

# Complexes of gold, silver and copper with $Z,Z$ - $\text{PPh}_2\text{CH}_2\text{CBu}^t=\text{N}-\text{N}=\text{C}(\text{Bu}^t)\text{CH}_2\text{PPh}_2$ containing a nine-membered chelate ring: crystal structure of $[\text{AuCl}\{\text{Z},\text{Z}-\text{PPh}_2\text{CH}_2\text{CBu}^t=\text{N}-\text{N}=\text{C}(\text{Bu}^t)\text{CH}_2\text{PPh}_2\}]$

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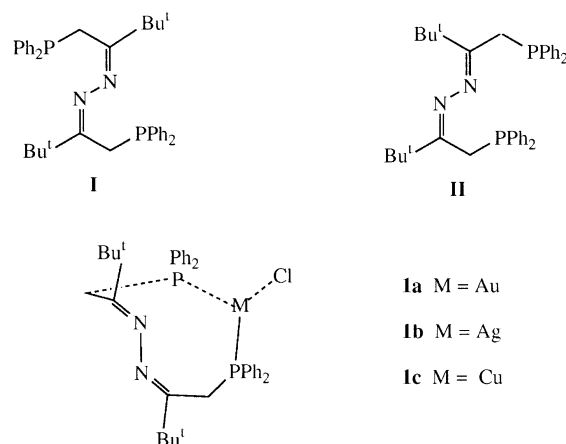
Complexes of gold, silver and copper with the azine diphosphine  $Z,Z$ - $\text{PPh}_2\text{CH}_2\text{CBu}^t=\text{N}-\text{N}=\text{C}(\text{Bu}^t)\text{CH}_2\text{PPh}_2$  have been prepared and shown to contain the diphosphine in an unusual nine-membered chelate ring; the crystal structure of the chlorogold derivative  $[\text{AuCl}\{\text{Z},\text{Z}-\text{PPh}_2\text{CH}_2\text{CBu}^t=\text{N}-\text{N}=\text{C}(\text{Bu}^t)\text{CH}_2\text{PPh}_2\}]$  was determined.

We have studied the interaction of the azine diphosphine  $Z,Z$ - $\text{PPh}_2\text{CH}_2\text{CBu}^t=\text{N}-\text{N}=\text{C}(\text{Bu}^t)\text{CH}_2\text{PPh}_2$  **I** with chromium, molybdenum and tungsten,<sup>1,2</sup> with platinum and palladium<sup>3</sup> and with iridium and rhodium.<sup>4</sup> When treated with the substitutionally labile palladium(II) and platinum(II) chloride complexes  $[\text{PdCl}_2(\text{NCPh})_2]$  or  $[\text{PtCl}_2(\text{NCMe})_2]$  this  $Z,Z$ -diphosphine gave large-ring polynuclear complexes of type  $\text{trans}-[\{\text{MCl}_2\{\text{Z},\text{Z}-\text{PPh}_2\text{CH}_2\text{CBu}^t=\text{N}-\text{N}=\text{C}(\text{Bu}^t)\text{CH}_2\text{PPh}_2\}_n]$ , probably with  $n = 2$  for Pd and 6 for Pt.<sup>3</sup> Frequently, however, when this diphosphine displaces other ligands from a metal, isomerisation around one of the C=N double bonds occurs and the resultant  $E,Z$ - $\text{PPh}_2\text{CH}_2\text{CBu}^t=\text{N}-\text{N}=\text{C}(\text{Bu}^t)\text{CH}_2\text{PPh}_2$  **II** can act as a bidentate chelate ( $P,P'$ -bonded) or terdentate ligand ( $P,N,P'$ -bonded) giving mononuclear complexes. Examples of mononuclear complexes which have a nine-membered chelate ring include  $[\text{Cr}(\text{CO})_4\{E,Z\text{-PPh}_2\text{CH}_2\text{CBu}^t=\text{N}-\text{N}=\text{C}(\text{Bu}^t)\text{CH}_2\text{PPh}_2\}]$ ,<sup>5</sup>  $[\text{PtMe}_2\{E,Z\text{-PPh}_2\text{CH}_2\text{CBu}^t=\text{N}-\text{N}=\text{C}(\text{Bu}^t)\text{CH}_2\text{PPh}_2\}]$ ,<sup>3</sup> and  $[\text{Pd}(\eta^3\text{-C}_3\text{H}_4\text{Me})\{E,Z\text{-PPh}_2\text{CH}_2\text{CBu}^t=\text{N}-\text{N}=\text{C}(\text{Bu}^t)\text{CH}_2\text{PPh}_2\}]$ .<sup>6</sup> However, more commonly the  $E,Z$ -diphosphine acts as a terdentate  $P,N,P'$ -bonded ligand, as in complexes of the types  $[\text{MX}\{E,Z\text{-PPh}_2\text{CH}_2\text{CBu}^t=\text{N}-\text{N}=\text{C}(\text{Bu}^t)\text{CH}_2\text{PPh}_2\}]\text{Y}$  ( $\text{M} = \text{Pd}, \text{X} = \text{Cl}, \text{Y} = \text{Cl}$  or  $\text{PF}_6$ ;  $\text{M} = \text{Pt}, \text{X} = \text{Cl}, \text{Y} = \text{PF}_6$  or  $\text{X} = \text{Y} = \text{I}$ ),<sup>3</sup>  $[\text{M}(\text{CO})_3\{E,Z\text{-PPh}_2\text{CH}_2\text{CBu}^t=\text{N}-\text{N}=\text{C}(\text{Bu}^t)\text{CH}_2\text{PPh}_2\}]$  ( $\text{M} = \text{Cr}, \text{Mo}$  or  $\text{W}$ ),<sup>1</sup> or  $[\text{Ir}(\text{CO})\{E,Z\text{-PPh}_2\text{CH}_2\text{CBu}^t=\text{N}-\text{N}=\text{C}(\text{Bu}^t)\text{CH}_2\text{PPh}_2\}]\text{X}$  ( $\text{X} = \text{Cl}$  or  $\text{PF}_6$ ).<sup>4</sup>

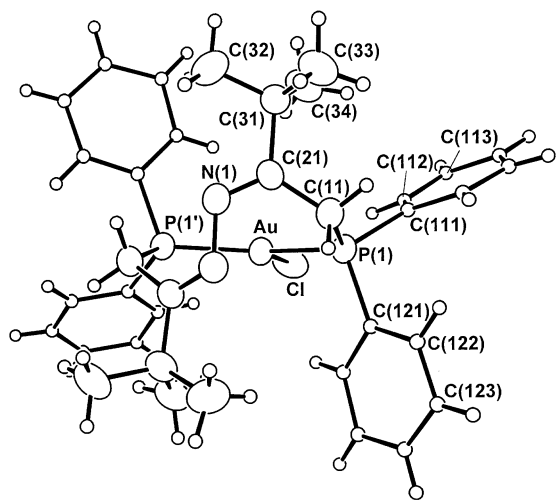
Previously, we thought that  $Z,Z$ - $\text{PPh}_2\text{CH}_2\text{CBu}^t=\text{N}-\text{N}=\text{C}(\text{Bu}^t)\text{CH}_2\text{PPh}_2$  would not chelate in a bidentate fashion through the two phosphorus atoms because of the  $Z,Z$  configuration around both C=N bonds.<sup>3</sup> However, we have studied the interaction of this  $Z,Z$ -diphosphine with gold(I), a valency state of gold which shows different co-ordination numbers (2 or 3) and allows bond angles at gold between 90 and 180°. We now report that  $Z,Z$ - $\text{PPh}_2\text{CH}_2\text{CBu}^t=\text{N}-\text{N}=\text{C}(\text{Bu}^t)\text{CH}_2\text{PPh}_2$  displaces  $\text{PPh}_3$  from  $[\text{Au}(\text{PPh}_3)\text{Cl}]$  to give a nine-membered  $P,P'$ -bonded chelate ring in which the  $Z$  configuration is retained around both C=N double bonds in the product  $[\text{AuCl}\{\text{Z},\text{Z}-\text{PPh}_2\text{CH}_2\text{CBu}^t=\text{N}-\text{N}=\text{C}(\text{Bu}^t)\text{CH}_2\text{PPh}_2\}]$  containing three-coordinate gold. In addition to a considerable interest in the chemistry and structures of gold(I)-tertiary phosphine complexes (see below), there is also interest in their medicinal properties, e.g. some such compounds have been shown to have anti-tumour activity and others have been used to treat arthritis.<sup>7,8</sup>

## Results and Discussion

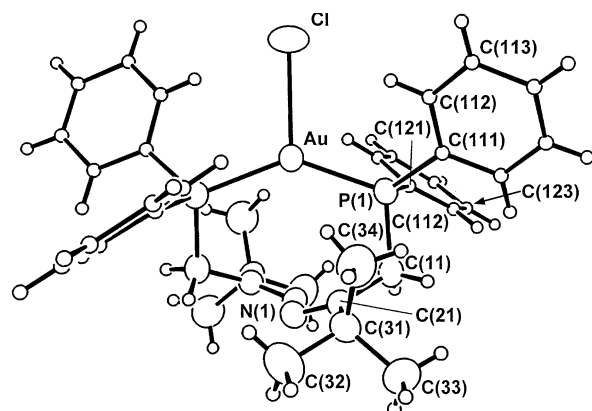
Addition of the azine diphosphine **I** to a dichloromethane solu-



tion of  $[\text{Au}(\text{PPh}_3)\text{Cl}]$  gave  $[\text{AuCl}\{\text{Z},\text{Z}-\text{PPh}_2\text{CH}_2\text{CBu}^t=\text{N}-\text{N}=\text{C}(\text{Bu}^t)\text{CH}_2\text{PPh}_2\}]$  **1a** as a white, air- and light-stable microcrystalline solid in high (>90%) yield. This complex was characterised by C, H, N and Cl analyses, mass spectrometry,  $^1\text{H}$ ,  $^1\text{H}\{-^{31}\text{P}\}$ ,  $^{31}\text{P}\{-^1\text{H}\}$  and  $^{13}\text{C}\{-^1\text{H}\}$  NMR spectroscopy (see Experimental section), its infrared spectrum ( $4000\text{--}200\text{ cm}^{-1}$ ), and by single-crystal X-ray diffraction analysis. The molecule (Fig. 1), which has  $C_2$  symmetry, contains a nine-membered chelate ring in which the azine diphosphine acts as a bidentate  $P,P'$ -bonded ligand and retains the  $Z,Z$  configuration. Selected bond lengths and angles are in the caption to Fig. 1. The geometry around the three-coordinate gold atom is trigonal planar and the gold and chlorine atoms lie on a  $C_2$  axis. The  $\text{C}(31)\text{--}\text{C}(21)=\text{N}(1)\text{--}\text{N}(1')$  moiety is very close to planarity with a dihedral angle of  $172.27(37)^\circ$ , i.e. it is essentially in the  $Z$  or extended configuration; the dihedral angle of  $\text{C}(31')\text{--}\text{C}(21')=\text{N}(1')\text{--}\text{N}(1)$  is the same (from symmetry). Both these four-atom moieties are presumably rigid. One would expect some rotation around the  $\text{N}(1)\text{--}\text{N}(1')$  single bond to be possible and the dihedral angle  $\text{C}(21)=\text{N}(1)\text{--}\text{N}(1')\text{--}\text{C}(21')$  is  $144.15(76)^\circ$ . The dihedral angle  $\text{P}(1)\text{--}\text{C}(11)\text{--}\text{C}(21)=\text{N}(1)$  of  $79.09(64)^\circ$  is less than that of  $\text{P}(1)\text{--}\text{C}(11)\text{--}\text{C}(21)\text{--}\text{C}(31)$   $102.97(54)^\circ$ ; this has the effect of reducing the non-bonding interaction between the sterically demanding *tert*-butyl and the  $\text{PPh}_2$  group. The relative arrangement of the two  $\text{Bu}^t$  and the two  $\text{PPh}_2$  groups is shown more clearly in Fig. 2, which also shows better the arrangement of the  $\text{Bu}^t\text{C}(21)=\text{N}(1)\text{--}\text{N}(1')\text{--}\text{C}(21')\text{Bu}^t$  moiety and that the very sterically demanding  $\text{Bu}^t$  groups occupy 'corner' positions on the chelate ring backbone.



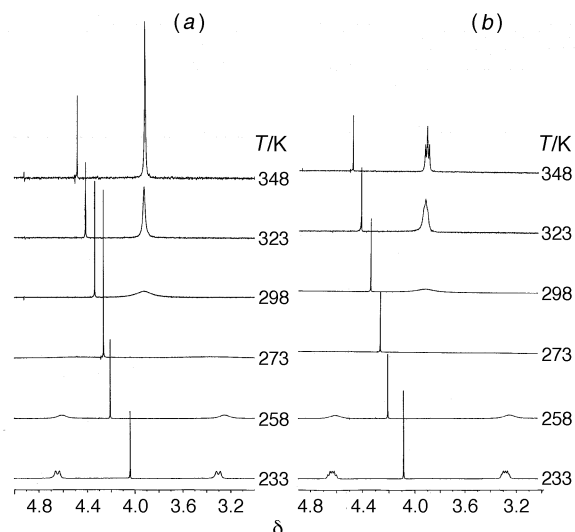
**Fig. 1** An ORTEP<sup>9</sup> drawing of the molecular structure of  $[\text{AuCl}\{\text{Z,Z-PPh}_2\text{CH}_2\text{CBu}^t\text{=N=N=C(Bu)}^t\text{CH}_2\text{PPh}_2\}]$  **1a**. Ellipsoids are shown at the 40% probability level. In the interests of clarity, phenyl carbon and all hydrogen atoms are drawn with an arbitrary radius. Disordered solvent (dichloromethane) is omitted for clarity. Selected interatomic distances (Å) and angles (°): Au–P(1) 2.316(2), Au–Cl 2.654(2), P(1)–C(111) 1.828(6), P(1)–C(121) 1.829(6), P(1)–C(11) 1.852(6), C(11)–C(21) 1.515(8), C(21)–N(1) 1.271(7), C(21)–C(31) 1.525(8) and N(1)–N(1') 1.417(8); P(1)–Au–P(1') 139.51(8), P(1)–Au–Cl 110.24(4), C(111)–P(1)–C(11) 107.6(3), C(121)–P(1)–C(11) 102.3(3), C(111)–P(1)–Au 115.9(2), C(121)–P(1)–Au 111.8(2), C(11)–P(1)–Au 112.0(2), C(21)–C(11)–P(1) 115.8(4), C(11)–C(21)–C(31) 119.8(5), N(1)–C(21)–C(11) 122.6(5), N(1)–C(21)–C(31) 117.6(5) and C(21)–N(1)–N(1') 115.8(5)



**Fig. 2** Alternative view of the molecule **1a** showing the arrangement of  $\text{Bu}^t$  groups relative to the  $\text{PPh}_2$  groups and the  $\text{Bu}^t\text{C}(21)=\text{N}(1)-\text{N}(1')-\text{C}(21)\text{Bu}^t$  moiety, see Discussion

The P–Au–P bond angle in complex **1a** is 139.51(8)°. A range of P–Au–P bond angles has been found for phosphine–gold(I) complexes, from 180° for two-co-ordinate gold in  $[\text{Au}(\text{P-MePh}_2)_2]\text{PF}_6$ ,<sup>10</sup> 176° in the three-co-ordinate complex chloro- $\{\text{bis}(\text{diphenylphosphinomethyl})\text{benzo}[c]\text{phenanthrene}\}$ -gold,<sup>11</sup> 173.2(1)° in  $[\text{AuCl}(\text{PPh}_2\text{CH}_2\text{NPh}_2)_2]$ ,<sup>8</sup> 155.9(1)° in  $[\text{Au}_2\text{Cl}_2(\text{PPh}_2\text{CH}_2\text{PPh}_2)_2]$ <sup>12</sup> and 132.1(1)° in  $[\text{AuCl}(\text{PPh}_3)_2]$ <sup>13</sup> to 120° (average) for  $[\text{Au}(\text{PPh}_3)_3][\text{BPh}_4]$ .<sup>14</sup>

Nine-membered chelate rings are very rare, mainly because of the destabilisation caused by non-bonding interactions within the nine-membered rings due to unfavourable torsion angles imposed by the ring size. With 'classical', potentially chelating ligands such as  $\text{H}_2\text{N}(\text{CH}_2)_n\text{NH}_2$  or  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ , five- or six-membered chelate rings are stable, *i.e.* with  $n = 2$  or 3, but as  $n$  increases the stability falls markedly so that for  $n = 5-8$  these ligands prefer to bridge metals to give polynuclear products rather than form a mononuclear chelate with 8–11-membered rings.<sup>15,16</sup> High strain in medium-sized rings pertains with cycloalkanes  $(\text{CH}_2)_x$  for which it is at a minimum for  $x = 6$  but



**Fig. 3** Changes with temperature in the  $^1\text{H}\{-^{31}\text{P}\}$  (a) and  $^1\text{H}$  (b) NMR spectra of the  $\text{CH}_2$  protons of complex **1a**, at 400.13 MHz and in deuteriotoluene. The sharp singlet above  $\delta$  4.0 is due to an impurity of constant concentration

risers and becomes quite large for  $x = 8-11$  before starting to fall for higher values of  $x$ .<sup>17</sup>

The other factor which destabilises rings is the loss of internal rotational entropy on cyclisation (*e.g.* on chelation); this is cumulative and increases with ring size. Since the nine-membered chelate ring in complex **1a** has two four-atom strain-free but rigid moieties, *e.g.*  $\text{C}(31)-\text{C}(21)=\text{N}(1)-\text{N}(1')$ , there will be less loss of internal rotational entropy on chelation than, for example, with a six-atom  $(\text{CH}_2)_6$  moiety. One would expect less ring strain to be introduced by chelation with a  $\text{CH}_2\text{C}=\text{N}-\text{N}=\text{CCH}_2$  moiety than with, for example, a  $(\text{CH}_2)_6$  moiety. The flexibility within the  $\text{PCH}_2\text{C}=\text{N}-\text{N}=\text{CCH}_2\text{P}$  backbone, around the N–N and two  $\text{CH}_2$  groups, allows the formation of the nine-membered ring. The presence of two  $\text{Bu}^t$  substituents on the backbone probably contributes to the stability of the nine-membered ring; it is well established that suitably positioned substituents contribute towards the stability of rings, an extension of the Thorpe–Ingold effect well established in organic chemistry. We have previously discussed the effects of sterically demanding substituents and internal rotational entropy effects on the stability of very large chelate rings;<sup>16,18</sup> the same effects could be used to stabilise medium-sized chelate rings such as the nine-membered chelate ring in **1a** and in the corresponding silver and copper complexes (see below).

Although the nine-membered chelate ring has rigid sections centred on the two C=N bonds, as mentioned above, one would expect some flexibility centred on the two  $\text{CH}_2$  groups and around the N–N single bond and possibly at the gold centre. This would be manifested as fluxional behaviour in the NMR spectra. At 348 K in the 400.13 MHz  $^1\text{H}\{-^{31}\text{P}\}$  NMR spectrum the four  $\text{CH}_2$  hydrogens of complex **1a** gave a sharp singlet (Fig. 3) and in the  $^1\text{H}$  NMR spectrum they gave a deceptively simple 1:2:1 triplet, due to virtual coupling with the two phosphorus nuclei [ $N = {}^2J(\text{PH}) + {}^4J(\text{P}'\text{H}) = 11.4$  Hz]. As the temperature was lowered the singlet of the  $^1\text{H}\{-^{31}\text{P}\}$  NMR spectrum broadened, disappeared at 273 K, and at 233 K gave a somewhat broadened AX pattern,  $\delta(\text{H}_x)$  3.37,  $\delta(\text{H}_y)$  4.58,  ${}^2J(\text{H}_x\text{H}_y) = 12.3$  Hz, *i.e.* at this temperature the two methylene hydrogens on C(11) are inequivalent, as in the crystal structure. Presumably at 348 K a rapid interconversion of the nine-membered ring causes equivalence of the methylene hydrogens on the NMR timescale. At 233 K in the  $^1\text{H}$  NMR spectrum the resonances were multiplets (see Fig. 3). Fluxional processes were previously observed with the nine-membered ring chelates of ligand **II** in  $[\text{Cr}(\text{CO})_4\{E,Z\text{-PPh}_2\text{CH}_2\text{CBu}^t\text{=N=N=C(Bu)}^t\text{CH}_2\text{PPh}_2\}]$ <sup>5</sup> and in  $[\text{Pd}(\eta^3\text{-C}_3\text{H}_4\text{Me})\{E,Z\text{-PPh}_2\text{CH}_2\text{CBu}^t\text{=N=N=C(Bu)}^t\text{CH}_2\text{PPh}_2\}]$ .<sup>6</sup>



parameters, and 26 restraints, goodness of fit (defined in ref. 24) = 1.008, maximum  $\Delta/\sigma = -0.078$ , maximum  $\Delta\rho = 0.568 \text{ e \AA}^{-3}$ . The absolute configuration (and by implication the space-group assignment) was shown to be correct by the refinement of the Flack parameter,  $x$ , to  $-0.029(9)$ .

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/312.

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