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Photoinitiated Oxidative Addition of CF_3I to Gold(I) and Facile Aryl-CF_3 Reductive Elimination

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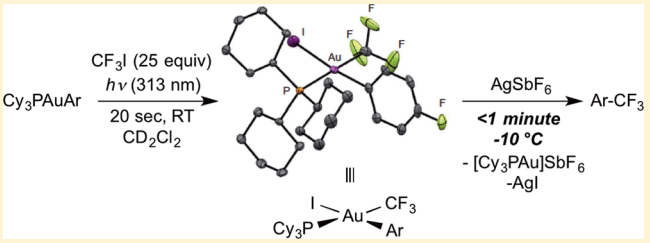
Supporting Information

ABSTRACT: Herein we report the mechanism of oxidative addition of CF_3I to Au(I), and remarkably fast C_{aryl}–CF_3 bond reductive elimination from Au(III) cations. CF_3I undergoes a fast, formal oxidative addition to R_3PAuR' (R = Cy, R′ = 3,5-F_2-C_6H_4, 4-F-C_6H_4, C_6H_5, 4-Me-C_6H_4, 4-MeO-C_6H_4, Me; R = Ph, R′ = 4-F-C_6H_4, 4-Me-C_6H_4). When R′ = aryl, complexes of the type $R_3PAu(aryl)(CF_3)I$ can be isolated and characterized. Mechanistic studies suggest that near-ultraviolet light (λ_{max} = 313 nm) photoinitiates a radical chain reaction by exciting CF_3I. Complexes supported by PPh_3 undergo reversible phosphine dissociation at 110 °C to generate a three-coordinate intermediate that undergoes slow reductive elimination. These processes are quantitative and heavily favor C_{aryl}–I reductive elimination over C_{aryl}–CF_3 reductive elimination. Silver-mediated halide abstraction from all complexes of the type $R_3PAu(aryl)(CF_3)I$ results in quantitative formation of Ar–CF_3 in less than 1 min at temperatures as low as −10 °C.



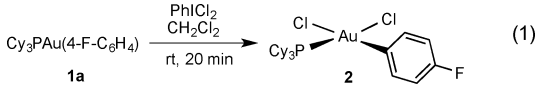
INTRODUCTION

Reports of organogold complexes undergoing redox processes are typically limited to slow oxidative additions and reductive eliminations.[1,2] However, organogold complexes are not necessarily unreactive; we recently showed that diaryl Au(III) complexes undergo remarkably fast aryl–aryl reductive elimination at temperatures as low as −50 °C.[3] These recent findings from our group, as well those established by Vicente,[4] Hashmi,[5] and Lloyd-Jones,[6] suggest that the barrier for challenging reductive eliminations might be substantially diminished at Au(III). C_{aryl}–CF_3 bond reductive elimination is typically a slow process requiring elevated temperatures and long reaction times, due to ground state stabilization afforded by exceptionally strong bonding between transition metals and CF_3 ligands.[7] For instance, (dppbz)Pd(2-Me-C_6H_4)(CF_3) (dppbz = 1,2-bis(diphenylphosphino)benzene) is stable at 130 °C for 3 days,[8] while (dppp)Pd(Ph)(CF_3) (dppp = 1,3-diphenylphosphinopropane) and (dppe)Pd(Ph)(CF_3) (dppe = 1,2-diphenylphosphinoethane) yield only 10% $PhCF_3$ after 3 days at 145 °C.[9] Reductive eliminations at temperatures between 50 and 80 °C can be achieved at Pd(II) by employing bulky ligands, such as Xantphos[10] and Brettphos.[11] Notably, while aryl-CF_3 reductive eliminations from Pd(IV) often require similarly high temperatures,[12a] Sanford has shown that they can occur at temperatures as low as 23 °C over 1 h.[12b] Despite advances in catalytic trifluoromethylation, C_{aryl}–CF_3 reductive elimination still remains a challenging step. Given the importance of trifluoromethylated arenes in pharmaceuticals and agrochemicals,[13] we were prompted to investigate potentially low-barrier C_{aryl}–CF_3 bond reductive elimination at Au(III).

To access complexes of the type $R_3PAu(aryl)(CF_3)I$, we were drawn to Puddephatt's report of the oxidative addition of CF_3I to Me_3PAuMe to afford *cis*/*trans* mixtures of $Me_3PAuMe_2(CF_3)$ and Me_3PAuI.[14] In one case, $Me_3PAu(Me)(CF_3)I$ was obtained exclusively, but its preparation could not be reproduced by the authors. Because reaction times varied from 5 min to 1 day, and rates dramatically slowed in the presence of galvinoxyl, the authors concluded that a free-radical chain mechanism was operative, with $^{\bullet}CF_3$ as the propagating species.

RESULTS AND DISCUSSION

Prior investigations by our group revealed that oxidation of Ph_3PAu(4-F-C_6H_4) rapidly generates 4,4′-difluorobiphenyl through a mechanism involving aryl group transfer.[3] However, the use of the bulkier PCy_3 prevents transfer of the arene ligand, instead resulting in clean, rapid oxidation of Cy_3PAu(4-F-C_6H_4) (**1a**) to the isolable Au(III) complex *cis*-(Cy_3P)Au(4-F-C_6H_4)Cl_2 (**2**) (eq 1).[15] Therefore, we began our investigations of Au(I) oxidation by CF_3I using **1a**, with the fluorinated arene ligand also providing a convenient ^{19}F NMR handle. Treatment of **1a** in CD_2Cl_2 with CF_3I (25 equiv) afforded the product of formal CF_3I oxidative addition **3a** in 1 h in good yield (eq 2 and Table 1). Both the CF_3 and PCy_3



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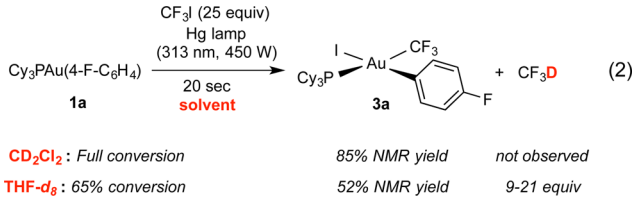
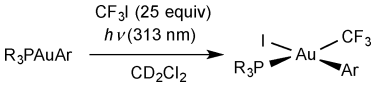


Table 1. Photoinitiated Oxidative Addition of CF_3I to Electronically Diverse Au(I) Aryl Complexes 1a–1f, 11a, and 11b



Au(I) reactant	PR_3	Ar	product	yield (%)
1a	PCy_3	4-F-C_6H_4	**3a**	64
1b	PCy_3	3,5-F_2-C_6H_3	**3b**	44
1c	PCy_3	C_6H_5	**3c**	59
1d	PCy_3	4-Me-C_6H_4	**3d**	38
1e	PCy_3	4-MeO-C_6H_4	**3e**	44
1f	PCy_3	2-Me-C_6H_4	–	NR
11a	PPh_3	4-F-C_6H_4	**12a**	71
11b	PPh_3	4-Me-C_6H_4	**12b**	63

ligands (doublet at δ = −24.5 and quartet at δ = 25.6 in the ^{19}F and ^{31}P NMR spectra, respectively) provide diagnostic NMR signals (Table 2). The substantial coupling ($^3J_{P-F}$ = 63 Hz) between fluorine and phosphorus are characteristic of a *trans* relationship between the CF_3 and phosphine ligands.[14] X-ray analysis of crystals of **3a** confirmed this stereochemical relationship around the square planar Au(III) (Figure 1A); other than the homoleptic anion $[Au(CF_3)_4]^-$,[16] complex **3a** contains a rare example of a crystallographically characterized Au(III)–CF_3 bond. Complex **3a** is not only stable to air and water but can be purified by column chromatography as well.

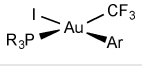
Mechanism of Oxidative Addition of CF_3I. The reaction of **1a** and CF_3I represents a rare oxidation of Au(I) to Au(III) that directly installs potentially reactive Au(III)–carbon bonds.[1] During our attempts to monitor the oxidative addition by ^{19}F NMR, we found that no reaction occurred when the reaction mixture was placed inside the dark NMR spectrometer. However, when the reaction mixture was exposed to ambient fluorescent light for 5 min, the formation of **3a** was detected (~20%). Given the reliance of numerous methods on CF_3I as a trifluoromethyl source,[17] we investigated its photochemical reactivity. Actinometry experiments were carried out to determine the overall quantum yield, using the Norrish II fragmentation of valerophenone as a standard.[18] The oxidative addition of CF_3I to **1a** was complete after 20 s of irradiation by a Hg vapor lamp (2 mM aq. K_2CrO_4 optical filter; transmittance λ_{max} = 313 nm), while the fragmentation of valerophenone (Φ = 1) took place over 24 h under identical conditions. This rate difference, in addition to the ability of ambient light to bring the reaction to full conversion over variable reaction times (between 15 min and 1 h), supports a radical chain reaction as the mechanism of Au(I) oxidation by CF_3I.

The reaction of excess CF_3I and **1a** is also fast in THF, but the conversion is never greater than 65% (52% yield of **3a**), even when irradiated by a Hg vapor lamp for 1 h (*vida infra*). Notably, an excess of fluoroform (HCF_3) is generated in THF, regardless of the light source (only DCF_3 is formed when THF-d_8 is used). GC-MS analysis of reaction mixtures reveals several products of THF oxidation, likely formed by $H^\bullet$ abstraction by $^\bullet CF_3$.

Several control experiments, using HCF_3 production relative to a standard as a probe to detect $^\bullet CF_3$ generation, support the involvement of Au(I) during the initiation of the chain reaction. The UV absorption of CF_3I is centered at 270 nm but tails beyond 350 nm.[19] When irradiated at 313 nm, CF_3I undergoes fast, reversible C–I bond homolysis. However, *in the absence of* ***1a***, only negligible amounts of HCF_3 are observed when THF solutions of CF_3I are irradiated for 30 min, indicating that carbon/iodine radical recombination is substantially faster than $H^\bullet$ abstraction from THF. Similarly insignificant quantities of HCF_3 are observed when 20 equiv (relative to CF_3I) of the $H^\bullet$ donors 1,4-cyclohexadiene, 9,10-dihydroanthracene, or triphenylmethane are added (Figure 2A). Additionally, $Cy_3PAu(2\text{-}(CH_2CH{=}CH_2)C_6H_4)$ (**4**), containing a pendent olefin to either capture a putative Au(II) intermediate and/or $^\bullet CF_3$, is fully consumed upon irradiation in the presence of excess CF_3I (Figure 2B). This oxidation affords multiple Au(III) products of indiscriminate $^\bullet CF_3$ addition to the terminal olefin and gold atom (and HCF_3 when THF is used as solvent) (see SI). Because 2-allylbromobenzene (**5**) does not react with CF_3I when irradiated under similar conditions (no HCF_3 is observed after 5 min, and less than 2% after 30 min), we conclude that the Au(I) aryl complex is necessary for chain initiation. These results are also consistent with an initiation mechanism involving $[CF_3I]^{\bullet-}$, which generates iodide and $^\bullet CF_3$ following C–I bond homolysis.

We envisioned two possible initiation mechanisms for generating $^\bullet CF_3$ as a propagating species from $[CF_3I]^{\bullet-}$ in a chain reaction: (1) initial photoexcitation of **6** followed by electron transfer to CF_3I, or (2) initial photoexcitation of CF_3I followed by electron transfer from **6** (Scheme 1).

Table 2. $^{31}P\{^1H\}$ and ^{19}F NMR Data for Complexes 3a–3e, 12a, and 12b



complex	PR_3	Ar	δ $^{31}P\{^1H\}$ (ppm)	δ ^{19}F (ppm)
3a	PCy_3	4-F-C_6H_4	25.6 (q, $^3J_{P-F}$ = 63 Hz)	−24.5 (d, $^3J_{P-F}$ = 63 Hz)
3b	PCy_3	3,5-F_2-C_6H_3	26.1 (q, $^3J_{P-F}$ = 63 Hz)	−22.0 (d, $^3J_{P-F}$ = 64 Hz)
3c	PCy_3	C_6H_5	25.5 (q, $^3J_{P-F}$ = 62 Hz)	−22.7 (d, $^3J_{P-F}$ = 62 Hz)
3d	PCy_3	4-Me-C_6H_4	25.5 (q, $^3J_{P-F}$ = 62 Hz)	−23.6 (d, $^3J_{P-F}$ = 62 Hz)
3e	PCy_3	4-MeO-C_6H_4	23.3 (q, $^3J_{P-F}$ = 63 Hz)	−20.6 (d, $^3J_{P-F}$ = 64 Hz)
12a	PPh_3	4-F-C_6H_4	20.0 (q, $^3J_{P-F}$ = 68 Hz)	−21.0 (d, $^3J_{P-F}$ = 68 Hz)
12b	PPh_3	4-Me-C_6H_4	20.4 (q, $^3J_{P-F}$ = 67 Hz)	−21.3 (d, $^3J_{P-F}$ = 67 Hz)

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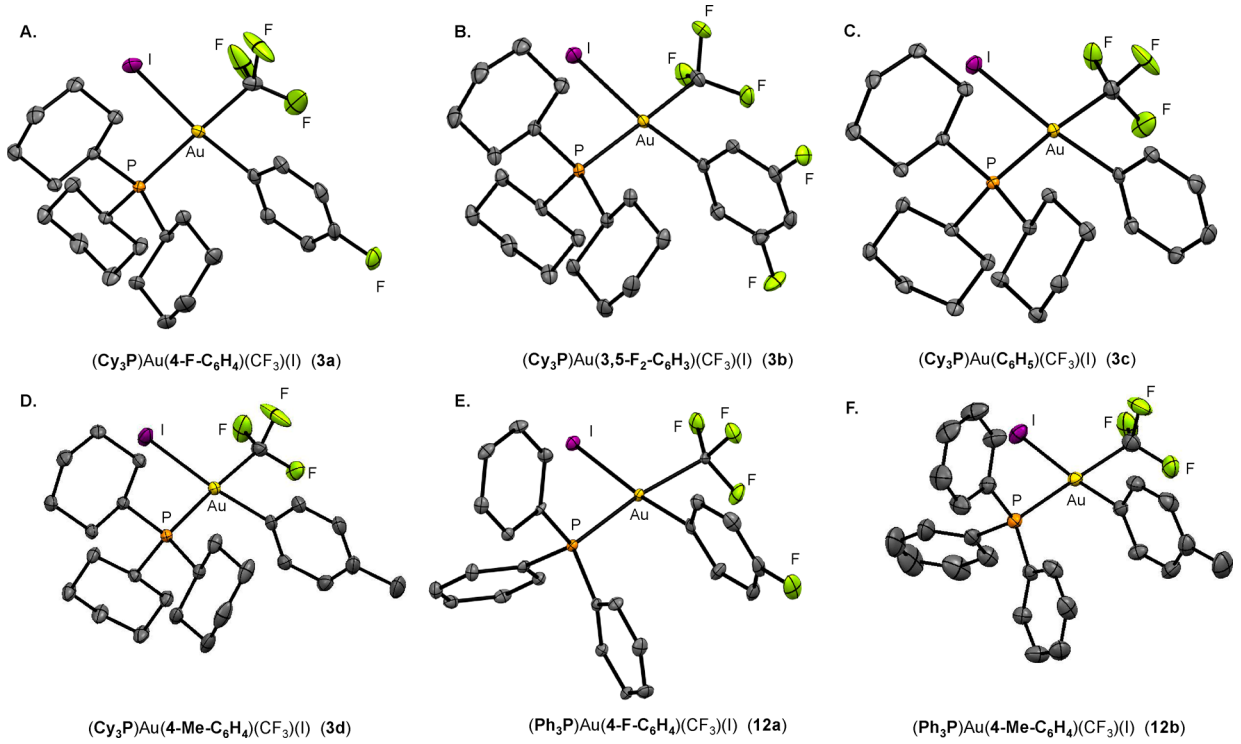


Figure 1. (A–F) Thermal ellipsoid representations of **3a–3d, 12a**, and **12b** at the 50% probability level. Hydrogens have been omitted for clarity. Atoms are color-coded: gray (carbon), yellow (fluorine), gold (gold), purple (iodine), orange (phosphorus). See Supporting Information (SI) for bond lengths and angles.

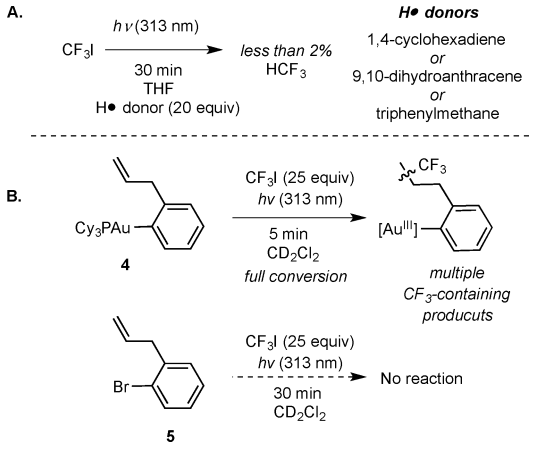
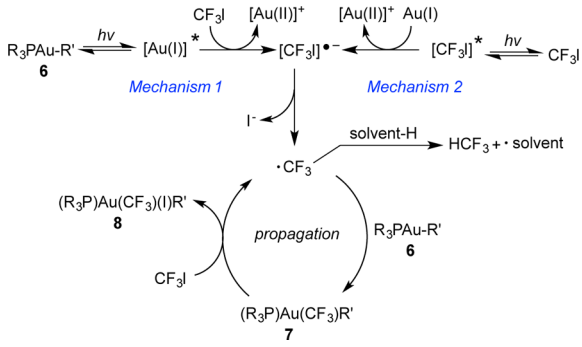


Figure 2. Control experiments to assess involvement of Au(I) in the initiation of the radical chain mechanism. (A) Irradiation of CF_3I solutions containing H• donors to detect CF_3H in the absence of gold. (B) Radical trapping using an olefin with and without a pendant gold center.

Au(I) aryl complexes are well-known chromophores, and their photophysical properties have been investigated previously.[20] While **1a** absorbs weakly above 310 nm (the cutoff for many laboratory fluorescent lamps[19]), excitation at 320 nm (ε = 37 M^{-1} cm^{-1}) results in a weak, broad luminescence from 340 to 460 nm, classified as fluorescence based on the lifetime of excited species **1a*** (<10 ns, quantum yield of fluorescence = 0.03).[21] Despite the short lifetime of **1a***, CF_3I effectively quenches its fluorescence (Stern–Volmer quenching constant K_{SV} = 30 M^{-1}, Figure 3). Although this energy transfer could conceivably generate $^{\bullet}CF_3$ and initiate a chain reaction (mechanism 1, Scheme 1), when CF_3I is removed from fluorimetry samples under vacuum, fluorescence is restored to the same intensity prior to introduction of the gas, indicating that consumption of Au(I) has not occurred.

Scheme 1. Possible Initiation Mechanisms Involving Photoexcitation of Either Au(I) Complex 6 (Mechanism 1) or CF_3I (Mechanism 2)



Surprisingly, fluorescence quenching by the Au(III) complex **3a** is more than 2 orders of magnitude more effective (K_{SV} = 4270 M^{-1}) than quenching by CF_3I (Figure 3). If propagating species terminate frequently, some critical concentration of Au(III) product exists that may impede productive energy transfer from an excited species, halting reinitiation of the chain reaction.

In light of Puddephatt's report, Au(I) alkyl complexes, such as Me_3PAuMe, clearly react with CF_3I.[14] However, there is no mention of the dependence of light on this process, although if the reaction is photoinitiated, mechanism 1 would seem especially unlikely given the absence of a chromophoric aryl ligand in Puddephatt's examples. To test this hypothesis, we irradiated Cy_3PAuMe (**9**) in the presence of CF_3I (Scheme 2).

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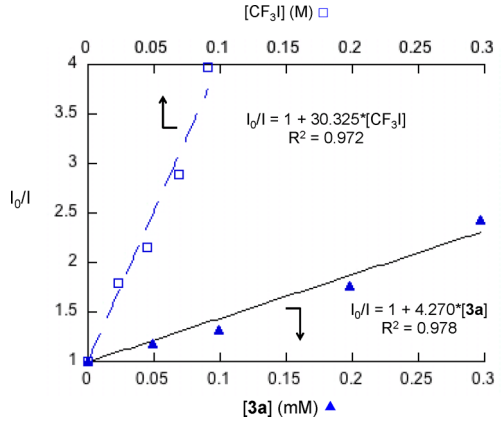
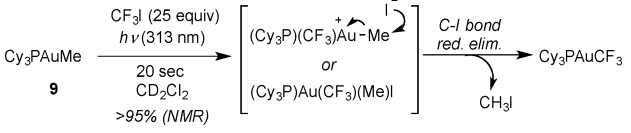


Figure 3. Stern–Volmer plots of fluorescence quenching of **1a** by different concentrations of CF_3I (blue boxes) and Au(III) complex **3a** (blue triangles) in CH_2Cl_2. Concentrations of Au(III) are in mol/L and CF_3I concentrations are in mmol/L.

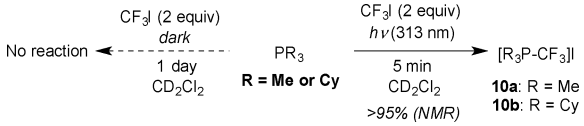
Scheme 2. Photochemical Oxidative Addition of CF_3I to 9 in CD_2Cl_2 and Spontaneous Reductive Elimination of CH_3I



While **9** does not absorb above 300 nm (see SI), the reaction is quantitative in CD_2Cl_2 when irradiated with ambient light, and *does not proceed in the dark*. The oxidized product is unobservable, eliminating CH_3I to generate Cy_3PAuCF_3 at room temperature.[22,23] In THF, the reaction generates excess HCF in THF_3, presumably also from solvent $H^{\bullet}$ abstraction by $^{\bullet}CF_3$.

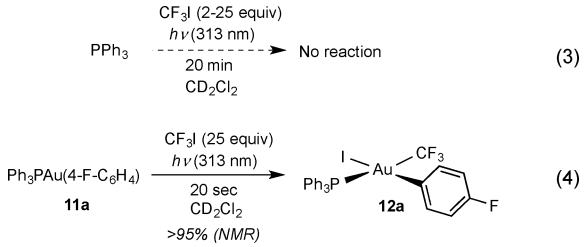
If initiation mechanism 2 is operative, then $^{\bullet}CF_3$ could be generated by irradiating CF_3I solutions containing electron donors other than Au(I), such as phosphines (Scheme 3).[24]

Scheme 3. Photochemical Oxidation of Trialkylphosphines by CF_3I



Indeed, irradiation of PMe_3 or PCy_3 in the presence of CF_3I results in formation of $[Me_3P\text{-}CF_3]I$ (**10a**, $^2J_{P-F}$ = 63 Hz) or $[Cy_3P\text{-}CF_3]I$ (**10b**, $^2J_{P-F}$ = 42 Hz);[25] neither reaction proceeds in the dark. Consistent with quenching of $[CF_3I]^*$ by Au(III), the oxidation of PCy_3 in THF stalls at roughly 45% conversion (by ^{31}P NMR) in the presence of 25 mol % Au(III) complex **3a**.

PPh_3 does not react with CF_3I (eq 3), presumably due to its lower oxidation potential relative to PMe_3 and PCy_3. When PCy_3 and PPh_3 are irradiated *together* with CF_3I, only PCy_3 is consumed, suggesting that PPh_3 neither initiates the chain nor reacts with $^{\bullet}CF_3$ during propagation. Contrary to our initial hypothesis that bulky phosphine ligands prevent aryl group transfer upon Au(I) oxidation, we found that $Ph_3PAu(4\text{-}F\text{-}C_6H_4)$ (**11a**) undergoes quantitative photoinitiated reaction with CF_3I in CD_2Cl_2 to generate **12a** (eq 4). Since PPh_3 is



unreactive toward CF_3I, oxidation of **11a** cannot be initiated by small amounts of dissociated PPh_3 (we cannot disprove the analogous mechanism for PCy_3-supported complex **1a**.) Complex **12a** was characterized by X-ray crystallography and shown to be isostructural to **3a** (Figure 1B).

On the basis of these results, we propose that while photoexcited $[CF_3I]^*$ undergoes rapid C–I bond homolysis and recombination, it also oxidizes Au(I) aryl and alkyl complexes by accepting electrons into a low-lying SOMO to generate radical anion $[CF_3I]^{\bullet-}$ (mechanism 2, Scheme 1). Homolysis of the C–I bond of $[CF_3I]^{\bullet-}$ generates iodide and $^{\bullet}CF_3$, which oxidizes $(R_3P)AuR'$ (**6**) to Au(II) intermediate **7**. Iodine atom abstraction of CF_3I by **7** affords Au(III) complex **8** and regenerates $^{\bullet}CF_3$. In THF, oxidation of **6** by $^{\bullet}CF_3$ is competitive with solvent $H^{\bullet}$ abstraction to make HCF_3 and terminate the radical chain. At sufficiently high concentrations, the Au(III) product (**8**) quenches $[CF_3I]^*$ before it can reinitiate the radical chain reaction.

Promisingly, the photoinitiated oxidative addition of CF_3I is general for electronically diverse complexes of the type $Cy_3PAu(aryl)$ (Tables 1 and 2). The resulting Au(III) products (see Figure 1 for their crystallographic analyses) can be purified by chromatography on silica. Complex **1b** (aryl = 3,5-F_2-C_6H_3), which is more electron-deficient than **1a** (aryl = 4-F-C_6H_4), reacts smoothly with CF_3I to afford **3b**. While complexes with more electron-rich ligands such as **1c** (aryl = C_6H_5) and **1d** (aryl = 4-Me-C_6H_4) also react with CF_3I to afford **3c** and **3d**, respectively, the most electron-rich complex **1e** (aryl = 4-MeO-C_6H_4) decomposes to Au nano particles and several CF_3-containing Au(III) complexes in solution and solid state (no products of C_{aryl}–I or C_{aryl}–CF_3 reductive elimination can be detected). Au(III) product **3e** is detectable, however, and its decomposition can be slowed substantially by addition of MeCN upon concentration of the reaction, allowing its solution-state characterization. The mechanism of decomposition has not yet been identified, although we speculate that the electron-rich arene may encourage PCy_3 dissociation at room temperature and subsequent aryl group transfer.

The complex **1f** (aryl = 2-Me-C_6H_4) does not react with CF_3I at all, suggesting that CF_3I oxidative addition is sensitive to the sterics of the aryl ligand and that relaxation of $[CF_3I]^*$ is faster than oxidation of the metal center to initiate the radical chain. Unsurprisingly, no HCF_3 is observed when **1f** is irradiated in THF for 20 min.

Reductive Elimination from Au(III) Complexes. We next probed C_{aryl}–CF_3 reductive eliminations from Au(III). To our surprise, **12a** undergoes quantitative C_{aryl}–I reductive elimination in toluene-d_8 at 110 °C to afford 4-fluoroiodobenzene and Ph_3PAuCF_3 over 20 min (Scheme 4).[22] No 4-fluoro(trifluoromethyl)benzene is observed by ^{19}F NMR or GC. This process is highly sensitive to free phosphine, stalling completely in the presence of PPh_3 (0.1 or 1.0 equiv) at 110 °C for 12 h. Treatment of **12a** with PPh_3-d_{15} at room temperature

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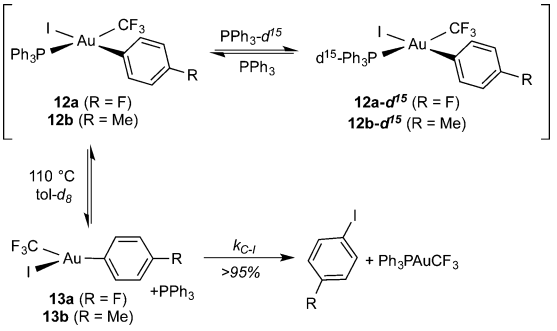
Scheme 4. Behavior of Au(III) Complex 12a and 12b in the Presence of Free PPh_3 and at Elevated Temperatures



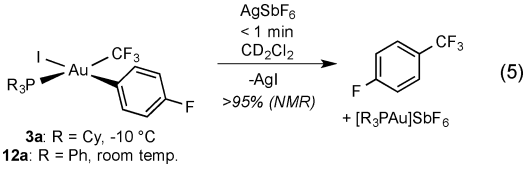
results in immediate formation of **12a-d_{15}**, presumably via an associative process.[2a−c]

More electron-rich aryl ligands, such as 4-methylphenyl (**12b**), do not significantly affect the relative rates of C_{aryl}–I and C_{aryl}–CF_3 reductive elimination (Scheme 4). At 110 °C, complex **12b** undergoes mostly C_{aryl}–I reductive elimination within 10 min to afford 4-methyliodobenzene.[26] Both C_{aryl}–I and C_{aryl}–CF_3 reductive eliminations are also completely inhibited in the presence of PPh_3 (0.1 or 1.0 equiv), while PPh_3-d_{15} reacts immediately at room temperature to afford **12b-d_{15}**, also via associative ligand exchange. These observations are consistent with a mechanism involving highly reversible PPh_3 dissociation from **12a** and **12b**, followed by slow C_{aryl}–I reductive elimination from **13a** or **13b**, respectively.

Clearly, the behaviors of **12a** and **12b** are similar to Au(III)alkyl complexes studied by Kochi, which not only reductively eliminate C_{alkyl}–C_{alkyl} bonds between 70 and 100 °C via a dissociative mechanism but also undergo associative ligand exchange at ambient temperature with excess phosphine.[2a−c] Unsurprisingly, analogous PCy_3-stabilized complexes **3a** and **3d** are stable at 110 °C for at least 12 h, presumably due to the greater σ-donating ability of PCy_3 relative to PPh_3. Phosphine exchange with excess P(*n*-Bu)$_3$, PBn_3, or PCy_3 does not occur even at these temperatures, precluding not only the lower-barrier associative exchange mechanism observed with the PPh_3-supported systems (attributed to the larger cone angle of PCy_3 relative to PPh_3), but also PCy_3 dissociation to form a three-coordinate complex.

Because C_{aryl}–I reductive elimination is significantly faster than C_{aryl}–CF_3 reductive elimination, a cycle for gold-catalyzed trifluoromethylation must necessarily involve iodide abstraction from the Au(III) product of CF_3I oxidative addition. Despite the apparent kinetic stabilities of the Au(III) complexes **3a**−**3e**, **12a**, and **12b**, they all undergo quantitative C_{aryl}–CF_3 reductive elimination *in less than 1 min upon treatment with $AgSbF_6$ at room temperature*.

To consider the effects of the phosphine ligand on the silver-mediated C_{aryl}–CF_3 reductive elimination of Au(III), we used variable-temperature NMR to follow the reductive elimination from **3a** and **12a** in the presence of $AgSbF_6$. PCy_3-substituted complex **3a** undergoes very fast (quantitative conversion in less than 1 min) C_{aryl}–CF_3 reductive elimination at −10 °C, while the analogous PPh_3-stabilized **12a** reacts similarly fast at room temperature (eq 5). At lower temperatures, several bridging species (most likely dimers) are observed by ^{19}F NMR upon halide abstraction in both cases. If C_{aryl}–CF_3 bond reductive elimination can only occur from a monomeric three-coordinate intermediate, then **12a** might be expected to undergo slower



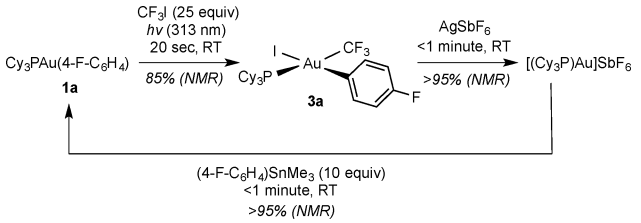
(5)

reductive elimination due to slower dimer dissociation and/or a dimer−monomer equilibrium that more favors the dimer, based on the smaller cone angle and weaker σ-donation of PPh_3 relative to PCy_3.

CONCLUSION

These results reported herein support the oxidative addition of CF_3I to Au(I) via a photoinitiated chain reaction. The reactions are fast at room temperature for both Au(I) aryl and alkyl complexes. Aryl-CF_3 reductive elimination is typically a high-barrier process but occurs in seconds at room temperature from a Au(III) cation. The Au(I)aryl species may be regenerated via one of the numerous transmetalation strategies available involving carbon nucleophiles.[27] For instance, excess (4-F-C_6H_4)$SnMe_3$ (10 equiv) undergoes fast, quantitative transmetalation with $[Cy_3PAu]SbF_6$ at room temperature to afford **1a**, thereby closing a hypothetical catalytic cycle based on the three elementary steps shown in Scheme 5. Silver-free halide

Scheme 5. Oxidation of 1a, Aryl-CF_3 Reductive Elimination, and Regeneration of 1a Supports the Feasibility of a Mild, Catalytic Trifluoromethylation



abstraction from Au(III) complexes could conceivably enable a practical and mild cycle for gold-catalyzed trifluoromethylation of aryl nucleophiles, although deleterious reactions between starting material and metalloradical intermediates and $^{\bullet}CF_3$ must be mitigated, as well as competitive aryl−aryl homocoupling.

While we initially set out to probe C_{aryl}–CF_3 reductive elimination at Au(III), we also explored the oxidative addition of CF_3I to Au(I), a process with potential implications beyond gold chemistry. The possibility of photoinitiated oxidation of transition metals or main group elements by CF_3I should not be discounted in methods employing this reagent as a trifluoromethyl source, particularly since ambient fluorescent laboratory lighting is sufficient to initiate a chain in the presence of a suitable reductant. The results presented also suggest that substrate photoexcitation may provide a low-barrier avenue to kinetically challenging oxidative additions by Au(I), providing access to potentially reactive Au(III) complexes.[28]

ASSOCIATED CONTENT

Supporting Information

Experimental details, characterization data, and crystallographic information (cif). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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(21) The excited state lifetime of **1a*** is shorter than the lower limit of detection of our fluorimeter (<10 ns).

(22) Cy_3PAuCF_3 and Ph_3PAuCF_3 were previously synthesized by the reaction of $R_3PAuOCH(CF_3)_2$ with TMS-CF_3. See: Usui, T.; Noma, J.; Hirano, M.; Komiya, S. *Inorg. Chim. Acta* **2000**, *309*, 151.

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(26) Upon full conversion of **12b**, we detect roughly 2% of 4-methyl-1-trifluoromethylbenzene, the product of C_{aryl}−CF_3 reductive elimination from **13b**, by ^{19}F NMR and GC.

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