.



Scheme 2. Plausible mechanism for the conversion of dimethyl sulfoxide into the MeS^- anion upon the action of TsCl and KOH.

Because adduct **4** could be easily converted into phosphanyl thioether Ph_2PfcCH_2SMe (**3**), which expands the family of donors that are homologues of the known functional phosphanylferrocene ligands (see the Introduction section), we decided to design a rational preparative route to this compound. Unfortunately, repeated attempts to improve the yield of **4**, either by optimizing the original reaction conditions or by altering the synthetic approach, were not successful. For instance, the reactions of the thiolate MeSNa with in situ generated sulfonates [resulting from alcohol **5** and tosyl chloride/DMAP or, similarly, from **5** and methanesulfonyl chloride/DMAP; DMAP = 4-(dimethylamino)pyridine] or acetates (generated in situ from **5** and Ac_2O with and without added $NaHCO_3$, or by treatment of **5** with trifluoroacetic anhydride) failed to provide **4** according to TLC analyses. Similarly, only traces of **4** were found in the crude reaction mixture resulting from the successive addition of the Vilsmeier–Haack–Arnold reagent ($[ClCH{=}NMe_2]Cl$)[13] and MeSNa to a solution of **5** in DMF.

Eventually, compound **4** was synthesized by using the method developed by Kajigaeshi and co-workers[14] based on the reactions between the in situ formed *S*-alkylisothiouronium salts and alcoholates. Thus, the reaction of $[(Me_2N)_2SMe]I$ with **5**/NaH (Scheme 3) afforded the protected phosphanyl thioether **4** in yields of 28 and 45 % when performed in *N*,*N*-dimethylformamide and acetonitrile, respectively. Finally, the best yield of **4** (63 %) was obtained when the reaction solvent was changed to anhydrous tetrahydrofuran. In a subsequent step, the borane protecting group was removed by treatment with 1,4-diazabicyclo[2.2.2]octane (dabco)[15] in warm toluene, which provided the target phosphanyl thioether **3** in virtually quantitative yield after flash chromatography.



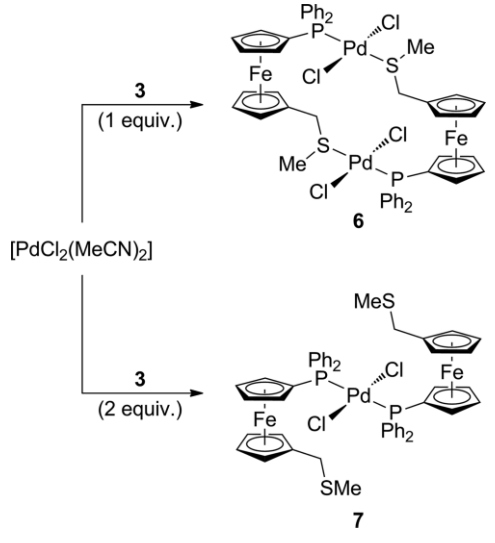
Scheme 3. Synthesis of 1-(diphenylphosphanyl)-1′-[(methylthio)methyl]ferrocene (**3**). dabco = 1,4-diazabicyclo[2.2.2]octane.

Compounds **3** and **4** were characterized by NMR spectroscopy, electrospray ionization (ESI) mass spectrometry, and elemental analysis. Their ^1H and ^{13}C NMR spectra show the characteristic signals of the 1,1′-disubstituted ferrocene unit and its diphenylphosphanyl substituent, which also gives rise to a characteristic broad feature at δ_P = 16.4 ppm in the ^{31}P NMR spectrum of **4** and a sharp singlet at δ_P = –16.3 ppm in the ^{31}P NMR spectrum of the free phosphane **3**. The signals of the thioether pendant in **3** are observed at δ_H = 1.97/δ_C = 15.47 ppm (SMe) and δ_H = 3.18/δ_C = 33.25 ppm (SCH_2).

Synthesis of Pd^{II} Complexes with Ligands 2 and 3

To compare the coordination properties of the phosphanyl thioether **3** with those of the previously studied ether analogue **2**,[6] we initially attempted to prepare simple Pd^{II} chloride complexes by treating **3** with $[PdCl_2(MeCN)_2]$ at various Pd/ligand ratios (Scheme 4). The reaction performed first with equimolar amounts of the starting materials and subsequent crystallization afforded a rusty-brown crystalline solid, which was structurally characterized as the ligand-bridged dipalladium(II) complex $[\{\mu(P,S)\text{-}\mathbf{3}\}PdCl_2]_2$ (**6**) rather than the originally anticipated monopalladium chelate $[PdCl_2(\mathbf{3}\text{-}\kappa^2P,S)]$. However, the analysis of the reaction mixture and even of the crystallized material revealed the presence of two species characterized by ^{31}P NMR resonances at δ_P = 24.5 and 29.9 ppm. Unfortunately, the ^1H NMR spectra of both the reaction mixture and the crystallized material provided little structural information about the species formed because of extensive signal broadening. Nonetheless, the splitting of the easily recognizable resonances due to the SMe groups, attributed to interactions with phosphorus, and their shift to lower field suggest that these moieties are coordi-

nated in both cases [SMe: δ_H = 2.45 ppm (d, J_{PH} = 4.6 Hz) and δ_H = 2.66 ppm (d, J_{PH} = 0.8 Hz)]. These facts and the NMR spectroscopic data previously reported for *trans*-[$PdCl_2$(Ph$_2$PfcCONHCH$_2$CH$_2$SMe-κ^2*S*,*P*)] (δ_P = 23.6 ppm)[16] led us to tentatively formulate the products as the structurally characterized dimer [{μ(P,S)-**3**}$PdCl_2$]$_2$ (**6**) and the plausible, but non-isolated, chelate [$PdCl_2$(**3**-κ^2*P*,*S*)]. However, the two species observed in solution could also be diastereoisomers of the same complex differing in the configuration of the two stereogenic sulfur atoms (i.e., *meso* form *RS*/*SR* and racemate *RR*/*SS*). Despite this ambiguity, it is clear that compound **3** behaves differently from the phosphanyl ether ligand **2**, which afforded the chloride-bridged dimer [Pd(μ-Cl)Cl(**2**-κ*P*)]$_2$ (δ_P = 31.7 ppm) as the sole product under similar conditions.[6]



Scheme 4. Synthesis of Pd^{II} chloride complexes with ligand **3**.

Upon increasing the amount of ligand **3** to 2 mol-equiv., the complexation reaction with [$PdCl_2$(MeCN)$_2$] took the expected course, producing the bis(phosphane) complex **7** as the sole product (Scheme 4), in analogy to the behavior of phosphanyl ether **2**. The ^{31}P NMR resonance of complex **7** can be observed at δ_P = 15.7 ppm, similarly to the corresponding complex featuring ligand **2** (δ_P = 15.4 ppm[6]). The formulation of **7** was further confirmed by its ^{13}C NMR spectrum, which shows the signals of the ^{31}P-coupled ferrocene and PPh_2 carbon atoms as characteristic apparent triplets due to virtual coupling in the AA'X spin system ^{13}C-^{31}P-Pd-^{31}P-^{12}C.[17] Finally, the presence of an uncoordinated thioether pendant was suggested by the practically negligible coordination shifts of its ^{1}H and ^{13}C NMR resonances [SMe: $\Delta\delta_H$(SMe) = 0.04 ppm, $\Delta\delta_C$(SMe) = 0.17 ppm].

Structure determination indicated that compound **6** crystallizes in the form of stoichiometric solvate **6**·3$CHCl_3$. Its structure is shown in Figure 1, and the relevant structural parameters are given in Table 1. Notably, the molecular structure of the complex lacks any imposed symmetry and has the (*S*) configuration at both sulfur atoms [the (*R*,*R*) enantiomeric molecules are also present in the centrosymmetric crystal].

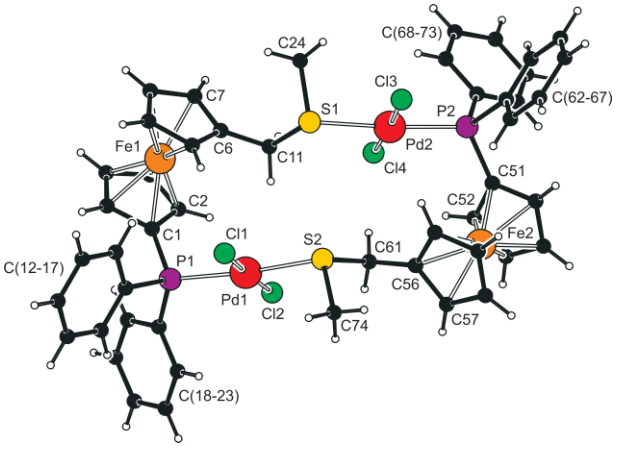


Figure 1. PLATON plot of the complex molecule in the structure of **6**·3$CHCl_3$.

The coordination spheres around the structurally independent, but chemically equivalent, palladium atoms are similar in terms of both interligand distances and angles and are essen-

Table 1. Selected geometric parameters for complex **6**·3$CHCl_3$.[a]

Pd1–Cl1	2.3099(5)	Pd2–Cl3	2.3057(5)
Pd1–Cl2	2.2874(5)	Pd2–Cl4	2.2892(5)
Pd1–P1	2.2852(5)	Pd2–P2	2.2708(5)
Pd1–S2	2.3871(5)	Pd2–S1	2.3754(5)
Cl1–Pd1–P1	94.30(2)	Cl3–Pd2–P2	95.06(2)
Cl1–Pd1–S2	81.97(2)	Cl3–Pd2–S1	82.55(2)
Cl2–Pd1–P1	89.70(2)	Cl4–Pd2–P2	88.15(2)
Cl2–Pd1–S2	94.11(2)	Cl4–Pd2–S1	94.19(2)
Fe1–Cg1	1.6465(9)	Fe2–Cg3	1.6492(9)
Fe1–Cg2	1.6441(9)	Fe2–Cg4	1.6522(9)
∠Cp1,Cp2	3.0(1)	∠Cp3,Cp4	1.3(1)
τ_1	67.2(1)	τ_2	70.2(1)
P1–C1	1.789(2)	P2–C51	1.792(2)
C–P1–C	102.45(9)–105.69(8)	C–P2–C	103.89(8)–104.62(8)
C11–S1	1.821(2)	C61–S2	1.824(2)
S1–C24	1.799(2)	S2–C74	1.802(2)
C6–C11–S1	109.3(1)	C56–C61–S2	108.9(1)
C11–S1–C24	99.0(1)	C61–S2–C74	100.34(9)

[a] Distances are given in Å and angles in °. The parameters are defined follows: Cp1 = C(1–5), Cp2 = C(6–10), Cp3 = C(51–55), Cp4 = C(56–60), Cg*n* (*n* = 1–4) are the corresponding ring centroids. τ_1 = C1–Cg1–Cg2–C6, τ_2 = C51–Cg3–Cg3–C56.

tially planar, as indicated by the sums of the *cis* interligand angles, which only marginally deviate from 360° (Table 1). According to a search in the Cambridge Structural Database,[18] complex **6** represents a rare example of a structurally characterized Pd^{II} complex with a $PSCl_2$ donor set having *trans*-P,S geometry rather than the *cis*-P,S configuration exhibited by the majority of similar, mostly chelate, complexes.[19] In fact, the only related example reported to date is the aforementioned complex [$PdCl_2(Ph_2PfcCONHCH_2CH_2SMe$-$\kappa^2S,P$)], which shows similar Pd–donor bond lengths (within ±0.025 Å).[16]

The $PdCl_2SP$ planes in the macrocyclic structure of **6**·$3CHCl_3$ are nearly parallel [dihedral angle: 4.07(2)°], but mutually offset [Pd1···Pd2 5.8544(5) Å]. The ferrocene moieties assume synclinal eclipsed conformations (compare the τ angles in Table 1 with the ideal value of 72°, see ref.[2b]). The cyclopentadienyl rings in the ferrocene unit comprising atom Fe1 are mutually tilted by approximately 3°, and the phosphane substituent is displaced from its bonding plane toward atom Pd1 by as much as 0.2510(4) Å, whereas the coordination of the other ferrocene moiety (Fe2) does not cause a similar distortion [tilt angle: 1°, distance of P2 from the C(51–55) plane: 0.0818(4) Å]. Both (methylthio)methyl substituents are directed below the ferrocene units (away from the iron atom) and coordinated in positions *trans* with respect to the phosphane moieties.

The molecular structure of compound **7** is shown in Figure 2, and the representative geometric data are given in Table 2. Apparently, the molecule of complex **7** adopts a geometry typical of *trans*-[$PdCl_2(Ph_2PfcX$-$\kappa P)_2$] complexes.[8d,9b,20] The coordination environment of the central palladium atom in **7** is ideally planar due to the imposed crystallographic symmetry (the Pd atom resides on an inversion center). However, the pairs of adjacent interligand angles differ from 90° by ±3.5°, most likely for steric reasons. Steric congestion may also account for a minor tilting [5.0(1)°] of the ferrocene cyclopentadienyl rings, which

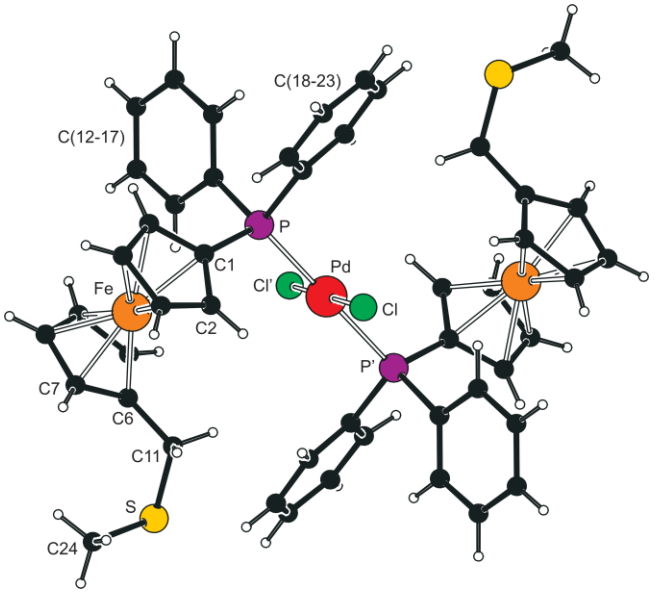


Figure 2. PLATON plot of the molecular structure of complex **7**. For simplicity, only one orientation of the disordered phenyl ring C(18–23) is shown. The atoms labelled with primes are generated by crystallographic inversion.

open toward the Pd^{II}, and, in particular, for a displacement of the phosphorus atom from the plane of the parent cyclopentadienyl ring C(1–5) and outward from the ferrocene core by 0.2387(6) Å. The 1,1′-disubstituted ferrocene moiety has an intermediate conformation characterized by the τ angle of 83.9(2)° (see Table 2). The CH_2SMe substituent is located on the side of the phosphanylferrocenyl moiety and directed away from the palladium center.

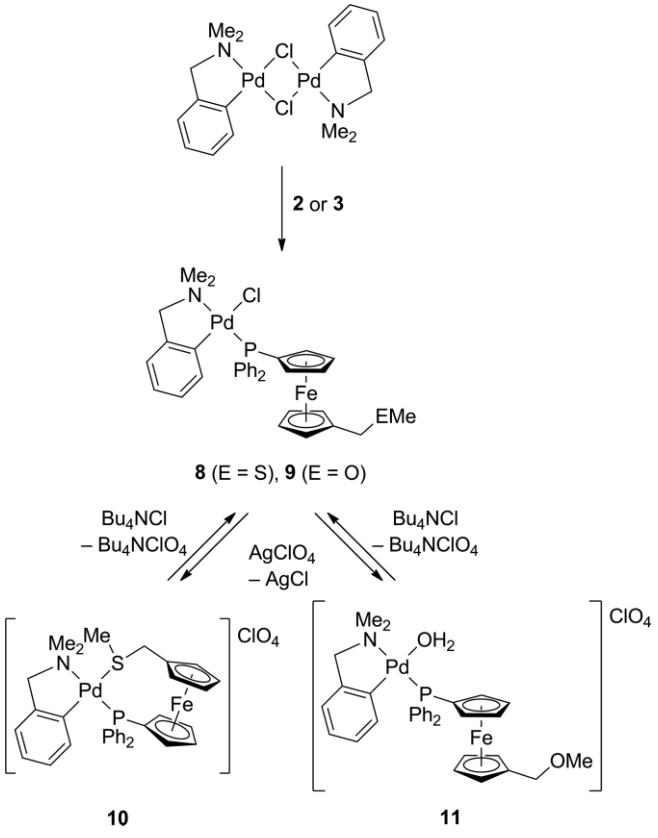
Table 2. Selected geometric parameters for **7**.[a]

Pd–Cl	2.2897(7)	Cl–Pd–P[b]	86.47(2)
Pd–P	2.3400(6)	Cl′–Pd–P[b]	93.53(2)
Fe–Cg1	1.645(1)	∠Cp1,Cp2	5.0(1)
Fe–Cg2	1.647(1)	τ	–83.9(2)
P–C6	1.799(3)	C–P–C[c]	102.6(1)–103.9(1)
C11–S	1.822(2)	C6–C11–S	114.1(2)
S–C24	1.798(3)	C11–S–C24	99.5(1)

[a] Distances are given in Å and angles in °. Definitions: Cp1 and Cp2 are the cyclopentadienyl rings C(1–5) and C(6–10), respectively. Cg1 and Cg2 denote their centroids. ∠Cp1,Cp2 is the dihedral angle of the least-squares cyclopentadienyl planes (tilt angle), and τ is the torsion angle C1–Cg1–Cg2–Cg6. [b] The adjacent interligand angles sum up to 180° because of the imposed symmetry. [c] Range of the C–P–C angles.

The reaction of **3** with di-μ-chlorobis{2-[(dimethylamino-κ*N*)methyl]phenyl-κC^1}dipalladium(II), [$(L^{NC})Pd(\mu$-$Cl)]_2$, in a ligand/Pd ratio of 1:1 proceeded as expected through the cleavage of the chloride bridges to generate the phosphane complex **8** (Scheme 5). The phosphanyl ether ligand **2** reacted similarly to furnish the analogous compound **9**. The ^1H and ^{13}C NMR spectra of complexes **8** and **9** display signals due to the auxiliary *ortho*-metalated ligand $C_6H_4CH_2NMe_2$ and the *P*-coordinated ferrocenylphosphane, with the $^3J_{PC}$ and $^4J_{PC}$ coupling constants of the phosphorus-coupled resonances of the CH_2NMe_2 moiety suggesting a *trans*-P,N arrangement in both cases.[20d,20f,20j,20l,21] The P-monodentate coordination of the phosphanylferrocene donors could also be inferred from a shift of the ^{31}P NMR signals to a lower field (δ_P = 33.0 ppm for both compounds; coordination shift: $\Delta_P \approx 49$ ppm) and from the fact that the signals of the terminal EMe (E = S and O) groups remained nearly unaffected by the coordination [cf. $\Delta\delta_H$(EMe) = 0.05 ppm for **8** and **9**, $\Delta\delta_C$(EMe) = 0.01 ppm for **8**, and 0.09 ppm for **9**]. Notably, the ^1H NMR signals of the SCH_2 groups are considerably more affected [$\Delta\delta_H(ECH_2)$ = 0.32 and 0.25 ppm, $\Delta\delta_C(ECH_2)$ = 0.12 and 0.04 ppm for **8** for **9**, respectively], being influenced by the coordinated phosphanylferrocene moiety. Finally, the positive-ion ESI mass spectra of **8** and **9** show peaks attributable to cations resulting from the loss of the chloride ligand, $[M - Cl]^+$, at *m*/*z* = 670 and 654, respectively.

The structures of the solvated complexes **8**·AcOEt and **9**·$1/2C_6H_{14}$ were determined by single-crystal X-ray diffraction analysis and are shown in Figure 3. Analysis of the geometric data collected in Table 3 shows that the coordination geometries of these complexes are very similar. In both cases, the coordination environment of Pd^{II} is significantly distorted due to varying Pd–donor bond lengths, different steric demands of the Pd-bonded ligands, and the presence of a small and rigid metallacycle. However, the geometric parameters are not significantly different from those reported for similar complexes [$(L^{NC})PdCl(Ph_2PfcX$-$\kappa P)$].[20d,20f,20j,20l,21]



Scheme 5. Synthesis and mutual interconversion of Pd^{II}–**2** and Pd^{II}–**3** complexes with an auxiliary [2-(dimethylamino-κ*N*)methyl]phenyl-κC^1 (L^{NC}) ligand.

The distortion of the coordination planes can be illustrated by the dihedral angles subtended by the half-planes {Pd,Cl,P} and {Pd,N,C25}, being 14.1(1) and 16.96(8)° in **8**·AcOEt and **9**·1/2C_6H_{14}, respectively (please note: the sums of the inter-

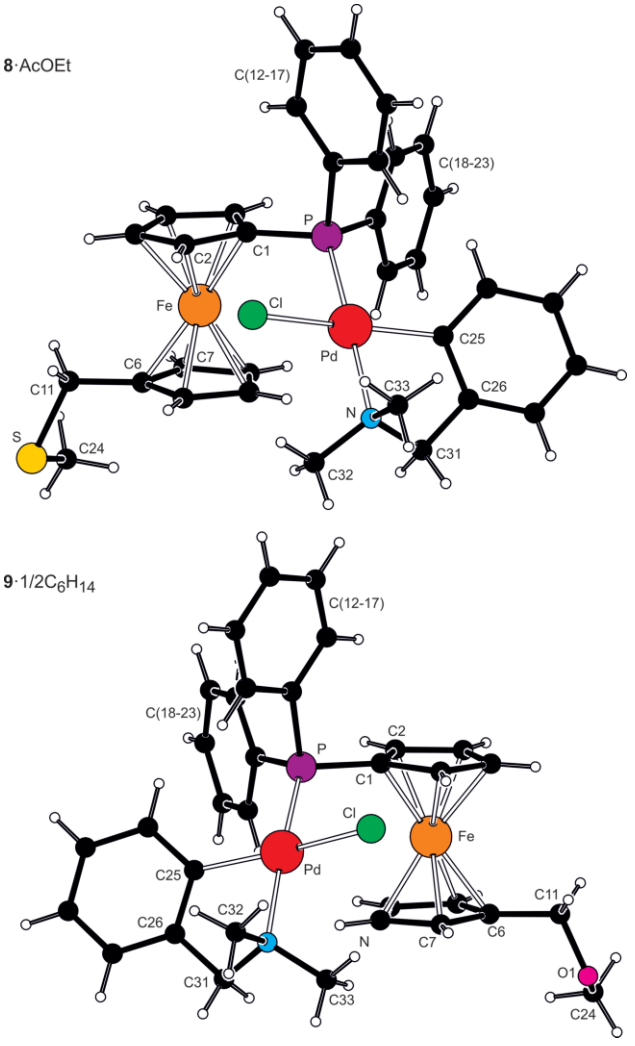


Figure 3. PLATON plots of the molecular structures of **8**·AcOEt (top) and **9**·1/2C_6H_{14} (bottom).

Table 3. Selected distances and angles for **8**·AcOEt, **9**·1/2C_6H_{14}, **10**·3/2$C_2H_4Cl_2$, and **11**.[a]

Parameter X/E	**8**·AcOEt Cl/S	**9**·1/2C_6H_{14} Cl/O1	**10**·3/2$C_2H_4Cl_2$ S/S[c]	**11** O1W/O1
Pd–X	2.3972(7)	2.3944(6)	2.4103(7)	2.169(1)
Pd–P	2.2531(7)	2.2505(6)	2.2552(6)	2.2546(6)
Pd–N	2.152(2)	2.158(2)	2.168(2)	2.145(2)
Pd–C25	2.010(2)	2.001(2)	2.035(2)	1.977(2)
P–Pd–X	92.37(2)	92.96(2)	96.93(2)	97.00(4)
P–Pd–C25	96.24(7)	96.25(6)	95.34(5)	93.20(6)
N–Pd–X	90.14(6)	90.77(5)	85.32(5)	89.14(6)
N–Pd–C25	82.50(9)	82.17(8)	82.30(7)	81.17(7)
Fe1–Cg1	1.645(1)	1.646(1)	1.642(1)	1.6439(8)
Fe1–Cg2	1.645(1)	1.643(1)	1.654(1)	1.6452(9)
∠Cp1,Cp2	3.6(2)	3.1(1)	5.2(1)	3.8(1)
τ	154.7(2)	–147.4(2)	2.1(2)	–144.1(1)
P–C1	1.808(2)	1.804(2)	1.795(2)	1.799(2)
C–P–C[b]	98.2(1)–105.0(1)	98.66(9)–104.62(9)	100.07(8)–111.02(9)	102.64(8)–103.25(8)
C11–E	1.829(3)	1.435(3)	1.811(2)	1.426(2)
E–C24	1.799(4)	1.421(4)	1.804(2)	1.417(3)
C6–C11–E	113.8(2)	112.4(2)	114.0(1)	113.3(2)
C11–E–C24	97.0(2)	112.4(2)	99.16(9)	112.5(2)

[a] Distances are given in Å and angles in °. Definitions: Cp1 and Cp2 are the cyclopentadienyl rings C(1–5) and C(6–10), respectively, Cg1 and Cg2 denote their respective centroids, ∠Cp1,Cp2 is the dihedral angle of the least-squares cyclopentadienyl planes (tilt angle), and τ is the torsion angle C1–Cg1–Cg2–C6. [b] The range of C–P–C angles. [c] X is identical to E in this particular case.

ligand angles are 361.3 and 362.2°). The five-membered palladacycles have similar geometries and envelope conformations, with their nitrogen atoms located in *endo* positions [cf. the ring-puckering parameters: φ = 41.8(4) and 220.6(3)° for **8**·AcOEt and **9**·1/2C_6H_{14}, respectively; the ideal envelope requires φ to be an integer multiple of 36°, see ref.[22]]. The ferrocene moieties in both structures assume open conformations with τ angles of around 150°, and their uncoordinated CH_2EMe (E = O, S) substituents are diverted away from the center of the ferrocene unit and the palladium(II) atom.

Preparation of complexes in which compounds **2** and **3** would possibly coordinate as P,E-chelate donors was attempted by removing the Pd-bonded chloride ligands from **8** and **9** (Scheme 5). Upon treatment with silver(I) perchlorate, compound **8** was, indeed, smoothly converted into the cationic bis(chelate) complex **10**. In contrast, a similar reaction with complex **9** was complicated by a partial decomposition, which resulted in the formation of green materials (most likely due to oxidation of the ferrocene ligand), and the product isolated after several crystallizations was characterized as the cationic aqua complex **11** featuring ligand **2** as a P-monodentate donor. After careful optimization, compound **11** was obtained in 30 % yield by using reagent-grade chloroform as the solvent and an excess of the silver salt (please refer to the Exp. Sect. for further details). Notably, both cationic complexes could be converted back into the neutral chloride complexes (i.e., their precursors) by adding tetrabutylammonium chloride, whereas repeated attempts to replace the coordinated water molecule in **11** with another ligand failed. For instance, adding cyclohexyl isocyanide, cyclohexyl cyanide, trimethylphosphane, or triphenylphosphane to **11** led, according to NMR analysis, to the formation of complicated mixtures that typically deposited intractable black materials during crystallization (a brown amorphous solid formed in the case of cyclohexyl cyanide). The reactions of **11** with ammonia or sulfane also led to brown amorphous solids, whereas the crystalline material isolated after adding benzyl methyl sulfide to **11** in $CDCl_3$ and crystallization from ethyl acetate/hexane was identified as the starting Pd^{II} complex.

Although structure determination provided definitive proof of the formulation, the NMR spectra had already suggested that complexes **10** and **11** have different structures. The ^{1}H NMR spectrum of **10** indicates coordination of the thioether moiety [$\Delta\delta_H$(SMe) = 0.46 ppm, $\Delta\delta_H$(SCH_2) = 0.08 ppm], whereas the spectrum of complex **11** suggests that the ether chain remains free [$\Delta\delta_H$(OMe) = 0.05 ppm, $\Delta\delta_H$(OCH_2) = 0.10 ppm]. A similar conclusion could be drawn from the ^{13}C NMR spectroscopic data [**10**: $\Delta\delta_C$(SMe) = 4.68 ppm; **11**: $\Delta\delta_C$(OMe) = 0.29 ppm], and the ^{31}P NMR spectra indicate coordination of the phosphane moieties (δ_P = 33.3 ppm for **10** and δ_P = 30.4 ppm for **11**). The IR spectra of the cationic complexes corroborate the presence of the perchlorate counter ions through strong composite bands at approximately 1090 cm^{-1} [$\nu_3(ClO_4)$][23] and, in the case of **11**, also indicated the presence of a water molecule (broad band at 3185 cm^{-1}). Conversely, the ESI mass spectra only show signals of the cations $[(L^{NC})Pd(L)]^+$ (L = **2** and **3**), which are isobaric to the ions $[M - Cl]^+$ resulting from the fragmentation of **8** and **9**.

The structure of solvate **10**·3/2$C_2H_4Cl_2$ is shown in Figure 4, and the pertinent geometric data are given in Table 3. Comparison of the structural parameters determined for the parent complex **8**·AcOEt and the cationic bis(chelate) complex **10** revealed a slight but statistically significant elongation of the Pd–N and Pd–C25 bonds in the latter complex (naturally, the Pd–S bond is also longer than the Pd–Cl bond in **8**[24]). Furthermore, the formation of a second chelate ring in **10** results in an opening of the P–Pd–S/Cl angle and a closure of the adjacent N–Pd–S/Cl angle by approximately 5°, whereas the remaining interligand angles remain practically unchanged. The dihedral angle of the {Pd,P,S} and {Pd,N,C25} planes associated with the chelate rings in **10** is 11.94(7)°, which is somewhat smaller than in the parent chloride complex.

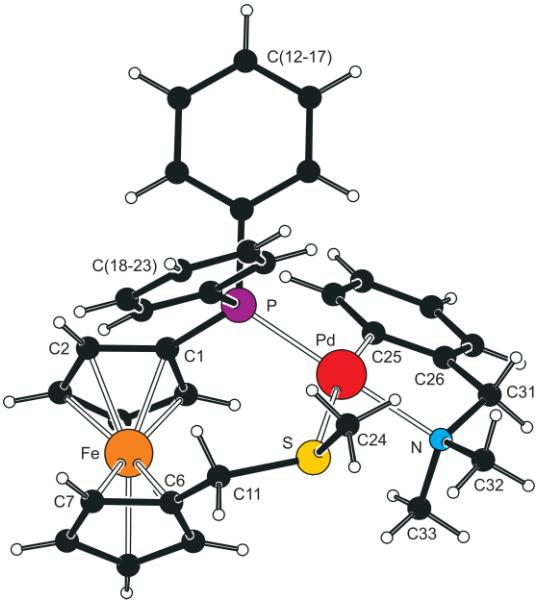


Figure 4. PLATON plot of the molecular structure of **10**·3/2$C_2H_4Cl_2$. The perchlorate anion and the solvent have been omitted for clarity.

Because of a simultaneous coordination of both attached donor moieties, the ferrocene unit in **10** adopts a synclinal eclipsed conformation ($\tau \approx 2°$) and is slightly tilted (by approximately 5°). Additionally, the formation of the P,S-chelate ring results in a displacement of the pivotal atom C11 by 0.208(2) Å from the plane of its parent cyclopentadienyl ring and twisting of the CH_2SMe pendant arm, as shown by the angles between the plane of the cyclopentadienyl ring C(6–10) and the S–C11 bond, which are 17.1(1)° in **10**·3/2$C_2H_4Cl_2$ and 65.1(1)° in **8**·AcOEt.

The presence of a coordinated water molecule in the structure of complex **11** (Figure 5, parameters in Table 3) reduces the mutual tilting of the coordination half-planes {Pd,P,O1W} and {Pd,N,C25} to 9.75(8)°. However, the range of the interligand angles in **11** is the largest in the entire set of $(L^{NC})Pd^{II}$ complexes reported in this paper. The Pd–N and Pd–C bonds in **11** are shorter than those in its precursor **9** and the other cationic complex **10**, whereas the length of the Pd–OH_2 bond is similar to the Pd–OH_2 distance determined for an analogous cationic complex with a PPh_2-substituted calix[4]arene ligand [2.171(2) or 2.186(2) Å depending on solvation].[25,26] The 1,1′-disubsti-

tuted ferrocene unit in **11** has an open conformation, similar to that in compound **9**, and its methoxymethyl substituent extends away from the ferrocene unit and the phosphane moiety. In the crystal, the coordinated water molecule forms O–H···O hydrogen bonds with a pair of proximal perchlorate anions, which are involved in similar interactions with the water molecule in a complex molecule related by crystallographic inversion (O1W–H1W···O2 and O1W–H2W···O4). These interactions result in the formation of closed centrosymmetric aggregates $[(L^{NC})Pd(H_2O)(\mathbf{2}\text{-}\kappa P)]_2(ClO_4)_2$ (Figure 6).

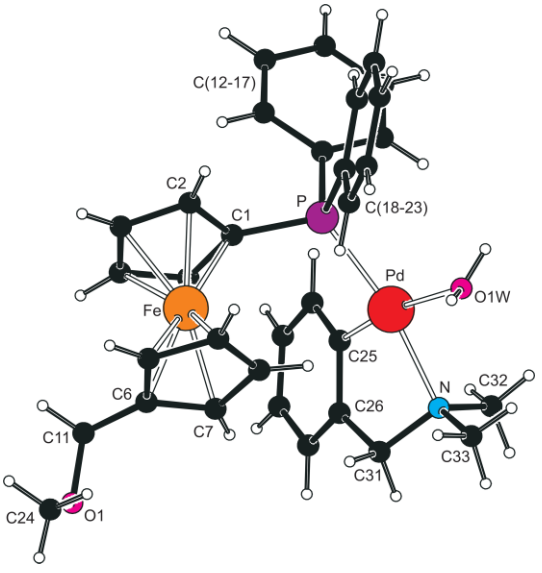


Figure 5. PLATON plot of the cation in the structure of **11**.

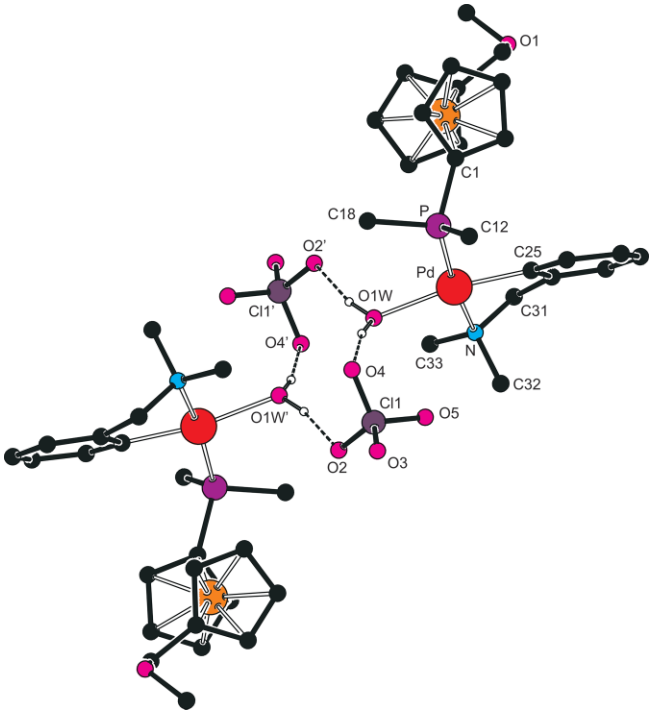


Figure 6. Hydrogen-bonding interactions in the structure of complex **11**. For clarity, only the pivotal atoms of the phosphorus-bonded phenyl groups are shown. The hydrogen bonds are indicated by dashed lines. Hydrogen-bond parameters: O1W···O2 2.859(2) Å (angle at H1W 160°), O1W···O4 2.802(2) Å (angle at H2W 168°). The atoms labeled with primes are generated by inversion operation.

Conclusions

The preparation of phosphanylferrocene thioether **3** described in this paper highlights the synthetic potential of the easily accessible adduct **5**[6,27] as a stable, *P*-protected precursor of new unsymmetric phosphanylferrocene donors. Furthermore, the study of the coordination of the congeneric ligands **2** and **3** to Pd^{II} with various supporting ligands revealed a remarkable difference in the coordination properties of these donors and the impact of the introduced methylene spacer. Obviously, the introduction of the methylene linking group considerably increases the flexibility of the 1′-functionalized phosphanylferrocene ligands, which may, in turn, decrease their tendency to form stable chelate complexes. For instance, compound **A** (Scheme 1) reacts with a $PdCl_2$ precursor (in a Pd/P ratio of 1:1) to afford the stable chelate complex $[PdCl_2(\mathbf{A}\text{-}\kappa^2 O,P)]$,[7] whereas ligand **2** only provides the chloride-bridged dimer $[Pd(\mu\text{-}Cl)Cl(\mathbf{2}\text{-}\kappa P)]_2$.[6] This trend is confirmed by the formation of the aqua complex **11** rather than a bis(chelate) cation when removing the Pd-bonded chloride from **9**. The replacement of the hard donor oxygen atom with the much softer sulfur atom apparently circumvents this problem (in the case of soft Pd^{II}), albeit only partly. As exemplified by the formation of a mixture of products from the reaction of $[PdCl_2(MeCN)_2]$ and **3** (in a ratio of 1:1), ligand **3** does not coordinate as a P,S-chelating donor preferentially, although it may form stable chelate rings, for example, in compound **10**, under appropriate conditions.

Experimental Section

Materials and Methods: All manipulations were carried out under argon using standard Schlenk techniques. Compounds **2**, **5**,[6] and $[(L^{NC})Pd(\mu\text{-}Cl)]_2$[28] were prepared according to literature methods. All other chemicals were purchased from commercial suppliers (Sigma–Aldrich and Alfa-Aesar) and used without any additional purification. Toluene was dried with sodium metal and distilled under argon. Unless stated otherwise, chloroform was dried with anhydrous potassium carbonate and distilled. Tetrahydrofuran was dried by using a PureSolv MD5 solvent purification system (Innovative Technology, USA). Solvents for crystallizations and chromatography were used as received (analytical grade, Lach-Ner, Czech Republic). NMR spectra were recorded at 25 °C with 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 given relative to internal $SiMe_4$ (^1H and ^{13}C) and external 85 % aqueous H_3PO_4 (^{31}P), all set to 0 ppm. In addition to the standard notation of the multiplicity of the NMR signals, vt and vq are used to denote virtual triplets and quartets,which arise from the CH_2- and phosphane-substituted cyclopentadienyl rings, respectively. IR spectra were measured with an FTIR Nicolet Magna 760 spectrometer in the range 400–4000 cm^{-1}. Electrospray ionization (ESI) mass spectra were recorded with a Bruker Esquire 3000 spectrometer for samples dissolved in HPLC-grade methanol. Elemental analyses were performed by using a PE 2400 Series II CHNS/O Elemental Analyzer

(Perkin–Elmer). The amount of residual solvent (if present) was corroborated by NMR analysis.

Synthesis of 1-(Diphenylphosphanyl)-1′-[(methylthio)methyl]-ferrocene–Borane (1:1) (4): Methyl iodide (71 mg, 0.50 mmol) was added to a solution of *N*,*N*,*N*′,*N*′-tetramethylthiourea (100 mg, 0.25 mmol) in dry THF (3 mL), and the resulting mixture was stirred under argon for 1 h, which resulted in a white precipitate {presumably $[(Me_2N)_2SMe]I$}. The borane adduct **5** (100 mg, 0.25 mmol) and sodium hydride (30 mg of a 60 % suspension in mineral oil, 0.75 mmol) were added successively to the reaction mixture, continuing stirring for another 1 h. Then the reaction was terminated by adding water, and the resulting mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$, and the solvents evaporated. Subsequent purification by column chromatography (silica gel, toluene) afforded pure compound **4** as an orange solid. Yield: 70 mg (63 %). ^{1}H NMR ($CDCl_3$): δ = 0.75–1.75 (br. m, 3 H, BH_3), 1.96 (s, 3 H, SMe), 3.11 (s, 2 H, SCH_2), 4.04 (vt, J' = 1.8 Hz, 2 H, fc), 4.16 (vt, J' = 1.9 Hz, 2 H, fc), 4.36 (vq, J' = 1.9 Hz, 2 H, fc), 4.50 (d of vt, J' = 1.1, 1.8 Hz, 2 H, fc), 7.38–7.50 (m, 6 H, PPh_2), 7.55–7.63 (m, 4 H, PPh_2) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 15.49 (s, SMe), 33.88 (s, SCH_2), 69.09 (d, $^1J_{PC}$ = 6 Hz, C-P of fc), 69.80 (s, CH of fc), 70.45 (s, CH of fc), 72.58 (d, J_{PC} = 7 Hz, CH of fc), 73.56 (d, J_{PC} = 10 Hz, CH of fc), 86.59 (s, *C*-CH_2 of fc), 128.43 (d, J_{PC} = 10 Hz, CH of PPh_2), 130.90 (d, $^4J_{PC}$ = 2 Hz, CH_{para} of PPh_2), 131.29 (d, $^1J_{PC}$ = 59 Hz, C_{ipso} of PPh_2), 132.63 (d, J_{PC} = 10 Hz, CH of PPh_2) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 16.4 (br. d) ppm. MS (ESI+): *m*/*z* = 467 $[M + H]^+$, 430 $[M - BH_3]^+$. $C_{24}H_{26}BFeP$ (444.2): calcd. C 64.90, H 5.90; found C 64.97, H 5.82.

Synthesis of 1-(Diphenylphosphanyl)-1′-[(methylthio)methyl]-ferrocene (3): Adduct **4** (222 mg, 0.50 mmol) and 1,4-diazabicyclo[2.2.2]octane (dabco; 60 mg, 0.53 mmol) were dissolved in anhydrous toluene (10 mL) in a reaction flask with a stirring bar. The reaction vessel was flushed with argon, sealed with a rubber septum, and transferred into an oil bath maintained at 60 °C. The reaction mixture was stirred at this temperature for 18 h and then cooled to room temperature and concentrated under reduced pressure, leaving a brown residue, which was purified by column chromatography (silica gel, diethyl ether/hexane, 1:1). A single orange band was collected and concentrated to afford compound **3** as a dark-amber oil that gradually solidified. Yield: 212 mg (quant.). ^{1}H NMR ($CDCl_3$): δ = 1.97 (s, 3 H, SMe), 3.18 (s, 2 H, SCH_2), 4.02 (vt, J' = 1.9 Hz, 2 H, fc), 4.06 (vq, J' = 1.8 Hz, 2 H, fc), 4.10 (vt, J' = 1.9 Hz, 2 H, fc), 4.35 (vt, J' = 1.8 Hz, 2 H, fc), 7.28–7.40 (m, 10 H, PPh_2) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 15.47 (s, SMe), 33.25 (s, SCH_2), 69.19 (s, CH of fc), 69.77 (s, CH of fc), 71.55 (d, J_{PC} = 4 Hz, CH of fc), 73.62 (d, J_{PC} = 15 Hz, CH of fc), 76.12 (d, $^1J_{PC}$ = 6 Hz, C-P of fc), 85.65 (s, *C*-CH_2 of fc), 128.14 (d, J_{PC} = 7 Hz, CH_{meta} of PPh_2), 128.51 (s, CH_{para} of PPh_2), 133.50 (d, J_{PC} = 19 Hz, CH_{ortho} of PPh_2), 139.06 (d, $^1J_{PC}$ = 9 Hz, C_{ipso} of PPh_2) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = –16.3 (s) ppm. MS (ESI+): *m*/*z* = 431 $[M + H]^+$. $C_{24}H_{23}FeP$ (430.3): calcd. C 66.99, H 5.39; found C 67.00, H 5.37.

Reaction of $[PdCl_2(MeCN)_2]$ with 1 equiv. of 3 and Isolation of Complex 6: Ligand **3** (22.0 mg, 0.05 mmol) and $[PdCl_2(MeCN)_2]$ (13.1 mg, 0.05 mmol) were dissolved in chloroform (2 mL). The mixture was stirred at room temperature for 30 min and then layered successively with *tert*-butyl methyl ether (5 mL) and hexane (5 mL). Crystallization by liquid-phase diffusion over several days afforded a crystalline solid, which was isolated by suction, washed with pentane, and dried under vacuum. Yield: 30.0 mg (quant). ^{1}H NMR ($CDCl_3$), selected resonances: δ = 2.45 (d, J_{PH} = 4.6 Hz, SMe), 2.66 (d, J_{PH} = 0.8 Hz, SMe) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 24.5 (s), 29.9 (s) ppm. $C_{48}H_{46}Cl_4Fe_2P_2Pd_2S_2$ (1215.3): calcd. C 47.44, H 3.82; found C 47.31, H 3.84.

Synthesis of $[PdCl_2(3\text{-}\kappa P)_2]$ (7): $[PdCl_2(MeCN)_2]$ (6.7 mg, 25 μmol) and ligand **3** (21.5 mg, 50 μmol) were mixed in chloroform (1 mL), and the resulting burgundy-red solution was stirred at room temperature for 90 min. Then the reaction mixture was filtered through a PTFE syringe filter (pore size 0.45 μm), and the filtrate was diluted with chloroform (1 mL) and then layered with *tert*-butyl methyl ether and hexane (5 mL each). Crystallization by liquid-phase diffusion furnished complex **7** as deep-red crystals, which were filtered off, washed with hexane and pentane, and, finally, dried under vacuum. Yield: 21.6 mg (83 %). ^{1}H NMR ($CDCl_3$): δ = 2.01 (s, 3 H, SMe), 3.42 (s, 2 H, SCH_2), 4.37 (m, 4 H, fc), 4.51 (vt, J' = 1.8 Hz, 2 H, fc), 4.53 (br. vt, J' = 1.8 Hz, 2 H, fc), 7.35–7.45 (m, 6 H, PPh_2), 7.61–7.67 (m, 4 H, PPh_2) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 15.64 (s, SCH_3), 33.44 (s, SCH_2), 70.36 (s, CH of fc), 71.11 (s, CH in fc), 71.67 (app. t, J' = 27 Hz, C-P of fc), 72.68 (app. t, J' = 4 Hz, CH of fc), 76.05 (app. t, J' = 5 Hz, CH of fc), 86.60 (s, *C*-CH_2 of fc), 127.72 (app. t, J' = 5 Hz, CH of PPh_2), 130.25 (s, CH_{para} of PPh_2), 131.34 (app. t, J' = 25 Hz, C_{ipso} of PPh_2), 134.16 (app. t, J' = 6 Hz, CH of PPh_2) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 15.7 (s) ppm. IR (Nujol): $\tilde{\nu}_{max}$ = 3056 (w), 2725 (w), 2672 (w), 1668 (br., vw), 1327 (vw), 1305 (m), 1244 (m), 1223 (vw), 1194 (w), 1185 (w), 1168 (m), 1131 (w), 1101 (m), 1093 (m), 1072 (w), 1061 (w), 1042 (m), 1034 (m), 1024 (m), 999 (w), 978 (w), 964 (vw), 927 (w), 917 (vw), 890 (w), 873 (w), 848 (w), 836 (w), 831 (w), 815 (s), 745 (s), 708 (m), 693 (vs), 624 (w), 544 (m), 517 (m), 506 (s), 496 (s), 469 (m), 458 (w), 442 (w) cm^{-1}. MS (ESI+): *m*/*z* = 571 $[M - Cl - \mathbf{3}]^+$, 1001 $[M - Cl]^+$. $C_{48}H_{46}Cl_2Fe_2P_2PdS_2 \cdot 0.25CHCl_3$ (1067.8): calcd. C 54.27, H 4.37; found C 54.21, H 4.33.

Synthesis of $[(L^{NC})PdCl(3\text{-}\kappa P)]$ (8): The dimer $[(L^{NC})Pd(\mu\text{-}Cl)]_2$ (13.8 mg, 25 μmol) and compound **3** (21.5 mg, 50 μmol) were dissolved in chloroform (1 mL), and the resulting solution was stirred at room temperature for 90 min and then concentrated under vacuum. The residue was dissolved in ethyl acetate (1 mL) and the solution filtered through a PTFE syringe filter (pore size 0.45 μm). The filtrate was diluted with ethyl acetate (1 mL) and layered with hexane (10 mL). Crystallization by liquid-phase diffusion afforded complex **8** in the form of orange crystals, which were filtered off, washed with hexane and pentane, and dried under vacuum. Yield: 26.1 mg (74 %). ^{1}H NMR ($CDCl_3$): δ = 2.02 (s, 3 H, SMe), 2.84 (d, $^4J_{PH}$ = 2.8 Hz, 6 H, NMe_2), 3.50 (s, 2 H, SCH_2), 4.12 (br. d, $^4J_{PH}$ = 2.4 Hz, 2 H, NCH_2), 4.32 (vtd, J' = 1.9, 1.0 Hz, 2 H, fc), 4.36 (vq, J' = 2.0 Hz, 2 H, fc), 4.43 (vt, J' = 1.9 Hz, 2 H, fc), 4.54 (vt, J' = 1.9 Hz, 2 H, fc), 6.29 (ddd, *J* = 7.8, 6.4, 1.3 Hz, 1 H, C_6H_4), 6.41 (br. td, *J* = 7.6, 1.5 Hz, 1 H, C_6H_4), 6.84 (td, *J* = 7.3, 1.2 Hz, 1 H, C_6H_4), 7.02 (dd, *J* = 7.4, 1.6 Hz, 1 H, C_6H_4), 7.30–7.35 (m, 4 H, PPh_2), 7.38–7.44 (m, 2 H, PPh_2), 7.53–7.59 (m, 4 H, PPh_2) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 15.48 (s, SMe), 33.37 (s, SCH_2), 50.15 (d, $^3J_{PC}$ = 3 Hz, NMe_2), 70.45 (s, CH of fc), 71.19 (s, CH of fc), 72.59 (d, J_{PC} = 7 Hz, CH of fc), 73.53 (d, $^1J_{PC}$ = 60 Hz, C-P of fc), 73.62 (d, $^3J_{PC}$ = 3 Hz, NCH_2), 76.02 (d, J_{PC} = 10 Hz, CH of fc), 86.42 (s, *C*-CH_2 of fc), 122.49 (s, CH of C_6H_4), 123.72 (s, CH of C_6H_4), 124.82 (d, J_{PC} = 5 Hz, CH of C_6H_4), 127.84 (d, J_{PC} = 11 Hz, CH of PPh_2), 130.46 (d, $^4J_{PC}$ = 2 Hz, CH_{para} of PPh_2), 131.77 (d, $^1J_{PC}$ = 49 Hz, C_{ipso} of PPh_2), 134.36 (d, J_{PC} = 12 Hz, CH of PPh_2), 138.46 (d, J_{PC} = 11 Hz, CH of C_6H_4), 148.24 (d, J_{PC} = 2 Hz, C_{ipso} of C_6H_4), 152.13 (s, C_{ipso} of C_6H_4) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 33.0 (s) ppm. IR (Nujol): $\tilde{\nu}_{max}$ = 3042 (w), 2724 (w), 2669 (w), 1733 (vs), 1579 (m), 1407 (vw), 1396 (w), 1304 (m), 1270 (vw), 1248 (m), 1200 (vw), 1182 (w), 1166 (m), 1100 (m), 1072 (vw), 1060 (w), 1042 (m), 1026 (m), 993 (m), 969 (w), 930 (w), 890 (vw), 865 (w), 854 (m), 846 (m), 817 (m), 752 (m), 741 (s), 708 (m), 697 (s), 654 (vw), 627 (m), 617 (vw), 605 (vw), 546 (m), 526 (m), 510 (vs), 478 (m), 462 (m), 447 (w), 433 (w), 424 (w) cm^{-1}. MS (ESI+): *m*/*z* = 670 $[M - Cl]^+$.

$C_{33}H_{35}ClFeNPPdS$ (706.4): calcd. C 56.11, H 4.99, N 1.98; found C 55.76, H 5.03, N 1.84.

Synthesis of [(L^{NC})PdCl(2-κ*P*)] (9): Compounds [(L^{NC})Pd(μ-Cl)]$_2$ (13.8 mg, 25 μmol) and **2** (20.7 mg, 50 μmol) were dissolved in chloroform (1 mL) in an argon-flushed reaction flask, and the resulting solution was stirred for 90 min and then concentrated under vacuum. The resulting orange residue was dissolved in ethyl acetate (1.5 mL) and the solution filtered through a PTFE syringe filter (pore size 0.45 μm) into a test tube. The filtrate was layered with hexane (10 mL) and set aside for crystallization. The orange crystals, which formed over several days, were filtered off, washed with hexane and pentane, and dried under vacuum. Yield: 30.2 mg (86 %). ^{1}H NMR ($CDCl_3$): δ = 2.85 (d, $^4J_{PH}$ = 2.8 Hz, 6 H, NMe_2), 3.29 (s, 3 H, OMe), 4.12 (br. d, $^4J_{PH}$ = 2.3 Hz, 2 H, NCH_2), 4.21 (s, 2 H, OCH_2), 4.31 (vtd, *J* = 1.9, 1.0 Hz, 2 H, fc), 4.37 (vq, *J′* = 2.0 Hz, 2 H, fc), 4.48 (vt, *J′* = 1.9 Hz, 2 H, fc), 4.60 (vt, *J′* = 1.9 Hz, 2 H, fc), 6.29 (ddd, *J* = 7.8, 6.5, 1.2 Hz, 1 H, C_6H_4), 6.41 (br. td, *J* = 7.5, 1.6 Hz, 1 H, C_6H_4), 6.84 (td, *J* = 7.3, 1.1 Hz, 1 H, C_6H_4), 7.02 (dd, *J* = 7.4, 1.6 Hz, 1 H, C_6H_4), 7.30–7.35 (m, 4 H, PPh_2), 7.37–7.43 (m, 2 H, PPh_2), 7.55–7.57 (m, 4 H, PPh_2) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 50.12 (d, $^3J_{PC}$ = 3 Hz, NMe_2), 57.77 (s, OMe), 70.35 (s, OCH_2), 71.06 (s, CH of fc), 71.83 (s, CH of fc), 72.12 (d, J_{PC} = 7 Hz, CH of fc), 73.62 (d, $^3J_{PC}$ = 3 Hz, NCH_2), 73.64 (d, $^1J_{PC}$ = 60 Hz, C-P of fc), 75.80 (d, J_{PC} = 10 Hz, CH of fc), 84.50 (s, *C*-CH_2 of fc), 122.49 (s, CH of C_6H_4), 123.71 (s, CH of C_6H_4), 124.84 (d, J_{PC} = 6 Hz, CH of C_6H_4), 127.85 (d, J_{PC} = 11 Hz, CH of PPh_2), 130.48 (d, $^4J_{PC}$ = 2 Hz, CH_{para} of PPh_2), 131.69 (d, $^1J_{PC}$ = 50 Hz, C_{ipso} of PPh_2), 134.37 (d, J_{PC} = 12 Hz, CH of PPh_2), 138.46 (d, J_{PC} = 11 Hz, CH of C_6H_4), 148.24 (d, J_{PC} = 2 Hz, C_{ipso} of C_6H_4), 152.22 (s, C_{ipso} of C_6H_4) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 33.0 (s) ppm. IR (Nujol): $\tilde{\nu}_{max}$ = 3067 (w), 3044 (w), 1734 (m), 1580 (w), 1305 (w), 1248 (m), 1236 (w), 1201 (vw), 1184 (w), 1167 (m), 1097 (m), 1083 (s), 1058 (vw), 1041 (m), 1028 (m), 993 (w), 970 (w), 931 (vw), 896 (w), 854 (m), 846 (m), 819 (m), 755 (m), 748 (m), 739 (s), 709 (m), 697 (m), 628 (w), 545 (m), 527 (m), 516 (s), 479 (m), 435 (vw) cm^{-1}. MS (ESI+): *m*/*z* = 654 $[M - Cl]^+$. $C_{33}H_{35}ClFeNOPPd{\cdot}0.1C_6H_{14}$ (698.9): calcd. C 57.74, H 5.25, N 2.00; found C 57.75, H 5.52, N 1.84.

Synthesis of [(L^{NC})Pd(3-κ^2*P*,*S*)]ClO_4 (10): The dimeric precursor [(L^{NC})Pd(μ-Cl)]$_2$ (13.8 mg, 25 μmol) and ligand **3** (21.5 mg, 50 μmol) were allowed to react in chloroform (1 mL) for 90 min, as described above. Then, the reaction solution was poured onto solid $AgClO_4$ (10.4 mg, 50 μmol), whereupon a greyish precipitate (AgCl) separated. After stirring for another 30 min, the reaction mixture was filtered through a PTFE syringe filter (pore size 0.45 μm), and the filtrate was concentrated. The residue was dissolved in 1,2-dichloroethane (2 mL), and the solution was layered with 1,2-dichloroethane/*tert*-butyl methyl ether (1:1; 2 mL) and pure *tert*-butyl methyl ether (11 mL). The mixture was set aside for crystallization by liquid-phase diffusion. The yellow crystals that formed after several days were filtered off, washed with *tert*-butyl methyl ether, and dried under vacuum. Yield: 21.7 mg (56 %). ^{1}H NMR ($CDCl_3$): δ = 2.43 (s, 3 H, SMe), 2.89 (d, $^4J_{PH}$ = 2.9 Hz, 6 H, NMe_2), 3.26 (s, 2 H, SCH_2), 4.31 (br. d, $^4J_{PH}$ = 1.8 Hz, 2 H, NCH_2), 4.37 (vt, *J′* = 1.9 Hz, 2 H, fc), 4.51 (vt, *J′* = 1.8 Hz, 2 H, fc), 4.65 (br. m, 2 H, fc), 4.69 (br. m, 2 H, fc), 6.24 (ddd, J_1 = J_2 = 7.5, J_3 = 1.1 Hz, 1 H, C_6H_4), 6.31 (br. t, *J* = 7.5 Hz, 1 H, C_6H_4), 6.81 (br. t, *J* = 7.3 Hz, 1 H, C_6H_4), 7.02 (dd, *J* = 7.4, 1.5 Hz, 1 H, C_6H_4), 7.36–7.44 (br. m, 6 H, PPh_2), 7.70–7.78 (br. m, 4 H, PPh_2) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 20.15 (s, SMe), 34.48 (s, SCH_2), 50.47 (d, $^3J_{PC}$ = 2 Hz, NMe_2), 69.69 (d, $^1J_{PC}$ = 59 Hz, C-P of fc), 69.73 (s, CH of fc), 70.36 (s, CH of fc), 73.01 (d, J_{PC} = 8 Hz, CH of fc), 73.61 (d, $^3J_{PC}$ = 3 Hz, NCH_2), 76.55 (d, J_{PC} = 12 Hz, CH of fc), 82.77 (s, *C*-CH_2 of fc), 123.19 (s, CH of C_6H_4), 125.17 (s, CH of C_6H_4), 125.51 (d, J_{PC} = 6 Hz, CH of C_6H_4), 128.80 (d, J_{PC} = 11 Hz, CH of PPh_2), 131.23 (d, $^4J_{PC}$ = 2 Hz, CH_{para} of PPh_2), 131.25 (d, $^1J_{PC}$ = 52 Hz, C_{ipso} of PPh_2), 133.33 (d, J_{PC} = 12 Hz, CH of PPh_2), 137.72 (d, J_{PC} = 13 Hz, CH of C_6H_4), 146.81 (d, J_{PC} = 2 Hz, C_{ipso} of C_6H_4), 152.07 (br. s, C_{ipso} of C_6H_4) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 33.3 (s) ppm. IR (Nujol): $\tilde{\nu}_{max}$ = 3049 (w), 2721 (w), 2671 (w), 1579 (m), 1406 (w), 1301 (w), 1276 (w), 1235 (vw), 1200 (w), 1184 (w), 1165 (m), 1093 (br. vs), 1057 (m), 1043 (w), 1033 (m), 1023 (m), 995 (m), 977 (m), 934 (w), 923 (w), 888 (w), 865 (w), 848 (m), 823 (m), 756 (m), 746 (s), 702 (s), 623 (m), 546 (w), 530 (s), 516 (m), 499 (m), 486 (m), 452 (m), 436 (w) cm^{-1}. MS (ESI+): *m*/*z* = 670 $[(L^{NC})Pd(\mathbf{3})]^+$. $C_{33}H_{35}ClFeNO_4PPdS$ (770.4): calcd. C 51.45, H 4.58, N 1.82; found C 51.20, H 4.57, N 1.65.

Synthesis of [(L^{NC})Pd(2-κ*P*)(H_2O)]ClO_4 (11): Complex **11** was prepared in unpurified reagent-grade chloroform. The dimer [(L^{NC})Pd(μ-Cl)]$_2$ (55.2 mg, 0.10 mmol) and compound **2** (82.8 mg, 0.20 mmol) were dissolved in chloroform (3 mL), and the solution was stirred for 90 min. The thus formed solution of complex **9** was added to solid silver(I) perchlorate (49.8 mg, 0.24 mmol; 2 mL of chloroform was used to wash the reaction flask) and the resulting mixture was stirred for another 30 min (a greyish precipitate separated immediately after the addition). The reaction mixture was filtered through a PTFE syringe filter (pore size 0.45 μm; an additional 2 mL of chloroform was used to rinse the reaction flask), and the filtrate was concentrated under vacuum, leaving a greenish residue, which was taken up with ethyl acetate (5 + 2 mL) by sonication in an ultrasound bath. The extract was filtered through the syringe filter and carefully layered with a mixture of ethyl acetate/hexane (1:1; 3 mL) and then with pure hexane (10 mL). Crystallization by liquid-phase diffusion provided green-brown crystals of the product, which were recrystallized once again as described above. The resulting yellow crystals of **11** were filtered off, washed with hexane and pentane, and dried under vacuum. Yield: 40.4 mg (30 %). ^{1}H NMR ($CDCl_3$): δ = 2.86 (d, $^4J_{PH}$ = 2.6 Hz, 6 H, NMe_2), 3.29 (s, 3 H, OMe), 3.98 (br. s, 2 H, fc), 4.06 (br. s, 2 H, OCH_2), 4.09 (br. d, J_{PH} = 1.7 Hz, 2 H, NCH_2), 4.36 (br. s, 2 H, fc), 4.42 (br. s, 2 H, fc), 4.49 (br. s, 2 H, fc), 6.34 (br. t, *J* = 7.0 Hz, 1 H, C_6H_4), 6.48 (br. t, *J* = 7.4 Hz, 1 H, C_6H_4), 6.92 (br. t, *J* = 7.2 Hz, 1 H, C_6H_4), 7.03 (br. dd, *J* = 7.4, 1.5 Hz, 1 H, C_6H_4), 7.39–7.45 (m, 4 H, PPh_2), 7.47–7.53 (m, 2 H, PPh_2), 7.59–7.66 (m, 4 H, PPh_2) ppm; please note: the signal due to coordinated water could not be identified. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 49.75 (d, $^3J_{PC}$ = 2 Hz, NMe_2), 57.97 (s, OMe), 70.06 (s, OCH_2), 70.72 (s, CH of fc), 71.29 (s, CH of fc), 71.99 (s, NCH_2), 72.60 (d, J_{PC} = 7 Hz, CH of fc), 74.80 (d, J_{PC} = 10 Hz, CH of fc), 85.05 (s, *C*-CH_2 of fc), 123.53 (s, CH of C_6H_4), 125.08 (s, CH of C_6H_4), 125.50 (d, J_{PC} = 6 Hz, CH of C_6H_4), 128.39 (d, J_{PC} = 11 Hz, CH of PPh_2), 129.34 (d, $^1J_{PC}$ = 50 Hz, C_{ipso} of PPh_2), 131.26 (s, CH_{para} of PPh_2), 134.36 (d, J_{PC} = 12 Hz, CH of PPh_2), 137.83 (d, J_{PC} = 12 Hz, CH of C_6H_4), 141.71 (br. s, C_{ipso} of C_6H_4), 147.78 (d, J_{PC} = 2 Hz, C_{ipso} of C_6H_4) ppm; the signal of *C*-P of fc was not found, presumably due to overlapping signals. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 30.4 (s) ppm. IR (Nujol): $\tilde{\nu}_{max}$ = 3374 (br., m), 3185 (br., w), 1582 (w), 1305 (w), 1234 (w), 1167 (m), 1129 (s), 1117 (s), 1097 (vs), 1085 (vs), 1064 (s), 1054 (s), 1041 (m), 1027 (m), 996 (m), 970 (m), 926 (w), 899 (w), 874 (vw), 842 (m), 820 (w), 756 (m), 747 (m), 710 (w), 695 (m), 660 (vw), 625 (m), 549 (m), 527 (m), 513 (s), 488 (m), 481 (m), 450 (w), 438 (w) cm^{-1}. MS (ESI+): *m*/*z* = 654 $[(L^{NC})Pd(\mathbf{2})]^+$. $C_{33}H_{37}ClFeNO_6PPd$ (772.3): calcd. C 51.32, H 4.83, N 1.81; found C 51.43, H 4.64, N 1.83.

Reactions of 10 and 11 with Bu_4NCl: Complex **10** (10 μmol) was dissolved in $CDCl_3$ (0.5 mL) by sonication in an ultrasound bath. Solid tetrabutylammonium chloride (3.0 mg, 10 μmol) was added, and the mixture was stirred for 30 min. After filtration through a syringe filter (PTFE, pore size: 0.45 μm), the mixture was analyzed by NMR spectroscopy, which confirmed the clean formation of com-

pound **8**. Under similar conditions, complex **11** was converted back into the chloride complex **9**.

X-ray Crystallography: The diffraction data (completeness ≥99.8 %, θ_{max} = 27.5°) were collected by using a Nonius-KappaCCD diffractometer equipped with a Bruker Apex-II image plate detector (**6**·3CHCl$_3$) or a Bruker D8 VENTURE Duo diffractometer equipped with a PHOTON100 detector and an IμS micro-focus X-ray tube (all other structures), both equipped with a Cryostream Cooler (Oxford Cryosystems). Mo-K_α radiation (λ = 0.71073 Å) was used in all cases. The structures were solved by direct methods (SHELXS-97[29]) and refined by a full-matrix least-squares procedure based on F^2 using SHELXL-2014.[30] The non-hydrogen atoms were refined by using anisotropic displacement parameters. All hydrogen atoms were included in their theoretical positions and refined by using the "riding model" with U_{iso}(H) set to a multiple of U_{eq} of their bonding atom. One of the *P*-phenyl substituents in the structure of **7** was disordered, and three of its carbon atoms had to be refined with two positions. Occupancies of the contributing orientations were refined to 31:69. In the case of **8**·AcOEt, the solvent molecules were heavily disordered around the inversion centers (two molecules of ethyl acetate per unit cell), and hence PLATON SQUEEZE[31] was used to compensate for this spread of electron density. Relevant crystallographic data, data collection details, and structure refinement parameters are presented in Table S1 in the Supporting Information. All geometric calculations were performed by using a recent version of the PLATON program,[32] which was also used to prepare the structural diagrams. CCDC 1569126 (for **6**·3CHCl$_3$), 1569127 (for **7**), 1569128 (for **8**·AcOEt), 1569129 (for **9**·1/2C$_6$H$_{14}$), 1569130 (for **10**·3/2C$_2$H$_4$Cl$_2$), and 1569131 (for **11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Supporting Information (see footnote on the first page of this article): NMR spectra and a summary of the crystallographic data.

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Keywords: Metallocenes · Phosphane ligands · Hybrid ligands · Palladium · Structure elucidation · X-ray diffraction

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