

Synthesis and reactivity of [Au(2-CH₂-6-RC₅H₃N)(PPh₃)] (R = H, Me). X-Ray structure of [Ag{Au(2-CH₂-6-MeC₅H₃N)(PPh₃)}₂][ClO₄]

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The reaction of Li(2-CH₂-6-RC₅H₃N) with [AuCl(PPh₃)] leads to the mononuclear complexes [Au(2-CH₂-6-RC₅H₃N)(PPh₃)] (R = H, Me). These react further with other copper, silver or gold compounds to give heteronuclear derivatives, [M{Au(2-CH₂-6-RC₅H₃N)(PPh₃)}₂][X] (M = Cu, X = PF₆ or M = Ag, X = ClO₄), or the dinuclear complex [Au(2-CH₂-6-MeC₅H₃N)]₂. The crystal structure of [Ag{Au(2-CH₂-6-MeC₅H₃N)(PPh₃)}₂][ClO₄] has been determined by X-ray diffraction studies and shows short interactions between the gold and silver centres.

One of the more interesting developments in gold chemistry¹ over the last few years has been in the area of di- and polynuclear systems. Potentially bidentate ligands, with the correct geometry to hold two metal centres close to each other, have been widely investigated. However, anionic ligands obtained from 2-methylpyridine or 2,6-dimethylpyridine (2-CH₂-6-RC₅H₃N, R = H, Me) have been studied far less, and no gold derivative has been described. The only related derivative is the dinuclear [Au{2-C(SiMe₃)₂C₅H₄N}]₂.²

This paper reports the preparation of [Au(2-CH₂-6-RC₅H₃N)(PPh₃)] (R = H, Me) and the homo- and hetero-nuclear derivatives obtained from the reactions with other copper, silver or gold compounds. The molecular structure of [Ag{Au(2-CH₂-6-RC₅H₃N)(PPh₃)}₂][ClO₄] has been established by single-crystal X-ray studies, showing short interactions between the gold and silver centres.

Results and discussion

The reaction of 2-CH₂-6-RC₅H₃N (R = H, Me) in diethyl ether with LiBuⁿ leads to the lithium derivatives Li(2-CH₂-6-RC₅H₃N),³⁻⁹ which react further with [AuCl(PPh₃)] to give the mononuclear complexes [Au(2-CH₂-6-RC₅H₃N)(PPh₃)] [R = H (1), Me (2)]. A similar reaction starting from tetramethylpyrazine (2,3,5,6-Me₄C₄N₂) gives the derivative [Au(2-CH₂-3,5,6-Me₃C₄N₂)(PPh₃)] 3. Complexes 1-3 are white air- and moisture-stable solids and are non-conducting in acetone solutions. Their IR spectra show the ν(C=N) and ν(C=C) vibrations of the heterocycle at 1587s and 1568s 1, 1589s and 1557s 2, and 1535s cm⁻¹ 3. The positive liquid secondary ion mass spectra (LSIMS) show the cation molecular peaks at *m/z* (%): 551 (26) 1, 565 (22) 2, or 594 (22) 3. Other peaks appear at *m/z* 459 ([AuPPh₃]⁺, 95 1, 70 2, or 100% 3) and 721 ([Au(PPh₃)₂]⁺, 98 1, 70 2, or 90% 3). The most intense peaks correspond to the cation [M + AuPPh₃]⁺ (*m/z* 1010 1, 1024 2, or 1053 3).

The ³¹P-{¹H} NMR spectra at room temperature show a singlet at *ca.* δ 42.9. The ¹H NMR spectra of complexes 1 and 2 are as expected and are summarised in Table 1. The methylene protons appear as doublets because of coupling with the phosphorus atom, confirming the coordination of the gold centre to the CH₂ group. Some resonances (H⁴ in 2, or H⁵ in 1) are apparent triplets, rather than doublets of doublets, which is

probably attributable to similar *J*(HH) constants. The methylenic protons of 3 are not equivalent and appear as singlets at δ 2.39, 2.44, and 2.59.

As suggested by the formation of [M + AuPPh₃]⁺ species in the mass spectra, complexes 1-3 can serve as building blocks for preparing heteronuclear complexes. We have studied their reactions with several silver or copper derivatives. Thus the treatment of complexes 1, 2 or 3 with AgClO₄ in molar ratio 2:1 gives the trinuclear derivatives [Ag{Au(2-CH₂-6-RC₅-H₃N)(PPh₃)}₂][ClO₄] (R = H 4, Me 5) or [Ag{Au(2-CH₂-3,5,6-Me₃C₄N₂)(PPh₃)}₂][ClO₄] 6. A similar reaction of complexes 1 or 2 with [Cu(NCMe)₄][PF₆] leads to the complexes [Cu{Au(2-CH₂-6-RC₅H₃N)(PPh₃)}₂][PF₆] (R = H 7, Me 8) (Scheme 1). They are white or pale brown air- and moisture-stable solids. Complexes 4, 7 and 8 behave as 1:1 electrolytes in acetone solution; however the silver complexes 5 and 6 show conductivities (188 and 228 Ω⁻¹ cm² mol⁻¹, respectively) higher than that of 1:1 electrolytes, probably because of interactions with the solvent forming new ions, such as [Ag(OCMe₂)₄]⁺. Their IR spectra show, apart from the bands arising from the heterocycle or the phosphine, those of the perchlorate at 1100vs (br) and 625m cm⁻¹ or hexafluorophosphate at 850s (br) and 558s cm⁻¹. The positive-ion LSIMS exhibit peaks corresponding to the cations [AuPPh₃]⁺ (*m/z* = 459), [Au(PPh₃)₂]⁺ (*m/z* = 721), [(2-CH₂-6-RC₅H₃N)(AuPPh₃)]⁺ [*m/z* = 552 (4 or 7) or 566 (5 or 8)], [(2-CH₂-3,5,6-Me₃C₄N₂)(AuPPh₃)]⁺ (*m/z* = 595, 6), [(2-CH₂-6-RC₅H₃N)(AuPPh₃)₂]⁺ [*m/z* = 1010 (4 or 7) or 1024 (5 or 8)], or [(2-CH₂-3,5,6-Me₃C₄N₂)(AuPPh₃)₂]⁺ (*m/z* = 1053, 6). The cation molecular peaks, [Ag{Au(2-CH₂-6-RC₅H₃N)(PPh₃)}₂]⁺ (*m/z* = 1211, 30%) or [Ag{Au(2-CH₂-3,5,6-Me₃C₄N₂)(PPh₃)}₂]⁺ (*m/z* = 1297, 30%) are only observed for complexes 4 and 6.

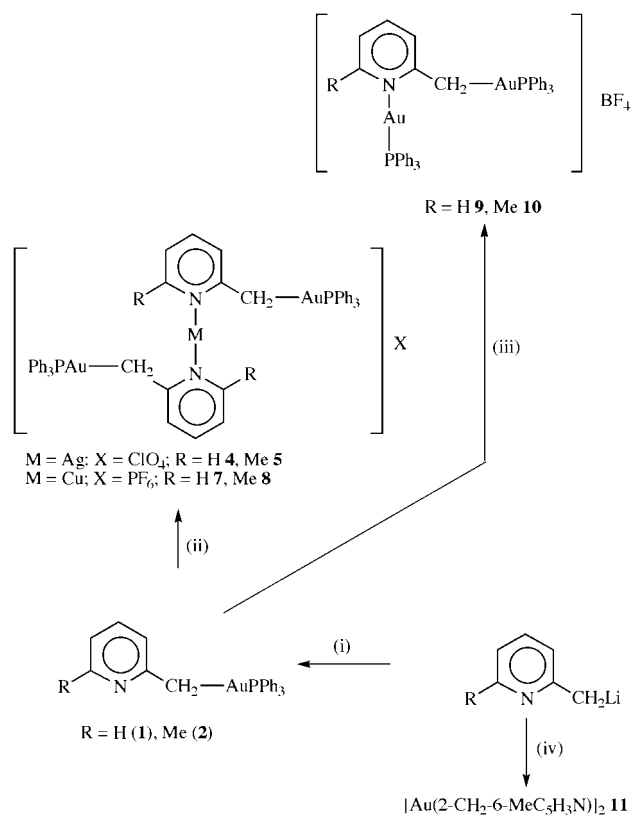
The ¹H NMR spectra show a doublet for the methylene protons, because of coupling with the phosphorus of the phosphine. Other resonances are collected in Table 1. Complex 6 presents a singlet for each of the three different methyl groups. The ³¹P-{¹H} NMR spectra present only one singlet for the two equivalent phosphorus atoms.

The crystal structure of complex 5 has been confirmed by an X-ray diffraction study; its cation is shown in Fig. 1, with a selection of bond lengths and angles in Table 2. The silver centre lies on a two-fold axis and thus only half of the molecule corresponds to the asymmetric unit. The gold atoms have a

Table 1 ^1H NMR data for complexes. ^a Coupling constants in parentheses

Complex	CH ₃	CH ₂	H ⁵	H ³	H ⁴	H ⁶
2-MeC ₅ H ₄ N	2.50 (s)		7.01 (t)	7.07 (d)	7.33 (dt)	8.42 (d)
2,6-Me ₂ C ₅ H ₃ N	2.42 (s)		6.83 (d)	6.83 (d)	7.33 (t)	
1		2.88 (d) (10.8)	6.67 (t) (3.1)	7.02 (d) (7.8)	^b	8.28 (d)
2	2.44 (s)	2.79 (d) (11.0)	6.58 (d) (7.3)	6.85 (d) (7.8)	7.25 (t)	
3	2.39 (s) 2.44 (s) 2.59 (s)	2.68 (d) (11.2)				
4		3.13 (d) (10.5)	6.54 (m)	7.02 (m)	^b	8.05 (m)
5	2.20 (s)	3.24 (d) (10.5)	6.72 (d) (7.3)	6.98 (d) (7.8)	^b	
6	2.41 (s) 2.56 (s) 2.59 (s)	2.88 (d) (9.5)				
7		3.10 (d) (9.5)	6.54 (m)	7.02 (m)	^b	8.05 (m)
8	2.06 (s)	3.28 (d) (10.2)	6.60 (d) (7.3)	6.98 (d) (7.3)	^b	
9		3.22 (d) (10.7)	^b	^b	^b	8.34 (m)
10	2.80 (s)	3.28 (d) (10.6)	6.74 (d) (6.0)	6.99 (d) (8.1)	^b	
11a	3.318 (s)	3.44 (s)	6.48 (d) (7.4)	7.0 (d) (7.4)	7.27 (t)	
11b	2.67 (s)	3.17 (s)	6.70 (d) (7.4)	7.03 (d) (7.4)	7.32 (t)	

^a In CDCl₃ solutions at -60 °C, δ from external SiMe₄; s = singlet, d = doublet, t = triplet, dt = doublet of triplets, m = multiplet. ^b Overlapped with the resonances of the phenyl groups.



Scheme 1 (i) [AuCl(PPh₃)]; (ii) 1/2 AgClO₄ or 1/2 [Cu(NCMe)₄][PF₆]; (iii) HBF₄; (iv) [AuCl(AsPh₃)].

slightly distorted linear geometry with a P–Au–C(1) angle of 175.3(2)°, possibly associated with a weak interaction with the silver centre, Au⋯Ag 3.428(1) Å; in contrast, the gold atoms are located far from each other, Au⋯Au# 5.115(2) Å

Table 2 Selected bond lengths (Å) and angles (°) for complex **5**

Au–C(1)	2.084(6)	P–C(31)	1.819(6)
Au–P	2.2813(16)	C(1)–C(11)	1.452(9)
Ag–N	2.162(5)	C(11)–N	1.347(7)
P–C(21)	1.815(6)	C(15)–N	1.346(8)
P–C(41)	1.818(6)		
C(1)–Au–P	175.32(17)	C(41)–P–Au	116.26(18)
N#1–Ag–N	159.6(2)	C(31)–P–Au	113.39(18)
C(21)–P–C(41)	105.7(2)	C(11)–C(1)–Au	112.3(4)
C(21)–P–C(31)	104.5(2)	C(15)–N–Ag	121.0(4)
C(41)–P–C(31)	104.6(2)	C(11)–N–Ag	116.2(4)
C(21)–P–Au	111.43(18)		

^a Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, y, -z + 1/2$.

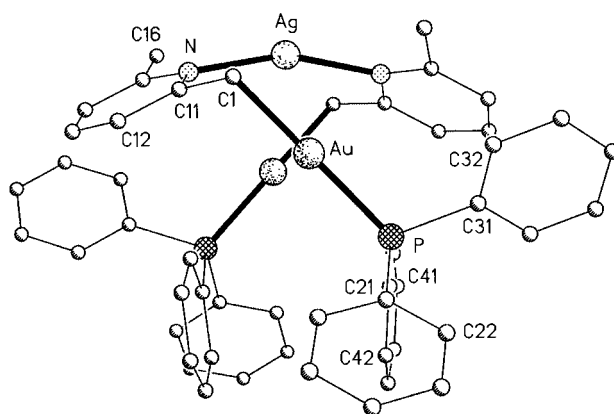


Fig. 1 Molecular structure of the cation of complex **5** showing the atom numbering scheme. Hydrogen atoms are omitted for clarity.

(#1: $1 - x, y, 0.5 - z$). The silver centre has a very distorted linear geometry, N–Ag–N# 159.6(2)°, probably attributable to weak contacts to oxygen atoms of the (disordered) perchlorate

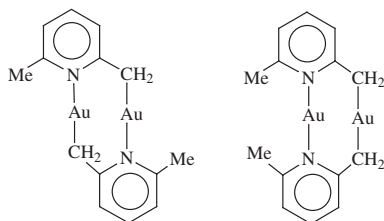


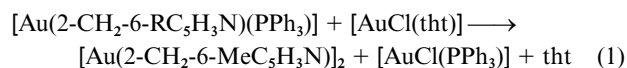
Fig. 2 The two isomers of complex 11.

anion, Ag...O 3.10, 3.16 Å. The silver–nitrogen bond length of 2.162(5) Å is similar to values reported for two-coordinate and pseudo two-coordinate complexes of silver(I) with σ-bonding ligands such as [Ag(2,6-Me₂py)₂][ClO₄] (2.166(4) Å),¹⁰ although shorter than in the complex [(Ph₃P)(O₃ClO)AgN(Ph₂PAuPPh₂)₂NAg(OClO₃)(PPh₃)] (2.239(4) Å),¹¹ perhaps as a consequence of the *trans* influence of the phosphine ligand.

The reaction of complexes **1** or **2** with HBF₄ in a 2:1 molar ratio leads to protonation of half of the heterocyclic ligand and to the formation of the dinuclear complexes [(2-CH₂-6-RC₅H₃N)(AuPPh₃)₂][BF₄] (R = H **9**, Me **10**). They are white air- and moisture-stable solids and behave as 1:1 electrolytes in acetone solution. In the IR spectra the vibrations from the anion appear at 1100s and 1053s (br) cm⁻¹. The ³¹P-{¹H} NMR spectra present two singlets at δ 42.7 and 30.3 **9** and δ 41.8 and 29.4 **10** from the two different phosphines and confirm the coordination of the second gold centre to the nitrogen atom. The ¹H NMR data are collected in Table 1. The mass spectra are similar to those of complexes **1** and **2** and the cations [M - BF₄]⁺ appear at *m/z* (%) 1010 (55) **9** or 1024 (30) **10**.

The reaction of the lithium derivative Li(2-CH₂-6-MeC₅H₃N) with [AuCl(AsPh₃)], with the weakly coordinating ligand AsPh₃, leads to the dinuclear complex [Au(2-CH₂-6-MeC₅H₃N)]₂ **11**. It is a white air- and moisture-stable solid and a non-conductor in acetone solution. The ν(Au–Cl) vibrations and those of the arsine are not present in its IR spectrum and only those of the 2-CH₂-6-MeC₅H₃N ligand are observed. The ¹H NMR spectrum (Table 1) is in agreement with the presence of two isomers (Fig. 2), in a molar ratio **11a**:**11b** = 4:1.

The same complex is obtained from the reaction of complex **2** with [AuCl(tht)] (tht = tetrahydrothiophene) (eqn. (1)), but now with a different molar ratio for the two isomers (**11a**:**11b** = 1:4), as observed from the ¹H NMR spectrum. Complex **11** reacts with PPh₃ to give the mononuclear derivative **2** (84% yield).



Experimental

Infrared spectra were recorded on a Perkin-Elmer 883 spectrophotometer, over the range 4000–200 cm⁻¹, using Nujol mulls between polyethylene sheets. Conductivities were measured in *ca.* 5 × 10⁻⁴ mol dm⁻³ solutions with a Philips 9509 conductimeter. C, H, and N analyses were carried out with a Perkin-Elmer 2400 microanalyser. Mass spectra were recorded on a VG Autospec, with the liquid secondary-ion mass spectra (LSIMS) technique, using 3-nitrobenzyl alcohol as matrix. ¹H and ³¹P-{¹H} NMR spectra were recorded on a Varian UNITY 300 or Bruker ARX 300 apparatus in CDCl₃ solutions (stored over Na₂CO₃); chemical shifts are quoted relative to SiMe₄ (external, ¹H) and 85% H₃PO₄ (external, ³¹P).

The starting materials [AuCl(tht)],¹² [AuCl(PPh₃)],¹² [AuCl(AsPh₃)],¹³ [Au(C₆F₅)(tht)],¹² and [Cu(NCMe)₄][PF₆]¹⁴ were prepared by published procedures. All other chemicals used were commercially available and used without further purification. **CAUTION**: perchlorate salts with organic cations may be explosive.

Syntheses

[Au(2-CH₂-6-RC₅H₃N)(PPh₃)] (R = H, **1**; Me, **2**) and [Au(2-CH₂-3,5,6-Me₃C₄N₂)(PPh₃)] **3**. To a solution of 2-CH₂-6-RC₅H₃N (R = H, 60 μl, 0.5 mmol; Me, 50 μl, 0.5 mmol) or 2,3,5,6-Me₄C₄N₂ (0.068 g, 0.5 mmol) in diethyl ether (40 cm³) was added a *n*-hexane solution of LiBuⁿ (0.31 ml, 1.6 M, 0.5 mmol) and the mixture was stirred for 10 min. An orange, Li(2-CH₂-6-RC₅H₃N), or red Li(2-CH₂-3,5,6-Me₃C₄N₂), precipitate was formed. To this suspension was added [AuCl(PPh₃)] (0.247 g, 0.5 mmol). After stirring for 1 h the mixture was filtered through a layer of celite and the solvent was evaporated to *ca.* 5 cm³. Addition of hexane (10 cm³) gave complexes **1–3** as white solids. Complex **1**: yield 59%. *M_w* 1 Ω⁻¹ cm² mol⁻¹. Elemental analysis (%), Found: C, 51.85; H, 3.8; N, 2.3. Calc. for C₂₄H₂₁AuNP: C, 52.27; H, 3.8; N, 2.5. ³¹P-{¹H} NMR, δ: 42.9 (s). Complex **2**: yield 67%. *M_w* 1 Ω⁻¹ cm² mol⁻¹. Elemental analysis (%), Found: C, 53.0; H, 4.15; N, 2.4. Calc. for C₂₅H₂₃AuNP: C, 53.1; H, 4.15; N, 2.45. ³¹P-{¹H} NMR, δ: 43.0 (s). Complex **3**: yield 77%. *M_w* 8 Ω⁻¹ cm² mol⁻¹. Elemental analysis (%), Found: C, 52.15; H, 4.7; N, 4.25. Calc. for C₂₆H₂₆AuN₂P: C, 52.55; H, 4.4; N, 4.7. ³¹P-{¹H} NMR, δ: 42.8 (s).

[M{Au(2-CH₂-6-RC₅H₃N)(PPh₃)₂}[X] (M = Ag, X = ClO₄, R = H, **4**; Me, **5**; M = Cu, X = PF₆, R = H, **7**; Me, **8**) or [Ag{Au(2-CH₂-3,5,6-Me₃C₄N₂)(PPh₃)₂}[ClO₄] **6**. To a solution of AgClO₄ (0.031 g, 0.15 mmol) or [Cu(NCMe)₄][PF₆] (0.028 g, 0.15 mmol) in diethyl ether (**4**, **5**) or dichloromethane (**6–8**) (30 cm³) was added complex **1** (0.165 g, 0.3 mmol), **2** (0.169 g, 0.3 mmol) or **3** (0.178 g, 0.3 mmol). The reaction mixture was stirred in the dark for 30 min. Evaporation of the diethyl ether to *ca.* 5 cm³ or concentration of the solution (dichloromethane) to *ca.* 5 cm³ and addition of diethyl ether (10 cm³) gave complexes **4–8** as white (**4–6**) or pale brown (**7**, **8**) solids. Complex **4**: yield 82%. *M_w* 152 Ω⁻¹ cm² mol⁻¹. Elemental analysis (%), Found: C, 45.15; H, 3.15; N, 2.0. Calc. for C₄₈H₄₂AgAu₂ClN₂O₄P₂: C, 44.9; H, 3.05; N, 2.15. ³¹P-{¹H} NMR, δ: 42.9 (s). Complex **5**: yield 86%. *M_w* 188 Ω⁻¹ cm² mol⁻¹. Elemental analysis (%), Found: C, 45.2; H, 3.4; N, 1.95. Calc. for C₅₀H₄₆AgAu₂ClN₂O₄P₂: C, 44.75; H, 3.5; N, 2.1. ³¹P-{¹H} NMR, δ: 43.8 (s). Complex **6**: yield 63%. *M_w* 227 Ω⁻¹ cm² mol⁻¹. Elemental analysis (%), Found: C, 52.15; H, 4.7; N, 4.25. Calc. for C₄₆H₄₀AgAu₂ClN₄O₄P₂: C, 52.55; H, 4.4; N, 4.7. ³¹P-{¹H} NMR, δ: 43.5 (s). Complex **7**: yield 61%. *M_w* 147 Ω⁻¹ cm² mol⁻¹. Elemental analysis (%), Found: C, 43.55; H, 2.85; N, 1.85. Calc. for C₄₈H₄₂Au₂CuF₆N₂P₃: C, 43.95; H, 3.05; N, 2.15. ³¹P-{¹H} NMR, δ: 42.7 (s). Complex **8**: yield 72%. *M_w* 164 Ω⁻¹ cm² mol⁻¹. Elemental analysis (%), Found: C, 44.3; H, 3.3; N, 3.25. Calc. for C₅₀H₄₆Au₂CuF₆N₂P₃: C, 44.8; H, 3.4; N, 2.1. ³¹P-{¹H} NMR, δ: 42.4 (s).

[(2-CH₂-6-RC₅H₃N)(AuPPh₃)₂][BF₄] (R = H, **9**; Me, **10**). To a solution of complex **1** (0.110 g, 0.2 mmol) or **2** (0.112 g, 0.2 mmol) in 40 cm³ of diethyl ether was added HBF₄ (54% diethyl ether solution, 13.6 μl, 0.1 mmol) and the mixture stirred for 15 min. A white precipitate of **9** or **10** was obtained. Complex **9**: yield 73%. *M_w* 103 Ω⁻¹ cm² mol⁻¹. Elemental analysis (%), Found: C, 45.6; H, 2.95; N, 1.35. Calc. for C₄₂H₃₆Au₂BF₄NP₂: C, 45.95; H, 3.3; N, 1.25. ³¹P-{¹H} NMR, δ: 42.7 (s, C-Au-PPh₃), 30.3 (s, N-Au-PPh₃). Complex **10**: yield 78%. *M_w* 120 Ω⁻¹ cm² mol⁻¹. Elemental analysis (%), Found: C, 46.0; H, 3.3; N, 1.6. Calc. for C₄₃H₃₈Au₂BF₄NP₂: C, 46.45; H, 3.45; N, 1.25. ³¹P-{¹H} NMR, δ: 41.8 (s, C-Au-PPh₃), 29.4 (s, N-Au-PPh₃).

[Au(2-CH₂-6-MeC₅H₃N)]₂ **11**. To a suspension of Li(2-CH₂-6-MeC₅H₃N) (0.5 mmol), prepared as above (complex **2**), in 40 cm³ of diethyl ether was added [AuCl(AsPh₃)] (0.269 g, 0.5 mmol). After stirring for 1 h the mixture was filtered through a layer of Celite and the solvent was evaporated to *ca.* 5

Table 3 Details of data collection and structure refinement for complex **5**

Formula	C ₅₀ H ₄₆ AgAu ₂ ClN ₂ O ₄ P ₂
<i>M</i>	1388.08
Crystal system	Monoclinic
Space group	<i>C2/c</i>
<i>a</i> /Å	14.593(5)
<i>b</i> /Å	17.237(6)
<i>c</i> /Å	19.330(7)
β /°	108.11(3)
<i>U</i> /Å ³	4621(3)
<i>Z</i>	4
<i>T</i> /°C	−95
μ (Mo-K α)/mm ^{−1}	6.927
No. of reflections measured	4382
No. of unique reflections	4052
<i>R</i> _{int}	0.018
<i>R</i> ^a (<i>F</i> , <i>F</i> > 4 σ (<i>F</i>))	0.031
<i>wR</i> ^b (<i>F</i> ² , all reflections)	0.081

^a $R(F) = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$; ^b $wR(F^2) = \frac{[\sum \{w(F_o^2 - F_c^2)^2\} / \sum \{w(F_o^2)^2\}]^{0.5}}{w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP}$, where $P = [F_o^2 + 2F_c^2]/3$ and *a* and *b* are constants adjusted by the program.

cm³. Addition of hexane (10 cm³) gave complex **11** as a white solid. Yield 42%. *M_r* 12 Ω^{−1} cm² mol^{−1}. Elemental analysis (%). Found: C, 28.0; H, 2.85; N, 4.2. Calc. for C₁₄H₁₆Au₂N₂: C, 27.75; H, 2.65; N, 4.6.

Crystallography

The crystal was mounted in inert oil on a glass fibre and transferred to the cold gas stream of a Siemens R3 diffractometer equipped with an LT-2 low temperature attachment. Data were collected using monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). Scan type ω . Cell constants were refined from setting angles of 50 reflections in the range 2θ 20–22°. An absorption correction was applied on the basis of ψ -scans. The structure was solved by the heavy-atom method and refined on *F*² using the program SHELXL-97.¹⁵ The perchlorate anion was refined with a two-fold disorder model. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included using a riding model. A system of restraints to light-atom displace-

ment factor components and to local ring symmetry was used. Further details are given in Table 3.

CCDC reference number 186/1548.

See <http://www.rsc.org/suppdata/dt/1999/2819/> for crystallographic files in .cif format.

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