Addition of Halogens to [{$Au(CH_2)_2PPh_2$}$_2$RX] Complexes. The Structures of *cis,trans*-[{$Au(CH_2)_2PPh_2$}$_2$(CH_2CF_3)Br_3] and *trans,trans*-[{$Au(CH_2)_2PPh_2$}$_2$-($CHCl_2$)Br_2Cl]†

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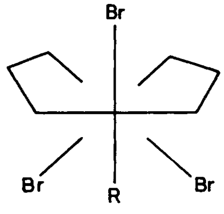
The syntheses and *X*-ray structures of the dinuclear gold(III) phosphorus ylide complexes *cis,trans*-[{$Au(CH_2)_2PPh_2$}$_2$(CH_2CF_3)Br_3] and *trans,trans*-[{$Au(CH_2)_2PPh_2$}$_2$($CHCl_2$)Br_2Cl] are reported. In $CDCl_3$, *cis,trans*-[{$Au(CH_2)_2PPh_2$}$_2$(CH_2CF_3)Br_3] is stable towards isomerisation after 4 d at 25 °C. The *cis,trans* and *trans,trans* complexes are obtained from the oxidative addition of Br_2 to the gold(II) alkyl halide complex [{$Au(CH_2)_2PPh_2$}$_2$(CH_2CF_3)I] and the reaction of [{$Au(CH_2)_2PPh_2$}$_2$] with an excess of $CHCl_2Br$, respectively. Crystallographic data: *cis,trans*-[{$Au(CH_2)_2PPh_2$}$_2$(CH_2CF_3)Br_3]·$(C_2H_5)_2O$, triclinic, space group $P\bar{1}$ (no. 2), a = 10.995(3), b = 13.056(3), c = 15.028(3) Å α = 93.35(2), β = 105.45(2), γ = 109.43(2)°, Z = 2, R = 0.058, R' = 0.058 for 2 782 unique reflections with $|F_o|^2 > 3\sigma(|F_o|^2)$; *trans,trans*-[{$Au(CH_2)_2PPh_2$}$_2$($CHCl_2$)$Br_2$Cl] triclinic, space group $P\bar{1}$ (no. 2), a = 11.716(4), b = 14.634(4), c = 9.619(3) Å, α = 94.44(3), β = 96.26(3), γ = 83.41(3)°, Z = 2, R = 0.081, R' = 0.086 for 2 254 reflections with $|F_o|^2 > 3\sigma(|F_o|^2)$. Both complexes contain four-co-ordinate gold atoms in the +3 oxidation state with an approximate square-planar arrangement of the bridging ligands. The metal atoms are separated by non-binding distances of 3.103(1) and 3.070(9) Å respectively.

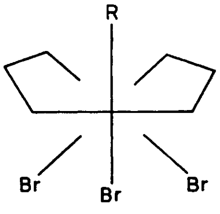
The oxidative addition of halogens or alkyl halides to the gold(I) phosphorus ylide dimer [{$Au(CH_2)_2PPh_2$}$_2$] (**1**) gives diamagnetic gold(II) complexes.[1] Further oxidative addition of the gold(II) dihalide complexes with halogens gives gold(III) tetrahalide complexes[2] except[3] where X = I. However, little is known[4] about gold(III) phosphorus ylide dimers of the general form [{$Au(CH_2)_2PR_2$}$_2X_3$R], containing both *halogen* and *alkyl* substituents. Five geometrical isomers, (A)—(E), can be drawn for this dimeric complex (X = Br), all containing non-equivalent gold centres. Such asymmetrical alkyl trihalides may be useful starting materials for the synthesis of heterovalent species by selectively reducing one of the gold(III) centres. By tagging one centre with a R group, interconversions of the five isomers can be followed. Studies of complexes of this type can lead to a better understanding of the nature of the interaction between the two metal centres in dimeric systems.

There are few[2a,5] structurally characterised gold(III) phosphorus ylide dimers derived from the parent complex of the general formula [{$Au(CH_2)_2PR_2$}$_2$] (R = Ph or Me). Although gold(III) tetrahalide dimers were first reported and structurally characterised[5] in 1975, the first gold(III) trihalide alkyl dimer to be characterised by an *X*-ray diffraction study has only recently been published.[4] The majority of gold(III) phosphorus ylide dimers structurally studied are A-frame complexes[6] of the general formula [{$Au(CH_2)_2PR_2$}$_2$(μ-CHR')X_2] (R' = H or NO_2; R = Me or Ph; X = halide or pseudohalide), the first[7] of which was structurally characterised in 1982.

Little is known about the gold(III) alkyl trihalide ylide dimers. A logical synthesis of such complexes is either the oxidative addition of alkyl halides to gold(II) dihalide complexes or the oxidative addition of a halogen to a gold(II) alkyl halide complex. Interestingly, although early studies[5] suggested that gold(III) tetrahalides could be obtained from gold(II) dihalide complexes,[8] there are no reports of the addition of halogens to stable dinuclear gold(II) alkyl halide species. This paper reports the results of such an investigation.



(A)



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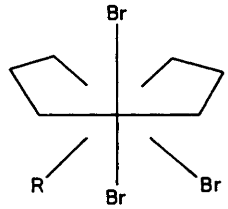

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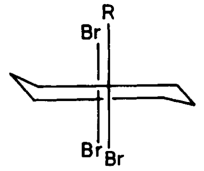

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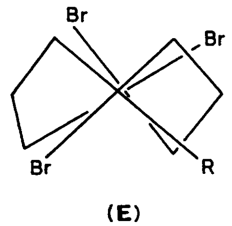

(E)

Results and Discussion

The two dinuclear gold(III) alkyl trihalide complexes we report here, *cis,trans*-[{$Au(CH_2)_2PPh_2$}$_2$(CH_2CF_3)Br_3] (**2**) and *trans,trans*-[{$Au(CH_2)_2PPh_2$}$_2$($CHCl_2$)Br_2Cl] (**3**), were obtained

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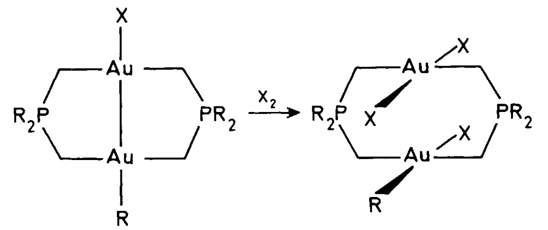
† In memory of T. A. Stephenson.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. Crystallographic data[a]

Complex	**(2)**	**(3)**
Formula	$C_{34}H_{40}Au_2Br_3F_3OP_2$	$C_{29}H_{29}Au_2Br_2Cl_3P_2$
Formula weight	1 217.26	1 099.61
a/Å	10.995(3)	11.716(4)
b/Å	13.056(3)	14.634(4)
c/Å	15.028(3)	9.619(3)
α/°	93.35(2)	94.44(3)
β/°	105.45(2)	96.26(3)
γ/°	109.43(2)	83.41(3)
U/Å^3	1 935.0(8)	1 625.1(9)
D_c/g cm^{-3}	2.09	2.25
Crystal size (mm)	0.40 × 0.35 × 0.20	0.25 × 0.25 × 0.20
F(000)	1 143.72	1 023.75
μ(Mo-K_α)/cm^{-1}	107.24	118.04
Orientation reflections, number, range (2θ)	20, 30—35	15, 20—25
Total reflections measured	5 047	4 272
Total with $F_o^2 > 3\sigma(F_o^2)$	2 782	2 254
Number of parameters refined	218	156
Transmission factors: max., min.	0.135, 0.049	0.033, 0.015
R[b]	0.058	0.081
R'[c]	0.058	0.086
Goodness-of-fit indicator[d]	1.216	1.429
Largest shift/e.s.d., final cycle	0.025	0.003
Largest peak, e Å^{-3}	1.64	3.74
g	0.0020	0.0047

[a] Details common to both complexes: space group $P\bar{1}$ (no. 2); no systematic absences; $Z = 2$; Mo-K_α radiation, $\lambda = 0.710\,73$ Å; 21 °C; scan method θ—2θ; data collection range 0—45°, 2θ; 3 check reflections every 97. [b] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [c] $R' = \Sigma w^{\frac{1}{2}}|F_o - F_c|/\Sigma w^{\frac{1}{2}}F_o$, $w^{-1} = [\sigma^2|F_o| + g|F_o|^2]$. [d] Goodness-of-fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_p)]^{\frac{1}{2}}$.



from the addition of Br_2 to $[\{Au(CH_2)_2PPh_2\}_2(CH_2CF_3)I]$ and the reaction of **(1)** with an excess of $CHCl_2Br$ respectively. Crystal data and details of the crystallographic experimental parameters for complexes **(2)** and **(3)** are summarised in Table 1, fractional positional parameters in Tables 2 and 3, and important interatomic dimensions in Tables 4 and 5. Views of **(2)** and **(3)** with the crystallographic numbering scheme for the atoms are shown in Figures 1 and 2.

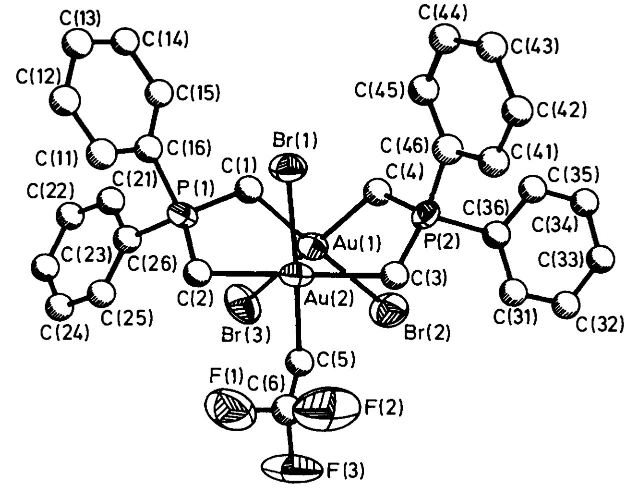


Figure 1. Perspective view of *cis,trans*-$[\{Au(CH_2)_2PPh_2\}_2(CH_2CF_3)Br_3]\cdot(CH_3CH_2)_2O$ **(2)**, showing the numbering scheme. Hydrogen atoms omitted and carbon atoms given an arbitrary radius for clarity, all other atoms are shown as 50% probability thermal ellipsoids. Diethyl ether not shown

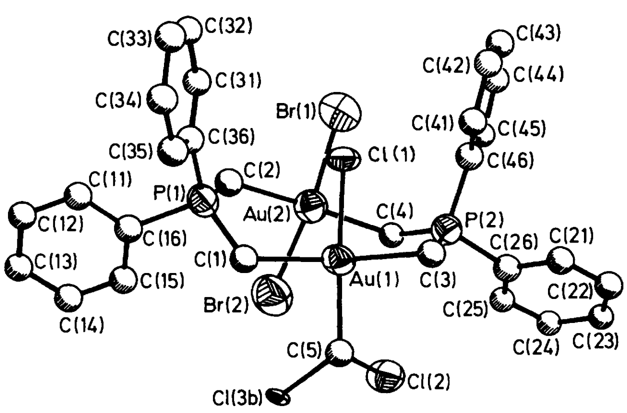


Figure 2. Perspective view of *trans,trans*-$[\{Au(CH_2)_2PPh_2\}_2(CHCl_2)Br_2Cl]$ **(3)**, showing the numbering scheme. Hydrogen atoms omitted and carbon atoms given an arbitrary radius for clarity, all other atoms shown as 50% probability thermal ellipsoids

cis,trans-$[\{Au(CH_2)_2PPh_2\}_2(CH_2CF_3)Br_3]$ **(2)**.—Complex **(2)** was obtained from the direct reaction of $[\{Au(CH_2)_2PPh_2\}_2(CH_2CF_3)I]$, with an excess of Br_2. The ^1H n.m.r. spectrum of the crude reaction product suggests that a mixture of gold(III) complexes is obtained.* However, the ^1H n.m.r. spectrum (Figure 3) of the recrystallised product is consistent with the isomer *cis,trans*-$[\{Au(CH_2)_2PPh_2\}_2(CH_2CF_3)Br_3]$ **(2)**, which has been structurally characterised (Figure 1).

The observation (^1H n.m.r. and *X*-ray)[9] of *trans,trans*-$[\{Au(CH_2)_2PPh_2\}_2Br_4]$ as a product from the reaction of excess of Br_2 and $[\{Au(CH_2)_2PPh_2\}_2(CH_2CF_3)I]$ shows that the CH_2CF_3 moiety can be replaced by Br. Whether this occurs on gold(II) before oxidative addition or a gold(III) centre after oxidative addition cannot be determined from the available data.

The possibility exists that the addition of halogen to dinuclear gold(II) alkyl halide ylide complexes initially gives a *trans,trans* isomer which then isomerises during the course of crystallisation. The type **(D)** isomer of complex **(2)** would suffer steric repulsions between the eclipsed CH_2CF_3 and Br ligands. These repulsions can be relieved either by buckling of the organometallic ring, as is the case for complex **(3)**, or by *trans* ⟶ *cis* isomerisation. When the *trans,trans* gold(III) tetrabromide stands in $CDCl_3$ for prolonged periods, the geometrical isomer with a *cis,trans* conformation is formed.[9] Further isomerisation of **(2)** to produce the *cis,cis* geometrical isomer **(E)** was not observed.

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* Upon crystallisation, a single crystal of $[\{Au(CH_2)_2PPh_2)\}_2(\mu\text{-}Br)Br_2][IBr_2]$ was obtained: monoclinic, space group $P2_1/c$ (no. 14), $a = 9.582(5)$, $b = 32.551(9)$, $c = 12.634(5)$ Å, $\beta = 109.91(3)$°, $U = 3\,705(3)$Å^3, $Z = 4$, $R = 0.087$, $R' = 0.086$ for 156 parameters and 899 unique reflections with $|F_o|^2 > 3\sigma(|F_o|^2)$. The complete description of this minor reaction product will be published elsewhere.

Table 2. Atomic co-ordinates (× 10^4) for *cis,trans*-$[\{Au(CH_2)_2PPh_2\}_2(CH_2CF_3)Br_3]\cdot(C_2H_5)_2O$ (**2**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Au(1)	3 931(1)	3 572(1)	3 870(1)	C(22)	9 397	7 059	4 512
Au(2)	3 415(1)	2 780(1)	1 770(1)	C(23)	10 272	6 510	4 453
Br(1)	2 531(3)	4 128(2)	979(2)	C(24)	9 791	5 510	3 852
Br(2)	3 002(4)	1 865(3)	4 487(2)	C(25)	8 434	5 060	3 311
Br(3)	6 263(3)	3 679(3)	4 663(2)	C(26)	7 559	5 610	3 370
P(1)	5 814(7)	5 111(5)	2 659(4)	C(31)	−277(18)	504(16)	3 130(12)
P(2)	751(7)	2 446(5)	2 414(4)	C(32)	−1 154	−183	3 549
F(1)	5 127(22)	1 444(16)	1 057(12)	C(33)	−2 127	142	3 790
F(2)	3 159(23)	453(16)	805(12)	C(34)	−2 223	1 154	3 611
F(3)	4 692(23)	118(16)	1 765(13)	C(35)	−1 345	1 841	3 192
C(1)	4 662(29)	5 010(24)	3 388(16)	C(36)	−372	1 516	2 951
C(2)	5 443(26)	3 877(25)	1 913(17)	C(41)	−1 416(18)	2 137(11)	897(11)
C(3)	1 509(26)	1 771(22)	1 782(17)	C(42)	−2 347	2 425	231
C(4)	1 924(27)	3 526(23)	3 276(16)	C(43)	−2 248	3 521	266
C(5)	4 133(26)	1 620(22)	2 239(15)	C(44)	−1 217	4 329	968
C(6)	4 280(30)	946(22)	1 501(17)	C(45)	−286	4 040	1 634
C(11)	6 187(18)	6 316(12)	1 251(11)	C(46)	−385	2 945	1 598
C(12)	6 306	7 249	822	C(7)	2 569(105)	7 924(87)	3 014(64)
C(13)	5 942	8 082	1 167	C(8)	3 357(65)	8 907(55)	3 808(41)
C(14)	5 459	7 983	1 939	C(9)	596(79)	7 909(64)	1 890(47)
C(15)	5 341	7 050	2 367	C(10)	−3(66)	8 351(53)	1 287(41)
C(16)	5 705	6 216	2 023	O	1 700(38)	8 712(34)	2 570(28)
C(21)	8 040(17)	6 609(13)	3 970(11)				

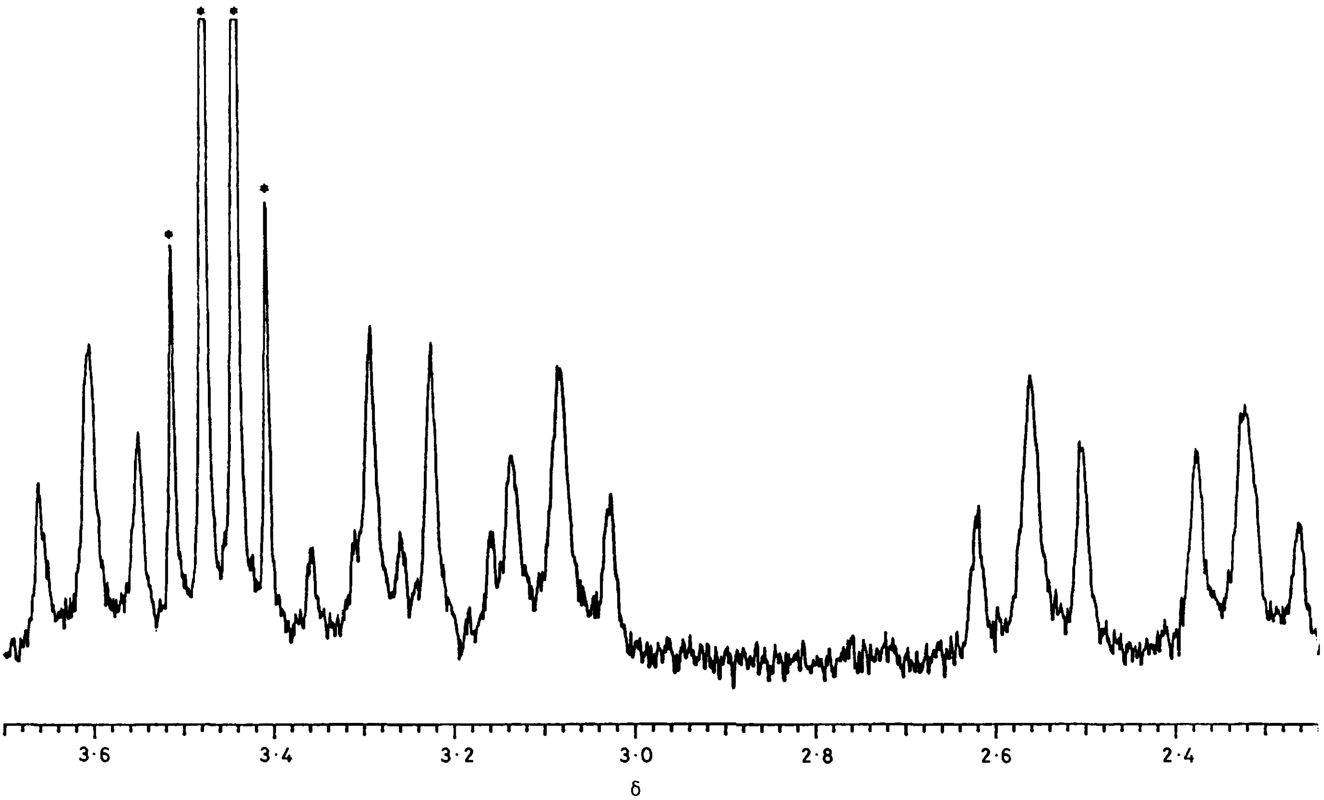

Figure 3. Proton n.m.r. spectrum ($CDCl_3$, 200 MHz) of *cis,trans*-$[\{Au(CH_2)_2PPh_2\}_2(CH_2CF_3)Br_3]$ at +22 °C, methylene region; 3.70—2.22 p.p.m. The asterisk identifies the methylene resonance of the diethyl ether

trans,trans-$[\{Au(CH_2)_2PPh_2\}_2(CHCl_2)Br_2Cl]$ (**3**).—Complex (**3**), an alkyl trihalide gold(III) dimer, is formed from the halogenation of the gold(II) alkyl halide adduct $[\{Au(CH_2)_2PPh_2\}_2(CHCl_2)Br]$, initially obtained in the reaction of neat $CHCl_2Br$ with (**1**). This gold(II) complex is observed by its ^1H n.m.r. spectrum but was not isolated. Presumably further oxidation of $[\{Au(CH_2)_2PPh_2\}_2(CHCl_2)Br]$ by Br_2 generates a alkyl tribromo gold(III) ylide dimer. The fully characterised product obtained upon crystallisation has a Cl, not a Br, *trans* to the $CHCl_2$ moiety (Figure 2). Product (**3**) apparently results from Cl in the solvent. The bromide *trans* to the alkyl group is expected to be labilised (*trans* effect) relative to the *trans* halides.

Table 3. Atomic co-ordinates (× 10^4) for *trans,trans*-[$\{Au(CH_2)_2PPh_2\}_2(CHCl_2)Br_2Cl$] (**3**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Au(1)	6 379(2)	7 519(2)	3 452(2)	C(16)	10 140	6 064	2 283
Au(2)	7 886(2)	6 718(1)	5 978(2)	C(21)	3 031(30)	8 402(19)	7 052(35)
Br(1)	8 537(6)	7 948(4)	7 578(7)	C(22)	1 977	8 328	7 560
Br(2)	7 554(6)	5 251(5)	4 756(7)	C(23)	1 753	7 490	8 017
Cl(1)	7 274(9)	8 894(7)	4 083(10)	C(24)	2 583	6 728	7 966
Cl(2)	4 518(10)	5 973(8)	3 629(11)	C(25)	3 637	6 802	7 458
Cl(3a)	4 189(15)	7 251(11)	1 357(15)	C(26)	3 861	7 640	7 001
Cl(3b)	5 808(15)	5 706(14)	1 197(18)	C(31)	10 491(31)	8 414(25)	4 123(28)
P(1)	9 234(11)	6 960(8)	3 214(11)	C(32)	10 926	9 231	3 890
P(2)	5 265(10)	7 784(8)	6 501(11)	C(33)	10 726	9 585	2 569
C(1)	7 815(34)	6 955(29)	2 414(41)	C(34)	10 090	9 121	1 481
C(2)	9 400(35)	6 626(30)	4 988(40)	C(35)	9 655	8 304	1 714
C(3)	5 061(37)	8 083(31)	4 742(42)	C(36)	9 855	7 951	3 035
C(4)	6 263(34)	6 794(28)	6 885(42)	C(41)	5 938(26)	9 568(20)	7 130(22)
C(5)	5 363(43)	6 527(34)	2 433(50)	C(42)	6 356	10 275	8 030
C(11)	11 177(23)	6 260(14)	1 845(27)	C(43)	6 570	10 164	9 465
C(12)	11 895	5 561	1 209	C(44)	6 366	9 345	10 000
C(13)	11 576	4 667	1 010	C(45)	5 948	8 638	9 100
C(14)	10 539	4 472	1 448	C(46)	5 734	8 749	7 665
C(15)	9 821	5 171	2 085				

Table 4. Selected distances (Å) and angles (°) for *cis,trans*-[$\{Au(CH_2)_2PPh_2\}_2(CH_2CF_3)Br_3$]·$Et_2O$ (**2**)

Au(1) ⋯ Au(2)	3.103(1)	Au(1)–C(4)	2.13(3)
Au(1)–Br(2)	2.470(3)	Au(2)–C(5)	2.01(3)
Au(1)–Br(3)	2.476(4)	Au(2)–C(2)	2.16(3)
Au(2)–Br(1)	2.493(3)	Au(2)–C(3)	2.08(3)
Au(1)–C(1)	2.04(3)		
Br(2)–Au(1)–Br(3)	90.4(1)	Br(1)–Au(2)–C(5)	172.3(7)
C(1)–Au(1)–C(4)	89.8(12)	C(2)–Au(2)–C(3)	174.0(10)
Br(2)–Au(1)–C(1)	177.7(10)		

Table 5. Selected distances (Å) and angles (°) for *trans,trans*-[$\{Au(CH_2)_2PPh_2\}_2(CHCl_2)Br_2Cl$] (**3**)

Au(1) ⋯ Au(2)	3.070(9)	Au(2)–Br(1)	2.412(10)
Au(2)–Br(2)	2.417(10)	Au(1)–Cl(1)	2.382(13)
Au(1)–C(5)	2.099(51)	Au(2)–C(2)	2.089(43)
Br(1)–Au(2)–Br(2)	165.9(3)	Br(1)–Au(2)–C(2)	90.8(11)
Cl(1)–Au(1)–C(5)	163.8(14)	Cl(1)–Au(1)–C(3)	87.0(13)
C(1)–Au(1)–C(3)	172.9(15)	C(1)–P(1)–C(2)	113.2(21)
C(2)–Au(2)–C(4)	176.6(15)		

Description of Structures.—The distinguishing feature of complex (**2**) is the unusual *cis,trans* geometry of the bridging ylide ligands. Although the *cis,trans* bridging ylide linkage might seem to be subject to internal strain, an examination of (*a*) the geometries about the phosphorus centres, (*b*) the Au–CH_2–P angle, (*c*) the co-ordination about the gold centres, and (*d*) the steric interaction of the Au-bond moieties across the ring from each other suggests that the *cis,trans* configuration of these four-co-ordinate gold(III) ylide dimers is strain free. Specifically, eleven of the twelve C–P–C angles fall within the range of 102.8(9)—114.4(13)°, with an average of 109.4°. These values are similar to those seen[1a,b] for the gold(I) parent complex [$\{Au(CH_2)_2PPh_2\}_2$] and the gold(II) trifluoroethyl iodide precursor, 105—113°. The Au–CH_2–P angles for the *trans* methylenes [C(2) and C(3)] are tetrahedral within 2.5 estimated standard deviations (e.s.d.s), 104.7(21) and 110.2(15)° respectively. The methylenes co-ordinated to Au(2) form angles of 124.3(27) and 121.7(23)° with the tetrahedral phosphorus. This 10 to 15° increase in the Au–CH_2–P angle seems to be where the greatest deviation from idealised geometries is observed.

As seen in Figure 1, the co-ordination about the gold centres is square planar (all angles are 90° within ±3 e.s.d.). Furthermore, the two square-planar gold(II) centres are staggered with respect to each other, thereby minimising the steric interaction of the CH_2CF_3 and Br across the ring.

The bromine ligands *trans* to methylene groups in (**2**), Au(1)–Br(2) and Au(1)–Br(3), have bond lengths which are longer by an average of 0.045 Å compared with those observed[9] in the more symmetrical *trans,trans* gold(III) tetrabromide complex, [$\{Au(CH_2)_2PPh_2\}_2Br_4$]. The Au–Br bond lengths in complex (**2**) show little variation regardless of whether the Br is co-ordinated *trans* to an ylide methylene carbon or the trifluoroethyl ligand.

The heterocyclic eight-membered ring of complex (**3**) assumes a twist-boat conformation in order to minimise the steric interaction of $CHCl_2$ and Br substituents (Figure 2). The phosphorus centres and methylene carbons are all tetrahedral within ±3 e.s.d. The Au–Br bond lengths are 2.412(10) Å and 2.417(10) Å, in good agreement with those in the *trans,trans* gold(III) tetrabromide[9] [2.411(3) and 2.440(3) Å]. Note that the Br–Au–Br angles in both complexes are very similar, 165.9(3) and 164.3(1)°.

The geometry about both gold centres is four-co-ordinate square planar. They are separated by 3.070(9) Å, a non-bonding distance. The gold-bound Cl in (**3**) is *trans* to a $CHCl_2$ unit [Au(1)–Cl(1) 2.382(13) Å]. This Au–Cl bond length (*trans* to the $CHCl_2$) is consistent with the Au–Cl bond lengths observed[9] for the *cis* Cl of *cis,trans*-[$\{Au(CH_2)_2PPh_2\}_2Cl_4$] [2.338(9) and 2.360(7) Å]. This contrasts with the Au–Cl distances *trans* to each other in *cis,trans*-[$\{Au(CH_2)_2PPh_2\}_2Cl_4$] [2.295(9) and 2.272(9) Å]. Again the *trans* influence of an alkyl group *versus* another halide accounts for this observation. This has been used to rationalise the formation of complex (**3**) which contains a Cl *trans* to the $CHCl_2$ moiety.

The angles formed between *trans* ligands of all four gold centres of complex (**2**) and (**3**) show small deviations from the ideal 180° angle. Any deviations are probably attributed to steric interactions and solid-state packing forces rather than metal–metal interactions across the 3.103(1) and 3.070(9) Å distances.

Proton N.M.R. Solution Spectroscopy of cis,trans-$[\{Au(CH_2)_2PPh_2\}_2(CH_2CF_3)Br_3]$.—The single-crystal *X*-ray diffraction study of (**2**) shows that the two halides on the gold centre are *cis* (Figure 1). This discrete molecule characterised in the solid state has point-group symmetry C_s and would have four unique methylene resonances in the ^{1}H n.m.r. spectrum (eight methylene protons, with *gem*-J_{HH} and J_{HP} splitting) if the solid-state *cis,trans* relationship is maintained in solution.

When a recrystallised sample of (**2**) is dissolved in $CDCl_3$ the ^{1}H n.m.r. spectrum obtained is consistent with the solid-state crystal structure, isomer (**A**). Note that interstitial diethyl ether was found in the crystal structure as well as in the ^{1}H n.m.r. spectrum of this sample. Figure 3 shows the ^{1}H n.m.r. spectrum of the methylene region of (**2**). This spectrum is also consistent with isomer (**B**). However, since the spectrum was obtained from the same recrystallised sample of complex (**2**) from which the single crystal used in the *X*-ray crystal structure determination was taken and since there is no reason to believe that isomer (**A**) has been converted completely into isomer (**B**) [the only other isomer of the five possible geometrical isomers which is of the appropriate symmetry to have an ^{1}H n.m.r. spectrum consistent with (**2**)] it is reasonable to assume that it is that of the discrete molecule whose structure is shown in Figure 1.

Experimental

Synthesis and ^{1}H *N.M.R. Spectra.*—All solvents were distilled and dried according to standard methods.[10] All reactions were carried out with exclusion of oxygen and water using Schlenk techniques.[11] The complexes $[\{Au(CH_2)_2PPh_2\}_2]$, $[\{Au(CH_2)_2PPh_2\}_2(CH_2CF_3)I]$, and $[\{Au(CH_2)_2PPh_2\}_2(CH_2Cl)Br]$ were synthesised according to published procedures. [1a,b,f] Proton n.m.r. spectra were obtained in $CDCl_3$ at 36 °C at 90 MHz with a Varian EM-390, using $SiMe_4$ as internal standard, or with a Varian XL-200 instrument (solvent $CDCl_3$) at 20 °C with concentration *ca.* 10^{-3} mol dm^{-3} unless otherwise stated. No attempt was made to obtain the sign of the coupling constants.

cis,trans-$[\{Au(CH_2)_2PPh_2\}_2(CH_2CF_3)Br_3]$ (**2**). To $[\{Au(CH_2)_2PPh_2\}_2(CH_2CF_3)I]$ (27.6 mg, 0.027 mmol) was added 3.9×10^{-2} mol dm^{-3} Br_2 (0.28 mmol, 7.3 cm^3) in CH_2Cl_2 at 25 °C and stirred for 25 min. The reaction was reduced to approximately 1/4 of its original volume *in vacuo* and the crude product precipitated with hexane leaving 27.5 mg of a yellow powder, m.p. 160 °C. Crystallisation from CH_2Cl_2 and diethyl ether gave complex (**2**) as yellow crystals containing interstitial $(C_2H_5)_2O$ (as determined from ^{1}H n.m.r. and an *X*-ray diffraction study), $[\{Au(CH_2)_2PPh_2\}_2Br_4]$ as dark orange crystals (^{1}H n.m.r.), and a dark red crystal of $[\{Au(CH_2)_2PPh_2\}_2(\mu\text{-}Br)Br_2][BrIBr]$, a cationic A-frame with a bridging Br. Proton n.m.r. of (**2**) (solvent $CDCl_3$, 200 MHz, 22 °C): δ 7.8—7.4 (20 H, m, Ph); 2.32, 2.55, 3.08, and 3.60 (8 H, dd, J_{HP} and J_{HH}, 11.6, 11.7, 10.8, and 10.9, Au–CH$_2$–P); 2.26 (2 H, q, J_{HF} 13.6 Hz, Au–CH$_2$CF$_3$). Crystals suitable for *X*-ray diffraction were obtained by crystallisation from a diethyl ether–dichloromethane solution.

trans,trans-$[\{Au(CH_2)_2PPh_2\}_2(CHCl_2)Br_2Cl]$ (**3**). Crystals were obtained by dissolving $[\{Au(CH_2)_2PPh_2\}_2]$ (30 mg) in $CHCl_2Br$ (*ca.* 1 cm^3) stirring for 5 min. The solvent was then removed under reduced pressure, the product was taken up in CH_2Cl_2, and allowed to crystallise by diffusion with diethyl ether in a closed system.

The reaction of $[\{Au(CH_2)_2PPh_2\}_2]$ (25 mg, 0.03 mmol) with $CHCl_2Br$ (slight excess) in CH_2Cl_2 (3 cm^3) at 25 °C for 20 min, followed by reduction of volume under reduced pressure and addition of hexane to precipitate the product, gave 20.5 mg (0.021 mmol) of $[\{Au(CH_2)_2PPh_2\}_2Br_2]$, approximately 70% yield.

A solution of $[\{Au(CH_2)_2PPh_2\}_2]$ in $CDCl_3$, when monitored by ^{1}H n.m.r. spectroscopy as a function of the addition of $CHCl_2Br$, reveals the predominant product to be $[\{Au(CH_2)_2PPh_2\}_2Br_2]$, δ_H 1.88 (d, J_{HP} 10.1 Hz, Au–CH$_2$–P). An asymmetrically substituted gold(II) product is also formed, assigned as $[\{Au(CH_2)_2PPh_2\}_2(CHCl_2)Br]$ on the basis of the ^{1}H n.m.r. spectrum: δ_H(200 MHz, $CDCl_3$, methylene region, 22 °C) 5.67 (1 H, s, Au–CHCl$_2$); 1.84 and 1.68 (4 H, d, J_{HP} 9.5 and 10.5 Hz, Au–CH$_2$–P). These values correspond very well to the ^{1}H n.m.r. data for the gold(II) bromoform adduct,[1c] $[\{Au(CH_2)_2PPh_2\}_2(CHBr_2)Br]$, δ_H(solvent $CDCl_3$, methylene region, 200 MHz, 22 °C) 5.56 (1 H, s, Au–CHBr$_2$); 1.90 and 1.71 (4 H, d, J_{HP} 10.5 and 10.5 Hz, Au–CH$_2$–P), and for the chloroiodomethane gold(II) adduct,[1c] $[\{Au(CH_2)_2PPh_2\}_2(CH_2Cl)I]$, δ_H(solvent $CDCl_3$, 90 MHz, 35 °C) 3.72 (2 H, s, Au–CH$_2$Cl), 1.55 and 2.00 (4 H, d, J_{HP} 11.4 and 11.1 Hz, Au–CH$_2$–P).

These results indicate that the product we have crystallographically characterised, *trans,trans*-$[\{Au(CH_2)_2PPh_2\}_2(CHCl_2)Br_2Cl]$ (**3**), is formed *via* the oxidative addition of halogen to a gold(II) precursor, $[\{Au(CH_2)_2PPh_2\}_2(CHCl_2)Br]$ followed by halogen exchange. Complex (**3**) is a minor component.

Addition of Br_2 *and* ICl *to Other Gold*(II) *Complexes and a Gold*(III) *A-Frame*: ^{1}H *N.M.R. Studies.*—The addition of an excess of Br_2 to the gold(II) dimer $[\{Au(CH_2)_2PPh_2\}_2(CH_2Cl)I]$ yields a yellow complex the ^{1}H n.m.r. spectrum of which contains two doublets, δ_H 2.53 and 2.43 (J_{HP} 10.5 and 10.5 Hz). The protons of the Au–CH$_2$Cl moiety resonate at 3.70 p.p.m. In this reaction a gold(III) alkyl trihalide ylide dimer $[\{Au(CH_2)_2PPh_2\}_2(CH_2Cl)Br_3]$ as well as the gold(III) tetrabromide, $[\{Au(CH_2)_2PPh_2\}_2Br_4]$, are formed. The latter, identified by its by its ^{1}H n.m.r. spectrum, is the only reaction product that can be isolated in crystalline form. Similarly, the addition of an excess of ICl to $[\{Au(CH_2)_2PPh_2\}_2(CH_2Cl)I]$ gave a light yellow complex the ^{1}H n.m.r. spectrum of which contains two doublets, δ_H ($CDCl_3$, 22 °C) 2.37 and 2.33 (J_{PH} 10.5 Hz each) and a singlet at 3.37 p.p.m. The complex $[\{Au(CH_2)_2PPh_2\}_2Cl_4]$ is also formed and is the only product that can be recrystallised.

The addition of an excess of Br_2 to the neutral gold(III) A-frame complex $[\{Au(CH_2)_2PPh_2\}_2(\mu\text{-}CH_2)Br_2]$ in CH_2Cl_2 generated the *trans,trans* gold(III) alkyl trihalide dimer $[\{Au(CH_2)_2PPh_2\}_2(CH_2Br)Br_3]$, as is evident from the ^{1}H n.m.r. specrum. Two methylene doublets at δ_H 2.62 and 2.52 (J_{HP} 10.5 and 11.2 Hz, Au–CH$_2$–P) and a singlet at 3.36 (Au–CH$_2$Br) are observed. This ^{1}H n.m.r. spectrum indicates oxidative cleavage of a Au–C bond of the bridging methylene giving Au–Br and Au–CH$_2$Br centres. This observation suggests that gold–carbon bond cleavage is more rapid for the μ-CH$_2$ than for the methylene groups on the ylide ligands.

Crystallography.—The structures of both complexes reported were determined from intensity data collected at room temperature as diffracted from suitably shaped single crystals sealed inside 0.5-mm glass capillaries. Data collection was carried out on a Nicolet R3m/E automated diffractometer using the θ—2θ scanning technique in bisecting geometry (graphite-monochromated Mo-K_α radiation). Triclinic symmetry was suggested for (**2**) and (**3**) on the basis of interaxial angles and confirmed using a Delaunay reduction[12] procedure. Axial lengths were verified by measuring the interlayer spacing observed in axial photographs and refined cell parameters were obtained from the setting angles of high-angle reflections. The data were corrected for standard decay, absorption, Lorentz and polarisation effects. Absorption corrections were estimated empirically on the basis of azimuthal scans of medium-intensity reflections spanning a range of 2θ values. Crystal data and details of the crystallographic experimental parameters for complexes (**2**) and (**3**) are summarised in Table 1. All structural results were obtained using the SHELXTL collection of crystallographic software.[9] Gold atom co-ordinates were determined from a sharpened Patterson map and used as an initial phasing model for a difference Fourier synthesis. Intensity statistics favoured the centrosymmetric space group $P\bar{1}$. Refinement was based on F using a weighting scheme of the form $w^{-1} = (\sigma^2|F_o| + g|F_o|^2)$. Neutral scattering factors, including terms for anomalous dispersion, were taken from ref. 13.

Refinement of the structure of complex (**2**) was uneventful and revealed that diethyl ether from recrystallisation was present in the lattice. Phenyl rings were refined as rigid bodies, C–C–C 120°, C–C 1.39 Å, hydrogens in calculated positions. All non-hydrogen atoms refined anisotropically except for carbons of the four phenyl groups and the carbon atoms of the diethyl ether.

During the later stages of refinement of the structure of complex (**3**) it became apparent that the dichloromethyl group was subject to some degree of rotational disorder or high-amplitude thermal motion. A difference Fourier map calculated using structure factors from a model with these atoms removed revealed three peaks of approximately equal electron density in the vicinity of C(5). These peaks were therefore assigned as chlorine atoms and given 2/3 site occupancy factors over three locations. All non-hydrogen atoms, except for the four phenyl rings of (**3**), were refined anisotropically. The phenyl rings were refined as rigid bodies as carried out in complex (**2**) and described in previous paragraphs. Positional parameters for complexes (**2**) and (**3**) are given in Tables 2 and 3 respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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