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Complexes of gold, silver and copper with Z,Z-$PPh_2CH_2CBu^t{=}N{-}N{=}C(Bu^t)CH_2PPh_2$ containing a nine-membered chelate ring: crystal structure of $[AuCl\{Z,Z\text{-}PPh_2CH_2CBu^t{=}N{-}N{=}C(Bu^t)CH_2PPh_2\}]$

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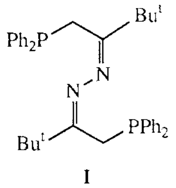
Complexes of gold, silver and copper with the azine diphosphine Z,Z-$PPh_2CH_2CBu^t{=}N{-}N{=}C(Bu^t)CH_2PPh_2$ have been prepared and shown to contain the diphosphine in an unusual nine-membered chelate ring; the crystal structure of the chlorogold derivative $[AuCl\{Z,Z\text{-}PPh_2CH_2CBu^t{=}N{-}N{=}C(Bu^t)CH_2PPh_2\}]$ was determined.

We have studied the interaction of the azine diphosphine Z,Z-$PPh_2CH_2CBu^t{=}N{-}N{=}C(Bu^t)CH_2PPh_2$ **I**[1] with chromium, molybdenum and tungsten,[1,2] with platinum and palladium[3] and with iridium and rhodium.[4] When treated with the substitution-labile palladium(II) and platinum(II) chloride complexes $[PdCl_2(NCPh)_2]$ or $[PtCl_2(NCMe)_2]$ this Z,Z-diphosphine gave large-ring polynuclear complexes of type *trans*-$[\{MCl_2[Z,Z\text{-}PPh_2CH_2CBu^t{=}N{-}N{=}C(Bu^t)CH_2PPh_2]\}_n]$, probably with $n = 2$ for Pd and 6 for Pt.[3] 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-$PPh_2CH_2CBu^t{=}N{-}N{=}C(Bu^t)CH_2PPh_2$ **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 $[Cr(CO)_4\{E,Z\text{-}PPh_2CH_2CBu^t{=}N{-}N{=}C(Bu^t)CH_2PPh_2\}]$,[5] $[PtMe_2\{E,Z\text{-}PPh_2CH_2CBu^t{=}N{-}N{=}C(Bu^t)CH_2PPh_2\}]$[3] and $[Pd(\eta^3\text{-}C_3H_4Me)\{E,Z\text{-}PPh_2CH_2CBu^t{=}N{-}N{=}C(Bu^t)CH_2PPh_2\}]$.[6] However, more commonly the E,Z-diphosphine acts as a terdentate P,N,P'-bonded ligand, as in complexes of the types $[MX\{E,Z\text{-}PPh_2CH_2CBu^t{=}N{-}N{=}C(Bu^t)CH_2PPh_2\}]Y$ (M = Pd, X = Cl, Y = Cl or PF_6; M = Pt, X = Cl, Y = PF_6 or X = Y = I),[3] $[M(CO)_3\{E,Z\text{-}PPh_2CH_2CBu^t{=}N{-}N{=}C(Bu^t)CH_2PPh_2\}]$ (M = Cr, Mo or W);[1] or $[Ir(CO)\{E,Z\text{-}PPh_2CH_2CBu^t{=}N{-}N{=}C(Bu^t)CH_2PPh_2\}]X$ (X = Cl or PF_6).[4]



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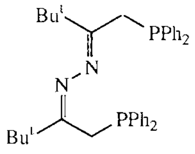

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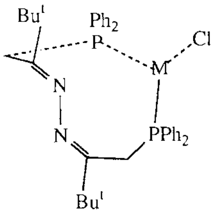

1a M = Au

1b M = Ag

1c M = Cu

Previously, we thought that Z,Z-$PPh_2CH_2CBu^t{=}N{-}N{=}C(Bu^t)CH_2PPh_2$ would not chelate in a bidentate fashion through the two phosphorus atoms because of the Z,Z configuration around both C=N bonds.[3] 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-$PPh_2CH_2CBu^t{=}N{-}N{=}C(Bu^t)CH_2PPh_2$ displaces PPh_3 from $[Au(PPh_3)Cl]$ 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 $[AuCl\{Z,Z\text{-}PPh_2CH_2CBu^t{=}N{-}N{=}C(Bu^t)CH_2PPh_2\}]$ containing three-co-ordinate 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.[7,8]

Results and Discussion

Addition of the azine diphosphine **I** to a dichloromethane solution of $[Au(PPh_3)Cl]$ gave $[AuCl\{Z,Z\text{-}PPh_2CH_2CBu^t{=}N{-}N{=}(Bu^t)CH_2PPh_2\}]$ **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, ^1H, $^1H\text{-}\{^{31}P\}$, $^{31}P\text{-}\{^1H\}$ and $^{13}C\text{-}\{^1H\}$ NMR spectroscopy (see Experimental section), its infrared spectrum (4000–200 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-co-ordinate gold atom is trigonal planar and the gold and chlorine atoms lie on a C_2 axis. The C(31)–C(21)=N(1)–N(1′) moiety is very close to planarity with a dihedral angle of 172.27(37)°, *i.e.* it is essentially in the Z or extended configuration; the dihedral angle of C(31′)–C(21′)=N(1′)–N(1) is the same (from symmetry). Both these four-atom moieties are presumably rigid. One would expect some rotation around the N(1)–N(1′) single bond to be possible and the dihedral angle C(21)=N(1)–N(1′)–C(21′) is 144.15(76)°. The dihedral angle P(1)–C(11)–C(21)=N(1) of 79.09(64)° is less than that of P(1)–C(11)–C(21)–C(31) 102.97(54)°; this has the effect of reducing the non-bonding interaction between the sterically demanding *tert*-butyl and the PPh_2 group. The relative arrangement of the two Bu^t and the two PPh_2 groups is shown more clearly in Fig. 2, which also shows better the arrangement of the $Bu^tC(21){=}N(1){-}N(1'){=}C(21')Bu^t$ moiety and that the very sterically demanding Bu^t groups occupy ‘corner’ positions on the chelate ring backbone.

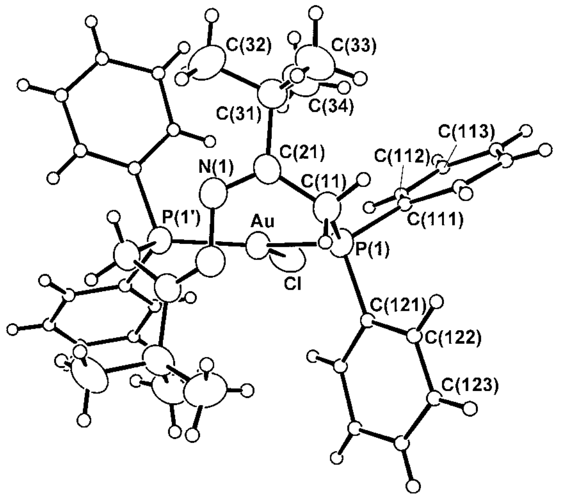

Fig. 1 An ORTEX[9] drawing of the molecular structure of [AuCl{Z,Z-$PPh_2CH_2CBu^t$=N–N=C(Bu^t)CH_2PPh_2}] **1a**. Ellipsoids are shown at the 40% probability level. In the interests of clarity, phenyl carbon and all hydrogen atoms are drawn with an arbitrary radius. Disordered solvent (dichloromethane) 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)

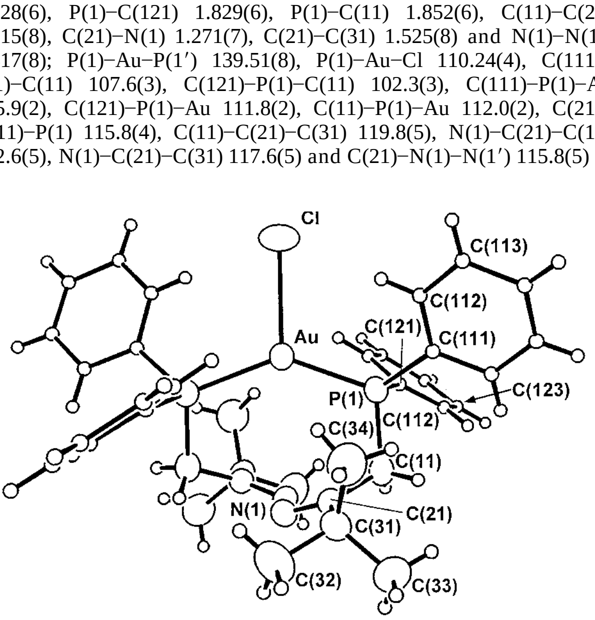

Fig. 2 Alternative view of the molecule **1a** showing the arrangement of Bu^t groups relative to the PPh_2 groups and the Bu^tC(21)=N(1)–N(1′)=C(21′)Bu^t moiety, see Discussion

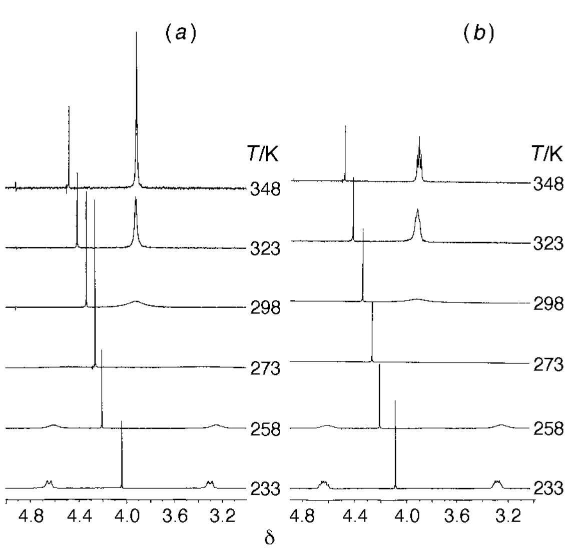

Fig. 3 Changes with temperature in the ^1H-{^{31}P} (*a*) and ^1H (*b*) NMR spectra of the CH_2 protons of complex **1a**, at 400.13 MHz and in deuteriotoluene. The sharp singlet above δ 4.0 is due to an impurity of constant concentration

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 [Au($PMePh_2$)$_2$]PF_6,[10] 176° in the three-co-ordinate complex chloro{bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene}gold,[11] 173.2(1)° in [AuCl($PPh_2CH_2NPh_2$)$_2$],[8] 155.9(1)° in [Au_2Cl_2($PPh_2CH_2PPh_2$)$_2$][12] and 132.1(1)° in [AuCl(PPh_3)$_2$][13] to 120° (average) for [Au(PPh_3)$_3$][BPh_4].[14]

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 $H_2N(CH_2)_nNH_2$ or $Ph_2P(CH_2)_nPPh_2$, 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.[15,16] High strain in medium-sized rings pertains with cycloalkanes $(CH_2)_x$ for which it is at a minimum for $x = 6$ but rises and becomes quite large for $x = 8$–11 before starting to fall for higher values of x.[17]

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.* C(31)–C(21)=N(1)–N(1′), there will be less loss of internal rotational entropy on chelation than, for example, with a six-atom $(CH_2)_6$ moiety. One would expect less ring strain to be introduced by chelation with a CH_2C=N–N=CCH_2 moiety than with, for example, a $(CH_2)_6$ moiety. The flexibility within the PCH_2C=N–N=CCH_2P backbone, around the N–N and two CH_2 groups, allows the formation of the nine-membered ring. The presence of two 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;[16,18] 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 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 ^1H-{^{31}P} NMR spectrum the four CH_2 hydrogens of complex **1a** gave a sharp singlet (Fig. 3) and in the ^1H NMR spectrum they gave a deceptively simple 1:2:1 triplet, due to virtual coupling with the two phosphorus nuclei [$N = |^2J(PH) + {}^4J(P'H)| = 11.4$ Hz]. As the temperature was lowered the singlet of the ^1H-{^{31}P} NMR spectrum broadened, disappeared at 273 K, and at 233 K gave a somewhat broadened AX pattern, $\delta(H_x)$ 3.37, $\delta(H_y)$ 4.58, $^2J(H_xH_y) = 12.3$ 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 ^1H NMR spectrum the resonances were multiplets (see Fig. 3). Fluxional processes were previously observed with the nine-membered ring chelates of ligand **II** in [$Cr(CO)_4${E,Z-$PPh_2CH_2CBu^t$=N–N=C(Bu^t)CH_2PPh_2}][5] and in [Pd(η^3-C_3H_4Me){E,Z-$PPh_2CH_2CBu^t$=N–N=C(Bu^t)CH_2PPh_2}].[6]

We have also prepared complexes of silver(I) chloride, **1b**, and copper(I) chloride, **1c**, with **I**. These appear to be analogous to **1a** and show similar fluxional behaviour. Treatment of $[Ag_4Cl_4(PPh_3)_4]$[19a] with **I** gave [AgCl{*Z*,*Z*-$PPh_2CH_2CBu^t$=N−N=C(Bu^t)CH_2PPh_2}] **1b** as white crystals, in 65% yield. This complex was characterised by elemental analysis (C, H, N and Cl) and by its mass spectrum, which gave the right *m/z* profile centred on 673, corresponding to $M - \mathrm{Cl}$. The infrared spectrum (4000–200 cm^{-1}) was very similar to that of **1a**. The ^{31}P-{^1H} NMR spectrum showed one type of phosphorus at δ 6.3 with $^1J(^{107}AgP) = 417$ and $^1J(^{109}AgP) = 479$ Hz. These values are typical for three-co-ordinate silver–tertiary phosphine complexes.[20] The spectrum remained sharp up to 333 K at 36.2 MHz, indicating that no intermolecular exchange of the phosphine was taking place. This contrasts with other phosphine complexes of silver(I) which exchange rapidly at ambient temperature.[20] In the 99.5 MHz ^1H NMR spectrum the slow-exchange limit was at *ca.* 258 K with non-equivalent CH_2 hydrogens, one of which was coupled to silver $^3J(AgH) \approx 4$ Hz and $^2J(HH) = 12.2$ Hz; both methylene hydrogens gave virtually coupled triplets in the low-temperature ^1H NMR spectrum. In the ^{13}C-{^1H} spectrum (at *ca.* 298 K) the PCH_2 carbon gave a virtual triplet with $N = |^1J(PC) + {}^3J(PC)| = 7.4$ Hz.

The copper(I) complex [CuCl{*Z*,*Z*-$PPh_2CH_2CBu^t$=N−N=C(Bu^t)CH_2PPh_2}] **1c** was prepared in a similar manner to the silver complex as white, air-stable crystals in 88% yield. It was characterised by elemental analysis (C, H, N and Cl), its mass spectrum (FAB) and by its infrared spectrum in which there was a strong band at 275 cm^{-1} (Nujol mull) tentatively assigned to ν(Cu−Cl) (terminal); this band was absent in the KBr disc, presumably due to replacement of Cl by Br. No analogous bands were observed for the complexes of Ag or Au. Complex **1c** also showed variable-temperature NMR spectra. The slow-exchange limit for CH_2 hydrogens was at ambient temperature, *i.e.* the rates of site exchange for the PCH_2 protons in the three complexes decreased in the order Au > Ag > Cu. We suggest that **1b** and **1c** are three-co-ordinate with similar structures to that of **1a**. The infrared spectra of **1a**–**1c**, recorded as Nujol mulls, were almost identical over the range 4000–300 cm^{-1}. The FAB mass spectra of all three complexes **1a**–**1c** showed strong signals due to loss of Cl from the parent ion.

Experimental

General methods and techniques were as reported in previous papers from this laboratory.[4b]

Preparation of the complexes

[AuCl{*Z*,*Z*-$PPh_2CH_2CBu^t$=N−N=C(Bu^t)CH_2PPh_2}] 1a. The azine diphosphine **I** (170 mg, 0.30 mmol) was added to a stirred solution of $[AuCl(PPh_3)]$[21] (150 mg, 0.30 mmol) in dichloromethane (5 cm^3). After 30 min the solution was filtered though a Celite plug and concentrated to low volume (*ca.* 0.5 cm^3) under reduced pressure. Addition of cyclohexane (*ca.* 2 cm^3) to the resultant residue gave the required complex as white microcrystals. Yield 220 mg, 92%. δ(^{31}P) ($CDCl_3$, 101.27 MHz) 35.9. δ(^1H) ($CDCl_3$, 99.5 MHz, 223 K) 0.70 (s, 18 H, CMe_3); 3.37 [dt, 2 H, $^2J(HH) = 12.3$, $|^2J(PH) + {}^4J(PH)| = 11.3$, PCH] and 4.58 [dt, 2 H, $^2J(HH) = 12.3$, $|^2J(PH) + {}^4J(PH)| = 12.9$ Hz, PCH]. δ(^{13}C) ($CDCl_3$, 62.5 MHz) 27.9 (s, 6 C, C*Me*$_3$), 29.3 [t, 2 C, $|^1J(PC) + {}^3J(PC)| = 20.6$ Hz, PCH_2] and 170.6 (s, 2 C, C=N). IR: ν(C=N) 1615 cm^{-1}. Mass spectrum: *m/z* 761 (100%), $M - \mathrm{Cl}$ (Found: C, 56.9; H, 6.15; Cl, 4.05; N, 3.3. $C_{36}H_{42}AuClN_2P_2 \cdot C_6H_{12}$ requires C, 57.25; H, 6.15; Cl, 4.0; N, 3.3%).

[AgCl{*Z*,*Z*-$PPh_2CH_2CBu^t$=N−N=C(Bu^t)CH_2PPh_2}] 1b. This complex was made similarly by adding **I** to a dichloromethane solution of $[Ag_4Cl_4(PPh_3)_4]$ in 4 : 1 mole proportion and isolated as above. It formed white microcrystals from cyclohexane. Yield 65%. δ(^{31}P) ($CDCl_3$, 101.27 MHz) 6.3 [$^1J(^{107}AgP) = 417$, $^1J(^{109}AgP) = 479$ Hz]. δ(^1H) ($CDCl_3$, 99.5 MHz, 258 K) 0.68 (s, 18 H, CMe_3), 3.31 [dt, 2 H, $^2J(HH) = 12.2$, $|^2J(PH) + {}^4J(PH)| = 9.7$, $^3J(AgH) = 3.9$, PCH] and 4.58 [dt, 2 H, $^2J(HH) = 12.2$, $|^2J(PH) + {}^4J(PH)| = 12.4$ Hz, PCH]. δ(^{13}C) ($CDCl_3$, 62.5 MHz) 27.7 (s, 6 C, C*Me*$_3$), 27.3 [t, 2 C, $|^1J(PC) + {}^3J(PC)| = 7.4$ Hz, PCH_2] and 173.5 (s, 2 C, C=N). IR: ν(C=N) 1620 cm^{-1}. Mass spectrum: *m/z* 673 (100%), $M - \mathrm{Cl}$ (Found: C, 61.65; H, 5.85; Cl, 4.75; N, 3.95. $C_{36}H_{42}AgClN_2P_2$ requires C, 61.05; H, 6.0; Cl, 5.0; N, 3.95%).

[CuCl{*Z*,*Z*-$PPh_2CH_2CBu^t$=N−N=C(Bu^t)CH_2PPh_2}] 1c. This complex was made from **I** and $[Cu_4Cl_4(PPh_3)_4]$[19b] and isolated similarly to **1b**, as white microcrystals. Yield 88%. δ(^{31}P) ($CDCl_3$, 101.27 MHz) −10.1. δ(^1H) ($CDCl_3$, 99.5 MHz) 0.68 (s, 18 H, CMe_3), 3.17 [dt, 2 H, $^2J(HH) = 12.5$, $|^2J(PH) + {}^4J(PH)| = 10.5$, PCH] and 4.49 [dt, 2 H, $^2J(HH) = 12.5$, $|^2J(PH) + {}^4J(PH)| = 12.3$, PCH]. δ($^{13}C$) ($CDCl_3$, 62.5 MHz) 27.7 (s, 6 C, C*Me*$_3$), 27.6 [t, 2 C, $|^1J(PC) + {}^3J(PC)| = 9.3$ Hz, PCH_2] and 170.8 (s, 2 C, C=N). IR: ν(C=N) 1622, ν(Cu−Cl) 275 cm^{-1}. Mass spectrum: *m/z* 627 (100%), $M - \mathrm{Cl}$ (Found: C, 67.45; H, 7.25; Cl, 5.05; N, 3.7. $C_{36}H_{42}ClCuN_2P_2 \cdot C_6H_{12}$ requires C, 67.45; H, 7.3; Cl, 4.75; N, 3.75%).

Crystallography

Colourless crystals of [AuCl{*Z*,*Z*-$PPh_2CH_2CBu^t$=N−N=C(Bu^t)CH_2PPh_2}] were obtained by diffusion of benzene into a solution of the complex in dichloromethane. A single crystal of dimensions 0.41 × 0.30 × 0.27 mm suitable for X-ray diffraction analysis was selected and mounted on a quartz glass fibre.

Crystal data. $C_{36}H_{42}AuClN_2P_2 \cdot CH_2Cl_2$, $M = 882.00$ (including solvate), tetragonal, space group $P4_32_12$ (no. 96) $a = 13.8156(8)$, $c = 20.874(2)$ Å, $U = 3984.2(5)$ Å^3, $Z = 4$, $D_c = 1.470$ Mg m^{-3}, $F(000) = 1760$, $T = 200$ K.

7256 Reflections were measured (3511 unique, $R_{int} = 0.0345$) on a Stoe STADI4 four-circle diffractometer in the range $3 < 2\theta < 50°$ operating in the ω–θ scan mode and using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Three standard reflections measured every hour showed a negligible variation in intensity. Data were corrected for Lorentz-polarisation effects and an absorption correction was applied based on azimuthal ψ scans [transmission factors 0.326–0.556, μ(Mo-Kα) = 4.00 mm^{-1}].

Structure solution and refinement. The two enantiomorphic space groups, $P4_12_12$ and $P4_32_12$, were consistent with the observed systematic absences; $P4_32_12$ was tried initially and shown to be correct by the refinement of the Flack parameter[22] (see below). The gold and chlorine atoms were located on special positions (a C_2 axis which runs diagonally across the *ab* face at $z = 0$, along the chlorine–gold vector and through the middle of the N−N bond) using Patterson heavy-atom methods (SHELXS 86);[23] subsequent Fourier-difference techniques located the remaining heavy atoms. Refinement was carried out by full-matrix least-squares analysis on F^2 (SHELXL 93)[24] using all the unique data. All non-hydrogen atoms were assigned anisotropic displacement parameters. Phenyl rings were restrained to be flat and of overall C_{2v} symmetry. All hydrogen atoms were included using a riding model with isotropic displacement parameters. Substantial electron density was evident on the residual Fourier-difference synthesis. This was modelled as a dichloromethane molecule positioned on the C_2 axis at $z = 0$ and disordered over four positions. All C−Cl distances were restrained to be equal and soft restraints were applied to the anisotropic displacement parameters of the chlorine atoms. The weighting scheme was $w = 1/[\sigma^2(F_o{}^2) + (0.0369P)^2]$ where $P = (F_o{}^2 + 2F_c{}^2)/3$. The final $wR(F^2)$ was 0.0760, with a conventional $R(F)$ of 0.0297 (*R* factors defined in ref. 24) for 2795 observed reflections [with $F > 4\sigma(F_o)$], 235 parameters, and 26 restraints, goodness of fit (defined in ref. 24) = 1.008, maximum $\Delta/\sigma = -0.078$, maximum $\Delta\rho = 0.568$ e $Å^{-3}$. 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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