How to cite: *Angew. Chem. Int. Ed.* **2025**, *64*, e202504162
doi.org/10.1002/anie.202504162

Nitrile–Ylides **Hot Paper**

Insertion of Nitriles Into a Gold(III)/Carbene Bond: A Direct and Powerful Entry to Imino-Substituted Carbenes

*Rui Wei, Nina Albouy, Sonia Mallet-Ladeira, Karinne Miqueu, and Didier Bourissou**

Dedicated to Anthony J. Arduengo and Guy Bertrand

Abstract: Strikingly, very little is known so far about reactive gold(III) carbenes. They have been proposed as key intermediates in a few reactions but remain chemical curiosities. Taking into account the enhanced electrophilicity of cationic Au(III) carbene complexes, we were intrigued by their reactivity with nitriles. Thus, we discovered a simple and efficient entry to imino-substituted carbenes. The transient (N^C^C)Au(III)←:CH(dmp)$^+$ carbene readily reacts with acetonitrile, benzonitrile, and diisopropyl cyanamide, affording stable and isolable Au(III) carbene complexes. Here, the imino group acts either as a strongly π-donating or a spectator substituent. Ligand exchange at Au(III) or protodeauration/deprotonation provides access to the corresponding free species, which display dual imino-carbene / nitrile-ylide reactivity, as substantiated by stoichiometric and catalytic dimerization, O─H insertion and [3 + 2] cycloaddition reactions.

Introduction

Since the pioneering work of Fischer and Schrock, transition metal carbene complexes have been recognized as extremely powerful and versatile reactive species involved in numerous synthetically useful transformations, including olefin metathesis, cycloaddition, and insertion reactions.[1–4] Varying the transition metal (and the surrounding ligands) enables to finely tune the structure and electronics of the carbene moiety, providing exquisite control over its chemical reactivity. Here, gold(I) carbenes have shown unique properties and have led to impressive synthetic as well as organometallic achievements over the past 20 years.[5–13] Comparatively, very little is known so far about reactive gold(III) carbenes, except a few catalytic and stoichiometric transformations in which Au(III)←:C(R)CO_2Et and Au(III)←:CF_2 complexes have been proposed as key intermediates.[14–16]

The very distinct electronic and geometric properties of gold(I) and gold(III) complexes[17] prompted us to launch studies aiming at preparing and stabilizing reactive Au(III) carbene complexes. To this end, cationic Au(III) carbene complexes are particularly attractive since they are expected to be extremely electrophilic.[18] In a first contribution, we have shown that the Au(III) complex **1** equipped with a N^C^C pincer ligand[19] is able to decompose aryl diazo compounds, such as (Dmp)CN_2H (Dmp = 2,6-dimesitylphenyl) (Figure 1a).[20] The ensuing Au(III) carbene complex is very short-lived. It tends to react with the diazo precursor to give the corresponding azine (preventing spectroscopic observation), but trapping with external reagents is possible and carbene transfer could be achieved under both stoichiometric and catalytic conditions via carbene–nitrene coupling, O─H insertion, and cyclopropanation.

Despite their significance, these first results do not address our initial paradigm: Can the extreme electrophilicity of Au(III) carbene complexes open new reactivity paths? In this light, we reasoned that nitriles, as ambiphilic unsaturated substrates (Lewis basic N center, electrophilic C center), could be ideal partners. They are susceptible to undergo 1,2-insertion and to afford imino-substituted carbenes (Figure 1b). Strikingly, reactions between carbene complexes and nitriles/cyanamides R─C≡N (R = alkyl, aryl, or amino) have very little precedents.[21–27] All contributions date back to the 1980's and involve Cr/Mo/W complexes, mainly alkoxy carbenes. It is also relevant to mention the trapping of transient free carbenes by nitriles.[28–31] The ensuing species are themselves highly reactive. They have been characterized and studied in inert matrices at few K or using time-resolved (nanosecond) laser spectroscopy (or laser-flash photolysis techniques). Their structure and reactivity are typically discussed within the imino-substituted

---

[*] R. Wei, D. Bourissou
CNRS/Université Paul Sabatier, Laboratoire Hetérochimie Fondamentale et Appliquée (LHFA, UMR 5069), 118 Route de Narbonne, Toulouse 31062, France
E-mail: didier.bourissou@univ-tlse3.fr

N. Albouy, K. Miqueu
CNRS/Université de Pau et des Pays de l'Adour, Institut des Sciences Analytiques et Physico-Chimie pour l'Environnement et les Matériaux (IPREM, UMR 5254), Hélioparc, 2 Avenue du Président Angot, Pau 64053, France

S. Mallet-Ladeira
Institut de Chimie de Toulouse (UAR 2599), 118 Route de Narbonne, Cedex 09, Toulouse 31062, France

Additional supporting information can be found online in the Supporting Information section

© 2025 The Author(s). Angewandte Chemie International Edition published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

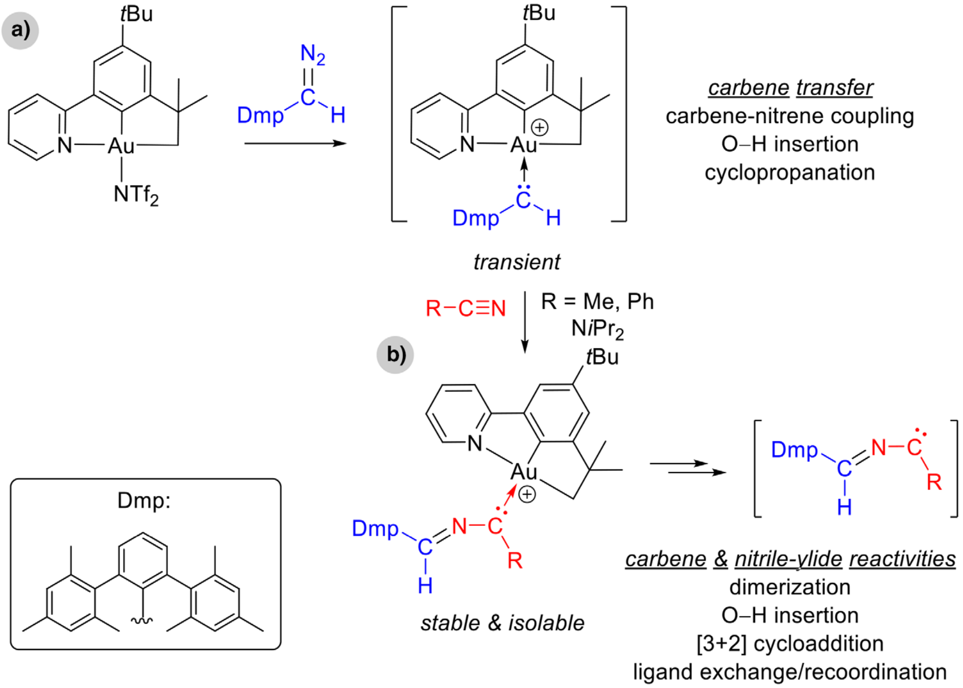
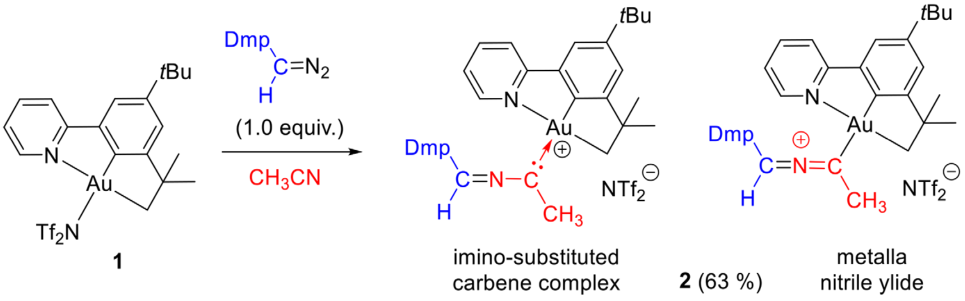


Figure 1. Formation and reactivity of the imino-substituted carbenes studied in this work.



Scheme 1. Synthesis of the imino-substituted carbene Au(III) complex **2**, and its resonance structure as metalla nitrile-ylide.

carbene / nitrile-ylide dichotomy.[32] Of note, one example of such a reaction involved a stable carbene, a phosphino-silyl-carbene, which was reported to give a 2*H*-azirine by [1 + 2] cycloaddition with benzonitrile.[33]

As described hereafter, reacting the transient Au(III)←:CH(Dmp) carbene with nitriles and cyanamides proved very fruitful. The ensuing imino-substituted carbene Au(III) complexes turned out to be stable and isolable. Their structure and stabilization mode have been thoroughly analyzed by experimental and computational means. The imino group was found to act either as a strongly π-donating or a spectator substituent. The corresponding *free* species could be generated by ligand dissociation or protodeauration/deprotonation. Their trapping with organic substrates and metal fragments have substantiated their dual imino-carbene / nitrile-ylide reactivity.

Results and Discussion

Nitrile Insertions

To start with, (Dmp)CN$_2$H was reacted with the (N^C^C)AuNTf$_2$ complex **1** in CH$_3$CN as solvent to directly trap the in situ generated Au(III)←:CH(Dmp) carbene (Scheme 1). Variable temperature NMR monitoring showed that the diazo decomposition occurred at −30 °C to afford a new Au(III) complex **2** with no detectable intermediate. After workup, complex **2** was isolated as a yellow solid in 63% yield. According to high-resolution mass spectroscopy (HRMS), it is a 1:1 adduct between the Au(III)←:CH(Dmp) carbene and CH$_3$CN. To help assigning the ^{1}H and ^{13}C NMR signals deriving from the incorporated CH$_3$CN motif, related D and ^{13}C-labeled complexes **2-D** and **2-C** were

© 2025 The Author(s). Angewandte Chemie International Edition published by Wiley-VCH GmbH

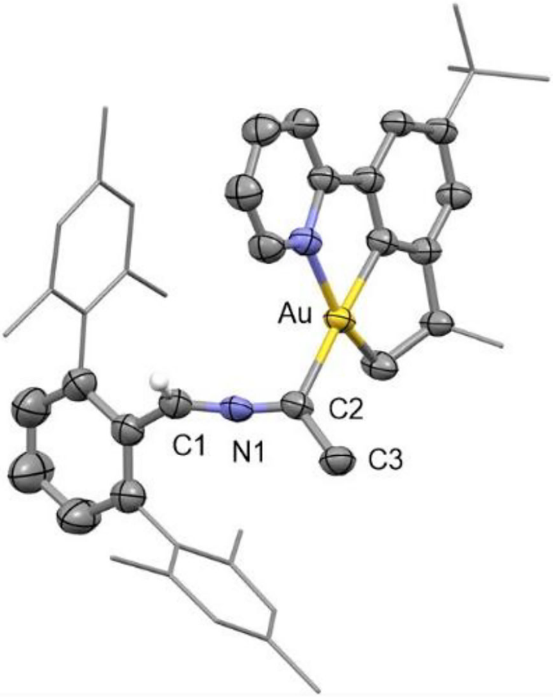


Figure 2. Molecular structure of complex **2**. For sake of clarity, the triflimide counter-anion and the hydrogen atoms, except the one at C1, are omitted, and the Mes/*t*Bu/Me groups are simplified. Ellipsoids are shown at 50% probability.

prepared using CD_3CN and $^{13}CH_3{}^{13}CN$, respectively.[34] The diagnostic imine ^1H NMR signal was found at δ 7.22 ppm as a quartet with small coupling to the CH_3 group found at δ 1.97 ppm ($^5J_{HH}$ 3.5 Hz). The ^{13}C NMR signal for the nitrile carbon atom shifts downfield to δ 183.0 ppm, while the (Dmp)CH signal shifts upfield to δ 116.9 ppm. Note that the ^{15}N NMR signal of the nitrile nitrogen atom (authenticated thanks to a ^1H-^{15}N HMQC experiment)[34] resonates at low field, δ 326 ppm. Of note, the same type of reaction occurs when trapping the Au(III)←:CH(Dmp) carbene in situ with PhCN (2 equiv.) in dichloromethane. The ensuing Au(III) complex **2′**, isolated in 78% yield as a pale-yellow solid, was characterized by ^1H and ^{13}C NMR spectroscopy, as well as HRMS.[34]

To gain more insight into the structure of the obtained complex, crystals suitable for single-crystal X-ray diffraction analysis were grown by diffusing *n*-pentane into an Et_2O solution of **2** at −20 °C.[35] Accordingly, complex **2** adopts a discrete ion-pair structure and results from 1,2-insertion of the C≡N triple bond into the Au←:CH(Dmp) bond of the transient carbene (Figure 2). The carbon atom bonded to Au (C2) is in a trigonal planar environment and the Au−C bond is long (2.115(4) Å), in the typical range for Au−C single bonds. Remarkably, the CNC fragment is close to linear (171.6(4)°) with short N−C bond lengths (1.249(5) and 1.246(5) Å), suggesting an azaallene-type structure. The planes of the CH(Dmp)=N imine and NC(C)Au carbene moieties are oriented quasi perpendicularly (86.9(3)°).

The bonding situation of complex **2** was further assessed by DFT calculations and Natural Bond Orbital (NBO) analyses. Calculations were performed at the B3PW91-D3(BJ)/SDD + f(Au), 6–31G**(other atoms) level of theory and the native (N^C^C)Au(III)←:CH(Dmp)$^+$ complex was also considered for comparison. The optimized geometry of complex **2** matched nicely that determined experimentally by XRD, with deviations of less than 0.042 Å and 2.24° in the key bond distances and bond angles, respectively (Table S2).[34] Inspection of the Natural Localized Molecular Orbitals (NLMOs) (Figure 3) shed light into the role of the substituents in the stabilization of the Au(III) carbenes. Accordingly, substantial Dmp→C_{carb} π-donation was found in the Au(III)←:CH(Dmp) complex (C_{carb} 19.0% and C_{ipso} 23.5%), while complex **2** is stabilized by strong N_{imino}→C_{carb} π-donation, as apparent from the N_{imino} and C_{carb} contributions in the associated NLMO (68.3 and 29.6%, respectively). Consistently, the Wiberg bond index for the $N_{imino}C_{carb}$ bond (1.7) indicates a double bond character. Note that in both Au(III) complexes, Au→C_{carb} back-donation is negligible. The d_{xy}(Au) orbital is only marginally delocalized over the $2p^{\pi}(C_{carb})$ orbital, even less in complex **2**, whose electrophilicity is tempered by the π-donating imino substituent (C_{carb} contributes to only 1.0% to the corresponding NLMO).

The mechanism of the 1,2-insertion of acetonitrile leading to the imino-substituted Au(III) carbene complex **2** was also investigated computationally. In line with what Fischer et al. proposed for the reaction of cyanamides with W/Mo/Cr carbene complexes,[22,24] a two-step process was found as the lowest energy path (Figure 4 and Figure S95).[34] It starts by the formation of a Lewis adduct between the N center of acetonitrile and the electrophilic carbene center (ΔG −12.4 kcal mol^{-1}, $\Delta G^{\neq}$ 4.6 kcal mol^{-1}). Then, the (N,C,C)Au(III) fragment undergoes a 1,3-shift from the CH(Dmp) to the C(CH_3) carbon center with temporary bending of the N center (CNC 83.87° at **TS2**). This step is rate-determining. Its activation barrier is estimated to be 22.0 kcal mol^{-1}, in agreement with a reaction proceeding at room temperature. The overall process is largely downhill in energy (ΔG −25.4 kcal mol^{-1}), in line with the strong stabilizing effect of the imino substituent.

Ligand Exchange/Dissociation

With complex **2** in hand, we were intrigued by its reactivity. We started our investigations by exploring the possibility of ligand exchange/dissociation, a key step in catalytic transformations involving carbene complexes. We chose PPh_3 as competitive ligand thanks to its simplicity and the advantageous ^{31}P NMR probe. Gratifyingly, an immediate and distinct color change from light to deep yellow was observed upon mixing complex **2** with PPh_3 (1 equiv.) at room temperature. The reaction afforded the 2,5-diazatriene **3₂** along with the [(N^C^C)Au(III)PPh_3]NTf_2 complex **4** (Scheme 2). Both compounds were isolated and fully characterized.[34] The 2,5-diazatriene **3₂** shows the characteristic ^{13}C NMR signal at δ 143.0 ppm for the central olefinic group. Additionally, its molecular structure was confirmed by sc-XRD analysis,[35] revealing an extended π-delocalized system. The formation

© 2025 The Author(s). Angewandte Chemie International Edition published by Wiley-VCH GmbH

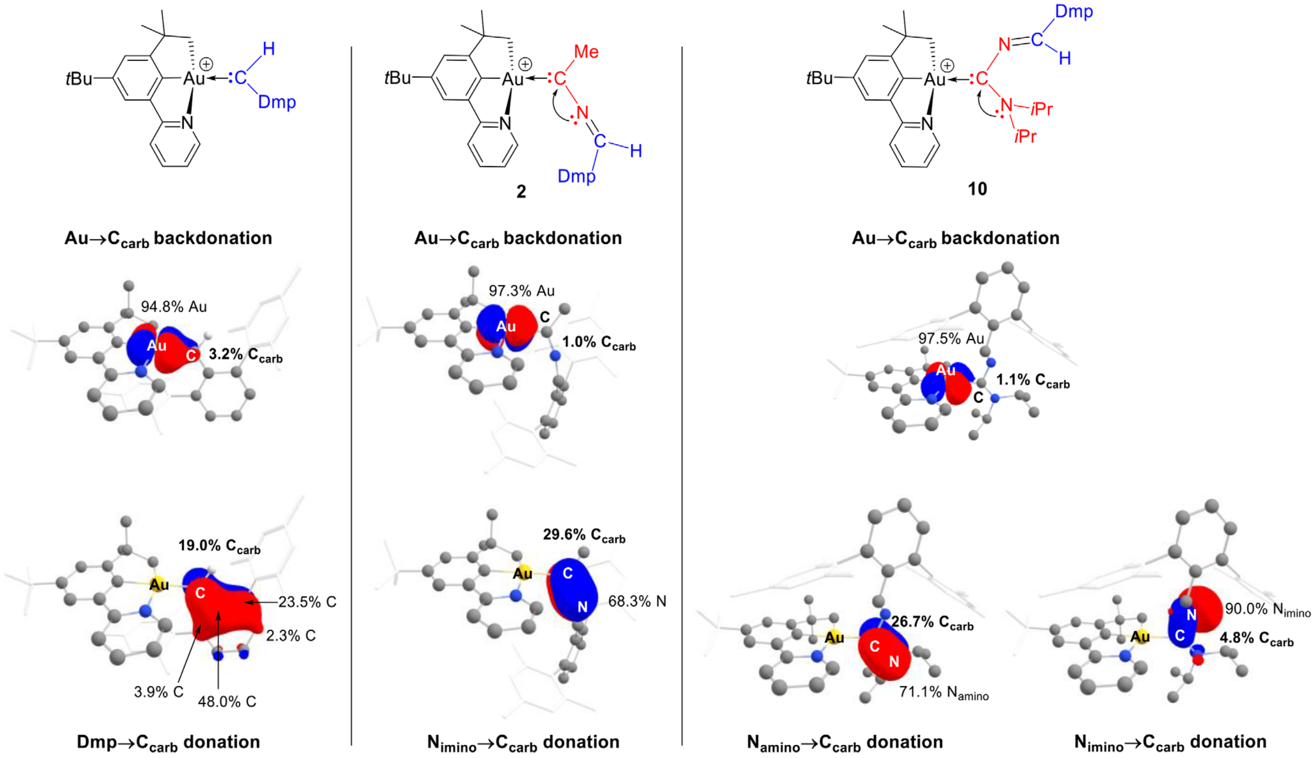
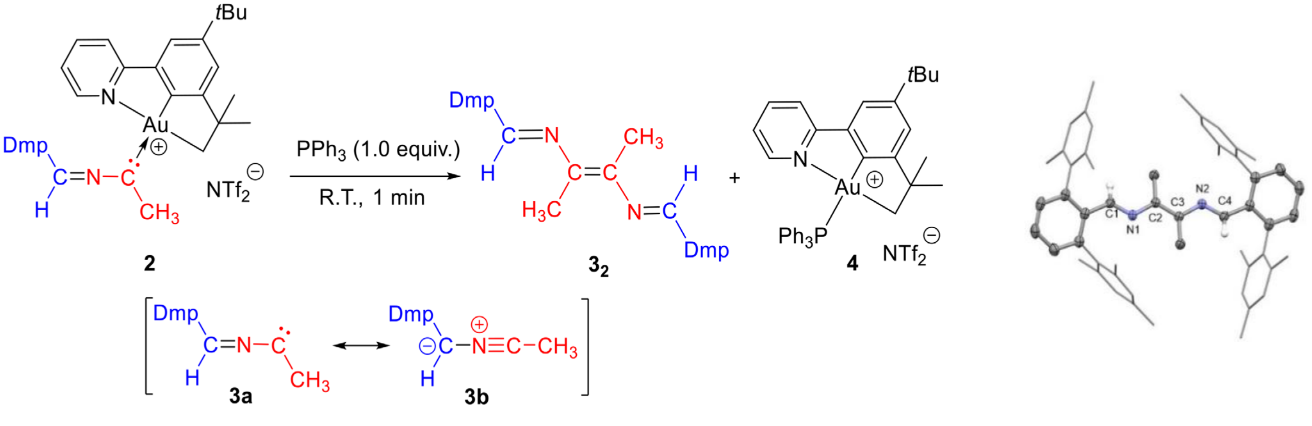


Figure 3. Bonding analyses of the (N^C^C)Au(III)←:CH(Dmp)$^+$, (N,C,C)Au(III)←:C(Me)N=CH(Dmp)$^+$ (**2**) and (N^C^C)Au(III)←:C(N*i*Pr$_2$)N=CH(Dmp)$^+$ (**10**) complexes at the B3PW91-D3(BJ)/SDD + f(Au), 6–31G**(other atoms) level of theory. Plot of the NLMOs (cutoff: 0.04) associated to Dmp→C$_{carb}$, N$_{imino}$→C$_{carb}$, N$_{amino}$→C$_{carb}$ and Au→C$_{carb}$ delocalizations with the contributions of the main atoms (in percent). For sake of clarity, the Mes/*t*Bu groups are simplified.

of **3$_2$** indicates that the free imino-substituted carbene (Dmp)HC=NCCH$_3$ **3a** released by ligand exchange at Au(III) spontaneously and quantitatively dimerizes. The formation of 2,5-diazatrienes was recognized early on by Hegarty et al. as a carbene-type reactivity path for nitrile-ylides.[32] Computationally, the dimerization of (Dmp)HC=NCCH$_3$ **3a** was found to be indeed very facile ($\Delta G^{\neq}$ 6.9 kcal mol^{-1}) and strongly exergonic (ΔG –62.6 kcal mol^{-1}).[34] The recent discovery by Bertrand et al. of a "masked" form for a bis(*N*-heterocyclic imino)carbene[36] prompted us to also consider the intramolecular rearrangement of (Dmp)HC=NCCH$_3$ via [3 + 2] cycloaddition of the nitrile-ylide form **3b** with one of the Mes group. The latter process was found much more demanding energetically ($\Delta G^{\neq}$ 32.5 kcal mol^{-1}, ΔG –25.7 kcal mol^{-1}) and not competitive with the dimerization.[34]

Interestingly, the same 2,5-diazatriene **3$_2$** was readily obtained when the ligand exchange reaction was conducted



Scheme 2. Formation and molecular structure of the 2,5-diazatriene **3$_2$**. For sake of clarity, the hydrogen atoms, except the ones at C1 and C4, are omitted and the Mes groups are simplified. Ellipsoids are shown at 50% probability.

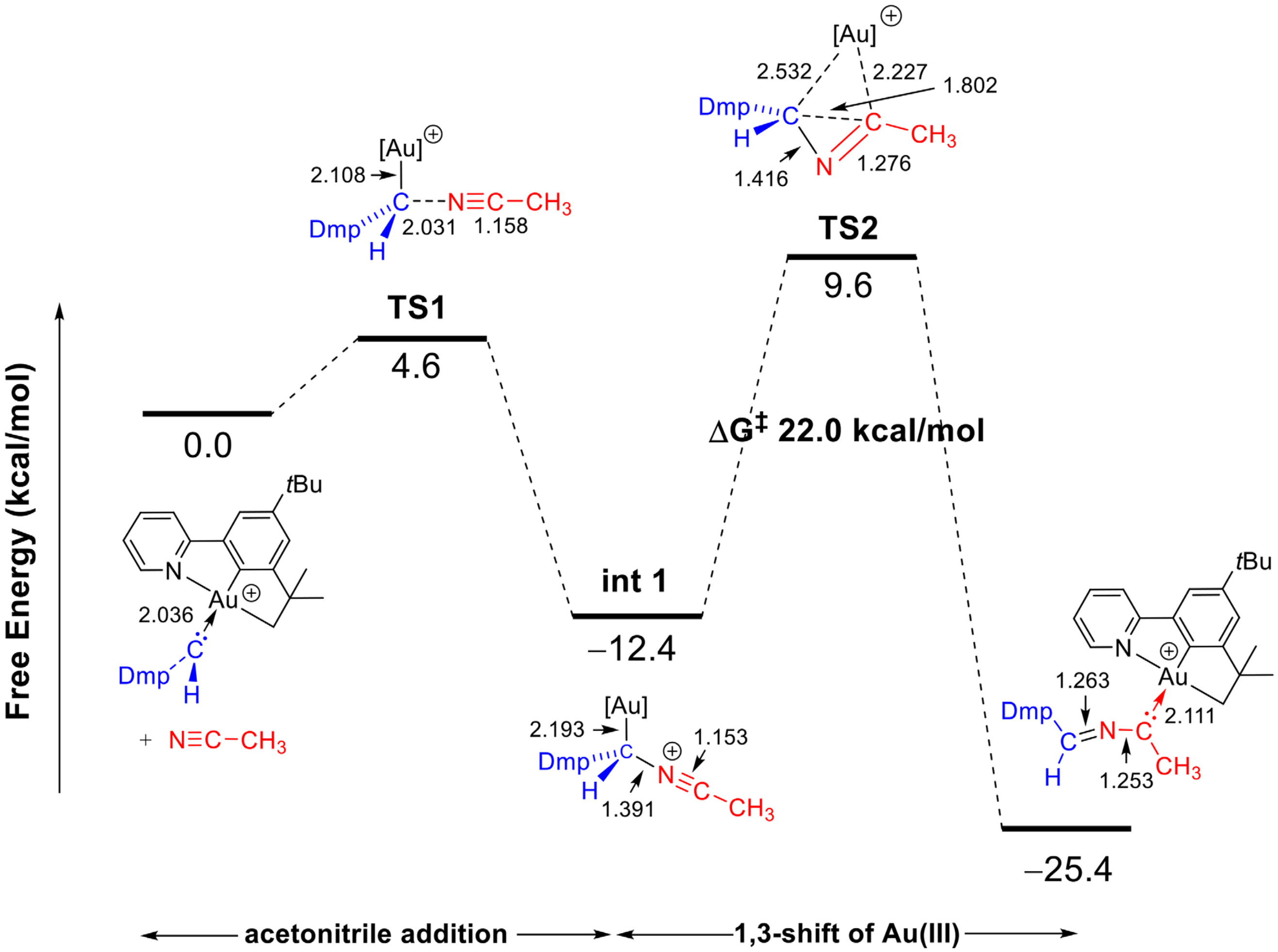
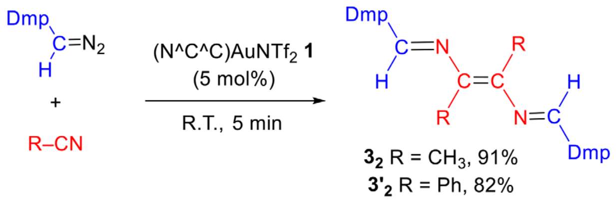


Figure 4. Energy profile computed for the reaction of the (N^C^C)Au(III)←:CH(Dmp)$^+$ complex with acetonitrile leading to the imino-substituted Au(III) carbene complex **2**. Calculations performed at the B3PW91-D3(BJ)/SDD + f(Au),6–31G**(other atoms) level of theory. Gibbs free energies (ΔG) in kilocalories per mole (kcal mol^{-1}). Main distances in ångström (Å).



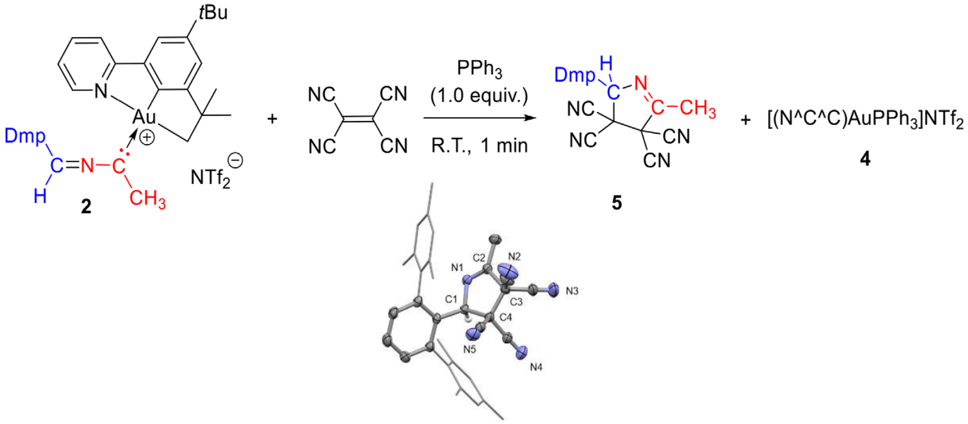
Scheme 3. Catalytic formation of the 2,5-diazatrienes **3**$_2$ and **3′**$_2$.

using (Dmp)CN$_2$H as a Lewis base instead of PPh$_3$. Upon mixing complex **2** with (Dmp)CN$_2$H in CH$_3$CN, the 2,5-diazatriene **3**$_2$ immediately and quantitatively precipitated.[34] This transformation paved the way for catalyzing the following sequence —diazo decomposition, nitrile insertion, iminocarbene dissociation and dimerization—using a catalytic amount of the (N^C^C)Au(III)NTf$_2$ complex **1**. Reacting the diazo (Dmp)CN$_2$H with 5 mol% of complex **1** in CH$_3$CN, the 2,5-diazatriene **3**$_2$ was indeed obtained in over 90% yield within only 5 min at room temperature (Scheme 3). The reaction proceeded similarly when PhCN (2 equiv. in dichloromethane) was used instead of CH$_3$CN, affording the corresponding 2,5-diazatriene **3′**$_2$ in 82% yield.[34] The structure of **3′**$_2$ was also unambiguously ascertained by NMR spectroscopy and sc-XRD analysis (Figure S93).[34,35] Of note, decomposition of (Dmp)CN$_2$H in the presence of acetonitrile under thermal (80 °C) or photochemical (Blue LED irradiation) conditions but without **1** showed no imino-carbene dimer formation.[34] The Au(III) complex thus not only induces diazo decomposition but also drives the carbene reactivity (nitrile insertion and dimerization).

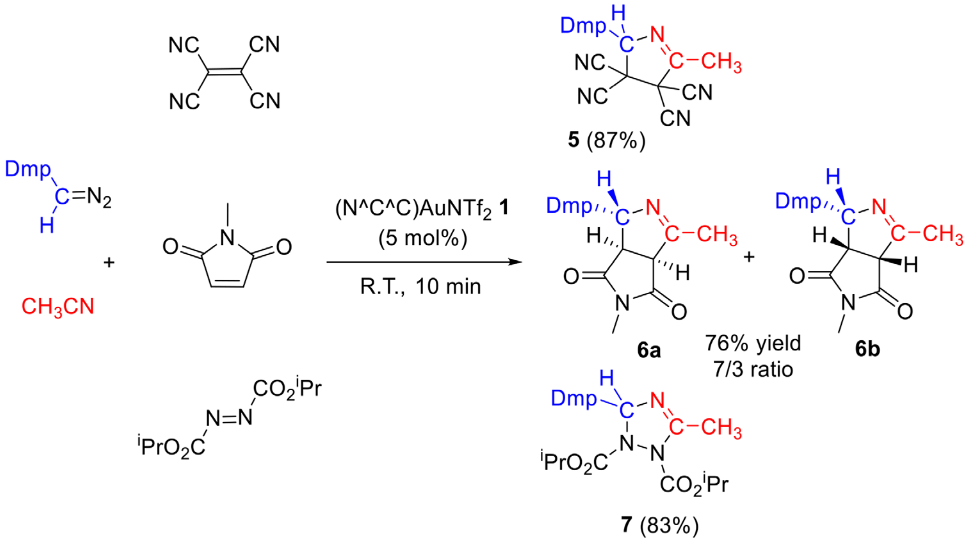
Trapping the Free Species, Imino-Substituted Carbene and/or Nitrile-Ylide Reactivity

The possibility to intercept the free species **3** before it dimerizes was then interrogated, and several trapping reagents were considered, starting with dipolarophiles.[37] Upon mixing tetracyanoethylene (TCE, 1 equiv.) with the Au(III) complex **2** in dichloromethane, no reaction occurred. However, when PPh$_3$ (1 equiv.) was subsequently added at room temperature,

© 2025 The Author(s). Angewandte Chemie International Edition published by Wiley-VCH GmbH



Scheme 4. Trapping of the free species **3** by tetracyanoethylene substantiating nitrile-ylide reactivity, molecular structure of the ensuing [3 + 2]-cycloaddition product **5**. For sake of clarity, the hydrogen atoms, except the one at C1, are omitted and the Mes groups are simplified. Ellipsoids are shown at 50% probability.

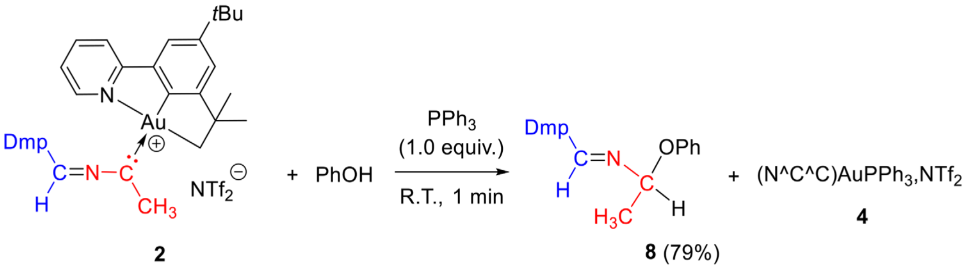


Scheme 5. Catalytic generation and [3 + 2]-cycloaddition trapping of the free species **3** with tetracyanoethylene, *N*-Me succinimide and diisopropyl azodicarboxylate.

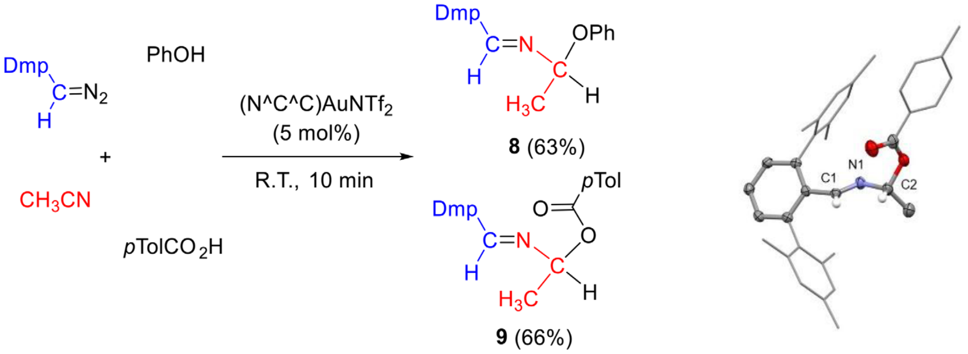
the reaction mixture immediately discolored. After workup, the [3 + 2]-cycloaddition product **5** was isolated in 81% yield, along with the Au(III) complex **4** (Scheme 4). To confirm that the observed reactivity originated from the transient free species **3**,[38] a control experiment was conducted with the 2,5-diazatriene **3₂**. Its reaction with TCE did not yield the [3 + 2]-cycloaddition product **5**, thereby excluding the involvement of the carbene dimer in the observed transformation. The structure of **5** was unequivocally determined by sc-XRD analysis.[35] Its formation substantiates the reactivity of the transient species as the nitrile-ylide **3b**. Product **5** was also obtained in quantitative yield when the reaction was performed in CH_3CN with $(Dmp)CN_2H$ instead of PPh_3 as Lewis base. This result prompted us to explore catalytic conditions using 5 mol% of the (NˆCˆC)Au(III)NTf_2 complex **1**, and the reaction indeed proceeded efficiently, affording product **5** in 87% yield within 10 min at room temperature. Similar reactivity was observed with *N*-Me succinimide and diisopropyl azodicarboxylate (DIAD) to give the corresponding [3 + 2]-cycloaddition products **6** and **7** in 76% and 83% yield, respectively (Scheme 5). Notably, in the case of *N*-Me succinimide, **6** was obtained as a mixture of diastereomers **6a/6b** (7:3 ratio), as determined by selective TOCSY (total correlation spectroscopy) and NOESY (nuclear overhauser effect spectroscopy) analyses.[34]

Carbene-type reactivity of the free species **3** was then targeted. The Au(III) complex **2** did not react by itself with phenol (1 equiv.) in dichloromethane at room temperature, but upon subsequent addition of PPh_3 (1 equiv.), the O—H insertion product **8** was readily obtained (79% isolated yield) along with the [(NˆCˆC)AuPPh_3]NTf_2 complex **4** (Scheme 6). The structure of the O—H insertion product was unambiguously established thanks to NMR and HRMS analyses. Here also, performing the reaction in CH_3CN with $(Dmp)CN_2H$ instead of PPh_3 quantitatively afforded product **8** and the reaction was amenable to catalysis. Using 5 mol% of the

© 2025 The Author(s). Angewandte Chemie International Edition published by Wiley-VCH GmbH



Scheme 6. Trapping of the free species **3** by phenol substantiating carbene reactivity.

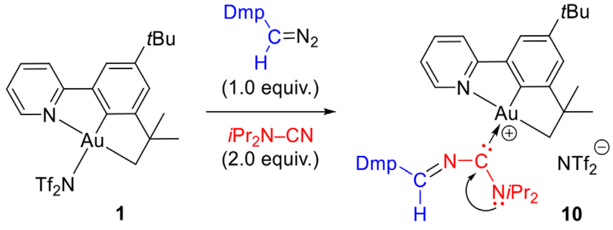


Scheme 7. Catalytic generation and O—H insertion trapping of the free species **3** with phenol and *p*-tolyl carboxylic acid. Molecular structure of the ensuing insertion product **9**. For sake of clarity, the hydrogen atoms, except the ones at C1 and C2, are omitted and the Mes/*p*Tol groups are simplified. Ellipsoids are shown at 50% probability.

(N^C^C)Au(III)NTf$_2$ complex **1**, the O—H insertion product **8** obtained in 63% yield within 10 min. at room temperature (Scheme 7). Similar O—H insertion reactivity was observed with *p*-tolylcarboxylic acid (*p*-TolCO$_2$H). The corresponding product **9**, obtained in 66% yield, was unequivocally characterized by sc-XRD analysis.[35] The key role of the free species **3**, in this case the imino-substituted carbene form **3a**, in the O—H insertion reactions was verified. Control experiments carried out with the 2,5-diazatriene **3$_2$** showed no transformation with both phenol and *p*-TolCO$_2$H.[34]

Cyanamide Insertion

The easy insertion of nitriles and the versatile reactivity of the ensuing imino-substituted Au(III) carbenes prompted us to investigate then the insertion of cyanamides R$_2$N—C≡N. We were intrigued by the impact the extra amino group may have on the formation, structure, bonding, and reactivity of the ensuing Au(III) carbene. Gratifyingly, a reaction proceeded readily by gently heating a mixture of the (N^C^C)AuNTf$_2$ complex **1**, the diazo compound (Dmp)CN$_2$H and *i*Pr$_2$NCN (2.0 equiv.) at 50 °C (Scheme 8). HRMS analysis indicated again the formation of a 1:1 adduct between the [(N^C^C)Au(III)←:CH(Dmp)]$^+$ complex and *i*Pr$_2$NCN. Multi-nuclear NMR spectroscopy provided the first insight into the structure of the obtained complex **10**. First, the nitrile N atom of the inserted *i*Pr$_2$N—C≡N moiety appeared at δ ^{15}N 339 ppm, very close to that observed for complex **2** deriving from MeCN insertion (δ 326 ppm), while



Scheme 8. Synthesis of the amino-imino-carbene Au(III) complex **10**.

the signal for the N*i*Pr$_2$ group was found at δ 206 ppm. Comparatively, the key ^{13}C NMR signals of complexes **10** and **2** turned to differ significantly. Indeed, the signals for the cyanamide and (Dmp)CH atoms (δ 220.5 and 155.5 ppm, respectively) appeared ~40 ppm more deshielded than the respective signals of complex **2**, suggesting substantially different bonding situations in both species.

To gain further insight into the precise structure of complex **10** and enable close comparison with complex **2**, single crystals of **10** were analyzed by XRD (Figure 5).[35] Here also, 1,2-insertion of the CN triple bond occurred into the Au←:CH(Dmp) bond, but in complex **10**, the 2-coordinate N center N1 is strongly bent (121.7(2)°) and the corresponding N1—C2(Au) bond is substantially elongated (1.384(2) Å), suggesting weak, if any, π-donation in this case. Conversely, the tricoordinate N center N2 is in planar environment, coplanar to the C2 coordination plane and the corresponding N2—C2(Au) bond is short (1.310(2) Å), indicating strong π-donation. As for the acetonitrile insertion complex **2**, the

© 2025 The Author(s). Angewandte Chemie International Edition published by Wiley-VCH GmbH

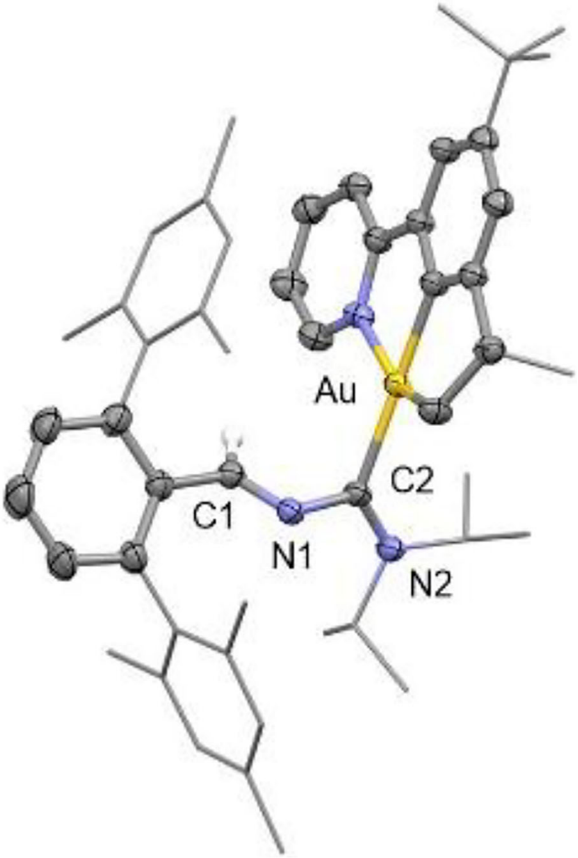


Figure 5. Molecular structure of **10**. For sake of clarity, the triflimide counter-anion and the hydrogen atoms, except the one at C1, are omitted, and the Mes/*t*Bu/*i*Pr groups are simplified. Ellipsoids are shown at 50% probability.

C2—Au bond is relatively long in **10** (2.103(2) Å), indicative of negligible π-backdonation from Au.

This picture with a merely spectator imino substituent and a strongly π-donating amino group was corroborated computationally by DFT and NBO. Here also, the optimized structure of the amino-imino gold(III) complex **10** very well reproduced the experimental one, with deviations of less than 0.008 Å and 0.6° in the key bond distances and bond angles, respectively (Table S4).[34] The two NLMOs accounting for the interactions of the amino and imino substituents with the carbene center are depicted in Figure 3. The first one shows significant delocalization of the N_{amino} lone pair to the carbene $2p^{\pi}(C_{carb})$ vacant orbital (with N_{amino} and C_{carb} contributions of 71.1% and 26.7%, respectively), whereas the second NLMO shows only low mixing of the N_{imino} lone pair with $2p^{\pi}(C_{carb})$ (with N_{imino} and C_{carb} contributions of 90.0% and 4.8%, respectively).

Similar to the 1,2-insertion of acetonitrile leading to complex **2**, a two-step process was computed for the reaction of the cyanamide with $[(N^{\wedge}C^{\wedge}C)Au(III)\leftarrow:CH(Dmp)]^{+}$ to give complex **10** (Figure 6).[34] The most notable difference is that the formation of the Lewis adduct is even more downhill (ΔG −27.0 kcal mol^{-1}), due to the higher Lewis basicity of the terminal N atom of the cyanamide compared to acetonitrile. The activation barrier for the subsequent 1,3-shift of the Au(III) fragment is essentially identical to that found for acetonitrile ($\Delta G^{\neq}$ 22.0 kcal mol^{-1}) and the overall process is again largely exergonic process (ΔG −52.1 kcal mol^{-1}).

Ligand Exchange/Dissociation

As for the acetonitrile insertion complex **2**, we first questioned the possibility to generate and transfer the amino-imino-carbene fragment from complex **10**. However, no reaction took place upon treatment with various Lewis bases (phosphines as well as the *N*-heterocyclic carbene IPr) (Scheme 9). Displacement of the amino-imino-carbene from Au(III) was actually computed to be 11.5 kcal mol^{-1} uphill in energy compared to that of the imino-carbene deriving from acetonitrile insertion.[34] As an alternative, we turned to protodeauration and treatment of the amino-imino-carbene Au(III) complex **10** with HCl afforded the imino-substituted iminium salt **11** in 43% yield. Single-crystal XRD analysis revealed strong π-donation from the amino group, as apparent from the coplanar environment of the amino N center N1 and carbon center C1. Of note, the C=N imino π-bond is also oriented parallel to the vacant $2p^{\pi}(C_{carb})$ orbital [the (Dmp)HC=N plane is rotated by < 2° with respect to the C1 coordination plane], indicating additional π-donation from the C=N imino group. Consistently, both C1—N distances are short and display double bond character [1.288(2) and 1.367(2) Å for C1N1 and C1N2, respectively]. The bonding situation was further confirmed by DFT calculations, two NLMOs accounting for C1=N1 and C1=N2 π-bonds.[34]

Deprotonation

Deprotonation of the imino-substituted iminium salt **11** was then investigated with the aim of generating the free amino-imino-carbene. KHMDS and LiHMDS were [HMDS = $N(SiMe_3)_2$] found to readily react with **11** in THF (tetrahydrofuran). Following the workup, the corresponding dimerization product, the 3,4-diamino 2,5-diazatriene **12$_2$**, was isolated in 59% yield (Scheme 10). According to sc-XRD analysis,[35] π-delocalization extends over the whole C=N—C=C—N=C skeleton, but not the amino groups in 3,4-positions, which are rotated about perpendicularly probably due to steric constraints.

We then tried to characterize the amino-imino-carbene prior to dimerization. Monitoring the deprotonation of **11** by LiHMDS or KHMDS in THF-d_8 at low temperature (−40 °C) revealed the transient formation of an intermediate. This intermediate rapidly and quantitatively evolved into the carbene dimer **12$_2$** preventing structural characterization. The most diagnostic NMR feature of the detected intermediate was the low-field ^{13}C NMR signal observed at δ 212.2–211.7 ppm, in the typical range for acyclic diaminocarbenes.[39] In addition, the ^{13}C NMR signal for the imino group, CH(dmp)=N, was found at δ 144.8–142.0 ppm. These

© 2025 The Author(s). Angewandte Chemie International Edition published by Wiley-VCH GmbH

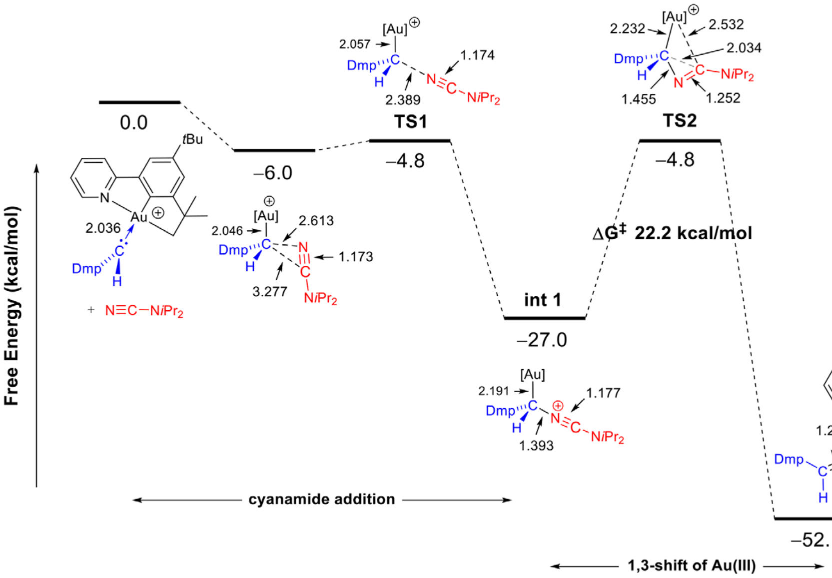
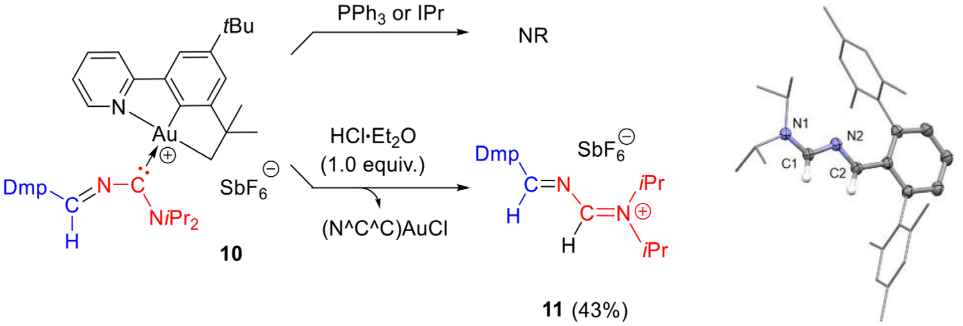


Figure 6. Energy profile computed for the reaction of the (N^C^C)Au(III)←:CH(Dmp)$^+$ complex with diisopropyl cyanamide leading to the amino-imino-substituted Au(III) carbene complex **10**. Calculations performed at the B3PW91-D3(BJ)/SDD + f(Au),6–31G**(other atoms) level of theory. Gibbs free energies (ΔG) in kcal mol^{-1}. Main distances in Å.



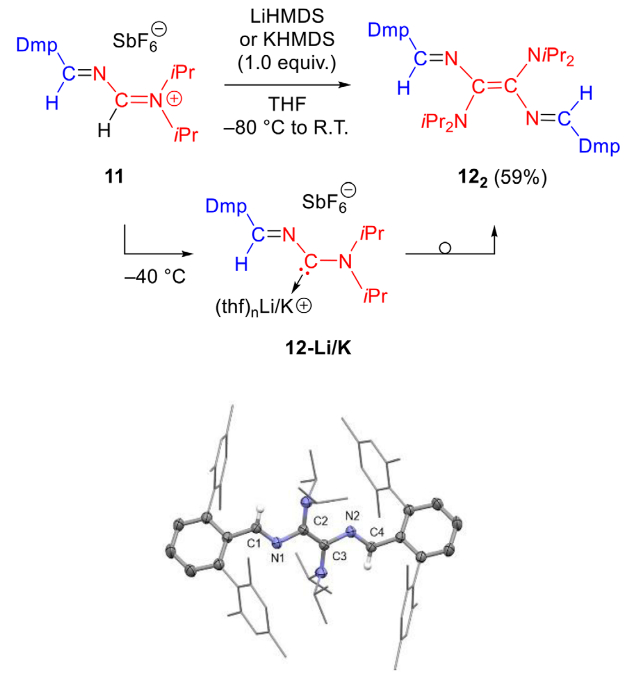
Scheme 9. Protodeauration of the amino-imino-carbene Au(III) complex **10**, molecular structure of the ensuing imino-substituted iminium salt **11**. For sake of clarity, the hexafluorostilbate counter-anion and the hydrogen atoms, except the ones at C1 and C2, are omitted, and the Mes/*i*Pr groups are simplified. Ellipsoids are shown at 50% probability.

chemical shifts are very similar to those of the amino-imino Au(III) carbene complex **10** (δ 220.9 and 155.5 ppm, respectively), suggesting that the intermediate retains bent geometry with a spectator imino substituent. Two structures were considered, the free amino-imino-carbene **12** and a lithium/potassium adduct Li/K(THF)$_n^+$ adduct **12-Li/K**. Following geometry optimizations, the ^{13}C NMR data of **12** and **12-Li** were computed using the ADF software at COSMO(THF)-BP86/TZ2P level of theory to help in the assignment.[34] A very good match was found for the lithium adduct **12-Li** ($\Delta\delta \leq 10$ ppm with δ_{carb} 219.4 ppm and $\delta_{\text{CH=N}}$ 132.0 ppm), while discrepancies of at least 45 ppm were predicted for the free species (with δ_{carb} 165.1 ppm and $\delta_{\text{CH=N}}$ 106.8 ppm) as the result of a different stabilization mode involving π-donation from both the amino and the imino groups.[34] We thus surmise that the observed intermediates are lithium/potassium adducts akin to **12-Li/K**. The propensity of *N*-heterocyclic carbenes to bind alkaline metals and the stabilization effect of such coordination are well documented.[40,41]

"Recoordination" of the Amino-Imino-Carbene

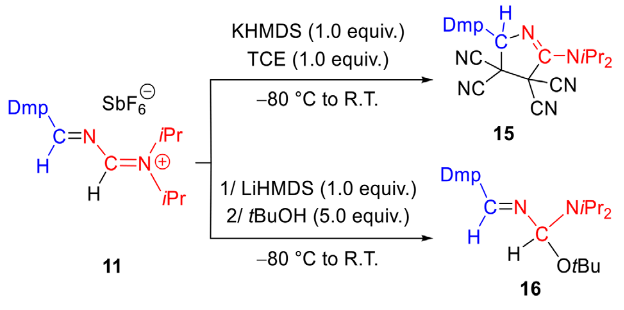
The possibility to detect the amino-imino-carbene prior to dimerization upon deprotonation of the imino-substituted iminium salt **11** prompted us to explore whether the free carbene could be trapped by coordination to metal fragments. Using this approach, the amino-imino Au(I) carbene complex **13** was synthesized in 47% yield using in situ generated $Ph_3PAuSbF_6$ (Scheme 11). The structure of **13** was unambiguously confirmed by sc-XRD analysis.[35] Strikingly, the geometry and bonding situation of the Au(I) carbene complex are very reminiscent of the initial Au(III) carbene complex **10**. The 2-coordinate N center is strongly bent (120.0(2)°), indicating that the imino group remains a spectator. In sharp

© 2025 The Author(s). Angewandte Chemie International Edition published by Wiley-VCH GmbH



Scheme 10. Formation and molecular structure of the 3,4-diamino-2,5-diazatriene $\mathbf{12_2}$. For sake of clarity, the hydrogen atoms, except the ones at C1 and C4, are omitted and the Mes/*i*Pr groups are simplified. Ellipsoids are shown at 50% probability. Low-temperature NMR characterization of the amino-imino-carbene as Li/K(thf)$_n^+$ adducts **12-Li/K**.

contrast, the tricoordinate nitrogen center is in a planar environment and the corresponding N─C(Au) bond is short at 1.303(3) Å, reflecting strong π-donation from the amino substituent. In addition, to probe the electronic properties of the amino-imino-carbene, the Rh(I) carbonyl complex **14** was prepared by trapping the carbene in situ with $[Rh(cod)Cl]_2$ followed by treatment with 2 bar of CO gas. Complex **14** displays CO stretching frequencies at ν 2072 and 1997 cm^{-1} in dichloromethane. These values fall in the upper range of those reported for acyclic amino-carbenes, close to those of amino-carbenes featuring an alkyl or silyl substituent,[42,43] in line with a spectator role of the imino substituent.



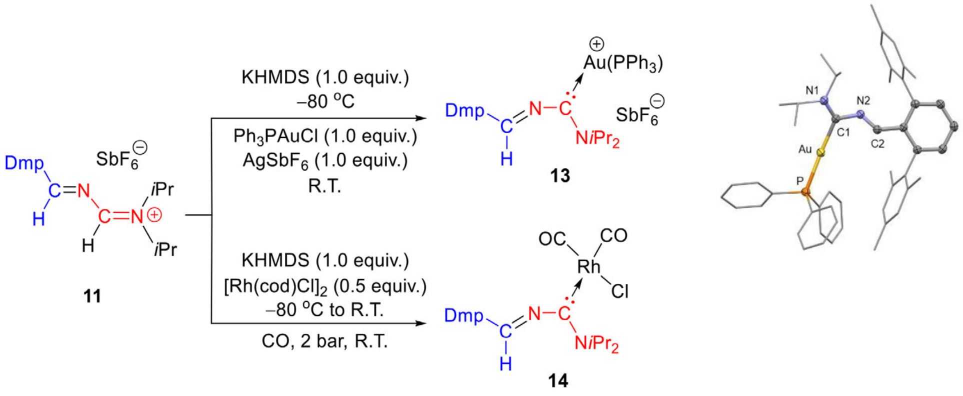
Scheme 12. Trapping the amino-imino carbene with tetracyanoethylene and *tert*-butanol substantiating nitrile-ylide and carbene reactivity.

Reactivity of the Amino-Imino-Carbene

Finally, trapping reactions with organic reagents were investigated. Deprotonation of the iminium salt **11** with KHMDS in the presence of tetracyanoethylene (1 equiv.) afforded the [3 + 2] cycloadduct **15** in 71% yield (Scheme 12). The structure of **15** was established by $^1H/^{13}C$ NMR spectroscopy and HRMS analyses.[34] In particular, the ^1H NMR signal for the CH(Dmp) moiety was found at δ 6.23 ppm, matching very well with the value observed for the closely related product **5** authenticated crystallographically (δ 6.29 ppm). The formation of **14** conveys 1,3-dipolar nitrile-ylide reactivity for the amino-imino-carbene. Further study involved deprotonation of the iminium salt with LiHMDS, followed by treatment with *t*-butanol (5 equiv.). This reaction produced compound **16** in 95% NMR yield (using 1,10-phenanthroline as internal standard), substantiating O─H insertion carbene reactivity. Notably, the carbene dimer $\mathbf{12_2}$ did not yield the [3 + 2]-cycloadduct **15** upon treatment with TCE and did not react with *t*-butanol under similar conditions, confirming that the observed reactivities originate from the amino-imino-carbene.[38]

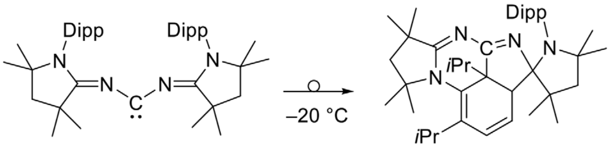
Conclusion

In conclusion, the very high electrophilicity of the transient (NˆCˆC)Au(III)←:CH(dmp) carbene was found to drive



Scheme 11. Coordination of the amino-imino carbene **12** to Au(I) and Rh(I).

© 2025 The Author(s). Angewandte Chemie International Edition published by Wiley-VCH GmbH



17 **17′**

Figure 7. Structure and rearrangement of the bis(*N*-heterocyclic imino)carbene **17**.

unusual reactivity toward nitriles and cyanamides. The terminal N center readily coordinates to the carbene center and the Au(III) metal fragment then easily undergoes 1,3-shift resulting in 1,2-insertion of the C≡N triple bond in the Au(III)←:CH(dmp) unit. The ensuing imino-substituted Au(III) carbene complexes are stable and isolable. They were fully characterized by multi-nuclear NMR spectroscopy as well as single-crystal X-ray diffraction. Their bonding situation was thoroughly analyzed by computational means. In complex **2** deriving from acetonitrile insertion, the imino group was found to act as a strong π-donor substituent, resulting in a linear azaallene-type geometry. Conversely, in complex **10** deriving from insertion of the diisopropyl cyanamide, the imino group remains spectator electronically, leading to a bent structure. From complex **2**, the free carbene **3** could be generated as a transient species by simple ligand displacement with PPh_3. The same route did not work for complex **10**, but protodeauration afforded the imino-substituted iminium salt **11,** which could be subsequently deprotonated with LiHMDS or KHMDS. Li/K^+ adducts of the amino-imino-carbene **12-Li/K** could be spectroscopically authenticated at low temperature. Reactivity studies involving organic substrates as well as metal fragments have substantiated dual behavior of both carbenes **3** and **12**. Dimerization, O─H insertions and metal coordinations illustrate carbene reactivity, while [3 + 2] dipolar cycloadditions showcase nitrile-ylide reactivity. In addition, the diazo decomposition, nitrile insertion and carbene transfer can be combined in three-component Au(III)-catalyzed transformations.

Besides their interest in the context of Au(III) carbene chemistry, these results point out the potential and versatility of the imino substituent in carbene chemistry.[39,44–46] Here, the >C═N substituent is forged by C≡N triple bond insertion into a Metal←:Carbene linkage. This is a very simple and efficient process that can certainly be extended beyond Au(III) complexes as studied here. Although transient imino-substituted carbenes have been extensively studied in the 1980′s, only one stable species **17**, reported by Bertrand et al. in 2023, is known so far, to the best of our knowledge.[36] It features two *N*-heterocyclic imino substituents at the carbene center (Figure 7). It is stable up to −20 °C and adopts at higher temperature a masked form **17′** resulting from intramolecular [3 + 2] cycloaddition.

Acknowledgements

Financial support from the Centre National de la Recherche Scientifique, the Université de Toulouse and the Agence Nationale de la Recherche (ANR-22-CE07-0037) is gratefully acknowledged. The NMR service of ICT, UAR 2599 (Pierre Lavedan, Marc Vedrenne) is acknowledged for assistance with the low-temperature and 2D HSQC NMR experiments. N.A. thanks MESRI (Ministère de l'Enseignement Supérieur, de la Recherche et de l'Innovation) and ENS–PSL for her Ph.D. fellowship (Contrat Doctoral Spécifique Normalien). The "Direction du Numérique" of the Université de Pau et des Pays de l'Adour and the Mésocentre de Calcul Intensif Aquitain (MCIA) are acknowledged for the support of computational facilities. This work was also granted access to the HPC resources of IDRIS under the allocation 2024-[AD010800045R3] made by GENCI.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Carbenes • Catalysis • Gold • Nitriles • Nitrile-ylides

---

[1] A. F. Hill, in *Organotransition Metal Chemistry*, Royal Society Of Chemistry, London **2002**.
[2] G. Parkin, K. Meyer, D. O'Hare, in *Comprehensive Organometallic Chemistry IV*, 4th ed., Elsevier, Amsterdam **2022**.
[3] J. F. Hartwig, in *OrganotransitionMetal Chemistry: From Bonding to Catalysis*, University Science Books, Sausalito **2009**.
[4] R. A. Moss, M. P. Doyle, in *Contemporary Carbene Chemistry*, John Wiley & Sons, Hoboken, NJ **2013**.
[5] D. Benitez, N. D. Shapiro, E. Tkatchouk, Y. Wang, W. A. Goddard, F. D. Toste, *Nat. Chem.* **2009**, *1*, 482–486.
[6] G. Seidel, A. Fürstner, *Angew. Chem. Int. Ed.* **2014**, *53*, 4807–4811.
[7] R. J. Harris, R. A. Widenhoefer, *Angew. Chem. Int. Ed.* **2014**, *53*, 9369–9371.
[8] M. W. Hussong, F. Rominger, P. Krämer, B. F. Straub, *Angew. Chem. Int. Ed.* **2014**, *53*, 9372–9375.
[9] Y. Wang, M. E. Muratore, A. M. Echavarren, *Chem. - Eur. J.* **2015**, *21*, 7332–7339.
[10] M. R. Fructos, M. M. Díaz-Requejo, P. J. Pérez, *Chem. Commun.* **2016**, *52*, 7326–7335.
[11] M. Navarro, D. Bourissou, *Adv. Organomet. Chem.* **2021**, *76*, 101–144.
[12] R. P. Herrera, M. C. Gimeno, *Chem. Rev.* **2021**, *121*, 8311–8363.
[13] L.-W. Ye, X.-Q. Zhu, R. L. Sahani, Y. Xu, P.-C. Qian, R.-S. Liu, *Chem. Rev.* **2021**, *121*, 9039–9112.
[14] I. Rivilla, B. P. Gómez-Emeterio, M. R. Fructos, M. M. Díaz-Requejo, P. J. Pérez, *Organometallics* **2011**, *30*, 2855–2860.
[15] M. D. Levin, T. Q. Chen, M. E. Neubig, C. M. Hong, C. A. Theulier, I. J. Kobylianskii, M. Janabi, J. P. O'Neil, F. D. Toste, *Science* **2017**, *356*, 1272–1276.
[16] A. V. Zhukhovitskiy, I. J. Kobylianskii, C.-Y. Wu, F. D. Toste, *J. Am. Chem. Soc.* **2018**, *140*, 466–474.

© 2025 The Author(s). Angewandte Chemie International Edition published by Wiley-VCH GmbH

[17] C.-Y. Wu, T. Horibe, C. B. Jacobsen, F. D. Toste, *Nature* **2015**, *517*, 449–454.
[18] A. Pujol, M. Lafage, F. Rekhroukh, N. Saffon-Merceron, A. Amgoune, D. Bourissou, N. Nebra, M. Fustier-Boutignon, N. Mézailles, *Angew. Chem. Int. Ed.* **2017**, *56*, 12264–12267.
[19] This N^C(sp^2)^C(sp^3) pincer ligand was introduced by Holmsen et al, see: M. S. M. Holmsen, A. Nova, K. Hylland, D. S. Wragg, S. Øien-Ødegaard, R. H. Heyn, M. Tilset, *Chem. Commun.* **2018**, *54*, 11104–11107.
[20] R. Wei, L. Ma, S. Mallet-Ladeira, D. Bourissou, *Organometallics* **2024**, *43*, 1775–1779.
[21] H. Fischer, U. Schubert, *Angew. Chem. Int. Ed.* **1981**, *20*, 461–463.
[22] H. Fischer, *J. Organomet. Chem.* **1980**, *197*, 303–313.
[23] H. Fischer, U. Schubert, R. Märkl, *Chem. Ber.* **1981**, *114*, 3412–3420.
[24] H. Fischer, R. Märkl, *Chem. Ber.* **1985**, *118*, 3683–3699.
[25] H. Fischer, S. Zeuner, *J. Organomet. Chem.* **1987**, *327*, 63–75.
[26] D. C. Yang, V. Dragisich, W. D. Wulff, J. C. Huffman, *J. Am. Chem. Soc.* **1988**, *110*, 307–309.
[27] W. D. Wulff, V. Dragisich, J. C. Huffman, R. W. Kaesler, D. C. Yang, *Organometallics* **1989**, *8*, 2196–2207.
[28] A. S. Kende, P. Hebeisen, P. J. Sanfilippo, B. H. Toder, *J. Am. Chem. Soc.* **1982**, *104*, 4244–4245.
[29] D. Griller, C. R. Montgomery, J. C. Scaiano, M. S. Platz, L. Hadel, *J. Am. Chem. Soc.* **1982**, *104*, 6813–6814.
[30] A. Padwa, J. R. Gasdaska, M. Tomas, N. J. Turro, Y. Cha, I. R. Gould, *J. Am. Chem. Soc.* **1986**, *108*, 6739–6746.
[31] N. J. Turro, Y. Cha, I. R. Gould, *J. Am. Chem. Soc.* **1987**, *109*, 2101–2107.
[32] S. Fergus, S. J. Eustace, A. F. Hegarty, *J. Org. Chem.* **2004**, *69*, 4663–4669.
[33] V. Piquet, A. Baceiredo, H. Gornitzka, F. Dahan, G. Bertrand, *Chem. - Eur. J.* **1997**, *3*, 1757–1764.
[34] See Supporting Information for details.
[35] Deposition Numbers CCDC-2424792 (for **2**), 2424793 (for $\mathbf{3_2}$), 2424794 (for **5**), 2424795 (for **9**), 2424796 (for **10**), 2424789 (for **11**), 2424791 (for $\mathbf{12_2}$), 2424790 (for **13**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.
[36] Y. K. Loh, M. Melaimi, D. Munz, G. Bertrand, *J. Am. Chem. Soc.* **2023**, *145*, 2064–2069.
[37] For a somewhat related 1,3-dipolar cycloaddition between *N*-aurated azomethine ylides and electron-deficient alkenes, see: A. D. Melhado, M. Luparia, F. D. Toste, *J. Am. Chem. Soc.* **2007**, *129*, 12638–12639.
[38] As recently pointed out, caution is needed when interpreting trapping experiments and carbene-like reactivity: J. Lorkowski, P. Yorkgitis, M. R. Serrato, M. Gembicky, C. Pietraszuk, G. Bertrand, R. Jazzar, *Angew. Chem. Int. Ed.* **2024**, *63*, e202401020.
[39] J. Vignolle, X. Cattoën, D. Bourissou, *Chem. Rev.* **2009**, *109*, 3333–3384.
[40] E. Aldeco-Perez, A. J. Rosenthal, B. Donnadieu, P. Parameswaran, G. Frenking, G. Bertrand, *Science* **2009**, *326*, 556–559.
[41] S. Bellemin-Laponnaz, S. Dagorne, *Chem. Rev.* **2014**, *114*, 8747–8774.
[42] V. Lavallo, J. Mafhouz, Y. Canac, B. Donnadieu, W. W. Schoeller, G. Bertrand, *J. Am. Chem. Soc.* **2004**, *126*, 8670–8671.
[43] Y. Canac, S. Conejero, B. Donnadieu, W. W. Schoeller, G. Bertrand, *J. Am. Chem. Soc.* **2005**, *127*, 7312–7313.
[44] D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39–92.
[45] D. Martin, M. Soleilhavoup, G. Bertrand, *Chem. Sci.* **2011**, *2*, 389–399.
[46] D. Martin, M. Melaimi, M. Soleilhavoup, G. Bertrand, *Organometallics* **2011**, *30*, 5304–5313.

Manuscript received: February 19, 2025
Revised manuscript received: March 28, 2025
Accepted manuscript online: March 31, 2025
Version of record online: April 14, 2025

© 2025 The Author(s). Angewandte Chemie International Edition published by Wiley-VCH GmbH