

Di- and Tetranuclear Palladium Complexes Incorporating Phospha- and Diphosphaferrocenes as Ligands**

Xavier Sava, Louis Ricard, François Mathey,* and Pascal Le Floch*[a]

Abstract: Monophosphaferrocenes **1** and **4** react with $[\text{Pd}(\text{COD})\text{Cl}_2]$ (COD = cyclooctadiene) to afford *cis*- $[\text{Pd}(\mathbf{1}$ or $\mathbf{4})_2\text{Cl}_2]$ complexes that slowly decompose in solution to give dimeric complexes **3** and **6** of general formula $[\{\text{Pd}(\mathbf{1}$ or $\mathbf{4})\text{Cl}\}_2]$. In these dimers, which incorporate a Pd–Pd bond, phosphaferrocenes act as four electron donors through the phosphorus-atom lone pair (μ_2 -bonded) and through one orbital of appropriate symmetry at iron. These dimers can also be more conventionally prepared from the reaction of *cis*- $[\text{Pd}(\mathbf{1}$ or $\mathbf{4})\text{Cl}_2]$ complexes with $[\text{Pd}(\text{dba})_2]$ (dba = dibenzylidene acetone). The reaction of octaethylphos-

phaferrocene (**7**) with $[\text{Pd}(\text{COD})\text{Cl}_2]$ yields a dinuclear complex $[\text{Pd}_2(\mathbf{7})_2\text{Cl}_4]$ (**8**) in which the two ligands **7** are coordinated in a *trans* fashion through the phosphorus-atom lone pairs. Decomposition of **8** in solution yields a dimeric dicationic complex of general formula $[\{\text{Pd}_2(\mathbf{7})_2\text{Cl}\}_2]^{2+}[\text{FeCl}_4]_2^-$ (**9a**) incorporating four palladium atoms. In each ligand, one phospholyl ring behaves as a two-electron donor through the phosphorus-atom lone pair whereas

the second binds two palladium centers in a μ_2 -fashion. A plausible mechanism that explains the formation of dimers **3**, **6**, and **9a** involves the preliminary oxidation of the mono- or diphosphaferrocene ligand. Parallel experiments aimed at confirming this hypothesis have shown that complex **9a** can be synthesized from the reaction of FeCl_2 with complex **8**. Also presented is another synthetic approach to the synthesis of the tetranuclear complex **9b** (counterion is GaCl_4^-) from the reaction of the palladium(0) complex $[\text{Pd}(\mathbf{7})_2]$ (**10**) with $[\text{Pd}(\text{COD})\text{Cl}_2]$ in the presence of GaCl_3 as chloride abstractor.

Keywords: coordination chemistry · palladium · phosphaferrocenes · phosphorus heterocycles · P ligands

Introduction

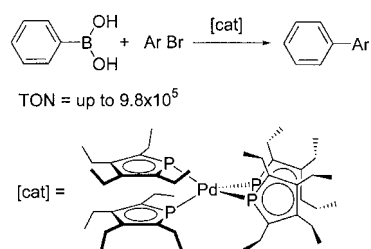
The combination of a ferrocene backbone and an sp^2 -hybridized phosphorus atom makes monophosphaferrocenes very attractive ligands for different purposes.^[1] A current and rewarding area of development concerns the elaboration of well-tailored ligands and their use in homogeneous catalysis, and recent studies have clearly demonstrated their potential in some catalytic processes of importance.^[2] A significant application was recently presented by Fu et al who showed that a diphenylphosphinomethylene-substituted phosphaferrocene could be successfully used as a ligand in the rhodium(i)-catalyzed enantioselective isomerization of allylic alcohols to aldehydes.^[2k] In all catalytic transformations known to date, phosphaferrocenes are supposed to act, like

classical phosphines, as two-electron-donor ligands η^1 -bonded to the metal through the phosphorus-atom lone pair. Although this coordinating mode is by far the most common for the coordination chemistry of mono- and diphosphaferrocenes, many other interesting structural and electronic features of the ligand can probably be exploited to devise very active catalytic systems. With this aim, we recently took advantage of the spherical character of the phosphorus-atom lone pair in diphosphaferrocenes to synthesize chelate-based catalysts. We discovered that species such as the bis(octaethylphosphaferrocene)palladium(0) chelate complex, which involves a side-on coordination of phosphorus-atom lone pairs, could catalyze the Suzuki cross-coupling reaction between phenylboronic acid and aryl bromides with turnover-numbers (TON) up to 9.8×10^5 (Scheme 1).^[2m]

This result is encouraging and constitutes, as far as we are aware, the highest TON ever recorded for a catalyst incorporating sp^2 -hybridized phosphorus derivatives as ligands.^[3] During further investigations on the catalytic activity of these phosphaferrocene-based palladium complexes we observed that, whereas palladium(0) species are particularly stable, palladium(II) derivatives exhibited a surprising reactivity. Therefore, we decided to explore in depth the coordination behavior of mono- and diphosphaferrocenes

[a] Prof. F. Mathey, Dr. P. Le Floch, Dr. X. Sava, Dr. L. Ricard
Laboratoire "Hétéroéléments et Coordination"
UMR CNRS 7653, École Polytechnique
91128 Palaiseau Cedex (France)
Fax: (+33)1-69-33-39-90
E-mail: francois.mathey@polytechnique.fr
lefloch@poly.polytechnique.fr

[**] This work constitutes part of X.S.'s Ph.D. thesis at the École Polytechnique.



Scheme 1. Suzuki Cross-coupling reaction of phenylboronic acid with aryl bromides catalyzed by the bis(octaethyl)diphosphaferrocene Pd^0 complex.

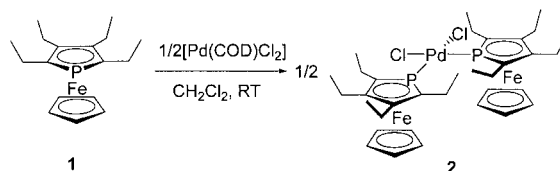
towards these Pd^{II} centers. This study led to the discovery of very unusual binding modes that involve both coordination of the phosphorus-atom lone pair and the central iron atom at the palladium center.

Results and Discussion

Our first experiments were carried out with the tetraethylphosphaferrocene **1**, which displays a high solubility in common organic solvents due to the presence of the four

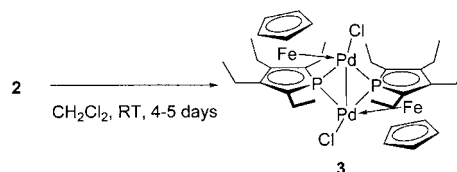
Abstract in French: Les monophosphaferrocènes **1** et **4** réagissent avec le complexe $[\text{Pd}(\text{COD})\text{Cl}_2]$ pour conduire aux complexes *cis*- $[\text{Pd}(\mathbf{1} \text{ ou } \mathbf{4})\text{Cl}_2]$ qui se décomposent lentement en solution pour donner les complexes dimères **3** et **6** de formule générale $[\text{Pd}(\mathbf{1} \text{ ou } \mathbf{4})\text{Cl}_2]_2$. Dans ces deux dimères, qui comportent une liaison palladium–palladium, les ligands phosphaferrocènes agissent comme des donneurs à quatre électrons, deux électrons étant apportés par la paire libre de l'atome de phosphore et deux autres par une orbitale de symétrie appropriée sur l'atome de fer central. D'une façon plus conventionnelle, ces dimères peuvent être également préparés par réaction des complexes *cis*- $[\text{Pd}(\mathbf{1} \text{ ou } \mathbf{4})\text{Cl}_2]$ avec le complexe $[\text{Pd}(\text{dba})_2]$. La réaction de l'octaéthyle diphosphaferrocène (**7**) avec le précurseur $[\text{Pd}(\text{COD})\text{Cl}_2]$ conduit au complexe dinucléaire $[\text{Pd}_2(\mathbf{7})_2\text{Cl}_4]$ (**8**) dans lequel les deux ligands **7** sont coordonnés d'une façon *trans* par l'intermédiaire des paires libres des atomes de phosphore. La décomposition du complexe **8** en solution conduit au dimère dicationique de formule générale $[\{\text{Pd}_2(\mathbf{7})_2\text{Cl}_4\}^{2+}[\text{FeCl}_4]^{2-}]$ (**9a**) qui contient quatre atomes de palladium. Dans chaque ligand, un cycle phospholyle se comporte comme un donneur à deux électrons par l'intermédiaire de la paire libre du phosphore alors que le second se lie aux deux atomes de palladium d'une façon μ_2 . Un mécanisme envisageable pouvant expliquer la formation des dimères **3**, **6** et **9a** fait intervenir une oxydation préliminaire du ligand mono ou diphosphaferrocène. Des expériences parallèles visant à confirmer cette hypothèse ont permis de montrer que le complexe **9a** peut être également synthétisé par réaction de FeCl_2 avec le complexe **8**. Une autre approche synthétique permettant de synthétiser le dimère **9b** (contre ion = GaCl_4^-) par réaction du complexe de palladium zérovalent $[\text{Pd}(\mathbf{7})_2]$ (**10**) avec le complexe $[\text{Pd}(\text{COD})\text{Cl}_2]$ en présence de GaCl_3 , qui est utilisé en qualité d'abstracteur d'ion chlorure, est également présentée.

ethyl substituents.^[2m] Reaction of **1** with $[\text{Pd}(\text{COD})\text{Cl}_2]$ in dichloromethane proceeded cleanly and afforded complex **2**, (Scheme 2), which was fully characterized. The *cis* geometry of complex **2** was established from ^{13}C NMR data (AXX' spin system). Estimation of the $^2J(\text{P},\text{P})$ coupling constant (50 Hz) was realized by simulation and examination of the pattern presented by the C_α carbon atoms (C_2 and C_5).



Scheme 2. Synthesis of complex **2**.

Further experiments aimed at exploring the stability of **2** in solution for long periods when stored led to a quite unexpected result. After several days, complex **2** partially decomposed to yield a new species that was isolated in low yields (<30%) as dark green microcrystals. The structure of **3** could not be unambiguously established on the basis of NMR data alone and was finally solved by an X-ray crystal structure analysis (Scheme 3). An ORTEP view of one molecule of **3** is presented in Figure 1; significant bond lengths and angles are given in the legend.



Scheme 3. Synthesis of complex **3** by decomposition of **2**.

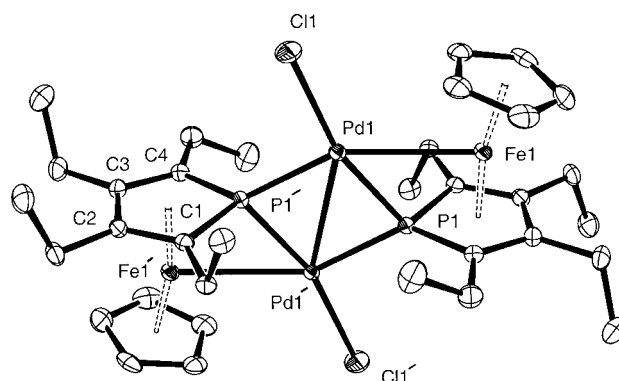


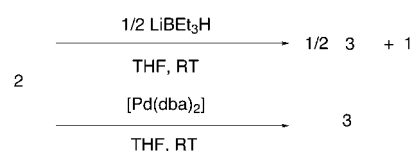
Figure 1. Molecular structure of **3** (ORTEP plot, 50% probability). Selected bond lengths [Å] and angles [°]: P1–Pd1 2.2633(4), Pd1–Pd1' 2.8442(2), P1–Pd1' 2.2417(4), Pd1–Cl1 2.3681(4), Pd1–Fe1 2.9566(3), P1–C1 1.767(2), C1–C2 1.426(2), C2–C3 1.441(2), C3–C4 1.425(2), C4–P1 1.764(2), P1–Pd1–Fe1 49.95(1), Pd1–P1–Pd1' 78.30(1), P1–Pd1–Pd1' 50.511, P1–Pd1'–Pd1 51.19(1), P1–Pd1–Cl1 163.90(1), C4–P1–C1 93.35(7).

As can be seen complex **2** has undergone a reduction, involving the loss of one molecule of **1** and one chloride ligand. The structure of **3** now consists of a dimeric arrangement incorporating two palladium(II) centers bonded through

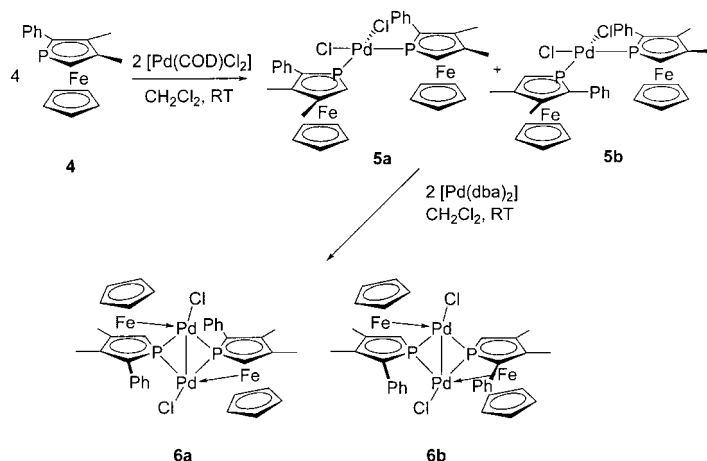
a metal–metal bond, two ligands **1** and two chloride ligands. The most interesting structural feature clearly concerns the presence of an iron–palladium bond. This Fe–Pd bond (2.9566(3) Å) appears to be quite long relative to those usually observed in bimetallic species, such as the dppm-based (dppm = bis(diphenylphosphino)methane) derivatives described by Braunstein et al. and others (usually about 2.6–2.7 Å).^[4] However, it is comparable to values observed in ferrocene complexes described by various authors (about 2.8–2.9 Å) with Group 10 divalent (M = Ni, Pd, Pt)^[5a–h] and Group 11 monovalent (M = Cu, Ag, Au) centers.^[5i–k] An interesting question evidently concerns the origin and nature of this very particular bonding. Phosphaferrocenes possess, as do their carbon analogues, a set of two nonbonding orbitals on iron that are parallel to the ring planes ($d_{y^2+z^2}$ and d_{xy} , e_{2g} degenerate in ferrocene),^[6] and we can confidently describe this bond as a dative bond between one of these two nonbonding orbitals and a vacant orbital of appropriate symmetry at the palladium atom. This type of bonding is not without precedent in the coordination chemistry of phospholide ligands. It was shown in 1994 that phosphacymantrenes, whose HOMOs also mainly consist of 3d(Mn) orbitals, react with Pd^{II} centers to yield similar dimeric structures to **3**.^[7]

The structure of **3** exhibits other interesting structural features. Another geometrical consequence of this particular Pd–Fe bonding is directly measurable on the slightly distorted ferrocenyl-type structure. Contrary to what is observed in the free ligand, the two rings are 16° from parallel resulting in a rather large Ct1–Fe–Ct2 angle of 168° (Ct being the centroid of the ring). This value is similar to that observed in the 1,2,3-trithia[3]ferrocenophane palladium complex reported by Seyferth.^[5] Also significant is the μ_2 -bonding mode of the two phosphorus atoms that share their lone pair with the two Pd atoms. Although the P–Pd bond lengths are slightly different (P1–Pd1 = 2.2633(4) and P1–Pd'1 = 2.2417(4) Å) they fall in the usual range. This kind of bonding, which has not been previously observed for phosphaferrocene complexes, is a specificity of sp²-hybridized phosphorus atoms, and many examples are known with other ligands such as phosphinines.^[8]

The formation of dimer **3** leads to an interesting point. Assuming one ligand has been lost, we can propose that the initial step of the mechanism relies on a monoelectronic reduction of the palladium center; this could be promoted by the iron atom of this ligand. Additional experiments carried out on a more sophisticated structure supports this proposal (see later). From a synthetic point of view, the synthesis of dimer **3** is not very efficient when carried out by decomposition of **2** as it consumes one equivalent of ligand and only affords **3** in low yields. However, we found two additional procedures to prepare **3** under more satisfactory conditions. The first relies on the use of “super-hydride” as the reducing agent. Addition of one equivalent of hydride to a solution of **2** in THF cleanly yields **3** with concomitant release of one molecule of ligand **1**. By using this procedure, **3** was obtained with a yield of 75%. The second, more convenient, approach involves the reaction of **2** with one equivalent of a Pd⁰ precursor such as [Pd(dba)₂] (Scheme 4; dba = dibenzylidene acetone).

Scheme 4. Synthesis of complex **3**.

To verify that the formation of this new type of dimer was not restricted to ligand **1**, similar experiments with a less sterically demanding ligand such as **4**, which only bears one phenyl group at one α position, were attempted. As can be seen in Scheme 5, the synthesis of the two Pd^{II} precursors **5**

Scheme 5. Syntheses of complexes **5a,b** and dimers **6a,b**.

could be carried out under the same experimental conditions. Owing to the planar chirality of ligand **4**, two diastereoisomers **5a** and **5b** are formed. The ³¹P NMR spectrum of the crude mixture shows that these two species are formed in the ratio **5a:5b** = 4:1. Complexes **5a,b** were characterized exclusively by ³¹P NMR spectroscopy. As previously observed in the synthesis of dimer **3**, reaction of these two species with one equivalent of [Pd(dba)₂] resulted in the formation of a mixture of diastereoisomers of dimer **6**; these only differ by the position of the phenyl rings towards the P₂Pd₂ core (Scheme 5). ³¹P NMR spectroscopy indicates that these two species are formed in the ratio **6a:6b** = 1:1. The configuration of these dimers could not be unambiguously established by analysis of the NMR spectrum of the mixture.

Fortunately, crystallization in dichloromethane at –20 °C afforded crystals of dimer **6a**, thus allowing the complete assignment of ³¹P NMR signals and the recording of ¹H and ¹³C NMR spectra. Interestingly, we noted that dimer **6a** slowly isomerizes in dichloromethane after several hours to yield a significant amount of dimer **6b**. ³¹P NMR experiments indicated that the equilibrium could be reached after one day. This clearly shows that the phosphaferrocenes are only weakly bound in these dimers and explains why dimers **6a,b** are formed in a similar ratio when they are prepared from a nonequimolar mixture of precursor **5a,b**. An ORTEP view of one molecule of **6a** is presented in Figure 2 and significant bond lengths and angles are listed in the legend. The structure

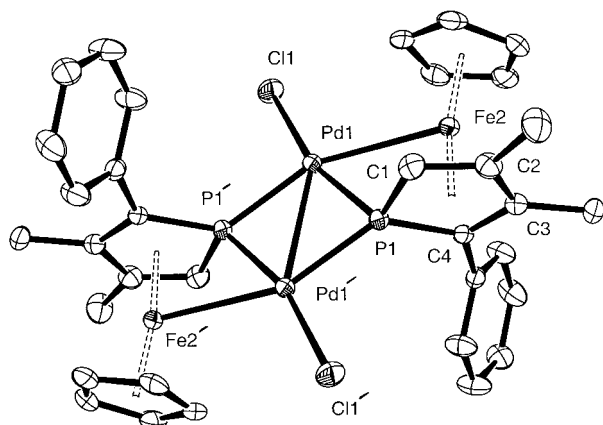
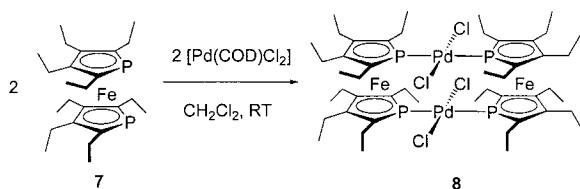


Figure 2. Molecular structure of **6a** (ORTEP plot, 50% probability). Selected bond lengths [Å] and angles [°]: P1–Pd1 2.262(1), Pd1–Pd1' 2.824(1), P1–Pd1' 2.238(1), Pd1–Cl1 2.369(1), Pd1–Fe2 2.941(1), P1–C1 1.760(4), C1–C2 1.413(6), C2–C3 1.439(6), C3–C4 1.423(5), C4–P1 1.769(4), P1–Pd1–Fe2 50.12(3), Pd1–P1–Pd1' 50.76(3), P1–Pd1–Pd1' 51.76(3), P1–Pd1'–Pd1 51.52(4), P1–Pd1–C1(1) 165.28(4), C4–P1–C1 92.1(2).

of **6a** deserves no special comments and is comparable to dimer **3**.

To complete our study, we also investigated the reactivity of diphosphaferrocenes towards Pd^{II} centers. Preliminary experiments carried out with the readily available 2,5-unsubstituted 3,3',4,4'-tetramethyldiphosphaferrocene only led to formation of insoluble materials, which were probably polymeric. To circumvent this problem we chose the octaethyldiphosphaferrocene (**7**), which proved to be highly soluble in the most common organic solvents. Reaction of ligand **7** with an equimolar amount of [Pd(COD)Cl₂] cleanly yielded complex **8** (Scheme 6). Although ³¹P and ¹H NMR data could be recorded, **8** proved to be too insoluble for a well-resolved ¹³C NMR spectrum to be obtained, thus precluding the determination of its geometry.



Scheme 6. Synthesis of complex **8**.

Fortunately, single crystals were obtained, and an X-ray crystal structure analysis was carried out. An ORTEP view of one molecule of **8** is shown in Figure 3; significant bond lengths and angles are given in the legend. As can be seen, complex **8** adopts *trans* geometry with the two diphosphaferrocenes facing each other. The preference for *trans* geometry very likely results from steric crowding between the ethyl groups of two diphosphaferrocene ligands. This steric hindrance is not present in complex **3**, which only bears four ethyl groups, so both ligands can probably freely rotate around the P–Pd bond axis. A surprising feature concerns the position of the two chloride ligands, which are not parallel to the planes defined by the rings. Nevertheless, the intramolecular

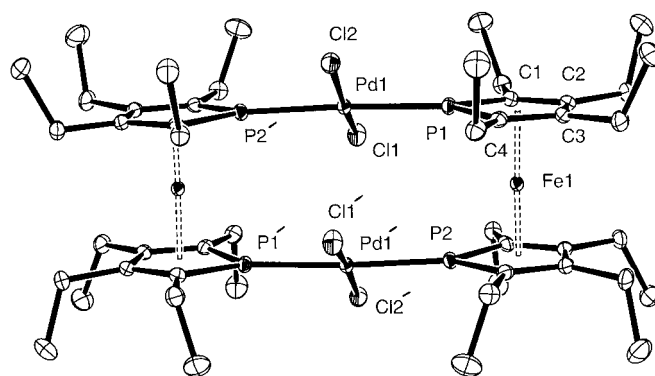
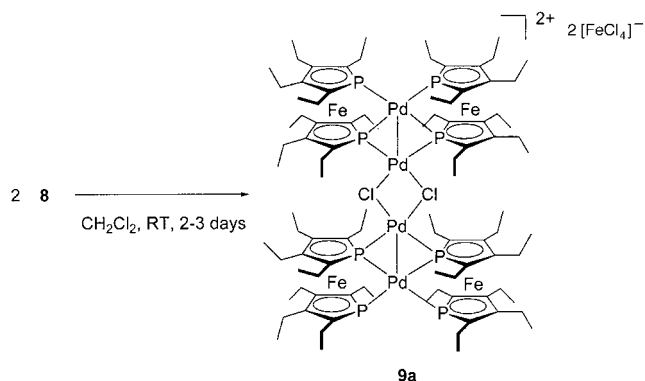


Figure 3. Molecular structure of **8** (ORTEP plot, 50% probability). Selected bond lengths [Å] and angles [°]: P1–Pd1 2.3001(5), Pd1–P2' 2.3040(5), Pd1–Cl1 2.3068(4), Pd1–Cl2 2.3040(4), P1–C1 1.769(2), C1–C2 1.430(2), C2–C3 1.442(2), C3–C4 1.428(2), C4–P1 1.766(2), P1–Pd1–P2' 176.25(2), P1–Pd1–Cl1 90.60(2), P1–Pd1–Cl2 89.43(2), C1–P1–C4 93.2(1).

Pd1–Cl1' and Pd1'–Cl1 contacts are too long to result from a μ_2 -coordination, and this particular arrangement is probably due to packing forces in the crystal.

Like complex **3** and **5a,b**, **8** slowly decomposed in dichloromethane to yield complex **9a**, which was recovered as black crystals in low yield (about 30%) after several days (Scheme 7). Unfortunately, **9a** proved to be highly insoluble,



Scheme 7. Synthesis of dimer **9a** by decomposition of complex **8**.

precluding the recording of ¹H and ¹³C NMR spectra. Interestingly, the ³¹P NMR spectrum reveals the presence of two magnetically nonequivalent phosphorus atoms which appear as poorly resolved broad singlets at δ (CDCl₃) = 10.6 and –264.4. Whereas the first signal is close to that recorded for complex **8**, the highly shielded signal at δ = –264.4 is quite unusual. However, it is in good agreement with a chelate structure. Indeed, although no theoretical studies have been undertaken yet, it appears that the chelating mode of diphosphaferrocene results in a strong shielding of ³¹P NMR signals. Hence, the ³¹P NMR chemical shift of the bis(octaethyldiphosphaferrocene)palladium(0) complex [Pd(**7**)₂] is δ = –125.5. Proof of the structure of **9a** was given by an X-ray crystal structure analysis. An ORTEP view of one molecule of **9** is presented in Figure 4; significant bond lengths and angles are given in the legend. It can be seen that complex **9a**, of general formula $[\text{Pd}_2(\text{7})_2\text{Cl}]_2^{2+}[\text{FeCl}_4]_2^{-}$, is a dimeric dicationic structure that incorporates four diphosphaferrocene

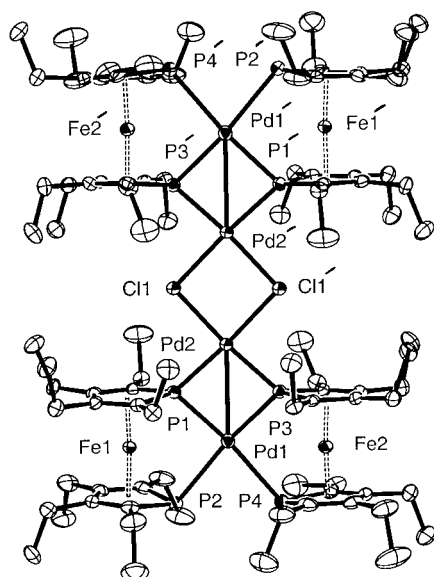
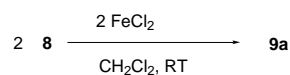


Figure 4. Molecular structure of **9a** (ORTEP plot, 50% probability). Selected bond lengths [Å] and angles [°]: P1–Pd1 2.3230(7), P2–Pd1 2.6076(8), P3–Pd1 2.3041(7), P4–Pd1 2.6350(8), P1–Pd2 2.2535(7), P3–Pd2 2.2449(7), Pd1–Pd2 3.0996(3), Pd2–Cl1 2.4364(7), Pd2–Cl1' 2.4407(7), P1–C1 1.760(3), C1–C2 1.430(4), C2–C3 1.446(4), C3–C4 1.417(4), C4–P1 1.765(3), P3–Pd1–P1 92.44(3), P2–Pd1–P3 170.64(3), P1–Pd1–P2 93.51(2), P3–Pd1–P4 93.85(2), P1–Pd1–P4 173.67(2), P2–Pd1–P4 80.16(2), P3–Pd1–Pd2, 46.25(2), P1–Pd1–Pd2 46.43(2), P2–Pd1–Pd2 139.90(2), P4–Pd1–Pd2 139.90(2), P3–Pd1–Fe2 46.66(2), P1–Pd1–Fe2 138.47(2), P2–Pd1–Fe2 126.15(2), P4–Pd1–Fe2 47.67(2), Pd2–Pd1–Fe2 92.87(1), P1–Pd2–P3 95.92(3), P3–Pd2–Cl1 173.76(3), P1–Pd2–Cl1 89.50(2).

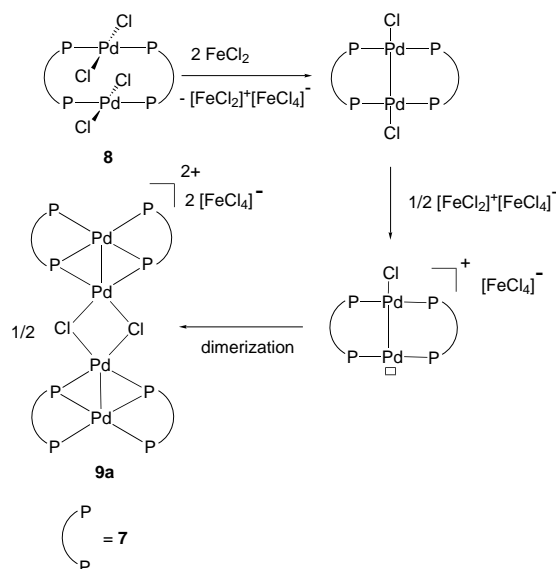
ligands, four palladium atoms, and two μ_2 -chloride ligands that ensure the connectivity between the two Pd_2P_4 units. An interesting feature concerns the electron count in the complex. A close examination of distances between metal atoms reveals that the interaction between Pd and Fe atoms is very weak and the quite long Pd–Fe distance average ($d(\text{Pd–Fe}) = 3.16 \text{ \AA}$) suggests that no dative bonding occurs. Assuming that the two Pd atoms in each subunit are connected through a metal–metal bond ($d(\text{Pd1–Pd2}) = 3.0996(3) \text{ \AA}$), 60 VE (VE = valence electron) are involved in the dimeric unit, leaving four 16-electron Pd^I centers.

The presence of two $[\text{FeCl}_4]^-$ counterions is of particular interest and shows that formation of complex **9a** involves the destruction of at least two ligands. To rationalize the formation of dimer **3**, we previously proposed that the reduction of Pd^{II} to Pd^I could be promoted by the oxidation of one phosphaferrrocene ligand. A similar mechanism is very probably operative in the formation of dimer **9a**. In 1989, Lemoine studied the stability of diphosphaferrocenium in the presence of chloride and bromide ligands.^[9] From this study it could be concluded that diphosphaferrocenium cations are decomposed by nucleophilic attack to yield a $[\text{FeCl}_2(\text{sol})_4]^+ [\text{FeCl}_4]^-$ complex (sol = solvent) and the corresponding 1,1'-biphosphole. That result leads us to propose that the synthesis of our dimers could be initiated by the decomposition of phosphaferrrocene ligands in $[\text{FeCl}_2]^+$ -solvated species. We verified this hypothesis by treating precursor **8** with FeCl_2 in dichloromethane. As expected complex **9a** was formed and obtained in 75% yield (Scheme 8).



Scheme 8. Synthesis of dimer **9a** from the reaction of FeCl_2 with complex **8**.

The mechanism summarized in Scheme 9, therefore, can be tentatively proposed. In a first step, FeCl_2 behaves as a reducing agent towards precursor **8** to yield a dimeric complex

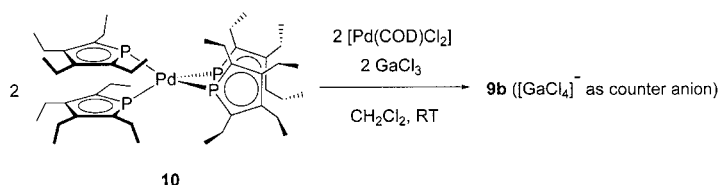


Scheme 9. Proposed mechanism for the formation of dimer **9a**.

of Pd^I and $[\text{FeCl}_2]^+[\text{FeCl}_4]^-$. In the second step, the $[\text{FeCl}_2]^+[\text{FeCl}_4]^-$ complex reacts with two molecules of the Pd^I dimer formed to yield two cationic dimers with a vacant site that can then dimerize. A recent study by Braunstein et al. concerning the assembly of dicationic tetrapalladium clusters that contain bis(diphenylphosphino)amine (dppa) and dppm bridging ligands from the corresponding Pd^I dimers supports this last step.^[10]

As shown previously in the synthesis of dimer **3**, the synthesis of complex **3** could be accomplished by treating one equivalent of precursor **2** with $[\text{Pd}(\text{dba})_2]$. Similarly, the same approach can also be employed to synthesize complex **9b** from the bis(octaethyldiphosphaferrocene)palladium(0) complex (**10**) and $[\text{Pd}(\text{COD})\text{Cl}_2]$. Reaction of the two complexes in the presence of $[\text{GaCl}_3]$, which was used as a chloride abstractor, produced complex **9b** in an 80% yield (Scheme 10).

In summary, a new bonding mode of phosphaferrrocenes has been discovered. The coordinating-ability of the lone pair on



Scheme 10. Synthesis of dimer **9b** from complex **10**, $[\text{Pd}(\text{COD})\text{Cl}_2]$ and GaCl_3 .

phosphorus and the possibility of dative bonding by iron adds an interesting new perspective to the template synthesis of new and original bimetallic species. This type of bonding is probably not limited to palladium and should also occur with other metal centers. Further investigations will now focus on this point, as well as on the reactivity and catalytic properties of the different dimers synthesized. The synthesis of the tetranuclear species **9** is another interesting result and shows that diphosphaferrocenes could be used for the elaboration of sophisticated homo- and heteronuclear polymetallic assemblies involving metal–metal bonding.

Experimental Section

General procedures: All reactions were routinely performed under an inert atmosphere of nitrogen by using standard Schlenk techniques and dry deoxygenated solvents. Dry hexane was obtained by distillation over Na/benzophenone and dry CH₂Cl₂ over P₂O₅. Dry Celite was used for filtration. Nuclear magnetic resonance spectra were recorded on a Bruker AC200 SY spectrometer. Chemical shifts are expressed with respect to external TMS (¹H and ¹³C) and 85% H₃PO₄ (³¹P); coupling constants are given in hertz. Mass spectra were obtained at 70 eV with an HP 5989B spectrometer coupled with an HP 5890 chromatograph by the direct inlet method. The following abbreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet; Ar, aromatic; v, virtual. Elemental analyses were performed by the "Service d'analyse du CNRS" at Gif sur Yvette, France. [Pd(COD)Cl₂]^[11] and [Pd(dba)₂]₂, and ^[12] phosphosphaferrocenes **1**^[13] and **4**^[2m] were prepared according to published procedures.

Synthesis of complex 2: [Pd(COD)Cl₂] (29 mg, 0.1 mmol) was added at RT to a solution of **1** (63 mg, 0.20 mmol) in dichloromethane (3 mL) causing an immediate change of color from yellow to deep violet. After evaporation of the solvent, the powder obtained was washed three times with hexane (20 mL) in order to remove 1,5-cyclooctadiene. After drying, complex **2** was obtained as a violet powder. Yield: 70 mg (87%); m.p. > 200 °C (decomp); ³¹P NMR (81 MHz, CDCl₃, 25 °C): δ = 29.3; ¹H NMR (200 MHz, CDCl₃, 25 °C): δ = 0.89 (t, ³J(H,H) = 7.50 Hz, 12H; 4 Me), 1.13 (t, ³J(H,H) = 7.50 Hz, 12H; 4 Me), 1.94 (m, 4H; CH₂), 2.41 (m, 8H; CH₂), 2.73 (m, 4H; CH₂), 4.40 (10H; Cp); ¹³C NMR (50 MHz, CDCl₃, 25 °C): δ = 17.0 (s, Me), 18.4 (s, Me), 22.0 (vt, AXX', ΣJ(P,C) = 14.0 Hz, CH₂), 22.5 (s, CH₂), 77.2 (s, Cp), 84.5 (vt, AXX', ΣJ(P,C) = 10.2, C_{3,4} of C₁₂H₂₀P), 96.2 (vt, AXX', ΣJ(P,C) = 10.0, C_{2,5} of C₁₂H₂₀P); elemental analysis calcd (%) for C₃₄H₅₀Cl₂Fe₂P₂Pd (809.72): C 50.43, H 6.22; found C 50.61; H 6.15.

Synthesis of dimer 3: Complex **2** was prepared as described above, by using the same amount of ligand **1** and [Pd(COD)Cl₂] in dichloromethane. After 10 minutes, [Pd(dba)₂]₂ (57 mg, 0.1 mmol) was added, and the resulting solution stirred for an additional 10 minutes. After reducing the volume of the solution by half, complex **3** was precipitated by addition of toluene (5 mL). After filtration, washing with toluene (3 × 5 mL), and drying, **3** was recovered as a dark green solid. Yield: 76 mg (83%); m.p. > 200 °C (decomp); ³¹P NMR (81 MHz, CDCl₃, 25 °C): δ = 106; ¹H NMR (200 MHz, CDCl₃, 25 °C): δ = 0.95 (s, 12H; 4Me), 1.42 (s, 12H; Me), 1.50 (m, 4H; CH₂), 1.88 (m, 4H; CH₂), 2.38 (m, 4H; CH₂), 3.02 (m, 4H; CH₂), 4.67 (10H; Cp); ¹³C NMR (50 MHz, CDCl₃, 25 °C): δ = 16.7 (s, Me), 18.6 (s, Me), 22.2 (vt, AXX', ΣJ(P,C) = 14.20 Hz, CH₂), 23.1 (s, CH₂), 75.2 (s, Cp), 89.7 (vt, AXX', ΣJ(P,C) = 22.20 Hz, Cq), 97.7 (vt, AXX', ΣJ(P,C) = 12.60 Hz, Cq); elemental analysis calcd (%) for C₃₄H₅₀Cl₂Fe₂P₂Pd₂ (916.14): C 44.57, H 5.29.

Syntheses of complexes 5a,b and dimers 6a,b: [Pd(COD)Cl₂] (29 mg, 0.1 mmol) was added at RT to a solution of **4** (62 mg, 0.20 mmol) in dichloromethane (3 mL). After stirring for ten minutes, ³¹P NMR spectro-

Table 1. Crystallographic data and experimental parameters for compounds **3**, **6a**, **8**, and **9a**.

	3	6a	8	9a
formula	C ₃₄ H ₅₀ Cl ₂ Fe ₂ P ₂ Pd ₂	C ₃₄ H ₃₂ Cl ₂ Fe ₂ P ₂ Pd ₂ ·CH ₂ Cl ₂	C ₄₈ H ₈₀ Cl ₄ Fe ₄ P ₄ Pd ₂	C ₉₆ H ₁₆₀ Cl ₁₀ Fe ₆ P ₈ Pd ₄ ·CH ₂ Cl ₂
<i>M_r</i>	458.04	448.97	1247.38	2762.13
crystal habit	red plate	orange cube	red plate	red plate
crystal size [mm]	0.22 × 0.22 × 0.22	0.20 × 0.20 × 0.16	0.22 × 0.18 × 0.12	0.20 × 0.20 × 0.14
crystal system	monoclinic	monoclinic	triclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> [Å]	9.3618(4)	8.362(5)	9.4598(2)	16.3140(3)
<i>b</i> [Å]	14.7832(7)	13.028(5)	15.1459(4)	16.2290(3)
<i>c</i> [Å]	13.0536(4)	17.732(5)	19.6691(4)	22.4050(4)
<i>α</i> [°]			83.8500(10)	90.0000(8)
<i>β</i> [°]	98.400(3)	101.350(5)	80.0140(10)	105.4220(10)
<i>γ</i> [°]			75.3620(10)	90.0000(9)
<i>V</i> [Å ³]	1787.20(13)	1893.9(14)	2679.42(11)	5718.36(18)
<i>Z</i>	4	4	1	2
<i>ρ</i> _{calcd} [g cm ⁻³]	1.702	1.575	1.599	1.604
<i>F</i> (000)	924	888	1322	2816
<i>μ</i> [cm ⁻¹]	2.048	1.931	1.593	1.784
max <i>θ</i> [°]	30.04	27.48	30.03	30.06
index ranges	−13 ≤ <i>h</i> ≤ 11 −16 ≤ <i>k</i> ≤ 20 −14 ≤ <i>l</i> ≤ 18	−10 ≤ <i>h</i> ≤ 8 −16 ≤ <i>k</i> ≤ 15 −22 ≤ <i>l</i> ≤ 23	−13 ≤ <i>h</i> ≤ 13 −20 ≤ <i>k</i> ≤ 21 −27 ≤ <i>l</i> ≤ 27	−17 ≤ <i>h</i> ≤ 22 −22 ≤ <i>k</i> ≤ 15 −31 ≤ <i>l</i> ≤ 28
reflections measured	11 692	6750	23 977	39 852
independent reflections	5203	4158	15 519	16 635
reflections used	4605	3583	13 542	13 438
<i>R</i> _{int}	0.0432	0.0242	0.0292	0.0467
refinement type	riding	riding	Fsqd	Fsqd
hydrogen atoms	mixed	mixed	mixed	mixed
parameters	194	223	861	593
reflections/parameter	23	16	15	22
<i>wR</i> ₂	0.0537	0.1202	0.0625	0.1051
<i>R</i> ₁	0.0217	0.0404	0.0259	0.0401
GOF	1.059	1.078	1.034	0.0401
difference peak/hole [e Å ⁻³]	0.628(0.078)/−0.451(0.078)	3.103(0.165)/−1.419(0.165)	0.551(0.084)/−0.673(0.084)	2.53(0.109)/−1.378(0.109)

copy data indicated the formation of complexes **5a** and **5b** with two singlets at $\delta = 37.4$ (for **5a**) and 22.2 (for **5b**). Then, $[\text{Pd}(\text{dba})_2]$ (57 mg, 0.1 mmol) was added and the resulting solution stirred for an additional 10 minutes. After reducing the volume by half, complexes **6a,b** were precipitated by addition of toluene. After filtration and drying, dimers **6a,b** were isolated as violet crystals. Crystals of **6a** were obtained from dichloromethane kept at -20°C for several days. Overall yield (**6a,b**): 72 mg (80%); **6a**: m.p. $> 200^\circ\text{C}$ (decomp); ^{31}P NMR (81 MHz, CDCl_3 , 25°C): $\delta = 94.0$ (**6a**), 103.8 (**6b**); ^1H NMR (200 MHz, CDCl_3 , 25°C , **6a**): $\delta = 2.29$ (s, 6H; Me), 2.35 (s, 6H; Me), 3.29 (m, AX X' , $\Sigma J(\text{P,H}) = 33.80$ Hz, 2H; CH), 4.78 (s, 10H; Cp), 7.09 (s, 10H; CH Ar); ^{13}C NMR (**6a**) (50 MHz, CDCl_3 , 25°C): $\delta = 15.4$ (s, Me), 17.4 (s, Me), 66.85 (m, AX X' , $\Sigma J(\text{P,C}) = 20.7$ Hz, C_5), 91.9 (m, C_2 , C_3 , or C_4), 93.7 (m, C_2 , C_3 , or C_4), 94.5 (m, C_2 , C_3 , or C_4), 127.5 (s, Ar), 128.5 (s, Ar), 129.6 (s, Ar), 144.00 (m, Ar); elemental analysis calcd (%) for $\text{C}_{34}\text{H}_{34}\text{Cl}_2\text{Fe}_2\text{P}_2\text{Pd}_2$ (900.02): C 45.37, H 3.81; found C 45.02; H 3.78.

Synthesis of complex 8: $[\text{Pd}(\text{COD})\text{Cl}_2]$ (32 mg, 0.11 mmol) was added at room temperature to a solution of **7** (50 mg, 0.11 mmol) in dichloromethane (3 mL). The color rapidly changed from yellow to deep violet. After having reduced the volume by half, addition of hexane caused precipitation of complex **8**. After filtration, **8** was washed three times with hexane (3×10 mL). After drying, **8** was obtained as a deep-violet solid. Yield: 61 mg (88%); m.p. $> 200^\circ\text{C}$ (decomp); ^{31}P NMR (81 MHz, CD_2Cl_2 , 25°C): $\delta = -9.34$; ^1H NMR (200 MHz, CD_2Cl_2 , 25°C): $\delta = 1.17$ (t, $^3J(\text{H,H}) = 7.50$ Hz, 24H; 8Me), 1.23 (t, $^3J(\text{H,H}) = 7.30$ Hz, 24H; 8Me), 1.68 (m, 8H; CH_2), 2.17 (m, 8H; CH_2), 2.37 (m, 8H; CH_2), 2.69 (m, 8H; CH_2); ^{13}C NMR (50 MHz, CD_2Cl_2 , 25°C): $\delta = 25.65$ (s, Me), 26.40 (s, Me), (s, CH_2), 29.45 (s, CH_2); elemental analysis calcd (%) for $\text{C}_{48}\text{H}_{80}\text{Cl}_4\text{Fe}_2\text{P}_4\text{Pd}_2$ (1247.38): C 46.22, H 6.46; found C 46.35, H 6.67.

Synthesis of $[(\text{Pd}_2(\text{7})_2\text{Cl}_2)[\text{FeCl}_4]]_2$ (9a**):** Complex **8** was prepared as described above from ligand **7** (45 mg, 0.1 mmol) and $[\text{Pd}(\text{COD})\text{Cl}_2]$ (29 mg, 0.1 mmol). After 10 minutes, a solution of FeCl_3 (13 mg, 0.1 mmol) in THF (10 mL) was added, causing a darkening of the reaction mixture and a rapid precipitation of complex **9a**. After evaporation of the solvent, **9a** was washed three times with hexane (3×10 mL). After drying, **9a** was recovered as black solid. Yield: 50 mg (75%). ^{31}P NMR (81 MHz, 25°C , CD_2Cl_2): $\delta = 9.9$, -247.1 ; ^1H and ^{13}C NMR data of **9a**, which is poorly soluble, could not be obtained; elemental analysis calcd (%) for $\text{C}_{96}\text{H}_{160}\text{Cl}_{10}\text{Fe}_6\text{P}_8\text{Pd}_4$ (2677.36): C 43.06, H 6.02; found C 42.40, H 5.90.

Synthesis of $[(\text{Pd}_2(\text{7})_2\text{Cl}_2)[\text{GaCl}_4]]_2$ (9b**):** A solution of ligand **7** (45 mg, 0.1 mmol) in CH_2Cl_2 (5 mL) was added to a solution of $[\text{Pd}(\text{dba})_2]$ (28 mg, 0.05 mmol). After 30 min, the solution turned green indicating the formation of complex **10**. $[\text{Pd}(\text{COD})\text{Cl}_2]$ (14 mg, 0.05 mmol) was then added at RT. The resulting black solution obtained was transferred to a glovebox and GaCl_3 (9 mg, 0.05 mmol) was added. After 15 min, the solvent was partially evaporated and hexane was added; complex **9b** was recovered by filtration. Yield: 53 mg (80%); m.p. $> 200^\circ\text{C}$ (decomp); ^{31}P NMR (81 MHz, CD_2Cl_2 , 25°C): $\delta = 7.4$, -249.8 ; ^1H and ^{13}C NMR data of **9b**, which is poorly soluble, could not be obtained; elemental analysis calcd (%) for $\text{C}_{96}\text{H}_{160}\text{Cl}_{10}\text{Fe}_4\text{Ga}_2\text{P}_8\text{Pd}_4$ (2705.12): C 42.62, H 5.96; found C 42.98, H 6.15.

Crystallography: Crystal data and details of the structure determinations of compounds **3**, **6a**, **8**, and **9a** are presented in Table 1. Crystals of **3**, **6a**, **8**, and **9a** were obtained from dichloromethane solutions of the complexes at RT. Data were collected at 150 K on a Nonius Kappa CCD diffractometer by using a $\text{MoK}\alpha$ ($\lambda = 0.71070$ Å) X-ray source and a graphite monochromator. The crystal structures were solved by using SIR 97^[14] and refined with SHELXL-97^[15] ORTEP drawings were made by using ORTEP III for Windows.^[16] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-156576 (**3**), CCDC-156577 (**6a**), CCDC-156578 (**8**), and CCDC-156579 (**9a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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