# Polynuclear Platinum–Silver, –Copper, and –Gold Acetylide Complexes. Molecular Structure of $[Pt_2Ag_4(C{\equiv}CBu^t)_8]$†

**Pablo Espinet, Juan Forniés,* Francisco Martinez, and Milagros Tomás**
*Departamento de Quimica Inorgánica, Instituto de Ciencias de Materiales de Aragón, Universidad de Zaragoza-Consejo Superior de Investigaciones Científicas, 50009 Zaragoza, Spain*
**Elena Lalinde,* M. Teresa Moreno, and Alejandro Ruiz**
*Colegio Universitario de la Rioja, Logroño, Spain*
**Alan J. Welch**
*Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ*

Hexanuclear complexes $[Pt_2Ag_4(C{\equiv}CR)_8]$ [R = Ph (**1**) or Bu$^t$ (**2**)] have been obtained by treating $[PtCl_2(tht)_2]$ (tht = tetrahydrothiophene) with $[Ag(C{\equiv}CR)]_n$(Pt/Ag 1:4). The complexes $[Pt_2M_4(C{\equiv}CR)_8]$ [M = Cu, R = Ph (**3**) or Bu$^t$ (**4**); M = Au, R = Bu$^t$ (**5**)] were obtained from $[Pt_2Ag_4(C{\equiv}CR)_8]$ with CuCl or [AuCl(tht)] respectively. Alternatively, the reactions between $[NBu_4]_2[Pt(C{\equiv}CR)_4]$ and $AgClO_4$, CuCl–$NaClO_4$, or [AuCl(tht)]–$NaClO_4$ yield respectively complexes (**1**)—(**5**). The molecular structure of $[Pt_2Ag_4(C{\equiv}CBu^t)_8]$ has been determined by an *X*-ray diffraction study: monoclinic, space group $C_2$ with $a$ = 37.062(7), $b$ = 12.0223(16), $c$ = 20.459(3) Å, $\beta$ = 107.485(15)°, $Z$ = 6, $R$ 0.0416, $R'$ 0.0465 for 5 613 reflections with $F > 6\sigma(F)$. The six metal atoms are arranged in a slightly irregular octahedron with the platinum atoms mutually *trans* and the silver atoms in the equatorial plane, with Pt · · · Ag and Ag · · · Ag distances longer than 3.0 Å. Each platinum atom is in an almost square-planar environment formed by four C≡CBu$^t$ ligands. Each acetylenic fragment also forms an asymmetric $\pi$ interaction with one silver atom of the equatorial positions so that each silver atom is bonded to two acetylenic fragments, of two different $Pt(C{\equiv}CBu^t)_4$ moieties. These moieties of each $[Pt_2Ag_4(C{\equiv}CBu^t)_8]$ unit are staggered.

Substituted acetylides are very useful ligands in the syntheses of polynuclear derivatives. These usually contain metal–metal bonds and in such species the acetylides can either be co-ordinated to the cluster as terminal ligands, *e.g.* $[Au_6Pt(C{\equiv}CBu^t)(PMe_3)_7][Au(C{\equiv}CBu^t)_2]$,[1] or as bridging ligands, *e.g.*: $\mu$–$\sigma$ in $[Cu_6(C{\equiv}CC_6H_4Me\text{-}p)_2R_4]$,[2] $\mu_3$–$\sigma$ in $[\{Cu(PPh_3)(C{\equiv}CPh)\}_4]$,[3] $\mu$–$\eta^2$ in $[Cu_4Ir(C{\equiv}CPh)_8(PPh_3)_2]$,[4] $\mu_3$–$\eta^2$ in $[RhAg_2(C{\equiv}CC_6F_5)_5(PPh_3)_3]$,[5] and $\mu_4$–$\eta^2$ in $[Ru_5(C{\equiv}CPh)(\mu\text{-}PPh_2)(CO)_{13}]$.[6]

Most of these complexes are prepared ty treating transition-metal derivatives with the polymeric acetylides $(M{-}C{\equiv}CR)_n$ (M = Cu, Ag, or Au) in refluxing organic solvents,[1,7–9] and in the course of the reaction metal–metal bonds are formed.

This paper deals with the reaction of $[PtCl_2(tht)_2]$ (tht = tetrahydrothiophene) with $[Ag(C{\equiv}CR)]_n$(R = Ph or Bu$^t$). Precipitation of AgCl affords solutions from which the hexanuclear $[Pt_2Ag_4(C{\equiv}CR)_8]$ compounds can be obtained. The analogous $[Pt_2M_4(C{\equiv}CR)_8]$ (M = Cu or Au) compounds can be obtained by metathetical reactions between $[Pt_2Ag_4(C{\equiv}CR)_8]$ and CuCl or [AuCl(tht)]. All these complexes can also be obtained by treating $[NBu_4]_2[Pt(C{\equiv}CR)_4]$ with $AgClO_4$ or, respectively, CuCl or [AuCl(tht)] in the presence of $NaClO_4$. The molecular structure of $[Pt_2Ag_4(C{\equiv}CBu^t)_8]$ has been established by a single-crystal *X*-ray diffraction study.

## Results and Discussion

(*a*) *Syntheses of the Platinum–Silver Complexes.*—Treatment of $[PtCl_2(tht)_2]$ with $[Ag(C{\equiv}CPh)]_n$ (Pt/Ag ratio 1:4), in boiling $CH_2Cl_2$, for 5 h results in the precipitation of silver chloride and the formation of a yellow solution from which, after partial evaporation and addition of acetone, a yellow solid (**1**) which analyses as $[PtAg_2(C{\equiv}CPh)_4]$ can be obtained [equation (1)]. However (**1**) is insoluble in common organic

$$2[PtCl_2(tht)_2] + \frac{8}{n}[Ag(C{\equiv}CR)]_n \longrightarrow AgCl + [Pt_2Ag_4(C{\equiv}CR)_8] + 4tht \quad (1)$$

solvents and this precludes the use of some structural techniques for its identification. An analogous reaction between $[PtCl_2(tht)_2]$ and 3,3-dimethylbutynylsilver(I), $[Ag(C{\equiv}CBu^t)]_n$, in acetone (see Experimental section) renders a very soluble yellow-green complex (**2**) which analogously analyses as $[PtAg_2(C{\equiv}CBu^t)_4]$. It seems sensible that both complexes show a similar formulation and we formulate them as hexanuclear complexes of the type $[Pt_2Ag_4(C{\equiv}CR)_8]$ on the basis of a molecular weight determination of (**2**) that gives the expected value (Found: 1 461. Calc.: 1 470). Furthermore, the structure of (**2**) has been determined by *X*-ray crystallography (see below).

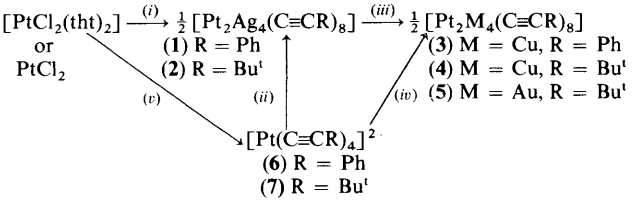
(*b*) *Synthesis of the Platinum–Copper and –Gold Complexes.*—Similar hexanuclear platinum–copper or –gold derivatives can be obtained by displacing the silver ion from the platinum–silver complexes (**1**) or (**2**). Thus, treatment of $[Pt_2Ag_4(C{\equiv}CR)_8]$ (**1**) or (**2**) with CuCl (ratio Ag/Cu 1:1) in $CH_2Cl_2$ (**1**) or acetone (**2**) results in the precipitation of AgCl and the formation of the corresponding $[Pt_2Cu_4(C{\equiv}CR)_8]$ clusters [R = Ph (**3**) or Bu$^t$ (**4**)]. An analogous reaction between $[Pt_2Ag_4(C{\equiv}CBu^t)_8]$ (**2**) and [AuCl(tht)][10] in acetone renders the polynuclear platinum–gold complex $[Pt_2Au_4(C{\equiv}CBu^t)_8]$ (**5**); however the reaction between $[Pt_2Ag_4(C{\equiv}CPh)_8]$ and [AuCl(tht)], in $CH_2Cl_2$, resulted in decomposition and the corresponding $[Pt_2Au_4(C{\equiv}CPh)_8]$ was not obtained.

(*c*) *Synthesis of the Polynuclear Complexes* (**1**)—(**5**) *from*

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix–xxii.

$[NBu_4]_2[Pt(C{\equiv}CR)_4]$.—Polynuclear complexes (**1**)—(**5**) can also be obtained by treating the anionic mononuclear derivatives $[NBu_4]_2[Pt(C{\equiv}CPh)_4]$ (**6**) or $[NBu_4]_2[Pt(C{\equiv}CBu^t)_4]\cdot 2H_2O$ (**7**) with $AgClO_4$, CuCl, or [AuCl(tht)]. Thus, $[NBu_4]_2[Pt(C{\equiv}CPh)_4]$ reacts with $AgClO_4$ (molar ratio 1:2) in acetone at room temperature and the sparingly soluble $[Pt_2Ag_4(C{\equiv}CPh)_8]$ (**1**) precipitates. The reaction between $[NBu_4]_2[Pt(C{\equiv}CBu^t)_4]\cdot 2H_2O$ and $AgClO_4$ was carried out in diethyl ether (room temperature); insoluble $NBu_4ClO_4$ precipitates, and from the resultant solution the hexanuclear $[Pt_2Ag_4(C{\equiv}CBu^t)_8]$ (**2**) was isolated. Complexes (**3**)—(**5**) were prepared in a similar manner by treating $[NBu_4]_2[Pt(C{\equiv}CPh)_4]$ with CuCl or [AuCl(tht)] in the presence of $NaClO_4$ (see Scheme). The reaction between $[NBu_4]_2[Pt(C{\equiv}CPh)_4]$ and [AuCl(tht)] in the presence of $NaClO_4$ takes place with decomposition so that this procedure does not allow the preparation of $[Pt_2Au_4(C{\equiv}CPh)_8]$.

Analytical data, molecular weights, and molar conductivities in acetone are collected in Table 1. The different routes to these hexanuclear $[Pt_2M_4(C{\equiv}CR)_8]$ complexes are summarized in the Scheme.




**Scheme.** (*i*) Ag(C≡CPh) in $CH_2Cl_2$ or Ag(C≡CBu$^t$) in acetone; (*ii*) $AgClO_4$ in acetone; (*iii*) [AuCl(tht)] or CuCl in acetone; (*iv*) [AuCl(tht)] and $NaClO_4$ in acetone or CuCl and $NaClO_4$ in acetone; (*v*) Li(C≡CR) and $NBu_4Br$ in diethyl ether

(*d*) *Structure of* $[Pt_2Ag_4(C{\equiv}CBu^t)_8]$ (**2**).—The structure of complex (**2**) has been determined by single-crystal *X*-ray diffraction (see Experimental section). Single crystals were grown by slow evaporation of a n-hexane solution of the complex at room temperature. Positional parameters are listed in Table 2. The crystal structure determination reveals that the unit cell (space group $C_2$, four-fold) contains six $[Pt_2Ag_4(C{\equiv}CBu^t)_8]$ molecules, two of which are located on two-fold axis, so that there are 1.5 independent $[Pt_2Ag_4(C{\equiv}CBu^t)_8]$ molecules per cell. In the following discussion, the molecule located on the two-fold axis is denoted A, and the other molecule B.

Interatomic distances for A and B are listed in Table 3 and bond angles are collected in Table 4. The complete molecular structures of $[Pt_2Ag_4(C{\equiv}CBu^t)_8]$ (A and B) are presented in Figures 1 and 2. The six metal atoms are arranged in a slightly irregular octahedron with the platinum atoms mutually *trans* while the silver atoms are in the equatorial plane. The platinum–silver and silver–silver distances are longer than 3.0 Å (see Table 3), which seems to indicate that no Pt–Ag or Ag–Ag bonds are present. Each platinum atom is σ bonded to four C≡CBu$^t$ groups in a slightly distorted square-planar environment. The Pt–C(α) distances are in the range 1.962(25)—2.062(22) (A), 1.951(22)—1.966(21) (B), the averages being 2.018 ± 0.002 (A) and 1.957 ± 0.001 Å (B). These distances are in the same range of those found in other platinum(II) acetylide complexes.[11–13] The angles C–Pt–C (two *cis*-acetylide groups) are in the range 86.2(9)—92.7(6) for A and 88.6(8)—91.5(9) for B. The C≡C bonds of the acetylide groups are π-co-ordinated to the Ag atoms in such a way that two Bu$^t$ acetylide units (one associated with each platinum atom) form unsymmetrical π bonds to each silver atom. Since in this compound no formal Pt–Ag or Ag–Ag bonds are present, formation of these silver acetylide π bonds appears to be the driving force in the synthesis of the hexanuclear derivative. The silver–acetylide π linkages are asymmetric, Ag–C(α) distances being in the range 2.220(23)—2.276(21) (average 2.247 ± 0.003) for A and 2.233(19)—2.270(18) (average 2.251 ± 0.001 Å) for B and Ag–C(β) in the range 2.337(34)—2.509(24) (average

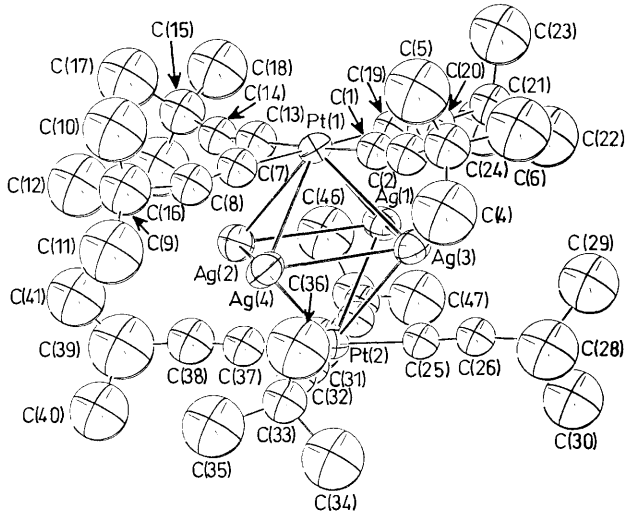



**Figure 1.** Complete molecular structure of $[Pt_2Ag_4(C{\equiv}CBu^t)_8]$ molecule A, showing the atom labelling scheme

**Table 1.** Analytical results, molecular weights, conductivities, and ν(C≡C) i.r. absorptions

| Complex | Analysis[a]/% C | Analysis[a]/% H | $M^b$ | $\Delta_M{}^c$/ $\Omega^{-1}$ cm$^2$ mol$^{-1}$ | μ(C≡C)[d]/cm$^{-1}$ |
|---|---|---|---|---|---|
| (**1**) $[Pt_2Ag_4(C{\equiv}CPh)_8]$ | 47.00 (47.15) | 2.30 (2.45) | *e* | *e* | 2 043m |
| (**2**) $[Pt_2Ag_4(C{\equiv}CBu^t)_8]$ | 39.35 (39.20) | 4.85 (4.95) | 1 461 (1 470.8) | 0 | 2 045m |
| (**3**) $[Pt_2Cu_4(C{\equiv}CPh)_8]$ | 52.65 (52.90) | 3.05 (2.75) | *e* | *e* | 2 034m |
| (**4**) $[Pt_2Cu_4(C{\equiv}CBu^t)_8]$ | 44.35 (44.55) | 5.60 (5.60) | 1 460 (1 293) | 0 | 2 017m |
| (**5**) $[Pt_2Au_4(C{\equiv}CBu^t)_8]$ | 31.50 (31.55) | 4.10 (3.95) | 1 974 (1 827) | 0 | 1 995m |

[a] Calculated values in parentheses. [b] In $CHCl_3$. [c] $\Lambda_M$: in acetone ($c \approx 5 \times 10^{-4}$ mol dm$^{-3}$). [d] Nujol mulls. [e] Not soluble enough for a measurement to be made.

**Table 2.** Fractional atomic co-ordinates ( $\times 10^4$) and their estimated standard deviations (e.s.d.s) for $[Pt_2Ag_4(C{\equiv}CBu^t)_8]$

| Molecule A | *x* | *y* | *z* | Molecule A | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| Pt(1) | 2 108(1) | 00 000(0) | 1 324(1) | C(24) | 1 187(6) | −2 579(38) | 2 378(19) |
| Pt(2) | 1 735(1) | 2 714(1) | 2 288(1) | C(25) | 1 985(6) | 2 042(18) | 3 193(10) |
| Ag(1) | 1 505(1) | 187(2) | 2 044(1) | C(26) | 2 173(6) | 1 612(21) | 3 746(11) |
| Ag(2) | 1 500(1) | 1 809(2) | 789(1) | C(27) | 2 349(6) | 1 160(20) | 4 475(10) |
| Ag(3) | 2 360(1) | 877(2) | 2 808(1) | C(28) | 2 762(7) | 1 581(30) | 4 677(20) |
| Ag(4) | 2 354(1) | 2 521(2) | 1 593(1) | C(29) | 2 354(10) | −107(19) | 4 594(19) |
| C(1) | 2 586(5) | −138(19) | 2 108(10) | C(30) | 2 140(9) | 1 727(29) | 4 932(20) |
| C(2) | 2 883(6) | −141(22) | 2 540(12) | C(31) | 2 221(6) | 3 541(19) | 2 412(10) |
| C(3) | 3 285(6) | −309(21) | 3 029(11) | C(32) | 2 517(6) | 3 986(19) | 2 467(11) |
| C(4) | 3 411(12) | 819(24) | 3 372(20) | C(33) | 2 880(6) | 4 682(19) | 2 645(11) |
| C(5) | 3 549(11) | −680(33) | 2 623(18) | C(34) | 2 936(10) | 5 171(33) | 3 365(12) |
| C(6) | 3 279(13) | −1 184(29) | 3 572(19) | C(35) | 2 850(11) | 5 637(27) | 2 128(15) |
| C(7) | 2 340(6) | 1 157(21) | 833(11) | C(36) | 3 229(9) | 3 965(28) | 2 659(18) |
| C(8) | 2 446(7) | 1 890(23) | 560(12) | C(37) | 1 506(7) | 3 395(23) | 1 387(13) |
| C(9) | 2 566(7) | 2 612(24) | 60(12) | C(38) | 1 342(9) | 3 689(29) | 798(17) |
| C(10) | 2 874(9) | 1 984(34) | −156(21) | C(39) | 1 171(8) | 4 300(27) | 101(14) |
| C(11) | 2 714(11) | 3 775(28) | 323(21) | C(40) | 1 218(10) | 5 553(29) | 248(20) |
| C(12) | 2 211(8) | 2 729(37) | −562(18) | C(41) | 1 332(10) | 3 999(36) | −489(20) |
| C(13) | 1 629(6) | 81(24) | 521(11) | C(42) | 749(9) | 3 986(35) | −108(22) |
| C(14) | 1 360(6) | 155(21) | 5(11) | C(43) | 1 248(6) | 1 807(20) | 2 176(10) |
| C(15) | 1 054(6) | −122(22) | −609(11) | C(44) | 968(6) | 1 297(19) | 2 026(10) |
| C(16) | 748(11) | 780(28) | −697(22) | C(45) | 558(6) | 968(20) | 1 728(11) |
| C(17) | 1 224(10) | −57(36) | −1 203(18) | C(46) | 480(11) | 180(27) | 1 109(14) |
| C(18) | 877(11) | −1 274(24) | −597(22) | C(47) | 450(11) | 386(30) | 2 311(14) |
| C(19) | 1 870(5) | −1 167(18) | 1 804(9) | C(48) | 320(11) | 2 030(23) | 1 520(17) |
| C(20) | 1 735(6) | −1 748(22) | 2 133(11) | Ag(1′) | 1 323(7) | 884(26) | 1 210(13) |
| C(21) | 1 619(6) | −2 643(20) | 2 509(11) | Ag(2′) | 1 902(8) | 2 492(29) | 852(13) |
| C(22) | 1 819(10) | −2 492(37) | 3 280(13) | Ag(3′) | 1 922(7) | 249(23) | 2 659(12) |
| C(23) | 1 719(10) | −3 797(29) | 2 285(20) | Ag(4′) | 2 513(6) | 1 947(22) | 2 290(17) |
| Molecule B | | | | Molecule B | | | |
| Pt(3) | 4 430(1) | 10 281(1) | 4 415(1) | C(60) | 4 133(7) | 6 393(35) | 3 189(18) |
| Ag(5) | 5 139(1) | 8 947(2) | 4 302(1) | C(61) | 4 289(6) | 9 524(19) | 5 145(11) |
| Ag(6) | 5 141(1) | 11 623(2) | 4 311(1) | C(62) | 4 186(5) | 9 081(18) | 5 654(10) |
| C(49) | 4 569(5) | 11 046(19) | 3 683(10) | C(63) | 3 997(5) | 8 692(17) | 6 122(9) |
| C(50) | 4 675(7) | 11 442(22) | 3 213(12) | C(64) | 4 193(9) | 9 102(31) | 6 849(13) |
| C(51) | 4 711(6) | 11 953(22) | 2 553(11) | C(65) | 3 981(10) | 7 412(18) | 6 109(19) |
| C(52) | 4 382(8) | 11 464(30) | 1 977(19) | C(66) | 3 592(7) | 9 160(29) | 5 866(18) |
| C(53) | 5 089(7) | 11 619(32) | 2 445(21) | C(67) | 4 335(5) | 11 708(18) | 4 804(9) |
| C(54) | 4 680(9) | 13 234(22) | 2 536(21) | C(68) | 4 277(5) | 12 619(19) | 5 065(10) |
| C(55) | 4 499(5) | 8 844(18) | 4 016(10) | C(69) | 4 108(5) | 13 631(17) | 5 256(10) |
| C(56) | 4 545(6) | 7 970(20) | 3 750(11) | C(70) | 3 779(8) | 14 115(34) | 4 679(14) |
| C(57) | 4 524(6) | 6 944(19) | 3 331(11) | C(71) | 3 967(9) | 13 364(36) | 5 878(13) |
| C(58) | 4 830(8) | 6 142(32) | 3 751(17) | C(72) | 4 429(8) | 14 495(31) | 5 477(18) |
| C(59) | 4 596(9) | 7 183(36) | 2 638(15) | | | | |

2.425 ± 0.004) for A and 2.397(23)—2.450(25) Å (average 2.423 ± 0.001 Å) for B.

Complexes containing simultaneously metal-acetylide σ bonds and acetylide–metal π bonds have been described previously. The interaction π–metal-acetylide is symmetric in $[\{Cu(C{\equiv}CPh)(PMe_3)\}_4]$[14] and $[\{Fe(\eta\text{-}C_5H_5)(CO)_2(C{\equiv}CPh)\text{-}CuCl\}_2]$[15] but asymmetric in $[Cu_4Ir_2(C{\equiv}CPh)_8(PPh_3)_2]$,[4] $[\{Au_2Ag_2(C{\equiv}CPh)_4(PPh_3)\}_2]$,[9] $[NBu_4][Au_3Cu_2(C{\equiv}CPh)_6]$,[8] and $[RhAg_2(C{\equiv}CC_6F_5)_5(PPh_3)_3]$.[5,16] In (**2**) the C(α)–C(β) distances are in the range 1.164(27)—1.248(28) (average 1.198 ± 0.003) for A and 1.219(28)—1.323(29) (average 1.261 ± 0.001 Å) for B, similar to those found in uncoordinated acetylenes[4] or σ, π acetylide complexes.[4,14,15,17] The Pt–C(α)–C(β)–C chains are not linear, the angles Pt–C(α)–C(β) being in the range 167.2(35)—174.8(26) (average 172.4 ± 5) for A, 171.4(18)—176.3(20) (average 176.6 ± 0.1) for B, while the C(α)–C(β)–Bu$^t$ angles range from 162.4(24) to 170.2(25) (average 166.9 ± 0.3) for A, 164.9(21) to 168.6(23) (average 167.1 ± 0.2°) for B. It seems sensible that as a consequence of the silver–acetylide π interaction the acetylide moiety loses its linearity forming a bent configuration. Usually *cis* bent arrangements have been found in acetylene—transition metal complexes,[18–22] but *cis* or *trans*[4,23,24] bent arrangements have been found in acetylide polynuclear complexes containing σ and π acetylide bonds. In our complex, both situations are present so that in molecule A the acetylide groups are *trans* [except the one formed by C(43)–C(44)–C(45) which is *cis*] and in B half of the acetylides are *trans* and the other half are *cis*.

Within the $[Pt_2Ag_4(C{\equiv}CBu^t)_8]$ unit, the two almost square-planar Pt(acetylide)$_4$ fragments are staggered. The average torsional angle Pt–C(α)–Pt–C(α) is 37.13(12) (A) and 32.84(5)° (B) (Figure 3).

The complex $[Pt_2Ag_4(C{\equiv}CBu^t)_8]$ shows a structure very similar to that found for $[Cu_4Ir_2(C{\equiv}CPh)_8(PPh_3)_2]$,[4] however in the latter, metal–metal bonds have been postulated on the bases of the metal–metal distances and the formal oxidation states of the metal centres. In our case, the intermetallic distances are long and no metal–metal bonds seem to be present. On the other hand, the formation of the iridium–copper complex involves a redox process while in our platinum–silver compound there is no change of the formal oxidation state of the metals. All these data suggest that the formation of the

**Table 3.** Bond distances (Å) and their e.s.d.s for $[Pt_2Ag_4(C{\equiv}CBu^t)_8]$

Molecule A

(*i*) With Ag atoms in holes type (*a*)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Ag(1)···Pt(1) | 3.034(2) | Ag(2)···Pt(1) | 3.086(2) | C(3)–C(2) | 1.539(28) | C(6)–C(3) | 1.535(9) |
| Ag(3)···Pt(1) | 3.082(2) | Ag(4)···Pt(1) | 3.164(2) | C(5)–C(3) | 1.527(9) | C(11)–C(9) | 1.538(10) |
| C(1)–Pt(1) | 2.006(19) | C(7)–Pt(1) | 2.049(24) | C(8)–C(7) | 1.172(32) | C(14)–C(13) | 1.219(28) |
| C(13)–Pt(1) | 2.027(22) | C(19)–Pt(1) | 2.058(21) | C(9)–C(8) | 1.508(35) | C(15)–C(14) | 1.456(28) |
| Ag(1)···Pt(2) | 3.154(2) | Ag(2)···Pt(2) | 3.121(2) | C(10)–C(9) | 1.539(10) | C(16)–C(15) | 1.539(10) |
| Ag(3)···Pt(2) | 3.146(2) | Ag(4)···Pt(2) | 3.047(2) | C(12)–C(9) | 1.538(10) | C(18)–C(15) | 1.536(10) |
| C(25)–Pt(2) | 1.978(20) | C(31)–Pt(2) | 2.005(21) | C(17)–C(15) | 1.529(10) | C(23)–C(21) | 1.542(10) |
| C(37)–Pt(2) | 1.962(25) | C(43)–Pt2 | 2.062(22) | C(20)–C(19) | 1.180(28) | C(26)–C(25) | 1.248(28) |
| Ag(2)···Ag(1) | 3.221(3) | Ag(3)···Ag(1) | 3.194(2) | C(21)–C(20) | 1.462(32) | C(27)–C(26) | 1.537(27) |
| C(19)–Ag(1) | 2.262(20) | C(20)–Ag(1) | 2.465(26) | C(22)–C(21) | 1.538(10) | C(29)–C(27) | 1.541(10) |
| C(43)–Ag(1) | 2.220(23) | C(44)–Ag(1) | 2.387(21) | C(24)–C(21) | 1.541(10) | C(32)–C(31) | 1.195(27) |
| Ag(4)···Ag(2) | 3.211(3) | C(13)–Ag(2) | 2.236(28) | C(28)–C(27) | 1.547(10) | C(33)–C(32) | 1.533(28) |
| C(14)–Ag(2) | 2.509(24) | C(37)–Ag(2) | 2.263(27) | C(30)–C(27) | 1.538(10) | C(34)–C(33) | 1.540(10) |
| C(38)–Ag(2) | 2.337(34) | Ag(4)···Ag(3) | 3.169(3) | C(35)–C(33) | 1.542(10) | C(36)–C(33) | 1.548(9) |
| C(1)–Ag(3) | 2.228(21) | C(2)–Ag(3) | 2.487(25) | C(38)–C(37) | 1.226(37) | C(41)–C(39) | 1.542(10) |
| C(25)–Ag(3) | 2.276(21) | C(26)–Ag(3) | 2.397(22) | C(39)–C(38) | 1.560(41) | C(44)–C(43) | 1.164(27) |
| C(7)–Ag(4) | 2.250(23) | C(8)–Ag(4) | 2.365(24) | C(40)–C(39) | 1.535(10) | C(45)–C(44) | 1.510(27) |
| C(31)–Ag(4) | 2.246(22) | C(32)–Ag(4) | 2.453(22) | C(42)–C(39) | 1.538(10) | C(46)–C(45) | 1.538(10) |
| C(2)–C(1) | 1.187(27) | C(4)–C(3) | 1.534(10) | C(47)–C(45) | 1.537(10) | C(48)–C(45) | 1.538(9) |

(*ii*) With Ag′ atoms in holes type (*b*)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Ag(1′)···Pt(1) | 3.040(26) | Ag(2′)···Pt(1) | 3.170(35) | Ag(4′)–C(31) | 2.252(33) | Ag(3′)–C(19) | 2.407(32) |
| Ag(3′)···Pt(1) | 3.027(26) | Ag(4′)···Pt(1) | 3.138(24) | Ag(4′)–C(32) | 2.478(35) | Ag(3′)–C(20) | 2.637(36) |
| Ag(1′)···Pt(2) | 3.163(23) | Ag(2′)···Pt(2) | 3.189(24) | Ag(1′)–C(43) | 2.356(32) | Ag(2′)–C(37) | 2.344(37) |
| Ag(3′)···Pt(2) | 3.085(28) | Ag(4′)···Pt(2) | 3.025(23) | Ag(1′)–C(44) | 2.467(32) | Ag(2′)–C(38) | 2.500(43) |
| Ag(1′)–C(13) | 2.272(34) | Ag(4′)–C(1) | 2.561(34) | Ag(2′)···Ag(1′) | 3.133(40) | Ag(3′)···Ag(1′) | 3.215(36) |
| Ag(1′)–C(14) | 2.659(32) | Ag(2′)–C(7) | 2.292(39) | Ag(4′)···Ag(2′) | 3.195(41) | Ag(4′)···Ag(3′) | 3.245(40) |
| Ag(3′)–C(25) | 2.397(34) | Ag(2′)–C(8) | 2.380(37) | | | | |

Molecule B

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Ag(5)···Pt(3) | 3.145(2) | Ag(6)···Pt(3) | 3.152(2) | C(56)–C(55) | 1.219(28) | C(57)–C(56) | 1.490(31) |
| C(49)–Pt(3) | 1.954(21) | C(55)–Pt(3) | 1.960(21) | C(58)–C(57) | 1.538(10) | C(59)–C(57) | 1.546(10) |
| C(61)–Pt(3) | 1.951(22) | C(67)–Pt(3) | 1.966(21) | C(60)–C(57) | 1.540(10) | C(62)–C(61) | 1.323(29) |
| Ag(6)···Ag(5) | 3.216(2) | C(55)–Ag(5) | 2.270(18) | C(63)–C(62) | 1.426(26) | C(64)–C(63) | 1.528(9) |
| C(56)–Ag(5) | 2.450(21) | Ag(5*)···Ag(5) | 3.313(4) | C(65)–C(63) | 1.539(9) | C(66)–C(63) | 1.539(10) |
| C(49)–Ag(6) | 2.233(19) | C(50)–Ag(6) | 2.397(23) | C(68)–C(67) | 1.266(29) | C(69)–C(68) | 1.474(28) |
| Ag(6*)···Ag(6) | 3.290(4) | C(50)–C(49) | 1.237(30) | C(70)–C(69) | 1.534(10) | C(71)–C(69) | 1.544(10) |
| C(51)–C(50) | 1.526(31) | C(52)–C(51) | 1.535(10) | C(72)–C(69) | 1.544(10) | | |
| C(53)–C(51) | 1.537(10) | C(54)–C(51) | 1.545(10) | | | | |

Starred atoms are related to unstarred ones by a two-fold axis.

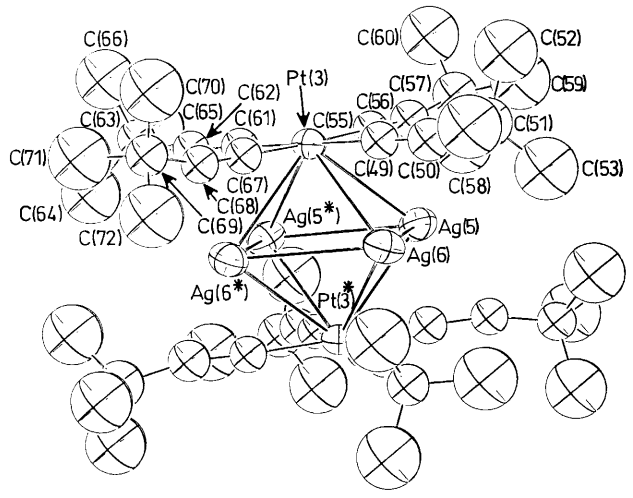



**Figure 2.** Complete molecular structure of $[Pt_2Ag_4(C{\equiv}CBu^t)_8]$ molecule B, showing the atom labelling scheme

silver–acetylide π bonds is the driving force in the formation of the compound.

*Disordering of* $[Pt_2Ag_4(C{\equiv}CBu^t)_8]$. Since the two 'Pt(C≡CBu$^t$)$_4$' fragments in each $[Pt_2Ag_4(C{\equiv}CBu^t)_8]$ molecule are staggered, the silver atoms could reasonably be located in holes type (*a*) or type (*b*) (see Figure 3). In molecule B all the silver atoms are located in holes type (*a*) and this molecule is ordered. However, molecule A shows partial disordering with occupancy factors of 0.92 [silver atoms in holes type (*a*)] and 0.08 [silver atoms in holes type (*b*)]. Silver atoms located in holes type (*b*) (Ag′) are in a very similar structural situation to those located in holes type (*a*) (Ag); the Ag′–C(α) distances are in the range 2.252(33)—2.561(34) (average 2.360 ± 0.012) and Ag′–C(β) distances range from 2.380(37) to 2.637(36) (average 2.520 ± 0.004 Å) only slightly longer than distances Ag–C(α) and Ag–C(β) found for silver atoms in type (*a*) holes.

*I.r. Spectra.*—The i.r. spectra of the mononuclear derivatives $[NBu_4]_2[Pt(C{\equiv}CPh)_4]$ (**6**) or $[NBu_4]_2[Pt(C{\equiv}CBu^t)_4]{\cdot}2H_2O$ (**7**) show a strong absorption at 2 075 and 2 081 cm$^{-1}$ respectively due to ν(C≡C) of the terminal acetylide groups.[7] Mention should be made that Shaw and co-workers[25] have reported that $[NBu_4]_2[Pt(C{\equiv}CPh)_4]$, obtained from the reaction between Li(C≡CPh) and $[PtCl_2(dppm\text{-}PP')]$ (dppm = $Ph_2PCH_2PPh_2$), shows ν(C≡C) at 2 100 cm$^{-1}$. Complex (**2**) shows absorptions at 3 421s, 3 303m, and 1 661s due to

**Table 4.** Bond angles (°) and their e.s.d.s for $[Pt_2Ag_4(C{\equiv}CBu^t)_8]$

Molecule A

(*i*) With Ag atoms in holes type (*a*)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C(1)–Pt(1)–C(13) | 177.84(99) | Ag(4)–Pt(2)–C(37) | 76.54(80) | Ag(1)–Pt(1)–C(19) | 48.19(56) | Ag(1)–Pt(2)–C(25) | 77.46(63) |
| C(1)–Pt(1)–C(7) | 92.76(92) | Ag(4)–Pt(2)–C(31) | 47.46(66) | Ag(1)–Pt(1)–C(13) | 78.24(70) | Ag(1)–Pt(2)–Ag(4) | 93.34(12) |
| Ag(4)–Pt(1)–C(19) | 135.42(53) | Ag(4)–Pt(2)–C(25) | 101.48(71) | Ag(1)–Pt(1)–C(7) | 131.81(68) | Ag(1)–Pt(2)–Ag(3) | 60.91(10) |
| Ag(4)–Pt(1)–C(13) | 103.38(75) | Ag(3)–Pt(2)–C(43) | 101.38(67) | Ag(1)–Pt(1)–C(1) | 102.72(58) | Ag(1)–Pt(2)–Ag(2) | 61.73(8) |
| Ag(4)–Pt(1)–C(7) | 45.10(67) | Ag(3)–Pt(2)–C(37) | 132.65(79) | Ag(1)–Pt(1)–Ag(4) | 93.46(11) | Pt(1)–Ag(1)–Pt(2) | 86.83(14) |
| Ag(4)–Pt(1)–C(1) | 78.54(62) | Ag(3)–Pt(2)–C(31) | 76.30(68) | Ag(1)–Pt(1)–Ag(3) | 62.96(14) | Pt(2)–Ag(1)–C(44) | 69.42(56) |
| Ag(3)–Pt(1)–C(19) | 79.03(50) | Ag(3)–Pt(2)–C(25) | 46.06(66) | Ag(1)–Pt(1)–Ag(2) | 63.50(11) | Pt(2)–Ag(1)–C(43) | 40.64(63) |
| Ag(3)–Pt(1)–C(13) | 135.60(71) | Ag(3)–Pt(2)–Ag(4) | 61.55(12) | C(37)–Pt(2)–C(43) | 89.95(102) | Pt(2)–Ag(1)–C(20) | 145.70(59) |
| Ag(3)–Pt(1)–C(7) | 101.71(66) | Ag(2)–Pt(2)–C(43) | 74.33(59) | C(31)–Pt(2)–C(43) | 177.68(92) | Pt(2)–Ag(1)–C(19) | 125.27(55) |
| Ag(3)–Pt(1)–C(1) | 46.19(58) | Ag(2)–Pt(2)–C(37) | 46.21(76) | C(13)–Pt(1)–C(19) | 91.25(92) | Pt(2)–Ag(1)–Ag(3) | 59.41(10) |
| Ag(3)–Pt(1)–Ag(4) | 60.98(8) | Ag(2)–Pt(2)–C(31) | 105.78(62) | C(7)–Pt(1)–C(19) | 179.17(81) | Pt(2)–Ag(1)–Ag(2) | 58.63(8) |
| Ag(2)–Pt(1)–C(19) | 106.05(59) | Ag(2)–Pt(2)–C(25) | 133.76(64) | C(7)–Pt(1)–C(13) | 87.96(91) | Pt(1)–Ag(1)–C(44) | 140.06(52) |
| Ag(2)–Pt(1)–C(13) | 46.39(73) | Ag(2)–Pt(2)–Ag(4) | 62.76(17) | C(31)–Pt(2)–C(37) | 91.75(99) | Pt(1)–Ag(1)–C(43) | 122.00(62) |
| Ag(2)–Pt(1)–C(7) | 73.57(66) | Ag(2)–Pt(2)–Ag(5) | 92.71(10) | C(25)–Pt(2)–C(43) | 92.08(93) | Pt(1)–Ag(1)–C(10) | 71.15(58) |
| Ag(2)–Pt(1)–C(1) | 135.77(63) | Ag(1)–Pt(2)–C(43) | 44.53(68) | C(25)–Pt(2)–C(37) | 177.82(112) | Pt(1)–Ag(1)–C(19) | 42.77(51) |
| Ag(2)–Pt(1)–Ag(4) | 61.86(8) | Ag(1)–Pt(2)–C(37) | 103.49(78) | C(25)–Pt(2)–C(31) | 86.20(93) | Pt(1)–Ag(1)–Ag(3) | 59.28(15) |
| Ag(2)–Pt(1)–Ag(3) | 94.65(8) | Ag(1)–Pt(2)–C(31) | 133.41(69) | Ag(4)–Pt(2)–C(43) | 131.61(61) | Pt(1)–Ag(1)–Ag(2) | 59.07(11) |
| C(43)–Ag(1)–C(44) | 28.99(84) | Ag(4)–Ag(2)–C(13) | 97.05(66) | Ag(1)–Ag(2)–C(13) | 71.49(66) | C(2)–Ag(3)–C(25) | 167.59(81) |
| C(20)–Ag(1)–C(44) | 142.82(82) | Pt(2)–Ag(3)–Ag(1) | 59.68(10) | Ag(1)–Ag(2)–Ag(4) | 89.10(13) | C(1)–Ag(3)–C(26) | 166.37(79) |
| C(20)–Ag(1)–C(43) | 166.01(78) | Pt(1)–Ag(3)–Ag(1) | 57.76(13) | Pt(2)–Ag(2)–C(38) | 69.61(84) | C(1)–Ag(3)–C(25) | 161.27(75) |
| C(19)–Ag(1)–C(44) | 161.52(73) | Pt(1)–Ag(3)–Pt(2) | 86.14(9) | Pt(2)–Ag(2)–C(37) | 38.76(65) | C(1)–Ag(3)–C(2) | 28.46(78) |
| C(19)–Ag(1)–C(43) | 164.62(83) | Ag(1)–Ag(3)–C(26) | 90.26(61) | Pt(2)–Ag(2)–C(14) | 147.96(53) | Ag(4)–Ag(3)–C(26) | 117.54(61) |
| C(19)–Ag(1)–C(20) | 28.45(79) | Ag(1)–Ag(3)–C(25) | 73.12(61) | Pt(2)–Ag(2)–C(13) | 123.20(61) | Ag(4)–Ag(3)–C(25) | 91.52(55) |
| Ag(3)–Ag(1)–C(44) | 124.22(54) | Ag(1)–Ag(3)–C(2) | 119.24(59) | Pt(2)–Ag(2)–Ag(4) | 57.53(15) | Ag(4)–Ag(3)–C(2) | 87.50(57) |
| Ag(3)–Ag(1)–C(43) | 96.40(61) | Ag(1)–Ag(3)–C(1) | 93.01(55) | Pt(1)–Ag(2)–C(38) | 146.83(83) | Ag(4)–Ag(3)–C(1) | 75.69(52) |
| Ag(3)–Ag(1)–C(20) | 86.49(58) | Ag(1)–Ag(3)–Ag(4) | 90.34(15) | Pt(1)–Ag(2)–C(37) | 120.98(68) | Ag(2)–Ag(4)–Ag(3) | 90.52(15) |
| Ag(3)–Ag(1)–C(19) | 73.99(53) | Pt(2)–Ag(3)–C(26) | 69.58(60) | Pt(1)–Ag(2)–C(14) | 69.95(58) | Pt(2)–Ag(4)–Ag(3) | 60.72(12) |
| Ag(2)–Ag(1)–C(44) | 81.03(53) | Pt(2)–Ag(3)–C(25) | 38.75(56) | Pt(1)–Ag(2)–C(13) | 41.00(65) | Pt(2)–Ag(4)–Ag(2) | 59.71(16) |
| Ag(2)–Ag(1)–C(43) | 70.47(58) | Pt(2)–Ag(3)–C(2) | 144.48(57) | Pt(1)–Ag(2)–Ag(4) | 60.28(10) | Pt(1)–Ag(4)–Ag(3) | 58.21(8) |
| Ag(2)–Ag(1)–C(20) | 123.33(55) | Pt(2)–Ag(3)–C(1) | 123.24(53) | C(37)–Ag(2)–C(38) | 30.91(108) | Pt(1)–Ag(4)–Ag(2) | 57.86(8) |
| Ag(2)–Ag(1)–C(19) | 97.11(49) | Pt(2)–Ag(3)–Ag(4) | 57.74(11) | C(14)–Ag(2)–C(38) | 140.11(97) | Pt(1)–Ag(4)–Pt(2) | 86.34(10) |
| Ag(2)–Ag(1)–Ag(3) | 90.01(13) | Pt(1)–Ag(3)–C(26) | 147.15(61) | C(14)–Ag(2)–C(37) | 168.61(91) | Ag(3)–Ag(4)–C(32) | 86.21(52) |
| Pt(2)–Ag(2)–Ag(1) | 59.64(8) | Pt(1)–Ag(3)–C(25) | 121.07(56) | C(13)–Ag(2)–C(38) | 166.67(100) | Ag(3)–Ag(4)–C(31) | 72.97(53) |
| Pt(1)–Ag(2)–Ag(1) | 57.43(10) | Pt(1)–Ag(3)–C(2) | 68.92(57) | C(13)–Ag(2)–C(37) | 161.34(88) | Ag(3)–Ag(4)–C(8) | 122.13(68) |
| Pt(1)–Ag(2)–Pt(2) | 86.49(10) | Pt(1)–Ag(3)–C(1) | 40.58(52) | C(13)–Ag(2)–C(14) | 29.04(78) | Ag(3)–Ag(4)–C(7) | 94.63(62) |
| Ag(1)–Ag(2)–C(38) | 121.40(82) | Pt(1)–Ag(3)–Ag(4) | 60.81(8) | Ag(4)–Ag(2)–C(38) | 87.07(85) | Ag(2)–Ag(4)–C(32) | 123.60(63) |
| Ag(1)–Ag(2)–C(37) | 94.73(66) | C(25)–Ag(3)–C(26) | 30.87(75) | Ag(4)–Ag(2)–C(37) | 69.54(71) | Ag(2)–Ag(4)–C(31) | 97.13(65) |
| Ag(1)–Ag(2)–C(14) | 88.91(57) | C(2)–Ag(3)–C(26) | 142.14(78) | Ag(4)–Ag(2)–C(14) | 121.39(61) | Ag(2)–Ag(4)–C(8) | 80.87(59) |
| Ag(2)–Ag(4)–C(7) | 68.74(62) | Ag(2)–C(14)–C(13) | 62.93(155) | C(2)–C(3)–C(6) | 109.81(241) | Pt(2)–C(26)–Ag(3) | 95.19(81) |
| Pt(2)–Ag(4)–C(32) | 70.15(56) | C(13)–C(14)–C(15) | 162.51(271) | C(2)–C(3)–C(5) | 109.71(210) | Ag(3)–C(25)–C(26) | 79.99(157) |
| Pt(2)–Ag(4)–C(31) | 41.11(60) | Ag(2)–C(14)–C(15) | 133.69(176) | C(2)–C(3)–C(4) | 106.48(209) | Pt(2)–C(25)–C(26) | 174.11(210) |
| Pt(2)–Ag(4)–C(8) | 140.52(65) | C(14)–C(15)–C(18) | 114.76(216) | C(9)–C(3)–C(6) | 110.18(250) | Ag(3)–C(26)–C(25) | 69.14(140) |
| Pt(2)–Ag(4)–C(7) | 120.89(65) | C(14)–C(15)–C(17) | 105.83(224) | C(4)–C(3)–C(6) | 110.50(241) | C(25)–C(26)–C(27) | 169.93(244) |
| Pt(1)–Ag(4)–C(32) | 144.04(53) | C(14)–C(15)–C(16) | 107.19(218) | C(4)–C(3)–C(5) | 110.50(277) | Ag(3)–C(26)–C(27) | 120.42(159) |
| Pt(1)–Ag(4)–C(31) | 122.40(59) | C(17)–C(15)–C(18) | 109.79(244) | Pt(1)–C(7)–Ag(4) | 94.70(93) | C(26)–C(27)–C(30) | 106.76(203) |
| Pt(1)–Ag(4)–C(8) | 69.44(63) | C(16)–C(15)–C(18) | 109.50(261) | Ag(4)–C(7)–C(8) | 80.79(173) | C(26)–C(27)–C(29) | 118.96(191) |
| Pt(1)–Ag(4)–C(7) | 40.20(62) | C(16)–C(15)–C(17) | 109.62(261) | Pt(1)–C(7)–C(8) | 173.38(230) | C(26)–C(27)–C(28) | 103.96(196) |
| C(31)–Ag(4)–C(32) | 29.04(80) | Pt(1)–C(19)–Ag(1) | 89.04(76) | Ag(4)–C(8)–C(7) | 69.91(155) | C(29)–C(27)–C(30) | 109.01(242) |
| C(8)–Ag(4)–C(32) | 144.29(89) | Ag(1)–C(19)–C(20) | 85.49(163) | Ag(4)–C(8)–C(9) | 124.97(176) | C(28)–C(27)–C(30) | 109.32(235) |
| C(8)–Ag(4)–C(31) | 164.64(86) | Pt(1)–C(19)–C(20) | 172.67(189) | C(7)–C(8)–C(9) | 164.96(257) | C(28)–C(27)–C(29) | 108.50(226) |
| C(7)–Ag(4)–C(32) | 167.65(92) | Ag(1)–C(20)–C(19) | 66.06(155) | C(8)–C(9)–C(12) | 105.07(226) | Pt(2)–C(31)–Ag(4) | 91.43(93) |
| C(7)–Ag(4)–C(31) | 161.51(88) | C(19)–C(20)–C(21) | 168.31(259) | C(8)–C(9)–C(11) | 115.65(235) | Ag(4)–C(31)–C(32) | 85.05(157) |
| C(7)–Ag(4)–C(8) | 29.31(82) | Ag(1)–C(20)–C(21) | 125.63(168) | C(8)–C(9)–C(10) | 107.93(243) | Pt(2)–C(31)–C(32) | 176.31(202) |
| Pt(1)–C(1)–Ag(3) | 93.23(81) | C(20)–C(21)–C(24) | 109.13(218) | C(11)–C(9)–C(12) | 109.43(276) | Ag(4)–C(32)–C(31) | 65.91(142) |
| Ag(3)–C(1)–C(2) | 88.09(163) | C(20)–C(21)–C(23) | 111.65(227) | C(10)–C(9)–C(12) | 109.39(258) | C(31)–C(32)–C(33) | 169.22(232) |
| Pt(1)–C(1)–C(2) | 173.52(205) | C(20)–C(21)–C(22) | 108.88(219) | C(10)–C(9)–C(11) | 109.19(271) | Ag(4)–C(32)–C(33) | 124.87(151) |
| Ag(3)–C(2)–C(1) | 63.45(149) | C(23)–C(21)–C(24) | 108.96(242) | Pt(1)–C(13)–Ag(2) | 92.61(88) | C(32)–C(33)–C(36) | 111.68(209) |
| C(1)–C(2)–C(3) | 170.17(255) | C(22)–C(21)–C(24) | 109.25(217) | Ag(2)–C(13)–C(14) | 88.03(183) | C(32)–C(33)–C(35) | 111.49(206) |
| Ag(3)–C(2)–C(3) | 125.99(156) | C(22)–C(21)–C(23) | 108.94(246) | Pt(1)–C(13)–C(14) | 174.49(208) | C(32)–C(33)–C(34) | 106.97(221) |
| C(35)–C(33)–C(36) | 108.36(241) | C(37)–C(38)–C(39) | 168.19(333) | C(40)–C(39)–C(41) | 109.62(289) | C(44)–C(45)–C(48) | 108.56(201) |
| C(34)–C(33)–C(36) | 108.85(267) | Ag(2)–C(38)–C(39) | 118.85(211) | Pt(2)–C(43)–Ag(1) | 94.83(97) | C(44)–C(45)–C(47) | 105.84(192) |
| C(34)–C(33)–C(35) | 109.44(223) | C(38)–C(39)–C(42) | 103.79(254) | Ag(1)–C(43)–C(44) | 83.51(170) | C(44)–C(45)–C(46) | 114.28(224) |
| Pt(2)–C(37)–Ag(2) | 95.02(105) | C(38)–C(39)–C(41) | 117.31(274) | Pt(2)–C(43)–C(44) | 171.49(182) | C(47)–C(45)–C(48) | 109.27(255) |
| Ag(2)–C(37)–C(38) | 77.89(206) | C(38)–C(39)–C(40) | 106.98(252) | Ag(1)–C(44)–C(43) | 67.51(160) | C(46)–C(45)–C(48) | 109.48(257) |
| Pt(2)–C(37)–C(38) | 171.72(264) | C(41)–C(39)–C(42) | 108.96(276) | C(43)–C(44)–C(45) | 162.44(240) | C(46)–C(45)–C(47) | 109.28(231) |
| Ag(2)–C(38)–C(37) | 71.20(203) | C(40)–C(39)–C(42) | 109.93(286) | Ag(1)–C(44)–C(45) | 126.36(155) | | |

**Table 4** (*continued*)

(*ii*) With Ag′ atoms in holes type (*b*)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Ag(3′)–Pt(1)–Ag(4′) | 63.48(77) | C(37)–Pt(2)–Ag(2′) | 47.04(94) | C(7)–Pt(1)–Ag(2′) | 46.17(92) | C(14)–C(13)–Ag(1′) | 94.40(180) |
| Ag(2′)–Pt(1)–Ag(4′) | 60.85(69) | C(37)–Pt(2)–Ag(1′) | 69.72(93) | C(7)–Pt(1)–Ag(1′) | 104.94(88) | C(13)–C(14)–Ag(1′) | 58.41(157) |
| Ag(2′)–Pt(1)–Ag(3′) | 94.71(71) | C(31)–Pt(2)–Ag(4′) | 48.07(82) | Ag(2′)–Pt(2)–Ag(4′) | 61.79(75) | C(15)–C(14)–Ag(1′) | 129.13(172) |
| Ag(1′)–Pt(1)–Ag(4′) | 93.05(73) | C(31)–Pt(2)–Ag(3′) | 108.55(85) | Ag(2′)–Pt(2)–Ag(3′) | 93.14(79) | Pt(1)–C(19)–Ag(3′) | 84.94(96) |
| Ag(1′)–Pt(1)–Ag(3′) | 64.04(70) | C(31)–Pt(2)–Ag(2′) | 75.08(77) | C(1)–Pt(1)–Ag(4′) | 54.44(83) | C(20)–C(19)–Ag(3′) | 87.74(168) |
| Ag(1′)–Pt(1)–Ag(2′) | 60.58(83) | C(31)–Pt(2)–Ag(1′) | 131.28(80) | C(1)–Pt(1)–Ag(3′) | 70.90(74) | C(19)–C(20)–Ag(3′) | 65.75(151) |
| C(19)–Pt(1)–Ag(4′) | 113.62(79) | C(25)–Pt(2)–Ag(4′) | 72.30(85) | C(1)–Pt(1)–Ag(2′) | 113.29(88) | C(21)–C(20)–Ag(3′) | 122.57(159) |
| C(19)–Pt(1)–Ag(3′) | 52.38(71) | C(25)–Pt(2)–Ag(3′) | 50.93(80) | C(1)–Pt(1)–Ag(1′) | 133.20(78) | Pt(2)–C(25)–Ag(3′) | 89.23(95) |
| C(19)–Pt(1)–Ag(2′) | 133.67(85) | C(25)–Pt(2)–Ag(2′) | 131.47(89) | Ag(1′)–Pt(2)–Ag(4′) | 92.82(74) | C(26)–C(25)–Ag(3′) | 89.54(167) |
| C(19)–Pt(1)–Ag(1′) | 74.69(79) | C(25)–Pt(2)–Ag(1′) | 111.15(84) | Ag(1′)–Pt(2)–Ag(3′) | 61.93(72) | C(25)–C(26)–Ag(3′) | 62.83(147) |
| C(13)–Pt(1)–Ag(4′) | 127.67(91) | Pt(1)–C(1)–Ag(4′) | 85.92(93) | Ag(1′)–Pt(2)–Ag(2′) | 59.10(89) | C(27)–C(26)–Ag(3′) | 121.80(162) |
| C(13)–Pt(1)–Ag(3′) | 110.20(85) | C(2)–C(1)–Ag(4′) | 90.55(178) | C(43)–Pt(2)–Ag(4′) | 129.86(84) | Pt(2)–C(31)–Ag(4′) | 90.42(114) |
| C(13)–Pt(1)–Ag(2′) | 68.62(97) | Pt(2)–C(7)–Ag(2′) | 93.63(119) | C(43)–Pt(2)–Ag(3′) | 69.14(84) | C(32)–C(31)–Ag(4′) | 86.17(180) |
| C(13)–Pt(1)–Ag(1′) | 48.39(86) | C(8)–C(7)–Ag(2′) | 79.75(200) | C(43)–Pt(2)–Ag(2′) | 105.01(74) | C(31)–C(32)–Ag(4′) | 65.06(166) |
| Ag(3′)–Pt(2)–Ag(4′) | 64.12(72) | C(9)–C(8)–Ag(2′) | 116.11(188) | C(43)–Pt(2)–Ag(1′) | 48.07(78) | C(33)–C(32)–Ag(4′) | 122.77(168) |
| C(7)–Pt(1)–Ag(4′) | 67.10(79) | C(7)–C(8)–Ag(2′) | 71.26(187) | C(37)–Pt(2)–Ag(4′) | 105.75(98) | Pt(2)–C(37)–Ag(2′) | 95.20(130) |
| C(7)–Pt(1)–Ag(3′) | 128.17(81) | Pt(1)–C(13)–Ag(1′) | 89.80(108) | C(37)–Pt(2)–Ag(3′) | 129.32(93) | C(38)–C(37)–Ag(2′) | 82.52(213) |
| C(37)–C(38)–Ag(2′) | 68.36(209) | C(7)–Ag(2′)–C(37) | 151.45(159) | C(44)–Ag(1′)–Ag(3′) | 77.57(97) | Pt(1)–Ag(2′)–Ag(4′) | 59.10(80) |
| C(39)–C(38)–Ag(2′) | 114.54(215) | C(7)–Ag(2′)–C(8) | 28.98(98) | C(44)–Ag(1′)–Ag(2′) | 125.16(131) | C(26)–Ag(3′)–Ag(1′) | 126.03(120) |
| Pt(2)–C(43)–Ag(1′) | 91.28(112) | Pt(2)–Ag(2′)–Ag(1′) | 60.03(70) | C(43)–Ag(1′)–Ag(3′) | 63.97(95) | C(25)–Ag(3′)–Ag(1′) | 98.77(113) |
| C(44)–C(43)–Ag(1′) | 81.44(175) | Pt(2)–Ag(2′)–C(38) | 66.70(96) | C(43)–Ag(1′)–Ag(2′) | 99.63(122) | C(25)–Ag(3′)–C(26) | 27.62(74) |
| C(43)–C(44)–Ag(1′) | 70.73(161) | Pt(2)–Ag(2′)–C(37) | 37.76(75) | C(14)–Ag(1′)–Ag(3′) | 124.26(121) | C(20)–Ag(3′)–Ag(1′) | 79.40(97) |
| C(45)–C(44)–Ag(1′) | 110.53(153) | Pt(2)–Ag(2′)–C(8) | 132.04(114) | C(14)–Ag(1′)–Ag(2′) | 75.92(100) | C(20)–Ag(3′)–C(26) | 150.94(127) |
| C(43)–Ag(1′)–C(44) | 27.82(84) | Pt(2)–Ag(2′)–C(7) | 114.12(109) | C(13)–Ag(1′)–Ag(3′) | 97.81(119) | C(20)–Ag(3′)–C(25) | 169.34(148) |
| C(14)–Ag(1′)–C(44) | 151.71(139) | Pt(1)–Ag(2′)–Ag(1′) | 57.65(80) | C(13)–Ag(1′)–Ag(2′) | 67.22(113) | C(19)–Ag(3′)–Ag(1′) | 67.35(91) |
| C(14)–Ag(1′)–C(43) | 170.27(152) | Pt(1)–Ag(2′)–C(38) | 132.70(143) | Pt(2)–Ag(1′)–Ag(3′) | 57.84(69) | C(19)–Ag(3′)–C(26) | 164.42(142) |
| C(13)–Ag(1′)–C(44) | 166.47(172) | Pt(1)–Ag(2′)–C(37) | 115.01(130) | Pt(2)–Ag(1′)–Ag(2′) | 60.86(77) | C(19)–Ag(3′)–C(25) | 160.63(134) |
| C(13)–Ag(1′)–C(43) | 158.04(157) | Pt(1)–Ag(2′)–C(8) | 69.18(104) | Pt(1)–Ag(1′)–Ag(3′) | 57.77(68) | C(19)–Ag(3′)–C(20) | 26.52(78) |
| C(13)–Ag(1′)–C(14) | 27.19(79) | Pt(1)–Ag(2′)–C(7) | 40.19(78) | Pt(1)–Ag(1′)–Ag(2′) | 61.76(81) | Pt(2)–Ag(3′)–Ag(1′) | 60.23(71) |
| Pt(2)–Ag(1′)–C(44) | 68.42(84) | Pt(1)–Ag(2′)–Pt(2) | 83.92(82) | Ag(2)–Ag(1′)–Ag(3′) | 91.74(102) | Pt(2)–Ag(3′)–C(26) | 67.36(79) |
| Pt(2)–Ag(1′)–C(43) | 40.65(71) | Ag(1′)–Ag(2′)–Ag(4′) | 90.23(110) | C(38)–Ag(2′)–Ag(1′) | 75.39(136) | Pt(2)–Ag(3′)–C(25) | 39.84(64) |
| Pt(2)–Ag(1′)–C(14) | 136.63(120) | C(38)–Ag(2′)–Ag(4′) | 120.52(144) | C(37)–Ag(2′)–Ag(1′) | 66.91(115) | Pt(2)–Ag(3′)–C(20) | 139.63(105) |
| Pt(2)–Ag(1′)–C(13) | 120.09(124) | C(37)–Ag(2′)–Ag(4′) | 92.01(128) | C(37)–Ag(2′)–C(38) | 29.12(104) | Pt(2)–Ag(3′)–C(19) | 122.51(104) |
| Pt(1)–Ag(1′)–C(44) | 135.34(114) | C(8)–Ag(2′)–Ag(4′) | 75.49(107) | C(8)–Ag(2′)–Ag(1′) | 124.19(153) | Pt(1)–Ag(3′)–Ag(1′) | 58.19(66) |
| Pt(1)–Ag(1′)–C(43) | 116.87(114) | C(7)–Ag(2′)–Ag(4′) | 64.04(105) | C(8)–Ag(2′)–C(38) | 156.63(164) | Pt(1)–Ag(3′)–C(26) | 133.61(113) |
| Pt(1)–Ag(1′)–C(14) | 68.97(82) | Ag(4)–Ag(2′)–Ag(4′) | 18.93(72) | C(8)–Ag(2′)–C(37) | 162.55(165) | Pt(1)–Ag(3′)–C(25) | 118.89(107) |
| Pt(1)–Ag(1′)–C(13) | 41.81(77) | Ag(2)–Ag(2′)–Ag(4′) | 109.81(151) | C(7)–Ag(2′)–Ag(1′) | 96.33(137) | Pt(1)–Ag(3′)–C(20) | 69.19(77) |
| Pt(1)–Ag(1′)–Pt(2) | 86.52(73) | Pt(2)–Ag(2′)–Ag(4′) | 56.58(79) | C(7)–Ag(2′)–C(38) | 170.12(183) | Pt(1)–Ag(3′)–C(19) | 42.68(61) |
| Pt(1)–Ag(3′)–Pt(2) | 88.18(64) | Ag(2′)–Ag(4′)–Ag(3′) | 90.12(108) | C(1)–Ag(4′)–Ag(2′) | 98.25(106) | Pt(2)–Ag(4′)–C(1) | 116.13(103) |
| Ag(1′)–Ag(3′)–Ag(4′) | 87.91(95) | C(32)–Ag(4′)–Ag(3′) | 124.29(121) | C(1)–Ag(4′)–C(32) | 173.58(138) | Pt(1)–Ag(4′)–Ag(3′) | 56.56(72) |
| C(26)–Ag(3′)–Ag(4′) | 73.71(90) | C(32)–Ag(4′)–Ag(2′) | 84.44(105) | C(1)–Ag(4′)–C(31) | 157.64(144) | Pt(1)–Ag(4′)–Ag(2′) | 60.05(68) |
| C(25)–Ag(3′)–Ag(4′) | 63.89(93) | C(31)–Ag(4′)–Ag(3′) | 97.42(116) | Pt(2)–Ag(4′)–Ag(3′) | 58.83(68) | Pt(1)–Ag(4′)–C(32) | 114.15(130) |
| C(20)–Ag(3′)–Ag(4′) | 126.22(116) | C(31)–Ag(4′)–Ag(2′) | 72.31(102) | Pt(2)–Ag(4′)–Ag(2′) | 61.63(74) | Pt(1)–Ag(4′)–C(31) | 123.34(124) |
| C(19)–Ag(3′)–Ag(4′) | 100.91(107) | C(31)–Ag(4′)–C(32) | 28.77(87) | Pt(2)–Ag(4′)–C(32) | 70.28(83) | Pt(1)–Ag(4′)–C(1) | 39.64(64) |
| Pt(2)–Ag(3′)–Ag(4′) | 57.04(68) | C(1)–Ag(4′)–Ag(3′) | 61.71(88) | Pt(2)–Ag(4′)–C(31) | 41.51(76) | Pt(1)–Ag(4′)–Pt(2) | 87.20(73) |
| Pt(1)–Ag(3′)–Ag(4′) | 59.96(66) | | | | | | |

Molecule B

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C(61)–Pt(3)–C(67) | 88.59(86) | C(50)–C(51)–C(53) | 110.30(220) | Pt(3)–Ag(5)–Ag(6) | 59.36(15) | Pt(3)–C(61)–C(62) | 175.85(190) |
| C(55)–Pt(3)–C(67) | 177.29(90) | C(50)–C(51)–C(52) | 105.24(213) | C(55)–Ag(5)–C(56) | 29.62(77) | C(61)–C(62)–C(63) | 167.69(214) |
| C(55)–Pt(3)–C(61) | 90.35(90) | C(53)–C(51)–C(54) | 108.90(235) | Ag(6)–Ag(5)–C(56) | 118.82(57) | C(62)–C(63)–C(66) | 106.10(193) |
| C(49)–Pt(3)–C(67) | 91.15(90) | C(52)–C(51)–C(54) | 109.17(229) | Ag(6)–Ag(5)–C(55) | 93.24(56) | C(62)–C(63)–C(65) | 109.92(183) |
| C(49)–Pt(3)–C(61) | 179.67(95) | C(52)–C(51)–C(53) | 109.94(236) | Pt(3)–Ag(6)–Ag(5) | 59.21(15) | C(62)–C(63)–C(64) | 111.25(201) |
| C(49)–Pt(3)–C(55) | 89.90(88) | Pt(3)–C(55)–Ag(5) | 95.83(88) | Ag(5)–Ag(6)–C(50) | 84.52(62) | C(65)–C(63)–C(66) | 109.31(223) |
| Ag(6)–Pt(3)–C(67) | 80.56(63) | Ag(5)–C(55)–C(56) | 83.49(157) | Ag(5)–Ag(6)–C(49) | 71.73(59) | C(64)–C(63)–C(66) | 110.06(212) |
| Ag(6)–Pt(3)–C(61) | 135.46(63) | Pt(3)–C(55)–C(56) | 177.68(189) | Pt(3)–Ag(6)–C(50) | 68.61(66) | C(64)–C(63)–C(65) | 110.11(201) |
| Ag(6)–Pt(3)–C(55) | 101.92(63) | Ag(5)–C(56)–C(55) | 66.89(144) | Pt(3)–Ag(6)–C(49) | 37.96(55) | Pt(3)–C(67)–C(68) | 178.95(163) |
| Ag(6)–Pt(3)–C(49) | 44.67(63) | C(55)–C(56)–C(57) | 168.61(239) | C(49)–Ag(6)–C(50) | 30.76(79) | C(67)–C(68)–C(69) | 164.99(210) |
| Ag(5)–Pt(3)–C(67) | 136.84(63) | Ag(5)–C(56)–C(57) | 123.13(164) | Pt(3)–C(49)–Ag(6) | 97.37(85) | C(68)–C(69)–C(72) | 106.16(193) |
| Ag(5)–Pt(3)–C(61) | 103.91(66) | C(56)–C(57)–C(60) | 110.40(205) | Ag(6)–C(49)–C(50) | 81.93(163) | C(68)–C(69)–C(71) | 108.80(202) |
| Ag(5)–Pt(3)–C(55) | 45.86(63) | C(56)–C(57)–C(59) | 112.26(225) | Pt(3)–C(49)–C(50) | 174.06(209) | C(68)–C(69)–C(70) | 114.34(185) |
| Ag(5)–Pt(3)–C(49) | 76.42(62) | C(56)–C(57)–C(58) | 107.20(203) | Ag(6)–C(50)–C(49) | 67.31(144) | C(71)–C(69)–C(72) | 108.68(216) |
| Ag(5)–Pt(3)–Ag(6) | 61.43(15) | C(59)–C(57)–C(60) | 108.60(223) | C(49)–C(50)–C(51) | 167.16(262) | C(70)–C(69)–C(72) | 109.55(231) |
| Pt(3)–Ag(5)–C(56) | 67.92(58) | C(58)–C(57)–C(60) | 109.25(240) | Ag(6)–C(50)–C(51) | 124.30(172) | C(70)–C(69)–C(71) | 109.15(213) |
| Pt(3)–Ag(5)–C(55) | 38.31(54) | C(58)–C(57)–C(59) | 109.09(230) | C(50)–C(51)–C(54) | 113.22(211) | | |

the presence of $H_2O$.[26] All the polynuclear derivatives (**1**)—(**5**) show a strong absorption at 2 000—2 050 $cm^{-1}$ (Table 1) due to ν(C≡C) of the acetylide group. These absorptions are shifted to lower wavelengths than is observed for $[Pt(C{\equiv}CR)_4]^{2-}$ as expected for bridging acetylide (μ—$\eta^2$) complexes.[7,22]

*Proton N.M.R. Spectra.*—t-Butylacetylide complexes (**2**), (**4**),

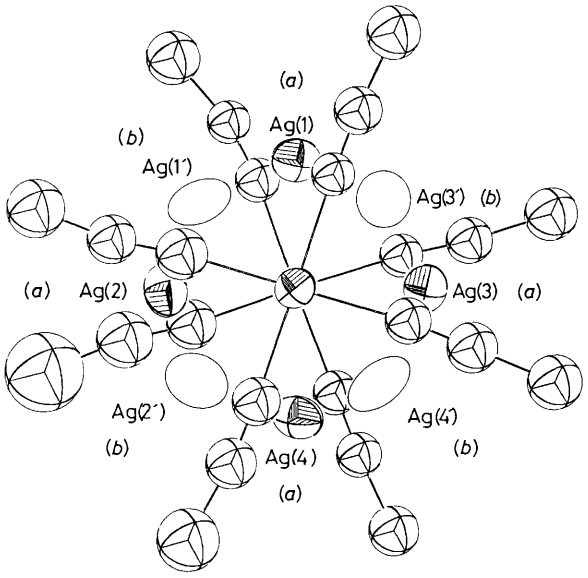



**Figure 3.** Perspective view of $[Pt_2Ag_4(C{\equiv}CBu^t)_8]$, molecule A, showing holes type (*a*) (Ag) and type (*b*) (Ag'). Terminal C atoms of the $Bu^tC{\equiv}C$ ligands have been omitted for clarity

(**5**), and (**7**) show a singlet due to $CH_3$ groups of the $Bu^t$[(**2**), δ 1.31; (**4**), 1.32; (**5**), 1.30 and (**7**), 1.14].

Complex (**7**) crystallizes with two molecules of $H_2O$ per Pt atom, which are observed as a singlet at δ 4.07; this assignment was confirmed by adding one drop of $D_2O$ to the $CDCl_3$ n.m.r. solution, whereupon exchange by deuterium took place, with the singlet decreasing in intensity, broadening, and shifting to δ 3.75.

Phenylacetylide complexes show a lower solubility and the n.m.r. spectrum of only the mononuclear complex $[NBu_4]_2[Pt(C{\equiv}CPh)_4]$ could be recorded, displaying signals due to the aromatic protons in the range δ 6.8—7.3 (5 H) in addition to the $[NBu_4]^+$ signals.

All anionic complexes showed signals of $NBu_4^+$ cation at δ 0.99 (t, $CH_3$), 1.58 (m, $CH_2$–$CH_2$), and 3.64 (m, N–$CH_2$).

## Experimental

Carbon, H, and N analyses were carried out with a Perkin-Elmer 240-B microanalyser. I.r. spectra were recorded on a Perkin-Elmer 830 spectrophotometer using Nujol mulls between polyethylene plates, $^1H$ n.m.r. spectra on a Varian X.L.-200 instrument (200 MHz for $^1H$). Molecular weights were determined in $CHCl_3$ solution with a Knauer apparatus (isopiestic method). Conductivities were measured for *ca.* $5 \times 10^{-4}$ mol $dm^{-3}$ acetone solutions with a Philips PW 9501/01 conductimeter. Silver acetylides were prepared by standard methods.[27]

Some of the following preparations use as reacting species acetylides and $AgClO_4$ which are potentially explosive. For this reason only small amounts of material have been prepared and in no cases were there any problems related to the stability of the reactants and products.

$[Pt_2Ag_4(C{\equiv}CPh)_8]$ (**1**).—(*a*) To a yellow solution of $[PtCl_2(tht)_2]$[28] (0.5125 g, 1.158 mmol) in $CH_2Cl_2$ (90 $cm^3$) was added $[Ag(C{\equiv}CPh)]$[27] (0.996 86 g, 4.63 mmol) (molar ratio Pt:Ag 1:4) and the mixture, with light excluded, was refluxed for 7 h. The AgCl was filtered off and the resulting yellow solution was evaporated to 15 $cm^3$. By adding acetone (40 $cm^3$) a yellow precipitate (**1**) (0.62 g, 76% yield) was obtained.

(*b*) The addition of $AgClO_4$ (0.0353 g, 0.170 mmol) to an acetone (30 $cm^3$) solution of $[NBu_4]_2[Pt(C{\equiv}CPh)_4]$ (0.0925 g, 0.0852 mmol) at room temperature caused the precipitation of a yellow solid. The suspension was stirred for 1 h and then the yellow solid was filtered off and washed with acetone, (**1**) (0.06 g, 90%).

$[Pt_2Ag_4(C{\equiv}CBu^t)_8]$ (**2**).—(*a*) To a yellow solution of $[PtCl_2(tht)_2]$ (0.2073 g, 0.469 mmol) in acetone (30 $cm^3$), was added $[Ag(C{\equiv}CBu^t)]_n$ (0.3544 g, 1.875 mmol) (Pt:Ag ratio 1:4), and the mixture, protected from the light, was stirred at room temperature for 72 h. After filtration of the AgCl, the resulting yellow solution was evaporated (*ca.* 1 $cm^3$) and the yellow crystalline precipitate (**2**) was filtered off and washed with acetone (5 $cm^3$) at −30 °C. Evaporation of the mother-liquor rendered additional complex (**2**) (0.22 g, 65%).

(*b*) The salt $[NBu_4]_2[Pt(C{\equiv}CBu^t)_4]{\cdot}2H_2O$ (0.1454 g, 0.1397 mmol) was added to a colourless solution of $AgClO_4$ (0.0579 g, 0.2794 mmol) in diethyl ether (50 $cm^3$). The mixture, protected from the light, was stirred for 4 h. The white precipitate ($NBu_4ClO_4$) was filtered off and the resulting solution was evaporated to dryness. The resulting yellow solid was washed with acetone (*ca.* 1 $cm^3$) at −30 °C, yielding complex (**2**) (0.036, 35%).

$[Pt_2Cu_4(C{\equiv}CPh)_8]$ (**3**).—(*a*) To a yellow solution of $[Pt_2Ag_4(C{\equiv}CPh)_8]$ in chloroform (60 $cm^3$) was added CuCl (0.0364 g, 0.3676 mmol). The mixture was refluxed for 4 h and then filtered to remove the AgCl. The resulting solution was partially evaporated (*ca.* 20 $cm^3$) and the addition of acetone (30 $cm^3$) rendered dark garnet crystals of complex (**3**) (0.077 g, 58%).

(*b*) To a suspension of $NaClO_4$ (0.0452 g, 0.3688 mmol) and CuCl (0.0366 g, 0.3688 mmol) in acetone (30 $cm^3$) was added $[NBu_4]_2[Pt(C{\equiv}CPh)_4]$ (0.2 g, 0.1844 mmol) and the mixture was stirred, at room temperature, for 6 h. The resulting garnet suspension was evaporated to dryness and the solid was extracted with $CH_2Cl_2$ (50 $cm^3$). Evaporation of the $CH_2Cl_2$ solution to a small volume (*ca.* 1 $cm^3$) and addition of acetone (30 $cm^3$) gave complex (**3**) (0.08 g, 62%).

$[Pt_2Cu_4(C{\equiv}CBu^t)_8]$ (**4**).—(*a*) A solution of $[Pt_2Ag_4(C{\equiv}CBu^t)_8]$ (0.1756 g, 0.119 mmol) in acetone (60 $cm^3$) was stirred with CuCl (0.0584 g, 0.59 mmol) for 8 d at room temperature and finally was refluxed for 10 h. The white-yellow precipitate (AgCl) was filtered off and the filtrate was evaporated to a small volume (*ca.* 2 $cm^3$) to give yellow crystals of complex (**4**) (0.054 g, 35%).

(*b*) To a solution of $NaClO_4$ (0.0471 g, 0.3844 mmol) in acetone (30 $cm^3$) were added CuCl (0.038 g, 0.3844 mmol) and $[NBu_4]_2[Pt(C{\equiv}CBu^t)_4]{\cdot}2H_2O$ (0.2 g, 0.1922 mmol), the mixture stirred at room temperature for 5 h and then evaporated to dryness. The residue was extracted with diethyl ether (30 $cm^3$) and the resulting solution was evaporated to dryness. By treating the residue with acetone (*ca.* 2 $cm^3$) and cooling at −30 °C, yellow crystals of (**4**) were obtained (0.047 g, 38%).

$[Pt_2Au_4(C{\equiv}CBu^t)_8]$ (**5**).—(*a*) Complex (**5**) was obtained in a similar way to that described for (**4**) [method (*a*)] by using $[AuCl(tht)]$[10] (0.1183 g, 0.369 mmol), $[Pt_2Ag_4(C{\equiv}CBu^t)_8]$ (0.135 g, 0.091 mmol) and acetone (30 $cm^3$). A shorter reaction time (2 h) was used. Yield of complex (**5**) 0.088 g (53%).

(*b*) To an acetone solution (25 $cm^3$) of $NaClO_4$ (0.0471 g, 0.3844 mmol) were added [AuCl(tht)] (0.123 23 g, 0.3844 mmol) and $[NBu_4]_2[Pt(C{\equiv}CBu^t)_4]{\cdot}2H_2O$ (0.2 g, 0.1922 mmol) and the mixture was refluxed for 45 min and then evaporated to dryness. The residue was extracted with $CH_2Cl_2$ (50 $cm^3$) and the resulting solution was treated with $MgSO_4$. After filtration the yellow solution was evaporated to dryness, and the residue was treated with diethyl ether (30 $cm^3$) in which $NBu_4ClO_4$ is

insoluble. The resulting solution was evaporated to dryness and treatment of the residue with acetone (1 $cm^3$) gave complex (**5**) (0.06 g, 75%).

$[NBu_4]_2[Pt(C{\equiv}CR)_4]$[R = Ph (**6**), Bu$^t$ (**7**)].—R = Ph. 2.46 mol $dm^{-3}$ n-Butyl-lithium (3.68 $cm^3$, 9.043 mmol) in n-hexane was added to a solution of HC≡CPh (0.92 g, 9.043 mmol) in dry diethyl ether (−10 °C). The mixture was stirred at −10 °C for 15 min and then $[PtCl_2(tht)_2]$ (0.5 g, 1.13 mmol) (8:1) was added. The mixture was stirred, under $N_2$, at 0 °C for 10 min and the resulting solution was evaporated to dryness and the residue treated, under $N_2$, with deoxygenated water. The resulting colourless solution was added dropwise to $NBu_4Br$ (0.911 g, 2.26 mmol) in isopropyl alcohol (1 $cm^3$), resulting in the formation of a pale yellow solid, which was dried over $P_2O_5$ under vacuum (1.1 g, 90%) (Found: C, 70.85; H, 8.25; N, 2.80. $C_{64}H_{92}N_2Pt$ requires C,70.90; H, 8.55; N, 2.60%).

The salt $[NBu_4]_2[Pt(C{\equiv}CBu^t)_4]{\cdot}2H_2O$ (**7**) was prepared by using a similar procedure to that described for (**6**). The following starting materials were used: LiBu (12.41 mmol); HC≡CBu$^t$ (1.02 g, 12.41 mmol); $PtCl_2$(0.6 g, 2.25 mmol) (5.5:1); $NBu_4Br$ (1.45 g, 45 mmol). The reaction between LiC≡CBu$^t$ and $PtCl_2$ was accomplished in 4 h (1.575 g, 67% yield) (Found: C, 64.70, H, 11.65; N, 2.60. $C_{56}H_{112}N_2O_2Pt$ requires C, 64.65; H, 10.80; N, 2.70%).

*X-Ray Structure Determination of Complex* (**2**).—*Crystal data.* $C_{48}H_{72}AgPt_2$, $M$ = 1 470.74, monoclinic, $a$ = 37.062(7), $b$ = 12.022 3(16), $c$ = 20.459(3) Å, β = 107.485(15)°, $U$ = 8 694.38 Å$^3$ (by least-squares refinement of diffractometer angles for 25 automatically centred reflections), Mo-$K_\alpha$ radiation (λ = 0.710 69 Å), space group $C_2$ (no. 5), $Z$ = 6, $D_c$ = 1.6848 g $cm^{-3}$, $F(000)$ = 4 223.44. Pale yellow plates, crystal dimensions 0.08 × 3 × 0.25 mm; μ(Mo-$K_\alpha$) = 63.48 $cm^{-1}$, $T$ = 273 K.

*Data collection and processing.* Enraf-Nonius CAD4 diffractometer, monochromated Mo-$K_\alpha$ radiation, 7 320 data measured (2θ max. 48°), 5 613 with $F > 6\sigma(F)$ used for all calculations. Empirical absorption correction was applied.[29] The programs SHELX 76[30] and SHELXS 86[31] were used for the crystallographic work; geometrical calculations were carried out using PARST.[32]

*Structure analysis and refinement.* Systematic absences were consistent with space groups $C_2$, $C_m$, or $C_{2/m}$. Statistics were fully consistent with a non-centrosymmetric lattice and no Harker lines corresponding to the plane $m$ (0, 2$y$, 0) could be found in the Patterson map. The structure was solved by direct methods and satisfactorily refined in the $C_2$ group. All heavy atoms anisotropic and all carbon atoms isotropic. The Bu$^t$ functions were refined as rigid groups. Thermal parameters of terminal C atoms, $U_{iso}$ (molecules A and B), were in the range 0.169(5)—0.183(5) Å$^2$. In the last stages of refinement four peaks (electronic density between 1.99 and 2.28 e Å$^{-3}$) appeared in the zone of molecule A. Since these peaks were located at distances greater than 1.5 Å from any atom and they have a similar environment to the silver atoms of the molecule, the possibility of disorder for the silver atoms was considered. Refinement of the occupation factor for silver atoms converged to 0.9159 (Ag) and 0.0841 (Ag′). The $R$ and $R'$ factors decreased from 0.0479, 0.0542 to 0.0416, 0.0465 respectively. The residual density was 0.81 e Å$^{-3}$. A weighting scheme $w^{-1} = 1/[\sigma^2(F) + 0.004\,336\,F^2]$ was applied. Largest parameter shift/estimated standard deviation (e.s.d.) in the final cycle 0.704. The enantiomorph was chosen on the basis of a lower $R$ factor.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters.

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