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Gold Difluorocarbenoid Complexes: Spectroscopic and Chemical Profiling

Alexander G. Tskhovrebov, Julia B. Lingnau, and Alois Fürstner*

Abstract: Gold carbenes of the general type $[LAu{=}CR_2]^+$ are sufficiently long-lived for spectroscopic inspection only if the substituents R compensate for the largely missing stabilization of the carbene center by the $[LAu]^+$ fragment. π-Donation by two fluorine substituents (R = F) is insufficient; rather, difluorocarbene complexes are so deprived in electron density that they sequester even "weakly coordinating" anions such as triflate or triflimide. This particular bonding situation translates into unmistakable carbenium ion chemistry upon reaction with stilbene as a model substrate.

Cationic gold carbene complexes can be thought as consisting of a singlet carbene fragment, the lone pair of which interacts with an orbital of appropriate symmetry of the $[LAu]^+$ unit to form a strong σ-bond; π-back donation from the metal to the empty carbene p-orbital is (very) modest.[1,2,3,4] This particular bonding situation allows the exceptional electrophilicity of gold carbenes to be rationalized, which surfaces in a plethora of catalytic transformations;[4,5,6,7] at the same time, it explains why spectroscopic characterization and isolation of these highly reactive species in pure form proved challenging. Known representatives have substituents at the carbene center that compensate for the largely missing stabilization that a more strongly π-donating metal would entail (Figure 1); if these substituents overdo their job, however, prototypical reactivity of an electrophilic carbene is internally "quenched" and the garnered structural information arguably loses relevance for a better understanding of gold catalysis.[8] In practice, the right balance has been reached by conjugation of the carbene with appropriately substituted arenes (**1**),[9] delocalization of the charge density within an aromatic ring system (**2**),[10] or simply by massive shielding that prevents any reaction partner from reaching the highly electrophilic site on steric grounds (**3**).[11,12,13]

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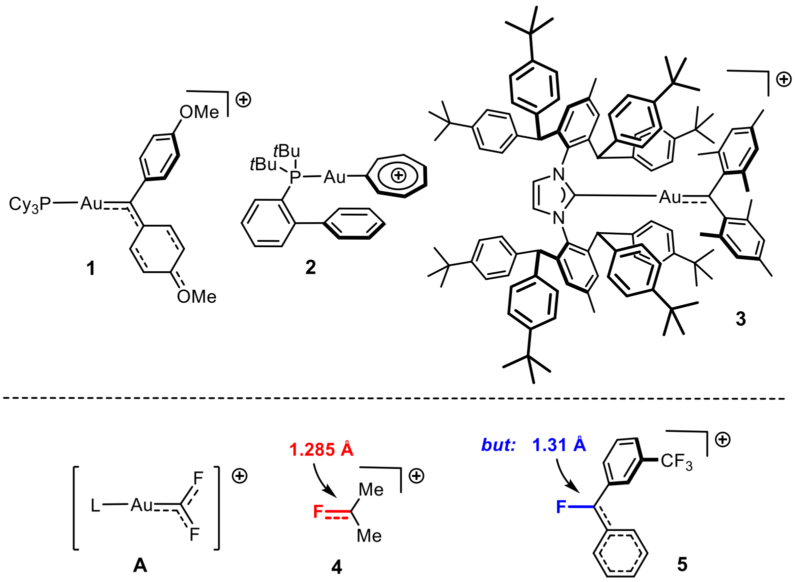
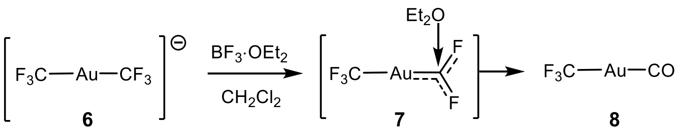


Figure 1. Top: Selected examples of reactive gold carbene complexes characterized by X-ray diffraction; the escorting counterions are not shown for clarity; bottom: targeted gold difluorocarbene complexes **A** stabilized by π-donation from the fluorine lone-pairs; this effect is operative in the carbenium ion **4** but largely offset by the aryl groups in **5**

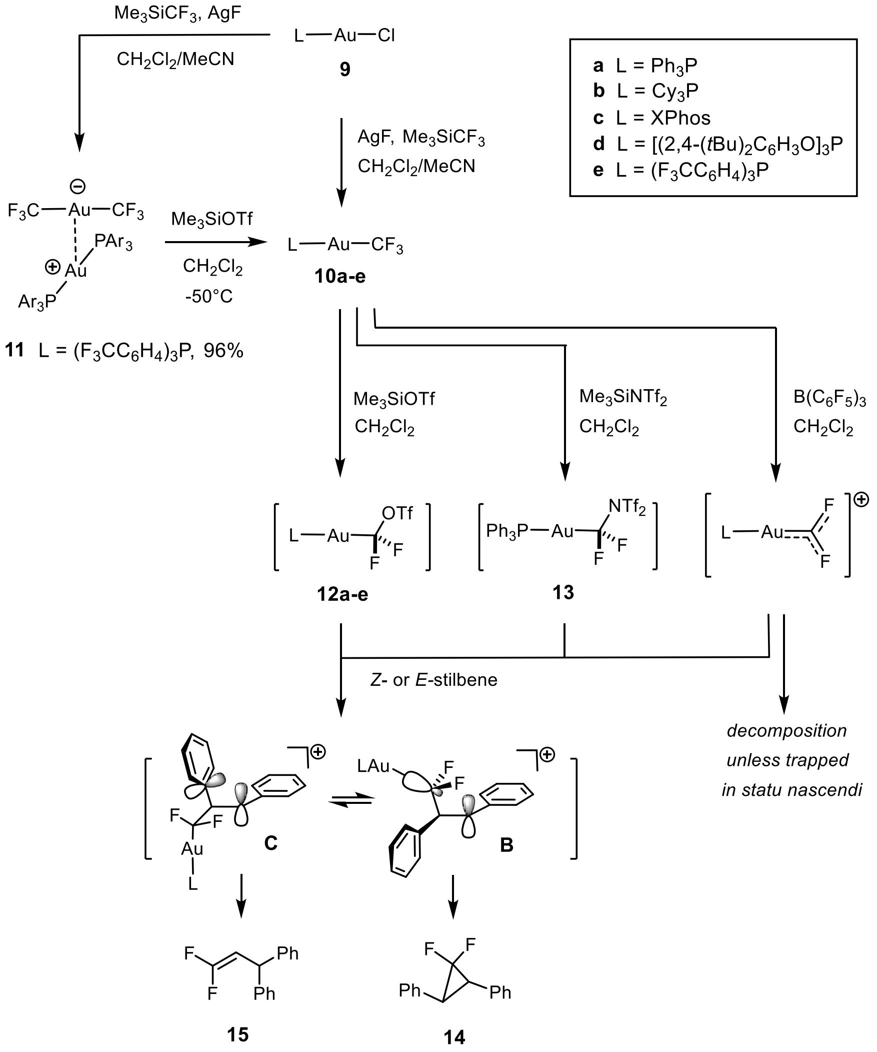


Scheme 1. An unsuccessful previous attempt at detecting a gold difluorocarbene (presumably in form of the ether adduct); only the corresponding carbonyl complex **8** was found even at very low temperature

Based on this analysis, we conjectured that gold difluorocarbenes of type **A** might be potentially observable entities (Figure 1): though fluorine substituents are strongly electron-withdrawing in the σ-framework, they act as decent π-donors. This effect is evident from the structures of other metal difluorocarbene complexes in the solid state;[14] the net stabilizing function notwithstanding, most examples that proved sufficiently stable for isolation in pure form do comprise a fairly strongly π-donating central metal fragment.[15] Cationic difluorocarbene complexes,[16] in contrast, as well as difluorocarbene complexes of platinum and gold as the most widely used carbophilic catalysts in synthesis are exceedingly rare.[17,18] Since the poor π-backdonation from $[LAu]^+$ in **A** imparts partial carbocation character onto the ground state of the coordinated carbene ligand,[19] it is also deemed relevant in the present context to recapitulate to which extent fluorine substituents can stabilize carbenium ions (Figure 1).[20] Their π-donor capability is clearly manifest, for example, in the structure of cation **4** in the solid state, in which the C–F distance is notably shorter (1.285(11) Å) than an average C_{sp2}–F bond ($\approx 1.333 \pm 0.005$ Å).[21] Interestingly, however, the analogous C–F distance in **5** is 1.31 Å and hence almost "normal", whereas the $C_{carbene}$–C_{ipso} bonds are contracted.[21] The comparison of **4** and **5** suggests that fluorine substituents can stabilize a carbenium center through π-donation but are less efficient in doing so than an ordinary aryl ring.

These data suggest that difluorocarbene complexes of type **A** are likely at the edge of being observable.[22] This supposition is in line with a previous study which showed that treatment of compound **6** with $BF_3 \cdot Et_2O$ solely afforded the carbonyl complex **8** (Scheme 1).[23] The transient gold difluorocarbene species **7** as the likely intermediate of this reaction could not be detected by ^{19}F NMR at –80°C; hydrolysis[24] must be extremely fast even under such notably mild conditions.

It is against this backdrop that our attempts at characterizing the intermediate formed upon Lewis-acid mediated α-fluoride elimination from dicoordinate $LAuCF_3$ complexes (**10**) have to be seen. The required precursors **10** were conveniently prepared from **9** by following a literature procedure and their structures in the solid state are contained in the Supporting Information (Scheme 2).[25] The only exception was **9e** (L = $(p\text{-}F_3CC_6H_4)_3P$), which, on treatment with Me_3SiCF_3 and AgF, underwent ligand scrambling with formation of **11** in high yield. The structure of this unique complex in the solid state (Figure 2) suggests that the pairing of the discrete $[L_2Au]^+$ and $[Au(CF_3)_2]^-$ ions is reinforced by an aurophilic interaction between them (Au1····Au2 2.88 Å);[26,27] the axes of the cationic unit and the bis(trifluoromethyl)aurate entity are almost orthogonal to each other likely for steric reasons (C1–Au1–Au2–P2 102.9°). This remarkable ensemble can be stored under inert conditions for extended periods of time; however, it was found to redistribute instantly on treatment with TMSOTf even at –50°C to give complex **10e**, which was identified by the very characteristic coupling pattern between the P- and F-nuclei.



Scheme 2. Generation and fate of gold difluorocarbenoid complexes

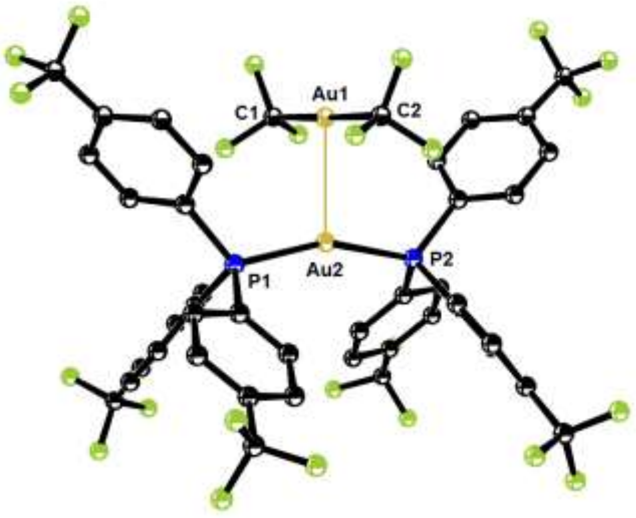
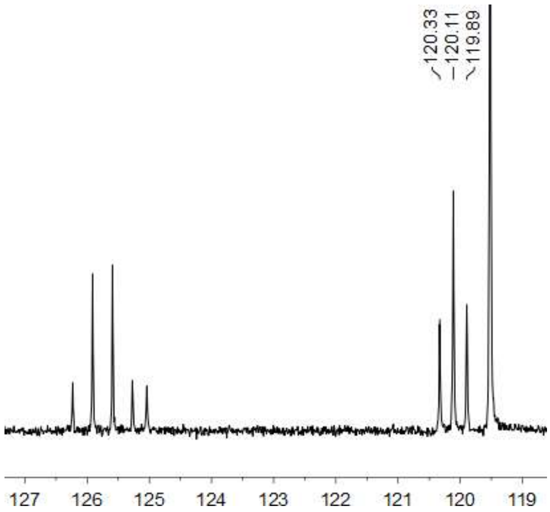


Figure 2. Structure of complex **11** in the solid state

Addition of TMSOTf to a solution of **10a** in CD_2Cl_2 at –78°C followed by short warming to –20°C resulted in the fairly clean formation of carbenoid **12a**,[28] provided that strictly inert conditions were ensured. While this reactive species was sufficiently long-lived at –50°C for spectroscopic inspection, it rapidly decomposed into purple gold colloid above this temperature. The structure assignment is based on the characteristic multiplicity of the signals in the ^{31}P NMR (δ_P = 36.1 ppm, t, $J_{P,F}$ = 31.0 Hz) and ^{19}F NMR spectra (δ_F = –30.7 ppm, d, $J_{P,F}$ = 31.0 Hz); this pattern and the identical coupling constant show that one phosphorous center and two fluorine atoms are mutually coupled. The ^{13}C NMR resonance of the carbenoid center itself is also highly informative, which appears as doublet of triplets centered at δ_C = 169.6 ppm ($J_{C,P}$ = 169.8, $J_{C,F}$ = 359.5 Hz). This shift speaks against a true "metal carbene", which one would expect to resonate at much lower field;[29] rather it suggests that the triflate anion is covalently bound.[30] This conclusion is in line by the cross peak observed in the ^{19}F COSY spectrum between the signal of the "carbenoid" $-CF_2-$ unit (δ_F = –30.7 ppm) and the $-OSO_2CF_3$ group (δ_F = –76.1 ppm, see the Supporting Information), which implies that the "weakly coordinating counterion" is at least in close vicinity. Unfortunately, all attempts at isolating complex **10a** in pure form failed because of rapid gold colloid formation.



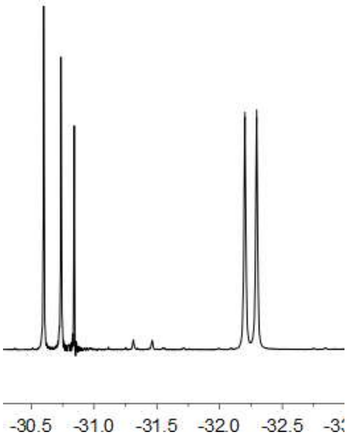


Figure 3 Strips from the ^{31}P NMR (top) and ^{19}F NMR spectra (bottom) of a crude reaction mixture formed from **10d** and TMSOTf in CD_2Cl_2 at –50°C at ≈45% conversion showing the starting complex and carbenoid **12d**

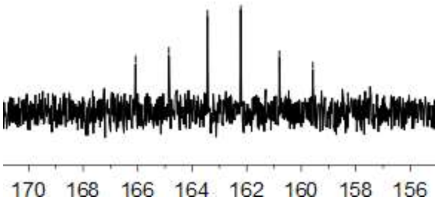


Figure 4 ^{13}C NMR signal (100 MHz, CD_2Cl_2, –50°C) of the carbenoid C-atom of complex [$(Ph_3P)AuCF_2(NTf_2)$] (**13**)

The overall bonding situation does not vary much upon changing the steric and electronic properties of the donor ligand *trans* to the carbenoid unit over a wide range. In all cases investigated were the spectral features of the resulting intermediates similar to those of **12a** (Figure 3 and the SI). Likewise, replacement of TMSOTf by $TMSNTf_2$ as the activating agent led to the same gross picture in that the triflimide unit seems to be bound to the resulting gold carbenoid **13** as manifest in the diagnostic spectral fingerprint (Figure 4 and the SI).[31] The use of activators with less coordinating counterions, however, was unrewarding: even though discrete carbene complexes seem to be generated in the first place, their extremely short lifetime made full characterization by low temperature NMR impossible; no carbene resonance, which is a multiplet with very low intensity, could be detected in any of the cases investigated.

In parallel, we probed the character of the gold difluorocarbenoids by chemical means. It is known for a long time that the chlorinated complexes [$R_3PAuCCl_3$] and [R_3PAuCH_2Cl], which are close relatives of **10**, afford (dichloro)cyclopropanes in high yield simply upon heating in the presence of an olefin in an inert solvent;[32] addition of a chloride scavenger allows the reaction to proceed at lower temperature, although carbene dimerization then seriously competes with cyclopropanation.[33] In contrast, complexes of type [$LAu(CF_3)$] (**10**) themselves are thermally stable: no reaction was observed by NMR upon heating of a mixture of **10a** or **10b** with *E*-stilbene in [D_8]-toluene for 72 h at 100°C. As expected, addition of TMSOTf or $B(C_6F_5)_5$ to a solution of $(Cy_3P)AuCF_3$ (**10b**) in CH_2Cl_2 at –20°C gave difluorocyclopropane **14** in 40% and 59% yield, respectively;[34,35] in all reactions, competing formation of volatile CO[23] and/or tetrafluoroethylene (δ_F = 131.5 ppm, 223K)[36] by hydrolysis or dimerization of the transient carbenoid, respectively, seem to make up for the rest. Surprisingly, however, use of the analogous gold precatalyst **10a** carrying the less donating Ph_3P ligand instead of Cy_3P furnished not only cyclopropane **14** (15%) but also difluoro-olefin **15** (26%). Formation of this unanticipated by-product mandates an 1,2-aryl shift, which in turn suggests that an intermediate of type **C** with significant carbocation character has been passed through. Under this premise, it seemed improbable that cyclopropane formation is a concerted process. Indeed, reaction of **10a**/TMSOTf with *Z*-stilbene furnished *trans*-**14** (and **15**);[37] this result is again consistent with a stepwise pathway in which a carbenium intermediate of type **B** opens the doorway to the thermodynamically more stable cyclopropane.[38] Such an ionic mechanism is strongly reminiscent of the reactivity of highly electrophilic cationic iron carbenes vis-à-vis unsaturated compounds, which are known to involve stabilized (e. g. benzylic) carbocations as key intermediates.[39]

In any case, formation of the rearranged difluoroolefin **15** lends further credence to the notion that the cornucopia of gold catalysis is rooted, to a significant extent, in reactive intermediates featuring considerable carbocationic character. The perhaps most notable manifestations thereof are cyclization cascades of polyunsaturated substrates that obey the “Stork-Eschenmoser postulate”,[40,41] as well as numerous reaction manifolds amalgamating π-acid catalysis with classical reactivity of the Wagner-Meerwein-, Friedel-Crafts-, Nazarov-, or Prins-type, to mention but a few.[4-7,42]

The first spectroscopic observation and chemical characterization of gold difluorocarbenoid complexes summarized above suggests that stabilization of such intermediates by electron donation from the metal to the empty carbene p-orbital is poor. As this deficiency is only partly compensated by overlap with the lone pairs of the fluorine substituents, these reactive species are so deprived in electron density that they retain even “weakly coordinating” anions such as triflate or triflimide. In accord with this analysis, gold difluorocarbenoids were found to react with stilbene in a stepwise rather than concerted fashion to generate benzylic carbocations in the first place as can be deduced from the downstream speciation. Further studies into structure, bonding and reactivity of late transition metal carbene complexes from this laboratory[43] are underway and will be reported in due course.

Acknowledgements

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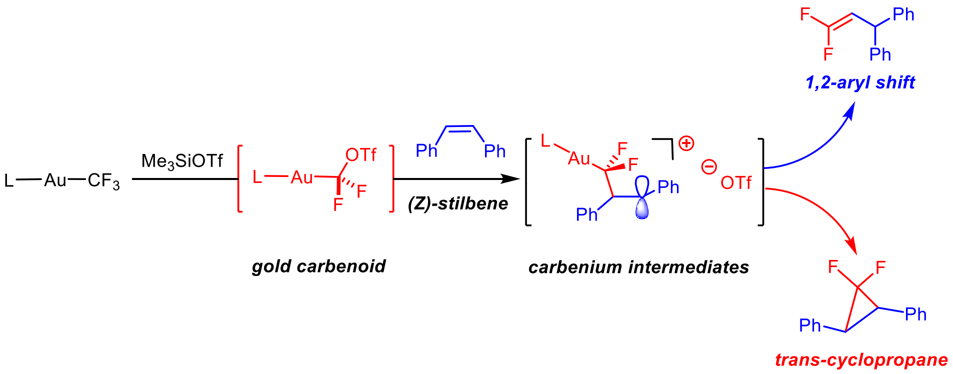

(Dis)Integrate: Gold carbenoids generated by Lewis-acid mediated α-fluoride elimination from LAuCF$_3$ are so deprived in electron density that they even retain poorly coordinating counteranions (triflate, triflimide); they disintegrate, however, on reaction with (*E*)- or (*Z*)-stilbene to give a carbenium intermediate that accounts for the observed downstream chemistry.

Keywords: Carbene Complexes · Carbenium Ions · Cyclopropanes · Gold · NMR · Organofluorine Chemistry

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[33] a) J. M. Sarria Toro, C. Garcia-Morales, M. Raducan, E. S. Smirnova, A. M. Echavarren, *Angew. Chem. Int. Ed.* **2017**, *56*, 1859-1863; when carrying a mesityl substituent, the corresponding gold carbene complexes could be observed by NMR, see: b) C. Garcia-Morales, X.-L. Pei, J. M. Sarria Toro, A. M. Echavarren, *Angew. Chem. Int. Ed.* **2019**, 58, 3957-3961.

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[34] For a general review on difluorocarbene, see: C. Ni, J. Hu, *Synthesis* **2014**, *46*, 842-863.

[35] Small amounts (≤ 10%) of difluoro-olefin **15** were also detected in the crude mixtures.

[36] Significant amounts of tetrafluoroethylene were detected by NMR and confirmed by GC/MS in the reaction promoted by $TMSNTf_2$.

[37] Traces of *cis*-**14** were detected in the crude mixture by ^{19}F NMR .

[38] It has not been firmly established if conversion of **B** into **14** proceeds via “backside attack”, as shown in Scheme 2; this drawing rests on the presumed analogy to the well-known behavior of electrophilic iron carbenes, cf. ref. 39

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