Cross Alkyl-Aryl Versus Homo Aryl-Aryl Coupling in Pd-catalyzed Coupling of Alkyl-Gold(I) and Aryl-X (X = Halide)

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ABSTRACT Experiments on palladium catalyzed cross-coupling of [AuMe(PPh3)] with aryl iodides show that Ar–Ar homo-coupling products are the major product or an abundant by-product of the reaction. The percentage of cross-coupling product is higher for aryls with larger 𝛼p, Hammet parameter. The scrambling of organic groups via bimetallic intermediates explains the formation of these products. This scrambling can be observed and the activation energies partially quantified in some cases using as aryl C6H3F3, which is relatively reluctant to coupling.

Introduction
In recent years many metal catalyzed processes involving organogold derivatives as stoichiometric reagents or as intermediates have been developed.1 Transmetalation reactions between organogold and zirconium,2 iron and ruthenium,3 rhodium,4 nickel,5 or palladium,6,7 have been reported. The use of gold has been particularly studied in palladium cross-coupling reactions, where gold complexes have been used not only as stoichiometric reagents,6,7 but also as cocatalysts in the gold-cocatalyzed Stille reaction,8,9 in Sonogashira-like cross-coupling,10 in the carbometalation of alkynes,11 and in processes combining gold-catalyzed cyclizations with cross-coupling processes.12,13,14

The kinetics and thermodynamics of the transmetallation involving Au and Pd8, which should influence the success of the bimetallic process,9,10,15,16 are only scarcely studied. Our seminal mechanistic studies on the Au8/Pd8 aryl transmetallation have shown that the formation of [PdRfL2] (Rf = C6H3F3) from [Pd(C6H3F3)2XL2] (X = Cl; L = AsPh3) and [AuRfL] is an endergonic process that occurs via intermediates and transition states stabilized by Pd-Au metalophilic interactions (Eq. 1). In other words, this exchange equilibrium is very shifted towards the formation of [PdRfL(AsPh3)] + [AuRfL]. The transmetallation occurs via replacement of one ancillary ligand in the palladium coordination sphere by the entering gold complex.15 Similar conclusions have been drawn in a recent computational study of the transmetallation between vinylgold and arylpalladium complexes.7

This suggests that the participation of intermediates type A formed by associative ligand substitution, and also the thermodynamic evolution indicated in Eq. 1 can be fairly general for Au8/Pd8 catalytic systems. The displacement of the equilibrium towards the right is expected to be more marked the more nucleophilic the hydrocarbyl groups.

In spite of the disfavored equilibrium, the cross-coupling processes from [PdRfXL2] and [AuRfL] do work, provided that the irreversible R1–R2 coupling is kinetically effective. However, since the transmetalation is a reversible equilibrium, concomitant reactions such as isomerization,18 or gold mediated ligand scrambling between metal centers (whether involving R, I, or X groups) can occur before the coupling takes place.9 These side-reactions are a potential complication, more likely to be influential in systems where the reductive elimination at the palladium center is slow, as it is the case for C(sp3) groups. It is well known that, for common aryl and alkyl groups, the reductive elimination occurs on cis-[Pd(RF)2L2] intermediates at a rate that follows the order CAr > CAr > CAr > CAr > CAr > CAr.19,20,21 According to this,22 Me–Ar coupling should be faster than Me–Me, but slower than Ar–Ar.23

In spite of this undesired complication, C(sp3) systems are particularly appealing for gold catalysis because the stability of alkylgold(I) complexes makes them potentially valuable reagents for C(sp3)–C(sp3) coupling in bimetallic processes.24 Sarandeses et al. have used [Au2(Bu)2(PPh3)] in alkyl-aryl palladium catalyzed cross-coupling experiments, but the results were not good for cross-coupling of [Au2(Bu)2(PPh3)] with 4-iodotoluene, which afforded only 4,4’-dimethylbiphenyl with 4-Br or 4-TIO-acetophenone the yields in cross-coupling product were low.5 However, Hashmi et al. have reported recently good yields in the cross coupling of [AuMe(PPh3)] with 4-iodobenzoimide (83% yield of 4-methyl benzoinonitrile after three days at 60 °C).2 Here we report an experimental mechanistic study of the Pd catalyzed Me–Ar coupling of AuMe and ArI systems, trying to better understand the circumstances of this coupling.

Results and discussion
In a typical process, the reaction of [AuMe(PPh3)] with p-CF3C6H4I catalyzed by trans-[Pd(C6H4CF3PPh3)2] (5%), NMR monitored in THF-d8 at 50 °C, led to the competitive formation of the cross-coupling product p-CF3C6H4Me and the homo-coupling product 4,4’-bistrifluoromethylbiphenyl, in 4:1 ratio (Eq. 2). Gold mirror was not observed and the products do not fit the expectations in case of redox incompatibility suggested by Webber and Gagné for other cases.15 Thus, as in a recent study by Blum,12a redox incompatibility can be discarded here.
The results of experiments with other aryl iodides are summarized in Table 1. A reasonable correlation is found between the percentage of cross-coupling product and the $\sigma_p$ Hammet parameter for the aryls, and aryls with larger $\sigma_p$ produce less Ar–Ar homocoupling.

Table 1. Hetero/ homocoupling ratios versus Hammet $\sigma_p$ values

<table>
<thead>
<tr>
<th>Ar-I</th>
<th>Hammet $\sigma_p$</th>
<th>Ar-Me/Ar-Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p$-NO$_2$C$_6$H$_4$I</td>
<td>0.78</td>
<td>6.3</td>
</tr>
<tr>
<td>$p$-CF$_3$C$_6$H$_4$I</td>
<td>0.54</td>
<td>4.4</td>
</tr>
<tr>
<td>$p$-FC$_3$H$_4$I</td>
<td>0.06</td>
<td>2.4</td>
</tr>
<tr>
<td>$p$-CH$_2$C$_6$H$_4$I</td>
<td>-0.17</td>
<td>2.8</td>
</tr>
<tr>
<td>$p$-CH$_3$OC$_6$H$_4$I</td>
<td>-0.26</td>
<td>2.4</td>
</tr>
</tbody>
</table>

In order to get insight into the mechanism we moved to use C$_6$H$_5$Cl$_3$F$_3$ (Rf) as aryl, which should slow down the different steps of the reaction and facilitate the detection of other possible intermediates or byproducts such as cis and trans-[PdRfR]$_2$[PF$_3$]$_2$ [Rf and Cl$_2$] (Pd(0) and subsequent isomerizations have formed the trans-[Pd(0)]$_2$ intermediate for both metals to avoid observational complications associated to L exchanges that we have studied elsewhere. The reaction of trans-[PdCl$_2$(PPh$_3$)$_2$] (1) with excess of [AuMeL] (2) in THF at 50 °C, was monitored by $^{19}$F NMR (Figure 1). Note that the use of large excess of [AuMeL] does not obscure perfect monitoring by $^{19}$F NMR.

The disappearance of 1 and the formation of [AuRfL] (3, L = PPh$_3$) as the main product were observed. The reaction was complete in about 10 h at rt. The presence of the other product, trans-[PdMeCl$_2$(PPh$_3$)$_2$] (4), was confirmed by $^{31}$P NMR. It is interesting to note that only a small amount of cross-coupling product RfMe and nothing of the homo-coupling RF–RF products was observed, as expected from the reluctance of Rf to participate in reductive elimination. After 17 h a small amount of ethene was also observed in the $^1$H NMR. The high activation energy of these coupling processes (RF–RF, RF–Me or Me–Me), and the different nature of the two organic groups allow for observation of some exchange processes in solution.

A kinetic study (initial rates method), based on the rate of consumption of 1, showed that the reaction kinetics is close to first order in gold complex (kinetic order for 2 = 0.8), and is retarded by addition of phosphine to the solution (kinetic order for [PPh$_3$] = -1). Moreover, the plot of 1/$k_{obs}$ vs. [PPh$_3$] gives a straight line. Applying the steady state approximation to an intermediate B (Eq. 3) in which one phosphine has been displaced, a rate constant $k_1$ ≈ 1.2 x 10$^{-3}$ is found, which affords $\Delta G^\circ_{25} = 23.3$ kcal mol$^{-1}$. The study of the reaction in the temperature range 280–327 K supports an associative phosphine substitution process in solution with $\Delta H = 63.9$ kJ mol$^{-1}$ and $\Delta S = 95.5$ J K$^{-1}$ mol$^{-1}$. This fits the expectations from our previous study on Au(aryl)/Pd(aryl) transmetallation.

The formation of 3 and 4 indicates the thermodynamic result of group exchange in the absence of coupling, but it does not mean that Eq. 3 is the only pathway from 1 and 2 to 3 and 4. For instance, the observation of some RF–Me proves that undetected cis-[PdRfMe(PPh$_3$)$_2$] (7) must have been formed too during the reaction, but having a high activation energy towards coupling and being high in energy compared to alternative products it never reaches observable concentration. Similarly, a small amount of the exchange product [AuC$_6$H$_5$(CF$_3$)$_2$P(OMe)$_3$] was detected by $^{31}$P NMR at early stages of the catalysis in Eq. 2. Overall, the molecules that are known to participate, either because they are observed directly or because they are deduced indirectly through observation of their byproducts, suggest that the reactions in equations 3-7 (L = PPh$_3$) are competitively operating in the process, even if some of them involve undetected products.

![Figure 1](image-url)  
**Figure 1.** Concentration/time plot of the reaction trans-[PdRfClL$_2$] (1) + [AuMeL] (2) in THF at 320 K. Initial conditions: [1]$_0$ = 0.01 M; [2]$_0$ = 0.03 M.
Direct kinetic data can be obtained only for some equations. Thus, complexes 5 and 7 can be prepared by alternative methods, and the reactions in equations 6 and 7 can be studied. The reaction of 5 with [AuCl(PPh₃)] (Eq. 6) takes place smoothly at 50 °C (for \([5]_0 = 0.01 M, k_\text{obs} = 3.4 \times 10^{-2} \text{ Lmol}^{-1} \text{s}^{-1} \); \( \Delta G^{\ddagger}\text{233} = 21.2 \text{ kcal mol}^{-1} \)). Not unexpectedly, the reaction is retarded by addition of PPh₃ (for [PPh₃] = \([5]_0 = 0.01 M, k_\text{obs} = 2.1 \times 10^{-2} \text{ Lmol}^{-1} \text{s}^{-1} \)). The reaction of the \( \text{cis} \) isomer 7 (Eq. 7) to cis-PdMe₃ to cis-PdMe₃ isomerization is too fast to be measured by NMR at this temperature, even in the presence of added [PPh₃], as in the time required to record a \(^{19}\text{F} \) NMR spectrum the reaction is finished. In the context of the reaction of 1 with 2, this confirms that complex 7, although formed during the reaction, will not be detected in the experiment due to its very high reactivity with the gold species.

Four other complexes, the precursors of the non-observed homocoupling products RF-RF and Me–Me, should be considered in order to have a complete picture of the exchanges. Homocoupling product RF–RF was not observed in the experiment in Fig. 1, as expected from the well-known inertness of cis-[PdRF₆L₂]. In fact this inertness made it possible our previous study using cis-[PdRF₆(AsPh₃)] and [AuCl(AsPh₃)] as reagents. Although study suggests that the equilibrium [PdRF₆Cl₂] + [AuRCl] to give cis-[PdRF₆L₂] (8) and [AuClL] (Eq. 8) should not produce NMR detectable concentrations of cis-[PdRF₆L₂], this equilibrium has to be taken into account for aryls less inert than RF/Ar in place of RF, such CdHCl(CF₃)₂ because then a faster reductive elimination from the intermediate cis-[PdAr₃PPh₃] will produce biphenyls, as observed (Eq. 1). For the shake of simplicity the pathways leading to PdMeCl₂ (similar to Eq. 8, with Me instead of Ph) will be omitted on the reasonable assumption that Me–Me coupling will be slower compared to any other coupling in the systems with conventional aryls and, in addition, the equilibrium for formation of the electron rich PdMeCl₂ should be the most unfavorable one. Note, however that some ethane is observed in our experimental reaction were the fluorinated aryl does not couple fast Finally, isomerization of the [PdRF₆Cl] and [PdRF₆(PPh₃)] complexes is not considered because these are usually slower processes than transmetalations, as we have previously found in related systems. For instance, under similar experimental conditions the isomerization of cis-[PdRF₆L₂] is too slow to be measured.

\[
\begin{align*}
\text{RF–Pd–L}^+ + \text{AuRCl} & \rightleftharpoons \text{RF–Pd–L}^+ + \text{AuCl} \\
\text{RF–Pd–L}^+ & \rightleftharpoons \text{RF–Pd–L}^+ + \text{AuCl}
\end{align*}
\]

The previous analysis shows that, in a general case, the Pd catalyzed reaction of aryl halides with alkyl gold complexes is a complicated process involving several competitive transmetalation pathways. This complex system can be simplified as shown in Scheme 1, where the formation of different intermediates via Au/Pd transmetalation is represented. From these, coupling should take place according to their respective rates for reductive elimination. All the equilibria have [PPh₃] dependent rates. Pathway (i) is unproductive as it forms, in a reversible way, trans-[PdArMePPh₃] which will not couple (a cis arrangement is required for coupling); pathway (ii) leads to cis-[PdArMePPh₃], producing cross-coupling; pathway (iii) produces [AuArL], which eventually leads via the fourth pathway (iv) to cis-[PdArPPh₃] and explains the Ar–Ar homocoupling observed in Eq. 1.

**Scheme 1.** Competitive pathways to homo- and heterocoupling. These equilibria are not necessarily one-step.

In fact the exchanges are more complex than shown in Scheme 1, as the transformations are not direct and involve the formation of bimetallic transition states and intermediates, related to the existence of more than one step. In this intricate scheme the number of unknowns is much larger than the number of parameters that can be experimentally modified, so determining all elementary rate constants from experimental measures on the overall reaction is not possible. However, some reasonable approximations can be made for our model reaction in the light of the kinetic data obtained.

**Analysis of the kinetic data.** The collection of experimental data was fitted to kinetic models using a non-linear fitting software package. The kinetic models consider a substitution of triphenylphosphine by the incoming [AuMePPh₃] consistent with the -1 reaction order on [PPh₃] observed above for Eq. 3; otherwise no acceptable fitting is obtained. The activation energy that the non-linear fitting affords for this substitution is 22.5 kcal mol⁻¹, in good agreement with the experimental values obtained above \( \Delta G^{\ddagger}\text{233} = 23.3 \text{ kcal mol}^{-1} \); \( \Delta H^\ddagger \text{= 63.9 kJ mol}^{-1} \) and \( \Delta S^\ddagger = -95.5 \text{ J K}^{-1} \text{ mol}^{-1} \), and with similar activation energy values in our previous studies on gold/Pd systems. The negative activation entropy for the reaction supports an associative substitution process of PPh₃ by the entering gold complex. From intermediate B, formed in this step, the reaction may proceed through different competitive pathways, which have different consequences when translated to a catalytic process. The possibilities considered are depicted in Figure 2.²⁰

**Figure 2.** Proposed competitive transmetalations. \( \Delta G^{\ddagger}\text{233} \) values in kcal mol⁻¹. The three activation energies (22.5, 27.4, and 26.8) are given by the kinetic fitting, taking as zero the stage 1 + 2. The
value 21.1 is an experimental value, as explained in the text, which is imposed in the fitting as a fixed value.

First of all, the transmetalation may produce trans-[PdRMeL₂] (5) via intermediate C. This is an improductive transmetalation since the cross coupling product cannot be formed from this isomer. In addition, since the cis-trans isomerization is slow, it cannot re-enter easily the catalytic cycle, except by a reversal transmetalation. Thus, 5, if formed, will react with [AuClL] (6) to go back to C and eventually produce the byproducts trans-[PdMeCIL₂] (4) and [AuRIL] (3) (blue lines in scheme 2). In the kinetic model, the known value of the rate constant was assigned to this transformation, with activation energy of 21.2 kcal mol⁻¹. This pathway is clearly detrimental for cross-coupling purposes since 3 is responsible (via transmetalation to I; see pathway IV in Scheme 1) for the formation of homocoupling products, and also because 4 further reacts with [AuMeL] (2) to produce ethane, consuming unproductively the organogold reagent.

According to the experimental data, a second pathway of reaction has to be proposed to account for a consumption of intermediate B, with an activation energy value of 26.8 kcal mol⁻¹. This second pathway can lead to the unobserved cis-[PdRMeL₂] (7) through intermediate D (red lines in Figure 2). From 7, the reductive elimination can proceed to the cross-coupling product Rf-Me. However, if the reductive elimination is slow, cis aryl-alkyl palladium(II) complexes can alternatively react with [AuClL] (6) via intermediate E, to produce the undesired aryl gold complex, which eventually gives rise to homocouplings Rf-Rf and Me-Me. This is the case of our model experimental system because fluoroaryls make fluoroaryl-coupling particularly difficult. Since the reductive elimination does not take place at a significant rate, almost all our cis product is consumed in a very fast reaction with [AuClL] to produce trans-[PdMeCIL₂] (4) and [AuRIL] (3).

Finally, a third pathway for the evolution of intermediate B can be considered: its transformation to intermediate E in an aryl/methyl exchange reaction, which eventually produces trans-[PdMeCIL₂] (4) and [AuRIL] (3) (black lines in Figure 2). Unfortunately, the existence of this pathway cannot be proved or disproved with the experimental data available. In case it effectivelly exists as a competitive pathway, the experimental activation energy 26.8 kcal mol⁻¹ would in fact correspond to the averaged rate of both pathways (red and black).

Thus, the selectivity to the desired cross coupling product Ar–Me depends at least on two critical steps: i) the transmetalation rate from intermediate B to produce cis-[PdArMeL₂], since the other pathways lead to the undesired [AuArL]; and ii) the reductive elimination rate of cis-[PdArMeL₂], because its accumulation in solution opens the possibility of a fast exchange with [AuClL] to produce again [AuArL].

The model proposed in Figure 2 provides qualitative information to understand why the cross-coupling of alkylgold complexes with aryl halides is difficult. An obvious reason is that the Ar–alkyl reductive elimination has higher activation energy than Ar–Ar coupling for conventional aryls.¹⁹,²⁰,²¹ This should allow for the formation of cis-[PdArL₂] via successive transmetalations (Eqs. 3, 6–8) with Ar in place of Rf, leading to the precursor on which a faster Ar–Ar homocoupling can occur. The efficiency of this undesired process should depend, in a general case, on the transmetalation rates as compared to the cross-coupling rates. In addition, the preference of palladium for the Me group and gold for the Ar group, remarked in Figure 1 and in equations 5 and 6, suggests that using [Au₅Bu₅P₂H₃] or alkyl complexes other than Me should produce alkyl-palladium complexes similar to 4, allowing for easy β–H elimination. Although the addition of phosphine could help to prevent this and slow down the undesired transmetalation reactions, it should have the same effect on the desired transmetalations, so it does not look that this could help to drive the reaction more selectively.

In summary, the result of the processes should be very much dependent on the compared rates of the reductive elimination for cross-coupling and homocoupling, and transmetalation steps. The experimental effective rate is summarized in Table 1. In our experience more electronegative aryl groups are slower towards coupling reductive elimination? (an extreme case is Rf, for which Rf–Rf coupling does not occur) and also slower towards transmetalation. Both effects, but specially the first one, should help to do the undesired transmetalation/homo-reductive elimination sequence less competitive for more electronegative groups, somehow protecting the desired homo-coupling reaction. Considering the complexity of the system, the rough correlation between the homo/hetero coupling ratios and the Hammet σᵢ supports this qualitative interpretation. The literature case of aryl-vinyl coupling, studied by Hasmi, Blum and Sarandeses group,⁶,⁷,¹¹,¹³ where the selectivity towards cross-coupling is very high, is also easily understood: Vinyl transmetalations are very fast, and in these conditions the reactions are dominated by the faster coupling rate (aryl-vinyl > aryl-aryl).

EXPERIMENTAL SECTION

All reactions were carried out under argon or nitrogen. Solvents were dried using a Solvent Purification System (SPS). NMR spectra were recorded on a Bruker AV 400 or a Varian 500/MR instrument equipped with a variable-temperature probe. Chemical shifts were reported in ppm from tetramethylsilane (H, CCl₄/F, 0 ppm), or 85% H₃PO₄ (³¹P), with positive shifts downfield, at ambient probe temperature unless otherwise stated. The NMR probe was calibrated using ethylene glycol as a temperature standard (T ≳ 300 K) and with a methanol standard (T < 300 K).¹¹ In the ¹⁹F and ³¹P spectra measured in non-deuterated solvents, a coaxial tube containing acetone-d₆ was used to maintain the lock ¹H signal. Combustion CHN analyses were made on a Perkin-Elmer 2400 CHN microanalyzer. Unless specified, all the compounds were used from commercial sources and used without further purification. The compounds trans-[PdRCl(C₆H₅)₂] (trans-[PdRCl(C₆H₅)₂] (26) [AuR₁][P₂H₃],) and RMe, and trans-[PdMeC(CH₃)(PPh₃)] were prepared as reported in the literature.

Synthesis of the complexes

[ transpose[Me(P₂H₃)]]. This synthesis is a modification of the procedure reported in the literature.³¹,³² 1.5 g of [AuCl(P₂H₃)] (3.03 mmol) were dissolved in THF (20 mL). The solution was cooled to -78 ºC and 7.58 mL of ZnMe₂ 2.0 M in toluene (15.2 mmol) were added. The reaction was stirred for four hours. After this time the solution was heated to 20 ºC, the solvent was removed a vacuo and 20 mL of cold hexane were added causing the precipitation of the gold complex as a white solid that was filtered, washed with cold hexane and vacuum dried. Yield: 1.30 g (60 %). ¹H NMR (acetone-d₆): δ 7.62-7.53 (m, 15H, Ph), δ 0.42 (d, J,P–H = 8.3 Hz, 3H, Me). ³¹P NMR (acetone-d₆): δ 46.7 (s). Cald. for C₁₉H₁₉AuC₂: C, 48.12; H, 3.83. Found: C, 47.93; H, 3.87.

Reactions of trans-[PdRClMe] and [AuMe(P₂H₃)]. Kinetic procedure. The kinetic experiments were studied by ¹H NMR. A volumetric NMR tube (5 mm) was charged with weighed amounts of trans-[PdRCl(C₆H₅)₂], [AuMe(P₂H₃)] and P₂H₃. The NMR tube was cooled down to -78 ºC and a small amount of THF (about 0.5 mL) was added to dissolve the solids. Then an additional amount of THF was added to reach a fixed volume of 0.6 mL. The tube was charged with an acetone-d₆ capillary for NMR lock, and placed into a thermostated probe. Series of NMR spectra (64 transients) were recorded at fixed time intervals of 5 minutes.
Concentration-time data were obtained from the integrated areas of trans-[PdRfCl(PPh₃)₂], [AuRf(PPh₃)], trans-[PdRfMe(PPh₃)₂] and Rf-Mc.

Cross-coupling experiments. Typical procedure. A NMR tube was charged with [AuMe₃(PPh₃)] (10 mg, 0.021 mmol), p-FC₆H₄H₁I (0.042 mmol), and trans-[Pd(p-FC₆H₄H₁I)(PPh₃)₂] as catalyst (0.95 mg, 0.0011 mmol). The solids were dissolved in 0.6 ml of THF-d₈ and the tube was placed in a thermostated bath at 50 °C. The evolution of the reaction was monitored by ⁵¹P NMR and ¹H NMR, and by ¹⁹F NMR when possible. The relative amount of homo- and cross-coupling products was taken from integrated areas of clean signals. The products were characterized according to the known NMR data: p-FC₆H₄H₁C₆H₄CF₃, p-NO₂C₆H₄H₁C₆H₄F₃ and p-FC₆H₄C₆F₁₄C₆H₄F₃.

ASSOCIATED CONTENT
Supporting Information
Kinetic data and details about the non-linear-least-squares fitting procedure are included. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interests.

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24 This oxidative addition is a well-known step. The oxidative addition of Rf-I gives initially cis-[PdRf2L2] but, in the conditions of this reaction, this intermediate isomerizes to trans-[PdRf2L2] at a much faster rate than the observed rate of transmetalation. See references 16, 18, and: Casado, A. L.; Espinet, P. Organometallics, 1998, 17, 904-930.
27 Note that the oxidative elimination processes on Pd are not being discussed here, but can occur on three- or tetra-coordinated intermediates. See, for instance Ananikov, V. P.; Musaev, D. G.; Morokuma, K. Eur. J. Inorg. Chem. 2007, 5390-5399. A complete discussion about this topic can be found in reference 19.
30 The structures of intermediates B and C in Figure 2 are proposed with a Pd-Au bond according to the calculated structures found in all DFT studies available. An alternative Pd-X-Au structure with bridging X ligand (X = Cl, Me) could be a kinetic equivalent, but this cannot be excluded. Structures with Pd interacting with both components of the X-Au bond have been found in the transition states of the associative substitution of the Pd leaving ligand by the entering complex AuXL. See references 7, 8 and 17.
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