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Synthesis, Structural Characterisation and Reactions of Some Vinylgold(I) Phosphane Complexes

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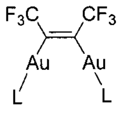
A series of vinylgold(I) complexes [Au(CR=CHR)L] (R = H, Me; L = PPh_3, PPh_2Me, $PPhMe_2$) were prepared from the reaction of the Grignard reagents [MgBr(CR=CHR)] (R = H, Me) with the gold(I) phosphane complexes [AuCl(L)] (L = PPh_3, PPh_2Me, $PPhMe_2$) at low temperature. The complexes were characterised by various spectroscopic techniques and, in the case of [Au(CMe=CHMe)(PPh_3)], by a single-crystal X-ray structure determination. The gold–carbon bonds of these vinylgold(I) complexes are easily cleaved by acids and, in the presence of potassium permanganate, by species containing acidic protons.

Introduction

Organometallic gold(I) complexes of the type [AuR(L)], where R is an alkyl, aryl or alkynyl group and L is a neutral donor ligand such as a tertiary phosphane or isocyanide, have been studied in depth over the years and numerous derivatives have been synthesised, many of which have been structurally characterised.[1–4] In marked contrast, analogous vinylgold(I) complexes [Au(CR=CR_2)(L)] have received very little attention to date. In the 1970s a group of Russian workers reported the synthesis and some reactions of [Au(CH=CH_2)(PPh_3)] but no X-ray structure was reported and the published experimental procedure seems dubious (see below).[5,6] Around the same time, other groups were studying reactions of [AuMe(L)] complexes with the fluorinated hydrocarbons $CF_3C{\equiv}CCF_3$ and $F_2C{=}CF_2$. Stone and Mitchell first observed that UV irradiation of a benzene solution of $CF_3C{\equiv}CCF_3$ and [AuMe(PPh_3)] afforded a colourless product, which, based on ^{19}F NMR spectroscopic data and elemental analysis, they formulated as the binuclear complex [Au_2(μ-$CF_3C{=}CCF_3$)(PPh_3)$_2$] (**1**).[7,8] The structure was later confirmed by an X-ray diffraction study, which showed that the complex consists of a $CF_3C{=}CCF_3$ molecule bridging two $AuPPh_3$ units.[9] Similar observations were made by Puddephatt and Johnson, who studied the reactions of [AuMe($PPhMe_2$)] and [AuMe(PMe_3)] with $CF_3C{\equiv}CCF_3$. The initial reaction products, formulated as [$AuMe_2$($CF_3C{\equiv}CCF_3$)L] (L = $PPhMe_2$, PMe_3), undergo ethane elimination in acetone to give the binuclear complexes [Au_2(μ-$CF_3C{=}CCF_3$)L_2] (**1**), which is analogous to those observed earlier by Stone.[10] In the case of L = PMe_3, the crystal structure of the complex was obtained and shown to be the mixed-valence gold(I)/gold(III) complex [$Me_3PAu^{III}(Me)_2C(CF_3){=}C(CF_3)Au^{I}PMe_3$] (**2**), which contains a bridging $CF_3C{=}CCF_3$ unit.[11]



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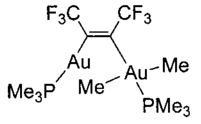

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L = PPh_3, $PPhMe_2$, PMe_3

More recently, Brisdon and co-workers have prepared and structurally characterised the vinylgold(I) complexes [AuCR=CF_2(PPh_3)] (R = Cl, F) by treating [AuCl(PPh_3)] with the organolithium reagent CF_2=CRLi.[12] Puddephatt and Treurnicht reported the synthesis of the very thermally unstable vinylgold(I) complex [Au(CH=CH_2)(CNMe)], which could only be characterised by ^1H NMR spectroscopy at –20 °C.[13] Other approaches for adding vinyl groups to an $AuPPh_3$ unit have also been investigated. The vinyl(methyl)titanium complex [Cp^*_2TiMe(CH=CH_2)] reacts with [AuCl(PPh_3)] to give [Cp^*_2TiCl(μ-C=CH_2)-$AuPPh_3$] (**3**), the structure of which contains a vinylidene unit bridging the titanium and gold atoms in an unsymmetrical fashion.[14] The vinylgold(I) complexes [Au{C(OR)=CH_2}(PPh_3)M(CO)$_5$] (**4**) (M = Cr, Mo, W; R = Me, Et), in which the vinyl group is π-coordinated (η^2) to the M(CO)$_5$ fragment, are formed by treating the deprotonated carbene species Li[(CO)$_5$M=C(OR)CH_2] with [AuCl(PPh_3)].[15] Addition of PPh_3 displaces the coordinated M(CO)$_5$ unit from **4** and produces the vinylgold(I) complex [Au{C(OR)=CH_2}(PPh_3)].

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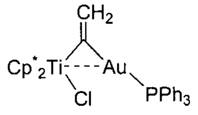

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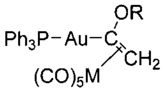

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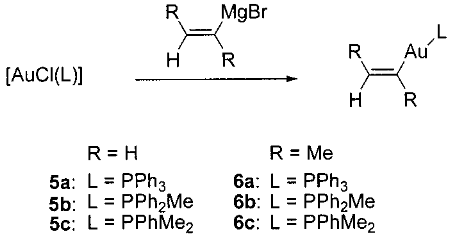
M = Cr, Mo, W; R = Me, Et

Our group has been studying the catalytic activity of various gold complexes in the addition of water or MeOH to terminal alkynes.[16] A vinylgold species has been suggested as a possible intermediate in this catalytic process. For this reason we were interested in preparing some vinylgold(I) complexes and studying their structures and reactivity. The results of this investigation are presented here.

Results and Discussion

Initially, we attempted to reproduce the Russian work to prepare $[Au(CH{=}CH_2)(PPh_3)]$ (**5a**). What seemed suspicious to us was the claim that the reaction between the vinyl Grignard reagent and $[AuCl(PPh_3)]$ was carried out at +50 °C and that the complex was obtained in 90% yield![5] In our hands, these conditions led to complete decomposition of the reaction mixture to metallic gold. However, when vinylmagnesium bromide was added to an ethereal suspension of $[AuCl(PPh_3)]$ at –78 °C the complex $[Au(CH{=}CH_2)(PPh_3)]$ (**5a**) could be isolated in 73% yield after work-up. We found that when a large excess of Grignard reagent was used in the reaction and the subsequent hydrolysis was carried out with large volumes of water or aqueous NH_4Cl, significant decomposition to metallic gold occurred. This decomposition can be avoided by using only a small excess of Grignard reagent (ca. 10%), and simply exposing the reaction mixture to air was sufficient to hydrolyse the excess Grignard reagent. Following this procedure the vinylgold(I) complexes $[Au(CR{=}CHR)(L)]$ (R = H, **5a**: L = PPh_3, **5b**: L = PPh_2Me, **5c**: L = $PPhMe_2$; R = Me, **6a**: L = PPh_3, **6b**: L = PPh_2Me, **6c**: L = $PPhMe_2$) were prepared in good to moderate yields (Scheme 1).



Scheme 1.

All the complexes prepared are colourless, crystalline solids (except for **5c** and **6c**, which were isolated as pale-brown oils) that are air- and thermally stable in the solid state; in solution, however, decomposition occurs slowly (2–3 days) for the PPh_3 and PPh_2Me complexes, whilst the $PPhMe_2$ derivatives are stable in solution for less than 12 h. The ^1H NMR spectra of the vinyl complexes **5a**–**5c** consists of three doublets of doublets displaying *trans,cis* and geminal coupling constants of 20, 14 and 5 Hz, respectively. The ^1H NMR spectra of the dimethyl analogues **6a**–**6c** display a broad singlet at $\delta \approx 6.4$ ppm due to the vinylic proton. Furthermore, the two methyl groups attached to the vinyl group resonate as a broad singlet (coupling unresolved) and doublet of quartets for the α- and β-Me groups, respectively; the coupling constants confirm that the methyl groups are *trans* to each other. In the ^{13}C NMR spectra of all six complexes we observed, in addition to the phenyl and Me signals, a singlet at $\delta \approx 129$ ppm due to the β-C of the vinyl group. The resonance of the α-C of the vinyl group attached to the gold atom could not be observed, presumably due to the large quadrupole moment of the proximal gold atom. As expected, the $^{31}P\{^1H\}$ NMR spectra of all six complexes show singlet resonances whose chemical shift varies depending on the phosphane ligands. The FAB+ mass spectra of most of the complexes show weak molecular-ion peaks as well as peaks due to loss of the vinyl group and formation of higher mass ions $[Au(phosphane)_2]^+$; the latter are frequently observed in FAB mass spectra of gold(I) phosphane complexes.[17] The vinylgold(I) structure was confirmed by a partial X-ray diffraction study of **6a**. Due to the limited stability of the complex in solution, the crystals obtained were of poor quality and, more importantly, signs of twinning were apparent. However, the data were of sufficient quality to establish the connectivity and to derive geometric parameters of middling accuracy but wholly consistent with all other experimental data reported here and elsewhere for this and analogous compounds. A displacement ellipsoid plot of one molecule is shown in Figure 1.[18]

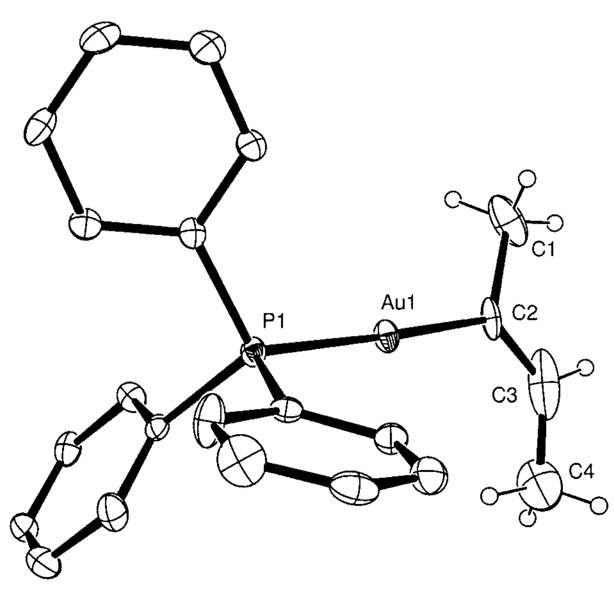


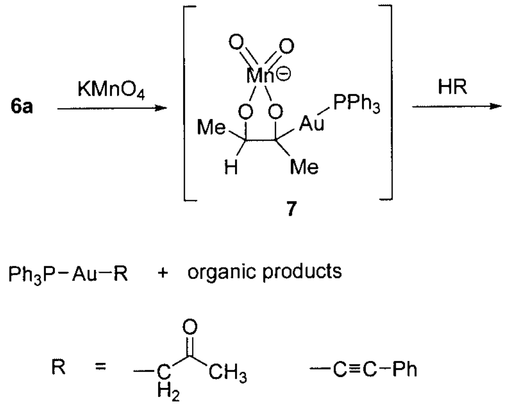
Figure 1. ORTEP view of one of the independent molecules of **6a**. Ellipsoids show 30% probability levels; phenyl hydrogen atoms have been omitted for clarity.

The structure was refined in the space group *C*2/*c* with two independent molecules in the asymmetric unit. Some bond lengths and angles differ slightly between the two molecules; but we do not wish to attribute chemical significance to this observation given that the differences are consistent with the inaccuracies evident in the diffraction data (vide infra) [wR_2 = 0.1482, R_1 = 0.0822, C–C bond precision 0.022 Å]. The structure of **6a** consists of a dimethylvinyl moiety (with the Me groups in a *trans* configuration) and a PPh_3 unit linearly [177.9(3)° and 175.4(4)°] coordinated to the gold(I) centre. The Au–P [2.3092(19) and 2.291(2) Å] and Au–C [2.004(7) and 2.053(10) Å] distances are similar to those in [Au(CF=CF_2)(PPh_3)] [Au–P = 2.272(3) and Au–C = 2.028(9) Å] and [Au(CCl=CF_2)(PPh_3)] [Au–P = 2.266(2) and Au–C = 2.026(10) Å].[12] The vinyl C=C distances [1.322(18) and 1.327(17) Å] are slightly longer than those in [Au(CF=CF_2)(PPh_3)] [C=C = 1.297(14) Å][12] but shorter than that in [AuC(OMe)=CH_2(PPh_3)Cr(CO)$_5$] [C=C = 1.345(11) Å].[15]

Reactions of Vinylgold(I) Complexes

The Russian workers studied the reactions of [Au(CH=CH_2)(PPh_3)] (**5a**) with HCl, $HgCl_2$ Br_2, $(SCN)_2$, benzoic acid and $KMnO_4$.[6] In the first five cases the gold–carbon bond is cleaved to give [AuX(PPh_3)] (X = Cl, Br, SCN, O_2CPh) as the gold-containing product. However, in the case of $KMnO_4$, neither metal–carbon bond cleavage nor oxidation of the carbon–carbon double bond occurs; instead, the acetonylgold(I) phosphane complex [Au{$CH_2C(O)CH_3$}(PPh_3)] is formed in high yield.[6,19] The X-ray crystal structure of this complex was reported later, but neither the method of preparation nor source of the sample was mentioned.[20] In order to examine the generality of these reactions we studied the reaction of hydrochloric acid and $KMnO_4$ with the new vinylgold(I) complex **6a**. Treatment of an acetone solution of **6a** with a solution of HCl or DCl in D_2O (the deuterated acid was more convenient to study by ^{1}H NMR spectroscopy) results in electrophilic cleavage of the gold–carbon bond and formation of [AuCl(PPh_3)] and *trans*-MeDC=CMeH, as was evident from the ^{1}H and ^{31}P NMR spectra; the chemical shift observed in the ^{31}P NMR spectrum is identical to that of an authentic sample of [AuCl(PPh_3)]. Treatment of an acetone solution of complex **6a** at 0 °C with $KMnO_4$ resulted in formation of a brown precipitate (MnO_2). After about 30 min reaction time a pale-yellow solid could be isolated from the mixture after filtration and removal of the solvent. On the basis of ^{1}H and ^{31}P{^{1}H} NMR spectroscopic data, this product was identified as the acetonylgold(I) complex [Au{$CH_2C(O)CH_3$}(PPh_3)], identical to that reported by Nesmeyanov.[19] We were interested in investigating this reaction in more detail in order to gain some understanding of the mechanism and the exact role of the permanganate. To test whether species containing acidic protons, such as acetone or phenylacetylene, can react with **6a** in the absence of permanganate we treated $CDCl_3$ solutions of complex **6a** with an equivalent amount of acetone or phenylacetylene and examined the ^{1}H and ^{31}P NMR spectra over time. Even after a period of 48 h there was no evidence that any reaction had occurred − only signals from the starting complex were observed in the NMR spectra − thus confirming that permanganate is indeed required for this reaction. If a solution of $KMnO_4$ in CD_3CN is then added to the NNR tubes containing complex **6a** and acetone or phenylacetylene a brown precipitate is observed after a few minutes and after about 30 min the main species in solution, determined by NMR spectroscopy, are [Au{$CH_2C(O)CH_3$}(PPh_3)] and [Au(C≡CPh)(PPh_3)], respectively. These results suggest that the permanganate reacts initially with the vinylgold(I) complex, probably oxidising the carbon–carbon double bond, via an intermediate gold(I)/manganese(V) cyclic ester **7** (Scheme 2). It is known that the oxidation of alkenes with permanganate proceeds via such cyclic Mn^V ester intermediates, which undergo decomposition reactions to give organic products and MnO_2.[21] Recently, this [3+2] mechanism via cyclic Mn^V esters has been confirmed by DFT calculations and kinetic isotope effect data.[22] In our case, the evidence presented above suggests that the presumed intermediate **7** causes deprotonation of acetone and phenylacetylene, thus producing the acetonyl- and alkynylgold(I) complexes as well as the diol, accompanied, perhaps even driven, by precipitation of insoluble MnO_2. We tried to identify the organic oxidation products by both ^{1}H NMR and GC/MS spectroscopy, but no conclusive results were obtained. In an attempt to observe the intermediate species **7** we treated a $CDCl_3$ solution of **6a** with a CD_3CN solution of $KMnO_4$ and observed immediate formation of a brown precipitate. The ^{31}P NMR spectrum of the supernatant solution shows a singlet resonance at δ = 44.50 ppm, slightly shifted relative to that of the starting complex (δ = 44.77 ppm), which may be due to the intermediate. However, the presence of a multiplet at δ = 6.4 ppm in the ^{1}H NMR spectrum, due to the vinylic proton, suggests that the C=C double bond in the vinyl ligand is still intact; in fact, the overall spectrum is almost identical to that of **6a**. When excess PhC≡CH is added to this solution the ^{31}P NMR spectrum shows, in addition to the original peak at δ = 44.50 ppm, a new signal at δ = 42.15 ppm. The latter resonance is consistent with the presence of [Au(C≡CPh)(PPh_3)], which was confirmed by comparison of chemical shifts of an authentic sample. Over a period of about 10 h the intensity of the signal due to [Au(C≡CPh)(PPh_3)] increases, whilst that of the starting complex **6a** decreases. After about 24 h the major species in solution is [Au(C≡CPh)(PPh_3)]. If the same experiment is carried out with acetone similar observations are made, namely the intensity of the ^{31}P NMR signal due to the acetonylgold(I) complex [Au{$CH_2C(O)CH_3$}(PPh_3)] increases over time, while that due to **6a** decreases. These results show that $KMnO_4$ is required for the vinylgold(I) complex to react with species containing acidic protons and, although we failed to detect any intermediate, the simple fact that addition of $KMnO_4$ to a solution of **6a** causes precipitation of

MnO_2 suggests that some reaction yielding an undetectable intermediate must be taking place. More detailed investigations are necessary to fully understand this process. Other oxidants including dichromate and H_2O_2 either do not react at all or, in the case of peroxide, oxidation of the phosphane occurs to give $Ph_3P{=}O$ and decomposition of the starting complex to gold metal.



Scheme 2.

In summary, we have shown that vinylgold(I) complexes can be prepared in good yields from the reaction of a vinyl Grignard reagent with $[AuCl(PPh_3)]$ at low temperatures. The gold–vinyl–C bond is easily cleaved by acids or, in the presence of $KMnO_4$, by species containing an acidic proton such as acetone and phenylacetylene. Further work is currently in progress to further elucidate the mechanism of this reaction and to study other reactions of vinylgold(I) compounds.

Experimental Section

General: All reactions were performed under an atmosphere of dry argon using Schlenk techniques. Solvents were dried by standard methods and freshly distilled under argon before use. ^1H, ^{13}C and $^{31}P\{^1H\}$ NMR spectra were recorded with a 400 MHz Bruker Avance spectrometer. Chemical shifts are quoted relative to external TMS (^1H and ^{13}C) or 85% H_3PO_4 (^{31}P). FAB mass spectra were measured on a VG Autospec spectrometer in positive ion mode using NBA as matrix. Elemental analyses were obtained in-house using a Perkin–Elmer 240B microanalyser. The chlorogold(I) precursor complexes were prepared by treating equivalent amounts of [AuCl(tht)] with the tertiary phosphanes in CH_2Cl_2. The vinyl Grignard reagents were obtained commercially (Aldrich).

$[Au(CH{=}CH_2)(PPh_3)]$ (5a): A suspension of $[AuCl(PPh_3)]$ (0.402 g, 0.929 mmol) in dry Et_2O (10 mL) was cooled to –78 °C and treated with a solution of vinylmagnesium bromide (1.0 mL 1 M solution in THF, 1.0 mmol). The mixture was warmed to room temperature over a period of 4 h. After this time the reaction vessel was exposed to air for about 10 min. to hydrolyze any unreacted Grignard reagent. The mixture was then filtered through anhydrous $MgSO_4$ and the filtrate evaporated to dryness in vacuo to afford 0.288 g (73%) of colourless product. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.42–7.61 (m, 15 H, Ph), 7.20 (dd, $J_{trans\text{-H,H}}$ = 20, $J_{cis\text{-H,H}}$ = 14 Hz, 1 H, AuC*H*), 6.04 (dd, $J_{trans\text{-H,H}}$ = 20, $J_{gem\text{-H,H}}$ = 5 Hz, 1 H, =C*H₂*), 5.53 (dd, $J_{cis\text{-H,H}}$ = 14, $J_{gem\text{-H,H}}$ = 5 Hz, 1 H, =C*H₂*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 134.3 (d, $^3J_{P,C}$ = 13 Hz, *meta*-Ph), 131.4 (s, AuC=*C*), 131.2 (s, *para*-Ph), 129.0 (d, $^2J_{P,C}$ = 10 Hz, *ortho*-Ph) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ = 44.40 ppm ppm. FAB MS: *m/z* (%) = = 486 (5) $[M]^+$, 459 (95) $[Au(PPh_3)]^+$, 721 (100) $[Au(PPh_3)_2]^+$. $C_{20}H_{18}AuP$ (486.3): calcd. C 49.40, H 3.73; found C 49.30, H 3.50.

Compounds **5b** and **5c** were prepared in a similar manner.

$[Au(CH{=}CH_2)(PMePh_2)]$ (5b): Colourless solid (0.252 g, 64% yield). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.60–7.70 (m, 4 H, Ph), 7.41–7.48 (m, 6 H, Ph), 7.14 (dd, $J_{trans\text{-H,H}}$ = 21, $J_{cis\text{-H,H}}$ = 14 Hz, 1 H, AuC*H*), 6.00 (dd, $J_{cis\text{-H,H}}$ = 14, $J_{gem\text{-H,H}}$ = 5 Hz, 1 H, =C*H₂*), 5.48 (dd, $J_{trans\text{-H,H}}$ = 21, $J_{gem\text{-H,H}}$ = 5 Hz, 1 H, =C*H₂*), 2.01 (d, $^2J_{P,H}$ = 8 Hz, 3 H, PCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 132.8 (d, $^3J_{P,C}$ = 13 Hz, *meta*-Ph), 132.7 (d, $^1J_{P,C}$ = 50 Hz, *ipso*-Ph), 131.5 (s, AuC=*C*), 131.0 (s, *para*-Ph), 129.0 (d, $^2J_{P,C}$ = 10 Hz, *ortho*-Ph), 13.9 (d, $^1J_{P,C}$ = 32 Hz, P*C*H₃) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ = 30.10 ppm ppm. FAB MS: *m/z* (%) = = 379 (60) $[Au(PMePh_2)]^+$, 597 (100) $[Au(PMePh_2)_2]^+$ 821 (35) $[M + Au(PPh_2Me)]^+$. $C_{15}H_{16}AuP$ (424.2): calcd. C 42.47, H 3.80; found C 42.84, H 3.71.

$[Au(CH{=}CH_2)(PPhMe_2)]$ (5c): Pale-brown oil (0.108 g, 55% yield). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.70–7.78 (m, 2 H, Ph), 7.45–7.50 (m, 3 H, Ph), 7.10 (dd, $J_{trans\text{-H,H}}$ = 21, $J_{cis\text{-H,H}}$ = 14 Hz, 1 H, AuC*H*), 5.98 (dd, $J_{cis\text{-H,H}}$ = 12, $J_{gem\text{-H,H}}$ = 5 Hz, 1 H, =C*H₂*), 5.46 (dd, $J_{trans\text{-H,H}}$ = 21, $J_{gem\text{-H,H}}$ = 5 Hz, 1 H, =C*H₂*), 1.73 (br. s, 6 H, PCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 133.8 (d, $^1J_{P,C}$ = 49 Hz, *ipso*-Ph), 131.77 (d, $^3J_{P,C}$ = 13 Hz, *meta*-Ph), 131.5 (s, AuC=*C*), 131.1 (s, *para*-Ph), 128.9 (d, $^2J_{P,C}$ = 10 Hz, *ortho*-Ph), 15.34 (d, $^1J_{P,C}$ = 31 Hz, P*C*H₃) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ = 18.65 ppm. FAB MS: *m/z* (%) = 335 (62) $[Au(PPhMe_2)]^+$, 473 (100) $[Au(PPhMe_2)_2]^+$.

The following complexes were prepared as described above using 1-methyl-1-propenylmagnesium bromide.

$[Au(CMe{=}CHMe)(PPh_3)]$ (6a): Colourless, crystalline solid (0.206 g, 63% yield). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.51–7.60 (m, 6 H, Ph), 7.40–7.51 (m, 9 H, Ph), 6.45 (m, 1 H, =C*H*Me), 2.06 (br. s, 3 H, AuC*Me*), 1.95 (dq, $^3J_{H,H}$ = 6, $^5J_{H,H}$ = 1 Hz, 3 H, =CH*Me*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 134.3 (d, $^3J_{P,C}$ = 13 Hz, *meta*-Ph), 131.4 (d, $^1J_{P,C}$ = 48 Hz, *ipso*-Ph), 130.8 (s, *para*-Ph), 129.2 (AuC=*C*), 128.9 (d, $^2J_{P,C}$ = 10 Hz, *ortho*-Ph), 30.4 (s, AuC*Me*), 20.9 (s, CH*Me*) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ = 44.77 ppm. FAB MS: *m/z* (%) = 514 (15) $[M]^+$, 459 (100) $[Au(PPh_3)]^+$, 721 (65) $[Au(PPh_3)_2]^+$. $C_{22}H_{22}AuP$ (514.4): calcd. C 51.37, H 4.31; found C 51.48, H 4.12. X-ray quality crystals were selected from the bulk sample.

$[Au(CMe{=}CHMe)(PPh_2Me)]$ (6b): Colourless solid (0.118 g, 73% yield). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.61–7.71 (m, 4 H, Ph), 7.39–7.48 (m, 6 H, Ph), 6.47 (m, 1 H, =C*H*Me), 2.06 (br. s, 3 H, AuC*Me*), 2.01 (d, $^2J_{P,H}$ = 6 Hz, 3 H, P*Me*) 1.96 (dq, $^3J_{H,H}$ = 6, $^5J_{H,H}$ = 1 Hz, 3 H, =CH*Me*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 133.2 (d, $^1J_{P,C}$ = 47 Hz, *ipso*-Ph), 132.7 (d, $^3J_{P,C}$ = 13 Hz, *meta*-Ph), 130.8 (s, *para*-Ph), 129.3 (s, AuC=*C*), 128.9 (d, $^2J_{P,C}$ = 10 Hz, *ortho*-Ph), 30.3 (s, AuC*Me*), 20.9 (s, CH*Me*), 13.7 (d, $^1J_{P,C}$ = 39 Hz, P*Me*) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ = 30.96 ppm. FAB MS: *m/z* (%) = 452 (10) $[M]^+$, 397 (100) $[Au(PPh_2Me)]^+$, 597 (55) $[Au(PPh_2Me)_2]^+$. $C_{17}H_{20}AuP$ (452.3): calcd. C 45.14, H 4.46; found C 45.28, H 4.32.

$[Au(CMe{=}CHMe)(PPhMe_2)]$ (6c): Pale-brown oil (0.170 g, 40% yield). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.68–7.80 (m, 2 H, Ph), 7.41–7.50 (m, 3 H, Ph), 6.45 (m, 1 H, =C*H*Me), 2.01 (br. s, 3 H, AuC*Me*), 1.92 (dq, $^3J_{H,H}$ = 6, $^5J_{H,H}$ = 1 Hz, 3 H, =CH*Me*), 1.70 (d, $^{2}J_{\mathrm{P,H}}$ = 6 Hz, 6 H, P*Me*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 131.8 (d, $^{3}J_{\mathrm{P,C}}$ = 13 Hz, *meta*-Ph), 131.1 (s, *para*-Ph), 129.4 (s, AuC=*C*), 129.0 (d, $^{2}J_{\mathrm{P,C}}$ = 11 Hz, *ortho*-Ph), 30.4 (s, AuC*Me*), 20.9 (s, CH*Me*), 15.3 (d, $^{1}J_{\mathrm{P,C}}$ = 32 Hz, P*Me*) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C): δ = 19.96 ppm. FAB MS: *m*/*z* (%) = 390 (11) [M]$^+$, 335 (100) [Au(PPhMe$_2$)]$^+$, 473 (90) [Au(PPhMe$_2$)$_2$]$^+$.

Reaction of 6a with Acid: A few drops of an approx. 1 M solution of DCl in D_2O was added to a sample of **6a** dissolved in [D$_6$]acetone in an NMR tube. ^{1}H and ^{31}P NMR spectra were recorded after about 10 min. ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C): δ = 7.53–7.66 (m, 15 H, Ph from Ph$_3$PAuCl), 5.35 (br. s, 1 H, C*H*Me), 1.54 (q, $^{3}J_{\mathrm{H,D}}$ = 1 Hz, 3 H, CD*Me*), 1.53 (s, 3 H, CH*Me*) ppm. ^{31}P{^{1}H} NMR (162 MHz, [D$_6$]acetone, 25 °C): δ = 33.97 ppm. This ^{31}P{^{1}H} NMR chemical shift is identical to that of an authentic sample of [AuCl(PPh$_3$)].

Reaction of 6a with $KMnO_4$: A sample of **6a** was dissolved in acetone and treated with an acetone solution of $KMnO_4$ at about 0 °C. After around 10 min a brown precipitate (MnO_2) was observed. The mixture was filtered and the filtrate was evaporated to dryness. ^{1}H and ^{31}P NMR spectra of the pale-yellow solid were recorded. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.40–7.59 (m, 15 H, Ph), 2.71 (d, $^{3}J_{\mathrm{H,P}}$ = 1 1 Hz, 2 H, AuC*H*$_2$), 2.22 (s, 3 H, C*Me*) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C): δ = 42.20 ppm. In addition, there are trace amounts of starting complex **6a** and a further unidentified species present (δ_{P} = 44.7 and 29.2 ppm, respectively).

NMR Reactions of 6a with $KMnO_4$ and Acetone or Phenylacetylene: A solution of $KMnO_4$ in CD_3CN was added to a $CDCl_3$ solution of **6a**. A brown solid (MnO_2) precipitated immediately. Acetone or phenylacetylene (4 µL) was then added to the NMR tube and ^{31}P and ^{1}H NMR spectra were recorded before and after the addition.

Reaction of 6a with H_2O_2: A sample of **6a** dissolved in acetone was treated with 30% H_2O_2. After stirring for about 30 min a gold mirror had formed on the inside of the flask. The solvents were removed in vacuo and the residue was analysed by ^{31}P spectroscopy. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C): δ = 29.69 ppm.

X-ray Crystallography of Complex 6a: Data were gathered twice, from two different crystals and using two different CCD-based diffractometers, with similar results in both cases. The results reported here were derived from data gathered using a four-circle diffractometer (Xcalibur2 with a Sapphire3 detector and sealed tube Mo Enhance source).[23] A crystal of dimensions 0.17×0.16×0.05 mm, and with a slight yellow tint as viewed under an optical microscope, was mounted with epoxy at the end of a quartz fibre and kept at 123 K for the measurements. A preliminary unit-cell determination yielded the same results that had been determined earlier using a Bruker Apex diffractometer, namely a monoclinic cell with one unusually long axis (ca. 45.8 Å). The cell dimensions were verified on the four-circle diffractometer using normal-beam axial photography. Because of the long axis, for the present data the crystal-to-detector distance was set to 90 mm and the data collection strategy was optimised accordingly. The faces of the crystal were indexed and absorption corrections were calculated numerically and applied to the integrated data. The structure was solved by direct methods and refined against F_o^2 using full-matrix least-squares.[24] Non-hydrogen atoms were refined anisotropically. Non-methyl hydrogen atoms were placed at calculated positions and refined as riders. Methyl hydrogen atoms were located successfully in local slant-Fourier calculations and refined as riding atoms but with a variable torsion angle about the local C–C bond. The refinement was stable and convergent, but the results showed effects that are normally considered characteristic of twinning, i.e. high residuals, some 20 difference peaks above 1 eÅ^{-3}, and unusual analysis of variance with the worst-fit reflections largely having F_o^2 greater than F_c^2. Several twin models were tested, each of which produced some improvement in the crystallographic indicators but did not influence the chemical implications of the results. Concurrent twin models were also tested, with similar results. The results reported here are those obtained with no twin model; more information on other models can be obtained from the authors. Commonly employed structure validation tools (PLATON[25]) did not reveal the presence of missed crystallographic symmetry elements. Visual examination of the structural results suggests pseudo-translational symmetry, but at the same time reveals that the two independent molecules have very different environments and participate in quite distinct fashions in the crystal packing. One of the phenyl groups (C50–C55) shows prolate displacement ellipsoids and a short average C–C distance. While these are normally taken to be definitive symptoms of libration, we cannot rule out an association between these effects and the presence of a putative minor twin component.

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[18] $C_{22}H_{22}AuP$, monoclinic, *C2/c*, a = 15.4392(6), b = 10.8911(5), c = 45.7928(18) Å, β = 98.404(4)°, V = 7617.4(5) Å^3, Z = 16, ρ = 1.794 gcm^{-3}, μ = 7.809 mm^{-1}, 31300 data measured, 8639 unique, 98.6% completeness, R_{int} = 0.0440, $R\sigma$ = 0.0653, wR_2 = 0.1482 (437 parameters), R_1 = 0.0822 [6532 data with $I > 2\sigma(I)$], quality-of-fit = 1.232. CCDC-286877 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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