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Mono-, Bi- and Trinuclear Bis(diphenylarsino)methane Gold Complexes. Crystal and Molecular Structure of $[\{(C_6F_5)_3Au(Ph_2AsCH_2AsPh_2)\}_2Ag(OClO_3)]$*

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Abstract

Addition of bis(diphenylarsino)methane (dpam) to neutral or cationic gold(I) or gold(III) complexes containing weakly coordinating ligands leads to the formation of mononuclear $\{R_3Au(dpam)$, $R_2ClAu(dpam)$, $[R_2Au(dpam)]ClO_4$ $(R = C_6F_5)\}$ or binuclear complexes $\{RAu(dpam)AuR$, $[Au_2(dpam)_2](ClO_4)_2\}$. Mixed gold(III)–gold(I) compounds can be synthesized either by oxidation of the gold(I) complexes or from mononuclear gold(III) derivatives. Reaction of $R_3Au(dpam)$ with ClAu(tht), $[Au(tht)_2]ClO_4$ or $AgClO_4$ leads to the trinuclear complexes $[\{R_3Au(dpam)\}_2Au]X$ ($X = [AuCl_2]$ or ClO_4) or $[\{R_3Au(dpam)\}_2Ag(OClO_3)]$, respectively. The structure of the silver complex has been determined by X-ray crystallography.

Introduction

Although in recent years the chemistry of the bis(diphenylphosphino)methane ligand has received a great deal of attention [1] and several gold derivatives have been prepared [2–4], no systematic study of the bis(diphenylarsino)methane (dpam) ligand in organometallic gold chemistry has been carried out until now.

In the present paper we describe the preparation of (a) mononuclear gold(III) complexes with uni- and bidentate dpam, (b) binuclear gold(I), gold(III), and mixed gold(III)–gold(I) complexes with dpam as bridging ligand, and (c) trinuclear mixed gold(III)–gold(I) or gold(III)–silver(I) complexes with bridging dpam.

Experimental

The instrumentation employed and general experimental techniques were as described earlier [5]. The yields, melting points, C, H and Au analyses, conductivities and molecular weights of the novel complexes are listed in Table I.

Preparation of the Complexes

All the reactions were run at room temperature.

$(C_6F_5)_3Au(dpam)$ (1)

A solution of $(C_6F_5)_3Au(tht)$ [6] (0.166 g, 0.21 mmol) and dpam (0.099 g, 0.21 mmol) in 25 ml of dichloromethane was stirred for 5 min. Concentration to *ca.* 5 ml and addition of hexane (20 ml) led to the precipitation of white crystals of **1**.

$(C_6F_5)_2ClAu(dpam)$ (2)

To a solution of $Bu_4N[(C_6F_5)_2AuCl_2]$ [7] (0.652 g, 0.76 mmol) in 50 ml of diethylether was added $AgClO_4$ (0.158 g, 0.76 mmol); the mixture was stirred for 90 min under exclusion of light. The precipitated AgCl and $[Bu_4N]ClO_4$ were removed. To the resulting solution was added dropwise a solution of dpam (0.359 g, 0.76 mmol) in 30 ml of diethylether and stirring continued for 30 min. Evaporation to ~5 ml and addition of hexane (20 ml) led to the white complex **2**.

$[(C_6F_5)_2Au(dpam)]ClO_4$ (3)

To a solution of complex **2** (0.250 g, 0.24 mmol) in 30 ml of dichloromethane was added $AgClO_4$ (0.050 g, 0.24 mmol); the mixture was stirred for 90 min under exclusion of light. Removal of AgCl, concentration of the filtrate to *ca.* 2 ml, and subsequent slow addition of diethyl ether (20 ml) led to the crystallization of complex **3**.

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*Dedicated to Professor Rafael Usón on his 60th birthday.

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TABLE I. Analytical Data for Complexes

Complex[a]	Yield (%)	Analysis, found (calculated) (%)			Λ_M[b]	Molecular weight[c], found (calculated)	Melting point (°C)
		C	H	Au			
1 $R_3Au(dpam)$	90	43.75	1.9	16.65	0	1091	197
		(44.1)	(1.9)	(16.85)		(1170)	
2 $R_2ClAu(dpam)$	82	42.45	2.35	19.25	0	1069	179
		(42.75)	(2.15)	(18.95)		(1039)	
3 $[R_2Au(dpam)]ClO_4$	76	39.65	1.95	17.45	108		100(d)
		(40.3)	(2.0)	(17.85)			
4 $R_2\overline{Au(AsPh_2CHAs}Ph_2)$	45	43.65	2.65	20.5	5	997	154(d)
		(44.35)	(2.1)	(19.65)		(1002)	
5 $RAu(dpam)AuR$	97	36.95	1.95	33.5	0	1191	189(d)
		(37.0)	(1.85)	(32.8)		(1200)	
6 $[Au_2(dpam)_2](ClO_4)_2$	92	39.15	2.9	25.15	196		228(d)
		(39.05)	(2.9)	(25.6)			
7 $RCl_2Au(dpam)AuR$	82	35.4	1.8	31.7	20	1248	136
		(34.95)	(1.75)	(31.0)		(1271)	
8 $[Cl_2Au(dpam)_2Au](ClO_4)_2$	90	37.35	2.85	24.35	224		130(d)
		(37.35)	(2.75)	(24.5)			
9 $[Cl_2Au(dpam)_2AuCl_2](ClO_4)_2\cdot 1/2OEt_2$	93	36.55	2.9	22.45	198		135(d)
		(36.4)	(3.1)	(22.95)			
10 $R_3Au(dpam)AuR_3$	94	39.5	1.2	21.2	3	1779	189(d)
		(39.2)	(1.2)	(21.1)		(1868)	
11 $[R_3Au(dpam)AuPPh_3]ClO_4$	62	43.15	2.5	22.8	116		199(d)
		(42.35)	(2.15)	(22.8)			
12 $[R_3Au(dpam)Au(dpam)AuR_3][AuCl_2]$	90	37.4	2.05	28.7	80	2554	138
		(36.8)	(1.6)	(28.05)		(2808)	
13 $[R_3Au(dpam)Au(dpam)AuR_3]ClO_4$	81	39.05	1.85	22.3	107		168(d)
		(39.15)	(1.7)	(22.4)			
14 $R_3Au(dpam)Ag(OClO_3)(dpam)AuR_3$	85	40.5	1.7	20.35	120		125(d)
		(40.55)	(1.75)	(19.7)			

[a] $R = C_6F_5$. [b] In acetone, $ohm^{-1}\ cm^2\ mol^{-1}$. [c] In chloroform.

$(C_6F_5)_2\overline{Au(Ph_2AsCHAs}Ph_2)$ (4)

To a suspension of NaH (0.3 g, 12.4 mmol) in diethylether (15 ml) was added complex **3** (0.298 g, 0.27 mmol). After 1 h stirring, the excess of NaH and the $NaClO_4$ precipitated were removed by filtration. Evaporation of the yellow filtrate to *ca.* 2 ml and addition of hexane under nitrogen led to the yellow complex **4**.

$C_6F_5Au(dpam)AuC_6F_5$ (5)

To a solution of $C_6F_5Au(tht)$ [8] (0.767 g, 1.70 mmol) in 50 ml of dichloromethane was added dpam (0.401 g, 0.85 mmol); the mixture was stirred for 30 min. Concentration to *ca.* 5 ml and addition of hexane (20 ml) gave a white solid of **5**, which was recrystallized from diethylether hexane.

$[Au_2(dpam)_2](ClO_4)_2$ (6)

To a dichloromethane solution (35 ml) of $[Au(tht)_2]ClO_4$ [9] (0.142 g, 0.3 mmol) was added dpam (0.142 g, 0.3 mmol); the mixture was stirred for 30 min. Concentration to *ca.* 5 ml and addition of hexane (20 ml) gave a white solid of **6**.

$(C_6F_5)Cl_2Au(dpam)Au(C_6F_5)$ (7) and $[Cl_2Au(dpam)_2Au](ClO_4)_2$ (8)

1.2 ml of chlorine solution in CCl_4 (0.1 M) was added to a dichloromethane solution (15 ml) of complex **5** (0.144 g, 0.12 mmol) or **6** (0.185 g, 0.12 mmol). The solution instantaneously turned orange but rapidly became yellow or colourless. Thereafter the solution was vacuum evaporated to *ca.* 5 ml. Addition of hexane (20 ml) gave a yellow (**7**) or white (**8**) solid.

$[Cl_2Au(dpam)_2AuCl_2](ClO_4)_2$ (9)

1.9 ml of chlorine solution in CCl_4 (0.1 M) was added to a dichloromethane solution (15 ml) of complex **6** (0.140 g, 0.09 mmol). The solution was stirred for 30 min and thereafter concentrated to 5 ml. Addition of diethylether (20 ml) precipitated **9** as a yellow solid.

$(C_6F_5)_3Au(dpam)Au(C_6F_5)_3$ (10) and $[(C_6F_5)_3Au(dpam)AuPPh_3]ClO_4$ (11)

To a solution of complex **1** (0.117 g, 0.1 mmol) in 20 ml of dichloromethane was added $(C_6F_5)_3Au$-

(OEt$_2$) [6] (0.074 g, 0.1 mmol) or a solution of (O$_3$ClO)AuPPh$_3$ [10] (0.1 mmol) in dichloromethane (20 ml), and the mixture stirred for 30 min. Evaporation to ~5 ml and addition of hexane (20 ml) led to the white complexes **10** or **11**.

[(C$_6$F$_5$)$_3$Au(dpam)Au(dpam)Au(C$_6$F$_5$)$_3$]X {X = [AuCl$_2$] (12) or ClO$_4$ (13)} and [(C$_6$F$_5$)$_3$Au(dpam)Ag(OClO$_3$)(dpam)Au(C$_6$F$_5$)$_3$] (14)

To a solution of complex **1** (0.164 g, 0.14 mmol) in 15 ml of dichloromethane was added ClAu(tht) [8] (0.044 g, 0.14 mmol), [Au(tht)$_2$]ClO$_4$ [9] (0.034 g, 0.07 mmol) or AgClO$_4$ (0.015 g, 0.07 mmol) and the mixture was stirred for 5 min [(**12**) or (**13**)] or 2 h under exclusion of light [(**14**)]. Thereafter the solution was evaporated to *ca.* 5 ml and addition of hexane (20 ml) gave white solids of **12**, **13** or **14**.

Crystal Structure Determination of 14

Colourless single crystals were obtained by diffusion of diethyl ether into a dichloromethane solution.

Crystal data

$C_{86}H_{44}AgAs_4Au_2ClF_{30}O_4$, $M_r = 2548$. Monoclinic, $P2_1/n$, $a = 13.103(2)$, $b = 37.886(7)$, $c = 17.199(3)$ Å, $\beta = 98.19(2)°$, $U = 8451$ Å^3, $Z = 4$, $D_x = 2.00$ g cm^{-3}, λ(Mo Kα) = 0.71069 Å, μ(Mo Kα) = 5.4 mm^{-1}, $F(000) = 4864$, crystal size 0.27 × 0.23 × 0.23 mm.

Data collection and processing

Stoe-Siemens four-circle diffractometer, 12661 profile-fitted intensities ($2\theta_{max}$ 45°), 11014 unique, 7549 with $F > 4\sigma(F)$ used for all calculations. Absorption correction based on ψ-scans; transmissions 0.57–0.64. Cell constants refined from 2θ values of 44 reflections in the range 20–23°.

Structure solution and refinement

Heavy-atom method; least-squares refinement on F to R 0.057, R_w 0.047 (all atoms except C and H anisotropic; aromatic rings as rigid groups with C–C 1.395 Å, C–H (where applicable) 0.96 Å, C–C–C and H–C–C 120°; methylene H using riding model with C–H 0.96 Å; U(H) = 1.2 U(C); weighting scheme $w^{-1} = \sigma^2(F) + 0.0002F^2$; 555 parameters). Program system SHELXTL. Final atomic coordinates and derived parameters are presented in Tables II and III.

Results and Discussion

Mononuclear Complexes

The action of the diarsine (dpam) on gold(III) complexes leads to mononuclear derivatives. Thus, displacement of a weakly coordinating ligand, such as tetrahydrothiophen (tht) (eqn. (1)),

TABLE II. Atom Coordinates (×10^4) and Isotropic Temperature Factors (Å^2 × 10^3) for **14**

	x	y	z	U^a
Au(1)	8547.8(.4)	1514.5(.1)	3768.3(.3)	36(1)*
Au(2)	2297.1(.4)	929.7(.1)	9197.4(.3)	37(1)*
Ag	4864(1)	1217.9(.3)	5952(1)	57(1)*
As(1)	6977(1)	1605.7(.3)	4371(1)	40(1)*
As(2)	3691(1)	997.1(.3)	8381(1)	37(1)*
As(3)	6129(1)	1724.2(.4)	6110(1)	41(1)*
As(4)	4221(1)	678.3(.3)	6588(1)	41(1)*
C(1)	9457(6)	1576(3)	4845(4)	46(3)
C(2)	9717	1911	5147	64(4)
C(3)	10295	1946	5889	97(6)
C(4)	10614	1647	6329	82(5)
C(5)	10353	1312	6028	82(5)
C(6)	9775	1276	5285	69(4)
C(7)	9865(5)	1440(2)	3262(5)	44(3)
C(8)	10492	1721	3101	68(4)
C(9)	11371	1657	2750	79(5)
C(10)	11623	1313	2561	80(5)
C(11)	10996	1032	2722	81(5)
C(12)	10117	1096	3072	62(4)
C(13)	7692(6)	1435(2)	2671(4)	41(3)
C(14)	7607	1698	2099	55(4)
C(15)	7068	1632	1353	62(4)
C(16)	6614	1303	1181	53(4)
C(17)	6699	1040	1753	58(4)
C(18)	7239	1106	2498	48(3)
C(19)	2992(6)	1300(2)	9999(4)	44(3)
C(20)	2842	1655	9804	53(4)
C(21)	3270	1916	10323	87(5)
C(22)	3847	1821	11038	90(5)
C(23)	3997	1466	11233	68(4)
C(24)	3569	1205	10713	53(4)
C(25)	1167(5)	848(2)	9903(4)	43(3)
C(26)	421	1104	9975	52(4)
C(27)	−374	1032	10412	65(4)
C(28)	−423	705	10776	75(5)
C(29)	322	449	10703	67(4)
C(30)	1118	521	10266	60(4)
C(31)	1468(6)	580(2)	8421(4)	50(4)
C(32)	1842	244	8283	47(3)
C(33)	1293	26	7719	62(4)
C(34)	369	143	7292	67(4)
C(35)	−5	478	7431	64(4)
C(36)	544	697	7995	63(4)
C(38)	5319(7)	1163(2)	3658(5)	61(4)
C(39)	4743	852	3560	80(5)
C(40)	4966	573	4087	76(5)
C(41)	5765	605	4712	75(5)
C(42)	6341	916	4810	64(4)
C(37)	6118	1195	4284	44(3)
C(44)	6698(5)	2264(2)	3583(5)	55(4)
C(45)	6154	2556	3252	84(5)
C(46)	5092	2580	3258	85(5)
C(47)	4575	2310	3594	73(5)
C(48)	5120	2018	3925	60(4)
C(43)	6181	1994	3919	44(3)
C(50)	4506(7)	2223(2)	5801(5)	62(4)

(continued)

TABLE II. *(Continued)*

	x	y	z	U^a
C(51)	4054	2556	5681	88(5)
C(52)	4674	2855	5684	89(5)
C(53)	5745	2822	5807	101(6)
C(54)	6197	2490	5927	85(5)
C(49)	5578	2190	5924	50(4)
C(56)	6783(7)	2052(2)	7632(6)	80(5)
C(57)	7334	2069	8387	87(5)
C(58)	8012	1798	8661	96(6)
C(59)	8139	1510	8179	99(6)
C(60)	7589	1493	7424	87(5)
C(55)	6910	1764	7150	47(3)
C(62)	2837(7)	515(2)	5191(6)	82(5)
C(63)	2062	328	4723	104(6)
C(64)	1703	10	4989	88(5)
C(65)	2119	- 22	5723	83(5)
C(66)	2894	64	6191	65(4)
C(61)	3254	382	5925	44(3)
C(68)	4970(5)	92(2)	7639(5)	51(4)
C(69)	5710	-152	7963	70(4)
C(70)	6695	-146	7745	67(4)
C(71)	6941	103	7204	71(4)
C(72)	6202	346	6880	64(4)
C(67)	5216	341	7098	46(3)
C(74)	4645(6)	1663(2)	8778(4)	53(4)
C(75)	4750	2028	8721	74(5)
C(76)	4213	2210	8084	75(5)
C(77)	3572	2026	7505	73(5)
C(78)	3467	1661	7561	53(4)
C(73)	4004	1479	8198	42(3)
C(80)	4910(5)	550(2)	9482(5)	53(4)
C(81)	5816	390	9837	71(4)
C(82)	6754	470	9582	68(4)
C(83)	6784	711	8973	72(5)
C(84)	5878	872	8618	53(4)
C(79)	4941	791	8873	41(3)
F(2)	9400(8)	2188(2)	4759(6)	120(5)*
F(3)	10555(10)	2260(4)	6169(8)	207(8)*
F(4)	11178(8)	1671(5)	7047(5)	199(8)*
F(5)	10727(9)	1030(4)	6413(7)	181(7)*
F(6)	9552(7)	961(2)	5005(5)	109(5)*
F(8)	10269(6)	2034(2)	3294(7)	114(5)*
F(9)	11988(8)	1923(3)	2632(8)	175(7)*
F(10)	12475(8)	1238(4)	2252(7)	168(7)*
F(11)	11270(7)	696(3)	2571(6)	140(6)*
F(12)	9560(6)	825(2)	3225(6)	103(4)*
F(14)	8038(6)	2004(2)	2227(4)	73(3)*
F(15)	6980(7)	1875(2)	797(4)	104(4)*
F(16)	6091(7)	1240(3)	464(4)	104(4)*
F(17)	6257(7)	721(2)	1586(5)	95(4)*
F(18)	7293(6)	855(2)	3022(4)	62(3)*
F(20)	2285(6)	1760(2)	9149(5)	80(4)*
F(21)	3151(9)	2254(2)	10153(7)	150(6)*
F(22)	4282(9)	2063(4)	11546(7)	180(7)*
F(23)	4521(7)	1367(4)	11898(5)	158(7)*
F(24)	3680(6)	871(2)	10892(4)	90(4)*
F(26)	429(6)	1418(2)	9651(5)	77(4)*
F(27)	-1085(7)	1267(2)	10488(6)	107(5)*
F(28)	-1181(8)	630(3)	11181(6)	127(5)*
F(29)	288(8)	130(2)	11028(6)	120(5)*
F(30)	1815(6)	274(2)	10201(5)	87(4)*
F(32)	2728(5)	127(2)	8649(4)	60(3)*
F(33)	1662(7)	-286(2)	7546(4)	86(4)*
F(34)	-163(8)	-66(3)	6735(5)	114(5)*
F(35)	-904(6)	588(3)	7041(6)	116(5)*
F(36)	187(6)	1012(2)	8114(5)	83(4)*
C(85)	3318(9)	771(3)	7365(6)	43(3)
C(86)	7279(9)	1707(3)	5495(7)	50(4)
Cl	2666(3)	1496(1)	4935(2)	75(2)*
O(1)	1909(8)	1268(3)	4563(7)	107(6)*
O(2)	3661(7)	1398(3)	4757(6)	90(5)*
O(3)	2740(9)	1450(4)	5764(6)	132(7)*
O(4)	2457(10)	1852(3)	4714(9)	148(7)*

[a] Asterisk indicates equivalent isotropic U calculated from anisotropic U.

$$R_3Au(tht) + dpam \rightarrow R_3Au(dpam) + tht \qquad (1)$$

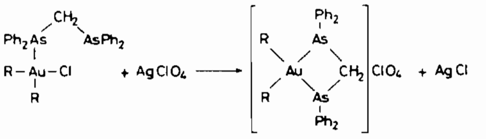
$R = C_6F_5$ (1)

gives rise to the mononuclear **1**, whilst $(C_6F_5)_2ClAu(OEt_2)$ (obtained by reaction of $Bu_4N[(C_6F_5)_2AuCl_2]$ and $AgClO_4$ (1:1) in diethyl ether) reacts with dpam (eqn. (2)) to give the mononuclear **2**

$$R_2ClAu(OEt_2) + dpam \rightarrow \underset{\mathbf{2}}{R_2ClAu(dpam)} + OEt_2 \qquad (2)$$

Complexes **1** and **2** are white, air- and moisture-stable solids that are non-conducting in acetone solution and monomeric in chloroform (Table I). If the geometry around the gold centre is, as usual, square planar, the diarsine is necessarily unidentate with one uncoordinated end. Similar structures are observed for $(C_6F_5)_3Au(dppm)$ [6] and $(C_6F_5)_2ClAu(dppm)$ [4]. The IR spectrum of compound **2** shows two bands at 815(s) and 800(s) cm^{-1}, which indicates that the C_6F_5 groups are mutually *cis*. ν(Au–Cl) cannot be assigned and is probably masked by absorptions of the dpam.

Chloride abstraction (with $AgClO_4$) from complex **2** gives a new mononuclear derivative **3**, according to eqn. 3



(3)

3

Complex **3** is a white solid, showing two IR bands at 1100(s,br) and 620(m) cm^{-1} characteristic [11] of the ClO_4^- anion and two bands at 820(s) and 805(s)

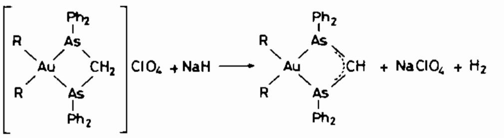
TABLE III. Selected Bond Lengths (Å) and Angles (°) for **14**

Au(1)–C(1)	2.067(8)	Au(1)–C(7)	2.060(9)
Au(1)–C(13)	2.075(7)	Au(2)–C(19)	2.083(9)
Au(2)–C(25)	2.066(9)	Au(2)–C(31)	2.075(9)
Ag–As(3)	2.524(3)	Ag–As(4)	2.520(3)
Ag–O(2)	2.500(11)	As(1)–Au(1)	2.457(2)
As(1)–C(37)	1.914(9)	As(1)–C(43)	1.905(9)
As(1)–C(86)	1.956(12)	As(2)–Au(2)	2.469(2)
As(2)–C(73)	1.909(10)	As(2)–C(79)	1.900(8)
As(2)–C(85)	1.946(12)	As(3)–C(49)	1.917(10)
As(3)–C(55)	1.937(10)	As(3)–C(86)	1.962(14)
As(4)–C(61)	1.937(10)	As(4)–C(67)	1.943(9)
As(4)–C(85)	1.938(13)	Cl–O(2)	1.428(12)
Cl–O(1)	1.398(13)	Cl–O(4)	1.419(15)
Cl–O(3)	1.426(12)		

As(1)–Au(1)–C(1)	91.0(3)	As(1)–Au(1)–C(7)	179.8(4)
C(1)–Au(1)–C(7)	89.1(4)	As(1)–Au(1)–C(13)	91.6(3)
C(1)–Au(1)–C(13)	177.0(4)	C(7)–Au(1)–C(13)	88.4(4)
As(2)–Au(2)–C(19)	91.0(3)	As(2)–Au(2)–C(25)	176.9(3)
C(19)–Au(2)–C(25)	89.7(4)	As(2)–Au(2)–C(31)	93.6(3)
C(19)–Au(2)–C(31)	174.4(4)	C(25)–Au(2)–C(31)	85.9(4)
As(3)–Ag–As(4)	145.5(2)	As(3)–Ag–O(2)	102.0(3)
As(4)–Ag–O(2)	111.6(3)	Au(1)–As(1)–C(37)	111.8(4)
Au(1)–As(1)–C(43)	112.3(4)	C(37)–As(1)–C(43)	108.4(4)
Au(1)–As(1)–C(86)	112.4(5)	C(37)–As(1)–C(86)	105.7(5)
C(43)–As(1)–C(86)	105.9(6)	Au(2)–As(2)–C(73)	112.8(3)
Au(2)–As(2)–C(79)	111.4(4)	C(73)–As(2)–C(79)	105.9(4)
Au(2)–As(2)–C(85)	110.7(5)	C(73)–As(2)–C(85)	107.8(5)
C(79)–As(2)–C(85)	108.0(5)	Ag–As(3)–C(49)	117.1(4)
Ag–As(3)–C(55)	114.3(4)	C(49)–As(3)–C(55)	102.7(5)
Ag–As(3)–C(86)	117.4(5)	C(49)–As(3)–C(86)	103.9(6)
C(55)–As(3)–C(86)	98.9(5)	Ag–As(4)–C(61)	116.4(4)
Ag–As(4)–C(67)	119.0(3)	C(61)–As(4)–C(67)	103.0(4)
Ag–As(4)–C(85)	115.3(5)	C(61)–As(4)–C(85)	95.6(5)
C(6)–As(4)–C(85)	104.2(5)	As(2)–C(85)–As(4)	126.8(7)
As(1)–C(86)–As(3)	118.4(7)	O(1)–Cl–O(2)	110.6(8)
O(1)–Cl–O(3)	108.9(9)	O(2)–Cl–O(3)	104.3(8)
O(1)–Cl–O(4)	111.6(8)	O(2)–Cl–O(4)	109.6(9)
O(3)–Cl–O(4)	111.5(10)	Ag–O(2)–Cl	112.5(7)

cm^{-1} from the mutually *cis* C_6F_5 groups. The complex is a 1:1 electrolyte both in acetone (Table I) and in nitromethane; in the latter the slope B of Onsager's equation, $\Lambda_e = \Lambda_0 - B\sqrt{c}$ (where Λ_e = equivalent conductivity, Λ_0 = conductivity at infinite dilution, and c = equivalent concentration) [12], is 218. The structure is presumably similar to that [4] of $[(C_6F_5)_2Au(dppm)]ClO_4$.

The reaction of complex **3** with NaH renders yellow solutions, from which the bis(diphenylarsino)-methanide complex **4** can be isolated upon partial evaporation (eqn. (4)). The yellow solid is stable at room temperature under nitrogen, but in solution it slowly decomposes to give gold(I) complexes. It is non-conducting in acetone and monomeric in chloroform

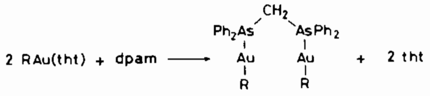
 (4)

4

The IR spectrum of **4** shows no ClO_4^- band, but a new band (which was not present in the starting perchlorato complex) appears at 1265(s) cm^{-1}. This absorption may be characteristic for the methanide system.

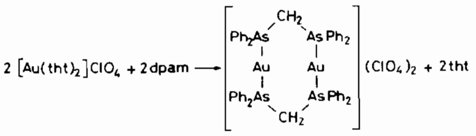
Binuclear Complexes

The tetrahydrothiophen in $C_6F_5Au(tht)$ or $[Au(tht)_2]ClO_4$ can be easily displaced by dpam to give binuclear gold(I) complexes (eqns. (5) and (6))



(5)

5



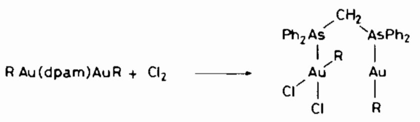
(6)

6

The phosphorus analogue of **6** has recently been reported [13].

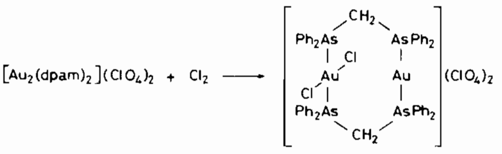
Complexes **5** and **6** are white, air- and moisture-stable solids at room temperature. Acetone solutions of **5** are non-conducting, whilst **6** is a 2:1 electrolyte both in acetone (Table I) and in nitromethane; in the latter the slope B of Onsager's equation, $\Lambda_e = \Lambda_0 - B\sqrt{c}$, is 760 [12]. The IR spectrum of **6** shows two bands at 1100(s,br) and 625(m) cm^{-1} from [11] the ClO_4 anion.

Addition of chlorine (1:1 molar ratio) to dichloromethane solutions of **5** or **6** give orange solutions that rapidly become yellow or colourless, respectively, and from which the mixed gold(III)–gold(I) derivatives can be isolated (eqns. (7) and (8)). It is probable that both oxidation reactions start



(7)

7

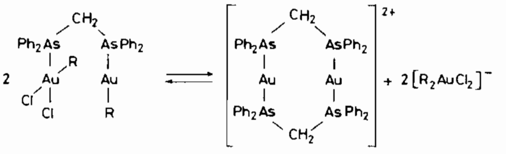


(8)

8

with the formation of an intermediate gold(II) derivative [14], which rapidly isomerises.

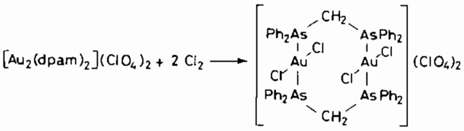
These complexes are yellow (**7**) or white (**8**) solids. Despite its apparent non-ionic nature, complex **8** is conducting in acetone solution (Table I), probably because of equilibria such as that in eqn. (9):



(9)

Its molecular weight (in chloroform) confirms the binuclear nature of **8**. Its acetone solutions behave as 2:1 electrolytes. ν(Au–Cl) cannot be assigned and are probably masked by absorptions of the diarsine.

When chlorine is used in a 2:1 molar ratio, a binuclear gold(III)–gold(III) compound is obtained (eqn. (10))

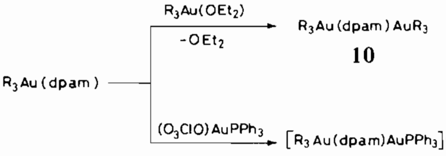


(10)

9

Complex **9** is also obtained from **8** and chlorine (1:1). It crystallizes as a yellow $\frac{1}{2}Et_2O$ solvate (as seen from the ^1H NMR spectrum) that is air- and moisture-stable. The complex is a 2:1 electrolyte in nitromethane (slope B of Onsager's equation, $\Lambda_e = \Lambda_0 - B\sqrt{c}$, 643). The IR spectrum shows an absorption at 350(m) cm^{-1}, assignable to ν(Au–Cl), which confirms a *trans* configuration [7].

Since in R_3Au(dpam) the dpam ligand has one uncoordinated arsenic atom, this complex is capable of displacing poorly coordinated neutral (OEt_2) or anionic ($OClO_3^-$) ligands from other complexes (eqn. (11)) to give binuclear derivatives



10

(11)

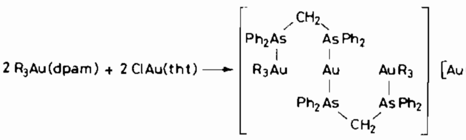
11

No reaction was observed with RAu(tht) or R_3Au(tht); the unchanged starting products were recovered after two days at room temperature.

Complexes **10** and **11** are white solids. **10** is non-conducting in acetone solutions and the molecular weight confirms its binuclear nature. **11** is an 1:1 electrolyte in acetone solutions.

Trinuclear Complexes

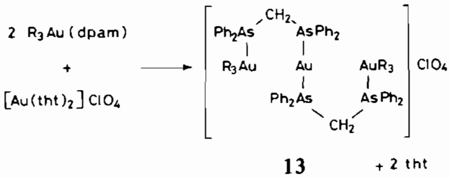
The reaction between complex **1** and ClAu(tht) does not follow the normal pattern (eqn. (11)); not only is the neutral ligand tht displaced but a ligand rearrangement takes place (eqn. (12))



(12)

12 + 2 tht

The same trinuclear cation is obtained by the reaction of **1** with $[Au(tht)_2]ClO_4$ (eqn. (13))

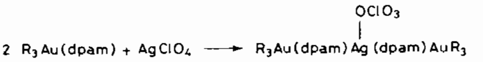


(13)

13

Complexes **12** and **13** are white, air- and moisture-stable solids that in acetone solution behave as 1:1 electrolytes. The IR spectrum of **13** shows two bands at 1100(s,br) and 625(m) cm^{-1} from the ClO_4^- anion. ν(Au–Cl) in **12** are masked by diarsine absorptions.

A similar trinuclear heterometallic complex **14** can be prepared by reaction with silver perchlorate (eqn. (14)). The IR spectrum of the white, light-sensitive complex **14** shows bands at 1115(s,br), 1080(s), 1070(s), 920(m), 630(m), 625(m) and 615(m) cm^{-1} from coordinated perchlorate [11]. It behaves as an 1:1 electrolyte in acetone solution, presumably by displacement of the perchlorate ligand by solvent molecules.



$$2\ R_3Au(dpam) + AgClO_4 \longrightarrow R_3Au(dpam)\overset{\overset{OClO_3}{|}}{Ag}(dpam)AuR_3 \qquad (14)$$

14

The structure of **14** was determined by single crystal X-ray diffraction (Fig. 1). The perchlorate ligand is weakly coordinated to silver [Ag–O(2) 2.500 Å], which thus displays irregular trigonal planar coordination (angle sum 359.1°). The As–Au bond lengths of 2.457 and 2.469 Å are similar to the 2.453 Å observed in $[(C_6F_5)_3Au(diars)]$, in which the diars ligand is monodentate [6]. An unusual feature of the structure is the very high As–C–As bond angles of 118 and 127°, for which there is no obvious explanation; in particular, there is no evidence for deprotonation of the methylene groups.

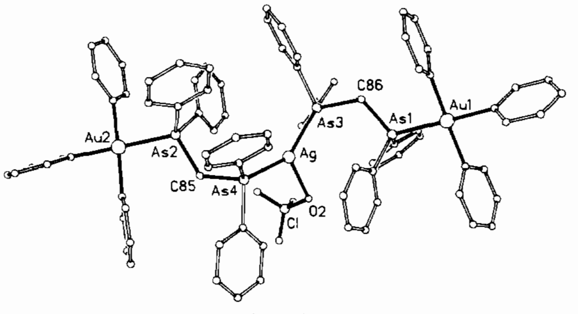


Fig. 1. The structure of **14** in the crystal. Radii arbitrary; H and F atoms omitted for clarity.

Supplementary Material

Additional crystallographic material (complete bond lengths and angles, H atom coordinates, structure factors, temperature factors) can be ordered from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, F.R.G. Please quote reference no. CSD 51947 and the names of the authors and the title of this communication.

Acknowledgement

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