On the Mechanistic Behavior of Highly Efficient Palladium−Tetraphosphine Catalytic Systems for Cross-Coupling Reactions: First Spectroscopic and Electrochemical Studies of Oxidative Addition on Pd(0)/Multidentate Ferrocenylpolyphosphine Complexes

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Electrochemical studies carried out in conjunction with ^{31}P NMR spectroscopy on the palladium(II)/palladium(0) halogeno complexes of the tetraphosphine 1,1′,2,2′-tetrakis(diphenylphosphino)-4,4′-di-*tert*-butylferrocene, termed Fc(P$_4$)^{t}Bu, are reported. Fc(P$_4$)^{t}Bu was chosen with regard to its good performances in pallado-catalyzed cross-coupling reactions, which resulted in catalytic turnover numbers (TONs) up to 1 000 000 [*Organometallics* **2003**, *22,* 4490–4499]. The complexes [PdX$_2${Fc(P)$_4$^{t}Bu}] (X = Cl, Br, I) are described with their X-ray molecular characterization in the solid state and multinuclear NMR in solution. The electrochemical behavior of Fc(P$_4$)^{t}Bu and [PdX$_2${Fc(P)$_4$^{t}Bu}] complexes was investigated by cyclic voltammetry and electrolysis: a formulation of the corresponding electro-generated Pd^0 species formed is proposed on the basis of their NMR characterization. The oxidative addition reaction of phenyl iodide on these zerovalent palladium/ferrocenyltetraphosphine complexes was also studied by combining electrochemistry and ^{31}P NMR. The Pd(II) species that result from phenyl iodide oxidative addition are described, and their rate of formation under standard conditions is given; the halogeno phenyl products obtained are identified and characterized. These results are discussed in light of the knowledge existing for more classical systems combining Pd(II) halides or zerovalent palladium with *n* monodentate tertiary phosphines (*n* = 2–4). In this respect, the system using Fc(P$_4$)^{t}Bu is relevant since its four triarylphosphine groups (Ph$_2$*P*Cp) are formally similar to a 4-fold excess of the triarylphosphine triphenylphosphine (*P*Ph$_3$) as ligand. However, the phosphorus atoms of the tetraphosphine ligand present a mutual spatial proximity that is absent in monophosphines, due to their implantation on the ferrocene platform. Therefore, the possible effects of multidentarity are discussed. Finally, the importance of palladium anionic species is confirmed in this study, and the rate value of Ph−I oxidative addition (130 ± 10 ms) on Pd(0) confirmed both the good reactivity and the enhanced stability provided to palladium species by the ferrocenyltetraphosphine ligand.

Introduction

Palladium-based catalysts emerged as powerful tools in reactions aimed at coupling organic halides with organometallic substrates based mainly on boron (Suzuki−Miyaura reaction), tin (Stille reaction), zinc (Negishi reaction), silicon (Hiyama reaction), copper (Castro−Sonogashira reaction), or magnesium reagents (Kumada−Corriu reaction).[1]

The development of ligand chemistry has been decisive in this prospect, and much progress was done on the fine understanding of the relevant catalytic cycles due to the systematic studies of Hartwig,[2] Fu,[3] Amatore and Jutand,[4] and others. These mechanistic studies mainly concerned palladium catalytic systems incorporating classical ligands such as PPh$_3$, dppp (=1,3-diphenylphosphinopropane), AsPh$_3$, or bi- and monodentate electron-rich phosphines. Besides traditional catalytic auxiliaries and bulky electron-rich phosphine ligands, other systems of interest in catalytic cross-coupling have been identified to address specific issues.[5] Recent investigations of the catalytic activity of various polyphosphines have highlighted

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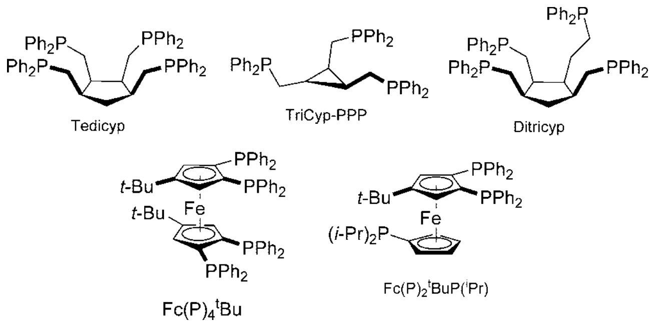
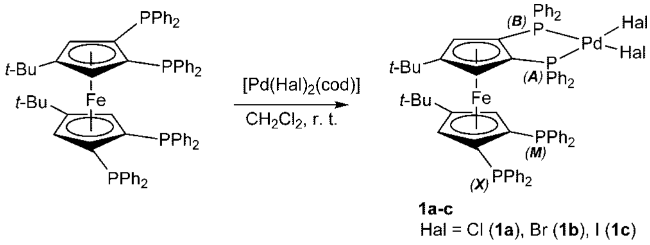


Figure 1. Polyphosphine ligands efficiently used under low palladium loading conditions.

several examples of polydentate ligands that have been employed under conditions of very low catalyst loadings. Various cross-coupling reactions carried out in the presence of catalyst amounts ranging from 10^{-1} to 10^{-6} mol % have been therefore described (Figure 1).[6] The main advantage of this class of ligand is to provide high catalytic turnover numbers (TONs) consistently with the use of very low [metal/ligand] loadings. The comparison of catalytic activity with some classical systems incorporating mono- or bidentate phosphines (such as PPh$_3$, dppe = 1,2-diphenylphosphinoethane, and dppb = 1,4-diphenylphosphinobutane) often indicated a higher efficiency for the systems based on polyphosphines. These performances have been generally attributed to a better stability under the reaction conditions, which is consistent with their efficiency during long periods of time ($\geq$20 h) at relatively high temperatures ($\geq$100 °C). From a mechanistic point of view only a few ^{31}P NMR studies of Pd(II) precatalytic systems are available so far to account for their behavior.[6a,f] In general, their good performance results have been hypothetically attributed to the catalyst longevity: the presence near the metal of several phosphorus coordinative sites might prevent catalyst deactivation and metallic palladium precipitation.

Electrochemical studies have greatly contributed to the mechanistic understanding of catalytic cross-coupling reactions, and electrochemistry encompasses valuable methods to investigate mechanistic features of Pd(II)/Pd(0) catalytic systems.[4] The present work is the first account of a research program aimed at identifying the parameters at the origin of the catalytic activity of palladium systems incorporating polyphosphines. The tetraphosphine 1,1′,2,2′-tetrakis(diphenylphosphino)-4,4′-di-*tert*-butylferrocene, Fc(P$_4$)^{t}Bu (see Figure 1), was chosen from different ferrocenylpolyphosphines[5] for its high performance in Heck and Suzuki cross-coupling reactions (with TONs up to 1 000 000 observed).[6a] The electrochemical behavior of the dihalogeno palladium(II) complexes of Fc(P)$_4{}^t$Bu, **1a** and **1b** (Scheme 1), is detailed. Electroreduction to the catalytically important corresponding palladium(0) species, and addition of Ph−I in the electrochemical medium has allowed the observation of the oxidative addition reaction. Quantitative information on kinetics of oxidative addition was obtained. The halogeno phenyl products have been therefore isolated and characterized in this series. We provide herein the first mechanistic information on the possible role and behavior of catalytically efficient polyphosphine ligands. These data are discussed and compared to available knowledge existing for more classical systems combining palladium(II) halides or zerovalent palladium with *n* monodentate tertiary phosphines (*n* = 2–4).

Scheme 1. Mononuclear Palladium Halide Complexes of the Tetraphosphine Fc(P)$_4{}^t$Bu



Results and Discussion

Palladium(II) Halide Complexes of the Ferrocenyltetraphosphine Ligand: Synthesis and Spectroscopic Characterization. The tetraphosphine ligand Fc(P)$_4{}^t$Bu is obtained in a one-step reaction using FeCl$_2$ with 2 equiv of the anionic cyclopentadienyl (Cp) moiety from [^{t}BuCp(PPh$_2$)$_2$]Li.[7a] The cyclopentadienyl lithium reagent results from two successive phosphorylation/lithiation reactions performed on [^{t}BuCp]Li. The salt [^{t}BuCp]Li is obtained from reaction of methyl lithium with dimethylfulvene.[7b] Reaction of Fc(P)$_4{}^t$Bu under high dilution conditions in chlorinated solvent with [Pd(Hal)$_2$(cod)] precursors (cod = 1,5-cyclooctadiene, Hal = Cl, Br, or I) selectively affords the expected palladium mononuclear complexes with suitable purity (Scheme 1). The NMR characterization and X-ray diffraction study of **1a** have been previously reported.[6a,8] The complex **1b** presents analogous features with, however, some differences: its ^{31}P NMR spectrum is depicted in Figure 2.

The four nonequivalent phosphorus atoms of **1b** give four multiplets that might be described as a first-order ABMX spin system (see Scheme 1, P$_A$, P$_B$, P$_M$, and P$_X$).[9] In the following, for clarity and accuracy reasons, the detailed peaks of the spectrum are given rather than the average chemical shift of the multiplets: δ_A (ddd) = 40.08, 40.07, 39.91, 39.90, 39.87, 39.86, 39.70, 39.69 ppm, J_{AB} = 20.6 Hz, J_{AM} = 25.6 Hz, J_{AX} = 1.9 Hz; δ_B (dd) = 37.49, 37.44, 37.32, 37.27 ppm, J_{BA} = 20.6 Hz, J_{BM} = 5.8 Hz, δ_M (ddd) = −24.88, −24.93, −24.98, −25.02, −25.09, −25.14, −25.19, −25.23 ppm, J_{MA} = 25.6

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(9) NMR spectra (and g-NMR simulation for **1b**) and X-ray data are available as Supporting Information.

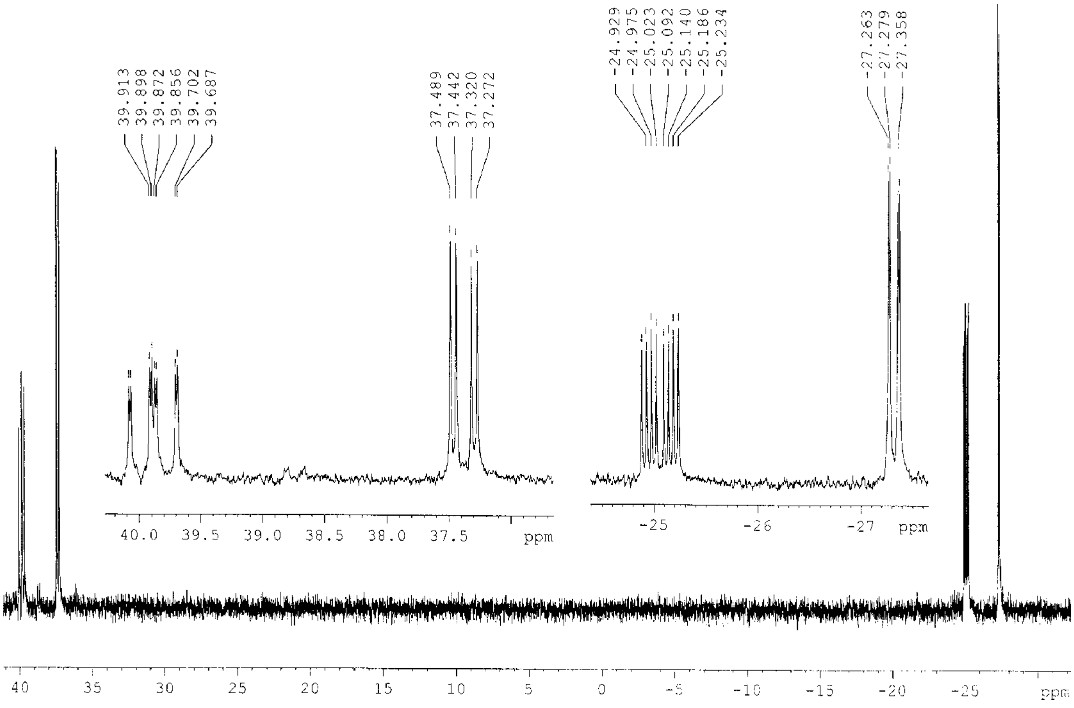


Figure 2. ^{31}P NMR spectrum of **1b** with signal enhancement.

Table 1. Correlation between the Heteroannular P···P Distance and J_{PP} Intensity

	P···P distance (Å)	coupling constant J_{PP} (Hz)[a]
d $P_A \cdots P_M / J_{AM}$	3.6765(12)	25.6
d $P_B \cdots P_M / J_{BM}$	4.4879(13)	5.8
d $P_A \cdots P_X / J_{AX}$	5.3971(13)	1.9
d $P_B \cdots P_X / J_{BX}$	6.7628(13)	none

[a] Values at ±0.1 Hz from spectra simulated with g-NMR.

Hz, $J_{MB} = 5.8$, $J_{MX} = 11.5$ Hz; δ_X (dd) = −27.26, −27.28, −27.36, −27.37 ppm, $J_{XA} = 1.9$ Hz, $J_{XM} = 11.5$ Hz. The set of coupling constants for this kind of highly unsymmetrical spin system has been thoroughly investigated previously with parent nickel and palladium coordination complexes, such as **1a**, and was found to originate from strong phosphorus−phosphorus J_{PP} through-space spin–spin couplings.[8] The NMR spectrum of **1b** confirmed the theory we developed, in which the intensity of the collected ^{31}P NMR J_{PP} coupling constants for a heteroannular nucleus is related to the through-space distance between phosphorus nuclei (determined from X-ray crystallographic data), as summarized in Table 1.[9] Due to the efficiency of the overlap of phosphorus' valence electron clouds, the intensity of J coupling between phosphorus atoms separated by at least four bonds increases exponentially with the decrease of the spatial distances between the phosphorus atoms.[8]

As formerly observed for **1a**,[6a,8] the complex **1b** conserves in solution a *cisoid* conformation, in which one of the noncoordinated phosphorus atoms is closer to one of the two palladium-bonded phosphorus atoms. This is evidenced by the strong through-space coupling constant $J_{AM} = 25.6$ Hz compared to only the analogous $J_{BM} = 5.8$ Hz. This general feature was supported by the X-ray structure determinations of **1a**,[6a] **1b**,[9] and **1c**, which are all similar (Figure 3 displays for example the molecular structure of **1c**).

Conversely, while the coupling constants between the phosphorus attached to the same Cp ring (homoannular) are of the same order of magnitude for **1a** ($J_{AB} = 14.7$ Hz and $J_{MX} = 15.3$ Hz), in **1b** they are substantially different ($J_{AB} = 20.6$ Hz, $J_{MX} = 11.5$ Hz), showing probably the influence of through-space spin–spin transmission contribution in addition to the classical through-bond ^3J couplings ($dP_A \cdots P_B = 3.061$ Å, while $dP_M \cdots P_X = 3.754$ Å). The spatial proximity of the phosphorus P_M to phosphorus atoms P_A and P_B is expected to play an important role in the reactivity of the tetraphosphine ligand toward a metal center, as confirmed by the electrochemical studies reported below.

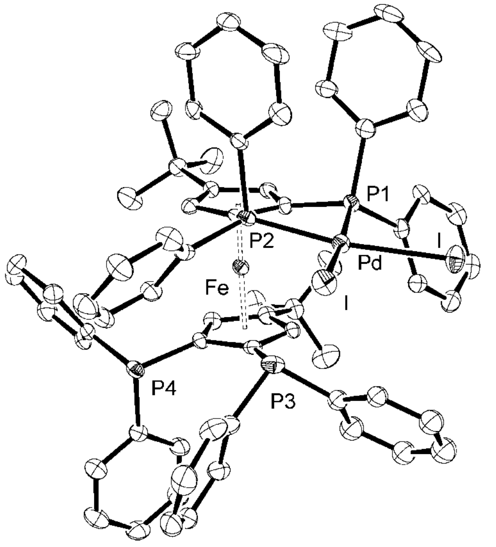


Figure 3. ORTEP view of the molecular structure determined for **1c**.

Electrochemical Behavior of the Ferrocenyltetraphosphine and of the Pd(II) Halide Coordination Complexes: Electrolysis to Pd(0) Species and Their Characterization. Studies on the anodic reactions of ferrocenylphosphine derivatives have been reported,[10a] but none deals with derivatives bearing more than one phosphino substituent per cyclopentadienyl ring. Owing to its role in homogeneous catalysis,[10b] most of these studies have been related to the diphosphine complex 1,1′-bis(diphenylphosphino)ferrocene (dppf)[11] and its coordination complexes with various metallic ions.[12]

Table 2. Half-Wave Potentials (V vs SCE) for the Ligand Fc(P)$_4{}^t$Bu and the Complexes [PdCl$_2${Fc(P)$_4{}^t$Bu}] (1a) and [PdBr$_2${Fc(P)$_4{}^t$Bu}] (1b) (oxidation potential for ferrocene is given for comparison, peak potential values recorded by cyclic voltammetry are in parentheses)

	E_{ox}(Fe)	E_{red}(Pd)	E_{red}(Fe)
Ferrocene	+0.68 (+0.69)		−2.93[a]
Fc(P)$_4{}^t$Bu	+0.67 (+0.68)		−2.37
[PdCl$_2${Fc(P)$_4{}^t$Bu}], **1a**	+0.92 (+0.94)	−1.30 (−1.37)	−2.42 (−2.50)
[PdBr$_2${Fc(P)$_4{}^t$Bu}], **1b**	(+1.06)[b]	−1.10 (−1.12)	−2.40 (−2.38)

[a] Recorded by polarography in DMF/NBu$_4$I.[13] [b] Because the oxidation wave is too close to the discharge to be properly determined, only the peak potential is given.

The tetraphosphine ligand Fc(P)$_4{}^t$Bu and the palladium complexes **1a** and **1b** were examined in an identical system [supporting electrolyte/solvent]: 0.2 mol L^{-1} of the salt [*n*-Bu$_4$N][BF$_4$] in THF. The rotating-disk electrode voltammograms (RDE voltammograms) of the three compounds have been recorded, and the resultant half-wave potentials ($E_{1/2}$) are collected in Table 2. The oxidation of Fc(P)$_4{}^t$Bu occurs at a potential of +0.67 V. Additionally, the RDE voltammogram of Fc(P)$_4{}^t$Bu displays in the cathodic part a reduction wave at $E_{1/2} = -2.37$ V. In comparison, the reduction of ferrocene, in DMF with 0.2 mol/L NBu$_4$I as supporting electrolyte, was observed at 10 °C as a well-defined one-electron reversible polarographic wave located at $E_{1/2} = -2.93$ (V vs SCE).[13] In Fc(P$_4$)^{t}Bu, this reduction process would mainly concern the ferrocene moiety, as the −PPh$_2$ groups are not expected to be reduced at this potential range. However, the large shift in reduction potential between the ferrocene and Fc(P$_4$)^{t}Bu is thought to result from an electron-withdrawing effect of the −PPh$_2$ groups.[14] In oxidation, no similar shift toward a more positive potential was observed. The oxidation reaction formally corresponds to the removal of one or several electrons from the highest occupied molecular orbital (HOMO); since the HOMO could possibly have a significant atomic orbital contribution from phosphorus, a strict comparison with the ferrocene is delicate. This is supported by recent reports on multiferrocenyl phosphines, in which were evidenced HOMOs having a substantial phosphine character.[10a]

Upon coordination to palladium halides, the oxidation attributed to the Fc(P)$_4{}^t$Bu ligand is shifted toward a more positive potential ($\Delta E_p = +0.26$ V for **1a** and +0.38 V for **1b**). A similar trend was noted for dppf, with a positive shift of +0.39 V between the reversible oxidation of the ligand compared to its complex [PdCl$_2$(dppf)].[12] This is attributed to an electron density decrease on the electroactive moiety of the ligand due to the σ-donation of bonded phosphorus donors to the palladium. The larger shift observed with complex **1b** incorporating bromides is indicative of a more important σ-donation. In the cathodic part of voltammograms, for **1a** and for **1b**, the first reduction process (referenced as R, potential value $E_{1/2} = -1.30$ for **1a** and −1.10 V for **1b**) is ascribed to the reduction of the Pd(II) center since the ferrocenylphosphine ligand is reduced at a more negative potential.

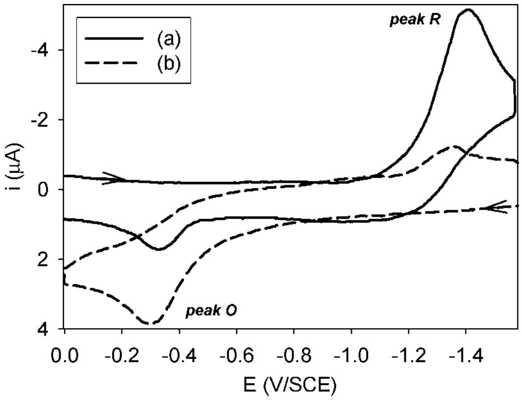
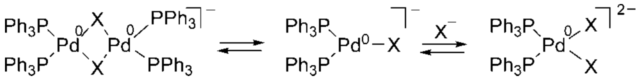


Figure 4. Cyclic voltammogram in THF on a carbon disk electrode of **1a** (1 mM) at a scan rate of 100 mV s^{-1}: (a) before electrolysis; (b) after bielectronic reduction at −1.5 V. Initial potential: 0 (a) and −1.6 V (b).

Scheme 2. Mixture of Three Pd(0) Species in Equilibrium from Electroreduction



In the cyclic voltammogram of the palladium halide complexes the corresponding reduction peak R is observed in the forward scan (Figure 4, line a). The reduction peak R is irreversible, and the electrogenerated zerovalent complex is oxidizable, as seen in the backward scan by the oxidation peak referenced as O in Figure 4 (line a, for a scan rate $v = 100$ mV s^{-1}, $E_p = -0.25$ V for **1a** and −0.12 V for **1b**). Thus, the voltammetry evidences one or several chemical reactions that follow the electron transfer process and ultimately give a product oxidized in O. Controlled-potential electrolysis has been performed at the potential of reduction process R. The electrolysis proceeds with a charge count of 2 Faradays per mole of **1a** (or **1b**) and leads to the same zerovalent palladium product found at the voltammetric scale (Figure 4, line b).[15] This product was found moderately stable with a lifetime of less than 1 h. The characterization by ^{31}P NMR spectroscopy of this zerovalent Pd(0)/ferrocenylpolyphosphine is difficult since either only weak peaks (three signals at 36.2, 34.5, and 22.9 ppm) or no signal at all was observed in our repeated experiments. This could possibly be due to decomposition of the electrolyzed species in the short delay between the electrolysis process and the NMR analysis. As an additional evidence of this uncontrolled evolution, the electrolyzed solutions for which ^{31}P NMR was silent did not give any oxidative addition reaction to Pd(0) in the presence of added Ph−I, in contrast to the freshly electrolyzed solutions (*vide infra*).

In the mechanistic studies by Amatore and Jutand, the halide ions were shown to play a significant role in the catalytic

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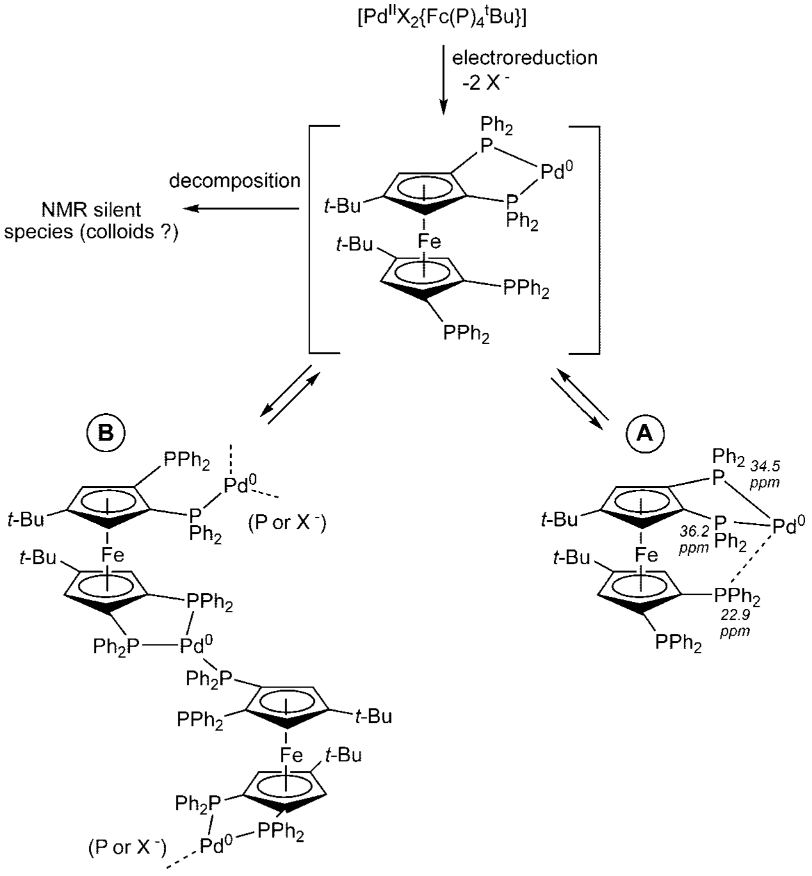
Scheme 3. Formation of Short-Lived Zerovalent Palladium Species A or B in the Absence of Additive



reaction, providing in the oxidative addition step an easier energetic pathway.[16] Noteworthy, in reactions under catalytic conditions, large amounts (stoichiometric) of halides are coproduced from the coupled aryl halide. To provide further informative data, electrolysis of **1a** was performed in the presence of an excess of chloride ions (10 equiv of $[n\text{-Bu}_4\text{N}][\text{Cl}]$ salt). ^{31}P NMR spectra collected after electrolysis repeatedly showed five ill-resolved signals located at low field ($\delta_P = 30.8$, 36.4, 37.9, 38.9, and 40.9 ppm, phosphorus atoms coordinated to palladium) and three other signals at high field ($\delta_P = -24.8$, -27.5, and -29.5 ppm, nonbonded phosphorus atoms).[9] Due to the magnetic inequivalence of the phosphorus atoms induced by bonding of this ferrocenyltetraphosphine (see spectrum of **1b** for instance), the eight signals detected in the ^{31}P NMR certainly reveal two different $[\text{Pd}^0/\{\text{Fc(P)}_4{}^t\text{Bu}\}/(\text{chloride})]$ units. The integration of the eight peaks was found fairly consistent with the hypothesis of the formation of two products in approximately equivalent amount. With regard to chemical shifts, a reasonable postulate is the existence of a first species for which two phosphines coordinate the palladium center while the other two remain dangling. Conversely, in the second species three phosphorus atoms are bonded to palladium, while only the last remains uncoordinated.

The possible formulation of the zerovalent palladium species formed in the presence of the ferrocenyltetraphosphine was examined in light of the Pd(II)/Pd(0) systems that were studied by complementary electrochemical techniques and NMR spectroscopy (as reported by Jutand and Amatore).[4a] In this respect, the ferrocenyltetraphosphine system is relevant since the four triarylphosphine groups (Ph_2PCp) are formally analogous to a 4-fold excess of the triarylphosphine triphenylphosphine ($P\text{Ph}_3$).

Formulation of the Electrogenerated Zerovalent Palladium Species Depending on the Reaction Conditions and Discussion of Their Structure. Our attention was first attracted by the resemblance of the electrochemical behavior of **1a** and **1b** to those earlier reported for complexes $\text{Pd}^{\text{II}}\text{X}_2(\text{PPh}_3)_2$ (X = Cl, Br).[4a,17,18] In these systems the electroreduction of Pd(II) generated a mixture of three Pd(0) species in equilibrium, in accordance with the three ^{31}P NMR signals observed at 27.1, 25.2, and 23.2 ppm in THF (species in Scheme 2). The coordination of halide ions, released during the reductive process, to the electronically highly unsaturated "$\text{Pd}^0(\text{PPh}_3)_2$" was proposed.[4a,17]

When the reduction was conducted in the presence of 1 equiv of added PPh$_3$, the halide ions were no longer involved in the coordination to the Pd^0 center, and the formation of $[\text{Pd}^0(\text{PPh}_3)_3]$ was quantitative (singlet at 20.5 ppm[17]) according to eq 1.[4a]

$$\text{Pd}^{\text{II}}(\text{PPh}_3)_2\text{X}_2 + 2e^- \xrightarrow{\text{PPh}_3} \text{Pd}^0(\text{PPh}_3)_3 + 2\text{X}^- \tag{1}$$

In the absence of added halides the electroreduction of $[\text{PdX}_2\{\text{Fc(P)}_4{}^t\text{Bu}\}]$ is better related to the latter experimental conditions. Three weak ^{31}P NMR signals were observed (at 36.2,

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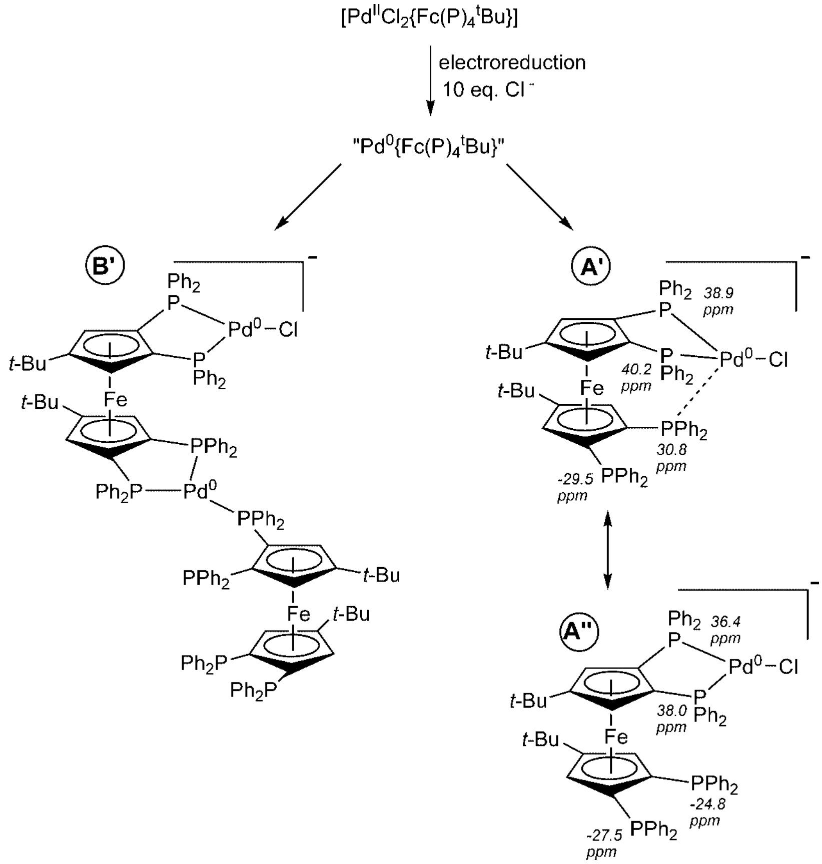
[15] Voltammetric investigation of the electrolyzed solution shows that peak O is observed in the first anodic scan (Figure 4, line b). Noticeably, the backward cathodic scan makes reduction peak R happen: the electrolysis product can be converted back to **1a** by oxidation.

[16] For a review see: Amatore, C.; Jutand, A. *Acc. Chem. Res.* **2000**, *33*, 314–321.

[17] Amatore, C.; Azzabi, M.; Jutand, A. *J. Organomet. Chem.* **1989**, *363*, C41–C45.

[18] The cyclic voltammogram of each Pd complex bearing PPh$_3$ similarly displays in the cathodic scan a two-electron chemically irreversible reduction around–1 V vs SCE, which is coupled upon scan inversion to an oxidation O more positive than R by nearly 1 V.

Scheme 4. Formation of Stabilized Zerovalent Palladium Species A′/A″ or B′ in the Presence of 10 equiv of [*n*-Bu$_4$N][Cl] Salt



34.5, and 22.9 ppm, X = Br). The spectra did not show any other signal of unbound tetraphosphine ligand nor of the starting complexes [PdX$_2${Fc(P)$_4$^{t}Bu}]. The accurate examination of phosphorus chemical shifts of the formed species is of special interest. In the hypothesis of the initial formation of only one species from electroreduction,[19] two phosphorus atoms are of very similar environment and more closely bonded to palladium (δ = 36.2, 34.5 ppm, deshielded by stronger σ-donation) than is the third one (δ = 22.9 ppm). The fourth phosphorus atom is barely detected at high field (an unclear broad signal around −28 ppm was occasionally found;[9] low-temperature NMR experiments did not allow a better characterization). This species appears to be more destabilized than [Pd^0(PPh$_3$)$_3$] with regard to its instability after electrolysis (*vide supra* experiments with Ph−I added on ^{31}P NMR-silent solutions). The problems encountered in ^{31}P NMR characterization after electrolysis in the absence of additive support this assessment (in several cases no signal at all was observed). The structure **A** depicted in Scheme 3 is proposed for the formed species based on the electrochemistry/NMR results and on the structure of [Fc(P)$_4$^{t}Bu]. Besides a possible intramolecular triligation due to blocked conformation of the ligand, another formulation consistent with the data is an intermolecular tridentate bonding with a neighboring unit. This would then form dimeric or even oligomeric compounds corresponding to the formulation **B** in Scheme 3.[20] Whatever the species resulting from electroreduction, ^{31}P NMR experiments are reasonably consistent with a tridentate coordination of the tetraphosphine ligand. In addition, these transient species **A** and/or **B** are very reactive, in accordance with the studies of Ph−I oxidative addition described below.

Conversely, electrolysis in the presence of an excess of chloride ions (10 equiv of [*n*-Bu$_4$N][Cl] salt) resulted in more stable zerovalent palladium species. As described above, the ^{31}P NMR spectra with five signals located at low field (δ_P = 30.8, 36.4, 37.9, 38.9, and 40.2 ppm) and three other signals at high field (δ_P = −24.8, −27.5, and −29.5 ppm) are consistent with the formation of two different [Pd^0/{Fc(P)$_4$^{t}Bu}/(halide)] units. This would correspond to a first compound in which two phosphorus atoms coordinate the palladium center and two others remain dangling. A second species would form, in which three palladium-bonded phosphorus atoms are observed and one is free. Consistently with the formulation of **A** or **B**, the formation of the two species **A′/A″** or of the dimeric assembly **B′** is proposed by addition/coordination of chloride (Scheme 4). The chemical shift attribution proposed in Scheme 4 is consistent with the NMR data obtained for palladium(II) halides reported in the first section. The "internal" pseudoeclipsed phosphorus atoms (corresponding to P$_A$ and P$_M$ in Scheme 3) are more deshielded than their corresponding homoannular paired P atoms in "external" positions (corresponding to P$_B$ and P$_X$ in Scheme 3). In this case as well, a connection can be made to the PPh$_3$ series, where addition of an excess of [*n*-Bu$_4$NCl] on [Pd^0(PPh$_3$)$_3$] led to a new tetraligated species formulated as [Pd(PPh$_3$)$_3$X]$^-$.[4a]

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[19] This case is much more probable because of the simplicity of the voltammograms and NMR spectra obtained.

[20] This intermolecular phosphorus bonding process toward palladium may possibly concern more than two ligand molecules to yield oligomers. In addition, it is worth noting that the coordination sphere of palladium for **A** and **B** might be completed with a halide ion to form anionic Pd^0 species; see ref 4a. However, the values of phosphorus chemical shift are not really in favor of this hypothesis compared to data reported by Jutand and Amatore and also to the other NMR chemical shifts obtained in the presence of excess halides.

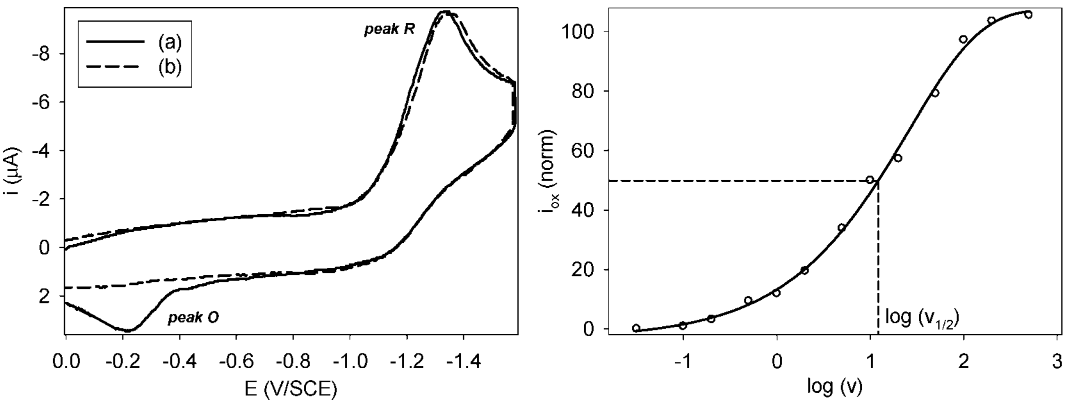

Figure 5. Left: cyclic voltammogram in THF on a platinum disk microelectrode at a scan rate of 100 mV s^{-1} of **1a** (2 mM) in the absence of additive (line a) and in the presence of 1 molar equiv of phenyl iodide (line b). Initial potential: 0 V. Right: variation of the normalized current peak of O [i_{ox}(norm) = $100 i_{p,O}$(with PhI)/$i_{p,O}$(without PhI)] as a function of the scan rate logarithm.

A′/A″ and **B′** could be regarded as resulting from halide addition on the previously identified species **A** or **B**. This halogenation seems to provide supplementary stability to the complexes and shifts the chemical equilibrium away from the highly destabilized “naked” bis-ligated form “$Pd^0\{Fc(P)_4{}^tBu\}$” (analogous to the “$Pd^0(PPh_3)_2$” earlier postulated[4a]), possibly preventing the formation of palladium colloids.[21]

Electrochemical Studies of the Phenyl Iodide Oxidative Addition Reaction on the Zerovalent Palladium/Ferrocenyltetraphosphine Complexes. The oxidative addition of aryl halides to palladium(0) complexes as the initiating step of most of the palladium-catalyzed cross-coupling reactions is often assumed to be rate-determining.[22] This is obviously dependent on the substrate/catalytic system employed and on the specific experimental conditions.[23] Consequently, the fine study of mechanisms and factors that influence the efficiency of oxidative addition in each system is very important. This topic has led to numerous relevant investigations on catalytic systems based on diphosphines and monophosphines.[24] Since the use in pallado-catalyzed cross-coupling of efficient tri- and tetradentate polyphosphine ligands is rapidly growing,[6a,b,d–h] investigations aimed at elucidating unidentified “multidentarity” effects associated with this emerging class of ligands are essential. Studies on the oxidative addition of aryl halides on palladium/polyphosphine systems are a first step toward this goal.

The generation of zerovalent palladium species by reduction of **1a** (or **1b**) offers the opportunity to investigate the oxidative addition process on the time scale of voltammetry and electrolysis. In the voltammogram of **1a** (Figure 5 line a), an oxidation peak O is associated with the oxidation of the low-stability zerovalent species formed after electroreduction (Scheme 3). In the presence of Ph–I the reduction peak R of **1a** remains unchanged (Figure 5 line b). Conversely, the oxidation peak O completely disappears at low potential scan rate (100 mV s^{-1} for Figure 5, line b), indicating a fast reaction between phenyl iodide and the electrochemically generated **A** or **B** species. Raising the potential scan rate shows the progressive recovery of peak O, until a value of nearly 100 V s^{-1} is reached, for which the oxidation peak O is totally restored.

The plot of the peak current as a function of the logarithm of the scan rate (peak current normalized as defined in Figure 5) led to extracting a half-life time $t_{1/2}$ of 130 ± 10 ms[25] for the zerovalent palladium species in the presence of 1 equiv of phenyl iodide under the conditions relevant to Figure 5.

The reaction of Ph–I on electrogenerated zerovalent palladium was extended at the electrolysis scale to perform spectroscopic characterization of the resultant species. The electrolysis of **1a** and **1b** in the presence of phenyl iodide proceeded with a transfer of 2 Faradays per mole of starting complex. The ^{31}P NMR spectra of electrolyzed solutions in the presence of Ph–I showed a quantitative conversion of the palladium(II) complexes and of the transiently formed zerovalent palladium compounds. In the resulting NMR patterns, six signals of different intensity centered on δ 36, 32, 16, 15, −21, and −27 ppm were observed.[9] The signal integration found nearly double for the upper field signals (−21 and −27 ppm) clearly evidenced two distinct species with four nonequivalent phosphorus atoms that have identical chemical shifts for the nonbonded phosphorus. Despite the poor resolution of the spectra (due to a low concentration for NMR spectroscopy), the signals associated with these species displayed, as expected, a multiplicity resulting from the existence of various J_{PP} nuclear spin couplings (see for instance Figure 6).

For these two species issued of Ph–I oxidative addition the ^{31}P NMR patterns are differentiated by the four signals of lower field region. This clearly indicates a structural difference in the palladium coordination sphere (Figure 6). The comparison of

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(25) $t_{1/2} = \{(E_{p,R} - E_{inv}) + (E_{p,O} - E_{inv})\}/v_{1/2}$; $E_{p,R}$: peak potential of R, $E_{p,O}$: peak potential of O, E_{inv}: inverting potential of the scan, $V_{1/2}$: rate corresponding to $i_{norm,O} = 50\%$.

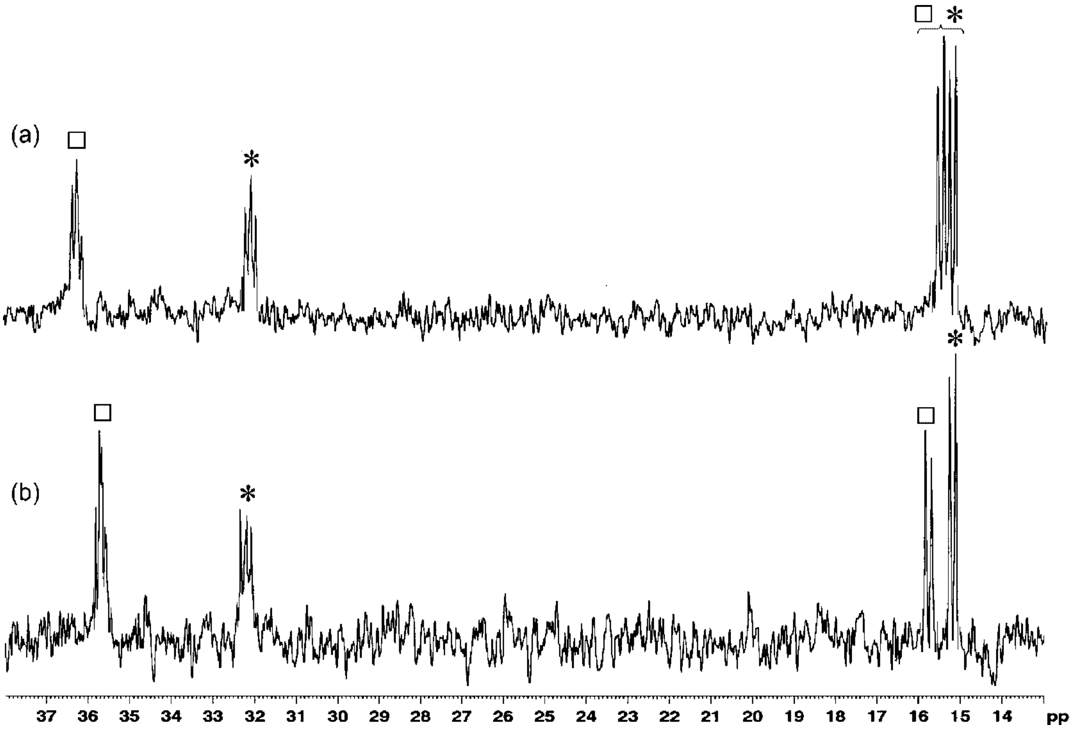


Figure 6. Lower field region of the ^{31}P NMR spectra in acetone-d_6 of the reductive electrolysis product originating from **1a** (top) and **1b** (bottom).

Table 3. Relative Intensity of the Resonances Observed in the Product of Oxidative Addition of Ph−I on Pd^0 Formed after Electrolysis, as a Function of the Starting Reagent

entry	palladium complex	additive	PhI equiv (vs Pd)	δ (ppm)				
				36[a]	32	15[b]	−21	−27
1	**1a**		1	0.48	0.59	1.10	1.0	1.14
2	**1a**		10	0.49	0.54	1.07	1.01	0.99
3	**1b**		1	0.52	0.39	0.35 0.49	1.00	0.99
4	**1a**	H_2O (100 μL)	1	0.42	0.54	1.08	1.02	0.98
5	**1a**	*n*-Bu_4NCl (10 equiv vs Pd)	1	0.91	0	1.01	1.00	0.95
6	**[Pd$^0_2$(dba)]$_3$**[c]	Fc(P)$_4$^{t}Bu (1 equiv vs Pd)	3	0	0.87	1.10	1.00	1.11

[a] The chemical shifts of signals are clearly different if X = Cl (δ: 36.2 ppm, entries 1, 3, 5, and 6) or X = Br (δ: 35.6 ppm, entries 2 and 4). [b] *Nota bene* that at this chemical shift two different signals are observed between 15 and 16 ppm (with no more overlapping in the cases of Pd/bromide product). [c] Starting from a Pd^0 reagent, no electrolysis was necessary in this case.

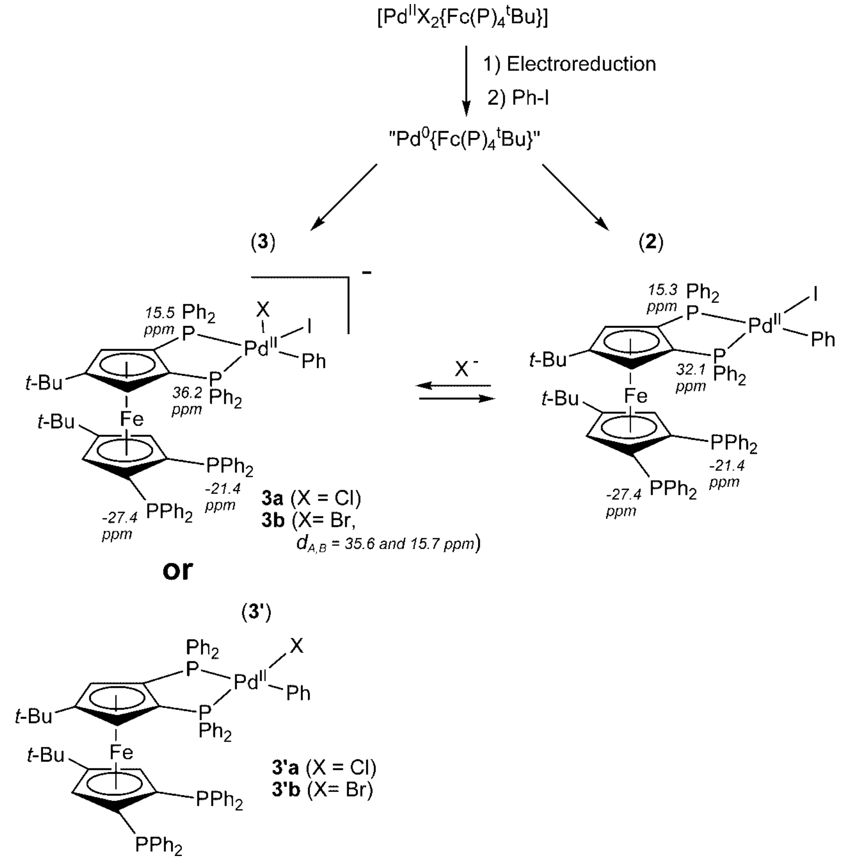
the NMR patterns resulting from electrolysis of the [PdX$_2$-{Fc(P)$_4$^{t}Bu}] complexes **1a** (X = Cl) and **1b** (X = Br) in the presence of Ph−I revealed in both cases the shift of only one set of signals (with the mark □ in Figure 6). These signals are attributed to a compound incorporating chlorine in the first case (Figure 6a) and bromine in the second case (Figure 6b). Consistently, the unchanged signals (with the mark * in Figure 6) can unambiguously be attributed to a palladium(II) complex that does not contain chlorine or bromine, since the corresponding signals are common to both spectra.

Electrolysis of **1a** or **1b** was conducted under modified conditions, and each of the two species originally observed could successfully be obtained as the only product. Table 3 summarizes the experiments performed with the integration of all ^{31}P NMR signals related to chemical shifts, depending on the electrolysis conditions.[9]

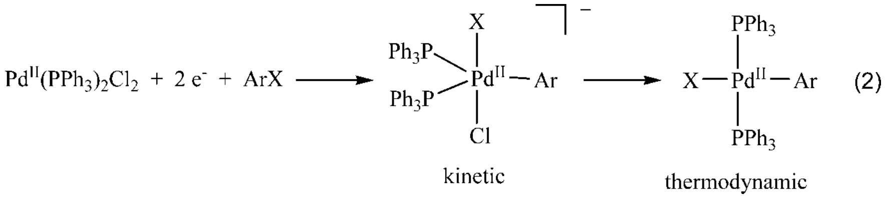
The electrolysis of **1a** in the presence of 1 or 10 equiv of Ph−I (entries 1 and 2) led to the same mixture of two species: a first one incorporating chlorine (δ_P 36.2, 15.5, −21.4, −27.4 ± 0.1 ppm) and the other without (δ_P 32.1, 15.3, −21.4, −27.4 ± 0.1 ppm). The electrolysis of **1b** under the same conditions (entry 3) led to the formation of the same halogen-free species (δ_P 32.2, 15.2, −21.3, −27.3 ppm) and a product analogous to the previous cases but incorporating bromine (δ_P 35.6, 15.7, −21.3, −27.3 ± 0.1 ppm). The halogen-free species (chlorine and bromine-free) was quantitatively obtained (δ_P 32.2, 15.4, −21.4, −27.3 ppm) from addition of 3 equiv of Ph−I to a mixture of zerovalent [Pd$_2$(dba)$_3$] with two Fc(P)$_4$^{t}Bu (entry 6, dba = *trans,trans*-dibenzylidene acetone). Conversely, this chlorine-free species is no longer formed when the electrolysis is conducted in the presence of an excess of [*n*-Bu$_4$N][Cl] salt (entry 5): only the first species incorporating chlorine (δ_P 36.4, 15.4, −21.4, −27.3 ppm) is quantitatively formed. We additionally observed that the presence of water does not affect the formation of the mixture of species (entry 4). From this set of experiments a picture could be proposed for the formation of oxidative addition products depending on the conditions.

Formulation of the Palladium Species from Phenyl Iodide Oxidative Addition and Reaction Rate under Standard Conditions. The NMR experiments conducted after electrolysis of **1a** and **1b** in the presence of phenyl iodide without any additive indicated the formation of two species. The first one is produced independently of the nature of the electroreduced palladium(II) halide: as a consequence, the formation of the *cis* four-coordinate palladium(II) complex **2** (Scheme 5) is proposed from the insertion of zerovalent palladium into the C−I bond

Scheme 5. Palladium Complexes Resulting from Ph–I Addition to Electrogenerated Pd(0) Species



Scheme 6. Pd Complexes Resulting from Ph–I Addition to Electrogenerated “Pd⁰PPh₃” Species



of phenyl iodide. This formulation was supported by the direct synthesis of **2** from zerovalent [Pd$_2$(dba)$_3$][26] and Ph–I in the presence of 2 equiv of ferrocenyltetraphosphine. Different possibilities can be envisioned for the formulation of the second species, whose formation depends on the starting Pd^{II}(halide). Taking into account that this species was quantitatively formed in the presence of an excess of chlorides ([*n*-Bu$_4$N][Cl] salt), a reliable formulation is either the anionic five-coordinate complex **3** from addition of X$^-$ or the neutral four-coordinate complex **3′** that results from a substitution of iodide by X$^-$ (Scheme 5).

To account for the formulation of **3**, in the PPh$_3$ series the anionic five-coordinate arrangement was observed as a kinetic product slowly evolving toward the *trans* aryl palladium(II) complex by chloride release (Scheme 6).[24i] In the present case, the energy barrier to change from **3** to **2** is expected to be much lower since the *cis* conformation is geometrically imposed by the chelating tetraphosphine. The formation of this anionic species would constitute another key common point with the results obtained for electrochemical studies of Pd/*n*[PPh$_3$] systems ($n \geq 2$). Noteworthy, by employing dppf as ligand and [Pd(dppf)$_2$] as palladium(0) source, the addition of Ph–I leads to the neutral 1,1′-bidentate *cis* complex comparable to **2**.[27]

The value of $t_{1/2} = 130$ ms for the half-life of zerovalent bis-ligated “Pd^0{Fc(P)$_4$^{t}Bu}” obtained from electroreduction of **1a** (Scheme 3) and due to oxidative addition of Ph–I has to be compared with the rate of 80 ms found in the PPh$_3$ series under similar conditions.[4a,17] The value obtained indicates a reactivity ca. 200 times more important than the chemically stable [Pd^0(PPh$_3$)$_4$] ($t_{1/2} = 30$ s)[17] and 1.5 times slower than for the zerovalent “Pd^0(PPh$_3$)$_2$” and its anionic halide derivatives. Considering Scheme 3, and before a detailed kinetic investigation, “Pd^0{Fc(P)$_4$^{t}Bu}” is certainly the more active species for oxidative addition of Ph–I.[28] With monodentate PPh$_3$, the oxidative addition operates on the anionic three-coordinate halide-ligated [Pd^0(PPh$_3$)$_2$Cl]$^-$,[24i] generated by reduction of the palladium(II) precursor [Pd(PPh$_3$)$_2$Cl$_2$]. In the present case, as outlined in Scheme 3, in the absence of deliberately added halide

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[26] Macé, Y.; Kapdi, A. R.; Fairlamb, I. J. S.; Jutand, A. *Organometallics* **2006**, *25*, 1795–1800.

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[28] Indeed, for diphosphines of moderate basicity the reaction has been established to proceed via insertion of the bis-ligated Pd^0(L-L) (L-L = diphosphine) into the C$_{arom}$–X bond; see ref 27.

salt, the halide ions were not found to play a role since spectroscopic evidence was more in favor of a triligation of palladium with phosphorus atoms, via either intra- (**A**) or intermolecular (**B**) processes. The effect of the equilibrium with **A** (or **B**) is to diminish the concentration of highly reactive "$Pd^0\{Fc(P)_4{}^tBu\}$" and might be at the origin of the slight decrease of oxidative addition rate compared to the PPh_3 series. Therefore reorganization of **A** or **B** certainly participates in the higher value of $t_{1/2}$ in our system compared to processes involving n PPh_3 monophosphines ($n = 2$–4). This clearly constitutes the first quantitative evidence of the stabilization of zerovalent palladium species due to the phosphine arrangement in *polyphosphine ligands*: in this particular ferrocenyltetraphosphine the palladium(0) center is in close proximity with at least three phosphorus donors.

Summary and Conclusions

Polyphosphine ligands can be at the origin of high catalytic performances in Heck and Suzuki cross-coupling reactions with TONs up to 1 000 000, while under similar low catalyst loading conditions classical mono- and diphosphines are ineffective. Electrochemical studies combined with NMR spectroscopy on the mononuclear palladium(II) halide complexes of the polydentate tetraphosphine 1,1′,2,2′-tetrakis(diphenylphosphino)-4,4′-di-*tert*-butylferrocene, $[PdX_2\{Fc(P)_4{}^tBu\}]$ (**1a**,**b**), provided several valuable insights into palladium(0/II)/ferrocenyltetraphosphine interactions and activity toward the oxidative addition of aryl halides. Hypotheses for further investigations are also envisioned:

(i) The 1,2-P bonded palladium complexes $[PdX_2\{Fc(P)_4{}^tBu\}]$ (**1a**−**c**, X = Cl, Br, I) have in the solid state and in solution analogous structures, in which is evidenced the proximity of one dangling phosphorus (P_M) with the coordination area Pd/(P_A, P_B).

(ii) The electroreduction of **1a** and **1b** quantitatively leads to the formation of destabilized zerovalent palladium species of short lifetime ("$Pd^0\{Fc(P)_4{}^tBu\}$", and **A** or **B**). The electroreduction conducted in the presence of an excess of chlorides stabilizes these zerovalent palladium species under an anionic form (**A′**/**A″** in possible equilibrium,[29] or **B′**). For these species two different kinds of palladium coordination sphere incorporating either two or three phosphorus donor atoms were evidenced. The involvement of three phosphorus donors in the coordination process is expected to be either intramolecular (species of **A** type) or intermolecular (species of **B** type).

(iii) In any case, the result is that a half-life time of 130 ms was observed for the zerovalent species in the presence of the oxidative reagent phenyl iodide. The half-life time obtained for Ph−I oxidative addition "$Pd^0\{Fc(P)_4{}^tBu\}$" species indicates a reactivity ca. 200 times greater than the chemically stable $[Pd^0(PPh_3)_4]$ and 1.5 times weaker than the zerovalent destabilized "$Pd^0(PPh_3)_2$" and its anionic halide derivatives. Although a quantitative description of the kinetics must await further investigation, this was presumably attributed to the effect of stabilization provided by the reversible formation of **A** and/or **B**.

(iv) The formation of a mixture of palladium(II) compounds **2** and **3** (or **3′**) is proposed from electroreduction in the presence of Ph−I. These species can be independently produced upon tuning of the electroreduction conditions.

Several connections were obtained in the present work with the pioneering electrochemical studies by Jutand and Amatore. The presence of excess halide, for instance, is of primary importance for the stability of the Pd^0 species of anionic form. However, one very important conclusion of this work is the involvement of the third phosphorus atom in the Pd^0 coordination sphere; the benefit is to preserve the Pd^0 complex from metal aggregation and possibly catalytic deactivation. Consistently, the oxidative addition rate we found revealed a stabilized system in comparison to zerovalent "$Pd^0(PPh_3)_2$"; nevertheless, that rate evidenced also a system much more reactive than $[Pd^0(PPh_3)_4]$.

Experimental Section

General Comments. ^{31}P and ^1H NMR spectra were recorded at the "Centre de Spectroscopie Moléculaire" of the "Université de Bourgogne" on a 300 MHz Bruker Avance and a 600 MHz Bruker Avance II spectrometer, operating respectively at 300.13 and 600.13 MHz (in $CDCl_3$, CD_2Cl_2, or acetone-d_6). All manipulations were performed using Schlenk techniques in an atmosphere of dry oxygen-free argon gas. The supporting electrolyte (tetrabutylammonium tetrafluoroborate) was degassed under vacuum before use and then solubilized at a concentration of 0.2 M. For cyclic voltammetry experiments, the concentration of the complexes was set at 10^{-3} M. Voltammetry was carried out in a standard three-electrode cell with a Tacussel UAP4 unit cell. The reference electrode was a saturated calomel electrode (SCE) separated from the solution by a sintered glass disk. The auxiliary electrode was a platinum wire. For all classical voltammetric measurements, the working electrode was a vitreous carbon electrode ($\Phi = 3$ mm). Under these conditions in THF, the formal potential for the ferrocene$^{+/0}$ couple is found to be +0.56 V vs SCE. High scan rate measurements were performed on a platinum disk electrode ($\Phi = 1$ mm) using a Autolab 50 potentiostat. The controlled potential electrolysis experiments were performed with a Amel 552 potentiostat coupled with a Tacussel IG5-N integrator. High-scale electrolysis was performed in a cell with three compartments separated with medium-porosity sintered glasses. A carbon gauze was used as the working electrode, a platinum plate, as the counter-electrode, and a saturated calomel electrode, as the reference electrode.

Chemicals. All solvents were purchased from Aldrich and purified according to standard procedures. Tetrabutylammonium tetrafluoroborate was purchased from Fluka and used without further treatment. The tetraphosphine ligand $Fc(P)_4{}^tBu$ and the $[Pd(cod)Cl_2]$ complex were prepared according to literature procedures.[6a,30,31]

Synthesis of $[Pd(cod)Br_2]$. $[Pd(cod)Cl_2]$ (0.35 mmol, 100 mg) was dissolved in 50 mL of acetone. After addition of excess KBr (3.36 mmol, 400 mg), the solution was stirred overnight. Filtration to remove KCl and evaporation to dryness of the resulting filtrate yielded $[Pd(cod)Br_2]$ (99 mg, 75% yield) as an orange powder, which was washed twice with water and ether. ^1H NMR ($CDCl_3$): 6.39 (s, 4 H, $-CH{=}CH-$), 2.80 (d, 4 H, $-CH_aH_b-CH_aH_b-$), 2.44 (q, 4 H, $-CH_aH_b-CH_aH_b-$).

Synthesis of $[PdCl_2\{Fc(P_4)^tBu\}]$, 1a. To $[Pd(cod)Cl_2]$ (0.35 mmol, 100 mg) in a CH_2Cl_2 solution (30 mL) was added $Fc(P)_4{}^tBu$ (0.35 mmol, 362.5 mg). The solution was stirred for 4 h and evaporated to dryness. The red-orange residue was washed with vigorous stirring overnight in 20 mL of hexane. The filtration of the mixture afforded pure complex **1a** as a red powder (318.5 mg, 75% yield). Anal. Calcd: C 65.4, H 5.2. Found: C 65.2, H 4.9. ^1H NMR ($CDCl_3$): δ 6.40–8.90 (m, 40 H, Ph), 4.79, 4.55, 4.31, 4.28 (s, 1 H each, Cp), 0.80, 0.71 (d, $J_{HP} = 1$ Hz, 9 H each, ^tBu). $^{31}P\{^1H\}$

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[29] The exchange energy barrier from **A′** to **A″** is expected to be rather low.

[30] (a) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purifications of Laboratory Chemicals*; Pergamon Press: Oxford, 1966. (b) Gordon, A. J.; Ford, R. A. *The Chemist's Companion, a Handbook of Practical Data, Techniques and References*; Wiley: New York, 1972; p 436.

[31] Schultz, R. G. *J. Organomet. Chem.* **1966**, *6*, 435–436.

NMR ($CDCl_3$): δ 41.7 (dd, $J = 14.3$, 24.0 Hz), 39.2 (dd, $J = 14.3$, 6.4 Hz), −22.5{pseudoheptuplet (ddd), $J = 24.0$, 15.7, 6.4 Hz}, −26.3 (d, $J = 15.7$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 30.8 and 31.6 (s, 1C each, ^{t}BuCCH$_3$), 31.8 and 31.9 (s, 3C each, ^{t}BuCH$_3$), 66.7 and 70.4 (d, 1C each, CpCH), 66.7 and 70.4 (d, 1C each, CpCH,), 71.4 (d, 1C, CpCH), 75.6 (m, 1C, CpCH), 80.0 (m, 2C, CpCP), 81.4 (dd, 1C, CpCP), 91.5 (dd, 1C, CpCP), 108.5, 119.5, 127–137 (C_6H_5).

Synthesis of [PdBr$_2${Fc(P$_4$)^{t}Bu}], 1b. This compound was obtained in a similar way to **1a**, in a 60% yield (0.03 mmol, 40 mg) after purification by employing [Pd(cod)Br$_2$] (0.05 mmol, 19 mg) instead of [Pd(cod)Cl$_2$], in 5 mL of CH_2Cl_2. Single crystals suitable for X-ray analysis were obtained from slow evaporation of a concentrated chloroform solution (see Supporting Information). ^1H NMR ($CDCl_3$): δ 6.40–8.60 (m, 40 H, Ph), 4.67, 4.54, 4.21, 4.18 (s, 1 H each, Cp), 0.71, 0.62 (s, 9 H each, ^{t}Bu). $^{31}P\{^1H\}$ NMR ($CDCl_2$): δ 39.9 (ddd, $J = 20.6$, 25.6, 1.9 Hz) 37.35 (dd, $J = 20.6$, 5.8 Hz), −25.1 (ddd, $J = 25.6$, 5.8, 11.5 Hz), (dd) −27.3 (dd, $J =$ 1.9, 11.5 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 30.4 and 31.4 (s, 1C each, ^{t}BuCCH$_3$), 31.8 and 31.5 (s, 6C, ^{t}BuCH$_3$), 66.2, 69.8, 69.9, 71.0, 75.4 (1C each, CpCH), some resonances missing in the area 80.0–90.0 ppm, 127–137 (C_6H_5).

Synthesis of [PdI$_2${Fc(P$_4$)^{t}Bu}], 1c. The synthesis of the precursor [Pd(cod)I$_2$] from [Pd(cod)Cl$_2$] and KI or NaI was unsuccessful. Therefore, this complex was quantitatively obtained at NMR scale from the reaction of 2.6 equiv of NaI with **1a** in acetone-d_6. Single crystals were grown in the NMR tube by slow evaporation of acetone, and X-ray experiments were carried out that confirm a structure analogous to **1a**[6a] and **1b**.[9] Excessively disordered solvent unfortunately precludes a proper report of the X-ray structure: while resolution for the main molecule was of good quality (ORTEP drawing is given), disordered solvent could not be solved (work is ongoing to resolve these problems with acetone solvent molecules). ^1H NMR ($CDCl_3$): δ 6.55–8.85 (m, 40 H, Ph), 4.90, 4.62, 4.62, 4.43 (s, 1 H each, $J_{HH} = 1.5$ Hz, HCp), 0.88, 0.80 (s, 9 H each, ^{t}Bu). $^{31}P\{^1H\}$ NMR ($CDCl_3$), due to signal broadness the accuracy of J_{PP} is poor: δ 36.08 (dd, $J = 15$ and 29 Hz), 34.2 (dd, $J = 15$ and 4 Hz), −27.0 (m), −28.4 (dd, $J = 24$ and 4 Hz).

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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