85% phosphoric acid; $^1$H and $^{13}$C, internal tetramethylsilane. The high-frequency-positive convention, recommended by IUPAC, has been used in reporting all chemical shifts. Line shape analyses of $^{31}$P NMR spectra were performed with an iterative analysis program, DNMR5,[12,13] on a VAX/VMS computer. Infrared spectra (resolution 2 cm$^{-1}$) were recorded from mineral oil mulls or dichloromethane solutions with a Perkin-Elmer 180 spectrometer. Electronic spectra were recorded on a Hewlett-Packard 8450A.

**X-ray Data Collection, Solution, and Refinement for $[Rh_2Pd(CO)_2(\mu\text{-}Cl)Cl_2(\mu\text{-}dpma)_2][BPh_4]\cdot 2CH_2Cl_2\cdot(C_2H_5)_2O$.** Well-formed red parallelepipeds were grown by slow diffusion of diethyl ether into a dichloromethane solution of the complex. The crystals were rapidly taken from the diffusion tube and covered with epoxy resin to reduce loss of solvent from the crystal. Crystal data, data collection procedures, and refinement of the structure are summarized in Table VI. The lattice was found to be monoclinic by standard procedures using the software associated with the Syntex $P2_1$ diffractometer. The data were corrected for Lorentz and polarization effects.

The structure was solved by locating the two rhodium and palladium atoms by using the Patterson method (FMAP 8 routine of SHELXTL, version 4, 1984, Nicolet Instrument Corp., Madison, WI). Other atoms were located from successive difference Fourier maps. Final cycles of refinement were made with anisotropic thermal parameters for iridium, rhodium, arsenic, phosphorus, and the five chlorine atoms, and isotropic thermal parameters for all remaining atoms. Hydrogen atoms were refined by using a riding model in which an idealized C-H vector of 0.96-Å length is recalculated with each cycle of refinement. Isotropic hydrogen thermal parameters were fixed at 1.2 times the equivalent isotropic thermal parameter of the bonded carbon. Scattering factors and corrections for anomalous dispersion were taken from a standard source.[14] An absorption correction (XABS) was applied.[15] One molecule of dichloromethane and the ether molecule exhibited large thermal motion. Ten reflections suffering from extinction were removed from the data set for the final cycles of refinement. A conventional $R$ factor of 0.071 was obtained. The final difference map showed some residual electron density (3.7 e Å$^{-3}$), which may be part of a disordered dichloromethane since it is approximately 3 Å from a symmetry-related site. The next four are all in the vicinity of the less well-behaved of the two dichloromethane molecules.

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**Registry No.** **1**, 97551-38-7; **2**, 97570-01-9; **5**, 97551-42-3; **5**·$2CH_2Cl_2\cdot(C_2H_5)_2O$, 97551-43-4; **6**, 108818-13-9; **7**, 108818-15-1; **8**, 108818-17-3; **9**, 97551-40-1; $PdCl_2(NCPh)_2$, 14220-64-5; Pd, 7440-05-3; Rh, 7440-16-6.

**Supplementary Material Available:** Listings of anisotropic thermal parameters, hydrogen atom positions, phenyl carbon and boron positions, and bond distances and bond angles and a figure of extensive $^{31}$P NMR data (12 pages); calculated and observed structure factor tables (65 pages). Ordering information is given on any current masthead page.

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# Synthesis and Structure of $Pt_2Au$ Cluster Complexes, Including $[Pt_2(C{\equiv}C\text{-}t\text{-}Bu)_2(\mu\text{-}AuI)(\mu\text{-}Ph_2PCH_2PPh_2)_2]$

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*Received October 7, 1986*

Reaction of $[Pt_2(\mu\text{-dppm})_3]$ (dppm = $Ph_2PCH_2PPh_2$) with AuCC-*t*-Bu gave the complex $[Pt_2(CC\text{-}t\text{-}Bu)_2(\mu\text{-}AuX)(\mu\text{-dppm})_2]$ (**1a** (X = CC-*t*-Bu)), and this could be converted to the derivatives **1b** (X = Cl) and **1c** (X = I). The compounds are the first $Pt_2Au$ clusters. The compound **1c**, fully characterized by X-ray diffraction, is a distorted molecular A-frame containing a 42-electron triangular $Pt_2Au$ cluster with 3-center 2-electron metal-metal bonding [Pt-Au = 2.656 (2), 2.661 (2) Å and Pt-Pt = 2.837 (1) Å]. The crystals of **1c** are orthorhombic, space group $Pna2_1$ (No. 33), with $Z = 4$, $a = 29.053$ (4) Å, $b = 16.131$ (3) Å, and $c = 13.956$ (3) Å; $R = 0.040$ for 225 parameters refined from 4442 unique reflections with $I \geqslant 3\sigma(I)$.

## Introduction

There has been much interest in the heteronuclear cluster complexes containing both a platinum-group metal and a coinage metal, and a number of synthetic routes to such compounds have been developed.[2-9] Most compounds containing Pt-Au bonds have been prepared by reactions of $Ph_3PAu^+$ with a platinum hydride[10] or an electron-rich cluster of platinum[11] and are based on the isolobal relationship for $H^+$ and $Ph_3PAu^+$.[12]

In this paper, the synthesis of the first $Pt_2Au$ cluster complexes is reported, based on the reactions of AuCC-*t*-Bu. The latter

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**Table I.** Selected Parameters of the Molecular Structure of [Pt$_2$(C≡C-*t*-Bu)$_2$($\mu$-AuI)($\mu$-dppm)$_2$] (**1c**)

| | | | |
|---|---|---|---|
| | Bond Lengths (Å) | | |
| Au–Pt(1) | 2.656 (2) | Pt(1)–P(3) | 2.279 (5) |
| Au–Pt(2) | 2.661 (2) | Pt(2)–P(2) | 2.274 (5) |
| Pt(1)–Pt(2) | 2.837 (1) | Pt(2)–P(4) | 2.289 (6) |
| Au–I | 2.580 (2) | C(3)–C(4) | 1.14 (3) |
| Pt(1)–C(3) | 2.01 (3) | C(9)–C(10) | 1.10 (3) |
| Pt(2)–C(9) | 2.02 (3) | C(4)–C(5) | 1.59 (5) |
| Pt(1)–P(1) | 2.283 (6) | C(10)–C(11) | 1.54 (3) |
| | Bond Angles (deg) | | |
| I–Au–Pt(1) | 147.5 (2) | C(9)–Pt(2)–P(2) | 85.3 (6) |
| I–Au–Pt(2) | 148.0 (2) | C(9)–Pt(2)–P(4) | 92.3 (6) |
| Pt(1)–Au–Pt(2) | 64.5 (1) | P(2)–Pt(2)–Pt(1) | 86.8 (2) |
| Au–Pt(1)–Pt(2) | 57.8 (1) | P(4)–Pt(2)–Pt(1) | 95.5 (2) |
| Au–Pt(2)–Pt(1) | 57.7 (1) | C(9)–Pt(2)–Pt(1) | 150.0 (7) |
| Au–Pt(1)–C(3) | 151.0 (7) | P(2)–Pt(2)–P(4) | 177.6 (3) |
| Au–Pt(1)–P(1) | 88.8 (2) | Pt(1)–P(1)–C(1) | 110.4 (7) |
| Au–Pt(1)–P(3) | 94.5 (2) | Pt(2)–P(2)–C(1) | 114.3 (7) |
| C(3)–Pt(1)–P(1) | 90.2 (7) | Pt(1)–P(3)–C(2) | 115.4 (6) |
| C(3)–Pt(1)–P(3) | 86.1 (6) | Pt(2)–P(4)–C(2) | 113.1 (7) |
| P(1)–Pt(1)–Pt(2) | 95.6 (2) | P(1)–C(1)–P(2) | 111 (1) |
| P(3)–Pt(1)–Pt(2) | 87.5 (2) | P(3)–C(2)–P(4) | 108 (1) |
| C(3)–Pt(1)–Pt(2) | 150.9 (7) | Pt(1)–C(3)–C(4) | 172 (2) |
| P(1)–Pt(1)–P(3) | 176.3 (3) | C(3)–C(4)–C(5) | 176 (3) |
| Au–Pt(2)–C(9) | 151.7 (6) | Pt(2)–C(9)–C(10) | 177 (2) |
| Au–Pt(2)–P(2) | 93.3 (2) | C(9)–C(10)–C(11) | 175 (3) |
| Au–Pt(2)–P(4) | 88.4 (2) | | |
| | Torsion Angles (deg) | | |
| P(1)–Pt(1)–Pt(2)–P(2) | −11.0 (2) | P(3)–Pt(1)–Pt(2)–P(4) | −1294 (2) |
| Pt(2)–Pt(1)–P(1)–C(1) | −13.2 (7) | Pt(1)–Pt(2)–P(4)–C(2) | −11.4 (7) |
| Pt(1)–P(1)–C(1)–P(2) | 40.7 (8) | Pt(2)–P(4)–C(2)–P(3) | 37.0 (7) |
| Pt(2)–P(2)–C(1)–P(1) | −55.1 (9) | Pt(1)–P(3)–C(2)–P(4) | −52.2 (8) |
| Pt(1)–Pt(2)–P(2)–C(1) | 36.3 (8) | Pt(2)–Pt(1)–P(3)–C(2) | 36.8 (7) |

complex is probably a tetramer, though its structure has not been determined.[13] The mononuclear fragment AuCC-*t*-Bu is neutral, is isolobal with H$^+$, and contains a robust Au–C bond. We therefore supposed that it might form neutral gold–metal clusters by reaction with electron-rich metal complexes, rather than the more common cationic complexes formed by reactions of Ph$_3$PAu$^+$. Contrary to this prediction, the reaction of AuCC-*t*-Bu with [Pt(PPh$_3$)$_3$] gave[14] the cationic cluster [Pt(PPh$_3$)(CC-*t*-Bu)(AuPPh$_3$)$_6$]$^+$, but it has now been shown that a neutral cluster [Pt$_2$(C≡C-*t*Bu)$_2$($\mu$-dppm)$_2$($\mu$-AuCC-*t*-Bu)] is formed by reaction with [Pt$_2$($\mu$-dppm)$_3$] (dppm = Ph$_2$PCH$_2$PPh$_2$).[15]

## Results and Discussion

Reaction of [Pt$_2$($\mu$-dppm)$_3$] with 4 equiv of AuCC-*t*-Bu in toluene gave a deep red solution, and evaporation of the solvent gave a deep red oil. Crystallization from acetone–pentane gave yellow crystals of the new cluster complex [Pt$_2$(C≡C-*t*Bu)$_2$($\mu$-AuCC-*t*-Bu)($\mu$-dppm)$_2$] (**1a**) in good yield. The mother liquor from this crystallization yielded a red oil, which could not be characterized. From the stoichiometry, the components Au$_3$(C≡C-*t*-Bu)(dppm) are unaccounted for, but from the complexity of the NMR spectra of this oil, it seems likely that a mixture of gold clusters is formed. No metallic gold was precipitated in the reaction. The required stoichiometry was determined by trial and error. Reaction of [Pt$_2$($\mu$-dppm)$_3$] with only 2 equiv of [AuCC-*t*-Bu] gave **1a** and 50% unreacted [Pt$_2$($\mu$-dppm)$_3$], as determined by $^{31}$P NMR spectroscopy of the reaction mixture, whereas with 4 equiv of [AuCC-*t*-Bu] all of the [Pt$_2$($\mu$-dppm)$_3$] was consumed.

Complex **1a** is an air-stable solid, but it reacted slowly with chlorinated solvents to give [Pt$_2$(C≡C-*t*-Bu)$_2$($\mu$-AuCl)($\mu$-dppm)$_2$] (**1b**). The gold–acetylide bond was cleaved to give the AuCl unit of **1b**, but the platinum–acetylide bonds were stable to these conditions. This reaction was complete in ~2 days in CDCl$_3$ solution as monitored by $^{31}$P NMR spectroscopy but took ~2 weeks to reach completion in CH$_2$Cl$_2$ solution. Reaction of **1b** with sodium iodide gave the cluster [Pt$_2$(C≡C-*t*-Bu)$_2$($\mu$-AuI)($\mu$-dppm)$_2$] (**1c**) by displacement of chloride.

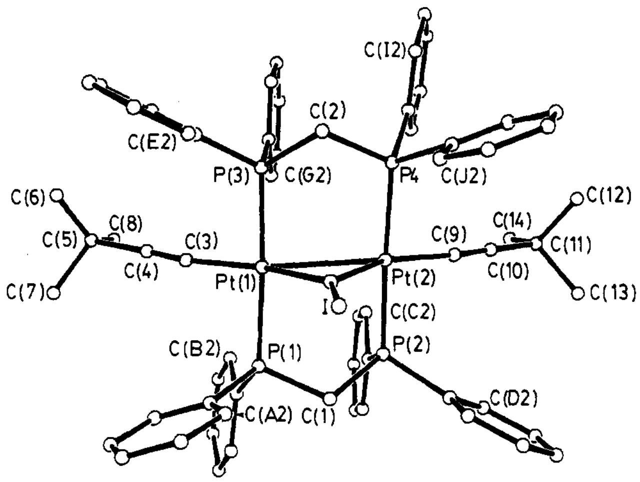

**Figure 1.** View of the molecular structure of [Pt$_2$(C≡C-*t*-Bu)$_2$($\mu$-AuI)($\mu$-dppm)$_2$] (**1c**), with atoms represented by spheres of arbitrary size. In the phenyl rings carbon atoms are numbered cyclically, C(n1)...C(n6), with C(n1) bonded to phosphorus and n = A, B, C, D, E, G, I, or J. Only the C(n2) atoms are labeled, for clarity.

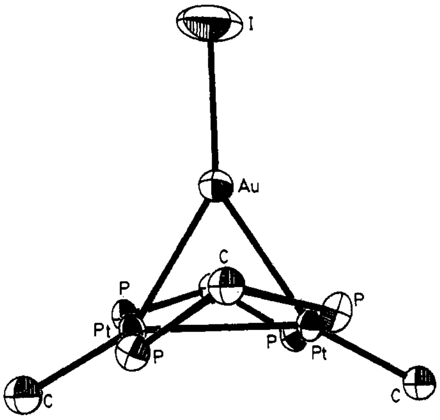

**Figure 2.** View of the molecular core of [Pt$_2$(C≡C-*t*-Bu)$_2$($\mu$-AuI)($\mu$-dppm)$_2$] (**1c**), with atomic vibrational ellipsoids displayed at 40% probability level.

**Table II.** Crystal Data for [Pt$_2$(C≡C-*t*-Bu)$_2$($\mu$-AuI)($\mu$-dppm)$_2$] (**1c**)

| | |
|---|---|
| formula | $C_{62}H_{62}AuIP_4Pt_2$ |
| fw | 1645.12 |
| space group | *Pna*2$_1$ (No. 33) |
| unit-cell params | |
| *a*, Å | 29.053 (4) |
| *b*, Å | 16.131 (3) |
| *c*, Å | 13.956 (3) |
| *V*, Å$^3$ | 6540.5 |
| *Z* | 4 |
| *F*(000) | 3128 |
| $\rho_{calcd}$, g cm$^{-3}$ | 1.671 |
| radiation | graphite monochromated; Mo K$\alpha$, $\lambda$ = 0.71069 Å |
| linear abs coeff, cm$^{-1}$ | 71.4 |

The new complexes **1a–c** were characterized by elemental analysis, by $^1$H and $^{31}$P NMR spectroscopy, and, for **1c**, by an X-ray structure determination.

**Structure of Complex 1c.** The molecular structure of **1c** is shown in Figure 1 and is characterized by the bond lengths and angles listed in Table I. It comprises two Pt(C≡C-*t*-Bu) groups spanned by two mutually trans dppm ligands and bridged symmetrically by an AuI fragment, to form a highly distorted molecular A-frame.[16] The distortions from the idealized A-frame

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geometry are similar to those reported for the $d^7$–$d^7$ species $[Rh_2Cl_2(\mu\text{-}SO_2)(\mu\text{-dppm})_2]$, in which the metal atoms form a Rh–Rh bond of 2.78 Å.[17] The Au–Pt–C angles are substantially decreased from 180° [151.0 (7) and 151.7 (6)°] and the Pt–Pt separation [2.837 (1) Å] is compatible with metal–metal bonding. Thus, both platinum atoms lie in locally highly distorted trigonal-bipyrimidal environments. An alternative view of the molecular structure of **1c** is to consider it as a heterometallic triangular cluster, in which each metal atom is coordinated by a monodentate ligand and an edge is spanned by two trans dppm ligands (Figure 2). The $IC_2$ donor set is roughly coplanar with the metal cluster, the C atoms being displaced by 0.10 (2) and –0.16 (2) Å from the $Pt_2Au$ plane.

The molecular geometry of **1c** approximates to $C_{2v}$ symmetry, with a mirror plane passing through the atoms Au, I, C(1), and C(2). The main distortion from idealized $C_{2v}$ symmetry arises from the twist of the T-shaped $PtP_2C$ fragments about the Pt–Pt bond, resulting in dihedral angles with the $Pt_2Au$ plane of 97.2 and 82.9° (Figure 2). The five-membered $Pt_2P_2C$ dimetallacycles display torsion angles (Table I) comparable with those in the half-chair form ($C_2$) of cyclopentane.[18] With respect to the $Pt_2P_4$ moiety, each methylene group is in a cisoid orientation with the AuI fragment. Such a configuration of the molecular core, usually found in dppm A-frame complexes, is thought to reflect the steric requirements of the phosphine substituents,[19] directing the axial phenyl groups (rings B, C, G, and I) away from the AuI fragment at the apex of the "A".

The $\eta^1$-acetylide ligands are essentially linear (Table I), and the C(3)–C(4) and C(9)–C(10) distances [1.14 (3) and 1.10 (3) Å] are consistent with retention of carbon–carbon triple bonds. The Pt–C distances [2.01 (3) and 2.02 (3) Å] are indicative of $\sigma$ covalent bonding, and the Pt–P distances [2.274 (5)–2.289 (6) Å] are comparable with those usually observed in the complexes containing *trans*-$Pt_2(\mu\text{-dppm})_2$ nuclei.[19-22] The Au–I distance [2.580 (2) Å] is slightly shorter than those in *trans*-$[AuI_2((p\text{-}MeC_6H_4NH)_2C)_2]^+$, where the formal oxidation state of the gold atom is higher than in **1c** and the iodine atoms are trans to one another [2.601 (2) and 2.606 (2) Å].[23]

In the *isosceles* $Pt_2Au$ triangle all three angles are close to 60° (Table I) and both Pt–Au [2.652 (2) and 2.661 (2) Å] and Pt–Pt [2.837 (1) Å] distances are within ranges considered typical of bonding interactions (2.60–3.03[2,11] and 2.53–2.89 Å,[11,20,24] respectively). In **1c** such interactions can be ascribed to 3-center 2-electron bonding formed by overlap of the $3a_1$ orbital[25] of the $[Pt_2(C{\equiv}C\text{-}t\text{-}Bu)_2(\mu\text{-dppm})_2]$ dimer and the $a_1$ orbital of the AuI fragment. Thus, the platinum atoms formally attain 16-electron configurations and the gold atom attains a 14-electron configuration. The cationic A-frame $[Pt_2Me_2(\mu\text{-}H)(\mu\text{-dppm})_2]^+$, in which the apex bridging ligand $H^+$ is isolobal with AuX, is thought to contain a 3-center 2-electron $Pt_2(\mu\text{-}H)^+$ group, although the Pt–Pt distance is even longer than in **1c** [2.932 (1) Å].[22,25]

**Table III.** $^{31}P\{^1H\}$ NMR Spectra of Complexes **1a–c**

| complex | $\delta(^{31}P)$ | $^1J(PtP)$, Hz | $^3J(PtP)$, Hz | $^2J(P^AP^{A''})$, Hz | $^4J(P^AP^{A'''})$, Hz |
|---|---|---|---|---|---|
| **1a**[a] | 6.31[b] | 2556 | –45 | 69 | 25 |
| **1b**[c] | 7.06 | 2480 | –24 | 60 | 30 |
| **1c**[c] | 6.50 | 2509 | –23 | 64 | 25 |

[a] Solvent $C_6D_6$. [b] $\delta$ = 5.72 in $CD_2Cl_2$. [c] Solvent $CD_2Cl_2$.

**Table IV.** $^1H$ NMR Spectra of Complexes **1a–c**[a]

| complex | $\delta(CH^a)$ | $\delta(CH^b)$ | $^2J(H^aH^b)$, Hz | $^3J(PtH^a)$, Hz | $\delta(t\text{-Bu})$ |
|---|---|---|---|---|---|
| **1a** | 5.74[b] | 4.73[c] | 14 | 99 | 0.54[d]<br>1.23[e] |
| **1b** | 5.14[f] | 4.54[g] | 13 | 90 | 0.58 |
| **1c** | 5.49[h] | 4.62[i] | 14 | 96 | 0.58 |

[a] Solvent $CD_2Cl_2$. [b] $^2J(PH) + {}^4J(PH)$ = 2 Hz. [c] $^2J(PH) + {}^4J(PH)$ = 6 Hz. [d] *t*-BuCCPt. [e] *t*-BuCCAu. [f] $^2J(PH) + {}^4J(PH)$ = 2 Hz. [g] $^2J(PH) + {}^4J(PH)$ = 6 Hz. [h] $^2J(PH) + {}^4J(PH)$ = 2 Hz. [i] $^2J(PH) + {}^4J(PH)$ = 6 Hz.

The electron-deficient $Pt_2Au$ cluster distinguishes **1c** from the essentially undistorted $d^8$–$d^8$ A-frames $[Pt_2XX'(\mu\text{-}CH_2)(\mu\text{-dppm})_2]^n$ (X = X′ = Cl, *n* = 0; X = Cl, X′ = $CH_2PPh_3$, *n* = 1+) in which the coordination geometry of the metal centers is square planar and the Cl–Pt–C($\mu$-methylene) angles are close to 180°.[19] In these complexes metal–metal bonding is not required for a 16-electron count of the platinum atoms nor indicated either by the Pt–Pt distances [3.151 (1) and 3.120 (2) Å][19] or by theoretical considerations based on extended Hückel molecular orbital calculations.[25] In the recently reported homonuclear trimetallic A-frame $[Pt_2(CNR)_2(\mu\text{-}Pt(CNR)_2)(\mu\text{-dppm})_2]^{2+}$ (R = 2,6-$Me_2C_6H_3$), where the bridging apex is occupied by a 14-electron $ML_2$ fragment isolobal with $CH_2$, the platinum atoms of the *trans*-$Pt_2(\mu\text{-dppm})_2$ nucleus are also at a distance that is considered too long to permit metal–metal bond formation [Pt–Pt = 3.304 (2) Å].[26]

**Characterization by NMR.** The NMR spectra are typical of A-frame complexes of platinum, as analyzed elsewhere[19-22,27,28] and so are discussed only briefly. Data are given in Tables III and IV.

It has been suggested previously that the long-range coupling constant $^2J(PtP)$ gives a correlation with the Pt–Pt distance in binuclear complexes with the *trans*-$[Pt_2(\mu\text{-dppm})_2]$ skeleton;[27,28] more negative values indicate a stronger Pt–Pt interaction. The values of –23 to –45 Hz for this coupling in **1a–c** suggest a significant bonding interaction between the platinum atoms. For comparison, $[Pt_2Me_2(\mu\text{-}H)(\mu\text{-dppm})_2]^+$ has *r*(PtPt) = 2.932 (1) Å and $^2J(PtP)$ = +24 Hz while $[Pt_2Cl_2(\mu\text{-dppm})_2]$ has *r*(PtPt) = 2.651 (1) Å and $^2J(PtP)$ = –136 Hz. The values of $^2J(PtP)$ for **1a–c** are in reasonable agreement with the value of *r*(PtPt) = 2.837 (1) Å found crystallographically for **1c**.

In the $^1H$ NMR spectra of **1a–c** the methylene resonance appeared as an "AB" multiplet, showing that there is no plane of symmetry containing the $Pt_2P_4C_2$ skeleton. This is, of course, due to the presence of the $\mu$-AuX group. The complexes do not undergo the A-frame inversion, which is observed for the analogous $\mu$-H complexes.[29] The $\mu$-H complexes undergo A-frame inversion in a one-step mechanism, with a linear Pt–H–Pt transition state, and this is obviously not possible for the $\mu$-AuX derivatives **1a–c**. Complex **1a** gave two resonances in a 2:1 ratio for the *t*-BuCCPt and *t*-BuCCAu groups, respectively. On reaction with the

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**Table V.** Atomic Fractional Coordinates and Displacement Parameters for $[Pt_2(C{\equiv}C\text{-}t\text{-}Bu)_2(\mu\text{-}AuI)(\mu\text{-dppm})_2]$ (**1c**)

| atom | *x* | *y* | *z* | $U$,[a] Å$^2$ | atom | *x* | *y* | *z* | $U$,[a] Å$^2$ |
|---|---|---|---|---|---|---|---|---|---|
| Au | −0.25895 (2) | −0.08035 (5) | −0.34304 (10) | 0.038 | C(C2) | −0.0788 (5) | −0.2063 (12) | −0.3740 (19) | 0.044 (6) |
| Pt(1) | −0.18162 (3) | −0.04520 (4) | −0.25000 | 0.028 | C(C3) | −0.0330 (5) | −0.2247 (7) | −0.3588 (8) | 0.077 (8) |
| Pt(2) | −0.18150 (3) | −0.11075 (4) | −0.43867 (6) | 0.029 | C(C4) | −0.0209 (4) | −0.2969 (13) | −0.3122 (17) | 0.079 (8) |
| I | −0.34774 (5) | −0.08312 (19) | −0.34077 (33) | 0.115 | C(C5) | −0.0546 (5) | −0.3508 (10) | −0.2808 (15) | 0.069 (8) |
| P(1) | −0.18701 (21) | −0.17045 (29) | −0.17463 (45) | 0.032 | C(C6) | −0.1005 (4) | −0.3324 (10) | −0.2960 (11) | 0.055 (7) |
| P(2) | −0.17191 (18) | −0.23749 (29) | −0.37015 (41) | 0.031 | C(D1) | −0.1944 (9) | −0.3272 (12) | −0.4403 (11) | 0.037 (5) |
| P(3) | −0.17365 (19) | 0.08286 (29) | −0.31697 (40) | 0.031 | C(D2) | −0.1637 (5) | −0.3785 (13) | −0.4870 (14) | 0.055 (6) |
| P(4) | −0.19040 (20) | 0.01440 (30) | −0.51374 (44) | 0.033 | C(D3) | −0.1798 (7) | −0.4409 (7) | −0.5459 (17) | 0.064 (7) |
| C(1) | −0.2021 (7) | −0.2509 (11) | −0.2597 (15) | 0.037 (5) | C(D4) | −0.2265 (8) | −0.4520 (10) | −0.5581 (10) | 0.056 (6) |
| C(2) | −0.2054 (7) | 0.0992 (10) | −0.4306 (15) | 0.035 (5) | C(D5) | −0.2572 (4) | −0.4007 (11) | −0.5114 (15) | 0.044 (6) |
| C(3) | −0.1482 (8) | 0.0021 (13) | −0.1360 (17) | 0.047 (6) | C(D6) | −0.2412 (8) | −0.3383 (5) | −0.4525 (18) | 0.050 (6) |
| C(4) | −0.1261 (9) | 0.0332 (13) | −0.0787 (17) | 0.054 (6) | C(E1) | −0.1941 (10) | 0.1676 (7) | −0.2439 (18) | 0.032 (5) |
| C(5) | −0.0986 (14) | 0.0770 (23) | 0.0055 (28) | 0.130 (13) | C(E2) | −0.2412 (9) | 0.1787 (13) | −0.2390 (8) | 0.037 (5) |
| C(6) | −0.1061 (12) | 0.1611 (20) | 0.0231 (25) | 0.118 (12) | C(E3) | −0.2593 (4) | 0.2416 (12) | −0.1835 (15) | 0.078 (8) |
| C(7) | −0.1130 (19) | 0.0338 (33) | 0.1006 (40) | 0.227 (25) | C(E4) | −0.2303 (8) | 0.2934 (6) | −0.1329 (15) | 0.061 (7) |
| C(8) | −0.0420 (24) | 0.0530 (33) | −0.0160 (53) | 0.291 (32) | C(E5) | −0.1833 (7) | 0.2823 (13) | −0.1378 (9) | 0.060 (7) |
| C(9) | −0.1471 (7) | −0.1590 (11) | −0.5510 (15) | 0.036 (5) | C(E6) | −0.1652 (5) | 0.2194 (12) | −0.1933 (18) | 0.057 (7) |
| C(10) | −0.1283 (8) | −0.1820 (12) | −0.6145 (15) | 0.043 (6) | C(G1) | −0.1145 (4) | 0.1053 (13) | −0.3461 (18) | 0.045 (5) |
| C(11) | −0.0984 (8) | −0.2143 (13) | −0.6970 (16) | 0.053 (6) | C(G2) | −0.0807 (5) | 0.0483 (7) | −0.3238 (13) | 0.063 (7) |
| C(12) | −0.1141 (12) | −0.1724 (20) | −0.7895 (24) | 0.118 (12) | C(G3) | −0.0354 (6) | 0.0644 (13) | −0.3468 (20) | 0.076 (7) |
| C(13) | −0.1128 (16) | −0.3060 (28) | −0.7263 (35) | 0.193 (19) | C(G4) | −0.0239 (4) | 0.1376 (11) | −0.3920 (15) | 0.088 (9) |
| C(14) | −0.0516 (14) | −0.2075 (23) | −0.6678 (29) | 0.153 (15) | C(G5) | −0.0576 (5) | 0.1947 (9) | −0.4142 (15) | 0.074 (8) |
| C(A1) | −0.2300 (7) | −0.1718 (6) | −0.0850 (15) | 0.037 (6) | C(G6) | −0.1029 (6) | 0.1785 (14) | −0.3912 (23) | 0.065 (7) |
| C(A2) | −0.2761 (8) | −0.1756 (14) | −0.1084 (9) | 0.041 (6) | C(I1) | −0.1405 (4) | 0.0617 (8) | −0.5802 (11) | 0.056 (7) |
| C(A3) | −0.3091 (5) | −0.1704 (12) | −0.0374 (15) | 0.064 (7) | C(I2) | −0.1476 (5) | 0.1348 (13) | −0.6295 (19) | 0.039 (6) |
| C(A4) | −0.2959 (6) | −0.1615 (6) | 0.0571 (13) | 0.065 (7) | C(I3) | −0.1115 (5) | 0.1723 (11) | −0.6768 (16) | 0.068 (8) |
| C(A5) | −0.2498 (7) | −0.1578 (13) | 0.0805 (11) | 0.056 (6) | C(I4) | −0.0683 (4) | 0.1368 (8) | −0.6748 (10) | 0.066 (7) |
| C(A6) | −0.2168 (4) | −0.1629 (12) | 0.0094 (17) | 0.052 (6) | C(I5) | −0.0612 (5) | 0.0637 (12) | −0.6255 (18) | 0.065 (7) |
| C(B1) | −0.1379 (4) | −0.2125 (16) | −0.1130 (20) | 0.031 (5) | C(I6) | −0.0973 (5) | 0.0262 (10) | −0.5782 (15) | 0.055 (6) |
| C(B2) | −0.0953 (5) | −0.1754 (10) | −0.1216 (15) | 0.049 (6) | C(J1) | −0.2395 (7) | 0.0142 (15) | −0.6053 (14) | 0.033 (5) |
| C(B3) | −0.0572 (5) | −0.2113 (10) | −0.0794 (10) | 0.069 (7) | C(J2) | −0.2842 (8) | 0.0150 (12) | −0.5720 (9) | 0.045 (6) |
| C(B4) | −0.0617 (4) | −0.2842 (13) | −0.0285 (17) | 0.082 (8) | C(J3) | −0.3204 (5) | 0.0088 (7) | −0.6356 (14) | 0.063 (7) |
| C(B5) | −0.1044 (5) | −0.3213 (8) | −0.0199 (12) | 0.062 (7) | C(J4) | −0.3119 (6) | 0.0018 (13) | −0.7326 (12) | 0.059 (7) |
| C(B6) | −0.1424 (5) | −0.2854 (13) | −0.0622 (14) | 0.064 (7) | C(J5) | −0.2672 (7) | 0.0010 (9) | −0.7659 (11) | 0.062 (7) |
| C(C1) | −0.1125 (4) | −0.2601 (15) | −0.3426 (20) | 0.035 (5) | C(J6) | −0.2310 (4) | 0.0072 (15) | −0.7022 (10) | 0.052 (6) |

[a] For Au, Pt, I, and P atoms, $U$ is the mean latent root of the $U_{ij}$ tensor; for C atoms $U$ is the isotropic displacement parameter.

chlorinated solvent $CD_2Cl_2$, these resonances slowly decayed and a new *t*-BuCCPt resonance due to **1b** appeared. The fate of the *t*-BuCC group cleaved from gold was not determined, but it gave a *t*-Bu resonance at $\delta$ = 1.27 ppm.

## Conclusions

The complexes **1a–c** are the first $Pt_2Au$ cluster complexes and the first 42-electron platinum–gold clusters.[2,10,11] The only other reported triangular platinum–gold cluster is the 40-electron $PtAu_2$ complex $[PtCl(PEt_3)_2(AuPPh_3)_2]$.[10] The $Pt_2Au$ unit in **1c** is clearly shown by the X-ray structure (Figures 1 and 2) to have the features of a 3c–2e bond. The 3c–2e bond is also expected by analogy with the corresponding $Pt_2(\mu\text{-}H)$ complexes, which are isolobal with the $Pt_2(\mu\text{-}AuX)$ complexes and which have had molecular orbital calculations performed on them.[25] It is probable that complex **1a** is formed by oxidation of $[Pt_2(\mu\text{-dppm})_3]$ to $[Pt_2(CC\text{-}t\text{-}Bu)_2(\mu\text{-dppm})_2]$ (**2**), followed by addition of AuCC-*t*-Bu to the Pt–Pt bond of **2**. The protonation of the Pt–Pt bond of complexes analogous to **2** is known to occur easily and provides a good precedent for the suggested mechanism involving the isolobal AuCC-*t*-Bu,[22] and it has recently been shown that both $HgCl_2$ and AuCl can be added across the Pt–Pt bond of $[Pt_2Cl_2(\mu\text{-dppm})_2]$ to give A-frame clusters.[30] Finally, we have verified that **1a** is formed by reaction of **2** with AuCC-*t*-Bu. The synthetic method using AuCC-*t*-Bu can be expected to lead to many other heteronuclear gold–metal clusters by reaction with appropriate electron-rich metal compounds.

## Experimental Section

NMR spectra were recorded with Varian XL200 ($^1H$) and XL300 ($^{31}P$) spectrometers. Chemical shifts are quoted with respect to $Me_4Si$ ($^1H$) and 85% phosphoric acid ($^{31}P$). Analyses were performed by Guelph Chemical Laboratories Ltd.

$[Pt_2(CC\text{-}t\text{-}Bu)_2(\mu\text{-dppm})_2(\mu\text{-}AuCC\text{-}t\text{-}Bu)]$ **(1a).** A solution of $[Pt_2(\mu\text{-dppm})_3]$ (0.2042 g, 0.132 mmol) in dry toluene (10.0 mL) was added dropwise under a dinitrogen atmosphere to a solution of $[AuC{\equiv}C\text{-}t\text{-}Bu]$ (0.1472 g, 0.529 mmol) in toluene (5.0 mL). The reaction mixture was stirred at room temperature for 20 h. The volatile components of the reaction mixture were removed under reduced pressure, yielding a dark red oil. The oil was redissolved in a minimum of toluene (5.0 mL), and pentane was slowly added. A dark red-brown solid precipitated and was isolated. Addition of a small volume of acetone (3.0 mL) to the solid resulted in formation of a red solution and some bright yellow solid. The red solution was filtered off, and the remaining yellow solid **1a** was again washed with acetone (2.0 mL) and then dried in vacuo. The first and second red solutions were combined, dissolved in acetone (5.0 mL), and layered with pentane. Slow diffusion of the solvents yielded a further crop of yellow crystals of **1a**: total yield 0.15 g; mp 195–220 °C dec. Anal. Calcd for $C_{68}H_{71}AuP_4Pt_2$: C, 51.07; H, 4.47. Found: C, 51.03; H, 4.91. No crystalline product could be obtained from the remaining red material.

$[Pt_2(CC\text{-}t\text{-}Bu)_2(\mu\text{-dppm})_2(\mu\text{-}AuCl)]$ **(1b).** Compound **1a** was also crystallized by slow diffusion of pentane into a $CH_2Cl_2$ solution. Under these conditions **1a** converted to **1b**. This conversion was shown by $^1H$ and $^{31}P$ NMR spectroscopy to take place in quantitative yield over several days. Crystals of **1b** were obtained from $CH_2Cl_2$/pentane. Anal. Calcd for $C_{62}H_{62}AuClP_4Pt_2$: C, 47.93; H, 4.02. Found: C, 48.01; H, 4.11.

$[Pt_2(CC\text{-}t\text{-}Bu)_2(\mu\text{-dppm})_2(\mu\text{-}AuI)]$ **(1c).** A solution of **1b** (0.05 g) in acetone (10 mL) was reacted with NaI (0.02 g) in acetone (10 mL) for 1 h. The solvents were evaporated, and the product was crystallized from $CH_2Cl_2$/pentane. Anal. Calcd for $C_{62}H_{62}AuIP_4Pt_2$: C, 45.26; H, 3.80. Found: C, 44.62; H, 4.16.

**X-ray Crystal Structure Analysis of** $[Pt_2(C{\equiv}C\text{-}t\text{-}Bu)_2(\mu\text{-}AuI)(\mu\text{-dppm})_2]$ **(1c).** Yellow, needlelike crystals of **1c** were obtained by recrystallization from an acetone/dichloromethane mixture. All diffraction measurements were made at room temperature (~22 °C), with Mo K$\alpha$ radiation, an Enraf-Nonias CAD4F diffractometer, and a crystal of approximate dimensions 0.60 × 0.15 × 0.12 mm. The unit cell dimensions (Table II) were determined by a least-squares treatment of the setting angles of 25 reflections with $13.5 < \theta(\text{Mo K}\alpha) < 17.5°$. Systematically absent reflections were compatible with space groups $Pna2_1$

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(No. 33) and *Pnam* (No. 62), but the former was indicated by the shape of a Patterson function and confirmed by structure analysis.

Intensities of 9704 reflections (*hkl* with $2 < \theta < 27°$ and $h\bar{k}l$ with $2 < \theta < 18°$) were measured by continuous $\theta/2\theta$ scans of $(0.70 + 0.35 \tan \theta)°$ in $\theta$; background was estimated by extending scans at both ends by 25%. The scan speeds were adjusted to give $\sigma(E)/I < 0.02$, subject to a time limit of 90 s. Two strong reflections were remeasured every 2 h, but their intensities displayed only random fluctuations not exceeding 3.4% of the mean values.

The integrated intensities of reflections, derived in the usual manner ($q = 0.03$),[31] were corrected for Lorentz, polarization, and absorption effects. The last correction, made by an empirical method,[32] yielded absorption factors (on $F$) of 0.78–1.47. Averaging 4604 symmetry-related structure amplitudes to get 2302 unique ones gave $R$(internal) of 0.032. Rejection of 2960 reflections with $I < 3\sigma(E)$ led to 4442 unique structure amplitudes, and only these were used in further analysis.

The positions of the platinum and gold atoms were determined from a Patterson function, and those of the remaining non-hydrogen atoms, from difference electron density syntheses. The dppm hydrogen atoms were included in the structural model in calculated positions and constrained so that $U(\text{H}) = U(\text{C})$ with C–H bonds of 1.0 Å. The $CH_2$ hydrogens were allowed to ride on the carbon atoms to which they are bonded, and the phenyl groups were treated as rigid bodies of $D_{6h}$ symmetry (C–C = 1.38 Å). Only Au, Pt, I, and P atoms were allowed anisotropic displacement parameters. The structure was refined by full-matrix least squares, minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(|F_o|)$. Neutral-atom scattering factors and anomalous dispersion corrections were taken from ref 33. The refinement of 225 parameters, including the polarity factor $\eta$,[34] converged at $R = 0.040$ and $R_w = 0.050$,[35] with $\eta = 0.94$ (6), the largest parameter-shift/error ratio of 0.19, and the error in observation of unit weight of 2.6. In the final difference electron density synthesis the function values were −0.19 to +0.18 e Å$^{-3}$. Disorder of the methyl carbon atoms C(6) to C(8) and C(12) to C(14) is possible in view of their large displacement parameters (Table V). Attempts to model the disorder were unsuccessful, and this may explain the large error in observation of unit weight and discrepancies between $|F_o|$ and $|F_c|$ for about 20 low-angle reflections. All calculations were performed on a GOULD SEL 32/27 minicomputer, using the locally developed GX program package.[36]

The final atomic parameters are listed in Table V. The calculated coordinates of hydrogen atoms, anisotropic displacement parameters of Pt, Au, I, and P atoms, complete lists of bond lengths and angles, and the observed and calculated structure amplitudes are presented as supplementary material (Tables VI–X).

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**Supplementary Material Available:** Calculated coordinates of hydrogen atoms, anisotropic displacement parameters of Pt, Au, I, and P atoms, and complete bond lengths and angles (Tables VI–IX) (6 pages); observed and calculated structure amplitudes (Table X) (20 pages). Ordering information is given on any current masthead page.

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# Complexes Containing Unbridged Homonuclear or Heteronuclear Quadruple Bonds. Crystal and Molecular Structures of $MoWCl_4(PMePh_2)_4$, $MoWCl_4(PMe_3)_4$, and $Cl_2(PMe_3)_2MoWCl_2(PMePh_2)_2$

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The reactions of Mo($\eta^6$-PhPMePh)$(PMePh_2)_3$ and Mo($\eta^6$-$PhPMe_2$)$(PMe_2Ph)_3$ with $MoCl_4(THF)_2$ yield the homonuclear unbridged quadruply bonded complexes $Mo_2Cl_4(PR_3)_4$ ($PR_3 = PMePh_2$ (**1**), $PMe_2Ph$ (**2**)). Complex **1** readily undergoes phosphine substitution with $PMe_3$ to yield $Mo_2Cl_4(PMe_3)_4$ (**3**). The reactions of Mo($\eta^6$-$PhPMe_2$)$(PMe_2Ph)_3$ and Mo($\eta^6$-PhPMePh)$(PMePh_2)_3$ with $WCl_4(PPh_3)_2$ yield the complexes $MoWCl_4(PR_3)_4$ ($PR_3 = PMe_2Ph$ (**4**), $PMePh_2$ (**5**)), which are among the first to contain an unbridged quadruple bond between two different elements. Complex **5** undergoes phosphine substitution reactions with $PMe_3$ to give sequentially $Cl_2(PMe_3)_2MoWCl_2(PMePh_2)_2$ (**6**) and then $MoWCl_4(PMe_3)_4$ (**7**). Complex **4** can also be synthesized by reacting **5** with $PMe_2Ph$. The $^{31}P$ and $^1H$ NMR spectra, electronic and visible spectra, and cyclic voltammograms of these complexes are interpreted, and the crystal and molecular structures of **5**–**7** are reported. Compounds **5** and **7** were found to have disordered arrangements of the metal atoms; compound **6** with the different phosphine ligands on the metal atoms is, however, ordered with a $\text{Mo}\overset{4}{-}\text{W}$ bond length of 2.207 (1) Å. In **6** and **7** the molecules have crystallographic 2-fold symmetry. In all three structures the ligand arrangement over the metal–metal bond defines an eclipsed geometry with chlorine next to phosphine across the bond in a pseudo-$D_{2d}$ arrangement. The metal–metal distances in **5** and **7** are 2.208 (4) (average) and 2.2092 (7) Å, respectively. These values are close to distances expected on the basis of homonuclear $\text{M}\overset{4}{-}\text{M}$ bonds, and therefore there is no extra shortening of these bonds due to electronegativity differences. Crystal data: **5**, monoclinic, space group $P2_1/a$, $a = 21.511$ (4) Å, $b = 12.176$ (6) Å, $c = 40.863$ (8) Å, $\beta = 92.65$ (2)°, $V = 10692$ Å$^3$, $D_{\text{calcd}} = 1.52$ g cm$^{-3}$ for $Z = 8$, $R = 0.0957$ for 3554 observed ($I > 3\sigma(I)$) reflections; **6**, monoclinic, space group $I2/a$, $a = 16.817$ (4) Å, $b = 11.925$ (3) Å, $c = 19.685$ (5) Å, $\beta = 103.87$ (2)°, $V = 3832.4$ Å$^3$, $D_{\text{calcd}} = 1.69$ g cm$^{-3}$ for $Z = 4$, $R = 0.0364$ for 2203 observed reflections; **7**, monoclinic, space group $I2/a$, $a = 17.312$ (4) Å, $b = 9.193$ (1) Å, $c = 19.085$ (3) Å, $\beta = 119.69$ (2)°, $V = 2638.9$ Å$^3$, $D_{\text{calcd}} = 1.57$ g cm$^{-3}$ for $Z = 4$, $R = 0.0312$ for 2084 observed reflections.

All of the compounds known to contain heteronuclear quadruple bonds involve combinations of the chromium group metals.[1] Two classes of complexes containing quadruple bonds between molybdenum and tungsten are now known in which the $\text{Mo}\overset{4}{-}\text{W}$ bond is either supported by bridging ligands or is free of bridging ligands. The members of the first class are $MoW(O_2CCMe_3)_4$[2,3] and $MoW(mhp)_4$, [mhp = 2-hydroxy-6-methylpyridine anion].[4,5]

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