

# A Spirocyclic Parabanic Acid Masked *N*-Heterocyclic Carbene as Thermally Latent Pre-Catalyst for Polyamide 6 Synthesis and Epoxide Curing

Hagen J. Altmann, Wolfgang Frey, and Michael R. Buchmeiser\*

1,3-Dicyclohexyl-6,9-dimethyl-1,3,6,9-tetraazaspiro[4.4]non-7-ene-2,4-dione, a spirocyclic parabanic acid derivative of *N,N*-dimethylimidazole, is used as thermally latent, protected *N*-heterocyclic carbene (NHC) in polymerizing anhydride-cured epoxide resins, and azepan-2-one, respectively. The protected carbene is synthesized from 1,3-dimethylimidazolium-2-carboxylate in the presence of two equivalents of cyclohexyl isocyanate. In the synthesis of epoxide resin thermosets, this class of latent NHC allows the production of fast and fully cured materials with high crosslinking content. Fast and complete conversion is found in the anionic ring opening polymerization (AROP) of azepan-2-one ( $\epsilon$ -caprolactam, CLA) with and without additional activators.

Protected *N*-heterocyclic carbenes (NHCs) have been successfully applied as thermally latent initiators in the polymerization of various monomers like, acrylates,<sup>[1–4]</sup> cyclotetrasiloxanes,<sup>[5]</sup> epoxides,<sup>[6–8]</sup> lactams,<sup>[9–11]</sup> cyclic esters (lactones and lactide),<sup>[12–17]</sup> and in polyurethane synthesis.<sup>[18,19]</sup> Latency is mostly achieved by protecting the free carbene by coordinating it to CO<sub>2</sub>, CS<sub>2</sub>,<sup>[20,21]</sup> or to metal salts (Lewis acids), respectively. Further known protecting groups are alcohols, carbonate species, and halogenated organic compounds.<sup>[22,23]</sup> Despite the structural relationship with CO<sub>2</sub>, isocyanate- as well as double isocyanate-protected carbenes so far received less attention in the field of latent catalysis.<sup>[24]</sup>

However, the structural motif of these compounds is not unknown. Winberg and Coffman reported the synthesis of double isothiocyanate—as well as mixtures of isothiocyanate—and isocyanate-protected structures.<sup>[25]</sup> Reglitz

and Hocker reported the synthesis of double isocyanate-protected carbenes.<sup>[26]</sup> Remarkably, both groups started their synthesis from peraminoethylenes (NHC dimers) and investigated this field before free NHCs were isolated in 1991.<sup>[27]</sup> Finally, the reaction of peraminoethylenes with heterocumulenes deserves to be mentioned.<sup>[28–31]</sup>

Free carbenes (1 equivalent) and phenyl isothiocyanate (1 equivalent) were shown to form a zwitterionic covalent compound.<sup>[32,33]</sup> Inter alia, the reverse fragmentation into a carbene and an isothiocyanate has been investigated. Temperature increase releases the free carbene, which was used to trimerize phenyl isocyanate or polymerize lactic acid in situ.

In 2013, Katritzky et al. already claimed that double isothiocyanate-protected NHCs, found before, could be used as latent catalysts.<sup>[34,35]</sup> They reported on a thermally triggered, partially reversible, stepwise fragmentation with a subsequent capturing of the released carbene by addition of elemental sulfur.

Here, the synthesis of 1,3-dicyclohexyl-6,9-dimethyl-1,3,6,9-tetraazaspiro[4.4]non-7-ene-2,4-dione (5u-Me-(OCN-Cy)<sub>2</sub>), a double cyclohexyl isocyanate-protected carbene, from 1,3-dimethylimidazolium-2-carboxylate (5u-Me-CO<sub>2</sub>) and its structure are outlined and discussed together with its ability to serve as thermally latent initiator for anhydride-hardened epoxide resins and polyamide 6 synthesis.


The synthesis of 5u-Me-(OCN-Cy)<sub>2</sub> is shown in **Scheme 1**. 5u-Me-CO<sub>2</sub> is prepared in a solvent-free reaction from 1-methylimidazol and dimethyl carbonate; ensuing washing steps provide the pure carboxylate in 78% isolated yield.<sup>[36]</sup> It is then reacted with 2 equivalents of cyclohexyl isocyanate in a mixture of acetonitrile and sulfolane to yield the target compound. The non-polar cyclohexyl groups of the product allow the extraction from the sulfolane/acetonitrile reaction medium with pentane and crystallization of the target compound from this solution.

5u-Me-(OCN-Cy)<sub>2</sub> (Scheme 1) crystallizes in form of yellow crystals in the monoclinic space group P2<sub>1</sub>/c with the unit cell dimensions  $a = 1909.01(15)$  pm,  $b = 691.33(7)$  pm,  $c = 1466.25(11)$  pm,  $\alpha = 90^\circ$ ,  $\beta = 99.127(4)^\circ$ ,  $\gamma = 90^\circ$ . Noteworthy bond length and angles are outlined in the supporting information (Table S1).

In CO<sub>2</sub>-protected NHCs, the torsions angle between the carboxylate and the imidazole moiety is an important measure for the release of CO<sub>2</sub> and the formation of the free carbene. A torsion angle of 90° delivers the lowest stability and the easiest

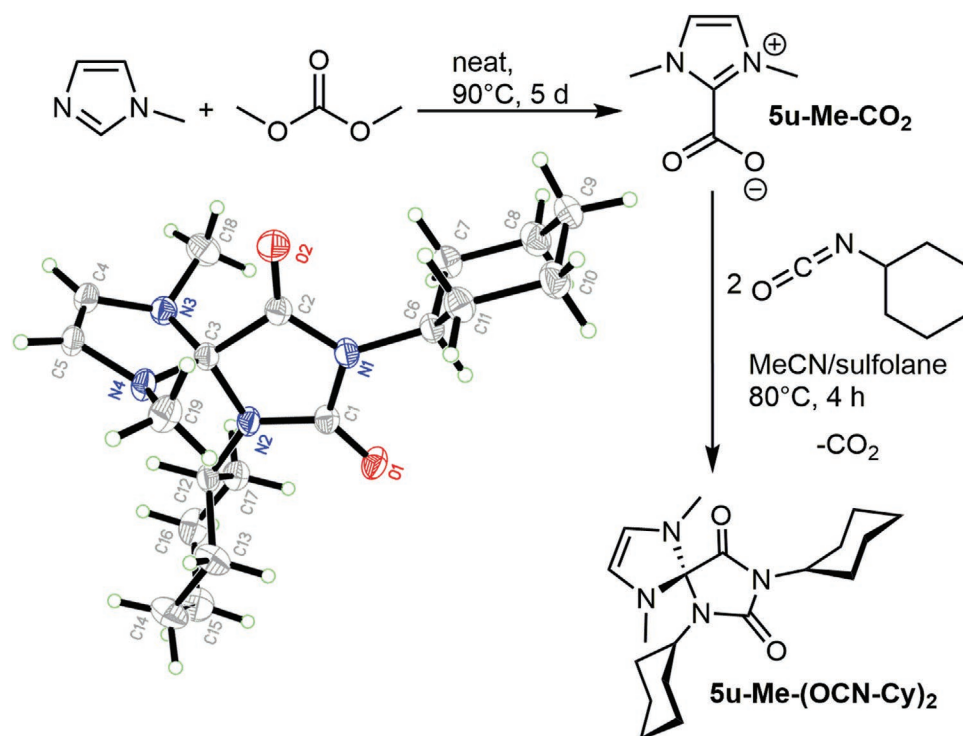
H. J. Altmann, Prof. M. R. Buchmeiser  
 Institute of Polymer Chemistry  
 University of Stuttgart  
 Pfaffenwaldring 55, Stuttgart 70569, Germany  
 E-mail: michael.buchmeiser@ipoc.uni-stuttgart.de

Dr. W. Frey  
 Institute of Organic Chemistry  
 University of Stuttgart  
 Pfaffenwaldring 55, Stuttgart 70569, Germany

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/marc.202000338>.

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**Scheme 1.** Two step synthesis and single X-ray structure of 5u-Me-(OCN-Cy)<sub>2</sub>.

release, respectively, due to a zero-overlap of the p-orbitals. 5u-Me-CO<sub>2</sub> features an angle of 29°. [22,37] By contrast, the areas formed by the two rings of the spirocycle are almost orthogonal. Such orthogonality has also been found for the benzoyl isothiocyanate adduct of 1,3-dimethylbenzimidazole. [34]

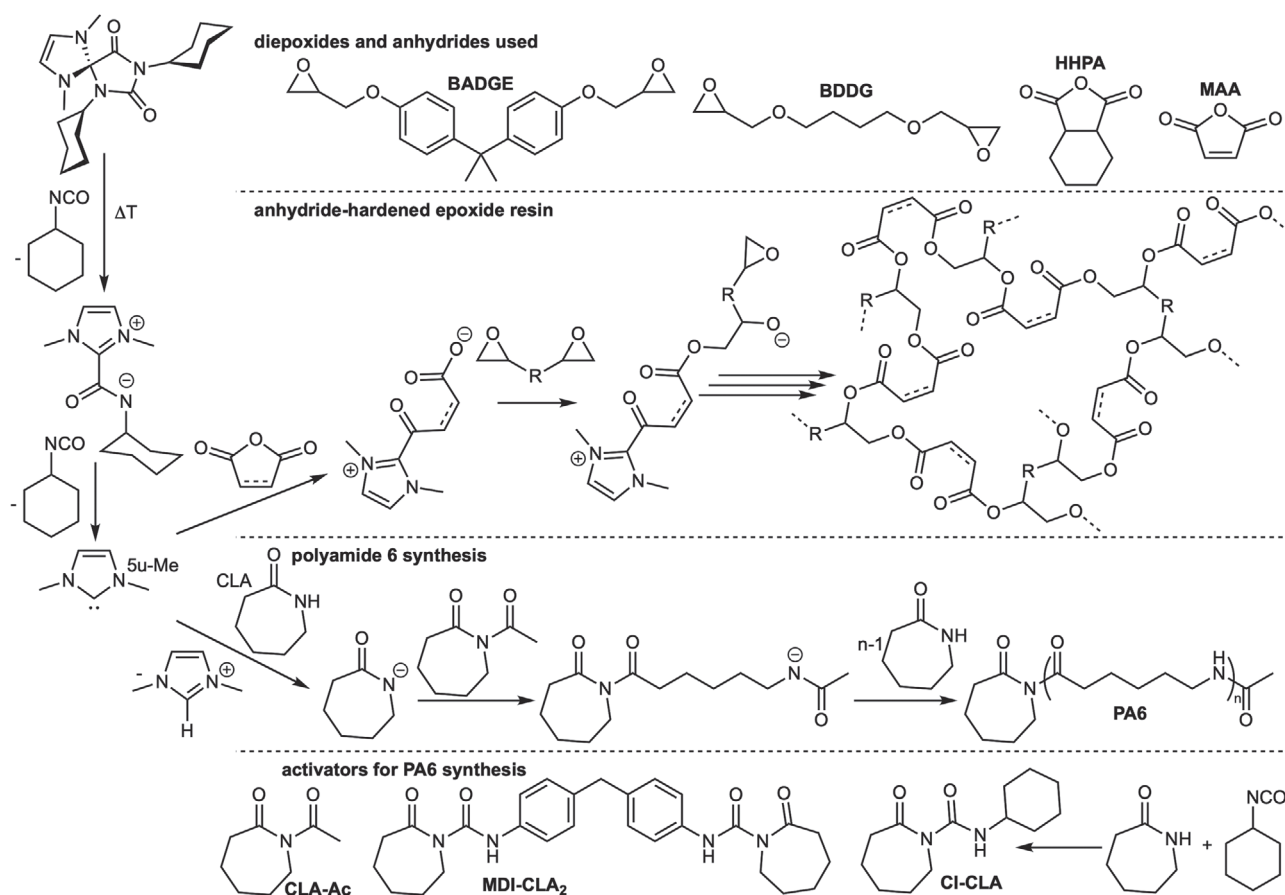
The two cyclohexyl groups and the neutral, non-betaine structure of 5u-Me-(OCN-Cy)<sub>2</sub> are the reasons for its excellent solubility even in non-polar solvents such as pentane. Beneficially, aside from water, 5u-Me-(OCN-Cy)<sub>2</sub> covers the full solubility range of 5u-Me-CO<sub>2</sub>. Whereas NMR spectra of the latter in D<sub>2</sub>O are common, [38] 5u-Me-(OCN-Cy)<sub>2</sub> decomposes under wet or aqueous conditions. Ambient conditions also lead to a slow decomposition of the spirocyclic molecule, probably to a 1,3-dimethylimidazolium derivative, as supported by two signals in the <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) at δ = 7.11 (2 H) and 3.91 ppm (6 H), respectively.

Curing of anhydride-hardened epoxide resins, initiated by latent NHCs, has been investigated before. [6–8] From these publications epoxides and anhydrides were selected and used for epoxide resin synthesis applying 5u-Me-(OCN-Cy)<sub>2</sub> (Scheme 2). Particularly hexahydrophthalic acid anhydride (HHPA) and bisphenol-A diglycidyl ether (BADGE) served as benchmark system. [39–41] Table 1 provides a comparison between 5u-Me-(OCN-Cy)<sub>2</sub> and 5u-Me-CO<sub>2</sub> as thermally latent initiator.

In hexahydrophthalic acid anhydride (HHPA) based systems, the maximum of the exothermic peak, *T*<sub>max</sub>, was 13–15 °C higher with 5u-Me-(OCN-Cy)<sub>2</sub> compared to 5u-Me-CO<sub>2</sub>. By contrast, in maleic anhydride based systems, *T*<sub>max</sub> was ≈10 °C lower with 5u-Me-(OCN-Cy)<sub>2</sub> compared to 5u-Me-CO<sub>2</sub>. Despite these subtle differences, the released energies with 5u-Me-(OCN-Cy)<sub>2</sub> were in good accordance with those found previously for

5u-Me-CO<sub>2</sub>. Further, literature known curing experiments of BADGE/HHPA applying 6-Cy-CO<sub>2</sub> (1,3-dicyclohexyl tetrahydroimidazolium-2-carboxylate) and 5u-*t*Bu-CO<sub>2</sub> (1,3-di-*tert*-butyl imidazolium-2-carboxylate) as initiator showed released energies of –296 and –337 J g<sup>–1</sup> with *T*<sub>max</sub> values of 146 and 154 °C, respectively, although the initiator loading was lower. [6] However, it is important to note that higher precursor loadings were used in order to allow for a meaningful comparison with the data presented in Table 1. In view of these data and the fact that no additional energy was released in a control heating cycle, quantitative conversion can be assumed. The fate of the released isocyanate remains somewhat speculative. It is conceivable that the monoisocyanate carbene adduct (cyclohexyl-(1,3-dimethylimidazolium-2-carbonyl)amide, Scheme 2, left), formed according to the findings of Katritzky et al., initiates the reaction by attacking an oxiranyl ring. [34,35] In accordance with the literature, the trimerization to isocyanurates and the formation of oxazolidinones seem most conceiving. [18,33,42] On a final remark it is worth mentioning that all mixtures, stored at ambient temperature and under nitrogen atmosphere, were usable as latent resins for seven days, indicating sufficient pot life.

Polyamide 6 (PA6) synthesis via anionic ring opening polymerization is initiated by strong bases. [43,44] The mechanism has been discussed elsewhere. [9,43–45] 5u-Me-(OCN-Cy)<sub>2</sub>, *N*-acetylazepan-2-one (CLA-Ac) and eventually MgCl<sub>2</sub> were dissolved in molten azepan-2-one (CLA) at 75 °C to form a homogeneous, latent one-component mixture. MgCl<sub>2</sub> serves as an activator for CLA-Ac, thereby increasing its electrophilicity. Three different mixtures containing 5u-Me-(OCN-Cy)<sub>2</sub> were prepared (Table 2, entries 1–3). Additionally, results for a mixture containing 5u-Me-CO<sub>2</sub> and 2 equivalents of cyclohexyl isocyanate instead of 5u-Me-(OCN-Cy)<sub>2</sub>,



**Scheme 2.** Release of the free carbene in two steps (left). Molecular structures and abbreviations of the diepoxides and anhydrides used in this work (top). Synthesis of anhydride-cured epoxide resin (middle top). Polyamide 6 synthesis applying CLA-Ac as activator (middle bottom). Azepan-2-one derivatives activated by electron-withdrawing moieties (bottom).

pre-homogenized at 75 °C for 1 h, are listed, too (Table 2, entry 4). All samples were heated to 180 °C for 1 h, although solidification occurred in less than 10 min in all cases. The use of 6-Cy-CO<sub>2</sub>, a precursor to a strongly basic carbene, applied without any activator in a initiator to monomer ratio of 1:160, was reported to allow for the isolation of 85% polymer.<sup>[9]</sup> A conceivable addition reaction

**Table 1.** Maximum of the exothermic peak ( $T_{\max}$ ) and the integral of the corresponding area as released energy ( $\Delta H$ ) of an anhydride/epoxide curing reaction executed in DSC; comparing two NHC precursors.

No.	Monomers <sup>a)</sup>	5u-Me-(OCN-Cy) <sub>2</sub>		5u-Me-CO <sub>2</sub> <sup>b)</sup>	
		$T_{\max}$ [°C]	$\Delta H$ [J g <sup>-1</sup> ] <sup>c)</sup>	$T_{\max}$ [°C]	$\Delta H$ [J g <sup>-1</sup> ] <sup>c)</sup>
1	BADGE/ HHPA	140	-281	125	-279
2	BADGE/MAA	141	-301	152	-263
3	BDDG/ HHPA	144	-395	131	-400
4	BDDG/MAA	131	-390	142	-399

<sup>a)</sup>100 equiv. diepoxides/200 equiv. anhydride/8 equiv. NHC precursor; <sup>b)</sup>literature values, same molar ratios;<sup>[8]</sup> <sup>c)</sup>the heating rate was 5 K min<sup>-1</sup> in the range from 30–250 °C. BADGE = bisphenol-A diglycidyl ether; BDDG = 1,4-butandiol diglycidyl ether; MAA = oxol-2,5-dione; HHPA = hexahydrophthalic acid anhydride.

of cyclohexyl isocyanate, as fragmentation product of the carbene release process, to CLA is postulated to form *N*-cyclohexyl-2-oxoazepane carboxamide (CI-CLA, Scheme 2, PA6 synthesis activators) in situ. This assumption is strengthened by the available literature where CI-CLA is synthesized from cyclohexyl isocyanate and CLA at elevated temperatures.<sup>[46–48]</sup> CI-CLA is an electron-deficient carbonyl easing the initial polymerization step comparable to CLA-Ac (Scheme 2, polyamide 6 synthesis).<sup>[48]</sup> In accordance with this proposal, the solidification times of mixtures containing 3 equivalents of activator (CLA-Ac and Cy-NCO, Table 2, entries 1 and 4) are significantly shorter than for mixtures containing 2 equivalents of activator (Cy-NCO, Table 2, entries 2–3). In line with the higher activator content, melting points ( $T_m$ ) of the resulting PA6 are somewhat lower (205–215 °C) than the one of PA6 prepared by anionic polymerization ( $T_m \approx 220$  °C).<sup>[49]</sup> Indeed, the reaction solidified in an acceptable time span with quantitative polymer yield even in the absence of CLA-Ac (Table 2, entry 3).

Spirocyclic 5u-Me-(OCN-Cy)<sub>2</sub> can be synthesized from 5u-Me-CO<sub>2</sub> in a simple one-pot process. Like related 5u-Me-CO<sub>2</sub>, 5u-Me-(OCN-Cy)<sub>2</sub> can be used as thermally latent pre-catalyst for both epoxide curing and polyamide 6 synthesis. Its neutral character provides better solubility in anhydride/epoxide mixtures. Compared to 5u-Me-CO<sub>2</sub> it also provides far longer pot life of up to 1 week, which renders it an attractive

**Table 2.** Composition, solidification times and yields of single-component mixtures homogenized at 75 °C for 1 h and polymerized at 180 °C.

No.	CLA <sup>a)</sup>	5u-Me-(OCN-Cy) <sub>2</sub> <sup>a)</sup>	MgCl <sub>2</sub> <sup>a)</sup>	CLA-Ac <sup>a,b)</sup>	5u-Me-CO <sub>2</sub> <sup>a)</sup>	Cy-NCO <sup>a)</sup>	Solidification time <sup>c)</sup>	Yield [%]	T <sub>m</sub> [°C] <sup>d)</sup>
1 <sup>e)</sup>	250	1	1	1	–	–	3	>96	208
2	250	1	1	–	–	–	9	>96	215
3	250	1	–	–	–	–	7	>96	211
4	250	–	1	1	1	2	3	>96	205

<sup>a)</sup>equivalents; <sup>b)</sup>N-acetylazepan-2-one; <sup>c)</sup>minutes; <sup>d)</sup>T<sub>m</sub> = melting point, determined by DSC at 30 K min<sup>-1</sup>, average of two runs; <sup>e)</sup>remained slightly cloudy at 75 °C, fully homogeneous at 180 °C.

alternative. In PA6 synthesis, 5u-Me-(OCN-Cy)<sub>2</sub> allows for fast and quantitative polymerizations. Due to the activating role of cyclohexyl isocyanate, full conversion is reached even without the use of any further activators.

## Experimental Section

**Synthesis of 5u-Me-(OCN-Cy)<sub>2</sub>:** Inside a glove box, 5u-Me-CO<sub>2</sub> (1.000 g, 1 equivalent, 7.136 mmol) was mixed with cyclohexyl isocyanate (1.7864 g, 2 equivalents, 14.271 mmol) in 10 mL acetonitrile and 15 mL sulfolane in a Schleck tube equipped with a magnetic stir bar. The closed tube was chambered outside and heated to 80 °C for 4 h. The red solution was brought inside the glove box and extracted with pentane until freshly added pentane remained colorless. The yellow/greenish/brownish combined pentane phases were reduced to dryness in vacuo, the residue was re-dissolved in pentane, filtered through a pad of celite and crystallized from this solution at –35 °C, after concentrating under reduced pressure.

**Epoxide Resin Curing:** Epoxide resins were prepared under inert gas atmosphere inside a glove box. A typical sample had a weight of 0.5 to 1 g. Stoichiometric amounts of anhydride (200 equivalents) and diepoxide (100 equivalents) were weighed in and homogenized at elevated temperature of 60 °C (1 h), before 5u-Me-(OCN-Cy)<sub>2</sub> (8 equivalents) was dissolved in parts of the formed resin within 3 to 4 h at ambient temperatures. Mixtures containing HHPA as anhydride form colorless or yellowish substances, mixtures containing MAA form reddish/brown mixtures. 1–5 mg of the resins was used to measure DSC.

**Polyamide 6 Synthesis:** Inside a glove box, azepan-2-one (CLA, 1.000 g, 250 equivalents, 8.836 mmol) was mixed with the NHC precursor (1 equivalent, 0.035 mmol), an activator (1 equivalent, 0.035 mmol). The mixture was heated to 75 °C and stirred until a homogeneous solution formed, typically within 1 h. Those were solidified by cooling to room temperature and stored under inert gas atmosphere. Samples were polymerized under inert gas at 180 °C. The formed polymers were dissolved under ambient conditions in methanoic acid (≥10 mL g<sup>-1</sup><sub>polymer</sub>), precipitated from propanone (≥35 mL g<sup>-1</sup><sub>polymer</sub>) and centrifuged (4500 rpm, for ≥15 min). The supernatant solutions were discarded and the residual solid dried under reduced pressure at 60 °C for 24 h. For further details, see Supporting Information.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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## Conflict of Interest

The authors declare no conflict of interest.

## Keywords

epoxide resins, latent initiators, N-heterocyclic carbenes, polyamide 6

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