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Calix[4]pyrrolato gallate: square planar-coordinated gallium(III) and its metal-ligand cooperative reactivity with CO_2 and alcohols

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S1. Materials and methods

All reagents and solvents used within this research project were purchased from commercial sources. Carbon dioxide gas (99.998%) was obtained from Air Liquide and was used without further purification. Unless otherwise noted, all manipulations were carried out under inert conditions. Solvents were degassed prior to use with four freeze-pump-thaw cycles and were stored in sealed Schlenk ampulla over activated molecular sieve (3 or 4 Å, respectively) under a dry argon atmosphere. All reactions on preparative scale were carried out in flame-dried standard laboratory glassware under a dry argon or nitrogen atmosphere using Schlenk line techniques and were permanently magnetically stirred, if not stated differently. Syringes, magnetic stirring bars, and needles were dried and/or flushed with argon prior to use. Reactions on the NMR sample scale were done in dry J. Young NMR tubes under a dry nitrogen atmosphere. Compounds sensitive to ambient conditions were handled and stored in a Sylatech glove box filled with dry nitrogen gas. Removal of solvents *in vacuo* was performed using a Heidolph VV2000 rotary evaporator or a Schlenk line. Literature-known compounds were synthesized following published procedures. The respective publications are cited below. Analytical data of known compounds were compared to reference data and were found to be consistent in all cases. Novel compounds were characterized to the reported structures and compositions to the best of our knowledge.

Nuclear magnetic resonance (NMR) spectra were collected with a Bruker DPX200, a Bruker Avance II 400, or a Bruker Avance III 600 spectrometers at 295 K. The Bruker Avance machines were operated by the NMR facility of the Inorganic Chemistry Department at Heidelberg University. All spectra were acquired with field-frequency lock on the ^{2}H signal of the used solvent prior to data collection. Chemical shifts δ of ^{1}H and ^{13}C nuclei are given in parts per million (ppm) relative to the tetramethylsilane resonance; ^{19}F and ^{31}P chemical shifts (in ppm) are reported relative to the trichlorofluoromethane and the H_3PO_4 (85% aq) reference system, respectively. ^{1}H and $^{13}C\{^{1}H\}$ spectra were calibrated after data processing on the solvent residual signals (CD_2Cl_2: ^{1}H: 5.32 ppm, ^{13}C: 53.84 ppm, THF-d_8: ^{1}H: 3.58 ppm, ^{13}C: 67.21 ppm, CD_3CN: ^{1}H: 1.94 ppm, ^{13}C: 1.32 ppm).[1] ^{19}F and ^{31}P NMR spectra were not manually calibrated after processing. Signal multiplicities are reported as s (singlet), d (doublet), t (triplet), q (quartet), sept (septet), dd (doublet of doublets), tq (triplet of quartets), and m (multiplet); "br" stand for a broadened signal. The protons of the aromatic pyrrole rings of the calix[4]pyrrolato ligands are denoted "β-H", the directly attached carbon atoms "β-C". The quaternary carbon atoms of the aromatic pyrrole rings in the ligand are named "C_q-pyrrole". The atoms of the ligand's methyl and methylene (in case of the *meso*-octaethyl ligand) groups are called "α-Me" and "α-methylene", respectively. The quaternary carbon atoms to which they are bound are denoted "α-C". NMR spectra were processed with TopSpin 4.0.7[2] and plotted with MestReNova v14.0.1-23559[3].

High resolution mass spectrometry (HR-MS) was done with a Bruker ApexQe FT-ICR instrument coupled to an electrospray ionization (ESI) source operating in negative ion mode. Samples were prepared with dichloromethane as solvent under inert conditions with an approximate analyte concentration of $c = 10^{-5}$ mol L^{-1}. They were immediately analyzed after being brought in contact with air.

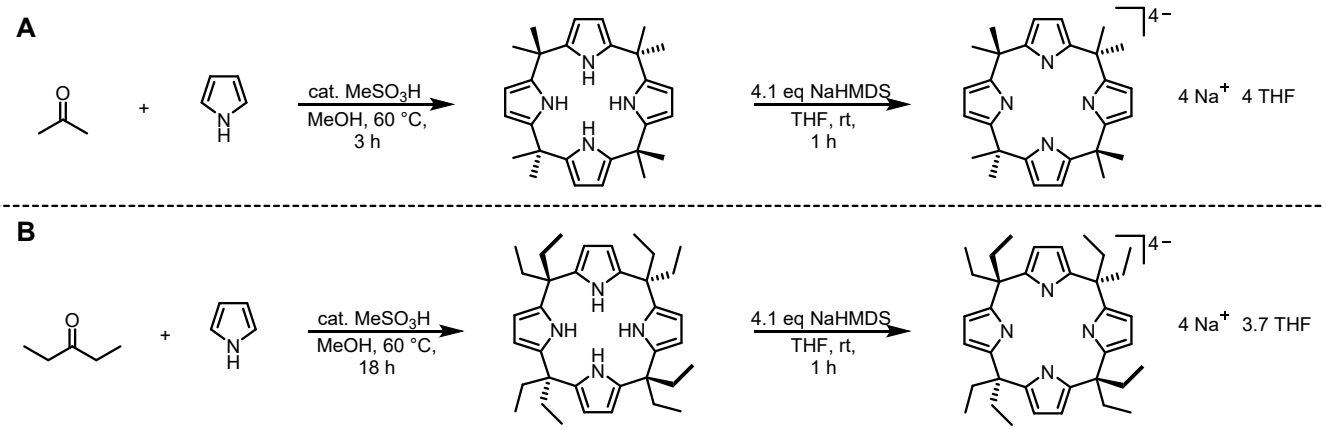
Fourier-transform attenuated total reflection infrared spectroscopy (FT-ATR-IR) was done with an Agilent Cary 630 spectrometer with solid material at room temperature inside a dry nitrogen-filled glove box. The obtained spectra were manually baseline-corrected. Data is reported as: maximum wavenumber $\tilde{\nu}_{max}$ [cm^{-1}] of the respective absorption band, intensity (s = strong, m = medium, w = weak).

For data handling and plotting OriginPro 2020[4] was used.

All quantum chemical calculations were done with Orca 5.0.1.[5-6] Details on the applied computational methods are given in Chapter S8.

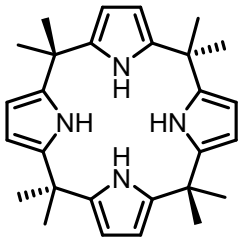
S2. Synthesis and characterization of the calix[4]pyrrolato ligands and of tetraphenylphosphonium tetrachloridogallate

meso-Octamethylcalix[4]pyrrole and *meso*-octaethylcalix[4]pyrrole were prepared as described below following modified procedures from literature (Scheme S1).[7-8] Deprotonation was achieved with sodium bis(trimethylsilyl)amide (NaHMDS) as described in the literature.[9] Tetraphenylphosphonium tetrachloridogallate was synthesized from tetraphenylphosphonium chloride and gallium(III)chloride following a reported procedure.[10]



Scheme S1. Synthetic schemes for the preparation of **A)** *meso*-octamethylcalix[4]pyrrole and **B)** *meso*-octaethylcalix[4]pyrrole and their subsequent deprotonation with sodium bis(trimethylsilyl)amide (NaHMDS) to give their tetrasodium salts.

meso-Octamethylcalix[4]pyrrole

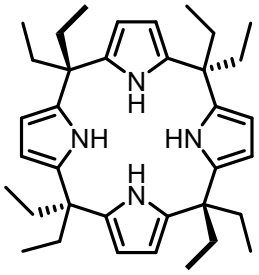


Procedure.[7-8] In a 500 mL round-bottom flask equipped with a reflux condenser, acetone (13.00 g, 16.5 mL, 223.6 mmol, 1.0 eq) was dissolved in methanol (160 mL). Pyrrole (15.00 g, 15.5 mL, 223.6 mmol, 1.0 eq), which was freshly distilled, was added in one portion. Methanesulfonic acid (4 drops) was added to the colorless solution. While the mixture was heated to 60 °C for 3 h, a colorless solid precipitated. The reaction mixture was allowed to cool down to room temperature. The solvent was removed under reduced pressure. A pale green solid was obtained as the crude reaction product, which was purified by flash column chromatography on silica gel with dichloromethane/petroleum ether (60:40, R_f = 0.53) as eluent. The solvent was removed from the combined product fractions and *meso*-octamethylcalix[4]pyrrole was isolated after drying under reduced pressure as a pale brown solid (13.7 g, 32.0 mmol, 57% yield), which is stable to ambient conditions.

^{1}H NMR (399.9 MHz, CD_2Cl_2, 295 K): δ_{1H} [ppm] = **7.02** (br s, 4H, N-H), **5.88** (d, $^3J_{HH}$ = 2.8 Hz, 8H, β-H), **1.49** (s, 24H, α-Me).

^{13}C{^{1}H} NMR (100.1 MHz, CD_2Cl_2, 295 K): δ_{13C} [ppm] = **138.8** (s, C_q, C_q-pyrrole), **103.1** (s, CH, β-C), **35.4** (s, C_q, α-C), **28.9** (s, CH_3, α-Me).

meso-Octaethylcalix[4]pyrrole

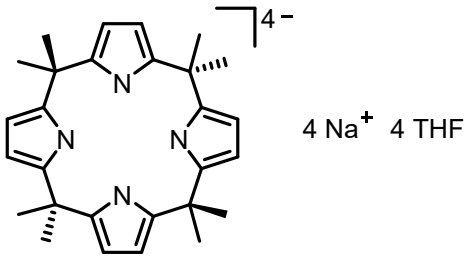


Procedure.[7-8] In a 1000 mL round-bottom flask equipped with a reflux condenser, pentan-3-one (25.7 g, 31.5 mL, 298.1 mmol, 1.0 eq) was dissolved in methanol (320 mL). Pyrrole (20.0 g, 20.1 mL, 298.1 mmol, 1.0 eq) and catalytic amounts of methanesulfonic acid (8 drops) were added. Upon stirring for 18 h at 60 °C, the reaction mixture turned dark brown, and a colorless solid precipitated. The crude product was separated by filtration and was washed with methanol (3 × 40 mL). The obtained beige solid was dried under reduced pressure. It was then purified by flash column chromatography on silica gel with dichloromethane/petroleum ether (40:60, R_f = 0.59) as eluent. The solvent was removed from the combined product fractions, and after drying under reduced pressure *meso*-octaethylcalix[4]pyrrole was obtained as a colorless solid (18.4 g, 34.0 mmol, 46% yield). It was previously recognized that over several weeks the color of the material changes to pale orange when stored under ambient conditions. Therefore, the compound was brought into a nitrogen-filled glovebox after completion of the synthesis and was stored there.

^{1}H NMR (600.2 MHz, CD_2Cl_2, 295 K): δ_{1H} [ppm] = **6.90** (br s, 4H, N-H), **5.90** (d, $^3J_{HH}$ = 2.6 Hz, 8H, β-H), **1.80** (br s, 16H, α-methylene), **0.58** (t, $^3J_{HH}$ = 7.4 Hz, 24H, α-Me).

^{13}C{^{1}H} NMR (150.9 MHz, CD_2Cl_2, 295 K): δ_{13C} [ppm] = **136.5** (s, C_q, C_q-pyrrole), **105.1** (s, CH, β-C), **43.1** (s, C_q, α-C), **28.4** (s, CH_2, α-methylene), **8.0** (s, CH_3, α-Me).

Deprotonation of *meso*-octamethylcalix[4]pyrrole to give its tetrasodium salt

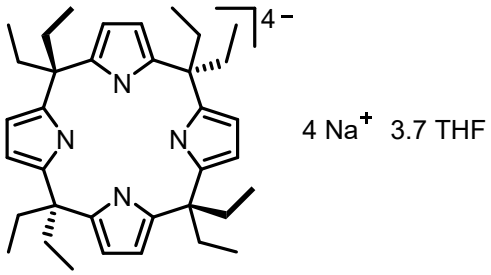


Procedure.[9] *meso*-Octamethylcalix[4]pyrrole (1.0 g, 2.33 mmol, 1.0 eq) was dissolved in THF (20 mL) in a Schlenk tube. Sodium bis(trimethylsilyl)amide (1 M solution in THF, 9.6 mL, 9.57 mmol, 4.1 eq) was added dropwise to the rapidly stirring solution within 5 min at room temperature. After approximately four fifths of the solution were added, a colorless precipitate formed. After complete addition, the reaction was stirred for 1 h at room temperature. The mixture was filtered over a fritted glass filter inside a nitrogen-filled glove box. The obtained solid was washed with THF (3 × 7 mL). Drying for 30 min under reduced pressure afforded the desired product as a colorless solid (1.8 g, 2.23 mmol, 95% yield). The acquired ^{1}H NMR spectrum showed the presence of four equivalents of THF as well as slight contamination. However, the material was found sufficient for subsequent usage.

^{1}H NMR (600.2 MHz, DMSO-d_6, 295 K): δ_{1H} [ppm] = **5.38** (s, 8H, β-H), **3.65-3.58** (m, 4 × 4H, THF), **1.80-1.74** (m, 4 × 4H, THF), **1.32** (s, 24H, α-Me).

^{13}C{^{1}H} NMR (150.9 MHz, DMSO-d_6, 295 K): δ_{13C} [ppm] = **148.8** (s, C_q, C_q-pyrrole), **96.5** (s, CH, β-C), **67.0** (s, CH, THF), **38.3** (s, C_q, α-C), **33.1** (s, CH_3, α-Me), **25.2** (s, CH, THF).

Deprotonation of *meso*-octaethylcalix[4]pyrrole to give its tetrasodium salt

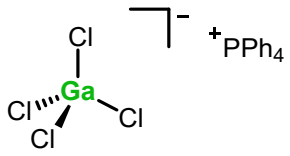


Procedure.[9] *meso*-Octaethylcalix[4]pyrrole (600 mg, 1.11 mmol, 1.0 eq) was dissolved in THF (6 mL) in a Schlenk tube. Sodium bis(trimethylsilyl)amide (1 M solution in THF, 4.6 mL, 4.55 mmol, 4.1 eq) was added dropwise to the rapidly stirring solution within 5 min at room temperature. The clear solution was stirred for 1 h at room temperature, and the solvent was evaporated at reduced pressure. The obtained solid was suspended in *n*-hexane (6 mL) and was filtered over a fritted glass filter inside a nitrogen-filled glove box. The obtained solid was washed with *n*-hexane (4 × 4 mL). Further purification was achieved by dissolving the entire material in THF (5 mL) and subsequent precipitation with *n*-pentane (approximately 80 mL). The solid was isolated by filtration using a fritted glass filter. After drying *in vacuo* for 30 min, the desired product was obtained as colorless solid (566 mg, 0.62 mmol, 57% yield). The acquired ^{1}H NMR spectrum showed the presence of 3.7 equivalents of THF as well as slight contamination. However, the material was found sufficient for subsequent usage.

^{1}H NMR (600.2 MHz, DMSO-d_6, 295 K): δ_{1H} [ppm] = **5.35** (s, 8H, β-H), **3.63-3.56** (m, 3.7 × 4H, THF), **1.80-1.73** (m, 3.7 × 4H, THF), **1.65** (br q, $^{3}J_{HH}$ = 6.7 Hz, 16H, α-methylene), **0.45** (t, $^{3}J_{HH}$ = 6.7 Hz, 24H, α-Me).

^{13}C{^{1}H} NMR (150.9 MHz, DMSO-d_6, 295 K): δ_{13C} [ppm] = **147.7** (s, C_q, C_q-pyrrole), **97.2** (s, CH, β-C), **67.0** (s, CH, THF), **45.4** (s, C_q, α-C), **28.7** (s, CH_2, α-methylene), **25.2** (s, CH, THF), **9.3** (s, CH_3, α-Me).

Tetraphenylphosphonium tetrachloridogallate(III) ([PPh_4][$GaCl_4$])



Procedure.[10] Gallium trichloride (1.00 g, 5.68 mmol, 1.0 eq) was dissolved in ice-cold concentrated hydrochloric acid (35 mL). Dry tetraphenylphosphonium chloride (2.13 g, 5.68 mmol, 1.0 eq) was dissolved in ethanol (25 mL). The latter solution was added to the former. This caused the immediate precipitation of a colorless solid. The mixture was stirred for 10 min at room temperature. The solid was isolated by filtration using a Büchner funnel. It was washed with ethanol (in total 60 mL over several washing steps) and diethyl ether (in total 40 mL over several washing steps). The product was obtained as a colorless solid after drying *in vacuo* (2.87 g, 5.20 mmol, 92% yield).

^{1}H NMR (600.2 MHz, CD_2Cl_2, 295 K): δ_{1H} [ppm] = **7.96-7.90** (m, 4H, $[PPh_4]^+$), **7.80-7.72** (m, 8H, $[PPh_4]^+$), **7.66-7.59** (m, 8H, $[PPh_4]^+$).

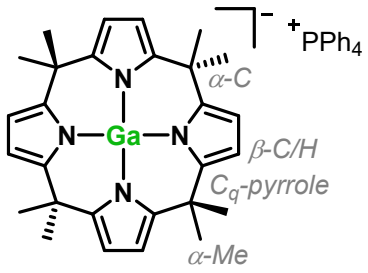
^{13}C{^{1}H} NMR (151.9 MHz, CD_2Cl_2, 295 K), δ_{13C} [ppm] = **136.1** (d, CH, $^{4}J_{PC}$ = 3.0 Hz, $[PPh_4]^+$), **134.8** (d, CH, $^{2}J_{PC}$ = 10.3 Hz, $[PPh_4]^+$), **131.0** (d, CH, $^{3}J_{PC}$ = 12.9 Hz, $[PPh_4]^+$), **117.9** (d, C_q, $^{1}J_{PC}$ = 89.7 Hz, $[PPh_4]^+$).

^{31}P{^{1}H} NMR (243.0 MHz, CD_2Cl_2, 295 K), δ_{31P} [ppm] = **23.3** (s, $[PPh_4]^+$).

^{71}Ga{^{1}H} NMR (183.0 MHz, CD_2Cl_2, 295 K), δ_{71Ga} [ppm] = **250.9** (s, $GaCl_4^-$).

S3. Synthesis and characterization of the calix[4]pyrrolato gallates

Tetraphenylphosphonium *meso*-octamethylcalix[4]pyrrolato gallate ([PPh_4][**[Me]1**])



[PPh_4][**[Me]1**]

Procedure. In a nitrogen-filled glove box, the tetrasodium salt of deprotonated *meso*-octamethylcalix[4]pyrrole (500 mg, 0.62 mmol, 1.0 eq) was dissolved in 1,2-dimethoxyethane (DME, 5 mL). [PPh_4][$GaCl_4$] (332 mg, 0.60 mmol, 0.97 eq) was added in one portion at room temperature. The reaction mixture turned intensively red. It was stirred for 3 h at room temperature. Over time, the color changed to pale orange and a colorless precipitate formed. The solid was separated from the orange solution by filtration over a fritted glass filter. It was washed with DME (3 × 2 mL) and *n*-pentane (2 × 2 mL) and was subsequently suspended in CH_2Cl_2 (5 mL). The suspension was stirred for 5 min at room temperature. It was filtered over a fritted glass filter covered with a pad of celite to remove NaCl. The product was isolated from its CH_2Cl_2 solution by precipitation with *n*-pentane (approximately 20 mL) and subsequent filtration. After drying *in vacuo,* it was obtained as a pale rose solid (390 mg, 0.43 mmol, 69% yield). The material was found to contain 0.9 equivalents of CH_2Cl_2 as determined by ^{1}H NMR spectroscopy using $CDCl_3$ as solvent. This is consistent with the obtained result from elemental analysis.

^{1}H NMR (600.2 MHz, CD_2Cl_2, 295 K), δ_{1H} [ppm] = **7.89-7.84** (m, 4H, [PPh_4]$^+$), **7.72-7.66** (m, 8H, [PPh_4]$^+$), **7.60-7.53** (m, 8H, [PPh_4]$^+$), **5.79** (s, 8H, β-H), **1.65** (s, 12H, α-Me), **1.46** (s, 12H, α-Me).

^{13}C{^{1}H} NMR (151.9 MHz, CD_2Cl_2, 295 K), δ_{13C} [ppm] = **146.2** (s, C_q, C_q-pyrrole), **136.2** (d, CH, $^4J_{PC}$ = 3.0 Hz, [PPh_4]$^+$), **134.8** (d, CH, $^2J_{PC}$ = 10.3 Hz, [PPh_4]$^+$), **131.0** (d, CH, $^3J_{PC}$ = 12.9 Hz, [PPh_4]$^+$), **117.8** (d, C_q, $^1J_{PC}$ = 89.6 Hz, [PPh_4]$^+$), **100.7** (s, CH, β-C), **42.4** (s, C_q, α-C), **35.6** (s, CH_3, α-Me), **25.0** (s, CH_3, α-Me).

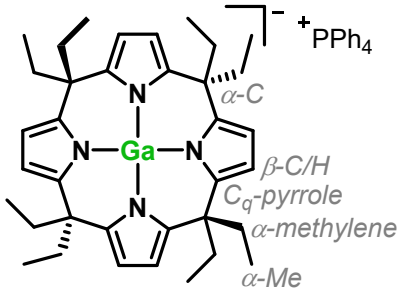
^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2, 295 K), δ_{31P} [ppm] = **23.2** (s, [PPh_4]$^+$).

HR-MS (ESI, negative ion mode): m/z calculated for $C_{28}H_{32}{}^{69}GaN_4$ [M]$^-$: **493.1888**, found: **493.1877**.

FT-ATR-IR (solid state, room temperature), $\tilde{\nu}_{max}$ [cm^{-1}] = **3094** (w), **3040** (w), **2966** (m), **2937** (m), **2902** (m), **2867** (w), **2840** (w), **1613** (w), **1587** (w), **1485** (m), **1460** (w), **1435** (s), **1371** (s), **1348** (s), **1316** (w), **1303** (w), **1278** (s), **1263** (s), **1224** (m), **1213** (m), **1190** (w), **1153** (s), **1107** (s), **1064** (s), **994** (m), **929** (w), **890** (w), **854** (w), **807** (w), **756** (s), **723** (s), **688** (s).

Elemental analysis: calc. **C 69.81**, **H 5.96**, **N 6.16** ([PPh_4][**[Me]1**] · 0.9 CH_2Cl_2), found: **C 69.80**, **H 5.71**, **N 6.59** (content of CH_2Cl_2 was verified by ^{1}H NMR spectroscopy in $CDCl_3$).

Tetraphenylphosphonium *meso*-octaethylcalix[4]pyrrolato gallate ([PPh_4][^{Et}**1**])



[PPh_4][^{Et}**1**]

Procedure. In a nitrogen-filled glove box, the tetrasodium salt of deprotonated *meso*-octaethylcalix[4]pyrrole (200 mg, 0.22 mmol, 1.0 eq) was dissolved in 1,2-dimethoxyethane (DME, 2 mL). [PPh_4][$GaCl_4$] (119 mg, 0.22 mmol, 0.97 eq) was added in one portion at room temperature. The reaction mixture turned intensively red. It was stirred for 3 h at room temperature. Over time, the color changed to pale orange and a colorless precipitate formed. The solid was separated from the orange solution by filtration over a fritted glass filter. It was washed with DME (3 × 0.5 mL) and *n*-pentane (2 × 1 mL) and was subsequently suspended in CH_2Cl_2 (3 mL). The suspension was stirred for 5 min at room temperature. It was filtered over a fritted glass filter covered with a pad of celite to remove NaCl. The product was isolated from its CH_2Cl_2 solution by precipitation with *n*-pentane (approximately 20 mL) and subsequent filtration. After drying *in vacuo,* it was obtained as a slightly pale rose solid (120 mg, 0.13 mmol, 57% yield).

^{1}H NMR (600.2 MHz, CD_2Cl_2, 295 K), δ_{1H} [ppm] = **7.90-7.84** (m, 4H, $[PPh_4]^+$), **7.73-7.66** (m, 8H, $[PPh_4]^+$), **7.61-7.53** (m, 8H, $[PPh_4]^+$), **5.77** (s, 8H, β-H), **2.04** (q, $^3J_{HH}$ = 7.3 Hz, 8H, α-methylene), **1.48** (q, $^3J_{HH}$ = 7.2 Hz, 8H, α-methylene), **1.07** (t, $^3J_{HH}$ = 7.2 Hz, 12H, α-Me), **0.52** (t, $^3J_{HH}$ = 7.2 Hz, 12H, α-Me).

^{13}C{^{1}H} NMR (151.9 MHz, CD_2Cl_2, 295 K), δ_{13C} [ppm] = **143.2** (s, C_q, C_q-pyrrole), **136.2** (d, CH, $^4J_{PC}$ = 3.0 Hz, $[PPh_4]^+$), **134.7** (d, CH, $^2J_{PC}$ = 10.3 Hz, $[PPh_4]^+$), **131.0** (d, CH, $^3J_{PC}$ = 12.9 Hz, $[PPh_4]^+$), **117.8** (d, C_q, $^1J_{PC}$ = 89.6 Hz, $[PPh_4]^+$), **102.4** (s, CH, β-C), **44.5** (s, C, α-methylene), **43.7** (s, C_q, α-C), **27.4** (s, CH_2, α-methylene), **10.5** (s, CH_3, α-Me), **10.2** (s, CH_3, α-Me).

^{31}P{^{1}H} NMR (243.0 MHz, CD_2Cl_2, 295 K), δ_{31P} [ppm] = **23.3** (s, $[PPh_4]^+$).

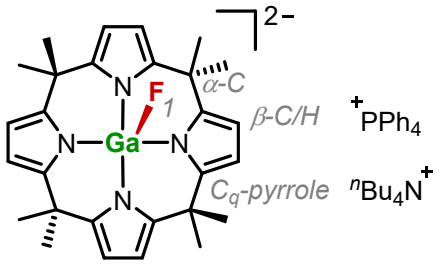
HR-MS (ESI, negative ion mode): m/z calculated for $C_{36}H_{48}{}^{69}GaN_4$ $[M]^-$: **605.3135**, found: **605.3154**.

FT-ATR-IR (solid state, room temperature), $\tilde{\nu}_{max}$ [cm^{-1}] = **3087** (w), **3056** (w), **2959** (m), **2923** (m), **2869** (m), **2834** (w), **1587** (m), **1483** (m), **1454** (m), **1439** (s), **1374** (s), **1319** (s), **1292** (m), **1246** (m), **1188** (w), **1149** (m), **1108** (s), **1073** (s), **1026** (m), **996** (m), **971** (m), **924** (m), **883** (m), **858** (m), **749** (s), **719** (s), **688** (s).

Elemental analysis: calc. **C 76.19**, **H 7.25**, **N 5.92**, found: **C 76.08**, **H 7.04**, **N 5.96**.

S4. Fluoride adduct formation

[PPh_4][(^{n}Bu)$_4$N][^{Me}**1**-F]



[^{n}Bu$_4$N][PPh$_4$][^{Me}**1**-F]

Procedure. In a nitrogen-filled glove box, tetraphenylphosphonium *meso*-octamethylcalix[4]pyrrolato gallate (15.0 mg, 16.48 µmol (0.9 eq of residual CH_2Cl_2 included), 1.0 eq) and tetrabutylammonium difluorotriphenylsilicate (8.9 mg, 16.48 µmol, 1.0 eq) were placed in a 10 mL snap cap vial and were dissolved in acetonitrile (1 mL) at room temperature. A pale-orange solution was obtained, which was stirred at room temperature for 4 h. Diethyl ether (3 mL) was added. Upon further addition of *n*-pentane (10 mL) an orange oil formed, which was separated by centrifugation. The clear and colorless supernatant was removed. The oil was washed with *n*-pentane (4 × 1 mL), what transformed it into a dark-orange, sticky solid. Drying under reduced pressure over night at room temperature gave the desired product as an orange solid (14.6 mg, 13.33 µmol, 80% yield).
A sample for mass spectrometry was prepared by mixing *meso*-octamethylcalix[4]pyrrolato gallate (7.0 mg, 7.69 µmol (0.9 eq of residual CH_2Cl_2 included), 1.0 eq) and tetrabutylammonium difluorotriphenylsilicate (12.5 mg, 23.07 µmol, 3.0 eq) in CH_2Cl_2 (0.5 mL). This solution was diluted with CH_2Cl_2 to approximately reach a concentration of c = 10^{-5} mol L^{-1} and was subsequently analyzed. However, it was later noted that the fluorido adduct of [^{Me}**1**]$^-$ is significantly more stable in acetonitrile.

^{1}H NMR (600.2 MHz, CD_3CN, 295 K), δ_{1H} [ppm] = **7.93-7.87** (m, 4H, [PPh_4]$^+$), **7.76-7.70** (m, 8H, [PPh_4]$^+$), **7.70-7.63** (m, 8H, [PPh_4]$^+$), **5.66** (d, $^3J_{HH}$ = 2.9 Hz, 4H, β-H), **5.61** (d, $^3J_{HH}$ = 2.9 Hz, 4H, β-H), **3.12-3.03** (m, 8H, [^{n}Bu$_4$N]$^+$), **1.74** (d, J_{FH} = 3.1 Hz, 6H, α-Me), **1.64-1.56** (m, 8H, [^{n}Bu$_4$N]$^+$), **1.61** (s, 6H, α-Me), **1.60** (s, 6H, α-Me), **1.36** (tq, $^3J_{HH}$ = 7.4, 7.4 Hz, 8H, [^{n}Bu$_4$N]$^+$), **1.22** (s, 6H, α-Me), **0.97** (t, $^3J_{HH}$ = 7.4 Hz, 12H, [^{n}Bu$_4$N]$^+$).

^{13}C{^{1}H} NMR (151.9 MHz, CD_3CN, 295 K), δ_{13C} [ppm] = **148.0** (s, C_q, C_q-pyrrole), **145.9** (s, C_q, C_q-pyrrole), **136.4** (d, CH, $^4J_{PC}$ = 3.0 Hz, [PPh_4]$^+$), **135.7** (d, CH, $^2J_{PC}$ = 10.4 Hz, [PPh_4]$^+$), **131.3** (d, CH, $^3J_{PC}$ = 12.9 Hz, [PPh_4]$^+$), **118.9** (d, C_q, $^1J_{PC}$ = 89.7 Hz, [PPh_4]$^+$), **100.2** (s, CH, β-C), **98.6** (s, CH, β-C), **59.3** (t, CH_2, $^1J_{NC}$ = 2.9 Hz, [^{n}Bu$_4$N]$^+$), **42.0** (s, CH_3, α-Me), **36.8** (s, C_q, α-C), **36.6** (d, CH_3, J_{FC} = 18.3 Hz, α-Me), **36.4** (s, C_q, α-C), **31.7** (s, CH_3, α-Me), **26.9** (s, CH_3, α-Me), **24.3** (s, CH_2, [^{n}Bu$_4$N]$^+$), **20.3** (t, CH_2, $^3J_{NC}$ = 1.5 Hz, [^{n}Bu$_4$N]$^+$), **13.8** (s, CH_3, [^{n}Bu$_4$N]$^+$).

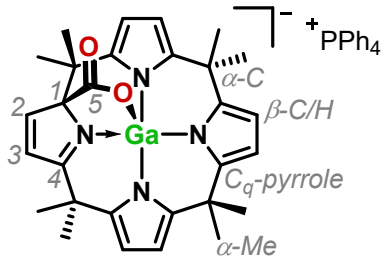
^{19}F NMR (376.3 MHz, CD_3CN, 295 K), δ_{19F} [ppm] = **−146.4** (br s, F-1).

^{31}P{^{1}H} NMR (243.0 MHz, CD_3CN, 295 K), δ_{31P} [ppm] = **22.9** (s, [PPh_4]$^+$).

HR-MS (ESI, negative ion mode): m/z calculated for $C_{28}H_{35}F^{69}GaN_4O$ [M+H_3O]$^-$: **531.2056**, found: **531.2075**.

S5. Reactivity with CO_2

[PPh_4][^{Me}**1***-CO_2]



[PPh_4][^{Me}**1***-CO_2]

Procedure. In a nitrogen-filled glove box, tetraphenylphosphonium *meso*-octamethylcalix[4]pyrrolato gallate (15 mg) was placed in a J. Young NMR pressure tube and was dissolved in CD_2Cl_2 (0.5 mL). To the sample, gaseous CO_2 (5 bar) was applied at room temperature. The reaction mixture was shaken with a rocking shaker at room temperature for 10 h. Over the course of the reaction, the color of the solution turned to yellow. The sample was analyzed by NMR spectroscopy and mass spectrometry. The ratio between free [^{Me}**1**]$^-$ and [^{Me}**1***-CO_2]$^-$ under the reaction conditions was determined to 1:24 by ^{1}H NMR spectroscopy. CO_2 elimination. The pressure was released from the sample, CH_2Cl_2 (1 mL) was added, and the solution was transferred by syringe to a normal J. Young NMR tube. The open NMR tube was placed inside a large Schlenk flask. The solvent was slowly evaporated at room temperature over the course of several hours. The obtained solid was kept under static vacuum overnight at room temperature and was analyzed by NMR spectroscopy. A 1:1 ratio between free [^{Me}**1**]$^-$ and [^{Me}**1***-CO_2]$^-$ was observed. Subsequently, this process was repeated twice to achieve quantitative CO_2 removal as found by ^{1}H NMR spectroscopy (see Figure S1).

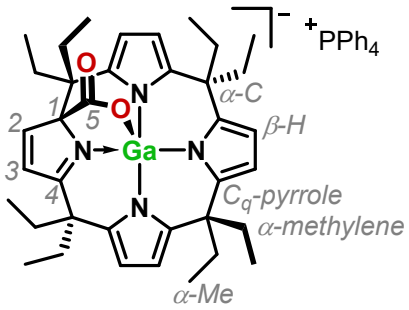
^{1}H NMR (600.2 MHz, CD_2Cl_2, 295 K), δ_{1H} [ppm] = **7.87-7.80** (m, 4H, [PPh_4]$^+$), **7.71-7.63** (m, 8H, [PPh_4]$^+$), **7.65** (1H, H-2, identified by ^{1}H,^{1}H COSY NMR spectroscopy, expected multiplicity is d), **7.60-7.53** (m, 8H, [PPh_4]$^+$), **6.64** (d, $^3J_{HH}$ = 5.0 Hz, 1H, H-3), **5.94** (d, $^3J_{HH}$ = 3.1 Hz, 1H, β-H), **5.91** (d, $^3J_{HH}$ = 3.1 Hz, 1H, β-H), **5.84** (d, $^3J_{HH}$ = 3.1 Hz, 1H, β-H), **5.81** (d, $^3J_{HH}$ = 3.1 Hz, 1H, β-H), **5.79** (d, $^3J_{HH}$ = 3.0 Hz, 1H, β-H), **5.77** (d, $^3J_{HH}$ = 3.0 Hz, 1H, β-H), **1.79** (s, 3H, α-Me), **1.78** (s, 3H, α-Me), **1.68** (s, 3H, α-Me), **1.66** (s, 3H, α-Me), **1.60** (s, 3H, α-Me), **1.38** (s, 3H, α-Me), **1.36** (s, 3H, α-Me), **0.95** (s, 3H, α-Me).

^{13}C{^{1}H} NMR (151.9 MHz, CD_2Cl_2, 295 K), δ_{13C} [ppm] = **184.8** (s, C_q, C-4), **168.0** (s, C_q, C-5), **158.1** (s, CH, C-2), **149.0** (s, C_q, C_q-pyrrole), **148.3** (s, C_q, C_q-pyrrole), **146.2** (s, C_q, C_q-pyrrole), **146.1** (s, C_q, C_q-pyrrole), **145.6** (s, C_q, C_q-pyrrole), **140.0** (s, C_q, C_q-pyrrole), **136.2** (d, CH, $^4J_{PC}$ = 3.0 Hz, [PPh_4]$^+$), **134.8** (d, CH, $^2J_{PC}$ = 10.3 Hz, [PPh_4]$^+$), **131.0** (d, CH, $^3J_{PC}$ = 12.9 Hz, [PPh_4]$^+$), **126.6** (s, CH, C-3), **117.9** (d, C_q, $^1J_{PC}$ = 89.6 Hz, [PPh_4]$^+$), **104.2** (s, CH, β-C), **102.5** (s, CH, β-C), **102.1** (s, CH, β-C), **101.9** (s, CH, β-C), **101.8** (s, CH, β-C), **100.1** (s, CH, β-C), **97.2** (s, C_q, C-1), **44.1** (s, C_q, α-C), **40.8** (s, CH_3, α-Me), **38.5** (s, C_q, α-C), **36.4** (s, C_q, α-C), **36.14** (s, CH_3, α-Me), **36.10** (s, C_q, α-C), **35.9** (s, CH_3, α-Me), **27.4** (s, CH_3, α-Me), **27.2** (s, CH_3, α-Me), **26.8** (s, CH_3, α-Me), **26.6** (s, CH_3, α-Me), **24.1** (s, CH_3, α-Me).

^{31}P{^{1}H} NMR (243.0 MHz, CD_2Cl_2, 295 K), δ_{31P} [ppm] = **23.2** (s, [PPh_4]$^+$).

HR-MS (ESI, negative ion mode): m/z calculated for $C_{29}H_{32}{}^{69}GaN_4O_2$ [M]$^-$: **537.1781**, found: **537.1769**.

[PPh_4][^{Et}**1***-CO_2]



[PPh_4][^{Et}**1***-CO_2]

Procedure. In a nitrogen-filled glove box, tetraphenylphosphonium *meso*-octaethylcalix[4]pyrrolato gallate (15 mg) was placed in a J. Young NMR pressure tube and was dissolved in CD_2Cl_2 (0.5 mL). To the sample, gaseous CO_2 (5 bar) was applied. The reaction mixture was shaken with a rocking shaker at room temperature for 10 h. Over the course of the reaction, the color of the solution turned to yellow. The sample was analyzed by NMR spectroscopy. The ratio between free [^{Et}**1**]$^-$ and [^{Et}**1***-CO_2]$^-$ under the reaction conditions was determined to 2:1 by ^{1}H NMR spectroscopy. Detection of the addition product by mass spectrometry was not possible. CO_2 elimination. The pressure was released from the sample, CH_2Cl_2 (1 mL) was added, and the solution was transferred by syringe to a normal J. Young NMR tube. The open NMR tube was placed inside a large Schlenk flask. The solvent was slowly evaporated under reduced pressure over the course of several hours at room temperature. The obtained solid was kept under static vacuum overnight at room temperature and was subsequently analyzed by ^{1}H NMR spectroscopy. Quantitative CO_2 removal was found (see Figure S2).

^{1}H NMR (600.2 MHz, CD_2Cl_2, 295 K), δ_{1H} [ppm] = **7.89-7.82** (m, 4H, [PPh_4]$^+$), **7.77** (d, $^3J_{HH}$ = 5.1 Hz, 1H, H-2), **7.72-7.65** (m, 8H, [PPh_4]$^+$), **7.60-7.53** (m, 8H, [PPh_4]$^+$), **6.54** (d, $^3J_{HH}$ = 5.1 Hz, 1H, H-3), **5.95** (d, $^3J_{HH}$ = 3.3 Hz, 1H, β-H), **5.89** (d, $^3J_{HH}$ = 3.1 Hz, 1H, β-H), **5.85** (d, $^3J_{HH}$ = 3.2 Hz, 1H, β-H), **5.81** (d, $^3J_{HH}$ = 3.0 Hz, 1H, β-H), **5.76** (d, $^3J_{HH}$ = 3.1 Hz, 1H, β-H), **5.74** (d, $^3J_{HH}$ = 3.0 Hz, 1H, β-H). Evaluation of the signals of the ethyl groups was not fully possible due to signal overlapping (with unreacted [^{Et}**1**]$^-$) and diastereotopicity of the methylene protons. Six of the eight methyl triplets were well resolved: **1.03** (t, $^3J_{HH}$ = 7.4 Hz, 3H, α-Me), **1.00** (t, $^3J_{HH}$ = 7.3 Hz, 3H, α-Me), **0.65** (t, $^3J_{HH}$ = 7.3 Hz, 3H, α-Me), **0.56** (t, $^3J_{HH}$ = 7.4 Hz, 3H, α-Me), **0.48** (t, $^3J_{HH}$ = 7.4 Hz, 3H, α-Me), **0.39** (t, $^3J_{HH}$ = 7.3 Hz, 3H, α-Me).

^{13}C{^{1}H}, NMR (151.9 MHz, CD_2Cl_2, 295 K), δ_{13C} [ppm] = Due to the low concentration of [^{Et}**1***-CO_2]$^-$, complete characterization by ^{13}C{^{1}H} NMR spectroscopy was not possible. Only the well resolved and reliably assignable signals of [^{Et}**1***-CO_2]$^-$ are listed. Some of them were identified by two-dimensional experiments. **184.6** (s, C_q, C-4), **168.6** (s, C_q, C-5), **158.6** (s, CH, C-2), **126.5** (s, CH, C-3), **105.0** (s, CH, β-C), **104.5** (s, CH, β-C), **103.5** (s, CH, β-C), **103.5** (s, CH, β-C), **102.4** (s, CH, β-C), **101.4** (s, CH, β-C), **97.3** (s, C_q, C-1), **11.1** (s, CH_3, α-Me), **11.0** (s, CH_3, α-Me), **10.7** (s, CH_3, α-Me), **10.0** (s, CH_3, α-Me), **9.7** (s, CH_3, α-Me), **9.1** (s, CH_3, α-Me), **8.7** (s, CH_3, α-Me).

^{31}P{^{1}H} NMR (243.0 MHz, CD_2Cl_2, 295 K), δ_{31P} [ppm] = **23.2** (s, [PPh_4]$^+$).

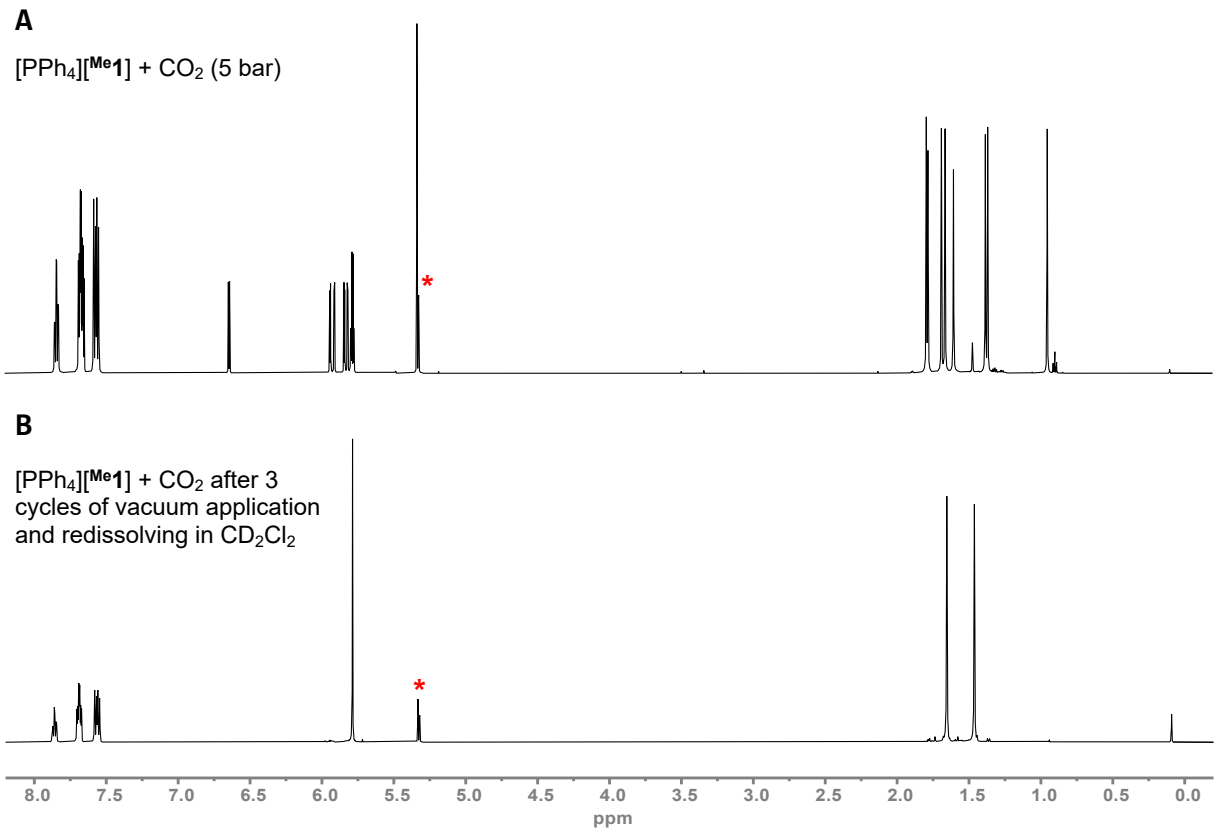


Figure S1. ^{1}H NMR spectra (600.2 MHz, CD_2Cl_2, 295 K) of $[PPh_4][^{Me}\mathbf{1}]$ **A**) in the presence of CO_2 (5 bar) and **B**) after three cycles of vacuum application. The signal of $CHDCl_2$ and of residual CH_2Cl_2 is marked with a red asterisk.

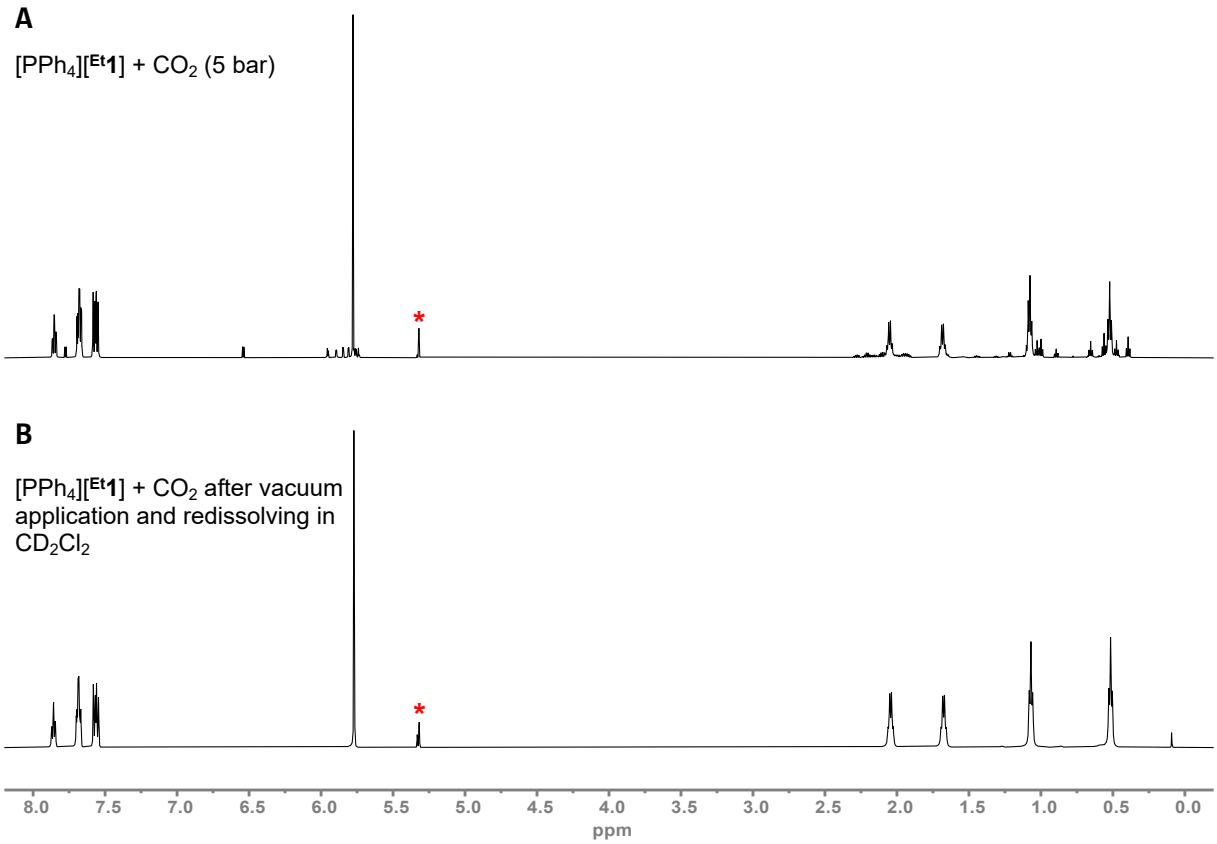


Figure S2. ^{1}H NMR spectra (600.2 MHz, CD_2Cl_2, 295 K) of $[PPh_4][^{Et}\mathbf{1}]$ **A**) in the presence of CO_2 (5 bar) and **B**) after one cycles of vacuum application. The signal of $CHDCl_2$ is marked with a red asterisk.

S6. Reactivity with $HNTf_2$ and isopropanol

Reactivity with isopropanol without $HNTf_2$ activation

Procedure. In a nitrogen-filled glove box, tetraphenylphosphonium *meso*-octamethylcalix[4]pyrrolato gallate and tetraphenylphosphonium *meso*-octaethylcalix[4]pyrrolato gallate (7 mg) were placed in two separate J. Young NMR tubes and were dissolved in CD_2Cl_2 (each 0.5 mL). To the samples, isopropanol ([PPh_4][^{Me}**1**]: 1.0 µL, [PPh_4][^{Et}**1**]: 0.7 µL) was added in one portion at room temperature using a piston pipette. No color change occurred in both cases. The samples were closed and were vigorously shaken. The samples were analyzed by ^{1}H NMR spectroscopy immediately after preparation and after standing 24 h at room temperature (Figure S3 and Figure S4). No reaction occurred.

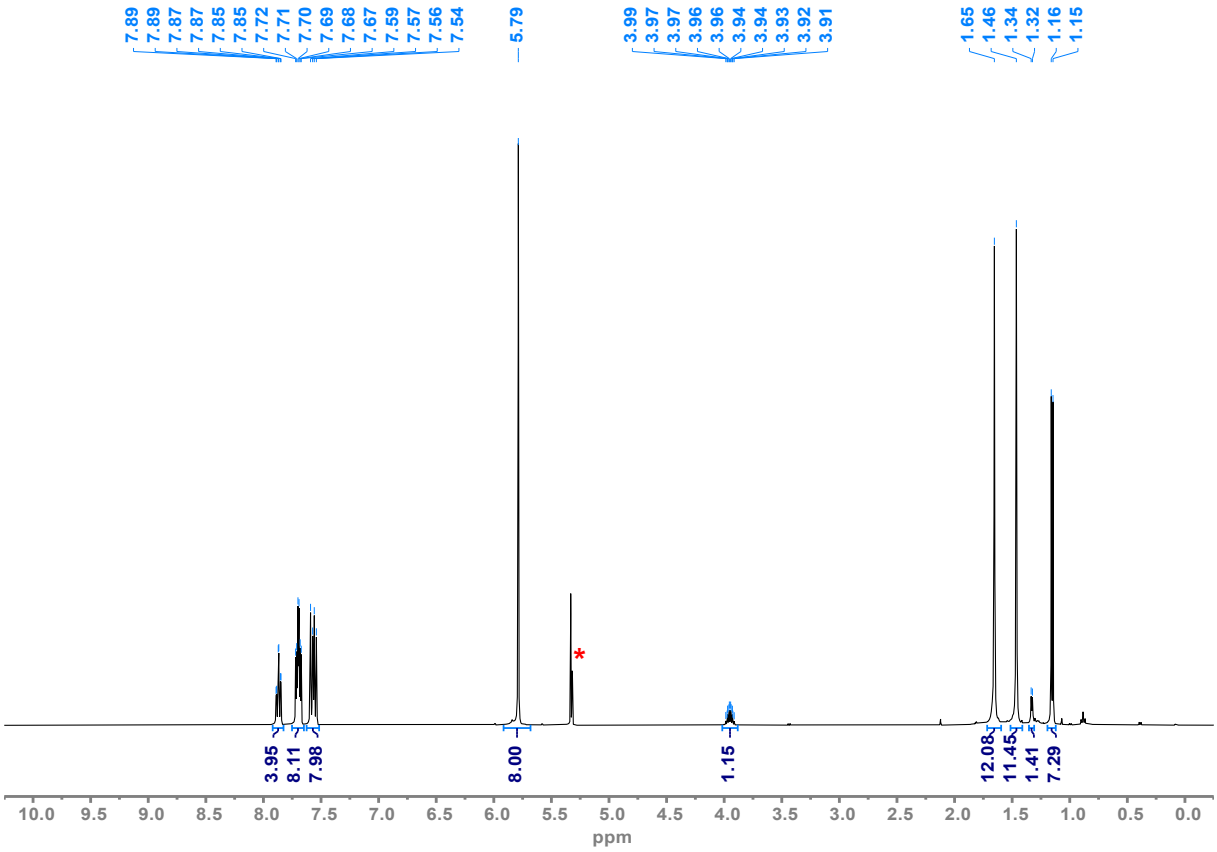


Figure S3. ^{1}H NMR spectrum (399.9 MHz, CD_2Cl_2, 295 K) of [PPh_4][^{Me}**1**] in the presence of approximately one equivalent of isopropanol. The signal of $CHDCl_2$ and of residual CH_2Cl_2 is marked with a red asterisk.

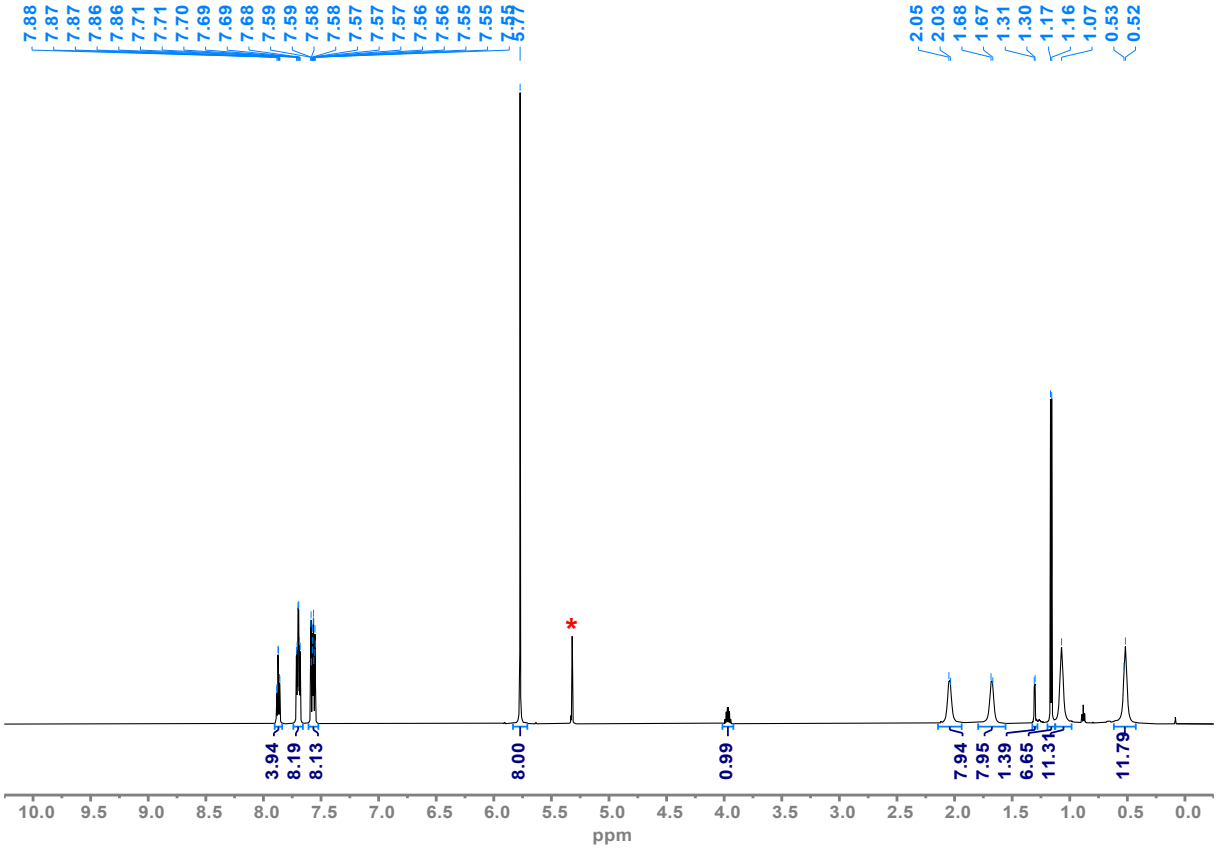
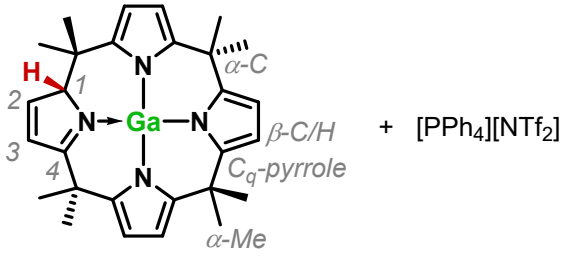


Figure S4. ^{1}H NMR spectrum (600.2 MHz, CD_2Cl_2, 295 K) of $[PPh_4][^{Et}\mathbf{1}]$ in the presence of approximately one equivalent of isopropanol. The signal of $CHDCl_2$ and is marked with a red asterisk.

Reactivity with $HNTf_2$

Reaction with THF-d_8 as solvent



+ $[PPh_4][NTf_2]$

$[H\text{-}^{Me}\mathbf{1}^*]$, dissolved in THF

Procedure. In a nitrogen-filled glove box, tetraphenylphosphonium *meso*-octamethylcalix[4]pyrrolato gallate (10.0 mg, 10.99 µmol (0.9 eq of residual CH_2Cl_2 included), 1.0 eq) and bis(trifluoromethyl)sulfonimide ($HNTf_2$, 3.0 mg, 10.66 µmol, 0.97 eq) were placed in a J. Young NMR tube. THF-d_8 (0.5 mL) was added, the sample was closed and was vigorously shaken. A yellow solution was obtained which was analyzed by NMR spectroscopy.

^{1}H NMR (600.2 MHz, THF-d_8, 295 K), δ_{1H} [ppm] = **7.95-7.90** (m, 4H, $[PPh_4]^+$), **7.85** (d, $^{3}J_{HH}$ = 5.4 Hz, 1H, H-2), **7.80-7.74** (m, 16H, $[PPh_4]^+$), **7.18** (dd, $^{3}J_{HH}$ = 5.4 Hz, $^{4}J_{HH}$ = 1.3 Hz, 1H, H-3), **6.08** (d, $^{3}J_{HH}$ = 3.3 Hz, 1H, β-H), **5.96** (d, $^{3}J_{HH}$ = 3.3 Hz, 1H, β-H), **5.95** (d, $^{3}J_{HH}$ = 3.2 Hz, 1H, β-H), **5.92** (d, $^{3}J_{HH}$ = 3.2 Hz, 1H, β-H), **5.81** (d, $^{3}J_{HH}$ = 3.1 Hz, 1H, β-H), **5.79** (d, $^{3}J_{HH}$ = 3.1 Hz, 1H, β-H), **5.02** (s, 1H, H-1), **1.77** (s, 3H, α-Me), **1.65** (s, 2 × 3H, α-Me), **1.56** (s, 3H, α-Me), **1.51** (s, 3H, α-Me), **1.47** (s, 3H, α-Me), **1.43** (s, 3H, α-Me), **0.86** (s, 3H, α-Me).

^{13}C{^{1}H} NMR (151.9 MHz, THF-d_8, 295 K), δ_{13C} [ppm] = **190.3** (s, C_q, C-4), **156.6** (s, CH, C-2), **150.0** (s, C_q, C_q-pyrrole), **149.5** (s, C_q, C_q-pyrrole), **147.3** (s, C_q, C_q-pyrrole), **145.6** (s, C_q, C_q-pyrrole), **145.5** (s, C_q, C_q-pyrrole), **141.3** (s, C_q, C_q-pyrrole), **136.1** (d, CH, $^{4}J_{PC}$ = 3.1 Hz, $[PPh_4]^+$), **135.5** (d, CH, $^{2}J_{PC}$ = 10.4 Hz, $[PPh_4]^+$), **131.2** (d, CH, $^{3}J_{PC}$ = 12.9 Hz, $[PPh_4]^+$), **129.5** (s, CH, C-3), **121.0** (q, CF_3, $^{1}J_{FC}$ = 322.4 Hz, $[NTf_2]^-$, the outer two peaks of the quartet were only barely visible), **118.9** (d, C_q, $^{1}J_{PC}$ = 89.5 Hz, $[PPh_4]^+$), **106.4** (s, CH,

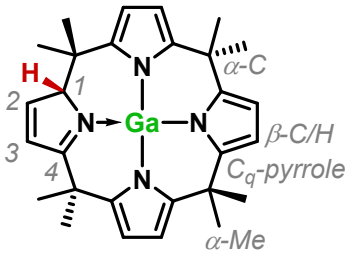
β-C), **103.8** (s, CH, β-C), **103.8** (s, CH, β-C), **103.6** (s, CH, β-C), **102.1** (s, 2 × CH, β-C), **87.6** (s, CH, C-1), **39.8** (s, C_q, α-C), **39.3** (s, C_q, α-C), **36.5** (s, C_q, α-C), **36.4** (s, C_q, α-C), **36.2** (s, CH_3, α-Me), **35.0** (s, CH_3, α-Me), **33.91** (s, CH_3, α-Me), **33.87** (s, CH_3, α-Me), **31.9** (s, CH_3, α-Me), **29.5** (s, CH_3, α-Me), **28.3** (s, CH_3, α-Me), **24.8** (s, CH_3, α-Me).

^{19}F NMR (188.1 MHz, THF-d_8, 295 K), δ_{19F} [ppm] = **−79.9** (s, $[NTf_2]^-$).

^{31}P{^{1}H} NMR (243.0 MHz, THF-d_8, 295 K), δ_{31P} [ppm] = **21.1** (s, $[PPh_4]^+$).

The ^{1}H,^{1}H COSY NMR spectrum showed characteristic cross peaks between the signals at 5.02 (transferred proton) and 7.18 ppm (H-3) and between the signals at 7.18 (H-3) and 7.85 ppm (H-2) (see Figure S25).

Reaction with CD_2Cl_2 / diethyl ether (2:1 %vol) as solvent



+ $[PPh_4][NTf_2]$

[H-^{Me}**1***], dissolved in CD_2Cl_2 / Et_2O (2:1 %vol)

Procedure. In a nitrogen-filled glove box, tetraphenylphosphonium *meso*-octamethylcalix[4]pyrrolato gallate (10.0 mg, 10.99 µmol (0.9 eq of residual CH_2Cl_2 included), 1.0 eq) were suspended in a mixture of CD_2Cl_2 and diethyl ether (2:1 %vol, 0.5 mL) in a 1 mL vial. bis(Trifluoromethyl)sulfonimide ($HNTf_2$, 2.8 mg, 10.66 µmol, 0.9 eq) was dissolved in the same solvent mixture (0.3 mL). The $HNTf_2$ solution was dropwise added to the gallate suspension over the course of 5 min at room temperature while shaking the latter. The reaction mixture turned yellow. It was filtered into a J. Young NMR tube and was analyzed by NMR spectroscopy.

^{1}H NMR (600.2 MHz, CD_2Cl_2 / Et_2O (2:1 %vol), 295 K), spectrum was calibrated with the signal of $CHDCl_2$ to 5.32 ppm, δ_{1H} [ppm] = **7.92-7.86** (m, 4H, $[PPh_4]^+$), **7.77-7.71** (m, 8H, $[PPh_4]^+$), **7.73** (1H, H-2, identified by ^{1}H,^{1}H COSY NMR spectroscopy, expected multiplicity is d), **7.66-7.59** (m, 8H, $[PPh_4]^+$), **7.05** (dd, $^3J_{HH}$ = 5.4 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, H-3), **6.14** (d, $^3J_{HH}$ = 3.3 Hz, 1H, β-H), **6.05** (d, $^3J_{HH}$ = 3.3 Hz, 1H, β-H), **6.03** (d, $^3J_{HH}$ = 3.3 Hz, 1H, β-H), **6.00** (d, $^3J_{HH}$ = 3.2 Hz, 1H, β-H), **5.90** (s, 2 × 1H, β-H), **4.91** (s, 1H, H-1), **1.82** (s, 3H, α-Me), **1.63** (s, 3H, α-Me), **1.574** (s, 3H, α-Me), **1.568** (s, 3H, α-Me), **1.52** (s, 3H, α-Me), **1.46** (s, 3H, α-Me), **1.44** (s, 3H, α-Me), **0.81** (s, 3H, α-Me).

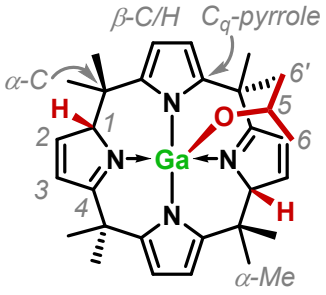
^{13}C{^{1}H} NMR (151.9 MHz, CD_2Cl_2 / Et_2O (2:1 %vol), 295 K), spectrum was calibrated with the signal of CD_2Cl_2 to 53.84 ppm, δ_{13C} [ppm] = **190.0** (s, C_q, C-4), **156.6** (s, CH, C-2), **151.1** (s, C_q, C_q-pyrrole), **150.7** (s, C_q, C_q-pyrrole), **148.3** (s, C_q, C_q-pyrrole), **146.0** (s, C_q, C_q-pyrrole), **145.3** (s, C_q, C_q-pyrrole), **141.4** (s, C_q, C_q-pyrrole), **136.4** (d, CH, $^4J_{PC}$ = 3.1 Hz, $[PPh_4]^+$), **135.1** (d, CH, $^2J_{PC}$ = 10.3 Hz, $[PPh_4]^+$), **131.3** (d, CH, $^3J_{PC}$ = 12.9 Hz, $[PPh_4]^+$), **129.8** (s, CH, C-3), **120.6** (q, CF_3, $^1J_{FC}$ = 321.2 Hz, $[NTf_2]^-$, the outer two peaks of the quartet were only barely visible), **118.3** (d, C_q, $^1J_{PC}$ = 89.7 Hz, $[PPh_4]^+$), **106.9** (s, CH, β-C), **104.7** (s, CH, β-C), **104.4** (s, CH, β-C), **104.1** (s, CH, β-C), **102.8** (s, CH, β-C), **102.4** (s, CH, β-C), **87.4** (s, CH, C-1), **42.7** (s, CH, α-Me), **40.5** (s, C_q, α-C), **39.1** (s, C_q, α-C), **37.5** (s, CH, α-Me), **36.43** (s, C_q, α-C), **36.38** (s, C_q, α-C), **35.5** (s, CH, α-Me), **32.2** (s, CH, α-Me), **31.7** (s, CH, α-Me), **26.7** (s, CH, α-Me), **25.3** (s, CH, α-Me), **25.2** (s, CH, α-Me).

^{19}F NMR (376.3 MHz, CD_2Cl_2 / Et_2O (2:1 %vol), 295 K), δ_{19F} [ppm] = **−79.8** (s, $[NTf_2]^-$).

^{31}P{^{1}H} NMR (243.0 MHz, CD_2Cl_2 / Et_2O (2:1 %vol), 295 K), δ_{31P} [ppm] = **23.2** (s, $[PPh_4]^+$).

The identical pattern in the ^{1}H,^{1}H COSY NMR spectrum as for the reaction in THF-d_8 was found.

Reactivity with isopropanol after *in situ* activation with $HNTf_2$



[HH-^{Me}**1****-O^{i}Pr]

Procedure. In a nitrogen-filled glove box, tetraphenylphosphonium *meso*-octamethylcalix[4]pyrrolato gallate (10.0 mg, 10.99 µmol (0.9 eq of residual CH_2Cl_2 included), 1.0 eq) was suspended in a mixture of CH_2Cl_2 and diethyl ether (2:1 %vol, 2 mL) in a 10 mL snap cap vial and was vigorously stirred at room temperature. bis(Trifluoromethyl)sulfonimide ($HNTf_2$, 3.0 mg, 10.66 µmol, 0.97 eq) was dissolved in the same solvent mixture (0.5 mL). The $HNTf_2$ solution was added dropwise to the gallate suspension over the course of 5 min at room temperature. The reaction mixture turned yellow. Isopropanol (0.9 µL, 11.79 µmol, 1.07 eq) was added in one portion at room temperature using a piston pipette. It was continued to stir for 1 min. All volatiles were removed under reduced pressure. From the obtained solid, it was extracted with a *n*-pentane/diethyl ether mixture (4:1 %vol, 2.5 mL in total, used over three extraction cycles). After removing the solvent from the extract under reduced pressure and drying *in vacuo*, a pale-yellow solid was isolated, which was characterized to [HH-^{Me}**1****-O^{i}Pr] by NMR spectroscopy (4.4 mg, 7.92 µmol, 72% yield).
It was noted by ^{1}H NMR spectroscopy (see Figure S28) that a small quantity (approximately 8% relative to the shown compound) of another molecule was formed. Based on the acquired NMR data, this is assigned to a constitutional isomer in which the two dearomatization-inducing protons are convertible into each other by means of a mirror plane. One proton is located at the 2- the other at the 5-position of the respective dearomatized pyrrole ring.

^{1}H NMR (600.2 MHz, CD_2Cl_2, 295 K), δ_{1H} [ppm] = **7.61** (dd, $^3J_{HH}$ = 5.4, 0.7 Hz, 2H, H-2), **7.00** (dd, $^3J_{HH}$ = 5.4, $^4J_{HH}$ = 1.4 Hz, 2H, H-3), **6.09** (d, $^3J_{HH}$ = 3.3 Hz, 2H, β-H), **6.00** (d, $^3J_{HH}$ = 3.3 Hz, 2H, β-H), **4.87** (br s, 2H, H-1), **3.52** (sept, $^3J_{HH}$ = 6.0 Hz, 1H, H-5), **1.88** (s, 6H, α-Me), **1.84** (s, 6H, α-Me), **1.57** (s, 6H, α-Me), **0.89** (d, $^3J_{HH}$ = 6.0 Hz, 3H, H-6), **0.69** (d, $^3J_{HH}$ = 6.0 Hz, 3H, H-6'), **0.44** (s, 6H, α-Me).

^{13}C{^{1}H} NMR (151.9 MHz, CD_2Cl_2, 295 K), δ_{13C} [ppm] = **188.4** (s, C_q, C-4), **155.3** (s, CH, C-2), **147.7** (s, C_q, C_q-pyrrole), **142.7** (s, C_q, C_q-pyrrole), **129.1** (s, CH, C-3), **104.7** (s, CH, β-C), **102.9** (s, CH, β-C), **87.1** (s, CH, C-1), **64.4** (s, CH, C-5), **39.4** (s, C_q, α-C), **38.8** (s, C_q, α-C), **32.4** (s, CH_3, α-Me), **28.7** (s, CH_3, α-Me), **28.4** (s, CH_3, α-Me), **27.2** (s, CH_3, C-6), **26.9** (s, CH_3, C-6'), **23.0** (s, CH_3, α-Me).

The ^{1}H,^{1}H COSY NMR spectrum showed characteristic cross peaks between the signals at 4.87 (protons at the 2-positions) and 7.00 ppm (H-3) and between the signals at 7.00 (H-3) and 7.61 ppm (H-2) (see Figure S30). Moreover, the ^{1}H,^{1}H NOESY NMR spectrum (see Figure S31) revealed spatial proximity of the isopropyl group and the ligand framework (both with the methyl groups and with the signal of the protons at the 2-positions). This further confirms the attachment of the [^{i}PrO]$^-$ group to the gallium center.

S7. X-ray crystallography

Crystals of the both gallates as their tetraphenylphosphonium salts ([PPh_4][^{Me}**1**] and [PPh_4][^{Et}**1**]) were grown by gas phase diffusion of *n*-pentane into dichloromethane solutions (approximately 30 mg mL^{-1}) at −40 °C. The THF adduct of [^{Me}**1**]$^-$ as its tetraphenylphosphonium salt ([PPh_4][^{Me}**1**-thf]) crystallized at room temperature when the synthesis of [PPh_4][^{Me}**1**] was attempted on NMR sample scale (J. Young NMR tube) in THF-d_8. However, not the sodium but rather the lithium salt of the deprotonated ligand (deprotonation carried out with *n*-butyllithium in THF)[11] was used in this reaction. Crystals formed overnight after mixing the deprotonated ligand (15.0 mg) and [PPh_4][$GaCl_4$] (10.4 mg) in THF-d_8 (0.5 mL) at room temperature.

For SCXRD measurements, crystals were immersed in perfluorinated polyether oil. A suitable crystal was picked and was fixed on top of a cryo loop. A Bruker APEX-III CCD diffractometer with a low-temperature unit using Mo-Kα radiation, chromated by mirror optics, was used for φ and ω scans. Data acquisition was done at 100.0 K. A strategy for data collection was calculated with Bruker's APEX3 software.[12-13] This program was also used for processing of collected data. Data reduction, scaling, and absorption corrections were done with SAINT.[14] SADABS-2016/2 was used for multi-scan absorption correction.[15] Structures were solved with direct methods as implemented in the ShelXT 2018[16-17] structure solution program. Structure refinement was carried out by full matrix least squares minimization on F^2 using the 2018/3 version of ShelXL[18-21]. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using a riding model. Handling of the structural data during refinement was performed with the ShelXle (Rev: 1246)[22] or Olex2 v1.3[23] graphical interface. Data finalization was done with FinalCif v104 (D. Kratzert, *FinalCif*, *V104*, https://dkratzert.de/finalcif.html).

For data visualization, Mercury 4.1.3 was used.[24-26] The thermal displacement ellipsoids are shown at a probability level of 50% (Figure S5, Figure S6, Figure S7).

[PPh_4][^{Me}**1**]

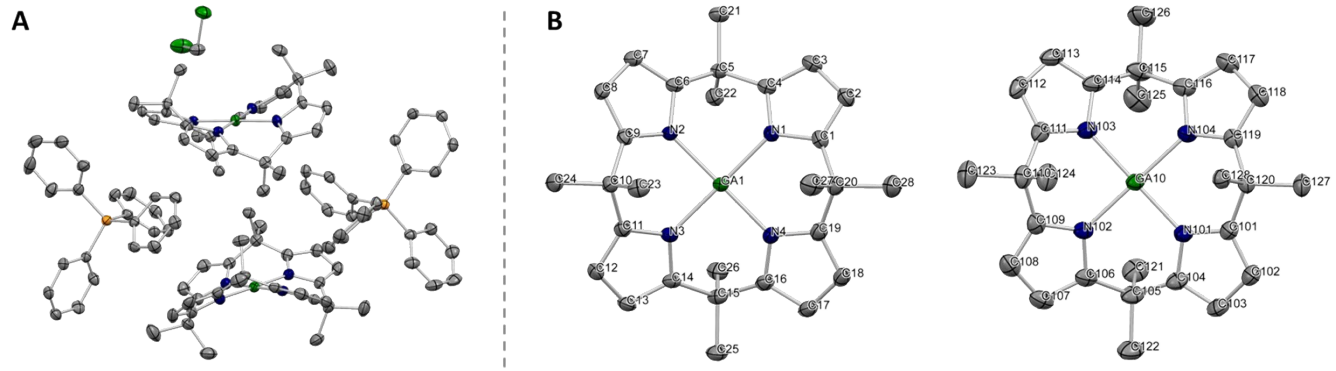


Figure S5. A) Asymmetric unit of the crystal lattice which was found for [PPh_4][^{Me}**1**] • 0.5 CH_2Cl_2 (monoclinic, $P2_1/c$), and **B)** molecular structures of the anions [^{Me}**1**]$^-$, with atom labels**.** All non-hydrogen thermal displacement ellipsoids are shown at a probability level of 50%.

Table S1. Crystal data and structure refinement for [PPh_4][^{Me}**1**] • 0.5 CH_2Cl_2 (mo_lmsnr006_ii_02a).

CCDC number	2175982
Empirical formula	$C_{52.50}H_{53}ClGaN_4P$
Formula weight	876.13
Temperature [K]	100.0
Crystal system	monoclinic
Space group (number)	$P2_1/c$ (14)
a [Å]	25.4110(18)
b [Å]	16.6359(13)
c [Å]	23.7139(18)
α [°]	90
β [°]	107.797(3)
γ [°]	90
Volume [Å^3]	9545.0(12)
Z	8
ρ_{calc} [gcm^{-3}]	1.219
μ [mm^{-1}]	0.704
F(000)	3672
Crystal size [mm^3]	0.144×0.113×0.086
Crystal colour	colourless
Crystal shape	block

Radiation	MoK_α (λ=0.71073 Å)
2Θ range [°]	4.11 to 54.00 (0.78 Å)
Index ranges	-32 ≤ h ≤ 32 -20 ≤ k ≤ 21 -30 ≤ l ≤ 30
Reflections collected	141733
Independent reflections	20825 R_{int} = 0.0912 R_{sigma} = 0.0553
Completeness to Θ = 25.242°	99.9 %
Data / Restraints / Parameters	20825/0/1088
Goodness-of-fit on F^2	1.027
Final R indexes [I≥2σ(I)]	R_1 = 0.0463 wR_2 = 0.1083
Final R indexes [all data]	R_1 = 0.0735 wR_2 = 0.1219
Largest peak/hole [eÅ^{-3}]	1.47/-0.81

Table S2. Solid state bond lengths found for [PPh_4][**^{Me}1**] • 0.5 CH_2Cl_2 (mo_lmsnr006_ii_02a).

Atoms		Length [Å]	Atoms		Length [Å]
Ga1	N3	1.938(2)	C119	C118	1.371(4)
Ga1	N2	1.946(2)	C302	C303	1.388(4)
Ga1	N1	1.935(2)	C302	C301	1.385(4)
Ga1	N4	1.929(2)	C22	C5	1.542(4)
Ga10	N101	1.928(2)	C307	C312	1.386(4)
Ga10	N103	1.938(2)	C307	C308	1.399(4)
Ga10	N104	1.951(2)	C7	C6	1.370(4)
Ga10	N102	1.935(2)	C3	C2	1.432(4)
P301	C313	1.790(3)	C6	C5	1.515(4)
P301	C319	1.798(3)	C21	C5	1.532(3)
P301	C307	1.807(3)	C14	C13	1.369(4)
P301	C301	1.791(3)	C14	C15	1.510(4)
P201	C213	1.791(3)	C206	C201	1.389(4)
P201	C219	1.797(3)	C206	C205	1.383(4)
P201	C201	1.792(3)	C101	C102	1.371(4)
P201	C207	1.796(3)	C111	C110	1.513(4)
Cl40	C401	1.764(3)	C111	C112	1.369(4)
Cl1	C401	1.748(3)	C17	C18	1.409(4)
N3	C11	1.384(3)	C17	C16	1.376(4)
N3	C14	1.388(3)	C216	C217	1.378(4)
N2	C9	1.388(3)	C18	C19	1.374(4)
N2	C6	1.384(3)	C201	C202	1.391(4)
N1	C4	1.392(3)	C303	C304	1.383(4)
N1	C1	1.384(3)	C205	C204	1.381(4)
N101	C101	1.380(4)	C321	C322	1.385(4)
N101	C104	1.382(4)	C301	C306	1.399(4)
N103	C111	1.389(4)	C19	C20	1.500(4)
N103	C114	1.388(4)	C204	C203	1.382(4)
N104	C119	1.387(4)	C323	C322	1.382(4)
N104	C116	1.382(4)	C323	C324	1.385(4)
N4	C19	1.396(3)	C109	C110	1.510(4)
N4	C16	1.377(3)	C109	C108	1.366(4)
N102	C109	1.386(4)	C110	C124	1.552(4)
N102	C106	1.390(4)	C110	C123	1.535(4)
C313	C314	1.400(4)	C15	C16	1.513(4)
C313	C318	1.399(4)	C15	C25	1.527(4)
C11	C10	1.500(4)	C315	C316	1.379(4)
C11	C12	1.377(4)	C106	C107	1.371(4)
C9	C10	1.511(4)	C106	C105	1.516(4)
C9	C8	1.377(4)	C104	C105	1.509(4)
C218	C213	1.398(4)	C104	C103	1.364(4)
C218	C217	1.394(4)	C118	C117	1.421(4)

C319	C320	1.399(4)	C114	C113	1.365(4)
C319	C324	1.390(4)	C114	C115	1.510(5)
C224	C219	1.389(4)	C116	C117	1.377(4)
C224	C223	1.386(4)	C116	C115	1.514(4)
C10	C23	1.551(4)	C312	C311	1.391(4)
C10	C24	1.529(4)	C304	C305	1.375(4)
C220	C219	1.392(4)	C202	C203	1.375(4)
C220	C221	1.385(4)	C102	C103	1.422(4)
C213	C214	1.394(4)	C112	C113	1.416(5)
C314	C315	1.380(4)	C208	C207	1.397(4)
C215	C214	1.384(4)	C208	C209	1.384(4)
C215	C216	1.388(4)	C317	C316	1.378(4)
C4	C3	1.368(4)	C20	C28	1.536(4)
C4	C5	1.510(4)	C20	C27	1.552(4)
C320	C321	1.388(4)	C107	C108	1.423(5)
C8	C7	1.419(4)	C207	C212	1.390(4)
C1	C2	1.372(4)	C105	C122	1.527(4)
C1	C20	1.511(4)	C105	C121	1.557(4)
C221	C222	1.381(4)	C308	C309	1.395(5)
C26	C15	1.545(4)	C212	C211	1.385(5)
C12	C13	1.414(4)	C306	C305	1.387(4)
C223	C222	1.382(4)	C309	C310	1.389(5)
C120	C119	1.519(4)	C209	C210	1.383(5)
C120	C101	1.510(4)	C210	C211	1.373(5)
C120	C128	1.548(4)	C311	C310	1.364(5)
C120	C127	1.535(4)	C115	C126	1.537(4)
C318	C317	1.386(4)	C115	C125	1.551(5)

Table S3. Solid state bond angles found for $[PPh_4][^{Me}\mathbf{1}] \cdot 0.5\ CH_2Cl_2$ (mo_lmsnr006_ii_02a).

Atoms			Angle	Atoms			Angle
N3	Ga1	N2	89.36(9)	N101	C101	C120	120.7(2)
N1	Ga1	N3	178.59(10)	C102	C101	N101	108.9(3)
N1	Ga1	N2	89.93(9)	C102	C101	C120	130.2(3)
N4	Ga1	N3	90.33(9)	N103	C111	C110	121.0(3)
N4	Ga1	N2	178.42(10)	C112	C111	N103	108.5(3)
N4	Ga1	N1	90.41(9)	C112	C111	C110	130.2(3)
N101	Ga10	N103	178.92(11)	C14	C13	C12	107.8(2)
N101	Ga10	N104	89.81(10)	C16	C17	C18	107.5(2)
N101	Ga10	N102	90.14(10)	C217	C216	C215	121.1(3)
N103	Ga10	N104	89.70(10)	C19	C18	C17	107.7(3)
N102	Ga10	N103	90.37(10)	C206	C201	P201	121.3(2)
N102	Ga10	N104	178.95(10)	C206	C201	C202	120.5(3)
C313	P301	C319	109.86(13)	C202	C201	P201	118.1(2)
C313	P301	C307	110.55(13)	C304	C303	C302	120.1(3)
C313	P301	C301	109.23(13)	C4	C5	C22	108.9(2)
C319	P301	C307	108.21(13)	C4	C5	C6	111.3(2)
C301	P301	C319	108.18(13)	C4	C5	C21	110.3(2)
C301	P301	C307	110.77(13)	C6	C5	C22	108.5(2)
C213	P201	C219	111.50(13)	C6	C5	C21	109.5(2)
C213	P201	C201	106.86(13)	C21	C5	C22	108.2(2)
C213	P201	C207	112.30(13)	C1	C2	C3	107.2(2)
C201	P201	C219	110.26(13)	C216	C217	C218	119.9(3)
C201	P201	C207	108.94(13)	C204	C205	C206	120.2(3)
C207	P201	C219	106.97(13)	C322	C321	C320	120.2(3)
C11	N3	Ga1	125.90(17)	C302	C301	P301	118.9(2)
C11	N3	C14	108.2(2)	C302	C301	C306	120.4(3)
C14	N3	Ga1	125.64(18)	C306	C301	P301	120.4(2)
C9	N2	Ga1	125.23(17)	N4	C19	C20	120.5(2)
C6	N2	Ga1	126.23(18)	C18	C19	N4	108.2(3)
C6	N2	C9	107.8(2)	C18	C19	C20	131.0(3)
C4	N1	Ga1	125.67(18)	C205	C204	C203	120.4(3)

C1	N1	Ga1	125.68(17)	C322	C323	C324	120.3(3)
C1	N1	C4	108.2(2)	N102	C109	C110	119.8(2)
C101	N101	Ga10	126.67(19)	C108	C109	N102	109.0(3)
C101	N101	C104	107.6(2)	C108	C109	C110	130.9(3)
C104	N101	Ga10	125.70(19)	C111	C110	C124	108.8(3)
C111	N103	Ga10	125.59(19)	C111	C110	C123	109.8(3)
C114	N103	Ga10	126.7(2)	C109	C110	C111	112.1(2)
C114	N103	C111	107.6(2)	C109	C110	C124	108.7(3)
C119	N104	Ga10	125.33(19)	C109	C110	C123	109.6(3)
C116	N104	Ga10	126.8(2)	C123	C110	C124	107.9(3)
C116	N104	C119	107.7(2)	C323	C322	C321	120.3(3)
C19	N4	Ga1	125.91(18)	C14	C15	C26	108.8(2)
C16	N4	Ga1	126.13(18)	C14	C15	C16	112.2(2)
C16	N4	C19	107.8(2)	C14	C15	C25	109.6(2)
C109	N102	Ga10	126.71(19)	C16	C15	C26	108.7(2)
C109	N102	C106	107.5(2)	C16	C15	C25	108.8(2)
C106	N102	Ga10	125.7(2)	C25	C15	C26	108.7(2)
C314	C313	P301	119.9(2)	C316	C315	C314	120.4(3)
C318	C313	P301	119.9(2)	N102	C106	C105	120.1(3)
C318	C313	C314	120.2(3)	C107	C106	N102	108.9(3)
N3	C11	C10	120.5(2)	C107	C106	C105	130.8(3)
C12	C11	N3	108.2(2)	N4	C16	C15	120.2(2)
C12	C11	C10	131.1(3)	C17	C16	N4	108.8(2)
N2	C9	C10	120.9(2)	C17	C16	C15	130.8(3)
C8	C9	N2	108.4(2)	C323	C324	C319	119.5(3)
C8	C9	C10	130.4(2)	N101	C104	C105	120.5(3)
C217	C218	C213	119.0(3)	C103	C104	N101	109.2(3)
C320	C319	P301	118.8(2)	C103	C104	C105	130.0(3)
C324	C319	P301	120.7(2)	C119	C118	C117	107.6(3)
C324	C319	C320	120.4(3)	N103	C114	C115	120.4(3)
C223	C224	C219	119.6(3)	C113	C114	N103	108.7(3)
C11	C10	C9	111.5(2)	C113	C114	C115	130.6(3)
C11	C10	C23	107.7(2)	N104	C116	C115	120.3(3)
C11	C10	C24	110.7(2)	C117	C116	N104	109.1(3)
C9	C10	C23	109.5(2)	C117	C116	C115	130.6(3)
C9	C10	C24	109.3(2)	C307	C312	C311	119.5(3)
C24	C10	C23	108.1(2)	C305	C304	C303	120.4(3)
C221	C220	C219	119.8(3)	C203	C202	C201	119.6(3)
C218	C213	P201	121.1(2)	C101	C102	C103	107.1(3)
C214	C213	P201	118.2(2)	C111	C112	C113	107.5(3)
C214	C213	C218	120.7(3)	C209	C208	C207	119.7(3)
C315	C314	C313	119.5(3)	C316	C317	C318	120.7(3)
C224	C219	P201	121.6(2)	C1	C20	C28	109.6(2)
C224	C219	C220	120.0(3)	C1	C20	C27	108.9(2)
C220	C219	P201	118.4(2)	C19	C20	C1	111.4(2)
C214	C215	C216	119.7(3)	C19	C20	C28	109.9(2)
N1	C4	C5	120.9(2)	C19	C20	C27	109.0(2)
C3	C4	N1	108.4(2)	C28	C20	C27	108.0(3)
C3	C4	C5	130.5(2)	C106	C107	C108	107.1(3)
C321	C320	C319	119.2(3)	C317	C316	C315	120.3(3)
C9	C8	C7	107.5(2)	C208	C207	P201	119.3(2)
N1	C1	C20	120.3(2)	C212	C207	P201	121.2(2)
C2	C1	N1	108.7(2)	C212	C207	C208	119.4(3)
C2	C1	C20	130.9(3)	C106	C105	C122	110.0(3)
C222	C221	C220	120.2(3)	C106	C105	C121	108.7(3)
C11	C12	C13	107.5(2)	C104	C105	C106	110.9(2)
C222	C223	C224	120.4(3)	C104	C105	C122	110.0(3)
C119	C120	C128	108.0(2)	C104	C105	C121	109.0(3)
C119	C120	C127	109.4(2)	C122	C105	C121	108.2(3)
C101	C120	C119	112.4(2)	C309	C308	C307	119.0(3)
C101	C120	C128	108.8(2)	C104	C103	C102	107.1(3)
C101	C120	C127	109.7(2)	C211	C212	C207	120.0(3)
C127	C120	C128	108.4(2)	C202	C203	C204	120.1(3)

C317	C318	C313	118.9(3)	C109	C108	C107	107.6(3)
N104	C119	C120	121.0(2)	C116	C117	C118	106.9(3)
C118	C119	N104	108.7(3)	C305	C306	C301	119.1(3)
C118	C119	C120	129.8(3)	C304	C305	C306	120.4(3)
C301	C302	C303	119.5(3)	Cl1	C401	Cl40	110.81(17)
C312	C307	P301	121.8(2)	C310	C309	C308	119.9(3)
C312	C307	C308	120.4(3)	C210	C209	C208	120.4(3)
C308	C307	P301	117.7(2)	C211	C210	C209	120.0(3)
C6	C7	C8	107.3(2)	C114	C113	C112	107.6(3)
C4	C3	C2	107.5(2)	C310	C311	C312	120.6(3)
C215	C214	C213	119.5(3)	C311	C310	C309	120.6(3)
C221	C222	C223	120.1(3)	C210	C211	C212	120.4(3)
N2	C6	C5	119.6(2)	C114	C115	C116	110.7(3)
C7	C6	N2	108.9(2)	C114	C115	C126	110.2(3)
C7	C6	C5	131.3(2)	C114	C115	C125	109.1(3)
N3	C14	C15	120.5(2)	C116	C115	C126	109.3(3)
C13	C14	N3	108.3(2)	C116	C115	C125	109.0(3)
C13	C14	C15	131.0(2)	C126	C115	C125	108.6(3)
C205	C206	C201	119.1(3)				

[PPh_4][^{Et}**1**]

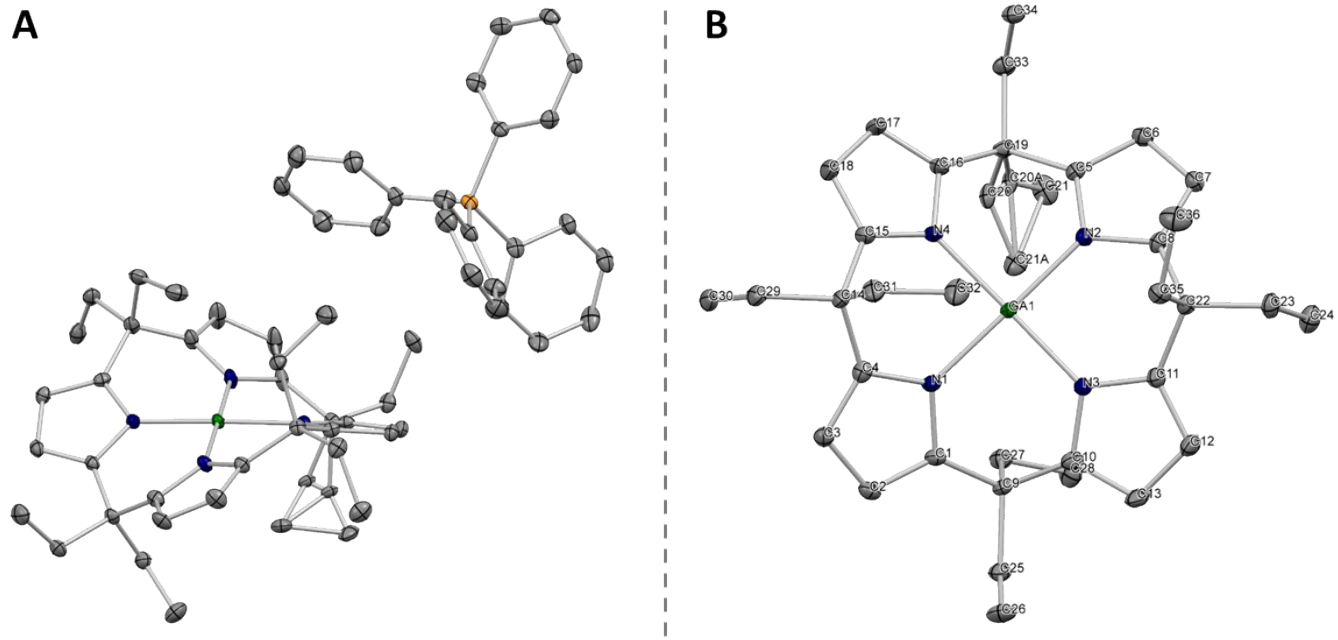


Figure S6. A) Asymmetric unit of the crystal lattice which was found for [PPh_4][^{Et}**1**] (monoclinic, $P2_1/n$), and **B)** molecular structures of the anion [^{Et}**1**]$^-$, with atom labels**.** All non-hydrogen thermal displacement ellipsoids are shown at a probability level of 50%.

Table S4. Crystal data and structure refinement for [PPh_4][^{Et}**1**] (mo_lmsee025_0m_a).

CCDC number	2175981
Empirical formula	$C_{60}H_{68}GaN_4P$
Formula weight	945.87
Temperature [K]	100.0
Crystal system	monoclinic
Space group (number)	$P2_1/n$ (14)
a [Å]	11.5827(6)
b [Å]	15.4151(5)
c [Å]	27.0610(12)
α [°]	90
β [°]	90.708(2)
γ [°]	90
Volume [Å^3]	4831.3(4)
Z	4
ρ_{calc} [gcm^{-3}]	1.300
μ [mm^{-1}]	0.648

F(000)	2008
Crystal size [mm^3]	0.231×0.182×0.113
Crystal colour	colourless
Crystal shape	block
Radiation	MoK_α (λ=0.71073 Å)
2Θ range [°]	4.40 to 57.61 (0.74 Å)
Index ranges	-15 ≤ h ≤ 15 -20 ≤ k ≤ 19 -36 ≤ l ≤ 36
Reflections collected	38808
Independent reflections	12354 R_{int} = 0.0785 R_{sigma} = 0.0785
Completeness to Θ = 25.242°	98.7 %
Data / Restraints / Parameters	12354/0/617
Goodness-of-fit on F^2	1.042
Final R indexes [I≥2σ(I)]	R_1 = 0.0547 wR_2 = 0.1224
Final R indexes [all data]	R_1 = 0.0791 wR_2 = 0.1368
Largest peak/hole [eÅ^{-3}]	0.63/-0.56

Table S5. Solid state bond lengths found for [PPh_4][^{Et}**1**] (mo_lmsee025_0m_a).

Atoms	Length [Å]	Atoms	Length [Å]
Ga1_1–N1_1	1.954(2)	C20_1–C21_1	1.519(6)
Ga1_1–N2_1	1.944(2)	C21A_1–C20A_1	1.497(13)
Ga1_1–N3_1	1.943(2)	C22_1–C23_1	1.543(3)
Ga1_1–N4_1	1.957(2)	C22_1–C35_1	1.567(3)
N1_1–C1_1	1.394(3)	C23_1–C24_1	1.534(4)
N1_1–C4_1	1.397(3)	C25_1–C26_1	1.526(3)
C1_1–C2_1	1.378(3)	C27_1–C28_1	1.532(3)
C1_1–C9_1	1.513(3)	C29_1–C30_1	1.523(4)
N2_1–C5_1	1.392(3)	C31_1–C32_1	1.526(4)
N2_1–C8_1	1.390(3)	C33_1–C34_1	1.526(4)
C2_1–C3_1	1.422(4)	C35_1–C36_1	1.525(4)
N3_1–C10_1	1.396(3)	P1_2–C1_2	1.801(3)
N3_1–C11_1	1.395(3)	P1_2–C7_2	1.789(3)
C3_1–C4_1	1.374(3)	P1_2–C13_2	1.796(3)
N4_1–C15_1	1.399(3)	P1_2–C19_2	1.802(3)
N4_1–C16_1	1.389(3)	C1_2–C2_2	1.397(4)
C4_1–C14_1	1.510(3)	C1_2–C6_2	1.399(4)
C5_1–C6_1	1.376(3)	C2_2–C3_2	1.392(4)
C5_1–C19_1	1.513(3)	C3_2–C4_2	1.378(4)
C6_1–C7_1	1.425(3)	C4_2–C5_2	1.386(4)
C7_1–C8_1	1.371(3)	C5_2–C6_2	1.389(4)
C8_1–C22_1	1.520(3)	C7_2–C8_2	1.393(4)
C9_1–C10_1	1.512(3)	C7_2–C12_2	1.398(3)
C9_1–C25_1	1.545(3)	C8_2–C9_2	1.392(4)
C9_1–C27_1	1.561(3)	C9_2–C10_2	1.392(4)
C10_1–C13_1	1.378(3)	C10_2–C11_2	1.384(4)
C11_1–C12_1	1.377(3)	C11_2–C12_2	1.388(4)
C11_1–C22_1	1.513(3)	C13_2–C14_2	1.399(4)
C12_1–C13_1	1.421(4)	C13_2–C18_2	1.394(4)
C14_1–C15_1	1.503(3)	C14_2–C15_2	1.390(4)
C14_1–C29_1	1.554(3)	C15_2–C16_2	1.384(4)
C14_1–C31_1	1.559(4)	C16_2–C17_2	1.388(4)
C15_1–C18_1	1.377(4)	C17_2–C18_2	1.388(4)
C16_1–C17_1	1.377(4)	C19_2–C20_2	1.398(4)
C16_1–C19_1	1.511(4)	C19_2–C24_2	1.397(4)
C17_1–C18_1	1.423(4)	C20_2–C21_2	1.386(4)
C19_1–C20_1	1.547(5)	C21_2–C22_2	1.383(4)
C19_1–C20A_1	1.651(10)	C22_2–C23_2	1.387(4)

C19_1–C33_1	1.544(3)	C23_2–C24_2	1.388(4)

Table S6. Solid state bond angles found for $[PPh_4][^{Et}1]$ (mo_lmsee025_0m_a).

Atoms	Angle [°]	Atoms	Angle [°]
N1_1–Ga1_1–N4_1	89.10(8)	C5_1–C19_1–C20_1	111.5(2)
N2_1–Ga1_1–N1_1	177.82(8)	C5_1–C19_1–C20A_1	104.2(4)
N2_1–Ga1_1–N4_1	90.20(8)	C5_1–C19_1–C33_1	110.2(2)
N3_1–Ga1_1–N1_1	90.41(8)	C16_1–C19_1–C5_1	111.6(2)
N3_1–Ga1_1–N2_1	90.28(8)	C16_1–C19_1–C20_1	101.8(2)
N3_1–Ga1_1–N4_1	179.48(9)	C16_1–C19_1–C20A_1	121.3(4)
C1_1–N1_1–Ga1_1	126.29(16)	C16_1–C19_1–C33_1	109.6(2)
C1_1–N1_1–C4_1	107.31(19)	C33_1–C19_1–C20_1	111.8(2)
C4_1–N1_1–Ga1_1	126.40(16)	C33_1–C19_1–C20A_1	98.9(4)
N1_1–C1_1–C9_1	120.7(2)	C21_1–C20_1–C19_1	114.1(3)
C2_1–C1_1–N1_1	108.9(2)	C21A_1–C20A_1–C19_1	113.7(7)
C2_1–C1_1–C9_1	130.2(2)	C8_1–C22_1–C23_1	110.27(19)
C5_1–N2_1–Ga1_1	125.79(16)	C8_1–C22_1–C35_1	109.6(2)
C8_1–N2_1–Ga1_1	126.66(16)	C11_1–C22_1–C8_1	110.89(19)
C8_1–N2_1–C5_1	107.41(19)	C11_1–C22_1–C23_1	110.5(2)
C1_1–C2_1–C3_1	107.3(2)	C11_1–C22_1–C35_1	107.58(19)
C10_1–N3_1–Ga1_1	126.04(16)	C23_1–C22_1–C35_1	107.88(19)
C11_1–N3_1–Ga1_1	126.78(17)	C24_1–C23_1–C22_1	117.8(2)
C11_1–N3_1–C10_1	107.2(2)	C26_1–C25_1–C9_1	118.1(2)
C4_1–C3_1–C2_1	107.7(2)	C28_1–C27_1–C9_1	116.1(2)
C15_1–N4_1–Ga1_1	126.09(17)	C30_1–C29_1–C14_1	117.3(2)
C16_1–N4_1–Ga1_1	126.54(17)	C32_1–C31_1–C14_1	117.2(2)
C16_1–N4_1–C15_1	107.3(2)	C34_1–C33_1–C19_1	116.2(2)
N1_1–C4_1–C14_1	121.8(2)	C36_1–C35_1–C22_1	116.5(2)
C3_1–C4_1–N1_1	108.8(2)	C1_2–P1_2–C19_2	110.69(12)
C3_1–C4_1–C14_1	129.2(2)	C7_2–P1_2–C1_2	108.31(12)
N2_1–C5_1–C19_1	122.7(2)	C7_2–P1_2–C13_2	107.14(12)
C6_1–C5_1–N2_1	108.7(2)	C7_2–P1_2–C19_2	110.08(12)
C6_1–C5_1–C19_1	128.2(2)	C13_2–P1_2–C1_2	111.43(12)
C5_1–C6_1–C7_1	107.5(2)	C13_2–P1_2–C19_2	109.13(12)
C8_1–C7_1–C6_1	107.1(2)	C2_2–C1_2–P1_2	120.45(19)
N2_1–C8_1–C22_1	121.7(2)	C2_2–C1_2–C6_2	119.9(2)
C7_1–C8_1–N2_1	109.3(2)	C6_2–C1_2–P1_2	119.68(19)
C7_1–C8_1–C22_1	128.8(2)	C3_2–C2_2–C1_2	119.7(2)
C1_1–C9_1–C25_1	110.31(19)	C4_2–C3_2–C2_2	120.3(3)
C1_1–C9_1–C27_1	107.78(19)	C3_2–C4_2–C5_2	120.3(2)
C10_1–C9_1–C1_1	111.2(2)	C4_2–C5_2–C6_2	120.4(3)
C10_1–C9_1–C25_1	110.6(2)	C5_2–C6_2–C1_2	119.5(2)
C10_1–C9_1–C27_1	108.85(19)	C8_2–C7_2–P1_2	120.92(19)
C25_1–C9_1–C27_1	108.0(2)	C8_2–C7_2–C12_2	119.8(2)
N3_1–C10_1–C9_1	120.8(2)	C12_2–C7_2–P1_2	119.3(2)
C13_1–C10_1–N3_1	109.0(2)	C9_2–C8_2–C7_2	119.8(2)
C13_1–C10_1–C9_1	129.2(2)	C8_2–C9_2–C10_2	120.0(2)
N3_1–C11_1–C22_1	121.8(2)	C11_2–C10_2–C9_2	120.3(2)
C12_1–C11_1–N3_1	108.9(2)	C10_2–C11_2–C12_2	119.9(2)
C12_1–C11_1–C22_1	128.9(2)	C11_2–C12_2–C7_2	120.2(2)
C11_1–C12_1–C13_1	107.5(2)	C14_2–C13_2–P1_2	119.2(2)
C10_1–C13_1–C12_1	107.3(2)	C18_2–C13_2–P1_2	121.7(2)
C4_1–C14_1–C29_1	109.9(2)	C18_2–C13_2–C14_2	119.0(2)
C4_1–C14_1–C31_1	110.6(2)	C15_2–C14_2–C13_2	120.4(3)
C15_1–C14_1–C4_1	112.0(2)	C16_2–C15_2–C14_2	119.9(3)
C15_1–C14_1–C29_1	109.3(2)	C15_2–C16_2–C17_2	120.4(3)
C15_1–C14_1–C31_1	109.7(2)	C18_2–C17_2–C16_2	119.9(3)
C29_1–C14_1–C31_1	105.1(2)	C17_2–C18_2–C13_2	120.5(3)
N4_1–C15_1–C14_1	122.2(2)	C20_2–C19_2–P1_2	120.5(2)
C18_1–C15_1–N4_1	108.8(2)	C24_2–C19_2–P1_2	119.1(2)
C18_1–C15_1–C14_1	128.9(2)	C24_2–C19_2–C20_2	120.2(2)

N4_1–C16_1–C19_1	121.4(2)	C21_2–C20_2–C19_2	119.4(2)
C17_1–C16_1–N4_1	109.2(2)	C22_2–C21_2–C20_2	120.6(3)
C17_1–C16_1–C19_1	129.1(2)	C21_2–C22_2–C23_2	120.0(3)
C16_1–C17_1–C18_1	107.3(2)	C22_2–C23_2–C24_2	120.5(3)
C15_1–C18_1–C17_1	107.4(2)	C23_2–C24_2–C19_2	119.4(2)

[PPh_4][^{Me}**1**-thf]

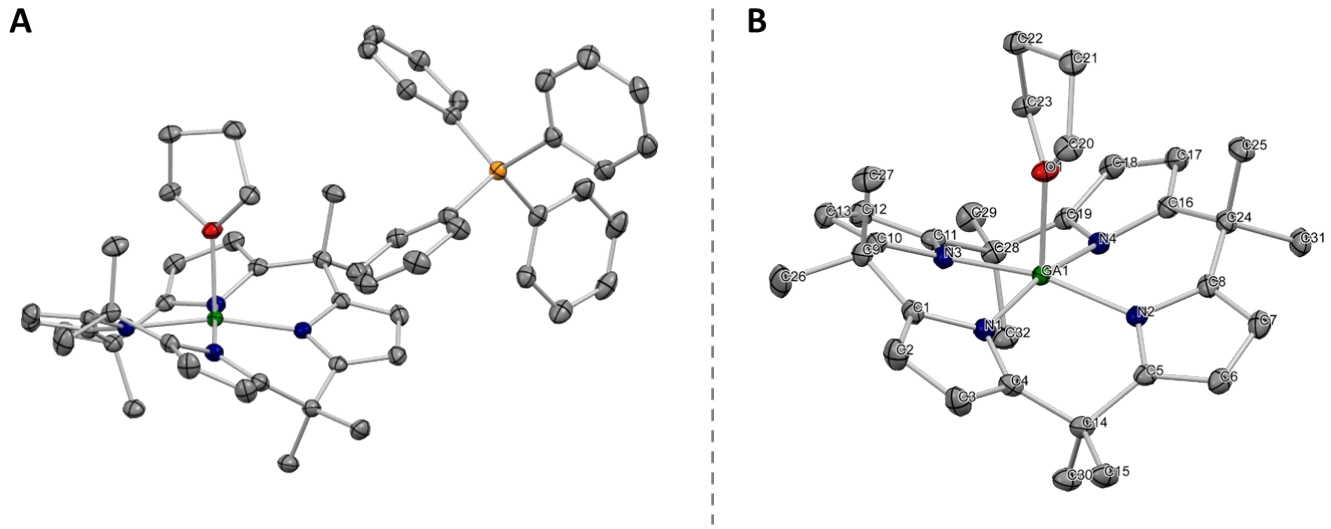


Figure S7. A) Asymmetric unit of the crystal lattice which was found for [PPh_4][^{Me}**1**-thf] (monoclinic, $P2_1/c$), and **B)** molecular structures of the anion [^{Me}**1**-thf]$^-$, with atom labels**.** All non-hydrogen thermal displacement ellipsoids are shown at a probability level of 50%.

Table S7. Crystal data and structure refinement for [PPh_4][^{Me}**1**-thf] (mo_LMSEE019_0m).

CCDC number	2175983
Empirical formula	$C_{56}H_{60}GaN_4OP$
Formula weight	905.77
Temperature [K]	100(2)
Crystal system	monoclinic
Space group (number)	$P2_1/c$ (14)
a [Å]	13.0677(6)
b [Å]	21.4060(11)
c [Å]	17.1423(7)
α [°]	90
β [°]	108.630(2)
γ [°]	90
Volume [Å^3]	4543.9(4)
Z	4
ρ_{calc} [gcm^{-3}]	1.324
μ [mm^{-1}]	0.687
F(000)	1912
Crystal size [mm^3]	0.694×0.453×0.342
Crystal colour	yellow
Crystal shape	block
Radiation	MoK_α (λ=0.71073 Å)
2Θ range [°]	3.80 to 55.15 (0.77 Å)
Index ranges	-16 ≤ h ≤ 16 -27 ≤ k ≤ 27 -22 ≤ l ≤ 22
Reflections collected	302121
Independent reflections	10488 R_{int} = 0.0585 R_{sigma} = 0.0183
Completeness to Θ = 25.242°	99.8 %
Data / Restraints /	10488/0/576

Parameters	
Goodness-of-fit on F^2	1.061
Final R indexes	R_1 = 0.0254
[$I \geq 2\sigma(I)$]	wR_2 = 0.0689
Final R indexes	R_1 = 0.0272
[all data]	wR_2 = 0.0700
Largest peak/hole [eÅ^{-3}]	0.43/-0.37

Table S8. Solid state bond lengths found for [PPh_4][^{Me}**1**-thf] (mo_LMSEE019_0m).

Atoms	Length [Å]	Atoms	Length [Å]
Ga1_1–N2_1	1.9841(10)	C18_1–C19_1	1.3757(16)
Ga1_1–N1_1	1.9853(10)	C19_1–C28_1	1.5064(16)
Ga1_1–N3_1	1.9992(10)	C20_1–C21_1	1.5273(17)
Ga1_1–N4_1	2.0041(9)	C21_1–C22_1	1.5239(18)
Ga1_1–O1_1	2.0230(8)	C22_1–C23_1	1.5173(16)
O1_1–C20_1	1.4611(14)	C24_1–C25_1	1.5485(16)
O1_1–C23_1	1.4673(14)	C24_1–C31_1	1.5513(15)
N1_1–C4_1	1.3851(15)	C28_1–C29_1	1.5371(16)
N1_1–C1_1	1.3916(14)	C28_1–C32_1	1.5473(16)
C1_1–C2_1	1.3763(17)	P1_2–C7_2	1.7895(12)
C1_1–C9_1	1.5086(16)	P1_2–C13_2	1.7933(12)
N2_1–C5_1	1.3857(15)	P1_2–C1_2	1.7933(12)
N2_1–C8_1	1.3926(14)	P1_2–C19_2	1.7986(12)
C2_1–C3_1	1.4139(18)	C1_2–C6_2	1.3991(16)
N3_1–C11_1	1.3851(14)	C1_2–C2_2	1.4053(16)
N3_1–C10_1	1.3923(14)	C2_2–C3_2	1.3848(17)
C3_1–C4_1	1.3755(17)	C3_2–C4_2	1.3928(17)
N4_1–C19_1	1.3855(15)	C4_2–C5_2	1.3905(17)
N4_1–C16_1	1.3935(15)	C5_2–C6_2	1.3890(17)
C4_1–C14_1	1.5051(16)	C7_2–C12_2	1.3917(17)
C5_1–C6_1	1.3762(16)	C7_2–C8_2	1.4010(17)
C5_1–C14_1	1.5083(16)	C8_2–C9_2	1.3868(17)
C6_1–C7_1	1.4121(18)	C9_2–C10_2	1.3868(18)
C7_1–C8_1	1.3800(17)	C10_2–C11_2	1.384(2)
C8_1–C24_1	1.5159(16)	C11_2–C12_2	1.3938(18)
C9_1–C10_1	1.5178(16)	C13_2–C14_2	1.3908(18)
C9_1–C26_1	1.5441(16)	C13_2–C18_2	1.3991(18)
C9_1–C27_1	1.5468(17)	C14_2–C15_2	1.3948(17)
C10_1–C13_1	1.3773(16)	C15_2–C16_2	1.385(2)
C11_1–C12_1	1.3739(16)	C16_2–C17_2	1.382(2)
C11_1–C28_1	1.5082(16)	C17_2–C18_2	1.3861(19)
C12_1–C13_1	1.4185(17)	C19_2–C24_2	1.3882(18)
C14_1–C15_1	1.5344(16)	C19_2–C20_2	1.3999(17)
C14_1–C30_1	1.5496(16)	C20_2–C21_2	1.3887(19)
C16_1–C17_1	1.3805(16)	C21_2–C22_2	1.380(2)
C16_1–C24_1	1.5160(16)	C22_2–C23_2	1.383(2)
C17_1–C18_1	1.4203(18)	C23_2–C24_2	1.3928(19)

Table S9. Solid state bond angles found for [PPh_4][^{Et}**1**] (mo_LMSEE019_0m).

Atoms	Angle [°]	Atoms	Angle [°]
N2_1–Ga1_1–N1_1	90.87(4)	N4_1–C16_1–C24_1	125.41(10)
N2_1–Ga1_1–N3_1	166.32(4)	C16_1–C17_1–C18_1	107.24(10)
N1_1–Ga1_1–N3_1	87.48(4)	C19_1–C18_1–C17_1	106.83(10)
N2_1–Ga1_1–N4_1	87.00(4)	C18_1–C19_1–N4_1	110.03(10)
N1_1–Ga1_1–N4_1	166.66(4)	C18_1–C19_1–C28_1	129.57(11)
N3_1–Ga1_1–N4_1	91.48(4)	N4_1–C19_1–C28_1	120.23(10)
N2_1–Ga1_1–O1_1	99.73(4)	O1_1–C20_1–C21_1	105.04(10)
N1_1–Ga1_1–O1_1	100.57(4)	C22_1–C21_1–C20_1	103.24(10)
N3_1–Ga1_1–O1_1	93.92(4)	C23_1–C22_1–C21_1	103.46(10)
N4_1–Ga1_1–O1_1	92.76(4)	O1_1–C23_1–C22_1	104.04(9)
C20_1–O1_1–C23_1	110.86(9)	C8_1–C24_1–C16_1	114.64(9)

C20_1–O1_1–Ga1_1	129.65(7)	C8_1–C24_1–C25_1	110.41(10)
C23_1–O1_1–Ga1_1	119.41(7)	C16_1–C24_1–C25_1	110.02(10)
C4_1–N1_1–C1_1	106.57(9)	C8_1–C24_1–C31_1	107.05(10)
C4_1–N1_1–Ga1_1	127.06(8)	C16_1–C24_1–C31_1	107.58(9)
C1_1–N1_1–Ga1_1	125.84(8)	C25_1–C24_1–C31_1	106.76(9)
C2_1–C1_1–N1_1	109.30(11)	C19_1–C28_1–C11_1	110.08(9)
C2_1–C1_1–C9_1	125.75(11)	C19_1–C28_1–C29_1	109.96(10)
N1_1–C1_1–C9_1	124.94(10)	C11_1–C28_1–C29_1	109.87(10)
C5_1–N2_1–C8_1	106.73(9)	C19_1–C28_1–C32_1	109.12(10)
C5_1–N2_1–Ga1_1	127.04(8)	C11_1–C28_1–C32_1	109.80(10)
C8_1–N2_1–Ga1_1	125.92(8)	C29_1–C28_1–C32_1	107.97(10)
C1_1–C2_1–C3_1	107.35(11)	C7_2–P1_2–C13_2	110.07(6)
C11_1–N3_1–C10_1	106.75(9)	C7_2–P1_2–C1_2	106.00(5)
C11_1–N3_1–Ga1_1	127.16(8)	C13_2–P1_2–C1_2	112.09(6)
C10_1–N3_1–Ga1_1	124.52(8)	C7_2–P1_2–C19_2	110.26(6)
C4_1–C3_1–C2_1	106.97(11)	C13_2–P1_2–C19_2	106.39(6)
C16_1–N4_1–Ga1_1	121.67(8)	C1_2–P1_2–C19_2	112.08(6)
C3_1–C4_1–N1_1	109.79(11)	C6_2–C1_2–C2_2	120.61(11)
C3_1–C4_1–C14_1	128.17(11)	C6_2–C1_2–P1_2	122.36(9)
N1_1–C4_1–C14_1	121.35(10)	C2_2–C1_2–P1_2	116.95(9)
C6_1–C5_1–N2_1	109.73(10)	C3_2–C2_2–C1_2	119.46(11)
C6_1–C5_1–C14_1	128.06(11)	C2_2–C3_2–C4_2	119.84(11)
N2_1–C5_1–C14_1	121.85(10)	C5_2–C4_2–C3_2	120.78(11)
C5_1–C6_1–C7_1	107.02(11)	C6_2–C5_2–C4_2	120.06(11)
C8_1–C7_1–C6_1	107.48(11)	C5_2–C6_2–C1_2	119.25(11)
C7_1–C8_1–N2_1	109.03(10)	C12_2–C7_2–C8_2	120.37(11)
C7_1–C8_1–C24_1	125.27(11)	C12_2–C7_2–P1_2	122.17(10)
N2_1–C8_1–C24_1	125.69(10)	C8_2–C7_2–P1_2	117.44(9)
C1_1–C9_1–C10_1	113.55(9)	C9_2–C8_2–C7_2	119.81(11)
C1_1–C9_1–C26_1	107.90(10)	C10_2–C9_2–C8_2	119.67(12)
C10_1–C9_1–C26_1	107.81(10)	C11_2–C10_2–C9_2	120.73(12)
C1_1–C9_1–C27_1	109.75(10)	C10_2–C11_2–C12_2	120.20(12)
C10_1–C9_1–C27_1	110.90(10)	C7_2–C12_2–C11_2	119.23(12)
C26_1–C9_1–C27_1	106.63(10)	C14_2–C13_2–C18_2	120.27(12)
C13_1–C10_1–N3_1	109.06(10)	C14_2–C13_2–P1_2	120.60(9)
C13_1–C10_1–C9_1	125.62(10)	C18_2–C13_2–P1_2	119.04(10)
N3_1–C10_1–C9_1	125.31(10)	C13_2–C14_2–C15_2	119.55(12)
C12_1–C11_1–N3_1	109.91(10)	C16_2–C15_2–C14_2	120.02(13)
C12_1–C11_1–C28_1	128.85(11)	C17_2–C16_2–C15_2	120.30(12)
N3_1–C11_1–C28_1	121.18(10)	C16_2–C17_2–C18_2	120.49(13)
C11_1–C12_1–C13_1	106.77(10)	C17_2–C18_2–C13_2	119.36(13)
C10_1–C13_1–C12_1	107.50(10)	C24_2–C19_2–C20_2	120.14(12)
C4_1–C14_1–C5_1	112.36(9)	C24_2–C19_2–P1_2	121.38(10)
C4_1–C14_1–C15_1	109.74(10)	C20_2–C19_2–P1_2	118.46(10)
C5_1–C14_1–C15_1	109.60(10)	C21_2–C20_2–C19_2	119.80(12)
C4_1–C14_1–C30_1	107.97(10)	C22_2–C21_2–C20_2	119.92(12)
C5_1–C14_1–C30_1	109.03(10)	C21_2–C22_2–C23_2	120.40(12)
C15_1–C14_1–C30_1	108.03(9)	C22_2–C23_2–C24_2	120.45(13)
C17_1–C16_1–N4_1	109.29(10)	C19_2–C24_2–C23_2	119.28(12)
C17_1–C16_1–C24_1	125.16(11)		

S8. Computational details and results

All quantum chemical calculations were carried out with Orca 5.0.1[5-6] making use of the computational resources of the bwForClusters JUSTUS2 at Ulm University within the Baden-Württemberg High Performance Computing program (bwHPC). Ball and stick representations and isodensity surfaces were rendered with Chemcraft 1.8[27]. xyz Coordinates and computed energies are given in Chapter S11.

General remarks

Conformational spaces, especially of structures of the ethyl version of the ligand, were initially explored with the conformer-rotamer ensemble sampling tool (CREST)[28] for the xtb program package[29] using the following command line input. The lowest-energy conformer was then reoptimized as described below.

```
crest [file_name].xyz --alpb CH2Cl2 --chrg [charge] --noreftopo > [file_name].out
```

Structure optimizations on the Kohn-Sham DFT level were done with the r^{2}SCAN-3c composite method.[30] The RIJCOSX Fock-matrix formation algorithm was used along with the respective automatically generated auxiliary basis sets (AutoAux)[31]. The RIJCOSX scheme combines the chain of spheres exchange approximation (COSX)[32] for the computation of the exchange matrix with the split-RI-J algorithm[33] for the calculation of the Coulomb matrix. All equilibrium structures were confirmed to possess only positive Hessian matrix eigenvalues by analytic frequency calculations. The following Orca keyword line was used.

```
! r2SCAN-3c RIJCOSX AutoAux VeryTightSCF Opt Freq
```

Transition structures were optimized toward a single negative Hessian matrix eigenvalue using the `OptTS` keyword. It was ensured that the correct first-order saddle point on the potential energy surface was located by animation of the imaginary frequency in Chemcraft and by following the intrinsic reaction coordinate (IRC) by invoking the `IRC` keyword. `TolRMSG` was set to `3e-5` a.u. and `TolMaxG` to `1e-4` a.u..

Structural constraints (for the structural optimization of [^{Me}**1**]$^-$ with a tetrahedral configuration around gallium) were introduced with the `Constraints` option inside the `%geom` block.

Final single point energies were calculated with the RI-DSD-PBEP86/2013 spin-component-scaled double hybrid functional[34-35], including the D3(BJ) correction[36-37]. The def2-QZVPP set of basis functions was used.[38] Again, the `RIJCOSX` combined with the `AutoAux` keywords were included. The `VeryTightSCF` convergence settings were kept, and the integration grid was changed to `DefGrid3`. The keyword line was:

```
! RI-DSD-PBEP86/2013 D3BJ def2-QZVPP RIJCOSX AutoAux DefGrid3 VeryTightSCF
```

Enthalpies and Gibbs free energies at 298.15 K and 1 atm were calculated with the electronic energies from the double hybrid functional calculations combined with the corrections to enthalpies and Gibbs free energies[39], respectively, from the frequency calculations.

Finally, solvent influences were included implicitly at T = 298.15 K with the conductor like screening model for real solvents (COSMO-RS)[40-42] as it is implemented[43] in the Amsterdam Modeling suite (ADF 2019.304)[44]. The ADF-preset parameters were used, except for the maximum number of iterations, which were set to zero. COSMO-RS corrections for enthalpies were achieved by calculating ΔG-corrections at five different temperatures (278.15, 288.15, 298.15, 308.15, 318.15 K) and with help of $\Delta G = \Delta H - T\Delta S$.

Natural population analysis were done on the PBE0/def2-TZVPP level of theory interfacing Orca 5.0.1 with the NBO6 program.[45] To get the molecular orbitals within a natural atomic orbital basis, the `NAOMO` keyword was included inside the `%nbo` block.

```
! PBE0 def2-TZVPP NoRI VeryTightSCF DefGrid3 NBO
%nbo
  NBOKEYLIST = "$NBO NAOMO $END"
end
```

Assessment of structural strain

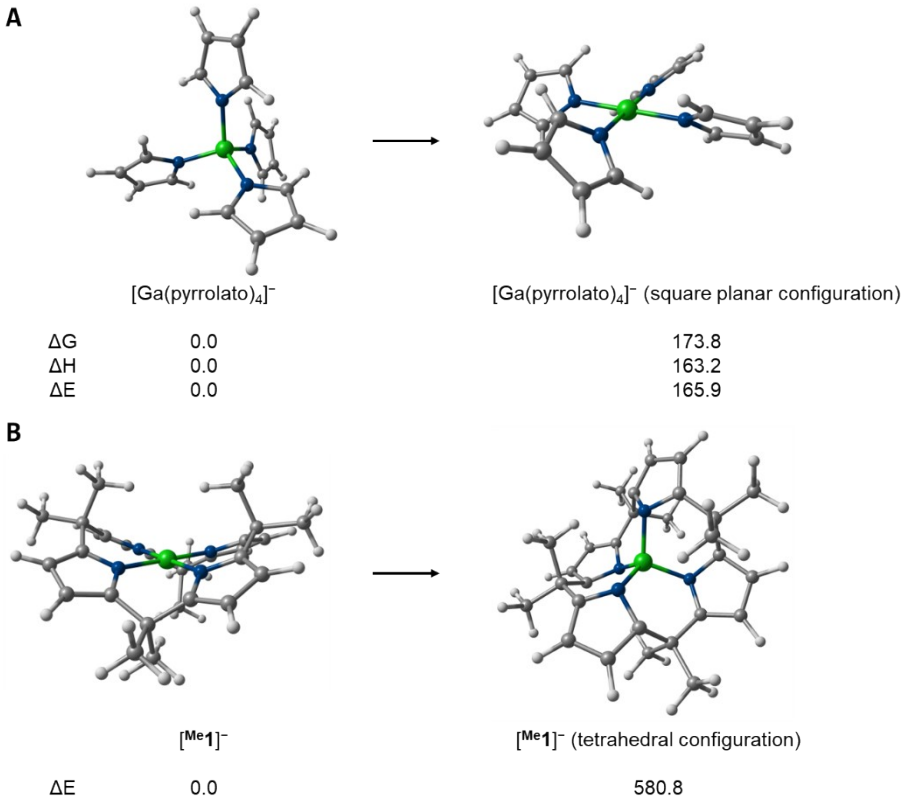


Figure S8. Energetic characteristics for **A**) the deformation of tetrapyrrolato gallate ([Ga(pyrrolato)$_4$]$^-$ toward square planarity, and of **B**) [^{Me}**1**]$^-$ toward a tetrahedral arrangement around the gallium center. The calculations were done on the RI-DSD-PBEP86/2013-D3(BJ)/def2-QZVPP//r^{2}SCAN-3c level of theory. All numbers are given in kJ mol^{-1}.

Fluoride ion affinities

Fluoride ion affinities (FIA, $\Delta_r H$ values) were calculated as described in the literature using the fluorotrimethylsilane anchoring system.[46] The anchoring enthalpy (952.5 kJ mol^{-1}, reaction enthalpy for the dissociation of fluorotrimethylsilane into the trimethylsilyl cation and the fluoride anion) was taken from the cited paper. To account for the solvation influences (CH_2Cl_2), the COSMO-RS scheme was used as described above for the fluoride adduct formation reaction of the molecule under investigation. The COSMO-RS correction to the enthalpy of the fluoride ion was calculated explicitly to −341.75 kJ mol^{-1}.

Table S10. Calculated gas and solution (CH_2Cl_2) phase fluoride ion affinities (FIA). The calculations were done on the RI-DSD-PBEP86/2013-D3(BJ)/def2-QZVPP//r^{2}SCAN-3c, COSMO-RS(CH_2Cl_2) level of theory. All numbers are given in kJ mol^{-1}.

	FIA$_{gasphase}$	**FIA$_{solution}$**
[^{Me}**1**]$^-$	80.1	149.0
[^{Et}**1**]$^-$	90.8	131.8
[^{Me}**1(Al)**]$^-$	129.5	196.4
[H-^{Me}**1***]	383.9	190.7
[Ga(pyrrolato)$_4$]$^-$	−41.4	57.7
Ph_3SiF	263.2	85.1

Reactivity with CO_2

The addition reaction of CO_2 to [^{Me}**1**]$^-$ was studied by quantum chemical calculations. In the case of the analogous aluminum compound ([^{Me}**1(Al)**]$^-$), a transition state accounting for the entrance of CO_2 into the coordination sphere of Al and the subsequent intermediate in which CO_2 is coordinating to Al was located.[47] Such structures are not accessible for [^{Me}**1**]$^-$. Structural optimization of the coordination intermediate resulted in constant dissociation of the two reactants. This was also found with various other DFT methods than the one described above (r^{2}SCAN-3c). The inclusion of the SMD model for dichloromethane did not change this outcome either.

The transition states for the C-C bond formation/cleavage and the gallium-ligand cooperative addition products were readily located for [^{Me}**1**]$^-$ and [^{Et}**1**]$^-$. The conformational space of [^{Et}**1***-CO_2]$^-$ was analyzed by CREST (see above for details) and the lowest-energy

conformer was reoptimized with the r^{2}SCAN-3c method. The ethyl group conformations as found for [^{Et}**1***-CO_2]$^-$ were kept for the transition structure optimization.

Following the IRC in the C-C cleavage direction with the [^{Me}**1**]$^-$ system also suggested the above-described non-existence of the coordination intermediate.

Table S11. Activation energies / enthalpies / Gibbs free energies in the gas phase and in solution (CH_2Cl_2) for the C-C bond formation/cleavage transition state for the element ligand cooperative addition of CO_2 (top part) and the respective reaction energies / enthalpies / Gibbs free energies. The calculations were done on the RI-DSD-PBEP86/2013-D3(BJ)/def2-QZVPP//r^{2}SCAN-3c, COSMO-RS(CH_2Cl_2) level of theory. All numbers are given in kJ mol^{-1}.

[^{R}**1**]$^-$ *or* [^{Me}**1(Al)**]$^-$ + CO_2 → C-C bond formation/cleavage transition state					
	$\Delta E^{\ddagger}_{gasphase}$	$\Delta H^{\ddagger}_{gasphase}$	$\Delta G^{\ddagger}_{gasphase}$	$\Delta H^{\ddagger}_{solution}$	$\Delta G^{\ddagger}_{solution}$
[^{Me}**1**]$^-$	30.6	31.6	79.8	50.7	90.3
[^{Et}**1**]$^-$	30.5	30.0	79.7	51.6	92.5
[^{Me}**1(Al)**]$^-$	20.8	20.9	68.8	35.6	76.2
[^{R}**1**]$^-$ *or* [^{Me}**1(Al)**]$^-$ + CO_2 → [^{R}**1***-CO_2]$^-$ *or* [^{Me}**1(Al)***-CO_2]$^-$					
	$\Delta_r E_{gasphase}$	$\Delta_r H_{gasphase}$	$\Delta_r G_{gasphase}$	$\Delta_r H_{solution}$	$\Delta_r G_{solution}$
[^{Me}**1**]$^-$	−39.2	−34.1	20.1	−46.0	5.9
[^{Et}**1**]$^-$	−32.7	−28.7	25.9	−33.8	17.8
[^{Me}**1(Al)**]$^-$	−68.2	−62.9	−8.7	−74.9	−23.1

Reactivity after protonation

The reactivity of [^{Me}**1**]$^-$ after protonation (to give [H-^{Me}**1***]) was studied (Figure S9). An energetically low-lying transition state (**TS-1**) accounting for the cleavage of the exopyrrolic C-C bond originating from the proton-bearing carbon atom was found. The subsequently obtained intermediate (**Int-1**) is essentially Gibbs free isoenergetic with [H-^{Me}**1***].

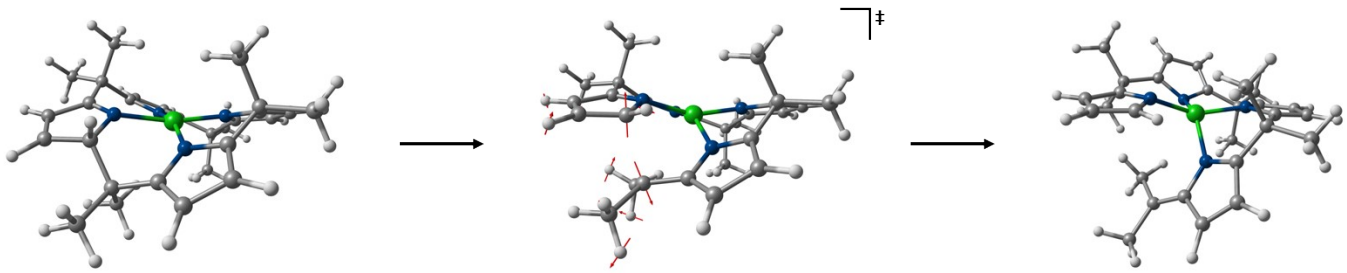


Figure S9. Reactivity of [H-^{Me}**1***] as suggested by calculations on the RI-DSD-PBEP86/2013-D3(BJ)/def2-QZVPP//r^{2}SCAN-3c, COSMO-RS(CH_2Cl_2) level of theory. All numbers are given in kJ mol^{-1}. The scaled displacement vectors illustrating the single imaginary mode of **TS-1** are shown in red.

The obtained results were then compared to calculations which included THF donor molecules explicitly coordinating to the gallium center (Figure S10). THF coordinating *syn* to the dearomatization-inducing proton was found energetically more favorable than *anti* coordination. The association of a second THF donor was calculated endergonic by 18 kJ mol^{-1}. The transition state searches for the C-C bond cleavage based on [H-^{Me}**1***-thf]$_{syn}$ and [H-^{Me}**1***-$(thf)_2$] as preceding intermediates remained unsuccessful. The transition structure optimizations did not converge. Only with THF coordinating *anti* to the proton resulted in a successful optimization (**TS-2**). Comparing [H-^{Me}**1***-thf]$_{syn}$ and **TS-2** gives a Gibbs free energy difference of 131 kJ mol^{-1}.

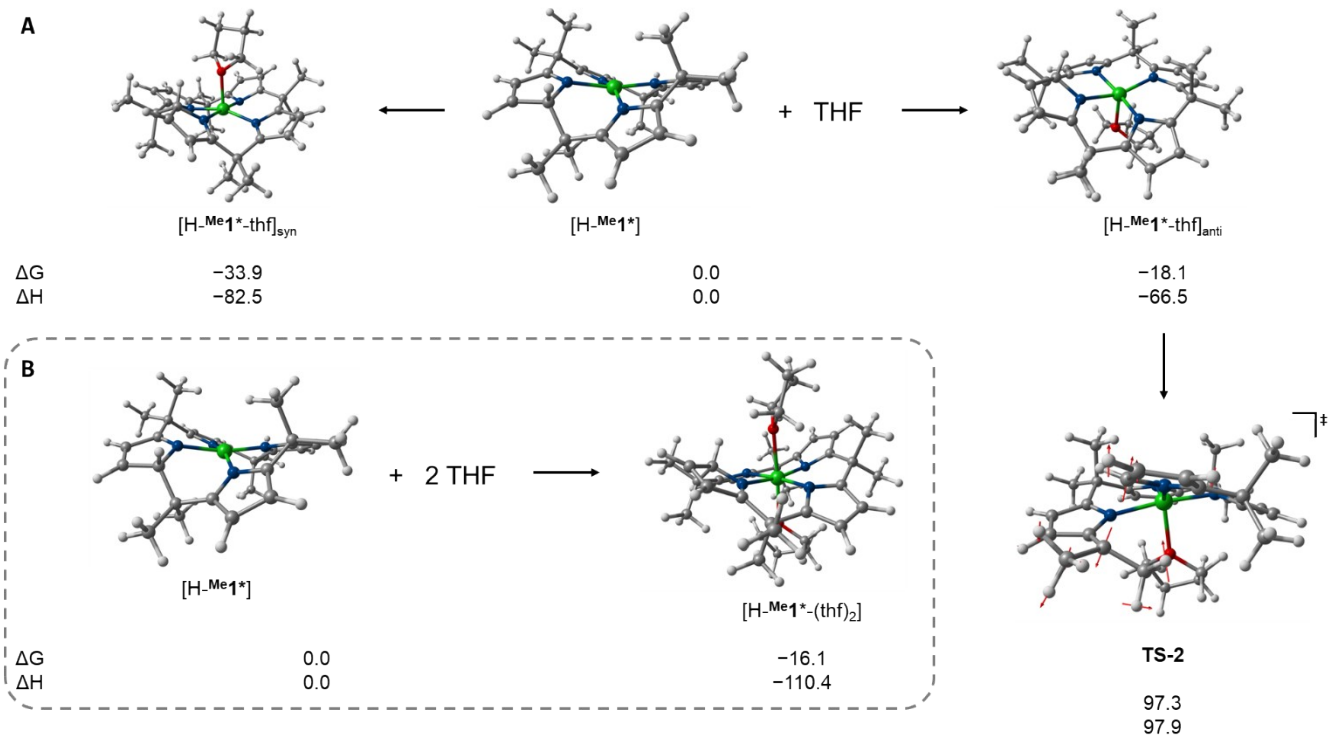


Figure S10. Reactivity of [H-^{Me}**1***] in the presence of THF as donor as suggested by calculations on the RI-DSD-PBEP86/2013-D3(BJ)/def2-QZVPP//r^{2}SCAN-3c, COSMO-RS(CH_2Cl_2) level of theory. All numbers are given in kJ mol^{-1}. The scaled displacement vectors illustrating the single imaginary mode of **TS-2** are shown in red.

S9. NMR spectra

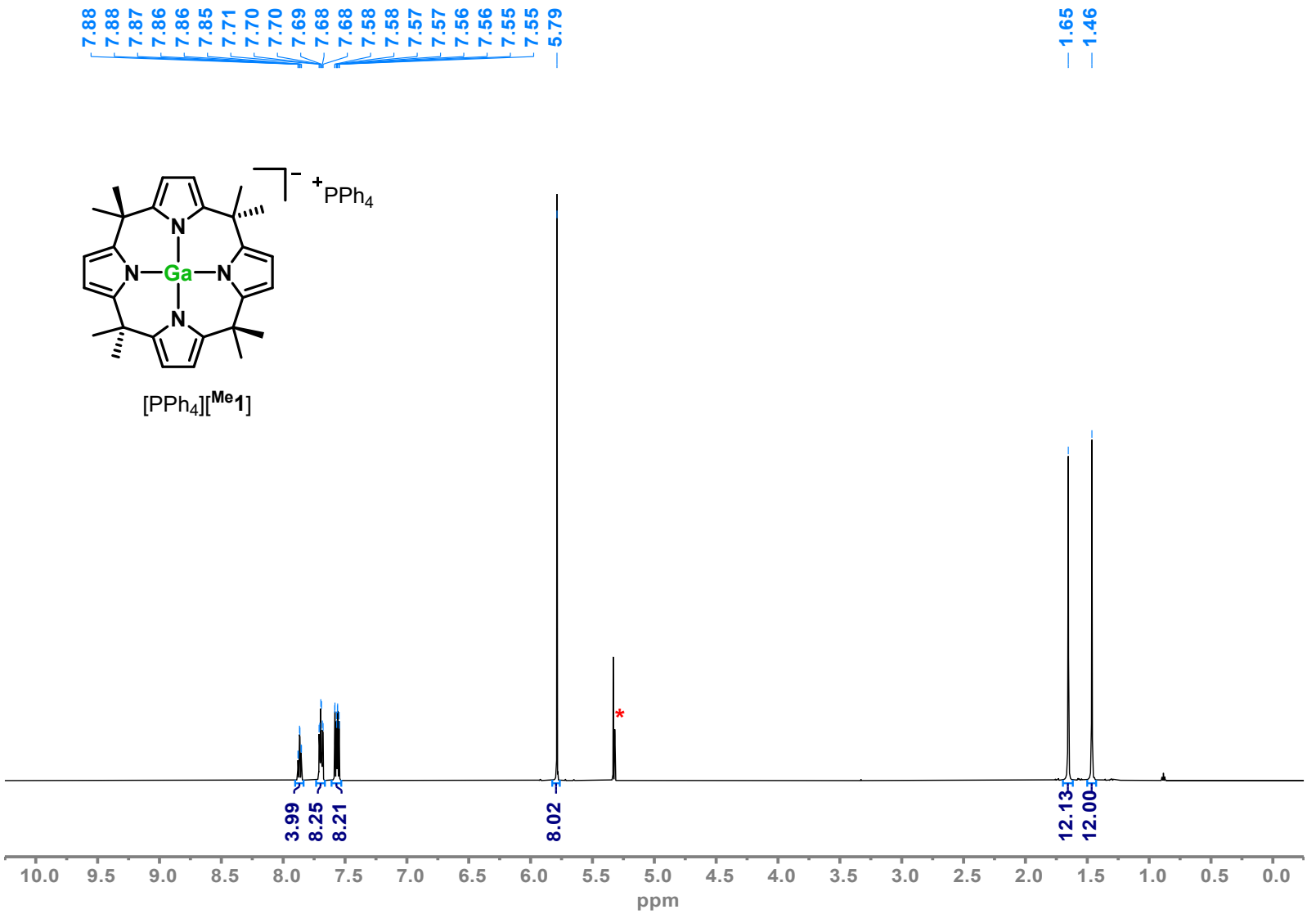


Figure S11. ^{1}H NMR spectrum (600.2 MHz, CD_2Cl_2, 295 K) of [PPh_4][^{Me}**1**]. The signal of $CHDCl_2$ and of residual CH_2Cl_2 is marked with a red asterisk.

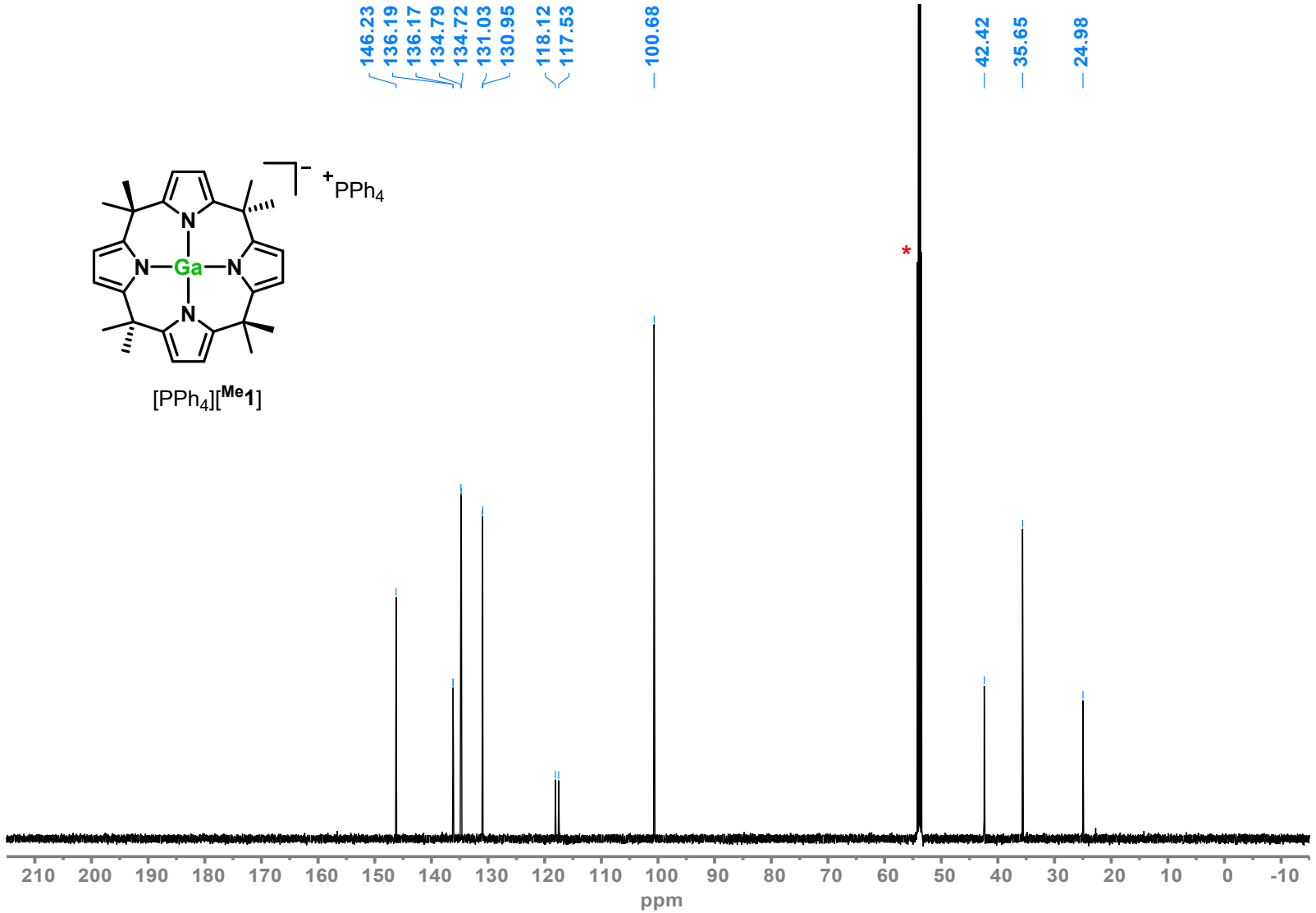
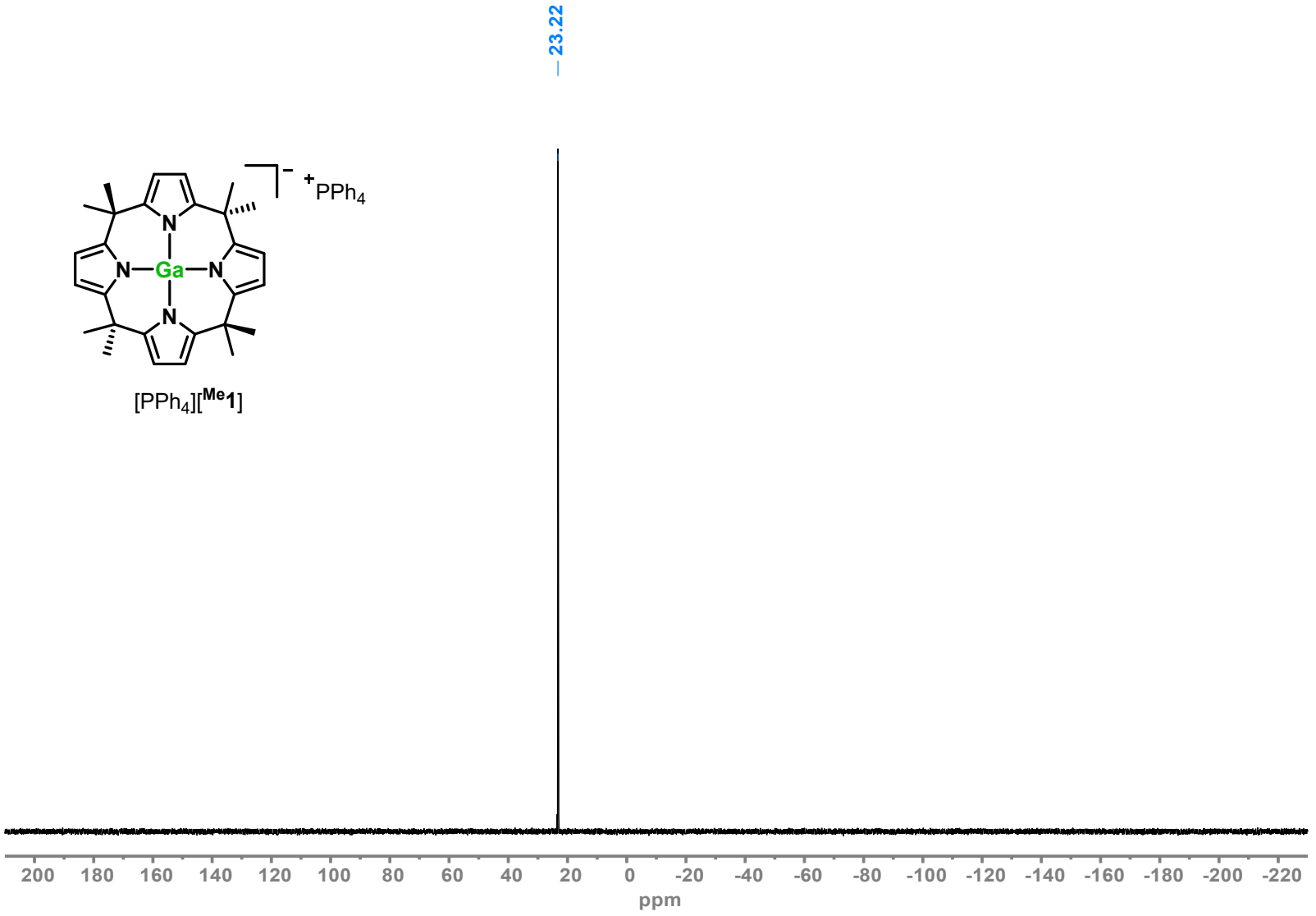


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum (150.9 MHz, CD_2Cl_2, 295 K) of $[PPh_4][^{Me}\mathbf{1}]$. The signal of CD_2Cl_2 is marked with a red asterisk.



[PPh_4][^{Me}**1**]

Figure S13. $^{31}P\{^1H\}$ NMR spectrum (161.9 MHz, CD_2Cl_2, 295 K) of [PPh_4][^{Me}**1**].

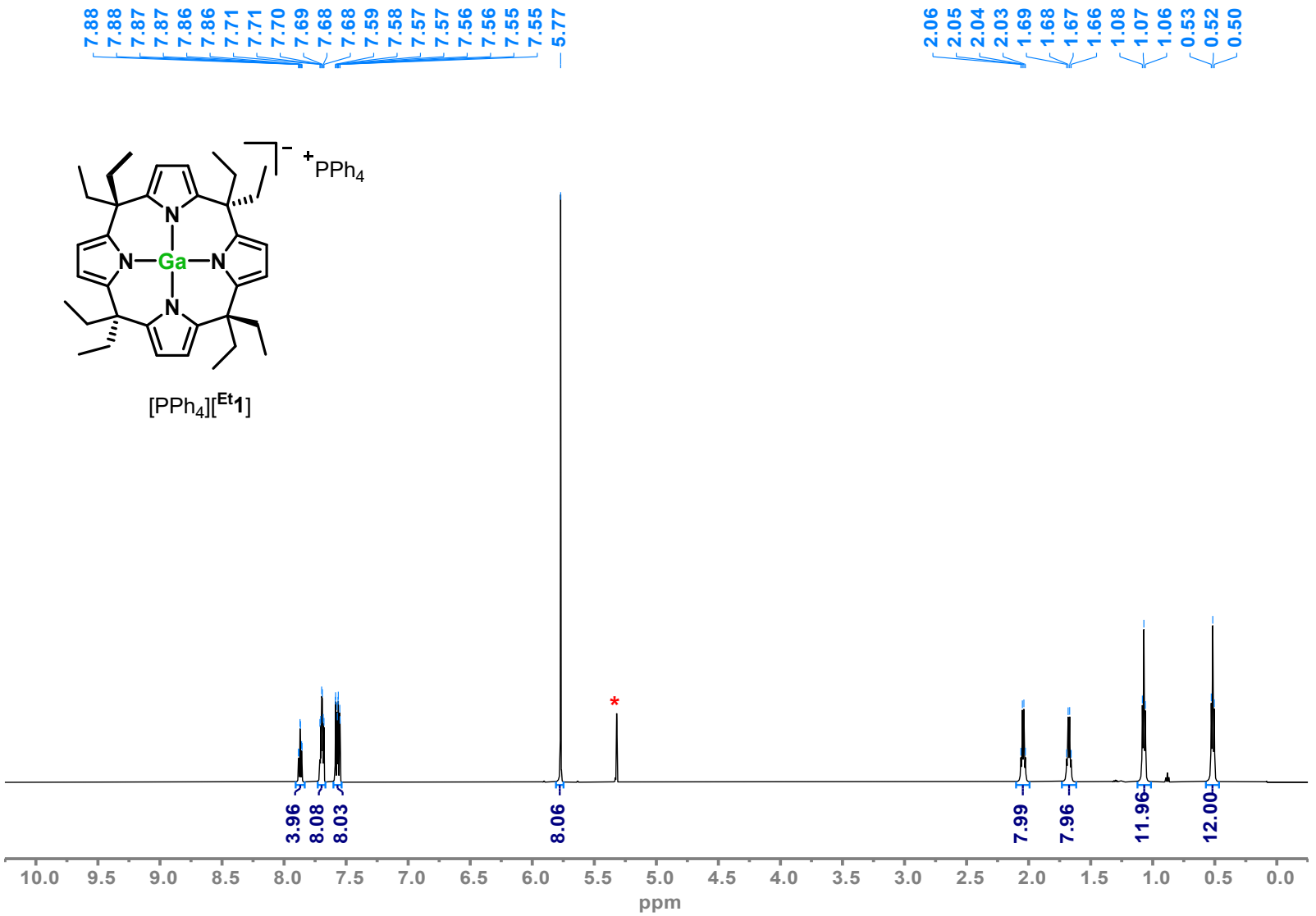


Figure S14. ^{1}H NMR spectrum (600.2 MHz, CD_2Cl_2, 295 K) of $[PPh_4][^{Et}\mathbf{1}]$. The signal of $CHDCl_2$ is marked with a red asterisk.

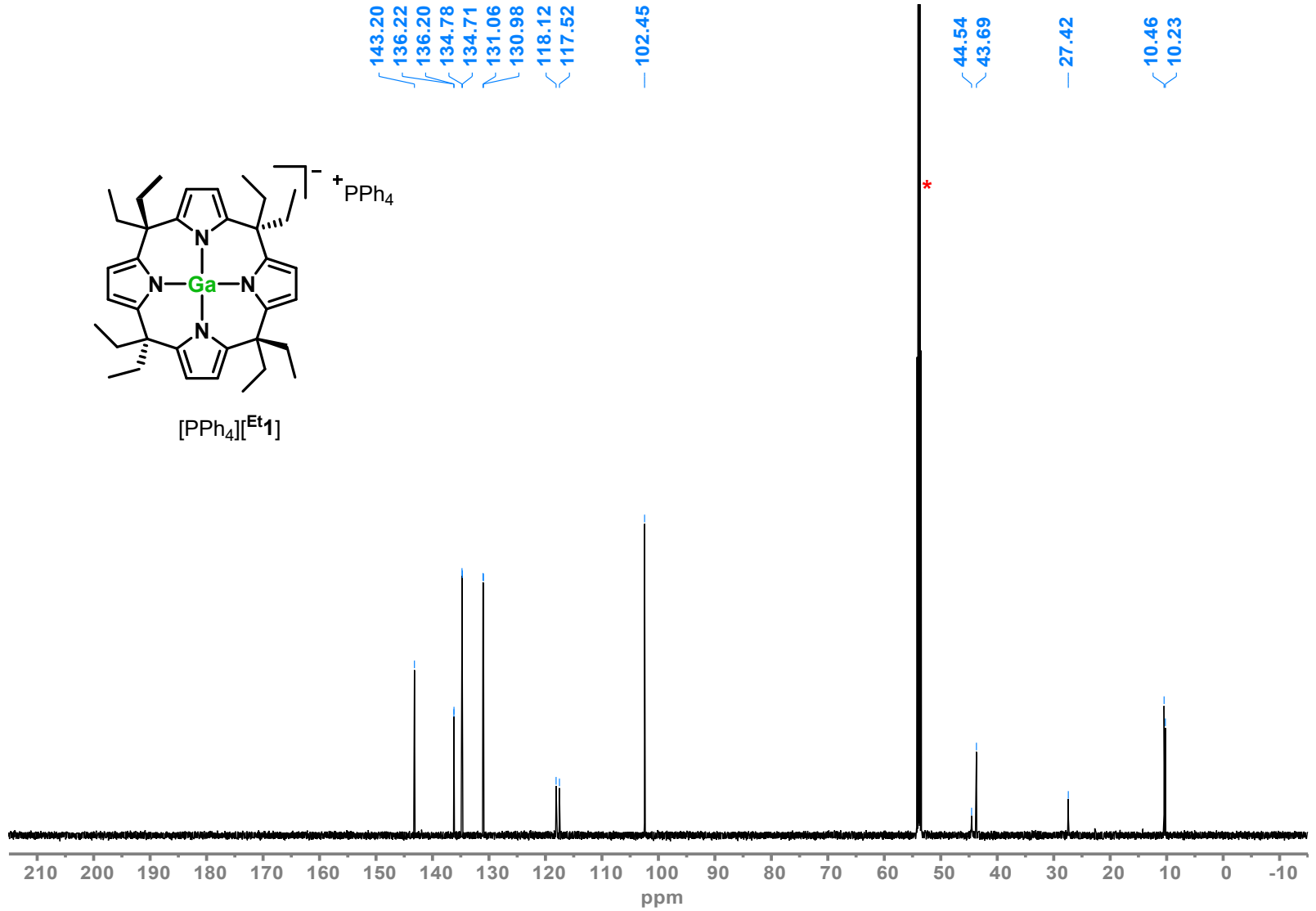


Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum (150.9 MHz, CD_2Cl_2, 295 K) of $[PPh_4][^{Et}\mathbf{1}]$. The signal of CD_2Cl_2 is marked with a red asterisk.

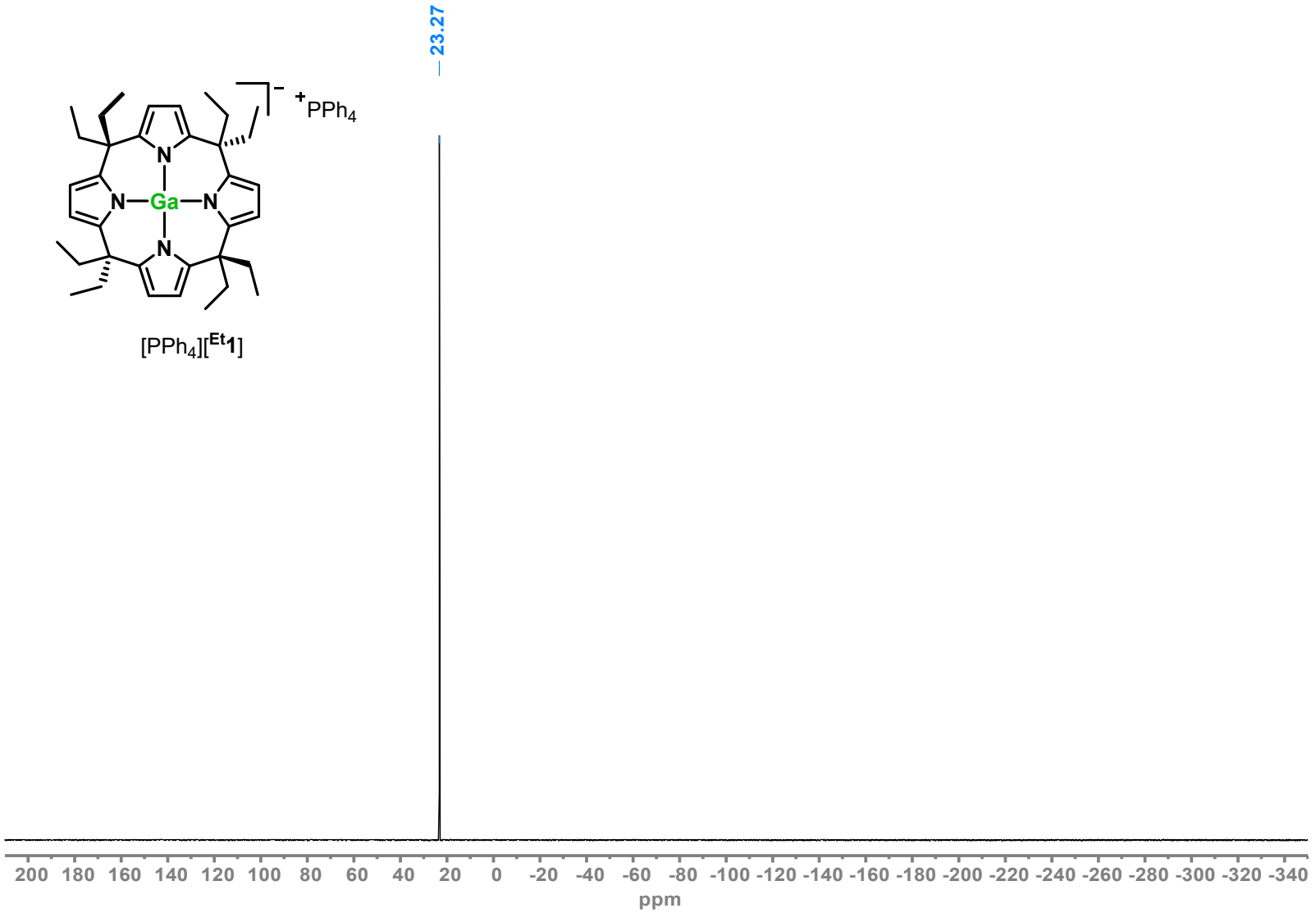


Figure S16. $^{31}P\{^{1}H\}$ NMR spectrum (243.0 MHz, CD_2Cl_2, 295 K) of $[PPh_4][^{Et}\mathbf{1}]$.

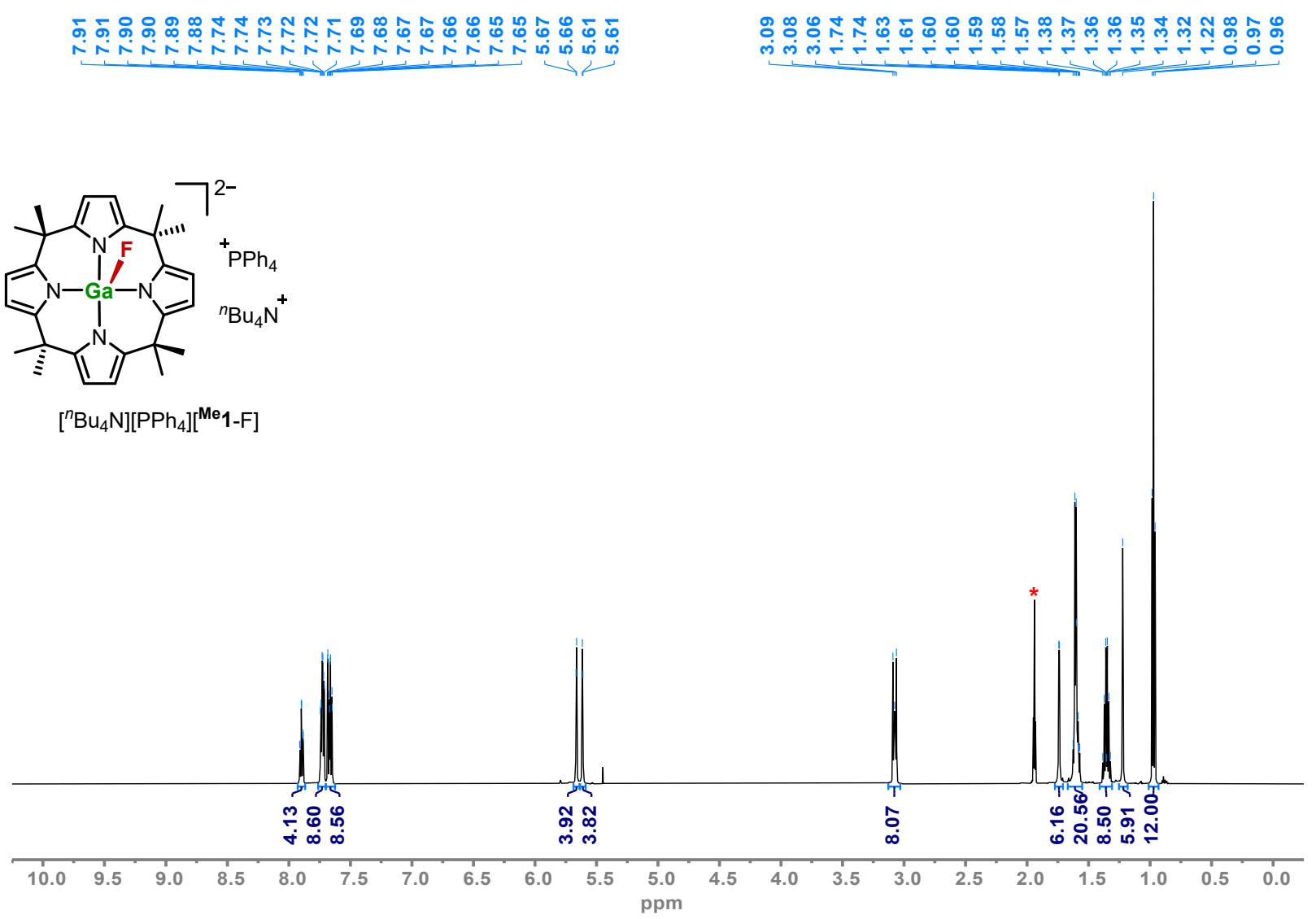


Figure S17. ^{1}H NMR spectrum (600.2 MHz, CD_3CN, 295 K) of [$^{n}Bu_4N$][PPh_4][^{Me}**1**-F]. The signal of CHD_2CN is marked with a red asterisk. The small singlet at 5.47 corresponds to a slight residual amount of CH_2Cl_2.

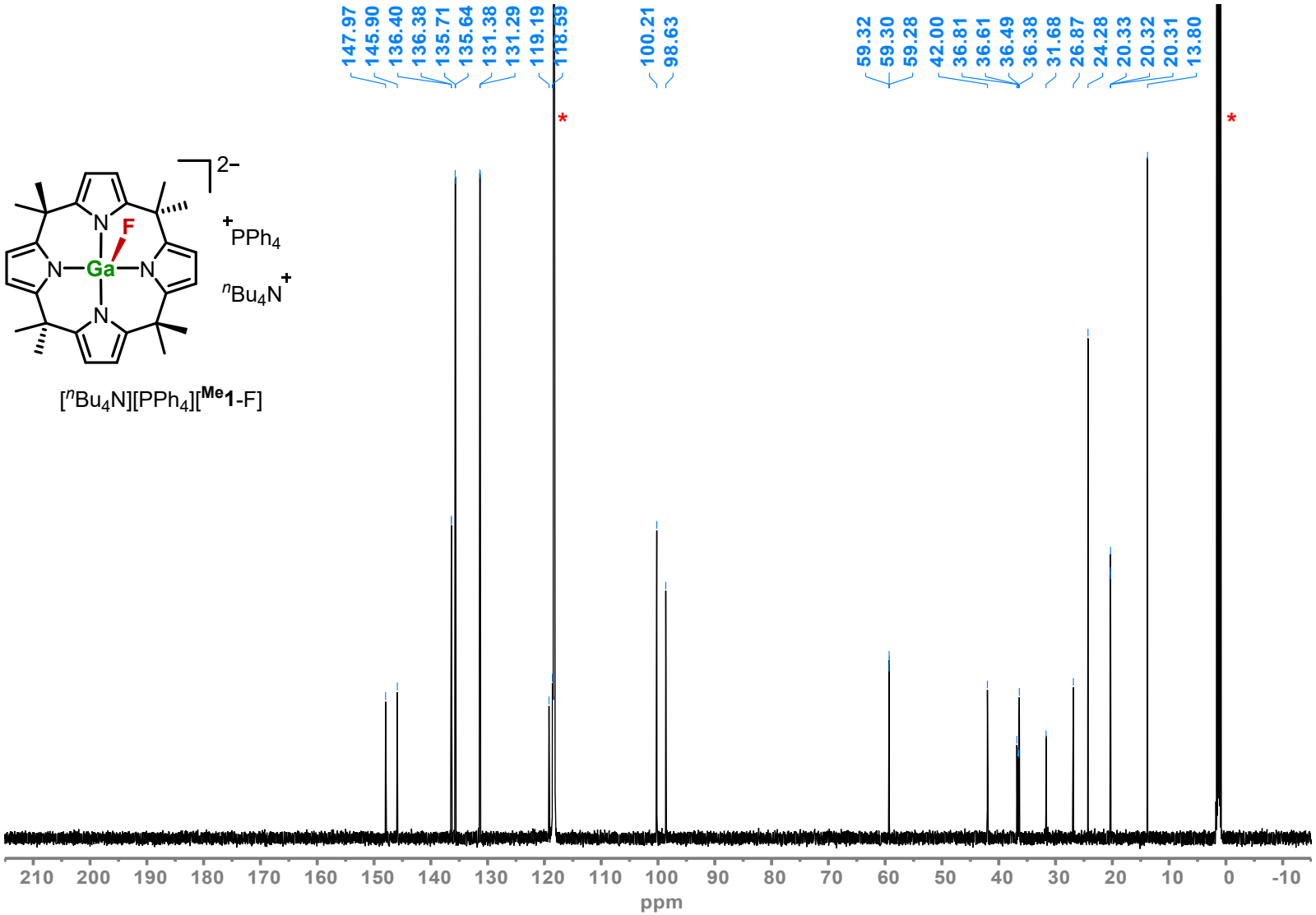


Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum (150.9 MHz, CD_3CN, 295 K) of [$^{n}Bu_4N$][PPh_4][^{Me}**1**-F]. The signals of CD_3CN are marked with red asterisks.

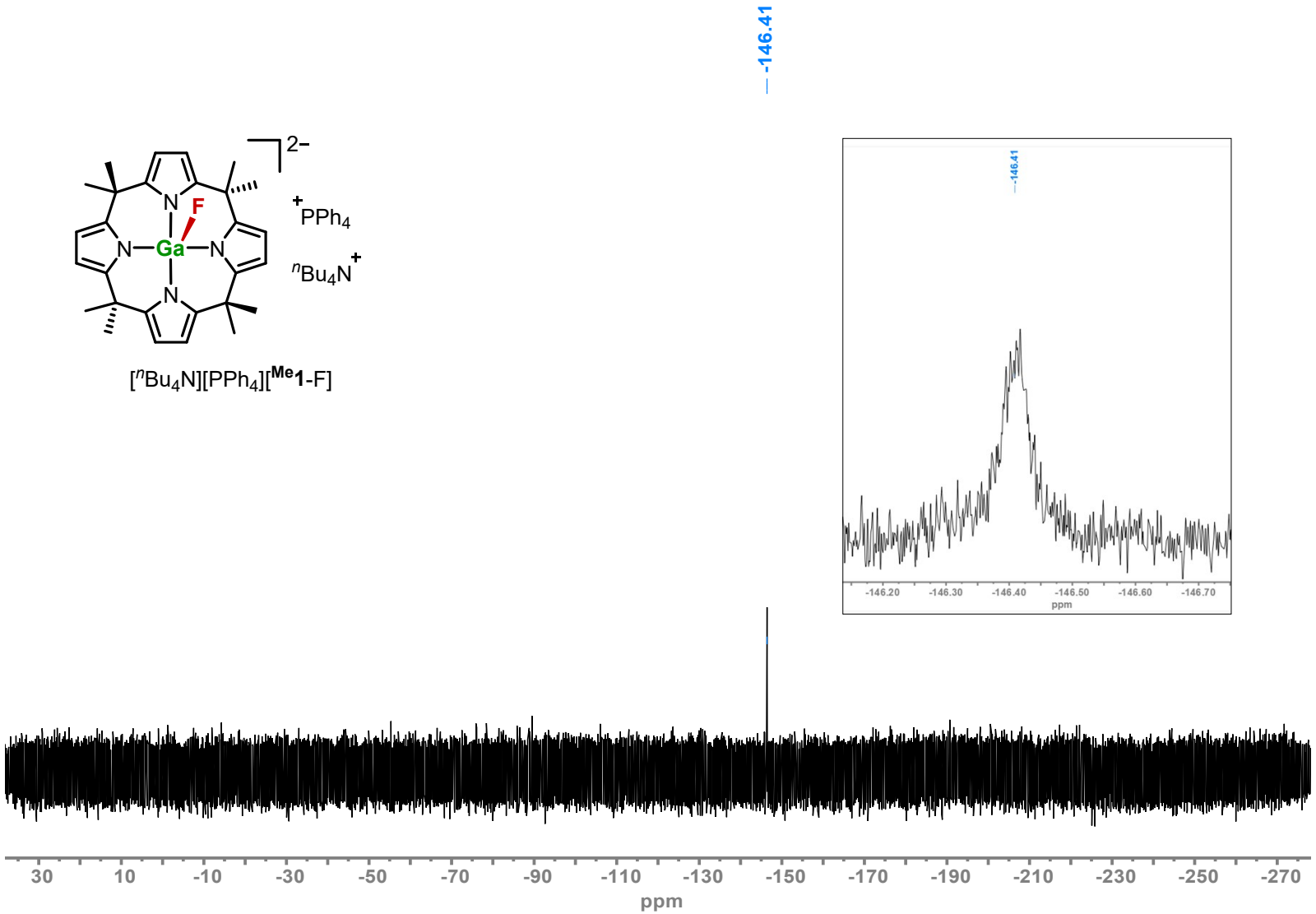


Figure S19. ^{19}F NMR spectrum (376.3 MHz, CD_3CN, 295 K) of $[^nBu_4N][PPh_4][^{Me}\mathbf{1}\text{-F}]$.

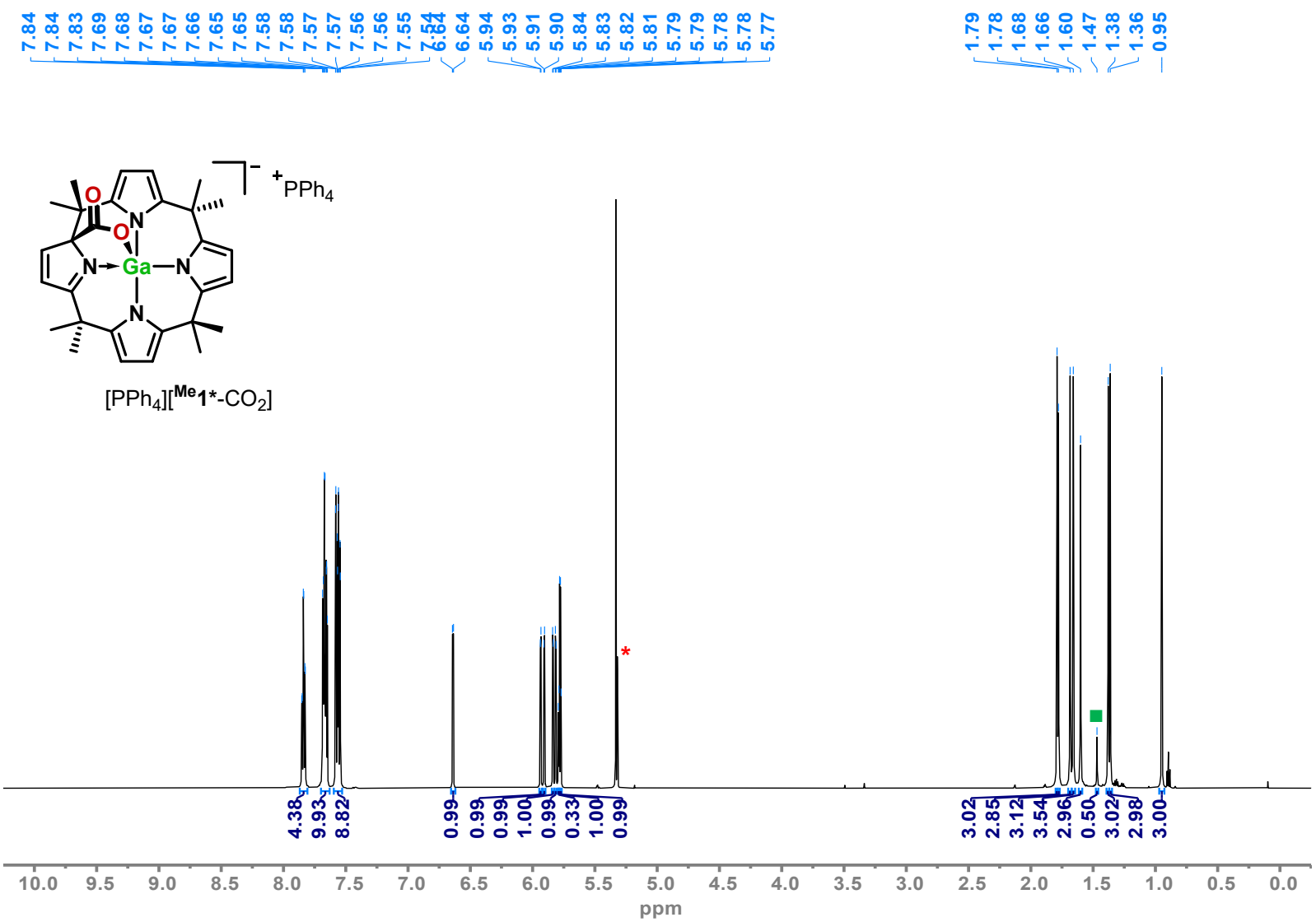


Figure S20. ^{1}H NMR spectrum (600.2 MHz, CD_2Cl_2, 295 K) of $[PPh_4][^{Me}\mathbf{1}]$ in the presence of CO_2 (5 bar). One well visible signal of free $[^{Me}\mathbf{1}]^-$ is marked with a green square. The ratio between $[^{Me}\mathbf{1}]^-$ and $[^{Me}\mathbf{1}^*\text{-}CO_2]^-$ was determined to 1:24 using this resonance. The signal of $CHDCl_2$ and residual CH_2Cl_2 is marked with a red asterisk.

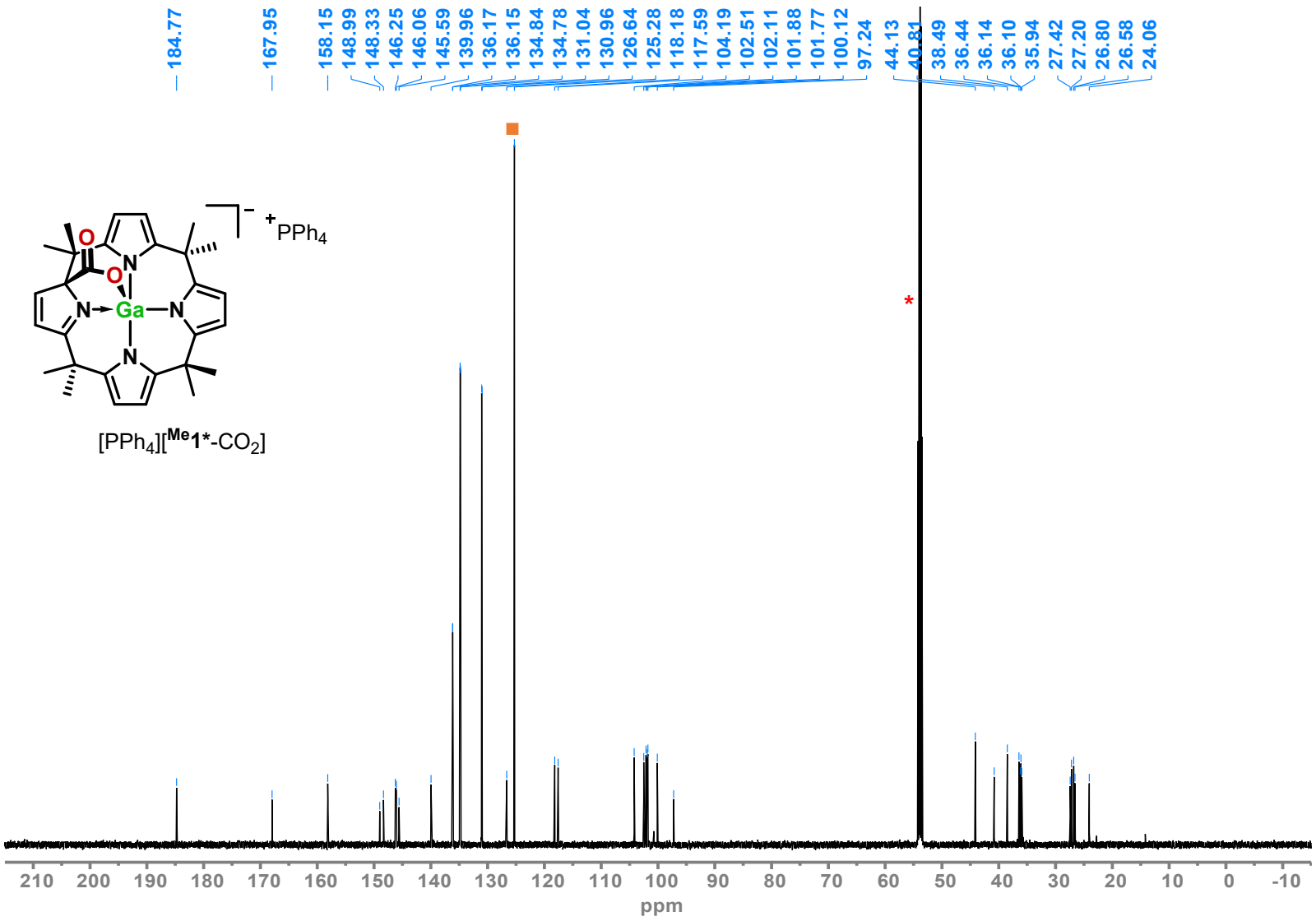


Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum (150.9 MHz, CD_2Cl_2, 295 K) of $[PPh_4][^{Me}\mathbf{1}]$ in the presence of CO_2 (5 bar). The signal of CD_2Cl_2 is marked with a red asterisk, that of free CO_2 with an orange square.

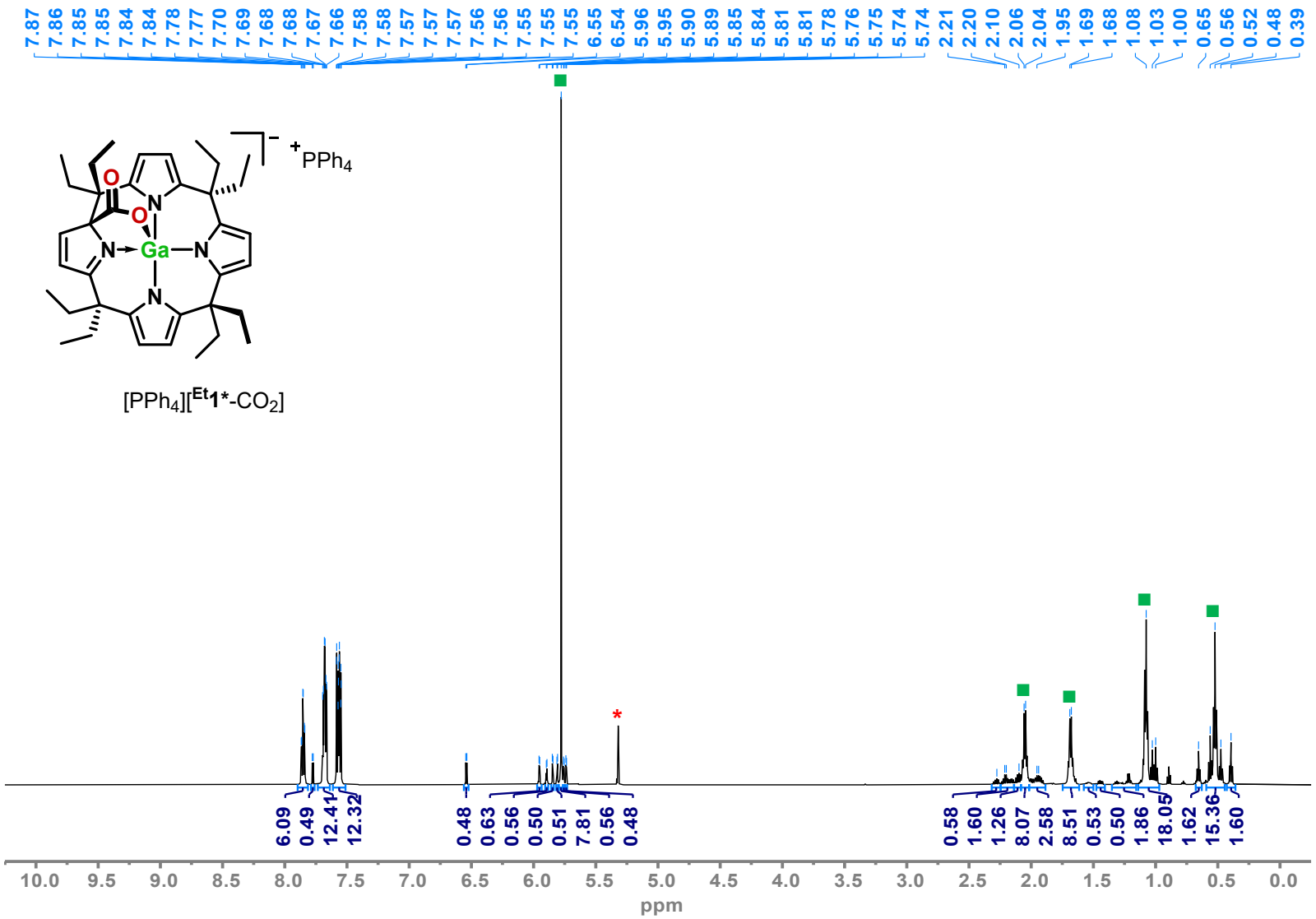


Figure S22. ^{1}H NMR spectrum (600.2 MHz, CD_2Cl_2, 295 K) of $[PPh_4][^{Et}\mathbf{1}]$ in the presence of CO_2 (5 bar). The signals of free $[^{Et}\mathbf{1}]^-$ are marked with green squares. The ratio between $[^{Et}\mathbf{1}]^-$ and $[^{Et}\mathbf{1}^*\text{-}CO_2]^-$ was determined to 2:1 using the resonances of the β-protons of the pyrrole rings. The signal of $CHDCl_2$ is marked with a red asterisk.

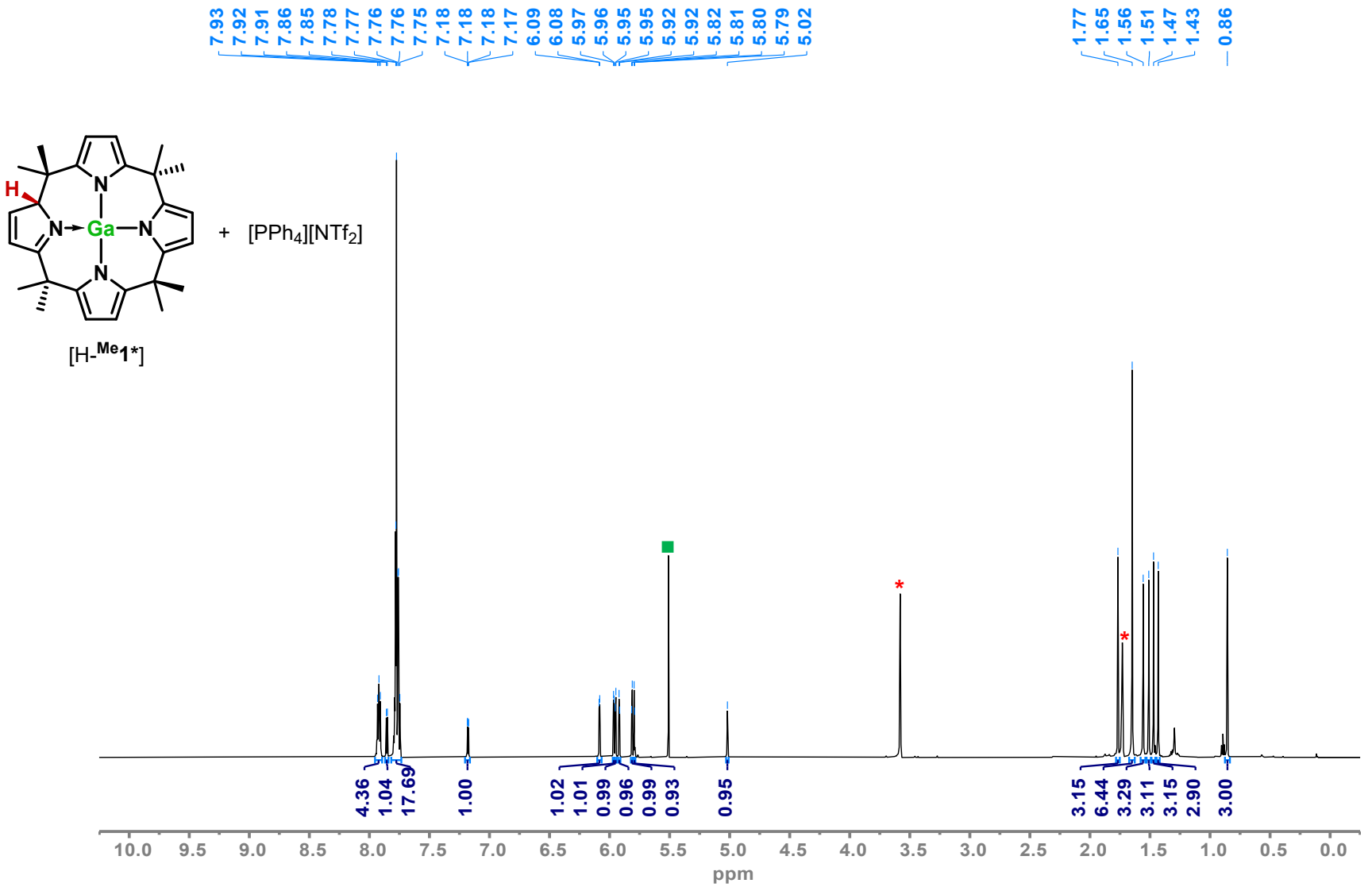


Figure S23. ^{1}H NMR spectrum (600.2 MHz, THF-d_8, 295 K) of [PPh_4][^{Me}**1**] in the presence of $HNTf_2$ (one equivalent). The signal of CH_2Cl_2, which is contained in [PPh_4][^{Me}**1**], is marked with a green square, those of THF-d_7 with red asterisks.

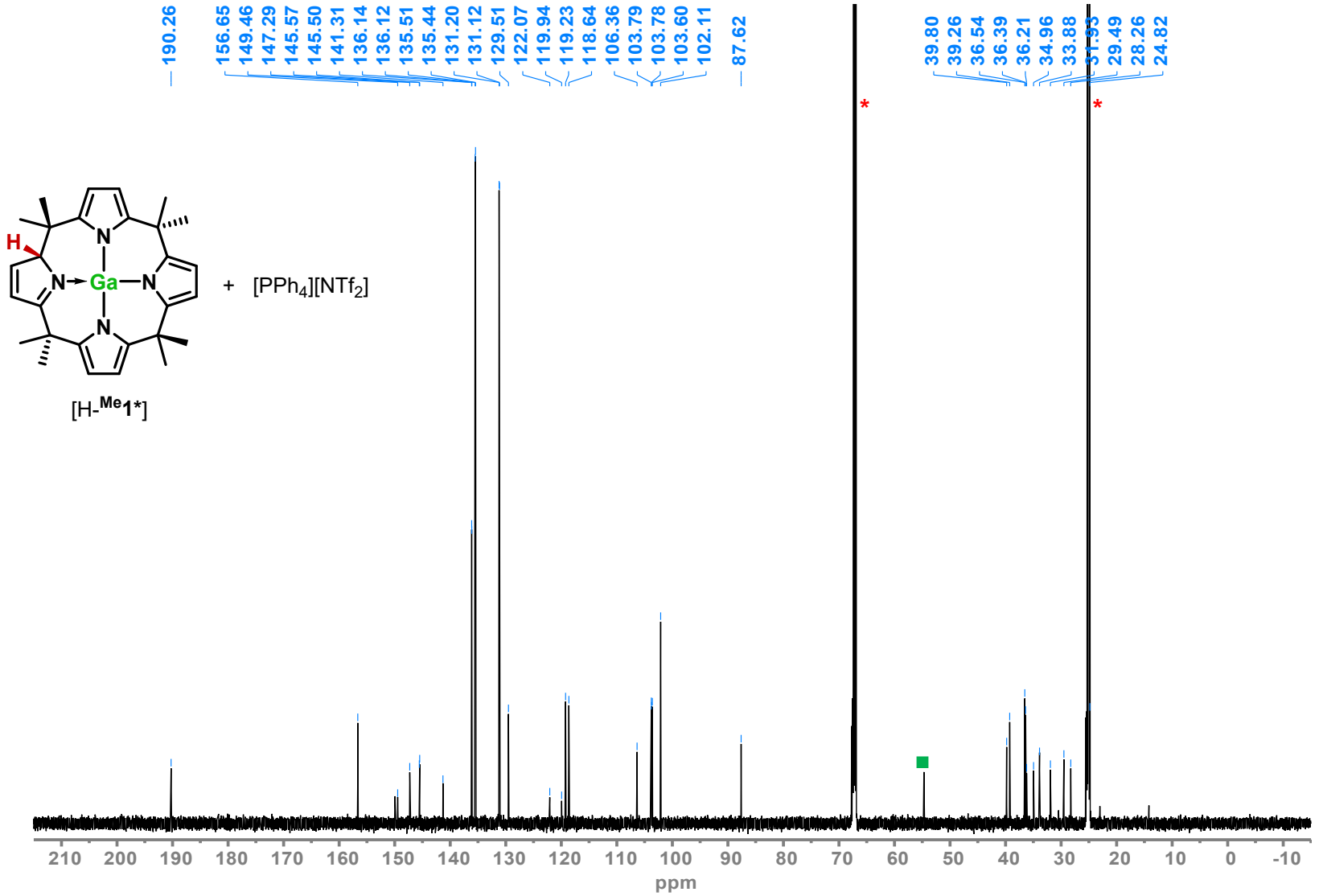


Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum (150.9 MHz, THF-d_8, 295 K) of $[PPh_4][^{Me}\mathbf{1}]$ in the presence of $HNTf_2$ (one equivalent). The signal of CH_2Cl_2, which is contained in $[PPh_4][^{Me}\mathbf{1}]$, is marked with a green square, those of THF-d_8 with red asterisks.

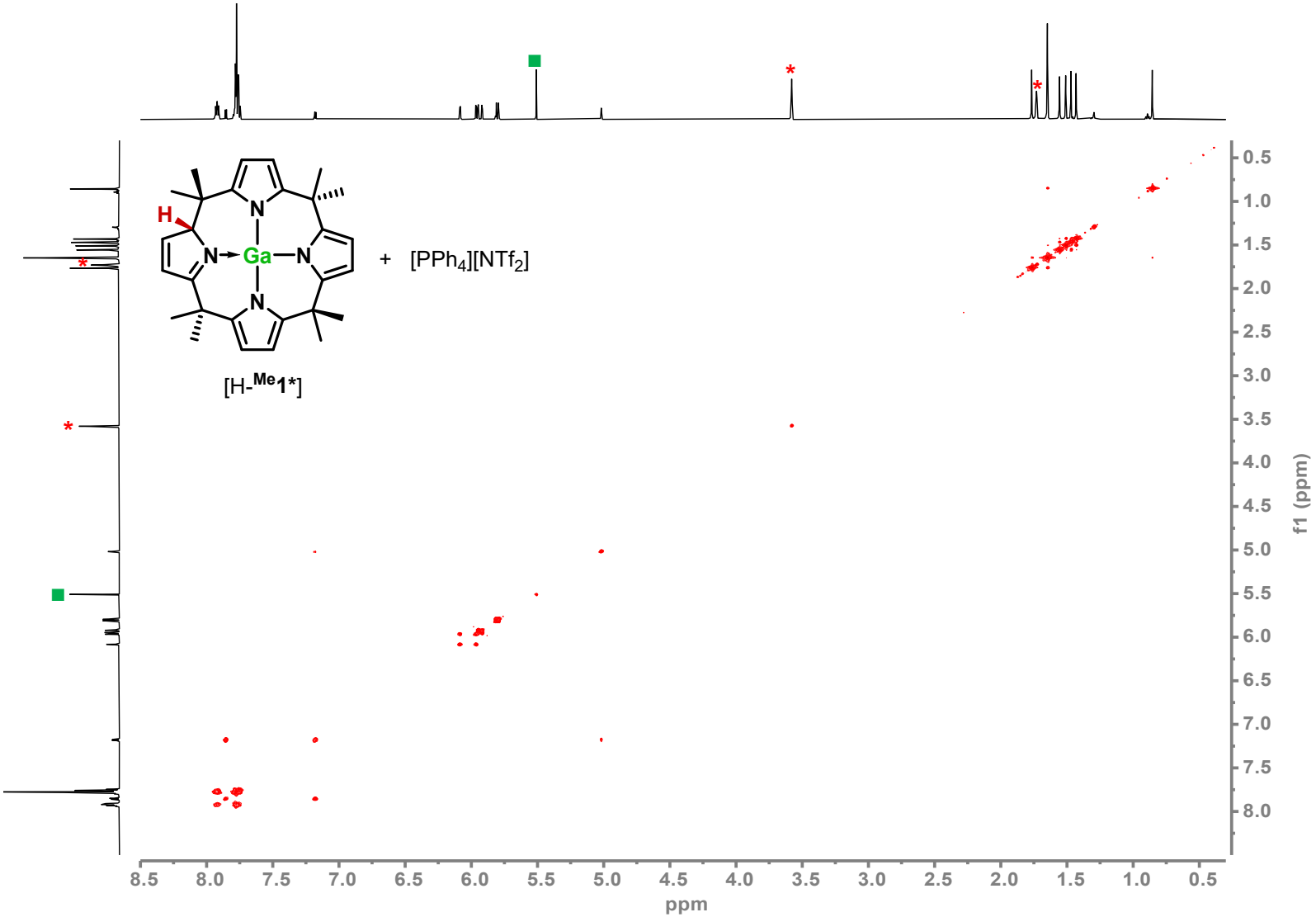


Figure S25. $^{1}H,^{1}H$ COSY NMR spectrum (600.2 MHz, THF-d_8, 295 K) of [PPh_4][^{Me}**1**] in the presence of $HNTf_2$ (one equivalent). The signal of CH_2Cl_2, which is contained in [PPh_4][^{Me}**1**], is marked with a green square, those of THF-d_7 with red asterisks.

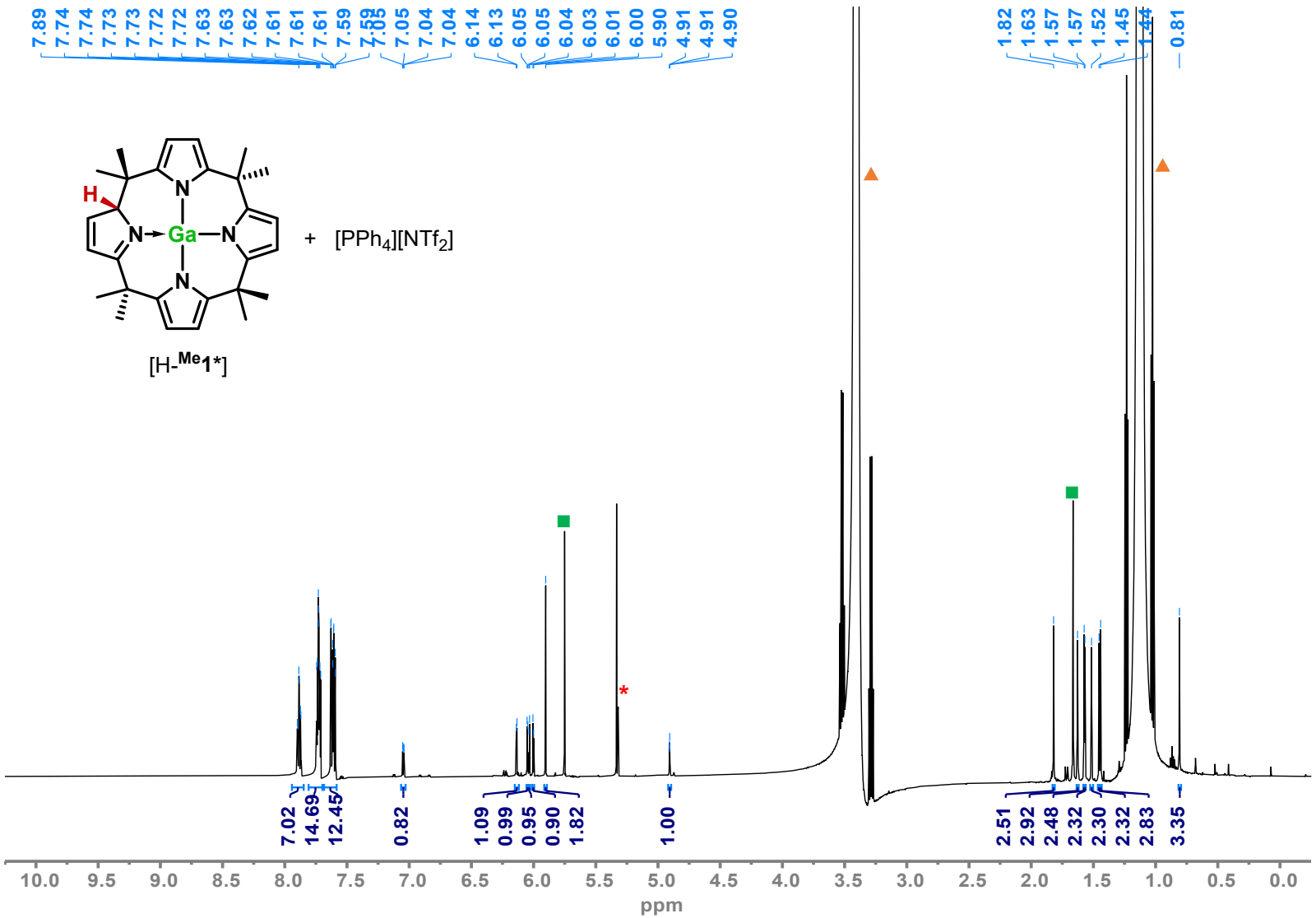


Figure S26. ^{1}H NMR spectrum (600.2 MHz, CD_2Cl_2 / Et_2O (2:1 %vol), 295 K) of $[PPh_4][^{Me}\mathbf{1}]$ in the presence of $HNTf_2$ (0.9 equivalents). The signals of unreacted $[^{Me}\mathbf{1}]^-$ are marked with green squares. Due to the donor properties of Et_2O, the methyl groups of $[^{Me}\mathbf{1}]^-$ resonate at the same frequency. The signal of $CHDCl_2$ and residual CH_2Cl_2 is marked with a red asterisk, those of diethyl ether with orange triangles. The spectrum was calibrated on the signal of $CHDCl_2$ (5.32 ppm).

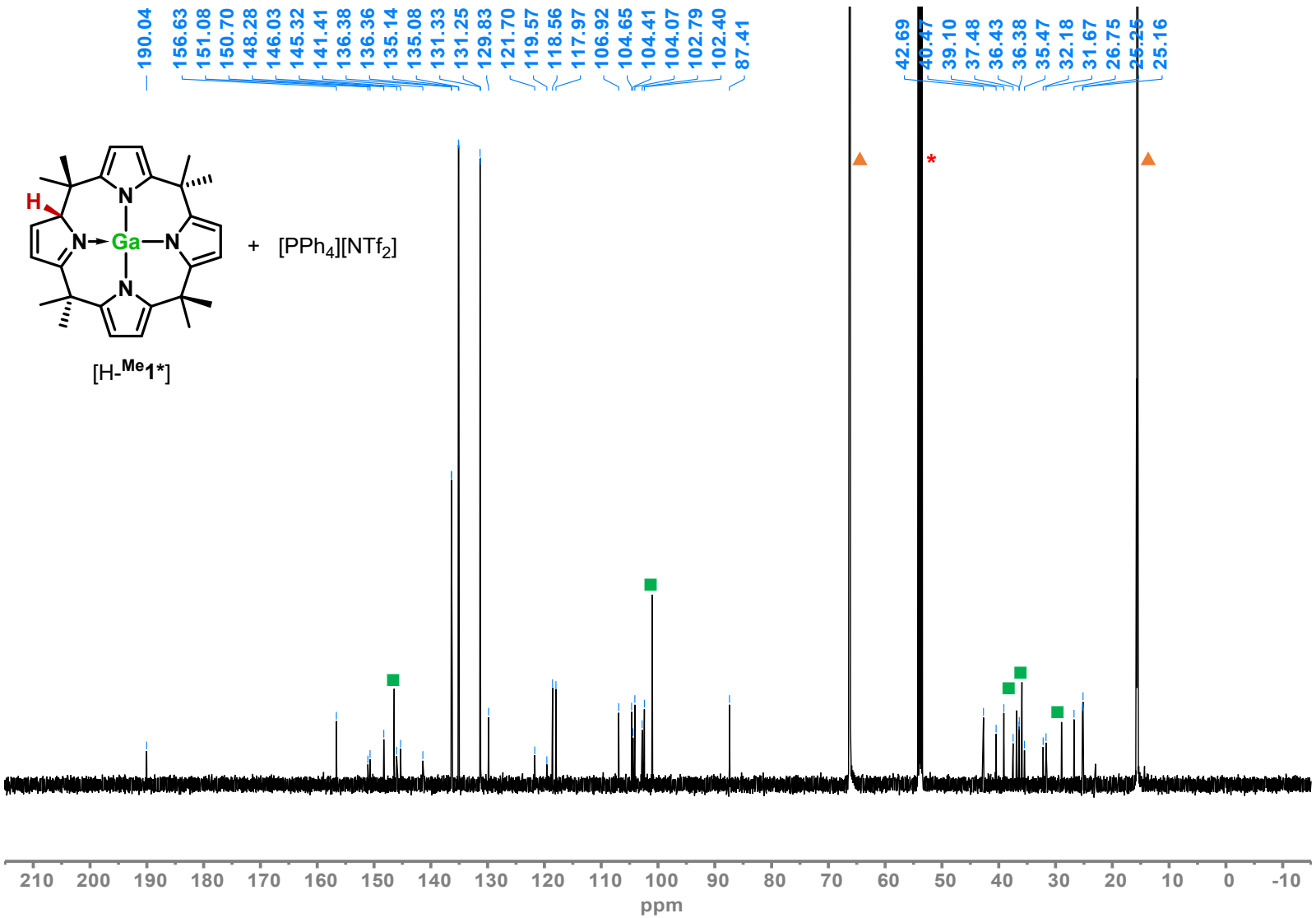


Figure S27. $^{13}C\{^{1}H\}$ NMR spectrum (150.9 MHz, CD_2Cl_2 / Et_2O (2:1 %vol), 295 K) of $[PPh_4][^{Me}\mathbf{1}]$ in the presence of $HNTf_2$ (0.9 equivalents). The signals of unreacted $[^{Me}\mathbf{1}]^-$ are marked with green squares. The signal of CD_2Cl_2 is marked with a red asterisk, those of diethyl ether with an orange triangle. The spectrum was calibrated on the signal of CD_2Cl_2 (53.84 ppm).

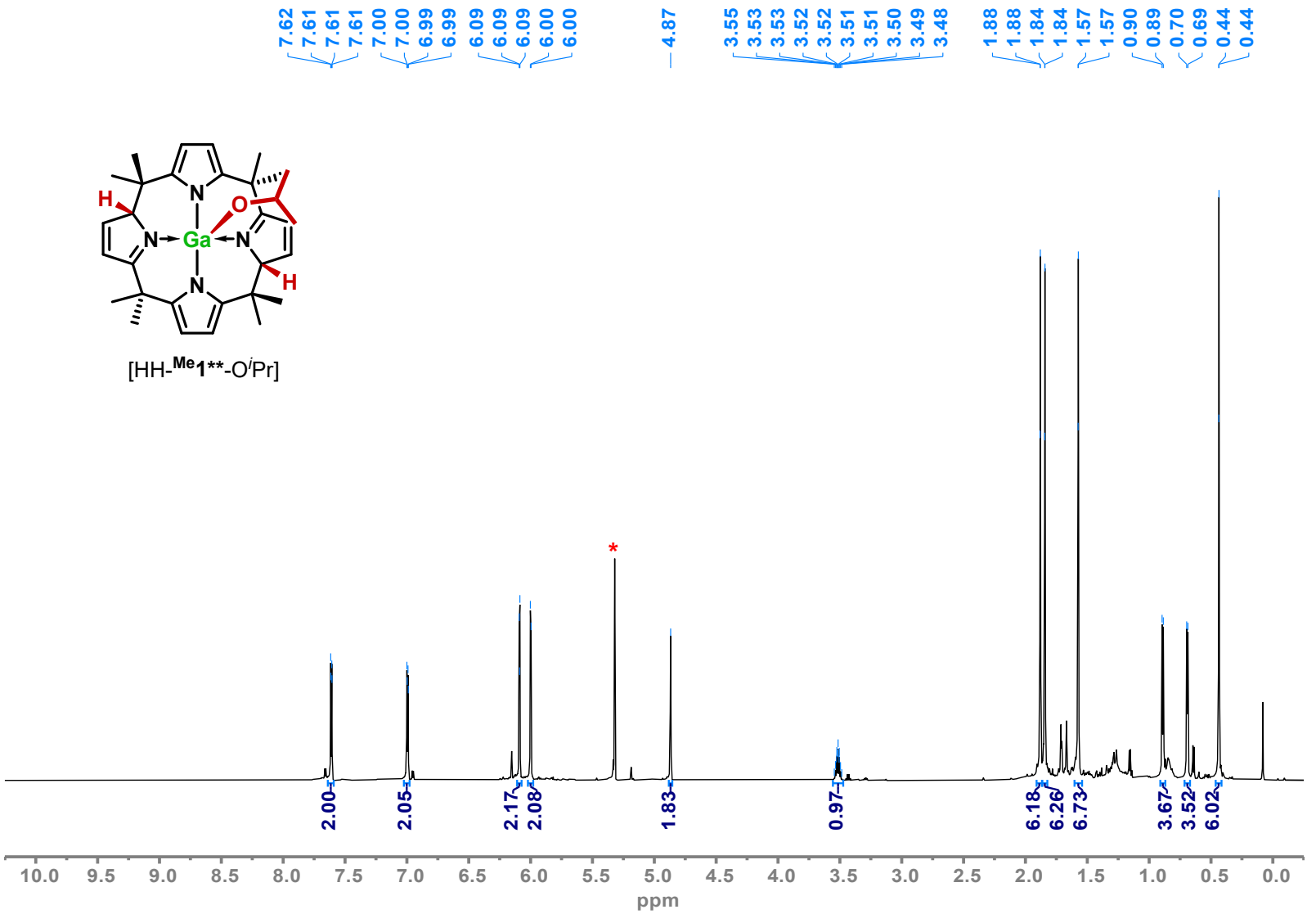


Figure S28. ^{1}H NMR spectrum (600.2 MHz, CD_2Cl_2, 295 K) of [HH-^{Me}**1****-O^{i}Pr]. The signal of $CHDCl_2$ is marked with a red asterisk. The small signals at 7.66, 6.95, 6.16, 5.19, 3.30, 1.71, 1.70, 1.69, and 0.64 ppm of an additional specie are ascribed to a constitutional isomer of the shown compound in which the two dearomatization-inducing protons are convertible into each other by means of a mirror plane. Its amount is estimated to approximately 8% relative to the main isomer.

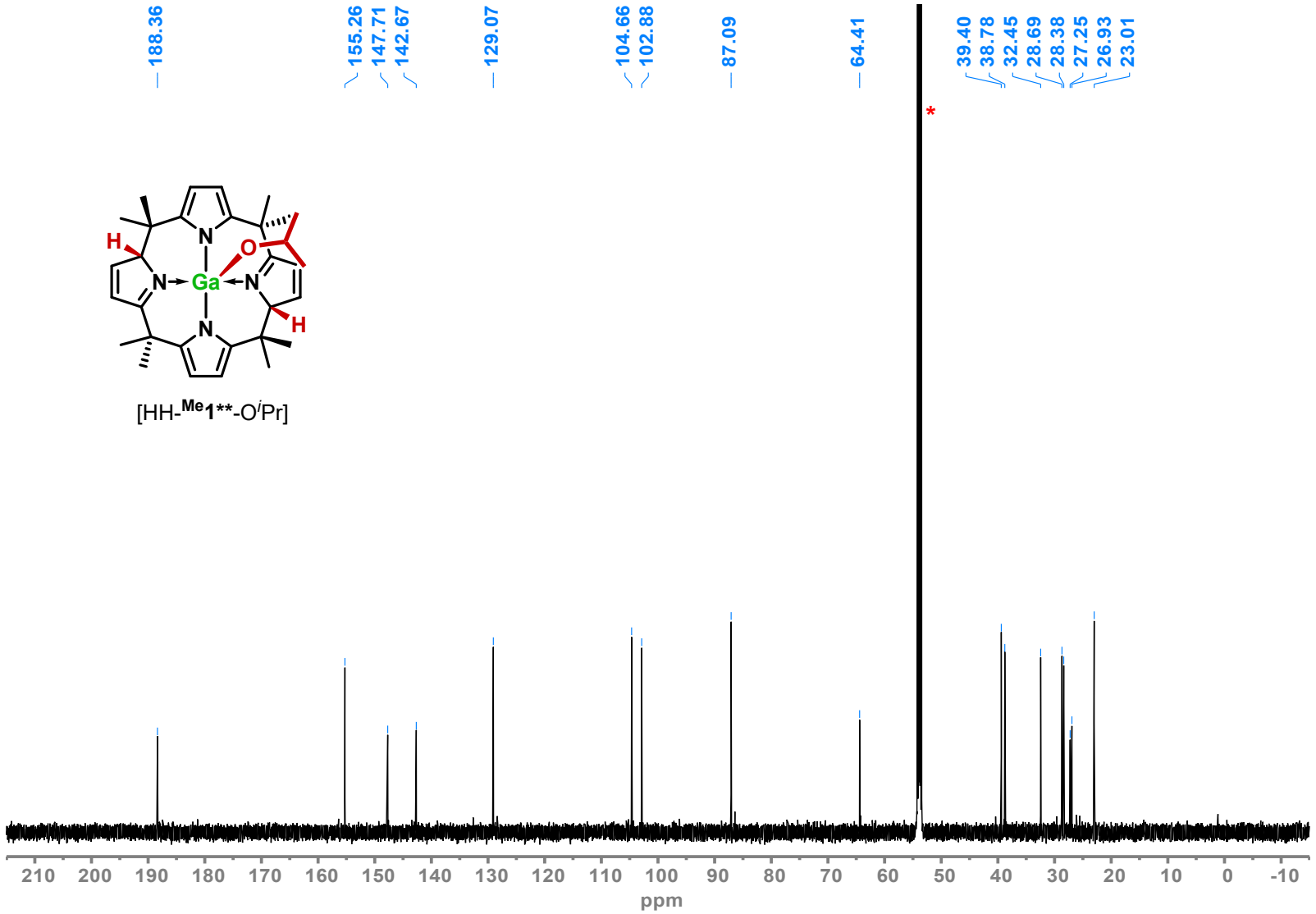


Figure S29. $^{13}C\{^{1}H\}$ NMR spectrum (150.9 MHz, CD_2Cl_2, 295 K) of [HH-^{Me}**1****-O^{i}Pr]. The signal of CD_2Cl_2 is marked with a red asterisk.

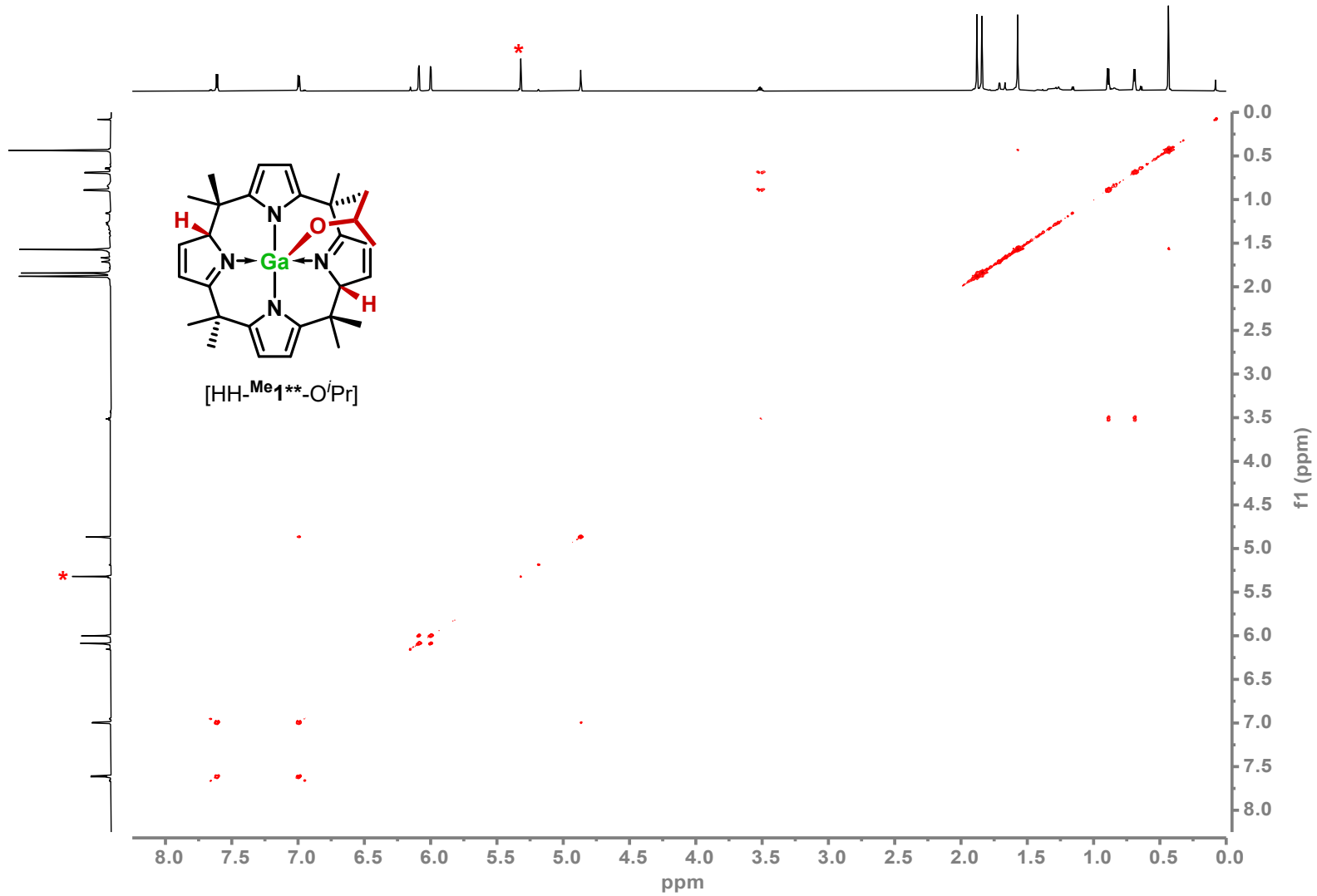


Figure S30. $^{1}H,^{1}H$ COSY NMR spectrum (600.2 MHz, CD_2Cl_2, 295 K) of [HH-^{Me}**1****-O^{i}Pr]. The signal of $CHDCl_2$ is marked with a red asterisk.

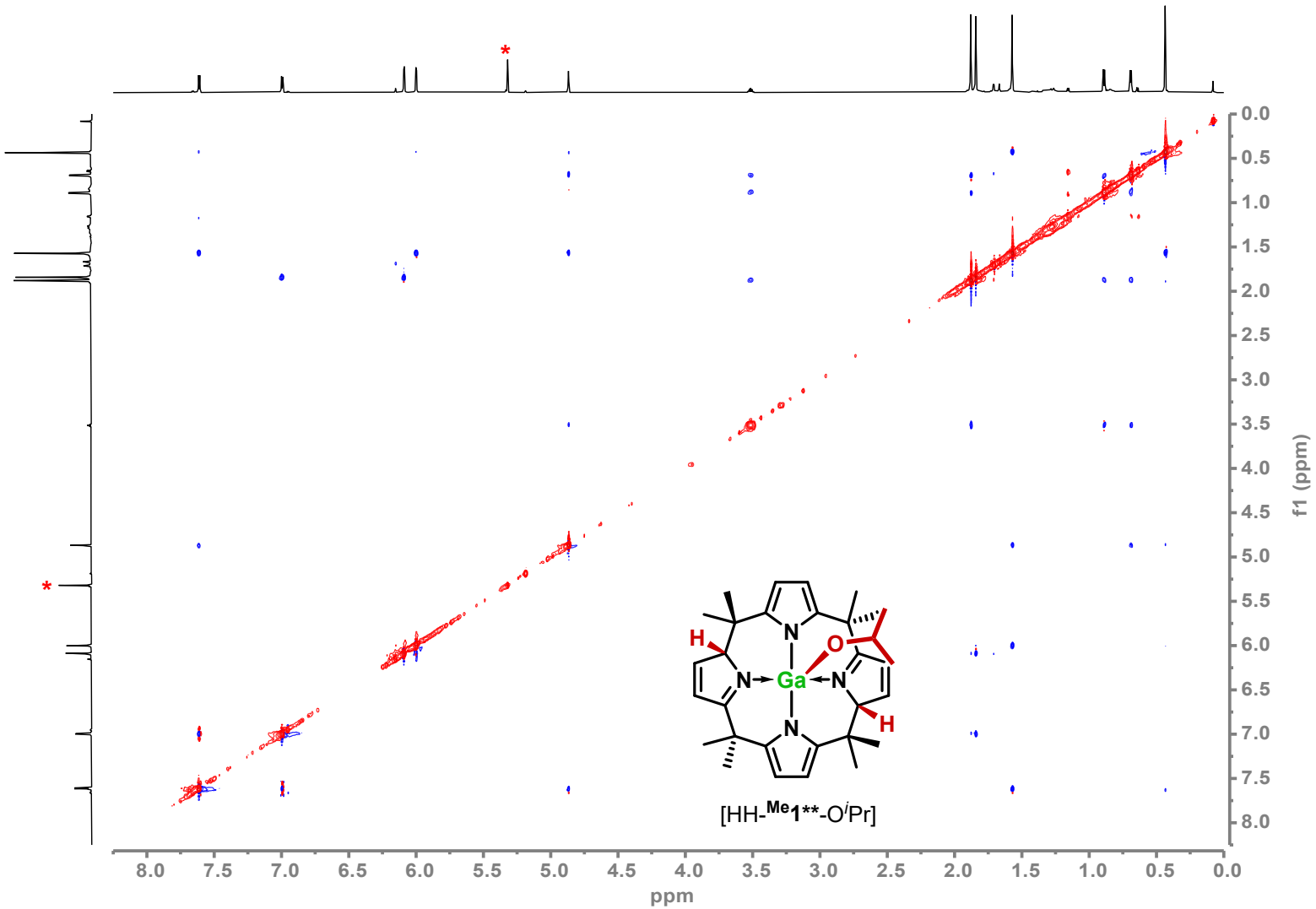


Figure S31. $^{1}H,^{1}H$ NOESY NMR spectrum (600.2 MHz, CD_2Cl_2, 295 K) of [HH-^{Me}**1****-O^{i}Pr]. The signal of $CHDCl_2$ is marked with a red asterisk.

S10. IR spectra

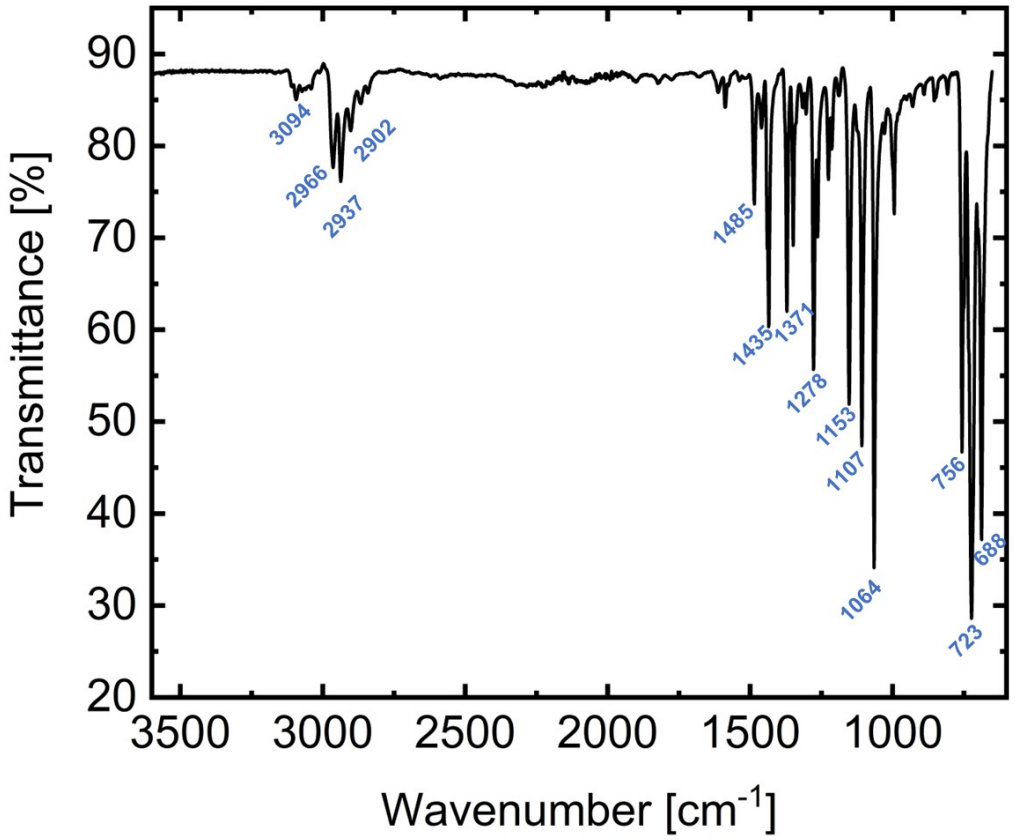


Figure S32. Solid state FT-ATR-IR spectrum of, $[PPh_4][^{Me}\mathbf{1}]$. The spectrum was acquired at room temperature.

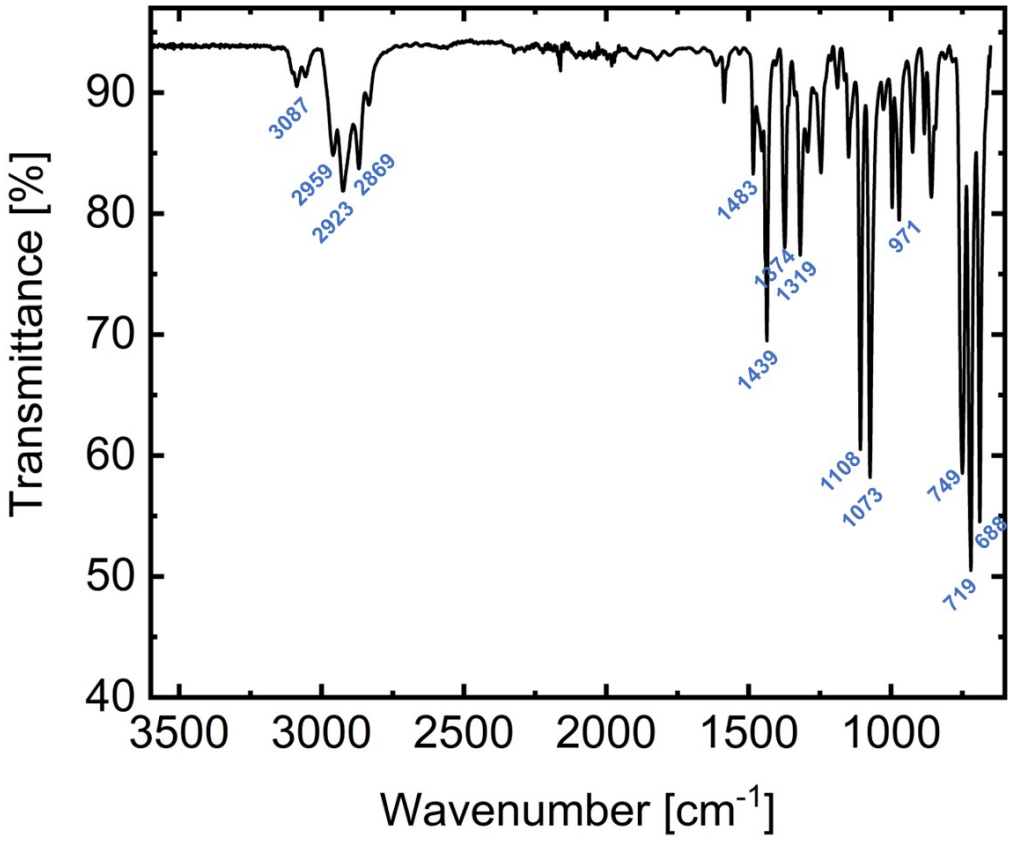


Figure S33. Solid state FT-ATR-IR spectrum of, $[PPh_4][^{Et}\mathbf{1}]$. The spectrum was acquired at room temperature.

S11. Xyz coordinates and energies from DFT calculations

[^{Me}1(Al)]$^-$

Total correction:	1492.6775 kJ/mol
Final entropy term:	218.5914 kJ/mol
Final single point energy:	-4058925.9228 kJ/mol
Final enthalpy:	-4057430.7663 kJ/mol
Final Gibbs free enthalpy:	-4057649.3577 kJ/mol
COSMO-RS correction (CH_2Cl_2, enthalpy):	-218.67 kJ/mol
COSMO-RS correction (CH_2Cl_2, Gibbs free energy):	-202.68 kJ/mol

xyz, charge: -1, multiplicity: 1

N	-0.138209	-2.216123	0.210180
C	-0.767462	-3.242779	0.893120
C	0.388090	-2.757013	-0.950417
C	-0.646370	-4.412331	0.173399
H	-1.048990	-5.378744	0.444614
C	0.101364	-4.104644	-0.997845
H	0.394298	-4.797605	-1.774749
N	-0.104342	-0.947039	2.590129
C	0.452540	-0.290646	3.674230
C	-0.739512	-2.076806	3.075875
C	0.179376	-0.997069	4.826108
C	-0.591616	-2.131227	4.445474
H	-0.991214	-2.889168	5.105397
N	0.101322	1.424022	1.322255
C	-0.336557	2.529515	0.613355
C	0.640786	1.885344	2.510679
C	-0.084091	3.670706	1.344487
H	-0.327563	4.684744	1.058074
C	0.550195	3.260398	2.550531
H	0.900700	3.904963	3.345077
N	0.068704	0.155001	-1.057089
C	0.577546	-0.580661	-2.113582
C	-0.364877	1.365222	-1.570784
C	0.472545	0.154211	-3.275243
H	0.799387	-0.150038	-4.260222
C	-0.139712	1.391850	-2.930623
H	-0.387038	2.198044	-3.607702
H	0.506213	-2.831305	-3.703989
C	1.458880	-2.644770	-3.198970
C	2.624039	-1.686385	-1.214915
C	1.236764	-1.915537	-1.870648
H	3.117602	-2.646006	-1.021380
H	1.958959	-3.603332	-3.026171
H	2.526549	-1.165189	-0.255226
H	-2.676431	-1.290126	1.274873
C	-2.868999	-2.240655	1.786474
C	-1.902085	-4.270969	2.860741
C	-1.543972	-2.959875	2.154835
H	-0.998227	-4.817282	3.147104
H	-3.465760	-2.864394	1.110670
H	-2.502775	-4.905440	2.200941
H	2.562963	-0.001283	1.920480
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C	1.567694	1.628491	4.810063
C	1.310484	0.933058	3.470062
H	2.077911	0.947676	5.499345
H	3.183054	-0.196872	3.565733
H	0.627452	1.951731	5.267137
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C	-2.512621	1.847767	-0.397454
C	-1.198854	3.708889	-1.406646
H	-3.068683	1.716912	-1.333270
H	-1.759766	3.592912	-2.339774
H	-2.491948	0.877279	0.112512
H	-0.209931	4.115734	-1.638949
H	-3.044211	2.552215	0.253012
H	-1.735259	4.426341	-0.777078
H	3.256105	-1.068982	-1.863865
H	2.095671	-2.046253	-3.858595

H	-2.490275	-4.067883	3.761697
H	-3.446563	-2.018225	2.691310
H	2.207772	2.504669	4.664295
H	3.319412	1.381016	2.725005
H	0.496046	-0.740302	5.827837
Al	-0.016213	-0.396149	0.766926

[^{Me}1]$^-$

Total correction:	1490.2337 kJ/mol
Final entropy term:	222.5634 kJ/mol
Final single point energy:	-8474889.7485 kJ/mol
Final enthalpy:	-8473397.0358 kJ/mol
Final Gibbs free enthalpy:	-8473619.5992 kJ/mol
COSMO-RS correction (CH_2Cl_2, enthalpy):	-217.23 kJ/mol
COSMO-RS correction (CH_2Cl_2, Gibbs free energy):	-201.56 kJ/mol
COSMO-RS correction (MeCN, Gibbs free energy):	-206.20 kJ/mol

xyz, charge: -1, multiplicity: 1

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C	0.351656	-2.783719	-0.984628
C	-0.628291	-4.453412	0.173479
H	-1.010740	-5.425584	0.453412
C	0.073489	-4.135267	-1.023269
H	0.344220	-4.825797	-1.810412
N	-0.105155	-0.960354	2.636057
C	0.419415	-0.277535	3.715852
C	-0.708616	-2.110276	3.105878
C	0.155248	-0.994050	4.865797
C	-0.570612	-2.155564	4.478662
H	-0.949971	-2.924384	5.138049
N	0.106963	1.470982	1.336285
C	-0.297972	2.569935	0.604132
C	0.609623	1.918672	2.542197
C	-0.057305	3.710128	1.344124
H	-0.279634	4.726855	1.049885
C	0.528830	3.296420	2.573355
H	0.856581	3.942033	3.376797
N	0.074212	0.169751	-1.103783
C	0.546663	-0.587471	-2.157738
C	-0.325598	1.395166	-1.599878
C	0.452230	0.156053	-3.316973
H	0.756234	-0.154873	-4.307228
C	-0.111605	1.414173	-2.963455
H	-0.337484	2.228077	-3.638919
H	0.407821	-2.841270	-3.741908
C	1.371767	-2.666216	-3.254322
C	2.586569	-1.726755	-1.291008
C	1.183168	-1.937063	-1.920007
H	3.071833	-2.693695	-1.113569
H	1.864539	-3.630330	-3.092817
H	2.513896	-1.209557	-0.327253
H	-2.666928	-1.362877	1.309274
C	-2.838079	-2.314357	1.825896
C	-1.822361	-4.326995	2.890063
C	-1.495386	-3.009030	2.180493
H	-0.905858	-4.856753	3.167462
H	-3.430775	-2.952101	1.159665
H	-2.417940	-4.972187	2.236340
H	2.553799	0.043088	1.993397
C	2.648086	0.547759	2.961923
C	1.481585	1.663131	4.860978
C	1.258594	0.963072	3.516480
H	1.985570	0.988791	5.560863
H	3.140686	-0.146615	3.652667
H	0.529120	1.976756	5.299229
C	-1.019814	2.402454	-0.712858
C	-2.465944	1.912059	-0.433371
C	-1.113489	3.752536	-1.431063
H	-3.014597	1.789973	-1.374712

H	-1.667444	3.644963	-2.369163
H	-2.463345	0.942218	0.077582
H	-0.116404	4.144577	-1.654178
H	-2.991753	2.626446	0.210913
H	-1.644966	4.477801	-0.806557
H	3.211885	-1.114533	-1.951316
H	2.002806	-2.073412	-3.924256
H	-2.405294	-4.134415	3.796494
H	-3.408549	-2.101116	2.737408
H	2.115074	2.545668	4.726652
H	3.277992	1.433081	2.816079
H	0.450566	-0.727659	5.871588
Ga	-0.013878	-0.395363	0.766606

[^{Me}**1**]$^-$ (tetrahedral configuration around gallium)

Final single point energy: -8474308.9351 kJ/mol

xyz, charge: -1, multiplicity: 1

Ga	-0.307682	-0.217675	0.701346
N	-1.449020	-1.530017	0.027451
N	0.821547	-0.973996	1.977396
N	0.711688	0.490224	-0.690632
N	-1.315620	1.140128	1.486998
C	-1.618675	-2.702809	0.756942
C	-1.112135	-1.958964	-1.302766
C	-1.875777	-3.741172	-0.120894
H	-2.115907	-4.763258	0.138178
C	-1.573119	-3.263489	-1.420485
H	-1.499108	-3.887262	-2.301410
C	1.083644	-0.257646	3.141067
C	0.400126	-2.274366	2.421542
C	1.307764	-1.151128	4.173827
C	0.893328	-2.425045	3.710877
H	0.774560	-3.297556	4.339500
C	-1.511766	2.319827	0.775585
C	-0.819992	1.552759	2.771681
C	-1.629047	3.367266	1.672301
H	-1.851783	4.398923	1.436684
C	-1.209126	2.875873	2.933779
H	-1.015642	3.495477	3.799402
C	0.818732	-0.232922	-1.874384
C	0.302481	1.808926	-1.089902
C	0.972585	0.653474	-2.926042
H	1.146145	0.402694	-3.963550
C	0.663684	1.942625	-2.424063
H	0.517547	2.821130	-3.038406
H	-0.418667	-1.534439	-3.980658
C	0.317512	-2.106433	-3.408797
C	1.328947	-2.582698	-1.174955
C	0.334625	-1.668447	-1.938372
H	1.050454	-3.635529	-1.281515
H	0.078197	-3.169134	-3.493102
H	1.366302	-2.356894	-0.105711
H	-1.983367	-0.896462	2.874811
C	-2.004683	-1.962627	3.116638
C	-1.178148	-4.267284	2.621377
C	-1.097619	-2.800405	2.177450
H	-0.501631	-4.893437	2.032858
H	-3.040650	-2.305273	3.002370
H	-2.202044	-4.636632	2.496877
H	1.537055	1.840989	1.316178
C	1.618817	2.068174	2.382813
C	0.830920	1.635029	4.712831
C	0.671782	1.197616	3.250219
H	1.855344	1.440505	5.049070
H	2.654614	1.867414	2.683588
H	0.135820	1.094735	5.361674
C	-1.138670	2.396631	-0.692102
C	-2.172954	1.599405	-1.529967
C	-1.203823	3.866237	-1.129509
H	-1.977021	1.712399	-2.600584

H	-1.047550	3.955931	-2.207061
H	-2.160620	0.530028	-1.302188
H	-0.446968	4.463542	-0.613266
H	-3.177424	1.974677	-1.297924
H	-2.194313	4.276596	-0.903989
H	2.335771	-2.424578	-1.581006
H	1.307245	-1.955415	-3.854044
H	-0.918678	-4.367088	3.678049
H	-1.693821	-2.073274	4.159903
H	0.647532	2.707021	4.816691
H	1.398015	3.131876	2.513258
H	1.600190	-0.909641	5.186560

CO_2

Total correction:	37.574 kJ/mol
Final entropy term:	63.7135 kJ/mol
Final single point energy:	-494668.7862 kJ/mol
Final enthalpy:	-494628.7332 kJ/mol
Final Gibbs free enthalpy:	-494692.4467 kJ/mol
COSMO-RS correction (CH_2Cl_2, enthalpy):	-10.78 kJ/mol
COSMO-RS correction (CH_2Cl_2, Gibbs free energy):	-4.79 kJ/mol

xyz, charge: 0, multiplicity: 1

C	0.000000	-0.000000	-0.000000
O	-0.000000	0.000000	1.163425
O	-0.000000	0.000000	-1.163425

$[^{Me}$**1(Al)***-$CO_2]^-$

Total correction:	1538.0601 kJ/mol
Final entropy term:	228.1614 kJ/mol
Final single point energy:	-4553662.9081 kJ/mol
Final enthalpy:	-4552122.369 kJ/mol
Final Gibbs free enthalpy:	-4552350.5304 kJ/mol
COSMO-RS correction (CH_2Cl_2, enthalpy):	-241.45 kJ/mol
COSMO-RS correction (CH_2Cl_2, Gibbs free energy):	-221.84 kJ/mol

xyz, charge: -1, multiplicity: 1

N	1.027226	-1.301385	0.944647
C	1.812849	-1.498191	3.215071
C	1.838531	-2.529802	4.346359
H	2.388766	-3.425594	4.035700
H	0.825394	-2.817527	4.644340
H	2.343865	-2.111357	5.221285
C	3.267297	-1.101635	2.865195
H	3.848778	-1.974790	2.541577
H	3.740163	-0.661302	3.748770
H	3.286888	-0.361292	2.060578
N	0.593920	0.670042	2.684922
C	-0.052100	1.664577	3.395680
C	1.001082	-0.278339	3.607045
C	-0.049086	1.348317	4.743316
H	-0.486009	1.929832	5.542779
C	0.621682	0.108636	4.878636
H	0.809358	-0.425899	5.800126
C	-0.742379	2.827668	2.711292
C	-2.116636	2.368108	2.157862
H	-2.735028	1.978608	2.975972
H	-2.013964	1.585043	1.404509
H	-2.627893	3.220389	1.694615
C	-1.015624	3.931774	3.743129
H	-1.529252	4.772392	3.266164
H	-0.084984	4.294361	4.190419
H	-1.667586	3.553952	4.537275
N	0.809946	2.563287	0.725874
C	1.515761	3.382765	-0.135562
C	0.120158	3.384736	1.601615
C	1.254595	4.703279	0.171423
H	1.672280	5.573240	-0.316617
C	0.361842	4.704379	1.274683

H	-0.040489	5.575736	1.772626
C	2.584585	2.828494	-1.049108
C	2.941645	3.859978	-2.124922
H	3.298664	4.783716	-1.659617
H	2.070876	4.096764	-2.744233
H	3.740457	3.476489	-2.768912
C	3.856820	2.563058	-0.199409
H	4.653354	2.139199	-0.823689
H	3.638595	1.853906	0.605607
H	4.204371	3.496749	0.257891
N	1.733597	0.468502	-0.933662
C	1.491933	-0.582311	-1.817820
C	2.164313	1.534177	-1.696718
C	1.768715	-0.168470	-3.106999
H	1.680798	-0.761873	-4.006985
C	2.206546	1.175800	-3.030106
H	2.504690	1.803077	-3.858530
C	1.153022	-1.997612	-1.397330
C	0.403373	-2.732565	-2.515306
H	1.040550	-2.787452	-3.402671
H	-0.526419	-2.225209	-2.778273
H	0.168764	-3.759187	-2.213826
C	2.464352	-2.760161	-1.105138
H	3.064557	-2.777336	-2.019901
H	2.270848	-3.793145	-0.789473
H	3.050181	-2.255035	-0.332541
C	1.162130	-2.064032	1.982630
C	0.276278	-1.984576	-0.083002
C	0.531388	-3.358972	1.752056
H	0.479937	-4.171214	2.465231
C	-0.021186	-3.311701	0.520915
H	-0.612919	-4.075893	0.034807
Al	0.736874	0.664178	0.732350
O	-0.913718	0.103904	0.070459
C	-1.030983	-1.122003	-0.330227
O	-1.997111	-1.637173	-0.859611

[^{Me}**1***-CO_2]$^-$

Total correction:	1535.4599 kJ/mol
Final entropy term:	232.1462 kJ/mol
Final single point energy:	-8969597.7595 kJ/mol
Final enthalpy:	-8968059.8206 kJ/mol
Final Gibbs free enthalpy:	-8968291.9668 kJ/mol
COSMO-RS correction (CH_2Cl_2, enthalpy):	-239.96 kJ/mol
COSMO-RS correction (CH_2Cl_2, Gibbs free energy):	-220.49 kJ/mol

xyz, charge: -1, multiplicity: 1

N	1.051056	-1.350948	0.951458
C	1.750108	-1.535900	3.255557
C	1.737938	-2.571474	4.383753
H	2.285178	-3.472090	4.082117
H	0.715021	-2.849628	4.656501
H	2.227236	-2.162006	5.271874
C	3.216758	-1.151882	2.943959
H	3.795818	-2.028954	2.626799
H	3.673063	-0.724015	3.842315
H	3.262169	-0.405368	2.146377
N	0.588797	0.668527	2.732556
C	-0.039259	1.678110	3.431943
C	0.950536	-0.304930	3.642761
C	-0.070188	1.346855	4.776825
H	-0.503449	1.932896	5.575119
C	0.558201	0.084811	4.911112
H	0.712182	-0.462331	5.831464
C	-0.694555	2.859183	2.739784
C	-2.057699	2.415959	2.146435
H	-2.699987	2.023237	2.944134
H	-1.942898	1.637243	1.389583
H	-2.550265	3.275556	1.676677
C	-0.981450	3.954752	3.776179
H	-1.475048	4.805184	3.295443

H	-0.058093	4.303686	4.248998
H	-1.654798	3.575391	4.551315
N	0.829111	2.616369	0.734465
C	1.535475	3.422174	-0.133385
C	0.186271	3.426742	1.649242
C	1.323956	4.742936	0.215313
H	1.751551	5.612329	-0.265211
C	0.463674	4.745897	1.344877
H	0.101281	5.618320	1.870987
C	2.551452	2.853472	-1.100939
C	2.857802	3.886326	-2.191867
H	3.243040	4.807234	-1.743969
H	1.956791	4.129806	-2.763392
H	3.619723	3.500221	-2.877511
C	3.863507	2.581576	-0.316095
H	4.624938	2.153619	-0.980026
H	3.684645	1.873339	0.499129
H	4.237978	3.514376	0.121114
N	1.770365	0.465131	-0.966047
C	1.489599	-0.582959	-1.839566
C	2.103301	1.559532	-1.737368
C	1.660326	-0.142944	-3.138817
H	1.526885	-0.726332	-4.039541
C	2.058095	1.215356	-3.074965
H	2.280889	1.858036	-3.915318
C	1.216468	-2.007702	-1.400205
C	0.518117	-2.791518	-2.517469
H	1.162761	-2.814718	-3.401039
H	-0.439780	-2.343124	-2.786755
H	0.344524	-3.827916	-2.208569
C	2.556503	-2.705631	-1.081085
H	3.158023	-2.737700	-1.994933
H	2.399195	-3.732418	-0.726322
H	3.122181	-2.151938	-0.327445
C	1.132669	-2.101147	2.003010
C	0.322269	-2.021935	-0.095497
C	0.502647	-3.394125	1.752979
H	0.413045	-4.202462	2.467054
C	0.005994	-3.351062	0.497485
H	-0.574861	-4.112125	-0.006220
Ga	0.756979	0.678705	0.738498
O	-0.959580	0.039573	0.039203
C	-1.004056	-1.184626	-0.371070
O	-1.930896	-1.734469	-0.938527

C-C bond formation/cleavage transition structure between CO_2 and [**Me1(Al)**]$^-$

Total correction:	1532.8285 kJ/mol
Final entropy term:	234.4021 kJ/mol
Final single point energy:	-4553573.8917 kJ/mol
Final enthalpy:	-4552038.5842 kJ/mol
Final Gibbs free enthalpy:	-4552272.9863 kJ/mol
COSMO-RS correction (CH_2Cl_2, enthalpy):	-214.77 kJ/mol
COSMO-RS correction (CH_2Cl_2, Gibbs free energy):	-200.13 kJ/mol

xyz, charge: -1, multiplicity: 1

Al	2.050345	7.999915	12.964976
O	3.191684	7.780519	11.240846
N	3.682885	7.537810	13.959969
N	0.333842	8.471385	12.240288
N	2.557028	9.847652	13.164760
N	1.463876	6.154005	13.091634
C	1.713785	10.936340	13.056443
C	-0.506407	7.655677	11.491535
C	1.881039	5.197116	14.004011
C	3.851486	10.327264	13.027744
C	2.812520	5.544902	15.137993
C	-0.309108	9.692814	12.368690
C	3.947876	6.359738	14.587083
C	2.054738	6.371112	16.206433
H	1.652527	7.296623	15.782104
H	2.725036	6.645272	17.030243

H	1.214006	5.787781	16.597899
C	-1.515311	9.657956	11.703688
H	-2.238226	10.459456	11.641155
C	4.899695	8.044567	13.492861
C	0.534224	5.533699	12.265602
C	2.449990	12.082673	12.841839
H	2.062274	13.085014	12.724116
C	0.392663	4.213075	12.644002
H	-0.254074	3.478988	12.184490
C	3.811284	11.692496	12.814408
H	4.664893	12.344691	12.678939
C	4.236457	7.199651	11.229997
C	1.246633	3.999781	13.754334
H	1.367631	3.079903	14.309746
C	-0.156177	6.235187	11.117829
C	0.234571	10.773239	13.266675
C	-1.637676	8.362987	11.139613
H	-2.467681	7.996979	10.551647
C	5.911168	7.146651	13.848541
H	6.968811	7.274015	13.653889
C	5.313138	6.083974	14.539832
H	5.805533	5.206699	14.935650
C	-1.448544	5.472929	10.775559
H	-2.124001	5.441926	11.635224
H	-1.214357	4.448258	10.470373
H	-1.961564	5.955625	9.938175
C	5.118692	9.519285	13.204976
C	-0.028686	10.381492	14.745237
H	0.458313	9.431856	14.991997
H	-1.104419	10.261145	14.919026
H	0.370770	11.147950	15.420389
C	0.719716	6.204766	9.837079
H	0.165521	6.648309	9.001365
H	0.982568	5.169576	9.587820
H	1.639468	6.774084	9.964569
C	3.342558	4.273615	15.806719
H	2.516885	3.707751	16.249451
H	4.045893	4.533704	16.605500
H	3.851857	3.630568	15.082257
C	-0.485985	12.097872	12.997849
H	-0.096011	12.879534	13.658337
H	-1.557815	11.993226	13.193438
H	-0.349380	12.412994	11.958707
C	5.862394	10.099783	14.443068
H	6.022639	11.176297	14.323897
H	6.830242	9.604021	14.580322
H	5.259231	9.939481	15.341977
C	6.037332	9.701852	11.977868
H	5.515643	9.441702	11.051032
H	6.934154	9.077045	12.061356
H	6.351796	10.746941	11.891582
O	5.110087	6.536341	10.843001

C-C bond formation/cleavage transition structure between CO_2 and [^{Me}**1**]$^-$

Total correction:	1531.267 kJ/mol
Final entropy term:	238.0944 kJ/mol
Final single point energy:	-8969527.9306 kJ/mol
Final enthalpy:	-8967994.1847 kJ/mol
Final Gibbs free enthalpy:	-8968232.2791 kJ/mol
COSMO-RS correction (CH_2Cl_2, enthalpy):	-208.91 kJ/mol
COSMO-RS correction (CH_2Cl_2, Gibbs free energy):	-195.80 kJ/mol

xyz, charge: -1, multiplicity: 1

Ga	2.015080	7.964577	12.985070
O	3.225496	7.620702	11.130081
N	3.743350	7.491287	13.931448
N	0.252475	8.464681	12.243857
N	2.591441	9.872700	13.103380
N	1.397829	6.077518	13.154366
C	1.768354	10.933338	12.780196
C	-0.648302	7.618683	11.611745

C	1.868093	5.121423	14.036793
C	3.898749	10.287095	12.873584
C	2.962038	5.416137	15.030683
C	-0.339414	9.714769	12.308764
C	4.030734	6.234053	14.362914
C	2.388409	6.215998	16.227676
H	1.931085	7.152191	15.894052
H	3.182355	6.464729	16.942790
H	1.617846	5.621413	16.730578
C	-1.585016	9.664307	11.721111
H	-2.284876	10.483131	11.628573
C	4.909756	8.030006	13.386310
C	0.362886	5.493956	12.437774
C	2.527974	11.995080	12.335139
H	2.160436	12.961280	12.018239
C	0.191493	4.192559	12.867577
H	-0.529970	3.481828	12.490055
C	3.883760	11.581324	12.389812
H	4.748210	12.182804	12.142944
C	4.404829	7.759439	11.015068
C	1.146768	3.956260	13.886285
H	1.285133	3.039226	14.442305
C	-0.339151	6.178710	11.290515
C	0.292839	10.858194	13.056809
C	-1.779047	8.333562	11.273811
H	-2.650906	7.951112	10.762062
C	5.919667	7.062214	13.486344
H	6.947116	7.185442	13.169344
C	5.365509	5.928522	14.100815
H	5.866996	4.995305	14.315988
C	-1.650166	5.435655	10.987460
H	-2.319386	5.445427	11.853040
H	-1.439755	4.397483	10.712977
H	-2.160202	5.902947	10.139764
C	5.088536	9.536264	13.417371
C	0.079120	10.651219	14.580354
H	0.528670	9.711391	14.916876
H	-0.992823	10.613689	14.806370
H	0.545744	11.467765	15.144777
C	0.528417	6.093215	10.006920
H	-0.010804	6.545816	9.166252
H	0.748223	5.044190	9.774617
H	1.473375	6.621745	10.126474
C	3.556923	4.111223	15.570490
H	2.795898	3.544628	16.115627
H	4.379163	4.330502	16.260483
H	3.933860	3.484444	14.756525
C	-0.381176	12.177675	12.665715
H	0.076569	13.009267	13.211863
H	-1.445162	12.149126	12.919982
H	-0.285321	12.363696	11.591449
C	5.228152	9.923267	14.920345
H	5.384399	11.004236	15.011719
H	6.074120	9.391772	15.373979
H	4.316422	9.655918	15.461365
C	6.378719	9.967386	12.709954
H	6.346714	9.765365	11.637551
H	7.240718	9.448207	13.141273
H	6.536770	11.040164	12.854597
O	5.426232	7.848296	10.448626

[^{Et}**1***-CO_2]$^-$

Total correction:	2159.3781 kJ/mol
Final entropy term:	288.7068 kJ/mol
Final single point energy:	-9794157.1075 kJ/mol
Final enthalpy:	-9791995.2504 kJ/mol
Final Gibbs free enthalpy:	-9792283.9572 kJ/mol
COSMO-RS correction (CH_2Cl_2, enthalpy):	-225.03 kJ/mol
COSMO-RS correction (CH_2Cl_2, Gibbs free energy):	-211.94 kJ/mol

xyz, charge: -1, multiplicity: 1

N	-1.715939	0.702610	-0.058000
C	-1.240228	2.816484	1.015391
C	-1.876591	4.209235	1.168540
H	-1.143806	4.870398	1.642580
H	-2.047322	4.622170	0.166408
C	-1.062665	2.121125	2.396341
H	-2.049535	1.938757	2.842786
H	-0.625498	1.133753	2.220468
N	0.830831	1.789797	-0.007941
C	2.046000	2.209043	-0.506921
C	0.100435	2.917175	0.311493
C	2.072392	3.595913	-0.522640
H	2.887688	4.219882	-0.863085
C	0.838847	4.046395	0.001183
H	0.545967	5.075726	0.157663
C	3.098767	1.262051	-1.058004
C	2.783228	1.062567	-2.579114
H	2.820062	2.054651	-3.050733
H	1.748838	0.718036	-2.672908
C	4.490711	1.930907	-0.935314
H	4.492847	2.823092	-1.575894
H	5.233353	1.252467	-1.369404
N	1.978214	-0.757072	0.009855
C	2.343707	-1.947411	0.605488
C	3.125387	-0.073759	-0.346892
C	3.726722	-2.028929	0.599473
H	4.325515	-2.831167	1.009678
C	4.218636	-0.851040	-0.008915
H	5.259117	-0.606861	-0.174545
C	1.411794	-2.875392	1.359181
C	1.899211	-4.334974	1.149380
H	1.301584	-4.994660	1.790621
H	2.930845	-4.410903	1.514857
C	1.550267	-2.560535	2.884783
H	2.607182	-2.679674	3.159365
H	0.970379	-3.312536	3.438710
N	-0.668160	-1.777169	0.319764
C	-2.020779	-2.062582	0.235947
C	-0.057324	-2.809438	0.995875
C	-2.261276	-3.263951	0.881349
H	-3.214290	-3.773449	0.950092
C	-1.021759	-3.736026	1.364726
H	-0.857651	-4.652905	1.914840
C	-3.058523	-1.313278	-0.584078
C	-3.511434	-2.185898	-1.798452
H	-3.987356	-1.536030	-2.544719
H	-4.291317	-2.863346	-1.425420
C	-4.324523	-1.101992	0.298665
H	-4.695500	-2.104231	0.543405
H	-5.104728	-0.631475	-0.318021
C	-2.084351	1.930578	0.134964
C	-2.532683	0.084925	-1.081010
C	-3.256873	2.242771	-0.681801
H	-3.758841	3.200046	-0.730502
C	-3.546590	1.136224	-1.394462
H	-4.315909	1.023053	-2.146934
Ga	0.186845	-0.093727	-0.256463
O	-0.340237	-0.157185	-2.132553
C	-1.603259	-0.053902	-2.381080
O	-2.129711	-0.056290	-3.478952
C	3.694937	0.087349	-3.320320
H	3.344231	-0.042161	-4.350395
H	4.732534	0.437146	-3.364505
H	3.691326	-0.892541	-2.831992
C	4.925136	2.313737	0.480043
H	5.938870	2.732907	0.469251
H	4.249560	3.057728	0.911230
H	4.921179	1.440317	1.138253
C	1.824270	-4.812716	-0.297398
H	0.792350	-4.768571	-0.660858
H	2.439286	-4.177312	-0.942672
H	2.179291	-5.846069	-0.387941
C	1.071615	-1.165206	3.269227

H	0.006067	-1.051405	3.037305
H	1.204338	-0.985096	4.342312
H	1.630034	-0.394879	2.724336
C	-2.432784	-3.038183	-2.467940
H	-2.867710	-3.575657	-3.318671
H	-1.598159	-2.447571	-2.849880
H	-2.030821	-3.769186	-1.760253
C	-4.141635	-0.331153	1.604381
H	-3.253373	-0.692220	2.133095
H	-4.033912	0.743535	1.441585
H	-5.011848	-0.483223	2.253375
C	-3.171529	4.236270	1.982371
H	-2.985149	4.034871	3.042044
H	-3.646398	5.221228	1.913479
H	-3.896391	3.491898	1.634079
C	-0.165302	2.893621	3.356098
H	0.019871	2.301661	4.258493
H	0.798469	3.111094	2.883635
H	-0.612036	3.844969	3.666767

[^{Et}**1**]$^-$

Total correction:	2115.313 kJ/mol
Final entropy term:	279.5584 kJ/mol
Final single point energy:	-9299455.5947 kJ/mol
Final enthalpy:	-9297337.8027 kJ/mol
Final Gibbs free enthalpy:	-9297617.3611 kJ/mol
COSMO-RS correction (CH_2Cl_2, enthalpy):	-209.14 kJ/mol
COSMO-RS correction (CH_2Cl_2, Gibbs free energy):	-199.11 kJ/mol

xyz, charge: -1, multiplicity: 1

N	1.901688	-0.235062	-0.092758
C	2.283303	1.907805	-1.377948
C	3.475516	2.841844	-1.682175
H	4.130285	2.322830	-2.395215
H	3.090753	3.722928	-2.208741
C	1.618662	1.492733	-2.736119
H	2.396642	1.028420	-3.358013
H	0.894033	0.693671	-2.521669
N	0.186264	1.947963	0.014885
C	-0.662902	2.877426	0.589723
C	1.259672	2.623565	-0.531500
C	-0.120422	4.136417	0.407720
H	-0.539691	5.073545	0.748225
C	1.087198	3.976942	-0.316161
H	1.736550	4.772059	-0.656427
C	-1.880043	2.507012	1.404557
C	-1.458945	2.290074	2.895535
H	-2.377037	2.132729	3.478894
H	-0.990166	3.219458	3.247866
C	-2.872564	3.698999	1.403516
H	-2.363991	4.564801	1.846985
H	-3.695022	3.454083	2.087500
N	-1.987438	0.273772	0.162278
C	-2.932033	-0.697652	-0.100149
C	-2.595551	1.273493	0.901719
C	-4.128261	-0.330895	0.482240
H	-5.060701	-0.877347	0.445272
C	-3.912345	0.916598	1.123934
H	-4.654484	1.498397	1.654658
C	-2.549093	-1.910168	-0.915034
C	-3.750958	-2.862615	-1.073628
H	-4.158090	-3.052718	-0.073116
H	-3.379770	-3.826606	-1.439869
C	-2.044532	-1.446154	-2.315861
H	-1.231226	-0.720209	-2.175276
H	-2.847000	-0.881615	-2.807307
N	-0.262716	-1.948788	0.099521
C	0.635345	-2.859145	0.629783
C	-1.428828	-2.626930	-0.199544
C	0.023360	-4.094758	0.697117
H	0.462616	-5.009458	1.072457

C	-1.283257	-3.951237	0.156917
H	-2.013751	-4.738586	0.032565
C	2.001942	-2.446836	1.127568
C	1.816788	-1.908286	2.586719
H	1.426571	-2.735264	3.196137
H	1.021733	-1.153589	2.561455
C	2.935341	-3.678400	1.175533
H	2.516045	-4.385939	1.903682
H	3.900521	-3.360583	1.587041
C	2.772213	0.636005	-0.723156
C	2.614453	-1.364142	0.272566
C	4.024574	0.056571	-0.766807
H	4.914128	0.479383	-1.213891
C	3.928558	-1.201874	-0.119130
H	4.742197	-1.892677	0.055807
Ga	-0.040450	0.004339	0.046132
C	-0.510984	1.120512	3.127528
H	-0.968606	0.180149	2.792539
H	0.439569	1.272137	2.601686
H	-0.278428	1.003828	4.192199
C	-3.438200	4.071053	0.035487
H	-2.635195	4.339906	-0.657185
H	-3.987729	3.227854	-0.394059
H	-4.122701	4.923683	0.119711
C	-4.860661	-2.381040	-2.012042
H	-5.159479	-1.351274	-1.796497
H	-4.547528	-2.423067	-3.060921
H	-5.745293	-3.020480	-1.911036
C	-1.534112	-2.571009	-3.210552
H	-1.138581	-2.167777	-4.149442
H	-0.734734	-3.126221	-2.708393
H	-2.327332	-3.284093	-3.462061
C	3.053591	-1.292685	3.235092
H	3.861090	-2.022374	3.359882
H	3.439100	-0.468369	2.626560
H	2.804117	-0.901762	4.228426
C	3.169816	-4.396963	-0.154675
H	2.231663	-4.775856	-0.567968
H	3.607265	-3.723397	-0.896059
H	3.852827	-5.243677	-0.013279
C	4.295487	3.299672	-0.473747
H	5.092163	3.982879	-0.792652
H	3.667207	3.819850	0.253642
H	4.753523	2.450874	0.039528
C	0.904074	2.605473	-3.497725
H	1.595264	3.390983	-3.821890
H	0.419889	2.200810	-4.393887
H	0.137925	3.071677	-2.870194

C-C bond formation/cleavage transition structure between CO_2 and [^{Et}**1**]$^-$

Total correction:	2154.8513 kJ/mol
Final entropy term:	293.5869 kJ/mol
Final single point energy:	-9794093.8576 kJ/mol
Final enthalpy:	-9791936.5273 kJ/mol
Final Gibbs free enthalpy:	-9792230.1142 kJ/mol
COSMO-RS correction (CH_2Cl_2, enthalpy):	-198.32 kJ/mol
COSMO-RS correction (CH_2Cl_2, Gibbs free energy):	-191.13 kJ/mol

xyz, charge: -1, multiplicity: 1

Ga	2.044038	7.996140	13.021553
O	3.264583	7.476879	11.244518
N	3.727382	7.546216	14.054527
N	0.343796	8.493036	12.185629
N	2.594988	9.891907	13.193043
N	1.401503	6.118033	13.191927
C	1.730279	10.969251	13.272790
C	-0.519750	7.643059	11.509090
C	1.937998	5.135058	14.001487
C	3.853865	10.343440	13.560884
C	2.877071	5.487693	15.129376
C	-0.250858	9.743586	12.237563

C	3.992339	6.298564	14.522283
C	2.132642	6.352453	16.188125
H	1.781698	7.267462	15.700437
H	2.851993	6.683683	16.948576
C	-1.467207	9.685568	11.583009
H	-2.172822	10.496202	11.464127
C	4.890035	8.046914	13.471305
C	0.545260	5.493870	12.298246
C	2.435021	12.084062	13.690987
H	2.032797	13.074992	13.852312
C	0.565967	4.131628	12.537204
H	-0.002819	3.379399	12.007171
C	3.778402	11.688642	13.866979
H	4.605863	12.329603	14.141703
C	4.455969	7.377251	11.174541
C	1.443506	3.903631	13.623275
H	1.667920	2.949257	14.078855
C	-0.226127	6.195494	11.200090
C	0.236286	10.895818	13.081200
C	-1.631421	8.364334	11.116393
H	-2.475809	7.987937	10.555781
C	5.885756	7.062034	13.596797
H	6.913305	7.159253	13.268008
C	5.321779	5.962248	14.254835
H	5.812995	5.028600	14.491288
C	-1.568941	5.443995	10.987608
H	-1.332705	4.432345	10.633012
H	-2.110306	5.925342	10.166632
C	5.130532	9.548661	13.448390
C	-0.444784	10.807139	14.488271
H	-1.532530	10.807855	14.333228
H	-0.180979	11.719515	15.041948
C	0.604598	6.068885	9.877307
H	0.773379	4.997263	9.703256
H	1.588030	6.509561	10.057057
C	3.427955	4.200517	15.771592
H	2.581461	3.552955	16.026209
H	4.001770	3.659469	15.009461
C	-0.247185	12.225337	12.441796
H	0.014169	13.045435	13.121345
H	-1.343310	12.210039	12.404191
C	6.023271	9.861543	14.692166
H	6.181366	10.946900	14.734713
H	7.007934	9.406668	14.513598
C	5.945459	10.004955	12.195277
H	6.638978	9.200666	11.916735
H	6.568464	10.857366	12.498851
O	5.470826	7.173770	10.624024
C	5.122327	10.442211	10.984042
H	5.775579	10.613241	10.120828
H	4.366795	9.710241	10.688013
H	4.581469	11.366874	11.206424
C	4.283917	4.414625	17.020958
H	3.681834	4.761360	17.867470
H	4.760945	3.474821	17.321678
H	5.071863	5.155149	16.849224
C	0.938975	5.655099	16.831889
H	0.250328	5.292106	16.061224
H	1.241247	4.797796	17.444339
H	0.394609	6.350745	17.479883
C	-0.006846	6.716346	8.636352
H	0.691239	6.646933	7.793988
H	-0.939245	6.229115	8.331028
H	-0.222913	7.774300	8.817165
C	-2.478964	5.363256	12.211871
H	-3.410369	4.839440	11.964101
H	-1.987629	4.825838	13.028237
H	-2.733666	6.364656	12.571591
C	-0.043970	9.588186	15.310862
H	-0.325430	8.657004	14.804468
H	1.038148	9.583948	15.490201
H	-0.540188	9.594649	16.288236
C	0.318402	12.506822	11.052866

H	1.411465	12.554332	11.088460
H	0.035507	11.714338	10.353167
H	-0.056861	13.461671	10.665681
C	5.458367	9.372141	16.020763
H	4.444443	9.758412	16.168952
H	5.414143	8.278778	16.055194
H	6.083679	9.715377	16.853352

[^{Me}1(Al)-F]$^{2-}$

Total correction:	1497.7336 kJ/mol
Final entropy term:	224.3199 kJ/mol
Final single point energy:	-4321015.6096 kJ/mol
Final enthalpy:	-4319515.397 kJ/mol
Final Gibbs free enthalpy:	-4319739.7169 kJ/mol
COSMO-RS correction (CH_2Cl_2, enthalpy):	-627.36 kJ/mol
COSMO-RS correction (CH_2Cl_2, Gibbs free energy):	-597.38 kJ/mol

xyz, charge: -2, multiplicity: 1

N	-0.275580	-2.249291	0.227659
C	-0.808187	-3.318247	0.920913
C	0.261339	-2.751327	-0.935184
C	-0.626305	-4.482625	0.188555
H	-0.935917	-5.480024	0.472572
C	0.062981	-4.121421	-0.996500
H	0.387027	-4.788895	-1.784716
N	-0.242362	-0.978070	2.611141
C	0.324155	-0.298196	3.664412
C	-0.776872	-2.143801	3.123955
C	0.143624	-1.009126	4.840097
C	-0.565746	-2.187010	4.494540
H	-0.869678	-2.975169	5.171110
N	-0.027546	1.480438	1.296877
C	-0.358810	2.613691	0.580064
C	0.517293	1.902609	2.487290
C	-0.043653	3.741426	1.324078
H	-0.185730	4.772541	1.027334
C	0.522258	3.287295	2.542000
H	0.900862	3.902716	3.348063
N	-0.059088	0.208972	-1.086240
C	0.455524	-0.550729	-2.111008
C	-0.391830	1.437598	-1.621956
C	0.440003	0.173397	-3.292361
H	0.793159	-0.157671	-4.260577
C	-0.107516	1.443265	-2.979933
H	-0.257944	2.264371	-3.668783
H	0.418581	-2.815817	-3.694415
C	1.358514	-2.618460	-3.168421
C	2.473006	-1.646235	-1.162878
C	1.098791	-1.888432	-1.845038
H	2.971635	-2.603079	-0.959722
H	1.864502	-3.572113	-2.981492
H	2.334180	-1.127010	-0.210526
H	-3.113027	-1.874941	1.601953
C	-2.989104	-2.832697	2.107479
C	-1.426025	-4.537581	2.993592
C	-1.484254	-3.178319	2.270629
H	-0.390732	-4.857438	3.149011
H	-3.481591	-3.615823	1.515166
H	-1.948207	-5.299540	2.404493
H	2.369791	-0.008138	1.869269
C	2.528853	0.487252	2.831134
C	1.461526	1.620492	4.775896
C	1.169082	0.930148	3.438150
H	1.978443	0.931282	5.452979
H	3.031691	-0.222075	3.501519
H	0.533679	1.952865	5.253173
C	-0.979869	2.569369	-0.802261
C	-2.525143	2.451149	-0.714214
C	-0.684139	3.901205	-1.518422
H	-2.952838	2.462149	-1.726052
H	-1.142842	3.903298	-2.513215

H	-2.813535	1.524514	-0.217732
H	0.393667	4.060255	-1.624253
H	-2.925497	3.300723	-0.144541
H	-1.112920	4.736177	-0.953563
H	3.111475	-1.022016	-1.801674
H	2.003430	-2.012779	-3.814752
H	-1.926624	-4.470037	3.965790
H	-3.462048	-2.778897	3.097466
H	2.107804	2.490886	4.617778
H	3.172633	1.360478	2.662675
H	0.491741	-0.729937	5.826343
Al	-0.550865	-0.354351	0.752231
F	-2.267535	-0.228664	0.706682

$[^{Me}\mathbf{1}\text{-F}]^{2-}$

Total correction:	1495.2033 kJ/mol
Final entropy term:	228.5276 kJ/mol
Final single point energy:	-8736930.021 kJ/mol
Final enthalpy:	-8735432.3387 kJ/mol
Final Gibbs free enthalpy:	-8735660.8663 kJ/mol
COSMO-RS correction (CH_2Cl_2, enthalpy):	-627.87 kJ/mol
COSMO-RS correction (CH_2Cl_2, Gibbs free energy):	-597.73 kJ/mol
COSMO-RS correction (MeCN, Gibbs free energy):	-616.80 kJ/mol

xyz, charge: -2, multiplicity: 1

N	-0.281186	-2.289109	0.219082
C	-0.779816	-3.357406	0.932003
C	0.229404	-2.774621	-0.960211
C	-0.600197	-4.519622	0.193676
H	-0.886930	-5.521830	0.484943
C	0.049154	-4.148982	-1.011466
H	0.360768	-4.814995	-1.805997
N	-0.246949	-0.993182	2.648726
C	0.293619	-0.290350	3.697938
C	-0.747990	-2.175309	3.149195
C	0.131204	-1.012378	4.871114
C	-0.538663	-2.212497	4.521308
H	-0.819600	-3.009617	5.197428
N	-0.027505	1.520109	1.305287
C	-0.324530	2.647430	0.570465
C	0.487957	1.929952	2.510753
C	-0.012106	3.773426	1.320272
H	-0.130337	4.805862	1.017485
C	0.511619	3.316160	2.556297
H	0.877419	3.932150	3.367909
N	-0.060498	0.223884	-1.124218
C	0.424376	-0.554991	-2.146500
C	-0.359000	1.463630	-1.646036
C	0.426845	0.176977	-3.324690
H	0.766476	-0.158655	-4.296242
C	-0.078405	1.463243	-3.005890
H	-0.205755	2.289723	-3.693068
H	0.346183	-2.826141	-3.723622
C	1.292797	-2.633870	-3.207729
C	2.434852	-1.669207	-1.213064
C	1.051554	-1.903475	-1.880722
H	2.930145	-2.629410	-1.017934
H	1.795981	-3.589991	-3.027044
H	2.309427	-1.151143	-0.258020
H	-3.073085	-1.916445	1.620295
C	-2.947906	-2.873843	2.128482
C	-1.373977	-4.574558	3.012447
C	-1.442452	-3.216132	2.290024
H	-0.336423	-4.888844	3.165334
H	-3.439979	-3.658583	1.537971
H	-1.893075	-5.339180	2.424290
H	2.348748	0.020273	1.917008
C	2.493167	0.517303	2.880506
C	1.395379	1.645293	4.812411
C	1.123035	0.951916	3.471618
H	1.908882	0.960018	5.495750

H	2.992239	-0.188061	3.557790
H	0.459966	1.972018	5.278770
C	-0.932365	2.600208	-0.819508
C	-2.477965	2.487693	-0.733721
C	-0.624801	3.929306	-1.534655
H	-2.904371	2.500074	-1.746087
H	-1.079855	3.933825	-2.530978
H	-2.769992	1.560719	-0.237625
H	0.454517	4.081395	-1.636985
H	-2.876214	3.337883	-0.163501
H	-1.049748	4.767136	-0.971349
H	3.068657	-1.047162	-1.858519
H	1.933663	-2.031009	-3.860360
H	-1.872317	-4.509818	3.985872
H	-3.419723	-2.817639	3.118860
H	2.037937	2.519398	4.661157
H	3.132336	1.395280	2.719664
H	0.467009	-0.727164	5.859958
Ga	-0.562016	-0.353541	0.752045
F	-2.387891	-0.218946	0.705247

$(CH_3)_3SiF$

Total correction:	318.1492 kJ/mol
Final entropy term:	107.9297 kJ/mol
Final single point energy:	-1335564.7624 kJ/mol
Final enthalpy:	-1335244.1342 kJ/mol
Final Gibbs free enthalpy:	-1335352.0639 kJ/mol
COSMO-RS correction (CH_2Cl_2, enthalpy):	-25.15 kJ/mol
COSMO-RS correction (CH_2Cl_2, Gibbs free energy):	-18.37 kJ/mol

xyz, charge: 0, multiplicity: 1

C	-5.642239	3.687375	-0.530028
Si	-5.671513	2.051753	0.368791
H	-4.614951	4.002335	-0.742713
H	-6.118826	4.473277	0.065811
H	-6.176497	3.620442	-1.484709
C	-7.410243	1.540490	0.815579
H	-7.902916	2.307397	1.422973
H	-7.412011	0.605938	1.386926
H	-8.017058	1.384398	-0.083680
C	-4.785190	0.719337	-0.591992
H	-5.284747	0.526555	-1.548321
H	-4.761257	-0.221323	-0.031271
H	-3.751059	1.009483	-0.806893
F	-4.861674	2.256250	1.759516

$[Ga(pyrrolato)_4]^-$

Total correction:	802.053 kJ/mol
Final entropy term:	182.1274 kJ/mol
Final single point energy:	-7250598.4355 kJ/mol
Final enthalpy:	-7249793.9035 kJ/mol
Final Gibbs free enthalpy:	-7249976.0309 kJ/mol
COSMO-RS correction (CH_2Cl_2, enthalpy):	-203.76 kJ/mol
COSMO-RS correction (CH_2Cl_2, Gibbs free energy):	-188.09 kJ/mol

xyz, charge: -1, multiplicity: 1

Ga	-1.892794	-1.204080	0.247673
N	-1.764846	0.605904	0.849135
N	-3.577685	-1.384546	-0.637065
N	-0.455860	-1.626493	-0.940365
N	-1.772806	-2.413628	1.723538
C	-4.145728	-0.467392	-1.490819
C	-4.383474	-2.498284	-0.624365
C	-5.461967	-2.291629	-1.461593
C	-5.309902	-0.992444	-2.016194
H	-5.976398	-0.497280	-2.710035
H	-3.684366	0.500283	-1.643332
H	-4.131052	-3.349893	-0.004950
H	-6.268511	-2.988770	-1.646345

C	-2.780077	1.344483	1.411523
C	-0.615899	1.358050	0.913465
C	-2.281532	2.563265	1.827686
C	-0.897023	2.571837	1.508739
H	-3.787576	0.950019	1.454444
H	-2.847420	3.356801	2.297634
H	-0.192291	3.373494	1.685829
H	0.314247	0.972385	0.515043
C	0.829569	-1.947364	-0.569361
C	-0.488011	-1.551404	-2.312650
C	0.768265	-1.827184	-2.815029
C	1.611451	-2.080207	-1.699869
C	-1.482728	-3.756246	1.644777
C	-2.082390	-2.129619	3.032563
C	-1.602305	-4.323714	2.897959
C	-1.985512	-3.282821	3.785778
H	-1.194586	-4.201619	0.700750
H	-1.426550	-5.361889	3.147140
H	-2.335333	-1.119382	3.329275
H	-2.161261	-3.365703	4.850150
H	-1.412143	-1.319896	-2.827403
H	1.045367	-1.852287	-3.860602
H	1.083809	-2.075930	0.475303
H	2.662228	-2.337469	-1.721699

$[(CH_3)_3Si]^+$

Total correction:	305.1236 kJ/mol
Final entropy term:	105.7794 kJ/mol
Final single point energy:	-1072644.0722 kJ/mol
Final enthalpy:	-1072336.4696 kJ/mol
Final Gibbs free enthalpy:	-1072442.249 kJ/mol
COSMO-RS correction (CH_2Cl_2, enthalpy):	-242.78 kJ/mol
COSMO-RS correction (CH_2Cl_2, Gibbs free energy):	-226.40 kJ/mol

xyz, charge: 1, multiplicity: 1

C	-5.666800	3.729659	-0.565179
Si	-5.966278	1.978068	-0.138811
H	-4.766510	4.076462	-0.034370
H	-6.500850	4.384755	-0.300888
H	-5.439680	3.831731	-1.634764
C	-7.457745	1.510707	0.808541
H	-7.591877	2.175029	1.672157
H	-7.448413	0.469096	1.139670
H	-8.342818	1.664962	0.171418
C	-4.775268	0.693119	-0.658519
H	-5.294126	-0.083353	-1.238933
H	-4.375136	0.181456	0.229180
H	-3.944889	1.090263	-1.247703

$[Ga(pyrrolato)_4]^-$ (square planar configuration)

Total correction:	799.4109 kJ/mol
Final entropy term:	171.5899 kJ/mol
Final single point energy:	-7250432.5802 kJ/mol
Final enthalpy:	-7249630.6904 kJ/mol
Final Gibbs free enthalpy:	-7249802.2803 kJ/mol

xyz, charge: -1, multiplicity: 1

Ga	-1.900395	-1.195733	0.248885
N	-0.715414	0.072300	1.191045
N	-3.085355	-2.463743	-0.693258
N	-1.064199	-0.702071	-1.468806
N	-2.736660	-1.689436	1.966716
C	-3.707632	-2.257971	-1.906172
C	-3.444773	-3.722037	-0.259351
C	-4.279953	-4.310258	-1.185719
C	-4.456542	-3.367679	-2.236538
H	-5.059419	-3.486397	-3.127481
H	-3.548078	-1.341746	-2.458473
H	-3.098481	-4.096166	0.694629

H	-4.711542	-5.300287	-1.115636
C	-1.069400	0.908396	2.228443
C	0.622013	0.286284	0.933584
C	0.026266	1.647506	2.621918
C	1.113095	1.241280	1.798639
H	-2.074463	0.895371	2.627957
H	0.043144	2.391788	3.407460
H	2.132201	1.603833	1.834575
H	1.120006	-0.241771	0.131674
C	-0.686966	0.564622	-1.861610
C	-0.744558	-1.560429	-2.499457
C	-0.167595	-0.850263	-3.531137
C	-0.139859	0.513252	-3.126385
C	-4.077495	-1.924796	2.185566
C	-2.090236	-1.864011	3.171991
C	-4.281600	-2.239756	3.512492
C	-3.006440	-2.210720	4.142584
H	-4.785597	-1.876424	1.369420
H	-5.234493	-2.463599	3.974275
H	-1.024205	-1.700624	3.253979
H	-2.785073	-2.418727	5.181373
H	-0.977893	-2.614323	-2.430923
H	0.191945	-1.262997	-4.464804
H	-0.812660	1.408129	-1.196397
H	0.234717	1.356193	-3.692515

[H-^{Me}**1***]

Total correction:	1525.3991 kJ/mol
Final entropy term:	222.2992 kJ/mol
Final single point energy:	-8476188.4437 kJ/mol
Final enthalpy:	-8474660.5656 kJ/mol
Final Gibbs free enthalpy:	-8474882.8648 kJ/mol
COSMO-RS correction (CH_2Cl_2, enthalpy):	-96.39 kJ/mol
COSMO-RS correction (CH_2Cl_2, Gibbs free energy):	-83.77 kJ/mol

xyz, charge: 0, multiplicity: 1

N	1.187635	-2.102603	2.205296
C	2.703864	-1.331381	4.059692
C	3.081413	-1.785765	5.473843
H	3.594662	-2.750238	5.432685
H	2.192191	-1.889726	6.102466
H	3.763683	-1.068054	5.939300
C	4.012992	-1.195126	3.233075
H	4.536180	-2.156389	3.200203
H	4.666699	-0.435662	3.676705
H	3.800281	-0.901179	2.198043
N	1.378716	0.575666	3.030284
C	0.913814	1.826092	3.407397
C	2.031423	0.018749	4.123524
C	1.297415	2.070143	4.708120
H	1.069581	2.949653	5.293429
C	2.007394	0.927994	5.158137
H	2.444299	0.795006	6.136986
C	-0.116350	2.578413	2.596671
C	-1.502904	1.897577	2.752665
H	-1.800176	1.945620	3.803924
H	-1.461186	0.844364	2.459512
H	-2.262094	2.398552	2.139982
C	-0.229745	4.027227	3.085862
H	-0.993056	4.571152	2.519917
H	0.726018	4.553922	3.004438
H	-0.533579	4.036453	4.134760
N	0.440041	1.402537	0.508544
C	0.717134	1.694708	-0.907642
C	0.245969	2.533611	1.137686
C	0.658848	3.176841	-0.981852
H	0.796503	3.742068	-1.894749
C	0.374366	3.667801	0.237763
H	0.252960	4.704983	0.517018
C	2.028374	1.005482	-1.448157
C	2.303295	1.521634	-2.864219

H	2.607622	2.572409	-2.850226
H	1.427386	1.409716	-3.512116
H	3.121917	0.946478	-3.305846
C	3.223946	1.360596	-0.549086
H	4.132104	0.916123	-0.966477
H	3.120702	0.980652	0.474001
H	3.362186	2.446152	-0.481494
N	1.224249	-1.090790	-0.370722
C	0.914403	-2.398124	-0.700612
C	1.744533	-0.468100	-1.487609
C	1.251145	-2.599300	-2.023532
H	1.123294	-3.514286	-2.584325
C	1.776154	-1.375594	-2.525130
H	2.126451	-1.196184	-3.532025
C	0.144505	-3.282870	0.263156
C	-1.299499	-2.730936	0.391814
H	-1.789421	-2.705898	-0.587945
H	-1.307883	-1.708988	0.793842
H	-1.881435	-3.357652	1.076018
C	0.061540	-4.707914	-0.289518
H	-0.452112	-4.712877	-1.255838
H	-0.504434	-5.344870	0.396857
H	1.060245	-5.135207	-0.418987
C	1.841786	-2.383356	3.392815
C	0.809504	-3.292897	1.617604
C	1.833441	-3.750594	3.573386
H	2.285370	-4.293602	4.391548
C	1.171865	-4.327194	2.451283
H	1.005944	-5.381398	2.278970
Ga	1.055309	-0.382707	1.401043
H	-0.105241	1.267206	-1.505774

[H-^{Me}**1***-F]$^-$

Total correction:	1532.4477 kJ/mol
Final entropy term:	228.558 kJ/mol
Final single point energy:	-8738534.5514 kJ/mol
Final enthalpy:	-8736999.6248 kJ/mol
Final Gibbs free enthalpy:	-8737228.1828 kJ/mol
COSMO-RS correction (CH_2Cl_2, enthalpy):	-244.91 kJ/mol
COSMO-RS correction (CH_2Cl_2, Gibbs free energy):	-225.28 kJ/mol

xyz, charge: -1, multiplicity: 1

N	1.152201	-2.191795	2.175602
C	2.610616	-1.361130	4.028267
C	3.028713	-1.819386	5.431137
H	3.565457	-2.770526	5.367807
H	2.153480	-1.953154	6.074672
H	3.700242	-1.088637	5.893274
C	3.903158	-1.160803	3.187151
H	4.467325	-2.099565	3.136346
H	4.529402	-0.376693	3.630995
H	3.649444	-0.866952	2.163816
N	1.225712	0.549178	3.058655
C	0.854932	1.823669	3.455370
C	1.904320	-0.026811	4.118575
C	1.301504	2.049570	4.745238
H	1.167431	2.948121	5.331193
C	1.966312	0.875413	5.164712
H	2.444998	0.719441	6.120842
C	-0.018521	2.761623	2.646946
C	-1.523500	2.428839	2.844175
H	-1.768827	2.563308	3.903008
H	-1.727500	1.396044	2.554054
H	-2.151225	3.103395	2.245839
C	0.208034	4.210255	3.112740
H	-0.465473	4.895872	2.587024
H	1.244508	4.527987	2.957241
H	-0.018016	4.291978	4.177941
N	0.405025	1.513997	0.563068
C	0.611064	1.760013	-0.857981
C	0.268144	2.650511	1.172223

C	0.578097	3.244400	-0.987964
H	0.683719	3.782509	-1.921592
C	0.361064	3.769528	0.228533
H	0.272929	4.817167	0.482469
C	1.886253	1.017753	-1.381291
C	2.194683	1.515483	-2.798450
H	2.511863	2.563507	-2.782305
H	1.327000	1.411668	-3.459821
H	3.013094	0.927732	-3.223389
C	3.087960	1.339802	-0.474407
H	3.987116	0.879479	-0.896259
H	2.953768	0.946258	0.536554
H	3.248463	2.423324	-0.397617
N	0.986614	-1.101816	-0.342543
C	0.838449	-2.431721	-0.693361
C	1.576298	-0.455000	-1.409292
C	1.319944	-2.614038	-1.978677
H	1.343508	-3.543638	-2.529590
C	1.787924	-1.358451	-2.436334
H	2.225985	-1.152494	-3.403508
C	0.197570	-3.465718	0.217952
C	-1.338462	-3.263738	0.267861
H	-1.754719	-3.338002	-0.745057
H	-1.603452	-2.292491	0.687844
H	-1.786337	-4.043558	0.896017
C	0.446774	-4.866766	-0.361398
H	-0.007012	-4.952797	-1.354511
H	-0.016424	-5.620822	0.282814
H	1.517249	-5.081226	-0.437139
C	1.799760	-2.445763	3.359208
C	0.816124	-3.394814	1.600053
C	1.846669	-3.815995	3.561136
H	2.312286	-4.334616	4.388385
C	1.215722	-4.419800	2.441873
H	1.100036	-5.481194	2.268207
Ga	0.532791	-0.457586	1.491289
H	-0.240815	1.322095	-1.405793
F	-1.278233	-0.470086	1.681184

[^{Et}**1**-F]$^{2-}$

Total correction:	2118.6879 kJ/mol
Final entropy term:	286.6686 kJ/mol
Final single point energy:	-9561504.9524 kJ/mol
Final enthalpy:	-9559383.7855 kJ/mol
Final Gibbs free enthalpy:	-9559670.4541 kJ/mol
COSMO-RS correction (CH_2Cl_2, enthalpy):	-591.91 kJ/mol
COSMO-RS correction (CH_2Cl_2, Gibbs free energy):	-568.99 kJ/mol

xyz, charge: -2, multiplicity: 1

N	1.542167	1.293756	-0.091926
C	0.204158	3.212862	0.794157
C	0.155201	2.595593	2.225150
H	0.160039	1.508213	2.114257
H	1.085577	2.846273	2.753154
C	0.290362	4.751233	0.879803
H	0.476606	5.130217	-0.132751
H	-0.691880	5.136972	1.177388
N	-1.338884	1.488604	-0.153170
C	-2.604822	1.419437	-0.692305
C	-1.055380	2.817540	0.061060
C	-3.105376	2.703638	-0.851297
H	-4.081494	2.972832	-1.236241
C	-2.121163	3.596646	-0.358707
H	-2.201445	4.674580	-0.305488
C	-3.306795	0.120661	-1.035030
C	-4.831539	0.312181	-0.806354
H	-5.345776	-0.614162	-1.087793
H	-5.178872	1.076174	-1.515356
C	-3.080548	-0.166982	-2.557468
H	-2.000317	-0.179367	-2.727049
H	-3.483159	0.693883	-3.111705

N	-1.500036	-1.272618	0.125530
C	-1.436416	-2.464524	0.810632
C	-2.824106	-1.044547	-0.196863
C	-2.716050	-2.992741	0.928172
H	-2.993768	-3.915706	1.421226
C	-3.592765	-2.097144	0.280679
H	-4.662493	-2.218839	0.169916
C	-0.199505	-3.037362	1.465657
C	-0.213903	-2.650386	2.980654
H	0.633580	-3.158037	3.465367
H	-1.143021	-3.043710	3.419612
C	-0.284332	-4.588737	1.405491
H	-1.192025	-4.906699	1.934563
H	0.557959	-5.001864	1.975028
N	1.340022	-1.460467	0.147724
C	2.693066	-1.381422	-0.118577
C	1.123216	-2.609963	0.870237
C	3.327474	-2.485749	0.433807
H	4.383062	-2.718770	0.380339
C	2.334580	-3.260757	1.070036
H	2.491037	-4.187172	1.607862
C	3.324188	-0.307658	-0.978812
C	4.852112	-0.265212	-0.695427
H	5.306572	0.417633	-1.426503
H	5.275254	-1.254954	-0.904128
C	3.122571	-0.633891	-2.496039
H	3.606847	0.171554	-3.067909
H	2.050199	-0.567591	-2.700344
C	1.405645	2.653457	0.069598
C	2.755211	1.071240	-0.705971
C	2.509588	3.298903	-0.463892
H	2.693864	4.365546	-0.482963
C	3.367492	2.287985	-0.965963
H	4.342331	2.436717	-1.414885
Ga	0.011237	-0.030501	-0.386397
C	-5.243533	0.709150	0.611952
H	-4.793251	1.668414	0.884110
H	-6.336057	0.798293	0.688750
H	-4.903969	-0.038746	1.334672
C	-3.686604	-1.467463	-3.084698
H	-3.330740	-2.319485	-2.495506
H	-4.783602	-1.469500	-3.048251
H	-3.389812	-1.624653	-4.129446
C	-0.122176	-1.149865	3.229713
H	-0.965350	-0.628119	2.762669
H	-0.133884	-0.923894	4.303471
H	0.804877	-0.746793	2.806516
C	-0.281558	-5.159499	-0.009629
H	-0.327419	-6.256593	0.007158
H	-1.141648	-4.780910	-0.571135
H	0.628911	-4.854521	-0.535782
C	5.244026	0.168931	0.716919
H	4.875754	1.180039	0.916456
H	4.805720	-0.502815	1.461138
H	6.336081	0.160752	0.838191
C	3.643601	-1.995508	-2.955782
H	4.736333	-2.074371	-2.890885
H	3.212680	-2.794778	-2.342752
H	3.360688	-2.174274	-4.000967
C	-1.066714	2.998616	3.046439
H	-1.983279	2.740557	2.504483
H	-1.074252	2.473656	4.009805
H	-1.092666	4.076790	3.250709
C	1.340987	5.302535	1.848909
H	2.309031	4.812143	1.711049
H	1.476366	6.381132	1.694782
H	1.038659	5.155973	2.892301
F	0.032986	-0.177657	-2.210290

Ph_3SiF

It was not possible to remove a slight imaginary mode (7 i*cm^{-1}) from the structure with the applied computational method (r^{2}SCAN-3c, see Chapter S8 for details). Therefore, for the calculation of the reaction Gibbs free energy of the fluoride exchange reaction between $[Ph_3SiF_2]^-$ and $[^{Me}\mathbf{1}]^-$ a value of 11.21 kJ mol^{-1} was subtracted from the Gibbs free energy obtained from Orca, to approximately account for the missing low real mode during the calculation of the entropy term. Below, the uncorrected value is given.

Total correction:	765.3287 kJ/mol
Final entropy term:	162.0527 kJ/mol
Final single point energy:	-2843686.9781 kJ/mol
Final enthalpy:	-2842919.1704 kJ/mol
Final Gibbs free enthalpy:	-2843081.2231 kJ/mol
COSMO-RS correction (CH_2Cl_2, enthalpy):	-54.65 kJ/mol
COSMO-RS correction (CH_2Cl_2, Gibbs free energy):	-46.92 kJ/mol
COSMO-RS correction (MeCN, Gibbs free energy):	-41.12 kJ/mol

xyz, charge: 0, multiplicity: 1

C	-2.789124	0.252226	-0.813474
C	-2.823907	-0.719677	0.184293
C	-1.593105	0.892385	-1.117279
C	-0.410244	0.570993	-0.433864
C	-0.463990	-0.409720	0.564726
C	-1.661443	-1.049753	0.873716
H	-3.695691	0.509329	-1.354224
H	-3.758515	-1.219994	0.422767
H	-1.577781	1.651183	-1.897422
H	0.442378	-0.678301	1.103231
H	-1.686300	-1.808993	1.650426
Si	1.173305	1.470702	-0.837792
C	1.068319	3.271083	-0.361423
C	1.993500	4.190049	-0.879257
C	0.108826	3.733222	0.548526
C	0.074850	5.071041	0.932845
C	1.958469	5.527436	-0.501146
C	0.999102	5.968622	0.407659
H	-0.623022	3.039452	0.957153
H	-0.676024	5.413804	1.639292
H	2.747684	3.855998	-1.589137
H	2.678843	6.227922	-0.914336
H	0.972014	7.013471	0.704665
C	2.646402	0.646882	-0.043486
F	1.383118	1.398602	-2.441465
C	3.134853	-0.568100	-0.546819
C	3.265556	1.197219	1.086146
C	4.337332	0.553044	1.698130
C	4.208343	-1.211022	0.059603
C	4.809490	-0.650861	1.184654
H	2.909434	2.143984	1.487189
H	4.807931	0.993385	2.572762
H	2.673115	-1.013561	-1.425832
H	4.578416	-2.149052	-0.344775
H	5.648167	-1.153098	1.658997

$[Ph_3SiF_2]^-$

Total correction:	772.8796 kJ/mol
Final entropy term:	169.9684 kJ/mol
Final single point energy:	-3105912.9102 kJ/mol
Final enthalpy:	-3105137.5516 kJ/mol
Final Gibbs free enthalpy:	-3105307.52 kJ/mol
COSMO-RS correction (CH_2Cl_2, enthalpy):	-218.25 kJ/mol
COSMO-RS correction (CH_2Cl_2, Gibbs free energy):	-202.65 kJ/mol
COSMO-RS correction (MeCN, Gibbs free energy):	-213.19 kJ/mol

xyz, charge: -1, multiplicity: 1

C	-2.581602	-0.992168	-0.123090
C	-2.257529	-1.499285	1.132524
C	-1.686216	-0.164161	-0.797495
C	-0.432271	0.165365	-0.259600
C	-0.126567	-0.369543	1.001529
C	-1.025271	-1.177685	1.695525
H	-3.539970	-1.237831	-0.577069

H	-2.957870	-2.138282	1.666745
H	-1.958797	0.243077	-1.766427
H	0.840015	-0.142923	1.441228
H	-0.759775	-1.563851	2.677955
Si	0.810795	1.298288	-1.206155
C	1.194431	3.070215	-0.546238
C	2.451912	3.404110	-0.019857
C	0.229415	4.089208	-0.568937
C	0.497023	5.367272	-0.082037
C	2.737957	4.686263	0.445518
C	1.757682	5.674838	0.422812
H	-0.750595	3.867361	-0.980536
H	-0.280105	6.129086	-0.102813
H	3.217744	2.635495	0.023213
H	3.729025	4.913215	0.834226
H	1.973855	6.674446	0.794625
C	1.673307	0.666490	-2.812951
F	-0.496004	1.935898	-2.157003
C	2.637738	-0.352496	-2.780998
C	1.370194	1.208413	-4.071745
C	2.002849	0.769707	-5.233415
C	3.258196	-0.815625	-3.939787
C	2.947757	-0.251093	-5.174096
H	0.619763	1.990686	-4.133320
H	1.751889	1.222465	-6.191047
H	2.903158	-0.786268	-1.821637
H	3.991556	-1.617680	-3.879090
H	3.437129	-0.603235	-6.079996
F	2.116667	0.660462	-0.255097

[Ga(pyrrolato)$_4$-F]$^{2-}$

It was not possible to remove a slight imaginary mode (18 i*cm^{-1}) from the structure with the applied computational method (r^{2}SCAN-3c, see Chapter S8 for details). This was not a problem, as this structure was only used for the calculation of the FIA (enthalpy scale) of [Ga(pyrrolato)$_4$]$^-$.

Total correction:	803.5672 kJ/mol
Final entropy term:	181.7155 kJ/mol
Final single point energy:	-7512513.7257 kJ/mol
Final enthalpy:	-7511707.6796 kJ/mol
Final Gibbs free enthalpy:	-7511889.3951 kJ/mol
COSMO-RS correction (CH_2Cl_2, enthalpy):	-644.61 kJ/mol
COSMO-RS correction (CH_2Cl_2, Gibbs free energy):	-611.61 kJ/mol

xyz, charge: -2, multiplicity: 1

Ga	0.106452	-0.168528	0.483900
N	0.076610	-0.012802	-1.597809
N	-1.366249	-1.522884	0.387897
N	-0.525341	1.698159	0.684385
N	2.100510	-0.373030	0.420541
C	-1.817678	-2.260655	1.455716
C	-2.159895	-1.839882	-0.687592
C	-3.110345	-2.774987	-0.312116
C	-2.889205	-3.047301	1.066884
H	-3.442904	-3.731993	1.699920
H	-1.337361	-2.147911	2.416904
H	-1.992020	-1.380407	-1.652716
H	-3.869163	-3.205122	-0.955924
C	-0.605649	0.910418	-2.342054
C	0.522423	-0.972614	-2.463853
C	-0.590984	0.549155	-3.683836
C	0.138851	-0.667891	-3.762606
H	-1.059879	1.770661	-1.865076
H	-1.044156	1.098545	-4.501203
H	0.357796	-1.248757	-4.651505
H	1.090950	-1.819154	-2.097019
C	-1.795402	2.076351	1.015213
C	0.190308	2.833713	0.431349
C	-0.619019	3.948630	0.602228
C	-1.899775	3.460259	0.977135
C	2.964820	0.043605	-0.561484
C	2.863540	-0.888286	1.437965

C	4.272526	-0.207240	-0.178106
C	4.206864	-0.811832	1.107769
H	2.584484	0.477590	-1.476248
H	5.161580	0.019009	-0.755714
H	2.378060	-1.246518	2.334557
H	5.036788	-1.145169	1.720830
H	1.230632	2.769286	0.134895
H	-0.322225	4.982753	0.472490
H	-2.541930	1.328266	1.254024
H	-2.787785	4.042913	1.192263
F	0.188320	-0.467323	2.345442

THF

Total correction:	317.5197 kJ/mol
Final entropy term:	88.5177 kJ/mol
Final single point energy:	-609538.3066 kJ/mol
Final enthalpy:	-609218.3079 kJ/mol
Final Gibbs free enthalpy:	-609306.8256 kJ/mol
COSMO-RS correction (CH_2Cl_2, enthalpy):	-24.62 kJ/mol
COSMO-RS correction (CH_2Cl_2, Gibbs free energy):	-16.44 kJ/mol

xyz, charge: 0, multiplicity: 1

C	-5.717755	1.102332	-0.233116
C	-5.575460	-0.367071	0.156899
C	-4.369997	1.667028	0.225294
C	-3.423676	0.525371	-0.141115
O	-4.182452	-0.687411	0.004586
H	-4.375276	1.827697	1.309935
H	-4.104089	2.609538	-0.262381
H	-2.542436	0.467310	0.508762
H	-3.081794	0.615207	-1.184523
H	-6.576495	1.585382	0.242318
H	-5.821594	1.201851	-1.320155
H	-6.160172	-1.043943	-0.477016
H	-5.873495	-0.526931	1.205652

[^{Me}**1**-thf]$^-$

Total correction:	1818.2677 kJ/mol
Final entropy term:	252.391 kJ/mol
Final single point energy:	-9084508.268 kJ/mol
Final enthalpy:	-9082687.5214 kJ/mol
Final Gibbs free enthalpy:	-9082939.9124 kJ/mol
COSMO-RS correction (CH_2Cl_2, enthalpy):	-219.28 kJ/mol
COSMO-RS correction (CH_2Cl_2, Gibbs free energy):	-204.05 kJ/mol

xyz, charge: -1, multiplicity: 1

N	-0.414273	-2.170128	0.382199
C	-1.259318	-3.032702	1.064112
C	-0.335515	-2.620210	-0.918036
C	-1.718826	-4.001795	0.186450
H	-2.354916	-4.842468	0.431669
C	-1.125814	-3.742590	-1.075685
H	-1.253937	-4.320816	-1.980640
N	-0.216189	-0.816384	2.790889
C	0.105927	0.024682	3.834753
C	-1.036979	-1.808382	3.300427
C	-0.515948	-0.405539	4.990645
C	-1.248339	-1.570799	4.649211
H	-1.813504	-2.193431	5.330737
N	0.084500	1.670634	1.395266
C	-0.121058	2.801285	0.617223
C	0.645669	2.094031	2.584989
C	0.293471	3.916587	1.322338
H	0.253001	4.943152	0.986005
C	0.784282	3.466771	2.571363
H	1.199680	4.079304	3.359695
N	-0.153702	0.324310	-1.039861
C	0.117257	-0.508450	-2.107473
C	-0.431325	1.579465	-1.561023

C	-0.001110	0.194757	-3.288749
H	0.162926	-0.189571	-4.286073
C	-0.354087	1.520947	-2.941522
H	-0.514658	2.338600	-3.630355
H	-0.435254	-2.682008	-3.683880
C	0.563255	-2.683443	-3.235127
C	2.019348	-1.936096	-1.355176
C	0.568960	-1.930438	-1.901454
H	2.358695	-2.964520	-1.181228
H	0.879185	-3.720846	-3.081339
H	2.083739	-1.395501	-0.406171
H	-3.531240	-2.856761	2.697778
C	-2.763373	-3.581534	2.985572
C	-0.325105	-4.149051	3.043452
C	-1.365699	-3.089203	2.570227
H	0.680503	-3.827018	2.755805
H	-2.997248	-4.539699	2.511543
H	-0.527885	-5.117595	2.571351
H	2.337780	-0.049054	2.232542
C	2.457658	0.487239	3.178970
C	1.365455	1.851389	4.956014
C	1.115847	1.120286	3.632986
H	1.701816	1.140920	5.718544
H	2.813694	-0.230692	3.928012
H	0.454646	2.344819	5.310029
C	-0.799340	2.790492	-0.732280
C	-2.338536	2.877734	-0.547770
C	-0.386930	4.058120	-1.505837
H	-2.834593	2.883879	-1.526427
H	-0.899288	4.096412	-2.471506
H	-2.705157	2.024919	0.021240
H	0.692970	4.076787	-1.677389
H	-2.599118	3.793496	-0.003022
H	-0.674218	4.954576	-0.948266
H	2.689196	-1.445372	-2.070835
H	1.258488	-2.213343	-3.937960
H	-0.357750	-4.254064	4.134113
H	-2.816547	-3.724243	4.069274
H	2.144085	2.610425	4.830409
H	3.210942	1.270308	3.033647
H	-0.438180	0.044047	5.971186
Ga	-0.349198	-0.215034	0.880314
O	-2.397099	-0.058043	0.900103
C	-3.177493	0.405131	2.040739
C	-3.241587	-0.650900	-0.133362
C	-4.601559	-0.788015	0.536304
C	-4.615448	0.373393	1.539995
H	-2.810072	1.402139	2.303901
H	-2.995820	-0.282505	2.877019
H	-4.866226	1.312489	1.032140
H	-5.324692	0.221206	2.359125
H	-2.794692	-1.604496	-0.427494
H	-3.252588	0.038700	-0.986664
H	-5.419519	-0.735771	-0.188346
H	-4.661321	-1.749165	1.058639

TS-1

Total correction:	1520.3926 kJ/mol
Final entropy term:	220.7647 kJ/mol
Final single point energy:	-8476125.7934 kJ/mol
Final enthalpy:	-8474602.9218 kJ/mol
Final Gibbs free enthalpy:	-8474823.6865 kJ/mol
COSMO-RS correction (CH_2Cl_2, enthalpy):	-86.90 kJ/mol
COSMO-RS correction (CH_2Cl_2, Gibbs free energy):	-75.95 kJ/mol

xyz, charge: 0, multiplicity: 1

N	1.100760	-2.108044	2.215271
C	2.646588	-1.392188	4.085628
C	2.953446	-1.848767	5.516975
H	3.410640	-2.841743	5.505682
H	2.042089	-1.889309	6.120578

H	3.663803	-1.166132	5.992622
C	3.986714	-1.357907	3.296254
H	4.453938	-2.348303	3.302004
H	4.669847	-0.627153	3.743630
H	3.821317	-1.077012	2.249150
N	1.452995	0.573466	3.008861
C	1.075467	1.864737	3.345462
C	2.073043	0.003268	4.112388
C	1.491313	2.118414	4.635287
H	1.322742	3.023946	5.200801
C	2.125041	0.944685	5.116820
H	2.556441	0.812201	6.098328
C	0.037887	2.636922	2.559987
C	-1.371757	2.151767	3.010343
H	-1.495854	2.359569	4.077130
H	-1.477149	1.073329	2.858297
H	-2.160367	2.663167	2.445936
C	0.152159	4.135374	2.868720
H	-0.650585	4.695475	2.379159
H	1.119082	4.535065	2.548079
H	0.054359	4.300138	3.943623
N	0.160755	1.171782	0.523760
C	0.192094	1.337815	-0.877579
C	0.109723	2.406795	1.074412
C	0.023562	2.714013	-1.154133
H	-0.054345	3.146168	-2.142772
C	0.024773	3.384319	0.053811
H	-0.017048	4.452948	0.204539
C	2.231608	0.916397	-1.390174
C	2.446614	1.600712	-2.716939
H	2.492581	2.684853	-2.592133
H	1.662521	1.355554	-3.437349
H	3.405556	1.267529	-3.135913
C	2.968306	1.558840	-0.251885
H	3.992914	1.759084	-0.592345
H	3.054929	0.932566	0.640258
H	2.528594	2.521816	0.034753
N	1.550001	-1.155571	-0.313094
C	1.092739	-2.377584	-0.708729
C	2.040309	-0.495084	-1.427948
C	1.362571	-2.540792	-2.077291
H	1.157310	-3.424047	-2.664598
C	1.928263	-1.348749	-2.534785
H	2.250283	-1.129923	-3.543954
C	0.216479	-3.246008	0.183806
C	-1.206911	-2.627632	0.181125
H	-1.604682	-2.572083	-0.838404
H	-1.215638	-1.611702	0.596905
H	-1.872871	-3.239064	0.798439
C	0.122137	-4.664084	-0.386998
H	-0.336602	-4.653193	-1.380210
H	-0.503261	-5.281895	0.263821
H	1.111330	-5.125722	-0.458143
C	1.750963	-2.409176	3.400747
C	0.771594	-3.286315	1.582624
C	1.761261	-3.783712	3.540851
H	2.208395	-4.342029	4.351093
C	1.139866	-4.340787	2.390011
H	1.006206	-5.392784	2.180214
Ga	1.034062	-0.382513	1.419732
H	-0.168693	0.532226	-1.504079

Int-1

Total correction:	1523.3881 kJ/mol
Final entropy term:	228.1835 kJ/mol
Final single point energy:	-8476179.1563 kJ/mol
Final enthalpy:	-8474653.2892 kJ/mol
Final Gibbs free enthalpy:	-8474881.4727 kJ/mol
COSMO-RS correction (CH_2Cl_2, enthalpy):	-94.70 kJ/mol
COSMO-RS correction (CH_2Cl_2, Gibbs free energy):	-82.58 kJ/mol

xyz, charge: 0, multiplicity: 1

N	-0.861215	-1.731906	-0.498853
C	-2.817616	-0.567826	-1.490834
C	-2.105986	-0.005513	-2.745696
H	-2.565308	0.935327	-3.070579
H	-2.193941	-0.740122	-3.551922
H	-1.039104	0.178026	-2.586136
C	-4.270637	-0.875229	-1.873906
H	-4.278587	-1.671415	-2.622863
H	-4.756331	0.001067	-2.313747
H	-4.851913	-1.211475	-1.010007
N	-1.698856	0.752416	0.360464
C	-2.021658	1.848832	1.185066
C	-2.778571	0.473999	-0.379286
C	-3.394706	2.196218	0.935667
C	-3.862050	1.346145	-0.018625
C	-1.143231	2.487877	2.013209
C	0.264924	2.058503	2.199942
H	0.889092	2.528489	1.419935
H	0.412633	0.976348	2.139385
H	0.650324	2.398244	3.166057
C	-1.526088	3.723042	2.755762
H	-0.796418	4.510865	2.527542
H	-1.454133	3.541875	3.835922
H	-2.522497	4.095310	2.523249
N	0.794127	1.467771	-1.013008
C	2.052175	1.948652	-0.670221
C	0.031758	2.550250	-1.417406
C	2.065652	3.317268	-0.876982
C	0.785489	3.696700	-1.353617
C	3.220626	1.103756	-0.191084
C	4.377132	1.288654	-1.196979
H	4.624016	2.349605	-1.291913
H	4.093989	0.908664	-2.182697
H	5.275542	0.762496	-0.859960
C	3.705589	1.621808	1.188676
H	4.616340	1.087079	1.476830
H	2.953257	1.438846	1.961019
H	3.919330	2.695732	1.154289
N	1.709532	-0.847882	0.469933
C	1.816092	-2.237141	0.541602
C	2.909780	-0.365694	-0.058143
C	3.070260	-2.609941	0.123127
H	3.457494	-3.617866	0.080737
C	3.759730	-1.429719	-0.257280
H	4.775139	-1.379575	-0.623267
C	0.661265	-3.091700	0.994304
C	1.090321	-4.561712	1.056259
H	1.949941	-4.676067	1.724060
H	1.359250	-4.935145	0.063993
H	0.275786	-5.178237	1.447101
C	0.229121	-2.650817	2.418519
H	1.076056	-2.726013	3.109815
H	-0.592581	-3.279671	2.776755
H	-0.119665	-1.611884	2.420790
C	-2.145910	-1.812753	-0.984571
C	-0.540352	-2.944721	0.081177
C	-2.629956	-3.087335	-0.768805
H	-3.602447	-3.466865	-1.049954
C	-1.605577	-3.806632	-0.100434
H	-1.659588	-4.834254	0.229975
Ga	0.085184	-0.108312	-0.189955
H	0.463459	4.689222	-1.638444
H	2.913597	3.972120	-0.727272
H	-1.001166	2.427762	-1.711142
H	-4.857441	1.317221	-0.435955
H	-3.952658	2.977008	1.431573

[H-^{Me}**1***-$(thf)_2$]

Total correction:	2180.5152 kJ/mol
Final entropy term:	286.2873 kJ/mol
Final single point energy:	-9695439.8223 kJ/mol
Final enthalpy:	-9693256.8282 kJ/mol
Final Gibbs free enthalpy:	-9693543.1155 kJ/mol
COSMO-RS correction (CH_2Cl_2, enthalpy):	-96.37 kJ/mol
COSMO-RS correction (CH_2Cl_2, Gibbs free energy):	-86.17 kJ/mol

xyz, charge: 0, multiplicity: 1

N	1.962521	-0.533119	0.141265
C	1.692636	-3.050747	0.163861
C	2.268501	-4.236447	-0.635265
H	2.102311	-4.100700	-1.708404
H	1.793275	-5.171585	-0.329705
H	3.343200	-4.335572	-0.453052
C	1.993573	-3.305207	1.664640
H	3.074922	-3.376495	1.826164
H	1.514866	-4.230931	2.003751
H	1.611544	-2.476628	2.264127
N	-0.568691	-1.907289	-0.372756
C	-1.888466	-2.341510	-0.477472
C	0.189363	-3.019582	-0.037425
C	-1.951122	-3.691963	-0.192356
H	-2.835631	-4.314666	-0.221920
C	-0.640011	-4.119588	0.090779
H	-0.334908	-5.128388	0.332735
C	-3.077843	-1.522344	-0.934574
C	-3.801084	-2.268736	-2.072929
H	-4.137622	-3.247355	-1.724287
H	-3.128961	-2.432773	-2.921605
H	-4.686242	-1.720158	-2.414119
C	-4.069353	-1.299431	0.221308
H	-3.620988	-0.700914	1.019538
H	-4.345232	-2.268130	0.647019
H	-4.982312	-0.797117	-0.119658
N	-1.857091	0.578829	-0.493267
C	-2.445510	1.717376	-0.282411
C	-2.595104	-0.160224	-1.507432
C	-3.600017	1.880216	-1.167035
H	-4.245889	2.746034	-1.208048
C	-3.683532	0.769179	-1.916267
H	-4.419546	0.554650	-2.680458
C	-2.032667	2.668439	0.800515
C	-2.579890	4.077305	0.492896
H	-3.674409	4.078754	0.453860
H	-2.182647	4.458258	-0.453172
H	-2.283255	4.768680	1.282941
C	-2.731866	2.156470	2.091417
H	-2.488906	2.833763	2.915823
H	-2.380233	1.152800	2.338613
H	-3.821554	2.130938	1.967354
N	0.400372	1.879309	0.413863
C	1.655635	2.349324	0.763091
C	-0.527633	2.744197	0.973973
C	1.515645	3.483222	1.545028
H	2.312408	4.096336	1.941799
C	0.134376	3.734081	1.676395
H	-0.313145	4.564382	2.205971
C	2.955817	1.829184	0.195035
C	3.338660	2.712282	-1.018858
H	4.293817	2.392120	-1.448640
H	3.424214	3.759565	-0.710796
H	2.574399	2.644678	-1.798377
C	4.065265	1.989221	1.263638
H	4.172502	3.032366	1.577898
H	5.023425	1.654666	0.856302
H	3.836535	1.379886	2.143681
C	2.404236	-1.790615	-0.245265
C	2.942002	0.375868	-0.219973
C	3.646058	-1.672491	-0.839409
H	4.261258	-2.476469	-1.217817

C	3.983337	-0.297880	-0.828284
H	4.913167	0.134364	-1.175004
Ga	0.072857	-0.046197	0.002387
H	-1.918033	-0.388924	-2.344591
O	-0.401218	-0.329284	2.137364
C	-0.416869	-1.644143	4.141783
C	0.725942	-0.614291	4.168543
C	0.255626	0.437372	3.182389
H	0.890710	-0.196279	5.165814
H	-0.475412	1.121961	3.634826
C	-1.055175	-1.480912	2.749920
H	-1.148790	-1.420789	4.924483
H	-2.130493	-1.273555	2.816651
H	1.665833	-1.053865	3.821551
H	-0.897787	-2.337640	2.090260
H	1.051379	1.022549	2.716638
H	-0.056888	-2.664651	4.298465
H	0.370705	2.434503	-2.112615
O	0.350328	0.379403	-2.193913
C	1.084289	-0.483257	-3.098291
C	1.921555	0.480137	-3.918773
C	0.968216	1.669974	-4.106777
C	0.104091	1.657317	-2.835286
H	1.666388	-1.177828	-2.487676
H	0.366127	-1.040921	-3.720479
H	2.248394	0.046964	-4.868387
H	2.804001	0.764683	-3.338058
H	0.343388	1.522151	-4.994205
H	1.499585	2.618717	-4.223747
H	-0.967669	1.743451	-3.063804

[H-^{Me}**1***-thf]$_{anti}$

Total correction:	1855.2126 kJ/mol
Final entropy term:	249.7951 kJ/mol
Final single point energy:	-9085842.1888 kJ/mol
Final enthalpy:	-9083984.4973 kJ/mol
Final Gibbs free enthalpy:	-9084234.2924 kJ/mol
COSMO-RS correction (CH_2Cl_2, enthalpy):	-81.88 kJ/mol
COSMO-RS correction (CH_2Cl_2, Gibbs free energy):	-73.67 kJ/mol

xyz, charge: 0, multiplicity: 1

N	1.924156	-0.203707	0.725066
C	2.523975	2.247512	0.798392
C	2.490863	2.383058	2.347855
H	1.711359	1.742186	2.769135
H	2.282247	3.420904	2.632144
H	3.454625	2.076510	2.768969
C	3.635198	3.163337	0.272570
H	4.597274	2.869895	0.700668
H	3.447173	4.198795	0.569301
H	3.712296	3.120075	-0.818812
N	0.018375	1.977144	0.490817
C	-1.036628	2.821124	0.148984
C	1.186212	2.704898	0.278775
C	-0.538999	4.027533	-0.297561
H	-1.116954	4.887418	-0.609262
C	0.870185	3.952702	-0.218739
H	1.565337	4.743615	-0.460081
C	-2.496996	2.504925	0.362682
C	-3.174476	3.680133	1.090972
H	-2.727185	3.844624	2.076851
H	-4.250807	3.511835	1.205796
H	-3.047000	4.598510	0.514170
C	-3.207995	2.273143	-0.982201
H	-4.272638	2.045249	-0.855362
H	-2.738409	1.464539	-1.547849
H	-3.121366	3.184857	-1.580262
N	-2.013031	0.103073	0.603228
C	-2.950859	-0.773039	0.374697
C	-2.600769	1.248867	1.290278
C	-4.209730	-0.361873	0.991556

H	-5.127902	-0.931737	0.982558
C	-3.998880	0.830790	1.569271
H	-4.717053	1.423799	2.120496
C	-2.776151	-1.972427	-0.506757
C	-3.852631	-3.025676	-0.172922
H	-3.714725	-3.903174	-0.805815
H	-4.859711	-2.641478	-0.366237
H	-3.779294	-3.347971	0.870188
C	-3.025842	-1.477821	-1.961203
H	-2.978885	-2.341514	-2.631264
H	-2.256647	-0.762106	-2.259206
H	-4.011975	-1.007789	-2.060720
N	-0.319154	-1.997076	0.262939
C	0.695081	-2.941774	0.276912
C	-1.404585	-2.591449	-0.368003
C	0.269456	-4.091872	-0.354350
H	0.834151	-5.004677	-0.477203
C	-1.064550	-3.868437	-0.766713
H	-1.705143	-4.585096	-1.262304
C	1.974630	-2.705448	1.030709
C	1.653262	-2.655040	2.547699
H	2.571964	-2.488238	3.120935
H	1.193728	-3.597809	2.865564
H	0.957824	-1.841099	2.771414
C	2.946627	-3.864666	0.790711
H	3.207760	-3.953878	-0.268694
H	2.499939	-4.806834	1.121790
H	3.864205	-3.707823	1.364885
C	2.841232	0.812975	0.478032
C	2.615618	-1.405365	0.630720
C	4.072646	0.256894	0.208535
H	4.988743	0.792174	0.003152
C	3.929642	-1.151890	0.307586
H	4.712643	-1.886154	0.182190
Ga	0.035486	-0.025078	0.257956
H	-2.034166	1.478042	2.204961
O	0.039452	0.034694	-1.821563
C	1.793766	1.097377	-3.027767
C	2.084412	-0.419209	-2.899626
C	0.733883	-1.031411	-2.553823
H	2.488980	-0.852356	-3.818817
H	0.128273	-1.245426	-3.444930
C	0.336123	1.249310	-2.587372
H	1.927689	1.467750	-4.048359
H	-0.353597	1.250112	-3.442298
H	2.794139	-0.601604	-2.086892
H	0.139539	2.112183	-1.951735
H	0.776915	-1.914930	-1.914946
H	2.451158	1.665014	-2.364930

[H-^{Me}**1***-thf]$_{syn}$

Total correction:	1853.8786 kJ/mol
Final entropy term:	251.5532 kJ/mol
Final single point energy:	-9085844.7664 kJ/mol
Final enthalpy:	-9083988.4089 kJ/mol
Final Gibbs free enthalpy:	-9084239.9621 kJ/mol
COSMO-RS correction (CH_2Cl_2, enthalpy):	-94.00 kJ/mol
COSMO-RS correction (CH_2Cl_2, Gibbs free energy):	-83.86 kJ/mol

xyz, charge: 0, multiplicity: 1

N	1.845960	-0.733073	0.349844
C	1.212603	-2.920997	1.355390
C	1.707200	-4.369806	1.360524
H	2.738433	-4.406456	1.724552
H	1.679813	-4.805516	0.356844
H	1.088835	-4.981859	2.024212
C	1.281696	-2.380548	2.804721
H	2.314703	-2.414791	3.167509
H	0.646308	-2.983913	3.462766
H	0.940437	-1.342688	2.855530
N	-0.912689	-1.662079	0.770235

C	-2.206570	-1.992931	0.345543
C	-0.214581	-2.860270	0.871268
C	-2.289603	-3.359328	0.170950
H	-3.166731	-3.918309	-0.121897
C	-1.030938	-3.908290	0.508298
H	-0.765097	-4.955238	0.500332
C	-3.371134	-1.037965	0.351337
C	-4.598697	-1.688726	-0.298733
H	-4.405365	-1.963763	-1.341249
H	-5.459617	-1.014904	-0.262806
H	-4.875186	-2.594377	0.246452
C	-3.719824	-0.656498	1.801705
H	-2.868340	-0.199419	2.311661
H	-3.978977	-1.568162	2.347894
H	-4.572604	0.031028	1.845947
N	-1.870843	0.905430	0.129493
C	-2.225715	2.103429	0.494894
C	-3.012323	0.242805	-0.482403
C	-3.594576	2.395538	0.088433
H	-4.110228	3.332133	0.250568
C	-4.068663	1.291376	-0.514743
H	-5.053323	1.155778	-0.943791
C	-1.285690	2.995874	1.258819
C	-1.850556	4.414060	1.380509
H	-1.134608	5.047599	1.910621
H	-2.784402	4.410150	1.952316
H	-2.039870	4.859713	0.398925
C	-1.115049	2.409207	2.681095
H	-2.076847	2.371326	3.206106
H	-0.423906	3.041455	3.246447
H	-0.700499	1.397091	2.652025
N	0.757782	1.840813	0.355213
C	1.919800	2.189694	-0.326800
C	0.022830	3.000339	0.515715
C	1.887691	3.546033	-0.599015
H	2.662802	4.119583	-1.087330
C	0.685094	4.062065	-0.063446
H	0.363847	5.093979	-0.080752
C	3.125086	1.289595	-0.489241
C	3.877196	1.653472	-1.779488
H	4.775608	1.039486	-1.883055
H	4.196801	2.698881	-1.763122
H	3.248653	1.500141	-2.662453
C	4.063673	1.586241	0.718699
H	4.976458	0.985925	0.640021
H	3.558875	1.326934	1.654166
H	4.325374	2.649748	0.745916
C	2.094368	-2.083142	0.470180
C	2.841712	-0.193276	-0.454004
C	3.223702	-2.411375	-0.250888
H	3.676480	-3.389740	-0.331883
C	3.694870	-1.210699	-0.844433
H	4.599080	-1.104552	-1.428340
Ga	0.033671	0.003072	0.232063
H	-2.749087	-0.105832	-1.492228
O	-0.188596	-0.303071	-1.790936
C	0.160074	-1.419176	-3.821073
C	0.683314	0.014116	-3.970351
C	0.032614	0.739870	-2.799471
H	1.773007	0.022572	-3.860624
H	0.652638	1.527457	-2.357351
C	0.219061	-1.617234	-2.319509
H	0.774832	-2.152541	-4.349582
H	1.236701	-1.826182	-1.970231
H	0.423513	0.473176	-4.928108
H	-0.482297	-2.350069	-1.909360
H	-0.953133	1.148385	-3.056201
H	-0.871770	-1.499634	-4.183913

TS-2

Total correction:	1848.2505 kJ/mol
Final entropy term:	250.1719 kJ/mol
Final single point energy:	-9085753.3809 kJ/mol
Final enthalpy:	-9083902.6515 kJ/mol
Final Gibbs free enthalpy:	-9084152.8234 kJ/mol
COSMO-RS correction (CH_2Cl_2, enthalpy):	-81.88 kJ/mol
COSMO-RS correction (CH_2Cl_2, Gibbs free energy):	-73.67 kJ/mol

xyz, charge: 0, multiplicity: 1

N	1.858244	-0.075700	0.863548
C	2.232627	2.320791	1.517870
C	1.686341	2.086804	2.952310
H	0.847839	1.383509	2.946461
H	1.344601	3.031429	3.389852
H	2.476942	1.662561	3.580236
C	3.399494	3.311736	1.606993
H	4.209037	2.874149	2.197949
H	3.086199	4.234338	2.103284
H	3.787152	3.562889	0.614773
N	0.111645	2.151566	0.173356
C	-0.879274	3.039315	-0.261928
C	1.108524	2.907290	0.699917
C	-0.447698	4.355552	-0.012084
H	-0.994220	5.256702	-0.253905
C	0.816718	4.275127	0.552578
H	1.450446	5.099227	0.844898
C	-2.203105	2.665672	-0.606892
C	-3.246453	3.754381	-0.552461
H	-3.197673	4.328673	0.374728
H	-4.246032	3.325448	-0.654994
H	-3.095315	4.447785	-1.391658
C	-2.546458	1.578657	-1.566131
H	-3.416141	1.001889	-1.223291
H	-1.719260	0.907346	-1.783548
H	-2.847384	2.064055	-2.505910
N	-1.896420	0.310222	0.901707
C	-2.932810	-0.532369	0.678194
C	-2.442251	1.521816	1.343665
C	-4.145467	0.098167	1.049735
H	-5.132418	-0.337078	0.975684
C	-3.828678	1.367609	1.501154
H	-4.505846	2.120544	1.881611
C	-2.862608	-1.928603	0.115161
C	-3.393709	-2.878852	1.227678
H	-3.411850	-3.905378	0.851048
H	-4.404267	-2.597850	1.543391
H	-2.732375	-2.842915	2.098382
C	-3.809900	-2.029717	-1.102545
H	-3.836647	-3.058828	-1.470533
H	-3.461289	-1.388276	-1.917569
H	-4.831424	-1.740752	-0.837959
N	-0.305806	-1.856916	0.182292
C	0.716291	-2.728805	-0.150647
C	-1.488999	-2.412140	-0.276106
C	0.186162	-3.818011	-0.816463
H	0.728258	-4.679299	-1.180563
C	-1.212263	-3.616027	-0.899755
H	-1.931124	-4.304054	-1.324495
C	2.100613	-2.564235	0.426226
C	2.026594	-2.990188	1.920467
H	3.014175	-2.900448	2.387013
H	1.679449	-4.026556	1.998584
H	1.327070	-2.347595	2.461829
C	3.083886	-3.501758	-0.282770
H	3.191431	-3.249848	-1.342814
H	2.740458	-4.536905	-0.205370
H	4.068461	-3.447831	0.190065
C	2.709014	1.015064	0.951821
C	2.615424	-1.146405	0.392033
C	3.973020	0.649697	0.543958
H	4.851472	1.279011	0.523883

C	3.911113	-0.721530	0.184005
H	4.741213	-1.332161	-0.141472
Ga	0.007086	0.087042	0.280369
H	-1.817599	2.243102	1.850446
O	0.387681	0.176514	-1.819744
C	2.012127	0.386128	-3.557872
C	1.539361	-1.064774	-3.435503
C	0.178678	-0.892068	-2.796437
H	1.488197	-1.587993	-4.394461
H	-0.569008	-0.540831	-3.523716
C	1.520901	1.017117	-2.258503
H	1.548130	0.865398	-4.427752
H	1.153798	2.041486	-2.370252
H	2.187398	-1.625715	-2.752766
H	2.278576	0.979082	-1.470886
H	-0.194262	-1.770261	-2.270207
H	3.097695	0.476402	-3.651660

[^{Et}**1**-thf]$^-$

Total correction:	2443.1009 kJ/mol
Final entropy term:	309.2535 kJ/mol
Final single point energy:	-9909082.7783 kJ/mol
Final enthalpy:	-9906637.1984 kJ/mol
Final Gibbs free enthalpy:	-9906946.4519 kJ/mol
COSMO-RS correction (CH_2Cl_2, enthalpy):	-206.33 kJ/mol
COSMO-RS correction (CH_2Cl_2, Gibbs free energy):	-197.52 kJ/mol

xyz, charge: -1, multiplicity: 1

Ga	0.019631	0.020973	0.129704
O	-0.002949	0.256230	-1.914545
N	1.596651	-1.242224	0.146994
N	-1.284454	-1.518153	0.088304
N	1.296831	1.501318	0.511089
N	-1.525102	1.229958	0.461384
C	-0.923385	-2.850480	0.098046
C	1.490561	-2.619379	0.141718
C	1.031236	2.644109	1.242631
C	2.653170	1.499517	0.218767
C	-3.619941	2.055889	0.516326
H	-4.684031	2.173774	0.364486
C	-1.496622	2.427007	1.152028
C	2.204761	3.358851	1.409409
H	2.321043	4.293884	1.939900
C	3.225824	2.639987	0.756331
H	4.264159	2.933444	0.683871
C	-2.776435	2.952727	1.200542
H	-3.078686	3.875837	1.675529
C	-3.492322	0.157369	-2.230409
H	-3.867965	-0.742644	-2.735958
H	-2.484611	0.322694	-2.620873
C	-1.851295	-3.592494	-0.605537
H	-1.842292	-4.662765	-0.759029
C	-2.837495	1.000434	0.075426
C	2.760369	-0.920270	-0.531268
C	-3.341313	-0.186827	-0.713366
C	-2.474967	-1.423715	-0.612671
C	-0.298372	2.389666	3.349958
H	0.524455	2.873962	3.894884
H	-1.242238	2.699128	3.820718
C	0.323021	-3.289263	0.820241
C	2.548053	-3.165334	-0.559466
H	2.741500	-4.216370	-0.725512
C	0.192364	1.205253	-4.066003
H	1.258973	1.324871	-4.284216
H	-0.369613	1.859013	-4.739639
C	3.404354	0.875461	-2.119661
H	2.377313	0.811874	-2.485253
H	3.967585	0.103071	-2.661373
C	0.450974	-4.823672	0.740662
H	-0.514664	-5.261250	1.021116
H	0.615594	-5.095232	-0.309219

C	-0.218360	-0.270756	-4.198672
H	0.313132	-0.779862	-5.007923
H	-1.293809	-0.355676	-4.386751
C	3.369556	0.462872	-0.612693
C	-0.091084	1.533658	-2.602125
H	0.638246	2.209497	-2.143454
H	-1.097778	1.935749	-2.438363
C	-0.293756	2.958539	1.890342
C	-2.832535	-2.681867	-1.068681
H	-3.734799	-2.934704	-1.611193
C	-4.748007	-0.572131	-0.159313
H	-5.169365	-1.345218	-0.815142
H	-5.417421	0.292348	-0.230856
C	0.127304	-0.866539	-2.839257
H	-0.568702	-1.642839	-2.504367
H	1.160025	-1.233101	-2.774376
C	3.352267	-2.083505	-0.993561
H	4.295259	-2.157862	-1.520474
C	-0.429348	4.497497	2.035607
H	0.394827	4.852086	2.666287
H	-1.344449	4.705637	2.603415
C	4.839343	0.351286	-0.107010
H	5.379129	-0.311144	-0.795830
H	5.324803	1.331201	-0.180667
C	0.255711	-2.831223	2.304695
H	0.217640	-1.738312	2.327290
H	1.198715	-3.101622	2.796760
C	3.969051	2.255971	-2.444460
H	5.029963	2.337389	-2.183572
H	3.879724	2.460305	-3.518721
H	3.432192	3.036542	-1.895764
C	4.968136	-0.178180	1.318482
H	4.450156	0.481212	2.021809
H	4.524749	-1.176337	1.396205
H	6.021741	-0.242638	1.615844
C	-4.722099	-1.076974	1.280221
H	-4.123340	-1.990784	1.354654
H	-4.279792	-0.323401	1.940216
H	-5.735675	-1.297077	1.635862
C	-4.370930	1.353423	-2.588121
H	-4.361269	1.517538	-3.672676
H	-5.413783	1.199845	-2.289850
H	-4.013755	2.263831	-2.096661
C	1.545400	-5.437084	1.616989
H	1.280795	-5.395069	2.679066
H	1.693802	-6.492214	1.358754
H	2.499948	-4.917631	1.491764
C	-0.940505	-3.375954	3.079935
H	-0.906568	-4.466838	3.181673
H	-0.971876	-2.948296	4.088437
H	-1.874595	-3.116561	2.569885
C	-0.148598	0.877052	3.453000
H	-0.977030	0.364618	2.949777
H	0.797643	0.547766	3.007399
H	-0.149663	0.554200	4.500584
C	-0.444693	5.279191	0.724303
H	-1.282326	4.963216	0.094872
H	-0.543288	6.354698	0.915786
H	0.482000	5.112698	0.166268

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