Reactivity of an Acetylenephosphino Gold(III) Precursor: Addition to the Triple Bond or Formation of Alkynyl Derivatives

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We have synthesized the gold(III) complex Au(C_6F_5)$_3$(PPh$_2$CCH) (**1**), containing an acetylene moiety. Reactions with sodium alkoxides lead chemoselectively and regioselectively to gold(III) complexes containing the new ligand (2-alkoxyethenyl)diphenylphosphine or (2,2-dialkoxyethyl)diphenylphosphine, via a single or double alcohol addition to the acetylene-phosphine fragment. Reaction of complex **1** with gold(I) or silver(I) acetylacetonato derivatives affords di-, tri-, or tetranuclear alkynylphosphino complexes, namely Au^{III}(C_6F_5)$_3$(PPh$_2$CC)-M^{I}(PPh$_3$) (M = Au, Ag), {Au^{III}(C_6F_5)$_3$(PPh$_2$CC)}$_2$Au^{I}, and {Au^{III}(C_6F_5)$_3$(PPh$_2$CC)Au^{I}}$_2$(μ-PPh$_2$-CH$_2$CH$_2$PPh$_2$). The crystal structures of Au(C_6F_5)$_3$(PPh$_2$CH$_2$CH(OMe)$_2$) and Au^{III}(C_6F_5)$_3$(PPh$_2$-CC)Au^{I}(PPh$_3$) have been determined by X-ray diffraction studies. Luminescence studies in the solid state show that only the tetranuclear derivative is luminescent at room temperature.

Introduction

Phosphinoalkynes, PR$_2$CCR′, are potentially bifunctional ligands, able to coordinate as a phosphine, an acetylene, or a combination of both; additionally, if R′ = H, the ligand can also act as an acetylide, by deprotonation of the C≡CH group. The coordination via the phosphorus lone pair usually dominates, mainly in complexes of metals in their normal oxidation states, although derivatives have been reported where this ligand behaves as a six- or even seven-electron (in the case of R = H) donor.[1] In some cases the alkyne fragment undergoes M−H or M−C insertion reactions, oxidative alkyne coupling processes, and even cleavage of the P−C bond to yield phosphide and alkynyl fragments that can give further reactions.[2]

There has been considerable activity concerning the synthesis of alkynylgold(I) derivatives. They can be prepared in various ways, but the most typical is the addition of a base, such as sodium alkoxide, in alcohol to the terminal alkyne, followed by that of a gold(I) halo derivative. Recently some other specific reagents have been used, such as [Au(NH$_3$)$_2$]$^+$ or the more generally applicable acetylacetonato gold(I) complexes, which already contain the base in the gold precursor.[3] Alkynyl gold(I) complexes have shown interesting optical properties, and generally the ancillary ligands are phosphines.[4] Thus, it would be promising to use phosphinoalkynyl ligands to study luminescence properties.

Accordingly, in this work we have prepared the acetylenephosphino gold(III) complex Au(C_6F_5)$_3$(PPh$_2$-CCH), from which we have tried to synthesize polynuclear acetylide derivatives by reaction with sodium alkoxide (methoxide, ethoxide) and chloro derivatives; unexpectedly, we have observed single and double alcohol addition to the triple bond, which to the best of our knowledge had not previously been reported in

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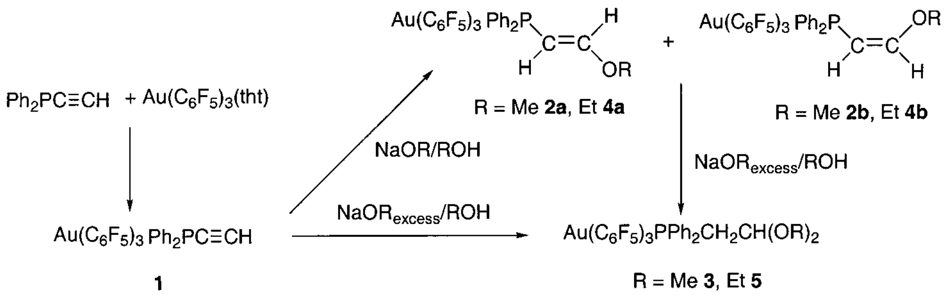
Scheme 1



metal complexes. We have also prepared for the first time (2-alkoxyethenyl)diphenylphosphines, although they are coordinated to a metal center. We have characterized by X-ray diffraction the final product of this reaction in the case of methoxide, namely $Au(C_6F_5)_3(PPh_2CH_2CH(OMe)_2)$, the first complex containing this phosphine to be structurally characterized. We have also prepared the "expected" mixed di-, tri-, and tetranuclear derivatives containing phosphino gold(III) and acetylide gold(I) or silver(I) fragments by using the "acac method",[5] and we have determined the crystal structure of $Au^{III}(C_6F_5)_3(PPh_2CC)Au^{I}(PPh_3)$.

Results and Discussion

Synthesis and Characterization of $Au(C_6F_5)_3(PPh_2CCH)$ and Reactivity toward Alkoxides. The reaction of ethynyldiphenylphosphine with $Au(C_6F_5)_3(tht)$ (tht = tetrahydrothiophene) led by displacement of tht to complex **1** with the acetylenephosphine ligand coordinated only through the phosphorus donor atom (Scheme 1). We have carried out the reaction of complex **1** with sodium methoxide, and surprisingly, we obtained complex **2** as a mixture of isomers (cis/trans) containing the new phosphine (2-methoxyethenyl)diphenylphosphine, coming from the anti-Markovnikov addition of methanol to the noncoordinated alkyne fragment. The addition of an excess of NaOMe to complex **1** led after 1 week to the (2,2-dimethoxyethyl)diphenylphosphino complex **3**, through a double anti-Markovnikov methanol addition. Analogous results were obtained by using sodium ethoxide, involving single or double anti-Markovnikov addition of ethanol to give complexes **4** and **5**.

Complexes **1**−**5** are air- and moisture-stable white solids. The IR spectrum of **1** shows a strong absorption at 3209 cm^{-1} from $\nu(C{\equiv}CH)$ and a signal at 2071 cm^{-1} from the asymmetric $C{\equiv}C$, which are not present for the other derivatives; all the spectra show absorptions corresponding to the pentafluorophenyl rings around 965 and 800 cm^{-1}.[6] Their acetone solutions are nonconducting. Selected ^1H and $^{31}P\{^1H\}$ NMR data are collected in Table 1. The $^{31}P\{^1H\}$ NMR spectra display a single resonance. The proton spectrum of **1** shows the acetylenephosphine ligand with a characteristic doublet ($^3J_{HP}$ = 9.3 Hz) due to $PC{\equiv}CH$, which disappears after reaction with alkoxide. The proton spectra of complexes **2** and **4** show two products in ratios of ca. 80:20 and 70:30, respectively, for the mixtures of derivatives **2a**/**2b** and **4a**/**4b**. Selective phosphorus decoupling, $^1H\{^{31}P\}$ NMR, and COSY experiments have been carried out to determine fully the relationships, the chemical shifts, and the coupling constants. The mixtures for the ethenyl−phosphino complexes can be assigned to the trans/cis isomers, whereby the main product is the trans isomer, because of the greatest H−H coupling ($^3J_{HH}$ = ca. 13.5 Hz) and the smallest P−H coupling ($^3J_{HP}$ = 10.6 and 12.5 Hz for derivatives **2a** and **4a**). Finally, the ^1H NMR spectra of complexes **3** and **5** show a single product, which must be the isomer $PPh_2CH_2CH(OR)_2$, because only one kind of alkoxide and two types of H in the ratio 1:2 are observed (in fact, for complex **5** with R = OCH_2CH_3 one observes one resonance for CH_3 but two resonances for CH_2, which are attributable to diastereotopic protons as confirmed by a COSY experiment).

Table 1. Selected ^1H and $^{31}P\{^1H\}$ NMR Resonances for Complexes 1−5[a]

	^1H			
complex	H^{α}	H^{β}	R^b	$^{31}P\{^1H\}$
1		3.51 d		−2.6
2a	5.20 dd	6.90 dd	3.84	9.0
2b	5.15 "t"	7.02 dd	4.01	−1.6
3	2.88 dd	4.28 "q"	3.11	10.6
4a	5.25 dd	7.06 dd	1.43 t, 4.10 q	8.5
4b	5.10 dd	6.95 dd	1.15 t, 3.99 q	1.1
5	2.89 dd	4.33 "q"	0.96 t, 3.11 m, 3.40 m	11.4

[a] In $CDCl_3$; proton assignment $-Au-PPh_2-CH^{\alpha}{}_x-CH^{\beta}(OR)_x$ (x = 0−2). [b] R = Me for complexes **2** and **3**; R = Et for complexes **4** and **5**.

The ^{19}F NMR spectra show the pattern of one $Au(C_6F_5)_3$ unit (two types of C_6F_5 rings in a 1:2 ratio) for complexes **1**, **3**, and **5** and of two different $Au(C_6F_5)_3$ units in the case of **2** and **4** (as expected for the mixture **2a**/**2b** and **4a**/**4b**). The reaction was monitored by NMR to verify that the first alcohol addition takes place very fast and only the starting complex **1**, **2a**, and **2b** (or **3a** and **3b**) are observed, but the second one occurs very slowly after adding an excess of alkoxide; a mixture of complexes **2a**, **2b**, and **3** (or **4a**, **4b**, and **5**) is observed, which finally leads to the double-addition complex **3** (or **5**).

The FAB^- mass spectra show a peak corresponding to $[Au(C_6F_5)_2]^-$ as the base peak and a peak for complex **1** at m/z 907 due to $[M - H]^-$. In the FAB^+ mass spectra the fragments $[Au(PPh_2R)]^+$ are observed, which are useful because the different phosphines can be distinguished. The peaks for **1**−**5** are as follows: m/z (% abundance, R) 407 (100, $C{\equiv}CH$), 439 (100, $CH{=}CHOMe$), 471 (48, $CH_2CH(OMe)_2$), 453 (100, $CH{=}CHOEt$), and 499 (37, $CH_2CH(OEt)_2$).

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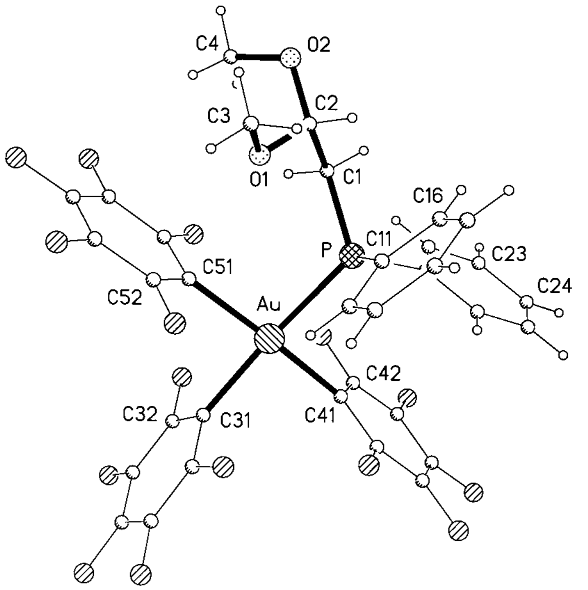

Figure 1. Molecular structure of complex **3**, Au(C_6F_5)$_3$(PPh$_2$CH$_2$CH(OMe)$_2$).

In contrast to our findings, it has been reported that the reaction of the gold(I) derivative AuCl(PR$_2$CCH) with NaOMe/MeOH leads, as expected, to the deprotonation of the terminal alkyne and the formation of [Au(PR$_2$CC)]$_n$ as insoluble polymeric chains.[7] In our case the formation of this polymer is prevented because of the high stability of the tris(pentafluorophenyl)gold fragment, and the acetylenic fragment is activated for nucleophilic attack. More closely related to our reaction are the reported alcohol additions to alkynes catalyzed by a gold(I) or a gold(III) derivative or to an olefinic double bond activated by metal complexation.[8]

We have thus found the first stoichiometric reaction where an alcohol is added to an alkyne−phosphino fragment in a metallic complex in two steps: first to give the (2-alkoxyvinyl)diphenylphosphino complex and then to give the (2,2-dialkoxyethyl)diphenylphosphino complex. The single addition of methanol to the ligand is chemoselective (100% to the alkene in a first step) and regioselective (100% anti-Markovnikov) but not stereoselective (mixed cis−trans); the double addition is chemoselective (100% to the alkane after 1 week) and regioselective (100% anti-Markovnikov). The regioselectivity could be associated with the steric hindrance of the pentafluorophenyl−phosphinogold(III) unit, consistent with the assignment of the trans isomer as the main isomer.

Crystal Structure of Complex 3. The nature of the gold(III) complex Au(C_6F_5)$_3$(PPh$_2$CH$_2$CH(OMe)$_2$) has been confirmed by X-ray diffraction studies. To the best of our knowledge, this is the first X-ray structure of a coordination derivative containing this phosphine. The molecular structure is shown in Figure 1, with selected bonds and angles in Table 2. The gold(III) center displays a slightly distorted square planar coordination (mean deviation from best plane 0.10 Å) with CAuC and CAuP angles ranging from 87.62(11) to 94.24(9)°. The acetylenephosphine starting ligand has clearly changed by the formal addition of two methanol molecules to the triple bond. The C(1)−C(2) distance is 1.509(5) Å, consistent with a single bond, and compares well to the corresponding single carbon−carbon bond in the isopropyl substituent in the related AuCl(^{i}Pr$_2$PCCH) (1.510(12)−1.526(13) Å);[7] it is clearly different from the carbon−carbon triple bond in the same derivative (1.204(7) Å). A search of the Cambridge Crystallographic Database for the acyclic fragment CH$_2$CH(OC)$_2$ yielded 25 hits with a mean C−C bond length of 1.507 Å. The C(2)−O distances are 1.360(5) and 1.414(5) Å. All of the bonds may be slightly vibrationally shortened, because the *U* values of the dimethoxyethyl fragment are marginally higher than in the rest of the molecule, although none of the values are strikingly high (maximum U_{eq} 0.079 Å^2 for C3). There are no significant differences in the P−C distances, which lie in the range 1.810(3)−1.835(4) Å.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex 3

Au−C(41)	2.065(3)	P−C(1)	1.835(4)
Au−C(51)	2.068(3)	C(1)−C(2)	1.509(5)
Au−C(31)	2.067(3)	C(2)−O(1)	1.360(5)
Au−P	2.3692(8)	C(2)−O(2)	1.414(5)
P−C(11)	1.810(3)	C(3)−O(1)	1.414(5)
P−C(21)	1.824(3)	C(4)−O(2)	1.398(6)
C(41)−Au−C(51)	171.15(11)	C(11)−P−Au	108.92(11)
C(41)−Au−C(31)	87.62(11)	C(21)−P−Au	112.12(10)
C(51)−Au−C(31)	88.60(11)	C(1)−P−Au	115.56(12)
C(41)−Au−P	90.17(8)	C(2)−C(1)−P	114.5(3)
C(51)−Au−P	94.24(9)	O(1)−C(2)−O(2)	113.8(3)
C(31)−Au−P	174.78(9)	O(1)−C(2)−C(1)	108.7(3)
C(11)−P−C(21)	104.40(14)	O(2)−C(2)−C(1)	112.7(4)
C(11)−P−C(1)	110.70(16)	C(2)−O(1)−C(3)	113.6(4)
C(21)−P−C(1)	104.54(16)	C(4)−O(2)−C(2)	115.0(3)

Au−C bond distances trans to the phosphine and trans to pentafluorophenyl are almost equal, 2.067(3) and 2.065(3), 2.068(3) Å, respectively. They are shorter than those found in Au(C_6F_5)$_3${PPh(CH$_2$PPh$_2$)$_2$} (2.078(6)−2.082(7) Å)[9] but similar to those found in other tris(pentafluorophenyl)gold(III) complexes, such as [Au(C_6F_5)$_3$(S$_2$C−PEt$_3$)] (2.067(4) and 2.076(4) Å trans to C),[10] [(μ-S$_2$C−PEt$_3$){Au(C_6F_5)$_3$}$_2$] (2.062(14)−2.090(13) Å trans to C),[10] NBu$_4$[{Au(C_6F_5)$_3$PPh$_2$CHPPh$_2$}$_2$Au] (2.063(8) and 2.080(8) trans to P, 2.057(8)−2.069(9) Å trans to C),[11] and [N(PPh$_3$)$_2$][{Au(C_6F_5)$_3$(μ-PPh$_2$)}$_2$Au] (2.073(6) Å trans to P, 2.052(5) and 2.058(6) Å trans to C).[12] The Au^{III}−P bond distance is 2.3692(8) Å, similar to those found in NBu$_4$[{Au(C_6F_5)$_3$PPh$_2$CHPPh$_2$}$_2$Au] (2.367(2) Å)[11] and in [N(PPh$_3$)$_2$][{Au(C_6F_5)$_3$(μ-PPh$_2$)}$_2$Au] (2.365(2) Å),[12] shorter than in [Au(C_6F_5)$_3${PPh$_2$C(=CH$_2$)PPh$_2$}Au(C_6F_5)] (2.382(2) Å),[13] but longer than reported in AuMe$_3$PPh$_3$ (2.350(6) and 2.347(6) Å)[14] or

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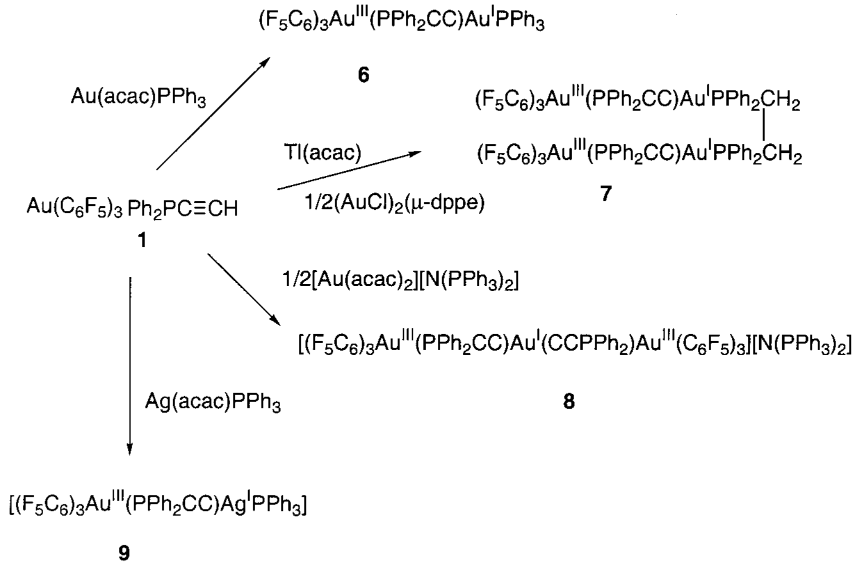
Scheme 2



in $Au(C_6F_5)_3\{PPh(CH_2PPh_2)_2\}$ (2.356(2) Å);[9] it is much longer than that found in the related gold derivative $AuCl(^iPr_2PCCH)$ (2.222(2) Å), although this is an $Au^I{-}P$ distance.

Synthesis and Characterization of Acetylide Complexes. To prepare acetylide derivatives, we tried a different approach. Instead of adding a base to the reaction mixture, we carried out reactions by using acetylacetonato (acac) derivatives of gold(I), silver(I), or thallium(I) (in this case together with a chlorogold(I) derivative) which are able to deprotonate an "acid" and to coordinate to the resulting "base" the corresponding gold(I) or silver(I) fragment (as result of the loss of the acac ligand); this is known as the "acac method".[5] Thus, we proceeded to react complex **1** with $Au(acac)(PPh_3)$, $Tl(acac) + AuCl(PPh_3)$, $Tl(acac) + (AuCl)_2(\mu\text{-}PPh_2CH_2CH_2PPh_2)$, $[Au(acac)_2](PPN)$ (PPN is $PPh_3{=}N{=}PPh_3$), and $Ag(acac)(PPh_3)$, giving the corresponding di-, tri-, or tetranuclear derivatives (see Scheme 2). Therefore, we have succeeded in functionalizing the alkyne fragment to produce alkynyl derivatives without any addition to the carbon−carbon triple bond.

Complexes **6**−**9** are air- and moisture-stable white solids at room temperature. Their acetone solutions behave as nonconducting for derivatives **6**, **7**, and **9** but as 1:1 electrolytes for derivative **8**. In the IR spectra the absorption corresponding to C≡CH disappeared but the asymmetric C≡C vibration is observed at 2082 (**6**), 2074 (**7**), 2052 (**8**), and 2049 and 2024 cm^{-1} (**9**), which confirms that the carbon−carbon triple bond has not reacted; all the spectra show absorptions corresponding to the pentafluorophenyl rings around 965 and 800 cm^{-1}. The ^1H NMR spectra show the disappearance of the PC≡CH doublet and display only phenyl resonances, except for complex **7**, where the methylene resonances of the diphosphine are observed. The ^{19}F NMR spectra display only one type of tris(pentafluorophenyl)gold(III) unit. The $^{31}P\{^1H\}$ NMR spectra show a singlet around −6.6 ppm for complexes **6** and **7** or around −8.5 ppm for complexes **8** and **9** due to the alkynylphosphino gold(III) fragment and a singlet at about 40 ppm or a broad resonance at 15.1 ppm for the phosphino gold(I) or silver(I) fragment; the broad phosphino silver resonances are transformed at −55 °C to a doublet of doublets centered at 16.7 ppm because of the P−Ag coupling. Finally, a resonance at 21.8 ppm is observed for complex **8** from the PPN^+ ion.

The FAB^- mass spectra show the base peak at *m*/*z* 531 due to $[Au(C_6F_5)_2]^-$; additionally, a peak at *m*/*z* 2011 corresponding to $[(F_5C_6)_3Au(PPh_2CC)Au(CCPPh_2)Au(C_6F_5)_3]^-$ is observed for complexes **6**−**8**. In the FAB^+ mass spectra the parent peaks are observed at *m*/*z* 459 ($[Au(PPh_3)]^+$), 1001 ($[Au_2(PPh_2CC)(PPh_2CH_2CH_2PPh_2)]^+$) and 369 ($[Ag(PPh_3)]^+$), respectively, for complexes **6**, **7**, and **9**; other significant peaks are observed as follows: *m*/*z* (% abundance, assignment, complex) 1825 (2, $[(F_5C_6)_3Au(PPh_2CC)(AuPPh_3)_2]^+$, **6**), 1407 (35, $[Au_3(PPh_2CC)_2(PPh_2CH_2CH_2PPh_2)]^+$, **7**).

We have carried out the same reaction with the previously reported[7] gold(I) precursor $AuCl(PPh_2CCH)$, but the dinuclear complex was not obtained (see eq 1); a phosphine substitution reaction takes place, accompanied by the formation of the very stable acetylidephosphino gold(I) polymer.

$$AuClPh_2PC{\equiv}CH + Au(acac)PPh_3 \rightarrow [Au(PPh_2CC)]_n + AuClPPh_3 + Hacac \quad (1)$$

Crystal Structure of Complex 6. The molecular structure of the dinuclear gold(III)−gold(I) complex $(F_5C_6)_3Au(PPh_2CC)Au(PPh_3)$ has been confirmed by X-ray diffraction studies. The molecular structure is shown in Figure 2, with selected bonds and angles in Table 3. The gold(I) center shows an almost linear geometry (175.7(2)°), which is connected with the linear ethynylphosphine ligand (C2−C1−P = 175.8(7)°) to give a five-atom linear chain. The intramolecular gold−gold distance is 6.069 Å, and the shortest intermolecular gold−gold distance is 7.37 Å, which prevents any metal−metal interactions, probably because of the steric hindrance of the two bulky end groups of the molecule (pentafluorophenyl and triphenylphosphine). The gold(III) center displays a square-planar coordination (mean deviation from best plane 0.02 Å) with C−Au−C and C−Au−P angles ranging from 88.5(3) to 91.56(19)°.

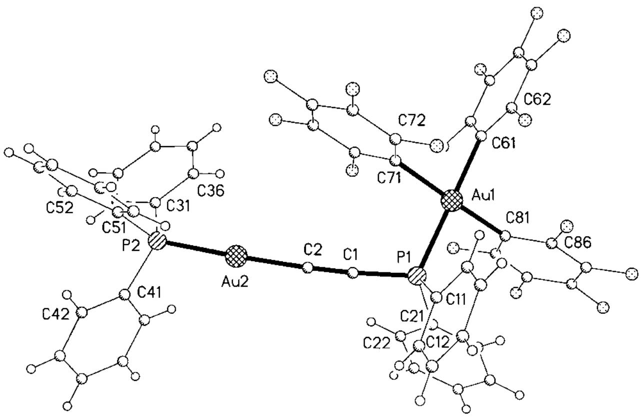


Figure 2. Molecular structure of complex **6**, $Au^{III}(C_6F_5)_3(PPh_2CC)Au^I(PPh_3)$.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex 6

Au(1)−C(81)	2.063(8)	P(1)−C(11)	1.803(8)
Au(1)−C(71)	2.067(8)	P(1)−C(21)	1.804(8)
Au(1)−C(61)	2.082(7)	P(2)−C(51)	1.809(8)
Au(1)−P(1)	2.3572(18)	P(2)−C(41)	1.815(8)
Au(2)−C(2)	1.982(8)	P(2)−C(31)	1.823(8)
Au(2)−P(2)	2.280(2)	C(1)−C(2)	1.220(11)
P(1)−C(1)	1.733(8)		

C(81)−Au(1)−C(71)	175.8(3)	C(11)−P(1)−Au(1)	113.1(2)
C(81)−Au(1)−C(61)	88.5(3)	C(21)−P(1)−Au(1)	113.6(2)
C(71)−Au(1)−C(61)	88.5(3)	C(51)−P(2)−C(41)	104.6(4)
C(81)−Au(1)−P(1)	91.36(18)	C(51)−P(2)−C(31)	107.1(4)
C(71)−Au(1)−P(1)	91.56(19)	C(41)−P(2)−C(31)	105.0(3)
C(61)−Au(1)−P(1)	179.12(19)	C(51)−P(2)−Au(2)	115.3(3)
C(2)−Au(2)−P(2)	175.7(2)	C(41)−P(2)−Au(2)	112.7(3)
C(1)−P(1)−C(11)	106.6(4)	C(31)−P(2)−Au(2)	111.4(2)
C(1)−P(1)−C(21)	105.9(4)	C(2)−C(1)−P(1)	175.8(7)
C(11)−P(1)−C(21)	105.9(3)	C(1)−C(2)−Au(2)	177.1(7)
C(1)−P(1)−Au(1)	111.3(3)		

The carbon−carbon bond triple distance is 1.220 (11) Å, close to that found in $AuCl(^iPr_2PCCH)$ (1.204(7) Å),[7] and it is clearly different from the carbon−carbon single bond distance found in complex **3** (1.509 (5) Å). The $P-C_{acetylide}$ bond distance is 1.733(8) Å, shorter than found for the other P−C bond distances (from 1.803(8) to 1.823(8) Å) or for the same bond in complex **3** (1.835 (4) Å). The $Au^{III}-C$ bond distances trans to the phosphine and trans to pentafluorophenyl are insignificantly different, taking account of the relatively high esd's, 2.082(7) and 2.063(8)−2.067(8) Å, respectively, and similar to those found for complex **3**. The $Au^{III}-P$ bond distance is 2.3572(18) Å, shorter than in complex **3** (2.3692(8) Å) and similar to that reported in $Au(C_6F_5)_3\{PPh(CH_2PPh_2)_2\}$ (2.356(2) Å).[9] The Au^I-P bond distance is normal for these alkynyl derivatives (2.280(2) Å) but longer than in many gold(I) phosphino complexes, as a consequence of the strong trans influence of the alkynyl group.[4] The Au^I-C bond distance is 1.982(8) Å, consistent with other reported gold(I) acetylide derivatives.[3,4]

Photophysical Studies. Alkynyl gold(I) derivatives often luminesce at room temperature, and the emission has been associated with intraligand electronic transitions, gold-centered transitions, Au−P to acetylide transitions, or even gold−gold bond to acetylide transitions.[4a] It is noteworthy that only derivative **7** is luminescent at room temperature in the solid state, the emission maxima being located at 445 and 455 nm, while the excitation maximum is located at 340 nm with a shoulder at 350 nm. The spectrum does not show any vibrational fine structure, and it is the only derivative able to possess short gold(I)−gold(I) distances (probably intermolecular short distances as in $(AuCCPh)_2(\mu\text{-dppe})$);[4b] besides, the acetylenephosphine ligand is not emissive in the solid state and therefore the nature of the emission could be tentatively assigned to metal-centered transitions.

Table 4. Excitation and Emission Data in the Solid State at 77 K for Complexes 1−9

complex	λ_{exc}/nm	λ_{emis}/nm
1		
2	334	445, 457, 482
3	300, 333	447, 458, 482, 517, 526
4	333	446
5	298, 343 (sh)	484
6	302, 330 (sh)	484, 517, 539
7	341	446
8	340, 386, 395	452, 458, 482 (sh)
9	314	483

However, complexes **2**−**9** luminesce at low temperature in the solid state, with excitation maxima in the range 298−395 nm and emission maxima between 445 and 539 nm. The results are summarized in Table 4. Complex **1** and the acetylenephosphine ligand are not emissive under the same conditions. Exchanging methoxide for ethoxide in complexes **2**−**5** leads to different emission spectra, which indicates that this phosphine ligand is involved in the electronic transitions. The spectrum of complex **7** is similar to that found at room temperature, except that the intensity has increased, and it is clearly different from that observed for the related complex **6**, indicating the role of the possible gold(I)−gold(I) contacts. The metal center attached to the alkynyl fragment has a role in the luminescence properties, and so the substitution of gold(I) by silver(I) leads to different spectra, as shown by comparison of the spectra of complexes **6** and **9**.

Experimental Section

General Considerations. All the reactions were carried out under an argon atmosphere at room temperature. IR spectra were recorded on a Perkin-Elmer 883 spectrophotometer, over the range 4000−200 cm^{-1}, by using Nujol mulls between polyethylene sheets. ^1H, ^{19}F, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Brüker ARX·300 or GEMINI 2000 apparatus in $CDCl_3$ solutions (if no other solvent is stated); chemical shifts are quoted relative to $SiMe_4$ (external, ^1H), $CFCl_3$ (external, ^{19}F), and 85% H_3PO_4 (external, ^{31}P). C, H, N, and S analyses were performed with a Perkin-Elmer 2400 microanalyzer. Conductivities were measured in acetone solution with a Philips PW 9509 apparatus. Mass spectra were recorded on a VG Autospec using the FAB technique (with Cs gun) and 3-nitrobenzyl alcohol as matrix. The luminescence spectra were recorded on a Perkin-Elmer LS-50B spectrofluorometer.

Preparation of $Au(C_6F_5)_3(PPh_2CCH)$ (1). To a 20 mL diethyl ether solution of $Au(C_6F_5)_3(tht)$[15] (0.393 g, 0.5 mmol) was added PPh_2CCH[7,16] (0.105 g, 0.5 mmol). After it was stirred for 2 h, the solution was concentrated to ca. 2 mL and the addition of petroleum ether afforded **1** as a white solid. A second fraction was obtained by concentration and addition

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of more petroleum ether. Yield of **1**: 381 mg, 84%. Data for **1**: ^{1}H NMR δ 3.51 (d, ^3J(HP) = 9.3 Hz, 1H, CH), 7.3−7.6 (m, 10H, Ph). ^{19}F NMR: δ −121.3 (m, 4F$_o$), −122.4 (m, 2F$_o$), −157.7 (t, 2F$_p$), −158.0 (t, 1F$_p$), −162.0 (m, 6F$_m$); ^{31}P{^{1}H} NMR δ −2.9 (s); IR 3209 (s, ν(C≡CH)), 2071 (s, ν(C≡C)), 967 (s, C_6F_5), 805 (s, C_6F_5), 796 (s, C_6F_5) cm^{-1}. Anal. Calcd for $C_{32}H_{11}AuF_{15}P$: C, 42.3; H, 1.2. Found: C, 41.9; H, 1.35. FAB$^-$ (*m/z* (%, assignment)): 531 (100, $[Au(C_6F_5)_2]^-$), 907 (2, [M − H]$^-$). FAB$^+$ (*m/z* (%, assignment)): 407 (100, $[Au(PPh_2CCH)]^+$), 617 (25, $[Au(PPh_2CCH)_2]^+$), 951 (15, $[Au(C_6F_5)_2(PPh_2CCH)_2]^+$). $\Lambda = 4\ \Omega^{-1}$ cm^2 mol^{-1}.

Preparation of $Au(C_6F_5)_3(PPh_2CH{=}CHOR)$ (R = Me, 2a (*trans*), 2b (*cis*); R = Et, 4a (*trans*), 4b (*cis*)). To $Au(C_6F_5)_3(PPh_2CCH)$ (91 mg, 0.1 mmol) was added a 10 mL methanol solution of NaOMe (6 mg, 0.1 mmol) or a 10 mL ethanol solution of 0.01 M NaOH. After the mixture was stirred for 2 h, the solvent was removed, dichloromethane was added, and the solution was filtered through Celite then concentrated to ca. 1 mL. Addition of petroleum ether afforded complexes **2** and **4** as white solids which were washed with petroleum ether. Yield of **2**: 71 mg, 75%. Data for *trans*-**2a**: ^{1}H NMR δ 3.84 (s, 3H, Me), 5.20 (dd, ^2J(HP) = 11.1 Hz, ^3J(HH) = 13.4 Hz, 1H, MeOCH═C*H*P), 6.90 (dd, ^3J(HH) = 13.4 Hz, ^3J(HP) = 10.6 Hz, 1H, MeOC*H*═CHP), 7.4−7.7 (m, 10H, Ph); ^{1}H{^{31}P} NMR δ 5.20 (d, ^3J(HH) = 13.4 Hz, 1H, MeOCH═C*H*P), 6.90 (d, 1H, MeOC*H*═CHP); ^{19}F NMR δ −121.3 (m, 4F$_o$), −122.6 (m, 2F$_o$), −158.2 (t, 2F$_p$), −158.4 (t, 1F$_p$), −162.0 (m, 4F$_m$), −162.3 (m, 2F$_m$); ^{31}P{^{1}H} NMR δ 9.0 (m). Data for *cis*-**2b**: ^{1}H NMR δ 4.01 (s, 3H, Me), 5.15 ("t", ^2J(HP) = ^3J(HH) = 6.9 Hz, 1H, MeOCH═C*H*P), 7.02 (dd, ^3J(HH) = 6.9 Hz, ^3J(HP) = 25.9 Hz, 1H, MeOC*H*═CHP), 7.4−7.7 (m, 10H, Ph); ^{1}H{^{31}P} NMR δ 5.15 (d, ^3J(HH) = 6.9 Hz, 1H, MeOCH═C*H*P), 7.02 (d, 1H, MeOC*H*═CHP); ^{19}F NMR δ −121.4 (m, 4F$_o$), −122.4 (m, 2F$_o$), −158.8 (t, 1F$_p$), −159.1 (t, 2F$_p$), −162.8 (m, 6F$_m$); ^{31}P{^{1}H} NMR δ −1.6 (m); IR 967 (s, C_6F_5), 795 (s, C_6F_5), 775 (sh, C_6F_5) cm^{-1}. Anal. Calcd for $C_{33}H_{15}AuF_{15}OP$: C, 42.15; H, 1.6. Found: C, 42.45; H, 1.7. FAB$^-$ (*m/z* (%, assignment)): 531 (100, $[Au(C_6F_5)_2]^-$), 865 (35, $[Au(C_6F_5)_4]^-$). FAB$^+$ (*m/z* (%, assignment)): 439 (100, $[Au(PPh_2CH{=}CHOMe)]^+$). $\Lambda = 8\ \Omega^{-1}$ cm^2 mol^{-1}.

Yield of **4**: 67 mg, 70%. Data for *trans*-**4a**: ^{1}H NMR δ 1.43 (t, ^3J(HH) = 7.1 Hz, 3H, C*H*$_3$CH$_2$O), 4.10 (q, 2H, CH$_3$C*H*$_2$O), 5.25 (dd, ^2J(HP) = 11.0 Hz, ^3J(HH) = 13.5 Hz, 1H, MeOCH═C*H*P), 7.06 (dd, ^3J(HP) = 12.5 Hz, 1H, MeOC*H*═CHP), 7.4−7.6 (m, 10H, Ph); ^{1}H{^{31}P} NMR δ 5.25 (d, ^3J(HH) = 13.5 Hz, 1H, MeOCH═C*H*P), 7.06 (d, 1H, MeOC*H*═CHP); ^{19}F NMR δ −121.3 (m, 4F$_o$), −122.6 (m, 2F$_o$), −158.3 (t, 2F$_p$), −158.4 (t, 1F$_p$), −162.0 (m, 4F$_m$), −162.3 (m, 2F$_m$); ^{31}P{^{1}H} NMR δ 8.5 (m). Data for *cis*-**4b**: ^{1}H NMR δ 1.15 (t, ^3J(HH) = 7.1 Hz, 3H, C*H*$_3$CH$_2$O), 3.99 (q, 2H, CH$_3$C*H*$_2$O), 5.10 (dd, ^2J(HP) = 12.7 Hz, ^3J(HH) = 7.1 Hz, 1H, MeOCH═C*H*P), 6.95 (dd, ^3J(HP) = 18.6 Hz, 1H, MeOC*H*═CHP), 7.4−7.6 (m, 10H, Ph); ^{1}H{^{31}P} NMR δ 5.10 (d, ^3J(HH) = 7.1 Hz, 1H, MeOCH═C*H*P), 6.95 (d, 1H, MeOC*H*═CHP); ^{19}F NMR δ −121.1 (m, 4F$_o$), −122.3 (m, 2F$_o$), −158.8 (t, 1F$_p$), −159.0 (t, 2F$_p$), −162.7 (m, 6F$_m$); ^{31}P{^{1}H} NMR δ 1.1 (m); IR 968 (s, C_6F_5), 795 (s, C_6F_5) cm^{-1}. Anal. Calcd for $C_{34}H_{17}AuF_{15}OP$: C, 42.8; H, 1.8. Found: C, 42.55; H, 1.7. FAB$^-$ (*m/z* (%, assignment)): 531 (100, $[Au(C_6F_5)_2]^-$), 865 (4, $[Au(C_6F_5)_4]^-$). FAB$^+$ (*m/z* (%, assignment)): 453 (100, $[Au(PPh_2CH{=}CHOEt)]^+$). $\Lambda = 4\ \Omega^{-1}$ cm^2 mol^{-1}.

Preparation of $Au(C_6F_5)_3(PPh_2CH_2CH(OR)_2)$ (R = Me, 3; R = Et, 5). To $Au(C_6F_5)_3(PPh_2CCH)$ (91 mg, 0.1 mmol) was added a 10 mL methanol solution of NaOMe (54 mg, 1 mmol) or a 20 mL ethanol solution of 0.05 M NaOH. After the mixture was stirred for 1 week, the solvent was removed, dichloromethane was added, and the solution was filtered through Celite and then concentrated to ca. 1 mL. Addition of petroleum ether afforded complexes **3** and **5** as white solids which were washed with petroleum ether. Yield of **3**: 84 mg, 86%. Data for **3**: ^{1}H NMR δ 2.88 (dd, ^2J(HP) = 10.4 Hz, ^3J(HH) = 5.4 Hz, 2H, CH$_2$P), 3.11 (s, 6H, Me), 4.28 ("q", ^3J(HH) = ^3J(HP) = 5.4 Hz, 1H, C*H*CH$_2$P), 7.4−7.6 (m, 10H, Ph); ^{19}F NMR δ −121.2 (m, 4F$_o$), −122.5 (m, 2F$_o$), −157.9 (t, 2F$_p$), −158.4 (t, 1F$_p$), −161.8 (m, 4F$_m$), −162.3 (m, 2F$_m$); ^{31}P{^{1}H} NMR δ 10.6 (m); IR 967 (s, C_6F_5), 795 (s, C_6F_5) cm^{-1}. Anal. Calcd for $C_{34}H_{19}AuF_{15}O_2P$: C, 42.0; H, 1.95. Found: C, 41.7; H, 2.25. FAB$^-$ (*m/z* (%, assignment)): 531 (100, $[Au(C_6F_5)_2]^-$), 865 (35, $[Au(C_6F_5)_4]^-$). FAB$^+$ (*m/z*, (%, assignment)): 383 (100, $[Au(PPh_2H)]^+$), 471 (48, $[Au(PPh_2CH_2CH(OMe)_2)]^+$), 607 (78, $[Au(C_6F_5)(PPh_2CH_2CHOMe)]^+$), 745 (4, $[Au(PPh_2CH_2CH(OMe)_2)_2]^+$), 941 (3, [M-OMe]$^+$). $\Lambda = 6\ \Omega^{-1}$ cm^2 mol^{-1}. Yield of **5**: 70 mg, 70%. Data for **5**: ^{1}H NMR δ 0.96 (t, ^3J(HH) = 7.0 Hz, 6H, C*H*$_3$CH$_2$O), 2.89 (dd, ^2J(HP) = 9.6 Hz, ^3J(HH) = 5.5 Hz, 2H, CH$_2$P), 3.11 (m, ABX$_3$ system, $^3J_{AX}$(HH) = 7.0 Hz, $^2J_{AB}$(HH) = 9.5 Hz, 2H, CH$_3$C*H*$_2$O), 3.40 (m, ABX$_3$ system, $^3J_{BX}$(HH) = 7.0 Hz, 2H, CH$_3$C*H*$_2$O), 4.33 ("q", ^3J(HH) = ^3J(HP) = 5.5 Hz, 1H, C*H*CH$_2$P), 7.4−7.6 (m, 10H, Ph); ^{1}H{^{31}P} NMR 2.89 (d, ^3J(HH) = 5.5 Hz, 2H, CH$_2$P), 4.33 (t, 1H, C*H*CH$_2$P); ^{19}F NMR δ −121.2 (m, 4F$_o$), −122.5 (m, 2F$_o$), −157.9 (t, 2F$_p$), −158.4 (t, 1F$_p$), −161.7 (m, 4F$_m$), −162.3 (m, 2F$_m$); ^{31}P{^{1}H} NMR δ 11.4 (m). IR 965 (s, C_6F_5), 795 (s, C_6F_5) cm^{-1}. Anal. Calcd for $C_{36}H_{23}AuF_{15}O_2P$: C, 43.2; H, 2.3. Found: C, 43.4; H, 2.6. FAB$^-$ (*m/z* (%, assignment)): 531 (100, $[Au(C_6F_5)_2]^-$), 698 (7, $[Au(C_6F_5)_4]^-$). FAB$^+$ (*m/z* (%, assignment)): 383 (100, $[Au(PPh_2H)]^+$), 499 (37, $[Au(PPh_2CH_2CH(OEt)_2)]^+$), 621 (55, $[Au(C_6F_5)(PPh_2CH_2CHOEt)]^+$). $\Lambda = 2\ \Omega^{-1}$ cm^2 mol^{-1}.

Preparation of $(F_5C_6)_3Au(PPh_2CC)Au(PPh_3)$ (6). This complex can be prepared in two different ways. (a) To a 5 mL dichloromethane solution of $Au(C_6F_5)_3(PPh_2CCH)$ (45 mg, 0.05 mmol) was added $Au(acac)(PPh_3)$[17] (28 mg, 0.05 mmol), and the mixture was stirred for about 1 h. The solution was concentrated to ca. 1 mL, and the addition of petroleum ether afforded **6** as a white solid. (b) To a 10 mL dichloromethane solution of $Au(C_6F_5)_3(PPh_2CCH)$ (45 mg, 0.05 mmol) was added Tl(acac)[18] (15 mg, 0.05 mmol), and the mixture was stirred for about 2 h. Then $AuCl(PPh_3)$[19] (25 mg, 0.05 mmol) was added. After the mixture was stirred for 1 h, TlCl was filtered off and the clear solution concentrated to ca. 1 mL. Addition of petroleum ether afforded **6** as a white solid. Yield of **6**: 44 mg, 65%. Data for **6**: ^{1}H NMR δ 7.4−7.7 (m, Ph); ^{19}F NMR δ −120.9 (m, 4F$_o$), −121.9 (m, 2F$_o$), −159.0 (t, 1F$_p$), −159.3 (t, 2F$_p$), −162.8 (m, 6F$_m$); ^{31}P{^{1}H} NMR δ -6.7 (s, 1P, PPh$_2$), 41.4 (s, 1P, PPh$_3$); IR 2082 (s, ν(C≡C)), 968 (s, C_6F_5), 810 (s, C_6F_5), 795 (s, C_6F_5) cm^{-1}. Anal. Calcd for $C_{50}H_{25}Au_2F_{15}P_2$: C, 43.95; H, 1.85. Found: C, 44.3; H, 2.2. FAB$^-$ (*m/z* (%, assignment)): 531 (100, $[Au(C_6F_5)_2]^-$), 2011 (25, $[(F_5C_6)_3Au(PPh_2CC)Au(CCPPh_2)Au(C_6F_5)_3]^-$). FAB$^+$ (*m/z* (%, assignment)): 459 (100, $[Au(PPh_3)]^+$), 721 (46, $[Au(PPh_3)_2]^+$), 1825 (2, $[M{+}Au(PPh_3)]^+$). $\Lambda = 4\ \Omega^{-1}$ cm^2 mol^{-1}.

Preparation of $[(F_5C_6)_3Au(PPh_2CC)Au(PPh_2CH_2CH_2PPh_2)Au(CCPPh_2)Au(C_6F_5)_3]$ (7). To a 10 mL dichloromethane solution of $Au(C_6F_5)_3(PPh_2CCH)$ (45 mg, 0.05 mmol) was added Tl(acac) (15 mg, 0.05 mmol), and the mixture was stirred for about 2 h. Then $(AuCl)_2(\mu\text{-}PPh_2CH_2CH_2PPh_2)$[19] (22 mg, 0.025 mmol) was added. After this mixture was stirred for 2 h, TlCl was filtered off and the clear solution concentrated to ca. 1 mL. Addition of petroleum ether afforded **7** as an off-white solid. Yield of **7**: 55 mg, 85%. Data for **7**: ^{1}H NMR: δ 2.70 (s, 4H, CH$_2$), 7.3−7.7 (m, 40H, Ph); ^{19}F NMR δ −121.1 (m, 4F$_o$), −122.1 (m, 42F$_o$), −159.1(t, 1F$_p$), −159.2 (t, 2F$_p$), −162.8 (m, 6F$_m$); ^{31}P{^{1}H} NMR δ -6.5 (s, 1P, PPh$_2$), 39.0 (s, 1P, PPh$_2$CH$_2$); IR 2074 (s, ν(C≡C)), 969 (s, C_6F_5), 797 (s, C_6F_5) cm^{-1}. Anal. Calcd for $C_{90}H_{44}Au_4F_{30}P_4$: C, 41.45; H, 1.7. Found: C, 41.8; H, 1.8. FAB$^-$ (*m/z* (%, assignment)): 531 (100, $[Au(C_6F_5)_2]^-$), 2011 (10, $[(F_5C_6)_3Au(PPh_2CC)Au(CCPPh_2)Au(C_6F_5)_3]^-$). FAB$^+$ (*m/z* (%, assignment)): 1001 (100, [$Au_2(PPh_2$-

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Table 5. Details of Crystal Data and Structure Refinement for Complexes 3 and 6

	3	**6**
empirical formula	$C_{34}H_{19}AuF_{15}O_2P$	$C_{52}H_{30}Au_2Cl_3F_{15}OP_2$
fw	972.43	1517.98
temp/K	143	133
wavelength/Å	0.710 73	0.710 73
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
a/Å	10.5562(10)	19.863(3)
b/Å	10.5950(10)	13.2995(18)
c/Å	15.7468(14)	19.928(3)
α/deg	109.378(3)	90
β/deg	104.321(3)	92.484(6)
γ/deg	91.630(3)	90
V/Å^3	1598.0(3)	5259.4(12)
Z	2	4
density (calcd)/(Mg/m^3)	2.021	1.917
abs coeff/mm^{-1}	4.775	5.877
F(000)	936	2896
cryst habit	colorless square prism	colorless needle
cryst size/mm	0.31 × 0.14 × 0.13	0.50 × 0.10 × 0.05
θ range for data collecn/deg	1.42−30.03	1.42−28.29
index ranges	$-14 \leq h \leq 14$, $-14 \leq k \leq 14$, $-21 \leq l \leq 22$	$-26 \leq h \leq 26$, $-17 \leq k \leq 17$, $-26 \leq l \leq 26$
no. of rflns collected	28 899	79 626
indep rflns	9287 (R(int) = 0.0387)	13044 (R(int) = 0.0881)
max, min transmission	0.802, 0.611	0.928, 0.597
no. of data/restraints/params	9287/146/480	13 044/204/676
goodness of fit on F^2	1.023	1.028
R1 ($I > 2\sigma(I)$)[a]	0.0299	0.0519
wR2 (all data)[b]	0.0700	0.1592
largest diff peak, hole/(e Å^{-3})	1.596, −2.842	3.044, −3.860

[a] $R1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2(F^2) = [\sum\{w(F_o^2 - F_c^2)^2\}/\sum\{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and a and b are constants adjusted by the program.

CC)($PPh_2CH_2CH_2PPh_2$)]$^+$), 1407 (35, [$Au_3(PPh_2CC)_2(PPh_2CH_2CH_2PPh_2)$]$^+$). $\Lambda = 9\ \Omega^{-1}\ cm^2\ mol^{-1}$.

Preparation of [(F_5C_6)$_3$Au(PPh_2CC)Au($CCPPh_2$)Au(C_6F_5)$_3$][PPN] (8). To a 15 mL dichloromethane solution of $Au(C_6F_5)_3(PPh_2CCH)$ (91 mg, 0.1 mmol) was added [Au(acac)$_2$][PPN][20] (47 mg, 0.05 mmol), and the mixture was stirred for about 4 h. The solvent was removed and the white residue washed with petroleum ether. Yield of **8**: 89 mg, 70%. Data for **8**: ^{1}H NMR δ 7.3−7.7 (m, Ph); ^{19}F NMR δ −121.3 (m, 6F$_o$), −159.6 (t, 2F$_p$), −159.7 (t, 1F$_p$), −163.0 (m, 6F$_m$); ^{31}P{^{1}H} NMR δ −8.6 (s, 1P, PPh$_2$), 21.8 (s, 1P, PPh$_3$); IR 2052 (s, ν(C≡C)), 966 (s, C_6F_5), 794 (s, C_6F_5) cm^{-1}. Anal. Calcd for $C_{100}H_{50}Au_3F_{30}NP_4$: C, 47.1; H, 2.0; N, 0.55. Found: C, 47.45; H, 2.3; N, 0.6. FAB$^-$ (m/z (%, assignment)): 531 (100, [$Au(C_6F_5)_2$]$^-$), 865 (3, [$Au(C_6F_5)_4$]$^-$), 2011 (2, [M − PPN]$^-$). $\Lambda = 100\ \Omega^{-1}\ cm^2\ mol^{-1}$.

Preparation of (F_5C_6)$_3$Au(PPh_2CC)Ag(PPh_3) (9). To a 5 mL dichloromethane solution of $Au(C_6F_5)_3(PPh_2CCH)$ (45 mg, 0.05 mmol) was added Ag(acac)(PPh$_3$)[17a] (24 mg, 0.05 mmol) and the mixture stirred for about 3 h, protected from light. The solvent was removed and the white residue washed with petroleum ether. Yield of **9**: 43 mg, 68%. Data for **9**: ^{1}H NMR δ 7.4−7.7 (m, Ph); ^{19}F NMR δ −120.9 (m, 4F$_o$), −121.9 (m, 2F$_o$), −159.1 (t, 1F$_p$), −159.3 (t, 2F$_p$), −162.7 (m, 2F$_m$), −163.0 (m, 4F$_m$); ^{31}P{^{1}H} NMR δ −8.4 (s, 1P, PPh$_2$), 15.1 (br s, 1P, PPh$_3$); ^{31}P{^{1}H} NMR (−55 °C) δ −8.5 (s, 1P, PPh$_2$), 16.7 (dd, ^1J(^{105,107}AgP) = 486.3 and 556.0 Hz, 1P, PPh$_3$); IR 2049 (s, ν(C≡C)), 2024 (s, ν(C≡C)), 967 (s, C_6F_5), 794 (s, C_6F_5) cm^{-1}. Anal. Calcd for $C_{50}H_{25}AgAuF_{15}P_2$: C, 47.0; H, 1.95. Found: C, 47.4; H, 2.2. FAB$^-$ (m/z (%, assignment)): 531 (100, [$Au(C_6F_5)_2$]$^-$), 865 (8, [$Au(C_6F_5)_4$]$^-$). FAB$^+$ (m/z (%, assignment)): 369 (100, [Ag(PPh$_3$)]$^+$), 631 (45, [Ag(PPh$_3$)$_2$]$^+$). $\Lambda = 12\ \Omega^{-1}\ cm^2\ mol^{-1}$.

Crystal Structure Determination of 3 and 6. Crystal data and details of the data collection and structure refinement of $Au(C_6F_5)_3(PPh_2CH_2CH(OMe)_2)$ and (F_5C_6)$_3$Au(PPh_2CC)Au(PPh$_3$) are given in Table 5. Data were measured on a Bruker SMART 1000 CCD diffractometer. An absorption correction was based on multiple scans (program SADABS). The structures were refined anisotropically on F^2 (program SHELXL-97[21]) using a system of restraints (to light atom U values and local ring symmetry). H atoms were included using a riding model. The structure refinement of **6** involved a region of badly resolved residual electron density, tentatively identified as one chloroform molecule and one methanol molecule, the last of which has been idealized using three different sites. However, this should be interpreted with caution.

Conclusions

We have carried out reactions of the acetylenephosphine ligand coordinated to the gold(III) complex **1** in two completely different ways. On one hand, we have carried out single or double anti-Markovnikov alcohol additions to the acetylene fragment to obtain (2-alkoxyvinyl)diphenylphosphine or (2,2-dialkoxyethyl)diphenylphosphine ligands. On the other hand, we have prepared di-, tri-, or tetranuclear alkynylphosphino complexes with gold(I), silver(I), and gold(III) centers.

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Supporting Information Available: X-ray crystallographic data for the structure determination of complexes **3** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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