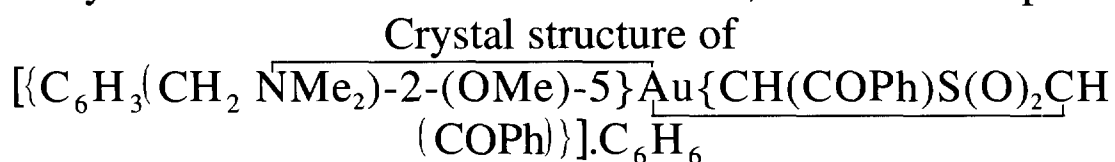# Organogold(III) metallacyclic chemistry

Part 1. Synthesis of the first auraoxodimethylenemethane (auracyclobutan-3-one) and aurathietane-3,3-dioxide complexes. Crystal structure of $[\{C_6H_3(CH_2\overline{NMe_2})\text{-}2\text{-}(OMe)\text{-}5\}\underline{Au\{CH(COPh)S(O)_2CH(COPh)\}}].C_6H_6$

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Abstract

The reactions of the cyclometallated gold complex $[\overline{Au\{C_6H_3(CH_2NMe_2)}\text{-}2\text{-}(OMe)\text{-}5\}Cl_2]$ (**5b**) with diphenacyl sulfone (**1**) or dimethyl 1,3-acetonedicarboxylate (**II**) using an excess of silver(I) oxide in refluxing dichloromethane afford in high yields, the aurathietane-3,3-dioxide (**6**) and auracyclobutan-3-one (**7**) complexes, containing $\overline{Au\text{-}C\text{-}S(O)_2\text{-}C}$ and $\overline{Au\text{-}C\text{-}C(O)\text{-}C}$ rings, respectively. Although analogous compounds of this type are known for platinum(II) and palladium(II), they are new for gold(III). A single crystal X-ray diffraction study has been carried out on $[\{C_6H_3(CH_2\overline{NMe_2})\text{-}2\text{-}(OMe)\text{-}5\}\overline{Au\{CH(COPh)S(O)_2CHCOPh)\}}].C_6H_6$ (**6**). The crystals are monoclinic, space group $P2_1/n$, $Z = 4$, in a unit cell with lattice parameters $a = 9.697(6)$, $b = 24.595(9)$, $c = 12.690(7)$ Å and $\beta = 107.84(4)°$. The structure was refined to R_1 0.0624 for 3784 reflections in the range $2 < \theta < 25°$ (Mo Kα X-radiation), collected at 130(2) K. The compound exhibits puckering of the aurathietane-3,3-dioxide ring [fold angle 18.6(12)°]. This, and a shortening of the C–S bonds, suggests a heteroallylic bonding contribution as previously seen in analogous platinum(II) and palladium(II) complexes. Detailed NMR data for the complexes are also reported, including the ^{1}H-ROESY spectrum of (**6**). The $^1J(CH)$ values of the $\overline{Au\text{-}C\text{-}X\text{-}C}$ ring carbons atoms have been measured for both (**6**) and (**7**), and used as indicators of their *s* character. © 1997 Elsevier Science S.A.

Keywords: Gold; Metallacycle; Organometallic; Crystal structure; Oxodimethylenemethane

1. Introduction

Four-membered ring metallacycles are involved in a wide range of metal-catalysed reactions of organic molecules [1,2], and are of fundamental interest for their structures and reactivities. The interest in the field is exemplified by the very large number of platinum(II) metallacycles which have been described over the years, including platinacyclobutanes (**1a**)–(**1e**) [3,4], platinathietane derivatives (**2a**)–(**2m**) [5–7], platinacyclobutanones (**3a**)–(**3f**) [8–10] (also known as 1,3-oxodimethylenemethane complexes) and platinaoxetanes (**4a**)–(**4d**) [11]. Palladium(II) also has an abundance of metallacycles; indeed $\overline{M\text{-}C\text{-}X\text{-}C}$ (X = C, N, O, S) ring systems are known for the vast majority of transition metals. Despite gold(III) being isoelectronic (d^8) with platinum(II) there is a paucity of information on similar gold metallacyclic complexes, and to the best of our knowledge no compounds containing the $\overline{Au\text{-}C\text{-}X\text{-}C}$ ring system have been reported. There has been some recent interest in cyclometallated gold(III) complexes [12,13], and the ready accessibility of the compounds $\overline{Au\{C_6H_3(CH_2NMe_2)}\text{-}2\text{-}R\text{-}5\}Cl_2]$ (**5a**) [14] or (**5b**) [15] suggested that these

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could be ideal precursors for the study of organogold(III) metallacycles analogous to those of platinum(II). In this paper, we report the synthesis [from (5b)] of two new gold(III) ring systems, together with an X-ray structure of an aurathietane dioxide derivative, containing the $\overline{Au-CHR-S(O)_2-CHR}$ ring.

2. Results and discussion

The silver(I) oxide mediated reaction of $[\overline{Au\{C_6H_3(CH_2NMe_2)\text{-}2\text{-}(OMe)\text{-}5\}Cl_2}]$ (5b) with diphenacyl sulfone (I) in refluxing dichloromethane affords a white air-stable, but somewhat light-sensitive, compound in 70% yield. This was characterised as the aurathietane-3,3-dioxide species (6), on the basis of elemental microanalysis, NMR analysis, electrospray mass spectrometry, and an X-ray crystallographic study. Similarly, the reaction of (5b) and dimethyl 1,3-acetonedicarboxylate (II) afforded in high yield the auracyclobutan-3-one complex (7) as a pale yellow oil that did not crystallise. Attempted purification of (7) by chromatography on a silica plate with ethyl acetate resulted in substantial decomposition of the complex.

The crystal structure of (6) · C_6H_6 was determined to fully characterise the reaction product of $[\overline{Au\{C_6H_3(CH_2NMe_2)\text{-}2\text{-}(OMe)\text{-}5\}Cl_2}]$ (5b) and diphenacyl sulfone (I), to examine the absolute geometry of the compound, and for comparison with analogous platinum(II) and palladium(II) systems. Selected bond lengths and angles for the structure are given in Tables 1 and 2. An ORTEP perspective view of the final structure is shown in Fig. 1, together with the atom labelling scheme.

2.1. Discussion of the structure

The structure confirms the expected product (6), which is overall very similar to the structures reported for $[\overline{Pt\{CH(COPh)S(O)_2CH(COPh)\}(PPh_3)_2}].2CH_2Cl_2$ (2a) and $[\overline{Pd\{CH(COPh)S(O)_2CH(COPh)\}(PMePh_2)_2}].CH_2Cl_2$ .H_2O (8) [5,6]. The compound crystallised with one molecule of benzene per molecule of complex. The benzene ring was somewhat disordered, but was modelled satisfactorily as a single rigid hexagon with strongly anisotropic temperature factors.

As expected for a d^8 metal centre, the gold atom is coordinated in a distorted square-planar arrangement, with the four- and five-membered metallacycles in the plane. The main distortion is the C(1)–Au–C(2) bite angle of 74.1(6)°, not significantly different to the bite angles reported for (2a) and (8), 75.4(4)° and 74.7(2)° respectively. The geometry about the central gold atom is planar, with a maximum deviation from the least-squares plane drawn through N(1), C(31), Au, C(1) and C(2) being 0.018(6) Å, for the gold atom.

The four-membered aurathietane-3,3-dioxide ring itself is non-planar with the fold angle between the C(1)–Au–C(2) and C(1)–S–C(2) planes being 18.6(12)°. This is slightly higher than the angle observed for the platinum system (2a) [15.3(6)°] but considerably lower than that reported for the palladium complex (8) [30.2(2)°]. The five-membered cyclometallated ring, incorporating an sp^2 hybridised carbon, is typically non-planar with deviations from the least-squares plane of 0.26(1)Å above the plane for C(6) and 0.278(9) Å below for N(1).

Table 1

Selected interatomic bond distances (Å) for (6)·C_6H_6 with estimated standard deviations in parentheses

Bond	Length
Au–C(1)	2.14(2)
Au–C(2)	2.05(2)
Au–C(31)	2.03(2)
Au–N(1)	2.14(1)
Au...S	2.833(4)
CH(COPh)S(O)$_2$CH(COPh) ligand	
C(1)–S	1.73(2)
C(2)–S	1.75(2)
S–O(3)	1.44(1)
S–O(4)	1.43(1)
C(1)–C(4)	1.51(2)
C(2)–C(3)	1.48(2)
C(3)–O(2)	1.24(2)
C(4)–C(11)	1.49(2)
C(3)–C(21)	1.52(2)

Table 2
Selected bond angles (°) for (6)·C$_6$H$_6$ with estimated standard deviations in parentheses

Bonds	Angle
C(1)–Au–C(2)	74.1(6)
C(1)–Au–N(1)	104.4(5)
C(2)–Au–C(31)	100.9(7)
N(1)–Au–C(31)	80.6(6)
CH(COPh)S(O)$_2$CH(COPh) ligand	
Au–C(1)–S	93.4(6)
Au–C(2)–S	95.9(8)
Au–C(1)–C(4)	105.7(11)
Au–C(2)–C(3)	115.0(12)
C(1)–S–C(2)	93.2(8)
C(1)–S–O(3)	108.1(7)
C(1)–S–O(4)	115.0(7)
C(2)–S–O(3)	109.7(8)
C(2)–S–O(4)	111.0(8)
C(1)–C(4)–O(1)	122(2)
C(1)–C(4)–C(11)	119.2(14)
C(2)–C(3)–O(2)	121(2)
C(2)–C(3)–C(21)	122.5(14)

The Au–C(1) and Au–C(2) bond lengths are not equal, as expected, with the former [2.14(2) Å] longer than the latter [2.05(2) Å]. This is attributable to C(31) having a higher *trans*-influence than N(1), a classically observed phenomenon in d^8 complexes [16]. The average bond distance of 2.10(2) Å is not significantly different to the average distances observed for (2a) [2.12(1) Å] and (8) [2.135(6) Å]. Additionally, the higher *trans*-influence of the C–C ligand vs. the chloride anion does, as expected, appear to significantly lengthen the Au–N(1) bond length [2.14(1) Å] for (6) compared with [2.05(3) Å] for [Au{C$_6$H$_3$(CH$_2$NMe$_2$)-2-(OMe)$_2$-5,6}Cl$_2$] [15] (9), a species closely related to
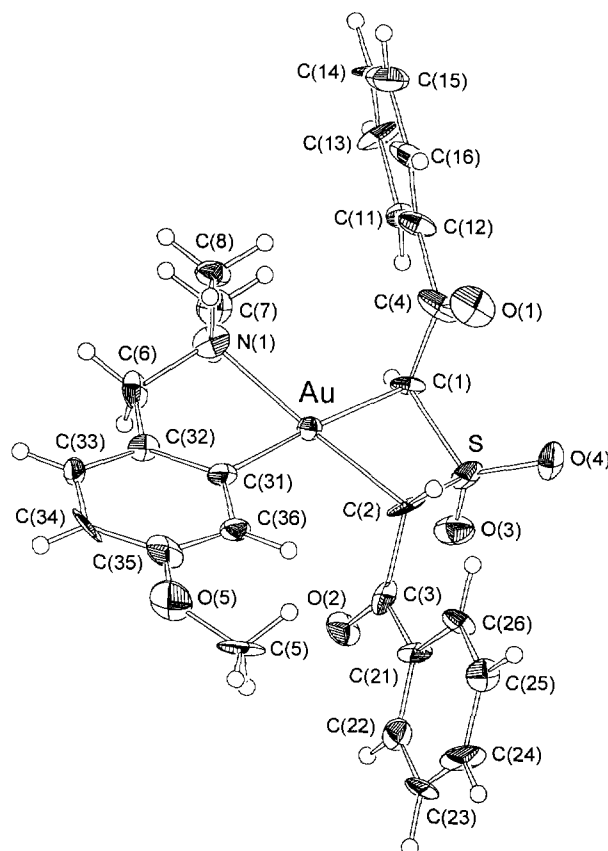

Fig. 1. Molecular structure of [{C$_6$H$_3$(CH$_2$NMe$_2$)-2-(OMe)-5}Au{CH(COPh)S(O)$_2$CH(COPh)}] (6), showing the atom numbering scheme. Atoms are shown as thermal ellipsoids at the 50% probability level. The benzene molecule of crystallisation has been omitted for clarity.

(5b). However, the Au–C(31) bond length [2.03(2) Å] of (6) does not appear to be greatly affected, and is of comparable length to that of (9) [2.08(2) Å].

The C–S bond lengths of 1.73(2) Å and 1.75(2) Å for C(1)–S and C(2)–S respectively, are also comparable to those reported for (2a) and (8), and are shorter than those measured in thietane-1,1-dioxides. A detailed comparison with starting materials and related compounds has been reported previously [5,6]. The short C–S bond distances, together with the puckering of the four-membered metallacycle, indicate contributions to the metallacyclic bonding (10a) from an η^3-heteroallylic representation (10b), with a degree similar to that observed for (2a).

2.2. Spectroscopic characterisation

Unambiguous NMR assignments of the complexes were achieved using a combination of HMBC (Heteronuclear Multiple Bond Correlation (long-range ^{13}C–^{1}H correlation, optimised for ^2J and ^3J coupling)), HMQC (Heteronuclear Multiple Quantum Correlation (short-range ^{13}C–^{1}H, optimised for ^1J coupling)), and ROESY (Rotating-frame Overhauser Effect SpectroscopY) inverse 2D experiments. The latter is a variation of the NOESY (Nuclear Overhauser Effect SpectroscopY) experiment, but with the NOE effects measured under spin-locked conditions. The ROESY spectrum of (6) is shown in Fig. 2, together with a structural representation illustrating the enhancements.

As expected, the differing *trans*-influences of the aryl carbon and nitrogen atoms markedly affects the environment of the ring CH proton and carbon atoms of both (6) and (7). For (6) 0.57 and 11.9 ppm differences in chemical shift are observed in the proton and carbon NMR spectra respectively. Similarly, 0.24 and 16.2 ppm differences are seen for the Au–CH groups of (7). However, rationalisation in terms of *trans*-influences is not clear, since the higher
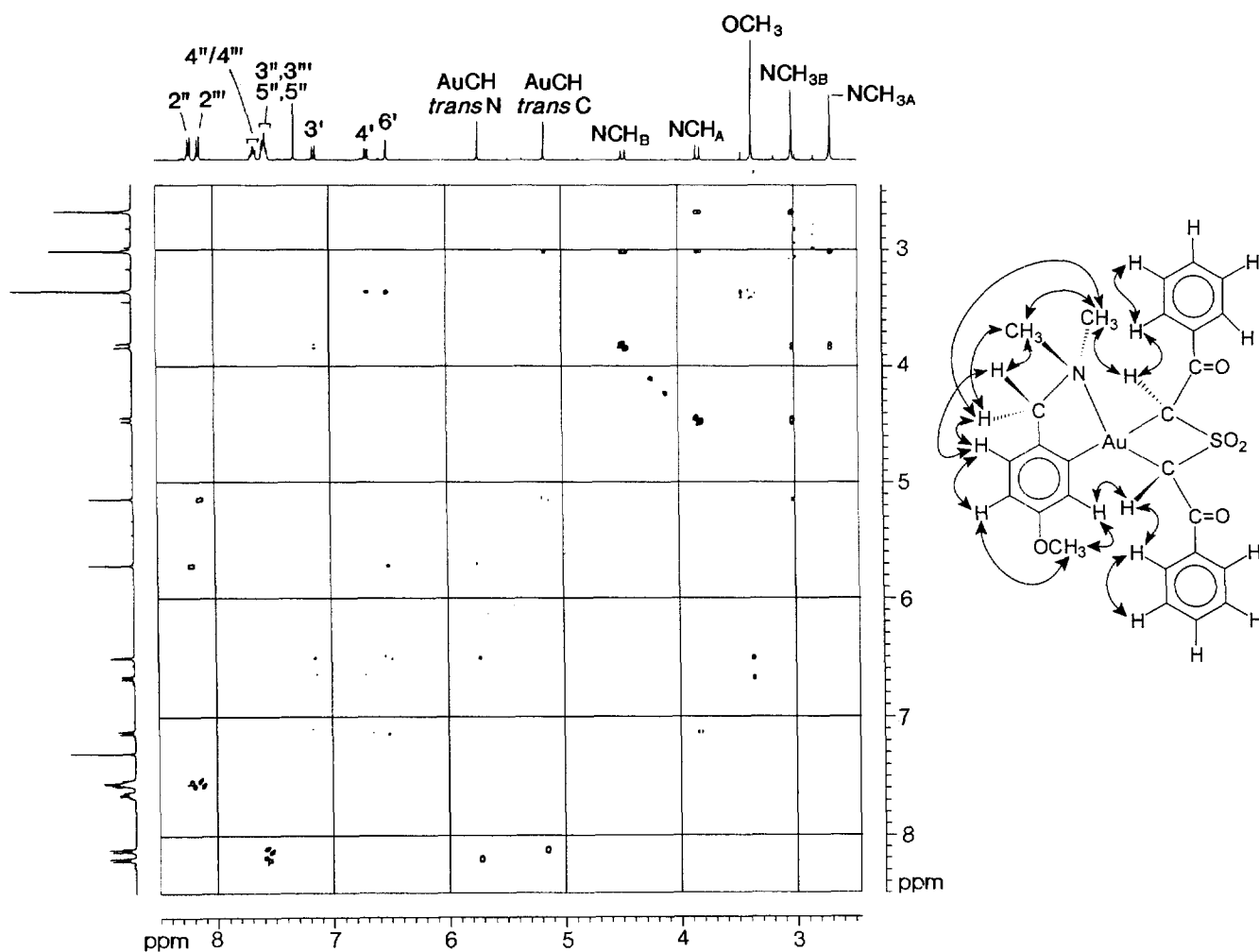

Fig. 2. ROESY spectrum of (6), with diagram illustrating observed NOE enhancements.

chemical shift proton is bonded to the lower chemical shift carbon. In the carbon spectra the upfield ^{13}C resonance is attributable to the *C*H *trans* to the lower *trans*-influence nitrogen.

The average carbon NMR Au–*C*H chemical shift of 62.1 ppm for (6) is significantly higher than that reported for analogous complexes (2a) and (8), with shifts of 54.6 ppm and 52.5 ppm respectively. This is not unexpected with a more electron-deficient, central metal atom (Zhang electronegativity values for platinum(II) and gold(III) are 1.5 and 1.7) [17]. The starting material, diphenacyl sulfone (I), shows the methylene carbon resonance at 60.0 ppm—slightly lower than the gold(III) derivative (6), but higher than the platinum(II) derivative (2a). A similar trend is seen in the proton spectra, with (6) having an average methine resonance of 5.40 ppm, compared with a value of 4.86 ppm for (2a) and 5.01 ppm for (I).

The ^{13}C chemical shift of the auracyclobutan-3-one ring C=O group of (7) occurs at 185.9 ppm, indicating the carbon atom is deshielded to a significantly greater degree than that for (3a), where the resonance for this moiety is observed at 178.3 ppm [8]. Again, this is consistent with more electronegative Au(III) vs. Pt(II) centres.

It was of interest to investigate the applicability of NMR in measuring the putative η^3-heteroallylic bonding contribution, which has been proposed to account for the non-planarity of the four-membered metallacyclic ring observed in X-ray crystal structure determinations [9]. Therefore the ^{1}H coupled ^{13}C spectra for (6) and (7) was measured, since it has been shown that there is a clear correlation of the percentage *s* character of carbon atoms and their $^1J(^{13}C-^1H)$ coupling constants [18], with larger values observed for *sp* carbons (e.g., ~ 250 Hz for alkynes) than for sp^2 carbons (e.g., ~ 160 Hz for aromatics), which in turn are higher than sp^3 (e.g., ~ 125 Hz for alkanes). For (6), values of 147.5 Hz for Au–*C trans* to C and 149.9 Hz for Au–*C trans* to N, were recorded. Comparing these with a value of 137.9 Hz for the starting material, diphenacyl sulfone (I), tentatively suggests that there is substantial sp^2 character in the Au–C ring carbon atoms, consistent with a heteroallylic bonding contribution. For (7), values of 148.7 Hz and 151.3 Hz were recorded, these being very similar to those of (6). However in this case the starting material (II) shows a ^{13}C–^{1}H coupling constant of 131.2 Hz, so the nett increase is greater. This is important since the electronegativity of adjacent atoms (CO, SO_2 and the metal centres themselves) also contribute to the magnitude of the ^1J value, with higher values observed for carbon atoms bonded to electron-withdrawing groups [18]. For the complex [Pt{CH(CO$_2$Me)C(O)CH(CO$_2$Me)}(PPh$_3$)$_2$] (3a), prepared by the literature procedure [8], a very similar value of 149.9 Hz was measured. It has been suggested that for sulfone derivatives (2) η^3-heteroallylic bonding is considered to be less than for oxodimethylenemethane complexes (3), since the metallacycle is considerably more puckered in the latter [e.g., 50.4(4)° in the case of (3a) [8]]. The new NMR evidence reported in this paper further supports this notion.

Electrospray mass spectrometric (ESMS) analyses of the title complexes (6) and (7) recorded in MeCN/H$_2$O solution show very strong parent ions (MH$^+$), with no observable fragmentation at low cone voltages (~ 20 V). Indeed, even when higher cone voltages (50–80 V) were used the complexes still show the MH$^+$ ion as the predominant signal, indicating appreciable stability. We believe that this resistance to fragmentation is at least partly due to the extra stability imparted by the presence of two ring systems.

3. Conclusions

The cyclometallated gold(III) complex (5b) appears to be an excellent precursor for the investigation of gold(III) metallacyclic chemistry. The compounds reported here are comparable to previously reported isoelectronic platinum(II) analogues. Further studies in gold metallacyclic chemistry will be described in subsequent papers.

4. Experimental

Melting points were measured in air on a Reichert hotstage apparatus and are uncorrected. Infrared spectra were recorded as KBr discs on a BioRad FTS-40 spectrophotometer. Electrospray mass spectra were determined in positive ion mode on a VG Platform II instrument, using a 1:1 mixture of CH$_3$CN/H$_2$O as the mobile phase. Elemental analyses were performed by the Campbell Microanalytical Laboratory, University of Otago.

Proton and all inverse 2D NMR experiments were recorded on a Bruker DRX 400 spectrometer at 400.13 MHz and 100.61 MHz for the proton and carbon channels respectively, with SiMe$_4$ (0.0 ppm) as the internal standard. The ^{13}C{^{1}H} NMR spectra were recorded on either the instrument above, or on a Bruker AC300 spectrometer at 75.47 MHz. All NMR analyses were carried out in CDCl$_3$. Fig. 3 illustrates the NMR numbering scheme.

All syntheses were carried out under a dry, oxygen-free, nitrogen atmosphere, using solvents which were dried and freshly distilled prior to use. The compound [Au{C$_6$H$_3$(CH$_2$NMe$_2$)-2-(OMe)-5}Cl$_2$] (5b) [15] was prepared as reported by transmetallation of the orthomercurated complex [Hg{C$_6$H$_3$(CH$_2$NMe$_2$)-2-(OMe)-5}Cl] [19] with Me$_4$NAuCl$_4$.
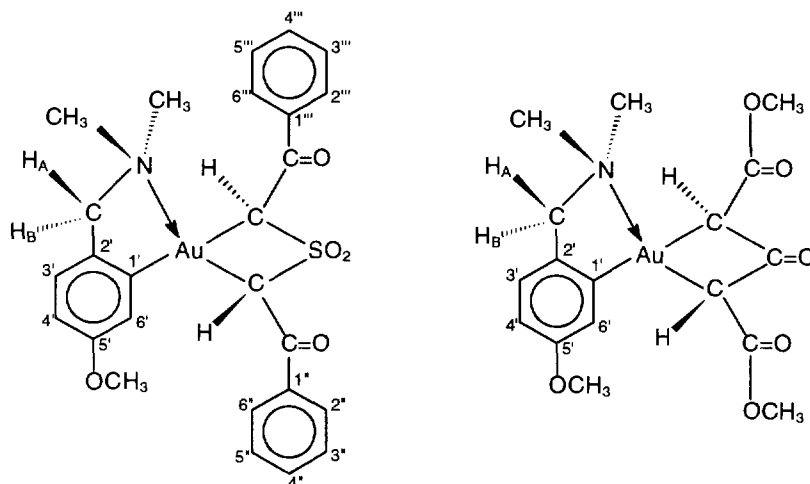
Fig. 3. NMR numbering scheme of (6) and (7).

Diphenacyl sulfone (I) [20], dimethyl 1,3-acetonedicarboxylate (II) [21,22] and [Pt{CH(CO$_2$Me)C(O)CH(CO$_2$Me)}(PPh$_3$)$_2$] (3a) [8] were prepared as described in the literature.

4.1. Preparation of (6)

To a nitrogen-flushed Schlenk flask containing dichloromethane (30 cm^3) was added [$\overline{Au\{C_6H_3(CH_2NMe_2)}$-2-(OMe)-5}Cl$_2$] (5b) (0.051 g, 0.118 mmol), diphenacyl sulfone (I) (0.035 g, 0.116 mmol), and silver(I) oxide (0.11 g, excess). The resulting mixture was stirred under reflux for 1 h in dark conditions, during which time the initial yellow solution became noticeably paler. Without further precautions to exclude air or light, the insoluble silver salts were filtered off to give an almost colourless solution. The solvent was removed under reduced pressure to give a colourless oil. This was subsequently recrystallised by vapour diffusion of ether into dichloromethane at 4°C to give colourless crystals which were dried in vacuo to yield (6) (0.054 g, 71%). The compound is air stable, but somewhat light sensitive, with slow decomposition occurring over several days as evidenced by purple colloidal gold formation on crystal surfaces.

Found: C, 47.1; H, 3.9; N, 2.2%; C$_{26}$H$_{26}$NO$_5$SAu requires: C, 47.2; H, 4.0; N, 2.1%. ESMS: (Cone voltage = 30 V) 662 (M + H$^+$, 100%); (Cone voltage = 80 V) 684 (M + Na$^+$, 18%), 662 (M + H$^+$, 100%).

IR: ν(CO region) 1668(s), 1647(s), 1592(s) cm^{-1}; ν(SO$_2$) 1276(s), 1130(vs) cm^{-1}. ^{1}H NMR: (400.13 MHz) δ 8.16 (2H, d, $^3J_{2'',3''} = 7.41$ Hz, H-2'',6''), 8.08 (2H, d, $^3J_{2''',3'''} = 7.39$ Hz, H-2''',6'''), 7.62–7.58 (2H, m, H-4'',4'''), 7.54–7.48 (4H, m, H-3'',3''',5'',5'''), 7.08 (1H, d, $^3J_{3',4'} = 8.28$ Hz, H-3'), 6.63 (1H, dd, $^3J_{4',3'} = 8.25$ Hz, $^4J_{4',6'} = 2.40$ Hz, H-4'), 6.46 (1H, d, $^4J_{6',4'} = 2.40$ Hz, H-6'), 5.68 (1H, s, AuCH trans N), 5.11 (1H, s, AuCH trans C), 4.42 (1H, d, $^2J_{H_B,H_A} = 13.56$ Hz, NCH$_B$), 3.78 (1H, d, $^2J_{H_B,H_A} = 13.58$ Hz, NCH_A), 3.32 (3H, s, OCH_3), 2.97 (3H, s, NCH_{3B}), 2.64 (3H, s, NCH_{3A}). ^{13}C NMR: (100.61 MHz) δ 193.6 (s, C=O trans C), 191.9 (s, C=O trans N), 158.2 (s, C-5'), 155.4 (s, C-1'), 139.0 (s, C-2'), 138.6 (s, C-1'''), 138.4 (s, C-1''), 133.8 (d, C-4'''), 133.6 (d, C-4''), 129.4 (d, C-3'''), 129.0–128.9 (d, C-2'',3'',2'''), 124.3 (d, C-3'), 117.9 (d, C-6'), 113.9 (d, C-4'), 73.9 (t, NCH$_2$), 68.0 (d, AuCH trans C), 56.1 (d, AuCH trans N), 54.8 (q, OCH$_3$), 52.7 (q, NCH$_{3B}$), 50.6 (q, NCH$_{3A}$).

4.2. Preparation of (7)

To a nitrogen-flushed Schlenk flask containing dichloromethane (30 cm^3) was added [$\overline{Au\{C_6H_3(CH_2NMe_2)}$-2-(OMe)-5}Cl$_2$] (0.050 g, 0.116 mmol), dimethyl 1,3-acetonedicarboxylate (II) (0.017 cm^3, 0.020 g, 0.115 mmol), and silver(I) oxide (0.08 g, excess). The resulting mixture was stirred under reflux for 1 h in dark conditions, during which time the initial yellow solution became noticeable paler. As described above, the insoluble silver salts were filtered off and subsequent evaporation of the filtrate gave a pale yellow oil which resisted crystallisation. ESMS and NMR revealed the product as (7) ($\sim$ 90% pure). Attempted purification by preparative layer chromatography resulted in substantial decomposition of the compound. The crude product is somewhat light and, possibly, air sensitive with decomposition occurring over several hours. This, and the difficulty in purification of the compound, rendered elemental analysis unfeasible.

ESMS: (Cone voltage = 20 V) 534 (M + H$^+$, 100%). (Cone voltage = 50 V) 534 (M + H$^+$, 100%), 502 ([M–OMe]$^+$, 52%), 402 (unidentified, 8%). (Cone voltage = 80 V) 556 (M + Na$^+$, 19%), 534 (M + H$^+$, 100%), 502 ([M–OMe]$^+$, 72%), 402 (unidentified, 40%).

IR: ν(CO region) 1772–1636(s) multiple signals, 1593(vs) cm^{-1}. ^{1}H NMR: (400.13 MHz) δ 7.15 (1H, d, $^3J_{3',4'}$ = 8.27 Hz, H-3'), 7.09 (1H, d, $^4J_{6',4'}$ = 2.55 Hz, H-6'), 6.70 (1H, dd, $^3J_{4',3'}$ = 8.26 Hz, $^4J_{4',6'}$ = 2.56 Hz, H-4'), 4.23 (1H, d, $^2J_{H_B,H_A}$ = 13.84 Hz, NCH$_B$), 4.15 (1H, s, AuC*H trans* N), 3.96 (1H, d, $^2J_{H_B,H_A}$ = 13.76 Hz, NC*H*$_A$), 3.91 (1H, s, AuC*H trans* C), 3.77 (3H, s, OC*H*$_3$), 3.680 (3H, s, C(O)OC*H*$_3$) 3.678 (3H, s, C(O)OC*H*$_3$), 3.17 (3H, s, NC*H*$_{3B}$), 2.79 (3H, s, NC*H*$_{3A}$). ^{13}C NMR: (75.47 MHz) δ 185.9 (s, C=O) 170.7 (s, *C*(O)OCH$_3$ *trans* C), 169.6 (s, *C*(O)OCH$_3$ *trans* N), 158.3 (s, C-5'), 156.8 (s, C-1'), 139.1 (s, C-2'), 124.1 (d, C-3'), 118.3 (d, C-6'), 113.4 (d, C-4'), 73.0 (t, N*C*H$_2$), 61.6 (d, Au*C*H *trans* C), 55.3 (q, O*C*H$_3$), 52.3 (s, C(O)O*C*H$_3$), 52.2 (q, N*C*H$_{3B}$), 51.4 (q, N*C*H$_{3A}$), 51.0 (s, C(O)O*C*H$_3$), 45.4 (d, Au*C*H *trans* N).

4.3. X-ray crystal structure of (6) · C$_6$H$_6$

Colourless rectangular blocks of (6) were obtained by liquid–liquid diffusion of benzene layered on a solution of (6) in chloroform, at 4°C. Cell parameters and intensity data were collected on an Nicolet R3 automatic four-circle diffractometer at the University of Canterbury, using a crystal of dimensions 0.35 × 0.30 × 0.16 mm, with monochromatic Mo Kα X-rays (λ = 0.71073 Å). A total of 3784 reflections in the range 2 < θ < 25° were collected at 130(2) K, of which 3745 were unique. These were subsequently corrected for Lorentz and polarisation effects, and for linear absorption by a Ψ scan method ($T_{max, min}$ = 0.55, 0.31).

4.4. Crystal data

C$_{26}$H$_{26}$NO$_5$SAu · C$_6$H$_6$, M_r = 739.61, monoclinic, space group $P2_1/n$, a = 9.697(6), b = 24.595(9), c = 12.690(7) Å, β = 107.84(4)°, U = 2881(3) Å^3, D_c = 1.705 g cm^{-3}, Z = 4, F(000) = 1464, μ(Mo Kα) = 5.22 mm^{-1}.

4.5. Solution and refinement

The structure was solved by the Patterson methods option of SHELXS-86 [23], and all further non-hydrogen atoms were located routinely (SHELXL-93 [24]). In the final cycle of the full-matrix least-squares refinement based on F^2, all non-hydrogen atoms were assigned anisotropic temperature factors, and all hydrogen atom positions determined by calculation. The refinement converged with R_1 = 0.0624 for data with $I \geq 2\sigma(I)$, 0.1071 for all data; wR_2 = 0.1420 $\{w = 1/[\sigma^2(F_o^2) + (0.0984P)^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^2)/3\}$, and GOF = 1.065. No parameter shifted in the final cycle, and the final difference map showed no peaks or troughs of electron density greater than + 3.31 and − 2.90 e Å^{-3} respectively (adjacent to the gold atom). The benzene solvate [C(41)...C(46)] was partially disordered (largely over two positions) so was modelled as a single rigid hexagon (all bond lengths 1.39 Å, bond angles 120°), with strongly anisotropic temperature factors.

Acknowledgements

Appendix A
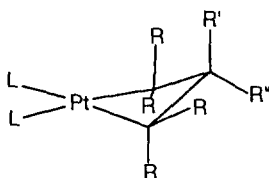
L = neutral donor ligand, e.g. PR₃,

½(1,5-cyclo-octadiene); AsPh₃

(**1a**) R = CN; R' = H; R" = H

(**1b**) R = CN; R' = Me; R" = Me

(**1c**) R = H; R' = Me; R" = Me

(**1d**) R = H; R' = CMe₂CO₂Me; R" = H

(**1e**) R = H, R' = H, R" = H
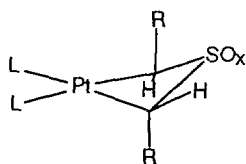
(**2a**)-(**2g**) L = PPh₃, PMePh₂, PMe₂Ph,

PMe₃, PBu₃, PEt₃, P(OPh)₃; R = C(O)Ph;

x = 2

(**2h**) L = PPh₃; R= CO₂Me; x = 2

(**2i**)-(**2j**) L = AsPh₃, L = P(OMe)₃; R = Ph;

x = 2

(**2k**)-(**2m**) L = PPh₃, PMePh₂, PMe₂Ph;

R = C(O)Ph; x = 1
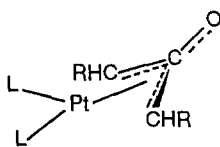
(**3a**)-(**3d**) L = PPh₃; R = CO₂Me,

CO₂Ph, Ph, H

(**3e**)-(**3f**) L = PPh₃, AsPh₃; R = Ph
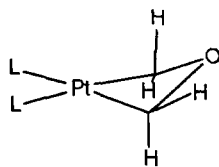
(4a)-**(4d)** L = PPh₃, PMe₃, dppe,

½(1,5-cyclo-octadiene)
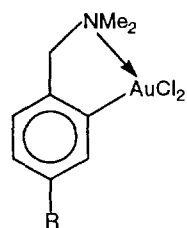
(5a) R = H

(5b) R = OMe
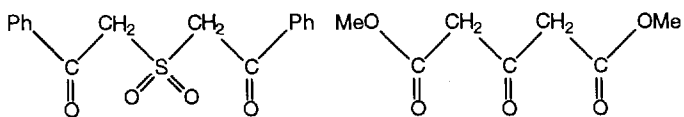
(I)

(II)
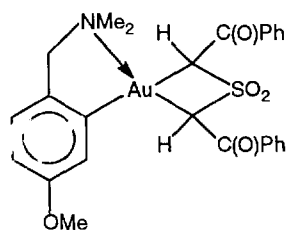
(6)

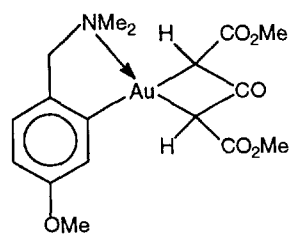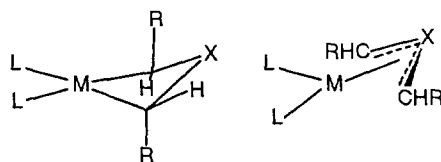**(7)**

$$X = CO, SO_2$$

(10a)   **(10b)**

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