
SUPPLEMENTARY INFORMATION

Synthesis and Structural Characterisation of Stable Cationic Gold(I)

Alkene Complexes

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Synthesis of 1

To [AuCl(PBu₃)₃] (0.087 g, 0.2 mmol) and AgSbF₆ (0.069 g, 0.2 mmol) was added a solution of norbornene (0.038 g, 0.4 mmol) in dichloromethane (5 cm³) at room temperature. The solution was stirred for 16 h in the absence of light and then filtered through celite, washing with dichloromethane (3 x 4 cm³). The resulting solution was evaporated to dryness *in vacuo* and the white solid redissolved in dichloromethane (~1 cm³). Diethyl ether (~5 cm³) was added until white precipitate began to form and after storage for 16 hrs at -18 °C compound **1** was isolated and dried *in vacuo* (0.115 g, 79%).

¹H NMR (300 MHz, 22 °C, CDCl₃): δ = 6.60 (s, 2H), 3.49 (s, 2H), 1.92 (m, 2H), 1.53 (d, ³J_{PH} 14.5 Hz, 2H), 1.45 (m, 1H), 1.07 (m, 1H), 0.99 (m, 2H) ppm. ¹³C{¹H} NMR (75.6 MHz, 22 °C, CDCl₃): δ = 132.3 (d, J_{CP} 9.2 Hz), 47.2 (s, CH₂), 44.3 (s, CH), 40.6 (d, C, J_{CP} 17.9 Hz), 32.4 (d, CH₃ J_{CP} 3.9 Hz), 24.0 (s, CH₂) ppm. ³¹P{¹H} NMR (121.4 MHz, 22 °C, CDCl₃): δ = 98.1 (s) ppm.

Elemental Analysis, found: C 31.3% H 5.1%. Calculated for (C₁₉H₃₇AuPF₆Sb): C 31.3% H 5.1%.

Mass spectrometry, ESI positive ion, *m/z*: 493.2 (M⁺, [C₁₉H₃₇AuP]⁺).

Melting Point: decomposed 152-157 °C to a grey/black solid

Synthesis of **2**

2 was synthesised by a similar method to **1** replacing norbornene with *trans*-cyclooctene, synthesised by the method of Cope and Bach,¹ (~0.05 cm³, 0.4 mmol). Compound **2** was isolated as colourless crystals and dried *in vacuo* (0.056 g, 38%). A further recrystallisation of the mother liquor yielded more colourless crystals of **2**, (0.021 g, 14%).

Single crystals of [Au(PBu^t₃)(C₈H₁₄)] [SbF₆] were recrystallised from a mixture of dichloromethane (~1 cm³) and diethyl ether (~5 cm³) at -18 °C, mounted in inert oil and transferred to the cold gas stream of the diffractometer.

Due to the carbon atoms of the *trans*-cyclooctene ring being disordered, atom pairs C3A and C3B, C4A and C4B, C7A and C7B and C8A and C8B were described using the EXYZ and EADP commands. The atoms C1A and C2A and C1B and C2B were described using the DELU command. Four of the fluorine atoms in the [SbF₆] anion were also disordered and the fluorine atom F3B was described using the EADP command using F5B.

¹H NMR (300 MHz, 22 °C, CDCl₃): δ = 6.04 (m, 2H), 2.91 (m, 2H), 2.25-2.02 (m, 6H), 1.81-1.67 (m, 2H), 1.53 (d, ³J_{PH} 14.5 Hz, 27H), 0.86 (m, 2H) ppm. ¹³C{¹H} NMR (75.6 MHz, 22 °C, CDCl₃): δ = 130.6 (s, =CH), 40.3 (d, C, ¹J_{CP} 17.9 Hz), 36.9 (s, CH₂), 35.9 (s, CH₂), 32.4 (d, CH₃, ²J_{CP} 3.9 Hz), 27.8 (s, CH₂) ppm. ³¹P{¹H} NMR (121.4 MHz, 22 °C, CDCl₃): δ = 99.1 (s) ppm.

Elemental Analysis, found: C 32.2% H 5.6%. Calculated for (C₂₀H₄₁AuPF₆Sb): C 32.2% H 5.6%.

Melting Point: decomposed 178-185 °C to a grey/black solid

Crystal Data for **2:** C₂₀H₄₁AuF₆PSb, *M* = 745.21, orthorhombic, *a* = 16.1038(5), *b* = 17.5224(6), *c* = 9.1760(3) Å, *V* = 2589.26(15) Å³, *T* = 100 K, space group *Pna*21 (no. 33), *Z* = 4, reflections measured 19702, 5963 unique (*R*_{int} = 0.0326) which were used in all calculations. The final *R*1 was 0.0279 and the final *wR*(*F*²) was 0.0436 (all data). Flack parameter = 0.089(5). CCDC 729112.

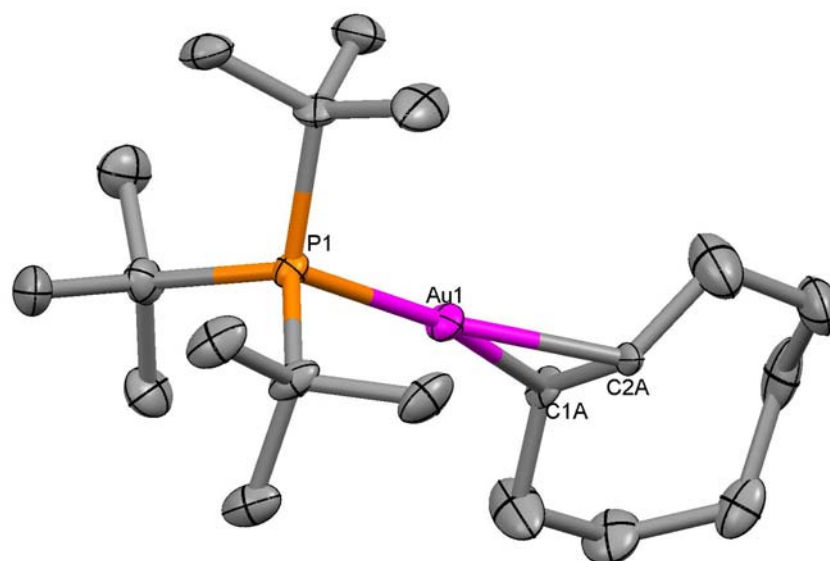


Fig. S1 Molecular structure of the cation of **2**. Thermal ellipsoids are at 50% probability; the $[\text{SbF}_6]^-$ anion and all hydrogen atoms have been omitted for clarity. The *trans*-cyclooctene ring was disordered over 2 sites (only one is shown above) and whilst the connectivity of the structure was established a detailed analysis of the bond lengths and angles in the alkene would be inappropriate.

Synthesis of **3**

3 was synthesised by a similar method to **1** replacing norbornene with norbornadiene, ($\sim 0.05 \text{ cm}^3$, 0.4 mmol). Compound **2** was isolated as a white solid and dried *in vacuo* (0.105 g, 72%).

Single crystals of $[\text{Au}(\text{PBU}^t_3)(\text{C}_7\text{H}_8)][\text{SbF}_6]$ were recrystallised from a mixture of dichloromethane ($\sim 1 \text{ cm}^3$) and diethyl ether ($\sim 5 \text{ cm}^3$) at $-18 \text{ }^\circ\text{C}$, mounted in inert oil and transferred to the cold gas stream of the diffractometer.

Upon isolation (ca. 10^{-2} torr, 30 mins), the solvent of recrystallisation was removed. The following spectroscopic data are for the solvent free material.

^1H NMR (300 MHz, $22 \text{ }^\circ\text{C}$, CDCl_3): $\delta = 7.62$ (br s, 2H, coordinated alkene), 6.81 (br s, 2H, non-coordinated alkene), 4.20 (br s, 2H), 2.10 (br s, 1H), 2.07 (br s, 1H), 1.52 (d, $^3J_{\text{PH}}$ 14.5 Hz, 27H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75.6 MHz, $22 \text{ }^\circ\text{C}$, CDCl_3): $\delta = 143.4$ (s non-coordinated alkene CH), 142.8 (d, J_{CP} 7.6 Hz, coordinated alkene CH), 73.6 (s,

CH₂) 52.7 (s, CH), 40.6 (d, C, J_{CP} 17.9 Hz), 32.4 (d, CH₃ J_{CP} 3.8 Hz) ppm. ³¹P{¹H} NMR (121.4 MHz, 22 °C, CDCl₃): δ = 97.8 (s) ppm.

Elemental Analysis, found: C 31.1% H 4.8%. Calculated for (C₁₉H₃₅AuPF₆Sb): C 31.4% H 4.9%.

Mass spectrometry, ESI positive ion, *m/z*: 491.2 (M⁺, [C₁₉H₃₅AuP]⁺).

Melting Point: decomposed 160-175 °C to a grey/black solid

Crystal Data for 3: C₂₀H₃₇AuCl₂F₆PSb, *M* = 812.08, monoclinic, *a* = 11.7603(7), *b* = 13.7090(8), *c* = 16.9906(10) Å, β = 100.338(3) °, *V* = 2694.8(3) Å³, *T* = 100 K, space group *P*21/*n* (no. 14), *Z* = 4, reflections measured 37200, 7510 unique (*R*_{int} = 0.0737) which were used in all calculations. The final *R*1 was 0.0472 and the final *wR*(*F*²) was 0.1237 (all data). CCDC 729113.

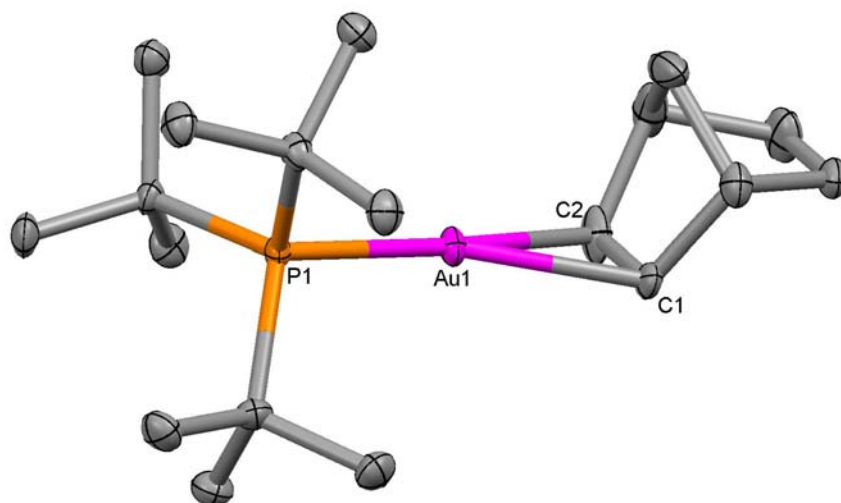


Fig. S2 Molecular structure of the cation of **3**. Thermal ellipsoids are at 50% probability; the [SbF₆]⁻ anion, solvent of crystallisation and all hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Au(1)-C(1) 2.273(5), Au(1)-C(2) 2.296(5), Au(1)-P(1) 2.2939(12), C(1)-C(2) 1.370(9); C(2)-Au(1)-C(1) 34.9(2), C(2)-C(1)-Au(1) 73.5(3), C(1)-C(2)-Au(1) 71.6(3).

Synthesis of **4**

To [AuCl(PBu^t₃)] (0.063 g, 0.14 mmol), AgSbF₆ (0.049 g, 0.14 mmol) and **3** (0.105 g, 0.14 mmol) was added dichloromethane (10 cm³). The solution was stirred in the absence of light for 16 h and worked up in a similar manner to **1**. Compound **4** was

isolated as a white solid and dried *in vacuo* (0.082 g, 42%). A further recrystallisation of the mother liquor yielded more crystals of **4**, (0.017 g, 9%).

Single crystals of $[\{\text{Au}(\text{P}^t\text{Bu})_3\}_2(\text{C}_7\text{H}_8)][\text{SbF}_6]_2$ were recrystallised from dichloromethane layered with *n*-hexane at room temperature, mounted in inert oil and transferred to the cold gas stream of the diffractometer.

Due to the carbon atoms of the $\text{P}(2)\text{Bu}^t_3$ ligand being disordered, atom pairs C30A and C31B, C28A and C27B, C27A and C28B, C24A and C23B were described using the EXYZ and EADP commands. Bond lengths C21A-C24A and C25A-C27A were restrained using the DFIX command to 1.54 Å.

^1H NMR (300 MHz, 22 °C, CD_2Cl_2): δ = 7.59 (br s, 4H), 4.76 (br s, 2H), 2.16 (br s, 2H), 1.54 (d, $^3J_{\text{PH}}$ 14.7 Hz, 54H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75.6 MHz, 22 °C, CD_2Cl_2): δ = 142.0 (br s), 40.8 (d, C, J_{CP} 17.9 Hz), 32.3 (d, CH_3 J_{CP} 3.6 Hz) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, 22 °C, CD_2Cl_2): δ = 100.0 (br s) ppm.

The broadness in the NMR spectra of this compound and the inability to observe two of the ^{13}C resonances of the norbornadiene cage might be interpreted as evidence that in solution the $[\text{Au}(\text{P}^t\text{Bu}_3)]^+$ fragments can slide easily back and forth along the C=C bonds *via* a low activation energy process, but the spectrum was complicated as a result of an exchange process arising from the presence of small amounts (~6% from ^1H NMR integration) of **3**. This exchange process was frozen out at -40 °C, but so far we have been unable to obtain a well resolved ^{13}C spectrum of **4** at low temperature owing to poor solubility and line broadening upon cooling. In support of the sliding mechanism, the ^1H NMR spectrum even at -80 °C showed only one signal for the alkene hydrogen atoms.

Elemental Analysis, found: C 27.8% H 4.6%. Calculated for $(\text{C}_{31}\text{H}_{62}\text{Au}_2\text{P}_2\text{F}_{12}\text{Sb}_2)$: C 27.3% H 4.6%.

Melting Point: decomposed 165-183 °C to a grey/black solid

Crystal Data for 4: $\text{C}_{31}\text{H}_{62}\text{Au}_2\text{F}_{12}\text{P}_2\text{Sb}_2$, $M = 1362.18$, monoclinic, $a = 20.3711(4)$, $b = 12.6067(3)$, $c = 17.0445(4)$ Å, $\beta = 104.6320(10)$ °, $V = 4235.28(16)$ Å³, $T = 100$ K, space group $P21/c$ (no. 14), $Z = 4$, reflections measured 60578, 11999 unique ($R_{\text{int}} =$

0.0527) which were used in all calculations. The final $R1$ was 0.0472 and the final $wR(F^2)$ was 0.0769 (all data). CCDC 729114.

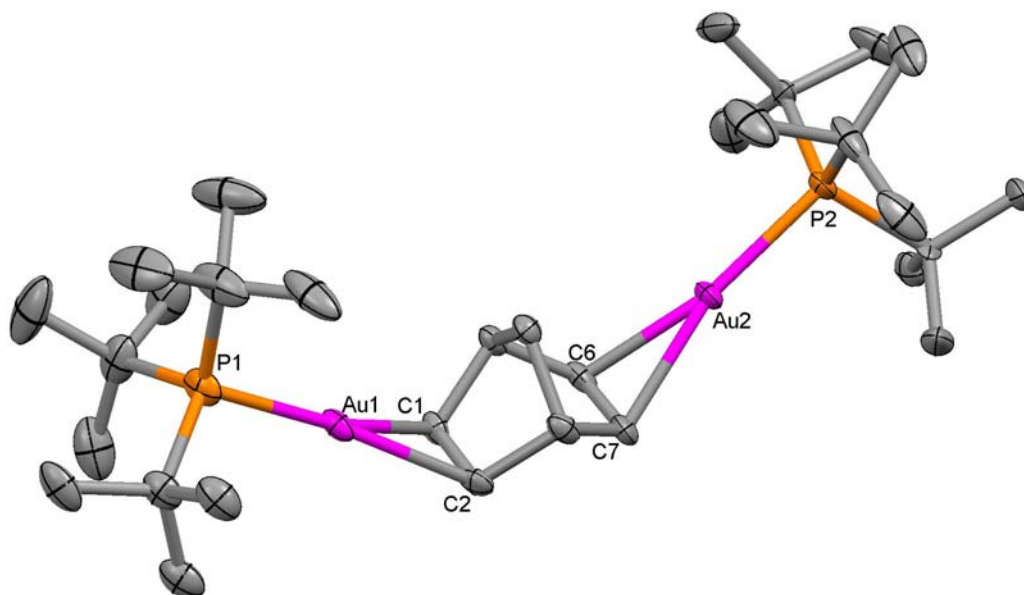


Fig. S3 Molecular structure of the dication of **4**. Thermal ellipsoids are at 50% probability; the $[\text{SbF}_6]^-$ anions and all hydrogen atoms have been omitted for clarity. All carbon atoms in the $\text{P}(2)\text{Bu}^t_3$ ligand were disordered over 2 sites but only one is shown above. Selected bond distances (\AA) and angles ($^\circ$): Au(1)-C(1) 2.254(4), Au(1)-C(2) 2.323(4), Au(1)-P(1) 2.2953(13), C(1)-C(2) 1.359(6), Au(2)-C(6) 2.260(4), Au(2)-C(7) 2.350(4), Au(2)-P(2) 2.3032(12), C(6)-C(7) 1.359(6); C(2)-Au(1)-C(1) 34.51(15), C(2)-C(1)-Au(1) 75.5(2), C(1)-C(2)-Au(1) 70.0(2), C(6)-Au(2)-C(7) 34.22(16), C(7)-C(6)-Au(2) 76.5(3), C(6)-C(7)-Au(2) 69.2(2).

Synthesis of **5**

Isobutylene was bubbled through dichloromethane (10 cm^3) for 10 mins and this solution was then added to $[\text{AuCl}(\text{PBU}^t_3)]$ (0.087 g, 0.2 mmol) and AgSbF_6 (0.069 g, 0.2 mmol). The flask was sealed and the contents stirred in the absence of light for 16 h and then worked up in a manner similar to **1**. Complex **5** was isolated and dried *in vacuo* to yield a white solid (0.114 g, 83%).

^1H NMR (300 MHz, 22 °C, CDCl_3): δ = 5.19 (br s, 2H), 2.38 (s, CH_3 , 6H), 1.53 (d, $^3J_{\text{PH}}$ 14.7 Hz, 27H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75.6 MHz, 22 °C, CDCl_3): δ = 162.1 (s, CMe_2), 96.2 (d, J_{CP} 11.5 Hz, CH_2), 40.1 (d, C, $^1J_{\text{CP}}$ 18.4 Hz), 32.4 (d, CH_3 $^2J_{\text{CP}}$ 3.6 Hz), 27.9 (s, CH_3) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, 22 °C, CDCl_3): δ = 100.4 (s) ppm.

Elemental Analysis, found: C 27.5% H 5.3%. Calculated for ($\text{C}_{16}\text{H}_{35}\text{AuPF}_6\text{Sb}$): C 27.8% H 5.1%.

Melting Point: decomposed 148-159 °C to a grey/black solid

The positions of the hydrogen atoms H1A and H1B were not well modelled using the HFIX command in SHELXTL so the atoms were located in the difference map and the C1-H1X bond lengths restrained to 0.98 Å using the DFIX command.

References

1. A. C. Cope and R. D. Bach, *Org. Synth.*, 1969, **49**, 39.