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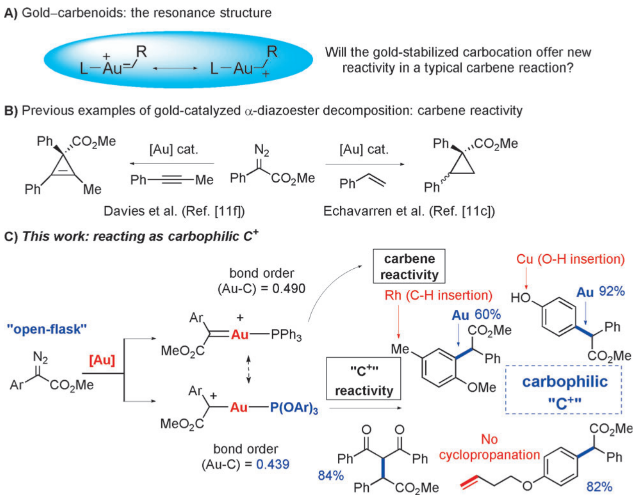
Gold–Carbenoids

Chemoselective Carbophilic Addition of α-Diazoesters through Ligand-Controlled Gold Catalysis**

Yumeng Xi, Yijin Su, Zhaoyuan Yu, Boliang Dong, Edward J. McClain, Yu Lan, and Xiaodong Shi**

Abstract: *The chemoselective addition of arenes and 1,3-diketones to α-aryldiazoesters was achieved through ligand-controlled gold catalysis. Unlike a dirhodium catalyst (which promotes C_{sp^3}–H insertion and cyclopropanation) and a copper catalyst (which catalyzes O–H and N–H insertions), the gold catalyst with an electron-deficient phosphite as the ancillary ligand exclusively gave the carbophilic addition product, thus representing a new and efficient approach to form "carbophilic carbocations", which selectively react with carbon nucleophiles.*



Scheme 1. Reactivity of gold–carbenoids: carbene versus carbocation.

The "push–pull" dual reactivity[1] of gold complexes renders them versatile compounds for the synthesis of complex molecules, because it allows the use of gold–carbenoid-type reactivity. Despite the early debut of gold–carbenoids, the direct proof of the existence of such an intermediate is largely missing and mostly relies on indirect evidences[2] and computational studies.[3] The nature of gold–carbenoids, i.e. gold–carbenes or gold-stabilized carbocations, remains elusive (Scheme 1 A). A recent comprehensive NMR study performed by Widenhoefer and co-workers suggested that only cationic gold intermediates were involved in gold–carbenoid-related transformations.[4] More strikingly, Fürstner and co-workers later reported the first structure of a reactive gold–carbenoid, which showed a very weak electron donation from gold to the carbene center.[5] Whereas these results provided insight into the nature of gold–carbenoids, most of the reported gold-catalyzed carbene transfer reactions proceed according to the typical carbene reactivity, i.e. in cyclopropanation and cyclopropenation reactions (Scheme 1 B). Herein, we report a chemoselective electrophilic aromatic substitution on α-diazoesters through ligand-controlled gold catalysis. With an electron-deficient phosphite $P(OAr)_3$ as the ligand, the gold–carbene intermediate acts as a "carbophilic carbocation", leading to a selective nucleophilic addition on carbon, without addition at typical carbene receptors such as phenol and alkene (Scheme 1 C).[6]

α-Diazoesters[7] are valuable compounds for carbene transfer reactions and have been applied in C–H and X–H insertion reactions catalyzed, e.g., by dirhodium[8] and copper[9] complexes. The first gold-catalyzed decomposition of a diazoester was reported in 2005[10] and since then many more followed.[11] However, compared to the π-acid activation mode, this type of gold catalysis is less explored and little mechanistic insight has been provided so far.

We hypothesized that in comparison to Rh and Cu cations, gold cations have a very different coordination ability, which was observed in numerous gold catalyzed reactions. Thus, the formation of a distinct Au=C bond should translate into a different reactivity when the proper conditions are found. This hypothesis proved correct when we observed the exclusive electrophilic aromatic substitution (EAS) of 4-methoxytoluene with methyl phenyldiazoacetate (Scheme 2 A), which was achieved through slow addition of the diazoester in the presence of PPh_3AuNTf_2. This result clearly indicated an orthogonal reactivity of the gold catalyst compared to a dirhodium catalyst, which exclusively promoted the benzylic C–H insertion without the occurrence of electrophilic aromatic substitution.[12]

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[*] Y. Xi,[+] Y. Su,[+] B. Dong, E. J. McClain, Prof. X. Shi
C. Eugene Bennett Department of Chemistry
West Virginia University
Morgantown, WV 26506 (USA)
E-mail: Xiaodong.Shi@mail.wvu.edu
Homepage: http://community.wvu.edu/~xs007/
Z. Yu, Prof. Y. Lan
School of Chemistry and Chemical Engineering
Chongqing University
400030, Chongqing (P.R. China)
E-mail: LanYu@cqu.edu.cn

[+] These authors contributed equally to this work.

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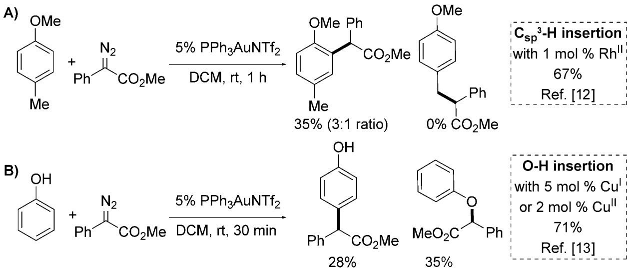


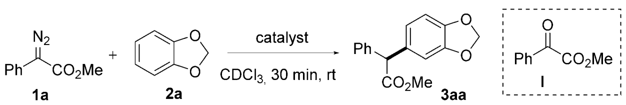
Scheme 2. The distinct chemoselectivities observed with gold–, rhodium–, and copper–carbenoids in C–H and O–H insertion reactions. Conditions: Nu (5 equiv) and $Ph_3PAuNTf_2$ (5 mol%) in dry DCM (0.1 mL) was added to a solution of methyl phenyldiazoacetate (0.2 mmol) in dry DCM (0.9 mL) over 1 h with a syringe pump, Ar. DCM is degassed with Ar. The NMR yield was calculated using 1,3,5-tribromobenzene as an internal standard.

A different chemoselectivity was also observed for the reaction between phenol and methyl phenyldiazoacetate: whereas a copper catalyst has been shown to efficiently catalyze the O–H insertion reaction,[13] the gold(I) complex surprisingly promoted the *para*-alkylation in modest yield (Scheme 2B).[6] These rather unexpected results prompted our interest in exploring the carbocation reactivity of gold–carbenoids to achieve a selective nucleophilic addition on carbon, even in the presence of carbene-sensitive functional groups such as phenol, alkene, and alkyne.

We began our study using methyl phenyldiazoacetate (**1a**) and 1,3-benzodioxole (**2a**) as the model substrates. Since gold(I) complexes exhibit a simple linear coordination pattern, the reactivity of the resulting gold–carbenoid should strongly depend on different ancillary ligands. As shown in Table 1, the cationic gold(I) complex with Ph_3P as the ligand, led to the complete conversion of **1a** and furnished the desired product **3aa** in 48% yield (entry 1). The catalyst with the electron-rich ligand IPr showed inferior reactivity toward the conversion of the diazo compound (entry 2). Electron-rich phosphine ligands, on the other hand, showed reactivities similar to that observed with the Ph_3P-substituted catalyst, although lower yields were obtained (entry 3–6). Interestingly, MorDalPhos,[14] a superior ligand for non-diazo gold–carbenoid chemistry,[15] also showed low reactivity (entry 7). A careful examination of the crude reaction mixture indicated the formation of at least five different by-products, with the major one being the α-oxoester **I**, which we propose to be a product of the reaction between the metal carbene and oxygen, a common side reaction observed in dirhodium–carbene chemistry.[16]

Based on these preliminary results, we hypothesized that the product selectivity could be altered by fine-tuning the electronic nature of the ligand.[17] Specifically, an electron-donating ligand might lead to the gold–carbene resonance form (Scheme 1A), whereas a π-acceptor ligand would favor the formation of the gold-stabilized carbocation resonance form. Thus, the latter type of catalyst could benefit the desired electrophilic aromatic substitution by eliminating the by-products resulting from the typical carbene pathway. Gratifyingly, the phosphite–gold(I) complex gave very good yields albeit a slower conversion was observed (entry 8). An extension of the reaction time to two hours led to full conversion and 87% yield of **3aa** (entry 9). Notably, this transformation (entry 10) was performed under open-flask conditions without solvent pretreatment and syringe pump, which is rarely seen in diazo chemistry.[18] Remarkably, the observed chemoselectivity is unique for gold–carbenoids, because dirhodium, copper, and silver catalysts gave only marginal amounts of product (entries 13–15).[19]

Table 1: Optimization of the reaction conditions.[a]

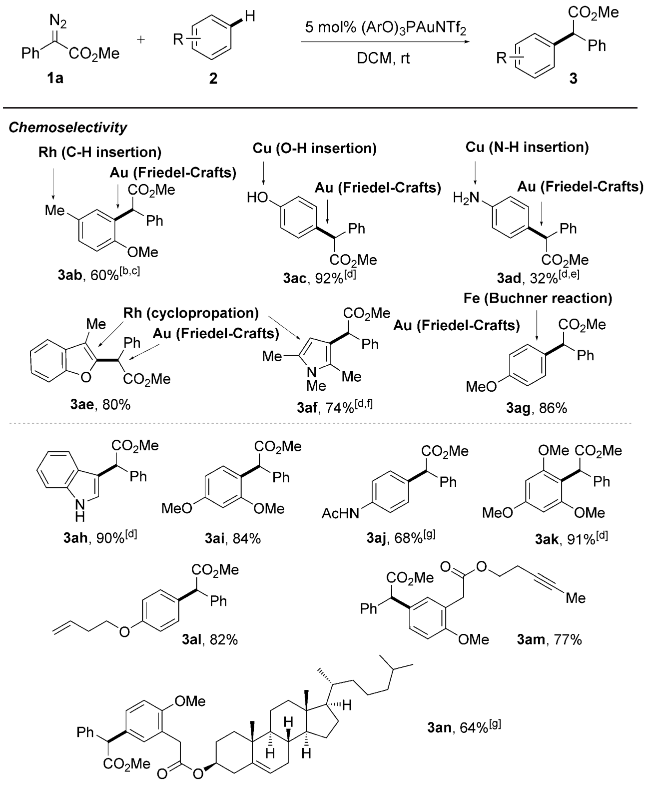


Entry	Catalyst (mol%)	Conv. [%][b]	**3aa** [%][b]	**I** [%][b]
1	$Ph_3PAuNTf_2$ (5)	100	48	13
2	$IPrAuNTf_2$ (5)	30	3	5
3	$JohnPhosAuNTf_2$ (5)	100	24	6
4	Di-Ad-BrettPhos$AuNTf_2$ (5)	100	18	8
5	$t$$Bu_3PAuNTf_2$ (5)	86	19	50
6	$Me_4$$t$BuXPhos$AuNTf_2$ (5)	100	12	16
7	MorDalPhos$AuNTf_2$ (5)	41	3	37
8	$(ArO)_3PAuNTf_2$ (5)	83	70	5
9[c]	**$(ArO)_3PAuNTf_2$ (5)**	**100**	**87**	**5**
10[c,d]	**$(ArO)_3PAuNTf_2$ (5)**	**100**	**82**	**6**
11	$(ArO)_3PAu$(TA-Me)OTf (5)	100	74	12
12[e]	$(ArO)_3PAuNTf_2$ (5)	89	0	22
13	$AgNTf_2$ (5)	100	13	3
14	$Cu(OTf)_2$ (5)	40	7	16
15	$Rh_2(OAc)_4$ (5)	100	0	41

[a] Reaction conditions: **2a** (5 equiv) and catalyst in $CDCl_3$ (0.1 mL) was added to a solution of **1a** (0.1 mmol) in $CDCl_3$ (0.9 mL) over 30 min using a syringe pump. [b] Conversion and yield were determined by ^{1}H NMR spectroscopy using 1,3,5-tribromobenzene as internal standard. [c] Reaction time: 2 h. [d] Open flask (air, wet solvent), syringe-pump-free. [e] **2a** is absent. Ar = 2,4-di-*tert*-butylphenyl. TA-Me: *N*-methyl-benzotriazole.

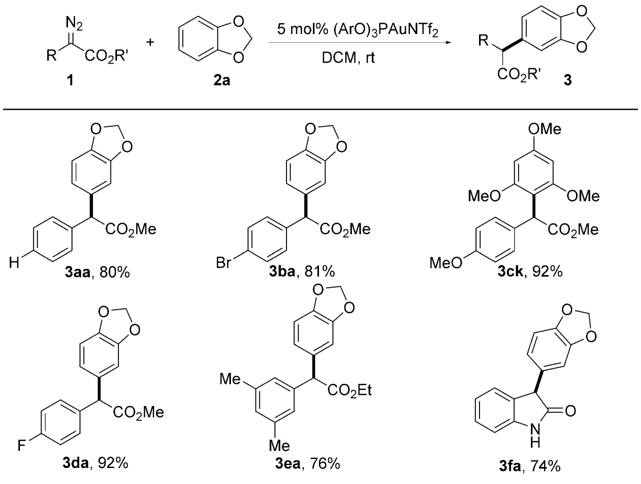
With these results in hand, we examined the general applicability of the reaction with regard to the chemoselectivity and the substrate scope. The results are summarized in Table 2. In general, electronically activated arenes undergo this transformation leading to the corresponding products in good to excellent yields. As shown in Scheme 2, the gold catalyst promoted the electrophilic aromatic substitution with 4-methoxytoluene and phenol, whereas the rhodium and copper catalyst promote the C–H and O–H insertion, respectively (**3ab**, **3ac**).[20] Notably, aniline, which is a potential ligand and a strong N nucleophile, also furnished the Friedel–Crafts-type product **3ad**, even though a low yield was obtained (the major product resulted from the N–H insertion).[21] This result supports the carbophilic nature of gold–carbenoids compared to copper–carbenoids (which exclusively gave the N–H insertion products). Electron-rich heterocycles, such as benzofuran and pyrrole, are also suitable substrates for this aromatic substitution (**3ae**, **3af**), whereas the cyclopropanation reaction is dominant when the dirhodium catalyst is used.[22] Similar results were obtained with anisole in an iron-promoted Buchner reaction with the identical diazoester.[23]

Table 2: Scope of arenes and chemoselectivity.[a]



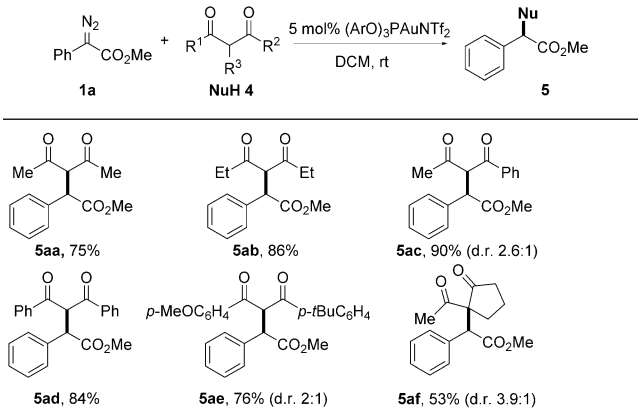
[a] General conditions: **1a** (0.2 mmol), **2** (0.8 mmol), $(ArO)_3PAuNTf_2$ (5 mol%) in DCM (1.0 mL), 30 min–2 h. Yield of the isolated compound. [b] 5 equiv of nucleophile was used, slow addition in 1 h, Ar. [c] Two regioisomers were formed (ratio 2.4:1). [d] 2 equiv of nucleophile was used. [e] 5 mol% $Ph_3PAuNTf_2$ was used. [f] Reaction time: 12 h. [g] 2 equiv of **1a** and 1 equiv of nucleophile were used.

Table 3: Scope of α-diazoesters.[a]



[a] General reaction conditions: **1** (0.2 mmol), **2a** (0.8 mmol), 5 mol% $(ArO)_3PAuNTf_2$ in DCM (1.0 mL), 30 min-2 h. Yield of the isolated product.

Table 4: 1,3-Diketones as effective carbon nucleophiles.[a]



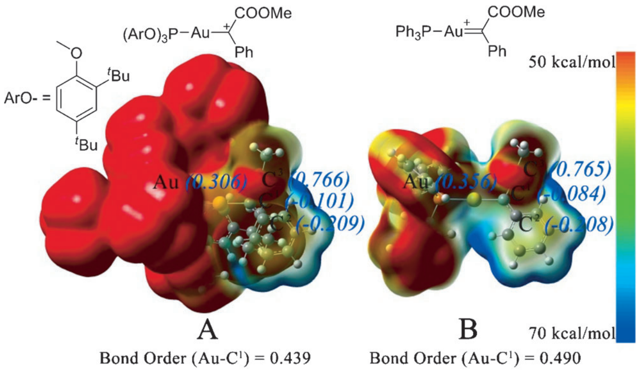
[a] General reaction conditions: a solution of **1a** (0.2 mmol) in 0.8 mL DCM was added to a solution of **4** (1.0 mmol) and $(ArO)_3PAuNTf_2$ (5 mol%) in 0.2 mL DCM with a syringe pump over 1 h. Yield of the isolated product.

The investigated transformation also shows good functional group compatibility as illustrated in the second part of Table 2. Indole, ester, and amide groups were well tolerated under the reaction conditions. More impressively, substrates bearing an olefin or an alkyne exclusively underwent Friedel–Crafts alkylation instead of cyclopropanation and cyclopropenation, which have been reported previously for similar gold catalysts (**3al**, **3am**).[24] In the case of **3am**, the alkyne also remained intact, demonstrating the potential tandem use of π-activation and diazo decomposition reactivity. Moreover, a cholesterol derivative also gave the alkylation product in satisfactory yield (**3an**), which highlights the potential usage of this transformation for the late-stage modification of complex molecules.

The scope of α-diazoesters was evaluated as shown in Table 3. This reaction tolerates both electron-rich and electron-poor α-aryldiazoesters, when **2a** is used as the nucleophile. Electron-poor diazoesters (**1b** and **1d**) showed better reactivity, whereas the electron-rich diazoester **1c** gave dimerization products under standard conditions. A more electron-rich nucleophile, 1,3,5-trimethoxybenzene, gave a higher yield of the product (**3ck**). Notably, the diazooxindole worked well under the optimal conditions (yielding **3fa**), which provides an efficient approach to incorporate various carbon-substituted groups at the C-3 position of indoles.[25]

After the successful application of this gold-catalyzed Friedel–Crafts-type alkylation, we envisioned that the use of other carbon nucleophiles in conjunction with the gold–carbenoid might lead to the discovery of novel methodologies. As showcased in Table 4, 1,3-dicarbonyl compounds successfully serve as the nucleophile[26] to furnish tricarbonyl compounds **5**, which are rarely found in the literature.[27] Again, this transformation gave exclusively the C-nucleophilic addition product over O-nucleophilic addition product,[28] which is consistent with the chemoselectivity observed with phenol.

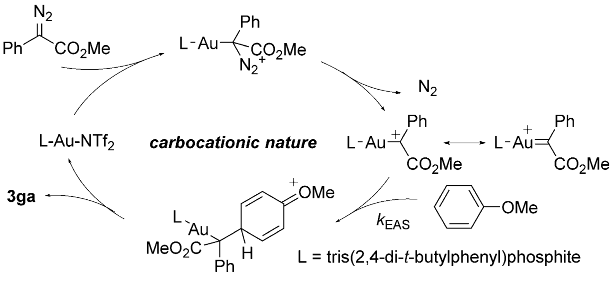
To gain more insight into how the ancillary ligand controls the gold–carbenoid reactivity,[29] we briefly investigated this new system with the density functional theory (DFT) method M11-L[30] using the standard basis set 6-311+G(d) (LanL08



Scheme 3. Electron static potential maps for compounds A and B with the tris(2,4-di-tert-butylphenyl)phosphite and triphenylphosphine ligand, respectively. The values in parentheses are M11-L-calculated NPA charges. The bond order for each gold–carbene bond is given below.

basis set[31] for Au).[32] The calculated bond order of the gold–carbene bond and the nature population analysis (NPA) charge distribution for compounds **A** and **B** are shown in Scheme 3. When the electron-deficient ligand tris(2,4-di-tert-butylphenyl)phosphite is used (compound **A**), the gold–carbene bond order is 0.439, which is 0.051 lower than that of compound **B** with the Ph$_3$P ligand. The difference of these bond orders indicates that the use of phosphite (ArO)$_3$P as the ligand leads to a complex with a lower fraction of the gold–carbene resonance form compared to the complex with Ph$_3$P as the ligand. The charge distribution shows that the positive charge of the Au atom in compound **A** is 0.306, which is 0.050 lower than in compound **B**. Accordingly, the charge of the C1 atom in compound **A** is only 0.017 lower than that in compound **B**.

Based on both, experimental and computational results, we propose a mechanism for this ligand-controlled gold-catalyzed electrophilic aromatic substitution with diazoester (Scheme 4). First, the cationic gold undergoes a ligand exchange with the diazoester to form the diazonium ion, which collapses to form the gold–carbenoid. This reactive gold–carbenoid serves as an electrophile to form a σ-complex with the substrate, followed by a 1,2-proton shift[33] to yield the product.



Scheme 4. Proposed mechanism for the gold-catalyzed Friedel–Crafts alkylation.

In summary, we have developed a ligand-controlled gold-catalyzed α-diazoester decomposition for the formation of a carbophilic carbocation. The observed chemoselectivity differs from the typical metal–carbenoid reactivity and largely depends on the choice of the ancillary ligand. Preliminary DFT calculations and our experimental observations imply that the nature of the gold–carbenoid, though varied with supporting ligands, better fits the description of a gold-stabilized carbocation, as Fürstner recently presented.[5a] The application of gold–carbenoids as carbocationic electrophiles for C–C bond forming reactions and detailed mechanistic investigations are currently underway in our laboratory.

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[32] Calculation results obtained with other DFT methods are summarized in the Supporting Information.

[33] It is not clear at this moment whether this 1,2-proton shift is concerted or stepwise.