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Synthesis of Different Classes of Six-Membered Gold(I) NHC Complexes by the Isonitrile Route

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Supporting Information

ABSTRACT: Different types of six-membered N-heterocyclic gold carbene complexes were prepared by using gold(I) isonitrile complexes as precursors in combination with suitably functionalized amines. The simple procedures provide an easy access to not only unsymmetrically substituted saturated carbene complexes but rarely reported types of carbene complexes such as six-membered N-heterocyclic oxo-carbene complexes, and six-membered partly unsaturated ligands can be obtained following the strategy.



1. INTRODUCTION

The major advantages of N-heterocyclic carbenes (NHCs), in contrast to ligands such as phosphanes, are their thermal stability, their low toxicity, and their stability against oxidation.¹ This enables the application of NHC-transition metal complexes in a manifold of different reactions.²

While most of the research is focusing on five-memberedring carbenes, recently publications also dealt with the concept of six-, seven-, and eight-membered NHC complexes.³ Due to their higher basicity^{3c,4} and larger $N-C_{\rm NHC}-N$ angles,^{3c} in contrast to their five-membered analogues, these expanded ring systems are promising scaffolds for transition metal catalysis.⁵

The most common protocol for the synthesis of saturated five-, six-, seven-, and eight-membered carbene systems starts with the formation of a diamine (or diimine) and its subsequent transformation into the corresponding amidinium salt by reaction with a formyl (C1) unit.^{3c,6} Nevertheless, this approach is practical only for a limited class of large ring systems. A different protocol, starting from a 1,3-diazaallyl anion fragment, was developed by Bertrand and co-workers.⁷ The ring closure in this approach is enabled by a dielectrophile such as a dibromoalkane. A drawback of this methodology is the requirement for moisture-free conditions, which are necessary because of the use of strong organolithium bases for the anion formation. A revised protocol by Fallis and Cavell circumvents these inert conditions by using potassium carbonate as base,⁸ but the methodology is still limited to certain substituents for the formation of unsymmetrically substituted expanded ring NHCs. The formation of NHCmetal complexes with expanded ring systems either by ligand transfers from silver(I) complexes to other metals 9^{a-c} or by deprotonation of amidinium salts^{9d} is still a challenge in that field of research.

An alternative approach toward NHC complexes is the template synthesis of metal-coordinated isonitriles with suitable amines as nucleophiles. Following this route, cyclic carbene complexes can be obtained either by suitable leaving groups that are attached to an intermoleculary offered nucleophile¹⁰ or by the use of functionalized isonitriles that can undergo ring closure in an intramolecular fashion.¹¹

Attracted by the simplicity of this strategy (especially for the synthesis of unsymmetrically substituted NHC complexes), we joined this field and have published the straightforward synthesis of five-membered saturated NHC-,¹² unsaturated NHC-,¹³ and N-heterocyclic oxo-carbene (NHOC)-metal complexes.¹⁴ Unusual (with respect to the connectivity, not with respect to the electronic structure) saturated NHC-metal complexes could also be obtained following a related strategy.¹⁵

Reports on the use of metal-coordinated isonitriles for the synthesis of six-membered NHC complexes are rare and yet limited to Pt^{16} and Pd^{17} complexes.

Herein we report our efforts to evaluate the utilization of the template strategy for the synthesis of six-membered gold carbene complexes by the isonitrile route. By variation of the electrophilic functionality attached to the amine building block, various classes of six-membered gold NHC complexes including completely new types of ligands were accessible.

2. RESULTS AND DISCUSSION

We first focused on the synthesis of six-membered saturated NHC gold chlorides. The 3-chloropropylamine hydrochlorides needed as a 3C/1N building block for the saturated carbene backbones were synthesized via a simple two-step procedure starting from commercially available 3-bromopropanol (1) (Table 1). After substitution of the bromine under elevated temperature, the resulting amino alcohols 3 were directly transformed to the corresponding chloro compounds without further purification. The final products were obtained as hydrochlorides (4), which were purified via crystallization from

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Table 1. Synthesis of the Amine Hydrochlorides 4

НО	`Br + H ₂ N ^{, R} b	$\xrightarrow{\Delta} HO N H^{R}$	$\xrightarrow{\text{SOCI}_2} \text{CI} \xrightarrow{\bigoplus} \text{R} \xrightarrow{\bigoplus}_{H_2} \text{R}$		
1	2	3	4		
entry		amine 2/amino alcohol 3	4 [yield (%)] ^{<i>a</i>}		
1		cyclohexylamine	4a (59)		
2		cyclooctylamine	4b (76)		
3		cyclododecylamine	$4c (89)^{5b}$		
4		cyclopentadecylamine	4d (77)		
5		2-(2-hydroxyethyl)piperidine ^b	4e (89)		

^aReaction conditions: 2 M solution of amine in benzonitrile; 1.25 equiv 3-bromopropan-1-ol, 12 h, 95 °C. After workup redissolved in DCM and addition of 3 equiv SOCl₂/reflux (yield over two steps). ^bStarting from commercially available amino alcohol.





^aReaction conditions: 0.1 M solution of isonitrile–gold(I) precursor in DCM, 1–2 equiv amine, 5 equiv NEt₃, rt, 1–3 d.

ethanol/petroleum ether. This two-step protocol led to high overall yields irrespective if open chained (entries 1-4) or cyclic secondary amines (entry 5) were applied.

With the 3C/1N building blocks in hand, we subjected them to gold isonitrile complexes **5**, which can simply be obtained from tetrahydrothiophene gold(I) chloride¹⁸ or dimethylsulfide gold(I) chloride by a ligand exchange reaction.¹⁹ In analogy to our recently published procedure for five-membered NHC complexes from metal-bound isonitriles,^{12,13} the reactions were performed in the presence of triethylamine in dichloromethane at room temperature. The results of the complex syntheses are summarized in Table 2. To our delight, our strategy toward the six-membered carbene complexes turned out to be highly versatile. All of the applied isonitriles precursors delivered good to excellent yields of the corresponding complexes (**6a–g**) and were obtained with all of the applied nucleophiles. No strong effect of the substitution pattern at the arene systems was visible, and besides the isonitriles with a biaryl substituent (**6a**, **6b**), an electron-withdrawing *ortho*-CF₃ group (**6c**) or the sterically demanding Dipp-isonitrile (**6d**–**g**) could be converted in high efficiency as well. A series with differently sized cyclic amines in combination with the same isonitrile precursor showed no effect of the ring size on the reaction yields (**6d**–**f**). The reaction with cyclic amino precursor **4e** delivered the bicyclic annelated six-membered carbene complex **6g** in good yield, too. For compound **6f** crystals suitable for X-ray crystal structure analysis could be obtained. The solid-state molecular structure is depicted in Figure 1.²⁰

A comparison of some key structural parameters of $6f^{20}$ with its five-membered unsaturated $(7)^{13}$ and saturated $(8)^{20}$ homologues is depicted in Table 3. The most significant difference between the different carbene classes is the angle between the two nitrogen atoms and the central carbene carbon. The smallest angle of 104.5° is observed for the



unsaturated five-membered carbene that possesses significant aromatic character. Shifting to its saturated derivative leads to a widening of the angle of about 4.9° . Not unexpectedly, the additional methylene unit in the six-membered carbene backbone induced a further widening of 9.6° compared to carbene complex 8. The differences in other structural parameters are less pronounced. While the unsaturated fivemembered system shows the shortest Au-carbene distance (197.4 pm), this distance is more or less the same for the other two carbene classes (199.2 and 199.8 pm). No significant differences are obtained for the distances of the adjacent nitrogen atoms to the central carbene atom.

Amines with additional functional groups in the tether were suitable substrates as well. This was demonstrated by the reaction of various aromatic isonitrile precursors with hydroxyl-functionalized amine 4f (Scheme 1).²¹ All of the corresponding carbene complexes 6h-j bearing a β -hydroxy moiety in the carbene backbone could be isolated in good yields. The incorporation of the hydroxyl functionality in the carbene

backbone is noteworthy, as it delivers the possibility for further derivatizations.

As we have already reported, palladium bis-isonitrile precursors **9** are also suitable substrates for the synthesis of six-membered NHC complexes.^{5b} In addition to the presented results, we were curious if cyclic amine **4e** as nucleophile would enable an entry toward annelated six-membered Pd-NHCs as well. As shown in Scheme 2, like in the case of the gold precursor, bicyclic NHC **10** could be obtained in high yield. In complete agreement with our previous findings, only one of the two isonitrile ligands reacted, while the other is preserved in the product. The structure of the obtained complex **10** could be verified by the results of an X-ray crystal structure investigation, too (Figure 2).

Inspired by these results on the synthesis of saturated sixmembered NHC complexes, we wondered whether our recently reported strategies on the isonitrile-based synthesis of five-membered saturated NHC complexes¹³ and the synthesis of five-membered NHOC complexes¹⁴ could be expanded toward the synthesis of their corresponding sixmembered-ring homologues, too.

First we focused on the synthesis of six-membered NHOC complexes, a class of carbene complexes that was only once mentioned in the literature.^{22,23} In analogy to our previous reports, an ester containing C3/N1 building block **11a** was used as a nucleophile in combination with the Dipp-Au isonitrile precursor **5f** (Scheme 3). Indeed a clean reaction took place, but unfortunately only the open-chain NAC²⁴ (nitrogen acyclic carbene) complex **12** was formed, and even after prolonged reaction times of 14 days or with different postreaction treatments we were not able to convert **12** into the desired cyclic carbene **13a**.

An explanation for this lack of reactivity was obtained by quantum chemical calculations. The thermochemistry of the intramolecular ring closure of the NAC complexes toward the cyclic NHOC complexes was calculated on model systems for the six-membered complexes as well as for its five-membered counterparts. The results summarized in Table 4 indicate that for both systems the formation of the NHOC complexes is an

Table 3. Comparison of Key Structural Parameters of Complexes 6f, 7, and 8









Figure 2. Solid-state molecular structure of carbene complex 10.

endothermic process. However, the observed trend is more pronounced in the case of the six-membered system, and in the case of the five-membered system the endothermicity can be overcompensated by the positive reaction entropy, leading to an overall exergonic process. In the case of the six-membered system this compensation leads only to a slightly negative free reaction enthalpy (calculations were performed for 25 °C (298.15 K) and 1 atm). These results combined with the increased steric limitations in the experimentally applied

Table 4. Thermochemistry of Model Systems for theTransformation of 12 to 13



^aB3LYP-d3, cc-pVTZ. ^bM06, cc-pVTZ. ^cElectronic energy. ^dSum of electronic and thermal enthalpies. ^eSum of electronic and thermal free energies. ^fGP = gas phase. ^gIEFPCM calculation. ^hSMD calculation. ⁱAll energies given in kcal/mol.

systems can explain the observed lack of reactivity of NAC complex **12**.

As a consequence, we then focused on the synthesis of, to the best of our knowledge, yet unknown six-membered unfunctionalized unsaturated NHC-gold chlorides 17 (Scheme 4).²⁵ The synthesis of the starting materials and applied reaction conditions were adopted from our recently reported synthesis of unsaturated five-membered NHC-gold chlorides based on the isonitrile strategy.¹³ To our surprise, instead of the expected unsaturated complexes 17, acidic treatment of NAC complexes 15 delivered an entirely new class of NHC complexes bearing a hemiaminal functionality attached to the N–C–N unit of the carbene. Most unfortunately the initial yields of this process were low (<10%).

After optimization of the reaction conditions, an increased yield was obtained by using technical grade dichloromethane as solvent (see Table 5). This led us to the assumption that the hydroxy functionality of complexes **16** was derived from traces of water present in the reaction mixture.

Under the optimized conditions four derivates of complexes 16 could be obtained in good to moderate yields (Table 5).

Scheme 3. Attempted Synthesis of Six-Membered NHOC Complex 13a



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Scheme 4. Unexpected Synthesis of Six-Membered Hemiaminal NHC-Gold(I) Chlorides 16



Table 5. Overview of the Synthesized Hydroxy-Functionalized Six-Membered NHC-Au(I) Chlorides



Furthermore, it was possible to obtain crystals of compound **16c** that were suitable for X-ray analysis.²⁰ The corresponding solid-state molecular structure is shown in Figure 3 together with selected bond lengths and angles. A comparison of the obtained structural data of **16c** with those of compound **6f** without the hydroxy functionality reveals only slight deviations in the measured structural parameters ($\Delta d < 1.50 \text{ pm}$, $\Delta \Phi <$



Figure 3. Molecular structure of 16c in the solid state; d_{CS-OS} : 142.8(7) pm, d_{N6-CS} : 147.0(9) pm, d_{N6-C1} : 135.4(3) pm, d_{N2-C1} : 133.1(3) pm, d_{C1-Au1} : 199.7(2) pm, $\Phi_{N6-C1-N2}$: 118.51(19)°.

 0.45°), which implies a limited influence of the hydroxy functionality on the carbene moiety of the six-membered NHC complexes.

With complexes 16 in hand, we were curious if it was possible to oxidize the hydroxyl group in these compounds and thus bypass the above-discussed thermodynamic problems for the synthesis of six-membered NHOC complexes.

16d as a representative example could be oxidized by using Dess-Martin periodinane, and the corresponding six-membered NHOC complex 18 could be isolated in 58% yield (Scheme 5).²⁶ The assignment of this new type of carbene ligand could be verified by its solid-state molecular structure (see Figure 4).²⁰







Figure 4. Molecular structure of **18** in the solid state; d_{OS-CS} : 122.1(4) pm, d_{CS-N6} : 140.6(4)pm, d_{N6-C1} : 138.1(4) pm, d_{C1-N2} : 132.3(4) pm, d_{C1-A1} : 199.3(3), $\Phi_{N6-C1-N2}$: 117.0(3)°.

A comparison of the structural parameters of 16c and 18 reveals that by the oxidation the C–O bond length in 18 is significantly reduced by 20.7 pm to 122.1 pm (a bond length slightly shorter than the typical C–O bond length observed in carboxamides). The N6–C5 bond with a bond length of 140.6 pm is elongated compared to that of typical carboxamides. The changes in the bond lengths of the N–C–N unit are less pronounced. The bond length of the N6–C1 bond is elongated

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by 2.7 pm, whereas the bond length of the C1–N2 bond is slightly contracted. Similar to the delocalization of the nitrogen lone-pair in carboxamides, the carbonyl group next to the N– C–N unit reduces the electron-donating abilities of N6. As a consequence, this effect is then compensated by a slightly stronger donation of N2.

After having accomplished the synthesis of a six-membered NHOC complex, we refocused on the realization of the synthesis of six-membered unsaturated gold chlorides. To get an insight into the synthetic difficulties, we again conducted quantum chemical calculations on the thermochemistry for the formation of complex 17 and compared the results to those of the five-membered system. The obtained results are presented in Table 6. They predict that the formation of both the

Table 6. Thermochemistry of Model Systems for theFormation of 17 Starting from 15

	() n >) n = N		Ø	∩ ()) n N → N Au Cl 17	+ 2	HOMn
B3LYP-d3 ^a ,	i GP $_{n=0}^{f}$	$\operatorname{solv}_{n=0}^{\mathbf{g}}$	$\operatorname{solv}_{n=0}^{h}$	$\operatorname{GP}_{n=1}^{f}$	$\operatorname{solv}_{n=1}^{g}$	$\operatorname{solv}_{n=1}^{h}$
$\Delta_{\rm R} E^{c}$	5.81	2.06	1.82	21.6	19.7	19.3
$\Delta_{\mathrm{R}} H^{d}$	2.02	-2.34	-2.17	17.5	15.4	15.0
$\Delta_{\rm R} G^{e}$	-21.8	-24.2	-26.0	-6.15	-8.53	-8.18
M06 ^{<i>b</i>,<i>i</i>}	$\operatorname{GP}_{n=0}^{f}$	$\operatorname{solv}_{n=0}^{g}$	$\operatorname{solv}_{n=0}^{h}$	$\operatorname{GP}_{n=1}^{f}$	$\operatorname{solv}_{n=1}^{g}$	$solv_{n=1}^{h}$
$\Delta_{\rm R} E^{c}$	11.1	7.22	6.83	25.9	23.6	23.5
$\Delta_{\mathrm{R}} H^d$	7.48	3.00	3.26	21.9	19.5	19.0
$\Delta_{\mathrm{R}}G^{e}$	-16.8	-20.3	-20.4	-2.47	-4.55	-5.53
						-

^{*a*}B3LYP-d3, cc-pVTZ. ^{*b*}M06, cc-pVTZ. ^{*c*}Electronic energy. ^{*d*}Sum of electronic and thermal enthalpies. ^{*e*}Sum of electronic and thermal free energies. ^{*f*}GP = gas phase. ^{*g*}IEFPCM calculation. ^{*h*}SMD calculation. ^{*i*}All energies given in kcal/mol.

unsaturated six- and five-membered carbene gold chlorides are exergonic processes. However, the trend is more pronounced in the case of the five-membered system.

Since these calculations delivered no explanation for the obtained experimental results, we included the formation of the possible hemiaminal ether intermediates **19** (which can be formed upon elimination of one equivalent of alcohol) into our thermochemical considerations.

The thermochemistry of these species relative to acetal 15 (Table 7) reveals that for both systems a similar negative free energy is obtained. However, while the final elimination toward the desired unsaturated product for the unsaturated five-membered system is exergonic as well, the corresponding process for the six-membered system is endergonic (see Table 8). Nevertheless, instead of the hemiaminal ether complexes 19 the hemiaminal complexes 16 are experimentally observed.

We postulate that these species are formed by the attack of external water (present in the reaction solvent) at an intermediate iminium species 20 that should easily be formed under acidic conditions. The overall preference of 16 over 20 results from water being present in excess compared to the ethanol concentration (Scheme 6).

To underline this hypothesis, we repeated the synthesis of 16 under as strict exclusion of water as experimentally possible with these reagents (Scheme 7).





^{*a*}B3LYP-d3, cc-pVTZ. ^{*b*}M06, cc-pVTZ. ^{*c*}Electronic energy. ^{*d*}Sum of electronic and thermal enthalpies. ^{*e*}Sum of electronic and thermal free energies. ^{*f*}GP = gas phase. ^{*g*}IEFPCM calculation. ^{*h*}SMD calculation. ^{*i*}All energies given in kcal/mol.





^aB3LYP-d3, cc-pVTZ. ^bM06, cc-pVTZ. ^celectronic energy. ^dSum of electronic and thermal Enthalpies. ^eSum of electronic and thermal Free Energies. ^fGP = gas phase. ^gIEFPCM calculation. ^hSMD calculation. ⁱAll energies given in kcal/mol.

Scheme 6. Mechanistic Hypothesis for the Formation of Products 16



Scheme 7. Synthesis of 19a under Exclusion of Water and Conversion of 19a to 16d



Indeed, under these conditions we were able to obtain the predicted hemiaminal ether complex **19a** together with the corresponding hemiaminal complex **16d**, which can be attributed to unavoidable traces of water that stem from the HCl in dioxane solution. A full spectroscopic characterization was possible for the hemiaminal ether species. The control experiment with the isolated hemiaminal ether complex **19a** in the presence of water cleanly delivered the hemiaminal complex **16d**, which further confirms our mechanistic proposal.

Our quantum chemical calculations and the obtained experimental results suggest that complexes like 19 and 16 are the thermodynamic sink of the investigated systems. In order to finally obtain the desired six-membered unsaturated gold chloride, we envisioned performing the reaction under strictly water-free conditions. In addition by removal of the lowboiling ethanol under reduced pressure, simple elimination of a proton from iminium intermediate 20 or direct elimination of ethanol from hemiaminal ether complex 19 should deliver the target NHC complex containing an enamine-like substructure. In order to realize this strategy, the higher boiling toluene was needed as the solvent. Furthermore, it was necessary to use a nonvolatile and completely water-free acid, for which the acidic anion exchanger Amberlyst 15 was selected. Indeed these reaction conditions in the presence of a reduced pressure (200 mbar) enabled us to isolate three differently substituted sixmembered unsaturated NHC-gold chlorides 17 in good to moderate yields (Table 9).

Table 9. Overview of the Synthesized Unsaturated Six-Membered NHC-Au(I) Chlorides 17



Compound 17b gave crystals suitable for an X-ray singlecrystal structure analysis. The resulting molecular structure in the solid state of one of two independent molecules present in the unit cell is depicted in Figure 5 together with selected bond lengths and angles.



Figure 5. Molecular structure of 17b in the solid state; d_{C5-N6} : 141.7(6) pm/142.6(6) pm, d_{N6-C1} : 134.6(7) pm/135.2(7) pm, d_{C1-N2} : 133.4(7) pm/132.7(6), d_{C1-Au1} : 199.0(5) pm/200.3(5) pm, d_{C4-C5} : 130.6(8) pm/130.5(8) pm, $\Phi_{N6-C1-N2}$: 117.8(4)°/118.0(5)°.

The analysis of the structural parameters of the N–C–N unit of 17b revealed no striking peculiarities compared to the saturated derivatives; therefore it can be assumed that the influence of the double bond on this unit is limited. Only the rather short bond length of the C4–C5 bond is noteworthy.

The reactivity of these new complexes was investigated, too. To complete our mechanistic picture, we used complex 17a and exposed it to the reaction conditions that usually delivered the hemiaminal complexes. Indeed 17a was cleanly converted to the hydrolyzed complex 16a (Scheme 8). Furthermore, it is important to note that, even against steric limitations, only 16a was observed and no formation of a species of type 21 could be detected. Thus, we assume that the reactivity of the double bonds is comparable to the usual reactivity of an enamine moiety. Further studies on the reactivity that can be explained by the lack of aromatic stabilization compared to the five-membered unsaturated complexes are currently ongoing in our group.

4. CONCLUSION

In summary we have shown that our previously reported isonitrile-based synthesis of unsymmetrically substituted six-

Scheme 8. Conversion of 17a to 16a



membered saturated NHC-Pd(II) complexes can be transferred to the synthesis of analogous Au(I) complexes. The use of prefunctionalized nucleophiles even enabled the synthesis of hydroxy-functionalized carbene backbones with great potential for further derivatization. During our search for the synthesis of so far rarely described six-membered NHOC complexes as well as six-membered unsaturated NHC-Au(I) chlorides we discovered a new class of NHC-Au(I) complexes bearing a hemiaminal functionality within the backbone of the NHC ligand. By careful quantum chemical studies we were able to explore the thermochemistry of these species and deduced a synthetic procedure for the synthesis of the six-membered NHOC-Au(I) chlorides as well as the six-membered unsaturated complexes. In contrast to the C-C double bond of the related five-membered systems, the C-C double bond of the six-membered homologues bears significant reactivity, and further studies exploring the potential for postmodifications of these species are under way.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.6b00023.

 1H and $^{13}C\{^1H\}$ NMR, HRMS, and IR data of all new compounds (PDF)

Computational details (PDF)

Crystallographic data (CIF)

Coordinate files of the model structures determined by quantum chemistry (ZIP)

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Notes

The authors declare no competing financial interest.

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