Binuclear and Trinuclear Gold–Platinum Complexes: The Crystal Structures of $[PtCl(C{\equiv}C\text{-}t\text{-}Bu)(\mu\text{-dppm})_2Au][Cl]\cdot CH_2Cl_2$ and $[Pt(C{\equiv}C\text{-}t\text{-}Bu)_2\{(\mu\text{-dppm})AuCl\}_2]$ (dppm = $Ph_2PCH_2PPh_2$)

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Reactions of *trans*-$[PtCl_2(SMe_2)_2]$ with 1 or 2 equiv of $AuC{\equiv}C\text{-}t\text{-}Bu$ give unstable complexes formulated as $[PtCl(C{\equiv}C\text{-}t\text{-}Bu)(SMe_2)_2(AuCl)]$ and $[Pt(C{\equiv}C\text{-}t\text{-}Bu)_2(SMe_2)_2(AuCl)_2]$ with the AuCl units probably bonded to the alkynylplatinum groups. Further reaction of these complexes with dppm, $Ph_2PCH_2PPh_2$, gave the binuclear *trans*-$[PtCl(C{\equiv}C\text{-}t\text{-}Bu)(\mu\text{-dppm})_2Au]^+Cl^-$ and *trans*-$[Pt(C{\equiv}C\text{-}t\text{-}Bu)_2(\mu\text{-dppm})_2Au]^+Cl^-$ and the trinuclear *trans*-$[Pt(C{\equiv}C\text{-}t\text{-}Bu)_2\{(\mu\text{-dppm})AuCl\}_2]$. A number of other routes to these and related complexes have been developed. The structures of *trans*-$[PtCl(C{\equiv}C\text{-}t\text{-}Bu)(\mu\text{-dppm})_2Au][Cl]\cdot CH_2Cl_2$ [space group $P2_1/a$, $Z = 4$, $a = 23.144$ (5) Å, $b = 23.752$ (3) Å, $c = 10.474$ (4) Å, $\beta = 99.15$ (2)°, $R = 0.034$] and of *trans*-$[Pt(C{\equiv}C\text{-}t\text{-}Bu)_2\{(\mu\text{-dppm})AuCl\}_2]$ [space group $P1$, $Z = 2$, $a = 9.703$ (3) Å, $b = 14.362$ (1) Å, $c = 23.646$ (3) Å, $\alpha = 75.805$ (8)°, $\beta = 83.87$ (2)°, $\gamma = 70.09$ (2) Å, $R = 0.027$] were determined by X-ray crystallography.

Introduction

There has been growing interest in heteronuclear complexes of gold and other transition metals. These complexes may contain gold–metal bonds or may have bridging ligands between gold and the second metal.[2-7] This paper describes the use of the oligomeric[8,9] $(AuC{\equiv}C\text{-}t\text{-}Bu)_n$ as a reagent for the synthesis of organometallic gold–platinum complexes. Evidence is presented that the reaction with $[PtCl_2(SMe_2)_2]$ takes place by acetylide for chloride exchange and that the resultant AuCl unit remains coordinated to the platinum acetylide unit, in a similar way as in complexes $[AuCl(RC{\equiv}CR)]$.[10,11] Trapping of these unstable complexes with bis(diphenylphosphino)methane, dppm, occurs with retention of the nuclearity and leads to binuclear or trinuclear organometallic gold–platinum complexes with bridging dppm ligands; the structures of two typical compounds have been determined by X-ray diffraction.

Results and Discussion

The complex $[AuC{\equiv}C\text{-}t\text{-}Bu]$ exists in a yellow tetrameric form and in a white form, which may have a polymeric chain structure. Both are presumed to contain σ-bonded $Au{-}C{\equiv}C\text{-}t\text{-}Bu$ units π-bonded through the acetylide triple bond to an adjacent molecule to give the usual linear structure of gold(I) complexes, though crystal structures have never been obtained. The π-bonds are easily broken by ligands, L, to give monomeric complexes, $[Au(C{\equiv}C\text{-}t\text{-}Bu)L]$,[8,9,12] but the following types of reactions appear to be new.

The reaction of *trans*-$[PtCl_2(SMe_2)_2]$ with 1 equiv of $[Au{-}C{\equiv}C\text{-}t\text{-}Bu]$ at low temperature in CH_2Cl_2 resulted in formation of a white solid, for which we tentatively assign structure 1 (Scheme I). This material could be stored at low temperatures, but after 24 h at −20 °C some discoloration was evident. Decomposition was substantially faster in solution. The unstable nature of 1 impaired attempts to obtain and store single crystals at either room or low temperature, and so it was characterized spectroscopically and by its chemical reactions. The ^1H NMR spectrum of 1 gave singlets due to Me_2S and *t*-Bu groups with the expected intensity ratio. The coupling constant $^3J(PtSMe_2) = 51.5$ Hz is characteristic for platinum(II) with two mutually trans SMe_2 groups (compare $^3J(PtSMe_2) = 54$ Hz in *trans*-$[PtClMe(SMe_2)_2]$).[13] The ^{13}C NMR spectrum clearly showed that the acetylide was σ-bonded to platinum, with a large coupling constant, $^1J(PtC^\alpha) = 1421$ Hz. No change in the NMR spectra occurred at low temperature. The mass spectrum of 1 gave a parent ion envelope at m/e 668 consistent with the formulation $[PtCl(C{\equiv}C\text{-}t\text{-}Bu)(SMe_2)_2AuCl]$. There is no direct evidence that gold is bound to the acetylide ligand, but the other likely formulations with the AuCl bound to a bridging SMe_2 ligand or to platinum are inconsistent with the above spectroscopic data. Indirect evidence that the $M{-}C{\equiv}C{-}t\text{-}Bu$ group is a stronger ligand for AuCl than is SMe_2 is provided by the observations that neither 1 nor $[(AuC{\equiv}C\text{-}t\text{-}Bu)_4]$ reacted with SMe_2. Thermal decom-

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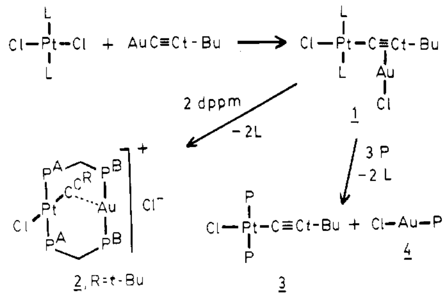
Scheme I



L = SMe_2; P = PPh_3

position of 1 gave metallic gold, and the product remaining was *trans*-[$PtCl(C{\equiv}C$-*t*-Bu$)(SMe_2)_2$].

Further evidence for the structure of 1 was obtained by treatment of the dinuclear species with either dppm or PPh_3. As expected, the addition of phosphine ligands leads to instantaneous breaking of the alkyne–gold π-bond (see Scheme I).

Reaction of 1 equiv of 1 with 2 equiv of dppm proceeded cleanly to give the yellow crystalline compound 2. The assigned structure for 2 is supported by the $^{31}P\{^1H\}$ NMR data, showing a pattern typical for an AA′BB′ spin system with ^{195}Pt satellites. The parameters correlate well with those obtained previously for [$PtCl(C{\equiv}CPh)(\mu$-dppm$)_2Au]^+$, though this complex was not isolated, and the assignments for its were therefore tentative.[3] As a result of the asymmetric substitution at the platinum center, the four methylene protons of the two dppm ligands resonate as two broadened AB signals in the ^1H NMR spectrum. The resolution of this pattern could not be improved by recording the ^1H NMR spectrum at lower temperature (−60 °C, −80 °C). Full structural characterization of 2 was achieved by a single-crystal X-ray diffraction study of its CH_2Cl_2 solvate. In the crystal structure of $2{\cdot}CH_2Cl_2$ the cations, anions, and solvent molecules are separated by normal contacts.

The structure of the cation, displaying the bond lengths and angles listed in Table I, is shown in Figure 1. It comprises a *trans*-$PtCl(C{\equiv}C$-*t*-Bu) fragment and a gold atom bridged by two mutually trans dppm ligands to form an eight-membered dimetallacycle, in which the gold(I) and platinum(II) centers lie in distorted linear and square-planar environments. The configuration of the $PtAu(\mu$-dppm$)_2$ nucleus is closely similar to that usually found in molecular A-frames: the dppm ligands show a virtually staggered conformation about each $P{-}CH_2$ bond (Table I), and the eight-membered $PtAuP_4C_2$ ring adopts a long boat conformation. The *trans*-$PtCl(C{\equiv}C$-*t*-Bu) fragment is inclined toward the $PtAuP_4$ plane, to yield the C(3)–Pt–Au angle of 59.9 (4)°. Thus the structural type of 2 can be considered derived from the molecular A-frame structure,[14] by loss of one terminal ligand.

The Pt–Au distance [3.082 (1) Å] is somewhat longer than those (2.60–3.03 Å)[2,5,7,15,16] associated with significant bonding interactions. The Pt–P and Au–P distances are as expected,[16-19] and the Pt–Cl distance [2.353 (4) Å] is

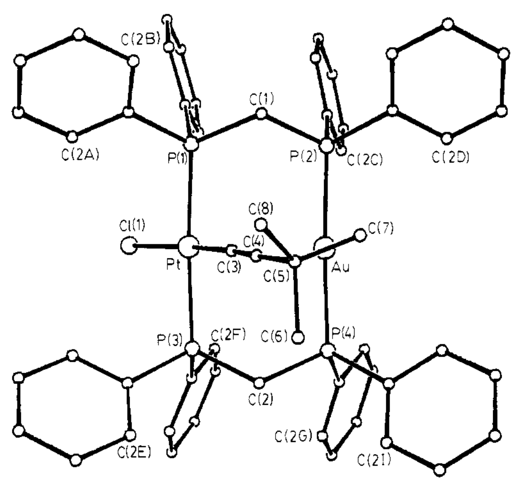


Figure 1. The structure of [$PtCl(C{\equiv}C$-*t*-Bu$)(\mu$-dppm$)_2Au]^+$, with atoms represented by spheres of arbitrary size. In the phenyl rings carbon atoms are numbered cyclically, C(1n)···C(6n), with n = A, B, C, D, E, F, G, or I and C(1n) bonded to phosphorus. Only the C(2n) atoms are labeled, for clarity.

Table I. Selected Interatomic Distances (Å) and Angles (deg) in *trans*-[$PtCl(C{\equiv}C$-*t*-Bu$)(\mu$-dppm$)_2Au]^+$

	Distances		
Pt–Cl(1)	2.353 (4)[a]	Au–P(4)	2.313 (4)
Pt–C(3)	1.98 (1)	C(3)–C(4)	1.18 (2)
Au–C(3)	2.70 (1)	C(4)–C(5)	1.49 (2)
Pt–P(1)	2.316 (4)	Pt···Au	3.082 (1)
Pt–P(3)	2.310 (3)	P(1)···P(2)	3.064 (4)
Au–P(2)	2.314 (4)	P(3)···P(4)	3.074 (4)
	Bond Angles		
Cl(1)–Pt–P(1)	93.4 (2)	Au–C(3)–C(4)	103.3 (9)
Cl(1)–Pt–P(3)	90.5 (2)	C(3)–C(4)–C(5)	175 (1)
C(3)–Pt–P(1)	88.3 (4)	Pt–C(3)–Au	80.7 (4)
C(3)–Pt–P (3)	88.0 (4)	P(1)–C(1)–P(2)	112.8 (6)
Cl(1)–Pt–C(3)	171.2 (4)	P(3)–C(2)–P(4)	114.3 (6)
P(1)–Pt–P(3)	176.0 (2)	Pt–P–C	110.1 (4)–118.4 (5)
P(2)–Au–P(4)	176.3 (2)	Au–P–C	110.4 (4)–116.8 (5)
Pt–C(3)–C(4)	175 (1)	C–P–C	102.5 (7)–108.0 (6)
	Torsion Angles		
Pt–P(1)–C(1)–P(2)	53.8 (5)	Pt–P(3)–C(2)–P(4)	−53.3 (5)
Au–P(2)–C(1)–P(1)	−55.8 (5)	Au–P(4)–C(2–)P(3)	48.6 (5)

[a] Estimated standard deviations in the least significant digit are shown in parentheses, here and throughout the paper.

indicative of relatively high trans influence of the acetylide ligand.

A novel structural feature of 2 is the semibridging coordination mode of the acetylide ligand (A). The Pt–C(3) distance [1.98 (1) Å] is within the range previously found for Pt(II)–C(acetylide) σ-bonds [1.91–2.09 Å].[3,16-18] However, the Au–C(3) distance [2.70 (1) Å] is substantially longer than the normal gold(I)–carbon single bonds (1.85–2.12 Å)[20] and yet too short to be considered a nonbonding contact. The Pt–C(3)–C(4), Au–C(3)–C(4), and Pt–C(3)–Au angles [175 (1), 103.3 (9), and 80.7 (4)°, respectively] are comparable with corresponding angles in complexes of the isoelectronic carbonyl group[21] for which the semibridging bonding mode is well established.[21,22] For the acetylide ligands spanning two metal centers, only the bridging mode (B), characterized by two approximately equal M—C≡C bond angles and a C≡C—C linkage perpendicular to the M—M vector, and the "side-on" mode

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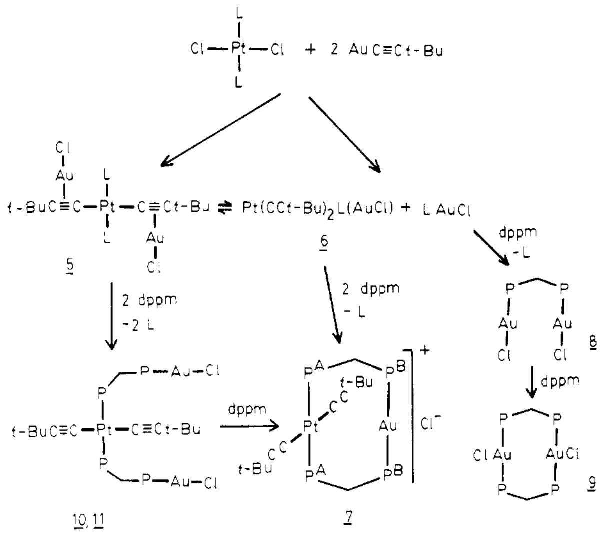
Scheme II



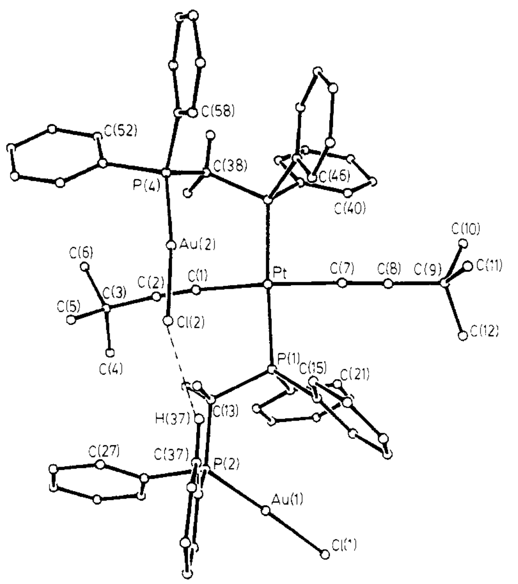
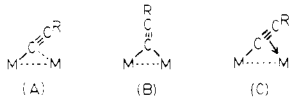


Figure 2. Molecular structure of *trans*-[Pt(C≡C-*t*-Bu)$_2${(μ-dppm)AuCl}$_2$] (11), with atoms represented by spheres of arbitrary size. For clarity, in each phenyl ring only the C(n+1) atom is labeled; it indicates direction of the progressive sequence C(n), C(n+1), ..., C(n+5), in which C(n) is the atom bonded to phosphorus. Only H(37) and methylenic hydrogen atoms are shown.

(C) have been previously found,[17,18,22] as far as we are aware.



Reasons for the occurrence of the semibridging acetylide in 2 are difficult to discern; in view of the inequality of the metal atom charges and of the steric crowding (evident from angular distortions, Table I), neither electronic nor steric effects can be discarded. It is, however, likely that the steric requirements of the bulky ligands force the Cl—Pt—C≡C-*t*-Bu fragment into the observed rotational orientation about the P—Pt—P linkage. Such orientation minimizes steric interactions of the Cl ligand with phenyl rings [Cl···C(6B) = 3.25 (1), Cl(1)···C(2F) = 3.35 (1) Å], but it also places the acetylide group in the vicinity of the gold center.

The reaction of 1 equiv of 1 with 3 equiv of triphenylphosphine (Scheme I), followed by immediate ^{1}H and ^{31}P{^{1}H} spectroscopic analysis, showed formation of *trans*-[PtCl(C≡C-*t*-Bu)(PPh$_3$)$_2$] (3) and [AuCl(PPh$_3$)] (4) in a 1:1 ratio. The products were separated and purified, and their formulations were confirmed by comparison of the NMR and MS with those of authentic samples.

Reactions of Scheme II. Reaction of *trans*-[PtCl$_2$(SMe$_2$)$_2$] with 2 equiv of AuC≡C-*t*-Bu gave in ~70% yield a complex formulated as 5 (Scheme II). In addition, the complex [AuCl(SMe$_2$)] and a complex presumed, from the NMR data and from the requirements of the reaction stoichiometry, to have the empirical formula [Pt(C≡C-*t*-Bu)$_2$(SMe$_2$)(AuCl)] (6) were formed in ~30% yield as analyzed by NMR and appeared to be in equilibrium with 5. Complex 5 was characterized by peaks in the ^{1}H NMR spectrum due to SMe$_2$ and *t*-Bu protons in the expected ratio of 12:18 and by the coupling constant ^3J(PtSMe$_2$) = 51.5 Hz which indicated trans SMe$_2$ ligands. The complex [AuCl(SMe$_2$)] was characterized from the MeS resonance by comparison with an authentic specimen. Complex 6, whose detailed structure could not be deduced, gave a broad Me$_2$SPt resonance in the ^{1}H NMR spectrum with ^3J(PtH) = 44 Hz and a *t*-Bu resonance with the expected intensity. The two *t*-BuC≡C groups appear to be nonequivalent since two CH$_3$ resonances could be attributed to this species in the ^{13}C NMR spectrum. The presence of a single gold atom is required by the reaction stoichiometry (Scheme II). The reaction products were again thermally unstable, and attempted crystallizations were unsuccessful. More stable derivatives were therefore prepared by reaction with dppm.

Reaction of the above mixture of 5, 6, and [AuCl(SMe$_2$)] with 3 equiv (based on Pt) on dppm gave mostly 7 and 9, which could be separated and fully characterized. Complexes analogous to 7, but with different alkynyl ligands, have been prepared previously, and complex 9 is also known.[3,23] Under these conditions therefore, the proposed trinuclear formulation for 5 could not be confirmed. However, treatment of the reaction mixture of Scheme II with exactly 2 equiv of dppm proved more informative. Complex 7 was again formed along with [Au$_2$Cl$_2$(μ-dppm)$_2$] (9), which is a known compound,[23] and a novel trinuclear complex, 10, was also formed. Complex 10 was separated and purified, but a further complication arose due to its slow conversion in solution to an isomeric form 11; the latter was characterized as shown below.

The chemistry described above can be rationalized in the following way. Reaction of [AuCl(SMe$_2$)] with dppm gives 8, and, with excess dppm, it gives 9. Reaction of the proposed binuclear 6 with dppm gives the binuclear complex 7 directly. Finally, reaction of 5 with dppm gives 10 as kinetic product, but 10 then isomerizes to 11 or reacts with excess dppm by cleavage of one AuCl unit to give 7 and 8 or 9.

The molecular structure of 11, shown in Figure 2 and characterized by bond lengths and angles listed in Table II, was determined by X-ray crystallography. It contains a *trans*-Pt(C≡C-*t*-Bu)$_2$ and two AuCl fragments bridged by two dppm ligands to form a novel trinuclear complex, in which the platinum(II) and gold(I) centers show square-planar and linear coordination geometries. The structure is subject to considerable strain, arising from steric interactions of the bulky ligands and balanced by substantial angular distortions (Table II). Especially large is the deviation of the P(1)–C(13)–P(2) angle [120.3 (4)°] from the tetrahedral value. Such large opening of the

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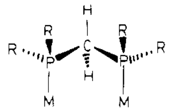
Table II. Selected Interatomic Distances (Å) and Angles (deg) in *trans*-[Pt(C≡C-*t*-Bu)$_2${(μ-dppm)AuCl}$_2$]

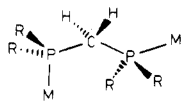
Bond Lengths			
Pt–P(1)	2.291 (2)	Pt–C(1)	2.051 (6)
Pt–P(3)	2.289 (2)	Pt–C(7)	2.007 (7)
Au(1)–P(2)	2.230 (2)	C(1)–C(2)	1.166 (9)
Au(2)–P(4)	2.230 (2)	C(7)–C(8)	1.211 (10)
Au(1)–C(1)	2.296 (3)	C(2)–C(3)	1.499 (10)
Au(2)–Cl(2)	2.297 (2)	C(8)–C(9)	1.491 (11)
Intramolecular Nonbonded Distances			
Au(2)···Pt	3.446 (1)	P(1)···P(2)	3.191 (2)
Au(2)···C(1)	3.137 (6)	P(3)···P(4)	3.052 (2)
Bond Angles			
P(1)–Pt–C(1)	89.3 (2)	Pt–C(7)–C(8)	174.1 (6)
P(1)–Pt–C(7)	87.4 (2)	C(1)–C(2)–C(3)	175.8 (7)
P(3)–Pt–C(1)	92.4 (2)	C(7)–C(8)–C(9)	175.5 (8)
P(3)–Pt–C(7)	90.5 (2)	Au(1)–P(2)–C(13)	116.8 (3)
P(1)–Pt–P(3)	175.1 (1)	P(1)–C(13)–P(2)	120.3 (4)
C(1)–Pt–C(7)	173.5 (3)	C(13)–P(1)–Pt	113.0 (2)
Cl(1)–Au(1)–P(2)	176.5 (1)	Pt–P(3)–C(38)	114.5 (2)
Cl(2)–Au(2)–P(4)	173.0 (1)	P(3)–C(38)–P(4)	112.9 (4)
Pt–C(1)–C(2)	175.2 (5)	C(38)–P(4)–Au(2)	114.8 (2)
Torsion Angles			
Pt–P(1)–C(13)–P(2)	−179.2 (5)	Pt–P(3)–C(38)–P(4)	67.8 (3)
Au(1)–P(2)–C(13)–P(1)	−21.8 (3)	Au(2)–P(4)–C(38)–P(3)	−40.0 (3)

P–CH$_2$–P angle is rarely found in dppm complexes.[24] The acetylide ligands are essentially linear, the Pt—C≡C and C≡C—C angles lying in the 174.1 (6)–175.8 (7)° range. The observed bond lengths are in agreement with acceptable values.[3,14-19]

Particularly interesting is the configuration of the Pt{(μ-dppm)AuCl}$_2$ fragment. The conformation of the dppm ligand linked to the Au(1) center is staggered about one and virtually eclipsed about the other P–CH$_2$ bond, while in the ligand attached to the Au(2) center it is practically staggered about both P–CH$_2$ bonds (Table II). The latter ligand approximates to coordination mode (D), which is common in di- and polymetallic complexes. However, the coordination mode (E), adopted by the former ligand, has not been previously found in dppm-bridged complexes, to the best of our knowledge. The rotational orientation of the dppm ligands about the P–Pt–P linkage is such to yield a syn arrangement of the two CH$_2$ groups and place a phenyl group hydrogen, H(37), in proximity of the Cl(2) ligand. The H(37)···Cl(2) distance (2.58 Å) is ca. 0.3 Å shorter than the sum of corresponding van der Waals radii, and the C(37)–H(37)···Cl(2) angle is 153.4°; they may indicate the presence of a weak intramolecular hydrogen bond of the type C–H···Cl and, therefore, of a 12-membered dimetallamacrocycle [Pt···Au(2) = 3.446 (1) Å].



(D)



(E)

Complexes 10 and 11 both give two multiplets in the ^{31}P NMR spectra due to AA′XX′ spin systems (Figure 3), and each gives very characteristic CH$_2$P$_2$ resonances in the ^{1}H NMR spectra. These give apparent doublets of triplets due to the complex spin system (Figure 4). The structure of the less stable conformer 10 may differ from that of 11 in having the anti rather than syn arrangement of the two CH$_2$ groups with respect to the P–Pt–P linkage. The restricted rotation is due to the steric congestion discussed above. Other possible structures for 10 that have been considered, for example the one containing only one PtC≡C-*t*-Bu group, are inconsistent with the spectroscopic data.

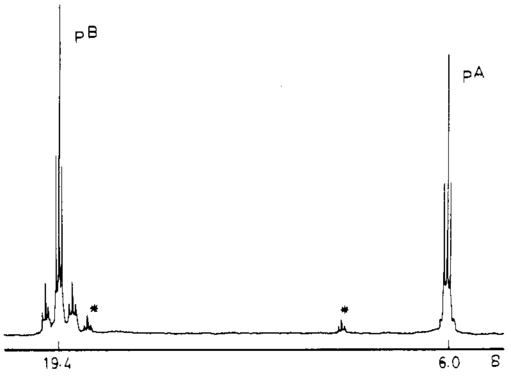


Figure 3. ^{31}P NMR spectrum of *trans*-[Pt(C≡C-*t*-Bu)$_2${(dppm)AuCl}$_2$] (11). The minor peaks are due to the less stable isomer 10.

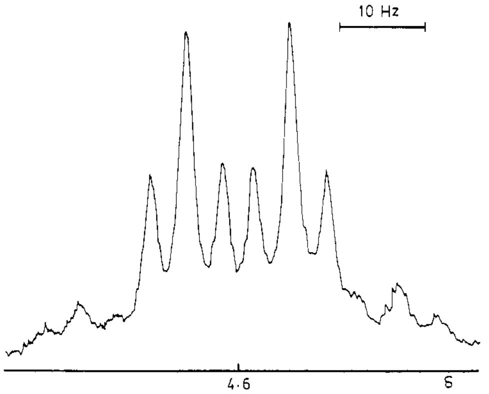
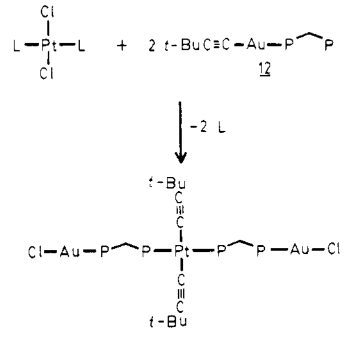


Figure 4. ^{1}H NMR spectrum of *trans*-[Pt(C≡C-*t*-Bu)$_2${(dppm)AuCl}$_2$] (11), showing only the characteristic C*H*$_2$P$_2$ resonance.

Further Routes to Trinuclear PtAu$_2$ Complexes. A second route to the complexes 10 and 11 was developed by reaction of [Au(C≡C-*t*-Bu)(η^1-dppm)] (12) with *trans*-[PtCl$_2$(SMe$_2$)$_2$] with displacement of the SMe$_2$ ligands as shown in eq 1.



···· (1)

Minor products of this reaction were [Pt(C≡C-*t*-Bu)$_2$(dppm)], [Au$_2$(C≡C-*t*-Bu)$_2$(μ-dppm)] (13), and the binuclear complex 2. The complex [Pt(C≡C-*t*-Bu)$_2$(dppm)] was identified by its ^{31}P NMR spectrum, and [Au$_2$(C≡C-*t*-Bu)$_2$(μ-dppm)], (13) was identified by comparison with an authentic sample prepared by reaction of [(AuC≡C-*t*-Bu)$_n$] with dppm. The reaction of eq 1 gave complex 10 initially, and this slowly rearranged over a period of several days to give 11.

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[24] Ling, S. S. M.; Jobe, I. R.; Manojlović-Muir, Lj.; Muir, K. W.; Puddephatt, R. J. *Organometallics* **1985**, *4*, 1198. Hutton, A. T.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1985**, 1677. A reviewer suggested that the PCP angle of ca. 120° perhaps indicates a deprotonated dppm ligand, but this is clearly inconsistent with the NMR data and with the analytical data.

Discussion

The primary reactions of Schemes I and II involve alkynyl for chloro ligand exchange reactions between gold and platinum. Related reactions have been reported recently,[25] but these reactions are novel in that the AuCl fragment(s) remain bonded weakly to the alkynylplatinum groups in the products **1** and **5**. Further, the nuclearities of **1** and **5** are maintained in the reactions with dppm to give the stable products **2** and **11**. Since an attempt to prepare complex **11** by reaction of $[Pt(C{\equiv}C\text{-}t\text{-}Bu)_2(\mu\text{-}dppm)_2Au]Cl$ with excess $[AuCl(SMe_2)]$ was unsuccessful, it seems that **11** is formed from complex **5** as a result of kinetic control, thus giving a trinuclear product from a trinuclear precursor, **5**. Complex **11** is of a new structural type, and **2** contains the first example of a semibridging acetylide.

Experimental Section

NMR spectra were recorded with Varian XL200 (^1H) and XL300 (^{31}P and ^{13}C) spectrometers in CD_2Cl_2 unless otherwise stated. Chemical shifts are quoted with respect to Me_4Si (^1H and ^{13}C) and trimethyl phosphate (^{31}P). Analyses were performed by Guelph Chemical Laboratories Ltd. *trans*-$[PtCl_2(SMe_2)_2]$, $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$, and $[AuCl(SMe_2)]$ were prepared according to published procedures.[13]

Preparation of [Au—C≡C—*t*-Bu]. Methyllithium solution (4.3 mL, 1.6 M) was diluted with dry diethyl ether (25.0 mL) under an atmosphere of N_2 at 0 °C. A solution of 3,3-dimethylbut-1-yne (0.578 g, 7.00 mmol) in diethyl ether (3.0 mL) was added. The mixture was warmed to room temperature and then added at −78 °C to a suspension of $[AuCl(SMe_2)]$ (1.00 g, 3.39 mmol) in diethyl ether (100.0 mL). The reaction mixture was allowed to warm to room temperature and stirred for 1 h. The excess lithiating reagent was hydrolyzed by addition at 0 °C of a saturated ammonium chloride solution (15.0 mL). The organic layer was separated, and the product (0.8680 g, 92%) was obtained as a yellow solid.

Reaction of *trans*-[PtCl₂(SMe₂)₂] with [Au—C≡C—*t*-Bu]. A solution of *trans*-$[PtCl_2(SMe_2)_2]$ (0.1000 g, 0.256 mmol) in CH_2Cl_2 (3.0 mL) was added dropwise to a solution of [Au—C≡C—*t*-Bu] (0.0713 g, 0.256 mmol) in CH_2Cl_2 (3.0 mL). Within 15 min the yellow suspension had become a colorless solution. The product was obtained by evaporation of the solvent and was purified by slow addition of pentane to a concentrated solution in CH_2Cl_2. The white solid **1** was washed with pentane and dried in vacuo. The product (0.1590 g, 93%) was stored at −20 °C.

NMR in CD_2Cl_2: ^1H, δ 2.59 [s, $^3J(PtH) = 51.5$ Hz, MeS], 1.31 (s, *t*-Bu); ^{13}C, δ 108.44 [$^2J(PtC_\beta) = 349$ Hz, C_β], 73.30 [$^1J(PtC_\alpha) = 1421$ Hz, C_α], 32.43 [$C{\equiv}CC(CH_3)_3$]; 31.33 [$^3J(PtC_\gamma) = 27$ Hz, C_γ], 23.97 [$S(CH_3)_2$]. MS (60 °C, m/e^+): 668, 553, 506, 390. HRMS: found, m/e 667.9773; calcd for $C_{10}H_{21}AuCl_2PtS_2$, m/e 667.9755.

Reaction of 1 with 2 Equiv of dppm. Product **1** (0.0500 g, 0.075 mmol) was dissolved in CH_2Cl_2 (3.0 mL). dppm (0.0575 g, 0.150 mmol) in CH_2Cl_2 (5.0 mL) was added dropwise. The colorless solution turned yellow within a few minutes. After 2 h the reaction mixture was taken to dryness, and the yellow product **2** was shown to be formed in essentially quantitative yield by ^{31}P NMR analysis. It was recrystallized from CH_2Cl_2/pentane: yield 0.089 g; mp 230 °C.

Anal. Calcd for $C_{56}H_{53}AuCl_2P_4Pt{\cdot}0.5CH_2Cl_2$: C, 50.1; H, 4.0. Found: C, 49.9; H, 3.9.

Reaction of 1 with 3 Equiv of PPh₃. Product **1** (0.0500 g, 0.075 mmol) was dissolved in CD_2Cl_2 (0.8 mL). Triphenylphosphine (0.0588 g, 0.225 mmol) in CD_2Cl_2 (0.5 mL) was added, and the $^{31}P\{^1H\}$ and ^1H NMR spectra were recorded immediately and showed the presence of only **3** and **4** in equimolar amounts. The two products were separated by extraction of **3** with acetone and recrystallization of both **3** and **4** from CH_2Cl_2/pentane solutions.

Table III. Crystallographic Data for [PtCl(C≡C-*t*-Bu)(μ-dppm)₂Au][Cl]•CH₂Cl₂ (2•CH₂Cl₂) and *trans*-[Pt(C≡C-*t*-Bu)₂{(μ-dppm)AuCl}₂] (11)

	$2{\cdot}CH_2Cl_2$	11
empirical formula	$C_{57}H_{55}AuCl_4P_4Pt$	$C_{62}H_{62}Au_2Cl_2P_4Pt$
fw	1397.8	1591.0
space group	$P2_1/a$	$P\bar{1}$
a, Å	23.144 (5)	9.703 (3)
b, Å	23.752 (3)	14.362 (1)
c, Å	10.474 (44)	23.646 (3)
α, deg		75.805 (8)
β, deg	99.15 (2)	83.87 (2)
γ, deg		70.09 (2)
V, Å^3	5684 (3)	3003 (1)
Z	4	2
$F(000)$, electrons	2728	1528
d_{calcd}, g cm^{-3}	1.633	1.760
cryst dimens, mm	0.25 × 0.16 × 0.16	0.50 × 0.20 × 0.10
temp, °C	23	22.5
radiatn (wavelength, Å)	Mo Kα (0.710 69)	
μ(Mo Kα), cm^{-1}	53.92	74.45
data collectn range (2θ), deg	4–50	4–50
absorptn factors (on F)	0.843–1.080	0.690–1.343
no. of unique reflectns with $I \geqslant 3\sigma(I)$	4212	7471
no. of parameters refined	242	640
R^a	0.034	0.027
$R_w{}^b$	0.043	0.036
s^c	1.68	1.74
parameter shifts/error	<0.01	<0.09

[a] $R = \sum||F_o| - |F_c||/|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. [c] $S = [\sum w(|F_o| - |F_c|)^2/(N_{observatns} - N_{parameters})]^{1/2}$.

trans-$[PtCl(C{\equiv}C\text{-}t\text{-}Bu)(PPh_3)_2]$ (**3**): MS (130 °C, m/e^+) 836, 801, 755, 719, 457. NMR in CD_2Cl_2: ^1H, δ 0.37 [s, 9 H, $-C{\equiv}CC(CH_3)_3$], 7.43 and 7.73 [m, 30 H, $6(C_6H_5\text{–}P)$]; ^{31}P, δ 19.56 [s, $^1J(PtP) = 27.15$ Hz]. Anal. Calcd for $C_{42}H_{39}ClP_2Pt$: C, 60.4; H, 4.7. Found: C, 59.9; H, 4.5.

$[AuCl(PPh_3)]$ (**4**): MS (80 °C, m/e^+) 494, 262. NMR in CD_2Cl_2: ^1H, δ 7.60 [m, C_6H_5–P]; ^{31}P, δ 32.88 (s, AuP). The spectral data were identical with those of an authentic sample.[12]

Reaction of *trans*-[PtCl₂(SMe₂)₂] with 2 Equiv of [Au—C≡C—*t*-Bu]. A solution of *trans*-$[PtCl_2(SMe_2)_2]$ (0.0500 g, 0.128 mmol) in CH_2Cl_2 (4.0 mL) was added dropwise to a stirring suspension of [Au—C≡C—*t*-Bu] (0.0713 g, 0.256 mmol) in CH_2Cl_2 (3.0 mL). After 3 h the volatile components of the reaction mixture were removed under reduced pressure, and the product mixture containing **5**, **6**, and $[AuCl(SMe_2)]$ was dried in vacuo.

Complex **5**, NMR in CD_2Cl_2: ^1H, δ 2.61 [s, $^1J(PtH) = 51.5$ Hz, *Me*S]; 1.35 (s, *t*-Bu); ^{13}C, δ 32.5 [$C{\equiv}CC(CH_3)_3$], 31.77 [br, $C{\equiv}CC(CH_3)_3$], 24.03 [PtS(*C*H)], C_α and C_β were not observed at this concentration. Complex **6**: ^1H, δ 2.59 [s, $^3J(PtH) = 44$ Hz, MeS], 1.33 (s, *t*-Bu); ^{13}C, δ 32.81 and 32.91 [$C{\equiv}CC(CH_3)_3$], 22.96 and 24.32 (PtSC). $[AuCl(SMe_2)]$: ^1H, δ 2.77 (s, MeS); ^{13}C, δ 25.16 (AuSC).

Reaction of 5 with 2 Equiv of dppm. The above reaction mixture was dissolved in CH_2Cl_2 (8.0 mL) and treated with 2 equiv (based on 0.128 mmol of platinum present) of dppm (0.0985 g, 0.256 mmol). The reaction mixture developed a stronger yellow color and was taken to dryness after 3 h. NMR analysis of the solid obtained showed the major product was **10** and minor products **7**, **9**, and **11** were also detected. The products were separated by fractional crystallization from CH_2Cl_2/pentane, during which it became evident that **10** converts to **11**.

Complex 7: mp 286–288 °C. Anal. Calcd for $C_{62}H_{62}AuClP_4Pt{\cdot}CH_2Cl_2$: C, 52.4; H, 4.5. Found: C, 52.6; H, 4.3. NMR in CD_2Cl_2: ^1H, δ 0.65 (s, *t*-Bu); 4.60 [q, $^2J + {}^4J(PH) = 10$, $^3J(PtH) = 30$ Hz, CH_2P_2]; ^{31}P, δ 5.98 [m, $^1J(PtP) = 2658$ Hz, Pt*P*]; 28.54 [m, $^3J(PtP) = 145$ Hz, Au*P*].

Complex 11: mp 230 °C dec. Anal. Calcd for $C_{62}H_{62}Au_2Cl_2P_4Pt$: C, 46.8; H, 3.9. Found: C, 46.6; H, 4.05. MS (180 °C, m/e^+): 1482, 1358, 1323, 1126, 1045, 964—no parent ion observed at m/e 1591. NMR in CD_2Cl_2: ^1H, δ 0.63 (s, *t*-Bu), 4.61 [dt, $^2J(PH) = 12$, $^2J(PH) + {}^4J(PH) = 8$ Hz, CH_2P_2]; ^{31}P, δ 6.04 [m, $^1J(PtP) = 2716$ Hz, Pt*P*], 19.42 [m, $^3J(PtP) = 118$ Hz, Au*P*].

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[25] Cross, R. J.; Davidson, M. F. *J. Chem. Soc., Dalton Trans.* **1986**, 411.

Table IV. Fractional Atomic Coordinates and Displacement Parameters (Å^2) for [PtCl(C≡C-*t*-Bu)(μ-dppm)$_2$Au][Cl]•CH$_2$Cl$_2$(2•CH$_2$Cl$_2$)

atom	*x*	*y*	*z*	*U*[a]
Au	0.23212 (2)	0.00303 (2)	0.19132 (4)	0.046
Pt	0.34737 (2)	0.00732 (2)	0.07933 (4)	0.031
Cl(1)	0.44070 (13)	−0.02491 (13)	0.17267 (32)	0.050
Cl(2)	0.80252 (17)	0.21656 (14)	0.24334 (40)	0.073
Cl(1S)	−0.0192	0.1715	0.5973	0.50 (1)
Cl(2S)	−0.1003	0.0870	0.5020	0.50
P(1)	0.36377 (13)	0.09723 (13)	0.16292 (29)	0.032
P(2)	0.25124 (14)	0.09125 (14)	0.28190 (31)	0.038
P(3)	0.32416 (13)	−0.08078 (12)	−0.00730 (30)	0.033
P(4)	0.20697 (14)	−0.08316 (13)	0.09560 (33)	0.041
C(1)	0.2948 (5)	0.1327 (5)	0.1854 (11)	0.038
C(2)	0.2452 (4)	−0.0946 (4)	−0.0417 (11)	0.034
C(3)	0.2738 (5)	0.0354 (5)	−0.0241 (11)	0.040
C(4)	0.2315 (5)	0.0509 (5)	−0.0936 (11)	0.038
C(5)	0.1754 (5)	0.0701 (6)	−0.1716 (15)	0.056
C(6)	0.1510 (9)	0.0208 (8)	−0.2643 (24)	0.155
C(7)	0.1329 (7)	0.0859 (9)	−0.0905 (18)	0.120
C(8)	0.1853 (7)	0.1188 (7)	−0.2547 (19)	0.107
C(1A)[b]	0.3973 (2)	0.1419 (2)	0.0546 (5)	0.036 (3)
C(2A)	0.4443 (4)	0.1192 (4)	0.0064 (12)	0.038 (3)
C(3A)	0.4745 (4)	0.1514 (4)	−0.0709 (12)	0.055 (4)
C(4A)	0.4576 (2)	0.2062 (2)	−0.1000 (5)	0.057 (4)
C(5A)	0.4106 (4)	0.2289 (4)	−0.0518 (12)	0.062 (4)
C(6A)	0.3804 (4)	0.1967 (3)	0.0255 (12)	0.045 (3)
C(1B)	0.4120 (5)	0.1055 (6)	0.3175 (7)	0.037 (3)
C(2B)	0.4363 (3)	0.1576 (4)	0.3506 (10)	0.047 (3)
C(3B)	0.4707 (5)	0.1654 (3)	0.4696 (8)	0.059 (4)
C(4B)	0.4807 (4)	0.1211 (5)	0.5555 (7)	0.059 (4)
C(5B)	0.4564 (3)	0.0690 (4)	0.5224 (9)	0.049 (3)
C(6B)	0.4220 (6)	0.0612 (4)	0.4034 (7)	0.042 (3)
C(1C)	0.2887 (5)	0.0907 (6)	0.4461 (7)	0.038 (3)
C(2C)	0.2898 (6)	0.0416 (5)	0.5168 (8)	0.048 (3)
C(3C)	0.3165 (4)	0.0406 (3)	0.6443 (10)	0.061 (4)
C(4C)	0.3422 (4)	0.0888 (5)	0.7012 (7)	0.065 (4)
C(5C)	0.3411 (5)	0.1379 (4)	0.6305 (8)	0.053 (4)
C(6C)	0.3144 (3)	0.1389 (4)	0.5030 (10)	0.049 (3)
C(1D)	0.1865 (5)	0.1332 (5)	0.2928 (16)	0.040 (3)
C(2D)	0.1400 (6)	0.1053 (3)	0.3320 (14)	0.072 (4)
C(3D)	0.0914 (4)	0.1350 (4)	0.3547 (6)	0.077 (5)
C(4D)	0.0893 (5)	0.1926 (4)	0.3382 (13)	0.078 (5)
C(5D)	0.1357 (5)	0.2206 (3)	0.2991 (11)	0.081 (5)
C(6D)	0.1843 (3)	0.1909 (4)	0.2764 (8)	0.061 (4)
C(1E)	0.3508 (5)	−0.0882 (3)	−0.1618 (10)	0.036 (3)
C(2E)	0.3179 (3)	−0.1106 (4)	−0.2714 (10)	0.057 (4)
C(3E)	0.3407 (6)	−0.1131 (5)	−0.3853 (6)	0.079 (5)
C(4E)	0.3964 (5)	−0.0932 (3)	−0.3897 (8)	0.065 (4)
C(5E)	0.4293 (4)	−0.0707 (5)	−0.2801 (9)	0.056 (4)
C(6E)	0.4065 (6)	−0.0682 (6)	−0.1661 (6)	0.047 (3)
C(1F)	0.3535 (3)	−0.1415 (5)	0.0884 (14)	0.045 (3)
C(2F)	0.3626 (6)	−0.1395 (3)	0.2218 (15)	0.047 (3)
C(3F)	0.3822 (5)	−0.1866 (5)	0.2927 (8)	0.072 (4)
C(4F)	0.3927 (3)	−0.2358 (4)	0.2302 (12)	0.071 (4)
C(5F)	0.3836 (6)	−0.2379 (3)	0.0968 (12)	0.076 (5)
C(6F)	0.3639 (5)	−0.1907 (6)	0.0260 (7)	0.061 (4)
C(1G)	0.2188 (3)	−0.1439 (6)	0.1978 (15)	0.053 (4)
C(2G)	0.2258 (6)	−0.1969 (6)	0.1486 (8)	0.059 (4)
C(3G)	0.2347 (7)	−0.2426 (4)	0.2308 (14)	0.092 (5)
C(4G)	0.2365 (3)	−0.2353 (5)	0.3620 (12)	0.096 (6)
C(5G)	0.2294 (6)	−0.1823 (6)	0.4112 (10)	0.114 (7)
C(6G)	0.2205 (7)	−0.1366 (3)	0.3290 (16)	0.083 (5)
C(1I)	0.1301 (5)	−0.0888 (8)	0.0295 (15)	0.050 (4)
C(2I)	0.1093 (7)	−0.1225 (5)	−0.0751 (18)	0.073 (5)
C(3I)	0.0498 (8)	−0.1280 (6)	−0.1150 (11)	0.102 (6)
C(4I)	0.0111 (4)	−0.0998 (7)	−0.0503 (13)	0.108 (6)
C(5I)	0.0319 (7)	−0.0661 (3)	0.0543 (16)	0.113 (7)
C(6I)	0.0914 (8)	−0.0606 (7)	0.0942 (8)	0.094 (6)
C(S)	−0.082	0.156	0.530	0.50

[a] The atoms Cl(1S), Cl(2S), and C(S) belong to the solvent molecule. For these and the phenyl carbon atoms *U* is the refined isotropic displacement parameter. For the other atoms *U* is one-third of the orthogonalized U_{ij} tensor. [b] Phenyl rings S–I were refined as rigid graphs.

Table V. Fractional Atomic Coordinates and Displacement Parameters (Å^2) for *trans*-[Pt(C≡C-*t*-Bu)$_2${(μ-dppm)AuCl}$_2$] (11)

atom	*x*	*y*	*z*	*U*[a]
Au(1)	−0.14619 (3)	−0.19665 (2)	−0.23119 (1)	0.052
Au(2)	0.17485 (3)	0.21486 (2)	−0.18254 (1)	0.052
Pt	−0.02354 (3)	0.20775 (2)	−0.29298 (1)	0.039
Cl(1)	−0.2298 (3)	−0.2658 (2)	−0.2927 (1)	0.092
Cl(2)	0.2860 (2)	0.0427 (1)	−0.1517 (1)	0.073
P(1)	−0.04141 (17)	0.04788 (11)	−0.27358 (7)	0.042
P(2)	−0.05462 (19)	−0.13881 (11)	−0.16961 (8)	0.046
P(3)	−0.01940 (19)	0.37117 (11)	−0.31865 (7)	0.043
P(4)	0.08038 (19)	0.38394 (12)	−0.20349 (7)	0.046
C(1)	−0.1371 (7)	0.2300 (4)	−0.2165 (2)	0.038
C(2)	−0.2002 (7)	0.2354 (4)	−0.1719 (3)	0.053
C(3)	−0.2774 (8)	0.2340 (5)	−0.1134 (3)	0.060
C(4)	−0.3891 (9)	0.1773 (6)	−0.1091 (4)	0.091
C(5)	−0.1634 (10)	0.1764 (6)	−0.0655 (3)	0.085
C(6)	−0.3553 (10)	0.3420 (6)	−0.1037 (4)	0.082
C(7)	0.0677 (7)	0.1834 (4)	−0.3706 (3)	0.051
C(8)	0.1104 (8)	0.1696 (5)	−0.4188 (3)	0.061
C(9)	0.1521 (9)	0.1592 (6)	0.4801 (3)	0.077
C(10)	0.0789 (14)	0.2587 (7)	−0.5229 (4)	0.121
C(11)	0.3174 (12)	0.1386 (10)	−0.4905 (4)	0.150
C(12)	0.1155 (15)	0.0693 (9)	−0.4889 (4)	0.152
C(13)	−0.0433 (7)	−0.0097 (4)	−0.1951 (3)	0.050
C(14)	0.1035 (7)	−0.0461 (4)	−0.3038 (3)	0.055
C(15)	0.2455 (8)	−0.0542 (6)	−0.2927 (4)	0.090
C(16)	0.3639 (10)	−0.1239 (7)	−0.3131 (6)	0.135
C(17)	0.3479 (11)	−0.1837 (7)	−0.3431 (6)	0.139
C(18)	0.2058 (13)	−0.1758 (6)	−0.3571 (4)	0.120
C(19)	0.0820 (9)	−0.1073 (5)	−0.3358 (3)	0.072
C(20)	−0.2111 (7)	0.0540 (4)	−0.3011 (3)	0.045
C(21)	−0.2251 (8)	0.0696 (5)	−0.3608 (3)	0.058
C(22)	−0.3547 (9)	0.0750 (6)	−0.3824 (3)	0.074
C(23)	−0.4721 (8)	0.0677 (5)	−0.3452 (4)	0.073
C(24)	−0.4631 (7)	0.0577 (5)	−0.2875 (4)	0.067
C(25)	−0.3346 (7)	0.0502 (5)	−0.2647 (3)	0.054
C(26)	−0.1625 (7)	−0.1291 (4)	−0.1027 (3)	0.048
C(27)	−0.1040 (8)	−0.1164 (5)	−0.0555 (3)	0.065
C(28)	−0.1883 (9)	−0.1045 (6)	−0.0038 (3)	0.074
C(29)	−0.3287 (9)	−0.1057 (6)	−0.0015 (3)	0.081
C(30)	−0.3879 (9)	−0.1175 (7)	−0.0499 (4)	0.096
C(31)	−0.3047 (8)	−0.1291 (6)	−0.0995 (3)	0.069
C(32)	0.1258 (7)	−0.2262 (5)	−0.1448 (3)	0.054
C(33)	0.1377 (8)	−0.3258 (4)	−0.1245 (3)	0.055
C(34)	0.2694 (9)	−0.3981 (5)	−0.1054 (3)	0.071
C(35)	0.3901 (10)	−0.3704 (6)	−0.1059 (5)	0.103
C(36)	0.3780 (11)	−0.2734 (7)	−0.1273 (7)	0.177
C(37)	0.2472 (10)	−0.1992 (6)	−0.1456 (6)	0.125
C(38)	−0.0617 (7)	0.4371 (4)	−0.2588 (3)	0.045
C(39)	−0.1518 (7)	0.4533 (4)	−0.3729 (3)	0.049
C(40)	−0.1385 (12)	0.4296 (7)	−0.4261 (4)	0.112
C(41)	−0.2330 (13)	0.4876 (8)	−0.4703 (4)	0.127
C(42)	−0.3417 (10)	0.5729 (6)	−0.4625 (3)	0.079
C(43)	−0.3575 (10)	0.5949 (6)	−0.4094 (4)	0.090
C(44)	−0.2600 (9)	0.5367 (5)	−0.3649 (3)	0.070
C(45)	0.1512 (7)	0.3921 (4)	−0.3487 (3)	0.051
C(46)	0.2786 (8)	0.3113 (5)	−0.3475 (3)	0.066
C(47)	0.4103 (9)	0.3283 (6)	−0.3641 (4)	0.088
C(48)	0.4107 (10)	0.j276 (7)	−0.3834 (4)	0.093
C(49)	0.2865 (10)	0.5069 (5)	−0.3846 (3)	0.076
C(50)	0.1533 (8)	0.4900 (5)	−0.3677 (3)	0.061
C(51)	−0.0150 (7)	0.4334 (5)	−0.1409 (3)	0.053
C(52)	−0.1281 (8)	0.5261 (5)	−0.1481 (3)	0.058
C(53)	−0.1975 (9)	0.5647 (6)	−0.1008 (4)	0.085
C(54)	−0.1543 (12)	0.5085 (7)	−0.0458 (4)	0.108
C(55)	−0.0426 (12)	0.4139 (7)	−0.0389 (3)	0.110
C(56)	0.0270 (11)	0.3787 (5)	−0.0858 (3)	0.074
C(57)	0.2146 (7)	0.4485 (5)	−0.2261 (3)	0.051
C(58)	0.3606 (8)	0.3946 (5)	−0.2310 (3)	0.064
C(59)	0.4654 (9)	0.4442 (7)	−0.2454 (4)	0.082
C(60)	0.4238 (9)	0.5471 (6)	−0.2541 (3)	0.086
C(61)	0.2795 (9)	0.6029 (6)	−0.2502 (4)	0.085
C(62)	0.1737 (8)	0.5545 (5)	−0.2369 (3)	0.066

[a] Equivalent isotropic displacement parameter *U* is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Complex 10: characterized by NMR in CD_2Cl_2 only; ^1H, δ 0.68 (s, *t*-Bu), 4.43 [dt, $^2J(PH) = 11$, $^2J(PH) + {}^4J(PH) = 8$ Hz, CH_2P_2]; ^{31}P, δ 9.79 [m, $^1J(PtP) = 2695$ Hz, Pt*P*], 18.58 [m, $^2J(PtP) = 89$ Hz, Au*P*].

Reaction of [Au—C≡C—*t*-Bu] with dppm. A solution of dppm (0.1382 g, 0.360 mmol) in CH_2Cl_2 (4.0 mL) was added dropwise to a suspension of [Au—C≡C—*t*-Bu] (0.1000 g, 0.360 mmol) in CH_2Cl_2 (3.0 mL). After being stirred for 3 h, the reaction mixture was concentrated and the product **12** precipitated by slow addition of pentane: yield 90%. Anal. Calcd for $C_{31}H_{31}AuP_2$: C, 56.2; H, 4.7. Found: C, 55.9; H, 4.7. MS (150 °C, m/e^+): 662, 384, 278. MW (calc) = 662. NMR in CD_2Cl_2: ^1H, δ 2.23 (s, *t*-Bu); ^{31}P, δ 31.75 (s, AuP), −24.81 (s, P free). Both ^{31}P resonances were broad, indicating some exchange process.

Reaction of 2 Equiv of [Au—C≡C—*t*-Bu] with dppm. A solution of dppm (0.0691 g, 0.180 mmol) in CH_2Cl_2 (4.0 mL) was added dropwise to a suspension of [Au—C≡C—*t*-Bu] (0.1000 g, 0.360 mmol) in CH_2Cl_2 (3.0 mL). After 3 h the reaction mixture was concentrated and the product **13**, precipitated by slow addition of pentane: yield 90%; mp, discolours to orange at 240 °C, 323–325 °C dec. Anal. Calcd for $C_{37}H_{40}Au_2P_2$: C, 47.2; H, 4.2. Found: C, 47.4; H, 4.3. MS (200 °C, m/e^+): 778, 662, 581, 384—no parent ion observed at m/e 940. NMR in CD_2Cl_2: ^1H, δ 3.43 [t, $^2J(PH) = 11$ Hz, CH_2P_2], 1.50 (s, *t*-Bu); ^{31}P, δ 28.65 (s, AuP).

Preparation of [Pt(C≡C-*t*-Bu)$_2$(dppm)$_2$]. A solution of *t*-BuC≡CLi (2.8 mmol) in ether (20 mL) was added at 0 °C to a suspension of [$PtCl_2$(dppm)] (0.7187 g, 1.105 mmol) and dppm (0.4248 g, 1.105 mmol) in diethyl ether (100.0 mL). The reaction mixture was warmed to room temperature and stirred for 2 h. Hydrolytic workup gave the product (1.1200 g, 90%) as a pale yellow solid.

The yellow product was confirmed to be [Pt(C≡C-*t*-Bu)$_2$(dppm)$_2$] by ^1H and ^{31}P (room and low temperature) NMR and mass spectrometry. NMR in CD_2Cl_2: ^1H, δ 4.84 [m, $^3J(PtH) = 44$ Hz, CH_2P_2], 0.72 (s, *t*-Bu); ^{31}P (−80 °C), δ 1.32 [m, $^1J(PtP) = 2540$ Hz, Pt*P*], −35.4 [m, $^2J(P^AP^B) + 4^J(P^AP^B) = 60$ Hz, free P]. MS (m/e^+) 1125, 841. Anal. Calcd for $C_{62}H_{62}P_4Pt{\cdot}0.25CH_2Cl_2$: C, 65.2; H, 5.45. Found: C, 65.3; H, 5.1. The presence of CH_2Cl_2 was confirmed by ^1H NMR.

X-ray Diffraction Studies of [PtCl(C≡C-*t*-Bu)(*μ*-dppm)$_2$Au][Cl]·CH_2Cl_2 (2·CH_2Cl_2) and [Pt(C≡C-*t*-Bu)$_2${(*μ*-dppm)AuCl}$_2$] (11). Crystals of 2·CH_2Cl_2 were grown from a CH_2Cl_2/pentane solution and those of **11** from a CD_2Cl_2/pentane solution. All diffraction measurements were made with graphite-monochromated molybdenum radiation and an Enraf-nonius CAD4 diffractometer.

The unit cell constants (Table III) were deterimined by a least-squares treatment of the setting angles for 25 reflections, with $12 < \theta < 17°$ for **2** and $14 < \theta < 17°$ for **11**. Preliminary investigation of the diffraction patterns showed that the Laue group is $2/m$ for **2** and $\bar{1}$ for **11** and that the crystal lattice is primitive for each compound. The observed systematic absences of reflections were compatible with space groups $P2_1/a$ for **2** and $P\bar{1}$ for **11**.

For each compound two strong reflections were remeasured every 2 h, but their intensities showed only random fluctuations not exceeding 3% of the mean values. The integrated intensities of reflections, derived in the usual manner,[26] were corrected for Lorentz, polarization, and absorption effects. For **2**, 528 symmetry related reflections were averaged to yield 264 independent ones and *R*(internal) of 0.024; for **11**, averaging 1360 symmetry related reflections to get 680 independent ones gave *R*(internal) of 0.017. Only unique reflections with $I \geq 3\sigma(I)$, 4212 for **2** and 7471 for **11**, were used in the structure analyses.

The crystal structures of both compounds were determined by the heavy-atom method. The positions of the metal atoms were obtained from Patterson functions and those of the remaining non-hydrogen atoms from difference electron density maps. The structures were refined minimizing the function $w(|F_o| - |F_c|)^2$, where $w = \sigma^{-2}(|F_o|)$.

The structure of **2** was refined by full-matrix least squares. At a later stage of refinement difference electron density maps showed three broad peaks indicating the presence of a disordered CH_2Cl_2 solvent molecule. Attempts to refine the positional parameters of its C and Cl atoms led to a highly distorted geometry; these atoms were therefore included in the structural model with fixed positions, and only their common isotropic thermal parameter was refined. All hydrogen atoms of the [PtCl(C≡C-*t*-Bu)(*μ*-dppm)$_2$Au]$^+$ cation, many of which could be found in low-angle difference maps, were included in the structural model in calculated positions (C–H = 1.00 Å) and with $U(H) = 1.2U(C)$, where $U(C)$ is the isotropic thermal parameter of the carbon atom to which the hydrogen is bonded. The phenyl rings were constrained to $6/mmm$ symmetry, C–C = 1.38 Å, and their carbon atoms were allowed only isotropic thermal parameters. The remaining non-hydrogen atoms were refined with anisotropic thermal parameters. The refinement converged at $R = 0.034$ and $R_w = 0.043$. In the final difference electron density synthesis the function values range from −1.32 to +0.93 e Å^{-3}, the extreme ones being associated with the positions of the metal atoms and of disordered solvent molecules. The final atomic coordinates are shown in Table IV.

The structure of **11** was refined by a two large block approximation to the normal least-squares matrix. In the final stages of refinement all non-hydrogen atoms were allowed anisotropic thermal parameters. Only the hydrogen atoms of the dppm ligands, most of which could be located in a low-angle difference map, were included in the structural model; they were allowed to ride on the carbon atoms to which they are bonded but were constrained to C–H = 1.07 Å and $U_{iso} = 0.05$ Å^2. The refinement converged at $R = 0.027$ and $R_w = 0.036$. The function values of the final difference electron density synthesis were in the −0.82 to +0.92 e Å^{-3} range, the extreme values being associated with the positions of the heavy atoms. The final atomic coordinates are listed in Table V.

All calculations were performed on a GOULD SEL 32/7 supermini computer, using the locally developed GX program package.[27] Neutral atom scattering factors and anomalous dispersion corrections were taken from ref 28.

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Supplementary Material Available: Listings of anisotropic displacement parameters, bond lengths, and bond angles for [PtCl(C≡C-*t*-Bu)(*μ*-dppm)$_2$Au][Cl]·CH_2Cl_2 and [Pt(C≡C-*t*-Bu)$_2${(*μ*-dppm)AuCl}$_2$] (Tables SI-SVI) (9 pages); listings of observed and calculated structure amplitudes (52 pages). Ordering information is given on any current masthead page.

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