Cross-Coupling

DOI: 10.1002/ange.201406712

Gold(I)-Catalyzed Diazo Coupling: Strategy towards Alkene Formation and Tandem Benzannulation**

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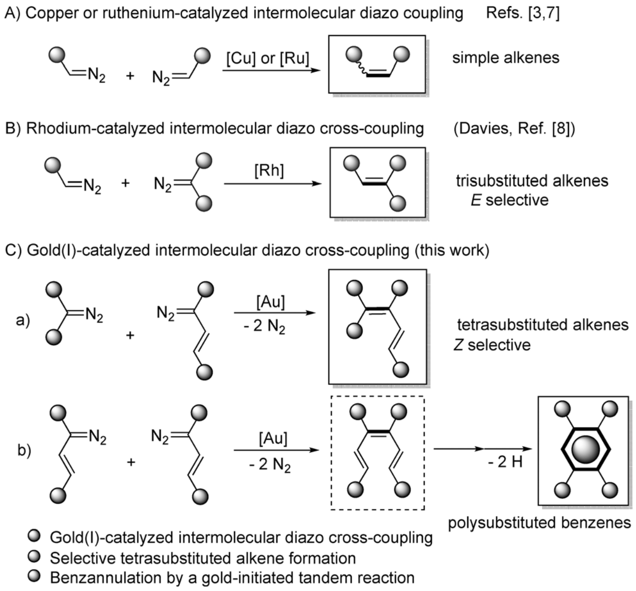
Dedicated to Professor Detlef Heller on the occasion of his 60th birthday

Abstract: *A gold(I)-catalyzed cross-coupling of diazo compounds to afford tetrasubstituted alkenes has been developed by taking advantage of a trivial electronic difference between two diazo substrates. A N-heterocyclic-carbene-derived gold complex is the most effective catalyst for this transformation. Based on this new strategy, a gold(I)-initiated benzannulation has been achieved through a tandem reaction involving a diazo cross-coupling, 6π electrocyclization, and oxidative aromatization.*

For the construction of $C{=}C$ bonds, Wittig-type reactions[1] and olefin metathesis[2] remain the most important and general approaches. Alternatively, the carbenoid-induced coupling of diazo compounds affords another possibility.[3] However, after the first discovery of this transformation,[3a] only a few synthetically useful processes have been reported and the most useful applications are metal-catalyzed intramolecular coupling of bis(diazocarbonyl) compounds or their synthetic surrogates developed by the groups of Doyle,[4] Che,[5] and Wang.[6] In contrast, the intermolecular diazo cross-coupling might be more challenging because of the inevitable competition between homo- and cross-coupling processes, as well as difficulties in controlling the stereoselectivity. Following the pioneering research on copper- and ruthenium-catalyzed intermolecular coupling of diazo compounds toward simple alkenes (Scheme 1 A),[3,7] a breakthrough was made by Davies et al., who reported rhodium(II)-catalyzed cross-couplings of diazo compounds to selectively produce *E*-configured trisubstituted alkenes for synthetically useful applications (Scheme 1 B).[8] However, no significant progress has been made since then, especially for the synthesis of tetrasubstituted alkenes through diazo coupling. Therefore, it would be useful if practical procedures could be established to this end.



Scheme 1. Alkene formation by metal-catalyzed diazo coupling.

In contrast, metal-catalyzed decomposition of diazo compounds and the subsequent transformation is one of the most powerful tools in organic synthesis.[9] Thus, much effort has been devoted to this research area and a series of novel and valuable transformations have been discovered recently.[10,11] Although Nolan et al. reported the first gold-catalyzed carbenoid transfer from ethyl diazoacetate in 2005,[12a] the application of gold complexes in carbene transfer has been investigated to a lesser degree compared to that with other noble metals (such as Rh, Cu, and Pd).[12] More specifically, recent studies revealed that gold-mediated carbene reactions displayed very different reactivity and selectivity compared to that of rhodium and other metal complexes.[13,14] In continuing with our interest in metal-catalyzed diazo transformations,[15] we describe herein the first successful gold-catalyzed cross-coupling of aryldiazoacetates and vinyldiazoacetates to selectively generate *Z*-configured tetrasubstituted alkenes,[16] as well as the discovery of a novel benzannulation which proceeds through a gold(I)-catalyzed cross-coupling of vinyldiazoacetates, 6π electrocyclization, and oxidative aromatization sequence (Scheme 1 C).

We began our study using phenyl diazoacetate (**1a**) and styryldiazoacetate (**2a**) as model substrates in the presence of various NHC/Au catalysts[17] (Table 1). Initial experiments to assess the yield of the diene **3a** revealed that $IPrAuNTf_2$/

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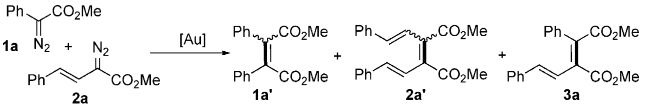
[**] This project is supported by NSFC (No. 21172023), A Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institution (PAPD) and Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology (BM2012110).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201406712.

Table 1: Optimization of diazo cross-coupling conditions.[a]



Entry	Catalyst	Solvent	**1a'**/**2a'**/**3a**[b]	*Z*/*E* (**3a**)[c]	Yield [%][d]
1	IPrAuCl/NaBAr$_F$	CH_2Cl_2	19:5:76	> 20:1	57
2	IMesAuCl/NaBAr$_F$	CH_2Cl_2	22:9:69	> 20:1	35
3	SIPrAuCl/NaBAr$_F$	CH_2Cl_2	–	–	0
4	IPrAuNTf$_2$/NaBAr$_F$	CH_2Cl_2	13:6:81	> 20:1	72
5	PPh$_3$AuCl/NaBAr$_F$	CH_2Cl_2	21:12:67	4:1	12
6	XPhosAuCl/NaBAr$_F$	CH_2Cl_2	16:19:65	3.2:1	26
7	*t*BuXPhosAuCl/NaBAr$_F$	CH_2Cl_2	12:24:64	5:1	18
8	IPrAuNTf$_2$/NaBAr$_F$	DCE	11:5:84	> 20:1	76
9	IPrAuNTf$_2$/NaBAr$_F$	toluene	–	–	–
10	IPrAuNTf$_2$/NaBAr$_F$	CH_3CN	26:11:63	> 20:1	40
11	IPrAuNTf$_2$	DCE	14:8:78	> 20:1	38
12[e]	IPrAuNTf$_2$/NaBAr$_F$	DCE	11:6:83	> 20:1	73
13[f]	IPrAuNTf$_2$/NaBAr$_F$	DCE	–	> 20:1	23

[a] Reaction conditions: **1a** and **2a** (1 mmol each) in CH_2Cl_2 (5 mL) were added slowly to the gold complex/NaBAr$_F$ (5 mol%) in 5 mL of CH_2Cl_2 at RT. Reaction time was 4 h. [b] Determined by NMR analysis of the crude reaction mixture. [c] Determined by NMR analysis of the crude reaction mixture. [d] Yield of isolated product. [e] Used 2.5 mol% of catalyst. Reaction time was 10 h. [f] The reaction was performed at 0 °C. DCE = 1,2-dichloroethane, Tf = trifluoromethanesulfonyl.

NaBAr$_F$ (Ar$_F$: tetrakis[3,5-bis(trifluoromethyl)phenyl]) was the most effective catalyst (entry 4). The diene **3a** was obtained in 72% yield with excellent stereoselectivity (> 20:1) for the *Z* isomer in dichloromethane along with a small amount of **1a'** and **2a'**. IPrAuCl/NaBAr$_F$ afforded **3a** in a slightly lower stereoselectivity and slightly lower yield (entry 1). Surprisingly, SIPrAuCl was inert in this reaction (entry 3). Attempts to use other gold catalysts bearing phosphine ligands such as PPh$_3$AuCl, XPhosAuCl, and *t*BuXPhosAuCl resulted in poor results (entries 5–7). The use of dichloroethane (DCE) as a solvent provided slightly better selectivity (**3a**/**2a'**/**1a'** = 84:5:11) and higher yield (entry 8). Other solvents failed to improve the yield and selectivity. Notably, NaBAr$_F$ was crucial for good reactivity and using IPrAuNTf$_2$ alone provided **3a** in low yield (entry 11). Low catalyst loading gave similar results but after a longer reaction time (entry 12). In addition, low temperature was detrimental to the reactivity (entry 13).

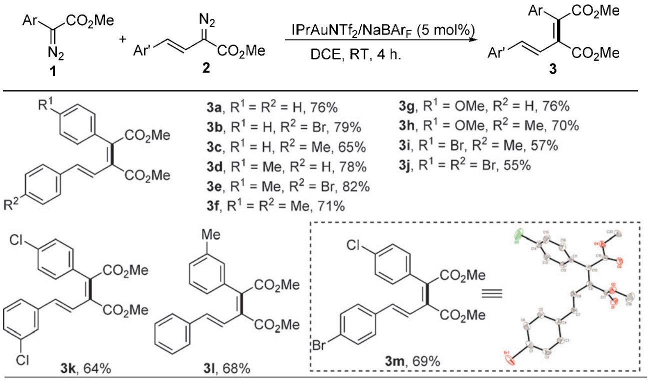
With the optimal reaction conditions in hand, various aryldiazoacetates and vinyldiazoacetates were tested (Table 2). In general, the reactions proceeded smoothly to produce the corresponding dienes in moderate to good overall yields (55% to 82%), thus favoring the *Z* isomer (*Z*/*E* ratio > 20:1). Both electron-donating and electron-withdrawing groups on the phenyl ring of the diazo substrates were tolerated. Reactions of aryldiazoacetates, having electron-donating groups, and vinyldiazoacetates gave the corresponding dienes (**3d**–**h**) in high yields. The highest yield was obtained for **3e** (82%). The configuration of **3m** was also confirmed by single-crystal X-ray crystallography.[18]

Encouraged by the success achieved, we set out to extend this approach by developing it into a sequential three-step reaction (Scheme 2). We envisioned gold-catalyzed intermolecular cross-coupling of two molecular of vinyldiazoaceates would provide the corresponding triene under the appropriate reaction conditions. Moreover, the resulting triene would be an ideal precursor for 6π electrocyclization, thus leading to the cyclization product at an elevated temperature, a product which could be further oxidized to generate a substituted benzene in the presence of a suitable oxidant. As a result, a novel benzannulation initiated by gold(I)-catalyzed triene formation by the cross-coupling of vinyldiazoacetates would be established.

Based on this hypothesis, the diazoacetate **2d** was employed for the initial study (Scheme 2). Under the optimal reaction conditions, the triene **2d'** was isolated in 86% yield with good stereoselection (*Z*/*E* = 9:1) when catalyzed by 2.5 mol% of IPrAuNTf$_2$/NaBAr$_F$. Furthermore, without isolation of **2d'**, the reaction mixture was directly heated to 80 °C and was continuously stirred for another 2 hours. The mixture was then cooled to room temperature, and oxidative aromatization occurred within 2 hours in the presence of two equivalents of DDQ. As a result, the desired product **4d** was obtained in 82% yield and **2d'** (both *Z* and *E* isomers) was not detected. In contrast, treatment of **2d** with [$Rh_2(OPiv)_4$][8] did not afford **2d'** but instead delivered pyrazole as the sole product (Scheme 2).[16d,19]

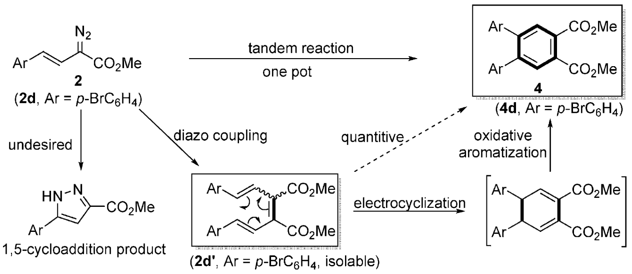
Given this newly established protocol, various vinyldiazoacetates were subjected to this one-pot procedure

Table 2: Substrates scope.[a,b]



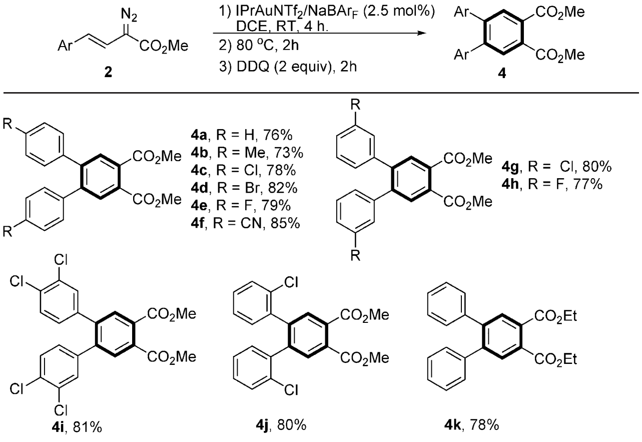
3a, $R^1 = R^2 = H$, 76%
3b, $R^1 = H$, $R^2 = Br$, 79%
3c, $R^1 = H$, $R^2 = Me$, 65%
3d, $R^1 = Me$, $R^2 = H$, 78%
3e, $R^1 = Me$, $R^2 = Br$, 82%
3f, $R^1 = R^2 = Me$, 71%
3g, $R^1 = OMe$, $R^2 = H$, 76%
3h, $R^1 = OMe$, $R^2 = Me$, 70%
3i, $R^1 = Br$, $R^2 = Me$, 57%
3j, $R^1 = R^2 = Br$, 55%
3k, 64%
3l, 68%
3m, 69%

[a] Reaction conditions: **1** and **2** (1 mmol each) in 5 mL of DCE was added slowly to IPrAuNTf$_2$/NaBAr$_F$ (5 mol%) in 5 mL of DCE at RT. Reaction time was 4 h. [b] Yield is that of isolated product.



Scheme 2. Synthetic strategy for a gold(I)-initiated tandem benzannulation.

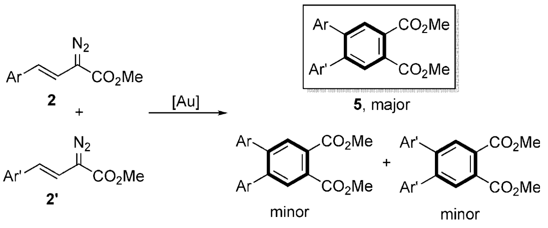
Table 3: Synthesis of symmetric polysubstituted benzenes.[a,b]



[a] Reaction conditions: **2** (1 mmol) in 5 mL of DCE was added to IPrAuNTf$_2$/NaBAr$_F$ (2.5 mol%) in 5 mL of DCE at RT. Reaction time was 4 hours. [b] Yield is that of isolated product. DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

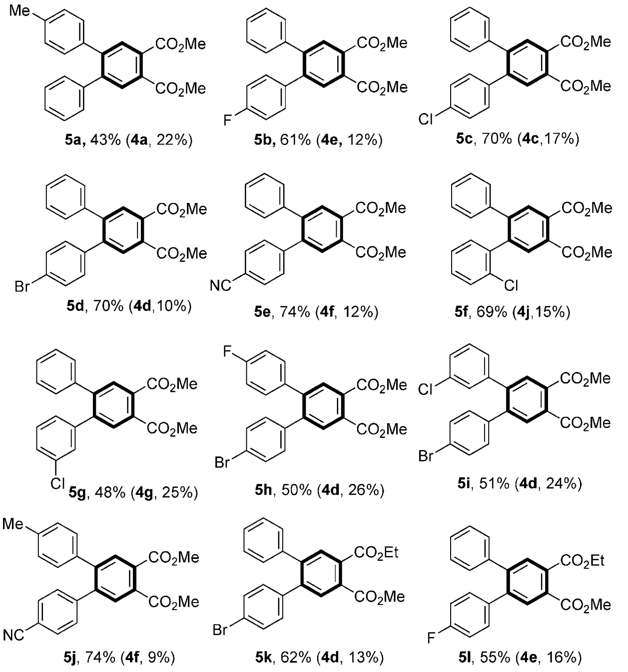
(Table 3). All the substrates reacted smoothly to produce the corresponding symmetric benzenes in moderate to high yields (73% to 85%). Both electron-poor and electron-rich aromatic rings were tolerated and the vinyldiazoacetates having electron-withdrawing substituents on the phenyl ring provided the corresponding products in higher yields than those with electron-donating substituents. The highest yield was obtained for the tandem benzannulation of *para*-cyanophenyl vinyldiazoacetate (**4f**, 85% yield).

The successful synthesis of symmetric benzenes led us wonder if unsymmetric polysubstituted benzenes could be prepared by this tandem benzannulation. However, compared with the homocoupling process, the cross-coupling between two different vinyldiazoacetates might be more complicated owing to their trivial electronic difference, which would probably cause serious competition between the homo- and cross-coupling processes (Scheme 3). Despite this disadvantage, the *E*/*Z* isomers of the newly formed trienes for each coupling process would be transformed into the same product simultaneously after sequential electrocyclization and aromatization according to previous observations. Thus only three different benzenes would be obtained after the tandem procedure. Moreover, the unsymmetrical polysubstituted benzene could be isolated as the major product if the cross-coupling is favored over two homocoupling processes.



Scheme 3. Synthesis of unsymmetric polysubstituted benzenes.

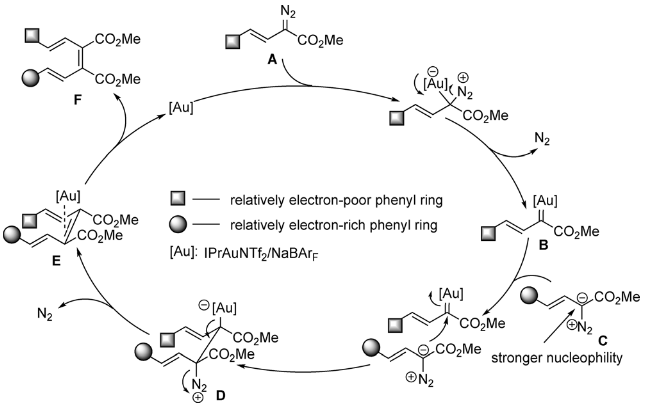
Table 4: Synthesis of unsymmetric polysubstituted benzenes.[a,b]



[a] Reaction conditions: **2** and **2′** (1 mmol each) in 5 mL of DCE was added slowly to IPrAuNTf$_2$/NaBAr$_F$ (5 mol%) in 5 mL of DCE at RT. Reaction time was 4 h. Then 80°C for 2 h, and cooled to RT for another 2 h in the presence of 2 equiv of DDQ. [b] Yield is that of the isolated product for each isomer (see Table 3 for structure of the products **4**).

Based on this hypothesis, the gold(I)-catalyzed cross-coupling of vinyldiazoacetates and subsequent aryl annulation was extended to an array of substrates. To our delight, the unsymmetrical polysubstituted benzenes were isolated as the major isomer in moderate to high yields for all cases (Table 4). Notably, only one homocoupling product was isolated in a small amount for each reaction. Specifically, the electronic effect of the vinyldiazoacetates had a key role in the selectivity. The cross-coupling reactions between electron-rich and electron-deficient styryldiazoacetates were liable to give better selectivity (**5c**–**f**, **5j**). The most impressive result was obtained for the reaction of *para*-methylphenyl vinyldiazoacetate and *para*-cyanophenyl vinyldiazoacetate, in which **5j** was isolated in 74% yield together with 9% yield of **4f**. In addition, the reaction of ethyl vinyldiazoacetates with methyl vinyldiazoacetates provided the unsymmetrical benzenes, having four different functional groups, in moderate yields (**5k**, **5l**).

The gold-catalyzed cross-coupling is the preferred process, which is consistent with Davies' previous investigation.[8] A plausible mechanism for the gold(I)-mediated cross-coupling of vinyldiazoacetates is proposed (Scheme 4). First, the preferential reaction of the relatively electron-poor vinyldiazoacetate **A** and the gold catalyst generates the gold-carbenoid **B**, which would be quickly attacked by the relatively electron-rich vinyldiazoacetate **C** (with stronger nucleophilicity), thus leading to the newly formed C–C bond and giving rise to the intermediate **D**. Next, loss of one molecule of nitrogen and subsequent migration of the C–Au



Scheme 4. Proposed reaction mechanism.

bond results in C=C bond formation to give the triene **F**. Clearly, the trivial electronic difference between **A** and **C** is responsible for the role they played during the reaction process.

In conclusion, we have achieved a challenging intermolecular cross-coupling reaction of diazo compounds by completely taking advantage of the electronic difference between reaction partners to produce tetrasubstituted alkenes using a IPrAuNTf$_2$/NaBAr$_F$ catalyst. Furthermore, a gold-initiated benzannulation was also developed, and demonstrates significant progress on the synthetic usefulness of this methodology. To our knowledge, this is the first selective and practical example to selectively produce *Z*-configured tetrasubstituted alkenes by intermolecular cross-coupling of diazo compounds. Studies are ongoing with regard to gold-catalyzed intramolecular diazo coupling as well as synthetic applications.

Received: June 30, 2014
Published online: August 25, 2014

Keywords: annulations · alkenes · cross-coupling · diazo compounds · gold

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