Inorganic Chemistry

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Kinetic and Electrochemical Studies of the Oxidative Addition of Demanding Organic Halides to Pd(0): the Efficiency of Polyphosphane Ligands in Low Palladium Loading Cross-Couplings Decrypted

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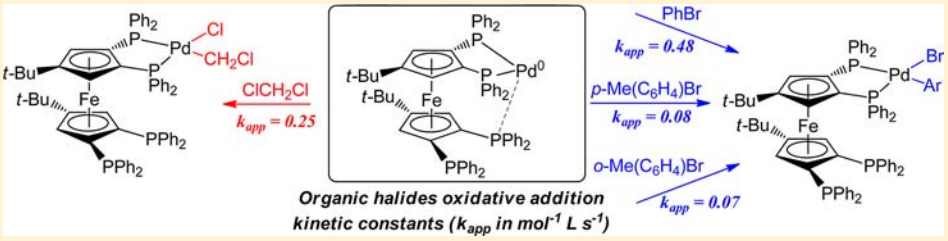
Supporting Information



ABSTRACT: Oxidative addition (OA) of organic halides to palladium(0) species is a fundamental reaction step which initiates the C−C bond formation catalytic processes typical of Pd(0)/Pd(II) chemistry. The use of structurally congested *polyphosphane* ligands in palladium-catalyzed C−C bond formation has generated very high turnover numbers (TONs) in topical reactions such as Heck, Suzuki, Sonogashira couplings, and direct sp^2C−H functionalization. Herein, the OA of aryl bromides to Pd(0) complexes stabilized by ferrocenylpolyphosphane ligands **L1** (tetraphosphane), **L2** (triphosphane), and **L3** (diphosphane) is considered. The investigation of kinetic constants for the addition of Ph−Br to Pd(0) intermediates (generated by electrochemical reduction of Pd(II) complexes coordinated by **L1**−**L3**) is reported. Thus, in the OA of halides to the Pd(0) complex coordinated by **L1** the series of rate constants k_{app} is found (mol^{-1} L s^{-1}): k_{app}(Ph−Br) = 0.48 > k_{app}($ClCH_2$−Cl) = 0.25 ≫ k_{app}(*p*-MeC_6H_4−Br) = 0.08 ≈ k_{app}(*o*-MeC_6H_4−Br) = 0.07 ≫ k_{app}(Ph−Cl). Kinetic measurements clarify the influence that the presence of four, three, or two phosphorus atoms in the coordination sphere of Pd has on OA. The presence of supplementary phosphorus atoms in **L1** and **L2** unambiguously stabilizes Pd(0) species and thus slows down the OA of Ph−Br to Pd(0) of about 2 orders of magnitude compared to the diphosphane **L3**. The electrosynthesis of the complexes resulting from the OA of organic halides to [Pd(0)/**L**] is easily performed and show the concurrent OA to Pd(0) of the sp^3C−Cl bond of dichloromethane solvent. The resulting unstable Pd/alkyl complex is characterized by NMR and single crystal X-ray structure. We additionally observed the perfect stereoselectivity of the OA reactions which is induced by the tetraphosphane ligand **L1**. Altogether, a clearer picture of the general effects of congested polydentate ligands on the OA of organic halides to Pd(0) is given.

INTRODUCTION

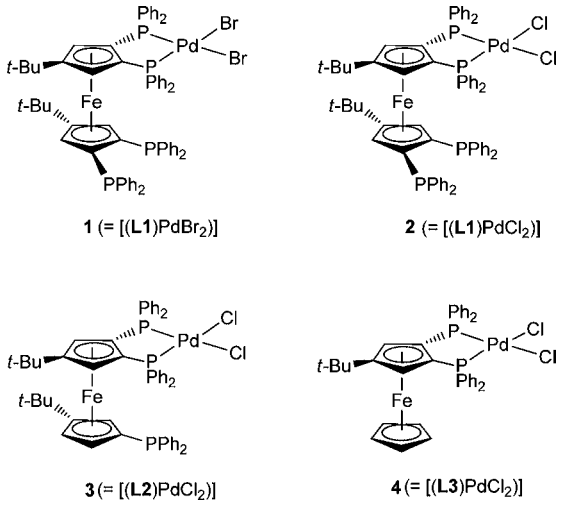
Oxidative addition (OA) of organic halides and pseudohalides is an ubiquitous elementary step of C−C and C−X (X = N, O, S, etc.) bond forming reactions catalyzed by palladium.[1,2] The fine understanding of the parameters that influence this chemical process is essential for progress in organic synthesis by employing palladium-based catalytic systems. In terms of catalytic efficiency, which can be quantified by the turnover numbers (TONs = ratio [substrate/catalyst] × yield in desired product), much progress has been made in the past decade concerning palladium-catalyzed C−C bond formation by cross-coupling reactions. High TONs are achieved by employing various polydentate phosphane ligands, and remarkable limits have been passed with TONs greater than 10,000.[3−7] A feature common to various branched polyphosphanes reported from several research groups is the congested environment provided to metal complexes by the implantation of three or four phosphino-groups lying in very close spatial proximity. These particular arrangements of phosphane groups have been achieved by their specific implantation onto various platforms such as, nonexclusively, cyclopentane, cyclopropane, cyclo-

Received: June 25, 2013
Published: October 9, 2013

dextrins, or ferrocene.[3−10] A remarkable illustration of the catalytic efficiency of congested polyphosphanes has been reported by Sollogoub, Madec, and co-workers who have reported an impressive TON world record of 3.4×10^{11} in the Suzuki cross-coupling reaction of phenylboronic acid with 4-bromoacetophenone from a cyclodextrin tetraphosphane.[7] Regarding other topical reactions catalyzed by transition metal, Beller and co-workers have also recently described the interest of robust linear polyphosphanes in the production of H_2 from formic acid.[11] Interestingly, sp^2C-H direct functionalization has also been very successful using polyphosphanes in the palladium-catalyzed coupling of aryl chlorides and hindered bromides.[12] Nevertheless, the influence of congested *poly*phosphanes (as opposed to *mono*phosphanes) in the elementary steps of cross-coupling is far from being well understood. Mechanistic studies concerning tri- and tetraphosphanes have been only recently addressed.[13,14] These studies have been focused on the OA to palladium(0) of phenyl iodide as a first approach for the starting chemical reaction of C−C cross-coupling catalytic cycles in Suzuki, Stille, Negishi, Sonogashira reactions, and so forth. While these studies have been meaningful, PhI as substrate is arguably less pertinent than the more demanding organic bromides and chlorides. These latter are the substrates generally employed for the high performance catalytic reactions mentioned above; in these cases the OA step is often assumed to be rate determining.

Kinetic investigations on the mechanism of catalytic reactions may allow rationalizing the relationship between the catalyst structure, the interaction between the components of the system, and the global reactivity (selectivity/reaction rates).[15] The usual approaches address either the catalytic reaction as a whole or the successive individualized elementary steps. In addition to methods such as multinuclear NMR,[16] calorimetric measurements,[17] and mass spectrometry,[18] analytical electrochemistry is well-suited to elucidate mechanisms relating to palladium-catalyzed C−C bond formation.[19−23] Electroanalytical studies allow generating the Pd(0)/Pd(II) catalytically active species and collecting qualitative and quantitative information on the short lifetime intermediates through analysis of their electrochemical traces. In the present work, the OA to palladium(0) of aryl bromides (i.e., phenyl bromide and electron-enriched *o*- and *p*-methylated analogues) is investigated in relation with the structure and coordination of various, structurally related, ferrocenyl polyphosphane ligands: **L1** (a tetraphosphane), **L2** (a triphosphane), and **L3** (a diphosphane), see Scheme 1.[24] Kinetic measurements clarify the influence that the presence of four, three, or two donor phosphorus atoms in the coordination sphere of palladium(0) has on the process of OA of organic halides (aryl bromides, alkyl chlorides) to [Pd(0)/polyphosphane] complexes. In the course of the electrosynthesis of the complexes resulting from the OA of aryl halides, we observed the concurrent easy OA to Pd(0) of the sp^3C-Cl bond of dichloromethane solvent at room temperature (quantitative). The resulting fairly unstable Pd(II) complex was characterized by ^{31}P NMR and single crystal X-ray diffraction. We evidenced a perfect stereoselectivity in the OA to [Pd(0)/**L1**] of the substrates studied whatever their steric and electronic features (Ph−I, Ph−Br, $ClCH_2-Cl$); most probably, this is induced by the congested conformation of the tetraphosphane ligand **L1**. Finally, the stabilizing effect provided by polyphosphanes (both tri- and tetraphosphane) to Pd(0) species is evidenced and even quantified. The properties reported herein are conceivably applicable to the case of many other polyphosphanes of congested structure, and justify, thus, the high TONs reported in C−C bond forming reactions using congested polyphosphanes.

Scheme 1. Palladium(II) Dihalide Complexes Stabilized by Polydentate Ferrocenylphosphane Ligands Structurally Related L1 (tetraphosphane), L2 (triphosphane), and L3 (diphosphane)



RESULTS AND DISCUSSION

Cyclic Voltammetry of the Pd(II) Complex [(L1)PdBr$_2$] (1), Reduction and Electroanalysis in the Presence of Phenyl Bromide. Initial studies focused on the palladium(II) dibromide complex **1** coordinated by the tetradentate ligand, **L1** (Scheme 1). The electroreductive behavior of **1** was examined in tetrahydrofuran (THF) with NBu_4PF_6 as supporting electrolyte. The corresponding cyclic voltammogram (CV) on a platinum electrode is presented in Figure 1a. Along the initial negative potential scan a large cathodic peak is found ($E_{p,R}$ = −1.26 V vs SCE) corresponding to the reduction of Pd(II) into Pd(0).[20,25−28] The backward scan displays an anodic peak O_1* ($E_{p,O1*}$ = −0.02 V) corresponding to the Pd(0) → Pd(II) reverse electrode reaction. The predominance of peak O_1* indicates the formation of a major species generated by reduction. Additionally, the irregular shape of this peak suggests the existence in minor amount of other Pd(0) species participating in the oxidation current in the potential range between 0.0 and 0.5 V. The effect on the cyclic voltammogram of the addition of PhBr on complex **1** has been examined in the presence of several hundred equivalents of PhBr, consistently with catalytic reactions conditions (Figure 1a). The oxidation peak O_1* decreases and finally vanishes with increasing amounts of PhBr from 100 to 800 equiv. The disappearance of peak O_1* renders clearly apparent the peak O_2* ($E_{p,O2*}$ = 0.25 V). Thus, the peak O_2* is present in the original cyclic voltammogram of **1** and is the trace we mentioned before, which affects the shape of O_1*. The oxidation peak O_2* is insensitive to the presence of PhBr (in any amount), and therefore corresponds to Pd(0) species that does not undergo PhBr OA at the time scale of voltammetry.

Figure 1b results from processing the peak current corresponding to O_1* at the amounts of added PhBr: $\ln(I_{before}/I_{after})$ is plotted against [PhBr]Δt, where Δt is the delay between the peaks R and O_1*, and I_{before} and I_{after} the O_1*

dx.doi.org/10.1021/ic401613w | Inorg. Chem. 2013, 52, 11923−11933

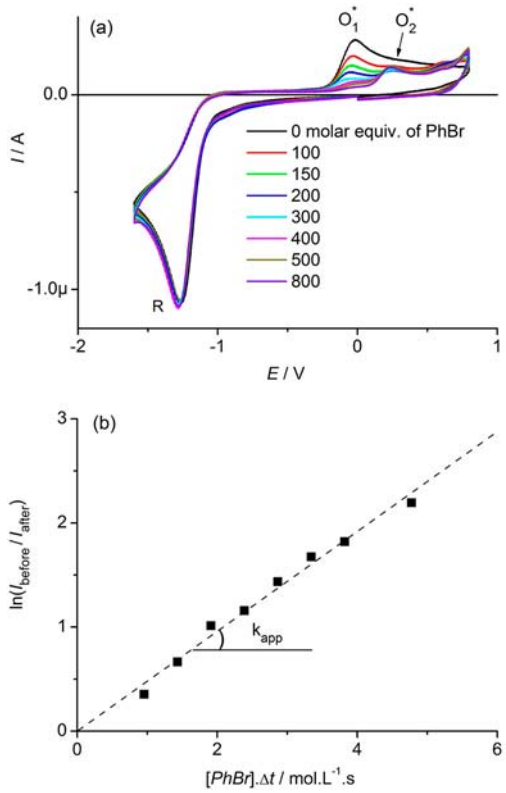
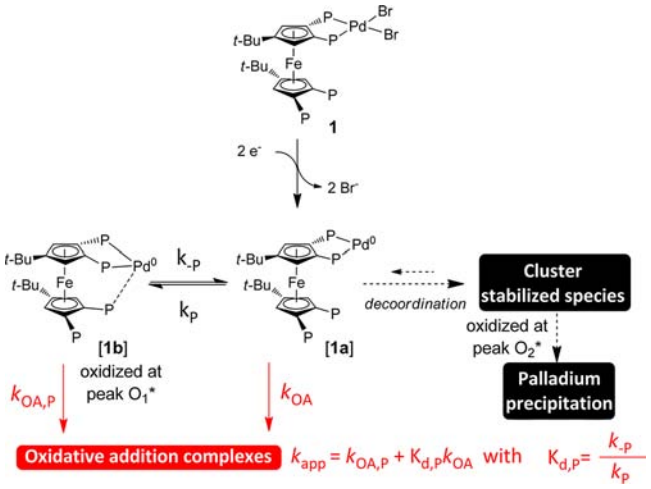


Figure 1. (a) Evolution of the reductive part of the CV of complex **1** with increasing addition of Ph−Br (scan rate = 100 mV s^{-1}, starting potential 0.0 V, working electrode: platinum disk). (b) Logarithm processing of the CV data (I_{before} and I_{after} = peak currents of O_1* before and after addition of Ph−Br, respectively; Δt = time evolved between peaks R and O_1*).

peak currents before and after addition of PhBr, respectively. The resulting relationship is linear with a regression coefficient r^2 = 0.993. This relationship indicates two reaction partners each associated to a kinetic order one. The apparent rate constant k_{app} = 0.48 mol^{-1} L s^{-1} is extracted from the slope of the line. These results can be rationalized according to the mechanism depicted in Scheme 2.

In the initial reduction step of generating Pd(0), the two-electron transfer to complex **1** is accompanied by the elimination of the two bromides coordinated to palladium.[13,29] In the absence of PhBr, the major complex formed is [**1b**],[14] in which the Pd center lies in a 16e$^-$ outer electronic shell.[30−32] Tricoordinated complex [**1b**] results from the chelating coordination of the phosphane groups from the upper cyclopentadienyl ring (Cp) and the additional weaker interaction of the phosphane group from the lower Cp. This coordination mode has been identified after reduction of the palladium dichloride complex **2** (Scheme 1).[14] This palladium complex is thus oxidized at peak O_1* ($E_{p,O1*}$ = −0.02 V) as supported by the oxidation potential found for the electronically similar tris(triphenylphosphino) palladium(0) complex [$Pd^0(PPh_3)_3$].[33] The weak interaction existing in [**1b**] between the Pd(0) center and the phosphane group from the lower Cp ring is consistent with NMR and kinetic observations reported early on.[14] In addition, the fairly short internuclear distance observed in the precursor Pd(II) complex **1** (Pd···P3 = 3.763 Å,[34] sum of van der Waals (Pd,P) radii = 3.43 Å) is a favorable structural feature, as it was previously experimentally observed in related complexes that such similar distances (Pd···P) can be

Scheme 2. Competing Pathways Leading to OA of PhBr to 1, or Palladium "Black" Precipitation[a]



[a]Ph groups on phosphorus are omitted for clarity.

shorten down to 2.618 Å.[35] Additionally, the shuttling of Pd(II) center between three phosphorus centers in such arrangement and the stabilization of the related Pd(0) intermediates by tridentate coordination have been also documented by density functional theory (DFT) calculations.[36]

Concerning the OA process, two pathways are envisioned from the isomeric palladium complexes [**1a**] or [**1b**]; however, their relative contribution to k_{app} cannot be distinguished from these kinetic experiments. Moderately bulky and bidentate chelating ligands are known to promote OA via reactive 14e$^-$ [PdL_2] intermediates.[37−39] This pathway may be also preferred from [Pd(0)/**L1**] and thus [**1b**] would preliminarily decoordinate one phosphino group to afford complex [**1a**], from which the OA may proceed more easily. Following this hypothesis, the expression of k_{app} is simplified into $k_{app} = K_{d,P}$ k_{OA}. An increased stability of [**1b**] leads to weaker $K_{d,P}$ and thus lower k_{app} and slower OA rate to Pd(0).

The determination of the exact structure of the species related to the peak O_2* is more delicate. In the time scale of cyclic voltammetry this species is unreactive toward PhBr addition, whatever the concentration in organic bromide. Electrolysis of **1** (in THF without PhBr) leads to a solution showing peak O_2* in cyclic voltammetry. The ^{31}P NMR analysis of the corresponding electrolyzed solutions is silent, consistent with the presence of unligated polynuclear Pd(0) species. Consequently, because of the absence of detectable coordination of phosphorus, and because of a higher oxidation potential in comparison with coordination complex [**1b**], this electroanalytical trace might be associated to polynuclear palladium(0) coming from the evolution of a minor part of complex [**1a**]. The formation of soluble palladium clusters has been discussed under homogeneous conditions when a portion of the metal is not coordinated by an auxiliary ligand, typically phosphanes.[15c,40] Such small clusters can possibly serve as source of reactive mononuclear palladium species which, then, could reenter into catalytic cycles. These clusters would make a connection between the mononuclear complexes *able to undergo demanding* OA (due to ligand influence) and the precipitation of colloidal palladium (Scheme 2). A recognized mode of catalytic deactivation operates through "palladium-black" formation. This process is mediated by phosphane

dx.doi.org/10.1021/ic401613w | Inorg. Chem. 2013, 52, 11923−11933

decoordination and palladium nuclei aggregation,[41,42] and competes with the OA reaction.[43] The profile of OA of PhBr to Pd(0) from dibromide complex **1**, for which a rate of 0.48 mol^{-1} L s^{-1} has been established, was of interest to compare with the corresponding profiles for complexes **2**−**4** (Scheme 1).

Influence of the Ligand Structure and Its Phosphorus Nuclearity on OA. Complexes **2**−**4** were studied according to the same electroanalytical methods used for **1**. Investigations focused on this series are pertinent to clarify the influence on OA profile of essential structural parameters of the Pd(II) precursor complexes. We investigated the influence of ancillary halide ligands (Br^- or Cl^-) from comparison of complexes **1** and **2**, and the effects induced by the number of phosphane donors at the proximity of the palladium center (with the series formed by **2**, **3**, and **4**). For the OA rate determination, the cyclic voltammetry was recorded as a function of added aliquots of PhBr. Figure 2 shows the initial cyclic voltammograms of

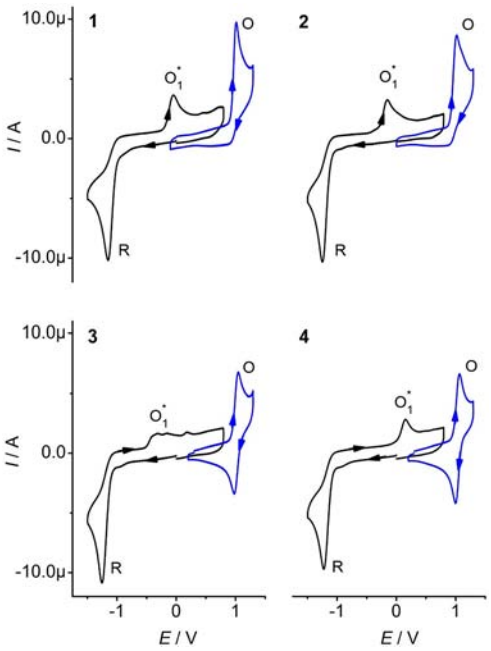


Figure 2. Cyclic voltammograms of complexes **1**−**4** in the reductive and oxidative initial potential scan directions (referred to SCE and vitreous carbon disk working electrode). Starting potentials in V for the reductive and oxidative scans, respectively: **1** (0.0; 0.0), **2** (0.0; 0.1), **3** (0.0; 0.3), **4** (0.0; 0.3).

complexes **1**−**4** on vitreous carbon electrode with both the reductive and oxidative forward potential scan, before any introduction of PhBr.

In Table 1 are collected the corresponding peak potentials. Complexes **2**−**4** are reduced similarly to **1**, along a two-electron process marked by peak R. The peak potential varies between −1.23 and −1.25 V (Table 1). In the series the most influential factor is the nature of the ancillary halide ligand. From complexes **1** and **2** the substitution of Br^- for Cl^- results in a negative shift of the reduction peak of 100 mV. This significant effect was somehow expectable as the halides pertain to the first coordination sphere of palladium.[44] For the backward scan following the reduction peak R, some significant differences in the oxidation peak pattern are observed between the complexes. The CV of complex **2** does not really differ from that of **1** in its profile, with a major large peak O_1*. However,

Table 1. Peak Potentials in the Cyclic Voltammograms of Complexes 1−4[a]

complex	forward cathodic peak $E_{p,R}$ (V)	backward anodic peak $E_{p,O1*}$ (V)	forward anodic peak[b] $E_{p,O}$ (V)
1	−1.15	−0.05	1.01^{irr}
2	−1.25	−0.15	1.02^{irr}
3	−1.25	−0.39	1.04^{r}
4	−1.23	0.15	1.07^{r}

[a]Potentials are indicated in Volts (V) and referred to the saturated calomel electrode (SCE); working electrode: vitreous carbon disk electrode; potential scan rate: 100 mV s^{-1}. [b]r: reversible; irr: irreversible.

the potential is shifted by −100 mV compared to the one observed for **1**. In contrast, for complex **3** (bearing triphosphane ligand **L2**), the oxidation pattern in the return sweep incorporates several peaks of weak intensity, poorly defined and overlapping, the most cathodic being positioned at −0.39 V. These peaks indicate that in comparison to **1** and **2** other Pd(0) species are generated by reduction of **3**. This is in agreement with some of our previous results.[45] We have shown that a ferrocenyl triphosphane similar to **L2** is able to accommodate several relatively stable modes of coordination. Particularly within Pd(II) and Pt(II) halide complexes an unprecedented bis-monodentate *trans*-configuration from the *trans*-coordination of two 1′-Cp-phosphino groups has been evidenced with [*trans*-P,P′-(**L**)MCl_2] (M = Pd or Pt). Such coordination mode has neither been detected with the ligands tetraphosphane **L1** and diphosphane **L3**, probably because the chelation from 1,2-Cp-phosphino groups strongly dominates the coordination behavior to group 10 metals in these cases.

Regarding complex **4**, a single oxidation peak O_1* is found with a peak potential which is much more positive in comparison to **1** and **2**, that corresponds to a shift up to 300 mV. In addition, the peak current is found to be lower, indicating a comparatively lesser concentration of phosphane-coordinated Pd(0) species formed in the case of **4**.

The complexes **1**−**4** can also be oxidized because of their electroactive ferrocene moiety and of the presence of phenylphosphane groups.[46] On vitreous carbon electrode, the corresponding peak O lies between 1.01 and 1.07 V (Table 1). In the case of complexes **3** and **4** the oxidation process is reversible. The peak current $i_{p,O}$ is nearly half to that of peak R in accordance with a one-electron transfer, and O is coupled on the backward scan with a reduction peak of equal intensity with a peak separation in the range 60−64 mV. Conversely, for the complexes **1** and **2** stabilized by the tetraphosphane ligand **L1** the oxidation process is fully irreversible with no peak on the backward scan. In comparison with $i_{p,R}$, the current peak $i_{p,O}$ is intermediate between one and two electrons transferred. Previously, the oxidative behavior of the related 1,1′-bis-(phosphino)ferrocene and its coordination complexes has been thoroughly studied.[47] The oxidative electrochemistry of the uncoordinated diphosphane has been found generally intricate, while oxidation of its chelating metal complexes was easily understandable as a fully reversible one-electron transfer process Fe(II)→Fe(III). The irreversibility in the oxidation process of the tetraphosphane complexes **1** and **2**, which illustrates a multielectron transfer accompanied by chemical reactions, obviously originates in the uncoordinated phosphino group which therefore takes part in the oxidation process.

Cyclic voltammetry measurements were achieved on complexes **2**−**4** after addition of PhBr. For each complex the OA of PhBr is confirmed by the disappearance of the Pd(0) oxidation peak (see CVs in the Supporting Information). Logarithmic processing was applied to the oxidation peak positioned at the most negative potential (O_1*); the resulting plots are displayed in Figure 3.

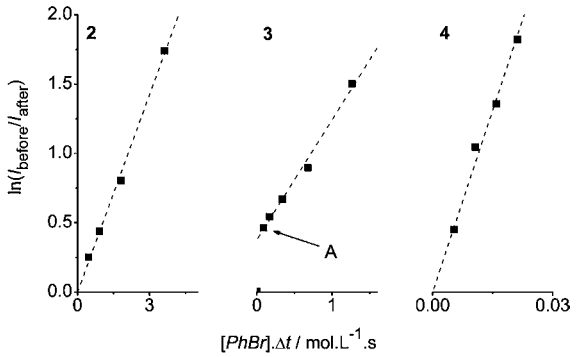


Figure 3. Logarithm processing of CV data resulting from addition of PhBr to complexes **2**−**4**.

For the complex **2** the plot is linear with a *y*-intercept near zero. The rate constant k_{app} = 0.47 mol^{-1} L s^{-1} (r^2 = 0.998) which is obtained from the graph slope (see also Table 2), is fully consistent with k_{app} obtained for the OA of PhBr to **1**; the difference between the two experimental values falls within the margin of error. This indicates that the intermediates ([**1a**] and [**1b**], Scheme 2) are identical in the oxidation processes involving **1** and **2**, and it establishes that halide incorporation in the first coordination sphere of Pd(0) does not occur from these species. Interestingly, early related works have addressed OA of aryl halides to palladium complexes stabilized by several equivalents of PPh_3 monophosphane ligands. These studies have in contrast demonstrated the coordination of bromide in the Pd(0) transient species generated by reduction of [$Pd(PPh_3)_2Br_2$].[1a,22,28,48] We assume that the structure of tetraphosphane **L1** allows in the Pd(0) complexes to override any interaction with bromide or chloride anions because of stabilizing interactions involving a third internal phosphane.

For the complex **3** which incorporates the triphosphane ligand **L2**, the logarithm plot is linear when the addition of PhBr is higher than 10 equiv. The corresponding rate constant k_{app} = 0.86 mol^{-1} L s^{-1} (r^2 = 0.996) is in the same magnitude range as for tetraphosphane complexes **1** and **2**, although slightly higher (1.8 times higher, Table 2). This suggests the formation of analogous reactive intermediates depicted as [**3a**] and [**3b**] in Scheme 3. However, at the lower PhBr concentration range (PhBr <10 equiv) the logarithmic plot significantly deviates from linearity. In the first instants of the process the decrease in the peak current, which is highly sensitive to the addition of PhBr, indicates the existence of another intermediate reacting faster than [**3b**]. The presence of other Pd(0) species reactive toward OA is in agreement with the cyclic voltammetry traces observed for **3** in the absence of PhBr, in which various coordination species were observed (see discussion above).[49] Accordingly, a consistent proposal is the formation of complex [**3c**] (Scheme 3) in which two **L2** ligands coordinate a Pd(0) center in a bis-monodentate *trans*-configuration via their 1′-Cp-phosphino group. Such 14e$^-$ Pd(0) species would participate in the OA at a rate different from [**3a,b**]. The relative decrease of peak O_1* in the nonlinear range of the logarithm plot (i.e., before point **A** in Figure 3) can be mostly attributed to the higher reactivity of [**3c**] toward OA. This decrease allows estimating the proportion of [**3c**] as limited to less than 1/3 of the species present in solution at low PhBr concentration.

For the complex **4**, which bears the diphosphane ligand **L3**, the logarithm plot is linear (Figure 3) with a resulting k_{app} = 87.4 mol^{-1} L s^{-1} (r^2 = 0.993) that is 2 orders of magnitude higher than the rates obtained from OA to complexes **2** and **3**. This OA is thus 185 fold faster than to [Pd(0)/**L1**], and is 100 fold faster than to [Pd(0)/**L2**]. The cyclic voltammetry experiments and linear plot are in accordance with a unique highly reactive intermediate. This Pd(0) complex is formulated as [**4a**] (Scheme 3), for which no supplementary intramolecular phosphane is in the vicinity for stabilizing the 14e$^-$ Pd(0) configuration. In addition, the chelating *cis*-coordination of 1,2-Cp-phosphino groups precludes any other coordination mode. Notably, the structure [**4a**] is consistent with the positive shift of O_1* peak potential of about 300 mV observed in the CV of complex **4** in comparison with the O_1* peak potential for complex **2** (Table 1, Figure 2). The complex [**4a**] bearing 14e$^-$ in the outer electronic shell (against 16e$^-$ for [**1b**] and [**3b**]) should be more difficult to oxidize. In addition, the comparatively poor intensity of peak O_1* in the CV of complex **4** can be regarded as related to the phosphino-group absence on the second Cp ring, absence which has clearly a dramatic effect on the stability of the Pd(0) intermediate and its presence in solution.

Influence on OA Rate of Electron-Donating Substituents on Aryl Bromide. In addition to these meaningful kinetic studies, which quantify for the first time the influence of congested polydentate phosphane structures on elusive Pd(0) species, we examined the effects that the presence of electron-donating substituents on aryl bromides has on OA. Indeed, while it is generally assumed that electronic and steric substituents effects are decisive for the course of the insertion of Pd(0) into the C−Br bond of organic substrates, these effects have been rarely quantified in terms of OA rates, and never on systems incorporating branched polydentate ligands. We measured the k_{app} rates of OA on [**1a,b**] of aryl bromides bearing an electron-donating methyl substituent respectively on the *C4* and *C2* position of the aryl. From OA of *p*-methylbromobenzene the logarithmic plot gives rise to a linear response (r^2 = 0.997), which is comparable to the one obtained in the case of the OA of PhBr to Pd(0) from complex **1** or **2**. The cyclic voltammetry experiments do not indicate any

Table 2. Kinetic Constants k_{app} with Margins of Error for OA of Phenyl Bromide and Methyl-Substituted Derivatives to Pd Complexes 1−4

Pd(II) precursor complex for OA	**1**	**2**	**3**	**4**	**1**	**1**
R Substituent on R(C_6H_4)Br	H	H	H	H	*p*-Me	*o*-Me
k_{app} (mol^{-1} L s^{-1})	0.48 ± 0.02	0.47 ± 0.03	0.86 ± 0.14	87.4 ± 8.1	0.080 ± 0.005	0.067 ± 0.003

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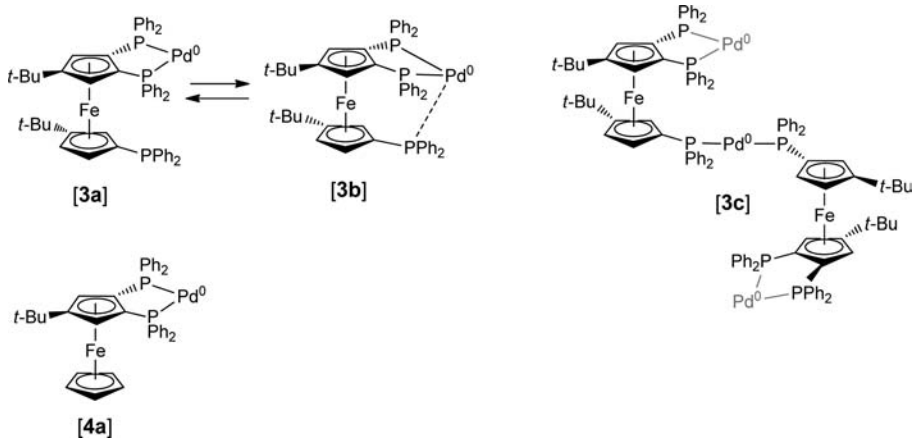
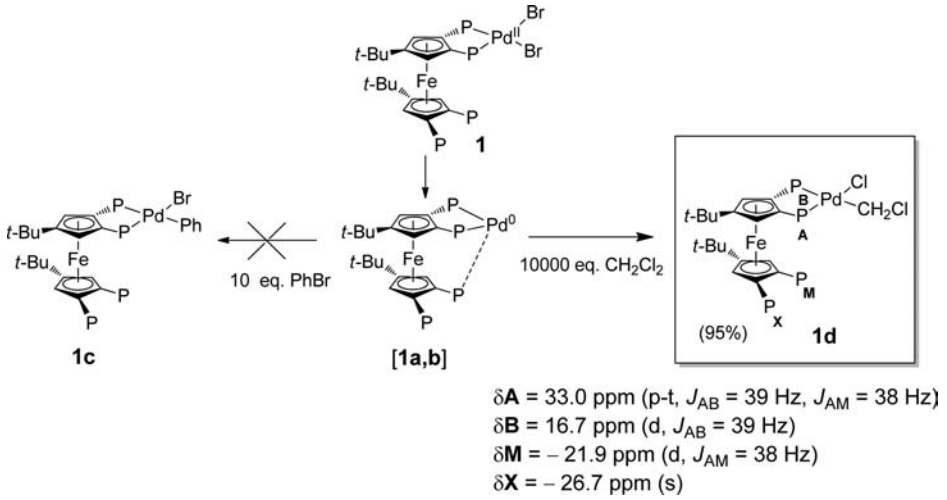
Scheme 3. Pd(0) Intermediate Complexes Postulated, as Generated by Reduction of Complexes 3 and 4



Scheme 4. Electrolysis of Complex 1 (1 equiv) in the Presence of PhBr (10 equiv) in Dichloromethane (10000 equiv), and ^{31}P NMR ($CDCl_3$) Characterization of the Resulting Complex 1d[a]



[a]Ph groups on phosphorus are omitted for clarity.

particular change in the Pd(0) intermediates which are formed. However, the extraction of the rate constant k_{app} = 0.08 mol^{-1} L s^{-1} (r^2 = 0.996) points out that the OA is slowed down about 1 order of magnitude in comparison to PhBr addition (6 times slower, Table 2). Interestingly, by employing the comparatively congested *o*-methylbromobenzene, the rate constant obtained k_{app} = 0.07 mol^{-1} L s^{-1} does not differ significantly. The decrease in rate induced by the methyl substituent is in accordance with its slightly electron-donating effect. But, by comparing the standard Hammet constant for the methyl in the *o*- and *p*- positions (respectively equal to −0.12 and −0.17)[50] this effect is less pronounced in the former case: thus, *o*-(Me)PhBr should be less electronically deactivated than *p*-(Me)PhBr, and thus should react more rapidly. This is experimentally not the case, possibly because the steric effect of the methyl group, although not very important, has a negative influence on the rate in the *o*-position and somewhat counter-balances a more favorable electronic situation. We also examined the addition of PhCl after reduction of complex **1**, but no significant change was observed in the CV even in the presence of large excess of PhCl. The OA did not occur at room temperature (RT) even within the longest periods of our CV experiments.

Synthesis and Characterization of the OA Complex of PhBr, Unexpected Effect of the Alkyl Chloride Solvent. One can achieve the isolation of [PhPd(II)Br/L] complexes from the successive electro-induced reactions of Pd(II) precursors in the presence of PhBr: [Pd(II)/L] → [Pd(0)/L] → [PhPd(II)Br/L]. Electrosynthesis can be very practical for clean generation of catalytic intermediates in high yield.[13] This has led to the successful isolation of the [PhPd(II)I/**L1**] OA complex obtained from PhI. The key issue for quantitative production of such OA product is the finding of an adequate couple electrolyte/solvent for the electrosynthesis, from which a clean separation of the resulting complex is feasible. A solution of 0.1 mol L^{-1} tetra-*n*-butyl ammonium hydrogen sulfate in dichloromethane has been found well-suited to isolate the OA complex of PhI to [Pd(0)/**L1**] by simply washing the electrolyzed solution several times with water. Most importantly, the isolation and structural characterization of this complex has allowed us to figure out the perfect stereoselectivity of the process induced by the unique structure of **L1**.[51] The optimized electrosynthesis conditions used with PhI were reproduced for the electrolysis of complex **1** in the presence of 10 equiv of PhBr. By operating a controlled potential electrolysis on a high surface carbon electrode at a

dx.doi.org/10.1021/ic401613w | Inorg. Chem. 2013, 52, 11923−11933

working potential of −1.3 V vs SCE, **1** is fully consumed after injection of a nearly stoichiometric quantity of electrons (2.1 F per mol of **1**). The subsequent treatment delivers a unique Pd(II) complex in a pure chromatographic fraction. However, instead of the expected bromo(phenyl)palladium complex **1c** (Scheme 4), the chloro(chloromethyl)palladium complex **1d** was quantitatively obtained.

The complex **1d** clearly results from the OA of one molecule of dichloromethane solvent on [**1a**,**b**]. The quantitative formation of **1d** apparently resulted from the fairly sluggish rate of PhBr addition with respect to the relative quantities of each organic halide, the molar ratio [PhBr]/[CH_2Cl_2] being about 1:1000. We then measured the rate of CH_2Cl_2 OA to [**1a**,**b**] in the absence of other halide. We found a value k_{app} = 0.25 mol^{-1} L s^{-1} (r^2 = 0.997), which is "only" twice slower than the rate of OA of PhBr, and is much faster than the rates involving PhBr methylated derivatives. Thus, in the situation where CH_2Cl_2 and aryl bromides are concurrent for OA to [Pd(0)/**L1**], and more precisely in the conditions we used, the formation of **1d** is favored as it may be estimated by the relationship:

$$\frac{[\mathbf{1d}]}{[\mathbf{1c}]} = \frac{k_{app}(CH_2Cl_2) \times [CH_2Cl_2]}{k_{app}(PhBr) \times [PhBr]} \approx 500$$

The complex **1d** was unambiguously identified by multinuclear NMR in solution and by X-ray diffraction in the solid state. The ^{31}P NMR spectrum exhibits a typical ABMX spin system in which the four phosphorus atoms of the tetraphosphane ligand are chemically nonequivalent. NMR signals are attributed (Scheme 4) on the basis of their chemical shift and spin multiplicity, the latter indicating intense intramolecular phosphorus−phosphorus "through-space" spin−spin couplings (in particular J_{AM} = 38 Hz).[52] The phosphorus NMR evidence also that **1d** is stereoselectively obtained as a unique diastereoisomer with the configuration depicted in Scheme 4. This is confirmed by the typical chemical shifts of phosphorus atoms located in *trans*-position either of a chlorine atom (33.0 ppm) or of an alkyl group (16.7 ppm). The ^{31}P NMR attribution is also consistent with the X-ray structure characterization (Figure 4). Surprisingly, **L1** thus not only ensure a perfect diastereoselectivity in the OA of phenyl iodide (as we observed and discussed previously),[13] but also in the OA of much less hindered alkyl chlorides. The reason for such selectivity in OA is at first sight unclear. Since the conformation of **L1** is blocked in solution at room temperature intricate steric effects are suspected. An interesting interpretation can be given from careful examination of the single crystals X-ray analyses for the products of R−X addition (RX = Ph−I, $ClCH_2$−Cl). These show (see **1d** example in Supporting Information) the arrangement of the R group in the less crowded coordination area left free halfway between the two phenyl groups of the proximate third phosphorus atom (namely 1′-PPh_2 group, spatially positioned just below the 1,2-PPh_2 chelating pair).

The formation of chloro(chloromethyl) bis(phosphane)Pd complexes via electrosynthesis is unprecedented. The previously reported parent complexes have been formed mostly from OA of dichloromethane on a chemically synthesized Pd(0) precursor.[53] An alternative way was the reaction of diazomethane with a palladium dichloride complex, which results in the insertion of methylene in one of the Pd−Cl bonds.[54] At room temperature these compounds are moderately stable, and they give the corresponding dichloride

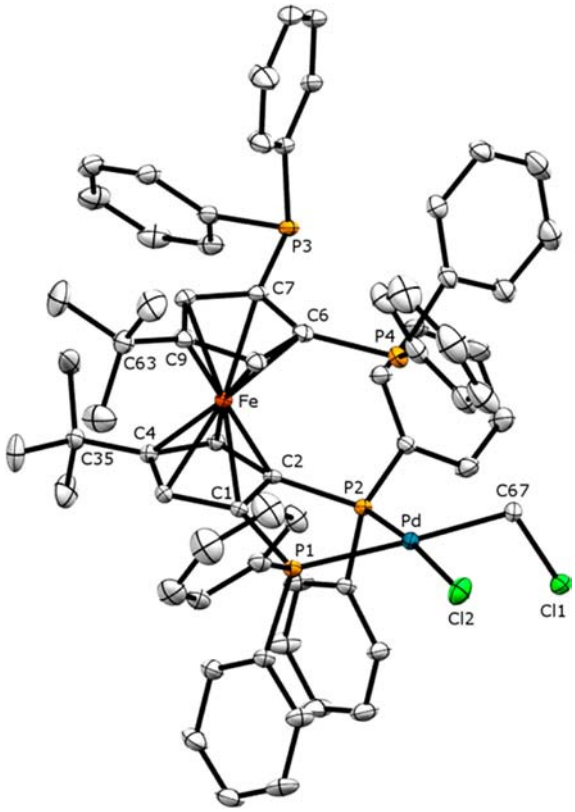


Figure 4. Molecular structure of **1d** (thermal ellipsoid plot at 30% probability, H atoms are omitted for clarity).

complex by loss of the methylene moiety. Consistently, we observed by ^{31}P NMR spectroscopy monitoring that complex **1d** in solution rapidly evolves over a few hours toward dichloride complex **2**. Single crystals of **1d** suitable for X-ray diffraction analysis were obtained by slow diffusion of *n*-heptane in an acetone solution of the complex. The molecular structure of **1d** is presented in Figure 4, and representative structural parameters are gathered in Table 3.

The structure shows a disorder around the Pd (see Supporting Information), which is due to the presence in the crystal of some palladium centers coordinated to two chloride atoms. This contamination of the crystal by a minor amount of the dichloride complex **2** (1:6 ratio of **2**:**1d**) is a direct consequence of the limited stability of **1d**, which spontaneously evolves toward **2** even during/after the crystallization process. Another X-ray structure has been reported for a chloro(chloromethyl)palladium(II) complex. This compound shows a *cis*-P,P-coordination from the chelating diphosphane [bis(dicyclohexyl)phosphino]ethane.[53d]

In the molecular structure of **1d** significantly different Pd−P1 and Pd−P2 distances (2.3129(14) *trans* to the CH_2Cl group, and 2.2499(13) *trans* to Cl, respectively) confirm the *trans* influence of ancillary chloride and alkyl ligands.[55] The Pd center lies 0.0669(17) Å slightly above the mean plane formed by P1−P2−C67−Cl2A atoms. This deviation from the planarity may be related to the fairly short nonbonding distance P4···Pd = 3.4326(17) Å observed between the Pd center and the phosphorus P4. This short distance is in accordance with a P4 lone-pair mainly pointing in the direction of the palladium center, and is consistent also with the strong "through-space" $^{TS}J_{AM}$ of 38 Hz observed by NMR in solution.[52] The transfer of electron density occurring upon

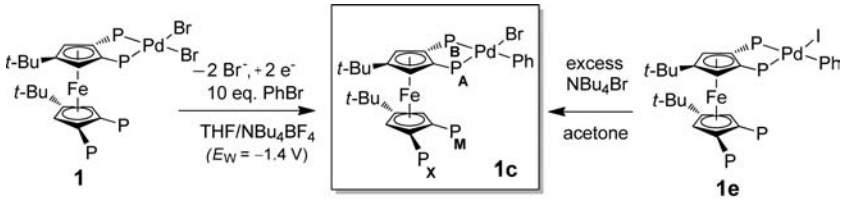
dx.doi.org/10.1021/ic401613w | *Inorg. Chem.* 2013, 52, 11923−11933

Table 3. Selected Distances (Å) and Bond Angles (deg) for Complex 1d

Pd−P1	2.3129(14)	P2−C2	1.810(4)	P1−Pd−P2	83.86(4)
Pd−P2	2.2499(13)	P3−C7	1.829(4)	P1−Pd−Cl2	95.1(1)
Pd−Cl2	2.357(4)	P4−C6	1.822(5)	Cl2−Pd−C67	88.87(18)
Pd−C67	2.065(5)	C4−C35	1.516(6)	C67−Pd−P2	92.26(16)
Pd···P4	3.4326(17)	C9−C63	1.521(6)	C67−Pd−P1	176.01(17)
C67−Cl1	1.793(7)	Fe···CT1[a]	1.676(5)	Pd−C67−Cl1	112.8(3)
P1−C1	1.796(4)	Fe···CT2[a]	1.689(5)	CT1−Fe−CT2	178.05(19)

[a]CT1 and CT2 are respectively the centroids of cyclopentadienyl groups C1−C5 and C6−C10.

Scheme 5. Synthetic Pathways to (Bromo)(phenyl)palladium Complex 1c from Pd(0) or Pd(II) (Electrolysis of 1 or Halide Exchange from 1e, Respectively), and ^{31}P NMR (Acetone-d_6) Characterization of 1c[a]



δ**A** = 35.1 ppm (ddd, J_{AB} = 35 Hz, J_{AM} = 23 Hz, J_{AX} = 2 Hz)
δ**B** = 15.0 ppm (dd, J_{AB} = 35 Hz, J_{BM} = 4 Hz)
δ**M** = − 21.4 ppm (d(p-t), J_{AM} = 23 Hz, J_{BM} = 4 Hz, J_{MX} = 4 Hz)
δ**X** = − 27.1 ppm (dd, J_{MX} = 4 Hz, J_{AX} = 2 Hz)

[a]Ph groups on phosphorus are omitted for clarity.

coordination of P1 and P2 to palladium has a discernible effect on the bond lengths of the corresponding functionalized cyclopentadienyl ring (Table 3) with a shortening of some bonds compared to the noncoordinated analogues (for instance C−C bond linking the *tert*-butyl group to the Cp rings and P−C bond attaching phosphanyl moieties to Cp rings).

In the absence of chlorinated solvent competing in the OA reaction to Pd(0), the formation of complex **1c** by reaction of PhBr to [**1a,b**] should be straightforward. Accordingly, we checked that when the electrolysis of **2** is conducted in the presence of PhBr in THF as solvent with NBu_4BF_4 as supporting electrolyte, after transfer of 2 equiv of electrons, a clean pattern of four signals is obtained in ^{31}P NMR spectroscopy monitoring. This pattern is consistent with the exclusive formation of **1c**, in this case also as a single diastereoisomer. The identity of **1c** was definitely established by its formation upon halide exchange from [(**L1**)Pd(Ph)(I)] (complex **1e** in Scheme 5).

Complex **1c** is cleanly formed by exchanging the iodide with a bromide in the presence of an excess of NBu_4Br, as attested by the identical ^{31}P NMR spectrum.[56] In the ^{31}P NMR of **1c** four signals are observed in which an outstanding multiplicity of consistent J couplings ranging between 35 and 2 Hz can be identified (see attribution in Scheme 5 and spectrum in Supporting Information). In particular δP_M at −21.4 ppm appears as a doublet of pseudotriplets because of the identical values of J_{BM} and J_{MX} = 4 Hz (the "through-space" $^{TS}J_{AM}$ = 23 Hz). The spin−spin coupling of distant nucleus P_X with P_A and P_M, although of weak intensity, is nevertheless a curiosity among the palladium complexes of **L1**.[57]

CONCLUSION

OA of organic halides to palladium(0) species is a fundamental reaction step which initiates the C−C bond formation processes typical of palladium catalysts. The general efficiency of specially designed structurally congested polyphosphane ligands in palladium C−C bond formation has been observed by several groups, with numerous reports of very high turnover numbers in topical reactions such as Heck, Suzuki, Sonogashira reactions, and others. Many of these high TONs have been obtained by using different congested tetraphosphanes and triphosphanes, in which a close proximity of phosphorus atoms is ensured. Yet, the quantification of their influence on OA had never been reported. Another issue related to this field of research could be formulated as the question of "*what may be the general differences induced in OA process by using a single congested polyphosphane able to polydentate coordination to a metal center instead of several equivalents of a mono- or a diphosphane, typically 2−4 equiv of* PPh_3 *or dppe* $(Ph_2P(CH_2)_2PPh_2)$". The present work discloses comparative kinetic data for the OA of phenyl bromide, *p*-methylbromobenzene, *o*-methylbromobenzene, and dichloromethane (relevant because it is a common solvent in metal chemistry and catalysis) to Pd(0) species coordinated by an archetypal ferrocenyl tetraphosphane **L1**. **L1** is structurally related to other pertinent polyphosphanes such as Tedicyp,[3a,b] α-Cytep,[7] and many others.[5,6,3c,4b] The series of OA apparent rates k_{app} was found as follows (mol^{-1} L s^{-1}): k_{app}(Ph−Br) = 0.48 > k_{app}(Cl−CH_2Cl) = 0.25 ≫ k_{app}(*p*-MeC_6H_4Br) = 0.08 ≈ k_{app}(*o*-MeC_6H_4Br) = 0.07 ≫ k_{app}(Ph−Cl).

We also determined kinetics for the OA of PhBr to Pd(0) intermediates; these latter were straightforwardly electrogenerated from the series of structurally related Pd(II) halide complexes incorporating tetraphosphane **L1** (complex **2**), triphosphane **L2** (complex **3**), and diphosphane **L3** (complex **4**): k_{app}(**4**) = 87.4 ≫ k_{app}(**3**) = 0.86 > k_{app}(**2**) = 0.47 (mol^{-1} L s^{-1}). Such kind of quantitative data are unprecedented for polyphosphanes and establish benchmarks for further progress in this field of ligand chemistry.

The presence of supplementary phosphorus atoms in **L1** and **L2** (in comparison to the chelating diphosphane **L3**), which are in close proximity to the coordination area, has a dramatic

dx.doi.org/10.1021/ic401613w | *Inorg. Chem.* 2013, 52, 11923−11933

effect on the stabilization of Pd(0) species. Such stabilization slows down the OA of PhBr to Pd(0) of about 2 orders of magnitude compared to the structurally related diphosphane **L3**. This steadying effect is the origin of the possibility of using polydentate ligands in low amounts (below 0.01 mol %), and may produce very high TONs in such catalytic reactions.

Cyclic voltammetry in reduction and oxidation of Pd(II) complexes **1**−**4** allowed determining the dominant coordination modes of the ligands. Electroanalysis showed also that a minor part of palladium remains soluble but uncoordinated, probably forming soluble clusters. These uncoordinated soluble Pd(0) species *do not* undergo OA of PhBr. In addition, the triphosphane **L2** displays another coordination mode (in contrast to **L1** and **L3**) forming thus a supplementary Pd^0 species, which is traceable from CV electroanalysis.

Electrosynthesis was successfully used to quantitatively yield the OA complexes bromo(phenyl)palladium(II) complex **1c** and chloro(chloromethyl)palladium(II) complex **1d**. The latter has been first fortuitously formed from dichloromethane solvent, illustrating an unexpected competition in OA between organic bromides (PhBr) and alkyl chlorides (CH_2Cl_2). The formation of **1c** and **1d** is perfectly stereoselective as demonstrated by the ^{31}P NMR of the complexes and confirmed by the X-ray diffraction structure of **1d**. In our previous works we found that the OA of PhI to [Pd^0/**L1**] complexes is also fully diastereoselective. Therefore, the stereoselectivity of OA of alkyl and aryl halides is seemingly independent of the substrate nature (and its steric hindrance), and is fully governed by the congested geometry and specific conformation of **L1**. This definitively establishes another relevant influence of the congested polyphosphanes on the course of OA reactions beyond the valuable stabilization of Pd(0) species which was demonstrated herein.

EXPERIMENTAL SECTION

General Procedures. All electrochemical measurements were carried out in a standard three electrode glass cell under an inert atmosphere of dry oxygen-free argon. A double junction saturated calomel electrode, with background electrolyte between two frits, was used as reference electrode. The formal potential of Fc/Fc^+ couple was found to be 0.53 V in 0.2 M $[NBu_4][HSO_4]$+CH_2Cl_2 and 0.52 V in 0.2 M $[NBu_4][PF_6]$+THF media vs SCE. CVs were registered with the use of a PGSTAT302N potentiostat (Autolab). Well-polished glassy carbon (diameter = 3 mm) and Pt (diameter = 1 mm) disks served as working electrodes. Pt wire was a counter electrode. Bulk electrolyses were performed with an Amel 552 potentiostat coupled with an Amel 721 electronic integrator. During these experiments, anodic and cathodic compartments were separated with a sintered glass disk. Carbon gauze and platinum plate served as working and counter electrodes, respectively. ^1H and ^{31}P NMR spectra were obtained with a 300 MHz Bruker Avance III spectrometer. The reference was the residual nondeuterated solvent. High resolution mass spectra (ESI) were recorded on a MicroTOF Q Bruker instrument. Elemental analyses (C, H, N, S) were performed with a Flash EA 1112 Thermo Electron analyzer. UV−visible absorption spectra were measured in quartz cuvettes (1 mm optical path; Hellma Benelux) with a Varian Cary 50 Scan UV−visible spectrophotometer.

Chemicals. Acetone-d_6 and $CDCl_3$ (99.8% D), acetone (>99.5%), *n*-heptane (for analysis), *p*-bromotoluene (98%+), NBu_4Br (99%+) and NBu_4Cl (>97%) were used as received. PhBr (99%), chlorobenzene (98%+), *o*-bromotoluene (98%+), CH_2Cl_2, and THF (for analysis) were distilled before use. Tetra-*n*-butylammonium hydrogen sulfate (>99%) $[NBu_4][HSO_4]$ was recrystallized twice from an acetone/*n*-heptane mixture and dried. For synthesis of $[NBu_4][PF_6]$, tetra-*n*-butylammonium hydroxide (40% w/w aq. sol.) was mixed with a stoichiometric amount of HPF_6 (60% w/w aq. sol.). The obtained salt was recrystallized three times from ethanol and kept in an oven at 80 °C for several days. Prior to use, $[NBu_4][HSO_4]$ and $[NBu_4][PF_6]$ salts were additionally dried in an electrochemical cell at 60 °C under reduced pressure for at least 5 h. Palladium complexes **1**, **1e**, **2**, and **4** were synthesized as previously described.[13,14,58] Polyphosphane **L1** and **L2** are commercially available from STREM (HiersoPHOS).

Synthesis of Dichloro[1,1′,2-tris(diphenylphosphino)-3′,4-di-*tert*-butyl ferrocene]palladium, 3. A mixture of 1,1′,2-tris-(diphenylphosphino)-3′,4-di-*tert*-butylferrocene, **L2** (308.5 mg, 0.363 mmol), and $PdCl_2$ (69.5 mg, 0.392 mmol) was refluxed under stirring in THF (15 mL) for 24 h. The brown solution was then filtrated through silica, and the solvent was evaporated under vacuum. Then, the crude product was purified by column chromatography (silica gel, h 30 cm, diameter 5.5 cm) using 3:2 heptane/Et_2O to give 0.305 g of pure **3** (yield = 82%). ^1H NMR (300 MHz, $CDCl_3$, 300 K): 0.56, 0.92 (s, 9H each, *t* Bu), 3.63, 4.29, 4.33, 4.37, 4.61 (s, 1H each, *H*-Cp), 6.75−8.01 ppm (m, 30H, *H*-Ph). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 300 K): −20.70 (s, 1′-PPh_2), 42.50 (ABq, 1,2-PPh_2, J_{AB} = 7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 139.9−126.7 (m, 36 C, C_6H_5), 118.2 (s, 1C, 4-Fc), 107.6 (s, 1C, 3′-Fc), 83.0 (dd, 1C, 1-Fc, $^1J_{CP}$ = 62 Hz, $^2J_{CP}$ = 40 Hz), 82.5 (dd, 1C, 2-Fc, $^1J_{CP}$ = 62 Hz, $^2J_{CP}$ = 40 Hz), 78.5 (d, 1C, 1′-Fc, $^1J_{CP}$ = 15 Hz), 72.9 (d, 1C, 3-Fc, $^2J_{CP}$ = 23 Hz), 70.4 (m, 1C, 5′-Fc), 69.9 (d, 1C, 4′-Fc, $^3J_{CP}$ = 4 Hz), 69.2 (d, 1C, 5-Fc, $^3J_{CP}$ = 4 Hz), 67.4 (d, 1C, 2′-Fc, $^2J_{CP}$ = 15 Hz), 30.7, 30.5 (s, 3C each, $C(CH_3)_3$), 30.6, 28.7 (s, 1C each, $C(CH_3)_3$). HRMS (ESI): *m*/*z* calcd (%) for $[C_{54}H_{53}FeP_3PdCl_2]$: 991.1445 $[M-Cl]^+$; found: 991.1413. Elemental analysis calcd (%) for $C_{54}H_{53}FeP_3PdCl_2$: C 63.09, H 5.20; found: C 63.03, H 5.27.

Synthesis of [(L1)Pd(Ph)(Br)], 1c. The complex **1c** was directly prepared in a NMR tube by mixing **1e** (3.7×10^{-6} mol, 0.005 g) and NBu_4Br (0.112 mmol, 0.036 g) in a small amount of acetone-d_6. Complex **1c** was also obtained by electrolysis of **1** (0.038 mmol, 0.050 g) with 10 equiv of PhBr (0.384 mmol, 40 μL) at fixed potential (E = −1.4 V vs SCE) in 0.2 M $[NBu_4][BF_4]$ + THF (25 mL). After evaporation of THF, the background salt is removed by washing with toluene (3 × 25 mL). The solid residue is then dissolved in acetone-d_6 for NMR analysis. ^1H NMR (300 MHz, acetone-d_6, 27 °C): 0.71 (br. s, 9H, *t*Bu); 0.84 (br. s, 9H, *t*Bu); 4.39 (br. s, 1H, HCp); 4.50 (br. s, 1H, HCp); 4.60 (br. s, 1H, HCp); 5.00 (br. s, 1H, HCp); 6.55−8.46 (m, 45H, Ph). $^{31}P\{^1H\}$ NMR (121.5 MHz, acetone-d_6, 27 °C): −27.1 (dd, J_1 = 4 Hz, J_2 = 2 Hz); −21.4 (d(p-t), J_1 = 23 Hz, J_2 = 4 Hz, J_3 = 4 Hz); 15.0 (dd, J_1 = 35 Hz, J_2 = 4 Hz); 35.1 (ddd, J_1 = 35 Hz, J_2 = 23 Hz, J_3 = 2 Hz). Elemental analysis calcd (%) for $C_{74}H_{73}FeP_4PdBr$: C 66.91, H 5.54; found: C 66.72, H 5.41.

Synthesis of [(L1)Pd(CH_2Cl)(Cl)], 1d. This complex was prepared by electrolysis of **2** (0.041 mmol, 0.050 g) at constant potential (E = −1.3 V vs SCE) in 0.2 M $[NBu_4][HSO_4]$+CH_2Cl_2 (25 mL). The reaction mixture was washed by water (3 × 25 mL) to remove the background salt, and then CH_2Cl_2 was evaporated under reduced pressure. Yield: 95% (0.048 g). ^1H NMR (300 MHz, acetone-d_6, 27 °C): 0.67 (br. s, 9H, *t*Bu); 0.76 (br. s, 9H, *t*Bu); 4.19 (br. s, 1H, HCp); 4.25 (br. s, 1H, HCp); 4.39 (br. s, 1H, HCp); 4.67 (br. s, 1H, HCp); 6.47−8.56 (m, 40H, Ph; 2H, CH_2). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 27 °C): −26.7 (s); −21.4 (d, J_1 = 38 Hz); 16.7 (d, J_2 = 39 Hz); 33.0 (p-t, J_1 = 38 Hz, J_2= 39 Hz,). HRMS (ESI): *m*/*z* calcd for $[C_{67}H_{64}FeP_4PdCl]$: 1189.20311 $[M-Cl]^+$; found: 1189.19776. Elemental analysis calcd (%) for $C_{67}H_{64}FeP_4PdCl_2{\cdot}2H_2O$: C 63.75, H 5.43; found: C 63.58, H 5.46. Single crystals of **1d** suitable for X-ray diffraction (XRD) measurements were prepared in a tube by solvent diffusion; a portion of *n*-heptane was carefully added to a concentrated solution of **1d** in acetone to form two layers. The tube closed with a silicon cap was left untouched for one week at 0 °C before collecting the needles formed.

Determination of k_{app} and Margin of Error. The apparent rate constants k_{app} (Table 2) for OA of phenyl bromide and methyl-substituted derivatives to Pd(II) complexes **1**−**4** are extracted from Figures 1b and 3 as the slopes of the corresponding regression lines (with $r^2 \geq 0.993$). For each system of *n* measurements, the margin of error for the k_{app} (Table 2) is equal to the standard error of the slope

dx.doi.org/10.1021/ic401613w | *Inorg. Chem.* 2013, 52, 11923−11933

SE_{slope} multiplied by the appropriate Student's t_{n-2} factor (for $n-2$ degrees of freedom) at 95% confidence level. Thus, the confidence interval for the k_{app} could be presented as $k_{app} \pm t_{n-2}SE_{slope}$.

Crystallographic Data. Diffraction data were collected from a suitable crystal (0.32 × 0.13 × 0.12 mm^3) on a Bruker Nonius ApexII CCD system using graphic-monochromated Mo−Kα radiation. The structure was solved using direct methods (SIR 92)[59] and refined with full-matrix least-squares methods based on F^2 (SHELX-97)[60] with the aid of the WINGX program.[61] Non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms attached to carbon atoms were included in their calculated positions and refined with a riding model. As illustrated in Supporting Information a disorder was found in the coordination sphere of the palladium atom, which is either bonded to a chloromethyl group and a chloride atom (major component of the disorder) or to two chloride atoms (minor component). The occupation factors converged to 0.84:0.16. Both dichloromethane molecules were found disordered around an inversion center and then refined with a multiplicity set to 0.5.

Crystal Data for 1d. 0.84($C_{67}H_{66}Cl_2FeP_4Pd$), 0.16-($C_{66}H_{64}Cl_2FeP_4Pd$), CH_2Cl_2; M_r = 1226.06 ; monoclinic; a = 14.3917(4), b = 20.0428(6), c = 25.2108(6) Å; β = 120.253(1)°; V = 6281.7(3) Å^3 ; D_{calc} = 1.386 g.cm^{-3}; μ = 0.829 mm^{-1}; T = 115(2) K, space group $P2_1/c$; Z = 4; 45553 reflections measured, index range: h = ± 18; k = −26/+25, l = ± 32, (sin θ)/λ = 0.65 Å^{-1}, 14200 independent reflections (R_{int} = 0.0536), final R values ($I > 2\sigma(I)$): R_1 = 0.0631, wR_2 = 0.1399, final R values (all data): R_1 = 0.0675, wR_2 = 0.1424, 759 parameters, 6 restraints, goodness of fit: 1.196; $\Delta\rho_{fin}$ (max/min)=1.41/−1.15 e Å^{-3}. CCDC-930900 contains the supplementary crystallographic data for the **1d** structure. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

■ ASSOCIATED CONTENT

Supporting Information

CVs of **1**−**4** before and after addition of organic halides; CV, UV−visible spectra, and ^{31}P NMR spectra after electrolysis of complexes **1** and **2**; evolution of ^{31}P NMR of complex **1d**, details of crystal data for **1d** (with spatial arrangement and space fill image); $^{31}P/^{1}H$ NMR spectra of **1c** and **1f** synthesized by halide exchange; CV and ^{31}P NMR spectrum of **1d** and **1c** obtained from electrosynthesis. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was funded by the Agence Nationale de la Recherche (programme *Chimie pour le Développement Durable* 2009-CP2D-03 "Camelot"). Additional support was provided by the CNRS, the Université de Bourgogne (uB-BQR 2012), and the Conseil Régional de Bourgogne (3MIM program and PARI-SMT08). Thanks are due to S. Royer for technical assistance.

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