A Facile One-Step Synthesis of a Lipophilic Gold(I) Carbene Complex – X-ray Crystal Structures of LAuCl and LAuC≡CH (L = 1,3-di-*tert*-Butyl imidazol-2-ylidene)

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The reaction of Au(CO)Cl with 1,3-di-*tert*-butylimidazol-2-ylidene and 1,3-dimesitylimidazol-2-ylidene in toluene at room temperature results in CO evolution and readily affords in high yield the adducts **1a** and **1b**, respectively. The reaction of **1a** and **1b** with ethynylmagnesium chloride in THF yields **2a** and **2b**, respectively. The crystal structures of **1a**, **1b**, and **2a** were determined.

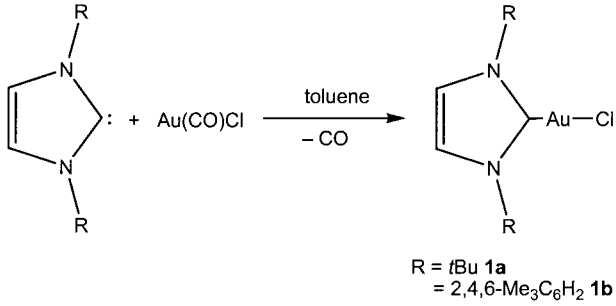
Introduction

Recently there has been a resurgence of interest in the chemistry of gold compounds in general and that of gold(I) compounds in particular. A major driving force for this interest has been the utility of soluble gold compounds in various applications ranging from precursor for gold nanoparticles[1,2] to drugs,[3] and catalysts.[4–6] Among Au^I compounds, there has been considerable success in the preparation of alkynyl gold complexes. These are among the most stable organogold complexes.[7] Although dinuclear complexes such as $R_3PAuC{\equiv}CAuPR_3$ have been known for some time,[8,9] Schmidbaur and co-workers have recently isolated terminal acetylides of gold in the form of gold ethynyl complexes $RAuC{\equiv}CH$ (R = $MePH_2$, Me_3P).[10] A key factor in this successful assembly is the utility of appropriate phosphane ligands in stabilizing such compounds. It has also been shown that these compounds can be used as reliable synthons in crystal engineering owing to strong and predictable aurophilic [Au^I–Au^I] interactions.[11] Another interesting aspect of these complexes has been the ability to exhibit rich photophysical and photochemical behaviour.[12–15]

One of the key challenges in Au^I chemistry remains the availability of reasonably stable synthons, which would allow simple substitution reactions. The use of sterically hindered N-heterocyclic carbenes[16] for such a purpose was regarded as ideal.[17,18] Accordingly, in this paper we describe a facile one-step, high yield synthesis of a lipophilic gold(I)-N-heterocyclic carbene complex LAuCl. We also demonstrate the synthetic utility of the latter by preparing the terminal acetylide $LAuC{\equiv}CH$. The X-ray crystal structures of LAuCl and $LAuC{\equiv}CH$ are described. During the preparation of this manuscript Baker and co-workers reported the synthesis of LAuCl **1a** complex by transmetallation of LAgCl and $(Me_2S)AuCl$.[19]

Results and Discussion

The reaction of Au(CO)Cl with a stoichiometric amount of N-heterocyclic carbene (1,3-di-*tert*-butylimidazol-2-ylidene or 1,3-dimesitylimidazol-2-ylidene) in toluene at room temperature results in a vigorous evolution of carbon monoxide and the formation of the corresponding carbene adducts **1a** and **1b**, respectively (Scheme 1). Thus this synthetic method represents a viable and rational route for the preparation of N-heterocyclic carbene adducts of Au^I.



Scheme 1. Synthesis of Au^I N-heterocyclic carbene complexes.

Compounds **1a** and **1b** have been unambiguously characterized by means of spectroscopic, spectrometric, and crystallographic techniques. Both **1a** and **1b** are colorless crystalline solids and are thermally stable. They decompose

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with melting at 170 °C and 210 °C respectively. The EI mass spectrum of **1a** revealed that the most intense peak appears at *m*/*z* 320 and corresponds to the loss of one *tert*-butyl group and the chlorine atom from the molecular ion. A similar peak at *m*/*z* 303 in **1b** is due to [M^+ – Cl – Au – H]. The ^{1}H NMR spectrum of **1a** exhibits two singlets (δ = 1.83 and 7.26 ppm) for the protons of the *tert*-butyl groups and (HC=CH) of the carbene. They are shifted downfield relative to the 1,3-di-*tert*-butylimidazol-2-ylidene (δ = 1.51 and 7.06 ppm). The resonances of *o*-Me and *p*-Me in **1b** (δ = 1.75 and 2.13 ppm) are observed upfield relative to the carbene (δ = 2.08 and 2.31 ppm) whereas the (HC=CH) protons in **1b** (δ = 7.46 ppm) are found downfield relative to the carbene (δ = 7.07 ppm). A weak ^{13}C NMR resonance (δ = 167.6 ppm for **1a**) can be assigned to the carbene carbon atom. However, in case of **1b** no resonance downfield to 150 ppm was detected which could be assigned to the carbene carbon.

Single crystals of **1a** and **1b** suitable for X-ray structural analysis were obtained from their toluene solutions. Compound **1a** crystallizes with one molecule of toluene. The molecular structures of **1a** and **1b** are shown in Figure 1 and Figure 2, respectively, and selected metric parameters are given in Table 1. Compound **1a** crystallizes in the monoclinic space group $P2_1/c$ whereas compound **1b** in the orthorhombic space group *Fdd*2, respectively. The X-ray crystal structures of **1a** and **1b** reveal that the compounds are monomeric adducts of the N-heterocyclic carbene Au^I chloride, no Au^I–Au^I interactions were observed.

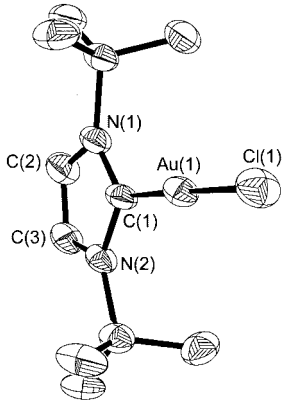


Figure 1. Molecular structure of **1a**. Toluene molecule and hydrogen atoms are omitted for clarity, thermal ellipsoids are shown with 50% probability.

The Au–Cl distances 2.290(2) Å in **1a** and 2.281(4) Å in **1b** are shorter than the Au–Cl distance in [Au(Me$_2$-bimy)Cl] [2.338(2) Å][17] but comparable to that in {PhCH$_2$N(CH)$_2$N(COPh)C}AuCl [2.286(2) Å][18] and [Au(Me$_2$-imyl)Cl] [2.288(3) Å].[20] The Au–C bond lengths 1.983(8) Å in **1a** and 1.933(1) Å in **1b** are similar to those found in [Au(Me$_2$-bimy)Cl][17] [1.985(1) Å], {PhCH$_2$N(CH)$_2$N(COPh)C}AuCl[18] [1.970(1) Å] and in [Au(Me$_2$-imyl)Cl][20] [1.98(1) Å]. The average N–C(1) distance of the ligand in **1a** 1.369 Å and 1.377 Å in **1b** are similar to those observed in [Au(Me$_2$-bimy)Cl] (1.371 Å)[17] and in

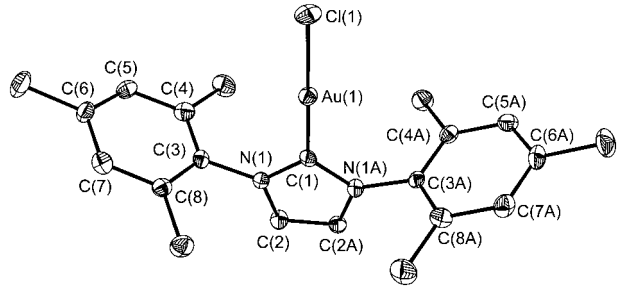


Figure 2. Molecular structure of **1b**. Hydrogen atoms are omitted for clarity, thermal ellipsoids are shown with 50% probability.

Table 1. Selected bond lengths [Å] and angles [°] of **1a**, **1b**, and **2a**.

	1a	**1b**	**2a**
Au(1)–C(1)	1.983(8)	1.933(1)	2.05(1)
Au(1)–Cl(1)	2.290(2)	2.281(4)	
N(1)–C(1)	1.376(9)	1.377(9)	1.37(2)
N(2)–C(1)*	1.362(1)	1.377(9)	1.34(2)
C(2)–C(3)*	1.315(1)	1.372(8)	1.34(2)
Au(1)–C(12)			2.04(2)
C(12)–C(13)			1.11(2)
C(1)–Au(1)–Cl(1)	178.9(2)	180.0(1)	
N(2)–C(1)–N(1)*	104.5(7)	102.6(9)	107(1)
N(1)–C(1)–Au(1)	128.4(5)	128.7(4)	125(2)
N(2)–C(1)–Au(1)*	127.1(5)	128.7(4)	128(1)
C(1)–Au(1)–C(12)			178.7(6)
Au(1)–C(12)–C(13)			171.3(2)

* N(2) corresponds to N(1A) and C(3) corresponds to C(2A) in case of **1b**.

{PhCH$_2$N(CH)$_2$N(COPh)C}AuCl (1.355 Å).[18] The N(1)–C(1)–N(2) angles within the N_2C_3 five-membered ring of the carbene ligand in **1a** 104.5(7)° and 102.6(9)° in **1b** are similar to that in {PhCH$_2$N(CH)$_2$N(COPh)C}AuCl 104.4(1)° but are slightly smaller than those in [Au(Me$_2$-bimy)Cl][17] 108(1)° and in [Au(Me$_2$-imyl)Cl][20] [106(10)°]. In the crystal lattice **1a** forms an extended network through agostic interaction of Au with one proton of the *t*Bu group from neighbouring molecule (2.96 Å) and also interacts with one *o*-H of the solvating toluene molecule (3.06 Å) present in the crystal lattice (Figure 3). These are in the range 1.95–3.20 Å reported for similar H···Au interactions.[21] In the case of **1b** all aromatic hydrogens are involved in hydrogen bonds. Hydrogen atoms on C(7) and C(7A) are bonded by agostic interactions to Au from two different neighbouring molecules with a H···Au distance of 3.18 Å which is comparable to the values in the range 1.95–3.20 Å reported for similar H···Au interactions[21] but slightly longer than those in **1a**. Hydrogen atoms present on C(5), C(5A), C(2) and C(2A) are bonded to Cl atoms of neighbouring molecules in a symmetrical manner as shown in Figure 4. The corresponding H···Cl distances are 2.88 Å and 2.90 Å which agrees with the reported values of intermediate to long range intermolecular interactions.[21,22]

Reaction of the adducts **1a** and **1b** with ethynylmagnesium chloride in THF smoothly affords the corresponding gold(I) ethynyls **2a** and **2b** in good yields (Scheme 2). Compounds **2a** and **2b** decompose with melting at 155 °C and

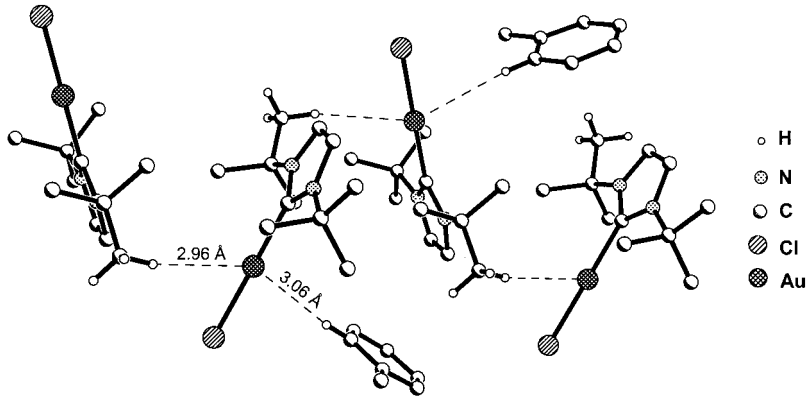


Figure 3. Perspective view of the agostic interactions of Au with *o*-H of the toluene molecule and with H atom of *t*Bu of the carbene ligand in the crystal state of **1a**, forming a zig-zag chain.

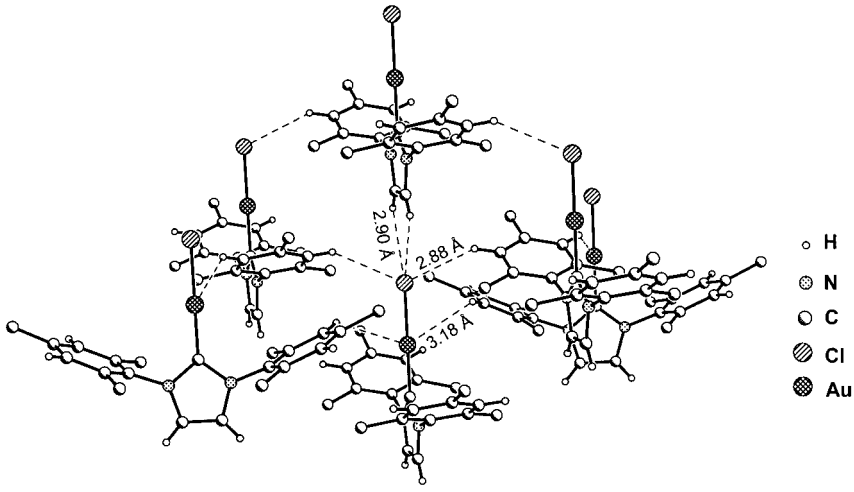
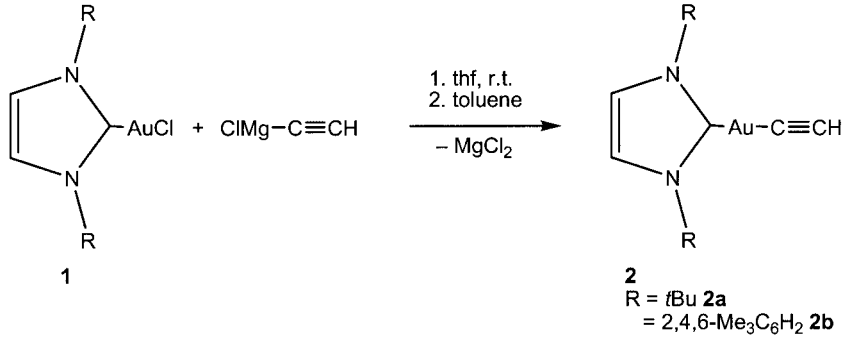


Figure 4. Perspective view of the chain formation through the agostic interaction of the aromatic protons of the carbene ligand with Au and Cl atoms in **1b**.

240 °C respectively. The EI mass spectrum of **2a** revealed the molecular ion peak as the most intense one (*m*/*z* 402), whereas the ion at *m*/*z* 303 in **2b** is the most intense peak and corresponds to the loss of Au and C_2H_2 units from the molecular ion. The IR spectrum of **2a** shows a sharp band (1979 cm^{-1}) which can be attributed to the ethynyl stretching frequency. The corresponding stretching mode for **2b** appears at 1982 cm^{-1}. The ^1H NMR spectrum of **2a** shows the ethynyl proton to resonate at δ = 1.22 ppm whereas the same proton in **2b** resonates at δ = 0.86 ppm. The resonances of the carbene ligand in **2a** and **2b** are shifted downfield relative to the free carbenes. The ^1H NMR spectrum of **2a** shows two singlets (δ = 1.84 and 7.29 ppm) for the protons of the *tert*-butyl groups and (HC=CH) of the carbene. They are shifted downfield relative to the free carbene, (δ = 1.51 and 7.06 ppm). The resonances of *o*-Me and *p*-Me in **2b** (δ = 2.13 and 2.34 ppm) are observed downfield (δ = 2.08 and 2.31 ppm) as well as the (HC=CH) protons



Scheme 2. Synthesis of the monomeric terminal ethynyl Au^I complexes **2a** and **2b**.

in **2b** (δ = 7.38 ppm) relative to the free carbene (δ = 7.07 ppm). A weak ^{13}C NMR resonance (δ = 187.9 ppm for **2a**) can be assigned to the N–C–N carbon atom and it is shifted downfield relative to **1a** (δ = 167.6 ppm).

Single crystals of **2a** suitable for X-ray structural analysis were obtained from its toluene solution. Repeated efforts to obtain a better data set for **2a** were not successful due to the fast crystal decomposition caused by liberation of the solvating toluene molecules. The most optimistic dataset is reported here. The molecular structure of **2a** is shown in Figure 5 and selected metric parameters are given in Table 1. Compound **2a** is isomorphous to **1a**. The X-ray crystal structure of **2a** reveals that the compound is a monomeric adduct of the N-heterocyclic carbene Au^I acetylide with no Au^I–Au^I interactions. The Au(1)–C(12) distance of 2.04(2) Å in **2a** is similar to that of [($MePh_2P$)AuC≡CH] 2.008(4) Å.[10] The C(12)–C(13) distance of the ethynyl moiety in **2a** [1.11(2) Å] is comparable to that in [($MePh_2P$)AuC≡CH] [1.187(6) Å].[10] The Au(1)–C(12)–C(13) angle of 171.3(2)° in **2a** is comparable to that in [($MePh_2P$)AuC≡CH] [178.9(4)°].[10] The C(1)–Au(1)–C(12) angle in **2a** is close to linearity. The N(1)–C(1)–N(2) angle [107(1)°] is slightly wider than that of the parent compound **1a** [104.5(7)°]. The H····Au agostic interactions observed in the crystal of **2a** are analogous to that of **1a** (Figure 6). Thus the contacts are 2.97 Å and 3.12 Å corresponding to the *o*-H of toluene and H atom of *t*Bu group of the carbene. Due to the disordered toluene molecule in **2a** in two positions with occupancy ratio 87:13 the 2.97 Å distance is attributed to the major 87% part and 3.04 Å distance is attributed to the minor 13% part.

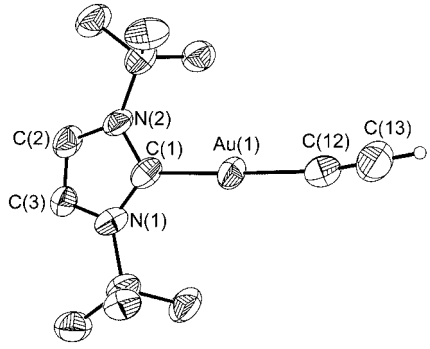


Figure 5. Molecular structure for **2a**. Only the hydrogen atom on the ethynyl group is shown. The toluene molecule is omitted for clarity, thermal ellipsoids are shown with 50% probability.

In summary, we have demonstrated a single step synthesis of N-heterocyclic carbene adducts of gold(I) chloride. The utility of complexes thus synthesized stems from the stability of these complexes which have been used to prepare the first N-heterocyclic carbene gold(I) ethynyl which contains a terminal –C≡CH group.

Experimental Section

All manipulations were performed under a dry and oxygen free atmosphere (N_2 or Ar) using Schlenk line and glove box techniques. Solvents were purified according to conventional procedures and were freshly distilled prior to use. Au(CO)Cl,[23] 1,3-di-*tert*-butylimidazol-2-ylidene and 1,3-dimesitylimidazol-2-ylidene[24] were synthesized according to literature.

Synthesis of (1,3-Di-*tert*-butylimidazol-2-ylidene)gold(I) Chloride (1a): In a glove box a 100 mL Schlenk flask was charged with Au(CO)Cl (1.90 g, 7.30 mmol) and topped with a dropping funnel containing 1,3-di-*tert*-butylimidazol-2-ylidene (1.31 g, 7.25 mmol). Toluene (50 mL) was added to the dropping funnel and the resulting solution was added dropwise to the flask at room temperature. The mixture was stirred until the CO evolution had ceased. It was filtered and the residue was washed with toluene (30 mL). The combined filtrate was concentrated until the compound begins to crystallize and then kept at 0 °C for two days to afford colorless crystals of (1,3-di-*tert*-butylimidazol-2-ylidene)gold(I) chloride **1a** (1.8 g), the mother liquor afforded another crop (0.6 g), combined yield 2.48 g, 83%, m.p. 170 °C (decomp.). $C_{11}H_{20}AuClN_2$ (412): calcd. C 32.04, H, 4.84, N, 6.79; found C 32.27, H, 5.01, N, 6.80. EI-MS: *m/z* (%) 412 (44) [M^+], 376 (14) [M^+ – H – Cl], 356 (14) [M^+ – *t*Bu – H], 320 (100) [M^+ – Cl – *t*Bu], 264 (36) [M^+ – 2 *t*Bu –

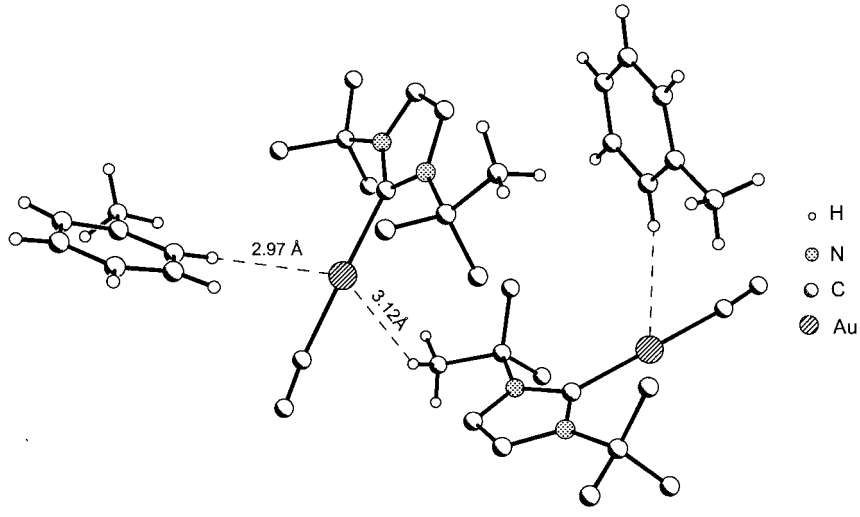


Figure 6. Perspective view of the agostic interactions of Au with *o*-H of the toluene molecule and with H atom of *t*Bu of the carbene ligand in the crystal leading to the formation of a zig-zag chain in the crystal lattice in **2a**.

Cl – H]. ^{1}H NMR (200 MHz, CD_3CN): δ = 1.83 (s, 18 H, *tBu*), 7.26 (s, 2 H, *HC*=C*H*) ppm. ^{13}C NMR (50 MHz, CD_3CN): δ = 31.2 (s, C*Me*$_3$), 59.0 (s, *C*Me$_3$), 117.7 (s, H*C*=*C*H), 167.6 (s, N*C*N) ppm. IR (KBr, Nujol): $\tilde{\nu}$ = 1646, 1543, 1515, 1406, 1387, 1304, 1262, 1236, 1209, 1183, 1097, 1021, 865, 801, 720, 693, 626 cm^{-1}.

Synthesis of (1,3-Dimesitylimidazol-2-ylidene)gold(I) Chloride (1b): The preparation of **1b** was carried out by using a similar procedure as that for **1a**. The quantities of the reactants used are Au(CO)Cl (1.72 g, 6.60 mmol) and 1,3-dimesitylimidazol-2-ylidene (1.97 g, 6.50 mmol). Yield 2.3 g, 67%, m.p. 210 °C (decomp.). $C_{21}H_{24}AuClN_2$ (536): calcd. C 47.01, H, 4.47, N, 5.22; found C 46.63, H, 4.51, N, 4.95. EI-MS: *m/z* (%) 536 (28) [M$^+$], 500 (92) [M$^+$ – Cl – H], 303 (100) [M$^+$ – Cl – Au – H]. ^{1}H NMR (300 MHz, [D$_8$]THF): δ = 1.75 (s, 12 H, *o*-C*H*$_3$), 2.13 (s, 6 H, *p*-C*H*$_3$), 6.99 (s, 4 H, *m*-*H*), 7.46 (s, 2 H, *HC*=C*H*) ppm. ^{13}C NMR (126 MHz, [D$_8$]-THF): δ = 17.4 (s, *o*-*C*H$_3$), 21.3 (s, *p*-*C*H$_3$), 123.6 (s, H*C*=*C*H), 124.3 (s, mesityl C^{3,5}), 130.0 (s, mesityl C^1), 135.6 (s, mesityl C^{2,6}), 140.2 (s, mesityl C^4).

Synthesis of (1,3-Di-*tert*-butylimidazol-2-ylidene)(ethynyl)gold(I) (2a): (1,3-Di-*tert*-butylimidazol-2-ylidene)gold(I) chloride (1.0 g, 2.43 mmol) was dissolved in THF (30 mL). To this solution was added 5.1 mL (2.55 mmol, 1.05 equiv.) of 0.5 M, THF solution of ethynylmagnesium chloride. The solution was stirred overnight at room temperature and after the removal of all the volatiles, the crude product was extracted with toluene (45 mL). Crude yield (0.72 g, 72%), m.p. 155 °C (decomp.). $C_{13}H_{21}AuN_2$ (402): calcd. C 38.80, H, 5.22, N, 6.96; found C 38.79, H, 5.10, N, 6.85. EI-MS: *m/z* (%) 402 (100) [M$^+$], 376 (20) [M$^+$ –H – HC=CH], 320 (60) [M$^+$ – *t*Bu – HC=CH], 290 (80) [M$^+$ – *t*Bu – HC=CH – 2 Me]. ^{1}H NMR (500 MHz, [D$_8$]THF) 1.22 (s, 1 H, –C≡C*H*), 1.84 (s, 18 H, *t*Bu) 7.29 (d, 2 H, *HC*=C*H*) ppm. ^{13}C NMR (126 MHz, [D$_8$]THF): δ = 32.0 (s, C*Me*$_3$), 59.2 (s, *C*Me$_3$), 89.6 (s, –*C*≡CH), 117.3 (s, H*C*=*C*H), 120.0 (s, –C≡*C*H),187.9 (s, N*C*N) ppm. IR (KBr, Nujol): $\tilde{\nu}$ = 1979, 1665, 1567, 1456, 1407, 1375, 1301, 1261, 1234, 1219, 1194, 1094, 1025, 933, 865, 801, 726, 696, 661, 627, 601 cm^{-1}.

Synthesis of (1,3-Dimesitylimidazol-2-ylidene)(ethynyl)gold(I) (2b): The preparation of **2b** was carried out by using a similar procedure as that for **2a**. The quantities of the reactants used are (1,3-dimesitylimidazol-2-ylidene)gold(I) chloride (1.0 g, 1.86 mmol) and 4.0 mL (2.0 mmol, 1.07 equiv.) of 0.5 M, THF solution of ethynylmagnesium chloride. Yield 0.67 g, 72%, m.p. 240 °C (decomp.). $C_{23}H_{25}AuN_2$ (526.5): calcd. C 52.42, H, 4.74, N, 5.32; found C 51.87, H, 4.82, N, 5.43. EI-MS: *m/z* (%) 526 (64) [M$^+$], 500 (60) [M$^+$ – C_2H – H], 303 (100) [M$^+$ – C_2H – Au – H]. ^{1}H NMR (300 MHz, [D$_8$]THF): δ = 0.86 (s, 1 H, –C≡C*H*), 2.13 (s, 12 H, *o*-C*H*$_3$), 2.34 (s, 6 H, *p*-C*H*$_3$), 7.04 (s, 4 H, *m*-*H*), 7.38 (s, 2 H, *HC*=C*H*) ppm. ^{13}C NMR (75 MHz, [D$_8$]THF): δ = 18.0 (s, *o*-*C*H$_3$), 21.0 (s, *p*-*C*H$_3$), 88.0 (s, –*C*≡CH), 123.5 (s, H*C*=*C*H), 124.4 (s, –C≡*C*H), 130.0 (s, mesityl C^{3,5}), 135.6 (s, mesityl C^1), 136.4 (s, mesityl C^{2,6}), 139.9 (s, mesityl C^4), 190.6 (s, N*C*N) ppm. IR (KBr, Nujol): $\tilde{\nu}$ = 1982, 1730, 1606, 1559, 1484, 1409, 1376, 1339, 1290, 1234, 1164, 1028, 926, 852, 755, 705, 629, 574 cm^{-1}.

X-ray Structure Determinations for 1a, 1b, and 2a: A suitable crystal of each compound was mounted on a glass fiber and coated with paraffin oil. Diffraction data for **1a** and **2a** were collected on a Siemens-Stoe AED2 four-circle instrument and the measurements were made with graphite-monochromated Mo-*K*α radiation (λ = 0.71073 Å). Data for **1b** was obtained on Bruker three circle diffractometer equipped with a SMART 6000 CCD detector using

Table 2. Crystallographic data for the structural analyses of compounds **1a, 1b**, and **2a**.

Compound	**1a**·C_7H_8	**1b**	**2a**·C_7H_8
Formula	$C_{18}H_{28}AuClN_2$	$C_{21}H_{24}AuClN_2$	$C_{20}H_{29}AuN_2$
Fw	504.84	536.84	494.42
T [K]	200(2)	100(2)	200(2)
λ [Å]	0.71073	1.54178	0.71073
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/c$	*Fdd*2	$P2_1/c$
a [Å]	9.355(3)	14.715(3)	9.459(4)
b [Å]	10.291(3)	28.748(6)	10.350(6)
c [Å]	20.56(3)	9.678(2)	20.714(12)
α [deg]	90.00	90.00	90.00
β [deg]	97.84(7)	90.00	98.25(6)
γ [deg]	90.00	90.00	90.00
V [Å^3]	1961(3)	4094(2)	2007(2)
Z	4	8	4
D(calcd.) [g·cm^{-3}]	1.710	1.742	1.636
μ(Mo-*K*α) [mm^{-1}]	7.637	–	7.322
μ(Cu-*K*α) [mm^{-1}]	–	14.732	–
F(000)	984	2080	968
θ Range [deg]	3.59 to 24.98	5.68 to 59.04	3.57 to 24.92
Index range	$-11 \le h \le 11$	$-16 \le h \le 16$	$-11 \le h \le 11$
	$-10 \le k \le 12$	$-31 \le k \le 31$	$-12 \le k \le 12$
	$-23 \le l \le 24$	$-10 \le l \le 10$	$-24 \le l \le 24$
Reflections collected	5093	7611	5214
Independent reflections	3416	1454	3471
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3416/0/206	1454/1/122	3471/263/278
R_1, R_2 [$I > 2\sigma(I)$][a]	0.0489, 0.1296	0.0127, 0.0299	0.0777, 0.1839
R_1, R_2 (all data)[a]	0.0532, 0.1348	0.0128, 0.0300	0.1021, 0.2084
S	1.092	1.106	1.075
Δρ(min.), Δρ(max.)/e·Å^3	2.660, –2.084	0.487, –0.422	2.814, –3.564

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $R_2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$.

mirror monochromated Cu-$K\alpha$ radiation (λ = 1.54178 Å) (Table 2). Compound **1b** was refined as a recemic twin with ratio of the components 35.3:64.7. The structures were solved by direct methods using SHELXS-97[25] and refined against F^2 on all data by full-matrix least-squares with SHELXL-97[26]. All non-hydrogen atoms were refined anisotropically. The disordered toluene molecule in **2a** was refined with distance and geometry restrains and restrains for anisotropic displacement parameters. Neutral-atom scattering factors (including anomalous scattering) were taken from the International Tables for X-ray Crystallography. Hydrogen atoms were included at geometrically calculated positions except for protons of the methyl group of disordered toluene molecule in **2a** and refined using a riding model.

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