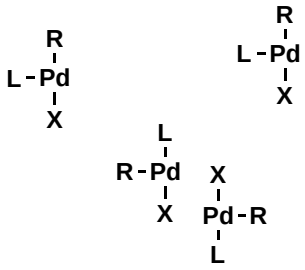
14-Electron T-shaped intermediates are cursorily depicted in catalytic cycles, substitution reactions, transmetalations... But, are they what they appear to be?

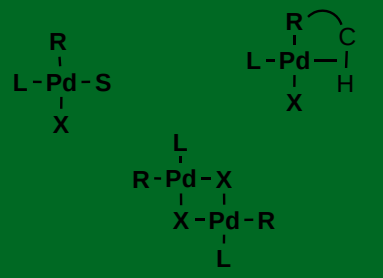
14-e intermediates



Deceptive appearance

or

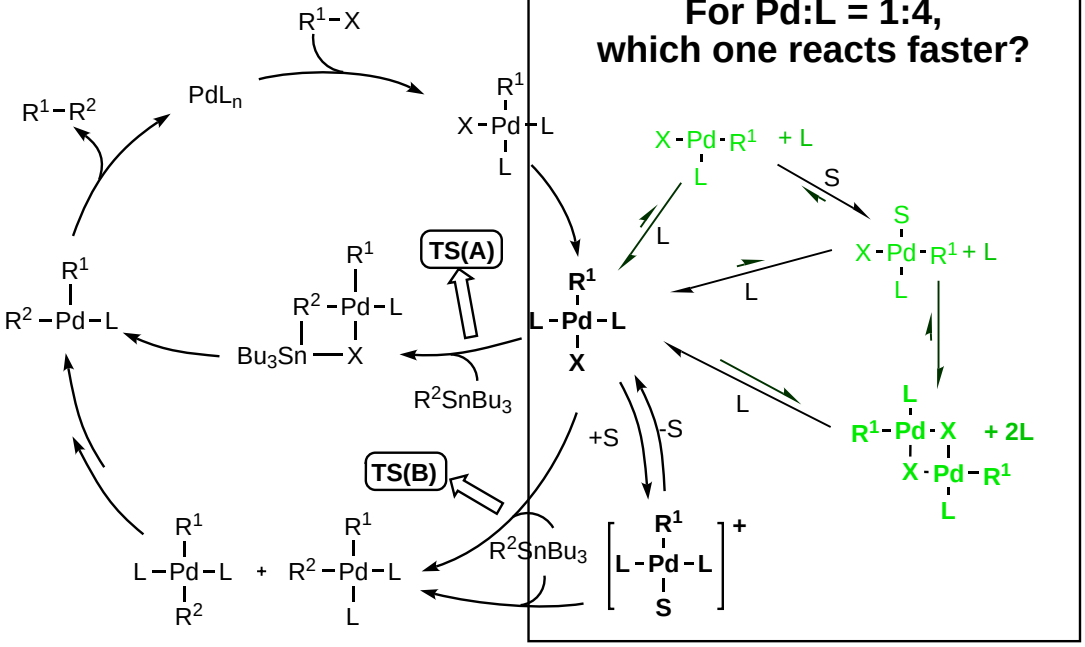
16-e intermediates?



unveiled

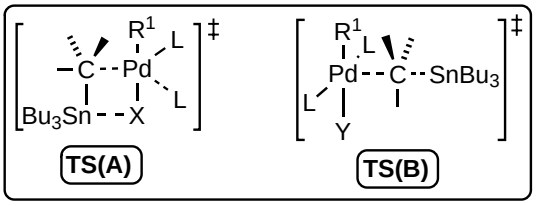
...

Stille Cycle: Dual Pathway



For Pd:L = 1:4, which one reacts faster?

Associative Transmetalation Possible Transition States:



Y = S or X
S = L or solvent

For more information see the following pages

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14-Electron T-Shaped [PdRXL] Complexes: Evidence or Illusion? Mechanistic Consequences for the Stille Reaction and Related Processes

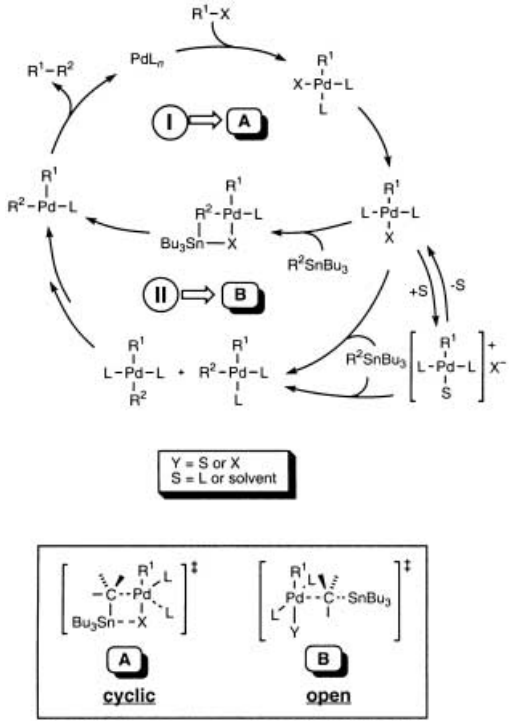
Juan A. Casares, Pablo Espinet,* and Gorka Salas[a]

Abstract: A recent claimed spectroscopic observation (by ^{1}H NMR) of 14-electron T-shaped 3-coordinated palladium complexes turns out to be a misinterpretation. A thorough study of the species formed by $[PdRX(AsPh_3)_2]$ (R = Ph, $C_6Cl_2F_3$; X = Cl, I) in different solvents (S = $CDCl_3$, THF, DMF) suggests that: 1) there is no NMR-detectable amount of $[PdRX(AsPh_3)]$, and 2) in the presence of free arsine ($AsPh_3$/$[PdRX(AsPh_3)_2]$ 2:1) the concentration of $[PdRX(AsPh_3)(S)]$ is negligible. This clearly settles matters in the controversy of dissociative or associative pathways for the transmetalation step involved in the Stille coupling in favor of the latter: under catalytic conditions the dominant pathway is the associative reaction of the stannane with the square-planar complex $[PdRX(AsPh_3)_2]$.

Keywords: cross-coupling · metalation · palladium · Stille coupling · tin

Introduction

To distinguish between dissociative and associative mechanisms in processes operating on square-planar 16-electron complexes is a hard task. This problem occurs in a number of fundamental steps common to many reaction mechanisms, such as ligand substitution, reductive elimination, or transmetalation. Recently we have been occupied with this problem in the context of our studies on the transmetalation step in the palladium-catalyzed coupling of organic halides or triflates with stannanes (Stille reaction).[1] In the course of a thorough study of the mechanism of this reaction we concluded that a more complete view of the possible pathways for the reaction was as shown in Scheme 1.[2, 3] Two main cycles are suggested, differing in the transmetalation step (and consequently in the subsequent reductive elimination steps). Pathway **I** involves a cyclic transition state **A**, leading to *associative L-for-R*^{2} substitution, and directly yields a *cis* arrangement for R^1 and R^2. This path is favored for organic halides as electrophiles, and in solvents with moderate coordinative ability towards Pd. Coordination of the halide to Sn assists the transmetalation, increasing the nucleophilicity of the a-carbon of the stannane and the electrophilicity of Pd, and reducing the free energy of the transition state. It also directs the stereochemistry of the transmetalation.[4]



Scheme 1. Complete view of the pathways that may be involved in the catalytic Stille cycle.

Pathway **II** involves an open transition state **B**, leading to *associative Y-for-R*^{2} substitution (either directly or via intermediates in which X has been associatively replaced by L or by a molecule of solvent), which results in a *trans* arrangement

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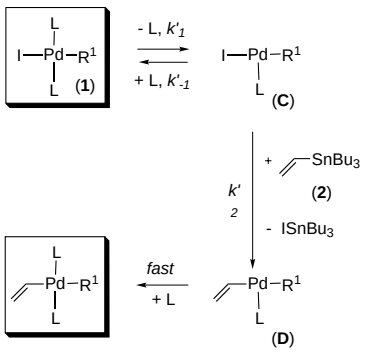
for R^1 and R^2; depending on the *trans* effects of R^1 and L, this takes place in competition with *associative L-for-R^2* substitution, which leads to a *cis* arrangement for R^1 and R^2. Pathway **II** is favored by good leaving groups (X) from Pd (OTf $\gg$ halides) and by solvents capable of acting as reasonably good ligands towards Pd. Our studies showed that, in the transmetalations with X = halide, L = $AsPh_3$, $R^1 = C_6Cl_2F_3$, and R^2 = vinyl, and with THF as the solvent, only pathway **I** seemed to be operating, whereas in those with X = OTf, L = PPh_3, $R^1 = C_6Cl_2F_3$, and R^2 = vinyl, and with THF or $CHCl_3$ as the solvent, pathway **II** was preferred.

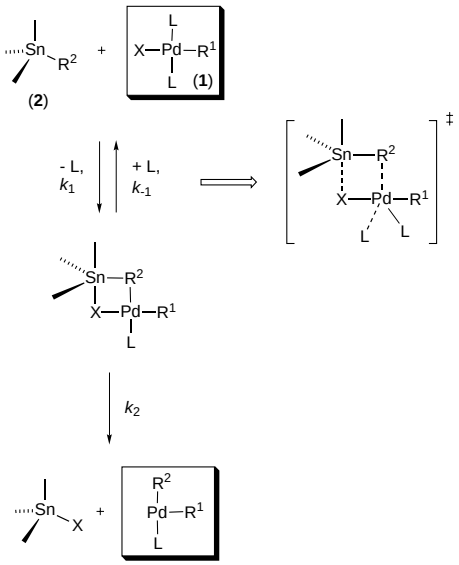
We also examined the species that could be detected in solution by ^{19}F NMR spectroscopy.[3] These varied depending on different factors (nature of X, L, and S, concentration of L, temperature). The conclusion was that the actual molecule undergoing transmetalation can change as a function of all these factors. Among the species that we were able to detect in solution, depending on the conditions, were: $[Pd(C_6Cl_2F_3)I(AsPh_3)_2]$ (in THF), $[Pd(C_6Cl_2F_3)I(PPh_3)_2]$ (in chloroform or THF), $[Pd(C_6Cl_2F_3)(OTf)(PPh_3)_2]$ (in chloroform or THF), $[Pd(C_6Cl_2F_3)(PPh_3)_2(THF)](OTf)$ (in THF), $[Pd(C_6Cl_2F_3)(PPh_3)_3](OTf)$ (in chloroform or THF), $[Pd(C_6Cl_2F_3)(PPh_3)_2(HMPA)]X$ (X = Cl, I, OTf) (in HMPA), $[Pd(C_6Cl_2F_3)(PPh_3)(HMPA)_2]X$ (X = Cl, I, OTf) (in HMPA), and $[Pd(C_6Cl_2F_3)Cl(PPh_3)_2(HMPA)]$ (in HMPA). Thus, the actual mechanism of transmetalation will have a complex dependence on the reaction conditions, and will need to be studied separately each case. Note, however, that in all cases we have proposed that the entrance of the R^2 group into the coordination sphere of Pd occurs by *associative* mechanisms: that is, through 5-coordinated (18-electron) transition states (**A** or **B** in Scheme 1). Under the conditions studied we have discounted *dissociative* mechanisms, which should involve 3-coordinated 14-electron transition states or intermediates.

Kinetic studies previous to our work had led to the proposal of a *dissociative* mechanism involving *X-for-R^2* transmetalation (Scheme 2, R^1 = Ph, L = $AsPh_3$, solvent = THF), basically because it was satisfactory to explain the retarding effect of the addition of L.[5] The intermediates **C** and **D** were depicted in different publications randomly as T-shaped 14-electron species $[PdR^1XL]$, or as so-called "solvent-stabilized" $[PdR^1XL(S)]$ (X = I, vinyl) intermediates. Note that the transmetalation leads to a *trans* complex, which should require isomerization before coupling.



Scheme 2. Dissociative transmetalation for halides, as proposed by Farina et al.

Our associative proposal (Scheme 3) explains the retarding effect of the addition of L equally well, and also accounts for other observations that cannot be explained by the mechanism in Scheme 2.[2, 3]



Scheme 3. Associative transmetalation for halides, as proposed by us.

Although the two transmetalation mechanisms are very different, to tell one from the other kinetically is not obvious because, as we have discussed previously,[2] the kinetic equations for Scheme 2 for a hypothesized fast preequilibrium [Eq. (1)] and for Scheme 3 [Eq. (2)] differ only in the coefficients but show the same dependence on the concentrations of the reagents.

$$r_{\text{dissociative}} = \frac{k'_2 K_{\text{dis}}[\mathbf{1}]}{K_{\text{dis}} + [AsPh_3]}[\mathbf{2}]; \quad K_{\text{dis}} = \frac{k'_1}{k'_{-1}} \tag{1}$$

$$r_{\text{associative}} = \frac{k_1 k_2[\mathbf{1}]}{k_{-1}[AsPh_3] + k_2}[\mathbf{2}] \tag{2}$$

An important point in our decision to discount the *dissociative* mechanism in Scheme 2 in favor of the *cyclic associative* mechanism in Scheme 3 was a quantitative con-

Abstract in Spanish: *La observación espectroscópica (por ^1H RMN) de complejos de paladio tricoordinados de 14 electrones anunciada en un reciente artículo resulta ser un error de interpretación. Un estudio completo de las especies formadas por $[PdRX(AsPh_3)_2]$ R = Ph, $C_6Cl_2F_3$; X = Cl, I) en distintos disolventes (S = $CDCl_3$, THF, DMF) lleva a las siguientes conclusiones: 1) No hay trazas detectables por RMN de $[PdRX(AsPh_3)]$; 2) en presencia de arsina libre ($AsPh_3$: $[PdRX(AsPh_3)_2]$ = 2:1) la concentración de $[PdRX(AsPh_3)(S)]$ es despreciable. Esto define claramente la cuestión en la controversia entre vías disociativas o asociativas para la etapa de transmetalación implicada en el acoplamiento de Stille, en favor de las últimas: En las condiciones catalíticas el camino dominante es la reacción asociativa del estannano con el complejo plano-cuadrado $[PdRX(AsPh_3)_2]$.*

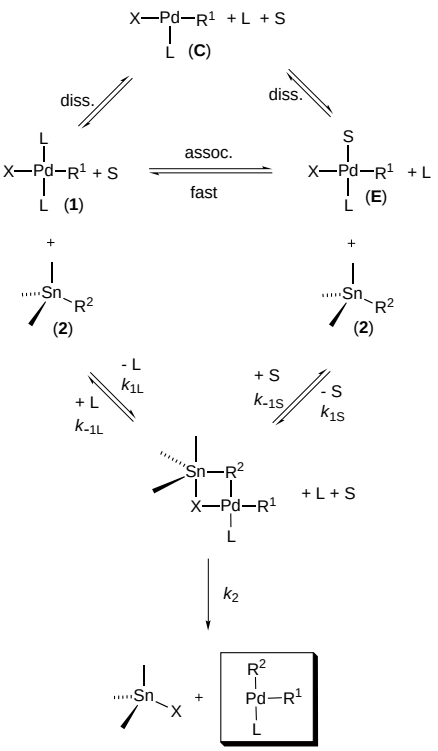
sideration of the data. We calculated that, in order to fit the kinetic results, the percentage of $[PdR^1I(AsPh_3)]$ in a solution of $[PdR^1I(AsPh_3)_2]$ should be 40% for $R^1 = Ph$ at 323 K in THF,[6] and 12% for $R^1 = C_6Cl_2F_3$ at 322.6 K in THF.[7] Our experience in Pd chemistry told us that these high percentages of dissociation were unacceptable for a T-shaped 14-electron species (we analyze the case of $[PdR^1XL(S)]$ intermediates later). It was even less likely that these intermediates would be abundant under catalytic conditions in which an excess of L (usually $Pd/AsPh_3$ 1:4) is used. Moreover, we argued that, if this high concentration was produced, the intermediate (**C**) should be easy to observe spectroscopically. In fact, we were unable to detect such intermediate in our system by the highly receptive ^{19}F NMR spectroscopy.

To our surprise the title of a recent paper announced "Evidence for the Formation of a T-Shaped Complex" and claimed in the text "the first spectroscopic evidence for the formation of the so-called T-shaped complex".[8] The news became less striking to us when we observed that the T-shaped complex was defined in several places in the text as $[PdPhI(AsPh_3)(S)]$ ($S = CDCl_3$, THF, DMF), which is not a T-shaped 14-electron complexes but a square-planar 16-electron complex. $[PdPhI(AsPh_3)(S)]$ appeared to be formed in solutions of $[PdPhI(AsPh_3)_2]$ along with the corresponding amount of free arsine, and was (or were) detected by ^1H NMR spectroscopy in $CDCl_3$, and by cyclic voltammetry in DMF. Although the discussion assumed a single identity for the complex, it was at the same time represented by $[PdPhI(AsPh_3)(solv)]$. The degree of "dissociation of arsine" at 293 K was reported to be 22% in $CDCl_3$, and 32% in dimethylformamide (DMF). If these observations corresponded to concentrations of a real T-shaped complex $[PdPhI(AsPh_3)]$ we should certainly consider our proposal of pathway **I** in Scheme 1 to be incorrect, or at least no better based than the alternative dissociative proposal. Even if the observed species were simply $[PdPhI(AsPh_3)(S)]$ in that high concentration, the consequences would deserve careful consideration and discussion. Thus, we decided to reexamine the systems with $C_6Cl_2F_3$ and Ph in our laboratory.

Results and Discussion

Setting out the concepts: For the discussion in this paper we need to define exactly the meaning of a few concepts that are frequent occasion of misunderstanding in mechanistic discussions. Let us consider the simple, rather common, and general system in Scheme 4, in which a complex $[PdR^1XL_2]$ (**1**, X = halide), in solution in a solvent S, exists in equilibrium with a T-shaped 14-electron complex $[PdPhXL]$ (**C**), and with a square-planar 16-electron complex $[PdR^1XL(S)]$ (**E**), in which a solvent molecule is one of the ligands. Note that we make a strict distinction between the two complexes, $[PdR^1XL]$ and $[PdR^1XL(S)]$, because they are very different, both conceptually and in their mechanistic implications.

A T-shaped 14-electron complex $[PdR^1XL]$ (**C**) could be formed by dissociation of L or S from a 16-electron precursor. It has a very low-lying empty orbital and reacts quickly with molecules with lone pairs (whether these molecules are



Scheme 4. Possible species in solution and competitive associative transmetalation for halides where L and S compete as ligands.

L or S) to fill this empty orbital. Obviously, high concentrations of such reactive species are incompatible with a high concentration of coordinating molecules (L or S) in the vicinity (special steric cases excluded), and will become less and less likely in solvents with progressively higher coordinating ability. The ability of solvents such as THF,[9] DMF,[10] and even CH_2Cl_2,[11] to act as ligands filling one or more coordination sites is well established, and complexes $[PdR^1XL(S)]$ are not and cannot be called T-shaped complexes.

A square-planar 16-electron complex $[PdR^1XL(S)]$ (**E**) is not essentially different from a 16-electron complex $[PdR^1XL_2]$ (**1**). Both have four ligands, and both could undergo ligand substitution by a dissociative mechanism (forming **C**), or by an associative mechanism, through an 18-electron 5-coordinate transition state.

The rate of the associative mechanism in $[PdR^1XL_2]$ complexes is faster by far than that for the dissociative mechanism, and no dissociative substitution for this kind of compound has ever been reported.[12, 13] In fact, we can safely discount, as discussed before, the possibility that the rate of transmetalation in the Stille reaction through a 14-electron complex $[PdR^1XL]$ (**C**) formed in a fast preequilibrium might be significant.[2] The high percentage of dissociated species required to fit the kinetic results is incompatible with the presence of a coordinating solvent (THF) and excess $AsPh_3$, either under Farina's conditions ($R^1 = Ph$),[5] or under ours ($R^1 = C_6Cl_2F_3$).[2] On the other hand, we have discussed,[2] and considered kinetically acceptable, the case of associative substitution (leading to transmetalation) on $[PdR^1XL_2]$ (**1**), which proved to explain satisfactorily all the observations on

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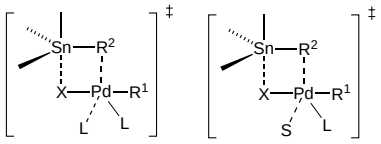
the system. Now we need to consider the case of weak ligands in coordinating solvents, in which there is the possibility of a preequilibrium that could produce a large degree of ligand-for-solvent exchange,[14] giving rise to a significant concentration of $[PdR^1XL(S)]$ (**E**) in solution (Scheme 4). In this case the transmetalation would be based on associative substitutions occurring competitively on both 16-electron complexes $[PdR^1XL_2]$ (**1**) and $[PdR^1XL(S)]$ (**E**) through their respective transition states shown below. In each case a ligand (L or S) will be associatively replaced by the entering nucleophile R^2-$SnBu_3$.



The reverse reaction (Scheme 4) will be the displacement of R^2-$SnBu_3$ by L or S. The rates of transmetalation through **1** and through **E** are obtained by application of the steady-state approximation, and are given in Equations (3) and (4), respectively.[15]

$$r(\mathbf{I})_{\text{associative}} = \frac{k_{1L}\,k_2[\mathbf{1}]}{k_{-1L}[AsPh_3] + k_{-1s}[S] + k_2}[\mathbf{2}] \quad (3)$$

$$r(\mathbf{E})_{\text{associative}} = \frac{k_{1S}\,k_2[\mathbf{E}]}{k_{-1L}[AsPh_3] + k_{-1s}[S] + k_2}[\mathbf{2}] \quad (4)$$

The ratio of the two rates [Eq. (5)], depends on two factors: i) the concentrations of **1** and **E**, which are determined by the thermodynamic equilibrium (K_{eq}, or ΔG^0 for the substitution reaction), and ii) the rate constants, which are determined by the $\Delta G^{\neq}$ values for the nucleophilic attack by the stannane on **1** or **E**, respectively. The complex with the worse ligand (expected to be **E**) is less stable (higher fundamental state) and more electrophilic (lower transition state towards attack by a nucleophile), hence it should give rise to a lower $\Delta G^{\neq}$ value and provide a faster reaction path, unless the ratio of concentrations compensates for this factor. It is thus important, from a theoretical point of view, to examine whether there is a significant concentration of **E** under the reaction conditions, in which case the reaction would probably take place mostly via **E**.

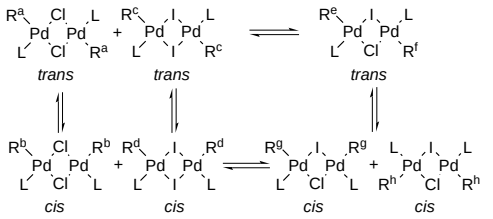
$$\frac{r(\mathbf{1})}{r(\mathbf{E})} = \frac{k_{1L}[\mathbf{1}]}{k_{1S}[\mathbf{E}]} \quad (5)$$

From a practical point of view, however, it must be noted that both transmetalations are *associative L-for-R*^{2} substitutions (L (= ligand) or S), both lead to a *cis* arrangement for R^1 and R^2, both are retarded by L, and both give the same product, following our proposed cycle **I** (Scheme 1). It is also interesting to note that addition of free $AsPh_3$ (the catalytic conditions often use a $Pd/AsPh_3$ ratio of 1:4), will produce a retardation of *both* rates. Moreover, it will displace the equilibrium towards the formation of more **1**, increasing the percentage of the reaction that proceeds via **1**. With the usual values of the equilibrium constants for the displacement of ligand by solvents, this effect is very pronounced, and small amounts of added L suffice to reduce the concentration of **E** to very small values. This is supported by the studies in solution that follow.

Studies in solution: With these premises in mind we can now examine the systems under discussion $[PdR^1X(AsPh_3)_2]$ (R^1 = Ph, $C_6Cl_2F_3$; X = halide) in $CDCl_3$, THF, and DMF. For this purpose we have prepared, characterized, and studied in different solutions the following compounds: $[Pd(C_6Cl_2F_3)X(AsPh_3)_2]$ (X = Cl (**3**), I (**4**)), $[(\mu\text{-}X)_2Pd_2(C_6Cl_2F_3)_2(AsPh_3)_2]$ (X = Cl (**5**), I (**6**)), $[PdPhX(AsPh_3)_2]$ (X = Cl (**7**), I (**8**)), and $[(\mu\text{-}X)_2Pd_2Ph_2(AsPh_3)_2]$ (X = Cl (**9**), I (**10**)). The compounds with $R = C_6Cl_2F_3$ were prepared by methods similar to others reported before.[16] The dimer $[(\mu\text{-}I)_2Pd_2Ph_2(AsPh_3)_2]$ was prepared from $[PdPhI(AsPh_3)_2]$ by use of $[Pd(C_6F_5)_2(OEt_2)_2]$ as an $AsPh_3$-sequestering agent [Eq. (5)], and metathesis with AgCl afforded $[(\mu\text{-}Cl)_2Pd_2Ph_2(AsPh_3)_2]$. All the compounds were fully characterized by elemental analysis and spectroscopically (see Experimental Section).

$$2\,[PdPhI(AsPh_3)_2] + [Pd(C_6F_5)_2(OEt_2)_2] \rightarrow [(\mu\text{-}I)_2Pd_2Ph_2(AsPh_3)_2] + [Pd(C_6F_5)_2(AsPh_3)_2] + 2\,OEt_2 \quad (6)$$

Two strategies used in this study are as follows. 1) A dimer $[(\mu\text{-}X)_2Pd_2(R^1)_2(AsPh_3)_2]$ is the best possible precursor to form the highest possible concentration of a solvent complex $[PdR^1X(AsPh_3)(S)]$, as there is no $AsPh_3$ set free in solution. 2) Dimers can be distinguished from monomers by NMR, by studying solutions of mixtures of complexes with different halides. An equimolar mixture of $[(\mu\text{-}Cl)_2Pd_2(R^1)_2(AsPh_3)_2]$ and $[(\mu\text{-}I)_2Pd_2(R^1)_2(AsPh_3)_2]$ will generate a new complex, the dimer with mixed bridges $[(\mu\text{-}Cl)(\mu\text{-}I)Pd_2(R^1)_2(AsPh_3)_2]$, in the statistical ratio (1:1:2). If the dimers give *cis* and *trans* isomers this could produce up to seven isomers and eight chemically inequivalent R groups (Scheme 5). A mixture of monomers $[PdR^1X(AsPh_3)(S)]$ will show only the sum of the two spectra of the monomers: two sets of R^1 signals if each monomer has a single isomer, or four sets of R^1 signals if the monomers are mixtures of the two possible isomers. The *cis* and *trans* percentages are thermodynamically (not statistically) imposed, and can be rather unequal.



Scheme 5. Possible species in solution in a mixture of two different dimers. The R groups are labeled according to their chemical equivalence or inequivalence.

Because ^{19}F NMR is very informative and the results with $R^1 = C_6Cl_2F_3$ are very clear, we start the discussion with this system.

Nature of the species detected in solutions of $[Pd(C_6Cl_2F_3)X(AsPh_3)_2]$ or $[(\mu\text{-}X)_2Pd_2(C_6Cl_2F_3)_2(AsPh_3)_2]$: Our previous experience had shown that halocomplexes $[PdRXL_2]$ with weak ancillary ligands often release ligand in $CDCl_3$. Specifically, we have reported that complexes $[Pd(C_6Cl_2F_3)ClL_2]$ (L = MeCN, SMe_2, or tetrahydrothiophene (tht)) have a high tendency, in solution, to enter into equilibria with the corresponding dimers $[(\mu\text{-}Cl)_2Pd_2(C_6Cl_2F_3)_2L_2]$ and free ligand.[16] We cursorily assigned a halobridged dimeric structure $[(\mu\text{-}X)_2Pd_2R_2L_2]$ to the products formed in solution, because these kinds of dimers are well known and many have been characterized by diffraction methods.[17] The dimers appeared as a mixture of *trans* (major) and *cis* (minor) isomers, their proportions changing with the polarity of the solvent. This tendency to displace free ligand is so high that it makes it difficult to isolate the monomeric compounds in a pure state, without contamination with some dimer. This is not apparently the case for the stronger ligand $AsPh_3$: the complex $[Pd(C_6Cl_2F_3)I(AsPh_3)_2]$, which we use profusely in our research, seems to remain unchanged in $CDCl_3$ and THF (we have never tried DMF). However, the results reported in the literature for the phenyl system warranted closer scrutiny.

$C_6Cl_2F_3$ complexes in $CDCl_3$ and in THF: In their ^{19}F NMR spectra, solutions of $[Pd(C_6Cl_2F_3)X(AsPh_3)_2]$ (X = Cl (**3**), I (**4**)) in $CDCl_3$ show only the two singlets (2:1) expected for the two equivalent F_{ortho} and the F_{para} of the perhaloaryl group. The corresponding dimers $[(\mu\text{-}X)_2Pd_2(C_6Cl_2F_3)_2(AsPh_3)_2]$ (X = Cl (**5**), I (**6**)) give rise to two sets of signals in very different proportions (7:93 for X = Cl, 10:90 for X = I), which we assign to the *cis* (minor) and the *trans* (major) isomers of the dimer. We have also found mixtures of *cis* and *trans* isomers in orthopalladated halo-bridged dimeric compounds.[18] Hartwig et al. have also reported similar mixtures,[17b] and this seems to be a frequent phenomenon. It could be argued that, if $[Pd(C_6Cl_2F_3)X(AsPh_3)(S)]$ was formed quantitatively by bridge splitting, the signals could correspond to the two possible isomers of that solvent complex. A mixing experiment can decide between monomers (no new signals arising in the mixture) and dimers. In fact the equimolar mixture of **5** and **6** produces new signals, as would be expected for the formation of $[(\mu\text{-}Cl)(\mu\text{-}I)\text{-}Pd_2(C_6Cl_2F_3)_2(AsPh_3)_2]$ (**11**). The mixed complex appears as a mixture of one *trans* (major) and two *cis* (minor) isomers (Figure 1, see Scheme 5 for labeling).

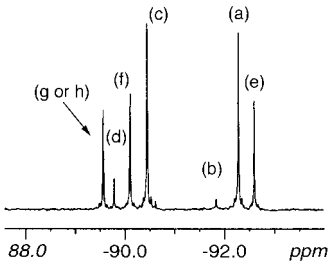


Figure 1. ^{19}F NMR spectrum of an equimolar mixture of **5** and **6** in $CDCl_3$. Only the range of the F_{ortho} signals is shown. (The small symmetric signals flanking the high singlets are spinning sidebands.) The signals are labeled as shown in Scheme 5.

The results in THF are identical, and no traces of $[Pd(C_6Cl_2F_3)I(AsPh_3)(THF)]$ can be detected. This supports the hypothesis that the transmetalation in $CDCl_3$ and in THF most probably takes place on $[Pd(C_6Cl_2F_3)I(AsPh_3)_2]$, as proposed,[2] even in the absence of added $AsPh_3$.

$C_6Cl_2F_3$ complexes in DMF: The behavior in DMF is far more complex. The dimer $[(\mu\text{-}I)_2Pd_2(C_6Cl_2F_3)_2(AsPh_3)_2]$ (**6**) shows signals for three species in an approximate ratio of 74:16:10. The signal with 16% intensity seems to correspond to the *trans* isomer of the dimer (the amount of *cis* isomer should be negligible or in fast exchange with the *trans*), whereas that of 10% intensity corresponds, unexpectedly, to $[Pd(C_6Cl_2F_3)I(AsPh_3)_2]$ (**4**). The dimer $[(\mu\text{-}Cl)_2Pd_2(C_6Cl_2F_3)_2(AsPh_3)_2]$ (**5**) also shows signals for three species in an approximate ratio of 6.5:80.5:13. The signal with 13% intensity corresponds to the *trans* isomer of the dimer (the small amount of *cis* isomer should be negligible or in fast equilibrium with the dominant *trans*), whereas that of 6.5% intensity corresponds to $[Pd(C_6Cl_2F_3)Cl(AsPh_3)_2]$ (**3**). A mixing experiment of **5** and **6** reveals that the major signals correspond to monomers, which are consequently assigned as the complexes arising from bridge-splitting by the solvent, $[Pd(C_6Cl_2F_3)X(AsPh_3)(DMF)]$ (X = Cl (**12**), I (**13**)). The surprising observation of **3** and **4**, containing additional arsine, without observation of a counterpart providing that arsine, required further checking to make sure that it was not due to accidental contamination of the dimers with some monomer. A sample of **6** was dissolved in $CDCl_3$ and was shown not to contain any significant amount of **4** (Figure 2). Successive addition of

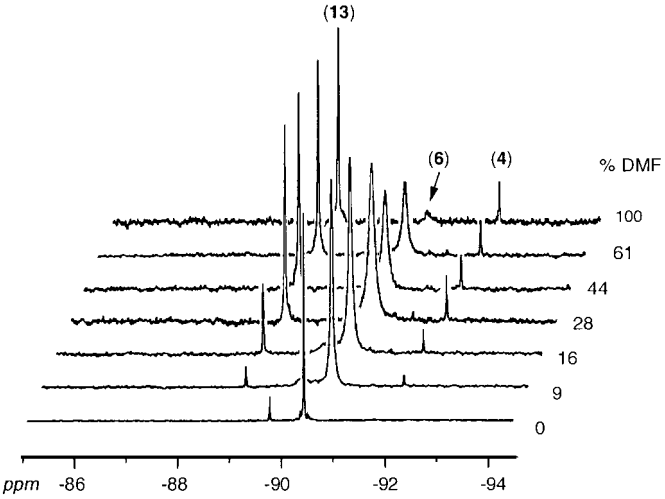


Figure 2. Changes in the ^{19}F NMR spectrum of a solution of **6** as the solvent changes from 100% $CDCl_3$ to 100% DMF, passing through mixtures. Only the range of the F_{ortho} signals is shown.

DMF unambiguously gave rise to increasing formation of **13** and **4**. This requires the formation of a counterpart that has lost $AsPh_3$ and cannot be detected. We suggest that this could be $[(\mu\text{-}I)_2Pd_2(C_6Cl_2F_3)_2(DMF)_2]$, and that the signals attributed to the dimers (which are somewhat broad) may in fact correspond to a fast equilibrium between the several possible dimers in solution.

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Fortunately, the systems simplify notably upon addition of $AsPh_3$ to produce a $Pd/AsPh_3$ ratio of 1:4, as under catalytic conditions. Then, only the signals of the monomers **3** and **4** are observed. Consequently, the likely candidates for transmetalation in DMF are also the monomeric $[Pd(C_6Cl_2F_3)X(AsPh_3)_2]$ species.

Ph complexes in $CDCl_3$ and in $[D_8]$THF: Only the 7.2–6.5 ppm range in the ^1H spectrum is informative. In that range, the H_{ortho} proton of the metallated phenyl (near 7 ppm) and the H_{para} and H_{meta} protons (near 6.5 ppm, partially overlapped with each other), are observed. As reported in the literature,[8] $[PdPhI(AsPh_3)_2]$ (**8**) gives rise in $CDCl_3$ to two sets of signals corresponding to two different chemical species (Figure 3a). Similar behavior (with a smaller proportion of the minor signal) is observed for $[PdPhCl(AsPh_3)_2]$ (**7**) (Figure 3b).

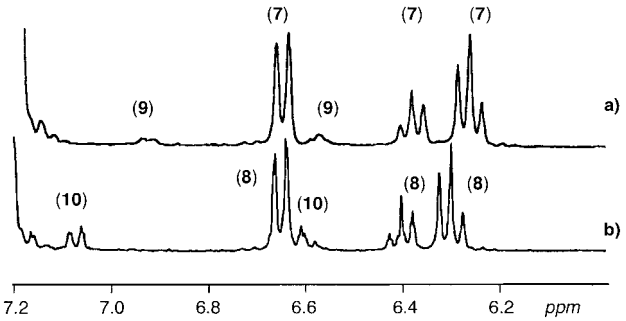

Figure 3. ^1H NMR spectrum of solutions of **7** (b) or **8** (a) in $CDCl_3$, showing the formation of the corresponding dimers in equilibrium. The major signals are, from left to right, $2H_{ortho}$ (d), $1H_{para}$ (t), $2H_{meta}$ (t).

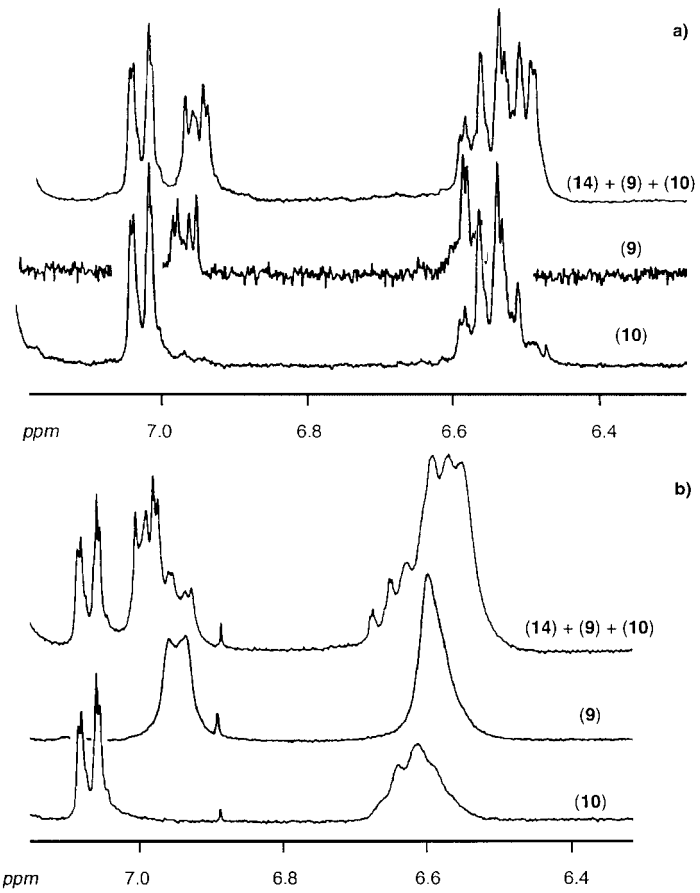

Figure 4. a) ^1H NMR spectra of solutions of the dimers **9** and **10** in $CDCl_3$. A mixture of them gives additional signals from the mixed dimer **14**. b) The same experiment in $[D_8]$THF.

The major species in each spectrum is $[PdPhX(AsPh_3)_2]$. The minor species in the solution of **8** was attributed in the literature to the so-called T-shaped $[PdPhI(AsPh_3)(S)]$,[8] but this is not correct. The signals of the minor species correspond to the only signals observed in the $CDCl_3$ solutions of the corresponding dimers $[(\mu\text{-}X)_2Pd_2Ph_2(AsPh_3)_2]$ (X = Cl (**9**), I (**10**)), and are in fact the unchanged dimers. This is supported by the following facts. 1) An equimolar mixture of $[(\mu\text{-}Cl)_2Pd_2Ph_2(AsPh_3)_2]$ (**9**) and $[(\mu\text{-}I)_2Pd_2Ph_2(AsPh_3)_2]$ (**10**) in $CDCl_3$ produced signals of the compound with mixed bridges $[(\mu\text{-}Cl)(\mu\text{-}I)Pd_2Ph_2(AsPh_3)_2]$ (**14**), as shown in Figure 4a. Although the partial overlap of the signals prevents integration, the signals appear to be approximately in the expected statistical ratio for **9**/**10**/**14** (1:1:2). 2) Vapor pressure determination on a solution of $[(\mu\text{-}I)_2Pd_2Ph_2(AsPh_3)_2]$ in $CHCl_3$ afforded a molecular weight in solution of 1245 (calculated for the dimer: 1234.48; a monomer should give half this value, while dimer/monomer equilibria should give intermediate values). The dimer does not therefore split in chloroform.

The behavior in $[D_8]$THF is identical to that described for $CDCl_3$, except for the fact that the signals of **14** overlap with those of **9** and **10** to a greater extent and are less distinctly seen (Figure 4b; the increased complexity of the signals at higher field in the mixture is particularly clear). It is likely that the $[(\mu\text{-}X)_2Pd_2Ph_2(AsPh_3)_2]$ dimers in $CDCl_3$ and in $[D_8]$THF consist of mixtures of *cis* and *trans* isomers, as this seems to be common behavior, but the lower discriminatory power of ^1H (in comparison to the previously used ^{19}F) does not permit this aspect to be recognized. Addition of excess of arsine (to make $Pd/AsPh_3$ (1:4), as in Stille catalytic conditions) generates the monomers as the only detected species.

Consequently, we can conclude that:

a) The second complex observed in solutions of $[PdPhI(AsPh_3)_2]$ in these solvents is not any kind of T-shaped complex as reported in the literature,[8] but the dimeric complex $[(\mu\text{-}I)_2Pd_2Ph_2(AsPh_3)_2]$ (**8**).
b) There is no perceptible concentration of $[PdPhI(AsPh_3)(THF)]$ or $[PdPhI(AsPh_3)]$.
c) Our decision to discount the dissociative mechanism and the intermediate proposed by Farina et al. (whether $[PdPhI(AsPh_3)]$ or $[PdPhI(AsPh_3)(THF)]$) seems correct.
d) The reaction under catalytic conditions most probably occurs on $[PdPhX(AsPh_3)_2]$.

Ph complexes in $[D_7]$DMF: The solutions in DMF are more problematic to study. The dimers give very broad signals (hardly observable) from room temperature to 223 K, suggesting the existence of at least two species in fast exchange, but any assignment is impossible. The monomers show rather broad but observable signals attributable to $[PdPhX(AsPh_3)_2]$ that integrate for about 97% of the initial monomer dissolved (by use of the CH_2 benzyl signal of $(NEt_3CH_2Ph)Cl$ for the chloro complex or the NCH_2 signal of $(NBu_4)I$ for the iodo

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complex as internal references for integration). The very minor species exchanging with the monomer are not detectable (although the broadening of those of $[PdPhX(AsPh_3)_2]$ suggests that they must exist in very small concentrations). A detailed experiment was carried out for $[PdPhI(AsPh_3)_2]$ (**8**), by dissolving it in $CDCl_3$ and adding increasing amounts of $[D_7]$DMF and finally $AsPh_3$ to produce $Pd/AsPh_3$ (1:4) (Figure 5). The successive addition of DMF produces increasing broadening of the signals of the dimer (in equilibrium with the monomer), which eventually becomes unobservable when the solvent is predominantly DMF. The signals of $[PdPhI(AsPh_3)_2]$ do not noticeably lose intensity, and undergo a slower broadening. All this suggests the existence of a third species in solution, probably $[PdPhI(AsPh_3)(S)]$, unobservable but in fast exchange with **8** (and with the remaining **10**), producing the broadening. This result is basically consistent with the observations by cyclic voltammetry reported in the literature.[8] The addition of a small amount of $AsPh_3$ very quickly restores a fairly sharp spectrum of **8**, which recovers 100% of integration relative to the internal reference, showing that the concentration of any other complex in solution must be extremely small. In DMF, in solutions of **8** with the excess of $AsPh_3$ conventionally used in catalysis, the absolutely dominant species and likely candidate to undergo transmetalation, is—as in the other solvents studied here—the monomer $[PdPhI(AsPh_3)_2]$.

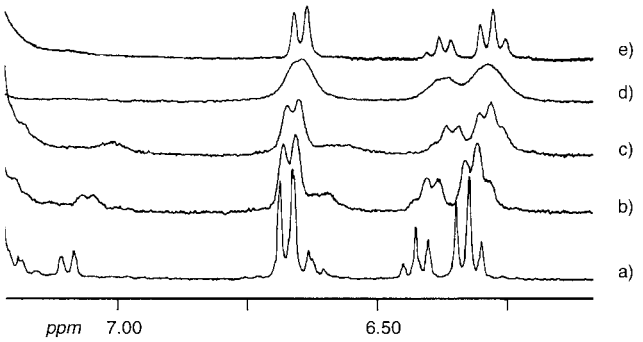
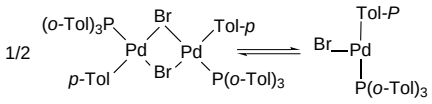


Figure 5. Changes in the ^1H NMR spectrum of a solution of **8** in $CDCl_3$/$[D_7]$DMF mixtures: a) 1:0, b) 1:0.6, c) 1:1, d) 0:1 in volume, e) solution of **8** + 2 $AsPh_3$ in $[D_7]$DMF.

Additional comments: The observations reported in this paper and in our previous publications afford the order of coordinating ability of the ligands involved as $AsPh_3$ > DMF > X–Pd > THF ≫ $CDCl_3$, although the solvents are in much higher concentration than $AsPh_3$ or X–Pd. In fact, solutions of dimers in $CDCl_3$ are not completely split by moderate amounts of DMF, showing that the real coordinating ability to Pd at comparable ligand concentrations should be $AsPh_3$ > X–Pd > DMF > THF ≫ $CDCl_3$. The results also indicate that the substitution of a better donating ligand for a worse donating ligand is easier for the more electron-rich complexes (Ph > $C_6Cl_2F_3$; I > Cl).

Although there are reports of cationic $ArPd(PPh_3)_2^+$ with TfO^- or BF_4^- as the counterion, it is even less likely that an observable cationic species will be a T-shaped 14-electron compound, since its tendency to coordinate any electron-donating moiety, to become 16-electron square-planar, must be higher than for the neutral species studied here. The triflate complexes (Ar = *p*-ClC_6H_4, *p*-$NO_2C_6H_4$) in DMF were described as separated ion-pairs $ArPd(PPh_3)_2^+ + TfO^-$ "strongly solvated by DMF"; in toluene as "not covalent but totally ion-paired" ($ArPd(PPh_3)_2^+$, TfO^-); and in THF as an equilibrium between "solvated" and "totally ion-paired" species.[19a] In view of our results here and in our previous paper,[3] it is clear that the solutions in coordinating solvents (such as DMF) must be formulated as solvent-coordinated (rather than "solvated") complexes $[ArPd(PPh_3)_2(S)](TfO^-)$ (S = DMF); solutions in THF as equilibria between $[ArPd(PPh_3)_2(S)](TfO^-)$ and $[ArPd(PPh_3)_2(TfO)]$; and in toluene solution or in the solid state as covalent triflato complexes $[ArPd(PPh_3)_2(TfO)]$, rather than as "ion-paired".[20] The same holds for the tetrafluoroborate complex (Ar = Ph).[19b, 21] Consistently with this reformulation, the substitution reactions assigned a dissociative S_N1 mechanism,[19b, 21] must in reality be associative S_N2 reactions involving the participation of solvent as ligand.

The best candidate for a true observation of a transmetalation on a T-shaped 14-electron complex is the report by Louie and Hartwig on the behavior of $[(\mu\text{-}Br)_2Pd_2(p\text{-}Tol)_2\{P(o\text{-}Tol)_3\}_2]$ (**15**). This complex undergoes stoichiometric transmetalation with organotin aryl, thiolate, and amide compounds. The transmetalation was described as "an unusual type of dissociative ligand substitution reaction", based on the fact that kinetic studies in a non-coordinating solvent afford a rate law dependence on the square root of the concentration of dimer ($[\mathbf{15}]^{1/2}$).[22] The properties of **15** are quite unique: addition of $P(o\text{-}Tol)_3$ does not split **15**, nor does it retard transmetalation on **15** from stannanes, showing that the formation of $[Pd(Tol\text{-}p)Br\{P(o\text{-}Tol)_3\}_2]$ is severely hindered. The rate law observed is only consistent with a preequilibrium in which a molecule of dimer gives two of monomer, but this is not conclusive proof of a 14-electron T-shaped complex.



On the assumption that the monomer formed is not $[Pd(Tol\text{-}p)Br\{P(o\text{-}Tol)_3\}(S)]$, since the solvent is non-coordinating, there is still another way to stabilize the monomer as a 16-electron complex, in the form of an agostic complex.[23] It is well known that bulky phosphines are prone to cyclometalation. For instance, $PR_2(Tol\text{-}o)$ or PR_2Mes ligands are metallated in the tolyl methyl or in the mesityl methyl group to give a five-membered metalla-ring.[24] The same kinds of bulky ligands propitiate the formation of agostic interactions between the metal and C–H bonds.[25] In fact, it is widely accepted that cyclometalation is initiated by an agostic interaction with the σ(C–H) orbital followed by back-donation to the σ^*(C–H) orbital. Thus, the existence of complexes with cyclopalladated *o*-tolyl phosphine suggests that agostic interaction is possible whenever a coordination

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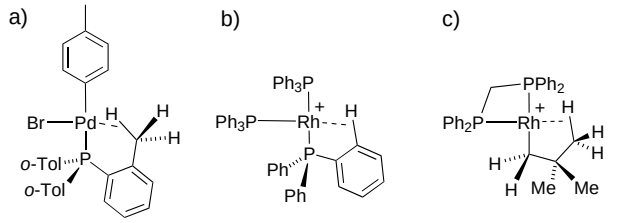
site *cis* to the phosphine is available. It seems reasonable that the monomeric species [Pd(Tol-*p*)Br{P(*o*-Tol)$_3$}] might be stabilized by an agostic interaction involving the empty orbital on Pd and the electron pair of the C–H bond of a methyl group (see below, a)). Since this intermediate is not spectroscopically observable because of its very low concentration, this hypothesis cannot be demonstrated or disproved, but existing crystallographic data on similar complexes make it a very attractive suggestion.



In effect, there are many X-ray structures that show agostic C–H bonds involved in agostic interaction to the empty coordination site of otherwise T-shaped d^8 complexes.[26] This evidence goes back to the pioneering study of the structure of [Rh(PPh$_3$)$_3$](ClO$_4$) (the proposed 14-electron species in Wilkinson's catalyst) in which the *ortho* C–H of one of the phenyl groups is involved in agostic bonding b) (see above),[27] and continues through many reports until the very recent [RhNp(κ^2-dtbpm)] (Np = neopentyl; dtbpm = Bu*t*PCH$_2$P-*t*Bu), where again an agostic interaction occupies the fourth coordination position (c).[28] These agostic ligands are very weakly bonded and can easily be displaced. For instance, [{RhNp(κ^2-dtbpm)}$_2$(μ-η^1:η^1-N$_2$)] is formed on subjection of [RhNp(κ^2-dtbpm)] to 1 bar of N$_2$. Thus, from a conciliatory point of view, if a formally 16-electron agostic complex is not quite a T-shaped 14-electron species, it is probably the existing intermediate closest to it.

Conclusion

Although 14-electron species are conceivable as transition states in many reactions—such as reductive elimination, isomerization, ligand rotations, and sometimes ligand substitution—it is unlikely that a detectable concentration of these highly unsaturated species can survive in a condensed state. In fact, close scrutiny of the reports of such observations always affords a more plausible interpretation in which the low-lying Pd orbital that should be empty in a T-shaped compound becomes involved in some kind of bonding. The determination of activation parameters for the reactions (particularly activation volumes) can convincingly support the nature of 3-coordinated *transition states*, but fragmentary kinetic results are misleading as evidence of the existence of 3-coordinated *intermediates*. Ligand associative substitution by the solvent or in an intramolecular process can easily be mistaken for a dissociation. Retardation of the rate by addition of the ligand being released, which is often taken as evidence of a dissociative preequilibrium, seems more often to be associated with an associative interchange mechanism (I_a),[29] which is the usual pathway for ligand substitution in Pd^{II} complexes. This is certainly the case for the transmetalation step in the conditions of the Pd-catalyzed coupling of organic halides or triflates and stannanes (Stille reaction), which is simply a variant of associative ligand substitution in Pd.

Experimental Section

Note Added in Proof

The X-ray structures of [PdArX(P*t*Bu$_2$R)](Ar = Ph, X = Br, R = adamantyl; Ar = 2,4-xylyl, X = I, R = *t*Bu) have been reported while this paper was in print. They come to support our view that apparently three-coordinated T-shaped Pd^{II} complexes do get involved in agostic bonds when no better possibility is available, to fill the supposedly open site and make the Pd^{II} tetracoordinate.[30]

General comments: All reagents were purchased from commercial sources and used as received. Solvents were dried by known procedures and distilled under nitrogen prior to use. ^{1}H NMR (300.16 MHz) and ^{19}F NMR (282.4 MHz) spectra were recorded on a Bruker ARX 300 instrument equipped with a VT-100 variable-temperature probe. Chemical shifts are reported in ppm from tetramethylsilane (^{1}H) or CCl$_3$F (^{19}F), with positive shifts downfield, at ambient probe temperature unless otherwise stated. In ^{19}F NMR spectra registered in non-deuterated solvents, a coaxial tube containing [D$_6$]acetone was used to maintain the lock ^{2}H signal, and the chemical shifts are reported from the CCl$_3$F signal in deuterated acetone. Combustion CHN analyses were made on a Perkin–Elmer 2400 CHN microanalyzer. Infrared spectra were recorded on a Perkin–Elmer 843 apparatus (range 4000–200 cm^{-1}) with Nujol mulls between polyethylene sheets or in dichloromethane solution between NaCl plates. The molecular weight measurements were performed in a Knauer vapor pressure osmometer in CHCl$_3$ at 303 K. The precursors [PdCl(C$_6$Cl$_2$F$_3$)(AsPh$_3$)$_2$] (**3**),[2] [PdI(C$_6$Cl$_2$F$_3$)(AsPh$_3$)$_2$] (**4**),[2] (NBu$_4$)$_2$[Pd$_2$(C$_6$F$_5$)$_4$(μ-Br)$_2$],[31] and [PdIPh(AsPh$_3$)$_2$] (**8**)[8] were prepared by published methods.

Synthesis and NMR data of the complexes

[Pd$_2$(μ-Cl)$_2$(C$_6$Cl$_2$F$_3$)$_2$(AsPh$_3$)$_2$] (5): PdCl$_2$ (17.9 mg, 0.101 mmol) was added to a solution of [Pd(C$_6$Cl$_2$F$_3$)$_2$(AsPh$_3$)$_2$] (112.9 mg, 0.101 mmol) in acetone (25 mL). The suspension was heated under reflux for 12 h and filtered through Celite. The resulting yellow solution was concentrated to 10 mL, *n*-hexane (10 mL) was added, and the solution was further concentrated until crystallization of the product. The yellow solid was filtered, washed with hexane, and vacuum-dried. The crude product was recrystallized from CH$_2$Cl$_2$/EtOH. Yield 110 mg (84%). ^{19}F NMR (CDCl$_3$; there are signals assigned to two isomers (*cis* and *trans*) in a *cis*/*trans* ratio of 7:93): δ_{cis} = −91.85 (s; F$_{ortho}$), −118.41 (s; F$_{para}$); δ_{trans} = −92.30 (s; F$_{ortho}$), −118.41 (s; F$_{para}$; overlapped with *cis* F$_{para}$); ^{19}F NMR (THF; *cis*/*trans* isomers (2:98)): δ_{cis} = −90.07 (s; F$_{ortho}$), −120.69 (s; F$_{para}$); δ_{trans} = −91.65 (s; F$_{ortho}$), −119.00 (s; F$_{para}$); ^{19}F NMR (DMF; the spectrum shows signals from three complexes): **3** (5%): δ = −90.17 (s; F$_{ortho}$), −120.44 (s; F$_{para}$); **12** (83%): δ = −90.43 (s; F$_{ortho}$), −120.70 (s; F$_{para}$); **5** (*cis* + *trans*) (12%): δ = −92.06 (s; F$_{ortho}$), −119.78 (s, *p*-F); elemental analysis calcd (%) for C$_{48}$H$_{30}$As$_2$Cl$_6$F$_6$Pd$_2$: C 44.48, H 2.33; found C 44.50, H 2.42.

[Pd$_2$(μ-I)$_2$(C$_6$Cl$_2$F$_3$)$_2$(AsPh$_3$)$_2$] (6): Solid NaI (29.7 mg, 0.1984 mmol) was added to a stirred solution of [Pd$_2$(μ-Cl)$_2$(C$_6$Cl$_2$F$_3$)$_2$(AsPh$_3$)$_2$] (59.1 mg, 0.0456 mmol) in CH$_2$Cl$_2$/acetone (5+5 mL). After one hour the solvent was evaporated and the product was extracted with CH$_2$Cl$_2$ (3 × 5 mL). The solution was filtered and concentrated to 5 mL. The product was precipitated by addition of *n*-hexane, filtered, recrystallized from CH$_2$Cl$_2$/EtOH, and vacuum-dried (28.5 mg, 42%). ^{19}F NMR (CDCl$_3$; signals assigned to two isomers (*cis*/*trans* 10:90)): δ_{cis} = −89.80 (s, 2F; F$_{ortho}$), −118.64 (s, 1F; F$_{para}$); δ_{trans} = −90.46 (s, 2F; F$_{ortho}$), −118.94 (s, 1F; F$_{para}$); ^{19}F NMR (THF; *cis*/*trans* (15:85)): δ_{cis} = −89.23 (s; F$_{ortho}$), −118.96 (s, 1F, F$_{para}$); δ_{trans} = −89.71 (s, 2F; F$_{ortho}$), −119.23 (s, 1F; F$_{para}$); ^{19}F NMR (DMF; the spectrum shows signals from three complexes): **13** (74%): δ_{13} = −87.95 (s; F$_{ortho}$), −121.10 (s; F$_{para}$); **4** (10%): δ = −91.05 (s; F$_{ortho}$), −120.09 (s; F$_{para}$); **6** (*cis* + *trans*) (16%): δ = −89.67 (s; F$_{ortho}$), −118.70 (s; F$_{para}$);

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elemental analysis calcd (%) for $C_{48}H_{30}As_2Cl_4F_6I_2Pd_2$: C 38.98, H 2.04; found C 39.17, H 2.08.

^1H NMR in $CDCl_3$/[D_7]DMF mixtures: The complex (9.8 mg, 6.6 μmol) was dissolved in $CDCl_3$ (0.5 mL) and spectra were recorded after the addition of increasing volumes of DMF (0.00, 0.05, 0.10, 0.20, 0.40, 0.60, and 0.80 mL). The starting signals from *cis* and *trans* **6** coalesced and gradually decreased, while signals of two new complexes, **13** and **4**, appeared at: $\delta =$ −87.95 (s; F_{ortho}), −91.05 (s; F_{ortho}), −120.09 (s; F_{para}), −121.10 (s; F_{para}) (chemical shifts reported relative to CCl_3F in DMF).

[PdIPh(AsPh$_3$)$_2$] (8) NMR data: ^{1}H NMR ($CDCl_3$; 17.4 mg in 0.5 mL solvent): samples of the pure compound show the signals due to **8** and **10** (78:22); ^{1}H NMR ([D_8]THF; 23.4 mg in 0.5 mL of solvent): $\delta = 7.46 - 7.22$ (m, 30 H; $AsPh_3$), 6.69 (d, $J = 7.3$ Hz, 2 H; H_{ortho} Ph−Pd), 6.39 (m, 1 H; H_{para} Ph−Pd), 6.29 (m, 2 H; H_{meta} Ph−Pd). The sample also shows signals due to **10** (chemical shifts reported below) with a relative intensity **8**/**10** 67:33; ^{1}H NMR ([D_7]DMF; 15.41 mg, 0.0167 mmol in 0.75 mL solvent): $\delta = 7.6 - 7.3$ (m, 30 H; $AsPh_3$), 6.83 (broad, 2 H; H_{ortho} Ph−Pd), 6.43 (m, 3 H; H_{para} and H_{meta} Ph−Pd). The integrals accounted for 97% of the dissolved product relative to the integrals of $(NBu_4)I$ (1.245 mg, 3.37 μmol) as internal standard. After the addition of $AsPh_3$ (10.2 mg, 0.0334 mmol) the intensity of the Ph−Pd signals increased until reaching a value of 100% relative to the internal standard. The same result was obtained for the chloro complex with $[C_6H_5CH_2(C_2H_5)_3N]Cl$ as internal standard.

[Pd$_2$(μ-I)$_2$Ph$_2$(AsPh$_3$)$_2$] (10): A solution of $[Pd(C_6F_5)_2(Et_2O)_2]$ was prepared as follows. $[Pd_2(\mu\text{-}Br)_2(C_6F_5)_4](NBu_4)_2$ (143.8 mg, 0.094 mmol) was added to a stirred solution of $AgBF_4$ (36.7 mg, 0.188 mmol) in acetone (30 mL). After one hour the AgBr was removed by filtration, and the solvent was evaporated. The product was extracted into diethyl ether (3 × 5 mL), filtered, and immediately used.

[PdIPh($AsPh_3$)$_2$] (348.4 mg, 0.377 mmol) was added to the freshly prepared solution of $[Pd(C_6F_5)_2(Et_2O)_2]$, cooled at 0 °C. The mixture was stirred for one hour, during which time $[Pd_2(\mu\text{-}I)_2Ph_2(AsPh_3)_2]$ precipitated as a brown solid. The crude product was recrystallized from CH_2Cl_2/hexane. Yield: 0.1375 g (59%). ^{1}H NMR ($CDCl_3$): $\delta = 7.32$ (m, 12 H; $AsPh_3$), 7.27 (m, 18 H; $AsPh_3$), 7.10 (d, $J = 8$ Hz, 4 H; H_{ortho} Ph−Pd), 6.64 (m, 4 H_{meta} and 2 H_{para} Ph−Pd); ^{1}H NMR ([D_8]THF): $\delta = 7.37 - 7.21$ (m, 30 H; $AsPh_3$), 7.03 (d, 4 H; *o*-Ph−Pd), 6.54 (m, 4 H_{meta} and 2 H_{para} Ph−Pd); elemental analysis calcd (%) for $C_{48}H_{40}As_2I_2Pd_2$: C 46.75, H 3.27; found C 46.13, H 3.03; M_w: calcd 1234.48; found 1245.86 g mol^{-1}.

^{1}H NMR ($CDCl_3$/[D_7]DMF mixtures): The complex (5 mg, 4.1 μmol) was dissolved in $CDCl_3$ (0.7 mL) and spectra were recorded after the addition of increasing amounts of [D_7]DMF (0.00, 0.05, 0.12, 0.22, 0.44, and 0.70 mL). The addition of DMF induces the coalescence of the signals. After the addition of 0.12 mL, the Ph−Pd signals appear as broad bumps. The coalescence is not resolved by cooling the sample to 213 K, nor by further addition of DMF.

[PdClPh(AsPh$_3$)$_2$] (7): Freshly prepared AgCl (102.3 mg, 0.714 mmol) was added to a solution of [PdIPh($AsPh_3$)$_2$] (0.3297 g, 0.357 mmol) in acetone (40 mL) under nitrogen atmosphere and the solution was stirred overnight. The desired product, which precipitated with the silver halides, was extracted from the precipitate with CH_2Cl_2 (5 × 5 mL) and the resulting solution was filtered through Celite. The solvent was evaporated to dryness and the residue was washed with ether, filtered, and vacuum-dried (0.2367 g, 80%). ^{1}H NMR ($CDCl_3$; 8.6 mg in 0.5 mL of solvent): $\delta = 7.4 - 7.2$ (m, 30 H; $AsPh_3$), 6.70 (d, 2 H, $J = 7$ Hz; H_{ortho} Ph−Pd), 6.43 (m, 1 H; H_{para} Ph−Pd), 6.31 (m, 2 H; H_{meta} Ph−Pd); signals of **9** (see below for chemical shift data) give integrals in a ratio **7**/**9** 90:10; ^{1}H NMR ([D_8]THF; 8.7 mg in 0.5 mL of solvent): $\delta = 7.46 - 7.19$ (m; $AsPh_3$), 6.70 (d, 2 H, $J =$ 7 Hz; H_{ortho} Ph−Pd), 6.34 (m, 1 H; H_{para} Ph−Pd), 6.24 (m, 2 H; H_{meta} Ph−Pd); **7**/**9** ratio 85:15; elemental analysis calcd (%) for $C_{42}H_{35}As_2PdCl$: C 60.58, H 4.23; found C 59.96, H 4.24.

[Pd$_2$(μ-Cl)$_2$Ph$_2$(AsPh$_3$)$_2$] (9): An excess of freshly prepared AgCl (69.2 mg, 0.483 mmol) was added to a solution of **2** (0.1598 g, 0.129 mmol) in acetone (40 mL). The suspension was stirred overnight. The solution was filtered through Celite to remove the silver halides and the insoluble residue was washed with CH_2Cl_2 (3 × 10 mL), the combined solutions was evaporated to 5 mL, and ether (10 mL) was added. The resulting precipitate was filtered, washed with ether, and vacuum-dried (65 mg, 48%). ^{1}H NMR ($CDCl_3$): $\delta = 7.4 - 7.2$ (m, 30 H; $AsPh_3$), 6.97 (m, 4 H; *o*-Ph−Pd), 6.63 (m, 6 H; *p*- and *m*-Ph−Pd); ^{1}H NMR ([D_8]THF): $\delta = 7.4 - 7.2$ (m, 30 H; $AsPh_3$), 6.92 (m, 4 H_{ortho} Ph−Pd), 6.56 (m, 4H_{meta} and 2H_{para} Ph−Pd); elemental analysis calcd (%) for $C_{48}H_{40}As_2Cl_2Pd_2$: C 54.88, H 3.84; found C 54.51, H 3.70.

1:1 Mixtures of [Pd$_2$(μ-Cl)$_2$(C$_6$Cl$_2$F$_3$)$_2$(AsPh$_3$)$_2$] and [Pd$_2$(μ-I)$_2$(C$_6$Cl$_2$F$_3$)$_2$(AsPh$_3$)$_2$]

In $CDCl_3$: $[Pd_2(\mu\text{-}Cl)_2(C_6Cl_2F_3)_2(AsPh_3)_2]$ (6.0 mg, 4.7 μmol) and $[Pd_2(\mu\text{-}I)_2(C_6Cl_2F_3)_2(AsPh_3)_2]$ (6.9 mg, 4.7 μmol) were dissolved in $CDCl_3$ (0.5 mL). The ^{19}F NMR spectrum shows signals of the *cis* and *trans* isomers of the starting complexes (29% of *trans*-**6**, 4% of *cis*-**6**, 25% of *trans*-**5**, and 2% of *cis*-**5**), and the groups of signals of two new compounds *trans*-**11** (28%) and *cis*-**11** (12%). ^{19}F NMR ($CDCl_3$): $\delta_{trans\text{-}11} = -90.12$ (s; F_{ortho}), −92.61 (s; F_{ortho}), −118.33 (s; F_{para}), −119.06 (s; F_{para}); $\delta_{cis\text{-}11} = -89.58$ (s; F_{ortho}), −118.75 (s; F_{para}).

In THF: A solution of $[Pd_2(\mu\text{-}Cl)_2(C_6Cl_2F_3)_2(AsPh_3)_2]$ (6.0 mg, 4.7 μmol) and $[Pd_2(\mu\text{-}I)_2(C_6Cl_2F_3)_2(AsPh_3)_2]$ (6.9 mg, 4.7 μmol) in THF (0.5 mL) was prepared. The ^{19}F NMR spectrum shows signals of the *cis* and *trans* isomers of the starting complexes, and the next groups of broad signals of *trans*-**11** and *cis*-**11**: ^{19}F NMR (THF): $\delta = -89.15$ (s), −89.40 (s), −91.94 (s), −118.81 (s), −119.07 (s), −119.45 (s).

The spectrum was recorded again after the addition of $AsPh_3$ (17.3 mg, 56.4 μmol) to the sample. Only signals of **3** and **4** were observed.

In DMF: $[Pd_2(\mu\text{-}Cl)_2(C_6Cl_2F_3)_2(AsPh_3)_2]$ (6.2 mg, 5.0 μmol) and $[Pd_2(\mu\text{-}I)_2(C_6Cl_2F_3)_2(AsPh_3)_2$ (7.4 mg, 5.0 μmol) were dissolved in DMF (0.5 mL). The spectrum shows the sum of the signals of the starting compounds in this solvent (see above) ^{19}F NMR (DMF): $\delta = -87.95$ (s), −88.5 (s), −89.0 (s), −89.69 (s), −90.17 (s), −90.44 (s), −91 (s), −92.08 (s), −118.70 (s), −119.73 (s), −120.13 (s), −120.44 (s), −120.71 (s), −121.14 (s).

The spectrum was recorded again after the addition of $AsPh_3$ (17.3 mg, 56.4 μmol) to the sample. Only signals of **3** and **4** were observed.

1:1 Mixtures of [Pd$_2$(μ-Cl)$_2$Ph$_2$(AsPh$_3$)$_2$] and [Pd$_2$(μ-I)$_2$Ph$_2$(AsPh$_3$)$_2$]

In $CDCl_3$: $[Pd_2(\mu\text{-}Cl)_2Ph_2(AsPh_3)_2]$ (1.95 mg, 1.85 μmol) and $[Pd_2(\mu\text{-}I)_2Ph_2(AsPh_3)_2]$ (2.30 mg, 1.85 μmol) were dissolved in $CDCl_3$ (0.5 mL). ^{1}H NMR: $\delta = 7.5 - 7.15$ (m, 30 H; $AsPh_3$), 7.08 – 6.99 (m, 4 H; H_{ortho} Ph−Pd), 6.75 – 6.59 (m, 6 H; H_{para} and H_{meta} −Pd).

The spectrum was recorded again after the addition of $AsPh_3$ (17.3 mg, 56.4 μmol) to the sample. Only signals of **7** and **8** were observed.

In [D_8]THF: $[Pd_2(\mu\text{-}Cl)_2Ph_2(AsPh_3)_2]$ (2.07 mg, 1.97 μmol) and $[Pd_2(\mu\text{-}I)_2Ph_2(AsPh_3)_2]$ (2.43 mg, 1.96 μmol) were dissolved in [D_8]THF (0.50 mL). ^{1}H NMR: $\delta = 7.4 - 7.2$ (m, 30 H; $AsPh_3$), 7.05 – 6.92 (m, 4 H; *o*-Ph−Pd), 6.6 – 6.5 (m, 6 H; *p*- and *m*-Ph−Pd).

The spectrum was recorded again after the addition of $AsPh_3$ (7.23 mg, 23 μmol) to the sample. Only signals of **7** and **8** were observed.

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