Electronic Supporting Information to

Oxidative Addition, Reduction and Reductive Coupling: The versatile reactivity of Subvalent Gallium cations.

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S-1 Experimental Details and Characterisation Techniques

All reactions and manipulations were carried out under an inert argon atmosphere, using standard Schlenk-line and glovebox techniques (box atmosphere kept below 1 ppm H_2O/O_2). Glassware has been stored over-night in an oven set to 180°C and flame dried under vacuum prior to use. **2**,[1] [H-PPh_3][BF_4][2], **1**[3] were prepared according to reported procedures. Pentane was collected from a solvent purification system (SPS) and oxygen removed by purging with Argon. PhF, *o*-DFB, CD_2Cl_2, hexane and heptane were refluxed/stirred over CaH_2 and distilled. All solvents were stored over activated 3 Å molecular sieves in gas tight ampoules.

ATR-IR Spectroscopy. ATR FT-IR spectra were recorded at ambient temperature on a Diamond crystal on a FTIR Bruker ALPHA with a QuickSnap Platinum ATR sampling module inside an inert atmosphere glovebox. Spectra were recorded in a range from 4000-500 cm^{-1}. The spectra were recorded with 64 scans and a resolution of 2 cm^{-1}. Data processing was carried out with the software package OPUS 7.5. For all spectra, signal intensity was normalised to and the relative band intensities were described as follows: $\geq$ 0.8 = very very strong (vvs), $\geq$ 0.7 = very strong (vs), $\geq$ 0.6 = strong (s), $\geq$ 0.5 = medium strong (ms), $\geq$ 0.4 = medium (m), $\geq$ 0.3 = medium weak (mw), $\geq$ 0.2 = weak (w), $\geq$ 0.1 = very weak (vw), $<$ 0.1 = very very weak (vvw).

Single crystal X-ray diffraction. Single crystal X-ray diffraction data were collected using either a Bruker SMART APEXII QUAZAR detector with fixed-Chi D8 Goniometer, INCOATEC Mo microsource or Bruker D8 VENTURE with PHOTONIII detector, fixed-Chi D8 Goniometer and INCOATEC Mo/Cu microsource. Crystals were selected under perfluoropolyether oil, mounted on 0.1 to 0.3 mm diameter CryoLoops and quench-cooled using an Oxford Cryostream 800 open flow N_2 cooling device.[4] Data were collected at 100 K using monochromated Cu Kα or Mo Kα radiation (λ = 1.5418/0.71073 Å). Data processing was done with SHELXS/XL and refined by least squares on weighted F^2 values for all reflections, disordering of fragments was done with the help of the implemented DSR tool.[5,6] Graphical representations have been prepared using Olex2-1.2. Finalisation of gathered data was done using final cif tool.[7]

NMR spectroscopy. NMR samples were prepared inside an inert atmosphere glovebox in either flame sealable NMR tubes or NMR tubes equipped with a gas-tight J.Young valve. ^{1}H, ^{13}C, ^{19}F, ^{27}Al, ^{31}P-NMR spectra were acquired either on a Bruker Biospin Avance II+ 400 MHz WB, a Bruker Avance 200 MHz or a Bruker Avance III HD 300 MHz spectrometer. ^{1}H and ^{13}C NMR spectra are reported relative to TMS and were calibrated to residual solvent resonances.[8] Data analysis was performed using the Bruker TOPSPIN 3.5 software. The broad resonance at δ = 70 ppm observed in ^{27}Al-NMR spectra corresponds

to a background from Al-nuclei in the probe head. Base line rolling (broad features) centred at δ = 0 ppm in ^{11}B-NMR spectra stem from borosilicate glass of the used NMR-tubes.

Quantum Chemical Calculations. All quantum chemical calculations were carried out with the TURBOMOLE program package using the BP86 functionals with def-SV(P) basis sets and D3(BJ) dispersion correction.[9–13] Vibrational frequencies were calculated using the AOFORCE-module.[14] All calculated structures were checked for consistency in terms of geometric conversion, sensible electron occupations and the absence of imaginary vibrational frequencies. Thermal contributions to the enthalpy and free energy of the systems were calculated with the FREEH application based on the analysis of the vibrations obtained by BP86/def-SV(P)/D3(BJ) calculations. Charge analysis was done by NPA[15], PABOON[16] and AIM[17] analysis on wfn files generated with TURBOMOLE using the program Multiwfn 3.6.[18]

S-2 Experimental

S-2.1 Synthesis of [H-PPh$_3$][Al(OR^F)$_4$].

[H-PPh$_3$][BF$_4$] (210 mg, 0.6 mmol) and Li[Al(OR^F)$_4$] (584 mg, 0.6 mmol, 1.0 eq.) were dissolved in CH_2Cl_2 (5 ml) and stirred at ambient temperature for 12 h. The supernatant solution was filtered and the precipitate extracted with CH_2Cl_2 (5 ml). The solvent was removed under reduced pressure and the obtained white solid washed with *n*-pentane (10 ml). [H-PPh$_3$][Al(OR^F)$_4$] was obtained as colourless solid (610 mg, 0.5 mmol, 82 %).

^{1}H-NMR (400.17 MHz, CD_2Cl_2, 298 K): δ = 8.76 (s, 1H, [*H*-PPh$_3$]$^+$), 7.83 (m, 3H, [H-PPh$_3$]$^+$, *p*-C$_6$*H*$_5$), 7.65 (m, 6H, BPh$_3$, *o*-C$_6$*H*$_5$), 7.57 (m, 6H, BPh$_3$, *m*-C$_6$*H*$_5$). ^{19}F-NMR (376.54 MHz, CD_2Cl_2, 298 K): δ = −75.8 (s, 36F, [Al(O(C(C*F*$_3$)$_3$)$_4$]$^-$) ppm. ^{27}Al-NMR (104.27 MHz, CD_2Cl_2, 298 K): δ = 34.4 (s, [*Al*(O(C(CF$_3$)$_3$)$_4$]$^-$) ppm. ^{31}P-NMR (161.99 MHz, CD_2Cl_2, 298 K): δ = 7.49 (d, ^{1}J(^{31}P-^{1}H) = 487 Hz, [H-*P*Ph$_3$]$^+$) ppm.

S-2.2 Reaction between **2** and [H-PPh$_3$][Al(OR^F)$_4$] with addition of PPh$_3$: Isolation of [H-Ga(PPh$_3$)$_3$][Al(OR^F)$_4$]$_2$ **3.**

2 (50 mg, 0.042 mmol) and [H-PPh$_3$][Al(OR^F)$_4$] (51 mg, 0.042 mmol, 1.0 eq.) were dissolved in *o*DFB (1 ml) and analysed by NMR showing only resonances of the two starting materials. Then PPh$_3$ (10 mg, 0.042 mmol, 1.0 eq.) was added to the NMR tube and the spectra recollected. The NMR solution was then layered with *n*-pentane to yield **45** as colourless crystals (24 mg, 0.042 mmol, 24 %).

^{1}H-NMR (300.18 MHz, 1,2-C$_6$H$_4$F$_2$, 298 K): δ = 7.99 (s, 1H, [*H*-PPh$_3$]$^+$), 7.66 – 7.15 (m, X-PPh$_3$, -C$_6$H$_5$), 6.65 (m, [*H*-Ga(PPh$_3$)$_x$]$^+$), 2.22 (s, 18 H, C$_6$Me$_6$) ^{19}F-NMR (282.45 MHz, 1,2-C$_6$H$_4$F$_2$, 298 K): δ = −75.3 (s, 36F, [Al(O(C(C*F*$_3$)$_3$)$_4$]$^-$) ppm. ^{27}Al-NMR (78.22 MHz, 1,2-C$_6$H$_4$F$_2$, 298 K): δ = 35.0 (s, [*Al*(O(C(CF$_3$)$_3$)$_4$]$^-$) ppm. ^{31}P-NMR (121.52 MHz, 1,2-C$_6$H$_4$F$_2$, 298 K): δ = 8.38 (d, ^{1}J(^{31}P-^{1}H) = 495.9 Hz, [H-*P*Ph$_3$]$^+$), 4.42 (d, ^{2}J(^{31}P-

^{1}H) = 33.6 Hz, [H-Ga(PPh$_3$)$_x$]$^+$) ppm. ^{71}Ga-NMR (91.55 MHz, 1,2-$C_6H_4F_2$, 298 K): δ = 717 (s, [Ga(HMB)$_n$]$^+$)ppm

S-2.3 Reaction between **1** and [H-PPh$_3$][Al(OR^F)$_4$] in presence of 2 eq. PPh$_3$.

1 (100 mg, 0.078 mmol) and [H-PPh$_3$][Al(OR^F)$_4$] (95 mg, 0.0743 mmol, 0.95 eq.) were dissolved in *o*DFB (1 ml) and cooled to −20°C. Next a cooled solution of PPh$_3$ (39 mg, 0.1487, 1.9 eq.) in *o*DFB was added to the reaction mixture. The reaction mixture was stirred for further 30 min at this temperature and then warmed to ambient temperature and concentrated to half-volume for NMR analysis.

^{1}H-NMR (300.18 MHz, 1,2-$C_6H_4F_2$, 298 K): δ = 7.57 – 7.13 (m, X-PPh$_3$, -C_6H_5), 6.70 (m, [H-Ga(PPh$_3$)$_x$]$^+$) ppm. ^{19}F-NMR (282.45 MHz, 1,2-$C_6H_4F_2$, 298 K): δ = −75.3 (s, 36F, [Al(O(C(CF_3)$_3$)$_4$]$^-$) ppm. ^{27}Al-NMR (78.22 MHz, 1,2-$C_6H_4F_2$, 298 K): δ = 35.0 (s, [Al(O(C(CF_3)$_3$)$_4$]$^-$) ppm. ^{31}P-NMR (121.52 MHz, 1,2-$C_6H_4F_2$, 298 K): δ = 8.43 (d, ^{1}J(^{31}P-^{1}H) = 495.8 Hz, [H-PPh$_3$]$^+$), 4.42 (d, ^{2}J(^{31}P-^{1}H) = 37.7 Hz, [H-Ga(PPh$_3$)$_x$]$^+$) ppm. ^{71}Ga-NMR (91.55 MHz, 1,2-$C_6H_4F_2$, 298 K): δ = 717 (s, [Ga(HMB)$_n$]$^+$)ppm.

IR (64 scans, ZnSe ATR, corrected): $\tilde{\nu}$/cm^{-1} (intensity) = 1443 (vw) 1350 (vw) 1297 (mw) 1273 (s) 1239 (vs) 1210 (vvs) 1163 (ms) 1114 (w) 1097 (w) 968 (vvs) 907 (vw) 889 (w) 829 (vw) 742 (w) 725 (vvs) 687 (m) 559 (vw).

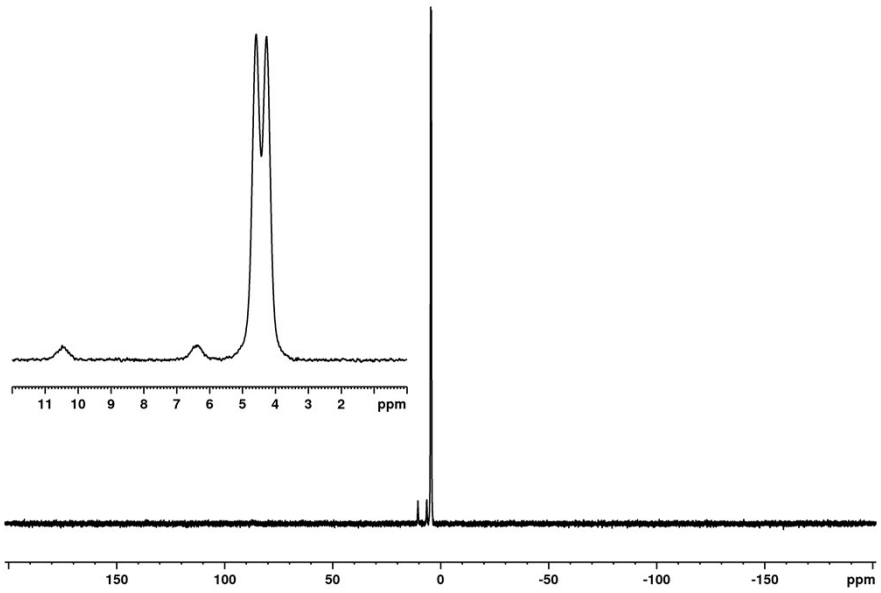


Fig. S 1: ^{31}P-NMR (121.52 MHz, 1,2-$C_6H_4F_2$, 298 K) spectrum of reaction between [Ga(PhF)$_{2.5}$][Al(OR^F)$_4$] and [H-PPh$_3$][Al(OR^F)$_4$] in presence of 2 eq. PPh$_3$

S-2.4 Reaction between **2** and PPh$_2$Cl: Isolation of [μ-(PPh$_2$)-(PPh$_2$)$_2$][Al(OR^F)$_4$]$_2$ **4**.

2 (68 mg, 0.057 mmol) was dissolved in *o*DFB (1 ml) and PPh$_2$Cl (10 µl, 0.0567 mmol, 1 eq.) was added to the reaction mixture. The reaction mixture was shaken thoroughly and submitted to NMR analysis.

The reaction mixture was then layered with *n*-pentane to yield yellow crystals of **47** (15 mg, 0.009 mmol, 52% with respect to three eq. of PPh_2Cl).

^{1}H-NMR (300.18 MHz, 1,2-$C_6H_4F_2$, 298 K): δ = 7.78 – 7.22 (m, X-PPh_2, -C_6H_5), 2.19 (18 H, C_6Me_6) ppm. ^{19}F-NMR (282.45 MHz, 1,2-$C_6H_4F_2$, 298 K): δ = −75.3 (s, 36F, $[Al(O(C(CF_3)_3)_4]^-$) ppm. ^{27}Al-NMR (78.22 MHz, 1,2-$C_6H_4F_2$, 298 K): δ = 35.0 (s, $[Al(O(C(CF_3)_3)_4]^-$) ppm. ^{31}P-NMR (121.52 MHz, 1,2-$C_6H_4F_2$, 298 K): δ = 72.3 (d, 1P, $^{1}J(^{31}P\text{-}^{31}P)$ = 393 Hz, $[PPh_2Cl\text{-}PPh_2]^+$),14.62 (m, $[\mu(PPh_2)\text{-}(PPh_2)_2]^+$), 1.66 (d, 1P, $^{1}J(^{31}P\text{-}^{31}P)$ = 393 Hz, $[PPh_2Cl\text{-}PPh_2]^+$), −18.09 (m, $[\mu(PPh_2)\text{-}(PPh_2)_2]^+$) ppm. ^{71}Ga-NMR (91.55 MHz, 1,2-$C_6H_4F_2$, 298 K): δ = 250 (br. s, $GaCl_3$), −711 (s, $[Ga(HMB)_n]^+$)ppm.

IR (64 scans, ZnSe ATR, corrected): $\tilde{\nu}$/cm^{-1} (intensity) = 1584 (vvw) 1509 (vvw) 1483 (vvw) 1440 (vw) 1351 (vw) 1297 (mw) 1273 (ms) 1238 (vs) 1209 (vvs) 1166 (m) 1103 (vw) 1094 (vw) 1026 (vvw) 998 (vw) 968 (vvs) 860 (vvw) 832 (vw) 744 (w) 725 (vvs) 704 (vw) 684 (m) 639 (vvw) 571 (vw) 560 (vw)

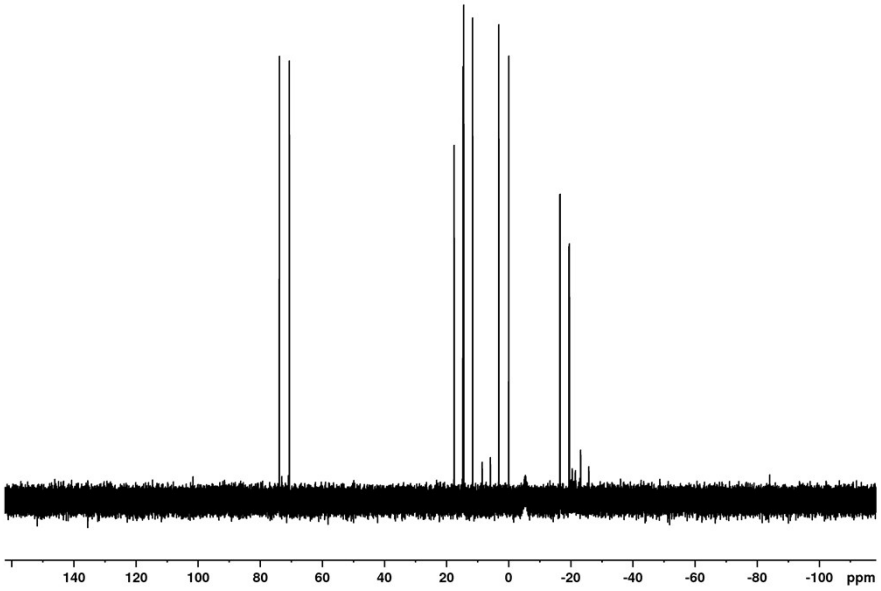


*Fig. S 2: ^{31}P-NMR (121.52 MHz, 1,2-$C_6H_4F_2$, 298 K) spectrum of reaction between **2** and PPh_2Cl.*

S-2.1 Reaction between **1** and PPh_2Cl: Isolation of $[\mu\text{-}(PPh_2)\text{-}(PPh_2)_2][Al(OR^F)_4]_2$ **4**.

1 (230 mg, 0.187 mmol) was dissolved in *o*DFB (2 ml) and PPh_2Cl (100 µl, 0.561 mmol, 3 eq.) was added at −30°C to the reaction mixture. The reaction mixture was stirred for 1h at ambient temperature and subsequently layered with n-pentane to yield yellow crystals of **4** (164 mg, 0.009 mmol, 58% crystalline yield).

^{1}H-NMR (300.18 MHz, CD_2Cl_2, 298 K): δ = 7.79 – 7.73 (m, $[\mu(P(C_6H_5)_2)\text{-}(PPh_2)_2]^+$), 7.53-7.42 (m, $[\mu(P(C_6H_5)_2)\text{-}(PPh_2)_2]^+$), 7.37 (m, $[\mu(P(Ph)_2)\text{-}(P(C_6H_5)_2)_2]^+$), 7.25 (m, $[\mu(P(Ph)_2)\text{-}(P(C_6H_5)_2)_2]^+$), 7.54 (m, $[PPh_2Cl\text{-}P(C_6H_5)_2]^+$), 7.93 (m, $[P(C_6H_5)_2Cl\text{-}P(Ph)_2]^+$), 7.73-7.63 (m, $[P(C_6H_5)_2Cl\text{-}P(Ph)_2]^+$) ppm. ^{19}F-NMR

(282.45 MHz, 1,2-$C_6H_4F_2$, 298 K): δ = −75.6 (s, 36F, $[Al(O(C(CF_3)_3)_4]^-$) ppm. ^{27}Al-NMR (78.22 MHz, 1,2-$C_6H_4F_2$, 298 K): δ = 34.6 (s, $[Al(O(C(CF_3)_3)_4]^-$) ppm. ^{31}P-NMR (121.52 MHz, 1,2-$C_6H_4F_2$, 298 K): δ = 72.6 (d, 1P, $^1J(^{31}P\text{-}^{31}P)$ = 390 Hz, $[PPh_2Cl\text{-}PPh_2]^+$), 14.33 (m, $[\mu(PPh_2)\text{-}(PPh_2)_2]^+$), 1.0 (d, 1P, $^1J(^{31}P\text{-}^{31}P)$ = 390 Hz, $[PPh_2Cl\text{-}PPh_2]^+$), −2.0 (br. s, $Cl_3Ga\text{-}P(Ph_2)\text{-}P(Ph_2)\text{-}GaCl_3$), −18.2 (m, $[\mu(PPh_2)\text{-}(PPh_2)_2]^+$) ppm.

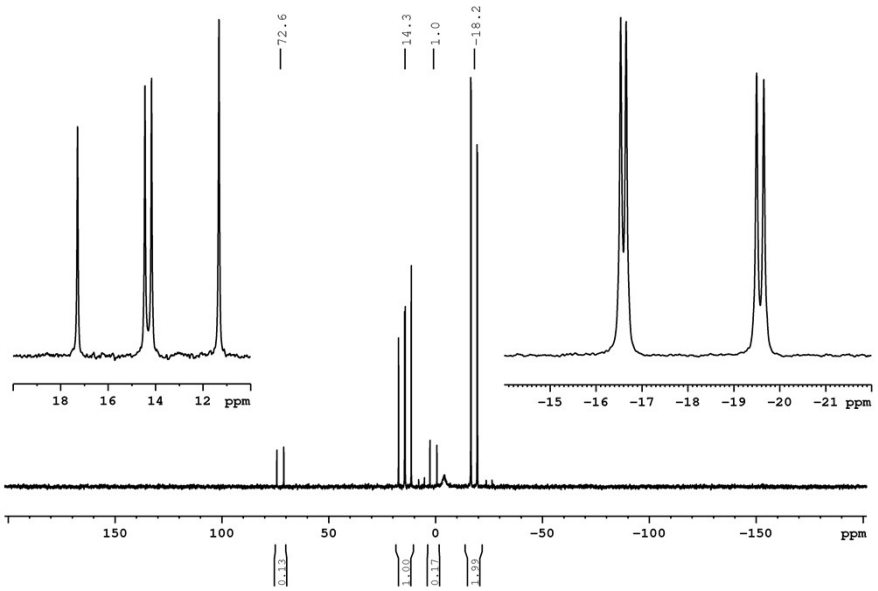
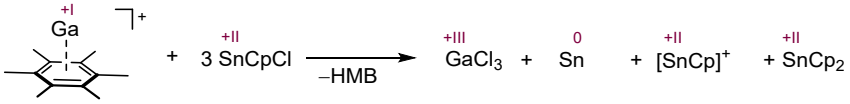


*Fig. S 3: ^{31}P-NMR (121.52 MHz, CD_2Cl_2, 298 K) spectrum of reaction between **1** and PPh_2Cl.*

S-2.2 Reaction between **2** and SnCpCl

In probing the reactivity of **2** with other main-group halide species a reaction between **2** and SnCpCl was carried out. Along with formation of $GaCl_3$ (NMR) precipitation of a grey precipitate (presumably Sn^0) was observed. Crystallisation of the obtained reaction mixture allowed for the isolation of known quadruple-decker $[CpSn(\mu\text{-}SnCp_2)SnCp][Al(OR^F)_4]_2$. The "excess" of Cp^- needed for the formation of this cation is attributed by loss of one equivalent of Sn as Sn^0 by reduction. The obtained results are therefore in line with the above described reactivity and show the reducing ability of the employed subvalent Gallium cation.

2 (150 mg, 0.123 mmol) and SnCpCl (81 mg, 0.369 mmol, 3 eq.) were dissolved in *o*DFB (4 ml) and stirred for 2 d at ambient temperature. The supernatant was filtered from formed grey precipitate (Sn^0) and submitted for NMR analysis. The reaction mixture was subsequently layered with *n*-pentane to yield needle shaped crystals revealing the molecular structure of $[CpSn(\mu\text{-}SnCp_2)SnCp][Al(OR^F)_4]_2$.



Scheme S 1: Proposed reaction sequence in the formation of [CpSn(μ-SnCp$_2$)SnCp][Al(OR^F)$_4$]$_2$. From the mixture of [Sn(Cp)]$^+$ and SnCp$_2$ the dication salt [CpSn(μ-SnCp$_2$)SnCp][Al(OR^F)$_4$]$_2$ crystallised.

^{1}H-NMR (300.18 MHz, 1,2-$C_6H_4F_2$, 298 K): δ = 6.63 (5 H, Cp), 2.12 (s, 18H, C_6Me_6) ppm. ^{19}F-NMR (282.45 MHz, 1,2-$C_6H_4F_2$, 298 K): δ = −75.3 (s, 36F, [Al(O(C(C*F*$_3$)$_3$)$_4$]$^-$) ppm. ^{27}Al-NMR (78.22 MHz, 1,2-$C_6H_4F_2$, 298 K): δ = 35.0 (s, [*Al*(O(C(CF$_3$)$_3$)$_4$]$^-$) ppm. ^{71}Ga-NMR (91.55 MHz, 1,2-$C_6H_4F_2$, 298 K): δ = 250 (s, $GaCl_3$), −615 (s, [*Ga*(μ-Cp)SnCp]$^+$)ppm. ^{119}Sn-NMR (111.94 MHz, 1,2-$C_6H_4F_2$, 298 K): δ = −2303 (s, 1 Sn, [CpSn(μ-SnCp$_2$)SnCp]$^{2+}$) ppm.

S-2.3 Reaction of **1** with 1.5 eq. of $PPhCl_2$. Isolation of $[P_6Ph_6Cl_2]^{2+}[A]^-_2$; $[A]^-$ = $[Ga_2Cl_7]^-$ **5a**, $[A]^-$ = $[Al(OR^F)_4]^-$ **5b**.

1 (200 mg, 0.157 mmol) was dissolved in oDFB (2 ml) and cooled to −30°C. Next a stock solution of $PPhCl_2$ (1 ml, 0.236 M, 0.236 mmol, 1.5 eq.) was added to the reaction mixture at this temperature for 30 min. Upon addition the colour of the reaction mixture darkened immediately. The reaction mixture was warmed to ambient temperature and stirred for additional 2h. During this time the dark brown colour faded to give a colourless suspension which slowly changed for a faint yellow clear solution. The solvent was removed under reduced pressure and the residue dissolved in CD_2Cl_2 for NMR analysis.

^{1}H-NMR (300.18 MHz, CD_2Cl_2, 298 K): **6** δ = 8.18-6.84 (several m, Ar-H, -P(C_6H_5)) ppm. ^{31}P-NMR (121.52 MHz, CD_2Cl_2, 298 K): 110.7(br. d, J_{PP} = 425 Hz, [(Ph)Cl$_2$*P*-PCl(Ph)-GaCl$_3$]$^+$),85.7 (br. d, J_{PP} = 425 Hz, [(Ph)Cl$_2$P-PCl(Ph)-GaCl$_3$]$^+$), 79.9 (m, 2 P, [$P_6Ph_6Cl_2$]$^{2+}$,>*P*Cl(Ph)),70.8 (d, J_{PP} = 395 Hz, [(Ph$_2$)Cl*P*-PCl(Ph)]$^+$), 57.9 (d, J_{PP} = 395 Hz, [(Ph$_2$)ClP-PCl(Ph)]$^+$),9.6 (m),-11.9 (m, 4 P, [$P_6Ph_6Cl_2$]$^{2+}$, >P(Ph)),-18.6 to -31.7 (several small m). ^{19}F-NMR (282.45 MHz, CD_2Cl_2, 298 K): δ = −75.3 (s, 36F, [Al(O(C(C*F*$_3$)$_3$)$_4$]$^-$) ppm. ^{27}Al-NMR (78.22 MHz, CD_2Cl_2, 298 K): δ = 34.8 (s, [*Al*(O(C(CF$_3$)$_3$)$_4$]$^-$) ppm. ^{71}Ga-NMR (91.55 MHz, CD_2Cl_2, 298 K): no resonances.

The reaction was repeated in analogy. The obtained faint yellow oDFB solution was layered with n-pentane for crystallisation. After 2 d, block shaped yellow crystals of $[P_6Ph_6Cl_2]^{2+}[Ga_2Cl_7]^-_2$ **5a** separated together with a yellow oil, which furnished a further crop of yellow crystals after 5 d at ambient temperature comprising of $[P_6Ph_6Cl_2]^{2+}[Al(OR^F)_4]^-_2$ **5b**.

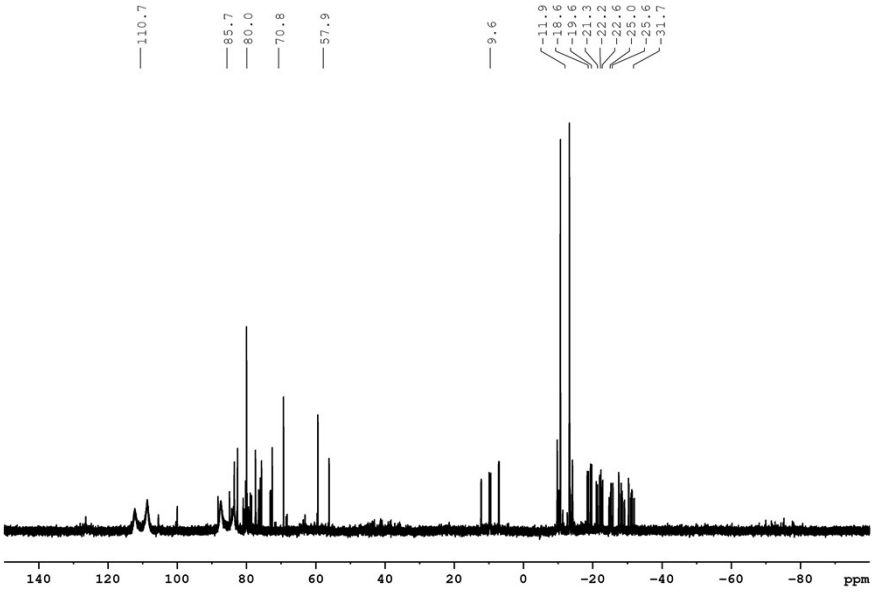


*Fig. S 4: ^{31}P-NMR (121.52 MHz, CD_2Cl_2, 298 K) spectrum of reaction between **1** and 1.5 eq. of $PPhCl_2$.*

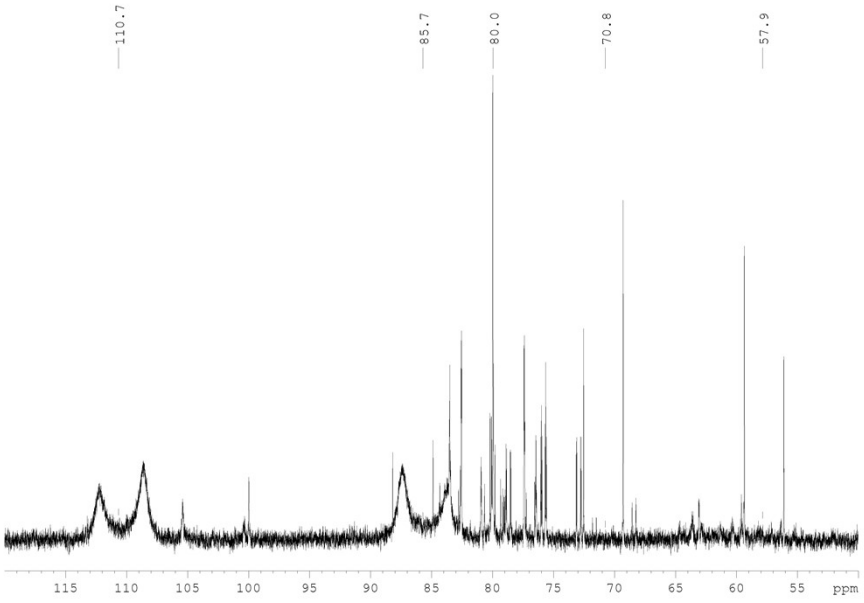


*Fig. S 5 ^{31}P-NMR (121.52 MHz, CD_2Cl_2, 298 K) spectrum of reaction between **1** and 1.5 eq. of $PPhCl_2$ region 120 to 50 ppm magnified.*

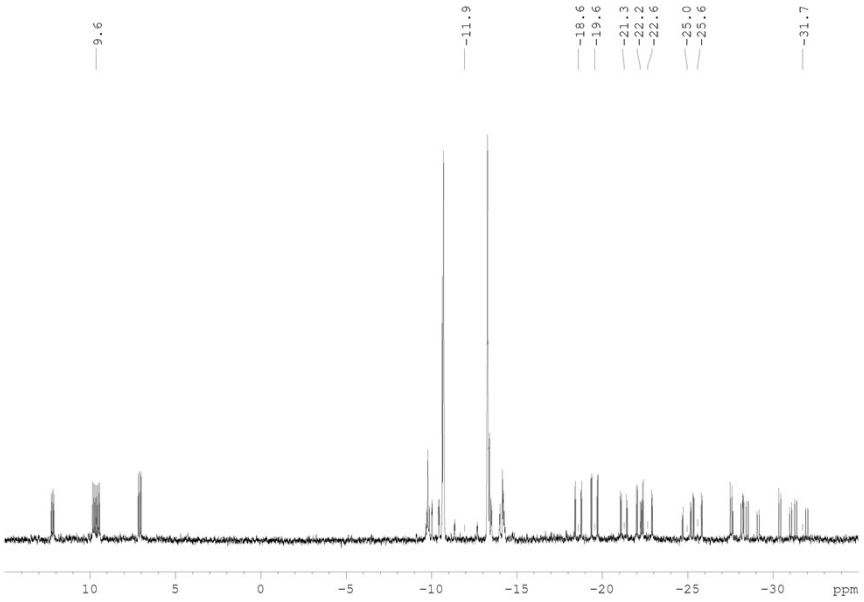


*Fig. S 6 ^{31}P-NMR (121.52 MHz, CD_2Cl_2, 298 K) spectrum of reaction between **1** and 1.5 eq. of $PPhCl_2$.region 20 to -35 ppm magnified.*

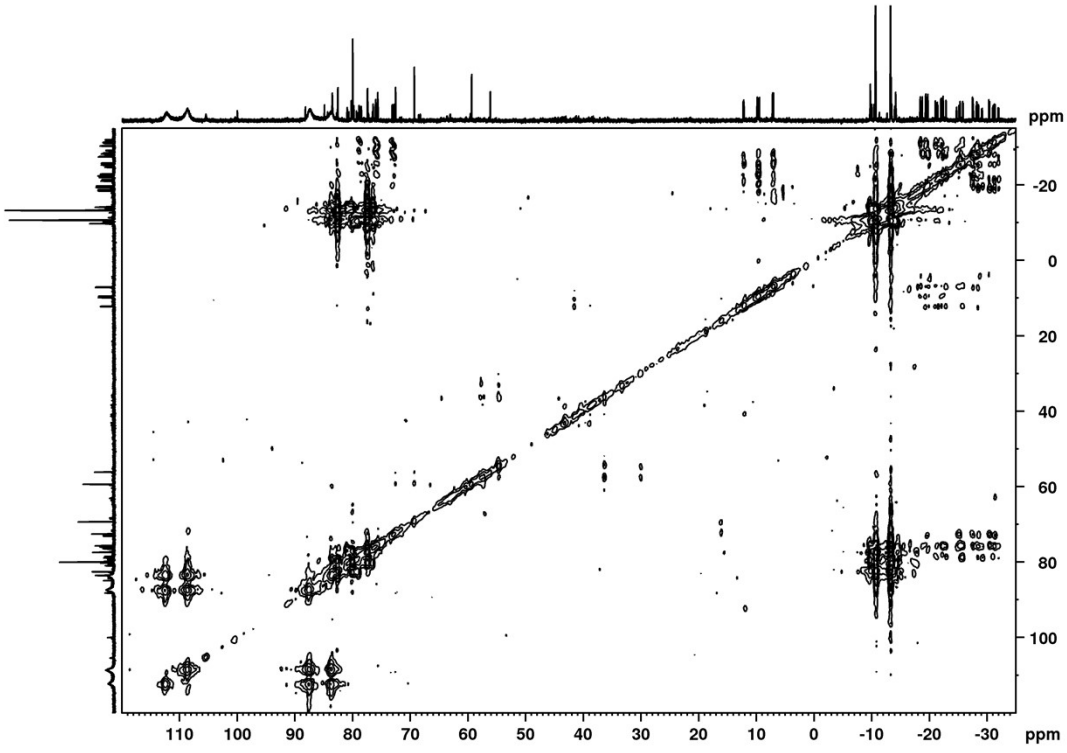


*Fig. S 7: ^{31}P-COSY-NMR (121.52 MHz, CD_2Cl_2, 298 K) spectrum of reaction between **1** and 1.5 eq. of $PPhCl_2$.*

S-2.4 Reactions between **1** and $SbCl_3$ in presence of dimpyr^{Dipp}.

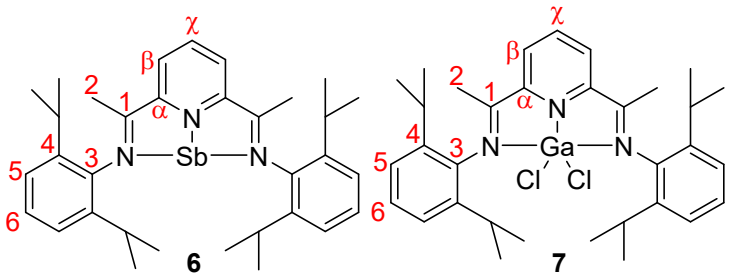
The following reaction was repeated several times with varying reaction conditions: temperature, order of addition, solvent media. Two syntheses have been exemplarily selected in the following.

S-2.4.1 Reaction between **1** and $SbCl_3$ in presence of dimpyr^{Dipp}. Isolation of [Sb(dimpyr^{Dipp})][Al(OR^F)$_4$] **6**.

$SbCl_3$ (35.7 mg, 0.157 mmol) and dimpyr^{Dipp} (75.4 mg, 0.157 mmol, 1.0 eq.) were suspended in fluorobenzene 4 ml. Next **1** (200 mg, 0.156 mmol, 1 eq.) dissolved in fluorobenzene (2 ml) was added with immediate formation of a dark green colour. The reaction mixture was stirred for 1 h at ambient temperature. The supernatant dark green solution was filtered from the formed dark precipitate. An aliquot (1 ml) was removed from the reaction mixture for NMR analysis. The remaining reaction mixtures was concentrated to half volume and layered with *n*-pentane for crystallisation. [Sb(dimpyr^{Dipp})][Al(OR^F)$_4$] **6** (170 mg, 0.108 mmol, 69%) was obtained as dark green needle shaped crystals suitable for scXRD analysis.

NMR analysis of the reaction mixture revealed contamination of **6** with **7** by 35 % whereas analysis of the isolated crystalline material revealed **7** to be the major isolated product (65%). However, attempts to purify **6** by fractional crystallisation (see below) have proven futile and all attempts to selectively extract either **6** or **7** by the use of CH_2Cl_2, toluene, Et_2O have proven unsuccessful and clean samples of **6** could not be obtained. EPR spectra were recorded on dilute *o*DFB solution at ambient temperature as well as solid samples at 100 K showing no resonances in each case. The obtained compound **6** is therefore diamagnetic as evidenced by missing EPR resonance together with sharp NMR resonances. QTAIM-Analysis suggest a charge of +1.04 at the central antimony atom allowing for the assignment of a formal oxidation state of +I.

ESI-MS (m/z): **7** (m/z found 622.42; clcd. 622.21), **6** (m/z found 602.58; clcd. 602.25).



^{1}H-NMR (300.18 MHz, PhF, 298 K): **6** δ = 8.36 (m, 2 H, dimpyr^{Dipp}, Pyr-β*H*), 7.63 (m, 1 H, dimpyr^{Dipp}, Pyr-γ*H*), 7.25 – 7.16 (6 H, -Dipp, Ar-*m*/*pH*), 2.50 (s, 6 H, dimpyr^{Dipp}, -CH_3), 2.03 (sept., 4 H, ^{3}J = 6.7 Hz, -Dipp, -C*H*(CH_3)$_2$), 1.04 (d, 12 H, ^{3}J = 6.7 Hz, -Dipp, -CH(C*H*$_3$)$_2$), 1.01 (d, 12 H, ^{3}J = 6.7 Hz, -Dipp, -CH(C*H*$_3$)$_2$) ppm. **7** δ = 8.72 (m, 1 H, dimpyr^{Dipp}, Pyr-γ*H*), 8.50 (m, 1 H, dimpyr^{Dipp}, Pyr-β*H*), 7.25 – 7.16 (6 H, -Dipp, Ar-

m/*pH*), 2.67 (sept., 4 H, ^{3}J = 6.6 Hz, -Dipp, -C*H*(CH_3)$_2$), 2.31 (s, 6 H, dimpyr^{Dipp}, -CH_3), 1.21 (d, 12 H, ^{3}J = 6.6 Hz, -Dipp, -CH(C*H*$_3$)$_2$), 0.98 (d, 12 H, ^{3}J = 6.6 Hz, -Dipp, -CH(C*H*$_3$)$_2$) ppm. ^{13}C-NMR (75.48 MHz, PhF , 298 K): **6** δ = 159.8 (C-1), 142.2 (C-α), 141.2 (C-3), 133.6 (C-4), 129.8 (C-β), 128.3 (C-γ), 123.4 - (C-5/C-6), 29.6 (-Dipp, -*C*H(CH_3)$_2$), 24.5 (-Dipp, -CH(*C*H_3)$_2$), 22.8 (-Dipp, -CH(*C*H_3)$_2$), 15.8 (-Me, C-2)). **7** δ = 168.6 (C-1), 148.4 (C-γ), 143.7 (C-α), 140.0 (C-3), 136.1 (C-4), 127.6 (C-β), 124.7 (C-5/C-6), 29.8 (-Dipp, -*C*H(CH_3)$_2$), 23.8 (-Dipp, -CH(*C*H_3)$_2$), 23.6 (-Dipp, -CH(*C*H_3)$_2$), 17.4 (-Me, C-2). ^{19}F-NMR (282.45 MHz, PhF, 298 K): δ = −75.3 (s, 36F, [Al(O(C(C*F*$_3$)$_3$)$_4$]$^-$) ppm. ^{27}Al-NMR (78.22 MHz, PhF, 298 K): δ = 35.0 (s, [*Al*(O(C(CF_3)$_3$)$_4$]$^-$) ppm. ^{71}Ga-NMR (91.55 MHz, 1,2-$C_6H_4F_2$, 298 K): no resonances.

IR (64 scans, ZnSe ATR, corrected): $\tilde{\nu}$/cm–1 (intensity) = 2958 (vw) 2923 (w) 2852 (vw) 1643 (vvw) 1596 (vvw) 1497 (vvw) 1465 (vw) 1440 (vw) 1418 (vw) 1351 (vw) 1300 (m) 1275 (ms) 1239 (s) 1213 (vvs) 1163 (mw) 1101 (w) 1057 (vw) 1040 (vw) 971 (vvs) 828 (vw) 796 (mw) 778 (w) 766 (vw) 755 (vw) 737 (vw) 727 (vvs) 696 (vw) 559 (vw).

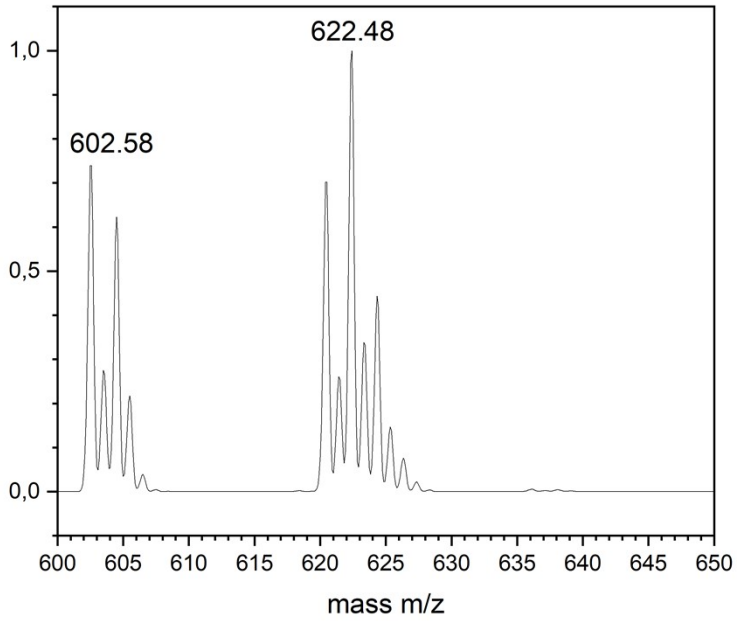


*Fig. S 8: positive ion mode ESI-mass spectrum of isolated crystalline material from reaction between **1** and $SbCl_3$ in presence of dimpyr^{Dipp}.*

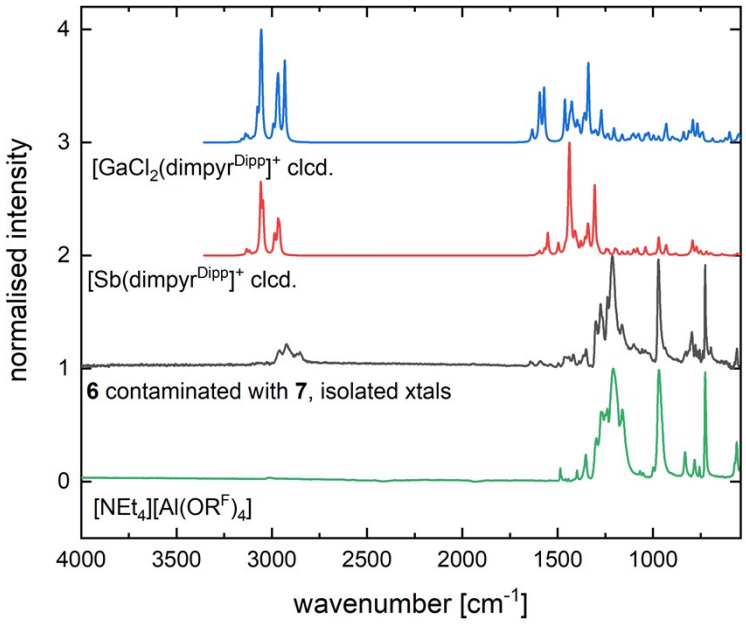


*Fig. S 9: ATR-IR spectrum of isolated crystalline material from reaction between **1** and $SbCl_3$ in presence of dimpyr^{Dipp} (black trace), together with [NEt_4][Al(OR^F)$_4$] (comparison of Anion bands, green trace) and calculated spectra of cationic part of **6** (red trace) and **7** (blue trace).*

S-2.4.2 Reaction between **1** and $SbCl_3$ in presence of dimpyr^{Dipp}. Isolation of [$GaCl_2$(dimpyr^{Dipp})][Al(OR^F)$_4$] **7**.

$SbCl_3$ (74 mg, 0.324 mmol) and dimpyr^{Dipp} (78 mg, 0.162 mmol, 0.5 eq.) were suspended in Toluene 10 ml and cooled to −30°C. Next **1** (199 mg, 0.162 mmol, 0.5 eq.) dissolved in fluorobenzene (3 ml) was added at −30°C with immediate formation of a dark green colour. The reaction mixture was stirred for 1 h at this temperature, warmed to ambient temperature and stirred for further 2h. The supernatant solution was filtered from the formed dark precipitate and the solvent removed in vacuo. NMR analysis of the crude reaction product revealed presence of both **6** and **7**. The crude reaction product was dissolved in fluorobenzene (2 ml), concentrated to half volume and stored at −30°C for crystallisation. Colourless block shaped crystals of [$GaCl_2$(dimpyr^{Dipp})][Al(OR^F)$_4$] **7** suitable for scXRD analysis were obtained.

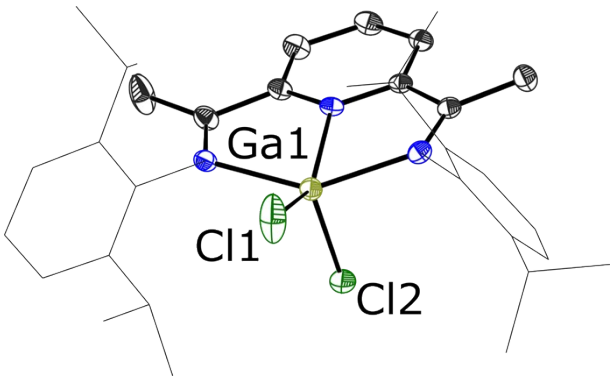


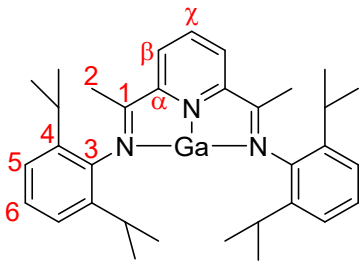
*Fig. S 10: Molecular structure of [$GaCl_2$(dimpyr^{Dipp})][Al(OR^F)$_4$ **7**. Protons, counter ion and solvent (fluorobenzene) omitted and Dipp groups drawn as wireframe for clarity. Thermal displacement ellipsoids set at 50% probability.*

NMR analysis of the obtained crystalline material revealed pure isolation of **7**. While the supernatant mother liquor still contained both **6** and **7**.

^{1}H-NMR (300.18 MHz, CD_2Cl_2, 298 K): δ = 9.02 (m, 1 H, dimpyr^{Dipp}, Pyr-γ*H*), 8.72 (m, 2 H, dimpyr^{Dipp}, Pyr-β*H*), 7.50 – 7.40 (6 H, -Dipp, Ar-*m*/*pH*), 2.72 (s, 6 H, dimpyr^{Dipp}, -CH_3), 2.66 (sept., 2 H, ^{3}J = 6.7 Hz, -Dipp, -C*H*(CH_3)$_2$), 1.31 (d, 12 H, ^{3}J = 6.7 Hz, -Dipp, -CH(C*H*$_3$)$_2$), 1.15 (d, 12 H, ^{3}J = 6.7 Hz, -Dipp, -CH(C*H*$_3$)$_2$) ppm.

S-2.5 Synthesis of [Ga(dimpyr^{Dipp}][Al(OR^{F})$_4$] **8** RT-34

1 (200 mg, 0.156 mmol) and dimpyr^{Dipp} (75.4 mg, 0.156 mmol, 1.0 eq.) were dissolved in *o*DFB (3 ml). Upon solvent addition, immediate formation of a deep red colour was observed. The reaction mixture was stirred for 1 h at ambient temperature and subsequently concentrated to a third of the volume and stored at −30°C for crystallisation. Dark red crystals of [Ga(dimpyr^{Dipp}][Al(OR^{F})$_4$] **8** (125 mg, 0.157 mmol, 53% crystalline yield) suitable for scXRD analysis were obtained. EPR measurements were conducted on dilute solutions of **8** in *o*DFB as well as solid samples at 100 K showed no resonances in each case. The obtained compound **8** is therefore diamagnetic as evidenced by missing EPR resonance together with sharp NMR resonances. QTAIM-Analysis suggest a charge of +0.77 at the central gallium atom allowing for the assignment of a formal oxidation state of +I.



^{1}H-NMR (300.18 MHz, 1,2-$C_6H_4F_2$, 298 K): δ = 8.38 (m, 1 H, dimpyr^{Dipp}, Pyr-γ*H*), 8.23 (m, 2 H, dimpyr^{Dipp}, Pyr-β*H*), 7.29 – 7.22 (6 H, -Dipp, Ar-*m*/*pH*), 2.58 (sept., 2 H, ^{3}J = 6.8 Hz, -Dipp, -C*H*(CH_3)$_2$), 2.40 (s, 6 H, dimpyr^{Dipp}, -CH_3), 1.16 (d, 12 H, ^{3}J = 6.8 Hz, -Dipp, -CH(C*H*$_3$)$_2$), 1.13 (d, 12 H, ^{3}J = 6.8 Hz, -Dipp, -CH(C*H*$_3$)$_2$) ppm. ^{13}C-NMR (75.48 MHz, 1,2-$C_6H_4F_2$, 298 K): δ = 167.9 (C-1), 150.6 (C-α), 144.3 (C-γ), 138.3 (C-3), 137.7 (C-4), 126.9 (C-β), 123.9 - 123.7 (C-5, C-6), 28.9 (-Dipp, -*C*H(CH_3)$_2$), 23.9 (-Dipp, -CH(*C*H$_3$)$_2$), 22.1 (-Dipp, -CH(*C*H$_3$)$_2$), 16.6 (-Me, C-2). ^{19}F-NMR (282.45 MHz, 1,2-$C_6H_4F_2$, 298 K): δ = −75.3 (s, 36F, [Al(O(C(C*F*$_3$)$_3$)$_4$]$^-$) ppm. ^{27}Al-NMR (78.22 MHz, 1,2-$C_6H_4F_2$, 298 K): δ = 35.0 (s, [*Al*(O(C(CF_3)$_3$)$_4$]$^-$) ppm. ^{71}Ga-NMR (91.55 MHz, 1,2-$C_6H_4F_2$, 298 K): no resonances.

S-2.6 Reaction between **2** and $RhCl_3$ in presence of COD. Isolation of $[Rh(HMB)COD][Al(OR^F)_4]$

2 (200 mg, 0.167 mmol) was dissolved in oDFB (2ml) and COD (0.1 ml, 1.50 mmol, ~9 eq., exc.) was added to the reaction mixture. Next the reaction mixture was added to $RhCl_3$ (34.9 mg, 0.167 mmol, 1.0 eq.). The reaction mixture was stirred for 24 h at ambient temperature, further 4 h at 60°C and subsequent sonication of the reaction mixture for 2 h with no noticeable change (no dissolution of $RhCl_3$ was observed). The reaction mixture was then spiked with a few drops of THF resulting in immediate formation of dark grey precipate (Ga^0?) from disproportionation of Ga^+ and stirred for further 2h. The reaction mixture was subsequently filtered and layered with n-pentane for crystallisation. The formation of few small yellow block shaped crystals together with many colourless crystals was observed which were both subsequently analysed by scXRD analysis. The obtained yellow crystals revealed the molecular structure of targeted $[Rh(HMB)COD][Al(OR^F)_4]$. The colourless crystals were of minor quality however they allowed the assignment of the constitution of the isolated material as the product of the presumed THF induced deterioration of Ga(I) starting material in the form of $[Ga\text{-}H(THF)_3(OR^F)][Al(OR^F)_4]$.

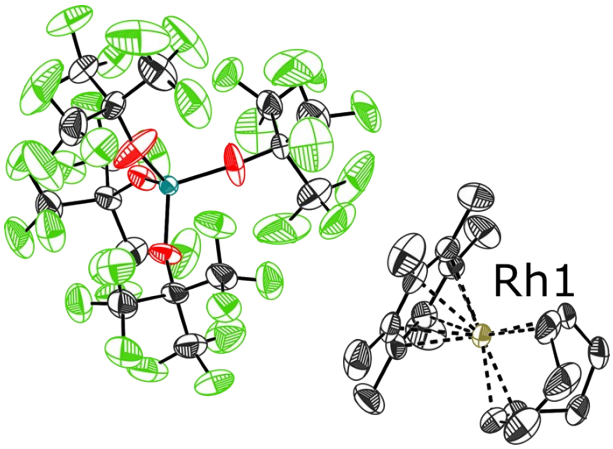


Fig. S 11: molecular structure of $[Rh(HMB)(COD)][Al(OR^F)_4]$. H atoms omitted for clarity. Thermal displacement ellipsoids drawn at 50% probability.

S-2.7 Reaction between **1** and $RhCl_3$ in presence of COD. Isolation of $[RhCOD_2][Al(OR^F)_4]$

1 (200 mg, 0.162 mmol) was dissolved in oDFB (2ml) and COD (0.1 ml, 1.50 mmol, ~9 eq., exc.) was added to the reaction mixture. Next the reaction mixture was added to $RhCl_3$ (34.0 mg, 0.162 mmol, 1.0 eq.). The reaction mixture was stirred for 1 h at ambient temperature and was subsequently sonicated for 2 h with no noticeable change (no dissolution of $RhCl_3$ was observed). The reaction mixture was then spiked with a few drops of THF resulting in immediate formation of dark grey precipate (Ga^0?) from disproportionation of Ga^+ and stirred for further 2h. The reaction mixture was subsequently filtered and layered with n-pentane for crystallisation. The formation of few small yellow

block shaped crystals together with many colourless crystals was observed. The yellow crystals were subsequently by scXRD and revealed the molecular structure of targeted and literature known $[RhCOD_2][Al(OR^F)_4]$.[19]

S-3 Crystallographic data

*Table S 1: Summary of crystallographic details of compounds **3**, **4**, **5a**, **5b**.*

	3	**4**	**5a**
Empirical formula	$C_{86}H_{46}Al_2F_{72}GaO_8P_3$	$C_{52}H_{30}AlF_{36}O_4P_3$	$C_{36}H_{30}Cl_{16}Ga_4P_6$
Formula weight	2791.81	1522.65	1494.50
Temperature/K	100(2)	130(2)	100(2)
Crystal system	monoclinic	monoclinic	triclinic
Space group	$C2/c$ (15)	$P2_1/c$ (14)	$P\overline{1}$ (2)
a/Å	49.8991(7)	15.6096(5)	12.113(4)
b/Å	15.6251(2)	14.4751(4)	15.422(8)
c/Å	28.3883(5)	26.9444(8)	15.880(6)
α/°	90	90	87.86(2)
β/°	102.8230(10)	102.457(2)	71.470(12)
γ/°	90	90	88.42(2)
Volume/Å^3	21581.7(6)	5944.8(3)	2810(2)
Z	8	4	2
ρ_{calc}g/cm^3	1.718	1.701	1.766
μ/mm^{-1}	0.492	0.273	2.857
F(000)	11008	3024	1464
Crystal size/mm^3	0.34×0.28×0.26	0.27×0.23×0.22	0.25×0.22×0.20
Radiation	MoK_α (λ=0.71073 Å)	MoK_α (λ=0.71073 Å)	MoK_α (λ=0.71073
2Θ range /°	1.67 to 57.64 (0.74 Å)	2.78 to 52.89 (0.80 Å)	2.64 to 55.75 (0.7
Index ranges	-57 ≤ h ≤ 67, -21 ≤ k ≤ 21, -38 ≤ l ≤ 28	-19 ≤ h ≤ 19, -18 ≤ k ≤ 17, -33 ≤ l ≤ 33	twin
Reflections collected	126483	81968	13243
Independent reflections	28039, [R_{int} = 0.0424; R_{sigma} = 0.0415]	12243, [R_{int} = 0.0384, R_{sigma} = 0.0274]	13243, [R_{int} = 0.05 = 0.0440]
Data/restraints/parameters	28039/22486/2018	12243/12582/1429	13243/0/570
Goodness-of-fit on F^2	1.086	1.004	1.131
Final R indexes [I>=2σ (I)]	R_1 = 0.0549; wR_2 = 0.1370	R_1 = 0.0780, wR_2 = 0.2246	R_1 = 0.0719, wR_2 =
Final R indexes [all data]	R_1 = 0.0847, wR_2 = 0.1545	R_1 = 0.0979, wR_2 = 0.2477	R_1 = 0.0903, wR_2 =
Largest diff. peak/hole / e Å^{-3}	1.35/-0.68	1.93/-0.71	2.25/-1.22
CCDC no.	2088450	2088451	2088452

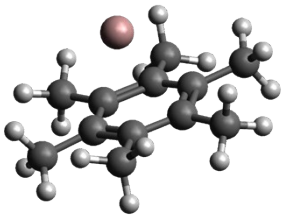
*Table S 2: Summary of crystallographic details of compounds **6**, **7**, **8**, **[Rh(COD)HMB][Al(OR^F)$_4$]**.*

	6	**7**	**8**
Empirical formula	$C_{56}H_{51}AlF_{36}N_3O_4Sb$	$C_{55}H_{48}AlCl_2F_{37}GaN_3O_4$	$C_{58}H_{49}AlF_{39}GaN_3O_4$
Formula weight	1662.72	1685.56	1689.70
Temperature/K	100(2)	101(2)	100(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$ (14)	$P2_1/c$ (14)	$C2/c$ (15)
a/Å	14.065(9)	13.9157(8)	36.379(2)
b/Å	20.990(9)	27.2818(16)	14.4021(7)
c/Å	22.636(10)	17.4384(10)	27.8948(14)
α/°	90	90	90
β/°	90.18(3)	94.017(2)	111.764(3)
γ/°	90	90	90
Volume/Å^3	6683(6)	6604.1(7)	13573.3(13)
Z	4	4	8
ρ_{calc}g/cm^3	1.653	1.695	1.654
μ/mm^{-1}	0.573	0.663	0.573
F(000)	3312	3368	6760
Crystal size/mm^3	0.32×0.24×0.18	0.29×0.25×0.24	0.32×0.28×0.21
Radiation	MoK_α (λ=0.71073 Å)	MoK_α (λ=0.71073 Å)	MoK_α (λ=0.71073
2Θ range /°	3.41 to 55.82 (0.76 Å)	2.93 to 54.32 (0.78 Å)	3.14 to 55.94 (0.7
Index ranges	twin	-17 ≤ h ≤ 17, -34 ≤ k ≤ 34, -22 ≤ l ≤ 22	twin
Reflections collected	15259	155659	16250
Independent reflections	15259, [R_{int} = 0.0534, R_{sigma} = 0.1714]	14626, [R_{int} = 0.0517, R_{sigma} = 0.0275]	16250, [R_{int} = 0.05 = 0.0147]
Data/restraints/parameters	15259/4440/1042	14626/8204/1319	16250/11165/158
Goodness-of-fit on F^2	0.842	1.071	1.001
Final R indexes [I>=2σ (I)]	R_1 = 0.0420, wR_2 = 0.0879	R_1 = 0.0377, wR_2 = 0.0866	R_1 = 0.0434, wR_2 =
Final R indexes [all data]	R_1 = 0.0877, wR_2 = 0.0943	R_1 = 0.0417, wR_2 = 0.0887	R_1 = 0.0483, wR_2 =
Largest diff. peak/hole / e Å^{-3}	1.09/-0.73	0.96/-1.28	1.24/-0.54
CCDC no.	2088454	2088455	2088456

Table S 3 SCF energy, FreeH energy and FreeH entropy of presented compounds. (*BP86/def2-def-SV(P)/D3(BJ)*)

npound	SCF /*Hartree*	FreeH energy [kJ/mol]	FreeH entropy [kJ/mol K]	HOMO/LUMO (
(HMB)]$^+$ **2**$^+$	-2392.531049289	726.50	0.54884	4.34
$(PPh_3)_2]^+$	-3996.471093043	1503.28	0.99042	2.59
$(PPh_3)_3]^+$	-5032.397108311	2256.50	1.30694	2.95
(dimpyr^{Dipp})]$^+$, 6$^+$	-1687.145459531	1861.80	1.05752	1.59
Cl_2(dimpyr^{Dipp})]$^+$, 7$^+$	-4291.988251008	1880.30	1.05484	1.31
(dimpyr^{Dipp})]$^+$, 8$^+$	-3371.628161077	1860.19	1.01301	1.53

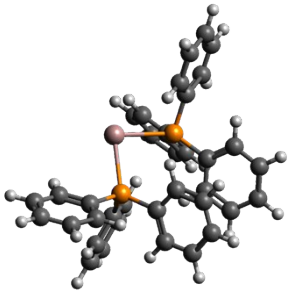
S-4 Quantum mechanical calculations



Symmetry: c3v
Method: (RI-)b-p/def-SV(P)

C	0.71600	1.24015	-0.03007
C	1.43182	0.00000	-0.06345
C	0.71600	-1.24015	-0.03007
C	-0.71591	-1.23999	-0.06345
C	-1.43200	0.00000	-0.03007
C	-0.71591	1.23999	-0.06345
C	1.47211	2.54977	0.01852
C	-1.47082	2.54754	-0.16722
C	2.94164	0.00000	-0.16722
C	1.47211	-2.54977	0.01852
C	-1.47082	-2.54754	-0.16722
C	-2.94422	0.00000	0.01852
Ga	0.00000	0.00000	2.29154
H	2.44365	2.44816	0.54073
H	1.68846	2.92449	-1.00881
H	0.89834	3.34034	0.54073
H	-2.42535	2.41975	-0.71411
H	-1.71841	2.97637	0.83103
H	-0.88289	3.31029	-0.71411
H	3.30824	0.89054	-0.71411
H	3.43682	0.00000	0.83103
H	3.30824	-0.89054	-0.71411
H	2.44365	-2.44816	0.54073
H	0.89834	-3.34034	0.54073
H	1.68846	-2.92449	-1.00881
H	-0.88289	-3.31029	-0.71411
H	-1.71841	-2.97637	0.83103
H	-2.42535	-2.41975	-0.71411
H	-3.34199	-0.89218	0.54073
H	-3.34199	0.89218	0.54073
H	-3.37692	0.00000	-1.00881

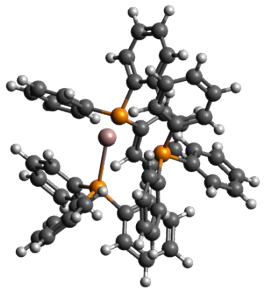
SCF energy GEOOPT = -2392.531049289 H
ZPE = 682.9 kJ/mol
FREEH energy = 726.50 kJ/mol
FREEH entropy = 0.54884 kJ/mol



Symmetry: c1
Method: (RI-)b-p/def-SVP
Energy =

Ga	0.6703898	2.1088171	1.0950043
P	-1.4751460	0.5257283	1.1192215
C	-2.8440523	1.6872214	1.4493875
C	-2.9228516	2.8607269	0.6691400
H	-2.1613495	3.0660627	-0.1019745
C	-3.9754449	3.7670486	0.8662033
H	-4.0355671	4.6802315	0.2562175
C	-4.9445641	3.5085092	1.8501720
H	-5.7661472	4.2220563	2.0108723
C	-4.8638969	2.3441337	2.6338902
H	-5.6227018	2.1458558	3.4052012
C	-3.8176727	1.4306788	2.4364324
H	-3.7531151	0.5186649	3.0484138
C	-1.1876903	-0.3673430	2.6941134
C	-0.6779555	0.3828843	3.7811852
H	-0.5621475	1.4757170	3.6959664
C	-0.3443081	-0.2559230	4.9839007
H	0.0465741	0.3351375	5.8250329
C	-0.5129964	-1.6452747	5.1128650
H	-0.2487580	-2.1461920	6.0558017
C	-1.0310260	-2.3907995	4.0406972
H	-1.1829683	-3.4753451	4.1453184
C	-1.3694942	-1.7585357	2.8332952
H	-1.7798681	-2.3479591	2.0013217
C	-2.1368662	-0.6975607	-0.0666271
C	-1.3257517	-1.7848487	-0.4638295
H	-0.3132334	-1.9055578	-0.0526388
C	-1.8086789	-2.7164844	-1.3906036
H	-1.1749541	-3.5637705	-1.6884749
C	-3.0888759	-2.5582824	-1.9492457
H	-3.4622264	-3.2871243	-2.6835060
C	-3.8878505	-1.4678670	-1.5726282
H	-4.8904539	-1.3409988	-2.0070505
C	-3.4188394	-0.5382369	-0.6306506
H	-4.0530987	0.3078914	-0.3299544
P	1.7364553	0.6337832	-0.8061548
C	2.6065519	-0.7062114	0.0841263
C	3.8604632	-1.1937808	-0.3421028
H	4.3526830	-0.7516952	-1.2213644
C	4.4799488	-2.2346314	0.3663153
H	5.4548717	-2.6172073	0.0297646
C	3.8633292	-2.7846580	1.5044297
H	4.3579561	-3.5967962	2.0573721
C	2.6242269	-2.2893628	1.9427496
H	2.1405368	-2.7021751	2.8400486
C	1.9989116	-1.2505166	1.2372980
H	1.0315238	-0.8686200	1.5967906
C	0.7832182	-0.1345747	-2.1596173
C	1.2122244	-1.3224741	-2.7854311
H	2.1307457	-1.8247235	-2.4472886
C	0.4563537	-1.8658934	-3.8346127
H	0.7900979	-2.7928784	-4.3239673
C	-0.7248111	-1.2323499	-4.2566847
H	-1.3183970	-1.6668068	-5.0743565
C	-1.1544927	-0.0494978	-3.6326440
H	-2.0845512	0.4401518	-3.9547799
C	-0.4035827	0.4978069	-2.5838764
H	-0.7484092	1.4156256	-2.0824235
C	3.0523104	1.6052874	-1.6214579
C	3.1216158	1.7423692	-3.0222928
H	2.3909620	1.2288928	-3.6640244
C	4.1316046	2.5325134	-3.5952087
H	4.1860545	2.6355280	-4.6890183
C	5.0694251	3.1844905	-2.7787740
H	5.8592268	3.8011890	-3.2323536
C	4.9990903	3.0513406	-1.3804609
H	5.7327468	3.5611544	-0.7388340
C	3.9908613	2.2702124	-0.7998625
H	3.9438350	2.1652463	0.2962260

SCF energy GEOOPT = -3996.471093043 H
ZPE = 1407. kJ/mol
FREEH energy = 1503.28 kJ/mol
FREEH entropy = 0.99042 kJ/mol



Symmetry: c1
Method: (RI-)b-p/def-SVP
Energy =

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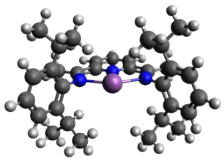
C	-1.9158785	1.4617976	-1.3483003
C	-1.9493033	0.0959673	-1.6944708
H	-1.0714877	-0.5374875	-1.5139835
C	-3.1096721	-0.4656473	-2.2441621
H	-3.1259976	-1.5364347	-2.4931654
C	-4.2479364	0.3346285	-2.4409619
H	-5.1663571	-0.1071457	-2.8551196
C	-4.2150871	1.7003269	-2.1058446
H	-5.1046827	2.3278844	-2.2649768
C	-3.0529434	2.2685394	-1.5611651
H	-3.0338667	3.3314679	-1.2805214
C	-0.8989879	3.7094196	0.1825200
C	-0.8304935	4.9127722	-0.5510310
H	-0.4401134	4.9085139	-1.5795914
C	-1.2586875	6.1128716	0.0365624
H	-1.2043955	7.0504479	-0.5364678
C	-1.7535965	6.1186234	1.3523992
H	-2.0859856	7.0624753	1.8096024
C	-1.8166133	4.9221143	2.0854572
H	-2.1992550	4.9200984	3.1163656
C	-1.3863094	3.7195264	1.5062587
H	-1.4401897	2.7860273	2.0862759
C	0.7210338	2.5565825	-1.9153287
C	1.9980144	3.0609322	-1.5835505
H	2.2852581	3.1902149	-0.5286146
C	2.8985066	3.4121840	-2.5969646
H	3.8889670	3.8062661	-2.3308185
C	2.5428972	3.2426193	-3.9458697
H	3.2568373	3.5076884	-4.7394921
C	1.2751696	2.7402960	-4.2801633
H	0.9900297	2.6185996	-5.3357680
C	0.3588015	2.4053879	-3.2694281
H	-0.6418682	2.0301504	-3.5305761
P	-1.2332914	-0.7841320	1.8500334
C	-2.5306935	0.3875187	2.4087697
C	-3.4846848	0.8669446	1.4831659
H	-3.5314885	0.4495291	0.4695464
C	-4.3810106	1.8777254	1.8566158
H	-5.1162966	2.2418296	1.1243642
C	-4.3365853	2.4237757	3.1499837
H	-5.0393188	3.2192609	3.4380612
C	-3.3945788	1.9454689	4.0756017
H	-3.3619460	2.3577303	5.0950362
C	-2.4934859	0.9321561	3.7105014
H	-1.7679471	0.5577444	4.4470856
C	-0.7427120	-1.7348972	3.3490749
C	0.2017056	-1.1697841	4.2358233
H	0.6177878	-0.1691690	4.0352045
C	0.6367949	-1.8873315	5.3595615
H	1.3713194	-1.4367597	6.0430988
C	0.1461787	-3.1815117	5.6007169
H	0.4927726	-3.7476313	6.4779538
C	-0.7824630	-3.7535892	4.7151925
H	-1.1670036	-4.7679617	4.8983888
C	-1.2283309	-3.0364015	3.5937235
H	-1.9511507	-3.4933753	2.9029550
C	-2.0930906	-2.0248580	0.8098256
C	-1.3209587	-2.7486921	-0.1210122
H	-0.2466686	-2.5440291	-0.2215892
C	-1.9177615	-3.7196281	-0.9363665
H	-1.3010471	-4.2642764	-1.6655777
C	-3.2956076	-3.9746377	-0.8276387
H	-3.7691581	-4.7303528	-1.4718677
C	-4.0681504	-3.2648592	0.1075119
H	-5.1450021	-3.4691974	0.2020507
C	-3.4722953	-2.2952019	0.9291564
H	-4.0822804	-1.7482369	1.6622192
P	2.1545269	-0.8166627	-0.5147836
C	2.9232771	-2.0901346	0.5593655
C	4.2475362	-2.5363349	0.3657890
H	4.8611100	-2.1054910	-0.4392945
C	4.7785445	-3.5266881	1.2062800
H	5.8119605	-3.8722470	1.0545279
C	3.9984576	-4.0747605	2.2404852
H	4.4241472	-4.8472533	2.8980478
C	2.6804496	-3.6315390	2.4375341
H	2.0615726	-4.0432315	3.2482339
C	2.1483292	-2.6399406	1.6006977
H	1.1203539	-2.2922507	1.7675074
C	1.5335669	-1.7672929	-1.9583284
C	1.6169355	-3.1746737	-2.0121044
H	2.1096049	-3.7283767	-1.1999412
C	1.0692287	-3.8676511	-3.1039256
H	1.1442801	-4.9647743	-3.1422832
C	0.4381437	-3.1672480	-4.1456243
H	0.0096976	-3.7147470	-4.9981279
C	0.3635453	-1.7646346	-4.0990984
H	-0.1220586	-1.2076845	-4.9140892
C	0.9053383	-1.0664393	-3.0108830
H	0.8489295	0.0310706	-2.9840804
C	3.5883921	0.1312607	-1.1578621
C	4.0067277	0.0764100	-2.5010896
H	3.4663275	-0.5506416	-3.2237389
C	5.1219203	0.8206125	-2.9184346
H	5.4440754	0.7708092	-3.9690791
C	5.8278094	1.6159310	-2.0022095
H	6.7047343	2.1922070	-2.3327366
C	5.4136607	1.6723887	-0.6596209
H	5.9653146	2.2902306	0.0643974
C	4.2967214	0.9382459	-0.2388261
H	3.9803095	0.9795891	0.8160999

SCF energy GEOOPT = -5032.397108311 H
ZPE = 2115. kJ/mol
FREEH energy = 2256.50 kJ/mol
FREEH entropy = 1.30694 kJ/mol



Method: (RI-)BP86(D3BJ)/def2-SVP
Symmetry: c1

Cartesian coordinates in Ångström:

C	-0.0559942	4.1923760	-2.3018510
C	-1.2480523	3.4867872	-2.0792430
C	-1.2230382	2.2564091	-1.4032057
N	-0.0227386	1.7358694	-0.9552397
C	1.1612572	2.4182899	-1.1665772
C	1.1529680	3.6501196	-1.8403327
H	-0.0689568	5.1555911	-2.8297260
H	-2.2085979	3.8877032	-2.4295188
C	-2.3938131	1.4478694	-1.1184206
Sb	0.0026918	-0.1460095	0.0761915
C	2.3516392	1.7684641	-0.6503858
H	2.1008864	4.1810390	-2.0008082
C	-3.1199504	-0.6198552	-0.0629257
C	3.1329700	-0.2146812	0.5201334

C	-3.3677229	-1.7434191	-0.8928598
C	-3.7491889	-0.4457270	1.1974144
C	3.3867607	-0.1141867	1.9121497
C	3.7816215	-1.1663236	-0.3094490
C	4.3344247	-0.9966727	2.4646093
C	4.7178864	-2.0238675	0.2977110
C	4.9945679	-1.9418142	1.6690352
C	3.4570085	-1.2965515	-1.7935179
H	5.2392556	-2.7724944	-0.3169066
H	4.5590554	-0.9405965	3.5402177
H	5.7309212	-2.6221197	2.1216135
C	-4.6591577	-1.4369933	1.6099732
C	-4.2885996	-2.7023200	-0.4295035
C	-4.9289915	-2.5536679	0.8074321
H	-5.6444273	-3.3155085	1.1502531
H	-4.5077749	-3.5826364	-1.0519734
C	-2.6707316	-1.9244699	-2.2366135
C	-3.4337044	0.7423178	2.0994742
H	-5.1650227	-1.3321065	2.5811869
C	2.6691465	0.9020774	2.7931563
C	-4.7048314	1.4902806	2.5387515
H	-2.8150248	1.4564954	1.5181164
C	-2.5892782	0.2946136	3.3086455
H	-3.1413478	-0.4350112	3.9353894
H	-2.3246575	1.1611802	3.9478114
H	-1.6460649	-0.1905216	2.9832711
H	-5.3112480	1.8073315	1.6667213
H	-4.4415848	2.3945789	3.1233062
H	-5.3501951	0.8593033	3.1827113
C	-3.6829033	-2.0142158	-3.3935311
C	-1.7254914	-3.1402217	-2.2091520
H	-2.0435922	-1.0265863	-2.4158202
H	-2.2829832	-4.0828837	-2.0350367
H	-0.9718529	-3.0450982	-1.4006427
H	-1.1845439	-3.2401667	-3.1717217
H	-4.3249906	-2.9139247	-3.3044859
H	-3.1577687	-2.0766058	-4.3678860
H	-4.3501761	-1.1294118	-3.4175259
N	-2.1279012	0.3282198	-0.4722049
N	2.1167026	0.6161994	-0.0515365
C	3.7221037	2.3587287	-0.7978448
H	2.8264751	-0.4303909	-2.0816095
C	2.6241754	-2.5671734	-2.0544209
C	4.7203255	-1.2546297	-2.6710688
H	1.6853733	-2.5613687	-1.4633483
H	3.1888256	-3.4801743	-1.7760391
H	2.3522260	-2.6478592	-3.1263165
H	5.3196977	-0.3426094	-2.4769068
H	4.4477942	-1.2663159	-3.7454695
H	5.3759237	-2.1302366	-2.4895797
C	1.7553081	0.1999435	3.8148122
H	2.0164783	1.5159621	2.1385078
C	3.6611341	1.8602066	3.4778031
H	4.3283332	1.3217032	4.1809877
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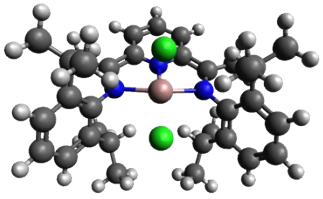
H	4.3041418	2.3754125	2.7363055
H	1.0158778	-0.4547255	3.3094189
H	1.1975917	0.9427789	4.4199879
H	2.3393024	-0.4343685	4.5121890
C	-3.7782123	1.8616920	-1.5192287
H	-3.8371942	2.0641454	-2.6072969
H	-4.0844347	2.7868659	-0.9890874
H	-4.5026295	1.0654593	-1.2700903
H	3.7620785	3.3876781	-0.3880948
H	4.0179090	2.4113029	-1.8657894
H	4.4650081	1.7387790	-0.2644505

SCF energy GEOOPT = -1687.145459531 H
ZPE = 1754. kJ/mol
FREEH energy = 1861.80 kJ/mol
FREEH entropy = 1.05752 kJ/mol



Method: (RI-)BP86(D3BJ)/def2-SVP
Symmetry: c1

Cartesian coordinates in Ångström:

Ga	0.4929433	0.0585993	-0.0671274
C	0.7235186	-2.1804370	1.8260180
N	0.5131996	-0.8571806	1.7950928
C	1.0699421	-2.8036642	3.0391943
H	1.2516467	-3.8853500	3.0876056
N	0.2623436	-2.0370892	-0.4779684
Cl	2.6949788	0.1852545	-0.1110557
N	0.0864697	1.6368489	1.3298374
C	1.1912237	-2.0020103	4.1877379
H	1.4683683	-2.4610964	5.1477318
Cl	-0.5404380	0.8649406	-1.8041894
C	0.9672822	-0.6159237	4.1150902
H	1.0684862	0.0168133	5.0065952
C	0.6238203	-0.0617276	2.8681204
C	0.3754337	2.3856436	3.6754528
H	-0.0724066	3.3387366	3.3414331
H	1.4282179	2.5873527	3.9679956
H	-0.1542052	2.0168118	4.5754012
C	0.3485926	1.3760952	2.5765425
C	0.6937759	-4.3244370	0.3758726
H	0.3103807	-4.6738105	-0.5995052
H	0.1686757	-4.8513479	1.1962978
H	1.7686859	-4.5990452	0.4381619
C	0.5489298	-2.8442517	0.5005896
C	-0.2776469	2.9417818	0.8708656
C	-0.0114521	-2.4951419	-1.8049910
C	-1.3712593	-2.4584213	-2.2155429
C	-1.6476498	3.1347177	0.5469704
C	-2.0293574	4.3995925	0.0730367
H	-3.0830066	4.5896259	-0.1736647
C	-1.0843798	5.4233161	-0.0916529
H	-1.4024195	6.4068705	-0.4673724
C	-1.6657195	-2.8824951	-3.5208324
H	-2.7082179	-2.8817270	-3.8677643
C	0.2626616	5.1933512	0.2084043
H	0.9982364	5.9959730	0.0510467
C	-0.6478781	-3.3055343	-4.3885781
H	-0.8982611	-3.6312250	-5.4088371
C	0.7050163	3.9468094	0.6939400
C	0.6853717	-3.3026241	-3.9645372
H	1.4772467	-3.6123477	-4.6624656
C	-2.6607216	2.0222831	0.7874639
H	-2.1197529	1.0593274	0.6474939
C	1.0421621	-2.8945567	-2.6640279
C	-3.8197567	2.0338882	-0.2158536
H	-4.4669258	2.9252487	-0.0900131
H	-4.4644863	1.1456874	-0.0661443
H	-3.4441927	2.0179202	-1.2568259
C	-2.4623867	-2.0480312	-1.2342533
H	-2.0058542	-1.3106049	-0.5361800
C	-3.1763708	2.0545076	2.2400233
H	-3.7103604	3.0048252	2.4435018
H	-2.3531164	1.9773343	2.9784421
H	-3.8811805	1.2193562	2.4285787
C	-3.6492462	-1.3500341	-1.9085671
H	-3.3104043	-0.4897789	-2.5171070
H	-4.3583811	-0.9763918	-1.1441627
H	-4.2176446	-2.0405942	-2.5636380
C	2.1909476	3.6986057	0.9181525
H	2.3178469	2.6778063	1.3331793

C	-2.9248516	-3.2543849	-0.3930638
H	-3.3729982	-4.0339987	-1.0420016
H	-3.6880933	-2.9487048	0.3510016
H	-2.0860136	-3.7279695	0.1557072
C	2.8027802	4.6983309	1.9162248
H	3.8648250	4.4489507	2.1124169
H	2.2648809	4.7022969	2.8857579
H	2.7763226	5.7343265	1.5218941
C	2.5103739	-2.8099111	-2.2671693
H	2.5697619	-2.5072009	-1.2016443
C	2.9377769	3.7186878	-0.4304050
H	2.4985790	2.9906083	-1.1387317
H	4.0045593	3.4545165	-0.2875913
H	2.8927724	4.7242182	-0.8957869
C	3.2113562	-1.7006612	-3.0766079
H	3.2309504	-1.9477650	-4.1575587
H	4.2580424	-1.5734235	-2.7352608
H	2.6927427	-0.7308835	-2.9534616
C	3.2326208	-4.1607880	-2.4202321
H	3.2759088	-4.4805539	-3.4810235
H	2.7290686	-4.9700390	-1.8538361
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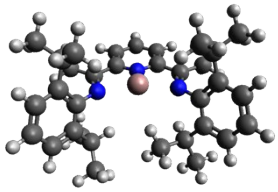
ZPE = 1766. kJ/mol
FREEH energy = 1880.30 kJ/mol
FREEH entropy = 1.05484 kJ/mol



Method: (RI-)BP86(D3BJ)/def2-SVP
Symmetry: c1

Cartesian coordinates in Ångström:

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C	-2.1246903	-1.7133752	-1.0438866
C	-2.7879390	-2.9301286	-1.2964516
H	-3.6918877	-2.9579586	-1.9187589
N	1.3014383	-1.4298396	0.9509010
C	-2.2662308	-4.1101193	-0.7439487
H	-2.7634404	-5.0731420	-0.9292370
N	-1.7608011	0.6002215	-1.3363204
C	-3.8114101	-0.3088193	-2.4107379
H	-3.7878115	-1.0450507	-3.2397535
H	-3.9287446	0.7036351	-2.8358998
H	-4.7057881	-0.5362042	-1.7946236
C	0.0370606	1.7144781	-3.2030171
H	-0.3006676	0.6592301	-3.2842493
C	-2.5547476	-0.3980975	-1.5954875
C	-0.4793443	-2.8098705	0.2434423
C	-1.0984508	-4.0581358	0.0318461
H	-0.6696562	-4.9754515	0.4556978
C	1.3906931	-3.7888446	1.7353448
H	0.7398916	-4.1105421	2.5748505
H	2.3808007	-3.5203233	2.1445813
H	1.5075339	-4.6593231	1.0587337
C	0.7885189	-2.6249415	1.0025816
C	-2.0305507	1.9388748	-1.7238119
C	-3.2367164	4.0242832	-1.5068627
H	-4.0375159	4.6248139	-1.0506793
C	-3.0838616	2.6779169	-1.1196181
C	-3.5467442	2.6916345	1.3520503
H	-4.1477224	2.2483747	2.1719136
H	-3.6966674	3.7900982	1.3752432
H	-2.4754318	2.4967871	1.5639409
C	-3.9626816	2.1047870	-0.0124339
H	-3.7872754	1.0109407	0.0442566
C	-1.1338229	2.5272818	-2.6597250
C	-1.3478955	3.8653551	-3.0244378
H	-0.6883206	4.3372621	-3.7658316
C	-2.3919541	4.6110570	-2.4548722
H	-2.5415141	5.6599673	-2.7498845
C	-5.4630722	2.3141913	-0.2821230
H	-6.0719446	1.8128743	0.4967180
H	-5.7644408	1.9108700	-1.2694225
H	-5.7339033	3.3890326	-0.2661296
C	0.5087896	2.1555661	-4.5957404
H	1.2795291	1.4574837	-4.9784753
H	0.9679961	3.1647995	-4.5768224
H	-0.3276216	2.1746112	-5.3221797
C	3.8516202	-2.3640531	-1.0098099
H	3.1559563	-3.0659291	-0.5085848
H	4.8813040	-2.6462089	-0.7097319
H	3.7591310	-2.5178917	-2.1041586
C	3.5607856	-0.8963951	-0.6325475
H	2.5114541	-0.6830839	-0.9382144
C	1.2048634	1.7487971	-2.1982199
H	2.0467378	1.1133710	-2.5355565
H	0.8989956	1.3857183	-1.1880067
H	1.5792940	2.7827847	-2.0590705
C	4.4831913	0.0603318	-1.3990821
H	4.3092052	1.1162618	-1.1120919
H	4.3140002	-0.0335328	-2.4905911
H	5.5537514	-0.1689226	-1.2224541
C	1.2119681	-1.1572728	3.9200881
H	0.4317299	-1.6084082	3.2721142
C	0.6461665	0.1837958	4.4298945
H	0.4239911	0.8723064	3.5892577
H	1.3698850	0.6939114	5.0974160
H	-0.2900088	0.0240781	5.0025618
C	1.4666664	-2.1358044	5.0806882
H	1.8876273	-3.0973074	4.7251174
H	0.5244034	-2.3503579	5.6237331
H	2.1802906	-1.7145271	5.8170899
C	2.4607901	-0.9212278	3.0765670
C	3.6428807	-0.4655710	3.6923085
H	3.6640360	-0.3441888	4.7855463
C	4.7847133	-0.1557921	2.9444048
H	5.6967302	0.1898905	3.4527255
C	4.7640277	-0.2754025	1.5466781
H	5.6634708	-0.0232561	0.9679559
C	3.6091114	-0.7103915	0.8775027
C	2.4705051	-1.0524161	1.6604730

SCF energy GEOOPT = -3371.628161077 H
ZPE = 1754. kJ/mol
FREEH energy = 1860.19 kJ/mol
FREEH entropy = 1.01301 kJ/mol

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