# ORGANOMETALLICS

### Gold Catalysis: Hydrolysis of Di(alkoxy)carbenium Ion Intermediates as a Sensor for the Electronic Properties of Gold(I) Complexes

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Supporting Information

ABSTRACT: Six different cationic gold(I) complexes LAu<sup>+</sup> were converted to the corresponding di(alkoxy)carbenium ions by reaction with ethyl 2,5-dimethylhexa-2,3-dienoate. These conversions were monitored by in situ IR spectroscopy; at room temperature they proceeded in only a few seconds. The ligands L are based on the most



popular ligand types in gold catalysis: phosphanes, phosphites, carbenes, and isonitriles. The di(alkoxy)carbenium ions were stable, not short-lived intermediates, and could be characterized. This allowed the kinetic study of the next step, the hydrolytic cleavage to the Hammond-type vinylgold species. Depending on the ligand on gold, large rate differences were detected. Computational chemistry revealed a correlation of the experimental reaction rates with the LUMO energies of the di(alkoxy)carbenium species and the direct influence of the ligand on gold on these LUMO energies. Thus, the di(alkoxy)carbenium ion could be utilized as an easy to use benchmark system for the electronic characterization of LAu<sup>+</sup> catalysts by theory, spectroscopy, and kinetic experiments.

### INTRODUCTION

Over the past few decades homogeneous gold catalysis has emerged as a powerful tool in organic synthesis.<sup>1</sup> However, despite its increasing significance and the stability of many organogold compounds, only a few intermediates of gold-catalyzed reactions have been isolated and characterized so far.<sup>2</sup> Many mechanistic proposals rely on careful considerations, calculations, observation of side products or analogies to other transition-metal-catalyzed reactions. As an example, vinylgold compounds have been proposed as intermediates of goldcatalyzed nucleophilic additions to unsaturated compounds such as alkynes or allenes for years. Finally, in 2008, Hammond and co-workers succeeded in isolating vinylgold(I) compounds formed by a gold(I)-catalyzed cyclization reaction of allenoates. They also characterized a di(alkoxy)carbenium intermediate by in situ <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy (Scheme 1).<sup>3</sup>

Since these important findings, several other groups have reported the isolation and characterization of vinylgold(I) compounds in gold-catalyzed reactions. Moreover, their role as intermediates has been established.<sup>4</sup> From these intermediates the gold catalyst is usually regenerated by a fast protodemetalation step. However, the C-Au bond can also be cleaved by other electrophiles, regenerating the gold catalyst.<sup>3,5</sup> The transmetalation of vinylgold(I) compounds to palladium electrophiles in palladium-catalyzed cross-coupling reactions has also been reported recently.6

In contrast to the case for vinylgold(I) compounds, the nature of gold(I)-coordinated carbenes as intermediates of gold-catalyzed reactions has caused a controversial discussion in the literature.<sup>7</sup> The discussion focuses on the extent of carbene

character versus gold-stabilized carbocation character in these intermediates (Scheme 2).

Recent work by Fürstner<sup>8</sup> and by Toste<sup>9</sup> indicates a continuum ranging from metal-stabilized singlet carbenes to metal coordinated carbocations, with the position of the gold species strongly depending on the carbene substituents and the ancillary ligand of gold(I). This discussion reveals the large influence of the ancillary ligand on the electronic properties and the reactivity of gold(I) complexes.

Here we present a new and feasible method to estimate the electronic properties of LAu<sup>+</sup> catalysts by simple NMR experiments. This is demonstrated for the rate of hydrolysis of di-(alkoxy)carbenium ions, true intermediates of a gold-catalyzed cyclization reaction of allenoates (Scheme 3). These intermediates turned out to be stable and can be isolated with a number of counterions. Thus, the electronic properties can be quantified in an elemental step of a catalysis reaction and can be correlated to electronic properties of the ligand L by computational chemistry.

### RESULTS AND DISCUSSION

Experimental Chemistry. For this investigation we prepared a number of different di(alkoxy)carbenium ions, bearing electronically different ligands (Figure 1).

As shown in Scheme 4, di(alkoxy)carbenium ions are formed by treatment of allenoate 4 with stoichiometric amounts of gold(I) salts. The cationic gold species 3-X activates the distal

Received: August 5, 2011 Published: October 12, 2011 Scheme 1. In Situ Characterization of Di(alkoxy)carbenium Intermediates Formed by Gold(I)-Catalyzed Cyclization of Allenoates



Scheme 2. Carbene or Gold-Stabilized Carbocation?



Scheme 3. Di(alkoxy)carbenium Intermediates



Figure 1. Ligands used in this study.

double bond toward nucleophilic attack by the carbonyl oxygen. Previously, these intermediates have only been characterized in situ by <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy but have not been isolated.<sup>3</sup> In fact, these intermediates are easily accessible and stable. Our own results as well as results from other groups indicated a very fast formation of di(alkoxy)carbenium ions for  $L = PPh_3$  (1a).<sup>3,6a-d</sup> Monitoring the di(alkoxy)carbenium ion formation with different gold(I) salts (LAuOTf (3-OTf), LAuNTf<sub>2</sub> (3-NTf<sub>2</sub>)) by ReactIR confirmed these observations. This is demonstrated for Ph<sub>3</sub>PAuNTf<sub>2</sub> (3a-NTf<sub>2</sub>) in Figure 2.

Allenoate 4 was consumed, and the corresponding di(alkoxy)carbenium species were formed within a few seconds in each case. Small differences in rate between the different gold salts were observed in this non-rate-determining step of the overall catalytic conversion of the allenoates. In further experiments we checked the influence of the counterion on the formation of the di(alkoxy)carbenium intermediates. In a detailed NMR study we reacted 4 with a series of complexes of the general structure  $Ph_3PAuX$  (**3a-X**; X = SbF<sub>6</sub>, OTf, OTs, NTf<sub>2</sub>). With the exception of  $Ph_3PAuOTs$  (**3a-OTs**), we observed for all compounds a fast formation of the cationic cyclization products.<sup>10</sup> Although we used different anions, the resulting cyclization products featured only slight variations concerning their NMR characteristics. For this reason, we excluded strongly anion dependent interactions.

In the presence of water, di(alkoxy)carbenium intermediates 5 are known to afford the corresponding vinylgold(I) compounds 6. This can proceed via two different pathways: water can either attack the carbenium carbon (path a, tetrahedral intermediate) or the ethoxy group (path b,  $S_N 2$ ). In both cases lactone 6 and ethanol are formed (Scheme 5a). To distinguish between both pathways, we added <sup>18</sup>O-labeled water to the in situ formed di(alkoxy)carbenium intermediates 5a-OTf, 5e-OTf, and 5g-OTf. We could determine high ratios of labeling at the carbonyl position in each case.<sup>11</sup> These results unambiguously prove that the nucleophilic attack occurs at the di(alkoxy)carbenium carbon atom. Asao and co-workers recently reported the use of primary cyclization products obtained by gold catalysis as a useful activation method for nucleophilic substitution reactions.<sup>12</sup> We also succeeded in trapping the corresponding intermediate  $8g-NTf_2$  by simple treatment of compound 6 with stoichiometric amounts of IPrAuNTf<sub>2</sub>  $(3g-NTf_2)$  in absolute DCM at room temperature (Scheme 5b). In this case, the intermediate is stabilized by the aromaticity of the resulting pyrylium salt, hampering the nucleophilic attack at the dioxocarbenium carbon atom.

Surprisingly, the use of  $NTf_2^-$  salts 3- $NTf_2$  resulted in a very slow hydrolysis.<sup>13</sup> Nevertheless, this enabled us to isolate the di(alkoxy)carbenium species 5a- $NTf_2$  as a pure compound for the first time and to characterize it by <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectroscopy and mass spectrometry. We also succeeded in isolating the allyloxy- and diethylamino-substituted carbenium ions 5h- $NTf_2$  and 5i- $NTf_2$  (Scheme 6). Allyloxy-substituted carbenium ions have previously been proposed as intermediates by Blum et al.<sup>6c</sup> The allene amide precursor for 5i- $NTf_2$  was easily accessible by a Wittig reaction.

To gain further insight into the mechanism, we decided to monitor the rate of hydrolysis of the salts **5-OTf** by <sup>1</sup>H NMR spectroscopy. We prepared the di(alkoxy)carbenium ions **5a-OTf** and **5c-OTf**–**5e-OTf** in situ in dry  $CD_2Cl_2$  and added  $H_2O$ (20.0 equiv) to the reaction mixtures. NMR samples were taken after certain intervals and were filtered through a short pad of MgSO<sub>4</sub> to remove traces of  $H_2O$  and AgCl. <sup>1</sup>H NMR signals have been normalized to *tert*-butyl methyl ether, which was used as an internal standard for quantification (Figure 3). We found the rate

### Scheme 4. Synthesis of Gold Compounds



Figure 2. Formation of the di(alkoxy)carbenium ion 5a-NTf<sub>2</sub> monitored by ReactIR (complete conversion in less than 30 s): (a) characteristic absorption bands of starting material and product; (b) consumption of starting material and product formation.

of hydrolysis to be highly dependent on the ligand coordinated to the gold(I) complex. In cases of 5a-OTf, 5c-OTf, and 5e-OTf, the hydrolysis proceeded quickly (30-80% product formation after 30 min). In contrast, gold complexes 5d-OTf and 5g-OTf reacted slowly (<5% product formation after 30 min). 6c seemed to be very sensitive and started to decompose unspecifically after several hours. Organogold compounds 6b-g have also been synthesized analogously to 6a with stoichiometric amounts of LAuCl (2) and AgOTf in  $CH_2Cl_2/H_2O$  and have been characterized.<sup>6b,d</sup> In some cases we were able to obtain suitable single crystals of compounds 6 for an X-ray structure analysis (Figure 4). Strong differences in reaction time and yield have also been observed here. Because of the large distances (Figure 4) between the reaction center  $C^1$  (for atom labeling, see Figure 5) and the ancillary ligand coordinated to gold(I), the observable significant differences in reaction time and rate of hydrolysis should originate from electronic effects of the ancillary ligands only. In order to understand these differences in reactivity, we turned our attention to the electronic structure of these intermediates.

The isonitrile carbon in **6e** is electrophilic and can be attacked by nucleophiles such as diethylamine.<sup>14</sup> The NAC gold compound **6j** was obtained in 98% yield (Scheme 7). In the future interpretation of data obtained with isonitrile complexes similar to **6e** or even **5e**, it will be important to keep in mind that subsequent nucleophilic additions are possible.

**Computational Methods.** The geometry optimizations of the gold complexes were performed using the Gaussian03 program

package<sup>15</sup> at the density functional theory (DFT) level, employing the Becke three-parameter B3LYP functional<sup>16</sup> together with a cc-pVDZ basis<sup>17</sup> on all atoms. Some representative systems were calculated with an increased cc-pVTZ basis set in order to examine basis set completeness. The increased basis only led to insignificant changes in the orbital energies and natural charge occupations, which means that the electronic characterization of the systems can safely be maintained in the cc-pVDZ basis. This finding is also relevant for the treatment of large ligands connected to the gold fragment, because there a triple- $\zeta$  calculation is not manageable. For gold a relativistic effective core potential (RECP) from ref 18 was employed, where 60 electrons are taken into the core. The corresponding valence basis suitable for this pseudopotential also had cc-pVDZ quality and was optimized by Peterson and Puzzarini.<sup>19</sup> The relativistic effects, especially s-orbital contraction and d-orbital expansion, are accurately accounted for by the RECP; DFT/RECP has proven to be very successful for calculations of organometallic compounds.<sup>20</sup> Mulliken and natural charges for the relevant atomic centers were calculated, where the former exhibit a considerable basis set dependence and are only included for completeness. The bonding situation was analyzed by employing the natural bond orbitals (NBOs)<sup>21</sup> in order to characterize the special electronic features in this system. All NBO-type calculations were done with the program GENNBO 5.0.<sup>22</sup> In order to analyze orbital energy trends in the systems under consideration, we also performed Hartree-Fock self-consistent field (SCF) calculations. Electron correlation is neglected in the SCF

Scheme 5. (a) Proposed Mechanism for the Gold-Catalyzed Cyclization of Allenoates. (b) Trapping of the Pyrylium Salt Intermediate 8g-NTf<sub>2</sub>

![](_page_3_Figure_3.jpeg)

### Scheme 6. Differently Substituted Carbenium Ions

![](_page_3_Figure_5.jpeg)

method, avoiding possible artifacts introduced in the calculation of DFT-LUMO energies. It turned out that despite different absolute values of orbital energies the trends are identical for both the DFT and SCF treatments.

**Theoretical Results.** Depending on the type of ligand on the gold center, the observed experimental reactivity of the di-(alkoxy)carbenium intermediates toward the nucleophilic attack of water varies considerably (Figure 3). In order to establish a relation between the observed rate of hydrolysis and the electronic properties inherent to the substrate, we investigated molecular orbital energies, orbital coefficients at the reactive center  $C^1$ , and natural charges of the di(alkoxy)carbenium intermediate for all ligands shown in Figure 1 (except **1b**) at various levels of theory.

At first we analyzed the positively charged prototype system of Scheme 3 using  $L = PMe_3$ , omitting the negative counterion in the calculations. Among the three possible mesomeric structures depicted in Scheme 3, the leftmost realization with a positive charge delocalized over the  $O^1/C^1/O^2$  system carries the highest weight (see Figure 5 for the atom labels in the di(alkoxy)-carbenium system). This is reflected by the partial double-bond character of the two oxygen–carbon bonds, possessing bond lengths of 129 and 130 pm, and a  $C^2-C^3$  distance of 137 pm, lying between a single and a double bond. The carbon atom  $C^1$  carries most of the positive charge and will therefore be the reactive center for the nucleophilic attack. A second important factor for a nucleophilic attack is a nonvanishing LUMO density at the reactive center in order to accommodate charge density

![](_page_3_Figure_9.jpeg)

Figure 3. Hydrolysis of di(alkoxy)carbenium ions 5a-OTf and 5c-OTf–5e-OTf monitored by <sup>1</sup>H NMR spectroscopy: (a) section of <sup>1</sup>H NMR spectrum 5e-OTf; (b) rate of product formation for different L (1).

originating from the nucleophile. It can be seen that the di-(alkoxy)carbenium LUMO is  $C^1-C^2$  bonding but antibonding

![](_page_4_Figure_2.jpeg)

Figure 4. Solid-state molecular structures of 6d-g. Thermal ellipsoids are shown at the 50% probability level.

![](_page_4_Figure_4.jpeg)

**Figure 5.** General numbering of the basic heterocyclic structure. The  $\pi$  system, the charge, and the counterion are omitted for clarity.

in  $C^1 - O^1$  and  $C^1 - O^2$ . Furthermore, strong contributions from the gold-bound vinyl carbon atom can be observed together with a small participation of a gold pd-hybrid orbital (Figure 6). The orbitals of the vinyl carbon  $C^3$  also participate in the LUMO, but due to its negative Mulliken and natural charge a nucleophilic attack will not occur there. For all ligands under consideration and for both SCF/DFT methods,  $C^1$  ( $C^3$ ) will always keep its positive (negative) partial charge in terms of both Mulliken and natural charges. The difference in reactivity will therefore be modulated by the varying  $\sigma$ -donor character of the chosen ligands bound to the opposite coordination site of gold. Hereby the metal atom acts as a mediator or relay of the electronic ligand properties, forwarding them to the di-(alkoxy)carbenium moiety. In contrast to the case for many other transition metals, gold in its +1 oxidation state maintains a nearly closed 5d shell, as detailed NBO analyses reveal (see below). As a consequence, a four-electron-three-center bond, in which the gold atom, the ligand moiety, and the carbon atom C<sup>3</sup> of the di(alkoxy)carbenium unit participate, is observed for all systems under consideration and is responsible for the electronic tunability.

In the following we investigate possible electronic factors relevant for the varying reaction rates. Even for bulky ligands steric effects can be excluded, due to the large distance to the reactive center on  $C^1$ , and we are left with the criteria of orbital energy, partial charge, and density.

As an obvious rate-determining factor one may first assume the partial charge on  $C^1$ . In Table 1 we summarize the calculated partial Mulliken and natural charges on the reactive center  $C^1$  for the SCF and DFT/B3LYP method. Although substantial differences in the partial charges can be observed between the SCF and DFT approaches and between the Mulliken and natural charges, they remain remarkably constant with respect to ligand change (column). Therefore, they are not able to explain any correlation to observed trends in reactivity. This is somehow surprising, because one is tempted to attribute a variation of  $\sigma$ -donor capabilities or electronegativities of the ligands to a change in partial charge of  $C^1$ , which is made possible by the conjugated  $\pi$  system.

Despite the low variability in the partial charge at  $C^1$ , we found a variation of the <sup>1</sup>H NMR shifts for the hydrogen atom bound to  $C^4$  but only little variation for the hydrogen atoms bound to  $C^5$ . At first, these results seem somehow contradictory, because one might assume that negative inductive effects should affect both positions in a comparable manner. On closer inspection of the system, it is obvious that the different NMR shifts should be due to the magnetic anisotropy being inherent in the heterocycle. The  $\pi$  substructure of the heterocycle resembles an electronically disturbed cyclopentadiene system, whereby the hydrogen atom at  $C^4$  is directly influenced by the electronic structure. The hydrogen at  $C^5$  is more separated, and therefore the influence of the  $\pi$  system (see also NBO analyses) is ineffective.

For a basis set completeness check with respect to an enhancement to triple- $\zeta$  quality, we picked four representative ligands from Table 1 that induce different hydrolysis rates and recalculated the partial charges on the reactive center (see Table 2).

Our results for the triple- $\zeta$  basis confirm the well-known observation of a pronounced basis set dependence in case of Mulliken charges and a considerably higher stability for the natural charges. The most important observation, however, is again the absence of a correlation between the partial charge and the reaction rate within the space of triple- $\zeta$  basis functions. In contrast to the natural charges at the reactive center, the LUMO energies together with the corresponding coefficients at C<sup>1</sup> exhibit a clear correlation to the reaction rates in the way that a decrease in the LUMO energy leads to an increase of the reaction rate. The experimental reaction rates are shown in Figure 3b, reflecting their capabilities in activating the ring system for a nucleophilic attack: phosphite (1c) > isonitrile (1e) > PPh<sub>3</sub> (1a)> NAC (1f) > XPhos (1d) > IPr (1g). Reaction rates for the ligands  $L = PH_3$ , PMe<sub>3</sub>,  $Cl^-$  are experimentally not accessible. However, their theoretical values are given for the sake of thoroughness. A theoretical value for a simplified NHC ligand derived from 1g is also given, where the two nitrogen-bound side chains are replaced by methyl groups (denoted as NHC). In Table 3 (see also Figure 7) we collect the LUMO energies for SCF and DFT/B3LYP and the C<sup>1</sup> orbital coefficients for these ligand systems following the experimentally measured rates. Both the SCF and DFT LUMO energies exhibit a clear correlation to reaction rates, although it is known that not much physical significance can be attributed to DFT virtual orbitals,<sup>24</sup> rendering the SCF virtual orbitals more significant for the interpretation.

The various ligands hereby determine the LUMO energy and the orbital coefficient on the reactive center. Due to the high number of possible rotamers and the number of atoms (n = 112!), we did not succeed in finding a global minimum structure for XPhos (1d), resulting in a possibly incorrect energetic value.

### Scheme 7. (a) Addition of Diethylamine to 6e. (b) Solid-State Molecular Structure of $6j^a$

![](_page_5_Figure_3.jpeg)

<sup>a</sup> Thermal ellipsoids are shown at the 50% probability level.

![](_page_5_Figure_5.jpeg)

Figure 6. LUMO of the di(alkoxy)carbenium ion 6f at an isocontour value of 0.05.

 Table 1. Partial Charges on the C<sup>1</sup> Reactive Center Obtained

 by Various Methods Employing a cc-pVDZ Basis<sup>a</sup>

	;	SCF	DFT		<sup>1</sup> H shift	NMR (ppm)
1. 1.7	. 1	N C 11:1	. 1	N 6 11:1	proton	protons
ligand L	naturai	Mulliken	natural	Mulliken	at C4	at CS
PH <sub>3</sub>	1.076	0.633	0.880	0.329		
phosphite	1.076	0.633	0.880	0.330	6.06	4.81
(1c)						
isonitrile $(1e)$	1.074	0.630	0.881	0.329	5.86	4.86
PMe <sub>3</sub>	1.072	0.631	0.873	0.324		
$PPh_3$ (1a)	1.070	0.630	0.874	0.324	5.92	4.85
NHC	1.069	0.627	0.871	0.321		
NAC (1f)	1.068	0.627	0.861	0.312	5.75	4.87
$NAC^{*}(1f^{*})$	1.068	0.625	0.862	0.311	5.73	4.73
XPhos (1d)	1.065	0.616	0.867	0.312	5.26	4.65
IPr (1g)	1.066	0.632	0.864	0.321	5.27	4.78
Cl <sup>-</sup>	1.040	0.618	0.838	0.308		
<sup>a</sup> The asterisk denotes the NAC conformational isomer. <sup>14b,23</sup>						

Both the energy and orbital coefficient determine the hardness or softness of the substrate according to the HSAB concept.<sup>25</sup> For a specific nucleophile with a definitive hardness, different affinities for the formation of a chemical bond between the two fragments are predicted by the HSAB concept. Hereby the absolute hardness of the nucleophile is not important, since the variation of the substrate's hardness induced by the various

![](_page_5_Figure_10.jpeg)

Table 2.	Partial Charg	ges on C <sup>1</sup>	for Some	Selected	Ligands
Employi	ng a cc-pVTZ	Basis			

	SCF		DFT		
ligand L	natural	Mulliken	natural	Mulliken	
$Cl^{-}$	0.9439	0.4386	0.7395	0.3039	
NHC	0.9672	0.4530	0.7637	0.3195	
IPr (1g)	0.9699	0.4471	0.7636	0.3159	
phosphite $(1c)$	0.9719	0.4495	0.7776	0.3286	

Table 3.	SCF and DFT/B3LY	P LUMO	<b>Energies</b> i	n eV o	of the
Di(alkox	y)carbenium System (	(cc-pVDZ	$(Z)^a$		

		E <sub>LUM</sub>	<sub>IO</sub> (eV)			
entry	ligand L	DFT	SCF	SCF orb coeff ( $\times 10^{-1}$ )		
1	phosphite (1c)	-1.93	-5.36	0.936		
2	$PH_3$	-1.87	-5.50	1.233		
3	isonitrile (1e)	-1.75	-5.32	1.101		
4	PMe <sub>3</sub>	-1.54	-5.18	1.417		
5	$PPh_3$ (1a)	-1.28	-5.01	1.689		
6	NHC	-1.28	-4.98	1.748		
7	NAC (1f)	-1.05	-4.87	1.502		
8	$NAC^{*}(1f^{*})$	-1.09	-4.84	1.995		
9	XPhos (1d)	-0.91	-4.78	2.259		
10	IPr (1g)	-1.04	-4.74	1.800		
11	$Cl^{-}$	1.36	-2.38	2.691		
<sup><i>a</i></sup> The last column shows the corresponding $p_z$ orbital coefficient on $C^1$ .						
For XPh	For XPhos (1d) see text.					

ligands will act as the probe for their electronic properties and will in turn always result in different affinities toward the nucleophile. According to our findings, the di(alkoxy)carbenium compound can therefore act as a probe for the  $\sigma$ -donor character of the ligands without the need for actual experiments. One can freely define an arbitrary reference point and classify the ligands to be analyzed according to the hardness induced in the heterocyclic ring system. Before analyzing the bonding situation via NBO analysis, we add some selected SCF and DFT LUMO energies obtained with the triple- $\zeta$  basis set. Due to the neglect of electron correlation effects, the SCF energies remain nearly unaltered. Still negligible but somewhat larger alterations are introduced by the DFT/cc-pVTZ treatment mainly by including slightly more electron correlation in comparison to the cc-pVDZ basis (Table 4). However, as in the case of the natural charges the

overall picture does not change and a calculation employing basis sets of double- $\zeta$  quality will be sufficient for the intended purposes.

In order to gain some insight into the metal-assisted transfer mechanism of electronic ligand properties to the heterocyclic ring system, we performed a detailed NBO analysis (Table 5). In accordance with the results obtained for the natural charges, the natural electron configuration is similarly stable and shows only slight variation upon ligand change.

Taking the complexes with the Cl<sup>-</sup> and PH<sub>3</sub> ligands as examples, we carried out a detailed analysis of the natural bond orders (Table 6). These two compounds are located at opposite positions in Table 3 and induce a large change in the hardness. Table 6 summarizes the natural bond orders and the bond length of the heterocyclic system. One clearly detects that the two compounds differ in all characteristic bond lengths and natural bond orders. In case of the Cl<sup>-</sup> ligand, the total bond order for Au–C<sup>3</sup> has a value of 0.87, exceeding the maximum value of 0.5 for a  $\sigma$  bond. The C<sup>3</sup>–C<sup>2</sup> bond has a length of 139.1 pm and a natural bond order of 1.59, showing an obvious deviation from a

![](_page_6_Figure_4.jpeg)

**Figure 7.** Graphical overview of the correlation between orbital coefficient and LUMO energy. The numbering corresponds to the results in Table 3.

Table 4. SCF and DFT/B3LYP LUMO Energies in eV for the Triple- $\zeta$  Basis

	$E_{\rm LUMO}~({\rm eV})$		
ligand L	SCF	DFT	
phosphite (1c)	-1.92	-5.57	
NHC	-1.29	-5.04	
IPr (1g)	-1.06	-4.83	
$Cl^{-}$	1.34	-2.48	

## Table 5. Summary of the Natural Electron Configuration at the Au Atom

	orbital	
ligand L	6s	5d
phosphite (1c)	0.86	9.74
PH <sub>3</sub>	0.81	9.75
isonitrile (1e)	0.84	9.66
PMe <sub>3</sub>	0.85	9.74
$PPh_3$ (1a)	0.83	9.74
NHC	0.85	9.68
$NAC^{*}(1f^{*})$	0.87	9.68
NAC (1f)	0.84	9.68
IPr (1g)	0.84	9.67
XPhos (1d)	0.80	9.75
Cl <sup>-</sup>	0.81	9.67

Table 6. Analysis of the Natural Bond Orders Taking the Complexes with  $Cl^-$  and  $PH_3$  Ligands as Examples<sup>*a*</sup>

![](_page_6_Figure_12.jpeg)

Cl	$Au-C^3$	$C^{3}-C^{2}$	$C^2 - C^1$	$C^1 - O^1$	$C^1 - O^2$
r	198.9	139.1	141.3	131.0	130.7
t	0.8721	1.5909	1.2714	1.3331	1.0883
с	0.2458	1.2708	1.0798	0.6697	0.6076
i	0.6263	0.3201	0.1916	0.6635	0.4808
$PH_3$	$Au-C^3$	$C^{3}-C^{2}$	$C^{2}-C^{1}$	$C^1 - O^1$	$C^{1}-O^{2}$
r	205.1	137.2	143.7	130.2	128.9
t	0.4757	1.7356	1.1471	1.3703	1.3886
с	0.1767	1.4574	1.0086	0.6823	0.6935
i	0.2990	0.2782	0.1385	0.6880	0.6951

<sup>*a*</sup> The charges and the counterions are omitted for clarity. r = bond length (pm); bond order split into t = total, c = covalent, and i = ionic.

![](_page_6_Figure_15.jpeg)

**Figure 9.** Stabilization of the carbenium ion in the heterocyclic system. The X stands for an atom with positive mesomeric effect.

![](_page_6_Figure_17.jpeg)

Figure 8. Lewis structures describing the bonding situation. In the case of the PH<sub>3</sub> ligand, the counterion was omitted for clarity.

![](_page_7_Figure_2.jpeg)

Figure 10. Comparison of the hydrolysis using D<sub>2</sub>O and H<sub>2</sub>O as nucleophiles.

![](_page_7_Figure_4.jpeg)

Figure 11. Mechanism in which water acts as nucleophile and as base.

localized double bond. Combining all the data presented, one could formulate Lewis structures, which are physically inadequate but descriptive. On the basis of the natural bond analysis for the Cl<sup>-</sup> ligand, partial double bonds for Au–C<sup>3</sup> and C<sup>2</sup>–C<sup>1</sup> as well as for C<sup>1</sup>–O<sup>1</sup> can be formulated (Figure 8a). The PH<sub>3</sub> ligand generates an opposite bonding situation. Moreover, it is obvious that in the case of the PH<sub>3</sub> ligand the Lewis structures with the positive charge localized at the O<sup>1</sup>–C<sup>1</sup>–O<sup>2</sup> motif are dominating (Figure 8b).

In contrast to the natural charge analysis and the natural electron configuration, we see a clear dependence of the natural bond order on the nature of the coordinated ligand. An explanation for these results could be anchored in the strongly delocalized bonding situation in these complexes. The electronic features of the ligands are directly transferred to the heterocyclic system, inducing concomitant structural adaptations. Nevertheless, the overall charges remain mainly unaltered, because the system acts like a relay with the gold atom and the two oxygen atoms as electronic buffers. In this context it might be useful to regard the gold atom as a substituent with a positive mesomeric effect (Figure 9).

In further calculations we checked solvent effects on our systems. All calculations were done as described before using the PCM (UAO and UFF) model.<sup>26</sup> Although the orbital energies were shifted, we found the same correlation with respect to LUMO energies and the orbital coefficients. Moreover, we included the counterion in one of the calculations and found the natural charges and natural electron configuration unaffected and the LUMO still localized on the heterocyclic system. All these data are available in the Supporting Information. For reasons of complexity of our systems it is not possible to run IRC calculations

on the reaction mechanism. Although the hydrolysis seems to be a simple single-step reaction, one must keep in mind that several deprotonation/reprotonation steps have to be considered. All these steps are multicentered problems, because the proton transfer mechanisms should include several water molecules and even the counterion. In order to get a first insight in the hydrolysis mechanism, we carried out the reaction with the isonitrile ligand in two separate experiments with  $H_2O$  and  $D_2O$  (Figure 10).

In contrast to other hydrolysis reactions, we could measure only a small kinetic isotopic effect.<sup>27</sup> This result is not in agreement with a mechanism consisting of a water-nucleophile/water-base principle (Figure 11). For this reason, the involvement of the counterion in the hydrolysis is much more likely (this might also be an explanation for the persistence of the NTf<sub>2</sub><sup>-</sup> analogues). Nevertheless, this result demonstrates that the rate-determining step is not largely dominated by the degree of solvation of the nucleophile or by a proton/deuteron transfer step.<sup>28</sup>

In the di(alkoxy)carbenium systems investigated, the ancillary ligand can influence the chemical properties of a reactive center located more than 600 pm away from the coordinating atom of the ligand. The pronounced dependence of LUMO energies and the orbital coefficients at the reactive center of the heterocyclic system clearly point to a transfer capability of electronic properties through the Au(I) bridge, resulting in different kinetics of the hydrolysis.

### CONCLUSION

The good accessibility of the organogold intermediates **5** is the basis for a fast experimental assessment of the electronic ligand properties in gold(I) catalysts. A corresponding theoretical investigation hereby reveals a stringent correlation between the reaction rate of the nucleophilic attack and specific electronic properties of the substrate, consisting of its LUMO energy and the corresponding p orbital coefficients at the reactive center C<sup>1</sup>. These properties define the hardness of the substrate according to the HSAB concept and are modulated by the  $\sigma$ -donor capability of the gold-bound ligands. The gold center hereby acts as an electronic relay via a three-center—four-electron bond

transferring the ligand properties to the opposite moiety. According to the HSAB concept various affinities toward a chosen nucleophile will result, allowing for a classification of ligands without performing actual experiments. Despite intuition, the natural charges at  $C^1$  do not exhibit any correlation to reaction rate and stay remarkably constant upon ligand change, whereas the <sup>1</sup>H NMR of the hydrogen atom bound to  $C^4$  is noticeably influenced by the varying electronic ligand properties.

### ASSOCIATED CONTENT

**Supporting Information.** Text, figures, tables, and CIF files giving experimental details, characterization data, crystal-lographic data, and details of the calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) The corresponding NMR spectra can be found in the Supporting Information.

(11) <sup>18</sup>O labeling was 88% for **5e-OTf**, 91% for **5a-OTf**, and 55% for **5g-OTf** (97% <sup>18</sup>O-labeled water), respectively. The small ratio of labeling for **5g-OTf** can be traced back to incomplete conversion of **5g-OTf** to **6g** under the reaction conditions and partial hydrolysis during workup. 3-Methyl-5-(propan-2-yl)furan-2(5*H*)-one, which was formed as a byproduct under reaction conditions by protodemetalation of **6g**, shows an <sup>18</sup>O labeling of 85%.

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