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The course of oxidative addition reactions of haloalkynes and haloalkenes to dimethyl- and dialkynylaurate(I) anions $[RAuR]^-$

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Dedicated to Professor D. Michael R. Mingos.

Abstract

The reactions of halo-alkynes Cl–C≡CH, C–lC≡C–Cl or PhC≡C–I with solutions of $Li^+[MeAuMe]^-$ in diethylether containing Ph_3P do not give the expected oxidative addition products $Me_2(RC{\equiv}C)Au(PPh_3)$ with R = H, Cl, Ph. A mixture of other complexes is obtained instead which are generated in secondary reactions involving reductive elimination of ethane and/or dialkyne. However, addition of the halo-alkene $H(Cl)C{=}CCl_2$ to the same substrate solution affords *trans*-Me_2[*trans*-$H(Cl)C{=}C(Cl)]Au(PPh_3)$ in good yield. Its molecular structure with *pseudo*-C_s symmetry has been determined by the solution NMR spectra and a single-crystal X-ray diffraction study. The reaction of methyl iodide with solutions of $Li^+[RC{\equiv}CAuC{\equiv}CR]^-$ in diethylether containing PPh_3 give the quaternary salts Ph_3PMe^+ $[RC{\equiv}CAuC{\equiv}CR]^-$ as the main products and only small amounts of *cis*-$Me_2(RC{\equiv}C)Au(PPh_3)$ complexes probably formed in a series of oxidative addition, reductive elimination, and substitution reactions. The structure of Ph_3PMe^+ $[PhC{\equiv}CAuC{\equiv}CPh]^-$ has been determined.

Keywords: Gold complexes; Oxidative addition; Reductive elimination; Alkenylgold(III) complex; Alkynylgold(III) complex; *cis*-Dialkylgold(III) complex

1. Introduction

In the last two decades, alkynylgold(I) complexes (L)Au–C≡C–R have received growing interest due to their potential for a range of applications, mainly in non-linear optical and optoelectronic devices, as well as in mesogenic and multidimensional arrays [1]. Their rigid-rod structures with highly polarizable π-systems parallel to the molecular axis can be tuned by introducing a large variety of donors L and substituents R. The research activities have led to an explosive growth of the literature [2–6], for which only a few key references can be given [7–12].

By contrast, alkynylgold(III) complexes have remained almost unknown, and it was only recently that the first complexes of the types $(L)AuR'_2(C{\equiv}CR)$ and $(L)Au(C{\equiv}CR)_3$ could be isolated and fully characterized [13,14]. The homoleptic tetraalkynylgold(III) anions $[Au(C{\equiv}CR)_4]^-$ were also finally discovered as components of salts with large quaternary cations [14]. All these alkynylgold(III) species were shown to undergo facile reductive elimination of alkanes R'_2 or dialkynes $RC{\equiv}CC{\equiv}CR$ to leave the corresponding alkynylgold(I) analogues $(L)AuC{\equiv}CR$ and $[Au(C{\equiv}CR)_2]^-$, respectively. For the mixed complexes of the type $(L)AuR'_2(C{\equiv}CR)$ only the *cis*-isomers have been confirmed.

In the course of complementary attempts to find better access to *alkynyl* gold(III) complexes in general, and to compounds *trans*-$Me_2(RC{\equiv}C)Au(L)$ in particular, the oxidative addition of alkynyl halides to lithium dimethylaurates(I), and of alkyl halides to dialkynylaurates(I), were also probed, but the results were not encouraging. As described below, all reactions of this type were quickly followed by substitution, redistribution or reductive elimination processes. However, from peripheral observations it became obvious that *alkenyl* gold(III) complexes can be

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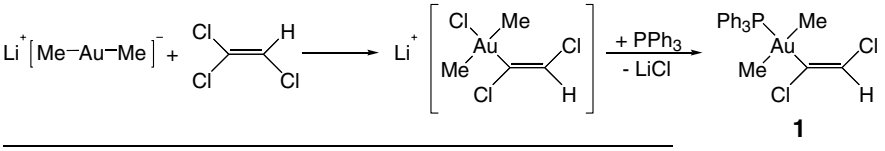
obtained via this route as demonstrated in detail for the addition of trichloroethene.

2. Preparative results

2.1. Oxidative addition of alkynyl halides to Li[MeAuMe]/PPh_3

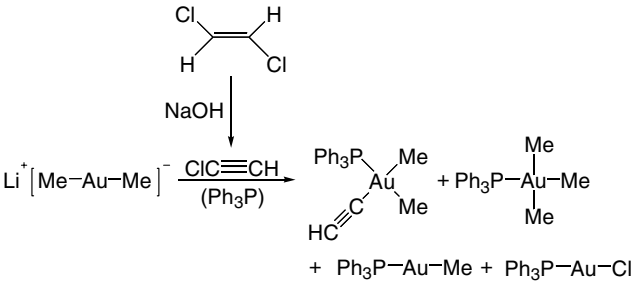
Following the pioneering work of Tobias and co-worker [15,16], lithium dimethylaurates(I) are readily obtained by treatment of Ph_3PAuCl with two equivalents of MeLi in diethylether. The solutions of the reagent thus obtained contain one equivalent of the Ph_3P ligand liberated in the process (Eq. (1)). In the present context, this is to be taken as an advantage, since the phosphine can function as a stabilizing ligand for the products of subsequent reactions

$$Ph_3P{-}Au{-}Cl \xrightarrow{+2MeLi} Li^+[Me{-}Au{-}Me]^- + PPh_3 + LiCl \quad (1)$$



1 (4)

Treatment of the solutions of Li[MeAuMe]/PPh_3 with an excess of HC≡C–Cl in diethylether gave a mixture of products, in which Ph_3PAuMe, Ph_3PAuMe_3, Ph_3PAuCl, and traces of *cis*-$Me_2(HC{\equiv}C)AuPPh_3$ were positively identified by their NMR spectra (Eq. (2))



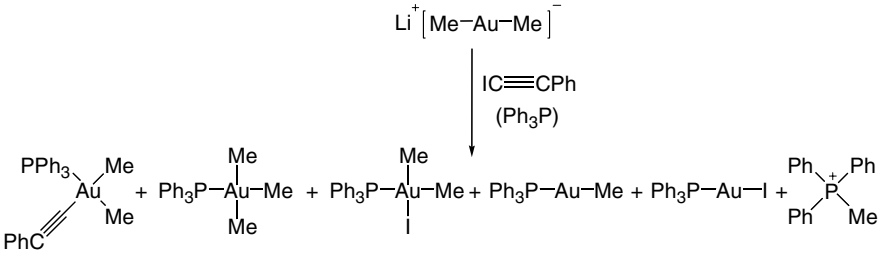
(2)

The same reaction with phenylethynyl iodide PhC≡C–I afforded Ph_3PAuMe, Ph_3PAuMe_3, Ph_3PAuI, *cis*-$Me_2IAuPPh_3$, and *cis*-$Me_2(PhC{\equiv}C)AuPPh_3$, and thus followed a similar pattern (Eq. (3)). According to the NMR data, the reaction mixture also contained a methyltriphenylphosphonium salt with an unknown anion, indicating quaternization of the tertiary phosphine.

When the reaction was first carried out with Cl–C≡C–Cl, an unexpected product was identified, which subsequently could be traced to an impurity in the dichloroethyne: Cl–C≡C–Cl had been prepared from trichloroethene by dehydrochlorination. With the conditions applied some $Cl_2C{=}C(Cl)H$ also evaporates and therefore some starting material is left in the product [17]. Addition of this alkene to the $[MeAuMe]^-$ anion appears to give the *trans*-(alkenyl)(chloro)dimethylaurate anion, of which the chlorine atom is finally substituted by the PPh_3 ligand (Eq. (4)). Further purified Cl–C≡C–Cl gave only traces of this product together with $(Ph_3P)AuMe$ and $(Ph_3P)AuCl$. It should be noted, that in neither case any evidence for the formation of isomeric *cis*-H(Cl)C=C(Cl)- or $Cl_2C{=}CH$-complexes could be found. The above observations suggest that *alkynyl* halide addition to [MeAuMe]$^-$ is very slow whilst *alkenyl* halide addition takes place easily

Compound **1** in Eq. (4) is a colourless crystalline solid which decomposes above 125 °C. It is readily soluble in di- and trichloromethane, but almost insoluble in pentane. The ^1H and $\{^1H\}^{13}C$ NMR spectra of solutions in CD_2Cl_2 show single doublets for the methyl hydrogen and carbon atoms at δ_H 0.14 and δ_C 9.7 ppm, respectively. Together with the small coupling constants ($^3J_{P,H} = 6.2$ Hz and $^2J_{P,C} = 4.7$ Hz) this is proof for the *trans*-position of the methyl groups. The alkenyl proton appears at δ_H 6.74 ppm as a doublet with $^4J_{P,H} = 15.6$ Hz. Of the two alkenyl carbon atoms, only C_β could be located by its signal at δ_C 113.8 ppm ($^3J_{P,C} = 3.1$ Hz). In the $\{^1H\}^{31}P$ NMR spectrum there is only a single resonance at δ_P 26.2 ppm, in a chemical shift range typical for R_3AuPPh_3 complexes.

Crystals of compound **1** are monoclinic, space group $P2_1/n$, with $Z = 4$ molecules in the unit cell. The molecules have no crystallographically imposed symmetry (Fig. 1). The metal atom is in a square planar coordination environment and has the two methyl groups in *trans* positions with Au1–C3 and Au1–C4 distances of 2.112(3) and 2.123(3) Å, respectively. These distances are in very good agreement with those of $(Ph_3P)AuMe_3$ (average 2.111 Å for its mutually *trans* methyl groups) [18].



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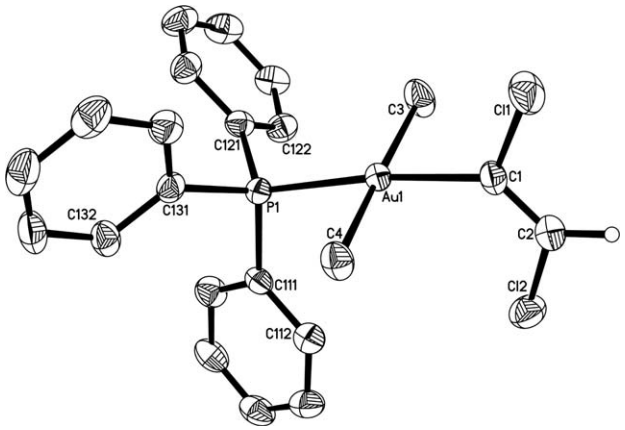


Fig. 1. Molecular structure of compound **1** (ORTEP, 50% probability ellipsoids; phenyl and methyl hydrogen atoms omitted, vinyl hydrogen atom with arbitrary radius.) Selected bond lengths (Å) and angles (°), standard deviations in parentheses: Au1–C1 2.038(3), Au1–C3 2.112(3), Au1–C4 2.123(3), Au1–P1 2.3241(8), C1–C2 1.307(5), C1–Cl1 1.758(4), C2–Cl2 1.741(4), C2–H2 1.01(4); C1–Au1–C3 88.37(14), C1–Au1–C4 88.19(13), C3–Au1–P1 94.46(11), C4–Au1–P1 89.22(10), Au1–C1–C2 126.5(3), Au1–C1–Cl1 118.59(18), C1–C2–Cl2 120.8(3), C2–C1–Cl1 114.9(3).

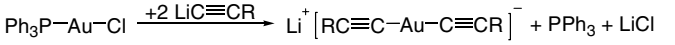
The Au–C distance involving the alkenyl carbon atom is distinctly shorter at Au1–C1 2.038(3) Å. This shortening may not only be due to the sp^2-hybridization of C1, but also to the *trans*-influence of the tertiary phosphine which is known to stabilize Au–C bonds. This is also reflected by the data for $(Ph_3P)AuMe_3$ with the Au–C bond *trans* to the phosphine at only 1.968 Å, and thus shorter than for the two mutually *trans* methyl groups (average 2.111 Å) [18].

The chlorine atoms of the alkenyl group are in *trans* positions and the plane of the olefin is roughly perpendicular to the coordination plane of the metal atom. The chlorine atom Cl1 is located in a plane bisecting the angle C121–P1–C131, and this staggered conformation places the more distant chlorine atom Cl2 in an eclipsed position relative to the phenyl group C111–C116.

In the crystal, the molecular units (**1**) are arranged in double-stacks along the *c*-axis without any specific intermolecular contacts discernible (Fig. 2).

2.2. Attempted oxidative addition of alkyl halides to *Li[RC≡CAuC≡CR]/PR₃*

Solutions containing salts Li[RC≡CAuC≡CR]/PPh_3 (R = H, Me, Ph) are obtained from Ph_3PAuCl and two equivalents of RC≡CLi in diethylether (Eq. (5))



(5)

Treatment of these solutions with methyl iodide gives mainly the quaternary salts Ph_3PMe^+ $[RC{\equiv}CAuC{\equiv}CR]^-$ with minor amounts of *cis*-$Me_2(RC{\equiv}C)AuPPh_3$ as the by-products (Eq. (6)). The latter have been identified previously [13]

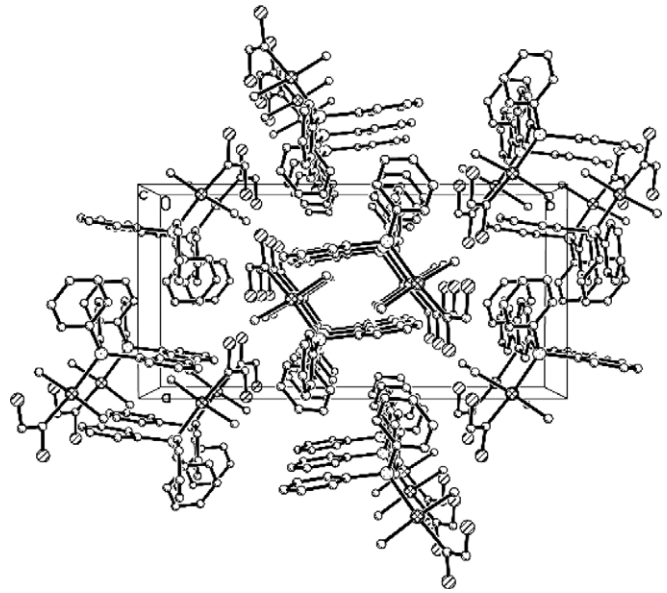
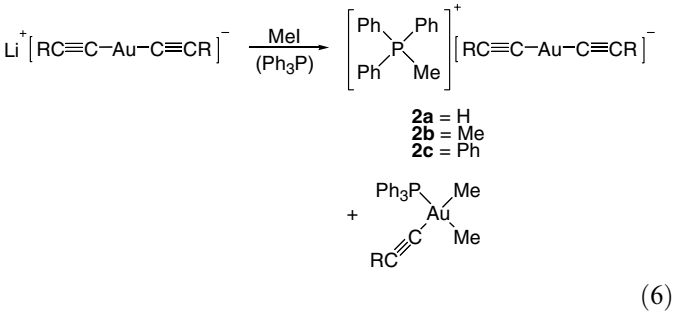


Fig. 2. Unit cell of crystals of compound **1** projected down the *c*-axis (arbitrary radii).



(6)

Maybe not unexpectedly, this result demonstrates that the quaternization of the tertiary phosphine with MeI is faster than the oxidative addition of MeI to the dialkynylaurate anion. The structures of the by-products suggest that the slow MeI addition to the anion is followed by fast ligand redistribution (probably involving reductive eliminations) to give the stable *cis*-dimethyl(alkynyl)gold complexes. It seems, that the formation of the gold(III) species does not take place at all, when the acetylene C≡C–R is substituted with an electron withdrawing group (R = Ph), but this observation has to be proven in further experiments.

Compounds **2a**–**c** are colourless, crystalline solids with melting points at 145–146, 109–110 and 137–139 °C, respectively. The complexes are readily soluble in di- and trichloromethane, but sparingly soluble in hydrocarbons. The NMR spectra of the solutions in CD_2Cl_2 show the same resonances for the Ph_3PMe^+ cation in each case. For the anions the signals of the hydrogen and carbon atoms are all in the expected shift ranges. As in previous cases, the Au–*C*≡ resonances were not detected. In the IR spectra of **2a**–**c** (in KBr) the *ν*(C≡C) stretching frequencies are found at 2219, 2119 and 2099 cm^{-1}, respectively. For **2a**, *ν*(≡C–H) was located at 3273 cm^{-1}.

Crystals of compound **2c** are monoclinic, space group $P2_1/c$, with $Z = 4$ formula units in the unit cell. The cations

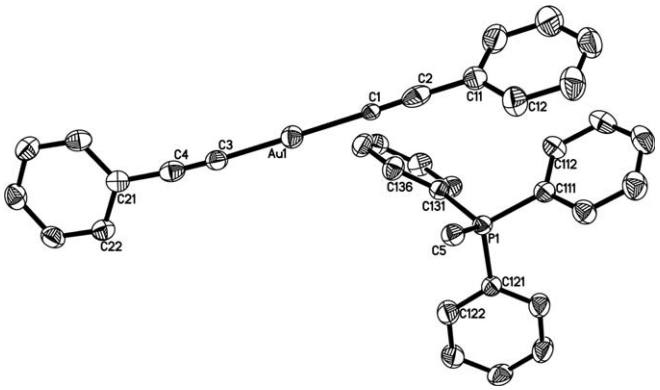


Fig. 3. Structure of the $[Ph_3PMe]^+$ cation and the $[PhC{\equiv}CAuC{\equiv}CPh]^-$ anion in crystals of compound **2c** (ORTEP, 50% probability ellipsoids, hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Au1–C1 2.042(4), Au1–C3 2.003(4), C1–C2 1.144(6), C3–C4 1.186(6), C1–C11 1.461(6), C4–C21 1.454(6); C1–Au1–C3 179.22(15), Au1–C1–C2 170.1(4), Au1–C3–C4 176.9(4), C1–C2–C11 177.1(5), C3–C4–C21 176.6(4).

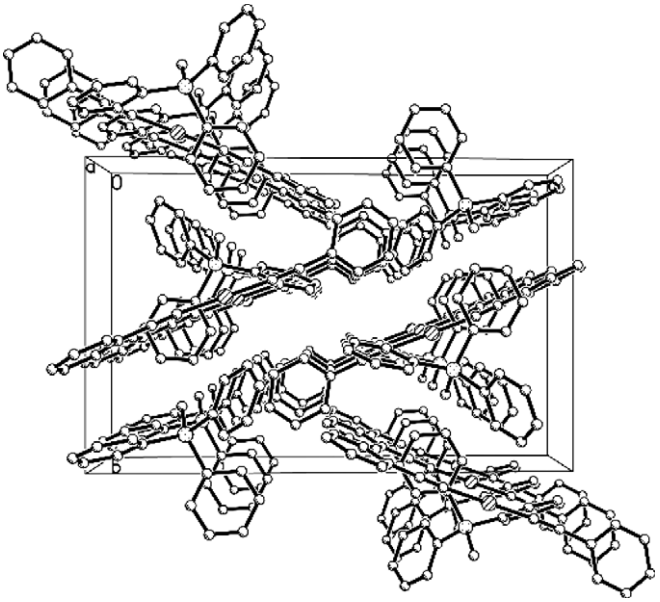


Fig. 4. Unit cell of crystals of compound **2c** projected along the *a*-axis (arbitrary radii).

and anions are fully separated and show no unusual details (Fig. 3). The structure of the anion is known from previous studies of the tetra(*n*-butyl)ammonium salt [14]. In stacks of alternating cations and anions along the *a*-axis (Fig. 4), the anions are separated by the cations and thus not aggregated through aurophilic bonding (Au–Au 7.708 Å). There is also no evidence for arene π–π stacking.

3. Discussion

The present study has shown that oxidative addition of alkynyl halides (chloro- and dichloro-ethyne, phenylethynyl iodide) to lithium dimethylaurate(I), $Li^+[MeAuMe]^-$, in diethylether solutions (containing PPh_3) offers no preparative advantages for the synthesis of alkynylgold(III) complexes. Although some of the expected products are formed in low yield, the major reactions take a different course to give mainly gold(I) complexes.

By contrast, the oxidative addition of an alkenyl halide – trichloroethene – was successful and led to an alkenyl(dimethyl)gold(III) complex of which NMR and single-crystal X-ray diffraction studies have shown that it has the two methyl groups in *trans* positions. This rare configuration has previously been encountered only in isolated cases such as $Li[AuMe_4]$ and $(L)AuMe_3$ with $L = PMe_3$ [19], PPh_3 [18], R_3PCH_2 [18] or $Me_2S(O)CH_2$ [20], where there is no choice of an isomeric ligand distribution, or in some cyclic ylide complexes where the *trans* orientation is required by the constraints of the metallacycle [21,22]. Mixed trialkylgold(III) complexes $R_nR'_{3-n}Au(L)$ ($R = Me$, $R' = Et$, *n*-Pro, *i*-Pro, etc.) show no distinct configurational preference and both isomers are available [2,23].

All previously described complexes of the type $Me_2R'Au(L)$, with $R' = \eta^1$-$CH_2C(Me){=}CH_2$, *trans*-$MeCH{=}CH$ [24,25], η^1-C_5H_5 [26], $C{\equiv}CH$, $C{\equiv}CMe$, $C{\equiv}CPh$ [13], and Ph [27], have the methyl groups in *cis* positions, arguably due to a kinetic effect, because the commonly employed substitution of a precursor molecule with a *cis*-configuration proceeds with retention of the *cis*-arrangement. In the absence of thermodynamic data on *cis*- and *trans*-isomers it therefore must be assumed that compound **1** is also the kinetically controlled product of the oxidative addition of $Cl_2C{=}CHCl$ to $[MeAuMe]^-$ followed by substitution of the Au-bound chlorine atom by the PPh_3 ligand (Eq. (1)). To date this is only the second reaction which gives access to *trans*-$Me_2R'Au(L)$ complexes: Addition of two equivalents of $MeAuPMe_3$ to $CF_3C{\equiv}CCF_3$ yielded $(Me_3P)AuC(CF_3){=}C(CF_3)AuMe_2(PMe_3)$ with the olefin-bound CF_3 groups in *cis*-, but the Au-bound methyl groups in *trans*-position [28].

It should be noted that the assignment of the *cis*-configuration to the two methyl groups in the reference compounds is unambiguous even in cases where it has not been confirmed by crystallographic data, because the NMR-equivalence of the two methyl groups leaves no alternative.

Attempts of oxidative addition of methyl iodide to dialkynylaurate anions, $[RC{\equiv}CAuC{\equiv}CR]^-$ in diethylether (containing PPh_3) led predominantly to the quaternization of the tertiary phosphine to give salts $Ph_3PMe^+[RC{\equiv}CAuC{\equiv}CR]^-$. There are only small amounts of by-products including the type *cis*-$Me_2(RC{\equiv}C)Au(PPh_3)$, which indicate that any oxidative addition of MeI to the anion is followed by ligand scrambling probably including reductive elimination steps. The observation that two methyl groups are finally ending up mutually *cis* can be taken as evidence for a thermodynamic preference of this configuration over the corresponding *trans* form. This idea is supported by the observation that compounds *cis*-$Me_2(RC{\equiv}C)Au(L)$ could not be isomerized upon prolonged heating in polar solvents. This is in contrast to results by Kochi et al. who were able to thermally isomerize trialkylgold(III) complexes

$R_2R'Au(L)$ [23], and also to the stability towards isomerization of the alkenyl compound **1** (above). It therefore appears that in their *cis*/*trans*-preference the alkynyl complexes are notably different from the alkyl and alkenyl analogues.

4. Experimental

General: All experiments were carried out in an atmosphere of dry and pure nitrogen. Solvents were dried, distilled and saturated with nitrogen, and glassware was oven-dried and filled with nitrogen. Standard equipment was used throughout. NMR: Jeol JNM-GX 270 and 400; chemical shifts in δ values rel. residual ^1H and ^{13}C resonances of the CD_2Cl_2 solvent converted to int. TMS, and ext. 85% aqueous H_3PO_4 for ^{31}P, respectively. $(Ph_3P)AuCl$ [29], HC≡CCl [30], ClC≡CCl [17], Li[C≡CH] [31] and Li[C≡CMe] [31] were prepared as described in the literature, all other reagents are commercially available.

4.1. Preparation of the lithium diorganoaurate(I) solutions and oxidative addition

Following the literature procedures, a suitable quantity of $(Ph_3P)AuCl$ was suspended in diethylether and treated with a solution of two equivalents of the organolithium reagent (MeLi, RC≡CLi) in diethylether at 25 °C with stirring. $(Ph_3P)AuCl$ was rapidly dissolved to give a turbid, colourless solution of $Li^+[R'AuR']^-$ with R′ = Me or RC≡C which contained one equivalent of Ph_3P. After cooling to −75 °C, equimolar quantities of the alkynyl, alkenyl or alkyl halides were slowly added. After a given time (below) the reaction mixtures were allowed to warm to room temperature and stirred for 2 h. The solvent was evaporated in a vacuum and the residue extracted with 3 × 10 mL of water to remove the lithium halides. The residue was taken up with dichloromethane, the solution filtered through dry $MgSO_4$, and the products precipitated by addition of pentane. Alternatively, $(Ph_3P)AuMe$ was used instead of $(Ph_3P)AuCl$ and treated with only one equivalent of organolithium reagent under the same conditions. The solutions of Li[RAuR] thus obtained are free of chloride.

4.1.1. Addition of Cl–C≡CH to $Li^+[MeAuMe]^-/PPh_3$

$(Ph_3P)AuMe$ (76 mg, 0.16 mmol) was dissolved in 20 mL of diethylether and 0.1 mL of a 1.6 M solution of MeLi in diethylether (0.16 mmol) added with stirring at 25 °C. After cooling to −75 °C an excess of freshly prepared gaseous ClC≡CH was condensed into the reaction mixture over a period of 45 min and the flask kept at this temperature for 12 h. After warming to room temperature and evaporation of the solvent the work-up gave a colourless precipitate consisting of $(Ph_3P)AuMe$ (NMR: δ_P 48.0, s; δ_H 0.43, d, $J = 7.7$ Hz, Me); $(Ph_3P)AuCl$ (δ_P 33.3, s); $(Ph_3P)AuMe_3$ (δ_P 28.9, s; δ_H −0.05, d, $J = 6.7$, Me_{cis}; 1.02, d, $J = 8.9$, Me_{trans}); *cis*-$Me_2(HC{\equiv}C)Au(PPh_3)$ (δ_P 26.5, s).

4.1.2. Addition of Cl–C≡C–Cl, containing residual starting material H(Cl)C=CCl_2, to $Li^+[MeAuMe]^-/PPh_3$

$(Ph_3P)AuCl$ (300 mg, 0.6 mmol) in 80 mL of diethylether and 0.75 mL of an 1.6 M solution of MeLi (1.2 mmol) were employed together with an excess of ca. 0.1 mol of the C_2Cl_2/C_2HCl_3 mixture. Complex **1** was obtained as the main product; 263 g (45% yield), colourless crystals, m.p. 125–126 °C with decomposition. Calc. for $C_{22}H_{22}AuCl_2P$ (585.23): C, 45.15; H, 3.79; Cl, 12.12. Found: C, 45.06; H, 3.75; Cl, 13.19%. NMR: δ_P 26.2, s, δ_H 0.14, d, $J = 6.2$, 6H, Me; 6.74, d, $J = 15.6$, 1H, C*H*Cl; 7.43–7.66, m, 15H, Ph. δ_C 9.7, d, $J = 4.7$, Me; 113.8, d, $J = 3.1$, *C*HCl; 117.4, d, $J = 55.5$, *i*-Ph; 129.2, d, $J = 11.4$, *m*-Ph; 132.0, d, $J = 2.6$, *p*-Ph; 134.8, d, $J = 11.4$, *o*-Ph; Au*C*Cl not observed.

4.1.3. Addition of Cl–C≡C–Cl to $Li^+[MeAuMe]^-/PPh_3$

The same process with purified C_2Cl_2 reagent gave very low yields (<10%) of $(Ph_3P)AuMe$ and $(Ph_3P)AuCl$.

4.1.4. Addition of Ph–C≡C–I to $Li^+[MeAuMe]^-/PPh_3$

$(Ph_3P)AuCl$ (79 mg, 0.16 mmol); 0.2 mL of a 1.6 M solution of MeLi (0.32 mmol) in diethylether; PhC≡C–I (68 mL, 0.30 mmol). Products: $(Ph_3P)AuMe$, $(Ph_3P)AuI$ (δ_P 39.7, s); *cis*-$Me_2(PhC{\equiv}C)Au(PPh_3)$ (δ_P 26.1, s; δ_H 0.32, d, $J = 8.2$, 3H, Me_{cis}; 1.38, d, $J = 9.2$, 3H, Me_{trans}); *cis*-$Me_2AuI(PPh_3)$ (δ_P 29.3, s; δ_H 1.13, d, $J = 8.2$, 3H, Me_{trans}; 1.49, d, $J = 9.1$, 3H, Me_{cis}); $(Ph_3P)AuMe_3$; Ph_3PMe^+ (δ_P 21.7, s; δ_H 3.1, d, $J = 13.4$, Me).

4.1.5. Addition of MeI to $Li^+[HC{\equiv}CAuC{\equiv}CH]^-/PPh_3$

$(Ph_3P)AuCl$ (100 mg, 0.2 mmol) in 25 mL of diethylether; LiC≡CH (6 mg, 0.4 mmol); MeI (71 mg, 0.5 mmol); colourless precipitate, 53 mg (51% yield), m.p. 145–146 °C. Calc. for $C_{23}H_{20}AuP$ (524.10): C, 52.68; H, 3.84. Found: C, 52.29; H, 3.43%. NMR: δ_P 22.0, s, δ_H 2.0, s, 2H, ≡C–H; 3.0, d, $J = 13.1$, 3H, Me; 7.64–7.96, m, 15H, Ph. δ_C 11.1, d, $J = 57.6$, Me; 87.8, s, ≡CH; 119.1, d, $J = 88.8$, *i*-Ph; 130.8, d, $J = 13.7$, *o*-Ph; 133.5, d, $J = 10.4$, *m*-Ph; 135.6, d, $J = 2.6$, *p*-Ph; AuC≡ not observed. IR(KBr): 2219 cm^{-1}, ν(C≡C); 3273 cm^{-1}, ν(≡C–H). Small amounts of the by-product *cis*-$Me_2(HC{\equiv}C)Au$- (PPh_3) were identified by δ_P 26.5, s.

4.1.6. Addition of MeI to $Li^+[MeC{\equiv}CAuC{\equiv}CMe]^-/PPh_3$

$(Ph_3P)AuCl$ (100 mg, 0.2 mmol); LiC≡CMe (18 mg, 0.4 mmol); MeI (71 mg, 0.5 mmol); colourless, microcrystalline product, 49 mg (44% yield), m.p. 109–110 °C. Calc. for $C_{25}H_{24}AuP \cdot 0.7CH_2Cl_2$ (611.85): C, 50.45; H, 4.18%. Found: C, 50.69; H, 4.04%. NMR: δ_P 21.7, s, δ_H 1.69, s, 6H, MeC≡; 3.1, d, $J = 13.4$, 3H, MeP; 7.68–7.93, m, 15H, Ph. δ_C 5.1, s, *Me*C; 11.0, d, $J = 57.0$, MeP; 96.6, s, Me*C*; 119.2, d, $J = 89.3$, *i*-Ph; 130.9, d, $J = 13.7$, *o*-Ph; 133.6, d, $J = 10.4$, *m*-Ph; 135.7, d, $J = 2.6$, *p*-Ph; Au–C not observed. IR(KBr): 2119 cm^{-1}, ν(C≡C). Small amounts of *cis*-$Me_2(MeC{\equiv})Au(PPh_3)$: δ_P 26.3, s.

Table 1
Crystal data, data collection and structure refinement details for **1** and **2c**

	trans-$Me_2Au(PPh_3)$[*trans*-(Cl)C=C(Cl)H] (**1**)	$[Ph_3PMe][Au(C{\equiv}CPh)_2]$ (**2c**)
Empirical formula	$C_{22}H_{22}AuCl_2P$	$C_{35}H_{28}AuP$
M	585.23	676.51
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
a (Å)	10.2331(2)	10.1034(2)
b (Å)	20.4398(4)	13.4080(2)
c (Å)	10.4376(3)	20.7363(5)
α (°)	90	90
β (°)	91.667(1)	94.122(1)
γ (°)	90	90
V (Å^3)	2182.23(9)	2801.89(10)
ρ_{calc} (g cm^{-3})	1.781	1.604
Z	4	4
$F(000)$	1128	1328
μ (Mo Kα) (cm^{-1})	70.63	53.29
T (K)	143	143
Reflections measured	75267	80526
Reflections unique (R_{int})	4448 (0.045)	5722 (0.066)
Refined parameters/restraints	239/0	334/0
R_1 [$I \geqslant 2\sigma(I)$]	0.0219	0.0307
wR_2[a]	0.0488	0.0637
Weighting scheme	$a = 0.0074$; $b = 3.1488$	$a = 0.0147$; $b = 4.8486$
σ_{fin}(max/min) (e Å^{-3})	0.688/−1.086	0.693/−0.714

[a] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$.

4.1.7. Addition of MeI to $Li^+[PhC{\equiv}CAuC{\equiv}CPh]^-/PPh_3$

$(Ph_3P)AuCl$ (100 mg, 0.2 mmol); LiC≡CPh (0.4 mL of a 1.0 M solution in tetrahydrofuran, 0.4 mmol); MeI (71 mg, 0.5 mmol); colourless crystals, 88 mg (65% yield), m.p. 137–139 °C. Calc. for $C_{35}H_{28}AuP$ (676.51): C, 62.14; H, 4.17. Found: C, 62.29; H, 4.23%. NMR: δ_P 21.5, s, δ_H 2.95, d, $J = 13.1$, 3H, Me; 6.93–7.54, m, 10H, Ph-C; 7.54–7.94, m, 15H, PhP. δ_C 10.3, d, $J = 57.6$, Me; 103.0, s, Ph-*C*; 125.2, 127.4, 128.1, and 131.5, all s, for *i*-, *o*-, *p*-, *m*-*Ph*C; 118.6 (d, $J = 89.3$), 130.6 (d, $J = 13.0$), 133.2 (d, 10.9), and 135.6 (d, $J = 2.6$), for *i*-, *o*-, *m*-, and *p*-PhP. IR(KBr): 2099 cm^{-1}, ν(C≡C).

4.2. Crystal structure determinations

Specimens of suitable quality and size were mounted on the ends of quartz fibers in F06206R oil and used for intensity data collection on a Nonius DIP2020 diffractometer, employing graphite-monochromated Mo Kα radiation. Intensity data were corrected for absorption effects (DELABS from PLATON). The structures were solved by a combination of direct methods (SHELXS-97) and difference-Fourier syntheses and refined by full-matrix least-squares calculations on F^2 (SHELXL-97) [32]. The thermal motion of all non-hydrogen atoms was treated anisotropically. Apart from the alkene hydrogen atom of **1** which was found and refined isotropically, all hydrogen atoms were calculated and allowed to ride on their parent atoms with fixed isotropic contributions. Further information on crystal data, data collection and structure refinement are summarized in Table 1.

5. Supplementary data

Important interatomic distances and angles are shown in the corresponding figure captions. Anisotropic thermal 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-291993 and/or -291994.

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