# Scope and Limitations of Palladium-Catalyzed Cross-Coupling Reactions with Organogold Compounds

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**Abstract:** Five different alkenylgold(I) phosphane complexes were prepared and then investigated in [1,1'-bis(diphenylphosphino)ferrocene]palladium(II) dichloride-catalyzed cross-coupling reactions with different aryl halides, heterocyclic halides, an alkenyl halide, an alkynyl halide, allylic substrates, benzyl bromide and an acid chloride. With regard to the halides, the iodides were highly reactive, bromides or chlorides gave significantly reduced yields or failed, allylic acetates failed, too. The cross-coupling partners contained a number of different functional groups, while free carboxylic acids did not deliver

# Introduction

To a large extent modern organic synthesis uses transition metal-catalyzed cross-coupling reactions for C-C bond formation. Among the transition metals employed for cross-coupling, palladium is still the most frequently used,<sup>[1]</sup> which includes the synthesis of natural products and pharmaceuticals.<sup>[2]</sup> The mechanism of these palladium-catalyzed cross-coupling reactions consists of three different steps, the oxidative addition of aryl or alkenyl halides, triflates etc., the transmetalation step and the reductive elimination which regenerates the active catalyst species and sets free the product of the C-C bond formation (Scheme 1). A number of organometallic compounds derived from electropositive metals has been used for the transmetalation step; the name reactions shown in Scheme 1 go along with the use of B, Sn, Zn and Mg. Unlike palladium, gold is not a good catalyst for cross-coupling reactions, it usually does not readily undergo a change in oxidation state (especially oxidative addition) under mild reaction conditions. Still, in the last years some examples have been reported, which incross-coupling products and *o*,*o*-disubstituted arenes failed as well, a broad range of other functional groups like nitro groups, nitrile groups, ester groups,  $\alpha$ , $\beta$ -unsaturated ester groups and lactones, aldehydes, alkoxy groups, pyridyl groups, thienyl groups, unprotected phenols and anilines, even aryl azides were tolerated. The structures of one alkenylgold(I) species and of four of the cross-coupling products were proved by crystal structure analyses.

**Keywords:** alkenes; allenes; cross-coupling; gold; heterocycles; palladium

clude cross-couplings<sup>[3]</sup> and homocouplings,<sup>[4]</sup> homocoupling using external stoichiometric oxidants<sup>[5]</sup> like BAIB,<sup>[5a]</sup> *t*-BuOOH,<sup>[5b]</sup> or Selectfluor<sup>[5c]</sup> and cross-coupling using stoichiometric Selectfluor.<sup>[6]</sup>

For a long time, alkenylgold species have been proposed as intermediates of gold-catalyzed reactions with allenes or alkynes.<sup>[7]</sup> These alkenylgold species usually regenerate the active catalyst by a fast protodeauration step, more seldom by trapping with alternative electrophiles.<sup>[8]</sup> Last year Hammond et al. succeeded in isolating a stabile alkenylgold(I) species derived from allenic substrates bearing an acceptor sub-stituent on the allene unit.<sup>[9]</sup> Other alkenylgold(I) species obtained recently from allenes<sup>[10]</sup> or alkynes were less stable.[11] A new dimension for gold catalysis would be the use of alkenylgold intermediates for a transmetalation to different transition metals like palladium, linking two catalytic cycles. The reluctance of gold to undergo a change in oxidation state would then become an advantage as the orthogonal reactivity of both metals should guarantee highly selective conversions. Although a few examples of the transmetalation of different organogold compounds to various





Scheme 1. Transmetalation as a key step in palladium-catalyzed cross-coupling.

transition metals were known,<sup>[12]</sup> no general study in combination with a cross-coupling catalytic cycle existed prior to our first communication on this subject.<sup>[13]</sup> Although these reactions were catalytic in Pd but stoichiometric in gold, a nearly quantitative reisolation of gold as Ph<sub>3</sub>PAuI could already render this method attractive. While the potential combination of gold and palladium catalysis is under investigation,<sup>[14]</sup> in the context of the known literature the interpretation has to be done with great care.<sup>[15]</sup>

Here we present the scope and limitations of the gold/palladium transmetalation in palladium-cata-lyzed cross-coupling.

### **Results and Discussion**

Allenoates **2a–f** were prepared according to literature protocols by a Wittig reaction of acyl chlorides with the Wittig reagents (Scheme 2).<sup>[16]</sup> The cyclization/ elimination to the alkenylgold species was conducted in analogy to a protocol by Hammond et al.<sup>[9]</sup> with stoichiometric amounts of Ph<sub>3</sub>PAuCl and AgOTf

(Scheme 3). Moderate to good yields were obtained. The only exception was **2f**, with  $R^1 = Ph$  no cyclization took place. This is in accordance with Hammond's results. We were able to crystallize compound **3b** and performed a crystal structure analysis (Figure 1). Two independent molecules are linked by an aurophilic interaction (Au–Au distance 3.1783 Å, Au–P distances 2.301 Å and 2.292 Å). This is in accordance with the results reported by Hammond et al. for **3d**.<sup>[9]</sup> A minor aberration from linearity is observed for the C–Au–P angles: 173.0° and 169.6°.

Based on our previous results, the cross-coupling reactions of alkenylgold compounds **3** with various C-electrophiles have been carried out at 60 °C under a nitrogen atmosphere in dry and degassed MeCN using 1 mol% of  $[PdCl_2(dppf)]$ .<sup>[13]</sup>

In general, the use of a nitrogen atmosphere was found to be crucial. For example, a cross-coupling product was not detectable by GC-MS analysis of the reaction of triphenylphosphine-alkenylgold(I) and iodobenzene under an atmosphere of air, an otherwise quite successful coupling. This has been attributed to



Scheme 2. Synthesis of allenoates by a Wittig reaction.

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duced cyclization/elimination.



Figure 1. Molecular structure of 3b in the solid state. Thermal ellipsoids shown at 50% probability.

the catalytically active Pd(0) species being sensitive towards oxygen. However, water is tolerated. The cross-coupling reaction between 3a and 4-methyliodobenzene has been carried out in a 9:1 mixture of MeCN and water (both degassed) to afford 4ai in 81% yield (Table 1, entry 12).

Table 1. Palladium-catalyzed cross-coupling of 3a with a variety of electrophiles (X=I, Br, Cl, OAc, C(=O)Cl).<sup>[a]</sup>



4a

Entry	R–X	Equiv. of R–X	Time [h]	<b>4</b> a	Yield
1	O <sub>2</sub> N	1.50	6	<b>4</b> aa	77%
2	NC	1.50	4	4ab	91% <sup>[b]</sup>
3	NC	1.50	45	4ab	39%

Table	Table I. (Continued)							
Entry	R-X	Equiv. of R–X	Time [h]	<b>4</b> a	Yield			
4	H L	1.50	4	4ac	85%			
5		1.50	4	4ad	83%			
6	ОН	1.50	26	4ae	0% <sup>[c]</sup>			
7	ONa	1.50	48	4ae	0%			
8		0.45	4	4af	73% <sup>[d]</sup>			
9	Br	0.45	18	4ag	95% <sup>[e]</sup>			
10		1.50	4	4ah	86%			
11	Br	1.50	10	4ah	0%			
12		1.50	4	4ai	81% <sup>[f]</sup>			
13		1.50	48	4aj	0% <sup>[g]</sup>			
14		1.50	4	4ak	84%			
15	HO	1.50	4	4al	89%			
16	H <sub>2</sub> N	1.50	4	4am	78%			
	N. A							

1.50

1.50

1.50

Ta

8

Adv. Synth. Catal. 2010, 352, 1307-1314

17

18

19

4

72

72

4an 71%

4a0

4ao

92%

37%

Table 1. (Continued)

Entry	R–X	Equiv. of R–X	Time [h]	<b>4</b> a	Yield
20		1.50	48	4ap	0% <sup>[h]</sup>
21	⟨	1.50	4	4aq	81%
22		1.50	4	4ar	73% <sup>[i]</sup>
23		1.50	4	4as	80%
24		1.50	48	4at	70%
25	Br	1.50	24	4at	traces
26	Ph Br	1.50	14 d	4au	traces
27	Ph	1.50	48	4au	0% <sup>[j]</sup>
28	Br	1.50	4	4av	87%
29	CI	1.20	4	4aw	82%

- <sup>[a]</sup> The reactions have been carried out under an inert gas atmosphere; Ph<sub>3</sub>PAuR (150 μmol), Ar–X (225 μmol), [PdCl<sub>2</sub>(dppf)] (1 mol%), MeCN (1.5 mL), 60 °C.
- <sup>[b]</sup> The reaction was also carried out on 2 mmol scale, 1.1 equiv. Ar-X, 95% cross-coupling product and 99% of [Ph<sub>3</sub>PAuI] were isolated.
- <sup>[c]</sup> Partial protodeauration of starting material but no crosscoupling (GC-MS).
- <sup>[d]</sup> 2 mol% [Pd] referred to halide, only disubstituted product was obtained.
- <sup>[e]</sup> Neither substitution of bromide nor substitution of both halides was observed (GC-MS).
- <sup>[f]</sup> In MeCN/H<sub>2</sub>O 9:1 (degassed).
- <sup>[g]</sup> Starting material [Ph<sub>3</sub>PAuR] reisolated in 97% yield.
- <sup>[h]</sup> No conversion (TLC).
- <sup>[i]</sup> (Z)-configuration,  ${}^{3}J_{\text{H,H}\,cis} = 12.6$  Hz.
- <sup>[j]</sup> No conversion (GC-MS).

Overall, the functional group tolerance turned out to be very high. Most of the cross-coupling reactions showed complete conversion of **3** within 4 h. The results of our studies are summarized in Table 1. The nitro group is tolerated (entry 1), the cyano group, too (entry 2). 1-Iodo-4-nitrobenzene and 4-iodobenzonitrile were effectively coupled with **3a** to afford **4aa** (77%) and **4ab** (91%) in excellent yields. The latter reaction has also been carried out on 2 mmol scale and **4ab** was obtained in 95% yield. Moreover, 99% of the gold could be reisolated as Ph<sub>3</sub>PAuI which can also be used for the synthesis of organogold compounds **3** after activation with AgOTf. 4-Bromobenzonitrile was found to be a less effective coupling partner (entry 3). Substrate **3a** was incompletely consumed even after a prolonged reaction time of 45 h. Crude **4ab** was isolated in a much lower yield (39%) than in entry 2 (91%). The latter two yields show clearly that as expected the iodide gives better results than the bromide, which is also visible in entry 9 and in the comparison of entries 10 and 11 as well as 18 and 19 or entries 24 and 25.

Further functional groups that were tolerated well are a formyl group (entry 4), an ester group (entry 5), but the coupling fails with a carboxylic acid (entries 6 and 7, protodeauration detectable). The corresponding cross-coupling products **4ac** (85%) and **4ad** (83%) could be isolated in excellent yields. No addition of the organogold nucleophile to the aldehyde or ester functionalities was observed. However, the use of 2iodobenzoic acid resulted in incomplete conversion, partial protodeauration of **3a** and formation of a gold mirror. No cross-coupling product **4ae** was observed by GC-MS analysis in this case.

With a diiodo substrate an efficient two-fold coupling was observed (entry 8). The yield of 73% for **4af** corresponds to 85% yield for each individual coupling. With the bromo-iodo compound a selective coupling of the iodo position was observed, no twofold coupling was detectable, **4ag** was isolated in 95% yield (entry 9).

An alkyl substituent was not a problem (entry 12), iodobenzene and 1-iodo-4-methylbenzene gave quite similar yields of 86% of **4ah** and 81% of **4ai**. Again a dramatic decrease in reactivity was observed with bromobenzene compared to iodobenzene (entries 10 and 11), no cross-coupling product **4ah** was obtained even after a prolonged reaction time. But an *o,o*-disubstitution leads to failure (entry 13), no conversion of **3a** took place with sterically demanding 2-iodo-1,3dimethylbenzene. After 48 h the starting material **3a** was reisolated in 97% yield. The *o*-methoxy group in entry 14 gives a good yield.

We also applied further electron-rich, deactivated, aryl halides in our cross-coupling (entry 14). Even an unprotected phenol is tolerated (entry 15), the same is true for an aniline (entry 16) and an aryl azide (entry 17)! 2-Iodoanisol, 4-iodophenol and 4-iodoaniline afforded the corresponding cross-coupling products **4ak** (84%), **4al** (89%), **4am** (78%) in excellent yields. A very important point is that no protodeauration of **3a** was observed with 4-iodophenol. From 4-azido-1-iodobenzene **4an** was isolated in 71% yield.

Different heterocycles also react, pyridines (entries 18 and 19), and thiophene (entry 21), but the chloropyrimidine fails (entry 20). Although a long reaction time (72 h) was necessary, cross-coupling of 2iodopyridine with **3a** afforded **4ao** in 92% yield, the corresponding bromide was less reactive (37%). In contrast, sulfur-containing 2-iodothiophene smoothly reacted with **3a** within only 4 h and the cross-coupling product **4aq** was isolated in 81% yield.

To demonstrate further the scope of our cross-coupling protocol, we also used alkenyl, allyl, alkynyl electrophiles, benzyl bromide and benzoyl chloride. An example for a (Z)-alkenyl iodide is shown in entry 22. The cross-coupling between 3a and ethyl (2Z)-3-iodoprop-2-enoate diastereoselectively afforded 4ar in 73% yield. A coupling constant of J =12.6 Hz for olefinic hydrogen atoms in the <sup>1</sup>H NMR spectrum indicates a (Z)-configuration for 4ar. An alkynyl iodide reacts (entry 23), from the cross-coupling reaction with 3a and (iodoethynyl)benzene 4as was isolated in 80% yield. Allylic iodides seem to be more difficult (entry 24), a slower reaction was observed for 3-iodoprop-1-ene (full conversion of **3a** only after 48 h). Cross-coupling product 4at was isolated in 70% yield. But the allylic bromides and acetate failed (entries 25–27), only traces of the corresponding crosscoupling products were detected by GC-MS with 3bromoprop-1-ene or (E)-(3-bromoprop-1-enyl)benzene (entries 25 and 26). No reaction took place with (2E)-3-phenylprop-2-en-1-yl acetate (entry 27). In contrast to other bromides, (bromomethyl)benzene smoothly reacted with 3a to afford 4av in 87% yield (entry 28).

The benzoyl chloride furnishes the ketone (entry 29), **4aw** was obtained in 82% yield. No decarbonylation was observed by GC-MS. Moreover, no reaction took place in the absence of a Pd source, which again underlines the catalytic nature of Pd and the lack of reactivity of the organogold compound towards an addition to carbonyl groups (entries 4, 5 and 28).

As described above (Scheme 3) we also synthesized organogold compounds **3b–e**. These have been used in the cross-coupling with 4-iodobenzonitrile. Our results are summarized in Table 2. Cross-coupling was successful in each case and products **4b–e** were isolated in excellent yields.

Entry 1 shows the yield obtained with **3a** in Table 1 for comparison. With the mono-substituted aurated lactone ring in **3b** also an excellent 88% yield of **4b** was isolated (entry 2). The disubstituted aurated lactones **3c** and **3d** with the benzyl and the ester functionalized side-chain delivered even better yields of 90% and 91% (entries 3 and 4). And even the trisubstituted lactone ring of the alkenylgold(I) species provided 91% of **4e** (entry 5).

The structure of the products has been proven unambiguously by a number of crystal structure analyses. The structures of **4aa**, **4ad**, **4ai** (Table 1) and **4d** (Table 2) are shown in Figure 2.<sup>[17]</sup> **Table 2.** Palladium-catalyzed cross-coupling of the alkenyl-<br/>gold(I) complexes 3a-e with 4-iodobenzonitrile.<sup>[a]</sup>



[a] Reactions have been carried out under inert gas atmosphere; Ph<sub>3</sub>PAuR (150 μmol), Ar–X (225 μmol), [PdCl<sub>2</sub> (dppf)] (1 mol%), MeCN (1.5 mL), 60 °C.

### Conclusions

The numerous successful cross-couplings described here show clearly that highly functionalized substrates can be tolerated in combinations of gold and palladium catalysis in the future. Especially the phenol and aniline derivatives and the unsaturated lactone rings illustrate the possibilities. This investigation also reveals the limitations when using the current conditions and thus provides a basis for the future finetuning of the palladium catalyst and the optimal transmetalation conditions.

# **Experimental Section**

#### **General Methods**

All reagents and solvents were obtained from Fisher Scientific, ABCR, Alfa Aesar, Sigma–Aldrich or VWR and were used without further purification unless otherwise noted. Deuterated solvents were purchased from Euriso-Top. Absolute solvents were dried by a MB SPS-800 using drying columns. Preparation of air- and moisture-sensitive materials



Figure 2. Molecular structures of a) 4aa, b) 4ad, c) 4ai and d) 4d. Thermal ellipsoids shown at 50% probability.

was carried out in flame-dried flasks under an atmosphere of nitrogen using Schlenk techniques. Cross-coupling reactions were performed in dry and degassed solvents. Thin layer chromatography (TLC) was performed using Polygram<sup>®</sup> precoated plastic sheets SIL G/UV<sub>254</sub> (SiO<sub>2</sub>, 0.20 mm thickness) from Macherey-Nagel. Column chromatography was performed using silica gel (40.0-63.0 nm particle size) from Macherey-Nagel. NMR spectra were recorded on Bruker Avance 500, Bruker Avance 300 and Bruker ARX-250 spectrometers at room temperature. Chemical shifts (in ppm) were referenced to residual solvent protons.[18] Signal multiplicity was determined as s (singlet), d (doublet), t (triplet), q (quartet) or m (multiplet). <sup>13</sup>C NMR assignment was achieved via DEPT 90, DEPT 135 or HSQC spectra. Mass spectra were recorded on a Vacuum Generators ZAB-2F, Finnigan MAT TSQ 700 or JEOL JMS-700 spectrometer. GC-MS were recorded on an Agilent 5890 Series II Plus with a HP 5972 mass analyzator. IR spectra were recorded on a Bruker Vector 22 FT-IR. Crystal structure analysis was accomplished on Bruker Smart CCD or Bruker APEX diffractometers. Elemental analysis was performed on an Elementar Vario EL.

#### General Procedure A (GPA), Synthesis of Allenoates

Under nitrogen, the phosphorus ylide (1.00 equiv.) was dissolved in dry DCM ( $5 \text{ mL mmol}^{-1}$ ), triethylamine (1.05 equiv.) was added and the mixture was stirred for 5 min. The acyl chloride (1.05 equiv.) was added dropwise and the mixture was stirred at room temperature overnight. The solvent was removed under reduced pressure and the residue was extracted with *n*-pentane  $(4 \times 5 \text{ mL mmol}^{-1})$ . The combined solutions were concentrated to one fourth of the original volume and filtered. The crude product was purified by column chromatography over silica.

# General Procedure B (GPB), Synthesis of Organogold Compounds

Under nitrogen, the allenoate (1.1 equiv.) was dissolved in dry DCM (10 mLmmol<sup>-1</sup> Ph<sub>3</sub>PAuCl). Ph<sub>3</sub>PAuCl (1.0 equiv.) and AgOTf (1.0 equiv.) were added and the mixture was stirred at room temperature for 2 h. Water (5 mLmmol<sup>-1</sup> Ph<sub>3</sub>PAuCl) was added and the mixture was stirred vigorously at room temperature for 1.5 h. The mixture was filtered and the layers were separated. The aqueous layer was extracted with DCM ( $3 \times 10$  mLmmol<sup>-1</sup> Ph<sub>3</sub>PAuCl). The combined organic layers were dried over MgSO<sub>4</sub>, filtered and the crude product was purified by column chromatography over silica.

# General Procedure C (GPC), Cross-Coupling Reactions

To the organogold compound (150  $\mu mol)$  under nitrogen was added [PdCl\_2(dppf)] (1 mM in dry and degassed MeCN,

1.5 mL) and the halide (225  $\mu$ mol). The mixture was stirred at 60 °C for the specified time. The mixture was filtered and the residue was washed with MeCN (2×1 mL). The crude product was purified by column chromatography over silica.

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## References

- For reviews on Pd-catalyzed cross-coupling reactions, see: a) R. Martin, S. L. Buchwald, Acc. Chem. Res. 2008, 41, 1461–1473; b) G. C. Fu, Acc. Chem. Res. 2008, 41, 1555–1564; c) R. Chinchilla, C. Nájera, Chem. Rev. 2007, 107, 874–922; d) E. A. B. Kantchev, C. J. O'Brien, M. G. Organ, Angew. Chem. 2007, 16, 2768–2813; e) A. F. Littke, G. C. Fu, Angew. Chem. 2002, 114, 4350–4386; Angew. Chem. Int. Ed. 2002, 41, 4176–4211; f) E. Negishi, J. Organomet. Chem. 2002, 653, 34–40; g) N. Miyaura, A. Suzuki, Chem. Rev. 1995, 95, 2457–2483.
- [2] K. C. Nicolaou, P. G. Bulger, D. Sarlah, Angew. Chem. 2005, 117, 4516–4563; Angew. Chem. Int. Ed. 2005, 44, 4442–4489.
- [3] a) C. González-Arellano, A. Abad, A. Corma, H. García, M. Iglesias, F. Sánchez, *Angew. Chem.* 2007, *119*, 1558–1560; *Angew. Chem. Int. Ed.* 2007, *46*, 1536–1538; b) P. Li, L. Wang, M. Wang, F. You, *Eur. J. Org. Chem.* 2008, 5946–5951; c) A. Corma, E. Gutiérrez-Puebla, M. Iglesias, A. Monge, S. Pérez-Ferreras, F. Sánchez, *Adv. Synth. Catal.* 2006, *348*, 1899–1907.
- [4] For examples of oxidative dimerization with substoichiometric/stoichiometric amounts of gold, see:
  a) A. S. K. Hashmi, M. C. Blanco, D. Fischer, J. W. Bats, *Eur. J. Org. Chem.* 2006, 1387–1389; b) A. K. Sahoo, Y. Nakamura, N. Aratani, K. S. Kim, S. B. Noh; H. Shinokubo, D. Kim, A. Osuka, *Org. Lett.* 2006, *8*, 4141–4144.
- [5] a) A. Kar, N. Mangu, H. M. Kaiser, M. Beller, M. K. Tse, *Chem. Commun.* 2008, 386–388; b) H. A. Wegner, S. Ahles, M. Neuburger, *Chem. Eur. J.* 2008, 14, 11310–11313; c) L. Cui, G. Zhang, L. Zhang, *Bioorg. Med. Chem. Lett.* 2009, 19, 3884–3887.
- [6] G. Zhang, Y. Peng, L. Cui, L. Zhang, Angew. Chem. 2009, 121, 3158–3161, Angew. Chem. Int. Ed. 2009, 48, 3112–3115.
- [7] For reviews on gold catalysis, see: a) A. S. K. Hashmi, G. J. Hutchings, Angew. Chem. 2006, 118, 8064–8105; Angew. Chem. Int. Ed. 2006, 45, 7896–7936; b) A. Fürstner, P. W. Davis, Angew. Chem. 2007, 119, 3478–3519; Angew. Chem. Int. Ed. 2007, 46, 3410–3449; c) A. S. K. Hashmi, Chem. Rev. 2007, 107, 3180–3211; d) A. Arcadi, Chem. Rev. 2008, 108, 3266–3325; e) E.

Jiménez-Núnez, A. M. Echavarren, *Chem. Rev.* **2008**, *108*, 3326–3350; f) Z. G. Li, C. Brouwer, C. He, *Chem. Rev.* **2008**, *108*, 3239–3265.

- [8] For selected examples, see: a) A. Buzas, F. Gagosz, Org. Lett. 2006, 8, 515–518; b) M. Yu, G. Zhang, L. Zhang, Org. Lett. 2007, 9, 2147–2150; c) A. S. K. Hashmi, T. D. Ramamurthi, F. Rominger, J. Organomet. Chem. 2009, 694, 592–597; d) B. Gockel, N. Krause, Eur. J. Org. Chem. 2010, 311–316.
- [9] a) L.-P. Liu, B. Xu, M. S. Mashuta, G. B. Hammond, J. Am. Chem. Soc. 2008, 130, 17642-17643; b) L.-P. Liu, G. B. Hammond, Chem. Asian J. 2009, 4, 1230-1236. For the previous invention of the catalytic allenoate to butenolide cyclization with tert-butyl esters, see: c) J.-E. Kang, E.-S. Lee, S.-I. Park, S. Shin, Tetrahedron Lett. 2005, 46, 7431-7433.
- [10] D. Weber, M. A. Tarselli, M. R. Gagné, Angew. Chem.
   2009, 121, 5843-5846; Angew. Chem. Int. Ed. 2009, 48, 5733-5736.
- [11] a) A. S. K. Hashmi, A. Schuster, F. Rominger, Angew. Chem. 2009, 121, 8396-8398; Angew. Chem. Int. Ed. 2009, 48, 8247-8249; b) X. Zeng, R. Kinjo, B. Donnadieu, G. Bertrand, Angew. Chem. 2010, 122, 954-957; Angew. Chem. Int. Ed. 2010, 49, 942-945; c) A. S. K. Hashmi, T. Dondeti Ramamurthi, F. Rominger, Adv. Synth. Catal. 2010, 352, 971-975; d) A. S. K. Hashmi, Gold Bull. 2009, 42, 275-279.
- [12] a) R. J. Cross, M. F. Davidson, A. J. McLennan, J. Organomet. Chem. 1984, 265, C37-C39; b) R. J. Cross, M. F. Davidson, J. Chem. Soc. Dalton Trans. 1986, 411-414; c) M. Contel, M. Stol, M. A. Casado, G. P. M. van Klink, D. D. Ellis, A. L. Spek, G. van Koten, Organometallics 2002, 21, 4556-4559; d) M. I. Bruce, M. E. Smith, N. N. Zaitseva, B. W. Skelton, A. H. White, J. Organomet. Chem. 2003, 670, 170-177; e) A. B. Antonova, M. I. Bruce, B. G. Ellis, M. Gaudio, P. A. Humphrey, M. Jevric, G. Melino, B. K. Nicholson, G. J. Perkins, B. W. Skelton, B. Stapleton, A. H. White, N. N. Zaitseva, Chem. Commun. 2004, 960-961; f) M. Ferrer, L. Rodríguez, O. Rossell, J. C. Lima, P. Gómez-Sal, A. Martín, Organometallics 2004, 23, 5096-5099; g) M. I. Bruce, P. A. Humphrey, G. Melino, B. W. Skelton, A. H. White, N. Zaitseva, Inor. Chim. Acta 2005, 358, 1453-1468; h) M. Robitzer, I. Bouamaed, C. Sirlin, P. A. Chase, G. van Koten, M. Pfeffer, Organometallics 2005, 24, 1756-1761; i) C.-L. Chan, K.-L. Cheung, W. H. Lam, E. C.-C. Cheng, N. Zhu, S. W.-K. Choi, V. W.-W. Yam, Chem. Asian. J. 2006, 1, 273-286; j) M. Stol, D. J. M. Snelders, H. Kooijman, A. L. Spek, G. P. M. van Klink, G. van Koten, Dalton Trans. 2007, 2589-2593; k) L. A. Jones, S. Sanz, M. Laguna, Catal. *Today* **2007**, *122*, 403–406; 1) Y. Shi, S. D. Ramgren, S. A. Blum, *Organometallics* **2009**, *28*, 1275–1277; m) W. M. Khairul, M. A. Fox, N. N. Zaitseva, M. Gaudio, D.S. Yufit, B.W. Skelton, A.H. White, J. A. K. Howard, M. I. Bruce, P. J. Low, Dalton Trans. 2009, 610-620; n) B. Panda, T. K. Sarkar, Tetrahedron Lett. 2010, 51, 301-305.
- [13] 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.

- [14] a) Y. Shi, K. E. Roth, S. D. Ramgren, S. A. Blum, J. Am. Chem. Soc. 2009, 131, 18022-18023. For the previous observation of C-C bond formation with stoichiometric amounts of organogold compounds under Sonogashira conditions with Pd(0) and Cu(I) or with organocobalt compounds, see: A. B. Antonova, M. I. Bruce, P. A. Humphrey, M. Gaudio, B. K. Nicholson, N. Scoleri, B. W. Skelton, A. H. White, N. N. Zaitseva, J. Organomet. Chem. 2006, 691, 4694-4707.
- [15] S. Ma, Z. Yu, J. Org. Chem. 2003, 68, 6149-6152.
- [16] R. W. Lang, H.-J. Hansen, Org. Synth. Coll. 1990, 7, 232–236.
- [17] CCDC 767465 (3b), 767468 (4aa), 767466 (4ad), 767467 (4ai) and 767464 (4d) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.
- [18] H. E. Gottlieb, V. Kotlyar, A. Nudelmann, J. Org. Chem. 1997, 62, 7512–7515.