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Nitrogen Acyclic Gold(I) Carbenes: Excellent and Easily Accessible Catalysts in Reactions of 1,6-Enynes

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Complexes [AuCl{C(NHR)(NHR′)}] and [AuCl{C(NHR)(NEt$_2$)}] (R = ^{t}Bu, *p*-Tol, Xylyl, *p*-C$_6$H$_4$-COOH, *p*-C$_6$H$_4$COOEt, R′ = Me, ^{n}Bu, ^{i}Pr, ^{n}heptyl, *p*-Tol) have been prepared by reaction of the corresponding isocyanogold complexes [AuCl(CNR)] with either primary amines or diethylamine. All the prepared carbenes are reactive and highly selective catalysts for skeletal rearrangement, methoxycyclization of 1,6-enynes, and other mechanistically related gold-catalyzed transformations. Overall, these easily accessible nitrogen acyclic carbene (NAC) gold complexes were not second to NHC complexes and were advantageous to obtain different products.

Introduction

The importance of gold complexes with nitrogen heterocyclic carbenes (NHCs) as catalysts in organic synthesis has been well demonstrated.[1−5]

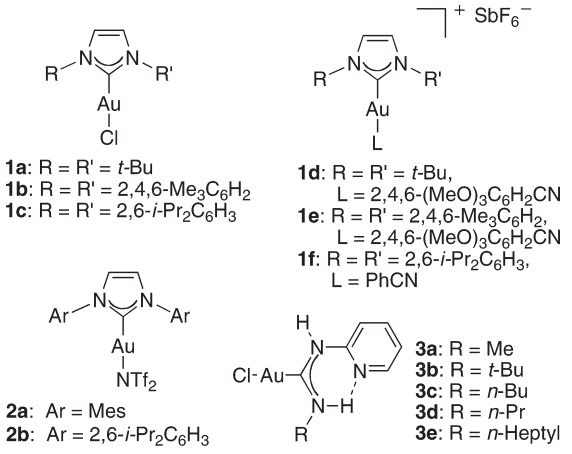

Figure 1. NHCs and HBHCs used as catalysts for skeletal rearrangement of enynes.

Many heterocyclic gold carbenes (Figure 1) have been found to be good precatalysts for reactions of enynes.[2,6−9] In these reactions, the catalyst is formed in solution from complexes such as **1a**−**c** after chloride abstraction with a silver salt. Alternatively, cationic complexes stabilized with benzonitrile ligands **1d**−**f** have also been used as catalysts.[10] Similar complexes with NTf$_2$ (Tf = trifluoromethanesulfonyl) as a labile ligand (**2a**,**b**),[11,12] are also catalytically active.

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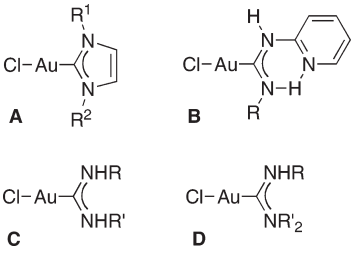


Figure 2. Gold(I) complexes with NHC (**A**), HBHC (**B**), and NAC (**C** and **D**) ligands.

The recently reported gold(I) carbene complexes of the type AuCl{C(NHR)-(NHPy-2)}][13] (**3**) also turned out to be good precatalysts in the skeletal rearrangement of enynes.[14] These carbenes have been called HBHCs (hydrogen bond supported heterocyclic carbenes) because the hydrogen-bonded cyclic structure (Figure 2, **B**) is maintained in solution.[13,14] These HBHCs also happened to catalyze efficiently the alkoxycyclization of enynes in alcohols as solvent.[14] As the intramolecular hydrogen bond is split in the presence of alcohols,[14] under the reaction conditions these catalysts should be acting as nitrogen acyclic carbene (NAC) gold complexes (Figure 2, **C** and **D**). This observation might be interesting for catalytic purposes because it is easier to prepare series of gold carbene complexes with a systematic variation of their steric and electronic properties in NAC than in NHC or HBHC systems. For this purpose, the rather general addition of primary or secondary amines to isocyanide gold complexes will yield the corresponding carbene gold complex combining the substituents provided by the two organic fragments.

Therefore, we decided to focus on the catalytic activity of nitrogen acyclic gold carbenes in the skeletal rearrangement, methoxycyclizations of 1,6-enynes, and mechanistically related processes, to compare the catalytic behavior of these NACs with the results obtained not only with the well-known NHCs but also with the recently reported HBHCs. For this purpose, we have synthesized different series of NAC gold(I) complexes of the type [AuCl{C(NHR)(NHR′)}] (Figure 2, **C**) or [AuCl{C(NHR)(NEt_2)}] (Figure 2, **D**) by nucleophilic addition of primary amines or diethylamine to isocyanogold complexes.

Results and Discussion

Synthesis and Structural Characterization of Gold Carbene Complexes. The neutral gold carbene catalysts **4**−**8** were synthesized by nucleophilic attack to gold alkyl or aryl isocyanide complexes [AuCl(CNR)] (R = *p*-C_6H_4COOH,[15] *p*-C_6H_4COOEt, ^{t}Bu,[16] *p*-Tol,[17] Xylyl[18]) with differently hindered primary amines or with a secondary amine such as diethylamine (Scheme 1). The starting isocyano-gold complexes had been previously reported, except [AuCl(CN*p*-C_6H_4COOEt)],

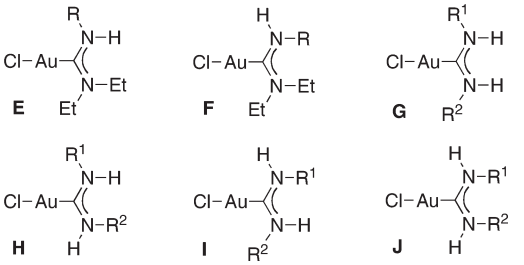
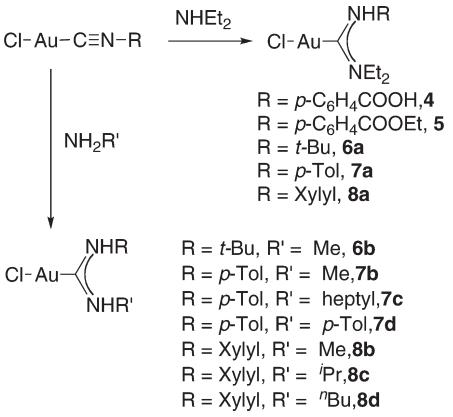


Figure 3. Possible stereoisomers for the NAC complexes.

Scheme 1. Synthesis of the Gold Carbene Derivatives



which was obtained from [AuCl(tht)] (tht = tetrahydrothiophene)[19] by substitution of tht with CN(*p*-C_6H_4-COOEt),[15] as reported for similar gold compounds.[20] The complexes [AuCl{C(NH^{t}Bu)(NEt_2)}][21] (**6a**) and [AuCl{C(NH*p*-Tol)(NH*p*-Tol)}][22] (**7d**) have already been published.

The gold NAC complexes were identified by elemental and spectroscopic analysis. The carbene C−N bond shows a considerable multiple character, which produces an important restriction to rotation and can give rise to stereoisomers (Figure 3).

Two stereoisomers (**E** and **F**) are possible for carbenes from secondary amines, but **F** looks clearly disfavored on the grounds of steric factors. In fact, for the latter, the less hindered **E** stereoisomer has been confirmed in the solid state by X-ray diffraction studies in the complexes [Au(C≡C*p*-R-C_6H_4){C(NH^{t}Bu)(NEt_2)}] (R = NO_2, *p*-NO_2-C_6H_4, (*E*)-CH=CH*p*-NO_2-C_6H_4),[23] [{AuC(NH^{t}Bu)(NEt_2)}$_2$-(μ-C≡CC_6H_4C≡C)],[24] [Au(*C*-acac){C(NH^{t}Bu)(NEt_2)}],[24] and [Au{C(NH^{t}Bu)(NEt_2)}{$CH_2S(O)Me_2$}]ClO_4,[24] whereas **F** has not been observed. The **E** stereoisomer was also confirmed in the solid state by X-ray diffraction studies, and in solution by NOE experiments, for the gold carbene complexes [AuCl{C(NEt_2)-(NHPy-2)}][13] and [AuR{C(NEt_2)(NHPy-4)}] (R = C_6F_5, Fmes).[25] Stereoisomer **E** is also the only one observed in this

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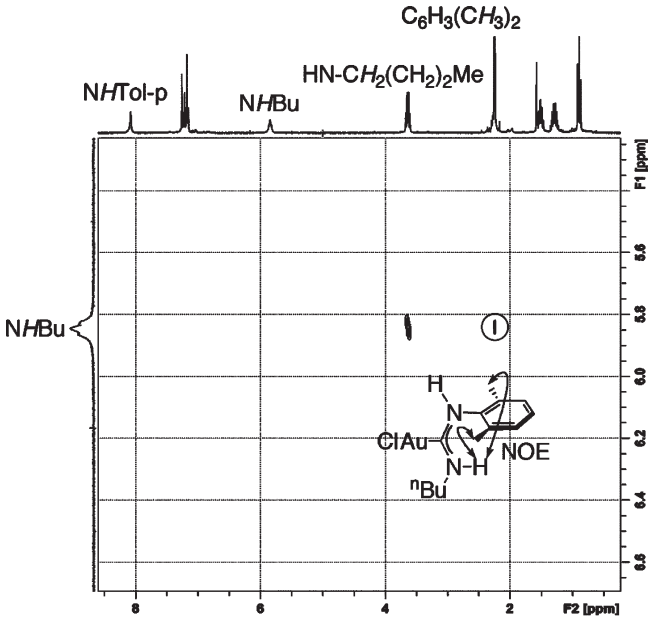

Figure 4. $^1H-^1H$ NOESY spectrum of **8d** (N*H*Bu region) registered at 295 K. The N*H*Bu shows a NOE with the methyl hydrogen atoms of the 2,6-xylyl group at 2.24 ppm (cross-peak in the circle), as well as with the hydrogen atoms of the contiguous methylene of the ^{n}Bu chain.

work in the ^1H NMR spectra of all the carbene gold complexes [AuCl{C(NHR)(NEt_2)}] (**4**, **5**, and **6a**−**8a**).

Up to four stereoisomers (**G**−**J**) are possible for complexes formed from primary amines. Often, more than one stereoisomer is observed, and these data are given in the Experimental Section. Although **J** is clearly the most disfavored for steric reasons, it is not easy to predict which of the other three stereoisomers should be preferred. The configuration of the major stereoisomer was assigned for all the complexes on the basis of NOE experiments (slow exchange was observed during the experiments at room temperature in some cases, and some NOE experiments were carried out at 243 K). Figure 4 shows the $^1H-^1H$ NOESY spectrum of **8d**, in which a NOE is observed between the hydrogen of the N*H*Bu group and the singlet of the methyl substituents of the 2,6-xylyl. The major stereoisomer for all the neutral complexes having at least one aryl group (R^1 = aryl; these are all, except **6b**) is stereoisomer **I**, having the aryl *anti* to the gold atom, regardless of R^2; moreover, **I** is the only stereoisomer observed for **8c** and **8d**. For complex **6b** (R^1 = ^{t}Bu; R^2 = Me) the major stereoisomer is **H**, with the bulky ^{t}Bu group *syn* to the gold atom.

Catalytic Reactions. The results obtained for the gold-catalyzed skeletal rearrangement of 1,6-enyne **9a** are summarized in Table 1. All the gold carbenes **4**−**8** catalyze this reaction, but the efficiency and selectivity observed change with the substituents of the carbene. Up to three different products have been isolated in the skeletal rearrangement reaction of **9a**: the product of exo cyclization, **10a**, the product of the endo cyclization, **12a**,[26] and the diene **11a** arising from the isomerization of the endo cyclic double bond of **10a**.[3a,c] Diene **11a** has been observed in reactions of **9a** catalyzed by $FeCl_3$ and as a minor product in reactions catalyzed by different Au(I) complexes.[3c] Then, in this

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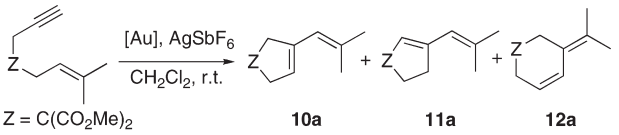
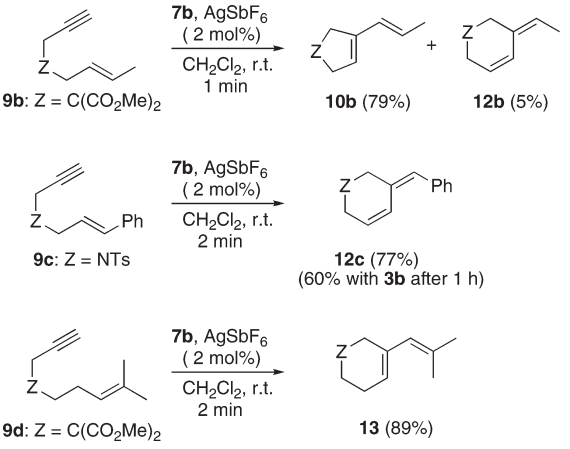
Table 1. Skeletal Rearrangement of Enyne 9a with the Series of Catalysts 4−8.[a]



entry	[Au]	product(s) (yield, %)
1	**4**	**10a** (74) + **11a** (6) + **12a** (2)[b]
2	**5**	**10a** (51) + **11a** (12)
3	**6a**	**10a** (81) + **12a** (2)[b]
4	**6b**	**10a** (35) + **11a** (21) + **12a** (1)[b]
5	**7a**	**10a** (50) + **11a** (15)
6	**7b**	**10a** (85) + **12a** (3)
7	**7b**	**10a** + **12a** (30:1) (88)[c]
8	**7c**	**10a** (98)
9	**7d**	**10a** (61) + **11a** (12)
10	**8a**	**10a** (100)
11	**8b**	**10a** (100)
12	**8c**	**10a** (8) + **11a** (17)
13	**8d**	**10a** (5) + **11a** (8)

[a] Reactions were carried out at room temperature with 2 mol % catalysts for 5 min. Yields were determined by GC. [b] Yield determined by ^1H NMR. [c] Isolated yield.

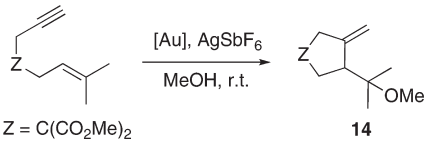
Scheme 2. Skeletal Rearrangements Catalyzed by 7b



respect, the new catalysts used here are more selective and are advantageous to obtain different products. Catalysts **6a**, **7b**, **7c**, **8a**, and **8b** give exclusively or almost exclusively the exo product **10a** (Table 1, entries 3, 6−11). Poor yields were observed using complexes **8c**,**d**, bearing bulkier substituents (Table 1, entries 12 and 13). Previous results using HBHC-Au(I) complexes **3a**−**e** as catalysts led also to **10a** and **12a** (≥30:1 ratio) in 73−89% yield.[14] All these results demonstrate that most NAC-Au(I) complexes are, at least, as reactive and selective as the previously reported more complex carbene-Au(I) complexes.

Additional experiments were performed with complex **7b** as catalyst using 1,6-enynes **9b**,**c** and 1,7-enyne **9d** as substrates (Scheme 2). Thus, the skeletal rearrangement of **9b** provided the exo product **10b** in 79% yield, along with 5% of the product of endo-type cyclization, **12b**, whereas **9c** led exclusively to exo **12c** in higher yield in much shorter reaction time than that using the HBHC-Au(I) catalyst **3b**. Rearrangement of 1,7-enyne **9d** was also fast, with catalyst **7b** leading to diene **13** in excellent yield. This result is comparable to that reported using the cationic catalyst

Table 2. Methoxycyclization of 1,6-Enyne 9a with the Series of Catalysts 4−8 and 1a−c[a]



entry	[Au]	time (h)	yield, %
1	**4**	2	85
2	**5**	2	74
3	**6a**	2	83
4	**6b**	2	65
5	**7a**	2	70
6	**7b**	2	83
7	**7c**	2	44
8	**7d**	2	72
9	**8a**	2	99
10	**8b**	2	92
11	**8c**	2	71
12	**8d**	2	85
13	**1a**	1.5	71
14	**1b**	5	87
15	**1c**	24	34

[a] Reactions were carried out at room temperature with 2 mol % catalyst for 2 h. Yields were determined by ^{1}H NMR.

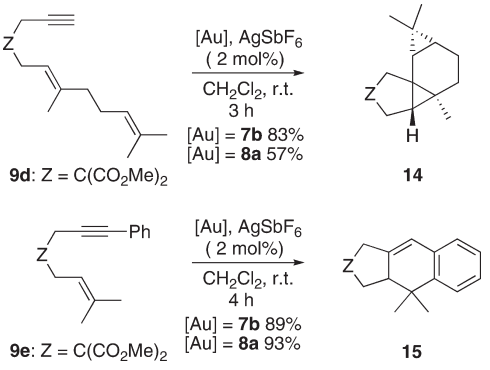
$[Au(PPh_3)(NCMe)]SbF_6$ (2 mol %), which led to **13** in 86% yield after 5 min.[27]

Reactions of 1,6-enynes in alcohols or water as solvent or cosolvent led to the cyclization of the enyne with concomitant addition of a molecule of the alcohol (alkoxy- or hydroxycyclization reaction).[3,28] Interestingly, although these processes are much slower than the skeletal rearrangements, no rearrangement is usually observed in the presence of alcohols, which suggests that the slower cyclization is due to the immediate in situ formation of complexes [AuL(ROH)]X, of lower catalytic activity, in which a molecule of alcohol or water strongly binds to the gold(I) center. These reactions are expected to show a higher dependence on the electronic and steric nature of the L ligands. Therefore, we studied the methoxycyclization of 1,6-enyne **9a** in pure methanol using the new complexes **4**−**8** as catalysts (Table 2). We also compared their performance with that of known catalysts **1a**−**c**.

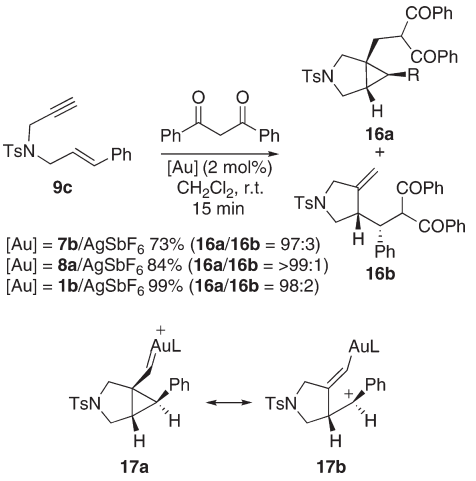
The cleanest reactions and better yields were obtained using catalysts **8a** and **8b** (Table 2, entries 9 and 10). The best NHC complexes **1a**−**c** do not outperform these results,[6a] and the HBHC-Au(I) complexes **3a**−**e** led to poorer yields (20−79%), even using 5 mol % catalyst.[14]

We also carried out the cyclization of dienyne **9d** using **7b** or **8a** and $AgSbF_6$ (Scheme 3). The cyclization led to the expected tetracyclic compound **14**[3a,29] in 83% and 57% yield, respectively. Under these conditions, less that 1% of the skeletal rearrangement product of **9d** was detected in the crude mixture. Skeletal rearrangement of **9d** was formed in significant amounts with some Au(I)- and Pt(II)-phosphine complexes.[29] Similarly, the [4+2] cycloaddition of **9e** proceeded smoothly at room temperature with **7b** or **8a** as precatalysts to give **15** in very good yields, comparable to those obtained under similar conditions using phosphine-Au(I) complexes.[6]

Scheme 3. Cyclization Reactions Catalyzed by 7b and 8a



Scheme 4. Reactions of 1,6-Enyne 9c with Dibenzoylmethane



Finally, we probed the site selectivity of the gold(I) complexes bearing NAC ligands in the reaction of 1,6-enyne **9c** with dibenzoylmethane as the nucleophile to give adducts **16a** and/or **16b** (Scheme 4). We have recently found that the site of nucleophilic attack on intermediate **17** depends on the nature of the L ligand[10] and reflects the dual character, carbene-like or carbocationic, of the intermediates involved in the cyclizations of enynes.[30,31] Thus, a highly electrophilic complex bearing a bulky phosphite ligand gave preferentially **16b** (up to 95:5 ratio) as a result of the attack at the cationic center of **17b**, whereas exclusive attack at the carbene carbon yielding **16a** occurred using the complex **1b** with the IMes ligand.[10] A complex with a bulky dialkylbiarylphosphine ligand, which is of intermediate electrophilicity, gave a 2:1 mixture of **16a** and **16b**.[10] Therefore, we decided to probe the site selectivity of gold(I) catalysts bearing NAC ligands in

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this reaction. In the event, using complexes **7b** and **8a**, adduct **16a** was obtained with high regioselectivity. The results obtained with **8a** are better than those with **1b** and as good as those obtained with the cationic complex obtained from **1b**, [Au(IMes)(2,4,6-$(MeO)_3C_6H_2CN$)]SbF_6, which were the best so far.[10] These results reflect the highly electron-donating character of the NAC, which leads to cyclization of enynes through intermediates that show a significant gold-carbene character.

Conclusions

The modern development of fascinating isolable NHC ligands and the catalytic properties of their complexes have somehow obscured so far the existence of the old, known nitrogen acyclic carbene complexes (NACs). The latter can be easily obtained from widespread isocyanide complexes of transition metals and primary or secondary amines. An advantage of this classic methodology over the NHCs is that, at least for late transition metals, it provides an easy way to obtain organized series of catalysts from a single isocyanide complex precursor, by varying the amine. Moreover, these catalysts will contain carbene ligands that are not otherwise accessible because they do not exist as free molecules.

We have shown here that these easily accessible NACs complexes are interesting catalysts that have been disregarded in favor of the more fashionable NHC complexes but, at least for some purposes, perform as efficiently as the latter. Actually, complexes [AuCl{C(NHR)(NHR′)}] and [AuCl{C(NHR)(NEt_2)}] with acyclic carbene ligands (NAC ligands) show a reactivity as catalysts in reactions of 1,6- and 1,7-enynes comparable to or higher than that displayed by gold(I) complexes with N-heterocyclic ligands. In methanol, these new NAC gold complexes are more reactive than those with hydrogen bond supported heterocyclic carbenes (HBHC). The complexes [AuCl{C(NHMe)(NH*p*Tol)}] (**7b**) and [AuCl{C(NEt_2)(NHXylyl)}] (**8a**) have proved particularly efficient.

It looks reasonable that this type of metal complexes of NAC ligands should be incorporated in the armory of metal-catalyzed reactions.

Experimental Section

General Conditions. All reactions were carried out under dry N_2. The solvents were purified according to standard procedures.[32] Enynes **9a**−**d** were prepared according to literature procedures.[3,26] The other reagents are commercially available. Infrared spectra were recorded in Perkin-Elmer 883 or 1720X equipment. NMR spectra were recorded with Bruker AC300, ARX 300, and Avance 400 Ultrashield instruments. ^{1}H NMR spectra are referred to TMS. Elemental analyses were performed with a Perkin-Elmer 2400B microanalyzer.

Synthesis of Carbenes. [AuCl{C(NH(*p*-C_6H_4COOH)-(NEt_2)}] (4). $HNEt_2$ (0.32 mmol, 33 μL) was added to a solution of [AuCl(CN*p*-C_6H_4COOH)] (120 g, 0.32 mmol) in THF (30 mL). After 15 min of stirring at room temperature, the solution did not show *ν*(CN) IR absorption. The volatiles were removed, and the white residue was washed with *n*-hexane to remove the excess of amine and crystallized from CH_2Cl_2/*n*-hexane. The white solid obtained was washed with *n*-hexane (3 × 5 mL) and vacuum-dried, yielding 0.134 g (92%). ^{1}H NMR (300 MHz, acetone-d_6): δ 9.35 (br s, 1H, NH), 8.03 (d, *J* = 8.8 Hz, 2H, ArH), 7.69 (d, *J* = 8.6 Hz, 2H, ArH), 4.09 (q, *J* = 7.1 Hz, 2H, CH_2), 3.75 (q, *J* = 7.2 Hz, 2H, CH_2), 1.37 (t, *J* = 7.1 Hz, 3H, CH_3), 1.33 (t, *J* = 7.2 Hz, 3H, CH_3). Anal. Calcd for $C_{12}H_{16}AuClN_2O_2$: C, 31.84; H, 3.56; N, 6.19. Found: C, 32.01; H, 3.46; N, 6.01.

[AuCl{C(NH(*p*-C_6H_4COOEt)(NEt_2)}] (5). $HNEt_2$ (1.32 mmol, 136 μL) was added to a solution of [AuCl(CN*p*-C_6H_4COOEt)] (0.540 g, 1.32 mmol) in CH_2Cl_2 (30 mL). Workup for **4** yielded 0.472 g (98%). ^{1}H NMR (300 MHz, acetone-d_6): δ 8.00 (AA′ part of a AA′BB′ system, 2H, ArH), 7.85 (br s, 1H, NH), 7.61 (BB′ part of a AA′BB′ system, 2H, ArH), 4.36 (q, *J* = 7.0 Hz, 2H, CH_2), 3.99 (q, *J* = 7.0 Hz, 2H, CH_2), 3.51 (q, *J* = 7.1 Hz, 2H, CH_2), 1.40 (t, *J* = 7.0 Hz, 3H, CH_3), 1.33−1.30 (m, 6H, CH_3). Anal. Calcd for $C_{14}H_{20}AuClN_2O_2$: C, 34.98; H, 4.19; N, 5.83. Found: C, 35.32; H, 4.25; N, 6.01.

[AuCl{C(NH^{t}Bu)(NHMe)}] (6b). $MeNH_2$ (2.50 mmol, 110 μL, 40% solution in water) was added to a solution of [AuCl(CN^{t}Bu)] (0.200 g, 0.633 mmol) in CH_2Cl_2 (30 mL). Workup for **4** yielded 0.140 g (64%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.78 (br s, 1H, NH major), 6.68 (br s, 1H, NH minor), 6.30 (br s, 1H, NH minor), 5.96 (br, 1H, N*H*Me, major), 3.24 (d, *J* = 5.2 Hz, 3H, CH_3 minor), 2.78 (d, *J* = 5.2 Hz, 3H, CH_3), 1.61 (s, 9H, $C(CH_3)_3$), 1.57 (s, 9H, $C(CH_3)_3$ minor). Stereoisomeric ratio: 4:1. Anal. Calcd for $C_6H_{14}AuClN_2$: C, 20.79; H, 4.07; N, 8.08. Found: C, 21.20; H, 3.80; N, 7.92.

[AuCl{C(NEt_2)(NHTol-*p*)}](7a). Et_2NH (0.60 mmol, 62 μL) was added to a solution of [AuCl(CNTol-*p*)] (0.175 g, 0.50 mmol) in CH_2Cl_2 (30 mL). Workup as for **4** yielded 0.189 g (89%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47 (br, 1H, N*H*$C_6H_4CH_3$), 7.34 (d, *J* = 8.3 Hz, 2H, NH$C_6H_4CH_3$), 7.14 (d, *J* = 7.9 Hz, 2H, NH$C_6H_4CH_3$), 4.01 (q, *J* = 7.2 Hz, 2H, N(CH_2CH_3)$_2$), 3.47 (q, *J* = 7.2 Hz, 2H, N(CH_2CH_3)$_2$), 2.32 (t, *J* = 7.2 Hz, 6H, N(CH_2CH_3)$_2$) Anal. Calcd for $C_{12}H_{18}AuClN_2$: C, 34.10; H, 4.29; N, 6.63. Found: C, 33.81; H, 4.03; N, 6.25.

[AuCl{C(NHMe)(NHTol-*p*)}] (7b). $MeNH_2$ (0.75 mmol, 65 μL, 40% solution in water) was added to a solution of [AuCl(CNTol-*p*)] (0.193 g, 0.50 mmol) in CH_2Cl_2 (30 mL). Workup as for **4** yielded 0.068 g (66%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.19 (br s, 1H, N*H*, major), 7.69 (br s, 1H, N*H*, minor), 7.44−6.89 (m, 3H, arom, major, 3H, arom, minor, 1H, N*H*, minor), 6.33 (br, 1H, N*H*Me, major), 3.24 (d, *J* = 4.6 Hz, 3H, CH_3, major), 2.97 (d, *J* = 5.2 Hz, 3H, CH_3, minor), 2.37 (s, 3H, Ar-CH_3, major), 2.31 (s, 3H, Ar-CH_3, minor). Stereoisomeric ratio: 2:1. Anal. Calcd for $C_9H_{12}AuClN_2$: C, 28.40; H, 3.18; N, 7.36; Found: C, 28.94; H, 2.80; N, 7.32.

[AuCl{C(NHC$_7$H$_{15}$)(NHTol-*p*)}] (7c). *n*-Heptylamine (0.75 mmol, 112 μL) was added to a solution of [AuCl(CNTol-*p*)] (0.175 g, 0.5 mmol) in CH_2Cl_2 (40 mL). Workup as for **4** yielded 0.168 g (72%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.64 (br, 1H, N*H*, minor 1), 8.00 (br, 1H, N*H*Tol-*p*), 7.67 (br, 1H, N*H*, minor 2), 7.44 (d, *J* = 5.7 Hz, 2H, NH$C_6H_4CH_3$, minor 1), 7.40 (d, *J* = 6.0 Hz, 2H, NH$C_6H_4CH_3$, minor 2), 7.27 (d, *J* = 6.2 Hz, 2H, NH$C_6H_4CH_3$), 7.15 (d, *J* = 6.0 Hz, 2H, NH$C_6H_4CH_3$, minor 2), 7.11 (d, *J* = 5.7 Hz, 2H, NH$C_6H_4CH_3$, minor 1), 7.08 (d, *J* = 6.2 Hz, 2H, NH$C_6H_4CH_3$), 6.98 (br, 1H, N*H*, minor 1 + minor 2), 6,37 (br, 1H, N*H*C_7H_{15}), 3.73 (br, 2H, NHC$H_2C_6H_{13}$, minor), 3.66 (q, *J* = 6.3 Hz, 2H, NHC$H_2C_6H_{13}$), 3.22 (q, *J* = 6.2 Hz, 2H, NHC$H_2C_6H_{13}$, minor), 2.38 (s, 3H, NH$C_6H_4CH_3$), 2.30 (s, 3H, NH$C_6H_4CH_3$, minor), 2.25 (s, 3H, NH$C_6H_4CH_3$, minor), 1.58 (m, 2H, NHC$H_2C_6H_{13}$), 1.27 (m, 8H, NHC$H_2C_6H_{13}$), 0.87 (t, *J* = 5.2 Hz, 3H, NHC$H_2C_6H_{13}$). Stereoisomeric ratio: 10:1:2. Anal. Calcd for $C_{15}H_{24}AuClN_2$: C, 38.76; H, 5.20; N, 6.03. Found: C, 39.10; H, 4.80; N, 6.19.

[AuCl{C(NHTol-*p*)(NHTol-*p*)}] (7d). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.29 (br, 2H, N*H*Tol-*p*, minor), 8.73 (br, 1H, N*H*Tol-*p*, major), 7.99 (8.73 (br, 1H, N*H*Tol-*p*, major), 7.50 (d, *J* = 8.0 Hz 4H, NH$C_6H_4CH_3$, minor), 7.35 (d, *J* = 8.2 Hz, 2H, NH$C_6H_4CH_3$), 7.31 (d, *J* = 8.2 Hz, 2H, NH$C_6H_4CH_3$), 7.20 (d, *J* = 7.9 Hz, 2H, NH$C_6H_4CH_3$), 7.11 (m, 2H, NH$C_6H_4CH_3$, major + 4H, NH$C_6H_4CH_3$, minor), 2.40 (s, 3H, NH$C_6H_4CH_3$,

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major), 2.30 (s, 3H, $NHC_6H_4CH_3$, major), 2.27 (s, 6H, $NHC_6H_4CH_3$, minor). Stereoisomeric ratio: 10:1.

[**AuCl{C(NHXylyl)(NEt$_2$)}**] (**8a**). $HNEt_2$ (1.098 mmol, 161 μL) was added to a solution of [AuCl(CNXylyl)] (0.200 g, 0.549 mmol) in CH_2Cl_2 (30 mL). Workup as for **4** yielded 0.190 g (79%). ^{1}H NMR (300 MHz, acetone-d_6): δ 8.47 (br s, 1 H, N*H*), 7.21−7.05 (m, 3H ArH),), 4.02 (q, J = 7.2 Hz, 2H, CH_2), 3.50 (q, J = 7.3 Hz, 2H, CH_2), 2.24 (s, 6H, Ar-CH_3), 1.36 (t, J = 7.3 Hz, 3H, CH_3), 1.35 (t, J = 7.2 Hz, 3H, CH_3). Anal. Calcd for $C_{13}H_{20}AuClN_2$: C, 35.75; H, 4.62; N, 6.41. Found: C, 35.74; H, 4.22; N, 6.53.

[**AuCl{C(NHXylyl)(NHMe)}**] (**8b**). $MeNH_2$ (1.098 mmol, 95 μL, 40% solution in water) was added to a solution of [AuCl(CNXylyl)] (0.200 g, 0.549 mmol) in CH_2Cl_2 (30 mL). Workup as for **4** yielded 0.163 g (75%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.27 (br s, 1H, N*H*, minor 1), 7.67 (br s, 1H, N*H*, major), 7.28−7.05 (m, 3H, major, 6H, minor 1, 6H, minor 2, 1H, N*H*, minor 2), 5.83 (br, 1H, N*H*Me, major), 5.70 (br, 1H, N*H*Me, minor 1), 5.08 (br, 1H, N*H*Me, minor 2), 3.24 (d, J = 4.7 Hz, 3H, C*H*$_3$, major), 3.13 (d, J = 4.7 Hz, 3H, C*H*$_3$, minor 1), 3.06 (d, J = 4.7 Hz, 3H, C*H*$_3$, minor 2), 2.34 (s, 6H, Ar-C*H*$_3$, minor 1), 2.28 (s, 6H, Ar-C*H*$_3$, minor 2), 2.24 (s, 6H, Ar-C*H*$_3$, major). Stereoisomeric ratio: 5:1:1. Anal. Calcd for $C_{10}H_{14}AuClN_2$: C, 30.43; H, 3.58; N, 7.10. Found: C, 30.93; H, 3.48; N, 6.91.

[**AuCl{C(NHXylyl)(NH^{i}Pr)}**] (**8c**). ^{i}PrNH$_2$ (0.825 mmol, 71 μL) was added to a solution of [AuCl(CNXylyl)] (0.200 g, 0.55 mmol) in CH_2Cl_2 (30 mL). Workup as for **4** yielded 0.197 g (85%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78 (br s, 1H NH), 7.26 (t, J = 6.2 Hz, 1H, ArH), 7.17 (d, J = 6.7 Hz, 2H, ArH), 5.57 (br d, J = 8.9 Hz, 1H, N*H*^{i}Pr), 4.49 (m, 1H, CH), 2.23 (s, 6H, Ar-CH_3), 1.17 (d, J = 6.6 Hz, 6H, CH_3). Anal. Calcd for $C_{12}H_{18}AuClN_2$: C, 34.10; H, 4.29; N, 6.63. Found: C, 34.52; H, 4.05; N, 6.87.

[**AuCl{C(NHXylyl)(NHBu)}**] (**8d**). $BuNH_2$ (0.824 mmol, 82 μL) was added to a solution of [AuCl(CNXylyl)] (0.150 g, 0.412 mmol) in CH_2Cl_2 (30 mL). Workup as for **4** yielded 0.091 g (51%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.73 (br s, 1H N*H*Xylyl), 7.27−7.16 (m, 3H, ArH), 5.86 (br, 1H, N*H*Bu), 3.64 (q, J = 7.1 Hz, 2H, CH_2), 2.24 (s, 6H, Ar-CH_3), 1.52 (q, J = 6.8 Hz, 2H, CH_2), 1.33−1.25 (m, 4H, CH_2), 0.90 (t, J = 7.2 Hz, 3H, CH_3). Anal. Calcd for $C_{13}H_{20}AuClN_2$: C, 35.75; H, 4.62; N, 6.41. Found: C, 35.59; H, 4.14; N, 6.16.

Catalytic Procedures. All the reactions were carried out under N_2 in solvents dried using a solvent purification system. Thin-layer chromatography was carried out using TLC-aluminum sheets with 0.2 mm of silica gel (Merck GF234). Chromatography purifications were carried out using flash grade silica gel (SDS S-2 Chromatogel 60 ACC, 40−60 μm). NMR spectra were recorded at 25 °C on a Bruker Avance 400 Ultrashield. Compounds **9a**−**14** tested in catalysis have been reported before.[3c]

General Procedure for Skeletal Rearrangement of 1,6-Enynes. Procedure with Catalysts 4−8. The enyne (0.15−0.2 mmol) and the gold(I) complex (2−5 mol %) were dissolved with stirring in a solution of $AgSbF_6$ in CH_2Cl_2 (2 mM, 2 mL; 2−5 mol % $AgSbF_6$). After the indicated time (monitored by TLC), the reaction was quenched with a solution of Et_3N in hexanes (0.1 M, 2 mL) and filtered through a pad of silica gel that was eluted with Et_2O. Isolated products were purified by flash column chromatography (EtOAc/hexane).

General Procedure for Methoxycyclizations of 1,6-Enynes. Procedure with Catalysts 4−8. The enyne (0.15−0.2 mmol) and the gold(I) complex (2 mol %) were dissolved with stirring in a solution of $AgSbF_6$ (2 mol %) in MeOH (2 mM, 2 mL). After 5 min, the reaction was quenched with a solution of Et_3N in hexanes (0.1 M, 2 mL) and filtered through a pad of silica gel that was eluted with Et_2O. Isolated products were purified by flash column chromatography (EtOAc/hexane).

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