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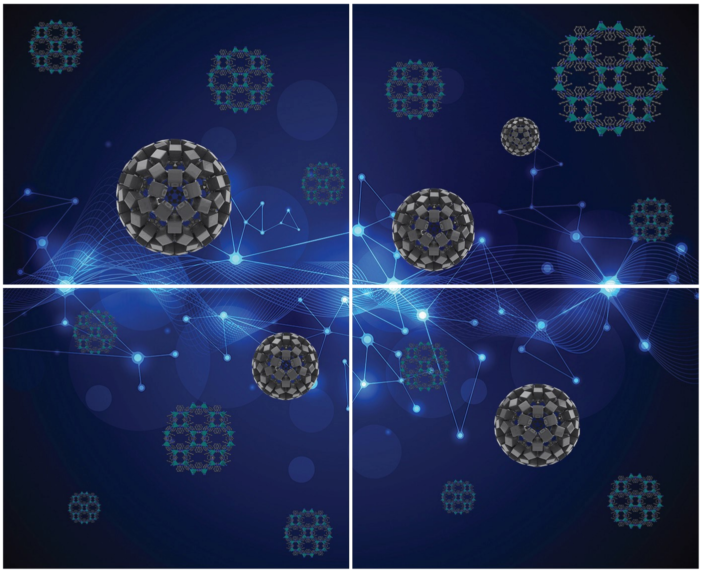

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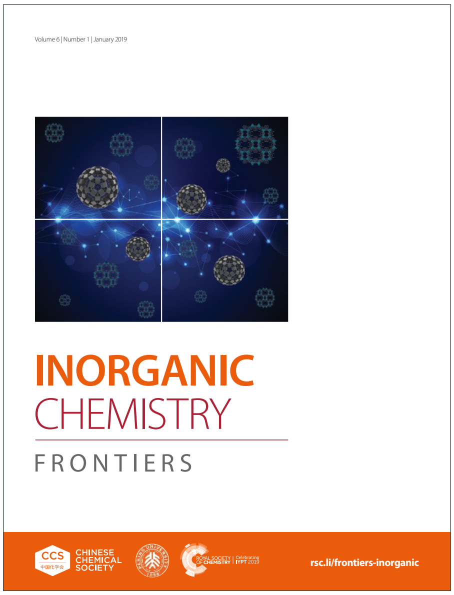

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ARTICLE

# Ethylene carbonate splitting and Claisen-type self-addition of γ-butyrolactone promoted by an oxygen-bridged Ga/P FLP

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The versatile reactivity of the geminal oxygen-bridged frustrated Lewis pair (FLP) $Bis_2Ga–O–P^tBu_2$ (Bis = $CH(SiMe_3)_2$; **GaOP**) is presented towards a series of C═O double bonds, strained oxygen-containing rings, alkynes plus alkenes and a C–Cl bond. By adding benzaldehyde, cyclopentanone (CP), γ-butyrolactone (GBL) or ethylene carbonate (EC), classical 1,2-adducts are formed. The reversibility of the **GaOP**·EC adduct stands out, enabling a splitting of EC after several days or when heated to 70 °C, resulting in FLP adducts of $CO_2$ and ethylene oxide (EO). The latter consists of a six-membered ring and is obtained *via* a ring-opening reaction, as verified by a further reaction involving the similar propylene oxide (PO). The **GaOP**·GBL adduct is further converted, with two adduct molecules combining to a 2:1 FLP adduct in a Claisen-type addition and ring-opening. Tests towards various acetylene containing species revealed that the ratio of deprotonation to ring-closure product can be adjusted. While PhC≡CH is almost exclusively bound as the deprotonation product, for $Me_3SiC≡CH$ also the ring-closure product forms. In the reaction with benzyl chloride, $Bis_2(Cl)Ga–O–P(Bn)^tBu_2$ is formed by a C–Cl bond activation.

## Introduction

Understanding the activation and transformation steps of small molecules is of crucial importance for many chemical applications. With the concept of frustrated Lewis pairs (FLPs), D. W. Stephan introduced a way to polarise substrates through the simultaneous action of Lewis acid (LA) and base (LB) functions.[1] Over the last two decades, this field of research has generated enormous interest, particularly within main-group chemistry and in the pursuit of transition metal-free catalysis.[2–5]

While many transition-metal-based systems boast catalysts for a variety of transformations,[6–13] the investigations of main-group-based FLP-mediated conversions has focused primarily on hydrogenation reactions, C–C couplings and $CO_2$ reductions.[14–19] Although FLPs are capable of activating many types of small molecules,[20–25] the majority form irreversible adducts, making the development of catalytic reactions difficult. Only a few undergo further transformation due to a conditional reversibility, which is essential for the broader application of FLPs as catalysts.[26,27]

Multiple reactivity studies have shed light on the following adjustment screws for tuning intramolecular FLP reactivity: the combination of LA and LB elements, their respective substituents and the linker unit. The literature predominantly features boron-containing FLP systems that have to bear strongly electron-withdrawing groups in order to be reactive.[28] Such groups are unnecessary for the heavier homologue aluminium, which is inherently more Lewis acidic.[29] However, its strong oxophilicity is a major drawback, particularly when it comes to the release of a transformed product that contains oxygen atoms.

Instead, the group 13 element gallium is on a similar Lewis acidity level but prefers softer Lewis bases according to the concept of hard and soft acids and bases (HSAB) by R. G. Pearson.[30,31] W. Uhl et al. took advantage of this tendency with the benzylidene-bridged E/P FLPs (E = Al, Ga) in a reaction involving carbon dioxide: the aluminium system irreversibly captures $CO_2$, while the gallium analogue binds it reversibly.[29,32]

Similarly, adjusting the linker unit, Y. Wang et al. have shown the reversibility of a $CO_2$ adduct with an oxygen-bridged B/P FLP.[33] Reducing the Lewis acidity by using donating atoms like oxygen, affects the reactivity. Recently, we demonstrated how to tune FLPs for specific reactivities with four chalcogen-bridged systems $Bis_2E–X–P^tBu_2$ (Bis = $CH(SiMe_3)_2$, E = Al, Ga, X = O, S).[34]

As $Bis_2Al–O–P^tBu_2$ (**AlOP**) imposes with $H_2$ and $CO_2$ activation, resulting in a reduction of carbon dioxide to the formate stage,[35] $Bis_2Ga–O–P^tBu_2$ (**GaOP**) forms an unusual temperature-dependent $H_2$ equilibrium by cleavage into $Bis_2GaH$ and $^tBu_2P(O)H$.[36] Especially this difference in oxophilicity prompted us to test reactivity towards molecules with C═O double bonds and small rings containing oxygen atoms.

In this work, we show impressive reactivities of $Bis_2Ga–O–P^tBu_2$: the cleavage of ethylene carbonate (EC) to ethylene oxide (EO) and $CO_2$, a Claisen addition of γ-butyrolactone (GBL), the ring opening of propylene oxide (PO) and deprotonation *versus* ring formation of phenyl- and trimethylsilylacetylene plus C–Cl bond activation of benzyl chloride.

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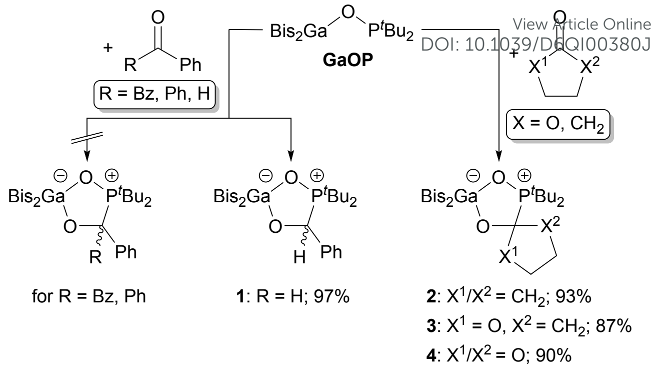
## Results and discussion

We probed the reactivity of the FLP $Bis_2Ga–O–P^tBu_2$ (**GaOP**) with a series of molecules containing C=O double bonds: benzil, benzophenone, benzaldehyde, cyclopentanone (CP), *γ*-butyrolactone (GBL) and ethylene carbonate (EC). Unlike the **AlOP** system, which forms a stable 1,2-addition product with benzil, the reaction of the **GaOP** system and benzil ends up in an unselective decomposition. As no reaction was observed with benzophenone, benzaldehyde with a less sterically demanding carbonyl unit was tested, affording the 1,2-adduct **1** (Scheme 1).

In the $^1H$ NMR spectrum, the resonances of the Bis and *tert*-butyl groups are split due to the implemented stereocentre. The chemical shifts of the methine protons at the gallium atom with –0.26 and –0.48 ppm indicate a tetra-coordination. The aldehyde proton resonance at 5.85 ppm is significantly shifted towards higher field compared to "free" benzaldehyde (9.64 ppm). The presence of a five-membered ring is confirmed by $^{13}C\{^1H\}$ NMR spectroscopy with the carbon stereocenter leading to a doublet at 75.5 ppm ($^1J_{P,C}$ = 40.4 Hz) and by $^{31}P\{^1H\}$ NMR with a signal at 70.9 ppm.

Tests towards CP, GBL and EC result in similar adducts **2**–**4** with five-membered ring motifs (Scheme 1). In all cases, the $^1H$ NMR signals of the adducts are broadened, indicating weak and potentially reversible adduct formation. In particular, the signals of the $CH_2$ groups show poor resolution and are lowfield-shifted in relation to their resonances in the free substrates.



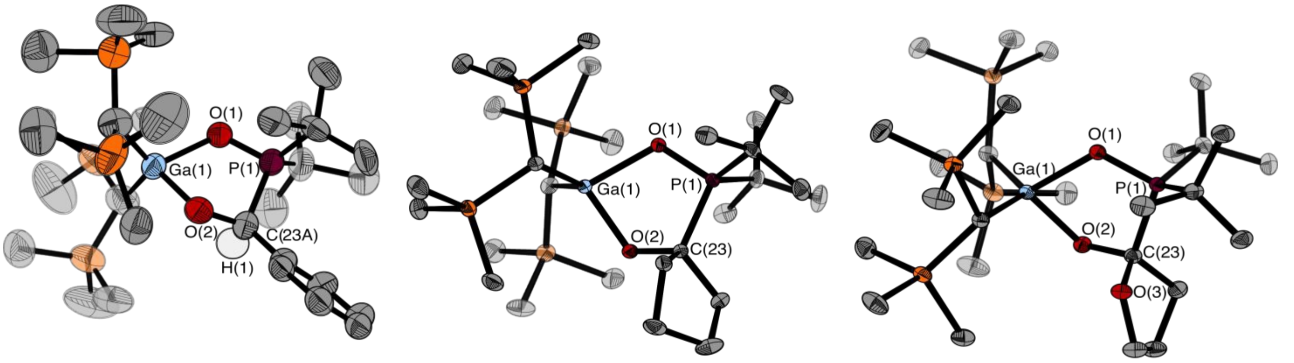
**Scheme 1.** Reactions of **GaOP** with benzaldehyde, cyclopentanone (CP), *γ*-butyrolactone (GBL) and ethylene carbonate (EC) to five-membered ring adducts **1**–**4**. Tests with benzil and benzophenone show decomposition or no reaction.

The $^1H$ NMR shifts of the methine protons range from –0.20 to –0.62 ppm, characteristic for quadruple coordinated gallium atoms (Table 1). Likewise, the $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR shifts as well as the $^1J_{P,C}$ coupling constants are consistent with normal 1,2-addition adducts.

Further confirmation was provided by elemental analysis and the determination of the molecular structures in the crystalline state, which verified the proposed connectivity for **1**, **2** and **3** (Figure 1). Despite numerous crystallizations attempts, the ethylene carbonate adduct **4** could only be obtained in a resin-like form.

**Table 1.** $^1H$, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopic data of **1**, **2**, **3**, **4**, **7** and **8**.

| Compound | No. | $\delta(^1H)$ (GaC**H**) / ppm | $\delta(^1H)$ ($^tBu$) / ppm | $\delta(^{13}C\{^1H\})$ (P**C**$X_3$) / ppm | $\delta(^{31}P\{^1H\})$ / ppm |
|---|---|---|---|---|---|
| **GaOP**·PhCHO | **1** | –0.48, –0.26 | 0.84 / 1.15 ($^3J_{P,H}$ = 13.4 / 13.3 Hz) | 75.5 ($^1J_{P,C}$ = 40.4 Hz) | 70.9 |
| **GaOP**·CP | **2** | –0.62, –0.39 | 0.99 / 1.11 ($^3J_{P,H}$ = 13.0 / 13.3 Hz) | 87.0 ($^1J_{P,C}$ = 40.0 Hz) | 77.2 |
| **GaOP**·GBL | **3** | –0.38, –0.20 br. | 1.10 br. | 109.9 ($^1J_{P,C}$ = 73.2 Hz) | 74.1 |
| **GaOP**·EC | **4** | –0.30 br. | 1.19 br. | 122.7 ($^1J_{P,C}$ = 120.4 Hz) | 70.6 |
| **GaOP**·EO | **7** | –0.40 br. | 0.87 ($^3J_{P,H}$ = 14.0 Hz) | 23.7 ($^1J_{P,C}$ = 54.5 Hz) | 75.1 |
| **GaOP**·PO | **8** | –0.49, –0.39 | 0.85 / 0.90 ($^3J_{P,H}$ = 13.9 / 14.0 Hz) | 30.0 ($^1J_{P,C}$ = 54.5 Hz) | 73.0 |



**1** **2** **3**

**Figure 1.** Molecular structures of **1**, **2** and **3** in the solid state. Hydrogen atoms (except H(1) in **1**) and minor occupied disordered parts are omitted for clarity. Ellipsoids are set at 50% probability level. Selected distances, bond length [Å] and angles [°]: **1**: Ga(1)···P(1) 2.989(1), Ga(1)–O(1) 2.004(2), Ga(1)–O(2A) 1.834(13), O(1)–P(1) 1.524(2), P(1)–C(23A) 1.891(16), O(2)–C(23) 1.44(2); Ga(1)–O(1)–P(1) 115.2(2), C(1A)–Ga(1)–C(8A) 126.9(8), O(1)–Ga(1)–O(2A) 86.4(4), O(2A)–Ga(1)–P(1)–C(23A) 25.0(9); **2**: Ga(1)···P(1) 2.990(1), Ga(1)–O(1) 1.986(1), Ga(1)–O(2) 1.894(1), O(1)–P(1) 1.538(1), P(1)–C(23) 1.897(2), O(2)–C(23) 1.404(2); Ga(1)–O(1)–P(1) 115.5(1), C(1)–Ga(1)–C(8) 119.1(1), O(1)–Ga(1)–O(2) 87.0(1), O(2)–Ga(1)–P(1)–C(23) 18.9(1); **3**: Ga(1)···P(1) 2.986(1), Ga(1)–O(1) 1.993(1), Ga(1)–O(2) 1.907(1), O(1)–P(1) 1.533(1), P(1)–C(23) 1.906(1), O(2)–C(23) 1.360(1); Ga(1)–O(1)–P(1) 115.2(1), C(1)–Ga(1)–C(8) 122.4(1), O(1)–Ga(1)–O(2) 86.9(1), O(2)–Ga(1)–P(1)–C(23) 18.4(1).

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A comparison of the molecular structures shows similar five-membered rings: the Ga(1)–O(1)–P(1) angles (115.2(2)–115.5(1)°) and the Ga(1)···P(1) distances (2.986(1)–2.990(1) Å) are identical. The gallium atoms are, as expected, in distorted tetrahedral environments, with the O(1)–Ga(1)–O(2) angles ranging from 86.4(4) to 87.0(1)°. Only the O(2)–C(23) bond length varies significantly with 1.44(2) (for **1**), 1.404(2) (for **2**) and 1.360(1) Å (for **3**). However, these values are higher than in the carbon dioxide adduct (**6**: 1.285(3) Å), evidencing an oxygen-carbon single bond.

Strikingly, the 1,2-addition adducts **3** and **4** undergo further conversions in solution within two days at ambient temperature (partially) or when heated to 70 °C for six hours (fully). The GBL adduct **3** is subject to a rearrangement, forming the adduct type **5** in a Claisen addition and ring-opening reaction (Scheme 2). In this reaction, two molecules of the adduct **3** react to a Claisen addition product, which then forms the α,β-unsaturated ketone resulting from a ring-opening. This molecule is bound to two FLP units. The reaction to **5** is presumably triggered by the deprotonation of the α-proton, resulting in the formation of the P–H unit (Scheme 2 or SI Scheme S1).

Multinuclear NMR spectroscopy analysis approves the formation of **5**. The $^{31}$P NMR spectrum shows a doublet of multiplets at 63.2 ppm ($^{1}J_{P,H}$ = 422.9 Hz), confirming the generation of phosphane oxide. The broadened signal indicates its interaction with the Lewis acid moiety. The $^{1}$H NMR shifts of the methine protons at –0.30 and –0.48 ppm verify tetra-coordinated gallium atoms and suggest the presence of two different Bis$_2$Ga-groups, also confirmed by $^{29}$Si NMR spectroscopy. The framework of the Claisen added and ring-opened product **5** is identified by $^{1}$H and $^{13}$C{$^{1}$H} NMR spectroscopy, with five CH$_2$ units observable in the $^{13}$C DEPT-135 NMR spectrum. The remaining quaternary carbon atoms show shifts of 188.0, 178.7 and 90.7 ppm, respectively. The $^{1}$H-$^{1}$H COSY NMR spectrum validates the correlation of the methylene protons at 3.68 and 2.49 ppm and of those at 4.07, 2.49 and 2.10 ppm. All these assignments are consistent within the corresponding 2D NMR spectra ($^{1}$H-$^{13}$C HSQC and HMBC). As for the 1,2-adduct **4**, multiple attempts to crystallize **5** failed and only yielded resin-like residues.

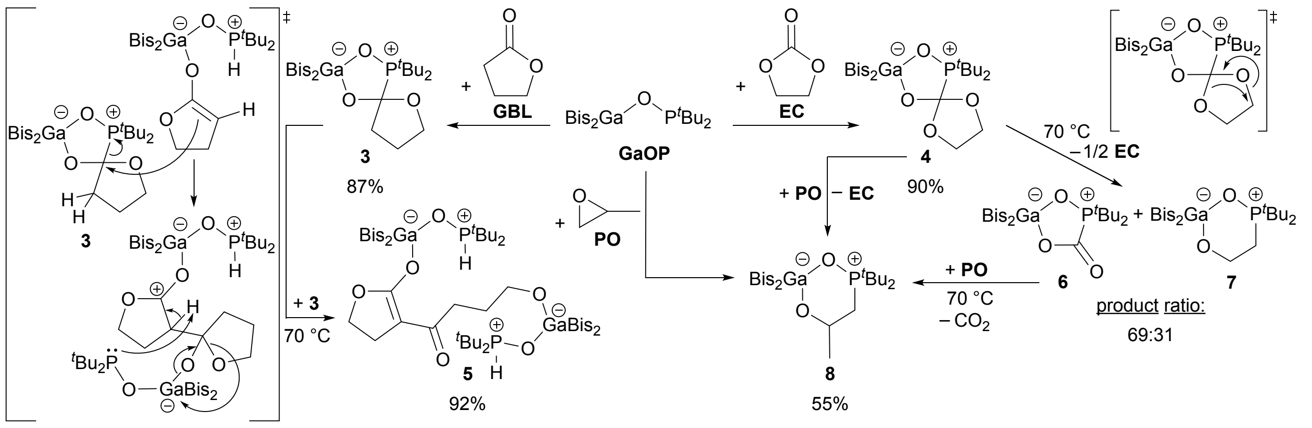
A different transformation is observed for **4**. The added ethylene carbonate (EC) is cleaved, resulting in the formation of the FLP adducts of carbon dioxide (**6**) and of ethylene oxide (EO) (**7**) accompanied by the release of half an equivalent of EC (Scheme 2). This observation lends support to the assumed reversible nature of the adduct formation with EC.

There are two main pathways for the splitting of EC (see SI, Scheme S2): the activation of the carbonyl unit followed by ring-opening (path A) or ring-opening, where the carbonate unit remains intact followed by an extrusion (retro-insertion) of CO$_2$ leading to the EO adduct **7** (path B). Both pathways have been reported in literature,[37,38] but the experimental outcome (formation of more CO$_2$ adduct **6**) matches only path A, as **7** is stable in the presence of CO$_2$.

In the $^{1}$H NMR spectrum one set of signals corresponds to the literature values of **6**.[34] Characteristic for the EO adduct **7** is the doublet of triplets of the oxygen-bound CH$_2$ group at 4.10 ppm ($^{3}J_{P,H}$ = 18.5 Hz, $^{3}J_{H,H}$ = 5.6 Hz). Due to overlapping resonances, it was not possible to localise a resonance for the second CH$_2$ unit exactly in the $^{1}$H NMR spectrum, even when using 2D NMR. In contrast, the $^{13}$C{$^{1}$H} NMR spectrum contains a resonance in this regard as a doublet at 23.7 ppm ($^{1}J_{P,C}$ = 54.5 Hz).

To further verify the formation of a six-membered ring, we reacted **GaOP** with the similar propylene oxide (PO). In a ring-opening reaction the adduct **8** was formed. Both **7** and **8** have comparable chemical shifts. For example, the $^{31}$P{$^{1}$H} NMR shifts differ slightly (**7**: 75.1 ppm; **8**: 73.0 ppm). In the $^{13}$C{$^{1}$H} NMR spectrum the carbon atom attached to the oxygen atom is detected at 60.5 (**7**) and 65.6 ppm (**8**), respectively. The propylene unit of **8** induces signals at 4.35, 1.63, 1.36 and 1.32 ppm in the $^{1}$H NMR spectrum, which are similar to those of **7**. Due to diastereotopic nature of the P–CH$_2$ protons, both resonances are split into doublets of multiplets with a characteristic $^{3}J_{P,H}$ coupling constant of 14.8 Hz (see SI, Figure S38).

Crystal structure determinations of both, the EO and PO adducts **7** and **8**, confirm the six-membered ring motif (Figure 2). Since they differ only by an exocyclic methyl group, the structural parameters are nearly the same. The Ga(1)···P(1) distances



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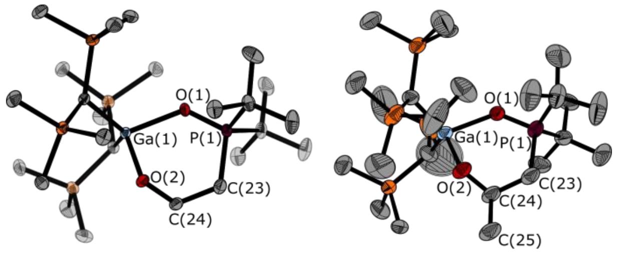
**Scheme 2.** The 1,2-adduct **3** is further converted in a Claisen-type addition, forming a 2:1 FLP Claisen addition adduct with subsequent ring-opening with the proposed mechanism and structure **5** (left). Heating **4** to 70 °C results in the splitting of EC, leading to the FLP $CO_2$ and EO adducts (**6**/**7**) and one half of an equivalent of EC (right). In a ring-opening reaction propylene oxide forms a six-membered ring adduct **8**. Also exchange reactions of **4** and **6** with propylene oxide (PO) result in adduct **8**.



**7** **8**

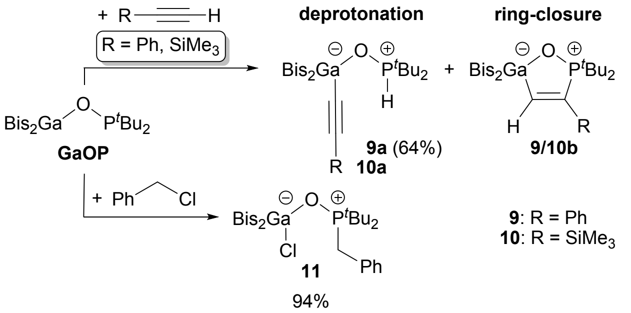
**Figure 2.** Molecular structures of **7** and **8** in the solid state. Hydrogen atoms and minor occupied parts are omitted for clarity. Ellipsoids are set at 50% probability level. Selected distances, bond length [Å] and angles [°]: **7**: Ga(1)···P(1) 3.198(1), Ga(1)–O(1) 2.007(1), Ga(1)–O(2) 1.866(1), O(1)–P(1) 1.527(1), P(1)–C(23) 1.826(1), C(23)–C(24) 1.535(2), O(2)–C(24) 1.401(1); Ga(1)–O(1)–P(1) 129.1(1), O(1)–Ga(1)–O(2) 92.3(1), O(2)–Ga(1)–P(1)–C(23) 15.2(1); **8**: Ga(1)···P(1) 3.191(1), Ga(1)–O(1) 2.001(2), Ga(1)–O(2) 1.854(3), O(1)–P(1) 1.523(2), P(1)–C(23) 1.847(4), C(23)–C(24) 1.520(6), O(2)–C(24) 1.393(5); Ga(1)–O(1)–P(1) 129.3(1), O(1)–Ga(1)–O(2) 93.1(1), O(2)–Ga(1)–P(1)–C(23) 14.3(3).

of 3.191–3.198(1) Å are longer than in free FLP **GaOP** (3.082(1) Å).[36] The Ga(1)–O(1)–P(1) angles in **7** (129.1(1)°) or **8** (129.3(1)°) are slightly wider than that in **GaOP** of 126.2(1)°.

In an NMR spectroscopic study, we tested the exchange reaction of the ethylene carbonate adduct **4** and the $CO_2$ adduct **6** with an excess of propylene oxide (PO). When **4** is reacted with PO, the formation of adduct **8** and free EC is observed at ambient temperatures. For **6**, heating to 70 °C is necessary to exchange the carbon dioxide with PO. These findings gave further insights and strengthened the proposed mechanism (path A) of the ethylene carbonate splitting (see SI, Scheme S2).

Relating to previous investigations of slightly polarized alkynes with the **AlOP** system,[39] we tested the reactivity of phenyl- and trimethylsilylacetylene with the **GaOP** FLP. Interestingly, there is a clear difference in the product ratio of deprotonation *vs.* ring-closure. Whereas deprotonation predominates in the case of phenylacetylene (>96%), and crystallization gave the deprotonation product **9a** in pure form, only mixtures with deprotonation/ring-closure ratios for of approximately 2:1 (**10a**:**10b**) were obtained for trimethylsilylacetylene (Scheme 3).

Heating the reaction to 70 °C for 24 h did not result in formation of the ring-closure products **9b** and **10b**. The same behaviour, along with a similar deprotonation/ring-closure ratio, was previously observed for **AlOP**·PhC≡CH (85:15).[39] Although the experimental outcome is consistent, quantum chemical calculations suggest that the ring-closure products **9b**/**10b** are thermodynamically favoured (see SI). To explain these contradictions, we assume that the deprotonation products **9a**/**10a** are kinetically preferred and the activation barriers of these meta-stable states to the ring-closure products **9b**/**10b** are too high. Furthermore, a partial separation of **9a** and **10a** into di-*tert*-butylphosphane oxide and $Bis_2GaC{\equiv}CR$ (R = Ph, $SiMe_3$) at higher temperatures, as we reported it for the $H_2$ adduct of the **GaOP** system,[36] would prevent a rearrangement to ring-closure.



**Scheme 3.** Reactions of **GaOP** with phenylacetylene and trimethylsilylacetylene result in deprotonation (**9a**/**10a**) or ring-closure (**10b**) products. Using benzyl chloride leads to $Bis_2(Cl)Ga–O–P(H)^tBu_2$ (**11**).

While the ring-closure product **10b** was identified by $^1H$ NMR spectroscopy by its characteristic doublet at 9.25 ppm ($^3J_{P,H}$ = 56.0 Hz), the deprotonation product **10a** has a typical doublet at 5.97 ppm with a $^1J_{P,H}$ coupling constant of 442.2 Hz. The $^{31}P$ NMR spectrum displays a doublet of multiplets with the same large coupling constant at 66.9 ppm (**10a**) and a single multiplet at 84.8 ppm (**10b**), confirming the identity of these two species. However, the $^1H$ NMR integral ratios of the deprotonation product **10b** do not match exactly; there is a surplus of phosphane oxide present. Besides hydrolysis, the aforementioned partial separation into the phosphane oxide species and $Bis_2GaC{\equiv}CSiMe_3$ is probably another plausible explanation for these mismatching integral ratios. The excess of phosphane oxide undergoes a dynamic exchange with the deprotonation product **10a**, meaning no "free" phosphane oxide being detected in the $^{31}P$ NMR spectrum. Elemental analyses confirm this hypothesis and the compositions of **9** and **10**.

We were able to determine the solid-state molecule structures of the deprotonation products **9a** and **10a** (Figure 3). Contrary to the structure of **AlOP**·PhC≡CH in both forms,[39] and although the formation of the ring-closure product **10b** is evident by NMR spectroscopy, the crystalline sample showed no evidence for different types of crystals. The determined bond lengths of C(23)–C(24) in the deprotonation products fall over the expected range for triple bonds (**9a**: 1.186(3) Å; **10a**: 1.206(2) Å). The angles ∠(Ga–C≡C) (**9a**: 175.3(2)°; **10a**: 177.5(2)°) and ∠(C≡C–R) (**9a**: 178.5(2)°; **10a**: 178.0(2)°) in the acetylide units are similar, nearly matching an idealized bond angle of 180°. In contrast, both structures differ in their Ga(1)–O(1)–P(1) angles (**9a**: 155.3(1)°; **10a**: 142.4(1)°) and their torsion angles τ(C(23)–Ga(1)–P(1)–H(1)) with 57.0(8)° for **9a** and 41.1(9)° for **10a**. These values for the heavier gallium homologue **9a** are significantly smaller than those of its aluminium analogue **AlOP**·PhC≡CH (168.8(2)°; 95.9(5)°).[39]

Activation attempts with the non-polar diphenylacetylene and the alkene species styrene, stilbene, 1,2-diphenylethene and 1-phenyl-1-(trimethylsiloxyl)ethylene remained

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unsuccessful. However, we demonstrated the versatility of the **GaOP** FLP by reacting it with benzyl chloride. After heating to 70 °C, the adduct $Bis_2(Cl)Ga–O–P(Bn)^tBu_2$ (**11**) was isolated and fully characterized by means of NMR spectroscopy, elemental analysis and single crystal X-ray diffraction experiments (Figure 3). Cleavage of the C–Cl bond resulted in the chloride ion bound to the Lewis acidic gallium and a benzyl group attached to the phosphorus atom.

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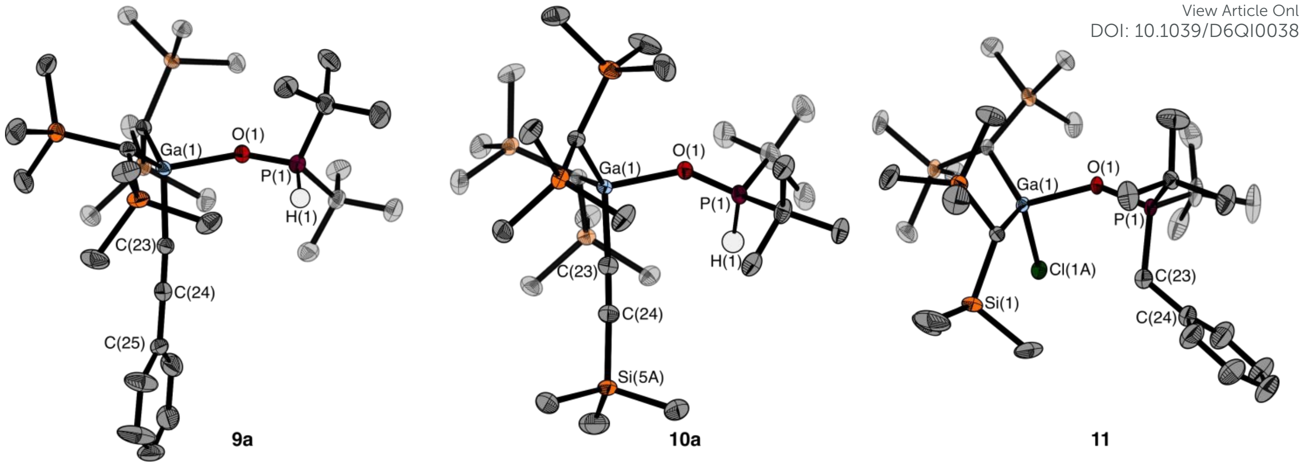

**Figure 3.** Molecular structures of **9a**, **10a** and **11** in the solid state. Hydrogen atoms except H(1) and minor occupied disordered parts are omitted for clarity. Ellipsoids are set at 50% probability level. Selected distances, bond length [Å] and angles [°]: **9a**: Ga(1)···P(1) 3.469(1), Ga(1)–O(1) 2.037(1), O(1)–P(1) 1.512(1), Ga(1)–C(23) 2.004(1), C(23)–C(24) 1.187(2); Ga(1)–O(1)–P(1) 155.3(1), C(1)–Ga(1)–C(8) 117.9(1), C(23)–Ga(1)–P(1)–H(1) 57.0(8); **10a**: Ga(1)···P(1) 3.338(1), Ga(1)–O(1) 2.008(1), O(1)–P(1) 1.514(1), Ga(1)–C(23) 1.978(2), C(23)–C(24) 1.206(2); Ga(1)–O(1)–P(1) 142.4(1), C(1)–Ga(1)–C(8) 121.6(1), C(23)–Ga(1)–P(1)–H(1) 41.1(9). **11**: Ga(1)···P(1) 3.371(1), Ga(1)–O(1) 2.014(2), O(1)–P(1) 1.528(2), Ga(1)–Cl(1A) 2.257(3), P(1)–C(23) 1.827(3); Ga(1)–O(1)–P(1) 143.8(1), C(1)–Ga(1)–C(8) 122.8(1), Cl(1A)–Ga(1)–P(1)–C(23) 45.9(1).

In the $^{1}H$ NMR spectrum the formation of **11** is proven by a doublet of the $CH_2$ group at 3.40 ppm ($^{3}J_{P,H} = 14.0$ Hz). The broad methine proton singlet at –0.06 ppm verifies the tetra-coordinated gallium atom. Besides the signal at 63.6 ppm, another species containing a P–H unit was detected by a doublet $^{31}P$ NMR resonance at 69.7 ppm ($^{1}J_{P,H} = 451.5$ Hz). This minor impurity was identified as the formal hydrogen chloride adduct $Bis_2(Cl)Ga–O–P(H)^{t}Bu_2$, likely originating from the partial hydrolysis of benzyl chloride. The chemical shifts are comparable with those of the recently published HBr adduct, **GaOP**·HBr.[36]

The molecular structure of **11** shows a tetrahedral environment at the gallium atom and the Ga(1)–Cl(1A) bond length of 2.257(3) Å is slightly longer than in the free $Bis_2GaCl$ (2.193(1) Å).[40] Compared with **GaOP**·HBr, the Ga(1)–O(1)–P(1) angles are almost identical (**GaOP**·HBr: 143.1(1)°; **11**: 143.8(1)°). As the value of $\tau$(C(23)–Ga(1)–P(1)–H(1)) = 45.9(1)° indicates, the chloride ion and benzyl group are twisted, in a similar manner to the proton and acetylide unit in the deprotonation adducts **9a** and **10a**.

## Conclusions

$Bis_2Ga–O–P^{t}Bu_2$ (**GaOP**) exhibits a remarkably broad and tuneable reactivity profile towards a wide variety of substrates, ranging from carbonyl compounds to strained oxygen heterocylces, alkynes and polar σ-bonds. In classical 1,2-additions to the C=O double bond of benzaldehyde, cyclopentanone (CP), γ-butyro-lactone (GBL) and ethylene carbonate (EC), FLP adducts with five-membered rings are observed. Beyond simple adduct formation, the system reveals unexpected secondary transformations such as the Claisen-type reaction of two GBL adducts and subsequent trapping of the resulting product as a 2:1 FLP adduct. The reversible activation of EC is particularly notable, as it enables a fragmentation into $CO_2$ and ethylene oxide (EO), which were both detected as the corresponding FLP adducts. This ring-opening reaction to a six-membered ring was proven by using propylene oxide (PO), which results in the formation of the similar adduct. Reactions involving phenyl- and trimethylsilylacetylene further demonstrate that subtle changes in the substrate structure allow deprotonation and ring-closure to be deliberately steered, providing rare insight into selectivity control in FLP chemistry. Activating the C–Cl bond in benzyl chloride broadens the scope of activation to include polar σ-bonds. Taken together, these findings establish the **GaOP** system as a highly versatile and adaptable FLP, capable of reversible activation, bond cleavage and multistep substrate transformation.

## Experimental section

### General methods

All reactions and manipulations with air and moisture sensitive compounds were carried out under conventional Schlenk techniques or in a glove box using argon as inert gas. Volatile compounds were handled in a vacuum line. The solvents *n*-hexane, toluene, toluene-$d_8$ and benzene-$d_6$ were dried over a Na/K alloy, distilled and degassed prior to use. $Bis_2Ga–O–P^{t}Bu_2$ (**GaOP**) was prepared according to literature procedure.[36] Benzaldehyde, cyclopentanone (CP), γ-butyrolactone (GBL), propylene oxide (PO), phenylacetylene, trimethylsilyl acetylene and benzyl chloride were degassed, dried over mole sieves (4 Å) and distilled prior to use. Ethylene carbonate (EC) was used without further purification. NMR spectra were recorded using a Bruker Avance III 500, Avance III 500 HD, Ascend 500 neo2K or Ascend 500 neo3K spectrometer at ambient temperature unless otherwise stated. Chemical shifts were referenced to the residual proton or carbon signal of the solvent (benzene-$d_6$: $^{1}H$: 7.16 ppm, $^{13}C$: 128.1 ppm; toluene-$d_8$: $^{1}H$: 2.09 ppm) or externally ($^{29}Si$: $SiMe_4$, $^{31}P$: 85% $H_3PO_4$ in $H_2O$). Elemental analyses were carried out using a HEKATECH EURO Elemental Analyzer.

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**Synthetic procedure**

Bis$_2$Ga–O–P$^t$Bu$_2$ (**GaOP**) was dissolved in toluene (2 mL), the substrate was added and the reaction was stirred for 24 h at room temperature, unless otherwise stated. All volatiles were removed under reduced pressure and the residue dried in *vacuo*.

**Bis$_2$Ga–O–P$^t$Bu$_2$**·PhCHO (**1**): Using benzaldehyde (5 µL, 4.8 mg, 45 µmol, 1.2 equiv.) and after an additional washing step with *n*-hexane, **1** was obtained as a colourless solid (24 mg, 37 µmol, 97%). $^1$H NMR (500 MHz, C$_6$D$_6$): $\delta$ [ppm] = –0.48 (s, 1H, GaC**H**), –0.26 (s, 1H, GaC**H**), 0.36 – 0.58 (m, 36H, Si(C**H**$_3$)$_3$), 0.84 (d, $^3J_{\mathrm{P,H}}$ = 13.4 Hz, 9H, C(C**H**$_3$)$_3$), 1.15 (d, $^3J_{\mathrm{P,H}}$ = 13.3 Hz, 9H, C(C**H**$_3$)$_3$), 5.85 (s, C**H**O), 7.02 (t, $^3J_{\mathrm{H,H}}$ = 7.2 Hz, 1H, *para*-**H**), 7.14 (t, $^3J_{\mathrm{H,H}}$ = 7.3 Hz, 2H, *meta*-**H**), 7.72 (d, $^3J_{\mathrm{H,H}}$ = 7.6 Hz, 2H, *ortho*-**H**). $^{13}$C{$^1$H} NMR (126 MHz, C$_6$D$_6$): $\delta$ [ppm] = 3.9 (s, Si(**C**H$_3$)$_3$), 4.6(s, Si(**C**H$_3$)$_3$), 4.6 (s, Si(**C**H$_3$)$_3$), 4.8 (s, Si(**C**H$_3$)$_3$), 6.6 (s, Ga**C**H), 27.1 (s, C(**C**H$_3$)$_3$), 28.2 (s, C(**C**H$_3$)$_3$), 35.3 (s, **C**(CH$_3$)$_3$), 37.0 (s, **C**(CH$_3$)$_3$), 75.5 (d, $^1J_{\mathrm{P,C}}$ = 40.4 Hz, **C**HO), 126.3 (s, *ortho*-**C**), 127.2 (s, *para*-**C**), 128.3 (s, *meta*-**C**), 141.6 (s, *ipso*-**C**). $^{29}$Si{$^1$H} NMR (99 MHz, C$_6$D$_6$): $\delta$ [ppm] = –1.1 (s). $^{31}$P{$^1$H} NMR (202 MHz, C$_6$D$_6$): $\delta$ [ppm] = 70.9 (s). Elemental analysis calcd (%) for C$_{29}$H$_{62}$GaO$_2$PSi$_4$ ($M_{\mathrm{r}}$ = 655.85): C 53.11, H 9.53; found C 53.57, H 9.54.

**Bis$_2$Ga–O–P$^t$Bu$_2$**·CP (**2**): Using cyclopentanone (10 µL, 9.5 mg, 113 µmol, 1.2 equiv.) and after an additional washing step with *n*-hexane, **2** was obtained as a colourless solid (58 mg, 91 µmol, 93%). $^1$H NMR (500 MHz, C$_6$D$_6$): $\delta$ [ppm] = –0.62 (s, 1H, GaC**H**), –0.39 (s, 1H, GaC**H**), 0.42 – 0.50 (s, 36H, Si(C**H**$_3$)$_3$), 0.99 (d, $^3J_{\mathrm{P,H}}$ = 13.0 Hz, 9H, C(C**H**$_3$)$_3$), 1.11 (d, $^3J_{\mathrm{P,H}}$ = 13.3 Hz, 9H, C(C**H**$_3$)$_3$), 1.48(m, 2H, C**H**$_2$), 1.66 (m, 2H, C**H**$_2$), 2.03 (m, 4H, C**H**$_2$). $^{13}$C{$^1$H} NMR (126 MHz, C$_6$D$_6$): $\delta$ [ppm] = 5.3 (s, Si(**C**H$_3$)$_3$), 6.8 (s, Ga**C**H), 9.9 (s, Ga**C**H), 23.5 (d, $^2J_{\mathrm{P,C}}$ = 11.9 Hz, **C**H$_2$), 23.8 (d, $^2J_{\mathrm{P,C}}$ = 12.4 Hz, **C**H$_2$), 28.2 (s, C(**C**H$_3$)$_3$), 28.8 (s, C(**C**H$_3$)$_3$), 35.8 (d, $^1J_{\mathrm{P,C}}$ = 41.4 Hz, **C**(CH$_3$)$_3$), 37.5 (d, $^1J_{\mathrm{P,C}}$ = 41.8 Hz, **C**(CH$_3$)$_3$), 41.1 (s, **C**H$_2$), 42.5 (s, **C**H$_2$), 87.0 (d, $^1J_{\mathrm{P,C}}$ = 40.0 Hz, P**C**O). $^{29}$Si{$^1$H} NMR (99 MHz, C$_6$D$_6$): $\delta$ [ppm] = –1.2 (s). $^{31}$P{$^1$H} NMR (202 MHz, C$_6$D$_6$): $\delta$ [ppm] = 77.2 (s). Elemental analysis calcd (%) for C$_{27}$H$_{64}$GaO$_2$PSi$_4$ ($M_{\mathrm{r}}$ = 633.84): C 51.16, H 10.18; found C 50.78, H 10.14.

**Bis$_2$Ga–O–P$^t$Bu$_2$**·GBL (**3**): Using γ-butyrolactone (10 µL, 11.3 mg, 131 µmol, 1.0 equiv.) and after an additional washing step with *n*-hexane, **3** was obtained as a colourless solid (70 mg, 110 µmol, 87%). $^1$H NMR (500 MHz, C$_6$D$_6$): $\delta$ [ppm] = –0.38 (br. s, 1H, GaC**H**), –0.20 (br. s, 1H, GaC**H**), 0.45 (s, 36H, Si(C**H**$_3$)$_3$), 1.10 (m, 18H, C(C**H**$_3$)$_3$), 1.44 (m, 1H, C**H**$_2$), 1.60 (br. m, 1H, C**H**$_2$), 1.93 (br. s, 1H, C**H**$_2$), 2.11 (br. s, 1H, C**H**$_2$), 3.32 (br. s, 1H, C**H**$_2$), 4.00 (br. s, 1H, C**H**$_2$). $^{13}$C{$^1$H} NMR (126 MHz, C$_6$D$_6$): $\delta$ [ppm] = 5.1 (s, Si(**C**H$_3$)$_3$), 9.2 (s, Ga**C**H), 24.7 (s, **C**H$_2$), 27.8 (s, C(**C**H$_3$)$_3$), 35.6 (d, $^1J_{\mathrm{P,C}}$ = 47.5 Hz, **C**(CH$_3$)$_3$), 36.4 (d, $^1J_{\mathrm{P,C}}$ = 48.5 Hz, **C**(CH$_3$)$_3$), 39.6 (s, **C**H$_2$), 67.1 (s, O**C**H$_2$), 109.9 (d, $^1J_{\mathrm{P,C}}$ = 73.2 Hz, P**C**O$_2$). $^{29}$Si{$^1$H} NMR (99 MHz, C$_6$D$_6$): $\delta$ [ppm] = –1.5 (s). $^{31}$P{$^1$H} NMR (202 MHz, C$_6$D$_6$): $\delta$ [ppm] = 74.1 (s). Elemental analysis calcd (%) for C$_{26}$H$_{62}$GaO$_3$PSi$_4$ ($M_{\mathrm{r}}$ = 635.82): C 49.12, H 9.83; found C 48.61, H 10.23.

**Bis$_2$Ga–O–P$^t$Bu$_2$**·EC (**4**): Using ethylene carbonate (9.1 mg, 103 µmol, 1.1 equiv.) and after an additional washing step with *n*-hexane, **4** was obtained in a colourless, resin-like form (52 mg, 82 µmol, 90%). $^1$H NMR (500 MHz, C$_6$D$_6$): $\delta$ [ppm] = –0.30 (br. s, 2H, GaC**H**), 0.45 (s, 36H, Si(C**H**$_3$)$_3$), 1.19 (m, 18H, C(C**H**$_3$)$_3$), 3.28 (br. s, 2H, C**H**$_2$), 3.80 (br. s, 2H, C**H**$_2$). $^{13}$C{$^1$H} NMR (126 MHz, C$_6$D$_6$): $\delta$ [ppm] = 4.9 (s, Si(**C**H$_3$)$_3$), 9.0 (s, Ga**C**H), 27.5 (s, C(**C**H$_3$)$_3$), 35.8 (br. m, **C**(CH$_3$)$_3$), 63.4 (s, O**C**H$_2$), 122.7 (d, $^1J_{\mathrm{P,C}}$ = 120.4 Hz, P**C**O$_3$). $^{29}$Si{$^1$H} NMR (99 MHz, C$_6$D$_6$): $\delta$ [ppm] = –1.3 (s). $^{31}$P{$^1$H} NMR (202 MHz, C$_6$D$_6$): $\delta$ [ppm] = 70.6 (s). Elemental analysis calcd (%) for C$_{25}$H$_{60}$GaO$_4$PSi$_4$ ($M_{\mathrm{r}}$ = 637.79): C 47.08, H 9.48; found C 46.99, H 9.56.

**Claisen addition ring-opening FLP adduct 5**: Heating a solution of **GaOP** (55.7 mg, 101 µmol) and GBL (7.9 µL, 8.9 mg ,104 µmol, 1.0 equiv.) in toluene (3 mL) to 70 °C for 6 h, full conversion of the FLP to **5** was observed. After removing all volatiles in *vacuo*, and an additional washing step with *n*-hexane, **5** was obtained in a resin-like form (59.4 mg, 47 µmol, 92%). $^1$H NMR (500 MHz, C$_6$D$_6$): $\delta$ [ppm] = –0.48 (s, 2H, GaC**H**), –0.30 (s, 2H, GaC**H**), 0.34 (s, 36H, Si(C**H**$_3$)$_3$), 0.34 (s, 18H, Si(C**H**$_3$)$_3$), 0.36 (s, 18H, Si(C**H**$_3$)$_3$), 0.99 (d, $^3J_{\mathrm{P,H}}$ = 15.0 Hz, 18H, C(C**H**$_3$)$_3$), 2.10 (tt, $J$ = 11.9, 5.8 Hz, 2H, C**H**), 2.49 (m, 2H, C**H**), 2.49 (t, $J$ = 8.3 Hz, 2H, C**H**), 3.68 (t, $J$ = 8.2 Hz, 2H, C**H**), 4.07 (t, $J$ = 6.0 Hz, 2H, C**H**$_2$). $^{13}$C{$^1$H} NMR (126 MHz, C$_6$D$_6$): $\delta$ [ppm] = 3.9/4.1/4.5 (s, Si(**C**H$_3$)$_3$), 7.5/10.3 (s, Ga**C**H), 25.8 (s, C(**C**H$_3$)$_3$), 26.0 (s, **C**H$_2$), 30.9 (s, **C**H$_2$), 33.6 (d, $^1J_{\mathrm{P,C}}$ = 59.0 Hz, **C**(CH$_3$)$_3$), 36.1 (s, **C**H$_2$), 65.7 (s, O**C**H$_2$), 67.8 (s, O**C**H$_2$), 90.7 (s, **C**CO$_2$Ga), 178.7 (s, **C**O$_2$Ga), 188.0 (s, **C**=O). $^{29}$Si{$^1$H} NMR (99 MHz, C$_6$D$_6$): $\delta$ [ppm] = –1.4 (s), –0.5 (s), –0.3 (s). $^{31}$P{$^1$H} NMR (202 MHz, C$_6$D$_6$): $\delta$ [ppm] = 63.2 (s).

**Bis$_2$Ga–O–P$^t$Bu$_2$**·EO (**7**): After heating a solution of **GaOP** (60.5 mg, 110 µmol) and EC (9.6 mg, 110 µmol, 1.0 equiv.) in toluene (3 mL) to 70 °C for 6 h, full conversion of the FLP to a mixture of Bis$_2$Ga–O–P$^t$Bu$_2$·CO$_2$ (**6**) and **7** was observed. The chemical shifts of **6** are in accordance with the literature values.[34] Crystals of **7**, suitable for X-ray diffraction experiments, were obtained by slow evaporation of a solution in C$_6$D$_6$. $^1$H NMR (500 MHz, C$_6$D$_6$): $\delta$ [ppm] = –0.40 (br. s, 2H, GaC**H**), 0.49 (s, 36H, Si(C**H**$_3$)$_3$), 0.87 (d, $^3J_{\mathrm{P,H}}$ = 14.0 Hz, 18H, C(C**H**$_3$)$_3$), 4.10 (dt, $^3J_{\mathrm{P,H}}$ = 18.5 Hz, $^3J_{\mathrm{H,H}}$ = 5.6 Hz, 2H, OC**H**$_2$); due to overlapping resonances, as well in 2D spectra, signals for PC**H**$_2$ could not be localized exactly. $^{13}$C{$^1$H} NMR (126 MHz, C$_6$D$_6$): $\delta$ [ppm] = 5.1 (s, Si(**C**H$_3$)$_3$), 10.5 (s, Ga**C**H), 23.7 (d, $^1J_{\mathrm{P,C}}$ = 54.5 Hz, P**C**H$_2$), 25.9 (s, C(**C**H$_3$)$_3$), 26.2 (s, C(**C**H$_3$)$_3$), 33.6 (d, $^1J_{\mathrm{P,C}}$ = 58.9 Hz, **C**(CH$_3$)$_3$), 35.4 (d, $^1J_{\mathrm{P,C}}$ = 58.3 Hz, **C**(CH$_3$)$_3$), 60.5 (d, $^2J_{\mathrm{P,C}}$ = 7.6 Hz, O**C**H$_2$). $^{29}$Si{$^1$H} NMR (99 MHz, C$_6$D$_6$): $\delta$ [ppm] = –0.5 (s). $^{31}$P{$^1$H} NMR (202 MHz, C$_6$D$_6$): $\delta$ [ppm] = 75.1 (s).

**Bis$_2$Ga–O–P$^t$Bu$_2$**·PO (**8**): Using propylene oxide (10 µL, 8.3 mg, 143 µmol, 1.5 equiv.), the ring-opening adduct **8** crystallized from *n*-hexane at –18 °C, giving colourless needles (32 mg, 53 µmol, 55%). $^1$H NMR (500 MHz, C$_6$D$_6$): $\delta$ [ppm] = –0.49 (s, 1H, GaC**H**), –0.39 (s, 1H, GaC**H**), 0.42 – 0.56 (m, 36H, Si(C**H**$_3$)$_3$), 0.85

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(d, ${}^3J_{\mathrm{P,H}}$ = 13.9 Hz, 9H, $\mathrm{C(C\mathbf{H}_3)_3}$), 0.90 (d, ${}^3J_{\mathrm{P,H}}$ = 14.0 Hz, 9H, $\mathrm{C(C\mathbf{H}_3)_3}$), 1.32 (ddd, $J$ =14.8, 3.7, 1.8 Hz, $\mathrm{PC\mathbf{H}_2}$), 1.36 (dd, $J$ =5.7, 2.7 Hz, $\mathrm{C\mathbf{H}_3}$), 1.63 (ddd, $J$ =14.8, 10.8, 8.8 Hz, $\mathrm{PC\mathbf{H}_2}$), 4.35 (m, 1H, $\mathrm{OC\mathbf{H}}$). ${}^{13}\mathrm{C}\{{}^1\mathrm{H}\}$ NMR (126 MHz, $\mathrm{C_6D_6}$): $\delta$ [ppm] = 4.8 (s, overlapped, from ${}^1$H-${}^{13}$C HSQC experiment, $\mathrm{Ga\mathbf{C}H}$), 4.9 (s, $\mathrm{Si(\mathbf{C}H_3)_3}$), 5.2 (s, $\mathrm{Si(\mathbf{C}H_3)_3}$), 5.6 (s, $\mathrm{Si(\mathbf{C}H_3)_3}$), 5.6 (s, overlapped, from ${}^1$H-${}^{13}$C HSQC experiment, $\mathrm{Ga\mathbf{C}H}$), 26.2 (s, $\mathrm{C(\mathbf{C}H_3)_3}$), 26.5 (s, $\mathrm{C(\mathbf{C}H_3)_3}$), 29.4 (d, ${}^3J_{\mathrm{P,C}}$ = 13.6 Hz, $\mathrm{\mathbf{C}H_3}$), 30.0 (d, ${}^1J_{\mathrm{P,C}}$ = 54.5 Hz, $\mathrm{P\mathbf{C}H_2}$), 35.1 (d, ${}^1J_{\mathrm{P,C}}$ = 57.7 Hz, $\mathrm{\mathbf{C}(CH_3)_3}$), 35.7 (d, ${}^1J_{\mathrm{P,C}}$ = 59.0 Hz, $\mathrm{\mathbf{C}(CH_3)_3}$), 65.6 (d, ${}^2J_{\mathrm{P,C}}$ = 5.9 Hz, $\mathrm{O\mathbf{C}H}$). ${}^{29}\mathrm{Si}\{{}^1\mathrm{H}\}$ NMR (99 MHz, $\mathrm{C_6D_6}$): $\delta$ [ppm] = –1.7 (s), –1.1 (s), –0.7 (s), –0.2 (s). ${}^{31}\mathrm{P}\{{}^1\mathrm{H}\}$ NMR (202 MHz, $\mathrm{C_6D_6}$): $\delta$ [ppm] = 73.0 (s). Elemental analysis calcd (%) for $\mathrm{C_{25}H_{62}GaO_2PSi_4}$ ($M_r$ = 607.81): C 49.40, H 10.28; found C 49.14, H 10.53.

**$\mathbf{Bis_2Ga–O–P^{\mathit{t}}Bu_2}$**$\cdot$PhC≡CH (**9**): Using phenylacetylene (10 µL, 9.3 mg, 91 µmol, 1.0 equiv.) and stirring at 70 °C, **9a** was recrystallized from *n*-hexane at –18 °C, giving colourless needles of the deprotonation product (38 mg, 59 µmol, 64%). ${}^1$H NMR (500 MHz, $\mathrm{C_6D_6}$): $\delta$ [ppm] = –0.31 (s, 2H, $\mathrm{GaC\mathbf{H}}$), 0.46 (s, 36H, $\mathrm{Si(C\mathbf{H}_3)_3}$), 0.95 (d, ${}^3J_{\mathrm{P,H}}$ = 15.7 Hz, 18H, $\mathrm{C(C\mathbf{H}_3)_3}$), 5.98 (d, ${}^1J_{\mathrm{P,H}}$ = 440.1 Hz, 1H, $\mathrm{P\mathbf{H}}$), 6.98 (t, ${}^3J_{\mathrm{H,H}}$ = 7.4 Hz, 1H, *para*-**H**), 7.05 (t, ${}^3J_{\mathrm{H,H}}$ = 7.3 Hz, 2H, *meta*-**H**), 7.62 (d, ${}^3J_{\mathrm{H,H}}$ = 7.8 Hz, 2H, *ortho*-**H**). ${}^{13}\mathrm{C}\{{}^1\mathrm{H}\}$ NMR (126 MHz, $\mathrm{C_6D_6}$): $\delta$ [ppm] = 4.6 (s, $\mathrm{Si(\mathbf{C}H_3)_3}$), 10.0 (s, $\mathrm{Ga\mathbf{C}H}$), 26.0 (s, $\mathrm{C(\mathbf{C}H_3)_3}$), 33.8 (d, ${}^1J_{\mathrm{P,C}}$ = 58.4 Hz, $\mathrm{\mathbf{C}(CH_3)_3}$), 109.7 (s, PhC≡**C**Ga), 126.1 (s, Ph**C**≡CGa), 127.6 (s, *para*-**C**), 128.4 (s, *ipso*-**C**), 128.6 (s, *meta*-**C**), 131.6 (s, *ortho*-**C**). ${}^{29}\mathrm{Si}\{{}^1\mathrm{H}\}$ NMR (99 MHz, $\mathrm{C_6D_6}$): $\delta$ [ppm] = –0.9 (s). ${}^{31}\mathrm{P}\{{}^1\mathrm{H}\}$ NMR (202 MHz, $\mathrm{C_6D_6}$): $\delta$ [ppm] = 67.3 (s). Elemental analysis calcd (%) for $\mathrm{C_{30}H_{62}GaOPSi_4}$ ($M_r$ = 651.86): C 55.28, H 9.59; found C 54.61, H 9.88.

**$\mathbf{Bis_2Ga–O–P^{\mathit{t}}Bu_2}$**$\cdot\mathrm{Me_3SiC{\equiv}CH}$ (**10**): Using trimethylsilylacetylene (10 µL, 7.1 mg, 72 µmol, 1.0 equiv.), stirring at 70 °C and after an additional washing step with *n*-hexane, **10** was obtained in a colourless resin-like form (41 mg, 63 µmol, 92%). *Deprotonation product* (**10a**): ${}^1$H NMR (500 MHz, $\mathrm{C_6D_6}$): $\delta$ [ppm] = –0.50 (s, 2H, $\mathrm{GaC\mathbf{H}}$), 0.27 (s, 9H, $\mathrm{Si(C\mathbf{H}_3)_3}$), 0.46 (s, 36H, $\mathrm{CH(Si(C\mathbf{H}_3)_3)_2}$), 0.96 (d, ${}^3J_{\mathrm{P,H}}$ = 15.6 Hz, 18H, $\mathrm{C(C\mathbf{H}_3)_3}$), 5.97 (d, ${}^1J_{\mathrm{P,H}}$ = 442.2 Hz, 1H, $\mathrm{P\mathbf{H}}$). ${}^{13}\mathrm{C}\{{}^1\mathrm{H}\}$ NMR (126 MHz, $\mathrm{C_6D_6}$): $\delta$ [ppm] = 0.3 (s, $\mathrm{Si(\mathbf{C}H_3)_3}$), 4.8 (s, $\mathrm{Si(\mathbf{C}H_3)_3}$), 8.2 (s, $\mathrm{Ga\mathbf{C}H}$), 26.2 (s, $\mathrm{C(\mathbf{C}H_3)_3}$), 33.8 (d, ${}^1J_{\mathrm{P,C}}$ = 58.3 Hz, $\mathrm{\mathbf{C}(CH_3)_3}$), 115.7 (s, $\mathrm{Me_3SiC{\equiv}\mathbf{C}Ga}$), 134.8 (s, $\mathrm{Me_3Si\mathbf{C}{\equiv}CGa}$). ${}^{29}\mathrm{Si}\{{}^1\mathrm{H}\}$ NMR (99 MHz, $\mathrm{C_6D_6}$): $\delta$ [ppm] = –22.9 (s), –0.7 (s). ${}^{31}\mathrm{P}\{{}^1\mathrm{H}\}$ NMR (202 MHz, $\mathrm{C_6D_6}$): $\delta$ [ppm] = 66.9 (s). Elemental analysis calcd (%) for $\mathrm{C_{27}H_{66}GaOPSi_5}$ ($M_r$ = 647.95): C 50.05, H 10.27; found C 49.81, H 10.37. *Ring-closure product* (**10b**): ${}^1$H NMR (500 MHz, $\mathrm{C_6D_6}$): $\delta$ [ppm] = –0.50 (br. s, 2H, $\mathrm{GaC\mathbf{H}}$), 0.18 (s, 9H, $\mathrm{Si(C\mathbf{H}_3)_3}$), 0.38 – 0.43 (s, 36H, $\mathrm{CH(Si(C\mathbf{H}_3)_3)_2}$), 1.02 (d, ${}^3J_{\mathrm{P,H}}$ = 14.0 Hz, 18H, $\mathrm{C(C\mathbf{H}_3)_3}$), 9.25 (d, ${}^3J_{\mathrm{P,H}}$ = 56.0 Hz, 1H, $\mathrm{PC\mathbf{H}}$). ${}^{13}\mathrm{C}\{{}^1\mathrm{H}\}$ NMR (126 MHz, $\mathrm{C_6D_6}$): $\delta$ [ppm] = 2.0 (s, $\mathrm{Si(\mathbf{C}H_3)_3}$), 5.1/5.4 (s, $\mathrm{Si(\mathbf{C}H_3)_3}$), 27.5 (s, $\mathrm{C(\mathbf{C}H_3)_3}$), 35.1 (d, ${}^1J_{\mathrm{P,C}}$ = 56.3 Hz, $\mathrm{\mathbf{C}(CH_3)_3}$), 139.9 (d, ${}^1J_{\mathrm{P,C}}$ = 41.4 Hz, $\mathrm{GaC{=}\mathbf{C}P}$), 206.7 (d, ${}^2J_{\mathrm{P,C}}$ = 5.9 Hz, $\mathrm{Ga\mathbf{C}{=}CP}$); a signal for $\mathrm{Ga\mathbf{C}H}$ could not be observed. ${}^{29}\mathrm{Si}\{{}^1\mathrm{H}\}$ NMR (99 MHz, $\mathrm{C_6D_6}$): $\delta$ [ppm] = –8.2 (s), –1.6 (s). ${}^{31}\mathrm{P}\{{}^1\mathrm{H}\}$ NMR (202 MHz, $\mathrm{C_6D_6}$): $\delta$ [ppm] = 84.8 (s).

**$\mathbf{Bis_2(Cl)Ga–O–P(Bn)^{\mathit{t}}Bu_2}$** (**11**): Using benzyl chloride (10 µL, 9.1 mg, 72 µmol, 1.0 equiv.), stirring at 70 °C and after an additional washing step with *n*-hexane, **11** was obtained as a light yellow solid (44 mg, 65 µmol, 94%). ${}^1$H NMR (500 MHz, $\mathrm{C_6D_6}$): $\delta$ [ppm] = –0.06 (s, 2H, $\mathrm{GaC\mathbf{H}}$), 0.36 (s, 36H, $\mathrm{Si(C\mathbf{H}_3)_3}$), 1.06 (d, ${}^3J_{\mathrm{P,H}}$ = 13.6 Hz, 18H, $\mathrm{C(C\mathbf{H}_3)_3}$), 3.40 (d, ${}^3J_{\mathrm{P,H}}$ = 14.0 Hz, 2H, $\mathrm{C\mathbf{H}_2}$), 7.00 (t, ${}^3J_{\mathrm{H,H}}$ = 7.3 Hz, 1H, *para*-**H**), 7.05 (t, ${}^3J_{\mathrm{H,H}}$ = 7.6 Hz, 2H, *meta*-**H**), 7.39 (d, ${}^3J_{\mathrm{H,H}}$ = 7.9 Hz, 2H, *ortho*-**H**). ${}^{13}\mathrm{C}\{{}^1\mathrm{H}\}$ NMR (126 MHz, $\mathrm{C_6D_6}$): $\delta$ [ppm] = 4.3 (s, $\mathrm{Si(\mathbf{C}H_3)_3}$), 15.8 (s, $\mathrm{Ga\mathbf{C}H}$), 27.5 (s, $\mathrm{C(\mathbf{C}H_3)_3}$), 31.2 (d, ${}^1J_{\mathrm{P,C}}$ = 48.4 Hz, $\mathrm{\mathbf{C}H_2}$), 36.7 (d, ${}^1J_{\mathrm{P,C}}$ = 56.3 Hz, $\mathrm{\mathbf{C}(CH_3)_3}$), 127.0 (d, ${}^4J_{\mathrm{P,C}}$ = 2.5 Hz, *para*-**C**), 128.7 (s, *meta*-**C**), 130.8 (d, ${}^3J_{\mathrm{P,C}}$ = 5.0 Hz, *ortho*-**C**), 134.3 (d, ${}^2J_{\mathrm{P,C}}$ = 6.0 Hz, *ipso*-**C**). ${}^{29}\mathrm{Si}\{{}^1\mathrm{H}\}$ NMR (99 MHz, $\mathrm{C_6D_6}$): $\delta$ [ppm] = –1.3 (s). ${}^{31}\mathrm{P}\{{}^1\mathrm{H}\}$ NMR (202 MHz, $\mathrm{C_6D_6}$): $\delta$ [ppm] = 63.6 (s). Elemental analysis calcd (%) for $\mathrm{C_{29}H_{63}GaOPSi_4}$ ($M_r$ = 676.31): C 51.50, H 9.39; found C 51.67, H 9.59.

## Author contributions

J. Buth: investigation, methodology, validation, visualization, writing (original draft), B. Neumann, J.-H. Lamm and H.-G. Stammler: investigation (SCXRD), Y. V. Vishnevskiy (quantum chemical calculations), N. W. Mitzel: funding acquisition, project administration, supervision, writing, reviewing and editing.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data that supports the findings of this study are available in the ESI† of this article. CCDC 2528994-2529001† contain the supplementary crystallographic data for this paper.

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The data supporting this article have been included as part of the Supplementary Information. Supplementary information: Experimental details, NMR spectra, Crystallographic details, Quantum Chemical Calculations, References. See DOI: [URL – format https://doi.org/DOI]

Crystallographic data for **1**, **2**, **7**, **8**, **9a**, **10a**, and **11** have been deposited at the CCDC under CCDC 2528994 – 2529001. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.