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CO_2, Magnesium, Aluminum, and Zinc Adducts of N-Heterocyclic Carbenes as (Latent) Catalysts for Polyurethane Synthesis

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

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A series of magnesium, aluminum, and zinc complexes of imidazol-2-ylidene-, imidazolin-2-ylidene-, and tetrahydropyrimidin-2-ylidene-derived N-heterocyclic carbenes (NHCs) was prepared. In addition, both symmetrical and unsymmetrical CO_2-protected imidazol-2-ylidenes and imidazolin-2-ylidenes were prepared. Selected single-crystal X-ray structures are reported. All compounds were investigated for their catalytic behavior in (poly)urethane (PUR) synthesis. Out of nine different compounds, the dimeric complex $[Zn(CH_3COO)_2$(1,3-dimesitylimidazol-2-ylidene)$]_2$ (**7**) proved to be the most active one, rivaling the industrially most relevant catalyst dibutyltin dilaurate in terms of catalytic activity. Even more important, the Mg- and Zn-derived NHC complexes as well as the CO_2-protected imidazol-2-ylidenes displayed pronounced latent behavior combined with high catalytic activity in selected cases, rivaling and exceeding the industrially relevant latent catalyst phenylmercury neodecanoate. This allows for creating one-component PUR systems with significant pot lives. Pseudo-second-order kinetics were found for all Mg- and Zn-based NHC complexes as well as for all CO_2-protected NHCs indicating fast precatalyst decomposition prior to (poly)urethane formation.

Introduction

N-Heterocyclic carbenes (NHCs) have become an important class of ligands for both main-group and transition metals.[1–7] The corresponding NHC–metal complexes have been introduced into organometallic catalysis some 15 years ago and now hold a strong position in that area of research. More recently, NHCs have established themselves as highly valuable catalysts in organic synthesis, thereby entering and further developing the field of organocatalysis.[8,9] During the last years, however, an increasing number of reports on the use of NHCs in polymer synthesis has emerged. Inspired by some excellent reports,[10–16] we were interested whether protected NHCs could be of some use as catalysts in polyurethane (PUR) synthesis and, if this was true, whether latent systems could be created. Such latent systems are of significant interest in industry, as they allow the premixing of all components including the precatalyst and, after triggering the catalyst, formation of the desired polymer or polymeric network. Here, we report on some selected results we have obtained so far.

Results and Discussion

NHC–metal complexes **1** and **7**–**9** (Figure 1) were prepared by reaction of the free NHC with the corresponding water-free metal salt in 83–93% yield. Compounds **5** and **6** were accessible in high yields (89 and 90%) by reaction of the corresponding CO_2-protected NHCs[17–19] 1,3-dimesitylimidazolium-2-carboxylate (**3**)[20] and 1,3-dimesityl-3,4,5,6-tetrahydropyridinium-2-carboxylate,[21] respectively, with anhydrous $ZnCl_2$. Compounds **2** and **4** were prepared in 93 and 70% yield by reaction of the corresponding imidazolium salt with potassium *tert*-butoxide and KH, respectively, followed by reaction with dry CO_2. Compound **1** crystallizes in the monoclinic space group $P2_1/n$, a = 1089.28(3) pm, b = 1236.14(4) pm, c = 2018.18(6) pm, β = 101.559(2)°, Z = 4 (Figure 2). Its structure and selected bond lengths and angles are summarized in Figure 2. The Mg–carbene distance in **1** [220.0(2) pm] is slightly shorter than the one in Mg(1,3-dimesitylimidazol-2-ylidene)-Et_2 (227.9 pm),[22] which is most probably a result of the stronger salt character of **1**. The ligand arrangement around the central Mg^{II} ion results in a distorted tetrahedral complex as supported by the angles C(1)–Mg(1)–Cl(1) [109.27(7)°], O(1)–Mg(1)–Cl(2) [101.09(6)°], C(1)–Mg(1)–Cl(2) [111.08(7)°], and Cl(1)–Mg(1)–Cl(2) [122.99(5)°].

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[a] Leibniz-Institut für Oberflächenmodifizierung (IOM),
Permoserstr. 15, 04318 Leipzig, Germany
Fax: +49-341-235-2584
E-mail: michael.buchmeiser@iom-leipzig.de
[b] Institut für Allgemeine Anorganische und Theoretische Chemie, Universität Innsbruck,
Innrain 52a, 6020 Innsbruck, Austria
[c] BAYER MaterialScience AG,
51368 Leverkusen
[d] Institut für Technische Chemie, Universität Leipzig,
Linnéstr. 3, 04103 Leipzig, Germany

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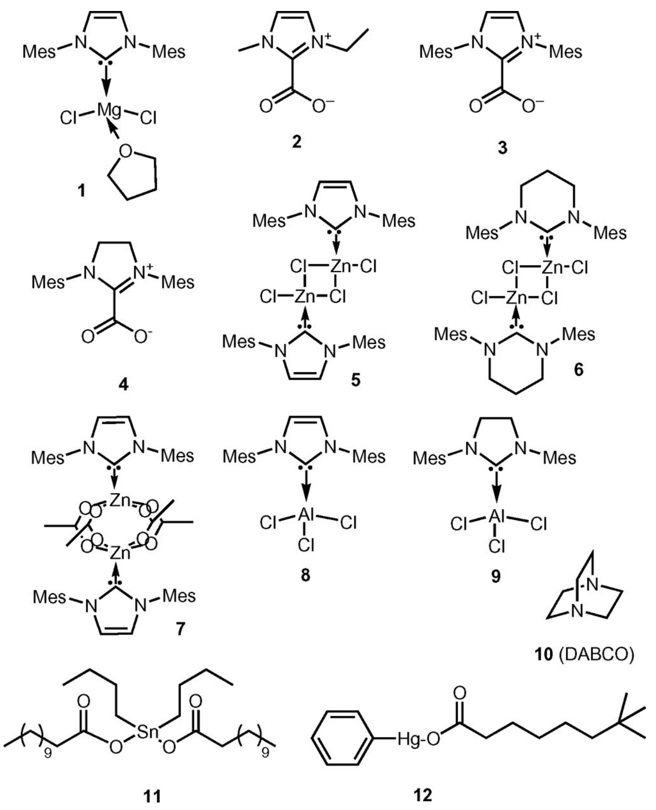

Figure 1. Structure of N-heterocyclic carbene derived compounds **1**–**9**, DABCO (**10**), DBTDL (**11**), and PMND (**12**).

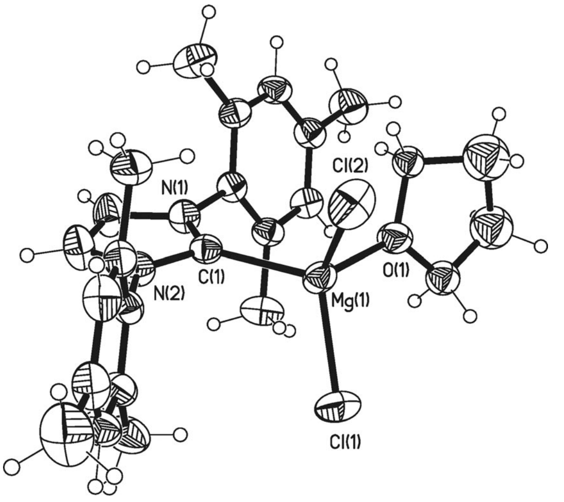

Figure 2. Single crystal X-ray structure of **1**. Selected bond lengths [pm] and angles [°]: Mg(1)–C(1) 220.0(2), Mg(1)–Cl(1) 228.12(11), Mg(1)–Cl(2) 228.52(11), Mg(1)–O(1) 201.4(2), C(1)–Mg(1)–Cl(1) 109.27(7), O(1)–Mg(1)–Cl(2) 101.09(6), C(1)–Mg(1)–Cl(2) 111.08(7), Cl(1)–Mg(1)–Cl(2) 122.99(5).

Compound **4** crystallizes in the orthorhombic space group *Pbcn*, a = 1622.83(7) pm, b = 724.73(4) pm, c = 1636.47(7) pm, Z = 4 (Figure 3). Its structure and selected bond lengths and angles are summarized in Figure 3 with a half molecule in the asymmetric unit, which can be completed by a twofold rotation axis. The distance C(1)–C(2) is 153.8(3) pm and is thus almost identical to the one found in other CO_2 adducts of NHCs.[21]

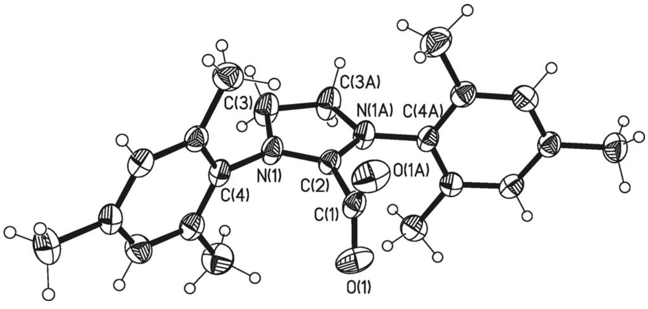

Figure 3. Single crystal X-ray structure of **4**. Selected bond lengths [pm] and angles [°]: N(1)–C(2) 131.9(2), C(1)–C(2) 153.8(3), N(1A)–C(2)–N(1) 111.5(2).

Compound **8** crystallizes in the orthorhombic space group *Pbcn*, a = 1559.94(5) pm, b = 1661.33(5) pm, c = 1800.38(6) pm, Z = 8 (Figure 4). Its structure as well as selected bond lengths and angles are summarized in Figure 4. The Al(1)–C(1) distance is 201.68(17) pm, the distances Al(1)–Cl(2) [210.2(8) pm], Al(1)–Cl(1) [211.2(9) pm], and Al(1)–Cl(3) [211.3(5) pm] are identical within experimental error. The ligands around the central Al^{III} ion form a slightly distorted tetrahedral complex as supported by the angles Cl(2)–Al(1)–Cl(3) [110.8(3)°], Cl(1)–Al(1)–Cl(3) [109.1(3)°], and Cl(2)–Al(1)–Cl(1) [109.2(3)°].

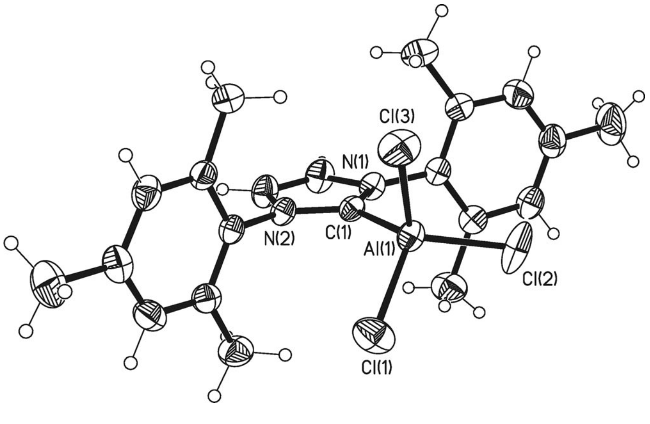

Figure 4. Single crystal X-ray structure of **8**. Selected bond lengths [pm] and angles [°]: Al(1)–C(1) 201.68(17), Al(1)–Cl(2) 210.2(8), Al(1)–Cl(1) 211.2(9), Al(1)–Cl(3) 211.3(5), Cl(2)–Al(1)–Cl(3) 110.8(3), Cl(1)–Al(1)–Cl(3) 109.1(3), Cl(2)–Al(1)–Cl(1) 109.2(3).

For our investigations on the activity of compounds **1**–**9** as potential (pre)catalysts for PUR synthesis, we focused on a technically relevant mixture of a polymeric hydroxyacrylate and trimeric hexamethylene diisocyanate (HMDI, RNCO/OH, 1:1). As already reported,[21] all compounds may be regarded as either CO_2-, Mg^{II}-, Al^{III}-, or Zn^{II}-protected NHCs, which, upon thermal initiation, should be able to generate the corresponding free carbene. Because free NHCs are both highly nucleophilic and basic, they should also catalyze polyurethane (PUR) formation through proton abstraction form the alcohol to thus form the more nucleophilic alcoholate. In addition to that, the decomposition of metal-containing complexes **1** and **5**–**9** additionally results in the formation of the free metal salt, which may well be expected to enhance the electrophilicity of the isocyanate.

We next monitored PUR formation in the absence and in the presence of compounds **1**–**9** by real-time-FTIR. The decrease in intensity of the isocyanate band at 2265 cm^{-1} was chosen as a measure for conversion. The results are summarized in Figure 5.

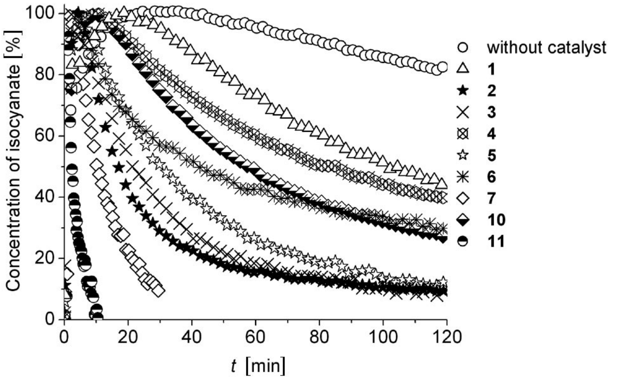

Figure 5. Reactivity of catalysts in comparison to **10** and **11**. T = 60 °C. Catalyst loading: 14 mmol-% with respect to DABCO.

Note that any initial increase in the isocyanate concentration is the sole result of the evaporation of the solvent that was used for premixing. Whereas Al-based NHC complexes **8** and **9** turned out to possess a comparably low activity (data not shown), all other protected NHCs displayed significant catalytic activity in PUR synthesis. Thus, CO_2-protected NHCs **2** and **3** as well as Zn-based complex **5** exceeded 1,4-diazabicyclooctane (DABCO), a technically relevant base, in catalytic activity. Compound **7** even rivaled dibutyltin dilaurate (DBTDL, **11**), the most active catalyst for PUR synthesis, in reactivity (Figure 5).

For externally catalyzed polyaddition reactions, for example, those catalyzed by a base, the number average degree of polymerization $\bar{X} = 1/\{1 - [(A_0 - A)/A_0]\} = 1 + kA_0t$, ($A_0$, A = initial and time-dependant isocyanate concentration, respectively; k = apparent rate constant), 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. As must be expected, this was in fact found to be true for the polyaddition reaction catalyzed by **10** (DABCO), but also for the PUR reaction catalyzed by compounds **1**–**6**, suggesting that for these (pre) catalysts decomposition and formation of the active catalyst is fast and quantitative compared to the polyaddition reaction (Figure 6). The slopes (proportional to k, average rate constant of polyaddition) clearly confirm the increased catalytic activity of **2**, **3**, **5**, and **7** compared to DABCO.

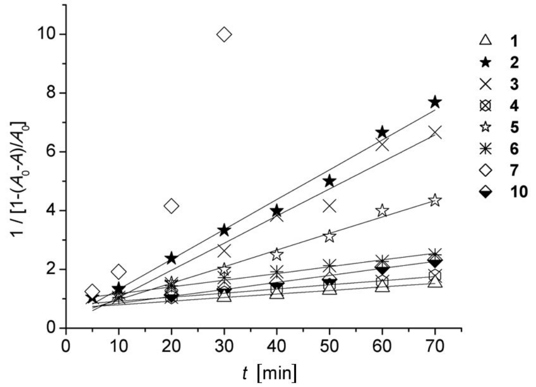

Figure 6. Graph of $1/[1 - (A_0 - A)/A_0]$ vs. t. Kinetic data taken from Figure 5.

Compound **7**, however, does not give pseudo-second order kinetics (Figure 6). Instead, an increase in k over time is observed. This clearly indicates that additional active species are also formed during the PUR reaction. This is in turn attributed to a comparatively slow dissociation of the dimeric bis(μ-acetato) complex.

We were then interested in the question whether any of compounds **1**–**7** that was found to be an active catalyst in PUR synthesis would display *latent* behavior. Such latent, delayed action catalysts allow the premixing of the components (i.e., the isocyanates, polyols, and the precatalyst) and their storage at room temperature and slightly above for a given time. Polyaddition is then triggered thermally. So far, in special applications phenylmercury neodecanoate (**12**, PMND) is the *only* catalyst that combines sufficient latency and high reactivity at elevated temperatures. In many markets the ban on heavy-metal-containing materials is increasingly implemented. As a consequence, a growing demand for the replacement of heavy metals, such as mercury, evolves.

Figure 7 shows the changes in isocyanate concentration as monitored by real-time FTIR in a mixture of trimeric hexamethylene diisocyanate, poly(hydroxyacrylate) and the corresponding precatalyst. The corresponding mixtures were stored at room temperature for 45 min and then heated to 65 °C. A precatalyst loading of 3.5 mmol-% was used in order to provide enough time to record the kinetics at elevated temperature and to distinguish between the different compounds. As can be deduced from these measurements, compounds **1**–**6** display pronounced latent behavior. Thus, no reaction was observed within 45 min at room temperature, whereas the PUR reaction commenced instantaneously after raising the temperature to 65 °C. In terms of reactivity, compounds **2**, **3**, **5**, and **6** even exceeded the catalytic activity of PMND (**12**).

Again, a graph of $1/\{1 - [(A_0 - A)/A_0]\}$ versus time was linear at least for compounds **1** and **3**–**5**, indicating that precatalyst decomposition at 65 °C was fast compared to PUR formation (Figure S1, Supporting Information).

Finally, we checked for the possibility to further tailor the polymer structure itself by using different (pre)catalysts.

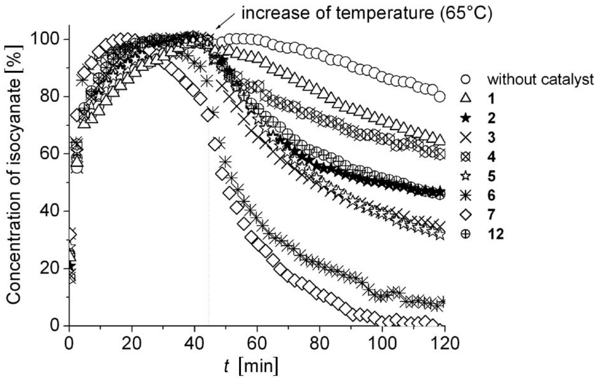

Figure 7. Reactivity and latent behavior of catalysts in comparison to **12**. T = 25 °C for 45 min, then T was raised to 65 °C. Catalyst loading: 3.5 mmol-% with respect to isocyanate.

Thus, certain NHCs have already been reported to catalyze the cyclotrimerization of isocyanates.[23]

In case a catalyst is capable of catalyzing *both* the PUR reaction and the trimerization of the isocyanate, different polymer structures (Figure 8) may be realized that are relevant to the area of macromolecular materials engineering. We therefore checked for the synthetic potential of compounds **1**–**7** for this reaction by simply using FTIR spectroscopy to follow the reaction of trimeric HMDI with compounds **1**–**7**. Whereas **1**, **2**, and **4**–**6** did not result in any trimerization reaction, compounds **3** and **7** were in fact identified as active catalysts for this task. In fact, trimeric HMDI was quantitatively polymerized and crosslinked by both **3** and **7** at a 1 mol-% base (Figures S6 and S7, Supporting Information). All together, these data illustrate the potential of these new delayed action catalysts in terms of tailoring the final polymer structure. However, it has to be underlined that the final tailor-made synthesis of a certain polymer backbone based on both the urethane and the isocyanurate motive requires a subtle tuning of the concentration of all reactants as well as of the process itself.

We next carried out some mechanistic investigations on the mode of action of these new catalysts. For CO_2-protected NHCs, the reaction pathway is comparably simple. Thus, an increase in temperature results in the release of CO_2 and the concomitant formation of the free carbene, which then immediately reacts with the alcohol to produce the corresponding imidazolium salts. In fact, quantitative formation of the latter was observed in the reaction of **2** with both the polyol and ethylene glycol in $C_2D_4Cl_2$ at 70 °C (Figure S2, Supporting Information). In both cases, the imidazolium salt was clearly identified by the typical ^1H NMR chemical shift of the imidazolium proton at δ = 10.7 and 9.93 ppm, respectively. Changes in the chemical shift result from the different anions that form. The same reaction occurs in a mixture of polyol and HMDI-trimer (imidazolium salt formation, δ_{NH} = 10.7 ppm). The concomitantly formed alcoholate then starts the PUR reaction, as evidenced by the formation of a solid block of crosslinked PUR.

The reactivity of NHC–metal complexes in PUR synthesis was also investigated by using compound **5**. In principle, one might regard **5** as a $ZnCl_2$-protected NHC. Upon heating **5** in the presence of ethylene glycol and TDI, it apparently decomposes into the corresponding NHC and most probably into (dispersed) $ZnCl_2$, which serves at least to a certain extent as a Lewis acid and speeds the isocyanate reaction (Figure S3, Supporting Information). The NHC itself is then proposed to deprotonate the alcohol, which then starts the PUR reaction. In fact, formation of the imidazolium salt in this reaction was evidenced by ^1H NMR spectroscopy (δ_{NH} = 8.73 ppm; Figure S4, Supporting Information). The same accounts for the reaction of the

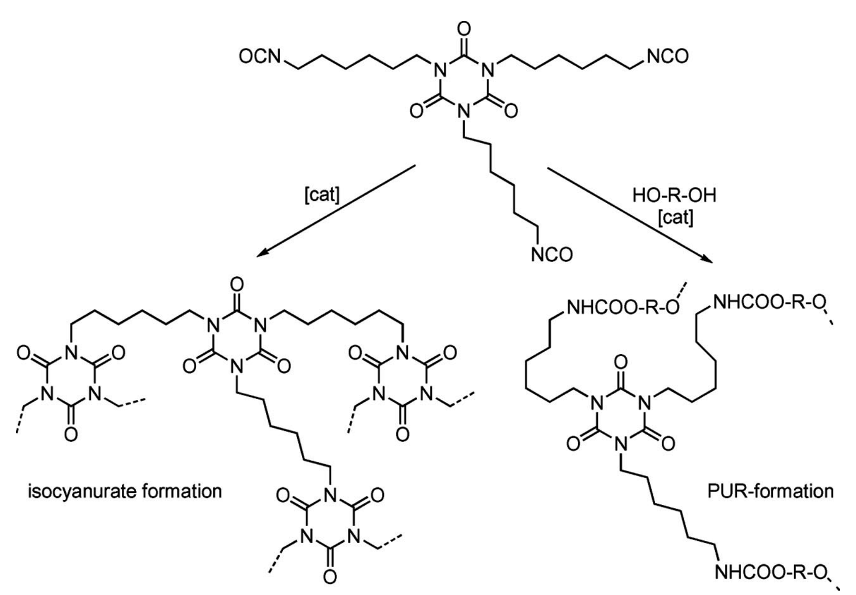

Figure 8. Different polymer structures that may form by PUR reaction (right) and isocyanate trimerization, that is, isocyanurate formation (left).

polyol and the polyisocyanate triggered by **5**. Rapid formation of imidazolium salt (δ_{NH} = 8.69 ppm) was observed, suggesting that decomposition of the parent NHC–Zn complex took place. A similar behavior was observed for compounds **1**, **7**, and **8** (Figure S5, Supporting Information), though decomposition times were different. Whether any free NHCs are involved in the PUR reaction for *a prolonged time* remains speculative. However, the finding that **1** catalyzes at least to a certain extent the PUR formation whereas $MgCl_2$ does not (Figure S3, Supporting Information) implies that the NHC must act as a catalyst for this reaction. Nevertheless, the finding that compounds **1** and **3** are capable of crosslinking the HMDI trimer whereas the reactive compounds **1** and **5**, which are based on the *same* NHC as **3** and **7**, do *not* catalyze this reaction (vide supra) and the finding that Zn complexes based on other NHCs also do not catalyze this reaction suggest a subtle role of both the nature and the concentration of the free NHC at a given time.

Conclusions

We have synthesized a series of novel CO_2- Mg^{II}-, Al^{III}-, and Zn^{II}-protected NHCs and investigated their use as catalysts and latent catalysts in PUR synthesis. Whereas all CO_2- Mg^{II}-, and Zn^{II}-protected NHCs displayed catalytic activity, particularly CO_2-protected imidazolium-derived NHCs **2** and **3** as well as dimeric Zn^{II} complex **5** displayed pronounced latent behavior. Complex **7** rivaled DBTDL in terms of reactivity. All compounds reported here do not contain any ionic Sn and may therefore well be expected to possess much lower toxic potential. Future work will be directed to the synthesis of different polyurethanes and their physicochemical properties as well as to the further elucidation of the mechanism.

Experimental Section

General: Except where noted, all manipulations were performed under a nitrogen atmosphere in a glove box (MBraun LabMaster 130) or by standard Schlenk techniques. Pentane, toluene, diethyl ether, dichloromethane, and tetrahydrofuran (thf) were dried by using a solvent purification system (SPS, MBraun, Garching, Germany). Benzene and *n*-hexane were distilled from sodium/benzophenone ketyl under an argon atmosphere. All commercially available starting materials were purchased from Aldrich or Fluka (Germany) and used without any further purification. The polyol (Desmophen A 870 BA), the triisocyanate (Desmodur N 3390 BA) dibutyltin dilaurate (DBDTL) were received from Bayer MaterialScience AG (BMS). Phenylmercury neodecanoate (PMND) was received from Thor Especialidades, S.A., Spain. NMR spectra were recorded with a Bruker Avance 250 (250.13 MHz for proton and 62.90 MHz for carbon) or a Bruker Avance II$^+$ 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 the internal solvent resonance and are reported in ppm. Mass spectra were recorded with a VG ZAB HS, Bruker Esquire 300 plus and Finnigan-MAT 8200, respectively. Infrared spectra were recorded in the 4000–400 cm^{-1} range with a Bruker Vector 2000 by using ATR technology. The absorption bands are reported in wavenumbers (cm^{-1}). Elemental analyses were carried out at the Mikroanalytisches Labor, Institut für Physikalische Chemie, Universität Wien, Austria. DSC measurements on latent catalysts were carried out with a DSC 7 (Perkin–Elmer) by using open Al pans. Temperature program: 25–100 °C, 10 °C min^{-1}; then at 100 °C for 120 min isothermal. All measurements were carried out under a nitrogen atmosphere. GC–MS investigations were carried out with a Shimadzu GCMS-QP5050 equipped with an AOC-20i Autosampler, an SPB fused silica (Rxi-5MS) column (30 m × 0.25 mm × 0.25 µm film thickness) run at 60.6 kPa. Temperature program: linear 70–300 °C within 25 min.

Investigations on the kinetics of the polyaddition reactions were carried out by 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.

Compounds **3**,[20] **7**,[24] 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene,[25] as well as 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene[26] were synthesized according to published procedures.

Compound 1: In a 100-mL Schlenk flask equipped with a stirring bar, 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (500.0 mg, 1.64 mmol) was dissolved in dry thf (50.0 mL). Then, $MgCl_2$ (156.5 mg, 1.64 mmol) was added to the reaction. The mixture was stirred for 5 h; then all volatiles were evaporated. The remaining white solid was dried in vacuo and recrystallized from tetrahydrofuran and diethyl ether (306.0 mg, 85.0%). Crystals suitable for single crystal X-ray analysis were obtained from tetrahydrofuran/diethyl ether. ^{1}H NMR ($CDCl_3$): δ = 1.71 (b, thf), 2.16 (s, 12 H, *o*-CH_3), 2.36 (s, 6 H, *p*-CH_3), 3.62 (b, thf), 7.02 (s, 4 H, Mes), 7.07 (s, 2 H, N-CH_2) ppm. ^{13}C NMR ($CDCl_3$): δ = 18.0, 21.2, 25.2 (thf), 69.3 (thf), 122.9, 129.3, 135.0, 135.7, 139.6, 181.9 ppm. FTIR (ATR): $\tilde{\nu}$ = 2916 (br), 1605 (m), 1538 (m), 1450 (br), 1227 (m), 1032 (br), 854 cm^{-1} (m).

Compound 2: 1-Ethyl-3-methylimidazolium bromide[27] (5.0 g, 26.18 mmol) was suspended in thf (100 mL). Potassium *tert*-butoxide (3.5 g, 31.19 mmol) was separately suspended in thf (10 mL) and added to the imidazolium bromide suspension. The reaction mixture was stirred for 16 h at room temperature. The resulting pink-colored reaction suspension was filtered through Celite to remove residual salts. The filtrate was transferred into a 250 mL Schlenk flask and removed from the glove box. Carbon dioxide was further bubbled through the solution at 0 °C for 30 min resulting in the precipitation of a white solid. The product was filtered and washed with diethyl ether (3.75 g, 93.0%). ^{1}H NMR (D_2O): δ = 1.36 (2 t, *J* = 7.5 Hz, 3 H), 3.80, 3.88 (s, 3 H), 4.09, 4.28 (2 q, *J* = 7.25 Hz, 2 H), 7.30 (dd, *J* = 2.0 Hz, 1 H), 7.37 (dd, *J* = 2.0 Hz, 1 H) ppm. ^{13}C NMR (D_2O): δ = 14.6, 15.3, 35.7, 36.7, 44.9, 45.3, 121.5, 122.0, 123.4, 123.6, 139.8, 158.7, 160.6 ppm. FTIR (ATR mode): $\tilde{\nu}$ = 3090 (w), 1624 (m, CO), 1325 (s), 1233 (m), 977 (m), 794 (m), 657 (m) cm^{-1}. MS (HRMS): calcd. for $C_7H_{10}N_2O_2$ 154.0742; found 309.1557 [2M + H]$^+$.

Compound 4: 1,3-Bis(2,4,6-trimethylphenyl)imidazolinium chloride (2.5 g, 7.30 mmol) was suspended in thf (50 mL). Potassium hydride (350 mg, 8.75 mmol) was separately suspended in thf (5.0 mL) and this suspension was added to the imidazolinium chloride suspension. The reaction mixture was stirred for 4 h and 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 resulting in the precipitation of a white solid. The product was filtered off and washed with diethyl ether (1.8 g, 70.0%). Single crystals suitable for X-ray analysis were obtained from CH_2Cl_2 at –5 °C. Absolutely identical ^{13}C NMR spectra, but different ^{1}H NMR spectra were obtained from different batches. Therefore, both ^{1}H NMR spectra are reported. ^{1}H NMR (CD_3OD): δ = 2.28, 2.32 (s, 6 H of *p*-mes), 2.40, 2.44 (s, 12 H, *o*-Mes), 4.36, 4.49 (s, 4 H, CH_2), 6.99, 7.09 (s, 4 H, Mes) ppm. ^{1}H NMR (CD_3OD): δ = 2.33 (s, 6 H, *p*-Mes), 2.40 (s, 12 H, *o*-Mes), 4.51 (s, 4 H, CH_2), 7.10 (s, 4 H, Mes) ppm. ^{13}C NMR (CD_3OD): δ = 17.6, 21.0, 52.4, 131.0, 131.9, 136.6, 142.0, 161.4 ppm. FTIR (ATR): $\tilde{\nu}$ = 2956 (w), 1674 (s, CO), 1547 (m), 1439 (m), 1264 (s), 855 (s) cm^{-1}. MS (ESI): *m*/*z* = 351.2 $[M + H]^+$.

Compound 5: In a 50 mL Schlenk tube equipped with a stirring bar, 1,3-dimesitylimidazolium-2-carboxylate[20] (300 mg, 0.86 mmol) was suspended in benzene (15 mL); zinc chloride (117.0 mg, 0.86 mmol) was then added to the suspension. The Schlenk tube was taken out of the glove box and placed in a 85 °C oil bath. After 2 h of stirring, the Schlenk tube was cooled to room temperature. The solvent was removed in vacuo, and the Schlenk tube was taken inside the box again. The crude reaction mixture was dissolved in dichloromethane. The solution was filtered through glass fiber filter paper. Evaporation of CH_2Cl_2 resulted in a white solid (338 mg, 89.0%). ^{1}H NMR ($CDCl_3$): δ = 7.04 (s, 2 H), 6.9 (s, 4 H), 2.31 (s, 6 H), 2.0 (s, 12 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 173.1, 139.3, 135.6, 133.9, 129.2, 123.0, 21.2, 17.9 ppm. FTIR (ATR mode): $\tilde{\nu}$ = 2919 (br), 1486 (m), 1403 (m), 1377 (m), 1230 (m), 1106 (m), 930 (m), 850 (s), 752 (s) cm^{-1}. MS (ESI): *m*/*z* = 845.16 $[M - Cl]^+$. $C_{42}H_{48}Cl_4N_4Zn_2$ (876.12): calcd. C 57.23, H 5.49, N 6.36; found C 57.01, H 5.51, N 6.28.

Compound 6: In a 50 mL Schlenk tube equipped with a stirring bar, 1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-1-ium-2-carboxylate (300 mg, 0.82 mmol) was suspended in benzene (15 mL); zinc chloride (113.0 mg, 0.82 mmol) was then added to the suspension. Then, the Schlenk tube was taken out of the glove box and placed in a 85 °C oil bath. After 2 h of stirring, the Schlenk tube was cooled to room temperature. The solvent was removed in vacuo, and the Schlenk tube was taken inside the box again. The crude reaction mixture was dissolved in dichloromethane. The solution was filtered through glass fiber filter paper. Evaporation of CH_2Cl_2 resulted in a white solid (340 mg, 90.0%). ^{1}H NMR ($CDCl_3$): δ = 6.96 (4 H, Mes), 3.45 (t, *J* = 2.25 Hz, 4 H, N-CH_2), 2.39 (2 H, CH_2), 2.36 (s, 12 H), 2.27 (s, 6 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 194.7, 153.3, 140.2, 139.7, 139.5, 136.8, 135.7, 134.7, 130.3, 130.0, 128.4, 47.6, 45.1, 21.2, 21.1, 20.4, 19.6, 18.2, 18.0 ppm. FTIR (ATR mode): $\tilde{\nu}$ = 2917 (br), 1663 (s), 1516 (m), 1310 (s), 1207 (s), 850 (s) cm^{-1}. MS (ESI): *m*/*z* = 877.21 $[M - Cl]^+$.

Compound 8: In a 10 mL vial equipped with a stirring bar, 1,3-bis-(2,4,6-trimethylphenyl)imidazol-2-ylidene (250.0 mg, 0.82 mmol) was dissolved in benzene. Then, aluminum chloride (110.0 mg, 0.81 mmol) was added. The reaction was stirred for 3 h, and then all volatiles were evaporated. The remaining white solid was dried in vacuo and recrystallized from CH_2Cl_2 and diethyl ether (306.0 mg, 85%). Crystals suitable for single crystal X-ray analysis were obtained from CH_2Cl_2/diethyl ether. ^{1}H NMR ($CDCl_3$): δ = 2.13 (s, 12 H, *o*-CH_3), 2.36 (s, 6 H, *p*-CH_3), 7.02 (s, 4 H, Mes), 7.21 (s, 2 H, N-CH_2) ppm. ^{13}C NMR ($CDCl_3$): δ = 17.7, 21.3, 124.7, 129.5, 133.2, 135.3, 140.4 ppm. HRMS: calcd. for $C_{21}H_{24}AlCl_3N_2$ 436.0820; found 436.0679. FTIR (ATR): $\tilde{\nu}$ = 2917 (br), 1603 (m), 1543 (m), 1480 (br), 1230 (s), 1127 (m), 1030 (m), 850 cm^{-1}.

Compound 9: In a 10 mL vial equipped with a stirring bar, 1,3-bis-(2,4,6-trimethylphenyl)imidazolin-2-ylidene (200.0 mg, 0.65 mmol) was dissolved in benzene. Then, aluminum chloride (87.0 mg, 0.65 mmol) was added. The reaction was stirred for 3 h; then all volatiles were evaporated. The remaining white solid was dried in vacuo and recrystallized from dichloromethane and diethyl ether (238.2 mg, 83% Yield). ^{1}H NMR ($CDCl_3$): δ = 2.31 (s, 6 H, *p*-CH_3), 2.37 (s, 12 H, *o*-CH_3), 4.06 (s, 4 H, N-CH_2), 6.97 (s, 4 H, Mes) ppm. ^{13}C NMR ($CDCl_3$): δ = 18.2, 21.2, 51.8, 130.0, 132.8, 136.2, 139.9 ppm. HRMS: calcd. for $C_{21}H_{26}AlCl_3N_2$ 438.0977; found 438.0988. FTIR (ATR mode): $\tilde{\nu}$ = 2921 (br), 1630 (m), 1494 (br), 1455 (m), 1276 (s), 1191 (m), 1033 (m), 948 (s), 850 cm^{-1}.

Typical Procedure for the Recording of the Reaction Kinetics: The catalyst (14.0 mmol-% with respect to DABCO; DABCO was used on 1.0 wt.-% base) was dissolved in a minimum amount of CH_2Cl_2. Then, 2 wt.-parts of Desmophen A870 BA (polyol), 1 wt.-part of Desmodur N 3390 BA (isocyanate) (corresponding to a 1:1 molar ratio) were added to the catalyst solution. The mixture was mixed for 3.0 min, and then a small drop was taken from the mixture and polyaddition kinetics were measured by real-time FTIR by using a BIO-RAD FTS 6000 spectrometer for 2 h.

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 CH_2Cl_2. Then, 2 wt.-parts of Desmophen A870 BA (polyol), 1 wt.-part of Desmodur N 3390 BA (isocyanate) (corresponding to a 1:1 molar ratio) were added to the catalyst solution. The mixture was mixed for 3.0 min, kept at room temperature for 45 min, and then the temperature was raised to 65 °C. The entire process was monitored by real-time FTIR by using a BIO-RAD FTS 6000 spectrometer.

Typical Procedure for Isocyanurate Formation: A solution of phenyl isocyanate (1:1 v/v in thf) was added to an oven-dried 25 mL Schlenk tube containing 1,3-dimesityl-4,5-imidazolinium-2-carboxylate (3.0 mg, 1.0 mol-% with respect to the isocyanate). The reaction mixture was stirred at 65 °C for 12 h. Yields were determined by GC–MS.

Typical Procedure for the Cyclotrimerization of HMDI Trimer: Catalyst **3** (1.0 mol-%, 3.5 mg; with respect to HMDI trimer) was dissolved in a minimum amount of dichloromethane; HMDI trimer (0.5 g) was added to the catalyst solution. The reaction mixture was mixed and heated to 65 °C for 1 h, during this time a white solid of polymeric HMDI trimer was obtained. Yield: 495.0 mg, 99.0%. FTIR (ATR mode): $\tilde{\nu}$ = 2931 (br), 2358 (br), 2264 (m, free NCO), 1675 (s, CO), 1454 (br), 1423 (br) cm^{-1}.

X-ray Analyses for 1, 4, and 8: Data were collected with a Nonius KappaCCD diffractometer equipped with graphite-monochromatized Mo-K_α-radiation and a nominal crystal to area detector distance of 36 mm. The structures were solved with direct methods SHELXS86 and refined against F^2 SHELX97. All non-hydrogen atoms were refined with anisotropic displacement parameters and positions of hydrogen atoms were calculated. CCDC-711502 (for **1**), -711503 (for **4**), and -711504 (for **8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge form The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): X-ray and structural data of compounds **1**, **4**, and **8**; pseudo-second-order kinetic graphs for compounds **1** and **3**–**5**, kinetic plots of PUR formation under the action of $MgCl_2$, $Zn(CH_3COO)_2$, $ZnCl_2$, **5**, and **7**.

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