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

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

We have studied the interaction of the azine diphosphine \( \text{Z}, \text{Z}-\text{PPPh}_2\text{C}_2\text{Bu}^\text{t}-\text{N} -\text{N} = \text{C} (\text{Bu}^\text{t}) \text{CH}_2\text{PPPh}_2 \) with chromium, molybdenum and tungsten, with platinum and palladium, and with iridium and rhodium. When treated with the substitution-labile palladium(II) and platinum(II) chloride complexes [PtCl(NCPh)] or [PtCl(NCM e)] this Z, Z-diphosphine gave large-ring polymeric complexes of type trans-[{MCl(\text{Z}, \text{Z}-\text{PPPh}_2\text{C}_2\text{Bu}^\text{t}-\text{N} -\text{N} = \text{C} (\text{Bu}^\text{t}) \text{CH}_2\text{PPPh}_2)]], probably with \( n = 2 \) for Pd and 6 for Pt. Frequently, however, when this diphosphine displaces other ligands from a metal, isomerisation around one of the C-N double bonds occurs and the resultant \( \text{E}, \text{Z}-\text{PPPh}_2\text{C}_2\text{Bu}^\text{t}-\text{N} -\text{N} = \text{C} (\text{Bu}^\text{t}) \text{CH}_2\text{PPPh}_2 \) II can act as a bidentate chelate (P, P-1 bonded) or terdentate ligand (P, P, P-3 bonded) giving mononuclear complexes. Examples of mononuclear complexes which have a nine-membered chelating ring include \([\text{Cr}(\text{CO})_3] (\text{Z}, \text{Z}-\text{PPPh}_2\text{C}_2\text{Bu}^\text{t}-\text{N} -\text{N} = \text{C} (\text{Bu}^\text{t}) \text{CH}_2\text{PPPh}_2)] \) \(^1\) \( \text{[PtCl(\text{Z}, \text{Z}-\text{PPPh}_2\text{C}_2\text{Bu}^\text{t}-\text{N} -\text{N} = \text{C} (\text{Bu}^\text{t}) \text{CH}_2\text{PPPh}_2)]} \) \(^3\) \( \text{[Pd(\eta^3-\text{C}_3\text{H}_5\text{M}e}) (\text{Z}, \text{Z}-\text{PPPh}_2\text{C}_2\text{Bu}^\text{t}-\text{N} -\text{N} = \text{C} (\text{Bu}^\text{t}) \text{CH}_2\text{PPPh}_2)]} \) \(^4\) However, more commonly the E, Z-diphosphine acts as a terdentate P, N, P-3 bonded ligand, as in complexes of the type [MX(\text{E}, \text{Z}-\text{PPPh}_2\text{C}_2\text{Bu}^\text{t}-\text{N} -\text{N} = \text{C} (\text{Bu}^\text{t}) \text{CH}_2\text{PPPh}_2)] (M = Pd, X = Cl, Y = Cl or PF\(_3\), M = Pt, X = Cl, Y = PF\(_3\) or X = Y = Cl). \(^8\) \( \text{[CO}] (\text{E}, \text{Z}-\text{PPPh}_2\text{C}_2\text{Bu}^\text{t}-\text{N} -\text{N} = \text{C} (\text{Bu}^\text{t}) \text{CH}_2\text{PPPh}_2]) \) \( \text{(M} = \text{Cr, Mo or W}) \) \(^9\) or \( \text{[IICO}] (\text{E}, \text{Z}-\text{PPPh}_2\text{C}_2\text{Bu}^\text{t}-\text{N} -\text{N} = \text{C} (\text{Bu}^\text{t}) \text{CH}_2\text{PPPh}_2)]X \) \( \text{(X} = \text{Cl or PF}_3) \) \(^4\) Furthermore, we thought that \( \text{Z}, \text{Z}-\text{PPPh}_2\text{C}_2\text{Bu}^\text{t}-\text{N} -\text{N} = \text{C} (\text{Bu}^\text{t}) \text{CH}_2\text{PPPh}_2 \) would not chelate in a bidentate fashion through the two phosphorus atoms because of the Z,Z configuration around both C=N bonds. 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 \( \text{Z}, \text{Z}-\text{PPPh}_2\text{C}_2\text{Bu}^\text{t}-\text{N} -\text{N} = \text{C} (\text{Bu}^\text{t}) \text{CH}_2\text{PPPh}_2 \) displaces PPPh2 from \( \text{[Au(PPh}_3\text{Cl}] \) to give a nine-membered P, P-3 bonded chelate ring in which the Z configuration is retained around both C=N double bonds in the product \( \text{[AuCl} [\text{Z}, \text{Z}-\text{PPPh}_2\text{C}_2\text{Bu}^\text{t}-\text{N} -\text{N} = \text{C} (\text{Bu}^\text{t}) \text{CH}_2\text{PPPh}_2] \) containing threecoordinate 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 antitumour activity and others have been used to treat arthritis. \(^8\)

**Results and Discussion**

A dition of the azine diphosphine to a dichloromethane solution of \( \text{[Au(PPh}_3\text{Cl}] \) gave \( \text{[AuCl} [\text{Z}, \text{Z}-\text{PPPh}_2\text{C}_2\text{Bu}^\text{t}-\text{N} -\text{N} = \text{C} (\text{Bu}^\text{t}) \text{CH}_2\text{PPPh}_2] \) 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, \(^1\)H- and \(^31\)P- 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 \( C_3 \) symmetry, contains a nine-membered chelate ring in which the azine diphosphine acts as a bidentate P, P-3 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 fouratom 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 PPh2 group. The relative arrangement of the two Bu3N and the two PPh2 groups is shown more clearly in Fig. 2, which also shows better the arrangement of the \( \text{Bu}(C(21)) - N(1') - C(21') - \text{Bu}^\text{t} \) moiety and that the very sterically demanding Bu3N groups occupy ‘corner’ positions on the chelate ring backbone.
MePh complexes, from 180 rings. Six-membered chelate rings are stable, [C(11)P(1) 1.417(8); P(1) of P 436 cycloalkanes (CH ligands such as H imposed by the ring size. With "classical", potentially chelating in the nine-membered rings due to unfavourable torsion angles of the destabilisation caused by non-bonding interactions with-

Gold, Fig. 2 Alternative view of the molecule 1a showing the arrangement of Bu groups relative to the PPh groups and the BuC(21)-N(1)–C(21) Bu 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 [Au(P-MeP)2]2PF6 at 176° in the three-co-ordinate complex chloro(bis(diphenylphosphinomethyl)benzyl)[phenanthrene]-gold11 173.21(1° in [Au2Cl4(PPh2CH2PPh2)2]12 and 132.11(1° in [AuCl(PPh3)2]13 to 120° (average) for [Au(PPh3)3]2BF4.14

N lone-pair chelated rings are very rare, mainly because of the destabilisation caused by non-bonding interactions within the n-membered rings due to unfavourable torsion angles imposed by the ring size. With "classical", potentially chelating ligands such as H:N(CH3)2N=H or PhPC6H4PPh2 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 (CH3)n for which it is a minimum for n = 6 but

Fig. 1 An ORTEP drawing of the molecular structure of [AuCl(Z- PPh2CH2C6Bu=NC(CBu)2PPh2)] 1a. Ellipsoids are shown at the 50% probability level. Anisotropic displacement parameters 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-C 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(21) 1.525(8) and N(1)-N(1') 1.417(8); P(1)-Au-P(1') 130.51(8), P(1)-Au-C 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 115.2(2), C(121)-P(1)-Au 112.8(2), C(121)-P(1)-Au 112.9(2), C(21)-P(1)-Au 111.8(2), C(121)-P(1)-Au 112.9(2), C(21)-P(1)-Au 111.8(2), C(111)-P(1)-Au 111.8(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)

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Fig. 3 Changes with temperature in the 1H-(PPh3) spectra of the CH3 protons of complex 1a, at 400.13 MHz and in deuteriotoluene. The sharp singlet above 6 4.0 is due to an impurity of constant concentration.
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 [AgCI(CPPh3)]2+ with 1 gave [AgClI(Z–Z-PPPh2CH,CBu–N–N–C(Bu')CH,CPPh3)] 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 – Cl. The infrared spectrum (9000–200 cm–1) was very similar to that of 1a. The 31P{1H} NMR spectrum showed one type of phosphorus at δ 6.3 with 131P A coupling of 417 and 133A coupling of 479 Hz. These values are typical for three-coordinate silver–tether phosphine complexes. The spectrum remained sharp up to 333 K at 36.2 M Hz, indicating that no intermolecular exchange of the phosphine face occurred. This contrasts with other phosphine complexes of silver(I) which exchange rapidly at ambient temperature. In the 99.5 M Hz 13C NMR spectrum the slow-exchange limit was at ca. 258 K with non-equivalent CH2 hydrogens, one of which was coupled to silver 31P (JAg = 4 Hz and 3J (H H) = 12.2 Hz); both methylene hydrogens gave virtually coupled triplets in the low-temperature 13C NMR spectrum. In the 31P{1H} (H) spectrum (at ca. 298 K) the PCH2 carbon gave a virtual triplet with N = 3J (PC) + 3J (PCC) = 7.4 Hz.

The copper(i) complex [CuClI(Z–Z-PPPh2CH,CBu–N–N–C(Bu')CH,CPPh3)] 1c also showed variable-temperature 13C and 31P spectra. The slow-exchange limit for CH2 hydrogens was at ambient temperature, i.e. the rates of site exchange for the CH2 protons in the three complex decreased in the order Cu > Ag > Cu. We suggest that 1b and 1c are three-coordinate with similar structures to that of 1a. The infrared spectra of 1a–1c, recorded as Nujol mulls, were almost identical over the range 4000–3000 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.

Preparation of the complexes

[AgClI(Z–Z-PPPh2CH,CBu–N–N–C(Bu')CH,CPPh3)] 1a. The azine diphosphine I (170 mg, 0.30 mmol) was added to a stirred solution of [AgClI(PPh3)]2 (150 mg, 0.30 mmol) in dichloromethane (5 cm3). A ter 30 min the solution was filtered through a Celite plug and concentrated to low volume (ca. 0.5 cm3) under reduced pressure. A dilution of cyclohexane (ca. 2 cm3) to the resultant residue gave the required complex as white microcrystals. Yield 220 mg, 92%. δ31P (CDCl3, 101.27 M Hz) 35.9. δ(1H) (CDCl3, 99.5 M Hz, 233 K) 0.70 (s, 18 H, CM eq); 3.37 (dt, 2 H, δ (H H) = 12.3, 3J (PH + δ (PCH2) = 11.3, 4J (H C) = 4.58 (dt, 2 H, δ (H H) = 12.3, 4J (PH + δ (PCH2) = 12.9 Hz, PCH2). δ31P (CDCl3, 62.5 M Hz) 27.9 (s, 6 C, CM eq), 29.3 (t, 2 C, 3J (PC) + 3J (PCC) = 20.6 Hz, PCH2 and 170.6 (s, 2 C, C=C), 1R): v(C–N) 1615 cm–1. Mass spectrum: m/z 761 (100%), M – Cl (Found: C, 56.9; H, 6.15; Cl, 4.05; N, 3.3. C20H20AgCuClI requires C, 57.25; H, 6.15; Cl, 4.0; N, 3.3%).

[AgClI(Z–Z-PPPh2CH,CBu–N–N–C(Bu')CH,CPPh3)] 1b. This complex was made similarly by adding I to a dichloromethane solution of [AgClI(PPh3)]2 in 4:1 mole proportion and isolated as above. It formed white microcrystals from cyclohexane. Yield 65%. δ31P (CDCl3, 101.27 M Hz) 6.3 J (133A coupling of 417, 135A coupling of 479 Hz). δ(1H) (CDCl3, 99.5 M Hz, 258 K) 0.68 (s, 18 H, CM eq), 3.31 (dt, 2 H, 3J (H H) = 12.2, 3J (PH + δ (PCH2) = 12.4 Hz, PCH2). δ31P (CDCl3, 62.5 M Hz) 27.7 (s, 6 C, CM eq), 27.3 (t, 2 C, 3J (PC) + 3J (PCC) = 7.4 Hz, PCH2 and 173.5 (s, 2 C, C=C). 1R): v(C–N) 1620 cm–1. Mass spectrum: m/z 763 (100%), M – Cl (Found: C, 61.65; H, 5.85; Cl, 4.75; N, 3.95. C24H24AgCuClI requires C, 61.05; H, 6.0; Cl, 5.0; N, 3.95%).

[CuClI(Z–Z-PPPh2CH,CBu–N–N–C(Bu')CH,CPPh3)] 1c. This complex was made from I and [CuClI(PPh3)]2 and isolated similarly to 1b, as white microcrystals. Yield 88%. δ31P (CDCl3, 101.27 M Hz) 10.1. δ(1H) (CDCl3, 99.5 M Hz) 0.68 (s, 18 H, CM eq), 3.17 (dt, 2 H, 3J (H H) = 12.5, 3J (PH + δ (PCH2) = 10.5, PCH2) and 4.49 (dt, 2 H, 3J (H H) = 12.5, 3J (PH + δ (PCH2) = 12.3, PCHI). δ31P (CDCl3, 62.5 M Hz) 27.7 (s, 6 C, CM eq), 27.6 (t, 2 C, 3J (PC) + 3J (PCC) = 9.3 Hz, PCH2 and 170.8 (s, 2 C, C=C). 1R): v(C–N) 1622, v(Cu–Cl) 275 cm–1. Mass spectrum: m/z 627 (100%), M – Cl (Found: C, 67.45; H, 7.25; Cl, 5.05; N, 3.7. C20H20CuClICuCu requires C, 67.45; H, 7.3; Cl, 4.75; N, 3.75%).

Crystallography

Colourless crystals of [CuClI(Z–Z-PPPh2CH,CBu–N–N–C(Bu’)CH,CPPh3)] were obtained by diffusion of benzene into a solution of the complex in dichloromethane A single crystal of dimensions 0.10 x 0.20 x 0.20 mm suitable for X-ray diffraction analysis was selected and mounted on a quartz glass fibre.

Crystal data. C50H32A2CuICuICuICuCl2, M = 882.00 (including solvate), tetragonal, space group P4212 (no. 96) a = 13.8156(8), c = 20.874(2) Å, U = 3984.24(5) Å3, Z = 4, D = 1.470 M g m–3, F(000) = 1760, T = 200 K

2756 Reflections were measured (3511 unique, Rint = 0.0345) on a Stoe STAD4 four-circle diffractometer in the range 3 < 20 < 50° in the 0-0 scan mode and using graphite-monochromated Mo-Kα radiation (λ = 0.71073 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 ω scans [transmission factors 0.326–0.356, μ(Mo-Kα) = 4.00 mm–1].

Structure solution and refinement. The two enantiomorphous space groups, P 4212 and P 4212, were consistent with the observed systematic absences; P 4212 was tried initially and shown to be correct by the refinement of the Flack parameter (see below). The gold and chlorine atoms were located on special positions (a C2 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) subsequent Fourier-difference techniques located the remaining heavy atoms. Refinement was carried out by full-matrix least-squares analysis on F2 (SHELXL 93) using all the unique data. All non-hydrogen atoms were assigned anisotropic displacement parameters. Phenyl rings were restrained to be flat and of overall C2 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 C2 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/[σ2(F2) + (0.0369P)2] where P = (F2 + 2F0)/3. The final wR(F2) was 0.0760, with a conventional R(F) of 0.0297 (R factors defined in ref. 24) for 2795 observed reflections [with F > 4σ(F)].
parameters, and 26 restraints, goodness of fit (defined in ref. 24) = 1.008, maximum ∆σ = 0.078, maximum ∆ρ = 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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