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Catalytic arylative *endo* cyclization of gold acetylides: access to 3,4-diphenyl isoquinoline, 2,3-diphenyl indole, and mesoionic normal NHC-gold complex

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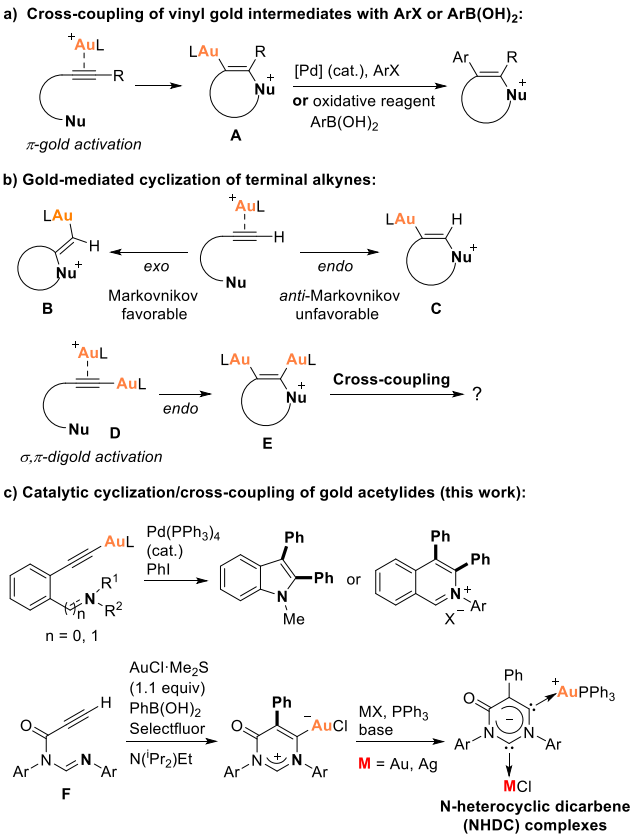
Abstract: 3,4-Diphenyl isoquinoline and 2,3-diphenyl indole are readily accessed by catalytic selective bis-arylative *endo* cyclization of gold acetylides. The synthetic approach could be also extended to prepare six-membered mesoionic NHC complex, which could further undergo deprotonation/complexation to afford 1,3-N-heterocyclic dicarbene (NHDCs) Au_2 and Au/Ag complexes. The key vicinal diaurated alkene intermediates have been isolated and the studies on their reactivities towards coupling partners reinforce the proposed mechanisms.

Gold catalysis has raised considerable attention, and emerged as efficient and versatile tool for C−C bond formation, mainly due to the capability of gold to activate C−C multiple bonds towards nucleophilic attack to initiate various novel transformations in organic synthesis.[1] Vinyl gold species **A** are commonly proposed as the key intermediates in gold-catalyzed intramolecular nucleophilic attack of alkynes (Scheme 1a).[2] Gold complexes are reluctant to undergo a redox process, due to the high redox potential of the Au^{I}/Au^{III} couple.[3] Therefore, cross-coupling of vinyl gold intermediates **A** generally requires stoichiometric amounts of strong external oxidants, such as $PhI(OAc)_2$ or Selectfluor, to promote $Au^{I}\rightarrow Au^{III}$ oxidation.[4] Alternatively, by combination of the powerful ability of gold to activate C−C multiple bonds for cyclizations with the C−C bond forming and efficient redox turnover of palladium, Au and Pd dual-catalyzed cyclization/cross-coupling reactions have attracted much interests in the past decade, wherein a key transmetalation of vinylgold with $ArPd^{+}$ intermediate, followed by reductive elimination at Pd center is involved.[5] In particular, such Au/Pd dual-catalyzed reactions could utilize weak internal oxidants, such as aryl halides, avoiding the use of strong external oxidants to avoid the low functional group tolerance typically going along with strong oxidants like Selectfluor and hypervalent iodine reagents.

So far, most alkyne substrates used in such cyclization/cross-coupling reactions had an internal alkynyl moiety, thus involving endocyclic vinyl gold species **A**.[2] When terminal alkynes are used, the intramolecular nucleophilic attack can process through *exo*−dig or *endo*−dig cyclization, corresponding to exocyclic (**B**) or endocyclic vinyl gold species (**C**), respectively (Scheme 1b). In



Scheme 1. Gold-mediated arylative cyclization of alkynes.

general, the *endo*−dig cyclization of terminal alkynes upon an anti-Markovnikov addition manner is kinetically unfavorable. Recent studies on the combination of computational, theoretical, and experimental data also show that nucleophilic *exo*-dig cyclizations of alkynes are intrinsically more favourable.[6] Indeed, we previously reported the Au-mediated cyclization of N-propiolic formamidine **F** to exclusively form an exocyclic vinyl gold species of type **B** through 5-*exo*-dig mode.[7] Later, we found that in the presence of base and two equivalents of Au salt, **F** could

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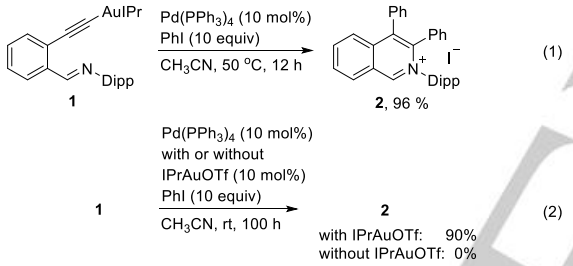
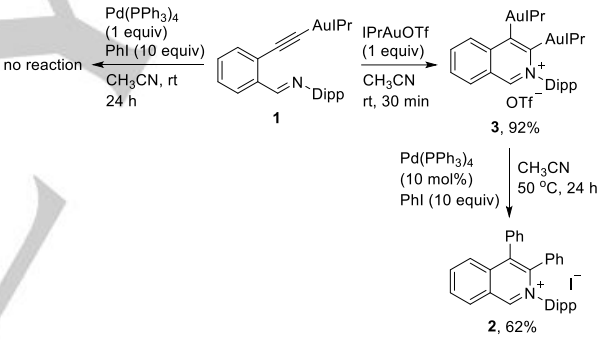
undergo 6-*endo*-dig cyclization to give six-membered vicinal diaurated alkene species of type **E**, indicating the involvement of the formation of a *σ*,*π*-digold acetylide species **D**.[8] In this case, gold in the acetylide acts as a directing group to realize the regioselective nucleophilic attack at the α-carbon in gold acetylide moiety. In addition, gold acetylides are generally quite stable and have been used as alternative substrates in C-C coupling reactions in the case that the corresponding terminal alkynes are unstable.[9] To date, studies on the reactivity of the vicinal diaurated alkene species **E** remain very rare. We previously reported **E** derived from **F** could undergo homocoupling to afford gold vinyl complexes.[8] We wonder whether **E** could undergo cross-couplings either with aid of either strong oxidative reagent or under Pd catalysis. Herein, firstly we reported catalytic bis-arylative *endo* cyclization of gold acetylides for the formation of 3,4-diphenyl isoquinoline and 2,3-diphenyl indole under Pd catalysis. Secondly, we have realized catalytic domino cyclization and oxidative coupling of in-situ prepared gold acetylide for the facile synthesis of six-membered NHC complex, a precursor for the synthesis of 1,3-NHDC (N-heterocyclic dicarbene) Au_2 and Au/Ag complexes. Moreover, two key active vicinal diaurated alkene intermediates have been isolated and fully characterized, and the studies on their reactivities towards coupling partners confirm the proposed mechanism.



Scheme 2. Cyclization/crossing coupling reaction of gold acetylide **1**.

of type **E**, which further undergoes cross-coupling with PhI under Pd catalysis.

To ascertain the mechanism, we attempted to isolate the proposed vicinal diaurated alkene intermediate. Delightfully, reacting gold acetylide **1** with one equivalent of IPrAuOTf led to form a vicinal diaurated alkene complex **3** in 92 % yield (Scheme 3). As expected, under catalysis of $Pd(PPh_3)_4$, digold **3** reacted with excess PhI in CH_3CN at 50 °C to give diarylation product **2** in a moderate yield of 62%. However, at room temperature, **3** cannot undergo such transformation to give **2** under the reaction conditions. Additionally, in the presence of excess PhI, no reaction was observed between **1** and stoichiometric amounts of $Pd(PPh_3)_4$ in CH_3CN at room temperature after 24 hours. These results suggest that the vicinal diaurated alkene complex **3** might be the reaction intermediate. Notably, the mechanism involving a vicinal Pd/Au alkene intermediate formed from the cyclization of *π*-Pd activated gold acetylide species cannot be completely ruled out. The structure of **3** was established by the single crystal X-ray diffraction analysis (Figure 1). The Au-C bond distances [Au1-C2, 2.043(6) and Au2-C3, 2.046(6) Å] in **3** are slightly longer than the gold carbene complexes (e.g., 2.015(3) Å[11a] and 2.010(10) Å[11b]), and similar with that of a C(sp^2)-Au single bond (e.g., 2.045(6) Å)[11c].



Scheme 3. Isolation of vicinal diaurated alkene **3** and its reactivity toward PhI.

The isoquinoline ring is present in many natural alkaloids, and 3,4-disubstituted isoquinolines could be synthesized by Pd-catalyzed cross-coupling of 2-(1-alkynyl)benzaldimines containing a internal alkynyl moiety with organic halides.[10] Firstly, we chose gold acetylide **1** (IPr = 2,6-bis(diisopropyl-phenyl)imidazol-2-ylidene) bearing a benzaldimine moiety as the model substrate for Pd-catalyzed cyclization/coupling with organic halide (Eqn 1, Scheme 2). In the presence of excess PhI, by using $Pd(PPh_3)_4$ as the catalyst, gold acetylide **1** underwent *endo* cyclization/crossing coupling to exclusively give diarylation product, 3,4-diarylisoquinoline **2** in a high yield of 96% at 50 °C in 12 h. However, at room temperature, the transformation didn't work (Eqn 2, Scheme 2). Interestingly, introduction of catalytic amount of IPrAuOTf (10 mol%) led to form the desired **2** in 90% yield within 100 h at room temperature. The structure of **2** was confirmed by X-ray diffraction analysis (please see Figure S1). These results indicate that the formation of **2** at room temperature probably involves a key vicinal diaurated alkene intermediate

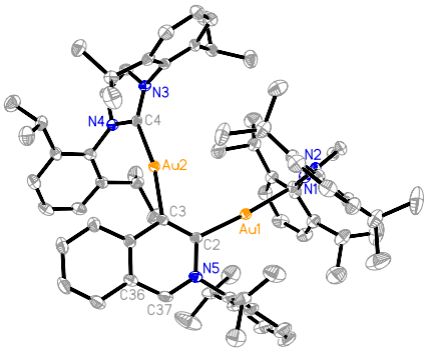
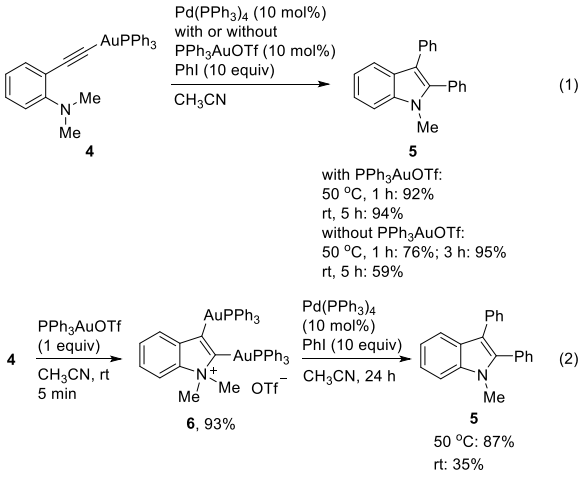
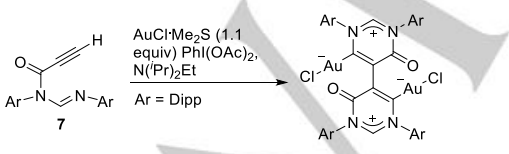


Figure 1. X-ray crystal structure of vicinal diaurated alkene **3**. The counter anion and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Au1−C1 2.033(6), Au1−C2 2.043(6), Au2−C3 2.046(6), Au2−C4 2.042(6), C2−C3 1.398(8).

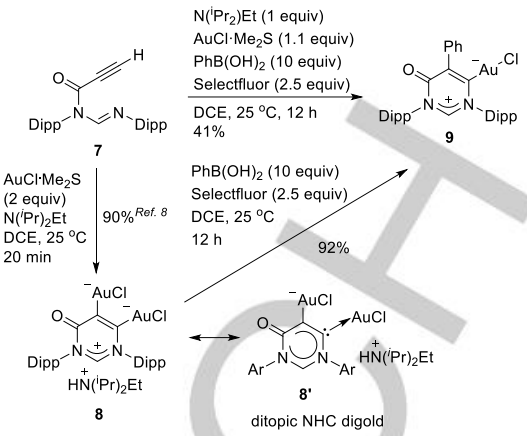


Scheme 4. Cyclization/crossing coupling reaction of **4**.

The increasing attention in outstanding biomedical applications of substituted indoles led to the recent development of methods for the access to 2,3-disubstituted indoles.[12] Therefore, we next tested the reactivity of gold acetylide **4** bearing a 2-*N*,*N*-dimethylaniline moiety in such cyclization/cross-coupling reaction. Under catalysis of $Pd(PPh_3)_4$, in the presence of PPh_3AuOTf as co-catalyst, cyclization/cross-coupling of **4** with excess PhI followed by a *N*-demethylation reaction led to the diarylation product 2,3-diphenyl indole **5** in a high yield 92%~94% either at elevated temperature (50 °C) within 1 h or at room temperature within 5 h (Eqn 1, Scheme 4). Without PPh_3AuOTf as co-catalyst, a decrease of reaction rate was observed. Under identical reaction condition, **5** was obtained in a 76% yield at 50 °C within 1 h or in a 59% yield at room temperature within 5 h (Eqn 1, Scheme 4). Again, addition of catalytic amounts of PPh_3AuOTf could accelerate the reaction rate in the same way as observed for the reaction of **1**. In the presence of stoichiometric PPh_3AuOTf, vicinal diaurated alkene intermediate **6** could also be obtained by the cyclization of **4** (Eqn 2, Scheme 4). A similar tetra-aurated indole complex, which was previously reported by Zhao group, has been synthesized through the cyclization of *o*-(trimethylsilylethynyl)aniline with $[(PPh_3Au)_3(\mu^3\text{-}O)](BF_4)$.[13] As expected, in the presence of a catalytic amount of $Pd(PPh_3)_4$, the digold **6** could also undergo cross-coupling with PhI to form **5** in 87% yield at 50 °C or in 35% yield at room temperature (Eqn 2, Scheme 4), suggesting the role of **6** as a reaction intermediate.



Scheme 5. Our previous work on cyclization/homo-coupling reaction of terminal alkyne **7**.[8]



Scheme 6. Cyclization/cross-coupling reactions of **7**.

Recently, we have reported the catalytic cyclization/oxidative homo-coupling reaction of gold acetylide, which was prepared in situ from terminal alkyne **7** (Scheme 5).[8] The vicinal diaurated alkene species **8** was isolated and identified as the key reactive intermediate *via* *σ*,*π*-digold-activated mechanism. Vicinal diaurated alkene species **8** also could be considered as the ditopic NHC digold **8'**, containing a gold-carbene bond at C4 position. However, neither **7** nor **8** could undergo cross-coupling with PhI under Pd catalysis. Inspired by the catalytic homo-coupling of **7**, we further investigated the cross-coupling reaction of **7** using $PhB(OH)_2$ as cross-coupling partner in the presence of strong external oxidant. Interestingly, when using Selectfluor as an oxidant, reacting of digold species **8** with $PhB(OH)_2$ at 25 °C led to monoarylated product **9**, instead of the diarylation product (Scheme 6). Finally, in the presence of 1.1 equivalent of $AuCl{\cdot}Me_2S$, excess $PhB(OH)_2$ and Selectfluor, **9** could also be directly prepared from **7**. Similar to the homo-coupling reaction, the cross-coupling also occurred at Au-C5 bond adjacent to the carbonyl moiety in **8**, whereas another Au–C4 bond adjacent to the N-substituent in **8** kept intact during cross-coupling step. The outcome is probably due to the stronger Au–carbene bond at C4 position, compared to the Au–C5 one adjacent to the carbonyl moiety.

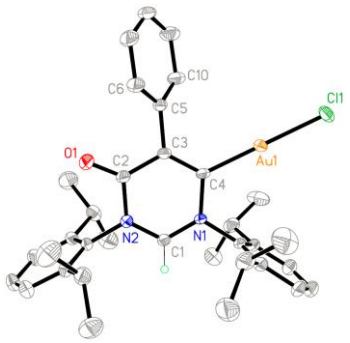


Figure 2. X-ray crystal structure of **9**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Au1−C4 1.985(4), Au1−Cl1 2.2909(15), C3−C4 1.368(6), C2−O1 1.221(5).

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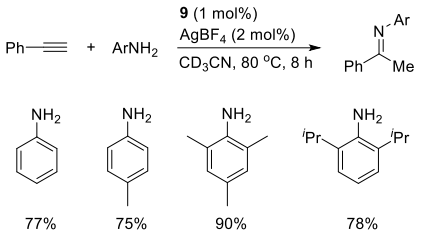
The structure of **9** was established by the single crystal X-ray diffraction analysis (Figure 2). The Au-C bond distance (1.985(4) Å) is similar to those in the abnormal carbene (*a*NHC) Au complexes (1.981(5) Å[14a]) and in the normal NHC Au complex IPrAuCl (1.942(3) Å[14b]). The ^{13}C resonance of the C4 carbon in **9** at 184.4 (s) ppm is deshielded compared to the C_{NHC} resonance in AuCl(IPr) (175.1 ppm).[14b] These observations indicate Au complex **9** can be better described as mesoionic normal NHC-gold complex.



Scheme 7. Gold complex **9** catalyzed addition of aryl amine into phenyl acetylene. Reaction conditon: 1.1 mmol of amine, 1 mmol of phenylacetylene, 1 mL of CD_3CN. Yields were determined by ^1H NMR spectroscopy on the basis of the amount of phenyl acetylene remaining in solution.

It's well-established that NHC-transition metal complexes bearing sterically bulky N-aryl substituents on the NHCs often exhibit high stability and catalytic performance in various organic reactions. Considering **9** contain bulky substituents at both nitrogen atom and at the α position of the carbene carbon atom, we were highlighted that **9** could be used as a potential candidate in gold catalysis (Scheme 7). The preliminary tests proved **9** an efficient catalyst in the addition of arylamine into alkyne with a comparable activity to IPrAuCl.[15]

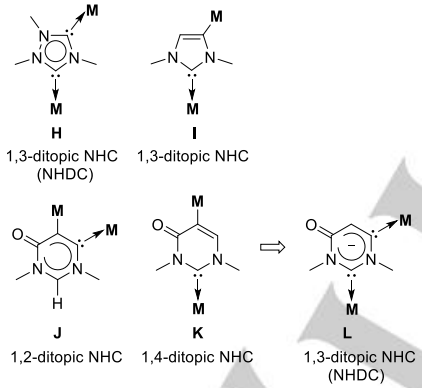
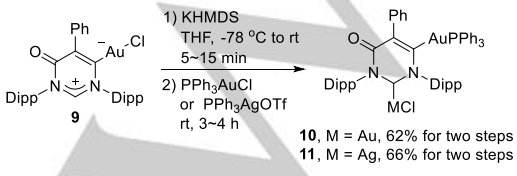


Figure 3. Known ditopic NHC complexes and the targeted six-membered ditopic NHC complex **L.**



Scheme 8. Synthesis of ditopic NHC metal complexes **10** and **11** from **9**.

Ditopic NHC ligands incorporating two carbene centers in a same heterocycle ring have recently emerged as the tuneable molecular scaffolds that can bridge transition metals.[16] Some ditopic NHC homo- and heterodimetallic complexes, such **H** and **I**, have found applications in a range of challenging catalytic tandem reactions.[17] Recently, we have developed coinage metal complexes **J** and **K**, based on 1,2- or 1,4-ditopic NHC.[8,18] So far, the known 1,3-ditopic NHC ligands are those having a five-membered heterocyclic ring. Since gold complex **9** has an H substituent at the C2-position, we suppose that the deprotonation of the C2-position of **9** followed by metal coordination, would offer a desirable six-membered 1,3-ditopic NHC digold complex **L**. Different from six-membered 1,2- and 1,4-ditopic NHCs, both containing one normal NHC centre, six-membered 1,3-ditopic NHC in **L**, could be described as anionic NHDC containing two normal NHC centres in the same heterocycle. As expected, upon deprotonation of **9** by potassium bis(trimethylsilyl)amide (KHMDS) and the subsequent complexation with PPh_3AuCl, a 1,3- ditopic NHC digold complex **10** was obtained (Scheme 8). Notably, upon treatment of **9** with KHMDS and PPh_3AuCl, the chloride ligand is exchanged by a PPh_3 in the resulting complex **10**. Ditopic NHC-based heterodinuclaer Au/Ag complex **11** could also be prepared by this synthetic approach. The single crystal X-ray crystallographic studies established the molecular structure of **10** (Figure 4) and **11** (please see Figure S2). In **10**, the Au–C4 bond [i.e., Au2–C2, 2.057(6) Å] is somewhat longer than the Au–C2 bond [i.e., Au1–C1, 1.994(6) Å], and the two Au-C bonds are marginally longer than those in the related five-membered NHDC digold complex [ClAu:C{[N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$CHCAu(PPh$_3$)}] [i.e., Au–C4, 2.022(5) Å; Au–C2, 1.975(5) Å],[19] respectively. The Au–C4 bond [i.e., Au1–C4, 2.046(4) Å] in **11** is similar to that in **10**. The Ag-C2 bond [i.e., Ag1–C1, 2.084(4) Å] in **11** is in the typical range for NHC-Ag complexes.[20]

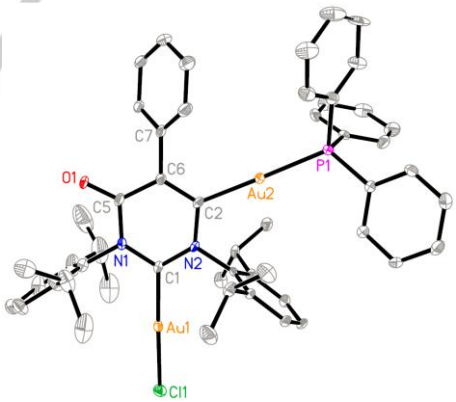


Figure 4. X-ray crystal structure of **10**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Au1−C1 1.994(6), Au2−C2 2.057(6), O1−C5 1.221(7), N2−C1 1.341(7), N2−C2 1.399(7), C2−C6 1.373(8), C5−C6 1.454(9).

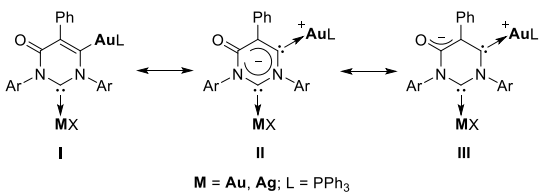


Figure 5. Various mesomeric structures for **10** and **11**.

NMR data can help us to assess the degree of carbene character of the donor atoms in the new ditopic NHC ligand in **10** and **11**. The ^{13}C signal for the carbene carbons of **10** appear at 195.7 ppm and 195.3 ppm, and those for the carbene carbons of **11** are observed at 208.89 ppm ($^{1}J_{C\text{-}Ag}$= 250.8 Hz and $J^{107}Ag\text{-}^{109}Ag$ = 18.3 Hz) and 194.48 ppm ($^{2}J_{C\text{-}P}$ = 114.3 Hz). All the carbene carbon signals are in the usual range for normal NHC metal complexes.[21] These NMR and structural data suggest that **II** and **III** are the major contributing resonance structures in the ditopic NHC complexes (Figure 5).

In summary, we have developed Pd-catalyzed or Au-catalyzed selective arylative *endo* cyclization of gold acetylides to synthesize 3,4-diphenyl isoquinoline and 2,3-diphenyl indole, as well as six-membered mesoionic NHC complex. The mesoionic NHC complex could further undergo deprotonation/complexation to prepare 1,3-NHDC Au_2 and Au/Ag complexes. Two key vicinal diaurated alkene intermediates have been isolated and fully characterized.

Acknowledgements

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Keywords: gold acetylides • arylative cyclization • isoquinoline • indole • NHC complexes

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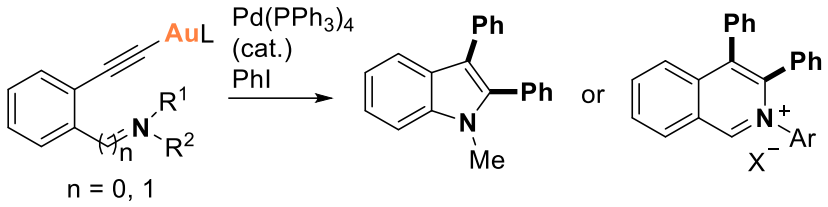

3,4-Diphenyl isoquinoline and 2,3-diphenyl indole have been synthesized by catalytic bis-arylative *endo* cyclization of gold acetylides. By using the synthetic approach six-membered mesoionic NHC complex has also been obtained, which could be used as precursor for the synthesis of 1,3-NHDC Au_2 and Au/Ag complexes. Catalytically relevant vicinal diaurated alkene intermediates have been isolated and fully characterized.