Articles

Novel BPPFA Palladium Complexes. P,P to P,N Rearrangements Promoted by Chelating κ^3-*N,P,P*-BPPFA Intermediates

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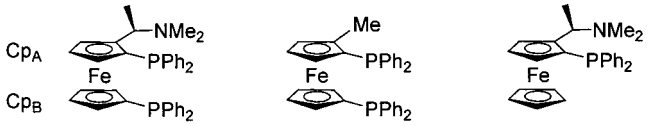
Novel palladium complexes with BPPFA (*N,N*-dimethyl-1-[2,1′-bis(diphenylphosphino)-ferrocenyl]ethylamine) and the newly prepared ligand 1,1′-bis(diphenylphosphino)-2-methylferrocene (BPPFMe, **1**) have been synthesized. Racemic BPPFA reacts with $Pd_2(dba)_3 \cdot CHCl_3$ in the presence of electron-withdrawing alkenes to give palladium(0) complexes Pd(BPPFA)(alkene), where alkene = dimethyl fumarate (**2**), maleic anhydride (**3**). Displacement of weak donor ligands from the appropriate palladium(II) precursors leads to the derivatives [Pd(η^3-2-Me-C_3H_4)(BPPFA)]TfO (**4**), $Pd(C_6F_5)_2$(BPPFA) (**5**), $Pd(C_6F_5)_2$(BPPFMe) (**6**), $PdMe_2$(BPPFA) (**7**), and PdClMe(BPPFA) (**8**). Complexes **2**−**4** and **8** each exist in solution as two diastereomers that do not interconvert at room temperature on the NMR time scale. In all mononuclear complexes BPPFA is P,P-coordinated to palladium. When PdClX(cod) (X = Cl, Me) is reacted with (R_C,S_P)-BPPFA in a Pd:L ratio higher than 1:1, polynuclear species are formed. A Pd:L ratio of 2:1 leads to the tetranuclear derivatives {*cis*-PdClX(μ-κ^3-BPPFA)}$_2$-{PdX(μ-Cl)$_2$PdX} (X = Me (**9**), Cl (**10**)), while a ratio of 1.5:1 gives the trinuclear complexes {*cis*-PdClX(μ-κ^3-BPPFA)}$_2$(*trans*-PdClX) (X = Me (**11**), Cl (**12**)) along with the corresponding tetra- and mononuclear derivatives. Mechanistic studies concerning the formation of the tetranuclear complexes have shown that a P,P to P,N coordination shift and Pd−P bond rupture are feasible processes. Variable-temperature ^{1}H NMR studies have provided evidence of Pd−N interactions in complexes **2**, **5**, **7**, and **8** that involve an unprecedented terdentate κ^3N,P,P chelate coordination of BPPFA to palladium. The pentafluorophenyl complexes **5** and **6** each exist in solution as two conformers that are interconvertible by torsional twisting of the Cp rings. In the case of complex **5** this interconversion process is slowed at low temperature to such an extent that both conformers can be observed separately by NMR spectroscopy. This phenomenon is presumably due to the Pd−N interaction. The molecular structures of **2M** and **8M** (**M** = major isomer) have been determined by X-ray diffraction.

Introduction

Bi- and multifunctional ferrocene derivatives have been used successfully as ligands in homogeneous catalysts for almost three decades.[1] The enantiopure aminophosphines PPFA[2] and BPPFA (Chart 1) are among the most widely used derivatives and are employed not only as catalyst ligands but also as starting materials for the synthesis of other bi- and multifunctional ferrocene derivatives. PPFA and BPPFA are easily prepared in both enantiomeric forms (R_C,S_P and S_C,R_P) as well as both diastereomeric forms (R_C,R_P and S_C,S_P) from enantiopure (*R*)- or (*S*)-*N,N*-dimethyl-1-ferrocenylethylamine.[3] Substitution of the dimethylamino group of aminophosphines PPFA or BPPFA with nucleophiles allows the preparation of a diverse range

Chart 1



(R_c,S_p)-BPPFA (S_p)-BPPFMe, **1** (R_c,S_p)-PPFA

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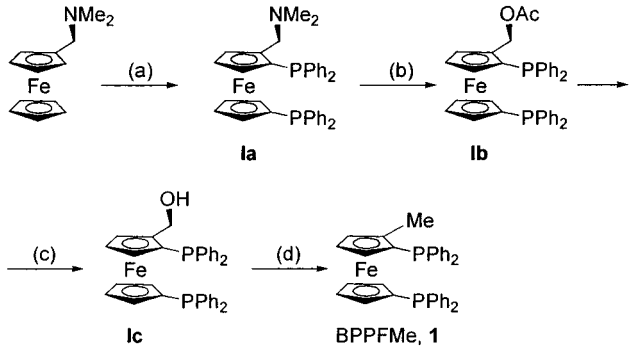
of ligands with amino, hydroxyl, thiol, phosphino, and other functional groups attached to the ethyl side chain.[4,5a,6] Coordination of such ferrocenyl−phosphine ligands to transition-metal units leads to precatalysts for a variety of homogeneous asymmetric reactions, including, among others, cross-coupling reactions, allylic substitutions, hydrogenation and hydrosilylation of olefins and ketones, and aldol-type condensations.[7−9] In several cases BPPFA-modified catalysts work far better than those derived from PPFA.[1]

In recent years we have been interested in the coordination properties of ferrocenyl ligands and have reported on the coordination and fluxional behavior of PPFA Pd[10] and Ru[11] complexes. For instance, we demonstrated by means of NMR spectroscopy that Pd−N bond cleavage is a feasible process for PPFA−Pd(0) and −Pd(II) derivatives but is of higher energy for other ferrocenylaminophosphine complexes.[10a] Further studies have been carried out to assess the influence of the metal oxidation state and the structure of ancillary ligands on the nature of this bond rupture process.[10b]

As a bidentate ligand PPFA must be P,N-coordinated while, at least in principle, BPPFA could be P,N or P,P coordinated. According to the reported X-ray structure of a mononuclear palladium complex, BPPFA is selectively P,P-coordinated.[12] An interesting aspect of this structure concerns the fact that the lone pair of the noncoordinated dimethylamino nitrogen is pointing almost directly toward the metal unit in a way that is essentially preorganized for metal coordination. On the basis of this structural property one could imagine a pentacoordinated species with BPPFA as a tridentate chelating ligand that could act as an intermediate in a P,P ↔ N,P coordination exchange process. With this idea in mind, the work described in this paper is focused on the different coordination modes of BPPFA Pd(0) and Pd(II) complexes with olefin, allyl, chloro, methyl, and pentafluorophenyl groups as ancillary ligands. The possible participation of the dimethylamino group in the coordination and fluxional behavior of BPPFA complexes in solution was anticipated. We also expected that a better knowledge of the coordination properties of BPPFA versus PPFA would contribute to our understanding of the similarities and differences between these ligands in catalytic systems.

Scheme 1



Results and Discussion

Synthesis of the New Derivatives. For the sake of comparison the new ligand BPPFMe (**1**) was synthesized from ((dimethylamino)methyl)ferrocene (see Scheme 1 for the reaction scheme employed), which was subsequently transformed into **Ia** using the method described by Hayashi et al.[5a] Treatment of **Ia** with acetic anhydride led to the acetate **Ib**. Subsequent reaction of this compound with *n*-BuLi gave, after hydrolysis, the corresponding alcohol **Ic**, which was then reduced with $LiAlH_4$ in the presence of $AlCl_3$ to give BPPFMe (**1**).

Palladium(0) complexes were prepared from $Pd_2(dba)_3.CHCl_3$, *rac*-BPPFA, and an electron-withdrawing alkene, such as dimethyl fumarate (DMFU) or maleic anhydride (MA), as shown in eq 1. Excess dba was removed by column chromatography.

$$Pd_2(dba)_3{\cdot}CHCl_3 + 2BPPFA + 2L \rightarrow 2Pd(BPPFA)L + 3dba \quad (1)$$
2, **3**

L = DMFU (**2**), MA (**3**)

Chloride was removed from the dimer $[Pd(\eta^3\text{-2-Me-}C_3H_4)Cl]_2$ in a coordinating solvent, and subsequent addition of BPPFA gave the allyl complex **4** (see eq 2).

$$[Pd(\eta^3\text{-2-Me-}C_3H_4)Cl]_2 + 2AgTfO \rightarrow 2\,[Pd(\eta^3\text{-2-Me-}C_3H_4)(S)_2]TfO + AgCl \xrightarrow{2BPPFA} 2\,[Pd(\eta^3\text{-2-Me-}C_3H_4)(BPPFA)]TfO \quad (2)$$
4

Complexes **5**−**7** were prepared by substitution of 1,5-cyclooctadiene (cod) or tetramethylethylenediamine (TMEDA) from the corresponding precursors (see eq 3) with either *rac*-BPPFA or *rac*-BPPFMe.

$$PdR_2(L') + Fec \rightarrow PdR_2(Fec) + L' \quad (3)$$
5−**7**

L′ = cod, R = C_6F_5, Fec = BPPFA, **5**; L′ = cod, R = C_6F_5, Fec = BPPFMe, **6**; L′ = TMEDA, R = Me, Fec = BPPFA, **7**

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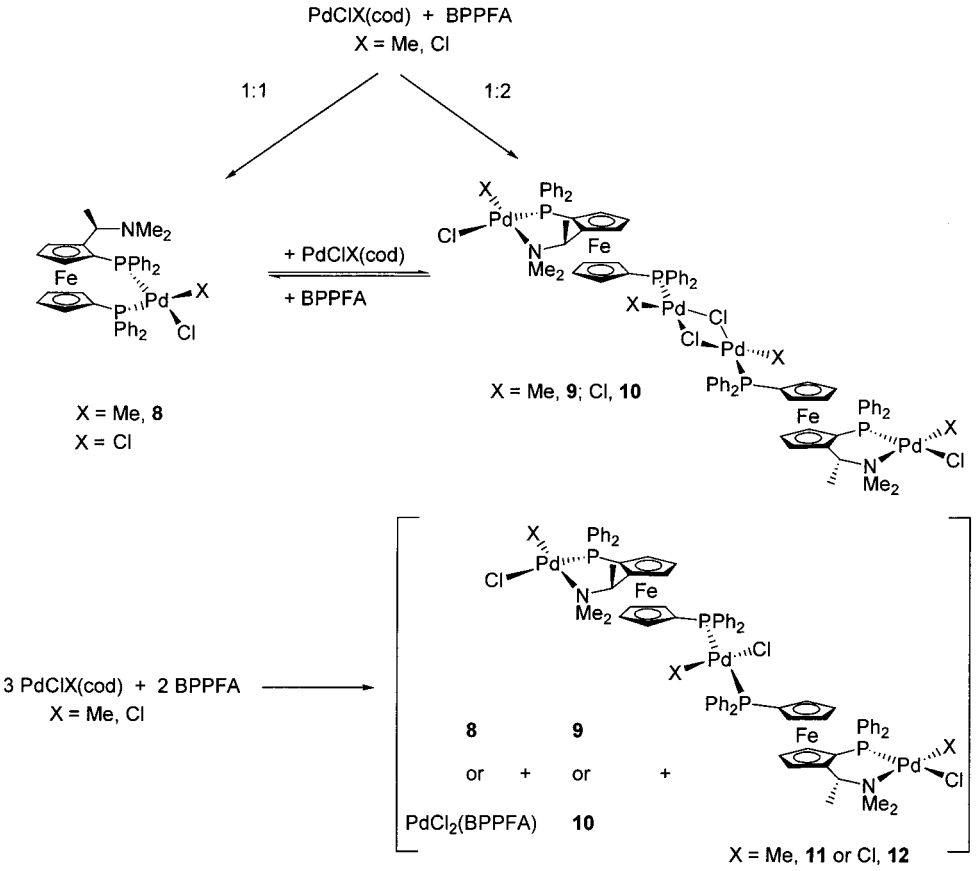
Scheme 2



Complex **7** reacts with halogenated solvents such as chloroform to give the corresponding chloromethyl derivative. The substitution of the second methyl group also takes place, but at a much slower rate. The synthesis of complex **5** was also carried out with an excess of the palladium precursor, but no other products were detected in this case.

In contrast, the outcome of the reaction between PdClMe(cod) or $PdCl_2$(cod) and BPPFA depends strongly on the stoichiometry. For these particular reactions enantiomerically pure (R_C,S_P)-BPPFA was used. When the reactions were carried out with a Pd:BPPFA ratio of 1:1, the expected mononuclear complex PdClMe(BPPFA) (**8**) or the previously described derivative $PdCl_2$(BPPFA)[12] was formed. With a Pd:BPPFA ratio of 2:1, the tetranuclear derivatives $[(PdClX)_2(BPPFA)]_2$ (X = Me (**9**), Cl (**10**)) were obtained (see Scheme 2 and Characterization of the New Derivatives). The use of a 1.5:1 ratio led to a more complicated situation: besides the corresponding mononuclear and tetranuclear derivatives, new trinuclear complexes of formula {*cis*-PdClX(μ-BPPFA)}$_2$(*trans*-PdClX) (X = Me (**11**), Cl (**12**)) were formed (see Scheme 2).

The same results were obtained after consecutive additions of 1, 0.5, and 0.5 equiv of PdClX(cod) to 1 equiv of BPPFA in an NMR tube. In the case where X = Cl, the addition of 0.5 equiv of $PdCl_2$(cod) to $PdCl_2$(BPPFA) was monitored by ^{31}P NMR spectroscopy at room temperature. Although three products were initially present ($PdCl_2$(BPPFA), **10**, and **12**), an increase in the amount of trinuclear complex **12** was observed with time along with a concomitant decrease in the amounts of $PdCl_2$(BPPFA) and **10**. After approximately 1 h the equilibrium ratio (**12**:$PdCl_2$(BPPFA):**10** = 3:2:1) was reached. This observation proves that **12** can be formed by reacting 2 equiv of $PdCl_2$(BPPFA) with 1 equivalent of tetranuclear **10**. Addition of 2 equiv of BPPFA to **9** or **10** resulted in the formation of **8** or $PdCl_2$(BPPFA), respectively. The different transformations specified above show that the mononuclear, trinuclear, and tetranuclear derivatives are present in a reversible equilibrium that mainly depends on the Pd:BPPFA stoichiometry.

Characterization of the New Derivatives. All new complexes were characterized by elemental analysis, IR spectroscopy, and ^{1}H, ^{19}F, ^{31}P{^{1}H} (see Table 1), and ^{13}C{^{1}H} NMR spectroscopy. COSY, NOE, and selective ^{31}P decoupling experiments were used to gain additional structural information. In some cases FAB mass spectra were also recorded.

All data for the BPPFMe ligand (**1**) are in accordance with the structure proposed (see Table 1 and Experimental Section).

(a) Mononuclear Derivatives. The ^{31}P{^{1}H} and ^{1}H NMR spectra of compounds **5**−**7** show only one species, whereas the spectra for **2**−**4** and **8** show the presence in solution of two isomers in different ratios. In the ^{31}P{^{1}H} NMR spectra, either two doublets or an AB system is observed for each product or isomer. The chemical shifts and the presence of P−P couplings are indicative of P,P-coordination. In complexes **5** and **6** the P−P coupling is not observed, probably due to signal broadening caused by multiple coupling with the fluorine nuclei of the pentafluorophenyl groups ($W_{1/2}$ = 70 Hz). The absence of diastereotopic methyl signals for the NMe_2 group in their respective ^{1}H or ^{13}C{^{1}H} NMR

Table 1. $^{31}P\{^1H\}$ NMR Data for Ligands and Complexes 2−12 at Room Temperature[a]

complex or ligand	M[b]	m
BPPFA[c]	−18.37, −23.93	
BPPFA[d]	−14.78, −20.57	
1[d]	−20.05, −24.81	
2[d]	15.45 (d), 14.86 (d), J_{PP} =9.2	AB system, 17.18, 17.03, J_{PP} = 13.6
3[c]	21.38 (d), 20.36 (d), J_{PP} = 25.0	22.43 (d), 19.52 (d), J_{PP} = 22.6
4[c]	AB system, 25.73 (d), 25.07 (d), J_{PP} = 37.3	AB system, 26.01, 24.41, J_{PP} = 37.5
5[d]	P_A, 17.33 (b s); P_B, 10.39 (b s)	
6[d]	P_A, 19.05 (b s); P_B, 17.26 (b s)	
7[d]	P_A = 20.93(d), P_B = 16.75(d), J_{PP} = 20.1	
8[d]	P_A = 36.03 (d), P_B = 8.22 (d), J_{PP} = 31.1	37.37 (d), 15.46 (d), J_{PP} = 28.0
9[d]	P_A, 25.51; P_B, 31.24	
10[e]	P_A, 11.53; P_B, 31.64	
11[d]	P_A, 25.13; P_B, 22.47	
12[e]	P_A, 11.44; P_B, 16.43	

[a] Singlets, if not indicated otherwise. δ in ppm, J in Hz. [b] For P_A and P_B see Chart 4. [c] In acetone-d_6. [d] In benzene-d_6. [e] In chloroform-d.

spectra and the position of the resonances are consistent with a noncoordinated dimethylamino nitrogen. A partial assignment of the phenyl protons was made, with the ortho protons that are coupled to phosphorus being the most easily recognized. In complexes **5** and **6** some of these protons are also coupled to fluorine. Interestingly, as in the case of (BPPFA)$PdCl_2$, the protons of the stereogenic center (C*H) in complexes **7** and **8** appear at high chemical shifts (5.80 (**7**) and 5.87 ppm (**8**)), while the corresponding protons in all other complexes appear in the range 3.98−4.94 ppm. This effect is likely to be the result of comparable preferred conformations of (BPPFA)$PdCl_2$, **7**, and **8** in solution. A more detailed structural comparison of (BPPFA)$PdCl_2$ and **8** is made in the discussion below.

Considering the asymmetry of the ferrocenyl diphosphine ligands and the results previously obtained with similar palladium complexes of ferrocenyl aminophosphine ligands,[10] the isomers of complexes **2**−**4** and **8** were assigned as follows: (i) face isomers in the case of complex **2** (either the *Si* or the *Re* face of the olefin is coordinated to Pd), (ii) rotamers in the case of **3** and **4** with the endocyclic oxygen (**3**) or the allyl fragment (**4**) oriented either endo or exo with respect to the CHMe-NMe_2 group, and (iii) geometrical isomers (**8**) with the chloride or methyl groups cis to either one or the other ferrocenyl phosphorus atom (see Chart 2).

At room temperature both isomers of complex **2** give rise to two resonances for the alkene protons (AB system for the minor isomer) and for the ester methyl groups (resonance ratio 77:23). This observation rules out a rapid alkene rotation about the Pd−alkene axis at this temperature. The same situation applies to complex **3**, since separate signals are observed at room temperature for the two isomers (isomer ratio 67:33). The allyl groups of both diastereomers (isomer ratio 62:38) of complex **4** are asymmetric, with the H_{syn} protons appearing as broad pseudotriplets while the H_{anti} protons give rise to doublets with higher phosphorus coupling constants.

NOE studies were performed in order to determine the structure of each diastereomer of complexes **2** and **8**. Complexes **2** and **8** were chosen, because in each case the solid-state structure of one diastereomer had been elucidated by an X-ray diffraction study (see below). Hence, it was of interest to find out whether the major diastereomers in solution (C_6D_6) were identical with those found in the solid state. In the case of **2** it is necessary to bear in mind that this complex was prepared from racemic BPPFA. To simplify the following discussion, we will refer to the (R_C,S_P)-BPPFA enantiomer only. The most important NOE interactions found for the major isomer **2M** (**M** = major isomer) are indicated with arrows in Chart 3.

When the dimethylamino group was irradiated, an NOE was found with the alkene signal at 4.84 ppm. This interaction could only arise when the alkene Re face is coordinated to the Pd[(R_C,S_P)-BPPFA] fragment. In addition, a very weak NOE with the other olefin resonance at 5.23 ppm was observed, which might be an indication of a certain degree of alkene rotation, albeit slow enough not to give rise to any signal broadening at room temperature. The structural assignment of the major isomer is also in agreement with the NOE observed between the methyl group at the

Chart 2

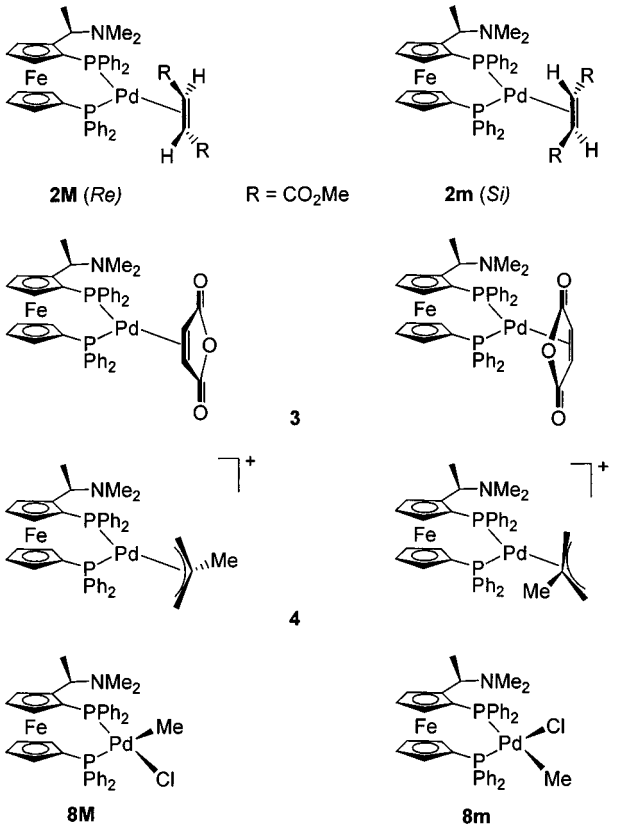


Chart 3

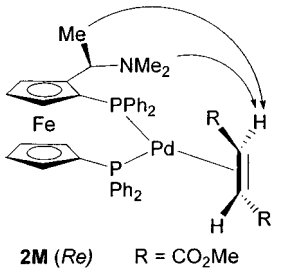
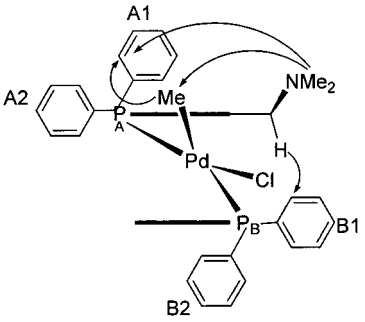


Chart 4



asymmetric carbon and the resonance at 4.84 ppm. In a similar NOE study the major diastereomer of complex **8** (**8M**) was found to be identical with that in the solid state. The phenyl ortho protons were first correlated with their respective phosphorus resonances. The cis or trans arrangement of the Pd−Me group with respect to the ligand phosphorus atoms was established by selective ^{31}P decoupling. The most important NOEs concerning the orientation of the methyl group are indicated in Chart 4 and are consistent with the methyl group being trans to the phosphorus P_B.

In the cases of complexes **5** and **6** the ^{19}F NMR spectra indicate the presence of two distinct pentafluorophenyl groups in a state of restricted rotation with respect to the Pd−C bond. Thus, for both derivatives four multiplets are observed for the ortho fluorines and two doublets of doublets for the para substituents. The resonances of the *m*-fluorine nuclei are partially overlapped. ^{19}F−^{19}F-COSY spectra were recorded for both complexes. In the spectrum of complex **6**, two sets of ^{19}F signals corresponding to the individual pentafluorophenyl rings could be identified by analyzing the cross-peaks between the F_{para}−F_{meta} and F_{meta}−F_{ortho} nuclei. Remarkably, the ^{19}F−^{19}F-COSY spectrum also shows inter-ring coupling interactions of different intensity between the ortho fluorines F_{a1}−F_{b1} and F_{a2}−F_{b2} (see Figure 1). This situation indicates a preferred conformation of the pentafluorophenyl rings in which the strongly coupled fluoro substituents F_{a1}−F_{b1} are in close proximity.[14] The accidental isochrony of three F_{meta} substituents in complex **5** did not allow the unambiguous assignment of all fluorine resonances of the two rings or allow evidence to be obtained for a coupling interaction between the ortho fluorines of nonidentical rings.

(b) Polynuclear Derivatives. As stated previously, derivatives **11** and **12** are always obtained as one component of a product mixture. However, the use of enriched samples, obtained by recrystallization, allowed a signal assignment to be made.

All polynuclear species show several common characteristics in their NMR spectra (i) Two singlets in the ^{31}P NMR spectra that are shifted to lower field with respect to those of free BPPFA, a situation in agreement with coordination to a Pd center. The absence of P−P coupling indicates that the two phosphorus atoms are

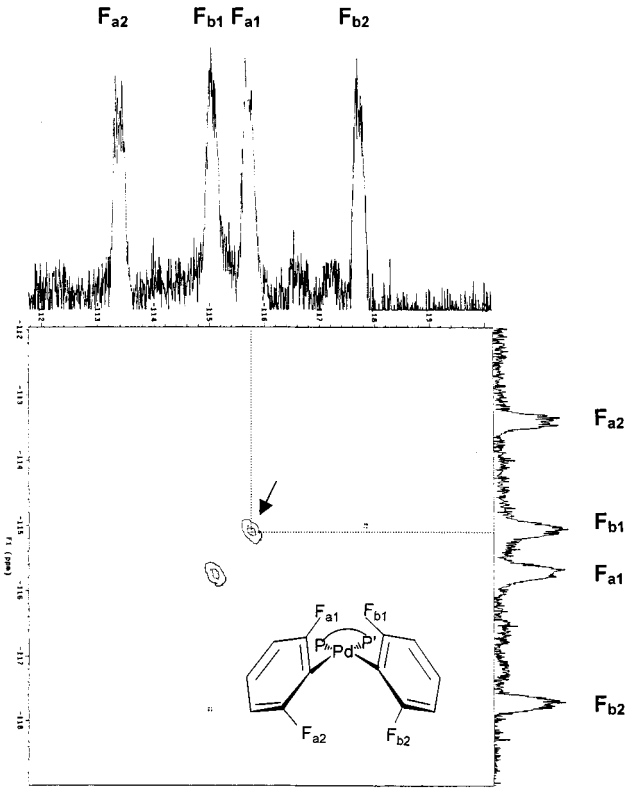


Figure 1. ^{19}F−^{19}F-COSY of complex **6** (F_{ortho} region). The cross-peak marked with the arrow reflects the interannular F_{a1}−F_{b1} coupling; the smaller cross-peak corresponds to an intraannular F_{b1}−F_{b2} coupling.

coordinated to different metal centers. (ii) In both the ^{1}H and ^{13}C NMR spectra, two different singlets, assigned to the aminomethyl groups, appear at frequencies higher than those of the free ligand. These diastereotopic signals are indicative of P,N coordination. (iii) Only one set of resonances is seen for each type of ferrocenyl ligand, reflecting a certain degree of symmetry in the complexes.

The resonances of the Pd−Me groups proved to be very useful in elucidating the structure of the chloromethyl derivatives **9** and **11**. For each complex two types of Pd−Me groups are observed, implying the presence of two different palladium centers. The values for the H−P coupling constants (4.1−6.4 Hz) are in accordance with a cis arrangement of the methyl groups and the phosphorus atoms. The absence of observable J_{CP} coupling constants in the corresponding ^{13}C NMR spectra also supports this view. In the ^{1}H NMR spectrum of complex **11**, the methyl groups give rise to a doublet and a triplet in a 2:1 ratio. All the data for complex **11** are consistent with the trinuclear structure shown in Scheme 2, in which a *trans*-PdClMe group connects two *cis*-PdClMe(μ-κ^3-BPPFA) units. For the tetranuclear complex **9**, two signals in a 1:1 ratio are observed for the methyl groups. For complex **9** we propose a structure in which the dinuclear central unit [MePd(μ-Cl)$_2$PdMe] connects two terminal *cis*-PdClMe(μ-κ^3-BPPFA) moieties (Scheme 2). Structures similar to those of **9** and **11** are proposed for complexes **10** and **12**. In these cases a central [$PdCl_2$] (**12**) or a [ClPd(μ-Cl)$_2$PdCl] (**10**) unit with a trans geometry is present that minimizes steric repulsions between the two terminal units. This effect is particularly important in complex

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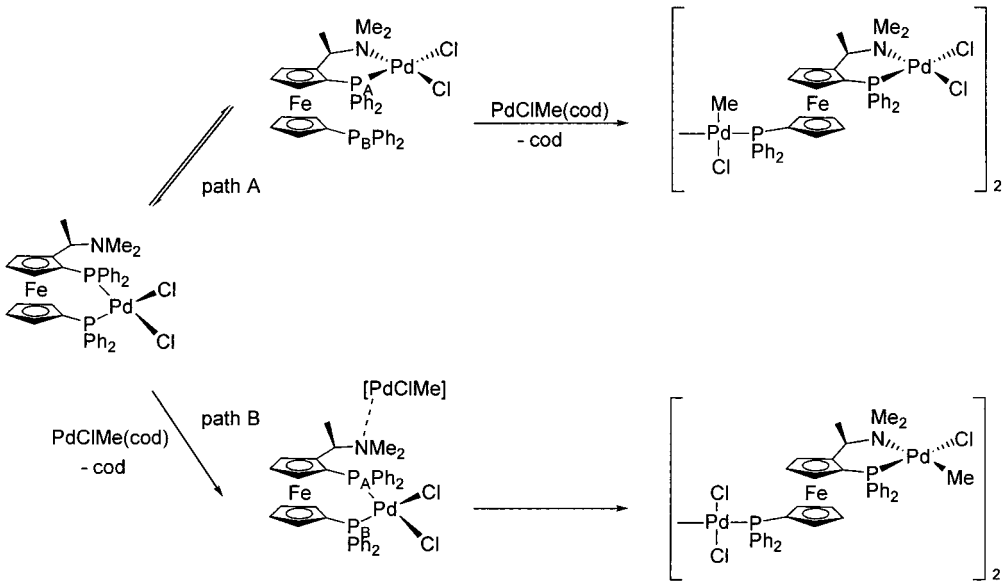
Scheme 3



12. Several of the ^{1}H and ^{13}C NMR resonances, as well as the ^{31}P NMR resonances, in the tetranuclear derivatives **9** and **10** are broad at room temperature. This could indicate a fluxional process that is likely to involve the central unit.

For the polynuclear compounds **9**−**12**, the ^{31}P NMR resonances (see Table 1) of the terminal κ^2-*P*,*N*-PdClX (X = Cl, Me) groups were assigned by comparison with those of the complexes PdClMe(PPFA)[10b] (24.09 ppm) and $PdCl_2$(PPFA)[15] (13.73 ppm). As expected, these chemical shifts are very similar for species with identical terminal units, e.g. **9** and **11** or **10** and **12**. The assignment of all other phosphorus resonances was straightforward.

A transfer of magnetization between the two aminomethyl groups was observed in complex **11** at room temperature. According to our previous studies with similar ligands[10] this interchange is due to a Pd−N bond rupture process, which is likely to be favored by the high trans influence of the methyl groups. Additional evidence for this process is provided by a pronounced broadening of the aminomethyl signals at 55 °C ($CDCl_3$) in the ^{1}H NMR spectrum. In the case of **9** (C_6D_6) the coalescence between the two aminomethyl resonances was actually reached at 331 K, indicating a free energy of activation of $\Delta G^{\ddagger}_{331} = 64.9$ kJ mol^{-1}, a value similar to those found for PPFA complexes.[10]

The FAB mass spectra of the isolated complexes **9** and **10** are in accordance with the proposed polynuclear compositions. Although the signal corresponding to the molecular ion was not detected, fragments with four or three palladium atoms, such as $[Pd_4Cl_4Me_2(BPPFA)_2]^+$ for **9** or $[Pd_3Cl_5(BPPFA)_2]^+$ for **10**, were identified (see Experimental Section for fragmentation details). The IR spectra of these complexes show bands assigned to Pd−$Cl_{terminal}$ and Pd−Cl_{bridge} (see Experimental Section).

To obtain additional information about the mechanism of formation of the polynuclear species, particularly the tetranuclear complexes, we monitored the reaction of $PdCl_2$(BPPFA) with 1 equiv of PdClMe(cod) by ^{31}P{^{1}H} NMR spectroscopy. A Pd:BPPFA ratio of 2:1 is appropriate for the formation of tetranuclear species. However, considering that two different palladium fragments are involved, it is feasible, from a statistical point of view, that eight other tetranuclear species can be formed in addition to complexes **9** and **10**. After the first few minutes of the reaction only two pairs of singlets (in a ratio of 8:2) were observed in the region of the P-coordinated BPPFA phosphorus nuclei (major, 31.00 and 12.05 ppm; minor, 31.38 and 27.38 ppm). These signals do not correspond to those of complexes **9** and **10** (see Table 1) but are due to two new compounds. After a reaction time of 30 min new signals with more complicated patterns appeared and the amount of the initial products, especially the major component, decreased. The simplicity of the ^{31}P NMR pattern for both initial products is consistent with C_2 symmetry. Apart from **9** and **10** only two dispositions fit this condition, those with terminal PdClMe and central $PdCl_2$ fragments or the reverse situation. All other isomers are C_1-symmetrical and would be expected to give rise to four ^{31}P signals. Comparison of the chemical shifts of signals for the initially formed compounds with those of complexes **9**, **10**, and PdClX(PPFA) (X = Cl, Me) revealed that the major isomer must be the complex {*cis*-$PdCl_2$(μ-κ^3-BPPFA)}$_2$(MePd(μ-Cl)$_2$PdMe) with terminal (*P*,*N*-BPPFA)$PdCl_2$ units, while the minor isomer corresponds to {*cis*-PdClMe(μ-κ^3-BPPFA)}$_2$(ClPd(μ-Cl)$_2$PdCl) with terminal (*P*,*N*-BPPFA)PdClMe units (see Scheme 3).

It is clear that the formation of both initial products proceeds in a highly selective manner, and this can be understood by invoking two different kinetically favored reaction pathways. The major isomer is likely to be the result of a P,P to P,N coordination shift of the $PdCl_2$ unit of $PdCl_2$(BPPFA), coordination of a PdClMe unit to P_B, and dimerization of two identical dinuclear units (Scheme 3, path A). The formation of the minor isomer, on the other hand, is represented in path B. The sequence involves coordination of the PdClMe fragment to the noncoordinated nitrogen of the $PdCl_2$(BPPFA) complex, cleavage of the $PdCl_2$−P_A bond, P,N coordina-

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tion of the PdClMe unit, and subsequent dimerization. Both C_2-symmetric initial products must be the result of kinetic control, while all other isomers are formed at a much slower rate, presumably through scrambling processes. In both pathways A and B, one Pd−P bond must be opened up for the process to proceed.

Pd−N Interactions in the Mononuclear Derivatives. To identify additional fluxional processes, including Pd−N interactions in the mononuclear complexes, variable-temperature NMR experiments with derivatives **2**, **3**, and **5**−**8** were carried out.

The ^{1}H NMR spectrum of complex **3** did not change significantly, even on cooling the sample down to −80 °C. In contrast, decreasing the temperature of complex **2** led to a splitting of the signal for the aminomethyl group in the ^{1}H NMR spectrum, a situation consistent with an interaction between the metal center and the aminomethyl nitrogen. The shift difference ($\delta\nu$) between the diastereotopic methyl groups in the slow exchange regime is similar to that observed for P,N-coordinated PPFA complexes.[10,15] These signals coalesce at 203 K, corresponding to a $\Delta G^{\ddagger}_{203}$ value for the Pd−N bond rupture of 38 kJ mol^{-1}. As mentioned above, this barrier is considerably higher in tetracoordinated κ^2-*N*,*P*-PPFA complexes.[10]

When the ^{1}H NMR spectrum of complex **7** (toluene-d_8) was recorded at 183 K, the aminomethyl signal was seen to broaden significantly ($W_{1/2}$ = 100 Hz at 183 K) but did not split into two separate signals. However, splitting of the aminomethyl group resonance was observed for the major isomer of the chloromethyl complex **8** when the temperature was decreased. As in complex **2**, the most plausible explanation for this fact is the existence of an interaction between the nitrogen atom of the side chain and the palladium center. The barrier associated with the exchange of the aminomethyl signals was calculated to be $\Delta G^{\ddagger}_{193}$ = 36 kJ mol^{-1}. In addition, at low temperature a splitting of the ortho proton resonances of rings A2 and B1 (Chart 4) was observed. This fact can be explained in terms of a restricted rotation of these phenyl groups at low temperature. No further splitting was observed in either the ^{1}H or ^{31}P NMR spectra.

Variable-temperature ^{1}H and ^{31}P{^{1}H} NMR studies were carried out on complex **5** over the temperature range 193 K to room temperature. The ^{31}P{^{1}H} NMR spectrum at 193 K contained four broad singlets corresponding to two P,P-coordinated BPPFA complexes in a 3:1 ratio. When the temperature was increased, these resonances coalesced in pairs ($\Delta G^{\ddagger}_{228}$ = 45.6 and $\Delta G^{\ddagger}_{253}$ = 44.9 kJ mol^{-1}), leading to the expected equilibrium of two rapidly interchanging species at room temperature. Unfortunately, severe signal overlap in the ^{1}H NMR spectrum at 193 K makes the aromatic and cyclopentadienyl regions rather complex. The presence of two species in a 3:1 ratio was, however, confirmed from the *C−Me signals.

From the coalescence of these signals a free energy of activation of 45.8 kJ mol^{-1} at 233 K was calculated, which is in good agreement with the values deduced from the ^{31}P NMR spectra. The aminomethyl signals show an interesting pattern (Figure 2): three resonances in a ratio of 1.5:1.5:1 were observed, indicating a mixture of two isomers. We interpret the diastereotopic nature of the methyl groups of the major component (A) as being caused by coordination of the amino nitrogen to the palladium center. All three aminomethyl signals broaden when the temperature is increased and only one resonance is observed at temperatures above 233 K, a fact consistent with the existence of two rapidly interconverting isomers. Consequently, and in contrast to the complexes described above, a second species with a noncoordinated aminomethyl group is observed for compound **5** at low temperature. To establish the influence of the aminomethyl group on the equilibrium between the two isomers of **5**, the bis(pentafluorophenyl)palladium complex of ligand **1**, i.e., complex **6**, was investigated. When the temperature was lowered to 193 K, neither a second isomer nor any other splitting of ^{31}P or ^{1}H NMR resonances of **6** was observed.

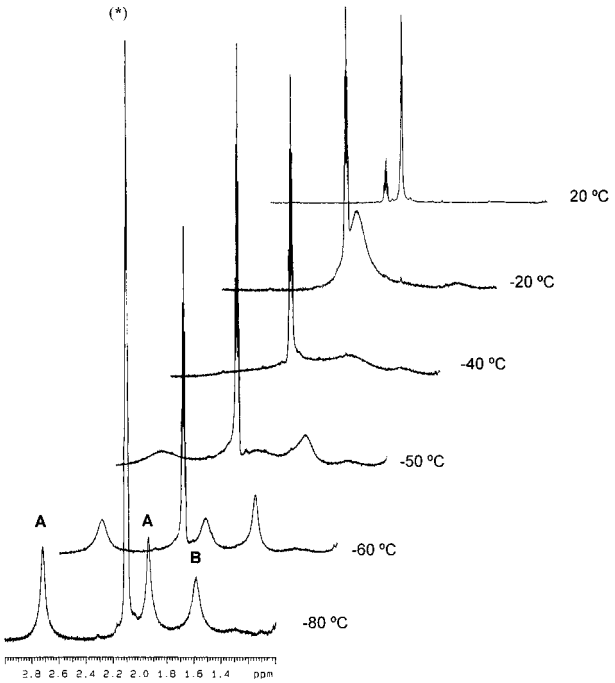
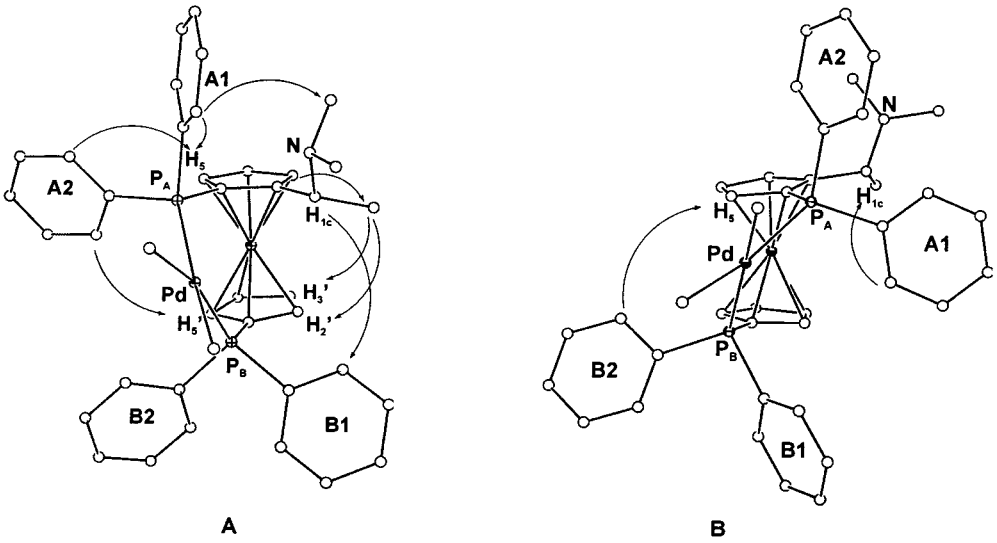


Figure 2. Variable-temperature NMR spectra of complex **5** (aminomethyl region). A and B indicate the signals corresponding to conformers A and B (Chart 5); the asterisk indicates a residual signal for toluene-d_8.

In accordance with the known X-ray structures of Pd complexes of BPPFA,[12] dppf[16] (1,1′-bis(diphenylphosphino)ferrocene), and similar ligands,[13c,17] the Cp rings always adopt a staggered or nearly staggered conformation. Such an arrangement means that two conformers (A and B in Chart 5) are possible for P,P-coordinated complexes and these would be interconvertible by a mutual twist of the Cp rings. It is generally assumed for dppf complexes that even at low temperatures such conformers are in a dynamic equilibrium with a very low energy barrier.[18] Hayashi et al.[12] have reported that for BPPFA derivatives conformer B is disfavored due to steric hindrance between the alkyl side chain and one of the phenyl groups (A2 in Chart 5). Indeed, conformer A has been found exclusively in all known X-ray structures of BPPFA complexes ($PdCl_2$·BPPFA,[12] **2** and **8**). As can be seen from Chart 5, in the case of BPPFA Pd(II) complexes conformer A is well-suited for an

Chart 5



interaction between the NMe_2 nitrogen and palladium while conformer B is not.

The minor isomer of **5** lacks such a Pd−N interaction, and therefore its conformation is likely to be B. It should be mentioned that conformer B is not unprecedented. Such a system has been found in the solid-state structure of a palladium dichloride complex with a C_2-symmetric BPPFA related ligand (2,2′-bis(1-(dimethylamino)ethyl)-1,1′-bis(diphenylphosphino)ferrocene).[17] To find further evidence to support this view, we carried out a number of room-temperature NOE experiments on complexes **5**−**8**. The observed NOE correlations are nearly identical for all complexes and are indicated in Chart 5. Practically the whole set of NOEs is consistent with the presence of conformer A in solution. In fact, some NOEs, for example those observed between the ortho Ph protons of rings A1 with H_5 and A2 with $H_{5'}$ (see Chart 5), are only possible in conformer A and not in conformer B. However, an additional NOE—between the ortho Ph protons of ring B2 and H_5 of Cp_A—was observed in complexes **5** and **6** but not in complexes **7** and **8**. Such an interaction is only possible in conformer B and constitutes indirect evidence for the presence of this conformer in solution for the pentafluorophenyl derivatives **5** and **6** but not for **7** and **8** (see Chart 5).

In summary, according to the VT-NMR and NOE results, only the pentafluorophenyl complexes **5** and **6** exist in solution in an equilibrium of rapidly interconverting conformers, with conformer A being the more stable. In addition, in comparison to **6** the interconversion barrier of the two conformers of **5** is sufficiently high to be measured by VT-NMR and is likely to be influenced by the Pd−N interaction in conformer A.

In conclusion, a Pd−N interaction has been found not only in Pd(II) complexes (**5**, **7**, **8**) but also in a Pd(0) complex (**2**). In all these cases, the low-temperature chemical shifts of the ^{31}P NMR resonances indicate that both phosphorus atoms are coordinated, thus showing the ability of BPPFA to act as a terdentate chelating κ^3N,P,P ligand. To the best of our knowledge, this type of coordination for BPPFA is described here for the first time. Although pentacoordinated palladium(II) complexes[19] have been described not only as being intermediates[19a,20] or being in equilibrium with the square-planar species[21] (in the presence of excess of ligand) but also as isolated compounds,[22] sometimes together with their

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Table 2. Crystal Data and Structure Refinement for 2 and 8·½C$_6$H$_6$

	2	**8**·½C$_6$H$_6$
empirical formula	$C_{44}H_{45}FeNO_4P_2Pd$	$C_{42}H_{43}ClFeNP_2Pd$
fw	876.00	821.42
temp, K	293(2)	297(2)
wavelength, Å	0.710 70	0.710 73
cryst syst, space group	monoclinic, $P2_1/c$	monoclinic, $P2_1$
unit cell dimens		
a, Å	10.696(3)	18.258(4)
b, Å	18.060(6)	10.126(3)
c, Å	20.672(8)	22.275(5)
β, deg	94.60(2)	113.61(2)
V, Å^3	3980(2)	3773.5(16)
Z; calcd density, Mg/m^3	4; 1.462	4; 1.446
abs coeff, mm^{-1}	0.940	1.047
max and min transmissn	1.000 and 0.715	1.00 and 0.90
F(000)	1800	1684
crystal size, mm	0.2 × 0.2 × 0.4	0.07 × 0.11 × 0.68
θ range for data collecn, deg	2.22−27.99	2.00−30.00
limiting indices	$0 \le h \le 14$ $0 \le k \le 23$ $-27 \le l \le 27$	$-25 \le h \le 25$ $-14 \le k \le 14$ $-31 \le l \le 31$
no. of rflns collected/ unique	9562/9562 (R(int) = 0.0000)	54 537/21 293 (R(int) = 0.037, $R(\sigma)$ = 0.053)
no. of data/restraints/ params	9562/0/478	21 293/1/865
goodness of fit on F^2	0.906	0.971
final R indices ($I > 2\sigma(I)$)	R1 = 0.0316, wR2 = 0.0532	R1 = 0.0353, wR2 = 0.0672
R indices (all data)	R1 = 0.0653, wR2 = 0.0642	R1 = 0.0584, wR2 = 0.0742
largest diff peak and hole, e Å^{-3}	0.482 and −0.531	0.322 and −0.337

solid-state structure,[23] the coordination number 5 is not common in palladium(II) chemistry.

X-ray Structures of Complexes 2 and 8. Crystallographic data of **2** and **8** are given in Table 2.

Complex **2** crystallizes in the monoclinic space group $P2_1/c$ with four molecules per unit cell. An ORTEP plot of the molecular structure of **2** is shown in Figure 3.

In agreement with the data obtained on the complex in solution, the alkene *Re* face is coordinated to a [(R_C,S_P)-BPPFA]Pd unit. The structural features of BPPFA are as expected, with average $C_{ar}-C_{ar}$ bond distances of 1.422(4) Å and the two Cp rings slightly tilted with respect to each other by 2.7(1)°. The alkene double-bond length C3−C4 was found to be 1.407(4) Å, which is similar to that in the corresponding PPFA derivative.[10a] The square-planar unit shows a slight pyramidal distortion, with the plane C3−Pd−C4 tilted with respect to the plane P1−Pd−P2 away from the dimethylamino group with normal distances of 0.273 Å for C4 and 0.202 Å for C3. The two phosphorus atoms lie almost in the plane of their respective Cp rings, with deviations of 0.045 Å for P1 and 0.008 Å for P2. As depicted in Figure 3 (right projection), the Cp rings adopt a synclinal staggered conformation with P1 situated between P2 and the 1-(dimethylamino)ethyl substituent. A rather large bite angle (P1−Pd1−P2) of 105.68(3)° was found.

Complex **8** crystallizes from benzene in the form of the stable solvate **8**·½C$_6$H$_6$, which adopts the monoclinic space group $P2_1$. The asymmetric unit contains two independent Pd complexes with very similar dimensions and shapes. The molecular structure of one independent complex molecule is shown in Figure 4.

The configuration of both molecules is identical with that found for the major isomer in solution, with the methyl group (attached to palladium, C11) positioned cis with respect to P1. The C_p rings adopt a staggered conformation with the bond C31−P2 bisecting the bond C21−C22 (Figure 4, right projection). All other structural features of BPPFA are as expected. In contrast to **2**, the P1−Pd−P2 bond angle is only slightly opened up to 98.0°.

Structural Comparison of 2, 8·½C$_6$H$_6$, and PdCl$_2$(BPPFA).[12] All three complexes adopt a similar overall conformation (conformation A, Chart 5) with staggered Cp rings. While the molecular structures of PdCl$_2$(BPPFA) and **8**·½C$_6$H$_6$ are almost superimposable, significant differences are seen in **2**. In particular, as compared to PdCl$_2$(BPPFA), the phenyl rings of the diphenylphosphino groups are rotated in order to minimize steric interactions with the DMFU unit. Interestingly, the position of the dimethylaminoethyl side chain is almost identical in all three complexes. Hence, the chemical shift differences seen for the *CH protons of **2** as compared to PdCl$_2$(BPPFA) and **8**·½C$_6$H$_6$ are likely to be caused by conformational changes of the diphenylphosphino phenyl groups rather than by changes in the (dimethylamino)ethyl unit.

Conclusions

BPPFA reacts with Pd(0) or Pd(II) fragments to give mononuclear P,P- but not P,N-coordinated complexes. With proper fragments (Pd(alkene), Pd(CH$_3$)Cl, and Pd(2-Me-C$_3$H$_4$)$^+$), diastereomers are formed with a certain degree of selectivity but in neither Pd(0) or Pd(II) complexes was an isomer interconversion observed at room temperature on the NMR time scale.

Depending on the Pd:BPPFA ratio, tri- or tetranuclear complexes containing PdClX (X = Cl, Me) fragments and μ-κ^3*N*,*P*,*P*-BPPFA ligands are formed. This implies that catalytic reactions carried out "in situ" using "Pd^{II}ClX" precursors and BPPFA must be performed with careful control of the Pd:BPPFA ratio in order to prevent a serious perturbation of regio- and enantioselectivity by polynuclear species with trans PdClX units. In a mechanistic study a crossover reaction between PdCl$_2$(BPPFA) and PdClMe(cod) complexes was carried out, and in the

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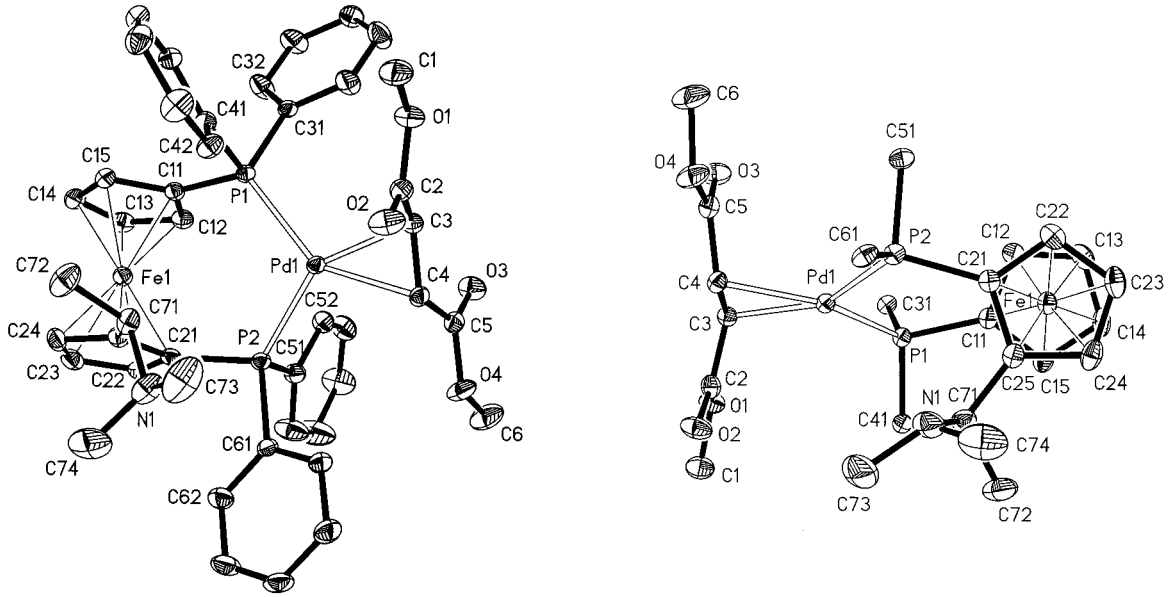

Figure 3. Molecular structure of Pd(BPPFA)(DMFU) (**2**) in the crystalline state showing 20% thermal ellipsoids (hydrogen atoms omitted, benzene rings in right view omitted). Selected bond lengths and angles (Å, deg): Pd(1)−P(1) = 2.3404(9), Pd(1)−P(2) = 2.3426(10), Pd(1)−C(3) = 2.131(3), Pd(1)−C(4) = 2.131(3), <Fe(1)−C> = 2.036(3), P(1)−C(11) = 1.808(3), P(2)−C(21) = 1.811(3), C(3)−C(4) = 1.407(4); P(1)−Pd(1)−P(2) = 105.68(3), P(1)−Pd(1)−C(3) = 107.6(1), P(1)−Pd(1)−C(4) = 146.2(1), P(2)−Pd(1)−C(3) = 146.2(1), P(2)−Pd(1)−C(4) = 107.3(1), C(3)−Pd(1)−C(4) = 39.0(1).

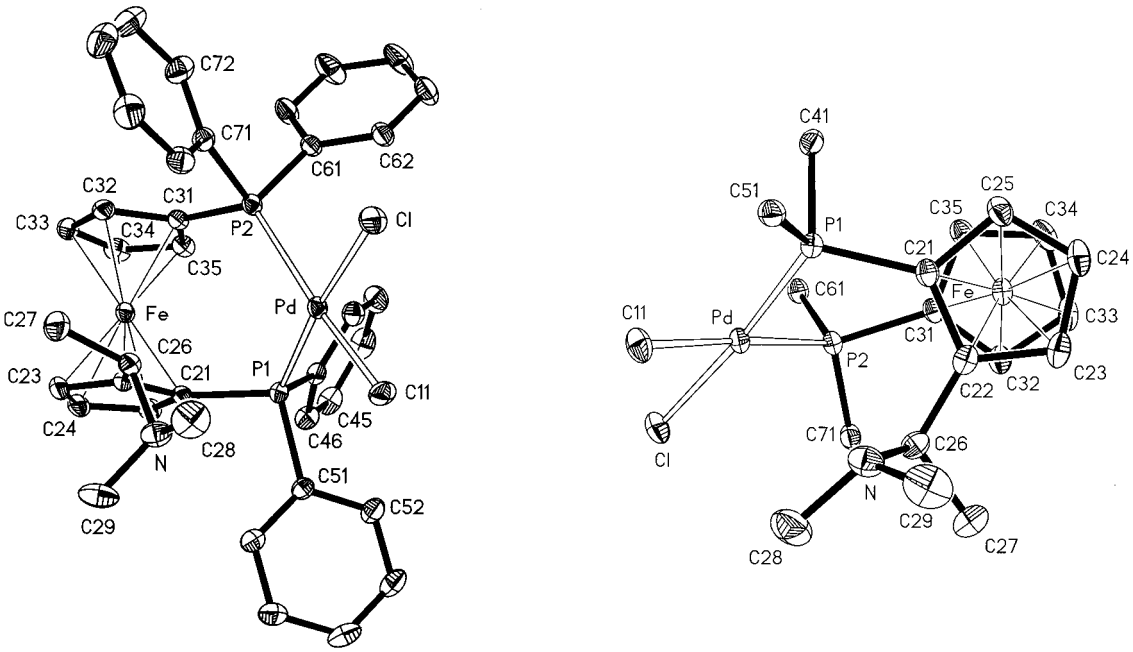

Figure 4. Molecular structure of PdClMe(BPPFA) (**8**·$^1/_2C_6H_6$) in the crystalline state showing one of the two independent but geometrically similar complexes with 20% thermal ellipsoids (hydrogen atoms omitted, benzene rings in right view omitted). Selected bond lengths and angles (Å, deg): Pd−P(1) = 2.2631(9), Pd−P(2) = 2.4276(9), Pd−Cl = 2.3713(9), Pd−C(11) = 2.089(3), <Fe−C> = 2.040(3), P(1)−C(21) = 1.816(3), P(2)−C(31) = 1.826(3); P(1)−Pd−P(2) = 97.99(3), P(1)−Pd−Cl = 173.62(3), P(1)−Pd−C(11) = 87.6(1), P(2)−Pd−Cl = 88.06(3), P(2)−Pd−C(11) = 174.3(1), Cl−Pd−C(11) = 86.3(1).

initial state only the two feasible C_2-symmetric tetranuclear products were formed. This fact implies that the BPPFA ligand can shift from a P,P to a P,N coordination involving a Pd−P bond rupture process.

Coordination of the NMe_2 group not only to Pd(II) but also to Pd(0) has been identified in mononuclear *P*,*P*-BPPFA−Pd complexes at low temperature. Consequently, an unprecedented chelating κ^3*P*,*P*,*N*-BPPFA coordination is present in solution in a dynamic equilibrium with the κ^2*P*,*P*-BPPFA form. An equilibrium was found in the pentafluorophenyl derivatives **5** and **6** between two conformers that are interconvertible by a torsional twist of the Cp rings. Only in the case of complex **5** could this interconversion process be slowed, presumably due to the palladium−nitrogen interaction.

In summary, we have demonstrated that in mononuclear *P*,*P*-BPPFA Pd(II) and Pd(0) complexes the dimethylamino nitrogen can interact with the metal center. This interaction can not only slow conformational interchanges but is also thought to facilitate structural rearrangements such as P,P to P,N changes in the BPPFA coordination mode.

Experimental Section

General Comments. All manipulations were carried out under an atmosphere of dry oxygen-free nitrogen using standard Schlenk techniques. Solvents were distilled from the appropriate drying agents and degassed before use. Elemental analyses were performed with a Thermo Quest FlashEA 1112 microanalyzer. IR spectra were recorded as KBr pellets or Nujol mulls on a Perkin-Elmer PE 883 IR spectrometer. FAB mass spectra were recorded with a VG BIOTECH Quattro spectrometer using 3-NBA as matrix. ^{1}H, ^{13}C{^{1}H}, ^{19}F, and ^{31}P-{^{1}H} NMR spectra were recorded on a Varian Unity 300 or Bruker AC-250 spectrometer. Chemical shifts (ppm) are relative to TMS (^{1}H, ^{13}C NMR), $CFCl_3$ (^{19}F), and 85% H_3PO_4 (^{31}P NMR). The abbreviation pt refers to pseudotriplet. COSY spectra: standard pulse sequence, acquisition time 0.214 s, pulse width 10 μs, relaxation delay 1 s, 16 scans, 512 increments. The NOE difference spectra were recorded with 5000 Hz, acquisition time 3.27 s, pulse width 90°, relaxation delay 4 s, and irradiation power 5−10 dB. For variable-temperature spectra, the probe temperature (±1 K) was controlled by a standard unit calibrated with a methanol reference. Free energies of activation were calculated[24] from the coalescence temperature (T_c) and the frequency difference between the coalescing signals (extrapolated at the coalescence temperature) with the formula $\Delta G_c^{\ddagger} = aT[9.972 + \log(T/\delta\nu)]$ ($a = 1.914 \times 10^{-2}$). The estimated error in the calculated free energies of activation is ±1.0−1.1 kJ mol^{-1}. $Pd_2(dba)_3$·$CHCl_3$,[25] $[Pd(\eta^3\text{-}2Me\text{-}C_3H_4)Cl]_2$,[26] PdClMe(COD),[27] $Pd(C_6F_5)_2$(COD),[28] $PdMe_2$(TMEDA),[29] and BPPFA[5a] were prepared according to literature methods. $PdCl_2$(cod)[30] was prepared by displacing benzonitrile from $PdCl_2(PhCN)_2$.

Synthesis of BPPFMe. For the reaction sequence see Scheme 1.

(a) Synthesis of 2-((Dimethylamino)methyl)-1,1′-bis-(diphenylphosphino)ferrocene (Ia). This compound was prepared according to a procedure reported by Hayashi et al.[5a]

(b) Synthesis of 2-(Acetoxymethyl)-1,1′-bis(diphenylphosphino)ferrocene (Ib). A solution of 3.67 g (6 mmol) of **Ia** in 40 mL of acetic anhydride is heated at 100 °C for 2 h. After the volume of the reaction mixture is reduced under low pressure to 5 mL, the product is purified by chromatography on silica: eluent, 3/1 hexane/ethyl acetate; yield, 2.146 g (57%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.50−7.05 (m, 20H, Ph), 4.90 (AB, J = 13 Hz, 2H, CH_2), 4.50 (s, 1H, Cp), 4.42 (s, 1H, Cp), 4.23−4.15 (m, 3H, Cp), 3.76 (s, 1H, Cp), 3.59 (s, 1H, Cp), 1.58 (s, 3H, CH_3CO_2).

(c) Synthesis of 2-(Hydroxymethyl)-1,1′-bis(diphenylphosphino)ferrocene (Ic). To a solution of 1.945 g (3.1 mmol) of **Ib** in 20 mL of diethyl ether is added at 0 °C 4.65 mL (7.45 mmol) of *n*-BuLi. The reaction mixture is stirred for 2 h at room temperature and then hydrolyzed with water (20 mL). The aqueous phase is extracted with diethyl ether (3 × 25 mL), and the combined organic phases are washed with water and dried over Na_2SO_4. After removal of solvent under reduced pressure the crude product is purified by chromatography on alumina: eluent, ethyl acetate; yield, 1.793 g (99%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.45−7.00 (m, 20H, Ph), 4.45 (s, 1H, Cp), 4.41−4.25 (m, 3H, Cp + CH_2), 4.20−4.05 (m, 3H, Cp), 3.79 (s, 1H, Cp), 3.56 (s, 1H, Cp).

(d) Synthesis of 2-Methyl-1,1′-bis(diphenylphosphino)-ferrocene (1). To 844.3 mg (22.24 mmol) of $LiAlH_4$ in 20 mL of dry dimethoxyethane is added 298.4 mg (2.238 mmol) of $AlCl_3$. After the mixture is stirred for 2 h at room temperature, 1.090 g (1.865 mmol) of **Ic** in 5 mL of dry DME is added dropwise. The reaction mixture is stirred for 15 h at 90 °C. Water (50 mL) is carefully added at 0 °C, the organic phase is separated, and the aqueous phase is extracted with diethyl ether (3 × 30 mL). The combined organic phases are washed with brine and dried over anhydrous Na_2SO_4. After filtration, the solvent is removed under reduced pressure and the product is purified by chromatography on alumina: eluent, 4/1 petroleum ether/ethyl acetate; yield, 594 mg (56%). Anal. Calcd for $C_{35}H_{30}FeP_2$: C, 73.96; H, 5.32. Found: C, 73.13; H, 4.96. ^{1}H NMR (300 MHz, benzene-d_6): δ 6.90−7.90 (m, 20H, Ph), 4.28 (m, 2H, Cp), 4.20 (m, 1H, Cp), 4.14 (m, 1H, Cp), 4.07 (t, J_{HH} = 2.4 Hz, 1H, Cp), 3.52 (m, 1H, Cp), 3.38 (m, 1H, Cp), 1.93 (s, Me). ^{13}C{^{1}H} NMR (75 MHz, benzene-d_6): δ 135.8 (d, J_{CP} = 21.0 Hz, C_{ortho} Ph), 134.6 (d, J_{CP} = 8.8 Hz, C_{meta} Ph), 134.2 (d, J_{CP} = 8.5 Hz, C_{meta} Ph), 133.0 (d, J_{CP} = 18.1 Hz, C_{ortho} Ph), 129.6 (s, C_{para} Ph), 90.7 (d, J_{CP} = 23.2 Hz, Cp), 77.5 (d, J_{CP} = 8 Hz, Cp), 75.9 (s, Cp), 75.0 (d, J_{CP} = 13.8 Hz, Cp), 74.0 (d, J_{CP} = 13.0 Hz, Cp), 73.8 (s, Cp), 72.2 (s, Cp), 71.0 (s, Cp), 14.2 (d, J_{CP} = 10.3 Hz, Me).

Synthesis of Pd(BPPFA)(DMFU) (2). A mixture of BPPFA (80.0 mg, 0.128 mmol), DMFU (27.4 mg, 0.190 mmol), and $Pd_2(dba)_3$·$CHCl_3$ (76.7 mg, 0.064 mmol) in toluene (15 mL) is stirred for 3.5 h. After the volume of toluene is reduced to 1 mL, the reaction mixture is separated by chromatography on silica. Toluene elutes unreacted dba and THF complex **2**. THF is removed in vacuo, and the remaining residue is washed with hexane. After it is dried in vacuo, complex **2** is obtained as a brown solid. Yield: 75.1 mg (67%). Ratio of isomers in benzene: **2M**:**2m** = 77:23. Crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether vapor over a toluene solution of **2**. Anal. Calcd for $C_{44}H_{45}FeNO_4P_2Pd$: C, 60.32; H, 5.18; N, 1.60. Found: C, 59.84; H, 5.33; N, 1.51. IR (cm^{-1}, KBr): 1685 (vs, ν(C=O)). ^{1}H NMR (300 MHz, benzene-d_6): **2M** *Re*, δ 8.2−6.9 (m, 20H, Ph), assigned ortho protons 8.11 (m, 2H, Ph_{ortho}), 8.04 (m, 2H, Ph_{ortho}), 7.68 (m, 2H, Ph_{ortho}), 4.92 (q, J_{HH} = 6.6 Hz, 1H, *C*H*CH$_3$), 5.23 (ddd, J_{HH} = 10.0 Hz, $J_{HP,trans}$ = 8.3 Hz, $J_{HP,cis}$ = 3.6 Hz, 1H, CH=), 4.84 (m, 1H, CH=), 4.39 (s, 1H, Cp), 3.98 (s, 1H, Cp_A), 3.96 (s, 1H, Cp), 3.80 (m, 2H, Cp), 3.74 (s, 1H, Cp), 3.65 (m, 1H, Cp), 3.24 (s, 3H, CO_2CH_3), 2.96 (s, 3H, CO_2CH_3), 1.81 (s, 6H, $N(CH_3)_2$), 0.62 (d, 3H, *CHCH_3); **2m** *Si*, δ 8.2−6.8 (m, 20H, Ph), assigned ortho protons 8.11 (m, 2H, Ph_{ortho}), 7.63 (m, 2H, Ph_{ortho}), 4.93, 4.86 (AB, J_{HH} = 10.1 Hz, 2H, CH=CH), 4.25 (q, J_{HH} = 6.3 Hz, 1H, *C*H*CH$_3$), 4.32 (s, 1H, Cp), 4.07 (s, 1H, Cp), 4.01 (s, 1H, Cp), 3.98 (s, 1H, Cp), 3.80 (s, 2H, Cp), 3.74 (s, 1H, Cp), 3.06 (s, 3H, CO_2CH_3), 3.01 (s, 3H CO_2CH_3), 1.88 (s, 6H, $N(CH_3)_2$), 0.56 (d, 3H, *CHCH_3). ^{13}C{^{1}H} NMR (75 MHz, chloroform-*d*): **2M**, δ 135.6 (d, J_{CP} = 16.6 Hz, C_{ortho} Ph), 135.5 (d, J_{CP} = 16.6 Hz, C_{ortho} Ph), 133.2 (d, J_{CP} = 14.1 Hz, C_{ortho} Ph), 133.2 (d, J_{CP} = 14.6 Hz, C_{ortho} Ph), 128.2 (d, J_{CP} = 9.6 Hz, C_{meta} Ph), 128.1 (d, J_{CP} = 9.6 Hz, C_{meta} Ph), 127.7 (d, J_{CP} = 10.7 Hz, C_{meta} Ph), 127.0 (d, J_{CP} = 9.6 Hz, C_{meta} Ph), 130.1 (d, J_{CP} = 1.3 Hz, C_{para} Ph), 129.6 (d, J_{CP} = 1.3 Hz, C_{para} Ph), 129.1 (d, J_{CP} = 1.3 Hz, C_{para} Ph), 129.0 (s, C_{para} Ph), 97.1 (d, J_{CP} = 15.1 Hz, Cp), 76.1 (s, Cp), 75.6 (s, Cp), 74.6 (s, Cp), 73.5 (d, J_{CP} = 15 Hz, Cp), 71.7 (d, J_{CP} = 7.5 Hz, Cp), 70.8 (d, J_{CP} = 5.7 Hz, Cp), 69.1 (d, J_{CP} = 1.9 Hz, Cp), 67.5 (d, J_{CP} = 1.9 Hz, Cp), 65.8 (s, *C*H−CH_3), 54.8 (dd, $J_{CP,trans}$ = 24.3 Hz, $J_{CP,cis}$ = 4.0 Hz, CH=), 54 (d, $J_{CP,trans}$ = 25 Hz, CH=), 50.5 (s, CO_2CH_3), 50.3 (s, CO_2CH_3), 38.2 (s, $N(CH_3)_2$), 7.1 (s, CH*CH$_3$).

Synthesis of Pd(BPPFA)(MA) (3). A mixture of BPPFA (70.0 mg, 0.112 mmol), MA (11.0 mg, 0.112 mmol), and $Pd_2(dba)_3$·$CHCl_3$ (61.0 mg, 0.051 mmol) in 15 mL of toluene is stirred at room temperature. Within 10 min the color of the solution changes from dark red to yellow. After 40 min the volume of toluene is reduced to 1 mL and the reaction mixture

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is separated as described for **2**. Crude **3** is obtained as a yellow solid. Recrystallization from toluene/pentane yields 29.6 mg (35%) of complex **3**. Ratio of isomers in acetone: **3M**/**3m** = 67/33. Anal. Calcd for $C_{42}H_{39}FeNO_3P_2Pd$: C, 60.80; H, 4.74; N, 1.69. Found: C, 60.23; H, 4.26; N, 1.67. IR (cm^{-1}, KBr): 1797 and 1730 (vs, ν(C=O)). ^1H NMR (300 MHz, acetone-d_6): δ 7.9−7.1 (m, Ph), assigned ortho protons 7.80 (m, 2H, Ph_{ortho}, **3m**), 7.75 (m, 2H, Ph_{ortho}, **3M**), 7.70 (m, 2H, Ph_{ortho}, **3m**),7.69 (m, 6H, Ph_{ortho}, **3M**), 7.50 (m, 2H, Ph_{ortho}, **3m**), 7.35 (m, 2H, Ph_{ortho}, **3m**), 4.94 (qt, J_{HH} = 6.6 Hz, J_{HP} = 1.7 Hz, 1H, *C*H*CH$_3$, **3M**), 4.63 (qt, J_{HH} = 6.6 Hz, J_{HP} = 1.7 Hz, 1H, *C*H*CH$_3$, **3m**), 4.61 (m, Cp), 4.59 (m, J_{HH} = 4.4 Hz, 1H, CH=, **3m**), 4.51 (m, Cp), 4.45 (m, Cp), 4.44 (m, J_{HH} = 4.4 Hz, 1H, CH=, **3M**), 4.40 (m, Cp), 4.36 (m, Cp), 4.36 (m, 1H, CH=, **3M**), 4.29 (m, Cp), 4.12 (m, Cp), 4.06 (m, Cp), 3.95 (m, 1H, CH=, **3m**), 3.93 (m, Cp), 3.73 (m, Cp), 1.81 (s, 6H, N(CH$_3$)$_2$, **3M**), 1.64 (s, 6H, N(CH$_3$)$_2$, **3m**), 1.02 (d, 3H, *CHC*H*$_3$, **3M**), 0.64 (d, 3H, *CHC*H*$_3$, **3m**). $^{13}C\{^1H\}$ NMR (75 MHz, acetone-d_6): **3M,** δ 171 (b s, *C*O), 137.4−127.6 (m, Ph), assigned ortho carbons 136.4 (d, J_{CP} = 17.6 Hz, C_{ortho} Ph), 135.5 (d, J_{CP} = 16.6 Hz, C_{ortho} Ph), 134.8 (d, J_{CP} = 15.6 Hz, C_{ortho} Ph), 133.7 (d, J_{CP} = 13.6 Hz, C_{ortho} Ph), 98.2 (d, J_{CP} = 16.1 Hz, Cp), 77.6 (d, J_{CP} = 5.0 Hz, Cp), 76.2 (s, Cp), 74.5 (d, J_{CP} = 11.6 Hz, Cp), 72.4 (d, J_{CP} = 5.5 Hz, Cp), 72.3 (d, J_{CP} = 5.0 Hz, Cp), 70.4 (d, J_{CP} = 4.0 Hz, Cp), 69.8 (d, J_{CP} = 4.0 Hz, Cp), 58.3 (pt, J_{CP} = 2.5 Hz, *C*HCH$_3$), 54.1 (dd, $J_{CP,trans}$ = 25.1 Hz, $J_{CP,cis}$ = 3.0 Hz, CH=), 53.7 (dd, $J_{CP,trans}$ = 25.1 Hz, $J_{CP,cis}$ = 3.5 Hz, CH=), 39.4 (s, N(*C*H$_3$)$_2$), 7.8 (s, CH-*C*H$_3$); **3m**, 137.4−127.6 (m, Ph), assigned ortho carbons 137.2 (d, J_{CP} = 16.1 Hz, C_{ortho} Ph), 136.4 (d, J_{CP} = 17.6 Hz, C_{ortho} Ph), 133.9 (d, J_{CP} = 14.6 Hz, C_{ortho} Ph), 132.6 (d, J_{CP} = 13.1 Hz, C_{ortho} Ph), 77.0 (d, J_{CP} = 2.5 Hz, Cp), 76.4 (s, Cp), 74.9 (d, J_{CP} = 15.1 Hz, Cp), 73.4 (d, J_{CP} = 6.0 Hz, Cp), 72.6 (d, J_{CP} = 6.0 Hz, Cp), 70.9 (d, J_{CP} = 4.0 Hz, Cp), 69.4 (d, J_{CP} = 4.5 Hz, Cp), 57.1 (dd, J_{CP} = 3.0, 1.5 Hz, *C*HCH$_3$), 54.9 (dd, $J_{CP,trans}$ = 28.2 Hz, $J_{CP,cis}$ = 3.5 Hz, CH=), 52.1 (dd, $J_{CP,trans}$ = 28.7 Hz, $J_{CP,cis}$ = 3.5 Hz, CH=), 38.7 (s, N(*C*H$_3$)$_2$), 7.4 (s, CH*C*H$_3$).

Synthesis of [Pd(η^3-2-Me-C$_3$H$_4$)(BPPFA)](CF$_3$SO$_3$)·(CH$_3$)$_2$CO (4·(CH$_3$)$_2$CO). A solution of 22.0 mg (0.056 mmol) of [(η^3-2-Me-C$_3$H$_4$)PdCl]$_2$ in acetone is added to a solution of light-protected AgCF$_3$SO$_3$ (28.7 mg, 0.112 mmol) in methanol. After it is stirred for 3.5 h, the reaction mixture is filtered over Celite and BPPFA (70.0 mg, 0.112 mmol) is added. The color of the initially yellow solution changes to orange. Stirring is continued for 2.5 h. The solvent is removed in vacuo, and the remaining orange oil solidifies when treated with hexane and ultrasound. After filtration and drying in vacuo complex **4** is obtained as an orange solid. Yield: 88.0 mg (79%). Ratio of isomers in acetone: **4M**:**4m** = 62;38. Anal. Calcd for $C_{43}H_{44}F_3FeNO_3P_2PdS\cdot C_3H_6O$: C, 55.57; H, 5.07; N, 1.41; S, 3.28. Found: C, 55.07; H, 4.92; N, 1.31; S, 2.93. IR (cm^{-1}, KBr): 1268 (s), 1220 (m), 1149 (m), and 636 (m) (CF$_3$SO$_3$); 1028 (s), 823 (m), and 834 (2-methylallyl). ^1H NMR (300 MHz, acetone-d_6): δ 7.9−7.3 (m, Ph), assigned ortho protons 7.45 (t, J = 7.7 Hz, 2H, Ph_{ortho}, **4M**), 7.31 (t, J = 7.7 Hz, 2H, Ph_{ortho}, **4m**), 4.83 (s, 1H, Cp, **4M**), 4.75 (s, 1H, Cp, **4m**), 4.58−4.40 (m, Cp), 4.49 (q, J_{HH} = 6.4 Hz, 1H, *C*H*−CH$_3$, **4M**), 4.33 (s, Cp), 4.25 (b pt, 1 H_{syn}), 4.16 (b s, Cp), 3.99 (s, Cp), 3.88 (b pt, 1 H_{syn}), 3.84 (d, J_{HP} = 7.1 Hz, 1 H_{anti}), 3.82 (s, Cp), 3.67 (d, J_{HP} = 9.8 Hz, 1 H_{anti}), 3.58 (d, J_{HP} = 9.3 Hz, 1 H_{anti}), 3.55 (d, J_{HP} = 7.6 Hz, 1 H_{anti}), 2.08 (s, 6H, N(CH$_3$)$_2$, **4m**), 2.03 (s, 6H, N(CH$_3$)$_2$, **4M**), 1.94 (s, 3H, C*H*$_3$C=, **4M**), 1.25 (d, 3H, *CHC*H*$_3$, **4M**), 1.20 (s, 3H, CH$_3$C=, **4m**), 1.04 (d, J_{HH} = 6.6 Hz, 3H, *CHC*H*$_3$, **4m**). $^{13}C\{^1H\}$ NMR (75 MHz, chloroform-d): δ 138.7−123.1 (m, Ph), 97.6 (m, Cp), 78.1 (s, Cp), 76.1 (s, Cp), 74.3 (m, Cp), 73.1 (s, Cp), 72.9 (s, Cp), 72.4 (m, Cp), 71.0 (m, Cp), 69.5 (s, Cp), 57.6 (s, *C*HCH$_3$, **4M**), 56.2 (s, *C*HCH$_3$, **4m**), 39.6 (s, N(*C*H$_3$)$_2$, **4M**), 39.1 (s, N(*C*H$_3$)$_2$, **4m**), 29.2 (s, *C*H$_3$C=, **4M**), 23.7 (s, *C*H$_3$C=, **4m**), 8.4 (s, CH*C*H$_3$, **4m**), 8.3 (s, CH*C*H$_3$, **4M**).

Synthesis of Pd(C$_6$F$_5$)$_2$(BPPFA) (5). A solution of Pd(C$_6$F$_5$)$_2$(cod) (43.8 mg, 0.080 mmol) and BPPFA (50.0 mg, 0.080 mmol) in 30 mL of toluene is stirred for 24 h. The solvent is removed in vacuo, and the remaining yellow oil solidifies when treated with hexane and ultrasound. Filtration and drying in vacuo yields complex **5** as a yellow solid. Yield: 61.3 mg (72%). Anal. Calcd for $C_{50}H_{37}F_{10}FeNP_2Pd$: C, 56.34; H, 3.50; N, 1.32. Found: C, 56.07; H, 3.28; N, 1.29. IR (cm^{-1}, KBr): 1495 (s) and 954 (s) (C$_6$F$_5$). ^1H NMR (300 MHz, benzene-d_6): δ 8.2−6.9 (m, 20H, Ph), assigned ortho protons 8.17 (m, 2H, $Ph_{ortho,A1}$), 7.77 (m, 4H, $Ph_{ortho,A2+B1}$), 7.44 (m, 2H, $Ph_{ortho,B2}$), 3.98 (q, J_{HH} = 6.1 Hz, 1H, *C*H*CH$_3$), 4.62 (m, 1H, Cp_B), 4.21 (m, 2H, Cp_{A+B}), 3.90 (m, 1H, Cp_A), 3.80 (m, 1H, Cp_B), 3.70 (s, 1H, Cp_A), 3.62 (s, 1H, Cp_A), 1.92 (s, 6H, N(CH$_3$)$_2$), 0.46 (d, 3H, *CHC*H*$_3$). ^{19}F NMR (282 MHz) δ −114.71 (m, 1F, $F_{ortho,a}$), −115.44 (m, 1F, F_{ortho}), −116.52 (m, 1F, F_{ortho}), −117.58 (m, 1F, F_{ortho}), −162.11 (dd, J_{FF} = 21.4, 18.3 Hz, 1F, $F_{para,a}$), −162. 84 (dd, J_{FF} = 21.3, 18.3 Hz, 1F, $F_{para,b}$), −163.20 (m, 1F, $F_{meta,a}$), −163.75 (m, 3F, $F_{meta,a+2b}$). $^{13}C\{^1H\}$ NMR (75 MHz, benzene-d_6): δ 148.4−128.5 (m, Ph), 146.8 (dd, J_{CF} = 227.2 Hz, J_{CP} = 21.7, 2C, $C_{orthoC_6F_5}$), 145.9 (dd, J_{CF} = 223.1 Hz, J_{CP} = 22.2 Hz, 2C, $C_{orthoC_6F_5}$), 138.3 (dm, J_{CF} = 249.3 Hz, 2C, $C_{paraC_6F_5}$), 137.7 Hz, (dm, J_{CF} = 236 Hz, 4C, $C_{metaC_6F_5}$), 97.0 (d, J_{CP} = 8.5 Hz, Cp), 80.3 (d, J_{CP} = 14.6 Hz, Cp), 76.7 (d, J_{CP} = 8.6 Hz, Cp), 75.4 (dd, J_{CP} = 41.3, 6.5 Hz, Cp), 74.4 (d, J_{CP} = 9.5 Hz, Cp), 73.7 (s, Cp), 73.2 (d, J_{CP} = 4.0 Hz, Cp), 72.6 (d, J_{CP} = 4.0 Hz, Cp), 72.1 (dd, J_{CP} = 40.3, 4.0 Hz, Cp), 71.4 (d, J_{CP} = 8.0 Hz, Cp), 55.4 (s, *C*HCH$_3$), 39.0 (s, N(*C*H$_3$)$_2$), 8.0 (s, CH*C*H$_3$).

Synthesis of Pd(BPPFMe)(C$_6$F$_5$)$_2$ (6). To a solution of **1** (51.8 mg, 0.091 mmol) in 15 mL of toluene is added Pd(C$_6$F$_5$)$_2$(cod) (50.0 mg, 0.091 mmol). After it is stirred for 16 h at room temperature, the solution is evaporated to dryness and the remaining orange solid is washed with hexane. Orange crystals are obtained from dichloromethane/pentane. Yield: 78.0 mg (85%). Anal. Calcd for $C_{47}H_{30}F_{10}FeP_2Pd$: C, 55.95; H, 3.00. Found: C, 55.48; H, 2.94. IR (cm^{-1}, Nujol): 1498 (s), 956 (s), and 785 (m) (C$_6$F$_5$). ^1H NMR (300 MHz, benzene-d_6): δ 8.2−6.7 (m, 20H, Ph), assigned ortho protons 8.12 (m, 2H, $Ph_{ortho,A2}$), 7.69 (m, 2H, $Ph_{ortho,B1}$), 7.46 (m, 2H, $Ph_{ortho,B2}$), 6.89 (m, 2H, $Ph_{ortho,A1}$), 4.13 (m, 1H, Cp_B), 4.00 (m, 1H, Cp_A), 3.96 (m, 1H, Cp_A), 3.91 (m, 1H, Cp_B), 3.66 (m, 2H, Cp_{A+B}), 3.60 (m, 1H, Cp_B), 2.52 (s, 3H, CpC*H*$_3$). ^{19}F NMR (282 MHz): δ −113.47 (m, 1F, $F_{ortho,a}$), −115.20 (m, 1F, $F_{ortho,b}$), −115.78 (m, 1F, $F_{ortho,a}$), −117.77 (m, 1F, $F_{ortho,b}$), −162.07 (pt, J_{FF} = 21.4 Hz, 1F, $F_{para,a}$), −162.70 (pt, J_{FF} = 19.8 Hz, 1F, $F_{para,b}$), −163.03 (m, 1F, $F_{meta,a}$), −163.40 (m, 2F, $F_{meta,a+b}$), −163.89 (m, 1F, $F_{meta,b}$). $^{13}C\{^1H\}$ NMR (75 MHz, benzene-d_6): δ 137.0−119.6 (m, Ph), assigned phenyl carbons 136.9 (d, J_{CP} = 14.6 Hz, C_{ortho} Ph), 135.8 (b d, J_{CP} = 11.0 Hz, C Ph), 133.8 (b d, J_{CP} = 9.4 Hz, C Ph), 130.6 (d, J_{CP} = 2.9 Hz, C_{para} Ph), 129.6 (d, J_{CP} = 2.9 Hz, C_{para} Ph), 91.0 (d, J_{CP} = 17.4 Hz, Cp), 78.2 (s, Cp), 77.7 (m, Cp), 76.1 (d, J_{CP} = 4.8 Hz, Cp), 75.7 (d, J_{CP} = 7.7 Hz, Cp), 75.4 (d, J_{CP} = 2.7 Hz, Cp), 73.8 (d, J_{CP} = 12.6 Hz, Cp), 73.0 (d, J_{CP} = 8.0 Hz, Cp), 71.3 (d, J_{CP} = 4.9 Hz, Cp), 70.3 (d, J_{CP} = 7.8 Hz, Cp), 30.1 (s, *C*H$_3$−Cp).

Synthesis of PdMe$_2$(BPPFA)·$^1/_2$C$_6$H$_{14}$ (7·$^1/_2$C$_6$H$_{14}$). To a solution of PdMe$_2$(TMEDA) (20.2 mg, 0.080 mmol) in 15 mL toluene is added 50 mg (0.080 mmol) of BPPFA. After the mixture is stirred for 20 h at room temperature, the volume of toluene is partially reduced and hexane is added. After 16 h at 4 °C, yellow crystals of **7** are obtained. Yield: 30.3 mg (47%). Anal. Calcd for $C_{40}H_{43}FeNP_2Pd\cdot{}^1/_2C_6H_{14}$: C, 64.15; H, 6.26; N, 1.74. Found: C, 64.37; H, 6.15; N, 1.74. IR (cm^{-1}, Nujol): 529 (ν(Pd−Me)).^1H NMR (300 MHz, benzene-d_6): δ 8.2−6.7 (m, 20H, Ph), assigned ortho protons 8.15 (m, 2H, $Ph_{ortho,B2}$), 8.04 (m, 2H, $Ph_{ortho,A2}$), 7.89 (m, 2H, $Ph_{ortho,B1}$), 7.38 (m, 2H, $Ph_{ortho,A1}$), 5.80 (q, J_{HH} = 6.8 Hz, 1H, *C*H*CH$_3$), 4.11 (m, 2H, Cp), 3.79 (t, J_{HH} = 2.6 Hz, 1H, Cp), 3.65 (m, 1H, Cp), 3.62 (m, 1H, Cp), 3.54 (m, 1H, Cp), 3.33 (m, 1H, Cp), 2.23 (s, 6H, N(CH$_3$)$_2$), 1.14 (dd, $J_{HP,trans}$ = 8.7 Hz, $J_{HP,cis}$ = 5.5 Hz, 3H, Me_2−Pd), 1.13 (d, 3H, *CHC*H*$_3$), 1.08 (dd, $J_{HP,trans}$ = 9.3 Hz, $J_{HP,cis}$ = 6.9 Hz, 3H, Me_1−Pd). $^{13}C\{^1H\}$ NMR (75 MHz, benzene-d_6): δ 137.9 (d, J_{CP} = 16.6 Hz, C_{ortho} Ph), 137.8 (d, J_{CP} = 16.1 Hz, C_{ortho} Ph), 136.0 (d, J_{CP} = 13.1 Hz, C_{ortho} Ph), 135.6 (d, J_{CP} =

13.6 Hz, C_{ortho} Ph), 134.3 (d, J_{CP} = 9.6 Hz, C_{meta} Ph), 126.8 (d, J_{CP} = 9.1 Hz, C_{meta} Ph), 130.3 (d, J_{CP} = 1.5 Hz, C_{para} Ph), 129.9 (d, J_{CP} = 1.5 Hz, C_{para} Ph), 129.6 (d, J_{CP} = 2.0 Hz, C_{para} Ph), 99.3 (d, J_{CP} = 19.1 Hz, Cp), 84.4 (dd, J_{CP} = 31.2, 6.5 Hz, Cp), 79.1 (dd, J_{CP} = 30.7, 4.6 Hz, Cp), 77.5 (d, J_{CP} = 4.6 Hz, Cp), 75.3 (s, Cp), 73.9 (d, J_{CP} = 9.6 Hz, Cp), 71.2 (d, J_{CP} = 6.1 Hz, Cp), 70.8 (d, J_{CP} = 4.0 Hz, Cp), 69.1 (d, J_{CP} = 3.1 Hz, Cp), 68.9 (d, J_{CP} = 3.1 Hz, Cp), 56.7 (d, J_{CP} = 2.5 Hz, *C*HCH$_3$), 39.7 (s, N(*C*H$_3$)$_2$), 13.2 (dd, $J_{CP,trans}$ = 102.9 Hz, $J_{CP,cis}$ = 11.3 Hz, *C*H$_3$-Pd), 8.3 (dd, $J_{CP,trans}$ = 102.2 Hz, $J_{CP,cis}$ = 10.1 Hz, *C*H$_3$Pd), 8.0 (s, CH*C*H$_3$).

Synthesis of PdClMe(BPPFA) (8). To a mixture of BPPFA (14 mg, 0.022 mmol) and PdClMe(cod) (5.9 mg, 0.022 mmol) in an NMR tube was added 0.5 mL of benzene-d_6. The ^{1}H and ^{31}P NMR spectra recorded immediately afterward showed that only complex **8** was formed. Crystallization by vapor diffusion of diethyl ether gave complex **8** as pale yellow crystals. Yield: 15.4 mg (88%). Ratio of isomers in benzene **8M**/**8m** = 85/15. Anal. Calcd for $C_{39}H_{40}ClFeNP_2Pd$: C, 59.87; H, 5.15; N, 1.79. Found: C, 60.04; H, 5.49; N, 1.76. ^{1}H NMR (300 MHz, toluene-d_8): δ 8.7−6.6 (m, 20H, Ph), assigned ortho protons 8.66 (m, 2H, $Ph_{ortho,B1}$), 8.09 (m, 2H, $Ph_{ortho,B2}$), 8.06 (m, 2H, $Ph_{ortho,A1}$), 7.19 (m, 2H, $Ph_{ortho,A2}$), 6.09 (q, J_{HH} = 6.8 Hz, 1H, *C*HCH$_3$), 4.16 (s, 1H, Cp_A), 4.10 (s, 1H, Cp_A), 3.77 (d, J_{HH} = 4.2 Hz, 1H, Cp_A), 3.60 (s, 1H, Cp_B), 3.54 (s, 1H, Cp_B), 3.41 (s, 1H, Cp_B), 3.24 (s, 1H, Cp_B), 2.17 (s, 6H, N(CH$_3$)$_2$), 1.64 (dd, $J_{HP,trans}$ = 8.1 Hz, $J_{HP,cis}$ = 5.1 Hz, 3H, CH$_3$Pd), 1.09 (d, 3H, *CHC*H$_3$). ^{13}C{^{1}H} NMR (75 MHz, benzene-d_6): δ 137.4−126.7 (Ph), 99.7 (d, J_{CP} = 25.5 Hz, Cp), 78.5 (d, J_{CP} = 6.1 Hz, Cp), 76.1 (s, Cp), 74.6 (d, J_{CP} = 14.3 Hz, Cp), 72.4 (d, J_{CP} = 11.0 Hz, Cp), 72.2 (d, J_{CP} = 3.8 Hz, Cp), 71.0 (d, J_{CP} = 7.9 Hz, Cp), 70.5 (d, J_{CP} = 3.8 Hz, Cp), 57.3 (s, *C*HCH$_3$), 40.3 (s, N(*C*H$_3$)$_2$), 19.0 (d, $J_{CP,trans}$ = 97.2 Hz, *C*H$_3$Pd), 8.0 (s, CH*C*H$_3$).

Synthesis of {*cis*-PdClMe(*μ*-*κ*^{3}-BPPFA)}$_2${MePd(*μ*-Cl)$_2$-PdMe} (9). Complex **9** was prepared as for **8**, using the following amounts: BPPFA (14 mg, 0.0224 mmol), PdClMe-(cod) (11.8 mg, 0.0448 mmol), and benzene-d_6 (0.5 mL). Yield: 19.8 mg (94%). Anal. Calcd for $C_{80}H_{86}Cl_4Fe_2N_2P_4Pd_4$: C, 51.15; H, 4.61; N, 1.49. Found: C, 51.12; H, 4.14; N, 1.52. IR (cm^{-1}, Nujol mull): 316 (w), 282 (w), and 269 (w), ν(Pd−Cl). ^{1}H NMR (300 MHz, benzene-d_6): δ 7.9−6.8 (m, 40H, Ph), assigned ortho protons 7.91 (m, 4H, $Ph_{ortho,B}$), 7.44 (m, 8H, $Ph_{ortho,A}$), 7.28 (m, 4H, $Ph_{ortho,B}$), 5.16 (b s, 2H, Cp), 4.87 (s, 2H, Cp), 4.32 (b s, 2H, Cp), 4.01 (s, 2H, Cp), 3.88 (s, 2H, Cp), 3.56 (s, 2H, Cp), 3.36 (b m, 2H, *C*HCH$_3$), 3.24 (s, 6H, NCH$_3$), 3.13 (s, 2H, Cp), 2.62 (s, 6H, NCH$_3$), 1.20 (d, J_{HP} = 4.1 Hz, 6H, Me−Pd), 1.04 (b s, 6H, Me−Pd), 1.06 (d, J_{HH} = 6.3 Hz, 6H, *CHC*H$_3$). ^{13}C-{^{1}H} NMR (75 MHz, benzene-d_6): δ 137−128 (Ph), 136.2 (d, J_{CP} = 14.1 Hz, C_{ortho} Ph), 134.2 (d, J_{CP} = 12.0 Hz, C_{ortho} Ph), 133.8 (d, J_{CP} = 12.1 Hz, C_{ortho} Ph), 132.8 (d, J_{CP} = 10.1 Hz, C Ph), 131.3 (b s, C_{para} Ph), 130.7 (b s, 4C, C_{para} Ph), 129.8 (b s, C_{para} Ph), 97.8 (d, J_{CP} = 20.2 Hz, Cp), 78.5 (d, J_{CP} = 20.2 Hz, Cp), 76.5 (d, J_{CP} = 7.4 Hz, Cp), 75.4 (d, J_{CP} = 54.9 Hz, Cp), 75.2 (d, J_{CP} = 7.6 Hz, Cp), 74.7 (d, J_{CP} = 6.5 Hz, Cp), 74.0 (d, J_{CP} = 4.0 Hz, Cp), 74.0 (s, Cp), 72.5 (d, J_{CP} = 42.8 Hz, Cp), 62.6 (s, *C*HCH$_3$), 49.3 (s, N(*C*H$_3$)), 44.9 (s, N(*C*H$_3$)), 18.6 (s, CH*C*H$_3$), 2.1 (s, *C*H$_3$Pd), 8.9 (b s, *C*H$_3$Pd). MS: *m*/*z* 1849 [M − C_2H_5], 1068 [M − BPPFA − Pd − Cl − C_3H_8], 959 [M − BPPFA − 2Pd − Cl − 3Me], 904 [M − BPPFA − 2Pd − 3Cl − 2Me].

Synthesis of {*cis*-PdCl$_2$(*μ*-*κ*^{3}-BPPFA)}$_2${ClPd(*μ*-Cl)$_2$PdCl} (10). Complex **10** was prepared as for **8** using the following amounts: BPPFA (14 mg, 0.0224 mmol), PdCl$_2$(cod) (12.8 mg, 0.0448 mol) and chloroform-*d* (0.5 mL). Yield: 22.6 mg (96%). Anal. Calcd for $C_{76}H_{74}Cl_8Fe_2N_2P_4Pd_4$: C, 46.56; H, 3.80; N, 1.43. Found: C, 45.61; H, 4.04; N, 1.36. IR (cm^{-1}, Nujol mull): 340 (m, br), 274 (m, br) (ν(Pd−Cl)). ^{1}H NMR (300 MHz, chloroform-*d*): δ 8.2−7.3 (m, 40H, Ph), assigned ortho protons 8.22 (m, 4H, Ph_{ortho}), 5.34 (s, 2H, Cp), 5.06 (s, 2H, Cp), 4.65 (s, 2H, Cp), 4.48 (s, 2H, Cp), 4.07 (s, 2H, Cp), 3.92 (s, 2H, Cp), 3.63 (s, 6H, NCH$_3$), 3.44 (s, 2H, Cp), 2.90 (s, 6H, NCH$_3$), 2.86 (q, J_{HH} = 6.4 Hz, 2H, *C*HCH$_3$), 1.54 (d, 6H, *CHC*H$_3$). ^{13}C-{^{1}H} NMR (75 MHz, chloroform-*d*): δ 135.7−128.2 (Ph), assigned phenyl carbons 135.6 (d, J_{CP} = 11.5 Hz, C Ph), 133.6 (d, J_{CP} = 9.5 Hz, C Ph), 128.7 (d, J_{CP} = 11.9 Hz, C_{meta} Ph), 128.3 (d, J_{CP} = 10.9 Hz, C_{meta} Ph), 98.9 (b s, Cp), 81.6 (m, Cp), 77.5 (s, Cp), 76.0 (b s, Cp), 75.1 (b s, Cp), 73.6 (b s, Cp), 64.7 (s, *C*HCH$_3$), 53.8 (s, NCH$_3$), 51.9 (s, NCH$_3$), 22.9 (s, CH*C*H$_3$). MS: *m*/*z* 1746 [M − Pd − 3Cl − H], 1157 [M − BPPFA − Pd − 2Cl], 980 [M − BPPFA − 2Pd − 4Cl − H], 944 [M − BPPFA − 2Pd − 5Cl], 766 [M − BPPFA − 3Pd − 7Cl], 804 [M − BPPFA − 3Pd − 6Cl + H].

Synthesis of {*cis*-PdClMe(*μ*-*κ*^{3}-BPPFA)}$_2$(*trans*-PdClMe) (11). To a mixture of BPPFA (14 mg, 0.0224 mmol) and PdClMe(cod) (11.8 mg, 0.0336 mmol) in an NMR tube was added 0.5 mL of benzene-d_6. Immediately afterward, sequences of ^{1}H (120 scans) and ^{31}P (240 scans) spectra were recorded for 3 h at 20 °C until an equilibrium ratio of complexes **11**, **9**, and **8** was reached. ^{1}H NMR (300 MHz, chloroform-*d*): δ 8.3−7.0 (m, 40H, Ph), assigned ortho protons 8.10 (m, 4H, Ph_{ortho}), 7.96 (m, 4H, Ph_{ortho}), 7.45 (m, 4H, Ph_{ortho}), 7.28 (m, 4H, Ph_{ortho}), 4.67 (s, 2H, Cp), 4.22 (s, 4H, Cp), 4.16 (s, 2H, Cp), 3.87 (s, 2H, Cp), 3.59 (q, J_{HH} = 6.6 Hz, 2H, *C*HCH$_3$), 3.16 (s, 2H, Cp), 3.15 (s, 6H, NCH$_3$), 3.12 (s, 2H, Cp), 2.48 (s, 6H, NCH$_3$), 1.29 (d, 6H, *CHC*H$_3$), 0.55 (d, J_{HP} = 3.7, 6H, Me−Pd), −0.21 (t, J_{HP} = 6.4 Hz, 3H, Me−Pd). ^{13}C{^{1}H} NMR (75 MHz, benzene-d_6): δ 137.9−126.9 (m, Ph), 99.3−69.6 (m, Cp), 62.5 (s, *C*HCH$_3$), 49.3 (s, N(*C*H$_3$)), 45.6 (s, N(*C*H$_3$)), 19.5 (s, CH*C*H$_3$), 14.3 (s, MePd), 1.3 (s, MePd).

Synthesis of {*cis*-PdCl$_2$(*μ*-*κ*^{3}-BPPFA)}$_2$(*trans*-PdCl$_2$) (12). A procedure similar to that described for complex **11** was used. An equilibrium mixture of **12** together with complexes PdCl$_2$-(BPPFA) and **10** was obtained. ^{1}H NMR (300 MHz, chloroform-*d*): δ 8.1−7.3 (m, 40H, Ph), assigned ortho protons 8.13 (m, 4H, Ph_{ortho}), 4.70 (s, 2H, Cp), 4.68 (s, 2H, Cp), 4.25 (s, 2H, Cp), 3.95 (s, 2H, Cp), 3.90 (s, 2H, Cp), 3.50 (s, 6H, NCH$_3$), 3.44 (s, 2H, Cp), 3.33 (s, 2H, Cp), 3.22 (q, J_{HH} = 6.4 Hz, 2H, *C*HCH$_3$), 2.75 (s, 6H, NCH$_3$), 1.33 (d, 6H, *CHC*H$_3$).

Reaction of PdCl$_2$(BPPFA) with PdClMe(cod). Formation of Mixed Tetranuclear Derivatives. To a mixture of complexes PdCl$_2$(BPPFA) (14 mg, 0.0174 mmol) and PdClMe-(cod) (4.6 mg, 0.0174 mmol) in an NMR tube was added 0.5 mL of chloroform-*d*. Sequences of ^{1}H (120 scans) and ^{31}P (240 scans) spectra were recorded at 20 °C for 3 h.

Transformations of Tetranuclear to Mononuclear Derivatives. (a) PdCl$_2$(BPPFA) from 10. A solution of **10** in chloroform-*d* was prepared as described above. BPPFA (14 mg, 0.0224 mmol) was added, and both ^{1}H and ^{31}P NMR spectra were recorded immediately afterward, showing the presence of PdCl$_2$(BPPFA) only.

(b) 8 from 9. A solution of **9** in benzene-d_6 was prepared as described above. According to the ^{1}H and ^{31}P NMR spectra, after the addition of BPPFA (14 mg, 0.0224 mmol), the complex PdClMe(BPPFA) (**8**) is formed exclusively.

X-ray Crystal Structure Determinations. Compound 2. Intensity data were collected with a Nonius MACH3 diffractometer and Mo Kα radiation. The structure was solved with direct methods and refined with SHELXL-97[31] against F^2 of all reflections using anisotropic displacement parameters for non-hydrogen atoms. Hydrogen atoms had isotropic displacement parameters and were calculated riding with the atoms to which they were bonded.

Compound 8·$^1/_2$C$_6$H$_6$. Intensity data were collected on a Bruker Smart CCD diffractometer and Mo Kα radiation. Of 54 537 reflections, 21 293 were independent (θ = 30°); R_{int} = 0.037 after absorption correction on the basis of multiple measured reflections (program SADABS[32]). The structure was solved with direct methods and refined with SHELXL97[31]

(31) Sheldrick, G. M. SHELXL-97, Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1997.

(32) Sheldrick, G. M. SADABS (version 2.03), Program for Area Detector Absorption and Other Corrections; University of Göttingen, Göttingen, Germany, 2001.

against F^2 of all reflections, using anisotropic displacement parameters for non-hydrogen atoms. Hydrogen atoms had isotropic displacement parameters and were calculated riding with the atoms to which they were bonded. The absolute structure was determined; Flack parameter 0.02(1).[33]

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Supporting Information Available: Tables giving crystal data for **2** and **8** as well as details of the structure determination, non-hydrogen atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates with isotropic displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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(33) Flack, H. D.; Bernardelli, G. *Acta Crystallogr.* **1999**, *A55*, 908.