Access to Gold(I) Protic N-Heterocyclic Carbene Complexes from Trinuclear Gold(I) Imidazolate Clusters

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ABSTRACT: A series of mononuclear gold(I) protic N-heterocyclic carbene (pNHC) complexes has been prepared by reaction of trinuclear gold(I) imidazolate clusters with acids of variable strength (pK_a ranging from -14 to 6.7), which induce the opening of the Au_3 ring cluster by protonation. Thus, reaction of $[Au_3(\mu\text{-Im})_3]$ (Im = N-alkyl or N-arylimidazolate) with weak acids such as phosphonium salts or 4-methoxythiophenol (HSR) yields mononuclear derivatives of general formula $[Au(pNHC)PR_3]^+$ or [Au(pNHC)SR], respectively, whereas with HCl complexes [Au(pNHC)Cl] are obtained. The non-coordinating strong acid CF_3SO_3H reacts with $[Au_3(\mu\text{-Im})_3]$ in the presence of isocyanide (CNR) to afford the cationic species $[Au(pNHC)CNR]^+$, from which the rare example of bis-carbene derivative $[Au(pNHC)(pADC)]^+$ (pADC = protic acyclic diamino carbene) is formed by reaction with $NHMe_2$. Additionally, a number of neutral complexes were obtained by substitution reactions of the chloride ligand in [Au(pNHC)Cl] with anions such as cyanide, thiocyanate and diethyldithiocarbamate.

INTRODUCTION

Despite the enormous development of N-heterocyclic carbenes (NHCs) chemistry and their metal complexes in the last three decades,[1] the chemistry of NHCs containing at least an N-H group within the heterocyclic skeleton (also called protic N-heterocyclic carbenes, pNHCs) still remains relatively underexplored.[2] However, this subclass of NHCs is also relevant, as they offer additional reactivity patterns such as easy post-functionalization, formation of hydrogen bonds for supramolecular assembly, and substrate recognition in cooperative catalysis.[2] The impossibility to isolate metal-free pNHCs, as their imidazole tautomers are much more stable,[3] leads to synthetic methodologies for the obtention of pNHC-metal complexes clearly differentiated from those normally used with their classical NR,NR-NHCs (R = alkyl or aryl) congeners. Methods based on metal-promoted tautomerization of azoles[4] and diverse cyclization processes of coordinated isocyanides by reactions with amines[5] are amongst the most popular. In the specific case of gold(I), a number of pNHC complexes have been obtained by reaction of the appropriate gold(I) precursor with lithiated azoles, followed by protonation of the azolyl intermediate derivatives.[6] Singular examples prepared by deprotection protocols[7] and by cyclization reactions from isocyanide complexes with propargyl amine have also been reported.[8]

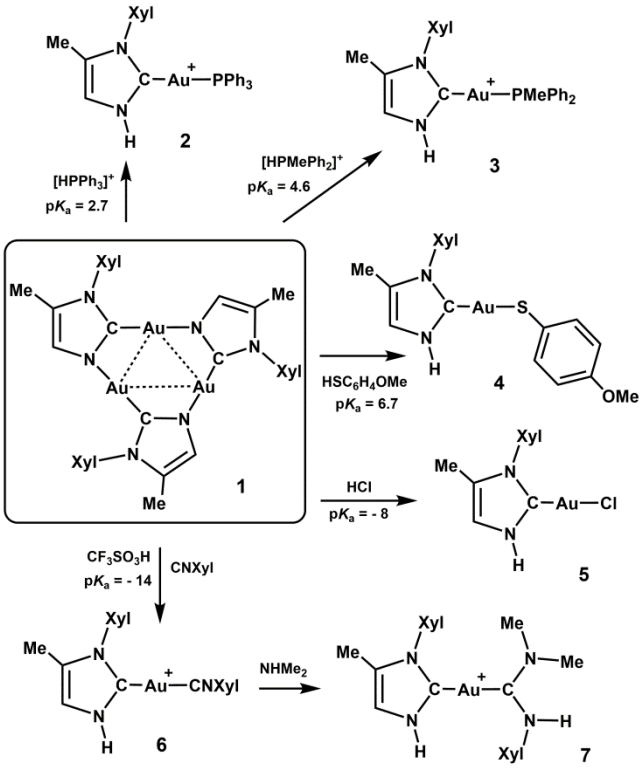
In this context we have now developed a new experimental approach to obtain diverse pNHC-gold(I) complexes from triangular gold(I) imidazolate clusters. Trinuclear gold(I) complexes bearing N-alkylimidazolate bridging groups have attracted widespread interest in the past several years.[9] These triangular clusters possess a Lewis base character forming sandwich metal structures when reacting with metal cations such as Ag^+,[10] as well as sandwich-like adducts with organic Lewis acids like hexafluorobenzene or octafluoronaphtalene and with the electron acceptor 7,7,8,8-tetracyanoquinodimethane.[11] They have also been enclosed within columnar coordination cages to produce highly conductive materials and stabilized triple-decker clusters.[12] In addition these triangular clusters and their derivatives usually exhibit photoluminescence.[13] Naturally, the nitrogen atoms of the imidazolate bridging groups directly bonded to gold still retain some basic character, and this feature prompted us to obtain a number of pNHC-Au(I) derivatives by reaction with proton donors of variable nature, as we will describe below.

RESULTS AND DISCUSSION

We have recently described the synthesis of the first trinuclear gold(I) N-arylimidazolate complex (**1**),[14] which is used in this work for the preparation of mononuclear pNHC-Au(I) derivatives as summarized in Scheme 1. The reaction of a dichloromethane solution of compound **1** with the phosphonium salt $[HPPh_3]BF_4$ affords the cationic complex **2**, whose formation implies protonation of the bridging imidazolate group and breaking of the gold-gold interactions, followed by coordination of the newly generated phosphine PPh_3 to gold. This result indicates that the triphenylphosphinum cation, with a pK_a value of 2.7,[15] is acidic enough to promote the opening of the Au_3 ring in cluster **1**. To evaluate the scope of this synthetic approach we used other protic reagents that gradually increase their pK_a. This is the case of methyldiphenylphosphonium with a pK_a of 4.6,[15] which also leads to the formation of the corresponding mixed-ligand pNHC/phosphine complex **3**, despite its lesser acid character. The treatment of **1** with 4-methoxythiophenol, which implies an additional increase of the pK_a to 6.7,[16] in similar reaction conditions, gives rise to the formation of the neutral thiolate complex **4** after protonation of the imidazolate bridging group.[17] However, when trying to produce a similar protonation reaction of **1** with NH_4PF_6 (pK_a = 9.2) the starting complex **1** was recovered unchanged, even

after prolonged reaction times and with an excess of the ammonium salt. This result appears to indicate that the p*K*a threshold for a substrate to produce the protonation of **1** and so formation of the pNHC-Au(I) derivative might be somewhere between 6.7 and 9.2. Naturally, reaction of **1** with a strong acid containing a coordinating anion such as HCl instantaneously affords the expected mononuclear neutral species pNHC-Au-Cl (**5**), as we have already described in a recent communication.[14] Other strong acids bearing weekly coordinating anions, like CF_3SO_3H, also readily produce the immediate protonation of **1** but, in order to stabilize the resulting pNHC-Au(I) complex a two electron ligand must be added. Thus, the treatment of a dichloromethane solution of **1** with 3 equivalents of triflic acid in the presence of another 3 equivalents of CNXyl (Xyl = 2,6-xylyl) yields the cationic complex **6**. Complexes **2**-**6** were characterized by spectroscopic method (see experimental section). The N-H group of the newly formed pNHC ligand is clearly observed in the ^{1}H NMR spectra, appearing as a broad singlet in the range 11.2-12.5 ppm. In the $^{13}C\{^1H\}$ NMR spectra the signal corresponding to the carbene carbon atom appears in the expected low field region (166.7-182.9 ppm).

Scheme 1. Reactions of the triangular gold(I) imidazolate cluster 1 with weak and strong acids to afford mononuclear pNHC-Au(I) complexes. Xyl = 2,6-xylyl.



Complexes **2**-**6** are stable by standing at room temperature at the solid state, but in dichloromethane solution most of them slowly evolve to give a mixture of complexes where the bis-carbene cation $[Au(pNHC)_2]^+$ is clearly identified.[8] For this reason, in occasions the spectroscopic characterization must be accomplished at low temperature. Nevertheless, some of these complexes can be used for further reactivity. This is the case of **6** that cleanly reacts with dimethylamine to afford complex **7** (Scheme 1) in a typical nucleophilic addition of the secondary amine to the coordinated isocyanide. Interestingly, **7** is the first example of a gold(I) complex that contains together a protic N-heterocyclic ligand and a protic acyclic diaminocarbene (pADC) ligand.[18] It is worth mentioning the high regioselectivity of the nucleophilic attack of the amine to **6**, as no deprotonation of the N-H group by the base was observed, contrary to that found in the treatment of other pNHC-Au(I) complexes with bases. For instance, reaction of **5** with NH_3 cleanly affords the triangular cluster **1** after deprotonation. The N-H group of each carbene ligand in **7** is observed in the ^{1}H NMR spectrum at 11.36 (pNHC) and 7.21 (pADC) ppm. In the $^{13}C\{^1H\}$ NMR spectrum the carbene carbon atoms appear at 180.9 and 205.9 ppm for the pNHC and pADC ligands, respectively.

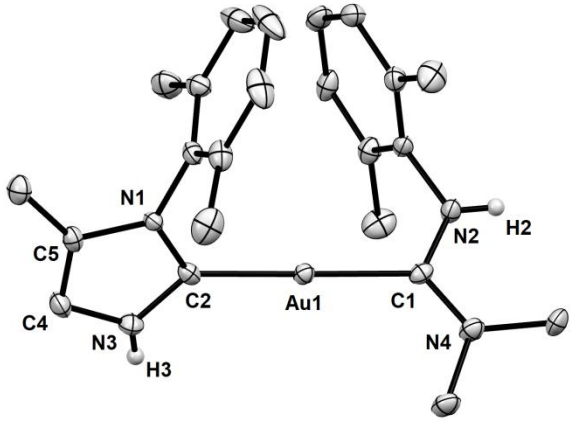
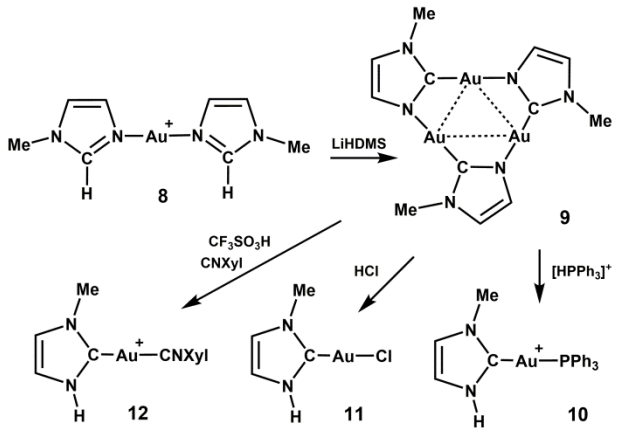


Figure 1. A view of the structure of **7**, shown with 50% thermal ellipsoids. Hydrogen atoms (except N2-H2 and N3H3) are omitted for clarity. Selected bond distances (Å) and angles (deg): Au1-C1 2.048(3), Au1-C2 2.021(3), C1-N2 1.339(4), C1-N4 1.328(4), C2-N1 1.361(4), C2-N3 1.341(4); C1-Au1-C2 177.94(13), N1-C2-N3 103.8(3), N2-C1-N4 117.0(3).

Colorless crystals of [**7**]CF_3SO_3 suitable for an X-ray study were obtained by slow diffusion of diethyl ether and hexane into a dichloromethane solution of the compound. A drawing of the cationic complex **7**, together with selected bond distances and angles, is showed in Figure 1. As it is well stablished, there is not free rotation around the C-N bonds in ADC ligands owing to its multiple bond character.[19] Consequently, two possible conformers of complex **7** could be formed depending on the relative disposition of the substituents at the nitrogen atom N2. The X-ray structure confirms the presence of just one conformer (in agreement with the spectroscopic characterization in solution), in which the bulky xylyl group is located *syn* with respect to the gold atom, presumably to avoid the steric repulsion of the NMe_2 group. The Ccarbene(pNHC)-Au distance is slightly shorter than the Ccarbene(pADC)-Au one, in consonance with that observed in non-protic NHC-Au(I) complexes,[18] even though ADCs are better overall donors than NHCs.[20] A tentative explanation for this behavior might be the stronger π-acceptor character of the pNHC with respect to the pADC in this particular case, which could make an important contribution to the shortening of the C2-Au bond.[21]

This synthetic methodology can be extended to N-alkylimidazolate gold(I) triangular clusters, as we have exemplified with the reactions included in Scheme 2. For this purpose, the N-methylimidazolate trinuclear cluster **9** has been employed, which furthermore was synthetized by a new experimental protocol. This consists of the treatment of the cationic bis(1-methylimidazole)gold(I) complex **8** with LiHMDS, which acts as deprotonating agent of a coordinated imidazole ligand, while the remaining imidazole molecule is liberated from the metal center. This procedure avoid the use of the stronger base *n*-BuLi employed in the classical method to deprotonate free 1-methylimidazole,[22,13b] as in the case of **8** the N_2C-H hydrogen atom has an enhanced acidic character owing to the coordination of the imidazole molecule to gold(I) and does not require such a strong base to be extracted.

Scheme 2. Synthesis and protonation reactions of the triangular gold(I) 1-methylimidazolate cluster 9 to afford mononuclear pNHC-Au(I) complexes. Xyl = 2,6-xylyl.



The reaction of **9** with the triphenylphosphonium salt yielded the pNHC-Au(I) mononuclear complex **10**, which is totally analogous to its N-aryl counterpart **2**, though considerably more unstable in solution. In fact, on standing in dichloromethane at room temperature a mixture of **10**, and the homoleptic cations $[Au(pNHC)_2]^+$ and $[Au(PPh_3)_2]^+$ is observed. As expected, the treatment of **9** with the strong acid HCl instantaneously produces complex **11**, similar to **5**. Finally, when the protonation reaction of **9** was carried out with CF_3SO_3H in the presence of xylylisocyanide complex **12** was readily formed, whose spectroscopic data are very similar to those of **6**, particularly the ν(CN) stretching frequency in the IR spectrum (2216 cm^{-1}) and chemical shifts for the donor carbon atoms of the carbene and isocyanide ligands in the $^{13}C\{^1H\}$ NMR spectrum. The structure of **12** was additionally confirmed by an X-ray single crystal diffraction study of the salt [**12**]CF_3SO_3 (Figure 2).

There are not significant differences between the structural parameters of **12** and those of similar non-protic NHC-Au(I) complexes described in the literature,[18] except from the existence of a N-H…O hydrogen bond involving the N-H group of the protic carbene and the triflate anion. There are not intermetallic contacts in the crystal, in spite of the low steric hindrance of the N-substituents in the carbene ligand (H and Me), with the shorter Au-Au distance between complex cations being 5.1041(3) Å.

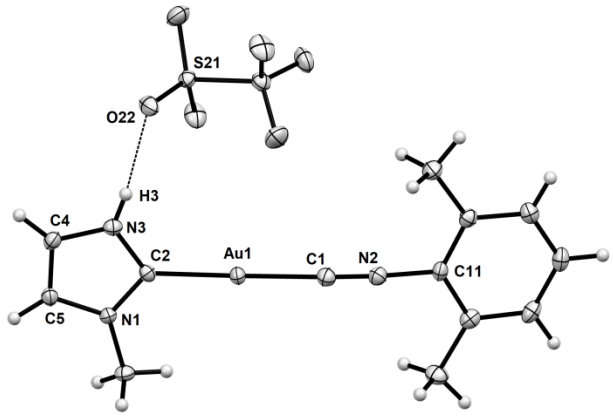


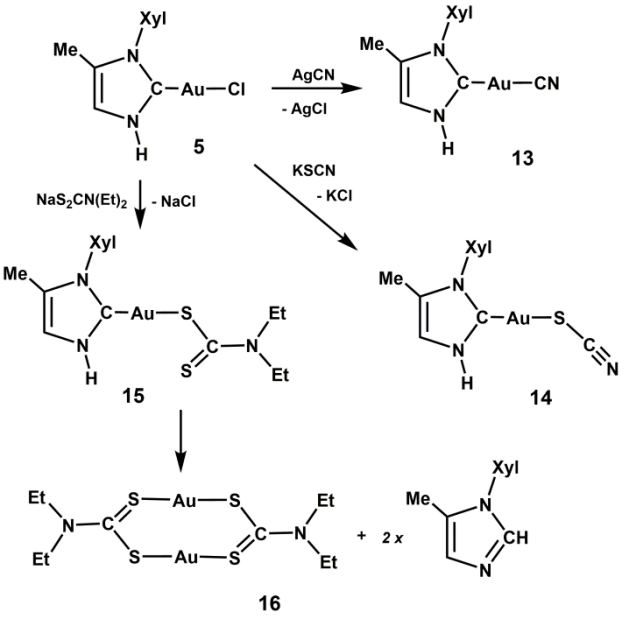
Figure 2. A view of the structure of [**12**]CF_3SO_3, shown with 50% thermal ellipsoids. Selected bond distances (Å) and angles (deg): Au1-C1 1.972(2), Au1-C2 2.0059(19), C1-N2 1.148(4), C2-N1 1.346(2), C2-N3 1.350(2), O22…H3 2.03(3); C1-Au1-C2 178.29(8), N1-C2-N3 105.04(16), Au1-C1-N2 176.59(18), N3-H3…O22 165(2).

Another source of pNHC-Au(I) complexes is provided by complex **5** which, as showed before, can be easily prepared from the triangular cluster **1**. In fact, the chloride ion in **5** can be substituted by different anionic ligands affording neutral pNHC-Au(I) derivatives, as summarized in Scheme 3.

Thus, the treatment of **5** with an equivalent of AgCN in CH_2Cl_2 as solvent leads to the formation of complex **13**, after precipitation of AgCl.[23] A characteristic ν(CN) band at 2145 cm^{-1} in the IR spectrum of **13** confirms the coordination of the cyanide ion to gold, while the other spectroscopic data proved the maintenance of the pNHC ligand in the complex. Rather interestingly, the X-ray crystal structure of **13** (Figure 3) showed a pairwise association of this molecule to allow the existence of intermolecular N-H…N hydrogen bonds involving the N-H residue of the pNHC ligand and the nitrogen atom of the cyanide ligand. The rather long intermolecular Au-Au distance of 4.0126(4) Å appears to exclude any significant interaction between the gold atoms. Another pseudohalogen gold(I) complex is obtained by reaction of **5** with KSCN in dichloromethane, which affords complex **14** featuring a thiocyanate ligand.[23] The ν(CN) band at 2124 cm^{-1} in the IR spectrum of **14** in dichloromethane solution suggests the formation of the S-bound linkage isomer rather than the N-bound one, as it would be expected considering the soft Lewis character of gold(I), and in consonance with that found in the literature for similar complexes with non-protic NHCs.[23]

Complex **5** also reacts under similar conditions with sodium N,N-diethyldithiocarbamate to afford complex **15**, whose spectroscopic data confirmed the presence of both pNHC and dithiocarbamate ligands in a 1:1 ratio.[24] It is worth noting that the signal corresponding to the N-H proton of the pNHC ligand is absent in the ^1H NMR spectrum recorded at room temperature, whereas a broad peak at 12.71 ppm appears at – 80º C. This behavior suggests the existence of a dynamic process in solution, perhaps affecting to possible N-H…S hydrogen bonds.

Scheme 3. Substitution reactions of the chloride ligand in complex 5 by cyanide, thiocyanate and diethyldithiocarbamate to afford neutral pNHC-Au(I) complexes 13, 14 and 15, respectively. Xyl = 2,6-xylyl.



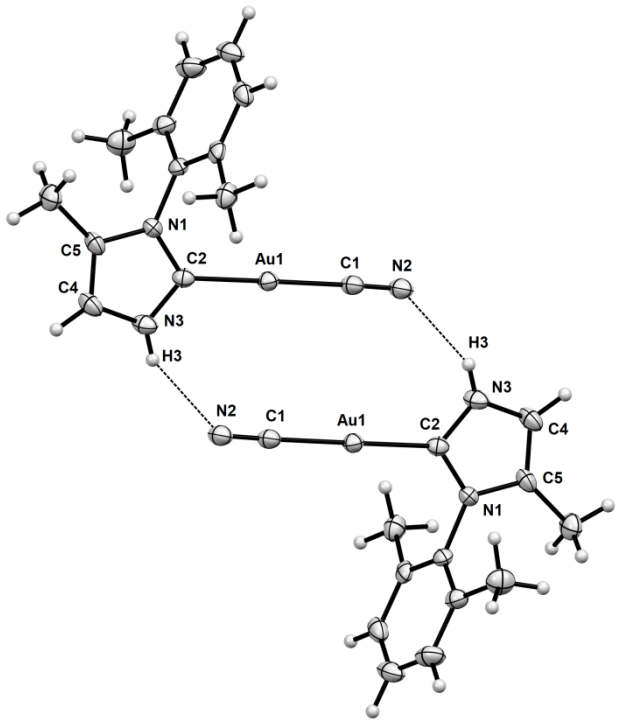


Figure 3. A view of the structure of **13**, shown with 50% thermal ellipsoids. Selected bond distances (Å) and angles (deg): Au1-C1 2.005(5), Au1-C2 2.016(5), C1-N2 1.137(6), C2-N1 1.349(6), C2-N3 1.336(6), H3…N2 2.22(5); C1-Au1-C2 179.57(18), N1-C2-N3 104.3(4), Au1-C1-N2 177.2(4), N3-H3…N2 150(5).

Furthermore, complex **15** is unstable on standing in solution of dichloromethane or other organic solvents at room temperature, affording pale red crystals of the dimeric gold(I) dithiocarbamate complex $[Au(S_2CN(C_2H_5)_2)]_2$ **16**, (circa 40% yield), with elimination of free 1-xylylimidazole. The indexed metric indicates that crystals of **16** correspond to the orthorhombic β-phase already described in the literature.[25] Apparently, complex **15** lacks the kinetic stabilization provide by substituents in classical N,N-dialkyl or diaryl substituted NHC gold(I) complexes, and this is a feature to be taken into account when planning future possible applications of pNHC-Au(I) complexes.

CONCLUSION

We have described herein a new experimental protocol to synthetize mononuclear gold(I) protic N-heterocyclic carbene (pNHC) complexes, based on the reaction of trinuclear gold(I) imidazolate clusters of general formula $[Au_3(\mu\text{-Im})_3]$ (Im = N-alkyl or N-arylimidazolate) with Bronsted acids of variable strength, which induce the opening of the Au_3 ring cluster by protonation. Weak or strong acids that release a good coordinating ligand on protonation, such as phosphonium salts, 4-methoxythiophenol (HSR) or HCl, afford the complexes $[Au(pNHC)PR_3]^+$, [Au(pNHC)SR] or [Au(pNHC)Cl], respectively. However, in the reaction of the non-coordinating acid CF_3SO_3H with $[Au_3(\mu\text{-Im})_3]$ the presence of a two electron ligand, such as isocyanide (CNR), is needed to stabilize the corresponding pNHC/Au(I) derivative, namely $[Au(pNHC)CNR]^+$. In addition, a number of neutral complexes are obtained by substitution reactions of the chloride ligand in [Au(pNHC)Cl] with anions such as cyanide, thiocyanate and diethyldithiocarbamate. Overall, the main difference of the pNHC/Au(I) complexes described herein with respect to classical NHC/Au(I) complexes is the involvement of the N-H residue of the pNHC ligand in intermolecular hydrogen bonds, as well as the lesser kinetic stability of the former owing to the low steric hindrance of the N-H group.

EXPERIMENTAL SECTION

General considerations. All reactions and manipulations were performed under an atmosphere of dry nitrogen by standard Schlenk techniques. Solvents were distilled over appropriate drying agents under dry nitrogen before use. The IR spectra were measured with a Perkin-Elmer Spectrum 100 spectrophotometer. NMR spectra were recorded on Bruker 300 and 400 MHz spectrometers. Coupling constants *J* are given in Hz. Chemical shifts of the NMR spectra were referenced to internal $SiMe_4$ (^1H and ^{13}C) or external H_3PO_4 (^{31}P). X-ray diffraction measurements were performed on a Bruker D8 VENTURE PHOTON-III C14 diffractometer. Mass Spectra were recorded on a Bruker Impact II spectrometer. All reagents were obtained commercially and used without further purification, except for the salts $[HPPh_3]BF_4$ and $[HPMePh_3]BF_4$, which were prepared by reaction of PPh_3 or $PMePh_2$ with HBF_4 following a similar procedure to that described elsewhere.[15]

Compound [2]BF_4: To a solution of the trinuclear cluster **1** (15 mg, 0.013 mmol) in CH_2Cl_2 (4 mL) $[HPPh_3]BF_4$ (14 mg, 0.04 mmol) was added and the resulting mixture stirred for 2 h. The solution was then concentrated under vacuum to circa 1 mL. Slow diffusion of diethyl ether (1 mL) and hexane (3 mL) afforded colorless crystals of the compound. Yield: 20 mg (71%). $^{31}P\{^1H\}$ NMR (121.5 MHz,

CD_2Cl_2, 25ºC, δ, ppm): 40.2 (s). ^{1}H NMR (400 MHz, CD_2Cl_2, 25ºC, δ, ppm): 11.44 (br, 1H, NH), 7.55-7.24 (19H, Ph, Xylyl and =CH), 2.04 (s, 6H, CH_3 Xylyl), 1.98 (s, 3H, =C-CH_3). ^{13}C{^{1}H} NMR (100.61 MHz, CD_2Cl_2, -40ºC, δ, ppm): 183.3 (d, ^2J(C,P) = 128.5 Hz, $C_{carbene}$), 136.1 (s, *o*-Xylyl), 135.7 (s, C_{ipso} Xylyl), 134.2 (d, ^2J(C,P) = 13.3 Hz, *o*-Ph), 132.1 (s, *p*-Ph), 129.9 (s, *p*-Xylyl), 129.7 (s, =*C*-CH_3), 129.4 (d, ^3J(C,P) = 11.1 Hz, *m*-Ph), 128.8 (s, *m*-Xylyl), 128.3 (d, ^1J(C,P) = 57.8 Hz, C_{ipso} Ph), 117.4 (s, =CH), 18.1 (s, CH_3 Xylyl), 9.7(s, =C-*C*H_3). MS (ESI): *m/z*: $[M - BF_4]^+$: calcd. for $C_{30}H_{29}AuN_2P$: 645.1734, found: 645.1725.

Compound [3]BF_4: This compound was similarly prepared by reacting **1** (15 mg, 0.013 mmol) with $[HPMePh_2]BF_4$ (11 mg, 0.039 mmol). Yield: 21 mg (81%). ^{1}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, δ, ppm): 25.5 (s). ^{1}H NMR (400 MHz, CD_2Cl_2, δ, ppm): 11.39 (br, 1H, NH), 7.52-7.27 (14H, Ph, Xylyl and =CH), 2.05 (s, 6H, CH_3 Xylyl), 2.02 (s, 3H, PCH_3), 1.98 (s, 3H, =C-CH_3). ^{13}C{^{1}H} NMR (100.61 MHz, CD_2Cl_2, δ, ppm): 136.7 (s, *o*-Xylyl), 136.3 (s, C_{ipso} Xylyl), 133.2 (d, ^2J(C,P) = 14.1 Hz, *o*-Ph), 132.3 (s, *p*-Ph), 131.0 (d, $^1J_{CP}$ = 57.4 Hz, C_{ipso} Ph), 130.4 (s, *p*-Xylyl), 130.3 (s, =*C*-CH_3), 129.9 (d, ^3J(C,P) = 11.1 Hz, *m*-Ph), 129.3 (s, *m*-Xylyl), 117.7 (s, =CH), 18.2 (s, CH_3 Xylyl), 13.6 (d, ^1J(C,P) = 36.2 Hz, PCH_3), 9.8 (s, =C-*C*H_3). MS (ESI): *m/z*: $[M - BF_4]^+$: calcd. for $C_{25}H_{27}AuN_2P$: 583.1577, found: 583.1563.

Compound 4: To a solution of **1** (15 mg, 0.013 mmol) in CH_2Cl_2 (4 mL) 4-methoxythiophenol (4.8 μL, d = 1.14 g/mL, 0.039 mmol) was added and the resulting mixture stirred for 2 h. The solvent was then evaporated to dryness under vacuum, and the remaining residue washed with hexane (2 x 3 mL). Diffusion of diethyl ether and hexane into a dichloromethane solution of the compound afforded pale yellow crystals. Yield: 17 mg (81%). ^{1}H NMR (400 MHz, CD_2Cl_2, 25ºC, δ, ppm): 12.10 (br, 1H, NH), 7.39 (t, ^3J(H,H) = 7.6 Hz, 1H, *p*-Xylyl), 7.25 (d, ^3J(H,H) = 7.6 Hz, 2H, *m*-Xylyl), 7.06 (d, ^3J(H,H) = 7.5 Hz, 2H, C_6H_4), 6.87 (s, 1H, =CH), 6.54 (d, ^3J(H,H) = 8.6 Hz, 2H, C_6H_4), 3.72 (s, 3H, OCH_3), 1.99 (s, 6H, CH_3 Xylyl), 1.88 (s, 3H, =C-CH_3). ^{13}C{^{1}H} NMR (100.61 MHz, CD_2Cl_2, -80ºC, δ, ppm): 176.6 (s, $C_{carbene}$), 155.4 (s, C-OCH_3), 135.9 (s, C_{ipso} Xylyl), 135.7 (s, *o*-Xylyl), 132.1 (s, =CH C_6H_4), 131.4 (s, C-S), 129.1 (s, *p*-Xylyl), 128.2 (s, *m*-Xylyl), 127.9 (s,=*C*-CH_3), 114.9 (s, =CH), 112.9 (s, =CH C_6H_4), 54.9 (s, OCH_3), 17.7 (s, CH_3 Xylyl), 9.7(s, =C-*C*H_3). MS (ESI): *m/z*: [*M+H*]: calcd. for $C_{19}H_{22}AuN_2OS$: 523.1118, found: 523.1113.

Compound [6]CF_3SO_3: To a solution of **1** (15 mg, 0.013 mmol) and 2,6-xylyl isocyanide (5 mg, 0.2039 mmol in CH_2Cl_2 (6 mL), CF_3SO_3H (3.4 μL, 0.039 mmol) was added and the resulting mixture stirred for 15 min. The solvent was then eliminated to dryness under vacuum and the remaining solid washed with hexane (2 x 3 mL). Colorless crystals were obtained by slow diffusion of diethyl ether and hexane into a dichloromethane solution of the compound. Yield: 29 mg (73%). IR (CH_2Cl_2, cm^{-1}): ν(CN) 2217. ^{1}H NMR (400 MHz, CD_2Cl_2, 25ºC, δ, ppm): 12.48 (br, 1H, NH), 7.37 (t, ^3J(H,H) = 7.6 Hz, 1H, *p*-Xylyl), 7.34 (t, ^3J(H,H) = 7.7 Hz, 1H, *p*-Xylyl), 7.27-7.25 (m, 3H, *m*-Xylyl and =CH), 7.17 (d, ^3J(H,H) = 7.7 Hz, 2H, *m*-Xylyl), 2.39 (s, 6H, CH_3 Xylyl), 2.04 (s, 6H, CH_3 Xylyl), 1.94 (s, 3H, =C-CH_3). ^{13}C{^{1}H} NMR (100.61 MHz, CD_2Cl_2, -40ºC, δ, ppm): 172.7 (s, $C_{carbene}$), 157.2 (br, CN), 136.8, 135.9 (s, *o*-Xylyl), 135.3, 123.6 (s, C_{ipso} Xylyl), 131.4, 129.9 (s, *p*-Xylyl), 130.1 (s, =*C*-CH_3), 128.8, 128.4 (s, *m*-Xylyl), 117.5 (s, =CH), 18.8, 18.0 (s, CH_3 Xylyl), 9.7 (s, =C-*C*H_3). MS (ESI): *m/z*: $[M - OTf]^+$: calcd. for $C_{21}H_{23}AuN_3$: 514.1557, found: 514.1550.

Compound [7]CF_3SO_3: To a solution of **[6]CF_3SO_3** (26 mg, 0.039 mmol) in CH_2Cl_2 (8 mL) a solution of $NHMe_2$ in THF (2 M, 19.5 μL, 0.039 mmol) was added and the resulting mixture stirred for 15 min. The solvent was then eliminated to dryness under vacuum and the remaining solid washed with diethyl ether (2 x 3 mL). Colorless crystals were obtained by slow diffusion of diethyl ether and hexane into a dichloromethane solution of the compound. Yield: 23 mg (85%). ^{1}H NMR (400 MHz, CD_2Cl_2, δ, ppm): 11.36 (br, 1H, NH_{NHC}), 7.34 (t, ^3J(H,H) = 7.6 Hz, 1H, *p*-Xylyl), 7.21 (1H) y 7.02 (1H) (br, NH_{ADC} and =CH), 7.16-7.10 (m, 3H, *m*-Xylyl and *p*-Xylyl), 6.97 (d, ^3J(H,H) = 7.5 Hz, 2H, *m*-Xylyl), 3.49 (s, 3H, NCH_3), 3.06 (s, 3H, NCH_3). 1.97 (s, 6H, CH_3 Xylyl), 1.78 (s, 3H, =C-CH_3), 1.72 (s, 6H, CH_3 Xylyl). ^{13}C{^{1}H} NMR (100.61 MHz, CD_2Cl_2, δ, ppm): 205.9 (s, $C_{carbene\ ADC}$), 180.9 (s, $C_{carbene\ NHC}$), 137.4, 136.1 (s, C_{ipso} Xylyl), 136.9, 136.2 (s, *o*-Xylyl), 129.9, 128.6 (s, *p*-Xylyl), 129.6 (s, =*C*-CH_3), 129.1, 128.8 (s, *m*-Xylyl), 116.8 (s, =CH), 47.3, 36.5 (s, NCH_3) 18.8, 17.9 (s, CH_3 Xylyl), 9.7(s, =C-*C*H_3). MS (ESI): *m/z*: $[M - OTf]^+$: calcd. for $C_{23}H_{30}AuN_4$: 559.2136, found: 559.2126.

Compound [8]PF_6: To a solution of $[AuCl(SMe_2)]$ (0.1 g, 0.339 mmol) in CH_2Cl_2 (10 mL) 2 equivalents of 1-methylimidazole (53 μL, 0.678 mmol) and $TlPF_6$ (0.118 g, 0.339 mmol) were added. The resulting suspension was vigorously stirred for 1 h. Then the solution was filtered over diatomaceous earth to eliminate the salt TlCl. Evaporation of the solvent to dryness under vacuum caused the formation of a white solid. Yield: 155 mg (90%). ^{1}H NMR (300 MHz, CD_2Cl_2, δ, ppm): 7.89 (s, 2H, NCHN), 7.19 (t, ^3J(H,H) = 1.5 Hz, 2H, =CH), 7.13 (t, ^3J(H,H) = 1.4 Hz, 2H, =CH), 3.82 (s, 3H, NCH_3). ^{13}C{^{1}H} NMR (75.46 MHz, CD_2Cl_2, δ, ppm): 140.4 (s, NCHN), 129.9 (s, =CH), 122.5 (s, =CH), 35.6 (s, NCH_3). MS (ESI): *m/z*: $[M - PF_6]^+$: calcd. for $C_8H_{12}AuIN_4$: 361.0727, found: 361.0718. Note: the synthesis of the triflate salt [8]CF_3SO_3 has been described elsewere.[26]

Compound 9: LiHMDS ($LiN(SiMe_3)_2$, 0.217 mL, 1 M in hexane, 0.217 mmol) was added to a solution of **[8]PF_6** (0.1 g, 0.198 mmol) in THF (10 mL). The mixture was stirred for 30 min and then treated with MeOH (1 mL). The solvents were evaporated to dryness under vacuum. The residue was dissolved in CH_2Cl_2 (10 mL) and the solution filtered over diatomaceous earth and concentrated under vacuum to 2 mL. Slow diffusion of hexane (4 mL) into the dichloromethane solution of the compound afforded colorless crystals. Yield: 120 mg (73%). The spectroscopic data are coincident with those already described in the literature.[22]

Compound [10]BF_4. To a solution of **9** (15 mg, 0.018 mmol) in CH_2Cl_2 (5 mL) at -20º C a solution of $[HPPh_3]BF_4$ (19 mg, 0.054 mmol) in CH_2Cl_2 (1 mL) was slowly added. The mixture was stirred at -20ºC for 1h. The solvent was then evaporated to dryness under vacuum to afford a white solid. Yield: 23 mg (68%). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, -20ºC, δ, ppm): 39.9 (s). ^{1}H NMR (400 MHz, CD_2Cl_2, -20ºC, δ, ppm): 7.54-7.46 (m, 15H, Ph,), 7.19 (s, 1H, =CH), 7.13 (s, 1H, =CH), 3.79 (s, 3H, NCH_3). ^{13}C{^{1}H} NMR (100.61 MHz, CD_2Cl_2, -20ºC, δ, ppm): 183.8 (br, $C_{carbene}$), 134.4 (d, ^2J(C,P) = 13.4 Hz, *o*-Ph), 132.3 (s, *p*-Ph), 129.6 (d, ^3J(C,P) = 10.8 Hz, *m*-Ph), 128.6 (d, ^1J(C,P) = 57.3 Hz, C_{ipso} Ph), 121.9 (s, =CH), 120.4 (s, =CH), 38.0 (s, NCH_3). MS (ESI): *m/z*: $[M - BF_4]^+$: calcd. for $C_{22}H_{21}AuN_2P$: 541.1108, found: 541.1005.

Compound 11. To a solution of **9** (50 mg, 0.06 mmol) in CH_2Cl_2 (5 mL) aqueous HCl (20 mL, d = 1.18 g/mL, 37%, 0.24 mmol) was added and the resulting mixture stirred for 10 min. The solvent was then evaporated to dryness under vacuum and the residue washed with diethyl ether (2 x 3 mL) to obtain a white solid. Yield: 46 mg (83%). ^{1}H NMR (400 MHz, CD_2Cl_2, δ, ppm): 11.20 (br, 1H, NH), 7.10 (s, 1H, =CH), 7.04 (s, 1H, =CH), 3.83 (s, 3H, NCH_3). ^{13}C{^{1}H} NMR (100.61 MHz, CD_2Cl_2, δ, ppm): 167.3 (s, $C_{carbene}$), 121.6 (s, =CH), 118.7 (s, =CH), 38.7 (s, NCH_3). MS (ESI): *m/z*: $[M + H]^+$: calcd. for $C_4H_7AuClN_2$: 314.9963, found:314.9961.

Compound [12]CF_3SO_3: To a solution of **9** (15 mg, 0.018 mmol) in CH_2Cl_2 (6 mL) 2,6-xylyl isocyanide (7 mg, 0.054 mmol) and CF_3SO_3H (4.8 μL, 0.054 mmol) were added and the resulting mixture stirred for 15 min. The solvent was evaporated to dryness under vacuum and the residue washed with diethyl ether (2 x 3 mL). Colorless crystals were obtained by slow diffusion of diethyl ether and hexane into a dichloromethane solution of the compound. Yield: 25 mg (83%). IR (CH_2Cl_2, cm^{-1}): ν(CN) 2216. ^{1}H NMR (400 MHz, CD_2Cl_2, 25ºC, δ, ppm): 12.30 (br, 1H, NH), 7.39 (t, ^3J(H,H) = 7.7 Hz, 1H, *p*-Xylyl), 7.27 (br, 1H, =CH), 7.22 (d, ^3J(H,H) = 7.7 Hz, 2H, *m*-Xylyl), 7.15 (br, 1H, =CH), 3.92 (s, 3H, NCH_3), 2.50 (s, 6H, CH_3 Xylyl). ^{13}C{^{1}H} NMR (100.61 MHz, CD_2Cl_2, 25ºC, δ, ppm): 174.7 (s, $C_{carbene}$), 158.6 (br, CN), 137.3, (s, *o*-Xylyl), 132.0 (s, *p*-Xylyl), 129.1 (s, *m*-Xylyl), 122.4, 120.7 (s, =CH), 38.6 (s, NCH_3) 19.0 (s, CH_3 Xylyl). MS (ESI): *m/z*: $[M - OTf]^+$: calcd. for $C_{13}H_{15}AuN_3$: 410.0931, found: 410.0927.

Compound 13. To a solution of compound **5** (40 mg, 0.095 mmol) in CH_2Cl_2 (10 mL) AgCN (13 mg, 0.095 mmol) was added and the

resulting suspension vigorously stirred for 30 min. The solution was filtered over diatomaceous earth and then the solvent evaporated to dryness under vacuum to give a white solid. Slow diffusion of hexane into a dichloromethane solution of the compound afforded colorless crystals. Yield: 32 mg (82%). IR (CH_2Cl_2, cm^{-1}): ν(CN) 2145. ^1H NMR (400 MHz, CD_2Cl_2, 25ºC, δ, ppm): 11.78 (br, 1H, NH), 7.36 (t, ^3J(H,H) = 7.6 Hz, 1H, *p*-Xylyl), 7.24 (d, ^3J(H,H) = 7.8 Hz, 2H, *m*-Xylyl), 7.00 (s, 1H, =CH), 1.99 (s, 6H, CH_3 Xylyl), 1.88 (s, 3H, =C-CH_3). $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2, 25ºC, δ, ppm): 179.7 (s, $C_{carbene}$), 136.4 (s, C_{ipso} Xylyl), 136.3, (s, *o*-Xylyl), 130.2 (s, *p*-Xylyl), 130.1 (s, =*C*-CH_3), 129.2 (s, *m*-Xylyl), 116.2 (s, =CH), 18.1 (s, CH_3 Xylyl), 9.8 (s, =C-*C*H_3). MS (ESI): *m/z*: [*M* + *H*]: calcd. for $C_{13}H_{15}AuN_3$: 410.0931, found: 410.0923.

Compound 14. To a solution of compound **5** (40 mg, 0.095 mmol) in acetone (10 mL) KSCN (9.3 mg, 0.095 mmol) was added and the resulting suspension vigorously stirred for 15 min. The solvent was then evaporated to dryness under vacuum. Dichloromethane (10 mL) was added to the residue and the solution filtered over diatomaceous earth. The dichloromethane solution was concentrated to 2 mL and hexane (7 mL) added to afford colorless crystals of the compound by slow diffusion. Yield: 28 mg (67%). IR (CH_2Cl_2, cm^{-1}): ν(CN) 2124. ^1H NMR (400 MHz, CD_2Cl_2, -20ºC, δ, ppm): 10.95 (br, 1H, NH), 7.35 (t, ^3J(H,H) = 7.6 Hz, 1H, *p*-Xylyl), 7.22 (d, ^3J(H,H) = 7.5 Hz, 2H, *m*-Xylyl), 7.03 (br, 1H, =CH), 1.97 (s, 6H, CH_3 Xylyl), 1.87 (s, 3H, =C-CH_3). $^{13}C\{^1H\}$ NMR (100.61 MHz, $(CD_3)_2CO$, -20ºC, δ, ppm): 173.0 (s, $C_{carbene}$), 136.4 (s, C_{ipso} Xylyl), 136.2, (s, *o*-Xylyl), 130.6 (s, *p*-Xylyl), 130.4 (s, =*C*-CH_3), 129.5 (s, *m*-Xylyl), 117.3 (s, =CH), 17.8 (s, CH_3 Xylyl), 9.6 (s, =C-*C*H_3). MS (ESI): *m/z*: $[M + H]^+$: calcd. for $C_{13}H_{15}AuN_3S$: 442.0652, found: 442.0648

Compound 15. To a solution of compound **5** (35 mg, 0.084 mmol) in acetone (10 mL) NaS_2CNEt_2 (19 mg, 0.084 mmol) was added and the mixture vigorously stirred for 15 min. The solvent was then evaporated to dryness under vacuum. Dichloromethane (10 mL) was added and the solution filtered over diatomaceous earth. Evaporation of the solvent afforded a brownish solid. Yield: 32 mg (73%). ^1H NMR (400 MHz, CD_2Cl_2, δ, ppm): 7.33 (t, ^3J(H,H) = 7.6 Hz, 1H, *p*-Xylyl), 7.21 (d, ^3J(H,H) = 7.6 Hz, 2H, *m*-Xylyl), 7.08 (s, 1H, =CH), 3.87 (q, ^3J(H,H) = 7.0 Hz, 4H, CH_2CH$_3$) 2.00 (s, 6H, CH_3 Xylyl), 1.87 (s, 3H, =C-CH_3), 1.22 (t, ^3J(H,H) = 7.0 Hz, 6H, CH_2CH_3). ^1H NMR (400 MHz, CD_2Cl_2, -80ºC, δ, ppm): 12.71 (br, 1H, NH), 7.33 (t, ^3J(H,H) = 7.4 Hz, 1H, *p*-Xylyl), 7.20 (d, ^3J(H,H) = 7.5 Hz, 2H, *m*-Xylyl), 6.99 (s, 1H, =CH), 3.72 (br, 4H, CH_2CH$_3$) 1.88 (s, 6H, CH_3 Xylyl), 1.77 (s, 3H, =C-CH_3), 1.11 (br, 6H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2 , -80ºC, δ, ppm): 203.4 (s, S-C), 173.8 (s, $C_{carbene}$), 135.6 (s, C_{ipso} Xylyl, *o*-Xylyl), 128.9 (s, *p*-Xylyl), 128.1 (s, *m*-Xylyl), 128.0 (s, =*C*-CH_3), 114.9 (s, =CH), 48.8 (s, CH_2 Et), 17.6 (s, CH_3 Xylyl), 11.4 (s, CH_3 Et), 9.7 (s, =C-CH_3). MS (ESI): *m/z*: $[M + H]^+$: calcd. for $C_{17}H_{25}AuN_3S_2$: 532.1155, found: 532.1156.

ASSOCIATED CONTENT

Supporting Information.

NMR spectra of the new compounds (pdf). The Supporting Information is available free of charge on the ACS Publications website.

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Notes

The authors declare no competing financial interests.

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