Synthesis, structures and reactions of cyclometallated gold complexes containing (2-diphenylarsino-*n*-methyl)phenyl ($n = 5, 6$)

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Reaction of $(C_6H_3\text{-}2\text{-}AsPh_2\text{-}n\text{-}Me)Li$ ($n = 5$ or 6) with $[AuBr(AsPh_3)]$ at −78 °C gives the corresponding cyclometallated gold(I) complexes $[Au_2\{(\mu\text{-}C_6H_3\text{-}n\text{-}Me)AsPh_2\}_2]$ [$n = 5$, (**1**); $n = 6$, (**9**)]. **1** undergoes oxidative addition with halogens and with dibenzoyl peroxide to give digold(II) complexes $[Au_2X_2\{(\mu\text{-}C_6H_3\text{-}5\text{-}Me)AsPh_2\}_2]$ [X = Cl (**2a**), Br (**2b**), I (**2c**) and O_2CPh (**3**)] containing a metal–metal bond between the $5d^9$ metal centres. Reaction of **2a** with AgO_2CMe or of **3** with C_6F_5Li gives the corresponding digold(II) complexes in which X = O_2CMe (**4**) and C_6F_5 (**6**), respectively. The Au–Au distances increase in the order **4** < **2a** < **2b** < **2c** < **6**, following the covalent binding tendency of the axial ligand. Like the analogous phosphine complexes, **2a**–**2c** and **6** in solution rearrange to form C–C coupled digold(I) complexes $[Au_2X_2\{\mu\text{-}2,2'\text{-}Ph_2As(5,5'\text{-}Me_2C_6H_3C_6H_3)AsPh_2\}]$ [X = Cl (**5a**), X = Br (**5b**), X = I (**5c**) and C_6F_5 (**7**)] in which the gold atoms are linearly coordinated by As and X. In contrast, the products of oxidative additions to **9** depend markedly on the halogens. Reaction of **9** with chlorine gives the gold(I)–gold(III) complex, $[ClAu\{\mu\text{-}2\text{-}Ph_2As(C_6H_3\text{-}6\text{-}Me)\}AuCl\{(6\text{-}MeC_6H_3)\text{-}2\text{-}AsPh_2\}\text{-}\kappa^2 As,C]$ (**10**), which contains a four-membered chelate ring, $Ph_2As(C_6H_3\text{-}6\text{-}Me)$, in the coordination sphere of the gold(III) atom. When **10** is heated, the ring is cleaved, the product being the digold(I) complex $[ClAu\{\mu\text{-}2\text{-}Ph_2As(C_6H_3\text{-}6\text{-}Me)\}Au\{AsPh_2(2\text{-}Cl\text{-}3\text{-}Me\text{-}C_6H_3)\}]$ (**11**). Reaction of **9** with bromine at 50 °C gives a monobromo digold(I) complex (**12**), which is similar to **11** except that the 2-position of the substituted aromatic ring bears hydrogen instead halogen. Reaction of **9** with iodine gives a mixture of a free tertiary arsine, $(2\text{-}I\text{-}3\text{-}MeC_6H_3)AsPh_2$ (**13**), a digold diiodo compound (**14**) analogous to **11**, and a gold(I)–gold(III) zwitterionic complex $[I_2Au^{III}\{(\mu\text{-}C_6H_3\text{-}2\text{-}AsPh_2\text{-}6\text{-}Me)\}_2Au^{I}]$ (**15**) in which the bridging units are arranged head-to-head between the metal atoms. The structures of **2a**–**2c** and **4–15** have been determined by single-crystal X-ray diffraction analysis. The different behaviour of **1** and **9** toward halogens mirrors that of their phosphine analogues; the 6-methyl substituent blocks C–C coupling of the aryl residues in the initially formed oxidative addition product. In the case of **9**, the greater lability of the Au–As bond in the initial oxidative addition product may account for the more complex behaviour of this system compared with that of its phosphine analogue.

Introduction

Binuclear complexes in which a pair of linearly coordinated gold(I) atoms (electron configurations $5d^{10}\cdots 5d^{10}$) are held closely together by a pair of 1,1-bifunctional ligands, such as bis(diphenylphosphino)methane,[1] dialkyldithiocarbamate,[2] phosphorus bis(ylides)[3,4] and methylenethiophosphinate,[5] have attracted interest because the complexes can undergo oxidative addition with halogens or pseudohalogens to give metal–metal bonded ($5d^9$–$5d^9$) digold(II) complexes. The homobinuclear complexes often rearrange spontaneously to heterobinuclear, mixed-valence, gold(I)–gold(III) species ($5d^8\cdots 5d^{10}$).[6]

Although the carbanion $2\text{-}C_6H_4PPh_2$ commonly forms mononuclear complexes derived by removal of a hydrogen atom from an *ortho*-position of coordinated triphenylphosphine, it can also function as a bridging ligand with later transition metals, such as Au, Pt, Pd and Rh.[7] The digold(I) complexes $[Au_2\{\mu\text{-}(2\text{-}C_6H_3\text{-}5\text{-}R)PPh_2\}_2]$ (R = H, Me), which are accessible from the reaction of $[AuBr(PEt_3)]$ with $(2\text{-}Li\text{-}4\text{-}RC_6H_3)PPh_2$, react with halogens to give initially homobinuclear digold(II) complexes $[Au_2X_2\{\mu\text{-}(2\text{-}C_6H_3\text{-}5\text{-}R)PPh_2\}_2]$ (X = Cl, Br, I). These isomerise subsequently in solution by C–C coupling (reductive elimination) of the aryl groups, forming biarylbis(diphenylphosphine)-bridged digold(I) complexes, $[XAu\{\mu\text{-}2,2'\text{-}Ph_2P(5,5'\text{-}R_2C_6H_3C_6H_3)PPh_2\}AuX]$.[8–13] In contrast, in the 6-methyl-substituted series, the dihalodigold(II) complexes formed by halogenation of complexes $[Au_2\{\mu\text{-}(2\text{-}C_6H_3\text{-}6\text{-}Me)PPh_2\}_2]$ rearrange rapidly to gold(I)–gold(III) complexes $[XAu\{\mu\text{-}2\text{-}Ph_2P(C_6H_3\text{-}6\text{-}Me)\}AuX\{(6\text{-}MeC_6H_3)\text{-}2\text{-}PPh_2\}\text{-}\kappa^2 P,C]$, in which one of the originally bridging units is chelated to the gold(III) atom.[10] Heterobineclear complexes of this type are likely intermediates in the C–C coupling reaction but this process is sterically blocked in the 6-methyl series.

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In the platinum(II) series, the monomeric bis(chelate) complexes [Pt{(C$_6$H$_3$-5-R)-2-PPh$_2$}$_2$-κ^2*P*,*C*] (R = H, Me), which are isolated from the reaction of (2-Li-4-RC$_6$H$_4$)PPh$_2$ with [PtCl$_2$(SEt$_2$)$_2$], isomerise in refluxing toluene to binuclear complexes [Pt$_2${μ-(2-C$_6$H$_3$-5-R)PPh$_2$}$_2${(2-C$_6$H$_3$-5-R)PPh$_2$-κ^2*P*,*C*}$_2$] (R = H, Me).[14–16] However, no corresponding bis(chelate) complex is obtained with the corresponding tertiary arsine (R = Me). The first product isolated is a mixture of two dimers, one of which is the arsenic analogue of the complex cited above. The second dimer, which is the final stable product of the reaction, is [Pt$_2${μ-(2-C$_6$H$_3$-5-Me)AsPh$_2$}$_4$], in which all four of the ligands bridge a pair of platinum atoms in a lantern or paddle-wheel structure.[17] These observations, which imply a preference for the bridging over the chelate mode for *ortho*-metallated tertiary arsines, prompted us to compare the gold chemistry of the (2-C$_6$H$_3$-*n*-Me)AsPh$_2$ ligands ($n = 5, 6$) with that of their PPh$_2$ analogues. The results are reported here.

Experimental

Materials and reagents

The compounds [AuBr(AsPh$_3$)] and PhICl$_2$ were prepared as described in the literature.[12] 2-Bromo-3-iodotoluene was prepared in a four-step sequence from *o*-toluidine and 3-bromo-4-iodotoluene in a two-step sequence from *p*-toluidine.[12] These compounds were converted into (2-bromo-3-methylphenyl)diphenylarsine and (2-bromo-4-methylphenyl)diphenylarsine by PdCl$_2$(NCMe)$_2$-catalyzed reaction[17] with diphenyl(trimethylsilyl)arsine in yields of 40 and 47%, respectively. All solvents were dried by standard procedures.

Physical measurements

^{1}H NMR spectra were recorded on a JEOL JNM-ECP 400 (400 MHz) or Varian Gemini 300 (300 MHz) Fourier transform NMR spectrometer with chemical shift values (δ, ppm) recorded relative to solvent. FAB and EI mass spectra were measured on a JEOL JMS-600H spectrometer and VG ZAB-2SEQ spectrometer, respectively. Elemental analyses were carried out on a Perkin-Elmer 2400 analyzer or in the Microanalytical Laboratory of the Research School of Chemistry, ANU. IR spectra were recorded on a Perkin-Elmer PE 683 spectrometer on samples prepared as Nujol mulls.

Synthesis of gold complexes

Most syntheses were performed under a dry argon atmosphere with use of standard Schlenk techniques, although the solid gold complexes once isolated were air-stable.

[Au$_2${μ-(2-C$_6$H$_3$-*n*-Me)AsPh$_2$}$_2$] (*n* = 5, 1; *n* = 6, 9). **1** and **9** were synthesized in a similar manner, and a typical preparation of **1** is described. A solution of (2-Br-4-Me-C$_6$H$_3$)AsPh$_2$ (0.544 g, 1.36 mmol) in ether (20 ml) was treated with a 1.6 M hexane solution of ^{n}BuLi (0.75 ml). To the solution was added solid [AuBr(AsPh$_3$)] (0.629 g, 1.08 mmol) at −78 °C. The mixture was stirred overnight at room temperature, and the resulting white solid was collected and washed with MeOH and ether. The solid was dissolved in hot dichloromethane, and the solution was filtered through Celite. Evaporation and addition of MeOH gave **1** as a white, air-stable solid. Yield: 0.453 g, 81%. ^{1}H NMR (CDCl$_3$): δ 2.27 (s, 6H, –CH$_3$), 6.89–7.59 (m, 26H, arom). Positive-ion FAB-MS: *m*/*z* 1034 {M + H}$^+$. Found: C, 43.90; H, 3.21%. C$_{38}$H$_{32}$As$_2$Au$_2$ requires C, 44.21; H, 3.12%.

9: Yield: 0.628 g, 89%. ^{1}H NMR (CDCl$_3$): δ 2.60 (s, 6H, –CH$_3$), 6.95–7.50 (m, 26H, arom). Positive-ion FAB-MS: *m*/*z* 1034 {M + H}$^+$. Found: C, 44.03; H, 3.11%. C$_{38}$H$_{32}$As$_2$Au$_2$ requires C, 44.21; H, 3.12%.

[Au$_2$X$_2${μ-(2-C$_6$H$_3$-5-Me)AsPh$_2$}$_2$] (X = Cl, 2a; X = Br, 2b; X = I, 2c). A stirred suspension of **1** (0.108 g, 0.105 mmol) in dichloromethane (10 ml) was treated with a solution of iodine, bromine or PhICl$_2$ (0.113 mmol) in dichloromethane at −78 °C. The suspension was stirred for 3 h while being shielded from light; during work-up the temperature was kept below −40 °C. The suspension was filtered through Celite and the solvent was removed under reduced pressure. The residue was washed with hexane (3 × 5 ml) and dried *in vacuo*.

2a: Yield, 73 mg, 63%. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 2.33 (s, 6H, –CH$_3$), 6.58–7.87 (m, 26H, arom). Positive-ion FAB-MS: *m*/*z* 1069 {M − Cl + H}$^+$. Found: C, 41.03; H, 2.84%. C$_{38}$H$_{32}$As$_2$Au$_2$Cl$_2$ requires C, 41.37; H, 2.92%.

2b: Yield: 141.3 mg, 61%. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 2.31 (s, 6H, –CH$_3$), 6.51–7.72 (m, 26H, arom). Positive-ion FAB-MS: *m*/*z* 1113 {M − Br + H}$^+$. Found: C, 37.99; H, 2.58%. C$_{38}$H$_{32}$As$_2$Au$_2$Br$_2$ requires C, 38.28; H, 2.71%.

2c: Yield: 71.2 mg, 57%. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 2.34 (s, 6H, –CH$_3$), 6.82–7.87 (m, 26H, arom). Positive-ion FAB-MS: *m*/*z* 1161 {M − I + H}$^+$. Found: C, 35.14; H, 2.29%. C$_{38}$H$_{32}$As$_2$Au$_2$I$_2$ requires C, 35.48; H, 2.51%.

Complexes **2a–2c** could be also prepared by the reaction of the bis(benzoato) complexes **3** (see below) with a solution of the appropriate lithium halide in methanol. The suspension was filtered through Celite and the product was precipitated by the addition of hexane to the filtrate. Yields were 80–90%. This procedure usually gave the purest samples.

[Au$_2$(O$_2$CPh)$_2${μ-(2-C$_6$H$_3$-5-Me)AsPh$_2$}$_2$] 3. A stirred suspension of **1** (0.230 g, 0.223 mmol) in dichloromethane (55 ml) was treated with an excess of solid dibenzoyl peroxide (0.338 g, 1.40 mmol) at room temperature. The mixture was stirred for 3 days, shielded from light, and filtered through Celite. The solvent was removed under reduced pressure. The yellow residue was stirred for 2 h with ether to remove the excess of dibenzoyl peroxide, and was dried again. The solid was dissolved in a small amount of dichloromethane, and hexane was added. The mixture was evaporated under reduced pressure until the product began to precipitate, then set aside at 0 °C. The solid was separated by filtration and washed with hexane. Yield, 0.221 g, 78%. **3**: ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 2.32 (s, 6H, –CH$_3$), 6.70–7.67 (m, 36H, arom). IR (Nujol, ν/cm^{-1}): 1629, 1573 (s) ν(C=O), 1321, 1300 (s) ν (C–O). Positive-ion FAB-MS: *m*/*z* 1156 {M − (O$_2$CPh) + H}$^+$. Found: C, 48.74; H, 3.41%. C$_{52}$H$_{42}$As$_2$Au$_2$O$_4$ requires C, 49.00; H, 3.32%.

[Au$_2$(O$_2$CMe)$_2${μ-(2-C$_6$H$_3$-5-Me)AsPh$_2$}$_2$] 4. A stirred solution of **2a** (25 mg, 0.023 mmol) in dichloromethane (5 ml) was treated with an excess of silver acetate (19 mg, 0.114 mmol) at room temperature. The mixture was stirred for 5 h, while being shielded from light. The insoluble silver salts were removed by centrifugation, the supernatant liquid was evaporated to dryness under reduced pressure, and the solid product was washed with hexane and dried *in vacuo*. Yield, 21 mg, 81%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.46 (s, 6H, $-CH_3$), 2.33 (s, 6H, $-CH_3$), 6.68–7.57 (m, 26H, arom). Positive-ion FAB-MS: *m/z* 1093 {M + H}$^+$. Found: C, 43.40; H, 3.24%. $C_{42}H_{38}As_2Au_2O_4$ requires C, 43.85; H, 3.33%.

[Au_2X_2{μ-2,2′-$Ph_2As(5,5'-Me_2C_6H_3C_6H_3)AsPh_2$}] (X = Cl, 5a; X = Br, 5b; X = I, 5c). A typical preparation of **5** is described. A stirred suspension of **1** (0.225 g, 0.218 mmol) in dichloromethane (20 ml) was treated with a solution of $PhICl_2$ (0.222 mmol) in dichloromethane (10 ml) at room temperature. After being stirred for 3 h, the suspension was filtered through Celite and the solvent was removed under reduced pressure to dryness. The residue was dissolved in toluene and heated at 50 °C until the solution became almost colourless. The solution was evaporated under reduced pressure, and the product was precipitated by addition of hexane. Yield, 0.195 mg, 70%.

5a: ^{1}H NMR ($CDCl_3$): δ 1.78 (s, 6H, $-CH_3$), 6.16–7.81 (m, 26H, arom). Positive-ion FAB-MS: *m/z* 1069 {M − Cl + H}$^+$. Found: C, 41.46; H, 2.99%. $C_{38}H_{32}As_2Au_2Cl_2$ requires C, 41.37; H, 2.92%.

5b: Yield: 165.5 mg, 68%. ^{1}H NMR ($CDCl_3$): δ 1.79 (s, 6H, $-CH_3$), 6.18–7.86 (m, 26H, arom). Positive-ion FAB-MS: *m/z* 1113 {M − Br + H}$^+$. Found: C, 38.26; H, 2.82%. $C_{38}H_{32}As_2Au_2Br_2$ requires C, 38.28; H, 2.71%.

5c: Yield: 36.7 mg, 29%. ^{1}H NMR ($CDCl_3$): δ 1.80 (s, 6H, $-CH_3$), 6.20–7.88 (m, 26H, arom). Positive-ion FAB-MS: *m/z* 1161 {M − I + H}$^+$. Found: C, 35.77; H, 2.50%. $C_{38}H_{32}As_2Au_2I_2$ requires C, 35.48; H, 2.51%.

[$Au_2(C_6F_5)_2${μ-(2-C_6H_3-5-Me)$AsPh_2$}$_2$] 6. A stirred solution of C_6F_5Br (0.069 mL, 0.55 mmol) in ether (25 ml) was treated with an equimolar amount of 1.6 M solution of ^{n}BuLi in hexane at −78 °C. The mixture was stirred at low temperature for 1 h, and the resulting solution of C_6F_5Li was treated over a 30 min period with a solution of **3** (0.211 g, 0.166 mmol) in toluene (50 ml). After being stirred for a further 30 min, the mixture was warmed to room temperature and was stirred for 1 h. The yellow solution was filtered through Celite, and the solvent was evaporated to dryness under reduced pressure. The yellow residue was purified by passing a toluene solution down a short column of neutral alumina and eluting with toluene–hexane (1 : 1). The yellow solution was evaporated under reduced pressure to dryness and washed with hexane. Yield, 178 mg, 79%. ^{1}H NMR ($CDCl_3$): δ 2.17 (s, 6H, $-CH_3$), 6.63–7.59 (m, 26H, arom). Positive-ion FAB-MS: *m/z* 1201 {M − (C_6F_5) + H}$^+$. Found: C, 43.44; H, 1.97%. $C_{50}H_{32}As_2Au_2F_{10}$ requires C, 43.95; H, 2.36%.

[$Au_2(C_6F_5)_2${μ-2,2′-$Ph_2As(5,5'-Me_2C_6H_3C_6H_3)AsPh_2$}] 7. A stirred solution of **14** (57.6 mg, 0.042 mmol) in toluene (15 ml) was heated at 70 °C for 5 h. The colourless solution was filtered through Celite and evaporated under reduced pressure to dryness. The residue was washed with hexane. Yield of **7**; 50.5 mg, 88%. ^{1}H NMR ($CDCl_3$): δ 1.84 (s, 6H, $-CH_3$), 6.20–7.58 (m, 26H, arom). Positive-ion FAB-MS: *m/z* 1201 {M − (C_6F_5) + H}$^+$. Found: C, 43.70; H, 1.97%. $C_{50}H_{32}As_2Au_2F_{10}$ requires C, 43.95; H, 2.36%.

2,2′-$Ph_2As(5,5'-Me_2C_6H_3C_6H_3)AsPh_2$ 8. A suspension of **5c** (51 mg, 0.040 mmol) in ethanol (2 ml) was stirred overnight with an aqueous solution of KCN (17 mg, 0.261 mmol) at room temperature. The white solid was separated by filtration and washed with water. Recrystallisation from hot hexane gave **6** as colourless needles. Yield, 18 mg, 71%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 2.12 (s, 6H, $-CH_3$), 6.69–7.36 (m, 26H, arom). Positive-ion EI-MS: *m/z* 560.5 {M − Ph}$^+$. Found: C, 71.86; H, 5.16%. $C_{38}H_{32}As_2$ requires C, 71.48; H, 5.05%.

[ClAu{μ-2-$Ph_2As(C_6H_3$-6-Me)}AuCl{(6-MeC_6H_3)-2-$AsPh_2$}-κ^2*As*,*C*] 10. A stirred solution of **9** (0.108 g, 0.105 mmol) in dichloromethane (10 ml) was treated with an equimolar amount of $PhICl_2$ in dichloromethane (5 ml) at room temperature. The solution was stirred for 2 h and filtered through Celite, then evaporated to dryness. The white residue was washed with hexane and dried *in vacuo*. Yield, 90 mg, 78%. ^{1}H NMR ($CDCl_3$): δ 1.65 (s, 3H, $-CH_3$), 2.56 (s, 3H, $-CH_3$), 6.91–7.82 (m, 26H, arom). Positive-ion FAB-MS: *m/z* 1069 {M − Cl + H}$^+$. Found: C, 41.39; H, 3.05; Cl, 6.49%. $C_{38}H_{32}As_2Au_2Cl_2$ requires C, 41.37; H, 2.92; Cl, 6.43%.

[ClAu{μ-2-$Ph_2As(C_6H_3$-6-Me)}Au{$AsPh_2$(2-Cl-3-Me-C_6H_3)}] 11. A stirred solution of **9** (0.252 g, 0.244 mmol) in toluene (25 ml) was treated with an equimolar amount of $PhICl_2$ in toluene (10 ml) at room temperature. The mixture was stirred for 1 h at room temperature, then heated at 70 °C overnight. The colourless solution was filtered through Celite, evaporated under reduced pressure, and hexane was added. The product was separated by filtration and washed with hexane. Yield, 208 mg, 77%. ^{1}H NMR ($CDCl_3$): δ 2.38 (s, 3H, $-CH_3$), 2.60 (s, 3H, $-CH_3$), 6.75–7.54 (m, 26H, arom). Positive-ion FAB-MS: *m/z* 1069 {M − Cl + H}$^+$. Found: C, 41.19; H, 2.67%. $C_{38}H_{32}As_2Au_2Cl_2$ requires C, 41.37; H, 2.92%.

[BrAu{μ-2-$Ph_2As(C_6H_3$-6-Me)}Au{$AsPh_2$(3-Me-C_6H_4)}] 12. A toluene solution (20 ml) of **9** (0.202 g, 0.196 mmol) was treated with an equimolar amount of Br_2 as in the same manner to that for **11** except that the reaction was carried out at 50 °C. Yield, 178 mg, 82%. ^{1}H NMR ($CDCl_3$): δ 2.35 (s, 3H, $-CH_3$), 2.60 (s, 3H, $-CH_3$), 6.95–7.50 (m, 27H, arom). Positive-ion FAB-MS: *m/z* 1115 {M + H}$^+$. Found: C, 41.24; H, 2.83%. $C_{38}H_{33}As_2Au_2Br$ requires C, 41.03; H, 2.90; Br, 7.18%.

Reaction of 9 with iodine. A stirred solution of **9** (0.520 g, 0.504 mmol) in dichloromethane (50 ml) was treated with an equimolar amount of I_2 in dichloromethane (25 ml). The mixture was stirred for 1 h, filtered through Celite and was evaporated under reduced pressure to dryness. The residue was washed with hexane and isolated by filtration. The product was obtained as a mixture of (2-I-3-Me-C_6H_3)$AsPh_2$ (**13**), [ClAu(μ-2-$Ph_2AsC_6H_3$-6-Me)$AuAsPh_2$(2-Cl-3-Me-C_6H_3)] (**14**) and [I_2Au{(μ-C_6H_3-2-$AsPh_2$-6-Me)}$_2$Au] (**15**), crystals of which were separated by hand and identified by X-ray crystallography (see text). 380 mg of the mixture of products was obtained.

Crystal structure determination

All diffraction data were collected with a Bruker SMART CCD area detector diffractometer (Mo-Kα radiation, graphite monochromator, $\lambda = 0.71073$ Å) at room temperature. Geometric and intensity data were collected using SMART software.[18] The data were processed using SAINT software,[19] and corrections for absorption were applied using SADABS software.[20]

All structures except **8** were solved by direct methods using the SHELX-TL package.[21] The structure of **8** was solved by the heavy atom method. All atoms were found by difference Fourier syntheses and all non-hydrogen atoms were anisotropically refined. Hydrogen atoms were located at the calculated positions and refined isotropically. Crystallographic data are summarized in Table 1.

CCDC reference numbers 290381–290397.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b516538e

Results

All the complexes described in this paper have been characterised by ^{1}H NMR spectroscopy, positive ion FAB-MS, and elemental analyses. The molecular structures of key complexes have also been determined by single-crystal X-ray structural analysis.

The digold(I) complexes [$Au_2\{\mu$-(2-C_6H_3-*n*-Me)$AsPh_2\}_2$] (*n* = 5 (**1**), 6 (**9**)) were prepared by the reaction of the appropriate aryllithium reagents with [$AuBr(AsPh_3)$] and obtained as air- and moisture-stable white powders. The positive-ion FAB mass spectra each show a parent-ion molecular peak at *m*/*z* 1035 and the ^{1}H NMR spectra show only one methyl signal (δ 2.3 for **1**, 2.6 for **9**). Complex **9** has crystallographically imposed twofold symmetry. The molecular structure, shown in Fig. 1, resembles that of the phosphorus analogue, [$Au_2\{\mu$-(2-C_6H_3-6-Me)$PPh_2\}_2$],[11] although the Au–Au distance is significantly greater [2.9543(10) *vs*. 2.861(2) Å]. Selected bond lengths and angles in **9** are listed in Table 2.

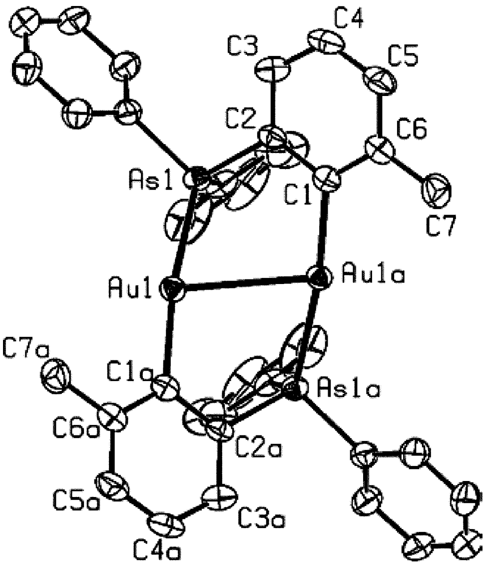
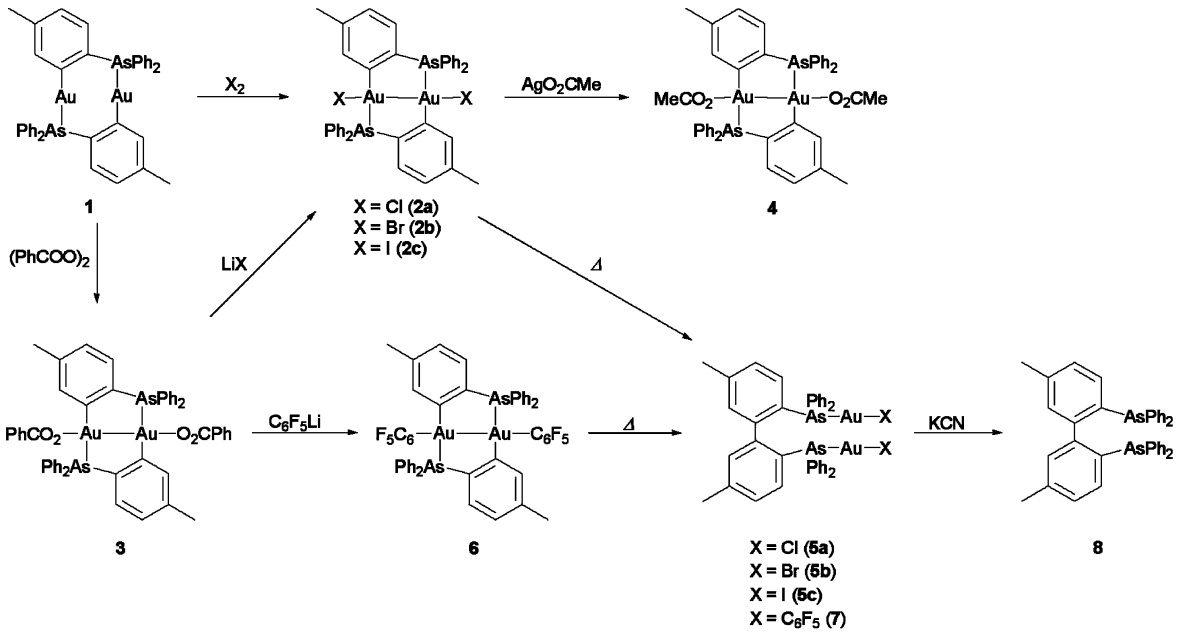


Fig. 1 Perspective drawing of **9** with atomic numbering. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level. The atoms having an additional letter "a" have coordinates at [$-x$, y, $1/2 - z$].

The oxidative addition reactions of **1** and **9** are summarized in Scheme 1 and 2, respectively. Thus, **1** reacted with $PhICl_2$ (acting as a source of Cl_2), Br_2 or I_2 at −78 °C to give the dihalodigold(II) complexes [$Au_2X_2\{\mu$-(2-C_6H_3-5-Me)$AsPh_2\}_2$] [X = Cl (**2a**), Br (**2b**), I (**2c**)] as yellow, orange and deep red solids, respectively. Reaction of **1** with an excess of dibenzoyl peroxide gave the bis(benzoato)digold(II) complex [$Au_2(O_2CPh)_2\{\mu$-(2-C_6H_3-5-Me)$AsPh_2\}_2$] (**3**) as a yellow powder whose IR spectrum showed typical carboxylate bands at 1629, 1573 cm^{-1} [ν(C=O)] and at 1321, 1300 cm^{-1} [ν(C–O)].[22] Complex **3** reacted with an excess of lithium halides to give the dihalodigold(II) complexes **2a**–**2c** in >80% yield. Treatment of **2a** with an excess of silver acetate at room temperature gave the pale yellow bis(acetato)digold(II) complex [$Au_2(O_2CMe)_2\{\mu$-(2-C_6H_3-5-Me)$AsPh_2\}_2$] (**4**). Although parent ions were absent from the FAB mass spectra of these complexes, peaks corresponding to the loss of one halide, benzoate or acetate ion were observed. The ^{1}H NMR spectra of **2a–c**, **3** and



Scheme 1 Reactivity of **1** with halogens.

Table 1 Crystal and refinement data for complexes **2a–2c** and **4–15**

Complex	**9**	**2a**	**2b**	**2c**	**4**	**5a**	**5b**	**5c**
Molecular formula	$C_{38}H_{32}As_2Au_2$	$C_{38}H_{32}As_2Au_2Cl_2$	$C_{38}H_{32}As_2Au_2Br_2$	$C_{38}H_{32}As_2Au_2I_2$	$C_{42}H_{38}As_2Au_2O_4$	$C_{38}H_{32}As_2Au_2Cl_2$	$C_{38}H_{32}As_2Au_2Br_2$	$C_{38}H_{32}As_2Au_2I_2$
M_w	1032.41	1103.31	1192.23	1286.21	1150.50	1103.31	1192.23	1286.21
Crystal colour	Colourless	Yellow	Orange	Red	Yellow	Colourless	Colourless	Colourless
Crystal size/mm	0.39 × 0.22 × 0.12	0.35 × 0.16 × 0.11	0.22 × 0.13 × 0.13	0.28 × 0.087 × 0.065	0.39 × 0.36 × 0.26	0.19 × 0.11 × 0.086	0.11 × 0.10 × 0.10	0.17 × 0.13 × 0.087
Collection range, *hkl*	−15 to 30 −11 to 10 −24 to 10	−23 to 19 −15 to 16 −22 to 22	−23 to 21 −15 to 16 −22 to 21	−23 to 23 −16 to 13 −22 to 19	−22 to 25 −14 to 13 −24 to 26	−25 to 21 −14 to 14 −24 to 23	−25 to 23 −14 to 13 −25 to 21	−25 to 18 −14 to 10 −25 to 23
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	*Pccn*	*Pccn*	*Pccn*	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*
a/Å	23.051(7)	17.4586(14)	17.6413(12)	17.8668(12)	18.9303(12)	19.1148(15)	19.2239(15)	19.4517(10)
b/Å	8.910(3)	12.1644(10)	12.2384(8)	12.4610(9)	10.8309(7)	10.7477(8)	10.7877(9)	10.8921(6)
c/Å	18.718(6)	16.7311(14)	16.7360(11)	16.7927(12)	19.5860(12)	18.6647(14)	18.8728(15)	19.1704(10)
α/°	90	90	90	90	90	90	90	90
β/°	121.310(13)	90	90	90	103.1240(10)	112.638(2)	112.499(2)	112.2280(10)
γ/°	90	90	90	90	90	90	90	90
V/Å^3	3284.4(18)	3553.2(5)	3613.3(4)	3738.7(5)	3910.9(4)	3539.1(5)	3616.0(5)	3759.8(3)
Z	4	4	4	4	4	4	4	4
F(000)	1936	2072	2216	2360	2184	2072	2216	2360
μ/mm^{-1}	10.948	10.273	12.166	11.272	9.213	10.314	12.157	11.209
D_c/g cm^{-3}	2.088	2.062	2.192	2.285	1.954	2.071	2.190	2.272
T/K	298(2)	293(2)	293(2)	298(2)	293(2)	298(2)	298(2)	298(2)
R	0.0591	0.0237	0.0262	0.0307	0.0217	0.0233	0.0281	0.0237
wR	0.1419	0.0564	0.0622	0.0664	0.0532	0.0536	0.0630	0.0531
Max shift $(\Delta/\sigma)_{max}$	0.000	0.002	0.002	0.002	0.077	0.001	0.015	0.010
Goodness-of-fit	0.979	1.028	1.031	1.037	0.869	1.023	1.026	1.025
No. data collected	5526	25230	25520	26626	14257	12922	13290	13750
No. unique data	3848	4443	4496	4667	4862	4405	4492	4682
R_{int}	0.1598	0.0327	0.0372	0.0438	0.0249	0.0212	0.0282	0.0214
No. data used in refinement	3848	4443	4496	4667	4862	4405	4492	4682
No. params refined	191	200	200	200	228	200	200	200
$\Delta\rho$/e A^{-3}	+3.415, −3.283	+2.114, −0.681	+2.183. −0.820	+1.472, −0.749	+1.241, −1.316	+0.843. −0.759	+1.021, −0.685	+0.826, −0.492

Table 1 (*Contd.*)

Complex	**6**	**7**	**8**	**10**	**11**	**12**	**13**	**14**	**15**
Molecular formula	$C_{50}H_{32}As_2Au_2F_{10}$	$C_{50}H_{32}As_2Au_2F_{10}$	$C_{38}H_{32}As_2$	$C_{38}H_{32}As_2Au_2Cl_2$	$C_{38}H_{32}As_2Au_2Cl_2$	$C_{38}H_{33}As_2Au_2Br$	$C_{19}H_{16}AsI$	$C_{38}H_{32}As_2Au_2I_2$	$C_{38}H_{32}As_2Au_2I_2$
M_w	1366.53	1366.53	638.48	1103.31	1103.31	1113.33	446.14	1286.21	1286.21
Crystal colour	Yellow	Colourless	Colourless	Colourless	Colourless	Colourless	Colourless	Colourless	Orange
Crystal size/mm	0.27 × 0.25 × 0.23	0.40 × 0.26 × 0.22	0.37 × 0.20 × 0.11	0.16 × 0.11 × 0.062	0.33 × 0.10 × 0.070	0.25 × 0.17 × 0.14	0.59 × 0.54 × 0.27	0.26 × 0.11 × 0.090	0.13 × 0.12 × 0.11
Collection range, *hkl*	−17 to 18 −28 to 27 −12 to 19	−16 to 14 −24 to 27 −24 to 21	−16 to 26 −9 to 8 −16 to 13	−21 to 34 −27 to 23 −25 to 24	−12 to 10 −21 to 18 −32 to 32	−10 to 11 −17 to 20 −33 to 33	−12 to 12 −13 to 9 −12 to 14	−12 to 11 −16 to 16 −27 to 18	−19 to 19 −17 to 18 −23 to 6
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$C2$	$C2/c$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a/Å	13.7505(8)	12.0980(9)	19.799(4)	25.691(2)	9.0921(12)	8.9939(7)	9.3408(6)	9.1944(9)	15.8379(15)
b/Å	21.7158(12)	20.5775(16)	6.8375(15)	20.4189(18)	15.991(2)	15.7013(13)	9.8564(6)	12.0156(11)	14.0363(15)
c/Å	14.9318(8)	18.6526(15)	12.489(3)	19.0832(17)	24.704(3)	25.199(2)	11.1989(7)	20.2994(19)	17.4504(17)
α/°	90	90	90	90	90	90	112.6130(10)	83.702(2)	90
β/°	95.7420(10)	97.678(2)	111.204(4)	130.1910(10)	97.868(3)	96.491(2)	111.2450(10)	81.403(2)	111.217(3)
γ/°	90	90	90	90	90	90	97.2830(10)	77.640(2)	90
V/Å^3	4436.3(4)	4601.9(6)	1576.3(6)	7647.0(12)	3558.0(8)	3535.7(5)	843.60(9)	2159.0(4)	3616.4(6)
Z	4	4	2	8	4	4	2	2	4
$F(000)$	2584	2584	652	4144	2072	2080	432	1180	2360
μ/mm^{-1}	8.164	7.871	2.144	9.547	10.259	11.302	3.836	9.760	11.653
D_c/g cm^{-3}	2.046	1.972	1.345	1.917	2.060	2.091	1.756	1.979	2.362
T/K	293(2)	293(2)	293(2)	298(2)	293(2)	293(2)	293(2)	293(2)	298(2)
R	0.0374	0.0405	0.0427	0.0416	0.0595	0.0420	0.0284	0.0641	0.0343
wR	0.0821	0.0954	0.0981	0.0904	0.1483	0.0812	0.0755	0.1960	0.0707
Max shift $(\Delta/\sigma)_{max}$	0.002	0.130	0.001	0.009	0.012	0.034	0.002	0.003	0.001
Goodness-of-fit	0.959	0.975	0.971	0.950	1.025	0.985	1.053	1.048	0.878
No. data collected	32838	33783	5585	27580	25596	26126	6289	16075	12188
No. unique data	11013	11431	3661	9609	8775	8765	4124	10595	8316
R_{int}	0.0498	0.0432	0.0300	0.0494	0.0610	0.0517	0.0131	0.0233	0.0487
No. data used in refinement	11013	11431	3661	9609	8775	8765	4124	10595	8316
No. params refined	578	579	182	399	399	390	191	399	390
$\Delta\rho$/e A^{-3}	+1.653. −0.901	+1.963, −1.093	+1.058, −0.483	+1.972. −0.705	+4.485, −1.154	+1.389, −0.566	+0.751, −1.086	+3.312, −1.393	+1.678, −1.275

$w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$, where p is $[F_o^2 + 2(F_c^2)]/3$.

Table 2 Selected bond distances (Å) and angles (°) in **9**

Au(1)···Au(1a)	2.9543(10)	Au(1a)–Au(1)–As(1)	74.03(3)
Au(1)–As(1)	2.4011(10)	Au(1a)–Au(1)–C(1a)	98.6(2)
Au(1)–C(1a)	2.040(7)	As(1)–Au(1)–C(1a)	169.9(2)
As–C	1.918(8)–1.944(8)	Au(1)–As(1)–C(2)	114.7(2)
		Au(1)–C(1a)–C(2a)	117.9(6)

4 showed just one aromatic methyl singlet at δ 2.3. The acetate methyl resonance of **4** appeared at δ 1.5.

The molecular structures of **2a–2c** and **4** have been determined by X-ray crystallography, those of **2a** and **4** being shown in Fig. 2 and 3, respectively. These four complexes have crystallographic twofold symmetry and **2a–2c** are isomorphous. The structures are very similar to those of the phosphorus-containing analogues, $[Au_2I_2\{(\mu\text{-}C_6H_4)PPh_2\}_2]$[8] and $[Au_2(O_2CPh)_2\{(\mu\text{-}C_6H_4)PEt_2\}_2]$.[9] The Au–Au distances are 2.5526(3) Å (**2a**), 2.5651(3) Å (**2b**), 2.5880(3) Å (**2c**) and 2.5306(2) Å (**4**). The separation for **2c** is identical, within experimental error, with that for $[Au_2I_2\{(\mu\text{-}C_6H_4)PPh_2\}_2]$ [2.5898(6) Å];[9] that for **4** is only slightly greater than that for $[Au_2(O_2CPh)_2\{(\mu\text{-}C_6H_4)PEt_2\}_2]$ [2.5243(7) Å].[10] Selected bond lengths and angles in **2a**, **2b**, **2c**, **4** and **6** are listed in Table 3.

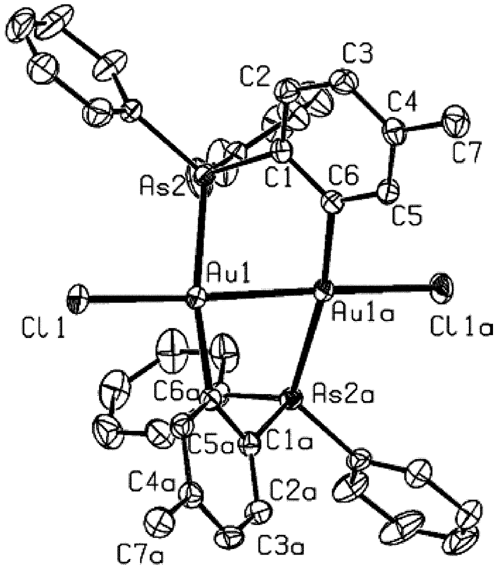


Fig. 2 Perspective drawing of **2a** with atomic numbering. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level. The atoms having an additional letter "a" have coordinates at [1/2 − *x*, 3/2 − *y*, *z*].

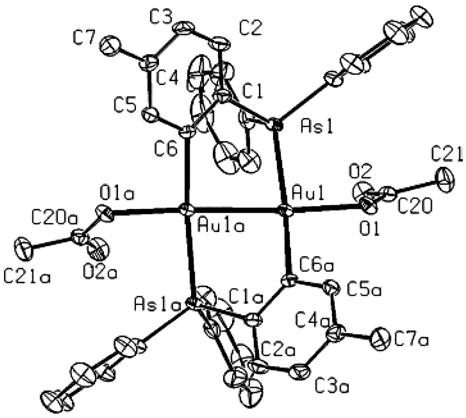


Fig. 3 Perspective drawing of **4** with atomic numbering. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level. The atoms having an additional letter "a" have coordinates at [1 − *x*, *y*, 1/2 − *z*].

Solutions of the digold(II) complexes **2a–2c** in toluene decolourized at 50 °C within a few hours and the digold(I) complexes $[Au_2X_2\{\mu\text{-}2,2'\text{-}Ph_2As(5,5'\text{-}Me_2C_6H_3C_6H_3)AsPh_2\}]$ **5a–5c** resulting from C–C coupling of the $(5\text{-}MeC_6H_3)AsPh_2$ units were isolated in good yield as colourless solids. Their ^1H NMR spectra show only one aromatic methyl singlet at δ 1.8. The crystals of **5a–5c** belong to the same space group and have similar cell dimensions to those of $[Au_2I_2\{\mu\text{-}2,2'\text{-}Ph_2P(5,5'\text{-}Me_2C_6H_3C_6H_3)PPh_2\}]$.[11] The molecular structure of **5c** is shown in Fig. 4. The molecules have crystallographic twofold symmetry. As in the PPh_2 iodo-complex,

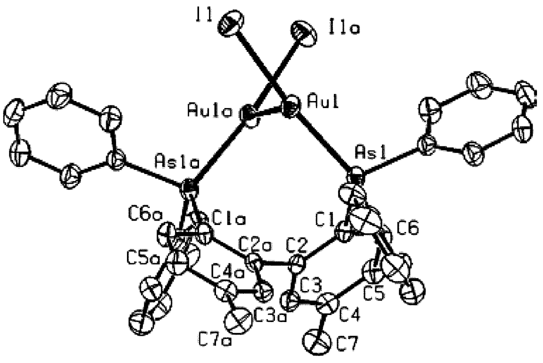


Fig. 4 Perspective drawing of **5c** with atomic numbering. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level. The atoms having an additional letter "a" have coordinates at [1 − *x*, *y*, 1/2 − *z*].

Table 3 Selected bond distances (Å) and angles (°) in **2a–2c**, **4** and **6**

	2a	**2b**	**2c**	**4**	**6**
Au(1)–Au(1a)	2.5526(3)	2.5651(3)	2.5880(3)	2.5306(2)	2.6337(3)
Au(1)–As(2)	2.4618(4)	2.4623(4)	2.4619(5)	2.4399(3)	2.4217(6)
Au(1)–C(6a)	2.070(3)	2.071(4)	2.072(4)	2.059(3)	2.079(5)
Au(1)–X(1)	2.3592(9)	2.4842(4)	2.6520(4)	2.116(2)	2.124(5)
Au(1a)–Au(1)–As(2)	79.401(10)	79.016(11)	78.486(13)	84.405(10)	80.289(16)
Au(1a)–Au(1)–C(6a)	89.36(9)	89.65(10)	89.86(12)	91.12(8)	*93.72(14)*
As(2)–Au(1)–X(1)	98.16(3)	98.089(15)	97.961(15)	93.36(7)	90.47(14)
C(6a)–Au(1)–X(1)	93.05(9)	93.34(10)	93.98(12)	90.69(11)	96.0(2)
Au(1a)–Au(1)–X(1)	177.52(3)	176.701(12)	174.035(10)	175.10(7)	168.81(14)
As(2)–Au(1)–C(6a)	168.20(9)	168.10(9)	167.68(12)	173.13(8)	172.44(14)

Table 4 Selected bond distances (Å) and angles (°) in **5a–5c** and **7**

	5a	**5b**	**5c**	**7**
Au(1) · · · Au(1a)	2.9963(3)	2.9913(3)	2.9932(3)	3.8139(4)
Au(1)–As(1)	2.3413(3)	2.3469(4)	2.3600(3)	2.3792(5)
Au(1)–X(1)	2.2772(9)	2.3927(5)	2.5421(3)	2.038(5)
As(1)–Au(1)–X(1)	173.28(3)	172.507(17)	170.931(11)	173.28(15)
As(1)–Au(1)–Au(1a)	*90.286(10)*	*91.947(12)*	*93.784(9)*	*78.07(1)*
X(1)–Au(1)–Au(1a)	95.57(3)	94.486(14)	94.084(7)	107.33(13)
C(1)–As(1)–Au(1)	119.60(8)	118.95(11)	118.31(9)	117.95(14)
α	88.79(8)	85.16(11)	79.74(9)	75.43(18)

the biphenyl backbone is twisted about the central C–C bond with the gold atoms in a mutually *syn*-orientation. In contrast to the variations observed in the digold(II) complexes, the Au · · · Au separations [2.9963(3) Å (**5a**), 2.9913(3) Å (**5b**) and 2.9932(3) Å (**5c**)] are independent of halide, though they are slightly greater than that in [Au_2I_2\{μ-2,2′-$Ph_2P(5,5'-Me_2C_6H_3C_6H_3)PPh_2$\}].[12] These distances are in the range expected for weak aurophilic interactions.[23] On the other hand, the As–Au–X angles and the dihedral angles (α) between the two phenyl rings of the biphenyl unit [173.28, 88.79° (**5a**), 172.51, 85.16° (**5b**), 170.93, 79.74° (**5c**)] decrease in the order Cl > Br > I, presumably to accommodate the larger halide. Selected bond lengths and angles in **5a**, **5b**, **5c** and **7** are listed in Table 4.

Reaction of **3** with C_6F_5Li gave the bis(pentafluorophenyl)-digold(II) complex [$Au_2(C_6F_5)_2$(μ-C_6H_3-5-Me)$AsPh_2]_2$] (**6**) as a yellow powder which showed only one aromatic-methyl resonance at δ 2.2 in its ^1H NMR spectrum. The molecular structure of **6** determined by X-ray crystallography is shown in Fig. 5; it is similar to that of **2c** and **4**, but the Au–Au distance [2.6337(3) Å] is significantly greater that in these compounds. It is also slightly greater than that in [$Au_2(C_6F_5)_2$(μ-C_6H_4)$PPh_2]_2$] [2.6139(4) Å].[11] The yellow solution of **6** in toluene turned colourless on heating for 5 h at 70 °C. The C–C coupled product [$Au_2(C_6F_5)_2$\{μ-2,2′-$Ph_2As(5,5'-Me_2C_6H_3C_6H_3)AsPh_2$\}] (**7**), which was isolated from the resulting solution, showed just one aromatic-methyl singlet at δ 1.8 in its ^1H NMR spectrum. There was no evidence for the formation of a zwitterionic species analogous to [$(C_6F_5)_2Au^{III}$\{μ-(2-C_6H_4)PPh_2\}$_2Au^I$], having a head–to–head arrangement of the bridging group, which was isolated as a minor product, together with the C–C coupled product, from the isomerisation of [$Au_2(C_6F_5)_2$\{μ-(2-C_6H_4)PPh_2\}$_2$].[11] In the molecular structure of **7**, determined by X-ray crystallography, the Au · · · Au separation [3.8139(4) Å] is significantly greater than those in **5a–5c** and in [$Au_2(C_6F_5)_2$(μ-2,2′-$Ph_2PC_6H_4C_6H_4PPh_2$)] [3.0688(8) Å].[11] The dihedral angle between the phenyl groups of the biphenyl unit (75.43(18)°) is also smaller than in these compounds.

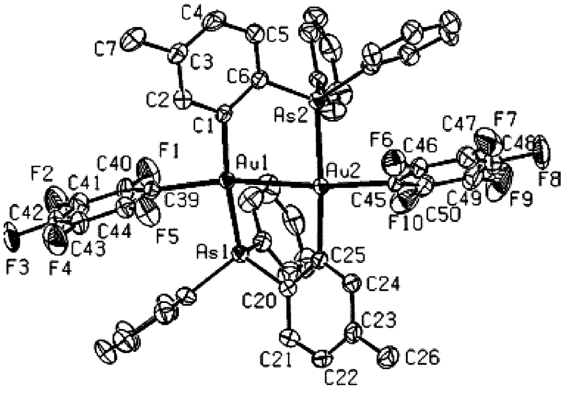


Fig. 5 Perspective drawing of **6** with atomic numbering. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

The ligand 2,2′-$Ph_2As(5,5'-Me_2C_6H_3C_6H_3)AsPh_2$ (**8**) was liberated from **5c** by reaction with KCN and its molecular structure determined (see Fig. 6), **8** also has crystallographic twofold symmetry. The dihedral angle between the phenyl groups of the biphenyl unit is 82.21(10)°, *i.e.*, similar to those in the digold(I) complexes **5a–5c**.

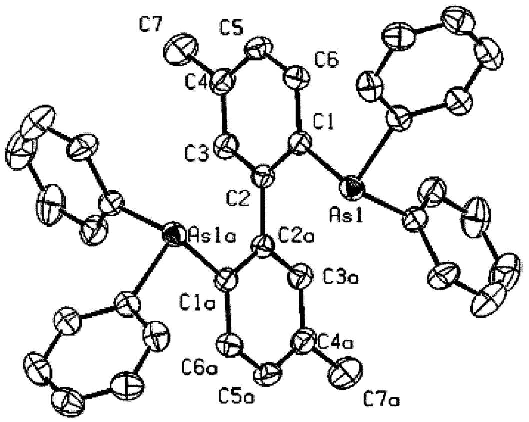


Fig. 6 Perspective drawing of **8** with atomic numbering. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level. The atoms having an additional letter "a" have coordinates at [$1 - x$, y, $1 - z$]. Distances (Å): As(1)–C(1) 1.969(4), C(2)–C(2a) 1.502(7); angles (°): As(1)–C(1)–C(2) 118.6(3), C(1)–C(2)–C(2a) 121.5(3), $\alpha = 82.27(10)$.

From the reaction of 6-methyl substituted digold(I) complex **9** with $PhICl_2$ at room temperature a colourless solid was isolated which showed two aromatic methyl singlets of equal intensity at δ 1.7 and 2.6 in its ^1H NMR spectrum, indicative of the 6-$MeC_6H_3AsPh_2$ group in different environments. As shown by X-ray crystal structure determination, this solid is a gold(I)–gold(III) complex, [ClAu\{μ-2-$Ph_2As(C_6H_3$-6-Me)\}AuCl\{(6-MeC_6H_3)-2-$AsPh_2$\}-κ^2*As*,*C*] (**10**), whose molecular structure is shown in Fig. 7. The gold(I) centre is coordinated linearly by one chlorine and one arsenic atom of a bridging group. The carbon atom of the latter is bound to the gold(III) atom, to which is also attached a chlorine atom and 6-MeC_6H_3-2-$AsPh_2$ acting as a bidentate ligand; the chlorine is *trans* to the σ-bonded carbon atom of the

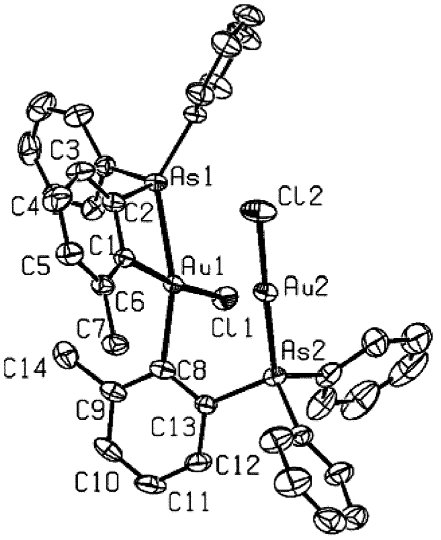


Fig. 7 Perspective drawing of **10** with atomic numbering. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

four-membered ring. The gold(III) atom is in distorted planar coordination and is located 0.174 Å above the least-squares plane formed by C(1), C(8), Cl(1) and As(1) with mean deviation of 0.106(3) Å. The structure of **10** is similar to that of the complex [IAu{μ-2-$Ph_2P(C_6H_3$-6-Me)}AuI{(6-MeC_6H_3)-2-PPh_2}-κ²*P*,*C*], which was isolated from the reaction of iodine with the iodogold(I) phosphine complex.[12] The Au–Au distance in **10**, 3.2062(5) Å, is greater than that in the precursor complex **9**, but is less than that in the iodogold-phosphine analogue [3.4692(7) Å]. **10** is only the second example of a structurally characterised orthometallated chelate complex derived from a triarylarsine. Selected bond lengths and angles in **10** are listed in Table 5.

Whereas the iodogold phosphine complex decomposed in heating in toluene to give unidentified materials, complex **10** gave a colourless solution in which the original methyl ¹H NMR singlet at δ 1.7 had been replaced by one at δ 2.4, the singlet at δ 2.6 remaining unchanged. The crystals obtained from this solution were identified as the digold(I) complex [ClAu{μ-(2-C_6H_3-6-Me)$AsPh_2$}Au{$AsPh_2$-2-Cl-3-Me-C_6H_3}] (**11**), which is derived from **10** by migration of Cl into the Au–C σ-bond of the four-membered ring. The gold atoms in **11** (Fig. 8) are 3.2510(6) Å apart and are, as expected, linearly coordinated. A similar compound, [BrAu{μ-2-$Ph_2P(C_6H_3$-6-Me)Au($AsPh_3$)}], has been isolated as a by-product of the reaction of 2-$Ph_2P(C_6H_3$-6-Me)Li with [AuBr($AsPh_3$)] to give [Au_2{μ-(2-C_6H_3-6-Me)PPh_2}$_2$].[24] The somewhat smaller Au···Au separation in the bromo-phosphine compound [3.0927(8) Å] is attributable to the smaller size of phosphorus compared with that of arsenic.

Table 5 Selected bond distances (Å) and angles (°) in **10**

Au(1) ··· Au(2)	3.2063(5)	Au(1)–Cl(1)	2.3491(18)
Au(1)–As(1)	2.4849(7)	Au(2)–As(2)	2.3305(8)
Au(1)–C(1)	2.071(7)	Au(2)–Cl(2)	2.267(2)
Au(1)–C(8)	2.077(7)		
Cl(1)–Au(1)–C(1)	170.17(19)	C(8)–Au(1)–C(1)	100.2(3)
Cl(1)–Au(1)–As(1)	100.20(5)	Au(1)–As(1)–C(2)	78.1(2)
Cl(1)–Au(1)–C(8)	88.46(19)	As(1)–C(2)–C(1)	105.1(5)
As(1)–Au(1)–C(8)	163.1(2)	Au(1)–C(1)–C(2)	106.4(5)
As(1)–Au(1)–C(1)	70.27(19)	Cl(2)–Au(2)–As(2)	177.42(8)

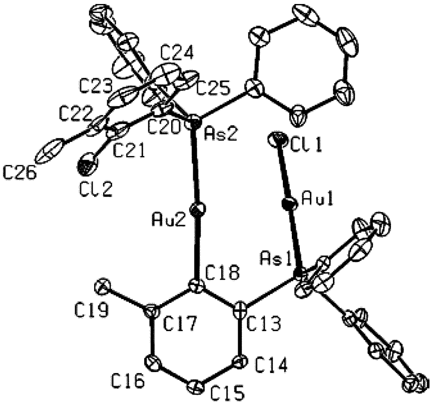


Fig. 8 Perspective drawing of **11** with atomic numbering. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

A pure product could not be isolated from the reaction of bromine with **9** at room temperature. At 50 °C, however, the complex isolated showed in its ¹H NMR spectrum two aromatic methyl resonances at δ 2.4 and 2.6, suggestive of a digold(I) structure similar to **11**, although elemental analysis was consistent with the presence of only one bromine atom. These features were confirmed by the single-crystal X-ray structure analysis, which showed the compound to be [BrAu{μ-(2-C_6H_3-6-Me)$AsPh_2$}Au{$AsPh_2$(3-MeC_6H_4)}] (**12**), the κ*As*–coordinated ligand being (3-tolyl)diphenylarsine rather than the expected (2-bromo-3-methylphenyl)diphenylarsine (Fig. 9). As in **11**, both gold atoms are coordinated almost linearly, the Au···Au separation, 3.1304(4) Å, being somewhat less than that in **11**. Selected bond lengths and angles in **11** and **14** are listed in Table 6 and of **12** in Table 7.

Table 6 Selected bond distances (Å) and angles (°) in **11** and **14**

11			
Au(1) ··· Au(2)	3.2510(6)	X(1)–Au(1)–As(1)	175.48(8)
Au(1)–As(1)	2.3392(10)	Au(1)–As(1)–C(13)	110.7(3)
Au(1)–X(1)	2.283(3)	As(2)–Au(2)–C(18)	174.8(2)
Au(2)–C(18)	2.089(9)	Au(2)–As(2)–C(20)	113.1(3)
Au(2)–As(2)	2.4302(11)		
14			
Au(1) ··· Au(2)	3.2806(7)	X(1)–Au(1)–As(1)	174.30(4)
Au(1)–As(1)	2.3556(11)	Au(1)–As(1)–C(13)	113.5(3)
Au(1)–X(1)	2.5367(10)	As(2)–Au(2)–C(18)	177.4(3)
Au(2)–C(18)	2.056(11)	Au(2)–As(2)–C(20)	115.8(4)
Au(2)–As(2)	2.4115(12)		

Table 7 Selected bond distances (Å) and angles (°) in **12**

Au(1) ··· Au(2)	3.1304(4)	As(1)–Au(1)–C(20)	172.98(17)
Au(1)–As(1)	2.4082(7)	Au(1)–As(1)–C(1)	108.4(2)
Au(1)–C(20)	2.063(6)	Br(1)–Au(2)–As(2)	175.27(3)
Au(2)–Br(1)	2.3839(7)	Au(2)–As(2)–C(25)	111.63(18)
Au(2)–As(2)	2.3379(6)		

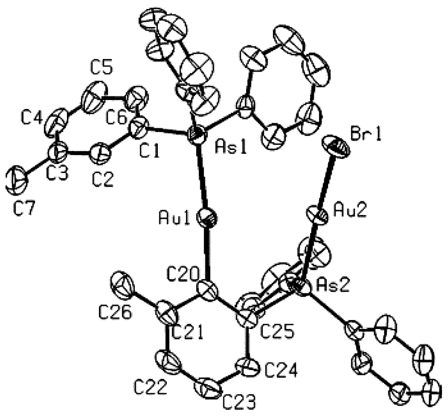


Fig. 9 Perspective drawing of **12** with atomic numbering. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

The reaction of iodine with **9** gave an orange solution together with a precipitate of elemental gold. The ^{1}H NMR spectrum in the aromatic methyl region showed a pair of equally intense singlets at δ 2.3 and 2.6 accompanied by two singlets at δ 2.5 and 2.7, indicating the presence of at least three species. Attempts to separate the constituents by fractional crystallization or chromatography were unsuccessful. Three crystals of different shape and colour were separated by hand under a microscope and their molecular structures were determined by X-ray diffraction analysis. The compounds are: (i) a mixed valence, zwitterionic complex $[I_2Au^{III}\{\mu\text{-}(2\text{-}C_6H_3\text{-}6\text{-}Me)AsPh_2\}_2Au^I]$ (**15**) (orange blocks), (ii) a digold(I) complex $[IAu\{\mu\text{-}(2\text{-}C_6H_3\text{-}6\text{-}Me)AsPh_2\}Au\{AsPh_2\text{-}2\text{-}I\text{-}3\text{-}Me\text{-}C_6H_3\}]$ (**14**) (colourless needles), which is the diiodo analogue of the dichloro complex **11**, and (iii) a free tertiary arsine $(2\text{-}I\text{-}6\text{-}MeC_6H_3)AsPh_2$ (**13**) (colourless blocks). ^{1}H NMR measurements on the separated compounds established that the signals at δ 2.5 and 2.7 belong to **13** and **15**, while the two peaks of equal intensity at δ 2.3 and 2.6 are due to **14**.

The molecular structure of **15** is shown in Fig. 10; selected bond distances and angles are in Table 8. As expected, the coordination about the cationic gold(I) centre is close to linear, while that about the anionic gold(III) centre is approximately planar. The Au···Au separation [2.9365(4) Å] is similar to that in the compound $[(C_6F_5)_2Au^{III}\{\mu\text{-}(2\text{-}C_6H_4)PPh_2\}_2Au^I]$ [2.931(1) Å], which was isolated as a by-product of the rearrangement of the digold(II) complex $[Au_2(C_6F_5)_2\{\mu\text{-}(2\text{-}C_6H_4)PPh_2\}_2]$ to the C–C coupled digold(I) compound and shown not to be an intermediate in that rearrangement.[11] A similar zwitterionic complex, which also has a head-to-head arrangement of its bridging groups, is $[Au^I(\mu\text{-mtp})_2Au^{III}I_2]$ [mtp = methylenethiophosphinate, $CH_2P(S)Ph_2$], which was isolated from the reaction of $[Au_2(\mu\text{-mtp})_2]$ with iodine in CH_2I_2–1,2-$C_2H_4Cl_2$.[5]

Table 8 Selected bond distances (Å) and angles (°) in **15**

Au(1)···Au(2)	2.9365(4)	Au(1)–I(2)	2.6043(5)
Au(1)–C(1)	2.120(6)	Au(2)–As(1)	2.3795(7)
Au(1)–C(8)	2.116(6)	Au(2)–As(2)	2.3820(7)
Au(1)–I(1)	2.5965(5)		
Au(1)–Au(2)–As(1)	87.115(17)	C(1)–Au(1)–I(1)	88.34(15)
Au(1)–Au(2)–As(2)	86.621(17)	C(1)–Au(1)–C(8)	174.2(2)
As(1)–Au(2)–As(2)	172.71(2)	C(1)–Au(1)–I(2)	90.78(15)
Au(2)–Au(1)–C(1)	92.46(16)	I(1)–Au(1)–C(8)	90.04(15)
Au(2)–Au(1)–C(8)	93.04(16)	I(1)–Au(1)–I(2)	176.81(2)
Au(2)–Au(1)–I(1)	86.512(19)	I(2)–Au(1)–C(8)	91.13(15)
Au(2)–Au(1)–I(2)	90.467(16)		

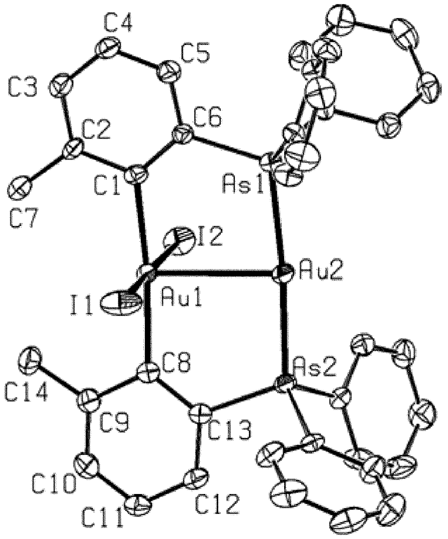
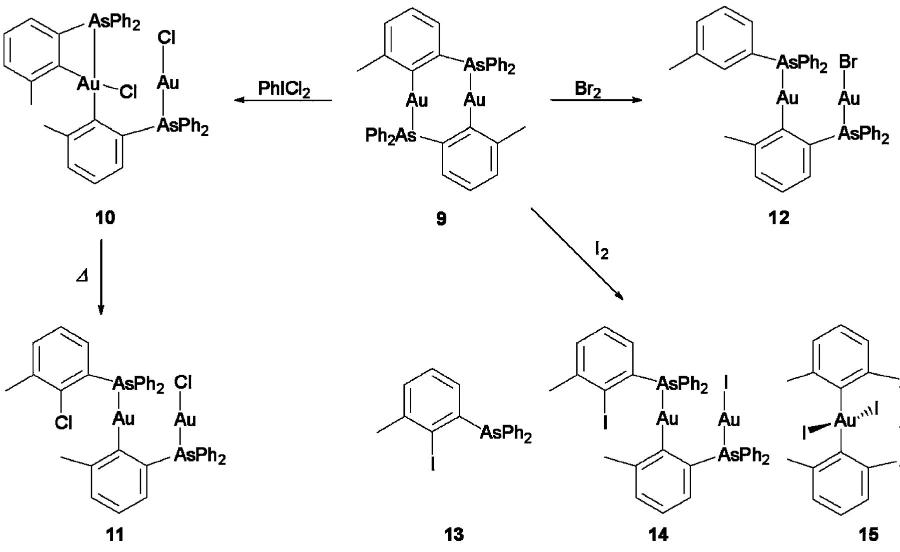


Fig. 10 Perspective drawing of **15** with atomic numbering. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

Discussion

The oxidative addition and subsequent C–C coupling reactions of $[Au_2\{\mu\text{-}(2\text{-}C_6H_3\text{-}5\text{-}Me)AsPh_2\}_2]$ **1** shown in Scheme 1 resemble those established for the tertiary phosphine analogues $[Au_2\{\mu\text{-}(2\text{-}C_6H_3\text{-}5\text{-}R)PPh_2\}_2]$ (R = H, Me). As in the phosphine compounds, no C–C coupling occurs in the bis(acetato)- or bis(benzoato)-digold(II) compounds, and possible reasons for this behaviour have been discussed.[10,13] The Au–Au distances in the dihalodigold(II) complexes **2a–2c**, the bis(acetato) complex **4**, and the bis(pentafluorophenyl) complex **6** increase in the order **4** < **2a** < **2b** < **2c** < **6**. Thus, the Au–Au distance increases, and the strength of the Au(II)–Au(II) interaction presumably decreases, as the bond between the axial ligand and the gold atom becomes more covalent. This *trans*-influence trend had been foreshadowed in earlier structural determinations, *viz*, $[Au_2X_2(\mu\text{-}2\text{-}C_6H_4PR_2)_2]$ [R = Ph, X = I,[9] C_6F_5;[11] R = Et, X = O_2CPh[10]], but the more extensive studies reported here, with a common bridging ligand, provide strong confirmation. The same trend is also evident from structural data available for a series of digold(II) bis(ylide) complexes $[Au_2X_2\{\mu\text{-}(CH_2)_2PPh_2\}_2]$ (X = OAc,[25] O_2CPh,[26] Cl,[27] Br,[28] NO_2,[29] CF_3,[30] and C_6F_5[30]) and bis(methylenethiophosphinate) complexes $[Au_2X_2\{\mu\text{-}CH_2P(S)Ph_2\}_2]$ (X = Cl,[31] I[5]). We note also that comparable dihalodigold(II) complexes containing bridging (aryl)PR_2 and (aryl)AsR_2 ligands have almost identical Au–Au bond lengths, despite the greater size of arsenic compared with that of phosphorus. By contrast, in the precursor digold(I) complexes $[Au_2\{\mu\text{-}(2\text{-}C_6H_3\text{-}6\text{-}Me)EPh_2\}_2]$ (E = P, As), in which metal–metal interaction is of the weaker aurophilic type, the larger arsenic atom causes a significantly greater Au···Au separation.



Scheme 2 Reactivity of **9** with halogens.

The oxidative addition of chlorine to [$Au_2\{\mu\text{-}(2\text{-}C_6H_3\text{-}6\text{-}Me)AsPh_2\}_2$] **9** is generally similar to the corresponding reaction with the phosphine analogue. Presumably, as in the latter case, the first stable product, the gold(I)–gold(III) complex **10**, is formed *via* a homobinuclear digold(II) intermediate similar to **2a**. Also, as in the (6-methylphenyl)phosphine series, no C–C coupling is observed, owing to steric hindrance to reductive elimination at the gold(III) centre by the methyl substitutent.[12,13] However, the isomerisation of **10** to **11** shows that the four-membered ring of **10** is cleaved more readily than that in its phosphorus counterpart. In the reaction of **9** with bromine and iodine, we have been unable so far to isolate the bromo and iodo analogues of **10**, though complex **14** must be form from the latter. The greater lability of the arsine relative to the phosphine system is demonstrated by the formation of the liberated ligand (2-iodo-3-methylphenyl)diphenylarsine **13**. Also, for the first time, a zwitterionic, mixed-valence complex **15** appears as a product isolated from direct halogenation. Since **14** and **15** do not interconvert on heating, **15** must arise by an alternative rearrangement pathway in a precursor, either the iodo-analogue of **10** or of its diiododigold(II) precursor analogous to **2a**.

At present we cannot account for the formation of complex **12** from the reaction of **9** with bromine. Presumably the bromo analogue of complex **10** is formed but the bromine in the aromatic ring is then replaced by hydrogen, perhaps derived from the solvent.

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References

1 H. Schmidbaur, A. Wohlleben, U. Schubert, A. Frank and G. Huttner, *Chem. Ber.*, 1977, **110**, 2751.
2 S. Åkerström, *Ark. Kemi.*, 1959, **14**, 387.
3 A. Grohmann and H. Schmidbaur, in *Comprehensive Organometallic Chemistry II*, ed. J. Wardell, E. Abel, F. G. A. Stone and G. Wilkinson, Pergamon, Oxford, 1995, vol. 3, p. 1, and references therein.
4 H. Schmidbaur, A. Grohmann and M. E. Olmos, in *Gold, Progress in Chemistry, Biochemistry and Technology*, ed. H. Schmidbaur, Wiley, Chichester, 1999, p 747, and references therein.
5 A. M. Mazany and J. P. Fackler Jr., *J. Am. Chem. Soc.*, 1984, **106**, 801.
6 A. Laguna and M. Laguna, *Coord. Chem. Rev.*, 1999, **193–195**, 837.
7 F. Mohr, S. K. Bhargava, S. Privér and M. A. Bennett, *Coord. Chem. Rev.*, in press.
8 M. A. Bennett, S. K. Bhargava, K. D. Griffiths, G. B. Robertson, W. A. Wickramasinghe and A. C. Willis, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 258.
9 M. A. Bennett, S. K. Bhargava, K. D. Griffiths and G. B. Robertson, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 260.
10 M. A. Bennett, S. K. Bhargava, D. C. R. Hockless, L. L. Welling and A. C. Willis, *J. Am. Chem. Soc.*, 1996, **118**, 10469.
11 M. A. Bennett, D. C. R. Hockless, A. D. Rae, L. L. Welling and A. C. Willis, *Organometallics*, 2001, **20**, 79.
12 S. K. Bhargava, F. Mohr, M. A. Bennett, L. L. Welling and A. C. Willis, *Organometallics*, 2000, **19**, 5628.
13 H. L. Hermann, P. Schwerdtfeger, S. K. Bhargava and F. Mohr, *Organometallics*, 2003, **22**, 2373.
14 M. A. Bennett, D. E. Berry, S. K. Bhargava, E. J. Ditzel, G. B. Robertson and A. C. Willis, *J. Chem. Soc., Chem. Commun.*, 1987, 1613.
15 M. A. Bennett, S. K. Bhargava, M. Ke and A. C. Willis, *J. Chem. Soc., Dalton Trans.*, 2000, 3537.
16 J. Messelhäuser, M. A. Bennett, S. K. Bhargava, E. J. Ditzel, G. B. Robertson, A. C. Willis and D. E. Berry, Presented at the XIIIth International Conference on Organometallic Chemistry, Turin, September 4–9, 1988.
17 M. A. Bennett, S. K. Bhargava, A. M. Bond, A. J. Edwards, S. Guo, S. H. Privér, A. D. Rae and A. C. Willis, *Inorg. Chem.*, 2004, **43**, 7752.
18 *SMART ver. 5.625 software for the CCD Detector System*, Bruker AXS Inc., Madison, WI, 2001.
19 *SAINTPLUS ver. 6.22 software for the CCD Detector System*, Bruker AXS Inc., Madison, WI, 2001.
20 SADABS program for absorption correction using SMART CCD data based on the method of Blessing: R. H. Blessing, *Acta Crystallogr., Sect A*, 1995, **33**, 51.
21 G. M. Sheldrick, *SHELXTL, ver. 6.10*, University of Göttingen, Göttingen, Germany, 1994.
22 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley-Interscience, New York, 3rd edn, 1978, p. 232.
23 H. Schmidbaur, *Gold Bull.*, 1990, **23**, 11; H. Schmidbaur, *Chem. Soc. Rev.*, 1995, **24**, 391.

24 S. K. Bhargava, F. Mohr and A. C. Willis, *Inorg. Chim. Acta*, 2003, **352**, 19.

25 L. C. Porter and J. P. Fackler, Jnr, *Acta Crystallogr., Sect. C*, 1986, **42**, 1646.

26 L. C. Porter and J. P. Fackler, Jnr, *Acta Crystallogr., Sect. C*, 1986, **42**, 1128.

27 H. H. Murray III, J. P. Fackler, Jr., L. C. Porter and A. M. Mazany, *J. Chem. Soc., Chem. Commun.*, 1986, 321.

28 R. Usón, A. Laguna, M. Laguna, J. Jiménez and P. G. Jones, *J. Chem. Soc., Dalton Trans.*, 1991, 1361.

29 B. Trzcinska–Bancroft, M. N. I. Khan and J. P. Fackler, Jr, *Organometallics*, 1988, **7**, 993.

30 H. H. Murray, J. P. Fackler, Jr., L. C. Porter, D. A. Briggs, M. A. Guerra and R. J. Lagow, *Inorg. Chem.*, 1987, **26**, 357.

31 L. C. Porter and J. P. Fackler, Jnr, *Acta Crystallogr., Sect. C*, 1987, **43**, 587.