

Carbenes

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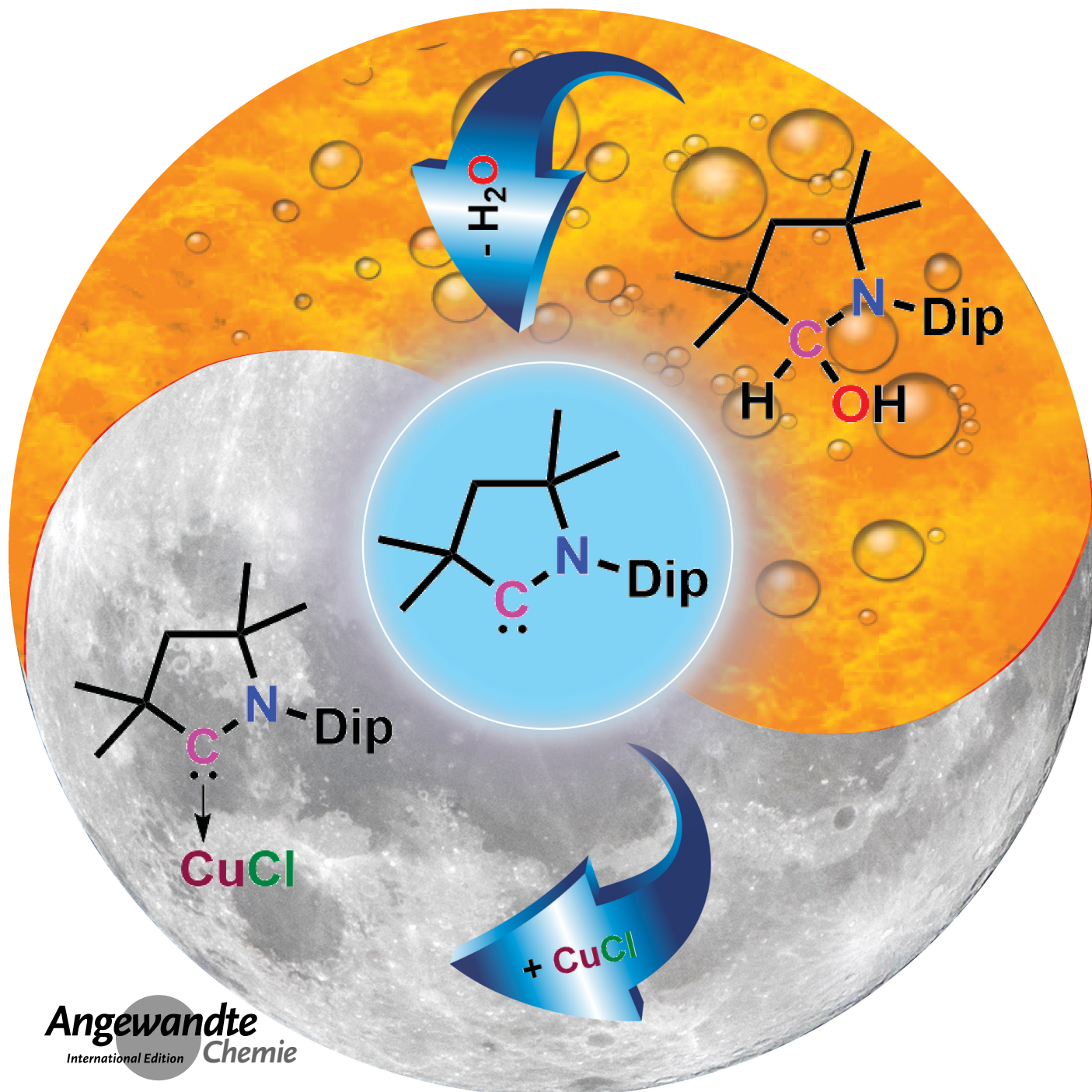
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# Realizing 1,1-Dehydration of Secondary Alcohols to Carbenes: Pyrrolidin-2-ols as a Source of Cyclic (Alkyl)(Amino)Carbenes

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Dedicated to all TIFR Hyderabad COVID-19 frontline helpers.



**Abstract:** Herein we report secondary pyrrolidin-2-ols as a source of cyclic (alkyl)(amino)carbenes (CAAC) for the synthesis of CAAC-Cu<sup>I</sup>-complexes and cyclic thiones when reacted with Cu<sup>I</sup>-salts and elemental sulfur, respectively, under reductive elimination of water from the carbon(IV)-center. This result demonstrates a convenient and facile access to CAAC-based Cu<sup>I</sup>-salts, which are well known catalysts for different organic transformations. It further establishes secondary alcohols to be a viable source of carbenes—realizing after 185 years Dumas' dream who tried to prepare *the* parent carbene (CH<sub>2</sub>) by 1,1-dehydration of methanol. Addressed is also the reactivity of water towards CAACs, which proceeds through an oxidative addition of the O–H bond to the carbon(II)-center. This emphasizes the ability of carbon-compounds to mimic the reactivity of transition-metal complexes: reversible oxidative addition and reductive elimination of the O–H bond to/from the C(II)/C(IV)-centre.

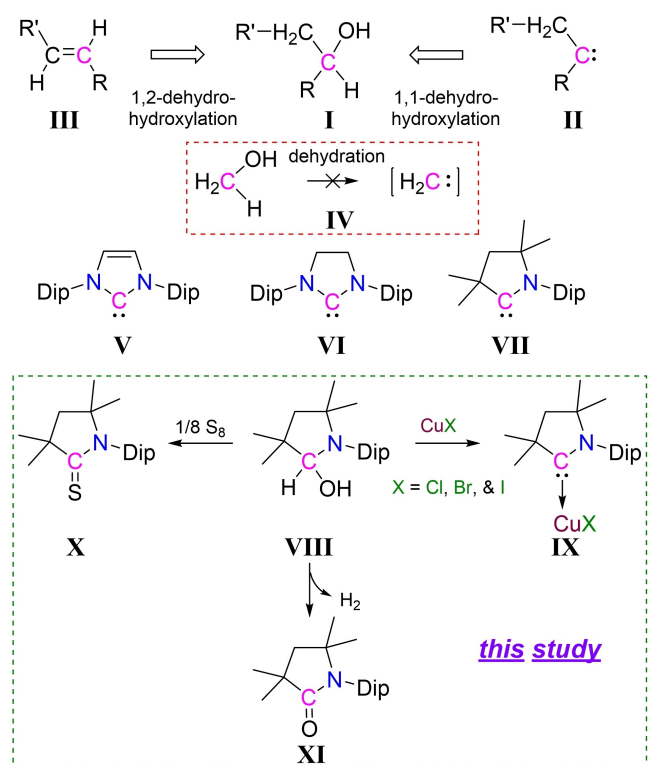
## Introduction

Retrosynthetically, a dehydration of primary and secondary alcohols **I** can be envisioned as leading either to typically reactive carbenes **II** (1,1-dehydrohydroxylation) or to more stable alkenes **III** (1,2-dehydrohydroxylation) (Scheme 1). Along this line, in 1835 Dumas attempted to synthesize *the* parent carbene (:CH<sub>2</sub>) by a 1,1-dehydration of methanol **IV**.<sup>[1]</sup> Subsequently, after the isolation of (phosphino)(silyl)-carbenes by Bertrand et al. in 1989<sup>[2]</sup> and *N*-heterocyclic carbenes by Arduengo et al. in 1991,<sup>[3]</sup> various kinds of carbenes such as imidazole-2-ylidene based *N*-heterocyclic carbene **V**,<sup>[4]</sup> imidazolidine-2-ylidene based *N*-heterocyclic carbene **VI**,<sup>[5]</sup> and cyclic (alkyl)(amino)carbene (CAAC) **VII**<sup>[6]</sup> were reported based on different precursors and

different synthetic routes (Scheme 1). Such species have become ubiquitous in different research areas ranging from advanced synthetic chemistry to materials.<sup>[7]</sup> Generally, carbenes (including examples given above) are mostly sensitive and decompose in the presence of air and moisture.<sup>[8]</sup> The first air stable carbene was reported in 1997 by Arduengo et al.<sup>[9]</sup> The synthesis of carbene-metal complexes under wet/moist conditions was established.<sup>[10]</sup> Similarly, it is known that free carbenes can form in situ in the course of organocatalytic reactions even without operating under strictly inert conditions.<sup>[11]</sup> Further reports have emphasized their versatility and effectiveness in various organocatalytic transformations.<sup>[12]</sup> Notably, there are no reports available to date for the formation of carbenes from their alcohol precursors.

Herein we report pyrrolidin-2-ol **VIII**, i.e. a secondary alcohol, used as the direct source of cyclic (alkyl)(amino)carbene (CAAC)<sup>[13]</sup> in the synthesis of CAAC-copper(I)-complexes **IX** and of cyclic thione **X** (Scheme 1). The reactions proceed through thermal 1,1-dehydrations and demonstrate, thereby, the successful formation of carbenes from alcohols via the release of water.

The synthesis of CAAC-copper(I)-complexes was addressed first. CAAC-metal complexes **IX** derived from “hydrated CAAC” pyrrolidin-2-ol **VIII** provide a convenient access to various catalytic properties,<sup>[14]</sup> functionalization to other targeted Cu<sup>I</sup>-complexes,<sup>[15]</sup> and transmetalation to other transition metal complexes.<sup>[16]</sup> Previously, a CAAC-CuCl species was also synthesized by the reaction of a corresponding conjugate acid of CAAC and Cu<sub>2</sub>O, in which



**Scheme 1.** Chemical structures of I–XI.

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water is eliminated in the course of the reaction.<sup>[14b]</sup> The more typical approach is the synthesis with free CAAC or in situ generated CAAC and CuCl.<sup>[14a]</sup> Since pyrrolidin-2-ol can be considered as hydrated CAAC, the reaction of a CAAC with water was investigated accordingly. It turns out that water for CAAC becomes a friend, instead of acting as foe as is commonly found for other carbenes.<sup>[8]</sup> The observed hydrated products, in fact, are even utilizable as an immediate source of CAACs via back reaction. Moreover, it was discovered that simple heating of **VIII** without any catalyst or in presence of PdCl<sub>2</sub> results in a dehydrogenation yielding the CAAC-based ketone **XI** (Scheme 1). Furthermore, to expand the substrate scope, other secondary cyclic-amino alcohols were considered and established as sources of carbenes by thermal 1,1-dehydration.

## Results and Discussion

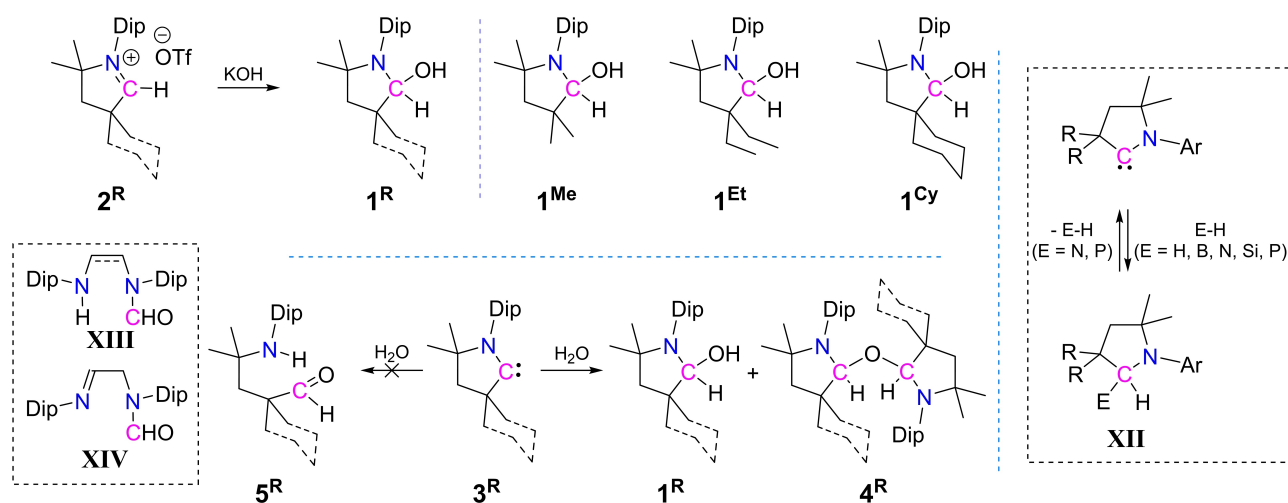
In this study, three pyrrolidin-2-ols **1<sup>Me</sup>/1<sup>Et</sup>/1<sup>Cy</sup>** were investigated as a source of cyclic (alkyl)(amino)carbenes (CAACs) via 1,1-dehydration. **1<sup>Me</sup>/1<sup>Et</sup>/1<sup>Cy</sup>** were obtained from the alkaline hydrolysis (aqueous KOH solution) of pyrrolinium cations **2<sup>Me</sup>/2<sup>Et</sup>/2<sup>Cy</sup>** in very good yields (Scheme 2).<sup>[18]</sup> The exclusive formation of pyrrolidin-2-ols **1<sup>Me</sup>/1<sup>Et</sup>/1<sup>Cy</sup>** indicates the aqueous KOH hydrolysis reaction to proceed through hydroxide addition to the 2-*H*-pyrrolinium cations **2<sup>Me</sup>/2<sup>Et</sup>/2<sup>Cy</sup>**, without the formation of free CAACs as in a pathway under deprotonation (see below). <sup>1</sup>H NMR spectra confirmed the formation of CAAC-based alcohols **1<sup>Me</sup>/1<sup>Et</sup>/1<sup>Cy</sup>** with the presence of two doublets at  $\delta=4.84/4.89/4.75$  and  $1.56/1.55/1.51$  ppm, respectively, for the *N*-C-*H* and O-*H* resonances with coupling constants of  $^3J_{(H, H)}=6.9/6.9/6.6$  Hz. Compounds **1<sup>Me</sup>/1<sup>Et</sup>/1<sup>Cy</sup>** can be considered as hydrated products of CAACs **3<sup>Me</sup>/3<sup>Et</sup>/3<sup>Cy</sup>**. Notably, reactions of CAACs with water or with any alcohol are unreported as of yet.<sup>[19]</sup> Reactions of CAACs are known, though, which involve different X-*H* bonds (X=H, B, N, Si, P)<sup>[20]</sup> **XII** or

the B-C bond<sup>[21]</sup> in a variety of molecules which proceeded through (reversible) oxidative additions<sup>[22]</sup> to the carbon(II)-center. In general, the reactions of water versus related compounds are strikingly different.<sup>[23]</sup> The classical example is water vs. ammonia reactivity towards metallic sodium. In the first case, this leads to the formation of NaOH along the evolution of dihydrogen gas, whereas in the latter case, ammonia acts as a solvent facilitating the transfer of electrons from metallic sodium to the solution or a substrate; this results in many modular chemical transformations such as the Birch reduction.<sup>[24]</sup>

Consequently, we have reacted CAACs **3<sup>Me</sup>/3<sup>Et</sup>/3<sup>Cy</sup>** with equivalent amounts of degassed water to test their respective reactivity (Scheme 2).<sup>[18]</sup> The <sup>1</sup>H NMR spectra of the crude reaction mixtures support the formation of alcohols **1<sup>Me</sup>/1<sup>Et</sup>/1<sup>Cy</sup>** and ethers **4<sup>Me</sup>/4<sup>Et</sup>/4<sup>Cy</sup>** as hydrated CAACs, while the later were the major products. Compounds **4<sup>Me</sup>/4<sup>Et</sup>/4<sup>Cy</sup>** can be described as the product of a double oxidative addition of both water O-*H* bonds onto the two carbon(II)-centers of two CAAC molecules. Such type of double O-*H* bond activation of water was previously reported for silylenes, i.e. the heavier analogues of carbenes.<sup>[26]</sup>

In order to obtain exclusively **1<sup>Me</sup>/1<sup>Et</sup>/1<sup>Cy</sup>** from the activation of only one O-*H* bond of water, we reacted **3<sup>Me</sup>/3<sup>Et</sup>/3<sup>Cy</sup>** with an excess (10 equiv) of water. However, in that case also two products **1<sup>Me</sup>/1<sup>Et</sup>/1<sup>Cy</sup>** and **4<sup>Me</sup>/4<sup>Et</sup>/4<sup>Cy</sup>** were obtained; the later still being the major product as in the 1:1 reaction. Due to distinct solubilities of **1<sup>Me</sup>/1<sup>Et</sup>/1<sup>Cy</sup>** and **4<sup>Me</sup>/4<sup>Et</sup>/4<sup>Cy</sup>**, it was possible to isolate the pure compounds **4<sup>Me</sup>/4<sup>Et</sup>/4<sup>Cy</sup>** from the crude reaction mixtures. The <sup>1</sup>H NMR spectra of these CAAC-based ethers exhibit singlets at  $\delta=4.69, 4.63,$  and  $4.70$  ppm, respectively, for the C-*H* resonance.

Notably, <sup>1</sup>H NMR spectra of all crude reaction mixtures indicate the complete absence of the potential ring-opened products **5<sup>Me</sup>/5<sup>Et</sup>/5<sup>Cy</sup>**, analogues of **XIII** and **XIV** which were observed in the case of *N*-heterocyclic carbenes **V** and **VI**.<sup>[8b,d]</sup> A computational investigation at the B3LYP-D3-(BJ)/6-311G(d,p) level of theory suggests that the calculated

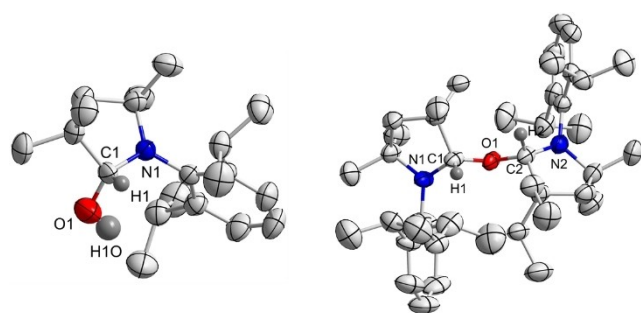


**Scheme 2.** Synthesis of **1** and reaction of **3** with H<sub>2</sub>O (Dip = 2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (Inserts: (reversible) oxidative addition to CAAC by different E-*H* bonds towards **XII** (right) and chemical structures of **XIII** and **XIV** (left – bottom)).

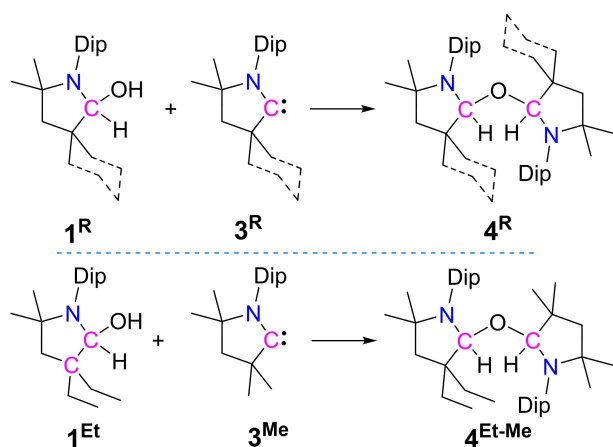
relative energy for the ring-opened product  $5^{\text{Me}}$  is higher in energy by  $9.7 \text{ kcal mol}^{-1}$  compared to that of  $1^{\text{Me}}$ . Solid-state molecular structure determinations of  $1^{\text{Me}}/1^{\text{Et}}/1^{\text{Cy}}$  confirm the presence of terminal hydroxide groups (Figure 1 and Figures S102, S103). Also the formation of  $4^{\text{Et}}$  and  $4^{\text{Cy}}$  is evidenced by solid-state molecular structure determination (Figures S104, S105).

The formation of  $4^{\text{Me}}/4^{\text{Et}}/4^{\text{Cy}}$  could generally result from a simultaneous and/or stepwise activation of both O–H bonds of water bound to the carbon(II)-centre of the CAAC. To support the stepwise pathway,  $1^{\text{Me}}/1^{\text{Et}}/1^{\text{Cy}}$  was reacted with  $3^{\text{Me}}/3^{\text{Et}}/3^{\text{Cy}}$  which led to the formation of  $4^{\text{Me}}/4^{\text{Et}}/4^{\text{Cy}}$  in a very good yield (Scheme 3). Additionally,  $1^{\text{Et}}$  was reacted with  $3^{\text{Me}}$  which gave indeed the heteroleptic ether  $4^{\text{Et-Me}}$  (Scheme 3).<sup>[18]</sup> The formation of  $4^{\text{Et-Me}}$  is evidenced by the presence of two singlets at  $\delta=4.75$  and  $4.73$  ppm in its  $^1\text{H}$  NMR spectrum. Moreover, the solid-state molecular structure of  $4^{\text{Et-Me}}$  on the basis of single crystal X-ray diffraction data unambiguously confirms its formation (Figure 1). These observations insinuate that CAACs are prone to oxidatively add the O–H bonds of alcohols in a similar manner and that this method even bears potential for the synthesis of hindered dialkyl ethers.<sup>[27]</sup>

To address the probable hydration mechanism accompanying CAAC, we considered the reaction of  $3^{\text{Me}}$  with one,



**Figure 1.** Molecular structures of  $1^{\text{Me}}$  (left) and  $4^{\text{Et-Me}}$  (right). All H atoms except for C1-H, C2-H and O1-H are omitted for clarity. Ellipsoids are drawn at the 50% probability level.

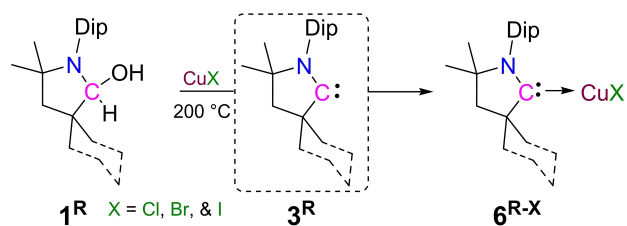


**Scheme 3.** Reactions of **1** and **3** (Dip = 2,6- $i\text{Pr}_2\text{C}_6\text{H}_3$ ).

two, and three water molecules at the B3LYP-D3(BJ)/6-311G(d,p) level of theory (Figures S112–S114).<sup>[18]</sup> In all cases we found the formation of a hydrogen-bonded structure as the initial intermediate. The next step in case of one and two water molecules is the concerted insertion of the carbenic carbon of  $3^{\text{Me}}$  into the O–H bond. Notably, for three water molecules the second step leads to the optimization of a pyrrolinium-hydroxide type structure, which could not be observed in case of one or two water molecules. The computational calculations indicate that reaction pathways are different for the hydration of CAAC with different stoichiometric amounts of water, resembling the hydrolysis of imidazole-2-ylidenes.<sup>[8a]</sup>

Compounds  $1^{\text{Me}}/1^{\text{Et}}/1^{\text{Cy}}$  are well stable in the open atmosphere and melted (M.P.:  $84^\circ\text{C}$ ,  $72^\circ\text{C}$ , and  $80^\circ\text{C}$ , respectively) without any indication of dehydration or decomposition. This was also investigated by thermogravimetric analysis (TGA). The determined onset/end point of decomposition temperatures are  $161/204$ ,  $181/219$ , and  $202/237^\circ\text{C}$  along with gradual weight losses up to 97.2, 100.0, and 100.0%, respectively, for  $1^{\text{Me}}/1^{\text{Et}}/1^{\text{Cy}}$  at a heating rate of  $10^\circ\text{C/min}$  under  $\text{N}_2$  atmosphere (Table S3 and Figure S86).<sup>[18]</sup> We were not able to observe the sudden elimination of small molecules such as  $\text{H}_2\text{O}$  in a step wise manner, not even at lower heating rates ( $1^\circ\text{C/min}$  and  $0.1^\circ\text{C/min}$ ) (Figure S87). It was then tested whether a reversion of the hydration could be enforced by reductive elimination of water from these pyrrolidin-2-ols  $1^{\text{Me}}/1^{\text{Et}}/1^{\text{Cy}}$  in presence of free-CAAC/carbene trapping reagents.<sup>[28]</sup> To address this, first the reaction of  $1^{\text{Me}}/1^{\text{Et}}/1^{\text{Cy}}$  with copper(I)-halides was studied, as the CAAC-Cu<sup>I</sup>-complexes are known for their catalytic ability in a variety of organic chemical transformations.<sup>[14]</sup> Moreover, CAAC-Cu<sup>I</sup>-halides are known for functionalizations on the Cu<sup>I</sup>-center to other CAAC-Cu<sup>I</sup>-complexes<sup>[15]</sup> and metathesis (transmetalation) reactions with other transition metal complexes.<sup>[16]</sup> The heating of 1:1 mixtures of  $1^{\text{Me}}/1^{\text{Et}}/1^{\text{Cy}}$  and Cu<sup>I</sup>-X (X = Cl, Br and I), without any solvents at  $200^\circ\text{C}$  leads to CAAC-CuX complexes  $6^{\text{R-X}}$  in fair to good yield (Scheme 4, Table 1).

In case of the  $1^{\text{Cy}}$  plus CuCl reaction, the isolated yield of  $6^{\text{Cy-Cl}}$  is with 75% as good as in the previously reported preparation using isolated CAAC  $3^{\text{Cy}}$  and CuCl.<sup>[14b,15h]</sup> Currently, we are optimizing the synthetic procedure for CAAC-Cu<sup>I</sup>X to reach excellent to quantitative yields by avoiding the formation of the conjugated acid of  $3^{\text{R}}$ . This result shows that for the synthesis of CAAC-Cu<sup>I</sup>-salts there is no need for isolated CAACs or in situ generated CAACs



**Scheme 4.** Reductive dehydration of **1<sup>R</sup>** in presence of Cu<sup>I</sup>-halides (Dip = 2,6- $i\text{Pr}_2\text{C}_6\text{H}_3$ ).

**Table 1:** Yields [%] of CAAC-Cu<sup>I</sup>-complexes and CAAC-thione.

| Compounds/Reagents    | CuCl | CuBr <sup>[a]</sup> | CuI <sup>[b]</sup> | S <sub>8</sub> |
|-----------------------|------|---------------------|--------------------|----------------|
| <b>1<sup>Me</sup></b> | 58   | –                   | –                  | 98             |
| <b>1<sup>Et</sup></b> | 53   | 48                  | 56                 | 99             |
| <b>1<sup>Cy</sup></b> | 75   | 57                  | 56                 | 98             |

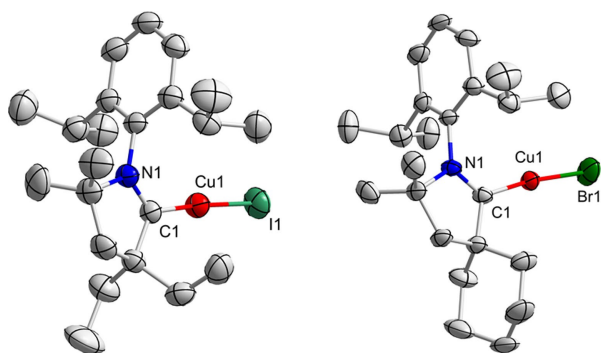
[a] The reaction of **1<sup>Me</sup>** and CuBr did not give a satisfactory yield. [b] The reaction of **1<sup>Me</sup>** and CuI did not allow isolating the desired product.

(by the deprotonation of pyrrolinium cation); the secondary alcohol pyrrolidin-2-ol can be used as a feedstock starting material instead. In the course of the reaction the ring-opened species (see below), a regioisomer of the initially formed CAAC, and pyrrolinium salts can be observed<sup>[29]</sup> as minor side products. Both of these side products can be recycled for the synthesis of pyrrolidin-2-ols **1<sup>Me</sup>/1<sup>Et</sup>/1<sup>Cy</sup>**. All CAAC-CuX complexes **6<sup>R-X</sup>** were characterized by solution state NMR spectroscopy. Moreover, we also determined the solid-state molecular structures of **6<sup>Et-I</sup>**, **6<sup>Cy-Br</sup>**, and **6<sup>Cy-I</sup>** complexes (Figure 2 and Figure S106) to unambiguously confirm their formation.

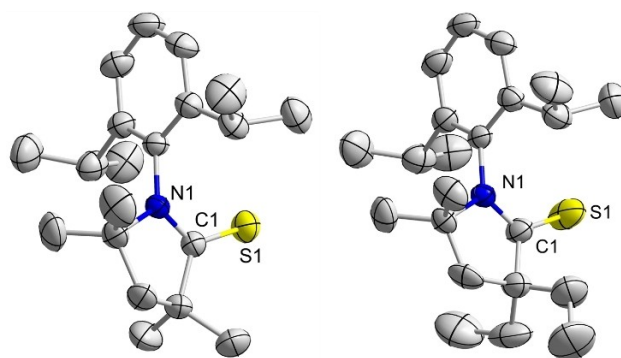
After utilizing pyrrolidin-2-ols **1<sup>Me</sup>/1<sup>Et</sup>/1<sup>Cy</sup>** as the source of CAACs for the synthesis of CAAC-Cu-halides, they were also reacted with elemental sulfur<sup>[30]</sup> without any solvent at 200 °C (Scheme 5). The <sup>1</sup>H NMR spectra of the crude reaction mixtures upon dissolving in CDCl<sub>3</sub> show the exclusive formation of thiones **7<sup>Me</sup>/7<sup>Et</sup>/7<sup>Cy</sup>**. It was possible to isolate these thiones almost quantitatively (Table 1). Carrying out these experiments in an open atmosphere (air) or under inert gas conditions (N<sub>2</sub>) did not change the reactions' outcome. Previously, **7<sup>Cy</sup>** was isolated from the correspond-

ing isolated CAAC in 58 % yield under inert atmosphere using dry and degassed solvents.<sup>[31]</sup> Formation of **7<sup>Me</sup>/7<sup>Et</sup>/7<sup>Cy</sup>** was confirmed by NMR-spectroscopy as well as solid-state molecular structure determination (Figure 3 and Figure S107).

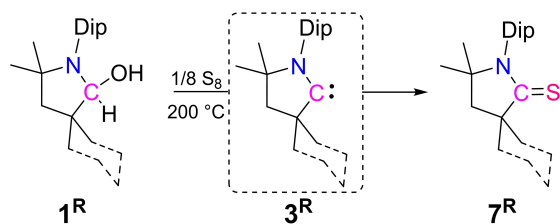
Consequently, the potential thermal dehydration of **1<sup>Me</sup>/1<sup>Et</sup>/1<sup>Cy</sup>** was studied without any free-CAAC trapping external reagents, by heating at 200 °C in open air as well as under N<sub>2</sub> atmosphere conditions (Scheme 6).<sup>[32]</sup> In all cases we observed the formation of **8<sup>Me</sup>/8<sup>Et</sup>/8<sup>Cy</sup>**, the ring-opened regioisomers of CAAC<sup>[33]</sup> and a very small amount of **9<sup>Me</sup>/9<sup>Et</sup>/9<sup>Cy</sup>**, a C–H activated regioisomer of CAAC (the Me-analogue was previously known to be thermally accessible from CAAC **3<sup>Me</sup>**<sup>[34]</sup>) along with CAAC-based ketone **10<sup>Me</sup>/10<sup>Et</sup>/10<sup>Cy</sup>** through dehydrogenation<sup>[35]</sup> (isolated yield: **10<sup>Me</sup>** = 31 %, **10<sup>Et</sup>** = 30 %, and **10<sup>Cy</sup>** = 33 %).<sup>[36]</sup> The product ratio remains the same irrespective of the atmosphere (open or inert). This can be considered indirect evidence that dehydrogenation of alcohol **1<sup>R</sup>** leads to ketone **10<sup>R</sup>**. Without direct proof, e.g. through <sup>18</sup>O labelling studies, it is impossible, though, to entirely rule out a potential reaction of in situ generated **3<sup>R</sup>** with adventitious sources of oxygen which could also lead to the ketone. The reaction of **1<sup>Me</sup>/1<sup>Et</sup>**



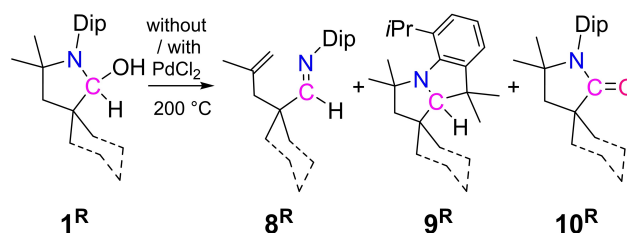
**Figure 2.** Molecular structures of **6<sup>Et-I</sup>** (left) and **6<sup>Cy-Br</sup>** (right). All H atoms are omitted for clarity. Ellipsoids are drawn at the 50% probability level.



**Figure 3.** Molecular structures of **7<sup>Me</sup>** (left) and **7<sup>Et</sup>** (right). All H atoms are omitted for clarity. Ellipsoids are drawn at the 50% probability level.



**Scheme 5.** Reductive dehydration of **1<sup>R</sup>** in presence of sulfur (Dip = 2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>).



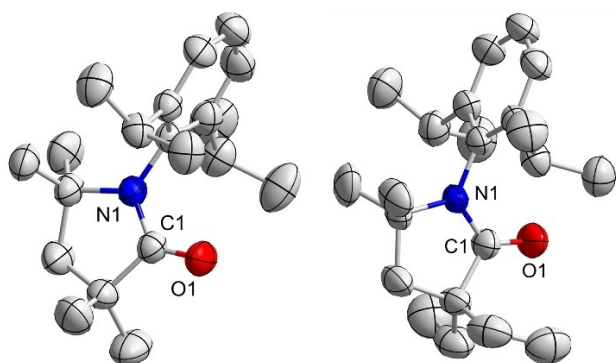
**Scheme 6.** Thermal heating of **1<sup>Me</sup>/1<sup>Et</sup>/1<sup>Cy</sup>** without and with PdCl<sub>2</sub>.

$1^{\text{Cy}}$  with  $\text{PdCl}_2$  under inert atmosphere at  $200^\circ\text{C}$ , results in the facile formation of  $10^{\text{Me}}/10^{\text{Et}}/10^{\text{Cy}}$ . In this case the yields for  $10^{\text{Me}}/10^{\text{Et}}/10^{\text{Cy}}$  are much better (isolated yield:  $10^{\text{Me}}=79\%$ ,  $10^{\text{Et}}=72\%$ , and  $10^{\text{Cy}}=62\%$ ) compared to experiments in absence of  $\text{PdCl}_2$  and otherwise similar reaction conditions. Notably, this observation contrasts those for the  $\text{CuX}$  reactions (Scheme 4) under similar conditions.  $\text{PdCl}_2$  apparently supports the dehydrogenation whereas  $\text{CuX}$  prefers coordination. This finding is along the line of well-known  $\text{Pd}^{\text{II}}$ -catalyzed aerobic oxidations of primary and secondary alcohols to aldehydes and ketones, respectively.<sup>[37]</sup> The formation of  $10^{\text{Me}}$  and  $10^{\text{Et}}$  was confirmed by molecular structure determination (Figure 4).

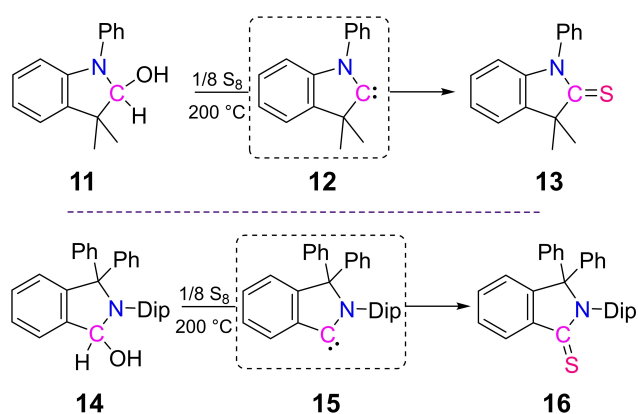
Further, to explore the ability of electronically distinct pyrrolidin-2-ols to similarly serve as source of carbenes through thermal dehydration, secondary alcohols **11** and **14** were investigated. These two pyrrolidin-2-ols could be synthesized in very good yields. The reactions of **11** and **14** with elemental sulfur, without any solvent at  $200^\circ\text{C}$  lead to thiones **13**<sup>[38]</sup> and **16**<sup>[39]</sup> respectively, in very good yields (Scheme 7). These two reactions validate pyrrolidin-2-ols **11** and **14** as sources of benz-annulated cyclic (alkyl)(amino)carbene (indol-2-ylidene) **12**<sup>[40]</sup> and cyclic (amino)-(aryl)carbene **15**<sup>[39]</sup>. In the course of the reactions no side products were observed. Also, carrying out these experiments in an open atmosphere (air) or under inert gas conditions ( $\text{N}_2$ ) did not change the reactions' outcome.

## Conclusion

In conclusion, we established the 1,1-dehydrohydroxylation (1,1-dehydration) of pyrrolidin-2-ols, the secondary alcohols, as a source of cyclic (alkyl)(amino)carbenes (CAACs) for the synthesis of CAAC- $\text{Cu}^{\text{I}}$ -complexes and cyclic thiones when reacted with  $\text{Cu}^{\text{I}}$ -salts and elemental sulfur, respectively, under the reductive elimination of water from the carbon(IV)-center. This validates alcohols as a source of carbenes—realizing after 185 years Dumas' dream who tried to prepare the parent carbene ( $:\text{CH}_2$ ) by the 1,1-dehydration of methanol.<sup>[1]</sup> In addition, the reactions of water with



**Figure 4.** Molecular structures of  $10^{\text{Me}}$  (left) and  $10^{\text{Et}}$  (right). All H atoms are omitted for clarity. Ellipsoids are drawn at the 50% probability level.



**Scheme 7.** Reductive dehydration of **11** and **14** in presence of sulfur (Dip = 2,6- $\text{Pr}_2\text{C}_6\text{H}_3$ ).

CAACs were studied and verified, which proceed through an addition of the O–H bond to the carbon(II)-center. This emphasizes the ability of carbon-compounds to mimic the reactivity of transition-metal complexes: reversible oxidative addition and reductive elimination of O–H bonds to or from  $\text{C}^{\text{II}}/\text{C}^{\text{IV}}$ -centres. Based on the results of this study, it is expected that further research efforts can develop (water-) protected CAACs<sup>[41]</sup> towards useful, broad, and convenient sources of CAACs similar to various protected precursor-derivatives of carbenes in different reactions including convenient access of various CAAC-based catalysts.<sup>[42]</sup> As a proof-of-principle other secondary amino-alcohols could be confirmed as sources of carbenes by the formation of cyclic thiones derived thereof. The secondary alcohols' potentially general efficacy as carbene sources is going to be explored further. Finally, it was proven that CAAC-based alcohols provide facile access to CAAC-based ketones through their dehydrogenation by simple heating or heating in presence of  $\text{PdCl}_2$ . All these results demonstrate pyrrolidin-2-ols/hydrated CAACs to be potential reagents for various applications from sources of carbene to possibly even a convenient source/storage form of molecular hydrogen. The results shared herein can be expected to stimulate further investigations under consideration of a broader variety of secondary alcohols as general source of carbenes for various purposes and even as direct sources of free carbenes. Currently, we continue focusing the research activity in this direction.

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### Conflict of Interest

We are working to file a patent on this work.

### Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

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