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Authors

Wong, Zeng Rong

Khanh, Binh

Berg, Willi R

et al.

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Reactions of Difluorocarbene with Organogold(I) and Organocopper(I) Complexes to Access *gem*-Difluoromethylene Organometallics.

Zeng Rong Wong,^a Binh Khanh Mai,^b Willi R. Berg,^{a,c} Alexander Kvitsinski,^a Thor L. F. Correia,^a Yu Zhang,^b Peng Liu,^{b*} F. Dean Toste.^{a*}

^aDepartment of Chemistry, University of California, Berkeley, California 94720, United States

^bDepartment of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, United States

^cDepartment of Chemistry and Biochemistry, Freie Universität Berlin, Berlin 14195, Germany

Supporting Information Placeholder

ABSTRACT: The *gem*-difluoromethylene functional group is an important motif in medicinal chemistry, and development of new fluoroalkyl-metal systems has been crucial to enable new syntheses of *gem*-difluoromethylenes. Herein we utilize reactions of difluorocarbene with to access novel examples of three classes of *gem*-difluoromethylene organometallics. Firstly, difluorocarbene insertion into the R-Au(I) bond of organogold(I) species was demonstrated for the first time, forming H-CF₂-Au(I), alkyl-CF₂-Au(I) and aryl-CF₂-Au(I) species. Secondly, on the isoelectronic Cu(I) system, PhCF₂Cu(I) was formed and detected for the first time via a similar difluorocarbene insertion into the aryl-Cu bond. Thirdly, via a difluorocarbene cycloaddition we isolate for the first time a κ^1 -difluorocyclopropenyl-transition metal complex, formed by reaction of alkynylAu(I) with difluorocarbene. Subsequent study of these reaction systems by density functional theory calculations facilitated a comparison of Au(I) and Cu(I) in the difluorocarbene insertion reactions, and a comparison of difluorocarbene insertion and cycloaddition pathways in the reaction of difluorocarbene and alkynylAu(I).

organometallics can advance new synthetic approaches towards fluoroalkyl-containing products

Organogold and organocopper chemistry has been intensively investigated in the synthesis of fluorine-containing products. In gold chemistry, both gold(I) and gold(III) complexes have been studied, [5] and our group has demonstrated difluorocarbene insertion into alkylgold(III) bonds to form alkylCF₂Au(III) species, that were subsequently cross-coupled with ¹⁸F-fluoride to form ¹⁸F-labelled R-CF₃ products.^{4a} In organogold(I) chemistry, while examples fluoridogold(I),⁶ difluoromethylgold(I),⁷ and perfluoroorganogold(I)⁸ complexes have been isolated, hydrocarbyl-substituted RCF₂Au(I) complexes remain notably unreported. Similarly, the isoelectronic copper(I) congeners, fluoridocopper(I),⁹ difluoromethylcopper(I),¹⁰ and perfluoroorganocopper(I)¹¹ have been isolated; however, the isolation of RCF₂Cu(I) for R = hydrocarbyl species remains elusive. Despite this, transient alkylCF₂Cu(I) species have been invoked as intermediates in catalytic three-component syntheses of *gem*-difluoromethylenes, often via difluorocarbene insertion into Cu(I) alkyl bonds,¹² followed by cross-coupling.¹³ Additionally, alkyl-CF₂Zn(II) nucleophiles, generated through difluorocarbene insertion into alkyl-Zn(II) bonds, have been engaged in Cu-catalyzed couplings via putative alkyl-CF₂Cu(I) intermediates.^{3c,14} However, the instability of aryl-CF₂Zn(II) species precludes transmetalation to form aryl-CF₂Cu(I),¹³ and no direct generation or detection of simple arylCF₂Cu(I) species has been reported. Beyond Au(III), Cu(I), and Zn(II), difluorocarbene insertion has also been applied to Co(III), Pd(II), and Pt(II) systems to access *gem*-difluoromethylene organometallics (**Figure 1a**).^{4e,15} Additionally, related processes have been developed to prepare *gem*-difluoromethylene groups in ring structures, such difluoromethylcyclopropenes and difluoromethylcyclopropanes.¹⁶ Cu-catalyzed cross-coupling of a difluorocyclopropenylzinc(II)

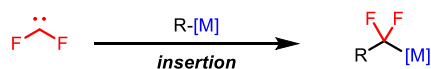
Introduction

The *gem*-difluoromethylene (R-CF₂-R') motif plays a significant role in medicinal chemistry, where it is utilized to modulate lipophilicity, function as a bioisostere, or confer greater metabolic stability when replacing methylene groups.¹ As a result, screening of pharmaceutical candidates is facilitated by modular synthesis of *gem*-difluoromethylene-containing products.² One such approach leverages difluorocarbene in three-component coupling reactions,³ often proceeding through transition metal-containing fluoroalkyl intermediates.⁴ Thus, the development and study fluoroalkyl

nucleophile with electrophiles has also been proposed to proceed via a difluorocyclopropenyl-Cu(I) intermediate,¹⁷ but this species proved too unstable for detection, even at -70 °C. To date, no difluorocyclopropenyl-transition metal complex has been isolated.

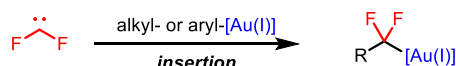
Figure 1. Reactions of organometallics with difluorocarbene to access difluoromethylene organometallics. **(a)** Previous work on difluorocarbene insertion into R-M bonds, **(b)** Controlled difluorocarbene insertion into R-Au(I) bond for isolation of

a. Previous work: Difluorocarbene insertion into metal-R bonds



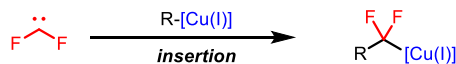
- Isolated examples: [M] = Au(III), Co(III), Pd(II), Pt(II)
- Generated as intermediates: [M] = Cu(I), Zn(II)

b. This work: Difluorocarbene insertion into Au(I)-R bonds



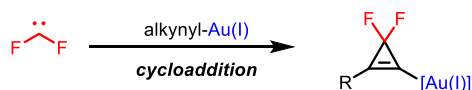
- Controlled single insertion
- Novel RCF₂-Au(I) products isolated
- Bench-stable without α-fluoride elimination

c. This work: Difluorocarbene insertion into Cu(I)-R bond



- Difluorocarbene insertion studied for R = simple aryl
- PhCF₂Cu formed and detected for the first time

d. This work: difluorocarbene cycloaddition with alkynyl-Au(I)



- First isolated κ¹-difluorocyclopropenyl transition metal complex
- Cycloaddition occurs exclusively with no insertion observed

RCF₂Au(I) complexes, **(c)** Detection of PhCF₂Cu(I) via difluorocarbene insertion into R-Cu(I) bond, **(d)** Isolation of a κ¹-difluorocyclopropenyl-transition metal species via difluorocarbene cycloaddition reaction with an alkynylAu(I) complex.

Herein, we utilize reactions of difluorocarbene with organometallics to access examples of the aforementioned classes of elusive *gem*-difluoromethylene-containing organometallics. Firstly, we demonstrated successful difluorocarbene insertions on the Au(I) platform to isolate the first examples of RCF₂Au(I) for R = hydrocarbyl. Next, we extended this successful difluorocarbene insertion approach to an isoelectronic copper(I) system, generating and detecting PhCF₂Cu(I) for the first time. Finally, we employed a difluorocarbene cycloaddition reaction to isolate the first κ¹-difluorocyclopropenyl-transition metal species via a cycloaddition reaction of alkynylgold(I) with difluorocarbene. These reaction systems were further probed by density functional theory (DFT) calculations, facilitating a comparison of gold(I) and copper(I) in the difluorocarbene insertion reactions, and a comparison of

difluorocarbene insertion and cycloaddition pathways in the reaction of difluorocarbene and alkynylAu(I).

Results and Discussion

Initially, the synthesis of novel R-CF₂Au(I) complexes (R = hydrocarbyl) by difluorocarbene insertion into the gold(I)-carbon bond was explored.¹⁸ Two important challenges associated with this process that needed to be addressed. The first involved preventing a multiple carbene-insertion, a process observed in multiple reports on isoelectronic copper(I) systems,^{12,13} and for which a low energy barrier of 7.6 kcal/mol was calculated for a second insertion event.^{13f} The second challenge concerned α-fluoride elimination, a decomposition pathway to which nucleophilic RCF₂M species are often susceptible¹⁹ (**Figure 2**).

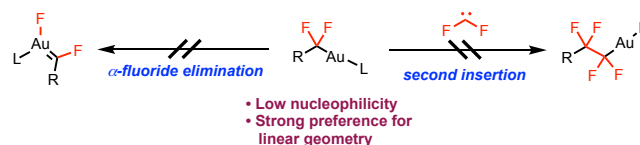


Figure 2. Leveraging characteristics of Au(I) to stabilize R-CF₂-Au(I) after a difluorocarbene insertion into the R-Au(I) bond.

Gold(I) complexes exhibit unique properties resulting from the strong relativistic effects and high electronegativity of gold,²⁰ large Pauli repulsion with ligands,²¹ and a well-established preference for linear geometry.²⁰ This tendency to form two coordinate linear complexes is associated with a strong reluctance towards β-hydride elimination.²² We envisioned that we could leverage these characteristics of gold(I) to address the aforementioned challenges (**Figure 2**). Specifically, the lower nucleophilicity of R-Au(I) was expected to promote controlled single difluorocarbene insertion without multiple insertions, while the strong preference of Au(I) for linear geometry anticipated to suppress α-fluoride elimination. Furthermore, the inherent resistance of alkylgold(I) complexes towards β-hydride elimination would provide a platform for studying the reactivity of alkyl-Au(I) complexes with difluorocarbene.

Prior reports on the synthesis of a difluoromethylgold(I) complexes via a transmetalation strategy suggested that these compounds exhibited “partial instability”.⁷ To address this, IPr (1,3-Bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene) was selected as a stabilizing ligand. Bulky N-heterocyclic carbene ligands such as IPr have been effectively utilized in previous studies to stabilize reactive Au(I) species.^{6, 20b, 23} The synthesis of organogold(I) complexes IPrAuEt (**3**) and IPrAuPh (**5**), bearing electronically unbiased alkyl and aryl groups, was achieved from IPrAuCl (**1**) (**Figure 3**).²⁴

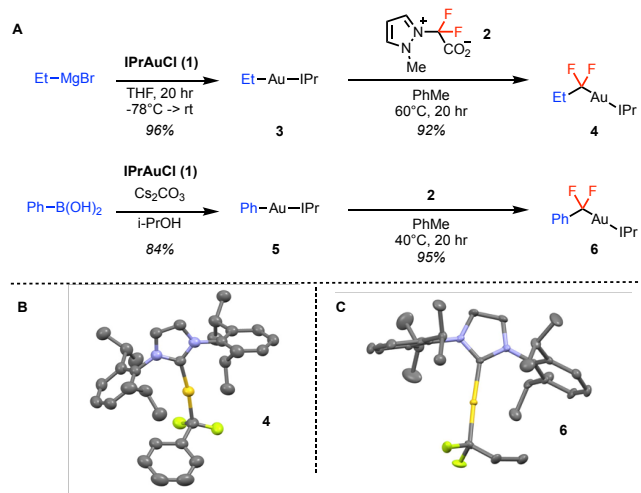


Figure 3. A. Synthesis of difluorocarbene insertion products **4** and **6**. **B** and **C.** X-ray structure of complexes **4** and **6**. Thermal ellipsoid plots are drawn at 50% probability, with hydrogen and solvent atoms omitted for clarity.

Nitrogen-based zwitterionic difluorocarbene sources such as **2** have been reported to release difluorocarbene under mild conditions without requiring an activator.²⁵ Heating **3** or **5** with an excess of **2** in toluene at 40°C led to the formation of the respective single insertion products IPrAuCF₂Et (**4**) and IPrAuCF₂Ph (**6**), which were isolated in excellent yields.²⁶ The structural connectivity of these difluoromethylenegold(I) complexes was confirmed by single-crystal XRD. Additionally, the competence of alternative difluorocarbene difluorocarbene sources for this insertion was briefly screened, and they exhibited varying competence for this insertion reaction (**Table 1**). Difluorocarbene source **2** was selected for subsequent reactions due to the excellent isolated yields obtained.

IPrAuPh		:CF ₂ source	Conditions		IPrAuCF ₂ Ph
5		1.5 equiv			6
Entry	Difluorocarbene (:CF ₂) source		Conditions ^a		Yield
1	2 (1.5 equiv.)		PhMe, 40°C, 20 h		95%
2	⁺ PPh ₃ CF ₂ CO ₂ ⁻ (1.5 equiv.)		PhMe, 60°C, 20 h		73%
3	KCO ₂ CF ₂ Br (4 equiv.)		PhMe, 60°C, 20 h		0%
4	TMSCF ₂ Br (4 equiv.), Bu ₄ N ⁺ Ph ₃ SiF ₂ ⁻ (4 equiv.)		THF, 0°C, 1 hr		10%

Table 1. Exploration of alternative difluorocarbene sources for the conversion of **5** to **6**. [a] Reactions were run on a 0.075 mmol scale.

The gold(I) complexes **4** and **6** were bench-stable, consistent with expectations based on the expected low nucleophilicity and good resistance towards α -fluoride elimination. Notably, the high resistance of alkylgold(I) complexes towards β -hydride elimination (with a reported activation barrier of 49.7 kcal/mol for **3**)^{22b} facilitated the study of difluorocarbene insertion into C(sp³)-metal bonds on the gold(I) system, with no β -hydride elimination observed for **3** or **4**. The reactivity of these new nucleophiles in palladium-catalyzed cross-coupling reactions with iodobenzene and electrophiles (Selectfluor) was also explored (**Scheme S1**).²⁸ Furthermore, we found that IPrAuH²⁹ could be engaged in desired

productive insertion reactions with **2** to cleanly form the desired IPrAuCF₂H product⁷ (see SI for further discussion and **Scheme S8** for DFT calculations). These results demonstrate that difluorocarbene insertion as a synthetic strategy not only for accessing previously described HCF₂Au(I) complexes, but also for the formation of alkyl-CF₂Au(I) and aryl-CF₂Au(I) species. Moreover, the gold(I) system effectively facilitated controlled single insertion without the occurrence of α -fluoride elimination.

Having successful difluorocarbene insertion into R-Au(I) bonds, potential extensions to the isoelectronic copper(I) system were considered. The formation of aryl-CF₂-Cu for an electronically unbiased aryl group remains an challenge in organocopper chemistry.³⁰ Known approaches towards RCF₂Cu(I) for R = hydrocarbyl include attack of external nucleophiles onto a copper(I)-difluorocarbene species^{13e,13f} and transmetalation of RCF₂Zn onto Cu(I).^{3c,14} The former was reported for R = alkyl, while the was described as successful for R = alkyl and not for R = aryl. We hypothesized that the isoelectronic PhCF₂Cu(I) could be successfully generated by an alternative third approach, namely attack of difluorocarbene onto a pre-existing arylcopper(I) species.^{12, 13}

Compared to the Au(I) congeners, reaction of **2** with IPrCuPh (**7**) proceeded less efficiently, yielding both single and double insertion products IPrCuCF₂Ph (**8**) and IPrCuCF₂CF₂Ph (**9**) (Figures S1 and S2).³¹ Notably, neither **8** or **9** were formed in yields exceeding 20%, and extended reaction times resulted in a complex mixture, likely due to decomposition.³² While **8** could not be isolated cleanly, its formation at room temperature suggests that, with an appropriately designed system, ArCF₂Cu(I) could be transiently generated and rapidly consumed in productive cross-coupling reactions for three-component *gem*-difluoromethylene synthesis. As the difluorocarbene insertion reaction was successful with IPrAuH, we also explored insertion reaction with analogous Cu(I)-hydride species. However, in our hands, attempts at demonstrating difluorocarbene insertion reactions into NHC-stabilized Cu(I)-hydrides to form (NHC)Cu(CF₂H) complexes were unsuccessful (see SI for further discussion and **Figure S9** for DFT calculations).

Following the successful development of difluorocarbene insertion chemistry to access difluoromethylene-bonded gold(I) and copper(I) organometallics, attention was directed toward a complementary difluorocarbene *cycloaddition* chemistry to produce and isolate a κ^1 -difluorocyclopropenyl-transition metal complex.³³ Based on prior reports of isolated cyclopropenyl-gold(I) complexes,³⁴ we considered it feasible to tame the strained and reactive difluorocyclopropenyl ligand on the gold(I) platform. Given the stronger and more directional bonding of Au-C(sp) compared to Au-C(sp²) and Au-C(sp³),³⁵ it was reasoned that the highest energy barrier for insertion would be associated with Au-C(sp), making difluorocarbene cycloaddition with the alkyne triple bond the preferred pathway.³⁶

Indeed, the application of of difluorocarbene cycloaddition chemistry to the gold(I) platform led to the successful isolation of two different cyclopropenyl-gold(I) complexes. The alkynyl gold complex **10**, derived from phenylacetylene and IPrAuOH,²³ was treated with excess of **2** under heating (**Figure 4**). A single product (**11**) was observed, successfully isolated in excellent yield, and identified as desired *gem*-difluorocyclopropenylgold(I), the first isolated difluorocyclopropenyl-transition metal complex. Furthermore, subsequent hydrolysis of moisture-sensitive **11** under

basic conditions generated a rare oxocyclopropenyl-Au(I) **12**. To the best of our knowledge, only two previous examples of oxocyclopropenyl-transitional metal complexes have been reported.³⁴

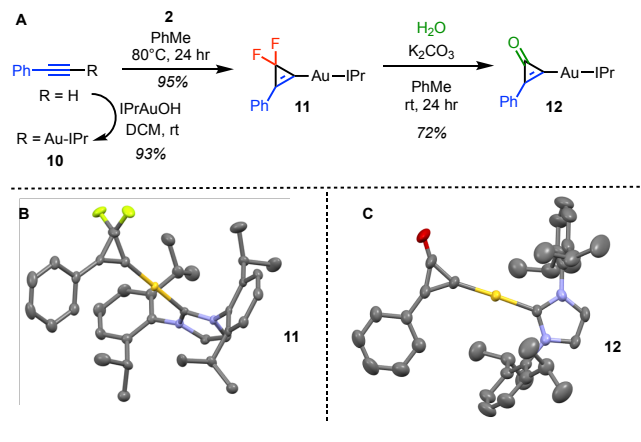


Figure 4. A. Synthesis of cyclopropenyl-gold species **11** and **12** via cycloaddition with difluorocarbene. B and C. X-ray structure of complexes **11** and **12**. Thermal ellipsoid plots are drawn at 30% probability, with hydrogen and solvent atoms omitted for clarity.

To gain better insight into the reaction systems above, we turned to density functional theory (DFT) calculations which were carried out at the M06/def2-TZVP/SMD(PhMe)//M06/6-31G(d)-LANL2DZ(Au,Cu) level of theory. We started by studying the difluorocarbene insertion mechanisms for the organogold(I) and organocopper(I) complexes. Two possible difluorocarbene insertion mechanisms with gold(I) and copper(I) complexes were considered: (a) a metal-difluorocarbene species is generated followed by a 1,1-migratory insertion to form the RCF₂M(I) product (Figure 5A); and (b) concerted insertion of difluorocarbene that breaks the metal-carbon bond and forms new metal-carbon and carbon-carbon bonds without forming metal-difluorocarbene intermediates (Figure 5B).

a. 1,1-Migratory insertion of :CF₂



b. Concerted addition of :CF₂

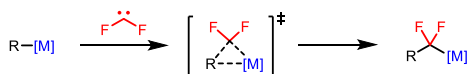


Figure 5. Two possible difluorocarbene insertion mechanisms into metal-carbon bonds

We first investigated difluorocarbene insertion into the Au-C(*sp*³) bond of IPrAuEt (**3**, Figure 6). The difluorocarbene generated from α,α-difluoroglycine precursor **2** (Figure S3)^{25,37} forms with **3** a van der Waals (vdW) complex **13**, which is 4.9 kcal·mol⁻¹ higher in Gibbs free energy than **3**. A T-shaped gold-difluorocarbene intermediate (**14**) is then formed, which is 6.8 kcal·mol⁻¹ higher in energy than **13**. The short Au-CF₂ bond distance (2.03 Å) in **14** suggests a relatively high Au-C bond order with both σ- and π-bonding characters.³⁸ The NPA atomic charges indicate the

difluorocarbene carbon in **14** is highly electrophilic with a +0.34 charge and the α-C of the ethyl is nucleophilic with a -0.75 charge. Therefore, gold-difluorocarbene **14** is highly reactive^{39,40} and undergoes facile 1,1-migratory insertion via **TS-1** with a low kinetic barrier of 1.8 kcal·mol⁻¹ relative to **14** and 13.5 kcal·mol⁻¹ with respect to the Au(I) complex **3**. This insertion process to produce IPrAu(I)CF₂Et (**4**) is highly exergonic by 54.4 kcal·mol⁻¹. Subsequent insertion of another difluorocarbene into the less nucleophilic and sterically more crowded Au-CF₂Et bond in **4** is kinetically much less favorable, requiring an activation free energy of 24.0 kcal·mol⁻¹ relative to **4**, substantially higher than the first difluorocarbene insertion that requires a 13.5 kcal·mol⁻¹ barrier. This result is consistent with the experimental findings that the only the single multiple insertion product was observed under the experimental conditions.

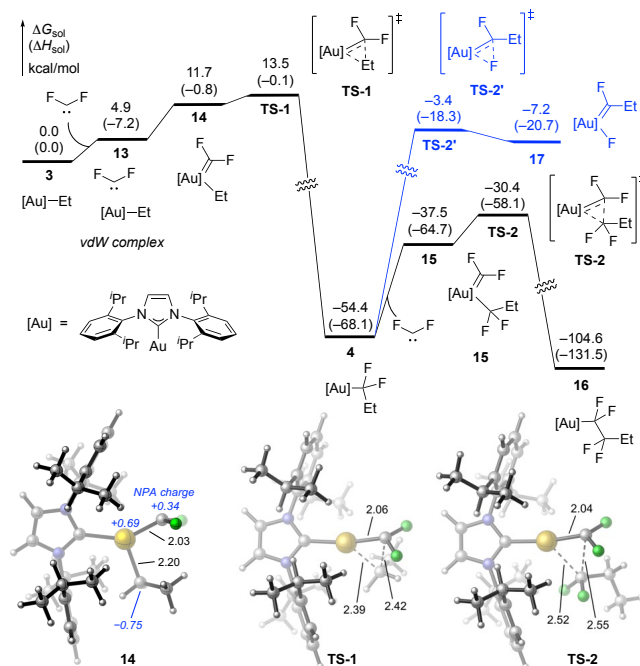


Figure 6. Computed reaction energy profile of difluorocarbene insertion into Au-C(*sp*³) bond of ethylgold(I) **3**. The second difluorocarbene insertion (**TS-2**) and α-fluoride elimination (**TS-2'**) were found to be kinetically less favorable. Bond distances in Å, NPA atomic charges in blue.

To confirm whether difluorocarbene insertion indeed involves gold-difluorocarbene **14** as a transient intermediate or occurs directly from vdW complex **13** (Figure 7), we performed intrinsic reaction coordinate (IRC) analysis of **TS1**. The IRC calculation reveals that the vdW complex **13** first leads to the T-shaped gold-difluorocarbene intermediate **14** without a transition state, which then rapidly undergoes 1,1-migratory insertion via transition state **TS-1**. Therefore, the IRC calculations support the formation of a transient gold-difluorocarbene intermediate **14** in the carbene insertion process.

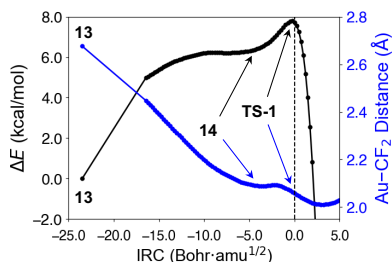


Figure 7. Intrinsic reaction coordinate (IRC) analysis for difluorocarbene insertion into **3**'s Au-Et bond at the M06/def2-TZVP/SMD(PhMe)//M06/6-31G(d)-LANL2DZ(Au) level of theory. Energies are relative to **13**.

Additionally, we have computed the α -fluoride elimination from **4** to form three-coordinate **17** (Figure 6). This process is highly unfavorable with an activation barrier of 51.0 kcal·mol⁻¹ (TS-2') due to the high endergonicity to form **17** (47.2 kcal·mol⁻¹). The DFT results are consistent with our hypothesis that Au(I)'s strong preference for linear geometry suppresses α -fluoride elimination. The [1+2] cycloaddition of difluorocarbene to gold-difluorocarbene intermediate **14** to form tetrafluoroauracyclopropane [IPrAu(C₂F₄)(Et)] was also considered (Figure S4).⁴¹ However, this process is 8.5 kcal/mol less favorable than TS-1. For difluorocarbene insertion into the Au-C(*sp*²) bond of IPrAuPh (**5**) (Figure S4), our calculations indicate that this reaction takes place *via* a similar 1,1-migratory insertion mechanism with a low activation barrier for the carbene insertion (16.1 kcal·mol⁻¹ with respect to **5**) and a very high barrier for the α -fluoride elimination (44.7 kcal·mol⁻¹).

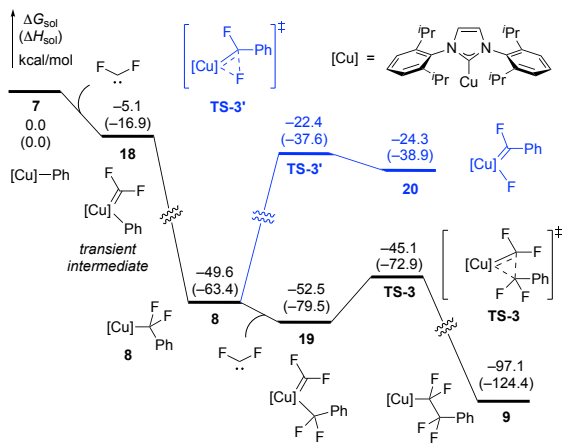


Figure 8. Computed reaction energy profile for difluorocarbene insertion into Cu-C(*sp*²) bond of IPrCuPh (**7**).

We then performed DFT calculations for difluorocarbene insertion into the Cu-C(*sp*²) bond of IPrCuPh (**7**) (Figure 8). A vdW complex between difluorocarbene carbene and **7** could not be located. Instead, the difluorocarbene directly binds to the copper center to form a transient T-shaped intermediate **18**, that is 5.1 kcal·mol⁻¹ more stable than **7**. The copper-difluorocarbene **18** undergoes rapid 1,1-migratory insertion giving IPrCuCF₂Ph product **8**. The failure to locate a transition state for the 1,1-migratory insertion, prompted the examined of Born-Oppenheimer molecular dynamics (BOMD) trajectory simulations initiated from **18** (see SI for computational details). In these simulations, the

difluorocarbene insertion product **8** is formed after an average of *ca.* 130 fs, highlighting the very short lifetime of the carbene intermediate **18**. NBO analysis indicates that the $\sigma_{\text{Cu-Ph}}$ bonding orbital in IPrCuPh (**7**) has a relatively high orbital energy of -7.4 eV, leading to the high reactivity of IPrCuPh with difluorocarbene. By contrast, the $\sigma_{\text{Au-R}}$ orbital energies are lower (-8.2, -8.8, -10.4 and eV for the Au-Et, Au-Ph, and Au-alkynyl bonds in IPrAuEt (**3**), IPrAuPh (**5**), and alkynylAu(I) complex **10**, respectively), consistent with the lower reactivity of difluorocarbene insertion to Au-C bonds. The second difluorocarbene insertion TS-3 into the Cu-CF₂Ph bond has a low activation barrier of 7.4 kcal·mol⁻¹ relative to T-shaped intermediate **19**, which is consistent with our experimental observation of both single and double insertion products (**8** and **9**). α -fluoride elimination from **8** has a barrier of 27.2 kcal·mol⁻¹ (TS-3'), which is substantially lower than α -fluoride elimination from **4** or **6**. Nonetheless, α -fluoride elimination from **8** is much less favorable than a second difluorocarbene insertion.

Finally, we investigated the competition between difluorocarbene insertion and cycloaddition pathways in reaction with alkynylAu(I) complex **10** (Figure 9). After the formation of vdW complex **21-A** and the T-shaped AuCF₂ intermediate **21-B**, difluorocarbene insertion (TS-4') requires an activation barrier of 22.4 kcal·mol⁻¹ with respect to **10**, significantly higher than those for insertion into Au-C(*sp*³) and Au-C(*sp*²) bonds in **3** and **7** ($\Delta G^\ddagger = 13.5$ and 16.1 kcal·mol⁻¹, respectively; see Figures 5 and S5). The breaking Au-C(*sp*) bond in TS-4' is shorter than the breaking Au-C(*sp*³) bond in TS-1, consistent with our hypothesis that the stronger Au-C(*sp*) bond leads to slower difluorocarbene insertion. Based on IRC calculation (Figure S7), difluorocarbene cycloaddition to the alkyne occurs through an asynchronous concerted mechanism⁴² *via* TS-4. This cycloaddition requires a 4.2 kcal·mol⁻¹ lower barrier than carbene insertion, consistent with the exclusive experimental formation of cycloaddition product **11**.

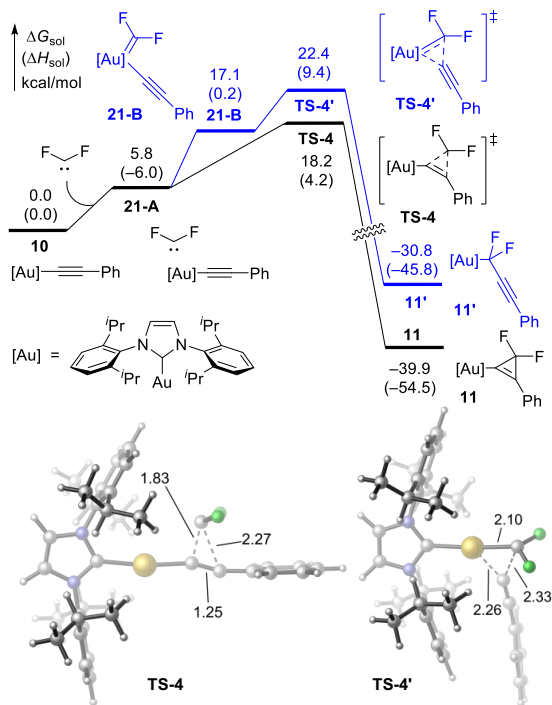


Figure 9. Computed reaction energy profiles of the difluorocarbene insertion (TS-4') and cycloaddition (TS-4) pathways with the alkynyl-Au complex **10**. Bond distances in Å.

Conclusion

The reactivities of difluorocarbene was utilized to isolate examples of three elusive classes of *gem*-difluoromethylene gold(I) and copper(I) complexes. A difluorocarbene insertion strategy enabled the formation of IPrAuCF₂H, IPrAuCF₂Et, and IPrAuCF₂Ph (**6**) through insertion of difluorocarbene into hydrido-, alkyl- and aryl-gold(I) bond, respectively. In the copper(I) system, difluorocarbene insertion into phenylcopper(I) (**7**) afforded PhCF₂Cu for the first time, indicating that ArCF₂Cu(I) synthons could be transiently generated for catalytic application. Additionally, a complementary difluorocarbene cycloaddition chemistry yielded the first difluorocyclopropenyl-transition metal complex **11**. These reactions were studied by DFT calculations, revealing difluorocarbene insertion to proceed via a 1,1-migratory insertion mechanism, and rationalizing the preference for the cycloaddition pathway of difluorocarbene with alkynylAu(I) **10**. These studies on novel fluoroalkyl-organometallics are expected to guide future developments in fluoroalkylation chemistry.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental and computational procedures and miscellaneous data (PDF)

X-ray crystal structure of **4** (CIF)
X-ray crystal structure of **6** (CIF)
X-ray crystal structure of **11** (CIF)
X-ray crystal structure of **12** (CIF)

AUTHOR INFORMATION

Corresponding Author

Peng Liu -- University of Pittsburgh, Pittsburgh, Pennsylvania 15260, United States; Email: pengliu@pitt.edu

F. Dean Toste -- University of California, Berkeley, California 94720, United States; Email: fdtoste@berkeley.edu

Authors

Zeng Rong Wong -- University of California, Berkeley, California 94720, United States.

Binh Khanh Mai -- University of Pittsburgh, Pittsburgh, Pennsylvania 15260, United States.

Willi Ragnar Berg -- Freie Universität Berlin, Berlin 14195, Germany.

Alexander Kvitsinski -- University of California, Berkeley, California 94720, United States.

Thor L. F. Correia -- University of California, Berkeley, California 94720, United States.

Yu Zhang -- University of Pittsburgh, Pittsburgh, Pennsylvania 15260, United States.

Notes

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