Supporting Information — X-Ray Crystallography

Manuscript: Gold(I) complexes bearing mixed-donor ligands derived from *N*-heterocylic carbenes

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The X-ray crystal structures of 2, 3 and 13

The methyl protons of the mesityl units in the structures of **2** and **3** were added in idealised tetrahedral positions and, as they are on an sp^3 centre bonded to an sp^2 centre, the groups were allowed to rotate about the associated $C_{(Ph)}$–$C_{(Me)}$ bond to find the best fit with the electron density map (*i.e.* the SHELX HFIX/AFIX 137 command).

The complex cation in the structure of **13** has C_2 symmetry about an axis that passes through the gold centre and bisects the Ag(1)···Ag(1A) vector. The $Ag_2(CF_3SO_3)_2$ unit was found to be disordered across the C_2 axis, and two orientations were identified of *ca*. 77 and 23% occupancy (see Fig. S4). The geometry of the unique triflate group of each orientation was optimised, and the thermal parameters of neighbouring, chemically equivalent atoms of the two orientations were restrained to be similar. Both the major and minor occupancy silver positions were refined anisotropically, as were the non-hydrogen atoms of the major occupancy triflate group; the non-hydrogen atoms of the minor occupancy triflate group were refined isotropically. The non-coordinated triflate anion and the included dichloromethane solvent molecule were both likewise found to be disordered across C_2 axes. In each case two unique orientations were identified, of *ca*. 26 and 24% for the triflate, and *ca*. 29 and 21% for the dichloromethane (two further orientations of the same pairs of occupancies are generated by the operation of the adjacent C_2 axes in each case). For both the anion and the solvent molecule, the geometries of the two orientations were optimised, the thermal parameters of the chemically equivalent atoms of the two orientations were restrained to be similar, and all of the atoms were refined isotropically.

Fig. S1 The molecular structure of the cation in **2** (50% probability ellipsoids).

Fig. S2 The molecular structure of the cation in **3** (50% probability ellipsoids).

Fig. S3 The molecular structure of the C_2-symmetric cation in **13** (30% probability ellipsoids).

Fig. S4 The disordered $Ag_2(CF_3SO_3)_2$ unit in **13**. The major occupancy orientation (*ca.* 77%) is shown with open bonds and the minor occupancy orientation (*ca.* 23%) is shown with dashed bonds.

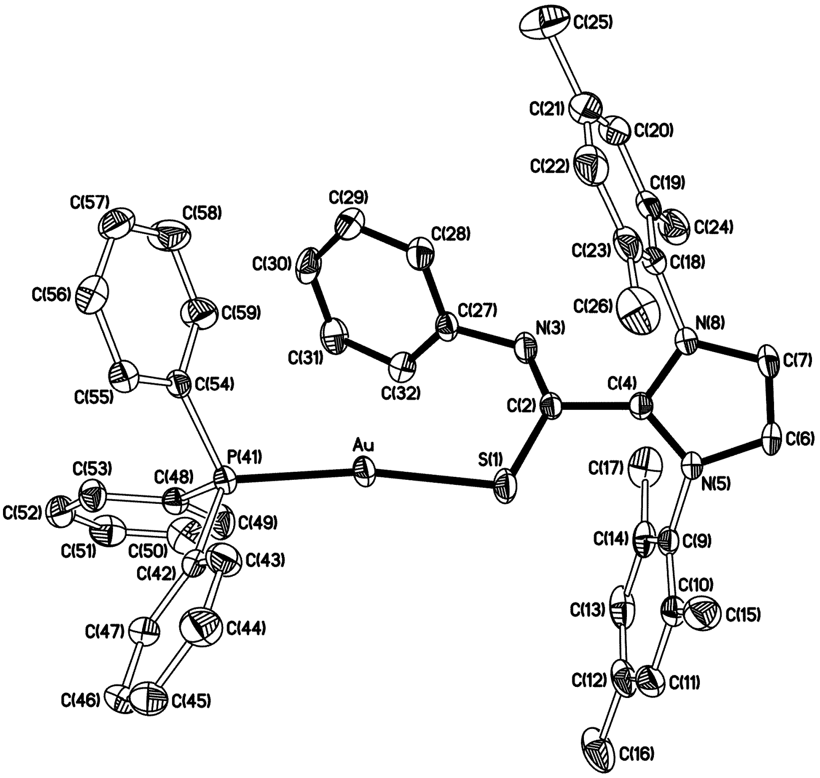


Fig. S1

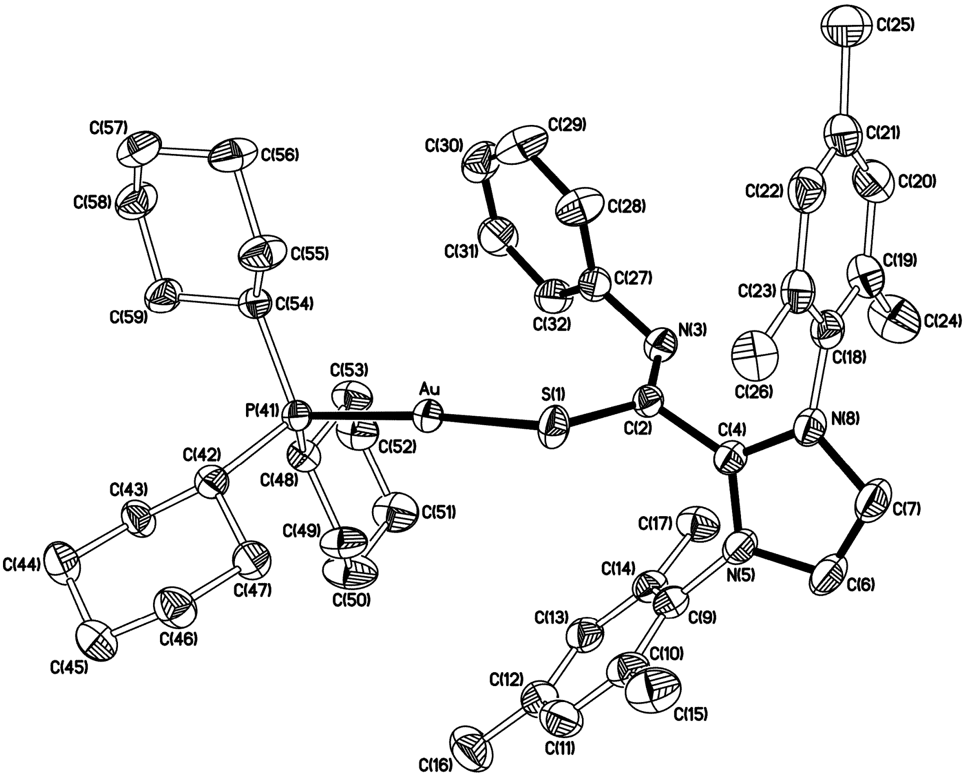
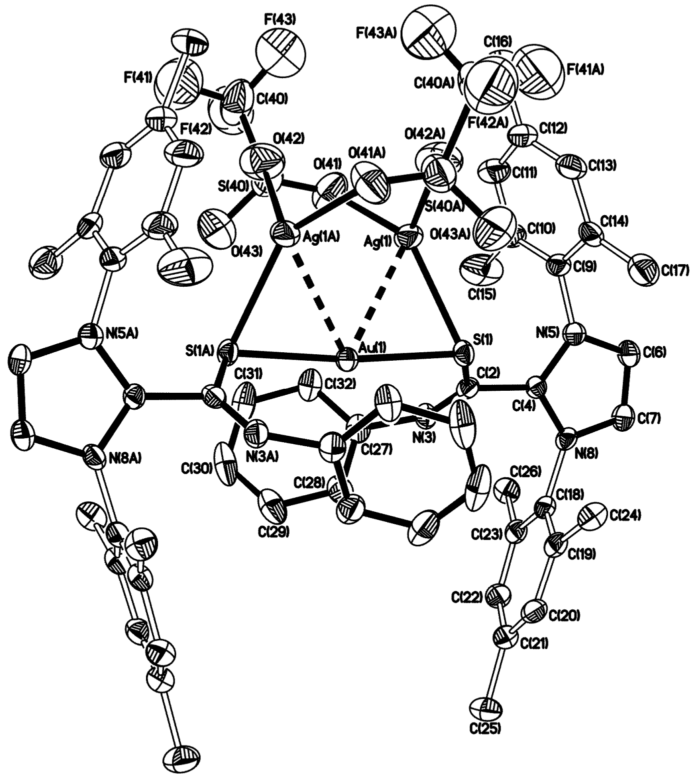

C(25)
C(57)
C(56)
C(30)
C(29)
C(21)
C(22)
C(20)
C(58)
C(28)
C(55)
C(31)
C(27)
C(19)
C(23)
C(59)
C(54)
C(32)
C(24)
N(3)
C(18)
C(53)
Au
S(1)
C(26)
P(41)
C(2)
C(4)
N(8)
C(52)
C(42)
C(48)
C(43)
C(51)
C(7)
C(17)
C(49)
C(44)
N(5)
C(14)
C(47)
C(6)
C(50)
C(13)
C(9)
C(46)
C(10)
C(45)
C(12)
C(15)
C(11)
C(16)

Fig. S2


F(43)
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C(16)
F(41)
F(41A)
C(40A)
C(40)
F(42A)
C(12)
F(42)
O(42A)
O(42)
O(41A)
O(41)
C(11)
C(13)
S(40)
S(40A)
C(14)
O(43)
Ag(1A)
Ag(1)
O(43A)
C(10)
C(9)
C(17)
C(15)
N(5A)
N(5)
S(1A)
Au(1)
S(1)
C(6)
C(31)
C(32)
C(2)
C(4)
C(7)
N(3)
C(27)
N(8)
N(3A)
N(8A)
C(30)
C(26)
C(28)
C(18)
C(24)
C(23)
C(29)
C(19)
C(22)
C(20)
C(21)
C(25)

Fig. S3

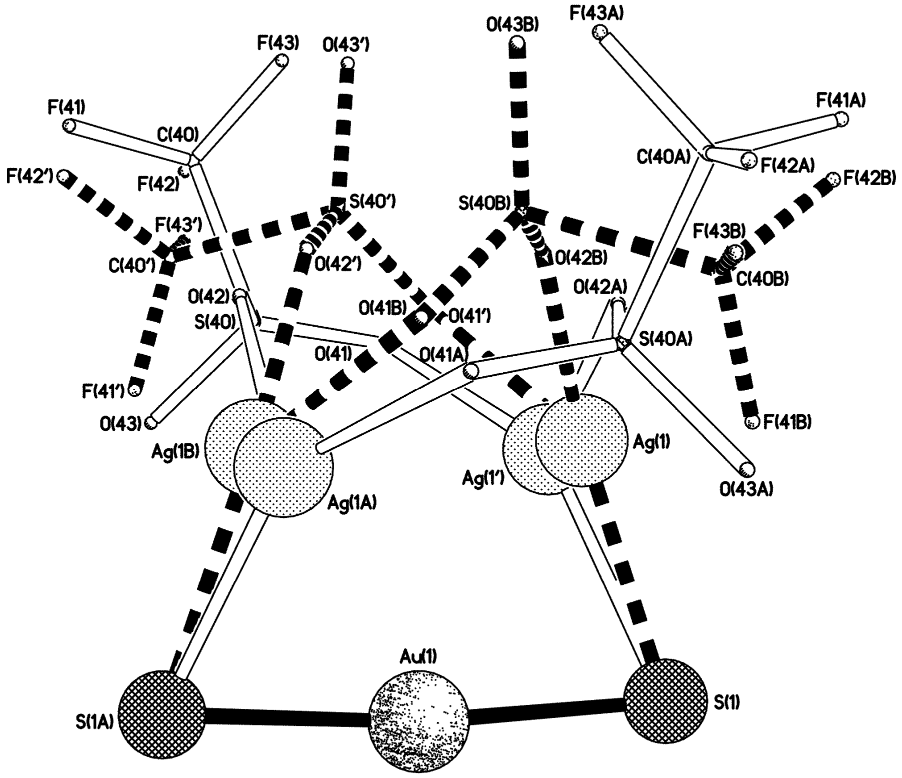
O(43B)
F(43A)
F(43)
O(43')
F(41)
F(41A)
C(40)
C(40A)
F(42A)
F(42')
F(42)
F(42B)
S(40')
S(40B)
F(43')
F(43B)
O(42')
O(42B)
C(40')
C(40B)
O(42)
O(42A)
O(41B)
O(41')
S(40)
S(40A)
O(41)
O(41A)
F(41')
F(41B)
O(43)
Ag(1B)
Ag(1)
Ag(1')
Ag(1A)
O(43A)
Au(1)
S(1A)
S(1)

Fig. S4