

Supporting Information for
A Carbene-stabilized Gold(I) Fluoride: Synthesis and Theory

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General Considerations. Unless stated otherwise, all synthetic manipulations were carried out using standard Schlenk techniques under an argon atmosphere, or in an Innovative Technologies glovebox under an atmosphere of purified nitrogen. Reactions were carried out in flame-dried glassware cooled under vacuum. Elemental analyses were performed by Atlantic Microlabs, Inc., Norcross, GA, or Desert Analytics, Tucson, AZ. Anhydrous toluene, hexanes, tetrahydrofuran, and diethyl ether were purchased from Aldrich in 18 L Pure-Pac™ solvent delivery kegs and sparged vigorously with argon for 40 minutes prior to first use. The solvents were further purified by passing them under argon pressure through two packed columns of neutral alumina (for diethyl ether and tetrahydrofuran; the tetrahydrofuran was also passed through a third column packed with activated 4Å molecular sieves) or through neutral alumina and copper(II) oxide (for toluene and hexanes). Benzene, and pentane, anhydrous, were purchased from Aldrich in Sure-Seal™ bottles, and stored in a glove box over 4Å molecular sieves. All non-dried solvents used were reagent grade or better.

IR spectra were recorded on a Nicolet Impact 410 spectrometer as KBr pellets. NMR solvents were dried as follows: C₆D₆ (Cambridge Isotope Laboratories) over sodium/benzophenone, CD₂Cl₂ (Cambridge Isotope Laboratories) over calcium hydride. All NMR solvents were degassed by three freeze-pump-thaw cycles and vacuum-transferred prior to use. ¹H NMR spectra were recorded on a

Varian 300 MHz instrument, with shifts reported relative to the residual solvent peak. ^{19}F NMR were recorded on a Varian 300 MHz instrument, with shifts referenced to an external standard of neat CFCl_3 (0 ppm). ^{13}C NMR spectra were recorded on a Varian 300 MHz or a Varian 500 MHz instrument, with shifts referenced relative to the solvent peak.

The starting materials silver(I) oxide (Strem), chloro(dimethylsulfide)gold(I) (Aldrich), sodium *tert*-butoxide (Aldrich), triethylamine trihydrogen fluoride (Aldrich), were used as received. 1,3-Bis(2,6-diisopropylphenyl)imidazolinium chloride¹ (*SIPr* $\bullet\text{HCl}$) was synthesized as described previously.

[1,3-Bis(2,6-diisopropylphenyl)imidazolin-2-ylidene]silver(I) chloride

This complex was synthesized by a route analogous to that developed by Wang and Lin:² In a fume hood, an Erlenmeyer was charged with *SIPr* $\bullet\text{HCl}$ (12.95 g, 30.92 mmol), silver(I) oxide (4.30 g, 18.55 mmol). Dichloromethane (200 mL) was added, and the mixture was stirred in the dark for 24 hours. The mixture was filtered and concentrated *in vacuo*. The resulting yellow solid was suspended in diethyl ether (20 mL), collected by filtration to give the title compound as a white solid (13.37 g, 81 %).

^1H NMR (CD_2Cl_2): δ 7.46 (t, $J = 7.8$ Hz, 2 H, *para*-CH), 7.29 (d, $J = 7.6$ Hz, 4 H, *meta*-CH), 4.08 (s, 4 H, NCH_2), 3.07 (sept., $J = 6.9$ Hz, 4 H, $\text{CH}(\text{CH}_3)_2$), 1.34 (pseudo t, $J = 6.8$ Hz, 24 H, $\text{CH}(\text{CH}_3)_2$). ^{13}C NMR (CD_2Cl_2): δ 207.9(d, $J_{\text{C}-^{109}\text{Ag}} = 253$ Hz, $J_{\text{C}-^{107}\text{Ag}} = 237$ Hz, $\underline{\text{C}_{\text{ipso}}-\text{Ag}}$)³, 147.3 (*ortho*-C), 135.2 (*ipso*-C), 130.4 (*para*-C), 125.1 (*meta*-C), 54.5 (d, $J_{\text{Ag-C}} = 8.6$ Hz, NCH_2), 29.3 ($\underline{\text{CH}}(\text{CH}_3)_2$), 25.7 ($\text{CH}(\underline{\text{CH}}_3)_2$), 24.3 ($\text{CH}(\underline{\text{CH}}_3)_2$). Anal. Calcd. for $\text{C}_{27}\text{H}_{38}\text{N}_2\text{AgCl}$: C, 60.74; H, 7.17. Found: C, 60.87; H, 7.11.

[1,3-Bis(2,6-diisopropylphenyl)imidazolin-2-ylidene]gold(I) chloride. This complex was synthesized by a route analogous to that of Lin and co-workers⁴: An Erlenmeyer flask was charged with (*SIPr*) AgCl (0.848 g, 1.61 mmol), and chloro(dimethylsulfide)-gold(I) (0.475 g, 1.61 mmol). Dichloromethane (50

mL) was added followed by dimethylsulfide (1 mL, 13.62 mmol). The mixture was stirred in the dark for 60 hours, filtered and concentrated *in vacuo*. The resulting yellow solid was washed with diethyl ether (2 x 5 mL) to afford the title compound as a cream-colored solid (0.902 g, 90%). ¹H NMR (CD₂Cl₂): δ 7.48 (t, *J* = 7.8 Hz, 2 H, *para*-CH), 7.29 (d, *J* = 7.6 Hz, 4 H, *meta*-CH), 4.06 (s, 4 H, NCH₂), 3.06 (sept., *J* = 6.9 Hz, 4 H, CH(CH₃)₂), 1.40 (d, *J* = 6.7 Hz, 12 H, CH(CH₃)₂), 1.34 (d, *J* = 6.9 Hz, 12 H, CH(CH₃)₂). ¹³C NMR (CD₂Cl₂): δ 196.3 (NCAu), 147.3 (*ortho*-C), 134.6 (*ipso*-C), 130.5 (*para*-C), 125.1 (*meta*-C), 54.1 (NCH₂), 29.4 (CH(CH₃)₂), 25.3 (CH(CH₃)₂), 24.4 (CH(CH₃)₂). Anal. Calcd. for C₂₇H₃₈N₂AuCl: C, 52.05; H, 6.15. Found: C, 51.81; H, 5.87.

[1,3-Bis(2,6-diisopropylphenyl)imidazolin-2-ylidene]gold (I) *tert*-butoxide (1). In a glove box, a scintillation vial was charged with (SIPr)AuCl (0.210 g, 0.34 mmol) and sodium *tert*-butoxide (0.033 g, 0.34 mmol). Benzene (10 mL) was added, and the mixture was stirred in the dark for 2 hours. The resulting suspension was filtered through Celite, and concentrated *in vacuo* to afford **1** as an off-white solid (0.210 g, 93 %). ¹H NMR (C₆D₆): δ 7.22 (t, *J* = 7.8 Hz, 2 H, *para*-CH), 7.07 (d, *J* = 7.6 Hz, 4 H, *meta*-CH), 3.18 (s, 4 H, NCH₂), 2.99 (sept., *J* = 6.9 Hz, 4 H, CH(CH₃)₂), 1.54 (d, *J* = 6.7 Hz, 12 H, CH(CH₃)₂), 1.31 (s, 9 H, O(CH₃)₃), 1.18 (d, *J* = 7.0 Hz, 12 H, CH(CH₃)₂). ¹³C NMR (C₆D₆): δ 196.0 (NCAu), 147.1 (*ortho*-C), 135.7 (*ipso*-C), 130.2 (*para*-C), 124.9 (*meta*-C), 71.5 (OC(CH₃)₃), 53.3 (NCH₂), 37.0 (OC(CH₃)₃, 29.5 (CH(CH₃)₂), 25.5 (CH(CH₃)₂), 24.7 (CH(CH₃)₂). Anal. Calcd. for C₃₁H₄₇N₂AuO: C, 56.36; H, 7.17. Found: C, 56.53; H, 7.30.

[1,3-Bis(2,6-diisopropylphenyl)imidazolin-2-ylidene]gold(I) fluoride (2). In a glove box, a round bottom flask wrapped in aluminum foil was charged with SIPrAuOt-Bu (0.551 g, 0.83 mmol). Benzene (20 mL) was added, the flask was sealed with a septum, and taken out of the glovebox. Triethylamine trihydrofluoride (0.045 mL, 0.28 mmol) was added via syringe, and the mixture was stirred for 2 hours.

The resulting suspension was collected by filtration in a glove box. The white solid was then dissolved in dichloromethane (2 mL) and hexanes were vapor diffused into it at -40°C . After 24 hours, crystals had grown, and the supernatant was decanted off to give **2** (0.244 g, 48 %). ^1H NMR (CD_2Cl_2): δ 7.48 (t, $J = 7.8$ Hz, 2 H, *para*-CH), 7.29 (d, $J = 7.6$ Hz, 4 H, *meta*-CH), 4.06 (s, 4 H, NCH_2), 3.06 (sept., $J = 6.9$ Hz, 4 H, $\text{CH}(\text{CH}_3)_2$), 1.40 (d, $J = 6.7$ Hz, 12 H, $\text{CH}(\text{CH}_3)_2$), 1.34 (d, $J = 6.9$ Hz, 12 H, $\text{CH}(\text{CH}_3)_2$). ^{19}F NMR (CD_2Cl_2): δ -247.0. ^{13}C NMR (CD_2Cl_2): δ 185.9 (d, $J_{\text{C}-\text{F}} = 60.5$ Hz, NCAu), 147.3 (*ortho*-C), 134.8 (*ipso*-C), 130.4 (*para*-C), 125.2 (*meta*-C), 53.9 (d, $J_{\text{C}-\text{F}} = 1.7$ Hz, NCH_2), 29.5 ($\text{CH}(\text{CH}_3)_2$), 25.3 ($\text{CH}(\text{CH}_3)_2$), 24.4 ($\text{CH}(\text{CH}_3)_2$). Anal. Calcd. $\text{C}_{27}\text{H}_{38}\text{N}_2\text{AuF}$: C, 53.46; H, 6.31. Found: C, 53.42; H, 6.50. IR (KBr pellet): 500 cm^{-1} (Au–F stretch).

Computational Details. Calculations were performed within the Gaussian 98 program suite,⁵ and employed the exchange functional of Becke⁶ along with the correlation functional of Perdew.⁷ Integrals over one-electron operators were evaluated throughout with a (75,302) grid that was pruned for nonmetal atoms. Nonmetal atoms were described with the 6-31+G(d,p) basis set.⁸ The gold orbitals were described with the Stuttgart effective core potential and their associated basis set,⁹ which was contracted as follows: Au, (8s,7p,6d) \rightarrow [6s,5p,3d]. Relativistic effects with the Stuttgart ECP and its associated basis set are introduced with a potential term (i.e., a one-electron operator) that replaces the two-electron exchange- and Coulomb operators resulting from interaction between core electrons and between core- and valence electrons. In this way, relativistic effects, especially the scalar effects, are included implicitly, rather than as explicit four-component, one-electron functions in the Dirac equation.

All calculations incorporate implicit solvation in methylene chloride through Tomasi's polarizable continuum model (PCM) at 298.15 K, with dielectric constant $\epsilon = 8.93$. Self-consistent field convergence was achieved with Pulay's direct inversion in the iterative subspace extrapolation.¹⁰

Equilibrium geometries of complexes lacking specific CH₂Cl₂ were optimized in redundant internal coordinates,¹¹ without imposed symmetry. Harmonic frequency calculations confirm the structures so generated to be energy minima. Geometry optimizations of specifically solvated complexes also proceeded in redundant internal coordinates, with implicit (PCM) methylene chloride solvation, and were unconstrained, except as follows: (i) distances between F and methylene chloride carbons were fixed at their crystallographic values, (ii) One F–C–Cl angle per solvent was constrained to the experimental value, and (iii) one Cl–C_(solv)–C_(carbene)–N dihedral angle per solvent molecule was fixed at the crystallographic value. Despite these constraints, net motion of CH₂Cl₂ is still possible. Force-constant matrix diagonalization found imaginary vibrational frequencies for all specifically solvated structures; the imaginary frequencies corresponded to CH₂Cl₂ libration or carbene rotation. Stability tests validated the integrity of all converged densities.

Population analyses were performed with the program AOMix by Gorelsky.^{12,13}

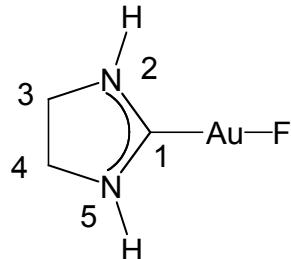


Table S1. Selected interatomic distances for **2** vs. **A**. Labels in parentheses refer to crystallographic designations.

Interatomic distance	Calculated	Observed
M = Au		
M–F	2.029	2.028(2)
M–C ₁	1.974	1.956(3)
C ₁ –N ₂ (C ₁ –N ₂ , .res)	1.349	1.342(3)
N ₂ –C ₃ (N ₂ –C ₃ , .res)	1.480	1.481(3)
C ₃ –C ₄ (C ₂ –C ₃ , .res)	1.551	1.534(4)
C ₄ –N ₅ (C ₂ –N ₁ , .res)	1.480	1.472(4)
C ₁ –N ₅ (C ₁ –N ₁ , .res)	1.349	1.338(3)
rms dev.	0.011	
av. dev.	+0.009	

Table S2. Calculated natural atomic charges.

BP86

	A , no specific solvation	A , with specific solvation ^a
Au	0.420	0.468
Carbene C ^b	0.200	0.226
Fluorine	−0.775	−0.796
Solvent carbons		−0.503, −0.502
Chlorines		−0.050, −0.051, −0.052, −0.053
Proximal CH ₂ Cl ₂ hydrogen		0.315, 0.316
Remote CH ₂ Cl ₂ hydrogen		0.279, 0.280

^a Correspondingly calculated charges on methylene chloride (PCM CH₂Cl₂ solvation): C, −0.530; Cl, −0.030; H, 0.295.

B3LYP

	A, no specific solvation	A, with specific solvation ^a
Au	0.462	0.468
Carbene C ^b	0.226	0.226
Fluorine	-0.804	-0.796
Solvent carbons		-0.502, -0.503
Chlorines		-0.050, -0.051, -0.052, -0.054
Proximal CH ₂ Cl ₂ hydrogen		0.315, 0.316
Remote CH ₂ Cl ₂ hydrogen		0.279, 0.279

^a Correspondingly calculated charges on methylene chloride (PCM CH₂Cl₂ solvation): C, -0.530; Cl, -0.030; H, 0.295.

Table S3. Calculated interatomic distances (\AA) associated with solvating methylene chlorides in **A**.

A	
F–proximal H	2.177, 2.132
Proximal H–C	1.103, 1.103
Remote H–C	1.097, 1.097
C–Cl	1.802, 1.802, 1.803, 1.803
M–F	2.050
M–C _(carbene)	1.975

Table S4. Mulliken electrostatic charges calculated for selected atoms of **A** with variations in basis set and functional.

	BP86/ 6-31+G(d,p)	BP86/6-31G(d)	BP86/6-31G	B3LYP/6- 31+G(d,p)
Au ^a	-0.714145	-0.176945	-0.162770	-0.560115
C _{carbene}	0.433350	0.387030	0.469926	0.408689
F	-0.473835	-0.400855	-0.378936	-0.541312

^a In all instances, the gold atom is described by the Stuttgart 1997 ECP and basis set.

X-ray Diffraction Study of [1,3-Bis(2,6-diisopropylphenyl)imidazolin-2-ylidene]gold(I) fluoride (2): Performed on a single crystal grown by the vapor diffusion of hexanes into dichloromethane solution of **2** at -40 °C. A colorless crystal was removed from the supernatant and transferred onto a microscope slide coated with Paratone N oil. The crystal was affixed to a glass fiber using the oil, frozen in a nitrogen stream, and optically centered. The data were collected on a Siemens three-circle platform goniometer equipped with a Bruker Smart Apex CCD detector with graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$), using both phi and omega scans at -173 °C. The structure was solved by direct methods (SHELXS)¹⁴ and refined against F^2 on all data by full matrix least squares with

SHELXL-97 (Sheldrick, G. M. *SHELXL* 97; Universität Göttingen: Göttingen, Germany, 1997). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at idealized positions and refined using a riding model. Four peaks of significant residual electron density was found less than one angstrom from gold ($1.32, 1.27, 1.23, 1.22, 1.02 \text{ e}/\text{\AA}^3$) and 1 peak was found less than 1 angstrom from Cl3 ($1.05 \text{ e}/\text{\AA}^3$)

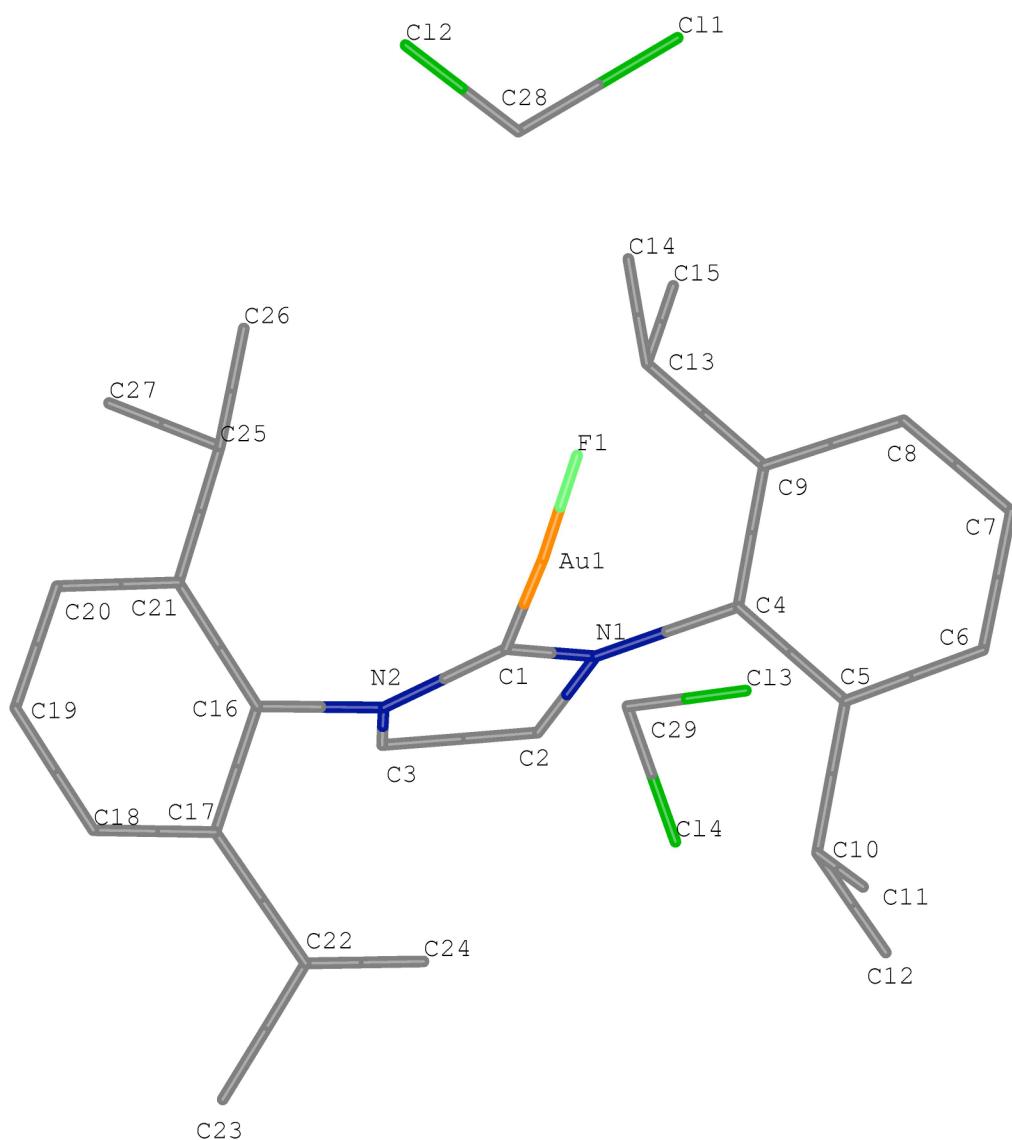


Figure S2. X-ray crystal structure of $(SIPr)AuF$ (2). Hydrogen atoms (calculated) omitted for clarity. Shown as stick representation for clarity in labeling.

Table S5. Crystal data and structure refinement for (*SIPr*)AuF (**2**).

Identification code	04166final	
Empirical formula	$C_{29}H_{42}N_2FCl_4Au$	
Formula weight	776.41	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	$a = 12.4390(4)$ Å	$\beta = 90^\circ$.
	$b = 16.3588(5)$ Å	$\gamma = 98.695 (1)^\circ$.
	$c = 15.7664(6)$ Å	$\alpha = 90^\circ$.
Volume	3171.3 (2) Å ³	
Z	4	
Density (calculated)	1.626 Mg/m ³	
Absorption coefficient	5.003 mm ⁻¹	
F(000)	1544	
Crystal size	0.20 x 0.20 x 0.20 mm ³	
Theta range for data collection	1.80 to 26.37°.	
Index ranges	-15≤h≤15, 0≤k≤20, 0≤l≤19	
Reflections collected	57714	
Independent reflections	6492 [R(int) = 0.0351]	
Completeness to theta = 26.37°	100.0 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.4344 and 0.4344
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6492 / 0 / 342
Goodness-of-fit on F^2	1.095
Final R indices [$I > 2\text{sigma}(I)$]	$R_1 = 0.0228, wR_2 = 0.0570$
R indices (all data)	$R_1 = 0.0308, wR_2 = 0.0628$
Largest diff. peak and hole	1.320 and -0.358 e. \AA^{-3}

Table S6. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $(SIPr)\text{AuF}$ (2). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Au(1)	5281(1)	2466(1)	4670(1)	15(1)
F(1)	6370(1)	2424(1)	5765(1)	17(1)
N(1)	3931(2)	1875(1)	3097(2)	15(1)
N(2)	3902(2)	3203(1)	3179(2)	14(1)
C(1)	4291(2)	2518(1)	3582(2)	13(1)
C(2)	3185(2)	2108(2)	2319(2)	18(1)
C(3)	3330(2)	3038(2)	2302(2)	18(1)
C(4)	4162(2)	1035(2)	3321(2)	16(1)
C(5)	3422(2)	600(2)	3738(2)	18(1)
C(6)	3662(3)	-219(2)	3941(2)	24(1)

C(7)	4600(3)	-577(2)	3743(2)	28(1)
C(8)	5311(3)	-139(2)	3327(2)	24(1)
C(9)	5112(2)	680(2)	3104(2)	19(1)
C(10)	2395(2)	984(2)	3965(2)	19(1)
C(11)	2393(3)	982(2)	4936(2)	29(1)
C(12)	1378(2)	565(2)	3488(2)	25(1)
C(13)	5919(2)	1162(2)	2667(2)	21(1)
C(14)	6951(3)	1318(2)	3306(2)	30(1)
C(15)	6196(2)	730(2)	1868(2)	25(1)
C(16)	4205(2)	4019(2)	3462(2)	16(1)
C(17)	3440(2)	4486(2)	3825(2)	17(1)
C(18)	3739(3)	5273(2)	4099(2)	20(1)
C(19)	4750(3)	5587(2)	4012(2)	22(1)
C(20)	5479(2)	5120(2)	3635(2)	20(1)
C(21)	5223(2)	4326(2)	3350(2)	17(1)
C(22)	2352(2)	4118(2)	3947(2)	18(1)
C(23)	1448(3)	4749(2)	3934(3)	36(1)
C(24)	2462(3)	3623(2)	4780(2)	27(1)
C(25)	6044(2)	3839(2)	2933(2)	20(1)
C(26)	7109(2)	3726(2)	3560(2)	26(1)
C(27)	6267(3)	4246(2)	2102(2)	26(1)
C(28)	8638(3)	2238(2)	4965(2)	29(1)
C(29)	4889(3)	2744(2)	7222(2)	31(1)

Cl(1)	9132(1)	1222(1)	5066(1)	39(1)
Cl(2)	9630(1)	2935(1)	5455(1)	51(1)
Cl(3)	5163(1)	2274(1)	8239(1)	37(1)
Cl(4)	3607(1)	2468(1)	6671(1)	32(1)

Table S7. Bond lengths [\AA] and angles [$^\circ$] for (*SIPr*)AuF (**2**).

Au(1)-C(1)	1.956(3)	C(8)-C(9)	1.398(4)
Au(1)-F(1)	2.028 (2)	C(9)-C(13)	1.521(4)
F(1)-C(29)	3.197(4)	C(10)-C(11)	1.531(4)
F(1)-C(28)	3.275(4)	C(10)-C(12)	1.532(4)
N(1)-C(1)	1.338(3)	C(13)-C(15)	1.528(4)
N(1)-C(4)	1.436(3)	C(13)-C(14)	1.528(4)
N(1)-C(2)	1.472(4)	C(16)-C(21)	1.398(4)
N(2)-C(1)	1.342(3)	C(16)-C(17)	1.407(4)
N(2)-C(16)	1.439(3)	C(17)-C(18)	1.392(4)
N(2)-C(3)	1.481(3)	C(17)-C(22)	1.520(4)
C(2)-C(3)	1.534(4)	C(18)-C(19)	1.384(4)
C(4)-C(5)	1.403(4)	C(19)-C(20)	1.387(4)
C(4)-C(9)	1.405(4)	C(20)-C(21)	1.395(4)
C(5)-C(6)	1.399(4)	C(21)-C(25)	1.522(4)
C(5)-C(10)	1.514(4)	C(22)-C(23)	1.523(4)
C(6)-C(7)	1.383(5)	C(22)-C(24)	1.531(4)
C(7)-C(8)	1.379(4)	C(25)-C(27)	1.532(4)

C(25)-C(26)	1.539(4)	C(9)-C(4)-N(1)	118.6(2)
C(28)-Cl(2)	1.769(3)	C(6)-C(5)-C(4)	117.4(3)
C(28)-Cl(1)	1.772(4)	C(6)-C(5)-C(10)	120.1(3)
C(29)-Cl(4)	1.756(4)	C(4)-C(5)-C(10)	122.5(2)
C(29)-Cl(3)	1.765(3)	C(7)-C(6)-C(5)	120.8(3)
		C(8)-C(7)-C(6)	120.7(3)
C(1)-Au(1)-F(1)	177.22(9)	C(7)-C(8)-C(9)	121.0(3)
Au(1)-F(1)-C(29)	102.91(9)	C(8)-C(9)-C(4)	117.3(3)
Au(1)-F(1)-C(28)	100.25(9)	C(8)-C(9)-C(13)	120.4(3)
C(29)-F(1)-C(28)	156.3 (1)	C(4)-C(9)-C(13)	122.2(2)
C(1)-N(1)-C(4)	125.0(2)	C(5)-C(10)-C(11)	111.4(2)
C(1)-N(1)-C(2)	112.8(2)	C(5)-C(10)-C(12)	111.2(2)
C(4)-N(1)-C(2)	122.0(2)	C(11)-C(10)-C(12)	111.3(2)
C(1)-N(2)-C(16)	124.7(2)	C(9)-C(13)-C(15)	112.4(2)
C(1)-N(2)-C(3)	112.2(2)	C(9)-C(13)-C(14)	109.5(3)
C(16)-N(2)-C(3)	121.6(2)	C(15)-C(13)-C(14)	110.4(2)
N(1)-C(1)-N(2)	108.7(3)	C(21)-C(16)-C(17)	122.4(3)
N(1)-C(1)-Au(1)	125.4 (2)	C(21)-C(16)-N(2)	119.6(2)
N(2)-C(1)-Au(1)	125.8 (2)	C(17)-C(16)-N(2)	117.9(2)
N(1)-C(2)-C(3)	102.2(2)	C(18)-C(17)-C(16)	117.6(3)
N(2)-C(3)-C(2)	101.9(2)	C(18)-C(17)-C(22)	121.9(3)
C(5)-C(4)-C(9)	122.7(3)	C(16)-C(17)-C(22)	120.4(2)
C(5)-C(4)-N(1)	118.7(2)	C(19)-C(18)-C(17)	121.1(3)

C(18)-C(19)-C(20)	120.1(3)	C(21)-C(25)-C(26)	110.7(3)
C(19)-C(20)-C(21)	121.2(3)	C(27)-C(25)-C(26)	110.6(2)
C(20)-C(21)-C(16)	117.5(3)	Cl(2)-C(28)-Cl(1)	110.84(19)
C(20)-C(21)-C(25)	119.4(3)	Cl(2)-C(28)-F(1)	110.89(16)
C(16)-C(21)-C(25)	123.1(2)	Cl(1)-C(28)-F(1)	111.07(14)
C(17)-C(22)-C(23)	113.6(2)	Cl(4)-C(29)-Cl(3)	111.98(19)
C(17)-C(22)-C(24)	110.6(2)	Cl(4)-C(29)-F(1)	100.45(15)
C(23)-C(22)-C(24)	109.9(3)	Cl(3)-C(29)-F(1)	121.91(18)
C(21)-C(25)-C(27)	111.2(2)		

Table S8. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (*SIPr*)AuF (**2**). The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Au(1)	17(1)	13(1)	16(1)	0(1)	3(1)	0(1)
F(1)	19(1)	19(1)	12(1)	1(1)	-2(1)	1(1)
N(1)	16(1)	11(1)	17(1)	-2(1)	1(1)	0(1)
N(2)	17(1)	12(1)	14(1)	0(1)	2(1)	0(1)
C(1)	12(1)	12(1)	14(1)	0(1)	4(1)	0(1)
C(2)	18(1)	15(1)	19(2)	-1(1)	0(1)	-2(1)
C(3)	22(2)	16(1)	14(1)	1(1)	-2(1)	0(1)
C(4)	19(1)	10(1)	17(1)	-1(1)	0(1)	0(1)
C(5)	20(2)	17(1)	17(1)	-2(1)	1(1)	-1(1)

C(6)	31(2)	13(1)	28(2)	3(1)	8(1)	-3(1)
C(7)	38(2)	11(1)	35(2)	1(1)	5(2)	1(1)
C(8)	23(2)	17(1)	32(2)	0(1)	6(1)	6(1)
C(9)	18(2)	15(1)	23(2)	-3(1)	3(1)	0(1)
C(10)	19(2)	19(1)	21(2)	0(1)	6(1)	-1(1)
C(11)	28(2)	37(2)	21(2)	-7(1)	4(1)	-1(1)
C(12)	21(2)	28(2)	26(2)	-1(1)	2(1)	-3(1)
C(13)	19(2)	16(1)	29(2)	-1(1)	7(1)	2(1)
C(14)	23(2)	34(2)	33(2)	-13(2)	7(1)	-6(1)
C(15)	20(2)	27(2)	27(2)	-2(1)	5(1)	2(1)
C(16)	19(1)	12(1)	15(1)	2(1)	1(1)	1(1)
C(17)	19(2)	16(1)	15(1)	5(1)	1(1)	2(1)
C(18)	29(2)	15(1)	15(1)	0(1)	4(1)	4(1)
C(19)	32(2)	13(1)	19(2)	0(1)	1(1)	-3(1)
C(20)	23(2)	14(1)	21(2)	1(1)	3(1)	-5(1)
C(21)	20(2)	14(1)	18(2)	1(1)	2(1)	-1(1)
C(22)	17(1)	20(1)	18(2)	-1(1)	3(1)	2(1)
C(23)	25(2)	32(2)	52(2)	2(2)	6(2)	10(1)
C(24)	24(2)	36(2)	23(2)	7(1)	7(1)	-3(1)
C(25)	18(2)	16(1)	27(2)	-1(1)	6(1)	-2(1)
C(26)	22(2)	28(2)	30(2)	8(1)	6(1)	2(1)
C(27)	21(2)	33(2)	26(2)	1(1)	5(1)	-1(1)
C(28)	27(2)	32(2)	26(2)	2(1)	2(1)	-7(1)

C(29)	36(2)	34(2)	23(2)	2(2)	2(2)	-9(2)
Cl(1)	37(1)	41(1)	37(1)	11(1)	2(1)	8(1)
Cl(2)	50(1)	70(1)	38(1)	-22(1)	18(1)	-35(1)
Cl(3)	36(1)	43(1)	30(1)	12(1)	1(1)	5(1)
Cl(4)	30(1)	38(1)	27(1)	-1(1)	0(1)	2(1)

Table S9. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2**.

	x	y	z	U(eq)
H(2A)	2425	1957	2365	21
H(2B)	3397	1849	1801	21
H(3A)	3774	3205	1861	21
H(3B)	2619	3322	2195	21
H(6)	3175	-532	4220	28
H(7)	4755	-1131	3895	34
H(8)	5947	-398	3190	29
H(10)	2379	1567	3773	23
H(11A)	2400	417	5143	43
H(11B)	1738	1259	5064	43
H(11C)	3039	1269	5221	43
H(12A)	1393	587	2869	38
H(12B)	727	846	3620	38
H(12C)	1364	-7	3672	38
H(13)	5584	1702	2487	25

H(14A)	6762	1604	3809	45
H(14B)	7454	1654	3033	45
H(14C)	7298	795	3485	45
H(15A)	6536	201	2031	37
H(15B)	6701	1069	1600	37
H(15C)	5529	644	1461	37
H(18)	3241	5601	4351	23
H(19)	4945	6123	4211	26
H(20)	6166	5345	3569	24
H(22)	2130	3732	3461	22
H(23A)	1602	5099	4443	54
H(23B)	752	4469	3936	54
H(23C)	1410	5085	3416	54
H(24A)	3047	3221	4785	41
H(24B)	1776	3340	4815	41
H(24C)	2634	3992	5271	41
H(25)	5729	3286	2785	24
H(26A)	7424	4263	3724	39
H(26B)	7623	3406	3282	39
H(26C)	6956	3438	4074	39
H(27A)	5582	4310	1710	40
H(27B)	6766	3904	1831	40
H(27C)	6597	4784	2234	40

H(28A)	8442	2377	4349	35
H(28B)	7974	2285	5237	35
H(29A)	4920	3345	7294	37
H(29B)	5456	2583	6876	37

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