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Gold(I) thiosulfonate complexes

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Dedicated to Professor Raphael Usón

Abstract

A series of seven gold(I) *p*-tolylthiosulfonate complexes of the general type (L)Au–$SS(O)_2C_6H_4$–4-Me have been prepared from the reaction of silver *p*-tolylthiosulfonate with the corresponding precursor complexes (L)AuCl in dichloromethane. Yields in excess of 90% were obtained throughout for tertiary phosphine and isocyanide ligands L = PMe_3, PPh_3, Ph_2(2-Py)P, (4-$Me_2NC_6H_4$)Ph_2P, ^{i}PrNC, and ^{t}BuNC. The complexes are surprisingly stable and undergo controlled decomposition well above 100 °C. The crystal and molecular structures have been determined for three representative examples. The Me_3P and Ph_3P complexes form dimers with short aurophilic bonding [Au–Au 2.9955(3) and 3.0509(2) Å] in a crossed-swords conformation, while for the ^{t}BuNC complex the monomers with their linear five-atom axes appear as only loosely aggregated dimers with a parallel head-to-tail arrangement [Au–Au 3.5423(3) Å]. In all cases the *p*-tolylthiosulfonate ligand is S-bonded to the metal center.

Keywords: Crystal structures; Thiosulfonate complexes; Gold complexes

1. Introduction

Gold(I) complexes of the type L–Au–X with a neutral and an anionic ligand (L/X) are of current interest owing to their fascinating structural chemistry and their potential for applications in a wide variety of classical and contemporary technologies, and in medicine [1]. Among the ligands L employed for tailoring the properties of the compounds the large family of tertiary phosphines and arsines are most prominent [1a,2], but isocyanides have recently also received considerable attention [3]. The heavier halides were the most common counterions X in most fundamental studies, but the current investigations have focussed almost exclusively on sulfur-functional components.

The thiosulfate complex $Na_3[Au(S_2O_3)_2]$ and thiolate complexes of the type $[RSAu]_n$ were among the early gold(I) complexes employed in chemotherapy (chrysotherapy) of common diseases like rheumatoid arthritis [4], and a (phosphine)gold thioglucose compound [(Et_3-P)AuSR] is presently the most successful oral gold drug [5]. Gold(I) sulfate (L)$AuOS(O)_2OAu$(L) and sulfonate complexes (L)$AuOS(O)_2R$ have also been described and have recently gained interest as homogeneous catalysts for addition reactions of alkynes [6]. This is particularly true for sulfonates with strongly electronegative substituents R = CF_3, C_2F_5 etc. [6g].

By contrast, gold(I) thiosulfonate and thiosulfinate complexes of the types (L)$AuSS(O)_2R$ and (L)AuS-S(O)R, respectively, with L a donor ligand and R an alkyl or aryl group, have not yet been investigated. Because compounds with these combinations of ligands may not only be of interest in pharmacy but also as precursor complexes for the deposition of gold films on substrates from solutions or pastes, in the present study a series of thiosulfonates was synthesized and their fundamental properties investigated. The compounds were also expected to have an interesting supramolecular chemistry based on aurophilic interactions between the individual molecules [1b].

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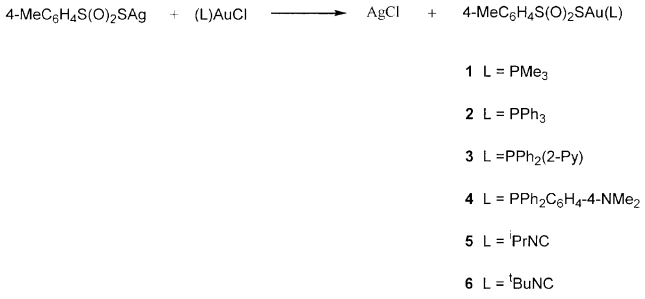
2. Preparative results

A series of six gold(I) *p*-tolylthiosulfonate compounds (L)Au–SS(O)$_2$C$_6$H$_4$–4-Me could readily be prepared by metathesis from silver *p*-tolylthiosulfonate (in slight excess) and the corresponding (L)AuCl complexes in dichloromethane at −78 °C with protection against incandescent light. Yields of the products in excess of 90% were obtained in all cases which include various tertiary phosphines and alkylisocyanides as ligands L. Silver chloride is the sole by-product which is easily separated by filtration.



All products were obtained as colorless solids which are stable at room temperature and soluble in moderately polar organic solvents, preferably di- and trichloromethane or tetrahydrofuran, but insoluble in hydrocarbons such as hexane, benzene or toluene.

The NMR spectra of the solutions in chloroform-d_1 or dichloromethane-d_2 are in full agreement with the proposed formulae, and elemental analyses have confirmed the composition. The molecular ions are detected in the mass spectra (FAB), but peaks for dinuclear cations with higher mass are also observed, which indicate association in the solid (matrix) state. The two isocyanide complexes show typical C≡N stretching frequencies in the IR spectra (KBr) with hypsochromic shifts relative to the free ligands which indicate direct end-on coordination of the isocyanide function to the metal atom. There are many reference data in the literature for this type of gold(I)–isocyanide coordination [1a].

It should be noted that most of the analytical and spectroscopic data would also be in agreement with an ionic formalism based on homoleptic cations $[L_2Au]^+$ and homoleptic anions $[(p\text{-TolSO}_2\text{S})_2\text{Au}]^-$. Structures of this kind are common for the corresponding phosphonates and other complexes of the seemingly simple composition 'LAuX' [6e,7]. Structural studies for representative compounds were therefore indispensable.

3. Structural studies

Crystals of (Me$_3$P)AuSS(O)$_2$C$_6$H$_4$–4-Me (**1**), are monoclinic, space group $P2_1/c$, with $Z = 8$ formula units in the unit cell. The asymmetric unit contains two independent molecules of very similar geometries. These two units are aggregated to pairs via a short aurophilic Au1–Au2 contact [2.9955(3) Å] (Fig. 1). The thiosulfonate ligands are S-bonded to their gold atoms with the two molecular axes P–Au–S close to 180° [P1–Au1–S11 179.83(5)°, P2–Au2–S21 176.03(5)°]. The angles at the bridging sulfur atoms S11 and S21 are Au1–S11–S12 99.73(7)° and Au2–S21–S22 103.15(6)°, respectively. The sulfonate sulfur atoms have a quasi-tetrahedral environment with two oxygen atoms, the *p*-tolyl carbon atom and a sulfur atom bridging to the gold atoms.

The two molecular axis P–Au–S have the crossed-swords conformation with torsional angles P1–Au1–Au2–P2 102.43(5)° and S1–Au1–Au2–S2 −77.50(5)°. These angles reflect the sterical requirement of the phosphine and thiosulfonate ligands. Parallel head-to-tail or head-to-head conformations would lead to significant sterical conflicts. The mutual approach of the gold atoms of the components relative to the P–Au–S axes is almost perpendicular as specified by the angles P1–Au1–Au2 94.52(4)° and P2–Au2–Au1 93.76(3)°, or S11–Au1–Au2 85.33(3)° and S21–Au2–Au1 85.86(3)°. These mutual orientations follow the data of a plethora of model systems reported in the literature on aurophilic interactions [1b].

Crystals of (Ph$_3$P)AuSS(O)$_2$C$_6$H$_4$–4-Me (**2**), are also monoclinic, space group $C2/c$, with $Z = 8$ formula units in the unit cell. The asymmetric unit contains only one independent molecule, which is part of a centrosymmetrical dimer associated via aurophilic bonding (Fig. 2).

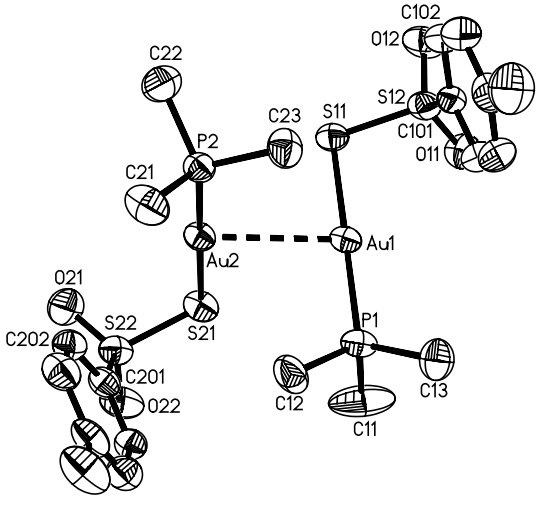


Fig. 1. Dimeric units of compound **1** (ORTEP drawing with 50% probability ellipsoids; H-atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Au1–P1 2.263(1), Au1–S11 2.340(1), Au2–P2 2.268(1), Au2–S21 2.332(1), S11–S12 2.033(2), S21–S22 2.039(2), S12–O11 1.437(4), S22–O21 1.442(4), S12–O12 1.450(4), S22–O22 1.448(4), S12–C101 1.769(6), S22–C201 1.764(5), Au1···Au2 2.9955(3); P1–Au1–S11 179.83(5), P2–Au2–S21 176.03(5).

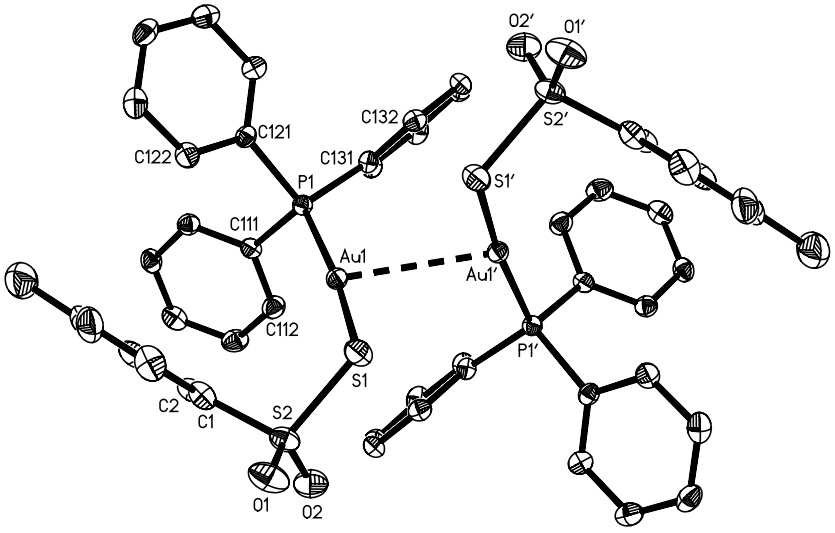


Fig. 2. Dimeric units of compound **2** (ORTEP drawing with 50% probability ellipsoids; H-atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Au1–P1 2.2662(7), Au1–S1 2.3286(7), S1–S2 2.043(1), S2–O1 1.448(2), S2–O2 1.441(2), S2–C1 1.777(3) Au1···Au1′ 3.0509(2); P1–Au1–S1 169.94(3).

The mutual approach of the monomers is similar to the situation described for the Me_3P analogue **1** (above). Owing to the greater bulk of the phosphine, the Au1–Au1′ contact is significantly longer [3.0509(2) Å] even though the axis P1–Au1–S1 is more strongly bent to facilitate the metal–metal contact [169.94(3)°]. The angles P1–Au1–Au1′ and S1–Au1–Au1′ [102.63(2), 84.09(2)°] and the dihedral angles P1–Au1–Au1′–P1′ and S1–Au1–Au1′–S1′ [−87.09(2), −71.90(2)°] also reflect the bulkiness of the phosphine ligand. The geometry of the S-bonded thiosulfonate ligand resembles that in **1**.

Crystals of $(Me_3CNC)AuSS(O)_2C_6H_4$–4-Me (**7**), are monoclinic, space group $P2_1/c$, with $Z = 4$ formula units in the unit cell. The asymmetric unit contains only one molecule. In the crystal lattice, the complex molecules are apparently only loosely aggregated into dimers (Fig. 3). The Au1–Au1′ distance is as long as 3.5423(3) Å and thus at the borderline of the range for which aurophilic bonding should be considered (2.85–3.50 Å). The individual molecule has a quasi-linear axis comprising no less than five atoms, with the angles at the three internal atoms all close to 180°: S1–Au1–C1 176.4(1), Au1–C1–N1 178.6(3), C1–N1–C11 176.5(4)°. This axis is bent at the sulfur end with an angle Au1–S1–S2 of 102.80(5)° and tetrahedrally branched at the carbon end C11. There are no anomalies regarding the thiosulfonate ligand, which is again S-coordinated to the gold atom.

The reluctance of compound **7** to undergo intimate aurophilic interaction is in agreement with structure reports on other (isocyanate)gold(I) complexes in the literature [3a,3b] and also with quantum-chemical calculations [3q]. These calculations not only predicted that Au–Au bonding for complexes with isocyanide

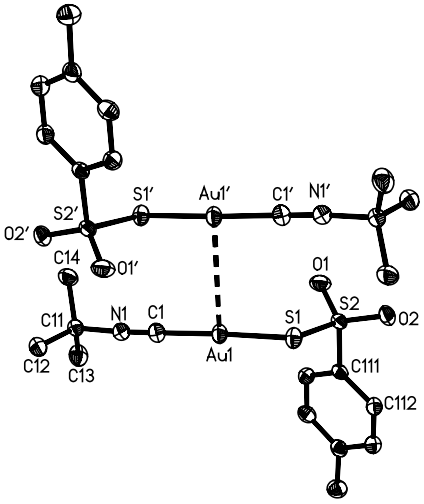


Fig. 3. Dimeric units of compound **7** (ORTEP drawing with 50% probability ellipsoids; H-atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Au1–C1 1.972(4), Au1–S1 2.288(1), S1–S2 2.045(1), S2–O1 1.445(3), S2–O2 1.444(3), S2–C111 1.771(3), C1–N1 1.135(6) Au1···Au1′ 3.5423(3); C1–Au1–P1 176.4(1), Au1–N1–C1 178.6(3).

should be longer and weaker, but also that the organization should be parallel head-to-tail. This is confirmed by the packing motif of compound **7** in the crystal.

In summary therefore the three structures reported for the new *p*-tolylthiosulfonates are fully consistent with previous variations in structure of L–Au–X molecules. All sulfonate complexes show remarkable thermal and chemical stability (to air and moisture) and thus represent a new class of robust gold(I) complexes. Their good solubility in common solvents and the broad choice of ligands L that can be employed suggest a variety of applications.

In conclusion it should be noted that gold(I) forms also a variety of phosphate, phosphonate, and phosphinate, as well as thiophosphate, thiophosphonate and thiophosphinate complexes with interesting structures and hitherto unexploited specific properties. The sulfur and phosphorus compounds show many analogies or are complementary [7].

4. Experimental

The experiments were carried out in an atmosphere of dry nitrogen. Solvents were dried and saturated with nitrogen, and glassware was oven-dried and filled with nitrogen. Standard equipment was used throughout. Reaction vessels were protected against incandescent light when silver salts were involved. The isocyanides and silver *p*-tolylthiosulfonate were prepared following literature methods [8], the phosphines were commercially available.

4.1. (Trimethylphosphine)gold(I) p-tolylthiosulfonate (1)

Silver *p*-tolylthiosulfonate (240 mg, 0.82 mmol) was suspended in CH_2Cl_2 (10 ml), cooled to −70 °C and a solution of (trimethylphosphine)gold(I) chloride (210 mg, 0.68 mmol) in 10 ml of the same solvent slowly added with stirring. Stirring was continued for 2 h with exclusion of light. The silver salt slowly converted into silver chloride. The reaction mixture was filtered, C_5H_{12} was added to the filtrate, and the solution allowed to warm to −30 °C and kept at this temperature over night. The colorless precipitate was recrystallized from CH_2Cl_2/C_5H_{12}, yield 295 mg (94%), m.p. 107 °C (dec.). NMR (CD_2Cl_2, 20 °C), ^{1}H: 7.91 and 7.23, 2 × d, $J = 8.1$ Hz, 2 × 2H, *o*/*m*-CH; 2.39, s, 3H, MeC; 1.55, d, $J = 1.2$ Hz, 9H, MeP. $^{13}C\{^1H\}$: 148.2, 142.9, 129.3, and 125.7, all s, i/*o*/*m*/*p*-CH; 21.2, s, MeC; 15.5, d, $J = 56.5$ Hz, MeP. $^{31}P\{^1H\}$: −5.5, s. MS(FAB) *m*/*z*: 733 (64%) $[(Me_3P)_2AuSSO_2Tol]^+$; 461 (7.3) $[M+1]^+$; 460 (59) $[M]^+$; 349 (41) $[(Me_3P)_2Au]^+$, 273 (100) $[(Me_3P)Au]^+$. *Anal.* Calc. for $C_{10}H_{16}AuO_2PS_2$ (460.29): C, 26.1; H, 3.5; S, 13.9. Found: C, 26.6; H, 3.5; S, 13.7%.

4.2. (Triphenylphosphine)gold(I) p-tolylthiosulfonate (2)

Following the procedure described for **1**, the compound was prepared with *p*-$TolSO_2SAg$ (295.1 mg, 0.81 mmol) and $(Ph_3P)AuCl$ (400 mg, 0.81 mmol), yield 490 mg (94%), m.p. 154 °C (dec.). NMR ($CHCl_3$, 20 °C), ^{1}H: 7.91 and 7.11, 2 × d, $J = 8.0$ Hz, 2 × 2H, C_6H_4; 7.60–7.38, m, 15H, Ph; 2.35, s, 3H, Me. $^{13}C\{^1H\}$: 148.9, 142.3, 128.5, and 125.8, all s, i/*o*/*m*/*p*-C_6H_4; 134.2, 132.0, 129.3, and 128.8, d/s/d/d with $J = 14.6$, –, 12.3, and 59.9 Hz, for *o*/*p*/*m*/i-Ph; 21.5, s, Me. $^{31}P\{^1H\}$: 39.2, s. MS (FAB): 1106 (17) $[(Ph_3P)_2Au_2SSO_2Tol+1]^+$; 721 (5) $[(Ph_3P)_2Au]^+$; 647 (57) $[M+1]^+$; 646 (8) $[M]^+$; 459 (100) $[(Ph_3P)Au]^+$. *Anal.* Calc. for $C_{25}H_{22}AuO_2S_2P$ (646.50): C, 46.4; H, 3.4; S, 9.9. Found: C, 46.1; H, 3.4; S, 9.1%.

4.3. [Diphenyl(2-pyridyl)phosphine]gold(I) p-tolylthiosulfonate (3)

As described for **1**, the compound was prepared with *p*-$TolSO_2SAg$ (120 mg, 0.41 mmol) and $[Ph_2(2\text{-}Py)P]AuCl$ (150 mg, 0.30 mmol); yield 180 mg (93%) m.p. 133 °C (dec.). NMR ($CDCl_3$, 20 °C), ^{1}H: 8.78 and 7.83–7.72, m, 4H, Py; 7.93 and 7.14, 2 × d, $J = 8.1$ Hz, 2 × 2H, C_6H_4; 7.68–7.34, m, 10H, Ph; 2.35, s, 3H, Me. $^{31}P\{^1H\}$: 38.5, s. MS (FAB): 1108 (6) $[L_2Au_2SSO_2Tol]^+$; 723 (4) $[L_2Au]^+$; 648 (46) $[M+1]^+$; 647 (5) $[M]^+$; 460 (100) $[LAu]^+$. *Anal.* Calc. for $C_{24}H_{21}AuNO_2S_2P$ (647.49): C, 44.5; H, 3.2; N, 2.2; S, 9.9. Found: C, 43.8; H, 3.3; N, 2.0; S, 10.5%.

4.4. [(p-Dimethylaminophenyl)diphenylphosphine]gold(I) p-tolylthiosulfonate (4)

As described for **1**, the compound was prepared from *p*-$TolSO_2SAg$ (170 mg, 0.58 mmol) and $[(p\text{-}Me_2NC_6H_4)Ph_2P]AuCl$ (300 mg, 0.56 mmol), yield 350 mg (91%), m.p. 127 °C (dec.). NMR ($CDCl_3$, 20 °C), ^{1}H: 7.93 and 7.13, 2 × d, $J = 7.8$ Hz, 2 × 2H, C_6H_4S; 7.77 and 6.76, 2 × d, $J = 6.9$ Hz, 2 × 2H, C_6H_4N; 7.43, m, 10H, Ph; 3.03, s, 6H, NMe_2; 2.35, s, 3H, C_6H_4Me. $^{31}P\{^1H\}$: 37.4, s. MS (FAB): 1192 (21) $[L_2Au_2SSO_2Tol+1]^+$; 690 (34) $[M+1]^+$; 689 (24) $[M]^+$; 502 (100) $[L_2Au]^+$. *Anal.* Calc. for $C_{27}H_{27}AuNO_2PS_2$ (689.57): C, 47.0; H, 3.9; N, 2.0; S, 9.3. Found: C, 45.8; H, 3.8; N, 1.9; S, 9.2%.

4.5. (Isopropylisocyanide)gold(I) p-tolylthiosulfonate (6)

As described for **1**, from *p*-$TolSO_2SAg$ (150 mg, 0.52 mmol) and (^{i}PrNC)AuCl (150 mg, 0.50 mmol), yield 210 mg (93%), m.p. 132 °C (dec.). NMR ($CDCl_3$, 20 °C), ^{1}H: 7.91 and 7.26, 2 × d, $J = 8.1$ Hz, 2 × 2H, C_6H_4; 4.09, sept, $J = 6.3$ Hz, 1H, CH; 2.41, s, 3H, MeC; 1.53, d, 6H, Me_2C. $^{13}C\{^1H\}$: 147.6, 142.7, 129.3, and 125.8, all s, i/*o*/*m*/*p*-CH; 49.5, s, *C*HMe_2; 22.2, s, Me_2; 21.5, s, Me; *C*N not detected. IR (KBr): 2246 cm^{-1}. *Anal.* Calc. for $C_{11}H_{14}AuNO_2S_2$ (453.34): C, 29.1; H, 3.1; N, 3.1; S, 14.1. Found: C, 28.9; H, 3.2; N, 3.1; S, 13.8%.

4.6. (^{t}Butylisocyanide)gold(I) p-tolylthiosulfonate (7)

As described for **1**, from *p*-$TolSO_2SAg$ (112 mg, 0.38 mmol) and (^{t}BuNC)AuCl (145 mg, 0.34 mmol), yield

Table 1
Crystal data, data collection, and structure refinement for compounds **1**, **2** and **7**

	1	**2**	**7**
Empirical formula	$C_{10}H_{16}AuO_2PS_2$	$C_{25}H_{22}AuO_2PS_2$	$C_{12}H_{16}AuNO_2S_2$
M	460.28	646.48	467.34
Temperature (K)	148	143	143
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$C2/c$	$P2_1/c$
a (Å)	10.9430(2)	28.3641(2)	11.2666(2)
b (Å)	14.4000(3)	10.1613(1)	7.9019(1)
c (Å)	18.8090(4)	19.5960(2)	16.4825(2)
β (°)	102.748(1)	124.293(1)	91.336(1)
U (Å^3)	2890.9(1)	4666.1(1)	1466.9(1)
Z	8	8	4
ρ_{calc} (g cm^{-3})	2.115	1.841	2.116
μ(Mo Kα) (cm^{-1})	105.56	65.73	103.06
F(000)	1744	2512	888
Absorption correction	DELABS	DELABS	DELABS
Measured reflections	37840	62023	36611
Unique reflections	6426 [$R_{int}=0.055$]	4973 [$R_{int}=0.039$]	3249 [$R_{int}=0.058$]
$T_{min/max}$	0.0767/0.1438	0.360/0.774	0.330/0.758
Refined parameters	289	280	163
R_1 [$I \geq 2\sigma(I)$]	0.0314	0.0206	0.0260
wR_2	0.0808	0.0518	0.0662
Weighting scheme [a]	$a=0.0403$ $b=5.15$	$a=0.0000$ $b=8.82$	$a=0.0301$ $b=1.15$
(Shift/error)$_{max}$	<0.001	<0.001	<0.001
σ_{fin}(max/min) (e Å^{-3})	2.015/−1.142	1.05/−0.592	1.631/−1.288

[a] $wR_2=\{[\Sigma w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w=1/[\sigma^2(F_o^2)+(ap)^2+bp]$; $p=(F_o^2+2F_c^2)/3$.

150 mg (93%), m.p. 115 °C (dec.). NMR ($CDCl_3$, 20 °C), ^{1}H: 7.76 and 7.36, 2 × d, $J=8.2$ Hz, 2 × 2H, C_6H_4; 2.41, s, 3H, Me; 1.57, s, 9H, Me_3. $^{13}C\{^1H\}$: 141.6, 134.2, 128.9, and 126.4, all s, i/*o*/*m*/*p*-CH; 30.1, s, Me_3; 21.4, s, Me; *C*N and *C*Me_3 not detected. IR (KBr): 2238 cm^{-1}. MS (FAB): 748 (43) $[L_2Au_2S_2O_2Tol]^+$; 692 (16) $[L_2Au_2S_2O_2Tol-C_4H_8]^+$; 468 (81) $[M+1]^+$; 467 (9) $[M]^+$; 412 (100) $[M-C_4H_8]^+$; 280 (6) $[L_2Au]^+$.

4.7. Crystallography

Specimens of suitable quality and size of compounds **1**, **2** and **7** were mounted on the ends of quartz fibers in F06206R oil and used for intensity data collection on a Nonius DIP2020 diffractometer, employing graphite-monochromated Mo Kα radiation. The structures were solved by a combination of direct methods (SHELXS-97) and difference-Fourier syntheses and refined by full-matrix least-squares calculations on F^2 (SHELXL-97). The thermal motion was treated anisotropically for all non-hydrogen atoms. All hydrogen atoms were calculated and allowed to ride on their parent atoms with fixed isotropic contributions. Further information on crystal data, data collection and structure refinement are summarized in Table 1. Important interatomic distances and angles are given in the corresponding Figure Captions.

5. Supplementary material

Crystallographic data for the structural analyses with thermal parameters and complete tables of interatomic distances and angles have been deposited with the Cambridge Crystallographic Data Centre CCDC Nos. 187777–18779. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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