ORGANOMETALLICS

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pubs.acs.org/Organometallics

Novel Mixed Coordination of N and C Donors to Gold−Gold Centers

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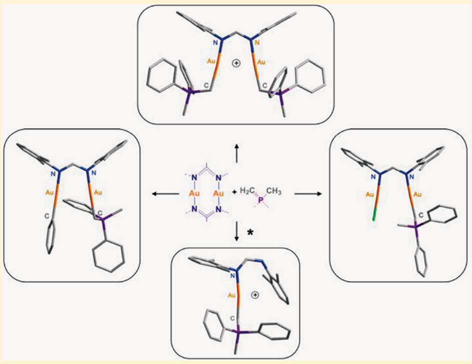
Supporting Information

ABSTRACT: Mixed-ligand gold(I) compounds featuring N and C connectivity from two dissimilar ligands, a formamidinate and a phosphorus ylide, are obtained by the reaction of a dinuclear gold(I) formamidinate with a phosphorus ylide in toluene solution under Schlenk conditions. When the reaction conditions such as polarity, basicity, and gold to ylide ratio are varied, a series of structures are produced, where the formamidinate (f = *N,N'*-bis(2,6-dimethylphenyl)methanimidamide) invariably bridges gold(I) centers. The aurophilic distances of Au(I)···Au(I) range around 3.00 Å, whereas the ylide (dimethyldiphenylphosphonium, $[H_2y]^+$) is monocoordinated as [Hy]. This produces open dinuclear species, with two terminal Hy's as the cation $[Au_2f(Hy)_2]^+$ (**1**), with the nitrate anion or terminal Hy and chloride anion in $[Cl\text{-}Au_2f(Hy)]$ (**2**), or Hy and phenyl in $[Ph\text{-}Au_2f(Hy)]$ (**3**). The activation of the ylide ligand by base liberates the phenyl group which produces **3**. A related cationic mononuclear moiety [Au(Hf)(Hy)] (**4**), with neutral amidinate and ylide, is produced from the neutral amidine upon reaction with [Au(THT)Cl] in a THF solution of ylide. These new compounds have been characterized by X-ray crystal structures, ^1H NMR, IR, and elemental analysis.



INTRODUCTION

Heterobridged dinuclear gold(I) complexes provide additional information about the role of the bridging ligand in comparison with related homobridged complexes (Chart 1). Such complexes may integrate disparate ligand properties, which has produced new chemistry with mixed donors such as a C,C-donor phosphorus ylide with S,S (dithiocarbamate, phosphoniodithioformate, xanthate)[1] and P,P (diphosphinomethanide)[2] ligands, a sulfur ylide with P,P (dppm),[3] and others, including P,P donor diphosphines with S,S (dithiophosphonate, dithiolates, and dangling thiolates)[4] and an S,S donor dithiolate with a P,C donor (C_6H_3-2-PPh_2-*n*-Me).[5]

Prior to this work, no digold(I) systems with combined C,C and N,N donors have been produced, with the exception of $[Au_3(C_6F_5)_3(\eta^3\text{-Fcterpy})]$,[6] which contains an *N,N,N*-terpyridine and three C-C_6F_5 ligands, and mononuclear complexes with N−Au^I−C linkages.[7,8] However, there are a large number of gold(III) complexes with Au−N and Au−C connectivities. One of the earliest reported is the heterocycle $[(CH_3)_2AuN(CH_3)_2]_2$, with two symmetrical amido bridges and methyl ligands.[9]

One approach to the study of dinuclear gold(I) complexes with N−Au−C connectivities has been to use pincerlike ligands with simultaneous C,N donation. Such ligands result from attaching pendant N moieties (pyridine, amine) to an imidazolium-based N-heterocyclic carbene (NHC),[10,11] to a phenyl ring,[12] or to ferrocene.[13] Conversely, a C-donor moiety appended to pyridine[14] produces such complexes. The most apparent N,C donor, however, is an azaallyl (RNC(R)CR) ligand.[15] Usually these ligands arrange in a head-to-tail fashion connecting two gold(I) atoms at aurophilic distances (less than 3 Å). Trinuclear gold(I) complexes with Au−N and Au−C bonds result from using ligands (pyridine, imidazoles, isocyanides, imidoyls) with adjacent N,C donors that require gold−gold separations to be larger than 3 Å. Tetranucleation with gold[16] can be obtained by a ligand designed with two C donors (NHC) tagged to a N,N donor (imidazole).

The nearly identical Pauling electronegativities of gold (2.54) and carbon (2.55) led to the early dinuclear gold chemistry with gold−carbon complexes of ylides, pioneered by Schmidbaur.[17] In contrast with nitrogen ligands, dinuclear and polynuclear gold(I,II) chemistry is a more recent research topic, dominated by amidinate ligands.[18] A mixed-ligand system involving both amidinate N-donor and ylide C-donor ligands offered an evaluation of the combined influence of a strong σ-donor (ylidic carbon, y) with a strong π-withdrawing ligand (formamidinate, f). Of special interest is the possible luminescent behavior known for the homoligand dinuclear complexes Au_2y_2 and Au_2f_2. These materials luminesce only faintly at room temperature, in contrast with the strongly luminescent Au_4f_4. While our focus was on the synthesis of the first mixed-ligand $[Au_2fy]$ complexes, the early stages of research produced the series of compounds reported here.

Prior to this report, only one cluster was known to connect dissimilar N donors (amidinate) and C donors (phosphorus ylide) in a neutral cubic assembly.[19] It turned out to be a special cluster

Received: June 27, 2011
Published: September 26, 2011

Chart 1. Dinuclear Gold(I) Complexes

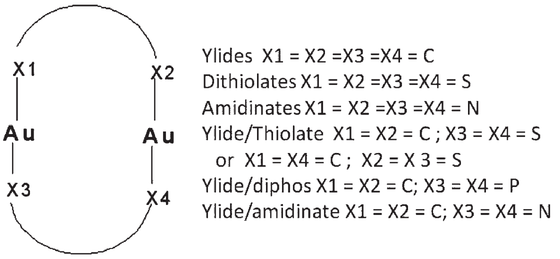
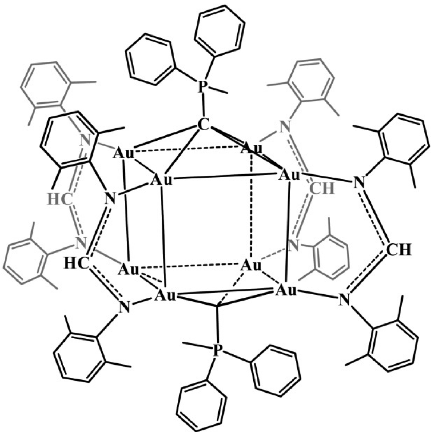


Chart 2. Cubic Gold(I) Cluster with Mixed Coordination of Bridging Formamidinates and Hypercoordinating Carbons from a Phosphorus Ylide



with eight gold(I) atoms at the corners of a distorted cube, bridged along the sides by four amidinates and capped above and below the cube by two hypercoordinating carbon atoms from the phosphorus ylide (Chart 2). This cluster showed green luminescence under UV light. The group of gold(I) complexes reported here is related to that cubic assembly in that they exhibit the same amidinate and ylide ligands in their structures.

■ RESULTS AND DISCUSSION

Synthetic Procedures. Due to the special affinity between gold and carbon, it was expected that Au−C bonds would form preferentially to Au−N bonds. Thermodynamically, the interaction of the carbon donor ylide (y) with the gold formamidinate $[Au_2f_2]$ would seem to favor the formation of mixed species $[Au_xf_yy_z]$ prior to forming $[Au_2y_2]$. The product would depend on the ratio of the ylide to Au_2f_2. Initially aiming to produce a dinuclear $[Au_2fy]$, the synthetic protocol was to react the dinuclear amidinate $[Au_2f_2]$ with the diphenylmethylmethylene-substituted phosphorus ylide, [Hy], in toluene at −20 °C, under nitrogen (Scheme 1).

The $[Au_2f_2]$ was synthesized by stirring [Au(THT)Cl] or $[Au(THT)NO_3]$ with potassium formamidinate in ethanol; a white solid formed, and the solvent was removed. The product was kept at 0 °C. The ylide $[CH_3CH_2(Ph)_2P]$ was produced by deprotonation of $[(CH_3)_2(Ph)_2P]NO_3$ or $[(CH_3)_2(Ph)_2P]PF_6$ with KH in THF at −20 °C; the THF was removed, and toluene was added to form a yellow solution, which was kept at −20 °C. Further reactions were performed at −20 °C, not only because of the instability of the ylide but because there is a tendency of gold(I) formamidinate solutions in toluene to oxidize in the presence of nitrate anions, yielding $[Au_2f_2(NO_3)_2]$.[20]

For compound **1**, $[Au_2f(Hy)_2]NO_3$, the gold to ylide ratio is 1:1 in toluene; the nitrate comes from the $[Au(THT)NO_3]$. With this ratio the mixed ligand complex being sought, $[Au_2fy]$, would be produced by proton exchange between two ylide molecules, giving the negatively charged ylide anion ligand. However, the high yield achieved for **1** indicates that gold−carbon bond formation is the favored process. Addition of 2 equiv of ylide to further promote ylide deprotonation leads to formation of the bridging ylide complex $[Au_2y_2]$ and **1**. A procedure which leads to the desired $[Au_2fy]$ required a process starting with the Au(II) amidinate.[21]

Compound **2**, $[Cl\text{-}Au_2f(Hy)]$, is obtained in a straightforward manner in a CH_3CN−toluene solution when [Au(THT)Cl] is the starting material and the ratio gold to ylide is 2:1. The formation of the strong Au−Cl bond appears to dominate this chemistry.

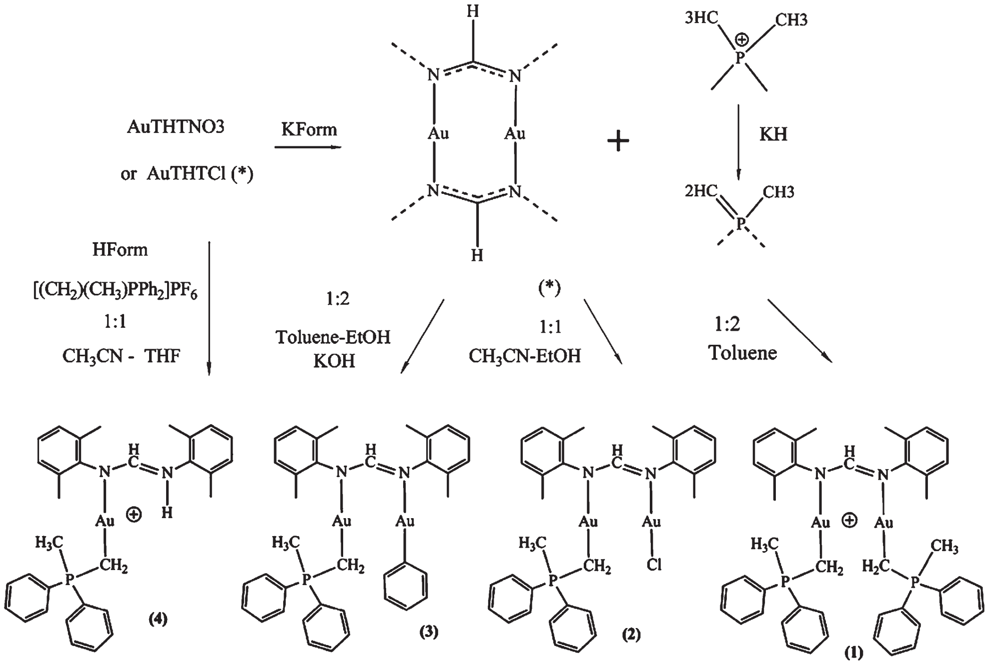
The mononuclear complex **4**, with the PF_6^- anion, is obtained by first reacting [Au(THT)Cl] and formamidine in a 1:2 ratio in CH_3CN, followed by addition of the ylide prepared from $[(CH_3)_2(Ph)_2P]PF_6$. The large anion is used to inhibit the tendency of gold(I) complexes to associate.

Compound **3**, $[Ph\text{-}Au_2f(Hy)]$, is obtained with a ratio of gold to ylide of 1:1, using KOH in a mixture of ethanol and toluene solvents. The KOH purportedly would remove the ylide methyl proton, but base reaction on the ylide releases a phenyl anion which ends up coordinating to gold and in smaller amounts as benzene in the solution. The modified ylide is found as crystalline $[Ph(CH_3)_2P{=}O]$.

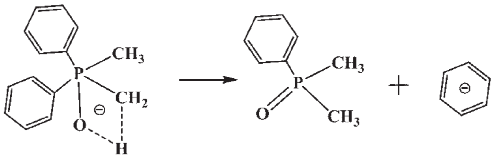
Phosphine oxides R_3PO are widely used as complexing agents of oxophilic metals such as lanthanides,[22,23] actinides,[24] and transition metals;[25−28] the methyl phosphine oxide is known[29] to be lithiated by nBuLi, tBuLi, and iPrLi at −78 °C as the first step in the Horner−Wittig reaction.[30] Usual syntheses involve oxidation of the phosphine PR_3 with hydrogen peroxide.[31] The basic path that converts ylides $[Ph_3P^+(R)]X^-$ into oxophosphanes has been studied in terms of solvent effects.[32] A low-polarity solvent is needed to speed up the hydrolysis, but a high-polarity solvent actually slows the reaction. This is coincident with the experimental observations here with a toluene to ethanol ratio of 10−20% v/v. The solvent polarity may be related to the polarity of the products. In the process the nucleophile OH^- attacks the onium center and the proton is transferred to a CH_2-Ph group, producing free Me-Ph and the P=O bond. In our synthesis a phenyl anion, Ph^-, is released from the neutral ylide $[Ph_2P(CH_2)CH_3]$ rather than the less stable Me^- anion (Scheme 2).

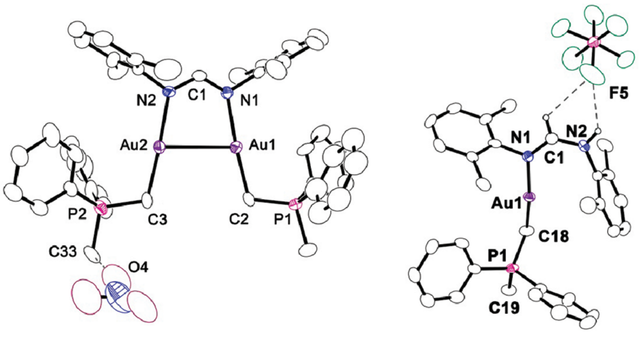
Structural Characteristics. The thermal ellipsoid structures of **1**−**4** are shown in Figures 1 and 2. The formamidine is a methanimidamide (NCHN) moiety N,N-substituted with 2,5-dimethylphenyl rings with two N donors; the ylide is an onium phosphine with two phenyls and two methyls, which upon losing a methyl proton monocoordinates through CH_2. Compounds **1**−**3** are open dinuclear structures (Scheme 1) exhibiting a formamidinate N−CH−N bridge (f) opposite to the two dangling neutral ylide ligands (Hy) coordinating through CH_2 in **1**. In **2**, instead of an ylide, there is a chloride, and in **3** there is a phenyl group. The N−Au−C (C-phenyl or C-ylide) and N−Au−Cl angles are close to linear (Table 1). In these compounds a

Scheme 1. Synthetic Conditions Originating Mixed-Ligand Compounds of Gold(I)



Scheme 2



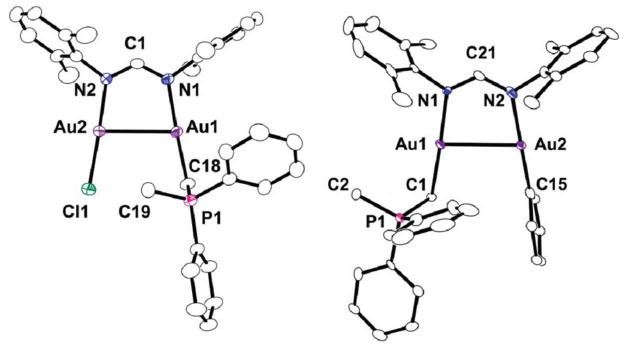


1, [Au$_2$f(Hy)$_2$]NO$_3$ **4, [Au(Hf)(Hy)]PF$_6$**

Figure 1. Structures of the mixed formamidinate−ylide ligand compounds **1** and **4** with displacement ellipsoids drawn at the 30% probability level.

formamidinate bridge connects Au(I) atoms, at distances greater than in [Au$_2$f$_2$] (2.711(3) Å) but still in the aurophilic range of <3.00 Å. The orientations of the formamidinate phenyl groups are the same as that found in the dinuclear gold(I) formamidinate: e.g., face to face.

In the cationic structure **1**, the methyl groups on the ylide are oriented away from the amidinate bridge. Close to them is a layer of nitrate anions parallel to the *bc* plane and to the Au−Au bond, with short $CH_3\cdots ONO_2^-$ contacts of 2.299(5) and 2.579(7) Å to the two nitrate anions on the same side of the molecule (Figure 3). On the opposite side another nitrate in the unit cell establishes contacts to an ylide CH$_2$ and a phenyl proton at 2.711(3) and 2.504(2) Å. This causes phenyls on both ylide ligands to point toward the formamidinate phenyls, though not establishing any short contact to them. The Au···Au distance stretches to 2.997(2) Å compared to 2.96[12] Å in **2** and **3** and cannot possibly be longer due to the angular constraints on the trigonal N donors. In **2** and **3** one ylide phenyl is pointing opposite the formamidinate bridge; in **3** this is because there is a short C−Ph contact between this ylide phenyl and the lone phenyl ligand on the vicinal molecule of 2.822(3) and 2.74(4) Å; in **2** it is the ylide methyl that comes closer to the coordinating chlorine at 2.96(4) Å.



2, [Au$_2$f(Hy)Cl] **3, [Au$_2$f(Hy)Ph]**

Figure 2. Structures of the mixed formamidinate−ylide ligand compounds **2** and **3** with displacement ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Mixed-Ligand Compounds of Gold(I)

compd	Au−Au	Au−N	Au−C	C−Au−N	Au−X
$[Au_2F(HY)_2]NO_3$(**1**)	2.997(2)	2.100[2]	2.059[2]	175.9[2]	
$[Au_2F(HY)Cl]$ (**2**)	2.9644(12)	2.038[2]	2.044(7)	176.9(3)	2.269(2) (X = Cl)
$[Au_2F(HY)Ph]$ (**3**)	2.9599(5)	2.062[2]	2.068 (10)	178.6(4)	1.973(12) (X = Ph)
$[Au(HF)(HY)]PF_6$ (**4**)		2.069(8)	2.020(11)	172.3(4)	

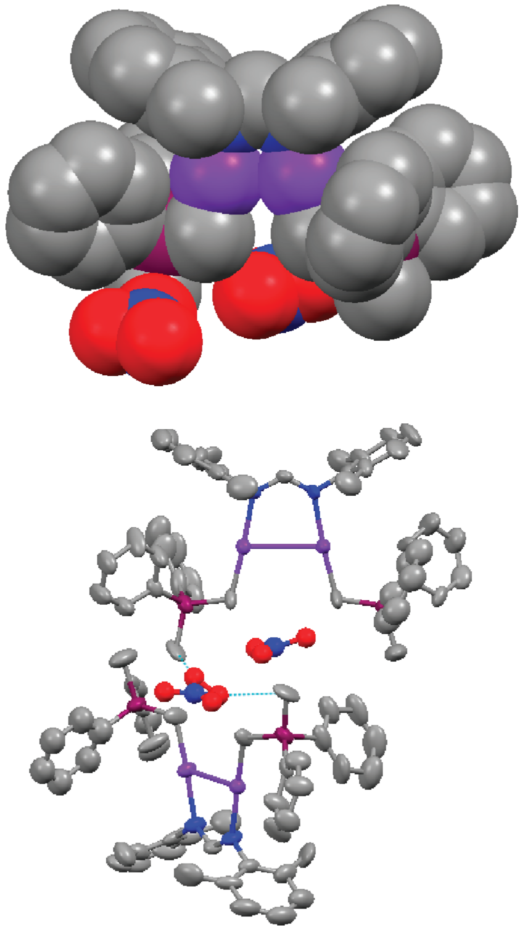
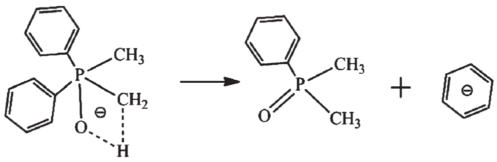


Figure 3. Space-filling picture of **1**, $[Au_2f(Hy)_2]NO_3$, showing an oxygen from the nitrate in short contact with the ylide methyl carbon (C33). This oxygen is disordered, and the short contact becomes the ylide methyl carbon of another cation.

The cationic mononuclear complex **4**, with neutral amidine and neutral ylide ligands, has a large PF_6^- anion presumably assisting in the prevention of an aurophilic gold−gold association. Here the formamidine NH proton is directed away from the N−Au−C bond, allowing the adjacent phenyl to be closer to this bond. The NH proton is H-bonded to two fluorides of a PF_6^- anion at 2.3927(10) and 2.433(9) Å. The anion shows additional short contacts through fluorines to the ylide methyl (2.283(7) Å), to ylide phenyls (2.403(12), 2.638(13) Å) to phenyls (2.382(13), 2.644(12), 2.638(13) Å), to a methyl phenyl (2.597(12) Å), and to the NCHN (2.582(14), 2.519(13) Å) on the surrounding formamidinates. This extensive net of short contacts governs the orientation of the ylide phenyls, so that one sits close to a formamidinate phenyl and the ylide methyl is pointing opposite to the Au−CH_2 bond. It also produces a spatial constraint on the N−Au−C bond ,which is more bent (172.52°) than in **1**−**3**.

Scheme 3. Base Hydrolysis of Ylide To Produce a Phenyl Anion and the Dimethyl Phenyl Phosphite



The Au−N distances are large compared to Au−N bonds in $[Au_2f_2]$ (2.035(4) Å),[17] revealing the strong σ-donor character of the ylide carbon atom. In **1** the elongation increases to 2.095(4) and 2.105(3) Å. In **2** the Au−N bond opposite to the ylide C is 2.051(3) Å, whereas that opposite to chlorine is 2.025(3) Å. In **3**, both Au−N bonds are elongated (2.047(4), 2.084(3) Å) but the effect is more pronounced on the bond opposite to the phenyl ligand. In **4**, the Au−N distance is 2.072(3) Å. Conversely, Au−C bonds to the ylide show a slight contraction in comparison to those in $[Au_2y_2]$ (2.075(5) Å), with distances of 2.052(4) Å in **1**, 2.051(4) Å in **2**, 2.047(3) Å in **3**, and 2.016(2) Å in **4**.

The constraint on the N−C−N angle imposed by an opposing bridge is no longer present in **1** and is reflected in the N−N distance of 2.278(5) Å, which is shorter than the 2.363(5) Å distance in $[Au_2f_2]$. This shortened distance in **1** compared with the eight membered ring compound[18] appears to occur because of the strain to maintain the linear N−Au−N angles in the bowed ring, a strain which is absent in **1**. This lack of strain in **1** shows even more distinctively in the separation between ylidic $CH_2 \cdots CH_2$ units of 3.982(17) Å.

H NMR Spectra. ^1H NMR spectra were taken in *d*-benzene from crystals. Signals in the aromatic region (6−8 ppm) are due to phenyl protons from both ligands, the formamidinate and the ylide. They usually overlap. Also in this region, characteristically at ~7.4 ppm, the N(CH)N signals appear. Signals in the aliphatic region (1−3 ppm) derive from methyls on the formamidinate and the methyl/methylene on the ylide. The latter are split due to $^{31}P-^1H$ coupling.

In $[Au_2fy_2]NO_3$ (**1**) the aromatic region shows phenyl signals spread from 7.7 to 6.90 ppm. There is a marked shift of the methyl/methylene signal to lower field arising from the positive charge on the molecule, an effect also observed in the ^1H NMR of the ylide precursor $[H_2y]NO_3$ with a CH_3 signal at 2.9 ppm and in the cationic mononuclear complex **4**. Additionally the proximity of the nitrate anion to the ylide methyl group, described in Structural Characteristics, causes this doublet to appear at 2.40−2.45 ppm (integrating to 6). It appears at a higher field than the coordinating ylide CH_2 at 2.17−2.13 ppm (integrating to 4). The formamidinate methyl signal is at 2.32 ppm. Phenyl signals from **4** in the aromatic region span from 7.8 to 6.7 ppm.

Table 2. Crystallographic Data

	1	2	3	4
chem formula	$Au_2C_{45}H_{49}N_3O_3P_2$	$Au_2C_{31}H_{34}N_2PCl$	$Au_2C_{37}H_{39}N_2P$	$C_{31}H_{35}N_2P_2F_6Au$
fw	1135.75	894.96	936.0	808.52
space group	$P2/c$	$P2_1/c$	$Fdd2$	$P\bar{1}$
a (Å)	20.034(16)	10.580(6)	22.1144(16)	8.594(8)
b (Å)	16.208(13)	16.133(9)	56.875(4)	12.966(12)
c (Å)	13.630(11)	18.634(10)	10.8177(7)	14.062(14)
α (deg)	90	90	90	92.895(17)
β (deg)	100.972(9)	104.024(8)	90	95.603(17)
γ (deg)	90	90	90	92.166(17)
V (Å^3)	4345(6)	3086(3)	13606.2(16)	1556(3)
Z	4	4	16	2
d_{calcd} (g cm^{-3})	1.736	1.926	1.829	1.726
μ (mm^{-1})	6.861	9.658	8.690	4.890
T (K)	213	213	110	213
R1^a (wR2^b)	0.0682 (0.1370)	0.0371 (0.0991)	0.0502 (0.1161)	0.0613 (0.1280)

[a] $R1 = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^{2}]^{1/2}$. [b] $wR2 = [\Sigma[w(F_o^{2} - F_c^{2})^2]/\Sigma w(F_o^{2})^2]^{1/2}$; $w = 1/[\sigma^2(F_o^{2}) + (aP)^2 + bP]$, where $P = [\max(F_o^{2},0) + 2(F_c^{2})]/3$.

There are formamidinate methyl signals at 2.34 and 2.28 ppm in **4**; the ylide methyl group which is in short contact with the anion shows up at a low field, 2.46−2.42 ppm, similar to the case for the cation **1**. The ylide methylene, with no short contacts to the anion, has its signal at 1.71−1.75 ppm, which compares well to signals found for **2** and **3**.

For [Au_2f(Hy)Cl] (**2**) the two formamidinate methyl signals are at 2.40 and 2.32 ppm. The ylide methylene signal is at 1.76−1.72 ppm and the methyl at 1.46−1.50 ppm. For [Au_2f(Hy)Ph] (**3**) the aromatic region shows the phenyl proton signal centered at 8.1 ppm. Since there are two different C-donor groups, there are two formamidinate methyl signals: 2.54 and 2.29 ppm. The ylide methylene doublet is at 1.79−1.75 ppm and the methyl at 1.45−1.49 ppm.

Two distinct factors influence the shifts of methylene and methyls on both the ylide and the formamidinate ligands: (a) short contacts with anions produce a deshielding effect on ylide methyl protons, moving the signal up to ∼2.4 ppm to a lower field in both cationic **1** and **4**; (b) the strong σ-donor character of the trans ligand across the gold(I) exerts a shielding effect on the coordinating methylene and on the formamidine methyl groups, moving these signals to a higher field. This is noted when comparing ^{1}H NMR data to data for Au_2f_2 and Au_2y_2. In the mixed-ligand compounds the N−Au−C linkage has a strong σ donor (ylide C) trans to a weaker σ donor (formamidinate N); therefore, the ylide methylene signals shift to lower field (1.71−1.79 ppm) in comparison with those for Au_2y_2 (1.42−1.38 ppm), while the formamidinate methyl signals (2.32−2.29 ppm) shift to a slightly higher field compared with Au_2f_2 (2.34 ppm). The shift of the formamidinate methyls is less marked, since these are more remote from the coordination.

CONCLUSIONS

Two dissimilar ligands, a N-donor formamidinate and a C-donor phosphorus ylide, are used to produce four gold(I) compounds with novel mixed N−Au−C coordination. Compounds **1**−**3** are open binuclear structures with bridging formamidinate and monocoordinating ylide and/or chloride and phenyl ligands. Compound **4** is a mononuclear complex with monocoordinating formamidine and ylide ligands. The N coordination on the dinuclear gold formamidinate is displaced by CH_2 donation from the strongly σ-donating ylide which produces the monocoordinate ylide ligand. Additional ylide favors further deprotonation, but the reaction produces the resulting dinuclear gold(I) ylide complex. Base activation of the ylide is observed upon addition of KOH, releasing a phenyl anion which ends up attached to a gold(I) center. It also produces benzene, as observed in the ^{1}H NMR.

The mixed coordination is reflected in the ^{1}H NMR as a shift of formamidinate methyl substituents to higher field and of ylide methyl/methylene signals to lower field in comparison with the signals for the homoligand dinuclear complexes. The effect is especially marked on the ylide methylene group. A screening of the luminescence of **3** and **2** under UV light at room temperature shows only a dull red emission. Additional studies of the emission spectra of these mixed-ligand species will be reported elsewhere.

EXPERIMENTAL SECTION

Syntheses were carried out under an inert atmosphere using standard Schlenk techniques, unless otherwise noted. Solvents (THF, toluene, ether, and hexane) were dried using a Glass Contour solvent system. Ethanol was used freshly distilled with Mg/I_2 under nitrogen. The phosphorus ylide [$PPh_2CH_3CH_2$] was prepared by stirring a 1/1 (mmol/mmol) mixture of [$PPh_2(CH_3)_2$]NO_3 and KH (25% slurry in mineral oil) in 10 mL of THF (−20 °C, dark, N_2) over 6 h. The THF was removed by vacuum pumping, keeping the flask at −20 °C. Then toluene (10−20 mL) was added and the yellow solution was stored at −20 °C. The potassium formamidinate was prepared by refluxing at 60 °C the formamidine [(2,6-Me_2Ph)$_2$NCHN] with KOH in a 1/1 ratio in ethanol; the solvent was slowly evaporated in air, which produced crystals that were rinsed with hexanes. Elemental analyses were performed by Robertson Microlit Laboratories, Inc., Madison, NJ. ^{1}H NMR spectra were recorded on a Mercury-300 NMR spectrometer.

X-ray Structure Determinations. Data for **1** and **3** were collected (Table 2) on a Bruker APEX-II 1000[33] CCD area detector system using ω scans of 0.3°/frame and 30 s per frame (2000 frames, 18 h 21 min) for **1** and 0.5°/frame and 10 s per frame (1208 frames, 4 h 33 min) for **3**, while data for **2** and **4** were collected on a Bruker SMART 1000 CCD area detector system using ω scans of 0.3°/frame and 40 s per frame (2000 frames, 28 h 41 min) for **2** and 0.3°/frame and 90 s per frame (2400 frames, 65 h 2 min) for **4**. For **1** and **3** cell parameters were determined using the program APEX. For **2** and **4** cell parameters were determined using the SMART software suite.[34] Data reduction and integration were performed with the software package SAINT,[35] which corrects for Lorentz and polarization effects, while absorption corrections were applied by using the program SADABS.[36]

The positions of the Au atoms were found via direct methods using the program SHELXTL.[37] Subsequent cycles of least-squares refinement followed by difference Fourier syntheses revealed the positions of the remaining non-hydrogen atoms. Hydrogen atoms were added in idealized positions. All hydrogen atoms were included in the calculation of the structure factors. All non-hydrogen atoms were refined with anisotropic displacement parameters.

Compound **1** crystallized in the monoclinic centrosymmetric space group $P2/c$; one of the NO_3^- anions in the structure was disordered in a special position. Compound **2** was refined in the monoclinic centrosymmetric space group $P2_1/c$. Compound **3** crystallized in the orthorhombic noncentrosymmetric space group $Fdd2$. Compound **4** was initially solved in the triclinic noncentrosymmetric space group $P1$ suggested by the XPREP program; however, following the recommendation of choosing the higher symmetry group advised by Marsh,[38] the final refinement was done in the centrosymmetric $P\bar{1}$. This structure has four fluorine atoms of the PF_6^- anion disordered; the positional disorder was treated by defining a second free variable,and the final refinement gave SOF = 0.56139 and 0.43861 for the major and minor components, respectively.

Additional crystallographic information for **1**−**4** are given in Table 2, and selected bond lengths are provided in Table 1.

Synthesis of [$Au_2f(Hy)_2$]NO_3 (1). To a suspension of [Au(THT)Cl] (0.0800 g, 0.25 mmol) and THT (0.25 mmol) in 20 mL of ethanol, at 0 °C, was added 0.25 mmol of $AgNO_3$, and the contents were stirred for 4 h. The white suspension was allowed to settle, and the liquid was canullated to a flask containing the potassium salt (0.0730 g, 0.25 mmol). The mixture was stirred for 3 h until a white solid formed. After the solvent was removed under vacuum, the flask with the gold(I) formamidinate was put in a dry ice bath and the ylide solution (0.25 mmol) in 20 mL of toluene (at −20 °C, in the dark) was transferred using a cannula. The mixture was stirred for 3 h at −20 °C. The toluene was removed under vacuum, and the residue was first extracted with 5 mL of ether and then with 5 mL of toluene. From the toluene solution layered with hexane colorless crystals of [Au_2fy_2] NO_3 grew in 1 week. Yield: 63%. Anal. Calcd for $C_{45}H_{49}N_3O_3P_2Au_2$: C, 47.57; N, 3.70, H, 4.32. Found: C, 47.85; N, 4.05; H, 4.37. IR (KBr): 3166 (ylide, m), 2966 (s), 2892 (ylide, s), 1604 (s), 1571 (s), 1470 (s), 1440 (s), 1373 (m), 1345 (m), 1300 (m), 1290 (m), 1255 (m), 1199 (m), 1160 (w), 1150 (ylide, m), 1090 (m), 1118 (ylide, m), 1031 (m), 982 (m), 943 (ylide, m), 915 (m), 819 (ylide, w), 755 (s), 725 (m), 691 (m), 663 (ylide, m), 618 (w), 475 (m), 425 (m). ^1H NMR (C_6D_6): δ 7.4 (NCHN), 2.32 (CH_3 form), 2.45−2.40 (CH_3 ylide), 2.17−2.13 (CH_2 ylide).

Synthesis of [Cl-$Au_2f(Hy)$] (2). A solution of [Au(THT)Cl] (0.0800 g, 0.25 mmol) and the potassium formamidinate salt (0.0730 g, 0.25 mmol) in 20 mL of CH_3CN was stirred for 2 h until a white suspension formed. The solvent was partially reduced to 10 mL by vacuum, and the flask under N_2 was cooled in a dry ice bath. In this flask the ylide solution (0.25 mmol) in 10 mL of toluene (at −20 °C, in the dark) was transferred using a cannula. The yellow suspension was stirred for 4 h until it cleared up. The solvents were removed under vacuum, and the residue was extracted first with 5 mL of CH_3CN and then with 10 mL of toluene. From the toluene solution layered with hexane bulky colorless crystals of [Cl-Au_2fy] grew in 1 week. Yield: 63%. Anal. Calcd for $C_{31}H_{34}N_2PClAu_2$: C, 41.61; N, 3.13; H, 3.80. Found: C, 41.10; N, 2.97; H, 4.20. IR: 3157 (ylide, m), 2965 (s), 2892 (ylide, s), 1607 (s), 1571 (s), 1473 (s), 1440 (s), 1374 (m), 1345 (m), 1290 (m), 1255 (m), 1199 (m), 1161 (w), 1150 (ylide, m), 1089 (m), 1117 (ylide, m), 1031 (m), 982 (m), 943 (ylide, m), 915 (m), 819 (ylide, w), 755 (s), 725 (m), 691 (m), 663 (ylide, m), 618 (w), 475 (m), 425 (m). ^1H NMR (C_6D_6): δ 7.4 (NCHN), 2.40−2.32 (CH_3 form), 1.76−1.72 (CH_2 ylide), 1.46−1.50 (CH_3 ylide).

Synthesis of [Ph-$Au_2f(Hy)$] (3). The gold(I) formamidinate was prepared as for **1** (with Au(THT)Cl 0.0800 g, 0.25 mmol), and the solvent (ethanol) was reduced to 1−2 mL under vacuum, and then the flask under N_2 was cooled in a dry ice bath. In this flask the ylide solution (0.25 mmol) in 10 mL of toluene (at −20 °C, in the dark) was transferred using a cannula. KOH (0.12 mmol) was added to the mixture, which was stirred for 4 h at −20 °C. The solvents were removed by vacuum, and the residue iswas extracted with 10 mL of ether. The ether solution layered with hexane produced large prismatic, colorless crystals of [Ph-$Au_2f(Hy)$] after 2 weeks. Yield: 40%. Anal. Calcd for $C_{37}H_{39}N_2PAu_2$: C, 47.44; N, 2.99; H, 4.17. Found: C, 47.64; N, 2.96; H, 4.09. IR: 3167 (ylide, m), 2964 (s), 2892 (ylide, s), 1605 (s), 1650 (phenyl, s), 1571 (s), 1470 (s), 1440 (s), 1373 (m), 1345 (m), 1290 (m), 1310 (phenyl, m), 1255 (m), 1199 (m), 1179 (phenyl, m), 1160 (w), 1150 (ylide, m), 1090 (m), 1117 (ylide, m), 1031 (m), 982 (m), 943 (ylide, m), 915 (m), 848 (phenyl, m), 819 (ylide, w), 755 (s), 725 (m), 691 (m), 663 (ylide, m), 618 (w), 475 (m), 425 (m). ^1H NMR (C_6D_6): δ 8.1 (Ph), 7.4 (NCHN), 2.54, 2.29 (CH_3 form), 1.79−1.75 (CH_2 ylide), 1.49−1.45 (CH_3 ylide).

Synthesis of [Au(Hf)(Hy)]PF_6 (4). A solution of [Au(THT)Cl] (0.0800 g, 0.25 mmol) and the neutral formamidine (0.0730 g, 0.50 mmol) in 20 mL of CH_3CN was stirred for 2 h until a white suspension formed. The solvent was partially reduced to 10 mL by vacuum, and the flask under N_2 was cooled in a dry ice bath. The ylide solution prepared from [$PPh_2(CH_3)_2$]PF_6 (0.25 mmol) in 10 mL of THF (at −20 °C, in the dark) was transferred into this flask using a cannula. The yellow suspension was stirred for 4 h until the cloudiness cleared up. The solvents were removed under vacuum, and the residue was rinsed with ether. The solid was dissolved in THF and layered with hexane; after 1 week small prismatic crystals grew. Yield: 60%. Anal. Calcd for $C_{31}H_{35}N_2P_2F_6Au$: C, 46.03; N, 3.46; H, 4.331. Found: C, 45.72; N, 3.18; H, 4.20. IR (KBr): 3166 (ylide, m), 2966 (s), 2892 (ylide, s), 1604 (s), 1571 (s), 1470 (s), 1440 (s), 1373 (m), 1345 (m), 1290 (m), 1255 (m), 1199 (m), 1160 (w), 1150 (ylide, m), 1090 (m), 1117 (ylide, m), 1031 (m), 982 (m), 943 (ylide, m), 915 (m), 819 (ylide, w), 755 (s), 725 (m), 691 (m), 663 (ylide, m), 618 (w), 475 (m), 425 (m). ^1H NMR (C_6D_6): δ 7.4 (NCHN), 2.40−2.32 (CH_3 form), 1.76−1.72 (CH_2 ylide), 1.46−1.50 (CH_3 ylide).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. CIF files giving X-ray crystallographic data for **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ ACKNOWLEDGMENT

This work was supported by the Robert A. Welch Foundation, Houston, TX, Grant No. A-0960.

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