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Gold(I) Complexes with Hydrogen-Bond Supported Heterocyclic Carbenes as Active Catalysts in Reactions of 1,6-Enynes

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Complexes [AuCl{C(NHR)(NHPy-2)}] (Py-2 = 2-pyridyl; R = Me, ^{t}Bu, ^{n}Bu, ^{i}Pr, ^{n}heptyl) have been prepared in a modular way from [AuCl(CNPy-2)]. The carbene moiety has a hydrogen-bond supported heterocyclic structure similar to the nitrogen heterocyclic carbenes in the solid state, and in CH_2Cl_2 or acetone solution, which is open in the presence of MeOH. The compounds are good catalysts for the skeletal rearrangement of enynes, and for the methoxycyclization of enynes. In contrast, the complexes [AuCl{C(NHR)(NHPy-4)}] are scarcely active due to the blocking effect of the coordination position required for the catalysis by the nitrogen of the NHPy-4 group.

Introduction

Gold(I) carbene complexes of the type AuCl{C(NRH)-(NHPy-*n*)}] (Py = pyridyl; n = 2,4), obtained by nucleophilic addition of primary amines to pyridylisocyanides coordinated to gold, have been reported recently.[1,2] In the case of gold(I) carbenes derived from 2-pyridyl isocyanide, a strong intramolecular hydrogen bond produces a planar cycle (structure **B**, Figure 1), somewhat reminiscent of that of the nitrogen heterocyclic carbenes (NHCs, structure **A**, Figure 1). We will refer to them as hydrogen bond supported heterocyclic carbenes (HBHCs). In all the HBHC carbenes synthesized, the hydrogen-bond-supported cyclic structure is observed in the solid state and maintained in solution in $CDCl_3$, and acetone-d_6.[1] By contrast, for carbenes derived from 4-pyridyl isocyanide, only intermolecular hydrogen bonds are formed in the solid state, which are broken in solution to give, predominantly, the noncyclic structures **C** and **D** in Figure 1.[2]

Gold NHC complexes, although known for more than 20 years,[3] have only recently become relevant in NHC chemistry because of their catalytic applications in organic synthesis.[4] The straightforward preparative method of their somehow related HBHCs complexes allows for the easy modular design and preparation of series of compounds where the R modifier can be easily varied in order to tune the steric and electronic properties of the complex. This invited us to check the catalytic performance of the HBHC carbenes derived from 2-pyridyl isocyanide and, for comparison, the related noncyclic carbenes derived from 4-pyridyl isocyanide.

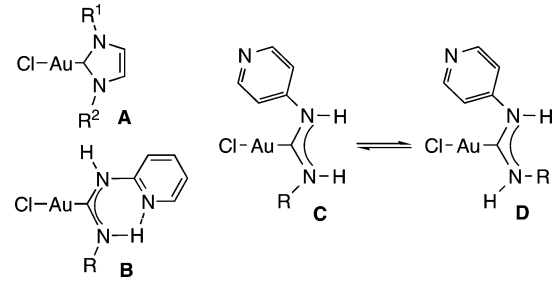

Figure 1. Gold(I) complexes with NHC (**A**), HBHC (**B**), and noncyclic (**C** and **D**) carbene derived from 4-pyridyl isocyanide.

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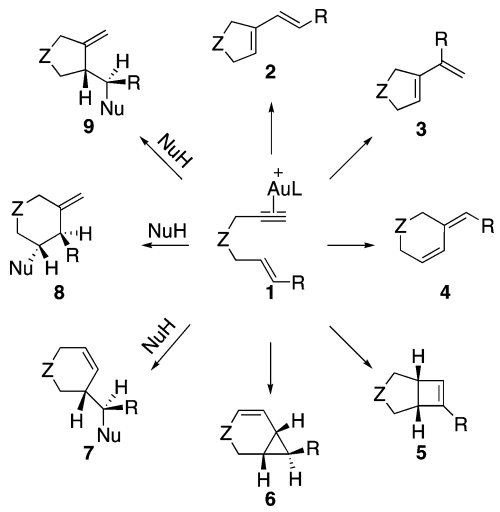
Scheme 1



In this respect, interesting gold catalyzed reactions are the skeletal rearrangements and other cyclization of enynes. The activation of 1,6-enynes via the η^2-alkyne gold complex **1** can afford a variety of compounds (Scheme 1).[5] In the absence of nucleophiles, enynes usually evolve by skeletal rearrangement to form dienes **2** (single cleavage) and/or **3** (double cleavage). Products of endocyclic skeletal rearrangement **4**,[5,6] cyclobutenes **5**,[5] and bicyclic products of intramolecular cyclopropanation **6**, have also been obtained.[7] In the presence of nucleophiles, adducts **7**−**9** have been produced in stereospecific processes.[5,8−11] More complex transformations are also possible starting from more functionalized enynes.[12]

Although most of the reactions in Scheme 1 use phosphines as the gold ligand, complexes with highly donating NHCs such as **10a**−**d** (Figure 2) have been found to be good precatalysts for some reactions of enynes.[12a,13] The actual catalyst is formed in solution by treatment with a silver salt to extract the chloride. Related complexes with NTf_2 as ligand (**11a**−**b**),[14,15] and cationic complexes (e.g., **12**) derived from **10d**,[16,17] or the phosphite complex **13**,[17] have also been reported active.

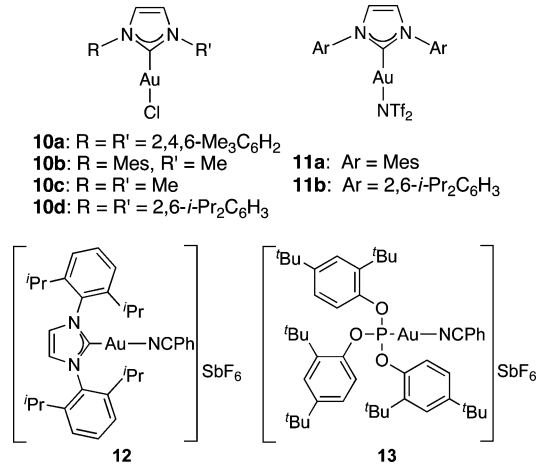


Figure 2. Gold complexes used as catalysts for skeletal rearrangement of enynes.

With these precedents in mind, the aim of this work is to check the catalytic activity of HBHC (**B**), and noncyclic (**C**−**D**) carbene complexes in the cyclization of 1,6-enynes, having the reported work with NHCs carbenes as reference. Thus selected AuCl{C(NRH)-(NHPy-*n*)}] ($n = 2, 4$) complexes prepared for this purpose have been tested in the skeletal rearrangement and in the methoxycyclizations of 1,6-enynes. The HBHC gold carbenes, derived from 2-pyridyl isocyanide, are highly active, whereas 4-pyridyl isocyanide derivatives are almost inactive. The steric and electronic features of the amine chosen for the nucleophilic attack to the coordinated isocyanide induce substantial changes in the catalytic activity of the complexes, and in the products formed.

Results and Discussion

Synthesis and Structural Characterization of the Gold Carbene Complexes. The neutral gold carbene catalysts **14a**−**e** were prepared by nucleophilic attack to the gold coordinated isocyanide with differently hindered primary amines to tune the steric requirement of the alkyl group

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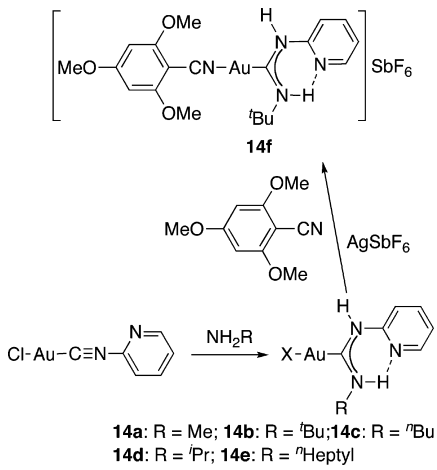
Scheme 2. Synthesis of the Gold Carbene Derivatives **14**



R (Scheme 2). All the complexes are white, air stable solids. The carbene [AuCl{C(NHMe)(NHPy-2)}] (**14a**) has been reported already.[1] Once the carbene has been formed, the R group will be located close to the gold atom, and might have some steric influence on the reaction. As observed in the ^{1}H NMR of **14a** in $CDCl_3$, there are two different signals for the two N−H protons, one at ca. 12.5 ppm and another in the range 9.5−8 ppm. The chemical shift of the low-field signal reveals the existence in solution of an intramolecular hydrogen bond between the amide proton and the nitrogen of the 2-pyridyl group forming a 6-member cycle. This feature is also observed in acetone-d_6 solution.

X-ray quality crystals suitable for single crystal diffraction were obtained for [AuCl{C(NH^{t}Bu)(NHPy-2)}] (**14b**), and the expected intramolecular hydrogen bond was confirmed. There are two very similar independent molecules of **14b** in the asymmetric unit. The molecular structure of one of them is shown in Figure 3, with selected bond lengths and angles.

The complex shows a nearly linear geometry for gold. The gold atom is located in the hinge defined by a CMe_2 fragment

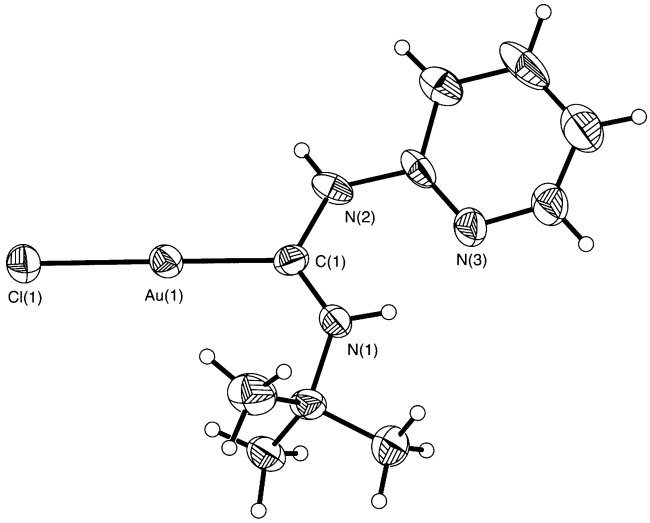


Figure 3. X-ray structure for [AuCl{C(NH^{t}Bu)(NHPy-2)}] (**14b**). Selected bond lengths (Å): Au(1)−Cl(1) = 2.301(3); Au(1)−C(1) = 2.016(12); C(1)−N(2) = 1.365(13); C(1)−N(1) = 1.309(13); N(3)−H(1A) = 1.786(1). Selected bond angles (°): C(1)−Au(1)−Cl(1) = 179.6(3); N(2)−C(1)−N(1) = 118.1(10); N(3)−H(1A)−N(1) = 138.41(5).

of the ^{t}Bu group. The Au−Cl distance in **14b** is longer than that for $[AuCl_2]^-$ (2.257 Å),[18] as a consequence of the high *trans* influence of the carbene ligand.[3,19] The Au−C distance is within the range found for similar gold(I) carbenes.[20] The C(1)−N(2) and C(1)−N(1) distances are within the range found for other Au(I) carbene complexes, and much shorter than the C(sp^2)−N single bond distance of 1.45 Å,[21] indicating a significant π-bonding contribution to the bond. The conformer found in this structure has the N−H of the formerly *tert*-butylamine group oriented toward the nitrogen of the pyridyl group. The H···N distance and the corresponding N−H···N angle are within the range of moderate intramolecular N···H hydrogen bonds.[22] The spectroscopic evidence discussed before supports that the conformation observed in the solid state is retained in solution in chloroform and in acetone, and is the same for all the complexes derived from 2-pyridyl isocyanide.

A cationic gold complex **14f** derivative was prepared from **14b** as a white, air stable solid, by chloride abstraction with $AgSbF_6$ in the presence of excess 2,4,6-trimethoxybenzonitrile. The 2,4,6-trimethoxybenzonitrile is a labile ligand, which is coordinated to gold in the solid state (ν_{CN} = 2261 cm^{-1}), but is displaced by the solvent in acetone (ν_{CN} = 2221 cm^{-1}). The ^{1}H NMR spectra in CD_2Cl_2 are complex and show two species in solution, as broad signals, probably due to competition of water in the solvent as ligand, along with slow exchange. In fact, addition of CD_3CN displaces the spectra to the formation of one single species, which is the same observed for **14f** in CD_3CN as solvent, and shows free 2,4,6-trimethoxybenzonitrile. Thus, it is concluded that acetonitrile has displaced the 2,4,6-trimethoxybenzonitrile from gold. The availability of this cationic precursor, which should allow for easy η^2-coordination of the reagent in the catalysis, avoids the presence of silver salts in the catalytic pot and reduces the possibility of silver promoted side reactions. In our cases, the catalytic behavior of **14f** and **14b** + $AgSbF_6$ are practically identical (see later).

Only one complex derived from 4-pyridyl isocyanide, [AuCl{C(NHMe)(NHPy-4)}] (**15**), was prepared and studied, in view of the poor catalytic behavior observed (see later). It was prepared as reported for analogous carbene complexes.[2] Up to four isomers might be formed, depending on the arrangement of the 4-pyridyl group and the Me group, but the ^{1}H NMR spectra showed only the two isomers depicted in Figure 4, which were assigned by irradiation and

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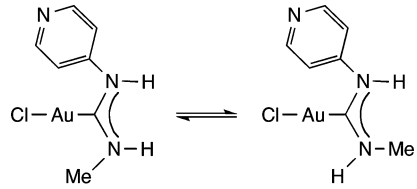
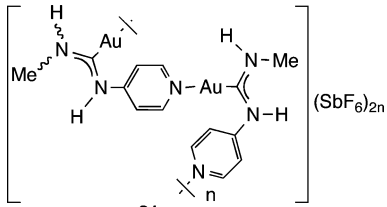


15

Figure 4. Conformers observed for **15** in solution.



21

Figure 5. Coordination polymer obtained by coordination of the dangling pyridyl group to the gold center.

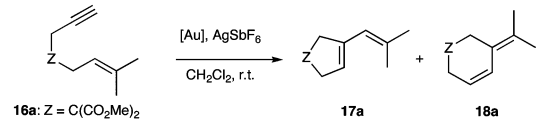
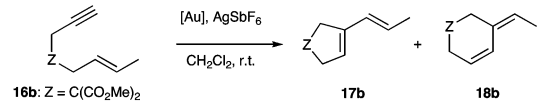
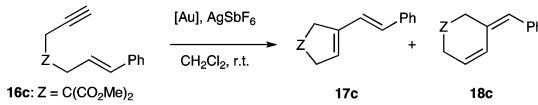
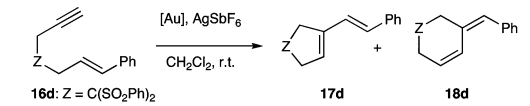
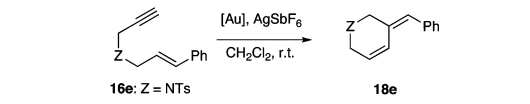
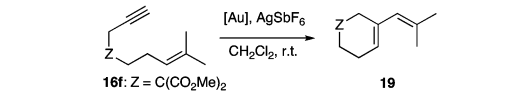
NOE experiments. These have a syn arrangement of the 4-pyridyl and Au moieties. The minor signals correspond to the isomer on the right of the figure, and the major to the less crowded isomer on the left. The isomer ratio changes with the polarity of the solvent (acetone-d_6 or $CDCl_3$), suggesting a slow exchange process in solution.

Catalytic Reactions. The reactions were carried out dissolving the catalyst and the 1,6-enyne in CH_2Cl_2 (skeletal rearrangements) or methanol (methoxycyclizations) and, except when the complex was cationic, adding $AgSbF_6$ to extract the chloride and allow for coordination of the enyne to the Au center. In general the catalysis with carbene gold complexes containing the 2-pyridyl group was very effective (somewhat less effective for the methoxycyclizations as observed also with other catalysts).[5c,12a] The different catalysts provided variations in yield (higher for bulkier R substituents), but also interesting variations in the major product when more than one was formed. The catalytic results for skeletal rearrangement of 1,6-enynes and for methoxycyclizations of 1,6-enynes using the gold catalysts derived from 2-pyridyl isocyanide afford fairly good yields (see later numeric results).

In contrast, the catalytic activity drops dramatically for the gold catalyst containing a 4-pyridyl group (complex **15**). The reaction conditions explain the poor activity of **15**. In the presence of a silver salt, the N atom of the pyridyl group, which in this case is not neutralized by a strong hydrogen bond interaction, can coordinate to the gold center, blocking the active site of the catalyst. Moreover, the resulting polymer is insoluble and the gold catalyst precipitates. In fact, treatment of **15** with $AgSbF_6$ in a separate reaction led to the formation of insoluble polymers **21** (Figure 5), which could not be separated from the insoluble silver chloride formed in the reaction but was easily detected by infrared. The weight of the precipitate accounted for the sum of the expected polymer plus the expected AgCl. The insolubility of the polymer precluded further characterization.

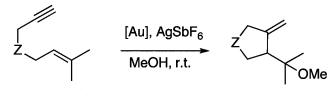
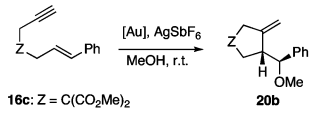
The catalytic results for the skeletal rearrangement of 1,6-enynes are listed in Table 1. The gold carbenes **14a**−**d** catalyze efficiently the skeletal rearrangement of 1,6-enynes

Table 1. Skeletal Rearrangement of 1,6-Enynes with Catalysts **14a**−**f** and **15**[a]

entry	[Au]	Time	Product(s) (Yield, %, ratio)
			
	16a: Z = $C(CO_2Me)_2$		**17a** **18a**
1	**14a**	2 min	**17a** + **18a** (89, 30:1)
2	**14b**	2 min	**17a** + **18a** (93, 31:1)
3	**14c**	5 min	**17a** (88)
4	**14d**	5 min	**17a** (73)
5	**14e**	5 min	**17a** (89)
6[b]	**14f**	5 min	**17a** + **18a** (94, 46:1)
7	**15**	24 h	**17a** + **18a** (5, 1:0)
			
	16b: Z = $C(CO_2Me)_2$		**17b** **18b**
8	**14a**	2 min	**17b** (85)
9	**14b**	2 min	**17b** + **18b** (80, 7:1)
10	**15**	24 h	**17b** (10)
			
	16c: Z = $C(CO_2Me)_2$		**17c** **18c**
11[c]	**14a**	35 min	**17c** + **18c** (100, 1:2.7)
12[c]	**14b**	35 min	**17c** + **18c** (100, 1:2.8)
13[c]	**15**	1 h	-[d]
			
	16d: Z = $C(SO_2Ph)_2$		**17d** **18d**
14	**14a**	30 min	**17d** + **18d** (81, 1.6:1)
15	**14b**	7 min	**17d** + **18d** (91, 1.6:1)
16	**15**	30 h	-[d]
			
	16e: Z = NTs		**18e**
17	**14a**	24 h	**18e** (16)
18	**14b**	1 h	**18e** (60)
19	**15**	24 h	**18e** (12)
			
	16f: Z = $C(CO_2Me)_2$		**19**
20	**14a**	10 min	**19** (90)
21	**14b**	5 min	**19** (96)
22	**15**	24 h	**19** (8)

[a] Reactions carried out in CH_2Cl_2 with 2 mol% catalyst. [b] Reaction run in the absence of $AgSbF_6$. [c] 5 mol% catalyst. [d] Starting material was recovered.

Table 2. Methoxycyclizations of 1,6-Enynes with Catalysts **14a**−**f** and **15**[a]

entry	[Au]	Time	Product(s) (Yield, %)
			
	16a: Z = $C(CO_2Me)_2$		**20a**
1	**14a**	3 h	**20a** (20)
2	**14b**	3 h	**20a** (70)
3	**14c**	2 h	**20a** (44)
4	**14d**	2 h	**20a** (33)
5	**14e**	2 h	**20a** (39)
6[b]	**14f**	2 h	**20a** (80)
7	**15**	3 h	**20a** (17)
			
	16c: Z = $C(CO_2Me)_2$		**20b**
8	**14a**	3 h	**20b** (55)
9	**14b**	3 h	**20b** (59)
10	**15**	3 h	-[b]

[a] Reactions carried out in CH_2Cl_2 with 5 mol% catalyst. [b] Starting material was recovered.

16a−**d** with similar efficiency (Table 1, entries 1−5, 8, 9, 11, 12, 14, 15, 20, and 21), although for the cyclization of **16e** and **16f** the most sterically hindered carbene **14b** affords better results than **14a** (compare Table 1, entries 17/18 and 20/21). The cationic complex **14f** and the mixture **14b** + $AgSbF_6$ catalyze the rearrangement of **14a** with similar efficiency (Table 1, entries 2 and 6). Finally, complex **15** results are very inefficient, for the reasons discussed above (Table 1, entries 7, 10, 13, 16, 19, and 22).

It is interesting to compare the performance of these new catalysts with the highly efficient cationic gold complexes **12** and **13** (Figure 2).[17] For example, whereas enyne **16c** reacts with catalysts **14a** and **14b** to give the product of endo cyclization **18c** as the major compound (ca. 1:3 **17c/18c**, Table 1, entries 11 and 12), complexes **12** and **13** favor the product of exo cyclization **17c** (50:1 for **12**, 73%, and 2.2:1 for **13**, 76%). For comparison, the reaction of **16c** with $[Au(PPh_3)Cl]/AgSbF_6$ gave and an almost equimolar ratio of **17c/18c**.[5c] Thus, the availability of a family of modular catalysts can be interesting to tune the reaction selectively toward different products, even at the expense of some loss of yield or activity.

The catalytic results for methoxycyclizations of 1,6-enynes are listed in Table 2. As for the cyclizations, the derivative with 4-pyridyl shows the poorest results (Table 2, entries 7 and 10), whereas the others display variable yields depending on the R group. The cationic complex **14f** and the combination **14b** + $AgSbF_6$ provide the product of methoxycyclization **20a** in the best yields (Table 2, entries 2 and 6). For comparison, catalysts **12** and **13** (5 mol%) afford similar yields in the methoxycyclization of enyne **16a** (68 and 76%, respectively) compared to those achieved using **14b**/$AgSbF_6$ or **14f** (Table 2, entries 2 and 6). However, although the reactions with **12** and **13** were faster (30 min vs 2−3 h), significant amounts (ca. 10%) of a methyl ketone, a product of a formal Markovnikov addition of water to the alkyne function of **16a**, were also observed. Thus, in this respect, the new catalysts used here are advantageous.

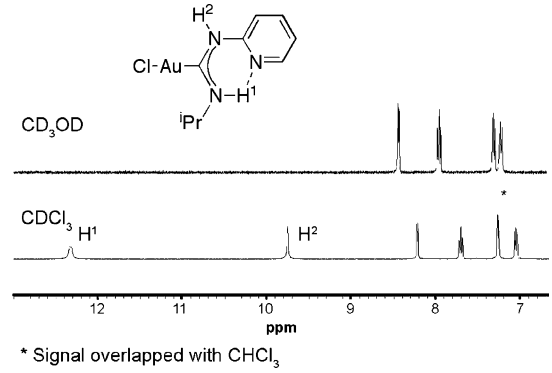


Figure 6. ^1H NMR of the aromatic and NH region for [AuCl{C(NH^{i}Pr)(NHPy-2)}] (**14d**) in $CDCl_3$ and CD_3OD at room temperature, showing that both N−H hydrogen atoms quickly exchange with CD_3OD.

Table 3. Crystal Data and Structure Refinement for [AuCl{C(NH*t*Bu)(NHPy-2)}] (**14b**)

empirical formula	$C_{10}H_{15}AuClN_3$
formula weight	409.67
temperature (K)	298(2)
wavelength (Å)	0.71073
crystal system	triclinic
space group	$P\bar{1}$
a (Å)	10.746(4)
b (Å)	10.834(4)
c (Å)	13.974(5)
α (deg)	109.282(7)
β (deg)	92.789(7)
γ (deg)	119.223(6)
V (Å^3)	1296.0(8)
Z	4
D_{calc} (g cm^{-3})	2.100
absorption coefficient (mm^{-1})	11.531
F(000)	768
crystal size (mm)	0.08 × 0.08 × 0.07
theta range for data collection	1.60 to 26.49°
reflections collected	11309
independent reflections	5293
absorption correction	semiempirical from equivalents
maximum and minimum transmission factor	1 and 0.758239
data/restraints/parameters	5293/0/277
goodness-of-fit on F^2	0.975
R_1 [$I > 2\sigma(I)$]	0.0472
wR_2 (all data)	0.1258

Since the methoxycyclizations require the presence of MeOH, the effect of this solvent on the intramolecular hydrogen bond was studied. It turned out that both N−H bonds exchange quickly with the deuterion of CD_3OD, supporting that the intramolecular hydrogen bond is split in the presence of MeOH (Figure 6).

In other words, the complexes **14** cannot be considered HBHCs when use in this solvent or in the presence of MeOH as reagent. Yet, the open carbene complexes formed in MeOH are very active catalysts, and the fall in yield observed in Table 2 should not necessarily be related to the splitting of the hydrogen bond supported ring, as the alkoxycycliza-

tions usually give lower yields with the carbene-gold complexes.[5c,12a] The splitting of the ring could have been a source of complication for reactions of skeletal rearrangements (Table 1), as any structural change of the catalyst can induce the formation of different products, but the HBHC structure of the ligand is well controlled in these reactions, since opening of the ring does not occur in CH_2Cl_2.

Conclusions

The complexes [AuCl{C(NHR)(NHPy-2)}] can be prepared in a modular way from [AuCl(CNPy-2)]. Depending on the solvent, they behave as hydrogen bond supported heterocyclic carbenes, structurally similar to the nitrogen heterocyclic carbenes (in acetone or CH_2Cl_2), or as noncyclic carbenes where the structural rigidity has been relaxed (in MeOH). The compounds are good catalysts for the skeletal rearrangement of enynes, affording somewhat different outcomes of the cyclizations as compared to other catalysts, and also for the alkoxycyclization of enynes. In contrast, the complexes [AuCl{C(NHR)(NHPy-4)}] are scarcely active due to the blocking effect by the nitrogen of the NHPy-4 group of the coordination position required for the catalysis. The modular construction of the catalysts makes them an attractive alternative to tune the catalysis.

Experimental Section

General Conditions. All reactions were carried out under dry N_2. The solvents were purified according to standard procedures.[23] [AuCl(CNPy-2)],[1] [AuCl(CNPy-4)],[2] and enynes **16a**−**f**,[5,6] were prepared according to literature procedures. The rest of the reactants are commercially available. Infrared spectra were recorded in Perkin-Elmer 883 or 1720X equipment. NMR spectra were recorded with Bruker AC300, ARX 300 and Bruker Avance 400 Ultrashield instruments. ^{1}H NMR spectra are referred to TMS. Elemental analyses were performed with a Perkin-Elmer 2400B microanalyzer. High resolution mass spectra were recorded in a Waters LCT Premier (ESI) spectrometer.

Synthesis of Carbenes 14b−**e. [AuCl{C(NH^{t}Bu)(NHPy-2)}] (14b).** tBuNH$_2$ (0.95 mmol, 100 μL) was added to a solution of [AuCl(CNPy-2)] (0.252 g, 0.75 mmol) in CH_2Cl_2 (30 mL). After 15 min stirring at room temperature, the solution did not show n(CN) IR absorption. The pale yellow solution was filtered through Celite, the volatiles were pumped off, and the pale-violet residue was crystallized from CH_2Cl_2/n-hexane. The colorless crystals obtained were washed with n-hexane (3 × 5 mL) and vaccuum-dried, yielding 0.202 g (66%). ^{1}H NMR (300 MHz, $CDCl_3$, 295 K): δ 12.96 (br, 1H, NHC(CH$_3$)$_3$), 9.64 (br, 1H, NHC$_5$H$_4$N), 8.20 (d, J = 5.2 Hz, 1H, NHC$_5H_4$N), 7.71 (m, 1H, NHC$_5H_4$N), 7.25 (d, J = 7.7 Hz, 1H, NHC$_5H_4$N), 7.05 (m, 1H, NHC$_5H_4$N), 1.66 (s, 9H, NHC(CH_3)$_3$). Anal. Calcd for $C_{10}H_{15}AuClN_3$: C, 29.32; H, 3.69; N, 10.26. Found: C, 29.65; H, 3.72; N, 10.10.

[AuCl{C(NH^{n}Bu)(NHPy-2)}] (14c). n-Butylamine (0.5 mmol, 50.0 μL) was added to a solution of [AuCl(CNPy-2)] (0.168 g, 0.5 mmol) in CH_2Cl_2 (40 mL). Work up as for **14b** yielded 0.151 g (74%). ^{1}H NMR (300 MHz, $CDCl_3$, 295 K): δ 12.46 (br, 1H, NH^nBu), 9.91 (br, 1H, NHC$_5$H$_4$N), 8.21 (d, J = 5.0 Hz, 1H, NHC$_5H_4$N), 7.68 (tm, J = 8.3 Hz, 1H, NHC$_5H_4$N), 7.29 (m, J = 8.3 Hz, 1H, NHC$_5H_4$N), 7.05 (m, J = 6.4 Hz, 1H, NHC$_5H_4$N), 3.78 (q, J = 6.8 Hz, 2H, NHCH_2C$_3$H$_7$), 1.67 (m, 2H, NHCH$_2$C$_3H_7$), 1.41 (m, 2H, NHCH$_2$C$_3H_7$), 0.92 (t, J = 7.4 Hz, 3H, NHCH$_2$C$_3H_7$). Anal. Calcd for $C_{10}H_{15}AuClN_3$: C, 29.32; H, 3.69; N, 10.26. Found: C, 29.60; H, 3.29; N, 10.36.

[AuCl{C(NH^{i}Pr)(NHPy-2)}] (14d). Isopropylamine (0.5 mmol, 43 μL) was added to a solution of [AuCl(CNPy-2)] (0.168 g, 0.5 mmol) in CH_2Cl_2 (40 mL). Work up as for **14b** yielded 0.171 g (86%). ^{1}H NMR (400 MHz, $CDCl_3$, 295 K): δ 12.32 (d, br, 1H, J = 6.5 Hz, NH^iPr), 9.76 (br, 1H, NHC$_5$H$_4$N), 8.21 (d, J = 5.3 Hz, 1H, NHC$_5H_4$N), 7.70 (tm, J = 6.7 Hz, 1H, NHC$_5H_4$N), 7.27 (d, J = 8.3 Hz, 1H, NHC$_5H_4$N), 7.05 (tm, J = 6.6 Hz, 1H, NHC$_5H_4$N), 4.38 (dsep, J = 8, 6.5 Hz, 1H, NHCH(CH$_3$)$_2$), 1.36 (d, J = 8.0 Hz. 6H, NHCH(CH_3)$_2$). Anal. Calcd for $C_9H_{13}AuClN_3$: C, 27.32; H, 3.31; N, 10.62. Found: C, 27.62; H, 3.06; N, 10.53.

[AuCl{C(NHC$_7$H$_{15}$)(NHPy-2)}] (14e). n-Heptylamine (0.15 mmol, 22.5 μL) was added to a solution of [AuCl(CNPy-2)] (0.051 g, 0.15 mmol) in CH_2Cl_2 (20 mL). Work up us for **14b** yielded 0.45 g (66%). ^{1}H NMR (400 MHz, $CDCl_3$, 295 K): δ 12.46 (br, 1H, NHC$_7$H$_{15}$), 9.77 (br, 1H, NHC$_5$H$_4$N), 8.20 (d, J = 4.1 Hz, 1H, NHC$_5H_4$N), 7.71 (tm, J = 6.8 Hz, 1H, NHC$_5H_4$N), 7.25 (m, 1H, NHC$_5H_4$N), 7.06 (m, 1H, NHC$_5H_4$N), 3.78 (q, J = 6.3 Hz, 2H, NHCH_2C$_6$H$_{13}$), 1.69 (m, 2H, NHCH$_2$C$_6H_{13}$), 1.26 (m, 8H, NHCH$_2$C$_6H_{13}$), 0.84 (t, J = 5.2 Hz, 3H, NHCH$_2$C$_6H_{13}$). Anal. Calcd for $C_{13}H_{21}AuClN_3$: C, 34.56; H, 4.69; N, 9.30. Found: C, 34.75; H, 4.45; N, 9.14.

[{Trimethoxybenzonitrile}Au{C(NH^{t}Bu)(NHPy-2)}]SbF$_6$ (14f). A solution of [AuCl{C(NH^{t}Bu)(NHPy-2)}] (**14b**) (41 mg, 0.10 mmol) and 2,4,6-trimethoxybenzonitrile (59 mg, 0.30 mmol, 3 equiv) in dry CH_2Cl_2 (1 mL) was added over a solution of $AgSbF_6$ (35 mg, 0.10 mmol) in CH_2Cl_2 (0.6 mL). A white precipitate appeared immediately. After stirring for 5 min, the mixture was filtered (double HPLC Teflon filter). Addition of Et_2O (5 mL) led to the formation of the cationic complex as a white air stable precipitate which was filtered, washed with Et_2O (2 × 5 mL) and air-dried (50 mg, 62%). ^{1}H NMR (400 MHz, CD_3CN) δ 13.29 (br s, 1H), 9.27 (br s, 1H), 8.32−8.31 (m, 1H), 7.87−7.83 (m, 1H), 7.20 (dd, J = 6.9, 5.6 Hz, 1H), 7.03 (d, J = 8.3 Hz, 1H), 6.23 (s, 2H), 3.88 (s, 6H), 3.86 (s, 3H), 1.63 (s, 9H); HRMS-ESI: 567.1698; Calcd for $C_{20}H_{26}AuN_4O_3$: 567.1671; Anal. Calcd for $C_{20}H_{26}AuF_6N_4O_3Sb$: C, 29.91; H, 3.26; N, 6.98; Found: C, 30.03; H, 3.26; N, 6.98. IR (solid): ν(CN) = 2261 cm^{-1}.

[AuCl{C(NHMe)(NHPy-4)}] (15). $MeNH_2$ (0.95 mmol, 100 μL) was added to a solution of [AuCl(CNPy-4)] (0.252 g, 0.75 mmol) in dichloromethane (30 mL). Work up us for **14b** yielded 0.202 g (66%). ^{1}H NMR (300 MHz, Me_2CO-D_6, 295 K): δ 9.50 (br, 1H, NHC$_5$H$_4$N, minor), 8,93 (br, 1H, NHC$_5$H$_4$N), 8.56 (m, 5H, NHCH$_3$ + NHC$_5H_4$N), 7.78 (m, 2H, NHC$_5H_4$N), 7.71 (m, 2H, NHC$_5H_4$N, minor), 3.38 (s, 3H, NHCH_3), 3.12 (d, J 4.1, 3H, NHCH_3, minor). Anal. Calcd for $C_7H_9AuClN_3$: C, 22.87; H, 2.47; N, 11.43; Found: C, 22.86; H, 2.76; N, 11.29.

Catalytic Procedures. All reactions were carried out under N_2 in solvents dried using a solvent purification system (SPS). 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 23 °C on a Bruker Avance 400 Ultrashield. Compounds **16a**−**20b** tested in catalysis have been reported before.[5c]

General Procedure for Skeletal Rearrangement of 1,6-Enynes. Procedure with Catalysts 14a−**e and 15.** 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 time indicated in Table 1 (monitored by TLC), the reaction was quenched with a drop of NEt_3 and then directly purified through a short column of silica (AcOEt/hexane) to give the corresponding compounds.

Procedure with the Cationic Complex 14f. The enyne (0.15−0.2 mmol) and the cationic gold(I) complex (2−5 mol%) were dissolved with stirring in CH_2Cl_2 (2 mL). After the time indicated in Table 1 (monitored by TLC), the reaction was quenched with 1 mL of a solution of NEt_3 (0.1 M) and then directly purified through a short column of silica (AcOEt/hexane) to give the corresponding compounds.

General Procedure for Methoxycyclizations of 1,6-Enynes. Procedure with Catalysts 14a-e and 15. 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 MeOH (2 mM, 2 mL; 2−5 mol% $AgSbF_6$). After the time indicated in Table 2 (monitored by TLC), the reaction was quenched with a drop of NEt_3 and then directly purified through a short column of silica (AcOEt/Hexane) to give the corresponding compounds.

Procedure with the Cationic Complex 14f. The enyne (0.15−0.2 mmol) and the cationic gold(I) complex (2−5 mol%) were dissolved with stirring in MeOH (2 mL). After the time indicated in Table 2 (monitored by TLC), the reaction was quenched with 1 mL from a solution of NEt_3 (0,1 M) and then directly purified through a short column of silica (AcOEt/Hexane) to give the corresponding compounds or mixtures.

Experimental Procedure for X-ray Crystallography. Suitable single crystals of **14b** were obtained by layering hexane in a dichloromethane solution of the corresponding compound. Crystals were mounted in glass fibers, and diffraction measurements were made using a Bruker SMART CCD area-detector diffractometer with Mo−K_α radiation (l = 0.71073 Å).[24] Intensities were integrated from several series of exposures, each exposure covering 0.3° in w, the total data set being a hemisphere.[25] Absorption corrections were applied, based on multiple and symmetry-equivalent measurements.[26] The structures were solved by direct methods and refined by least-squares on weighted F^2 values for all reflections (see Table 3).[27] All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. All the hydrogen atoms, including those involved in hydrogen bonding, were calculated with a riding model. Complex neutral-atom scattering factors were used.[28] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary publications with the deposition number CCDC-696928. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.)+44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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