C(sp^3)−F Reductive Elimination From Alkylgold(III) Fluoride Complexes

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Supporting Information

General synthetic considerations. Unless otherwise stated, all manipulations were conducted under ambient air. Air-sensitive manipulations were conducted using standard Schlenk techniques under N_2 atmosphere. The starting materials (IPr)AuCl,[1] (IPr)Au(*t*Bu),[2] (IPr)$AuCH_2CH_2$*t*Bu,[3] $Cp_2Zr(D)Cl$,[4] and 1-adamantylmethyl bromide[5] were prepared according to literature methods (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene). All other reagents were purchased from commercial vendors and used as received. Toluene, tetrahydrofuran, diethyl ether, and dichloromethane used for handling air- and moisture-sensitive reagents were dried by passage through a packed column of activated neutral alumina under argon pressure.[6] Chloroform-*d* and dichloromethane-d_2 were dried by distillation from phosphorous pentoxide and calcium hydride, respectively. 1,2-Dichloroethane was purchased as "extra dry" grade under Acros-Seal from Acros. All other solvents were used as received without further drying. ^1H, ^2H, $^{13}C\{^1H\}$, ^{19}F, and $^{19}F\{^1H\}$ NMR spectra were recorded at room temperature unless otherwise indicated with Brüker AV-300, AVB-400, AVQ-400, DRX-500, and AV-600 spectrometers. ^1H, ^2H, and $^{13}C\{^1H\}$ NMR spectra were referenced to the residual solvent peaks. ^{19}F NMR spectra were referenced to external $CFCl_3$ ($\delta = 0$). Combustion analysis data were obtained at the Micro-Mass Facility at the University of California, Berkeley.

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[1] de Frémont, P.; Scott, N. M.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2005**, *24*, 2411.

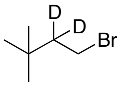
[2] Mankad,N. P.; Toste, F. D. *J. Am. Chem. Soc.* **2010**, *132*, 12859.

[3] Tkatchouk, E.; Mankad, N. P.; Benitez, D.; Goddard, W. A., III; Toste, F. D. *J. Am. Chem. Soc.* **2011**, *ASAP*, doi: 10.1021/ja2012627.

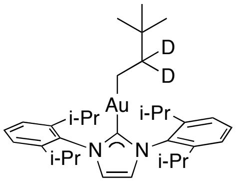
[4] (a) Buchwald, S. L.; LaMaire, S. J.; Nielsen, R. B.; Watson, B. T.; King, S. M. *Tet. Lett.* **1987**, *28*, 3895. (b) Buchwald, S. L.; LaMaire, S. J.; Nielsen, R. B.; Watson, B. T.; King, S. M. *Org. Synth.* **1998**, *9*, 77.

[5] (a) Davies, A. G.; Neville, A. G. *J. Chem. Soc., Perkin Trans. 2* **1991**, 2021. (b) Barfield, M.; Conn, S. A.; Marshall, J. L.; Miiller, D. E. *J. Am. Chem. Soc.* **1976**, *98*, 6253.

[6] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.



Preparation of $BrCH_2CD_2$*t*Bu. This procedure was adapted from literature precedent by Gladysz et al.[7] In a flame-dried Schlenk flask under dinitrogen atmosphere, $Cp_2Zr(D)Cl$ (5.00 g, 19.3 mmol) was suspended in dichloromethane (50 mL) and cooled to 0°C. 3,3-dimethyl-1-butyne (2.40 mL, 19.5 mmol) was added by syringe. The mixture was then stirred at room temperature for 30 min, resulting in a clear, orange solution. The solution was cooled to 0°C, and methanol (0.80 mL, 19.8 mmol) was added by syringe. The solution was then stirred at room temperature for 1 h, causing the color to fade to dull yellow. The solution was cooled to 0°C, and another portion of $Cp_2Zr(D)Cl$ (5.14 g, 19.9 mmol) was added along with additional dichloromethane (30 mL). After stirring at room temperature for 1 h, the resulting cloudy yellow solution was cooled to 0°C and *N*-bromosuccinimide (3.52 g, 19.8 mmol) was added, immediately causing the mixture to change to clear and colorless. The solution was stirred at room temperature for 2 h, and then the dichloromethane was removed by distillation at ambient pressure. The desired product was then isolated by Kugelrohr distillation with minor impurities and used without further purification. ^1H NMR ($CDCl_3$, δ): 3.38 (s, 2H, $C\underline{H}_2$), 0.92 (s, 9H, $C\underline{H}_3$). ^2H NMR ($CDCl_3$, δ): 1.82 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 47.0 (m, J_{CD} = 19.5 Hz, $\underline{C}D_2$), 31.9 (s, $\underline{C}H_2$), 29.9 (s, $\underline{C}(CH_3)_3$), 29.3 (s, $C(\underline{C}H_3)_3$). These data match expectations based on literature values for other isotopologues.[7]



4

Preparation of (IPr)$AuCH_2CD_2$*t*Bu. Under argon atmosphere, Mg powder (0.28 g, 12 mmol) was suspended in THF (3 mL) and activated with 1,2-dibromoethane (0.10 mL, 1.2 mmol) and gentle heating. After the resulting ethylene bubbles had subsided, the mixture was heated to a reflux. A solution of $BrCH_2CD_2$*t*Bu (0.20 mL, 1.4 mmol) in THF (7 mL) was then added dropwise to the refluxing solution. The mixture was refluxed for 45 min and then cooled to room

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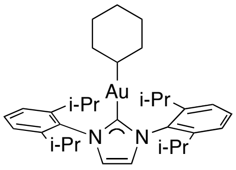
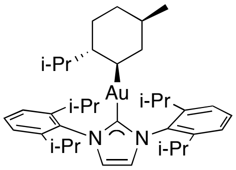
[7] Igau, A.; Gladysz, J. A. *Organometallics* **1991**, *10*, 2327.

temperature and allowed to settle. The supernatant was transferred by cannula to a stirring solution of (IPr)AuCl (0.245 g, 0.395 mmol) in THF (10 mL) at -78°C. Stirring was continued at room temperature overnight. Volatiles were removed. Diethyl ether (50 mL) and H_2O (30 mL) were added, the layers were separated, and the ethereal layer was washed with additional H_2O (2 x 20 mL). The combined aqueous washes were extracted with additional diethyl ether (2 x 25 mL). The combined organic fractions were then washed with brine (30 mL), dried over Na_2SO_4, filtered through a plug of basic alumina, and concentrated to a white solid. The product was then extracted into diethyl ether/pentane (1:1, 40 mL), filtered through Celite, and concentrated by rotary evaporation to yield the product as a fluffy white powder (0.243 g, 91%). ^{1}H NMR (CD_2Cl_2, δ): 7.52 (t, J = 7.8 Hz, 2H, p-C$\underline{H}$), 7.32 (d, J = 7.8 Hz, 4H, m-C$\underline{H}$), 7.10 (s, 2H, NC$\underline{H}$), 2.65 (sept., J = 6.9 Hz, 4H, C$\underline{H}$(CH_3)$_2$), 1.35 (d, J = 7.2 Hz, 12H, CH(C$\underline{H}_3$)$_2$), 1.21 (d, J = 6.6 Hz, 12H, CH(C$\underline{H}_3$)$_2$), 0.61 (s, 9H, C(C$\underline{H}_3$)$_3$), 0.49 (s, 2H, AuC$\underline{H}_2$). ^{2}H NMR (CD_2Cl_2, δ): 1.06 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2, δ): 202.5 (N$\underline{C}$N), 146.5, 135.7, 130.5, 124.4, 123.2, 45.1 (m, J_{CD} = 19.2 Hz, $\underline{C}D_2$), 32.2, 29.5, 29.3, 24.6, 24.2, 14.8 (Au$\underline{C}H_2$). Anal. Calcd. for $C_{33}H_{47}D_2AuN_2$: C, 58.92; H, 7.64; N, 4.16. Found: C, 59.26; H, 7.67; N, 4.05.



5

Preparation of (IPr)Au(*cyclo*-C_6H_{11}). Under argon atmosphere, Mg powder (0.32 g, 13 mmol) was suspended in diethyl ether (2 mL) and activated with 1,2-dibromoethane (0.10 mL, 1.2 mmol) and gentle heating. After the resulting ethylene bubbles had subsided, the suspension was heated to 35°C. A solution of cyclohexyl chloride (0.15 mL, 1.3 mmol) in diethyl ether (10 mL) was then added dropwise by addition funnel over 15 min. After addition was completed, the mixture was refluxed for 3.5 h, then cooled to room temperature and allowed to settle. The supernatant was transferred by cannula to a stirring solution of (IPr)AuCl (0.173 g, 0.279 mmol) in THF (10 mL). Stirring was continued at room temperature overnight. Volatiles were removed. Diethyl ether (30 mL) and H_2O (30 mL) were added, the layers were separated, and the ethereal layer was washed with additional H_2O (2 x 20 mL). The organic fraction was then dried over Na_2SO_4 and concentrated to a white solid that was washed with pentane (2 x 3 mL) to yield a white powder. An additional crop was crystallized by placing the pentane filtrate in a freezer overnight. Total yield: 0.137 g, 73%. ^{1}H NMR ($CDCl_3$, δ): 7.47 (t, *J* = 7.7 Hz, 2H, *p*-$C\underline{H}$), 7.28 (d, *J* = 7.5 Hz, 4H, *m*-$C\underline{H}$), 7.07 (s, 2H, $NC\underline{H}$), 2.65 (sept., *J* = 6.7 Hz, 4H, $C\underline{H}(CH_3)_2$), 1.62 (m, 2H), 1.44 (m, 5H), 1.36 (d, *J* = 6.5 Hz, 12H, $CH(C\underline{H}_3)_2$), 1.20 (d, *J* = 6.5 Hz, 12H, $CH(C\underline{H}_3)_2$), 1.09 (m, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 202.9 ($N\underline{C}N$), 146.0, 135.2, 130.0, 123.9, 122.4, 39.5, 37.2, 30.1, 28.9, 28.4, 24.4, 24.2. Anal. Calcd. for $C_{33}H_{47}AuN_2$: C, 59.27; H, 7.08; N, 4.19. Found: C, 57.96; H, 7.16; N, 4.19.



6

Preparation of (IPr)Au[(-)-menthyl]. This procedure is adapted from Glueck and coworkers.[8] Under argon atmosphere, Mg powder (0.30 g, 13 mmol) was suspended in THF (2 mL) and activated with 1,2-dibromoethane (0.10 mL, 1.2 mmol) and gentle heating. After the resulting ethylene bubbles had subsided, additional THF (8 mL) was added and the suspension was heated to 50°C. (-)-Menthyl chloride (0.20 mL, 1.1 mmol) was then added slowly by syringe. After addition was completed, the mixture was refluxed for 5 h, then cooled to room temperature and allowed to settle. The supernatant was transferred by cannula to a stirring suspension of (IPr)AuCl (0.173 g, 0.279 mmol) in diethyl ether (10 mL). Stirring was continued at room temperature overnight. H_2O (20 mL) was added and the layers were separated. The organic phase was washed with additional H_2O (2 x 20 mL). The combined aqueous washes were then extracted with diethyl ether (2 x 10 mL). The combined organic fractions were washed with brine (2 x 20 mL), dried over $MgSO_4$, and filtered through a short pad of basic alumina. The colorless filtrate was evaporated to dryness and washed with pentane (3 x 1 mL) to yield the product as a white powder (36 mg, 20%). Additional material was obtained by placing the pentane filtrate in a freezer overnight. ^{1}H NMR (CD_2Cl_2, δ): 7.47 (t, *J* = 7.7 Hz, 2H, *p*-$C\underline{H}$), 7.29 (d, *J* = 8.0 Hz, 4H, *m*-$C\underline{H}$), 7.12 (s, 2H, $NC\underline{H}$), 2.66-2.62 (two overlapping sept., 4H, $C\underline{H}(CH_3)_2$), 1.53 (m, 2H), 1.33 (d, *J* = 7.0 Hz, 12H, $CH(C\underline{H}_3)_2$), 1.21-1.18 (two overlapping d, 12H,

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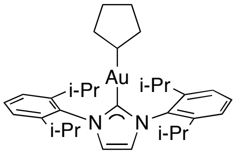
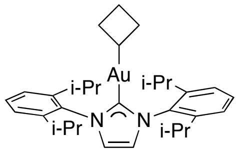
[8] Zuzek, A. A.; Reynolds, S. C.; Glueck, D. S.; Golen, J. A.; Rheingold, A. L. *Organometallics* **2011**, *30*, 1812.

CH(C$\underline{H}_3$)$_2$), 1.09 (m, 4H), 0.93-0.85 (m, 2H), 0.60-0.58 (m, 11H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ): 203.5 (N$\underline{C}$N), 146.42, 146.39, 135.7, 130.2, 124.2, 124.1, 122.9, 46.5, 44.7, 37.5, 34.9, 33.9, 29.2, 24.5, 24.4, 24.13, 24.10, 23.2, 21.8, 21.2. Anal. Calcd. for $C_{37}H_{55}AuN_2$: C, 61.36; H, 7.65; N, 3.86. Found: C, 61.36; H, 7.76; N, 3.81.



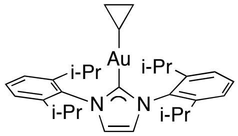
7

Preparation of (IPr)Au(*cyclo*-C_5H_9). Under argon atmosphere, Mg powder (0.29 g, 12 mmol) was suspended in diethyl ether (2 mL) and activated with 1,2-dibromoethane (0.10 mL, 1.2 mmol) and gentle heating. After the resulting ethylene bubbles had subsided, additional diethyl ether (8 mL) was added. Cyclopentyl bromide (0.20 mL, 1.9 mmol) was then added slowly, causing the solution to reflux gently without external heating. The mixture was stirred for 0.5 h at room temperature and then allowed to settle. The supernatant was transferred by cannula to a stirring solution of (IPr)AuCl (0.313 g, 0.504 mmol) in THF (8 mL) at -78°C. Stirring was continued at room temperature overnight. Diethyl ether (10 mL) and H_2O (20 mL) were added, the layers were separated, and the ethereal layer was washed with additional H_2O (2 x 10 mL). The combined aqueous washes were extracted with diethyl ether (2 x 10 mL). The combined organic fractions were then dried over Na_2SO_4, filtered through a short plug of basic alumina, and concentrated to an off-white solid. Yield: 0.164 g, 81%. ^1H NMR ($CDCl_3$, δ): 7.46 (t, *J* = 7.5 Hz, 2H, *p*-C$\underline{H}$), 7.27 (d, *J* = 7.8 Hz, 4H, *m*-C$\underline{H}$), 7.05 (s, 2H, NC$\underline{H}$), 2.62 (sept., *J* = 6.6 Hz, 4H, C$\underline{H}$(CH_3)$_2$), 1.35 (d, *J* = 6.6 Hz, 12H, CH(C$\underline{H}_3$)$_2$), 1.21 (d, *J* = 6.6 Hz, 12H, CH(C$\underline{H}_3$)$_2$), 1.043 (br, 2H), 0.89 (br, 2H), 0.07 (s, 1H, AuC$\underline{H}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 202.6 (N$\underline{C}$N), 146.0, 135.1, 130.0, 124.0, 122.4, 38.2, 35.2, 28.9, 25.7, 24.5, 24.1. Anal. Calcd. for $C_{32}H_{45}AuN_2\cdot O(C_2H_5)_2$: C, 59.33; H, 7.61; N, 3.84. Found: C, 59.35; H, 7.57; N, 3.98.



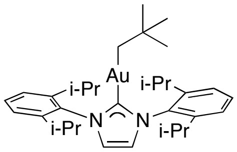
8

Preparation of (IPr)Au(*cyclo*-C_4H_7). Under argon atmosphere, Mg powder (0.29 g, 12 mmol) was suspended in THF (2 mL) and activated with 1,2-dibromoethane (0.10 mL, 1.2 mmol) and gentle heating. After the resulting ethylene bubbles had subsided, additional THF (8 mL) was added and the mixture was heated to a reflux. Cyclobutyl bromide (0.20 mL, 2.1 mmol) was then added slowly to the refluxing solution. The mixture was stirred for 1 h at reflux and then allowed to cool to room temperature and settle. The supernatant was transferred by cannula to a stirring solution of (IPr)AuCl (0.174 g, 0.280 mmol) in THF (10 mL) at -78°C. Stirring was continued at room temperature overnight. Diethyl ether (10 mL) and H_2O (20 mL) were added, the layers were separated, and the ethereal layer was washed with additional H_2O (2 x 10 mL). The combined aqueous washes were extracted with diethyl ether (2 x 10 mL). The combined organic fractions were then dried over Na_2SO_4, filtered through a short plug of basic alumina, and concentrated to an off-white solid. Yield: 0.131 g, 73%. ^{1}H NMR ($CDCl_3$, δ): 7.47 (t, *J* = 7.8 Hz, 2H, *p*-C$\underline{H}$), 7.28 (d, *J* = 7.8 Hz, 4H, *m*-C$\underline{H}$), 7.07 (s, 2H, NC$\underline{H}$), 2.65 (sept., *J* = 6.6 Hz, 4H, C$\underline{H}$(CH_3)$_2$), 2.01 (m, 3H), 1.84 (m, AuC$\underline{H}$), 1.69 (m, 3H), 1.38 (d, *J* = 6.6 Hz, 12H, CH(C$\underline{H}_3$)$_2$), 1.21 (d, *J* = 6.6 Hz, 12H, CH(C$\underline{H}_3$)$_2$. ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 202.1 (N$\underline{C}$N), 146.0, 135.2, 130.1, 124.0, 122.5, 35.7, 33.0, 29.0, 26.4, 24.5, 24.2. Anal. Calcd. for $C_{31}H_{43}AuN_2$: C, 58.12; H, 6.77; N, 4.37. Found: C, 58.21; H, 6.89; N, 4.26.



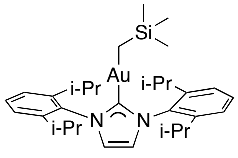
9

Preparation of (IPr)Au(*cyclo*-C_3H_5). Under argon atmosphere, Mg powder (0.32 g, 13 mmol) was suspended in diethyl ether (5 mL) and activated with 1,2-dibromoethane (0.10 mL, 1.2 mmol) and gentle heating. After the resulting ethylene bubbles had subsided, additional diethyl ether (5 mL) was added. Cyclopropyl bromide (0.20 mL, 2.5 mmol) was then added slowly, causing the solution to reflux gently without external heating. The mixture was stirred for 0.5 h at room temperature and then allowed to settle. The supernatant was transferred by cannula to a stirring solution of (IPr)AuCl (0.313 g, 0.504 mmol) in THF (8 mL) at -78°C. Stirring was continued at room temperature overnight. Diethyl ether (10 mL) and H_2O (20 mL) were added, the layers were separated, and the ethereal layer was washed with additional H_2O (2 x 10 mL). The combined aqueous washes were extracted with diethyl ether (2 x 10 mL). The combined organic fractions were then dried over Na_2SO_4, filtered through a short plug of basic alumina, and concentrated to an off-white solid. Yield: 0.291 g, 92%. ^{1}H NMR ($CDCl_3$, δ): 7.46 (t, *J* = 7.5 Hz, 2H, *p*-C$\underline{H}$), 7.27 (d, *J* = 7.5 Hz, 4H, *m*-C$\underline{H}$), 7.06 (s, 2H, NC$\underline{H}$), 2.61 (sept., *J* = 6.7 Hz, 4H, C$\underline{H}(CH_3)_2$), 1.34 (d, *J* = 6.5 Hz, 12H, $CH(C\underline{H}_3)_2$), 1.21 (d, *J* = 6.5 Hz, 12H, $CH(C\underline{H}_3)_2$), 0.29 (d, *J* = 8.5 Hz, 2H, $C\underline{H}_2$), -0.08 (d, *J* = 5.5 Hz, 2H, $C\underline{H}_2$), -0.58 (pseudo-quint., *J* = 8.1 Hz, 1H, AuC$\underline{H}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 199.2 (N$\underline{C}$N), 145.9, 135.0, 130.2, 124.0, 122.6, 28.9, 24.5, 24.1, 14.3, 9.5, 4.2. Anal. Calcd. for $C_{30}H_{41}AuN_2$: C, 57.50; H, 6.59; N, 4.47. Found: C, 57.46; H, 6.50; N, 4.31.



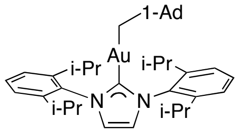
10

Preparation of (IPr)AuCH$_2$*t*Bu. Under flow of N_2, solid (IPr)AuCl (0.199 g, 0.320 mmol) was added to a solution of *neo*-pentyllithium (0.0743 g, 0.952 mmol) in toluene (10 mL) that had been pre-cooled to -78°C. The resulting mixture was allowed to warm gradually to room temperature overnight and then poured into a separatory funnel, diluted with Et_2O (10 mL), and washed with H_2O (3 x 10 mL). The organic fraction was dried over Na_2SO_4, filtered through Celite, and concentrated by rotary evaporation to a tan-colored solid. After washing the residue with pentane (2 x 2 mL), the target compound was obtained as an off-white powder (0.124 g, 59%). ^{1}H NMR ($CDCl_3$, δ): 7.45 (t, *J* = 6.6 Hz, 2H, *p*-C$\underline{H}$), 7.27 (d, *J* = 7.2 Hz, 4H, *m*-C$\underline{H}$), 7.06 (s, 2H, NC$\underline{H}$), 2.65 (sept., *J* = 6.6 Hz, 4H, C$\underline{H}(CH_3)_2$), 1.36 (d, *J* = 6.6 Hz, 12H, $CH(C\underline{H}_3)_2$), 1.21 (d, *J* = 7.2 Hz, 12H, $CH(C\underline{H}_3)_2$), 0.80 (s, 2H, $AuC\underline{H}_2C(CH_3)_3$), 0.56 (s, 9H, $AuCH_2C(C\underline{H}_3)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 203.4 (N$\underline{C}$N), 146.0, 135.3, 130.0, 124.0, 122.4, 41.5, 36.0, 34.8, 28.9, 24.4, 24.3. Anal. Calcd. for $C_{32}H_{47}AuN_2$: C, 58.53; H, 7.21; N, 4.27. Found: C, 58.31; H, 6.96; N, 4.0.



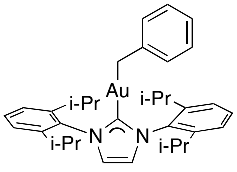
11

Preparation of (IPr)AuCH$_2$SiMe$_3$. In a flamed-dried flask under N_2 atmosphere, (IPr)AuCl (0.207 g, 0.333 mmol) was dissolved in THF (10 mL) and cooled to -78°C. Trimethylsilylmethylmagnesium chloride (1.0 M in Et_2O, 1.0 mL, 1.0 mmol) was added by syringe, and the resulting mixture was stirred at -78°C for 5 min then at room temperature overnight. Volatiles were removed by rotary evaporation. CH_2Cl_2 (40 mL) and H_2O (10 mL) were added, and after separation the organic phase was washed with H_2O (2 x 10 mL) and brine (10 mL). The organic phase was then dried over Na_2SO_4, filtered through Celite, and concentrated to a white powder (0.173 g, 77%). ^{1}H NMR (CDCl$_3$, δ): 7.46 (t, *J* = 8.0 Hz, 2H, *p*-C$\underline{H}$), 7.27 (d, *J* = 8.0 Hz, 4H, *m*-C$\underline{H}$), 7.06 (s, 2H, NC$\underline{H}$), 2.63 (sept., *J* = 6.5 Hz, 4H, C$\underline{H}$(CH$_3$)$_2$), 1.35 (d, *J* = 6.5 Hz, 12H, CH(C$\underline{H}_3$)$_2$), 1.20 (d, *J* = 6.5 Hz, 12H, CH(C$\underline{H}_3$)$_2$), -0.45 (s, 9H, AuCH$_2$Si(C$\underline{H}_3$)$_3$), -0.54 (s, 2H, AuC$\underline{H}_2$C(CH$_3$)$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, δ): 201.1 (N$\underline{C}$N), 145.9, 135.2, 130.1, 124.0, 122.4, 28.9 ($\underline{C}$H(CH$_3$)$_2$), 24.5 (CH($\underline{C}$H$_3$)$_2$), 24.2 (CH($\underline{C}$H$_3$)$_2$), 4.8 (Au$\underline{C}$H$_2$Si(CH$_3$)$_3$), 3.2 (AuCH$_2$Si($\underline{C}$H$_3$)$_3$). Anal. Calcd. for $C_{31}H_{47}AuN_2Si$: C, 55.34; H, 7.04; N, 4.16. Found: C, 55.47; H, 7.10; N, 4.05.



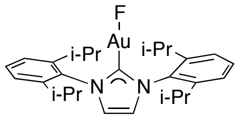
12

Preparation of (IPr)AuCH$_2$(1-Ad). Under argon atmosphere, Mg powder (0.315 g, 13.0 mmol) was suspended in diethyl ether (2 mL) and with rapid stirring was activated by addition of 1,2-dibromoethane (0.10 mL, 1.2 mmol). After the resulting ethylene bubbles had subsided, a solution of 1-bromomethyladamantane (0.285 g, 1.24 mmol) in diethyl ether (10 mL) was added dropwise by addition funnel over 40 min. The resulting mixture was stirred for 1.5 h, at which point stirring was stopped to let excess Mg powder settle. The supernatant was then transferred by cannula to a stirring solution of (IPr)AuCl (0.204 g, 0.328 mmol) in THF (10 mL), and stirring was continued overnight. Volatiles were removed by rotary evaporation. The residue was extracted with dichloromethane (50 mL), washed with H_2O (3 x 25 mL), dried over Na_2SO_4, filtered through Celite, and concentrated to a white powder. Diethyl ether (40 mL) was added, and after stirring for 5 min the solution was filtered once more and concentrated by rotary evaporation to a white solid. This solid was collected on a fritted funnel, washed with pentane (3 x 5 mL), and dried to yield a fine white powder. An additional crop was crystallized by placing the pentane filtrate in a freezer overnight. Total yield: 0.154 g, 64%. ^{1}H NMR ($CDCl_3$, δ): 7.44 (t, *J* = 7.7 Hz, 2H, *p*-C$\underline{H}$), 7.26 (d, 4H, *m*-C$\underline{H}$), 7.06 (s, 2H, NC$\underline{H}$), 2.65 (sept., *J* = 6.7 Hz, 4H, C$\underline{H}$(CH_3)$_2$), 1.66 (br, 3H), 1.44 (br m, 6H), 1.36 (d, *J* = 6.5 Hz, 12H, CH(C$\underline{H}_3$)$_2$), 1.20 (d, *J* = 7.0 Hz, 12H, CH(C$\underline{H}_3$)$_2$), 1.08 (br, 6H), 0.67 (s, 2H, AuC$\underline{H}_2$Ad). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 203.7 (N$\underline{C}$N), 145.9, 135.2, 130.0, 124.0, 122.4, 48.9, 41.9, 37.5, 36.5, 29.9, 28.9, 24.4, 24.3. Anal. Calcd. for $C_{38}H_{53}AuN_2$: C, 62.11; H, 7.27; N, 3.81. Found: C, 62.06; H, 7.26; N, 3.75.



13

Preparation of (IPr)AuCH$_2$Ph. In a flame-dried flask under N_2 atmosphere, (IPr)AuCl (0.197 g, 0.317 mmol) was suspended in toluene (10 mL) and cooled to -78°C. Benzylmagnesium chloride solution (2.0 M in THF, 0.50 mL, 1.0 mmol) was added by syringe. The resulting mixture was stirred at -78°C for 5 min and then at room temperature overnight. The mixture was then poured into a separatory funnel and washed with H_2O (3 x 10 mL) and brine (10 mL). The organic layer was then dried over Na_2SO_4, filtered through Celite, and concentrated to a white solid. After washing with hexanes (3 x 3 mL), a white solid was obtained. An additional crop was crystallized by placing the combined hexanes filtrate in a freezer overnight. Total yield: 0.124 g, 58%. ^{1}H NMR ($CDCl_3$, δ): 7.47 (t, *J* = 7.8 Hz, 2H, IPr *p*-C$\underline{H}$), 7.23 (d, *J* = 7.8 Hz, 4H, IPr *m*-C$\underline{H}$), 7.06 (s, 2H, NC$\underline{H}$), 6.80 (t, *J* = 7.2 Hz, 2H, benzyl *m*-C$\underline{H}$), 6.58 (t, *J* = 7.2 Hz, 1H, benzyl *p*-C$\underline{H}$), 6.52 (d, *J* = 7.8 Hz, 2H, benzyl *o*-C$\underline{H}$), 2.55 (sept., *J* = 6.6 Hz, 4H, C$\underline{H}$(CH_3)$_2$), 2.03 (s, 2H, AuC$\underline{H}_2$Ph), 1.22 (d, *J* = 7.2 Hz, 12 H, CH(C$\underline{H}_3$)$_2$), 1.18 (d, *J* = 6.6 Hz, 12H, CH(C$\underline{H}_3$)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 198.3 (N$\underline{C}$N), 153.3, 145.9, 135.0, 130.2, 127.6, 127.1, 124.0, 122.5, 119.5, 28.9, 28.8, 24.4, 24.2. Anal. Calcd. for $C_{34}H_{43}AuN_2$: C, 60.35; H, 6.40; N, 4.14. Found: C, 60.25; H, 6.30; N, 4.09.



Preparation of (IPr)AuF. In a N_2-filled glovebox, benzene (2 mL) was added to (IPr)AuCH$_2$Ph (136.0 mg, 0.201 mmol) and XeF$_2$ (34.3 mg, 0.203 mmol) in a scintillation vial. A precipitate formed immediately. The mixture was stirred for 20 min at room temperature, and then the precipitate was collected by filtration and washed with pentane (2 x 2 mL) to yield (IPr)AuF as a white powder (64.7 mg, 53%). ^{1}H and ^{13}C{^{1}H} NMR spectroscropy indicated the presence of minor (^{19}F NMR-silent) impurities which precluded combustion analysis. Crystals suitable for X-ray diffraction were grown by diffusion of pentane into a concentrated CH$_2$Cl$_2$ solution. ^{1}H NMR (CDCl$_3$, δ): 7.50 (t, *J* = 7.8 Hz, *p*-C$\underline{H}$), 7.29 (d, *J* = 7.6 Hz, 4H, *m*-C$\underline{H}$), 7.17 (s, 2H, NC$\underline{H}$), 2.54 (sept., *J* = 6.8 Hz, 4H, C$\underline{H}$(CH$_3$)$_2$), 1.35 (d, *J* = 6.8 Hz, 12H, CH(C$\underline{H}_3$)$_2$), 1.21 (d, *J* = 6.8 Hz, 12H, CH(C$\underline{H}_3$)$_2$). ^{1}H NMR (CD$_2$Cl$_2$, δ): 7.57 (t, *J* = 7.7 Hz, *p*-C$\underline{H}$), 7.35 (d, *J* = 7.5 Hz, 4H, *m*-C$\underline{H}$), 7.25 (s, 2H, NC$\underline{H}$), 2.54 (sept., *J* = 6.7 Hz, 4H, C$\underline{H}$(CH$_3$)$_2$), 1.35 (d, *J* = 6.5 Hz, 12H, CH(C$\underline{H}_3$)$_2$), 1.23 (d, *J* = 6.5 Hz, 12H, CH(C$\underline{H}_3$)$_2$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, δ): [C$_{\text{carbene}}$ peak not located], 146.3, 134.6, 131.3, 124.5, 124.1, 29.4, 24.6, 24.4. ^{19}F NMR (CDCl$_3$, δ): −256 (s). ^{19}F NMR (CD$_2$Cl$_2$, δ): −249 (s).

Fluorination of gold(I) alkyls. In a typical experiment, approximately 15 mg of a (IPr)AuR complex and an internal standard (either 1,3-dinitrobenzene or 1,3,5-trifluorobenzene) were dissolved in chloroform-*d* (0.7 mL) and placed in a J. Young tube. Crystals of xenon difluoride (1.1 equiv per Au) were added and the tube was sealed immediately. After inverting the tube 3-4 times to achieve dissolution of the xenon difluoride crystals, the reaction was monitored by ^{1}H and ^{19}F NMR spectroscopy. In some cases, a *cis*-$F_2Au(R)(IPr)$ intermediate was identified by its characteristic ^{19}F NMR properties (by comparison to the previously reported methyl derivative[2]) and observed to decay over time (typically several hours at room temperature); these data are summarized in Table S1. Note: no evidence was observed for $[Au^{III}{}_2(\mu\text{-}F)_2]^{2+}$ dimers as reported previously for similar compounds.[2] For cases not shown in Table S1, Au(III) intermediates were not observed directly, and product mixtures observed after ~5 min did not change over time. In all cases, (IPr)AuF was observed as a major component of the product mixtures (>80%), though its yield could not be determined accurately due to its slow decomposition in chlorinated solvents.[9] NMR yields of the organic products were determined by integration relative to the internal standard. Characterization data for the organic products matched literature data.[10] Extremely similar yields were obtained when reactions were carried out in CD_2Cl_2 or 1,2-dichloroethane. Furthermore, yields were highly reproducible regardless of whether the reactions solvents had been dried rigorously or not. In cases where β-H elimination was a viable pathway, additional ^{19}F peaks in the region of inorganic fluoride (i.e., F^-, F_2H^-, and related species) were also evident.

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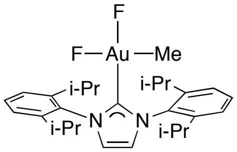
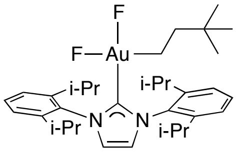
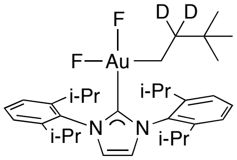
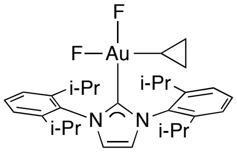
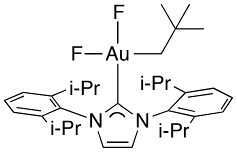
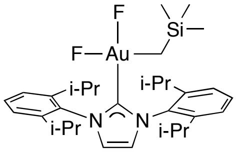
[9] Laitar, D. S.; Müller, P.; Sadighi, J. P. *Organometallics* **2005**, *24*, 4503.

[10] For an excellent compilation of ^{19}F NMR data, see (a) Weigert, F. J. *J. Org. Chem.* **1980**, *45*, 3476. Other sources of ^{19}F NMR data used, see: (b) Rahman, M.; McKee, M. L.; Shevlin, P. B. *J. Am. Chem. Soc.* **1986**, *108*, 6296. (c) Kanie, K.; Tanaka, Y.; Suzuki, K.; Kuroboshi, M.; Hiyama, T. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 471. (d) Schneider, H. J.; Gschwendtner, W.; Heiske, D.; Hoppen, V.; Thomas, F. *Tetrahedron* **1977**, *33*, 1769. (e) Kraft, B. M.; Lachicotte, R. J.; Jones, W. D. *J. Am. Chem. Soc.* **2001**, *123*, 10973. (f) Liu, E. K. S.; Lagow, R. J. *J. Organometal. Chem.* **1978**, *145*, 167. (g) Hairston, T. J.; O'Brien, D. H. *J. Organometal. Chem.* **1971**, *29*, 79. (h) Walter, S. R.; Marshall, J. L.; McDaniel, C. R., Jr.; Canada, E. D.; Barfield, M. *J. Am. Chem. Soc.* **1983**, *105*, 4185.

Table S1. ^{19}F NMR characterization data for observable *cis*-F_2Au(R)(IPr) complexes.

Complex	**$-\delta_{F1}$ (ppm)**	**$-\delta_{F1}$ (ppm)**	**$^2J_{FF}$ (Hz)**
 **1-F$_2$**	200[a]	233[a]	81[a]
 **3-F$_2$**	195	212	83
 **4-F$_2$**	195	214	78
 **9-F$_2$**	206	209	79
 **10-F$_2$**	184	232	n.d.[b]
 **11-F$_2$**	191	225	85

[a] Taken from Mankad,N. P.; Toste, F. D. *J. Am. Chem. Soc.* **2010**, *132*, 12859. [b] Peaks too broad to determine $^2J_{FF}$ accurately.

Iodination of gold(I) alkyls. An analogous procedure was used, substituting I_2 for XeF_2. In no case was an alkylgold(III) intermediate observable by ^{1}H NMR. Characterization data for the (IPr)AuI byproduct matched those of independently-synthesized (IPr)AuI.[11]

Kinetics measurements.

First-order plot and Eyring analysis. A stock solution of **11** (31 mM) and the internal standard 1,3,5-trifluorobenzene (12.0 mM) in 1,2-dichloroethane was prepared. An aliquot (0.80 mL) of this stock solution was added to an oven-dried J. Young tube containing XeF_2 crystals (5.0 mg). The tube was sealed and immediately inserted into a Brüker AV-600 NMR probe that was pre-heated to the appropriate temperature. (Eyring measurements were conducted at 315 K, 320 K, 325 K, and 334 K.) The reaction was then monitored by taking ^{19}F NMR spectra (number of scans = 1, d1 = 5 s) every 30 s until **11-F₂** had completely disappeared and ethylfluorodimethylsilane had stopped growing in. (Reliable integrals were not obtained for trimethylsilylmethyl fluoride due to low concentration.) After baseline correction, each spectrum was individually phased and integrated against the internal standard. Plots of -ln([**11-F₂**]/[**11-F₂**]$_0$) versus time exhibited linear relationships (for example, Figure S1), indicating first-order kinetics. The slopes of the ln plots were used as k_{obs} to determine Eyring parameters. An example of a first-order plot at 320 K is shown in Figure S1, and the Eyring plot is shown in Figure S2.

Fluoride dependence. A stock solution of **11** (32.4 mM), H_2O (90.1 mM), and the internal standard 1,3,5-trifluorobenzene (9.61 mM) in dichloromethane was prepared. For each data point, an aliquot (1.00 mL) of this stock solution was added to an oven-dried J. Young tube containing XeF_2 crystals (5.5 mg). The tube was sealed and inverted twice to dissolve the XeF_2 and generate **11-F₂** *in situ*. The tube was reopened and microliter quantities of a commercial THF solution containing TBAF (1.0 M) and H_2O (2.5 M) were added by microsyringe. (Initial TBAF concentrations ranged from 0 mM to 56.6 mM.) The tube was sealed and immediately inserted into a Brüker AV-600 NMR probe that was pre-heated to 300 K, and the reaction was monitored by ^{19}F NMR as described above. Fluoride dependence was measured using the method of initial rates. k_{obs} was calculated in units of s^{-1} by dividing initial rate (Δ[**11-F₂**]/Δt) by [**11-F₂**]$_0$. A plot of k_{obs} vs [TBAF] is shown in Figure 2, and k_{obs} vs 1/[TBAF] is plotted in Figure S3.

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[11] Scott, V. J.; Labinger, J. A.; Bercaw, J. E. *Organometallics*, **2010**, *29*, 4090.

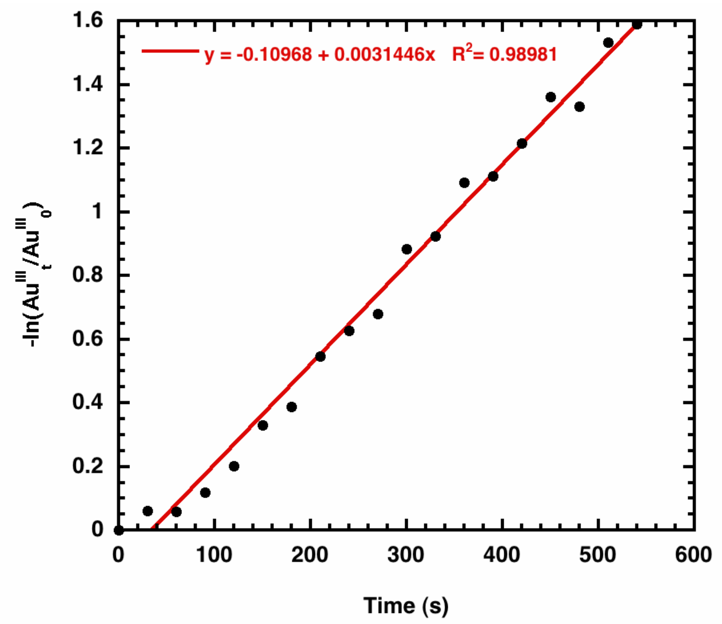

Figure S1. An example of a first-order plot for the decay of **11-F$_2$** in 1,2-dichloroethane solution at 320 K.

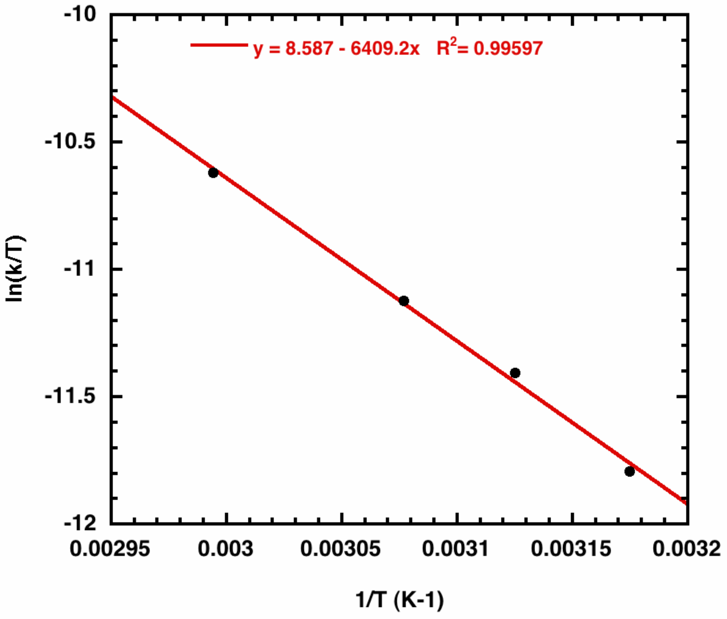

Figure S2. Eyring plot of the decay of **11-F$_2$** in 1,2-dichloroethane solution over the temperature range 315 K – 334 K.

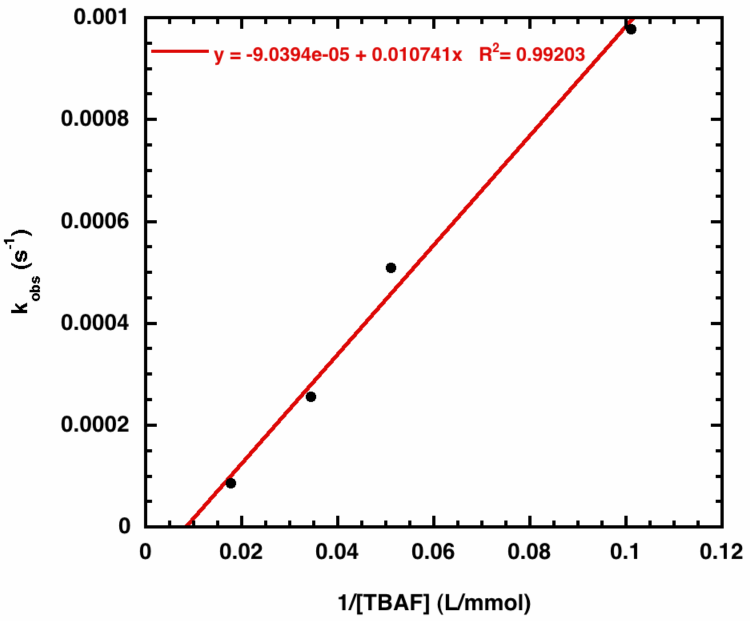

Figure S3. Dependence of the decay of **11-F$_2$** on 1/[TBAF] at 300 K in CH_2Cl_2 solution with excess H_2O. k_{obs} was determined by the method of initial rates.

X-ray crystallography. Low-temperature diffraction data were collected at the UC-Berkeley CHEXRAY crystallographic facility. Measurements were made with a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods using SHELXS[12] and refined against F^2 on all data by full-matrix least squares with SHELXL-97[13] using established methods.[14] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the *U* value of the atoms they are linked to (1.5 times for methyl groups). Details of the data quality and a summary of the residual values of the refinements are listed below.

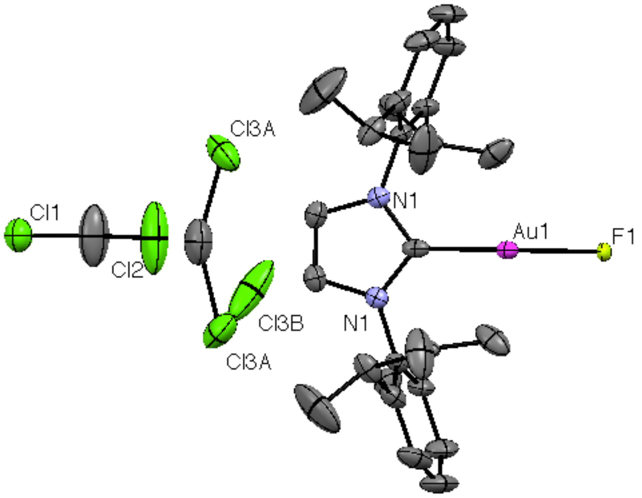

Figure S4. Representation of (IPr)AuF·2CH_2Cl_2 as 50% ellipsoids. Hydrogen atoms have been omitted for clarity. Disordered chloride components Cl3A and Cl3B each refined to 0.50 occupancy. An extended packing structure is shown in the main text (Figure 1).

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[12] Sheldrick, G. M. *Acta Cryst.* **1990**, *A46*, 467.
[13] Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112.
[14] Müller, P. *Crystallography Reviews* **2009**, *15*, 57.

Table S2. Crystal data and structure refinement for IPrAuF·2CH_2Cl_2.

Empirical formula	$C_{29}H_{40}AuCl_4FN_2$	
Formula weight	774.40	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/m$	
Unit cell dimensions	a = 9.3108(10) Å	α = 90°.
	b = 16.3917(17) Å	β = 103.594(2)°.
	c = 10.7713(11) Å	γ = 90°.
Volume	1597.9(3) $Å^3$	
Z	2	
Density (calculated)	1.610 Mg/m^3	
Absorption coefficient	4.964 mm^{-1}	
F(000)	768	
Crystal size	0.80 x 0.60 x 0.10 mm^3	
θ range for data collection	2.25 to 27.15°.	
Index ranges	$-11 \leq h \leq 11$, $-21 \leq k \leq 20$, $-13 \leq l \leq 13$	
Reflections collected	51743	
Independent reflections	3646 [R(int) = 0.0372]	
Completeness to θ = 27.15°	99.6 %	
Absorption correction	SADABS	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3646 / 24 / 198	
Goodness-of-fit on F^2	1.062	
Final R indices [I>2σ(I)]	R1 = 0.0282, wR2 = 0.0674	
R indices (all data)	R1 = 0.0309, wR2 = 0.0693	
Largest diff. peak and hole	2.576 and -3.025 e.$Å^{-3}$	

DFT calculations. Density functional calculations were carried out at the UC-Berkeley Molecular Graphics and Computational Facility using the Gaussian09 suite.[15] Calculations were conducted using the BPV86 functional and the LANL2DZ basis set for Au and I. The 6-31G(d) basis set was used for C, H, N, F, Cl, and Br during geometry optimizations. The 6-311G++(d,p) basis set was used for C, H, N, F, Cl, and Br during final energy calculations, population analyses, and charge analyses. Implicit dichloromethane solvation was included in all calculations using the default PCM model. Molecular orbital plots were created using the program VMD 1.8.7.[16] Mülliken population analysis was used to determine relative atomic orbital contributions to molecular orbitals. NBO analysis was used to examine electrostatic charge distribution. Optimized XYZ coordinates for all calculated molecules are enclosed below.

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[15] Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

[16] Humphrey, W., Dalke, A. and Schulten, K., "VMD - Visual Molecular Dynamics", *J. Molec. Graphics* **1996**, *14*, 33-38.

Table S3. Geometric parameters for optimized alkylgold(III) fluoride complexes[a]

Complex	d(Au-C$_{carbene}$)	d(Au-C$_{alkyl}$)	d(Au-F)[b]	d(Au-F)[c]
cis-$F_2Au(CH_2$*t*Bu)(IPr)	1.992	2.110	2.014	2.112
[FAu(CH_2*t*Bu)(IPr)]$^+$	1.995	2.180	1.995	N/A

[a] Distances measured in Å. [b] Corresponds to fluoride *cis* to the alkyl. [c] Corresponds to fluoride *trans* to the alkyl.

Table S4. Summary of computational results for [(IPr)Au(CH_2*t*Bu)(X)]$^+$ as a function of X

Complex	d(Au-C$_{alkyl}$)	%Au in LUMO	%C in LUMO	Au natural charge	CH_2 natural charge	Halide natural charge
[(IPr)Au(CH_2*t*Bu)(F)]$^+$	2.180	0.20	0.43	0.861	0.113	-0.621
[(IPr)Au(CH_2*t*Bu)(Cl)]$^+$	2.215	0.18	0.42	0.690	0.144	-0.527
[(IPr)Au(CH_2*t*Bu)(Br)]$^+$	2.215	0.17	0.42	0.607	0.138	-0.421
[(IPr)Au(CH_2*t*Bu)(I)]$^+$	2.224	0.17	0.41	0.480	0.136	-0.294

Optimized XYZ coordinates for *cis*-$F_2Au(CH_2{}^tBu)$(IPr) (**10-F$_2$**)

Au	0.00028	0.00185	-1.36731
C	-0.01616	-0.41878	0.57936
C	-0.7211	-1.18176	2.58843
H	-1.4469	-1.46274	3.34542
C	0.64436	-1.2055	2.59455
H	1.35286	-1.51291	3.35756
C	2.47028	-0.53355	1.00978
C	3.10193	0.65183	1.468
C	4.46859	0.80983	1.16669
H	4.99036	1.71116	1.50146
C	5.16906	-0.16615	0.45036
H	6.23038	-0.02061	0.22403
C	4.51933	-1.33216	0.02925
H	5.08329	-2.08996	-0.52121
C	3.15537	-1.55584	0.30229
C	2.38475	1.70888	2.30988
H	1.29549	1.56539	2.19013
C	2.72075	1.52796	3.81028
H	3.80386	1.65577	3.98323
H	2.43685	0.52894	4.18101
H	2.18687	2.28136	4.41563
C	2.71082	3.15234	1.87133
H	3.76039	3.41856	2.08591
H	2.07321	3.86294	2.42474
H	2.53815	3.30371	0.79251
C	2.48695	-2.87073	-0.09786
H	1.41943	-2.67149	-0.29442
C	2.61305	-3.90666	1.04467
H	3.67387	-4.13182	1.25848
H	2.11572	-4.85012	0.75765
H	2.1477	-3.55229	1.9804
C	3.0407	-3.45613	-1.41185
H	2.98926	-2.72065	-2.23197
H	2.43375	-4.33009	-1.70428
H	4.08565	-3.80253	-1.31768
C	-2.51027	-0.45569	0.98833
C	-3.22699	-1.4706	0.30232
C	-4.58489	-1.21292	0.02929
H	-5.17257	-1.96477	-0.50432
C	-5.19888	-0.02036	0.429
H	-6.25662	0.15106	0.20403
C	-4.46667	0.95064	1.12011
H	-4.95972	1.87484	1.43534
C	-3.10421	0.75859	1.42033
C	-2.59654	-2.80953	-0.07982
H	-1.52328	-2.6423	-0.27461
C	-2.75735	-3.83	1.07207
H	-2.28514	-3.48085	2.00627
H	-2.28712	-4.79051	0.79606
H	-3.82514	-4.02173	1.28377
C	-3.16307	-3.39122	-1.3901
H	-4.21789	-3.70613	-1.29592
H	-2.58073	-4.285	-1.67248
H	-3.08778	-2.66507	-2.21658

C	-2.34902	1.81414	2.22996
H	-1.26573	1.64252	2.09368
C	-2.66155	1.67117	3.73928
H	-3.73848	1.82482	3.929
H	-2.10151	2.42571	4.31907
H	-2.39035	0.67433	4.125
C	-2.64747	3.25597	1.76696
H	-2.49977	3.3786	0.68068
H	-1.97649	3.96075	2.28738
H	-3.68322	3.55643	2.00276
C	0.04675	2.07189	-0.96381
H	-0.8612	2.2343	-0.35855
H	0.92734	2.18573	-0.30931
F	0.01293	0.18955	-3.37245
N	1.06738	-0.72849	1.35308
N	-1.11647	-0.69136	1.34299
F	-0.0507	-2.09315	-1.62738
C	0.10636	3.0674	-2.13603
C	1.38338	2.8684	-2.97959
C	-1.14931	2.96184	-3.02726
C	0.1458	4.47823	-1.48697
H	2.28906	2.92361	-2.34702
H	1.3479	1.88399	-3.47085
H	1.46379	3.65368	-3.75366
H	-2.07117	3.09444	-2.43043
H	-1.13726	3.74454	-3.80785
H	-1.17243	1.97309	-3.51035
H	0.17596	5.25169	-2.27644
H	-0.74755	4.66581	-0.86423
H	1.04014	4.60985	-0.85139

Optimized XYZ coordinates for (F)Au(CH_2tBu)(IPr) (**10-F**$^+$)

Au	0.09866	-0.00006	-1.3337
C	0.06199	0.42838	0.61433
C	0.80338	1.11056	2.63681
H	1.5423	1.34939	3.39593
C	-0.56099	1.22026	2.63557
H	-1.25258	1.57682	3.39271
C	-2.40484	0.74342	0.99213
C	-3.20914	-0.31513	1.4899
C	-4.55938	-0.33137	1.09061
H	-5.21366	-1.1304	1.45104
C	-5.08027	0.657	0.24692
H	-6.13224	0.61919	-0.05267
C	-4.26516	1.7031	-0.19937
H	-4.69123	2.48444	-0.83597
C	-2.90795	1.78205	0.16954
C	-2.69035	-1.37072	2.46875
H	-1.58601	-1.33534	2.46757
C	-3.16404	-1.05121	3.90772
H	-4.26618	-1.0729	3.9697
H	-2.82902	-0.05544	4.24379
H	-2.76751	-1.80093	4.61414
C	-3.10848	-2.80613	2.08568
H	-4.19853	-2.95285	2.17376

H	-2.62405	-3.52897	2.76391
H	-2.8182	-3.05984	1.05222
C	-2.0793	2.99458	-0.25298
H	-1.02556	2.8126	0.02343
C	-2.54284	4.25298	0.51861
H	-3.58827	4.50687	0.27014
H	-1.91066	5.11721	0.25048
H	-2.48019	4.10513	1.61024
C	-2.11955	3.23697	-1.77656
H	-1.77493	2.35144	-2.33852
H	-1.46664	4.08697	-2.03955
H	-3.13762	3.48185	-2.12554
C	2.54952	0.35742	0.99307
C	3.25747	1.37652	0.30894
C	4.60231	1.11103	-0.015
H	5.18437	1.87328	-0.54207
C	5.20734	-0.10159	0.33329
H	6.25547	-0.28201	0.07492
C	4.47856	-1.08424	1.01464
H	4.96614	-2.02565	1.28407
C	3.12962	-0.88241	1.36286
C	2.64568	2.73037	-0.04707
H	1.56983	2.70274	0.20136
C	3.28183	3.85953	0.79599
H	3.16005	3.67524	1.87695
H	2.80752	4.82682	0.55575
H	4.36217	3.95062	0.58708
C	2.76084	3.03462	-1.55673
H	3.81407	3.13565	-1.87122
H	2.25187	3.98577	-1.7896
H	2.30352	2.23797	-2.16972
C	2.36754	-1.95657	2.13856
H	1.28886	-1.71971	2.08839
C	2.77482	-1.94917	3.63094
H	3.84771	-2.18439	3.74402
H	2.19858	-2.70811	4.18809
H	2.59296	-0.96793	4.10103
C	2.55592	-3.36565	1.53656
H	2.32037	-3.3855	0.4583
H	1.89476	-4.08456	2.04995
H	3.59096	-3.72825	1.65786
C	-0.54463	-2.04514	-0.93707
H	0.19373	-2.32403	-0.17217
H	-1.53309	-1.82214	-0.50821
F	0.25458	-0.09627	-3.31983
N	-1.00564	0.78684	1.38943
N	1.17211	0.61445	1.39029
C	-0.56323	-2.93421	-2.15618
C	-1.61501	-2.50514	-3.19576
C	0.82505	-3.10433	-2.80322
C	-0.99883	-4.3039	-1.51197
H	-2.61209	-2.38482	-2.73651
H	-1.30702	-1.55065	-3.6504
H	-1.69391	-3.26755	-3.98939
H	1.58863	-3.39143	-2.05845

H	0.78645	-3.89374	-3.57303
H	1.12461	-2.15904	-3.283
H	-1.04732	-5.04047	-2.33326
H	-0.27049	-4.66502	-0.76735
H	-1.99568	-4.24723	-1.0445

Optimized XYZ coordinates for (Cl)Au(CH$_2$*t*Bu)(IPr) (**10-Cl**$^+$)

Au	0.24085	-0.3085	-1.19918
C	0.16847	0.47643	0.66189
C	0.99527	1.39536	2.55488
H	1.7598	1.65878	3.28019
C	-0.34435	1.67061	2.50889
H	-0.98472	2.23107	3.18326
C	-2.24349	1.15376	0.94954
C	-3.17482	0.36005	1.67199
C	-4.52079	0.426	1.26294
H	-5.26971	-0.17059	1.79227
C	-4.91808	1.24382	0.19844
H	-5.96965	1.27377	-0.10329
C	-3.97877	2.04	-0.46613
H	-4.30848	2.7002	-1.27376
C	-2.61742	2.02739	-0.10299
C	-2.79079	-0.49383	2.88315
H	-1.68961	-0.56607	2.92725
C	-3.26947	0.1849	4.18951
H	-4.37052	0.26424	4.20861
H	-2.85993	1.20293	4.30317
H	-2.95537	-0.41047	5.06413
C	-3.33589	-1.93523	2.80565
H	-4.43894	-1.96068	2.81734
H	-2.98396	-2.51253	3.67775
H	-2.994	-2.45437	1.89539
C	-1.65086	3.00384	-0.77323
H	-0.62145	2.74555	-0.46927
C	-1.92518	4.44324	-0.2761
H	-2.93975	4.77415	-0.55979
H	-1.20084	5.14438	-0.72576
H	-1.83897	4.51502	0.82147
C	-1.70276	2.93134	-2.31328
H	-1.48857	1.91174	-2.6775
H	-0.952	3.61482	-2.74552
H	-2.68883	3.23306	-2.70684
C	2.63338	0.21574	1.05101
C	3.45581	1.11302	0.3243
C	4.7527	0.6683	0.00218
H	5.41977	1.32797	-0.56125
C	5.20323	-0.59771	0.39388
H	6.21626	-0.92007	0.13359
C	4.36693	-1.4514	1.12379
H	4.73751	-2.43398	1.43177
C	3.05855	-1.06759	1.47412
C	3.00501	2.51203	-0.09121
H	1.95161	2.64515	0.21242
C	3.83194	3.59977	0.63148
H	3.76192	3.50095	1.72819

H	3.46526	4.6026	0.35179
H	4.89874	3.54123	0.35345
C	3.06634	2.69415	-1.62365
H	4.10056	2.61021	-1.99988
H	2.68774	3.69274	-1.90211
H	2.45537	1.93428	-2.14183
C	2.17973	-2.00571	2.29836
H	1.16943	-1.564	2.36429
C	2.72056	-2.14234	3.7401
H	3.7291	-2.59154	3.74259
H	2.05785	-2.79374	4.3358
H	2.78405	-1.16288	4.24382
C	2.03598	-3.39098	1.63131
H	1.65942	-3.30452	0.59716
H	1.33321	-4.01762	2.20724
H	3.00068	-3.92565	1.59111
C	-1.21543	-1.85204	-0.56605
H	-0.61952	-2.30296	0.24001
H	-1.99339	-1.16955	-0.19647
Cl	0.7703	-0.72911	-3.46389
N	-0.84452	1.09184	1.34403
N	1.29441	0.65735	1.41474
C	-1.67185	-2.80706	-1.63378
C	-2.4491	-2.13218	-2.77767
C	-0.5711	-3.74754	-2.15326
C	-2.69602	-3.66803	-0.78458
H	-3.23127	-1.45686	-2.38917
H	-1.76796	-1.54943	-3.41849
H	-2.93744	-2.89791	-3.40345
H	-0.04221	-4.24739	-1.32303
H	-1.01779	-4.52824	-2.79193
H	0.16396	-3.19021	-2.75548
H	-3.09455	-4.43661	-1.46962
H	-2.21137	-4.18041	0.06233
H	-3.53942	-3.0631	-0.41512

Optimized XYZ coordinates for (Br)Au(CH_2*t*Bu)(IPr) (**10-Br**$^+$)

Au	-0.24816	-1.04654	-0.19403
C	-0.00907	0.84936	0.49145
C	-0.63907	2.825	1.39092
H	-1.32859	3.61771	1.66666
C	0.7046	2.67966	1.60576
H	1.42258	3.31769	2.1125
C	2.44833	0.95986	1.04789
C	3.38733	1.56656	0.17162
C	4.70306	1.06494	0.19829
H	5.4561	1.50678	-0.46114
C	5.06558	0.02032	1.05638
H	6.09397	-0.35407	1.05655
C	4.12152	-0.53274	1.92848
H	4.42479	-1.32786	2.61581
C	2.79001	-0.07329	1.95725
C	3.04963	2.75483	-0.7321
H	1.95314	2.88262	-0.7477
C	3.66612	4.05492	-0.16235

H	4.7683	3.9919	-0.14768
H	3.32928	4.25516	0.86888
H	3.38248	4.91744	-0.78979
C	3.50315	2.54741	-2.19244
H	4.60033	2.46521	-2.27614
H	3.18913	3.40932	-2.80575
H	3.06136	1.63829	-2.63269
C	1.82595	-0.6306	3.00456
H	0.80618	-0.27982	2.76706
C	2.18562	-0.07649	4.40374
H	3.19448	-0.40378	4.71122
H	1.46501	-0.44419	5.15472
H	2.16754	1.02657	4.41935
C	1.7859	-2.173	3.01549
H	1.52284	-2.57846	2.02343
H	1.03069	-2.52253	3.7403
H	2.75542	-2.60743	3.31509
C	-2.44404	1.44623	0.30751
C	-3.27926	0.72883	1.20129
C	-4.61962	0.54448	0.81067
H	-5.29869	-0.00146	1.4724
C	-5.09957	1.05314	-0.40184
H	-6.14642	0.8985	-0.68126
C	-4.24818	1.7653	-1.25507
H	-4.63856	2.16508	-2.19594
C	-2.89756	1.98381	-0.92254
C	-2.80035	0.20751	2.55513
H	-1.6996	0.296	2.59104
C	-3.37348	1.0713	3.70295
H	-3.08968	2.13213	3.59565
H	-2.99642	0.71091	4.67575
H	-4.4761	1.01628	3.7239
C	-3.13912	-1.28368	2.76547
H	-4.22875	-1.45712	2.79369
H	-2.72524	-1.62783	3.72907
H	-2.714	-1.91151	1.96353
C	-2.00444	2.79929	-1.85526
H	-0.96772	2.73996	-1.47971
C	-2.41361	4.29057	-1.84587
H	-3.44632	4.41992	-2.21458
H	-1.7435	4.87338	-2.50147
H	-2.361	4.721	-0.83133
C	-2.00796	2.23924	-3.29369
H	-1.73053	1.17115	-3.31191
H	-1.28895	2.79627	-3.9187
H	-3.0009	2.33461	-3.7661
C	1.03998	-0.53188	-1.92086
H	0.50824	0.36975	-2.25575
H	1.95283	-0.30153	-1.35231
Br	-0.98808	-3.39598	-0.38459
N	1.08263	1.46357	1.03978
N	-1.0632	1.69372	0.70069
C	1.19296	-1.60402	-2.9666
C	1.94847	-2.85157	-2.47647
C	-0.11708	-1.9669	-3.6885

C	2.12653	-0.83945	-3.99245
H	2.89133	-2.57882	-1.97116
H	1.32819	-3.4309	-1.77306
H	2.1942	-3.5019	-3.33278
H	-0.6398	-1.06657	-4.05607
H	0.09926	-2.61401	-4.55511
H	-0.79391	-2.51435	-3.01189
H	2.3011	-1.53682	-4.83023
H	1.65146	0.07058	-4.39297
H	3.10217	-0.58179	-3.55036

Optimized XYZ coordinates for (I)Au(CH_2*t*Bu)(IPr) (**10-I**$^+$)

Au	-0.38425	-0.81083	-0.06536
C	0.23371	1.10103	0.29188
C	-0.02785	3.29858	0.75699
H	-0.56173	4.24072	0.84004
C	1.26237	2.95934	1.06096
H	2.08053	3.54555	1.46838
C	2.65875	0.87488	0.93653
C	3.72569	1.14727	0.039
C	4.91642	0.41815	0.22402
H	5.76232	0.59823	-0.44604
C	5.03993	-0.52336	1.2524
H	5.97464	-1.07969	1.37331
C	3.97977	-0.7396	2.14026
H	4.10181	-1.45373	2.95975
C	2.76321	-0.04055	2.01456
C	3.6557	2.21976	-1.05078
H	2.60741	2.55277	-1.14867
C	4.50493	3.44749	-0.64216
H	5.571	3.17306	-0.55756
H	4.19039	3.86426	0.32972
H	4.41624	4.24256	-1.40239
C	4.09956	1.70535	-2.43603
H	5.16067	1.40221	-2.443
H	3.98106	2.50695	-3.18508
H	3.49779	0.84208	-2.76372
C	1.67533	-0.21545	3.07373
H	0.74298	0.23938	2.6956
C	2.07095	0.5455	4.36177
H	2.99466	0.12669	4.79854
H	1.26869	0.46115	5.11525
H	2.24565	1.61666	4.16216
C	1.36533	-1.69552	3.37854
H	1.06435	-2.23999	2.46693
H	0.53743	-1.76138	4.10505
H	2.23203	-2.21736	3.81965
C	-2.04687	2.05354	-0.09936
C	-3.00096	1.79408	0.91673
C	-4.34846	1.70921	0.51524
H	-5.11889	1.5085	1.26596
C	-4.71973	1.88633	-0.82268
H	-5.77397	1.81831	-1.10881
C	-3.75073	2.16231	-1.79543
H	-4.05895	2.31488	-2.83431

C	-2.38657	2.25401	-1.46045
C	-2.63655	1.6565	2.39511
H	-1.5381	1.71473	2.49136
C	-3.23075	2.82586	3.21434
H	-2.89776	3.80388	2.82707
H	-2.9158	2.74753	4.2693
H	-4.33439	2.81023	3.18953
C	-3.07484	0.29607	2.97808
H	-4.16923	0.16275	2.92218
H	-2.78377	0.23087	4.04083
H	-2.60311	-0.54362	2.43915
C	-1.35418	2.60148	-2.53123
H	-0.34693	2.46292	-2.09914
C	-1.47757	4.08644	-2.94545
H	-2.46646	4.29055	-3.39198
H	-0.70728	4.33872	-3.69488
H	-1.35085	4.76081	-2.08149
C	-1.45805	1.67772	-3.76373
H	-1.39485	0.61312	-3.47915
H	-0.64014	1.89923	-4.47079
H	-2.40918	1.82292	-4.30448
C	1.15721	-0.95728	-1.66136
H	0.77915	-0.14569	-2.29902
H	2.01731	-0.65515	-1.04786
I	-1.80739	-3.07507	0.13958
N	1.4144	1.60643	0.76038
N	-0.64593	2.14586	0.28415
C	1.31666	-2.2861	-2.34888
C	1.7889	-3.41963	-1.42095
C	0.11859	-2.70323	-3.21747
C	2.51764	-1.91959	-3.31859
H	2.64435	-3.10275	-0.79898
H	0.97496	-3.74404	-0.75162
H	2.10336	-4.28981	-2.02108
H	-0.18389	-1.89392	-3.90434
H	0.38479	-3.58469	-3.82476
H	-0.74817	-2.9704	-2.59115
H	2.72671	-2.8286	-3.90912
H	2.25727	-1.10803	-4.01698
H	3.42938	-1.64872	-2.76316