Preparation and Ligand-exchange Reactions of Phosphinegold Ethynyl Complexes

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Phosphinegold chlorides, [AuClL], react readily with terminal alkynes RC≡CH in ethanolic sodium ethoxide to produce high yields of ethynyl complexes [Au(C≡CR)L] [L = PPh_3; R = Me, Et, Ph, or CF_3: L = $P(C_6H_4Me\text{-}p)_3$, R = Ph]. When R = H a second reaction leads to formation of [LAuC≡CAuL] [L = PPh_3, $P(C_6H_4Me\text{-}p)_3$, or $P(C_6H_4OMe\text{-}p)_3$]. In a similar manner, the cyclopentadienyl complex $[Au(C_5H_5)(PPh_3)]$ can conveniently be made from $[AuCl(PPh_3)]$, Na(OEt), and C_5H_6. The phosphine of [Au(C≡CPh)L] rapidly exchanges in solution with free phosphines. The compounds $[Au(C{\equiv}CPh)(PPh_3)]$ and $[AuCl\{P(C_6H_4Me\text{-}p)_3\}]$ readily equilibrate with $[AuCl(PPh_3)]$ and $[Au(C{\equiv}CPh)\{P(C_6H_4Me\text{-}p)_3\}]$, a reaction which could also involve exchange of phosphines, but the exchange of Cl for C≡CPh is another possible pathway. Phenylethynyl groups from $[Au(C{\equiv}CPh)(PPh_3)]$ exchange with both chlorides of $HgCl_2$, *cis*-$[PtCl_2(PMePh_2)_2]$, and *cis*-$[PtCl_2(CO)(PMePh_2)]$. With the latter complex the exchange is non-stereospecific, unlike related reactions with organomercurials.

Ethynyls are amongst the most stable organogold(I) compounds.[1–3] Several examples of linear complexes [Au(C≡CR)L] (L = tertiary phosphine, arsine, stibine, isocyanide, or amine) have previously been made either by adding L to polymeric $[\{Au(C{\equiv}CR)\}_n]$ or by treating [AuClL] by Grignard reagent.[4] Neither of these methods is convenient, however, and each involves steps liable to be accompanied by substantial reduction to gold metal. A recent variation, treatment of $[\{Au(C{\equiv}CPh)\}_n]$ first by Cl^- to form $[Au(C{\equiv}CPh)Cl]^-$, then by PPh_3 to displace chloride, is unlikely to be more convenient.[5]

We report here details of an easy and high-yield route to $[Au(C{\equiv}CR')(PR_3)]$ complexes, involving treatment of $[AuCl(PR_3)]$ by a terminal alkyne and a base. A preliminary note has appeared,[6] and a report published at the same time by Bruce *et al.*[7] describes a closely related procedure.

Results and Discussion

When a suspension of $[AuCl(PPh_3)]$ in ethanol is treated with sodium ethoxide and phenylethyne a smooth conversion into $[Au(C{\equiv}CPh)(PPh_3)]$ takes place [equation (1)]. The product is

$$(Ph_3P)AuCl + PhC{\equiv}CH + Na(OEt) \longrightarrow (Ph_3P)Au(C{\equiv}CPh) + NaCl + EtOH \quad (1)$$

sparingly soluble in ethanol, and can be obtained essentially pure by filtration. The presence of water in the solvent does not affect the reaction, indicating that hydroxide is a strong enough base.[7] Treatment of $[AuCl(PPh_3)]$ by sodium ethoxide in the absence of an alkyne produced no reaction, so the reaction path is probably abstraction of a proton from the alkyne, followed by displacement of chloride from gold by the alkynyl. Co-ordination of the multiple bond to gold at some stage could also be involved.

This method for preparing gold alkynyls appears to be quite versatile. The compound $[AuCl\{P(C_6H_4Me\text{-}p)_3\}]$ reacts in a similar fashion to give $[Au(C{\equiv}CPh)\{P(C_6H_4Me\text{-}p)_3\}]$, and bubbling the relevant gaseous alkynes into suspensions of $[AuCl(PPh_3)]$ in alcoholic sodium ethoxide afforded the new materials [Au(C≡CMe)L], [Au(C≡CEt)L], and $[Au(C{\equiv}CCF_3)L]$ (L = PPh_3). Physical and spectroscopic data for the new compounds are presented in the Table. Other compounds have been prepared by Bruce *et al.*[7] in methanol, using KOH or Na(OMe) as base.

The compound $[AuCl(PPh_3)]$ in alcoholic sodium ethoxide reacts with C_2H_2 to produce $[Au(C{\equiv}CH)(PPh_3)]$ (Table). This compound was not obtained in pure form, and was difficult to recrystallise. It readily reacted further with $[AuCl(PPh_3)]$ and base to form $[(Ph_3P)AuC{\equiv}CAu(PPh_3)]$ [equation (2)]. This

$$(Ph_3P)AuCl + C_2H_2 \xrightarrow{Na(OEt)} (Ph_3P)Au(C{\equiv}CH) \xrightarrow[Na(OEt)]{(Ph_3P)AuCl} (Ph_3P)AuC{\equiv}CAu(PPh_3) \quad (2)$$

latter compound proved too insoluble to recrystallise, and prolonged heating in solvents at temperatures in excess of 60 °C led to decomposition. The more soluble analogues prepared from [AuClL] [L = $P(C_6H_4Me\text{-}p)_3$ or $P(C_6H_4OMe\text{-}p)_3$] were amenable to recrystallisation, however. Both of these chlorogold complexes reacted directly with basic ethyne to form the digold complexes and no intermediate [Au(C≡CH)L] could be detected. Recrystallisation of these digold acetylene complexes from chloroform or dichloromethane resulted in the isolation of the well defined solvates $[\{(p\text{-}MeC_6H_4)_3P\}AuC{\equiv}CAu\{P(C_6H_4Me\text{-}p)_3\}]\cdot3CHCl_3$, $[\{(p\text{-}MeC_6H_4)_3P\}AuC{\equiv}CAu\{P(C_6H_4Me\text{-}p)_3\}]\cdot2CH_2Cl_2$, and $[\{(p\text{-}MeOC_6H_4)_3P\}AuC{\equiv}CAu\{P(C_6H_4OMe\text{-}p)_3\}]\cdot2CHCl_3$. Prolonged heating (50 °C) of the last two compounds *in vacuo* resulted in the removal of the solvent molecules. This could not be achieved with the tris(chloroform) adduct and it is possible that this molecule might behave as a clathrate host. Few digold acetylides have previously been prepared. The only simple ethynyl-bridged materials that fall into this category are the anionic species $[RAuC{\equiv}CAuR]^{2-}$ prepared from gold carbide, $[(Au_2C_2)_n]$.[8]

Finally, the versatility of the synthetic method was further demonstrated by its application to another acidic hydrocarbon, cyclopentadiene. Triphenylphosphinegold cyclopentadienide[9] was cleanly prepared in a manner exactly analogous to the gold ethynyls [equation (3)], and this probably represents the easiest synthesis of this compound.

$$(Ph_3P)AuCl + C_5H_6 \xrightarrow[EtOH]{Na(OEt)} (Ph_3P)Au(C_5H_5) \quad (3)$$

Ligand-exchange Reactions.—Addition of small amounts of PPh_3 to solutions of either $[AuCl(PPh_3)]$ or

Table.

Compound	M.p./°C	$\tilde{\nu}(C\equiv C)$[a]/cm^{-1}	$\delta(^{31}P)$[b]/p.p.m.	$\delta(^{1}H)$[c]/p.p.m.
$[Au(C\equiv CH)(PPh_3)]$		1 975[d]	41.9	1.75
$[Au(C\equiv CMe)(PPh_3)]$	148—150	2 120	41.8	1.98
$[Au(C\equiv CEt)(PPh_3)]$	154—155	2 115	41.1	1.27, 2.40
$[Au(C\equiv CCF_3)(PPh_3)]$	155	2 128	41.2	
$[Au(C\equiv CPh)(PPh_3)]$	163—165[e]	2 118	42.3	
$[(Ph_3P)AuC\equiv CAu(PPh_3)]$		2 040 (R)		
$[\{(p\text{-}MeC_6H_4)_3P\}AuC\equiv CAu\{P(C_6H_4\text{-}p)_3\}]$	110—115[f]	2 025 (R)	40.7	
$[\{(p\text{-}MeOC_6H_4)_3P\}AuC\equiv CAu\{P(C_6H_4OMe\text{-}p)_3\}]$	125		38.3	
$[Au(C\equiv CPh)\{P(C_6H_4Me\text{-}p)_3\}]$	146—148	2 120	40.2	

[a] R = Raman. [b] In $CDCl_3$: positive is downfield with respect to external 85% H_3PO_4. [c] For the organic substituent on the ethynyl: relative to internal $SiMe_4$ in $CDCl_3$. [d] $\nu(\equiv C\text{-}H)$ at 3 278 cm^{-1}. [e] Lit.,[4] 162 °C. [f] For tris(chloroform) adduct.

$[Au(C\equiv CPh)(PPh_3)]$ caused broadening of the ^{31}P n.m.r. signals at room temperature, presumably due to a fast exchange process. The ^{31}P n.m.r. spectrum of a mixture of these compounds with 0.2 mol equivalent of PPh_3 consisted of a broad single resonance centred at δ 37.5 p.p.m. at room temperature. On cooling to −60 °C this separated into two resonances for two individual components (δ 32.7 and 41.7 p.p.m., respectively) as the exchange processes slowed, though the slow-exchange limit was not reached and no signal for PPh_3 was apparent.

Treatment of the phosphinegold ethynyls with a different tertiary phosphine also involves fast exchange. Thus the room-temperature ^{31}P n.m.r. spectrum of $[Au(C\equiv CPh)\{P(C_6H_4\text{-}Me\text{-}p)_3\}]$ and 0.1 mol equivalent of PPh_3 consisted of one broad signal. Addition of sulphur to react with and remove the excess of phosphine as phosphine sulphides then led to two sharp resonances of $[Au(C\equiv CPh)\{P(C_6H_4Me\text{-}p)_3\}]$ and $[Au(C\equiv CPh)(PPh_3)]$ (10:1 ratio), indicative of phosphine displacement [equation (4)].

$$\{(p\text{-}MeC_6H_4)_3P\}Au(C\equiv CPh) + Ph_3P \rightleftharpoons (Ph_3P)Au(C\equiv CPh) + (p\text{-}MeC_6H_4)_3P \quad (4)$$

According to ^{31}P n.m.r. spectroscopy, solutions of $[Au(C\equiv CPh)(PPh_3)]$ and $[AuCl\{P(C_6H_4Me\text{-}p)_3\}]$ in $CDCl_3$ rapidly equilibrate [equation (5)]. Clearly this exchange could be caused by a trace of free phosphine in solution, and this could conceivably originate from some decomposition of either material. A straightforward exchange of ethynyl for chloride could also produce the observed products, however, and other reactions do proceed by this type of process (see below). At present we are unable to assign the pathway involved.

$$(Ph_3P)Au(C\equiv CPh) + \{(p\text{-}MeC_6H_4)_3P\}AuCl \rightleftharpoons (Ph_3P)AuCl + \{(p\text{-}MeC_6H_4)_3P\}Au(C\equiv CPh) \quad (5)$$

The ethynyl groups of $[Au(C\equiv CR')(PR_3)]$ readily transfer from gold to mercury or platinum in exchange for chloride. Mercury(II) chloride is readily converted into $[Hg(C\equiv CPh)_2]$ by $[Au(C\equiv CPh)(PPh_3)]$ [equation (6)]. So complete are the transfers that no trace of gold ethynyl can be detected in solution by ^{31}P n.m.r. spectroscopy when $[AuCl(PPh_3)]$ is treated with either $[Hg(C\equiv CPh)_2]$ or $[Hg(C\equiv CMe)_2]$.

$$2(Ph_3P)Au(C\equiv CPh) + HgCl_2 \longrightarrow 2(Ph_3P)AuCl + Hg(C\equiv CPh)_2 \quad (6)$$

Reactions between $[Au(C\equiv CPh)(PPh_3)]$ and $\mathit{cis}\text{-}[PtCl_2(PMePh_2)_2]$ are complicated by isomerisations. The 1:1 reaction produces $\mathit{trans}\text{-}[PtCl(C\equiv CPh)(PMePh_2)_2]$ [equation (7)]. The *trans* isomers of mono-organoplatinum complexes of this type are thermodynamically favoured,[10] and it is likely in this case that stereospecific ligand substitution has been followed by isomerisation. The reaction of $\mathit{cis}\text{-}[PtCl_2(PMePh_2)_2]$ with 2 mol equivalents of the gold ethynyl complex follows one of two pathways. When observed in $CDCl_3$ solution by ^{31}P n.m.r. spectroscopy at ambient temperatures, the products are either $\mathit{cis}\text{-}[Pt(C\equiv CPh)_2(PMePh_2)_2]$, or $\mathit{trans}\text{-}[PtCl(C\equiv CPh)(PMePh_2)_2]$ followed by a slow formation of $\mathit{trans}\text{-}[Pt(C\equiv CPh)_2(PMePh_2)_2]$ [equation (8): L = $PMePh_2$].

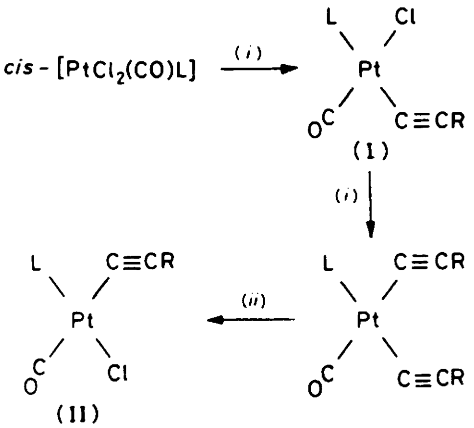
$$(Ph_3P)Au(C\equiv CPh) + \mathit{cis}\text{-}[PtCl_2(PMePh_2)_2] \longrightarrow (Ph_3P)AuCl + \mathit{trans}\text{-}[PtCl(C\equiv CPh)(PMePh_2)_2] \quad (7)$$

$$\begin{tikzcd} \mathit{cis}\text{-}[PtCl_2L_2] \arrow[r, "2(Ph_3P)Au(C\equiv CPh)"] \arrow[d, "(Ph_3P)Au(C\equiv CPh)"'] & 2(Ph_3P)AuCl + \mathit{cis}\text{-}[Pt(C\equiv CPh)_2L_2] \\ \mathit{trans}\text{-}[PtCl(C\equiv CPh)L_2] + (Ph_3P)AuCl \arrow[r, "(Ph_3P)Au(C\equiv CPh)"] & 2(Ph_3P)AuCl + \mathit{trans}\text{-}[Pt(C\equiv CPh)_2L_2] \quad (8) \end{tikzcd}$$

In the reactions which produced *trans* products, the n.m.r. signals of the gold complexes were noticeably broadened, indicative of the rapid exchange of phosphines observed previously. A tentative explanation for the two pathways can be based on this. The straightforward reaction involves ready formation of $\mathit{cis}\text{-}[PtCl(C\equiv CPh)(PMePh_2)_2]$, followed by a rapid second substitution to form $\mathit{cis}\text{-}[Pt(C\equiv CPh)_2(PMePh_2)_2]$. If, on the other hand, a trace of free phosphine is present in solution, perhaps by some decomposition of a gold complex, this would catalyse isomerisation of $\mathit{cis}\text{-}[PtCl(C\equiv CPh)(PMePh_2)_2]$.[10] The *trans* isomer subsequently reacts with more $[Au(C\equiv CPh)(PPh_3)]$. An experiment performed in the presence of S_8 to scavenge any free phosphine yielded substantially $\mathit{cis}\text{-}[Pt(C\equiv CPh)_2(PMePh_2)_2]$.

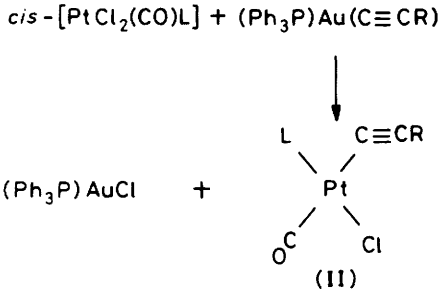
Mercury ethynyls also transfer their organic groups to platinum in reactions of this type,[11] so the ethynyl-transfer sequence is established as $Au^{I} > Hg^{II} > Pt^{II}$. Interestingly this sequence may not apply to other organic groups, as nitroaryl groups have been transferred from mercury(II) to both gold(I)[12] and gold(III).[13]

The most interesting exchange reactions of this type are those between the gold ethynyl complexes and $\mathit{cis}\text{-}[PtCl_2(CO)L]$. Reactions between ethynylmercury compounds and these carbonylphosphineplatinum halides have been examined,[11] and they follow a highly specific pathway (Scheme 1). When



Scheme 1. L = $PMePh_2$. (*i*) $[Hg(C{\equiv}CR)_2]$, $-[HgCl(C{\equiv}CR)]$; (*ii*) *cis*-$[PtCl_2(CO)L]$

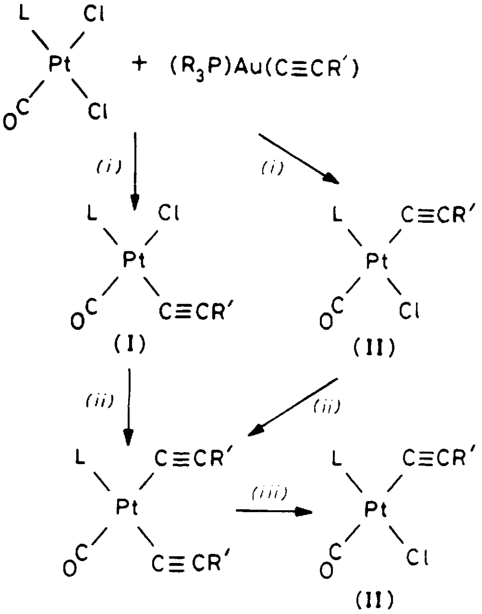
mercury ethynyls are replaced by gold ethynyls in these reactions the same final product (**II**) is obtained (Scheme 2).



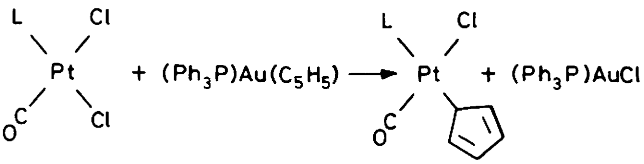
Scheme 2.

When monitored at −20 °C by ^{31}P n.m.r. spectroscopy, however, the presence of $[PtCl(C{\equiv}CR)(CO)L]$ [isomer (**I**) as well as (**II**)] and *cis*-$[Pt(C{\equiv}CR)_2(CO)L]$ (R = Me or Ph, L = $PMePh_2$) are observed as intermediates. The reaction sequences differ from those with $[Hg(C{\equiv}CR)_2]$ in that both isomers (**I**) and (**II**) of $[PtCl(C{\equiv}CR)(CO)L]$ are formed before any *cis*-$[Pt(C{\equiv}CR)_2(CO)L]$ appears, and both isomers appear to react with $[Au(C{\equiv}CR)(PR_3)]$ (R = Ph or C_6H_4Me-*p*) more readily than does *cis*-$[PtCl_2(CO)L]$. No exchange of tertiary phosphine appears to accompany these reactions, though they involve the formation and disappearance of small amounts (< 10%) of an unknown phosphine-containing material [$\delta(^{31}P) = -6.4$ p.p.m.]. Scheme 3 summarises these reactions.

Past work has indicated that halide-substitution reactions of *cis*-$[PtCl_2(CO)L]$ are generally very stereospecific (ref. 11 and refs. therein), and the lack of specificity in this case is noteworthy. The reactions with organomercurials probably involve an S_E2(cyclic) route or oxidative addition to platinum followed by reductive elimination (or some pathway intermediate between the two).[11] The gold compounds may well react in the same way as the mercurials. The fact that propynyl groups are transferred more rapidly than phenylethynyls from both gold and mercury to platinum could support this. The change in specificity, though, becomes difficult to explain. It is possible, however, that an alternative pathway could operate for the gold complexes. Oxidative addition *to* gold(I), followed by reductive elimination, can lead to the observed products. Such a process is unlikely for mercury(II), and could conceivably account for the change of specificity. The reaction of $[Au(C_5H_5)(PPh_3)]$ with *cis*-$[PtCl_2(CO)L]$ (L = $PMePh_2$) produced only one isomer (Scheme 4). This same material is produced from both $[Hg(C_5H_5)_2]$ or $Tl(C_5H_5)$.[14]



Scheme 3. (*i*) $-[AuCl(PR_3)]$; (*ii*) $[Au(C{\equiv}CR')(PR_3)]$, $-[AuCl(PR_3)]$; (*iii*) *cis*-$[PtCl_2(CO)L]$



Scheme 4.

Experimental

The ^{31}P and ^{1}H n.m.r. spectra were recorded on a Varian XL 100 spectrometer (operating in the Fourier-transform mode) and a Perkin-Elmer R32 90-MHz spectrometer, respectively. I.r. spectra were recorded as KBr discs on a PE 580 spectrometer. The compounds [AuClL] [L = PPh_3 or $P(C_6H_4Me$-*p*$)_3$] and *cis*-$[PtCl_2(CO)(PMePh_2)]$ were prepared by reported methods.[15,16]

Chloro[*tris*(4-*methoxyphenyl*)*phosphine*]*gold*.—A solution of $HAuCl_4$ (5 g) and $P(C_6H_4OMe$-*p*$)_3$ (5.69 g) in ethanol (100 cm^3) was stirred for 3 h at 0 °C. A pale yellow solution and precipitate developed, and addition of a further small amount of phosphine failed to remove the colour. The precipitate was filtered off and dissolved in CH_2Cl_2. The solution was dried over anhydrous $MgSO_4$, and diethyl ether was added until precipitation was about to begin, after which colourless crystals of $[AuCl\{P(C_6H_4OMe$-*p*$)_3\}]$ grew on standing (5.23 g, 61%), m.p. 206—207 °C, ν(Au–Cl) 330 cm^{-1} (Found: C, 43.2; H, 3.25. $C_{21}H_{21}AuClO_3P$ requires C, 43.1; H, 3.6%).

Phenylethynyl(*triphenylphosphine*)*gold*.—To a suspension of $[AuCl(PPh_3)]$ (1 g, 2.0 mmol) in dry ethanol (40 cm^3) was added Na(OEt) [freshly prepared from Na (48.7 mg, 2.1 mmol) in ethanol (5 cm^3)] and $PhC{\equiv}CH$ (208.2 mg, 2.0 mmol). The solution was refluxed for 1 h, cooled and concentrated, after which a white precipitate of pure [Au($C\equiv CPh$)(PPh_3)] (0.89 g, 78%) was removed by filtration.

Phenylethynyl[*tris*(p-*tolyl*)*phosphine*]*gold*.—This compound was prepared in analogous manner from [AuCl{P(C_6H_4-Me-*p*}$_3$] (0.49 g, 0.97 mmol) and Ph$C\equiv CH$ (99 mg, 0.97 mmol) at room temperature (2 h), and recrystallised from ethanol, yield 77% (Found: C, 57.3; H, 4.4. $C_{29}H_{16}AuP$ requires C, 57.8; H, 4.3%).

Propynyl(*triphenylphosphine*)*gold*.—Propyne was slowly bubbled through a suspension of [AuCl(PPh_3)] (0.5 g, 1.9 mmol) in ethanol (25 cm^3) to which sodium ethoxide (from 23.2 mg sodium) had been added. After 1 h at 60 °C, during which the suspension thinned, then appeared to reform, the solution was cooled and concentrated. The [Au($C\equiv CMe$)(PPh_3)] obtained was filtered off and recrystallised from $CHCl_3$–pentane, yield 0.28 g (56%) (Found: C, 50.35; H, 4.4. $C_{21}H_{18}AuP$ requires C, 50.6; H, 3.6%).

Similarly prepared were 1-*butynyl*(*triphenylphosphine*)*gold* from 1-butyne, yield 63% (Found: C, 51.5; H, 3.75. $C_{22}H_{20}AuP$ requires C, 51.6; H, 3.9%), and *trifluoromethylethynyl*(*triphenylphosphine*)*gold* from $CF_3C\equiv CH$ at 0 °C, yield 44% (Found: C, 45.5; H, 2.6. $C_{21}H_{15}AuF_3P$ requires C, 45.7; H, 2.7%).

Reaction of Ethyne with [AuCl(PPh_3)].—Bubbling C_2H_2 through a suspension of [AuCl(PPh_3)] in ethanolic sodium ethoxide at 0 °C produced white, solid *ethynyl*(*triphenylphosphine*)*gold*. At no stage did the solution become clear. Low solubility prevented purification (see Table for spectroscopic data). The impure [Au($C\equiv CH$)(PPh_3)] (0.36 g, 0.74 mmol) was added to another suspension of [AuCl(PPh_3)] (0.36 g, 0.74 mmol) in ethanolic Na(OEt), and the mixture stirred for 1 h at ambient temperatures. Upon filtration colourless solid [(Ph_3P)-Au$C\equiv C$Au(PPh_3)] (0.66 g, 95%) was obtained. The compound is very sparingly soluble in organic solvents, and attempts to purify it by recrystallisation failed (see Table for spectroscopic data).

μ-*Ethynylene-bis*[*tris*(p-*tolyl*)*phosphinegold*].—Bubbling C_2H_2 through a suspension of [AuCl{P(C_6H_4Me-*p*)$_3$}] (1.0 g, 1.9 mmol) in ethanolic Na(OEt) (1 mol equivalent) for 45 min caused disappearance then reappearance of a white solid. Upon filtration [{(*p*-MeC_6H_4)$_3$P}Au$C\equiv C$Au{P(C_6H_4Me-*p*)$_3$}] was obtained (Found: C, 50.7; H, 4.2. $C_{44}H_{42}Au_2P_2$ requires C, 51.7; H, 4.1%). Recrystallisation from CH_2Cl_2 produced the corresponding 2CH_2Cl_2 solvate (Found: C, 46.3; H, 3.5; Cl, 12.1. $C_{46}H_{46}Au_2Cl_4P_2$ requires C, 46.3; H, 3.9; Cl, 11.9%), from which the unsolvated material could be obtained by heating *in vacuo* at 50 °C for 12 h. Recrystallisation from a mixture of $CHCl_3$ and pentane produced the corresponding 3$CHCl_3$ solvate (Found: C, 40.7; H, 2.9; Cl, 22.8; P, 4.9. $C_{47}H_{45}Au_2Cl_9P_2$ requires C, 40.85; H, 3.25; Cl, 23.1; P, 4.5%). Prolonged heating under vacuum failed to remove the chloroform.

μ-*Ethynylene-bis*[*tris*(4-*methoxyphenyl*)*phosphinegold*].—Bubbling C_2H_2 through a suspension of [AuCl{P(C_6H_4-OMe-*p*)$_3$}] (4.5 g, 7.7 mmol) in ethanolic NaOH as above produced [{(*p*-MeOC_6H_4)$_3$P}Au$C\equiv C$Au{P(C_6H_4OMe-*p*)$_3$}] which was recrystallised from methanol (Found: C, 46.7; H, 3.8; P, 5.4. $C_{44}H_{42}Au_2O_6P_2$ requires C, 47.1; H, 3.8; P, 5.5%). Recrystallisation from $CHCl_3$ produced the corresponding 2$CHCl_3$ solvate (Found: C, 40.1; H, 3.5; Cl, 14.3; P, 4.5. $C_{46}H_{44}Au_2Cl_6O_6P_2$ requires C, 40.8; H, 3.3; Cl, 15.6; P, 4.55%).

Cyclopentadienyl(*triphenylphosphine*)*gold*.—To a suspension of [AuCl(PPh_3)] (0.5 g, 1.0 mmol) in ethanol (20 cm^3) was added sodium ethoxide (from Na, 23.2 mg, in ethanol) and cyclopentadiene (66.5 mg, 1.0 mmol). After stirring overnight, a pale yellow precipitate of [Au(C_5H_5)(PPh_3)] (0.404 g, 76%) was produced [i.r. and ^{1}H n.m.r. spectra identical to those in the literature:[9] δ(^{31}P) 36.4 p.p.m.].

Exchange Reactions.—These were mainly performed on a small scale and followed by ^{31}P n.m.r. spectroscopy. The δ and *J* values for the platinum-containing products have already been published,[11,14,16] and allowed identification. In a typical example, *cis*-[$PtCl_2$(CO)($PMePh_2$)] (20.3 mg, 41 μmol) and [Au($C\equiv CPh$)(PPh_3)] (22.7 mg, 40.5 μmol) were dissolved in $CDCl_3$ at −60 °C. The solution was placed in an n.m.r. tube and maintained at −20 °C, the spectra being recorded at this temperature at regular intervals.

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References

1 R. J. Puddephatt, 'The Chemistry of Gold,' Elsevier, Amsterdam, 1978.
2 G. K. Anderson, *Adv. Organomet. Chem.*, 1982, **20**, 39.
3 K. I. Grandberg, *Russ. Chem. Rev.*, 1982, **51**, 249.
4 G. E. Coates and C. Parkin, *J. Chem. Soc.*, 1962, 3220.
5 O. M. Abu-Salah and A. R. Al-Ohaly, *Inorg. Chim. Acta*, 1983, **77**, L159.
6 R. J. Cross, M. F. Davidson, and A. J. McLennan, *J. Organomet. Chem.*, 1984, **265**, C37.
7 M. I. Bruce, E. Horn, J. G. Matisons, and M. R. Snow, *Aust. J. Chem.*, 1984, **37**, 1163.
8 R. Nast, P. Scheller, and A. Hengefeld, *J. Organomet. Chem.*, 1981, **214**, 273.
9 R. Huttel, U. Raffay, and H. Reinheimer, *Angew. Chem., Int. Ed. Engl.*, 1967, **6**, 862.
10 G. K. Anderson and R. J. Cross, *Chem. Soc. Rev.*, 1980, **9**, 185.
11 R. J. Cross and J. Gemmill, *J. Chem. Soc., Dalton Trans.*, 1984, 199, 205.
12 J. Vicente, A. Arcas, and M. T. Chicote, *J. Organomet. Chem.*, 1983, **252**, 257.
13 J. Vicente, M. T. Chicote, A. Arcas, M. Artigao, and R. Jimenez, *J. Organomet. Chem.*, 1983, **247**, 123.
14 R. J. Cross and A. J. McLennan, *J. Chem. Soc., Dalton Trans.*, 1983, 359.
15 F. G. Mann, A. F. Wells, and D. Purdie, *J. Chem. Soc.*, 1937, 1828.
16 G. K. Anderson and R. J. Cross, *J. Chem. Soc., Dalton Trans.*, 1979, 1246.

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