Solvolysis of Palladium-Carbon Bonds in Palladium(II) Complexes containing Diphosphine Ligands.

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Citation for published version (APA):
Chapter 2

The Coordination Behavior of Diphosphine Ligands having a Large Natural Bite Angle towards Methylpalladium(II) Complexes.

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Abstract: The structures of neutral and ionic methylpalladium(II) complexes containing bidentate phosphine ligands were investigated in solution and in the solid state. Diphosphine ligands having a xanthene and a ferrocene backbone were used. New bis(dialkylphosphino) substituted Xantphos ligands were synthesized. $^1$H NMR and $^{31}$P NMR spectroscopy, conductivity measurements, UV-Vis spectroscopy, and X-ray crystallography were used to elucidate the structures of the complexes. Subtle changes of the phosphine ligands and the palladium center govern the coordination mode of the ligand. A variety of bidentate cis-, and trans-coordination and terdentate P-O-P, P-S-P and P-Fe-P coordination modes of the ligands were observed.
**Introduction**

Metal complexes containing chelating phosphine ligands are active catalysts for a plethora of important reactions\(^1\) and the performance of such catalysts is extremely sensitive toward changes in the ligand environment. In general, steric and electronic properties\(^2\) of a ligand strongly influence the rate, selectivity and stability of the catalyst. More recently it has been recognized that the geometry of ligands around the metal center also influence the rate and selectivity of a reaction considerably.\(^3,4\) Palladium complexes containing phosphine ligands are known to catalyze important reactions such as carbon-carbon\(^5-9\) and carbon-heteroatom coupling reactions,\(^10\) allylic substitution reactions,\(^11,12\) carbonylation and CO / alkene copolymerization reactions.\(^13,14\)

**Scheme 1**

![Scheme 1](image)

Basically, all coupling reactions with chelating diphosphine ligands proceed *via* the reaction sequence presented in scheme 1. First, one of the reactants oxidatively adds to a palladium(0) species, to form a square planar palladium(II) compound. In the next step, a coordination site for the other substrate has to be created. This vacant site can be created *via* dissociation of one of the phosphine ligands or *via* dissociation of the anion, X\(^-\). After coordination of the second substrate and reductive elimination of the product, the palladium(0) species is regenerated. If Y is an alkene, as in the Heck reaction,\(^15-18\) the sequence followed is: insertion, β-elimination of the product and base assisted reductive elimination of HX. The reaction pathway depends on the coordinating and chelating properties of the ligand, the coordinating properties of X, the substrates and the solvent. The CO / alkene copolymerization reaction is a reaction that proceeds through Pd(II) intermediates only. The reaction depends very much on the ligand environment. The use of monodentate ligands such as triphenylphosphine, which forms a *trans*-complex, leads to the selective formation of methyl propionate. In contrast, the use of *cis*-chelating diphosphine
ligands such as 1,2-bis(diphenylphosphino)ethane (dppe) or 1,3-bis(diphenylphosphino)propane (dppp) produces a high molecular weight copolymer.\textsuperscript{13,14} Pd(0) species are important intermediates in catalytic reactions (scheme 1) and have been thoroughly investigated using a wide range of diphosphine ligands. The crystal structures of (L-L)Pd(0)(alkene) complexes show a large range of P-Pd-P angles from 84.8° for (dppe)Pd(dbm) to 115.1° for (PMe\textsubscript{3})\textsubscript{2}Pd(η\textsuperscript{2}-CH\textsubscript{2}=C\textsubscript{5}Me\textsubscript{4}), depending on the steric demands of the ligand.\textsuperscript{19-24}

Recently, our group has developed a series of diphosphine ligands based on xanthene type backbones.\textsuperscript{25-27} These ligands were designed to enforce large phosphorus-metal-phosphorus angles, and have proven to be successful in tuning the activity and selectivity in the palladium catalyzed allylic alkylation,\textsuperscript{28,29} cross-coupling reaction,\textsuperscript{30} propionic acid synthesis,\textsuperscript{31} rhodium catalyzed hydroformylation,\textsuperscript{25} and the nickel catalyzed hydrocyanation of alkenes.\textsuperscript{32} The crystal structures of Pd(0)(tetracyanoethylene) complexes containing DPEphos, Sixantphos and Xantphos ligands have been determined.\textsuperscript{33} The largest phosphorus-palladium-phosphorus angle in these zerovalent palladium complexes containing bidentate ligands was found to be 104.6°.

The effect of ligands inducing wide bite-angles, such as Xantphos, dppf and analogs on catalytic performance of palladium complexes has not been understood completely yet. We rigorously changed the electronic and steric properties of these ligands to study the effects on the geometry of the Pd(II) complexes. In this study we systematically investigate neutral and ionic methylpalladium(II) complexes in solution and in the solid state. The effects of the diphosphine ligand and the anion on the structural properties of the palladium complexes are discussed.

**Results**

**Synthesis.**

The syntheses of arylphosphine ligands a-f have been reported previously (a-f, scheme 2).\textsuperscript{25,26,34,35} New bis(dialkyl)phosphine ligands of the Xantphos-series (ligands a-tBu, a-iPr and b-Me, scheme 2) were synthesized.
Scheme 2

Ligand a-tBu and a-iPr were prepared from the reaction of dilithiated diphenyl ether with chlorodi-tert-butylphosphine and chlorodi-iso-propylphosphine. Ligand b-Me was prepared by the reaction of methylmagnesium bromide with 9,9-dimethyl-4,5-bis(dichlorophosphino)xanthene. Attempts to synthesize a ligand containing two tert-butyl groups bonded to phosphorus based on the Xantheine backbone failed. Probably steric crowding prevents the coupling of two tert-Butyl groups to the same phosphorus. Neither by starting from the dilithiated backbone, nor by starting from 9,9-dimethyl-4,5-bis(dichlorophosphino)xanthene could the desired ligand be obtained.

Scheme 3

\[(\text{COD})\text{Pd(CH}_3\text{)}(\text{X}) + \text{C}_6\text{H}_6 \rightarrow (\text{L-L})\text{Pd(CH}_3\text{)}(\text{X}) \]

\[\text{AgY} \rightarrow \begin{cases} [ (\text{L-L})\text{PdCH}_3]^+ \text{Y}^- & \text{or} \\ [ (\text{L-L})\text{PdCH}_3(\text{CH}_3\text{CN})]^+ \text{Y}^- \end{cases} \]

X = Cl, Br
L-L = diphosphine ligand
X = Cl (1)
Br (2)
Y = CF$_3$SO$_3$ (3)
CF$_3$CO$_2$ (4)

The complexes (L-L)Pd(CH$_3$)Cl (L-L = diphosphine ligand, 1) and (L-L)Pd(CH$_3$)Br (2) were prepared by reaction of (COD)Pd(CH$_3$)Cl and (COD)Pd(CH$_3$)Br with 1.1 equivalents of the appropriate diphosphine ligand (scheme 3). The ionic complexes [(L-L)PdCH$_3$]$^+$ [X]$^-$ and [(L-L)PdCH$_3$(CH$_3$CN)]$^+$ [X]$^-$ (X = CF$_3$SO$_3$ (3), CF$_3$CO$_2$ (4)) were prepared by abstracting the chloride anion from 1 in dichloromethane / acetonitrile (10:1, v/v) using AgX. Alternatively, the ionic complexes could be obtained by the addition of one
equivalent of acid (HX) to a dichloromethane / acetonitrile solution of (L-L)Pd(CH₃)₂. The latter method could not be used to generate the ionic methylpalladium complexes with the ligands based on the ferrocene back-bone. Reaction of the dimethyl palladium complexes with ferrocene-based ligands with acids resulted in mixtures of monocationic methylpalladium, and dicationic palladium complexes.

**Solution and Solid State Structures of Methylpalladium(II) Complexes.**

In view of the flexible ligand properties a variety of coordination geometries can be envisaged for complexes 1-4 (scheme 4).

**Scheme 4**

\[
\begin{array}{cccccccc}
\text{cis} & \text{neutral} & \text{trans} & \text{cis} & \text{trans} & \text{trans} \\
\text{neutral} & \text{ionic} & \text{ionic} & \text{ionic} & (\text{not observed})
\end{array}
\]

**Ligands based on the diphenyl ether backbone.** The structure of methylpalladium complexes in solution can be studied by \(^1\)H NMR and \(^{31}\)P NMR spectroscopy. The methyl chloride and methyl bromide complex 1a and 2a display a double doublet in the \(^1\)H NMR for the methyl group and an AB system in the \(^{31}\)P NMR spectra. In all these cases the ligand is cis-coordinating (cis, neutral, scheme 4). The ionic methylpalladium complex 3a, could only be stabilized in the presence of acetonitrile. Suitable crystals of compound 3a for an X-ray analysis were obtained from CH₂Cl₂ / Et₂O (selected data, table 1). The metal center adopts a square planar geometry and the ligand is coordinated in a cis fashion to palladium (figure 1). Acetonitrile is coordinated to palladium. The P-Pd-P angle (103.24(7)°) is larger than that observed for its neutral counterpart 4a (vide infra). Despite the large P-Pd-P angle, no out of plane bending is observed for any of the ligands around the metal center. The Pd-N bond distance (2.085(8) Å) is in accordance with other reported N-Pd(II) bonds.\(^{37,38}\) Because of the large Pd-O distance (3.548(5) Å), a bonding interaction between these atoms can be ruled out.
Figure 1. Displacement ellipsoid plot of 3a. The ellipsoids are drawn at the 50% probability level. The triflate anion, the non-coordinating solvent molecule and the hydrogen atoms have been omitted for clarity.

The ionic methylpalladium analog without coordinated acetonitrile could only be observed in NMR spectra in CD$_2$Cl$_2$ at low temperatures, when it was synthesized from (DPEphos)Pd(CH$_3$)$_2$ and CF$_3$SO$_3$H. The cis-complex without a palladium-oxygen bond (cis, ionic, scheme 4), and the trans-complex, with a palladium-oxygen bond (trans, ionic, scheme 4), were observed as indicated by the singlet in $^{31}$P NMR spectra and the triplet for the methyl group in $^1$H NMR spectra. In contrast to the triflate complexes, the trifluoroacetate complex 4a is a neutral complex in CH$_2$Cl$_2$ solution as proven by conductivity measurements. The trifluoroacetate anion is too strongly bound to palladium to generate an ionic compound in CH$_2$Cl$_2$. When 4a is dissolved in a dichloromethane / acetonitrile mixture, the compound becomes ionic. Obviously the acetonitrile ligand assists in the dissociation of the trifluoroacetate anion from the palladium center. Suitable crystals for an X-ray analysis were obtained for compound 4a from CH$_2$Cl$_2$ / Et$_2$O (selected data, table 1, figure 2).
Figure 2. Displacement ellipsoid plot of 4a. The ellipsoids are drawn at the 50% probability level. The hydrogen atoms have been omitted for clarity.

Table 1. Selected bond lengths (Å) and bond angles (°) for [(DPEphos)PdCH₃(CH₃CN)]⁺ [CF₃SO₃]⁻ (3a) and (DPEphos)PdCH₃(CF₃CO₂) (4a).

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<td>2.443(2)</td>
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<td>3.548(5)</td>
<td>Pd-O1</td>
<td>3.531(6)</td>
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<td>Pd-N</td>
<td>2.085(8)</td>
<td>Pd-N</td>
<td>2.076(11)</td>
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<td>C1-Pd-P2</td>
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<td>C1-Pd-P1</td>
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<td>C1-Pd-P1</td>
<td>84.8(3)</td>
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<td>P1-Pd-N</td>
<td>89.4(2)</td>
<td>P1-Pd-N</td>
<td>166.9(2)</td>
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The structure of 4a is very similar to that of (DPEphos)Pd(4-C₆H₄-CN)Br. The DPEphos ligand is coordinated in a cis fashion to palladium (P-Pd-P angle = 100.89(7)°) and the palladium-phosphorus distances are in the same range. The trifluoroacetate anion is
coordinated to palladium via the oxygen atom of the carboxylate group (Pd-O2 = 2.122(6) Å), whereas there is no bonding interaction between the oxygen atom of the ligand backbone and palladium (Pd-O1 = 3.531(6) Å).

The dialkylphosphine substituted DPEphos ligands show a complexation behavior that differs from the diphenylphosphine substituted DPEphos ligand. Complex 1a-tBu, possessing tert-Bu groups at the phosphorus atoms, shows a singlet in the 31P NMR spectrum (48.3 ppm) and a triplet for PdCH₂ in the 1H NMR spectrum indicative of a trans-compound (1.44 ppm, 3J_HP = 5.1 Hz). The trflate complex 3a-tBu showed similar NMR characteristics, which in combination with conductivity measurements, proved that 1a-tBu is ionic and contains a palladium-oxygen bond. In contrast, the methylpalladium chloride complex 1a-iPr shows NMR characteristics different from the ionic analog, 3a-iPr. In 1a-iPr the ligand is coordinated in a cis fashion, whereas in complex 3a-iPr the ligand is coordinated in a trans fashion and a bond between palladium and oxygen is present.

Ligands based on xanthene-type backbones. The methylpalladium complexes containing the xanthene diphosphine ligands 1b-d show broad signals in 1H NMR and in 31P NMR spectra at room temperature. At low temperatures (below -60 °C) sharp NMR spectra were obtained. The 1H and 31P NMR spectra of 1d at different temperatures are shown in figure 3. Complex 1c shows an AB system only, whereas complexes 1b, 1d and 2b show an AB system (major compound) and a singlet in the 31P NMR spectra. The 1H NMR spectra show a double doublet and a triplet for the methyl group bonded to palladium. The integration ratio of the AB system and the singlet in 31P NMR spectra match the double doublet to triplet ratio in the 1H NMR spectra. The NMR signals originate from the neutral, cis and the neutral, trans complexes (scheme 4). The effect of a change of the temperature on the ratio of cis-compound over trans-compound could only be investigated over a narrow temperature range (-90 to -50 °C) due to line-broadening in the NMR spectra. Over this temperature range, the ratios do not change. When 1b-1d were stored in solution for one day at room temperature, decomposition occurred and several unidentified complexes were formed. Suitable crystals of 1b for X-ray analysis were obtained from CH₂Cl₂ / Et₂O (selected data, table 2, figure 4).
Figure 3. Variable Temperature $^1$H and $^{31}$P NMR spectra of (Thixantphos)Pd(CH$_3$)Cl (1d) in CDCl$_3$ from $-60$ °C to $+40$ °C.
Table 2. Selected bond lengths (Å) and bond angles (°) for (Xantphos)Pd(CH3)Cl (1b).

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<td>Pd-C1</td>
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<td>P1-Pd-P2</td>
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<td>92.02(19)</td>
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<td>P1-Pd-Cl</td>
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Figure 4. Displacement ellipsoid plot of 1b. The ellipsoids are drawn at the 50% probability level. The solvent molecule in 1b and the hydrogen atoms have been omitted for clarity.

Complex 1b shows a *trans*-coordination mode (*trans*, neutral, scheme 4) with a P-Pd-P angle of 152.61(6)° (table 2, figure 4). The Pd-O distance (2.658(4) Å) is in the same range as for a five-coordinate palladium complex reported by Cavell *et al.*40; therefore a weak bonding interaction seems to be present. The complex has a distorted square pyramid geometry, which may be caused by the steric demands of the ligand. The complex is
neutral and contains a coordinating chloride anion. The oxygen atom of the ligand backbone is forced into the apical position and the coordinating ability of the oxygen atom is obviously not strong enough to displace the chloride anion to yield an ionic complex. When silver triflate was added to solutions of 1b-1d new singlets appeared in the $^{31}$P NMR spectra and the signals of the starting compounds disappeared. The chemical shifts in the $^{31}$P NMR spectra match those of the ionic complexes 3b-3d, which show a singlet in the $^{31}$P NMR spectra (20.2 - 20.4 ppm) and a triplet for the methyl group in the $^1$H NMR spectra ($J_{PH} = 5.4 - 6.6$ Hz). The isolated complexes 3b-3d show a high molar conductivity, which is characteristic of ionic complexes. This implies that the trans-compound observed in solutions of 1b-1d is not the ionic complex, but a neutral complex (trans, neutral, scheme 4, figure 3). In the ionic compounds, the oxygen donor atom in the ligand backbone is coordinated like in $[(\text{Xantphos})\text{Pd}(4-C_6H_4-CN)]^+ [\text{CF}_3\text{SO}_3]^-$ (figure 5).39

![Figure 5. Displacement ellipsoid plot of $[(\text{Xantphos})\text{Pd}(4-C_6H_4-CN)]^+ [\text{CF}_3\text{SO}_3]^-$](image)

The ellipsoids are drawn at the 50% probability level. The triflate anion, the solvent molecule and the hydrogen atoms have been omitted for clarity.
Compounds 1e and 1d did not show conductivity in CH$_2$Cl$_2$. In contrast, the Xantphos complexes 1b and 2b, showed a molar conductivity of 3.5 and 4.6 S cm$^{-2}$ mol$^{-1}$ resp. The NMR spectra of these two compounds did not show any sign of ionic complexes, since the singlet in the $^{31}$P NMR spectrum did not have the same chemical shift as the ionic complex 3b. The complex with the bromide anion, 2b, contains a larger amount of the trans-compound than the chloride complex, 1b (cis : trans = 0.90 (1b), 0.52 (2b)). When 2b was dissolved in a mixture of CD$_2$Cl$_2$ and CD$_3$CN the equilibrium shifted towards the cis-complex. The signals in $^{31}$P NMR spectra broaden upon the addition of CD$_3$CN. Lowering the temperature of the solution results in sharpening of the signals. Compound 1b-Me is a pure cis-complex according to the AB system in the $^{31}$P NMR spectrum (-29.0 ppm and -13.5 ppm, d, $^2$J$_{PP}$ = 34.3 Hz). This is confirmed by the double doublet for PdCH$_3$ (0.66 ppm, $^3$J$_{PH}$ = 4.6 Hz and $^3$J$_{PH}$ = 7.7 Hz) in the $^1$H NMR spectrum. The ionic compound 3b-Me, however, is a trans-complex. The singlet in the $^{31}$P NMR spectrum (-5.0 ppm), the triplet in the $^1$H NMR spectrum (1.21 ppm, $^3$J$_{PH}$ = 6.6 Hz) and the high molar conductivity confirm that this compound is a trans-compound and presumably contains a Pd-O bond analogous to 3b-3d and [(Xantphos)Pd(4-C$_6$H$_4$-CN)]$^+$ [CF$_3$SO$_3$]$^-$.  

Palladium complexes containing the Thioxantphos ligand, e, are different from the ligands containing oxygen in their ligand backbone. Complex 1e gives a singlet in the $^{31}$P NMR spectrum (40.5 ppm) and a triplet for PdCH$_3$ in the $^1$H NMR spectrum (1.08 ppm, $^3$J$_{PH}$ = 8.5 Hz) at room temperature, indicative of a trans-complex. The NMR spectra do not change when silver triflate was added to a solution of 1e in CDCl$_3$, which yields 3e. The Thioxantphos complex 1e has a molar conductivity in the same range as the ionic complexes, showing that the chloride anion is substituted by the sulfur donor atom in the ligand backbone.

**Ligands based on the ferrocene-type backbones.** Previous studies showed that the dpdpf ligand behaves generally as a cis-coordinating ligand in methylpalladium(II) compounds. We studied the complexation behavior of dialkylphosphine substituted ferrocene ligands in methylpalladium(II) complexes. All complexes containing ligand f-tBu (1,1'-bis(di-tert-butylphosphino)ferrocene), compounds 1f-tBu, 3f-tBu and 4f-tBu, yield complexes showing a singlet in the $^{31}$P NMR spectra (29.3 ppm) and a triplet in the $^1$H NMR spectra for the PdCH$_3$ group (1.70 ppm, $^3$J$_{PH}$ = 4.8 Hz). These observations support a trans-geometry in these complexes. The large chemical shift difference between the $\alpha$ and the $\beta$ hydrogen atoms of the cyclopentadienyl rings in the complexes (1.0-1.3 ppm) in
comparison with the differences in the free ligand (0.14 ppm) indicate that these rings are slightly tilted. Such NMR characteristics indicate that an interaction between palladium and iron is present in solution.\textsuperscript{41} UV-Vis spectra showed just one absorption around 349 nm.

![Diagram](image)

**Figure 6.** Displacement ellipsoid plot of 3f-tBu. The ellipsoids are drawn at the 50% probability level. The triflate anion and the hydrogen atoms have been omitted for clarity.

**Table 3.** Selected bond lengths (Å) and bond angles (°) for [(dtpf)PdCH\textsubscript{3}]\textsuperscript{+} [CF\textsubscript{3}SO\textsubscript{3}]\textsuperscript{-} (5f-tBu).

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<td>Pd-P2</td>
<td>2.2979(5)</td>
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<tr>
<td>Pd-Fe</td>
<td>3.0683(3)</td>
<td>Pd-C1</td>
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<td>Fe-Pd-C1</td>
<td>178.97(8)</td>
</tr>
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</table>

27
Suitable crystals of 3f-tBu for an X-ray analysis were obtained from CH$_2$Cl$_2$ / Et$_2$O (selected data, table 3). The metal center in 3f-tBu adopts a square planar geometry (figure 6).

Like the Xantphos ligand in 3b (vide supra) and [(Xantphos)Pd(4-C$_6$H$_4$-CN)]$^+$. [CF$_3$SO$_3$]$^-$, the ferrocene ligand in 3f-tBu behaves as a terdentate ligand. The phosphorus atoms are trans-coordinated (P-Pd-P angle = 158.21(2)$^\circ$) and the iron atom of the ligand back-bone is weakly coordinated to the palladium center (Pd-Fe distance = 3.0683(3) Å). Pd-Fe bonds were found previously in dicaticonic complexes,\textsuperscript{41}\textsuperscript{42} this is the first example of a monocationic methylpalladium compound with a palladium-iron bond. The interatomic Pd-Fe distance in complex 3f-tBu is larger than other Pd-Fe bonds, which have been reported by Sato \textit{et al}, such as [(dppf)Pd(PPh$_3$)] [BF$_4$]$_2$ (2.88 Å)\textsuperscript{41} and [(1,5,9-trithia[9]ferrocenophane)Pd(CH$_3$CN)] [BF$_4$]$_2$ (2.83 Å)\textsuperscript{42}, but it is in the same range as that in [(1,4,7-trithia[7]ferrocenophane)Pd(CH$_3$CN)] [BF$_4$]$_2$ (3.10 Å).\textsuperscript{42} The Pd-P distances are in the range generally found for trans-coordinating phosphorus atoms (Pd-P1 = 2.2862(5) Å and Pd-P2 = 2.2979(5) Å).\textsuperscript{39}\textsuperscript{43}

The complexes containing ligand f-iPr (1,1'-bis(di-iso-propylphosphino)ferrocene) show NMR characteristics that are similar to that of the dppf ligand, f. The ionic complex 3f-iPr shows an AB system in the $^3$P NMR spectrum (54.1 and 32.7 ppm, $^2$J$_{PP}$ = 21.3 Hz) and a double doublet in the $^1$H NMR spectrum for PdCH$_3$ (0.73 ppm, $^3$J$_{PH}$ = 4.8 Hz and $^3$J$_{PH}$ \approx 1 Hz). According to $^1$H NMR spectroscopy, acetonitrile is coordinated to the palladium center. The singlet in the $^3$P NMR spectrum (4.5 ppm) for the methylpalladium chloride complex 5 (ligand f-Et), the triplet for PdCH$_3$ (0.51 ppm, $^3$J$_{PH}$ = 5.9 Hz) in the $^1$H NMR spectrum and the large chemical shift differences between the $\alpha$ and $\beta$ hydrogen atoms of the cyclopentadienyl rings in the complex (0.75 ppm), suggest a similar coordination as observed for complex 1f-tBu. Molecular weight determination in solution, however, showed that 5 is a dimeric compound. When a solution of 5 was allowed to stand at room temperature in CD$_2$Cl$_2$, a slow reaction was observed. A new AB system appeared in the $^3$P NMR spectrum (30.1 and 10.7 ppm, $^2$J$_{PP}$ = 28.2 Hz) and a double doublet for the methyl group appeared in the $^1$H NMR spectrum (0.75 ppm, $^3$J$_{PH}$ = 7.5 Hz and $^3$J$_{PH}$ = 3.6 Hz.). The new compound, 6, was shown to be a monomeric cis-compound analogous to 1f and 1f-iPr. At low palladium concentrations, 5 was not present in solution after three days, but at higher palladium concentrations ([Pd] > 2.5x10$^{-2}$ M) 5 can still be observed, even after allowing
the solution to stand for more than three days. This proves that at higher palladium concentrations an equilibrium exists between 5 and 6.

Discussion

The complexes containing the DPEphos ligand are cis-coordinated and show no sign of a bonding palladium-oxygen interaction. The reasons may be that the DPEphos ligand prefers a smaller bite-angle than the other ligands in the Xanthphos-series, and possesses a larger flexibility. Ionic complexes containing the DPEphos ligand need a coordinating solvent during synthesis to stabilize the ionic metal center. The crystal structures of complexes with the DPEphos ligand show that the two aryl rings of the ligand backbone can rotate around the carbon-oxygen bond. One of the aryl rings of the ligand backbone has a π-π interaction with one of the phenyl rings bonded to the phosphorus atom. This causes the DPEphos ligand to narrow the P-Pd-P angle relative to the other ligands in the Xanthphos series, which lack such a large flexibility. Only at low temperatures the ionic complex possessing a palladium-oxygen bond was observed. In the absence of coordinating solvents the smallest natural bite-angle ligand in the Xantphos series, DPEphos, has the tendency to form a palladium-oxygen bond, which shows the capability of the ligand to coordinate in a trans-fashion.

The size of the substituents on phosphorus influences the coordination mode of the ligand. tert-Butyl groups on phosphorus (ligand a-tBu) stabilize the ionic complex containing a palladium-oxygen bond. The cis-complexes cannot be formed due to steric crowding around the metal center. The strength of the palladium-oxygen bond is illustrated by the fact that in the methylpalladium chloride complex, 1a-tBu, the chloride anion is displaced from the metal center. However, the less crowded iso-propyl substituted ligand, a-iPr, behaves as a cis-ligand.

The solid state structure of complex 1b, which contains the less flexible, large natural bite-angle ligand Xantphos, b, shows that the oxygen atom of the P-O-P ligand back-bone in the trans-complexes is located at the apical position of the square pyramidal complex. The weak palladium-oxygen interaction can stabilize the trans-complex relative to the cis-complex, which lacks such a bonding interaction. The methylpalladium complexes (1b-1d) are mainly cis-coordinated in solution, whereas the bromide compound 3b exists as a 1:1 ratio of the cis and the trans-compound. The alkylphosphine ligand b-Me forms a cis-complex only. The higher electron density on palladium and less steric hindrance makes
a bonding palladium-oxygen interaction less favorable and therefore the trans-complex is not observed.

Scheme 5

The nearby oxygen atom can also play a role in the stabilization of an ionic intermediate that can be formed during the interchange from the cis- to the trans-complexes (scheme 5). Only in the case of complex 1b and 2b a significantly higher conductivity could be measured than for other neutral complexes, which suggests the presence of such an ionic intermediate but this could not be verified using NMR spectroscopy. The amount of cis-complex increased when a more polar co-solvent (acetonitrile) was added to a dichloromethane solution of 2b. The polar solvent stabilizes the more polar cis-complex. The rate of interconversion between the cis- and trans-complexes was higher in the more polar solvent as the interconversion reaction occurred at lower temperatures than in pure dichloromethane, which is probably caused by the stabilization of the ionic intermediate (scheme 5). Complex 1e is ionic, as concluded from the molar conductivity of complex 1e, which is of the same magnitude as that of the triflate complex 3e, which means that the chloride anion is not coordinated to the metal center. In 1e the chloride anion is substituted by the sulfur donor of the ligand back-bone. The soft sulfur atom can displace the coordinated anions, since it binds more strongly to the soft palladium metal center than the hard oxygen atom. Addition of acetonitrile or coordinating anions (chloride or bromide anions) to solutions of ionic complexes having a Pd-O or Pd-S bond did not affect the structures of the complexes. Such additives obviously cannot compete with the intramolecular Pd-O and Pd-S bonds. The activity and selectivity of the catalyst can be influenced by the presence of a Pd-Fe bond. Complexes which contain a palladium-iron bond are generally strongly colored according to Sato et al. In contrast, the complexes described in this study are not strongly colored and in the visible range no other absorptions were observed than those originating from the ferrocene unit. Although the solid state
structure of $3f$-$tBu$ has been determined and clearly shows the existence of a bonding palladium-iron interaction, the NMR spectra of $1f$-$tBu$ and $4f$-$tBu$ show the same characteristics in solution as $3f$-$tBu$. These complexes show a large chemical shift difference between the $\alpha$ and $\beta$ hydrogens of the cyclopentadieny ligand. The methylpalladium chloride complex $1f$-$tBu$ is ionic in dichloromethane solution, which indicates that the chloride anion is no longer bonded to palladium and the fourth coordination site is occupied by iron. These observations indicate that in these complexes a bonding Pd-Fe interaction is present as well (scheme 6).

The main difference between the complexes described here and the ones described by Sato, is that the complexes reported by Sato are dicationic. The difference in electrophilicity of the palladium center accounts for the changes in the UV-Vis spectra. The bulkiness of the ligand (large tert-Bu groups) hampers a cis-coordination to palladium. Because the phosphorus atoms are positioned trans, the iron atom is forced into the proximity of the palladium center enforcing the iron-palladium interaction. The slightly less bulky iso-propyl ligand, $f$-$iPr$, leads to the normal cis-coordination. No spectroscopic evidence was found for
a palladium-iron interaction. The same was observed by Butler et al in the crystal structure of (dipf)PdCl$_2$.\textsuperscript{46}

The least bulky substituted diphosphine ligand based on the ferrocene backbone, f-Et, yields a different complex (scheme 6). The $^1$H NMR chemical shift difference of the $\alpha$ and $\beta$ hydrogens is large, which indicates that the cyclopentadienyl rings are tilted, and suggests the presence of a bonding palladium-iron interaction. In addition, a triplet for the methyl group is observed. The large chemical shift difference between the PdCH$_3$ signals in the $^1$H NMR spectra (1.70 ppm for 1f-tBu and 0.51 ppm for 5) and the low molar conductivity, indicative of a neutral complex, suggest that a different complex is formed. Molecular weight determination in solution proved that 5 is a dimeric compound, which is an analog of the previously reported compound [(dppm)Pd(CH$_3$)$_2$Cl].\textsuperscript{47} The formation of a dimer is surprising if we consider that the ligands in compound 1f and 1f-iPr,\textsuperscript{36} are chelated in a cis-fashion. The observation of the slow formation of the monomeric cis-complex, 6, in dichloromethane solution provided an answer to this dilemma (scheme 6).\textsuperscript{47} Obviously, the dimer is formed as the kinetic product during the synthesis in benzene, whereas the cis-complex is the thermodynamically favored compound.

Conclusions

Solid state structures and structures in solution of neutral and ionic palladium(II) complexes bearing diphosphine ligands based on the diphenyl ether, xanthene and ferrocene backbone have been studied. The subtle changes in the steric and electronic properties of the diphosphine ligands and the electron density on the palladium metal were shown to influence the structure of the palladium complexes dramatically.

Experimental Section

General Synthetic Procedures. All reactions were carried out using standard Schlenk techniques under an atmosphere of purified argon or nitrogen. Benzene and toluene were distilled from sodium, diethylether was distilled from sodium/benzophenone and hexane and pentane were distilled from sodium/benzophenone/triglyme. Dichloromethane and acetonitrile were distilled from CaH$_2$. Chemicals were purchased from Aldrich Chemical Co. and Acros Chimica. (COD)Pd(CH$_3$)$_2$, (COD)Pd(CH$_3$)Br, (dppf)Pd(CH$_3$)Cl,\textsuperscript{36} Na[B(3,5-(CF$_3$)$_2$C$_6$H$_3$)],\textsuperscript{48} chloro-bis(diethylamino)phosphine,\textsuperscript{49} DPEphos,\textsuperscript{25} Thixantphos,\textsuperscript{25} Sixantphos,\textsuperscript{25} Xantphos,\textsuperscript{25} Thioxantphos,\textsuperscript{26} dtpe,\textsuperscript{50} dipf,\textsuperscript{51}
depf,52 and 10,11-dihydrodibenzo[b,f]oxepine53 were synthesized according to literature procedures. NMR spectra were recorded on a Bruker AMX 300, a Varian Mercury 300, and a Bruker DRX 300. 31P and 13C spectra were measured 1H decoupled (unless stated otherwise). Deuterated solvents were first degassed and then vacuum transferred from a drying agent. CD2Cl2 and CD3CN were distilled from CaH2. TMS was used as a standard for 1H and 13C NMR spectroscopy and H3PO4 for 31P NMR spectroscopy. Infrared spectra were recorded on a Nicolet 510 FT-IR spectrophotometer. Elemental analyses were performed on a Hereaus Elementar Vario EL.

Ligand synthesis.

General remarks. All alkylphosphine ligands are very sensitive towards oxygen. Therefore, these ligands were synthesized and handled under an argon atmosphere. The products were purified by column chromatography under a nitrogen atmosphere.

2,2'-Dilithiodiphenylether-(N,N,N',N'-tetramethylethylene diamine). To a solution of 7.18 g (42.2 mmol) diphenylether and 14.0 mL (92.7 mmol) of TMEDA in 40 mL of hexane, 44.3 mL of a 2.1 M solution (93.0 mmol) of n-BuLi in hexane was added in 30 min. at 0 °C. The reaction mixture stirred at room temperature for 16 hours. The dilithio-salt was precipitated at −20 °C and the suspension was filtered. The residue was washed with 20 mL of hexane. The off-white powder was isolated and used in synthesis without further analysis. Yield: 8.26 g (27.7 mmol, 65 %).

2,2'-Bis-(di-tert-butylphosphino)diphenylether (DPEphos-tBu, a-tBu). 2.09 g (7.01 mmol) of 2,2'-dilithiodiphenylether was suspended in 40 mL of hexane. 2.66 mL (14.0 mmol) of chlorodi-tert-butylphosphine was added. The reaction mixture was stirred at room temperature for 60 hours and refluxed for four hours. The reaction mixture was quenched using 5 mL of degassed water and 5 mL of brine. The organic phase was dried over MgSO4. The solution was filtered and the solvent was removed in vacuo. The yellowish oil was purified by column chromatography (neutral alumina, eluent 7:3 mixture of diethyl ether and hexanes). The solvents were removed in vacuo and a colorless viscous oil was isolated. Yield: 1.74 g (3.79 mmol, 54 %) of a colorless oil which solidified upon standing. 1H NMR (300 MHz, CDCl3, 25 °C): 7.79 (Ph, m, 2H), 7.24 (Ph, m, 2H), 7.05 (Ph, m, 2H), 6.73 (Ph, m, 2H), 1.24 (C(CH3)3, dd, 3JPH = 11.6 Hz, 44H). 31P NMR (121.5 MHz, CDCl3, 25 °C): 13.0 ppm (s).

2,2'-Bis-(di-iso-propylphosphino)diphenylether (DPEphos-iPr, a-iPr). The same procedure was followed as for DPEphos-tBu (a-tBu). Chlorodi-iso-propylphosphine was used instead of chlorodi-tert-butylphosphine. Yield: 0.85 g (0.021 mmol, 37 %) colorless oil.
NMR, CDCl₃, δ (ppm): 7.50 (Ph, m, 2H), 7.26 (Ph, m, 2H), 7.08 (Ph, t, 3J_HH = 6.0 Hz, 2H), 6.74 (Ph, dd, 3J_HH = 6.0 Hz, 3J_PH = 3.0 Hz, 2H), 2.31 (CH(CH₃)₂, d, sept, 3J_PH = 3.2 Hz, 3J_HH = 7.0 Hz, 4H), 1.16 (CH(CH₃)₂, dd, 3J_HH = 7.0 Hz, 3J_PH = 14.5 Hz, 20H), 1.01 (CH(CH₃)₂, dd, 3J_HH = 7.0 Hz, 3J_PH = 12.6 Hz, 16H).³¹P NMR (300 MHz, CDCl₃, 25 °C): 2.0 (s).

9,9-Dimethyl-4,5-bis-(dichlorophosphino)xanthene. 2.19 g (10.2 mmol) 9,9-Dimethylxanthene and 4.7 mL (31 mmol) TMEDA were dissolved in 30 mL of hexane / diethyl ether (1 : 1, v/v). 14 mL of a 2.2 M (31 mmol) solution of n-BuLi in hexane was slowly added to the solution at 0 °C. The reaction mixture was allowed to warm to room temperature and was stirred for 24 h. The reaction mixture was cooled to −78 °C and 5.6 mL (30.7 mmol) of chloro-bis(diethylamino)phosphine was added. The reaction mixture was allowed to warm to room temperature and it was stirred for another 24 h. The solvents were removed in vacuo and the dark oil was dissolved in 50 mL of hexane. The solution was filtered and the solvent in vacuo was removed again. The brownish oil was dissolved again in 150 mL of hexane and a large excess of HCl gas was bubbled through the solution at −78 °C. The ammonium salt was removed by filtration of the reaction mixture and the crude product was recrystallized from hexane at −20 °C. Yield: 3.58 g (8.6 mmol, 84 %) of a yellow microcrystalline solid.¹H NMR (300 MHz, CDCl₃, 25 °C): 7.91 (Ph, d, 3J_HH = 7.5 Hz, 2H), 7.60 (Ph, d, 3J_HH = 7.5 Hz, 2H), 7.30 (Ph, t, 3J_HH = 7.5 Hz, 2H), 1.63 (C(CH₃)₂, s, 4H).³¹P NMR (121.5 MHz, CDCl₃, 25 °C): 159.0 (s).

9,9-Dimethyl-4,5-bis-(dimethylphosphino)xanthene (Xantphos-Me, b-Me). 1.40 g (3.40 mmol) of 9,9-Dimethyl-4,5-bis-(dichlorophosphino)xanthene was dissolved in 30 mL of THF. To this solution 5.7 mL of a 3.0 M solution (17.0 mmol) of methylmagnesium bromide in THF was slowly added at −78 °C. The reaction mixture was stirred for 0.5 h, after which it was allowed to warm to room temperature. The reaction mixture was stirred for 16 h. The solvent was removed in vacuo and the resulting oil was dissolved again in hexane and 10 mL of degassed water was added. The organic layer was dried over MgSO₄ and filtered over neutral alumina. The solvent was removed in vacuo. Yield: 0.61 g (1.85 mmol, 54 %) of a yellowish oil.¹H NMR (300 MHz, CDCl₃, 25 °C): 7.38 (Ph, m, 2H), 7.21-7.00 (Ph, m, 4H), 1.62 (C(CH₃)₂, s, 6H), 1.45 (P(CH₃)₂, m, 6H), 1.24 (P(CH₃)₂, s, 6H).³¹P NMR (121.5 MHz, CDCl₃, 25 °C): -58.53 (s).

Complex synthesis.

General remarks. The alkylphosphine ligands used in complex synthesis were used in a larger excess in cases where the ligand had partially oxidized prior to use. The oxidized
alkylphosphine ligands did not coordinate to palladium. Palladium complexes containing bidentate alkylphosphine ligands could be handled and stored under ambient conditions.

**Synthesis of (L-L)Pd(CH\textsubscript{3})Cl (1).** To a solution of 0.36 mmol (1.05 equiv.) (COD)Pd(CH\textsubscript{3})Cl in 5 mL of benzene, 0.37 mmol of ligand (L-L) was added. The solution was stirred for one hour. The suspension was filtered and the residue was washed with benzene and diethylether. The product was dried *in vacuo*.

**(DPEphos)Pd(CH\textsubscript{3})Cl (1a).** Yield: ca. 85%. \textsuperscript{1}H NMR (CD\textsubscript{2}Cl\textsubscript{2}, 25 °C): 7.8-6.8 (Ph, m, 25H), 6.5-6.2 (Ph, m, 3H), 0.92 (PdCH\textsubscript{3}, dd, \textsuperscript{3}J\textsubscript{PH} = 6.3 Hz and \textsuperscript{3}J\textsubscript{PH} = 4.5 Hz). \textsuperscript{31}P NMR (CD\textsubscript{2}Cl\textsubscript{2}, 25 °C): 30.6 (d, \textsuperscript{2}J\textsubscript{PP} = 29.9 Hz), 8.6 (d, \textsuperscript{2}J\textsubscript{PP} = 29.9 Hz). Anal. Calcd. for (C\textsubscript{37}H\textsubscript{3}IC\textsubscript{10}P\textsubscript{2}Pd): C, 63.90; H, 4.50. Found: C, 64.25; H, 4.68.

**(2,2'-Bis-(di-fc7^burylphosphino)diphenylether)Pd(CH\textsubscript{3})Cl (la-tBu).** Yield: ca. 85%. \textsuperscript{1}H NMR (CD\textsubscript{2}Cl\textsubscript{2}, 25 °C): 7.8-6.8 (Ph, m, 25H), 6.5-6.2 (Ph, m, 3H), 0.92 (PdCH\textsubscript{3}, dd, \textsuperscript{3}J\textsubscript{PH} = 6.3 Hz and \textsuperscript{3}J\textsubscript{PH} = 4.5 Hz). Anal. Calcd. for (C\textsubscript{37}H\textsubscript{3}IC\textsubscript{10}P\textsubscript{2}Pd): C, 63.90; H, 4.50. Found: C, 64.25; H, 4.68.

**(Xantphos)Pd(CH\textsubscript{3})Cl (lb).** Yield: ca. 78%. \textsuperscript{1}H NMR (CD\textsubscript{2}Cl\textsubscript{2}, 25 °C): 7.7-7.1 (Ph, m, 26H), 1.76 (C(CH\textsubscript{3})\textsubscript{2}, s, 6H), 0.38 (PdCH\textsubscript{3}, s, 3H). \textsuperscript{31}P NMR (CD\textsubscript{2}Cl\textsubscript{2}, 25 °C): 15.8 (br,s). \textsuperscript{1}H NMR (CD\textsubscript{2}Cl\textsubscript{2}, -70 °C): 8.3-6.6 (Ph, m, 26H), 2.0-1.4 (C(CH\textsubscript{3})\textsubscript{2}, br, s, 6H), 0.53 (PdCH\textsubscript{3} (cis-complex), dd, \textsuperscript{3}J\textsubscript{PH} = 7.2 Hz and \textsuperscript{3}J\textsubscript{PH} = 3.6 Hz, 3H), -0.16 (PdCH\textsubscript{3} (trans-complex), t, \textsuperscript{3}J\textsubscript{PH} = 6.0 Hz, 3H). \textsuperscript{31}P NMR (121.5 MHz, CD\textsubscript{2}Cl\textsubscript{2}, -70 °C): 27.6 (cis-complex, d, \textsuperscript{2}J\textsubscript{PP} = 31.7 Hz), 12.0 (trans-complex, s), 11.2 (cis-complex, d, \textsuperscript{2}J\textsubscript{PP} = 31.6 Hz). Anal. Calcd. for (C\textsubscript{40}H\textsubscript{35}ClO\textsubscript{2}Pd): C, 65.32; H, 4.80. Found: C, 65.20; H, 5.19.

**Crystal structure determination of (1b):**
C\textsubscript{40}H\textsubscript{35}OP\textsubscript{2}ClPdC\textsubscript{4}H\textsubscript{10}O, M\textsubscript{r} = 735.5 g/mole, yellow cube, 0.20 x 0.40 x 0.60 mm, monoclinic, P2\textsubscript{1}/n, a = 12.7823(9), b = 17.954(1), c = 16.961(2) Å, β = 93.290(5)°, V = 3886.0(6) Å\textsuperscript{3}, Z = 4, ρ = 1.380 g/cm\textsuperscript{3}. 7967 reflections were measured on an Enraf-Nonius CAD-4 (λ = 1.5418) at room temperature. Analytical absorption correction with the program ABSCAL (Watenpaugh and Stewart, 1992) using ψ-scans of the [-2 6 3] reflection, with coefficients in the range 1.0-3.04. The structure was solved with the PATTY option of
the DIRDIF96 program system.\textsuperscript{54} Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were calculated. R-values: \( \langle \Delta / \sigma \rangle_{\text{max}} = 0.27, S = 0.93 \) a weighting scheme \( w = [10 + 0.001 * ( \sigma (F_{\text{obs}}) )^2 + 0.0001 / ( \sigma (F_{\text{obs}}) )]^{-1} \) was used (R = 0.061, R\(_w\) = 0.064. All calculations were performed with XTAL.\textsuperscript{55} unless stated otherwise.

**(Xantphos-Me)Pd(CH3)Cl (1b-Me).** Yield: ca. 64 %. White solid. \(^1^H\) NMR (300 MHz, CDCl\(_3\), 25 °C): 7.49 (Ph, dd, \( J = 6.6 \) Hz and \( J = 2.1 \) Hz, 1H), 7.43 (Ph, dd, \( J = 7.2 \) Hz and \( J = 1.5 \) Hz, 1H), 7.23 (Ph, m, 2H), 7.19 (Ph, m, 2H), 1.88 (P(CH3)_2, d, \( J_{\text{PH}} = 9.9 \) Hz, 6H), 1.81 (P(CH3)_2, d, \( J_{\text{PH}} = 7.2 \) Hz, 6H), 1.63 (C(CH3)_2, s, 6H), 0.66 (PdCH3, dd, \( J_{\text{PP}} = 4.6 \) Hz and \( J_{\text{PH}} = 7.7 \) Hz, 3H). \(^3^P\) NMR (121.5 MHz, CDCl\(_3\), 25 °C): -29.0 (d, \( J_{\text{PP}} = 33.9 \) Hz), -13.5 (d, \( J_{\text{PP}} = 34.3 \) Hz). Anal. Calcd. for (C\(_{20}\)H\(_{27}\)ClO\(_2\)Pd): C 49.30; H, 5.59. Found: C, 50.09; H, 5.72.

**(Sixantphos)Pd(CH3)Cl (1c).** Yield: ca. 86 %. \(^1^H\) NMR (300 MHz, CD\(_2\)Cl\(_2\), -40 °C): 7.9-6.7 (Ph, m, 26H), 1.66 (PdCH3, dd, \( J_{\text{PH}} = 7.0 \) Hz and 3.8 Hz, 3H), 0.47 (Si(CH3)_2, s, 6H). \(^3^P\) NMR (121.5 MHz, CD\(_2\)Cl\(_2\), -40 °C): 30.6 (d, \( J_{\text{PP}} = 33.9 \) Hz), 14.2 (d, \( J_{\text{PP}} = 33.9 \) Hz). Anal. Calcd. for (C\(_{39}\)H\(_{35}\)ClO\(_2\)SiPd): C, 62.32; H, 4.69. Found: C, 62.58; H, 4.42.

**(Thixantphos)Pd(CH3)Cl (1d).** Yield: ca. 65 %. \(^1^H\) NMR (300 MHz, CD\(_2\)Cl\(_2\), -60 °C): 8.3-6.5 (Ph, m, H), 2.20 and 2.17 (C(CH3), s, 6H), 0.74 (PdCH3 (cis-complex), dd, \( J_{\text{PH}} = 7.2 \) Hz and \( J_{\text{PH}} = 2.7 \) Hz, 3H), -0.21 (PdCH3 (trans-complex), t, \( J_{\text{PH}} = 6.0 \) Hz, 3H). \(^3^P\) NMR (CD\(_2\)Cl\(_2\), -60 °C): 32.0 (cis-complex, d, \( J_{\text{PP}} = 34.0 \) Hz), 15.9 (trans-complex, s), 15.5 (cis-complex, d, \( J_{\text{PP}} = 34.1 \) Hz). Anal. Calcd. for (C\(_{39}\)H\(_{35}\)ClO\(_2\)SdPd): C, 62.16; S, 4.25; H, 4.41. Found: C, 61.68; S, 4.66; H, 4.39.

**(Thioxantphos)Pd(CH3)Cl (1e).** Yield: ca. 57 %. \(^1^H\) NMR (300 MHz, CDCl\(_3\), 25 °C): 7.9-7.2 (Ph, m, 26H), 2.15 (C(CH3)_3, s, 3H), 1.63 (C(CH3)_3, s, 3H), 1.08 (PdCH3, t, \( J_{\text{PH}} = 8.5 \) Hz, 3H). \(^3^P\) NMR (121.5 MHz, CDCl\(_3\), 25 °C): 40.5 (s). \(^{13}\)C NMR (75.4 MHz, CD\(_2\)Cl\(_2\), 25 °C): 147.5, 139.7 and 137-128 (Ph, m), 45.1 (C(CH3)_2, s), 27.0, 26.8 (C(CH3)_2, s), 8.9 (PdCH3, s).

\([\text{dipf}]\text{PdCH}_{3}^+\) \text{Cl}^- (1f-tBu).** Yield: ca. 92 %. \(^1^H\) NMR (300 MHz, CDCl\(_3\), 25 °C): 5.45 (Cp, m, 4H), 4.20 (Cp, m, 4H), 1.69 (PdCH3, m, 3H), 1.47 (C(CH3)_3, dd, \( J_{\text{PH}} = 7.4 \) Hz, 36H). \(^3^P\) NMR (121.5 MHz, CDCl\(_3\), 25 °C): 29.4 (s). Anal. Calcd. for (C\(_{27}\)H\(_{39}\)ClFeP\(_2\)Pd): C, 52.03; H, 6.31. Found: C, 51.84; H, 6.12.

\([\text{dipf}]\text{Pd(CH}_{3})\text{Cl (1f-IPr).** Yield: ca. 83 %. \(^1^H\)NMR (300 MHz, CDCl\(_3\), 25 °C): 4.4-4.3 (Cp, m, 8H), 2.69 and 2.43 (C(CH3)_3, m, \( J_{\text{HH}} = 7.1 \) Hz, 4H), 1.50 (dd, 6H, \( J_{\text{HH}} = 7.1 \) Hz and \( J_{\text{PH}} = 15.9 \) Hz, CH(C(CH3)_2), 1.29-1.13 (C(CH3)_2, m, 18H), 0.91 (PdCH3, dd, \( J_{\text{PH}} = 36^\text{°}\).
3.0 Hz and $^{3}J_{PH} = 6.9$ Hz, 3H). $^{31}$P NMR (121.5 MHz, CDCl$_3$, 25 °C): 49.5 (d, $^{2}J_{PP} = 21.6$ Hz), 29.5 (d, $^{2}J_{PP} = 21.6$ Hz). Anal. Calcd. for (C$_{23}$H$_{39}$ClFeP$_{2}$Pd): C, 48.03; H, 6.83. Found: C, 48.21; H, 6.98.

**Synthesis of (L-L)Pd(CH$_3$)Br (2).** To a solution of 0.36 mmol (1.05 equiv.) (COD)Pd(CH$_3$)Br in 5 mL of benzene, 0.37 mmol of ligand (L-L) was added. The solution was stirred for one hour. The suspension was filtered and the residue was washed with benzene and diethyl ether. The product was dried *in vacuo.*

(DPEphos)Pd(CH$_3$)Br (2a). Yield: ca. 89 %. $^{1}$H NMR (CD$_2$Cl$_2$, 25 °C): 7.8-6.9 (Ph, m, 25H), 6.5-6.3 (Ph, m, 3H), 1.00 (PdCH$_3$, d, $^{3}J_{PH} = 2.1$ Hz). $^{31}$P NMR (CD$_2$Cl$_2$, 25 °C): 30.8 (d, $^{2}J_{PP} = 30.0$ Hz), 8.9 (d, $^{2}J_{PP} = 30.0$ Hz). Anal. Calcd. for (C$_{37}$H$_{31}$BrOP$_{2}$Pd): C, 60.06; H, 4.22. Found: C, 60.00; H, 4.21. (Xantphos)Pd(CH$_3$)Br (2b). Yield: ca. 65 %. $^{1}$H NMR (300 MHz, CD$_2$Cl$_2$, -80 °C): 8.2-6.5 (Ph, m, 26H), 2.1-1.5 (C(CH$_3$)$_2$, br, s, 6H), 0.56 (PdCH$_3$, cis-complex, dd, $^{3}J_{PH} = 7.2$ Hz and $^{3}J_{PH} = 3.6$ Hz, 3H), -0.09 (PdCH$_3$, trans-complex, t, $^{3}J_{PH} = 6.0$ Hz, 3H). $^{31}$P NMR (121.5 MHz, CD$_2$Cl$_2$, -80 °C): 29.6 (cis-complex, d, $^{2}J_{PP} = 31.4$ Hz), 15.3 (trans-complex, s), 12.3 (cis-complex, d, $^{2}J_{PP} = 31.4$ Hz).

**Synthesis of ionic methylpalladium complexes (3 and 4).** 0.190 mmol 1 was suspended in 2 mL of CH$_2$Cl$_2$ / CH$_3$CN (10 : 1, v/v). 0.191 mmol of AgX (X = CF$_3$SO$_3$, CF$_3$CO$_2$) was added to the suspension. After stirring for 10 minutes, the suspension was filtered over celite. Then 10 mL diethyl ether was added to crystallize the product.

[(DPEphos)PdCH$_3$(CH$_3$CN)]$^{+}$ [CF$_3$SO$_3$]$^{-}$ (3a). Yield: ca. 65 %. $^{1}$H NMR (300 MHz, CDCl$_3$, -20 °C): 7.8-6.2, (Ph, m, 28H), 1.79 (CH$_3$CN, s, 3H), 0.88 (PdCH$_3$, dd, $^{3}J_{PH} = 6.6$ Hz and $^{3}J_{PH} = 2.9$ Hz, 3H). $^{31}$P NMR (121.5 MHz, CDCl$_3$, -20 °C): 31.8 (d, $^{2}J_{PP} = 31.7$ Hz), 7.7 (d, $^{2}J_{PP} = 31.7$ Hz). $^{13}$C NMR (75.4 MHz, CD$_2$Cl$_2$, -20 °C): 159.0, 157.6, 137-120 (Ph, m), 118.3 (CH$_3$CN, s), 2.3 (PdCH$_3$, d, $^{2}J_{PP} = 100.3$ Hz), -3.5 (CH$_3$CN, s). Anal. Calcd. for (C$_{40}$H$_{34}$F$_{3}$O$_{2}$PdSNPd): C, 56.51; H, 4.03; N, 1.65. Found: C, 56.16; H, 4.05; N, 1.57. 

**Crystal structure determination of 3a:**

C$_{39}$H$_{34}$NOP$_2$Pd:CF$_3$SO$_3$, M$_r$ = 850.1 g/mole, colorless cube, 0.20 x 0.25 x 0.30 mm, monoclinic, P2$_1$/n, a = 10.8261(6), b = 26.801(2), c = 13.8267(8) Å, β = 109.637(9)°, V = 3778.5(5) Å$^3$, Z = 4, ρ = 1.49 g/cm$^3$. 7751 reflections were measured on an Enraf-Nonius CAD-4 (λ = 1.5418) at -20 °C. Analytical absorption correction was made using the program ABSCAL (Watenpaugh and Stewart 1992) using ψ-scans of the [0 1 4 6] reflection, with coefficients in the range 1.0-1.24. The structure was solved with the PATTY option of the DIRDIF96.
Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were calculated. R-values: \( [(\Delta/\sigma)_{\text{max}} = 0.54, S = 1.12] \) a weighting scheme \( w = [20 + 0.001*(\sigma(F_{\text{obs}}))^2 + 0.0001 / (\sigma(F_{\text{obs}}))] \) was used \( (R = 0.070, R_w = 0.074) \). All calculations were performed with XTAL, unless stated otherwise.

\[(2,2'-\text{Bis-(di-tert-butylphosphino)diphenylether})\text{PdCH}_3]^+ [\text{CF}_3\text{SO}_3]^-(3a-\text{tBu}).\]

Yield: ca. 84 %. \(^1\)H NMR (300 MHz, CDCl\(_3\), 25 \(^\circ\)C): 8.0-7.4 (Ph, m, 8H), 1.49 (C(\(\text{CH}_3\))\(_3\), dd, \( ^3J_{\text{PH}} = 7.6 \) Hz, 36H), 1.44(PdCH\(_3\), t, \( ^3J_{\text{PH}} = 4.9 \) Hz). \(^{31}\)P NMR (121.5 MHz, CDCl\(_3\), 25 \(^\circ\)C): 48.4 (s). Anal. Calcd. for (C\(_{30}\)H\(_{47}\)F\(_3\)O\(_4\)P\(_2\)Pd): C, 49.42; H, 6.50. Found: C, 49.02; H, 6.60.

\[(2,2'-\text{Bis-(di-iso-propylphosphino)diphenylether})\text{PdCH}_3]^+ [\text{CF}_3\text{SO}_3]^-(3a-\text{iPr}).\]

Yield: ca. 56 %. \(^1\)H NMR (300 MHz, CDCl\(_3\), 25 \(^\circ\)C): 7.73 (Ph, dd, \( ^3J_{\text{PH}} = 3.6 \) Hz, \( ^3J_{\text{HH}} = 7.4 \) Hz, 2H), 7.64 (Ph, d, \( ^3J_{\text{HH}} = 7.9 \) Hz, 2H), 7.49 (Ph, d, \( ^3J_{\text{HH}} = 7.9 \) Hz, 2H), 7.42 (Ph, t, \( ^3J_{\text{HH}} = 7.4 \) Hz, 2H), 2.71 (CH(CH\(_3\))\(_2\)) \( \text{br m} \), \( ^3J_{\text{HH}} = 6.9 \) Hz, 4H), 1.42-1.20 (PdCH\(_3\), m, \( ^2J_{\text{PH}} = 6.9 \) Hz, 27H). \(^{31}\)P NMR (121.5 MHz, CDCl\(_3\), 25 \(^\circ\)C): 35.8 (s). Anal. Calcd. for (C\(_{26}\)H\(_{39}\)F\(_3\)O\(_4\)P\(_2\)SPd): C, 46.40; S, 4.76; H, 5.84. Found: C, 46.02; S, 4.81; H, 5.79.

\[(\text{Xantphos})\text{PdCH}_3]^+ [\text{CF}_3\text{SO}_3]^-(3b).\]

Yield: ca. 78 %. \(^1\)H NMR (300 MHz, CDCl\(_3\), 25 \(^\circ\)C): 7.9-7.4 (Ph, m, 26H), 1.75 (C(\(\text{CH}_3\))\(_2\), s, 6H), 1.50 (PdCH\(_3\), t, \( ^3J_{\text{PH}} = 5.7 \) Hz). \(^{31}\)P NMR (121.5 MHz, CDCl\(_3\), 25 \(^\circ\)C): 20.4 (s). Anal. Calcd. for (C\(_{41}\)H\(_{35}\)O\(_4\)P\(_2\)SF\(_3\)Pd): C, 58.00; S, 3.78; H, 4.15. Found: C, 57.94; S, 3.63; H, 4.30.

\[(\text{Xantphos-Me})\text{PdCH}_3]^+ [\text{CF}_3\text{SO}_3]^-(3b-\text{Me}).\]

Yield: ca. 45 %. \(^1\)H NMR (300 MHz, CDCl\(_3\), 25 \(^\circ\)C): 7.8-7.6 (Ph, m, 4H), 7.43 (Ph, t, \( ^3J_{\text{HH}} = 7.8 \) Hz, 2H), 1.82 (P(CH\(_3\))\(_2\), s, 12H), 1.68 (C(\(\text{CH}_3\))\(_2\), s, 6H), 1.21 (PdCH\(_3\), t, \( ^3J_{\text{PH}} = 6.6 \) Hz, 3H). \(^{31}\)P NMR (121.5 MHz, CDCl\(_3\), 25 \(^\circ\)C): -5.0 (s).

\[(\text{Sixantphos})\text{PdCH}_3]^+ [\text{CF}_3\text{SO}_3]^-(3c).\]

Yield: ca. 45 %. \(^1\)H NMR (300 MHz, CDCl\(_3\), 25 \(^\circ\)C): 7.9-7.5 (Ph, m, 26H), 1.51 (PdCH\(_3\), t, \( ^3J_{\text{PH}} = 5.7 \) Hz), 0.58 (Si(\(\text{CH}_3\))\(_2\), s, 6H). \(^{31}\)P NMR (121.5 MHz, CDCl\(_3\), 25 \(^\circ\)C): -20.2 (s).

\[(\text{Thixantphos})\text{PdCH}_3]^+ [\text{CF}_3\text{SO}_3]^-(3d).\]

Yield: ca. 65 %. \(^1\)H NMR (300 MHz, CDCl\(_3\), -20 \(^\circ\)C): 7.7-7.4 (Ph, m, 20H), 7.16, 7.00 (Ph, s, 2H), 2.25 (C(\(\text{CH}_3\)), s, 6H), 1.44 (PdCH\(_3\), t, \( ^3J_{\text{PH}} = 5.4 \) Hz, 3H). \(^{31}\)P NMR (121.5 MHz, CDCl\(_3\), -20 \(^\circ\)C): 20.4 (s).

\[(\text{dtpf})\text{PdCH}_3]^+ [\text{CF}_3\text{SO}_3]^-(3f-\text{tBu}).\]

Yield: ca. 85 %. \(^1\)H NMR (300 MHz, CDCl\(_3\), 25 \(^\circ\)C): 5.25 (\(\text{Cp}\), m, 4H), 4.20 (\(\text{Cp}\), m, 4H), 1.70 (PdCH\(_3\), t, \( ^3J_{\text{PH}} = 4.8 \) Hz, 3H), 1.46 (C(\(\text{CH}_3\))\(_3\), dd, \( ^3J_{\text{PH}} = 7.5 \) Hz, 36H). \(^{31}\)P NMR (121.5 MHz, CDCl\(_3\), 25 \(^\circ\)C): 29.3 (s). Anal.
Calcd. for (C_{28}H_{47}F_{3}FeO_{3}P_{2}SPd): C, 45.15; S, 4.30; H, 6.36. Found: C, 45.14; S, 4.32; H, 6.47.

Crystal structure determination of 3f-tBu. [s2201a]:
C_{27}H_{47}FeP_{2}CF_{3}SO_{3}, Fw = 744.91, orange block, 0.33 x 0.24 x 0.15 mm, monoclinic, P2\textsubscript{1}/c (No. 14), a = 11.7515(1), b = 16.9323(2), c = 16.8170(2) Å, β = 105.8589(6)°, V = 3218.88(6) Å\textsuperscript{3}, Z = 4, ρ = 1.537 g/cm\textsuperscript{3}. 53974 reflections were measured on a Nonius KappaCCD diffractometer with rotating anode (λ = 0.71073 Å) at a temperature of 150(2) K. 7369 reflections were unique (R\textsubscript{int} = 0.0459). Absorption correction with PLATON [56] (MULABS, μ = 1.218 mm\textsuperscript{-1}, 0.75-0.82 transmission). The structure was solved with Patterson methods (DIRDIF97 [57]) and refined with SHELXL97 [58] against F\textsuperscript{2} of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were refined with isotropic displacement parameters. 540 refined parameters, no restraints. R-values [I > 2σ(I)]: R\textsubscript{1} = 0.0249, wR\textsubscript{2} = 0.0561. R-values [all refl.]: R\textsubscript{1} = 0.0323, wR\textsubscript{2} = 0.0587. Molecular illustration, structure checking and calculations were performed with the PLATON package [56].

[(dipf)PdCH\textsubscript{3}(CH\textsubscript{3}CN)]\textsuperscript{+} [CF\textsubscript{3}SO\textsubscript{3}]\textsuperscript{-} (3f-iPr). Yield: ca. 56 %. \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}, -40 °C): 4.49, 4.48, 4.41, 4.35 (Cp, s, 8H), 2.58 (CH\textsubscript{3}CN, s, 3H), 2.43, 2.31 (CH(CH\textsubscript{3})\textsubscript{2}, q, \textsuperscript{3}J\textsubscript{HH} = 6.9 Hz, 2H), 2.06 (CH(CH\textsubscript{3})\textsubscript{2}, br s, 2H), 1.36-1.06 (CH(CH\textsubscript{3})\textsubscript{2}, dd, \textsuperscript{3}J\textsubscript{HH} = 6.9 Hz and \textsuperscript{3}J\textsubscript{PH} = 14 Hz, 24H), 0.73 (PdCH\textsubscript{3}, br d, \textsuperscript{3}J\textsubscript{PH} = 4.8 Hz, 3H). \textsuperscript{31}P NMR (121.5 MHz, CDCl\textsubscript{3}, -40 °C): 54.1 (d, \textsuperscript{2}J\textsubscript{PP} = 21.3 Hz), 32.7 (d, \textsuperscript{2}J\textsubscript{PP} = 21.3 Hz). \textsuperscript{13}C NMR (75.4 MHz, CDCl\textsubscript{3}, 25 °C): 160.2 (CF\textsubscript{3}CO\textsubscript{2}, q, \textsuperscript{2}J_{CF} = 36.2 Hz), 159.1, 138-117 (Ph, m), 116.0 (CF\textsubscript{3}CO\textsubscript{2}, q, \textsuperscript{1}J_{CF} = 292 Hz), 15.1 (PdCH\textsubscript{3}, dd, \textsuperscript{2}J_{PC} = 83.8 Hz and \textsuperscript{2}J_{PC} = 2.7 Hz). Anal. Calcd. for (C\textsubscript{26}H\textsubscript{42}F\textsubscript{3}FeNO\textsubscript{3}P\textsubscript{2}SPd): C, 42.78; S, 4.39; N, 1.92; H, 5.84; Found: C, 42.72; S, 4.11; N, 1.78; H, 5.97.

(DPEphos)PdCH\textsubscript{3}(CF\textsubscript{3}CO\textsubscript{2}) (4a). Yield: ca. 87 %. \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}, 25 °C): 7.8-6.2 (Ph, m, 28H), 0.87 (PdCH\textsubscript{3}, dd, \textsuperscript{3}J_{PH} = 6.9 Hz and \textsuperscript{3}J_{PH} = 2.4 Hz). \textsuperscript{31}P NMR (121.5 MHz, CDCl\textsubscript{3}, 25 °C): 32.1 (d, \textsuperscript{2}J_{PP} = 28.7 Hz), 9.1 (d, \textsuperscript{2}J_{PP} = 28.7 Hz). \textsuperscript{13}C NMR (75.4 MHz, CDCl\textsubscript{3}, 25 °C): 160.2 (CF\textsubscript{3}CO\textsubscript{2}, q, \textsuperscript{2}J_{CF} = 36.2 Hz), 159.1, 138-117 (Ph, m), 116.0 (CF\textsubscript{3}CO\textsubscript{2}, q, \textsuperscript{1}J_{CF} = 292 Hz), 15.1 (PdCH\textsubscript{3}, dd, \textsuperscript{2}J_{PC} = 83.8 Hz and \textsuperscript{2}J_{PC} = 2.7 Hz). Anal. Calcd. for (C\textsubscript{39}H\textsubscript{31}F\textsubscript{3}O\textsubscript{3}P\textsubscript{2}Pd): C, 60.60; H, 4.05. Found: C, 60.31; H, 4.03.

Crystal structure determination of 4a.
C\textsubscript{39}H\textsubscript{31}O\textsubscript{3}F\textsubscript{3}P\textsubscript{2}Pd, M\textsubscript{r} = 773 g/mole, colorless cube, 0.30 x 0.40 x 0.50 mm, triclinic, P\textbar, a = 10.976(1), b = 11.516(1), c = 15.503(5) Å, α = 98.14(1), β = 97.05(1), γ = 113.89(1)°, V=1738.2(7) Å\textsuperscript{3}, Z = 2, ρ = 1.48 g/cm\textsuperscript{3}. Final R = 0.078 for 6886 observed reflections.
7751 reflections were measured on a Enraf-Nonius CAD-4 ($\lambda = 1.5418$) at room temperature. Absorption correction was performed with the program PLATON following the method of North et al. using $\Psi$-scans of five reflections, with coefficients in the range 0.630-0.978. The structure was solved by the PATTY option of the DIRDIF96 program system. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were calculated. R-values: $[(\Delta/\sigma)_{\text{max}}=0.55$, S=0.87] a weighting scheme $w=\left[7.5+0.01*(\sigma(F_{\text{obs}}))^2 + 0.001/(\sigma(F_{\text{obs}}))^2\right]^{-1}$ was used ($R=0.078$, $R_w=0.083$). All calculations were performed with XTAL unless stated otherwise.

$$[\text{dipf} \text{PdCH}_3]^+ \left[\text{CF}_3\text{CO}_2\right]^-(4\text{-fBu})$$ Yield: ca. 72%. $^1$H NMR (300 MHz, CDCl$_3$, 25 °C): 5.25 ($\text{Cp}$, s, 4H), 4.17 ($\text{Cp}$, s, 4H), 1.68 ($\text{PdCH}_3$, t, $^3J_{\text{PH}} = 4.5$ Hz, 3H), 1.44 ($\text{C(CH}_3)_3$, m, 36H). $^31$P NMR (121.5 MHz, CDCl$_3$, 25 °C): 29.1 (s). Anal. Calcd. for (C$_{29}$H$_{47}$F$_3$FeP$_2$Pd): C, 43.49; H, 4.42. Found: C, 39.42; H, 3.99.

$$[\text{dipf} \text{PdCH}_3\left(\text{CF}_3\text{CO}_2\right)(4\text{-iPr})]$$ Yield: ca. 73%. $^1$H NMR (300 MHz, CDCl$_3$, 25 °C): 4.40-4.35 ($\text{CH}$, m, 8H), 2.38, 2.35, 2.20, 2.18 ($\text{CH(CH}_3)_2$, m, 4H), 1.38, 1.27, 1.21, 1.17 ($\text{CH(CH}_3)_2$, dd, $^3J_{\text{HH}} = 7.0$ Hz, $^3J_{\text{PH}} = 15.3$ Hz, 24H), 0.81 ($\text{PdCH}_3$, dd, $^3J_{\text{PH}} = 2.0$ Hz and $^3J_{\text{PP}} = 6.8$ Hz, 3H). $^31$P NMR (121.5 MHz, CDCl$_3$, 25 °C): 47.35 (d, $^2J_{\text{PP}} = 22.1$ Hz), 25.8 (d, $^2J_{\text{PP}} = 22.1$ Hz). Anal. Calcd. for (C$_{25}$H$_{39}$F$_3$FeO$_2$P$_2$Pd): C, 46.00; H, 6.02. Found: C, 45.34; H, 6.04.

Synthesis of $[\text{dipf} \text{Pd(CH}_3\text{)}\text{Cl}]_2$ (5). To a solution of 0.36 mmol (1.05 equiv.) (COD)Pd(CH$_3$)Cl in 5 mL of benzene, 0.37 mmol of f-Et was added. The solution was stirred for one hour. The suspension was filtered and the residue was washed with benzene and diethylether. The product was dried in vacuo. Yield: ca. 80%. $^1$H NMR (300 MHz, CDCl$_3$, 25 °C): 5.19 ($\text{Cp}$, s, 4H), 4.34 ($\text{Cp}$, d, 4H), 2.39 ($\text{CH}_2\text{CH}_3$, br s, 2H), 2.08 ($\text{CH}_2\text{CH}_3$, br s, 4H), 1.80 ($\text{CH}_2\text{CH}_3$, br s, 2H), 1.24 ($\text{CH}_2\text{CH}_3$, br s, 6H), 1.01 ($\text{CH}_2\text{CH}_3$, br s, 6H), 0.51 ($\text{PdCH}_3$, t, $^3J_{\text{PH}} = 5.9$ Hz, 3H). $^31$P NMR (121.5 MHz, CDCl$_3$, 25 °C): 9.0 (s). Anal. Calcd. for (C$_{19}$H$_{31}$ClFeP$_2$Pd): C 43.96; H, 6.02; Found: C, 43.54; H, 6.01.

Synthesis of (dipf)Pd(CH$_3$)Cl (6). An NMR tube was filled with 15 mg of 5 and 0.7 mL of CDCl$_3$. The solution was allowed to stand at room temperature for one night. Complete conversion of 7 was observed. $^1$H NMR (300 MHz, CDCl$_3$, 25 °C): 4.37, 4.35, 4.34, 4.30 ($\text{Cp}$, s, 8H), 2.1-1.8 ($\text{CH}_2$, m, 8H), 1.3-1.1 ($\text{CH}_3$, m, 12H), 0.75 ($\text{PdCH}_3$, dd, $^3J_{\text{PH}} = 7.5$ Hz, $^3J_{\text{PP}} = 3.6$ Hz, 3H). $^31$P NMR (121.5 MHz, CDCl$_3$, 25 °C): 30.1 (d, $^2J_{\text{PP}} = 28.2$ Hz), 10.7 (d, $^2J_{\text{PP}} = 28.2$ Hz).
Literature


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