Versatile coordination of a reactive P,N-ligand toward boron, aluminum and gallium and interconversion reactivity†

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The synthesis and reactivity of the first Group 13 complexes bearing a dearomatized phosphino-amido ligand L are reported, i.e. alane AlEt2(L) 1, gallane GaCl3(L) 2 and borane B(Cl)(Ph)(L) 3. The three complexes react very differently with Group 13 trihalogenides, providing access to zwitterionic anti-3 GaCl3 and the unique bis(metalloid) 5 BCl3, with the boron center part of a highly unusual anionic four-membered ring (charge on C) and Ga bound to P. The coordination chemistry and the various transformations are supported by DFT calculations, X-ray crystallography and multinuclear NMR spectroscopic data.

Introduction

The synthetic chemistry and reactivity of Group 13 complexes has recently attracted much attention, both with respect to the preparation of unsaturated derivatives1 and for application in bond activation processes and homogeneous catalysis,2 often in combination with a Lewis base as a “Frustrated Lewis Pair” (FLP).3 At the same time, the bioinspired strategy to combine proton-responsive (‘reactive’) ligands and (transition) metal centers has become prominent, resulting in novel coordination chemistry with applications in small molecule activation and metal–ligand bifunctional catalysis.4

One particular strategy that has come to the forefront in this context is the use of lutidine- and picoline-based P,N donor ligands that can undergo reversible dearomatization.5 Many transition metals coordinate strongly to both phosphorus and nitrogen in these ligands,6 and deprotonation of the ligand backbone merely generates a nucleophilic carbon center that does not engage in any direct interaction with the metal coordination sphere. No examples of transmetallation on complexes bearing lutidine- or picoline-derived P,N-ligands are known, to the best of our knowledge.7 The coordination chemistry of Group 13 metals and metalloids such as boron and aluminum is unexplored with this type of reactive ligand scaffold. Hence, the fundamental reactivity of complexes bearing a dearomatized P,N ligand is currently unknown but it could be envisioned that other ligand coordination modes may be accessible with these elements.

To address both challenges, we decided to exploit the reversible dearomatization chemistry of P,N-ligands to generate the first examples of Group 13 species with a dearomatized pyridine ligand (see Scheme 1). This approach has allowed access to highly reactive aluminum, gallium and boron compounds stabilized by an anionic P,N-scaffold and to study their versatile reactivity with G13 trihalogenides.

Results and discussion

Reaction of the known bidentate P,N-ligand 2-(diphenylphosphinomethyl)-6-methyl-pyridine L4 with one molar equivalent of n-BuLi followed by electrophilic trapping with chlorodiethylaluminum (Scheme 2) resulted in the high yield synthesis of complex AlEt2(L) 1 as a red oil, which was characterized by multinuclear NMR spectroscopy. Contrary to what was previously observed for the anion of lutidine,8 this reaction selectively generates an N-Group 13 element bond, with deprotonation of the N-heterocycle, rather than a C-Group 13 bond. The 1H NMR spectrum contained three different resonances in the olefinic region (δ 5.28, 6.07 and 6.42) and a broad signal at δ 3.46 attributed to the methine proton of the tert-butyl groups connected to phosphorus and both Et-groups at aluminum are also equivalent, confirming the C4 symmetry of the molecule. This compound features a clear P ↔ Al interaction, as evidenced by the broad 31P NMR signal at δ ~0.9 (Δδ ~36.2 relative to L4) and the 27Al NMR resonance at δ 162, which is characteristic of a four-coordinated amido-alane.9
Strikingly, the analogous reaction of \( \text{LH} \) with \( \text{AlCl}_3 \) failed to generate any well-defined product.

To get insight into the geometric and electronic features of \( \text{1} \), we optimized its structure using DFT calculations (Fig. 1). The ligand framework adopts an almost planar configuration, with the phosphine and alane fragments slightly out of the N-heterocycle plane (\( \angle \text{P}2-\text{C}4-\text{C}5-\text{C}6 177.8^\circ \), \( \angle \text{Al1}-\text{N}1-\text{C}6-\text{C}7 174.6^\circ \)). The N-heterocycle shows clear alternation of C–C and C=C bonds. The HOMO is mainly located on the C1 carbon (64.1%), suggesting that this alane complex with an anionic P,N ligand would likely react with electrophiles at the methine site, as previously established for e.g. \( \text{MeOTf}, \text{CO}_2 \) and nitrile electrophiles with either Cu and Ru complexes bearing dearomatized P,N pincers.\(^{10}\) However, common inorganic Lewis acids have not been employed as electrophiles, to the best of our knowledge.

We thus explored its reactivity toward gallium trichloride as a prototypical Lewis acid (Scheme 2). After addition of \( \text{GaCl}_3 \) to a solution of \( \text{1} \) in toluene at room temperature and work-up, the \( ^{31}\text{P} \) NMR spectrum contained only a very broad resonance at \( \delta -3.1 \), while the \( ^1\text{H} \) NMR spectrum still showed the characteristic pattern for a dearomatized P,N backbone, but was lacking any signals for an AlEt\(_2\) fragment. These spectroscopic data indicate a formal transmetallation from Al to Ga to generate \( \text{GaCl}_2(\text{L})_2 \), which was detected by HR-MS data (FD\(^+\), \( m/z = 390.04338 \)), and AlClEt\(_2\). The structure of this gallane complex \( \text{2} \) was confirmed by X-ray structure determination on air-sensitive orange crystals of \( \text{GaCl}_2(\text{L})_2 \), obtained from a diethyl ether-toluene solution at r.t. (Fig. 2). In the crystal structure, the geometry around gallium is strongly pyramidal due to the interaction with the phosphine donor (sum of angles 331.9°). The N-heterocycle shows alternation of single and double C–C bonds, while the external C–C double bond lies in-between (C1–C2 = 1.394(2) Å) and the C1 carbon is clearly sp\(^3\) hybridized.

The intriguing conversion of \( \text{1} \) into \( \text{2} \) may be envisioned to involve initial formation of a bis-metalloid intermediate \( \text{1·GaCl}_3 \) with a C–Ga bond and a formally cationic Al-center, but this proposed intermediate could not be detected using \( \text{1} \), despite various attempts. We hypothesized that such a bis-
metallloid structure could be more readily accessible with B instead of Al, as boron cations are known to be stable in tetra-coordinated environments (commonly termed boroniums).\(^{11}\)

The boron analogue of 1 could be accessed via deprotonation of \(\text{L}^{11}\) and subsequent addition of \(\text{Cl}_3\text{BPh}\) (Scheme 3). Complex \(\text{B(Cl)(Ph)(L)}\) was obtained in 53% yield as a very air-sensitive red oil that was completely characterized by multinuclear NMR and HR-MS (\([\text{M + H}]^+\), 374.1976). The \(^{31}\text{P}\) NMR spectrum of 3 shows a broad resonance at \(\delta = 9.5\) ppm and a doublet at \(\delta = 24.5\) (\(\Delta\delta = 0.5\) ppm). The presence of a doublet at \(\delta = 3.46\) (\(J_{\text{HP}} = 5.1\) Hz) attributed to the proton of the \(=\text{CH}–\text{PPh}_2\) arm.

Addition of 1 eq. of \(\text{GaCl}_3\) to 3 instantaneously yielded a yellow precipitate, which was characterized by a broad signal at \(\delta = 34.0\) in the \(^{31}\text{P}\) NMR spectrum (\(\Delta\delta = 9.5\) ppm) and a slightly upfield shifted \(^{11}\text{B}\) NMR signal (\(\delta = 5.6\); \(\Delta\delta = 0.5\) ppm). The presence of a doublet at \(\delta = 3.67\) in the \(^1\text{H}\) NMR spectrum with a relatively large \(J_{\text{HP}}\) coupling constant of 13.4 Hz (\(J = 8.3\) Hz compared to 3) indicates rearomatization of the N-heterocycle and supports addition of \(\text{GaCl}_3\) to the methylene carbon spacer. Single crystal X-ray structure determination confirmed the diastereoselective formation of the formally zwitterionic \(\text{anti-3-GaCl}_3\) (\(\text{anti}\) refers to the relative positions of the chloride at boron and the \(\text{GaCl}_3\) fragment with respect to the \(\text{G13-pyridine plane}\), Fig. 3). The new \(\text{C1–Ga1}\) bond is in the range of previously reported carbogallates.\(^{12}\) DFT calculations (Gaussian 09, B3PW91, 6-31G**) show that the \(\text{syn-3-GaCl}_3\) diastereoisomer is 3.7 kcal mol\(^{-1}\) higher in energy, which is within the upper limit of the precision of the methods. Heating a solution of \(\text{anti-3-GaCl}_3\) for 10 h at 100 °C led to partial isomerization to \(\text{syn-3-GaCl}_3\), as evidenced by multinuclear NMR spectroscopy.

Although there is some precedent for nucleophilic attack of deaeromatized pincer transition metal complexes on a Group 13 Lewis acid,\(^{11}\) this reactivity is unprecedented for main group elements or metalloids. Moreover, given the propensity of \(\text{GaCl}_3\) to act as halide scavenger toward main group halides, including boron for the generation of boron cations,\(^{14}\) the observed preference to act as electrophile in a carbon–gallium bond formation step is deemed highly remarkable. This bond is indeed reactive, as evidenced by the reaction of \(\text{anti-3-GaCl}_3\) with HCl, which led to protonation at the methylene carbon with the formation of tetrachlorogallate salt 4 (Scheme 4), which was fully characterized, including by single crystal X-ray structure determination (Fig. 4).
The electronegativity of Ga lies in-between that of B and Al. We decided to explore the reaction of gallane 2 with boron tribromide as Lewis acid in order to probe whether the resulting reactivity of these Group 13 elements bound to a deaeromatized P,N ligand follows the same trend. Upon addition of BCl3 to 2, the bright orange reaction mixture turned colorless, which is diagnostic of re-aromatization (Scheme 5).

The broad 31P NMR signal appeared at lower field (δ 31.1 ppm, Δδ ~10.8 ppm) with no evidence for P–B coupling, indicative that the phosphine is still connected to gallium. In the 1H NMR spectrum, the δ 3.93 ppm) and broadened due to scalar proximity of a 11B nucleus (confirmed by 1H{11B} NMR analysis). Single crystal X-ray structure determination of 5–BCl2 confirmed the incorporation of both Ga and B (Fig. 5). However, concomitant with exchange of Ga for B for the coordination to the heterocycle nitrogen atom, the latter has undergone an unprecedented change from a P,N to a C,N binding pocket.

The boron atom is incorporated in a rare four-membered ring that is fused to a rearomatized pyridine ring (judging from the almost identical carbon–carbon bond lengths in the ring). The carbon atom binds to boron while the pendant phosphine binds the trichlorogallane. The C1–B1 bond length of 1.682(3) Å likely reflects the ring-strain in this structure. To the best of our knowledge, this is the first example wherein the methine spacer of a deaeromatized lutidinylphosphine engages in direct coordination to a metal(loid). The only two structurally characterized fused heterobicyclic structures with boron and pyridine resulted either from (i) C–H activation of a lutidine–borenium adduct in the presence of an external Lewis base15 or (ii) ring-closure of a bis(pentafluorophenyl)boryl derived FLP.16 In both cases, extremely strong Lewis acids are involved.

Given its unique nature, we decided to get further insight into the bonding situation within 5–BCl2 by DFT calculations. Natural bond order (NBO) analysis demonstrated that the C1–B1 and the N1–B1 bonds are very polarized toward C and N (70% and 80%, respectively). In line with this observation, the Natural Population Analysis (NPA) showed a positively charged boron atom (+0.4). Interestingly, the C1 carbon atom bears a significant negative charge (~0.9). As a result, 5–BCl2 is best described as the combination of a boronium and an anionic C,N ligand. The carbaborane might be partially stabilized by negative hyperconjugation into the σ(P–C) orbitals as in reported α-monolithiated17 and α-dilithiated18 phosphineboranes, although second order NBO analysis does not provide clear evidence for this. The analogous 5–B(Cl)(Ph) was obtained as a mixture of diastereomers by reacting 2 with BCl3 · Ph.

Compounds 3-GaCl 3 and 5-B(Cl)(Ph) are linkage isomers (Scheme 6). The average DFT calculated energy differences of the linkage isomers 3-GaCl 3 and 5-B(Cl)(Ph) (syn and anti) are within the upper limit of the precision of the methods (3.6 kcal mol−1 in favor of 5-B(Cl)(Ph)). Given this small energy difference, we speculated that 5-B(Cl)(Ph) could conceivably still be of relevance in the formal transmetallation of 2 with BCl3 · Ph to provide 3-GaCl3 under forcing conditions. To verify this hypothesis, a solution of 5-B(Cl)(Ph) in CD2Cl2 was heated in pressure tube to 100 °C for 6 hours, which cleanly generated 3-GaCl 3 as a mixture of diastereoisomers. It is plausible that this structural rearrangement, involving both C–B and
P–Ga bond cleavage and C–Ga as well as P–B bond formation, proceeds via reconstitution of a mixture of 3 (with the de-aromatized N-heterocycle) and GaCl₃, which were found to react instantaneously at room temperature.

With the well-defined coordination chemistry for the heterodinuclear species in hand, we wondered if the reaction of 1 with boron trichloride would also lead to selective transmetallation and generation of product BCl₂(L) (as observed with GaCl₃) or an analogous reaction as observed for 3 to 5 but with a phosphino-alane pendant arm. The addition of one equivalent of BCl₃ to a solution of alane 1 at room temperature led to only 50% conversion of starting material, but the reaction smoothly went to completion when two equivalents of BCl₃ were used (Scheme 7).

The new species gives rise to a quadruplet in ³¹P NMR at δ 22.8, which is characteristic of the direct coordination of the phosphine to a boron atom. In line with the required stoichiometry, the ¹¹B NMR shows two signals, a doublet at δ 4.7 with a J₊₋ = 139.4 Hz and a broad singlet at δ 6.6. Single crystal X-ray structure determination of 6 confirmed the incorporation of two boron atoms in the molecule (Fig. 6). Complex 6 is structurally related to borane–gallane 5.BCl₄, with the same strained four-membered ring including the boron atom, but featuring a trichloroborane-coordinated phosphine arm. It is likely that the interaction of AlClEt₂ with the pendant phosphine is relatively weak (perhaps partly due to steric hindrance), resulting in facile displacement by an additional equivalent of BCl₃.

In summary, we demonstrate the first examples of Group 13 complexes (boron, gallium and aluminum) stabilized by a de-aromatized P,N ligand. Depending on the nature of the metal(loid) involved, very different reactivity toward Group 13 halogenides is observed. The rich coordination chemistry of this reactive ligand scaffold with G13 elements may open up e.g. new avenues for non-transition metal based small molecule activation and cooperative catalysis. Research in this direction is currently ongoing in our laboratories.

Experimental section

General comments

All reactions and manipulations were carried out under an atmosphere of dry dinitrogen using standard Schlenk techniques or in a glove-box. All solvents were purged with dinitrogen and dried using an MBRAUN Solvent Purification System (SPS). ¹H, ¹³C, ³¹P, ¹¹B and ²⁷Al NMR spectra were recorded on Bruker AV 300, Bruker DRX 300 or Bruker AV 400 spectrometers. Chemical shifts were expressed in positive sign, in parts per million, calibrated to residual ¹H (5.32 ppm) and ¹³C (53.84 ppm) solvent signals, external BF₃·Et₂O, 85% H₃PO₄ and Al(NO₃)₃ 1 M in D₂O (0 ppm) respectively. Mass spectra were recorded on an AccuTOF LC, JMS-T100LP or an AccuTOF GC v 4 g, JMS-T100GCV Mass spectrometer. Di-(tert-butylphosphino)methyl-6-methyl-pyridine L⁴ was prepared according to a literature procedure.¹⁹

Complex 1. A solution of nBuLi (2.5 M in hexanes, 0.25 mL, 0.63 mmol, 1 eq.) was added dropwise to an ice-cooled stirred solution of 2-(di-tert-butylphosphino)methyl-6-methyl-pyridine L⁴ (157 mg, 0.63 mmol) in diethylether (6.5 mL) and the resulting orange solution was allowed to react for 1 h at the same temperature. Then, the reaction mixture was cooled down to −78 °C and chlorodiethylaluminum (0.32 M in toluene, 1.98 mL, 1.01 eq.) was added dropwise. The reaction mixture was allowed to warm up to room temperature over 1 h, giving an orange solution and a white precipitate. After elimination of the salts by filtration and removal of the volatiles under reduced pressure, 1 was obtained as a red oil in 95% yield.
solution and a white precipitate. Only 1 eq.) was added dropwise. The reaction mixture was allowed to cool, forming a solution of 2-(di-tert-butylphosphino)methyl-6-methylpyridine (150 mg, 0.52 mmol) in diethyl ether (5 mL) under stirring at room temperature and the resulting mixture was stirred for an additional 4.5 h. Then, volatiles were removed under vacuum leading to an orange residue. This residue was extracted with a mixture of dichloromethane/pentane (0.3 mL/10 mL) and filtered. The resulting solution was concentrated to 2 mL, resulting in the crystallization of 2 at room temperature as sticky orange blocks in 96% yield. Crystals suitable for X-ray crystallography were obtained from a saturated solution of 2 in a toluene/diethyl ether mixture at room temperature. 1H NMR (300 MHz, CD2Cl2, δ): 1.40 (d, 18H, JHH = 6.1 Hz, tBu), 2.35 (3H, CH3), 3.46 (d, 1H, JHP = 3.3 Hz, C=C(H)[P(tBu)]), 5.53 (d, 1H, JHH = 6.6 Hz, Csp2-H), 6.24 (d, 1H, JHH = 9.0 Hz, Csp2-H), 6.62 (dtd, 1H, JHH = 9.0 Hz, JHP = 1.3 Hz, Csp2-H). 31P 1H NMR (121 MHz, CD2Cl2, δ): -3.1 (br.). 13C 1H NMR (75 MHz, CD2Cl2, δ): 22.7 (s, 1C, CH3), 28.9 (d, 6C, JCP = 2.8 Hz, CH2Bu), 36.8 (d, 2C, JCP = 30.4 Hz, P-CBu), 50.7 (d, 1C, JCP = 67.6 Hz, P-CBu), 105.5 (d, 1C, JCP = 1.2 Hz, Csp2-H), 119.2 (d, 1C, JCP = 12.0 Hz, Csp2-H), 135.7 (d, 1C, JCP = 2.3 Hz, Csp2-H), 151.2 (d, 1C, JCP = 4.3 Hz, Cquat), 166.7 (d, 1C, JCP = 6.7 Hz, Cquat). HRMS (FD): exact mass (monoisotopic) calcd for [C21H30BCl4GaNP35Cl2+H]+, 390.04357; found 390.04338. Despite several attempts, no satisfactory combustion analysis data was obtained for this compound, likely as a result of its air-sensitive nature.

**Complex 3.** A solution of nBuLi (2.5 M in hexanes, 0.21 mL, 0.52 mmol, 1 eq.) was added dropwise under stirring to an ice-cold solution of 2-(di-tert-butylphosphino)methyl-6-methylpyridine (150 mg, 0.52 mmol) in diethyl ether (5 mL) and the resulting orange solution was allowed to react for 1 h at the same temperature. Then, the reaction mixture was cooled down to -78 °C and dichlorophenylborane (77 μL, 0.52 mmol, 1 eq.) was added dropwise. The reaction mixture was allowed to warm up to room temperature over 30 minutes and was further stirred for 1 h at room temperature, giving an orange solution and a white precipitate. Only 3 was detected in the crude mixture by 31P 1H NMR analysis. After removal of the volatiles, the residue was extracted with pentane (3 mL) and dried affording the expected compound in a mixture with the starting material (7:1) (yield = 53%) due to partial hydrolysis. 1H NMR (300 MHz, CD2Cl2, δ): 0.95 (d, 9H, JHH = 13.7 Hz, tBu), 1.51 (d, 9H, JHH = 13.3 Hz, tBu), 1.92 (3H, CH3), 3.46 (d, 1H, JCP = 5.1 Hz, C=C(H)[P(tBu)]), 5.40 (d, 1H, JHH = 6.5 Hz, Csp2-H), 6.25 (d, 1H, JHH = 8.9 Hz, Csp2-H), 6.59 (dd, 1H, JHH = 8.9 Hz, JHP = 6.5 Hz, Csp2-H), 7.10-7.24 (m, 3H, Csp2-H), 7.33 (t, 1H, JHH = 7.4 Hz, Csp2-H), 7.91 (d, 1H, JHH = 7.4 Hz, Csp2-H). 1B 1H NMR (96 MHz, CD2Cl2, δ): 5.1 (d, JHP = 106.0 Hz). 31P 1H NMR (121 MHz, CD2Cl2, δ): 24.5 (s br.). 13C 1H NMR (75 MHz, CD2Cl2, δ): 22.6 (s, 1C, CH3), 28.7 (3C, CH2Bu), 29.4 (3C, CH2Bu), 34.7 (d, 1C, JCP = 24.4 Hz, P-CBu), 38.8 (d, 1C, JCP = 23.1 Hz, P-CBu), 53.0 (d, 1C, JCP = 65.2 Hz, P-Cbu), 106.0 (d, 1C, JCP = 1.7 Hz, Csp2-H), 116.2 (d, 1C, JCP = 14.3 Hz, Csp2-H), 127.2 (d, 1C, JCP = 1.2 Hz, Csp2-H), 127.3 (d, 1C, JCP = 2.3 Hz, Csp2-H), 127.8 (d, 1C, JCP = 1.6 Hz, Csp2-H), 133.4 (d, 1C, JCP = 2.9 Hz, Csp2-H), 135.0 (d, 1C, JCP = 2.1 Hz, Csp2-H), 136.0 (d, 1C, JCP = 2.3 Hz, Csp2-H), 151.3 (d, 1C, JCP = 9.1 Hz, Cquat), 167.6 (d, 1C, JCP = 13.8 Hz, Cquat), the aromatic carbon connected to boron is not observed. HRMS (CS1, -30 °C): exact mass (monoisotopic) calcd for [C21H30BCl4GaNP35Cl2+H]+, 374.1976; found 374.1980. This compound proved too hydrolysis-sensitive for satisfactory combustion analysis data.

**Complex anti-3-GaCl3.** A solution of 3 (445 mg, 1.19 mmol) in ether (15 mL) was added slowly to a solution of gallium trichloride (210 mg, 1.19 mmol, 1 eq.) in toluene (4 mL) at r. t. under stirring. The reaction mixture was then further stirred for 30 minutes leading to an orange solution and a yellowish precipitate. After removal of the mother liquor via cannula filtration, the precipitate was extracted with dichloromethane (20 mL), filtered and the limpid dichloromethane solution thus obtained was layered with pentane (21 mL), affording colorless crystals of anti-3-GaCl3 in a yield of 40%. Crystals suitable for X-ray diffraction analysis were obtained under the same conditions. 1H NMR (300 MHz, CD2Cl2, δ): 1.31 (d, 9H, JHH = 15.8 Hz, tBu), 1.50 (d, 9H, JHH = 13.6 Hz, tBu), 2.42 (s, 3H, CH3), 3.67 (d, 1H, JHH = 13.4 Hz, P-C(H)-Ga), 7.04 (m, 1H, H arom), 7.18 (m, 1H, H arom), 7.29 (m, 1H, H arom), 7.34 (m, 1H, H arom), 7.43 (m, 1H, H arom), 7.96-8.05 (m, 2H, H arom), 8.51 (d, 1H, JHH = 8.2 Hz, H arom). 31P 1H NMR (121 MHz, CD2Cl2, δ): 34.0 (br.). 11B 1H NMR (96 MHz, CD2Cl2, δ): 5.6. 13C 1H NMR (75 MHz, CD2Cl2, δ): 23.4 (s, 1C, CH3), 28.8 (s, 3C, CH2Bu), 30.0 (s, 3C, CH2Bu), 32.6 (br., P-C(H)-Ga), 36.6 (d, 1C, JCP = 24.4 Hz, P-CBu), 39.6 (d, 1C, JCP = 23.1 Hz, P-CBu), 123.5 (d, 1C, JCP = 9.2 Hz, CH3 arom), 127.1 (d, 1C, JCP = 1.9 Hz, CH3 arom), 128.4 (s, 2C, CH3 arom), 129.2 (d, 1C, JCP = 2.3 Hz, CH3 arom), 134.7 (d, 1C, JCP = 2.2 Hz, CH3 arom), 135.1 (d, 1C, JCP = 2.9 Hz, CH3 arom), 143.0 (d, 1C, JCP = 1.7 Hz, CH3 arom), 157.9 (d, 1C, JCP = 7.4 Hz, Cquat), 164.5 (d, 1C, JCP = 3.7 Hz, Cquat), the aromatic carbon connected to boron is not observed. Anal. Calcd For C21H30BCl4GaNP; C, 45.88; H, 5.50; N, 2.55. Found: C, 45.81; H, 5.43; N, 2.49. m. p.: decomposition above 200 °C.

**Isomerization of anti-3-GaCl3.** A solution of anti-3-GaCl3 (14.6 mg, 26.6 μmol) in CD2Cl2 (0.4 mL) was heated at 100 °C.
for 10 h, leading to partial isomerization to its diastereoisomer syn-3-GaCl1 in a 0.70/0.1 (anti/syn) ratio (as determined by integration of each =CHPPh2 signal in the 1H NMR spectrum, D1 = 10 s). The mixture of diastereoisomers was fully characterized by NMR spectroscopy: anti-3-GaCl1 = A; syn-3-GaCl1 = B. 

1H NMR (400 MHz, CD2Cl2, δ): 1.29 (d, 9H, JHH = 15.3 Hz, tBu(B)), 1.31 (d, 9H, JHH = 15.5 Hz, tBu(A)), 1.50 (d, 9H, JHH = 13.3 Hz, tBu(A)), 1.53 (d, 9H, JHH = 12.7 Hz, tBu(B)), 2.42 (s, 3H, CH3(A)), 2.53 (s, 3H, CH3(B)), 3.27 (d, 1H, JHH = 13.6 Hz, P-C(H)-Ga(B)), 3.68 (d, 1H, JHH = 13.5 Hz, P-C(H)-Ga(A)), 4.34 (s, 1H, JHH = 7.3 Hz, Harmom(B)), 7.14 (m, 2Harom.(A) + 1Harom.(B)), 7.26–7.37 (m, 2Harom.(A) + 1Harom.(B)), 7.95–8.04 (m, 1Harom.(A) + 1Harom.(B)), 8.07 (d br., 1H, JHH = 7.4 Hz, Harmom(B)), 8.13 (t, 1H, JHH = 8.0 Hz, Harmom(B)), 8.51 (d, 1H, JHH = 8.5 Hz, Harmom(A)), 8.60 (d, 1H, JHH = 8.1 Hz, Harmom(B)). 31P{1H} NMR (121 MHz, CD2Cl2, δ): 34.1 (br., A), 43.4 (br., B). 1B {1H} NMR (128 MHz, CD2Cl2, δ): 5.3 (br.), 13C {1H} NMR (101 MHz, CD2Cl2, δ): 23.4 (s, 1C, CH3(A)), 24.4 (s, 1C, CH3(B)), 28.1 (br., 1C, P-C(H)-Ga(B)), 28.8 (s, 1C, CH3(Br)), 29.3 (s, 2C, CH3(Br)), 30.0 (s, 1C, CH3(1Bu)), 32.6 (br., 1C, P-C(H)-Ga(A)), 35.2 (d, 1C, JCP = 22.3 Hz, P-C(Ph)(B)), 36.3 (d, 1C, JCP = 24.5 Hz, P-C(Ph)(A)), 38.3 (d, 1C, JCP = 22.2 Hz, P-C(Ph)(B)), 39.5 (d, 1C, JCP = 23.0 Hz, P-C(Ph)(A)), 42.3 (d, 1C, JCP = 7.8 Hz, CH3(1Bu)), 123.5 (d, 1C, JCP = 9.1 Hz, CH3(1Bu)), 126.2 (d, 1C, JCP = 7.8 Hz, CH3(1Bu)), 127.1 (d, 1C, JCP = 1.9 Hz, CH3(1Bu)), 128.4 (br., 2C, CH3(1Bu)), 128.7 (br., 1C, CH3(1Bu)), 128.9 (d, 1C, JCP = 2.4 Hz, CH3(1Bu)), 129.0 (br., 1C, CH3(1Bu)), 129.2 (d, 1C, JCP = 2.4 Hz, CH3(1Bu)), 129.4 (d, 1C, JCP = 2.2 Hz, CH3(1Bu)), 131.6 (s br., 1C, CH3(1Bu)), 134.7 (d, 1C, JCP = 2.2 Hz, CH3(1Bu)), 135.1 (d, 1C, JCP = 1.6 Hz, CH3(1Bu)), 136.1 (s br., 1C, CH3(1Bu)), 143.0 (d, 1C, JCP = 1.6 Hz, CH3(1Bu)), 143.3 (s br., 1C, CH3(1Bu)), 157.9 (d, 1C, JCP = 7.8 Hz, Cquat(A)), 159.0 (d, 1C, JCP = 7.2 Hz, Cquat(B)), 161.3 (d, 1C, JCP = 2.5 Hz, Cquat(B)), 164.4 (d, 1C, JCP = 3.7 Hz, Cquat(A)), the aromatic ipso-carbon connected to boron is not observed for A or B.

Complex 4. A solution of hydrochloric acid in diethylether (1 M, 0.65 mL, 0.65 mmol, 1 eq.) was added dropwise at room temperature to a solution of diethyl ether (2 (255 mg, 0.65 mmol) in toluene (5 mL) under stirring. Upon addition, the solution changed from orange to colorless. Then, pentane (20 mL) was added and the reaction mixture was slowly concentrated until a white powder precipitated. After removal of the surfactant via cannula filtration, the solid material was dried under reduced pressure. The solid was then dissolved in dichloromethane (3 mL) and filtered again. Layering of this solution with pentane (8 mL) led to the crystallization of 5-BCl2 at room temperature in 3 days as colorless crystals with a yield of 34%. Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane into a saturated dichloromethane solution of 5-BCl2 at room temperature. 1H NMR (300 MHz, CD2Cl2, δ): 1.54 (d, 9H, JHH = 16.8 Hz, tBu), 1.68 (d, 9H, JHH = 15.5 Hz, tBu), 2.75 (s, 3H, CH3), 3.82 (d br., 1H, JHH = 12.3 Hz, P-C(H)-B), 7.46 (d, 1H, JHH = 8.0 Hz, Harmom), 8.12 (pseudo-t, 1H, JHH = 8.0 Hz, Harmom), 8.32 (d, 1H, JHH = 8.1 Hz, Harmom). 31P {1H} NMR (121 MHz, CD2Cl2, δ): 31.1 (br.), 13C {1H} NMR (96 MHz, CD2Cl2, δ): 6.4. 13C {1H} NMR (75 MHz, CD2Cl2, δ): 18.1 (s, 1C, CH3), 29.3 (d, 3C, JCP = 1.5 Hz, CH3(Br)), 30.3 (s, 3C, JCP = 2.5 Hz, CH3(Br)), 32.9–36.1 (br., 1C, P-C(H)-B), 37.5 (d, 1C, JCP = 20.8 Hz, P-C(Ph)), 38.5 (d, 1C, JCP = 15.2 Hz, P-C(Ph), 123.8 (s, 1C, CH3), 126.1 (s, 1C, CH3), 144.7 (s, 1C, JCP = 1.2 Hz, CH3), 153.6 (s, 1C, Cquat), 159.0 (s br., 1C, Cquat). HRMS (CSI, −35 °C): exact mass (monoisotopic) calced for [C21H31BCl5GaNP + (GaCl) + H]+: 532.1726; found 532.1730. Anal. Calcd for C21H31BCl5GaNP: C, 35.46; H, 4.96; N, 2.76. Found: C, 35.56; H, 4.86; N, 2.67. M. p.: decomposition above 177 °C.

Complex 5-B(Ph)Cl(Ph). Dichlorophenylborane (49.8 µl, 0.38 mmol, 1 eq.) in toluene (0.4 mL) was added dropwise at room temperature to a solution of 2 (155 mg, 0.38 mmol) in toluene (3 mL) under stirring, leading to a colorless solution. Analysis of the crude mixture by 1H NMR showed the formation of a mixture of diastereoisomers in a 1.9/1 ratio. After removal of the volatiles under reduced pressure, the residue was dissolved in dichloromethane (4 mL) and filtered in order to have a limpid solution. Layering of this solution with pentane (14 mL) afforded colorless crystals of 5-B(Ph)Cl(Ph) in one day at room temperature with a yield of 51%. The mixture of diastereoisomers was fully characterized by NMR spectroscopy and the relative configuration of each isomer was attributed based on 2D NOEY NMR spectroscopy (in the case
of syn-5-BClPh, correlations are found between the B-(H)-
PPh₂ proton and the protons of the phenyl ring due to their
spatial proximity, no correlation is observed with the anti
isomer). For NMR: A = syn-5-B(Cl)(Ph) B = anti-5-B(Cl)(Ph). ¹H
NMR (400 MHz, CD₂Cl₂, δ): 0.95 (d, 9H, J₃arbon = 16.4 Hz, tBu(B)),
1.44 (d, 9H, J₃arbon = 15.4 Hz, tBu(A)), 1.61 (d, 9H, J₃arbon = 17.9 Hz,
tBu(A)), 1.61 (d, 9H, J₃arbon = 15.0 Hz, tBu(B)), 2.30 (s, 3H,
CH₃(A)), 2.48 (s, 3H, CH₃(B)), 2.74 (d, 1H, J₃arbon = 15.2 Hz, P-C
(H)-B), 3.77 (d, 1H, J₃arbon = 12.5 Hz, P-(C)-B (A)), 7.23-7.42
(m, 5 HPh (B) and 5 HPh (A) and 1 Hpy (B)), 7.49 (d, 1H, J₃arbon = 8.0
Hz, Hpy (B)), 8.10 (pseudo-t, 1H, J₃arbon = 8.0 Hz, Hpy (A)),
8.16 (pseudo-t, 1H, J₃arbon = 8.0 Hz, Hpy (B)), 8.34 (d, 1H,
J₃arbon = 8.1 Hz, Hpy (B)), 8.38 (d, 1H, J₃arbon = 8.1 Hz, Hpy (B)).
³¹P (¹H) NMR (121 MHz, CD₂Cl₂, δ): 32.6 (br.). ¹³C (¹H) NMR (96 MHz,
CD₂Cl₂, δ): 7.4; ¹³C (¹H) NMR (75 MHz, CD₂Cl₂, δ): 18.0 (s, 1C,
CH₃(B)), 29.4 (s, 3C, CH₃(B)), 30.0 (s, 3C, CH₃(B)), 35.2 (br., 1C, B–
C), 37.4 (d, 1C, J₃arbon = 27.0 Hz, P-Carbon), 38.0 (d, 1C, J₃arbon = 21.1
Hz, P-Carbon), 124.9 (s, 1C, CHprep), 125.7 (s, 1C, CHprep), 144.3
(s, 1C, CHprep), 153.0 (s, 1C, CHprep), 159.7 (br., 1C, CHprep). Anal.
Calcd For C₁₃H₂₄B₂Cl₅NP: C, 45.61; H, 5.46; N, 2.50.

Complex 6. –

X-ray crystallography

X-ray intensities were measured on a Bruker D8 Quest Eco
diffractometer equipped with a Triumph monochromator (λ =
0.71073 Å) and a CMOS Photon 50 detector at a temperature of
150(2) K. Intensity data were integrated with the Bruker APEX2
software. Absorption correction and scaling were performed
with SADABS. ¹¹ The structures were solved with the program
SHELXL. ¹² Least-squares refinement was performed with
SHELXL-2013 ¹³ against F² of all reflections. Non-hydrogen
atoms were refined with anisotropic displacement parameters.
The H atoms were placed at calculated positions using the
instructions AFIX 13, AFIX 43 or AFIX 137 with isotropic
displacement parameters having values 1.2 or 1.5 times
Ueq of the attached C atoms. CCDC 1455266-1455269 contain the
supplementary crystallographic data for this paper.

Details for 2. C₁₂H₂₀B₂Cl₄GaNP, Fw = 451.00, colorless,
0.327 × 0.210 × 0.152 mm, monoclinic, P2₁/c (no: 14), a = 9.049(3),
b = 9.165(3), c = 22.163(9) Å, β = 91.028°(8), V = 1837.9(20) Å³,
Z = 4, Ddens = 1.643 g cm⁻³, μ = 1.893 mm⁻¹. 39 709 reflections were
measured up to a resolution of (sin θ/λ)max = 0.65 Å⁻¹. 7005
reflections were unique (Rint = 0.0634), of which 5482 were
observed [I > 2σ(I)]. 188 Parameters were refined with 0
restraints. R₁/Fw, R₁[I > 2σ(I)] = 0.0329/0.0687. R₁/wR₁ [all refl.]:
0.0517/0.0752. S = 1.008. Residual electron density between
–0.760 and 0.667 e Å⁻³. CCDC 1455266.

Details for anti-3-GaCl₃. C₁₂H₂₀B₂Cl₄GaNP, Fw = 549.76, colorless,
0.478 × 0.201 × 0.199 mm, monoclinic, P2₁/c (no: 14), a = 10.152(10),
b = 16.382(9), c = 15.393(12) Å, β = 93.68(3)°, V =
2555.5(5) Å³, Z = 4, Ddens = 1.467 g cm⁻³, μ = 1.609 mm⁻¹. 29 499
reflections were measured up to a resolution of (sin θ/λ)max =
0.84 Å⁻¹. 4370 reflections were unique (Rint = 0.0384), of which
3954 were observed [I > 2σ(I)]. 269 Parameters were refined with
252 restraints. R₁/Fw, R₁[I > 2σ(I)] = 0.0240/0.0563. R₁/wR₁
[all refl.]: 0.0288/0.0591. S = 1.091. Residual electron density
between –0.382 and 0.431 e Å⁻³. CCDC 1455267.

Details for 4. C₁₃H₁₃Cl₂B₂Cl₄GaNP, Fw = 550.77, colorless,
0.452 × 0.240 × 0.240 mm, triclinic, P₁ (no: 1), a = 9.7845(7),
b = 11.8465(9), c = 12.0322(9) Å, α = 83.458(3), β = 83.640(3), γ =
77.501(3)°, V = 1437.41(17) Å³, Z = 2, Ddens = 1.385 g cm⁻³, μ =
1.486 mm⁻¹. 70 054 reflections were measured up to a resolution
of (sin θ/λ)max = 0.64 Å⁻¹. 10 873 reflections were unique
(Rint = 0.0501), of which 8259 were observed [I > 2σ(I)]. 278
Parameters were refined with 0 restraints. R₁/Fw, R₁[I > 2σ(I)]:
0.3770/0.746. R₁/wR₁ [all refl.]: 0.647/0.897. S = 1.076. Residual
electron density between –1.04 and 0.86 e Å⁻³. CCDC 1455269.

Details for 5-BCl₃. C₁₃H₂₁Cl₂B₂Cl₄GaNP, Fw = 508.11, colorless,
0.312 × 0.268 × 0.108 mm, triclinic, P₁ (no: 1), a = 8.483(6), b =
8.751(5), c = 16.791(7) Å, α = 87.39(2), β = 80.71(2), γ =
63.25(3)°, V = 1098.0(16) Å³, Z = 2, Ddens = 1.560 g cm⁻³, μ =
1.963 mm⁻³.
33 460 reflections were measured up to a resolution of \((\sin \theta/\lambda)_{\text{max}} = 0.74 \ \text{Å}^{-1}\). 5489 reflections were unique \((R_{\text{int}} = 0.0589)\), of which 4453 were observed \([I > 2\sigma(I)]\). 224 Parameters were refined with 252 restraints. \(R_f/\sigma(R_f)\; [I > 2\sigma(I)];\) 0.323/0.628. \(R_f\; [\text{all refl.}];\) 0.491/0.685. \(S = 1.008.\) Residual electron density between \(-0.469\) and \(0.503\) e Å\(^{-3}\). CCDC 1455268.

**Details for 6.** \(\text{C}_{12}\text{H}_{22}\text{B}_{2}\text{Cl}_{2}\text{NP}\), \(F_w = 449.20\), colorless, 0.391 × 0.311 × 0.184 mm, triclinic, \(\text{PI}\) (no: 1), \(a = 8.2835(19)\), \(b = 8.3491(18)\), \(c = 16.876(4)\) Å, \(\alpha = 87.103(6)\), \(\beta = 81.076(7)\), \(\gamma = 61.850(5)\). \(V = 1040.6(4)\) Å\(^3\), \(Z = 2\), \(D_p = 1.434\) g cm\(^{-3}\), \(\mu = 0.773\) mm\(^{-1}\). 34 045 reflections were measured up to a resolution of \((\sin \theta/\lambda)_{\text{max}} = 0.75 \ \text{Å}^{-1}\). 5215 reflections were unique \((R_{\text{int}} = 0.658)\), of which 4319 were observed \([I > 2\sigma(I)]\). 227 Parameters were refined with 0 restraints. \(R_f/\sigma(R_f)\; [I > 2\sigma(I)];\) 0.357/0.722. \(R_f\; [\text{all refl.}];\) 0.502/0.774. \(S = 1.072.\) Residual electron density between \(-0.32\) and \(0.58\) e Å\(^{-3}\). CCDC 1418174.

**DFT calculations**

Calculations were carried out with the Gaussian09 software\(^{23}\) at the DFT level, using the hybrid functional B3PW91.\(^{24}\) Aluminum, gallium, chlorine and phosphorus atoms were treated with small-core pseudopotentials from the Stuttgart group, with additional polarization orbitals.\(^{25}\) Nitrogen, carbon, boron and H atoms have been treated with the all-electron 6-31G** Pople basis set. The geometry optimizations were done without any symmetry constraints. Analytical calculations of the vibrational frequencies of the optimized geometries were performed to confirm that the structures obtained were minimaums, and also obtained the thermal corrections over the energies. The Natural Bond Orbital analysis was done over the optimized structure, with the version of the NBO software included in Gaussian09.\(^{26}\)

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