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Synthesis and characterization of cationic heteronuclear complexes of platinum(II) and silver(I) bridged by alkynyl ligands

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Abstract

The dialkynyl complexes *cis*-$[Pt(C\equiv CR)_2L_2]$ [R = Ph, $L_2 = 2PPh_3$, $2PEt_3$, dppe (dppe = 1,2-bis(diphenylphosphino)ethane]; $R = {}^tBu$, $L_2 = 2PPh_3$, dppe) react with silver perchlorate in a molar ratio 1:0.5 to give platinum–silver perchlorate salts of the type $[Pt_2Ag(C\equiv CR)_4L_4](ClO_4)$ in excellent yield. The X-ray crystal structure of $[Pt_2Ag(C\equiv CPh)_4(PPh_3)_4](ClO_4)$ **1** shows that the cation is formed by two nearly orthogonal *cis*-$[Pt(C\equiv CPh)_2(PPh_3)_2]$ units connected through a silver cation which is unsymmetrically π-bonded to all four acetylene fragments. Similar reactions of *cis*-$[Pt(C\equiv CR)_2L_2]$ with one equivalent of $AgClO_4$ afford cationic complexes of general formula $[PtAg(C\equiv CR)_2L_2](ClO_4)$, which are believed to be salts, $[Pt_2Ag_2(C\equiv CR)_4L_4](ClO_4)_2$.

Keywords: Platinum; Pentafluorophenyl; Alkynyl; X-ray diffraction

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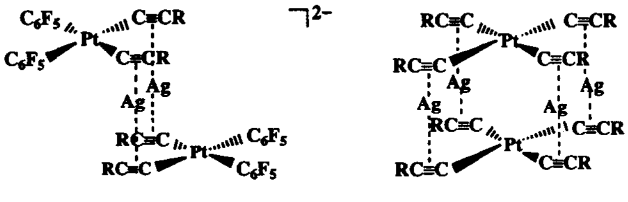
1. Introduction

Polynuclear acetylide complexes are of considerable current interest because of both their unusual structural features and their novel reactivity and chemistry [1]. Very recently we have been involved in the preparation of heteropolynuclear platinum–silver complexes containing alkynyl bridges [2].

We have described the synthesis and chemical properties of the alkynyl mixed complexes of general formula $(NBu_4)_2[Pt_2Ag_2(C_6F_5)_4(C\equiv CR)_4]$ [2b] or $[Pt_2Ag_4(C\equiv CR)_8]$ [2a], which have been prepared by addition of $AgClO_4$ or AgCl to mononuclear *cis*-$[PtX_2(C\equiv CR)_2]^{2-}$ ($X = C_6F_5$ or $C\equiv CR$). The structures of $(NBu_4)_2[Pt_2Ag_2(C_6F_5)_4(C\equiv CPh)_4]$ and $[Pt_2Ag_4(C\equiv C^tBu)_8]$ reveal that in both complexes two dianionic platinum units are linked by silver cations in such a way that only two acetylene fragments, one associated with each platinum atom, are unsymmetrically η^2-coordinated to Ag (see Diagram I). These complexes add to the number of mixed silver–transition metal complexes containing alkynyl ligands σ-bonded to the transition metal and η^2-coordinated to silver, synthesized by reaction of the polymeric metal acetylides $\{Ag(C\equiv CR)\}_x$ with transition metal complexes, or by the interaction of alkynyl metal compounds with appropriate silver species [3].

In this paper we report that, from neutral *cis*-$[Pt(C\equiv CR)_2L_2]$ and $AgClO_4$, two different types of cationic mixed heteronuclear complex can be prepared: trinuclear derivatives (2:1 adducts) containing a silver tetrahedrally coordinated by four acetylene fragments; and 1:1 adducts, which are believed to be salts of the type $[Pt_2Ag_2(C\equiv CR)_4L_4](ClO_4)_2$, where the silver ions are coordinated by two alkynyl units. The molecular structure of one trinuclear complex $[Pt_2Ag(C\equiv CPh)_4(PPh_3)_4](ClO_4)$ (**1**) has been established by a single-crystal X-ray study and confirms that the silver cation is unusually coordinated to four alkynyls. Recently Deem-



R = Ph, Bu^t

Diagram I.

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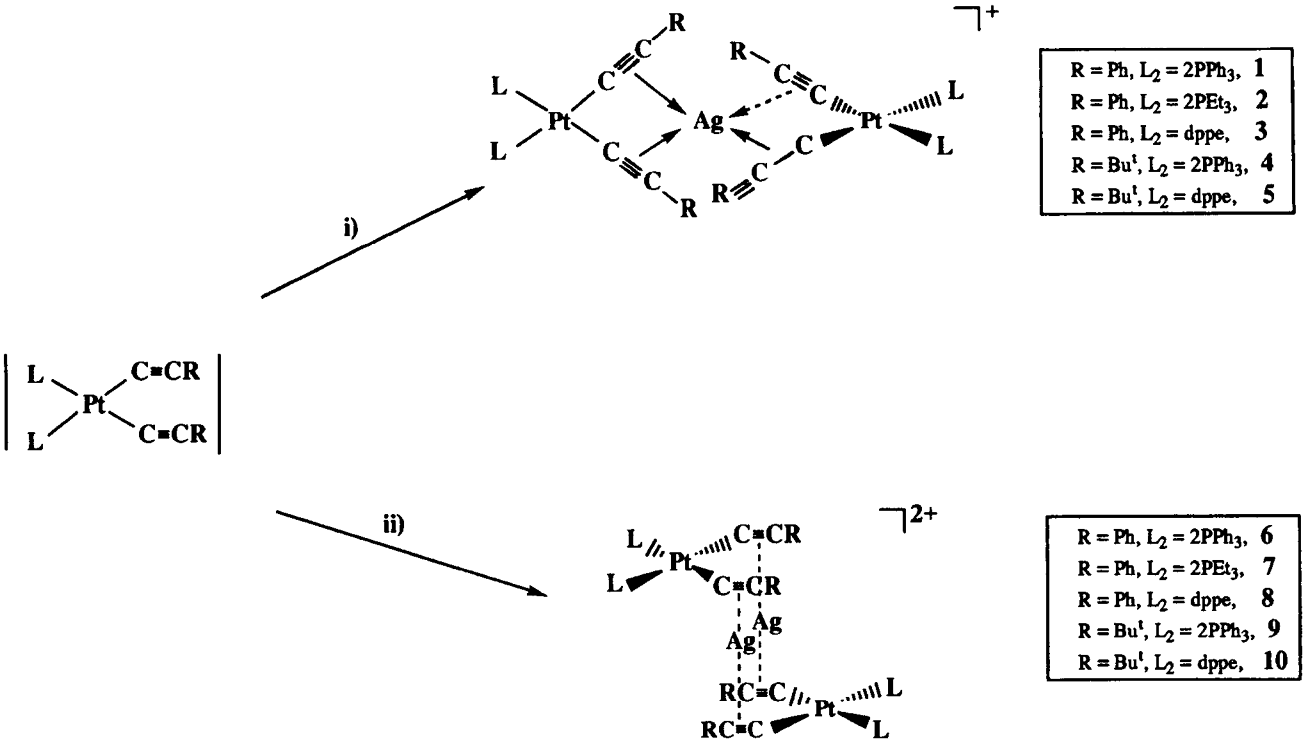

Scheme 1. (i) 0.5 equivalents of $AgClO_4$ in acetone; (ii) 1 equivalent of $AgClO_4$ in acetone.

Table 1
Elemental analyses [a], yields and relevant IR and NMR data [b]

Compound	Colour	Analysis (%)		Yield (%)	Λ_M [c]	IR (cm^{-1}) $\nu(C{=}C)$	$^{31}P\{^1H\}$NMR [d]	^1H NMR
		C	H					
1 $[Pt_2Ag(C\equiv CPh)_4(PPh_3)_4](ClO_4)$	white	60.47 (60.90)	3.55 (3.95)	90	127	2085 (w)	13.9 (2454)	7.23 (m), 7.04, 6.80 (d) (Ph)
2 $[Pt_2Ag(C\equiv CPh)_4(PEt_3)_4](ClO_4)$	white	45.53 (45.60)	5.53 (5.42)	84	139	2068 (m)	3.6 (2381)	7.43, 7.13 (m, Ph); 1.94 (m), 1.07 (m) (PEt_3)
3 $[Pt_2Ag(C\equiv CPh)_4(dppe)_2](ClO_4)$	white	55.61 (56.10)	3.95 (3.80)	84	135	2094 (w) 2077 (w)	40.6 (2431)	7.85–6.92 (m, Ph); 2.56 (m, CH_2, dppe)
4 $[Pt_2Ag(C\equiv C^tBu)_4(PPh_3)_4](ClO_4)$	white	58.50 (58.50)	4.80 (4.90)	96	150	2074 (w)	14.2 (2442)	7.32, 7.11 (m, Ph); 0.85 ($C\equiv C^tBu$)
5 $[Pt_2Ag(C\equiv C^tBu)_4(dppe)_2](ClO_4)$	white	52.53 (53.11)	4.48 (4.92)	88	141	[e]	40.8 (2430)	7.84, 7.41 (m, Ph); 2.37 (m, CH_2, dppe); 1.05 (s, ^tBu)
6 $[Pt_2Ag_2(C\equiv CPh)_4(PPh_3)_4](ClO_4)_2$	beige	55.21 (55.30)	3.05 (3.55)	86	272	2086 (w)	11.9 (2560)	7.34–6.95, 6.58 (m, Ph);
7 $[Pt_2Ag_2(C\equiv CPh)_4(PEt_3)_4](ClO_4)_2$	pale yellow	39.56 (40.00)	4.96 (4.76)	85	265	[e]	2.3 (2459)	7.46, 7.33 (m, Ph); 1.99 (m), 1.08 (m) (PEt_3)
8 $[Pt_2Ag_2(C\equiv CPh)_4(dppe)_2](ClO_4)_2$	beige	49.85 (50.30)	3.62 (3.40)	81	265	2024 (w)	41.8 (2517)	7.67, 7.32, 7.03, 6.66 (m, Ph); 2.76 (m, CH_2, dppe)
9 $[Pt_2Ag_2(C\equiv C^tBu)_4(PPh_3)_4](ClO_4)_2$	white	52.42 (52.93)	4.11 (4.44)	51	248	[e]	12.81 (2518)	7.33, 7.19 (m, Ph); 0.78 ($C\equiv C^tBu$)
10 $[Pt_2Ag_2(C\equiv C^tBu)_4(dppe)_2](ClO_4)_2$	white	46.86 (47.40)	4.21 (4.40)	80	247	2023 (m)	41.6 (2503)	7.69, 7.49 (m, Ph); 2.54 (m, CH_2, dppe); 0.88 (s, ^tBu)

[a] Calculated values in parentheses;
[b] in $CDCL_3$, δ external references H_3PO_4 (80%) and TMS;
[c] in acetone solution (5×10^{-4} M) (Ω^{-1} cm^2 mol^{-1});
[d] $J_{^{195}Pt,^{31}P}$ in square brackets;
[e] not detected.

ing et al. have reported the crystal structure of a similar platinum–copper derivative [4].

2. Results and discussion

The results of the reactions are summarized in Scheme 1. Treatment of *cis*-$[Pt(C \equiv CR)_2L_2]$ ($R = Ph$, $L_2 = 2PPh_3$, $2PEt_3$ or dppe; $R = {}^tBu$, $L_2 = 2PPh_3$ or dppe) with 0.5 equivalents of $AgClO_4$ in acetone (Scheme 1, i) afford colourless solutions (pale yellow for $R = Ph$, $L_2 =$ dppe) from which the corresponding trinuclear bridging alkynyl cationic derivatives **1**–**5** are isolated as white solids, in almost quantitative yield (see Table 1 for analytical and spectroscopic data).

Complexes **1**–**4** show a weak $\nu(C \equiv C)$ absorption (2074–2094 cm^{-1}) at lower frequencies than those of the starting platinum σ-alkynyls, suggesting the side-on π coordination of the $C \equiv CR$ ligands. In addition, compounds **1**–**5** behave as 1:1 electrolytes in acetone solution and their IR spectra show the typical absorptions of uncoordinated perchlorate at ca. 1100 and 620 cm^{-1} [5]. For complexes **1** and **4** the presence of an intense absorption at ca. 540 cm^{-1} in their IR spectra may be considered as a proof of the presence of two *cis* triphenylphosphine molecules [6]. The retention of the phosphines is evident from the ^{31}P NMR spectra, which exhibit a singlet flanked by two platinum satellites, and the values of $^1J_{Pt-P}$ (2381–2454 Hz) are similar to those previously reported for mono- or di-nuclear complexes having phosphine *trans* to a σ-alkynyl group [7]. The structure of complex **1**, determined by X-ray diffraction (see below), confirms that for the formation of the trinuclear cation $[Pt_2Ag(C \equiv CPh)_4(PPh_3)_4]^+$ two *cis*-$[Pt(C \equiv CPh)_2(PPh_3)_2]$ units are bidentate and chelating, binding the silver cation through the alkynyls.

Similar treatment of *cis*-$[Pt(C \equiv CR)_2L_2]$ with 1 equivalent of $AgClO_4$ in acetone (Scheme 1, ii) led to the isolation of the corresponding salts $[Pt_2Ag_2(C \equiv CR)_4L_4](ClO_4)_2$ (**6**–**10**) (**7** yellow; **6**, **8** beige and **9**, **10** white). Elemental analyses and selected spectroscopic properties are listed in Table 1. The formulation of these complexes as tetranuclear ionic species is consistent with the presence in their IR spectra of bands at ca. 1095 and 622 cm^{-1} due to uncoordinated perchlorate in the solid state. Furthermore, they behave as 2:1 electrolytes in acetone solution, consistent with their formulation. In particular, conductivity measurements in acetone solution for complex **6** (10^{-4}–10^{-3} M range) gave a slope for the Onsager equation of 787 confirming that it is a 2:1 electrolyte [8]. Unfortunately, we have not been able to obtain crystals suitable for X-ray studies, but on the basis of their spectroscopic properties (see Table 1) a plausible structure is the one shown in Scheme 1 (ii). Presumably, the tetranuclear cations are formed by two *cis*-$Pt(C \equiv CR)_2L_2$ units holding

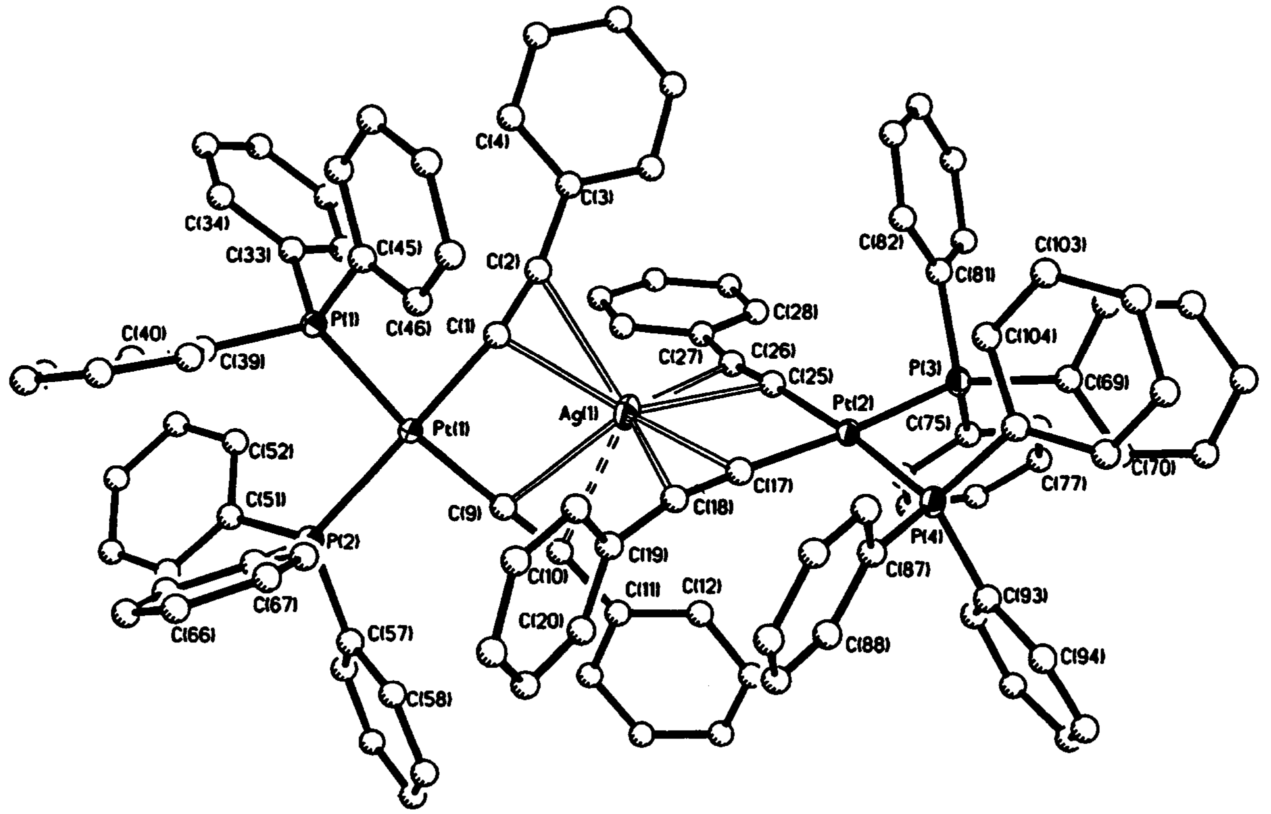

Fig. 1. View of the structure of the cation $[Pt_2Ag(C{=}CPh)_4(PPh_3)_4]^+$ in complex **1** with the atomic numbering scheme.

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for $[Pt_2Ag(C \equiv CPh)_4(PPh_3)_4](ClO_4) \cdot 2CHCl_3$ ($1 \cdot 2CHCl_3$): U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U_{eq}
Pt(1)	2136(1)	2482(1)	4011(1)	22(1)
Pt(2)	3830(1)	2471(1)	7207(1)	24(1)
Ag(1)	2715(1)	2367(1)	5703(1)	42(1)
Cl(1)	7214(2)	2403(1)	1507(2)	55(1)
P(1)	2474(1)	1399(1)	3402(1)	23(1)
P(2)	1831(1)	3435(1)	3030(1)	26(1)
P(3)	3388(1)	2225(1)	8408(1)	26(1)
P(4)	5200(2)	2796(1)	7332(1)	28(1)
O(1)	8073(5)	1978(5)	1769(4)	75(2)
O(2)	6540(5)	1966(4)	1721(5)	85(2)
O(3)	6937(6)	3135(5)	1712(7)	157(5)
O(4)	7362(7)	2451(6)	742(5)	114(3)
C(1)	2348(5)	1657(4)	4871(4)	28(2)
C(2)	2386(5)	1102(5)	5339(4)	30(2)
C(3)	2379(5)	347(4)	5784(4)	25(2)
C(4)	2394(5)	−296(4)	5439(4)	32(2)
C(5)	2354(6)	−1001(5)	5839(4)	41(2)
C(6)	2295(6)	−1092(5)	6578(5)	46(2)
C(7)	2301(6)	−473(5)	6906(4)	40(2)
C(8)	2348(6)	252(5)	6523(4)	35(2)
C(9)	1891(5)	3312(4)	4653(4)	27(2)
C(10)	1808(5)	3792(4)	5050(4)	32(2)
C(11)	1689(6)	4455(4)	5436(4)	33(2)
C(12)	2130(7)	4417(5)	6037(5)	59(3)
C(13)	2030(8)	5059(6)	6376(6)	72(3)
C(14)	1443(8)	5754(6)	6131(6)	61(3)
C(15)	974(7)	5820(5)	5541(6)	62(3)
C(16)	1099(7)	5162(6)	5194(5)	55(3)
C(17)	4097(5)	2644(4)	6146(4)	25(2)
C(18)	4263(5)	2781(4)	5518(4)	29(2)
C(19)	4633(6)	3027(4)	4809(4)	31(2)
C(20)	4353(6)	3792(5)	4488(4)	42(2)
C(21)	4804(7)	4047(6)	3855(5)	50(3)
C(22)	5491(7)	3543(6)	3530(5)	54(3)
C(23)	5747(7)	2768(6)	3825(4)	57(3)
C(24)	5321(6)	2505(5)	4468(4)	45(2)
C(25)	2598(6)	2267(5)	7035(4)	34(2)
C(26)	1842(6)	2215(5)	6943(4)	35(2)
C(27)	895(6)	2117(5)	7008(4)	36(2)
C(28)	437(7)	2045(6)	7683(5)	65(3)
C(29)	−451(8)	1947(7)	7752(7)	83(4)
C(30)	−880(7)	1910(6)	7178(7)	70(3)
C(31)	−439(7)	1965(6)	6510(6)	61(3)
C(32)	463(6)	2069(5)	6418(5)	48(2)
C(33)	1528(5)	902(4)	3548(4)	26(2)
C(34)	1456(6)	377(4)	3099(5)	39(2)
C(35)	731(7)	20(5)	3203(5)	53(3)
C(36)	74(7)	160(5)	3760(6)	54(3)
C(37)	141(6)	688(5)	4211(5)	41(2)
C(38)	858(5)	1048(5)	4092(4)	34(2)
C(39)	2755(5)	1481(4)	2433(4)	26(2)
C(40)	2075(6)	1645(4)	1953(4)	32(2)
C(41)	2314(7)	1659(5)	1232(5)	44(2)
C(42)	3228(7)	1504(5)	978(4)	49(3)
C(43)	3912(7)	1354(5)	1452(5)	49(2)
C(44)	3681(6)	1340(5)	2178(4)	37(2)
C(45)	3511(5)	664(4)	3721(4)	25(2)
C(46)	4240(6)	930(5)	3911(4)	38(2)
C(47)	5078(6)	407(5)	4072(5)	51(3)
C(48)	5192(6)	−386(5)	4053(5)	52(3)
C(49)	4463(6)	−647(5)	3880(4)	41(2)
C(50)	3642(6)	−122(4)	3701(4)	30(2)
C(51)	817(6)	3418(4)	2580(4)	33(2)
C(52)	322(6)	2856(4)	2859(5)	39(2)
C(53)	−454(6)	2811(5)	2516(5)	45(2)
C(54)	−718(7)	3329(6)	1918(6)	61(3)
C(55)	−252(7)	3900(6)	1653(5)	61(3)
C(56)	501(6)	3948(5)	19821(5)	47(2)
C(57)	1614(6)	4454(4)	3171(4)	28(2)
C(58)	2351(7)	4748(6)	3277(5)	56(3)
C(59)	2189(9)	5528(6)	3391(6)	72(4)
C(60)	1323(11)	6002(6)	3399(6)	86(4)
C(61)	586(9)	5712(6)	3301(6)	77(4)
C(62)	740(7)	4938(5)	3205(5)	48(2)
C(63)	2822(6)	3340(4)	2384(4)	26(2)
C(64)	2778(7)	3509(5)	1649(4)	44(2)
C(65)	3577(8)	3440(5)	1215(5)	52(3)
C(66)	4428(7)	3213(5)	1488(5)	49(3)
C(67)	4489(6)	3025(5)	2207(4)	39(2)
C(68)	3698(6)	3094(5)	2646(4)	36(2)
C(69)	4234(6)	2099(5)	9065(4)	33(2)
C(70)	4418(6)	2762(5)	9283(4)	38(2)
C(71)	5094(6)	2666(6)	9751(4)	46(2)
C(72)	5595(6)	1932(7)	10027(5)	52(3)
C(73)	5408(6)	1293(6)	9814(4)	47(2)
C(74)	4748(6)	1358(5)	9345(4)	38(2)
C(75)	2383(6)	2955(4)	8726(4)	30(2)
C(76)	2193(6)	3011(5)	9444(4)	37(2)
C(77)	1398(7)	3516(5)	9673(5)	47(2)
C(78)	792(7)	3969(6)	9205(6)	57(3)
C(79)	966(7)	3945(6)	8483(6)	61(3)
C(80)	1771(6)	3434(5)	8249(5)	45(2)
C(81)	3048(5)	1284(4)	8595(4)	25(2)
C(82)	3534(6)	680(5)	8221(4)	38(2)
C(83)	3336(6)	−45(5)	8386(5)	44(2)
C(84)	2672(7)	−176(5)	8907(5)	53(3)
C(85)	2184(7)	421(5)	9271(5)	55(3)
C(86)	2382(6)	1153(5)	9118(4)	42(2)
C(87)	5911(6)	2969(6)	6512(4)	40(2)
C(88)	5672(8)	3671(6)	6072(5)	60(3)
C(89)	6179(11)	3827(9)	5447(6)	83(4)
C(90)	6960(11)	3264(12)	5254(7)	111(7)
C(91)	7216(8)	2558(11)	5676(7)	106(6)
C(92)	6687(7)	2403(7)	6308(5)	63(3)
C(93)	4975(6)	3737(5)	7659(4)	33(2)
C(94)	5688(7)	4084(5)	7747(4)	45(2)
C(95)	5498(8)	4785(6)	8006(5)	57(3)
C(96)	4583(9)	5166(6)	8176(5)	62(3)
C(97)	3878(7)	4859(5)	8060(5)	50(3)
C(98)	4079(7)	4135(5)	7814(4)	43(2)
C(99)	6000(6)	2040(5)	7878(4)	32(2)
C(100)	6635(6)	2176(5)	8311(4)	38(2)
C(101)	7264(7)	1568(7)	8658(5)	58(3)
C(102)	7301(7)	795(7)	8592(5)	59(3)
C(103)	6701(7)	641(5)	8158(5)	56(3)
C(104)	6047(6)	1260(5)	7806(4)	40(2)
Cl(2)	9335(3)	1010(2)	−170(2)	109(1)
Cl(3)	10245(3)	836(2)	1098(2)	115(1)
Cl(4)	9992(3)	2277(2)	152(2)	119(1)
C(105)	9495(8)	1517(6)	506(6)	69(3)
Cl(5)	7990(3)	4746(3)	119(2)	131(2)
Cl(6)	6264(3)	4517(2)	−195(2)	125(2)
Cl(7)	7912(4)	3959(3)	−1054(3)	175(2)
C(106)	7476(10)	4100(8)	−192(8)	103(5)

two dicoordinated silver cations in a similar way to that previously found for the dianionic tetranuclear derivative $[Pt_2Ag_2(C\equiv CPh)_4(C_6F_5)_4]^{2-}$ [2b] (Diagram I).

The FAB^+ mass spectra show the molecular peak $[M]^+$ for complexes **1**–**3** at $m/z = 1951$ (100%, **1**), 1376 (100%, **2**), 1699 (93%, **3**). Other peaks at $m/z = 1873$ (29%, **4**) and 1620 (28%, **5**) are due to $[MH]^+$; at $m/z = 1951$ (100%, **6**), 1873 (6%, **9**) and 1620 (15%, **10**) are due to $[M-Ag]^+$; and at $m/z = 1582$ (6%, **7**) and 1906 (19%, **8**) are due to $\{[M](ClO_4)\}^+$.

3. Structure of $[Pt_2Ag(C{=}CPh)_4(PPh_3)_4](ClO_4)\cdot 2CHCl_3$ ($1\cdot 2CHCl_3$)

The structure of complex **1** has been established by single-crystal X-ray diffraction. A drawing of the cation is presented in Fig. 1. Atomic coordinates are shown in Table 2 and selected bond distances and angles are listed in Table 3.

The cation is a trinuclear species formed by two approximately orthogonal *cis*-$Pt(C\equiv CPh)_2(PPh_3)_2$ units (the dihedral angle formed by the best least-squares coordination planes of both platinums is 75.82(8)°) linked through a silver atom. Examination of Fig. 1 shows that each of the two *cis*-$Pt(C\equiv CPh)_2(PPh_3)_2$ units is acting as a bidentate diyne since the Ag atom is bonded to the four $C\equiv C$ triple bonds in an approximately tetrahedral arrangement. The dihedral angle between the planes each containing the mid-point [C(n,m)] of the η^2-coordinated $C\equiv C$ bonds and the Ag atom is 75.77(4)° [i.e. Ag, C(1,2), C(9,10) and Ag, C(17,18), C(25,26)] and the "bite angles" are 95.21(4)° for C(1,2)–Ag–C(9,10) and 95.88(5)° for C(17,18)–Ag–C(25,26).

The silver–acetylide η^2 linkages are slightly asymmetric, the Ag–C(α) distances being in the range 2.367(7)–2.584(7) Å and the Ag–C(β) in the range 2.577(8)–2.709(7). Moreover, the distance between the silver atom and the mid-points of the $C\equiv C$ triple bonds [Ag–C(1,2) 2.431(1) Å; Ag–C(9,10) 2.579(1) Å; Ag–C(17,18) 2.467(1) Å; Ag–C(25,26) 2.477(1) Å] are also somewhat different, with Ag appearing more symmetrically bonded to the Pt(2) fragment. These distances are significantly larger than the corresponding ones previously observed in $[Pt_2Ag_2(C\equiv CPh)_4(C_6F_5)_4]^{2-}$ [2b] and $[Pt_2Ag_4(C\equiv C^tBu)_8]$ [2a], suggesting that the interaction with four acetylene fragments is probably weaker. The Ag–C(acetylenic) distances are comparable to those Ag–C(olefin) found in the isoelectronic derivative $[Ag(COD)_2]BF_4$ 2.50(2)Å] [9] (COD = cycloocta-1,5-diene).

The geometrical details of the two organometallic platinum units in **1** are similar to those previously reported for *cis*-$[Pt(C\equiv CPh)_2(PPh_3)_2]$ [10]. Notwithstanding, the high standard deviations reported there [10] preclude any meaningful comparison. As a consequence of the η^2-interaction of the phenylethynyl groups with Ag^+ and steric interactions between the ligands, the bond angles at platinum differ from 90°, ranging from 83.3(2) to 96.93(7)° at Pt(1) and from 85.5(2) to 97.77(7)° at Pt(2), the largest values involving the bulky *cis*-triphenylphosphines (Table 3). The Pt–C distances are in the range of values quoted in the literature for σ-alkynylplatinum complexes [2,6b,10,11]. The distortion of the acetylide ligands is negligible. Thus, the

Table 3
Selected bond lengths (Å) and angles (°) for $[Pt_2Ag(C\equiv CPh)_4(PPh_3)_4](ClO_4)\cdot 2CHCl_3(1\cdot 2CHCl_3)$

Pt(1)–C(1)	2.005(7)	Pt(1)–C(9)	2.007(7)
Pt(1)–P(2)	2.306(2)	Pt(1)–P(1)	2.328(2)
Pt(2)–C(17)	2.008(8)	Pt(2)–C(25)	2.033(8)
Pt(2)–P(4)	2.310(2)	Pt(2)–P(3)	2.319(2)
Ag(1)–C(1)	2.367(7)	Ag(1)–C(17)	2.498(7)
Ag(1)–C(25)	2.506(8)	Ag(1)–C(18)	2.577(8)
Ag(1)–C(9)	2.584(7)	Ag(1)–C(26)	2.588(8)
Ag(1)–C(2)	2.635(7)	Ag(1)–C(10)	2.709(7)
C(1)–C(2)	1.212(10)	C(2)–C(3)	1.467(10)
C(9)–C(10)	1.205(10	C(10)–C(11)	1.452(11)
C(17)–C(18)	1.196(10)	C(18)–C(19)	1.448(11)
C(25)–C(26)	1.189(11)	C(26)–C(27)	1.459(11)
C(1)–Pt(1)–C(9)	89.1(3)	C(9)–Pt(1)–P(2)	90.6(2)
C(1)–Pt(1)–P(1)	83.3(2)	P(2)–Pt(1)–P(1)	96.93(7)
C(17)–Pt(2)–C(25)	88.5(3)	C(17)–Pt(2)–P(4)	88.3(2)
C(25)–Pt(2)–P(3)	85.5(2)	P(4)–Pt(2)–P(3)	97.77(7)
C(2)–C(1)–Pt(1)	169.4(7)	C(1)–C(2)–C(3)	167.4(8)
C(10)–C(9)–Pt(1)	175.3(7)	C(9)–C(10)–C(11)	171.6(8)
C(18)–C(17)–Pt(2)	176.9(6)	C(17)–C(18)–C(19)	166.1(8)
C(26)–C(25)–Pt(2)	174.1(7)	C(25)–C(26)–C(27)	166.9(9)

$C\equiv C$ distances [range 1.189(11)–1.212(10) Å] are not very different from those observed in complexes with terminal alkynyls [6b,10,11] and the $PtC_\alpha \equiv C_\beta$–C(Ph) fragments do not deviate significantly from linearity (Table 3).

The silver interacts more strongly with the fragment containing the Pt(2) atom. The Ag atom is displaced only 0.01 Å from the Pt(2) coordination plane, while it is 0.8 Å above the Pt(1) coordination plane.

Finally, the Pt(1)...Ag and Pt(2)...Ag distances are 3.384(1) Å and 3.513(1) Å respectively, indicating that no metal–metal interactions are present.

4. Experimental section

Elemental analyses were carried out with a Perkin-Elmer 240-B microanalyzer, IR spectra were recorded on a Perkin-Elmer 883 spectrophotometer and NMR spectra with a Bruker ARX 300 spectrometer. Mass spectra (FAB$^+$) were obtained in a VG Autospec spectrometer. *cis*-$[Pt(C\equiv CR)_2L_2]$ (R = Ph, $L_2 = 2PPh_3$ [12, 6b], $2PEt_3$ [13] or dppe [4, 13b, 14]; R = ^{t}Bu, $L_2 = 2PPh_3$ or dppe) were prepared in a similar manner to the reported synthesis of the corresponding *cis*-$[Pt(C\equiv C^tBu)_2L_2]$ ($L_2 = 2PPh_3$ or dppe) [7a] derivatives.

4.1. Preparation of $[Pt_2Ag(C\equiv CR)_4L_4](ClO_4)$ (R = Ph, $L_2 = 2PPh_3$ 1, $2PEt_3$ 2, dppe 3; R = ^{t}Bu, $L_2 = 2PPh_3$ 4, dppe 5)

A typical preparation (complex **1** R = Ph, L = PPh_3) was as follows: to a solution of *cis*-$[Pt(C\equiv CPh)_2(PPh_3)_2]$ (0.105 g, 0.114 mmol) in acetone (20 cm^3) was added $AgClO_4$ (0.012 g, 0.058 mmol) and the mixture, protected from the light, was stirred for 15 min. The solution was concentrated to ca. 5 cm^3, hexane (3 cm^3) added and the resulting mixture refrigerated (−30 °C) overnight to give **1** as a white crystalline product which was filtered off, washed with hexane and air dried.

Complexes **2**, **3** and **5** were prepared similarly using the appropriate starting material. For complex **4** the resulting reaction mixture was evaporated to dryness and the residue triturated with diethyl ether, giving the required product.Yields and other data are given in Table 1.

Table 4
Crystal data and structure refinement for $[Pt_2Ag(C\equiv CPh)_4(PPh_3)_4](ClO_4)\cdot 2CHCl_3$(**1** · $2CHCl_3$)

Empirical formula	$C_{106}H_{82}AgCl_7O_4P_4Pt_2$
Formula weight	2289.80
Temperature	200(1) K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	$P-1$
Unit cell dimensions	$a = 14.933(2)$ Å $\alpha = 80.60(1)°$
	$b = 17.786(3)$ Å $\beta = 84.09(1)°$
	$c = 19.058(2)$ Å $\gamma = 74.98(1)°$
Volume	4813.4(12) Å^3
Z	2
Density (calc.)	1.580 Mg m^{-3}
Absorption coefficient	3.413 mm^{-1}
$F(000)$	2264
Crystal size	0.36 × 0.24 × 0.18 mm
θ range for data collection	2.07 to 24.00°
Index ranges	$-1 \le h \le 16$, $-19 \le k \le 20$, $-21 \le l \le 21$
Reflections collected	16944
Independent reflections	14973 ($R_{int} = 0.0938$
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	13465/0/1118
Goodness-of-fit on F^2	1.036
R indices [10335 reflns. with $I > 2\sigma(I)$]	$R_1 = 0.0458$, $wR_2 = 0.0854$
R indices (all 14973 data)	$R_1 = 0.0898$, $wR_2 = 0.1025$
Mean, max. |shift/esd|, final cycle	0.000, −0.001
Largest diff. peak and hole	0.691 and −1.058 e Å^{-3}

$R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$
$wR_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$
Goodness-of-fit = $[\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$
$w = [\sigma^2(|F_o|) + (0.0314\ P)^2 + 3.21\ P]^{-1}$; $P = [\max(F_o^2; 0) + 2F_c^2]/3$

4.2. Preparation of $[Pt_2Ag_2(C\equiv CR)_4L_4](ClO_4)_2$ ($R = Ph$, $L_2 = 2PPh_3$ **6**, $2PEt_3$ **7**, dppe **8**; $R = {}^tBu$, $L_2 = 2PPh_3$ **9**, dppe **10**)

Preparation of **7** ($R = Ph$, $L = PPh_3$): to a solution of *cis*-$[Pt(C\equiv CPh)_2(PEt_3)_2]$ (0.100 g, 0.158 mmol) in acetone (20 cm^3) was added $AgClO_4$ (0.033 g, 0.158 mmol) (ratio Pt/Ag 1:1), and the mixture, protected from the light, was stirred for 15 min. The resulting solution was evaporated to dryness and the addition of diethyl ether to the oily residue causes the separation of **7** as a pale yellow solid. The product was filtered off, washed with diethyl ether and air dried.

Complexes **8** and **10** were obtained similarly using the appropriate starting materials.

For complex **6** ($R = Ph$, $L = PPh_3$), the resulting acetone solution was concentrated to small volume (3 cm^3). Then, addition of hexane (2 cm^3) and cooling to −30 °C (2 days), gave **6** as a beige solid.

For complex **9** ($R = {}^tBu$, $L_2 =$ dppe), the reaction mixture was stirred for 8 h and evaporated to dryness. Addition of 2-propanol (3 cm^3) gave **9** as a white solid which was filtered and washed with 2-propanol (3 cm^3).

4.3. X-ray crystallographic study of $[Pt_2Ag(C\equiv CPh)_4(PPh_3)_4](ClO_4)\cdot 2CHCl_3$ ($1\cdot 2CHCl_3$)

Suitable crystals of complex **1** were grown by slow diffusion of hexane into a $CHCl_3$ solution of the compound at room temperature. Crystallographic data and other information are summarized in Table 4. Measurements were made on a Siemens P4 automated diffractometer with graphite-monochromated Mo Kα radiation. Data were collected at 200 K using the ω scan technique. Unit cell dimensions with estimated standard deviations were obtained from least-squares refinement of the setting angles of 25 well centered reflections. Three standard reflections were monitored periodically; they showed no change during data collection. A semi-empirical absorption correction based on Ψ scans was applied (minimum and maximun transmission factors = 0.734, 0.971).

The stucture was solved by the Patterson method. Non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 (SHELX-93). Two $CHCl_3$ lattice molecules per formula unit were found and included in the calculations. H-atoms, except those of the solvent molecules, were located at fixed positions using a riding model with a common isotropic thermal parameter (0.053 Å^2). Of 14973 independent reflections, 13465 data with non-negative intensities were used to refine 1118 parameters. Final R indices were $R_1 = 0.0458$ and $wR_2 = 0.0854$ for 10353 data with $F_o > 4\sigma F_o$, and $R_1 = 0.0898$ and $wR_2 = 0.1025$ for all 14973 data. No residual peaks of more than 1 e Å^{-3} remained in the final density map.

All calculations were performed on a local area VAX cluster (VAX/VMS V5.5) with the Siemens SHELXTL PLUS [15] and SHELX-93 [16] software packages.

Additional material available from the Cambridge Crystallographic Data Centre comprises H atom coordinates, thermal parameters and full lists of bond lengths and angles.

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