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Coordination and Catalytic Properties of a Semihomologous Dppf Congener, 1-(Diphenylphosphino)-1′-[(diphenylphosphino)methyl]ferrocene

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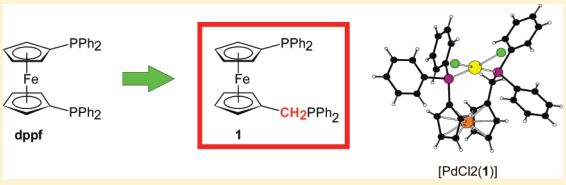
Supporting Information

ABSTRACT: Alcohol Ph_2PfcCH_2OH (**2**, fc = ferrocene-1,1′-diyl) reacts smoothly with Ph_2PH and Me_3SiCl/NaI in acetonitrile to give 1-(diphenylphosphino)-1′-[(diphenylphosphino)methyl]ferrocene (**1**), a new ferrocene diphosphine that fills the obvious gap left between the well-studied 1,1′-bis(diphenylphosphino)ferrocene (dppf) and its bis-spaced analogue, 1,1′-bis[(diphenylphosphino)methyl]ferrocene. The P-oxidized alcohols $Ph_2P(E)fcCH_2OH$ (E = O, **3**; S, **4**) behave similarly, yielding the corresponding semichalcogenides $Ph_2P(E)fcCH_2PPh_2$ (E = O, **5**; S, **6**). Exhaustive oxidations of **1** with hydrogen peroxide or elemental sulfur produce $Ph_2P(E)fcCH_2P(E)Ph_2$ (E = O, **7**; S, **8**), while similar oxidations of **5** and **6** afford the unsymmetric bis-chalcogenides $Ph_2P(O)fcCH_2P(S)Ph_2$ (**9**) and $Ph_2P(S)fcCH_2P(O)Ph_2$ (**10**), respectively. Compounds **1** and **3**−**10** were characterized by spectral methods, and the crystal structures of **3** and **8**−**10** were determined by single-crystal X-ray diffraction analysis. Compound **1** reacts with group 10 metal dichloride precursors to give the respective chelate complexes $[MCl_2(\mathbf{1}\text{-}\kappa^2P,P')]$ (**11**, M = Ni; **12**, M = Pd; and **13**, M = Pt). The Ni complex is paramagnetic and tetrahedral; the Pd and Pt complexes are expectedly square-planar and diamagnetic. Crystal structures of **11**−**13** reveal less acute ligand bite angles (P−M−P′) than those observed in the analogous dppf complexes, the difference being considerably larger for the Ni complex than in the less flexible square-planar complexes. Similarly to dppf and $fc(CH_2PPh_2)_2$, ligand **1** reacts with $[(L^{NC})PdCl]_2$ (L^{NC} = [2-(dimethylamino)methyl]phenyl) to give a diphosphine-bridged complex, $[(\mu\text{-}\mathbf{1})\{(L^{NC})PdCl\}_2]$ (**14**), whereas the reaction with the mononuclear precursor $[(L^{NC})Pd(MeCN)_2]ClO_4$ yields a mixture of isomeric bis-chelates $[(L^{NC})Pd(\mathbf{1}\text{-}\kappa^2P,P')]ClO_4$ (**15a**,**b**). Catalytic tests in Pd-catalyzed Suzuki−Miyaura cross-coupling and in Pd-catalyzed cyanation of aryl halides with $K_4[Fe(CN)_6]\cdot 3H_2O$ suggest that introduction of one methylene spacer group into the structure of dppf influences catalytic performance only marginally.



INTRODUCTION

Phosphinoferrocene ligands received considerable attention in the recent past owing to their versatile coordination properties and numerous successful applications in catalysis.[1,2] So far, there have been reported a vast number of ferrocene phosphines differing by the number and type of donor groups and also by the substitution patterns. The design of ferrocene ligands thus obviously follows two established major approaches: the design of new ligand types and modifications of known structures. Despite the enormous progress in the chemistry of ferrocene donors, the archetypal diphosphine, 1,1′-bis(diphenylphosphino)-ferrocene (dppf, Scheme 1),[3] still dominates the field, representing the most frequently studied and practically utilized ferrocene ligand, which also became a subject of extensive structural modifications.[1,4]

Typically, the modification of the basic dppf skeleton has been achieved through changing the substituents at the phosphorus atoms. Representative examples of such modified ligands are symmetrical dppf analogues bearing bulky and/or electron-donating substituents[4−7] or P-chiral phosphino moieties[4,8] (**B** in Scheme 2). In contrast, donor-unsymmetric derivatives in which *only one* PPh_2 group is replaced by another P-donor moiety remain very rare.[9,10] Another approach toward modification of the dppf molecule is (formally) represented by the attachment of an additional functional (donor) group and subsequent manipulations. A typical example of this approach is the vast family of donors related to BPPFA (Scheme 2)[1,2,11] and compounds having an additional donor group *directly* attached to the cyclopentadienyl ring (type **C** in Scheme 2).[1,2,12]

Recently, we[13] decided to go beyond the rather straightforward "substitution approach" outlined above and set about to modify bidentate ferrocene ligands by introducing a methylene spacer between *one* of the donor groups and the ferrocene moiety.[14] Such an approach has already proved warranted for many donors with organic backbones, typically resulting in changed coordination preferences, ligand bite angles, and catalytic performance.[15] This prompted us to prepare 1-(diphenylphosphino)-1′-[(diphenylphosphino)methyl]ferrocene (**1**, Scheme 1) as a unsymmetric dppf congener. This compound, whose donor-asymmetry

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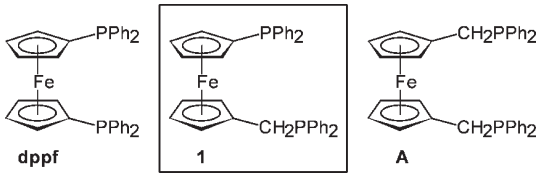
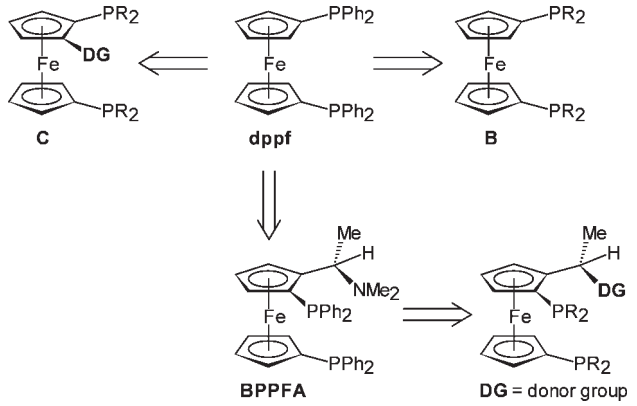
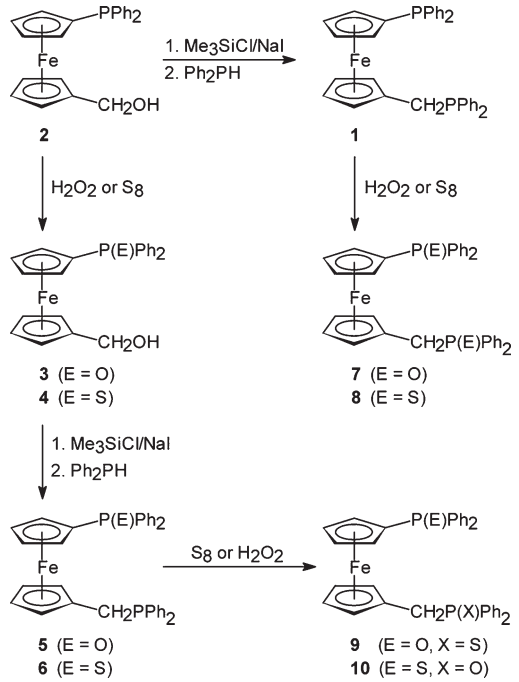
Scheme 1



Scheme 2. "Standard" Modifications of the Dppf Structure As Established in the Literature



Scheme 3. Synthesis of Diphosphane 1 and Its Chalcogenide Derivatives



arises exclusively from the presence of a single methylene spacer, has not yet been reported in the literature. It represents a missing link between dppf[3,16] and its doubly spaced counterpart, 1,1′-bis[(diphenylphosphino)methyl]ferrocene (**A** in Scheme 1).[17,18] In this contribution, we describe the preparation of diphosphine **1** and its several P-chalcogenide derivatives. Also reported are the results of our coordination and catalytic study aimed at a comparison of this new donor with the well-studied dppf.

RESULTS AND DISCUSSION

Synthesis of Diphosphine 1 and Chalcogenide Derivatives Thereof. Compound **1** was prepared by phosphinylation of 1′-(diphenylphosphino)ferrocenyl]methanol (**2**)[19] with an excess of Ph_2PH and chlorotrimethylsilane/sodium iodide[20,21] in acetonitrile (Scheme 3). The compound was isolated by column chromatography, resulting in a viscous, amber brown oil in good yield (typically ca. 75%). It is noteworthy that although the diphosphine is moderately air-sensitive, no special precautions are required in the isolation steps since the unreacted Ph_2PH prevents its oxidation during the aqueous workup and chromatography. Similar phosphinylation reactions with P-oxidized alcohols **3** and **4** furnished the corresponding semichalcogenides **5** and **6** (Scheme 3). Like any other diphosphine, compound **1** was readily oxidized with aqueous hydrogen peroxide or elemental sulfur, affording air-stable bis-chalcogenide derivatives **7** and **8**. Similar oxidations of semichalcogenides **5** and **6** led to a pair of mutually isomeric bis-chalcogenide derivatives **9** and **10** (Scheme 3).

The formulation of compounds **1** and **3**−**10** was established from NMR and mass spectra and further corroborated by X-ray diffraction analysis for compounds **3**[22] and **8**−**10**. In ^{1}H and ^{13}C NMR spectra, diphosphine **1** displays characteristic signals due to ferrocene-1,1′-diyl moiety and the PPh_2 substituents. Diagnostic resonances of the methylene linker are seen at δ_H 2.86 (singlet) and δ_C 29.55 (doublet, $^2J_{PC}$ = 15 Hz). The ^{31}P NMR spectrum of **1** corroborates the presence of two nonequivalent PPh_2 groups (δ_P −16.2 and −11.4). Oxidation of the phosphorus groups such as in chalcogenides derivatives **5**−**10** is reflected by characteristic shifts of the ^{31}P NMR signals to lower fields (to δ_P ca. 29 for P═O and 41−42 for P═S) and further by changes in the order of ^{13}C NMR signals of carbons within the PPh_2 groups and in the magnitude of the associated $^nJ_{PC}$ (n = 1−4) coupling constants.

The solid-state structures of **8**, **9**, and **10**·H_2O (Figures 1 and S2−4) show the usual ferrocene geometries with alike Fe−Cg distances and tilt angles less than ca. 2°. The P═O and P═S distances compare very well with those reported earlier for $dppfE_2$[23] and [Fe(η^5-C_5H_3-1-CO_2H-2-CH_2P(E)Ph_2)(η^5-C_5H_5)] (E = O, S).[21b] In all cases, the CH_2PPh_2 arm is directed away from the ferrocene unit (C6−C11−P2 = 110.8(1)−114.5(1)°) and the disubstituted ferrocene moiety assumes a conformation close to synclinal eclipsed (τ = 71° for **8**, 63° for **9**, and 72° for **10**; ideal value: 72°).

Preparation and Characterization of Group 10 Metal Complexes. For the sake of structural comparison, diphosphine **1** was subjected to complexation reactions for which *analogies* in the chemistry of dppf can be found using the catalytically relevant group 10 metals. Thus, reaction of **1** with one equivalent of [$NiCl_2$(dme)] (dme = 1,2-dimethoxyethane) in acetone/ethanol produced complex [$NiCl_2$(**1**-κ^2*P*,*P*′)] (**11**) as a dark green microcrystalline solid in a 95% isolated yield (Scheme 4).

Since solution NMR spectra suggested the complex to be paramagnetic, a solid sample of **11** was subjected to magnetic susceptibility measurements. The magnetic susceptibility (Figure 2) was found to be independent of the magnetic field (except for very low temperatures) as expected for a standard paramagnetic

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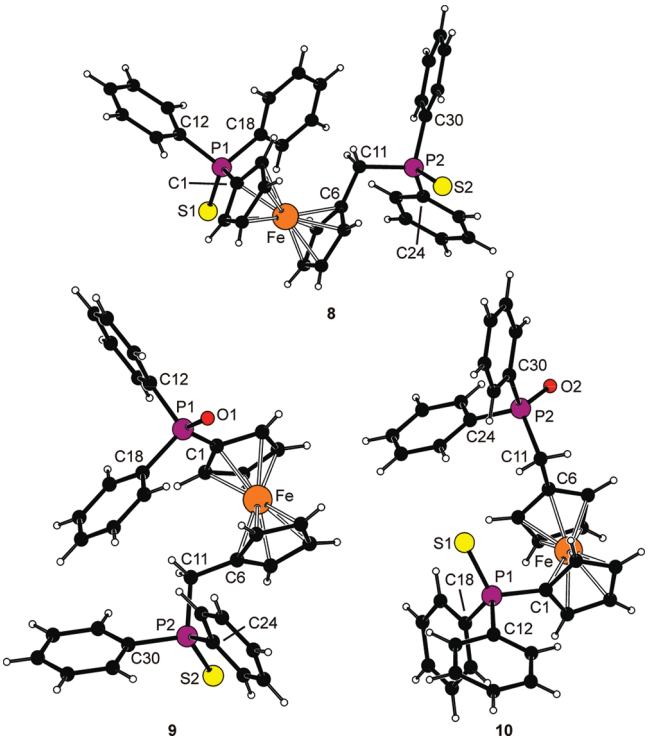


Figure 1. Views of the molecular structures of **8**, **9**, and **10**·H_2O (for conventional displacement ellipsoid plots, see Supporting Information). Selected distances and angles (in Å and deg): **8**, Fe−Cg1 1.638(1), Fe−Cg2 1.647(1), tilt 0.9(1); P1−S1 1.9509(8), P2−S2 1.9565(8); **9**, Fe−Cg1 1.6445(7), Fe−Cg2 1.6502(7), tilt 1.58(9); P1−O1 1.489(1), P2−S2 1.9460(5); **10**, Fe−Cg1 1.6418(8), Fe−Cg2 1.6504(8), tilt 1.6(1); P1−S1 1.9593(6), P2−O2 1.493(1). Definitions: Cg1 and Cg2 are the ring centroids of the rings Cp1 = C(1−5) and Cp2 = C(6−10), respectively; tilt = the dihedral angle of the Cp1 and Cp2 least-squares planes. Note: Atom labeling and plane definitions used for all complexes of ligand **1** are strictly analogous.

system.[24] The molar susceptibility data (within the field-independent interval) were evaluated using the Curie−Weiss law:

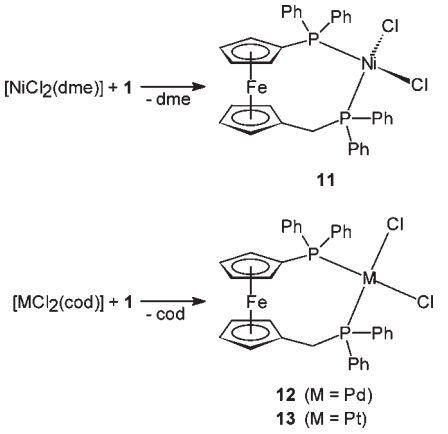
$$\chi_m = \frac{N_A g^2 \mu_B{}^2}{3k_B} \frac{S(S+1)}{T-\theta_p} = \frac{N_A \mu_{eff}{}^2}{3k_B} \frac{1}{T-\theta_p} = \frac{C}{T-\theta_p}$$

where N_A and k_B are the Avogadro and Boltzmann constants, respectively, θ_p is the paramagnetic Curie temperature, μ_{eff} is the effective magnetic moment, μ_B is the Bohr magneton, S is the spin quantum number, and C is the Curie constant.

Assuming that that there is no significant contribution of the spin−orbital interaction, the g factor was fixed to 2.00. The analysis then gave $\mu_{eff} = 3.05(4)\ \mu_B$ and $\theta_P = 1.5(5)$ K. The value of the effective magnetic moment is slightly higher than the theoretical one ($\mu_{eff}/\mu_B = [S(S+1)]^{1/2} \approx 2.82$ for $S = 1$) but corresponds well with the values reported for other Ni^{2+} complexes with tetrahedral coordination.[25] The paramagnetic Curie temperature indicates a weak ferromagnetic exchange interaction, which is in line with the field-dependent behavior of magnetic susceptibility at low temperatures (Figure 2).

Altogether, the data collected suggest **11** to be a "standard" tetrahedral $[Ni^{II}Cl_2P_2]$ complex, which was indeed confirmed by single-crystal X-ray diffraction analysis (Figures 3 and S5). The Ni−P and Ni−Cl distances observed for **11** are quite similar to those reported for $[NiCl_2(dppf\text{-}\kappa^2P,P')]$.[26] On the other hand,

Scheme 4. Synthesis of $[MCl_2(1)]$ Complexes with Group 10 Metals[a]



[a] dme = 1,2-dimethoxyethane; cod = cycloocta-1,5-diene.

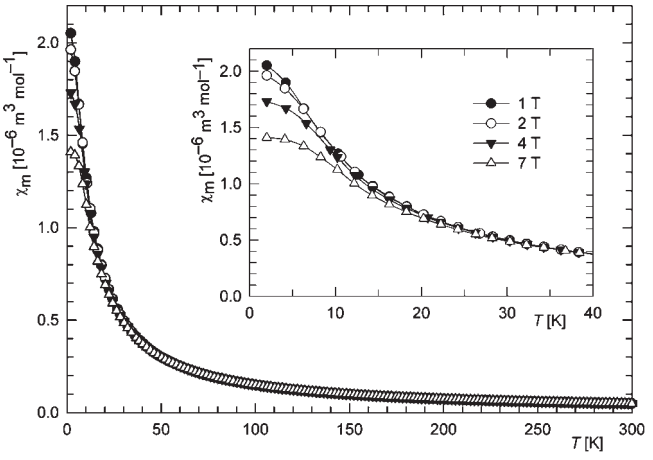


Figure 2. Temperature dependence of molar magnetic susceptibility of complex **11** at different magnetic fields (specified in the figure). The inset shows the expansion of the low-temperature region. For plots of $1/\chi$ vs T and a magnetization curve, see Supporting Information.

the associated interligand angles notably differ in both complexes, ranging from 101.41(4)° to 128.86(6)° for **11** and 95.6(1)° to 124.5(1)° for $[NiCl_2(dppf\text{-}\kappa^2P,P')]$. A wider span of the interligand angles in the dppf complex suggests a more severe deformation of the tetrahedral coordination environment, resulting from a lower flexibility of dppf, which is already manifested by a considerably more acute bite angle (cf. P1−Ni−P2 = 111.76(4)° for **11** and 105.0(1)° for the dppf complex). Accordingly, the $NiCl_2$ and NiP_2 planes in **11** subtend a dihedral angle of 87.70(8)°, which is close to the 90° expected for a regular tetrahedron. In the dppf complex, this dihedral angle is only 83.9(1)°.[27] On the other hand, the geometry of coordinated **1** is regular, showing similar Fe−Cg distances and negligible tilting (1.9(3)°; cf. 4.5° for the dppf analogue). Unlike the structurally characterized chalcogenides **8**−**10**, the CH_2PPh_2 moiety is oriented toward the cyclopentadienyl-bound PPh_2 group to allow for an efficient chelation.[28]

Analogous complexation reactions of **1** with $[MCl_2(cod)]$ (M = Pd or Pt, cod = η^2:η^2-cycloocta-1,5-diene) in dichloromethane afforded diamagnetic, square-planar *cis*-chelate complexes

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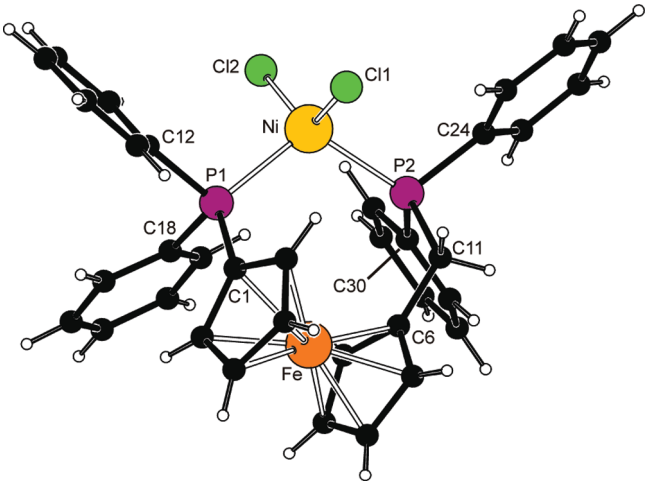


Figure 3. View of the molecular structure of complex **11** (conventional PLATON plot is available as Supporting Information). Selected distances and angles for **11** (in Å and deg): Ni−Cl1 2.214(2), Ni−Cl2 2.201(1), Ni−P1 2.312(1), Ni−P2 2.335(1), Cl1−Ni−Cl2 128.86(6), P1−Ni−P2 111.76(4); Fe−Cg1 1.630(2), Fe−Cg2 1.644(2), P1−C1 1.793(4), P2−C11 1.830(4), C6−C11 1.521(6), P2−C11−C6 117.5(3), tilt 1.9(3). Cg1/2 are defined as for **8** (see Figure 1).

$[MCl_2(\mathbf{1}\text{-}\kappa^2P,P')]$ (**12**, M = Pd; **13**, M = Pt). These compounds are air-stable but separate as crystalline solvates highly prone to desolvation under ambient conditions. ESI mass spectra support the formulation of **12** and **13** by showing signals due to $[MCl(\mathbf{1})]^+$ with characteristic isotopic patterns. Coordination of the phosphorus atoms of ligand **1** is manifested through a shift of both ^{31}P NMR resonances to lower fields (**12**: δ_P 18.2 and 24.6, **13**: δ_P 0.6 and 5.0) and, in the case of **13**, also by a scalar coupling between the chemically nonequivalent phosphorus nuclei ($^2J_{PP}$ = 18 Hz) and by ^{195}Pt satellites. The associated one-bond coupling constants ($^1J_{PtP}$ = 3537 and 3655 Hz) suggest the *cis*-P−P arrangement.[29] It is worth noting that whereas **1** behaves similarly to dppf for all the "MCl_2" fragments, diphosphine **A** reacts with hydrated $NiCl_2$ and $[PdCl_2(MeCN)_2]$ under the formation of *P,P′*-bridged dimers, $[(\mu\text{-}\mathbf{A})MCl_2]_2$.[17,30]

The crystal structures of solvated complexes **12** and **13** (Figures 4, S6, and S7) reveal similar coordination geometries. For instance, the interligand distances and angles differ by as little as 0.035 Å and 1.7° in the respective pairs. Moreover, the individual M-donor bond lengths compare well with those of $[PdCl_2(dppf)]\cdot Solv$ (Solv = $CHCl_3$[31] or CH_2Cl_2[32]) and $[PtCl_2(dppf)]\cdot Solv$ (Solv = $^1/_2Me_2CO$[33] or $CHCl_3$[34]). The ligand bite angles in **12** and **13** are more acute than in the respective dppf complexes. Yet, the differences are considerably smaller than that for the nickel complexes discussed above (ca. 2.2° for Pd and ca. 1.4° for Pt), probably due to a higher rigidity of the square-planar coordination environment.

Atoms constituting the coordination planes in **12** and **13**, {M, Cl1/2, P1/2}, are coplanar within less than 0.1 Å, and the planes are oriented nearly perpendicular to the ferrocene backbone (the dihedral angle of the coordination and Cp1 planes is 85° in both structures). Formation of the chelate ring is aided by the ferrocene unit adopting a conformation close to synclinal eclipsed (τ = 14° for **12** and 15° for **13**; tilts ≤3°) and further by rotation of the CH_2PPh_2 pendant toward P1 (the arm is more opened than in **8**−**10**; C6−C11−P2 = 120−122°).[35] All phenyl groups are directed away from the coordination plane and the ferrocene unit.

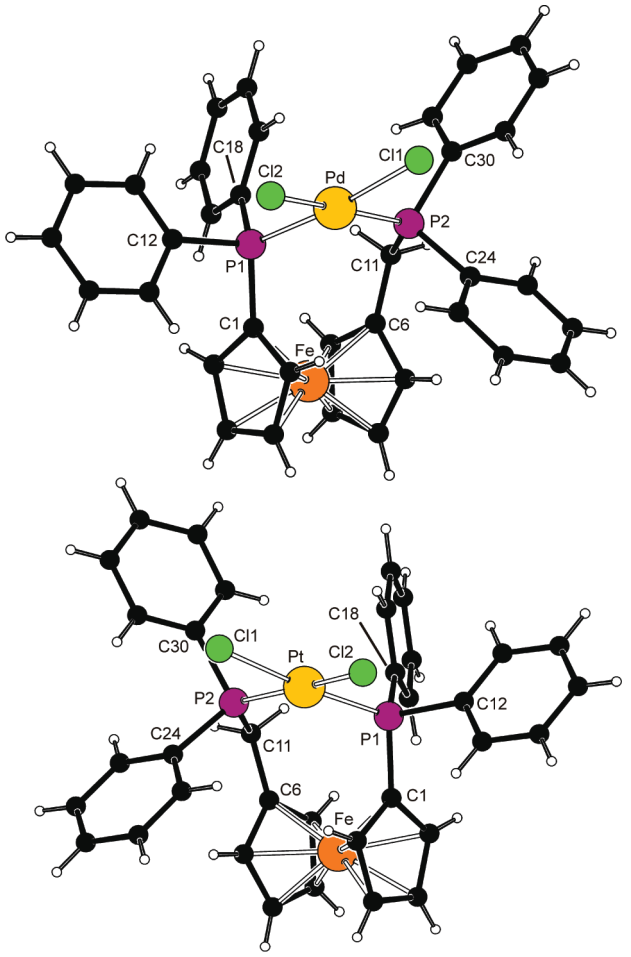
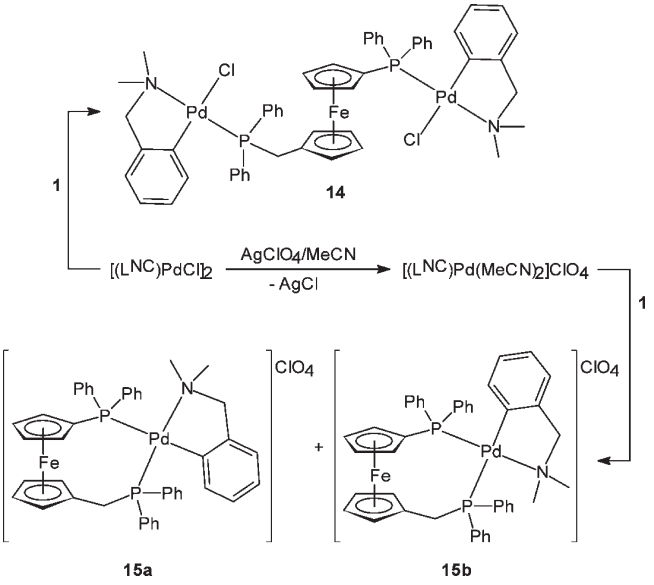


Figure 4. View of the complex molecules in the structure of $\mathbf{12}\cdot 2CH_2Cl_2$ (top) and $\mathbf{13}\cdot 0.8CH_2Cl_2$ (bottom). Conventional PLATON plots are available as Supporting Information. Selected distances and angles for $\mathbf{12}\cdot 2CH_2Cl_2$ [analogous parameters for $\mathbf{13}\cdot 0.8CH_2Cl_2$ in square brackets] (in Å and deg): M−Cl1 2.3582(8) [2.3555(8)], M−Cl2 2.3304(9) [2.3351(7)], M−P1 2.2624(8) [2.2484(7)], M−P2 2.2892(8) [2.2554(7)], Cl1−M−Cl2 88.74(3) [86.97(2)], P1−M−P2 96.31(3) [97.90(2)]; Fe−Cg1 1.644(2) [1.638(1)], Fe−Cg2 1.646(2) [1.646(1)], P1−C1 1.793(3) [1.796(3)], P2−C11 1.851(4) [1.845(3)], C6−C11 1.500(5) [1.509(4)], P2−C11−C6 121.6(2) [120.3(2)], tilt 1.7(2) [3.1(2)]. Cg1/2 are defined as for **8** (see Figure 1).

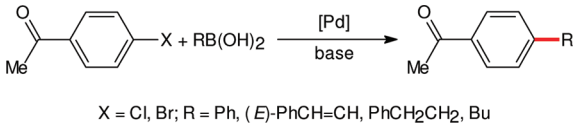
In analogy to dppf and **A**,[36] **1** reacts with the dimeric precursor $[(L^{NC})Pd(\mu\text{-}Cl)]_2$ under bridge cleavage to afford diphosphine-bridged dipalladium(II) complex **14** (Scheme 5). A replacement of acetonitrile ligands from the bis-solvento complex $[(L^{NC})Pd(MeCN)_2]ClO_4$ with an equimolar amount of **1** affords a mixture of isomeric bis-chelate complexes **15a** and **15b** in a ca. 40:60 ratio according to integration of the ^{31}P NMR spectrum. This suggests that the nonequivalent phosphine groups of **1** are differentiated only insignificantly by the dissymmetric $(L^{NC})Pd$ fragment.

Catalytic Tests. Catalytic properties of **1** were evaluated in palladium-catalyzed C−C bond forming reactions, namely, in Suzuki−Miyaura cross-coupling[37] of aromatic halides with various boronic acids and in cyanation of the same substrates with $K_4[Fe(CN)_6]\cdot 3H_2O$.[38] Both reactions hold particular value for organic synthesis:[39] The first one is typically used to build up a molecular skeleton, while the latter represents a convenient

Scheme 5. Preparation of Palladium Complexes with an Auxiliary [2-(Dimethylamino-κN)methyl]phenyl-κC^1 (L^{NC}) Ligand



Scheme 6. Pd-Catalyzed Suzuki–Miyaura Cross-Coupling Reactions



X = Cl, Br; R = Ph, (*E*)-PhCH=CH, $PhCH_2CH_2$, Bu

alternative to the standard, often hazardous, conventional methods used for the preparation of synthetically valuable nitriles.

Initial tests in the Suzuki–Miyaura cross-coupling were performed for the reaction of 4-bromoacetophenone with phenylboronic acid to give 4-acetylbiphenyl (Scheme 6) using 0.1 or 0.01 mol % Pd catalyst either as a defined complex (i.e., $[PdCl_2(L)]$ (L = **1** or dppf)) or generated *in situ* from palladium(II) acetate and the respective diphosphine. The results are summarized in Table 1.

All reactions performed at 0.1 mol % Pd loading (in dioxane at 100 °C for 24 h) proceeded with complete or very good conversions regardless of the type of catalyst. Upon lowering the amount of Pd catalyst to 0.01 mol %, the defined precatalyst still performed very well, while the activity of their *in situ* formed counterparts significantly decreased (Table 1). Kinetic profiles determined for the model reaction (Figure 5) showed that both *in situ* generated catalysts ($Pd(OAc)_2$/diphosphine) are "activated" very rapidly and achieve complete conversions within 2 h (0.1 mol % Pd). In contrast, the catalysts formed from the defined complexes $[PdCl_2(L)]$ exert relatively slower reaction rates and also differ significantly for both chelating ligands (rate: **1** ≫ dppf).

When the less reactive 4-chloroacetophenone[37,40] was employed as the substrate in the Suzuki–Miyaura reaction, the yields of the coupling product were fairly low even at 1 mol % Pd loading. The defined precatalysts still performed better than their *in situ* generated counterparts (cf. $[PdCl_2(L)]$: 24% for L = **1** and 35% for L = dppf; $Pd(OAc)_2$/L: 15% for L = **1** and 12% for L = dppf; $Pd_2(dba)_3$/L: 9% for L = **1** and 25% for L = dppf; in dioxane at 100 °C after 24 h).

Table 1. Summary of Catalytic Results Obtained with Defined and *in Situ* Generated Catalysts in Suzuki–Miyaura Reactions of 4-Bromoacetophenone with Boronic Acids[a]

	boronic acid			
catalyst	$PhB(OH)_2$[b]	$PhCH{=}CHB(OH)_2$[c]	$Ph(CH_2)_2B(OH)_2$[c]	$BuB(OH)_2$[c]
$[PdCl_2(1)]$	92 (91)	42	56	36
$[PdCl_2(dppf)]$	100 (86)	52	51	29
$Pd(OAc)_2$/**1**	100 (63)	73	20	8
$Pd(OAc)_2$/dppf	97 (78)	100	12	11
$Pd_2(dba)_3$/**1**	n.a.	61	53	41
$Pd_2(dba)_3$/dppf	n.a.	100	26	18

[a] For detailed conditions, see Experimental Section (n.a. = not available). [b] Conversions with 0.1 mol % (0.01 mol %) Pd catalyst. [c] Reactions with 5 mol % Pd catalyst.

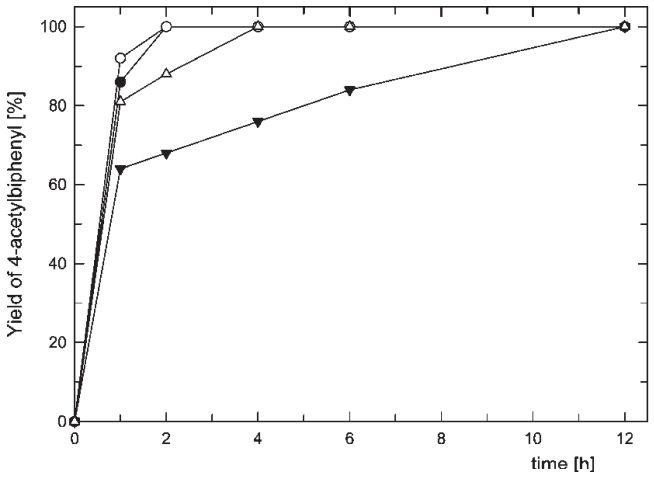
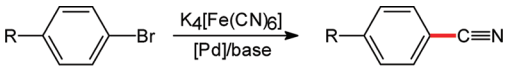


Figure 5. Kinetic profiles for Suzuki–Miyaura cross-coupling reaction of 4-bromoacetophenone with phenylboronic acid. Conditions: 0.1 mol % of Pd-catalyst (● $Pd(OAc)_2$/dppf, ○ $Pd(OAc)_2$/**1**, Δ $[PdCl_2(1)]$, ▼ $[PdCl_2(dppf)]$), dioxane, 100 °C.

Scheme 7. Pd-Catalyzed Cyanation of Aryl Bromides



R = Me, MeO, MeC(O), NO_2

The results obtained in reactions of 4-bromoacetophenone with other boronic acids (Table 1) were rather modest despite using the typically higher amounts of the Pd catalyst (5 mol %). In the case of styrylboronic acid, dppf-based catalysts performed somewhat better than those derived from **1**. In other cases (phenethyl- and butylboronic acid), either the catalytic performance of the pairs of structurally related catalysts were very similar ($[PdCl_2(L)]$ and $Pd(OAc)_2$/L) or the catalysts obtained from **1** reacted slightly better ($Pd_2(dba)_3$/L system).

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Table 2. Catalytic Results for Pd-Catalyzed Cyanation of 4-Substituted Bromobenzenes (4-RC_6H_4Br) with $K_4[Fe(CN)_6]\cdot 3H_2O$[a]

	conversion [%]			conversion [%]	
R	$[PdCl_2(dppf)]$	$[PdCl_2(\mathbf{1})]$	R	$[PdCl_2(dppf)]$	$[PdCl_2(\mathbf{1})]$
Ac	100	100	MeO	85	80
Me	100	100	NO_2	70	77

[a] 4-RC_6H_4Br (1.0 mmol), Na_2CO_3 (1.0 mmol), and $K_4[Fe(CN)_6]\cdot 3H_2O$ (0.25 mmol) were reacted in the presence of Pd-catalyst (5 μmol) in DMF at 130 °C for 16 h.

Palladium-catalyzed cyanation of 4-substituted bromobenzenes was carried out only with the defined precatalysts $[PdCl_2(L)]$ (Scheme 7 and Table 2). At 0.5 mol % palladium loading (in DMF at 130 °C for 16 h), both complexes behaved similarly, affording complete conversions with 4-bromoacetophenone and 4-bromotoluene and ca. 80% conversions for the remaining substrates (4-bromoanisole and 4-nitrobromobenzene).

CONCLUSIONS

Compound **1**, a semihomologous derivative of the popular dppf, is readily obtained upon reacting alcohol **2** with $HPPh_2$ and Me_3SiCl/NaI. Such a synthetic approach is highly versatile because the phosphorus substituents are introduced in a stepwise manner and can be also independently manipulated, which was demonstrated by the preparation of a series of chalcogenide derivatives, **5**−**10**.

As a ligand in group 10 metal complexes, diphosphine **1** binds more flexibly than dppf, which is reflected mainly in the ligand bite angles. Introduction of a methylene group lowers the overall molecular symmetry and results in an enhanced solubility of **1** and its complexes in organic solvents in comparison with dppf. On the other hand, the presence of the flexible methylene linker does not affect much the catalytic performance of both the defined complexes and precatalysts generated *in situ* from **1** and a metal source. This warrants further catalytic and structural studies with libraries of **1**-type ligands in which the phosphino groups and the nature of the single spacer unit are varied. In summary, the results presented in this work demonstrate that homologation of the known ligand structures is a viable route to new ferrocene donors with modified ligating properties.

EXPERIMENTAL SECTION

Unless noted otherwise, the syntheses were carried out under an argon atmosphere and with exclusion of direct daylight. Alcohol **2**,[19] $[MCl_2(cod)]$ (M = Pd and Pt),[41] $[(L^{NC})Pd(\mu\text{-}Cl)]_2$,[42] and $[(L^{NC})Pd(MeCN)_2]ClO_4$[43] were synthesized according to literature procedures. Dichloromethane and chloroform were dried over anhydrous potassium carbonate and distilled. Toluene and (1,4-)dioxane were distilled from sodium metal. Other chemicals, anhydrous acetonitrile, and solvents used for crystallizations and in chromatography were used as received (Fluka, Aldrich; solvents from Lach-Ner).

NMR spectra were measured with a Varian UNITY Inova 400 spectrometer at 298 K. Chemical shifts (δ/ppm) are given relative to internal $SiMe_4$ (^1H and ^{13}C) or to external 85% H_3PO_4 (^{31}P). In addition to the standard notation of signal multiplicity, vt and vq are used to denote virtual multiplets due to protons constituting the AA′BB′ and AA′BB′X spin systems of the Ph_2PCH_2- and PPh_2-substituted cyclopentadienyl rings, respectively (fc = ferrocene-1,1′-diyl). IR spectra were recorded with an FT IR Nicolet Magna 760 instrument. Magnetic susceptibilities were measured using a Quantum Design superconducting quantum interference device (SQUID) MPMS 7XL magnetometer at 1.0, 2.0, 4.0, and 7.0 T over the temperature range 2−300 K. A magnetization curve (see Supporting Information) was measured at 2 K up to a magnetic field of 7 T. The sample was loaded into a gelatin capsule and fixed in a plastic straw. Low-resolution electrospray ionization (ESI) mass spectra were obtained with an Esquire 3000 (Bruker) spectrometer. High-resolution ESI MS spectra were recorded with an LTQ Orbitrap XL spectrometer (Thermo Fisher Scientific).

Synthesis of [1′-(Diphenylphosphinoyl)ferrocenyl]methanol (3). In air, a solution of alcohol **2** (1.41 mg, 3.5 mmol) in acetone (25 mL) was treated with ca. 30% aqueous hydrogen peroxide solution (1 mL, ca. 10 mmol) while stirring and cooling in ice. After 30 min, the reaction mixture was diluted with brine (10 mL) and excess hydrogen peroxide was destroyed by addition of saturated aqueous $Na_2S_2O_3$ (10 mL). The acetone was removed under reduced pressure, and the residue extracted twice with ethyl acetate. The combined organic extracts were washed with brine, dried over $MgSO_4$, and filtered through a pad of silica gel (chromatographic grade, elution with ethyl acetate). The eluate was evaporated under vacuum, and the residue was subsequently crystallized from ethyl acetate/hexane. Yield: 1.31 g, 90%; orange-brown crystals.

^1H NMR ($CDCl_3$): δ 4.01 (vt, 2 H, J' = 1.9 Hz, fc), 4.35 (m, 4 H, fc), 4.43 (d, 2 H, $^3J_{HH}$ = 6.7 Hz, CH_2OH), 4.53 (vq, 2 H, J' = 1.9 Hz, fc), 5.87 (td, 1 H, $^3J_{HH}$ = 6.7, J = 1.2 Hz, CH_2OH), 7.41−7.72 (m, 10 H, PPh_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 59.81 (CH_2OH), 67.73, 68.25, 71.97 (d, J_{PC} = 10 Hz) (3 × CH of fc); 72.74 (d, $^1J_{PC}$ = 117 Hz, C-P(O)Ph_2 of fc), 72.81 (d, J_{PC} = 13 Hz, CH of fc), 93.14 (C-CH_2OH of fc), 128.33 (d, $^3J_{PC}$ = 12 Hz, CH_{meta} of PPh_2), 131.40 (d, $^2J_{PC}$ = 10 Hz, CH_{ortho} of PPh_2), 131.76 (d, $^4J_{PC}$ = 3 Hz, CH_{para} of PPh_2), 133.32 (d, $^1J_{PC}$ = 107 Hz, C_{ipso} of PPh_2). ^{31}P NMR ($CDCl_3$): δ 31.8 (s). IR (Nujol): 3340 br s, 3097 vw, 3080 w, 3071 vw, 3060 w, 2719 w, 2611 w, 2013 w, 1911 w, 1896 w, 1815 w, 1733 m, 1591 m, 1358 w, 1347 w, 1310 m, 1248 m, 1235 m, 1196 s, 1180 s, 1165 s, 1123 s, 1104 s, 1071 m, 1044 m, 1033 m, 1016 s, 998 m, 978 w, 948 m, 922 m, 882 w, 853 m, 837 s, 822 m, 752 s, 738 m, 708 s, 697 s, 670 m, 633 m, 621 m, 570 s, 528 s, 518 s, 500 s, 483 s, 466 m, 439 s cm^{-1}. Anal. Calcd for $C_{23}H_{21}FeO_2P$ (416.22): C 66.37, H 5.09. Found: C 66.28, H 5.05.

Synthesis of [1′-(Diphenylthiophosphinoyl)ferrocenyl]methanol (4). A solution of alcohol **2** (1.203 g, 3.0 mmol) and sulfur (97.5 mg, 3.0 mmol) in dry toluene (20 mL) was heated at reflux for 90 min. After cooling, the solvent was evaporated under vacuum and the yellow-brown residue was crystallized from ethyl acetate/hexane. Yield: 1.10 g, 84%, orange-brown crystals.

^1H NMR ($CDCl_3$): δ 2.70 (t, 1 H, $^3J_{HH}$ = 6.3 Hz, CH_2OH), 3.97 (vt, 2 H, J' = 1.6 Hz, fc), 4.28 (d, 2 H, $^3J_{HH}$ = 6.3 Hz, CH_2OH), 4.28 (vt, 2 H, J' = 1.6 Hz, fc), 4.46 (vq, 2 H, J' = 1.6 Hz, fc), 4.53 (q, 2 H, J' = 2.0 Hz, fc), 7.39−7.76 (m, 10 H, PPh_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 60.09 (CH_2OH), 69.19, 69.59, 72.10 (d, J_{PC} = 10 Hz), 73.39 (d, J_{PC} = 13 Hz) (4 × CH of fc); 75.18 (d, $^1J_{PC}$ = 98 Hz, C-P(S)Ph_2 of fc), 90.95 (C-CH_2OH of fc), 128.25 (d, $^3J_{PC}$ = 13 Hz, CH_{meta} of PPh_2), 131.35 (d, $^4J_{PC}$ = 3 Hz, CH_{para} of PPh_2), 131.58 (d, $^2J_{PC}$ = 1 Hz, CH_{ortho} of PPh_2), 134.18 (d, $^1J_{PC}$ = 87 Hz, C_{ipso} of PPh_2). ^{31}P NMR ($CDCl_3$): δ 42.5 (s). IR (Nujol): 3609 w, 3571 m, 3471 br m, 3072 vw, 3055 vw, 3044 vw, 2723 w, 1734 w, 1307 m, 1265 w, 1228 m, 1181 m, 1171 s, 1104 s, 1070 w, 1025 s, 1003 s, 936 w, 920 m, 871 m, 838 m, 822 m, 754 s, 717 s, 697 s, 655 s, 627 m, 614 m, 544 s, 521 w, 504 s, 494 s, 449 m, 436 w, 429 w cm^{-1}. Anal. Calcd for $C_{23}H_{21}FeOPS$ (432.04): C 63.90, H 4.90. Found: C 63.83, H 4.70.

1-(Diphenylphosphino)-1′-[(diphenylphosphino)methyl]ferrocene (1). Chlorotrimethylsilane (0.8 mL, 6 mmol) was added to a stirring solution of alcohol **5** (1.00 g, 2.5 mmol) and sodium iodide (750 mg, 7.5 mmol) in dry acetonitrile (50 mL). A white precipitate (NaCl) formed immediately. After 5 min, neat diphenylphosphine

(1.15 mL, 6.6 mmol) was introduced, and stirring was continued for 24 h. Then, the reaction mixture was diluted with saturated aqueous NaCl and diethyl ether. The organic phase was separated, dried over $MgSO_4$, and co-evaporated with alumina (chromatographic grade, neutral). The preadsorbed crude product was transferred onto the top of an alumina column (hexane), and the column was eluted with hexane to remove an excess of diphenylphosphine. Subsequent elution with hexane/diethyl ether (1:1 v/v) gave a yellow band, which, after evaporation under reduced pressure, afforded analytically pure **1** as a viscous, amber-brown oil. Yield: 1.09 g (77%). Note: Ph_2PH and **1** may co-elute during the chromatography if the acetonitrile is not removed *completely*.

^{1}H NMR ($CDCl_3$): δ 2.86 (s, 2 H, CH_2), 3.84 and 3.89 (2 × vt, J' = 1.8 Hz, 2 H, fc); 4.01 (vq, J' = 1.9 Hz, 2 H, fc), 4.32 (vt, J' = 1.8 Hz, 2 H, fc), 7.24−7.37 (m, 20 H, PPh_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 29.55 (d, $^1J_{PC}$ = 15 Hz, CH_2), 68.58 (2 C), 70.27 (d, 2 C, J_{PC} = 4 Hz), 71.68 (d, 2 C, J_{PC} = 4 Hz), 73.71 (d, 2 C, J_{PC} = 15 Hz) (CH of fc); 75.70 (d, $^1J_{PC}$ = 7 Hz, *C*-PPh_2 of fc), 84.81 (d, $^2J_{PC}$ = 15 Hz, *C*-CH_2PPh_2 of fc), 128.08 and 128.23 (2 × d, 4 C, $^3J_{PC}$ = 7 Hz, CH_{meta} of PPh_2); 128.44 and 128.58 (2 × s, 2 C, CH_{para} of PPh_2); 132.86 (d, 4 C, $^2J_{PC}$ = 18 Hz) and 133.50 (d, 4 C, $^2J_{PC}$ = 20 Hz) (2 × CH_{ortho} of PPh_2); 138.40 (d, 2 C, $^1J_{PC}$ = 15 Hz) and 139.12 (d, 2 C, $^1J_{PC}$ = 10 Hz) (2 × C_{ipso} of PPh_2). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −16.2 (s, fcPPh_2), −11.4 (s, CH_2PPh_2). IR (neat): 3069 m, 3051 m, 3027 w, 3014 w, 3000 w (ν_{CH}); 1954, 1888, 1813, 1749, 1662 (all m; $\nu_{C=C}$ aromatics); 1585 m, 1479 s, 1433 vs, 1307 m, 1192 m, 1160 s, 1068 m, 1026 s, 924 m, 828 s br, 813 m, 743 vs, 699 vs, 632 m, 496 s br, 456 m cm^{-1}. HR MS (ESI+): calcd for $C_{35}H_{30}{}^{56}FeP_2$ (M^+) 568.1168, found 568.1163.

1-(Diphenylphosphinoyl)-1′-[(diphenylphosphino)methyl]-ferrocene (5). Alcohol **3** (416 mg, 1.0 mmol) and NaI (300 mg, 2.0 mmol) were dissolved in dry acetonitrile (20 mL). The resultant solution was treated with chlorotrimethylsilane (0.3 mL, ca. 2.4 mmol). A white precipitate formed immediately. After stirring for 5 min, neat diphenylphosphine (0.45 mL, 2.5 mmol) was added and stirring was continued overnight. The reaction mixture was quenched with brine and diluted with diethyl ether. The clear, orange organic layer was separated, dried over $MgSO_4$, and evaporated with chromatographic alumina. The preadsorbed crude product was transferred onto the top of a chromatographic column, and the column was eluted first with hexane/ethyl acetate (1:1) to remove excess Ph_2PH and then with ethyl acetate to elute the product. After evaporation of the second fraction under vacuum, the product was chromatographed once again on silica gel using ethyl acetate to give, after evaporation, pure compound **5** as an orange solid. Yield: 392 mg (67%). ^{1}H NMR ($CDCl_3$): δ 2.90 (s, 2 H, CH_2), 3.98 and 4.03 (2 × vt, $J' \approx$ 1.8 Hz, 2 H, fc); 4.28 and 4.42 (2 × vq, $J' \approx$ 1.9 Hz, 2 H, fc); 7.27−7.67 (m, 20 H, PPh_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 29.36 (d, $^1J_{PC}$ = 15 Hz, CH_2), 69.09 (2 C), 70.73 (d, 2 C, J_{PC} = 4 Hz), 72.52 (d, 2 C, J_{PC} = 10 Hz) (CH of fc); 72.81 (d, $^1J_{PC}$ = 118 Hz, *C*-$P(O)Ph_2$ of fc), 73.03 (d, 2 C, J_{PC} = 13 Hz, CH of fc); 85.85 (d, $^2J_{PC}$ = 16 Hz, *C*-CH_2PPh_2 of fc), 128.13 (d, 4 C, $^3J_{PC}$ = 12 Hz, CH_{meta} of $P(O)Ph_2$), 128.24 (d, 4 C, $^3J_{PC}$ = 7 Hz, CH_{meta} of PPh_2), 128.60 (2 C, CH_{para} of PPh_2), 131.40 (d, 4 C, $^2J_{PC}$ = 10 Hz, CH_{ortho} of $P(O)Ph_2$), 131.40 (d, 2 C, $^4J_{PC}$ = 3 Hz, CH_{para} of $P(O)Ph_2$), 132.85 (d, 4 C, $^2J_{PC}$ = 19 Hz, CH_{ortho} of PPh_2), 134.47 (d, 2 C, $^1J_{PC}$ = 106 Hz, C_{ipso} of $P(O)Ph_2$), 138.29 (d, 2 C, $^1J_{PC}$ = 15 Hz, C_{ipso} of PPh_2). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −11.1 (s, PPh_2), 29.2 (s, $P(O)Ph_2$). HR MS (ESI+): calcd for $C_{35}H_{31}{}^{56}FeOP_2$ ([M + H]$^+$) 585.1194, found 585.1195.

1-(Diphenylthiophosphinoyl)-1′-[(diphenylphosphino)-methyl]ferrocene (6). Compound **4** was prepared similarly from alcohol **9** (432.5 mg, 1.0 mmol), NaI (453 mg, 3.0 mmol), chlorotrimethylsilane (0.35 mL, ca. 3 mmol), and diphenylphosphine (0.7 mL, 4 mmol) in dry MeCN (20 mL). The reaction mixture was worked up as described for **5**, and the preadsorbed crude product was transferred onto the top of a chromatographic column. The column was eluted first with hexane to remove unreacted Ph_2PH and then with hexane/diethyl ether (1:1, v/v) to wash out the product. Evaporation of the second fraction afforded **6** as an orange solid. Yield: 374 mg (62%).

^{1}H NMR ($CDCl_3$): δ 2.92 (s, 2 H, CH_2), 3.92 and 3.96 (2 × vt, $J' \approx$ 1.9 Hz, 2 H, fc); 4.34 and 4.44 (2 × vq, $J' \approx$ 1.9 Hz, 2 H, fc); 7.28−7.74 (m, 20 H, PPh_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 29.20 (d, $^1J_{PC}$ = 13 Hz, CH_2), 69.30 (2 C), 71.26 (d, 2 C, J_{PC} = 4 Hz), 72.54 (d, 2 C, J_{PC} = 10 Hz), 73.85 (d, 2 C, J_{PC} = 13 Hz) (CH of fc); 75.03 (d, $^1J_{PC}$ = 98 Hz, *C*-$P(S)Ph_2$ of fc), 84.42 (d, $^2J_{PC}$ = 16 Hz, *C*-CH_2PPh_2 of fc), 128.13 (d, 4 C, $^3J_{PC}$ = 13 Hz, CH_{meta} of $P(S)Ph_2$), 128.29 (d, 4 C, $^3J_{PC}$ = 7 Hz, CH_{meta} of PPh_2), 128.71 (2 C, CH_{para} of PPh_2), 131.12 (d, 2 C, $^4J_{PC}$ = 3 Hz, CH_{para} of $P(S)Ph_2$), 131.61 (d, 4 C, $^2J_{PC}$ = 11 Hz, CH_{ortho} of $P(S)Ph_2$), 132.89 (d, 4 C, $^2J_{PC}$ = 18 Hz, CH_{ortho} of PPh_2), 134.65 (d, 2 C, $^1J_{PC}$ = 87 Hz, C_{ipso} of $P(S)Ph_2$), 138.34 (d, 2 C, $^1J_{PC}$ = 15 Hz, C_{ipso} of PPh_2). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −11.0 (s, PPh_2), 42.2 (s, $P(S)Ph_2$). HR MS (ESI+): calcd for $C_{35}H_{31}{}^{56}FeP_2S$ ([M + H]$^+$) 601.0966, found 601.0967.

1-(Diphenylphosphinoyl)-1′-[(diphenylphosphinoyl)methyl]-ferrocene (7). In air, 30% aqueous hydrogen peroxide (0.2 mL) was added to a solution of diphosphine **1** (114 mg, 0.20 mmol) in acetone (10 mL) while stirring and cooling in an ice bath. After stirring for 1 h, sodium thiosulfate solution (5 mL of 30% solution in water) was introduced, and the stirring was continued at the same temperature for another 30 min to destroy an excess of H_2O_2. The acetone was removed under vacuum, and the residue was diluted with water and extracted with chloroform. The organic extract was dried ($MgSO_4$), evaporated, and then purified by column chromatography (silica gel, dichloromethane/methanol, 10:1 v/v). The single yellow band was collected and evaporated under vacuum to afford pure **7** as a brown, viscous oil. Yield: 113 mg (93%).

^{1}H NMR ($CDCl_3$): δ 3.32 (d, $^2J_{PH}$ = 12.2 Hz, 2 H, CH_2), 4.00 (vt, J' = 1.9 Hz, 2 H, fc), 4.16 (td, J = 1.9, ca. 0.8 Hz, 2 H, fc), 4.25 (vq, J' = 1.9 Hz, 2 H, fc), 4.44 (vq, J' = 1.9 Hz, 2 H, fc), 7.37−7.72 (m, 20 H, PPh_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 32.39 (d, $^1J_{PC}$ = 67 Hz, CH_2), 69.47 (2 C), 71.52 (d, 2 C, J_{PC} = 2 Hz), 72.41 (d, 2 C, J_{PC} = 10 Hz), 73.30 (d, 2 C, J_{PC} = 13 Hz) (CH of fc); 73.06 (d, $^1J_{PC}$ = 117 Hz, *C*-PPh_2 of fc), 79.70 (d, $^2J_{PC}$ = 3 Hz, *C*-CH_2PPh_2 of fc), 128.20 and 128.39 (2 × d, 4 C, $^3J_{PC}$ = 12 Hz, CH_{meta} of PPh_2); 131.20 (d, 4 C, $^2J_{PC}$ = 9 Hz) and 131.39 (d, 4 C, $^2J_{PC}$ = 10 Hz) (CH_{ortho} of PPh_2); 131.49 and 131.68 (2 × d, 2 C, $^4J_{PC}$ = 3 Hz, CH_{para} of PPh_2); 132.38 (d, 2 C, $^1J_{PC}$ = 98 Hz) and 134.37 (d, 2 C, $^1J_{PC}$ = 106 Hz) (2 × C_{ipso} of PPh_2). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 28.9 and 29.3 (2 × s, $P(O)Ph_2$). HR MS (ESI+): calcd for $C_{35}H_{31}{}^{56}FeO_2P_2$ ([M + H]$^+$) 601.1143, found 601.1144.

1-(Diphenylthiophosphinoyl)-1′-[(diphenylthiophosphinoyl)-methyl]ferrocene (8). Compound **1** (114 mg, 0.20 mmol) and sulfur (25.5 mg, 0.80 mmol) were mixed with dry toluene (10 mL). The resulting solution was heated at gentle reflux for 90 min, cooled, and filtered through a pad of silica gel, eluting with diethyl ether. The filtrate was evaporated, and the residue was dissolved in hot glacial acetic acid (20 mL). The solution was diluted with hot water (5 mL) and allowed to crystallize by slow cooling first to room temperature and then to 4 °C. The separated product was filtered off, washed successively with 50% acetic acid and water, and dried under vacuum. Yield of solvate **8**·AcOH: 107 mg (77%), yellow-brown needles. Note: Depending on the crystallization conditions, the compound separates either unsolvated or in the form of acetic acid solvate, **8**·AcOH.

^{1}H NMR ($CDCl_3$): δ 3.64 (d, $^2J_{PH}$ = 11.7 Hz, 2 H, CH_2), 3.86 (vt, J' = 1.8 Hz, 2 H, fc), 4.08 (br m, 2 H, fc), 4.31 and 4.47 (2 × vq, $J' \approx$ 1.8 Hz, 2 H, fc), 7.34−7.86 (m, 20 H, PPh_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 35.99 (d, $^1J_{PC}$ = 51 Hz, CH_2), 69.39 (2 C), 72.30 (d, 2 C, J_{PC} = 10 Hz), 72.44 (d, 2 C, J_{PC} = 2 Hz), 74.02 (d, 2 C, J_{PC} = 13 Hz) (CH of fc); 75.30 (d, $^1J_{PC}$ = 98 Hz, *C*-PPh_2 of fc), 79.62 (*C*-CH_2PPh_2 of fc), 128.21 and 128.40 (2 × d, 4 C, $^3J_{PC}$ = 12 Hz, CH_{meta} of PPh_2); 131.34 (d, 2 C, $^4J_{PC}$ = 3 Hz) and 131.41 (d, 2 C, $^4J_{PC}$ = 2 Hz) (2 × CH_{para} of PPh_2); 131.57 (d, 4 C, $^2J_{PC}$ = 11 Hz) and 131.64 (d, 4 C, $^2J_{PC}$ = 10 Hz) (CH_{ortho} of PPh_2); 132.24 (d, 2 C, $^1J_{PC}$ = 79 Hz) and 134.37 (d, 2 C, $^1J_{PC}$ = 87 Hz) (2 × C_{ipso} of PPh_2). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 41.3 and 42.2 (2 × s, $P(S)Ph_2$). HR MS (ESI+): calcd for $C_{35}H_{31}{}^{56}FeP_2S_2$ ([M + H]$^+$) 633.0686, found 633.0690.

1-(Diphenylphosphinoyl)-1′-[(diphenylthiophosphinoyl)-methyl]ferrocene (9). Compound **5** (59 mg, 0.10 mmol) and sulfur (5 mg, ca. 0.16 mmol) were dissolved in toluene (2 mL). The solution was stirred overnight, whereupon it deposited a yellow precipitate. The reaction mixture was evaporated to dryness, and the residue was dissolved in warm ethyl acetate (5 mL). Crystallization by addition of hexane (5 mL) as a top layer and standing for several days afforded orange-brown needles of **9**, which were filtered off, washed with pentane, and dried under vacuum. Yield: 44 mg (71%).

^{1}H NMR ($CDCl_3$): δ 3.56 (d, $^2J_{PH}$ = 11.8 Hz, 2 H, CH_2), 3.98 (vt, $J' \approx$ 1.9 Hz, 2 H), 4.12 (m, 2 H), 4.26 and 4.45 (2 × vq, $J' \approx$ 1.9 Hz, 2 H) (CH of fc); 7.35−7.83 (m, 20 H, PPh_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 36.02 (d, $^1J_{PC}$ = 51 Hz, CH_2), 69.39 (2 C), 71.85 (d, 2 C, J_{PC} = 2 Hz), 72.30 (d, 2 C, J_{PC} = 10 Hz) (CH of fc); 73.02 (d, $^1J_{PC}$ = 117 Hz, *C*-P(O)Ph_2 of fc), 73.26 (d, 2 C, J_{PC} = 13 Hz, CH of fc); 79.61 (*C*-CH_2P(S)Ph_2 of fc), 128.21 and 128.38 (2 × d, 4 C, $^3J_{PC}$ = 12 Hz, CH_{meta} of P(O/S)Ph_2); 131.38 (d, 4 C, $^3J_{PC}$ = 10 Hz, CH_{meta} of P(O/S)Ph_2), 131.41 and 131.50 (2 × d, 2 C, $^4J_{PC}$ = 3 Hz, CH_{para} of P(O/S)Ph_2), 131.62 (d, 4 C, $^3J_{PC}$ = 10 Hz, CH_{meta} of P(O/S)Ph_2), 132.20 (d, 2 C, $^1J_{PC}$ = 79 Hz, C_{ipso} of P(S)Ph_2), 134.35 (d, 2 C, $^1J_{PC}$ = 106 Hz, C_{ipso} of P(O)Ph_2). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 29.3 (s, P(O)Ph_2), 41.4 (s, P(S)Ph_2). HR MS (ESI+): calcd for $C_{35}H_{31}{}^{56}FeOP_2S$ ($[M + H]^+$) 617.0915, found 617.0915.

1-(Diphenylthiophosphinoyl)-1′-[(diphenylphosphinoyl)-methyl]ferrocene (10). A solution of compound **6** (60 mg, 0.10 mmol) in acetone (2 mL) was treated with 30% aqueous hydrogen peroxide (0.1 mL) while stirring in air and cooling in an ice bath. After 30 min, saturated aqueous $Na_2S_2O_3$ (1 mL) was added, and stirring was continued for another 15 min to decompose an excess of H_2O_2. The organic layer was separated and the aqueous residue was washed with diethyl ether. The combined organic layers were dried over $MgSO_4$ and evaporated, leaving a residue, which was taken up with ethyl acetate and crystallized by addition of hexane (5 mL each). The orange-brown crystals of solvate **10**·H_2O were filtered off, washed with pentane, and dried under vacuum. Yield: 45 mg (71%).

^{1}H NMR ($CDCl_3$): δ 3.39 (d, $^2J_{PH}$ = 12.2 Hz, 2 H, CH_2), 3.87 (vt, $J' \approx$ 1.9 Hz, 2 H), 4.12 (m, 2 H), 4.30 and 4.47 (2 × vq, $J' \approx$ 1.9 Hz, 2 H) (CH of fc); 7.345−7.75 (m, 20 H, PPh_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 32.41 (d, $^1J_{PC}$ = 67 Hz, CH_2), 69.50 (2 C), 72.10 (d, 2 C, J_{PC} = 2 Hz), 72.39 (d, 2 C, J_{PC} = 10 Hz), 74.02 (d, 2 C, J_{PC} = 12 Hz) (CH of fc); 75.31 (d, $^1J_{PC}$ = 98 Hz, *C*-P(S)Ph_2 of fc), 79.69 (d, $^2J_{PC}$ = 2 Hz, *C*-CH_2P(O)Ph_2 of fc), 128.19 and 128.41 (2 × d, 4 C, $^3J_{PC}$ = 12 Hz, CH_{meta} of P(O/S)Ph_2); 131.21 (d, 2 C, $^4J_{PC}$ = 3 Hz, CH_{para} of P(O/S)Ph_2), 131.22 and 131.58 (2 × d, 4 C, $^3J_{PC}$ = 10 Hz, CH_{meta} of P(O/S)Ph_2), 131.68 (d, 2 C, $^4J_{PC}$ = 3 Hz, CH_{para} of P(O/S)Ph_2), 132.39 (d, 2 C, $^1J_{PC}$ = 98 Hz, C_{ipso} of P(O)Ph_2), 134.42 (d, 2 C, $^1J_{PC}$ = 87 Hz, C_{ipso} of P(S)Ph_2). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 28.8 (s, P(O)Ph_2), 42.2 (s, P(S)Ph_2). HR MS (ESI+): calcd for $C_{35}H_{31}{}^{56}FeOP_2S$ ($[M + H]^+$) 617.0915, found 617.0915.

Dichlorido{1-(diphenylphosphino)-1′-[(diphenylphosphino)-methyl]ferrocene-κ^2*P,P*′}nickel(II) (11). A solution of **1** (59 mg, 0.10 mmol) in acetone (3 mL) was added to a suspension of [$NiCl_2$(dme)] (22 mg, 0.10 mmol) in absolute ethanol (3 mL). The reaction mixture turned brown, and the product started to separate. The mixture was stirred at room temperature for 30 min and then stored at 0 °C overnight. The solid product was filtered off, washed with diethyl ether and pentane, and dried under vacuum to afford complex **11** as a dark olive green microcrystalline solid. Yield: 66.5 mg (95%).

ESI+ MS: *m*/*z* 661 ($[NiCl(\mathbf{1})]^+$), 627. Anal. Calcd for (%) for $C_{35}H_{30}Cl_2FeNiP_2$ (698.0): C 60.22, H 4.33. Found: C 60.17, H 4.39.

Dichlorido{1-(diphenylphosphino)-1′-[(diphenylphosphino)-methyl]ferrocene-κ^2*P,P*′}palladium(II) (12). A solution of **1** (58 mg, 0.10 mmol) in dichloromethane (4 mL) was added to solid [$PdCl_2$(cod)] (28.5 mg, 0.10 mmol). The resulting deep red-orange solution was stirred for 1 h, filtered (PTFE syringe filter, 0.45 μm), and layered with diethyl ether (12 mL). Crystallization by liquid-phase diffusion at 4 °C over several days afforded red crystals, which were filtered off, washed with pentane, and dried under vacuum to afford **12**·0.2CH_2Cl_2 as a brick red solid. Yield: 64 mg (84%).

^{1}H NMR ($CDCl_3$): δ 2.74 (dd, 2 H, $^2J_{PH}$ = 11.2, $^4J_{PH}$ = 1.8 Hz, CH_2), 3.41 (br t, 2 H), 4.13 (vt, $J' \approx$ 1.8 Hz, 2 H), 4.68 (d of vt, $J' \approx$ 0.9, 1.9 Hz, 2 H), 5.11 (br s, 2 H) (CH of fc), 7.33−7.89 (m, 20 H, PPh_2). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 18.2, 24.6 (2 × s). ESI ± MS: *m*/*z* 709/711 ($[Pd(\mathbf{1})Cl]^+$); 781 ($[Pd(\mathbf{1})Cl_3]^-$). Anal. Calcd for $C_{35}H_{30}Cl_2FeP_2Pd$·0.2CH_2Cl_2 (762.7): C 55.43, H 4.02. Found: C 55.25, H 4.04.

Dichlorido{1-(diphenylphosphino)-1′-[(diphenylphosphino)-methyl]ferrocene-κ^2*P,P*′}platinum(II) (13). A solution of **1** (59 mg, 0.10 mmol) in dichloromethane (6 mL) was added to solid [$PtCl_2$(cod)] (37.5 mg, 0.10 mmol). The resulting yellow solution was stirred for 1 h, filtered (PTFE syringe filter, 0.45 μm), and layered with diethyl ether (ca. 10 mL). Subsequent crystallization at room temperature over several days afforded beautiful yellow crystals, which were filtered off, washed with pentane, and dried under vacuum. During isolation in the air, the crystals became opaque and then disintegrated due to extensive desolvation, finally affording the product as a nonstoichiometric solvate. Yield: 80 mg (94%) of **13**·0.15CH_2Cl_2, a yellow powdery solid.

^{1}H NMR ($CDCl_3$): δ 2.83 (d, $^2J_{PH}$ = 11.5 Hz with ^{195}Pt-satellites: $^3J_{PtH} \approx$ 47 Hz, 2 H, CH_2), 3.36 (br s, 2 H, fc), 4.11 (vt, $J' \approx$ 1.8 Hz, 2 H, fc), 4.69 (m, 2 H, fc), 5.11 (br s, 2 H, fc), 7.32−7.89 (m, 10 H, PPh_2). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 0.6 (d, $^2J_{PP}$ = 18 Hz with ^{195}Pt-satellites: $^1J_{PtP}$ = 3537 Hz), 5.0 (d, $^2J_{PP}$ = 18 Hz with ^{195}Pt-satellites: $^1J_{PtP}$ = 3655 Hz). ESI+ MS: *m*/*z* 799 ($[Pt(\mathbf{1})Cl]^+$), 762 ($[Pt(\mathbf{1}) - H]^+$). Anal. Calcd for $C_{35}H_{30}Cl_2FeP_2Pt$·0.15CH_2Cl_2 (847.1): C 49.83, H 3.61. Found: C 49.79, H 3.67.

{μ-1κ*P*:2κ*P*′-1-(Diphenylphosphino)-1′-[(diphenylphosphino)-methyl]ferrocene}bis{[(2-(dimethylamino-κ*N*)methyl)phenyl-κ*C*^{1}]palladium(II)} (14). A solution of **1** (58 mg, 0.10 mmol) in dichloromethane (2 mL) was added to solid [{(L^{NC})Pd(μ-Cl)}$_2$] (55 mg, 0.10 mmol). The resulting clear orange solution was stirred for 1 h and then slowly added to pentane (ca. 30 mL). The precipitated product was filtered off, washed successively with diethyl ether/pentane (1:1) and pentane, and dried under vacuum to give **14** as an orange solid in quantitative yield (110 mg).

^{1}H NMR ($CDCl_3$): δ 2.72 (d, $^4J_{PH}$ = 2.7 Hz, 6 H, NMe_2), 2.80 (d, $^4J_{PH}$ = 2.6 Hz, 6 H, NMe_2), 3.69 (d, $^2J_{PH}$ = 10.1 Hz, 2 H, PCH_2), 3.93 (d, $^4J_{PH}$ = 2.2 Hz, 2 H, NCH_2), 3.96 (d, $^4J_{PH}$ = 2.1 Hz, 2 H, NCH_2), 4.19 (vq, $J' \approx$ 2.0 Hz, 2 H), 4.24 (br vt, 2 H), 4.27 (d of vt, $J' \approx$ 0.5 and 1.8 Hz, 2 H), 4.44 (vt, $J' \approx$ 1.8 Hz, 2 H) (CH of fc); 6.24−6.32 (m, 2 H, C_6H_4), 6.40 (tt, $J \approx$ 7.6, 2.0 Hz, 2 H, C_6H_4), 6.77 (td, J = 7.3, 1.1 Hz, 1 H, C_6H_4), 6.84 (td, J = 7.3, 1.1 Hz, 1 H, C_6H_4), 6.92 (dd, J = 7.4, 1.1 Hz, 1 H, C_6H_4), 7.00 (dd, J = 7.4, 1.1 Hz, 1 H, C_6H_4), 7.24−7.66 (m, 20 H, PPh_2). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 33.0 and 36.6 (2 × s). ESI+ MS: *m*/*z* 1083/1085 ($[(\mathbf{1})(L^{NC})_2Pd_2Cl]^+$), 808 ($[(\mathbf{1})(L^{NC})_2Pd_2]^+$). Anal. Calcd $C_{53}H_{54}Cl_2FeN_2P_2Pd_2$ (1120.47): C 56.81, H 4.86, N 2.50. Found: C 56.82, H 5.22, N 2.36.

Reaction of [(L^{NC})Pd(MeCN)$_2$]ClO_4 with 1. Complex [(L^{NC})-Pd(MeCN)$_2$]ClO_4 (42.5 mg, 0.10 mmol) and **1** (58 mg, 0.10 mmol) were dissolved in dichloromethane (3 mL). After stirring for 90 min, the mixture was filtered through a pad of Celite and the filtrate was evaporated under vacuum, leaving a residue, which was washed with diethyl ether and pentane and dried under vacuum. Yield: 91 mg (quant.), ochre powdery solid.

^{31}P{^{1}H} NMR ($CDCl_3$): δ 2.4 and 27.7 (2 × d, $^2J_{PP}$ = 40 Hz; isomer A); 8.0 and 34.4 (2 × d, $^2J_{PP}$ = 42 Hz; isomer B). IR (Nujol): 1645 m, 1580 m, 1163 m, $\nu_3(ClO_4)$ 1097 vs, 1026 w, 998 w, 839 m, 725 s, 698 s, $\nu_4(ClO_4)$ 623 s, 487 s cm^{-1}. ESI+ MS: *m*/*z* 808 ($[(L^{NC})Pd(\mathbf{1})]^+$), 675 ($[Pd(\mathbf{1}) + H]^+$). Anal. Calcd for $C_{44}H_{42}ClFeNO_4P_2Pd$ (908.4): C 58.17, H 4.66, N 1.54. Found: C 57.81, H 4.85, N 1.72.

Suzuki−Miyaura Cross-Coupling with Phenylboronic Acid. A Schlenk tube was charged with 4-bromacetophenone (398 mg, 2.0 mmol), phenylboronic acid (293 mg, 2.4 mmol), potassium carbonate (663 mg, 4.8 mmol), bis(2-methoxyethyl) ether (internal standard; 134 mg, 1.0 mmol), and dioxane (10 mL). Palladium precatalyst (2.0 or 0.2 μmol) was added as a stock solution in 1,2-dichloroethane, and the reaction mixture was heated at 100 °C in an oil bath for 24 h under an argon atmosphere. Conversions were determined by ^{1}H NMR spectroscopy. The reactions with 4-chloroacetophenone were carried out similarly using 4-chloracetophenone (155 mg, 1.0 mmol), phenylboronic acid (146 mg, 1.2 mmol), potassium carbonate (332 mg, 2.4 mmol), and bis(2-methoxyethyl) ether (67 mg, 0.5 mmol) in dioxane (5 mL). Palladium precatalyst (10 μmol) was introduced as a solution in 1,2-dichloroethane (0.25 mL), and the reaction mixture was heated at 100 °C in an oil bath for 24 h under an argon atmosphere. "Instant" catalysts were prepared by stirring the Pd source (10 μmol of Pd) with the appropriate ligand (11 μmol) in 1,2-dichloroethane (0.25 mL) for 5 min.

Suzuki−Miyaura Cross-Coupling Reactions with Butyl-, 2-Phenylethyl-, and Styrylboronic Acids. A Schlenk tube was charged with 4-bromacetophenone (19.9 mg, 0.1 mmol), appropriate boronic acid (0.12 mmol), potassium carbonate (33.2 mg, 0.24 mmol), bis(2-methoxyethyl) ether (internal standard; 6.7 mg, 0.05 mmol), and dry dioxane (1 mL). Palladium precatalyst (5.0 μmol) was dissolved in 1,2-dichloroethane (0.25 mL) and added to the mixture, and the reaction vessel was transferred to an oil bath preheated to 100 °C. The reaction mixture was analyzed by standard proton NMR spectroscopy. When palladium(II) acetate or tris(dibenzylideneacetone)-dipalladium(0) were employed as the Pd source, the precatalyst was generated *in situ* by reacting the Pd-precursor (5.0 μmol) with the appropriate ligand (5.5 μmol) in 1,2-dichloroethane (0.25 mL) for 5 min.

Pd-Catalyzed Cyanation of Aryl Bromides. A pressure Schlenk tube was charged with aryl halide (1.0 mmol), Na_2CO_3 (106 mg; 1.0 mmol), and $K_4[Fe(CN)_6]\cdot 3H_2O$ (106 mg; 0.25 mmol). A solution of catalyst precursor (5 μmol) in dry DMF (3 mL) was added, and the reaction vessel was sealed and heated in an oil bath maintained at 130 °C for 16 h. Conversions were determined from ^{1}H NMR spectra.

X-ray Crystallography. Single crystals suitable for X-ray diffraction measurements were grown by cooling solutions in warm aqueous acetic acid (**8**: yellow-orange prism, 0.10 × 0.13 × 0.30 mm^3) or ethyl acetate/hexane (**3**: orange plate, 0.20 × 0.26 × 0.62 mm^3; **9**: orange prism, 0.24 × 0.42 × 0.56 mm^3; **10**·H_2O: orange prism, 0.13 × 0.31 × 0.46 mm^3) or, alternatively, by liquid-phase diffusion from dichloromethane/hexane (**12**·$2CH_2Cl_2$: orange-red prism, 0.10 × 0.20 × 0.35 mm^3) and from dichloromethane/diethyl ether (**13**·$0.8CHCl_3$: yellow plate, 0.08 × 0.18 × 0.25 mm^3). Full-set diffraction data ($\pm h \pm k \pm l$, $2\theta = 55°$; completeness ≥99.6%) were collected with a Bruker Apex2 (**3**, **9**, and **10**·H_2O) or Nonius KappaCCD (all other) diffractometers equipped with Cryostream cooler (Oxford Cryosystems) using Mo Kα radiation (λ = 0.71073 Å). When appropriate, the data were corrected for absorption by the methods included in the diffractometer software. Data collection, structure solution, and refinement parameters are summarized in Table S1 (see Supporting Information).

The phase problems were solved by direct methods (SIR-97[44] or SHELXS-97[45]), and the models refined by full-matrix least-squares routine based on F^2 (SHELXL-97[46]). The non-hydrogen atoms were refined with anisotropic displacement parameters, and the hydrogen atoms were included in their calculated positions and refined as riding atoms. The solvent molecules in the structure of **13**·$0.8CH_2Cl_2$ were disordered in structural voids located around the symmetry elements, and, therefore, their contribution to the overall scattering was numerically subtracted using the SQUEEZE[47] routine as incorporated in the PLATON program.[48] Within the 4 × 253 Å^3 of void space per unit cell, a total of 264 electrons were calculated, which compares well with 269 electrons expected for 8 × 0.8 molecules of CH_2Cl_2 per unit cell.

All geometric calculations were performed with a recent version of the PLATON program, and the numerical values are rounded with respect to their estimated standard deviations given with one decimal. CCDC-822092−822098 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

■ ASSOCIATED CONTENT

Supporting Information. Crystal structure of **3**, conventional displacement ellipsoid plots for all crystal structures presented in this article, additional plots of magnetochemical data, a summary of X-ray crystallographic data, and CIF files for all structurally characterized compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ DEDICATION

Dedicated to Professor Jaroslav Podlaha on the occasion of his 75th birthday.

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