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The Difluoromethylated Organogold(III) Complex *cis*-[Au(PCy$_3$)(4-F-C$_6$H$_4$)(CF$_2$H)(Cl)]: Preparation, Characterization, and Its C(sp^2)–CF$_2$H Reductive Elimination

Shuanshuan Liu,[†] Kai Kang,[‡] Shihan Liu,[§] Decai Wang,[†] Ping Wei,*[,†] Yu Lan,*[,§,∥] and Qilong Shen*[,‡]

[†]Biotechnology and Pharmaceutical Engineering, Nanjing Tech University, Nanjing, Jiangsu Province 210009, People's Republic of China

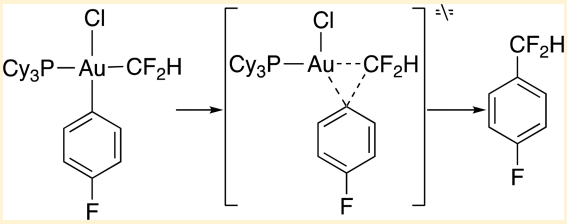
[‡]Key Laboratory of Organofluorine Chemistry, Center for Excellence in Molecular Synthesis, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Sciences, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, People's Republic of China

[§]School of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400030, People's Republic of China

[∥]College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450001, People's Republic of China

Supporting Information

ABSTRACT: The preparation of the difluoromethylated organogold(III) complex *cis*-[Au(PCy$_3$)(4-F-C$_6$H$_4$)(CF$_2$H)(Cl)] (**3**) and its Ar–CF$_2$H reductive elimination are described. In the presence of 1.0 equiv of AgSbF$_6$ or AgPF$_6$, compound **3** underwent a quantitative Ar–CF$_2$H reductive elimination in less than 1.0 min at 25 °C, while the lack of silver salt resulted in Ar–CF$_2$H reductive elimination from complex **3** in 1,1,2,2-tetrachloroethane (CCl$_2$HCCl$_2$H) after 80 min at 115 °C to afford the elimination product *p*-F-PhCF$_2$H (**4**) and (Cy$_3$P)Au(Cl) in quantitative yields. On the basis of the mechanistic studies of the kinetics of the reaction and DFT calculation, a concerted Ar–CF$_2$H bond-forming pathway for the Ar–CF$_2$H reductive elimination from organogold(III) complex **3** is proposed.



INTRODUCTION

Due to their exceptional properties that may bring favorable changes in the molecule's performance, fluoroalkyl groups including trifluoromethyl (−CF$_3$), difluoromethyl (−CF$_2$H), and trifluoromethylthio (−SCF$_3$) have attracted substantial interest from the pharmaceutical/agrochemical industry as well as academia.[1] Consequently, numerous efforts from many teams around the world have resulted in the development of a variety of efficient methods for the strategic incorporation of these functional groups.[2] One general approach accessing the fluoroalkylated compounds involves the tranistion-metal-mediated/-catalyzed fluoroalkylation of the corresponding substrates under mild conditions.[3,4] Despite this widespread interest, the fundamental organometallic chemistry of the transition-metal-catalyzed fluoroalkylation reactions is much less developed than that of hydrocarbons.[5−9] In particular, reports of isolated complexes bearing the difluoromethyl group, which is considered as a biostere of a hydroxy or thiol group[10] in drug molecule design, are rare[11] and very few elementary reactions of difluoromethylated transition-metal complexes have been reported previously. To the best of our knowledge, the only report for Ar–CF$_2$H reductive elimination from a well-characterized [(DPPF)Pd(Ar)(CF$_2$H)] complex was reported previously by Shen's group,[12] which shed light on the understanding of the fundamentals of the Ar–CF$_2$H bond-forming process. Nevertheless, the preparation of difluoromethylated transition-metal complexes and studies of their elementary reactions are still imperatively needed.

Herein, we report the preparation of the stable difluoromethylated gold(III) complex *cis*-[Au(PCy$_3$)(4-F-C$_6$H$_4$)(CF$_2$H)(Cl)] (**3**) and its Ar–CF$_2$H bond-forming reductive elimination in 1,1,2,2-tetrachloroethane in the absence and presence of silver salt.[13,14] In the presence of 1.0 equiv of AgSbF$_6$ or AgPF$_6$, which is presumably to abstract the chloride, complex **3** underwent a quantitative Ar–CF$_2$H reductive elimination in less than 1.0 min at 25 °C. In the absence of silver salt, Ar–CF$_2$H reductive elimiantion from complex **3** in 1,1,2,2-tetrachloroethane (CCl$_2$HCCl$_2$H) occurred after 80 min at 115 °C to afford the elimination product *p*-F-PhCF$_2$H (**4**) and (Cy$_3$P)Au(Cl) in quantitative yields. Kinetic studies and investigation on the effects of the temperature and added free phosphine ligand and chloride, as well as DFT calculations, let us conclude that a concerted carbon–carbon bond-forming pathway is preferred for the Ar–CF$_2$H reductive elimination from *cis*-[Au(PCy$_3$)(4-F-C$_6$H$_4$)(CF$_2$H)(Cl)] (**3**),

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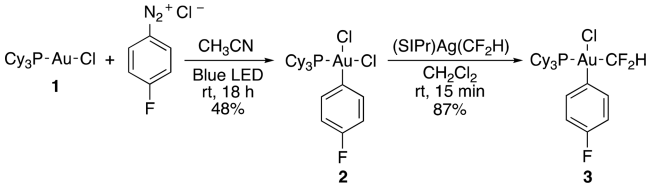
which differed significantly from the mechanism for Ar−CF_3 reductive elimination from the trifluoromethylated complex *cis*-[Au(PPh_3)(4-F-C_6H_4)(CF_3)(Cl)] that was proposed to proceed via a phosphine ligand dissociation pathway.

RESULTS AND DISCUSSION

Preparation of *cis*-[Au(PCy_3)(4-F-C_6H_4)(CF_2H)(Cl)] (3) and Its X-ray Structure. The difluoromethylated organogold(III) complex *cis*-[Au(PCy_3)(4-F-C_6H_4)(CF_2H)(Cl)] **3** was prepared via a two-step process from the readily available starting material [(Cy_3P)AuCl] (**1**), as shown in Scheme 1. Initially, *cis*-[Au(PCy_3)(4-F-C_6H_4)Cl_2] (**2**) was

Scheme 1. Synthesis of Difluoromethylgold(III) Complexes 3



prepared in 48% yield by oxidative addition of 4-fluorobenzenediazonium chloride to [(Cy_3P)Au(Cl)] in CH_3CN at 25 °C under irradiation of blue LED light, following the general procedure developed by Hashmi.[15] Treatment of a solution of complex **2** in dichloromethane with 1.5 equiv of (SIPr)Ag(CF_2H) (SIPr = 1,3-bis(2,6-diisopropylphenylimidazolin-2-ylidene),[12,16] gave the difluoromethylated gold(III) complex *cis*-[Au(PCy_3)(4-F-C_6H_4)(CF_2H)(Cl)] (**3**) after 15 min at room temperature in 87% yield. Complex **3** is a shelf-stable, air- and moisture-insensitive white crystalline solid that could be purified by column chromatography.

In general, the trans influence of a phosphine ligand is stronger than that of an aryl group.[17] Therefore, the gold−chloro bond trans to a phosphine ligand in *cis*-[Au(PCy_3)(4-F-C_6H_4)Cl_2] (**2**) is more easily transmetalated than the gold−chloro bond trans to an aryl group. As a result, complex **3** is thought to have a cis configuration. The NMR spectra of complex **3** are consistent with the proposed structure. For example, there is a peak at 6.68 ppm (triplet of doublets with coupling constants J = 52.0 and 20.0 Hz, respectively) in the ^{1}H NMR spectrum and a triplet peak at −97.61 ppm with the coupling constant J = 50.8 Hz in the ^{19}F NMR spectrum, which represent two characteristic splitting patterns for a difluoromethyl group. In addition, the peak in the proton NMR spectrum shows a doublet with the coupling constant J = 20.0 Hz, which indicates that the difluoromethyl group is *trans* to PCy_3 in complex **3**, as shown in Figure 1A.

Single crystals of complex **3** were obtained by diffusion of *n*-pentane vapors into a CH_2Cl_2 solution of complex **3**, and its X-ray structure is shown in Figure 1B. Likewise, its trifluoromethylated analogue *cis*-[Au(PCy_3)(4-F-C_6H_4)(CF_3)(Cl)] (**3a**) was synthesized following a similar procedure, and its single-crystal structure is shown in Figure 1C. In both complexes, the phosphines are located trans to the difluoromethyl or trifluoromethyl group. As found in Table 1, the sums of the four bond angles surrounding the gold metal center in complexes **3** and **3a** are 360.08 and 359.97°, respectively, which is consistent with the NMR data which suggest that the configuration of complexes **3** and **3a** is square planar. The Au−C(Ar) and Au−C(CF_3) bond distances in *cis*-[Au(PCy_3)(4-F-C_6H_4)(CF_3)(Cl)] (**3a**) are longer than the Au−C(Ar) and Au−C(CF_2H) bond distances in *cis*-[Au(PCy_3)(4-F-C_6H_4)(CF_2H)(Cl)] (**3**), presumably because the trifluoromethyl group is more sterically hindered than the difluoromethyl group.

C(sp^2)−CF_2H Bond Reductive Elimination. Having successfully synthesized stable difluoromethylated organogold(III) complex **3**, we then studied its Ar−CF_2H reductive elimination in the presence/absence of silver salt. Addition of 1.0 equiv of $AgSbF_6$ or $AgPF_6$ to a solution of complex **3** in 1,1,2,2-tetrachloroethane (CCl_2HCCl_2H) resulted in an immediate reductive elimination to give *p*-F-PhCF_2H (**4**) in quantitative yield (Scheme 2). Presumably, the cationic Y-shaped intermediate [Au(PCy_3)(4-F-C_6H_4)(CF_2H)] is formed, which undergoes a fast reductive elimination to give compound **4**. In the absence of silver salt, complex **3** is stable in 1,1,2,2-tetrachloroethane at room temperature and the formation of reductive elimination product **4** was not observed. On the other hand, full conversion of complex **3** and the quantitative formation of the elimination product *p*-F-PhCF_2H

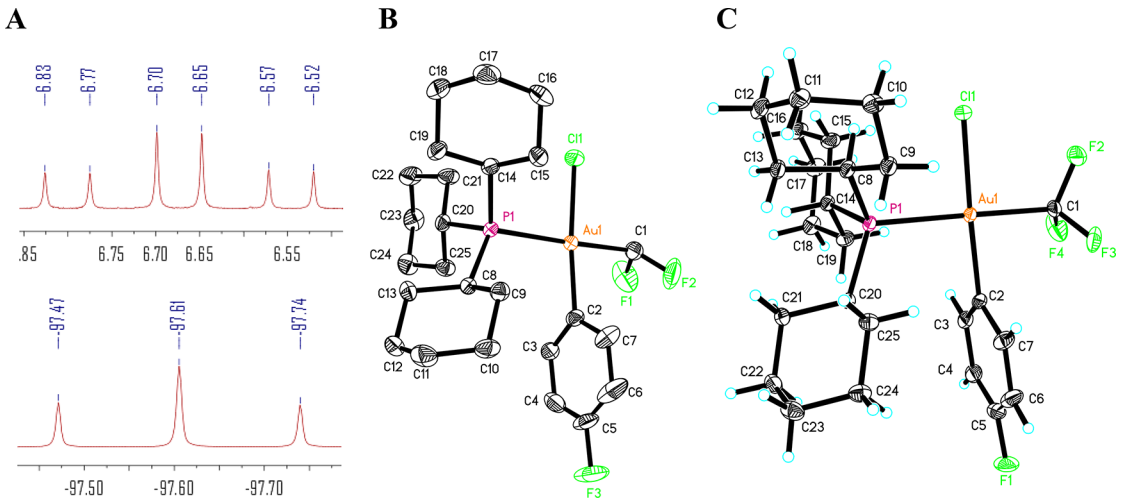


Figure 1. (A) ^{1}H (top) and ^{19}F NMR (bottom) spectra for the difluoromethyl group of complex **3** ($CDCl_3$, 298 K, 400 MHz). (B) ORTEP diagram of complex **3**. (C) ORTEP diagram of complex **3a**. Thermal ellipsoids are shown at the 50% probability level.

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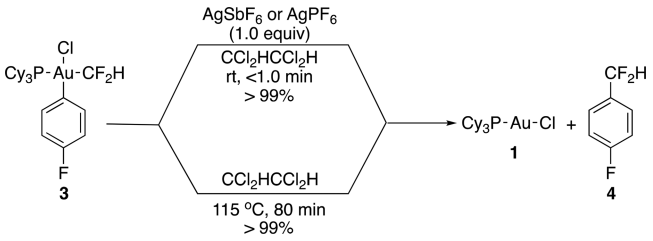
Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for Complexes 3 and 3a

cis-[Au(PCy_3)(4-F-C_6H_4)(CF_2H)(Cl)] (**3**)				*cis*-[Au(PCy_3)(4-F-C_6H_4)(CF_3)(Cl)] (**3a**)			
bond distance (Å)		bond angles (deg)		bond distance (Å)		bond angle (deg)	
Au−C(CF_2H)	2.071(4)	Cl−Au−C(CF_2H)	87.17(13)	Au−C(CF_3)	2.093(5)	Cl−Au−C(CF_3)	92.18(15)
Au−C(Ar)	2.020(4)	C(CF_2H)−Au−C(Ar)	87.36(16)	Au−C(Ar)	2.048(5)	C(CF_3)−Au−C(Ar)	85.1(2)
Au−P	2.3964(9)	C(Ar)−Au−P	95.57(10)	Au−P	2.3855(12)	C(Ar)−Au−P	93.74(14)
Au−Cl	2.3459(10)	P−Au−Cl	89.98(3)	Au−Cl	2.3487(13)	P−Au−Cl	88.95(4)
C(CF_2H)−F(1)	1.337(5)	F(2)−C(CF_2H)−F(1)	105.0(4)	C(CF_3)−F(1)	1.343(6)	F(2)−C(CF_3)−F(3)	103.7(4)
C(CF_2H)−F(2)	1.328(5)	H−C(CF_2H)−F(2)	103(2)	C(CF_3)−F(2)	1.337(6)	F(2)−C(CF_3)−F(4)	104.6(5)
C(CF_2H)−H	1.00(4)	H−C(CF_2H)−F(1)	111.7(3)	C(CF_3)−F(3)	1.343(6)	F(3)−C(CF_3)−F(4)	105.7(4)

Scheme 2. Reductive Elimination from Complex 3 in $CHCl_2CCl_2H$ in the Presence or Absence of Silver Salt



(**4**) and (Cy_3P)Au(Cl) was observed after 80 min at 115 °C in 1,1,2,2-tetrachloroethane (CCl_2HCCl_2H) (Scheme 2). The yields for the formation of the compound **4** in other solvents were much lower. For example, thermolysis of complex **3** in solvents such as diglyme, acetonitrile, DMF, and DMSO occurred to roughly 90% conversion after 2.0 h at 120 °C for 2 h to to give compound **4** in 39%, 50%, 62%, and 64% yields, respectively.

To gain some insight into the thermal reductive elimination process, we investigated the kinetics of the Ar−CF_2H bond-forming process from complex **3**. Experimentally, a solution of complex **3** with the internal standard 1-fluoronaphthalene in

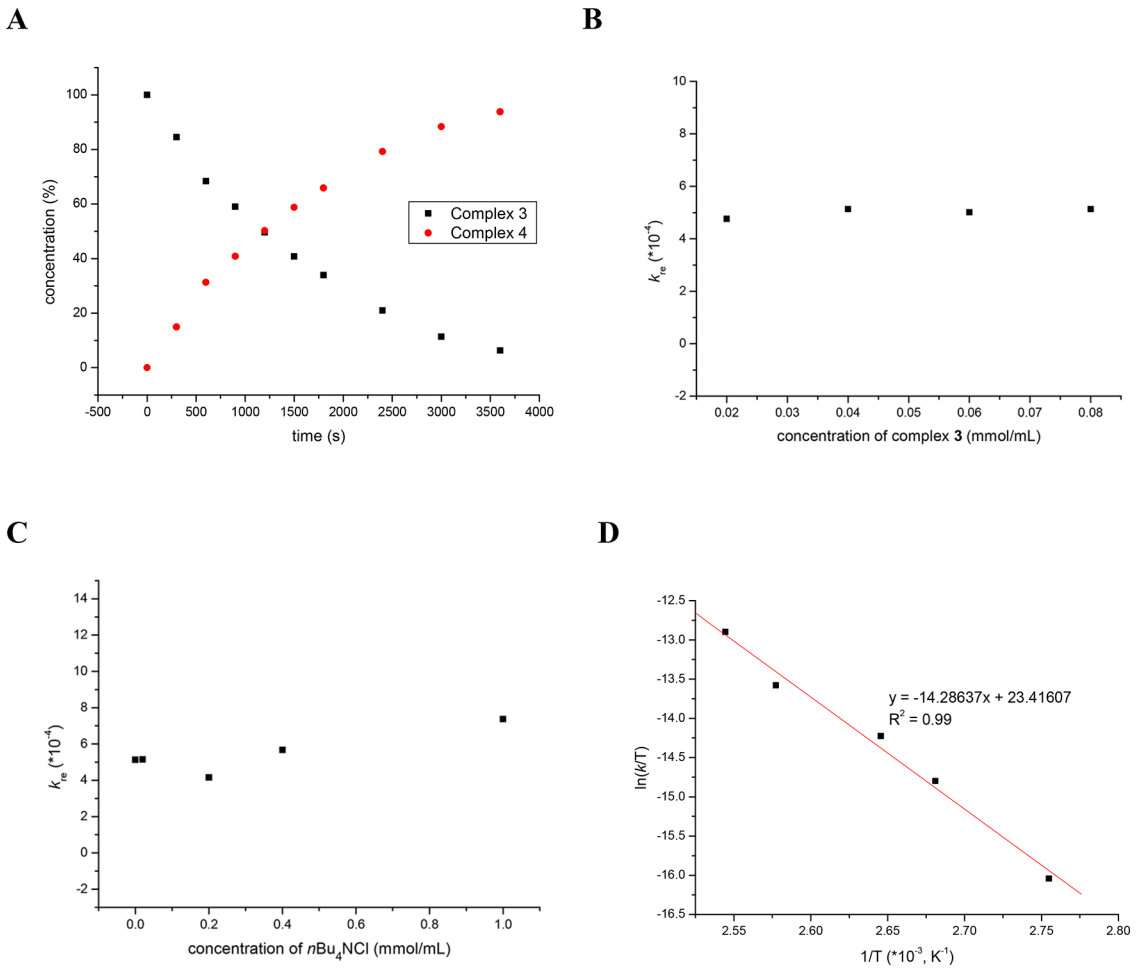


Figure 2. (A) Thermolysis of complex **3** in CCl_2HCCl_2H at 115 °C and the kinetic profile of the product complex **4**. (B) Rate constant of reductive elimination of complex **3** in CCl_2HCCl_2H at different initial concentration at 115 °C. (C) Effect of the concentration of nBu_4NCl on reductive elimination of complex **3**. (D) Eyring plot for the thermolysis of complex **3** over the temperature range 90−120 °C in CCl_2HCCl_2H.

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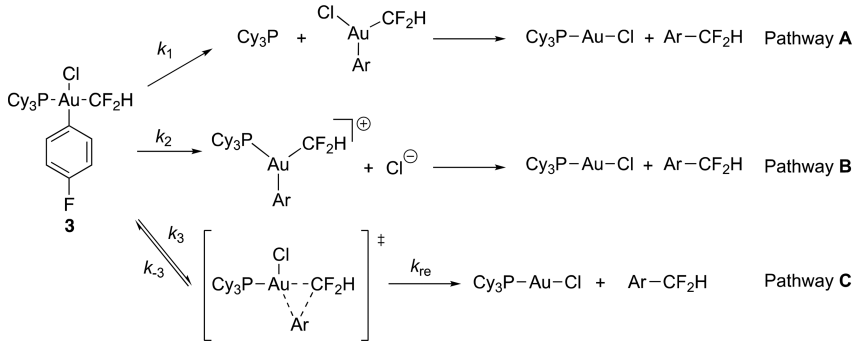
Scheme 3. Possible Pathways for the Ar−CF_2H Reductive Elimination from Complex 3



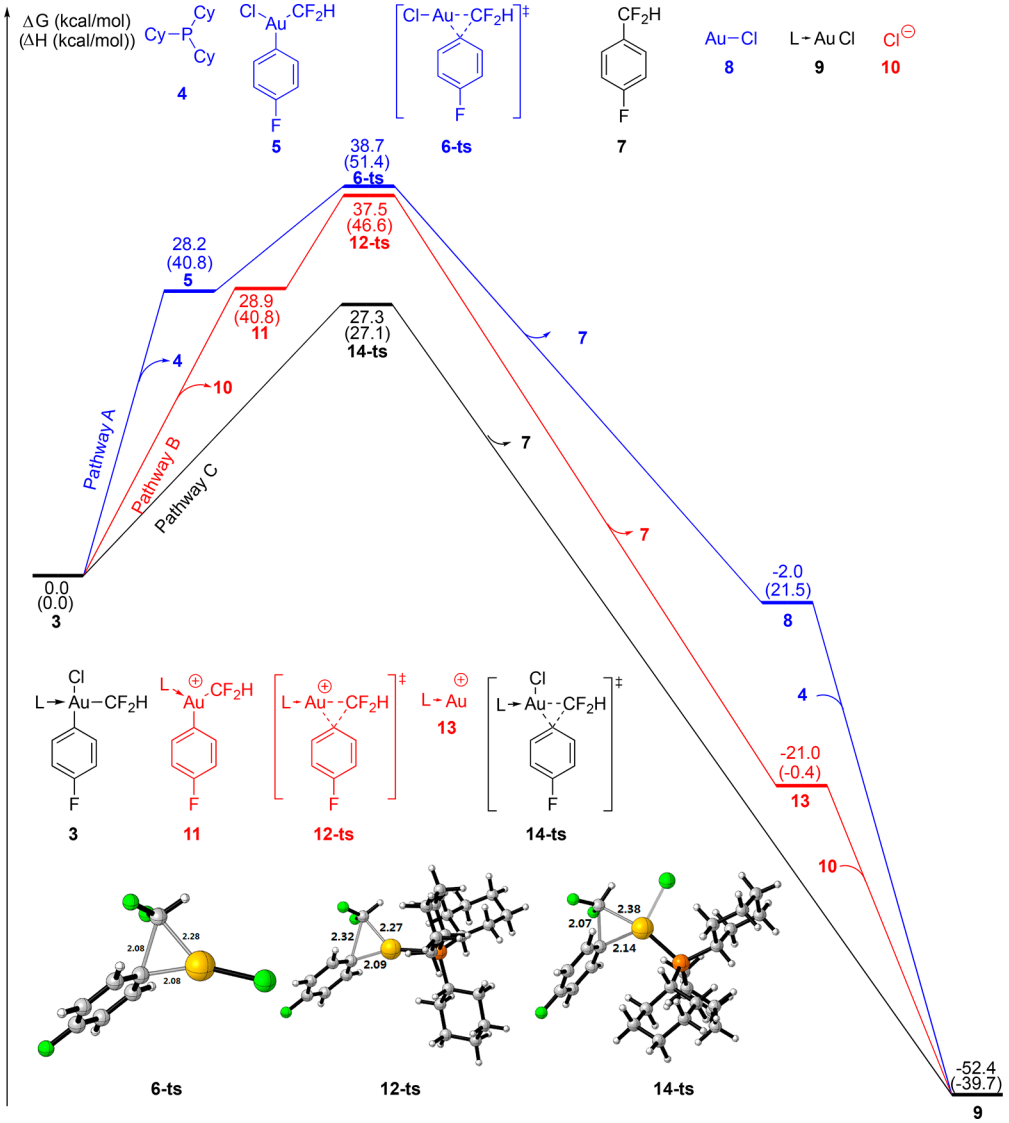


Figure 3. Calculated activation free energies for the Ar−CF_2H reductive elimination of *cis*-[Au(PCy_3)(4-F-C_6H_4)(CF_2H)(Cl)] (**3**). Optimized structures for all the transition states are shown. Selected bond distances (Å) are provided.

1,1,2,2-tetrachloroethane was placed in a NMR tube. The solution was heated at 115 ± 0.1 °C, and periodically, a ^{19}F NMR spectrum of the reaction mixture was acquired. The change in concentration of complex **3** vs time was then plotted, and it showed that the decay of the concentration followed first-order kinetics (Figure 2A). Further studies showed that the rate constants did not change with different initial concentrations of complex **3** (Figure 2B), consistent with the first-order kinetic behavior of the reductive elimination process.

Previously, Komiya reported that the rate of the C(sp^2)−CH_3 bond-forming process from complexes *cis*-[(Ar_3P)Au-$(Me)_2$(Ar)] was significantly suppressed by the addition of even a small amount of free tertiary phosphine.[18] Likewise,

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Toste reported that the addition of small amount of free phosphine ligand inhibited the C(sp^2)−CF_3 bond-forming process from the complex [$(Ph_3P)Au(4\text{-F-}C_6H_4)(CF_3)(I)$].[19] In both cases, a ligand dissociation pathway was proposed for these reductive elimination processes. To probe whether Ar−CF_2H reductive elimination from complex **3** proceeds via a similar ligand dissociation pathway (Scheme 3), we studied the reaction in the presence/absence of 1.0 equiv of PCy_3 at 115 °C. As shown in Figure 2A, reaction in the presence of 1.0 equiv of PCy_3 occurred to full conversion after 80 min to generate *p*-F-PhCF_2H in 78% yield and the unidentified side product with chemical shifts at −85.43 and −76.97 ppm in ^{19}F NMR spectroscopy in 18% yield. Nevertheless, kinetic studies disclosed that the reaction in the presence of PCy_3 followed the first-order decay. Interestingly, the rate was 1.36 times faster than that in the absence of phosphine ligand (6.99×10^{-4} vs 5.13×10^{-4} s^{-1}, respectively). These results differed greatly from the previous observations by Komiya and Toste for the reductive elimination from [$(Ar_3P)Au(Me)_2(Ar)$] or [$(Ph_3P)Au(4\text{-F-}C_6H_4)(CF_3)(I)$], thus clearly ruling out the phosphine ligand dissociation pathway (pathway A in Scheme 3).

An alternative mechanistic pathway for the Ar−CF_2H bond-forming process from complex **3** would be a rate-determining chloride dissociation to form the Y-shaped ionic species [$Au(PCy_3)(4\text{-F-}C_6H_4)(CF_2H)]^+$, followed by a fast Ar−$CF_2H$ bond-forming elimination from this intermediate (pathway B in Scheme 3). If this is the case, addition of a small amount of *n*-Bu_4NCl would significantly retard the reductive elimination process. Experimentally, thermolysis of complex **3** with 0.01−0.5 equiv of *n*-Bu_4NCl in 1,1,2,2-tetrachloroethane at 115 °C for 80 min gave the elimination product in 73−99% yield and an unknown side product with a chemical shift at −90.69 ppm in ^{19}F NMR spectroscopy in 1−24% yields. Kinetic studies showed the rate constants changed slightly with the increase of the amount of *n*-Bu_4NCl, even though the magnitude of difference is small (Figure 2C). More specifically, the reaction was 1.4 times slower when it conducted in absence of *n*-Bu_4NCl than that with *n*-Bu_4NCl (5.13×10^{-4} s^{-1}vs 7.37×10^{-4} s^{-1}, respectively). Thus, it is clear that the addition of *n*-Bu_4NCl did not inhibit the Ar−CF_2H bond forming process and the increase in the rate constant in the presence of *n*-Bu_4NCl might due to a kinetic salt effect. Overall, these results suggest a chloride dissociation pathway for Ar−CF_2H bond-forming process from complex **3** is unlikely (pathway B in Scheme 3).

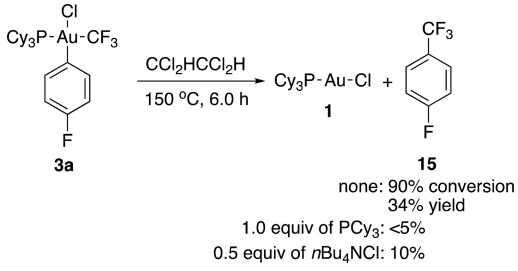
To further elucidate the mechanism of the process, we studied the effect of reaction temperature on the reaction of complex **3**. Experimentally, we investigated the kinetics of the Ar−CF_2H bond-forming process at a temperature from 90 to 120 °C. These results revealed that the rates constants were linearly dependent on the reaction temperature, as shown in Figure 2D. The activation parameters of $\Delta H^{\ddagger} = 28.40 \pm 1.86$ kcal/mol and $\Delta S^{\ddagger} = -0.68 \pm 0.07$ eu were then extracted, and the small negative entropy change suggests a pathway that involves a rate-determining phosphine ligand dissociation or chloride dissociation followed by a fast Ar−CF_2H reductive elimination from the three-coordinated intermediate is highly unlikely. Instead, the observed experimental results indicate that reductive elimination might proceed via a direct carbon−carbon bond-forming pathway involving a three-centered transition state (pathway C in Scheme 3).

Computational Investigation. To further deepen our understanding of the Ar−CF_2H reductive elimination from complex **3**, we conducted density functional theory (DFT) calculations of three possible pathways shown in Scheme 3. *cis*-[$Au(PCy_3)(4\text{-F-}C_6H_4)(CF_2H)(Cl)$] (**3**) was chosen as a starting point, and the free energy profiles of three pathways are shown in Figure 3. It was found that, in pathway A, the dissociation of the tricyclohexylphosphine from complex **3** is an endothermic process (28.2 kcal/mol), while reduction elimination of the resulting tricoordinated intermediate **4** via the three-membered-ring transition state **6-ts** requires overcoming an additional barrier of 10.5 kcal/mol. Overall, the total energy barrier of pathway A (38.7 kcal/mol) is 11.4 kcal/mol greater than that of pathway C, suggesting that pathway A is unfavorable. Likewise, in path B, the dissociation of chloride from complex **3** requires overcoming a barrier of 28.9 kcal/mol, while the barrier for the Ar−CF_2H bond-forming process from the resulting cationic tricoodinated intermediate **11** via the three-membered-ring transition state **12-ts** is 8.6 kcal/mol. The activation energy barrier of pathway B is 10.2 kcal/mol greater than that from pathway C (37.5 kcal/mol vs 27.3 kcal/mol), which rules out a chloride dissociation pathway. Overall, DFT calculations also support that the Ar−CF_2H bond-forming process from complex **3** proceeds via a classic concerted pathway with the three-membered-ring transition state **14-ts**, as illustrated in pathway C in Scheme 3.

Comparison with C(sp^2)−CF_3 Reductive Elimination from Complex 3a. Interestingly, the proposed concerted Ar−CF_2H bond-forming process from complex **3** is different from that for the Ar−CF_3 bond-forming process from the analogous trifluoromethylated complex [$(Ph_3P)Au(4\text{-F-}C_6H_4)(CF_3)(I)$], where a mechanism of rate-limiting phosphine dissociation and then elimination from the resulting Y-shaped cationic complex was proposed by Toste and co-workers.[19]

As a comparison, we prepared the trifluoromethyl-substituted organogold(III) complex *cis*-[$Au(PCy_3)(4\text{-F-}C_6H_4)(CF_3)(Cl)$] (**3a**), which bears an phosphine ligand (PCy_3) identical with that of complex **3** and studied its C(sp^2)−CF_3 reductive elimination. As shown in Scheme 4, thermolysis of a solution of complex **3a** in 1,1,2,2-tetrachloroethane (CCl_2HCCl_2H) occurred in >90% conversion after 6.0 h at 150 °C to generate *p*-F-PhCF_3 (**15**) in 34% yield, while the formation of *p*-F-PhCl was not observed, as monitored by GC-MS and ^{19}F NMR spectroscopy. In addition, the yield decreased significantly to less than 10% upon addition of 1.0 equiv of tricyclohexylphosphine or *n*Bu_4NCl. These experimental results suggest that reductive elimination from trifluoromethylated complex **3a** is significantly slower than that from difluoromethylated complex **3** and the underlying

Scheme 4. Thermolysis of Complex 3a in CCl_2HCCl_2H at 150 °C



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mechanisms for the two carbon−carbon reductive elimination processes might be different. A comparison of the X-ray structures of complexes **3** and **3a** showed that the Au−C(Ar) and Au−C(CF_3) bond distances in complex **3a** are 0.028 and 0.022 Å, respectively, longer than the Au−C(Ar) and Au−C(CF_2H) bond distances in complex **3**. The longer Au−C(Ar) and Au−C(CF_3) bond distances in complex **3a** suggest that the formation of the three-membered-ring transition state is much more difficult than that from complex **3**, even though a detailed mechanism for the Ar−CF_3 bond-forming process from complex **3a** is unclear at this stage.

CONCLUSION

In summary, we have systematically studied the Ar−CF_2H bond-forming reductive elimination from the PCy_3-ligated difluoromethylated organogold(III) complex *cis*-[Au(PCy_3)(4-F-C_6H_4)(CF_2H)(Cl)] (**3**). These investigations suggest that the Ar−CF_2H bond-forming process proceeds through a classic concerted pathway with a three-membered-ring transition state. A comparative study of thermolysis of its analogous trifluoromethyl-substituted organogold(III) complex *cis*-[Au(PCy_3)(4-F-C_6H_4)(CF_3)(Cl)] (**3a**) disclosed that Ar−CF_3 reductive elimination from the trifluoromethylated complex **3a** is significantly slower than that from the difluoromethylated complex **3** and the underlying mechanisms for the two carbon−carbon reductive elimination processes differ greatly.

EXPERIMENTAL SECTION

General Information. All glassware was oven or flame-dried immediately prior to use. Solvents were freshly degassed according to the procedures in *Purification of Laboratory Chemicals* prior to use. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc., and were degassed and stored over activated 4 Å molecular sieves. Unless otherwise noted, all other reagents and starting materials were purchased from commercial sources and used without further purification. The ^{1}H, ^{19}F, ^{31}P, and ^{13}C NMR spectra were obtained at 293 K on a 400 or 500 MHz spectrometer, and chemical shifts were recorded relative to the solvent resonance. ^{19}F shifts were determined relative to $CFCl_3$ as an outside standard, and low field is positive. Coupling constants are reported in hertz. The following abbreviations were used to explain the multiplicities: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br = broad.

Preparation of *cis*-[Au(PCy_3)(4-F-C_6H_4)$(Cl)_2$] (2). *cis*-[Au(PCy_3)(4-F-C_6H_4)$(Cl)_2$] (**2**) was synthesized by oxidative addition of 4-fluorobenzenediazonium chloride to [(Cy_3P)Au(Cl)] in CH_3CN at room temperature under blue LED irradiation, following a procedure developed by the Hashmi group. 4-Fluoroaniline (44.4 mg, 0.400 mmol) and acetonitrile (0.4 mL) were placed in a Schlenk tube equipped with a magnetic stir bar. A solution of concentrated HCl (60 mg, 0.60 mmol) in CH_3CN (0.4 mL) was added at 0 °C, and the mixture was stirred for 5 min. ^{t}BuONO (60 μL, 0.44 mmol) was added dropwise. The mixture was stirred for another 15 min at 0 °C. The resulting mixture was then frozen with liquid nitrogen and Cy_3PAuCl (102 mg, 0.200 mmol) was added. The mixture was degassed with freeze−pump−thaw for three cycles and was then irradiated with blue LEDs for 18 h at room temperature. A 10 mL portion of diethyl ether was added, and the precipitate were filtered as a white solid (50 mg, 48%). ^{1}H NMR (400 MHz, chloroform-*d*): δ 7.28 (dd, *J* = 8.5, 5.5 Hz, 2 H), 6.94 (t, *J* = 8.7 Hz, 2 H), 2.48 (d, *J* = 12.2 Hz, 3 H), 1.92 (t, *J* = 9.2 Hz, 6 H), 1.85−1.77 (m, 6 H), 1.68 (dtd, *J* = 13.7, 9.7, 9.3, 5.1 Hz, 9 H), 1.24 (dt, *J* = 13.2, 3.7 Hz, 3 H), 1.13−1.01 (m, 6 H). ^{19}F NMR (376 MHz, $CDCl_3$, 298 K): δ −103.61 to −135.72 (m, 1 F). ^{31}P NMR (162 MHz, $CDCl_3$, 298 K): δ 29.20 ppm.

Preparation of *cis*-[Au(PCy_3)(4-F-C_6H_4)(CF_2H)(Cl)] (3). In a glovebox, *cis*-[Au(PCy_3)(4-F-C_6H_4)$(Cl)_2$] (**2**; 320 mg, 0.486 mmol, 1.00 equiv) and (SIPr)Ag(CF_2H)[2] (399 mg, 0.729 mmol, 1.50 equiv) were placed in a 10 mL Schlenk tube that was equipped with a stirrer. Then 4.0 mL of freshly distilled CH_2Cl_2 was added and the reaction mixture was stirred at room temperature for 15 min. The mixture was then filtered through a short plug of Celite. The solvent was removed under vacuum. The residue was purified by flash chromatography on silica gel (*n*-pentane/dichloromethane = 5/1 to 3/1) to give *cis*-[Au(PCy_3)(4-F-C_6H_4)(CF_2H)(Cl)] (**3**) as a white solid (278 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, TMS): δ 7.34−7.26 (m, 2 H), 6.99−6.86 (m, 2 H), 6.84−6.50 (m, 1 H), 2.19 (d, *J* = 12.3 Hz, 3 H), 1.80 (dt, *J* = 14.3, 7.6 Hz, 12 H), 1.72−1.64 (m, 3 H), 1.52 (dt, *J* = 12.7, 3.5 Hz, 6 H), 1.28−1.19(m, 3 H), 1.19−0.93 (m, 6 H). ^{19}F NMR (376 MHz, $CDCl_3$, 298 K): δ −97.61 (t, *J* = 50.5 Hz), −117.58 (ddd, *J* = 8.8, 6.1, 2.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$, 298 K): δ 29.19 (t, *J* = 49.4 Hz) ppm. Anal. Calcd for $C_{25}H_{38}AuClF_3P$: C, 45.57; H, 5.81. Found: C, 45.56; H, 5.83.

Preparation of *cis*-[Au(PCy_3)(4-F-C_6H_4)(CF_3)(Cl)] (3a). In a glovebox, AgF (40 mg, 0.31 mmol), $TMSCF_3$ (92 μL, 0.62 mmol), and MeCN (2.0 mL) were placed in a 4 mL Schlenk tube that was equipped with a stirring bar. The reaction mixture was stirred in the dark for 3 h. The complex *cis*-[Au(PCy_3)(4-F-C_6H_4)$(Cl)_2$] (**2**; 200 mg, 0.310 mmol) was added, and the reaction mixture was stirred at room temperature in the dark for 12 h. The mixture was then filtered through a short plug of Celite. The solvent was removed under vacuum. The residue was purified by flash chromatography on silica gel (*n*-pentane/dichloromethane = 5/1) to give the complex *cis*-[Au(PCy_3)(4-F-C_6H_4)(CF_3)(Cl)] (**3a**) as a white solid (162 mg, 77%). ^{1}H NMR (400 MHz, chloroform-*d*): δ 7.24 (dd, *J* = 8.2, 6.1 Hz, 2 H), 6.98 (dd, *J* = 10.2, 7.8 Hz, 2 H), 5.32 (s, 2 H), 2.18 (dd, *J* = 13.6, 10.7 Hz, 3 H), 1.85 (dd, *J* = 10.9, 5.9 Hz, 12 H), 1.79−1.68 (m, 3 H), 1.54 (dtd, *J* = 12.8, 9.6, 9.1, 3.5 Hz, 6 H), 1.35−1.19 (m, 3 H), 1.18−1.01 (m, 6 H). ^{19}F NMR (376 MHz, $CDCl_3$, 298 K): δ −32.19 (d, *J* = 65.2 Hz), −116.65 (m, 1 F). ^{31}P NMR (162 MHz, $CDCl_3$, 298 K): δ 28.43 (q, *J* = 64.7 Hz) ppm. Anal. Calcd for $C_{25}H_{37}AuClF_4P$: C, 44.36; H, 5.51. Found: C, 44.19; H, 5.38.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00579.

X-ray diffraction data of complexes **3** and **3a**, data for kinetics, and DFT calculation of Ar−CF_2H bond formation from complex **3** (PDF)

Accession Codes

CCDC 1848595−1848596 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Authors

*E-mail for P.W.: weiping@njtech.edu.cn.
*E-mail for Y.L.: lanyu@cqu.edu.cn.
*E-mail for Q.S.: shenql@sioc.ac.cn.

ORCID

Yu Lan: 0000-0002-2328-0020
Qilong Shen: 0000-0001-5622-153X

Notes

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