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Synthesis of Luminescent Alkynyl Gold Metalaligands Containing 2,2′-Bipyridine-5-yl and 2,2′:6′,2″-Terpyridine-4-yl Donor Groups

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[AuCl(SMe$_2$)] reacts with HC$\equiv$CR (R = bpyl = 2,2′-bipyridine-5-yl (**1**), phtpyl = phenyl-4-(2,2′:6′,2″-terpyridine-4-yl) (**2**)) and NEt$_3$ (1:1:3) to afford the polymers [Au(C$\equiv$CR)]$_n$ (R = bpyl (**3**), phtpyl (**4**)). The new alkyne HC$\equiv$Cphccbpyl (**5**, phccbpyl = 4-C$_6$H$_4$C$\equiv$Cbpyl) has been prepared by Sonogashira coupling of 4-Me$_3$SiC$\equiv$CC$_6$H$_4$I and **1** followed by desilylation of the resulting alkyne 4-Me$_3$SiC$\equiv$Cphccbpyl. The alkynyl Au(I) complexes [Au(C$\equiv$CR)L] (R = bpyl, L = PPh$_3$ (**6**), PTol$_3$ (**7**, Tol = 4-MeC$_6$H$_4$), PEt$_3$ (**8**); R = phtpyl, L = XyNC (**9**), PPh$_3$ (**10**); R = phccbpyl, L = PPh$_3$ (**11**)) have been prepared by reacting: (1) **3** or **4** with L or (2) the corresponding alkyne **1**, **2**, or **5** with [Au(acac)(PPh$_3$)] (acac = acetylacetonato). The reaction of **3** or **4** with diphosphines gives [{Au(C$\equiv$CR)}$_2$(μ-Ph$_2$P(CH$_2$)$_x$PPh$_2$)] (R = bpyl, x = 1 (**12**), 2 (**13**), 4 (**14**), 10 (**15**); R = phtpyl, x = 10 (**16**)). ESI mass spectrometric studies show that complexes **12–14** are in equilibrium with the salts [Au$_3$(C$\equiv$Cbpyl)$_2$(μ-Ph$_2$P(CH$_2$)$_x$PPh$_2$)$_2$][Au(C$\equiv$Cbpyl)$_2$], although only when x = 1 (**17**) was a significant concentration of the salt detected by NMR spectroscopy and isolated. The anionic complexes PPN[Au(C$\equiv$CR)$_2$] (R = bpyl (**18**), phtpyl (**19**), or phccbpyl (**20**)) have been prepared by reaction of the corresponding alkynes with PPN[Au(acac)$_2$]. Complexes **6**, **10**, **13**, **14**, **17**, and **18** have been characterized by single-crystal X-ray diffraction studies. The alkynyl complexes are luminescent at room temperature, displaying dual emissions.

Introduction

Au(I) alkynyl complexes[1–4] have generated much interest associated with their use in the synthesis of organometallic rigid oligomers, polymers,[3,5,6] molecular triangles,[7] macrocycles, and catenanes.[8,9] Another interesting feature of these complexes is their luminescence, which can be employed for the design of sensors or optical devices and is strongly influenced by the presence of aurophilic interactions.[10] Several examples of luminescent chemosensors containing Au(I)-alkynyl units have been described.[11,12] In these systems, the alkynyl ligands contain a crown ether, a calixarene, or a calix crown host, which interacts with metal ions, giving rise to a detectable perturbation of the luminescence of the Au-alkynyl unit.

Ethynyl-substituted oligopyridines or -phenanthrolines have been used as conjugated linking units in the synthesis of polynuclear complexes, some of which display interesting photophysical or electrochemical properties.[13,14] Metalaligands containing [Au]C$\equiv$CR$_L$ (R$_L$ = 1,10-phenanthroline-x-yl (x =

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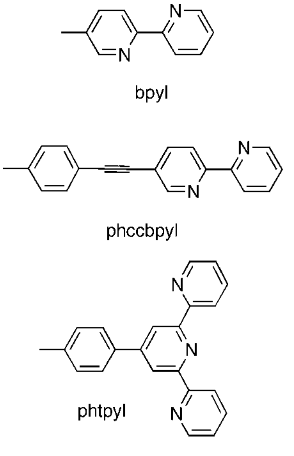
10.1021/om7009123 CCC: $40.75

Chart 1



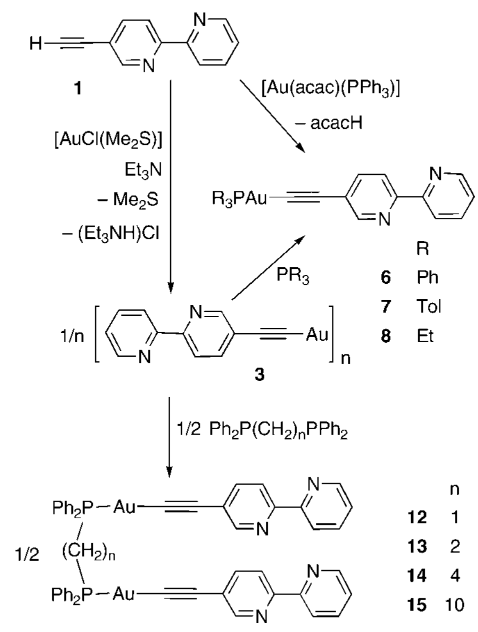
3,[15] 5[16]), pyridine-*x*-yl ($x = 2, 4$)[17–19]), or $[Au_2]\{\mu\text{-}(C\equiv C)_2R_L$ (R_L = pyridine-3,5-diyl)[13] units have been recently reported, as have several heteronuclear complexes where the R_L group is coordinated to $Ru(bpy)_2^{2+}$,[20] $ReCl(CO)_3$,[16,21] $Re(CO)_3(bpy)^+$,[18] $Au(PTol_3)^+$, or $PtCl(PPh_3)_2^+$.[13] The photophysical properties of some of these complexes have been studied in detail.[15,16,18–21]

Herein we report the synthesis and characterization of a family of metalaligands [Au]C≡Cbpyl, [Au]C≡Cphtpyl, or [Au]C≡Cphccbpyl (see Chart 1). Owing to their strong coordination ability and luminescence, these compounds are potential candidates for use as chemosensors. In addition, they can be used as building blocks for the synthesis of new heterometallic oligomers and polymers by reaction with metal ions.

Results and Discussion

Synthesis of Complexes. The reaction between HC≡CR (R = bpyl (**1**), phtpyl (**2**)) (see Chart 1) and $[AuCl(SMe_2)]$ affords the corresponding $[Au(C\equiv CR)]_n$ (R = bpyl (**3**), phtpyl (**4**)) in high yield as yellow solids (Schemes 1 and 2). The low solubility of **3** and **4** precluded their characterization by NMR in solution and the preparation of single crystals for an X-ray structural determination. The structural analysis by *ab initio* XRPD, which has recently proved successful in the determination of the structures of group 11 metal acetylides,[22] was not possible because of the amorphous character of **3** and **4**. In their IR spectra, the $\nu(\equiv C{-}H)$ bands of the starting alkynes are absent and the $\nu(C\equiv C)$ mode appears as weak bands at 2106 and 2112 cm^{-1}, respectively, which fall into the usual range for terminal σ-coordinated alkynyls. $\nu(C\equiv C)$ bands at a lower frequency, which could indicate a π-coordination of the C≡C bond,[22–24] were not observed. On the basis of these data, oligo- or polymeric structures based on AuC≡Cbpy or AuC≡Cphtpyl units linked by Au−N bonds can be tentatively proposed for **3** and **4**, respectively. The insolubility of this type of complexes prevents recrystallization and, in some cases, prevents obtaining good analytical data.[4,13] However, elemental analyses (C, H, N, and Cl for **4**) suggest the formulation of the present complexes as $\mathbf{3}\cdot(H_2O)_{0.5}$ and $\mathbf{4}\cdot H_2O\cdot(HCl)_{0.4}$. Both species, HCl and H_2O, can be trapped by the N atoms not involved in Au−N bonds.

Scheme 1



The new alkyne HC≡Cphccbpyl (**5**, phccbpyl = $C_6H_4C\equiv Cbpyl$) was prepared by palladium-catalyzed coupling of $Me_3SiC\equiv CC_6H_4I$-4 and **1**, followed by desilylation of the resulting alkyne $Me_3SiC\equiv Cphccbpyl$. The mononuclear complexes $[Au(C\equiv CR)L]$ (R = bpyl, L = PR'_3, R′ = Ph (**6**), tol (**7**, tol = 4-MeC_6H_4), Et (**8**); R = phtpyl, L = XyNC (**9**, Xy = 2,6-dimethylphenyl); Schemes 1 and 2) were prepared in good yields by reacting **3** or **4** with the corresponding neutral ligand. Alternatively, complexes **6** and $[Au(C\equiv CR)(PPh_3)]$ (R = phtpyl (**10**), phccbpyl (**11**), Schemes 2 and 3) were obtained by the

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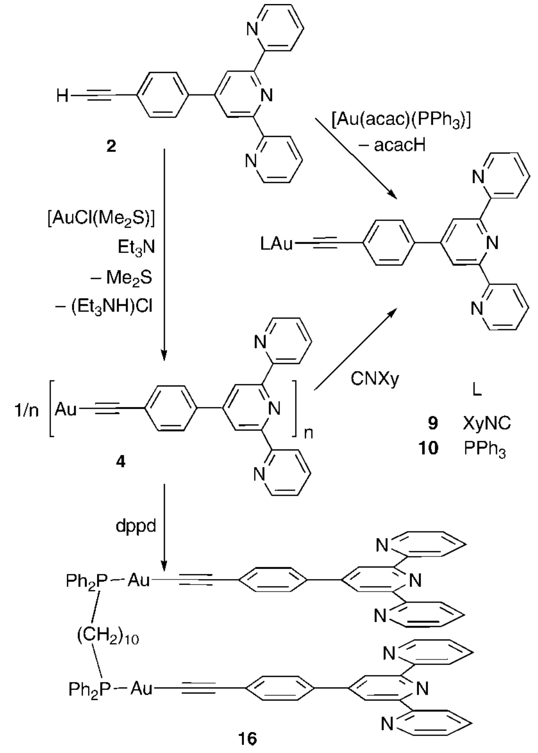
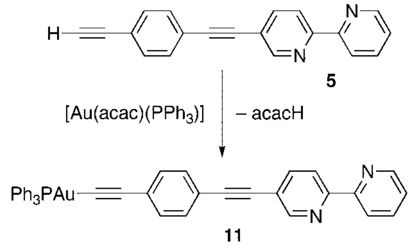
Scheme 2



Scheme 3



"acac method",[2,25] i.e., by reacting the alkynes **1**, **2**, and **5** with [Au(acac)(PPh$_3$)]. Complexes **6–10** were characterized by analytical and spectroscopical means and, in the case of **6** and **10**, by X-ray diffraction studies (Figures 1 and 2).

The dinuclear complexes [{Au(C≡Cbpyl)}$_2$(μ-Ph$_2$P(CH$_2$)$_x$-PPh$_2$)] (x = 1 (**12**), 2 (**13**), 4 (**14**), 10 (**15**)) (Scheme 1) were obtained in good yields by reacting **3** with the corresponding diphosphines. Similarly, [{Au(C≡Cphtpyl)}$_2$(μ-Ph$_2$P(CH$_2$)$_{10}$-PPh$_2$)] (**16**) was obtained by reacting **4** with Ph$_2$P(CH$_2$)$_{10}$PPh$_2$. Their analytical, IR, and NMR spectroscopical data in CDCl$_3$ solution are in agreement with the proposed structures, which were confirmed for **13** and **14** by single-crystal X-ray diffraction studies (Figures 3 and 4). However, in complex **12** a solvent dependence of the NMR spectra was observed. Thus, its ^{31}P{^{1}H} NMR spectrum in CDCl$_3$ at room temperature shows the expected singlet at 32.1 ppm (Figure 5), but in (CD$_3$)$_2$CO at 20 °C, two different sets of signals appear: a singlet at 32.7 ppm, corresponding to **12**, and two broad multiplets due to a new species **17** (Figure 5). These multiplets become sharper on lowering the temperature to 0 °C or by measuring the spectrum in a higher field NMR spectrometer. This part of the spectrum can be reproduced by computer simulation assuming an AA′XX′ spin system (see Supporting Information). On raising the temperature (60 °C), all signals coalesce into a unique, broad signal. In addition, the room-temperature ^{1}H NMR spectrum in CDCl$_3$ shows the signal of the PCH$_2$P protons as a triplet by coupling with two equivalent P nuclei, as expected for **12**. However, in (CD$_3$)$_2$CO, at 20 °C, a broad signal is observed, which at T < –40 °C splits into two multiplets from **17** and a

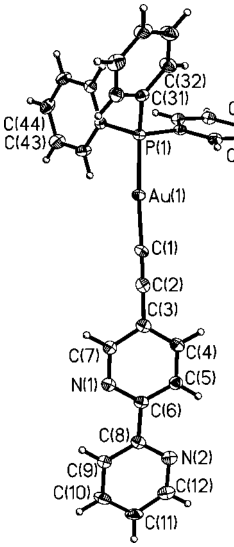


Figure 1. Molecular structure of **6** (50% thermal ellipsoids).

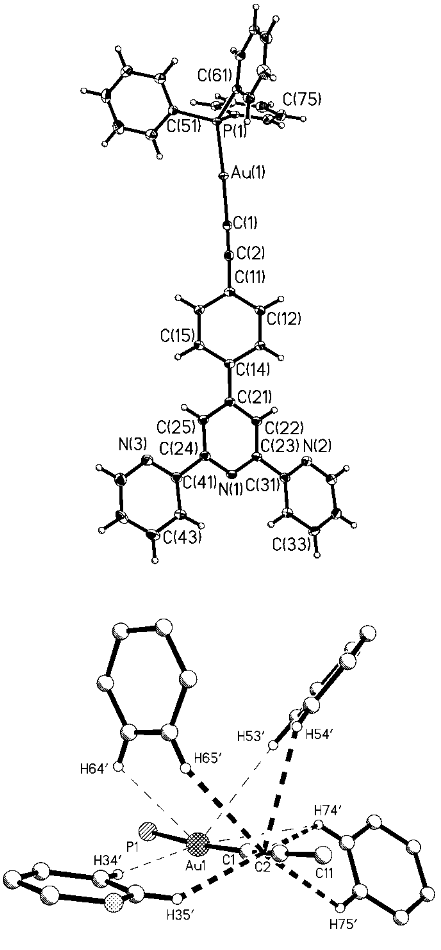


Figure 2. (Top) Molecular structure of **10** (50% thermal ellipsoids). (Bottom) Clustering of C–H···Au (thin dashed bonds) and C–H···π contacts (thick dashed bonds) at the P–Au–C≡C center of compound **10**. For symmetry operators, see Supporting Information.

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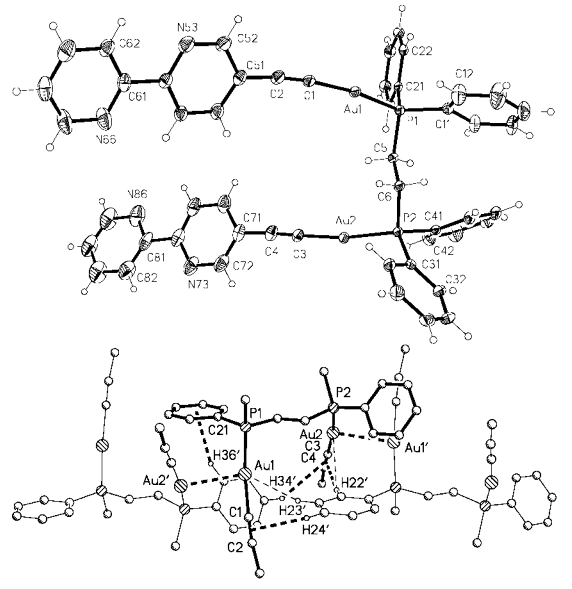


Figure 3. (Top) Molecular structure of **13** (50% thermal ellipsoids). (Bottom) C−H···Au (thin dashed bonds), C−H···π, and Au···Au contacts (thick dashed bonds) in compound **13**. For symmetry operators, see Supporting Information. Only interactions to the parent molecule (thick continuous bonds) are shown; other molecules are generated by the 2_1 screw axis.

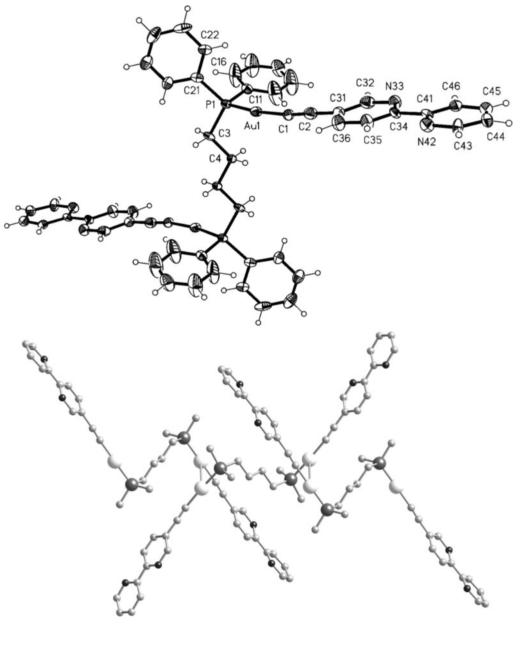


Figure 4. (Top) Structure of **14** (30% thermal ellipsoids). (Bottom) View of the chain structure showing the Au···Au interactions, the H atoms have been omitted, and only the *ipso* carbons of the Ph groups are shown.

triplet from **12**. A similar behavior was observed in CD_3CN, DMF, or a $CD_3OD/CDCl_3$ mixture. It can be concluded from the NMR data that, in polar solvents, complex **12** is in equilibrium with **17**. Slow evaporation of a solution of **12** in acetone gave single crystals suitable for an X-ray diffraction study. However, the crystals consisted not of **12** but instead of the complex $[Au_3(C{\equiv}Cbpyl)_2(\mu\text{-dppm})_2][Au(C{\equiv}Cbpyl)_2]$ (dppm = 1,2-bis(diphenylphosphino)methane; Figure 6), whose expected NMR spectra agree with those of the new species **17** found in polar solvent solutions of **12** (Scheme 4). The ^{13}C NMR spectrum measured in $(CD_3)_2CO$ shows the expected signals for a mixture of **12** and **17** (see Experimental Section).

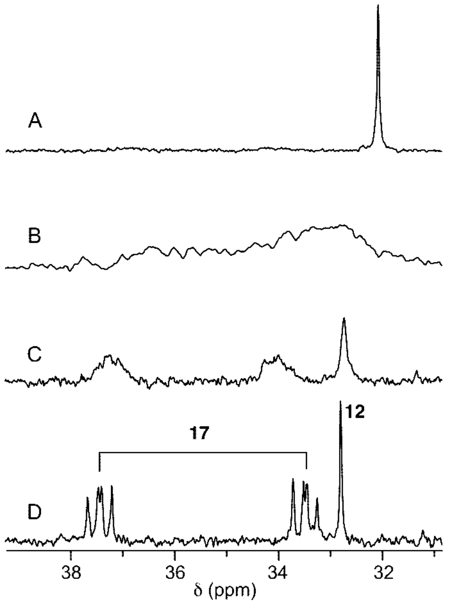


Figure 5. $^{31}P\{^1H\}$ NMR spectra (162.3 MHz) of complexes **12** and **17**. Solvent/temperature (°C): $CDCl_3/25$ (A); $CD_3COCD_3/60$ (B); $CD_3COCD_3/20$ (C); $CD_3COCD_3/0$ (D).

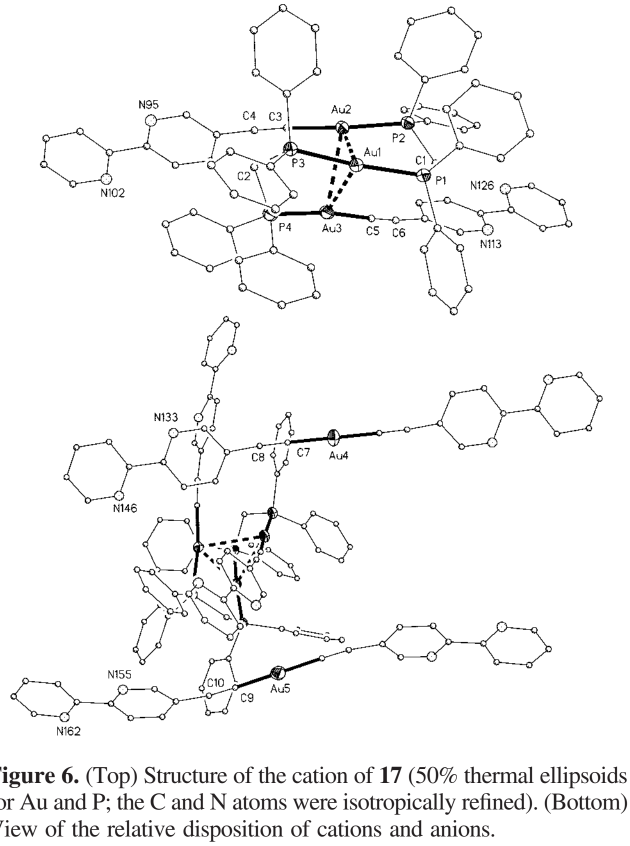
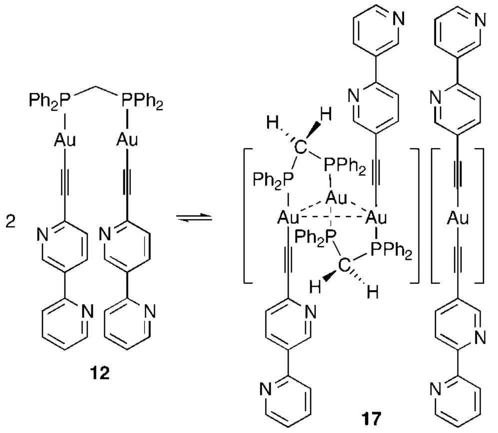


Figure 6. (Top) Structure of the cation of **17** (50% thermal ellipsoids for Au and P; the C and N atoms were isotropically refined). (Bottom) View of the relative disposition of cations and anions.

The presence of the salt **17** in solution was also confirmed by ESI MS spectroscopy, which showed the expected peaks for the $[Au_3(C{\equiv}Cbpyl)_2(\mu\text{-dppm})_2]^+$ cation and the $[Au(C{\equiv}Cbpyl)_2]^-$ anion in positive and negative mode, respectively. The ESI MS spectra of complexes **13** and **14** also show the peaks corresponding to the ions $[Au_3(C{\equiv}Cbpyl)_2\{\mu\text{-}Ph_2P\text{-}(CH_2)_nPPh_2\}_2]^+$ (n = 2 or 4) and $[Au(C{\equiv}Cbpyl)_2]^-$, in spite of the fact that their NMR spectra showed at room temperature only the singlet corresponding to the neutral dinuclear complexes in $CDCl_3$, Me_2CO, or $Me_2CO/CDCl_3$ with no significant

Scheme 4

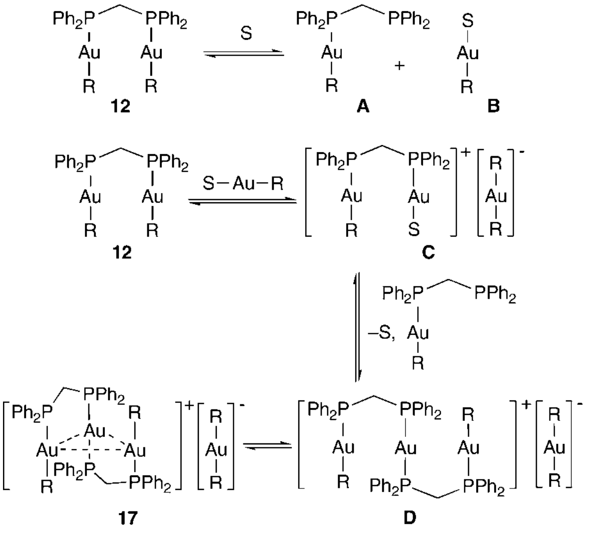


chemical shift variation. This suggests that **13** and **14** are ionized under the ESI-MS measurement conditions, but the concentration of the salt is too small to be detected by NMR spectroscopy. The NMR spectra of **15** did not show signals for new species when they were recorded in CD_3CN instead of $CDCl_3$ at room temperature, and in its ESI-MS spectra the anion $[Au(C\equiv Cbpyl)_2]^-$ was detected, but the only cationic species observed were $[Au_2(C\equiv Cbpyl)\{Ph_2P(CH_2)_{10}PPh_2\}]^+$ and $[Au\{Ph_2P(CH_2)_{10}PPh_2\}_2]^+$.

In view of these results, we propose that an equilibrium between **12** and **17** is established in solution (Scheme 4). Complex **12** is the main species in $CDCl_3$, but in more polar solvents, the ionization process is favored, giving a mixture where the main component is **17** (**17**:**12** = 1.3 in $(CD_3)_2CO$ at 20 °C). When an acetone solution containing **12** and **17** was evaporated to dryness and the solid residue was redissolved in $CDCl_3$, the main component turned out to be **12**, showing that the process is reversible. A similar ionization process could also take place for **13** and **14**, as shown by their ESI-MS spectra; however, the amounts of ionic species formed in solution must be very small because they are not observed by NMR. For complex **15**, the cationic trinuclear species was not detected by ESI-MS. This suggest that dppm could stabilize the trinuclear cation better than 1,2-bis(diphenylphosphino)ethane (dppe) and 1,4-bis(diphenylphosphino)butane (dppb), and it will not be stable with 1,10-bis(diphenylphosphino)decane (dppd).

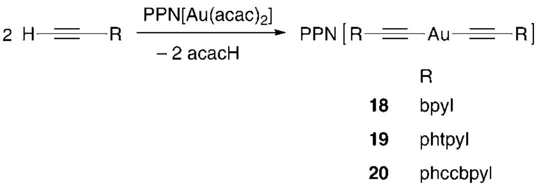
The interconversion between **12** and **17** could take place (Scheme 5) by substitution of one of the phosphine donor groups of **12** by a solvent molecule, followed by the transfer of an alkynyl group from **12** to the intermediate **B**. The resulting ionic species **C** would react with the $[Au(C\equiv Cbpyl)(\kappa^1\text{-dppm})]$ (**A**) intermediate to generate the trinuclear cation of the salt **D**, which, by closing of the Au_3 ring, would finally give the salt **17**. According to this mechanism, the formation of **17** is favored in donor solvents.

Scheme 5



S = $(CD_3)_2CO$, CD_3CN, DMF or CD_3OD
R = $C\equiv CBpyl$

Scheme 6



Some salts with structures similar to **17** have been previously described. Thus, the reaction of $[Au(C\equiv CPh)]_n$ with dppm has been reported to give $[Au_3(C\equiv CPh)_2(\mu\text{-dppm})_2][Au(C\equiv CPh)_2]$, which was characterized by a single-crystal X-ray diffraction study, but its structure in solution was not reported.[26] The isolation of a series of complexes of composition $[Au_3(C\equiv CR')_2(\mu R_2PCH_2PR_2)_2][Au(C\equiv CR')_2]$ by reaction of $[Au_2Cl_2(\mu\text{-}R_2PCH_2PR_2)]$ (R = Ph, Tol, Cy, Me) with 1-alkynes in the presence of a base has also been reported.[27] The structural characterization of these complexes was based on a single-crystal X-ray study and ESI-MS measurements that showed the expected masses for the cations and anions. However, their reported ^1H NMR spectra ($CDCl_3$, 298 K) suggest a dynamic behavior in solution similar to that between complexes **12** and **17**, because in all cases except one, single sets of resonances for the R and R′ groups and a triplet for the PCH_2P protons were observed. Finally, very few $[\{Au(C\equiv CR)\}_2(\mu\text{-dppm})]$ complexes have been described.[28]

The $PPN[Au(C\equiv CR)_2]$ salts (R = bpyl (**18**), phtpyl (**19**), and phccbpyl (**20**)) were prepared by reaction of the alkyne **1**, **2**, or **5** with $PPN[Au(acac)_2]$ (Scheme 6).[29] They were characterized by spectroscopical and analytical means and also by an X-ray diffraction analysis of **18** (Figure 8).

Crystallographic Studies. The structures of the complexes **6**, **10**, **13**, **14**, **17**, and **18** have been determined by single-crystal X-ray diffraction (Figures 1–4, 6, and 7). The structure of **14** involves two independent molecules, each with the gold atom on an inversion center. In **17**, there are two independent anions, each with the gold atom on an inversion center. In **18**, the gold atom lies on a 2-fold axis. The Au−C and C≡C distances and X−Au−C and Au−C≡C angles (Table 1) are in the usual ranges for Au(I) alkynyl complexes.[30]

Au···Au Contacts. The crystal structures of **6**, **10**, and **18** do not show Au···Au contacts. Complex **13** forms infinite

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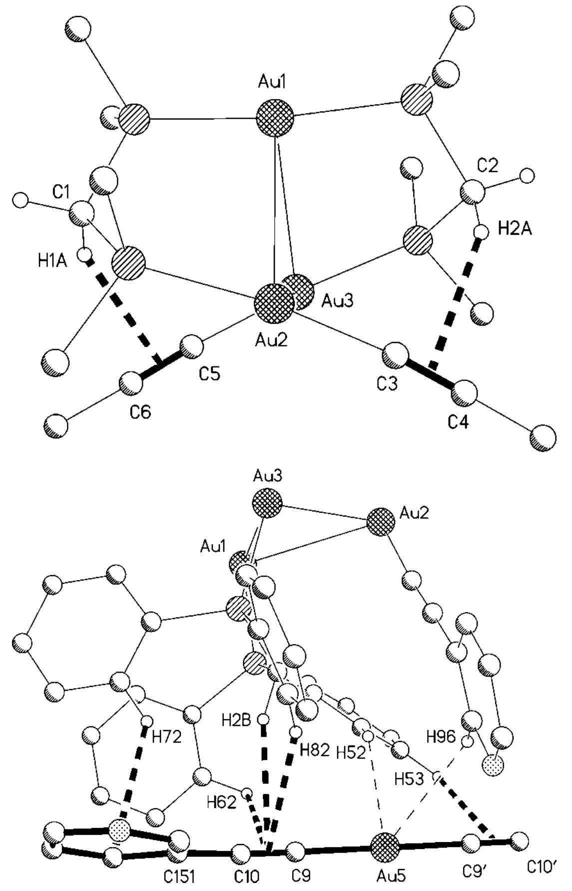

Figure 7. (Top) C−H···(C≡C) interactions within the cation of compound **15**. (Bottom) Clustering of five C−H···π (thick dashed bonds) and two C−H···Au contacts (thin dashed bonds) between the cation and one anion of **15**. For symmetry operators, see Supporting Information.

chains that are arranged in a parallel fashion (Figure 3) through intermolecular short aurophilic contacts (3.0214(3) Å) via the 2_1 axis. The chains have a helical twist as a result of the conformation of the Au−P−C−C−P−Au unit (the Au−P···P−Au dihedral angle is 70.6°). In contrast, in [$Au_2(C{\equiv}C\text{-}Ph)_2(\mu\text{-}dppe)$][31] and [$Au_2Cl_2(\mu\text{-}dppe)$],[32] two molecules interact with each other to form an isolated dimer.

One independent molecule of **14** is shown in Figure 4. The PC_4P chain is in a fully elongated form and the AuC≡Cbpyl units are perpendicular to the P···P vector (90°, 88° in the two molecules) in an *anti* configuration. Each molecule is linked to two neighboring molecules by weak Au···Au interactions[10,33] (3.6355(5) Å) to form infinite chains, which lie with Au···Au vectors very approximately parallel (27°). A similar arrangement has been found in [$Au_2X_2(\mu\text{-}dppb)$] complexes (X = I,[34] SPh,[35] STol,[36]), where the molecules are linked by short aurophilic contacts.

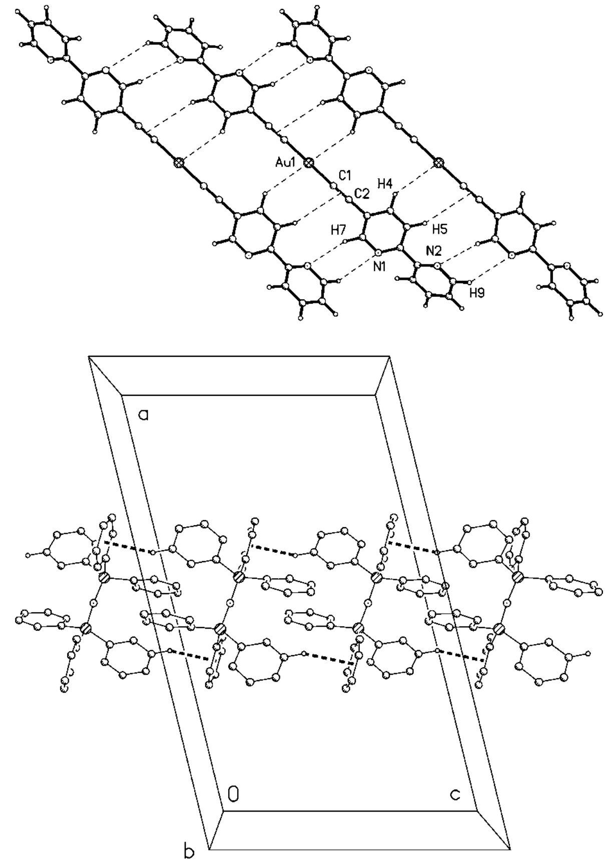

Figure 8. Neighboring anions (top) and cations (bottom) in the structure of compound **18**. Weak interactions (see text) are indicated by dashed lines.

In complex **17**, the structure of the cation [$Au_3(C{\equiv}Cbpyl)_2(\mu\text{-}dppm)_2$]$^+$ can be formally viewed as two AuC≡Cbpyl units linked to an Au^+ cation by two dppm ligands (Figure 6). The alkynyl groups point to opposite sides of the Au_3 plane. Remarkably, in the Au_3 triangle, the Au···Au distances between Au atoms linked by a dppm ligand are longer (3.1938(3) and 3.3298(3) Å) than the other Au−Au distance (3.0217(3) Å).

Weak Hydrogen Bonds. Short C−H···Au[4,6,7,9,37–39] and C−H···π(C≡CAu)[38,40,41] contacts have been found in the determined structures except for compound **6**, where no H···Au

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Table 1. Bond Distances and Angles for Complexes 6, 10, 13, 14, 17, and 18

	bond distances (Å)				bond angles (deg)	
complex	Au−P	Au−C	C≡C	Au−Au	X−Au−Y	Au−C≡C
6	2.2724(9)	2.004(3)	1.201(5)		172.38(10)[f]	168.1(3)
10	2.2729(5)	1.9995(19)	1.199(3)		176.23(6)[f]	176.39(18)
13	2.2737(12)	2.024(5)	1.192(7)	3.0214(3)[d]	172.22(16)[f]	169.7(5)
	2.2812(13)	2.024(5)	1.179(8)		172.26(16)[f]	177.1(5)
14	2.2719(18)	2.027(8)	1.145(9)	3.6355(5)[d]	172.0(2)[f]	166.8(8)
	2.273(2)	2.036(10)	1.074(11)		178.6(3)[f]	175.2(10)
17	2.2964(13)[a]	2.002(5)[b]	1.214(7)[b]	3.1938(3)	170.93(16)[f]	173.5(5)[b]
	2.3023(13)[a]	2.006(5)[b]	1.199(7)[b]	3.3298(3)	171.28(16)[f]	175.6(5)[b]
	2.2864(13)	1.988(6)[c]	1.209(8)[c]	3.0217(3)[e]	172.37(5)[h]	177.2(5)[c]
	2.2866(13)	1.996(7)[c]	1.199(9)[c]		180.0(2)[g,i]	177.2(5)[c]
18		1.976(4)	1.209(6)		179.6(2)[g]	177.5(4)

[a] For the mutually *trans* P atoms. [b] For the cation. [c] For the anion. [d] Intermolecular. [e] Between the Au atoms bonded to bpylC≡C. [f] P−Au−C. [g] C−Au−C. [h] P−Au−P. [i] By symmetry.

distance shorter than 3.13 Å was observed. Although the interpretation of these contacts as weak hydrogen bonds should be made very cautiously,[39] the packing features described below suggest that these interactions could be structurally significant, particularly when several interactions of the same or of different type act cooperatively.

For the following discussion, it should be noted that the C−H bond lengths have been normalized to 1.08 Å. Contacts with angles less than 130° have generally been excluded unless they form part of multicenter or multicontact systems (see individual discussion). Tables with the hydrogen bond distances and angles are given as Supporting Information.

In compound **6**, two C–H···N and three C−H···π interactions were observed, which involve different symmetry operators in all cases (see Supporting Information). The result is a complex three-dimensional packing without easily identifiable features.

In complex **10**, at first sight there seems to be no clearly recognizable packing feature; indeed, the eight C−H···π(C≡C) interactions observed are all quite long and narrow-angled (see Supporting Information). However, a closer inspection reveals that the interactions are coupled, each C−H···Au with one or two C−H···π(C≡C) from the same ring to the adjacent triple bond and with the same operator (Figure 2). Although believing that such contacts are structurally significant, we have cautiously pointed out the ease of assembling contacts at a linear and thus sterically accessible gold(I) center.[4,42] Nevertheless, the large number of contacts in **10** remains impressive.

The molecules of **10** are assembled such that the terpyridyl groups of neighboring molecules are approximately parallel. There are recognizable π-stacking interactions from the ring (N1,C21−C25) to itself at $-x$, $2-y$, $2-z$ (rings exactly parallel, intercentroid distance 3.73 Å, perpendicular distance 3.44 Å, offset 1.4 Å) and to the ring (N2,C31−C35) at $-1-x$, $2-y$, $2-z$ (interplanar angle 9°, distances 3.78, 3.24, ca. 1.9 Å).

The structure of compound **13** shows again a wide variety of contacts, many of which are rather long (see Supporting Information). Closer inspection shows that about half of these, from hydrogens of the diphenylphosphino groups, involve the 2_1 screw axis that also generates the Au···Au interactions (Figure 3). These interactions may thus be regarded as acting cooperatively.

In compound **14** again there is a broad and heterogeneous mixture of contacts (see Supporting Information), many of which are borderline in terms of lengths and/or angles. In contrast to **13**, there is also no concentration of contacts via any particular operator; all four notably short contacts involve different operators.

There are three striking features of the packing in the structure of compound **15**:

(i) Some of the contacts are extremely short (H···N 2.40, H···Au 2.69, H···ring centroid 2.30, H···triple bond 2.40 Å; more details are given in the Supporting Information). This may be promoted, at least in part, by favorable electrostatic interactions between oppositely charged ions ("charge assistance").

(ii) Three of the four methylene protons of dppm are involved in short contacts (see Supporting Information). We have already pointed out the marked tendency of these atoms to act as H bond donors.[43] The contacts H2A···(C3≡C4) and H1A···(C5≡C6) act within the cation (Figure 7) and may well help to determine or at least stabilize the configuration.

(iii) The extended and exposed linear sections of the anions, particularly the anion involving Au5, lead to a clustering of contacts at those regions (Figure 7).

Stacking interactions may be assumed between rings C41–46 and C111–116 within the cation (interplanar angle 7.8°, intercentroid distance 3.71 Å) and C91–96 and C101–106 via the operator $1-x$, $1-y$, $1-z$ (parallel, distance 3.67 Å).

Compound 18. The anions pack parallel to each other to form ribbons parallel to the z axis (Figure 8). Some of the "weak" interactions between the anions, especially those of the C−H···N type, are much longer than most of those discussed for the other structures (see Supporting Information), but in total they may serve to determine the anion substructure. Both independent C−H···N contacts are connected across inversion centers to form rings of graph set R (6).

The structures of PPN[Au(C≡CAr)$_2$] (Ar = C$_6$H$_4$X-4, X = Me, NO$_2$)[39,44] also contain ribbons of anions, but linked by Au···H contacts. In all cases the space group is *C*2/*c*, both ions have 2-fold symmetry, and the cell contant c is ca. 15 Å. Closer inspection shows that the cations form chains parallel to the z axis (Figure 8), with two cations per axis translation, in which neighboring ions are connected by two C−H···π contacts (symmetry-related) from *meta* hydrogens. It may well be that the large cations determine the packing to a great extent. The anion and cation substructures are then linked by other weak interactions (see Supporting Information).

Photophysical Studies. Absorption Spectra. The absorption spectra of complexes containing the Au−C≡Cbpyl unit (**6**, **8–15**, and **18**) display two maxima at 316–324 and 329–332 nm (Table 2 and Figure 9). The spectra are very similar throughout the series. In contrast, larger variations in the λ_{max}

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Table 2. UV–Visible Absorption and Emission Data for HC≡Cbpyl (1) and Its Au–Alkynyl Derivatives

	absorption[a]	emission	
complex	λ_{max}/nm (10^{-4} ϵ/dm^3 mol^{-1} cm^{-1})	medium (T/K)	λ_{max}/nm (τ/μs)
1	258 (2.9), 300 (4.2)	CH_2Cl_2 (298)	355,[b] 374
6	316 (3.4), 330 (3.1)	CH_2Cl_2 (298)	391, 492,[c] 533[c]
		solid (298)	392, 410,[b] 496, 536 (28, 184),[d] 557
8	316 (3.1), 329 (2.8)	CH_2Cl_2 (298)	390, 499, 532
		solid (298)	396, 426, 497, 544 (16, 136),[d] 577[b]
		solid (77)	525, 545, 572
		n-PrCN (77)	490 (172), 520, 532
12	318, (7.2), 332 (6.3)	CH_2Cl_2 (298)	376, 398, 501, 533[b]
		MeCN (298)	391, 500, 532[b]
		solid (298)	418, 516,[b] 550, 592, 655
13	316 (4.2), 330 (4.0)	CH_2Cl_2 (298)	378, 397, 496,[c] 529[d]
		solid (298)	393, 498, 541 (19, 158),[d] 557[b]
		n-PrCN (77)	496 (194), 536
14	317 (5.9), 330 (5.5)	CH_2Cl_2 (298)	394, 492,[c] 527[d]
		solid (298)	400, 420, 498, 539, 576[b]
15	317 (10.5), 330 (9.7)	CH_2Cl_2 (298)	393, 506, 546, 580[b]
		solid (298)	402, 516,[b] 546, 578,[b] 650[b]
		solid (77)	514, 538, 553,[b] 576[b]
		n-PrCN (77)	497, 537, 554[b]
18	324 (4.1), 333[b] (3.9)	CH_2Cl_2 (298)	376, 390, 506, 539
		solid (298)	400, 510 (76), 545
		n-PrCN (77)	495 (244), 535

[a] Measured in CH_2Cl_2 solution at 298 K. [b] Shoulder. [c] Weak. [d] Double exponential decay.

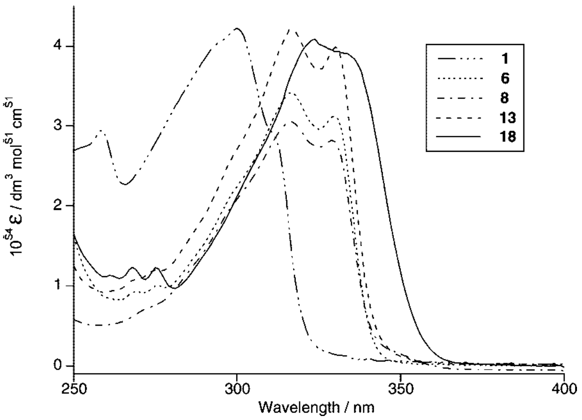

Figure 9. Absorption spectra (CH_2Cl_2) of compounds **1**, **6**, **8**, **13**, and **18**.

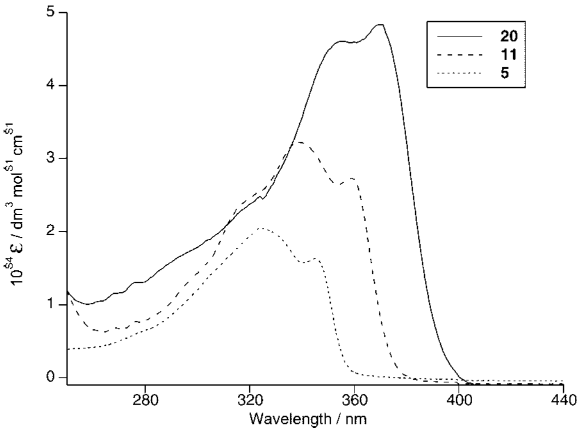

Figure 10. Absorption spectra (CH_2Cl_2) of compounds **5**, **11**, and **20**.

values of the lowest energy absorptions are observed on going from the neutral **9**–**11** to the corresponding anionic complexes **19** and **20** (Table 2 and Figure 10). In all cases, the λ_{max} values are higher in the dialkynyl aurate(I) than in the neutral complexes.

In accord with previously reported spectroscopic studies of Au(I) alkynyl complexes,[11,18,19,21,31,45,46] we tentatively propose that the transitions involved are mostly of intraligand [$\pi \rightarrow \pi^*$-(C≡CAr)] character with some participation of Au orbitals. Hence, the red shift of the absorptions of **5**, **11**, and **20** with respect to those of **1**, **6**, and **18**, respectively, can be attributed to the increase in π-electron delocalization on introducing a $C{\equiv}CC_6H_4$ group.

Emission Spectra. All complexes are emissive at room temperature in solution, as well as in the solid state. They present dual emissions, with higher energy maxima around 400 nm and lower energy maxima around 500 nm or higher. When the spectra are measured in deoxygenated CH_2Cl_2 at 298 K, the higher energy emissions are more intense than those at lower energy (Figure 11), except for complexes **8** and **19**, where the lower energy emissions are the most intense ones (Figure 12). Measuring the spectra in nondeoxygenated CH_2Cl_2 solutions gave rise to a significant decrease in the intensities of the lower energy emissions. In the solid state at 298 K, the intensity of both emissions is comparable, except for complexes **9–11** and **20**, where no maxima at low energy appeared, but the higher energy emission tailed up to 600 nm. At 77 K, in the solid state or in glassy ^{n}PrCN, the lower energy emissions are dominant (Figures 12 and 13), except for complex **11**. The low-energy emission displays vibrational structure in most cases, but it was not well resolved because of the broadness of the peaks, except for complexes **11** and **20**, in glassy ^{n}PrCN, at 77 K (Figure 13). The observed vibronic spacings in these conditions were around 1100–1200, 1500–1600, 2100 and 2200 cm^{-1}, which can be assigned to aromatic ring and C≡C vibrational modes.

The similarity of the emission spectra of different complexes containing the same alkynyl ligand suggests that the involved states are located mainly in the Au-alkynyl units. The difference

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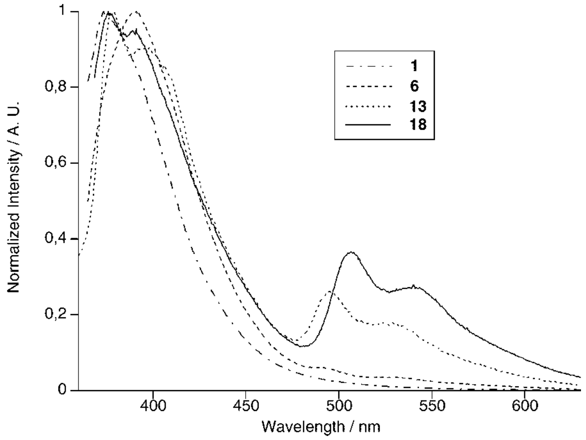

Figure 11. Emission spectra (CH_2Cl_2, 298 K) of compounds **1**, **6**, **13**, and **18**.

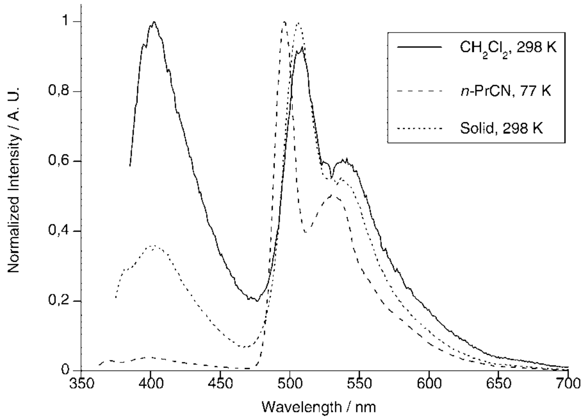

Figure 12. Emission spectra of **19**.

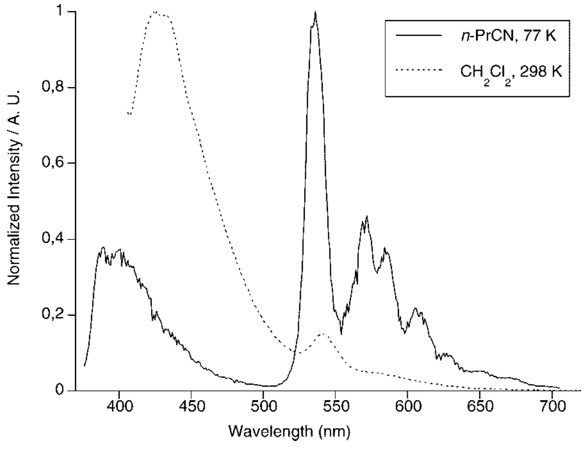

Figure 13. Emission spectra of **20**.

in the Stokes shifts of both emissions, the quenching of the lower energy emissions by oxygen, and its decrease in solution at room temperature suggest that both emissions are different in character. Studies of the photophysics of 5-ethynyl-2,2′-bipyridines have shown that they display strong fluorescence at 345–414 nm and very weak phosphorescence at 505–550 nm.[47] In our case, the positions of the high-energy emissions are close to the emission maxima of the free alkynes **1**, **2**, and **5** (374, 362, and 379 nm, respectively, in CH_2Cl_2, at 298 K). In addition, it is known that, in $[Au(C{\equiv}CR)(PR_3)]$ complexes, the $AuPR_3$ unit is able to efficiently enhance the emission from the triplet states (phosphorescence) of the C≡CR luminomophores.[19,23,40,46,48] Therefore, we tentatively assign the emitting states to metal-perturbed, alkynyl ligand based, ^{1}IL [$\pi\rightarrow\pi^*$] (higher energy emission) and ^{3}IL [$\pi\rightarrow\pi^*$] (lower energy emission) states. Lifetime measurements are in agreement with their respective singlet and triplet character. Thus, the lifetime of the higher energy emissions could not be accurately determined owing to instrumental limitations, but we observed that the emissions decayed completely after a few nanoseconds. In contrast, the τ values of the lower energy emissions are in the microsecond range (Tables 2–4). Finally, it should be noted that similar dual emissions have been recently reported in the related complexes $[Au(C{\equiv}Cphenl)(PPh_3)]$ (phenl = 1,10-phenanthrolin-3-yl or 1,10-phenanthrolin-5-yl), $[Au(C{\equiv}Cphenl)_2]^-$ (phenl = 1,10-phenanthrolin-3-yl), and $[(PPh_3)Au(C{\equiv}CphenlC{\equiv}C)Au(PPh_3)]$ (phenl = 1,10-phenanthrolin-3,8-ylidene).[15,16]

Concluding Remarks. A series of Au(I) alkynyl complexes containing the 2,2′-bipyridine-5-yl or 2,2′:6′,2′′-terpyridine-4-yl groups have been prepared and structurally characterized. An exchange process between the dinuclear complex $[Au_2(C{\equiv}Cbpyl)_2(\mu\text{-dppm})]$ (**12**) and the salt $[Au_3(C{\equiv}Cbpyl)_2(\mu\text{-dppm})_2][Au(C{\equiv}Cbpyl)_2]$ (**17**) has been observed in solution. The salt is the main component in solutions of highly polar solvents, while the dinuclear complex is virtually the only species present in $CDCl_3$. The crystal structures of the complexes $[Au_2(C{\equiv}Cbpyl)_2(\mu\text{-}PPh_2(CH_2)_xPPh_2)]$ (x = 2 (**13**) and 4 (**14**)) display Au···Au interactions that give rise to the formation of chains. All prepared complexes are luminescent at room temperature and display dual emissions that are assigned to metal-perturbed alkynyl ligand based transitions. These compounds are potential candidates for use as chemosensors or, by reaction with metal ions, as building blocks for the synthesis of new heterometallic oligomers and polymers. Studies of their reactivity toward transition metal cations, in particular with Fe^{2+}, are in progress and will be reported in due course.

Experimental Section

General Considerations. The preparation of compounds $IC_6H_4C{\equiv}CSiMe_3$-4,[49] **1**, **2**,[50] PPN[Au(acac)$_2$] ($PPN^+ = (Ph_3P{=}N{=}PPh_3)^+$), $[Au(acac)(PR_3)]$[51] (R = Ph, Tol), and $[AuCl(SMe_2)]$[52] was carried out as previously described. Other reagents were obtained from commercial sources—CNXy (Fluka), $Ph_2P(CH_2)_nPPh_2$, n = 1 (dppm, Fluka), 2 (dppe, Aldrich), and 4 (dppb, Fluka)—and used without further purification. All manipulations were carried out under an air atmosphere and at room temperature unless otherwise stated. Tetrahydrofuran, toluene, and Et_2O were distilled over sodium-benzophenone; CH_2Cl_2 was distilled over CaH_2 and bubbled before use with N_2 to remove traces of HCl.

Infrared spectra were recorded in the range 4000−200 cm^{-1} on a Perkin-Elmer 16F PC FT-IR spectrometer with Nujol mulls between polyethylene sheets. C, H, N, and S analyses were carried out with Carlo Erba 1108 and LECO CHS-932 microanalyzers. NMR spectra were measured on Bruker Avance 200, 300, 400, and 600 instruments. ^{1}H chemical shifts were referenced to residual $CHCl_3$ (7.26 ppm) or CHD_2COCD_3 (2.05 ppm).

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Table 3. UV–Visible Absorption and Emission Data for HC≡Cphtpyl (2) and Its Au−Alkynyl Derivatives

	absorption[a]	emission	
complex	λ_{max}/nm (10^{-4} ϵ/dm^3 mol^{-1} cm^{-1})	medium (T/K)	λ_{max}/nm (τ/μs)
2	256 (2.3), 284 (3.7), 315^b (0.8)	CH_2Cl_2 (298)	362
			409, 440^b
9	233 (5.4), 250 (5.3), 266 (3.8), 289^b (4.9), 306^b (5.8), 320 (6.3)	CH_2Cl_2 (298)	418, 489,^{c} 523^d
		solid (298)	403, 447, 491,^{b} 523^b
		n-PrCN (77)	370,^{c} 486 (449), 520
10	235 (8.2), 304^b (6.9), 314 (7.2)	CH_2Cl_2 (298)	378, 492,^{c} 524^d
		solid (298)	392, 444
		n-PrCN (77)	362, 427, 485 (875), 518
16	233 (10.4), 305^b (8.7), 315 (9.0)	CH_2Cl_2 (298)	391, 504,^{c} 533^c
		solid (298)	399, 509 (11, 93),^{d} 537
19	232 (11.9), 276 (6.3), 287 (6.5), 342 (9.1)	CH_2Cl_2 (298)	403, 506, 537
		solid (298)	403, 509, 541 (8.9, 94)^d
		n-PrCN (77)	399,^{c} 496 (519), 530

[a] Measured in CH_2Cl_2 solution at 298 K. [b] Shoulder. [c] Weak. [d] Double exponential decay.

Table 4. UV–Visible Absorption and Emission Data for HC≡C−C_6H_4−C≡Cbpyl (5) and Its Au−Alkynyl Derivatives

	absorption[a]	emission	
complex	λ_{max}/nm (10^{-4} ϵ/dm^3 mol^{-1} cm^{-1})	medium (T/K)	λ_{max}/nm (τ/μs)
5	324 (2.1), 345 (1.6)	CH_2Cl_2 (298)	379, 393^b
11	320^b (2.5), 339 (3.2), 359 (2.7)	CH_2Cl_2 (298)	400
		Solid (298)	417, 430
		n-PrCN (77)	400, 535 (1099), 569,^{c} 584,^{c} 606^c
20	356 (4.6), 371 (4.8)	CH_2Cl_2 (298)	427, 541,^{c} 577^{b,c}
		solid (298)	430
		n-PrCN (77)	389, 535, 571, 584, 606,^{c} 627,^{c} 649,^{b,c}669^{b,c}

[a] Measured in CH_2Cl_2 solution at 298 K. [b] Shoulder. [c] Weak.

Table 5. Crystal Data for 6, 10, 13, 14, 17, and 18.

	6	**10**	**13**·$2C_2H_4Cl_2$	**14**·½$C_4H_{10}O$	**17**	**18**
formula	$C_{30}H_{22}AuN_2P$	$C_{41}H_{29}AuN_3P$	$C_{54}H_{46}Au_2Cl_4N_4P_2$	$C_{54}H_{47}Au_2N_4O_{0.5}P_2$	$C_{98}H_{72}Au_4N_8P_4$	$C_{60}H_{44}AuN_5P_2$
cryst size (mm^3)	0.19 × 0.12 × 0.12	0.28 × 0.21 × 0.15	0.28 × 0.17 × 0.07	0.30 × 0.12 × 0.04	0.35 × 0.1 × 0.1	0.25 × 0.15 × 0.05
cryst syst	triclinic	triclinic	monoclinic	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$C2/c$
a (Å)	10.0469(4)	8.6401(4)	15.8653(11)	13.5520(14)	13.0631(16)	25.492(3)
b (Å)	10.6781(4)	9.4232(4)	14.3420(8)	14.0520(16)	15.8893(8)	12.3916(12)
c (Å)	13.1309(5)	19.5947(8)	22.9292(14)	15.1890(16)	20.2091(8)	15.1409(15)
α (deg)	76.667(2)	85.165(2)	90	69.737(5)	104.761(4)	90
β (deg)	68.524(2)	86.406(2)	104.006(4)	66.133(5)	93.429(4)	103.802(2)
γ (deg)	68.910(2)	85.237(2)	90	66.901(5)	90.574(4)	90
V (Å^3)	1215.14(8)	1581.69(12)	5062.2(5)	2371.8(4)	4047.6(3)	4644.7(8)
Z	2	2	4	2	2	4
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
ρ(calc) (Mg m^{-3})	1.745	1.662	1.770	1.702	1.865	1.564
F(000)	620	780	2616	1182	2184	2192
T (K)	100(2)	100(2)	173(2)	133(2)	133(2)	100(2)
μ (mm^{-1})	6.141	4.737	6.105	6.288	7.361	3.284
transmissions	0.38–0.53	0.35–0.54	0.40–0.67	0.23–0.77	0.40–0.67	0.49–0.85
θ range (deg)	1.68–28.08	2.09–26.37	1.32–30.04	1.50–26.37	1.33–30.51	1.65–26.37
index ranges	$-13 \le h \le 13$	$-10 \le h \le 10$	$-22 \le h \le 22$	$-16 \le h \le 16$	$-18 \le h \le 18$	$-31 \le h \le 31$
	$-13 \le k \le 13$	$-11 \le k \le 11$	$-20 \le k \le 20$	$-17 \le k \le 17$	$-22 \,'\, k \le 22$	$-15 \le k \le 15$
	$-17 \le l \le 17$	$-24 \le l \le 24$	$-32 \le l \le 32$	$-18 \le l \le 18$	$-28 \le l \le 28$	$-18 \le l \le 18$
no. of reflns collected	14 233	17 430	95 857	38 801	92 816	25 052
no. of indep reflns	5450	6421	14 798	9665	24 553	4752
R_{int}	0.0237	0.0139	0.0744	0.0776	0.0398	0.0440
abs corr	semiempirical from equivalents			face-indexing	semiempirical from equivalents	
refinement method	full-matrix least-squares on F^2					
no. of data/restraints/params	5450/24/307	6421/0/415	14798/127/595	9665/0/541	24553/196/500	4752/304/308
GOF on F^2	1.122	1.088	1.034	0.847	1.037	1.254
R1^a	0.0255	0.0147	0.0369	0.0478	0.0398	0.0372
wR2^b	0.0585	0.0370	0.0961	0.0868	0.1004	0.0808
largest diff peak (e Å^{-3})	1.329 and −0.685	0.672 and −0.462	1.704 and –1.216	2.115 and –1.222	2.624 and –1.466	1.462 and −1.236

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

$^{13}C\{^1H\}$ spectra were referenced to $CDCl_3$ (77.1 ppm). ^{19}F and $^{31}P\{^1H\}$ NMR spectra were referenced to external $CFCl_3$ (0 ppm) and H_3PO_4 (0 ppm). The temperature values in NMR experiments were not corrected. Abbreviations used: v = virtual; br = broad; $N = {}^xJ_{PC} + {}^{(x+y)}J_{PC}$, where $x = 2$ (C2, Ph) or 3 (C3, Ph) and $y = 2$ (dppm) or $y = 3$ (dppe). NMR simulations were performed with the gNMR (version 5.0.5.0) program. Melting points were determined on a Reichert apparatus in an air atmosphere.

UV–visible absorption spectra were recorded on a Unicam UV 500 spectrometer in 1 cm path length quartz cuvettes. Steady state excitation and emission spectra were measured on a Jobin Yvon Fluorolog 3-22 spectrofluorimeter with a 450 W xenon lamp, double-grating monochromators, and a Hamamatsu R-928P photomultiplier. The solutions for luminescence measurements were deoxygenated by bubbling N_2 or by four freeze–pump–thaw cycles and placed inside 1 cm path length quartz fluorescence cuvettes (298 K) or quartz tubes (77 K) under an atmosphere of N_2. Low-temperature measurements were carried out in an optical Dewar sample holder filled with liquid N_2 or using an Oxford Instruments OptistatDN cryostat and ITC503 temperature controller. The solid samples were placed between quartz coverslips or, for low-temperature measurements, were ground with added KBr and placed into 5 mm quartz NMR tubes. Phosphorescence lifetimes were measured using an incorporated Jobin Yvon FL-1040 phosphorimeter. The excitation source was a pulsed Xenon lamp, with a pulse full-width half-maximum of 3 μs. Solutions for τ measurements were rigorously degassed by no less than four freeze–pump–thaw cycles. A ±10% error is estimated for the given τ values.

$Ph_2P(CH_2)_{10}PPh_2$ (dppd). This was prepared by a literature method.[53] ^1H NMR (200.1 MHz, $CDCl_3$): δ 7.47–7.30 (m, 20 H, Ph), 2.40 (m, 4 H, CH_2P), 1.54–1.22 (m, 16 H, CH_2). $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): δ 138.8 (d, $^1J_{PC}$ = 14.2 Hz, C1, Ph), 132.7 (d, $^2J_{PC}$ = 18.2 Hz, *C*2, Ph), 128.4 (s, C4, Ph), 128.3 (d, $^3J_{PC}$ = 6.9 Hz, C3, Ph), 31.2 (d, $^3J_{PC}$ = 12.8 Hz, $PCH_2CH_2CH_2$), 29.4 (s, CH_2), 29.2 (s, CH_2), 28.0 (d, $^1J_{PC}$ = 10.6 Hz, PCH_2), 25.9 (d, $^2J_{PC}$ = 15.8 Hz, PCH_2CH_2). $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6): δ −15.5 (s). HRMS (FAB) exact mass: 511.2684 (MH^+), calcd for $C_{34}H_{41}P_2$: 511.2691.

$[Au(C{\equiv}Cbpyl)]_n$ (3). $[AuCl(SMe_2)]$ (327 mg, 1.11 mmol) and NEt_3 (0.46 mL, 3.33 mmol) were added to a solution of **1** (200 mg, 1.11 mmol) in CH_2Cl_2 (15 mL). The mixture was stirred for 30 min and concentrated to about half of its volume. MeOH (60 mL) was added and the resulting yellow-brownish precipitate was filtered off, washed with acetone (3 × 5 mL), CH_2Cl_2 (3 × 5 mL), and Et_2O (3 × 5 mL), and dried under vacuum. Yield: 261 mg, 70%. Mp: 145 °C (dec). Anal. Calcd for $C_{12}H_7AuN_2$: C, 38.32; H, 1.88; N, 7.45. Found: C, 37.13; H, 1.81; N, 7.19. IR (Nujol, cm^{-1}): $\nu(C{\equiv}C)$ 2106. The insolubility of **3** prevented its characterization by NMR spectroscopy in solution as well as its recrystallization.

$[Au(C{\equiv}Cphtpyl)]_n$ (4). This was prepared in the same way as **3** from $[AuCl(SMe_2)]$ (221 mg, 0.75 mmol), NEt_3 (0.31 mL, 2.25 mmol), and **2** (250 mg, 0.75 mmol) in CH_2Cl_2 (26 mL). Yield: 309 mg, 79%. Mp: 169 °C (dec). Anal. Calcd for $C_{23}H_{14}AuN_3\cdot(HCl)_{0.4}$: C, 50.79; H, 2.67; N, 7.73; Cl, 2.61. Found: C, 49.12; H, 2.74; N, 7.35; Cl, 2.70. IR (Nujol, cm^{-1}): $\nu(C{\equiv}C)$ 2112. The insolubility of **4** prevented its characterization by NMR spectroscopy in solution as well as its recrystallization.

$HC{\equiv}Cphccbpyl$ (5). To a solution of 4-$Me_3SiC{\equiv}CC_6H_4I$ (1124 mg, 4.03 mmol) in dry THF (40 mL) under nitrogen, **1** (725 mg, 4.03 mmol), *trans*-$[PdCl_2(PPh_3)_2]$ (283 mg, 0.403 mmol), CuI (123 mg, 0.64 mmol), and diisopropylamine (8 mL) were added. The mixture was stirred for 23 h at room temperature, and the volatiles were removed under vacuum. The residue was chromatographed on silica gel using *n*-hexane/Et_2O (3:1) as eluent. Evaporation of the solvent gave bpyl-$C{\equiv}CC_6H_4C{\equiv}CSiMe_3$-4 as a colorless solid, which was desilylated by treatment with KF (468 mg, 8.05 mmol) in MeOH (200 mL) overnight. The solvent was evaporated under vacuum, the residue was extracted with $CHCl_3$ (50 mL), and the extract was dried over Na_2SO_4 and filtered. Evaporation of the solution gave **5** as a colorless solid. Yield: 850 mg, 75%. Mp: 132–135 °C. Anal. Calcd for $C_{20}H_{12}N_2$: C, 85.69; H, 4.31; N, 9.99. Found: C, 85.34; H, 4.38; N, 10.01. IR (KBr, cm^{-1}): $\nu({\equiv}C{-}H)$ 3274, $\nu(C_6H_4C{\equiv}C)$ 2214, $\nu(C{\equiv}CH)$ 2102. ^1H NMR (600.1 MHz, $CDCl_3$): δ 8.81 (dd, $^4J_{HH}$ = 2.1 Hz, $^5J_{HH}$ = 0.5 Hz, 1 H, H6), 8.69 (ddd, $^3J_{HH}$ = 4.7, $^4J_{HH}$ = 1.8 Hz, $^5J_{HH}$ = 0.8 Hz, 1 H, H6′), 8.42 (d, $^3J_{HH}$ = 9.0 Hz, 1 H, H3′), 8.41 (d, $^3J_{HH}$ = 8.2 Hz, 1 H, H3), 7.93 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 2.2 Hz, 1 H, H4), 7.82 (td, $^3J_{HH}$ = 7.8 and $^4J_{HH}$ = 1.8 Hz, 1H, H4′), 7.52–7.48 (m, 4 H, C_6H_4), 7.31 (ddd, $^3J_{HH}$ = 7.5 and 4.8 Hz, $^4J_{HH}$ = 1.2 Hz, 1 H, H5′), 3.20 (s, 1 H, ${\equiv}C{-}H$). $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): δ 155.4 (C2′), 155.0 (C2), 151.6 (C6), 149.3 (C6′), 139.4 (C4), 137.0 (C4′), 132.2 (CH, C_6H_4), 131.6 (CH, C_6H_4), 124.0 (C5′), 123.0 (quaternary, C_6H_4), 122.5 (quaternary, C_6H_4), 121.4 (C3′), 120.4 (C3), 120.0 (C5), 92.9 (bpylC≡*C*), 88.3 (bpyl*C*≡C), 83.1 (*C*≡CH), 79.2 (C≡*C*H). HRMS (EI) exact mass: 280.1001 (M^+), calcd for $C_{20}H_{12}N_2$ 280.1000.

$[Au(C{\equiv}Cbpyl)(PPh_3)]$ (6). Method A. A suspension of **3** (196 mg, 0.52 mmol) in CH_2Cl_2 (30 mL) was treated with PPh_3 (137 mg, 0.52 mmol) and stirred for 30 min. The resulting solution was concentrated under vacuum to about 1 mL and treated with *n*-pentane (20 mL) to give a colorless precipitate, which was filtered off, washed with Et_2O (3 × 5 mL), and dried under vacuum. Yield: 300 mg, 90%. Mp: 139–144 °C (dec). Anal. Calcd for $C_{30}H_{22}AuN_2P$: C, 56.43; H, 3.47; N, 4.39. Found: C, 56.17; H, 3.79; N, 4.29. IR (Nujol, cm^{-1}): $\nu(C{\equiv}C)$ 2108. ^1H NMR (300.1 MHz, $CDCl_3$): δ 8.80 (br s, 1 H, H6), 8.66 (d, $^3J_{HH}$ = 4.5 Hz, 1 H, H6′), 8.37 (d, $^3J_{HH}$ = 8.1 Hz, 1 H, H3′), 8.30 (d, $^3J_{HH}$ = 8.1 Hz, 1 H, H3), 7.89 (dd, $^3J_{HH}$ = 8.4, $^4J_{HH}$ = 2.1 Hz, 1 H, H4), 7.78 (td, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ 1.8 Hz, 1 H, H4′), 7.60–7.43 (m, 15 H, Ph), 7.26 (t, $^3J_{HH}$ = 8.4 Hz, 1 H, H5′). $^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$): δ 156.0, 153.4 (C2 and C2′), 152.6 (C6), 149.2 (C6′), 140.1 (C4), 137.7 (d, $^2J_{CP}$ = 141.9 Hz, C≡*C*Au), 136.9 (C4′), 134.4 (d, $^2J_{PC}$ = 13.9 Hz, C2, Ph), 131.7 (d, $^4J_{PC}$ = 1.8 Hz, C4, Ph), 129.6 (d, $^1J_{PC}$ = 56.3 Hz, C1, Ph), 129.3 (d, $^3J_{CP}$ = 11.3 Hz, C3, Ph), 123.5 (C5′), 122.1 (C5), 121.2 (C3′), 120.2 (C3), 100.9 (d, *C*≡CAu, $^3J_{CP}$ = 25.7 Hz). $^{31}P\{^1H\}$ (121.50 MHz, $CDCl_3$): δ 42.6 (s).

Method B. A solution of **1** (90 mg, 0.50 mmol) in CH_2Cl_2 (15 mL) was treated with $[Au(acac)(PPh_3)]$ (279 mg, 0.50 mmol). The mixture was stirred for 3 h at room temperature and concentrated to about 1 mL under vacuum, and Et_2O (20 mL) was added to give a colorless precipitate, which was filtered off, washed with Et_2O (3 × 4 mL), and dried *in vacuo*. Yield: 184 mg, 58%.

$[Au(C{\equiv}Cbpyl)\{P(Tol)_3\}]$ (7). This was prepared in the same way as **6** from **3** (151 mg, 0.40 mmol) and Tol_3P (122 mg, 0.40 mmol) in CH_2Cl_2 (15 mL). Colorless solid. Yield: 184 mg, 68%. Mp: 96–102 °C. Anal. Calcd for $C_{33}H_{28}AuN_2P$: C, 58.24; H, 4.15; N, 4.12. Found: C, 58.17; H, 4.09; N, 3.97. IR (Nujol, cm^{-1}): $\nu(C{\equiv}C)$ 2112. ^1H NMR (300.1 MHz, $CDCl_3$): δ 8.80 (br s, 1 H, H6), 8.66 (d, $^3J_{HH}$ = 4.7 Hz, 1 H, H6′), 8.37 (d, $^3J_{HH}$ = 8.1 Hz, 1 H, H3′), 8.30 (dd, $^3J_{HH}$ = 8.2 Hz, $^5J_{HH}$ = 0.7 Hz, 1 H, H3), 7.89 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 2.1 Hz, 1 H, H4), 7.78 (td, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.8 Hz, 1 H, H4′), 7.60–7.43 (m, 13 H, C_6H_4 and H5′), 2.40 (s, 9 H, Me). $^{13}C\{^1H\}$ NMR (100.8 MHz, $CDCl_3$): δ 156.0 (C2′), 153.2 (C2), 152.5 (C6), 149.2 (C6′), 142.0 (s, C4, Ph), 140.0 (C4), 136.8 (C4′), 134.2 (d, $^2J_{PC}$ = 14.1 Hz, *C*2, Ph), 129.9 (d, $^3J_{PC}$ = 11.7 Hz, C3, Ph), 126.6 (d, $^1J_{PC}$ = 58.3 Hz, C1, Ph), 123.4 (C5′), 122.1 (s, C5), 121.1 (C3′), 120.1 (C3), 100.8 (s, *C*≡CAu), 21.5 (Me). The signal of C≡*C*Au was not observed. $^{31}P\{^1H\}$ NMR (121.50 MHz, $CDCl_3$): δ 40.5 (s).

$[Au(C{\equiv}Cbpyl)(PEt_3)]$ (8). This was prepared in the same way as **6** from **3** (200 mg, 0.53 mmol) and PEt_3 (118 μL, 0.80 mmol) in CH_2Cl_2 (30 mL). Pale yellow solid. Yield: 190 mg, 73%. Mp: 112–120 °C (dec). Anal. Calcd for $C_{18}H_{22}AuN_2P$: C, 43.73; H, 4.49; N, 5.67. Found: C, 43.60; H, 4.36; N, 5.74. IR (Nujol, cm^{-1}): $\nu(C{\equiv}C)$ 2106. ^1H NMR (400.9 MHz, $CDCl_3$): δ 8.78 (dd, $^4J_{HH}$ = 2.1 Hz, $^5J_{HH}$ = 0.9 Hz, 1 H, H6), 8.66 (ddd, $^3J_{HH}$ = 4.8 Hz, $^4J_{HH}$ = 1.7 Hz, $^5J_{HH}$ = 0.9 Hz, 1 H, H6′), 8.36 (dd, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.0 Hz, 1 H, H3′), 8.28 (dd, $^3J_{HH}$ = 8.3 Hz, $^5J_{HH}$ = 0.9 Hz, 1 H, H3), 7.87 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 2.1 Hz, 1 H, H4), 7.79 (td, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.8 Hz, 1 H, H4′), 7.26 (td, 1 H, $^3J_{HH}$ = 4.8 Hz, $^4J_{HH}$ = 1.1 Hz, H5′), 1.83 (dq, $^2J_{PH}$ = 9.6 Hz, $^3J_{HH}$ = 7.7 Hz, 6 H, CH_2), 1.22 (dt, $^3J_{PH}$ = 18.1 Hz, $^3J_{HH}$ = 7.6 Hz, 9 H, Me).

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^{13}C{^{1}H} NMR (100.8 MHz, CDCl$_3$): δ 155.8 (C2′), 153.1 (C2), 152.4 (C6), 149.1 (C6′), 141.0 (br s, C≡*C*Au) 139.9 (C4), 136.8 (C4′), 123.4 (C5′), 122.1 (C5), 121.0 (C3′), 120.0 (C3), 100.6 (s, *C*≡CAu), 17.7 (d, $^{1}J_{PC}$ = 33 Hz, CH$_2$), 8.8 (s, Me). ^{31}P{^{1}H} (162.3 MHz, CDCl$_3$): δ 38.0 (s).

[Au(C≡Cphtpyl)(CNXy)] (9). A suspension of **4** (132 mg, 0.25 mmol) was treated with XyNC (33 mg, 0.25 mmol). The mixture was stirred for 30 min at room temperature and then filtered through Celite. The filtrate was concentrated to about 1 mL under vacuum. By addition of Et$_2$O (30 mL), a pale yellow solid precipitated, which was filtered off, washed with Et$_2$O (3 × 5 mL) and acetone (3 × 5 mL), and dried under vacuum. Yield: 115 mg, 70%. Mp: 167 °C (dec). Anal. Calcd for C$_{32}$H$_{23}$AuN$_4$: C, 58.19; H, 3.51; N, 8.48. Found: C, 57.93; H, 3.45; N, 8.56. IR (Nujol, cm^{-1}): *ν*(C≡N) 2202, *ν*(C≡C) 2124. ^{1}H NMR (400.9 MHz, CDCl$_3$): δ 8.73–8.72 (overlapped s and m, 4 H, H3 and H6′), 8.66 (d, $^{3}J_{HH}$ = 7.9 Hz, 2 H, H3′), 7.87 (td, $^{3}J_{HH}$ = 8.1 Hz, $^{4}J_{HH}$ = 1.9 Hz, 2 H, H4′), 7.83 (vd, *J* = 8.6 Hz, 2 H, C$_6$H$_4$), 7.62 (vd, *J* = 8.6 Hz, 2 H, C$_6$H$_4$), 7.35 (ddd, $^{3}J_{HH}$ = 7.6 and 4.8 Hz, $^{4}J_{HH}$ = 1.2 Hz, 2 H, H5′), 7.33 (t, $^{3}J_{HH}$ = 8.0 Hz, 1 H, H4 of Xy), 7.17 (d, $^{3}J_{HH}$ = 8.0 Hz, 2 H, H3 of Xy), 2.45 (s, 6 H, Me). ^{13}C{^{1}H} NMR (100.8 MHz, CDCl$_3$): δ 156.2, 155.9 (C2 and C2′), 149.7 (C4), 149.1 (C6′), 136.8 (C4′), 136.7 (C≡*C*Au), 136.2 (C4, C$_6$H$_4$), 133.0 (CH, C$_6$H$_4$), 130.9 (C4, Xy), 128.4 (C3, Xy), 126.9 (CH, C$_6$H$_4$), 125.4 (*C*-C≡CAu), 124.1 (C2, Xy), 123.8 (C5′), 121.3 (C3′), 118.6 (C3), 103.8 (*C*≡CAu), 18.7 (s, Me). The signals of the C≡N−C carbons were not observed.

[Au(C≡Cphtpyl)(PPh$_3$)] (10). A solution of **2** (119 mg, 0.36 mmol) in CH$_2$Cl$_2$ (15 mL) was treated with [Au(acac)(PPh$_3$)] (200 mg, 0.36 mmol). The solution was stirred for 3 h, filtered through Celite, and concentrated to about 1 mL under vacuum. By addition of Et$_2$O (20 mL), a colorless solid precipitated, which was filtered off, washed with Et$_2$O (3 × 5 mL) and acetone (3 × 5 mL), and dried under vacuum. Yield: 231 mg, 83%. Mp: 254–253 °C. Anal. Calcd for C$_{41}$H$_{29}$AuN$_3$P: C, 62.20; H, 3.69; N, 5.31. Found: C, 62.31; H, 3.80; N, 5.29. IR (Nujol, cm^{-1}): *ν*(C≡C) not observed. ^{1}H NMR (400.9 MHz, CDCl$_3$): δ 8.73 (s, 2 H, H3), 8.72 (ddd, $^{3}J_{HH}$ = 4.8 Hz, $^{4}J_{HH}$ = 1.7 Hz, $^{5}J_{HH}$ = 0.8 Hz, 2 H, H6′), 8.66 (d, $^{3}J_{HH}$ = 7.9 Hz, 2 H, H3′), 7.86 (td, $^{3}J_{HH}$ = 7.7 Hz, $^{4}J_{HH}$ = 1.5 Hz, 2 H, H4′), 7.83 (vd, *J* = 8.3 Hz, 2 H, C$_6$H$_4$), 7.65 (vd, *J* = 8.3 Hz, 2 H, C$_6$H$_4$), 7.60–7.44 (m, 15 H, Ph), 7.34 (ddd, $^{3}J_{HH}$ = 7.6 and 4.0 Hz, $^{4}J_{HH}$ = 1.0 Hz, 2 H, H5′). ^{13}C{^{1}H} NMR (100.8 MHz, CDCl$_3$): δ 156.2, 155.9 (C2 and C2′), 149.7 (C4), 149.1 (C6′), 136.8 (C4′), 136.5 (C4, C$_6$H$_4$), 134.3 (d, $^{2}J_{CP}$= 14.0 Hz, C2, Ph), 134.0 (d, $^{2}J_{CP}$= 141.1 Hz, C≡*C*Au), 132.9 (CH, C$_6$H$_4$), 131.6 (d, $^{4}J_{CP}$ = 2.1 Hz, C4, Ph), 129.7 (d, $^{1}J_{CP}$ = 56.0 Hz, C1, Ph), 129.1 (d, $^{3}J_{CP}$ = 11.1 Hz, C3, Ph), 126.9 (CH, C$_6$H$_4$), 125.7 (d, $^{4}J_{CP}$ = 3.0 Hz, *C*-C≡CAu), 123.8 (C5′), 121.3 (C3′), 118.6 (C3), 103.9 (d, $^{3}J_{CP}$ = 26.7 Hz, *C*≡CAu). ^{31}P{^{1}H} NMR (81.0 MHz, CDCl$_3$): δ 42.8 (s).

[Au(C≡Cphccbpyl)(PPh$_3$)] (11). A solution of **5** (90 mg, 0.33 mmol) in CH$_2$Cl$_2$ (10 mL) was treated with [Au(acac)(PPh$_3$)] (184 mg, 0.33 mmol). The solution was stirred for 3 h, filtered through Celite, and concentrated to about 1 mL under vacuum. By addition of Et$_2$O (20 mL), a colorless solid precipitated, which was filtered off, washed with Et$_2$O (3 × 5 mL), and dried under vacuum. Yield: 181 mg, 74%. Mp: 167 °C (dec). Anal. Calcd for C$_{38}$H$_{26}$AuN$_2$P: C, 61.79; H, 3.55; N, 3.79. Found: C, 61.73; H, 3.59; N, 3.56. IR (KBr, cm^{-1}): *ν*(C$_6$H$_4$C≡C) 2210, *ν*(C≡CAu) 2110. ^{1}H NMR (600.1 MHz, CDCl$_3$): δ 8.79 (d, $^{4}J_{HH}$ = 1.1 Hz, 1 H, H6), 8.68 (d, $^{3}J_{HH}$ = 4.5 Hz, 1 H, H6′), 8.41 (d, $^{3}J_{HH}$ = 8.7 Hz, 1 H, H3′), 8.40 (d, $^{3}J_{HH}$ = 8.3 Hz, 1 H, H3), 7.91 (dd, $^{3}J_{HH}$ = 8.2 Hz, $^{4}J_{HH}$ = 2.0 Hz, 1 H, H4), 7.81 (td, $^{3}J_{HH}$ = 7.9 Hz, $^{4}J_{HH}$ = 1.7 Hz, 1 H, H4′), 7.57–7.45 (m, 19 H, Ph and C$_6$H$_4$), 7.31 (dd, $^{3}J_{HH}$ = 7.4 and 4.8 Hz, 1 H, H5′). ^{13}C{^{1}H} NMR (50.3 MHz, CDCl$_3$): δ 155.5 (C2′), 154.7 (C2), 151.6 (C6), 149.3 (C6′), 139.3 (C4), 137.0 (C4′), 134.3 (d, $^{2}J_{CP}$ = 13.8 Hz, C2, Ph), 132.4 (CH, C$_6$H$_4$), 131.7 (C4, Ph), 131.41 (quaternary, C$_6$H$_4$), 129.7 (d, $^{1}J_{CP}$= 55.6 Hz, C1, Ph), 129.2 (d, $^{3}J_{CP}$ = 11.4 Hz, C3, Ph), 125.6 (quaternary, C$_6$H$_4$), 123.9 (C5′), 121.4 (C3′), 120.7 (quaternary, C$_6$H$_4$), 120.4 (C3 and C5), 103.8 (d, $^{3}J_{CP}$ = 26.1 Hz, *C*≡CAu), 93.8 (bpylC≡*C*), 87.5 (bpyl*C*≡C); the signal of C≡*C*Au was not observed. ^{31}P{^{1}H} NMR (121.5 MHz, CDCl$_3$): δ 42.7 (s).

[{Au(C≡Cbpyl)}$_2$(*μ*-dppm)] (12). A suspension of **3** (139 mg, 0.37 mmol) in CH$_2$Cl$_2$ (20 mL) was treated with dppm (71 mg, 0.185 mmol). The mixture was stirred for 30 min and concentrated under vacuum to about 1 mL. By addition of Et$_2$O (20 mL) a colorless solid precipitated, which was filtered off, washed with Et$_2$O (3 × 5 mL), and dried under vacuum. Yield: 180 mg, 85%. Mp: 152–159 °C. Anal. Calcd for C$_{49}$H$_{36}$Au$_2$N$_4$P$_2$: 51.77; H, 3.19; N, 4.93. Found: C, 51.63; H, 3.35; N, 4.87. IR (Nujol, cm^{-1}): *ν*(C≡C) 2101. ^{1}H NMR (400.9 MHz, CDCl$_3$, 25 °C): δ 8.73 (br s, 2 H, H6), 8.56 (br s, 2 H, H6′), 8.23 (d, $^{3}J_{HH}$ = 7.7 Hz, 2 H, H3′), 8.12 (d, $^{3}J_{HH}$ = 8.0 Hz, 2 H, H3), 7.80 (br d, $^{3}J_{HH}$ = 7.6 Hz, 2 H, H4), 7.67–7.36 (m, 22 H, Ph and H4′), 7.19 (br t, $^{3}J_{HH}$ = 4.9 Hz, 2 H, H5′), 3.62 (t, $^{2}J_{PH}$ = 10.7 Hz, 2 H, CH$_2$). ^{13}C{^{1}H} NMR (100.8 MHz, CDCl$_3$, 25 °C): δ 156.1, 152.9 (C2 and C2′), 152.5 (C6), 149.1 (C6′), 139.9 (C4), 136.7 (C4′), 133.6 (vt, *N* = 14.7 Hz, C2, Ph), 132.2 (C4, Ph), 129.5 (vt, *N* = 11.1 Hz, C3, Ph), 129.2 (br m, C1, Ph), 123.2 (C5′), 122.6 (C5), 121.2 (C3′), 120.1 (C3), 101.9 (br vt, *N* = 24 Hz, *C*≡CAu), 29.5 (t, $^{1}J_{PC}$ = 25.0 Hz, CH$_2$). The signal of C≡*C*Au was not observed. ^{31}P{^{1}H} NMR (162.3 MHz, CDCl$_3$, 25 °C): δ 32.1 (s).

Solution Data of 12 + 17 Mixture. ^{1}H NMR (400.9 MHz, CD$_3$COCD$_3$, −60 °C): δ 8.78–7.09 (several m, bpyl and Ph), 5.54 and 5.30 (both m, CH$_2$ of [Au$_3$(C≡Cbpyl)$_2$(dppm)$_2$]$^+$), 4.64 (t, $^{2}J_{PH}$ = 12.3 Hz, CH$_2$ of **12**). ^{13}C{^{1}H} NMR (150.9 MHz, CD$_3$COCD$_3$/CDCl$_3$ 4:1, 25 °C): δ 155.0, 154.7, 154.5, 152.4, 151.5, 151.0, 150.9, 150.8, 150.5, 148.3, 148.1, 148.0 (all s, C2, C2′, C6 and C6′ of **12** and **17**), 141.8–140.4 (s and two m, C≡*C*Au of **12** and **17**), 138.2, 138.0, 137.8 (C4 of **12** and **17**), 136.0, 135.64, 135.55 (C4′ of **12** and **17**), 132.7–128.2 (Ph), 124.0, 122.9, 122.4, 122.2, 120.7, 119.8, 119.6, 119.4, 118.9, 118.6 (all s, C5, C5′, C3, and C3′ of **12** and **17**), 102.2 (d, $^{3}J_{PC}$ = 26.6 Hz, [Au$_3$(C≡*C*bpyl)$_2$(dppm)$_2$]$^+$), 99.6 (vt, *N* = 27.2 Hz, AuC≡*C* of **12**), 98.2 (s, [Au(C≡*C*bpyl)$_2$]$^-$), 26.0 (t, $^{1}J_{PC}$ = 28.0 Hz, CH$_2$ of **12**), 24.7 (m, CH$_2$ of **17**). ^{31}P{^{1}H} NMR (162.3 MHz, CDCl$_3$, 25 °C): δ 32.1 (s); (CD$_3$COCD$_3$, −60 °C): δ 37.6–37.1 (*A* part of an AA′XX′ system, P−Au−P of **17**), 32.8 (s, P−Au−C≡C of **12**), 32.3–31.9 (X part of an AA′XX′ system, P−Au−C≡C of **17**). MS (+ESI, MeCOMe): *m*/*z* 1716 ([M – H]$^+$, M = [Au$_3$(C≡Cbpyl)$_2$-(dppm)$_2$]), 1537 ([M − HC≡Cbpyl]$^+$), 1357 ([M – 2 HC≡Cbpyl]$^+$), 1333 ([M – dppm]$^+$), 1189, 957 ([Au$_2$(C≡Cbpyl)-(dppm)]$^+$); (−ESI, MeCOMe): *m*/*z* 555 ([Au(C≡Cbpyl)$_2$]$^-$).

[{Au(C≡Cbpyl)}$_2$(*μ*-dppe)] (13). This was prepared in the same way as **12** from **3** (132 mg, 0.35 mmol) and dppe (70 mg, 0.18 mmol). Colorless solid. Yield: 180 mg, 89%. Mp: 217–220 °C. Anal. Calcd for C$_{50}$H$_{38}$Au$_2$N$_4$P$_2$: C, 52.18; H, 3.33; N, 4.87. Found: C, 51.97; H, 3.28; N, 4.55. IR (Nujol, cm^{-1}): *ν*(C≡C) 2099. ^{1}H NMR (400.9 MHz, CDCl$_3$): δ 8.81 (d, $^{4}J_{HH}$ = 1.2 Hz, 2 H, H6), 8.66 (d, $^{3}J_{HH}$ = 4.0 Hz, 2 H, H6′), 8.37 (d, $^{3}J_{HH}$ = 8.0 Hz, 2 H, H3′), 8.32 (d, $^{3}J_{HH}$ = 8.3 Hz, 2 H, H3), 7.90 (dd, $^{3}J_{HH}$ = 8.4 Hz, $^{4}J_{HH}$ = 2.0 Hz, 2 H, H4), 7.80 (td, $^{3}J_{HH}$ = 8.0 Hz, $^{4}J_{HH}$ = 1.6 Hz, 2 H, H4′), 7.68–7.48 (m, 20 H, Ph), 7.28 (ddd, $^{3}J_{HH}$ = 4.8 and 7.5 Hz, $^{4}J_{HH}$ = 1.0 Hz, 2 H, H5′), 2.68 (br s, 4 H, CH$_2$). ^{13}C{^{1}H} NMR (100.8 MHz, CDCl$_3$): δ 155.9, 153.6 (C2 and C2′), 152.6 (C6), 149.3 (C6′), 140.0 (C4), 140.5 (br s, C≡*C*Au), 136.9 (C4′), 133.5 (vt, *N* = 13.6 Hz, C2, Ph), 132.4 (s, C4, Ph), 129.7 (vt, *N* = 11.1 Hz, C3, Ph), 128.6 (m, C1, Ph), 123.6 (C5′), 121.9 (C5), 121.2 (C3′), 120.3 (C3), 101.1 (s, *C*≡CAu), 24.1 (vt, *N* = 38.4 Hz, CH$_2$). ^{31}P{^{1}H} NMR (162.3 MHz, CDCl$_3$): δ 39.8 (s). MS (+ESI, CH$_2$Cl$_2$): *m*/*z* 1745 ([Au$_3$(C≡Cbpyl)$_2$(dppe)$_2$]$^+$), 1601 ([Au$_3$(C≡Cbpyl)Cl(dppe)$_2$]$^+$), 1369 ([Au$_2$(C≡Cbpyl)(dppe)$_2$]$^+$), 1347 ([Au$_3$-

(C$\equiv$Cbpyl)$_2$(dppe)]$^+$), 1225 ([Au$_2$(dppe)$_2$Cl]$^+$), 993 ([Au(dppe)$_2$]$^+$), 595 ([Au(dppe)]$^+$); ($-$ESI, CH$_2$Cl$_2$): *m/z* 555 ([Au(C$\equiv$Cbpyl)$_2$]$^-$).

[{Au(C$\equiv$Cbpyl)}$_2$(μ-dppb)] (14). This was prepared in the same way as **12** from **3** (150 mg, 0.40 mmol) and dppb (85 mg, 0.20 mmol). Colorless solid. Yield: 222 mg, 94%. Recrystallization from CH$_2$Cl$_2$/Et$_2$O and drying under vacuum (<1 mbar, 120 °C) gave analytically pure **14**. Mp: 156–159 °C. Anal. Calcd for C$_{52}$H$_{42}$Au$_2$N$_4$P$_2$: C, 52.98; H, 3.59; N, 4.75. Found: C, 52.74; H, 3.59; N, 4.63. IR (Nujol, cm^{-1}): ν(C$\equiv$C) 2113. ^{1}H NMR (400.9 MHz, CDCl$_3$): δ 8.79 (dd, $^4J_{HH}$ = 2.1 Hz, $^5J_{HH}$ = 0.9 Hz, 2 H, H6), 8.66 (ddd, $^3J_{HH}$ = 4.8 Hz, $^4J_{HH}$ = 1.7 Hz, $^5J_{HH}$ = 0.9 Hz, 2 H, H6′), 8.37 (dt, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = $^5J_{HH}$ = 0.9 Hz, 2 H, H3′), 8.30 (dd, $^3J_{HH}$ = 7.3 Hz, $^5J_{HH}$ = 0.7 Hz, 2 H, H3), 7.88 (dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 2.0 Hz, Hz, 2 H, H4), 7.79 (dt, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.7 Hz, 2 H, H4′), 7.68–7.44 (m, 20 H, Ph), 7.27 (ddd, $^3J_{HH}$ = 4.8 and 7.4 Hz, $^4J_{HH}$ = 1.0 Hz, 2 H, H5′), 2.42 (br m, 4 H, CH$_2$), 1.80 (br m, 4 H, CH$_2$). ^{13}C{^{1}H} NMR (75.5 MHz, CDCl$_3$): δ 155.8, 153.4 (C2 and C2′), 152.5 (C6), 149.2 (C6′), 140.0 (C4), 136.8 (C4′), 133.3 (d, $^2J_{CP}$= 13.2 Hz, C2, Ph), 131.8 (s, C4, Ph), 129.8 (d, $^1J_{CP}$= 55.5 Hz, C1, Ph), 129.4 (d, $^3J_{CP}$= 11.3 Hz, C3, Ph), 123.5 (C5′), 121.9 (C5), 121.1 (C3′), 120.2 (C3), 100.9 (br s, *C*$\equiv$CAu), 27.8 (d, $^1J_{CP}$ = 13.2 Hz, CH$_2$), 27.1 (d, $^2J_{CP}$ = 18.0 Hz, CH$_2$). The signal of C$\equiv$*C*Au was not observed. ^{31}P{^{1}H} NMR (121.5 MHz, CDCl$_3$): δ 37.5 (s). MS (+ESI, CH$_2$Cl$_2$/MeCOMe): *m/z* 1801 (M$^+$ = [Au$_3$(C$\equiv$Cbpyl)$_2$(dppb)$_2$]$^+$), 1375 ([M $-$ dppb $-$ H]$^+$), 1281 ([Au$_2$(dppb)$_2$Cl]$^+$), 999 ([Au$_2$(C$\equiv$Cbpyl)(dppb)]$^+$), 623 ([Au(dppb)]$^+$); ($-$ESI, CH$_2$Cl$_2$/MeCOMe): *m/z* 555 ([Au(C$\equiv$Cbpyl)$_2$]$^-$).

[{Au(C$\equiv$Cbpyl)}$_2$(μ-dppd)] (15). This was prepared in the same way as **12** from **3** (200 mg, 0.53 mmol) and dppd (136 mg, 0.26 mmol). The mixture was stirred at room temperature for 45 min and concentrated up to about 1 mL. A pale yellow solid precipitated by addition of *n*-pentane (20 mL). It was filtered off, washed with *n*-pentane (3 × 5 mL), and dried under vacuum. Yield: 210 mg, 62%. Mp: 91–95 °C. Anal. Calcd for C$_{58}$H$_{54}$Au$_2$N$_4$P$_2$: C, 55.16; H, 4.31; N, 4.44. Found: C, 54.83; H, 4.39; N, 4.44. IR (KBr, cm^{-1}): ν(C$\equiv$C) 2104. ^{1}H NMR (400.9 MHz, CDCl$_3$): δ 8.80 (s, 2 H, H6), 8.66 (d, $^3J_{HH}$ = 4.3 Hz, 2 H, H6′), 8.36 (d, $^3J_{HH}$ = 7.9 Hz, 2 H, H3′), 8.30 (d, $^3J_{HH}$ = 8.3 Hz, 2 H, H3), 7.89 (dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 2.4 Hz, 2 H, H4), 7.79 (td, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.4 Hz, 2 H, H4′), 7.70–7.65 (m, 8 H, Ph), 7.47–7.44 (m, 12 H, Ph), 7.27 (dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 2.4 Hz, 2 H, H5′), 2.40 (m, 4 H, CH$_2$P), 1.65 (m, 4 H, CH$_2$), 1.43 (m, 4 H, CH$_2$), 1.21 (m, 8 H, CH$_2$). ^{13}C{^{1}H} NMR (100.8 MHz, CDCl$_3$): δ 155.8, 153.2 (C2 and C2′), 152.4 (C6), 149.1 (C6′), 139.9 (C4), 136.8 (C4′), 133.2 (d, $^2J_{PC}$ = 13.0 Hz, *C*2, Ph), 131.5 (s, C4, Ph), 130.3 (d, $^1J_{PC}$ = 53.2 Hz, C1, Ph), 129.1 (d, $^3J_{PC}$= 11 Hz, C3, Ph), 123.4 (C5′), 121.98 (C5), 121.0 (C3′), 120.1 (C3), 100.7 (s, *C*$\equiv$CAu), 30.9 (d, $^3J_{PC}$ = 16.0 Hz, CH$_2$), 29.1, 28.9 (both s, CH$_2$), 27.9 (d, $^1J_{PC}$ = 34 Hz, CH$_2$P), 25.4 (d, $^2J_{PC}$ = 3.4 Hz, CH$_2$). The signal of C$\equiv$*C*Au was not observed. ^{31}P{^{1}H} NMR (162.3 MHz, CDCl$_3$): δ 36.8 (s). MS (+ESI, MeCOMe): *m/z* 1083 ([Au$_2$(C$\equiv$Cbpyl)(dppd)]$^+$), 707 ([Au(dppd)]$^+$); ($-$ESI, MeCOMe): *m/z* 555 ([Au(C$\equiv$Cbpyl)$_2$]$^-$).

[{Au(C$\equiv$Cphtpyl)}$_2$(μ-dppd)] (16). This was prepared in the same way as **12** from **4** (130 mg, 0.25 mmol) and dppd (64 mg, 0.13 mmol). Yield: 117 mg, 59%. Mp: 139–145 °C. Anal. Calcd for C$_{80}$H$_{68}$Au$_2$N$_6$P$_2$: C, 61.22; H, 4.37; N, 5.35. Found: C, 60.93; H, 4.56; N, 5.35. IR (nujol, cm^{-1}): ν(C$\equiv$C) 2102. ^{1}H NMR (300.1 MHz, CDCl$_3$): δ 8.73–8.72 (overlapped s and m, 8 H, H3 and H6′), 8.63 (d, $^3J_{HH}$ = 8.4 Hz, 4 H, H3′), 7.86 (td, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.5 Hz, 4 H, H4′), 7.83 (vd, *J* = 8.4 Hz, 4 H, C$_6$H$_4$), 7.72–7.43 (several m, 24 H, Ph and C$_6$H$_4$), 7.34 (ddd, $^3J_{HH}$ = 7.6 and 4.0 Hz, $^4J_{HH}$ = 1.0 Hz, 4 H, H5′), 2.41 (m, 4 H, CH$_2$P), 1.69–1.22 (m, 16 H, CH$_2$). ^{13}C{^{1}H} NMR (75.5 MHz, CDCl$_3$): δ 156.2, 155.9 (C2 and C2′), 149.7 (C4), 149.1 (C6′), 136.8 (C4′), 136.5 (C4 of C$_6$H$_4$), 133.3 (d, $^2J_{CP}$ = 13.0 Hz, C2, Ph), 132.9 (CH, C$_6$H$_4$), 131.5 (C4, Ph), 130.6 (d, $^1J_{CP}$ = 53.5 Hz, C1, Ph), 129.2 (d, $^3J_{CP}$ = 10.9 Hz, C3, Ph), 126.9 (CH, C$_6$H$_4$), 125.8 (*C*-C$\equiv$CAu), 123.8 (C5′), 121.3 (C3′), 118.6 (C3), 103.8 (br s, *C*$\equiv$CAu), 30.9 (d, $^3J_{CP}$ = 15.9 Hz, CH$_2$), 29.2, 28.9 (both s, CH$_2$), 28.0 (d, $^1J_{CP}$ = 33.8 Hz, CH$_2$P), 25.5 (s, CH$_2$). The signal of C$\equiv$*C*Au was not observed. ^{31}P{^{1}H} NMR (81.0 MHz, CDCl$_3$): δ 37.8 (s).

PPN[Au(C$\equiv$Cbpyl)$_2$] (18). A solution of **1** (61 mg, 0.34 mmol) in CH$_2$Cl$_2$ (10 mL) was treated with PPN[Au(acac)$_2$] (156 mg, 0.17 mmol). The solution was stirred at room temperature for 3 h, filtered through Celite, and concentrated under vacuum to about 4 mL. By addition of Et$_2$O (15 mL) a pale beige solid precipitated, which was filtered off, washed with Et$_2$O (3 × 5 mL), and dried under vacuum. Yield: 165 mg, 90%. Recrystallization from CH$_2$Cl$_2$/Et$_2$O and drying under vacuum (<1 mbar, 55 °C) gave analytically pure **18**. Mp: 73–76 °C. Anal. Calcd for C$_{60}$H$_{44}$AuN$_5$P$_2$: C, 65.87; H, 4.05; N, 6.40. Found: C, 66.20; H, 3.98; N, 6.44. IR (Nujol, cm^{-1}): ν(C$\equiv$C) 2114. ^{1}H NMR (400.9 MHz, CDCl$_3$): δ 8.66 (br s, 2 H, H6), 8.63 (d, $^3J_{HH}$ = 3.6 Hz, 2 H, H6′), 8.31 (d, $^3J_{HH}$ = 7.9 Hz, 2 H, H3′), 8.16 (d, $^3J_{HH}$ = 7.9 Hz, 2 H, H3), 7.75 (m, 4 H, H4 and H4′), 7.68–7.43 (m, 30 H, Ph), 7.24 (dd, $^3J_{HH}$ = 6.3 and 5.0 Hz, 2 H, H5′). ^{13}C{^{1}H} NMR (50.3 MHz, CDCl$_3$): δ 156.4 (C2 or C2′), 152.6 (C6), 151.6 (C2′ or C2), 149.1 (C6′), 140.6 (C$\equiv$*C*Au), 139.8 (C4), 136.8 (C4′), 134.0 (C4, PPN), 132.1, 129.7 (both m, C2 and C3, PPN), 127.0 (d, $^1J_{PC}$ = 118.1 Hz, C1, PPN), 124.7 (C5), 123.1 (C5′), 120.9 (C3′), 119.9 (C3), 99.8 (*C*$\equiv$CAu). ^{31}P{^{1}H} NMR (162.3 MHz, CDCl$_3$): δ 21.2 (s).

PPN[Au(C$\equiv$Cphtpyl)$_2$] (19). This was prepared in the same way as **18** from **2** (18 mg, 0.054 mmol) and PPN[Au(acac)$_2$] (25 mg, 0.027 mmol). **19** was obtained as a colorless solid by precipitation with Et$_2$O. Yield: 31 mg, 82%. Mp: 241–243 °C. Anal. Calcd for C$_{82}$H$_{58}$AuN$_7$P$_2$: C, 70.33; H, 4.17; N, 7.00. Found: C, 70.32; H, 4.15; N, 7.19. IR (nujol, cm^{-1}): ν(C$\equiv$C) 2100. ^{1}H NMR (300.1 MHz, CDCl$_3$): δ 8.69–8.67 (overlapped m and s, 8 H, H6′ and H3), 8.63 (d, $^3J_{HH}$ = 7.9 Hz, 4 H, H3′), 7.84 (td, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.8 Hz, 4 H, H4′), 7.68–7.39 (m, 38 H, PPN and C$_6$H$_4$), 7.32 (ddd, $^3J_{HH}$ = 7.6 and 4.7 Hz, $^4J_{HH}$ = 0.9 Hz, 4 H, H5′). ^{13}C{^{1}H} NMR (75.5 MHz, CDCl$_3$): δ 156.3, 155.7 (C2 and C2′), 150.0 (C4), 149.0 (C6′), 137.4 (C$\equiv$*C*Au), 136.8 (C4′), 134.3 (C4, C$_6$H$_4$), 133.9 (m, C4, PPN), 132.7 (CH, C$_6$H$_4$), 132.0, 129.6 (both m, C2 and C3, PPN), 128.8 (*C*-C$\equiv$CAu), 126.9 (vdd, $^1J_{CP}$ + $^1J_{CP}$ = 109.4 Hz, C1, PPN), 126.3 (CH, C$_6$H$_4$), 123.7 (C5′), 121.3 (C3′), 118.3 (C3), 102.6 (s, *C*$\equiv$CAu). ^{31}P{^{1}H} NMR (81.0 MHz, CDCl$_3$): δ 21.2 (s).

PPN[Au(C$\equiv$Cphccbpyl)$_2$] (20). This was prepared in the same way as **18** from **5** (41 mg, 0.146 mmol) and PPN[Au(acac)$_2$] (68 mg, 0.073 mmol). **20** was precipitated with Et$_2$O as a beige solid. Yield: 91 mg, 96%. Mp: 190–196 °C (dec). Anal. Calcd for C$_{76}$H$_{52}$AuN$_5$P$_2$: C, 70.53; H, 4.05; N, 5.41. Found: C, 70.24; H, 3.98; N, 5.52. IR (KBr, cm^{-1}): ν(C$_6$H$_4$C$\equiv$C) 2210, ν(C$\equiv$CAu) 2096. ^{1}H NMR (600.1 MHz, CDCl$_3$): δ 8.76 (d, $^3J_{HH}$ = 1.3 Hz, 2 H, H6), 8.68 (d, $^3J_{HH}$ = 3.9 Hz, 2 H, H6′), 8.39 (d, $^3J_{HH}$ = 7.9 Hz, 2 H, H3′), 8.37 (d, $^3J_{HH}$ = 8.2 Hz, 2 H, H3), 7.88 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 2.1 Hz, 2 H, H4), 7.82 (td, $^3J_{HH}$ = 7.6 Hz and $^4J_{HH}$ = 1.7 Hz, 2 H, H4′), 7.66 (m, 6 H, PPN), 7.50–7.43 (m, 24 H, PPN), 7.36 (m, 4 H, H2, C$_6$H$_4$), 7.32–7.29 (m, 6 H, H3 of C$_6$H$_4$ and H5′). ^{13}C{^{1}H} NMR (150.9 MHz, CDCl$_3$): δ 155.6 (C2′), 154.6 (C2), 151.5 (C6), 149.3 (C6′), 139.2 (C4), 138.8 (C$\equiv$*C*Au), 137.0 (C4′), 134.0 (s, C4, PPN), 132.3 (C2, C$_6$H$_4$), 132.1 (m, C2 or C3, PPN), 131.0 (C3, C$_6$H$_4$), 129.7 (m, C3 or C2, PPN), 128.7 (C4, C$_6$H$_4$), 127.0 (d, $^1J_{CP}$ = 109.1 Hz, C1, PPN), 123.9 (C5′), 121.4 (C3′), 120.7 (C5), 120.4 (C3), 118.5 (C1, C$_6$H$_4$), 102.8 (*C*$\equiv$CAu), 94.6 (bpylC$\equiv$*C*), 86.7 (bpyl*C*$\equiv$C). ^{31}P{^{1}H} NMR (162.3 MHz, CDCl$_3$): δ 21.2 (s).

Crystallography. Compounds **6**, **10**, and **18** were measured on a Bruker Smart APEX diffractometer; **13**, **14**, and **17** on a Bruker Smart 1000 diffractometer. Data were collected using monochromated Mo Kα radiation by ω and φ scans. Crystals of **13** disintegrated at –140 °C and were therefore measured at the slightly higher temperature of –100 °C. The structures of **10**, **17**, and **18** were solved by direct methods; others by the heavy atom method. All were refined anisotropically on F^2. Restraints to local aromatic ring symmetry or light atom displacement factor components were applied in some cases. The hydrogens were refined using a riding model. Special features/exceptions: Compound **14** displayed an ill-resolved region of residual electron density associated with an inversion center. Because no appropriate refinement model for this (assumed) half-molecule of diethyl ether could be found, the effect of the electron density was subtracted mathematically from the intensity data using the program SQUEEZE (A. L. Spek, Univ. of Utrecht, Netherlands). For compound **17**, C and N atoms were refined isotropically to avoid the need for blocked refinement.

In general, there may be a problem in distinguishing the C and N atoms in the pyridinic ring systems in the presence of heavy atoms, especially when the N atoms are not involved in further interactions such as metal coordination or H bonds. This problem is exacerbated in terminal rings of bipyridyl moieties, where the displacement factors may be appreciably larger. The following diagnostic factors may be useful: (i) *U* values. With the correct assignment, the *U* values should be approximately equal; if C is assigned as N and *vice versa*, the *U* values of the “C” atom will be too low and that of the “N” atom too high. (ii) Direct localization of H atoms in difference syntheses. This may be difficult in the presence of heavy atoms, especially if the crystal quality is not ideal. (iii) Analysis of C−H contacts. If an H atom is geometrically positioned (falsely) at a C atom that is really N, then it may make impossibly short contacts to other atoms. (iv) Bond lengths. C−N should be shorter than C−C. (v) Usually the N atoms are *trans* across the ring-connecting C−C bond. Finally, it should be remembered that the C/N sites may indeed be disordered. On the basis of the above-mentioned criteria, the following assignments were made Compounds **6**, **10**, **18**: All pyridinic ring H were found directly except for H12 of compound **6**. Compound **13**: N73 and N86 are probably reliable, N53 and N66 are highly tentative. Compounds **14** and **17**: N atoms assigned with reasonable confidence. However, the assignment of these atoms cannot be completely unambiguous using X-ray methods alone, and the results should be interpreted with caution.

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Supporting Information Available: ORTEP diagram of compound **18**, crystallographic data in CIF format for **6**, **10**, **13**, **14**, **17**, and **18**, hydrogen bond distances and angles, simulated $^{31}P\{^1H\}$ NMR spectrum of **17**. These materials are available free of charge via the Internet at http://pubs. acs.org.

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