Polyurethanes, manufactured from aromatic and aliphatic isocyanates (1), are an important class of high-performance materials. Aliphatic polyisocyanates are the preferred building blocks for coatings and most are based on hexamethylene disiocyanate (HDI). For the majority of applications, oligomers of HDI with significantly lower vapor pressure than that of the monomer are required. These oligomers are predominantly cyclo-oligomers, such as uretdiones 2, isocyanurates 3, and iminoxadiazinediones 4, which can be prepared by catalytic cyclo-oligomerization of monomeric isocyanates.

Although phosphines, including tri-n-butylphosphine (5), have been used commercially as catalysts for more than 20 years, no information is available on the mechanism of the reaction. Based on the reactivity of nucleophiles towards heterocumulenes, the reaction may start by the nucleophilic attack of the phosphine on the carbonyl group of the isocyanate to form a zwitterionic intermediate A, followed by reaction with another isocyanate moiety to result in a second zwitterionic intermediate B (Scheme 1). Although an intramolecular nucleophilic attack by the \(^{-}\text{O(RN)}^{-}\) ion on the carbonyl group of B could lead to the formation of 2 and 5, the addition of another isocyanate moiety could result in the formation of zwitterionic intermediates \(\text{C}_1\) and \(\text{C}_2\). Similarly,
intramolecular nucleophilic attack by the $-\overset{\infty}{O}(\text{RN})-$ ion on the carbonyl group of C1 and C2 could lead to the formation of isocyanurates 3 or iminooxadiazinediones 4, respectively, and the reformation of 5. We report herein the first structural characterization of B by in situ spectroscopic studies.

The cyclo-oligomerization of alkyl isocyanates (RNCO: $R = n$-butyl and $n$-hexyl 1a and 1b, respectively) was studied by in situ IR spectroscopy in the presence of various amounts of 5 in the temperature range 20–80°C.[8] Even in the presence of a slight excess of 5 (4.8 mmol) in relation to 1a (4.4 mmol), only the peaks assigned to products 2a, 3a, and 4a (1771; 1694; and 1791, 1719, and 1687 cm$^{-1}$, respectively) could be observed at 20°C (Figure 1).[9] At the beginning of the reaction, the rate of the formation of 2a is higher than that of 3a and 4a, but its concentration reaches a maximum after five hours, thus indicating that the reaction of 2a with 1a or yields 3a and 4a in almost constant ratios. When 12.2 mmol of 2a was treated with 1.22 mmol of 5, the formation of free isocyanates 1a, 3a, and 4a was observed (Figure 2), thus providing direct evidence that the formation of 2a is a reversible process.

As the in situ IR investigations only showed the formation of the products, we used in situ $^1$H, $^{13}$C, and $^{31}$P NMR spectroscopy to confirm these results and to structurally characterize the intermediates. During the tri-n-butylphosphine-catalyzed cyclo-oligomerization of 1a, we observed again the initial formation of 2a followed by the appearance of 3a and 4a.[10] The concentration of 2a goes to a maximum value, as expected, and at the end of the reaction the ratio of 2a/3a/4a is always equal to 0.2:2:1. The in situ NMR spectroscopic analysis of the reaction of 2a with 5 also confirmed the formation of free 1a, 3a, and 4a. On the contrary, no reaction was observed when the mixture of 3a and 4a was treated with 5, thus indicating that neither the ring opening of 3 and 4 nor the interconversion between 3 and 4 occurs.[10] Similar results were obtained when 1b was used as the monomer.

Next, we used $^{31}$P NMR spectroscopy to observe the possible intermediate(s) in the reaction between 1b and 5 in ratios of 1:1, 2:1, and 3:1, thus leading to A, B, and C1 and C2, respectively. Only one resonance at $\delta = -32.9$ ppm (linewidth (LW) = 1 Hz) was observed for 5 at 297 K (Figure 3). By lowering the temperature to 250 K, the appearance of a new, sharp peak is observed at $\delta = -54.0$ ppm (LW = 7 Hz). This peak begins to broaden when the temperature increases from 250 to 270 K (Figure 3) and finally disappears into the baseline at 275 K. It should be noted that below 250 K there is no change in the linewidth of this resonance and that there is no variation in the linewidth of free 5 over the whole temperature range studied. The observed dynamic phenomena can be explained by the fast exchange between the intermediate(s) and free isocyanate. The exact structure of the intermediate was delineated by using 99.0% $^{13}$C-labelled...
\textit{n}-hexyl isocyanate. The $^{31}$P NMR spectrum shows a doublet at $\delta = -54.0$ ppm, with a coupling constant of $J = 154$ Hz, thus indicating P–C coupling over a single bond ($J_{PC}$; Figure 3). This observation was confirmed by a doublet of doublets at $\delta = 166.7$ ppm in the $^{13}$C NMR spectrum. Besides the coupling constant exhibited by $J_{PC}$, a coupling constant of $J_{CC} = 2.5$ Hz indicates coupling to another C atom in a second -NC(O)- moiety. Accordingly, a doublet with the same $J_{CC}$ value appears at $\delta = 153.9$ ppm (Figure 4). The integral ratio of the peaks at $\delta = 166.7$ and 153.9 ppm is 1:1. These results confirm the presence of a P-$^{13}$C-N-$^{13}$C fragment and, thus, the formation of intermediate \textbf{B}. Finally, the temperature variation monitored by $^{13}$C[\textit{H}] spectra shows line broadening and disappearance for this intermediate at 275 K, as expected (Figure 5).

In conclusion, we have developed an understanding of the mechanism of the \textit{tri}-\textit{n}-butylphosphine-catalyzed cyclo-oligomerization of alkyl isocyanates at the molecular level and have structurally characterized one of the key catalytic intermediates for the first time. This information can be used to design new catalysts with built-in selectivity towards various oligomers. Finally, this reaction is a good example for organocatalysis—a rapidly developing field of contemporary homogeneous catalysis.

**Experimental Section**

\textit{n}-Butyl isocyanate, \textit{n}-hexyl isocyanate, and \textit{tri}-\textit{n}-butylphosphine were purified by vacuum distillation. Preparation of \textit{$^{13}$C}$\textit{n}$-hexyl isocyanate: \textit{n}-hexylamine (40.4 g, 0.4 mol) and triethylamine (121.4 g, 1.2 mol) were combined with CH$_2$Cl$_2$ (43.3 g, solvent) in a steel vessel, cooled to 0$^\circ$C, and pressurized with $^{12}$CO$_2$. The steel vessel containing the amine solution was connected with a lecture bottle containing 10 L of $^{13}$CO$_2$ (99.0% isotopic purity, 0.45 mol; Cambridge Isotope) and occasionally shaken. The pressure dropped from 4 to 2.6 bar within 15 h and remained constant thereafter. The vessel containing the carbamate salt solution was 17 g heavier than before, thus indicating an uptake of 0.38 mol of $^{13}$CO$_2$. After cooling to $24^\circ$C, the content of the steel vessel was transferred to a cooled (20$^\circ$C) solution of POCl$_3$ (73.6 g, 0.48 mol) in CH$_2$Cl$_2$ (50 mL). The resulting yellow–orange turbid mixture was extracted with deionized water (3 X 250 mL), the organic phase was dried with sodium sulfate and distilled to yield 23.6 g of product (99.6% pure, GC analysis; 0.18 mol, 48% yield based on $^{13}$CO$_2$ uptake). B.p. 39–40$^\circ$C at 5 mbar; $^1$H NMR (CDCl$_3$): $\delta = 3.3$ (t/d, $^3J_{HH} = 6.6$ Hz, $^3J_{CH} = 4.5$ Hz, 2H), 1.6 (quin, $^3J_{HH} = 6.6$ Hz, 4.5 Hz, 2H), 1.25–1.45 (m, 6H), 0.9 (t, $^3J_{HH} = 7$ Hz, 3H); $^{13}$C NMR (CDCl$_3$) intense signals at $\delta = 121.9$, 42.9 (d, $^3J_{CC} = 3.7$ Hz), 31.2, 31.1, 26.2, 22.5, 13.9 ppm.

IR spectra were collected under nitrogen on a ReactIR 1000 instrument using a SiComp probehead. A typical in situ IR experiment was performed by placing the alkyl isocyanate (I) onto a...
thermostated (± 0.5 °C) schlenk flask fitted with the IR probehead, a nitrogen inlet, a magnetic stirrer, and a septum. Tri-n-butylphosphine (5) was syringed into the schlenk flask after the data collection of the ReactIR 1000 was started.

\(^1\)H, \(^{13}\)C, and \(^{31}\)P NMR spectra were recorded on a Bruker AC 250 spectrometer. In a typical in situ NMR experiment, 1 was added into an NMR tube under nitrogen and 5 was added by syringe. The tube was immediately capped with a rubber septum and placed into the magnet for measurements at the preset temperature (± 0.05 °C) using standard Bruker pulse sequences.

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[6] Compounds of general formula P(NR\(_2\))\(_3\) are very selective catalysts for the formation of 2 (DE-A 3030513) but the carcinogenicity of their oxides prohibits a technical-scale application. Special aminopyridines (DE-A 3739549) selectively catalyze the formation of 2 from isophorone diisocyanate, but not for HDI or isocyanates containing exclusively NCO groups bound to a secondary carbon atom like hydrogenated methane diisocyanate or cyclohexyl isocyanate.
[9] Compounds 2a, 3a, and 4a were prepared and IR spectra (neat) were collected for the reference values.
[10] See the Supporting Information.