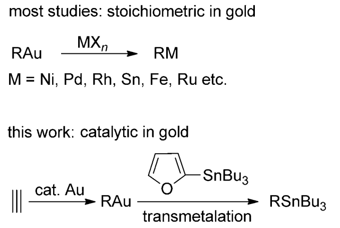
Gold Catalysis

DOI: 10.1002/anie.201201523

Gold-Catalyzed Cyclization of 1,6-Diyne-4-en-3-ols: Stannyl Transfer from 2-Tributylstannylfuran Through Au/Sn Transmetalation**

*Yifeng Chen, Ming Chen, and Yuanhong Liu**

In recent years, gold complexes and salts have emerged as powerful homogeneous catalysts for a wide variety of synthetic transformations owing to their superior chemoselectivity and activity.[1] For example, gold species can act as efficient alkynophilic Lewis acids, which can activate π systems towards nucleophilic attack. Despite significant diversity in the types of exisiting gold catalyzed reactions, the development of reactions that involve the functionalization of organogold intermediates containing a gold–carbon σ bond still remains a major challenge in this area. Such gold-containing intermediates are captured most frequently by a proton,[1] and much less frequently with alternative electrophiles such as carbocation,[2] sulfonyl,[3] silicon,[4] and halogen[5] electrophiles. Recent research has indicated that transmetalation of the in situ formed gold intermediates could extend the scope of the gold-catalyzed reactions to include, for example, C–C cross-coupling reactions.[6] Organogold complexes are good precursors for transmetalation reactions involving nickel,[7] palladium,[6e,7a,8] rhodium,[9] tin,[10] iron,[7a,11] ruthenium,[11] and other metal species,[7a,12] as demonstrated by the research groups of van Koten, Blum, Hashmi, and others (Scheme 1). However, whereas most of these studies involved the use of stoichiometric amounts of pre-formed organogold reagents, the transmetalation of a gold intermediate generated in situ within a gold-catalyzed reaction is quite rare.[8c,10,11,13] Blum and co-workers showed that the use of a mixture of gold and palladium catalysts was effective for the carbostannylation of electron-deficient alkynes and that it proceeds through successive palladium-to-gold and gold-to-tin transmetalation steps.[10] However, reactions that are catalyzed by a gold catalyst, in the absense of other metal catalysts, thus featuring a direct transmetalation from gold to tin and allowing for a direct access to organostannanes, are not known. During our ongoing research program on gold-catalyzed cyclization reactions of alkynes for the synthesis of polycyclic aromatic compounds,[14] we found that gold(I) complexes can be used as catalysts for the regioselective incorporation of a stannyl functional group into alkyne substrates (Scheme 1). Herein, we describe our discovery of a highly efficient gold-catalyzed cycloisomerization/stannylation cascade reaction of 1,6-diyne-4-en-3-ols, [15] thus leading to synthetically useful stannyl naphthalenes; 2-tributylstannylfurane is used as the source of stannane. Investigations into the mechanism of the reaction reveal that tin-to-gold as well as gold-to-tin transmetalation steps are involved in the process.



Scheme 1. Transmetalation reactions of organogold intermediates.

Recently, we developed a highly efficient gold-catalyzed cascade reaction between 1,6-diyne-4-en-3-ols and furans to give phenanthryl ketones; the reaction involved a Friedel—Crafts alkylation, furan-yne cyclization, and a heteroenyne metathesis reaction.[14a] Interestingly, when 2-tributylstannylfuran was used as the furan component, and the reaction was conducted in dichloroethane for a period of 1.5 hours, in the presence of 5 mol % of $[(PPh_3)AuCl]$ and 5 mol % of $AgSbF_6$, diyne **1a** was not converted into the expected phenanthrene. Instead, 2-stannyl naphthalene **2a** was obtained in 53 % yield, together with dihydroisobenzofuran **3a** in 19 % yield, the latter resulting from an intramolecular O–H bond addition to the alkyne moiety (Table 1, entry 1). The presence of the stannyl group in **2a** reveals that the stannyl group was transferred from 2-tributylstannylfuran to the diyne substrate during the reaction. The use of a OTf^--containing gold complex, which was prepared in situ by treating $[(PPh_3)AuCl]$ with AgOTf, improved the yield of **2a** to 71 %; however, significant amounts of **3a** and an isomeric isochromene derivative, 3-phenyl-1-(phenylethynyl)-1*H*-isochromene (**4a**), were also obtained (Table 1, entry 2). Further experiments revealed that the use of Echavarren's catalyst (**A**), which contains a bulky biarylphosphine ligand, gave much improved yields of **2a**. When 5 mol % of **A** was used, a clean conversion of diyne **1a** into the stannane was achieved (88 % yield) and only trace amounts of **3a** was detected (Table 1, entry 3). The use of a lower loading of catalyst **A** (2 mol %) afforded **2a** in a comparable yield of 87 % upon isolation (Table 1, entry 4). These results indicate that the nature of the

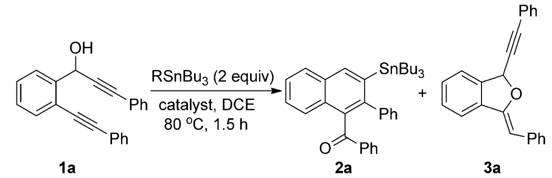
---

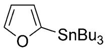
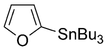
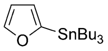
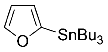
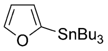
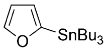
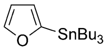
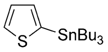
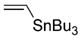
[*] Y.-F. Chen, M. Chen, Prof. Y.-H. Liu
State Key Laboratory of Organometallic Chemistry
Shanghai Institute of Organic Chemistry
Chinese Academy of Sciences
345 Lingling Lu, Shanghai 200032 (P. R. China)
E-mail: yhliu@mail.sioc.ac.cn

[**] We thank the National Natural Science Foundation of China (Grant Nos. 20872163, 21121062, and 21125210), the Chinese Academy of Science, and the Major State Basic Research Development Program (Grant No. 2011CB808700) for financial support.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201201523.

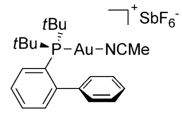
Table 1: Optimization studies for gold-catalyzed cyclization/stannyl transfer reactions.

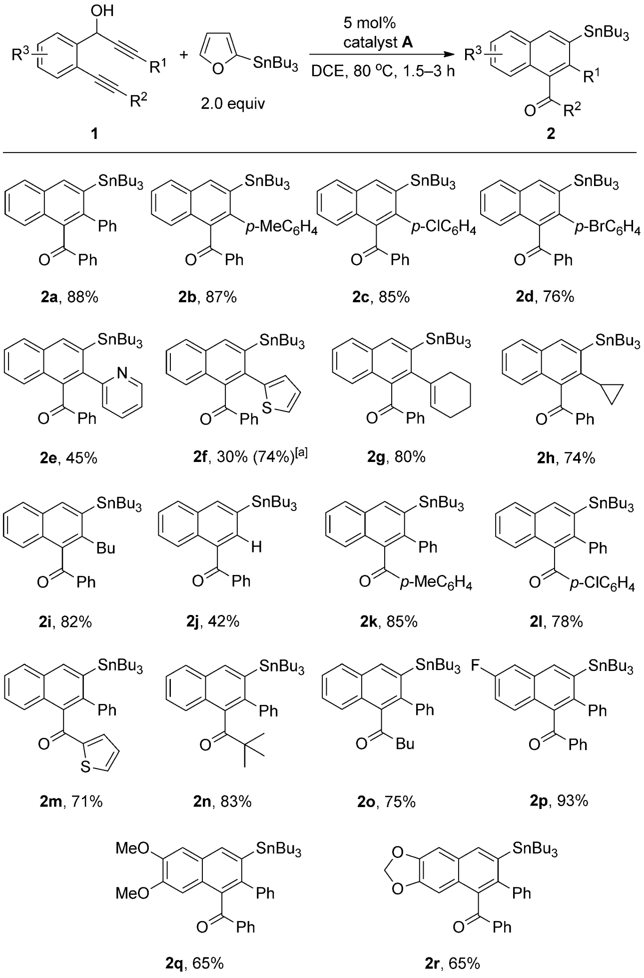


Entry	Catalyst (mol %)	RSnBu$_3$	Yield [%] **2a**[a]	Yield [%] **3a**[a]
1	[(PPh$_3$)AuSbF$_6$] (5)		53	19
2	[(PPh$_3$)AuOTf] (5)		71	26 (3.6:1)[b]
3	**A** (5)		88	4
4	**A** (2)		87	6
5[c]	**A** (2)		59	23 (2.9:1)[b]
6[d]	**A** (2)		76	10
7	AuCl$_3$ (5)		45	38 (1:2.3)[b]
8	**A** (2)		45	–[e]
9	**A** (2)	PhSnBu$_3$	24	–[e]
10	**A** (2)		22	12

[a] Yield of isolated product. [b] 3-phenyl-1-(phenylethynyl)-1*H*-isochromene **4a** was also formed. The ratio **3a**/**4a** is shown in parentheses. [c] 50 °C, 16 h. [d] 1.2 equiv of 2-tributylstannylfuran was used. [e] Not determined.

A =



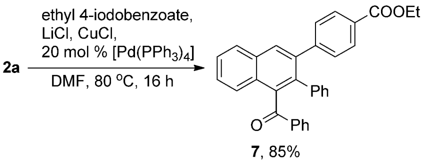


Scheme 2. Yields of isolated products. [a] The yield in parentheses was obtained by using 5 mol % of [(PPh$_3$)AuCl]/AgOTf and 1.2 equiv of 2-tributylstannylfuran. DCE = dichloroethane.

ligand on the gold(I) complex influences the chemoselectivity of the reaction. Decreasing the amount of 2-stannylfuran from 2 equivalents to 1.2 equivalents resulted in a lower yield of **2a** (76 % yield, Table 1, entry 6). The use of other tin reagents, such as 2-thienyl-, phenyl-, and vinylstannane resulted in lower product yields (22–45 %, Table 1, entries 8–10). When the reaction was conducted in the absence of 2-tributylstannylfuran at room temperature for a period of 15 minutes using 2 mol % of catalyst **A**, phenyl(2-phenylnaphthalen-1-yl)methanone (**5**)[15a] was isolated in 68 % yield, albeit containing a very small amount of an impurity. The reaction of **1a** using 1 equivalent of Bu$_3$SnOTf, in the absense of a gold catalyst, resulted in rapid decomposition of the starting material.

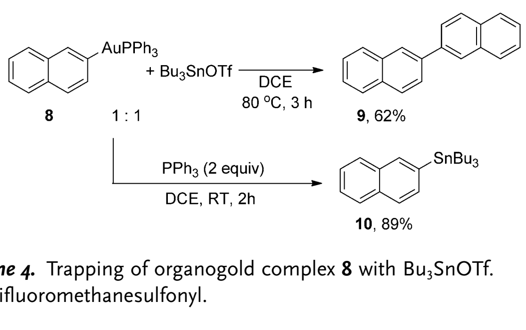
With conditions for an efficient reaction established, we next investigated the scope of the reaction using a variety of substituted diynes (Scheme 2). The reaction proved to be quite general with respect to variation of the R^1 and R^2 groups on the alkyne moieties; the presence of aryl-, heteroaryl-, and alkyl groups at these positions were tolerated, thus facilitating access to a diverse series of products. When R^1 was an aryl group containing electron-withdrawing or electron-donating groups, the desired stannyl naphthalenes **2b**–**2d** were obtained in good yields ranging from 76 % to 87 %. As the aryl substituent R^1 became more electron deficient, the reaction efficiency decreased (product **2d**, Scheme 2). The presence of heteroaryl substituents such as 2-pyridyl and 2-thienyl groups were also tolerated under the reaction conditions, thus giving **2e**, **2f**, and **2m** in 45–74 % yields. Notably, when R^1 is a thienyl group (product **2f**, Scheme 2), the use of [(PPh$_3$)AuOTf] afforded better results than the use of catalyst **A**. The presence of alkenyl and cyclopropyl groups was also tolerated in the reaction: **2g** and **2h** were obtained in 80 % and 74 % yields, respectively. The use of substrates containing alkyl substituents also resulted in good yields of the desired products (**2i** and **2o**, Scheme 2). The substrate containing a terminal alkyne (R^1 = H) underwent the reaction smoothly to give **2j** in 42 % yield. When R^2 was a bulky *tert*-butyl group, the efficiency of this reaction was not compromised, and the corresponding product **2n** was obtained in 83 % yield. Substrates containing fluoro, methoxy, or methylenedioxy groups on the parent phenyl ring were also suitable for this reaction, and good to high yields of the expected products were obtained in these cases (**2p**–**2r**).

Organostannanes are versatile building blocks for organic synthesis. The utility of the stannyl-containing products **2** was demonstrated in further transformations. For example, destannylation of **2a** with TsOH·H_2O in CH_2Cl_2 afforded naphthyl ketone **5** in 93% yield (see the Supporting Information). Treatment of **2a** with iodine gave the C2-iodinated product **6** in 84% yield. The structure of **6** was unambiguously confirmed by X-ray crystallography (see the Supporting Information).[16] In general, sterically encumbered stannanes, such as **2**, are not good substrates for Stille coupling reactions; however, after much investigation, we found that the cross coupling of **2a** with ethyl-4-iodobenzoate proceeded smoothly in the presence of Pd^0/CuCl/LiCl[17] to give **7** in high yield (85%, Scheme 3).

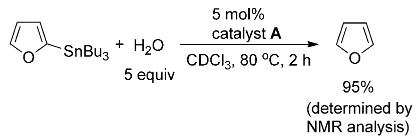


Scheme 3. Transformation of **2a**. DMF = *N*,*N*-dimethylformamide.

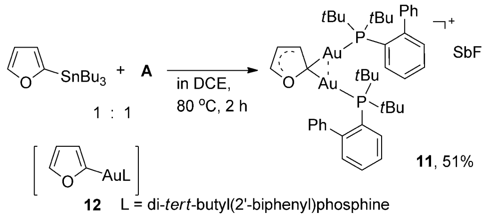
With regards to the mechanism, it occurred to us that the stannylation might proceed by the trapping of an aryl gold intermediate with a highly electrophilic tin species. To gain a better understanding of the transmetalation of an aryl gold species into an aryl tin species, we prepared the known complex [2-naphthylAu(PPh_3)] (**8**).[18] Treatment of **8** with Bu_3SnOTf[5e] afforded the product arising from a homocoupling reaction, 2,2′-binaphthyl (**9**, Scheme 4). We conducted the reaction in the presence of 2 equivalents of PPh_3 so that the released gold triflate would be trapped as $[AuL(PPh_3)]^+$, thus mimicking the conditions of our cyclization/stannylation reaction more closely; in the event, the desired tributyl(naphthalene-2-yl)stannane (**10**) was obtained in 89% yield (Scheme 4).[8d] Compound **8** could also react directly with 2-tributylstannylfuran at 80 °C to generate **10**, albeit in a low yield of 22%. However, the addition of 10 mol% of catalyst **A** to the reaction mixture improved the yield of **10** to 51%; the addition of 1 equivalent of catalyst **A** further improved the yield of **10** to 65%, and also gave the product arising from a cross-coupling reaction, 2-(naphthalen-2-yl)furan, in 20% yield. The above results suggest that the electrophilic Bu_3Sn^+ ion is formed in situ and then reacts with the gold intermediate. We wondered whether the Bu_3Sn^+ ion is generated through a gold-catalyzed destannylation of 2-stannylfuran. In a control experiment, 2-tributylstannylfuran in $CDCl_3$ at 80 °C, in the presence of 5 equivalents of H_2O and 5 mol% of **A**, underwent destannylation (Scheme 5);[19] in the absense of the gold catalyst, no reaction was observed. 2-tributylstannylfuran was treated with a stoichiometric amount of catalyst **A** in dichloroethane at 80 °C for 2 hours to determine whether a transmetalation from tin to gold was possible. Interestingly, an air-stable *gem*-diaurated complex **11** was obtained in 51% yield, a value based on the initial amount of gold complex **A** (Scheme 6). The structure of **11** was confirmed by X-ray crystallographic analysis (Figure 1).[16] The Au1–C41 and Au2–C41 bond lengths, 2.098(7) and 2.144(6) Å, respectively, are longer than those of the normal 2 center/2 electron bonds that are formed between gold and aryl groups (2.04–2.08 Å).[20] The Au1-C41-Au2 angle of 85.7(2)° is much smaller than those associated with normal tetrahedral carbon atoms, and the distance between the two gold atoms (2.8844(4) Å) is close to that observed in metallic gold (2.88 Å), thus indicating a strong aurophilic interaction. In addition, the large deviation of the P-Au-C *ipso* angle from the linear configuration (180°) also supports the existence of a Au···Au interaction. The C42–C43 bond length of 1.376(13) Å is significantly shorter than that of the corresponding C–C bond in 2-[(triphenyl)phosphine]gold]furan (1.431(5) Å),[21] thus indicating that the positive charge is delocalized over the ring and that the aromaticity of the furan moiety is reduced. Such gold moieties have been found in various aryl gold(I) complexes,[21,22] including a structurally characterized 2,2-diaurated furan complex $[C_4H_3O(AuPPh_3)_2][BF_4]$.[21] These results indicate that transmetalation has indeed occurred, and we believe that the diaurated furan complex **11** is formed through the addition of a second



Scheme 4. Trapping of organogold complex **8** with Bu_3SnOTf. Tf = trifluoromethanesulfonyl.



Scheme 5. Gold-catalyzed destannylation reaction.



Scheme 6. Transmetalation of gold complex **A** with 2-tributylstannylfuran.

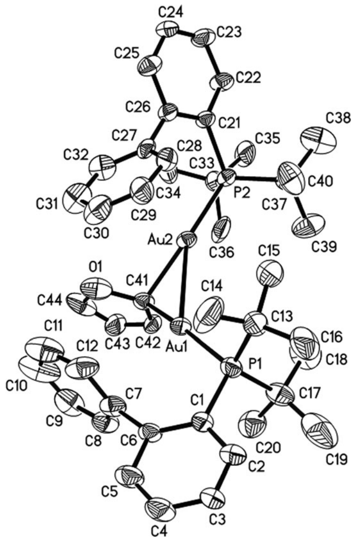
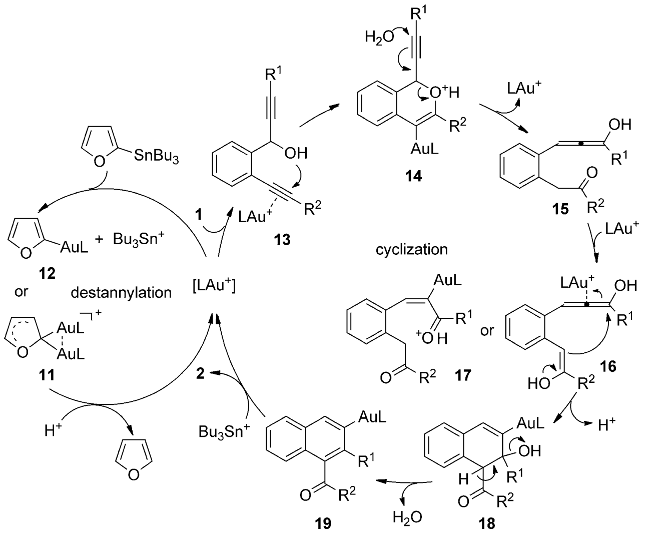


Figure 1. Molecular structure of complex **11** (H atoms and counter anion, SbF_6^-, are omitted for clarity). Thermal ellipsoids are shown at 30% probability. Selected bond lengths [Å] and angles [deg]: Au1–C41 2.098(7), Au1–P1 2.298(2), Au1···Au2 2.8844(4), Au2–C41 2.144(6), Au2–P2 2.2793(18); Au1-C41-Au2 85.7(2), C41-Au1-P1 167.5(3), C41-Au2-P2 158.1(2).



Scheme 7. Proposed reaction mechanism.

equivalent of catalyst **A** to the monoaurated furan complex **12**.[21] To the best of our knowledge, there are no crystallographic data associated with a transmetalation reaction between an organostannane and a cationic gold complex.[23] Interestingly, the catalytic activity of complex **11** was similar to that of the catalyst **A** under the standard conditions (2.0 equivalents of 2-(tributylstannyl)furan, dichloroethane, 80 °C, 2 hours), thus affording **2a** in 87% yield; the use of a *gem*-diaurated species as a catalyst has recently been reported.[16d] The transmetalation from tin to gold may proceed through a mechanism involving an interaction of the furanyl π system with gold followed by elimination of the Bu_3Sn^+ ion; this mechanism is analogous to that previously reported for the transmetalation reaction between 2-stannylfuran and a palladium complex.[24]

Although a detailed mechanism has yet to be determined,[25] we propose the following mechanism for this cascade reaction, based on the above observations (Scheme 7). The reaction is probably initiated by the nucleophilic attack of the hydroxy group onto the gold-coordinated alkyne to give oxacyclic species **14**, which could then undergo C–O bond cleavage, with the assistance of one molecule of water, to give allenol **15**. The allene moiety in **15** could be further activated by gold to form complex **16**. Subsequent cyclization of **16**, or alternatively its involvement in an aldol-condensation via intermediate **17**, would afford 2-naphthyl gold intermediate **19**. A trace amount of water should be sufficient to induce the cyclization reaction because although it would be consumed in the formation of allenol **15**, it is released during the aromatization process. In an adjoining catalytic cycle, the gold complex could catalyze the destannylation of 2-tributylstannylfuran through transmetalation and protodemetalation; furan was indeed detected in the crude reaction mixture. The resulting highly electrophilic Bu_3Sn^+ ion would then react with **19** to yield stannylnaphthalene **2** and regenerate the gold catalyst. However, a direct transmetalation of **19** with 2-tributylstannylfuran to give **2** cannot be ruled out. Although **1a** decomposed in the presence of stoichiometric amounts of Bu_3SnOTf, we did not observe such decomposition in the reaction, presumably because Bu_3SnOTf is generated catalytically and only reacts with the naphthyl gold intermediate preferentially.

To elucidate the reaction mechanism of the cyclization process, ^{18}O isotope labeling experiments were carried out.[26] Treatment of **1a** with 1 equivalent of $H_2{}^{18}O$, 2-tributylstannylfuran (2 equivalents), and 5 mol% of catalyst **A** resulted in the formation of **2a** without external ^{18}O atom incorporation at the carbonyl oxygen as indicated by EI-MS data. We also prepared ^{18}O-labelled **1a** ([^{18}O]-**1a**) wherein 49% of the molecules contained the ^{18}O atom. The treatment of [^{18}O]-**1a** with 2 equivalents of 2-tributylstannylfuran and 1 equivalent of H_2O (natural isotopic abundance) in the presence of 5 mol% of catalyst **A** afforded [^{18}O]-**2a** and [^{18}O]-**3a** without any loss of ^{18}O content as indicated by ESI-MS analysis. These results strongly support our proposed mechanism in which oxygen transfers from the benzylic postion to the triple bond.[27,28]

In conclusion, we have described the first example of a gold catalyzed cyclization and stannyl-transfer reaction of 1,6-diyne-4-en-3-ols using 2-tributylstannylfuran as the source of stannyl group and without the use of additional metals. This regioselective transformation provides an attractive new route to a diverse range of stannyl substituted naphthylstannanes and, when coupled with palladium-catalyzed Stille cross-coupling reactions, leads to highly functionalized naphthalenes. Investigations toward understanding the mechanism revealed that a gold to tin transmetalation reaction and a gold-catalyzed destannylation reaction might be involved in the domino process. We have also provided the first direct crystallographic evidence that supports a tin to gold transmetalation reaction involving cationic gold complexes. The method may find further application in the functionalization of organogold intermediates that have been proposed in other gold-catalyzed reactions.

Received: February 24, 2012
Revised: March 26, 2012

Keywords: alkynes · domino reactions · gold · stannanes · transmetalation

---

[1] For recent reviews on gold-catalyzed reactions, see: a) A. S. K. Hashmi, *Chem. Rev.* **2007**, *107*, 3180; b) A. Fürstner, P. W. Davies, *Angew. Chem.* **2007**, *119*, 3478; *Angew. Chem. Int. Ed.* **2007**, *46*, 3410; c) B. H. Lipshutz, Y. Yamamoto, *Chem. Rev.* **2008**, *108*, 2793; d) E. Jime’nez-Nu’n~ez, A. M. Echavarren, *Chem. Rev.* **2008**, *108*, 3326; e) D. J. Gorin, B. D. Sherry, F. D. Toste, *Chem. Rev.* **2008**, *108*, 3351; f) J. Muzart, *Tetrahedron* **2008**, *64*, 5815; g) A. Corma, A. Leyva-Pérez, M. J. Sabater, *Chem. Rev.* **2011**, *111*, 1657.

[2] a) L. Wang, G. Li, Y. Liu, *Org. Lett.* **2011**, *13*, 3786; b) I. Nakamura, T. Sato, Y. Yamamoto, *Angew. Chem.* **2006**, *118*, 4585; *Angew. Chem. Int. Ed.* **2006**, *45*, 4473; c) L. Zhang, *J. Am. Chem. Soc.* **2005**, *127*, 16804.

[3] I. Nakamura, U. Yamagishi, D. Song, S. Konta, Y. Yamamoto, *Angew. Chem.* **2007**, *119*, 2334; *Angew. Chem. Int. Ed.* **2007**, *46*, 2284.

[4] I. Nakamura, T. Sato, M. Terada, Y. Yamamoto, *Org. Lett.* **2007**, *9*, 4081.

[5] a) A. Buzas, F. Gagosz, *Org. Lett.* **2006**, *8*, 515; b) S. F. Kirsch, J. T. Binder, B. Crone, A. Duschek, T. T. Haug, C. Liébert, H. Menz, *Angew. Chem.* **2007**, *119*, 2360; *Angew. Chem. Int. Ed.* **2007**, *46*, 2310; c) M. Yu, G. Zhang, L. Zhang, *Org. Lett.* **2007**, *9*, 2147; d) A. S. K. Hashmi, T. D. Ramamurthi, F. Rominger, *J. Organomet. Chem.* **2009**, *694*, 592; e) A. S. K. Hashmi, T. D. Ramamurthi, M. H. Todd, A. S.-K. Tsang, K. Graf, *Aust. J. Chem.* **2010**, *63*, 1619.

[6] For reviews, see: a) J. J. Hirner, Y. Shi, S. A. Blum, *Acc. Chem. Res.* **2011**, *44*, 603; b) H. A. Wegner, M. Auzias, *Angew. Chem.* **2011**, *123*, 8386; *Angew. Chem. Int. Ed.* **2011**, *50*, 8236; c) P. Garcia, M. Malacria, C. Aubert, V. Gandon, L. Fensterbank, *ChemCatChem* **2010**, *2*, 493; for Au/Pd-catalyzed Sonogashira-type reactions, see: d) B. Panda, T. K. Sarkar, *Chem. Commun.* **2010**, *46*, 3131; e) T. Lauterbach, M. Livendahl, A. Rosellón, P. Espinet, A. M. Echavarren, *Org. Lett.* **2010**, *12*, 3006.

[7] a) 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; b) J. J. Hirner, S. A. Blum, *Organometallics* **2011**, *30*, 1299.

[8] a) A. L. Casado, P. Espinet, *Organometallics* **1998**, *17*, 3677; b) A. S. K. Hashmi, C. Lothschütz, R. Döpp, M. Rudolph, T. D. Ramamurthi, F. Rominger, *Angew. Chem.* **2009**, *121*, 8392; *Angew. Chem. Int. Ed.* **2009**, *48*, 8243; c) Y. Shi, K. E. Roth, S. D. Ramgren, S. A. Blum, *J. Am. Chem. Soc.* **2009**, *131*, 18022; d) Y. Shi, S. D. Ramgren, S. A. Blum, *Organometallics* **2009**, *28*, 1275; e) A. S. K. Hashmi, R. Döpp, C. Lothschütz, M. Rudolph, D. Riedel, F. Rominger, *Adv. Synth. Catal.* **2010**, *352*, 1307; f) M. Peña-López, M. Ayán-Varela, L. A. Sarandeses, J. Pérez Sestelo, *Chem. Eur. J.* **2010**, *16*, 9905; g) B. Panda, T. K. Sarkar, *Tetrahedron Lett.* **2010**, *51*, 301.

[9] Y. Shi, S. A. Blum, *Organometallics* **2011**, *30*, 1776.

[10] Y. Shi, S. M. Peterson, W. W. Haberaecker, S. A. Blum, *J. Am. Chem. Soc.* **2008**, *130*, 2168.

[11] A. S. K. Hashmi, L. Molinari, *Organometallics* **2011**, *30*, 3457.

[12] For transmetalation with other metals, see: a) R. J. Cross, M. F. Davidson, *J. Chem. Soc. Dalton Trans.* **1986**, 411; b) M. I. Bruce, M. E. Smith, N. N. Zaitseva, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **2003**, *670*, 170; c) M. Ferrer, L. Rodríguez, O. Rossell, J. C. Lima, P. Gómez-Sal, A. Martín, *Organometallics* **2004**, *23*, 5096; d) M. Robitzer, I. Bouamaied, C. Sirlin, P. A. Chase, G. van Koten, M. Pfeffer, *Organometallics* **2005**, *24*, 1756; e) M. I. Bruce, P. A. Humphrey, G. Melino, B. W. Skelton, A. H. White, N. N. Zaitseva, *Inorg. Chim. Acta* **2005**, *358*, 1453; f) A. V. Chuchuryukin, R. Huang, M. Lutz, J. C. Chadwick, A. L. Spek, G. van Koten, *Organometallics* **2011**, *30*, 2819.

[13] It has been recently shown that one example from Ref. [8c] needs only palladium to give the desired product in 37% yield, see: 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.

[14] a) Y. Chen, G. Li, Y. Liu, *Adv. Synth. Catal.* **2011**, *353*, 392; b) Y. Chen, Y. Lu, G. Li, Y. Liu, *Org. Lett.* **2009**, *11*, 3838; c) G. Li, Y. Liu, *J. Org. Chem.* **2010**, *75*, 2903; d) Y. Chen, Y. Liu, *J. Org. Chem.* **2011**, *76*, 5274; e) X. Xie, X. Du, Y. Chen, Y. Liu, *J. Org. Chem.* **2011**, *76*, 9175.

[15] For gold-catalyzed intramolecular 6-*endo*-dig cyclization of 1,6-diyne-4-en-3-ols to form naphthyl ketones, see: a) J. J. Lian, R. S. Liu, *Chem. Commun.* **2007**, 1337; for gold-catalyzed cycloisomerization of Ac- or Piv-protected 1,6-diyne-4-en-3-ols to 2-naphthyl ketone via allene intermediates, see: b) J. Zhao, C. O. Hughes, F. D. Toste, *J. Am. Chem. Soc.* **2006**, *128*, 7436.

[16] CCDC 868756 (**6**) and 868757 (**11**) 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. So far only a very small number of diaurated species have been isolated from gold-catalyzed reactions, see: a) D. Weber, M. A. Tarselli, M. R. Gagné, *Angew. Chem.* **2009**, *121*, 5843; *Angew. Chem. Int. Ed.* **2009**, *48*, 5733; b) A. S. K. Hashmi, I. Braun, M. Rudolph, F. Rominger, *Organometallics* **2012**, *31*, 644; c) A. S. K. Hashmi, M. Wieteck, I. Braun, P. Nösel, L. Jongbloed, M. Rudolph, F. Rominger, *Adv. Synth. Catal.* **2012**, *354*, 555; d) A. S. K. Hashmi, I. Braun, P. Nösel, J. Schädlich, M. Wieteck, M. Rudolph, F. Rominger, *Angew. Chem.* **2012**, *124*, 4532; *Angew. Chem. Int. Ed.* **2012**, *51*, 4456.

[17] X. Han, B. M. Stoltz, E. J. Corey, *J. Am. Chem. Soc.* **1999**, *121*, 7600.

[18] M. Osawa, M. Hoshino, D. Hashizume, *Dalton Trans.* **2008**, 2248.

[19] For a study on protodeauration of organogold complexes involving the C–C π system, see: a) K. E. Roth, S. A. Blum, *Organometallics* **2010**, *29*, 1712; for a related report on protodemetalation reaction, see: b) H. J. Berwin, *J. Chem. Soc. Chem. Commun.* **1972**, 237.

[20] M. Osawa, M. Hoshino, D. Hashizume, *Chem. Phys. Lett.* **2007**, *436*, 89.

[21] K. A. Porter, A. Schier, H. Schmidbaur, *Organometallics* **2003**, *22*, 4922.

[22] a) S. Gambarotta, C. Floriani, A. Chiesi-Villa, C. Guastini, *J. Chem. Soc. Chem. Commun.* **1983**, 1304; b) R. Usón, A. Laguna, E. J. Fernandez, A. Mendia, P. G. Jones, *J. Organomet. Chem.* **1988**, *350*, 129.

[23] For the transmetalation of vinyl boron with cationic gold to form a *gem*-diaurated complex, see: G. Seidel, C. W. Lehmann, A. Fürstner, *Angew. Chem.* **2010**, *122*, 8644; *Angew. Chem. Int. Ed.* **2010**, *49*, 8466.

[24] W. D. Cotter, L. Barbour, K. L. McNamara, R. Hechter, R. J. Lachicotte, *J. Am. Chem. Soc.* **1998**, *120*, 11016.

[25] For review on the mechanism of gold-catalyzed reactions, see: A. S. K. Hashmi, *Angew. Chem.* **2010**, *122*, 5360; *Angew. Chem. Int. Ed.* **2010**, *49*, 5232.

[26] See the Supporting Information for details.

[27] Liu et al (Ref. [15a]) proposed a mechanism for a cyclization process involving the attack of water to a cationic vinylgold(I) intermediate followed by enol–ketone tautomerization and

aromatization. Our results suggest that this mechanism is unlikely because if it was operating, incorporation of ^{18}O at the carbonyl oxygen in the product **6a** would be observed in the gold-catalyzed reaction of **1a** (natural isotopic abundance) and 2-tributylstannylfuran in the presence of 1 equivalent of $H_2{}^{18}O$.

[28] For gold-catalyzed intramolecular oxygen transfer reactions, see a) A. S. K. Hashmi, S, Schäfer, M. Wölfle, C. D. Gil, P. Fischer, A. Laguna, M. C. Blanco, M. C. Gimeno, *Angew. Chem.* **2007**, *119*, 6297; *Angew. Chem. Int. Ed.* **2007**, *46*, 6184; b) A. S. K. Hashmi, M. Bührle, R. Salathé, J. W. Bats, *Adv. Synth. Catal.* **2008**, *350*, 2059; c) J. M. Tang, T. A. Liu, R. S. Liu, *J. Org. Chem.* **2008**, *73*, 8479.