Syntheses and X-ray Crystal Structures of Cationic, Two-Coordinate Gold(I) π-Alkene Complexes that Contain a Sterically Hindered *o*-Biphenylphosphine Ligand

Timothy J. Brown, Marina G. Dickens, and Ross A. Widenhoefer*

French Family Science Center

Duke University

Durham, NC 27708-0346

Supporting Information

Experimental procedures, analytical and spectroscopic data for new gold(I) phosphine complexes, X-ray crystallographic data, and kinetic data (66 pages).

Experimental

General Methods. Reactions were performed under a nitrogen atmosphere employing standard Schlenk and glovebox techniques unless specified otherwise. NMR spectra were obtained on a Varian spectrometer operating at 500 MHz for ^{1}H NMR, 125 MHz for ^{13}C NMR, and 202 MHz for ^{31}P NMR in CD_2Cl_2 at 25 °C unless noted otherwise. IR spectra were obtained on a Nicolet Avatar 360-FT IR spectrometer. Elemental analyses were performed by Complete Analysis Laboratories (Parsippany, NJ). Mass spectra were obtained on an Applied Biosystems Voyager-DE Pro MALDI mass spectrometer operating at a mass range of 500-4000u with a dihydroxyacetophenone matrix (10 mg/1 mL DCM) and was calibrated with PEG1000.

Methylene chloride was purified by passage through columns of activated alumina under nitrogen. $CDCl_3$ and CD_2Cl_2 were dried over CaH_2 prior to use. [P(*t*-Bu)$_2$*o*-bipheny]AuCl (**S1**) was synthesized using a published procedure.[1] Hexanes, $AgSbF_6$, isobutylene, propene, ethylene, methylenecyclohexane, 2-methyl-2-butene, 2,3-dimethyl-2-butene, *cis*-2-butene, 1-hexene, 4-methylstyrene, *trans*-2-butene, 4-vinylanisole, styrene, 4-bromostyrene, and 4-trifluoromethylstyrene were purchased from major chemical suppliers and used as received.

Synthesis of di-*t*-butyl *o*-biphenylphosphine gold(I) complexes

{[P(*t*-Bu)$_2$*o*-bipheny]Au(NCAr$_F$)}$^+$ SbF$_6^-$ (2). A suspension of **S1** (160 mg, 0.30 mmol), $AgSbF_6$ (103.6 mg, 0.301 mmol), and 3,5-bis(trifluoromethyl)benzonitrile (72.0 mg, 0.30 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature for 6 hours. The resulting suspension was filtered and the filtrate concentrated to ~2 mL, diluted with hexanes (20 mL) and cooled at 4 ^{o}C overnight to promote precipitation of the product. The mother liquor was decanted and resulting solid rinsed with cold hexanes. Evaporation of the solid under vacuum provided **2** as a colorless powder (263 mg, 90 %). ^{1}H NMR: δ 8.41 (s, 2 H), 8.38 (s, 1 H), 7.91 (t, J = 8.5 Hz, 1 H), 7.65 – 7.60 (m, 2 H), 7.57 (t, J = 7.5 Hz, 2

H), 7.48 (t, *J* = 7.5 Hz, 1 H), 7.40 - 7.33 (m, 1 H), 7.28 (d, *J* = 7.0 Hz, 2 H), 1.45 (d, *J* = 16.5 Hz, 18 H). $^{13}C\{^1H\}$ NMR: δ 148.8 (d, *J* = 12.6 Hz), 143.1 (d, *J* = 5.9 Hz), 133.8 (d, *J* = 2.9 Hz), 133.6, 133.1, 131.6, 129.9 (d, *J* = 8.8 Hz), 129.6, 129.1, 127.6 (d, *J* = 43 Hz), 125.2, 123.6 (d, *J* = 52 Hz), 123.0, 120.8, 118.7, 114.7, 110.4, 38.1 (d, *J* = 27 Hz), 30.6. $^{31}P\{^1H\}$ NMR: δ 57.9. Anal. calcd (found) for $C_{29}H_{30}AuF_{12}NPSb$: H, 3.12 (3.06); C, 35.90 (36.10); N, 1.44 (1.29).

Synthesis of di-*t*-butyl *o*-biphenylphosphine Gold(I) π-Alkene Complexes

{[P(*t*-Bu)$_2$*o*-bipheny]Au[η^2-H$_2$C=C(CH$_2$)$_5$]}$^+$ SbF$_6^-$ (1a). A solution of **S1** (35 mg, 0.066 mmol) and $AgSbF_6$ (22.7 mg, 0.066 mmol) in CH_2Cl_2 (2 mL) was stirred at room temperature for 5 min. Methylene cyclohexane (25 mg, 0.26 mmol) was added dropwise via syringe and the resulting suspension was stirred in a sealed flask at room temperature for 6 hours. The resulting suspension was filtered and the filtrate concentrated to ~2 mL, diluted with hexanes (2 mL), and cooled at 4 °C for 24 h to form **1a** (54 mg, 99%) as a white solid. ^1H NMR ($CDCl_3$): δ 7.87 (t, *J* = 8 Hz, 1 H), 7.62 – 7.52 (m, 5 H), 7.22 - 7.16 (m, 3 H), 3.93 (d, *J* = 4.5 Hz, 2 H), 2.46 – 2.36 (m, 2 H), 2.36 – 2.24 (m, 2 H), 1.98 – 1.86 (m, 2 H), 1.68 (br. s, 1 H), 1.60 – 1.46 (m, 3 H), 1.39 (d, *J* = 16.5 Hz, 18 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 169.4, 148.4, 143.2, 133.9, 133.5, 131.6, 130.0, 129.6 (d, *J* = 18.5 Hz), 128.1, 127.9, 124.7 (d, *J* = 48.1 Hz), 91.8 (d, *J* = 14.7 Hz), 39.9, 37.7 (d, *J* = 22.9 Hz), 30.6 (d, *J* = 5.9 Hz), 25.5. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 64.7. Anal. calcd (found) for $C_{27}H_{39}PF_6AuSb$: H, 4.75 (4.65); C, 39.20 (39.31).

{[P(*t*-Bu)$_2$*o*-bipheny]Au[η^2-*cis*-CH$_3$C(H)=C(H)CH$_3$]}$^+$ SbF$_6^-$ (1b). Complex **1b** was isolated in 94% yield as a light yellow solid from reaction of *cis*-2-butene with a mixture of **S1** and $AgSbF_6$ employing a procedure similar to that used to synthesize **1a**. ^1H NMR (400 MHz, $CDCl_3$): δ 7.90 – 7.82 (m, 1 H), 7.68 – 7.50 (m, 5 H), 7.21 (d, *J* = 7.2 Hz, 3 H), 5.37 (br. s, 2 H), 1.85 (d, *J* = 4.8 Hz, 6 H), 1.38 (d, *J* = 16.4 Hz, 18 H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 148.4, 143.1, 133.8, 133.4, 131.7, 129.7, 129.3, 127.9, 124.2, 121.6, 110.0, 37.9 (d, *J* = 23.9 Hz), 30.7 (d, *J* = 6.2 Hz), 15.4. ^{31}P{^{1}H} NMR: δ 66.1. Anal. calcd (found) for $C_{24}H_{35}PF_6AuSb$: H, 4.48 (4.38); C, 36.62 (36.46).

{[P(*t*-Bu)$_2$*o*-biphenyl]Au[η^2-$H_2C{=}C(CH_3)_2$]}$^+$ SbF_6^- (1c). Complex **1c** was isolated in 93% yield as a white solid from reaction of isobutylene with a mixture of **S1** and $AgSbF_6$ employing a procedure similar to that used to synthesize **1a**. ^{1}H NMR: δ 7.94 – 7.90 (m, 1 H), 7.68 – 7.58 (m, 5 H), 7.30 – 7.26 (m, 1 H), 7.24 (d, *J* = 6.5 Hz, 2 H), 3.92 (d, *J* = 4.5 Hz, 2 H), 2.174 (s, 6 H), 1.42 (d, *J* = 16.5 Hz, 18 H). ^{13}C{^{1}H} NMR: δ 163.3, 148.7 (d, *J* = 13.7 Hz), 143.8 (d, *J* = 6.8 Hz), 134.3, 133.9 (d, *J* = 6.8 Hz), 132.2, 130.1, 130.0, 128.4, 124.7 (d, *J* = 47 Hz), 95.1 (d, *J* = 14.7 Hz), 37.8 (d, *J* = 23.6 Hz), 30.9 (d, *J* = 5.9 Hz), 28.6 (d, *J* = 6.9 Hz). ^{31}P{^{1}H} NMR: δ 64.9. Anal. calcd (found) for $C_{24}H_{35}PF_6AuSb$: H, 4.48 (4.34); C, 36.62 (36.53).

{[P(*t*-Bu)$_2$*o*-biphenyl]Au[η^2-$H_2C{=}CH(CH_2)_3CH_3$]}$^+$ SbF_6^- (1d). Complex **1d** was isolated in 95% yield as a white solid from reaction of 1-hexene with a mixture of **S1** and $AgSbF_6$ employing a procedure similar to that used to synthesize **1a**. ^{1}H NMR: δ 7.94 – 7.87 (m, 1 H), 7.70 – 7.56 (m, 5 H), 7.32 – 7.20 (m, 3 H), 6.22 – 6.10 (m, 1 H), 4.39 (d, *J* = 9 Hz, 1 H), 4.36 (d, *J* = 18 Hz, 1 H), 2.50 – 2.34 (m, 1 H), 2.30 – 2.16 (m, 1 H), 1.55 – 1.25 (m, 4 H), 1.41 (d, *J* = 16.5 Hz, 18 H), 0.91 (t, *J* = 7 Hz, 3 H). ^{13}C{^{1}H} NMR: δ 148.7 (d, *J* = 14.6 Hz), 143.7 (d, *J* = 6.8 Hz), 141.9 (d, *J* = 12.7 Hz),134.4, 133.8, 132.2, 129.9, 128.4, 124.7 (d, *J* = 48.0 Hz), 111.4, 100.1 (d, *J* = 10.7 Hz), 38.7 (d, *J* = 23.6), 35.6, 30.9, 22.3, 13.8. ^{31}P{^{1}H} NMR: δ 66.5. Anal. calcd (found) for $C_{26}H_{39}PF_6AuSb$: H, 4.82 (4.69); C, 38.30 (38.16).

{[P(*t*-Bu)$_2$*o*-biphenyl]Au[η^2-$(CH_3)_2C{=}C(CH_3)_2$]}$^+$ SbF_6^- (1e). Complex **1e** was isolated in 94% yield as a white solid from reaction of 2,3-dimethyl-2-butene with a mixture of **S1** and $AgSbF_6$ employing a procedure similar to that used to synthesize **1a**. ^{1}H NMR: δ 7.96 – 7.87 (m, 1 H), 7.74 – 7.50 (m, 5 H), 7.32 – 7.14 (m, 3 H), 1.88 (d, *J* = 1.0 Hz, 12 H), 1.47 – 1.38 (m, 18 H). ^{31}P{^{1}H} NMR: δ 65.5. Anal. calcd (found) for $C_{26}H_{39}PF_6AuSb$: H, 4.82 (4.69); C, 38.30 (38.35).

{[P(*t*-Bu)$_2$*o*-bipheny]Au[η^2-*trans*-CH$_3$C(H)=C(H)CH$_3$]}$^+$ SbF$_6^-$ (1f). Complex **1f** was isolated in 92% yield as a white solid from reaction of *trans*-2-butene with a mixture of **S1** and AgSbF$_6$ employing a procedure similar to that used to synthesize **1a**. ^{1}H NMR: δ 7.93 – 7.88 (m, 1 H), 7.70 – 7.58 (m, 5 H), 7.32 – 7.20 (m, 3 H), 5.23 (br. s, 2 H), 1.84 (br. s, 6 H), 1.44 (d, *J* = 16 Hz, 9 H), 1.41 (d, *J* = 16.5 Hz, 9 H). ^{31}P{^{1}H} NMR: δ 65.5 Hz. Anal. calcd (found) for C$_{24}$H$_{35}$PF$_6$AuSb: H, 4.48 (4.35); C, 36.62 (36.71).

{[P(*t*-Bu)$_2$*o*-bipheny]Au[η^2-(CH$_3$)$_2$C=CH(CH$_3$)]}$^+$ SbF$_6^-$ (1g). Complex **1g** was isolated in 98% yield as a white solid from reaction of 2-methyl-2-butene with a mixture of **S1** and AgSbF$_6$ employing a procedure similar to that used to synthesize **1a**. ^{1}H NMR: δ 7.94 – 7.87 (m, 1 H), 7.70 – 7.56 (m, 5 H), 7.28 – 7.18 (m, 3 H), 4.20 (quint, *J* = 6 Hz, 1 H), 2.04 (s, 3 H), 1.97 (s, 3 H), 1.67 (d, *J* = 6 Hz, 3 H), 1.42 (d, *J* = 11.5 Hz, 9 H), 1.38 (d, *J* = 11.5 Hz, 9 H). ^{13}C{^{1}H} NMR: δ 148.8 (d, *J* = 13.7 Hz), 146.1 (d, *J* = 3.9 Hz), 143.9 (d, *J* = 6.8 Hz), 134.2, 133.9, 132.2, 130.4 (d, *J* = 10.7 Hz), 129.9 (d, *J* = 11.7 Hz), 129.7, 128.5, 124.2 (d, *J* = 47 Hz), 111.4, 37.9 (dd, *J* = 23.6, 31.4 Hz), 31.0, 29.4 (d, *J* = 3.9 Hz), 22.7 (d, *J* = 5.9 Hz), 16.1. ^{31}P{^{1}H} NMR: δ 66.2. Anal. calcd (found) for C$_{25}$H$_{37}$PF$_6$AuSb: H, 4.65 (4.56); C, 37.47 (37.60).

{[P(*t*-Bu)$_2$*o*-bipheny]Au[η^2-H$_2$C=CHC$_6$H$_5$]}$^+$ SbF$_6^-$ (1h). Complex **1h** was isolated in 91% yield as a white solid from reaction of styrene with a mixture of **S1** and AgSbF$_6$ employing a procedure similar to that used to synthesize **1a**. ^{1}H NMR (CDCl$_3$): δ 7.83 – 7.78 (m, 1 H), 7.72 – 7.63 (m, 3 H), 7.55 (ddd, *J* = 1.5, 3.5, 5.5 Hz, 2 H), 7.42 – 7.34 (m, 5H), 7.22 (d, *J* = 6.5 Hz, 3 H), 6.84 (dd, *J* = 9, 17 Hz, 1 H), 4.84 (br. s, 1 H), 4.42 (br. s, 1 H), 1.17 (d, *J* = 16.0 Hz, 18 H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 148.4 (d, *J* = 13.7 Hz), 143.1 (d, *J* = 6.8 Hz), 134.8, 133.8 (d, *J* = 12.7 Hz), 133.4 (d, *J* = 6.8 Hz), 133.2 (d, *J* = 7.8 Hz), 132.3, 131.6 (d, *J* = 21.7 Hz), 129.9 (d, *J* = 16.6 Hz), 129.4 (d, *J* = 17.6 Hz), 128.0, 127.9, 124.5 (d, *J* = 47.0 Hz), 91.1, 37.8 (d, *J* = 23.6 Hz), 30.3. ^{31}P{^{1}H} NMR: δ 66.7. Anal. calcd (found) for C$_{28}$H$_{35}$PF$_6$AuSb: H, 4.22 (4.03); C, 40.26 (40.35).

{[P(*t*-Bu)$_2$*o*-bipheny]Au[η^2-H$_2$C=CH-4-C$_6$H$_4$CH$_3$]}$^+$ SbF$_6^-$ (1i). Complex **1i** was isolated in 96% yield as a light yellow solid from reaction of 4-methylstyrene with a mixture of **S1** and $AgSbF_6$ employing a procedure similar to that used to synthesize **1a**. ^{1}H NMR ($CDCl_3$): δ 7.83 – 7.78 (m, 1 H), 7.72 – 7.63 (m, 3 H), 7.55 (ddd, *J* = 2, 3.5, 6 Hz, 2 H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.24 – 7.16 (m, 5 H), 6.82 (dd, *J* = 9.5, 17 Hz, 1 H), 4.75 (br. s, 1 H), 4.32 (br. s, 1 H), 2.34 (s, 3 H), 1.18 (d, *J* = 16.0 Hz, 18 H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 148.4 (d, *J* = 13.7 Hz), 143.1 (d, *J* = 6.8 Hz), 134.8, 133.8 (d, *J* = 12.7 Hz), 133.4 (d, *J* = 6.8 Hz), 133.2 (d, *J* = 7.8 Hz), 132.3, 131.6 (d, *J* = 21.7 Hz), 129.9 (d, *J* = 16.6 Hz), 129.4 (d, *J* = 17.6 Hz), 128.0, 127.9, 124.5 (d, *J* = 47.0 Hz), 91.1, 37.8 (d, *J* = 23.6 Hz), 30.3. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 67.0. Anal. calcd (found) for $C_{29}H_{37}PF_6AuSb$: H, 4.39 (4.26); C, 41.01 (41.38).

{[P(*t*-Bu)$_2$*o*-bipheny]Au[η^2-H$_2$C=CH-4-C$_6$H$_4$Br]}$^+$ SbF$_6^-$ (1j). Complex **1j** was isolated in 90% yield as a light yellow solid from reaction of 4-bromostyrene with a mixture of **S1** and $AgSbF_6$ employing a procedure similar to that used to synthesize **1a**. ^{1}H NMR (-60 °C): δ 7.78 (t, *J* = 8 Hz, 1 H), 7.72 – 7.61 (m, 2 H), 7.61 – 7.47 (m, 3 H), 7.42 (d, *J* = 8.5 Hz, 1 H), 7.32 – 7.10 (m, 5H), 6.71 (dd, *J* = 9.5, 16.5 Hz, 1 H, bound), 6.63 (dd, *J* = 11, 17.5 Hz, 1 H, free), 5.77 (d, *J* = 18 Hz, 1 H, free), 5.27 (d, *J* = 11 Hz, 1 H, free), 4.68 (dd, *J* = 4, 17 Hz, 1 H, bound), 4.23 (dd, *J* = 4.5, 9 Hz, 1 H, bound), 1.38 – 1.25 (m, 6 H), 1.19 (d, *J* = 16.5 Hz, 6 H), 1.04 (d, *J* = 16.5 Hz, 6 H). ^{13}C{^{1}H} NMR (-60 °C): δ 147.6 (d, *J* = 13.6 Hz), 142.9 (d, *J* = 7.8 Hz), 135.1, 133.7, 132.9 (d, *J* = 6.9 Hz), 132.4, 132.0, 131.4, 129.6 (d, *J* = 14.6 Hz), 129.5, 127.9 (d, *J* = 6.8 Hz), 127.6, 126.4, 123.9 (d, *J* = 47.0 Hz), 121.1, 114.5, 91.0 (d, *J* = 11.7 Hz), 37.3 (d, *J* = 23.6 Hz), 37.1 (d, *J* = 23.6 Hz), 29.8 (d, *J* = 5.8 Hz), 29.6 (d, *J* = 6.9 Hz). ^{31}P{^{1}H} NMR: δ 67.1. Anal. calcd (found) for $C_{28}H_{34}BrPF_6AuSb$: H, 3.75 (3.69); C, 36.79 (36.82).

{[P(*t*-Bu)$_2$*o*-bipheny]Au[η^2-H$_2$C=CH-4-C$_6$H$_4$CF$_3$]}$^+$ SbF$_6^-$ (1k). Complex **1k** was isolated in 93% yield as a light yellow solid from reaction of 4-trifluoromethyl styrene with a mixture of **S1** and $AgSbF_6$ employing a procedure similar to that used to synthesize **1a**. ^{1}H NMR (-60 °C): δ 7.88 – 7.46 (m, 10 H), 7.77 (t, *J* = 7.5 Hz, 1 H), 7.28 – 7.14 (m, 2 H), 6.76 (dd, *J* = 9.5, 16.5 Hz, 1 H), 4.82 (dd, *J* =

4.17 Hz, 1 H), 4.31 (dd, *J* = 4.9 Hz, 1 H), 1.18 (d, *J* = 16.5 Hz, 9 H), 1.00 (d, *J* = 16.5 Hz, 9 H). $^{13}C\{^1H\}$ NMR (-60 °C): δ 147.6 (d, *J* = 13.7 Hz), 143.0 (d, *J* = 7.8 Hz), 135.9, 133.7 (d, *J* = 2.9 Hz), 132.9 (d, *J* = 7.8 Hz), 132.4 (q, *J* = 33.3 Hz), 131.5, 129.8 (d, *J* = 13.7 Hz), 129.0 (d, *J* = 30.4 Hz), 128.0, 127.8, 126.2 (d, *J* = 3.9 Hz), 124.3, 123.9 (d, *J* = 47.0 Hz), 122.1, 93.3 (d, *J* = 12.7 Hz), 37.4 (d, *J* = 22.6 Hz), 37.1 (d, *J* = 23.4 Hz), 29.8 (d, *J* = 5.8 Hz), 29.5 (d, *J* = 5.9 Hz). $^{31}P\{^1H\}$ NMR: δ 67.4. Anal. calcd (found) for $C_{29}H_{34}PF_9AuSb$: H, 3.79 (3.75); C, 38.56 (38.82).

***In situ* characterization of Gold(I) π-Alkene Complexes**

$\{[P(t\text{-Bu})_2o\text{-bipheny}]Au[\eta^2\text{-}H_2C{=}CH(CH_3)]\}^+ SbF_6^-$ (S2). Propene (0.51 mL, 0.021 mmol) was added via gas tight syringe to the head space of an NMR tube sealed with a rubber septum that contained a solution of **2** (20 mg, 0.021 mmol) in CD_2Cl_2 (0.5 mL) at –60 °C. The tube was shaken and placed in the probe of an NMR spectrometer cooled at –60 °C. Formation of **S2** was established by the disappearance of resonances corresponding to bound $NCAr_F$ [δ 8.41, 8.38 (2:1)] and the appearance of resonances corresponding to the internal olefinic (δ 6.16) and vinyl protons (δ 4.26, 4.10) of bound propene in the ^1H NMR spectrum that were shifted relative to the resonances corresponding to free propene (δ 4.98, 4.87). Complex **S2** was characterized without isolation by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. ^1H NMR: δ 7.90 – 7.78 (m, 1 H), 7.68 – 7.48 (m, 5 H), 7.28 – 7.10 (m, 3 H), 6.28 – 6.02 (m, 1 H), 4.26 (d, *J* = 16.0 Hz, 1 H), 4.10 (br. s, 1 H), 2.02 (s, 3 H), 1.44 – 1.24 (m, 18 H). $^{13}C\{^1H\}$ NMR: δ 147.7 (d, *J* = 13.7 Hz), 142.9, 136.8, 133.8, 133.0, 131.5, 129.5, 127.7, 124.0 (d, *J* = 47.0 Hz), 115.2, 100.6 (d, *J* = 11.8 Hz), 37.5, 30.2, 22.3. $^{31}P\{^1H\}$ NMR: δ 66.5.

$\{[P(t\text{-Bu})_2o\text{-bipheny}]Au[\eta^2\text{-}H_2C{=}C(H)4\text{-}C_6H_4OCH_3]\}^+ SbF_6^-$ (S3). Gold π-alkene complex **S3** was synthesized and characterized without isolation by NMR employing procedures similar to that used to synthesize **S2**. ^1H NMR: δ 7.86 – 7.72 (m, 1 H), 7.70 – 7.42 (m, 5 H), 7.33 (d, *J* = 6.5 Hz, 2 H), 7.26 – 7.10 (m, 3 H), 6.89 (d, *J* = 7 Hz, 2 H), 6.76 (dd, *J* = 9, 16 Hz, 1 H), 4.47 (d, *J* = 17 Hz, 1 H), 4.07

(br. s, 1 H), 3.80 (s, 3 H), 1.18 (d, *J* = 16 Hz, 9 H), 1.04 (d, *J* = 16 Hz, 9 H). $^{13}C\{^1H\}$ NMR: δ 162.6, 147.8 (d, *J* = 14.7 Hz), 143.0, 135.8, 133.7, 132.9, 131.3, 129.3, 127.8, 127.7, 127.1, 124.9, 124.0 (d, *J* = 47.1 Hz), 86.0 (d, *J* = 13.7 Hz), 55.6, 37.3, 29.8 (d, *J* = 28.5 Hz). $^{31}P\{^1H\}$ NMR: δ 67.1.

Table S1. ^{1}H and ^{13}C data for olefinic resonances for cationic gold π-alkene complexes. Resonances corresponding to free alkene are shown in parentheses for comparison.

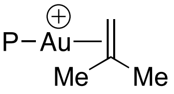
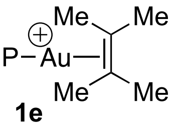
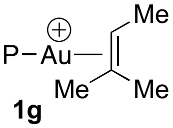
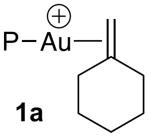
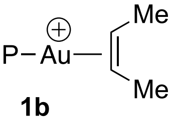
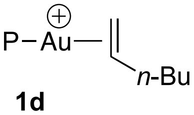
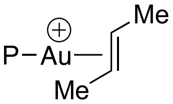
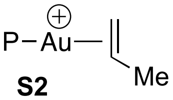
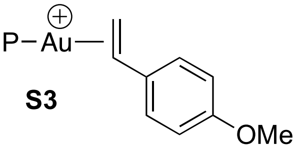
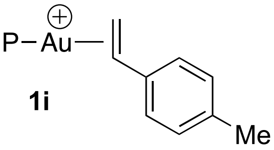
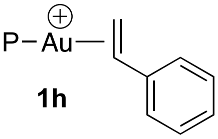
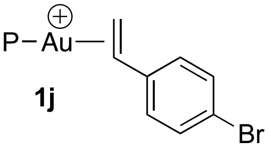
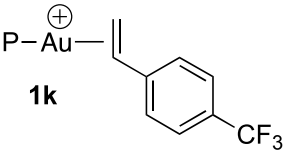
Complex	$H_2\underline{C}=$	$R_2\underline{C}=$	$\underline{H}_2C$	$RH\underline{C}=$	$R\underline{H}C=$
 **1c**	δ 95.1 (δ 110.5)	δ 163.3 (δ 142.4)	δ 3.92 (δ 4.60)		
 **1e**		δ 125.2 (δ 123.7)			
 **1g**		δ 146.1 (δ 132.0)		δ 111.4 (δ 118.0)	δ 4.20 (δ 5.12)
 **1a**	δ 91.8 (δ 106.4)	δ 169.4 (δ 150.0)	δ 3.93 (δ 4.55)		
 **1b**				δ 110.0 (δ 124.9)	δ 5.37 (δ 5.41)
 **1d**	δ 100.1 (δ 116.0)		δ 4.39, 4.36 (δ 4.87, 4.95)	δ 141.9 (δ 139.0)	δ 6.15 (δ 5.78)
 **1f**				δ 123.9 (δ 126.2)	δ 5.23 (δ 5.39)
 **S2**	δ 100.6 (δ 116.1)		δ 4.26, 4.10 (δ 4.87, 4.98)	δ 136.8 (δ 134.0)	δ 6.16 (δ 5.82)

Table S1 (Continued).

Complex	$H_2\underline{C}$=	$\underline{H}_2C$	$RH\underline{C}$=	$R\underline{H}C$=
 **S3**	δ 86.0 (δ 111.5)	δ 4.57, 4.07 (δ 5.61, 5.09)	δ 135.8 (δ 136.2)	δ 6.76 (δ 6.62)
 **1i**	δ 89.5 (δ 112.7)	δ 4.75, 4.32 (δ 4.70, 5.16)	δ 135.5 (δ 136.7)	δ 6.82 (δ 6.65)
 **1h**	δ 91.1 (δ 113.8)	δ 4.84, 4.42 (δ 5.77, 5.22)	δ 132.3 (δ 137.0)	δ 6.84 (δ 6.68)
 **1j**	δ 91.0 (δ 114.5)	δ 4.68, 4.23 (δ 5.77, 5.27)	δ 135.1 (δ 136.4)	δ 6.71 (δ 6.62)
 **1k**	δ 93.3 (δ 116.2)	δ 4.82, 4.31 (δ 5.90, 5.39)	δ 135.9 (δ 135.6)	δ 6.76 (δ 6.78)

Determination of alkene binding constants

Isobutylene (1.20 mg, 0.021 mmol) was added via gas tight syringe to an NMR tube sealed with a rubber septum that contained a CD_2Cl_2 solution of **2** (20 mg, 0.021 mmol) at –60 °C. The tube was shaken, placed in the probe of an NMR spectrometer cooled at –60 °C and allowed to equilibrate for 10 min. The relative concentrations of **2**, **1c**, $NCAr_F$, and isobutylene were determined by integrating the resonances corresponding to the aromatic protons of bound [δ 8.41, 8.38 (2:1)] and free [δ 8.15, 8.14 (2:1)] $NCAr_F$ and the resonances corresponding to the vinyl protons of bound (δ 3.77) and free (δ 4.60) isobutylene (Table S1). An equilibrium constant of K_{eq} = [**1c**][NCAr$_F$]/[**2**][isobutylene] = 136 ± 9 was determined.

To ensure that equilibrium was achieved under these conditions, the following control experiment was performed. NCAr$_F$ (4.9 mg, 0.02 mmol) was added via syringe to an NMR tube sealed with a rubber septum that contained a CD_2Cl_2 solution of isobutylene complex **1c** (16 mg, 0.02 mmol) at –60 °C. The tube was shaken, placed in the probe of an NMR spectrometer cooled at –60 °C and allowed to equilibrate for 10 min. The relative concentrations of **2**, **1c**, NCAr$_F$, and isobutylene were determined as was described in the preceding paragraph. The equilibrium constant determined from this experiment {K_{eq} = [**1c**][NCAr$_F$]/[**2**][isobutylene] = 145 ± 11} was not significantly different from that obtained from treatment of **2** with isobutylene.

Similar procedures were employed to determine the equilibrium constants for the displacement of NCAr$_F$ from **2** with 1-hexene, 2,3-dimethyl-2-butene, 2-methyl-2-butene, *cis*-2-butene, *trans*-2-butene, propene, 4-methylstyrene, 4-methoxystyrene, styrene, 4-bromostyrene, and 4-trifluoromethylstyrene in CD_2Cl_2 at –60 °C. Equilibrium data are collected in Table 2.

***cis*-2-Butene.** Integration of the resonances corresponding to the aromatic protons bound [δ 8.41, 8.38 (2:1)] and free [δ 8.15, 8.14 (2:1)] NCAr$_F$ and the resonances corresponding to the internal olefinic protons of bound (δ 5.20) and free (δ 5.41) *cis*-2-butene (Table S1) provides an equilibrium constant of K_{eq} = [**1b**][NCAr$_F$]/[**2**][*cis*-2-butene] = 126 ± 9.

1-Hexene. Integration of the resonances corresponding to the aromatic protons of bound [δ 8.41, 8.38 (2:1)] and free [δ 8.15, 8.14 (2:1)] NCAr$_F$ and the resonances corresponding to the internal olefinic protons of bound (δ 6.21) and free (δ 5.79) 1-hexene at –60 °C (Table S1) provided an equilibrium constant of K_{eq} = [**1d**][NCAr$_F$]/[**2**][1-hexene] = 133 ± 10.

2,3-Dimethyl-2-butene. Integration of the resonances corresponding to the aromatic protons of bound [δ 8.41, 8.38 (2:1)] and free [δ 8.15, 8.14 (2:1)] $NCAr_F$ and the resonances corresponding to the allylic protons of bound (δ 1.81) and free (δ 1.58) 2,3-dimethyl-2-butene at –60 °C (Table S1) provided an equilibrium constant of K_{eq} = [**1e**][$NCAr_F$]/[**2**][2,3-dimethyl-2-butene] = 0.44 ± 0.02. In a control experiment, $NCAr_F$ (4.8 mg, 0.02 mmol) was added via syringe to an NMR tube sealed with a rubber septum that contained a CD_2Cl_2 solution of 2,3-dimethyl-2-butene complex **1e** (16 mg, 0.02 mmol) at –60 °C. The tube was shaken, placed in the probe of an NMR spectrometer cooled at –60 °C and allowed to equilibrate for 10 min. The relative concentrations of **2**, **1e**, $NCAr_F$, and 2,3-dimethyl-2-butene were determined as was described above. The equilibrium constant determined from this experiment {K_{eq} = [**1e**][$NCAr_F$]/[**2**][2,3-dimethyl-2-butene] = 0.36 ± 0.02} was not significantly different from that obtained from treatment of **2** with 2,3-dimethyl-2-butene.

***trans*-2-Butene.** Integration of the resonances corresponding to the aromatic protons bound [δ 8.41, 8.38 (2:1)] and free [δ 8.15, 8.14 (2:1)] $NCAr_F$ and the resonances corresponding to the internal olefinic protons of bound (δ 5.12) and free (δ 5.39) *trans*-2-butene (Table S1) provides an equilibrium constant of K_{eq} = [**1f**][$NCAr_F$]/[**2**][*trans*-2-butene] = 14.1 ± 0.4.

2-Methyl-2-butene. Integration of the resonances corresponding to the aromatic protons of bound [δ 8.41, 8.38 (2:1)] and free [δ 8.15, 8.14 (2:1)] $NCAr_F$ and the resonances corresponding to the internal olefinic protons of bound (δ 3.99) and free (δ 5.12) 2-methyl-2-butene (Table S1) provided an equilibrium constant of K_{eq} = [**1g**][$NCAr_F$]/[**2**][2-methyl-2-butene] = 156 ± 8.

Styrene. Integration of the resonances corresponding to the aromatic protons of bound [δ 8.41, 8.38 (2:1)] and free [δ 8.15, 8.14 (2:1)] $NCAr_F$ and the resonances corresponding to the vinyl protons of bound (δ 4.68) and free (δ 5.77) styrene (Table S1) provided an equilibrium constant of K_{eq} = [**1h**][$NCAr_F$]/[**2**][styrene] = 2.3 ± 0.2.

4-Methylstyrene. Integration of the resonances corresponding to the aromatic protons of bound [δ 8.41, 8.38 (2:1)] and free [δ 8.15, 8.14 (2:1)] $NCAr_F$ and the resonances corresponding to the vinyl resonances of bound (δ 4.60, 4.17) and free (δ 5.70, 5.16) 4-methylstyrene (Table S1) provided an equilibrium constant of K_{eq} = [**1i**][$NCAr_F$]/[**2**][4-methylstyrene] = 9.4 ± 1.8.

4-Bromostyrene. Integration of the resonances corresponding to the aromatic protons of bound [δ 8.41, 8.38 (2:1)] and free [δ 8.15, 8.14 (2:1)] $NCAr_F$ and the resonances corresponding to the vinyl protons of bound (δ 4.67) and free (δ 5.77) 4-bromostyrene (Table S1) provided an equilibrium constant of K_{eq} = [**1j**][$NCAr_F$]/[**2**][4-bromostyrene] = 0.47 ± 0.05.

4-Trifluoromethylstyrene. Integration of the resonances corresponding to the aromatic protons of bound [δ 8.41, 8.38 (2:1)] and free [δ 8.15, 8.14 (2:1)] $NCAr_F$ and the resonances corresponding to the vinyl protons of bound (δ 4.80, 4.32) and free (δ 5.90, 5.38) 4-trifluoromethylstyrene (Table S1) provided an equilibrium constant of K_{eq} = [**1k**][$NCAr_F$]/[**2**][4-trifluoromethylstyrene] = 0.05 ± 0.01.

Propene. Integration of the resonances corresponding to the aromatic protons bound [δ 8.41, 8.38 (2:1)] and free [δ 8.15, 8.14 (2:1)] $NCAr_F$ and the the resonances corresponding to the internal olefinic protons of bound (δ 6.16) and free (δ 5.79) propene (Table S1) provided an equilibrium constant of K_{eq} = [**S2**][$NCAr_F$]/[**2**][1-propene] = 38 ± 2.

4-Methoxystyrene. Integration of the resonances corresponding to the aromatic protons of bound [δ 8.41, 8.38 (2:1)] and free [δ 8.15, 8.14 (2:1)] $NCAr_F$ and the resonances corresponding to the vinyl protons of bound (δ 4.47, 4.08) and free (δ 5.61, 5.09) 4-methoxystyrene (Table S1) provided an equilibrium constant of K_{eq} = [**S3**][$NCAr_F$]/[**2**][4-vinylanisole] = 32 ± 2.

Kinetics of Isobutylene Exchange with 1c

An NMR tube capped with a rubber septum that contained a solution of **1c** (14 mg, 0.018 mmol) and 1,3-dimethoxybenzene (1.0 μL, 7.6 μmol; internal standard) in CD_2Cl_2 (0.45 mL) was placed in the probe of an NMR spectrometer maintained at 298 K. Analysis of the singlet at δ 3.92 corresponding to the olefinic protons of the isobutylene ligand of **1c** in the ^{1}H NMR spectrum gave a peak width a half height of $\Delta v_{1/2}$ = 2.32 Hz. The tube was removed from the probe and isobutylene gas (0.03 mL, 1.3 μmol) was added into the head space of the tube via a gas-tight syringe. The tube was shaken well, returned to the probe, allowed to equilibrate for 10 min. The concentration of free isobutylene was determined ([isobutylene] = 3.0 mM) by integrating the olefinic resonance of free isobutylene at δ 4.60 relative to the methoxy resonance of the 1,3-dimethoxybenzene at δ 3.80. The peak width at half height of the singlet at δ 3.92 was determined: $\Delta v_{1/2}$ = 2.72 Hz, which corresponds to excess broadening of $\Delta v_{1/2\ (\text{excess})} = v - v_o$ = 0.4 Hz. Using this value, the rate of exchange of the isobutylene ligand of **1c** (k_{obs}) was determined through application of the slow exchange approximation: $k_{\text{obs}} = \pi(\Delta v_{1/2\ (\text{excess})}) = 1.3\ s^{-1}$. The rate of isobutylene exchange with **1c** was determined as a function of [isobutylene] from 3 - 71 mM through successive iterations of the above procedure (Table S2). The second-order rate constant for the rate of exchange of the isobutylene ligand of **1c** was determined from the slope of a plot of k_{obs} versus [isobutylene] where $k_{\text{ex}} = 75 \pm 3\ M^{-1}\ s^{-1}$ ($\Delta G^{\ddagger} = 14.89 \pm 0.02$ kcal mol^{-1}) (Table S2, Figure S1). The second-order rate constants (k_{ex}) for isobutylene exchange with **1c** were determined also determined at 11 °C and at 40 °C employing procedures similar to those outlined above (Figures S1, Table S3, S4, and S5). An Eyring plot of these data [$\ln(k_{\text{ex}}/T)$ versus 1/T] provided the activation parameters for isobutylene exchange of **1c**: $\Delta H^{\ddagger} = 5 \pm 1$ kcal mol^{-1} and $\Delta S^{\ddagger} = -33 \pm 4$ eu (Figure S2).

The plots of k_{obs} versus [isobutylene] possessed non-zero intercepts (Figure S1). These intercepts do not correspond to a potential solvent-assisted pathway for isobutylene exchange, as this information cannot be extracted from line-broadening analysis.[1] Rather, we attribute theses non-zero intercepts to the loss of isobutylene from **1c** in solution in the absence of isobutylene. The initial addition of isobutylene reconstitutes **1c**, thereby increasing its concentration, which leads to line broadening both due to the presence of free isobutylene and to the increase in [**1c**]. In support of this contention, the concentration of bound isobutylene increased ~10% upon the first addition of isobutylene and remained constant throughout successive isobutylene additions.

Table S2. Line broadening data and observed rate constants (k_{obs}) for the exchange of the isobutylene ligand of **1c** ([**1c**] = 40 mM) with free isobutylene at 24.6 °C.

[isobutylene] (mM)	$\nu_{1/2}$ (Hz)	$\Delta\omega$ (Hz)	k_{obs} (s^{-1})
0	2.3	—	—
3	2.7	0.4	1.3
8	2.9	0.6	1.8
15	3.1	0.8	2.5
21	3.3	1.0	3.0
48	3.9	1.6	4.9
71	4.4	2.0	6.4

Table S3. Second-order rate constants (k_{ex}) for exchange of the isobutylene ligand of **1c** with free isobutylene at 11, 25, and 40 °C.

T (K)	k_{ex} ($M^{-1}s^{-1}$)	$\Delta G^{\ddagger}$ (kcal mol^{-1})
284	53 ± 1	14.36 ± 0.02
298	75 ± 3	14.89 ± 0.02
313	135 ± 8	15.30 ± 0.04

Table S4. Line broadening data and observed rate constants (k_{obs}) for the exchange of the isobutylene ligand of **1c** ([**1c**] = 40 mM) with free isobutylene at 11 °C.

[isobutylene] (mM)	$\nu_{1/2}$ (Hz)	$\Delta\omega$ (Hz)	k_{obs} (s^{-1})
0	2.1	—	—
6	2.3	0.2	0.6
13	2.4	0.3	1.0
27	2.6	0.6	1.8
40	2.8	0.8	2.4
62	3.2	1.1	3.5
74	3.4	1.4	4.3

Table S5. Line broadening data and observed rate constants (k_{obs}) for the exchange of the isobutylene ligand of **1c** ([**1c**] = 40 mM) with free isobutylene at 40 °C.

[isobutylene] (mM)	$\nu_{1/2}$ (Hz)	$\Delta\omega$ (Hz)	k_{obs} (s^{-1})
0	2.6	—	—
6	4.5	1.8	5.8
17	4.9	2.2	7.0
26	5.4	2.8	8.7
52	6.2	3.6	11.3
70	7.3	4.7	14.7

Figure S1. Plots of k_{obs} versus [isobutylene] for the exchange of the isobutylene ligand of **1c** ([**1c**] = 40 mM) with free isobutylene at 40 °C (×), 25 °C (o), and 11 °C (Δ) in CD_2Cl_2.

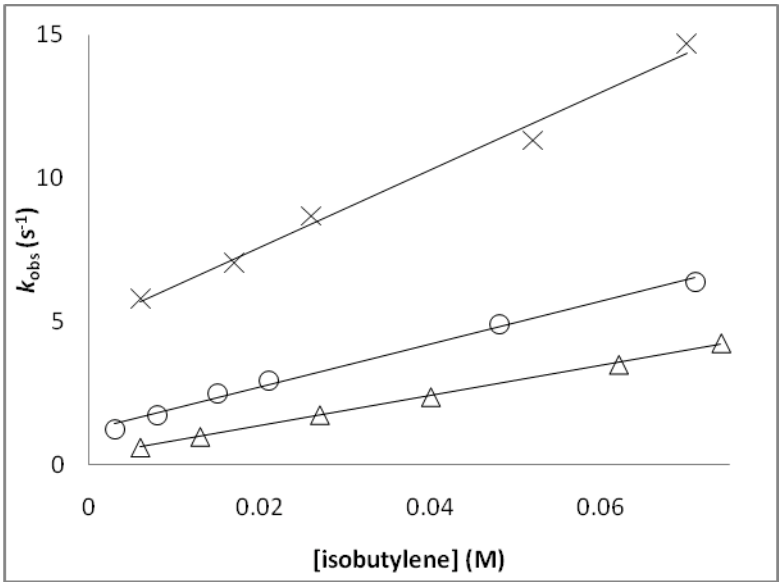
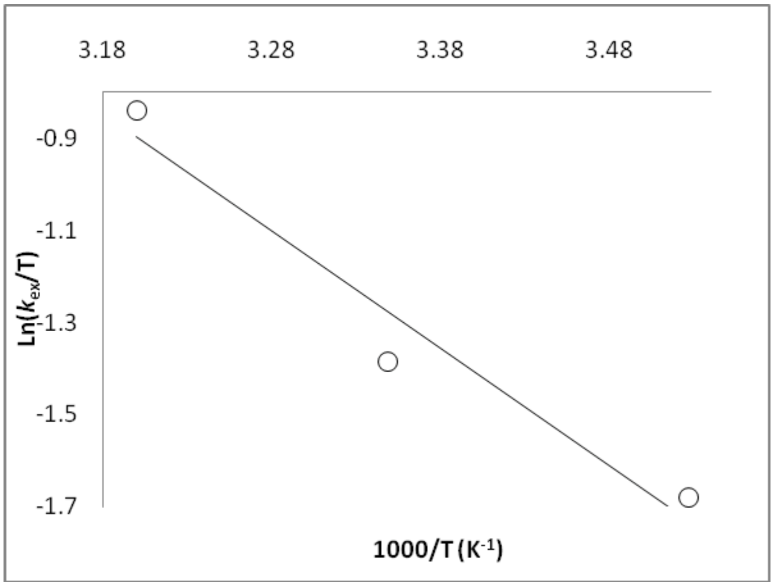


Figure S2. Eyring plot of the second-order rate constants (k_{ex}) for the exchange of the isobutylene ligand of **1c** with free isobutylene at 11, 25, and 40 °C, where $\Delta H^{\ddagger} = 5 \pm 1$ kcal mol^{-1} and $\Delta S^{\ddagger} = 33 \pm 4$ eu.



X-ray Crystal Structure of [(L)Au(η^2-H$_2$C=C(CH$_2$)$_5$)] SbF$_6^-$ (1a). Slow diffusion of hexane into a CH_2Cl_2 solution of **1a** at 4 °C gave crystals of **1a** suitable for X-ray diffraction. Diffraction data were obtained with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) on a Brüker Kappa Apex II diffractometer using the ω scan mode (Tables 1, and S6 – S11; Figures 1 and S3). Of the 73553 reflections, 11601 independent, observed reflections ($I > 2.0\sigma(I)$) were obtained with maximum h, k, l values of 12, 27, and 31, respectively. An absorption correction was applied (SADABS). The structure was refined by full matrix, least squares on F^2; H atoms were fixed, all other atoms were refined anisotropically (Table S7).

Figure S3. ORTEP diagrams of **1a**. Ellipsoids are shown at 50%. Counterion and hydrogen atoms are omitted for clarity.

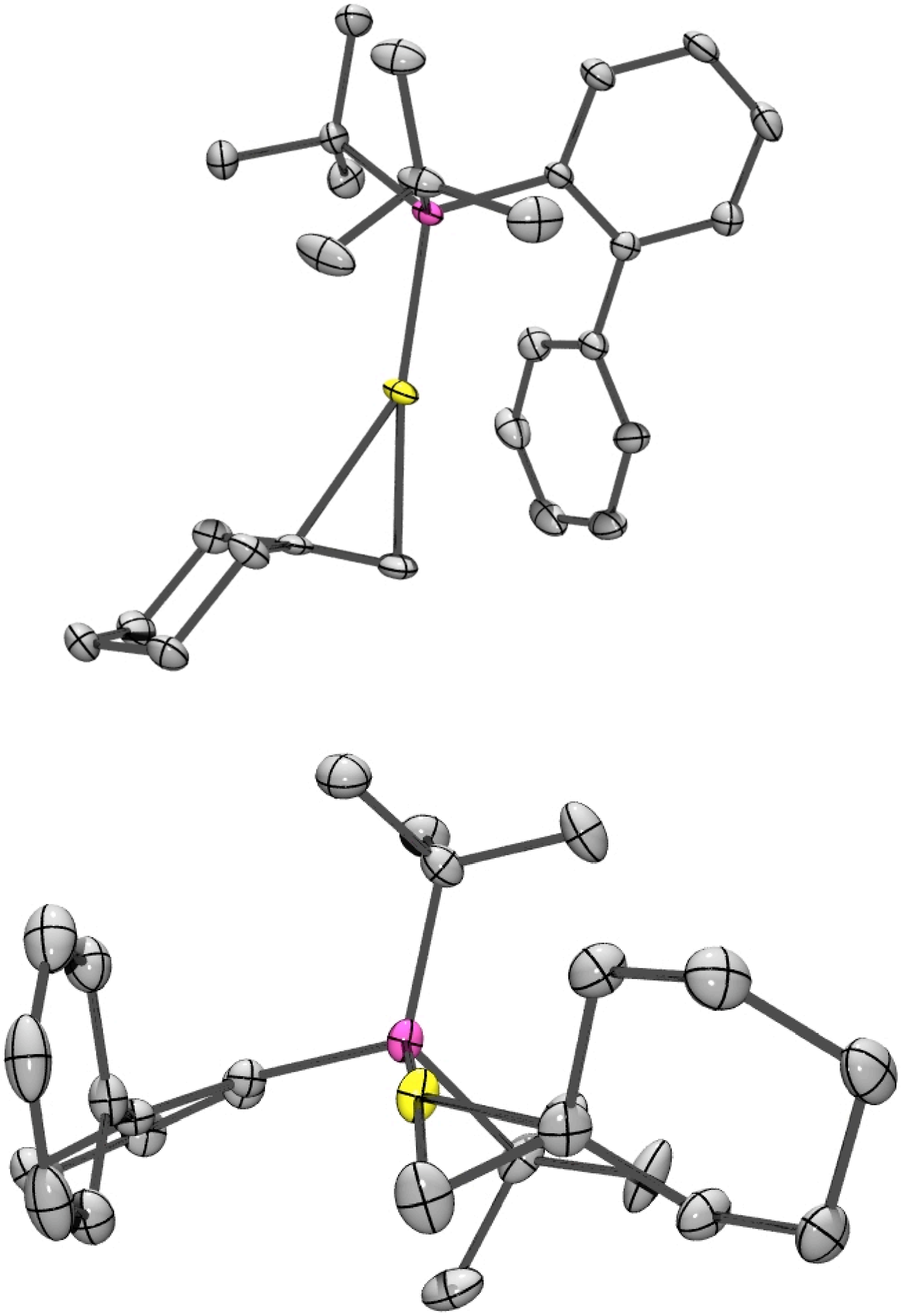


Table S6. Crystal data and structure refinement for **1a**.

Identification code	md97	
Empirical formula	$C_{27}H_{39}$ Au F_6PSb	
Formula weight	827.27	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 8.1045(9) Å	α= 90°.
	b = 17.2929(19) Å	β= 95.833(6)°.
	c = 20.611(2) Å	γ = 90°.
Volume	2873.7(6) Å^3	
Z	4	
Density (calculated)	1.912 Mg/m^3	
Absorption coefficient	6.149 mm^{-1}	
F(000)	1600	
Crystal size	.21 x .19 x .12 mm^3	
Crystal color and habit	colorless prism	
Diffractometer	Bruker SMART Apex II	
Theta range for data collection	2.87 to 34.65°.	
Index ranges	-12<=h<=12, -27<=k<=27, -30<=l<=31	
Reflections collected	73553	
Independent reflections	11601 [R(int) = 0.0587]	
Observed reflections (I > 2sigma(I))	9446	
Completeness to theta = 34.65°	94.2 %	
Absorption correction	Semi-empirical from equivalents	
Solution method	SHELXS-97 (Sheldrick, 2008)	
Refinement method	SHELXL-97 (Sheldrick, 2008)	
Data / restraints / parameters	11601 / 0 / 325	
Goodness-of-fit on F^2	1.142	
Final R indices [I>2sigma(I)]	R1 = 0.0285, wR2 = 0.0612	
R indices (all data)	R1 = 0.0436, wR2 = 0.0650	

Largest diff. peak and hole 1.860 and -1.859 e.Å^{-3}

Table S7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **1a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Au(1)	4031(1)	7579(1)	1733(1)	18(1)
P(1)	4972(1)	7953(1)	766(1)	15(1)
C(1)	3576(4)	7149(2)	2709(1)	28(1)
C(2)	3097(3)	7906(1)	2749(1)	19(1)
C(3)	4219(3)	8515(2)	3067(1)	22(1)
C(4)	3554(3)	8772(2)	3709(1)	25(1)
C(5)	1772(3)	9047(2)	3586(1)	28(1)
C(6)	670(3)	8424(2)	3251(1)	28(1)
C(7)	1324(3)	8155(2)	2612(1)	24(1)
C(8)	6873(3)	8551(2)	1032(1)	22(1)
C(9)	7458(3)	9102(2)	520(1)	28(1)
C(10)	8261(3)	7979(2)	1256(2)	32(1)
C(11)	6513(4)	9043(2)	1629(1)	34(1)
C(12)	3379(3)	8476(1)	216(1)	20(1)
C(13)	3928(3)	8686(2)	-457(1)	25(1)
C(14)	2850(4)	9203(2)	567(2)	30(1)
C(15)	1870(3)	7937(2)	95(2)	28(1)
C(16)	5722(3)	7138(1)	310(1)	16(1)
C(17)	5503(3)	6362(1)	497(1)	16(1)
C(18)	6422(3)	5791(1)	218(1)	22(1)
C(19)	7468(3)	5961(2)	-259(1)	26(1)
C(20)	7594(3)	6715(2)	-472(1)	24(1)
C(21)	6743(3)	7292(1)	-184(1)	21(1)
C(22)	4297(3)	6090(1)	951(1)	19(1)

C(23)	4839(3)	5741(1)	1543(1)	24(1)
C(24)	3694(4)	5431(2)	1937(1)	31(1)
C(25)	2010(4)	5468(2)	1744(2)	32(1)
C(26)	1463(3)	5817(2)	1159(2)	30(1)
C(27)	2595(3)	6116(1)	760(1)	25(1)
Sb(1)	-1365(1)	5966(1)	3236(1)	23(1)
F(1)	-3502(3)	5548(1)	3152(1)	67(1)
F(2)	743(2)	6381(1)	3308(1)	57(1)
F(3)	-1515(3)	6151(2)	2340(1)	68(1)
F(4)	-1149(3)	5778(2)	4128(1)	84(1)
F(5)	-527(3)	4994(1)	3105(1)	67(1)
F(6)	-2285(4)	6935(1)	3338(2)	101(1)

Table S8. Bond lengths [Å] and angles [°] for **1a**.

Au(1)-C(1)	2.210(3)	C(9)-H(9B)	0.9800
Au(1)-P(1)	2.2996(6)	C(9)-H(9C)	0.9800
Au(1)-C(2)	2.365(2)	C(10)-H(10A)	0.9800
P(1)-C(16)	1.832(2)	C(10)-H(10B)	0.9800
P(1)-C(12)	1.863(2)	C(10)-H(10C)	0.9800
P(1)-C(8)	1.890(2)	C(11)-H(11A)	0.9800
C(1)-C(2)	1.369(4)	C(11)-H(11B)	0.9800
C(1)-H(1A)	0.9900	C(11)-H(11C)	0.9800
C(1)-H(1B)	0.9900	C(12)-C(14)	1.532(3)
C(2)-C(3)	1.499(3)	C(12)-C(15)	1.538(4)
C(2)-C(7)	1.499(3)	C(12)-C(13)	1.544(3)
C(3)-C(4)	1.544(3)	C(13)-H(13A)	0.9800
C(3)-H(3A)	0.9900	C(13)-H(13B)	0.9800
C(3)-H(3B)	0.9900	C(13)-H(13C)	0.9800
C(4)-C(5)	1.517(4)	C(14)-H(14A)	0.9800
C(4)-H(4A)	0.9900	C(14)-H(14B)	0.9800
C(4)-H(4B)	0.9900	C(14)-H(14C)	0.9800
C(5)-C(6)	1.521(4)	C(15)-H(15A)	0.9800
C(5)-H(5A)	0.9900	C(15)-H(15B)	0.9800
C(5)-H(5B)	0.9900	C(15)-H(15C)	0.9800
C(6)-C(7)	1.540(4)	C(16)-C(21)	1.401(3)
C(6)-H(6A)	0.9900	C(16)-C(17)	1.413(3)
C(6)-H(6B)	0.9900	C(17)-C(18)	1.395(3)
C(7)-H(7A)	0.9900	C(17)-C(22)	1.496(3)
C(7)-H(7B)	0.9900	C(18)-C(19)	1.393(3)
C(8)-C(10)	1.533(4)	C(18)-H(18A)	0.9500
C(8)-C(9)	1.533(3)	C(19)-C(20)	1.384(4)
C(8)-C(11)	1.548(4)	C(19)-H(19A)	0.9500
C(9)-H(9A)	0.9800	C(20)-C(21)	1.382(3)

C(20)-H(20A)	0.9500	C(26)-C(27)	1.392(4)
C(21)-H(21A)	0.9500	C(26)-H(26A)	0.9500
C(22)-C(23)	1.391(4)	C(27)-H(27A)	0.9500
C(22)-C(27)	1.396(4)	Sb(1)-F(5)	1.843(2)
C(23)-C(24)	1.400(4)	Sb(1)-F(2)	1.8457(18)
C(23)-H(23A)	0.9500	Sb(1)-F(6)	1.855(2)
C(24)-C(25)	1.384(4)	Sb(1)-F(4)	1.858(2)
C(24)-H(24A)	0.9500	Sb(1)-F(3)	1.866(2)
C(25)-C(26)	1.381(4)	Sb(1)-F(1)	1.8679(19)
C(25)-H(25A)	0.9500		

C(1)-Au(1)-P(1)	169.97(8)	C(7)-C(2)-Au(1)	106.85(16)
C(1)-Au(1)-C(2)	34.62(9)	C(2)-C(3)-C(4)	109.1(2)
P(1)-Au(1)-C(2)	149.83(6)	C(2)-C(3)-H(3A)	109.9
C(16)-P(1)-C(12)	107.91(11)	C(4)-C(3)-H(3A)	109.9
C(16)-P(1)-C(8)	105.49(11)	C(2)-C(3)-H(3B)	109.9
C(12)-P(1)-C(8)	113.92(11)	C(4)-C(3)-H(3B)	109.9
C(16)-P(1)-Au(1)	112.64(8)	H(3A)-C(3)-H(3B)	108.3
C(12)-P(1)-Au(1)	113.15(8)	C(5)-C(4)-C(3)	110.9(2)
C(8)-P(1)-Au(1)	103.53(8)	C(5)-C(4)-H(4A)	109.5
C(2)-C(1)-Au(1)	78.88(15)	C(3)-C(4)-H(4A)	109.5
C(2)-C(1)-H(1A)	115.4	C(5)-C(4)-H(4B)	109.5
Au(1)-C(1)-H(1A)	115.4	C(3)-C(4)-H(4B)	109.5
C(2)-C(1)-H(1B)	115.4	H(4A)-C(4)-H(4B)	108.0
Au(1)-C(1)-H(1B)	115.4	C(4)-C(5)-C(6)	111.0(2)
H(1A)-C(1)-H(1B)	112.4	C(4)-C(5)-H(5A)	109.4
C(1)-C(2)-C(3)	122.4(2)	C(6)-C(5)-H(5A)	109.4
C(1)-C(2)-C(7)	122.4(2)	C(4)-C(5)-H(5B)	109.4
C(3)-C(2)-C(7)	114.0(2)	C(6)-C(5)-H(5B)	109.4
C(1)-C(2)-Au(1)	66.50(13)	H(5A)-C(5)-H(5B)	108.0
C(3)-C(2)-Au(1)	108.69(15)	C(5)-C(6)-C(7)	111.4(2)

C(5)-C(6)-H(6A)	109.3	H(11A)-C(11)-H(11B)	109.5
C(7)-C(6)-H(6A)	109.3	C(8)-C(11)-H(11C)	109.5
C(5)-C(6)-H(6B)	109.3	H(11A)-C(11)-H(11C)	109.5
C(7)-C(6)-H(6B)	109.3	H(11B)-C(11)-H(11C)	109.5
H(6A)-C(6)-H(6B)	108.0	C(14)-C(12)-C(15)	108.5(2)
C(2)-C(7)-C(6)	109.5(2)	C(14)-C(12)-C(13)	110.6(2)
C(2)-C(7)-H(7A)	109.8	C(15)-C(12)-C(13)	107.0(2)
C(6)-C(7)-H(7A)	109.8	C(14)-C(12)-P(1)	108.76(18)
C(2)-C(7)-H(7B)	109.8	C(15)-C(12)-P(1)	107.20(17)
C(6)-C(7)-H(7B)	109.8	C(13)-C(12)-P(1)	114.53(16)
H(7A)-C(7)-H(7B)	108.2	C(12)-C(13)-H(13A)	109.5
C(10)-C(8)-C(9)	109.8(2)	C(12)-C(13)-H(13B)	109.5
C(10)-C(8)-C(11)	107.9(2)	H(13A)-C(13)-H(13B)	109.5
C(9)-C(8)-C(11)	107.7(2)	C(12)-C(13)-H(13C)	109.5
C(10)-C(8)-P(1)	106.60(17)	H(13A)-C(13)-H(13C)	109.5
C(9)-C(8)-P(1)	116.04(18)	H(13B)-C(13)-H(13C)	109.5
C(11)-C(8)-P(1)	108.52(17)	C(12)-C(14)-H(14A)	109.5
C(8)-C(9)-H(9A)	109.5	C(12)-C(14)-H(14B)	109.5
C(8)-C(9)-H(9B)	109.5	H(14A)-C(14)-H(14B)	109.5
H(9A)-C(9)-H(9B)	109.5	C(12)-C(14)-H(14C)	109.5
C(8)-C(9)-H(9C)	109.5	H(14A)-C(14)-H(14C)	109.5
H(9A)-C(9)-H(9C)	109.5	H(14B)-C(14)-H(14C)	109.5
H(9B)-C(9)-H(9C)	109.5	C(12)-C(15)-H(15A)	109.5
C(8)-C(10)-H(10A)	109.5	C(12)-C(15)-H(15B)	109.5
C(8)-C(10)-H(10B)	109.5	H(15A)-C(15)-H(15B)	109.5
H(10A)-C(10)-H(10B)	109.5	C(12)-C(15)-H(15C)	109.5
C(8)-C(10)-H(10C)	109.5	H(15A)-C(15)-H(15C)	109.5
H(10A)-C(10)-H(10C)	109.5	H(15B)-C(15)-H(15C)	109.5
H(10B)-C(10)-H(10C)	109.5	C(21)-C(16)-C(17)	118.6(2)
C(8)-C(11)-H(11A)	109.5	C(21)-C(16)-P(1)	118.48(17)
C(8)-C(11)-H(11B)	109.5	C(17)-C(16)-P(1)	122.26(17)

C(18)-C(17)-C(16)	118.2(2)
C(18)-C(17)-C(22)	116.4(2)
C(16)-C(17)-C(22)	125.3(2)
C(19)-C(18)-C(17)	122.0(2)
C(19)-C(18)-H(18A)	119.0
C(17)-C(18)-H(18A)	119.0
C(20)-C(19)-C(18)	119.5(2)
C(20)-C(19)-H(19A)	120.2
C(18)-C(19)-H(19A)	120.2
C(21)-C(20)-C(19)	119.2(2)
C(21)-C(20)-H(20A)	120.4
C(19)-C(20)-H(20A)	120.4
C(20)-C(21)-C(16)	122.1(2)
C(20)-C(21)-H(21A)	118.9
C(16)-C(21)-H(21A)	118.9
C(23)-C(22)-C(27)	118.5(2)
C(23)-C(22)-C(17)	121.1(2)
C(27)-C(22)-C(17)	120.2(2)
C(22)-C(23)-C(24)	120.3(3)
C(22)-C(23)-H(23A)	119.8
C(24)-C(23)-H(23A)	119.8
C(25)-C(24)-C(23)	120.6(3)
C(25)-C(24)-H(24A)	119.7
C(23)-C(24)-H(24A)	119.7
C(26)-C(25)-C(24)	119.4(3)
C(26)-C(25)-H(25A)	120.3
C(24)-C(25)-H(25A)	120.3
C(25)-C(26)-C(27)	120.4(3)
C(25)-C(26)-H(26A)	119.8
C(27)-C(26)-H(26A)	119.8
C(26)-C(27)-C(22)	120.8(3)
C(26)-C(27)-H(27A)	119.6
C(22)-C(27)-H(27A)	119.6
F(5)-Sb(1)-F(2)	90.82(11)
F(5)-Sb(1)-F(6)	177.37(14)
F(2)-Sb(1)-F(6)	91.06(12)
F(5)-Sb(1)-F(4)	89.27(13)
F(2)-Sb(1)-F(4)	89.68(9)
F(6)-Sb(1)-F(4)	92.58(15)
F(5)-Sb(1)-F(3)	89.94(12)
F(2)-Sb(1)-F(3)	88.82(9)
F(6)-Sb(1)-F(3)	88.26(15)
F(4)-Sb(1)-F(3)	178.29(11)
F(5)-Sb(1)-F(1)	89.18(11)
F(2)-Sb(1)-F(1)	179.27(10)
F(6)-Sb(1)-F(1)	88.91(12)
F(4)-Sb(1)-F(1)	91.05(10)
F(3)-Sb(1)-F(1)	90.45(10)

Symmetry transformations used to generate equivalent atoms:

Table S9. Anisotropic displacement parameters ($Å^2$x 10^3) for **1a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Au(1)	23(1)	19(1)	13(1)	-1(1)	8(1)	-4(1)
P(1)	18(1)	16(1)	12(1)	-1(1)	5(1)	-2(1)
C(1)	42(2)	25(1)	19(1)	6(1)	16(1)	0(1)
C(2)	26(1)	24(1)	9(1)	3(1)	7(1)	-1(1)
C(3)	21(1)	32(1)	15(1)	-4(1)	4(1)	-1(1)
C(4)	32(1)	29(1)	15(1)	-5(1)	3(1)	1(1)
C(5)	33(1)	29(1)	22(1)	-3(1)	9(1)	8(1)
C(6)	24(1)	34(1)	26(2)	0(1)	9(1)	3(1)
C(7)	23(1)	29(1)	20(1)	0(1)	3(1)	-3(1)
C(8)	23(1)	28(1)	16(1)	-2(1)	5(1)	-11(1)
C(9)	30(1)	32(1)	24(1)	0(1)	6(1)	-15(1)
C(10)	22(1)	44(2)	29(2)	3(1)	-5(1)	-8(1)
C(11)	42(2)	38(2)	23(2)	-14(1)	12(1)	-22(1)
C(12)	20(1)	20(1)	20(1)	2(1)	5(1)	4(1)
C(13)	27(1)	29(1)	18(1)	3(1)	4(1)	4(1)
C(14)	36(2)	22(1)	34(2)	1(1)	14(1)	8(1)
C(15)	20(1)	31(1)	32(2)	2(1)	2(1)	1(1)
C(16)	16(1)	18(1)	13(1)	0(1)	4(1)	1(1)
C(17)	15(1)	19(1)	15(1)	1(1)	1(1)	0(1)
C(18)	24(1)	20(1)	24(1)	0(1)	5(1)	2(1)
C(19)	23(1)	28(1)	29(2)	-5(1)	11(1)	4(1)
C(20)	24(1)	28(1)	20(1)	-2(1)	12(1)	0(1)
C(21)	20(1)	24(1)	20(1)	-1(1)	8(1)	-1(1)
C(22)	24(1)	15(1)	19(1)	-1(1)	7(1)	-1(1)
C(23)	32(1)	22(1)	20(1)	2(1)	5(1)	1(1)
C(24)	53(2)	18(1)	24(1)	3(1)	15(1)	0(1)

C(25)	45(2)	19(1)	38(2)	-5(1)	25(1)	-8(1)
C(26)	26(1)	26(1)	42(2)	-5(1)	14(1)	-6(1)
C(27)	25(1)	21(1)	29(1)	0(1)	6(1)	-2(1)
Sb(1)	24(1)	21(1)	27(1)	-2(1)	11(1)	-5(1)
F(1)	35(1)	78(2)	87(2)	26(1)	2(1)	-24(1)
F(2)	34(1)	84(2)	50(1)	26(1)	-4(1)	-27(1)
F(3)	53(1)	107(2)	41(1)	38(1)	-8(1)	-18(1)
F(4)	111(2)	123(2)	22(1)	-13(1)	21(1)	-81(2)
F(5)	88(2)	36(1)	78(2)	-8(1)	14(1)	18(1)
F(6)	82(2)	40(1)	187(4)	-26(2)	47(2)	7(1)

Table S10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **1a**.

	x	y	z	U(eq)
H(1A)	2674	6764	2715	33
H(1B)	4579	7003	2997	33
H(3A)	4261	8964	2771	27
H(3B)	5356	8307	3159	27
H(4A)	3616	8333	4018	30
H(4B)	4254	9195	3908	30
H(5A)	1726	9516	3310	33
H(5B)	1357	9185	4007	33
H(6A)	-470	8628	3154	33
H(6B)	622	7976	3548	33
H(7A)	645	7718	2424	29
H(7B)	1242	8584	2292	29
H(9A)	8448	9381	706	42
H(9B)	6575	9473	385	42
H(9C)	7726	8804	140	42
H(10A)	9278	8265	1398	48
H(10B)	8461	7637	893	48
H(10C)	7931	7669	1619	48
H(11A)	7489	9356	1774	51
H(11B)	6257	8700	1985	51
H(11C)	5564	9383	1508	51
H(13A)	3026	8959	-715	37
H(13B)	4199	8212	-685	37
H(13C)	4909	9020	-399	37
H(14A)	2014	9484	281	45
H(14B)	3817	9536	675	45

H(14C)	2379	9053	968	45
H(15A)	1004	8194	-195	42
H(15B)	1441	7817	511	42
H(15C)	2203	7458	-110	42
H(18A)	6331	5270	358	27
H(19A)	8091	5561	-436	32
H(20A)	8258	6834	-813	28
H(21A)	6853	7811	-325	25
H(23A)	5992	5714	1681	29
H(24A)	4077	5192	2339	37
H(25A)	1237	5255	2012	39
H(26A)	308	5854	1028	36
H(27A)	2205	6340	352	30

Table S11. Torsion angles [°] for **1a**.

C(1)-Au(1)-P(1)-C(16)	61.6(4)
C(2)-Au(1)-P(1)-C(16)	170.52(14)
C(1)-Au(1)-P(1)-C(12)	-175.7(4)
C(2)-Au(1)-P(1)-C(12)	-66.75(15)
C(1)-Au(1)-P(1)-C(8)	-51.9(4)
C(2)-Au(1)-P(1)-C(8)	57.06(15)
P(1)-Au(1)-C(1)-C(2)	123.2(4)
Au(1)-C(1)-C(2)-C(3)	-97.9(2)
Au(1)-C(1)-C(2)-C(7)	95.7(2)
P(1)-Au(1)-C(2)-C(1)	-163.14(15)
C(1)-Au(1)-C(2)-C(3)	118.0(3)
P(1)-Au(1)-C(2)-C(3)	-45.2(2)
C(1)-Au(1)-C(2)-C(7)	-118.6(2)
P(1)-Au(1)-C(2)-C(7)	78.3(2)
C(1)-C(2)-C(3)-C(4)	-110.2(3)
C(7)-C(2)-C(3)-C(4)	57.2(3)
Au(1)-C(2)-C(3)-C(4)	176.29(16)
C(2)-C(3)-C(4)-C(5)	-56.0(3)
C(3)-C(4)-C(5)-C(6)	56.5(3)
C(4)-C(5)-C(6)-C(7)	-55.8(3)
C(1)-C(2)-C(7)-C(6)	110.9(3)
C(3)-C(2)-C(7)-C(6)	-56.5(3)
Au(1)-C(2)-C(7)-C(6)	-176.60(17)
C(5)-C(6)-C(7)-C(2)	54.4(3)
C(16)-P(1)-C(8)-C(10)	-41.6(2)
C(12)-P(1)-C(8)-C(10)	-159.78(17)
Au(1)-P(1)-C(8)-C(10)	76.92(17)
C(16)-P(1)-C(8)-C(9)	81.0(2)
C(12)-P(1)-C(8)-C(9)	-37.1(2)

Au(1)-P(1)-C(8)-C(9)	-160.43(18)
C(16)-P(1)-C(8)-C(11)	-157.63(19)
C(12)-P(1)-C(8)-C(11)	84.2(2)
Au(1)-P(1)-C(8)-C(11)	-39.1(2)
C(16)-P(1)-C(12)-C(14)	-174.90(17)
C(8)-P(1)-C(12)-C(14)	-58.1(2)
Au(1)-P(1)-C(12)-C(14)	59.78(18)
C(16)-P(1)-C(12)-C(15)	67.95(19)
C(8)-P(1)-C(12)-C(15)	-175.28(16)
Au(1)-P(1)-C(12)-C(15)	-57.37(18)
C(16)-P(1)-C(12)-C(13)	-50.6(2)
C(8)-P(1)-C(12)-C(13)	66.2(2)
Au(1)-P(1)-C(12)-C(13)	-175.94(15)
C(12)-P(1)-C(16)-C(21)	72.1(2)
C(8)-P(1)-C(16)-C(21)	-50.0(2)
Au(1)-P(1)-C(16)-C(21)	-162.26(17)
C(12)-P(1)-C(16)-C(17)	-116.9(2)
C(8)-P(1)-C(16)-C(17)	120.9(2)
Au(1)-P(1)-C(16)-C(17)	8.7(2)
C(21)-C(16)-C(17)-C(18)	5.2(3)
P(1)-C(16)-C(17)-C(18)	-165.77(18)
C(21)-C(16)-C(17)-C(22)	-171.8(2)
P(1)-C(16)-C(17)-C(22)	17.3(3)
C(16)-C(17)-C(18)-C(19)	-3.4(4)
C(22)-C(17)-C(18)-C(19)	173.8(2)
C(17)-C(18)-C(19)-C(20)	-0.9(4)
C(18)-C(19)-C(20)-C(21)	3.3(4)
C(19)-C(20)-C(21)-C(16)	-1.4(4)
C(17)-C(16)-C(21)-C(20)	-2.9(4)
P(1)-C(16)-C(21)-C(20)	168.4(2)
C(18)-C(17)-C(22)-C(23)	66.2(3)

C(16)-C(17)-C(22)-C(23)	-116.8(3)
C(18)-C(17)-C(22)-C(27)	-107.7(3)
C(16)-C(17)-C(22)-C(27)	69.3(3)
C(27)-C(22)-C(23)-C(24)	-0.5(4)
C(17)-C(22)-C(23)-C(24)	-174.5(2)
C(22)-C(23)-C(24)-C(25)	-0.2(4)
C(23)-C(24)-C(25)-C(26)	-0.2(4)
C(24)-C(25)-C(26)-C(27)	1.3(4)
C(25)-C(26)-C(27)-C(22)	-2.0(4)
C(23)-C(22)-C(27)-C(26)	1.6(4)
C(17)-C(22)-C(27)-C(26)	175.6(2)

Symmetry transformations used to generate equivalent atoms:

X-ray Crystal Structure of [(P)Au(η^2-$Me_2C{=}CMe_2$)•CH_2Cl_2] SbF_6^- (1e•CH_2Cl_2). Slow diffusion of hexane into a CH_2Cl_2 solution of **1e** at 4 °C gave crystals of **1e**•CH_2Cl_2 suitable for X-ray diffraction. Diffraction data were obtained with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) on a Brüker Kappa Apex II diffractometer using the ω scan mode (Tables 1, and S12 – S17; Figures 1 and S4). Of the 61645 reflections, 8078 independent, observed reflections ($I > 2.0\sigma(I)$) were obtained with maximum *h*, *k*, *l* values of 12, 19, and 28, respectively. An absorption correction was applied (SADABS). The structure was refined by full matrix, least squares on F^2; H atoms were fixed, all other atoms were refined anisotropically (Table S13).

Figure S4. ORTEP diagrams of **1e•CH_2Cl_2**. Ellipsoids are shown at 50%. Solvent, counterion and hydrogen atoms are omitted for clarity.

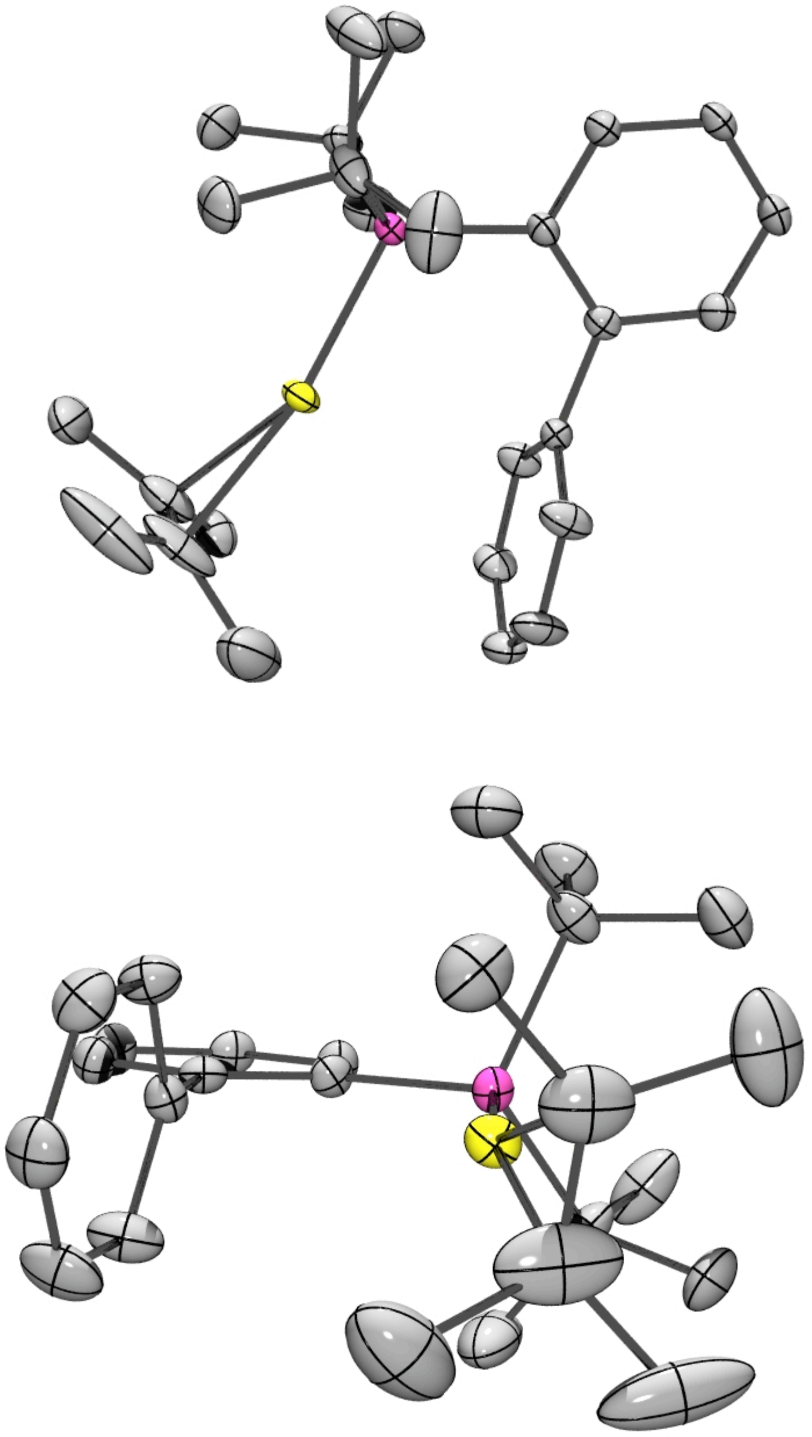


Table S12. Crystal data and structure refinement for **1e**•CH_2Cl_2.

Identification code	tetra	
Empirical formula	$C_{27}H_{41}AuCl_2F_6PSb$	
Formula weight	900.18	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 9.4018(9) Å	α = 90°.
	b = 16.0494(16) Å	β = 93.985(5)°.
	c = 21.377(2) Å	γ = 90°.
Volume	3217.9(5) $Å^3$	
Z	4	
Density (calculated)	1.858 Mg/m^3	
Absorption coefficient	5.660 mm^{-1}	
F(000)	1744	
Crystal size	0.22 x 0.18 x 0.11 mm^3	
Crystal color and habit	colourless prism	
Diffractometer	Bruker SMART Apex II	
Theta range for data collection	3.43 to 28.59°.	
Index ranges	-12<=h<=12, -21<=k<=19, -28<=l<=28	
Reflections collected	61645	
Independent reflections	8078 [R(int) = 0.0406]	
Observed reflections (I > 2sigma(I))	7221	
Completeness to theta = 28.59°	98.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5749 and 0.3690	
Solution method	SHELXS-97 (Sheldrick, 2008)	
Refinement method	SHELXL-97 (Sheldrick, 2008)	
Data / restraints / parameters	8078 / 0 / 343	
Goodness-of-fit on F^2	1.307	

Final R indices [I>2sigma(I)]	R1 = 0.0253, wR2 = 0.0652
R indices (all data)	R1 = 0.0310, wR2 = 0.0670
Largest diff. peak and hole	1.708 and -0.862 e.Å^{-3}

Table S13. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **1e**•CH_2Cl_2. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Au(1)	1222(1)	7236(1)	3461(1)	22(1)
Sb(1)	6419(1)	8476(1)	1710(1)	21(1)
F(1)	7216(2)	9340(1)	1264(1)	37(1)
F(2)	5885(3)	9237(1)	2314(1)	43(1)
F(3)	5608(2)	7596(1)	2142(1)	33(1)
F(4)	6950(3)	7705(1)	1114(1)	38(1)
F(5)	4666(2)	8643(1)	1254(1)	35(1)
F(6)	8166(2)	8308(1)	2170(1)	42(1)
P(1)	-112(1)	7176(1)	4315(1)	18(1)
C(1)	3360(5)	7227(2)	3007(2)	43(1)
C(2)	2524(5)	7760(3)	2683(3)	61(2)
C(3)	3658(4)	6332(2)	2850(2)	36(1)
C(4)	4435(5)	7604(3)	3510(2)	56(1)
C(5)	2479(6)	8683(3)	2737(3)	83(2)
C(6)	1767(6)	7526(4)	2047(2)	67(1)
C(7)	1072(3)	6703(2)	4964(1)	26(1)
C(8)	2391(4)	7255(2)	5098(2)	36(1)
C(9)	1563(4)	5854(2)	4701(2)	39(1)
C(10)	343(4)	6513(2)	5568(2)	37(1)
C(11)	-709(4)	8276(2)	4470(2)	29(1)
C(12)	496(4)	8882(2)	4324(2)	36(1)
C(13)	-1033(5)	8456(2)	5160(2)	49(1)
C(14)	-1995(5)	8433(2)	4029(2)	52(1)
C(15)	-1701(3)	6516(2)	4250(1)	19(1)
C(16)	-2032(3)	5976(2)	3743(1)	19(1)
C(17)	-3253(3)	5482(2)	3756(2)	24(1)

C(18)	-4147(3)	5516(2)	4241(2)	26(1)
C(19)	-3834(3)	6055(2)	4734(1)	23(1)
C(20)	-2620(3)	6544(2)	4741(2)	23(1)
C(21)	-1243(3)	5906(2)	3159(1)	19(1)
C(22)	-145(3)	5326(2)	3106(2)	26(1)
C(23)	406(4)	5191(2)	2525(2)	29(1)
C(24)	-115(4)	5634(2)	2005(2)	30(1)
C(25)	-1171(4)	6211(3)	2060(2)	37(1)
C(26)	-1738(4)	6349(2)	2634(2)	32(1)
Cl(1)	3344(2)	5788(1)	1064(1)	72(1)
Cl(2)	6083(2)	5075(1)	822(1)	81(1)
C(1X)	5091(5)	5582(3)	1368(3)	67(1)

Table S14. Bond lengths [Å] and angles [°] for **1e**•CH_2Cl_2.

Au(1)-P(1)	2.2876(8)
Au(1)-C(2)	2.293(4)
Au(1)-C(1)	2.292(4)
Sb(1)-F(4)	1.8682(19)
Sb(1)-F(2)	1.870(2)
Sb(1)-F(1)	1.8691(18)
Sb(1)-F(6)	1.875(2)
Sb(1)-F(5)	1.874(2)
Sb(1)-F(3)	1.8780(18)
P(1)-C(15)	1.829(3)
P(1)-C(7)	1.877(3)
P(1)-C(11)	1.888(3)
C(1)-C(2)	1.325(6)
C(1)-C(3)	1.505(5)
C(1)-C(4)	1.546(6)
C(2)-C(5)	1.486(7)
C(2)-C(6)	1.537(8)
C(3)-H(3A)	0.9600
C(3)-H(3B)	0.9600
C(3)-H(3C)	0.9600
C(4)-H(4A)	0.9600
C(4)-H(4B)	0.9600
C(4)-H(4C)	0.9600
C(5)-H(5A)	0.9600
C(5)-H(5B)	0.9600
C(5)-H(5C)	0.9600
C(6)-H(6A)	0.9600
C(6)-H(6B)	0.9600
C(6)-H(6C)	0.9600
C(7)-C(8)	1.535(5)
C(7)-C(10)	1.535(4)
C(7)-C(9)	1.557(5)
C(8)-H(8A)	0.9600
C(8)-H(8B)	0.9600
C(8)-H(8C)	0.9600
C(9)-H(9A)	0.9600
C(9)-H(9B)	0.9600
C(9)-H(9C)	0.9600
C(10)-H(10A)	0.9600
C(10)-H(10B)	0.9600
C(10)-H(10C)	0.9600
C(11)-C(14)	1.502(6)
C(11)-C(12)	1.541(4)
C(11)-C(13)	1.556(5)
C(12)-H(12A)	0.9600
C(12)-H(12B)	0.9600
C(12)-H(12C)	0.9600
C(13)-H(13A)	0.9600
C(13)-H(13B)	0.9600
C(13)-H(13C)	0.9600
C(14)-H(14A)	0.9600
C(14)-H(14B)	0.9600
C(14)-H(14C)	0.9600
C(15)-C(16)	1.406(4)
C(15)-C(20)	1.404(4)
C(16)-C(17)	1.397(4)
C(16)-C(21)	1.501(4)
C(17)-C(18)	1.381(4)

C(17)-H(17A)	0.9300
C(18)-C(19)	1.381(4)
C(18)-H(18A)	0.9300
C(19)-C(20)	1.384(4)
C(19)-H(19A)	0.9300
C(20)-H(20A)	0.9300
C(21)-C(26)	1.381(4)
C(21)-C(22)	1.401(4)
C(22)-C(23)	1.394(4)
C(22)-H(22A)	0.9300
C(23)-C(24)	1.381(5)
C(23)-H(23A)	0.9300
C(24)-C(25)	1.368(5)
C(24)-H(24A)	0.9300
C(25)-C(26)	1.390(4)
C(25)-H(25A)	0.9300
C(26)-H(26A)	0.9300
Cl(1)-C(1X)	1.755(5)
Cl(2)-C(1X)	1.745(5)
C(1X)-H(1XA)	0.9700
C(1X)-H(1XB)	0.9700

P(1)-Au(1)-C(2)	160.82(13)
P(1)-Au(1)-C(1)	152.05(12)
C(2)-Au(1)-C(1)	33.60(16)
F(4)-Sb(1)-F(2)	179.26(9)
F(4)-Sb(1)-F(1)	90.47(9)
F(2)-Sb(1)-F(1)	90.22(10)
F(4)-Sb(1)-F(6)	89.74(11)
F(2)-Sb(1)-F(6)	89.98(10)
F(1)-Sb(1)-F(6)	90.37(9)
F(4)-Sb(1)-F(5)	90.43(10)
F(2)-Sb(1)-F(5)	89.85(10)
F(1)-Sb(1)-F(5)	89.89(9)
F(6)-Sb(1)-F(5)	179.69(10)
F(4)-Sb(1)-F(3)	88.47(9)
F(2)-Sb(1)-F(3)	90.84(9)
F(1)-Sb(1)-F(3)	178.77(10)
F(6)-Sb(1)-F(3)	90.25(9)
F(5)-Sb(1)-F(3)	89.49(9)
C(15)-P(1)-C(7)	105.14(14)
C(15)-P(1)-C(11)	107.67(14)
C(7)-P(1)-C(11)	114.64(16)
C(15)-P(1)-Au(1)	117.04(10)
C(7)-P(1)-Au(1)	106.05(10)
C(11)-P(1)-Au(1)	106.63(10)
C(2)-C(1)-C(3)	127.7(5)
C(2)-C(1)-C(4)	116.5(4)
C(3)-C(1)-C(4)	113.9(4)
C(2)-C(1)-Au(1)	73.2(2)
C(3)-C(1)-Au(1)	106.4(2)
C(4)-C(1)-Au(1)	104.7(3)
C(1)-C(2)-C(5)	128.4(6)
C(1)-C(2)-C(6)	121.8(5)
C(5)-C(2)-C(6)	107.4(5)
C(1)-C(2)-Au(1)	73.2(2)
C(5)-C(2)-Au(1)	106.8(3)
C(6)-C(2)-Au(1)	108.4(3)
C(1)-C(3)-H(3A)	109.5
C(1)-C(3)-H(3B)	109.5

H(3A)-C(3)-H(3B)	109.5
C(1)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5
C(1)-C(4)-H(4A)	109.5
C(1)-C(4)-H(4B)	109.5
H(4A)-C(4)-H(4B)	109.5
C(1)-C(4)-H(4C)	109.5
H(4A)-C(4)-H(4C)	109.5
H(4B)-C(4)-H(4C)	109.5
C(2)-C(5)-H(5A)	109.5
C(2)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(2)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
C(2)-C(6)-H(6A)	109.5
C(2)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(2)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(8)-C(7)-C(10)	111.1(3)
C(8)-C(7)-C(9)	108.4(3)
C(10)-C(7)-C(9)	107.0(3)
C(8)-C(7)-P(1)	109.6(2)
C(10)-C(7)-P(1)	115.2(2)
C(9)-C(7)-P(1)	105.2(2)
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(7)-C(9)-H(9A)	109.5
C(7)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(7)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(7)-C(10)-H(10A)	109.5
C(7)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(7)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(14)-C(11)-C(12)	109.8(3)
C(14)-C(11)-C(13)	111.2(3)
C(12)-C(11)-C(13)	105.6(3)
C(14)-C(11)-P(1)	106.5(2)
C(12)-C(11)-P(1)	108.9(2)
C(13)-C(11)-P(1)	114.9(2)
C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(11)-C(13)-H(13A)	109.5
C(11)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(11)-C(13)-H(13C)	109.5

H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(11)-C(14)-H(14A)	109.5
C(11)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(11)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(16)-C(15)-C(20)	118.7(3)
C(16)-C(15)-P(1)	123.4(2)
C(20)-C(15)-P(1)	117.8(2)
C(17)-C(16)-C(15)	118.2(3)
C(17)-C(16)-C(21)	115.3(3)
C(15)-C(16)-C(21)	126.3(3)
C(18)-C(17)-C(16)	122.5(3)
C(18)-C(17)-H(17A)	118.8
C(16)-C(17)-H(17A)	118.8
C(19)-C(18)-C(17)	119.3(3)
C(19)-C(18)-H(18A)	120.3
C(17)-C(18)-H(18A)	120.3
C(18)-C(19)-C(20)	119.6(3)
C(18)-C(19)-H(19A)	120.2
C(20)-C(19)-H(19A)	120.2
C(19)-C(20)-C(15)	121.6(3)
C(19)-C(20)-H(20A)	119.2
C(15)-C(20)-H(20A)	119.2
C(26)-C(21)-C(22)	119.0(3)
C(26)-C(21)-C(16)	118.7(3)
C(22)-C(21)-C(16)	121.8(3)
C(23)-C(22)-C(21)	119.8(3)
C(23)-C(22)-H(22A)	120.1
C(21)-C(22)-H(22A)	120.1
C(24)-C(23)-C(22)	120.3(3)
C(24)-C(23)-H(23A)	119.9
C(22)-C(23)-H(23A)	119.9
C(25)-C(24)-C(23)	119.8(3)
C(25)-C(24)-H(24A)	120.1
C(23)-C(24)-H(24A)	120.1
C(24)-C(25)-C(26)	120.6(3)
C(24)-C(25)-H(25A)	119.7
C(26)-C(25)-H(25A)	119.7
C(21)-C(26)-C(25)	120.4(3)
C(21)-C(26)-H(26A)	119.8
C(25)-C(26)-H(26A)	119.8
Cl(2)-C(1X)-Cl(1)	111.7(3)
Cl(2)-C(1X)-H(1XA)	109.3
Cl(1)-C(1X)-H(1XA)	109.3
Cl(2)-C(1X)-H(1XB)	109.3
Cl(1)-C(1X)-H(1XB)	109.3
H(1XA)-C(1X)-H(1XB)	107.9

Symmetry transformations used to generate equivalent atoms:

Table S15. Anisotropic displacement parameters (Å^{2}x 10^3) for **1e•CH$_2$Cl$_2$**. The anisotropic displacement factor exponent takes the form: -2π^2[h^2 a*^{2}U^{11} + ... + 2 h k a* b* U^{12}].

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Au(1)	20(1)	30(1)	18(1)	3(1)	6(1)	-1(1)
Sb(1)	21(1)	21(1)	21(1)	3(1)	5(1)	0(1)
F(1)	35(1)	33(1)	44(1)	14(1)	10(1)	-6(1)
F(2)	56(1)	38(1)	37(1)	-8(1)	13(1)	5(1)
F(3)	32(1)	30(1)	37(1)	14(1)	14(1)	-2(1)
F(4)	55(1)	33(1)	31(1)	-1(1)	22(1)	5(1)
F(5)	28(1)	33(1)	44(1)	8(1)	-6(1)	0(1)
F(6)	30(1)	38(1)	55(1)	12(1)	-12(1)	-2(1)
P(1)	17(1)	21(1)	17(1)	0(1)	4(1)	-3(1)
C(1)	38(2)	52(2)	41(2)	12(2)	21(2)	4(2)
C(2)	48(3)	72(3)	68(3)	31(2)	45(3)	20(2)
C(3)	31(2)	34(2)	43(2)	0(2)	13(2)	0(1)
C(4)	39(2)	85(3)	44(3)	-14(2)	16(2)	-24(2)
C(5)	81(4)	64(3)	113(5)	57(3)	72(4)	39(3)
C(6)	52(3)	105(4)	45(3)	19(3)	4(2)	-7(3)
C(7)	24(2)	39(2)	16(1)	4(1)	2(1)	-1(1)
C(8)	29(2)	47(2)	32(2)	0(2)	-6(2)	-4(2)
C(9)	43(2)	37(2)	37(2)	8(2)	0(2)	9(2)
C(10)	37(2)	51(2)	23(2)	9(2)	4(2)	-1(2)
C(11)	30(2)	16(1)	43(2)	-1(1)	14(2)	-2(1)
C(12)	41(2)	24(2)	45(2)	1(2)	9(2)	-11(1)
C(13)	67(3)	31(2)	53(3)	-8(2)	37(2)	-8(2)
C(14)	41(2)	30(2)	81(3)	5(2)	-7(2)	5(2)
C(15)	19(1)	21(1)	19(1)	2(1)	3(1)	-3(1)
C(16)	19(1)	18(1)	19(1)	4(1)	2(1)	3(1)
C(17)	26(2)	24(1)	23(2)	0(1)	2(1)	-3(1)

C(18)	22(2)	30(2)	27(2)	2(1)	6(1)	-7(1)
C(19)	21(2)	25(2)	23(2)	4(1)	7(1)	-2(1)
C(20)	24(2)	25(2)	20(2)	-1(1)	4(1)	-4(1)
C(21)	18(1)	22(1)	17(1)	0(1)	2(1)	-3(1)
C(22)	30(2)	24(1)	24(2)	3(1)	6(1)	5(1)
C(23)	31(2)	27(2)	30(2)	-5(1)	10(1)	3(1)
C(24)	36(2)	36(2)	20(2)	-4(1)	8(1)	-3(2)
C(25)	39(2)	54(2)	18(2)	9(2)	5(1)	11(2)
C(26)	29(2)	41(2)	25(2)	9(1)	8(1)	13(1)
Cl(1)	62(1)	58(1)	97(1)	12(1)	7(1)	14(1)
Cl(2)	82(1)	89(1)	77(1)	-1(1)	36(1)	17(1)
C(1X)	59(3)	72(3)	72(4)	-17(3)	9(3)	11(3)

Table S16. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **1e**•CH_2Cl_2.

	x	y	z	U(eq)
H(3A)	4550	6297	2659	53
H(3B)	2908	6125	2564	53
H(3C)	3705	6005	3227	53
H(4A)	5366	7618	3352	83
H(4B)	4460	7268	3882	83
H(4C)	4146	8160	3607	83
H(5A)	3008	8928	2416	125
H(5B)	2892	8848	3141	125
H(5C)	1507	8869	2689	125
H(6A)	2296	7743	1715	101
H(6B)	824	7758	2016	101
H(6C)	1708	6931	2011	101
H(8A)	2997	7012	5429	55
H(8B)	2098	7800	5222	55
H(8C)	2904	7298	4726	55
H(9A)	2179	5577	5012	59
H(9B)	2070	5949	4332	59
H(9C)	745	5511	4595	59
H(10A)	1023	6273	5872	55
H(10B)	-425	6128	5479	55
H(10C)	-26	7020	5732	55
H(12A)	202	9443	4401	54
H(12B)	702	8825	3893	54
H(12C)	1336	8755	4589	54
H(13A)	-1331	9025	5198	73
H(13B)	-190	8362	5431	73

H(13C)	-1780	8093	5279	73
H(14A)	-2340	8988	4092	77
H(14B)	-2728	8039	4110	77
H(14C)	-1740	8374	3604	77
H(17A)	-3472	5118	3425	29
H(18A)	-4953	5179	4235	31
H(19A)	-4436	6090	5061	27
H(20A)	-2407	6899	5078	27
H(22A)	215	5032	3457	31
H(23A)	1127	4802	2489	35
H(24A)	252	5541	1618	36
H(25A)	-1514	6512	1710	44
H(26A)	-2455	6743	2666	38
H(1XA)	5556	6102	1490	81
H(1XB)	5060	5238	1740	81

Table S17. Torsion angles [°] for **1e**•CH_2Cl_2.

C(2)-Au(1)-P(1)-C(15)	133.8(5)
C(1)-Au(1)-P(1)-C(15)	-135.7(2)
C(2)-Au(1)-P(1)-C(7)	-109.3(5)
C(1)-Au(1)-P(1)-C(7)	-18.8(2)
C(2)-Au(1)-P(1)-C(11)	13.3(5)
C(1)-Au(1)-P(1)-C(11)	103.8(2)
P(1)-Au(1)-C(1)-C(2)	-143.6(3)
P(1)-Au(1)-C(1)-C(3)	91.2(4)
C(2)-Au(1)-C(1)-C(3)	-125.3(5)
P(1)-Au(1)-C(1)-C(4)	-29.8(4)
C(2)-Au(1)-C(1)-C(4)	113.8(5)
C(3)-C(1)-C(2)-C(5)	-163.5(4)
C(4)-C(1)-C(2)-C(5)	0.0(6)
Au(1)-C(1)-C(2)-C(5)	98.4(4)
C(3)-C(1)-C(2)-C(6)	-3.5(6)
C(4)-C(1)-C(2)-C(6)	160.1(4)
Au(1)-C(1)-C(2)-C(6)	-101.5(4)
C(3)-C(1)-C(2)-Au(1)	98.1(4)
C(4)-C(1)-C(2)-Au(1)	-98.4(3)
P(1)-Au(1)-C(2)-C(1)	122.1(4)
P(1)-Au(1)-C(2)-C(5)	-3.8(8)
C(1)-Au(1)-C(2)-C(5)	-125.9(6)
P(1)-Au(1)-C(2)-C(6)	-119.2(5)
C(1)-Au(1)-C(2)-C(6)	118.7(5)
C(15)-P(1)-C(7)-C(8)	-175.1(2)
C(11)-P(1)-C(7)-C(8)	-57.1(3)
Au(1)-P(1)-C(7)-C(8)	60.3(2)
C(15)-P(1)-C(7)-C(10)	-49.0(3)
C(11)-P(1)-C(7)-C(10)	69.0(3)

Au(1)-P(1)-C(7)-C(10)	-173.6(2)
C(15)-P(1)-C(7)-C(9)	68.5(2)
C(11)-P(1)-C(7)-C(9)	-173.5(2)
Au(1)-P(1)-C(7)-C(9)	-56.1(2)
C(15)-P(1)-C(11)-C(14)	-44.3(3)
C(7)-P(1)-C(11)-C(14)	-160.9(3)
Au(1)-P(1)-C(11)-C(14)	82.1(3)
C(15)-P(1)-C(11)-C(12)	-162.6(2)
C(7)-P(1)-C(11)-C(12)	80.8(3)
Au(1)-P(1)-C(11)-C(12)	-36.2(3)
C(15)-P(1)-C(11)-C(13)	79.3(3)
C(7)-P(1)-C(11)-C(13)	-37.3(3)
Au(1)-P(1)-C(11)-C(13)	-154.4(3)
C(7)-P(1)-C(15)-C(16)	-109.2(3)
C(11)-P(1)-C(15)-C(16)	128.2(3)
Au(1)-P(1)-C(15)-C(16)	8.2(3)
C(7)-P(1)-C(15)-C(20)	69.7(3)
C(11)-P(1)-C(15)-C(20)	-53.0(3)
Au(1)-P(1)-C(15)-C(20)	-173.0(2)
C(20)-C(15)-C(16)-C(17)	-0.9(4)
P(1)-C(15)-C(16)-C(17)	178.0(2)
C(20)-C(15)-C(16)-C(21)	175.3(3)
P(1)-C(15)-C(16)-C(21)	-5.9(4)
C(15)-C(16)-C(17)-C(18)	0.9(5)
C(21)-C(16)-C(17)-C(18)	-175.6(3)
C(16)-C(17)-C(18)-C(19)	0.0(5)
C(17)-C(18)-C(19)-C(20)	-1.0(5)
C(18)-C(19)-C(20)-C(15)	1.0(5)
C(16)-C(15)-C(20)-C(19)	-0.1(4)
P(1)-C(15)-C(20)-C(19)	-179.0(2)
C(17)-C(16)-C(21)-C(26)	80.7(4)

C(15)-C(16)-C(21)-C(26)	-95.6(4)
C(17)-C(16)-C(21)-C(22)	-90.8(4)
C(15)-C(16)-C(21)-C(22)	93.0(4)
C(26)-C(21)-C(22)-C(23)	-1.5(5)
C(16)-C(21)-C(22)-C(23)	169.9(3)
C(21)-C(22)-C(23)-C(24)	0.8(5)
C(22)-C(23)-C(24)-C(25)	0.3(5)
C(23)-C(24)-C(25)-C(26)	-0.6(6)
C(22)-C(21)-C(26)-C(25)	1.1(5)
C(16)-C(21)-C(26)-C(25)	-170.6(3)
C(24)-C(25)-C(26)-C(21)	-0.1(6)

Symmetry transformations used to generate equivalent atoms:

X-ray Crystal Structure of [(P)Au(η^2-$H_2C{=}CH$-4-$C_6H_4CH_3$)] SbF_6^- (1i). Slow diffusion of hexane into a CH_2Cl_2 solution of **1i** at 4 °C gave crystals of **1i** suitable for X-ray diffraction. Diffraction data were obtained with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) on a Brüker Kappa Apex II diffractometer using the ω scan mode (Tables 1, and S18 – S23; Figures 1 and S5). Of the 104499 reflections, 6695 independent, observed reflections ($I > 2.0\sigma(I)$) were obtained with maximum *h*, *k*, *l* values of 16, 24, and 29, respectively. An absorption correction was applied (SADABS). The structure was refined by full matrix, least squares on F^2; H atoms were fixed, all other atoms were refined anisotropically (Table S19).

Figure S5. ORTEP diagrams of **1i**. Ellipsoids are shown at 50%. Counterion and hydrogen atoms are omitted for clarity.

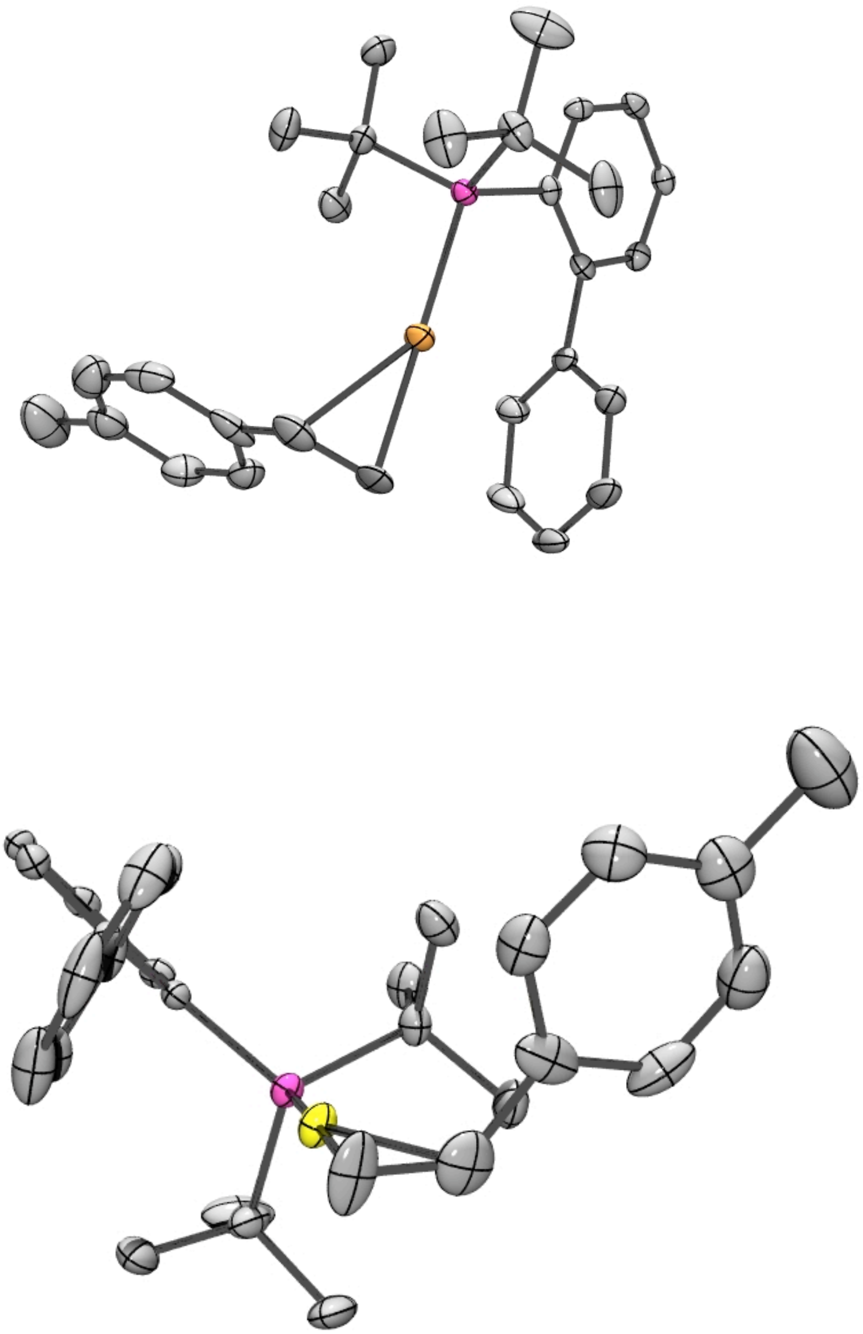


Table S18. Crystal data and structure refinement for **1i**.

Identification code	o1	
Empirical formula	$C_{29}H_{37}AuF_6PSb$	
Formula weight	849.27	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 12.702(4) Å	α= 90°.
	b = 18.693(6) Å	β= 90°.
	c = 25.481(7) Å	γ = 90°.
Volume	6050(3) $Å^3$	
Z	8	
Density (calculated)	1.865 Mg/m^3	
Absorption coefficient	5.844 mm^{-1}	
F(000)	3280	
Crystal size	0.28 x 0.10 x 0.07 mm^3	
Crystal color and habit	colourless prism	
Diffractometer	Bruker SMART Apex II	
Theta range for data collection	3.08 to 27.20°.	
Index ranges	-16<=h<=16, -23<=k<=24, -32<=l<=29	
Reflections collected	104499	
Independent reflections	6695 [R(int) = 0.0826]	
Observed reflections (I > 2sigma(I))	5501	
Completeness to theta = 27.20°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6851 and 0.2915	
Solution method	SHELXS-97 (Sheldrick, 2008)	
Refinement method	SHELXL-97 (Sheldrick, 2008)	
Data / restraints / parameters	6695 / 0 / 343	
Goodness-of-fit on F^2	1.426	

Final R indices [I>2sigma(I)]	R1 = 0.0291, wR2 = 0.0649
R indices (all data)	R1 = 0.0415, wR2 = 0.0683
Largest diff. peak and hole	1.190 and -1.002 e.Å^{-3}

Table S19. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **1i**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Au(1)	7179(1)	1959(1)	6492(1)	22(1)
Sb(1)	1678(1)	779(1)	6621(1)	27(1)
F(1)	806(3)	1136(2)	7136(1)	88(1)
F(2)	520(2)	648(2)	6188(1)	47(1)
F(3)	1801(4)	1720(2)	6367(2)	103(2)
F(4)	2562(3)	500(3)	6103(1)	145(3)
F(5)	2829(2)	922(2)	7067(1)	75(1)
F(6)	1545(4)	-115(2)	6902(2)	99(2)
P(1)	6177(1)	2975(1)	6498(1)	17(1)
C(1)	8153(4)	988(2)	6531(2)	45(1)
C(2)	7231(4)	757(2)	6698(2)	42(1)
C(3)	6429(4)	391(2)	6399(2)	38(1)
C(4)	5494(4)	168(3)	6657(2)	41(1)
C(5)	4749(4)	-215(3)	6402(2)	46(1)
C(6)	4850(4)	-411(3)	5893(2)	42(1)
C(7)	5753(4)	-204(3)	5636(2)	40(1)
C(8)	6528(3)	197(2)	5870(2)	34(1)
C(9)	4020(5)	-849(3)	5628(3)	72(2)
C(10)	4774(3)	2664(2)	6467(2)	23(1)
C(11)	4714(3)	2174(2)	5986(2)	31(1)
C(12)	3945(3)	3250(2)	6400(2)	31(1)
C(13)	4521(4)	2231(2)	6961(2)	35(1)
C(14)	6561(3)	3508(2)	7092(2)	26(1)
C(15)	7710(4)	3717(3)	6997(2)	38(1)
C(16)	5911(5)	4178(3)	7194(2)	51(2)
C(17)	6536(4)	3023(2)	7582(2)	41(1)

C(18)	6374(3)	3556(2)	5932(1)	17(1)
C(19)	7056(3)	3383(2)	5516(2)	18(1)
C(20)	7094(3)	3836(2)	5082(2)	21(1)
C(21)	6518(3)	4451(2)	5053(2)	19(1)
C(22)	5859(3)	4635(2)	5468(1)	20(1)
C(23)	5788(3)	4189(2)	5898(1)	18(1)
C(24)	7796(3)	2761(2)	5500(2)	22(1)
C(25)	7601(4)	2187(2)	5166(2)	29(1)
C(26)	8358(4)	1659(2)	5092(2)	38(1)
C(27)	9300(4)	1704(2)	5350(2)	42(1)
C(28)	9505(4)	2260(2)	5691(2)	41(1)
C(29)	8747(3)	2790(2)	5768(2)	30(1)

Table S20. Bond lengths [Å] and angles [°] for **1i**.

Au(1)-C(1)	2.199(4)	C(9)-H(9B)	0.9600
Au(1)-P(1)	2.2863(11)	C(9)-H(9C)	0.9600
Au(1)-C(2)	2.308(5)	C(10)-C(12)	1.529(6)
Sb(1)-F(4)	1.809(3)	C(10)-C(13)	1.530(5)
Sb(1)-F(6)	1.825(3)	C(10)-C(11)	1.533(6)
Sb(1)-F(1)	1.844(3)	C(11)-H(11A)	0.9600
Sb(1)-F(2)	1.855(2)	C(11)-H(11B)	0.9600
Sb(1)-F(5)	1.871(3)	C(11)-H(11C)	0.9600
Sb(1)-F(3)	1.882(4)	C(12)-H(12A)	0.9600
P(1)-C(18)	1.822(4)	C(12)-H(12B)	0.9600
P(1)-C(10)	1.877(4)	C(12)-H(12C)	0.9600
P(1)-C(14)	1.877(4)	C(13)-H(13A)	0.9600
C(1)-C(2)	1.319(7)	C(13)-H(13B)	0.9600
C(1)-H(1A)	0.9700	C(13)-H(13C)	0.9600
C(1)-H(1B)	0.9700	C(14)-C(16)	1.522(6)
C(2)-C(3)	1.445(7)	C(14)-C(15)	1.530(6)
C(2)-H(2A)	0.9800	C(14)-C(17)	1.542(5)
C(3)-C(8)	1.403(6)	C(15)-H(15A)	0.9600
C(3)-C(4)	1.419(7)	C(15)-H(15B)	0.9600
C(4)-C(5)	1.352(7)	C(15)-H(15C)	0.9600
C(4)-H(4A)	0.9300	C(16)-H(16A)	0.9600
C(5)-C(6)	1.354(7)	C(16)-H(16B)	0.9600
C(5)-H(5A)	0.9300	C(16)-H(16C)	0.9600
C(6)-C(7)	1.377(7)	C(17)-H(17A)	0.9600
C(6)-C(9)	1.497(7)	C(17)-H(17B)	0.9600
C(7)-C(8)	1.372(6)	C(17)-H(17C)	0.9600
C(7)-H(7A)	0.9300	C(18)-C(23)	1.401(5)
C(8)-H(8A)	0.9300	C(18)-C(19)	1.407(5)
C(9)-H(9A)	0.9600	C(19)-C(20)	1.393(5)

C(19)-C(24)	1.497(5)
C(20)-C(21)	1.365(5)
C(20)-H(20A)	0.9300
C(21)-C(22)	1.391(5)
C(21)-H(21A)	0.9300
C(22)-C(23)	1.380(5)
C(22)-H(22A)	0.9300
C(23)-H(23A)	0.9300
C(24)-C(29)	1.388(6)
C(24)-C(25)	1.392(6)
C(25)-C(26)	1.390(6)
C(25)-H(25A)	0.9300
C(26)-C(27)	1.367(7)
C(26)-H(26A)	0.9300
C(27)-C(28)	1.379(7)
C(27)-H(27A)	0.9300
C(28)-C(29)	1.395(6)
C(28)-H(28A)	0.9300
C(29)-H(29A)	0.9300

C(1)-Au(1)-P(1)	177.02(16)
C(1)-Au(1)-C(2)	33.92(17)
P(1)-Au(1)-C(2)	145.44(13)
F(4)-Sb(1)-F(6)	94.6(3)
F(4)-Sb(1)-F(1)	175.5(2)
F(6)-Sb(1)-F(1)	89.7(2)
F(4)-Sb(1)-F(2)	91.19(16)
F(6)-Sb(1)-F(2)	92.28(15)
F(1)-Sb(1)-F(2)	89.68(15)
F(4)-Sb(1)-F(5)	89.99(19)
F(6)-Sb(1)-F(5)	88.02(16)
F(1)-Sb(1)-F(5)	89.11(17)
F(2)-Sb(1)-F(5)	178.76(16)
F(4)-Sb(1)-F(3)	88.1(3)
F(6)-Sb(1)-F(3)	176.9(2)
F(1)-Sb(1)-F(3)	87.5(2)
F(2)-Sb(1)-F(3)	89.09(15)
F(5)-Sb(1)-F(3)	90.56(17)
C(18)-P(1)-C(10)	106.33(17)
C(18)-P(1)-C(14)	106.68(18)
C(10)-P(1)-C(14)	116.41(19)
C(18)-P(1)-Au(1)	114.46(13)
C(10)-P(1)-Au(1)	105.71(13)
C(14)-P(1)-Au(1)	107.54(14)
C(2)-C(1)-Au(1)	77.6(3)
C(2)-C(1)-H(1A)	115.6
Au(1)-C(1)-H(1A)	115.6
C(2)-C(1)-H(1B)	115.6
Au(1)-C(1)-H(1B)	115.6
H(1A)-C(1)-H(1B)	112.6
C(1)-C(2)-C(3)	127.7(5)
C(1)-C(2)-Au(1)	68.5(3)
C(3)-C(2)-Au(1)	108.7(3)
C(1)-C(2)-H(2A)	114.0
C(3)-C(2)-H(2A)	114.0
Au(1)-C(2)-H(2A)	114.0
C(8)-C(3)-C(4)	116.4(4)
C(8)-C(3)-C(2)	124.6(5)
C(4)-C(3)-C(2)	119.0(5)
C(5)-C(4)-C(3)	121.2(4)

C(5)-C(4)-H(4A)	119.4
C(3)-C(4)-H(4A)	119.4
C(4)-C(5)-C(6)	122.5(5)
C(4)-C(5)-H(5A)	118.8
C(6)-C(5)-H(5A)	118.8
C(5)-C(6)-C(7)	117.3(5)
C(5)-C(6)-C(9)	121.0(5)
C(7)-C(6)-C(9)	121.7(5)
C(8)-C(7)-C(6)	123.0(5)
C(8)-C(7)-H(7A)	118.5
C(6)-C(7)-H(7A)	118.5
C(7)-C(8)-C(3)	119.6(4)
C(7)-C(8)-H(8A)	120.2
C(3)-C(8)-H(8A)	120.2
C(6)-C(9)-H(9A)	109.5
C(6)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(6)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(12)-C(10)-C(13)	109.0(3)
C(12)-C(10)-C(11)	107.8(3)
C(13)-C(10)-C(11)	109.3(4)
C(12)-C(10)-P(1)	115.9(3)
C(13)-C(10)-P(1)	109.2(3)
C(11)-C(10)-P(1)	105.4(3)
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(10)-C(12)-H(12A)	109.5
C(10)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(10)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(10)-C(13)-H(13A)	109.5
C(10)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(10)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(16)-C(14)-C(15)	109.5(4)
C(16)-C(14)-C(17)	109.6(4)
C(15)-C(14)-C(17)	107.4(4)
C(16)-C(14)-P(1)	115.6(3)
C(15)-C(14)-P(1)	104.7(3)
C(17)-C(14)-P(1)	109.6(3)
C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(14)-C(16)-H(16A)	109.5
C(14)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(14)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5

C(14)-C(17)-H(17A)	109.5
C(14)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(14)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(23)-C(18)-C(19)	118.2(3)
C(23)-C(18)-P(1)	118.7(3)
C(19)-C(18)-P(1)	123.0(3)
C(20)-C(19)-C(18)	118.7(3)
C(20)-C(19)-C(24)	115.4(3)
C(18)-C(19)-C(24)	125.8(3)
C(21)-C(20)-C(19)	122.3(4)
C(21)-C(20)-H(20A)	118.8
C(19)-C(20)-H(20A)	118.8
C(20)-C(21)-C(22)	119.4(3)
C(20)-C(21)-H(21A)	120.3
C(22)-C(21)-H(21A)	120.3
C(23)-C(22)-C(21)	119.5(3)
C(23)-C(22)-H(22A)	120.3
C(21)-C(22)-H(22A)	120.3
C(22)-C(23)-C(18)	121.8(3)
C(22)-C(23)-H(23A)	119.1
C(18)-C(23)-H(23A)	119.1
C(29)-C(24)-C(25)	119.1(4)
C(29)-C(24)-C(19)	120.2(4)
C(25)-C(24)-C(19)	120.3(4)
C(26)-C(25)-C(24)	120.4(4)
C(26)-C(25)-H(25A)	119.8
C(24)-C(25)-H(25A)	119.8
C(27)-C(26)-C(25)	119.8(5)
C(27)-C(26)-H(26A)	120.1
C(25)-C(26)-H(26A)	120.1
C(26)-C(27)-C(28)	120.9(4)
C(26)-C(27)-H(27A)	119.5
C(28)-C(27)-H(27A)	119.5
C(27)-C(28)-C(29)	119.6(5)
C(27)-C(28)-H(28A)	120.2
C(29)-C(28)-H(28A)	120.2
C(24)-C(29)-C(28)	120.2(4)
C(24)-C(29)-H(29A)	119.9
C(28)-C(29)-H(29A)	119.9

Table S21. Anisotropic displacement parameters ($Å^2$x 10^3) for **1i**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Au(1)	22(1)	18(1)	27(1)	7(1)	3(1)	5(1)
Sb(1)	21(1)	39(1)	20(1)	3(1)	-1(1)	-6(1)
F(1)	97(3)	132(4)	35(2)	-30(2)	-8(2)	55(3)
F(2)	36(2)	65(2)	41(2)	-13(1)	-16(1)	-4(1)
F(3)	107(3)	83(3)	120(4)	60(3)	-56(3)	-52(3)
F(4)	84(3)	323(8)	29(2)	-4(3)	0(2)	129(4)
F(5)	45(2)	127(3)	52(2)	31(2)	-26(2)	-36(2)
F(6)	142(4)	35(2)	120(3)	27(2)	-66(3)	-33(2)
P(1)	19(1)	15(1)	18(1)	2(1)	1(1)	2(1)
C(1)	39(3)	20(2)	77(4)	23(2)	19(3)	17(2)
C(2)	48(3)	24(2)	54(3)	12(2)	-1(2)	13(2)
C(3)	48(3)	17(2)	48(3)	-2(2)	-20(2)	11(2)
C(4)	57(3)	41(3)	26(2)	8(2)	11(2)	25(3)
C(5)	38(3)	45(3)	55(3)	15(3)	2(2)	1(2)
C(6)	40(3)	30(3)	56(3)	3(2)	-4(2)	9(2)
C(7)	41(3)	38(3)	39(3)	-9(2)	3(2)	8(2)
C(8)	25(2)	35(3)	44(3)	8(2)	5(2)	9(2)
C(9)	57(4)	52(4)	106(5)	2(4)	-26(4)	-6(3)
C(10)	19(2)	21(2)	29(2)	2(2)	4(2)	-1(2)
C(11)	25(2)	28(2)	40(3)	0(2)	-7(2)	-2(2)
C(12)	21(2)	33(2)	40(3)	2(2)	4(2)	3(2)
C(13)	28(2)	40(3)	37(3)	11(2)	4(2)	-8(2)
C(14)	38(3)	23(2)	18(2)	2(2)	-4(2)	-2(2)
C(15)	48(3)	38(3)	29(2)	2(2)	-12(2)	-20(2)
C(16)	77(4)	45(3)	31(3)	-18(2)	-17(3)	19(3)
C(17)	59(3)	44(3)	19(2)	6(2)	-10(2)	-12(3)

C(18)	18(2)	16(2)	16(2)	1(2)	-3(1)	-4(2)
C(19)	22(2)	13(2)	20(2)	-2(2)	-2(2)	-1(2)
C(20)	20(2)	22(2)	21(2)	-1(2)	0(2)	-3(2)
C(21)	23(2)	17(2)	17(2)	4(2)	-3(2)	-3(2)
C(22)	20(2)	16(2)	24(2)	0(2)	-7(2)	2(2)
C(23)	16(2)	21(2)	18(2)	-2(2)	-2(1)	3(2)
C(24)	21(2)	17(2)	26(2)	7(2)	12(2)	3(2)
C(25)	35(2)	24(2)	29(2)	-2(2)	11(2)	4(2)
C(26)	53(3)	22(2)	38(3)	-2(2)	24(2)	8(2)
C(27)	42(3)	24(2)	61(3)	18(2)	35(3)	15(2)
C(28)	24(2)	30(3)	69(3)	23(2)	14(2)	10(2)
C(29)	23(2)	22(2)	44(3)	9(2)	4(2)	4(2)

Table S22. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **1i**.

	x	y	z	U(eq)
H(1A)	8384	798	6196	54
H(1B)	8711	994	6791	54
H(2A)	7207	658	7076	50
H(4A)	5393	288	7008	50
H(5A)	4145	-348	6584	55
H(7A)	5842	-341	5288	47
H(8A)	7114	339	5678	41
H(9A)	4220	-934	5270	107
H(9B)	3362	-596	5636	107
H(9C)	3944	-1298	5807	107
H(11A)	4009	1996	5948	47
H(11B)	5190	1779	6031	47
H(11C)	4906	2438	5678	47
H(12A)	3257	3038	6390	47
H(12B)	4072	3504	6079	47
H(12C)	3986	3577	6690	47
H(13A)	3803	2073	6947	52
H(13B)	4623	2526	7265	52
H(13C)	4980	1824	6980	52
H(15A)	7961	3997	7287	57
H(15B)	7759	3993	6680	57
H(15C)	8130	3293	6963	57
H(16A)	6168	4415	7502	76
H(16B)	5187	4047	7244	76
H(16C)	5966	4494	6898	76
H(17A)	6733	3296	7885	61

H(17B)	7022	2635	7536	61
H(17C)	5839	2837	7629	61
H(20A)	7529	3715	4802	25
H(21A)	6565	4744	4759	23
H(22A)	5469	5056	5455	24
H(23A)	5341	4312	6172	22
H(25A)	6960	2156	4991	35
H(26A)	8225	1277	4868	45
H(27A)	9809	1355	5295	51
H(28A)	10144	2282	5868	49
H(29A)	8878	3164	6000	36

Table S23. Torsion angles [°] for **1i**.

C(2)-Au(1)-P(1)-C(18)	-143.5(3)
C(2)-Au(1)-P(1)-C(10)	-26.8(3)
C(2)-Au(1)-P(1)-C(14)	98.2(3)
Au(1)-C(1)-C(2)-C(3)	97.6(5)
P(1)-Au(1)-C(2)-C(1)	-174.8(3)
C(1)-Au(1)-C(2)-C(3)	-124.0(6)
P(1)-Au(1)-C(2)-C(3)	61.1(5)
C(1)-C(2)-C(3)-C(8)	2.3(8)
Au(1)-C(2)-C(3)-C(8)	79.2(5)
C(1)-C(2)-C(3)-C(4)	178.3(5)
Au(1)-C(2)-C(3)-C(4)	-104.8(4)
C(8)-C(3)-C(4)-C(5)	0.5(7)
C(2)-C(3)-C(4)-C(5)	-175.9(4)
C(3)-C(4)-C(5)-C(6)	0.5(8)
C(4)-C(5)-C(6)-C(7)	-0.1(8)
C(4)-C(5)-C(6)-C(9)	178.6(5)
C(5)-C(6)-C(7)-C(8)	-1.2(7)
C(9)-C(6)-C(7)-C(8)	-179.9(5)
C(6)-C(7)-C(8)-C(3)	2.2(7)
C(4)-C(3)-C(8)-C(7)	-1.7(6)
C(2)-C(3)-C(8)-C(7)	174.4(4)
C(18)-P(1)-C(10)-C(12)	-51.0(3)
C(14)-P(1)-C(10)-C(12)	67.7(3)
Au(1)-P(1)-C(10)-C(12)	-173.0(3)
C(18)-P(1)-C(10)-C(13)	-174.5(3)
C(14)-P(1)-C(10)-C(13)	-55.9(3)
Au(1)-P(1)-C(10)-C(13)	63.4(3)
C(18)-P(1)-C(10)-C(11)	68.1(3)
C(14)-P(1)-C(10)-C(11)	-173.2(3)

Au(1)-P(1)-C(10)-C(11)	-53.9(3)
C(18)-P(1)-C(14)-C(16)	62.0(4)
C(10)-P(1)-C(14)-C(16)	-56.5(4)
Au(1)-P(1)-C(14)-C(16)	-174.8(3)
C(18)-P(1)-C(14)-C(15)	-58.7(3)
C(10)-P(1)-C(14)-C(15)	-177.1(3)
Au(1)-P(1)-C(14)-C(15)	64.6(3)
C(18)-P(1)-C(14)-C(17)	-173.6(3)
C(10)-P(1)-C(14)-C(17)	68.0(4)
Au(1)-P(1)-C(14)-C(17)	-50.3(3)
C(10)-P(1)-C(18)-C(23)	63.2(3)
C(14)-P(1)-C(18)-C(23)	-61.7(3)
Au(1)-P(1)-C(18)-C(23)	179.5(2)
C(10)-P(1)-C(18)-C(19)	-114.1(3)
C(14)-P(1)-C(18)-C(19)	121.0(3)
Au(1)-P(1)-C(18)-C(19)	2.2(3)
C(23)-C(18)-C(19)-C(20)	-2.0(5)
P(1)-C(18)-C(19)-C(20)	175.3(3)
C(23)-C(18)-C(19)-C(24)	175.4(4)
P(1)-C(18)-C(19)-C(24)	-7.3(5)
C(18)-C(19)-C(20)-C(21)	2.0(6)
C(24)-C(19)-C(20)-C(21)	-175.7(3)
C(19)-C(20)-C(21)-C(22)	-0.5(6)
C(20)-C(21)-C(22)-C(23)	-0.8(5)
C(21)-C(22)-C(23)-C(18)	0.7(6)
C(19)-C(18)-C(23)-C(22)	0.7(5)
P(1)-C(18)-C(23)-C(22)	-176.7(3)
C(20)-C(19)-C(24)-C(29)	98.8(4)
C(18)-C(19)-C(24)-C(29)	-78.6(5)
C(20)-C(19)-C(24)-C(25)	-73.0(5)
C(18)-C(19)-C(24)-C(25)	109.5(4)

C(29)-C(24)-C(25)-C(26)	-1.5(6)
C(19)-C(24)-C(25)-C(26)	170.5(4)
C(24)-C(25)-C(26)-C(27)	0.0(7)
C(25)-C(26)-C(27)-C(28)	1.2(7)
C(26)-C(27)-C(28)-C(29)	-0.9(7)
C(25)-C(24)-C(29)-C(28)	1.7(6)
C(19)-C(24)-C(29)-C(28)	-170.2(4)
C(27)-C(28)-C(29)-C(24)	-0.6(6)

Symmetry transformations used to generate equivalent atoms:

References

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