

(Phenylethynyl)trimethylphosphonium Bromide and Bromoaurates(I)

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(Phenylethynyl)trimethylphosphonium bromide (**1**) has been reinvestigated by NMR spectroscopy and its crystal structure determined. In the monoclinic crystals, the cations are arranged in layers in the *a-c* planes, with their P-C≡C-Ph axes parallel within one layer, but alternating in consecutive layers. The bromide anions are accommodated in channels between the cations. The spectroscopic and structural results are in agreement with the special reactivity pattern documented for ethynylphosphonium salts, in particular with the sensitivity to nucleophiles which *e. g.* prevents standard ylide formation. A slurry of polymeric phenylethynylgold [PhC≡CAu]_n in dichloromethane reacts with [Me₃PC≡CPh]Br to give a clear solution of [Me₃PC≡CPh]⁺ [PhC≡CAuBr]⁻ (**2**). In a similar reaction, with soluble pentafluorophenylgold(tetrahydrothiophene), C₆F₅Au(tht), the salt [Me₃PC≡CPh]⁺ [C₆F₅AuBr]⁻ (**3**) is produced. All attempts to generate gold(I) complexes of the corresponding phosphonium ylide [Me₂(PhC≡C)P=CH₂] by treatment of the two phosphonium salts (**2**, **3**) with strong base were not successful owing to side reactions induced by base.

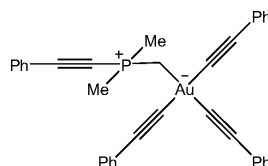
Key words: Ethynylphosphonium Salts, Phosphonium Salts, Bromoaurates(I), Aurates(I)

Introduction

In recent work the first examples of tri(alkynyl)gold(III) complexes (RC≡C)₃Au(L) have been prepared. A strong trialkylphosphine donor L is required in order to obtain stable compounds which can be isolated and structurally characterized, as shown *e. g.* for (PhC≡C)₃Au(PMe₃) and its dichloromethane solvate. The donor capacity of triarylphosphines like Ph₃P is not sufficient to lend a comparable stability [1].

However, in the series of exploratory experiments it was observed by serendipity that *phosphonium ylides* may also function as auxiliary ligands L, as demonstrated for the complex [Me₂(PhC≡C)PCH₂]Au(C≡CPh)₃ (**1**). This compound was obtained as a minor by-product in the reaction of (thf)AuCl₃ or (thf)AuBr₃ with PhC≡CLi (molar ratio 1 : 3) followed by the addition of Me₃P and fully characterized by structural methods [1].

To rationalize the unexpected result the following steps were assumed for the overall reaction: a) The partial substitution, PhC≡C for Cl/Br, in (thf)AuCl₃ or (thf)AuBr₃ is accompanied by some reductive elimination of PhC≡C-C≡C or PhC≡CCl/Br leaving the corresponding gold(I) complexes. b) The alkynyl halides



Formula I.

produced in step a) can quaternize the Me₃P ligand present in the reaction mixture to give the phosphonium salts [Me₃PC≡CPh]⁺ Cl⁻/Br⁻. c) After reductive elimination of alkynes in step a) there is an excess of PhC≡CLi left in solution which can act on the phosphonium salts as a base to generate the ylide Me₂(PhC≡C)P=CH₂. d) This ylide can trap any solvated Au(C≡CPh)₃ or react with its Me₃P adduct to give the ylide complex. (It has been established previously beyond doubt that non-stabilized phosphonium ylides like Me₃PCH₂ are superior ligands for gold(I) and gold(III) as compared to most other donors including in particular tertiary phosphines [2–4].)

In an attempt to prove this reaction sequence, some of the proposed intermediates have been prepared and subsequently subjected to the respective treatment, but the expected gold(I) complex [Me₂(PhC≡C)PCH₂]AuC≡CPh could not be detected. Because of the failure of this crucial step, there

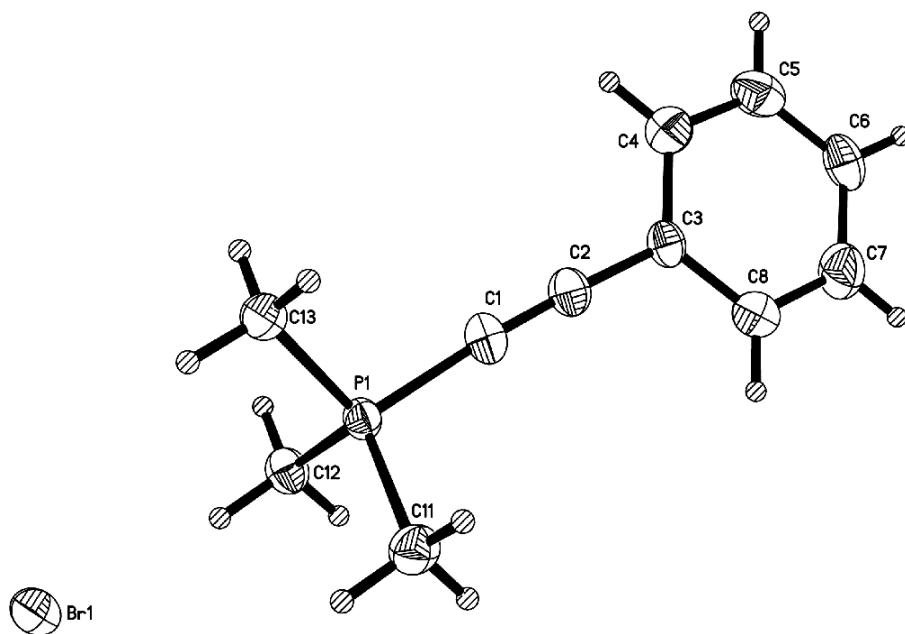


Fig. 1. Cation and anion of compound **1** with atomic numbering (ORTEP, 50% probability ellipsoids, H atoms with arbitrary radii). Selected bond lengths [Å] and angles [°]: P1-C1 1.739(3), P1-C11 1.778(3), P1-C12 1.777(2), P1-C13 1.776(3); C1-C2 1.202(4), C2-C3 1.431(4). P1-C1-C2 175.6(3), C1-C2-C3 177.5(3), C1-P1-C11 108.75(12), C1-P1-C12 108.69(12), C1-P1-C13 108.56(13), C11-P1-C12 109.75(13), C11-P1-C13 110.70(12), C12-P1-C13 110.52(12).

was no substrate basis for the oxidative addition using $[\text{PhC}\equiv\text{C})_2\text{TiCl}]_2$, which could finally have afforded the target gold(III) complex (**I**). This addition had been carried out successfully with $\text{PhC}\equiv\text{CAu}(\text{PMe}_3)$ [1].

The present report is an account of the pertinent investigations.

Results

(Phenylethynyl)trimethylphosphonium Bromide (**1**)

There is only a limited number of mixed ethynylphosphonium salts of the type $[\text{R}_3(\text{R}'\text{C}\equiv\text{C})\text{P}]^+\text{X}^-$ (with $\text{R}/\text{R}' = \text{alkyl and/or aryl}$) in the literature [5–11]. Their preparation generally followed the most obvious route, *vic.* the quaternization of tertiary phosphines with alkynyl halides, but other routes have also been described [5, 6, 11]. For the present case, oriented at the substitution pattern of the target molecule (**I**) and the proposed step b) of its formation (*v. s.*), trimethylphosphine and phenylethynyl bromide were chosen as the reactants. In agreement with literature observations [11], the reaction was found to be fast and exothermic in a tetrahydrofuran / toluene mixed solvent at r. t. The product precipitated as a colourless crystalline solid which could be recrystallized from dichloromethane/pentane (86% yield).



The compound is readily soluble in dichloro- and

trichloromethane. The solutions in CD_2Cl_2 show a $\{^1\text{H}\}^{31}\text{P}$ NMR signal at $\delta = 5.4$ ppm. The ^1H NMR spectrum features the doublet of the methyl protons at $\delta = 2.57$ with $^2J(\text{P},\text{H}) = 15.2$ Hz (9H) and the phenyl multiplet at 7.41–7.67 ppm (5H). The $\{^1\text{H}\}^{13}\text{C}$ resonance of the methyl groups appears at $\delta = 12.6$ with $^1J(\text{P},\text{C}) = 15.2$ Hz. The ethynyl carbon atoms give rise to two doublets at $\delta = 72.9$ and 112.5 with $^{1/2}J(\text{P},\text{C}) = 163.7/29.2$ Hz, respectively. The phenyl ^{13}C resonances include a doublet for C-1 at $\delta = 117.8$ with $^1J(\text{P},\text{C}) = 4.5$ Hz and singlets for C-2, C-3 and C-4 at $\delta = 129.0$, 132.9 and 132.4. The data follow trends already demonstrated in previous studies for homologous ethynylphosphonium salts [7, 8]. The IR spectrum of the solid in KBr has a band of the $\nu(\text{C}\equiv\text{C})$ vibration at 2186 cm^{-1} [11]. These spectroscopic data are important benchmarks for the bromoaurate(I) complexes (below) which have the same cation.

Crystals of compound **1** are monoclinic, space group $P2_1/c$, with $Z = 4$ formula units in the unit cell (Figs 1–3). In the cation, the phosphorus atom has an only slightly distorted tetrahedral environment. All C-P-C angles are in the narrow range from 108.55(12)–110.75(13)°. The three P-C(Me) distances are equal (1.777 ± 0.001 Å) within the standard deviations (0.003 Å), and significantly longer than the P-C1(ethynyl) distance of 1.739(3) Å clearly reflecting the different hybridization of the carbon atoms and a resonance effect. The ethynyl group is

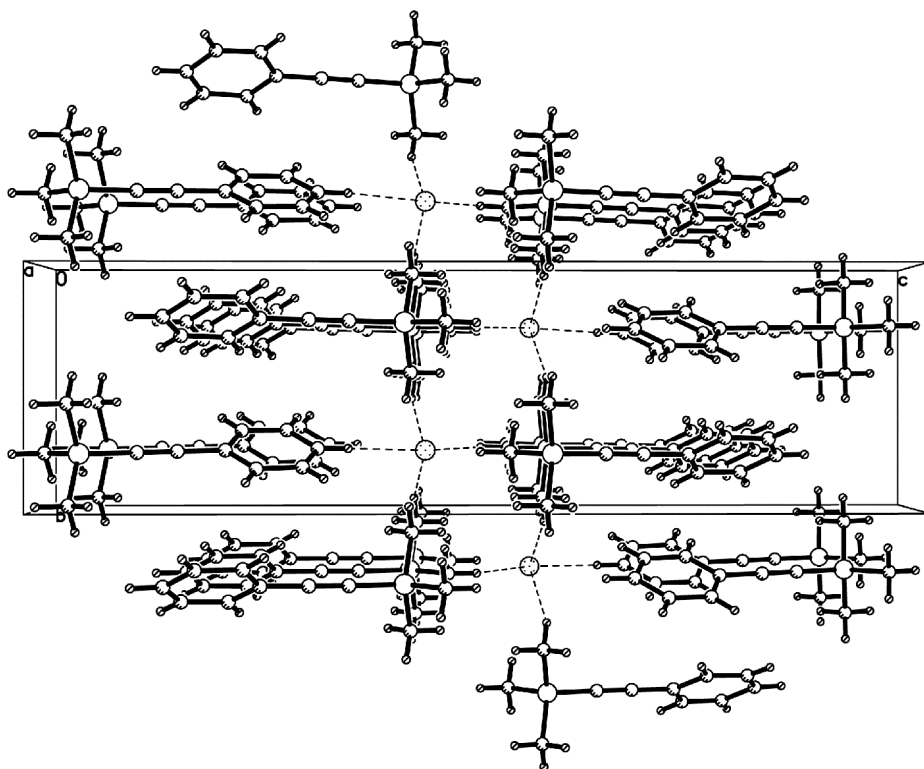
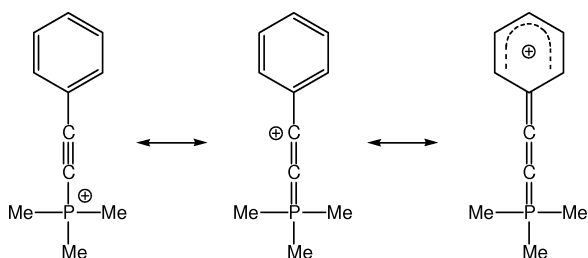


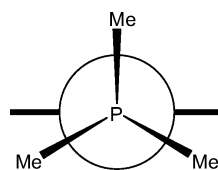
Fig. 2. Projection of the crystal structure of compound **1** along the *a* axis (arbitrary radii). Br-H-C contacts are indicated by thin broken lines. [(Ph)C6-H-Br 2.971, (Me)C-H-Br 2.865, 2.897, 2.986 Å. Only two layers of bromine atoms are shown.]



Formula II.

quasi-linear with angles P1-C1-C2 and C1-C2-C3 at 175.6(3) and 177.5(3)°, respectively. The bond lengths C1-C2 = 1.202(4) and C2-C3 = 1.431(4) Å are also as expected for a triple bond in conjugation with a phenyl substituent. Finally, there is a concomitant significant shortening of the bonds C3-C4 and C3-C8 (average 1.402 Å), which are longer than the remainder four bonds of the phenyl ring (average 1.379 Å) indicating resonance involving electron redistribution as indicated by Formula II.

The orientation of the plane of the phenyl group with respect to the threefold rotor of the Me₃P group corresponds to the most strain-free (minimal eclipse) conformation, *vic.* perpendicular to the projection of one



Formula III.

P-C(Me) bond along the main axis of the cation (Formula III and Fig. 3).

In the crystal, the cations form layers in the *a-c* planes. The orientation of the main axes of the cationic units is opposite in consecutive layers, but unidirectional and parallel to the *c*-axis in each individual layer (Figs 2, 3). The bromide anions are accommodated in channels between the cations and have long C-H...Br contacts with three methyl groups and one phenyl group (in its *p*-position) which are indicated by thin dotted lines in Fig. 2.

(Phenylethynyl)trimethylphosphonium bromo(phenylethynyl)aurate(I) (2)

A suspension of polymeric phenylethynylgold(I), [(PhC≡C)Au]_n, in dichloromethane reacts with an equivalent quantity of compound **1** to give a clear so-

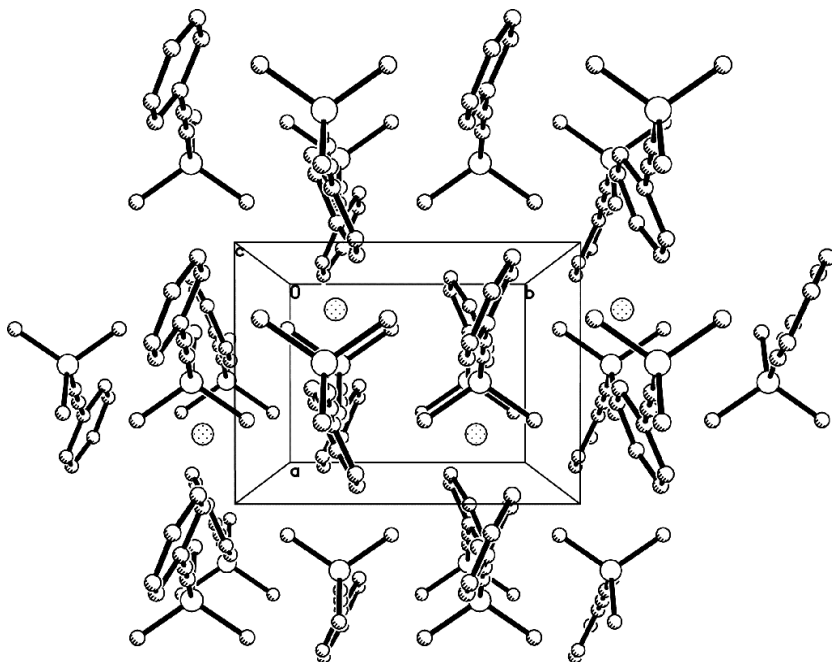
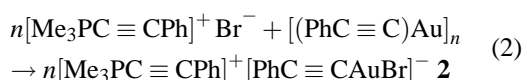


Fig. 3. Projection of the crystal structure of compound **1** along the *c* axis (arbitrary radii).

lution. Upon addition of pentane the product **2** precipitates as a colourless solid (90% yield, m. p. 91–93 °C).

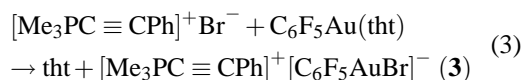


The NMR spectra of solutions of compound **2** in dichloromethane show the ^{31}P signal at $\delta = 5.9$ ppm, virtually unchanged as compared to the value for **1**, and the same is true for the ^{13}C and ^1H cation resonances (Exp. Section). The anion has separate resonances for its $\text{PhC}\equiv\text{C}$ group which are readily assigned referring to literature data of other salts with the $[\text{PhC}\equiv\text{CAuX}]^-$ anions ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) [12–15].

These reference salts have been prepared in analogous reactions employing tetraalkylammonium bromides $[\text{R}_4\text{N}]^+\text{Br}^-$ with $\text{R} = \text{Et}, ^n\text{Bu}$ as the reagents for $[(\text{PhC}\equiv\text{C})\text{Au}]_n$ [12]. Related compounds were obtained with $[(\text{Ph}_3\text{P})_2\text{N}]^+$ as the cation and simple $\text{HC}\equiv\text{C}$ [14] or substituted phenylethynyl groups [15] in the anion. In all cases their spectroscopic data are different from those of the related homoleptic $[(\text{RC}\equiv\text{C})_2\text{Au}]^-$ anions which were identified unequivocally [13]. For product **2**, therefore, an isomeric constitution with two different homoleptic anions $[\text{AuBr}_2]^-$ and $[\text{PhC}\equiv\text{C})_2\text{Au}]^-$ in the ratio 1:1 can be excluded.

(Phenylethynyl)trimethylphosphonium Bromo(pentafluorophenyl)aurate(I) (**3**)

Compound **1** reacts with (tetrahydrothiophene) pentafluorophenylgold(I), $\text{C}_6\text{F}_5\text{Au}(\text{tht})$, in homogeneous dichloromethane solution to give compound **3** and tht. The phosphonium salt is isolated as colourless plates (80% yield, m. p. 81–82 °C).

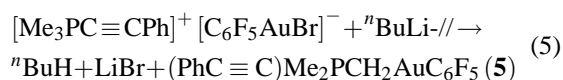
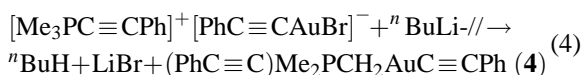


In the NMR spectra of compound **3** in dichloromethane solution the signals of the cation show the same chemical shifts and multiplicities as those of **1** and **2** (Exp. Section). For the anion, the usual multiplet ^{13}C resonances of the pentafluorophenyl group are detected. Salts with anions $[\text{C}_6\text{F}_5\text{AuX}]^-$ with $\text{X} = \text{Cl}, \text{Br}, \text{I}$ were prepared in the course of several previous studies [16–20]. The bromo complex anion in particular was also observed in the phosphonium salts with the cations MePh_3P^+ , EtPh_3P^+ and $^n\text{PrPh}_3\text{P}^+$ [16] and in the ammonium salt with the cation $^n\text{Bu}_4\text{N}^+$ [20]. The chloro complex has been isolated with the “PPN” cation, $[(\text{Ph}_3\text{P})_2\text{N}]^+[\text{C}_6\text{F}_5\text{AuCl}]^-$ [16] and the crystal structure of $[\text{BzPh}_3\text{P}]^+[\text{C}_6\text{F}_5\text{AuCl}]^-$ has been determined [18]. Closely related compounds were obtained with the 2,4,6-trifluorophenyl ligand [19]. Based on the

data of **3** and of these reference compounds a structure with homoleptically coordinated anions can again be excluded.

Attempted conversion of **2** and **3** into ylide complexes

In attempts to convert compounds **2** and **3** into the corresponding gold(I) ylide complexes (**4**, **5**) the compounds were reacted with strong base (ⁿBuLi) in diethylether or tetrahydrofuran solution under mild conditions (0° and –78 °C). The expected products [eq. (4) and (5)] could not be isolated or detected in the reaction mixtures (by NMR spectroscopy).



Therefore, no further experiments could be carried out aiming at the preparation of the original target complex, *vic.* the gold(III) complex $[(\text{PhC}\equiv\text{C})_3\text{AuCH}_2\text{PMe}_2(\text{C}\equiv\text{CPh})]$, **I**.

Discussion

Although quite a number of trialkyl- and triaryl-(ethynyl)phosphonium salts have been prepared and used in a variety of transformations [5–11], to the best of our knowledge no compound has been structurally characterized. The structure of compound **1**, a very simple, representative example has now been determined. Its structural details nicely reflect the resonance situation proposed on the basis of the reactivity pattern observed in previous experiments. Thus, the hydrolysis of $[\text{Ph}_3\text{PC}\equiv\text{CPh}]^+ \text{Br}^-$ was found to lead either to Ph_3PO , $\text{PhC}\equiv\text{CH}$ and HBr , or to $[\text{Ph}_3\text{PCH}_2\text{C}(\text{O})\text{Ph}]^+ \text{Br}^-$, depending on the reaction conditions [5, 6], indicating a primary nucleophilic attack of H_2O at the β carbon atom P-C \equiv C-Ph. Similar results were obtained with amines R_2NH , phosphines R_2PH and thiols RSH [6]. Compound **1** was shown to undergo base-catalyzed polymerization at only slightly elevated temperatures. The mechanism proposed for this polymerization involves a primary nucleophilic attack of pyridine or picoline at C- β [11].

The bond lengths in the P-C \equiv C-Ph unit of compound **1** are in agreement with a delocalization of the positive charge over P, C- β and the periphery of the phenyl ring (**II**). The evaluation of the chemical shifts

of the atoms of the P-C \equiv C-Ph unit of compound **1** and of reference compounds [7, 8] leads to the same conclusions.

In previous work, most reactions were carried out with triaryl(ethynyl)phosphonium salts for which standard ylide formation is excluded. Reactions with base in all cases took a different course including either P-C bond breaking or even an increase of the coordination number of the phosphorus atom to give hypercoordinated species such as $\text{Ph}_3\text{P}(\text{C}\equiv\text{CP})_2$ [10].

However, among the reactions and transformations of the few trialkyl(ethynyl)phosphonium salts reported in the literature, which are homologues of compound **1**, there is also no example for the formation of the corresponding ylides. It is therefore very likely that attack of a strong base on the $[\text{Me}_3\text{PC}\equiv\text{CPh}]^+$ cation of compounds **2** and **3** is not taking the course formulated in equations (4, 5) but leads to either P-C bond cleavage or to a reversible or irreversible addition of the nucleophile to C- β , possibly followed by polymerization [11]. Deprotonation at a methyl group by base is therefore overruled and no ylide can be generated. The original concept of the present work was based on the hope that in the presence of the metal center of the anions in compounds **2** and **3** any “hot” ylide intermediate would be trapped and stabilized, but the experiments proved that this is not the case. It remains even more surprising then that compound **I** was formed in the reaction mentioned in the introduction [1].

Experimental Section

General

All experiments were routinely carried out under an atmosphere of pure and dry nitrogen. Solvents were thoroughly dried using conventional methods and saturated with nitrogen, glassware was oven-dried and filled with nitrogen. Standard equipment was used throughout. Me_3P [21], $\text{PhC}\equiv\text{CBr}$ and $[\text{Me}_3\text{PC}\equiv\text{CPh}]\text{Br}$ [11], $[(\text{PhC}\equiv\text{C})\text{Au}]_n$ [22] and $[\text{C}_6\text{F}_5\text{Au}(\text{tht})]$ [12] were prepared according to literature procedures. NMR: Jeol JNM-GX-270/400 and Jeol JNM-LA-400; residual resonances of the deuterated solvent, converted to TMS, as standards for ^1H and ^{13}C signals; conc. aqueous H_3PO_4 as an external standard for ^{31}P ; δ values in [ppm], J values in [Hz].

Compound **1**

The solution of $\text{PhC}\equiv\text{CBr}$ (0.5 g, 2.8 mmol) in 25 ml of tetrahydrofuran was combined with 3 ml of a 1.0 M solution of Me_3P in toluene at r. t. with efficient stirring. A colourless

Table 1. Crystal and structure solution data of compound **1**.

	[Me ₃ PC≡CPh]Br
Empirical formula	C ₁₁ H ₁₄ BrP
<i>M_r</i>	257.10
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> [Å]	5.7525 (1)
<i>b</i> [Å]	7.6158 (2)
<i>c</i> [Å]	27.3932(6)
β [°]	91.308(1)
<i>V</i> [Å ³]	1199.78(5)
ρ _{calc} [g cm ⁻³]	1.423
<i>Z</i>	4
<i>F</i> (000)	520
μ (Mo-Kα) [cm ⁻¹]	35.16
<i>T</i> [K]	143
Reflections measured	27506
Reflections unique	2204 [R _{int} = 0.034]
Refined parameters	122
<i>R</i> 1 [<i>I</i> ≥ 2σ(<i>I</i>)]	0.0299
<i>wR</i> 2 ^a	0.0809
Weighting scheme	<i>a</i> = 0.0420 <i>b</i> = 0.9455
σ _{fin} (max/min)/eÅ ⁻³	0.528 / -0.517

^a $wR2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$.

precipitate was formed in an exothermic reaction. The suspension was stirred for 12 h at 40 °C and filtered. The product was recrystallized from dichloromethane/pentane; yield 0.61 g (86%), m. p. 217–220 °C (lit. 218–221 °C [11]). C₁₁H₁₄BrP (257.10): calcd. C 51.39, H 5.49; found C 50.76, H 5.50. IR (KBr): ν(C≡C) 2186 cm⁻¹. NMR (CD₂Cl₂, 25 °C), ³¹P{¹H}: 5.4, s, ¹³C{¹H}: 12.6, d, ¹J_{P,C} 62.3, Me; 72.9, d, ¹J_{P,C} 163.7, P-C≡C; 112.5, d, ²J_{P,C} 29.2, C≡C-Ph; 117.8, d, ⁴J_{P,C} 4.5, *i*-Ph; 129.0, s, *o*-Ph; 132.4, s, *p*-Ph; 132.9, s, *m*-Ph. ¹H: 2.57, d, ²J_{P,H} 15.2, 9H, *Me*; 7.41–7.67, m, 5H, *Ph*.

Compound **2**

Compound **1** (77 mg, 0.3 mmol) was added to a suspension of [(PhC≡C)Au]_n (90 mg, 0.3 mmol) in 25 ml of dichloromethane at 20 °C. After 1 h a clear colourless solution was obtained. Pentane was added to precipitate the product, which was filtered off and dried in a vacuum; yield 150 mg (90%), m. p. 91–93 °C. C₁₉H₁₉AuBrP (555.20): calcd. C 41.10, H 3.45; found C 40.90, H 3.21%. NMR (CD₂Cl₂, 25 °C), ³¹P{¹H}: 5.9, s, ¹³C{¹H}: 14.2, d, ¹J_{P,C} 61.8, Me; 73.0, d, ¹J_{P,C} 170.4, P-C≡C; 99.7, s, Au-C≡C-

Ph; 115.3, d, ²J_{P,C} 31.7, P-C≡C; Au-C not observed. 117.1, 127.4, 129.4, and 133.4, all s, for *i*, *o*, *p*, and *m* of PhC₂Au, respectively. 118.3, d, ³J_{P,C} 4.2, *i*-PhC₂P; 130.3, 134.0, 134.5, all s, for *o*, *p*, *m* of PhC₂P, respectively. ¹H: 2.44, d, ²J_{P,H} 14.8, 9H, *Me*; 7.11–7.42, m, 5H, Ph(C₂Au); 7.42–7.76, m, 5H, Ph(C₂P).

Compound **3**

(C₆F₅)Au(tht) (91 mg, 0.2 mmol) was treated with compound **1** (51 mg, 0.2 mmol) in 25 ml of dichloromethane at 20 °C. A clear solution was obtained. The product was precipitated by adding pentane, filtered off and dried in a vacuum; yield 99 mg (80%), m. p. 81–82 °C. C₁₇H₁₄AuBrF₅P (621.13): calcd. C 32.87, H 2.27; found C 32.77, H 2.01. NMR (CD₂Cl₂, 25 °C), ³¹P{¹H}: 5.7, s, ¹³C{¹H}: 13.0, s, ¹J_{P,C} 62.3, Me; 71.1, d, ¹J_{P,C} 173.0, P-C≡C; 114.6, d, ²J_{P,C} 32.7, P-C≡C; 117.2, d, ⁴J_{P,C} 4.7, *i*-Ph; 129.0, 132.8 and 133.1, all s, for *o*, *p* and *m* of Ph, respectively; 135.2, 138.8, 146.7, and 150.0, all br m., for *i*, *o*, *p*, and *m* of C₆F₅, respectively. ¹H: 2.38, d, ²J_{P,H} 14.6, 9H, *Me*; 7.41–7.69, m, 5H, *Ph*.

Crystal structure determination

The single crystal of **1** was placed in inert oil on the top of a glass pin and transferred to the cold gas stream of the diffractometer. Crystal data was collected using a Nonius DIP2020 system with monochromated Mo-Kα (λ = 0.71073 Å) radiation at -130 °C. The structure was solved by direct methods (SHELXS-97) and refined by full matrix least-squares calculations on *F*² (SHELXL-97) [23]. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and refined using a riding model with fixed isotropic contributions. Further information on crystal data, data collection and structure refinement are summarized in Table 1. Important interatomic distances and angles are given in the caption of Fig. 1. Complete lists of displacement parameters and tables of interatomic distances and angles have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. The data are available on request on quoting CCDS-606390.

Acknowledgements

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