Angewandte
International Edition Chemie

DOI: 10.1002/anie.201209262

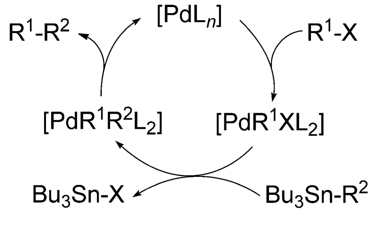
Cross-Coupling

Stille Coupling Involving Bulky Groups Feasible with Gold Cocatalyst**

Juan delPozo, Desirée Carrasco, Mónica H. Pérez-Temprano, Max García-Melchor, Rosana Álvarez, Juan A. Casares, and Pablo Espinet**

There is a growing interest in bimetallic catalysis, a synthetic approach combining two or more non-main-group-metal catalysts working in tandem.[1] A main-group metal is often involved as the nucleophilic reagent. The aim of bimetallic catalysis is to take advantage of the specific behavior of each catalyst in new one-pot synthetic routes. For the Au/Pd couple it is known that the Au/Pd transmetalation, a step which is hoped to connect the palladium and the gold catalytic cycles, is kinetically feasible,[2,3] even for fairly bulky groups.[4] However, so far only a few Au/Pd bimetallic catalyzed processes have been reported, including the Sonogashira-like cross-coupling,[5] the carbometallation of alkynes,[6] and processes combining cyclization with cross-coupling steps.[7,8] Herein we examine the potential of the Au/Pd pair in a Stille reaction, where tin is the third metal involved in the system, thus providing the nucleophile.

The classic palladium-catalyzed Stille reaction (Scheme 1) is a well-known, efficient, and deeply studied process.[9,10] The reaction is sometimes cocatalyzed by addition of CuX salts. The so-called copper effect is frequently deemed to be the result of the copper(I) mediating the aryl transfer from organotin to palladium.[11] However, it has also been shown that in some cases the kinetic effect observed is simply because of the ability of copper(I) to sequestrate the excess ligand in solution.[12] Blum and co-workers have recently succeeded in using gold as a vinyl carrier from tin to palladium in the carbostannylation of alkynes.[1b,6a]



Scheme 1. Classical Stille reaction.

We speculated that using AuXL complexes as the transmetalation cocatalyst to [PdR^{1}L$_2$] intermediates (L is identical in both species), instead of CuX salts, we might produce a Stille reaction cocatalyzed by gold(I) instead of copper(I). Moreover, should this cocatalysis occur, we could avoid the L sequestration or any ligand scrambling (for different ligands on palladium and gold) and thus observe a nonperturbed effect of the gold catalyst on the transmetalation. Furthermore, this reaction might be a good model to check the compatibility of palladium and gold as cocatalysts, and to explore the thermodynamic and kinetic parameters controlling this bimetallic system. In fact the results show that the intermediacy of gold can be critical to making Stille reactions involving bulky stannanes feasible.

The thermodynamics of the Au/Sn transmetalation equilibria are important. There are only very few reports of isolated transmetalations from tin to gold and vice versa. The transmetalation of Ar groups from SnArMe$_3$ (Ar = Ph, naphtyl, or 8-iodonaphtyl) to [AuCl(EPh$_3$)] (E = P, As) complexes has been reported, whereas the same reaction fails with SnPh(nBu)$_3$.[13] Attempts at performing Ar transmetalations with SnAr$_4$ or SnClAr$_3$ (Ar = C$_6$F$_5$, C$_6$F$_3$Cl$_2$, C$_6$Cl$_5$) were also unsuccessful.[14] These results suggest that the thermodynamics of the Sn/Au transmetalation might be shifted in either direction, depending on the specific groups involved.

We have studied the equilibrium for different combinations of reagents (X = Cl, I; R = vinyl, aryl, alkynyl) and ligands (L = PPh$_3$, AsPh$_3$), and the K_{eq} values are shown in Table 1. For L = AsPh$_3$ the equilibria were measured in MeCN, and for L = PPh$_3$ the equilibria were measured in THF (the complexes are only sparingly soluble in MeCN) in the presence of added L (L/Au = 2:1) to stabilize the gold complexes. Most equilibria were achieved within 5 minutes (for L = AsPh$_3$) or 24 hours (for L = PPh$_3$) at room temperature. More time was needed for systems with bulky aryl groups. Numerical values were obtained for a few cases with L = PPh$_3$, by integration of the peaks for the two gold complexes at equilibrium as observed in the ^{31}P NMR spectrum. For the rest, only reagents or only products were observed, thus restricting us to fix a minimum or maximum value for K_{eq}, assuming that a 1 % (for ^{31}P) or 0.1 % (for ^{1}H

---

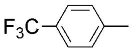
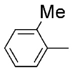
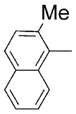
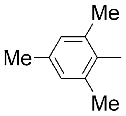
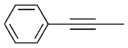
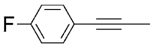
[*] J. delPozo, D. Carrasco, Dr. M. H. Pérez-Temprano, Prof. J. A. Casares, Prof. P. Espinet
Química Inorgánica, I. U. CINQUIMA, Facultad de Ciencias
Universidad de Valladolid, 47071 Valladolid (Spain)
E-mail: casares@qi.uva.es
espinet@qi.uva.es
Homepage: http://gircatalisishomogenea.blogs.uva.es/
Prof. R. Álvarez
Dpto. Química Orgánica, Facultad de Química
Universidade de Vigo
Lagoas-Marcosende s/n, 36310 Vigo (Spain)
Dr. M. García-Melchor
Química Física, Edifici C.n. Universitat Autònoma de Barcelona
08193 Bellaterra, Catalonia (Spain)

[**] We thank the Spanish Ministerio de Ciencia e Innovación (CTQ2010-18901/BQU) and the Junta de Castilla y León (VA281A11-2 and VA373A11-2) for financial support.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201209262.

Table 1: K_{eq} for Sn/Au transmetalation ($L^1 = PPh_3$; $L^2 = AsPh_3$).[a]

$$\mathrm{R^2SnBu_3 + AuXL} \xrightleftharpoons{K_{eq}} \mathrm{XSnBu_3 + AuR^2L}$$

Entry	R^2	K_{eq} (X = I)	K_{eq} (X = Cl)
1	vinyl	$<10^{-5}$ (L^1)	$<10^{-5}$ (L^1)
2		$<10^{-5}$ (L^1) $<10^{-4}$ (L^2)	$<10^{-5}$ (L^1) 2×10^{-2} (L^2)
3		$<10^{-5}$ (L^1) $<10^{-4}$ (L^2)	2×10^{4} (L^1) $>10^{6}$ (L^2)
4		$<10^{-5}$ (L^1) $<10^{-4}$ (L^2)	39 (L^1) $>10^{6}$ (L^2)
5		0.02 (L^1) $>10^{6}$ (L^2)	0.30 (L^1) $>10^{6}$ (L^2)
6		0.12 (L^1)	0.50 (L^1)
7		0.15 (L^1)	0.20 (L^1)

[a] The same results shown for p-$CF_3C_6H_4$ are obtained for C_6H_5, or p-$MeOC_6H_4$ and L^1.

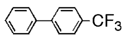
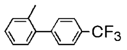
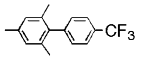
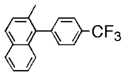
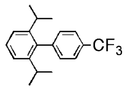
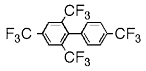
and ^{19}F) concentration or higher should be observable by NMR spectroscopy.

As suspected, the picture obtained is more complex than known so far. Table 1 shows that for X = I all the equilibria studied are shifted to the left, that is, the desired transmetalation from tin to gold is counter-thermodynamic. This shift is very pronounced for vinyl and most aryls groups (entries 1–4), and less so for alkynyl groups (entries 6 and 7) and for mesityl (entry 5). Importantly, electronic and steric factors can tune or modify this observed trend. Thus, all the equilibria are shifted less to the left for L = $AsPh_3$ than for L = PPh_3, probably because the hard-base PPh_3 (compared to the softer $AsPh_3$) interacts better with the hard AuXL. The halide is very influential, and these equilibria shift more to the right for X = Cl. This effect is more clearly observed in entries 3–5, and is mostly a result of the energetic balance of the markedly different Sn-X bond energies (Sn-Cl = 350 kJ mol^{-1}; Sn-I = 235 kJ mol^{-1}) compared to the similar Au–X bond energies (Au-Cl = 280 kJ mol^{-1}; Au-I = 276 kJ mol^{-1}).[15] Steric features of the transmetalated group are also influential: for bulky R^2 groups (entries 4 and 5) the equilibrium is more shifted to the right than for electronically similar but smaller R^2 groups. This trend probably results from some steric constraint at the tetrahedral tin center is released upon transmetalation of the bulky group to a linear gold(I) complex.

The thermodynamic results suggest that, as far as the reaction rate might depend on a higher concentration of the expected organogold intermediate, addition of LiCl should produce better results. Preliminary tests showed that in the presence of added LiCl, $[PdCl_2(AsPh_3)_2]$ was a faster catalyst than $[PdCl_2(PPh_3)_2]$. This is a well-known effect in Stille reactions when transmetalation is the rate-determining state, and results from the easier displacement of arsane ligands.[9,16] So, $AsPh_3$ was chosen for this study, and was complemented with some experiments with PPh_3. Stille coupling reactions, with and without a gold cocatalyst, and with or without added LiCl, were tested using p-$CF_3C_6H_4I$ (**1**), which allows for easy quantification of the products by ^{19}F NMR spectroscopy. All our results in this study show that transmetalation is the rate-determining step.

The cross-coupling results with $AsPh_3$ are shown in Table 2. The percentages of untransformed **1** and the main side-products p-$CF_3C_6H_4$–$C_6H_4CF_3$-p (**2**) and $CF_3C_6H_5$ (**3**) are given in the column labeled other products. In experiments with nonbulky aryltributyltin derivatives (entries 1 and 2), the effect of using a gold cocatalyst is small. But as the bulkiness of the aryl group substituents increases, a large beneficial effect is observed for the gold cocatalyst, as compared to the classic reaction (entries 3 versus 4, 5 versus 6, 7 versus 8, and 9 versus 10): the yields are negligible without the gold cocatalyst, and very satisfactory with the gold cocatalyst, although the bulkiest aryl groups still require longer reaction times. Overall, the presence of a gold cocatalyst clearly provides a more efficient pathway for the coupling with bulky stannylated groups.

Table 2: Palladium-catalyzed cross-coupling of p-$CF_3C_6H_4I$ (**1**) with various $ArSn(nBu)_3$ compounds using L = $AsPh_3$, and added LiCl in both the absence and presence of a gold cocatalyst.[a]

Entry	Au cat.	Product	t [h]	Yield [%]	Other products (Yield [%])
1	yes		5	83	**2**(7), **3**(10)
2	–		5	68	**1**(22), **2**(5), **3**(5)
3	yes		6	89	**2**(8), **3**(3)
4	–		6	4	**1**(80), **2**(3), **3**(12)
5	yes		24	84	**1**(<1), **2**(8), **3**(6)
6	–		24	<1	**1**(85), **2**(3), **3**(10)
7	yes		24	90	**2**(4), **3**(6)
8	–		24	0	**1**(81), **2**(5), **3**(11)
9	yes		48	64	**1**(1), **2**(19), **3**(1)
10	–		48	0	**1**(19), **2**(38), **3**(29)
11	yes		48	0	**1**(22), **2**(36), **4**(42)
12	–		48		**1**(90), **2**(2), **4**(2)

[a] Reaction conditions: MeCN, 80 °C, [p-$CF_3C_6H_4I$] = 0.10 M, [$ArSn(nBu)_3$] = 0.11 M, [$AsPh_3$] = 4.07×10^{-3} M, [LiCl] = saturated solution. Pd catalyst: $[PdCl_2(AsPh_3)_2] = 2\times10^{-3}$ M, Au catalyst: $[AuCl(AsPh_3)] = 2\times10^{-3}$ M. The reactions were monitored until total conversion of the starting p-$CF_3C_6H_4I$ was observed, or for the time indicated. Yields were determined by peak integration of the ^{19}F NMR spectra, and are average of two runs.

The fluoromesityl group (Table 2, entries 11 and 12) could not be coupled by using a gold cocatalyst, even after a long reaction time. Interestingly, under the reaction conditions for the cocatalyzed reaction (entry 11), considerable amounts of the homocoupling product **2** and the hydrolysis product $(CF_3)_3C_6H_3$ (**4**) were formed, both of which were are almost absent in the reaction attempted without the gold cocatalyst (entry 12). Homocoupling by-products such as **2** are typically formed in the classical Stille reactions where a slow coupling results in undesired transmetalations.[11h,12,17] In our experience the hydrolysis by-products like **4** are also observed in processes frustrated at the coupling step (e.g. $[Pd(C_6F_5)_2L_2]$ hardly undergoes reductive elimination to C_6F_5-C_6F_5 and formation of C_6F_5H is observed). Thus, it appears that the unsuccessful cocatalysis in entry 11 of Table 2 is due to the difficulty with the final reductive elimination, rather than at any of the two successive transmetalation steps.

Furthermore, experiments were carried out to check the influence of the added LiCl, the ligand L, and other effects (Table 3). The reactions can be carried out with similarly good yields using either $[PdCl_2(AsPh_3)_2]$ or the intermediate formed after the first oxidative addition to Pd, $[Pd(C_6H_4CF_3)I(AsPh_3)_2]$, prepared independently,[18] as far as excess LiCl is used (entries 1 and 2; also entries 6 and 7). The suppression of added LiCl is very detrimental to the gold cocatalyzed reaction with $AsPh_3$. The reaction still works albeit poorly when chloride is introduced in the catalytic system because it is part of the Pd and Au catalysts (entry 4), but it fails completely when the catalysts are iodide complexes and there is no other chloride source in the system (entry 3). This chloride effect is clearly related to the fact that the oxidative addition step to Pd^0 complexes with weak ligands such as arsanes does not take place without the addition of chloride.[9,10a,19] In fact, a similar reaction using PPh_3 catalysts runs perfectly in the absence of chloride, although very slowly (entry 5). In this case a 5% of undesired homocoupling product **2** is formed initially but does not increase with a prolonged reaction time. With added LiCl the homocoupling disappears (entry 6)and the reaction with PPh_3 is as efficient as that with $AsPh_3$, although noticeably slower (entry 2 versus 6 and 1 versus 7). The reactions with PPh_3 still continued slowly after 110 hours. This effect is well known in the classic Stille process, and results from the facile displacement of weaker ligands during the associative transmetalation to palladium.[10a] Other positive effects of a large excess of LiCl are that it exchanges I for Cl in the metal complexes. This reduces the energetic barrier of the tin to palladium transmetalation step.[10a,20] Also, excess LiCl helps to keep the gold cocatalyst in the $[AuCl(AsPh_3)]$ form,[21] which, as shown in Table 1, shifts the tin to gold transmetalation equilibrium towards the gold arylated compound. Furthermore, LiCl improves the overall thermodynamic balance of the coupling (whether it be the classical or the gold cocatalyzed) because of the higher stability of $SnCl(nBu)_3$.

Table 3: Results of the cross-coupling experiments between p-$CF_3C_6H_4I$ and mesityltributyltin under other reaction conditions.[a]

Entry	Pd catalyst (cocatalyst, LiCl)	t [h]	Yield [%]
1	$[PdCl_2(AsPh_3)_2]$ $[AuCl(AsPh_3)]$, LiCl	24	84
2	$[Pd(C_6H_4CF_3)I(AsPh_3)_2]$ $[AuCl(AsPh_3)]$, LiCl	24	84
3	$[Pd(C_6H_4CF_3)I(AsPh_3)_2]$ $[AuI(AsPh_3)]$, no LiCl	24	<1
4	$[PdCl_2(AsPh_3)_2]$ $[AuCl(AsPh_3)$, no LiCl	24	33
5	$[Pd(C_6H_4CF_3)I(PPh_3)_2]$ $[AuI(PPh_3)]$, no LiCl	110	58(+5)
6	$[Pd(C_6H_4CF_3)I(PPh_3)_2]$ $[AuI(PPh_3)]$, LiCl	110	75
7	$[PdCl_2(PPh_3)_2]$ $[AuCl(PPh_3)]$, LiCl	84	83
8	$[Pd(C_6H_4CF_3)I(AsPh_3)_2]$ CuCl, LiCl	24	13

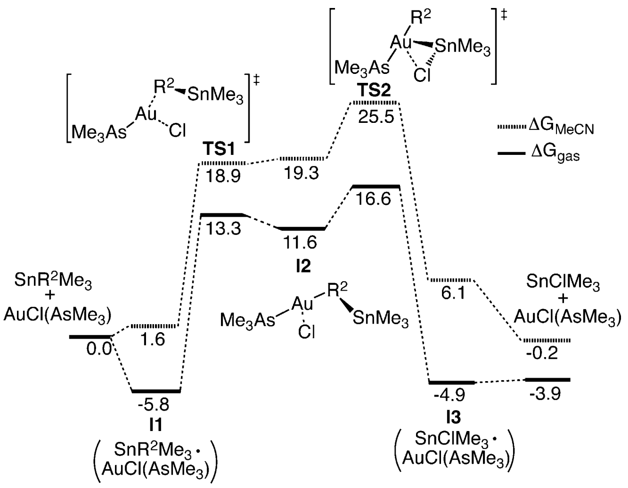
[a] General reaction conditions as in Table 2, except for the catalysts used and for the addition or not of LiCl, as indicated.

Finally, it is interesting that under similar experimental conditions, $[AuCl(AsPh_3)]$ and $[AuCl(PPh_3)]$ were much more efficient cocatalysts than CuCl (Table 3, entries 1, 2, 6, and 7 versus 8), as shown by the yields achieved for entries 2 and 8 (84% for the gold complex versus 13% for CuCl).

The ability of gold to promote the cross-coupling of sterically encumbered aryltin derivatives is remarkable. Thus far, these cross-coupling processes required the use of bulky and strong σ-donor phosphanes to facilitate the reaction going through tricoordinated palladium intermediates.[22] Apparently, when gold (and expectedly when Cu) complexes act as intermediates in the transmetalation, the steric hindrance for direct transmetalation with tetracoordinated tin and palladium compounds is circumvented via the less sterically demanding linear gold complexes. Moreover, in the direct Sn/Pd transmetalation the bulky group ($Sn(nBu)_3$) is directly involved in the bridging system, producing a very encumbered high-energy transition state, whereas with gold the bulky substituent on gold (the ancillary ligand) is one bond away from the bridging system , further relaxing the steric encumbrance and reducing the energy of the corresponding transmetalation transition state (see below and Figure 1). This improvement allows the process to occur using palladium and gold complexes with inexpensive common ligands.

Our hypothesis was confirmed by DFT calculations, which estimated the energy of the transmetalation transition states from tin to palladium (involved in the direct Stille reaction), or from tin to gold and from gold to palladium (involved in the gold cocatalyzed pathway). The calculations were performed for the formation of (2-methyl-1-(4-(trifluoromethyl)-phenyl)naphthalene (Table 2, entry 7) with the real molecules, except for the $Sn(nBu)_3$ group, which was simplified to $SnMe_3$. The transmetalation mechanisms from tin to palladium and from gold to palladium have been studied before for sterically nondemanding groups.[3,23] The transmetalation mechanism from tin to gold has not been studied so far, and is depicted in Scheme 2. The structures of the three rate-determining transition states and their free energies in vacuum and in MeCN are shown in Figure 1.[24]

The transition energies very clearly show that there is a considerable difference in favor of the bimetallic pathway,



Scheme 2. DFT calculated pathway for the tin to gold transmetalation.

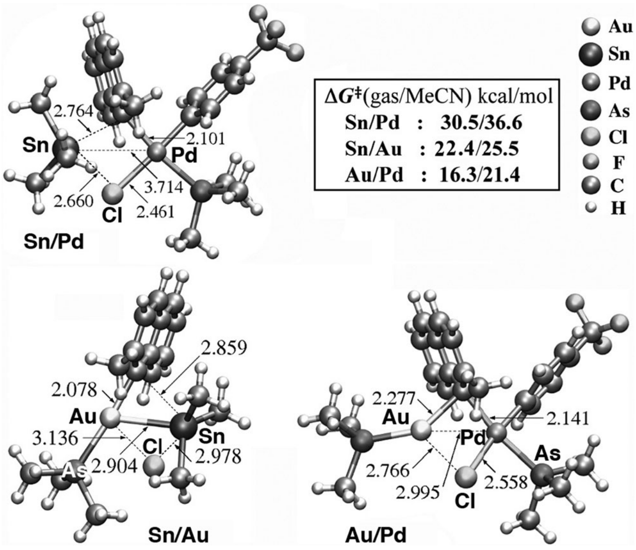
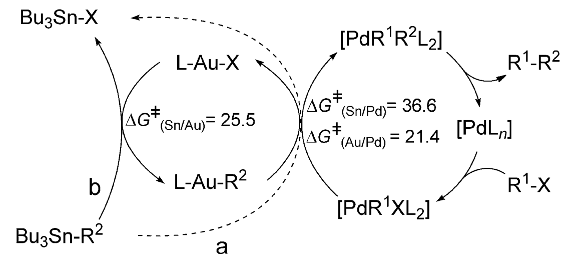


Figure 1. Transition states and ΔG^+ for the transmetalations.

thus predicting that, for this case, the direct Stille transmetalation should not take place, and the bimetallic process should be facile, as observed. Interestingly the two transition states involving gold show intermetallic distances much shorter than the sum of the van der Waals radii (in fact not far from the sum of covalent radii) for Sn-Au (2.904 versus 3.83 Å) and for Pd-Au (2.995 versus 3.29 Å), thus suggesting metallophilic interactions in the transition states. In contrast, the sum of the van der Waals radii is found for Sn-Pd (3.714 versus 3.80 Å), thereby suggesting no interaction.

This study shows that gold(I) complexes in the presence of LiCl efficiently catalyze the transmetalation step of bulky groups from tin to palladium, thus making possible some cross-couplings that would not proceed under the classical Stille reaction conditions. The effect of gold in the reaction might be limited by the unfavorable thermodynamics of the transmetalation equilibrium from organotin to gold if the concentrations of the arylgold intermediate were kinetically insufficient for the process to go on to the next step. Fortunately this transmetalation, which involves the replacement of aryl-Sn for X-Sn bonds, is favored in the presence of LiCl because of the high Sn−Cl bond energy, and is also more favorable for hindered aryl groups on the stannane, when the mediation of gold is more necessary. Thus the combination of a gold cocatalyst and LiCl provides an interesting modification of the Stille process for its application to bulky reagents that were not accessible so far in the classic way.

DFT calculations for the classic Stille and for the two successive transmetalations in the bimetallic processes (including the first study of a tin to gold transmetalation) show that, for a fairly bulky aryl group, the intermediacy of gold drives the reaction through transition states (Scheme 3) much lower in energy than the classic direct Stille processes. This reduction of the energetic barrier is associated with a lower crowding that additionally allows formation of metallophilic Au-Pd and Au-Sn stabilizing interactions, which are non-existent in the Sn-Pd transition state of the classic process. Obviously the effect of gold is expected to be very important for crowded systems, and less so for conventional aryls where the classic process is still sufficiently fast, as observed.



Scheme 3. Pathways for a) the classical Stille and b) the gold cocatalyzed processes, including the transition-state energies for the rate-determing step when X = Cl and R² = 2-methyl-1-(4-(trifluoromethyl)-phenyl)naphthalene.

Received: November 19, 2012

Keywords: density functional calculations · gold · homogeneous catalysis · palladium · tin

---

[1] Recent reviews: a) M. H. Pérez-Temprano, J. A. Casares, P. Espinet, *Chem. Eur. J.* **2012**, *18*, 1864–1884; b) S. A. Blum, J. J. Hirner, Y. Shi, *Acc. Chem. Res.* **2011**, *44*, 603–613.

[2] A. L. Casado, P. Espinet, *Organometallics* **1998**, *17*, 3677–3683.

[3] M. Pérez-Temprano, J. A. Casares, A. R. de Lera, R. Álvarez, P. Espinet, *Angew. Chem.* **2012**, *124*, 5001–5004; *Angew. Chem. Int. Ed.* **2012**, *51*, 4917–4920.

[4] a) A. S. K. Hashmi, C. Lothschütz, R. Döpp, M. Rudolph, T. D. Ramamurthi, F. Rominger, *Angew. Chem.* **2009**, *121*, 8392–8395; *Angew. Chem. Int. Ed.* **2009**, *48*, 8243–8246; b) A. S. K. Hashmi, R. Döpp, C. Lothschütz, M. Rudolph, D. Riedel, F. Rominger, *Adv. Synth. Catal.* **2010**, *352*, 1307–1314.

[5] For Sonogashira-like cross-coupling employing palladium/gold instead of palladium/copper systems, see: a) L. A. Jones, S. Sanz,

M. Laguna, *Catal. Today* **2007**, *122*, 403 – 406; b) B. Panda, T. K. Sarkar, *Tetrahedron Lett.* **2010**, *51*, 301 – 305.

[6] a) Y. Shi, S. M. Peterson, W. W. Haberaecker III, S. A. Blum, *J. Am. Chem. Soc.* **2008**, *130*, 2168 – 2169; b) Y. Shi, S. D. Ramgren, S. A. Blum, *Organometallics* **2009**, *28*, 1275 – 1277.

[7] a) Y. Shi, K. E. Roth, S. D. Ramgren, S. A. Blum, *J. Am. Chem. Soc.* **2009**, *131*, 18022 – 18023; b) Y. Shi, S. D. Ramgren, S. A. Blum, *Organometallics* **2011**, *30*, 4811 – 4813.

[8] A. S. K. Hashmi, C. Lothschütz, R. Döpp, M. Ackermann, J. D. B. Becker, M. Rudolph, C. Scholz, F. Rominger, *Adv. Synth. Catal.* **2012**, *354*, 133 – 147.

[9] P. Espinet, A. M. Echavarren, *Angew. Chem.* **2004**, *116*, 4808 – 4839; *Angew. Chem. Int. Ed.* **2004**, *43*, 4704 – 4734.

[10] a) A. L. Casado, P. Espinet, *J. Am. Chem. Soc.* **1998**, *120*, 8978 – 8985; b) A. L. Casado, P. Espinet, *J. Am. Chem. Soc.* **2000**, *122*, 11771 – 11782.

[11] a) J. P. Marino, J. F. Long, *J. Am. Chem. Soc.* **1988**, *110*, 7916 – 7917; b) L. S. Liebeskind, R. W. Fengl, *J. Org. Chem.* **1990**, *55*, 5359 – 5364; c) L. S. Liebeskind, J. Wand, *Tetrahedron Lett.* **1990**, *31*, 4293 – 4296; d) L. S. Liebeskind, M. S. Yu, R. H. Yu, J. Wang, K. S. Hagen, *J. Am. Chem. Soc.* **1993**, *115*, 9048 – 9055; e) L. S. Liebeskind, S. W. Riesinger, *J. Org. Chem.* **1993**, *58*, 408 – 413; f) J. R. Falck, R. K. Bhatt, J. Ye, *J. Am. Chem. Soc.* **1995**, *117*, 5973 – 5982; g) G. D. Allred, L. S. Liebeskind, *J. Am. Chem. Soc.* **1996**, *118*, 2748 – 2749; h) X. Han, B. M. Stoltz, E. J. Corey, *J. Am. Chem. Soc.* **1999**, *121*, 7600 – 7605; i) R. D. Mazzola, S. Giese, C. L. Benson, F. G. West, *J. Org. Chem.* **2004**, *69*, 220 – 223; j) E. Flöistrup, P. Goede, R. Strömberg, J. Malm, *Tetrahedron Lett.* **2011**, *52*, 209 – 211.

[12] a) A. L. Casado, P. Espinet, *Organometallics* **2003**, *22*, 1305 – 1309; b) V. Farina, S. Kapadia, B. Krishnan, C. Wang, L. S. Liebeskind, *J. Org. Chem.* **1994**, *59*, 5905 – 5911.

[13] N. Meyer, S. Sivanathan, F. Mohr, *J. Organomet. Chem.* **2011**, *696*, 1244 – 1247.

[14] R. V. Bojan, J. M. López-de-Luzuriaga, M. Monge, M. E. Olmos, *J. Organomet. Chem.* **2010**, *695*, 2385 – 2393.

[15] *CRC Handbook of Chemistry and Physics, Internet Version 2005* (Ed.: D. R. Lide), CRC, Boca Raton, FL, **2005**; http://www.hbcpnetbase.com.

[16] M. H. Pérez-Temprano, A. Nova, J. A. Casares, P. Espinet, *J. Am. Chem. Soc.* **2008**, *130*, 10518 – 10520.

[17] D. Milstein, J. K. Stille, *J. Am. Chem. Soc.* **1979**, *101*, 4992 – 4998.

[18] For the isomers arising from the oxidative addition and their isomerization, see the following paper and references therein: M. H. Pérez-Temprano, A. M. Gallego, J. A. Casares, P. Espinet, *Organometallics* **2011**, *30*, 611 – 617.

[19] R. Álvarez, M. Pérez, O. Nieto-Faza, A. R. de Lera, *Organometallics* **2008**, *27*, 3378 – 3389.

[20] A. Ariafard, Z. Lin, I. J. S. Fairlamb, *Organometallics* **2006**, *25*, 5788 – 5794. Probably the effect on the tin to gold transmetalation should be similar, as this barrier is related to the electrophilicity of the metal center.

[21] The coupling reaction is continuously producing $\mathrm{ISn}(n\mathrm{Bu})_3$. Should no other source of Cl be available, this $\mathrm{ISn}(n\mathrm{Bu})_3$ would react with $[\mathrm{AuCl}(\mathrm{AsPh}_3)]$ to give $\mathrm{ClSn}(n\mathrm{Bu})_3$ and $[\mathrm{AuI}(\mathrm{AsPh}_3)]$, which is undesired.

[22] a) G. C. Fu, *Acc. Chem. Res.* **2008**, *41*, 1555 – 1564; b) J. R. Naber, S. L. Buchwald, *Adv. Synth. Catal.* **2008**, *350*, 957 – 961; c) M. Dowlut, D. Mallik, M. G. Organ, *Chem. Eur. J.* **2010**, *16*, 4279 – 4283; d) R. D. Mazzola, S. Giese, C. L. Benson, F. G. West, *J. Org. Chem.* **2004**, *69*, 220 – 223; e) M. García-Melchor, G. Ujaque, F. Maseras, A. Lledós in *Phosphorus Compounds: Advanced Tools in Catalysis and Material Sciences*, *Vol. 37* (Eds.: M. Peruzzini, L. Gonsalvi), Springer, Berlin, **2011**, chap. 3, pp. 57 – 84.

[23] A. Nova, G. Ujaque, F. Maseras, A. Lledós, P. Espinet, *J. Am. Chem. Soc.* **2006**, *128*, 14571 – 14578.

[24] Calculated using *Gaussian09* and the ωB97X-D hybrid functional.