Synthesis, Reactivity, and Electrochemical Studies of Gold(I) and Gold(III) Complexes Supported by N-Heterocyclic Carbenes and Their Application in Catalysis

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In the present study we describe the efficient synthesis of various Au(I) complexes supported by NHC ligands. Some of these ligands have a pendant pyridine arm that is linked with various tethers $(CH_2)_n$ to the NHC backbone (n = 0-2). The chloride in the Au(I) complexes is easily and cleanly replaced by an aryl group upon reaction with an aryl-Grignard reagent. The thus obtained aryl Au(I) complexes are cleanly oxidized to the corresponding Au(III) complexes with phenyliodoso dichloride, as are the corresponding halide Au(I) complexes. The attempted salt metathesis with the parent Au(III) complex led to the oxidative coupling of the aryl residues with formation of the Au(I) complex. Some of the complexes are promising catalysts in the cycloisomerization of an ω -alkynylfuran to isobenzofuranol in the presence of a silver salt. For those precursors with pendant pyridine arms, a cationic dimeric Au complex was isolated and characterized, which represents a catalyst resting state and forms under reaction conditions.

Introduction

Although the first efforts to prepare organogold compounds were made ca. 160 years ago,¹ it took nearly 50 years until their existence was proven by Pope and Gibson in 1907.² It took a further ca. 40 years for Gilman to isolate the first trialkyl gold complex³ and another 20 for Coates to introduce phosphines as ligands in gold complexes.⁴ From that point on the field of organogold chemistry "exploded", and the application of the meanwhile uncountable number of various Au(I) and Au(III) complexes spans

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from homogeneous and heterogeneous catalysis^{5–16} to medicinal chemistry.^{17,18}

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In homogeneous catalysis both simple salts and welldefined Au(I) and Au(III) complexes have been used, with the latter usually supported by good σ donors. Among these, *N*-heterocyclic carbenes (NHCs) have recently excelled in supporting Au(I) as well as Au(III) complexes.^{13,19–21} Here, we report the synthesis of some new Au(I) and Au(III) complexes containing both simple NHCs and NHCs with pendant arms containing pyridine moieties. The redox chemistry of these complexes, their molecular structure, and their application in the synthesis of phenols are reported. The importance of the pyridine arms in supporting cationic Au(I) catalysts is also discussed.

Results and Discussion

Synthesis and Characterization. The *N*-heterocyclic carbene ligands used in this work are depicted in Figure 1. While the imidazolium salt $L1a \cdot HCl$ is commercially available, in analogy to a procedure reported by Echavarren et al. the

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Figure 1. Various NHC ligands L1a-c and L2a-c used to prepare Au(I) complexes 1a-f.



Figure 2. ORTEP diagram of $L2c \cdot HI \cdot H_2O$ with 50% probability ellipsoids. Most hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C1–N1 1.333(3), C1–N2 1.330(3), C4–N2 1.373(3), C3–N1 1.384(3), C3–C4 1.354(4), N3–O1 2.848, I1–O1 3.640, N3–H1b 2.061, I1–H1a 2.864, C1–N2–C21–N3 0.43.

ligand precursors L1b,²² L2a,²³ and L2b,²³ i.e., L1b·HI, L2a·HBr, and L2b·HBr, were prepared in 78%, 95%, and 82% yield, respectively. The new imidazolium salts L1c·HI and L2c·HI were synthesized by alkylation of the correspondingly substituted alkyl and aryl imidazoles with subsequent crystallization in 86% and 91% yield, respectively (*cf.* Experimental Section). The hygroscopic imidazolium salt L2c·HI crystallized as a water adduct L2c·HI·H₂O, giving suitable crystals for single-crystal X-ray diffraction. The solid-state molecular structure is depicted in Figure 2 and shows that the imidazolium and the pyridine rings are almost parallel (0.43°). The water molecule forms hydrogen bridges to both the nitrogen of the pyridine (2.061 Å) and the iodide (2.864 Å).

The Au(I) complexes 1a-f were obtained from the corresponding imidazolium salts by transmetalation of the *in situ* generated silver carbenes with (Me₂S)AuCl²⁴ and were isolated in moderate to almost quantitative yields (57–99%) after column chromatography on basic alumina (*cf.* Scheme 1). Recrystallization from hexanes yielded single crystals suitable for X-ray analysis of the known Au(I) complex $1b^{22.25}$ as well as of the new Au(I) complexes 1c-f. They show spectroscopic and geometric features expected for Au(I) NHC complexes, namely, a ¹³C NMR carbene signal at around 170 ppm (*cf.* Table 1) and a quasi linear geometry around the Au atom (*cf.* Table 3 and Figure 3). Interestingly, the pendant pyridine arm in complexes 1d-f does not interact with the Au center, as deduced from the rather long Au–N distance (*cf.* Table 3).

Complexes 1a-f were successfully oxidized with PhICl₂²⁶⁻²⁹ to give the corresponding Au(III) complexes [AuCl₃(L)] 2a-f in very good yields (92–97%), as recently reported by Nolan *et al.* for 2a.²⁷ PhICl₂ acts both as oxidant and as chlorinating agent. The presence of chlorine proved crucial in the stabilization of the Au(III) centers, as observed both in preparative reactions and in the electrochemical studies (*cf.* below). The attempted oxidation of 1e with oxidants other than PhICl₂, e.g., Ph₂IBr, PhI(O₂CCH₃)₂, or PhI(O₂CCF₃)₂ failed or gave a complex product mixture.

The solid-state molecular structures of complexes 2b-f are depicted in Figure 4. A comparison between corresponding complexes 1a-f and 2a-f revealed that a higher oxidation state does not translate into the shortening of the Au-carbene or the Au- Cl_{trans} distances (*cf.* Table 2; Au- $C_{carbene}$ for 1a-f ranges from 1.972(4) to 1.999(5) Å compared to 1.977(6)-2.010(4) Å for 2a-f and Au- Cl_{trans} ranges from 2.2758(12) to 2.3183(15) Å for 1a-f compared to 2.306-(2)-2.3201(13) Å for 2a-f), which correlates well to available structural data for this type of compounds.²⁴

The $\delta(C_{carbene})$ is shifted between 20 and 30 ppm upfield for complexes **2a**-**f** when compared to the chemical shifts observed for the Au(I) complexes **1a**-**f** (cf. Table 1). This correlates well with the increasing number of good σ donors in the coordination sphere^{30,31} of the metal for such complexes.^{24,27} The geometry around the Au center is essentially square planar (C_{carbene}-Au-Cl_{trans} angle ranges from 176° to 180° for **1a**-**f** compared to 178–179° for **2a**-**f**, *cf*. Table 3). There is no interaction between the pyridine and the Au center for **2d**-**f**, due to the large N···Au distances (*cf*. Table 3), nor is there an interaction between the pyridine's π system and the metal center for complexes **2e** and **2f**. The closest distances of the pyridine carbon atoms to the Au center are around 3.3 and 4.0 Å, respectively.

The reaction of **1a** with the Grignard reagents $BrMgC_6H_6$ and $BrMgC_6F_5$ gave, according to Hashmi's protocol,³² after flash column chromatography on alumina and subsequent crystallization from THF/hexane mixtures, $[Au(C_6H_5)(L1a)]$ (**3a**) (in 96% yield) and $[Au(C_6F_5)(L1a)]$ (**3b**) (in 77% yield), respectively (Scheme 1). Both **3a** and **3b** decompose upon long contact times on alumina, as indicated by the formation of purple Au-nanoparticles. Nevertheless, complexes **3a** and **3b** were fully characterized (for X-ray structures, cf. Figure 5). Compared to the parent complex **1a**, the chemical shifts of

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 $\begin{array}{l} \mbox{Table 1. Chemical Shifts (ppm) of the Carbon (δ_C) of the NHC Salts L1a \cdot HCl, L1b, c \cdot HI, L2a, b \cdot HBr, L2c \cdot HI, [AuCl(L)] ($1a-f$), [AuCl_3(L)] (2a-f$), [AuAr(L)] (3a,b), [AuArCl_2(L)] (4a,b), and [Au(L)NTf_2]_2 (5a,b) \end{array}$

L	$\delta_{\rm C}$ (ppm) of L · HX ^{<i>a</i>}	$\delta_{\rm C}$ (ppm) of $1a-f^a$	$\delta_{\rm C}$ (ppm) of 2a - f	$\delta_{\rm C}$ (ppm) of 3a , b ^{<i>a</i>}	$\delta_{\rm C}$ (ppm) of 4a , b ^{<i>a</i>}	δ_{C} (ppm) of 5a , b ^b	$\Delta \delta_{\rm C} (\rm ppm) = \\ \delta_{\rm C}(1) - \delta_{\rm C}(2)$
L1a	141.11	173.44	144.72 ^{<i>a</i>}	195.81, 190.58	180.35, 167.13		28.72
L1b	137.46	172.82	143.01 ^{<i>a</i>}				29.81
L1c	135.12	169.36	138.50 ^a				30.86
L2a	135.61	170.90	149.40^{c}				21.50
L2b	137.50	172.33	152.51 ^a			165.03	19.82
L2c	137.03	171.57	146.56 ^{<i>a</i>}			164.67	25.01

^a NMR in CDCl₃. ^b NMR in CD₂Cl₂. ^c NMR in THF-d₈.



Figure 3. ORTEP diagram of 1b-f with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths and angles are depicted in Tables 2 and 3, respectively.

the carbene carbons are deshielded (173.44 ppm for **1a** vs 195.81 and 190.58 ppm for **3a** and **3b**, respectively, cf. Table 1). This implies a poorer π -donor ability of the aromatic rings in **3a** and **3b** in comparison to chloride, a fact that is explainable by the torsion angle between the NHC and the aromatic rings, which allows only a poor overlap between the orbitals involved in NHC coordination and the π system of the aromatic rings (see Table 3).

The oxidation of complexes **3a** and **3b** in the presence of PhICl₂ proceeds smoothly to give $[Au(C_6H_5)Cl_2(L1a)]$ (**4a**) and $[Au(C_6F_5)Cl_2(L1a)]$ (**4b**) in high yields (78% and 93%, respectively, cf. Scheme 1). Both compounds were precipi-

tated from THF/water mixtures and purified by flash column chromatography on basic alumina. Again, after long contact with alumina, the complexes decomposed, as indicated by the formation of purple Au-nanoparticles. Besides **4a**, ca. 17% of **2a** was isolated from the reaction mixture. This is possibly originated from the reductive elimination of chlorobenzene, a common decomposition product,³³ from **4a**, with subsequent oxidation of the Au(I) species **1a** to **2a** under reaction conditions. A transmetalation route cannot

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Figure 4. ORTEP diagram of 2b-f with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths and angles are depicted in Tables 2 and 3, respectively.

 $\begin{array}{l} \text{Table 2. Selected Au-C}_{carbene, Au-X}_{trans} (X = Cl, C, N), Au-Cl_{cis}, Au\cdots Au, \text{ and } Au-N(py) \text{ Distances (Å) for } [AuCl_{L}] (1a-f), \\ & \quad [AuCl_{3}(L)] (2a-f), [AuAr(L)] (3a,b), [AuArCl_{2}(L)] (4a,b), \text{ and } [Au(L)NTf_{2}]_{2} (5a,b) \end{array}$

complex	Au-C _{carbene}	Au-X _{trans}	Au-Cl _{cis}	Au-Cl _{cis}	Au···Au	Au-N(py)
$1a^{62-64}$	1,999(5)	$2.2758(12)^{a}$			8.446	
1b	1.975(4)	$2.2892(10)^{a}$			3.764	
1c	1.995(4)	$2.3143(11)^{a}$			6.249	
1d	1.992(7)	$2.3183(15)^{a}$			3.3491(5)	4.817
1e	1.974(4)	$2.3183(9)^{a}$			4.020	4.969
$\mathbf{1f}^{b}$	1.972(4)	$2.290(4)^{a}$			3.324-6.708	3.606-4.822
2a ²⁷	1.977(6)	$2.306(2)^{a}$	2.276(2)	2.268(2)	9.398	
2b	1.994(4)	$2.3160(13)^{a}$	2.2614(14)	2.2886(13)	6.415	
2c	2.010(4)	$2.3154(12)^{a}$	2.2859(12)	2.2812(12)	10.305	
2d	2.003(5)	$2.3112(14)^{a}$	2.3036(14)	2.2970(14)	6.943	2.737
2e	1,999(5)	$2.3201(13)^{a}$	2.2906(12)	2.2905(11)	7.598	3.836
2f	1.997(5)	$2.3162(11)^{a}$	2.2787(11)	2.2802(11)	8.888	4.393
3a	2.002(11)	$2.072(13)^{c}$	()	()	9.704	
3b	2.001(4)	$2.034(5)^{c}$			10.867	
4a	2.077(6)	$2.085(6)^{c}$	2.2805(17)	2.2872(16)	9.904	
4b	2.051(10)	$2.063(12)^{c}$	2.276(3)	2.276(3)	8.773	
5a	1.984(8)	$2.066(7)^d$	(2)	()	3.407	е
Cu	1.960(9)	$2.068(6)^d$			21107	
5b	1.992(4)	$2.077(3)^d$			3.2269(3)	е

 ${}^{a}X_{trans} = Cl. {}^{b}Four independent molecules. {}^{c}X_{trans} = C. {}^{d}X_{trans} = N(py). {}^{e}Not relevant.$

be excluded, however.⁵ Compounds **4a** and **4b** are, to the best of our knowledge, the first NHC complexes of Au(III) of the type [AuArCl₂(L)], although complexes of this type with

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other σ -donor ligands³⁴⁻⁴⁰ or with alkyl instead of aryl residues^{41,42} have been reported. A comparison of the chemical shifts for the $\delta(C_{carbene})$ for **3a,b** and **4a,b** shows a clear upfield shift of 15–23 ppm, resulting from the presence of more σ donors in the metal's coordination sphere (Table 1).^{30,31} The structural parameters of complexes **3a,b** and **4a,b** are comparable to **1a–f** and **2a–f** (*cf*. Figure 6; Tables 1–3).

Curiously, the reaction of complex 2e and *p*-methoxyphenylmagnesium bromide gave 1e in 87% yield instead of the expected aryl-Au(III) complex of type 4. This is accompanied by the formation of 4,4'-bismethoxybiphenyl in 81% isolated yield (Scheme 1). C-C coupling reactions involving

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Table 3. Selected Angles and Torsion Angles (deg) for [AuCl(L)] (1a-f), [AuCl ₃ (L)] (2a-f), [AuAr(L)] (3a,b), [AuArCl ₂ (L)] (4a,b), and
$[Au(L)NTf_2]_2$ (5a,b)

complex	Ccarbene-Au-Xtrans	Ccarbene-Au-Clcis	X _{trans} -Au-Cl _{cis}	Cl _{cis} -Au-Cl _{cis}	torsion angle
$1a^{62-64}$	180.0 ^a				
1b	$178.25(11)^{a}$				
1e	$177.74(13)^{a}$				
1d	$175.7(2)^{a}$				
1e	$176.89(12)^{a}$				
1f ^b	$175.5 - 179.6^{a}$				
$2a^{27}$	178 10(18)	88 50(18)	90.01(10)	178.53(7)	73.9^{c}
2h	$179 \ 19(14)^a$	88 52(13)	91.43(5)	176.53(5)	71.09^{c}
	1,5115(11)	88.42(13)	91.61(5)	1/0100(0)	/ 110 /
2c	$179.21(14)^{a}$	88.70(14)	$90.54(6)^a$	174.38(6)	89.04^{c}
		88.86(14)	91.88(6)		
2d	$177.70(14)^{a}$	91.94(14)	90.25(6)	179.66(6)	86.44^{c}
	1,,,,,,(1,))	88 17(14)	89 65(5)	1/2/00(0)	00111
2e	$178, 16(14)^a$	90.15(13)	91.56(4)	178, 12(4)	66.97^{c}
	1,0110(11)	88 01(13)	90.28(5)	1/0112(1)	00177
2f	$177.68(13)^{a}$	89 09(12)	90.82(4)	178 95(4)	62.60°
	1,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	90.20(12)	89 92(4)		02100
39	$1785(5)^d$	90.20(12)	09.92(1)		44.81^{e}
3h	$176.52(17)^d$				16.71^{e}
49	$178.6(2)^d$	90.37(17)	88 54(18)	178 53(7)	14.11^{e}
iu ii	170.0(2)	91.04(17)	90.06(18)	1/0.05(7)	1
4h	$180,00(2)^d$	91.19(6)	88 81(6)		21.41^{e}
59	$174.6(3)^{f}$)1.1)(0)	00.01(0)		3453^{g}
Cu .	$170.9(3)^{f}$				45.68^{g}
5b	$175.24(14)^{f}$				67.87^{g}

 ${}^{a}X_{trans} = CL^{b}$ Four independent molecules. ${}^{c}Angle N$ -C_{carbene}-Au-Cl_{cis}. ${}^{d}X_{trans} = CL^{e}Angle between the aromatic and the carbene rings. <math>{}^{f}X_{trans} = N(py)$.



Figure 5. ORTEP diagrams of 3a and 3b with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths and angles are depicted in Tables 2 and 3, respectively.

Grignard reagents in the presence of Au(III) centers^{43–47} usually occur by radical coupling, in which case the Au(III) complex **2e** would act as an oxidant. In that case reduction would be faster than chloride substitution. This has been shown previously for several C–C coupling reactions mediated by Au(I) and Au(III) complexes, although the fate of the Au species often remained unclear.^{46,48,49} An innersphere reductive elimination pathway cannot be excluded, however.^{5,42}

The abstraction of one chloride ligand in complexes le and 1f by means of a silver salt (Scheme 1) gave in very good yields (93% and 96%, respectively) the cationic Au(I) complexes [Au(L2b)]₂(NTf₂)₂ (5a) and [Au(L2c)]₂(NTf₂)₂, (5b), respectively. Now, the pyridine pendant arm stabilizes the cationic Au(I) center as an L-type donor, similarly to what has been reported for other cationic Au(I) complexes.^{24,50} Due to the preference for a linear coordination geometry of Au(I) centers, the pyridine arm coordinates to a second Au(I) center, thus giving a dimeric bicationic structure with two triflimide units as counterions (*cf.* Figure 7). The ${}^{13}C{}^{1}H{}$ NMR chemical shifts for the carbon observed for these two complexes (165.03 ppm for 5a and 164.67 ppm for 5b) agree with the chemical shifts reported for cationic complexes of the type $[Au(NHC)(L)]^+$ (from 165.7 to 190.4 ppm), cf. Table 3.²⁴ Although the Au \cdots Au distance for both complexes is short (3.407 and 3.2269(3) Å for 5a and 5b, respectively), there is no Au-Au bond. This is believed to be partly due to the aurophilic attraction between two Au(I)

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Figure 6. ORTEP diagram of 4a and 4b with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths and angles are depicted in Tables 2 and 3, respectively.



Figure 7. ORTEP diagram of 5a and 5b with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths and angles are depicted in Tables 2 and 3, respectively.

ions (typical values for these interaction are reported between 2.75 and 3.4 Å)¹¹ and partly due to the geometry of the complex. Here, packing obviously plays a key role, since substitution of the mesityl group in **L2b** for a methyl group causes a significant shortening of the Au···Au distance $(3.407 \text{ Å for } 5a vs 3.1730(5) \text{ Å for } [Au_2(CH_3im(CH_2py))_2]-(BF_4)_2).^{51}$ Furthermore, Au(I) complexes **1d** and **1f** also show similar Au···Au distances in the solid state (see Table 2), but the electrochemical studies on these complexes rule out the presence of Au(II) species in the oxidation of these complexes (see below).

Electrochemical Studies. The electrochemistry of the Au(I) complexes 1b and 1d-f and the Au(III) analogues 2b and 2d-f was studied by cyclic voltammetry (CV) in acetonitrile using nBu_4NPF_6 (0.1 M) as electrolyte (*cf.* Figure 8, Table 4).

The cyclic voltammograms of the Au(I) complexes **1b** and **1d-f** show a reduction wave at -914, -1160, -980, and -1130 mV, respectively, versus the redox couple ferrocene/ ferrocenium, indicating the reduction of the complex to metallic Au(0). Upon reversal of the scanning direction, no oxidation wave was detected in the absence of nBu_4NCl (Figure 8a). For the Au(III) complexes **2b** and **2d-f** a reduction wave was obtained at -247, -120, -300, and -400 mV, respectively, to give the corresponding Au(I) complexes (Figure 8b). Complexes **2d** and **2e** were in turn further reduced to Au(0) at -1030 and -1140 mV. In case of **2b** and **2f** no reduction wave from Au(I) to Au(0) was observed. Reoxidation from Au(I) to Au(II) was observed for **2d** and **2e** at -950 and -1000 mV, respectively, but not for **2b** and **2f**.

When the CV experiment for **1f** was repeated in the presence of $nBu_4NCl(3.6 \text{ mM})$ the Au(I) complex (5.7 mM) was reduced to Au(0) at -1130 mV and was not reoxidized going back to anodic potential. When the same experiment was run with reversion of the scanning direction, we observed the oxidation of Cl⁻ to Cl₂ at -1360 mV,⁵² but no further oxidation wave from Au(I) to Au(III) was detected. On the basis of literature,⁵³ we believe that once chloride is oxidized to chlorine, the Au(I) centers present in the vicinity of the electrode is then rapidly oxidized to Au(III) by Cl₂ (the reaction is analogous to the one described above for PhICl₂). The oxidation to the chemically formed Au(III) is then evident once the scanning direction is again reversed, since now a reduction wave from Au(III) to Au(I) at -400 mV is indeed observed (Figure 8c).

The potential values measured do not seem to correlate with the presence of the tethered pyridine or with the length of the tether.

Catalytic Studies. Complexes **1b**–**f** and **2e** were tested as catalysts in the cycloisomerization of the ω -alkynylfuran **6** to give 4-isobenzofuranol (**7**, Scheme 2). This reaction has been reported by Hashmi et al.⁵⁴ as a standard test reaction for new Au complexes and also by others using platinum.^{55–57} More recently cationic Au(I) complexes supported by phosphines⁵⁸ and 1,2,3-triazoles were also used in this reaction.⁵⁹

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Figure 8. Electrochemical study. (a) and (b) GC, Pt, SCE in acetonitrile 0.1 M solution of nNBu₄PF₆ (initial potential 0 V vs ferrocene, vertex potential -1.5 V vs ferrocene, final potential 0 V vs ferrocene, scan rate 25 mV/s). (c) For compound **1f**, GC, Pt, SCE in acetonitrile 0.1 M solution of nNBu₄PF₆ (all potentials vs ferrocene, scan rate 25 mV/s). (c) For (3.6 mM) added as source of chloride). The concentration of the gold complexes ranges from 5.0 to 6.9 mM.

Table 4. Electrochemical Study of Gold(I) [AuCl(L2a)] (1d), [AuCl(L2b)] (1e), and [AuCl(L2c)] (1f) and Gold(III) Complexes [AuCl₃(L2a)] (2d), [AuCl₃(L2b)] (2e), and [AuCl₃(L2c)] (2f)

complex	reduction (III-I) [mV]	reduction (I-0) [mV]	oxidation (I–III) [mV]
1b		-914	
1d		-1160	
1e		-980	
1f		-1130	
2b	-247		
2d	-120	-1030	-950
2e	-300	-1140	-1000
2f	-400		

All reactions were done at room temperature in NMR tubes, with the exception of one preparative experiment (Table 5, entry 16). Conversion and yield were monitored by ¹H NMR. The reactions turned out to be complete within one hour. Control NMR experiments after 24 h showed no

Scheme 2



further conversion of the starting material, pointing to a fast catalyst deactivation.

The Au(I) complexes **1b**-**f** (Table 5, entries 1–5) gave a low overall conversion to **7**, with a maximum yield of 57% (with **1f**) but decent turnover numbers of 40–228 [mol]/[mol] at a catalyst loading of 0.25 mol % in chloroform. The length of the tether (CH₂)_n between the pyridine ring and the NHC backbone has a major influence on the reaction outcome; that is, in the series of complexes **1d**-**f** with increasing *n*, yields increase from 10% (n = 0) to over 37% (n = 1) to 57% (n = 2), respectively (entries 3–5). Au(III) complex **2e** gives slightly lower yields when compared to the corresponding Au(I) analogue **1e** under the same conditions (28% vs 37%, entry 6 vs entry 4).

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 Table 5. Gold-Catalyzed Synthesis of Dihydroisobenzofuran-4-ol

 (7), cf. Scheme 2,^a

entry	catalyst	catalyst (mol %)	yield (%)	TON^b
1	1b	0.25	30 ^c	120
2	1c	0.25	42^{c}	168
3	1d	0.25	10^{c}	40
4	1e	0.25	37^c	148
5	1f	0.25	57^c	228
6	2e	0.25	28^c	112
7	1f	2.00	70^c	35
8	1f	0.50	67^c	134
9	1f	0.25	82^d	328
10	1f	0.10	38 ^c	380
11	1f	0.05	30^c	600
12	1d	0.25	30^d	120
13	1e	0.25	24^d	96
14	1f	0.25	$25^{d,e}$	100
15	1f	0.25	$4^{d,f}$	16
16	1f	0.25	87^g	348
17	5a	0.13	$74^{d,h}$	569
18	5b	0.13	$72^{d,h}$	554

^{*a*} All reactions were done in an NMR tube with the exception of entry 16. All reactions were done at room temperature and monitored by NMR after one hour. ^{*b*} TON = n(7)/n(catalyst). ^{*c*} NMR experiment in CDCl₃. ^{*d*} NMR experiment in CD₂Cl₂. ^{*e*} AgSbF₆ was used instead of AgNTf₂. ^{*f*} AgOTf was used instead of AgNTf₂. ^{*g*} Isolated yield of double scaled reaction. ^{*h*} No silver salt added.

For catalyst **1f** a systematic reduction of the catalyst loading from 2 to 0.05 mol % led to a decrease in yield (from 57% to 30%, entries 5, 9, 10, 11, 16) but to an increase in TON (from 35 to 600 [mol]/[mol]). A strong dependency of yield and TON was observed by solvent change from chloroform to dichloromethane for **1f** (57% vs 82% yield and 228 vs 328 TON, entry 5 vs 9) and **1d** (10% vs 30% yield and 40 vs 120 TON, entry 3 vs 12), but not for **1e** (37% vs 24% yield and 148 vs 96 TON, entry 4 vs 13, respectively).

The counterions had a crucial impact on the yield and TON: replacement of Gagosz's⁶⁰ NTf₂⁻ by SbF₆⁻ or TfO⁻ in dichloromethane decreased the yields and TONs dramatically (82% vs 25% and 4% yield, 328 vs 100 and 16 TON, entry 9 vs 14 and 15, respectively). This is in agreement with the stabilization of Au(I) cations by coordinating ligands, which has been associated with higher conversions in this reaction by slowing catalyst decomposition pathways.^{50,59}

The most active catalyst under the screening conditions (NMR scale) is **1f**, which gave **7** in 82% yield (328 TON, entry 9). The same reaction on a preparative scale (entry 16) gave **7** in an isolated yield of 87%, indicated by an even higher TON of 348. This by far exceeds the yield of 68% obtained with state-of-the-art Au(I) phosphine complexes.⁵⁸

Interestingly, both complexes **1e** and **1f**, which both bear a pyridine pendant arm linked via a methylene and ethylene tether to the NHC's backbone, dimerize in the presence of AgNTf₂ to give **5a** and **5b** (Figure 7). As the conditions leading to the formation of the dimer are similar to the conditions for the cycloisomerization, we presume that **5a** and **5b** form *in situ* under reaction conditions and represent at least a catalyst resting state. We therefore tested **5a** and **5b**, without any added base and with the same concentration of Au (i.e., with half of the catalyst loadings of **5a** and **5b**) and obtained 7 in dramatically higher yield and TON (**1e** vs **5a**: 24% vs 74% yield, 96 vs 569 TON, entry 13 vs 17, respectively) or similar TON and yield (**1f** vs **5b**: 82% vs 72% yield, 328 vs 554

TON, entry 9 vs 18, respectively). As **5a** and **5b** are both coordinatively saturated due to the proximity of the twocoordinate Au(I) centers, they have no open coordination sites to act as catalytically active species. However, they could break up under reaction conditions into monomeric species or decoordinate one or two pyridine arms to allow for substrate coordination.

Conclusions

We reported new NHC gold complexes, supported by both tethered and untethered ligands. In the case of ligands bearing a NHC with a pyridine side arm, it was found that pyridine is only coordinated to the gold center in the case of dimeric cationic complexes, which formed under reaction conditions and turned out to be at least a catalyst resting state in a cycloisomerization reaction.

(NHC)AuCl complexes were successfully oxidized to their Au(III) counterparts by use of PhICl₂ in good yields. It was found that the presence of chlorine in the media is crucial for the formation of the Au(III) complexes. By cyclovoltammetry we have shown that chlorine is first generated *in situ* by oxidation of chloride, which in turn oxidizes complexes of the type (NHC)AuCl.

The same oxidation methodology was used to synthesize $(NHC)AuArCl_2$ from (NHC)AuAr, a reaction that have not yet been reported in Au-NHC chemistry. The attempted synthesis of $(NHC)AuArCl_2$ via arylation of $(NHC)AuCl_3$ failed, with bisaryl and (NHC)AuCl as byproduct.

In the cycloisomerization of ω -alkynylfurans these new organogold complexes are active even with a problematic substrate. Here, the pendant pyridine arm with the NHC backbone possibly stabilizes intermediates such as **5a** and **5b**. These turned out to be exceptionally effective precatalysts in this reaction.

Experimental Section

All reactions and manipulations were performed under an argon atmosphere using standard Schlenk techniques. Hexane, tetrahydrofuran, and dichloromethane were dried with an MBraun solvent purification system. Pentane, heptane, acetonitrile, diethyl ether, and chloroform were purchased as highpurity anhydrous solvents and used as received. All solvents were saturated with argon prior to use. All deuterated solvents were degassed via freeze-pump-thaw cycles and stored over molecular sieves (4 Å). ¹H and ¹³C{¹H} spectra were recorded at room temperature on a Bruker 250 spectrometer operating at 200 and 50 MHz. Additionally $^1H,\,^{13}C\{^1H\},$ and $^{19}F\{^1H\}$ NMR were recorded on a Bruker Avance II 400 operating at 400, 100, and 376 MHz, respectively, or on a Bruker 300, operating at 300 and 75 MHz with chemical shifts (δ , ppm) reported relative to the solvent peaks (¹H NMR, ¹³C NMR). Peak assignment of the carbene of **3b** and **4b** was accomplished by gHMBC. For X-ray crystal structure analyses suitable crystals were mounted with a perfluorinated polyether oil on nylon loops and cooled immediately on the goniometer head. Data collection was performed with Mo Ka radiation (graphite monochromator) on a Bruker Smart (1d, 2c-f, 3a, 4a, 4b, 5a, 5b) or a Bruker APEX (1b, 1c, 1e, 1f, 2b, 3b) at 200 K. Structures were solved by direct methods and refined by full-matrix least-squares against F^2 . All nonhydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were included in calculated positions. Calculations were performed using the SHELXTL software package.⁶¹ Melting points and IR were carried out on a Stuart SMP 30 instrument with a gradient of 1 °C/min and on a Varian

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2000 FT-IR Scimitar Series, respectively. TLC analyses were performed on commercially available Macherey-Nagel Polygram SILG/UV₂₅₄ and ALOX/UV₂₅₄ precoated plastic sheets. Elemental analyses were determined on an Elementar Vario EL CHN analyzer, and mass spectra (FAB⁺, HR FAB⁺) were obtained on a JEOL MStation JMS 700 instrument. All electrochemical experiments were conducted with a Princeton Applied Research potentiostat/galvanostat model 263A and the corresponding software PowerSuite 2.11. The three-electrode system was used. A glassy carbon (GC) working electrode (2 mm diameter) was employed. The pseudo-reference electrode was a platinum wire immersed in a solution of 0.1 M tetrabutylammonium hexafluorophosphate (nBu_4NPF_6) in acetonitrile. Platinum wire was used as the auxiliary electrode. In each case, IR compensation was applied in order to reduce the acetonitrile resistance. The scan rate for all CV measurements was 25 mV/s. Ferrocene was added for each measurement as an internal standard. Experiments were conducted under strict inert conditions to exclude interactions with oxygen and moisture. Measurements were taken at room temperature (25 °C) in acetonitrile as solvent. nBu₄NPF₆ and/or nBu₄NCl were used as supporting electrolyte. All other starting materials were purchased in reagent grade purity from Acros, Aldrich, Fluka, or Strem and used without further purification. Ligand precursor L1a·HCl was purchased from Aldrich and used as received, while **6** was prepared according to a literature procedure.²

3-Adamantylmethylimidazolium Iodide (L1c·HI). Methyl iodide (3.80 mL, 8.80 g, 61.8 mmol) was added dropwise to a solution of *N*-adamantylimidazole (2.50 g, 12.4 mmol) in THF (8 mL). The mixture was heated to reflux for 48 h. The product was isolated as a white solid by filtration (3.64 g, 86% yield). The solid was used without any further purification: mp 227–230 °C (THF); ¹H NMR (200 MHz, CDCl₃) 1.78 (s, 6H), 2.23 (s, 6H), 2.31 (s, 3H), 4.19 (s, 3H), 7.44 (br s, 2H), 10.17 (s, 1H); ¹³C{¹H} NMR (50 MHz, CDCl₃) 29.54, 35.41, 37.36, 43.03, 60.88, 118.95, 124.01, 135.12; IR (CH₂Cl₂) 3456, 3062, 2909, 2849, 1555, 1448, 1166, 918, 812. Anal. Calcd for $C_{14}H_{21}IN_2$: C 48.85, H 6.15, N 8.14. Found: C 48.96, H 6.02, N 8.28.

1-(2-Pyridinylethyl)-3-mesitylimidazolium Iodide (L2c·HI). 2-(2-Chloroethyl)pyridine (1.42 g, 10.0 mmol), 1-mesitylimidazole (2.05 g, 11.0 mmol), and sodium iodide (1.50 g, 10.0 mmol) were dissolved in acetone (10 mL). This solution was sealed in a high-pressure tube (50 mL) and heated to 60 °C for 24 h. The contents of the reaction vessel were poured into dichloromethane (20 mL) and filtered through Celite. Diethyl ether (10 mL) was then added, which caused an oil to separate. This was recrystallized from dichloromethane/diethyl ether to yield a highly hygroscopic solid, which was dried under vacuum and kept under argon (4.20 g, 91% yield): mp 112-115 °C (hexane); ¹H NMR (CDCl₃, 200 MHz) 1.94 (s, 6H), 2.31 (s, 3H), 3.60 (t, 2H, J = 6.0 Hz), 5.17 (t, 2H, J = 6.0 Hz), 6.96 (s, 2H), 7.06(m, 1H), 7.15 (m, 1H), 7.44 (m, 1H), 7.63 (m, 1H), 7.87 (m, 1H), 8.46 (m, 1H), 9.75 (br s, 1H); ¹³C{¹H} NMR (CDCl₃, 50 MHz) 17.51, 21.01, 37.60, 48.99, 122.23, 123.10, 124.06, 124.25, 129.62, 130.37, 134.06, 136.94, 137.03, 141.04, 149.17, 155.87; IR $(CH_2Cl_2):$ 3466, 3063, 2193, 1593, 1568, 1477, 1438, 1202, 1158, 919, 731. Anal. Calcd for $C_{19}H_{22}IN_3:$ C 54.42, H 5.29, N 10.02. Found: C 55.55, H 5.42, N 10.25; HRMS (FAB) calcd for $C_{19}H_{22}IN_3 m/z$ 292.18136 (M)⁺, found 292.18079.

General Procedure for the Synthesis of Au(I) Complexes 1c–f. A mixture of silver(I) oxide (1.80 mmol) and ligand precursor (2.90 mmol) in dichloromethane (50 mL) was stirred for 24 h in the dark at room temperature. The mixture was filtered, and $[AuCl(SMe_2)]$ (2.70 mmol) was added. The resulting mixture was stirred for 24 h at room temperature in the dark before it was filtered through Celite. The solvent was removed under vacuum and the residue redissolved in a minimum amount of dichloromethane. The product was precipitated as a white solid upon addition of pentane and purified by column chromatography on basic alumina (hexane/THF, 10:1–1:100).

Chloro[**1,3-dihydro-1-methyl-3-adamantyl-2***H***-imidazol-2-ylidene]gold [AuCl(L1c)] (1c): 700 mg, 57% yield; mp 202–204 °C (hexane); R_f = 0.43 (THF/hexane, 1:1); ¹H NMR (200 MHz, CDCl₃) 1.76 (s, 6H), 2.25 (s, 3H), 2.49 (s, 6H), 3.90 (s, 3H), 6.91 (br s, 1H), 7.10 (br s, 1H); ¹³C{¹H} NMR (50 MHz, CDCl₃) 30.04, 35.95, 39.94, 44.52, 59.57, 117.78, 119.96, 169.36; HRMS (FAB) calcd for C₁₄H₂₀N₂Au m/z 413.1292 (M)⁺, found 413.1304; for C₁₄H₂₀N₂³⁵ClAu m/z 448.0981 (M)⁺, found 448.0999. Anal. Calcd for C₁₄H₂₀AuN₂Cl: C 37.47, H 4.49, N 6.24. Found: C 37.37, H 4.50, N 6.10.**

Chloro[**1,3-dihydro-1-(2-pyridinyl)-3-(2,4,6-trimethylphenyl)-2H-imidazol-2-ylidene]gold** [**AuCl(L2a**)] (**1d):** 570 mg, 84% yield; mp 209–212 °C (hexane); $R_f = 0.57$ (THF/hexane, 1:1); ¹H NMR (CDCl₃, 200 MHz) 2.02 (s, 6H), 2.27 (s, 3H), 6.92 (s, 2H), 6.98 (d, 1H, J = 2.0 Hz), 7.38 (ddd, 1H, J = 7.5 Hz, J = 2.0 Hz, J = 1.0 Hz), 7.87 (ddd, 1H, J = 7.5 Hz, J = 2.0 Hz, J = 1.0 Hz), 7.87 (ddd, 1H, J = 7.5 Hz, J = 2.0 Hz, J = 1.0 Hz), 8.75 (dd, 1H, J = 8.0 Hz, J = 1.0 Hz), 8.75 (dd, 1H, J = 8.0 Hz, J = 1.0 Hz), 8.75 (dd, 1H, J = 8.0 Hz, J = 1.0 Hz), 17.94, 21.16, 117.34, 120.36, 122.47, 124.11, 129.56, 134.60, 135.05, 139.10, 139.93, 148.80, 150.26, 170.90; HRMS (FAB) calcd for C₁₇H₁₈³⁵ClN₃Au m/z 496.0855 (M – H)⁺, found 496.0894. Anal. Calcd for C₁₇H₁₇ClN₃Au: C 41.19, H 3.46, N 8.48. Found: C 41.75, H 3.63, N 8.09.

Chloro[1,3-dihydro-1-(2-pyridinylmethyl)-3-(2,4,6-trimethylphenyl)-2H-imidazol-2-ylidene]gold [AuCl(L2b)] (1e): 640 mg, 92% yield; mp 181–184 °C (hexane); $R_f = 0.40$ (THF/hexane, 1:1); ¹H NMR (CDCl₃, 200 MHz) 2.01 (s, 6H), 2.33 (s, 3H), 5.59 (s, 2H), 6.89 (d, 1H, J = 2.0 Hz), 6.95 (s, 2H), 7.27 (m, 1H), 7.36(d, 1H, J = 2.0 Hz), 7.46 (d, 1H, J = 8.0 Hz), 7.74 (ddd, 1H, J =8.0 Hz, J = 8.0 Hz, J = 2.0 Hz), 8.62 (d, 1H, J = 4.0 Hz); ¹³C{¹H} NMR (CDCl₃, 50 MHz) 17.83, 21.11, 56.50, 121.39, 122.52, 123.50, 129.10, 129.39, 134.64, 134.73, 137.45, 139.65, 149.75, 154.84, 172.33; HRMS (FAB) calcd for $C_{18}H_{20}^{35}ClN_3Au m/z 510.1011 (M - H)^+$, found 510.1004. Anal. Calcd for C₁₈H₁₉ClN₃Au: C 42.41, H 3.76, N 8.24. Found: C 42.46, H 3.89, N 8.04.

Chloro[1,3-dihydro-1-(2-pyridinylethyl)-3-(2,4,6-trimethylphenyl)-2*H*-imidazol-2-ylidene]gold [AuCl(L2c)] (1f): 620 mg, 87% yield; mp 127–130 °C (hexane); $R_f = 0.26$ (THF/hexane, 1:1); ¹H NMR (CDCl₃, 200 MHz) 1.94 (s, 6H), 2.32 (s, 3H), 3.45 (t, 2H, J = 8.0 Hz), 4.74 (t, 2H, J = 8.0 Hz), 6.72 (d, 1H, J = 2.0 Hz), 6.93 (s, 2H), 6.97 (m, 1H), 7.19 (d, 2H, J = 8.0 Hz), 7.61 (ddd, 1H, J = 8.0 Hz, J = 8.0 Hz, J = 2.0 Hz), 8.58 (d, 1H, J = 4.0Hz); ¹³C{¹H} NMR (CDCl₃, 50 MHz) 17.74, 21.10, 30.33, 34.22, 39.53, 50.72, 121.32, 121.55, 122.15, 124.08, 125.51, 129.33, 134.65, 134.76, 135.77, 136.86, 139.54, 149.60, 156.82, 171.57; HRMS (FAB) calcd for C₁₉H₂₂³⁵ClN₃Au m/z 524.1168 (M – H)⁺, found 524.1163. Anal. Calcd for C₁₉H₂₁ClN₃Au: C 43.57, H 4.04, N 8.02. Found: C 46.06, H 4.51, N 7.47.

General Procedure for the Oxidation of 1b–f with PhICl₂ to Give Au(III) Complexes 2b–f. At 0 °C to a solution of complex 1b–f (700 μ mol) in dichloromethane (20 mL) was added dropwise a solution of PhICl₂ (800 μ mol) in dichloromethane (10 mL). The reaction mixture was stirred for 24 h in the dark at room temperature. The solvent was then evaporated, and the yellow solid was washed with hexane. The pure product was dried under high vacuum.

Trichloro[1,3-dihydro-1-methyl-3-(2,4,6-trimethylphenyl)-2*H*imidazol-2-ylidene]gold [AuCl₃(L1b)] (2b): 320 mg, 92% yield; mp 215–218 °C (hexane); ¹H NMR (200 MHz, CDCl₃) 2.15 (s, 6H), 2.36 (s, 3H), 4.12 (s, 3H), 7.00 (s, 2H), 7.12 (d, 1H, J = 2.0Hz), 7.38 (d, 1H, J = 2.0 Hz); ¹³C{¹H} NMR (50 MHz, CDCl₃)

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18.67, 21.36, 38.72, 125.31, 125.66, 130.09, 132.38, 135.62, 141.21, 143.01; HRMS (FAB) calcd for $C_{13}H_{16}N_2Au m/z$ 397.0979 (M)⁺, found 397.0984; for $C_{13}H_{16}N_2^{35}ClAu m/z$ 432.0668 (M)⁺, found 432.0653. Anal. Calcd for $C_{13}H_{16}AuN_2Cl_3$: C 31.00, H 3.20, N 5.56. Found: C 30.70, H 3.12, N 5.41.

Trichloro[**1,3-dihydro-1-methyl-3-adamantyl-2***H***-imidazol-2ylidene]gold [AuCl₃(L1c)] (2c): 330 mg, 94% yield; mp 265– 268 °C (hexane); ¹H NMR (200 MHz, CDCl₃) 1.79 (br s, 6H), 2.35 (br s, 3H), 2.48 (br s, 6H), 4.04 (s, 3H), 7.22 (br s, 1H), 7.43 (br s, 1H); ¹³C{¹H} NMR (50 MHz, CDCl₃) 30.04, 35.55, 39.23, 44.12, 62.84, 121.36, 124.54, 138.50; HRMS (FAB) calcd for C_{14}H_{20}N_2Au m/z 413.1292 (M)⁺, found 413.1327. Anal. Calcd for C_{14}H_{20}AuN_2Cl_3: C 32.36, H 3.88, N 5.39. Found: C 32.34, H 3.85, N 5.33.**

Trichloro[1,3-dihydro-1-(2-pyridinyl)-3-(2,4,6-trimethylphenyl)-2*H*-imidazol-2-ylidene]gold [AuCl₃(L2a)] (2d): 55 mg, 96% yield; mp 213–216 °C (hexane); ¹H NMR (THF- d_8 , 200 MHz) 2.13 (s, 6H), 2.25 (s, 3H), 6.97 (s, 2H), 7.47 (dd, 1H, J = 8.0 Hz, J = 4.0Hz), 7.63 (d, 1H, J = 2.0 Hz), 7.98 (m, 2H), 8.25 (d, 2H, J = 2.0Hz), 8.60 (dd, 1H, J = 4.0 Hz, J = 2.0 Hz); ¹³C{¹H} NMR (THF- d_8 , 50 MHz) 17.96, 20.30, 116.98, 122.99, 124.88, 129.64, 135.64, 139.62, 140.73, 149.40; HRMS (FAB) calcd for C₁₇H₁₇N₃³⁵Cl₂Au *m*/*z* 530.0465 (M)⁺, found 530.0459. Anal. Calcd for C₁₇H₁₇AuCl₃N₃: C 36.03, H 3.02, N 7.42. Found: C 35.57, H 3.28, N 7.90.

Trichloro[**1,3-dihydro-1-(2-pyridinylmethyl)-3-(2,4,6-trimethyl-phenyl)-2***H***-imidazol-2-ylidene]gold [AuCl₃(L2b)] (2e): 540 mg, 95% yield; mp 187–190 °C (hexane); ¹H NMR (CDCl₃, 200 MHz) 2.06 (s, 6H), 2.26 (s, 3H), 5.59 (s, 2H), 6.90 (s, 2H), 7.04 (d, 1H, J = 2.0 Hz), 7.27 (dd, 1H, J = 8.0 Hz, J = 6.0 Hz), 7.52 (d, 1H, J = 4.0 Hz, J = 1.0 Hz); ¹³C{¹H} NMR (CDCl₃, 50 MHz) 18.50, 21.13, 56.21, 124.07, 124.23, 124.51, 125.24, 129.86, 132.32, 135.37, 137.77, 140.94, 143.24, 150.23, 152.51; HRMS (FAB) calcd for C₁₈H₁₉N₃³⁵Cl₂Au** *m/z* **544.0622 (M)⁺, found 544.0639. Anal. Calcd for C₁₈H₁₉Cl₃N₃Au: C 37.23, H 3.30, N 7.24. Found: C 37.69, H 3.40, N 6.94.**

Trichloro[**1,3-dihydro-1-(2-pyridinylethyl)-3-(2,4,6-trimethyl-phenyl)-2***H***-imidazol-2-ylidene]gold [AuCl₃(L2c)] (2f): 220 mg, 97% yield; mp 203–206 °C (hexane); ¹H NMR (CDCl₃, 200 MHz) 2.02 (s, 6H), 2.27 (s, 3H), 3.51 (t, 2H, J = 2.0 Hz), 4.88 (t, 2H, J = 2.0 Hz), 6.83 (d, 1H, J = 1.0 Hz), 6.91 (s, 2H), 7.04 (d, 1H, J = 1.0 Hz), 7.14 (m, 2H), 7.57 (dd, 1H, J = 6.0 Hz, J = 1.0 Hz), 8.55 (br s,1H); ¹³C{¹H} NMR (CDCl₃, 50 MHz) 18.38, 21.14, 124.73, 129.87, 132.20, 135.34, 137.10, 140.95, 142.64, 146.56; HRMS (FAB) calcd for C₁₉H₂₁N₃³⁵Cl₂Au** *m/z* **558.0778 (M)⁺, found 558.0810; for C₁₉H₂₂N₃³⁵Cl₃Au** *m/z* **594.0545 (M + H)⁺, found 594.0491. Anal. Calcd for C₁₉H₂₁Cl₃N₃Au: C 38.37, H 3.56, N 7.07. Found: C 37.27, H 3.69, N 6.62.**

General Procedure for Arylation of 1a to Give Au(I) Complexes 3a,b. At 0 °C to a solution of complex 1a (3.80 mmol) in THF (80 mL) was added a solution of Grignard reagent (C₆H₅MgBr for 3a and C₆F₅MgBr for 3b, each 15.0 mmol). The mixture was stirred at room temperature for 3–5 h. Water (drops) was added, and a precipitate crashed out of solution. This solid was filtered off, the solution was concentrated, and the residue was purified on neutral alumina eluted with THF/hexane (1:9–1:1) (this has to be done quickly since the TLC showed complex decomposition to purple Au-nanoparticles). The products were crystallized from CHCl₃/heptane as colorless solids.

Phenyl[1,3-dihydro-1,3-bis(2,4,6-trimethylphenyl)-2*H*-imidazol-2-ylidene]gold [Au(C₆H₅)(L1a)] (3a): 2.11 g, 96% yield; mp 242– 245 °C (heptane); $R_f = 0.46$ (THF/hexane, 3:10); ¹H NMR (CDCl₃, 200 MHz) 2.19 (s, 12H), 2.37 (s, 6H), 6.84–7.18 (m, 11H); ¹³C{¹H} NMR (CDCl₃, 50 MHz) 18.21, 21.38, 122.01, 124.70, 126.97, 129.39, 135.14, 135.54, 139.27, 140.67, 169.34, 195.81; HRMS (FAB) calcd $C_{27}H_{30}N_2Au m/z$ 579.2075 (M + H)⁺, found 579.2065. Anal. Calcd for $C_{27}H_{29}N_2Au$: C 56.06, H 5.05, N 4.84. Found: C 55.46, H 4.89, N 5.06. Pentafluorophenyl[1,3-dihydro-1,3-bis(2,4,6-trimethylphenyl)-2*H*-imidazol-2-ylidene]gold [Au(C₆F₅)(L1a)] (3b): 1.16 g, 77% yield; mp 180–183 °C (heptane); $R_f = 0.52$ (THF/hexane, 3:10); ¹H NMR (CHCl₃, 200 MHz) 2.18 (s, 12H), 2.36 (s, 6H), 7.03 (br s, 4H), 7.13 (s, 2H); ¹³C{¹H} NMR (CDCl₃, 50 MHz) 17.86, 21.17, 122.17, 129.21, 129.30, 134.73, 134.82, 139.48, 190.58; ¹⁹F NMR (CDCl₃, 376 MHz) –163.67, –160.80, –116.02; HRMS (FAB) calcd for C₂₇H₂₄N₂F₅Au *m*/*z* 668.1525 (M)⁺, found 668.1535. Anal. Calcd for C₂₇H₂₄N₂F₅Au: C 48.51, H 3.62, N 4.19. Found: C 47.10, H 3.61, N 3.76.

Phenyl[1,3-dihydro-1,3-bis(2,4,6-trimethylphenyl)-2*H*-imidazol-2-ylidene]gold Dichloride [Au(C₆H₅)Cl₂(L1a)] (4a). To a solution of 3a (1.20 g; 2.10 mmol) in dichloromethane (30 mL) was added PhICl₂ (710 mg; 2.60 mmol) at 0 °C. The reaction mixture was stirred for 3 h in the dark at room temperature, and the conversion was monitored by ¹H NMR until completion. Evaporation of the solvent, purification of the residue by flash chromatography on neutral alumina (THF/hexane, 1:9–1:1), and drying under high vacuum yielded 4a as a colorless solid (1.05 g, 78% yield). Additional washing of the column with THF gave a second fraction, which was crystallized from dichloromethane/hexane to give 2a (220 mg, 17% yield) as a yellow solid.

4a: mp 203–206 °C (heptane); $R_f = 0.46$ (THF/hexane, 3:10); ¹H NMR (CDCl₃, 200 MHz) 2.30 (s, 12H), 2.40 (s, 6H), 6.85-7.00 (m, 5H), 7.05 (s, 4H), 7.18 (s, 2H); ¹³C{¹H} NMR (CHCl₃, 50 MHz) 18.41, 21.21, 123.76, 125.62, 128.21, 129.46, 132.72, 133.88, 135.60, 139.84, 146.12, 180.35; HRMS (FAB) calcd for C₂₇H₃₀N₂³⁵Cl₂Au m/z 649.1452 (M + H)⁺, found 649.1474. Anal. Calcd for C₂₇H₂₉N₂Cl₂Au: C 49.94, H 4.50, N 4.31. Found: C 49.98, H 4.51, N 4.25. **2a**: ¹H NMR (CDCl₃, 200 MHz) 2.23 (s, 12H), 2.34 (s, 6H), 7.00 (s, 4H), 7.23 (s, 2H); ¹³C{¹H} NMR (CHCl₃, 50 MHz) 18.61, 21.19, 125.61, 129.97, 132.36, 135.32, 141.03, 144.72.

Pentafluorophenyl[1,3-dihydro-1,3-bis(2,4,6-trimethylphenyl)-2*H*-imidazol-2-ylidene]gold Dichloride [Au(C₆F₅)Cl₂(L1a)] (4b). To a solution of 3b (800 mg; 1.2 mmol) in dichloromethane (20 mL) was added PhICl₂ (460 mg; 1.7 mmol) at 0 °C. The reaction mixture was stirred for 18 h in the dark at room temperature. The solvent was evaporated and the solid was washed with hexane. Drying under high vacuum yielded 4b as a colorless solid (820 mg, 93% yield): mp 232–235 °C (heptane); $R_f = 0.45$ (THF/hexane, 3:10); ¹H NMR (CDCl₃, 200 MHz) 2.29 (s, 12H), 2.40 (s, 6H), 7.08 (s, 4H), 7.27 (s, 2H); ¹³C NMR (CDCl₃, 50 MHz) 18.40, 21.21, 124.38, 129.55, 133.04, 135.25, 140.43, 167.13; ¹⁹F NMR (CDCl₃, 376 MHz) –162.31, –158.47, –125.58; HRMS (FAB) calcd for C₂₇H₂₄N₂³⁵ClF₅Au *m/z* 705.1184 (M)⁺, found 703.1185; C₂₇H₂₄N₂³⁷ClF₅Au *m/z* 705.1184 (M)⁺, found 705.1193. Anal. Calcd for C₂₇H₂₄N₂Cl₂F₅Au: C 43.86, H 3.27, N 3.79. Found: C 43.72, H 3.48, N 3.59.

Reaction between 2e and *p*-Methoxyphenylmagnesium Bromide. At -20 °C to a solution of 2e (50 mg, 86.1 µmol) in dry THF (2 mL) was added dropwise *p*-methoxyphenylmagnesium bromide (100 µL; 103 µmol; 1 M in THF). The reaction mixture was stirred for 1 h at this temperature, and then slowly the temperature was raised to 0 °C. After slow addition of water the product was filtered through a plug of Celite and concentrated to dryness. The crude reaction mixture was purified on basic alumina (dichloromethane/ethanol gradient mixtures). 4,4'-Bismethoxy-1,1'-biphenyl (first fraction) was isolated as a colorless oil (15 mg, 81% yield) followed by 1e (38 mg, 87% yield).

4,4'-Bismethoxy-1,1'-biphenyl: ¹H NMR (CDCl₃, 200 MHz) 2.01 (s, 6H), 2.33 (s, 3H), 5.59 (s, 2H), 6.89 (d, 1H, J = 2.0 Hz), 6.95 (s, 2H), 7.27 (m, 1H), 7.36 (d, 1H, J = 2.0 Hz), 7.46 (d, 1H, J = 8.0 Hz), 7.74 (ddd, 1H, J = 8.0 Hz, J = 8.0 Hz, J = 2.0 Hz), 8.62 (d, 1H, J = 4.0 Hz).

General Procedure for the Synthesis of the Cationic Au(I) Complexes 5a,b. To a solution of 1e or 1f ($200 \mu mol$) in dichloromethane (3 mL) was added AgNTf₂ ($200 \mu mol$). The solution was stirred for 5 min and filtered over Celite. The pad of Celite was further washed twice with dichloromethane (2 mL), and the resulting solution was reduced under vacuum to 1 mL. Pentane (10 mL) was added, resulting in the immediate precipitation of a white solid. The product was filtered, further washed with pentane (3×5 mL), and dried under high vacuum.

[Au(L2b)]₂(NTf₂)₂ (5a): 140 mg, 93% yield; mp 85−88 °C (heptane); $R_f = 0.40$ (THF/hexane, 1:1); ¹H NMR (CD₂Cl₂, 400 MHz) 1.98 (br s, 6H), 2.33 (s, 3H), 5.97 (br s, 1 H), 7.04 (s, 2H), 7.14 (s, 1H), 7.62 (s, 1H), 7.68 (dd, 1H, J = 4.0 Hz, J = 8.0 Hz), 8.07 (d, 1H, J = 8.0 Hz), 8.12 (d, 1H, J = 4.0 Hz), 8.24 (dd, 1H, J = 8.0 Hz, J = 8.0 Hz); ¹³C{¹H} NMR (CD₂Cl₂, 100 MHz) 18.19, 21.29, 57.40, 118.69, 121.88, 123.10, 125.04, 127.33, 128.77, 129.95, 134.67, 135.09, 141.08, 143.16, 152.57, 155.03, 165.03; ¹⁹F NMR (CD₂Cl₂, 376 MHz) −79.40; MS (FAB) for C₃₆H₃₈N₆Au m/z 751.28 (M)⁺, (L2bAuL2b)⁺. Anal. Calcd for C₂₀H₁₉AuF₆N₄O₄S₂: C 31.84, H 2.54, N 7.43. Found: C 31.93, H 2.72, N 7.36.

[Au(L2c)]₂(NTf₂)₂ (5b): 150 mg, 96% yield; mp 180 °C (dec, heptane); $R_f = 0.29$ (THF/hexane, 1:1); ¹H NMR (CD₂Cl₂, 400 MHz) 1.78 (s, 6H), 2.32 (s, 3H), 3.66 (t, 2H, J = 8.0 Hz), 5.11 (t, 2H, J = 8.0 Hz), 7.00 (br s, 3H), 7.56 (m, 2H), 7.67 (d, 1H, J = 8.0 Hz), 7.98 (dd, 1H, J = 8.0 Hz, J = 8.0 Hz), 8.15 (d, 1H, J = 4.0 Hz); ¹³C{¹H} NMR (CD₂Cl₂, 100 MHz) 17.92, 21.24, 39.69, 50.20, 121.98, 122.99, 124.62, 125.75, 129.23, 129.88, 134.50, 134.96, 140.98, 142.01, 151.90, 157.58, 164.67; ¹⁹F NMR (CD₂Cl₂, 376 MHz) −79.35; MS (FAB) for C₃₈H₄₂N₆Au m/z 779.31 (M)⁺, (L2CAuL2c)⁺. Anal. Calcd for C₂₁H₂₁AuF₆. N₄O₄S₂: C 32.82, H 2.75, N 7.29. Found: C 32.20, H 2.86, N 7.17.

General Procedure for the Catalytic Studies. To a solution of 6 (30.0 mg, 200 μ mol) in deuterated solvent (CDCl₃ or CD₂Cl₂, 0.5 mL) containing internal standard (1,3,5-tri-*tert*-butylbenzene, 2 mg) was added a 1:1 mixture of gold complex and silver salt (0.05–4 mol %). The NMR tube was shaken for 1 h, and the yield was determined by integration of the corresponding ¹H NMR signals in comparison to the internal standard.

4-Isobenzofuranol (7). To a solution of 2-methyl-5-[(2-propyn-1-yloxy)methyl]furan (6, 60.8 mg, 405 μ mol) in dichloromethane (1 mL) were added gold complex **If** (529 μ g, 1.00 μ mol) and AgNTf₂ (392 μ g, 1.00 μ mol). The solution was stirred for 3 h and purified by flash column chromatography (petroleum ether/ ethyl acetate, 5:1, $R_f = 0.24$). The product was isolated as colorless solid (53 mg, 87% yield): ¹H NMR (CDCl₃, 300 MHz) 2.26 (s, 3H), 4.96 (s, 1H), 5.08–5.15 (m, 4H), 6.72 (d, 1H, J = 7.5 Hz), 7.05 (d, 1H, J = 7.5 Hz); ¹³C{¹H} NMR (CDCl₃, 75 MHz) 15.22, 71.77, 74.14, 113.02, 121.83, 125.27, 130.63, 139.28, 148.40.

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Supporting Information Available: Crystallographic information files (CIF) of compounds $L2c \cdot HI$, 1b-f, 2b-f, and 3-5; cyclic voltammetry data and NMR spectra of all compounds. This material is available free of charge via the Internet at http:// pubs.acs.org. Files CCDC 771118 (ligand L2c), 771119 (1b), 771120 (1c), 771121 (1d), 771122 (1e), 771123 (1f), 771124 (2b), 771125 (2c), 771126 (2d), 771127 (2e), 771128 (2f), 771129 (3a), 771130 (3b), 771131 (4a), 771132 (4b), 771133 (5a), and 771134 (5b) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam. ac.uk/data_request/cif.