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# Synthesis of Lewis Acid-Base Adducts Between $\text{PCO}^-$ and Group 13 Lewis Acids

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Lewis acid–base adducts between  $[\text{Na}(\text{diox})\text{PCO}]$  (diox = 1,4-dioxane) and trimethyltriels  $\text{EMe}_3$  ( $\text{E} = \text{B-In}$ ) were synthesized and crystallized using 18-crown-6 (18c6) as ligand for the sodium ions. In the course of these investigations, we were able to characterize the compounds  $[\text{Na}(18\text{c}6)][\text{PCO}(\text{EMe}_3)_2]$  (1:  $\text{E} = \text{B}$ ; 2:  $\text{E} = \text{Al}$ ) and  $[\text{Na}(18\text{c}6)][\text{PCO}(\text{EMe}_3)]$  (3:  $\text{E} = \text{Ga}$ ; 4:  $\text{E} = \text{In}$ ). All

compounds were examined by NMR spectroscopy, IR spectroscopy, and elemental analysis. X-ray structure analysis was performed for compounds 1, 3, and 4. The obtained adducts of negatively charged  $\text{PCO}^-$  anions with Lewis acids illustrate the HSAB concept, as the soft Lewis acids  $\text{GaMe}_3$  and  $\text{InMe}_3$  always coordinated at the soft phosphorus atom.

## 1. Introduction

Multiple bonds between elements of higher homologs greater than period two were long considered inaccessible because of the double bond rule.<sup>[1,2]</sup> In recent decades, this theory has been disproved by the presentation of numerous different compounds containing multiple bonds with heavier elements. These compounds are mainly stabilized by sterically demanding substituents. Prominent examples are, among many others, phosphorus-carbon triple bonds with organic groups on the C atom, such as  $\text{tBuCP}$  or  $\text{MesCP}$ .<sup>[3–17]</sup>

In contrast, multiple bonds that manage without additional substituents are much rarer. A classic example of such a compound is represented by the 2-phosphaethynolate anion ( $\text{PCO}^-$ ). This is the phosphorus homolog of the cyanate anion, which was first described as a lithium salt by Becker in 1992.<sup>[18]</sup> The stabilization of the P–C multiple bond in this type of compound is caused by coulomb repulsion preventing oligomerization of the monomer units.

The lithium compound described by Becker et al. is very susceptible to decomposition due to the pronounced covalent

bonds between lithium and the  $\text{PCO}^-$  anion.<sup>[19,20]</sup> Subsequent work on the synthesis of sodium and potassium homologs made this class of compounds more stable and accessible at a multi-gram scale.<sup>[21–26]</sup> Building on this research, various studies have been devoted to the reactivity of the  $\text{PCO}^-$  anion in recent years. For example the preparation of phosphorus-containing heterocycles<sup>[23,25,27–30]</sup> or the use of the  $\text{PCO}^-$  anion as a phosphide transfer reagent are described in literature.<sup>[31–34]</sup> The focus of these works was on salt elimination reactions and the investigation of the subsequent chemistry of the compounds obtained, such as cyclization. The group of Goicoechea et al. also investigated the  $\text{PCO}^-$  anion as a Lewis base. As part of their work, they were able to synthesize the Lewis acid–base adducts complexes  $[\text{K}(\text{crypt-222})][\text{W}(\text{CO})_5(\text{PCO})]$  and  $[\text{K}(18\text{c}6)][\text{W}(\text{CO})_5(\text{PCO})]$  (18c6 = 18-crown-6).<sup>[35]</sup> Furthermore, Stephan et al. investigated the adduct formation of  $\text{PCO}^-$  with  $\text{BR}_3$  ( $\text{R} = \text{H, Ph, C}_6\text{F}_5$ ) (Figure 1).<sup>[36]</sup> Based on this, we report here on the formation of Lewis acid–base adducts of  $\text{PCO}^-$  with the Lewis acids  $\text{BMe}_3$ ,  $\text{AlMe}_3$ ,  $\text{GaMe}_3$ , and  $\text{InMe}_3$ .

## 2. Results and Discussion

In a first step, the compound  $[\text{Na}(18\text{c}6)(\text{diox})\text{PCO}]$  (**A**, diox = 1,4-dioxane) was synthesized by literature known pathways.<sup>[35]</sup> The subsequent reactions were carried out as shown in Scheme 1.

In order to study the reactivity of compound **A** towards the lightest trimethyltriels,  $\text{BMe}_3$  was obtained according to the known synthesis based on  $\text{AlMe}_3$  and  $\text{B}(\text{OnBu})_3$ .<sup>[37]</sup> The reaction of  $\text{BMe}_3$  with **A** was carried out at  $-72^\circ\text{C}$  in an *n*-pentane/THF mixture and worked up at  $-32^\circ\text{C}$ . Crystals of compound  $[\text{Na}(18\text{c}6)]_2[\{\text{PCO}\}_2(\text{BMe}_3)_4]\cdot 4\text{thf}$  (**1-4thf**) were obtained which were suitable for X-ray structure analysis. **1-4thf** crystallizes in the triclinic space group  $P\bar{1}$  with one formula unit in the asymmetric unit. In the solid state, dimers of the  $\text{PCO}^-$  anion are formed. One  $\text{BMe}_3$  coordinates to each exocyclic oxygen atoms, which corresponds to the expectations based on the HSAB concept. Furthermore, the solid

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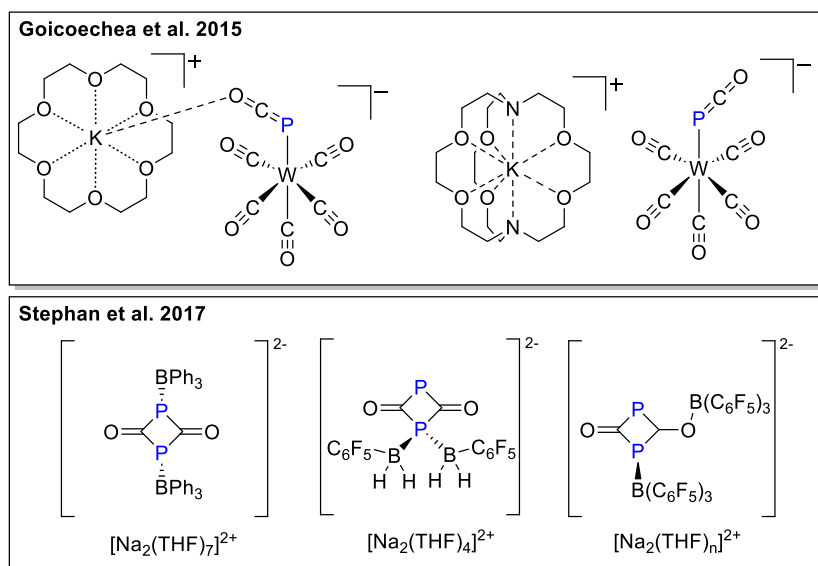
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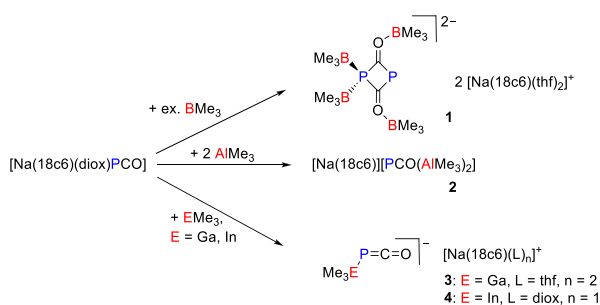
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**Figure 1.** Known Lewis acid–base adducts between  $\text{PCO}^-$  and different Lewis acids.<sup>[35,36]</sup>

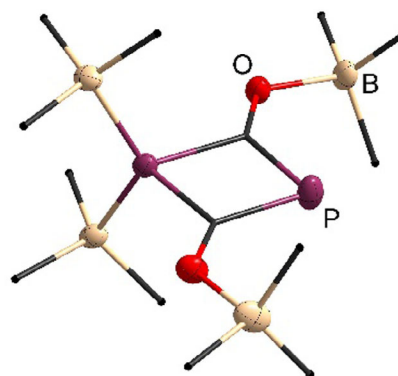


**Scheme 1.** General synthesis of the compounds 1, 3, and 4, diox = 1,4-dioxane.

state structure shows that one phosphorus atom is coordinated by two additional  $\text{BMe}_3$  units. The bond lengths of the anion in compound 1-4thf observed by us are in very good agreement with compounds described in the literature (e.g.  $[\{\text{Na}_2(\text{thf})_7\}(\text{BPh}_3)\text{PCO}]_2$ ;  $[\{\text{Na}_2(\text{thf})_4\}(\text{B}(\text{C}_6\text{F}_5)_2)\text{PCO}]_2$ ,  $[\{\text{Na}_2(\text{thf})_7\}(\text{B}(\text{C}_6\text{F}_5)_3)\text{PCO}]_2$ ). These include the P–C, C–O and P–B atomic distances (see **Figure 2**).<sup>[36]</sup>

The isolated compound 1 loses  $\text{BMe}_3$  very rapidly at room temperature. For this reason, it was not possible to characterize this compound by NMR spectroscopy. The  $^{31}\text{P}$  NMR spectrum obtained shows only one signal at  $-392.69$  ppm, which can be attributed to the free  $\text{PCO}^-$  ion. In the  $^1\text{H}$ ,  $^{11}\text{B}$ , and  $^{13}\text{C}$  NMR spectra, only traces of  $\text{BMe}_3$  can be detected next to the crown ether.

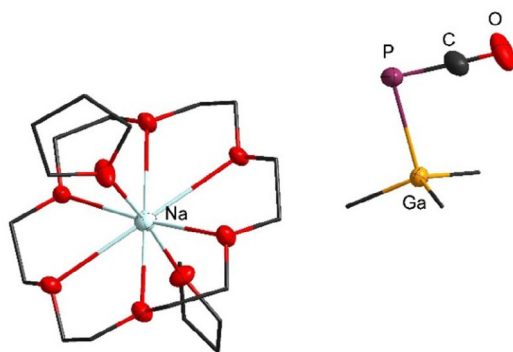
Similarly, compound A was reacted with  $\text{AlMe}_3$ . After working up at  $-32^\circ\text{C}$  and crystallizing at  $-72^\circ\text{C}$ , a slightly yellow solid was isolated. NMR spectroscopic investigations suggest that, as observed for compound 1, two Lewis acid molecules are bound to each anion, which results in the composition  $[\text{Na}(\text{18c6})][\text{PCO}(\text{AlMe}_3)_2]$  (2). The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum shows only one signal at  $-352.4$  ppm. Therefore, a structure such as that of compound 1-4thf in the solid state can be ruled out, at least in solution. Whether the solid compound 2 is a dimer, as observed



**Figure 2.** Molecular structure of the anion of 1 in the solid state. The  $[\text{Na}(\text{18c6})(\text{thf})_2]^+$  cations are not shown for reasons of clarity. Hydrogen atoms are omitted for clarity. Ellipsoids are shown at a 50% probability level. Selected bond lengths (pm) and angles ( $^\circ$ ): B–O 163.8(4), 163.1(3), B–P 203.2(3), 203.3(3); C–O 125.7(3), 126.4(3); (B)P–C 183.9(3), 184.6(3); P–C 178.6(3), 178.5(3); C–(B)P–C 77.0(1); C–P–C 80.0(1); P–C–O 133.7(3), 133.8(3); (B)P–C–O 124.8(3), 124.5(3).

for compound 1-4thf, cannot be determined from the data. Nevertheless, the composition mentioned above is confirmed by elemental analysis (see ESI). Despite various attempts, it was not possible to successfully investigate compound 2 using X-ray structure analysis on a single crystal. This was due to the compound's poor crystallization habits and rapid decomposition outside the mother solution. Instead, the structure was clarified by combining measured and calculated IR and NMR data, see below.

The reaction of  $[\text{Na}(\text{18c6})(\text{diox})\text{PCO}]$  with  $\text{GaMe}_3$  in *n*-pentane proceeds smoothly while warming up to room temperature. By adding THF, a clear colorless solution could be obtained from the previous suspension, from which crystals of compound 3 could be obtained at  $-72^\circ\text{C}$  after filtration, which were suitable for X-ray structure analysis. The compound  $[\text{Na}(\text{18c6})][\text{PCO}(\text{GaMe}_3)_2]\cdot 2\text{thf}$



**Figure 3.** Molecular structures of anion and cation in **3**-2thf in the solid state. Hydrogen atoms are omitted for clarity. Ellipsoids are shown at a 50% probability level. Selected bond lengths (pm) and angles (°): Ga–P 254.43(13), P–C 161.3(6), C–O 117.2(7), Ga–P–C 88.4(2), P–C–O 178.2(6).

(**3**-2thf) crystallizes in the monoclinic space group *Cc* with one molecular formula in the asymmetric unit (Figure 3). The  $\text{GaMe}_3$  is exclusively coordinated by the phosphorus atom of the  $\text{PCO}^-$  anion. Even when using an excess of  $\text{GaMe}_3$ , no compounds with a higher content of  $\text{GaMe}_3$  are observed. This is in agreement with the HSAB principle, which postulates that the relatively soft Lewis base (P) preferentially coordinates the relatively soft Lewis acid (Ga). Interestingly in compound **3**-2thf, discrete ions are observed in which the sodium cation is coordinated by two THF molecules in addition to the crown ether. The bond length of 254.43(13) pm between phosphorus and gallium is significantly longer than in the recently published  $[\text{PH}_2(\text{GaMe}_3)_2]^-$  anion (P–Ga = 242.21(14) pm).<sup>[38]</sup> We attribute this to the delocalized charge in the  $\text{PCO}^-$  ion, which leads to a significantly lower Lewis basicity compared to the  $\text{PH}_2^-$  ion. However, the Ga–P bond in **3**-2thf is shorter than in the neutral Lewis acid base complexes  $\text{Ph}_3\text{PGaMe}_3$ : 253.75(5) pm or  $\text{Ph}_3\text{PGa}t\text{Bu}_3$ : 271.26(5) pm.<sup>[39–41]</sup> A comparison of the PCO fragment in **3**-2thf (P–C: 161.3(6) pm; C–O: 117.2(7) pm) with the compound  $[\text{K}(\text{crypt-222})][(\text{CO})_5\text{WPCO}]$  described by Goicoechea et al. (P–C: 161.6(4) pm; C–O: 117.6(5) pm) shows very similar values for these bonds.<sup>[35]</sup> Further characterization of compound **3** was carried out using NMR spectroscopy, IR spectroscopy, and elemental analysis (Table 1).

The compound  $[\text{Na}(\text{18c6})][\text{PCO}(\text{InMe}_3)]$  (**4**) was obtained from the reaction of  $[\text{Na}(\text{18c6})(\text{diox})\text{PCO}]$  and  $\text{InMe}_3$  in toluene. Crystals which were suitable for X-ray structure were obtained from a saturated solution of compound **4** in toluene at  $-72^\circ\text{C}$ . Compound

**4**-diox crystallizes in the monoclinic space group  $P\bar{1}$  with four molecular formulas in the asymmetric unit. The anion  $[\text{PCO}(\text{InMe}_3)]^-$  observed in compound **4**-diox is strongly disordered in the solid state, and despite several attempts, no better data set could be obtained from this compound. Nevertheless, a bond length of 261.8(5)–266.6(3) pm between phosphorus and indium could be observed, which is slightly shorter than in neutral Lewis acid base compounds described in the literature, such as  $\text{Ph}_3\text{PInMe}_3$ : 273.33(2) pm,  $\text{Ph}_3\text{PInEt}_3$ : 274.53(5) pm, or  $\text{Ph}_3\text{PInCp}_3$ : 269.92(4) pm.<sup>[39,42,43]</sup>

The ionic species  $[\text{K}(\text{18c6})(\text{thf})_2\text{P}(\text{SiMe}_3)_2(\text{InMe}_3)_2]$  described recently shows a very similar P–In bond length of 263.42(9) pm.<sup>[38]</sup> Analogous to the previously described compound **3**, compound **4** also shows no significant differences in the bond lengths between P–C and C–O compared to the reference compound  $[\text{K}(\text{crypt-222})][(\text{CO})_5\text{WPCO}]$ .<sup>[35]</sup> Within the scope of this project, the double adducts of compounds **3** and **4** were also targeted. However, various reactions with the addition of an excess of the respective Lewis acid always yielded the one fold adduct.

A comparison of the  $^{31}\text{P}$  NMR shift of **A** and of compounds **3** and **4** shows no significant differences. It can be assumed that in the polar solvent THF, only little interaction is observed between the  $\text{PCO}^-$  anion and the respective Lewis acid used due to the competitive coordination with THF. In contrast, a  $^{31}\text{P}$  NMR shift of  $-352.44$  ppm is observed for compound **2**. Examining the solids reveals a shift in the CO stretching vibration to higher wave numbers in the IR spectrum. This indicates that the C–O bond is strengthened under the coordination of the anion with a Lewis acid. The CO band at  $1768\text{ cm}^{-1}$  in compound **A** is shifted to wave numbers  $1839\text{ cm}^{-1}$  for **3** and  $1833\text{ cm}^{-1}$  for **4**. Similar observations were made by Goicoechea et al.<sup>[35]</sup> In contrast, the C–O stretching vibrations of compound **1** ( $1763\text{ cm}^{-1}$ ) and **2** ( $1768\text{ cm}^{-1}$ ) are at lower wave numbers compared to compounds **3** and **4** and very close to the free  $\text{PCO}^-$  anion. Similar observations were also made by Stephan et al.<sup>[36]</sup>

A further indication of the more pronounced phosphaketenide character ( $\text{P}=\text{C}=\text{O}$ ) of the  $\text{PCO}^-$  anion in compounds **3** and **4** can be observed by comparing the  $^1J_{\text{PC}}$  couplings in  $^{13}\text{C}$  NMR spectra with literature known compounds. Values in the range from 41.5 to 62.0 Hz are found in the literature for the simple compounds  $[\text{M}(\text{L})][\text{PCO}]$  ( $\text{M} = \text{Li}, \text{Na}, \text{K}$ ;  $\text{L} = \text{dimethoxyethane, dioxane, 18c6}$ ) which speak for a pronounced phosphoethynolate character ( $\text{P}=\text{C}=\text{O}^-$ ).<sup>[44]</sup> The coupling constants observed by us are 72.8 (**3**) and 80.0 (**4**). This effect is even more pronounced for the literature known compound  $[\text{K}(\text{crypt-222})][\text{W}(\text{CO})_5(\text{PCO})]$  with 94.9 Hz. An increase in the coupling constant is therefore generally observed with a softer character of the Lewis acid used bond to phosphorus.<sup>[44]</sup>

Density functional calculations were employed to systematically investigate the preferred coordination site of  $\text{EMe}_3$  ( $\text{E} = \text{B}, \text{Al}, \text{Ga}, \text{In}$ ) to the  $\text{PCO}^-$  anion and to determine the most probable structure of **2**.

As noted above, from the HSAB concept, one would expect  $\text{BMe}_3$  and  $\text{AlMe}_3$  to coordinate rather at the O site and  $\text{GaMe}_3$  and  $\text{InMe}_3$  rather at the P site of  $\text{PCO}^-$ . Indeed, calculations indicate the P site to be preferred over the O site by  $26(36)\text{ kJ mol}^{-1}$  for

**Table 1.** Selected bond lengths (pm), angles (°),  $^{31}\text{P}$  NMR shifts, and CO stretching vibration ( $\text{cm}^{-1}$ ) of compounds **A**, **2**, **3**, and **4**.

	<b>A</b>	<b>2</b>	<b>3</b>	<b>4</b>
P–E/pm	–	–	254.43(13)	261.8(5)–266.6(3)
P–C/pm	162 <sup>[35]</sup>	–	161.3(6)	148.3(15)–153.8(13)
C–O/pm	120 <sup>[35]</sup>	–	117.2(7)	126.5(14)–130.4(16)
$^{31}\text{P}$ NMR shift/ppm	–392.8	–352.4	–386.3	–400.0
$\nu\text{-CO}/(\text{cm}^{-1})$	1768	1768	1839	1833

Ga(In); the preference for O is not as clearly visible from the calculations: for Al, we find an undecided situation (less than 1 kJ mol<sup>-1</sup> difference), and for B again, the P site is slightly preferred by 10 kJ mol<sup>-1</sup>. Depending on the functional, or when accounting for solvent effects or including the zero-point vibration energy or a dispersion correction, these numbers are shifted by very few kJ mol<sup>-1</sup>, but the sequence for the P-preference (Al < B < Ga < In) is always preserved; see ESI. For better foundation of the mainly electrostatically based HSAB concept, one might consider to extract the electrostatic contribution from the bond energy by an energy decomposition analysis.<sup>[45]</sup> Indeed, this contribution clearly points in favor of O for E = Al by 26 kJ mol<sup>-1</sup> and in favor of P for E = Ga by 60 kJ mol<sup>-1</sup>; see ESI. Nevertheless, one has to be aware that this is only one of four (no-uniquely defined) quantities contributing to the interaction energy (with different signs) and that this interaction energy still differs from the bond energy by the energy difference of the educts in their isolated and their coordinated geometric structure. For a detailed discussion, see ESI.

The structure of **2** was clarified by comparing calculated IR and NMR spectra for different models with the experimental data. The models may be characterized as follows. In model OO, both AlMe<sub>3</sub> groups bind to the O atom of the PCO unit, in PP both to the P atom, and in PO one to O and one to P. Further, we investigated a dimer, where each of the P and O atoms binds to one AlMe<sub>3</sub> unit. For this dimer, the calculated <sup>31</sup>P shift, +105 ppm, is far from the experiment, -352 ppm; it thus can be ruled out. Further, also a dimer analogously to **1** can be ruled out from the NMR spectrum, as one would expect two different <sup>31</sup>P signals, but observes only one. It remains to find the most probable isomer among PO, OO, and PP. Their <sup>31</sup>P shifts amount to -404, -342, and -402 ppm and thus are all not dramatically out of range of the experiment. For correcting the systematic error (from the functional and the fact that the free H<sub>3</sub>PO<sub>4</sub> molecule might not be the most adequate reference), we add the difference between shifts calculated for **3**, -431 ppm, and measured, -386 ppm, to these values to get -359, -297, and -357 ppm for PO, OO, and PP. Thus, OO can be ruled out, whereas PO and PP very reasonably match with the measurement, -352 ppm. This is in line with the relative stabilities: PO and PP are almost of the same energy (in fact, PP is 3 kJ mol<sup>-1</sup> more stable than PO), but OO is less stable than PP by 28 kJ mol<sup>-1</sup>. Final clarification is possible with the help of IR spectra, which significantly differ only in the position of the asymmetric P-C-O stretch vibration; see figure SX. For PO, OO, and PP, one gets 1816, 1668, and 1945 cm<sup>-1</sup>. Again, we correct this by the error of the method using a molecule that is similar in this respect, CO<sub>2</sub>, where calculation yields 2361 cm<sup>-1</sup> and measurement 2349, to get 1804, 1656, and 1933 cm<sup>-1</sup>; among these, the agreement with the experimental value, 1768 cm<sup>-1</sup>, is significantly better for PO than for PP, which makes the former the most probable isomer for compound **2**. The analogous procedure but with employing the conductor-like screening model (with default parameters) to account for environment effects yields 1761, 1633 and 1893 cm<sup>-1</sup>, thus an almost on-spot agreement for PO, i.e., (Me<sub>3</sub>Al-OCP-AlMe<sub>3</sub>)<sup>-</sup>. Overall, with the above-described calibration-extrapolation procedure, the variation of the results with the calculation level, about 30 cm<sup>-1</sup> for the O-C-P vibration

frequency and about 10 ppm for the <sup>31</sup>P shifts (see ESI), is smaller than the differences between the different models and thus allows for this assignment. We finally note that employing **4** instead of **3** for the extrapolation of NMR shifts changes their values systematically by 3 ppm, probably due to neglect of spin-orbit effects, which may become relevant in presence of 5p elements.

In addition to reactivity studies of the PCO<sup>-</sup> anion, subsequent work also dealt with studies of the AsCO<sup>-</sup> anion. In various reactions, we always observe the decomposition of [Na(18c6)AsCO] at room temperature and formation of an insoluble orange solid, which is presumably a polyarsane. Similar observations were also made by Goicoechea et al. starting from [Na(18c6)AsCO].<sup>[46]</sup> In the course of our investigations, we were only able to obtain compounds of the composition [Na(18c6)][EMe<sub>4</sub>] (E = Al, Ga, In).<sup>[47-49]</sup> We assume that the desired Lewis acid base adducts are formed in the short term, which, however, is a strong methylation reagent and leads to the formation of the observed salts under decomposition. Similar results were observed in Lewis acid-base studies starting from [K(18c6)(thf)AsH<sub>2</sub>] and [K(18c6)(thf)SbH<sub>2</sub>].<sup>[38,50]</sup>

Future studies will involve reactions of the anions PCS<sup>-</sup> and AsCS<sup>-</sup> with different Lewis acids.

### 3. Experimental Section

Unless otherwise specified, all manipulations were carried out under an argon atmosphere using a standard Schlenk technique. All solvents used in the reactions and for crystallizations were dried via standard techniques, distilled, and stored under argon. Solvents were never stored longer than one month before use. The starting [Na(18c6)(diox)PCO] was prepared according to literature procedures.<sup>[35]</sup> GaMe<sub>3</sub> and InMe<sub>3</sub> were provided by Dockweiler Chemicals GmbH. NMR spectra were recorded using Bruker Avance III HD 250 MHz, a Bruker Avance II 300 MHz, a Bruker Avance III 500 MHz, or a Avance III HD 500 MHz spectrometer at 298 K. The IR spectra were run on a BrukerFT IR spectrometer using the attenuated total reflectance (ATR) mode at room temperature. Elemental analysis was run on a Elementar vario Micro cube in CHN operating mode. X-ray structure analysis was carried out on the D8 Quest and Venture devices from Bruker.

**Synthesis of [Na(18c6)]<sub>2</sub>{[PCO]<sub>2</sub>(BMe<sub>3</sub>)<sub>4</sub>}** (**1**): First, the BMe<sub>3</sub> was freshly synthesized from AlMe<sub>3</sub> and B(OnBu)<sub>3</sub> according to known literature.<sup>[37]</sup> Subsequently, [Na(18c6)(diox)PCO] (150 mg, 0.38 mmol, 1.00 eq) was suspended in 10 mL *n*-pentane at -78 °C, and BMe<sub>3</sub> was added to the solution by condensation in excess. The reaction solution was then slowly warmed to -32 °C. After addition of 10 mL THF, the slightly cloudy solution was filtered at this temperature and stored at -72 °C for crystallization. The solid obtained was then freed from the supernatant solvent and washed twice with 3 mL *n*-pentane. The product was obtained in the form of yellow crystals in a yield of 65%. Crystals suitable for X-ray structure analysis had the composition 1.4thf. Further analysis could not be obtained due to rapid decomposition of the solid at temperatures above -32 °C. The NMR spectra obtained (see ESI) show residues of BMe<sub>3</sub> and free PCO<sup>-</sup> ions, which are residues from the decomposition of the Lewis acid-base adduct.

**Synthesis of [Na(18c6)][PCO(AlMe<sub>3</sub>)<sub>2</sub>]** (**2**): [Na(18c6)(diox)PCO] (150 mg, 0.38 mmol, 1.00 eq) was suspended in 10 mL *n*-pentane at -78 °C. Subsequently, AlMe<sub>3</sub> (56 mg, 0.76 mmol, 2.00 eq.) was



added to the solution. The reaction solution was then slowly warmed to  $-32^{\circ}\text{C}$ . After addition of 10 mL THF, the slightly cloudy solution was filtered at this temperature and stored at  $-72^{\circ}\text{C}$  for crystallization. The solid obtained was then freed from the supernatant solvent and washed twice with 3 mL *n*-pentane. The product was obtained in the form of yellow crystals in a yield of 54%. Elemental analysis after thorough vacuum drying:  $\text{C}_{19}\text{H}_{42}\text{Al}_2\text{NaO}_7\text{P}$  calcd: C, 46.53; H, 8.63; found: C, 46.18; H, 8.21;  $^1\text{H}$  NMR (300 MHz,  $\text{THF-d}_8$ , 298 K)  $\delta$ :  $-0.99$  (s, 18H,  $\text{AlMe}_3$ ), 3.65 (s, 24H, 18c6);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{THF-d}_8$ , 298 K)  $\delta$ :  $-6.70$  ( $\text{AlMe}_3$ ), 70.79 (s, 18c6);  $^{31}\text{P}\{^1\text{H}\}$  (130 MHz  $\text{THF-d}_8$ , 298 K)  $\delta$ :  $-352.44$  (s, PCO). IR ( $\text{cm}^{-1}$ ): 2884 (m), 2857 (m), 1768 (s), 1621 (m), 1472 (m), 1454 (m), 1351 (m), 1286 (m), 1251 (m), 1101 (s), 961 (m), 894 (m), 880 (m), 837 (m), 813 (m), 616 (m), 535 (m), 491 (m).

**Synthesis of  $[\text{Na}(18\text{c}6)][\text{PCOGaMe}_3]$  (3):**  $[\text{Na}(18\text{c}6)(\text{diox})\text{PCO}]$  (150 mg, 0.38 mmol, 1.00 eq) was suspended in 10 mL *n*-pentane at  $-78^{\circ}\text{C}$ . Subsequently,  $\text{GaMe}_3$  (44 mg, 0.38 mmol, 1.00 eq) was added dropwise to the solution. The reaction solution was then slowly warmed to room temperature. Three milliliters of THF was then added to the resulting suspension until almost clarity. Subsequently, the solution was separated from insoluble components by filtration and stored at  $-32^{\circ}\text{C}$  for crystallization. The solid obtained was then freed from the supernatant solvent and washed twice with 3 mL *n*-pentane. The product was obtained in the form of colorless crystals in a yield of 78%. Crystals suitable for X-ray structure analysis had the composition  $3\cdot 2\text{thf}$ . Elemental analysis after thorough vacuum drying:  $\text{C}_{20}\text{H}_{41}\text{GaNaO}_8\text{P}$  ( $3\cdot 2\text{thf}$ ) calcd: C, 45.05; H, 7.75; found: C, 44.73; H, 7.42;  $^1\text{H}$  NMR (300 MHz,  $\text{THF-d}_8$ , 298 K)  $\delta$ :  $-0.54$  (s, 9H,  $\text{GaMe}_3$ ), 3.64 (s, 24H, 18c6);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{THF-d}_8$ , 298 K)  $\delta$ :  $-2.18$  (s,  $\text{GaMe}_3$ ), 70.90 (s, 18c6), 175.93 (d,  $^1J_{\text{PC}} = 72.8$ , PCO);  $^{31}\text{P}\{^1\text{H}\}$  (130 MHz  $\text{THF-d}_8$ , 298 K)  $\delta$ :  $-386.29$  (s, PCO). IR ( $\text{cm}^{-1}$ ): 2898 (m), 2830 (m), 1839 (s), 1771 (m), 1470 (m), 1451 (m), 1353 (m), 1285 (m), 1249 (m), 1173 (m), 1105 (s), 965 (m), 838 (m), 734 (m), 536 (m), 517 (m), 506 (m), 415 (m).

**Synthesis of  $[\text{Na}(18\text{c}6)][\text{PCOInMe}_3]$  (4):**  $[\text{Na}(18\text{c}6)(\text{diox})\text{PCO}]$  (150 mg, 0.38 mmol, 1.00 eq) was suspended in 10 mL toluene at  $-78^{\circ}\text{C}$ . Subsequently,  $\text{InMe}_3$  (63 mg, 0.38 mmol, 1.00 eq) was added to the solution as a solid. The reaction solution was then slowly warmed to room temperature. The slightly cloudy solution was then filtered and stored at  $-32^{\circ}\text{C}$  for crystallization. The solid obtained was then freed from the supernatant solvent and washed twice with 3 mL *n*-pentane. The product was obtained in the form of colorless crystals in a yield of 74%. Crystals suitable for X-ray structure analysis had the composition  $4\cdot 1\text{diox}$ . Elemental analysis after thorough vacuum drying:  $\text{C}_{16}\text{H}_{33}\text{InNaO}_7\text{P}$  (4) calcd: C, 37.96; H, 6.57; found: C, 38.00; H, 6.74;  $^1\text{H}$  NMR (300 MHz,  $\text{THF-d}_8$ , 298 K)  $\delta$ :  $-0.59$  (s, 9H,  $\text{InMe}_3$ ), 3.64 (s, 24H, 18c6);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{THF-d}_8$ , 298 K)  $\delta$ :  $-6.53$  (s,  $\text{InMe}_3$ ), 70.94 (s, 18c6), 175.93 (d,  $^1J_{\text{PC}} = 80.0$ , PCO);  $^{31}\text{P}\{^1\text{H}\}$  (130 MHz  $\text{THF-d}_8$ , 298 K)  $\delta$ :  $-399.99$  (s, PCO). IR ( $\text{cm}^{-1}$ ): 2949 (m), 2898 (m), 2861 (m), 2829 (m), 1833 (m), 1470 (m), 1454 (m), 1351 (m), 1283 (m), 1247 (m), 1104 (s), 966 (m), 875.15 (m), 837.03 (m), 683.35 (m), 616 (m), 535 (m), 512 (m), 484 (m), 466 (m).

**X-Ray Diffraction Analysis:** Single crystal X-ray diffraction analysis was conducted using a Bruker D8 Quest or a Bruker D8 Venture diffractometer. The diffractometer uses  $\text{Mo-K}\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation and respective X-ray optics. Structures were solved via intrinsic phasing using SHELXT-2015. Structure refinement was performed via full-matrix-least-squares against  $F^2$  using SHELXL-2015. All structures were solved and refined using the OLEX2 platform. Deposition Numbers CCDC 2476033 (1), 2476032 (3), and 2476031 (4) contain the supplementary crystallographic data for this article. These data can be obtained free of charge via [https://www.ccdc.cam.ac.uk/data\\_request/cif](https://www.ccdc.cam.ac.uk/data_request/cif). For details of the crystal structures, see also ESI.

**Quantum-Chemical Calculations:** Density functional calculations with the program suite TURBOMOLE<sup>[51]</sup> were done with functional PBE<sup>[52]</sup> using def2-TZVP basis sets,<sup>[53]</sup> fine grids (gridsize 5),<sup>[54]</sup>

corresponding auxiliary basis sets,<sup>[55]</sup> and an effective core potential for In.<sup>[56]</sup> Results at other calculation levels are shown in the ESI. The conductor-like screening model<sup>[57]</sup> with default parameters was employed for solvent effects, where explicitly mentioned. Cartesian coordinates of calculated structures are collected in the ESI.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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