

Diazo Decomposition and Carbene Transfer Mediated by a Pincer Gold(III) Complex

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Abstract:

The pincer triflimide Au(III) complex ($N^{\wedge}C^{\wedge}C$)AuNTf₂ **2** is shown to decompose aryl diazo compounds Ph₂CN₂, (Dmp)CN₂H (Dmp = 2,6-dimesitylphenyl) and (*p*-F₃CPh)CN₂H and generate the corresponding Au(III) carbene complexes. Azine compounds resulting from carbene/diazo coupling have been isolated and structurally characterized. Carbene transfer to external reagents such as trimethylsilyl azide, methanol and styrene affords the corresponding imine, ether and cyclopropane under both stoichiometric and catalytic conditions.

Gold plays a major role in transition metal-mediated carbene chemistry.¹⁻⁴ Here, the key carbene complex is usually generated from alkynes or diazo compounds.⁵⁻⁷ Gold(I) undoubtedly occupies a forefront position in the field, and over the past 20 years, a number and variety of stable / persistent complexes have been reported,⁸⁻¹⁰ including diaryl carbenes,¹¹⁻¹³ monosubstituted carbenes,^{14,15} α -oxo carbenes¹⁶ and trifluoromethyl carbenes.¹⁷ Comparatively, much less is known for gold(III) carbene complexes, but few recent contributions from the Pérez and Toste groups have pointed out the high reactivity and synthetic potential of such species.¹⁸⁻²¹ (NHC)AuBr₃ precatalysts were first used to promote the functionalization of aromatic C–H bonds with diazoesters (Figure 1a).¹⁸ In 2017, difluoro Au(III) carbene complexes have been proposed as key intermediates in the formation of C(sp³)–CF₃ bonds assisted by B(C₆F₅)₃ (Figure 1b).¹⁹ The reaction does not proceed by direct reductive elimination but involves 1,1-migratory insertion of the carbene into the Au–C(sp³) bond. Insertion of α -oxo carbenes into 2,2'-biphenyl Au(III) metalacycles leading to fluorene derivatives has also been reported in 2018 (Figure 1c).²⁰

Given the spectacular progress achieved in Au(III) chemistry with cyclometalated complexes over the past few years,^{22, 23} we wondered about the possibility to take advantage of a pincer Au(III) fragment to generate and transfer carbene moieties. To do so, we turned to the $N^{\wedge}C(sp^2)^{\wedge}C(sp^3)$ framework introduced by Tilset *et al*²⁴ as it is readily accessible and impart high stability. Here we report the study of diazo decomposition by ($N^{\wedge}C^{\wedge}C$)Au(III) complexes and follow-up stoichiometric and catalytic reactions, including carbene/diazo coupling as well as carbene transfer to external reagents (Figure 1d).

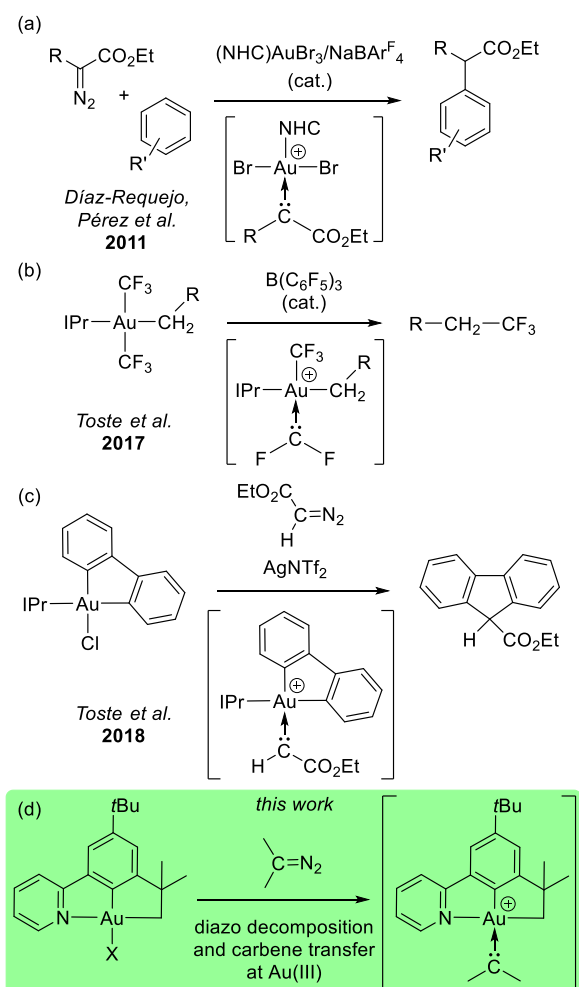


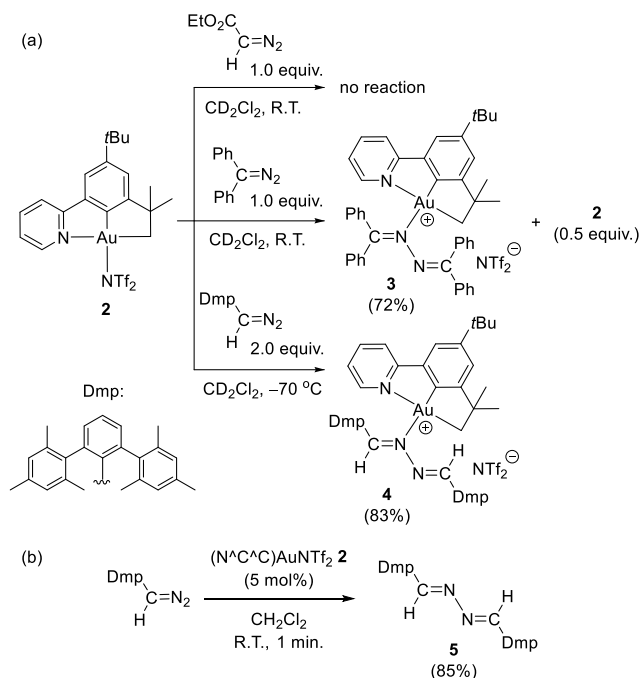
FIGURE 1. Reactive (electrophilic) Au(III) carbene complexes proposed as intermediates in gold-catalyzed aromatic C–H bond functionalization (a), C(sp³)–CF₃ bond formation at gold(III) (b), insertion into 2,2'-biphenyl Au(III) metalacycles (c) and targeted in this work (d).

Taking into account the lability of the trifluoroacetate group at Au(III),^{24–27} we first considered the (N^{^C^C})AuOAc^F complex **1** as a good candidate to achieve diazo decomposition and generate Au(III) carbenes. Complex **1** was prepared as described,²⁴ by microwave-assisted double cyclometalation of the corresponding phenylpyridine with Au(OAc)₃ in trifluoroacetic acid / water mixture. Disappointingly, no reaction occurred when **1** was treated with ethyl diazoacetate, diphenyl diazomethane or (Dmp)CN₂H (Dmp = 2,6-dimesitylphenyl). Given that diazo decomposition at transition metals usually starts by coordination of the terminal N atom or carbon atom, we assumed that the electrophilicity of Au(III) was not high enough and/or the OAc^F group was not labile enough in complex **1**. We thus turned to the corresponding triflimide complex (N^{^C^C})AuNTf₂. Complex **2** was readily obtained in two steps and 79% yield by reacting **1** with aqua regia^{28,29} and then silver triflimide.³⁰

Ethyl diazoacetate remained intact when exposed to complex **2**, but not the other diazo precursors, gratifyingly (Scheme 1a). With diphenyl diazomethane,¹³ decomposition occurs only at room temperature, as proved by the observation of dinitrogen bubbling and color fade upon mixing at –70 °C and slow warm up. After work-up, the corresponding azine, *ie* the coupling product between the carbene and its diazo precursor, was isolated as the Au(III) complex **3**. Its structure was ascertained by multi-nuclear NMR spectroscopy and high-resolution mass spectrometry (HRMS).³⁰ Most diagnostic for the coordination of the azine to Au(III) is the shielding of the CH₂ ¹H NMR signal of the N^{^C^C} ligand directly bound to gold. From δ 3.22 ppm in the triflimide precursor **2**, it shifts to δ 2.41 ppm in complex **3**. In the meantime, the ¹⁹F NMR signal for the triflimide moiety shifts upfield from δ –75.3 ppm for **2** to δ –79.4 ppm for **3**, indicating NTf₂ dissociation from Au(III) and formation of an ion pair.³¹ Alongside the Au(III) azine complex **3**, half an equivalent of the Au(III) triflimide precursor **2** is recovered intact. No sign of olefin formation by carbene dimerization was detected by NMR spectroscopy or mass spectrometry. We surmise that the higher reactivity of diphenyl diazomethane over ethyl diazoacetate towards **2** is due to the absence of strong electron-withdrawing group at the carbon atom.

With the hope to make diazo decomposition even easier, we then turned to the diazo compound (Dmp)CN₂H. Mono aryl diazo derivatives were shown to be substantially more nucleophilic than diaryl ones³² and we previously used the huge 3D steric shielding of the Dmp substituent to prepare a monosubstituted Au(I) carbene stable at –10 °C.¹⁵ The addition of one equivalent of Au(III) triflimide complex **2** to (Dmp)CN₂H in dichloromethane at –70 °C resulted in immediate color change

from orange to yellow-brown. Here the diazo decomposition proceeded at temperature as low as -70°C as evidenced by low-temperature multi-nuclear NMR spectroscopy. The thereby generated Au(III) carbene reacted spontaneously with the diazo precursor to give the corresponding azine, again as an Au(III) complex. Complex **4** was characterized by NMR spectroscopy and HRMS.³⁰ The ^1H NMR signal at δ 2.33 ppm for the ($\text{N}^{\wedge}\text{C}^{\wedge}\text{C}$)Au group and the ^{19}F NMR signal at δ -79.4 ppm support here also the coordination of the azine to Au(III) and the dissociation of the triflimide moiety. In addition to **4**, the crude mixture contains again about half of an equivalent of the Au(III) triflimide complex **2**. When the stoichiometric ratio was adjusted to 2 equivalents of diazo compound *per* Au(III) precursor, the Au(III) azine complex **4** was obtained cleanly and isolated in 83% yield.



SCHEME 1. (a) Stoichiometric reactions of the Au(III) complex **2** with diazo compounds. (b) Catalytic decomposition of the diazo compound (Dmp)CN₂H with the Au(III) complex **2**.

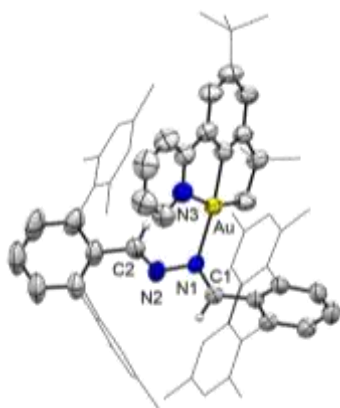
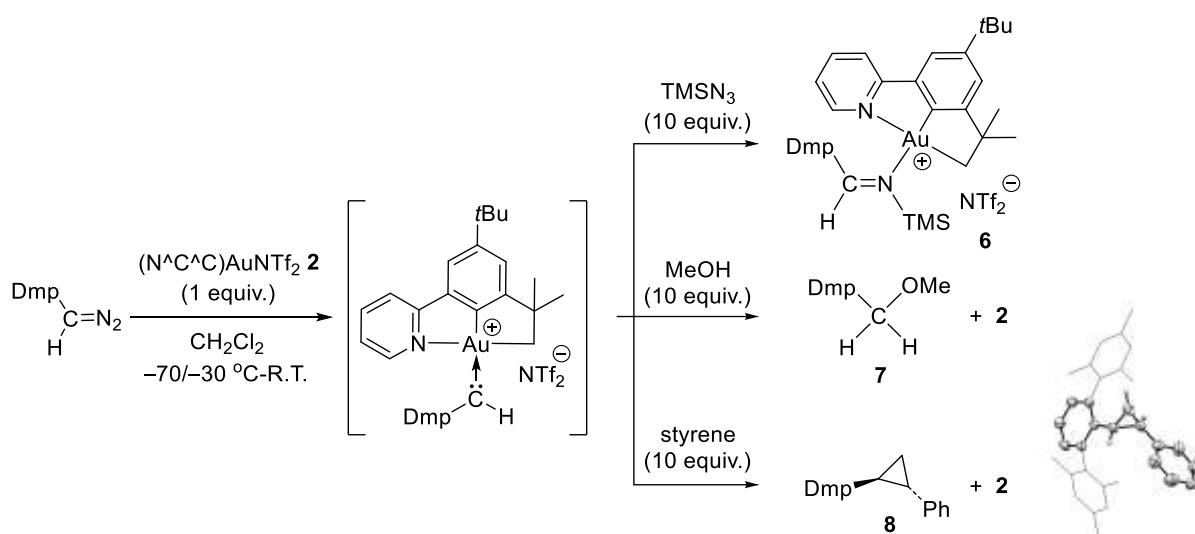


FIGURE 2. Molecular structure of complex **4'**. The H atoms of the Dmp substituent and $\text{N}^{\wedge}\text{C}^{\wedge}\text{C}$ ligand as well as the SbF_6^- counter-anion are omitted, for the sake of clarity. Ellipsoids are shown at 50% probability. Selected bond distances (in Å) and angles (in $^{\circ}$): Au-N1 2.155(4); Au-N3 2.165(4); N1-N2 1.419(6); C1-N1 1.269(6); C2-N2 1.208(6); Au-N1-N2 116.7(3); Au-N1-C1 133.0(3); N1-Au-N3 98.58(16); C1-N1-N2 110.3(4); N1-N2-C2 118.8(5).

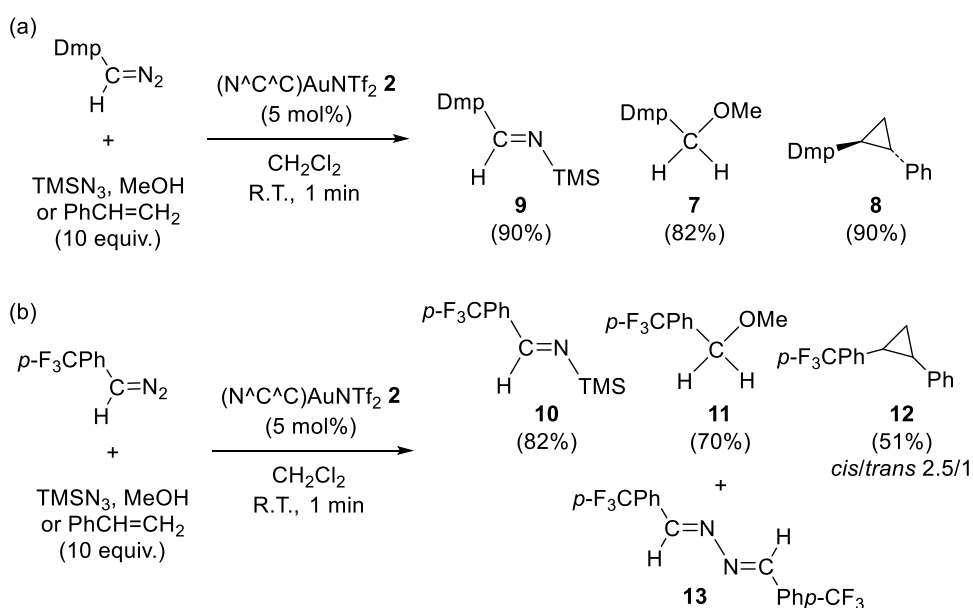
One step further, the possibility to induce diazo decomposition using a catalytic amount of Au(III) complex was tested. Pleasingly, when (Dmp)CN₂H was reacted with 5 mol% of Au(III) triflimide complex **2** at room temperature, complete conversion was reached within only 1 min. and the azine **5** was obtained in 85% yield, this time in free form (Scheme 1b). Besides NMR and HRMS, both the free azine **5** and its Au(III) complex **4'** (with SbF_6^- counter-anion instead of NTf_2^- , to impart higher crystallinity) were analyzed by single-crystal X-ray diffraction (SC-XRD).³⁰ The molecular structure of **4'** is shown in Figure 2 (see Figure S32 for that of **5**). In both cases, the azine moiety adopts *s-trans* configuration with anti arrangement of the two C=N double bonds. The C=N=N=C skeleton is quasi-planar in **5** but slightly rotated in **4'** (torsions angles of 168.76 and 145.77 $^{\circ}$, respectively), probably due to the additional steric constraints induced by the ($\text{N}^{\wedge}\text{C}^{\wedge}\text{C}$)Au fragment. In complex

4', the N(azine)–Au distance is very similar to the N(pyridine)–Au bond length within the (N[^]C[^]C)Au pincer unit [2.155(4) Å and 2.165(4) Å, respectively], indicating strong coordination.

The formation of the azine products **4** and **5** strongly suggests the transient formation of the Au(III) carbene complex, and its fast reaction with the diazo precursor. The following question is whether it is possible to compete with the carbene/diazo coupling and trap the carbene with external reagents. To this end, we successively considered trimethyl silyl azide, methanol and styrene as reaction partners with the aim to test carbene / nitrene coupling, O–H insertion and cyclopropanation, three complementary transformations typical of carbene complexes. These carbene transfer reactions were first attempted under stoichiometric conditions (1 equiv. of Au(III) complex **2** per diazo) with an excess of trapping reagent (10 equiv.). In all cases, the orange color characteristic of the diazo compound (Dmp)CN₂H rapidly vanished at –70/–30 °C. Gratifyingly, ¹H NMR analyses of the resulting mixtures showed formation of the corresponding imine, ether and cyclopropane products **6–8** without detectable amounts of azine byproducts **4** and **5** (Scheme 2). The imine product **6** was obtained as an Au(III) complex. The respective CH=N signal resonates at δ9.58 ppm in ¹H NMR spectroscopy, versus δ8.38 ppm for the corresponding free imine **9** (see below). The structure of the methyl ether **7** was unequivocally determined thanks to SC-XRD analysis. The presence of a single set of ¹H and ¹³C NMR signals for **8** indicates that the cyclopropanation proceeds with complete diastereoselectivity. The *trans* relationship of the Dmp and Ph substituents was ascertained thanks to X-ray diffraction analysis.³⁰



SCHEME 2. Carbene transfer reactions using stoichiometric amounts of Au(III) complex **2**. Molecular structure of cyclopropane **8**. The H atoms of the Dmp and phenyl substituents are omitted, the mesityl groups are simplified for the sake of clarity. Ellipsoids are shown at 50% probability.



SCHEME 3. Au(III)-catalyzed diazo decomposition and carbene transfer from (Dmp)CN₂H (a) and (*p*-F₃CPh)CN₂H (b).

The successful trapping of the $(N^{\wedge}C^{\wedge}C)Au(III)=CH(Dmp)^+$ carbene complex prompted us to then move to catalytic conditions, using 5 mol% of the Au(III) triflimide complex **2** per diazo, and again 10 equiv. of trapping reagent. The reactions proceeded nicely and the corresponding products **9** (the free imine), **7** and **8** were thereby obtained in high yields (82-90 %) confirming the efficiency of the $(N^{\wedge}C^{\wedge}C)Au(III)$ fragment to trigger diazo decomposition and carbene transfer (Scheme 3a).

To probe the generality of the transformation, the monosubstituted diazo compound (*p*-F₃CPh)CN₂H^{33,34} featuring a less sterically demanding aryl group was then evaluated. The *p*-CF₃ substitution increases the thermal and shock stability of the diazo compound,³⁵ and it provides a useful ¹⁹F NMR probe. Complex **2** was found to also readily react with this diazo precursor and catalytic carbene transfer afforded the corresponding imine, ether and cyclopropane products **10-12** (51-82% yields) alongside with some azine byproduct **13** (Scheme 3b).³⁰ Herealso, no sign of olefin formation by carbene dimerization was detected by NMR spectroscopy.

In conclusion, the $[N^{\wedge}C(sp^2)^{\wedge}C(sp^3)]AuNTf_2$ complex **2** was shown to trigger diazo decomposition and carbene transfer. The reactions are amenable to catalytic conditions. They represent first examples of carbene transfer catalyzed by a well-defined cyclometalated Au(III) complex. These results echo the following analysis and projection of Rocchigiani and Bochmann in the conclusion of their 2021 *Chemical Review* about Gold(III) chemistry: «Some intermediates and reaction pathways that are common for other late-transition metals, still remain unknown for gold(III). Notable examples are reactive gold(III) carbenes $Au\leftarrow CR_2 \leftrightarrow Au-C(+)R_2$ and carbene insertion catalysis, whose potential remains to be tapped.²² The difference in electronics and geometry between Au(III) and Au(I) (hard/soft character, four-coordinate square-planar versus two-coordinate linear) is likely to result in complementary reactivity profiles of the two oxidation state. Future work will aim to explore this chemistry further, in terms of synthetic applications as well as structural diversification, varying the substitution pattern of the carbene moiety as well as the nature of the ancillary ligand at Au(III).

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