Synthesis and Structure of $[Au(CH_2)_2PPh_2]_2[SSC(NPh)(NHPh)]_2$, a Gold(II) Ylide Dimer containing the First Example of a Sulphur-rich Thiourea

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The reaction of $SC(NHPh)_2$ with $[Au(CH_2)_2PPh_2]_2Cl_2$ followed by addition of base has led to the isolation and *X*-ray crystal structure analysis of a gold(II) ylide dimer, $[Au(CH_2)_2PPh_2]_2[SSC(NPh)(NHPh)]_2$ which is the first example of a thiourea containing catenated disulphide co-ordinated to a metal centre.

The continued interest in the co-ordination chemistry of gold ylide dimers, and our recent discovery of gold–polysulphide compounds which contain 12- or 13-atom gold–sulphur rings[1] have led us to investigate other sulphur containing ligands in the pursuit of interesting gold–sulphur compounds. Although considerable work has been done on gold(I) mononuclear compounds with sulphur bound ligands because of interest in relation to anti-arthritic drugs,[2] little work has been done on dinuclear compounds of gold which contain sulphur ligands, especially compounds in which the gold centres are in the 2+ oxidation state.

One method we are pursuing to prepare dinuclear compounds with sulphur ligands is through ligand substitution reactions in mixed solvent systems, usually $CHCl_3$ and H_2O (phase transfer conditions), in order to remove ionic components formed during the course of the reaction. One such reaction has led to the isolation and characterization of the title compound, $[Au(CH_2)_2PPh_2]_2[SSC(NPh)(NHPh)]_2$ (**1**), which contains two co-ordinated sulphur-rich thioureas. This appears to be the first example of a sulphur-rich thiourea, stabilized by co-ordination to a metal centre.

Complex (**1**) was isolated from the reaction of 1,3-diphenylthiourea, $SC(NHPh)_2$, with the gold(II) ylide dimer $[Au(CH_2)_2PPh_2]_2Cl_2$ (**2**), followed by the addition of base.† Crystals of (**1**) were grown by slow diffusion of ether into a CH_2Cl_2 solution of the product. Complex (**1**) was found in low yields as deep red, well formed needles suitable for *X*-ray crystal diffraction studies.‡ Other products isolated from the reaction include the previously characterized polysulphide compound,[1] $\{[Au(CH_2)_2PPh_2]_2\}_2S_8$, and the gold(I) ylide dimer, $[Au(CH_2)_2PPh_2]_2$.

X-Ray analysis of (**1**) has shown the asymmetric unit to contain one complete molecule (Figure 1), consisting of a pair of gold atoms bridged by two phosphorus ylide anions, and having a sulphur-rich thiourea bound to each gold centre. The two gold atoms are separated by 2.651(1) Å, a distance consistent with the two gold(II) atoms being bonded by a Au–Au single bond.[3–5] For the carbon atoms in the 5-membered gold–ylide rings, the gold–carbon distances average 2.088(13) Å and the carbon–phosphorus distances average 1.749(14) Å. The C–Au–C angles average 173.8(6)°. The co-ordination geometry of the carbon and phosphorus atoms in the gold–ylide ring is tetrahedral. All other bond distances and angles of the ylide bridge are consistent with previously characterized gold(II) ylide dimers.[3–5] The orientation of the two 5-membered gold–ylide rings with respect to each other produces a boat configuration for the dimer.

The most unusual feature of this structure involves the ligand bonded to each gold atom. The ligand can best be viewed as a deprotonated 1,3-diphenyl-2-thiourea to which an additional sulphur atom has been added, bonded to the gold atom and the sulphur atom of the ligand. The average Au–S distance of 2.391(5) Å is consistent with gold–sulphur distances in other gold(II) ylide dimers that contain bonded sulphur atoms.[1,6] The S–S distances of 2.013(7) and 2.028(5) Å are nearly identical to those found in gold–polysulphide ring complexes of the gold(II) ylide dimer.[1] In fact, the Au–S–S linkage is structurally very similar to the gold–polysulphide ring complexes, with the notable exception that where in the polysulphide ring complexes the second sulphur of the Au–S–S linkage is bonded to another sulphur of a second gold(II) ylide dimer, the second sulphur in compound (**1**) is bonded to the carbon of the thiourea unit. This S–C bond distance averages 1.830(17) Å for the two independent sulphur-rich thioureas of compound (**1**). This distance is appropriate for a C–S single bond, and approximately 0.1 Å longer than the C–S double bond observed for thiourea.[7]

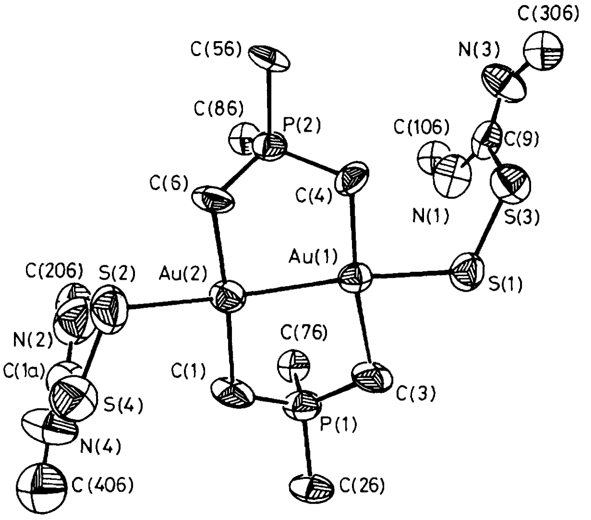

Figure 1. The molecular structure of (**1**) and its atomic labelling scheme (phenyl rings shown only as *ipso* carbon atoms). Selected bond distances (Å) and (°): Au(1)–Au(2) 2.651(1), Au(1)–S(1) 2.395(4), Au(2)–S(2) 2.388(5), S(1)–S(3) 2.028(5), S(2)–S(4) 2.013(7), S(3)–C(9) 1.820(16), S(4)–C(1a) 1.839(18), C(9)–N(1) 1.338(19), C(9)–N(3) 1.276(20), C(1a)–N(2) 1.327(22), C(1a)–N(4) 1.274(20), Au(1)–Au(2)–S(2) 175.0(1), Au(2)–Au(1)–S(1) 175.8(1), Au(1)–S(1)–S(3) 114.0(2), Au(2)–S(2)–S(4) 113.5(3), C(3)–Au(1)–C(4) 173.7(6), C(1)–Au(2)–C(6) 174.0(5), S(1)–S(3)–C(9) 104.1(5), S(2)–S(4)–C(19) 102.9(5), S(3)–C(9)–N(1) 114.4(12), S(3)–C(9)–N(3) 118.8(11), N(1)–C(9)–N(3) 126.8(15), S(4)–C(1a)–N(2) 111.3(11), S(4)–C(1a)–N(4) 116.3(13), N(2)–C(1a)–N(4) 132.4(17).

The carbon–nitrogen distances are different for C(9)–N(1) and C(9)–N(3), with values of 1.34(2) and 1.27(2) Å, respectively. Similarly, the C–N distances in the other thiourea are different, with values of 1.33(2) Å for C(1a)–N(2) and 1.27(2) Å for C(1a)–N(4). The shortened bond distance of one C–N bond in both thiourea ligands indicates deprotonation has occurred on N(3) and N(4), producing considerable double bond character between C(9)–N(3) and C(1a) and N(4). This is consistent with the observed planarity of C(9) and C(1a), and with each sulphur-rich thiourea ligand contributing a −1 charge to the overall neutral molecule.

While the presence of an anionic ligand bound to the gold centres in this dimeric complex is not unusual, the presence of the observed Au–S–S–C linkage is novel and unexpected. Its occurrence, combined with the recent observation of gold–polysulphide ring compounds, illustrates the potential wealth of unexplored chemistry involving gold dimers and sulphur compounds, especially in the preparation and characterization of sulphur-rich compounds.

We thank the National Science Foundation (CHE-8408414), the donors of the Petroleum Research Fund as

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† In the presence of air, 1,3-diphenylthiourea (2 mol. equiv.) was added to a mixture of $CHCl_3$ (3 ml) and H_2O (7 ml) containing $[Au(CH_2)_2PPh_2]_2Cl_2$ (0.042 mmol) and the mixture stirred vigorously overnight resulting in a colour change in the $CHCl_3$ layer from yellow to light red. The $CHCl_3$ layer was separated from the H_2O layer, dried with $CaCO_3$, and evaporated *in vacuo*, leaving a red non-crystalline residue. The residue was taken up in tetrahydrofuran (3 ml), then KOH (0.14 mmol) in MeOH (1 ml) was added to deprotonate the thiourea. The light red solution quickly darkened to deep red. The solution was filtered and evaporated to dryness. Complex (**1**) was crystallized as a minor product by slow diffusion of diethyl ether into a CH_2Cl_2 solution of this product. Yield of the pure crystalline (**1**): 2.5% based on Au.

‡ *Crystal data for* (**1**): $C_{54}H_{50}Au_2N_4P_2S_4$; $M = 1339.14$, monoclinic, space group $P2_1/c$ (from systematic absences), $a = 14.729(6)$, $b = 13.269(4)$, $c = 27.198(11)$ Å, $\beta = 99.64(3)°$, $U = 5240.6(35)$ Å^3, $F(000) = 2623.38$, $Z = 4$, $D_c = 1.69$ g cm^{-1}, Mo-K_α radiation, $\lambda = 0.71073$ Å, μ (Mo-K_α) = 59.9 cm^{-1}. A total of 4140 unique reflections with $F_O^2 > 3\sigma(F_O^2)$ were collected on a Nicolet R3M/E diffractometer over $2\theta = 3$—$45°$ using graphite monochromated Mo-K_α radiation and measuring 3 check reflections every 97 reflections as standards. The structure was determined using standard heavy atom and difference Fourier techniques on a Data General Eclipse S140 minicomputer with the SHELXTL collection of crystallographic programs. All non-hydrogen atoms were refined anisotropically, with hydrogen atoms fixed at idealized positions; $R = 0.0548$, $R_w = 0.0466$.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

administered by the American Chemical Society, the Welch Foundation, and the Texas A & M Center for Energy and Mineral Resources for financial support.

Received, 29th December 1986; Com. 1830

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