CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200800423

When Are Tricoordinated Pd^{II} Species Accessible? Stability Trends and Mechanistic Consequences

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Dedicated to Professor Jan Reedijk on the occasion of his 65th birthday

Abstract: The ease of access to Pd^{II} tricoordinated species (whether intermediates or transition states) in organometallic and catalytic reactions has been assessed with DFT methods to analyze the relative stability of tricoordinated [PdArXL] complexes versus their tetracoordinated derivatives formed by two most common processes of filling the fourth coordination site: solvent coordination (with tetrahydrofuran), or dimerization to give $[Pd_2Ar_2(\mu\text{-}X)_2L_2]$. The effect of each ligand ($L=PH_3$, PMe_3, PPh_3, $PtBu_3$, 1-AdPtBu$_2$; $Ar=C_6F_5$, C_6H_5, C_6H_4OH, $C_6H_4OCH_3$, $C_6H_4NH_2$, $C_6H_2(NH_2)_3$; X=F, Cl, Br, I, OH, SH, NH_2, PH_2, CH_3) on these two processes has been systematically considered, and the results have been compared with the experimental information available. The trends observed, match the experimental results and suggest that: 1) the formation of bridged dimeric complexes is strongly preferred; 2) electronic effects are in general less important compared to steric effects; 3) when steric effects prevent formation of bridges and coordination of a fourth external ligand, intramolecular agostic interactions are established with C–H groups of one ligand; 4) as an exception, for $X=NR_2$ true tricoordinated complexes, not showing agostic interactions, become stable. In the later case NR_2 seems to act as π-donor with its lone pair to the empty orbital at the fourth coordination site of palladium, thus avoiding a true 14e configuration for the tricoordinated Pd^{II} complex.

Keywords: coordination modes • density functional calculations • electronic structure • homogeneous catalysis • palladium

Introduction

The coordination number of transition metal complexes, whether in the ground state, in intermediates, or in transition states, is an important characteristic with mechanistic implications. In isolated Pd^{II} (d^8) complexes, square-planar tetracoordination, with a formal 16-electron counting, is absolutely dominant. There are much fewer pentacoordinated complexes (formally 18 electron),[1] but this coordination number is not a rarity. In the case of complexes of PdArXL stoichiometry with unexceptional ligands, a common way to satisfy the fourth coordination site is the dimerization to give $[Pd_2Ar_2(\mu\text{-}X)_2L_2]$ or, in solution in coordinating solvents, the coordination of a solvent molecule to give [PdArXL(s)].[2]

A different case has appeared with the recent use of hindered ligands with large steric demand and extraordinary catalytic performance,[3–15] and an increasing number of monomeric Pd^{II} complexes with only three ligands are being reported. However, when these species have been X-ray characterized, the tricoordination has been found somewhat deceptive, as the fourth coordination site is, in general, occupied by agostic interaction with the ligand.[16–18] For instance, for the T-shaped complexes with only three coordinated ligands reported by Hartwig and co-workers, [PdArXL] (X = halide, Ar = aryl ring, L = 1-AdPtBu$_2$ or PtBu$_3$), the authors could show, by ^1H NMR analysis along with computational studies on the characterized compounds, the existence in all cases of an agostic interaction with a C–H bond of the phos-

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200800423.

phine ligand, occupying the vacant site of the Pd center, although certainly in some cases these interactions were extremely weak.[17] Similar agostic coordinations have been found for related isoelectronic complexes of Ni^{II},[19] Pt^{II},[20–22] and Rh^{I}.[23,24] Strictly speaking, counting the agostic coordination, these complexes are tetracoordinated. However, the related complexes [PdArXL] (Ar = C_6H_4-OMe-*p*; X = NAr′$_2$, Ar′ = 3,5-$(CF_3)_2C_6H_3$; L = P*t*Bu$_3$, FcP*t*Bu$_2$, (Ph$_5$Fc)P*t*Bu$_2$; Fc = ferrocenyl), also reported by Yamashita and Hartwig, do not present agostic interactions and are unambiguously true tricoordinated complexes, the only ones reported so far for Pd^{II}.[25] Interestingly, one of them crystallized with two independent molecules in the asymmetric unit, one without and one with agostic interactions, revealing that the difference in energy between the two coordination modes is very small in this case.

It is clear that a stoichiometry of three ligands per Pd atom only rarely corresponds to a true tricoordinated complex. Even in encumbered coordinations impeding the approach of a fourth external ligand, the tendency to square planar coordination is fulfilled by agostic interactions, with the three exceptions just mentioned. It is equally true that the extreme weakness and lability of the agostic interactions make the tricoordinated species very accessible, so that it is not exaggerated to consider these complexes as "operationally tricoordinated" in a kinetic sense.[26]

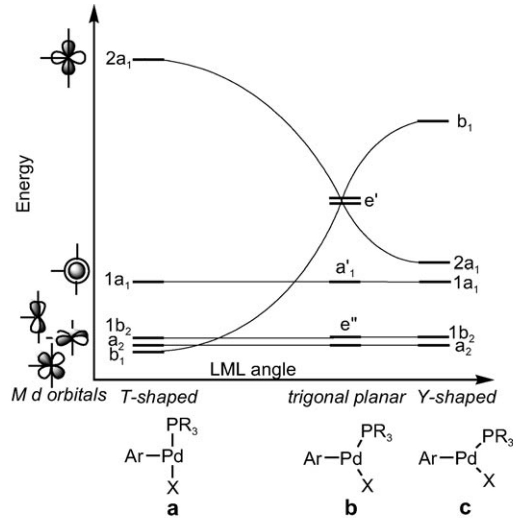
The abundance of the different coordination numbers observed in Pd^{II} isolated complexes ($4 \geqslant 5 \geqslant 3$) somehow reflects the accessibility of the alternative reaction pathways in reactions requiring a change in coordination number throughout the reaction. Typically, ligand substitution and transmetalation reactions on square-planar Pd^{II} complexes in catalytic processes should take place through *associative* or *dissociative* mechanisms involving penta- and tricoordinated intermediates, respectively. These pathways are not always easy to differentiate kinetically.[2] In cases studied in depth for conventional ligands, the mechanisms were found to be associative, the dissociative pathway having a higher activation barrier.[3,27] This is consistent with the scarcity of tricoordinated compared to pentacoordinated Pd^{II} complexes. Dissociative mechanisms have been experimentally supported in a few cases[28,29] and some involving bulky ligands,[30,31] which should render dissociative reaction mechanisms more accessible.

It looks reasonable that, in contrast with the traditional 16e–18e–16e textbook associative sequence of reactivity for conventional Pd^{II} complexes, the factors disfavoring tetracoordination (such as the use of hindered ligands, which is now fairly common) can alter the accessibility of tri- versus pentacoordinated species or transition states, introducing a change in the mechanisms and favoring 16e-14e-16e dissociative processes. This panorama deserves closer attention. With this aim we have undertaken a systematic computational study of the factors affecting the *relative stability* of Pd^{II} tricoordinated species (with or without agostic interactions), as a function of the properties of the different ligands employed.

Results and Discussion

The system under study: Probably the transmetalation step in cross-coupling processes is the most important reaction in which the involvement of tricoordination (whether in the ground or in the transition state) is a critical question. In these reactions the Pd^{II} complex comes usually from the oxidative addition of an aromatic halide to a Pd^0 complex. In addition to the aryl and the halide, the resulting complex contains often phosphines, as the most common ligands used in these reactions. As a result of substitution or transmetalation reactions on these Pd^{II} complexes, other complexes with ligands containing N, O, or S as coordinating atoms, different halides or pseudohalides, or a second hydrocarbyl ligand, can also be formed. Therefore, to get a fairly general panorama for the plausible real systems, three families of ligands were selected to study the feasibility of tricoordinated [PdArXL] complexes: phosphines (L = PR$_3$), different aromatic rings (Ar) and anionic ligands (X). As a reference, the complexes existing as T-shaped tricoordinated should be predicted by calculation.

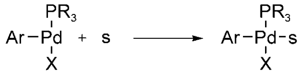
The geometry of the T-shaped complex: The first question is to establish whether the complexes will adopt a T-shaped or a Y-shaped structure.[32,33] The Walsh diagram in Scheme 1 shows the energy change of the metal valence orbitals for the conversion between T-shaped (C_{2v} symmetry) and Y-shaped (C_{2v} symmetry) structures through a trigonal-planar structure (D_{3h} symmetry), for an ideal ML$_3$ tricoordinated complex.[34] A Pd^{II}, with a low spin d^8 electronic configuration, should display a T-shaped structure (**a**), which leaves a 2a$_1$ vacant orbital pointing towards the empty coordination position. Test calculations performed on a model complex [PdPh(NH$_2$)(PH$_3$)] confirmed this prediction: Geometry optimizations starting from Y-shaped (**c**) or trigonal planar (**b**) structures always end in the T-shaped structure. The potential energy difference in gas phase between the trigonal



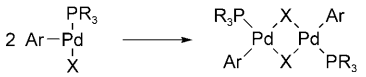
Scheme 1. Walsh diagram for an ideal ML$_3$ tricoordinated d^8 structure. In the lower part, tricoordinated structures for a [PdArX(PR$_3$)] complex: a) T-shaped; b) trigonal planar; c) Y-shaped.

planar structure (constrained geometry in the singlet state) and the T-shaped structure (fully optimized) was found to be 20.3 kcal mol^{-1}. The most stable triplet state structure (trigonal planar) is 34.6 kcal mol^{-1} less stable than the singlet state T-shaped structure. The most stable tricoordinated isomer is that with the aromatic ligand trans to the vacant site, in agreement with its higher σ-donor ability. The formation of a 4-coordinated complex is easier from a T-shaped structure.[35]

Stability criteria: The concept "stability" of a chemical compound has not a single meaning and needs to be referred to particular conditions. It is frequent to define stability with respect to: 1) chemical decomposition (IUPAC definition); 2) reactivity with common substances in environment (air or water stable compounds); or 3) reactivity with other substances. In this work we are interested in the relative stability of tricoordinated Pd^{II} complexes with respect to the formation of square-planar structures, which are more commonly found. To evaluate this stability we selected to calculate the energy change associated to the occupation of the vacant site in two different reactions likely to occur in the flask: solvent coordination, represented by coordination of tetrahydrofuran [Eq. (1), s = THF], and dimerization through double bridge formation [Eq. (2)]. Accordingly, the less negative (or more positive) the energy balance, the higher the relative stability of the tricoordinated species as compared to the tetracoordinated alternatives. The trends observed for the stability of the tricoordinated species as a function of the ligands involved are valuable information.



$$\mathrm{Ar{-}\overset{\displaystyle PR_3}{\underset{\displaystyle X}{Pd}}} + \mathrm{s} \longrightarrow \mathrm{Ar{-}\overset{\displaystyle PR_3}{\underset{\displaystyle X}{Pd}}{-}s} \quad (1)$$



$$2\ \mathrm{Ar{-}\overset{\displaystyle PR_3}{\underset{\displaystyle X}{Pd}}} \longrightarrow [\mathrm{(R_3P)ArPd(\mu\text{-}X)_2PdAr(PR_3)}] \quad (2)$$

THF was selected as the solvent for a number of reasons: it is one of the most common solvents used in the laboratory; it was the solvent used to prepare some of the experimentally characterized tricoordinated Pd^{II} complexes; it is moderately coordinating and small, therefore, appropriate to occupy the vacant site of tricoordinated species in the absence (either because of the stoichiometry used or because the extra ligand is too bulky to coordinate) of other fourth ligand. Note, that the absolute stability of tetracoordinated [PdArX(PR$_3$)(s)] (s = coordinating solvent) might be higher for other smaller or better coordinating molecules than THF; however, this does not affect the purpose of the study, which is to study the trends of stabilization of the tricoordinated species. As for the dimerization process, to obtain comparable results, the same type of dimer was always considered, with X acting as the bridging ligand. In fact this is the reasonable structure since in our model system only the X groups have lone pairs and can make non-deficient bridges.

Effect of the X ligand: To study the effect of the anionic ligands X, a systematic study was carried out keeping the two other ligands constant: L = PH$_3$, Ar = C$_6$H$_5$. The X ligands studied include four halides (F$^-$, Cl$^-$, Br$^-$, and I$^-$), two ligands with a group 16 coordinating atom (OH$^-$ and SH$^-$), two from group 15 (NH$_2^-$ and PH$_2^-$), and CH$_3^-$ from group 14. Note that the latter is different from the rest because it has only one electron pair available for bonding and can form only electron deficient bridges (three centers two electrons); this should reflect in the corresponding energy balance of Equation (2). The results of the calculations are gathered in Table 1.

The trends are better seen in the plots of the values for ΔE_{solv} and ΔG_{solv}, shown in Figure 1. The potential energy or

Table 1. Calculated ΔE, ΔE_{solv}, ΔG, and ΔG_{solv} [kcal mol^{-1}] for the coordination of a solvent molecule and the dimerization process, varying X in [PdPhX(PH$_3$)].

	Solvent Coordination [Eq. (1)]				Dimerization [Eq. (2)]			
X	ΔE[a]	ΔE_{solv}[b]	ΔG[a]	ΔG_{solv}[c]	ΔE	ΔE_{solv}	ΔG	ΔG_{solv}
F	−21.2	−17.0	−8.7	−4.4	−25.4	−19.7	−18.1	−12.3
Cl	−19.9	−16.0	−7.3	−3.4	−19.5	−14.1	−12.5	−7.1
Br	−19.3	−16.0	−6.6	−3.3	−18.4	−13.4	−11.4	−6.4
I	−18.9	−15.9	−5.8	−2.9	−17.7	−13.4	−11.3	−7.0
OH	−20.6	−15.9	−8.5	−3.8	−26.5	−23.2	−18.0	−14.7
SH	−18.3	−16.1	−5.5	−3.3	−23.7	−20.4	−15.1	−11.8
NH$_2$	−14.8	−11.8	−3.0	0.0	−28.6	−26.9	−19.7	−18.0
PH$_2$	−15.7	−14.7	−4.1	−3.1	−21.9	−22.1	−13.5	−13.6
CH$_3$	−15.8	−15.2	−3.4	−2.8	−6.9	−7.4	0.8	0.3

[a] Values in gas phase. [b] Potential energy including solvation effects by means of continuum PCM methods; solvent is THF. [c] $\Delta G_{solv} = \Delta E_{solv} + (\Delta G - \Delta E)$.

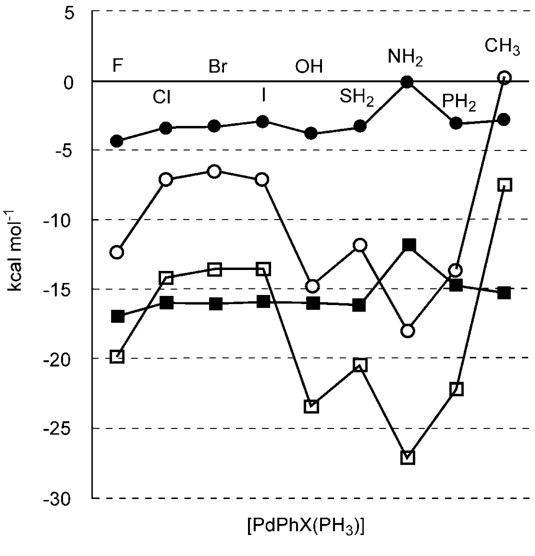


Figure 1. Effect of X ligand on the processes of solvent coordination and dimerization for [PdPhX(PH$_3$)] (numeric values in Table 1). ■: ΔE_{solv}; □ ΔE_{dimer}; ●: ΔG_{solv}; ○: ΔG_{dimer}.

Gibbs energy of each tricoordinated monomer (plus one molecule of free THF for the case of Equation (1) is taken as a zero point in the abscissa axis for each X ligand. The plot shows that the entropic contribution, although probably overestimated,[36] is, as expected, unfavorable to the tetracoordinated monomer in an amount (independent of X) of about 12.5 $kcal\,mol^{-1}$ for the solvent coordination process and 8.0 $kcal\,mol^{-1}$ for the dimerization process.[37] Despite the entropic contribution, both the solvent coordination and the dimerization processes are clearly favorable, and more favorable for the formation of dimers than for THF solvento complexes.

Overall, the relative stability of tricoordinated versus tetracoordinated species is more clearly estimated in the solvent coordination process (even when these complexes are less stable than the dimers), since the dimerization process further depends on the variation of the ability of the anionic ligand to act as a bridging ligand between the two Pd centers.

Considering the results obtained for the halide ligands and the solvent coordination process, the relative stability of the tricoordinated compounds increases slowly on going down in the group. This can be directly related to the electronegativity of the halide: tricoordinated Pd^{II} is an electron-deficient center, thus the more electron-withdrawing the halide, the less stable the tricoordinated species relative to the addition of a fourth ligand. The same trend is observed for the dimerization process within the group. Similar trends are observed for the anionic ligands of group 16. The reaction energy values for the solvent coordination process are similar to those obtained for the halides. Considering the dimerization process the reaction energies are larger for ligands of group 16, showing the greater ability of these ligands to act as bridging ligands. Note also the effect of the size of the donor atom: within a group, the smallest donor atom gives more stable bridges.

It is worth remarking the singular behavior of two cases. For $X=CH_3$, as an exception, the methyl-bridged dimer is less stable than its solvento monomer, owing to the weakness of the electron-deficient methyl bridges.[38] For $X=NH_2$, the solvento complex is particularly destabilized (or the tricoordinated complex stabilized), to the point that its stability is similar to the tricoordinated complex; however, NH_2 bridges are particularly strong and the dimer has by far the highest stability of the series.

The results of the calculations are clear enough to support that, for conventional ligands with small steric requirements, the tricoordinated species is highly disfavored in general and, for THF, the dimers are favored over the solvento complexes. It is clear that for a sufficiently more coordinating molecule than THF (e.g. phosphine, or DMF = dimethylformamide) the tetracoordinated monomer (e.g. $[PdArX(PH_3)_2]$, $[PdArX(PH_3)(DMF)]$) could become even more stable than the dimer. In no case there is chance for the formation of detectable amounts of the tricoordinated species. However, if dimerization was prevented (e.g. by the use of bulky ligands), NH_2 looks the most promising X ligand of the series to stabilize a tricoordinated species. It is somehow surprising that for the other X ligands (including CH_3!) the energy differences for tetracoordinated monomers are quite small compared to steric effects (see below).

The striking case of amide, the best ligand among those tested for stabilizing tricoordinated Pd^{II} species, was further investigated. We hypothesized that the NH_2 ligand could generate some Pd–N double bond character by donation of its electron lone pair to the "empty" Pd orbital, therefore acting as a single-faced π-donor ligand as suggested for related cases in other transition metal complexes.[39,40] The Pd–N bond was analyzed for two analogous isoelectronic monomeric [PdArXL] complexes ($X=NH_2^-$ and NH_3 ligands; the latter is unambiguously a single Pd–N bond), by using Bader QTAIM theory.[50] A bond critical point was found in both cases, with electron densities of 0.133 for Pd–N_{amide} and 0.082 for Pd–N_{amine}, respectively. These electron densities are lower compared to those obtained for organic compounds with strong presence of a resonance form with a C–N double bond character: for instance, for Ph–NH_2 and HOC–NH_2 these values are 0.302 and 0.319, respectively. Yet, the electron density at the critical point of the Pd–N_{amide} bond is notably higher than for the Pd–N_{amine} bond. An index used in QTAIM analysis to recognize double bond character is the ellipticity (ε). For the case of Ph–NH_2 and HOC–NH_2 compounds the ellipticity values are 0.062 and 0.092, respectively, in the same range than that for the Pd–N_{amide} bond 0.072. Surprisingly, the same value of ellipticity is found for the Pd–N_{amine} bond. However, it should be noted that, as the geometry of the compound suggests, this bond is unusual in the sense that the putative π-bond interaction is not symmetrical relative to the bond direction (Figure 2). Finally, the rotational barrier for both ligands (NH_2 and NH_3) was calculated, which afforded a significant result in favor of the suspected multiple bond character: in gas phase the rotational barrier for NH_2 is 10.3 $kcal\,mol^{-1}$, compared to only 0.4 $kcal\,mol^{-1}$ for NH_3.

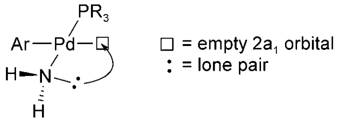


Figure 2. Sketch of the π donation of the electron lone pair of the amide ligand to the empty Pd orbital.

Overall, the analysis seems to support a certain double bond character for the Pd–N_{amide} bond, involving interaction of the highly nucleophilic lone pair of the amide ligand and the empty orbital of the Pd center. In such case the rotational conformation of the coordinated NH_2^- should be that arranging the lone pair in the coordination plane and in the direction towards the Pd empty position, and this is the case (see some structures below). This extra interaction, introducing additional electron density in the unsaturated Pd^{II} center, explains the peculiar behavior of NH_2^-. Note that the effect is not noticeable for PH_2^-, as it typically happens for additional π-bond interactions in bonds involving heavier elements compared with π-bond interactions involving second row elements.

Effect of the aromatic ligand (Ar): Gathered in Table 2 are the results obtained for the solvent coordination and dimerization processes on $[PdAr(NH_2)(PH_3)]$ complexes with different aromatic ligands. These values are plotted in Figure 3.

Table 2. Calculated ΔE, ΔE_{solv}, ΔG and ΔG_{solv} [kcal mol^{-1}] for the coordination of a solvent molecule and the dimerization process, varying the aromatic (Ar) ligand in $[PdAr(NH_2)(PH_3)]$.

	Solvent Coordination				Dimerization			
Ar	ΔE	ΔE_{solv}	ΔG	ΔG_{solv}	ΔE	ΔE_{solv}	ΔG	ΔG_{solv}
C_6F_5	−18.3	−15.6	−5.8	−3.1	−32.4	−31.9	−23.9	−23.5
C_6H_5	−14.8	−11.8	−3.0	0.0	−28.6	−26.9	−19.7	−18.0
C_6H_4OH-*p*	−14.9	−11.9	−2.9	0.1	−28.8	−27.0	−20.1	−18.2
$C_6H_4OCH_3$-*p*	−14.8	−11.8	−2.5	0.5	−28.6	−27.1	−19.9	−18.3
$C_6H_4NH_2$-*p*	−14.4	−11.4	−2.4	0.5	−28.3	−26.5	−19.6	−17.8
$C_6H_2(NH_2)_3$-2,4,6	−14.0	−10.0	−1.9	2.2	−27.8	−24.3	−20.5	−17.0

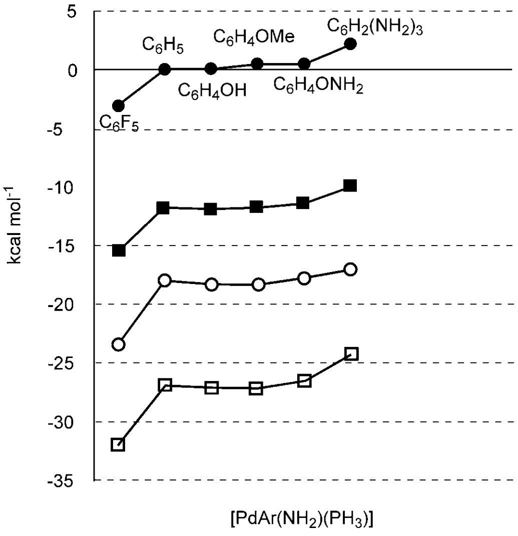


Figure 3. Effect of Ar ligand on the processes of solvent coordination and dimerization for $[PdAr(NH_2)(PH_3)]$ (numeric values in Table 2). ■: ΔE_{solv}; □: ΔE_{dimer}; ●: ΔG_{solv}; ○: ΔG_{dimer}.

The calculations were performed on $[PdAr(NH_2)(PH_3)]$, thus choosing the X group that favors better the stabilization of the tricoordinated species ($X = NH_2$). Again the plots of ΔE_{solv} and ΔG_{solv} run fairly parallel, separated by about 12.0 kcal mol^{-1} for the solvent coordination process and 8.5 kcal mol^{-1} for the dimerization process. Except for the most electron withdrawing aryl, C_6F_5, the variations with the aryl substituents are moderate. The values obtained for the dimerization process show clearly that the formation of dimers is strongly favored in all cases, with values for ΔG_{solv}, ranging from −17.0 to −18.3 kcal mol^{-1}. Interestingly, the plot of ΔG_{solv} would suggest that, if dimerization could be prevented, the stability of the tricoordinated species is as good as or superior to the solvento complex (ΔG_{solv} for the solvent coordination process are in the range 0.0–2.2 kcal mol^{-1}), and increases moderately with the electron-donating ability of the aryl substituents.

Effect of the phosphine ligand (PR_3): As deduced from the results above, it is mostly the large stabilization associated with dimerization that prevents the formation of the tricoordinated complex as a stable species. In this respect the role of the size of the ligands to hinder dimerization is expected to be more decisive than the electronic effects examined so far. Thus the influence of the phosphine ligand (PR_3) was analyzed, C_6H_5 was kept as the aromatic ligand, for two X ligands: Br^- (a very common ligand in practice) and NH_2^- (the ligand found to favor better tricoordination). The phosphine ligands selected increase in size progressively from PH_3 to 1-AdP*t*Bu$_2$ (1-adamantylbis(*tert*-butyl)phosphine). The results obtained for the set of phosphanes studied are gathered in Tables 3 and 4, and plotted in Figure 4.

Table 3. Calculated ΔE, ΔE_{solv}, ΔG and ΔG_{solv} [kcal mol^{-1}] for the coordination of a solvent molecule and the dimerization process, varying the phosphine (PR_3) ligand in $[PdPhBr(PR_3)]$.

	Solvent Coordination				Dimerization			
PR_3	ΔE	ΔE_{solv}	ΔG	ΔG_{solv}	ΔE	ΔE_{solv}	ΔG	ΔG_{solv}
PH_3	−19.3	−16.0	−6.6	−3.3	−18.4	−13.4	−11.4	−6.4
PMe_3	−18.1	−15.0	−4.9	−1.7	−18.2	−12.3	−10.8	−4.8
PPh_3	−15.0	−11.6	−1.1	2.3	−13.7	−6.1	−5.7	1.9
P*t*Bu$_3$	−8.0	−5.9	7.1	9.2	−5.2	0.9	3.8	10.0
1-AdP*t*Bu$_2$	−6.3	−4.6	8.9	10.6				

Table 4. Calculated ΔE, ΔE_{solv}, ΔG, and ΔG_{solv} [kcal mol^{-1}] for the coordination of a solvent molecule and the dimerization process, varying the phosphine (PR_3) ligand in $[PdPh(NH_2)(PR_3)]$.

	Solvent Coordination				Dimerization			
PR_3	ΔE	ΔE_{solv}	ΔG	ΔG_{solv}	ΔE	ΔE_{solv}	ΔG	ΔG_{solv}
PH_3	−14.8	−11.8	−3.0	0.0	−28.6	−26.9	−19.7	−18.0
PMe_3	−14.0	−10.2	−1.9	1.9	−28.9	−25.7	−20.3	−17.2
PPh_3	−12.3	−9.2	2.1	5.1	−27.0	−21.9	−18.4	−13.3
P*t*Bu$_3$	−6.6	−4.4	8.3	10.4	−17.6	−15.1	−6.6	−4.1
1-AdP*t*Bu$_2$	−3.5	−0.3	10.8	14.0				

Analogous to the results previously discussed, when Gibbs energies are taken into account, the reaction energies become smaller, therefore reflecting an increase in relative stability of the tricoordinated species. The general trends observed in Tables 3 and 4 show that the relative stability of the tricoordinated Pd complex increases very fast with the size of the phosphine: $PH_3 < PMe_3 < PPh_3 <$ P*t*Bu$_3 <$ 1-AdP*t*Bu$_2$. Moreover, the bridged dimers get destabilized with the size of the phosphine more steeply than the solvento complexes. As a result, for X = Br there is, around $PR_3 =$ P*t*Bu$_3$, a crossover of the two lines. These data mean that

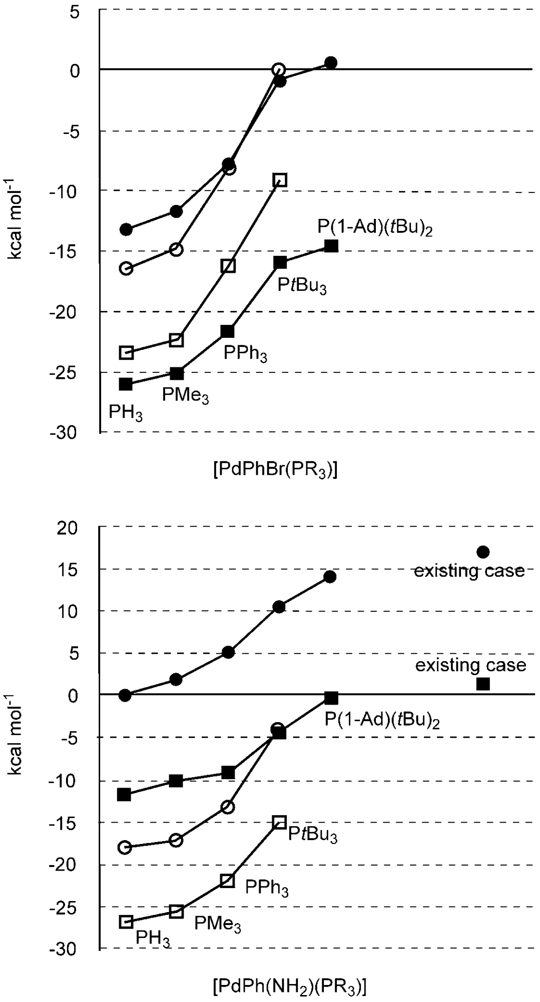


Figure 4. Effect of PR_3 ligand on the processes of solvent coordination and dimerization for $[PdPhBr(PR_3)]$ (upper plot, numeric values in Table 3), and $[PdPh(NH_2)(PR_3)]$ (lower plot, numeric values in Table 4). The values calculated for one existing case (see text) are plotted in the last graphics (at right). ■: ΔE_{solv}; □: ΔE_{dimer}; ●: ΔG_{solv}; ○: ΔG_{dimer}.

the relative stability of the low coordinated species becomes more and more accessible fairly rapidly.

According to Figure 4, for the solvent coordination process ΔG_{solv} is negative (this indicates that the tetracoordinated species $[Pd(C_6H_5)Br(PR_3)(THF)]$ is more stable than the tricoordinated one) only for the two smallest phosphines (PH_3, PMe_3) in the case of X = Br; for X = NH_2 the tricoordinated species is always more stable than the solvento complex, confirming the NH_2 effect already observed in the sections above. Looking at the values for the dimerization process, for X = NH_2 dimerization to $[Pd_2(C_6H_5)_2(\mu\text{-}NH_2)_2(PR_3)_2]$ is always spontaneous, even for a phosphine ligands as bulky as $Pt Bu_3$, owing to the strength of these bridges. However, the calculated data for X = Br would suggest the formation of tricoordinated $[Pd(C_6H_5)Br(PR_3)]$, instead of $[Pd_2(C_6H_5)_2(\mu\text{-}Br)_2(PR_3)_2]$, for PPh_3 or bigger phosphines. Moreover, with the energy differences calculated, the tetracoordinated complexes should be undetectable in equilibrium for X = Br and R ≥ Ph.

Although the calculations suggest that a tricoordinated complex with NH_2^- and $Pt Bu_3$ is not stable with respect to dimerization, and that even solvento complexes become more stable than dimers beyond that point, similar trimeric complexes have been experimentally synthesized and characterized, simply using more hindered substituted amides (e.g. $N(C_6H_3(CF_3)_2\text{-}3,5)_2$).[25] Hence, we performed the calculations for the solvent coordination reaction in a complex with the set of ligands observed in one experimental case: X = $N(C_6H_3(CF_3)_2\text{-}3,5)_2$, Ar = $C_6H_4OCH_3$-*p* and L = $Pt Bu_3$ (Figure 5). The ΔE_{solv} and ΔG_{solv} energies for solvent coordination, depicted in Figure 4 (lower plot, right), are 1.2 and 17.0 kcal mol^{-1}, respectively, predicting a reluctance to coordinate solvent, and the stability of the low coordinated complex that has been experimentally observed. This shows that the hindrance associated to the X group also contributes to the stability of the tricoordinated complex by destabilizing solvent coordination.

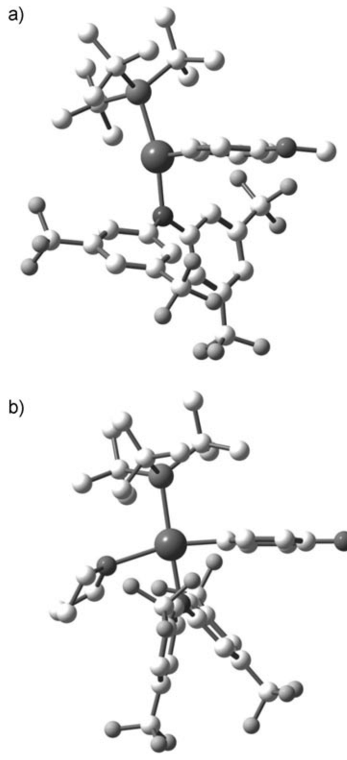


Figure 5. Optimized structures for a) $[Pd(Pt Bu_3)(C_6H_4OCH_3\text{-}p)(N(C_6H_3\text{-}(CF_3)_2\text{-}3,5)_2]$, and b) the THF-solvated counterpart. Hydrogen atoms are omitted for clarity.

A closer look at the tricoordinated predictions versus the experimental facts: Although the validity of the observed trends (particularly those for solvent coordination) as a description of the relative stabilization of tricoordinated species is out of question, the quantitative predictions need to be looked at more carefully.

First of all, in contrast to the prediction, many X-ray structures of tetracoordinated dimers and monomers, and none of tricoordinated complexes, are known for PPh_3 and even more crowded ligands.[40,41] This experimental evidence suggests that, as suspected, the values of Gibbs energy are overestimated and a more realistic picture should bring them somewhat closer to the ΔE values.

On the other hand, for the bulkier phosphanes such as $PtBu_3$ and $1\text{-}AdPtBu_2$ the prediction of [PdArXL] as the thermodynamic product meets, initially, with experimental support,[16,17,25] although the fourth coordination site could be occupied by an agostic interaction, rather than be left empty.

The calculated complexes susceptible to establish agostic interactions were analyzed in more detail. Table 5 collects selected geometrical calculated data. For $L = PtBu_3$ and $X = Br$ (Figure 6a), the C–H bond located closest to the metal center has a bond length of 1.102 Å in the calculated structure, and the Pd···H distance is 2.450 Å. These data, particularly the slightly elongated C–H bond length, would suggest that in this case there is a weak γ-agostic interaction. Indeed this complex had been characterized experimentally by single crystal X-ray diffraction, and the authors suggested an agostic interaction, with a Pd···H distance of 2.18 Å.[17] In the adamantyl case (Figure 6b), the calculated geometrical parameters are similar and a weak agostic interaction (a little stronger) would be assigned, also supported by the experimental observation (with a Pd···H distance of 2.27 Å).[17] Interestingly the two distances assigned in the solid state X-ray structure are shorter than those calculated for the solvated molecule in silico, suggesting that the packing pressure favors these agostic interactions.

Table 5. Calculated geometrical parameters concerning possible agostic interactions for tris(*tert*-butyl)phosphine and 1-adamantylbis(*tert*-butyl)-phosphine complexes. Distances in Å.

PR_3	X	$d(Pd–H)_{min}$ [Å]	$d(C–H)$ [Å]	Agostic interaction?
$PtBu_3$	Br	2.450	1.102	Yes
$1\text{-}AdPtBu_2$	Br	2.358	1.106	Yes
$PtBu_3$	NH_2	2.622	1.098	No
$1\text{-}AdPtBu_2$	NH_2	2.514	1.103	Yes

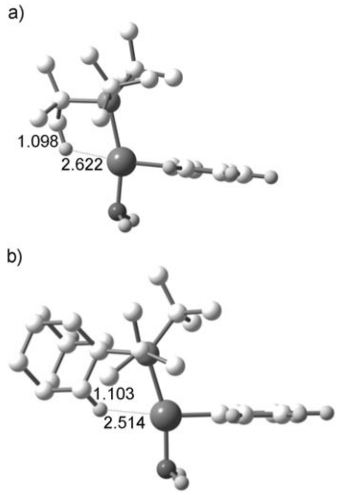


Figure 6. Optimized structures for a) $[Pd(PtBu_3)(C_6H_5)(NH_2)]$, and b) $[Pd(1\text{-}AdPtBu_2)(C_6H_5)(NH_2)]$. Hydrogen atoms on phosphine ligands are omitted for clarity.

For $X = NH_2$ and $L = PtBu_3$, the calculated C–H bond length is 1.098 Å, whereas the Pd···H distance is 2.622 Å, supporting that there is no agostic interaction, in coincidence with the experimental case. In contrast, the C–H and Pd···H distances found for the adamantyl phosphine ligand, would indicate a weak agostic interaction. It must be said, however, that the assignment of agostic interactions in the cases just discussed are within the limit, is a matter of opinion. Nevertheless, it seems that these weak interactions are extremely sensitive to small changes in the system.

Considering the agostic interaction as a fourth ligand, only in the case of $X = NH_2$ and $L = PtBu_3$ would it be strictly correct to say that Pd is tricoordinated. Moreover, the coexistence of π-donation from the coordinated amide and agostic interactions, as a cooperative mechanism to reduce the electronic unsaturation of a tricoordinated Pd^{II} center, is perfectly possible.

It is interesting to note, as compared with coordination of external ligands, that these intramolecular weak interactions are much less affected by entropy and, because of their intramolecular nature, their existence or not is not easy to assess from kinetic studies.

Conclusions

The calculations on the relative stability of coordinatively unsaturated tricoordinated Pd^{II} species versus tetracoordinated complexes report very nicely on the accessibility of the former as possible transition states or undetected intermediates in catalytic reactions. The tricoordinated Pd^{II} species become more accessible for more electron donating ligands and more electron donating substituents on the aryl groups, but the most important stabilizing effect of tricoordinated Pd^{II} species is the hindrance of the ligands. This is well illustrated by the effect of the phosphines PH_3 and PMe_3 that show behavior more similar to the smaller PPh_3 than to the electronically similar $PtBu_3$ or $1\text{-}AdPtBu_2$.

As for the observation of Pd^{II} tricoordination in the ground state, the hindrance of one ligand can be enough to exclude the formation of dimers, but also the hindrance of the second ligand cis to the empty coordination site is important in order to exclude solvent coordination. It seems that only NR_2 is able to produce true tricoordinated complexes. Otherwise ($X = Br$) the fourth position is occupied by an agostic interaction with a C–H bond of the phosphine ligand, and the phosphine can be considered an extreme case of hemilabile chelating ligand. Certainly this agostic interaction is very weak and the tricoordinated complex must be very close in energy to the ground state. Consequently, in practice the agostically stabilized complexes can be thought of as a resting state of the tricoordinated species or, in terms of reactivity as a synthon of the tricoordinated reactive species.

The role of the NR_2^- ligand seems to be critical to reduce the formation of agostic interactions. It seems that the avidity of the empty Pd orbital directed towards the empty coordination site can be satisfied by π-electron donation from the lone pair of this ligand, then reducing or eliminating the strong tendency for agostic bond formation. Although in the case of agostic interactions the concept of tricoordination cannot be maintained, in the case represented by the amido complex it seems fully correct to speak of three coordinated complexes, although the π-bond component reminds us that ligand counting should not be strictly associated to electron counting, even having an X-ray structure in front of our eyes. These tricoordinated complexes are not 14 electron species.

In this respect the electronic involvement of NR_2^- in π bonding is somewhat reminiscent of classical textbook cases.[42] For instance, $Mn(CO)_4(NO)$ shows second order rate law and negative ΔS in ligand substitution reactions, in contrast with first order rate law for the isoelectronic $Fe(CO)_5$;[43] this has been explained considering that the 18e $[Mn(CO)_4(NO)]$ can accept an extra ligand while avoiding a 20e configuration by rearranging the NO coordination from linear NO (3e donor) to bent NO (1e donor). In the case of the so-called indenyl effect, indenyl complexes react faster in associative substitutions in part because they can better switch from η^5 to η^3 coordination, again avoiding a 20e configuration in the transition state.[44] In the case discussed here the dissociation of an ancillary ligand from a 16e square-planar Pd^{II} complex containing a NR_2^- initially 2e bonded, can be compensated in part by concomitantly involving the lone pair in a π-interaction (formally making NR_2^- a 4e ligand), which would produce a tricoordinated complex while avoiding a 14e configuration.

The results discussed in this paper can be related to the extraordinary activity of bulky ligands in transition-metal catalyzed reactions. In Pd^{II} the use of hindered ligands should make more accessible tricoordinated transition states or intermediates, although disfavoring more crowded pentacoordinated ones. This will eventually switch the substitution and transmetalation steps of the catalytic cycles (for instance cross-coupling reactions) from the classical associative pathways to dissociative mechanisms. In such dissociative substitution the reacting complex will just need to release an agostic interaction with the phosphine, and reaching the tricoordinated TS might require less activation energy. Moreover, the catalytic reactions with conventional ligands, going though tetracoordinated intermediates and associative transmetalations, are usually carried out in the presence of excess ligand, in order to stabilize the Pd^0 species formed after the reductive elimination step; this excess of ligand is detrimental for the rate of dissociative transmetalation, where one of the two ligands on Pd has to be released. In a process in which the (usually rate determining) transmetalation takes place on a tricoordinated complex (whether or not agostically stabilized), the rate of this step will not be retarded by the presence of excess ligand, since no ligand needs to be released during the transmetalation.

Experimental Section

Computational details: The calculations were performed by using the Gaussian03 package.[45] All the geometries were fully optimized using density functional theory with the B3PW91 functional.[46] For the Pd, Cl, Br, I, S, and P atoms the lanl2dz effective core potential was used to describe the inner electrons,[47] along with their associated double-ζ basis set for the remaining electrons. An extra series of d-polarization functions was added for P, Cl, Br, I, and S, with exponent values of 0.387, 0.640, 0.428, 0.289, and 0.503, respectively.[48] Other atoms were described with a 6-31G basis, adding an extra d-polarization function in O, N, and F atoms, as well as the C atoms in phosphanes or aromatic ligands. Frequency analysis let us to identify all the optimized structures as minima within the potential energy surface. Single point calculations including solvent effects were performed at the optimized gas-phase geometries (ΔE_{solv}), using the PCM approach[49] in Gaussian03. Tetrahydrofuran was chosen as solvent (dielectric constant $\varepsilon = 7.58$). Topological analysis of the electron density was performed by means of the Bader's AIM theory,[50] by using the Xaim 1.0 program.[51]

ΔE is the potential energy and ΔG is the Gibbs energy in gas phase. ΔE_{solv} and ΔG_{solv} stand for the potential and Gibbs energies including the solvent effects, respectively. The ΔG_{solv} is calculated according to the following formula: $\Delta G_{solv} = \Delta E_{solv} + (\Delta G - \Delta E)$.[36] ΔE, ΔE_{solv}, ΔG and ΔG_{solv} values are included in the tables, though those commented in the text or represented in the figures refer to the values including solvent effects, unless otherwise specified.

Acknowledgements

We thank the Ministerio de Ciencia y Tecnología for financial support (Projects CTQ2007-67411/BQU, CTQ2005-09000-C02-01, INTECAT Consolider Ingenio-2010 (CSD2006-0003) and Consolider Ingenio-2010 (CSD2007-00006)). The Spanish MEC is also acknowledged for a fellowship to S.M. and a "Ramón y Cajal" contract to G.U.

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Received: March 8, 2008