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Preparative Routes to the First Tri- and Tetra(alkynyl)gold(III) Compounds: (L)Au(C≡CR)$_3$ and [ER$_4$]$^+$ [Au(C≡CR)$_4$]$^-$

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(Me$_3$P)Au(C≡CPh)$_3$ (**1**) was prepared as the first trialkynylgold(III) complex via three different routes: Treatment of solvated AuCl$_3$ with 3 equiv of PhC≡CLi in the presence of PMe$_3$, or of (Me$_3$P)AuBr$_2$Cl with the same reagent, gives high to medium yields of the product (**1**), which is also available from equimolar quantities of (Me$_3$P)AuC≡CPh and (PhC≡C)$_2$-TlCl. The same reactions fail with less powerful donors (PPh$_3$) or more bulky ligands (P^{i}Pr$_3$). The products of reductive elimination, PhC≡CC≡CPh and (R$_3$P)AuC≡CPh, are obtained instead. The molecular structure of compound **1** has been determined from single crystals of a monoclinic, solvent-free phase and a triclinic 1:1 solvate (**1**)·CH$_2$Cl$_2$. In the square-planar environment of the gold(III) center one of the three phenylethynyl groups exhibits the *trans* influence of the PMe$_3$ ligand. The reactions of **1** with PPh$_3$, HCl, and I$_2$ were studied, but no stable functional poly(alkynyl)gold(III) compounds could be isolated. Serendipitously, single crystals of a byproduct, [(PhC≡C)Me$_2$PCH$_2$Au(C≡CPh)$_3$], were found to grow from one of the reaction mixtures. The molecular structure has been determined, but no efficient synthetic pathway could be found. Salts with the tetra(phenylethynyl)aurate(III) anion [Au(C≡CPh)$_4$]$^-$ were obtained from compound **1** upon treatment with PhC≡CLi. The complex ion undergoes facile reductive elimination of PhC≡CC≡CPh to produce the [Au(C≡CPh)$_2$]$^-$ anion. After metathesis with ^{n}Bu$_4$N$^+$Br$^-$, mixed-anion salts with nonstoichiometric composition were precipitated as colorless, diamagnetic solids. From this product mixture, single crystals with the anion ratio 1:1 could be grown for structure determination: [^{n}Bu$_4$N]$_2$[Au(C≡CPh)$_4$][Au(C≡CPh)$_2$]·(CH$_2$Cl$_2$). The structure of the reference compound [^{n}Bu$_4$N][Au(C≡CPh)$_2$] has also been determined. The anions have square-planar and linear structures, respectively, with very small variations in the bond distances and angles.

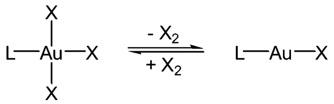
Introduction

Cyanide complexes of gold(I) are key compounds in gold chemistry and technology.[1] Most of the gold recovered from ores, or recycled after usage, is processed by reactions with aqueous solutions of alkali cyanides, and most electrochemical gilding techniques rely on cyanide baths.

By contrast, cyanide complexes of gold(III) are, due to their low redox stability, a virtually unexplored class of compounds. This fact can be traced back to the observation reported in the earliest literature, that the complex ion, tetracyanoaurate(III), [Au(CN)$_4$]$^-$, is easily reduced to dicyanoaurate(I), [Au(CN)$_2$]$^-$, and dicyanogen, (CN)$_2$, upon warming (eq 1).[2]

$$\mathrm{KAu(CN)_4} \longrightarrow \mathrm{K[Au(CN)_2] + (CN)_2} \qquad (1)$$

The stability of square-planar gold(III) complexes [(L)$_n$AuX$_{4-n}$]$^{(n-1)}$ (n = 0, 1, 2) generally depends very strongly on the specific properties of the neutral donor ligands L and anionic substituents X (Scheme 1). The relation between gold(III) and gold(I) species is best illustrated by the redox equilibrium represented by eq 2, which combines a reductive elimination of X$_2$ from a gold(III) complex (L)AuX$_3$ and an oxidative addition of X$_2$ to the corresponding gold(I) complex (L)AuX.

 (2)

$$\mathrm{L{-}Au(X)_2{-}X} \underset{+\,X_2}{\overset{-\,X_2}{\rightleftharpoons}} \mathrm{L{-}Au{-}X} \qquad (2)$$

For X representing the halogens X = Cl, Br, the equilibrium is known to be shifted to the left-hand side under standard conditions and with water and most other solvents as the medium.[2] However, for X = I the gold(III) complexes are only stable with strong and small donor ligands L, e.g., PMe$_3$ or PEt$_3$. The donor capacity of PPh$_3$ is insufficient, and the steric effect of P(^{i}Pr)$_3$ is prohibitive, for the formation of the corresponding (R$_3$P)AuI$_3$ complexes. Gold(I) polyiodides (R$_3$P)AuI·xI$_2$ are formed instead.[3]

Gold(III) pseudohalide complexes (L)AuY$_3$ with Y representing not only cyanide but also Y = cyanate,

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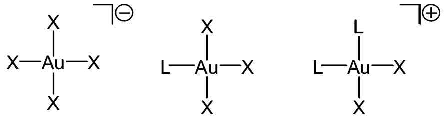
10.1021/om050038q CCC: $30.25

Scheme 1



isocyanate, thiocyanate, etc., appear to resemble the iodide complexes, and very little information is available on their range of stability.[2]

This is also true for complexes with alkynyl (acetylide) substituents, which can be classified as isoelectronic with cyanides. Solely three references can be quoted in which organogold complexes with an alkynyl group attached to a gold(III) center have been identified.[4−7] In all cases only one $-C{\equiv}C-R$ group is associated with two alkyl groups and a tertiary phosphine ligand: *cis*-$R_2(R'C{\equiv}C)Au(PR''_3)$. The compounds were found to undergo facile reductive elimination of R_2 and/or $R-C{\equiv}C-R'$ on heating, depending on the nature of the substituents.

In the present account we report the first synthesis of tri- and tetra(alkynyl)gold(III) complexes. This work is an extension of our earlier studies of alkynylgold(I) chemistry.[8] Alkynylgold compounds are important building blocks for the construction of extended one- or two-dimensional frameworks.[9−17] The rigid-rod nature of the acetylide group combined with the linear or rectangular motif at the gold centers is ideal for the design of square-grid materials.

Preparation, Reactions, and Stability of Tris(alkynyl)gold(III) Complexes: $(PhC{\equiv}C)_3Au(PR_3)$. Several routes were probed for the preparation of tri(alkynyl)gold(III) complexes, three of which were finally found to give access to significant yields of the expected products.

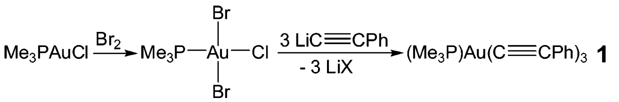
The seemingly most obvious pathway that uses anhydrous gold trichloride and 3 equiv of an alkynyllithium reagent requires carefully controlled conditions and a powerful tertiary phosphine as an auxiliary ligand in order to be successful. Thus, the reaction of a solution of $AuCl_3$ in tetrahydrofuran (THF) with a solution of 3 equiv of $LiC{\equiv}CPh$ in the same solvent at −78 °C, upon subsequent addition of a toluene solution of 1 equiv of PMe_3 at this temperature, afforded a 51% isolated yield of $(PhC{\equiv}C)_3Au(PMe_3)$ (**1**) as a colorless crystalline solid [eq 3].

$$AuCl_3 \xrightarrow[-\,3\,LiCl]{3\,LiC{\equiv}CPh} Au(C{\equiv}CPh)_3 \xrightarrow{Me_3P} (Me_3P)Au(C{\equiv}CPh)_3 \qquad (3)$$

By contrast, the same reaction with the PPh_3 ligand gave only products of reductive elimination, i.e., $PhC{\equiv}CAu(PPh_3)$ and $PhC{\equiv}CC{\equiv}CPh$ or $PhC{\equiv}CX$ (X = Br, Cl), regardless if $AuCl_3$ or $AuBr_3$ was employed as THF solvate or as the PPh_3 complex, respectively [eq 4, 5]. Treatment of the mixed-halide complex $(Me_3P)AuClBr_2$, obtained from $(Me_3P)AuCl$ and an equimolar quantity of Br_2 in dichloromethane at 0 °C, with 3 equiv of $PhC{\equiv}CLi$ also led to product **1**, but with only 30% yield [eq 6]. Recrystallization from dichloromethane/pentane gave, next to familiar crystals of **1**, very few differently shaped crystals suitable for X-ray diffraction studies. The byproduct was identified as [dimethyl(phenylethynyl)phosphoniummethylide]tri(phenylethynyl)gold(III), $(PhC{\equiv}C)Me_2PCH_2Au(C{\equiv}CPh)_3$, **2**. Several routes for a rational sythesis of this complex have been probed, but all attempts were unsuccessful.

$$Ph_3PAuBr_3 \xrightarrow[-\,2\,LiBr]{2\,LiC{\equiv}CPh} (Ph_3P)AuC{\equiv}CPh + PhC{\equiv}CBr \qquad (4)$$

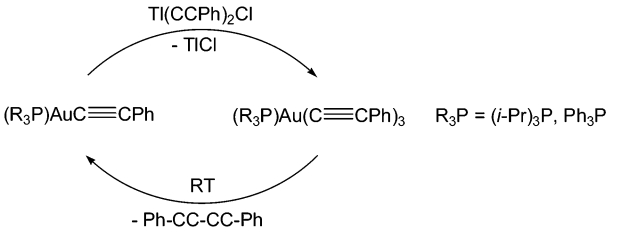
$$AuCl_3 \xrightarrow[-\,3\,LiCl]{3\,LiC{\equiv}CPh} \xrightarrow{Ph_3P} (Ph_3P)AuC{\equiv}CPh + PhC{\equiv}C-C{\equiv}CPh \qquad (5)$$



$$Me_3PAuCl \xrightarrow{Br_2} Me_3P-\overset{Br}{\underset{Br}{Au}}-Cl \xrightarrow[-\,3\,LiX]{3\,LiC{\equiv}CPh} (Me_3P)Au(C{\equiv}CPh)_3\ \mathbf{1} \qquad (6)$$

In a third variant, bis(phenylethynyl)thallium(III) chloride was used as an oxidant for phenylethynylgold(I) complexes. This reaction was again successful with the PMe_3 complex (giving a 36% yield of **1**). With PPh_3 or P^iPr_3 the desired products could be obtained but showed very low thermal stability and decomposed within minutes. Only the products of reductive elimination could be isolated. By immediate analysis of the reaction mixtures, however, ^1H and ^{31}P NMR data of the intermediates were obtained [eqs 7, 8].

$$(Me_3P)AuC{\equiv}CPh \xrightarrow[-\,TlCl]{Tl(CCPh)_2Cl} (Me_3P)Au(C{\equiv}CPh)_3\ \mathbf{1} \qquad (7)$$



(8)

The thallium(III) reagent employed in the preparation of the gold(III) complex has been synthesized for the first time from anhydrous $TlCl_3$ and $PhC{\equiv}CLi$, in the molar ratio 1:2, in tetrahydrofuran at −78 °C. The product was isolated in 69% yield as a colorless, microcrystalline solid and characterized by analytical and spectroscopic data. The NMR spectra recorded in THF-d_8 showed no multiplicity due to separate coupling to

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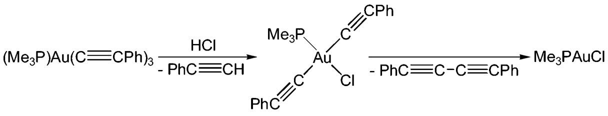
^{205}Tl and ^{203}Tl (I = 1/2; natural abundance 70.5 and 29.5%, respectively). Only broad signals were recorded.

(Trimethylphosphine)tri(phenylethynyl)gold(III), **1**, forms colorless crystals that melt at 114−115°C with decomposition to give equimolar quantities of $(Me_3P)AuC{\equiv}CPh$ and $PhC{\equiv}CC{\equiv}CPh$. The crystals are readily soluble but show limited stability in polar solvents. Decomposition is discernible within days. The solutions in CD_2Cl_2 show NMR spectra that are fully compatible with the proposed structure. Owing to the rigid square-planar configuration at the gold(III) center (5d^8), separate ^{13}C signals are recorded for *cis* and *trans* ethynyl groups, with small and large J(PC) coupling constants, respectively (Experimental Section). In the IR spectrum of the solid (in KBr) there are two $\nu(C{\equiv}C)$ absorption bands at 2107 and 2144 cm^{-1}.

Attempts to substitute the PMe_3 ligand by PPh_3 in CH_2Cl_2 or THF solution were not successful in the temperature range from 20 to 60 °C, indicating that the stronger donor is not readily replaced by the weaker one even if an excess of the latter is employed and/or reduced pressure applied to evaporate the volatile PMe_3. At higher temperatures decomposition of the substrate with reductive elimination of $PhC{\equiv}CC{\equiv}CPh$ is observed.

The reaction of complex **1** with hydrogen chloride in dichloromethane affords $(Me_3P)AuCl$, $PhC{\equiv}CH$, and $PhC{\equiv}CC{\equiv}CPh$, which clearly can be classified as the products of a substitution followed or accompanied by a reductive elimination. This result shows that the di(ethynyl)gold(III) complexes *cis*- or *trans*-$(Me_3P)Au(C{\equiv}CPh)_2Cl$, with one tertiary phosphine and one chloride ligand, are unstable [eq 9].

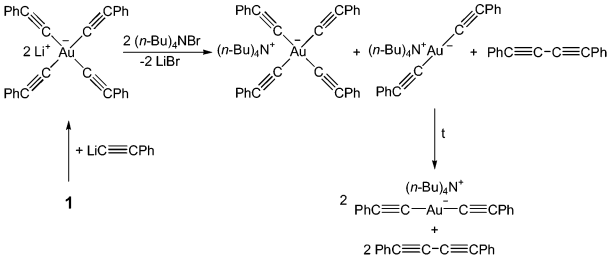


(9)

The reaction of complex **1** with iodine in dichloromethane was followed by NMR spectroscopy and shown to produce Me_3PAuI and an unstable compound that can be assigned the formula *trans*-$(Me_3P)Au(C{\equiv}CPh)_2I$ but could also not be isolated. Attempts to trap it by methylation with MeLi under mild conditions [to give $(Me_3P)Au(C{\equiv}CPh)_2Me$] or by quaternization with PMe_3 [to give $(Me_3P)_2Au(C{\equiv}CPh)_2{}^+\ I^-$] were not successful. NMR evidence for the former was obtained, however, in the reaction mixture obtained from equimolar quantities of $(Me_3P)AuMe$ and $(PhC{\equiv}C)_2TlCl$ in dichloromethane at −78 °C. The compound could not be separated from the byproduct $(Me_3P)AuC{\equiv}CPh$. The same reaction with $(Ph_3P)AuMe$ instead of $(Me_3P)AuMe$ yielded soleley the gold(I) complexes $(Ph_3P)AuC{\equiv}CPh$ and $(Ph_3P)AuMe$ together with elimination products. This observation confirms the stabilizing role of trimethylphosphine in alkynylgold(III) complexes not matched by triphenylphosphine.

Preparation and Reactions of Tetra(phenylethynyl)aurates(III): $M[Au(C{\equiv}CPh)_4]$. Several routes to the elusive tetra(alkynyl)aurates(III) were probed and proved unsuitable. These included the reaction of tetrahalogenoaurates(III) with an excess of alkynyllithium or -Grignard reagents and the oxidative addition of halogen to dialkynylaurates(I) followed by alkynylmetal agents. In all cases only the products of reductive elimination were obtained.

It was only in the reaction of $PhC{\equiv}CLi$ with the complex $(Me_3P)Au(C{\equiv}CPh)_3$ (**1**)—with its Me_3P-induced stability—that a product containing the symmetrical $[Au(C{\equiv}CPh)_4]^-$ anion could be obtained [eq 10]. Since this complex ion shows limited thermal stability, the fairly slow metathesis with $^nBu_4N^+Br^-$ at room temperature is accompanied by reductive elimination of $PhC{\equiv}CC{\equiv}CPh$, generating the anion $[Au(C{\equiv}CPh)_2]^-$. The isolated polycrystalline solid contained the gold(III) and gold(I) anions in a ratio of ca. 1:3. Recrystallization from dichloromethane/pentane finally afforded colorless single crystals with a clean 1:1 stoichiometry (**3**, mp 129−130 °C). Unexpectedly, the solutions of the compounds in CD_2Cl_2 gave only one set of ^{1}H and ^{13}C resonances for the alkynyl groups of the anions. The sp-carbon atoms neigbouring the metal centers, which should be most affected by a change in the oxidation state of the metal, show either no signal (C_1) or only a signal of very low (C_2) intensity. Thus no assignments could be made. Similar results were obtained by Bayón et al. in an investigation of the ^{1}H NMR spectra of gold(I) and (III) complexes with isocyanide ligands (isolobal to ethynyl groups).[18] Rapid interionic exchange of alkynyl groups cannot be ruled out as the origin of the phenomenon.



(10)

The presence of large amounts of the gold(I) salt in the reaction mixture obtained from a gold(III) precursor indicates extensive reductive elimination of $PhC{\equiv}CC{\equiv}CPh$. This byproduct was indeed discovered in all experiments, and the yield was approximately equivalent to that of the gold(I) compound.

For comparison, the corresponding "pure" di(phenylethynyl)gold(I) salt $^nBu_4N^+[Au(C{\equiv}CPh)_2]^-$ (**4**) was prepared from $Ph_3PAuC{\equiv}CPh$ and $PhC{\equiv}CLi$ in diethyl ether. The slurry of the reactants cleared, and upon addition of $^nBu_4N^+Br^-$, a precipitate of LiBr was observed. The product was isolated in 69% yield from the solid that remained after evaporation of the diethyl ether by extraction with benzene and again evaporating the solvent (mp 111−113 °C, from dichloromethane/pentane). Solutions of **4** in CD_2Cl_2 provided the same set of NMR parameters as **3**. The anion $[Au(C{\equiv}CPh)_2]^-$ has been reported previously with a variety of counterions.[19−32]

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Structural Studies. Compound **1** crystallizes in a solvent-free triclinic form, space group $P\bar{1}$, with $Z = 2$ molecules in the unit cell. The molecule has no crystallographically enforced symmetry. A dichloromethane solvate of 1:1 stoichiometry can be obtained as monoclinic crystals (space group $P2_1/c$, $Z = 4$). There are no unusual sub-van der Waals contacts between the complex and solvent molecules.

Both types of crystals feature similar, equivalent molecules (**1**) with the gold atom in a square-planar coordination distinguishing the singular *trans* from the two equivalent *cis* phenylethynyl ligands (Figure 1). Owing to the *trans* influence of the powerful PMe$_3$ donor, the Au−C bond lengths for the *trans* substituents [2.018(3) and 2.026(5) Å] are slightly, but significantly longer than for the *cis* substituents [2 × 2.003(5) and 2.001(3)/2.006(3) Å, respectively]. The C$\equiv$C distances are not affected by the *trans* influence and show only marginal variations [*trans*: 1.197(5); *cis*: 1.201(5), 1.203(5); *trans*: 1.195(7); *cis*: 1.200(7), 1.207(7) Å]. The two Au−P distances [2.3191(9) and 2.3218(14) Å] show no significant difference in the solvent-free and solvated form. All P−Au−C and C−Au−C angles are almost linear or rectangular, and the linearity is extended in the ethynyl carbon chains with only a slight curvature.

Crystals of (PhC$\equiv$C)Me$_2$PCH$_2$Au(C$\equiv$CPh)$_3$·CH$_2$Cl$_2$, **2**, are triclinic (space group $P\bar{1}$, $Z = 2$) with one ylide complex and one solvent molecule in the asymmetric unit (Figure 2). The gold atom is in a square-planar environment with the ylide ligand as a monodentate σ-donor. The overall geometry of the (PhC$\equiv$C)$_3$Au unit resembles very closely that of the PMe$_3$ complex **1**. The bond Au1−C1 connecting the ylide function with the metal atom is a true σ single bond [2.125(10) Å] complemented by a P1−C1 single bond of 1.790(10) Å at a quasi-tetrahedral carbon atom with an angle Au1−C1−P1 of 113.7(5)°. The phosphorus atom is a tetrahedral onium center with one phenylalkynyl and two methyl substituents. There is ample precedent for this type of ylide coordination to gold(I) and gold(III),[1] but complex **2** is the first case in which a tri(alkynyl)gold unit is stabilized by a phosphorus ylide. The packing of the zwitterionic complex molecules and the solvent in the unit cell shows no anomalies or peculiarities. The intermolecular Au···Au contact [3.744 Å] is beyond the limit commonly considered to be the threshold between aurophilic and van der Waals bonding.

Crystals of the reference compound **4** are orthorhombic (space group *Pbca*, $Z = 8$) with one cation and one anion in the asymmetric unit, which contains no solvent. The cation has the standard conformation of extended *n*-butyl groups at a tetrahedrally coordinated nitrogen atom, while the anion resembles a weightlifting gear unit with the planes of the terminal phenyl groups approximately at a right angle. The two Au−C bonds are of equal length at 1.989(5) and 1.995(6) Å, as are the two C$\equiv$C distances at 1.209(6) and 1.200(6) Å (Figure 3). The anions are separated from each other by the cations such that no aurophilic interactions are discernible. There is no evidence for π−π stacking of the phenyl groups or phenyl embrace of aryl hydrogen atoms.

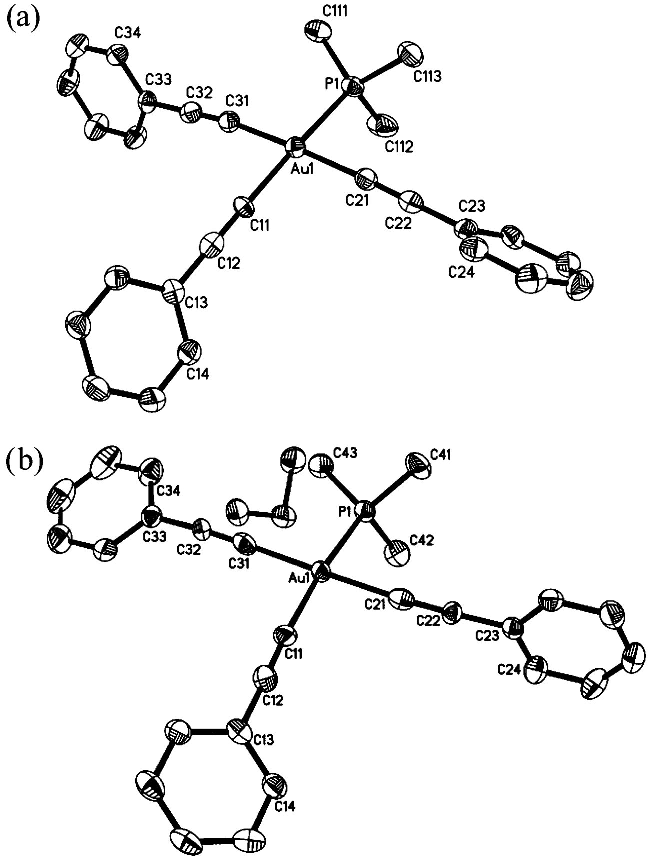

Figure 1. Molecular structure of compound (Me$_3$P)Au(C$\equiv$CPh)$_3$, **1** (ORTEP drawing with 50% probability ellipsoids; H atoms omitted for clarity). (a) Solvent-free; selected bond lengths [Å] and angles [deg]: Au1−P1 2.3191(9), Au1−C11 2.018(3), Au1−C21 2.006(3), Au1−C31 2.001(3), C11−C12 1.197(5), C21−C22 1.201(5), C31−C32 1.203(5); P1−Au1−C11 176.70(10), P1−Au1−C21 88.74(11), P1−Au1−C31 91.73(11), Au1−C11−C12 177.4(3), Au1−C21−C22 174.6(3), Au1−C31−C32 172.8(3), C11−Au1−C21 90.79(14), C11−Au1−C31 88.53(12), C21−Au1−C31 176.31(12). (b) 1:1 CH$_2$Cl$_2$ solvate; selected bond lengths [Å] and angles [deg]: Au1−P1 2.3218(14), Au1−C11 2.026(5), Au1−C21 2.003(5), Au1−C31 2.003(6), C11−C12 1.195(7), C21−C22 1.207(7), C31−C32 1.200(7); P1−Au1−C11 173.27(15), P1−Au1−C21 84.92(14), P1−Au1−C31 91.52(14), Au1−C11−C12 174.5(5), Au1−C21−C22 172.5(4), Au1−C31−C32 173.2(5), C11−Au1−C21 91.1(2), C11−Au1−C31 92.2(2), C21−Au1−C31 175.58(19).

The mixed-anion salt **3** crystallizes as a dichloromethane solvate (triclinic, space group $P\bar{1}$, $Z = 1$). In both types of anions the gold atom resides in a center of inversion, such that the asymmetric unit of the crystals contains one cation and one-half of each anion (Figure 4). The cation has a conformation similar to that of salt **4**, and the solvent molecule has no sub-van der Waals contacts with the ions.

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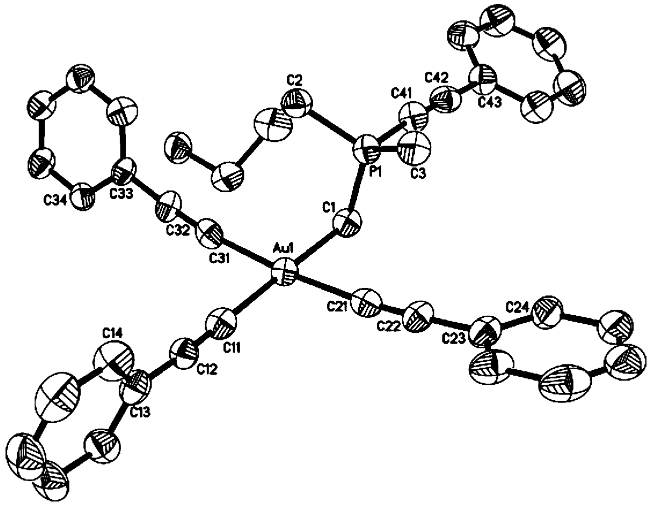

Figure 2. Molecular structure of $[(\mathrm{PhC{\equiv}C})\mathrm{Me_2PCH_2}]\mathrm{Au}(\mathrm{C{\equiv}CPh})_3\cdot\mathrm{CH_2Cl_2}$, **2** (ORTEP drawing with 50% probability ellipsoids; H atoms omitted for clarity). Selected bond lengths [Å] and angles [deg]: Au1−C1 2.125(10), Au1−C11 2.056(12), Au1−C21 2.114(11), Au1−C31 2.143(11), C11−C12 1.196(15), C21−C22 1.281(14), C31−C32 1.269(14), P1−C1 1.790(10), P1−C2 1.844(11), P1−C3 1.887(10), P1−C41 1.727(12), C41−C42 1.240(16); C1−Au1−C11 178.9(4), C1−Au1−C21 85.2(4), C1−Au1−C31 92.3(4), Au1−C11−C12 175.5(9), Au1−C21−C22 174.5(9), Au1−C31−C32 173.4(9), C11−Au1−C21 94.3(4), C11−Au1−C31 88.3(4), C21−Au1−C31 174.6(4), C1−P1−C41 109.3(5), P1−C41−C42 174.6(10).

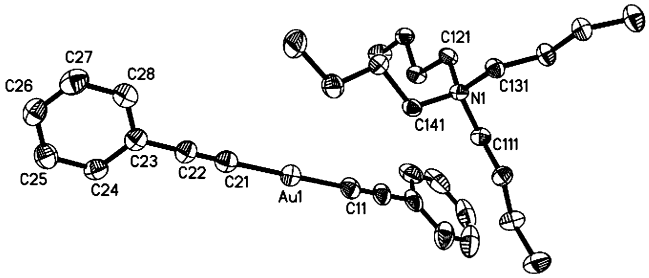

Figure 3. Molecular structure of $[(n\text{-}\mathrm{Bu})_4\mathrm{N}][\mathrm{Au}(\mathrm{C{\equiv}CPh})_2]$, **4** (ORTEP drawing with 50% probability ellipsoids; H atoms omitted for clarity). Selected bond lengths [Å] and angles [deg]: Au1−C11 1.989(5), Au1−C21 1.995(5), C11−C12 1.209(6), C21−C22 1.200(6); C11−Au1−C21 176.69(17), Au1−C11−C12 171.3(4), Au1−C21−C22 178.2(4).

The Au−C distances of the $[\mathrm{Au}(\mathrm{C{\equiv}CPh})_2]^-$ anion [1.995(7) Å] are similar to those in the reference salt **4**, but significantly shorter than those in the $[\mathrm{Au}(\mathrm{C{\equiv}CPh})_4]^-$ anion [2.017(6) and 2.018(6) Å]. The difference of the C≡C bond lengths is smaller, but follows the same trend: 1.189(9) Å for Au(I) vs 1.197(8) and 1.199(9) Å for Au(III). This result suggests weaker bonding of the phenylethynyl groups in the Au(III) case as also shown by the low stability of this square-planar anion toward reductive elimination of PhC≡CC≡CPh.

The planes of the phenyl groups of *trans* ethynyl groups are parallel for the $[\mathrm{Au}(\mathrm{C{\equiv}CPh})_2]^-$ and the $[\mathrm{Au}(\mathrm{C{\equiv}CPh})_4]^-$ anions, and for the latter the orientation is roughly perpendicular to the $\mathrm{AuC_4}$ reference plane. Note that in compound **4** the planes of the two phenyl rings are perpendicular to each other.

Conclusions

The results of the present study have shown that tri(alkynyl)gold(III) complexes $(\mathrm{RC{\equiv}C})_3\mathrm{Au(L)}$ can be prepared as metastable compounds if a small and strong trialkylphosphine donor is introduced as an auxiliary ligand L. Already a switch to tri*aryl*phosphines or to a bulky tri*alkyl*phosphine lowers the stability threshold toward reductive elimination of the dialkyne RC≡CC≡CR, and only alkynylgold(I) complexes $(\mathrm{RC{\equiv}C})\mathrm{Au(L)}$ are obtained. The complex with L $=\mathrm{PMe_3}$ has been crystallized in a solvent-free form and as a 1:1 solvate with $\mathrm{CH_2Cl_2}$. In the two forms the complex has the same square-planar structure. Determination of the molecular structure of $(\mathrm{PhC{\equiv}C})\mathrm{Me_2PCH_2Au}(\mathrm{C{\equiv}CPh})_3$ (**2**), a byproduct of the synthesis of **1**, provided the proof that ylides also have the capability to stabilize tri(alkynyl)gold(III) complexes.

Tetra(alkynyl)aurates(III) $[\mathrm{Au}(\mathrm{C{\equiv}CR})_4]^-$ can be prepared with large, nonpolarizing counterions such as $^n\mathrm{Bu_4N^+}$, but all preparative routes probed in the study led to significant side reactions producing also the dialkyne and leaving the $[\mathrm{Au}(\mathrm{C{\equiv}CR})_2]^-$ anion. Both types of anions cocrystallize with the cation in different stoichiometries.

Single crystals were obtained for the 1:1 ratio of anions as a dichloromethane solvate, $[^n\mathrm{Bu_4N}]_2[\mathrm{Au}(\mathrm{C{\equiv}CPh})_2][\mathrm{Au}(\mathrm{C{\equiv}CPh})_4]\cdot(\mathrm{CH_2Cl_2})$ (**3**). The reference compound $[^n\mathrm{Bu_4N}]\ [\mathrm{Au}(\mathrm{C{\equiv}CPh})_2]$ (**4**) has also been structurally characterized. The geometry of the anions and of the $[(\mathrm{PhC{\equiv}C})_3\mathrm{Au}(\mathrm{PMe_3})]$ complex (**1**) and its dichloromethane solvate shows only minor variations, which in the latter cases can be ascribed to the *trans* influence of the trialkylphosphine ligand. Two alkynyl groups in *trans* position at a gold(III) center appear to lower the stability of the complexes greatly such that reductive elimination of dialkynyl is easily induced either in the reaction mixture of any preparative attempts or upon heating of the products.

The stability of polyalkynyl complexes of gold(III) centers appears to be generally lower than that of the isoelectronic platinum(II) centers, for which a greater variety of coordination compounds is readily available.[33] It remains to be demonstrated that there are donors, other than phoshines and ylides, that can be successfully employed as auxiliary ligands L for $(\mathrm{RC{\equiv}C})_3\mathrm{Au(L)}$ complexes.

Experimental Section

General Procedures. All organometallic syntheses were performed in a dry deoxygenated dinitrogen atmosphere using standard Schlenk techniques. All solvents were distilled from an appropriate drying agent and stored over molecular sieves (4 Å) and under nitrogen. Unless otherwise stated solutions were protected against light. Most standard chemicals were purchased from Aldrich or Fluka and used without further purification, or prepared by literature procedures: $\mathrm{AuCl_3}$,[34] $\mathrm{TlCl_3}$,[35] $(\mathrm{Me_3P})\mathrm{AuCl}$,[36] $(\mathrm{Ph_3P})\mathrm{Au}(\mathrm{C_2Ph})$,[37] $(\mathrm{Me_3P})\mathrm{Au}(\mathrm{C_2Ph})$,[7] $[(i\text{-}\mathrm{Pr})_3\mathrm{P}]\mathrm{Au}(\mathrm{C_2Ph})$,[7] and $(\mathrm{Me_3P})\mathrm{AuMe}$.[37]

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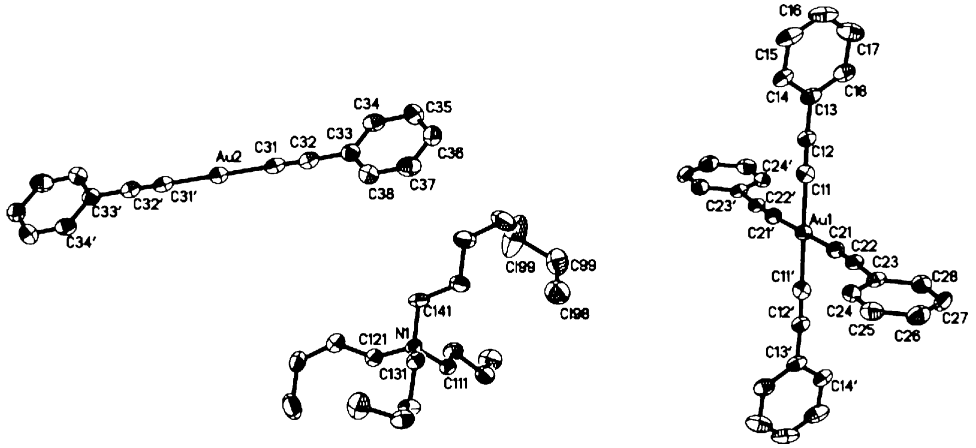

Figure 4. Crystal structure of $[(n\text{-Bu})_4N]_2[Au(C{\equiv}CPh)_4][Au(C{\equiv}CPh)_2]\cdot 2CH_2Cl_2$, **3** (ORTEP drawing with 50% probability ellipsoids; H atoms omitted for clarity). Selected bond lengths [Å] and angles [deg]:Au1−C11 2.017(6), Au1−C21 2.018(6), Au1−C31 1.995(7), C11−C12 1.197(8), C21−C22 1.199(9), C31−C32 1.189(9); C11−Au1−C21 91.7(2), Au1−C11−C12 179.4(6), Au1−C21−C22 177.1(5).

NMR spectra were obtained on JEOL-400 or JEOL-270 spectrometers. Chemical shifts are reported in δ values relative to the residual solvent resonances converted to TMS (^{1}H, ^{13}C). ^{31}P{^{1}H} NMR spectra are referenced to external aqueous H_3PO_4 (85%). IR spectra were measured on a Perkin-Elmer FT-IR 577 spectrometer.

Warnings. Thallium compounds are toxic and must be handled with care. Although thallium is classified as a cumulative poison, as are lead and mercury, it must be emphasized that it is gradually excreted from the body as a result of soft-tissue turnover.[38]

Chloro[bis(phenylethynyl)thallium(III). $TlCl_3$ (1.24 g, 4.0 mmol), dissolved in 15 mL of THF, was treated with 2 equiv (8 mL, 8 mmol, 1.0 M in THF) of LiCCPh at −78 °C. With continued stirring, the resultant solution was allowed to warm to room temperature and stirred for 30 min. After filtration a few drops of diluted aqueous HCl were added before the solvents were removed in vacuo. Recrystallization of the residue from dichloromethane/*n*-pentane at −30 °C gave 1.24 g (69% yield) of a white microcrystalline product; mp (dec) 135 °C. ^{1}H NMR (THF-d_8, RT): δ 7.28−7.55 [m, C_6H_5]. ^{13}C{^{1}H} NMR (THF-d_8, RT): δ 106.6 [d, $^1J_{TlC}$ = 2161.2 Hz, Tl-*C*≡C-Ph]. 122.9 [d, $^2J_{TlC}$ = 189.0 Hz, Tl-C≡*C*-Ph], 128.2 [s, *i*-(C_6H_5)], 128.4 [s, *o*-(C_6H_5)], 131.5 [s, *p*-(C_6H_5)], 132.2 [s, *m*-(C_6H_5)]. IR (KBr) [cm^{-1}]: 2160 (s), ν (*C*≡*C*). Anal. Calc for $C_{16}H_{10}ClTl$ (442.09 g·mol^{-1}): C, 43.47; H, 2.28. Found: C, 43.39; H, 2.18.

***trans*-Bis(phenylethynyl)methyl(trimethylphosphine)-gold(III).** A sample of $(Me_3P)AuMe$ (29 mg, 0.1 mmol) was dissolved in 2 mL of dichloromethane and cooled to −78 °C. After addition of $(PhC_2)_2TlCl$ (44 mg, 0.1 mmol) the mixture was stirred for 30 min and subsequently drawn into a syringe. Therein it was allowed to warm with shaking. Thirty seconds after the precipitation of TlCl was observed, the suspension was immediately filtered through a syringe filter into *n*-pentane kept at −78 °C. A colorless precipitate consisting of $(Me_3P)Au(C_2Ph)_2Me$ and $(Me_3P)Au(C_2Ph)$ was obtained, which could not be separated. Residual $(Me_3P)AuMe$ was detected in the mother liquor by NMR spectroscopy. ^{1}H NMR (CD_2Cl_2, RT): δ 1.36 [d, $^3J_{HP}$ = 10.4 Hz, 3 H, *trans*-P-Au-C*H*$_3$], 1.80 [d, $^2J_{HP}$ = 11.6 Hz, 9 H, P(C*H*$_3$)], 7.18−7.48 [m, C_6*H*$_5$]. ^{31}P{^{1}H} NMR (CD_2Cl_2, RT): δ −5.3 [s, *P*(CH_3)].

(Trimethylphosphine)tris(phenylethynyl)gold(III), 1. Route a. A 1.0 mL portion of a solution of LiCCPh (1.0 mmol, 1 M in THF) was added dropwise to a suspension of 100 mg (0.33 mmol) of $AuCl_3$ in THF (40 mL) at −78 °C. After 1 h of stirring 0.33 mL of PMe_3 (0.33 mmol, 1 M in toluene) was added and the mixture allowed to warm to room temperature. After removal of the solvent at room temperature, a brown slurry remained, which was redissolved in dichloromethane, and LiCl was removed by extraction with 3 × 50 mL of water. After filtration of the organic phase through anhydrous $MgSO_4$, *n*-pentane was added to precipitate 102 mg (51% yield) of colorless crystals; mp (dec) 114−115 °C.

Route b. The reaction of freshly prepared $(Me_3P)AuX_3$ [from 1.24 g (4.0 mmol) of $(Me_3P)AuCl$ by adding 0.21 mL (4.0 mmol) of bromine in dichloromethane at 0 °C] with 3 equiv (12.0 mL, 12.0 mmol, 1.0 M) of LiCCPh at −78 °C in THF yielded, after workup as described for route a, 717 mg (30% yield) of colorless crystals; mp (dec) 112−114 °C.

Route c. The synthesis was carried out with 77 mg (0.2 mmol) of $(Me_3P)Au(C_2Ph)$ and 91 mg (0.2 mmol) of $(PhC_2)_2$-TlCl using the same procedure as described for *trans*-$(Me_3P)Au(CCPh)_2Me$. Colorless crystals (44 mg, 36% yield) were collected after recrystallization from dichloromethane/*n*-pentane at −30 °C; mp (dec) 114−117 °C. ^{1}H NMR (CD_2Cl_2, RT): δ 1.97 [d, $^2J_{HP}$ = 12.8 Hz, 9 H, P(C*H*$_3$)], 7.21−7.58 [m, 15 H, C_6*H*$_5$]. ^{13}C{^{1}H} NMR (CD_2Cl_2, RT): δ 13.8 [d, $^1J_{CP}$ = 41.5 Hz, P(*C*H$_3$)], 93.3 [d, $^2J_{CP}$ = 12.3 Hz, *cis*-Au-*C*≡C-Ph], 94.1 [d, $^2J_{CP}$ = 212.5 Hz, *trans*-Au-*C*≡C-Ph], 104.1 [d, $^3J_{CP}$ = 40.7 Hz, *trans*-Au-C≡*C*-Ph], 105.7 [d, $^3J_{CP}$ = 3.0 Hz, *cis*-Au-C≡*C*-Ph], 125.8 [s, *cis-i*-(C_6H_5)], 126.0 [d, $^4J_{CP}$ = 23.0 Hz, *trans-i*-(C_6H_5)], 127.3 [s, *trans-o*-(C_6H_5)], 127.7 [s, *cis-o*-(C_6H_5)], 128.4 [s, *trans-p*-(C_6H_5)], 128.5 [s, *cis-p*-(C_6H_5)], 131.8 [s, *cis-m*-(C_6H_5)], 132.0 [s, *trans-m*-(C_6H_5)]. ^{31}P{^{1}H} NMR (CD_2Cl_2, RT): δ −9.0 [s, *P*(CH_3)]. IR (KBr) [cm^{-1}]: 2107 (vw), ν (*trans-C*≡*C*); 2144 (m), ν (*cis-C*≡*C*). Anal. Calc for $C_{27}H_{24}AuP\cdot 0.33CH_2Cl_2$ (604.73 g·mol^{-1}): C, 54.29; H, 4.11. Found: C, 54.33; H, 4.11.

(Triphenylphosphine)tris(phenylethynyl)gold(III) and [Tri(isopropyl)phosphine]tris(phenylethynyl)gold-(III). Samples of the corresponding $(R_3P)Au(C_2Ph)$ complexes were dissolved in CD_2Cl_2 and reacted with an excess of $(PhC_2)_2$-TlCl. NMR spectra were recorded immediately. *(Ph$_3$P)Au-(C$_2$Ph)$_3$:* ^{1}H NMR (CD_2Cl_2, RT): δ 6.95−7.77 [m, C_6*H*$_5$]. ^{31}P{^{1}H} NMR (CD_2Cl_2, RT): δ 20.0 [s, *P*(C_6H_5)]. *[(i-Pr)$_3$P]Au-(C$_2$Ph)$_3$:* ^{1}H NMR (CD_2Cl_2, RT): δ 1.49 [dd, $^3J_{HP}$ = 16.1 Hz, $^3J_{HH}$ = 7.2 Hz, 18 H, P(CH(C*H*$_3$)$_2$)], 3.20 [m, 3 H, P(C*H*(CH_3)$_2$)], 7.15−7.40 [m, 15 H, C_6*H*$_5$]. ^{31}P{^{1}H} NMR (CD_2Cl_2, RT): δ 68.7 [s, *P*(CH(CH_3)$_2$)].

[(Phenylethynyl)dimethylphosphoniummethylide]tri-(phenylethynyl)gold(III), 2. Crystals of this compound were obtained as a byproduct of the synthesis of complex **1** via route b; mp 129−130 °C.

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Table 1. Crystal Data, Data Collection and Structure Refinement Details

	$(Me_3P)Au(C_2Ph)_3$	$(Me_3P)Au(C_2Ph)_3\cdot CH_2Cl_2$	$[(PhCC)Me_2PCH_2Au(CCPh)_3\cdot CH_2Cl_2$
empirical formula	$C_{27}H_{24}AuP$	$C_{28}H_{26}AuCl_2P$	$C_{36}H_{28}AuCl_2P$
M_r	576.40	661.32	759.42
cryst syst	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a/Å	9.2632(1)	13.1163(2)	8.9539(5)
b/Å	11.1278(2)	16.2269(3)	12.9892(4)
c/Å	12.1561(2)	14.1022(3)	15.4944(11)
α/deg	82.9382(6)	90	83.782(5)
β/deg	73.8315(6)	117.6935(7)	79.916(5)
γ/deg	78.4370(9)	90	78.659(2)
V/Å^3	1176.05(3)	2657.64(9)	1734.47(19)
ρ_{calc}/g cm^{-3}	1.628	1.653	1.454
Z	2	4	2
F(000)	560	1288	744
μ (Mo Kα) (cm^{-1})	63.32	58.10	44.62
T/K	143	143	143
refls measd	25 643	67 806	69 364
refls unique	4054 [R_{int} = 0.042]	4834 [R_{int} = 0.084]	5443 [R_{int} = 0.076]
refined params/restraints	265/0	292/0	373/0
R1 [$I \geq 2\sigma(I)$]	0.0231	0.0372	0.0597
wR2[a]	0.0615	0.0961	0.1425
weighting scheme	a = 0.0366	a = 0.0532	a = 0.0697
	b = 0.6137	b = 4.6363	b = 1.9959
σ_{fin}(max/min)/e Å^{-3}	1.200/−1.421	2.295/−2.518	1.982/−1.712

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

Table 2. Crystal Data, Data Collection, and Structure Refinement Details

	$[(n\text{-}Bu)_4N][Au(C_2Ph)_2]$	$[(n\text{-}Bu)_4N]_2[Au(C_2Ph)_2][Au(C_2Ph)_4]\cdot 2CH_2Cl_2$
empirical formula	$C_{32}H_{46}AuN$	$C_{82}H_{106}Au_2Cl_4N_2$
M_r	641.66	1655.42
cryst syst	orthorhombic	triclinic
space group	$Pbca$	$P\bar{1}$
a/Å	17.2772(1)	8.9747(2)
b/Å	18.3213(2)	12.4383(3)
c/Å	18.6586(2)	17.9334(5)
α/deg	90	78.1633(12)
β/deg	90	84.1125(13)
γ/deg	90	78.1765(19)
V/Å^3	5906.21 (10)	1913.93(8)
ρ_{calc}/g cm^{-3}	1.443	1.436
Z	8	1
F(000)	2592	838
μ (Mo Kα) (cm^{-1})	50.00	40.11
T/K	143	143
refls measd	124 873	53 832
refls unique	5427 [R_{int} = 0.072]	6583 [R_{int} = 0.061]
refined params/restraints	311/0	413/0
R1 [$I \geq 2\sigma(I)$]	0.0400	0.0400
wR2[a]	0.1260	0.0848
weighting scheme	a = 0.0895	a = 0.0136
	b = 6.5974	b = 4.6269
σ_{fin}(max/min)/e Å^{-3}	1.728/−1.508	0.943/−0.878

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

Tetra(*n*-butyl)ammonium [bis(phenylethynyl)]aurate(I), 4. A suspension of 112 mg of $(Ph_3P)Au(C_2Ph)$ (0.2 mmol) in diethyl ether (50 mL) was treated with 1 equiv of LiCCPh (0.2 mL, 0.2 mmol, 1 M in THF) to give a clear solution. A white precipitate (LiBr) formed overnight upon addition of 64 mg of $[(n\text{-}Bu)_4N]Br$ (0.2 mmol). The solvents were removed and the residue was extracted with benzene (2 × 30 mL). Removal of the solvent from the combined benzene extracts and recrystallization of the residue from dichloromethane/*n*-pentane yielded 83 g (69% yield) of colorless crystals; mp 111−113 °C. ^{1}H NMR (CD_2Cl_2, RT): δ 0.98, t, $^2J_{HH}$ = 7.4 Hz, 12 H, N-CH_2-CH_2-CH_2-CH_3], 1.39−1.48 [m, 8 H, N-CH_2-CH_2-CH_2-CH_3], 1.55−1.72 [m, 8 H, N-CH_2-CH_2-CH_2-CH_3], 3.20−3.28 [m, 8 H, N-CH_2-CH_2-CH_2-CH_3], 7.05−7.43 [m, 10 H, Au-C≡C-C_6H_5]. ^{13}C{^{1}H} NMR (CD_2Cl_2, RT): δ 13.7 [s, N-CH_2-CH_2-CH_2-CH_3], 20.1 [s, N-CH_2-CH_2-CH_2-CH_3], 24.4 [s, N-CH_2-CH_2-CH_2-CH_3], 59.4 [s, N-CH_2-CH_2-CH_2-CH_3], 102.6 [s, Au-C≡*C*-Ph], 125.3 [s, *i*-(C_6H_5)], 127.5 [s, *o*-(C_6H_5)], 127.9 [s, *p*-(C_6H_5)], 131.7 [s, *m*-(C_6H_5)], Au-*C*≡C-Ph was not observed. IR (KBr) [cm^{-1}]: 2098 (s), ν (C≡C). Anal. Calc for $C_{32}H_{46}AuN$ (641.68 g·mol^{-1}): C, 59.90; H, 7.23. Found: C, 59.80; H, 7.04.

Bis[tetra(*n*-butyl)ammonium] bis(phenylethynyl)aurate(I) tetrakis(phenylethynyl)aurate(III), 3. The compound was synthesized in the same manner as described for **3** from 115 mg of $(Me_3P)Au(C_2Ph)_3$ (0.2 mmol), 0.2 mL of LiCCPh (0.2 mmol, 1 M in THF), and 64 mg of $[(n\text{-}Bu)_4N]Br$ (0.2 mmol) in diethyl ether. Extraction and recrystallization from dichloromethane/pentane afforded two kinds of crystals: **3** and $[(n\text{-}Bu)_4N]_2Au(C_2Ph)_4Au(C_2Ph)_2$; mp 129−130 °C. ^{1}H NMR (CD_2Cl_2, RT): δ 0.98, t, $^2J_{HH}$ = 7.4 Hz, 12 H, N-CH_2-CH_2-CH_2-CH_3], 1.35−1.48 [m, 8 H, N-CH_2-CH_2-CH_2-CH_3], 1.56−1.71 [m, 8 H, N-CH_2-CH_2-CH_2-CH_3], 3.18−3.27 [m, 8 H, N-CH_2-CH_2-CH_2-CH_3], 7.08−7.49 [m, Au-C≡C-(C_6H_5)]. ^{13}C{^{1}H} NMR (CD_2Cl_2, RT): δ 13.8 [s, N-CH_2-CH_2-CH_2-CH_3], 20.2 [s, N-CH_2-CH_2-CH_2-CH_3], 24.5 [s, N-CH_2-CH_2-CH_2-CH_3], 59.6 [s, N-CH_2-CH_2-CH_2-CH_3], 102.8 [s, Au-C≡*C*-Ph], 125.7 [s, *i*-(C_6H_5)], 126.8 [s, *o*-(C_6H_5)], 128.3 [s, *p*-(C_6H_5)], 132.0 [s, *m*-(C_6H_5)], Au-*C*≡C-Ph was not observed. Anal. Calc for product mixture [Au(III)/Au(I) = 1/3]: C, 62.46; H, 7.06; N, 2.02. Found: C, 61.75; H, 6.29; N, 1.82.

Crystal Structure Determinations. The single crystals were placed in inert oil on the top of a glass pin and transferred to the cold gas stream of the diffractometer. Crystal data were collected using a Nonius DIP2020 system with monochromated Mo K_α ($\lambda = 0.71073$ Å) radiation at −130 °C. The structures were solved by direct methods (SHELXS-97) and refined by full matrix least-squares calculations on F^2 (SHELXL-97).[39] Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and refined using a riding model with fixed isotropic contributions. Further information on crystal data, data collection, and structure refinement are summarized in Tables 1 and 2. Important interatomic distances and angles are shown in the figure captions. Complete lists of displacement parameters and tables of interatomic distances and angles have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. The data are available on request on quoting CCDS-266848−266852.

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Supporting Information Available: Details of crystal data, data collection, and structure refinement and tables of atomic coordinates, isotropic and anisotropic thermal parameters, and all bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

OM050038Q

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