SUPPORTING INFORMATION

Synthesis and Properties of “Sandwich” Diimine-Coinage Metal Ethylene Complexes

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General Considerations

All manipulations of air and water sensitive compounds were carried out under nitrogen atmosphere using standard glove box and Schlenk techniques. Column chromatography was performed on 60Å silica gel (Dynamic Adsorbents Inc.) using mixtures of EtOAc/hexanes or EtOAc/toluene as eluent. Analytical thin layer chromatography was performed on silica gel on TLC Al foils with fluorescent indicator (254 nm) from Fluka. The $^1$H NMR, $^{13}$C{$^1$H} NMR, and 2D-NMR spectra were recorded on JEOL EC-400, JEOL EC-500 or JEOL EC-600 spectrometers using residual solvent peak as a reference (CDCl$_3$: 7.26 ppm ($^1$H), 77.1 ppm ($^{13}$C), CD$_2$Cl$_2$: 5.32 ppm ($^1$H), 53.8 ppm ($^{13}$C), C$_2$D$_2$Cl$_4$ 5.90 ppm ($^1$H) and CDCl$_2$F 7.47 ppm ($^1$H)).

Compounds for HRMS were analyzed by positive mode electrospray ionization (ESI) using Agilent 6150 mass spectrometer at the Mass Spectrometry Facility of the Department of Chemistry and Biochemistry of University of Texas-Austin. Elemental analyses were performed by Atlantic Microlabs Inc. (Norcross, GA, USA). IR-spectra were obtained using Perkin Elmer Spectrum 100 FT-IR spectrometer. Ethylene (Polymer purity) was purchased from Matheson Tri-Gas. Deuterated solvents (CD$_2$Cl$_2$, CDCl$_3$, C$_2$D$_2$Cl$_4$, dried over 3Å molecular sieves prior use) and ethylene-$d_4$ were purchased from Cambridge Isotope Laboratories. Silver (I) hexafluoroantimonate (Strem Chemicals) and silver (I) tetrafloroborate (Strem Chemicals), were dried at 80 °C under high vacuum for 24 h and stored in a glove box. Gold (I) chloride (Sigma Aldrich), (CuOTf)$_2$PhH (Sigma Aldrich) and CuI (Strem Chemicals) were stored in a glove box and used as received. Dichloromethane, pentane and ether were dried by passing through commercial activated alumina columns. Methylcyclohexane was dried over chunks of sodium.

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Synthesis and Characterization

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\begin{align*}
\text{Cl} & \quad \text{Cl} & \quad \text{O} \\
\text{H} & \quad \text{N} & \quad \text{N}
\end{align*}
\]

\textit{N-(8-(3,5-dichlorophenyl)naphthalen-1-yl)picolinamide (4)}

Compound was synthesized following literature procedure.\(^2\)

\(\text{N-(Naphthalen-1-yl)picolinamide (19.9 g, 80.0 mmol),}^3 \quad \text{Pd(OAc)}_2 (898 \text{ mg, 4.00 mmol), AgOAc (20.0 g, 120 mmol), and 3,5-dichloriodobenzene (87.3 g, 320 mmol) were placed in a 350 mL pressure vessel equipped with a magnetic stir bar. The obtained mixture was stirred at 140 °C for 72 hours or until completion determined by TLC (SiO}_2, \text{EtOAc/toluene 1/5). After cooling to room temperature reaction mixture was diluted with CH}_2\text{Cl}_2 (200 mL) and filtered through a pad of Celite®. Solids were thoroughly washed with CH}_2\text{Cl}_2 (200 mL). Combined filtrate and washings were concentrated in vacuum. The residue was purified by flash chromatography in EtOAc/toluene (1/10 to 1/5) affording product (24.1 g, 77%) as beige solid. R}_f = 0.54 (SiO}_2, 1/5 EtOAc/toluene), mp = 160 – 162 °C (from hexanes).\)

\(^1\text{H NMR (500 MHz, CDCl}_3, \text{ppm) } \delta 9.42 (s, 1H), 8.36 (ddd, } ^3\text{J}_{\text{HH}} = 4.7 \text{ Hz, } ^4\text{J}_{\text{HH}} = 1.6 \text{ Hz, } ^5\text{J}_{\text{HH}} = 0.9 \text{ Hz, 1H}), 8.15 (dt, } ^3\text{J}_{\text{HH}} = 7.8 \text{ Hz, } ^4\text{J}_{\text{HH}} = 1.0 \text{ Hz, 1H}), 8.08 (dd, } ^3\text{J}_{\text{HH}} = 7.5 \text{ Hz, } ^4\text{J}_{\text{HH}} = 0.7 \text{ Hz, 1H}), 7.92 (dd, } ^3\text{J}_{\text{HH}} = 8.2 \text{ Hz, } ^4\text{J}_{\text{HH}} = 1.2 \text{ Hz, 1H}), 7.83 (m , 2H), 7.60 (t, } ^3\text{J}_{\text{HH}} = 7.8 \text{ Hz, 1H}), 7.48 (dd, } ^3\text{J}_{\text{HH}} = 8.2 \text{ Hz, } ^3\text{J}_{\text{HH}} = 7.1 \text{ Hz, 1H}), 7.42 (dd, } ^3\text{J}_{\text{HH}} = 7.6 \text{ Hz, } ^3\text{J}_{\text{HH}} = 4.7 \text{ Hz, } ^4\text{J}_{\text{HH}} = 1.2 \text{ Hz, 1H}), 7.32 – 7.20 (m, 2H, overlaps with CDCl}_3), 6.85 (t, } ^4\text{J}_{\text{HH}} = 1.9 \text{ Hz, 1H}).\)

\(^{13}\text{C NMR (126 MHz, CDCl}_3, \text{ppm) } \delta 162.0, 149.3, 147.4, 145.9, 137.4, 135.5, 134.9, 134.6, 132.2, 130.3, 129.8, 127.7, 127.2, 126.7, 126.5, 126.4, 125.6, 125.0, 124.4, 122.3. HRMS (+ESI): Calculated for C}_22\text{H}_16\text{Cl}_2\text{N}_2\text{O } [\text{M+Na}]^+ 420.03541, found 420.03590.\)

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8-(3,5-Dichlorophenyl)naphthalen-1-amine (5)
A solution of KOH (34.2 g, 610 mmol) in the mixture of EtOH/H$_2$O (10/1 v/v, 98 mL) was added to N-(8-(3,5-dichlorophenyl)naphtalen-1-yl)picolinamide (24.0 g, 61.0 mmol) in a 350 mL pressure vessel equipped with a magnetic stir bar. The resulting mixture was stirred at 130 °C for 4 h or until completion determined by TLC (SiO$_2$, EtOAc/hexanes 1/10). After cooling to room temperature, the reaction was diluted with H$_2$O (250 mL) and transferred to a separatory funnel. The aqueous layer was extracted with EtOAc (3×150 mL). Combined organic layers were dried over MgSO$_4$, filtered and concentrated in vacuum. The residue was purified by flash chromatography EtOAc/hexanes (gradient 1/20 to 1/10) affording product as a light yellow solid (13.8 g, 79%). R$_f$ = 0.53 (SiO$_2$, 1/10 EtOAc/hexanes), mp = 108 – 110 °C (from hexanes). $^1$H NMR (500 MHz, CDCl$_3$, ppm) δ 7.82 (dd, $^3$J$_{HH}$ = 8.2 Hz, $^4$J$_{HH}$ = 1.2 Hz, 1H), 7.44 (t, $^4$J$_{HH}$ = 1.9 Hz, 1H), 7.42 – 7.28 (m, 5H), 7.13 (dd, $^3$J$_{HH}$ = 7.0 Hz, $^4$J$_{HH}$ = 1.3 Hz, 1H), 6.68 (dd, $^3$J$_{HH}$ = 7.2 Hz, $^4$J$_{HH}$ = 1.4 Hz, 1H), 3.66 (s, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$, ppm) δ 146.4, 143.2, 135.9, 135.5, 134.5, 129.7, 128.5, 127.9, 127.6, 126.9, 124.6, 120.2, 119.4, 112.0. HRMS (+ESI): Calculated for C$_{16}$H$_{11}$Cl$_2$N [M+H]$^+$ 288.03413, found 288.03410.

2,3-Butanedione bis(8-(3,5-dichlorophenyl)naphthalen-1-imine) (6)
2,3-Butanedione (224 mg, 2.60 mmol), 8-(3,5-dichlorophenyl)naphthalen-1-amine (1.65 g, 5.72 mmol), MeOH (11 mL) and HCO$_2$H (2 drops) were placed in a 50 mL round bottom flask equipped with a magnetic stir bar and a reflux condenser. Reaction mixture was stirred at reflux for 48 h. Yellow precipitate formed. After cooling to room temperature, solid was collected by filtration, washed with cold MeOH and dried.
in vacuo affording product as a yellow solid (1.40 g, 86%). Rf = 0.60 (SiO2, 1/10 EtOAc/hexanes). 1H NMR (500 MHz, CDCl3, ppm) δ 7.91 (d, 3JHH = 8.1 Hz, 2H), 7.72 (d, 3JHH = 8.2 Hz, 2H), 7.58 (t, 3JHH = 7.7 Hz, 2H), 7.51 – 7.43 (m, 2H), 7.30 (t, 3JHH = 1.8 Hz, 2H), 7.23 – 7.16 (m, 2H), 7.11 – 7.08 (m, 4H), 6.58 (d, 3JHH = 7.2 Hz, 2H), 1.51 (s, 6H).

13C NMR (126 MHz, CDCl3, ppm) δ 166.7, 147.7, 147.5, 136.2, 135.4, 133.9, 129.4, 129.2, 127.9, 126.6, 126.4, 125.2, 125.0, 122.9, 114.7, 15.6. HRMS (+ESI): Calculated for C36H24Cl4N2 [M+H]+ 627.07423, found 627.07434. Anal. Calcd. for C36H24Cl4N2: C 69.03; H 3.86; N 4.47. Found: C 68.98; H 4.01; N 4.51.

(Cl2ArN(CMe))2Cu(C2H4)OTf (7a)

Inside the glove box (CuOTf)2PhH (138 mg, 0.275 mmol) and 6 (313 mg, 0.500 mmol) were placed in a 50 mL flame dried Schlenk flask equipped with a magnetic stir bar. Outside the glove box CH2Cl2 (25 mL, presaturated with C2H4) was added and additional C2H4 was gently bubbled through the mixture for 1 min. The red orange solution was stirred for 1 h at RT, and then filtered through a pad of Celite® into a 50 mL Schlenk tube. Solution was concentrated in vacuum to about 1 mL of a volume, and then dried using strong stream of C2H4 affording product as a red solid (370 mg, 85%). The pure compound is stable and can be stored outside the glovebox at room temperature under inert atmosphere for years without any signs of decomposition as evident by 1H NMR and single crystal crystallography. 1H NMR (400 MHz, CDCl3, ppm) δ 8.04 (dd, 3JHH = 8.2 Hz, 4JHH = 0.7 Hz, 2H), 8.00 (d, 3JHH = 8.0 Hz, 2H), 7.73 (m, 2H), 7.61 (m, 2H), 7.47 (t, 4JHH = 1.8 Hz, 2H), 7.39 (dd, 3JHH = 7.1 Hz, 4JHH = 1.0 Hz, 2H), 7.08 (m, 2H), 6.98 (m, 2H), 6.76 (dd, 3JHH = 7.3 Hz, 4JHH = 0.6 Hz, 2H), 4.01 (bs, 4H, C2H4), 2.37 (s, 6H). 13C NMR (126 MHz, CDCl3, ppm) δ 171.4, 146.4, 141.6, 135.6, 135.5, 134.9, 133.8, 131.1, 130.6, 130.0, 128.3, 127.7, 127.6, 126.8, 126.4, 123.5, 118.4, 19.9. 13C Signal for C2H4 was not observed in 13C NMR spectra from -20 to +40 °C. However, shift for bound C2H4 can be located using 2D-HMQC NMR spectra (88.9 ppm). IR: solid, selected values = 1641, 1584, 1556, 1524 cm⁻¹. Anal. Calcd. for C39H28N2Cl4CuF3O3S: C 54.02; H 3.25; N 3.23; found C 53.61; H 3.45; N 3.25%.
X-Ray quality crystals were grown by layering Et₂O over the solution of 7a in CH₂Cl₂ at -20 °C.

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\begin{align*}
\text{Cl} & \quad \text{ArN} \quad \text{Cu} \quad \text{N} \quad \text{Ar} \\
\downarrow & \quad \downarrow & \quad \downarrow & \quad \downarrow
\end{align*}
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**Synthesis of (Cl₂ArN(CMe))₂Cu(C₂H₄)SbF₆ (7b)**

Synthesis of Cu(C₂H₄)₃SbF₆ intermediate was adopted from Dias.⁴ Inside the glovebox CuI (105 mg, 0.550 mmol) and AgSbF₆ (172 mg, 0.500 mmol) were placed in a 25 mL flame dried Schlenk flask equipped with a magnetic stir bar. Outside the glove box the flask was covered with tin foil and CH₂Cl₂ (10 mL, presaturated with C₂H₄) was added. Reaction mixture was stirred at RT for 2.5 h, during this period of time C₂H₄ was gently bubbled through the mixture every 45 min for 1 min period (4 times overall). Yellow precipitate of AgI was formed. Reaction was filtered through a pad of Celite® into a 50 mL Schlenk flask. Glass frit was exchanged for a rubber septum and a suspension of 6 (219 mg, 0.350 mmol) in CH₂Cl₂ (10 mL, presaturated with C₂H₄) was added to the colorless filtrate. The resulting red solution was stirred at RT for 1 h followed by filtration through a pad of Celite® into a 50 mL Schlenk tube. Solution was concentrated in vacuum and obtained orange solid was recrystallized by layering pentane (3 mL) over the solution of solid in CH₂Cl₂ (2 mL) at – 20 °C affording product as an orange solid (270 mg, 81%). The pure compound is stable and can be stored outside the glove box at room temperature in air for years without any signs of decomposition as evident by ¹H NMR, and it does not lose complexed ethylene if kept under vacuum for short periods of time (ca. 30 min).

¹H NMR (500 MHz, CD₂Cl₂, ppm) δ 8.11 (dd, ³J_HH = 8.3 Hz, ⁴J_HH = 1.1 Hz, 2H), 8.08 (dd, J = 8.3, 0.9 Hz, 2H), 7.76 (m, 2H), 7.68 (m, 2H), 7.53 (t, ⁴J_HH = 1.9 Hz, 2H), 7.44 (dd, ³J_HH = 7.1 Hz, ⁴J_HH = 1.1 Hz, 2H), 7.07 (t, ⁴J_HH = 1.7 Hz, 2H), 6.97 (t, ⁴J_HH = 1.6 Hz, 2H), 6.75 (dd, ³J_HH = 7.3, ⁴J_HH =1.1 Hz, 2H), 4.01 – 3.93 (m, 2H, C₂H₄), 3.86 – 3.77 (m, 2H, C₂H₄), 2.35 (s, 6H). ¹³C NMR (126 MHz, CD₂Cl₂, ppm ) δ 171.7, 146.8, 141.8, 136.1, 136.0, 135.1, 134.1, 131.6, 131.1, 130.6, 128.8, 128.2, 128.1, 127.3, 126.7, 123.9, 118.8, 88.0 (C₂H₄), 20.1. IR: solid, selected values = 1584, 1556 cm⁻¹.

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Anal. Calcd. for C_{38}H_{28}N_{2}Cl_{4}SbF_{6}Cu: C 47.85; H 2.96; N 2.94; found C 47.55; H 2.95; N 2.94%.

Synthesis of (Cl_{2}ArN(CMe))_{2}Ag(C_{2}H_{4})SbF_{6} (8a)

Inside the glove box AgSbF_{6} (206 mg, 0.600 mmol) and 6 (413 mg, 0.660 mmol) were placed in a flame dried 50 mL Schlenk flask equipped with magnetic stir bar. Outside the glove box the flask was covered with tin foil and cooled to -75 °C in a dry ice/acetone bath. Then CH_{2}Cl_{2} (25 mL, presaturated with C_{2}H_{4} and predried over activated MS 3Å) was slowly added, additional C_{2}H_{4} was gently bubbled through reaction mixture for 1 min. The light orange mixture was then stirred at -75 °C for 2.5 hours in the dark. Reaction was filtered through a pad of Celite® into a 50 mL Schlenk tube that was placed in a cold bath at -35 °C and covered with tin foil. Orange solution was then concentrated in vacuum maintaining bath temperature between -35 to -30 °C to ca. 1 mL volume. To the obtained dark orange solution pentane (10 mL) was added and solvents were vigorously mixed to precipitate the product. Solvent was canula transferred away from the precipitate and residue was washed with pentane (2 × 5 mL) at – 30 °C. Dark orange solid was dried at RT under vigorous stream of C_{2}H_{4} affording product (470 mg, 78%). Complex is sensitive to air, temperature and light. It decomposes at RT within one day as a solid and within few hours in solution under inert atmosphere. It can be stored for several months as a solid under inert atmosphere at -20 °C. ^1H NMR (500 MHz, 293 K, CDCl_{3}, ppm) δ 8.03 (d, 3J_{HH} = 7.9 Hz, 2H), 7.99 (d, 3J_{HH} = 8.3 Hz, 2H), 7.71 (t, 3J_{HH} = 7.8 Hz, 2H), 7.61 (t, 3J_{HH} = 7.5 Hz, 2H), 7.45 (m, 2H), 7.38 (d, 3J_{HH} = 6.9 Hz, 2H), 7.17 (m, 2H), 6.97 (m, 2H), 6.75 (d, 3J_{HH} = 7.2 Hz, 2H), 4.94 (s, 4H, C_{2}H_{4}), 2.34 (s, 6H). ^13C NMR (126 MHz, 283 K, CDCl_{3}, ppm) δ 166.5, 146.7, 143.6, 135.6, 135.1, 134.7, 133.7, 131.0, 130.6, 129.3, 128.1, 127.4, 127.0, 126.7, 126.4, 123.2, 117.1, 105.4 (C_{2}H_{4}), 19.8. IR: solid, selected values = 1641, 1583, 1556, 1524 cm⁻¹. Anal. Calcd. for C_{38}H_{28}N_{2}Cl_{4}SbF_{6}Ag: C 45.73; H 2.83; N 2.81; found C 45.53; H 2.99; N 2.90%.
Synthesis of (Cl_2ArN(CMe))_2Ag(C_2H_4)BF_4 (8b)

Procedure for the synthesis of (Cl_2ArN(CMe))_2Ag(C_2H_4)SbF_6 was followed by employing silver tetrafluoroborate (39 mg, 0.2 mmol), 6 (138 mg, 0.220 mmol), and CH_2Cl_2 (10 mL). Product was obtained as an orange/brown solid (150 mg, 88%). Complex is sensitive to air, temperature, and light. It can be stored for several months as a solid under inert atmosphere at -20 °C. 

_1H NMR (500 MHz, 273 K, CD_2Cl_2, ppm )

δ 8.09 (dd, J_HH = 8.1, J_HH = 0.8 Hz, 2H), 8.05 – 7.98 (m, 2H), 7.72 (t, J_HH = 7.68 Hz, 2H), 7.65 (dd, J_HH = 8.0, J_HH = 7.1 Hz, 2H), 7.46 (t, J_HH = 1.8 Hz, 2H), 7.42 (dd, J_HH = 6.9, J_HH = 0.9 Hz, 2H), 7.14 (s, 2H), 7.00 (s, 2H), 6.74 – 6.62 (m, 2H), 4.94 (s, 4H, C_2H_4), 2.22 (s, 6H).

_13C NMR (126 MHz, 273 K, CD_2Cl_2, ppm ) δ 166.7, 147.1, 143.9, 135.9, 135.3, 134.8, 134.1, 131.2, 130.8, 129.44, 128.4, 127.7, 127.4, 126.9, 126.7, 123.5, 117.4, 105.9 (C_2H_4), 20.1. IR: solid, selected values = 1633, 1581, 1557 cm\(^{-1}\). Anal. Calcd. for C_{38}H_{38}N_2Cl_4BF_4Ag: C 53.75; H 3.32; N 3.30; found C 53.93; H 4.04; N 3.13%. X-Ray quality crystals were grown by layering methylcyclohexane over the solution of 8b in CH_2Cl_2 at -20 °C.

Synthesis of (Cl_2ArN(CMe))_2Au(C_2H_4)SbF_6 (9)

Procedure for the synthesis of Au(C_2H_4)_3SbF_6 intermediate was adopted from Dias. Inside the glove box AuCl (102 mg, 0.440 mmol) and AgSbF_6 (137 mg, 0.400 mmol) were placed in a flame dried 10 mL Schlenk flask, equipped with magnetic stir bar. Outside the glove box the flask was covered with tin foil and CH_2Cl_2 (10 mL, presaturated with C_2H_4) was added. Reaction mixture was stirred at RT for 3 h, during this period of time C_2H_4 was gently bubbled through the mixture every 30 min for 1 min period (5 times overall). Yellow precipitate of AgCl was formed. Reaction was filtered through a pad of Celite® into a 25 mL Schlenk flask covered with tin foil and cooled to -75 °C in a dry ice/acetone bath. Solids were washed once with CH_2Cl_2 (2
mL). Glass frit was exchanged for a rubber septum and a suspension of 6 (150 mg, 0.240 mmol) in CH₂Cl₂ (10 mL, presaturated with C₂H₄) was added to the colorless filtrate. The resulting dark red solution was stirred at -75 °C for 1 h followed by filtration through a pad of Celite® into a 50 mL Schlenk tube covered with tin foil and precooled to -75 °C. To the red solution pentane (30 mL) was added slowly and solvents were mixed by purging with stream of C₂H₄ to precipitate product. The fine red precipitate was left to settle for 20 min at -75 °C and solvent was removed via canula to a separate flask. Solids were washed with pentane (2 × 10 mL). Flask was taken out of the cold bath and product was dried with strong stream of C₂H₄ at RT affording product as a dark red solid (106 mg, 42%). Analysis by ¹H NMR shows that compound contains minor amount of an unidentified impurity. Complex 9 is unstable and decomposes in solution within an hour at room temperature, therefore it is important to precipitate product at low temperatures to avoid contamination. Solid product can be stored at -20 °C under inert atmosphere for several months. At room temperature complex decomposes within one day. ¹H NMR (500 MHz, CDCl₃, ppm) δ 8.11 – 8.00 (m, 4H), 7.73 (t, ³J_HH = 7.7 Hz, 2H), 7.65 (dd, ³J_HH = 8.0, ²J_HH = 7.2 Hz, 2H), 7.44 – 7.40 (m, 4H), 7.14 (t, ⁴J_HH = 1.6 Hz, 2H), 7.00 (t, ⁴J_HH = 1.6 Hz, 2H), 6.92 (dd, ³J_HH = 7.4 Hz, ⁴J_HH = 1.2 Hz, 2H), 3.31 – 3.30 (m, 2H, C₂H₄), 3.28 – 3.27 (m, 2H, C₂H₄), 2.11 (s, 6H). Due to the low solubility of complex at low temperature and its instability, a good quality ¹³C-NMR spectra was not obtained. ¹³C Shift for bound C₂H₄ can be located using 2D-HMQC NMR spectra (65.4 ppm). IR: solid, selected values = 1642, 1584, 1556, 1524 cm⁻¹. Anal. Calcd. for C₃₈H₂₈N₂Cl₄SbF₆Au: C 41.98; H 2.60; N 2.58; found C 41.94; H 2.62; N 2.60%.

X-Ray quality crystals were grown by layering pentane over the solution of 9 in CH₂Cl₂ at -20 °C.

![Chemical structure](image)

**Synthesis of (Cl₂ArN(CMe))₂Au(C₂D₄)SbF₆ (9-d₄)**

Inside the glove box (Cl₂ArN(CMe))₂Au(C₂H₄)SbF₆ (9) (52 mg, 0.05 mmol) was placed in a flame dried 25 mL Schlenk tube equipped with magnetic stir bar. Outside the glove box the flask was covered with tin foil and placed in a -30 °C dry ice/acetone
bath. CH$_2$Cl$_2$ (3 mL) was added slowly on the walls of the flask and the solution was purged with one rubber balloon filled with C$_2$D$_4$ (ca. 30 mL). Reaction mixture was stirred at -30 °C under C$_2$D$_4$ atmosphere for 1.5 h. Pentane (9 mL) was layered over the solution and solvents were mixed to precipitate the product. Solvents were decanted via canula and residue was washed with pentane (3 × 3 mL). Remaining solvent was concentrated in vacuum at -30 °C affording product as a dark red solid (44 mg, 81 %).

$^1$H-NMR indicates 97% conversion to a labeled complex. $^1$H NMR (500 MHz, CD$_2$Cl$_2$, ppm ) δ 8.15 – 8.10 (m, 2H), 8.10 – 8.06 (m, 2H), 7.75 (dd, $^3$J$_{HH}$ = 8.2 Hz, $^3$J$_{HH}$ = 7.5 Hz, 2H), 7.69 (dd, $^3$J$_{HH}$ = 8.2 Hz, $^3$J$_{HH}$ = 7.1 Hz, 2H), 7.50 – 7.43 (m, 4H), 7.12 – 7.08 (m, 2H), 7.08 – 7.05 (m, 2H), 6.91 (dd, $^3$J$_{HH}$ = 7.3 Hz, $^4$J$_{HH}$ = 1.1 Hz, 2H), 2.09 (s, 6H).

**Variable Temperature NMR Experiments**

Temperature was calibrated using MeOH (low temperatures) or ethyleneglycol (high temperatures) standards measuring the difference between -OH and -CH$_3$-CH$_2$-chemical shifts as a function of temperature.

**Determination of ligand exchange mechanism in (Cl$_2$ArN(CMe))$_2$Cu(C$_2$H$_4$)SbF$_6$ (7b) system**

Inside the glove box (Cl$_2$ArN(CMe))$_2$Cu(C$_2$H$_4$)SbF$_6$ (7b) (5 × 9.5 mg, 5 × 0.010 mmol) was placed in 5 separate NMR tubes. Outside the glove box CD$_2$Cl$_2$ was added (5 × 0.5 mL) and the mixture was briefly shaken to dissolve materials. Then necessary amount of C$_2$H$_4$ was transferred via syringe into NMR tubes (the exact quantity of added C$_2$H$_4$ was determined from integration of NMR signals) and samples were placed in an NMR spectrometer for spectra acquisition.

![Figure S1](image-url)  
*Figure S1.* Dependence of bound ethylene NMR line shape as a function of added free ethylene measured on 400MHZ JEOL-EC in CD$_2$Cl$_2$. 

S-10
Ethylene self exchange in (Cl$_2$ArN(CMe))$_2$Cu(C$_2$H$_4$)SbF$_6$ (7b) system

Procedure for experiments with and without added free ethylene.

Inside the glove box (Cl$_2$ArN(CMe))$_2$Cu(C$_2$H$_4$)SbF$_6$ (7b) (9.5 mg, 0.010 mmol) was placed in an NMR tube. Outside the glove box C$_2$D$_2$Cl$_4$ (0.5 mL) was added and the mixture was briefly shaken to dissolve materials. (For the experiment with added free ethylene: C$_2$H$_4$ was added to the red solution via syringe (approximately 2.24 mL, 0.1 mmol) and the exact quantity of added C$_2$H$_4$ (8.8 equiv) was determined from integration of NMR signals.)

The tube was then transferred to NMR spectrometer for spectra acquisition. The sample was allowed to equilibrate for 5 min at the indicated probe temperature prior each measurement. Data were analyzed by line shape analysis of the ethylene region of spectra. First order rate constants ($k_{obs}$, s$^{-1}$) were obtained by matching observed $^1$H-NMR spectra with those simulated using the WinDNMR program until coalescence of bound ethylene signals was reached.$^5$ The spectrum when there is no exchange (no added ethylene, 293 K), was used to set up the starting parameters in WinDNMR for $k_{obs} = 0$ s$^{-1}$.

Figure S2. a) Variable temperature $^1$H-NMR of (Cl$_2$ArN(CMe))$_2$Cu(C$_2$H$_4$)SbF$_6$ (7b) (ethylene region) on 600MHZ JEOL-EC in C$_2$D$_2$Cl$_4$. b) Variable temperature $^1$H-NMR of (Cl$_2$ArN(CMe))$_2$Cu(C$_2$H$_4$)SbF$_6$ (7b) (ethylene region) with added free ethylene on 600MHZ JEOL-EC in C$_2$D$_2$Cl$_4$.

Figure S3. a) Eyring plot of $(\text{Cl}_2\text{ArN(CMe)}_2)\text{Cu(C}_2\text{H}_4)\text{SbF}_6$ (7b). b) Eyring plot of ethylene exchange between $(\text{Cl}_2\text{ArN(CMe)}_2)\text{Cu(C}_2\text{H}_4)\text{SbF}_6$ (7b) and C$_2$H$_4$ in C$_2$D$_2$Cl$_4$.

Table S1. Measured and calculated parameters of ethylene exchange between Cl$_2$ArN(CMe)$_2$Co(C$_2$H$_4$)SbF$_6$ (7b) and C$_2$H$_4$ in C$_2$D$_2$Cl$_4$.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$k_{obs}$ (s$^{-1}$)</th>
<th>Activation Param.$^a$</th>
<th>[C$_2$H$_4$] (M)</th>
<th>$T$ (K)</th>
<th>$k_{obs}$ (s$^{-1}$)</th>
<th>$k_{exch}$ (M$^{-1}$s$^{-1}$)</th>
<th>Activation Param.$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>No added ligand</td>
<td></td>
<td></td>
<td></td>
<td>With added C$_2$H$_4$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>304</td>
<td>15</td>
<td></td>
<td></td>
<td>256</td>
<td>59</td>
<td>335</td>
<td></td>
</tr>
<tr>
<td>314</td>
<td>32</td>
<td></td>
<td></td>
<td>266</td>
<td>89</td>
<td>505</td>
<td></td>
</tr>
<tr>
<td>324</td>
<td>61</td>
<td>$\Delta G_{298}^{\ddagger}=15.9 \pm 0.1$</td>
<td></td>
<td>0.176</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>333</td>
<td>87</td>
<td>$\Delta H^{\ddagger}=9.9 \pm 0.2$</td>
<td></td>
<td>275</td>
<td>140</td>
<td>794</td>
<td>$\Delta G_{298}^{\ddagger}=12.9 \pm 0.1$</td>
</tr>
<tr>
<td>343</td>
<td>120</td>
<td>$\Delta S^{\ddagger}=-20.1 \pm 1.5$</td>
<td></td>
<td>285</td>
<td>219</td>
<td>1248</td>
<td>$\Delta H^{\ddagger}=6.2 \pm 0.5$</td>
</tr>
<tr>
<td>353</td>
<td>183</td>
<td></td>
<td></td>
<td>295</td>
<td>299</td>
<td>1697</td>
<td>$\Delta S^{\ddagger}=-22.5 \pm 1.7$</td>
</tr>
<tr>
<td>362</td>
<td>304</td>
<td></td>
<td></td>
<td>304</td>
<td>499</td>
<td>2832</td>
<td></td>
</tr>
<tr>
<td>372</td>
<td>425</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ $\Delta G_{298}^{\ddagger}$ (kcal/mol), $\Delta H^{\ddagger}$ (kcal/mol), $\Delta S^{\ddagger}$ (eu).

Ethylene self exchange in (Cl$_2$ArN(CMe)$_2$)Co(C$_2$H$_4$)SbF$_6$ (8a) system

Inside the glove box (Cl$_2$ArN(CMe)$_2$)Co(C$_2$H$_4$)SbF$_6$ (8a) (15 mg, 0.015 mmol) was placed in a tin-foil wrapped screw cap NMR tube. Outside the glove box after cooling to -75 °C CDCl$_3$F (0.45 mL) was added. The mixture was briefly shaken to dissolve materials. The solution was purged with C$_2$H$_4$ and the exact quantity of added C$_2$H$_4$ (5 equiv) was determined by $^1$H NMR. The tube was then transferred to a precooled NMR probe for spectra acquisition. The temperature was lowered to attempt to achieve the separation of coalesced ethylene signals. However, signal separation was not achieved when the lower limit of the cryoprobe was reached. The difference of the coalesced ethylene signal bandwidth at fast exchange (253 K) and slower exchange (146 K) was
used to estimate $k$. For calculation of $k$, the reaction was considered to follow pseudo first-order kinetics and the equation used for cases of equally populated sites was employed (this can lead to some inaccuracy in $k$, however with a small impact on the value of $\Delta G^{\ddagger}$). Since some broadening of other signals was also observed at low temperatures, the calculated $\Delta G^{\ddagger}$ value was considered to be the upper limit of $\Delta G^{\ddagger}$.

Table S2. Measured and calculated parameters of ethylene exchange between (Cl$_2$ArN(CMe))$_2$Ag(C$_2$H$_4$)SbF$_6$ (8a) and C$_2$H$_4$ in CDCl$_2$F.

<table>
<thead>
<tr>
<th>[C$_2$H$_4$] (M)</th>
<th>$T$ (K)</th>
<th>$\Delta \nu$ (Hz)</th>
<th>$\Delta W^{b}$ (Hz)</th>
<th>$k_{\text{obs}}^{c}$ ($10^3$ s$^{-1}$)</th>
<th>$k_{\text{exch}}$ (10$^3$ mol$^{-1}$·s$^{-1}$)</th>
<th>$\Delta G_{146}^{\ddagger}$ kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.167</td>
<td>146</td>
<td>250</td>
<td>6.27</td>
<td>15.6</td>
<td>93.9</td>
<td>&lt;5.0</td>
</tr>
</tbody>
</table>

$^{a}$ $\Delta \nu$ calculated from $\Delta \nu = \nu_{\text{free}} - \nu_{\text{bound}}$; where $\nu$ – chemical shift (Hz);

$^{b}$ $\Delta W$ calculated from $\Delta W = W^* - W_f$, where $W^*$ – width at half height at 146 K; $W_f$ – width at half height at fast exchange (253 K);

$^{c}$ $k_{\text{obs}}$ calculated from $k_{\text{obs}} = \frac{\pi \Delta \nu^2}{2 \Delta W}$.

Ethylene self exchange in (Cl$_2$ArN(CMe))$_2$Au(C$_2$H$_4$)SbF$_6$ (9) system

Inside the glove box (Cl$_2$ArN(CMe))$_2$Au(C$_2$D$_4$)SbF$_6$ (9-d4) (11 mg, 0.010 mmol) was placed in a tin foil-wrapped NMR tube. Outside the glove box after cooling to -75 °C CD$_2$Cl$_2$ (0.5 mL) was added and the mixture was briefly shaken to dissolve materials. To the red solution C$_2$H$_4$ was added via syringe (approximately 2.24 mL, 0.1 mmol) at -75 °C and the tube was quickly transferred to a precooled NMR probe for spectra acquisition. The exact quantity of added C$_2$H$_4$ was determined from NMR as a sum of intensity of free ethylene and bound ethylene formed from progressing reaction. Spectra acquisition was repeated every 10 min until equilibrium was nearly reached. Formation of (Cl$_2$ArN(CMe))$_2$Au(C$_2$H$_4$)SbF$_6$ (9) was monitored and pseudo first-order rate constants were calculated graphically. This was repeated for four different temperatures.
Figure S4. a) Plot of ethylene exchange between (Cl2ArN(CMe))2Au(C2D4)SbF6 (9-d4) and C2H4 at -75 °C in CD2Cl2. b) Plot of ethylene exchange between (Cl2ArN(CMe))2Au(C2D4)SbF6 (9-d4) and C2H4 at -70 °C in CD2Cl2.

Figure S5. a) Plot of ethylene exchange between (Cl2ArN(CMe))2Au(C2D4)SbF6 (9-d4) and C2H4 at -65 °C in CD2Cl2. b) Plot of ethylene exchange between (Cl2ArN(CMe))2Au(C2D4)SbF6 (9-d4) and C2H4 at -60 °C in CD2Cl2.

Table S3. Measured and calculated parameters of ethylene exchange between (Cl2ArN(CMe))2Au(C2D4)SbF6 (9-d4) and C2H4 in CD2Cl2.

<table>
<thead>
<tr>
<th>Nr.</th>
<th>T (K)</th>
<th>[C2H4] (equiv)</th>
<th>[C2H4] (M)</th>
<th>kobs (10^4 s⁻¹)</th>
<th>kexch (10^4 M⁻¹s⁻¹)</th>
<th>Activation parameters⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>199</td>
<td>15.0</td>
<td>0.30</td>
<td>1.38 ± 0.10</td>
<td>4.59 ± 0.6</td>
<td>ΔG298° = 16.7 ± 0.1</td>
</tr>
<tr>
<td>2.</td>
<td>204</td>
<td>13.5</td>
<td>0.27</td>
<td>2.59 ± 0.16</td>
<td>9.59 ± 1.1</td>
<td>ΔH° = 10.0 ± 1.4</td>
</tr>
<tr>
<td>3.</td>
<td>209</td>
<td>7.80</td>
<td>0.16</td>
<td>2.58 ± 0.24</td>
<td>16.3 ± 2.5</td>
<td>ΔS° = -22.5 ± 4.8</td>
</tr>
<tr>
<td>4.</td>
<td>214</td>
<td>7.90</td>
<td>0.16</td>
<td>4.73 ± 0.48</td>
<td>30.1 ± 4.4</td>
<td></td>
</tr>
</tbody>
</table>

⁴ ΔG298° (kcal/mol), ΔH° (kcal/mol), ΔS° (eu).
**Figure S6.** Eyring plot of ethylene exchange between (Cl₂ArN(CMe))₂Au(C₂D₄)SbF₆ (9-d4) and C₂H₄.

**Equations and notes**

**Eyring equation:**

\[
k = \kappa \frac{k_B T}{h} e^{-\Delta G^\ddagger / RT} = \kappa \frac{k_B T}{h} e^{-\Delta H^\ddagger - T \Delta S^\ddagger) / RT},
\]

(1)

**Eyring equation in linear form:**

\[
\ln \left(\frac{k}{T}\right) = -\frac{\Delta H^\ddagger}{R} \times \frac{1}{T} + \ln \left(\frac{k_B}{h}\right) + \frac{\Delta S^\ddagger}{R},
\]

(2)

\(\Delta S^\ddagger\) and \(\Delta H^\ddagger\) were calculated from Eyring plot ([ln(k/T] vs [1000/T] coordinates):

\[
\Delta S^\ddagger = R \times (\text{intercept} - \ln \left(\frac{k_B}{h}\right))
\]

(3)

\[
\Delta H^\ddagger = -(R \times \text{slope} \times 1000)
\]

(4)

\(\Delta G^\ddagger\) was calculated from:

\[
\Delta G_T^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger);
\]

(5)

or

\[
\Delta G_T^\ddagger = RT \left[\ln \left(\frac{k_B T}{h}\right) - \ln(k_{exch})\right].
\]

(6)

Errors in \(\Delta S^\ddagger\) and \(\Delta H^\ddagger\) values were calculated using error propagation formulas reported by Girolami.\(^6\) Error in \(\Delta G^\ddagger\) was obtained as a difference between \(\Delta G^\ddagger\) and calculated \(\Delta G^\ddagger\) for higher/lower error in \(T\) and \(k\). The error in \(k_{obs}\) for complex 9-d4 was taken as a twice that of the standard deviation value calculated using the LINEST

\(^6\) Morse, P. M.; Spencer, M. D.; Wilson, S. R.; Girolami, G. S. *Organometallics* 1994, **13**, 1646 – 1655.
function in the MS Excel program. The error in $k_{\text{obs}}$ where $k_{\text{obs}}$ values are simulated is taken as 10% of the obtained value. Error in $T$ was assumed to be +/- 1 K.
X-ray Crystallographic Data

Crystallographic Information for (Cl₂ArN(CMe))₂Cu(C₂H₄)OTf

Figure S7. ORTEP view (50% probability ellipsoids) of 7a showing atom labeling. Hydrogens are omitted for clarity.

A total of 1830 frames were collected. The total exposure time was 15.25 hours. CellNow was used to identify the 2 twin domains. The corresponding twin law is a 180° rotation around the reciprocal axis (1 0 1). The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 31,836 reflections. For further analyses only reflections containing a contribution of component#1 were considered. A total of 5368 independent reflections to a maximum θ angle of 61.00° (0.88 Å resolution) were used (completeness = 96.1%, R_int = 8.09%, R_sig = 2.49%) and 4474 (83.35%) were greater than 2σ(F²). The final cell constants of a = 11.7606(6) Å, b = 12.1587(6) Å, c = 12.8938(7) Å, α = 85.000(3)°, β = 88.881(3)°, γ = 87.642(3)°, volume = 1834.92(16) Å³, are based upon the refinement of the XYZ-centroids of 6254 reflections above 20 σ(I) with 4.679° < 2θ < 60.82°. Data were corrected for absorption effects using the multi-scan method (TWINABS). The ratio of minimum to maximum apparent transmission was 0.904. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8080 and 0.9800.
The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P\bar{1}$, with $Z = 2$ for the formula unit, $C_{39}H_{28}Cl_{4}CuF_{3}N_{2}O_{3}S$. The final anisotropic full-matrix least-squares refinement on $F^2$ with 581 variables converged at $R1 = 4.97\%$, for the observed data and $wR2 = 16.43\%$ for all data. The ratio of the two twin components refined to 0.97:0.03. The goodness-of-fit was 1.191. The largest peak in the final difference electron density synthesis was 0.796 e/Å$^3$ and the largest hole was -0.841 e/Å$^3$ with an RMS deviation of 0.110 e/Å$^3$. On the basis of the final model, the calculated density was 1.569 g/cm$^3$ and F(000), 880 e$^-$. 

**Table S4.** Crystal data, data collection and structure refinement for 7a.

<table>
<thead>
<tr>
<th>Chemical formula</th>
<th>$C_{39}H_{28}Cl_{4}CuF_{3}N_{2}O_{3}S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula weight</td>
<td>867.03</td>
</tr>
<tr>
<td>$T$ (K)</td>
<td>240(2)</td>
</tr>
<tr>
<td>$\lambda$ (Å)</td>
<td>1.54184</td>
</tr>
<tr>
<td>Crystal size (mm)</td>
<td>0.077 x 0.072 x 0.014</td>
</tr>
<tr>
<td>Crystal system</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>$P\bar{1}$</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>11.7606(6)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>12.1587(6)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>12.8938(7)</td>
</tr>
<tr>
<td>$\alpha$ (°)</td>
<td>85.000(3)</td>
</tr>
<tr>
<td>$\beta$ (°)</td>
<td>88.881(3)</td>
</tr>
<tr>
<td>$\gamma$ (°)</td>
<td>87.642(3)</td>
</tr>
<tr>
<td>$V$ (Å$^3$)</td>
<td>1834.92(16)</td>
</tr>
<tr>
<td>$Z$</td>
<td>2</td>
</tr>
<tr>
<td>$\rho_{\text{calc}}$ (g/cm$^3$)</td>
<td>1.569</td>
</tr>
<tr>
<td>$\mu$ (mm$^{-1}$)</td>
<td>4.543</td>
</tr>
<tr>
<td>F(000)</td>
<td>880</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>3.44 to 61.00°</td>
</tr>
</tbody>
</table>

S-18
Reflections collected 31836 for both domains;

Independent reflections 5368 [R(int) = 0.080]; only reflection with a contribution from domain#1 were used

Coverage of independent reflections 96.1%

Refinement program SHELXL-97 (Sheldrick, 2008)

Data / restraints / parameters 5368 / 1 / 581

Twin ratio 0.97:0.03

GOF on $F^2$ 1.191

R1 ($I > 2\sigma(I)$) 0.0497

wR2 all data 0.1643

Weighing Scheme $w=1/[\sigma^2(F_o^2)+(0.0677P)^2+4.4389P]$

where $P=(F_o^2+2F_c^2)/3$

Largest diff. peak and hole (e Å$^{-3}$) 0.796 and -0.841

Crystallographic Information for \((\text{Cl}_2\text{ArN(CMe)}_2\text{Ag(C}_2\text{H}_4\text{)}\text{BF}_4\text{)}_2(\text{CH}_2\text{Cl}_2)/(\text{C}_7\text{H}_14)\)

Figure S8. ORTEP view (50% probability ellipsoids) of 8b showing atom labeling. Hydrogens are omitted for clarity.
A crystal was picked and cut with Paratone oil and mounted onto a Mitegen loop. The data collection was performed using a Bruker APEXII DUO CCD area detector diffractometer with graphite-monochromated MoKa radiation ($\lambda = 0.71073 \text{ Å}$) at 123(2) K. The data were collected as $\omega$ scan frames at 45 sec. and 0.3°/frame. Cell parameters refinement and data reduction were performed using SAINT. An empirical absorption correction was applied using SADABS in Apex2. The structure was solved by direct methods and all nonhydrogen atoms were anisotropically refined using the SHELXTL package. Hydrogen atom positions were calculated.

**Table S5.** Crystal data, data collection and structure refinement for 8b.

<table>
<thead>
<tr>
<th>Chemical formula</th>
<th>C$<em>{47}$H$</em>{46}$AgBCl$_8$F$_4$N$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula weight</td>
<td>1117.14</td>
</tr>
<tr>
<td>$T$ (K)</td>
<td>123(2)</td>
</tr>
<tr>
<td>$\lambda$ (Å)</td>
<td>0.71073</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>$I\ 2/m$</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>11.982(4)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>23.133(8)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>17.482(9)</td>
</tr>
<tr>
<td>$\alpha$ (°)</td>
<td>90</td>
</tr>
<tr>
<td>$\beta$ (°)</td>
<td>94.631(4)</td>
</tr>
<tr>
<td>$\gamma$ (°)</td>
<td>90</td>
</tr>
<tr>
<td>$V$ (Å$^3$)</td>
<td>4830(3)</td>
</tr>
<tr>
<td>$Z$</td>
<td>4</td>
</tr>
<tr>
<td>$\rho_{\text{calc}}$ (g/cm$^3$)</td>
<td>1.536</td>
</tr>
<tr>
<td>$\mu$ (mm$^{-1}$)</td>
<td>0.911</td>
</tr>
<tr>
<td>$F$(000)</td>
<td>2264</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.463 to 27.918°</td>
</tr>
<tr>
<td>$hkl$ range</td>
<td>-15$\leq h \leq$15, -30$\leq k \leq$29, -22$\leq l \leq$21</td>
</tr>
</tbody>
</table>

S-20
Reflections collected: 4943
Independent reflections: 5851 [R(int) = 0.0235]
Coverage of independent reflections: 98.6%
Refinement program: SHELXL-2014/7 (Sheldrick, 2014)
Data / restraints / parameters: 5851 / 9 / 331
GOF on \( F^2 \): 1.046
R1(I > 2\sigma(I)): 0.0489
wR2 all data: 0.1344
Weighting scheme: 
\[
    w = \frac{1}{\sigma^2(F_o^2) + (0.0662P)^2 + 20.8996P}
\]
where \( P = (F_o^2 + 2F_c^2)/3 \)
Largest diff. peak and hole (e\(\text{Å}^{-3}\)): 1.945 and -1.062

Crystallographic Information for (Cl\(_2\)ArN(CMe))\(_2\)Au(C\(_2\)H\(_4\))SbF\(_6\).

Figure S9. ORTEP view (50% probability ellipsoids) of 9 showing atom labeling. Hydrogens are omitted for clarity.
A total of 1464 frames were collected. The total exposure time was 16.27 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 58,721 reflections to a maximum θ angle of 30.13° (0.71 Å resolution), of which 11,177 were independent (average redundancy 5.254, completeness = 99.6%, R_int = 4.79%) and 8,228 (73.62%) were greater than 2σ(F^2). The final cell constants of a = 17.6898(10) Å, b = 12.1398(7) Å, c = 17.9911(10) Å, β = 100.3306(8)°, volume = 3801.0(4) Å^3, are based upon the refinement of the XYZ-centroids of 9,880 reflections above 20 σ(I) with 4.602° < 2θ < 60.15°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.838.

The final anisotropic full-matrix least-squares refinement on F^2 with 469 variables converged at R1 = 4.60%, for the observed data and wR2 = 14.24% for all data. The goodness-of-fit was 1.048. The largest peak in the final difference electron density synthesis was 3.411 e^-/Å^3 and the largest hole was -3.023 e^-/Å^3 with an RMS deviation of 0.225 e^-/Å^3. On the basis of the final model, the calculated density was 1.900 g/cm^3 and F(000), 2088 e^-.

**Table S6.** Crystal data, data collection and structure refinement for 9.

<table>
<thead>
<tr>
<th>Chemical formula</th>
<th>C_{38}H_{28}AuCl_{4}F_{6}N_{2}Sb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula weight</td>
<td>1087.14</td>
</tr>
<tr>
<td>T (K)</td>
<td>140(2)</td>
</tr>
<tr>
<td>λ (Å)</td>
<td>0.71073</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P12/m1</td>
</tr>
<tr>
<td>a (Å)</td>
<td>17.6898(10)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>12.1398(7)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>17.9911(10)</td>
</tr>
<tr>
<td>α (°)</td>
<td>90</td>
</tr>
<tr>
<td>β (°)</td>
<td>100.3306(8)</td>
</tr>
</tbody>
</table>
\( \gamma (^\circ) \) & 90 \\
\( V (\text{Å}^3) \) & 3801.0(4) \\
\( Z \) & 4 \\
\( \rho_{\text{calc}} (\text{g/cm}^3) \) & 1.900 \\
\( \mu (\text{mm}^{-1}) \) & 4.908 \\
\( F(000) \) & 2088 \\
Theta range for data collection & 1.49 to 30.13° \\
hkl range & \(-24 \leq h \leq 24, -17 \leq k \leq 17, -25 \leq l \leq 25\) \\
Reflections collected & 58721 \\
Independent reflections & 11177 [R(int) = 0.0479] \\
Coverage of independent reflections & 99.6% \\
Refinement program & SHELXL-2013 (Sheldrick, 2013) \\
Data / restraints / parameters & 11177 / 0 / 469 \\
GOF on \( F^2 \) & 1.048 \\
R1(I > 2\sigma(I)) & 0.0460 \\
wR2 all data & 0.1424 \\
Weighting scheme & w=1/[\sigma^2(F_o^2)+(0.0598P)^2+42.5152P] \\
& where P=(F_o^2+2F_c^2)/3 \\
Largest diff. peak and hole (e Å\(^{-3}\)) & 3.411 and -3.023
$^1$H NMR (CDCl$_3$, 500 MHz)
$^{13}$C NMR (CDCl$_3$, 126 MHz)
^1H NMR (CDCl\textsubscript{3}, 500 MHz)
$^{13}$C NMR (CDCl$_3$, 126 MHz)
$^1$H NMR (CDCl$_3$, 500 MHz)
$^{13}$C NMR (CDCl$_3$, 126 MHz)
$^{1}$H NMR (CDCl$_3$, 400 MHz)
$^{13}$C NMR (CDCl$_3$, 126 MHz)

$\text{Ar-N-Cu-N-Ar}$

$^{2}$OTf$^-$
2D-HMQC (CDCl₃)

Ar – N – Cu – N – Ar

7a

^OTf⁻

S-32
$^{13}$C NMR (CD$_2$Cl$_2$, 126 MHz)

Ar–N–Cu–N–Ar

$^+$SbF$_6^-$

$^{13}$C NMR (CD$_2$Cl$_2$, 126 MHz)
2D-HMQC (CD$_2$Cl$_2$)
$\text{Ar-N}^+\text{Ag}^{-}\text{N-Ar}$

$^1$H NMR (CDCl$_3$, 500 MHz, 293 K)
$\text{SbF}_6^-$

Ar-N-Ar

$\text{Ag}$

$\text{^{13}C NMR (CDCl}_3, 126 \text{ MHz, 283 K)}$

$8a$
DEPT 135 deg (CDCl₃, 126 MHz, 283 K)
$^1$H NMR (CD$_2$Cl$_2$, 500 MHz, 273 K)
$^{13}$C NMR (CD$_2$Cl$_2$, 126 MHz, 273 K)

![Chemical structure and NMR spectrum](image)
2D-HMQC (CD$_2$Cl$_2$, 273 K)

$^1$H(C$_2$H$_4$)

$^{13}$C(C$_2$H$_4$)
$^{1}H$ NMR (CDCl$_3$, 500 MHz)

Ar - N - N - Ar

SbF$_6$
2D-HMQC (CDCl₃)

Ar–N–N–Ar

SbF₆⁻

1H(C₂H₄)

65.4 ppm

13C(C₂H₄)
$^1$H NMR (CD$_2$Cl$_2$, 500 MHz)  

$^{9-}d^4$