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Gold(I) α -Trifluoromethyl Carbenes: Synthesis, Characterization and Reactivity Studies

Mathilde Rigoulet, David Vesseur, Karinne Miqueu, and Didier Bourissou*

Abstract: Aryl trifluoromethyl diazomethanes **2-R** (R = Ph, OMe, CF₃) are readily decomposed by the (*o*-carboranyl)-diphosphine gold(I) complex **1**. The resulting α -CF₃ substituted carbene complexes **3-R** have been characterized by multi-nuclear NMR spectroscopy as well as X-ray crystallography (for **3-Ph**). The bonding situation was thoroughly assessed by computational means, showing stabilization of the electrophilic carbene center by π -donation from the aryl substituent and backdonation from Au, as enhanced by the chelating P⁺P ligand. Reactivity studies under stoichiometric and catalytic conditions substantiate typical carbene-type behavior for **3-Ph**.

Introduction

The interplay of gold and fluorine, two peculiar elements within the periodic table, has turned out to a very active field of research in recent years (Figure 1).^[1] Accordingly, fluoro, trifluoromethyl and pentafluorophenyl Au^I and Au^{III} complexes have become well-known and powerful species from both mechanistic and synthetic viewpoints.^[2–7] Highly reactive gold complexes featuring organofluoro moieties are also starting to be investigated. Toste et al. proposed in 2017 a F-rebound mechanism involving Au^{III} difluorocarbenes as key intermediates to account for C(sp³)-CF₃ coupling at gold.^[8] In 2019, Fürstner et al. spectroscopically characterized at low temperature a series of gold(I) difluorocarbenoids supported by phosphine ligands.^[9] Our interest in highly reactive gold complexes and the ability of *o*-carboranyl diphosphine ligands to stabilize gold(I) carbene species thanks to enhanced π -backdonation^[10] prompted us to investigate α -CF₃ complexes (Figure 1). A comprehensive study combining synthesis, NMR and crystallographic characterization, theoretical analysis of the bonding situation and reactivity studies is reported hereafter.

α -CF₃ carbene complexes are important and powerful intermediates in transition metal-catalyzed transformations enabling the rapid construction of CF₃-containing derivatives. They are typically generated via diazo decomposition and engaged in cycloaddition or insertion reactions. Ru and Cu are the most used and studied metals in this context,^[11] but recently, major achievements have been reported with Fe,^[12] Ag^[13] and Pd^[14] catalysts as well. Strikingly, despite the great interest and potential of gold carbene complexes,^[15,16] we found only two isolated examples involving an α -CF₃ species, namely the C–H functionalization of phenothiazine/carbazole with PhC(=N₂)CF₃ catalyzed by (phosphite)AuCl/AgSbF₆.^[17]

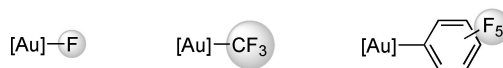
In parallel to the synthetic developments, efforts have been made to prepare and characterize α -CF₃ carbene complexes, but only very few such species have been reported so far (Figure 2): the porphyrin Ru complex **A**,^[18] the Fischer-type W complexes **B**^[19] and the Schrock-type Ir, Co and Ni fluoro complexes **C–E**.^[20] Of note, the Co and Ni carbene complexes **D** and **E** display reactivity relevant to the metathesis/polymerization of fluoro alkenes, but none of the isolated α -CF₃ carbene complexes was shown to undergo cyclopropanation or insertion reactions.

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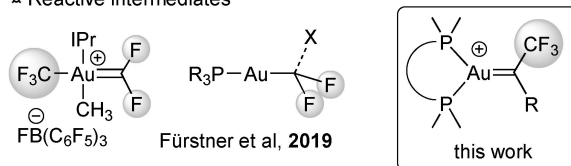
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▣ Well-known complexes, both Au(I) and Au(III)



▣ Reactive intermediates



Toste et al., 2017

Figure 1. Different classes of F-containing gold complexes.

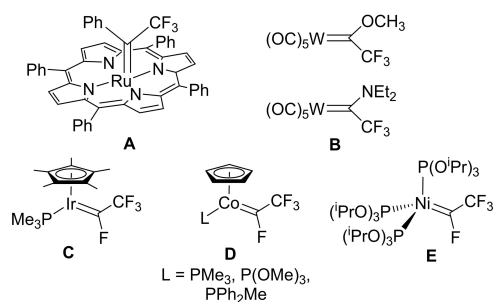


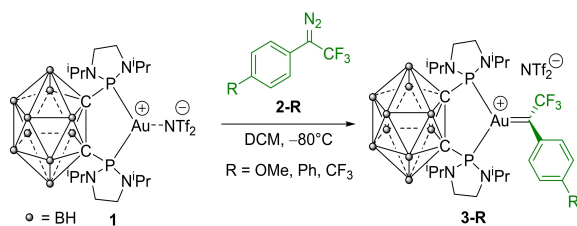
Figure 2. Known α -CF₃ carbene complexes.

Results and Discussion

Synthesis, Spectroscopic and Structural Characterization

To generate the targeted carbene complexes, diazo decomposition was chosen as a mild and versatile route, with only N₂ as byproduct.^[21] One equivalent of biphenyl trifluoromethyl diazomethane **2-Ph** was added at -80°C to the tricoordinate pseudo-cationic complex (P[^]P)AuNTf₂ **1**^[22] in dichloromethane (DCM) (Scheme 1). The diphosphine *o*-carboranyl (DPCb) ligand was used for its unique chelation property, resulting in a bent L₂Au⁺ fragment with higher π -backdonation capacity.^[15d] With monodentate phosphines such as JohnPhos, no sign of a Au^I trifluoromethyl carbene could be observed by NMR spectroscopy even at low temperature.

Small bubbles of dinitrogen immediately evolved and the solution turned deep blue. After quick work up at -40°C , the formed species was spectroscopically characterized. The ³¹P NMR signal (Figure 3a) appears at very similar chemical shift as the gold precursor (δ 137.8 and 138.2 ppm, respectively), but as a quartet instead of a singlet. The quartet multiplicity results from PF coupling, as unambiguously established by the presence of a triplet signal in the ¹⁹F NMR spectrum with similar coupling (23.2 Hz). These patterns suggest the formation of the desired (P[^]P)Au=C(CF₃)(biphenyl)⁺ complex **3-Ph**, something that was definitely confirmed by ¹³C NMR spectroscopy. The ¹⁹F-decoupled spectrum (Figure 3b) shows a diagnostic signal at δ 269.8 ppm. In line with the blue color, a strong absorption is found at 623 nm in UV/Vis spectroscopy. Carbene **3-Ph** proved to be moderately stable at room temperature, about 30 % decomposition being observed after 24 hours in DCM.



Scheme 1. Formation of the gold(I) trifluoromethyl carbenes **3** by diazo decomposition.

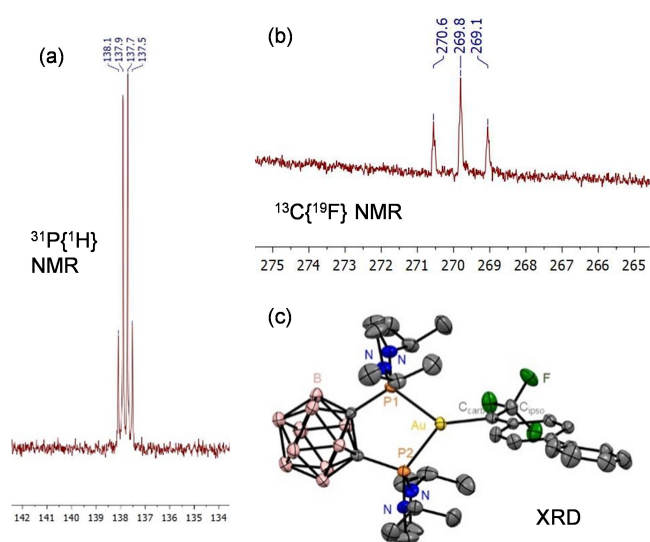


Figure 3. Diagnostic ³¹P{¹H} and ¹³C{¹⁹F} NMR signals for **3-Ph** (243 K, CD₂Cl₂, 121 and 126 MHz, respectively); molecular structure of **3-Ph**. Thermal ellipsoids drawn at 50% probability, hydrogen atoms, counter anion and disordered atoms are omitted. Selected bond lengths [Å] and bond angles [°]: Au–C_{carb} 1.971(2), Au–P1 2.347(1), Au–P2 2.348(1), C_{carb}–C_{ipso} 1.444(6), C_{carb}–CF₃ 1.500(6); P1–Au–P2 90.59(4), P1–Au–C_{carb} 135.7(1), P2–Au–C_{carb} 133.7(1).

The *para*-substituent at the phenyl ring was then changed for OMe and CF₃ to assess the impact of electron-donating/withdrawing groups. In both cases, the corresponding carbene complexes **3-OMe** and **3-CF₃** were formed (Scheme 1) and NMR data in line with those of **3-Ph** were obtained.^[23] Some features deserve comment: *i*) the diagnostic ¹³C NMR signal barely shifts (δ 268.5 ppm for **3-OMe**, 265.8 ppm for **3-CF₃**); *ii*) the ²J_{PC} and ⁴J_{PF} coupling constants decrease in the series *p*-CF₃ > *p*-Ph > *p*-OMe (from 109.0 to 79.5 Hz for ²J_{PC}, and from 32.1 to 14.0 Hz for ⁴J_{PF}), the carbene becomes less electron-deficient and the Au=C bond order/double bond character decreases (see the DFT optimizations and bonding analyses below); *iii*) the carbene **3-CF₃** displays a long-range ⁸J_{PF} coupling of 10.8 Hz, as apparent in the ³¹P and ¹⁹F NMR spectra.^[24] It is also worth noting that if the carbene complex **3-OMe** survives for a few hours at room temperature, as **3-Ph**, **3-CF₃** is much less stable. All attempts to work it up at room or low temperature resulted in complete degradation. It was thus characterized *in situ* at low temperature.

Efforts were then made to obtain crystallographic data to know more about the structure of the obtained carbene. Gratifyingly, crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane into a dichloromethane solution of **3-Ph** at -40°C (Figure 3c).^[23,25] The asymmetric unit contains two molecules of very similar geometries (Table S2).^[23] For sake of simplicity, the key features of only one will be discussed here. Accordingly, the carbene complex adopts an ion pair structure. The DPCb ligand symmetrically chelates gold with Au–P bond lengths of 2.347(1)/2.348(1) Å and a P–Au–P bite angle of 90.59(4)°. The carbene center is in a perfectly planar environment (as

apparent from the sum of bond angles of 360.0°) and it is oriented perpendicularly to the P–Au–P coordination plane (the mean planes around Au and C_{carb} make an angle of 89.76°). This orientation minimizes steric repulsions between the carbene and phosphorus substituents, it also maximizes the d(Au) to $2p^\pi(\text{C}_{\text{carb}})$ backdonation (see below). The Au=C bond length (1.971(2) Å) is in the lower range of those reported for gold(I) carbene complexes.^[26] The carbene center is also stabilized by π -donation from the biphenyl substituent, as indicated by their coplanar arrangement (the mean plane of the phenyl ring bonded to C_{carb} is rotated by only 2.5° from the carbene coordination plane) and from the relatively short C_{carb}–C_{ipso} bond length (1.444 (6) Å).

Structure and Bonding Analysis

To gain more insight into the bonding situation and stabilization mode of the $\alpha\text{-CF}_3$ gold(I) carbenes **3**,^[27] DFT (Density Functional Theory) calculations (B3PW91/SDD+f(Au),6-31G** (other atoms)) were performed.^[23] The geometry optimized for **3-Ph** (Table 1) matches well that determined crystallographically with deviations of less than 0.08 Å and 2.2° in the key bond lengths and angles (Table S2).^[23] The carbenes **3-OMe** and **3-CF₃** were also computed, showing similar structures as **3-Ph**. The small

Table 1: Data computed for the Au^I $\alpha\text{-CF}_3$ carbene complexes **3-Ph**, **3-OMe**, **3-CF₃** at the B3PW91/SDD+f(Au),6-31G** (other atoms) level of theory: selected bond lengths/angles, Wiberg bond indexes (WBI), charge transfer (CT) from the carbene to the (P⁺)Au⁺ fragment, NLMO associated with the aryl-to-C_{carb} π -donation and Au-to-C_{carb} backdonation (contribution of C_{carb}), donation/backdonation (d/b) ratio as estimated by Charge Decomposition Analysis (CDA).

	3-OMe	3-Ph	3-CF₃
Geometric parameters			
Au=C _{carb} [Å]	1.987	1.983	1.971
C _{carb} –C _{ipso} [Å]	1.423	1.429	1.442
Au–C–C _{CF₃} [°]	114.57	114.76	114.97
Au–C–C _{Aryl} [°]	128.56	128.42	128.31
C _{Aryl} –C–C _{CF₃} [°]	116.85	116.82	116.71
PAuP [°]	89.81	89.88	89.79
NBO Analysis			
WBI (Au=C _{carb})	0.677	0.687	0.710
WBI (C _{carb} –C _{ipso})	1.312	1.289	1.234
CT (e)	–0.10	–0.14	–0.25
d _{xz} (Au)→C _{carb} backdonation	7.3%	9.7%	15.5%
%C _{carb} in NLMO d _{xz} (Au)			
$\pi_{\text{C=Caryl}} \rightarrow \text{C}_{\text{carb}}$ donation	24.2%	16.3%	10.1%
%C _{carb} in NLMO $\pi_{\text{C=Caryl}}$			
CDA Analysis			
d/b ratio	2.16	2.09	1.86

variations found in the Au=C/C_{carb}–C_{ipso} bond lengths and associated Wiberg bond indexes (WBI) (Table 1) are in line with the electron bias induced by the *para* substituent, i.e. stronger arene-to-C_{carb} π -donation and weaker Au-to-C_{carb} backdonation from **3-CF₃** to **3-Ph**, and **3-OMe** (see below). The NMR data for **3-CF₃**, **3-Ph** and **3-OMe** were also calculated. The trends observed experimentally for the $^2J_{\text{PC}}$ and $^4J_{\text{PF}}$ couplings were nicely reproduced (Table S3).^[23]

The bonding situation was then assessed in detail via Natural Bond Orbital (NBO) and Charge Decomposition Analyses (CDA) (Table 1). The C_{carb}-to-Au charge transfer (CT) is slightly negative for the three carbenes, a little more for the electron-deprived carbene **3-CF₃** (–0.25 e) than for the electron-enriched one **3-OMe** (–0.10 e). CT values close to zero suggest that overall the C_{carb}-to-Au donation and Au-to-C_{carb} backdonation roughly compensate each other. The donation/backdonation ratio (d/b), as estimated by CDA, falls in the 1.8–2.2 range (slightly lower for the electron-deprived carbene **3-CF₃**, slightly higher for the electron-enriched carbene **3-OMe**), indicating C_{carb}-to-Au donation prevails, but Au-to-C_{carb} backdonation is significant.

Inspection of the molecular orbitals provides useful insight. The HOMO is centered on gold and is associated with an in-plane d(Au) orbital in bonding combination with the $2p^\pi(\text{C}_{\text{carb}})$ orbital. Reciprocally, the LUMO is centered on the carbene center and corresponds to the $2p^\pi(\text{C}_{\text{carb}})$ vacant orbital in anti-bonding combination with the d(Au) orbital (Figure 4, top). In addition, the π -system of the aryl substituent is involved in these frontier orbitals, in line with π -donation from the biphenyl substituent to the carbene center. This description is confirmed by referring to the Natural Localized Molecular Orbitals (NLMO). The Au-to-C_{carb} backdonation and aryl-to-C_{carb} π -donation are apparent from the contributions of $2p^\pi(\text{C}_{\text{carb}})$ in the d(Au)-centered and π -aryl orbitals, 9.7 and 16.3 %, respectively (Figure 4,

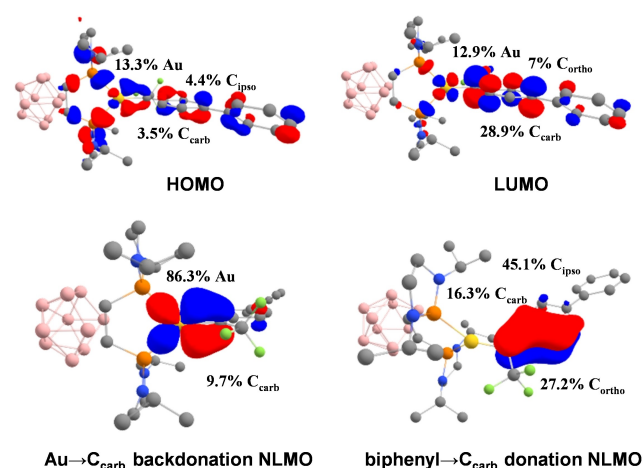


Figure 4. HOMO, LUMO and NLMO (cutoff: 0.04) associated with the arene-to-C_{carb} π -donation and Au-to-C_{carb} backdonation computed for the Au^I $\alpha\text{-CF}_3$ carbene complex **3-Ph** at the B3PW91/SDD+f(Au),6-31G** (other atoms) level of theory. Contribution of the main atoms (in %) in the frontier orbitals and NLMO.

bottom). Both interactions stabilize the carbene by filling partially its vacant orbital. The strength of the two interactions mildly evolves in the **3-CF₃**, **3-Ph**, **3-OMe** series. As expected from the electron-withdrawing/releasing effect of the *para* substituent, the C_{carb} contribution is the largest in the d(Au) NLMO for **3-CF₃**, while for **3-OMe**, it is in the $\pi(\text{arene})$ NLMO (Table 1 and Figure S37). Of note, the energy gap between the HOMO/LUMO frontier orbitals is relatively small (2.34 eV from DFT, 1.95 eV from TD-DFT (Time-Dependent Density Functional Theory) for **3-Ph**, Figure S38).^[23] Consistently, TD-DFT calculations taking into account solvent effects (DCM) by SMD (solvation model based on density) predict a low-energy symmetry-allowed electronic transition at 635 nm (HOMO→LUMO) that nicely matches the absorption band found experimentally at 623 nm (Figure S39 and Table S5).^[23]

To assess further the stabilization effect and relative importance of the arene-to- C_{carb} π -donation and Au-to- C_{carb} backdonation,^[28] the “dynamics” of the parent $\alpha\text{-CF}_3$ gold(I) carbene **3-H** were analyzed. A first transition state was located on the potential energy surface (PES) for the rotation about the Au= C_{carb} bond (Figure S41 and Table S7) with the two phosphine arms coordinated to gold (**TS_{rot AuC}**).^[29,30] It lies 20.5 kcal mol⁻¹ above **3-H** (Figure 5). From **3-H** to **TS_{rot AuC}**, we notice an elongation of the metal-carbene bond from 1.975 to 2.023 Å and a shortening of the $C_{\text{carb}}\text{-}C_{\text{ipso(Ph)}}$ bond from 1.438 to 1.427 Å (Tables S6 and S7). CDA and NBO Analyses of the bonding situation in **TS_{rot AuC}** substantiate a decrease of the Au-to- C_{carb} backdonation,

as deduced from the CT (−0.05 e vs −0.20 e in **3-H**), the d/b ratio (3.01 vs 1.94 in **3-H**) and the contribution of the C_{carbene} in the d(Au) NLMO (7.5 vs 14.8 % in **3-H**). In addition, arene-to- C_{carb} π -donation increases, as visible from the contribution of the C_{carbene} in the $\pi_{\text{C=C(phenyl)}}$ NLMO (17.5 % in **TS_{rot AuC}** vs 10.6 % in **3-H**).

Rotation about the $C_{\text{carb}}\text{-}C_{\text{ipso}}$ bond is also possible and actually turned out to be easier. Forcing the phenyl group to be perpendicular to the carbene center costs ca. 10 kcal mol⁻¹ only (**TS_{rot Ph}**). It induces some shortening of the Au= C_{carb} bond length (from 1.975 to 1.934 Å). In the absence of π -donation from the phenyl substituent, Au-to- C_{carb} backdonation is further enhanced in **TS_{rot Ph}**, as apparent from the more negative $C_{\text{carb}}\text{-to-Au}$ CT (−0.34 e vs −0.20 e in **3-H**), the higher $2p^{\pi}(C_{\text{carb}})$ contribution in the d(Au) NLMO (17.6 vs 14.8 % in **3-H**, Table S7) and the lower d/b ratio (1.49 vs 1.95 in **3-H**).

Forcing one of the P atom to dissociate from gold is more energetically demanding, the corresponding structure (**3-H_{dissoc P}**) being located 16.6 kcal mol⁻¹ above **3-H**. This results in T-shape instead of trigonal geometry. The Au center is now about linear (with P–Au distances of 2.343/3.496 Å and a P–Au– C_{carb} bond angle of 179.99°) while the Au= C_{carb} bond length increases to 2.020 Å. In the absence of P[^]P-chelation, Au-to- C_{carb} backdonation is decreased and the carbene center is mainly stabilized by π -donation from the phenyl substituent. Accordingly, the $C_{\text{carb}}\text{-to-Au}$ CT turns positive (0.19 e), the $2p^{\pi}(C_{\text{carb}})$ participation to the d(Au) NLMO decreases to 4.4 % and the d/b ratio increases to 3.60. The stability and bonding analysis of **3-H**, **3-H_{dissoc P}**, **TS_{rot AuC}** and **TS_{rot Ph}** emphasize that arene-to- C_{carb} π -donation and Au-to- C_{carb} backdonation act in concert to stabilize the carbene center, with key contribution of P[^]P-chelation.

Of note, the absence of free rotation about the Au= C_{carb} bond at the NMR timescale is apparent from the inequivalency of the CH, CH₂ and CH₃ groups of the diazaphospholane moiety in the ¹³C NMR spectra. Conversely, the presence of a single set of signals for the *ortho* and *meta* CH groups of the phenyl substituent in the ¹H and ¹³C NMR spectra is consistent with free rotation about the $C_{\text{carb}}\text{-}C_{\text{ipso}}$ bond.

Then the reactivity of the $\alpha\text{-CF}_3$ gold(I) carbenes was investigated.

Electrophilic Behavior

Upon addition of pyridine (2 equiv) at −40 °C, the blue color characteristic of **3-Ph** rapidly vanished, indicating rapid reaction. After work-up, the carbene-pyridine adduct **4** was isolated in 70 % yield as a pale-yellow solid (Scheme 2). The NMR data are diagnostic for the addition of pyridine to the carbene center, not to gold. The ¹³C NMR signal at 269.8 ppm for the carbene center is shifted by more than 170 ppm and now appears at δ 98.4 ppm (quartet, ² J_{CF} = 38.0 Hz). The ¹H NMR signals for the H_{ortho} atoms of pyridine are significantly deshielded at δ 8.98 ppm, while the ⁴ J_{PF} coupling constant decreases from 23.2 to 5.8 Hz upon coordination of the Lewis base. Since all our attempts to

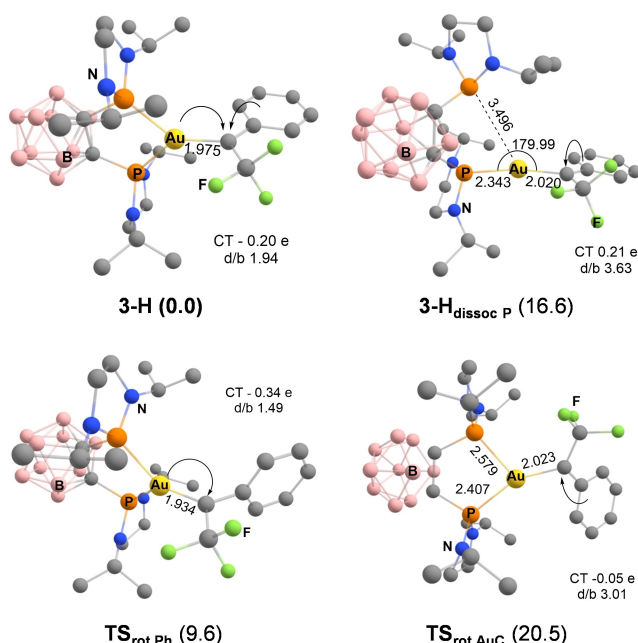
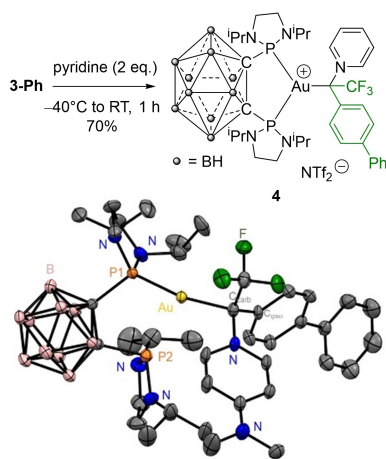


Figure 5. Optimized geometry of the parent $\alpha\text{-CF}_3$ Au^I carbene **3-H**, the form resulting from dissociation of one P atom (**3-H_{dissoc P}**) and the transition states associated with rotations about the $C_{\text{carb}}\text{-}C_{\text{ipso}}$ (**TS_{rot Ph}**) and AuC (**TS_{rot AuC}**) bonds at the B3PW91/SDD+f(Au),6-31G** (other atoms) level of theory. Charge transfer (CT) and donation-to-backdonation (d/b) ratio. In parenthesis, related Gibbs free energy, in kcal mol⁻¹.



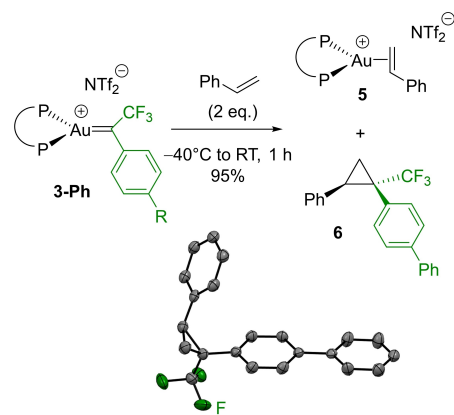
Scheme 2. Reaction of the α -CF₃ Au^I carbene **3-Ph** with pyridine; molecular structure of the related DMAP adduct **4'** (bottom). Thermal ellipsoids drawn at 50% probability, hydrogen atoms, counter anion and disordered atoms are omitted. Selected bond lengths [Å] and bond angles [°]: Au–C_{carb} 2.108(4), Au–P1 2.254(1), Au–P2 3.606(1), C_{carb}–C_{ipso} 1.530(5), C_{carb}–CF₃ 1.521(5), C_{carb}–N 1.499(5); P1–Au–P2 68.14(3), P1–Au–C_{carb} 167.8(1), P2–Au–C_{carb} 116.9(1).

crystallographically characterize **4** failed, we prepared the analogous 4-dimethylamino-pyridine (DMAP) adduct **4'**. Gratifyingly, crystals suitable for X-ray diffraction analysis could be obtained in this case,^[25] unambiguously confirming the addition of the N-Lewis base to the carbene center (Scheme 2, bottom). The pyridine N atom of DMAP is tightly coordinated to the former carbene center (N–C 1.499(5) Å) which is now in tetrahedral environment. Of note, only one of the P atom is coordinated to gold which adopts a quasi-linear dicoordinate geometry (P–Au–C 167.81(11)°). The coordination of the Lewis base reduces the electrophilicity of the carbene center and gold atom. Combined with higher steric shielding, this prevents the two P atoms of the DPCb ligand from chelating to gold. It is likely that the gold fragment swings in between the two phosphorus atoms, as previously observed in the (DPCb)AuCl complexes.^[31] The reactions of **3-Ph** with pyridine and DMAP substantiate its C-centered electrophilic behavior, in line with a Fischer-type carbene complex.

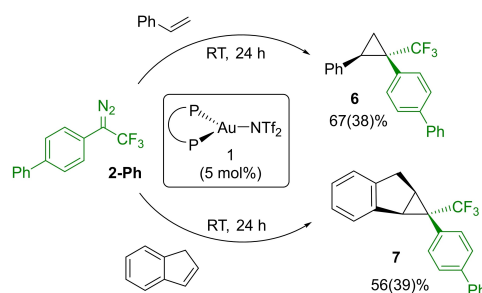
Cyclopropanation Reactions

The α -CF₃ gold(I) carbene **3-Ph** also readily reacts with styrene (Scheme 3).^[32] Two equivalents of alkene are needed for the reaction to reach completion (>95% spectroscopic yield of cyclopropane **6**). The π -alkene gold(I) complex **5** is obtained concomitantly, as deduced from ³¹P and ¹H NMR spectroscopy.^[33]

The transformation is amenable to catalysis (Scheme 4). Starting from the diazo compound **2-Ph**, the transformation can be performed under catalytic conditions. Using 5 mol% of the “cationic” complex (P[^]P)AuNTf₂ **1** and 1.05 equivalent of styrene, **6** is obtained in 67% yield after 24 hours at room temperature. Of note, the cyclopropanation is fully



Scheme 3. Reaction of the α -CF₃ Au^I carbene **3-Ph** with styrene; molecular structure of the ensuing cyclopropane **6** (bottom) showing the *syn* relationship of the phenyl and biphenyl moieties (thermal ellipsoids drawn at 50% probability, hydrogen atoms are omitted).

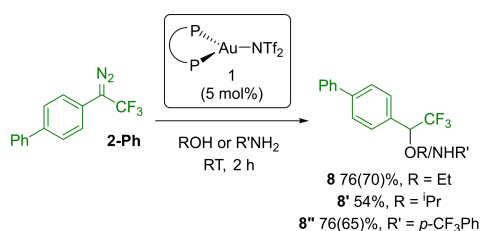


Scheme 4. Gold-catalyzed cyclopropanation reactions from the α -CF₃ diazo derivative **2-Ph** (NMR yields determined by ¹⁹F NMR using 4,4'-difluorobiphenyl as internal standard, isolated yields in parentheses).

diastereoselective. The *syn* relationship of the phenyl and biphenyl groups was first deduced from {¹H,¹⁹F} HOESY (Heteronuclear Overhauser Effect Spectroscopy) NMR experiments, and then definitely confirmed by X-ray diffraction analysis.^[23,25] Under similar conditions, indene is smoothly converted into **7** (56% spectroscopic yield), with again complete diastereoselectivity for the *syn* cyclopropane.

Insertion Reactions

With alcohols, O–H insertion reactions also proceed readily under similar conditions (Scheme 5). The corresponding α -CF₃ ethers **8** and **8'** are obtained thereby in 76 and 54% yields from ethanol and isopropanol, respectively.^[34] With anilines, N–H insertion occurs, as substantiated by the formation of the α -CF₃ amine **8''**.^[11c,d] Notably, attempts of C–H insertion from *N*-heterocycles (N–H or N–Me indole/carbazole) led to complex mixtures.^[35]



Scheme 5. Gold-catalyzed O–H/N–H insertion reactions from the α -CF₃ diazo derivative **2-Ph** (NMR yields determined by ¹⁹F NMR using 4,4'-difluorobiphenyl as internal standard, isolated yield in parentheses).

Conclusion

Using an (*o*-carboranyl)diphosphine ligand, we have been able to prepare and fully characterize α -CF₃ gold(I) carbenes. The bonding situation was thoroughly analyzed by experimental and computational means. Accordingly, the carbene is stabilized by a combination of Au-to-C_{carb} back-donation and arene-to-C_{carb} π -donation, whose balance finely depends on the electronic properties of the aryl substituent (OMe, Ph, CF₃).

Further studies will aim to explore and extend further the chemistry of α -CF₃ gold(I) carbene complexes. More generally, it is likely that other highly reactive (organo)fluoro gold complexes can be stabilized, isolated and exploited employing suitable ligands.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

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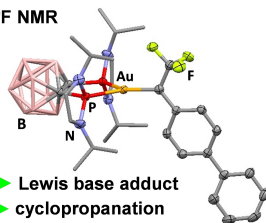
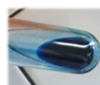
Research Articles

Gold Carbenes

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Gold(I) α -Trifluoromethyl Carbenes: Synthesis, Characterization and Reactivity Studies

- ✓ ^{31}P , ^1H , ^{13}C , ^{19}F NMR
- ✓ UV-vis
- ✓ XRD
- ✓ DFT
- ✓ NBO, CDA



Using an (*o*-carboranyl)diphosphine ligand, α -CF₃ gold(I) carbenes were isolated and fully characterized. Their stabilization involves Au-to-C_{carb} backdonation and arene-to-C_{carb} π -donation. They readily engage in carbene-type transformations under both stoichiometric and catalytic conditions.