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Exploring the Scope of Nitrogen Acyclic Carbenes (NACs) in Gold-Catalyzed Reactions

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The catalytic activity of the recently reported nitrogen acyclic carbene (NAC) complexes of gold(I) has been investigated and compared with the reported activity of other gold(I) and gold(III) complexes. The complexes studied, [AuCl{C(NEt_2)(NHTol-*p*)}], [AuCl{C(NEt_2)(NHXylyl)}], and [Au(NTf_2){C(NEt_2)(NHXylyl)}], are very active in processes such as the rearrangement of homopropargylsulfoxides, the intramolecular hydroamination of *N*-allenyl carbamates, the intramolecular hydroalkoxylation of allenes, the hydroarylation of acetylenecarboxylic acid ester, and the benzylation of anisole. Although the NAC ligands have not been optimized for the reactions tested, the yields obtained are usually similar and sometimes better than those reported with other catalysts, showing that the presence of N−H bonds and the wider N−C−N angle in the NAC (as compared to the NHC) complexes are not detrimental for the catalysis. For the hydroarylation reaction (where two competing products can be formed), the NAC complexes allow favoring one over the other. For the benzylation of anisole the selectivity is complementary to that obtained using H[$AuCl_4$] as catalyst, and depending on the substrate, the NAC gold(III) complexes outperform the activity of H[$AuCl_4$]. On average, the reactivity found suggests that the basicity of NACs toward gold(I) is very similar to that of NHCs and higher than that of phosphines.

Introduction

In contrast to the scarce attention paid just twenty years ago to gold complexes as catalysts, they are now recognized as very active compounds in many organic transformations.[1] Much research in the topic has been carried out on classical complexes with phosphine ligands, but in the last years nitrogen heterocyclic carbene ligands (NHCs) have gained attention,[2] because, as an advantage on phosphines, they are not prone to oxidation. Moreover, recently, Bertrand et al. have successfully used very interesting cationic gold(I) complexes with five-membered cyclic (alkyl)(amino)-carbene (CAAC) ligands as catalysts in some organic transformations.[3]

To the widely used NHC catalysts and the much less exploited CAACs, we recently added two other carbene types, the so-called hydrogen-bonded heterocyclic complexes (HBHCs)[4,5] and the nitrogen acyclic complexes (NACs),[6] both shown in Scheme 1. Although gold(I) complexes of the NAC type have been long known,[7−9] they had never been applied in catalysis previous to our works showing their high catalytic activity in the skeletal rearrangement and in the alkoxycyclization of 1,6-enynes.[5,6,10]

As we showed by NMR in our previous works,[5,6] depending on the ability of the solvent to break the intramolecular

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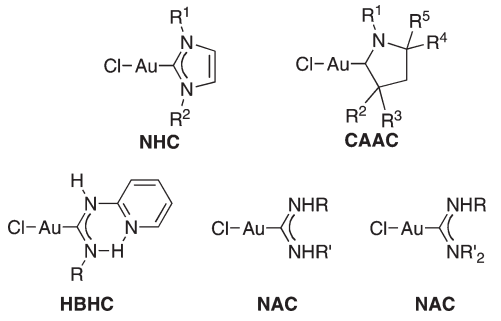
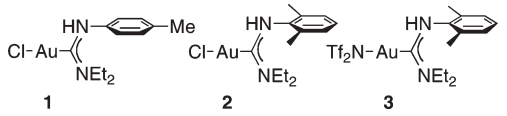
Scheme 1. Types of Gold(I) Carbene Complexes

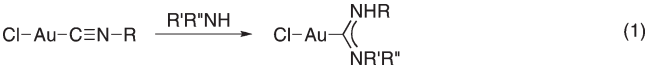


Scheme 2. Types of Carbene Gold(I) Complexes



hydrogen bond in HBHCs, these are structurally similar (cyclic) to the NHC carbenes (in acetone or CH_2Cl_2) or become similar to the NACs in solvents where the intramolecular hydrogen bond has been split (in MeOH). The fact that the HBHC gold complexes were similarly active in methoxycyclization of enynes, where their cyclic structure is broken,[5] and in cyclization reactions in CH_2Cl_2, where its cyclic structure is preserved, suggested that, except for the possible influence in the spatial arrangement of the substituents, the cyclic or acyclic structure of the carbene is not a crucial difference. In fact both types of gold complexes (NACs and HBHCs) showed similar catalytic activity.[5,6]

The HBHC ligands require the cumbersome low-yield synthesis of 2-pyridyl isocyanide, but the easy synthesis of NAC metal complexes by simple nucleophilic attack of amines to gold(I) isocyanide complexes (even from commercial isocyanides and amines) (eq 1)[11] makes NAC advantageous over NHC complexes to produce a series of gold catalysts and easily tune their electronic and steric characteristics.



(1)

However, these NAC complexes (also the HBHCs) have two peculiar features that make them different from the NHCs: (i) In the absence of structural distortions by the substituents, the N−C−N angle at the carbene atom should be about 60°, compared to about 72° for the NHCs, which means that, for similar electronic influences by the substituents, the expected order of carbene basicity should be NACs < NHCs.[12] (ii) Due to the method of synthesis, the coordinated carbenes have at least one (for secondary amines) or two (for primary amines) active N−H hydrogen atoms, which might interfere for some applications. These two features could be detrimental for the activity of NACs catalysts, so we decided to examine their scope of application by examining their performance, compared to the best results found in several reported gold-catalyzed processes.

(11) For other metal complexes with NACs, see: (a) Michelin, R. A.; Pombeiro, A. J. L.; Guedes da Silva, M. F. C. *Coord. Chem. Rev.* **2001**, *218*, 75–112. (b) Vignolle, J.; Cattoe, X.; Bourissou, D. *Chem. Rev.* **2009**, *109*, 3333–3384.

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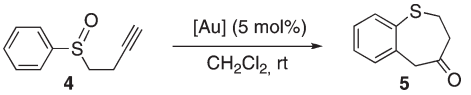
Table 1. NAC Gold-Catalyzed Rearrangement of Homopropargylsulfoxide



entry	[Au]	AgX	yield [%]
1	**1**	$AgSbF_6$	62[a]
2	**1**	$AgNTf_2$	75[a]
3	**2**	$AgNTf_2$	82[a]
4	**2**	$AgSbF_6$	76[a]
5	**3**		60[a]
6	$[AuCl(PPh_3)]$	$AgSbF_6$	30[a] (34[b])
7	$[AuCl(PPh_3)]$	$AgNTf_2$	30[a]
8	$[AuCl(P(p\text{-}CF_3C_6H_4)_3)]$	$AgSbF_6$	25[b]
9	[AuCl(IMes)]	$AgSbF_6$	76[a] (94[b])
10	[AuCl(IMes)]	$AgNTf_2$	77[a]
11	$[AuCl_2(N{-}O)]$[c]		93

[a] Our result, ^1H NMR yield. [b] Literature, isolated yield, see ref 16. [c] See ref 15.

This should give us information about the feasibility of application of the NAC-type carbenes in gold catalysis and about the actual nucleophilicity of this structural type of carbenes compared to other ligands used in gold(I) catalysis.

Results and Discussion

Complexes **1** and **2** have been reported before[6] and were chosen for the tests because they had been found particularly efficient and highly selective in the skeletal rearrangement and methoxycyclization of 1,6-enynes (Scheme 2).[6] Complex **3**, with the weakly coordinated counteranion bis(trifluoromethanesulfonyl)imidate, was synthesized by reaction of the neutral gold(I) carbene **2** with $AgNTf_2$,[13] affording in good yield a white and fairly stable solid.

The catalytic reactions chosen to test the activity of the NAC gold(I) complexes were carried out under the standard conditions used for the reported references (this means that the performance with NACs was not optimized) and, except for $[Au(NTf_2)\{C(NEt_2)(NHXylyl)\}]$ (**3**), adding a silver salt to extract the chloride *in situ* to allow for the coordination of the substrate to the Au center.[14]

1. Rearrangement of Homopropargylsulfoxides. Zhang and Li have demonstrated that dichloro(pyridine-2-carboxylato)gold(III) is active for this reaction in the absence of a silver salt (Table 1, entry 11).[15] With gold(I), Saphiro and Toste have reported that phosphine complexes [AuClL] (L = PPh_3, $P(p\text{-}CF_3C_6H_4)_3$) are active catalysts for the rearrangement of the homopropargylsulfoxide **4** to 1-benzothiepin-4-one **5** in the presence of $AgSbF_6$.[16] However, the yield obtained with PPh_3 was low (34%, Table 1, entry 6[b]), and it was even worse with the poorer donor phosphine $P(p\text{-}CF_3C_6H_4)_3$ (25%, Table 1, entry 8).[16] In our hands (entries 6[a] and 7), similar poor results have been obtained by using $[AuCl(PPh_3)]$ and $AgNTf_2$ instead of $AgSbF_6$ (Table 1, entry 7).

(13) Ricard, L.; Gagosz, F. *Organometallics* **2007**, *26*, 4704–4707.

(14) The reactions in the literature have been repeated in our lab, as suggested by one reviewer, for better comparison. When there is a significant difference, both results are given in the tables.

(15) Zhang, L.; Li, G. *Angew. Chem., Int. Ed.* **2007**, *46*, 5156–5159.

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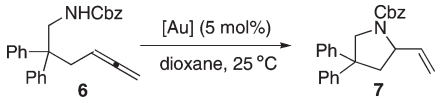
Table 2. NAC Gold-Catalyzed Intramolecular *exo*-Hydroamination of *N*-Allenyl Carbamate



entry	[Au]	AgX	yield [%]
1	**2**	AgOTs	92[a]
2	**3**		78[a]
3	[AuClP(*t*-Bu)$_2$(*o*-biphenyl)]	AgOTf	95[b]

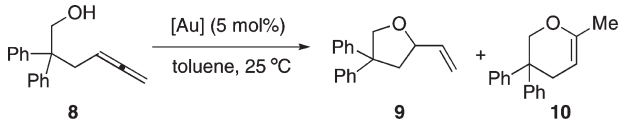
[a] Our result, isolated yield. [b] Literature, ref 18.

The better donor NHC ligand IMes was reported by Toste to afford 94% yield (Table 1, entry 9[b]);[16] in the same reaction conditions, our yield calculated by ^{1}H NMR was not as high, whether with $AgSbF_6$ or with $AgNTf_2$ as chloride scavenger (entries 9[a] and 10). The results obtained with **1**−**3**, shown in Table 1, are in the range of activity of their analogous NHC (somewhat better or worse depending on the experiment reference (our own or the data in the literature), which is consistent with the presumption that NACs should be in the order of basicity of NHCs, maybe a bit less basic than them. Under the same conditions NAC complexes compare favorably with phosphines, as expected.[17] Thus, the yields in this reaction seem to follow the order of basicity of the ligand.

2. Intramolecular Hydroamination of *N*-Allenyl Carbamates. As nitrogen and oxygen heterocycles are a part of the structure of a wide range of biologically active systems, the design of new catalysts for the synthesis of heterocyclic compounds is a very attractive field. The gold(I)-catalyzed intramolecular hydroamination of *N*-allenyl carbamates such as **6** (Table 2) has been reported with an equimolecular mixture of [AuClP(*t*-Bu)$_2$(*o*-biphenyl)] and AgOTf (Table 2, entry 3) and is very selective toward *exo*-hydroamination.[18] We find that the NAC gold(I) complexes **2** and **3** are also very active catalysts for this *exo*-hydroamination. When a mixture of **2** and AgOTs was used, the hydroamination of the allenyl carbamate **6** led to isolation of 2-vinylpyrrolidine **7** in 92% yield (Table 2, entry 1), similar to the yield reported using [AuClP(*t*-Bu)$_2$(*o*-biphenyl)] as precatalyst and AgOTf. The reaction carried out using **3** as catalyst with NTf_2 as ligand was about as effective (Table 2, entry 2).

3. Intramolecular *exo*-Hydroalkoxylation of Allenes. NAC gold(I) complexes are also active catalysts in the intramolecular hydroalkoxylation of 2,2-diphenyl-4,5-hexadienol **8**. Widenhoefer et al. reported that the regioselectivity of this reaction has a very strong dependence on the counterion.[18] For instance, the reaction carried out using a mixture of [AuClP(*t*-Bu)$_2$(*o*-biphenyl)] and AgOTf had a very low regioselectivity (Table 3, entry 3), producing a 1.3:1 mixture of tetrahydrofuran **9** and dihydropyran **10** in 85% yield; however, the same reaction using AgOTs instead of AgOTf to extract the chloride was highly regioselective, again in favor of the *exo*-hydroalkoxylation product **9** (Table 3, entry 4). In the presence of AgOTs, the NAC complex **2** was not only very efficient for the hydroalkoxylation but also highly selective toward **9** (Table 3, entry 1). The reaction using **3**, with the labile ligand NTf_2, afforded lower yields,

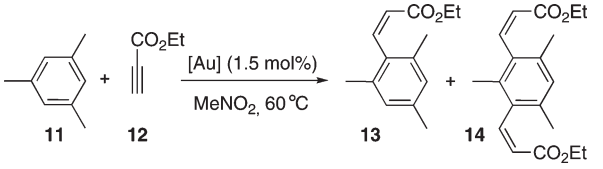
Table 3. NAC Gold-Catalyzed Intramolecular Hydroalkoxylation of 2,2-Diphenyl-4,5-hexadienol



entry	[Au]	AgX	Yield [%]
1	**2**	AgOTs	94/< 1[a]
2	**3**		45/< 1[a]
3	[AuClP(*t*-Bu)$_2$(*o*-biphenyl)]	AgOTf	48/37[b]
4	[AuClP(*t*-Bu)$_2$(*o*-biphenyl)]	AgOTs	91[c]

[a] Isolated yield. [b] Yield determined by GC analysis vs internal standard (see ref 18). [c] Isolated yield in ref 18.

Table 4. NAC Gold-Catalyzed Hydroarylation of Acetylenecarboxylic Acid Ester



entry	[Au]	AgX	Yield [%]
1	**2**	$AgNTf_2$	76/7[a]
2	**3**		78/7[a]
3	[AuCl(PEt$_3$)]	AgOTf	67/20[b]
4	[AuCl(PPh$_3$)$_3$)]	$AgBF_4$	63/6[a] (57/16[c])
5	[AuCl(PPh$_3$)$_3$)]	$AgSbF_6$	77/7[a]

[a] Our results, ^{1}H NMR yield. [b] Reaction run at 25 °C, 5% mol of catalyst. Yield determined by GC analysis vs internal standard (see ref 19.). [c] Reaction run at 60 °C with 5% mol of catalyst. Yield determined by GC analysis vs internal standard (see ref 19).

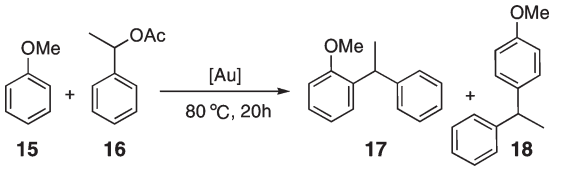
but with high regioselectivity toward the *exo*-hydroalkoxylation product **9**.

4. Intermolecular Hydroarylation of Alkynes. The formation of C−C bonds as a result of the activation of an aromatic C−H bond is an interesting alternative to the use of halogenated derivatives. Reetz and Sommer have reported that [AuCl(PR$_3$)] (R = Et, Ph) are active precatalysts in the intermolecular hydroarylation of alkynes.[19] The reactions of mesitylene **11** with the electron-poor alkyne **12**, catalyzed with [AuCl(PR$_3$)] and a silver salt (Table 4, entries 3−5), produced the desired product **13** in moderate yields. Although high *Z*-selectivity was obtained in both cases, considerable percentages of the second alkyne addition product **14** were also formed. In this case both the NAC precatalyst **2** (with an equimolecular amount of $AgNTf_2$) and catalyst **3** were apparently more active and more chemoselective than the phosphine complexes used in the original paper, leading to the formation of **13** in better yields and with a much lower percentage of **14** (Table 4, entries 1 and 2). However, repeating the reactions with PPh_3 and analyzing the results by ^{1}H NMR, we found that the results with both types of ligand are very similar in our hands.

5. Benzylation of Arenes. Beller et al. have reported that H[AuCl$_4$] is active in the benzylation of arenes and heteroarenes.[20]

(17) Phosphines have been ranked as less basic than NHCs in ref 12.
(18) Zhang, Z.; Liu, C.; Kinder, R. E.; Han, X.; Qian, H.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2006**, *128*, 9066–9073.
(19) Reetz, M. T.; Sommer, K. *Eur. J. Org. Chem.* **2003**, 3485–3496.

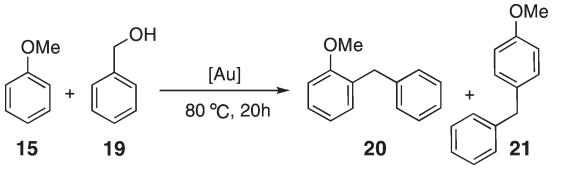
Table 5. NAC Gold-Catalyzed Benzylation of Anisole with 1-Phenylethyl Acetate



entry	[Au]	AgX	yield [%] (ratio)
1	**1**	$AgNTf_2$	95 (22/78)[a,b]
2	**1**	$AgNTf_2$	96 (19/81)[a,c]
3	**3**		94 (18/82)[a,b]
4	**3**		97 (23/77)[a,c]
5	$H[AuCl_4]$		82 (22/78)[a,b]
6	$H[AuCl_4]$		99 (13/87)[d]

[a] Our results, ^{1}H NMR yield. [b] 10 mol %. [c] 5 mol %. [d] Reaction run with 10% mol of catalyst. Yield determined by GC analysis vs internal standard (see ref 20).

Table 6. NAC Gold-Catalyzed Benzylation of Anisole with Benzyl Alcohol



entry	[Au]	AgX	yield[a] [%] (ratio)
1	**1**[b]	$AgNTf_2$	96 (40/60)
2	**1**[c]	$AgNTf_2$	91 (40/60)
3	**3**[b]		94 (40/60)
4	**3**[c]		66 (40/60)
5	$H[AuCl_4]$[b]		15 (33/67)

[a] ^{1}H NMR yield. [b] 10 mol %. [c] 5 mol %.

We have also explored the activity of this process with our gold(I) NACs. The benzylation of anisole **15** with 1-phenylethyl acetate **16** catalyzed with $HAuCl_4$ was reported to give the corresponding *para*-isomer **18** in very good yield. The reaction is not regioselective, and *ortho*-isomer **17** is also observed (Table 5, 99% yield determined by GC (o/p = 13/87), entry 6,[20] and 82% yield determined by ^{1}H NMR (o/p = 22/78), entry 5, our result). Our gold(I) NAC complexes are also active in this reaction, affording also excellent yields (Table 5, entries 1−4). The regioselectivity is nearly the same as with $HAuCl_4$, and the major regioisomer in this case is still **18**. The load of catalyst can be reduced, compared to the use of $HAuCl_4$, from 10 to 5 mol %, affording the same excellent yields.

Additional experiments were performed using a different benzylating agent (**19**, not reported in ref 20). The results obtained for the gold-catalyzed benzylation of anisole with benzyl alcohol are summarized in Table 6. The gold carbenes **1** and **3** catalyze this reaction (Table 6, entries 1−4). It is remarkable that, in contrast with the reported related reaction in Table 5, entry 6), the yields are here much better (about 90% versus 15%) than those obtained using the reported Au(III) system (Table 6, entry 5), even with lower load of catalyst (entry 2).

(20) Mertins, K.; Iovel, I.; Kischel, J.; Zapf, A.; Beller, M. *Adv. Synth. Catal.* **2006**, *348*, 641–695.

Conclusions

The scope of application of NACs as ligands for gold-catalyzed reactions looks very large. The catalyzed reactions are not disturbed by the presence of N−H bonds in the NAC ligand. Considering that the ground properties of a ligand can be tuned by changing substituents, the catalytic system [AuX(NAC)] looks extremely flexible and interesting for gold(I)-catalyzed processes: changes are particularly accessible for NACs, as they are directly made from accessible isocyanides and amines. In different reactions, these ligands behave (as far as yields are concerned) as well as or better than phosphines (even without optimization of the reaction) and are comparable to NHCs. Furthermore, in the benzylation of arenes, reported in the literature with $H[AuCl_4]$, our gold(I) ligands perform much better than the gold(III) catalyst. Taking the yields as a rough indication of reactivity, the trends observed do not contradict the expectations from the calculated order of basicity of ligands PR_3 < NACs < NHCs,[12] although practically there is no difference in behavior between NACs and NHCs.

Experimental Section

General Conditions. All reactions were carried out under dry N_2 atmosphere. The solvents were purified according to standard procedures. Complexes [AuCl{C(NEt_2)(NHTol-*p*)}] (**1**),[6] [AuCl{C(NEt_2)(NHXylyl)}] (**2**),[6] $AgNTf_2$,[21] **4**,[16] **6**,[18] **8**,[18] and **16**[22] 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 and ARX 300 and Bruker Avance 400 Ultrashield instruments. ^{1}H NMR spectra are referred to TMS.

[Au(NTf_2){C(NEt_2)(NHXylyl)}] (3). $AgNTf_2$ (89 mg, 0.229 mmol) was added to a solution of [AuCl{C(NEt_2)(NHXylyl)}] (**2**) (100 mg, 0.229 mmol) in dry CH_2Cl_2 (15 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 solid, which was filtered, washed with Et_2O (2 × 5 mL), and vacuum-dried (122 mg, 78%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.25−7.05 (m, 3 H, Ar*H*), 6.76 (br s, 1 H, N*H*), 3.94 (q, J = 7.1 Hz, 2 H, NCH_2CH$_3$), 3.55 (q, J = 7.5 Hz, 2 H, NCH_2CH$_3$), 2.24 (s, 6 H, Ar-CH_3), 1.41 (t, J = 7.5 Hz, 3 H, NCH_2CH$_3$), 1.40 (t, J = 7.1 Hz, 3 H, NCH_2CH$_3$). ^{19}F NMR (282.5 MHz, $CDCl_3$): δ −75.87 (s, N(SO_2CF_3)$_2$, 6 F). Anal. Calcd for $C_{15}H_{20}N_3AuF_6O_4S_2$: C, 26.44; H, 2.96; N, 6.17. Found: C, 26.82; H, 2.66; N, 6.20.

Catalytic Procedures. The general procedures followed for the rearrangement of homopropargylsulfoxide,[16] intramolecular *exo*-hydroamination of *N*-allenyl carbamate,[18] intramolecular hydroalkoxylation of 2,2-diphenyl-4,5-hexadienol,[18] hydroarylation of acetylenecarboxylic acid ester,[19] and benzylation of anisole with 1-phenylethyl acetate[20] are similar to those reported (the procedure was also analogous when benzyl alcohol was used as benzylating agent). The ^{1}H NMR yields were obtained by using 1,2-dichloroethane as an internal reference.

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