

## Beryllium

## 2019 IYPT Beryllium-Induced Conversion of Aldehydes

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**Abstract:** Aldehydes play a key role in the human metabolism. Therefore, it is essential to know their reactivity with beryllium compounds in order to assess its effects in the body. The reactivity of simple aldehydes towards beryllium halides (F, Cl, Br, I) was studied through solution and solid-state techniques and revealed distinctively different reactivities of the beryllium halides, with BeF<sub>2</sub> being the least and BeI<sub>2</sub> the most reactive. Rearrangement and aldol condensation reactions were observed and monitored by in situ NMR

spectroscopy. Crystal structures of various compounds obtained by Be<sup>2+</sup>-catalyzed cyclization, rearrangement, and aldol addition reactions or ligation of beryllium halides have been determined, including unprecedented one-dimensional BeCl<sub>2</sub> chains and the first structurally characterized example of an 1-iodo-alkoxide. Long-term studies showed that only aldehydes without a β-H can form stable beryllium complexes, whereas other aldehydes are oligo- and polymerized or decomposed by beryllium halides.

## Introduction

It is known that hard Lewis acids are able to catalyze the conversion of glucose into 5-(hydroxymethyl)furfural and subsequently into humins.<sup>[1–4]</sup> Hence, inhaled beryllium species should perform in a similar way in lung tissue, in which hexoses are abundant.<sup>[5]</sup> To what extent the Be<sup>2+</sup> cation is able to catalyze the conversion of carbonyl groups is therefore a subject of immense interest with regards to the alleged toxicity of beryllium in general and especially to understand the localization of beryllium-associated diseases to the lung.<sup>[6,7]</sup>

Lewis acids—especially aluminum chloride species—promote a wide variety of reactivities in aldehydes and are important for C–C bond formation, such as the carbonyl en reaction.<sup>[8–10]</sup> Furthermore, Lewis acidic metal chlorides are able to induce aldol condensation<sup>[11–13]</sup> and rearrangement reactions<sup>[14]</sup> or cyclization into trioxanes.<sup>[11–13]</sup> The latter is also well catalyzed by metal oxides or Me<sub>3</sub>SiCl.<sup>[15–17]</sup> Among the various Lewis acids, the activity of which towards aldehydes was examined, beryllium species, which are among the hardest known Lewis acids, have never been investigated. Only one beryllium aldehyde compound—a benzaldehyde adduct towards BeCl<sub>2</sub>

of which no reactivity had been investigated—was known so far.<sup>[18]</sup> The formation of BeCl<sub>2</sub> adducts towards carbonyl groups is also observed in esters<sup>[18,19]</sup> and ketones,<sup>[20]</sup> but to the best of our knowledge no experimental studies regarding a potentially altered reactivity of beryllium-coordinated carbonyl groups had been performed so far. Here, we present our findings regarding the reactivity of various simple aldehydes towards beryllium halides.

## Results and Discussion

All our experiments with BeF<sub>2</sub>, which is in theory the hardest Lewis acid of the investigated beryllium halides, showed that it does neither react with the investigated aldehydes nor dissolve in them or any of the used solvents. This is presumably caused by the significantly higher lattice energy of BeF<sub>2</sub> relative to those of the other beryllium halides<sup>[21]</sup> and is in line with the fact that only reactions of BeF<sub>2</sub> in water or liquid ammonia are known.<sup>[22,23]</sup>

Contrarily, BeCl<sub>2</sub> readily reacts in a wide variety of organic solvents. We started our investigations with pivaldehyde that has neither a proton in α position nor the direct ability for an aldol condensation reaction and was assumed to be the least reactive aliphatic aldehyde. Therefore, a reaction of BeCl<sub>2</sub> was performed with pivaldehyde in various stoichiometries on NMR scale. A brief summary of the obtained results is illustrated in Scheme 1. When few milligrams of BeCl<sub>2</sub> were dissolved in several milliliters of pivaldehyde the reaction mixture solidified within hours. This colorless solid can be sublimated in vacuo to yield centimeter-long single crystals of 2,4,6-tris-*tert*-butyl-1,3,5-trioxane (**1 a**, Figure 1) that crystallized in the monoclinic space group C2/c. This cyclization reaction is also known to be catalyzed by Lewis acids such as Me<sub>3</sub>SiCl, FeCl<sub>3</sub>, or metal oxides. BeCl<sub>2</sub> as a Lewis acid is therefore no exception. Subsequent reactions of pivaldehyde with catalytic amounts of BeBr<sub>2</sub>

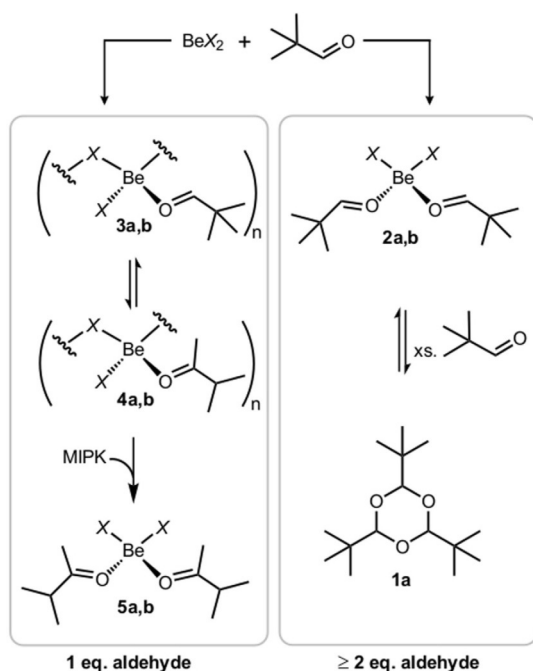
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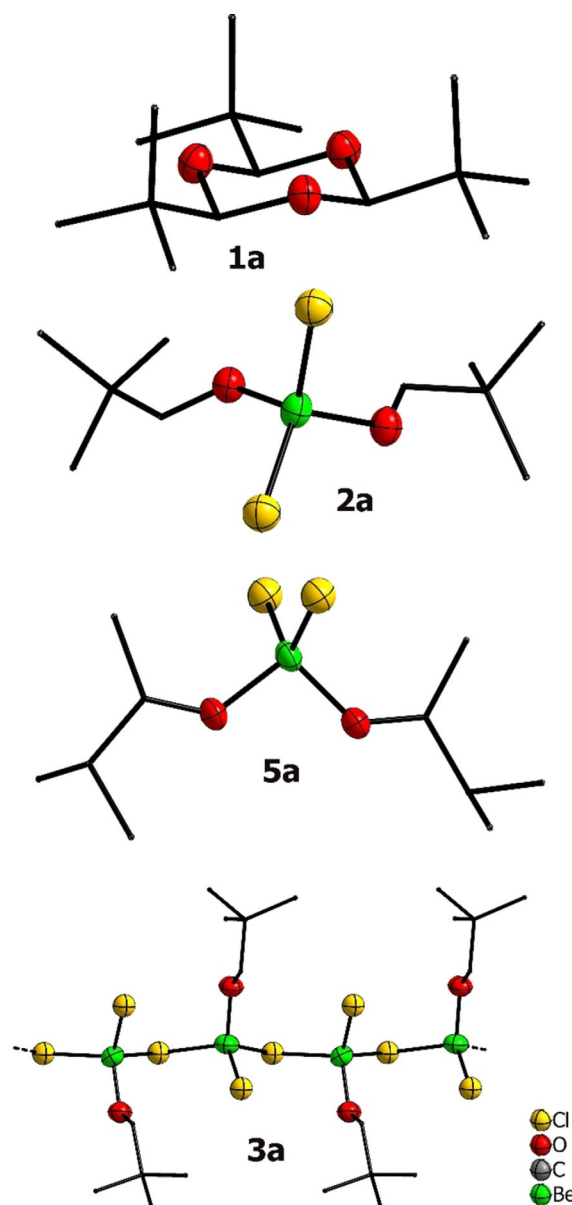
In celebration of the International Year of the Periodic Table.



**Scheme 1.** Schematic illustration of the reaction pathways for the formation of compounds **1 a**, **2 a,b**, **3 a,b**, **4 a,b**, and **5 a,b** depending on the amount of pivaldehyde (a: X = Cl; b: X = Br; MIPK = methyl isopropyl ketone).

and  $\text{BeI}_2$  led also to the formation of trioxane **1 a**, which was analyzed by X-ray diffraction, IR and NMR spectroscopy. The latter revealed its instability in polar solvents. Although stable in  $\text{C}_6\text{D}_6$ , it decomposes in  $\text{CDCl}_3$  to pivaldehyde. The same decomposition occurs when beryllium halides were added in stoichiometric amounts. Therefore, we used **1 a** instead of pivaldehyde as an aldehyde precursor for the following experiments because of its supreme purity and ease of use compared to the free aldehyde.

If  $\text{BeCl}_2$  was treated with two or more equivalents of pivaldehyde in  $\text{CDCl}_3$  a clear colorless solution was obtained.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopic experiments revealed that the pivaldehyde moiety was stable for several weeks, whereas the different chemical shifts of the signals, in comparison to the free ligand, indicated a coordination towards  $\text{BeCl}_2$  (see also Table 1). In the  $^9\text{Be}$  NMR spectrum we observed one sharp singlet at 5.8 ppm ( $\omega_{1/2} = 4.9$  Hz) that is typical for tetrahedral coordinated Be nuclei.<sup>[24]</sup> By removing the solvent, crystals of dichlorobis(2,2-dimethylpropanal)beryllium(II) (**2 a**) could be obtained as colorless blocks. Compound **2 a** crystallizes in the monoclinic space group  $P2_1/c$ . In this compound  $\text{BeCl}_2$  is coordinated by two pivaldehyde molecules leading to a tetrahedral coordination sphere around the beryllium atom, which is a typical structural motive for  $\text{BeCl}_2$  coordinated by electron-donating functional groups.<sup>[18,19,25]</sup> The molecular structure of **2 a** is illustrated in Figure 1. The Be–Cl atomic distances of 1.9595(18) and 1.9717(17) Å correspond to those in the  $\text{BeCl}_2$  benzaldehyde adduct with 1.9623(19) and 1.982(2) Å. The Be–O atomic distances in **2 a** of 1.6819(18) and 1.6925(19) Å are, however, significantly longer than those in the benzaldehyde



**Figure 1.** Molecular structures of compounds **1 a**, **2 a**, **5 a**, and **3 a** (from top to bottom). Ellipsoids are depicted at 70% probability at 100 K. Hydrogen atoms are omitted and carbon atoms are shown as wire frame for clarity (see Supporting Information Figures 1, 2, 4, 5 for molecular structures with all non-hydrogen atoms represented as ellipsoids). Subfigures are not to scale with each other.

complex [1.664(2) and 1.665(2) Å].<sup>[18]</sup> This might be caused by the larger steric bulk of the pivaldehyde. In the IR spectrum of **2 a** we observed a bathochromic shift for the C=O-stretching frequency of  $61\text{ cm}^{-1}$  relative to that of non-coordinated pivaldehyde, indicating a weakening of the C=O double bond because of the coordination towards  $\text{BeCl}_2$ . This is in agreement with our findings on the benzaldehyde adduct.<sup>[18]</sup>

When  $\text{BeCl}_2$  was treated with only one equivalent of pivaldehyde we also obtained a clear and colorless solution. The in situ NMR spectra recorded a few hours after the reaction was initiated, showed the same set of peaks as that of compound **2 a** though with different chemical shifts. A broad singlet in

**Table 1.** Selected chemical shifts and coordination shifts of the investigated compounds.  $\Delta\delta(^1\text{H})$ : shift of aldehyde proton ( $\text{CH}(\text{O})$ ) relative to that of free ligand,  $\delta(^9\text{Be})$ : chemical shift of Be nucleus,  $\Delta\delta(^{13}\text{C})$ : shift of aldehyde carbon atom ( $\text{CH}(\text{O})$ ) relative to that of free ligand.

	$\Delta\delta(^1\text{H})$ [ppm]	$\delta(^9\text{Be})$ [ppm]	$\Delta\delta(^{13}\text{C})$ [ppm]
<b>2a</b>	0.11	5.8	17.2
<b>2b</b>	0.30	5.4	18.6
<b>2c</b>	0.47	2.7	20.0
<b>3a</b>	0.25	5.0	17.8
<b>3b</b>	0.33	2.6	19.2
<b>4a</b>	–	4.3	22.1
<b>4b</b>	–	2.7	20.9
<b>4c</b>	–	–1.0	20.8
<b>5a</b>	–	4.7	18.8
<b>5b</b>	–	3.4	20.1
<b>5c</b>	–	2.7	24.1
<b>6</b>	0.47	4.1	20.0
<b>11</b>	–	3.0	–
<b>14</b>	0	5.3	9.6

the  $^9\text{Be}$  NMR spectrum at 5.0 ppm ( $\omega_{1/2}=21.1$  Hz) speaks for an increase in electron density around the beryllium nucleus relative to that in **2a**, whereas the significantly broader line width is indicative of a more fluxional compound in solution. When the solvent of a solution with 1:1 ratio of  $\text{BeCl}_2$ / pivaldehyde was removed in vacuo immediately after the starting materials had dissolved, single crystals of poly[dichloro- $\mu_2$ -2,2-dimethylpropanalberyllium(II)]- $\text{C}_6\text{H}_6$  (**3a**) were obtained from a colorless oil. A detail of its crystal structure is illustrated in Figure 1. It features one-dimensional  $\mu_2$ -Cl linked  $\text{BeCl}_2$  chains coordinated by one pivaldehyde per beryllium atom. The Be–Cl atomic distances of the terminal chloride atoms are 1.946(4) and 1.952(4) Å, comparable with those of compound **2a**, whereas the  $\mu_2$ -Cl–Be atomic distances range from 2.056(4) to 2.066(4) Å and are therefore significantly longer. These distances are comparable to those reported for  $[\text{Be}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{PCy}_3)_2]$ .<sup>[26]</sup> The Be–O atomic distances are 1.643(4) and 1.646(4) Å; significantly shorter than the corresponding distances for the aldehyde adducts mentioned above. This stronger interaction is expected because of the coordination of only one aldehyde towards this  $\text{BeCl}_2$  chain, which results in less steric repulsion. This is also supported by the larger coordination shifts observed in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, and the broad line widths of the NMR signals suggest that various oligomers are present in solution that exchange relatively rapidly on the NMR time scale. However, in the IR spectra of the dry residue of the reaction mixture of **3a** we observed a set of bands nearly identical to that of **2a**, and the C=O-stretching frequency of  $1662\text{ cm}^{-1}$  equals that of compound **2a**.

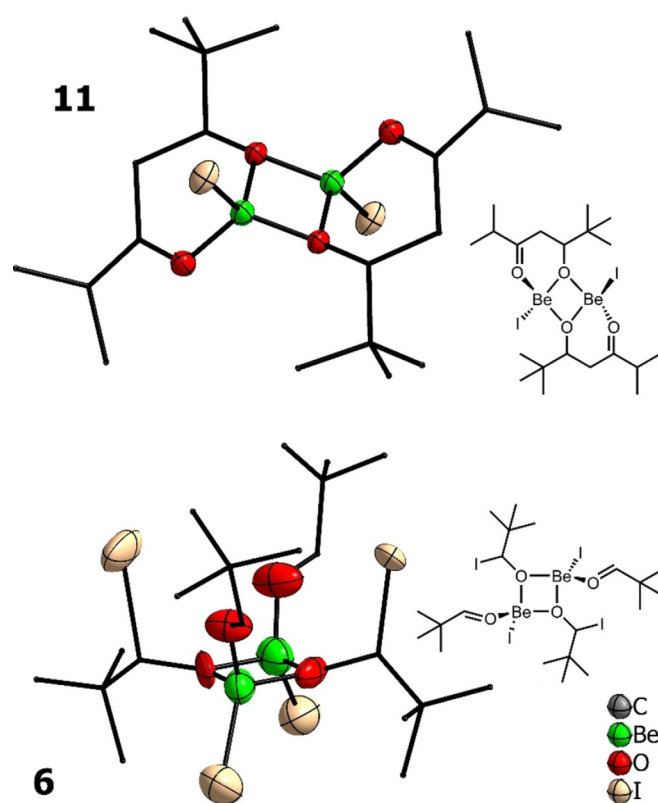
When the solution with a 1:1 ratio of  $\text{BeCl}_2$ /pivaldehyde was stored for several weeks, the NMR spectra changed (see also Supporting Information Figures 10–12). The former singlet in the  $^9\text{Be}$  NMR spectrum at 5.0 ppm shifted within six weeks to 4.3 ppm ( $\omega_{1/2}=13.9$  Hz) indicating the formation of a new, less fluxional species with increased electron density at the beryllium nucleus. We also observed a new signal set in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, which could be assigned to 3-methyl-2-butanone (methyl isopropyl ketone, MIPK) coordinated to  $\text{BeCl}_2$

(**4a**). To verify this we treated  $\text{BeCl}_2$  with one equivalent of MIPK and obtained matching NMR spectra. To figure out if MIPK can be converted to pivaldehyde by  $\text{BeCl}_2$  we monitored a 1:1 reaction mixture of MIPK and  $\text{BeCl}_2$  in  $\text{CDCl}_3$  over time. However, even after several weeks we did not observe any change in the NMR spectra, which leads to the conclusion that the rearrangement reaction is nonreversible in the presence of  $\text{BeCl}_2$ . In an additional control experiment  $\text{BeCl}_2$  was treated with two equivalents of MIPK. In the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra we observed only signals for MIPK and even several weeks later no change was observed. In the  $^{13}\text{C}$  NMR spectra we noticed a downfield shift of 18.8 ppm for the carbonyl carbon atom relative to that of the free butanone, which is similar to the coordination shift of compound **2a** relative to that of free pivaldehyde (see Table 1). This indicates a depletion of electron density at the carbonyl group. In the  $^9\text{Be}$  NMR spectrum one singlet is observed at 4.7 ppm ( $\omega_{1/2}=8.0$  Hz) and therefore shifted downfield in relation to the signal of compound **4a**. This shift difference is comparable to the one observed between compounds **2a** and **3a** and indicates that the electron density at the beryllium nuclei is higher in complexes in which only one carbonyl oxygen atom is coordinated. By removing the solvent in vacuo, we obtained rod-shaped crystals of dichloridobis(3-methyl-2-butanone)beryllium(II) (**5a**). This butanone adduct of  $\text{BeCl}_2$  crystallizes in the monoclinic space group  $C2/c$  and shows the same coordination around the Be atom as that described for **2a** with Be–Cl atomic distances of 1.983(3) and 1.987(3) Å, which are slightly longer than those of **2a**. On the other hand, the Be–O atomic distances of 1.659(3) and 1.669(3) Å are slightly shorter than the corresponding distances in **2a** suggesting that MIPK coordinates stronger to  $\text{BeCl}_2$  than pivaldehyde. This is in agreement with the upfield shift of the  $^9\text{Be}$  NMR signal. However, in the IR spectrum of **5a** the bathochromic shift for the C=O-stretching frequency of  $61\text{ cm}^{-1}$  is identical to that of **2a**.

If  $\text{BeBr}_2$  was treated with two or more equivalents of pivaldehyde a clear brownish solution was obtained. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra recorded initially showed a signal set for pivaldehyde shifted downfield from that of free pivaldehyde in a scale comparable to that of **2a**. In the  $^9\text{Be}$  NMR spectrum we observed a singlet at 5.4 ppm ( $\omega_{1/2}=3.0$  Hz). After removal of the solvent in vacuo we obtained colorless needle-shaped crystals of dibromobis(2,2-dimethylpropanal)beryllium(II) (**2b**, Supporting Information, Figure 2) from an oily residue. Compound **2b** crystallizes isotopic to **2a** in the monoclinic space group  $P2_1/c$ . The Be–O atomic distances are 1.653(5) and 1.657(6) Å and therefore shorter than those in **2a** but within the standard deviation identical to those in **3a**. This indicates a stronger interaction between pivaldehyde and  $\text{BeBr}_2$  relative to  $\text{BeCl}_2$  and is supported by the more pronounced NMR coordination shifts of the aldehyde proton and the carbonyl carbon nuclei in **2b** relative to **2a**. The Be–Br atomic distances are 2.118(5) and 2.141(5) Å, comparable to those in the acetonitrile compound  $[\text{BeBr}_2(\text{CH}_3\text{CN})_2]$  [2.146(5); 2.147(5) Å]<sup>[27]</sup> but shorter than those in adduct  $[\text{BeBr}_2(\text{Et}_2\text{O})_2]$  [2.170(8); 2.176(8) Å].<sup>[28]</sup> The IR spectrum of **2b** is similar to that of **2a** with a comparable coordination shift of the C=O-stretching frequency of  $66\text{ cm}^{-1}$ .

When  $\text{BeBr}_2$  was treated with only one equivalent of pivaldehyde we also observed the initial formation of the mono-aldehyde adduct to  $\text{BeBr}_2$  (**3b**) as evident from the downfield coordination shifts of the aldehyde proton and carbonyl carbon signals in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, which are comparable to those of **3a**. Compound **3b** gives rise to a  $^9\text{Be}$  NMR signal at 2.6 ppm ( $\omega_{1/2} = 13.5$  Hz). After six weeks we also observed the quantitative conversion of pivaldehyde to MIPK as well as the emergence of a new singlet at 2.7 ppm ( $\omega_{1/2} = 8.7$  Hz) in the  $^9\text{Be}$  NMR spectrum, leading to the conclusion that the same rearrangement reaction occurs like that described for  $\text{BeCl}_2$ . This was also verified by the reaction of one equivalent of  $\text{BeBr}_2$  with one equivalent of MIPK, which resulted in matching NMR spectra. Reaction of  $\text{BeBr}_2$  with two equivalents of MIPK in  $\text{CDCl}_3$  led, in analogy to  $\text{BeCl}_2$ , to the formation of the bis-ketone adduct **5b** with a  $^9\text{Be}$  NMR signal at 3.4 ppm ( $\omega_{1/2} = 4.1$  Hz). Solutions of complex **5b** proved to be stable for over six weeks such as those of **5a**. However, it was neither possible to obtain single crystals of the butanone adduct **5b** nor of the mono-pivaldehyde adduct **3b** similar to **3a**. In both cases a brownish oil was obtained.

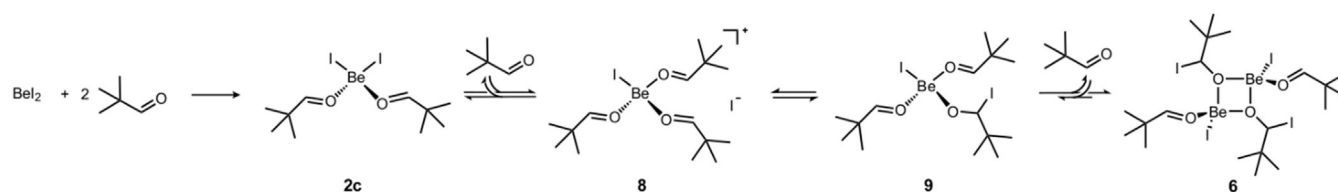
Finally, we investigated how  $\text{BeI}_2$  interacts with pivaldehyde and trioxane **1a**. Although it behaved like  $\text{BeCl}_2$  and  $\text{BeBr}_2$  when applied in catalytic amounts, it showed a distinctively different behavior when applied in equimolar amounts. When  $\text{BeI}_2$  was treated with three equivalents of pivaldehyde in  $\text{CDCl}_3$  we obtained a brownish solution that darkened within two weeks to give a brown opaque solution. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of a freshly prepared solution showed primarily signals for pivaldehyde coordinating towards beryllium iodide (Figure S18). Therefore, we assume that the formation of diiodobis(2,2-dimethylpropanal)beryllium(II) (**2c**) analogous to **2a** and **2b** occurred. However, the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra recorded directly after the reagents were dissolved already showed additional signals to those assigned to **2c**. In the  $^9\text{Be}$  NMR spectrum three signals at 4.1, 2.7, and 4.9 ppm were observed. On the basis of the assignment of the signals from **2a** and **2b** the singlet at 2.7 ppm ( $\omega_{1/2} = 36.3$  Hz) was assigned to **2c**. Over the course of a week, the intensity of the  $^9\text{Be}$  NMR signal at 4.1 ppm increased while the other two declined accordingly (Figure S19). In the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra the intensity of the signals of pivaldehyde also decreased and a variety of new signals could be observed. After  $\text{CDCl}_3$  was removed in vacuo a brown oil was obtained that contained rod-shaped single crystals of bis(2,2-dimethylpropanal)bis( $\mu_2$ -[1-iodo-2,2-dimethylpropan-1-ol])diiododiberyllium(II) (**6**, Figure 2), which crystallizes in the orthorhombic space group  $Pna2_1$ . This is the compound from which the  $^9\text{Be}$  NMR signal at 4.1 ppm originates. Compound **6** features a four-membered ring of two beryllium atoms that are linked through two  $\mu_2$ -oxygen atoms of two corresponding 1-iodo-2,2-dimethylpropan-1-olate (**7**) molecules, which is, to the best of our knowledge, the first structurally characterized example of an 1-iodo-alkoxide. Each beryllium atom is also coordinated by an iodine atom and an oxygen atom of a pivaldehyde molecule to complete the tetrahedral coordination sphere around the beryllium atom. The Be–O atomic distances inside the ring in **6** range from 1.56(4)



**Figure 2.** Molecular structures of compounds **6** (bottom) and **11** (top), including their formula. Ellipsoids are depicted at 70% probability at 100 K. Hydrogen atoms are omitted and carbon atoms are shown as wire frame for clarity (see Supporting Information Figures 6 and 7 for molecular structures with all non-hydrogen atoms represented as ellipsoids). Subfigures are not to scale with each other.

to 1.70(4) Å and those to the pivaldehyde molecule are 1.63(4) and 1.68(4) Å, which are within the standard deviation identical. The Be–O atomic distances between the beryllium atoms and the pivaldehyde molecules are within the standard deviation also identical to those of the adducts **2a** and **2b** because of the low precision of the data obtained. The Be–I atomic distances are 2.30(3) and 2.36(4) Å, thus comparable to the Be–I atomic distances found in  $\text{BeI}_2$  that range from 2.403(1) to 2.446(1) Å.<sup>[29]</sup> A few crystals were separated from the oil and an IR spectrum was recorded subsequently. The carbonyl stretching frequency of 1664  $\text{cm}^{-1}$  is similar to that of compounds **2a** and **2b**. The formation of 1-iodo-2-methylpropan-1-ol could additionally be verified by NMR spectroscopy. In the reaction mixture of **6** a singlet at 6.71 ppm in the  $^1\text{H}$  NMR spectrum was assigned to the *t*Bu-CHOI proton because of its  $^3J_{\text{CH}}$  coupling to a *tert*-butyl group observed in the HMBC NMR spectrum and no coupling in the COSY NMR spectrum as expected. The singlet at 1.08 ppm in the  $^1\text{H}$  NMR spectrum that is also present in the  $^1\text{H}$  NMR spectrum recorded initially was assigned to the *tert*-butyl group. This means that the conversion of the pivaldehyde to 1-iodo-2-methylpropan-1-ol takes place rapidly. However, we did not observe complete conversion even after several weeks. A plausible reaction pathway for this conversion is illustrated in Scheme 2; higher pivaldehyde concentrations also led to the formation of 1-iodo-2-methyl-



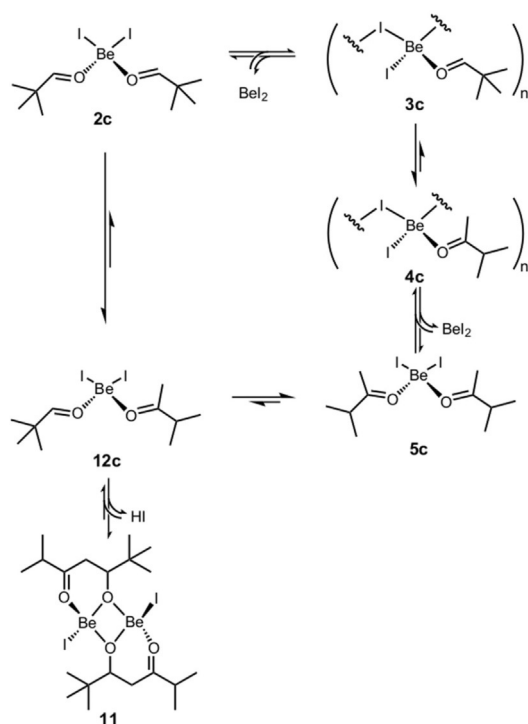


**Scheme 2.** Schematic illustration of the reaction pathway for the formation of compound **6**.

propan-1-ol. After coordination of two aldehydes one iodo ligand is displaced by a third aldehyde because of the weak Be–I bond generating the cationic tris-aldehyde complex **8**.<sup>[30]</sup> Because of the increased Lewis acidity of the cationic complex subsequent nucleophilic attack of iodide at one of the coordinated aldehydes is then facilitated. This leads to the formation of alcoholate **9**. After dissociation of one aldehyde, compound **6** is formed, which is presumably due to the superior coordination abilities of the negatively charged alcoholate compared to those of the aldehyde. We therefore assume that the signal at 4.9 ppm in the <sup>9</sup>Be NMR spectrum, which was observed in the beginning of the reaction, is caused by cationic species **8**.

Furthermore, reaction mixtures of BeI<sub>2</sub> with two or less equivalents of pivaldehyde showed a completely different reactivity, which is summarized in Scheme 3. When a reaction of pivaldehyde with BeI<sub>2</sub> was performed in a one-to-one ratio, one signal set for beryllium-coordinated pivaldehyde was observed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, indicating the formation of mono-aldehyde adduct **3c**. However, three broad singlets at 4.9, 4.1, and 2.7 ppm, which were also present in the three-to-one reaction mixture and belong to compounds **8**, **6**,

and **2c**, respectively, were observed by <sup>9</sup>Be NMR spectroscopy. This was presumably caused through an initial excess of aldehyde that was due to undissolved BeI<sub>2</sub>. While the signal at 4.9 and 4.1 ppm disappeared within one week and the one at 2.7 ppm decreased, two additional signals appeared at 0.9 and –1.0 ppm. During this reaction an additional organic intermediate was formed, which was identified by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy as well as mass spectrometry as 5-hydroxy-2,6,6-trimethylheptan-3-one (**10**). This is the aldol addition product of pivaldehyde and MIPK. After two weeks, only the signal at –1.0 ppm ( $\omega_{1/2}$  = 3.7 Hz) remained and only one signal set for MIPK was observable in the <sup>1</sup>H and <sup>13</sup>C NMR spectra with no pivaldehyde left; therefore, poly[diiodo- $\mu_2$ -3-methyl-2-butanoneberyllium] (**4c**) was formed (see also Supporting Information, Figures 20–22). To confirm this assumption we performed a reaction of BeI<sub>2</sub> with MIPK in a one-to-one ratio in CDCl<sub>3</sub> and obtained the same signals in the <sup>1</sup>H, <sup>13</sup>C, and <sup>9</sup>Be NMR spectra. Thus, BeI<sub>2</sub> shows a higher potential in promoting the rearrangement reaction of pivaldehyde into MIPK compared to BeCl<sub>2</sub> and BeBr<sub>2</sub>. However, no single crystals of **4c** were obtained. Compound **10** together with MIPK was also obtained when two equivalents of pivaldehyde were treated with one equivalent of BeI<sub>2</sub> in CDCl<sub>3</sub>. In situ <sup>9</sup>Be NMR reaction monitoring revealed the formation of **8** and **2c** within the first hour of reaction because of an initial excess of aldehyde caused by undissolved BeI<sub>2</sub> (see also Supporting Information, Figures 23–25). After four weeks one major signal at 3.0 ppm, which we assign to a beryllium species (**11**) coordinated to **10**, together with three smaller signals at 4.1 (**6**), 2.7 (**5c**), and 0.9 ppm were observed. The signal assignments to **5c** (2.7 ppm,  $\omega_{1/2}$  = 7.3 Hz) were confirmed through the reaction of BeI<sub>2</sub> with two equivalents of MIPK. Additionally, HI was observed in the <sup>1</sup>H NMR spectra evident from a sharp singlet at –11.33 ppm. We assumed that the <sup>9</sup>Be NMR signals at 0.9 ppm arose from the presence of BeI<sub>2</sub> coordinated to one aldehyde and one ketone **12c** and that this species was responsible for the condensation reaction. Therefore, we performed a reaction with one equivalent of pivaldehyde, MIPK, and BeI<sub>2</sub> each in CDCl<sub>3</sub> to promote the aldol addition reaction (see also Supporting Information, Figures 26–29). The recorded NMR spectra of the obtained brownish solution after four weeks of storage at ambient temperature showed that **10** was obtained as main organic moiety. After six weeks of storage colorless cubic crystals swam on top of the solution. The X-ray structure analysis revealed bis( $\mu_2$ -[5-hydroxy-2,6,6-trimethylheptan-3-one])diiododiberyllium(II) (**11**) as the main complex in solution. Compound **11** crystallizes in the triclinic space group *P* $\bar{1}$  and features a four-membered Be–O ring similar to that in compound **6**. Like

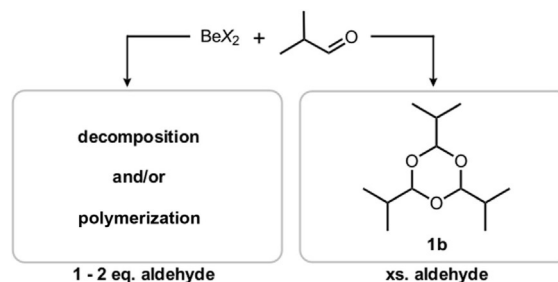


**Scheme 3.** Schematic illustration of the reactions of BeI<sub>2</sub> with one and two equivalents of pivaldehyde and proposed pathway for the formation of compound **11**.

in **6** the beryllium atoms are coordinated by one iodine atom and three oxygen atoms each. The hydroxy group acts as  $\mu_2$ -link while the oxygen atom of the carbonyl group completes the tetrahedral coordination around the Be atom (Figure 2). The Be–O atomic distances within the four-membered ring are 1.591(4) and 1.616(4) Å, which is comparable to the values found in **6** and those reported for tetrakis( $\mu_2$ -*t*-butoxy)-dichloro-tri-beryllium [from 1.540(2) to 1.635(2) Å].<sup>[31]</sup> The Be–O atomic distance to the carbonyl group is 1.655(4) Å, thus longer than that reported for Be(acac)<sub>2</sub> [1.62(1) Å].<sup>[20]</sup> The Be–I atomic distance is 2.390(4) Å, thus within the standard deviation identical to those of **6**. Compound **11** is obtained by cleavage of HI after the aldol addition and subsequent coordination towards “BeI<sup>+</sup>”. A similar increase of the acidity is described for diketones upon the coordination to BeCl<sub>2</sub>.<sup>[32]</sup> While **11** represents the major product, **4c**, **5c**, and an unknown compound were also observed in the <sup>1</sup>H and <sup>13</sup>C NMR spectra. EXSY NMR experiments showed that there is a fast exchange between the ketones coordinated to compounds **4c** and **5c** on the NMR time scale, whereas no NOE cross-peaks between the signals of ligand **10** and any MIPK moiety were observed. This leads to the deduction that complex **11** does not dissociate in solution. Furthermore, solutions of di-ketone **5c** also proved to be unstable and led to the formation of a mixture of compounds **11**, **4c**, and **5c** after several weeks. Therefore, in contrast to BeCl<sub>2</sub> and BeBr<sub>2</sub>, BeI<sub>2</sub> is able to convert MIPK into pivaldehyde. The analogous reaction of one equivalent of pivaldehyde and MIPK with BeCl<sub>2</sub> showed signals of both ligands in <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and one signal in the <sup>9</sup>Be NMR spectrum at 5.1 ppm, which is in between the signals observed for **2a** and **5a** as expected. This solution was stable for weeks and did not show any conversion to condensation product **10**. We therefore deduced that the corresponding mixed aldehyde ketone adduct of BeCl<sub>2</sub> (**12a**) is stable and that a cationic intermediate is necessary for the condensation, which is only available from BeI<sub>2</sub> adducts because of the weak Be–I bond.<sup>[30]</sup>

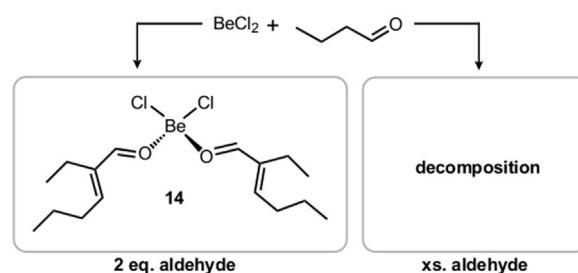
In comparison to pivaldehyde, isobutyraldehyde features a proton at the  $\alpha$ -C atom that enables it to form enols that can react further with the aid of a Lewis acid such as BeCl<sub>2</sub>. If isobutyraldehyde was exposed to catalytic amounts of BeCl<sub>2</sub>, the trimerization product 2,4,6-tris-isopropyl-1,3,5-trioxane (**1b**) was obtained (Scheme 4). The same applies to BeBr<sub>2</sub> and BeI<sub>2</sub>. Trioxane **1b** was subsequently used as precursor for isobutyraldehyde because of the easier handling. When BeCl<sub>2</sub> was treated with two equivalents of isobutyraldehyde in CDCl<sub>3</sub> or C<sub>6</sub>D<sub>6</sub> a brownish solution was obtained within a few hours. The <sup>1</sup>H NMR spectra showed a broad multiplet, which ranges from 0.5 to 3.0 ppm. In the <sup>13</sup>C NMR spectra we were not able to observe discrete signals. After the solvent was removed in vacuo we obtained a brown waxy residue that did not show any discrete bands in the IR spectrum. The same results were obtained for other stoichiometries and with BeBr<sub>2</sub> and BeI<sub>2</sub>. Therefore, we assume that isobutyraldehyde undergoes undirected polymerization.

For butyraldehyde we did not obtain the trimer when it was exposed to catalytic amounts of beryllium halides. Instead, an opaque beige solution of undefined composition was ob-



Scheme 4. Schematic illustration of the reaction pathways of isobutyraldehyde with beryllium halides (X = Cl, Br, I); xs. = excess.

tained. Because of this unselective reaction behavior, the decomposition of isobutyraldehyde and the complex reactivity of pivaldehyde with respect to BeI<sub>2</sub>, we limited our studies to the stoichiometric reactivity of butyraldehyde to BeCl<sub>2</sub> (Scheme 5). If two equivalents of butyraldehyde were treated with BeCl<sub>2</sub> in low concentrations in CDCl<sub>3</sub> the solution remained clear. The recorded <sup>1</sup>H and <sup>13</sup>C NMR spectra showed discrete signals for



Scheme 5. Schematic illustration of the reaction pathways of butyraldehyde with BeCl<sub>2</sub>.

the butyraldehyde and its aldol condensation product 2-en-2-ethyl-1-hexanal (**13**) in a one-to-four ratio. The signals of the carbonyl as well as of the allylic carbon atom are shifted downfield by 9.5 and 16.6 ppm, respectively, indicating a coordination of **13** towards BeCl<sub>2</sub>. In the <sup>9</sup>Be NMR spectrum a singlet at 5.3 ppm ( $\omega_{1/2}$  = 12.5 Hz) is observed, which is in a similar region as the signals of adducts **2a** and **5a** and evidence for a fourfold-coordinated beryllium species in solution. We assumed that this is a simple adduct of two ligands **13** to BeCl<sub>2</sub> (**14**). This was confirmed by the NMR spectra of a solution of two equivalents of **13** with one equivalent of BeCl<sub>2</sub>, which was prepared as a control experiment, and showed an identical set of signals with the same chemical shifts. However, if these solutions were stored for more than two weeks at ambient temperature they turned black and an unknown black solid precipitated, which indicates polymerization or decomposition. Therefore, attempts to obtain single crystals of that compound remained unsuccessful.

## Conclusion

We observed a rising reactivity among the halides from  $\text{BeF}_2$  to  $\text{BeI}_2$  when aldehydes were exposed to them. The aldehydes also showed distinctly different reactivities. The presence of a  $\beta$ -H was the decisive factor for different behaviors towards the beryllium halides. We were able to catalyze the formation of trioxans **1 a** and **1 b** through exposure of pivaldehyde and isobutyraldehyde, respectively, towards minute quantities of  $\text{BeCl}_2$ ,  $\text{BeBr}_2$ , or  $\text{BeI}_2$ , whereas  $\text{BeF}_2$  stayed inert in all the experiments we carried out. This cyclization was reversed when the trioxanes were exposed to higher quantities of beryllium halides (Cl, Br, I). If two equivalents of pivaldehyde were treated with  $\text{BeCl}_2$  or  $\text{BeBr}_2$ , the adducts **2 a** and **2 b** were obtained, whereas use of the same amounts of  $\text{BeI}_2$  resulted in the rearrangement reaction of pivaldehyde to MIPK and subsequent aldol addition to **10**, which then coordinates towards  $\text{BeI}_2$  to form compound **11** under evolution of HI. The respective isomerization to methyl isopropyl ketone could also be achieved when pivaldehyde was treated with equimolar amounts of  $\text{BeCl}_2$  or  $\text{BeBr}_2$ , and the corresponding adducts **4 a** and **4 b** were also obtained by direct reaction of one equivalent of MIPK with  $\text{BeCl}_2$  or  $\text{BeBr}_2$ , respectively. In addition, the adducts of two ketones to  $\text{BeCl}_2$  (**5 a**),  $\text{BeBr}_2$  (**5 b**), and  $\text{BeI}_2$  (**5 c**) were synthesized and characterized as well as mono-aldehyde adducts **3 a**, **3 b**, and **3 c**. The solid-state structure of compound **3 a** could be determined, which is the first example of a linear beryllium halide chain. While the reaction of  $\text{BeCl}_2$  or  $\text{BeBr}_2$  with three or more equivalents of pivaldehyde led to the formation of the bisaldehyde adducts **2 a** and **2 b**, 1-iodo-alkoxide **6** was formed in the case of  $\text{BeI}_2$ . This compound is generated through the formation of the cationic tris-aldehyde complex **8** and subsequent nucleophilic attack of iodine at one of the coordinated aldehydes. This leap in reactivity from  $\text{BeBr}_2$  to  $\text{BeI}_2$  is caused by the weak Be–I bond, which is cleaved easily and leads to the generation of cationic beryllium species. This proves on the one hand the potential of beryllium compounds to catalyze a vast amount of reactions as one of the hardest Lewis acids. On the other hand are complexes **6** and **11** model systems for transition states that have been proposed for proton-induced conversions of carbonyl groups.<sup>[33]</sup> Therefore,  $\text{Be}^{2+}$ —which is significantly smaller than any other metal ion—can be used as a proton substitute to isolate and structurally characterize transition-state-related compounds.

Polysaccharide binding to glycan-binding proteins is essential for immune recognition<sup>[34]</sup> and even slight changes of these polysaccharides can lead to an immune response.<sup>[35]</sup> Therefore, it is plausible that beryllium-induced alterations of the glycocalyx lead to an attack against the body's own cells by the immune system. Thus, the various observed conversion reactions of aldehydes and ketones enable the evaluation of potential pathways, in which carbohydrates are altered or decomposed when exposed to beryllium compounds in the human body, especially in lung tissue, in which hexoses are abundant. Accordingly, an examination of the glycocalyx in the lung tissue of berylliosis patients or corresponding animal

models with use of biochemical and immunologic techniques seems highly relevant.

## Experimental Section

**Caution!** Beryllium and its compounds are regarded as toxic and carcinogenic. As the biochemical mechanisms that cause beryllium-associated diseases are still unknown, special (safety) precautions are strongly advised.<sup>[7]</sup>

### General experimental techniques

All manipulations were performed either under solvent vapor pressure or dry argon by using glovebox and *Schlenk* techniques. Chloroform was dried by heating to reflux over  $\text{CaH}_2$ , and benzene over sodium and subsequent distillation under argon.  $\text{CDCl}_3$  was dried with  $\text{CaH}_2$  and  $\text{C}_6\text{D}_6$  with Na/K-alloy and vacuum-transferred directly into the *J. Young* NMR tubes.  $\text{BeF}_2$ ,  $\text{BeCl}_2$ ,  $\text{BeBr}_2$ , and  $\text{BeI}_2$  were prepared according to literature procedures<sup>[36,37]</sup> and the aldehydes and ketones were purchased from *VWR*. Because of the expected extreme toxicity of the obtained compounds no elemental analysis or mass spectrometry could be performed of the beryllium-containing species. The purity of the compounds was therefore determined by NMR and IR spectroscopy.

### NMR spectroscopy

$^1\text{H}$ ,  $^9\text{Be}$  and  $^{13}\text{C}$  NMR spectra were recorded with *Bruker* Avance III HD 300 and Avance III 500 NMR spectrometers. The latter was equipped with a *Prodigy* cryo-probe.  $^1\text{H}$  NMR (300/500 MHz) and  $^{13}\text{C}$  NMR (76/126 MHz) chemical shifts are given relative to the solvent signal for  $\text{C}_6\text{D}_6$  (7.16 and 128.1 ppm)/ $\text{CDCl}_3$  (7.26 and 77.2 ppm) and  $^9\text{Be}$  (42 MHz) used 0.43 M  $\text{BeSO}_4$  in  $\text{D}_2\text{O}$  as an external standard. NMR spectra were processed with the *MestReNova* software package.<sup>[38]</sup>

### IR spectroscopy

IR spectra were recorded with a *Bruker* alpha FTIR spectrometer equipped with a diamond ATR unit in an argon filled glovebox. Processing of the spectra was performed with the *OPUS* software package<sup>[39]</sup> and *OriginPro* 2017.<sup>[40]</sup> Either single crystals of the compounds (when possible) or bulk material were used for the IR spectroscopic measurements.

### Single-crystal X-ray diffraction

Single crystals were selected under exclusion of air in perfluorinated polyether (Fomblin YR 1800, *Solvay Solexis*) and mounted by using the *MiTeGen* MicroLoop system. X-ray diffraction data were collected with use of either the monochromated  $\text{Cu}_{\text{K}\alpha}$  radiation of a *Stoe* StadiVari diffractometer equipped with a *Xenocs* microfocus source and a *Dectris* Pilatus 300 K detector or monochromated  $\text{Mo}_{\text{K}\alpha}$  radiation of a *Stoe* IPDS II equipped with an image plate detector. The diffraction data were reduced with the *X-Area* software package.<sup>[41]</sup> The structures were solved by using direct methods (SHELXT-2018/2) and refined against  $F^2$  (SHELXL-2018/3) with use of the *ShelXle* software package.<sup>[42–44]</sup> All atoms were located by Difference Fourier synthesis and non-hydrogen atoms refined anisotropically. Hydrogen atoms were refined isotropically.

## Mass spectrometry

Mass spectrometry was performed with a *Thermo Fischer Scientific* LTQ-FT Ultra equipped with a combined ESI, APCI, and nanospray ionization source.

## NMR and IR spectroscopic data of purchased compounds

**Pivaldehyde:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.05$  (s, 9H,  $\text{CH}_3$ ), 9.45 ppm (s, 1H, C(O)H);  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 0.75$  (s, 9H,  $\text{CH}_3$ ), 9.19 ppm (s, 1H, C(O)H);  $^{13}\text{C}$  NMR (76 MHz,  $\text{CDCl}_3$ ):  $\delta = 23.6$  ( $\text{CH}_3$ ), 42.7 ( $\text{C}(\text{CH}_3)_3$ ), 206.1 ppm (C(O)H);  $^{13}\text{C}$  NMR (76 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 23.3$  ( $\text{CH}_3$ ), 42.1 ( $\text{C}(\text{CH}_3)_3$ ), 204.3 ppm (C(O)H); FTIR:  $\tilde{\nu} = 2966.5$  (m), 2871.3 (w), 2808.9 (w), 2697.8 (w), 1767.8 (w), 1724.4 (s), 1478.3 (s), 1463.3 (w), 1402.5 (s), 1365.3 (w), 1210.5 (w), 1037.7 (w), 942.7 (w), 882.3 (s), 763.3 (m), 593.6  $\text{cm}^{-1}$  (m).

**3-Methyl-2-butanone (MIPK):**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.09$  (d,  $^3J(\text{H,H}) = 7.0$  Hz, 6H,  $\text{CH}_3$ ), 2.13 (s, 3H,  $\text{CH}_3$ ), 2.58 ppm (hept,  $^3J(\text{H,H}) = 7.0$  Hz, 1H, CH);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta = 18.3$  ( $\text{CH}_3$ ), 27.7 ( $\text{CH}_3$ ), 41.8 (CH) 213.1 ppm (CO); FTIR:  $\tilde{\nu} = 2971.7$  (m), 2937.0 (w), 2877.9 (w), 1711.2 (s), 1466.5 (m), 1427.7 (w), 1382.8 (w), 1358.4 (m), 1193.2 (m), 1144.2 (m), 1099.3 (m), 956.6 (w), 724.1 (w), 603.7 (w), 575.2 (w), 526.2 (w), 438.5  $\text{cm}^{-1}$  (w).

**Isobutyraldehyde:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.10$  (d,  $^3J(\text{H,H}) = 7.0$  Hz, 6H,  $\text{CH}_3$ ), 2.40 (dhept,  $^3J(\text{H,H}) = 1.4$ , 7.0 Hz, 1H, CH), 9.61 ppm (d,  $^3J(\text{H,H}) = 1.4$  Hz, 1H, C(O)H);  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 0.73$  (d,  $^3J(\text{H,H}) = 7.1$  Hz, 6H,  $\text{CH}_3$ ), 1.80 (dhept,  $^3J(\text{H,H}) = 1.2$ , 7.0 Hz, 1H, CH), 9.25 ppm (d,  $^3J(\text{H,H}) = 1.2$  Hz, 1H, C(O)H);  $^{13}\text{C}$  NMR (76 MHz,  $\text{CDCl}_3$ ):  $\delta = 15.5$  ( $\text{CH}_3$ ), 41.1 (CH), 205.2 ppm (C(O)H);  $^{13}\text{C}$  NMR (76 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 15.3$  ( $\text{CH}_3$ ), 40.8 (CH), 203.2 ppm (C(O)H); FTIR:  $\tilde{\nu} = 2970.0$  (m), 2935.4 (m), 2876.2 (w), 2811.8 (w), 2712.7 (w), 1726.4 (s), 1466.1 (m), 1397.6 (m), 1368.3 (w), 1133.1 (w), 1108.0 (w), 910.2 (m), 842.4 (w), 796.6 (m), 630.3 (w), 546.8  $\text{cm}^{-1}$  (w).

**Butyraldehyde:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 0.94$  (t,  $^3J(\text{H,H}) = 7.3$  Hz, 3H,  $\text{CH}_3$ ), 1.65 (p,  $^3J(\text{H,H}) = 7.3$  Hz, 2H,  $\text{CH}_2$ ), 2.38 (dt,  $^3J(\text{H,H}) = 1.9$ , 7.3 Hz, 2H,  $\text{CH}_2$ ), 9.74 ppm (t,  $^3J(\text{H,H}) = 1.9$  Hz, 1H, C(O)H);  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 0.66$  (t,  $^3J(\text{H,H}) = 7.4$  Hz, 3H,  $\text{CH}_3$ ), 1.29 (p,  $^3J(\text{H,H}) = 7.3$  Hz, 2H,  $\text{CH}_2$ ), 1.79 (dt,  $^3J(\text{H,H}) = 1.7$ , 7.2 Hz, 2H,  $\text{CH}_2$ ), 9.31 ppm (t,  $^3J(\text{H,H}) = 1.7$  Hz, 1H, C(O)H);  $^{13}\text{C}$  NMR (76 MHz,  $\text{CDCl}_3$ ):  $\delta = 13.8$  ( $\text{CH}_3$ ), 15.7 ( $\text{CH}_2$ ), 45.9 ( $\text{CH}_2$ ), 202.9 ppm (C(O)H);  $^{13}\text{C}$  NMR (76 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 13.6$  ( $\text{CH}_3$ ), 15.7 ( $\text{CH}_2$ ), 45.6 ( $\text{CH}_2$ ), 200.9 ppm (C(O)H); FTIR:  $\tilde{\nu} = 3416.9$  (m), 2960.0 (s), 2936.5 (s), 2874.3 (s), 1714.1 (w), 1464.6 (w), 1416.1 (w), 1379.2 (w), 1336.2 (w), 1248.8 (w), 1149.2 (s), 1107.6 (m), 969.4 (s), 945.7 (s), 901.2 (vw), 829.8  $\text{cm}^{-1}$  (vw).

## Synthesis and characterization

**2,4,6-Tris-tert-butyl-1,3,5-trioxane (1a):**  $\text{BeCl}_2$  (10 mg, 0.125 mmol) was weighed into a *J. Young* Schlenk tube and pivaldehyde (5.0 mL, 46.04 mmol) was added under an argon stream. The tube was sealed and after 1 h of storage at ambient temperature rod-shaped crystals grew from the solid  $\text{BeCl}_2$ . After another 16 h pivaldehyde was completely converted into a colorless crystalline solid. Compound **1a** was obtained in quantitative yield (3.97 g) after sublimation at 50 °C in vacuo.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 0.90$  (s, 9H,  $\text{CH}_3$ ), 4.35 ppm (s, 1H, C(O)H);  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 1.0$  (s, 9H,  $\text{CH}_3$ ), 4.24 ppm (s, 1H, C(O)H);  $^{13}\text{C}$  NMR (76 MHz,  $\text{CDCl}_3$ ):  $\delta = 24.2$  ( $\text{CH}_3$ ), 35.0 ( $\text{C}(\text{CH}_3)_3$ ), 105.4 ppm (C(O)H);  $^{13}\text{C}$  NMR (76 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 24.5$  ( $\text{CH}_3$ ), 35.3 ( $\text{C}(\text{CH}_3)_3$ ), 105.8 ppm (C(O)H); FTIR:  $\tilde{\nu} = 2959.0$  (m), 2908.8 (w), 2868.7 (w), 2830.4 (w), 1480.0 (m), 1463.6 (w), 1428.3 (w), 1395.8 (m), 1362.8 (m), 1342.5 (m), 1209.2 (m),

1104.5 (s), 1060.9 (m), 1032.78 (w), 997.1 (m), 961.4 (w), 938.3 (w), 915.5 (w), 780.8 (w), 740.7 (w), 508.9 (w), 442.9 (w), 418.2  $\text{cm}^{-1}$  (w).

**Dichlorobis(2,2-dimethylpropanal)beryllium(II) (2a):** 2,4,6-Tris-tert-butyl-1,3,5-trioxane (**1a**) (32.3 mg, 0.125 mmol) and  $\text{BeCl}_2$  (10.0 mg, 0.125 mmol) were weighed into a *J. Young* NMR tube, which was subsequently filled with  $\text{CDCl}_3$  by vacuum condensation. The solvent was removed in vacuo after 2 weeks of storage. Single crystals of **2a** were isolated from an oily orange residue, which were suitable for single-crystal structure analysis.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.15$  (s, 9H,  $\text{CH}_3$ ), 9.59 ppm (s, 1H, C(O)H);  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 0.66$  (s, 9H,  $\text{CH}_3$ ), 9.54 ppm (s, 1H, C(O)H);  $^9\text{Be}$  NMR (42 MHz,  $\text{CDCl}_3$ ):  $\delta = 5.8$  ppm ( $\omega_{1/2} = 4.9$  Hz);  $^9\text{Be}$  NMR (42 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 6.6$  ppm ( $\omega_{1/2} = 8.1$  Hz);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta = 23.4$  ( $\text{CH}_3$ ), 43.3 ( $\text{C}(\text{CH}_3)_3$ ), 223.3 ppm (C(O)H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 22.9$  ( $\text{CH}_3$ ), 42.6 ppm ( $\text{C}(\text{CH}_3)_3$ ); FTIR:  $\tilde{\nu} = 2971.3$  (w), 2938.4 (w), 2873.4 (w), 1664.5 (s), 1482.0 (w), 1462.2 (w), 1404.4 (w), 1379.9 (w), 1369.9 (w), 1221.4 (w), 1046.4 (w), 951.3 (w), 897.5 (m), 775.3 (m), 658.5 (s), 570.1 (s), 534.6 (s), 414.2  $\text{cm}^{-1}$  (m).

**Dibromobis(2,2-dimethylpropanal)beryllium(II) (2b):** 2,4,6-Tris-tert-butyl-1,3,5-trioxane (**1a**) (32.3 mg, 0.125 mmol) and  $\text{BeBr}_2$  (21.1 mg, 0.125 mmol) were weighed into a *J. Young* NMR tube, which was subsequently filled with  $\text{CDCl}_3$  by vacuum condensation. The solvent was removed in vacuo after 3 d of storage. Single crystals of **2b** were isolated from an oily brownish residue, which were suitable for single-crystal structure analysis.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.26$  (s, 9H,  $\text{CH}_3$ ), 9.80 ppm (s, 1H, C(O)H);  $^9\text{Be}$  NMR (42 MHz,  $\text{CDCl}_3$ ):  $\delta = 5.4$  ppm ( $\omega_{1/2} = 3.6$  Hz);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta = 23.4$  ( $\text{CH}_3$ ), 43.9 ( $\text{C}(\text{CH}_3)_3$ ), 224.7 ppm (C(O)H); FTIR:  $\tilde{\nu} = 2972.0$  (w), 2936.7 (w), 2906.8 (w), 2872.8 (w), 1658.7 (s), 1479.6 (m), 1463.8 (m), 1404.0 (m), 1369.7 (m), 1272.9 (w), 1214.4 (w), 1152.9 (w), 1104.2 (w), 1046.0 (w), 950.4 (w), 895.8 (m), 774.8 (m), 679.9 (s), 646.4 (s), 590.1 (s), 540.1 (s), 408.0  $\text{cm}^{-1}$  (m).

**Poly[dichloro- $\mu_2$ -2,2-dimethylpropanalberyllium(II)] (3a):** 2,4,6-Tris-tert-butyl-1,3,5-trioxane (**1a**) (21.5 mg, 0.083 mmol) and  $\text{BeCl}_2$  (20.0 mg, 0.250 mmol) were weighed into a *J. Young* Schlenk tube, which was subsequently filled with benzene. The reaction mixture was heated to 100 °C for several minutes until the  $\text{BeCl}_2$  dissolved. While the solution cooled down, colorless needle-shaped crystals of **3a** precipitated in quantitative yield (41.5 mg).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.30$  (s, 9H,  $\text{CH}_3$ ), 9.72 ppm (s, 1H, C(O)H);  $^9\text{Be}$  NMR (42 MHz,  $\text{CDCl}_3$ ):  $\delta = 5.0$  ppm ( $\omega_{1/2} = 21.2$  Hz);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta = 23.5$  ( $\text{CH}_3$ ), 43.9 ( $\text{C}(\text{CH}_3)_3$ ), 223.9 ppm (C(O)H); FTIR:  $\tilde{\nu} = 2973.7$  (m), 2937.0 (w), 2912.5 (w), 2871.7 (w), 1662.2 (s), 1478.7 (m), 1405.2 (m), 1384.8 (m), 1370.6 (m), 1215.5 (w), 1038.1 (w), 899.4 (m), 783.2 (s), 717.9 (s), 675.1 (s), 601.6 (m), 554.7 (m), 530.2  $\text{cm}^{-1}$  (m).

**Poly[dichloro- $\mu_2$ -3-methyl-2-butanoneberyllium(II)] (4a):** 3-Methyl-2-butanone (MIPK) (21.3  $\mu\text{L}$ , 0.200 mmol) and  $\text{BeCl}_2$  (16.0 mg, 0.200 mmol) were weighed into a *J. Young* Schlenk tube, which was subsequently filled with benzene. The reaction mixture was heated to 100 °C for several minutes until the  $\text{BeCl}_2$  dissolved. The clear colorless solution was dried in vacuo. A beige polycrystalline solid of compound **4a** was obtained in quantitative yield (33.2 mg).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.27$  (d,  $^3J(\text{H,H}) = 6.9$  Hz, 6H,  $\text{CH}_3$ ), 2.74 (s, 3H,  $\text{CH}_3$ ), 3.03 ppm (hept,  $^3J(\text{H,H}) = 6.9$  Hz, 1H, CH);  $^9\text{Be}$  NMR (42 MHz,  $\text{CDCl}_3$ ):  $\delta = 4.3$  ppm ( $\omega_{1/2} = 13.9$  Hz);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta = 18.0$  ( $\text{CH}_3$ ), 28.5 ( $\text{CH}_3$ ), 43.9 (CH), 235.2 ppm (CO); FTIR:  $\tilde{\nu} = 3457.1$  (br), 2975.7 (m), 2937.0 (w), 2879.8 (vw), 1650.0 (s), 1466.4 (m), 1388.9 (w), 1366.5 (m), 1272.7 (w), 1211.5 (m), 1152.3 (w), 1103.4 (w), 997.4 (vw), 962.7 (vw), 844.4 (w), 764.8 (m), 728.1 (m), 632.2 (s), 554.8 (s), 520.9  $\text{cm}^{-1}$  (m).



**Dichloridobis(3-methyl-2-butanone)beryllium(II) (5a):** 3-Methyl-2-butanone (MIPK) (21.3  $\mu\text{L}$ , 0.200 mmol) and (8.0 mg  $\text{BeCl}_2$ , 0.100 mmol) were weighed into a *J. Young* NMR tube, which was subsequently filled with  $\text{CDCl}_3$  by vacuum condensation. The solvent was removed in vacuo after 2 weeks of storage. Single crystals of **5a** were isolated from an oily brownish residue, which were suitable for single-crystal structure analysis.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.09 (d,  $^3J(\text{H,H})$  = 7.0 Hz, 6H,  $\text{CH}_3$ ), 2.13 (s, 3H,  $\text{CH}_3$ ), 2.58 ppm (hept,  $^3J(\text{H,H})$  = 6.9 Hz, 1H,  $\text{CH}$ );  $^9\text{Be}$  NMR (42 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 4.7 ppm ( $\omega_{1/2}$  = 8.0 Hz);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 17.9 ( $\text{CH}_3$ ), 27.9 ( $\text{CH}_3$ ), 43.4 (CH), 231.8 ppm (CO); FTIR:  $\tilde{\nu}$  = 2975.0 (w), 2937.0 (w), 2879.9 (w), 1650.0 (s), 1466.5 (m), 1391.0 (m), 1366.5 (m), 1270.7 (w), 1213.6 (m), 1154.4 (w), 1105.5 (m), 1105.5 (w), 1105.5 (w), 764.8 (m), 634.3 (s), 556.8 (s), 522.1  $\text{cm}^{-1}$  (s).

**Bis(2,2-dimethylpropanal)bis( $\mu_2$ -[1-iodo-2,2-dimethyl-propan-1-ol])diiodoberyllium(II) (6):** 2,4,6-Tris-*tert*-butyl-1,3,5-trioxane (**1a**) (32.3 mg, 0.125 mmol) and  $\text{BeI}_2$  (32.8 mg, 0.125 mmol) were weighed into a *J. Young* NMR tube, which was subsequently filled with  $\text{CDCl}_3$  by vacuum condensation. The solvent was removed in vacuo after 2 d of storage. Single crystals of **6** were isolated from an oily brownish residue, which were suitable for single-crystal structure analysis.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.08 (s, 9H,  $\text{CH}_3$ ), 1.26 (s, 9H,  $\text{CH}_3$ ), 6.71 (s, 1H,  $\text{CHOH}$ ), 9.89 ppm (s, 1H,  $\text{C(O)H}$ );  $^9\text{Be}$  NMR (42 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 4.1 ppm ( $\omega_{1/2}$  = 35.6 Hz);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 24.1 ( $\text{CH}_3$ ), 26.5 ( $\text{CH}_3$ ), 43.8 ( $\text{C}(\text{CH}_3)_3$ ), 71.5 ( $\text{CCHOH}$ ), 226.0 ppm ( $\text{C(O)H}$ ); FTIR:  $\tilde{\nu}$  = 2967.9 (m), 2934.6 (w), 2905.0 (w), 2870.0 (w), 1662.4 (s), 1477.4 (m), 1462.3 (m), 1403.9 (m), 1382.7 (m), 1365.7 (m), 1309.6 (w), 1256.5 (w), 1210.8 (w), 1149.8 (w), 1104.3 (m), 1061.7 (s), 1014.3 (w), 941.5 (w), 891.0 (s), 776.4 (s), 721.8 (s), 679.0 (s), 600.0 (s), 553.8 (s), 526.5  $\text{cm}^{-1}$  (s).

**Bis( $\mu_2$ -[5-hydroxy-2,6,6-trimethylheptan-3-one])diiodoberyllium(II) (11):** 2,4,6-Tris-*tert*-butyl-1,3,5-trioxane (**1a**) (10.8 mg, 0.042 mmol) and  $\text{BeI}_2$  (32.8 mg, 0.125 mmol) were weighed into a *J. Young* NMR tube, which was subsequently filled with  $\text{CDCl}_3$  by vacuum condensation. The reaction mixture was stored for 6 weeks and monitored weekly by NMR spectroscopy. Single crystals of **11** grew after 6 weeks as colorless blocks, which were suitable for single-crystal structure analysis.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.04 (s, 9H,  $\text{CH}_3$ ), 1.25 (d,  $^3J(\text{H,H})$  = 6.9 Hz, 3H,  $\text{CH}_3$ ), 1.31 (d,  $^3J(\text{H,H})$  = 6.9 Hz, 3H,  $\text{CH}_3$ ), 2.71 (dd,  $^3J(\text{H,H})$  = 11.2 Hz,  $^2J(\text{H,H})$  = 14.4 Hz, 1H,  $\text{CHH}$ ), 3.04 (m, 1H,  $\text{CH}$ ), 3.21 (dd,  $^3J(\text{H,H})$  = 2.9 Hz,  $^2J(\text{H,H})$  = 14.4 Hz, 1H,  $\text{CHH}$ ), 4.15 ppm (dd,  $^3J(\text{H,H})$  = 2.9, 11.2 Hz, 1H,  $\text{CH}$ );  $^9\text{Be}$  NMR (42 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 3.0 ppm ( $\omega_{1/2}$  = 10.7 Hz);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 17.1 (*iPr*- $\text{CH}_3$ ), 17.7 (*iPr*- $\text{CH}_3$ ), 26.2 (*tBu*- $\text{CH}_3$ ), 36.1 (*tBu*-C), 39.3 ( $\text{CH}_2$ ), 43.9 (CH), 233.9 ppm ( $\text{C(O)}$ ); FTIR:  $\tilde{\nu}$  = 2972.2 (m), 2872.6 (w), 1631.6 (s), 1464.4 (m), 1388.9 (m), 1364.4 (m), 1311.4 (w), 1264.5 (w), 1213.5 (m), 1152.3 (w), 1078.9 (m), 1025.9 (m), 1011.6 (w), 993.3 (w), 960.6 (w), 921.9 (m), 852.5 (vw), 779.1 (s), 740.4 (s), 660.8 (s), 605.8 (m), 567.0 (w), 532.3 (m), 456.9 (w), 440.5  $\text{cm}^{-1}$  (vw).

**2,4,6-Tris-isopropyl-1,3,5-trioxane (1b):**  $\text{BeCl}_2$  (10 mg, 0.125 mmol) was weighed into a *J. Young* Schlenk tube and isobutyraldehyde (5.0 mL, 54.78 mmol) was added under an argon stream. The tube was sealed and after a few hours of storage at ambient temperature rod-shaped crystals grew from the solid  $\text{BeCl}_2$ . After 1 d the isobutyraldehyde was completely converted into a colorless crystalline solid. Compound **1b** was obtained in quantitative yield (3.95 g) after sublimation at 50 °C in vacuo.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.93 (d,  $^3J(\text{H,H})$  = 6.9 Hz, 6H,  $\text{CH}_3$ ), 1.84 (dhept,  $^3J(\text{H,H})$  = 5.5, 6.8 Hz, 1H,  $\text{CH}$ ), 4.49 ppm (d,  $^3J(\text{H,H})$  = 5.5 Hz, 1H,  $\text{C(O)H}$ );  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 1.01 (d,  $^3J(\text{H,H})$  = 6.9 Hz, 6H,  $\text{CH}_3$ ), 1.94 (dhept,  $^3J(\text{H,H})$  = 5.0, 6.8 Hz, 1H,  $\text{CH}$ ), 4.39 ppm (d,  $^3J(\text{H,H})$  = 5.0 Hz, 1H,  $\text{C(O)H}$ );  $^{13}\text{C}$  NMR (76 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 16.8 ( $\text{CH}_3$ ), 32.6 (CH),

104.9 ppm ( $\text{C(O)H}$ );  $^{13}\text{C}$  NMR (76 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 16.8 ( $\text{CH}_3$ ), 32.9 (CH), 104.7 ppm ( $\text{C(O)H}$ ); FTIR:  $\tilde{\nu}$  = 2980.5 (m), 2962.9 (m), 2923.7 (w), 2905.2 (w), 2875.2 (w), 1472.1 (m), 1457.8 (w), 1405.4 (w), 1378.4 (m), 1362.1 (m), 1302.4 (w), 1289.3 (w), 1190.3 (m), 1159.5 (m), 1133.7 (s), 1096.1 (m), 1046.8 (m), 1023.6 (w), 956.8 (m), 929.3 (w), 885.7 (w), 852.6 (w), 746.9 (w), 504.1 (w), 473.6 (m), 433.0  $\text{cm}^{-1}$  (w).

**2-En-2-ethyl-1-hexanal (13):** Butyraldehyde (2 mL, 22.2 mmol), water (2 mL), and NaOH (40 mg, 1.00 mmol) were heated to 120 °C for 2 h in a *J. Young* Schlenk tube. The reaction mixture was extracted with ethyl acetate, and the organic phase was dried with  $\text{MgSO}_4$  and filtered. Ethyl acetate was removed in vacuo and 2-en-2-ethyl-1-hexanal (**13**) was obtained as a colorless liquid by subsequent distillation at 180 °C. Yields were not determined.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.95 (t,  $^3J(\text{H,H})$  = 7.6 Hz, 3H,  $\text{CH}_3$ ), 0.97 (t,  $^3J(\text{H,H})$  = 7.4 Hz, 3H,  $\text{CH}_3$ ), 1.53 (p,  $^3J(\text{H,H})$  = 7.4 Hz, 2H,  $\text{CH}_2$ ), 2.25 (q,  $^3J(\text{H,H})$  = 7.6 Hz, 2H,  $\text{CH}_2$ ), 2.33 (q,  $^3J(\text{H,H})$  = 7.4 Hz, 2H,  $\text{CH}_2$ ), 6.41 (t,  $^3J(\text{H,H})$  = 7.5 Hz, 1H,  $\text{CH}$ ), 9.35 ppm (s, 1H,  $\text{C(O)H}$ );  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 0.70 (t,  $^3J(\text{H,H})$  = 7.4 Hz, 3H,  $\text{CH}_3$ ), 0.92 (t,  $^3J(\text{H,H})$  = 7.5 Hz, 3H,  $\text{CH}_3$ ), 1.13 (p,  $^3J(\text{H,H})$  = 7.4 Hz, 2H,  $\text{CH}_2$ ), 1.83 (q,  $^3J(\text{H,H})$  = 7.6 Hz, 2H,  $\text{CH}_2$ ), 2.19 (q,  $^3J(\text{H,H})$  = 7.5 Hz, 2H,  $\text{CH}_2$ ), 5.79 (t,  $^3J(\text{H,H})$  = 7.4 Hz, 1H,  $\text{CH}$ ), 9.25 ppm (s, 1H,  $\text{C(O)H}$ );  $^{13}\text{C}$  NMR (76 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 13.5 ( $\text{CH}_3$ ), 14.0 ( $\text{CH}_3$ ), 17.4 ( $\text{CH}_2$ ), 22.1 ( $\text{CH}_2$ ), 30.8 ( $\text{CH}_2$ ), 145.5 ( $\text{C}=\text{CH}$ ), 154.6 ( $\text{C}=\text{CH}$ ), 195.2 ppm ( $\text{C(O)H}$ );  $^{13}\text{C}$  NMR (76 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 13.6 ( $\text{CH}_3$ ), 13.9 ( $\text{CH}_3$ ), 17.6 ( $\text{CH}_2$ ), 22.1 ( $\text{CH}_2$ ), 30.5 ( $\text{CH}_2$ ), 145.7 ( $\text{C}=\text{CH}$ ), 152.8 ( $\text{C}=\text{CH}$ ), 193.9 ppm ( $\text{C(O)H}$ ); FTIR:  $\tilde{\nu}$  = 2964.0 (m), 2935.1 (m), 2875.2 (w), 2815.7 (vw), 2710.6 (vw), 1739.5 (vw), 1683.1 (s), 1641.8 (m), 1462.1 (m), 1402.1 (w), 1377.0 (w), 1337.5 (w), 1279.2 (w), 1236.6 (m), 1202.0 (m), 1149.3 (w), 1081.1 (m), 1061.7 (m), 1003.3 (w), 979.5 (w), 902.5 (w), 798.1 (m), 642.0 (vw), 560.6  $\text{cm}^{-1}$  (vw).

**Dichloridobis(2-en-2-ethyl-1-hexanal)beryllium(II) (14):** 2-En-2-ethyl-1-hexanal (**13**) (40.0  $\mu\text{L}$ , 0.250 mmol) and  $\text{BeCl}_2$  (10 mg, 0.125 mmol) were weighed into a *J. Young* NMR tube, which was subsequently filled with  $\text{CDCl}_3$  by vacuum condensation. The solvent was removed in vacuo after several hours. A clear colorless oil was obtained from which an IR spectrum was recorded. The oil darkened within 1 d of storage at ambient temperature.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.00 (t,  $^3J(\text{H,H})$  = 7.4 Hz, 3H,  $\text{CH}_3$ ), 1.01 (t,  $^3J(\text{H,H})$  = 7.6 Hz, 3H,  $\text{CH}_3$ ), 1.61 (p,  $^3J(\text{H,H})$  = 7.4 Hz, 2H,  $\text{CH}_2$ ), 2.39 (q,  $^3J(\text{H,H})$  = 7.6 Hz, 2H,  $\text{CH}_2$ ), 2.51 (q,  $^3J(\text{H,H})$  = 7.4 Hz, 2H,  $\text{CH}_2$ ), 7.21 (t,  $^3J(\text{H,H})$  = 7.5 Hz, 1H,  $\text{CH}$ ), 9.35 ppm (s, 1H,  $\text{C(O)H}$ );  $^9\text{Be}$  NMR (42 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 5.3 ppm ( $\omega_{1/2}$  = 12.5 Hz);  $^{13}\text{C}$  NMR (76 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 13.0 ( $\text{CH}_3$ ), 14.0 ( $\text{CH}_3$ ), 17.5 ( $\text{CH}_2$ ), 21.6 ( $\text{CH}_2$ ), 32.6 ( $\text{CH}_2$ ), 144.7 ( $\text{C}=\text{CH}$ ), 171.9 ( $\text{C}=\text{CH}$ ), 204.8 ppm ( $\text{C(O)H}$ ); FTIR:  $\tilde{\nu}$  = 2963 (m), 2932 (m), 2877 (w), 1601 (s), 1463 (m), 1408 (m), 1334 (w), 1287 (w), 1232 (w), 1208 (w), 1084 (m), 1060 (m), 982 (w), 912 (vw), 881 (vw), 803 (s), 694 (m), 662 (s), 577 (s), 515 (m), 452 (w), 429  $\text{cm}^{-1}$  (w).

## NMR spectroscopically monitored reactions

$\text{BeCl}_2$  (8.0 mg),  $\text{BeBr}_2$  (16.9 mg), or  $\text{BeI}_2$  (26.2 mg, 0.10 mmol, 1 equiv) and a corresponding amount of each of the respective ligands were weighed into a *J. Young* NMR tube inside a glovebox. Deuterated benzene or deuterated chloroform (0.5 mL) was added by vacuum distillation. The NMR tube was sealed immediately and NMR spectra collection commenced. The so prepared NMR tubes were stored for long-term investigations.

**Diiodobis(2,2-dimethylpropanal)beryllium(II) (2c):**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.30 (s, 9H,  $\text{CH}_3$ ), 9.95 ppm (s, 1H,  $\text{C(O)H}$ );  $^9\text{Be}$  NMR (42 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.7 ppm ( $\omega_{1/2}$  = 36.3 Hz);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 23.3 ( $\text{CH}_3$ ), 44.3 ( $\text{C}(\text{CH}_3)_3$ ), 226.1 ppm ( $\text{C(O)H}$ ).

**Poly[dibromo- $\mu_2$ -2,2-dimethylpropanalberyllium(II)] (3 b):**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.31$  (s, 9H,  $\text{CH}_3$ ), 9.78 ppm (s, 1H, C(O)H);  $^9\text{Be}$  NMR (42 MHz,  $\text{CDCl}_3$ ):  $\delta = 2.6$  ppm ( $\omega_{1/2} = 13.5$  Hz);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta = 23.6$  ( $\text{CH}_3$ ), 44.3 ( $\text{C}(\text{CH}_3)_2$ ), 225.3 ppm (C(O)H).

**Poly[dibromo- $\mu_2$ -3-methyl-2-butanoneberyllium(II)] (4 b):**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.28$  (d,  $^3J(\text{H,H}) = 6.8$  Hz, 6H,  $\text{CH}_3$ ), 2.82 (s, 3H,  $\text{CH}_3$ ), 3.04 ppm (hept,  $^3J(\text{H,H}) = 6.8$  Hz, 1H, CH);  $^9\text{Be}$  NMR (42 MHz,  $\text{CDCl}_3$ ):  $\delta = 2.7$  ppm ( $\omega_{1/2} = 8.7$  Hz);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta = 18.0$  ( $\text{CH}_3$ ), 28.8 ( $\text{CH}_3$ ), 43.9 (CH), 234.0 ppm (CO).

**Poly[diiodo- $\mu_2$ -3-methyl-2-butanoneberyllium(II)] (4 c):**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.26$  (d,  $^3J(\text{H,H}) = 6.9$  Hz, 6H,  $\text{CH}_3$ ), 2.87 (s, 3H,  $\text{CH}_3$ ), 3.06 ppm (hept,  $^3J(\text{H,H}) = 6.9$  Hz, 1H, CH);  $^9\text{Be}$  NMR (42 MHz,  $\text{CDCl}_3$ ):  $\delta = -1.0$  ppm ( $\omega_{1/2} = 3.7$  Hz);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta = 17.8$  ( $\text{CH}_3$ ), 29.8 ( $\text{CH}_3$ ), 44.1 (CH), 233.9 ppm (CO).

**Dibromidobis(3-methyl-2-butanone)beryllium(II) (5 b):**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.25$  (d,  $^3J(\text{H,H}) = 6.9$  Hz, 6H,  $\text{CH}_3$ ), 2.81 (s, 3H,  $\text{CH}_3$ ), 3.01 ppm (hept,  $^3J(\text{H,H}) = 6.8$  Hz, 1H, CH);  $^9\text{Be}$  NMR (42 MHz,  $\text{CDCl}_3$ ):  $\delta = 3.4$  ppm ( $\omega_{1/2} = 4.1$  Hz);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta = 17.9$  ( $\text{CH}_3$ ), 28.7 ( $\text{CH}_3$ ), 43.7 (CH), 233.2 ppm (CO).

**Diiodidobis(3-methyl-2-butanone)beryllium(II) (5 c):**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 0.98$ – $1.46$  (m, 6H,  $\text{CH}_3$ ), 2.83 (bs, 3H,  $\text{CH}_3$ ), 3.25 ppm (bs, 1H, CH);  $^9\text{Be}$  NMR (42 MHz,  $\text{CDCl}_3$ ):  $\delta = 2.7$  ppm ( $\omega_{1/2} = 7.3$  Hz);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta = 18.2$  ( $\text{CH}_3$ ), 30.7 ( $\text{CH}_3$ ), 44.4 (CH), 237.2 ppm (CO).

**Dichlorido(2,2-dimethylpropanal)(3-methyl-2-butanone)beryllium(II) (12 a):**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.21$  (d,  $^3J(\text{H,H}) = 6.9$  Hz, 6H,  $\text{CH}_3$ ), 1.24 (s, 9H,  $\text{CH}_3$ ), 2.74 (s, 3H,  $\text{CH}_3$ ), 2.97 (hept,  $^3J(\text{H,H}) = 6.9$  Hz, 1H, CH), 9.69 ppm (s, 1H, C(O)H);  $^9\text{Be}$  NMR (42 MHz,  $\text{CDCl}_3$ ):  $\delta = 5.1$  ppm ( $\omega_{1/2} = 11.0$  Hz);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta = 17.9$  ( $\text{CH}_3$ ), 23.4 ( $\text{CH}_3$ ), 28.0 ( $\text{CH}_3$ ), 43.4 ( $\text{C}(\text{CH}_3)_2$ ), 43.6 (CH), 222.6 (C(O)H), 232.8 ppm (CO).

### Preparation of samples for mass spectrometry

Beryllium-containing compounds were dissolved in chloroform. The chloroform solution was treated with water to extract the  $\text{Be}^{2+}$  cations from the organic phase. The chloroform solution was then diluted with dichloromethane to obtain a 1 mM solution that was subsequently analyzed by mass spectrometry. MS (ESI<sup>+</sup>):  $m/z$  (%): 173.2 [ $10^+$ ] (35), 195.2 [ $10 + \text{Na}^+$ ] (100).

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### Conflict of interest

The authors declare no conflict of interest.

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