DOI: 10.1002/ejic.201101158

Catalytic Hydrocarbon Functionalization with Gold Complexes Containing N-Heterocyclic Carbene Ligands with Pendant Donor Groups

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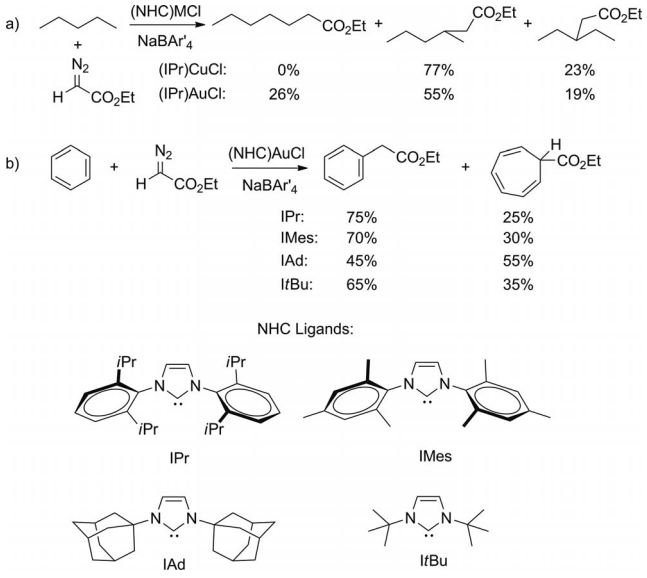
Keywords: Carbenes / Carbene complexes / NHC ligands / Silver / Gold / C–H functionalization / Metalation

A series of silver and gold complexes bearing N-heterocyclic carbene ligands with a $–CH_2CO_2Et$ pendant group attached to one N atom of the NHC ligand have been prepared. The catalytic properties of the gold complexes toward the decomposition of ethyl diazoacetate (N_2CHCO_2Et) and the transfer of the carbene $CHCO_2Et$ group to benzene and hexane have been investigated. A somewhat different reaction outcome has been found for this family of gold catalysts compared with the parent IPrAuCl catalyst.

Introduction

In the last decade, N-heterocyclic carbene complexes of the coinage metal have been widely employed in numerous catalytic processes in the homogeneous phase.[1,2] Our group has participated in this area developing a catalytic system based on the use of NHC–M (M = Cu, Au) to induce the transfer of carbene units from diazo compounds to saturated and unsaturated fragments.[3] In particular, the gold complex IPrAuCl efficiently catalyzed the C–H bond functionalization of aliphatic hydrocarbons with commercially available ethyl diazoacetate (EDA). Simple, non-activated alkanes such as *n*-pentane could be converted into a mixture of esters by the formal insertion of the $:CHCO_2Et$ group into the different primary or secondary C–H bonds (Scheme 1, a) using an equimolar mixture of IPrAuCl and $NaBAr'_4$ as a halide scavenger [IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene; Ar′ = 3,5-bis(trifluoromethyl)-phenyl].

Although the copper analogue also promoted the same transformation, the regioselection was clearly affected by the metal center, the gold complex being preferred for the activation of primary sites.[3c] The same catalytic system was tested for the less common functionalization of the aromatic C–H bonds of benzene, which was preferentially converted into the product derived from the formal insertion of the carbene moiety into the C_{sp^2}–H bond under very mild conditions (Scheme 1, b). The chemoselectivity, in this case, was influenced by the nature of the NHC ligand, and the IPr derivative was the most selective toward the desired target.[3b,3d]



Scheme 1. Functionalization of pentane and benzene with EDA.

The ligands employed in our previous work are monodentate, the carbenic atom being the only donor binding the metal center. We wondered about the effect that additional donor atoms, located at the N-substituents, could induce in the catalytic activity of these compounds in the aforementioned transformations. Although these (NHC)-MCl compounds are linear in geometry, the cationic species generated upon interaction with $NaBAr'_4$ could transiently form tricoordinate species, which are known for gold(I)

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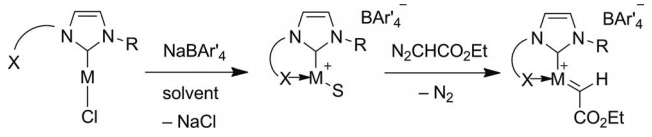
complexes such as dppomf(AuCl) [dppomf = 1,1′-bis(diphenylphosphanyl)octamethylferrocene][4] and (phosphane)gold(I)-azadipyrromethene.[5] In our commitment to developing more active and selective catalysts for these transformations, we wondered if combinations of a strong donor such as the N-heterocyclic carbene ligand, with a more weakly coordinating donor, would allow us to gain access to a class of catalysts that benefit from the hemilabile behavior of one of its ligands (Scheme 2). Thus, a tricoordinate geometry involving the NHC ligand, the hemilabile arm, and the carbene group could induce a distinct catalytic behavior in the targeted C–H bond functionalization reactions. With this objective in mind we decided to synthesize new gold complexes with N-heterocyclic carbene ligands functionalized with ester groups to check their catalytic activity in C–H bond functionalization of aliphatic and aromatic hydrocarbons with diazo compounds.

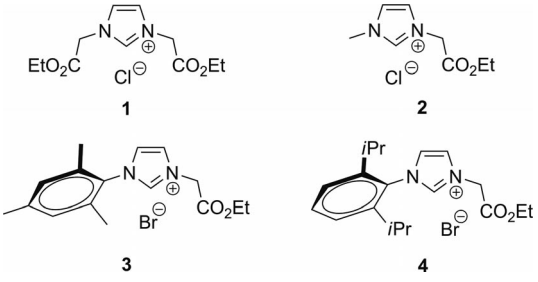


Scheme 2. Plausible coordination modes of NHC ligands with a weak donor in a pendant arm.

Results and Discussion

Syntheses of the Imidazolium Salts and Silver Complexes

The imidazolium salts **1**–**2** were readily prepared in quantitative yields according to literature procedures,[6] while compounds **3**–**4** (Scheme 3) were obtained by direct alkylation of *N*-mesityl- and *N*-(2,3-diisopropylphenyl)-imidazole with slight modifications of the procedure reported for the synthesis of the mesityl derivative.[7] These hygroscopic imidazolium salts were characterized by spectroscopic and analytical methods. In their ^{1}H NMR spectra, in addition to the ring and N-substituents, all of them showed a typical resonance in the downfield region within the 9.0–10.5 ppm range assigned to 2-H of the heterocyclic ring.

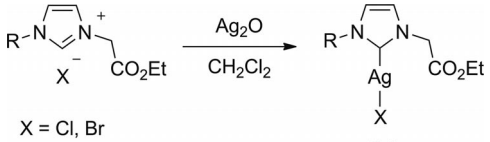


Scheme 3. Imidazolium salts employed in this work.

Once we obtained the above NHC precursors, we tried the direct synthesis of the gold complexes (NHC)AuCl. However, the direct reaction of the imidazolium salts **1**–**4** with AuCl(SMe$_2$) as the Au^I source in the presence of several bases was unsuccessful, with extensive decomposition and appearance of colloidal gold being observed. Therefore, we decided to move to the well-known strategy of ligand transmetallation[8] from silver derivatives of the general formula (NHC)AgX (X = Cl, Br).

The preparation of the silver complexes was first attempted following the described procedures for the synthesis of related NHC–sulfonate silver complexes.[9] The procedure consisted of refluxing the imidazolium salt in $CHCl_3$ in the presence of 3 equiv. of Ag_2O. However, in our case intractable mixtures were obtained. Moving to a less acidic medium and softer conditions such as CH_2Cl_2 as the solvent and only 1.2 equiv. of Ag_2O at room temperature afforded the silver complexes **5** and **7**, from the imidazolium salts **1** and **3**, respectively, in 87% and 60% yields (Table 1, Entries 1 and 3). Although low conversions were obtained with the imidazolium salts **2** and **4** at room temperature, the same protocol at 40 °C proved suitable to prepare the corresponding silver complexes **6** and **8** in 60 and 90% yields, respectively (Entries 2 and 4). While complexes **5**, **6**, and **8** display a high stability under an inert atmosphere, complex **7** decomposes rather quickly in both the solid state and in solution.

Table 1. Synthesis of the silver complexes (NHC)AgX **5**–**8**.



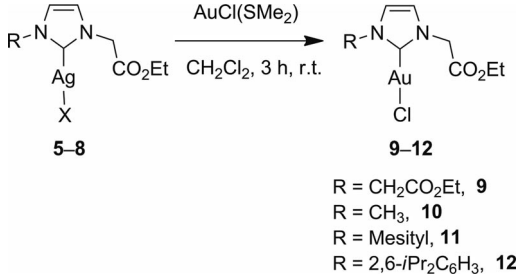
Entry	R	X	Silver complexes	Temp. [°C]	Time [h]	Yield [%]
1	CH_2CO_2Et	Cl	**5**	r. t.	14	87
2	CH_3	Cl	**6**	40	7	60
3	mesityl	Br	**7**	r. t.	24	60
4	2,6-$Pr_2C_6H_3$	Br	**8**	40	12	90

The ^{1}H NMR spectra of the C_2-symmetric complex **5** show single resonances centered at δ = 7.10 and 4.92 ppm for the unsaturated backbone of the imidazole ring and the methylene protons of the *N*-alkyl chain, respectively. Complexes **6**, **7** and **8** display single resonance signals between 4.90 and 5.03 ppm for the methylene protons of the arm, the imidazole ring protons appearing between 6.85 and 7.27 ppm as doublets or broad singlets from the loss of the C2 symmetry. The ^{13}C NMR spectra of complexes **5**–**8** show two low-field signals attributed to the carbonyl carbon (167–169 ppm) and to the carbenic carbon (183–184 ppm). The similar values in chemical shift of the carbenic carbon clearly evidenced the lack of a significant effect in the electronic-donor properties of the NHC ligands in complexes **5**–**8**. Additionally, these values of chemical shift are similar to those described for the unsaturated NHC-Ag complexes, such as (IMes)AgCl (δ = 185.0 ppm) or (IPr)-AgCl (δ = 184.6 ppm).[10] On the other hand, complexes **5**

and **6** show sharp singlets for the carbenic carbon characteristic of fast exchange equilibrium of the carbene moiety with the metal center.[11] The non-observance of Ag-carbene coupling in the NMR time-scale indicates that these complexes are useful carbene transfer reagents.[12] The carbenic carbon resonances in complexes **7** and **8** appeared as broad singlets, in this case characteristic of a slow exchange, that could be related to a higher steric hindrance in these complexes induced by the aromatic substituents.

Synthesis of the Gold Complexes (NHC)AuCl

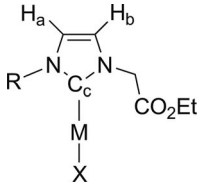
Once the silver complexes were prepared, we applied the methodology, which was described by Lin[8] and was further developed by the group of Nolan,[13] for the synthesis of the gold analogues by a transmetalation process. The complexes (NHC)AgX **5**–**8** were treated with $AuCl(SMe_2)$ as the gold source (Scheme 4). In all cases, the reaction took place at room temperature over 3 h affording the corresponding complexes **9**–**12** with the general formula (NHC)AuCl in 60–67% yields.



Scheme 4. Synthesis of the gold complexes **9**–**12**.

The novel Au^I–NHC complexes were characterized by spectroscopic methods and elemental analysis. The ^1H NMR spectra of complexes **10**–**12** containing the asymmetric NHC ligands showed two distinct resonances at low field for the two backbone-ring protons (6.92–7.24 ppm), as well as signals characteristic of their corresponding side-chain R groups. As expected, in the case of the C_2-symmetric complex **9**, bearing two CH_2CO_2Et substituents, the backbone hydrogens appear as a single resonance centered at δ = 7.10 ppm (Table 2). The carbenic carbons in these compounds give rise to resonances in the 173.1–174.4 ppm interval, similar to those reported for IPrAuCl and IMesAuCl (175.1 and 173.4 ppm, respectively).[13] As already mentioned for the silver analogues, there is no significant electronic effect of the substituents in the electronic density around the carbenic carbon. Nevertheless, the signals for the gold compounds appeared to be shifted upfield by 10 ppm (Table 2) compared with those for each silver analogue, possibly a result of the different effect of the metal center in the π-back donation, as proposed by Herrmann and coworkers.[11b]

Table 2. Selected chemical shifts (δ values, ppm) for the complexes (NHC)MX (M = Ag, Au; X = Cl, Br).[a]



M	R	Complex	H_a	H_b	C_c
Ag	CH_2CO_2Et	**5**	7.10	7.10	183.9
Au	CH_2CO_2Et	**9**	7.10	7.10	174.4
Ag	CH_3	**6**	7.02	7.06	183.1
Au	CH_3	**10**	7.00	7.04	173.1
Ag	Mesityl	**7**	6.85	6.96	173.5
Au	Mesityl	**11**	6.92	6.94	174.1
Ag	2,6-$iPr_2C_6H_3$	**8**	7.04	7.24	183.6
Au	2,6-$iPr_2C_6H_3$	**12**[b]	7.04	7.24	173.8

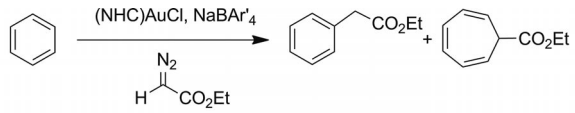
[a] $CDCl_3$ was the solvent used in all cases. [b] For complex **12**, a mixture of $CDCl_3$ and CD_2Cl_2 was employed to ensure complete dissolution.

Catalytic Experiments

As mentioned in the Introduction, we have previously reported the catalytic capabilities of a series of copper[3a,3c] and gold[3b–3d] complexes containing N-heterocyclic carbene ligands (NHC), to induce the carbene insertion into the carbon–hydrogen bond of different hydrocarbons, using ethyl diazoacetate (EDA) as the carbene source. We have now screened the potential of complexes **9**–**12** for such transformations, wondering about the role of donor atoms in the N-pendant groups of the NHC ligands. As representative hydrocarbons, we have chosen benzene and *n*-hexane for C_{sp^2}–H and C_{sp^3}–H functionalization, respectively.

The reaction of benzene and ethyl diazoacetate in the presence of the complexes **9**–**12** and $NaBAr_4'$ as halide scavenger led to mixtures of ethyl phenylacetate and the cycloheptatriene shown in Scheme 5. Ethyl phenylacetate arose from the gold-catalyzed formal insertion of the carbene **:**$CHCO_2Et$ into the aromatic C–H bond, whereas the cycloheptatriene was the product of a Buchner reaction also mediated by the metal center. In all cases EDA was consumed quantitatively, although benzene was functionalized with a variable yield of 11–66% (the remaining initial diazo compound was converted into a mixture of diethyl fumarate and maleate). This is in contrast with the catalytic activity of the parent IPrAuCl,[3b] which displayed a very high chemoselectivity toward benzene. This difference could be the result of a certain deactivation of the metal center due to the presence of the carboxylate groups. Actually, the less active catalyst is that bearing two carboxylate fragments, **9**, whereas the three compounds with one carboxylate group showed similar activities toward benzene (55–66%). With regard to the regioselectivity between the formation of phenylacetate and cycloheptatriene, again a decrease from that of IPrAuCl (75:25) was observed. Interestingly, complexes **11** and **12**, having a mesityl and a 2,6-diisopropylphenyl substituent, respectively, at one of the nitrogen

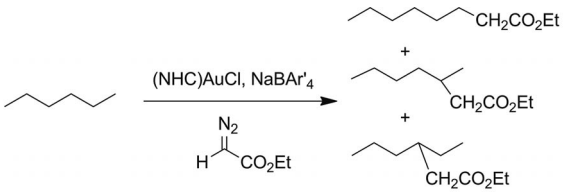
atoms were less productive toward the insertion product than **10**, with a simple methyl group at that position. Since NMR spectroscopic data for the series of four complexes showed little or no difference for the carbenic carbon atom, the observed differences in catalytic behavior should be due to local effects at the metal center, in two senses: the possible coordination of the carboxylate group and/or the steric effect of the substituents at the NHC ring (see below).



Gold complex	% EDA consumed	% EDA incorporated to benzene	% Regioselectivity	
			insert.	cyclohept.
9	> 95%	11%	42%	58%
10	> 95%	66%	50%	50%
11	> 95%	55%	31%	69%
12	> 95%	61%	38%	62%

Scheme 5. Reaction of benzene and ethyl diazoacetate in the presence of **9**–**12** and NaBAr′$_4$ as the catalyst precursor (5% catalyst loading with respect to EDA).

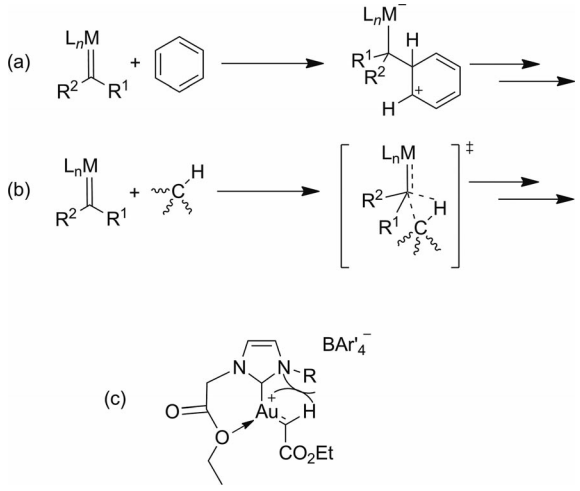
When *n*-hexane was treated with ethyl diazoacetate at room temperature in the presence of **9**–**12** and NaBAr′, the formation of a mixture of three products derived from the formal insertion of the carbene unit into the C–H bonds of primary as well as of the two distinct secondary sites were observed (Scheme 6). A 1:1 mixture of hexane and dichloromethane was employed as the reaction solvent, since the catalysts were insoluble in the hydrocarbon itself. In addition, a gradual decomposition was observed during the process (24 h), explaining the lack of complete consumption of the diazo compound. However, the results deserve some comments, particularly regarding the regioselective functionalization of primary versus secondary sites.



Gold complex	% EDA consumed	% EDA incorporated to hexane	% Distrib. of products	
			1^{ry} C-H	2^{ry} C-H
9	40%	15%	< 5%	> 95%
10	65%	10%	< 5%	> 95%
11	45%	40%	31%	69%
12	70%	25%	25%	75%

Scheme 6. Reaction of hexane and ethyl diazoacetate in the presence of **9**–**12** and NaBAr′$_4$ (5% catalyst loading with respect to EDA).

The incorporation of the carbene group to benzene or to hexane takes place by different mechanisms. As shown in Scheme 7 (a), it has been proposed that benzene undergoes an electrophilic attack of the metallacarbene to give a Wheland-like intermediate[14] from which both the insertion or the cycloheptatriene products evolve. The reverse process (gold-catalyzed retro-Buchner reaction) has recently been observed from cycloheptatrienes and cationic Au^{I} complexes.[15] In the case of a saturated C–H bond (Scheme 7, b), a concerted process in which the C–H bond acts as a (poor) nucleophile and interacts with the carbenic carbon atom occurs.[16] In the system we describe herein, it could be thought that a transient carboxylate coordination would affect the catalytic process. In our previous work with IPrAuCl and related catalysts these transformations are likely to occur through linear, two-coordinate intermediates of the type NHC–Au=C(H)CO$_2$Et$^+$. At variance with those catalysts, the system reported herein could proceed through the intermediacy of a gold–carbene tricoordinate species (Scheme 7, c). The additional electron density from oxygen coordination would decrease the electrophilicity of the gold atom, decreasing the catalytic activity. The proximity of the carbene group to the second substituent of the NHC ligand would also explain the observed steric effect in the hexane case: the 2,6-diisopropylphenyl substituent seems to disfavor the functionalization of the primary sites in this system.[3c]



Scheme 7. The accepted pathways for the functionalization of C–H bonds of benzene (a) and alkanes (b) by carbene transfer from diazo compounds. (c) Proposed tricoordinate intermediate in the case of complexes **9**–**12** and NaBAr′$_4$ as the catalyst precursor.

In order to assess the validity of the above proposal, we have carried out DFT calculations [DFT, B3LYP, 6-31G(d) (C, O, N, H), and SDD (Au)] on the model carbenes **13** (with CH_2 as the carbene unit, Figure 1) and **14** (with $CHCO_2Me$ as the carbene unit, Figure 1). Identical minima were calculated when solvent corrections (CH_2Cl_2) were included in the calculations. The NBO analysis of **13** and **14** failed to locate any significant bonding interaction between Au^{I} and the ester group. For comparison, we have included the structure of **15** with two phenyl substituents at the

NHC, which shows a similar natural atomic charge at the Au^I center. The Au–O distances found fall within the range 4.4–4.5 Å, indicating that this secondary interaction between Au^I and the ester at the arm is, at most, very weak. Therefore, our proposal of a transient tricoordinate species seems to be disfavored on the basis of such calculations.

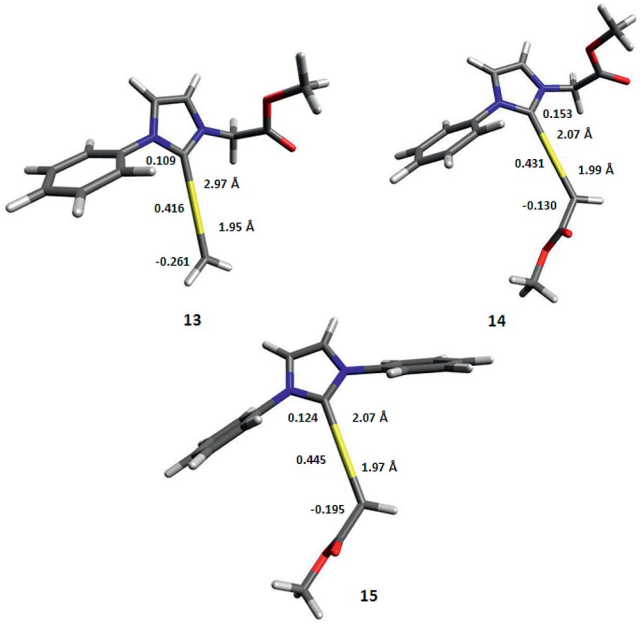


Figure 1. Minimum structures for model cationic intermediates **13**, **14**, and **15** [DFT, B3LYP, 6-31G(d) (C, N, O, H), and SDD (Au), CH_2Cl_2] showing selected bond lengths (boldface) and natural atomic charges (italics).

Conclusions

We have prepared a series of imidazolium salts with their corresponding silver and gold (NHC)MX derivatives (M = Ag, Au; X = Cl, Br) with a CH_2CO_2Et pendant group. The gold complexes have been tested as catalysts for the functionalization of benzene and hexane by means of the metal-catalyzed diazo compound (ethyl diazoacetate) decomposition and subsequent carbene ($CHCO_2Et$) transfer. Although catalytic activities are moderate, the observed trends suggest a somewhat distinct behavior of these gold complexes when employed as catalysts compared to the previous NHCAuCl (NHC) IPr, IMes, I*t*Bu, IAd catalyst precursors for the same transformations. Work aimed to ascertain the origin of such differences as well as to design other ligands in which the electronic and steric effect would enhance the catalytic activity is currently underway in our laboratories.

Experimental Section

General: All preparations and manipulations were carried out under an oxygen-free nitrogen atmosphere using Schlenk techniques. NMR experiments were carried out with a Varian Mercury 400 MHz. GC data were collected with a Varian 3900 instrument. All the reagents were purchased from commercial sources and used without further purification. Ligands **1** and **2** were prepared following literature procedures.[4] Elemental analyses were carried out with a Perkin–Elmer EA 2400 analyzer.

***N*-(Ethylacetyl)-*N*′-(mesityl)imidazolium Bromide (3):** *N*-Mesitylimidazole (600 mg, 3.22 mmol), ethyl bromoacetate (0.39 mL, 3.54 mmol), and THF (1 mL) were placed in a flask. The reaction mixture was stirred for 24 h at 130 °C. Volatiles were removed under vacuum and the residue was washed with diethyl ether and dried under vacuum (935 mg, 97%). $C_{16}H_{21}BrN_2O_2$ (353.25): calcd. C 54.40, H 5.99, N 7.93; found C 54.45, H 6.02, N 7.90. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.32 (t, J = 7 Hz, 3 H, CH_3CH$_2$O), 2.10 (s, 6 H, *o*-CH_3), 2.34 (s, 3 H, *p*-CH_3), 4.28 (q, J = 7.2 Hz, 2 H, CH$_3$CH_2O), 5.89 (s, 2 H, CH_2CO$_2$Et), 7.01 (s, 2 H, C*H*, arom.), 7.15 (d, J = 1.6 Hz, 1 H, C*H*, imidazole), 7.86 (d, J = 2 Hz, 1 H, C*H*, imidazole), 10.17 (s, 1 H, NC*H*N) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 14.3 (*C*H$_3$CH$_2$O), 17.8 (*o*-*C*H$_3$), 21.3 (*p*-*C*H$_3$), 50.9 (*C*H$_2$CO$_2$Et), 63.0 (CH$_3$*C*H$_2$O), 122.7, 125.3, 129.9, 130.8, 134.5, 139.1, 141.5 (N*C*HN), 166.6 (*C*=O) ppm.

***N*-(2,6-Diisopropylphenyl)-*N*′-(ethylacetyl)imidazolium Bromide (4):** *N*-(2,6-Diisopropylphenyl)imidazole (641 mg, 2.81 mmol), ethyl bromoacetate (0.34 mL, 3.10 mmol), and THF (1 mL) were placed in a flask. The reaction mixture was stirred for 24 h at 130 °C. Volatiles were removed under vacuum, and the residue was purified by silica gel chromatography (CH_2Cl_2/CH_3OH 10:1) to give **4** as a brown solid (818 mg, 74%). $C_{19}H_{27}BrN_2O_2$ (395.33): calcd. C 57.72, H 6.88, N 7.09; found C 57.91, H 6.97, N 7.17. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.15 [d, J = 6.8 Hz, 6 H, CH(CH_3)$_2$], 1.24 [d, J = 6.8 Hz, 6 H, CH(CH_3)$_2$], 1.33 (t, J = 7 Hz, 2 H, CH_3CH$_2$O), 2.30–2.41 [m, 2 H, C*H*(CH$_3$)$_2$], 4.30 (q, J = 7.2 Hz, 2 H, CH$_3$CH_2O), 5.93 (s, 2 H, CH_2CO$_2$Et), 7.16 (br. s, 1 H, C*H*, imidazole), 7.30 (d, J = 7.6 Hz, 2 H, C*H*, arom.), 7.53 (t, J = 7.8 Hz, 1 H, C*H*, arom.), 7.76 (br. s, 1 H, C*H*, imidazole), 10.31 (s, 1 H, NC*H*N) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 14.2 (*C*H$_3$CH$_2$O), 24.5 [CH(*C*H$_3$)$_2$], 24.6 [CH(*C*H$_3$)$_2$], 28.7 [*C*H(CH$_3$)$_2$], 50.9 (*C*H$_2$CO$_2$Et), 62.9 (CH$_3$*C*H$_2$O), 123.7 (*C*H, imidazole), 124.8 (*C*H, arom.), 125.3 (*C*H, imidazole), 125.4 (*C*H, arom.), 130.3 (*C*H, arom.), 132.1 (*C*H, arom.), 139.3 (*C*H, arom.), 145.6 (N*C*HN), 166.5 (*C*=O) ppm.

[*N*,*N*′-Bis(ethylacetyl)imidazolin-2-ylidene]silver Chloride (5): A Schlenk flask was charged with **1** (99 mg, 0.36 mmol), silver oxide (100 mg, 0.434 mmol), and CH_2Cl_2 (15 mL). The reaction mixture was stirred at room temperature for 14 h in the dark and then filtered through Celite. The solvent was removed under vacuum to give **5** as a white solid (120.6 mg, 87%). $C_{11}H_{16}AgClN_2O_4$ (383.58): calcd. C 34.44, H 4.20, N 7.30; found C 34.18, H 4.24, N 7.69. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.24 (t, J = 7.2 Hz, 6 H, CH_3CH$_2$O), 4.17 (q, J = 7.2 Hz, 4 H, CH$_3$CH_2O), 4.92 (s, 4 H, CH_2CO$_2$Et), 7.10 (s, 2 H, C*H*, imidazole) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 14.3 (*C*H$_3$CH$_2$O), 52.9 (*C*H$_2$CO$_2$Et), 62.5 (CH$_3$*C*H$_2$O), 122.9 (*C*H$_2$, imidazole), 167.7 (*C*=O), 183.9 (*C*-carbene) ppm.

[*N*-(Ethylacetyl)-*N*′-(methyl)imidazolin-2-ylidene]silver Chloride (6): As with the procedure described for **5**, a mixture of **2** (100 mg, 0.49 mmol) and silver oxide (137 mg, 0.59 mmol) in CH_2Cl_2 (15 mL) was stirred at 40 °C for 7 h in the dark and then filtered through Celite. The solvent was removed under vacuum to give **6** as a white solid (92.9 mg, 60%). $C_8H_{12}AgClN_2O_2$ (311.51): calcd. C 30.84, H 3.88, N 8.99; found C 30.81, H 3.94, N 9.13. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.31 (t, J = 7.2 Hz, 3 H, CH_3CH$_2$O), 3.85 (s, 3 H, CH_3N), 4.25 (q, J = 7.2 Hz, 2 H, CH$_3$CH_2O), 4.90 (s, 2 H, CH_2CO$_2$Et), 7.02 (d, J = 1.2 Hz, 1 H, C*H*, imidazole), 7.06 (d, J = 2 Hz, 1 H, C*H*, imidazole) ppm. ^{13}C{^{1}H} NMR (100 MHz,

$CDCl_3$): δ = 15.1 (CH_3CH_2O), 39.9 (CH_3N), 53.5 (CH_2CO_2Et), 63.3 (CH_3CH_2O), 123.5 (*C*H, imidazole), 123.7 (*C*H, imidazole), 168.7 (*C*=O), 183.1 (*C*-carbene) ppm.

[*N*-(Ethylacetyl)-*N*′-(mesityl)imidazolin-2-ylidene]silver Bromide (7): A mixture of **3** (116 mg, 0.33 mmol) and silver oxide (93 mg, 0.40 mmol) in CH_2Cl_2 (15 mL) was stirred at room temperature for 24 h in the dark. After filtration with Celite and solvent removal, complex **7** was isolated as an off-white solid (93 mg, 60%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.30 (t, *J* = 7 Hz, 3 H, CH_3CH_2O), 1.82 (br. s, 6 H, CH_3), 2.38 (s, 3 H, CH_3), 4.25 (q, *J* = 7 Hz, 2 H, CH_3CH_2O), 5.02 (s, 2 H, CH_2CO_2Et), 6.85–6.99 (m, 2 H, C*H*, arom., C*H*, imidazole), 7.35–7.38 (m, 2 H, C*H*, arom., C*H*, imidazole) ppm. ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ = 13.9 (CH_3CH_2O), 17.3 (CH_3), 20.9 (CH_3), 52.5 (CH_2CO_2Et), 62.3 (CH_3CH_2O), 122.6, 122.9, 128.8, 129.2, 134.8, 135.1, 135.3, 167.4 (*C*=O), 183.8 (br. s, *C*-carbene) ppm.

[*N*-(2,6-Diisopropylphenyl)-*N*′-(Ethylacetyl)imidazolin-2-ylidene]-silver Bromide (8): Following the above protocol, **4** (51 mg, 0.13 mmol) and silver oxide (35 mg, 0.15 mmol) were stirred at 40 °C for 12 h in the dark in CH_2Cl_2 (15 mL) as the solvent. Filtration through Celite prior to removal of volatiles afforded complex **8** as an off-white solid (58.7 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.13 [d, *J* = 7.2 Hz, 6 H, $CH(CH_3)_2$], 1.23 [d, *J* = 7.2 Hz, 6 H, $CH(CH_3)_2$], 1.35 (t, *J* = 7.2 Hz, 3 H, CH_3CH_2O), 2.40 [sept, *J* = 7.2 Hz, 2 H,$CH(CH_3)_2$], 4.31 (q, *J* = 7.2 Hz, 2 H,CH_3CH_2O), 5.03 (s, 2 H, CH_2CO_2Et), 7.04 (br. s, 1 H, C*H*, imidazole), 7.25–7.27 (m, 3 H, C*H*, arom., C*H*, imidazole), 7.47 (t, *J* = 7.6 Hz, 1 H, C*H*, arom.) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 14.07 (CH_3CH_2O), 24.3 [$CH(CH_3)_2$], 24.6 [$CH(CH_3)_2$], 28.2 [$CH(CH_3)_2$], 52.6 (CH_2CO_2Et), 62.6 (CH_3CH_2O), 121.9 (*C*H, imidazole), 122.0 (*C*H, imidazole), 124.3 (*C*H, arom.), 130.6 (*C*H, arom.), 134.4 (*C*H, arom.), 145.7 (*C*H, arom.), 167.2(*C*=O), 183.6 (br. s, *C*-carbene) ppm.

[*N*,*N*′-Bis(ethylacetyl)imidazolin-2-ylidene]gold Chloride (9): A mixture of the silver complex **5** (102 mg, 0.33 mmol) and (dimethyl sulfide)gold(I) chloride (115 mg, 0.39 mmol) in dichloromethane (50 mL) was stirred for 3 h at room temperature. After filtration, activated carbon was added to the filtrate and the mixture was filtered through Celite. The volatiles were then removed under reduce pressure to afford complex **9** as a white solid (30.1 mg, 64%). $C_{11}H_{16}AuClN_2O_4$ (472.05): calcd. C 27.95, H 3.41, N 5.93; found C 27.71, H 3.49, N 6.66. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.32 (t, *J* = 7.2 Hz, 6 H, CH_3CH_2O), 4.26 (q, *J* = 7.2 Hz, 4 H, CH_3CH_2O), 5.00 (s, 4 H, CH_2CO_2Et), 7.10 (s, 2 H, C*H*, imidazole) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 14.3 (CH_3CH_2O), 52.1 (CH_2CO_2Et), 62.7 (CH_3CH_2O), 122.3 (*C*H, imidazole), 166.9 (*C*=O), 174.4 (*C*-carbene) ppm.

[*N*-(Ethylacetyl)-*N*′-(methyl)imidazolin-2-ylidene]gold Chloride (10): Following the procedure described for **9**, complex **10** was prepared from **6** and isolated as a white solid (75.1 mg, 60%). $C_8H_{12}AuClN_2O_2$ (400.03): calcd. C 23.98, H 3.02, N 6.99; found C 23.61, H 3.21, N 6.88. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.32 (t, *J* = 7.2 Hz, 3 H, CH_3CH_2O), 3.84 (s, 3 H, CH_3N), 4.24 (q, *J* = 7.2 Hz, 2 H, CH_3CH_2O), 4.97 (s, 2 H, CH_2CO_2Et), 7.00 (d, *J* = 1.9 Hz, 1 H, C*H*, imidazole), 7.05 (d, *J* = 1.9 Hz, 1 H, C*H*, imidazole) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 14.3 (CH_3CH_2O), 38.8 (CH_3N), 52.0 (CH_2CO_2Et), 62.8 (CH_3CH_2O), 122.1 (*C*H, imidazole), 167.5 (*C*=O), 173 (*C*-carbene) ppm.

[*N*-(Ethylacetyl)-*N*′-(mesityl)imidazolin-2-ylidene]gold Chloride (11): This complex was prepared as above, using **7** as the starting material; yield 163.5 mg, 65%. $C_{16}H_{20}AuClN_2O_2$ (504.1): calcd. C 38.07, H 3.99, N 5.55; found C 38.48, H 4.36, N 5.83. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.32 (t, *J* = 7.2 Hz, 3 H, CH_3CH_2O), 2.01 (s, 6 H, CH_3), 2.32 (s, 3 H, CH_3), 4.28 (q, *J* = 7.2 Hz, 2 H, CH_3CH_2O), 5.09 (s, 2 H, CH_2CO_2Et), 6.92 (d, *J* = 1.7 Hz, 1 H, C*H*, imidazole), 6.95 (s, 2 H, C*H*, arom.), 7.24 (d, *J* = 1.7 Hz, 1 H, C*H*, imidazole) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 14.3 (CH_3CH_2O), 18.0 (CH_3), 21.4 (CH_3), 52.1 (CH_2CO_2Et), 62.7 (CH_3CH_2O), 122.1, 122.7, 129.7, 134.6, 135.0, 140.0, 167.1 (*C*=O), 173.4 (*C*-carbene) ppm.

[*N*-(2,6-Diisopropylphenyl)-*N*′-(ethylacetyl)imidazolin-2-ylidene]gold Chloride (12): A method of preparation similar to that used above, with **8** as the starting material, gave **12** as a yellowish solid (120 mg, 67%). $C_{19}H_{26}AuClN_2O_2{\cdot}CH_2Cl_2$ (631.5): calcd. C 38.0, H 4.43, N 4.43; found C 39.25, H 4.53, N 4.43. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.06 [d, *J* = 6.8 Hz, 6 H, $CH_3(CH_3)_2$], 1.20 [d, *J* = 6.8 Hz, 6 H, $CH_3(CH_3)_2$], 1.22–1.26 (m, 2 H, CH_3CH_2O), 2.36 [sept, *J* = 6.8 Hz, 2 H, $CH(CH_3)_2$], 4.23 (q, *J* = 7.2 Hz, 2 H, CH_3CH_2O), 5.02 (s, 2 H, CH_2CO_2Et), 7.04 (d, *J* = 1.9 Hz, 1 H, C*H*, imidazole), 7.24 (d, *J* = 1.9 Hz, 1 H, C*H*, imidazole), 7.31–7.34 (m, 2 H, C*H*, arom.), 7.42 (t, *J* = 7.6 Hz, 1 H, C*H*, arom.) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 13.8 (CH_3CH_2O), 24.0 [$CH(CH_3)_2$], 24.2 [$CH(CH_3)_2$], 28.3 [$CH(CH_3)_2$], 52.0 (CH_2CO_2Et), 62.4 (CH_3CH_2O), 121.7 (*C*H, imidazole), 123.7 (*C*H, imidazole), 124.1 (*C*H, arom.), 130.6 (*C*H, arom.), 145.9 (*C*H, arom.), 168.9 (*C*=O), 175.5 (*C*-carbene) ppm.

Catalytic Experiments. (a) Benzene: An equimolar mixture of the gold complex **9**–**12** and $NaBAr'_4$ (0.025 mmol) was dissolved in neat benzene (1–3 mL). After 15 min of stirring, EDA (0.5 mmol) was added in one portion. After 12 h of additional stirring, the mixture was analyzed by GC. The volatile components were removed, and the residue analyzed by NMR spectroscopy to identify the products.[3b]

(b) *n*-Hexane: An equimolar mixture of the gold complex **9**–**12** and $NaBAr'_4$ (0.025 mmol) was dissolved in a mixture of CH_2Cl_2 (5 mL) and *n*-hexane (5 mL). After 15 min of stirring, EDA (0.5 mmol) was added with the aid of a syringe pump (dissolved in 5 mL of CH_2Cl_2 and hexane, 1:1) for 24 h. The mixture was analyzed by GC and NMR spectroscopy.[3c]

Computational Details: Calculations were performed with the GAUSSIAN 09 series of programs.[17] The geometries were optimized at the DFT level using the B3LYP functional.[18] The LANL2DZ basis set, which includes the relativistic effective core potential (ECP) of Hay and Wadt and employs a split-valence (double-ζ) basis set, was used for Au.[19]

Acknowledgments

We thank Ministerio de Ciencia e Innovación (MICINN) (CTQ2008-00042BQU, CTQ2010-16088/BQU, Consolider Ingenio 2010 grant number CSD-2006-0003), Junta de Andalucía (P07-FQM-02870), the Agència de Gestió d'Ajuts Universitaris i de Reserca (AGAUR) (2009 SGR 47), and the ICIQ Foundation for financial support. M. D. R. thanks the Ministerio de Educación y Ciencia (MEC) for a FPU fellowship.

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Received: October 21, 2011
Published Online: January 9, 2012

