Halide-Dependent Mechanisms of Reductive Elimination from Gold(III)

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Supporting Information

ABSTRACT: Two unique organometallic halide series (Ph₃P)Au(4-Me-C₆H₄)(CF₃)(X) and (Cy₃P)Au(4-F-C₆H₄)(CF₃)(X) (X = I, Br, Cl, F) have been synthesized. The PPh₃-supported complexes can undergo both Caryl−X and Caryl−CF₃ reductive elimination. Mechanistic studies of thermolysis at 122 °C reveal a dramatic reactivity and kinetic selectivity dependence on halide ligand. For X = I or F, zero-order kinetic behavior is observed, while for X = Cl or Br, kinetic studies implicate product catalysis. The selectivity for Caryl−CF₃ bond formation increases in the order X = I < Br < Cl < F, with exclusively Caryl−I bond formation when X = I, and exclusively Caryl−CF₃ bond formation when X = F. Thermodynamic measurements show that Au(III)−X bond dissociation energies increase in the order X = I < Br < Cl, and that ground state Au(III)−X bond strength ultimately dictates selectivities for Caryl−X and Caryl−CF₃ reductive elimination.

INTRODUCTION

Transition metal-catalyzed transformations proceed through a series of fundamental steps, i.e., oxidative addition, migratory insertion, and reductive elimination. To minimize deleterious side reactions and maximize overall catalyst efficiency, the metal must undergo the proper series of reactions with excellent selectivity. A fundamental understanding of the factors that affect the selectivity of these elementary steps is critical in designing and improving new metal-catalyzed transformations.

We have recently shown that complexes of the type (Ph₃P)Au(aryl) (aryl = 4-F-C₆H₄, 4-Me-C₆H₄) undergo a photochemical oxidative addition to CF₃I to give the air- and moisture-stable Au(III) complexes (Ph₃P)Au(aryl) (aryl = 4-F-C₆H₄, 4-Me-C₆H₄) undergo a photochemical oxidative addition to CF₃I to give the air- and moisture-stable Au(III) complexes (Ph₃P)Au(aryl)(I). These complexes undergo rapid Caryl−CF₃ reductive elimination when treated with AgSbF₆ (Scheme 1). This transformation presumably proceeds via the cation [(Ph₃P)Au(aryl)(CF₃)]⁺. Although this step demonstrates the oxidizing ability of Au(III) cations, a reliance on stoichiometric Ag(I) salts to generate the reactive cation is ultimately impractical if a catalytic process involving such Au(III) intermediates is to be realized. Due to our failed efforts to induce iodide dissociation either photochemically or with Lewis acids, we also investigated thermolytic routes, and found that neutral (Ph₃P)Au(aryl)−(CF₃)(I) underwent solely Caryl−I reductive elimination at high temperatures (122 °C) (Scheme 1). Although Caryl−I reductive elimination from these complexes is facile, the factors controlling selectivity of C−X versus C−C bond formation are unclear due to a lack of other members of the halide family that could allow a comparative study.

In a seminal study, Hartwig has shown that the rates of reversible Caryl−X reductive elimination from three-coordinate Pd(II) increase with halide polarizability (X = Cl < Br < I), while the thermodynamic driving force increases in the order X = I < Br < Cl. However, because C−X (X = halide) reductive elimination is often endothermic, studies typically rely on using high-valent late metals such as Cu(III), Pd(IV) and Pt(IV) to establish a thermodynamic driving force. In this vein, Au-catalyzed halogenations likely involve C(sp²)−X reductive elimination from Au(III), and C(sp³)−X reductive eliminations from Au(III) have also been demonstrated.

Caryl−X reductive elimination is not necessarily productive, and may be a decomposition pathway for high-valent organometallic species with halide ligands. Importantly, Au(III) catalysts, which are often generated using dihalogen (or formal dihalogen) oxidants and stabilized by halide ligands, could undergo deleterious, irreversible Caryl−X bond formation to deplete active catalyst concentrations. With access to a full family of Au(III) halides, trends in the rates of Caryl−X reductive elimination from Au(III) could be established. Perhaps slower Caryl−X bond formation could also be exploited to promote selectivity for otherwise challenging reductive eliminations, such as Caryl−CF₃ bond formation in complexes of the type (R₃P)Au(aryl)(CF₃)(X). Indeed, studies of competitive

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resultive eliminations should inform factors dictating selectivity in catalytic cycles.4c,k

Herein, we report the synthesis and characterization of a series of well-defined complexes of the type (R3P)Au(aryl)-(CF3)(X) (X = I, Br, Cl, F) that undergo both Caryl−X and Caryl−CF3 reductive elimination with different, halide-dependent kinetic ratios. These ratios vary systematically among the halide series, showing that halide ligands, often considered spectators, can dramatically influence reaction behavior.

■ RESULTS AND DISCUSSION

Sonicating 1-I or 2-I with excess AgX (X = Br, Cl, F) afforded metathesis products 1-X and 2-X (X = Br, Cl, F) in high yield (Scheme 2). Interestingly, 1-F represents a rare example of an isolable, terminal organometallic Au(III) fluoride (Figure 1).

All complexes within the 1-X halide series underwent thermolysis to products of Caryl−X and Caryl−CF3 reductive elimination, and (when X = F) solvent activation. All reactions were followed by19F NMR at 122 °C in toluene-d8 ([1-X]=14.0−16.0 mM). All values were quantified relative to 1-trifluoromethylnaphthalene (19F δ = −59 ppm) as an internal standard. Due to irreversible formation of a new Au(III) species upon treatment with [Bu4N]X (presumably the aurates [Bu4N][Au(aryl)(CF3)(X)2] (19F NMR singlet at δ = −21 to −25 ppm), the kinetic order of halide anions could not be determined. Reactions run in the significantly more polar 9PhNO2 were only slightly affected (see Supporting Information), providing evidence against an ionic mechanism involving tight or dissociated ion pairs.

**Scheme 2. Synthesis of Au(III) Halide Series**

![Scheme 2](Image)

**Figure 1.** (A) Thermal ellipsoid representation of 1-F at the 50% probability level. (B) 19F NMR signal corresponding to the Au−CF3 functionality. (C) 31P{1H} NMR signal in CD2Cl2 corresponding to the Au-PPh3 functionality.

As previously reported, complex 1-I underwent thermolysis at 122 °C to exclusively generate Ph3PAuCF3 and 4-Me-C6H4−I (t1/2 = 2.5 min). Consumption of 1-I followed unusual zero-order kinetics over a range of concentrations (kobs = 4.5 × 10−5 M s−1 from 6 to 35 mM [1-I], Figure 2 and Supporting Information Figure S1). When 0.005 equiv PPh3 (70 μM) was added, the rate slowed substantially (t1/2 = 28 min), and the reaction exhibited first-order behavior in 1-I (kobs = 4.1 × 10−5 s−1). The observed rate constant (kobs) is inverse first-order in PPh3, implicating PPh3 predissociation from 1-I and reductive elimination from a short-lived three-coordinate Au(III) complex 3-I under these conditions (Scheme 3). Consistent with this sequence, PCy3-supported 2-I did not react at 122 °C over 2 days, presumably due to the increased donor strength of the trialkylphosphine.

The zero-order kinetics in the absence of PPh3 suggest reversible reaction inhibition by starting material. If reductive elimination proceeds through the coordinatively unsaturated 3-I, a reasonable origin of this unusual behavior is trapping by 1-I to μ-iodo bimetallic adduct 4-I (Scheme 3). Indeed, μ-halide bridges between Au(III) atoms form readily to avoid coordinative unsaturation at the metal; in addition, bimetallic complexes such as [AuCl3]2, [Me2AuI]2, [(F3C)2AuX]2 (X = I, Br), and ([SIPr)Au(Me)F] 2)2+ (SIPr = 1,3-bis(2′,6′-
The recombination of $\text{PPh}_3$ and $k$ added, the rate law simplifies to
\[
-\frac{d[1\text{-}1]}{dt} = \frac{k_{C,\text{PPh}_3}[^1\text{-}1] + k_{C,[\text{PPh}_3]}[1\text{-}1] + k_{C,[\text{PPh}_3]}[^1\text{-}1]}{k_{C,[\text{PPh}_3]}[^1\text{-}1] + k_{C,[\text{PPh}_3]}[1\text{-}1] + k_{C,[\text{PPh}_3]}[^1\text{-}1]}
\]

Since $[4\text{-}1]$ must be less than $[3\text{-}1]$, the assumption that $[4\text{-}1]$ is valid if the formation of $4\text{-}I$ is significantly faster than the recombination of $\text{PPh}_3$ and $3\text{-}I$, then $k_2[^1\text{-}1] \gg k_2[\text{PPh}_3]$ and eq 1 simplifies to the zero-order rate law $-\frac{d[^1\text{-}1]}{dt} = k_2[^1\text{-}1]$, which at 122 °C is $4.5 \times 10^{-5} \text{ M s}^{-1}$.

In steady-state, $[\text{PPh}_3]$ must be very low. Since even small amounts of $\text{PPh}_3$ dramatically alter the reaction behavior, $k_{C,\text{PPh}_3}$ must be substantially larger than $k_2$. Therefore, when $\text{PPh}_3$ is added, the rate law simplifies to
\[
-\frac{d[^1\text{-}1]}{dt} = \frac{k_{C,\text{PPh}_3}[^1\text{-}1]}{k_{C,[\text{PPh}_3]}}
\]

where $k_{C,\text{PPh}_3}/k_{C,[\text{PPh}_3]} = 2.9 \times 10^{-8} \text{ M s}^{-1}$. Thus, $k_{C,[\text{PPh}_3]} = (1600)k_{C,\text{PPh}_3}$ in accordance with our previous conclusion that $k_{C,\text{PPh}_3} \gg k_2$.

**Thermolyses of Au(III)–Bromide 1-Br and Au(III)–Chloride 1-Cl.** Qualitatively, the thermolyses of 1-Br and 1-Cl were notably slower ($t_{1/2} \sim 75$ and 400 min, respectively) than 1-I, and products of both $C_{\text{aryl}}\text{-}X$ and $C_{\text{aryl}}\text{-}\text{CF}_3$ reductive elimination were detected after full conversion ($[4\text{-}\text{Me}_2\text{C}_6\text{H}_4\text{-}\text{Br}]\text{/}[4\text{-}\text{Me}_2\text{C}_6\text{H}_4\text{-}\text{CF}_3] = 1.5:1$ for 1-Br, and $[4\text{-}\text{Me}_2\text{C}_6\text{H}_4\text{-}\text{Cl}]\text{/}[4\text{-}\text{Me}_2\text{C}_6\text{H}_4\text{-}\text{CF}_3] = 1:4.5$ for 1-Cl). To our surprise, reaction rates increased with time for both thermolyses (Figures 3A and 4A), suggestive of catalysis by products or nanoparticles. Indeed, in the presence of excess $\text{Ph}_3\text{PAuCF}_3$, the rates of these thermolyses dramatically accelerated, behaving first-order in 1-Br or 1-Cl and $\text{Ph}_3\text{PAuCF}_3$ (Figures 3B and 4B, see Supporting Information). The addition of 0.01 equiv (0.014 mM) $\text{PPh}_3$ dramatically slowed thermolysis of 1-Br and 1-Cl with and without excess $\text{Ph}_3\text{PAuCF}_3$, consistent with phosphine dissociation preceding reductive elimination in both the nonaccelerated and product-accelerated pathways.

Consistent with at least two processes with different product-determining steps, the ratios $[4\text{-}\text{Me}_2\text{C}_6\text{H}_4\text{-}X]/[4\text{-}\text{Me}_2\text{C}_6\text{H}_4\text{-}\text{CF}_3]$ vary over time during the thermolyses of 1-Br and 1-Cl. For instance, when $t < 20$ min, the accelerated pathway had not significantly contributed to consumption of 1-Br, and there was only a kinetic preference for $C_{\text{aryl}}\text{-}\text{Br}$ or $C_{\text{aryl}}\text{-}\text{CF}_3$ bond formation ($[4\text{-}\text{Me}_2\text{C}_6\text{H}_4\text{-}\text{Br}]\text{/}[4\text{-}\text{Me}_2\text{C}_6\text{H}_4\text{-}\text{CF}_3]$ is roughly 2:1). However, in the presence of a large excess of $\text{Ph}_3\text{PAuCF}_3$ (140 mM), the accelerated pathway dominated even at early reaction times, and $C_{\text{aryl}}\text{-}\text{Br}$ reductive elimination was slightly favored (2.3:1, presumably the intrinsic kinetic product distribution of the accelerated pathway.) For 1-Cl, the product ratio $[4\text{-}\text{Me}_2\text{C}_6\text{H}_4\text{-}\text{Cl}]\text{/}[4\text{-}\text{Me}_2\text{C}_6\text{H}_4\text{-}\text{CF}_3]$ for the nonaccelerated pathway was roughly 1:2.8, while the accelerated .
pathway heavily favored C\textsubscript{aryl}-CF\textsubscript{3} reductive elimination (1:7.6).

We propose that the electron-withdrawing effect\textsuperscript{12} of the CF\textsubscript{3} ligand renders Ph\textsubscript{3}PAuCF\textsubscript{3} sufficiently Lewis acidic to coordinate the halide of 1-Br or 1-Cl in a μ-bridging fashion\textsuperscript{13}, effectively withdrawing electron density from the Au(III) center and perturbing the relative kinetic preferences for C\textsubscript{aryl}−X and C\textsubscript{aryl}−CF\textsubscript{3} reductive elimination from 6-X. Inhibition by PPh\textsubscript{3}, the absence of saturation behavior at high [Ph\textsubscript{3}PAuCF\textsubscript{3}], and unobservables intermediates suggest a process involving fast, reversible coordination of Ph\textsubscript{3}PAuCF\textsubscript{3} to 1-Br or 1-Cl, followed by PPh\textsubscript{3} dissociation and slow C\textsubscript{aryl}−X and C\textsubscript{aryl}−CF\textsubscript{3} reductive elimination (Scheme 4).

**Scheme 4. Proposed Mechanism for Accelerated Thermolysis of 1-X (X = Br, Cl)**

![Scheme 4](image)

For both 1-Br and 1-Cl, kinetic details of the nonaccelerated pathway were masked by the accelerated reaction. However, the slower pathway is likely analogous to 1-I thermolysis (Scheme 3), given the reaction’s sensitivity to excess phosphine and the diversity of Au(III)-supported μ-halide bridges.\textsuperscript{11} The unambiguous first-order behavior in the presence of excess Ph\textsubscript{3}PAuCF\textsubscript{3} clearly indicates that the accelerated reaction is substantially faster than the nonaccelerated process (see Supporting Information for rate laws.)

**Thermolysis of Au(III)−Fluoride 1-F.** The thermolysis of 1-F was slower (\(t_{1/2} = 33\) min) than that of 1-I, but significantly faster than that of 1-Br and 1-Cl. Consistent with the apparent trend of decreasing selectivity of C\textsubscript{aryl}−X reductive elimination in the order X = I > Br > Cl, we observed no 4-Me-C\textsubscript{6}H\textsubscript{4}−F elimination from a putative species Au(4-MeC\textsubscript{6}H\textsubscript{4})(aryl−1-F) and was dramatically inhibited by PPh\textsubscript{3}, consistent with slow C\textsubscript{aryl}−CF\textsubscript{3} reductive elimination and slow solvent activation from three-coordinate intermediate 3-F, which can be trapped by starting material (Scheme 3). Although solvent activation is in all likelihood a bimolecular process, [toluene-\(d^8\)] can activate solvent implicates an ionic Au(III)−F bond that imparts sufficient Lewis acidity for formal C−H activation by electrophilic aromatic substitution, fluoride-assisted deprotonation, or σ-bond metathesis.\textsuperscript{17}

Like 1-I, addition of 0.1 equiv PPh\textsubscript{3} (1.4 mM) slowed the reaction (\(t_{1/2} = 300\) min) and altered the order in 1-F from zero to first (see Supporting Information ). However, only biaryl-d\textsuperscript{7} was formed under these conditions, suggesting an alternative, slower solvent activation pathway that does not involve 3-F. Although the Au(III) center in 1-F is less electron-deficient and more sterically shielded than in 3-F due to coordinative saturation, it may still be sufficiently Lewis acidic to activate solvent (Scheme 6). Consistent with this proposal, the reaction rate was independent of [PPh\textsubscript{3}] from 1.4 to 14 mM, and the more electron-rich, sterically encumbered 2-F did not react with toluene-\(d^8\).

A rate law consistent with the mechanism of 1-F thermolysis is shown in eq 3 where the zero-order term is significantly larger than the pseudo-first-order term in the absence of PPh\textsubscript{3}, and \(k_2(k_{C-CF_3} + k_{Ar}[toluene-\(d^8\)])/k_2 = 3.9 \times 10^{-6} \text{ M s}^{-1}\) (see Supporting Information for derivation).

\[
-\frac{d[1-F]}{dt} = \frac{k_1}{k_2}([C_{C-CF_3} + k_{Ar}[toluene-\(d^8\)]) + k_{Ar}[toluene-\(d^8\)][1-F]
\]

(3)

These kinetic investigations reveal that selectivity for C\textsubscript{aryl}−X versus C\textsubscript{aryl}−CF\textsubscript{3} reductive elimination from Au(III) decreases in the order X = I > Br > Cl > F (Figure 6). While rate of C\textsubscript{aryl}−
X bond formation corresponds to halide polarizability,7 thermodynamic studies were necessary to determine the role of ground state effects in the reaction selectivities.

**Relative Au(III)–X Bond Dissociation Enthalpies (X = I, Br, Cl).** To gain insight into what extent thermodynamics govern reductive elimination selectivity, van’t Hoff analyses between 2-X and trityl halides were carried out. The halide metathesis equilibria were monitored in toluene-d8 by 19F NMR at temperatures between 25 and 78 °C. Complexes 2-I and 2-Br were treated with an excess of Ph3C–Cl (30 equiv) to ensure fast approach to equilibrium, and to hold [Ph3C–Cl] constant for determination of the equilibrium constant.18 The equilibrium between 2-CI (+ Ph3C–I) and 2-I (+ Ph3C–Cl) was moderately exothermic (∆H° = −4.8 kcal/mol) with a negligible loss of entropy (∆S° = −2.1 e.u.) (Figure 7).

Similarly, the equilibrium between 2-CI (+ Ph3C–Br) and 2-Br (+ Ph3C–Cl) also lies to the right (∆H° = −3.1 kcal/mol) with a negligible entropy loss (∆S° = −1.8 e.u.) (Figure 8).

Using the thermodynamic parameters above, and differences in Benson group increments for tertiary alkyl halide groups (see Supporting Information for derivation),19 we obtain the differences in heats of formation (∆∆H°) of 2-CI, 2-Br, and 2-I: ∆H°(2-I) is 13 kcal/mol greater than ∆H°(2-Br), and 21 kcal/mol greater than ∆H°(2-CI).

The differences in bond dissociation energies (∆BDE) of each Au(III)–X bond are functions of ∆H°(2-X) and BDEs of the diatomic halogens (see Supporting Information for derivation).20 Although rough approximations, these values suggest that the Au(III)–I bond in 2-I is 18 kcal/mol weaker than the Au(III)–Br bond in 2-Br, and 33 kcal/mol weaker than the Au(III)–Cl bond in 2-Cl.21 The trend in Au(III)–X bond strengths follows Caryl–X bond strengths, with the variation in Au(III)–X BDEs only slightly greater. That the bond dissociation energies decrease in the order Au(III)–Cl > Au(III)–Br > Au(III)–I suggests that selectivities for Caryl–X and Caryl–CF3 reductive elimination are strongly influenced by the strength of the Au(III)–X bond in the starting material (Figure 8), and that Au–X bonding must be substantially diminished in the transition state to Caryl–X reductive elimination. Halide polarizability, or softness, is correlated with nucleophilicity, and may also play a role in dictating relative rates of Caryl–X bond formation, as noted by Hartwig for Pd(II) systems.22

**CONCLUSIONS**

We have accessed full Au(III) halide families through formal oxidative addition of CF3I to Au(I) followed by halide metathesis, and have systematically studied the thermolysis of 1-X (X = F, Cl, Br, I) and the competitive Caryl–X and Caryl–CF3 reductive eliminations from Au(III). The mechanisms and kinetic selectivities for these steps are highly dependent on the identity of the halide ligand. When X = I, thermolysis exclusively generates the products of Caryl–I bond formation. The selectivity for Caryl–CF3 reductive elimination increases in the order X = I < Br < Cl < F, and is completely selective for Caryl–CF3 bond formation when X = F (Figure 6). Thermodynamic studies reveal that the Au(III)–X bond strength increases in the order X = I < Br < Cl, a trend that mirrors selectivity for Caryl–CF3 reductive elimination. These...
Halide Metathesis between 1-I or 2-I with AgX. 1-I (75 mg, 0.10 mmol) or 2-I (77 mg, 0.10 mmol) was dissolved in CH2Cl2 (5 mL) in a vial. AgX (X = Br, Cl, F) (1.0 mmol) was added at once, and the reaction was capped and sonicated for 5 min in the dark, followed by a second addition of AgX (1.0 mmol) and further sonication for 5 min. When X = Br or Cl, the solid turned increasingly yellow with the formation of AgI. The suspension was filtered through a bed of Celite, and concentrated in vacuo to a white powder that was recrystallized twice in 1:3 CH2Cl2/pentane to afford 1-Br (52 mg, 0.074 mmol), 2-Br (61 mg, 0.081 mmol), 1-Cl (51 mg, 0.078 mmol), 2-Cl (60 mg, 0.089 mmol), 1-F (45 mg, 0.071 mmol), or 2-F (55 mg, 0.083 mmol) in analytical purity as white solids.

**Halide Metathesis between 1-I or 2-I with AgX.**

**Halide Metathesis between 1-I or 2-I with AgX.**

**METHODS**

General Considerations. Unless otherwise stated, all manipulations were carried out at ambient temperature (20 °C) under an atmosphere of purified nitrogen in a Vacuum Atmospheres Corp. glovebox or with a double manifold vacuum line using standard Schlenk techniques. All glassware was dried at 150 °C for 12 h prior to use. Solvents were dried by passage through a column of activated alumina under nitrogen pressure and degassed by sparging with dry nitrogen. Toluene-d8 was distilled from sodium ketyl. CF3I was purchased from Sigma-Aldrich and used as received. Ph3P–F was prepared according to a recent publication from our lab.1

**General Considerations.**

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**Improved Procedure for the Synthesis of 1-I and 2-I.** A 25 mL Pyrex Schlenk tube was charged with Ph3PAu(4-Me-C6H4)Br or Cy3PAu(4-F-C6H4) (up to 3 mmol) and the solid was dissolved in CH2Cl2 to give a 0.2 M solution. The tube was sealed and degassed with three freeze–pump–thaw cycles. CF3I gas was introduced (1 atm) and the reaction vessel was sealed and placed in direct sunlight for 15 min. The reaction mixture turned yellow within seconds of irradiation. After irradiation, the excess CF3I was vented and the reaction mixture adsorbed to neutral alumina and concentrated to dryness. The alumina mixture was then loaded onto a silica column and the desired Au(III) compounds were eluted in benzene/hexanes (1:1 (v/v), Rf = 0.2 for 1-I, Rf = 0.55 for 2-I). Yields typically range between 60 and 90%. All spectroscopic data match those previously reported.1

**Improved Procedure for the Synthesis of 1-I and 2-I.**

**Improved Procedure for the Synthesis of 1-I and 2-I.**

observations suggest that selectivity for reductive elimination is strongly dictated by the Au(III)–X bond strength in the reactant, and possibly halide polarizability. Highlighting stark reactivity differences between fluoride and higher halide ligands, we have also shown that the Au(III)–F bond is relatively ionic, and can activate C–H/B bonds in arenne solvent at elevated temperatures. Surprisingly, the thermolyses of 1-Br and 1-Cl are accelerated by Ph3PAuCF3, presumably via coordination of Ph3PAuCF3 to the Au(III)–bound halide.

In conclusion, Caryl–X reductive elimination can be facile from Au(III) at elevated temperatures, a process that is rarely observable and probed systematically at other d8 metal centers.2,3 Depending on the nature of the halide ligand, this process can outcompete Caryl–CF3 bond formation. Thus, irreversible Caryl–X reductive elimination should not be discounted as a possible, deleterious thermodynamic sink in studies of organometallic Au(III) halides or Au(I) under oxidative conditions. These studies also suggest that challenging Caryl–X reductive elimination from Au(III) halides is favored when X = Cl or F, due to relatively stronger Au(III)–X bonds compared to the higher halides. More broadly, reductive elimination is a fundamental step in many catalytic cycles, and judicious choice of halide, often considered a spectator ligand, may in fact be essential to achieving challenging C–C bond formation.

**METHODS**
Kinetic Experiments. A 14–16 mM solution of 1-X in tolu-
đ was prepared in an inert atmosphere glovebox. Standard (1-
tri-}
fl]

Thermodynamic Experiments. A 14–16 mM solution 2-X in
tolu-
đ was prepared in an inert atmosphere glovebox. Standard (3,5-
fluorotoluene) was added by microsyringe, and 500 μL aliquots of the solution were transferred to oven-dried NMR tubes. The tubes were capped with greased rubber septa and sealed with Teflon tape. When appropriate, PPh3 or Ph3PAuCF3 were added directly to the NMR tube as a solid prior to injection of the tolu-
đ solution of 1-X and standard.

The thermolyses of 1-I and 1-F were carried out in a Bruker DRX-
500 NMR probe that was temperature calibrated using ethylene glycol and preheated to 122 °C for 30 min. The spectrometer was shimmed and tuned with a solution of standard, then the NMR tube containing the solution of interest was lowered into the probe. All other reactions were carried out at 122 °C in an oil bath shielded from light and the solution of interest was cooled to room temperature, and monitored by19F NMR.

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was reached, the reaction was cooled to 25 °C. Likewise, the anodic peak potential of (SIPr)CuCH3. Likewise, the anodic peak potential of (dbpe)Ni(CF3)2 is 1.17 V greater than the potential of (dbpe)Ni(CH3)2. See: Kieltsch, I.; Dubinina, G. G.; Hamacher, C.; Kaiser, A.; Torres-Nieto, J.; Hutchison, J. M.; Klein, A.; Budnikova, Y.; Vicić, D. A. Organometallics 2010, 29, 1451.

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(11) To discount heterogeneous effects, nanoparticles isolated by heating 1-Br, 1-Cl or Ph3PAuCF3 at 122 °C over 3 days did not accelerate the reaction, nor did any solids (unobservable to the naked eye) centrifuged from a reaction halfway to completion. Filtration of reaction mixtures (0.2 μm PTFE filter) at 50% conversion also did not affect the reaction rates when thermolyses were resumed.
(12) The anodic peak potential of (SiPr)CuCF3 is 0.59 V greater than the potential of (SiPr)CuCH3. Likewise, the anodic peak potential of (dbpe)Ni(CF3)2 is 1.17 V greater than the potential of (dbpe)Ni(CH3)2. See: Kieltsch, I.; Dubinina, G. G.; Hamacher, C.; Kaiser, A.; Torres-Nieto, J.; Hutchison, J. M.; Klein, A.; Budnikova, Y.; Vicić, D. A. Organometallics 2010, 29, 1451.
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đ activation, respectively, we observe several silyl fluoride species by19F NMR resulting from facile Ph,PAuF ionization and quenching of fluoride and DF with the borosilicate NMR tube.
PhNO₂ is substantially less active toward electrophilic aromatic substitution, selectivity for arene activation in PhNO₂ increases by a factor of 18 (see Supporting Information). Given the greater acidity of aromatic protons of PhNO₂ relative to the deuterons of toluene-d₈, we favor a mechanism involving fluoride-assisted deprotonation. We observe no benzylic activation of toluene-d₈, suggesting that activation at the arene is kinetically preferred. Such selectivity has been observed in σ-bond metatheses at late metals, see: (c) Butschke, B.; Schwarz, H. Organometallics 2011, 30, 1588.

(18) Since [Ph₃C−X] = [2-Cl], the equilibrium constant expression simplifies to $K_{eq} = [2-X][Ph₃C−Cl]_o/[2-Cl]^2$, and can be solved from the relative intensities of 19F NMR signals for 2-Cl and 2-Br or 2-I.


(21) The qualitative trend of decreasing Au(III)−X BDEs with higher halides is in marked contrast with gas-phase diatomic Au(I)−X BDEs, which are lowest for Au(I)−Br and highest for Au(I)−Cl and Au(I)−I, see: Reuben Brown, J.; Schwerdtfeger, P.; Schröder, D.; Schwarz, H. J. Am. Soc. Mass Spectrom. 2002, 13, 485.