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CO_2 and Sn^{II} Adducts of N-Heterocyclic Carbenes as Delayed-Action Catalysts for Polyurethane Synthesis

Bhasker Bantu,[a] Gajanan Manohar Pawar,[a] Ulrich Decker,[a] Klaus Wurst,[c] Axel M. Schmidt,[b] and Michael R. Buchmeiser*[a, d]

Abstract: A series of CO_2-protected pyrimidin-2-ylidenes as well as 1,3-dimesitylimidazol-2-ylidene and dimesitylimidazolin-2-ylidene complexes of Sn^{II} have been prepared. Selected single-crystal X-ray structures are reported. The new compounds were investigated for their catalytic behavior in polyurethane (PUR) synthesis. All compounds investigated showed excellent catalytic activity, rivaling the industrially most relevant catalyst dibutyltin dilaurate. Even more important, all compounds displayed pronounced latent behavior, in selected cases rivaling and exceeding the industrially relevant latent catalyst phenylmercury neodecanoate both in terms of latency and catalytic activity. This allows for creating one-component PUR systems with improved pot lifetimes. Pseudo-second-order kinetics were found for both CO_2-protected tetrahyropyrimidin-2-ylidenes and for [$SnCl_2$(1,3-dimesityldihydroimidazol-2-ylidene)], indicating a fast pre-catalyst decomposition prior to polyurethane formation. 1,3-Di(2-propyl)tetrahydropyrimidin-2-ylidene was additionally found to be active in the cyclotrimerization of various isocyanates, offering access to a broad variability in polymer structure, that is, creating both urethane and isocyanurate moieties within the same polymer.

Keywords: catalysts · N-heterocyclic carbenes · polyaddition · polyurethanes · tin

Introduction

Since Otto Bayer's discovery of polyurethanes (PURs),[1,2] this class of polymers experienced a fantastic success story and created a multi-billion Euro business.[3,4] Polyurethanes are produced through a polyaddition reaction of an at least difunctional alcohol (polyol) to an at least difunctional isocyanate in the presence of a catalyst. Catalysts commonly used in PUR synthesis are tertiary amines, for example, diazabicyclooctane (DABCO) and *N*-alkylmorpholines, as well as organometallic compounds, such as dibutyltin dilaurate (DBTDL, **A**). The former activate the alcohol, thus increasing its nucleophilicity, while the latter are Lewis acids and thus activate the isocyanates and make them more electrophilic. DBTDL is among the most active catalysts, outrivaling most organic bases including DABCO. Many applications require a long pot lifetime combined with fast curing. Therefore, in reaction injection molding (RIM) applications, phenylmercury neodecanoate (PMND, **B**) is still used as a latent curing catalyst. In combination with suitable polyols and isocyanates, such latent, delayed-action catalysts allow for the premixing of the components and their storage at room temperature and slightly above for a given time (pot life). Polyaddition is then usually triggered thermally. Unfortunately, in special applications PMND is the *only* catalyst so far that combines sufficient latency and high reactivity at elevated temperatures. In many markets the ban on heavy metal containing materials is increasingly implement-

[a] B. Bantu, G. M. Pawar, Dr. U. Decker, Prof. Dr. M. R. Buchmeiser
Leibniz-Institut für Oberflächenmodifizierung e.V. (IOM)
Permoserstr. 15, 04318 Leipzig (Germany)
Fax: (+49) 341-235-2584
Homepage: http://www.iom-leipzig.de
E-mail: michael.buchmeiser@iom-leipzig.de

[b] Dr. A. M. Schmidt
BAYER MaterialScience AG
51368 Leverkusen (Germany)

[c] Dr. K. Wurst
Institut für Allgemeine
Anorganische und Theoretische Chemie
Universität Innsbruck
Innrain 52a, 6020 Innsbruck (Austria)

[d] Prof. Dr. M. R. Buchmeiser
Institut für Technische Chemie
Universität Leipzig
Linnéstr. 3, 04103 Leipzig (Germany)

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ed. As a consequence, a growing demand for the replacement of heavy metals, such as mercury, evolves.

In view of this unsatisfying situation, we aimed on the development of novel delayed-action catalysts for PUR synthesis that would satisfy the requirements of i) being stable at room temperature, ii) displaying high activity upon thermal initiation, iii) displaying low, or even better, no toxicity. With the reports on the use of (protected) N-heterocyclic carbenes (NHCs) for the polymerization of lactide published by Waymouth et al. in mind,[5–7] we started to design protected NHCs for the use as latent catalysts in PUR synthesis.

Results and Discussion

We commenced our investigations with the haloform and alkoxide protected NHCs based on imidazol-2-ylidenes and imidazolin-2-ylidenes, which have been reported by Waymouth et al. to present latent catalysts for the ring-opening polymerization of cyclic esters (Figure 1).[8,9]

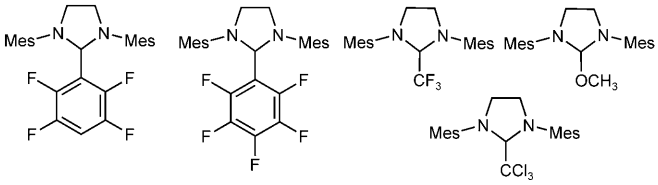


Figure 1. Structure of haloform- and alkoxide-protected NHCs.

Disappointingly, we found them unsuitable for our purposes. Though many of these compounds were stable up to 100 °C in the absence of a polyol based on a hydroxy-functionalized poly(acrylate) and a commercial triisocyanate, that is, cyclotrimeric hexamethylene diisocyanate (HDI-cyclotrimer, Figure 2), and some of these compounds were in fact active catalysts for PUR synthesis, no *latent* behavior was observed at all when these compounds were mixed with both the polyol and the HDI-cyclotrimer. We therefore prepared a series of CO_2-protected NHCs[10] based on tetrahydropyrimidin-2-ylidenes,[11,12] of which catalysts **1** and **2** (Figure 2) in fact turned out to satisfy our demands. The high latency of these pre-catalysts can be rationalized by the fact that tetrahydropyrimidin-2-ylidenes are characterized by a small angle defined by the two substituents at N-1 and N-3, which provides sufficient steric protection of the C-2 carbon as well as by the efficient charge delocalization (vide infra). Both are expected to lead to a lower proneness of the C-2 carbon to nucleophilic attacks, e.g., by alcoholates.

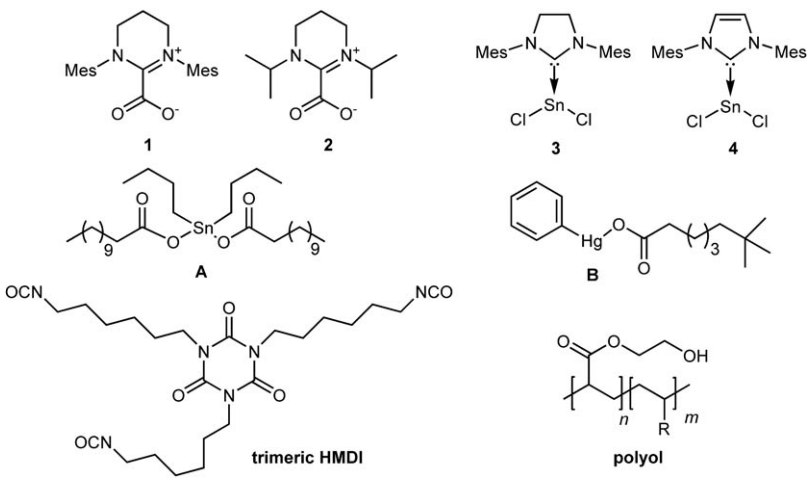


Figure 2. Structure of catalysts **1**–**4**, **A**, **B** and of the monomers used.

The X-ray structure of catalyst **1** is shown in Figure 3. Compound **1** crystallizes in the monoclinic space group

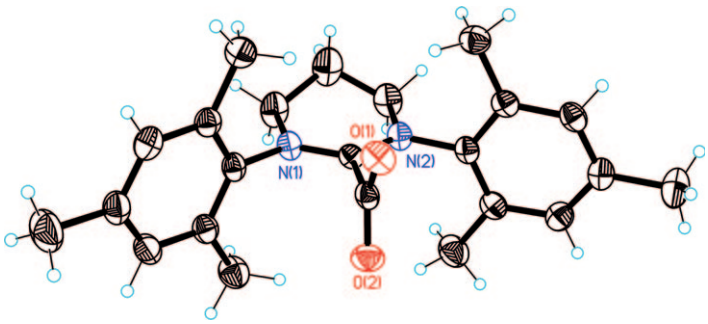


Figure 3. X-ray structure of **1**.

$P2_1/n$ with $a=738.75(2)$ pm, $b=2140.81(7)$ pm, $c=1472.40(3)$ pm, $\beta=95.612(2)°$, $Z=4$. As expected, both the two C–O [123.4(2) and 123.0(2) pm] and the two C–N bonds [132.6(2) versus 132.3(2) pm] are almost identical, indicating uniform charge distribution. In addition, we prepared a series of Sn^{II}–NHC complexes of which catalysts **3** and **4** also displayed latent behavior, as well as high activity. The X-ray structures of both **3** and **4** were also solved.

Compound **3** (Figure 4) crystallizes in the orthorhombic space group $Pna2_1$ with $a=2220.94(4)$ pm, $b=787.15(1)$ pm, $c=1281.83(2)$ pm, $\alpha=\beta=\gamma=90°$, $Z=4$. The angles C-Sn-Cl(1), C-Sn-Cl(2) and Cl(1)-Sn-Cl(2) are 95.89(7)°, 92.63(6)° and 94.22(5)° respectively. The Sn(1)–C(1) bond length is 233.9(2) pm.

Compound **4** (Figure 5) crystallizes in the triclinic space group $P\bar{1}$ with $a=873.38(2)$ pm, $b=1500.20(3)$ pm, $c=1849.40(4)$ pm, $\alpha=111.564(1)$, $\beta=100.736(1)$, $\gamma=90.266(1)°$, $Z=4$. The angles C-Sn-Cl(1), C-Sn-Cl(2) and Cl(1)-Sn-Cl(2) are 95.89(7)°, 92.63(6)° and 94.22(5)°, respectively. The Sn(1)–C(1) bond length is 231.1(3) pm.

The values for the bond lengths and angles found for both **3** and **4**, as well as the chemical shift in the ^{119}Sn NMR ($\delta=-61.5$ and -63.9 ppm, respectively) are comparable to the corresponding

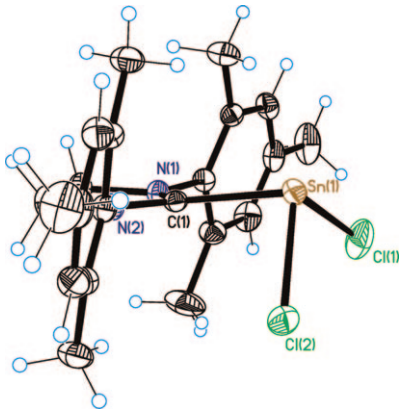


Figure 4. X-ray structure of **3**.

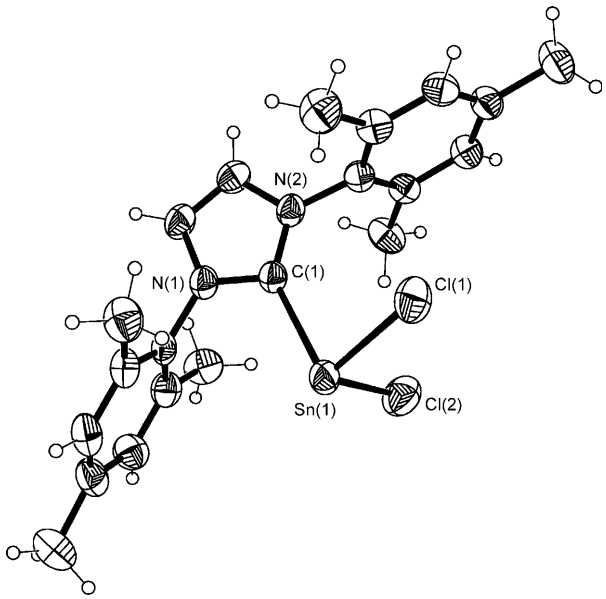


Figure 5. X-ray structure of **4**.

values found for [$SnCl_2$(1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene)],[13] for which a pyramidal coordination geometry for Sn and a strong s-character of the non-binding electron pair has been suggested.

Both the activity of the initiators and their latency were monitored by real-time FT-IR. For these purposes, the polyaddition reaction between a commercial polyol based on a hydroxy-functionalized poly(acrylate) and a commercial triisocyanate, that is, cyclotrimeric hexamethylene diisocyanate (HDI-cyclotrimer, Figure 2) was monitored. The decrease in intensity of the isocyanate band at $\tilde{\nu}=2265\ cm^{-1}$ was chosen as a measure for conversion (Figure S1 in the Supporting Information). The results are summarized in Figure 6.

Note that any initial *increase* in the isocyanate concentration is the sole result of the evaporation of the solvent (butylacetate) that was used for the premixing of the educts. As can be deduced there from, catalysts **1**–**4** and PMND (**B**) displayed excellent latency at room temperature for at least

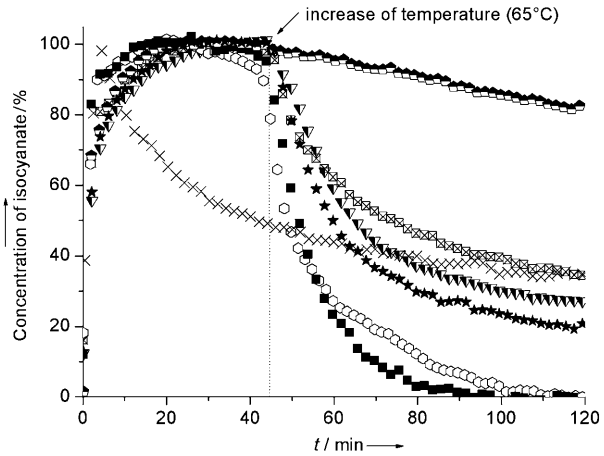


Figure 6. Reactivity and latent behavior of catalysts **1**–**4** in comparison to **A** and **B** in the polyaddition reaction of the polyol with HDI-cyclotrimer: without catalyst (◓), **1** (⋆), **2** (▽), **3** (■), **4** (◌), **A** at room temperature for 120 min (×), **B** (⊠).

45 minutes, while DBTDL (**A**) did not at all. Following heating to 65 °C the polyaddition reaction commenced instantly, triggered by either **1**–**4** or **B**.

Using identical amounts of catalyst, that is, 3.5 mmol % (0.63–1.8 wt. %) based on the HDI-cyclotrimer, catalysts **1**–**4** clearly outrivaled **B** in terms of activity as evidenced by the slopes in the graph of isocyanate concentration vs. time. In fact catalysts **3** and **4** displayed the highest activity of all compounds measured.

For externally catalyzed polyaddition reactions, e.g., those catalyzed by a base, the number average degree of polymerization $=1/(1-((A_0-A)/A_0))=1+kA_0t$, ($A_0$, $A=$initial and time-dependant isocyanate concentration, respectively, and $k=$rate constant of polymerization), provided the fact that the reaction is pseudo-second-order kinetics, that is, the initial concentration of the base is constant and not a function of time. In that case, the graph $1/(1-((A_0-A)/A_0))$ versus time should be linear. This was in fact found to be true for the polyaddition reactions catalyzed by **1**, **2**, **4** and **B**, suggesting that for these pre-catalysts decomposition and formation of the active catalyst is fast and quantitative compared to the polyaddition reaction (Figure 7). Since A_0 was identical in all experiments, the slopes of the graphs in Figure 7 are proportional to k and clarify the order of reactivity, which is **3** > **4** > **1** > **2** > **B**.

We next turned to possible modifications in the polymer structure. NHCs have already been reported to catalyze the cyclotrimerization of isocyanates.[14] While **1**, **3** and **4** were inactive in the cyclotrimerization of many aliphatic and aromatic isocyanates up to catalyst loadings of 0.1 mol % (yields ≪5 %), **2** allowed for the cyclotrimerization of a series of aromatic isocyanates in virtually quantitative yields down to catalyst loadings of 1 mmol % (Table 1). Interestingly, cyclohexylisocyanate could not be cyclotrimerized by the action of **2**, while cyclotrimeric HDI, which is also an aliphatic isocyanate, can be subject to cyclotrimerization resulting in a crosslinked polymer (vide infra). Similarly, the

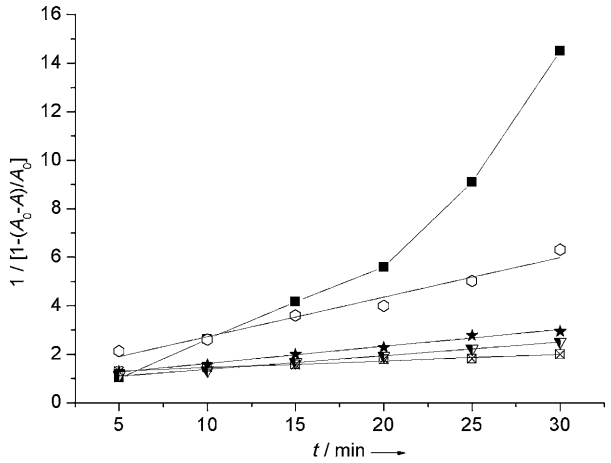


Figure 7. Graph of $1/(1-((A_0-A)/A_0))$ versus time (A_0 = initial isocyanate concentration, A = time-dependant isocyanate concentration) for the polyaddition reaction of polyol with HDI-cyclotrimer catalyzed by **1**–**4** and **B**. **1** (⋆), **2** (▼), **3** (■), **4** (⬡), **B** (⊠).

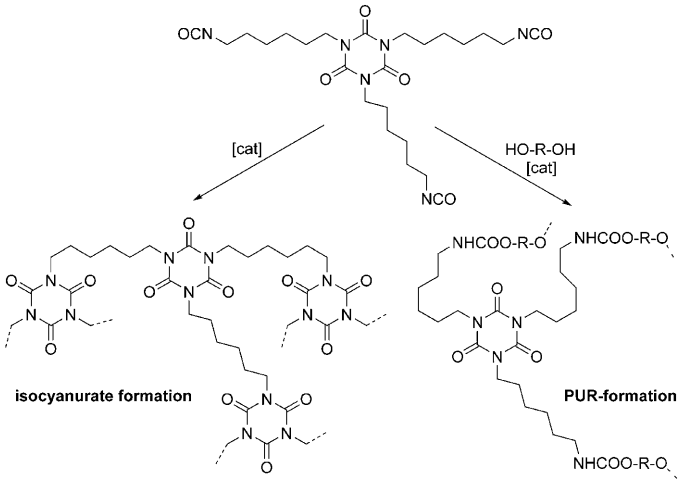
Table 1. Results for the cyclotrimerization of isocyanates by the action of **2**.

Substrate	t [h][a]	**2**, Yield [%][b]
phenyl isocyanate	0.5	99
4-(benzyloxy)phenyl isocyanate	1	99
4-methoxyphenyl isocyanate	1	99
3-methylphenyl isocyanate	1	95
4-methylphenyl isocyanate	1	99
4-fluorophenyl isocyanate	0.5	100
4-chlorphenyl isocyanate	1	99
cyclohexyl isocyanate	1	0

[a] 10^{-3} mol % of **2** were used. [b] Isolated yields.

cyclotrimerization reaction of 2,4-toluene diisocyanate (TDI) triggered by **2** occurred (isocyanurate band at $\tilde{\nu}=1701\ cm^{-1}$) while no reaction was observed with **1**. The capability of **2** to cyclotrimerize isocyanates is attributed to the more basic character that may be anticipated for the free NHC that forms from **2** compared to the NHC formed from **1** ($+I$ versus $-I$ and M effect of the 2-Pr and mesityl group, respectively).

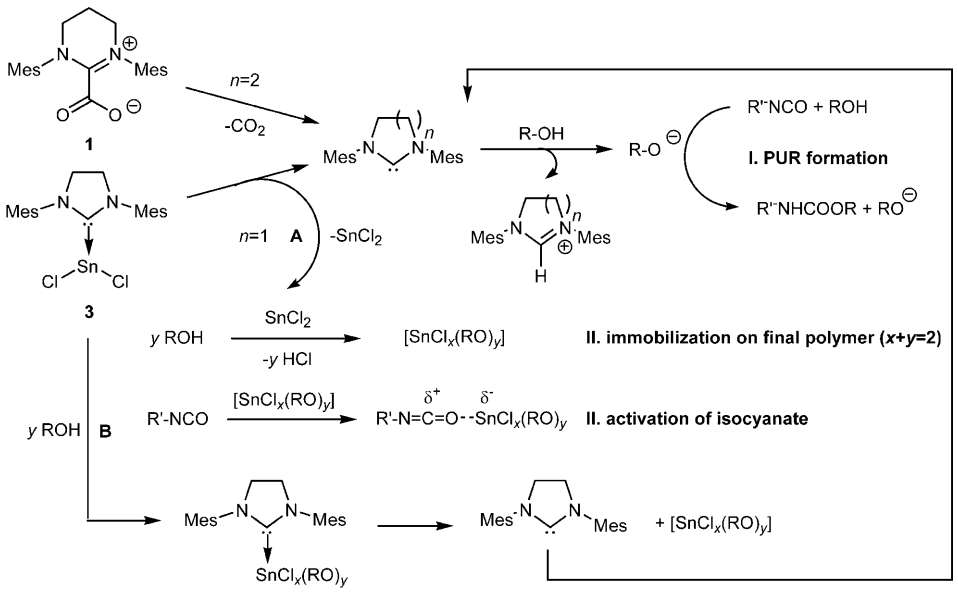
Consequently, compound **2** was used for the reaction of ethylene glycol with TDI to form PUR containing additional isocyanurate moieties. Isocyanurate formation was confirmed by IR spectroscopy (Figures S2 and S3 in the Supporting Information). Thus, in addition to the typical broad PUR bands at $\tilde{\nu}=1700$ and $1221\ cm^{-1}$, the band around $\tilde{\nu}=1530\ cm^{-1}$ (δ_{NH}) split into two signals at $\tilde{\nu}=1531$ and $1514\ cm^{-1}$.[15] Treating HDI-cyclotrimer with **2** also resulted in cyclotrimerization and the reaction mixture solidified. In the FT-IR, the peak around $\tilde{\nu}=1426\ cm^{-1}$ became stronger (Figure S4 in the Supporting Information). Again, the use of **1** resulted in no conversion at all. Consequently, a mixture of the polyol and the HDI-cyclotrimer prepared by the action of **2** contained additional isocyanurate moieties while PUR prepared by the action of **1** did not. Accordingly, the IR spectrum of PUR prepared from the polyol and the HDI-cyclotrimer by the action of **2** was characterized by two bands at $\tilde{\nu}=1461$ and $1429\ cm^{-1}$, while PUR prepared from the same educts by the action of **1** only showed only one band at $\tilde{\nu}=1460\ cm^{-1}$ (Figure S5 in the Supporting Information). These data illustrate the potential of these new delayed-action catalysts in terms of tailoring the final polymer structure (Scheme 1): PURs with or without additional cyanurate moieties can be realized.



Scheme 1. Different polymer structures that may form through the PUR reaction (right) and isocyanate cyclotrimerization, that is, isocyanurate formation (left).

We next focused on some mechanistic investigations on the mode of action of these new catalysts. The mechanism of initiation is a quite simple one for CO_2-protected NHCs. As might be anticipated, an increase in temperature results in the release of CO_2 and concomitant formation of the free carbene, which immediately reacts with the alcohol to produce the alcoholate and the corresponding tetrahydropyrimidinium salts (Scheme 2). In fact, quantitative formation of the latter was observed in the reaction of **1** with ethylene glycol in $C_2D_4Cl_2$ at 70 °C (Figure S6 in the Supporting Information). It was clearly identified by the typical ^1H NMR chemical shift of the pyrimidinium proton at $\delta=7.87$ ppm and by the corresponding signal for the pyrimidinium carbon at $\delta=155.1$ ppm, respectively. Concomitantly, in the ^{13}C NMR we observed resonances for the 2-hydroxy-1-ethanolate at $\delta=67.34$ and 62.51 ppm, respectively. Similar results were found for the reaction of **1** with the polyol or with the polyol and the HDI-cyclotrimer. Thus, heating a mixture of these three compounds in CD_2Cl_2 to 70 °C results in the quantitative formation of the pyrimidinium salt (Figure S6 in the Supporting Information) and the polyaddition reaction occurs.

The role of compounds **3** and **4** in PUR synthesis, however, was less obvious. In principle, one might regard both compounds as $SnCl_2$-protected NHCs, which, upon heating decompose into the corresponding free NHC and $SnCl_2$ (Scheme 2). To shed some light on that issue, we carried out



Scheme 2. Proposed pre-catalyst activation and PUR reaction ($x+y=2$).

some ^{1}H- and ^{119}Sn-NMR experiments. The reaction of **3** with ethylene glycol and TDI in $C_2D_4Cl_2$ at 70 °C resulted in the quantitative formation of a 1,3-dimesityl-4,5-dihydroimidazolium salt as evidenced by ^{1}H NMR ($\delta_{H\text{-}2}=8.15$ ppm) and ^{13}C NMR ($\delta_{C\text{-}2}=159.0$ ppm, Figure S7, Supporting Information). No signal for a Sn-species (any) was observed in the ^{119}Sn NMR, strongly suggesting a polymer-bound Sn-species that precipitates with the polymer. Again, the same accounts for the reaction of the polyol and the HDI-cyclotrimer triggered by **3**. Rapid formation of a 1,3-dimesityl-4,5-dihydroimidazolium salt was observed, again no Sn-signal was observable. Evidence for a polymer-bound Sn-species was provided by FT-IR. Thus, reaction of ethylene glycol with TDI in the presence of 1 equiv of **3** resulted in the formation of PUR. Its IR-spectrum displayed the corresponding signals, in addition signals at $\tilde{\nu}=1098$ and 1045 cm^{-1} could be assigned to those for a Sn-O-CH_2-R species.[16] To provide further proof for the reaction of compounds **3** or **4** with the alcohol, we reacted both **3** and **4** with Li(OC_2H_5) to form the corresponding NHC-Sn-alcoholate species. Our attempts to isolate [Sn(1,3-dimesitylimidazolin-2-ylidene)-$(OEt)_2$] revealed that this compound was thermally labile, resulting in the rapid formation of [$Sn(OEt)_2$] (^{119}Sn NMR $\delta=-146.3$ ppm, ^{1}H NMR $\delta=3.79$ (m, 2H; CH_2), 1.19 ppm (t, 3H; CH_3) and the free carbene $IMesH_2$. Together, these findings now allow for identifying the actual role of both **3** and **4** in the thermally triggered polyaddition reaction. Thus, both **3** and **4** are inactive pre-catalysts, Upon heating, both **3** and **4** decompose (pathway A, Scheme 2) or reaction with the alcohol occurs and the resulting Sn(NCH)-alcoholates decompose (pathway B, Scheme 2). As found for both **1** and **2**, the free carbenes formed from either **3** or **4** then deprotonate the polyol, thus simply serving as bases and catalyzing the base reaction. The Sn^{II}-alcoholates (any) that form, however, act as Lewis acids, which are known to catalyze the isocyanate reaction through coordination to the isocyanate oxygen. This way, upon activation both building blocks of **3** and **4**, that is, the $SnCl_2$ and the NHC, act as catalysts. This explains for the high catalytic activity of these compounds compared to other systems as well as for their latency.

Conclusion

In summary, we have established two classes of latent ("delayed action") catalysts based on CO_2-protected NHCs and NHC–Sn complexes for polyurethane synthesis that may be triggered thermally and exceed existing systems both in activity and latency. Particularly the CO_2-protected pre-catalysts circumvent the use of toxic heavy metals such as Hg^{II} or Sn^{IV}. Current work focuses on the investigation of other metal- and CO_2-protected NHCs as (latent) pre-catalysts for PUR synthesis.

Experimental Section

General: Except where noted, all manipulations were performed under a dinitrogen atmosphere in a glove box (MBraun LabMaster 130) or by standard Schlenk techniques. Pentane, toluene, diethyl ether, methylene chloride and tetrahydrofuran (THF) were dried using a solvent purification system (SPS, MBraun). Benzene and *n*-hexane were distilled from sodium/benzophenone ketyl under argon. All commercially available starting materials were purchased from Aldrich or Fluka and were used without any further purification. The polyol, the HDI-cyclotrimer, dibutyltin dilaurate (DBTDL, **A**) were received from BAYER MaterialScience (BMS). Phenylmercury neodecanoate (PMND, **B**) was received from Thor Especialidades, S.A., Spain. NMR spectra were recorded by using a Bruker Avence 250 (250.13 MHz for proton and 62.90 MHz for carbon) or a Bruker Avence 600 (600.25 MHz for proton and 150.93 MHz for carbon) spectrometer at room temperature unless specified otherwise. Proton and carbon spectra were referenced to an internal solvent resonance and are reported in ppm relative to tetramethylsilane. ^{119}Sn NMR spectra were recorded at room temperature by using a Bruker AVANCE II^{+} 600 spectrometer at 224 MHz for ^{119}Sn. Each sample was dissolved in [D_8]tetrahydrofuran or $CDCl_3$ up to concentrations of 10 wt.% in NMR-tubes (5 mm o.d.). ^{119}Sn NMR spectra were referenced to [$Sn(CH_3)_4$]/10 vol.% C_6D_6 according to the recommended UPAC Ξ-scale. Mass spectra were recorded on a VG ZAB HS, Bruker Esquire 300 plus and Finnigan-MAT 8200, respectively. Infrared spectra were recorded from $\tilde{\nu}=4000$–400 cm^{-1} by means of a Bruker Vector 22 using ATR technology. The absorption bands are reported in wave numbers (cm^{-1}). Elemental analyses were carried out at the Mikroanalytisches Labor, Institut für Physikalische Chemie, Universität Wien, Austria.

1,3-Dimesityl-3,4,5,6-tetrahydropyrimidin-1-ium-2-carboxylate (1): In a 250 mL Schlenk flask equipped with a stirring bar, 1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-1-ium bromide[11] (5.0 g, 12.46 mmol) was suspended in 100 mL of THF. Potassium *tert*-butoxide (1.68 g, 14.95 mmol) was sepa-

rately suspended in THF (10 mL) and added to the suspension of 1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-1-ium bromide. Then carbon dioxide was bubbled through the reaction mixture at 0 °C for 1 hour. During this procedure a sticky white precipitate formed. The solvent was removed in vacuo, and the residue was recrystallized from dichloromethane and diethyl ether (4.07 g, 90.0 %). Single crystals suitable for X-ray analysis were obtained from acetonitrile/diethyl ether. ^{1}H NMR (250.13 MHz, $CDCl_3$): $\delta = 2.24$, 2.28 (s, 6H), 2.34, 2.44 (s, 12H), 2.64 (m, 2H), 3.60 (t, 2H), 4.15 (t, 2H), 6.87, 6.95 ppm (s, 4H); ^{13}C NMR (62.89 MHz, $CDCl_3$): $\delta = 17.7$, 18.0, 19.5, 20.3, 21.0, 46.5, 46.7, 129.7, 130.1, 134.3, 135.5, 136.4, 137.2, 139.1, 140.5, 163.0 ppm; FTIR (ATR mode): $\tilde{\nu} = 2968$ (w), 1672 (s, CO), 1573 (s), 1305 (s), 1475(m), 851 cm^{-1} (s); elemental analysis (%) calcd for $C_{23}H_{28}N_2O_2$: C 75.79, H 7.74, N 7.69; found: C 75.47, H 7.42, N 7.59.

1,3-Diisopropyl-3,4,5,6-tetrahydropyrimidin-1-ium-2-carboxylate (2): 1,3-Diisopropyl-3,4,5,6-tetrahydropyrimidin-1-ium tetrafluoroborate[11] (1.0 g, 3.90 mmol) was suspended in 20 mL of THF. Potassium *tert*-butoxide (0.52 g, 4.68 mmol) was suspended in THF (5.0 mL) and added to this suspension. The reaction mixture was stirred for 16 h. It was then filtered through celite to remove residual salts. The filtrate was transferred to a 100 mL Schlenk flask and removed from the glove box. Carbon dioxide was bubbled through the solution at 0 °C for 30 min, during this time a white precipitate formed. The solvent was removed in vacuo, and the residue was washed with diethyl ether (0.70 g, 85.0 %). ^{1}H NMR (250.13 MHz, CD_3OD): $\delta = 1.27$ (d, 12H; of CH_3), 2.00 (m, 2H; of CH_2), 3.36 (t, 4H; N-CH_2), 4.13 ppm (m, 2H; CH); ^{13}C NMR (62.89 MHz, CD_3OD): $\delta = 19.6$, 20.2, 38.5, 55.8, 160.3, 162.7 ppm; FTIR (ATR mode): $\tilde{\nu} = 2971$ (w), 1651 (s, CO), 1591 (s), 1312 (m), 1166 (s), 863 (s), 760 cm^{-1} (s); ESI-MS: *m*/*z* calcd for $C_{11}H_{20}N_2O_2$: 212.15, found: 213.2 $[M+H]^+$.

[$SnCl_2$(1,3-dimesitylimidazolin-2-ylidene)] (3): In a 50.0 mL Schlenk flask equipped with a stirring bar, 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene (100 mg, 0.32 mmol) was dissolved in 20.0 mL of dry THF. Then $SnCl_2$ (62.0 mg, 0.33 mmol) was added. The mixture was stirred for 3 h; then all volatiles were evaporated. The resulting white solid was dissolved in dichloromethane and filtered through glass fiber filter paper. The solvent was evaporated and the white solid was recrystallized from dichloromethane and diethyl ether (145.0 mg, 90.0 % yield). Single crystals suitable for X-ray analysis were obtained from dichloromethane: diethyl ether. ^{1}H NMR (600.25 MHz, $CDCl_3$): $\delta = 2.31$ (s, 6H; *p*-CH_3), 2.40 (s, 12H; *o*-CH_3), 4.01 (s, 4H; N-CH_2), 6.97 ppm (s, 4H; Mes); ^{13}C NMR (150.92 MHz, $CDCl_3$): $\delta = 18.3$, 20.2, 51.94, 129.9, 132.9, 136.1, 139.7, 204.7 ppm; ^{119}Sn NMR (192.5 MHz, THF): $\delta = -61.5$ ppm; FTIR (ATR mode): $\tilde{\nu} = 2915$ (br), 1623 (m), 1481 (br), 1262 (m), 1030 (br), 850 cm^{-1} (m); elemental analysis (%) calcd for $C_{21}H_{26}Cl_2N_2Sn$: C, 50.85, H, 5.28, N, 5.65; found: C, 50.49, H, 5.30, N, 5.58.

[$SnCl_2$(1,3-dimesitylimidazol-2-ylidene)] (4): In a 100.0 mL Schlenk flask equipped with a stirring bar, 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene[17,18] (0.5 g, 1.64 mmol) was dissolved in 50.0 mL of dry THF. Then $SnCl_2$ (0.31 g, 1.64 mmol) was added to the reaction. The mixture was stirred for 3 h; then all volatiles were evaporated. The resulting white solid was dissolved in dichloromethane and filtered through glass fiber filter paper. The solvent was evaporated and the remaining white solid was recrystallized from dichloromethane and diethyl ether (730.0 mg, 90.0 % yield). Single crystals suitable for X-ray analysis were obtained from dichloromethane: diethyl ether. ^{1}H NMR (600.25 MHz, $CDCl_3$): $\delta =$ 2.18 (s, 12H; *o*-CH_3), 2.36 (s, 6H; *p*-CH_3), 7.03 (s, 4H; Mes), 7.17 ppm (s, 2H; N-CH_2); ^{13}C NMR (150.92 MHz, $CDCl_3$): $\delta = 17.8$, 21.3, 123.3, 129.2, 133.2, 135.0, 140.6, 181.6 ppm; ^{119}Sn NMR (192.5 MHz, THF) $\delta =$ −63.9 ppm; FTIR (ATR mode): $\tilde{\nu} = 2915$ (br), 1600 (m), 1540 (m), 1476 (br), 1226 (m), 1030 (br), 852 cm^{-1} (s); HR-MS: *m*/*z* calcd for $C_{21}H_{24}C_{l2}N_2Sn$: 494.03; found: 494.03.

Real-time FTIR-ATR spectroscopy: Investigations on the kinetics of the polyaddition reactions were carried out by means of real-time FTIR-ATR spectroscopy by using a Digilab FTS 6000 spectrometer and a heatable Golden Gate diamond ATR accessory (Specac). The monomer was applied as a small droplet to the ATR crystal, which was preheated to the appropriate temperature. Infrared spectra with a spectral resolution of 4 cm^{-1} were taken every 10 s over a period a 120 min. Conversion of the isocyanates was monitored by the decrease of absorbance of the NCO band at 2265 cm^{-1}.

Typical procedure for the recording of the reaction kinetics (latency): The catalyst (3.5 mmol %) with respect to isocyanate was dissolved in a minimum amount of dichloromethane (typically 0.5–1 mL); then 2 parts of the polyol (30 wt.-% in butylacetate), 1 part cyclotrimeric HDI (10 wt. % in butylacetate) (molar ratio of OH/NCO = 1:1) was added to the catalyst solution. The mixture was mixed for 3.0 min, kept at room temperature for 45 min; then the temperature was raised to 65 °C. The entire process of PUR formation (3D-crosslinked) was monitored by real-time FT-IR using a BIO-RAD FTS 6000 spectrometer.

Typical procedure for the cyclotrimerization of isocyanates: A solution of 4-methylphenyl isocyanate (1:1 v/v in THF) was added to 1,3-diisopropyl-3,4,5,6-tetrahydropyrimidin-1-ium-2-carboxylate (3.0 mg, 1.0 mmol %). The reaction mixture was stirred at 75 °C for 1 h. The resulting precipitate was filtered off, washed with pentane, and dried in vacuo to afford the isocyanurate as a white solid in 99 % yield.

1,3,5 Triphenyl-1,3,5-triazanine-2,4,6-trione: ^{1}H NMR (250.13 MHz, $CDCl_3$): $\delta = 7.38$–7.5 ppm (m, 15H; of phenyl); ^{13}C NMR (62.89 MHz, $CDCl_3$): $\delta = 148.8$, 133.6, 129.5, 128.5 ppm; FTIR (ATR mode): $\tilde{\nu} = 3044$ (br), 1688 (s, CO), 1488 (m), 1395 (m), 758 (s), 686 cm^{-1} (s); ESI-MS *m*/*z* calcd for $C_{21}H_{15}N_3O_3$: 357.11; found: 380.10 $[M+Na^+]$.

1,3,5-Tris(4-methoxyphenyl)-1,3,5-triazinane-2,4,6-trione: ^{1}H NMR (250.13 MHz, $CDCl_3$): $\delta = 7.29$ (d, 2H), 6.98 (d, 2H), 3.8 ppm (s, 3H); ^{13}C NMR (62.89 MHz, $CDCl_3$): $\delta = 160.0$, 149.2, 129.5, 126.38, 114.7, 55.6 ppm; FTIR (ATR mode): $\tilde{\nu} = 2938$ (br), 1688 (s, CO), 1508 (s), 1409 (m),1248 (m), 1168 (s), 1026 (s), 818 (s), 756 cm^{-1} (s); ESI-MS *m*/*z* calcd for $C_{24}H_{21}N_3O_6$: 447.14, found: 470.13 $[M+Na^+]$.

1,3,5-Tris(3-methlyphenyl)-1,3,5-triazinane-2,4,6-trione: ^{1}H NMR (250.13 MHz, $CDCl_3$): $\delta = 7.25$ (m, 9H), 7.41 (m, 3H), 2.43 ppm (s, 9H); ^{13}C NMR (62.89 MHz, $CDCl_3$): $\delta = 148.9$, 139.6, 133.6, 130.3, 129.3, 129.0, 125.5, 21.3 ppm; FTIR (ATR mode): $\tilde{\nu} = 2917$ (m), 1698 (s, CO), 1488 (s), 1404 (br), 875 (m), 785 (s), 690 cm^{-1} (s); ESI-MS *m*/*z* calcd for $C_{24}H_{21}N_3O_3$: 399.16; found: 422.15 $[M+Na^+]$.

1,3,5-Tris(4-methlyphenyl)-1,3,5-triazinane-2,4,6-trione: ^{1}H NMR(250.13 MHz, $CDCl_3$): $\delta = 7.28$ (s, 12H), 2.39 ppm (s, 9H); ^{13}C NMR (62.89 MHz, $CDCl_3$): $\delta = 148.9$, 139.3, 131.1, 130.0, 128.1, 21.32 ppm; FTIR (ATR mode): $\tilde{\nu} = 2916$ (br), 1696(m, CO), 1509 (s), 1402 (br), 807 (s), 749 cm^{-1} (s); ESI-MS *m*/*z* calcd for $C_{24}H_{21}N_3O_3$: 399.16; found: 422.15 $[M+Na^+]$.

1,3,5-Tris(4-fluoro)-1,3,5-triazinane-2,4,6-trione: ^{1}H NMR (250.13 MHz, $CDCl_3$): $\delta = 7.5$ (m), 7.36 (m), 7.18 (m), 7.10 (m), 7.05 (m), 7.01 ppm (m); ^{13}C NMR (62.89 MHz, $CDCl_3$): $\delta = 163.7$, 162.0, 161.2, 60.7, 159.6, 159.1, 151.0, 148.6, 130.4 (d), 129.3 (d), 126.2 (d), 118.7 (d), 116.7 ppm (m); FTIR (ATR mode): $\tilde{\nu} = 3294$ (br), 2291 (br), 1697(m, CO), 1505 (s), 1403 (m), 828 cm^{-1} (s); ESI-MS *m*/*z* calcd for $C_{21}H_{12}F_3N_3O_3$: 411.08; found: 434.0. $[M+Na^+]$.

1,3,5-Tris(4-chloro)-1,3,5-triazinane-2,4,6-trione: ^{1}H NMR(250.13 MHz, $CDCl_3$): $\delta = 7.32$ (d, 6H), 7.46 ppm (d, 6H); ^{13}C NMR (62.89 MHz, $CDCl_3$): $\delta = 129.8$, 131.8, 135.6, 148.2 ppm; FTIR (ATR mode): $\tilde{\nu} = 2976$ (br), 2852 (br), 1701 (m, CO), 1489 (m), 1419 (br), 1086 cm^{-1} (m); ESI-MS *m*/*z* calcd for $C_{21}H_{12}Cl_3N_3O_3$: 460.70, found: 460.0.

1,3,5-Tris(4-benzyloxyphenyl)-1,3,5-triazinane-2,4,6-trione: ^{1}H NMR (250.13 MHz, $CDCl_3$): $\delta = 7.42$ (m), 7.29 (m), 7.14 (d), 7.06 (d), 6.93 (d) (aromatic 27H), 5.12 (s), 5.08 (s), 5.04 ppm (s, 6H CH_2); ^{13}C NMR (62.89 MHz, $CDCl_3$): $\delta = 159.2$, 158.8, 149.2, 137.0, 131.0, 129.5, 128.7, 128.1, 127.6, 127.5, 122.6, 116.6, 115.6, 115.3, 70.4 ppm; FTIR (ATR mode): $\tilde{\nu} = 3292$ (br), 3034 (br), 1711 (br), 1640 (s), 1507 (s), 1235 cm^{-1} (br); ESI-MS *m*/*z* calcd for $C_{42}H_{33}N_3O_6$: 675.24, found: 698.2 $[M+Na^+]$.

X-ray measurement and structure determination of 1, 3 and 4: Data collection was performed by using a Nonius Kappa CCD equipped with graphite-monochromatized MoK_α radiation ($\lambda = 0.71073$ Å) and a nominal crystal to area detector distance of 36 mm. Intensities were integrated using DENZO and scaled with SCALEPACK.[19] Several scans in φ and ω direction were made to increase the number of redundant reflections, which were averaged in the refinement cycles. This procedure replaces in a good approximation an empirical absorption correction. The structures

were solved with direct methods SHELXS86 and refined against F^2 SHELX97.[20] All non-hydrogen atoms were refined with anisotropic displacement parameters. CCDC 715973 (**1**), 715974 (**3**) and 715975 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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