SUPPLEMENTARY INFORMATION

Synthetic strategies to bicyclic tetraphosphanes using P_1, P_2 and P_4 building blocks

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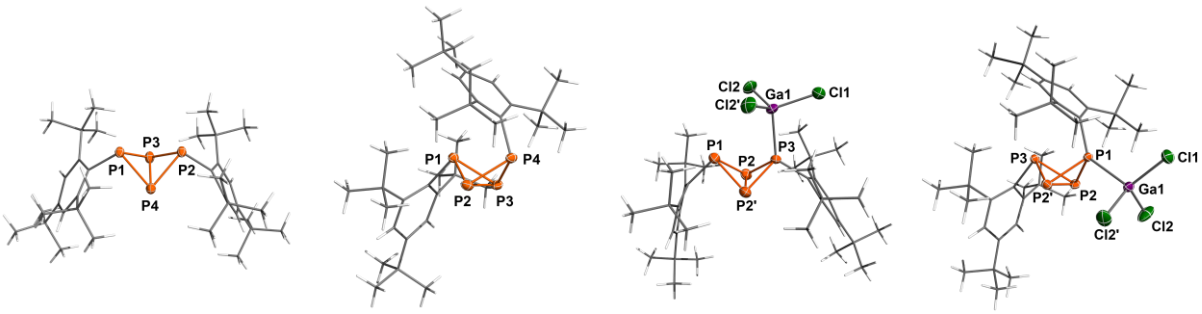


This file includes:

1 Experimental

General Information. All manipulations were carried out under oxygen- and moisture-free conditions under argon using standard Schlenk or Drybox techniques.

Solvents and reactants were obtained from commercial sources or were synthesized. Dichloromethane (CH_2Cl_2) was purified according to a literature procedure,[1] dried over P_4O_{10}, stored over CaH_2 and freshly distilled prior to use. Diethyl ether (Et_2O) and tetrahydrofuran (THF) were dried over Na/benzophenone and freshly distilled prior to use. *n*-Pentane and *n*-hexane were dried over Na/benzophenone/tetraglyme (tetraglyme = $Me(OCH_2CH_2)_3OMe$) and freshly distilled prior to use. Fluorobenzene (PhF) and Me_3SiCl (Merck, 99 %) were dried over CaH_2, freshly distilled and degassed prior to use. Deuterated dichloromethane (CD_2Cl_2) and PCl_3 (Merck, for synthesis) were dried over P_4O_{10}, freshly distilled and degassed. $GaCl_3$ (Acros, 99.9 %) was sublimed prior to use. $LiAlH_4$ (abcr, 95 %), $MgSO_4$ (dried, 99 %, Grüssing), *n*-Butyllithium (Acros, 2.5 mol/L in hexanes) and Mg turnings (Merck, 99 %) were used as received. Mes*H, Mes*Br and $(i\text{-Pr})_2NPCl_2$ were prepared according to literature procedures.[2–4]

NMR spectra were obtained on a Bruker AVANCE 250, 300 or 500 MHz spectrometer and were referenced internally to the deuterated solvent (^{13}C: CD_2Cl_2 δ_{ref} = 54.0 ppm), to protic impurities in the deuterated solvent (^{1}H: $CHDCl_2$ δ_{ref} = 5.31 ppm; CHD_5 δ_{ref} = 7.16 ppm) or externally (^{31}P: 85% H_3PO_4 δ_{ref} = 0 ppm). All measurements were carried at room temperature unless denoted otherwise. For NMR spectra simulation, the experimental ^{31}P NMR spectra were transferred to gNMR.[5] The full line-shape iteration procedure of gNMR was applied to give the best fit to the experimental spectrum. The signs of $^{n}J(^{31}P,^{31}P)$ coupling constants were derived from the calculated spectra (see Computational Details, p. 45).

IR spectra of crystalline samples were recorded on a Nicolet 380 FT-IR spectrometer equipped with a Smart Orbit ATR unit at ambient temperature.

Raman spectra of crystalline samples were recorded using a LabRAM HR 800 Horiba Jobin YVON Raman spectrometer equipped with an Olympus BX41 microscope with variable lenses. The samples were excited by an infrared laser (785 nm, 65 mW), a red laser (633 nm, 12 mW), or a green laser (532 nm, 23 mW). All measurements were carried out at ambient temperature unless stated otherwise.

Elemental analyses were obtained using a Thermoquest Flash EA 1112 CHNS analyzer.

Melting points (uncorrected) were determined using a Stanford Research Systems EZ Melt at a heating rate of 20 °C/min. **DSC** analyses were carried out at a heating rate of 5 °C/min using a Mettler-Toledo DSC 823e.

Mass spectra were recorded on a Finnigan MAT 95-XP (Thermo Electron) using crystalline samples.

2 Structure Elucidation

X-Ray Structure Determination: X-Ray quality crystals were selected in Fomblin YR-1800 perfluoroether (Alfa Aesar) at ambient temperature. The samples were cooled to 173(2) K during measurement. The data were collected on a Bruker Apex Kappa II CCD diffractometer or a Bruker-Nonius Apex X8 CCD diffractometer using graphite mono-chromated Mo K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods (SHELXS-2013)[6] and refined by full matrix least squares procedures (SHELXL-2013).[7] Semi-empirical absorption corrections were applied (SADABS).[8] All non-hydrogen atoms were refined anisotropically, hydrogen atoms were included in the refinement at calculated positions using a riding model.

Disordered groups or molecules were split in parts. The occupancy of each part was refined freely. In **5a**, this applied to one of the *p*-*t*-Bu groups (0.487(4), 0.39(2), 0.12(2)). In **5b_1**, both *p*-*t*-Bu groups were disordered (0.873(3), 0.127(3); 0.509(5), 0.491(5)). In **5a**·$GaCl_3$·½ *n*-hexane, both *p*-*t*-Bu groups were found to disordered with respect to the

crystallographic mirror plane. One of the *p*-*t*-Bu groups exhibited an additional disorder, so it was additionally split in two parts (0.374(16), 0.126(16)). In **5b**·$GaCl_3$·toluene, the solvent molecule was found to be disordered (0.82(6), 0.18(6)). In both **30** and **34**, the *p*-*t*-Bu group was disordered (0.810(4), 0.190(4); 0.958(3), 0.042(3)).

In **5a**·$GaCl_3$·½ *n*-hexane and **5b**·$GaCl_3$·1.5 CH_2Cl_2, the solvent molecules were found to be strongly disordered, so they were excluded from the model using the PLATON/SQUEEZE algorithm.[9]

Table S1: Crystallographic details of **5a** and **5b** (monoclinic, triclinic).

Compound	**5a**	**5b_1**	**5b_2**
Chem. Formula	$C_{36}H_{58}P_4$	$C_{36}H_{58}P_4$	$C_{36}H_{58}P_4$
Formula weight [g/mol]	614.70	614.70	614.70
Colour	colourless	colourless	colourless
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a [Å]	16.7738(4)	15.0599(7)	10.4770(5)
b [Å]	10.7853(2)	18.3797(8)	13.2999(8)
c [Å]	20.6732(5)	14.3330(7)	13.5005(7)
α [°]	90	90	102.674(4)
β [°]	95.943(1)	109.316(3)	93.615(4)
γ [°]	90	90	90.136(4)
V [Å^3]	3719.9(1)	3744.0(3)	1831.5(2)
Z	4	4	2
$\rho_{calc.}$ [g/cm^3]	1.098	1.091	1.117
μ [mm^{-1}]	0.225	0.223	0.228
T [K]	173(2)	173(2)	173(2)
Measured reflections	50752	52969	37485
Independent reflections	9868	10962	7574
Reflections with $I > 2\sigma(I)$	7015	6386	3504
R_{int}	0.0472	0.0836	0.1593
$F(000)$	1336	1336	670
$R_1(R[F^2>2\sigma(F^2)])$	0.0499	0.0539	0.0616
w$R_2(F^2)$	0.1346	0.1342	0.1226
GooF	1.029	1.020	0.980
No. of Parameters	415	423	379
CCDC #	1413820	1413821	1413822

Table S2: Crystallographic details of **5a**·$GaCl_3$·½ *n*-hexane, **5b**·$GaCl_3$·toluene, and **5b**·$GaCl_3$·1.5 CH_2Cl_2.

Compound	**5a**·$GaCl_3$·½ *n*-hexane	**5b**·$GaCl_3$·toluene	**5b**·$GaCl_3$·1.5 CH_2Cl_2
Chem. Formula	$C_{36}H_{58}P_4GaCl_3$ 0.5 (C_6H_{14})	$C_{36}H_{58}P_4GaCl_3$·C_7H_8	$C_{36}H_{58}P_4GaCl_3$ 1.5 (CH_2Cl_2)
Formula weight [g/mol]	833.86	822.91	918.16
Colour	colourless	colourless	colourless
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	*Pnma*	$P2_1/m$	$P2_1/m$
a [Å]	26.7411(7)	13.2689(4)	13.3333(4)
b [Å]	13.5063(4)	12.9252(5)	12.9538(4)
c [Å]	12.5618(3)	14.1556(5)	14.1349(5)
α [°]	90	90	90
β [°]	90	90.676(2)	91.834(2)
γ [°]	90	90	90
V [Å^3]	4537.0(2)	2427.6(2)	2440.1(1)
Z	4	2	2
$\rho_{calc.}$ [g/cm^3]	1.221	1.208	1.250
μ [mm^{-1}]	0.95	0.89	1.05
T [K]	173(2)	173(2)	173(2)
Measured reflections	69297	48175	43086
Independent reflections	6840	9856	8787
Reflections with $I > 2\sigma(I)$	5540	6949	7521
R_{int}	0.044	0.053	0.035
F(000)	1764	932	958
$R_1(R[F^2>2\sigma(F^2)])$	0.051	0.039	0.026
$wR_2(F^2)$	0.136	0.095	0.073
GooF	1.06	1.02	1.09
No. of Parameters	267	311	256
CCDC #	1413823	1413824	1413825

Table S3: Crystallographic details of **30** and **34**.

Compound	**30**	**34**
Chem. Formula	$C_{24}H_{43}NP_2$	$C_{24}H_{47}PSi_2$
Formula weight [g/mol]	407.53	422.77
Colour	yellow	colourless
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a [Å]	10.0058(5)	9.3749(6)
b [Å]	26.484(1)	16.953(1)
c [Å]	9.9173(5)	17.687(1)
α [°]	90	90
β [°]	101.035(2)	101.224(3)
γ [°]	90	90
V [Å^3]	2579.4(2)	2757.2(3)
Z	4	4
$\rho_{calc.}$ [g/cm^3]	1.049	1.018
μ [mm^{-1}]	0.18	0.19
T [K]	173(2)	173(2)
Measured reflections	45447	33224
Independent reflections	7502	6891
Reflections with $I > 2\sigma(I)$	5859	4340
R_{int}	0.035	0.060
$F(000)$	896	936
$R_1(R[F^2>2\sigma(F^2)])$	0.050	0.048
$wR_2(F^2)$	0.141	0.115
GooF	1.03	1.00
No. of Parameters	288	269
CCDC #	1413826	1413827

Scheme S1. Numbering scheme of **5a**.

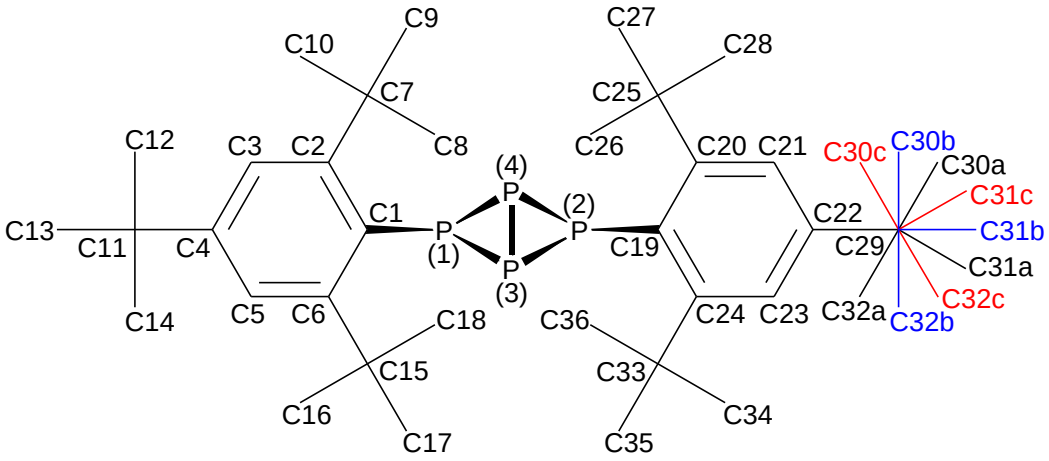


Table S4: Selected bond lengths (Å), angles (°) and dihedral angles (°) of **5a**.

P1–C1	1.875(2)	P2–C19	1.875(2)
P1–P3	2.2310(7)	P2–P3	2.2294(7)
P1–P4	2.2171(7)	P2–P4	2.2236(7)
P3–P4	2.1634(8)	P4–P1–P3	58.20(2)
C1–P1–P3	97.64(6)	C19–P2–P3	99.53(6)
C1–P1–P4	98.73(6)	C19–P2–P4	98.05(6)
P4–P2–P3	58.13(2)	P4–P3–P2	60.80(2)
P4–P3–P1	60.58(2)	P2–P3–P1	80.52(3)
P3–P4–P1	61.22(2)	P3–P4–P2	61.07(2)
P1–P4–P2	80.96(3)	C6–C1–C2	118.7(2)
C2–C1–P1	120.6(1)	C6–C1–P1	119.8(1)
C20–C19–P2	120.2(1)	C24–C19–P2	120.3(1)
P1–P3–P4–P2	−95.66(3)	P3–P1–C1–C2	109.4(2)
P3–P1–C1–C6	−59.4(2)	P4–P1–C1–C2	50.6(2)
P4–P1–C1–C6	−118.3(1)	P1–C1–C2–C3	−153.8(2)
C1–C2–C3–C4	−4.7(3)	P3–P2–C19–C24	54.3(1)
P3–P2–C19–C20	−115.6(1)	P4–P2–C19–C24	113.2(1)
P4–P2–C19–C20	−56.7(1)	P2–C19–C20–C21	156.7(1)

Scheme S2. Numbering scheme of **5b_1** (monoclinic modification).

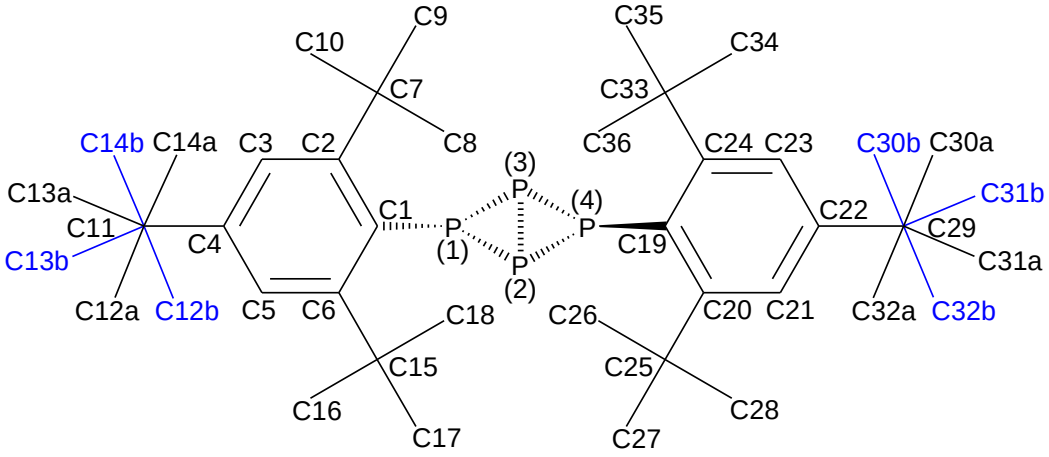


Table S5: Selected bond lengths (Å), angles (°) and dihedral angles (°) of **5b_1**.

P1–C1	1.880(2)	P4–C19	1.862(2)
P1–P2	2.2244(7)	P2–P4	2.2131(8)
P1–P3	2.2326(8)	P3–P4	2.2101(8)
P2–P3	2.1773(8)	P2–P1–P3	58.49(2)
C1–P1–P2	96.61(6)	P3–P2–P1	60.94(2)
C1–P1–P3	95.85(6)	P3–P2–P4	60.44(3)
P4–P2–P1	89.58(3)	P4–P3–P1	89.44(3)
P2–P3–P1	60.57(2)	C19–P4–P2	106.33(7)
P3–P4–P2	58.98(3)	C19–P4–P3	105.46(7)
C2–C1–C6	118.3(2)	C20–C19–C24	118.9(2)
C2–C1–P1	119.3(1)	C20–C19–P4	120.8(2)
C6–C1–P1	120.6(1)	C24–C19–P4	119.3(2)
P1–P2–P3–P4	107.78(3)	P1–C1–C2–C3	147.1(2)
P2–P1–C1–C2	−114.5(1)	P2–P4–C19–C20	53.6(2)
P3–P1–C1–C2	−55.7(2)	P3–P4–C19–C20	115.1(2)

Scheme S3. Numbering scheme of **5b_2** (triclinic modification).

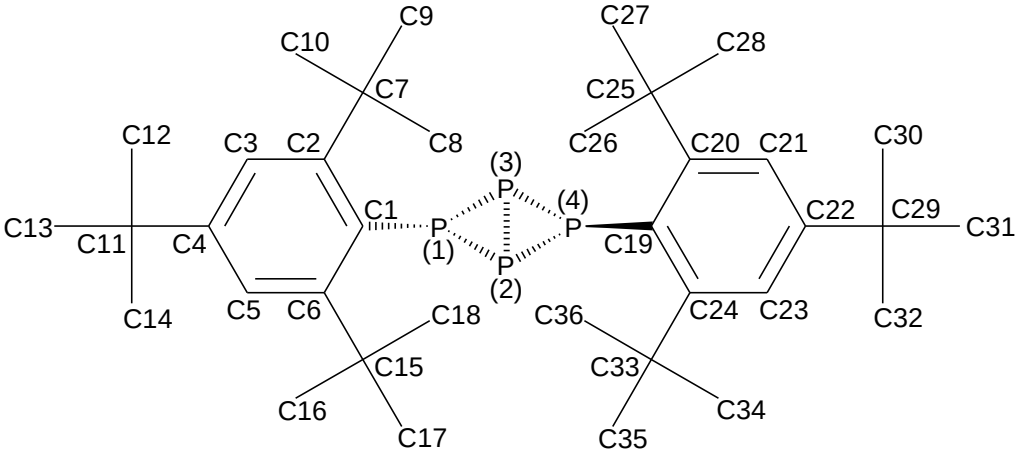


Table S6: Selected bond lengths (Å), angles (°) and dihedral angles (°) of **5b_2**.

P1–C1	1.870(3)	P4–C19	1.863(3)
P1–P2	2.229(1)	P2–P4	2.213(1)
P1–P3	2.234(1)	P3–P4	2.210(1)
P2–P3	2.177(2)	P2–P1–P3	58.39(4)
C1–P1–P2	102.5(1)	P3–P2–P1	60.92(4)
C1–P1–P3	99.9(1)	P3–P2–P4	60.45(5)
P4–P2–P1	88.09(5)	P4–P3–P1	88.04(5)
P2–P3–P1	88.04(5)	C19–P4–P2	106.7(1)
P3–P4–P2	58.96(5)	C19–P4–P3	104.7(1)
C2–C1–C6	118.4(3)	C20–C19–C24	119.2(3)
C2–C1–P1	122.2(3)	C20–C19–P4	119.3(3)
C6–C1–P1	119.0(3)	C24–C19–P4	120.1(3)
P1–P2–P3–P4	105.75(5)	P1–C1–C2–C3	−155.5(2)
P2–P1–C1–C2	52.1(3)	P2–P4–C19–C20	−114.3(2)
P3–P1–C1–C2	111.7(3)	P3–P4–C19–C20	−52.8(3)

Scheme S4. Numbering scheme of **5a**·$GaCl_3$·½ *n*-hexane.

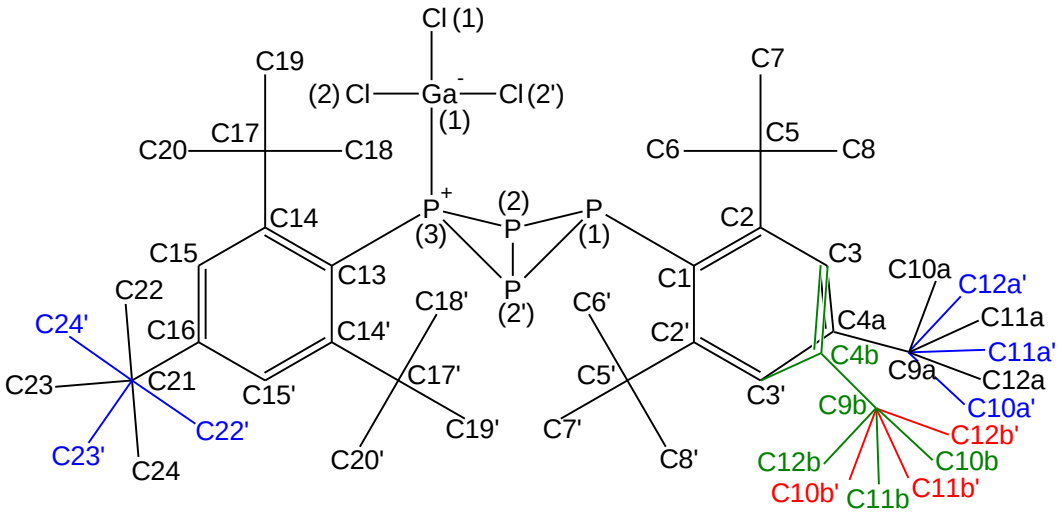


Table S7: Selected bond lengths (Å), angles (°) and dihedral angles (°) of **5a**·$GaCl_3$·½ *n*-hexane.

P1–P2	2.228(1)	Ga1–P3	2.4206(8)
P1–P2^{i}	2.228(1)	Ga1–Cl1	2.1794(9)
P2–P2^{i}	2.200(1)	Ga1–Cl2	2.1559(6)
P2–P3	2.1805(9)	P1–C1	2.4206(8)
P3–P2^{i}	2.1805(9)	P3–C13	1.859(4)
P2^{i}–P1–P2	59.15(4)	Cl1–Ga1–P3	103.83(3)
P2^{i}–P2–P1	60.42(2)	Cl2–Ga1–P3	108.44(2)
P3–P2–P2^{i}	59.71(2)	Cl2^{i}–Ga1–Cl2	112.90(4)
P3–P2–P1	82.41(4)	C2–C1–P1	119.1(2)
P2–P3–P2^{i}	60.59(4)	C2–C1–C2^{i}	119.2(3)
P2–P3–Ga1	119.95(4)	C14–C13–P3	118.8(1)
C13–P3–Ga1	126.7(1)	C14^{i}–C13–C14	120.4(3)
P1–P2–P2^{i}–P3	98.96(3)	C2–C3–C4A–C3^{i}	−13.2(2)
Cl1–Ga1–P3–C13	0.0	C1–C2–C3–C4B	−9(3)
P1–C1–C2–C3	−145.1(3)	C2–C3–C4B–C3^{i}	2(6)
P1–C1–C2–C5	39.9(4)	C2^{i}–C1–C2–C3	16.8(5)
C1–C2–C3–C4A	−1.4(9)	P3–C13–C14–C15	153.0(2)
P3–C13–C14–C17	−33.0(4)	C3–C4A–C9A–C11A^{i}	−51(2)

Symmetry code: (i) *x*, −*y*+1/2, *z*.

Table S7 continued.

C13–C14–C15–C16	2.4(4)	C3–C4A–C9A–C12A^{i}	63(1)
C14–C15–C16–C15^{i}	5.7(5)	C3–C4B–C9B–C10B	−27(5)
C14^{i}–C13–C14–C15	−10.9(4)	C3–C4B–C9B–C11B	−148(4)
C3–C4A–C9A–C10A	−12(2)	C3–C4B–C9B–C12B	97(4)
C3–C4A–C9A–C11A	−134(1)	C3–C4B–C9B–C10B$_{i}$	−157(4)
C3–C4A–C9A–C12A	111(1)	C3–C4B–C9B–C11B$_{i}$	−36(5)
C3–C4A–C9A–C10A^{i}	−173(1)	C3–C4B–C9B–C12B^{i}	79(4)

Symmetry code: (i) *x*, −*y*+1/2, *z*.

Scheme S5. Numbering scheme of **5b**·$GaCl_3$·toluene.

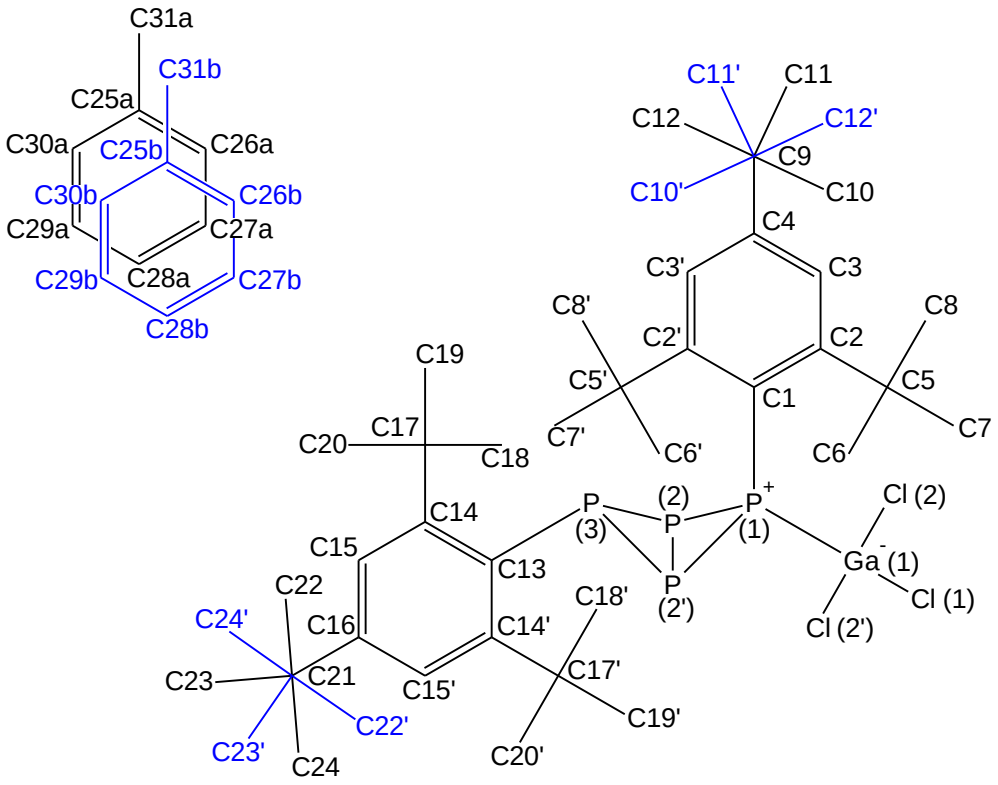


Table S8: Selected bond lengths (Å), angles (°) and dihedral angles (°) of **5b**·$GaCl_3$·toluene.

P1–Ga1	2.3966(5)	P3–P2^{i}	2.2365(6)
P1–P2	2.1854(5)	Ga1–Cl1	2.1550(5)
P1–P2^{i}	2.1854(5)	Ga1–Cl2	2.1560(5)
P2–P2^{i}	2.2074(8)	P1–C1	1.823(2)
P2–P3	2.2365(6)	P3–C13	1.864(2)
P2–P1–P2^{i}	60.67(2)	C1–P1–Ga1	136.15(6)
P1–P2–P2^{i}	59.67(1)	C13–P3–P2	96.02(6)
P2^{i}–P2–P3	60.43(1)	Cl1–Ga1–Cl2	111.84(2)
P2–P3–P2^{i}	59.14(2)	Cl2–Ga1–Cl2^{i}	110.72(3)
P1–P2–P3	85.13(2)	Cl1–Ga1–P1	112.85(2)
P2–P1–Ga1	105.23(2)	C2–C1–P1	117.91(9)
C1–P1–P2	112.34(5)	C2^{i}–C1–C2	120.6(2)
C14–C13–P3	119.72(9)	C14–C13–C14^{i}	119.2(2)

Symmetry code: (i) *x*, −*y*+3/2, *z*

Table S8 continued.

P1–P2–P2^{i}–P3	102.64(2)	C2^{i}–C1–C2–C3	−16.8(3)
C1–P1–Ga1–Cl1	0.0	P3–C13–C14–C15	150.4(1)
C1–P1–Ga1–Cl2	−121.78(2)	P3–C13–C14–C17	−34.5(2)
P1–C1–C2–C3	141.5(1)	C13–C14–C15–C16	3.3(3)
P1–C1–C2–C5	−43.8(2)	C14–C15–C16–C15^{i}	9.2(3)
C1–C2–C3–C4	2.9(2)	C14^{i}–C13–C14–C15	−16.2(3)
C2–C3–C4–C3^{i}	10.3(3)		

Symmetry code: (i) *x*, −*y*+3/2, *z*

Scheme S6. Numbering scheme of **5b**·$GaCl_3$·1.5 CH_2Cl_2.

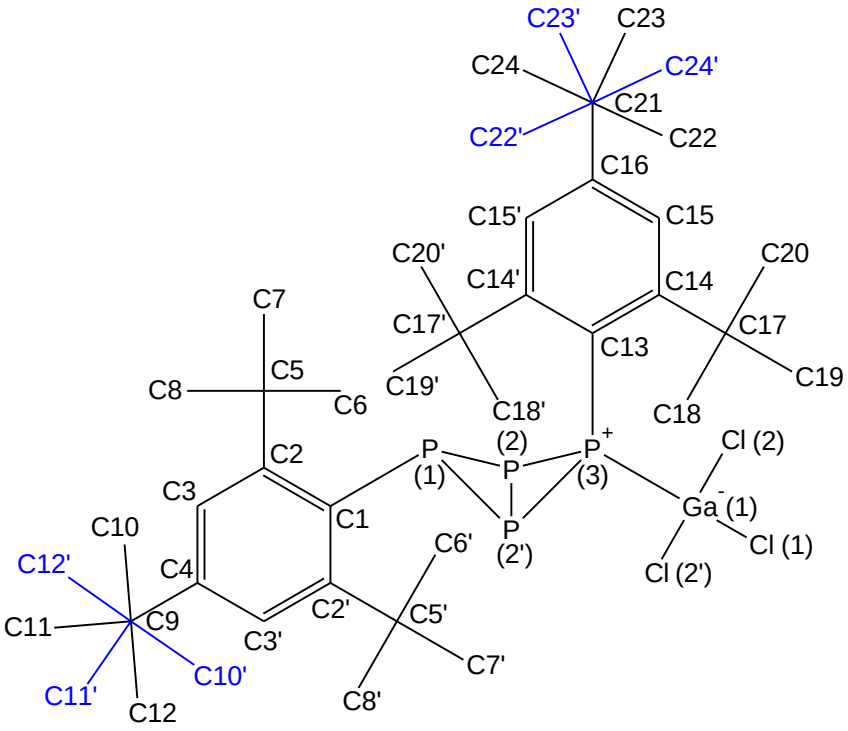


Table S9: Selected bond lengths (Å), angles (°) and dihedral angles (°) of **5b**·$GaCl_3$·1.5 CH_2Cl_2.

P3–Ga1	2.3999(3)	P3–P2^{i}	2.1878(3)
P1–P2	2.2373(4)	Ga1–Cl1	2.1576(4)
P1–P2^{i}	2.2373(4)	Ga1–Cl2	2.1617(3)
P2–P2^{i}	2.2092(5)	P1–C1	1.868(1)
P2–P3	2.1878(3)	P3–C13	1.827(1)
P2–P1–P2^{i}	59.17(1)	C13–P3–P2	112.83(3)
P1–P2–P2^{i}	60.415(7)	Cl1–Ga1–Cl2	112.11(1)
P2^{i}–P2–P3	59.675(7)	Cl2–Ga1–Cl2^{i}	110.49(2)
P2–P3–P2^{i}	60.65(1)	Cl1–Ga1–P3	112.34(1)
P1–P2–P3	85.49(1)	C2–C1–P1	119.66(5)
P2–P3–Ga1	105.57(1)	C2^{i}–C1–C2	119.0(1)
C13–P3–Ga1	135.18(4)	C14–C13–P3	118.23(5)
C1–P1–P2	94.81(4)	C14–C13–C14^{i}	120.3(1)
P1–P2–P2^{i}–P3	103.1(1)	C2^{i}–C1–C2–C3	−16.9(2)

Symmetry code: (i) *x*, −*y*+3/2, *z*

Table S9 continued.

C13–P3–Ga1–Cl1	0.0	P3–C13–C14–C15	143.56(7)
C13–P3–Ga1–Cl2	121.87(1)	P3–C13–C14–C17	−42.0(1)
P1–C1–C2–C3	148.28(8)	C13–C14–C15–C16	2.8(1)
P1–C1–C2–C5	−37.7(1)	C14–C15–C16–C15^{i}	9.5(2)
C1–C2–C3–C4	3.5(2)	C14^{i}–C13–C14–C15	−15.6(2)
C2–C3–C4–C3^{i}	9.7(2)		

Symmetry code: (i) *x*, −*y*+3/2, *z*

Scheme S7. Numbering scheme of **30**.

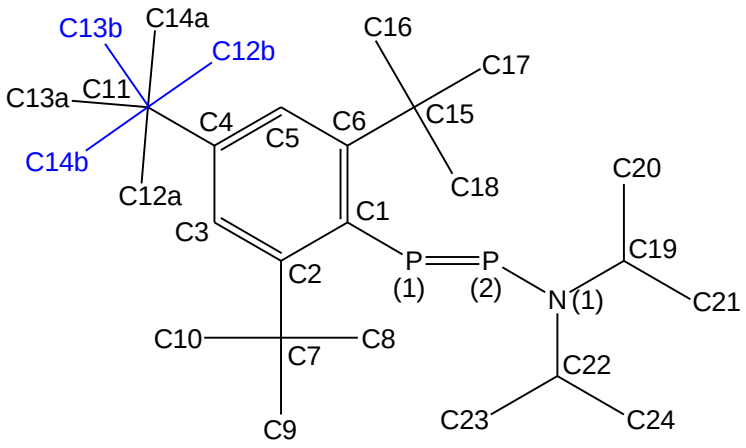


Table S10: Selected bond lengths (Å), angles (°) and dihedral angles (°) of **30**.

P1–C1	1.864(1)	C19–C21	1.518(3)
P1–P2	2.0380(6)	C19–C20	1.521(2)
P2–N1	1.669(1)	C22–C23	1.516(3)
N1–C19	1.472(2)	C22–C24	1.527(3)
N1–C22	1.486(2)	C19–N1–C22	117.4(1)
C1–P1–P2	92.44(5)	C19–N1–P2	125.3(1)
N1–P2–P1	108.38(5)	C22–N1–P2	117.3(1)
C6–C1–C2	119.3(1)	C3–C2–C1	117.9(1)
C6–C1–P1	120.0(1)	C5–C6–C1	118.1(1)
C2–C1–P1	120.5(1)	C1–P1–P2–N1	−174.18(7)
C6–C1–C2–C3	−11.0(2)	P1–P2–N1–C19	6.4(2)
C1–C2–C3–C4	2.9(2)	P1–P2–N1–C22	−170.5(1)
P1–C1–C2–C3	164.2(1)	P2–P1–C1–C6	86.2(1)
P1–C1–C2–C7	−20.5(2)	P2–P1–C1–C2	−89.0(1)

Scheme S8. Numbering scheme of **34**.

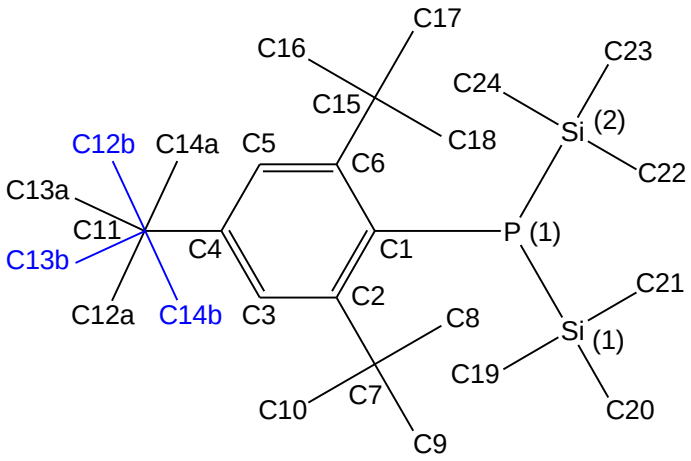
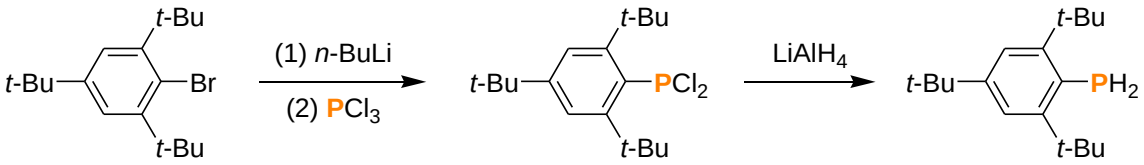


Table S11: Selected bond lengths (Å), angles (°) and dihedral angles (°) of **34**.

P1–C1	1.867(2)	C1–C2	1.420(2)
P1–Si1	2.2550(7)	C1–C6	1.432(2)
P1–Si2	2.2364(7)	C2–C3	1.397(2)
Si1–C19	1.871(2)	C2–C7	1.560(2)
Si1–C20	1.866(2)	C3–C4	1.384(2)
Si1–C21	1.871(2)	C4–C5	1.388(2)
Si2–C22	1.870(2)	C4–C11	1.532(2)
Si2–C23	1.872(2)	C5–C6	1.390(2)
Si2–C24	1.867(2)	C6–C15	1.545(2)
C1–P1–Si1	104.71(6)	C6–C1–P1	126.8(1)
C1–P1–Si2	127.39(6)	C2–C1–C6	117.9(1)
Si2–P1–Si1	109.3(1)	C1–C2–C7	125.6(1)
C2–C1–P1	113.3(1)	C1–C6–C15	124.0(2)
C1–P1–Si1–C20	−4.7(1)	P1–C1–C2–C7	31.8(2)
C1–P1–Si2–C22	172.2(1)	P1–C1–C6–C15	−35.6(2)
Si1–P1–C1–C2	97.0(1)	C1–C2–C3–C4	−4.5(3)
Si2–P1–C1–C2	−131.9(1)	C2–C3–C4–C5	−7.6(3)
P1–C1–C2–C3	−149.5(1)	C3–C4–C5–C6	8.8(3)
P1–C1–C6–C5	148.4(1)	C2–C3–C4–C11	175.1(2)

3 Syntheses of Starting Materials

3.1 2,4,6-Tri-*tert*-butylphenylphosphane

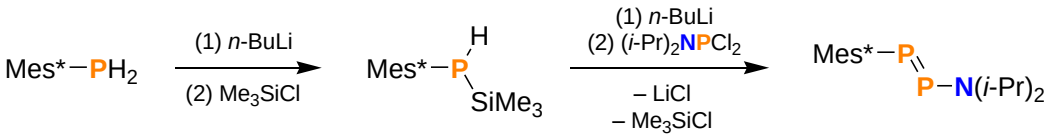


Mes^*PH_2 is prepared according to a modified literature procedure.[3] A solution of *n*-butyllithium (2.5 M in hexanes, 48 mL, 120 mmol) is added dropwise to a stirred solution of Mes*Br (32.6 g, 100 mmol) in THF (400 mL) at −80 °C over a period of 15 minutes. After stirring at −80 °C for one hour, PCl_3 (27.5 g, 200 mmol) is added over a period of two minutes, whereupon the solution turns yellow. The reaction vessel is warmed to ambient temperature over a period of one hour and heated to a brief reflux afterwards (ca. 10 min), resulting in the precipitation of a white solid. After cooling to ambient temperature, the solvent and excess PCl_3 are removed *in vacuo*. The resulting solid is extracted with Et_2O (400 mL); the insoluble residue is separated by filtration. The filtrate is added to $LiAlH_4$ (4.56 g, 120 mmol) at −80 °C and stirred overnight at ambient temperature. After cooling to −20 °C, excess hydrides are destroyed by *slowly* adding aqueous HCl (1 mol/L, 100 mL). Caution: Vigorous H_2 gas evolution is possible! *n*-Pentane (100 mL) is added, the slightly yellow organic layer is separated and subsequently washed with distilled water. The organic phase is dried over $MgSO_4$. After separating the inorganic solids by filtration, the solvents are evaporated. The crude product is recrystallized from boiling ethanol, yielding colourless needles of Mes^*PH_2, which are washed with cold ethanol and subsequently dried *in vacuo*. Yield: 19.29 g (69 mmol, 69 %).

Mp. 175 °C. CHN calc. (found) in %: C 77.65 (77.71), H 11.22 (11.07). $^{31}P\{^1H\}$-NMR (CD_2Cl_2, 121.5 MHz): δ = −130.9 (s). ^1H-NMR (CD_2Cl_2, 300.1 MHz): δ = 1.29 (s, 9 H, *p*-*t*-Bu), 1.55 (s, 18 H, *o*-*t*-Bu), 4.20 (d, $^1J(^1H,^{31}P)$ = 210 Hz, 2 H, P*H*$_2$), 7.41 (d,

$^4J(^1H,^{31}P)$ = 2.5 Hz, 2 H, *m*-H). $^{13}C\{^1H\}$-NMR (CD_2Cl_2, 75.5 MHz): δ = 31.6 (s, *p*-C(CH_3)$_3$), 32.8 (d, $^4J(^{13}C,^{31}P)$ = 7.2 Hz, *o*-C(CH_3)$_3$), 35.3 (s, *p*-*C*(CH_3)$_3$), 38.4 (s, *o*-*C*(CH_3)$_3$), 122.6 (d, $^3J(^{13}C,^{31}P)$ = 2.8 Hz, *m*-C), 149.6 (s, *p*-C), 154.7 (d, $^2J(^{13}C,^{31}P)$ = 7.2 Hz, *o*-C), *ipso*-C not observed. IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3102 (w), 2958 (s), 2904 (m), 2868 (m), 2743 (w), 2711 (w), 2350 (w), 2283 (w), 1765 (w), 1597 (m), 1547 (w), 1533 (w), 1473 (m), 1461 (m), 1410 (m), 1394 (m), 1361 (s), 1283 (w), 1238 (m), 1213 (m), 1189 (m), 1128 (w), 1106 (m), 1027 (w), 924 (w), 746 (w), 731 (m), 715 (w), 646 (w), 614 (w), 596 (w), 584 (w), 549 (w). Raman (785 nm, 40 s, 4 scans, cm^{-1}): $\tilde{\nu}$ = 3110 (1), 2965 (8), 2926 (7), 2904 (8), 2878 (4), 2780 (1), 2708 (1), 2408 (2), 2351 (2), 2285 (3), 1600 (8), 1462 (6), 1449 (7), 1396 (4), 1363 (4), 1285 (5), 1243 (5), 1204 (6), 1193 (6), 1178 (4), 1163 (4), 1130 (6), 1110 (3), 1048 (6), 1028 (3), 925 (8), 907 (3), 889 (2), 821 (10), 774 (2), 746 (3), 732 (5), 639 (2), 597 (2), 569 (10), 491 (3), 410 (5), 335 (4), 313 (4), 271 (10), 248 (8).

3.2 Synthesis of Mes*PPN(*i*-Pr)$_2$ (30)



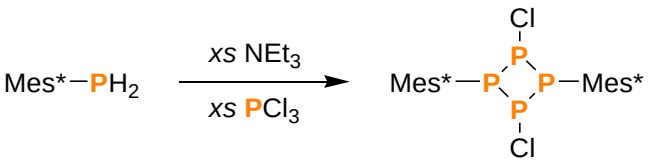
A solution of *n*-butyllithium in hexanes (2.5 mol/L, 4.1 mL, 10.2 mmol) is added dropwise to a stirred solution of Mes*PH_2 (2.34 g, 8.4 mmol) in THF (50 mL) at −80 °C over a period of ten minutes. Stirring is continued for 30 minutes at −80 °C, whereupon a solution of Me_3SiCl (0.940 g, 8.6 mmol) in THF (9 mL) is added over a period of ten minutes, resulting in a clear orange solution. This is slowly warmed to ambient temperature over a period of 1.5 hours. A second crop of *n*-butyllithium in hexanes (4.1 mL, 10.2 mmol) is added over a period of 10 minutes, resulting in a dark red colouration of the reaction mixture. This is stirred for further 2.5 hours, then cooled to −80 °C and a solution of (*i*-Pr)$_2$$NPCl_2$ (1.69 g, 8.4 mmol) in THF (6 mL) is added dropwise over a period of 15 minutes. The mixture is again warmed to ambient temperature over a period of one hour, resulting in the precipitation of a white solid. The solvent is

removed *in vacuo* and the residue is extracted with *n*-hexane (20 mL). The solution is filtered off using a glass sinter frit and the solids are extracted again with *n*-hexane (15 mL). The combined yellow filtrates are concentrated to *ca.* 10 mL. Crystallization at 5 °C yields yellow crystals, which are isolated and washed with *n*-hexane at −60 °C. The supernatant is again concentrated and crystallized, yielding a second crop of product, which is treated in the same manner. Total yield: 1.74 g (4.3 mmol, 51 %).

Mp. 125 °C. CHN calc. (found) in %: C 70.73 (69.47), H 10.63 (9.86), N 3.44 (3.69). $^{31}P\{^{1}H\}$-NMR (CD_2Cl_2, 121.5 MHz): δ = 269.9 (d, $^{1}J(^{31}P,^{31}P)$ = −540 Hz, 1 P, Mes*PPN(*i*-Pr)$_2$), 442.1 (d, $^{1}J(^{31}P,^{31}P)$ = −540 Hz, 1 P, Mes*PPN(*i*-Pr)$_2$). ^{1}H-NMR (CD_2Cl_2, 300.1 MHz): δ = 1.26 (d, $^{3}J(^{1}H,^{1}H)$ = 6.61 Hz, 12 H, CH(CH_3)$_2$), 1.34 (s, 9 H, *p*-*t*-Bu), 1.50 (s, 18 H, *o*-*t*-Bu), 4.27 (m, 2 H, CH(CH$_3$)$_2$), 7.41 (s, 2 H, *m*-H). $^{13}C\{^{1}H\}$-NMR (CD_2Cl_2, 75.5 MHz): δ = 23.8 (d, $^{3}J(^{13}C,^{31}P)$ = 4.9 Hz, CH(CH$_3$)$_2$), 31.7 (s, *p*-C(CH$_3$)$_3$), 34.7 (d, $^{4}J(^{13}C,^{31}P)$ = 7.7 Hz, *o*-C(CH$_3$)$_3$), 35.3 (s, *p*-C(CH$_3$)$_3$), 39.2 (s, *o*-C(CH$_3$)$_3$), 52.9 (d, $^{2}J(^{13}C,^{31}P)$ = 11.6 Hz, CH(CH$_3$)$_2$), 122.1 (d, $^{3}J(^{13}C,^{31}P)$ = 1.7 Hz, *m*-C), 149.1 (d, $^{4}J(^{13}C,^{31}P)$ = 2.8 Hz, *p*-C), 157.9 (d, $^{2}J(^{13}C,^{31}P)$ = 8.8 Hz, *o*-C), *ipso*-C not observed. IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 2961 (s), 2902 (m), 2865 (m), 1626 (w), 1591 (w), 1538 (w), 1478 (m), 1455 (m), 1388 (m), 1359 (s), 1310 (w), 1241 (w), 1211 (w), 1194 (m), 1168 (m), 1152 (m), 1117 (s), 1015 (w), 965 (s), 902 (w), 870 (m), 840 (m), 752 (m), 714 (w), 642 (m), 606 (w), 581 (w). Raman (532 nm, 70 s, 4 scans, cm^{-}): $\tilde{\nu}$ = 2968 (2), 2930 (1), 2909 (1), 2875 (1), 1593 (1), 1457 (1), 1384 (1), 1360 (1), 1285 (1), 1199 (1), 1171 (1), 1127 (1), 1039 (1), 1017 (1), 967 (1), 929 (1), 873 (1), 853 (1), 823 (1), 754 (1), 651 (3), 606 (10), 568 (1), 520 (3), 441 (1), 423 (1), 342 (1), 250 (1).

Crystals suitable for single crystal X-ray diffraction can be grown from saturated *n*-hexane solution at 5 °C.

3.3 Synthesis of [ClP(μ-PMes*)]$_2$ (32)

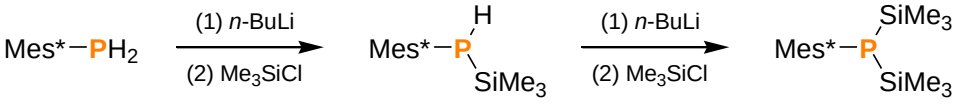


PCl_3 (7.7 g, 56 mmol) is added to a solution of Mes*PH_2 (7.9 g, 28.4 mmol) and NEt_3 (14.2 g, 140 mmol) in Et_2O (150 mL) at −80 °C. The reaction mixture is warmed to ambient temperature and stirred for 18 hours. Afterwards, all volatile components are removed *in vacuo*. The solid residue is thoroughly dried *in vacuo* at 50 °C for at least one hour and is then extracted with *n*-pentane. The suspension is filtered over a glass sinter frit yielding a clear, dark red filtrate. This extraction procedure is repeated two or three times by back-condensation of the solvent. Subsequently, the solvent is evaporated and the solid residue is solved in CH_2Cl_2. The solution is kept at 5 °C overnight, whereupon it turns yellow. Again, the solvent is removed *in vacuo*. The solid residue is crystallized from PhF at ambient temperature, yielding block-shaped, slightly yellowish crystals. The supernatant is separated using a syringe and concentrated, yielding another crop of product. To remove adhering impurities, the product is re-crystallized from PhF (15 mL) and dried *in vacuo*, resulting in pure [ClP(μ-PMes*)]$_2$ (**32**). Total yield: 4.42 g (6.4 mmol, 45 %).

Mp. 154 °C. CHN calc. (found) in %: C 63.06 (64.06), H 8.53 (8.28). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz): δ = −8.1 (t, $^1J(^{31}P,^{31}P)$ = −218 Hz, 2 P, *P*Mes*), 131.3 (t, $^1J(^{31}P,^{31}P)$ = −218 Hz, 2 P, *P*Cl). ^1H NMR (CD_2Cl_2, 300.1 MHz): δ = 1.29 (s, 18 H, *p*-*t*-Bu), 1.40 (s, 36 H, *o*-*t*-Bu), 7.28 (m, 4 H, *m*-H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz): δ = 31.5 (s, *p*-C(CH_3)$_3$), 34.1 (m, *o*-C(CH_3)$_3$), 35.2 (s, *p*-*C*(CH_3)$_3$) 39.6 (s, *o*-*C*(CH_3)$_3$), 123.9 (s, *m*-C), 151.2 (s, *p*-C), 157.8 (m, *o*-C), 163.5 (d, $^1J(^{13}C,^{31}P)$ = 245 Hz, *i*-C). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 2954 (s), 2902 (m), 2864 (m), 2743 (w), 2713 (w), 1592 (m), 1581 (m), 1521 (w), 1493 (m), 1474 (s), 1461 (s), 1441 (m), 1391 (s), 1361 (s), 1278 (w), 1235 (m), 1212 (s), 1178 (m), 1152 (m), 1122 (m), 1064 (m), 1020 (m), 947 (w), 932 (w), 920 (m), 893 (m), 875 (s), 830 (w), 804 (m), 753 (s), 740 (s), 714 (w), 684 (m), 650 (m), 646 (m), 637 (m), 597 (m), 581 (m), 574 (m), 546 (w),

539 (w). Raman (633 nm, 30 s, 4 scans, cm^{-1}): $\tilde{\nu}$ = 3086 (1), 3067 (2), 2969 (4), 2962 (4), 2922 (4), 2902 (5), 2864 (2), 2781 (1), 2709 (1), 1590 (5), 1579 (3), 1458 (2), 1444 (2), 1384 (2), 1359 (1), 1281 (4), 1239 (2), 1204 (3), 1172 (4), 1151 (2), 1122 (5), 1008 (10), 931 (2), 920 (3), 891 (1), 876 (1), 819 (6), 803 (3), 772 (1), 748 (2), 642 (1), 596 (3), 580 (3), 564 (6), 516 (3), 488 (4), 461 (6), 445 (8), 435 (8), 400 (4), 385 (2), 360 (1), 322 (2), 298 (2), 254 (4), 232 (4), 172 (3), 163 (4). MS (CI positive, *iso*-butane, m/z): 685 $[M+H]^+$, 649 $[M-Cl]^+$, 627 $[M-t\text{-Bu}]^+$, 557 $[M-t\text{-Bu}-Cl_2]^+$, 343 $[MesPPCl+H]^+$.

3.4 Synthesis of Mes*P(SiMe$_3$)$_2$ (34)



A solution of *n*-butyllithium in hexanes (2.5 mol/L, 1.9 mL, 4.8 mmol) is added dropwise to a stirred solution of Mes*PH$_2$ (1.11 g, 4.0 mmol) in THF (30 mL) at 0 °C over a period of five minutes. Stirring is continued for 30 minutes at ambient temperature, whereupon Me$_3$SiCl (0.538 g, 4.8 mmol) is added at 0 °C, resulting in a colourless solution. After stirring for one hour at ambient temperature, a second crop of *n*-butyllithium in hexanes (1.9 mL, 4.8 mmol) is added at 0 °C over a period of three minutes, resulting in a dark red colouration of the reaction mixture. This is stirred for further 45 minutes, then re-cooled to 0 °C and a second crop of Me$_3$SiCl (0.538 g, 4.8 mmol) is added quickly. The mixture is again warmed to ambient temperature and stirred for 45 minutes, resulting in a slightly yellow solution. The solvent is removed *in vacuo* and the residue is extracted with *n*-hexane (20 mL). The solution is filtered off using a celite padded glass sinter frit. The filtrate is concentrated to incipient crystallization and kept at ambient temperature overnight, yielding slightly yellow crystals with an unpleasant odour. The supernatant is removed by syringe and subsequently concentrated and crystallized again, yielding a second crop of product. Total yield: 1.12 g (2.6 mmol, 66 %).

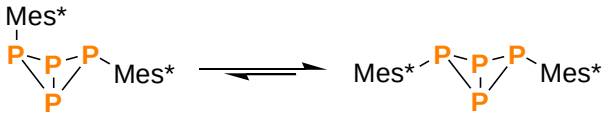
Mp. 93 °C. CHN calc. (found) in %: C 68.18 (68.26), H 11.21 (10.58). $^{31}P\{^{1}H\}$-NMR (CD_2Cl_2, 121.5 MHz): δ = −142.6 (s). ^{1}H-NMR (CD_2Cl_2, 300.1 MHz): δ = 0.15 (d, $^{3}J(^{1}H,^{31}P)$ = 6.23 Hz, 18 H, $SiMe_3$), 1.26 (s, 9 H, *p*-*t*-Bu), 1.60 (s, 18 H, *o*-*t*-Bu), 7.32 (d, $^{4}J(^{1}H,^{31}P)$ = 2.83 Hz, 2 H, *m*-H). $^{13}C\{^{1}H\}$-NMR (CD_2Cl_2, 75.5 MHz): δ = 2.8 (d, $^{2}J(^{13}C,^{31}P)$ = 17.6 Hz, $SiMe_3$), 31.6 (s, *p*-$C(CH_3)_3$), 34.1 (d, $^{4}J(^{13}C,^{31}P)$ = 5.5 Hz, *o*-$C(CH_3)_3$), 35.2 (s, *p*-$C(CH_3)_3$), 39.1 (d, $^{3}J(^{13}C,^{31}P)$ = 3.3 Hz, *o*-$C(CH_3)_3$), 121.8 (d, $^{3}J(^{13}C,^{31}P)$ = 8.8 Hz, *m*-C), 149.5 (d, $^{4}J(^{13}C,^{31}P)$ = 2.8 Hz, *p*-C), 159.2 (d, $^{2}J(^{13}C,^{31}P)$ = 9.4 Hz, *o*-C), *ipso*-C not observed. IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3004 (w), 2953 (s), 2903 (m), 2869 (m), 1590 (m), 1535 (w), 1519 (w), 1469 (m), 1453 (w), 1388 (m), 1354 (m), 1284 (w), 1244 (s), 1211 (m), 1179 (w), 1126 (w), 1028 (w), 923 (w), 903 (w), 873 (m), 854 (s), 826 (vs), 746 (s), 714 (m), 681 (s), 648 (m), 623 (s), 596 (m), 577 (m), 543 (w). Raman (785 nm, 50 s, 4 scans, cm^{-}): $\tilde{\nu}$ = 2971 (5), 2906 (8), 1604 (2), 1481 (2), 1458 (3), 1445 (2), 1298 (2), 1268 (2), 1253 (2), 1220 (2), 1197 (2), 1173 (1), 1141 (1), 1044 (1), 1031 (2), 960 (1), 947 (2), 941 (2), 918 (1), 894 (1), 838 (7), 789 (1), 771 (2), 757 (1), 706 (3), 696 (2), 647 (10), 611 (2), 592 (3), 579 (4), 521 (2), 497 (1), 444 (3), 425 (4), 399 (2), 364 (1), 340 (2), 300 (2), 266 (3).

Crystals suitable for single crystal X-ray diffraction can be grown from saturated *n*-hexane solution at 5 °C.

4 Syntheses of Compounds

4.1 Synthesis of *exo-exo*-Mes*P$_4$Mes* (5a)

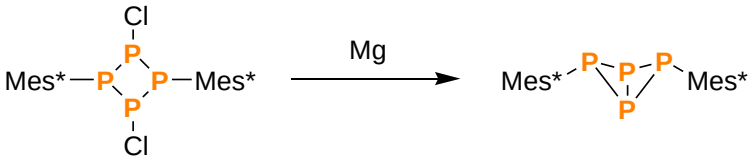
4.1.1 Isomerization of *endo-exo*-Mes*P$_4$Mes* (5b)



In an NMR tube equipped with a young valve, a mixture of *exo-exo* and *endo-exo*-Mes*P$_4$Mes* (25 mg, 0.04 mmol, isomeric ratio *ca.* 1:4) is dissolved in THF (0.5 mL) and C_6D_6 (0.1 mL). The solution is degassed by three freeze-pump-thaw cycles and the sample is subsequently heated to 75 °C in a drying oven. The reaction is monitored by NMR spectroscopy. After *ca.* 20 days, equilibrium state is achieved; the isomeric ratio is *ca.* 9:1.

$^{31}P\{^1H\}$ NMR (C_6D_6, 121.5 MHz, relative integrals given): δ = −303.0 (m, 0.6 %), −273.6 (t, $J_{AX}(^{31}P,^{31}P)$ = −177 Hz, 2 P, **5a**, 42.8 %), −220.4 (dd, $J_{AM}(^{31}P,^{31}P)$ = −208 Hz, $J_{AX}(^{31}P,^{31}P)$ = −229 Hz, 2 P, **5b**, 5.1 %), −130.4 (t, $J_{AX}(^{31}P,^{31}P)$ = −177 Hz, 2 P, **5a**, 46.1 %), −96.4 (td, $J_{AM}(^{31}P,^{31}P)$ = −208 Hz, $J_{MX}(^{31}P,^{31}P)$ = −31 Hz, 1 P, **5b**, 2.6 %), −56.3 (td, $J_{AX}(^{31}P,^{31}P)$ = −229 Hz, $J_{MX}(^{31}P,^{31}P)$ = −31 Hz, 1 P, **5b**, 1.2 %), −13.2 (s, 0.3 %), 2.5 (s, 1.2 %).

4.1.2 Reduction of [ClP(μ-PMes*)]$_2$ (32)



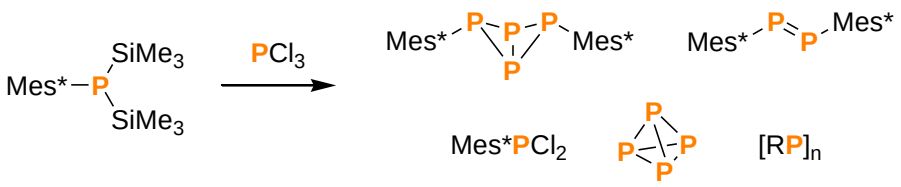
A solution of [ClP(μ-PMes*)]$_2$ (206 mg, 0.30 mmol) in THF (3 mL) is added to magnesium turnings (10 mg, 0.42 mmol) and stirred at ambient temperature overnight.

Subsequently, the solvent is removed *in vacuo* and the solid residue is extracted with *n*-hexane (5 mL). After filtration, the filtrate is concentrated and stored at 5 °C, resulting in crystallization of colourless *exo*-*exo*-Mes*P_4Mes*. Yield: 135 mg (0.22 mmol, 73 %).

Mp. 185 °C (decomposition). CHN calc. (found) in %: C 70.34 (70.32), H 9.51 (9.35). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz): δ = −273.2 (t, $^1J_{AX}(^{31}P,^{31}P)$ = −177 Hz, 2 P, $P_{bridgehead}$), −128.3 (t, $^1J_{AX}(^{31}P,^{31}P)$ = −177 Hz, 2 P, *P*Mes*). ^1H NMR (CD_2Cl_2, 300.1 MHz): δ = 1.19 (s, 18 H, *p*-*t*-Bu), 1.63 (s, 36 H, *o*-*t*-Bu), 7.07 (m, 4 H, *m*-H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz): δ = 31.4 (s, *p*-C(CH_3)$_3$), 34.8 (m, *p*-*C*(CH_3)$_3$), 35.0 (m, *o*-C(CH_3)$_3$) 39.9 (m, *o*-*C*(CH_3)$_3$), 123.6 (s, *m*-C), 149.3 (s, *p*-C), 156.2 (m, *o*-C), *ipso*-Cs not observed. IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3070 (w), 2958 (m), 2902 (w), 2864 (w), 1587 (m), 1525 (w), 1475 (m), 1462 (m), 1441 (m), 1392 (m), 1362 (m), 1306 (m), 1236 (vs), 1209 (s), 1184 (s), 1126 (vs), 1030 (m), 982 (s), 935 (m), 920 (m), 897 (m), 879 (s), 808 (m), 769 (m), 746 (s), 717 (m), 661 (m), 646 (s), 640 (m), 590 (s), 580 (s), 542 (m), 530 (m). Raman (633 nm, 15 s, 10 scans, cm^{-1}): $\tilde{\nu}$ = 3075 (1), 2963 (2), 2924 (2), 2903 (3), 2863 (1), 2777 (1), 2709 (1), 1588 (1), 1527 (1), 1473 (1), 1461 (1), 1442 (1), 1396 (1), 1365 (1), 1292 (1), 1281 (1), 1241 (1), 1208 (1), 1201 (1), 1175 (1), 1152 (1), 1128 (1), 1033 (2), 1020 (1), 934 (1), 921 (1), 891 (1), 822 (2), 775 (1), 637 (1), 592 (10), 563 (1), 490 (1), 475 (1), 463 (1), 447 (1), 432 (1), 412 (1), 387 (1), 351 (4), 294 (1), 259 (2), 211 (1), 191 (1), 177 (1), 136 (1), 125 (2), 107 (3), 86 (3). MS (CI positive, *iso*-butane, m/z): 615 $[M]^+$, 557 $[M - t\text{-}Bu]^+$.

Crystals suitable for single crystal X-ray diffraction can be grown from saturated *n*-hexane solution at ambient temperature.

4.1.3 Reaction of Mes*P(SiMe$_3$)$_2$ (34) with PCl$_3$



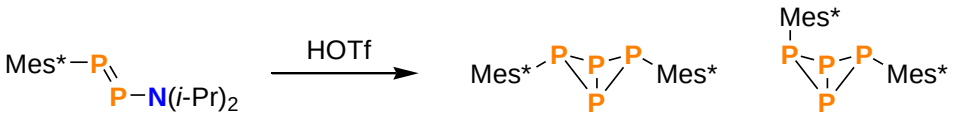
In an NMR tube equipped with a Young valve, PCl_3 (52 mg, 0.38 mmol) and THF (1.5 mL) are condensed onto Mes*P(SiMe$_3$)$_2$ (160 mg, 0.38 mmol) at −196 °C. Afterwards, the

sample is heated to 75 °C in a drying oven for several days, resulting in a mixture of products. Main species are Mes*PPMes* *exo-exo*-Mes*P_4Mes*, and higher aggregates with multiple P atoms ("$[RP]_n$") of uncertain composition. Minor species include P_4, Mes*PCl_2 and *endo-exo*-Mes*P_4Mes*.

$^{31}P\{^1H\}$ NMR (C_6D_6, 121.5 MHz): δ = −525.7 (s, P_4), −303.4 (m), −299.3 (m), −273.0 (t, **5a**), −241.8 (t), −219.7 (t, **5b**), −173.7 (m), −150.8 (m), −129.6 (t, **5a**), −111.2 (m), −106.9 (td), −97.7 (m), −95.5 (td, **5b**), −90.9 (m), −55.5 (td, **5b**), −31.4 (td), 9.9 (m), 13.4 (m), 19.2 (ddd), 41.8 (m), 55.1 (s), 76.0 (m), 76.4 (s), 82.9 (m), 91.2 (m), 111.7 (m), 133.6 (d), 139.4 (d), 153.4 (s, Mes*PCl_2), 160.9 (dd), 196.6 (s), 200.9 (s), 493.2 (s, Mes*PPMes*).

4.2 Synthesis of *endo-exo*-Mes*P_4Mes* (5b)

4.2.1 Protolysis of Mes*PPN(*i*-Pr)$_2$

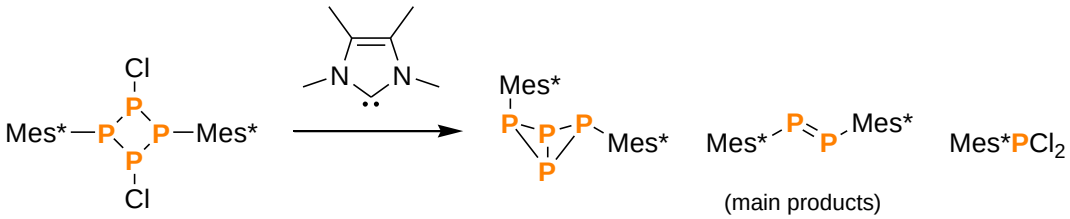


HOTf (180 mg, 1.12 mmol) is condensed onto a degassed solution of Mes*PPN(*i*-Pr)$_2$ (489 mg, 1.12 mmol) in CH_2Cl_2 (8 mL) at −196 °C. The reaction mixture is slowly warmed to ambient temperature overnight. The solvent is removed *in vacuo* and the residue is extracted with *n*-hexane (5 mL). Insoluble solids are filtered off. The clear orange filtrate is concentrated, resulting in crystallization of a mixture of *exo-exo* and *endo-exo*-Mes*P_4Mes* (1:4 ratio). Yield: 120 mg (0.20 mmol, 35 %). Re-crystallization yields pure *endo-exo*-Mes*P_4Mes*.

Mp. 161 °C (decomposition). CHN calc. (found) in %: C 70.34 (70.70), H 9.51 (9.43). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz): δ = −220.4 (dd, $^1J_{AX}(^{31}P,^{31}P)$ = −234 Hz, $^1J_{AM}(^{31}P,^{31}P)$ = −213 Hz, 2 P, $P_{bridgehead}$), –94.8 (td, $^1J_{AM}(^{31}P,^{31}P)$ = −213 Hz, $^2J_{MX}(^{31}P,^{31}P)$ = −27 Hz, 1 P, P_{exo}), −54.7 (td, $^1J_{AX}(^{31}P,^{31}P)$ = −234 Hz, $^2J_{MX}(^{31}P,^{31}P$ = −27 Hz, 1 P, P_{endo}). ^1H NMR (CD_2Cl_2, 300.1 MHz): δ = 1.19 (s, 9 H, *exo*-Mes*, *p-t*-Bu), 1.30 (s, 9 H, *endo*-Mes*, *p-t*-Bu),

1.49 (s, 18 H, *exo*-Mes*, *o*-*t*-Bu), 1.66 (m 18 H, *endo*-Mes*, *o*-*t*-Bu), 7.02 (m, 2 H, *exo*-Mes*, *m*-H), 7.05 (m, 2 H, *endo*-Mes*, *m*-H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz): δ = 31.4 (s, *p*-C(CH_3)$_3$), 31.6 (s, *p*-C(CH_3)$_3$), 34.4–34.9 (m, 2x *o*-C(CH_3)$_3$), 34.9 (s, *p*-C(CH_3)$_3$) 39.5 (m, *o*-C(CH_3)$_3$), 39.6 (m, *o*-C(CH_3)$_3$), 119.7 (s, *m*-C), 123.6 (s, *m*-C), 148.8 (s, *p*-C), 149.7 (s, *p*-C), 154.7 (m, *o*-C), 162.0 (m, *o*-C), *ipso*-Cs not observed. Raman (785 nm, 25 s, 4 scans, cm^{-1}): $\tilde{\nu}$ = 3070 (1), 3052 (1), 2960 (1), 2924 (1), 2902 (1), 2868 (1), 2777 (1), 2712 (1), 1584 (1), 1476 (1), 1466 (1), 1444 (1), 1397 (1), 1392 (1), 1361 (1), 1293 (1), 1283 (1), 1252 (1), 1204 (1), 1183 (1), 1174 (1), 1149 (1), 1132 (1), 1034 (2), 1017 (1), 933 (1), 919 (1), 897 (1), 879 (1), 822 (3), 818 (2), 773 (1), 751 (1), 747 (1), 739 (1), 646 (1), 638 (1), 591 (2), 583 (1), 568 (10), 540 (1), 499 (1), 490 (1), 472 (1), 434 (1), 420 (2), 412 (2), 388 (2), 380 (2), 362 (2), 330 (1), 308 (1), 290 (1), 256 (3), 197 (1), 186 (1), 175 (2), 171 (2), 144 (5), 137 (5), 102 (7), 77 (8). MS (CI positive, *iso*-butane, m/z): 615 $[M]^+$, 553 $[M-P_2]^+$.

4.2.2 Degradation of [ClP(μ-PMes*)]$_2$



A mixture of $Me_4C_3N_2$ (302 mg, 2.44 mmol) and [ClP(μ-PMes*)]$_2$ (835 mg, 1.22 mmol) is dissolved in CH_2Cl_2 (10 mL) at −80 °C, resulting in a dark red solution. The reaction vessel is warmed to ambient temperature over a period of one hour, whereupon the solution is concentrated and stored at 5 °C, resulting in the crystallization of orange, block shaped crystals that were identified as Mes*PPMes*. Yield: 110 mg (0.20 mmol, 16 %).

Mp. 169 °C (decomposition). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz): δ = 489.0 (s). ^1H NMR (CD_2Cl_2, 300.1 MHz): δ = 1.36 (s, 18 H, *p*-*t*-Bu), 1.45 (s, 36 H, *o*-*t*-Bu), 7.42 (m, 4 H, *m*-H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz): δ = 31.6 (s, *p*-C(CH_3)$_3$), 34.6 (m, *o*-C(CH_3)$_3$), 35.2 (s, *p*-C(CH_3)$_3$) 39.1 (s, *o*-C(CH_3)$_3$), 123.0 (s, *m*-C), 149.8 (s, *p*-C), 155.1 (m, *o*-C), *ipso*-C not observed. IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3076 (w), 2960 (s), 2951 (s), 2902 (m), 2864 (m),

1591 (m), 1537 (w), 1524 (m), 1477 (s), 1462 (s), 1446 (s), 1402 (m), 1390 (s), 1360 (vs), 1236 (s), 1209 (s), 1198 (s), 1176 (m), 1122 (s), 1026 (m), 1018 (m), 939 (m), 924 (m), 899 (m), 874 (vs), 854 (m), 768 (m), 744 (vs), 646 (s), 613 (s), 590 (s), 575 (s), 544 (s). Raman (633 nm, 4 s, 30 scans, cm^{-1}): $\tilde{\nu}$ = 3077 (1), 2974 (1), 2967 (1), 2957 (1), 2952 (1), 2906 (1), 2871 (1), 2775 (1), 2705 (1), 1592 (3), 1523 (1), 1465 (1), 1459 (1), 1448 (1), 1398 (1), 1389 (1), 1358 (1), 1298 (1), 1282 (1), 1253 (1), 1237 (1), 1201 (1), 1177 (1), 1157 (1), 1125 (1), 1070 (1), 1031 (5), 1015 (1), 923 (1), 914 (1), 900 (1), 886 (1), 875 (1), 820 (1), 773 (1), 750 (1), 696 (1), 649 (1), 639 (1), 613 (10), 591 (2), 572 (1), 565 (1), 545 (1), 480 (1), 443 (1), 428 (1), 401 (1), 378 (1), 355 (1), 329 (1), 312 (1), 283 (1), 257 (1), 217 (1), 140 (1), 99 (2), 69 (4). MS (CI positive, *iso*-butane, m/z): 553 $[M]^+$.

Crystallization of the supernatant at 5 °C yields large colourless crystals of *endo*-*exo*-Mes*P_4Mes*. Yield: 105 mg (0.17 mmol, 14 %).

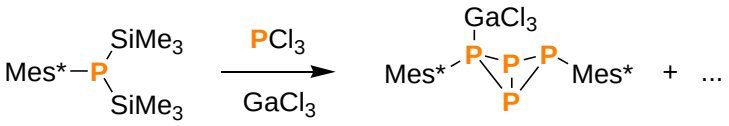
Mp. 161 °C (decomposition). CHN calc. (found) in %: C 70.34 (70.04), H 9.51 (9.47). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz): δ = −220.4 (dd, $^1J_{AX}(^{31}P,^{31}P)$ = −234 Hz, $^1J_{AM}(^{31}P,^{31}P)$ = −213 Hz, 2 P, $P_{bridgehead}$), –94.8 (td, $^1J_{AM}(^{31}P,^{31}P)$ = −213 Hz, $^2J_{MX}(^{31}P,^{31}P)$ = −27 Hz, 1 P, P_{exo}), −54.7 (td, $^1J_{AX}(^{31}P,^{31}P)$ = −234 Hz, $^2J_{MX}(^{31}P,^{31}P$ = −27 Hz, 1 P, P_{endo}). ^1H NMR (CD_2Cl_2, 300.1 MHz): δ = 1.19 (s, 9 H, *exo*-Mes*, *p*-*t*-Bu), 1.30 (s, 9 H, *endo*-Mes*, *p*-*t*-Bu), 1.49 (s, 18 H, *exo*-Mes*, *o*-*t*-Bu), 1.66 (m 18 H, *endo*-Mes*, *o*-*t*-Bu), 7.02 (m, 2 H, *exo*-Mes*, *m*-H), 7.05 (m, 2 H, *endo*-Mes*, *m*-H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz): δ = 31.4 (s, *p*-C(CH_3)$_3$), 31.6 (s, *p*-C(CH_3)$_3$), 34.4–34.9 (m, 2x *o*-C(CH_3)$_3$), 34.9 (s, *p*-*C*(CH_3)$_3$) 39.5 (m, *o*-*C*(CH_3)$_3$), 39.6 (m, *o*-*C*(CH_3)$_3$), 119.7 (s, *m*-C), 123.6 (s, *m*-C), 148.8 (s, *p*-C), 149.7 (s, *p*-C), 154.7 (m, *o*-C), 162.0 (m, *o*-C), *ipso*-Cs not observed. IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3068 (vw), 3055 (vw), 2960 (s), 2951 (s), 2901 (m), 2864 (m), 1583 (m), 1531 (w), 1518 (w), 1473 (s), 1460 (m), 1441 (m), 1390 (s), 1360 (vs), 1308 (m), 1238 (vs), 1209 (s), 1186 (s), 1147 (m), 1128 (s), 1068 (w), 1026 (m), 984 (m), 943 (w), 931 (m), 922 (m), 897 (m), 874 (vs), 814 (w), 773 (w), 741 (vs), 646 (m), 638 (m), 584 (m), 577 (m), 567 (m), 540 (m). Raman (633 nm, 15 s, 20 scans, cm^{-1}): $\tilde{\nu}$ = 3168 (1), 3074 (1), 3055 (1), 2959 (4), 2924 (4), 2902 (5), 2865 (2), 2778 (1), 2712 (1), 1584 (3), 1520 (1), 1475 (1), 1466 (2), 1444 (2), 1399 (1), 1392 (1), 1360 (1), 1283 (2), 1251 (1), 1203 (1), 1186 (1), 1182 (1),

1173 (1), 1148 (1), 1132 (2), 1033 (3), 1017 (2), 932 (1), 919 (2), 897 (1), 877 (1), 822 (4), 772 (1), 744 (1), 740 (1), 647 (1), 638 (1), 591 (2), 584 (2), 568 (10), 500 (2), 490 (1), 473 (1), 435 (1), 419 (2), 412 (2), 381 (4), 363 (2), 330 (1), 309 (1), 295 (1), 256 (2), 200 (1), 177 (1), 143 (4), 139 (3), 103 (7), 78 (6). MS (CI positive, *iso*-butane, m/z): 615 $[M]^+$, 553 $[M - P_2]^+$.

Crystals suitable for single crystal X-ray diffraction can be grown from saturated *n*-hexane or CH_2Cl_2 solution at 5 °C.

4.3 Synthesis of *exo-exo*-Mes*P$_4$Mes*·GaCl$_3$ (5a·GaCl$_3$)

4.3.1 Reaction of Mes*P(SiMe$_3$)$_2$ (34) with PCl$_3$ and GaCl$_3$



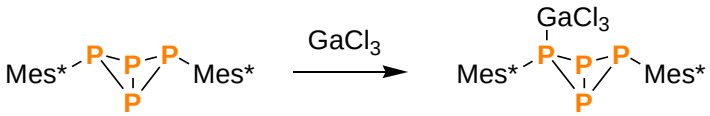
Solutions of PCl_3 (130 mg, 0.95 mmol) and $GaCl_3$ (168 mg, 0.95 mmol) in *n*-hexane (2 mL each) are added consecutively to a stirred solution of Mes*P(SiMe$_3$)$_2$ (403 mg, 0.95 mmol) in *n*-hexane (5 mL) at −80 °C. The mixture is warmed to ambient temperature, resulting in the deposition of an intensively red oil. Overnight, large colourless crystals grow at the phase interface at ambient temperature. Yield: 45 mg (0.07 mmol, 8 %).

Mp. 100 °C (decomposition). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz): δ = −246.4 (t, $^1J_{AX}(^{31}P,^{31}P)$ = −198 Hz, 2 P, $P_{bridgehead}$), −97.1 (broad, 2 P, *P*Mes*). ^1H NMR (CD_2Cl_2, 300.1 MHz): δ = 1.20 (s, 18 H, Mes*, *p*-*t*-Bu), 1.68 (s, 36 H, *o*-*t*-Bu), 7.24 (s, 4 H, *m*-H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz): δ = 31.2 (s, *p*-C(CH_3)$_3$), 35.2 (s, *o*-C(CH_3)$_3$ + *p*-*C*(CH_3)$_3$), 40.0 (s, *o*-*C*(CH_3)$_3$), 125.8 (s, *m*-C), 152.8 (s, *p*-C), 157.8 (s, *o*-C), *ipso*-C not observed. Raman (785 nm, 30 s, 4 scans, cm^{-1}): $\tilde{\nu}$ = 3064 (1), 2976 (1), 2960 (2), 2928 (2), 2904 (3), 2869 (1), 2786 (1), 2717 (1), 1593 (3), 1582 (2), 1536 (1), 1477 (2), 1465 (3), 1443 (2), 1393 (2), 1362 (1), 1284 (3), 1250 (2), 1208 (2), 1176 (3), 1031 (3), 1025 (3), 1016 (2), 920

(2), 891 (1), 819 (5), 772 (1), 747 (1), 638 (1), 613 (3), 597 (9), 561 (4), 502 (1), 497 (1), 480 (2), 470 (1), 451 (2), 436 (2), 406 (3), 395 (4), 385 (3), 366 (4), 343 (10), 294 (2), 260 (4). MS (CI positive, *iso*-butane, m/z): 615 $[M - GaCl_3]^+$, 277 $[Mes^*PH]^+$.

The crystals described above are suitable for single crystal X-ray diffraction.

4.3.2 Reaction of *exo*-*exo*-Mes*P$_4$Mes* (5a) with GaCl$_3$



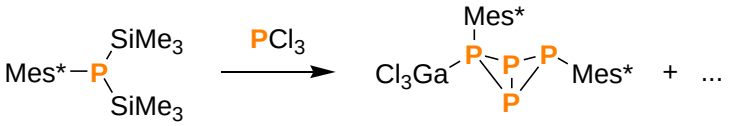
A solution of $GaCl_3$ (10 mg, 0.057 mmol) in CH_2Cl_2 (1 mL) is added to a solution of *exo*-*exo*-Mes*P_4Mes* (35 mg, 0.057 mmol) in CH_2Cl_2 (2 mL). The mixture is stirred for ten minutes and the solvent is removed *in vacuo*, yielding an analytically pure powder of *exo*-*exo*-Mes*P_4Mes*·$GaCl_3$. Yield: 30 mg (0.038 mmol, 67 %).

Mp. 100 °C (decomposition). CHN calc. (found) in %: C 54.68 (53.97), H 7.39 (6.89). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz): δ = −246.4 (t, $^1J_{AX}(^{31}P,^{31}P)$ = −198 Hz, 2 P, $P_{bridgehead}$), −97.1 (broad, 2 P, *P*Mes*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz, −80 °C): δ = −248.1 (dd, $^1J_{AM}(^{31}P,^{31}P)$ = −182 Hz, $^1J_{AX}(^{31}P,^{31}P)$ = −216 Hz, 2 P, $P_{bridgehead}$), −114.0 (dt, $^1J_{AM}(^{31}P,^{31}P)$ = −182 Hz, $^2J_{MX}(^{31}P,^{31}P)$ = +225 Hz, 1 P, *P*Mes*), −74.8 (dt, $^1J_{AX}(^{31}P,^{31}P)$ = −216 Hz, $^2J_{MX}(^{31}P,^{31}P)$ = +225 Hz, 1 P, *P*(Ga)Mes*). ^1H NMR (CD_2Cl_2, 300.1 MHz): δ = 1.20 (s, 18 H, Mes*, *p*-*t*-Bu), 1.68 (s, 36 H, *o*-*t*-Bu), 7.24 (s, 4 H, *m*-H). ^1H NMR (CD_2Cl_2, 300.1 MHz, −80 °C): δ = 1.09 (s, 9 H, Mes*, *p*-*t*-Bu), 1.13 (s, 9 H, Mes*, *p*-*t*-Bu), 1.59 (s, 18 H, *o*-*t*-Bu), 1.61 (s, 18 H, *o*-*t*-Bu), 7.08 (s, 2 H, *m*-H), 7.24 (s, 2 H, *m*-H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz): δ = 31.2 (s, *p*-C(CH_3)$_3$), 35.2 (s, *o*-C(CH_3)$_3$ + *p*-C(CH_3)$_3$), 40.0 (s, *o*-*C*(CH_3)$_3$), 125.8 (s, *m*-C), 152.8 (s, *p*-C), 157.8 (s, *o*-C), *ipso*-C not observed. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz, −80 °C): δ = 30.3 (broad, *p*-C(CH_3)$_3$), 30.5 (broad, *p*-C(CH_3)$_3$), 34.2 (broad, 2x *o*-C(CH_3)$_3$ + 2x *p*-C(CH_3)$_3$), 39.2 (broad, 2x *o*-*C*(CH_3)$_3$), 124.4 (s, *m*-C), 125.7 (m, *m*-C), 150.1 (s, *p*-C), 153.2 (s, *p*-C), 155.6 (s, *o*-C), 157.4 (s, *o*-C), *ipso*-C not observed. IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3074 (vw), 2958 (vs), 2902 (m), 2866 (m), 1587 (m), 1525 (w), 1475 (s), 1462 (s), 1443 (m), 1392 (s), 1362 (vs), 1279 (w), 1246 (s), 1209 (m), 1201 (m), 1184

(m), 1126 (s), 1057 (m), 1026 (m), 985 (m), 933 (m), 924 (m), 897 (s), 872 (s), 839 (m), 744 (s), 714 (s), 648 (m), 638 (m), 609 (s), 590 (s), 580 (s), 544 (s). Raman (785 nm, 30 s, 4 scans, cm^{-1}): $\tilde{\nu}$ = 3064 (1), 2976 (1), 2960 (2), 2928 (2), 2904 (3), 2869 (1), 2786 (1), 2717 (1), 1593 (3), 1582 (2), 1536 (1), 1477 (2), 1465 (3), 1443 (2), 1393 (2), 1362 (1), 1284 (3), 1250 (2), 1208 (2), 1176 (3), 1031 (3), 1025 (3), 1016 (2), 920 (2), 891 (1), 819 (5), 772 (1), 747 (1), 638 (1), 613 (3), 597 (9), 561 (4), 502 (1), 497 (1), 480 (2), 470 (1), 451 (2), 436 (2), 406 (3), 395 (4), 385 (3), 366 (4), 343 (10), 294 (2), 260 (4). MS (CI positive, *iso*-butane, m/z): 615 $[M - GaCl_3]^+$, 277 $[Mes^*PH]^+$.

4.4 Synthesis of *endo-exo*-Mes*P$_4$Mes*·GaCl$_3$ (5b·GaCl$_3$)

4.4.1 Reaction of Mes*P(SiMe$_3$)$_2$ (34) with PCl$_3$ and GaCl$_3$



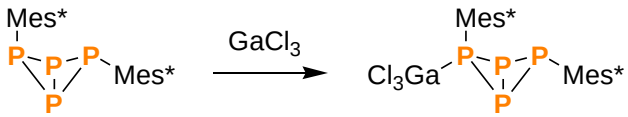
A solution of PCl_3 (131 mg, 0.95 mmol) in CH_2Cl_2 (1 mL) and a solution of $GaCl_3$ (168 mg, 0.95 mmol) in CH_2Cl_2/toluene (1:1, 2 mL) are added consecutively to a stirred solution of Mes*P(SiMe$_3$)$_2$ (403 mg, 0.95 mmol) in CH_2Cl_2 (5 mL) at −80 °C. The mixture is warmed to −50 °C, whereupon the solution turns red. After further stirring at −50 °C for two hours, the solution is concentrated and subsequently warmed to ambient temperature overnight, resulting in crystallization of *endo-exo*-Mes*P$_4$Mes*·GaCl$_3$ (CH_2Cl_2 solvate) in colourless, block-shaped crystals. The solvent is removed by drying *in vacuo*. Yield: 50 mg (0.08 mmol, 9 %).

Mp. 50–60 °C (decomposition). CHN calc. (found) in %: C 54.68 (54.15), H 7.39 (7.15). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz): δ = −224.5 (dd, $^1J_{AM}(^{31}P,^{31}P)$ = −192 Hz, $^1J_{AX}(^{31}P,^{31}P)$ = −249 Hz, 2 P, $P_{bridgehead}$), −114.5 (td, $^1J_{AM}(^{31}P,^{31}P)$ = −192 Hz, $^1J_{MX}(^{31}P,^{31}P)$ = +24 Hz, 1 P, P_{exo}), −50.0 (broad, 1 P, P_{endo}). ^1H NMR (CD_2Cl_2, 300.1 MHz): δ = 1.21 (s, 9 H, *exo*-Mes*, *p*-*t*-Bu), 1.33 (s, 9 H, *endo*-Mes*, *p*-*t*-Bu), 1.49 (s, 18 H, *exo*-Mes*, *o*-*t*-Bu), 1.70 (m 18 H, *endo*-Mes*, *o*-*t*-Bu), 7.11 (d, $J(^1H,^{31}P)$ = 1.9 Hz, 2 H, *exo*-Mes*, *m*-H), 7.32 (d, $J(^1H,^{31}P)$ =

5.0 Hz, 2 H, *endo*-Mes*, *m*-H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz): δ = 31.2 (s, *p*-C(CH_3)$_3$), 31.3 (s, *p*-C(CH_3)$_3$), 34.5 (m, *o*-C(CH_3)$_3$), 34.7 (m, *o*-C(CH_3)$_3$), 34.9 (s, *p*-C(CH_3)$_3$), 35.5 (m, *p*-C(CH_3)$_3$), 39.7 (m, *o*-C(CH_3)$_3$), 39.8 (m, *o*-C(CH_3)$_3$), 122.6 (m, *m*-C), 124.9 (s, *m*-C), 151.2 (m, *p*-C), 156.3 (m, *p*-C), 164.8 (m, *o*-C), 165.9 (m, *o*-C), *ipso*-Cs not observed. Raman (633 nm, 10 s, 4 scans, cm^{-1}): $\tilde{\nu}$ = 3055 (2), 3035 (1), 2973 (5), 2966 (6), 2905 (7), 2866 (3), 2782 (1), 2714 (1), 1603 (1), 1582 (4), 1525 (1), 1463 (2), 1441 (2), 1394 (1), 1362 (1), 1284 (2), 1208 (2), 1173 (1), 1133 (2), 1029 (3), 1011 (2), 1002 (3), 924 (1), 818 (3), 784 (2), 741 (2), 618 (3), 567 (7), 518 (1), 508 (1), 438 (3), 407 (2), 391 (2), 372 (2), 348 (10), 302 (1), 258 (3), 213 (1). MS (CI positive, *iso*-butane, m/z): 615 [M $-GaCl_3]^+$, 557 [M $-t$-Bu]$^+$, 277 [Mes*PH]$^+$.

Crystals suitable for single crystal X-ray diffraction can be obtained from saturated CH_2Cl_2 or toluene solution at ambient temperature.

4.4.2 Reaction of *endo-exo*-Mes*P$_4$Mes* (5b) with $GaCl_3$



A solution of $GaCl_3$ (15 mg, 0.085 mmol) in CH_2Cl_2 (1 mL) is added to a solution of *endo-exo*-Mes*P$_4$Mes* (52 mg, 0.085 mmol) in CH_2Cl_2 (2 mL). The mixture is stirred for ten minutes and the solvent is removed *in vacuo*, yielding an analytically pure powder of *endo-exo*-Mes*P$_4$Mes*·$GaCl_3$. Yield: 51 mg (0.064 mmol, 75 %).

Mp. 50–60 °C (decomposition). CHN calc. (found) in %: C 54.68 (54.23), H 7.39 (7.50). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz): δ = −224.5 (dd, $^1J_{AM}(^{31}P,^{31}P)$ = −192 Hz, $^1J_{AX}(^{31}P,^{31}P)$ = −249 Hz, 2 P, $P_{bridgehead}$), −114.5 (td, $^1J_{AM}(^{31}P,^{31}P)$ = −192 Hz, $^1J_{MX}(^{31}P,^{31}P)$ = +24 Hz, 1 P, P_{exo}), −50.0 (broad, 1 P, P_{endo}). ^1H NMR (CD_2Cl_2, 300.1 MHz): δ = 1.21 (s, 9 H, *exo*-Mes*, *p*-*t*-Bu), 1.33 (s, 9 H, *endo*-Mes*, *p*-*t*-Bu), 1.49 (s, 18 H, *exo*-Mes*, *o*-*t*-Bu), 1.70 (m 18 H, *endo*-Mes*, *o*-*t*-Bu), 7.11 (d, $J(^1H,^{31}P)$ = 1.9 Hz, 2 H, *exo*-Mes*, *m*-H), 7.32 (d, $J(^1H,^{31}P)$ = 5.0 Hz, 2 H, *endo*-Mes*, *m*-H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz): δ = 31.2 (s, *p*-C(CH_3)$_3$), 31.3 (s, *p*-C(CH_3)$_3$), 34.5 (m, *o*-C(CH_3)$_3$), 34.7 (m, *o*-C(CH_3)$_3$), 34.9 (s, *p*-C(CH_3)$_3$), 35.5 (m,

p-*C*(CH_3)$_3$), 39.7 (m, *o*-*C*(CH_3)$_3$), 39.8 (m, *o*-*C*(CH_3)$_3$), 122.6 (m, *m*-C), 124.9 (s, *m*-C), 151.2 (m, *p*-C), 156.3 (m, *p*-C), 164.8 (m, *o*-C), 165.9 (m, *o*-C), *ipso*-Cs not observed. IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3064 (w), 2960 (vs), 2902 (m), 2866 (m), 1585 (s), 1475 (s), 1462 (s), 1444 (m), 1392 (s), 1362 (vs), 1240 (s), 1211 (m), 1186 (m), 1126 (s), 1026 (m), 924 (m), 897 (m), 879 (s), 771 (m), 741 (s), 714 (m), 648 (m), 636 (m), 619 (s), 588 (s), 577 (m), 540 (m). Raman (633 nm, 10 s, 4 scans, cm^{-1}): $\tilde{\nu}$ = 3055 (2), 3035 (1), 2973 (5), 2966 (6), 2905 (7), 2866 (3), 2782 (1), 2714 (1), 1603 (1), 1582 (4), 1525 (1), 1463 (2), 1441 (2), 1394 (1), 1362 (1), 1284 (2), 1208 (2), 1173 (1), 1133 (2), 1029 (3), 1011 (2), 1002 (3), 924 (1), 818 (3), 784 (2), 741 (2), 618 (3), 567 (7), 518 (1), 508 (1), 438 (3), 407 (2), 391 (2), 372 (2), 348 (10), 302 (1), 258 (3), 213 (1). MS (CI positive, *iso*-butane, m/z): MS (CI positive, *iso*-butane, m/z): 615 [M $-GaCl_3]^+$, 557 [M $-t$-Bu]$^+$, 277 [Mes*PH]$^+$.

5 Additional spectroscopic data

5.1 Static NMR data

Table S12. ^{31}P NMR data of **5a** at ambient temperature (A_2X_2 spin system). Calculated values (GIAO method) are given in brackets.

X	***δ* [ppm]**	***J* [Hz]** P_A-X
P_A	−273.2 (−271.5)	–
P_X	−128.3 (−138.0)	−177 (−145)

Table S13. ^{31}P NMR data of **5a**·$GaCl_3$ at −80 °C (A_2MX spin system). Calculated values (GIAO method) are given in brackets.

X	***δ* [ppm]**	***J* [Hz]**	
		P_A-X	P_M-X
P_A	−248.1 (−245.0)	–	–
P_M	−114.0 (−138.5)	−182 (−154)	–
P_X	−74.8 (−106.9)	−216 (−178)	+225 (+192)

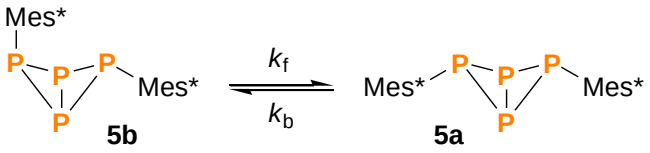
Table S14. ^{31}P NMR data of **5b** at ambient temperature (A_2MX spin system). Calculated values (GIAO method) are given in brackets.

X	***δ* [ppm]**	***J* [Hz]**	
		P_A-X	P_M-X
P_A	−220.4 (−217.8)	–	–
P_M	–94.8 (−100.2)	−213 (−169)	–
P_X	−54.7 (−68.0)	−234 (−195)	−27 (−49)

Table S15. ^{31}P NMR data of **5b**·$GaCl_3$ at ambient temperature (A_2MX spin system). Calculated values (GIAO method) are given in brackets.

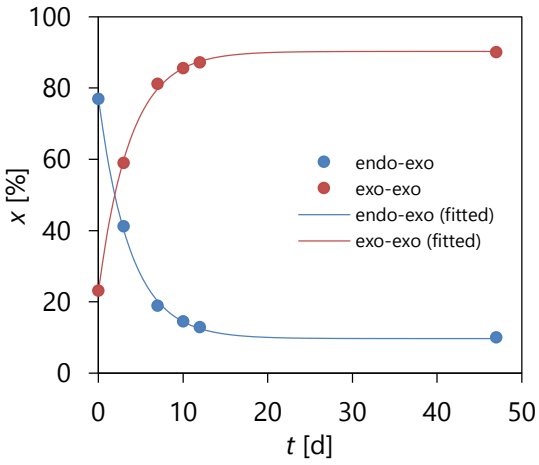
X	***δ* [ppm]**	***J* [Hz]**	
		P_A-X	P_M-X
P_A	−224.5 (−225.5)	–	–
P_M	−114.5 (−127.1)	−192 (−159)	–
P_X	−50.0 (−61.4)	−249 (−222)	+24 (+218)

5.2 Equilibrium between 5a and 5b



In an NMR tube equipped with a young valve, a mixture of *exo-exo* and *endo-exo*-Mes*P_4Mes* (25 mg, 0.04 mmol, isomeric ratio *ca.* 1:4) was dissolved in THF (0.5 mL) and C_6D_6 (0.1 mL). The solution was degassed by three freeze-pump-thaw cycles. Afterwards, the sample was heated to 75 °C in a drying oven for 50 days. NMR spectra were recorded every few days at ambient temperature, making the approximation that the reaction was paused during these periods (Figure S1).

Figure S1. Mole fraction of **5a** and **5b** *versus* time.



The mathematical model was adapted from Levine's "Physical Chemistry".[10] Let $[\mathrm{A}]$ and $[\mathrm{B}]$ be the concentrations of substances A and B, respectively. For a reversible first order reaction, A ⇌ B, the reaction rate is defined as

$$\frac{d[\mathrm{A}]}{dt} = -k_\mathrm{f}[\mathrm{A}] + k_\mathrm{b}[\mathrm{B}] \tag{1a}$$

$$\frac{d[\mathrm{B}]}{dt} = k_\mathrm{f}[\mathrm{A}] - k_\mathrm{b}[\mathrm{B}] \tag{1b}$$

where k_f is the rate constant of the forward and k_b the rate constant of the backward reaction, respectively. If $[\mathrm{A}]_0$ and $[\mathrm{B}]_0$ denote the initial concentrations at $t = 0$, it follows that

$$[\mathrm{A}]_0 + [\mathrm{B}]_0 = [\mathrm{A}] + [\mathrm{B}] \qquad \text{or} \qquad [\mathrm{B}] = [\mathrm{A}]_0 + [\mathrm{B}]_0 - [\mathrm{A}] \tag{2}$$

according to the conservation of mass. Therefore, the rate of the reaction can be expressed as

$$\frac{d[\mathrm{A}]}{dt} = -k_\mathrm{f}[\mathrm{A}] + k_\mathrm{b}([\mathrm{A}]_0 + [\mathrm{B}]_0 - [\mathrm{A}]) = -(k_\mathrm{f} + k_\mathrm{b})[\mathrm{A}] + k_\mathrm{b}([\mathrm{A}]_0 + [\mathrm{B}]_0) \tag{3}$$

When the system reaches equilibrium ($t \to \infty$), the concentrations of A and B remain constant, so the reaction rate becomes zero. Therefore

$$0 = -(k_\mathrm{f} + k_\mathrm{b})[\mathrm{A}]_\infty + k_\mathrm{b}([\mathrm{A}]_0 + [\mathrm{B}]_0)$$

$$k_\mathrm{b}[\mathrm{B}]_0 = (k_\mathrm{f} + k_\mathrm{b})[\mathrm{A}]_\infty - k_\mathrm{b}[\mathrm{A}]_0 \tag{4}$$

Using equation 4 in equation 3 gives

$$\frac{d[\mathrm{A}]}{dt} = -(k_\mathrm{f} + k_\mathrm{b})([\mathrm{A}] - [\mathrm{A}]_\infty) \tag{5}$$

Integration of equation 5 gives

$$\int_{[A]_0}^{[\mathrm{A}]} ([\mathrm{A}] - [\mathrm{A}]_\infty)\, d[\mathrm{A}] = -(k_\mathrm{f} + k_\mathrm{b}) \int_0^t dt$$

$$\ln\left(\frac{[\mathrm{A}] - [\mathrm{A}]_\infty}{[\mathrm{A}]_0 - [\mathrm{A}]_\infty}\right) = -(k_\mathrm{f} + k_\mathrm{b})t \tag{6}$$

The concentration at equilibrium $[A]_\infty$ can be calculated from equation (4):

$$[A]_\infty = \frac{k_b}{k_f + k_b}([A]_0 + [B]_0) \tag{7}$$

Therefore, the concentration of [A] at any time t is given by

$$[A] = [A]_\infty + \left([A]_0 - [A]_\infty\right) e^{-(k_f + k_b)t} \tag{8a}$$

$$[A] = \frac{k_b}{k_f + k_b}([A]_0 + [B]_0) + \left([A]_0 - \frac{k_b}{k_f + k_b}([A]_0 + [B]_0)\right) e^{-(k_f + k_b)t} \tag{8b}$$

Using the definition of concentration ($c_i = n_i/V$) and mole fraction ($x_i = n_i/n$), equation 6 can be written as

$$\ln\left(\frac{\frac{x_A n}{V} - \frac{x_{A,\infty} n}{V}}{\frac{x_{A,0} n}{V} - \frac{x_{A,\infty} n}{V}}\right) = \ln\left(\frac{x_A - x_{A,\infty}}{x_{A,0} - x_{A,\infty}}\right) = -(k_f + k_b)t \tag{9}$$

In a two component system, $x_A + x_B = 1$. It follows that

$$x_A = \frac{k_b}{k_f + k_b} + \left(x_{A,0} - \frac{k_b}{k_f + k_b}\right) e^{-(k_f + k_b)t} \tag{10}$$

Hence, knowledge of the mole fractions of suffices to derive the rate constants. This is convenient as the mole fractions can be derived from NMR integrals without knowledge of further quantities.

Table S16. Mole fractions derived from NMR integrals.

t [d]	0	3	7	10	12	47
x_A	0.769	0.411	0.189	0.145	0.129	0.100
x_B	0.231	0.589	0.811	0.855	0.871	0.900

x_A = *endo*-*exo*-isomer (**5b**), x_B = *exo*-*exo*-isomer (**5a**)

Using a fitting procedure, the square differences $\left(x_{A,exptl} - x_{A,calcd}\right)^2$ were minimized by alteration of the parameters k_f, k_b and $x_{A,0}$ from equation 10. Hence, the rate constants could be derived:

$$k_{\mathrm{f}} = 2.77(11) \times 10^{-6}\ \mathrm{s}^{-1} \tag{11a}$$

$$k_{\mathrm{b}} = 0.30(3) \times 10^{-6}\ \mathrm{s}^{-1} \tag{11b}$$

The equilibrium constant $K = k_{\mathrm{f}}/k_{\mathrm{b}}$ amounts to 9.3(1.4). The Gibbs energy of the reaction is

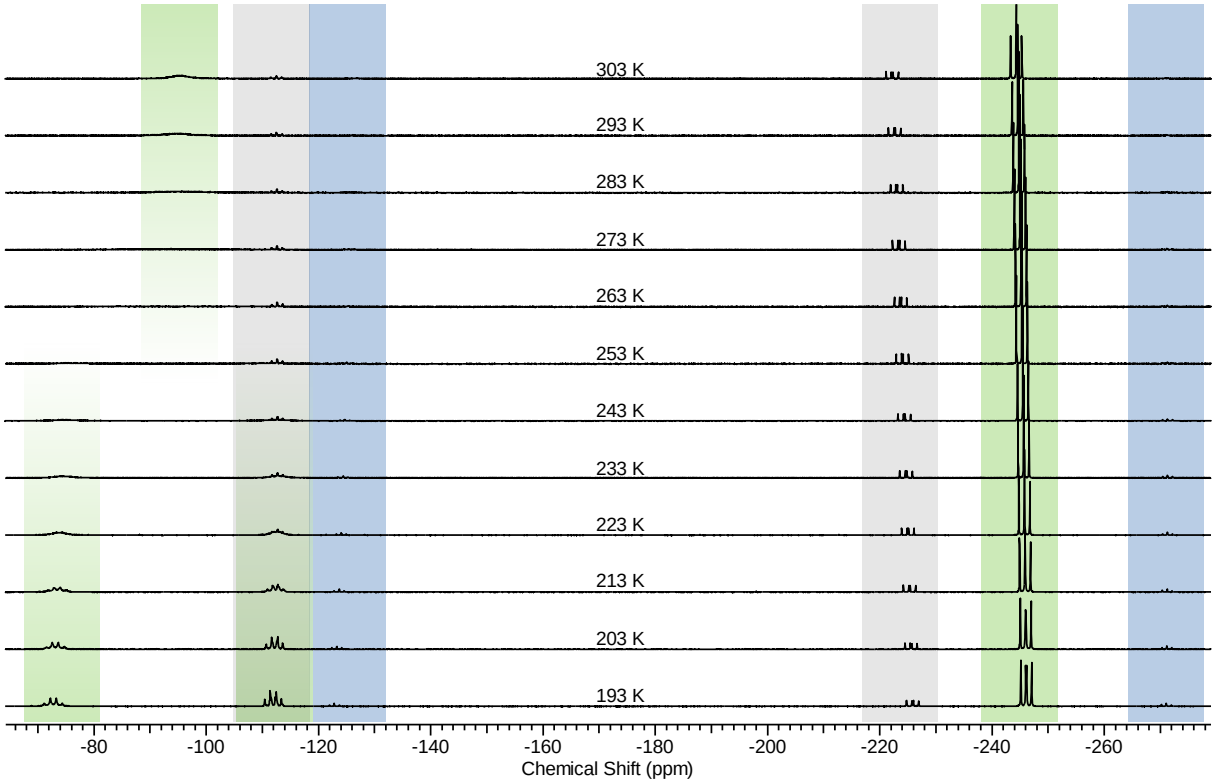
$$\Delta_{\mathrm{R}}G = -RT \ln K = -6.4(3)\ \mathrm{kJ/mol} \tag{12}$$

Accordingly, the *exo*-*exo*-isomer **5a** is energetically favoured by −6.4(3) kJ/mol.

5.3 Dynamic intramolecular exchange of $GaCl_3$ in 5a·$GaCl_3$

In an NMR tube, *exo*-*exo*-Mes*P_4Mes* (40 mg, 0.065 mmol) and $GaCl_3$ (11 mg, 0.062 mmol, 0.95 eq.) were combined and dissolved in CD_2Cl_2 (0.5 mL). The sample was measured in a temperature range from −80 to +30 °C in 10 K steps (Figure S2).

Figure S2. Variable temperature ^{31}P NMR spectrum of **5a**·$GaCl_3$ (green). Further species: free phosphane **5a** (blue) and *endo*-*exo* isomer **5b**·$GaCl_3$ (grey, impurity).



$GaCl_3$ was added in sub-stoichiometric amounts, so the non-coordinating bicyclic phosphane could be detected in the NMR spectrum. In this vein, it was possible to determine that the dissociation process is independent of the intramolecular exchange. In pure Mes*P_4Mes*·$GaCl_3$ (either isomer), the dissociation equilibrium is basically shifted completely to the side of the adduct, so the free phosphane is not detectable. Hence, both processes would not be clearly distinguishable.

The rate constants at each temperature were derived using the full lineshape iteration feature of gNMR.[5] The static line width was evaluated at slow exchange (193 K) and was estimated to be 17 Hz (A, M part) or 60 Hz (X part) without dynamic broadening. The chemical shifts and coupling constants were freely refined at that temperature. For all other temperatures, the coupling constants (Table S13) as well as the shift difference between M and X parts (7930 Hz) were fixed.

Table S17. Rate constants derived by full lineshape analysis.

T [K]	193	203	213	223	233	243
k [1/s]	1.35×10^1	5.25×10^1	2.10×10^2	6.10×10^2	1.34×10^3	2.88×10^3
T [K]	253	263	273[a]	283	293	303
k [1/s]	6.65×10^3	1.42×10^4	2.79×10^4	5.91×10^4	1.08×10^5	1.87×10^5

[a] The chemical shifts of M and X part had to be fixed for convergence.

The Eyring equation relates the rate constant to the Gibbs energy of activation:

$$k = \kappa \frac{k_B T}{h} \exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right) \tag{13}$$

Using a least squares fitting procedure, the parameters $\Delta G^{\ddagger}$ (39.5 kJ/mol) and κ (0.19) could be derived (Figure S3, left). Linearization of equation 13 gives

$$\ln\left(\frac{k}{T}\right) = -\frac{\Delta H^{\ddagger}}{R} \cdot \frac{1}{T} + \frac{\Delta S^{\ddagger}}{R} + \ln\left(\kappa \frac{k_B}{h}\right) \tag{14}$$

which is obtained using the Gibbs-Helmholtz equation:

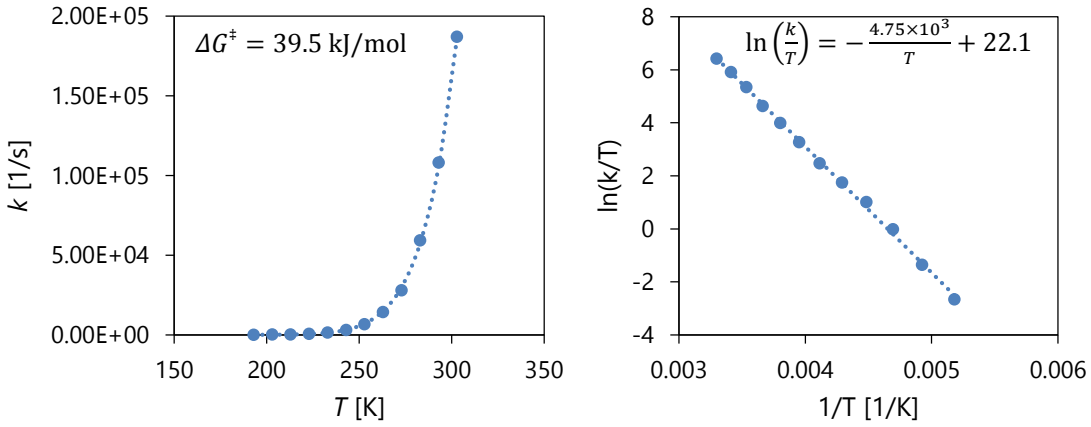
$$\Delta G = \Delta H - T\Delta S \tag{15}$$

Usually, κ is near unity, so $\ln(\kappa\, k_B/h) \approx \ln(k_B/h)$. Therefore, equation 16 is commonly used to evaluate the so-called Eyring plot ($\ln(k/T)$ *vs.* $1/T$).

$$\ln\left(\frac{k}{T}\right) = -\frac{\Delta H^{\ddagger}}{R}\cdot\frac{1}{T} + \frac{\Delta S^{\ddagger}}{R} + \ln\left(\frac{k_B}{h}\right) \tag{16}$$

The enthalpy and entropy of activation were determined to be 39.5(4) kJ/mol and −0.20(2) J/(mol K), respectively (Figure S3, right). The resulting Gibbs energy of activation (39.5(4) kJ/mol) agrees with the result obtained by least squares fitting.

Figure S3. Left: Temperature *versus* rate constant. Right: Eyring plot.



5.4 Intermolecular exchange of $GaCl_3$ in 5a·$GaCl_3$ and 5b·$GaCl_3$

In an NMR tube, *exo*-*exo*-Mes*P_4Mes* (25 mg, 0.041 mmol) and $GaCl_3$ (3.6 mg, 0.020 mmol, 0.5 eq.) were combined and dissolved in CD_2Cl_2 (0.5 mL). The sample was measured in a temperature range from −80 to +30 °C in 10 K steps. Broadening of the NMR signals of the free phosphane was detectable above 253 K (Figure S4). The rates of the intramolecular exchange and intermolecular exchange were fitted independently; the derived activation barrier of the former amounted to 39.5(4) kJ/mol (equivalent to the previous experiment), the latter exhibited an activation barrier of 30.9(1.6) kJ/mol (Figure S6, left).

Figure S4. Variable temperature ^{31}P NMR spectrum of a mixture of **5a**·$GaCl_3$ (green) and free phosphane **5a** (blue).

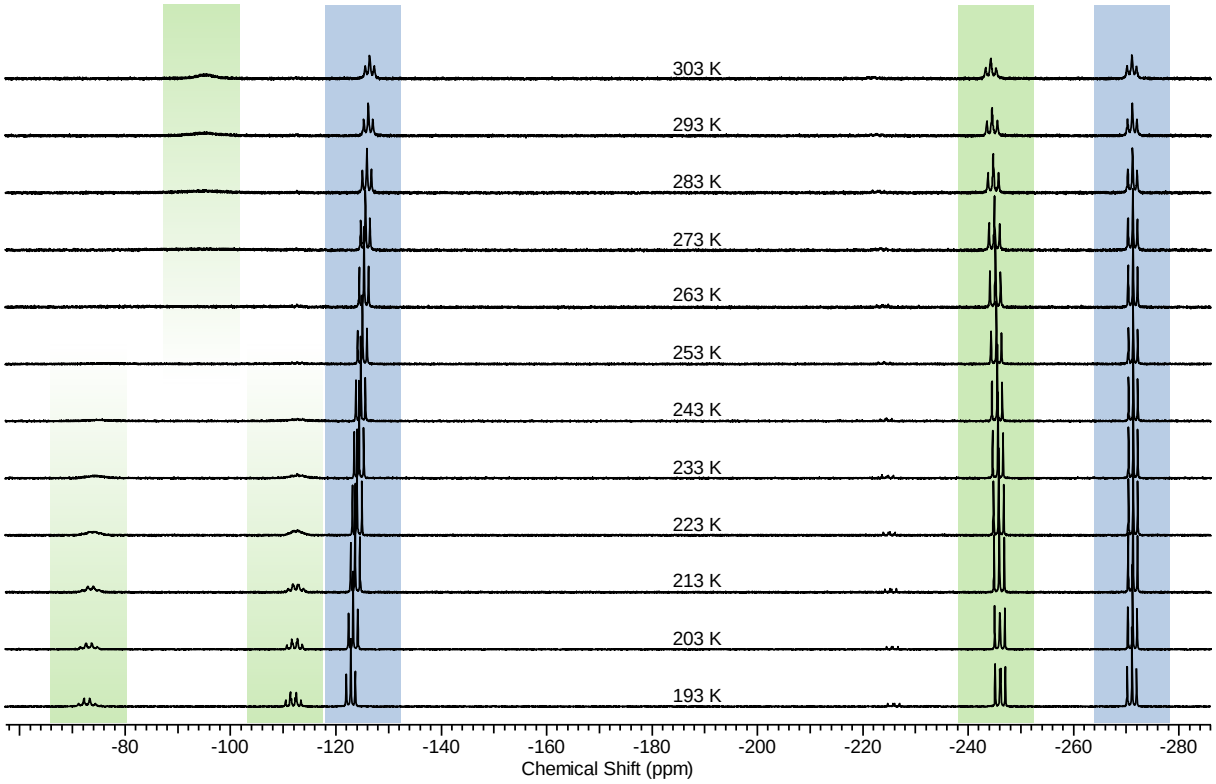
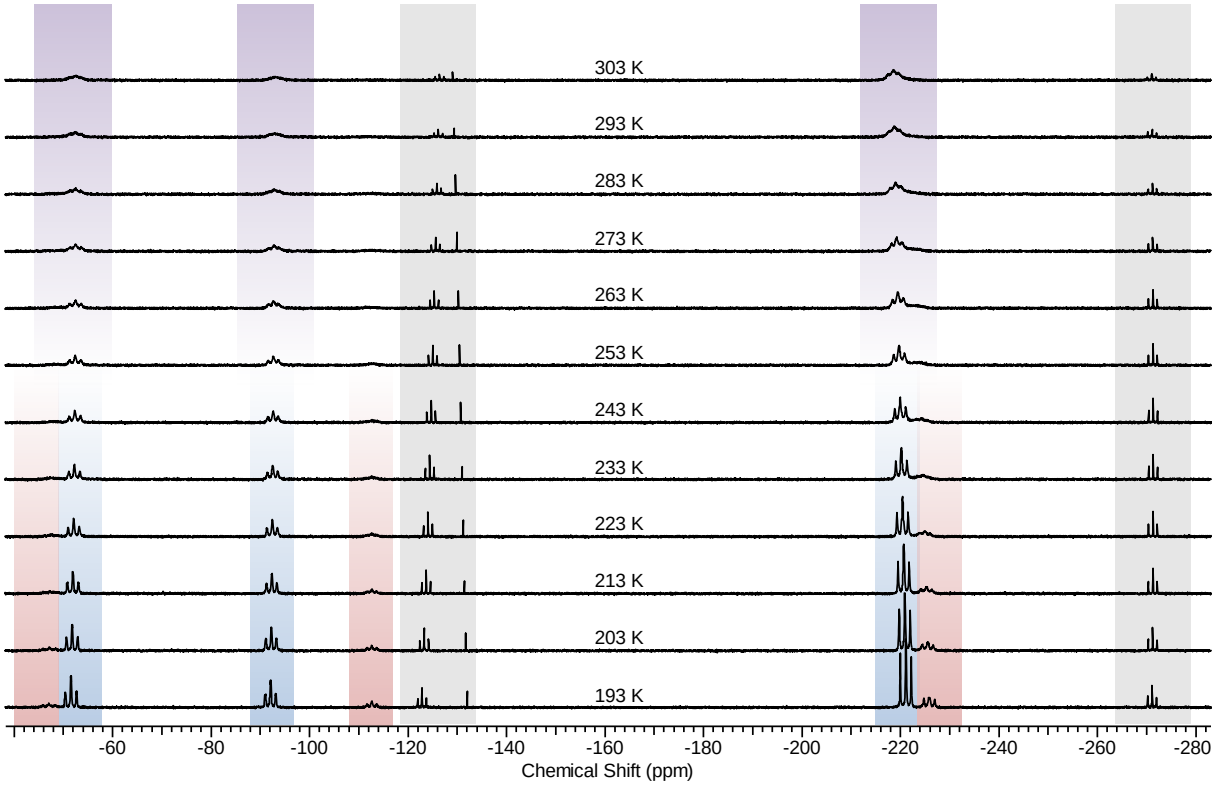
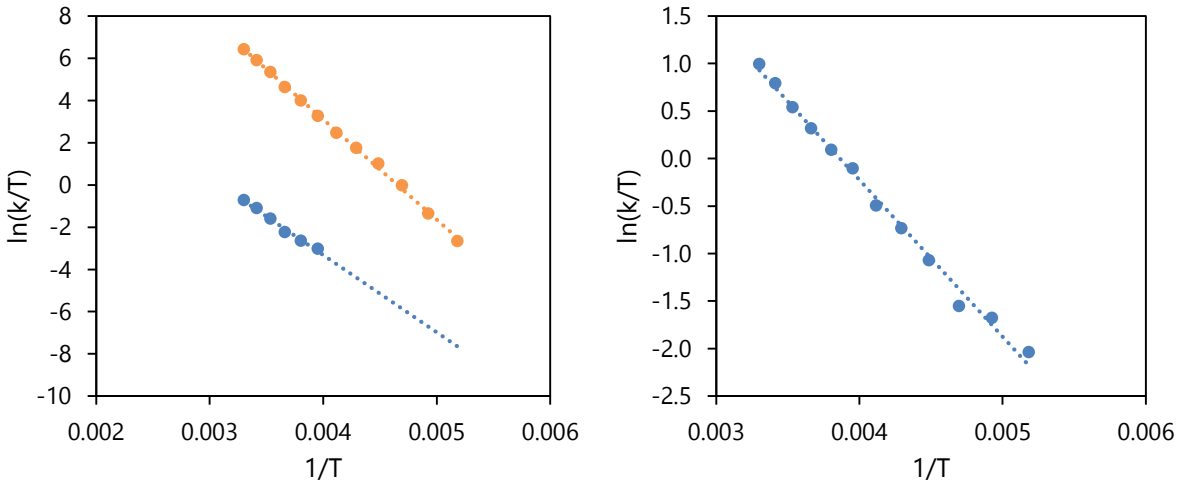


Figure S5. Variable temperature ^{31}P NMR spectrum of a mixture of **5b**·$GaCl_3$ (red) and free phosphane **5b** (blue; violet for fast exchange). Further species: **5a** (grey, impurity).

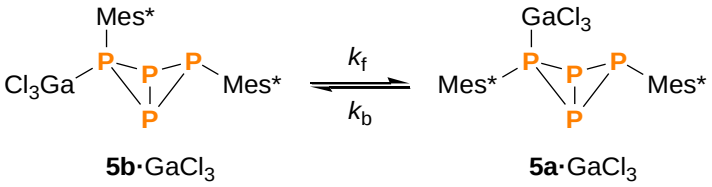


In a second experiment, *endo-exo*-Mes*P_4Mes* (20 mg, 0.033 mmol) and $GaCl_3$ (1.3 mg, 0.007 mmol, 0.22 eq.) were combined and dissolved in CD_2Cl_2 (0.5 mL). The sample was again measured in a temperature range from −80 to +30 °C in 10 K steps (Figure S5). Exchange between free phosphane and adduct was detectable even at −80 °C. The activation barrier was determined to be 14.3(3) kJ/mol (Figure S6, right).

Figure S6. Eyring plots of the intermolecular exchange reactions (blue). Left: *exo-exo* isomer (intramolecular exchange in yellow). Right: *endo-exo* isomer.



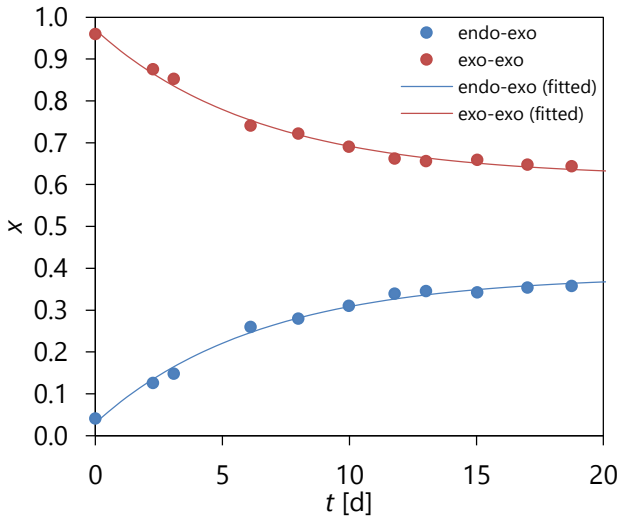
5.5 Equilibrium between 5a·$GaCl_3$ and 5b·$GaCl_3$



5b·$GaCl_3$ **5a**·$GaCl_3$

In an NMR tube equipped with a young valve, *exo-exo*-Mes*P_4Mes* (40 mg, 0.05 mmol) was dissolved in CD_2Cl_2 (0.5 mL). The sample was kept at ambient temperature for several days. NMR spectra were recorded every few days at ambient temperature.

Figure S7. Mole fraction of **5a**·$GaCl_3$ and **5b**·$GaCl_3$ *versus* time.



Using the procedure described above, the rate constants were derived ($1.11(11) \times 10^{-6}\ s^{-1}$ and $0.69(4) \times 10^{-6}\ s^{-1}$). Hence, the equilibrium constant is 1.6(2) and the Gibbs energy of reaction amounts to −1.2(4) kJ/mol.

6 Computational Details

All computations were carried out using the Gaussian09 program package[11] and the standalone version of NBO 6.0.[12–15] The Kohn-Sham wave function was calculated using the hybrid DFT functional PBE0[16–18] and a 6-31g(d,p) basis[19–28] (NMR, NBO data) or a cc-pVDZ basis at H and C, an aug-cc-pVDZ basis at P and Cl,[29–34] as well as an energy consistent pseudopotential of the Stuttgart/Cologne group for Ga (ECP10MDF)[35] in combination with a suitable aug-cc-pVDZ basis (thermodynamic data).[36] All structures were fully optimized and confirmed as minima by frequency analyses. Partial charges were determined by Natural Population analysis using the NBO program. Chemical shifts and coupling constants were derived by the GIAO method.[37–41] The calculated absolute shifts ($\sigma_{calc,X}$) were referenced to the experimental absolute shift of 85 % H_3PO_4 in the gas phase ($\sigma_{ref,1}$ = 328.35 ppm),[42] using PH_3 ($\sigma_{ref,2}$ = 594.45 ppm) as a secondary standard:[43]

$$\delta_{calc,X} = (\sigma_{ref,1} - \sigma_{ref,2}) - (\sigma_{calc,X} - \sigma_{calc,PH_3})$$
$$= \sigma_{calc,PH_3} - \sigma_{calc,X} - 266.1 \text{ ppm}$$

At the PBE0/6-31G(d,p) level of theory, σ_{calc,PH_3} amounts to +604.92 ppm. It should be emphasized that all computations were carried out for single, isolated gas phase molecules. There may well be significant differences between gas phase, solution and solid state data.

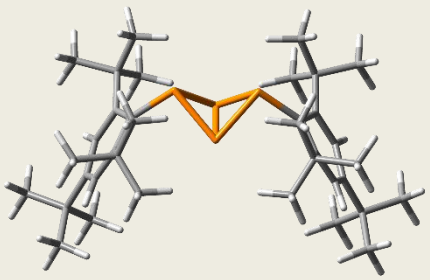
6.1 PH_3 (NMR standard)

6.1.1 Optimized structure

Atom	x	y	z
P	0.00000	0.00000	0.12862
H	0.00000	1.19440	-0.64311
H	1.03438	-0.59720	-0.64311
H	-1.03438	-0.59720	-0.64311

6.2 *exo-exo*-Mes*P_4Mes* (5a)

6.2.1 Optimized structure (PBE0/6-31g(d,p))

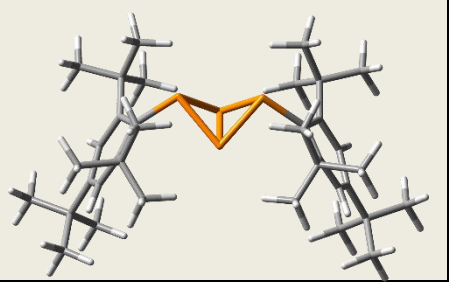


Atom	x	y	z
C	-5.30321	1.18628	3.56222
C	5.30257	1.18622	3.56253
C	-2.61468	3.65207	0.00450
C	2.61473	3.65207	0.00461
C	-5.08665	-0.18063	2.90749
C	-4.86212	3.15556	-0.98232
C	-4.19764	-1.02307	3.83668
C	4.19782	-1.02357	3.83659
C	-6.45540	-0.86351	2.75343
C	5.08653	-0.18065	2.90755
C	-4.12014	1.14698	0.93284
C	-3.39499	2.67662	-0.89027
C	4.86216	3.15557	-0.98226
C	4.12011	1.14697	0.93289
C	6.45554	-0.86300	2.75339
C	-4.41074	-0.06713	1.54025
C	3.39502	2.67665	-0.89021
C	4.41065	-0.06714	1.54030
C	-3.42725	1.25110	-0.28005
C	-2.85242	2.77861	-2.32102
C	3.42727	1.25111	-0.28003
C	2.85243	2.77868	-2.32095
C	-4.11558	-1.21384	0.80634
C	4.11551	-1.21384	0.80637
C	-2.92610	0.05883	-0.86607
C	2.92614	0.05885	-0.86610
C	-3.42660	-1.19317	-0.40694
C	3.42662	-1.19316	-0.40696
C	-3.40041	-2.54349	-1.17050
C	-4.86951	-3.00189	-1.31598
C	3.40046	-2.54348	-1.17052
C	2.62621	-3.61464	-0.38721
C	-2.62613	-3.61463	-0.38717
C	4.86958	-3.00184	-1.31599
C	-2.85550	-2.48881	-2.60249
C	2.85557	-2.48882	-2.60252
H	-5.75434	1.05362	4.55080
H	-4.35917	1.72451	3.69754
H	-5.97889	1.81792	2.97577
H	5.75345	1.05355	4.55121
H	4.35836	1.72420	3.69764
H	-3.02560	3.69265	1.01763
H	5.97826	1.81812	2.97635
H	-2.66108	4.66355	-0.41473
H	3.02568	3.69259	1.01773
H	2.66115	4.66357	-0.41458
H	-5.35429	3.20754	-0.00860
H	-4.66814	-1.12803	4.82080
H	-4.43837	2.06250	1.41680
H	-6.94760	-0.95228	3.72846
H	-1.56211	3.36482	0.08283
H	-4.89297	4.15832	-1.42262

H	3.21915	-0.55290	3.97348
H	4.66836	-1.12851	4.82069
H	1.56216	3.36483	0.08295
H	-3.21914	-0.55200	3.97350
H	4.43831	2.06249	1.41687
H	-7.10894	-0.28470	2.09286
H	5.35434	3.20750	-0.00854
H	6.94782	-0.95166	3.72839
H	4.89301	4.15835	-1.42251
H	-5.44954	2.48622	-1.61907
H	7.10883	-0.28389	2.09283
H	-4.03061	-2.02784	3.43710
H	-3.09092	3.77279	-2.71464
H	4.03118	-2.02834	3.43687
H	-6.36414	-1.87045	2.33493
H	3.09090	3.77288	-2.71454
H	-1.76879	2.66576	-2.38381
H	5.44956	2.48625	-1.61904
H	6.36463	-1.86994	2.33481
H	1.76880	2.66581	-2.38373
H	-3.31769	2.04417	-2.98671
H	-4.43920	-2.17398	1.19637
H	4.43909	-2.17400	1.19642
H	3.31771	2.04427	-2.98668
H	3.04573	-3.77115	0.61109
H	-5.36386	-3.15387	-0.35385
H	-3.04568	-3.77119	0.61110
H	-5.45208	-2.26523	-1.87847
H	1.57465	-3.33842	-0.26728
H	5.36390	-3.15386	-0.35385
H	-1.57459	-3.33835	-0.26720
H	-3.31556	-1.68239	-3.18297
H	5.45214	-2.26515	-1.87843
H	-1.77133	-2.37522	-2.65114
H	-4.90606	-3.95235	-1.85981
H	3.31564	-1.68241	-3.18301
H	1.77140	-2.37524	-2.65118
H	2.66836	-4.57154	-0.91970
H	-2.66820	-4.57151	-0.91970
H	4.90616	-3.95228	-1.85986
H	-3.09753	-3.43156	-3.10561
H	3.09760	-3.43158	-3.10562
P	0.00002	1.13069	-0.65247
P	-1.44946	0.11848	-2.01736
P	0.00003	-1.03155	-0.76551
P	1.44949	0.11850	-2.01738

6.2.2 Optimized structure (PBE0/aug-cc-pVDZ)

Atom	x	y	z
C	-5.28531	1.17309	3.57992
C	5.28534	1.17312	3.57990
C	-2.63203	3.65541	0.00419
C	2.63224	3.65545	0.00419
C	-5.07365	-0.19165	2.92084
C	-4.88106	3.15423	-0.97321
C	-4.17601	-1.03551	3.83910
C	4.17600	-1.03545	3.83913



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C	-4.12491	1.14452	0.94047
C	-3.41344	2.67940	-0.88809
C	4.88112	3.15410	-0.97345
C	4.12493	1.14451	0.94045
C	6.44241	-0.87452	2.77409
C	-4.40842	-0.07379	1.54786
C	3.41348	2.67936	-0.88815
C	4.40842	-0.07379	1.54786
C	-3.43965	1.25364	-0.27859
C	-2.87515	2.77946	-2.31962
C	3.43967	1.25361	-0.27861
C	2.87504	2.77941	-2.31963
C	-4.11806	-1.21947	0.80620
C	4.11804	-1.21948	0.80623
C	-2.94163	0.06220	-0.87200
C	2.94162	0.06217	-0.87199
C	-3.43731	-1.19358	-0.41375
C	3.43728	-1.19360	-0.41372
C	-3.41698	-2.53866	-1.18650
C	-4.88663	-2.99291	-1.32711
C	3.41695	-2.53870	-1.18644
C	2.64078	-3.61567	-0.41414
C	-2.64091	-3.61568	-0.41417
C	4.88659	-2.99302	-1.32695
C	-2.87726	-2.47151	-2.61898
C	2.87732	-2.47155	-2.61896
H	-5.73376	1.03844	4.57618
H	-4.33569	1.71411	3.71293
H	-5.96678	1.81153	2.99660
H	5.73379	1.03848	4.57615
H	4.33573	1.71416	3.71289
H	-3.04334	3.69746	1.02382
H	5.96681	1.81153	2.99655
H	-2.67843	4.67289	-0.41674
H	3.04366	3.69751	1.02377
H	2.67866	4.67292	-0.41679
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H	-4.63883	-1.14494	4.83329
H	-4.44596	2.06256	1.42989
H	-6.93231	-0.96681	3.75698
H	-1.57307	3.36701	0.08206
H	-4.91746	4.16274	-1.41530
H	3.19067	-0.56164	3.96897
H	4.63882	-1.14487	4.83332
H	1.57327	3.36713	0.08218
H	-3.19067	-0.56171	3.96894
H	4.44599	2.06256	1.42985
H	-7.10469	-0.29191	2.11491
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H	6.93230	-0.96681	3.75699
H	4.91754	4.16258	-1.41560
H	-5.47354	2.48018	-1.61127
H	7.10469	-0.29194	2.11491
H	-4.01059	-2.04492	3.43346
H	-3.11743	3.77706	-2.71824
H	4.01056	-2.04487	3.43351
H	-6.35357	-1.88642	2.35068
H	3.11734	3.77698	-2.71830

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H         -1.78570        2.66409       -2.38415
H          5.47349        2.47998       -1.61155
H          6.35353       -1.88644        2.35071
H          1.78557        2.66411       -2.38402
H         -3.34203        2.03736       -2.98581
H         -4.44176       -2.18618        1.19508
H          4.44172       -2.18619        1.19513
H          3.34179        2.03726       -2.98584
H          3.05953       -3.78146        0.58981
H         -5.37810       -3.15153       -0.35748
H         -3.05973       -3.78148        0.58975
H         -5.47478       -2.24670       -1.88363
H          1.58262       -3.33935       -0.29372
H          5.37799       -3.15162       -0.35729
H         -1.58275       -3.33940       -0.29367
H         -3.33913       -1.65321       -3.19295
H          5.47480       -2.24684       -1.88345
H         -1.78731       -2.35496       -2.66888
H         -4.92913       -3.94426       -1.88126
H          3.33925       -1.65327       -3.19291
H          1.78738       -2.35498       -2.66894
H          2.68373       -4.57455       -0.95570
H         -2.68387       -4.57455       -0.95575
H          4.92908       -3.94438       -1.88107
H         -3.12338       -3.41332       -3.13424
H          3.12346       -3.41338       -3.13419
P         -0.00000        1.14576       -0.64056
P         -1.45566        0.12585       -2.02652
P         -0.00001       -1.03925       -0.75942
P          1.45565        0.12584       -2.02652
```

6.2.3 Thermodynamic data

```
 Absolute energy=-2770.0708682
 T = 298 K
 Zero-point correction=                           0.858910 (Hartree/Particle)
 Thermal correction to Energy=                    0.907605
 Thermal correction to Enthalpy=                  0.908549
 Thermal correction to Gibbs Free Energy=         0.778776
 Sum of electronic and zero-point Energies=          -2769.211959
 Sum of electronic and thermal Energies=             -2769.163264
 Sum of electronic and thermal Enthalpies=           -2769.162320
 Sum of electronic and thermal Free Energies=        -2769.292092
 T = 348 K
 Zero-point correction=                           0.858907 (Hartree/Particle)
 Thermal correction to Energy=                    0.923725
 Thermal correction to Enthalpy=                  0.924827
 Thermal correction to Gibbs Free Energy=         0.755816
 Sum of electronic and zero-point Energies=          -2769.211961
 Sum of electronic and thermal Energies=             -2769.147143
 Sum of electronic and thermal Enthalpies=           -2769.146041
 Sum of electronic and thermal Free Energies=        -2769.315053
```

6.2.4 NBO analysis (excerpt)

		Natural Population			
Atom No	Natural Charge	Core	Valence	Rydberg	Total
C 1	-0.71992	1.99940	4.70928	0.01125	6.71992
C 2	-0.71992	1.99940	4.70928	0.01125	6.71992
C 3	-0.70215	1.99937	4.69188	0.01090	6.70215
C 4	-0.70215	1.99937	4.69188	0.01090	6.70215
C 5	-0.07151	1.99910	4.06082	0.01159	6.07151
C 6	-0.70198	1.99939	4.69179	0.01080	6.70198
C 7	-0.70551	1.99938	4.69546	0.01067	6.70551
C 8	-0.70552	1.99938	4.69546	0.01067	6.70552
C 9	-0.70492	1.99938	4.69484	0.01070	6.70492
C 10	-0.07151	1.99910	4.06082	0.01159	6.07151
C 11	-0.24481	1.99896	4.23364	0.01220	6.24481
C 12	-0.07520	1.99910	4.06387	0.01223	6.07520
C 13	-0.70198	1.99939	4.69179	0.01080	6.70198
C 14	-0.24481	1.99896	4.23364	0.01220	6.24481
C 15	-0.70492	1.99938	4.69484	0.01070	6.70492
C 16	-0.00658	1.99897	3.98751	0.02010	6.00658
C 17	-0.07520	1.99910	4.06387	0.01223	6.07520
C 18	-0.00658	1.99897	3.98751	0.02010	6.00658
C 19	-0.00498	1.99893	3.98485	0.02120	6.00498
C 20	-0.72144	1.99938	4.70926	0.01279	6.72144
C 21	-0.00499	1.99893	3.98485	0.02120	6.00499
C 22	-0.72144	1.99938	4.70926	0.01279	6.72144
C 23	-0.23952	1.99897	4.22839	0.01217	6.23952
C 24	-0.23953	1.99897	4.22839	0.01217	6.23953
C 25	-0.34607	1.99881	4.32731	0.01995	6.34607
C 26	-0.34607	1.99881	4.32731	0.01995	6.34607
C 27	-0.00707	1.99893	3.98680	0.02135	6.00707
C 28	-0.00707	1.99893	3.98680	0.02135	6.00707
C 29	-0.07506	1.99910	4.06376	0.01220	6.07506
C 30	-0.70176	1.99939	4.69155	0.01082	6.70176
C 31	-0.07506	1.99910	4.06376	0.01220	6.07506
C 32	-0.70209	1.99937	4.69183	0.01089	6.70209
C 33	-0.70209	1.99937	4.69183	0.01089	6.70209
C 34	-0.70176	1.99939	4.69155	0.01082	6.70176
C 35	-0.72164	1.99938	4.70945	0.01281	6.72164
C 36	-0.72164	1.99938	4.70945	0.01281	6.72164
H 37	0.25196	0.00000	0.74674	0.00130	0.74804
H 38	0.25029	0.00000	0.74830	0.00141	0.74971
H 39	0.24555	0.00000	0.75305	0.00140	0.75445
H 40	0.25196	0.00000	0.74674	0.00130	0.74804
H 41	0.25029	0.00000	0.74830	0.00141	0.74971
H 42	0.24355	0.00000	0.75523	0.00121	0.75645
H 43	0.24555	0.00000	0.75305	0.00140	0.75445
H 44	0.24432	0.00000	0.75424	0.00145	0.75568
H 45	0.24355	0.00000	0.75523	0.00121	0.75645
H 46	0.24432	0.00000	0.75424	0.00145	0.75568
H 47	0.24336	0.00000	0.75544	0.00120	0.75664
H 48	0.24392	0.00000	0.75467	0.00141	0.75608
H 49	0.24400	0.00000	0.75431	0.00169	0.75600
H 50	0.24472	0.00000	0.75385	0.00142	0.75528
H 51	0.25080	0.00000	0.74679	0.00241	0.74920
H 52	0.24476	0.00000	0.75384	0.00139	0.75524
H 53	0.25323	0.00000	0.74546	0.00131	0.74677

```
   H 54    0.24392      0.00000     0.75467    0.00141     0.75608
   H 55    0.25080      0.00000     0.74679    0.00241     0.74920
   H 56    0.25323      0.00000     0.74546    0.00131     0.74677
   H 57    0.24400      0.00000     0.75431    0.00169     0.75600
   H 58    0.25039      0.00000     0.74828    0.00133     0.74961
   H 59    0.24336      0.00000     0.75544    0.00120     0.75664
   H 60    0.24472      0.00000     0.75386    0.00142     0.75528
   H 61    0.24476      0.00000     0.75384    0.00139     0.75524
   H 62    0.25223      0.00000     0.74644    0.00133     0.74777
   H 63    0.25039      0.00000     0.74828    0.00133     0.74961
   H 64    0.24499      0.00000     0.75380    0.00121     0.75501
   H 65    0.25345      0.00000     0.74508    0.00148     0.74655
   H 66    0.24498      0.00000     0.75381    0.00121     0.75502
   H 67    0.24317      0.00000     0.75560    0.00122     0.75683
   H 68    0.25345      0.00000     0.74508    0.00148     0.74655
   H 69    0.25111      0.00000     0.74581    0.00309     0.74889
   H 70    0.25223      0.00000     0.74644    0.00133     0.74777
   H 71    0.24318      0.00000     0.75560    0.00122     0.75682
   H 72    0.25111      0.00000     0.74581    0.00309     0.74889
   H 73    0.25332      0.00000     0.74468    0.00200     0.74668
   H 74    0.23860      0.00000     0.75987    0.00153     0.76140
   H 75    0.23860      0.00000     0.75987    0.00153     0.76140
   H 76    0.25332      0.00000     0.74468    0.00200     0.74668
   H 77    0.24286      0.00000     0.75594    0.00121     0.75714
   H 78    0.24297      0.00000     0.75585    0.00118     0.75703
   H 79    0.24286      0.00000     0.75594    0.00121     0.75714
   H 80    0.25237      0.00000     0.74630    0.00132     0.74763
   H 81    0.25122      0.00000     0.74641    0.00238     0.74878
   H 82    0.24297      0.00000     0.75585    0.00118     0.75703
   H 83    0.25121      0.00000     0.74641    0.00238     0.74879
   H 84    0.25334      0.00000     0.74465    0.00202     0.74666
   H 85    0.25237      0.00000     0.74630    0.00132     0.74763
   H 86    0.25126      0.00000     0.74566    0.00309     0.74874
   H 87    0.24467      0.00000     0.75394    0.00139     0.75533
   H 88    0.25334      0.00000     0.74465    0.00202     0.74666
   H 89    0.25126      0.00000     0.74566    0.00309     0.74874
   H 90    0.24439      0.00000     0.75417    0.00144     0.75561
   H 91    0.24439      0.00000     0.75417    0.00144     0.75561
   H 92    0.24467      0.00000     0.75394    0.00139     0.75533
   H 93    0.25357      0.00000     0.74496    0.00147     0.74643
   H 94    0.25357      0.00000     0.74496    0.00147     0.74643
   P 95   -0.00274      9.99898     4.95477    0.04900    15.00274
   P 96    0.27014      9.99877     4.68394    0.04716    14.72986
   P 97   -0.00179      9.99898     4.95395    0.04886    15.00179
   P 98    0.27014      9.99877     4.68394    0.04716    14.72986
 =======================================================================
 * Total *  0.00000    111.96611   221.25992    0.77398   334.00000
```

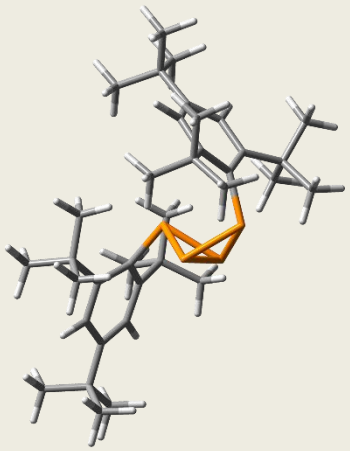
```
   (Occupancy)   Bond orbital / Coefficients / Hybrids
------------------ Lewis ----------------------------------------------------
[...]
163. (1.95604) BD ( 1) P 95- P 96
              ( 50.43%)   0.7101* P 95 s(  8.95%)p10.08( 90.20%)d 0.10(  0.85%)
                                       0.0000  0.0000  0.2991 -0.0040 -0.0023
                                       0.0000 -0.7026 -0.0063  0.0000 -0.1321
                                       0.0168  0.0000 -0.6249  0.0036  0.0483
                                       0.0626  0.0441  0.0114  0.0148
```

```
              ( 49.57%)   0.7041* P 96 s(  8.44%)p10.76( 90.80%)d 0.09(  0.76%)
                                        0.0000  0.0000  0.2903  0.0109 -0.0021
                                        0.0000  0.4545  0.0086  0.0000  0.6788
                                       -0.0105  0.0000  0.4904 -0.0073  0.0421
                                        0.0551  0.0502  0.0133  0.0114
164. (1.97348) BD ( 1) P 95- P 97
              ( 50.01%)   0.7072* P 95 s(  7.95%)p11.48( 91.23%)d 0.10(  0.82%)
                                        0.0000  0.0000  0.2818 -0.0068 -0.0035
                                        0.0000  0.0000  0.0000  0.0000 -0.8983
                                        0.0005  0.0000  0.3229  0.0348  0.0000
                                        0.0000  0.0055 -0.0746 -0.0511
              ( 49.99%)   0.7070* P 97 s(  7.97%)p11.45( 91.21%)d 0.10(  0.82%)
                                        0.0000  0.0000  0.2821 -0.0068 -0.0035
                                        0.0000  0.0000  0.0000  0.0000  0.8596
                                       -0.0041  0.0000  0.4149  0.0340  0.0000
                                        0.0000  0.0116 -0.0743 -0.0505
165. (1.95604) BD ( 1) P 95- P 98
              ( 50.43%)   0.7101* P 95 s(  8.95%)p10.08( 90.20%)d 0.10(  0.85%)
                                        0.0000  0.0000  0.2991 -0.0040 -0.0023
                                        0.0000  0.7026  0.0063  0.0000 -0.1321
                                        0.0168  0.0000 -0.6249  0.0036 -0.0483
                                       -0.0626  0.0441  0.0114  0.0148
              ( 49.57%)   0.7041* P 98 s(  8.44%)p10.76( 90.80%)d 0.09(  0.76%)
                                        0.0000  0.0000  0.2903  0.0109 -0.0021
                                        0.0000 -0.4545 -0.0086  0.0000  0.6788
                                       -0.0105  0.0000  0.4904 -0.0073 -0.0421
                                       -0.0551  0.0502  0.0133  0.0115
166. (1.95584) BD ( 1) P 96- P 97
              ( 49.58%)   0.7041* P 96 s(  8.42%)p10.78( 90.82%)d 0.09(  0.76%)
                                        0.0000  0.0000  0.2900  0.0109 -0.0021
                                        0.0000  0.4541  0.0087  0.0000 -0.7267
                                        0.0108  0.0000  0.4167 -0.0061 -0.0475
                                        0.0504 -0.0525  0.0078  0.0021
              ( 50.42%)   0.7101* P 97 s(  8.93%)p10.10( 90.22%)d 0.10(  0.85%)
                                        0.0000  0.0000  0.2988 -0.0039 -0.0023
                                        0.0000 -0.7027 -0.0062  0.0000  0.1967
                                       -0.0168  0.0000 -0.6078  0.0019 -0.0546
                                        0.0572 -0.0470  0.0066  0.0065
167. (1.95584) BD ( 1) P 97- P 98
              ( 50.42%)   0.7101* P 97 s(  8.93%)p10.10( 90.22%)d 0.10(  0.85%)
                                        0.0000  0.0000  0.2988 -0.0039 -0.0023
                                        0.0000  0.7026  0.0062  0.0000  0.1967
                                       -0.0168  0.0000 -0.6078  0.0019  0.0546
                                       -0.0572 -0.0470  0.0066  0.0065
              ( 49.58%)   0.7041* P 98 s(  8.42%)p10.78( 90.82%)d 0.09(  0.76%)
                                        0.0000  0.0000  0.2900  0.0109 -0.0021
                                        0.0000 -0.4541 -0.0087  0.0000 -0.7267
                                        0.0108  0.0000  0.4167 -0.0061  0.0475
                                       -0.0504 -0.0525  0.0078  0.0021
```

6.3 *endo-exo*-Mes*P_4Mes* (5b)

6.3.1 Optimized structure (PBE0/6-31g(d,p))

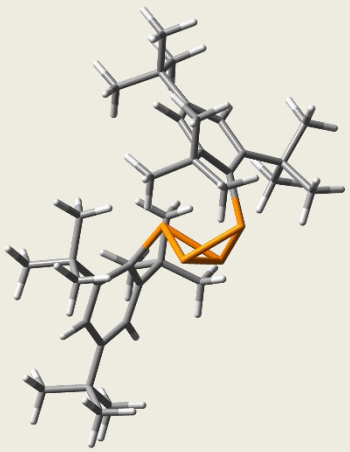
Atom	x	y	z
C	-4.10308	1.20463	0.29336
C	-4.80950	0.03152	0.06099
C	-4.11622	-1.15896	0.27211
C	-2.74793	-1.21203	0.53870
C	-2.01014	0.00619	0.49765
C	-2.72904	1.22966	0.56200
C	-2.20727	-2.59294	0.98682
C	-3.10383	-3.07794	2.14844
P	-0.18090	0.00024	0.05830
P	-0.31382	1.09515	-1.89280
P	1.48696	0.00579	-2.60953
P	-0.31347	-1.08700	-1.89616
C	-6.29044	0.00525	-0.31967
C	-6.85819	1.41054	-0.53505
C	-2.16949	2.59664	1.02833
C	-2.22346	3.64694	-0.09079
C	-2.27926	-3.62753	-0.14578
C	-0.78842	-2.56554	1.56517
C	-6.45801	-0.78591	-1.62707
C	-7.09834	-0.67634	0.79670
C	-0.75304	2.54135	1.61061
C	-3.06192	3.07993	2.19402
C	2.71777	0.00913	-1.20905
C	3.12114	-1.21480	-0.60514
C	3.55007	-1.16984	0.72084
C	3.68509	0.01642	1.44048
C	3.54278	1.19700	0.72197
C	3.11391	1.23269	-0.60976
C	3.22426	-2.59432	-1.30442
C	3.10891	-2.55291	-2.83392
C	4.04088	-0.02094	2.92722
C	4.11259	1.37966	3.54130
C	3.21043	2.61267	-1.30864
C	2.18321	3.60488	-0.74573
C	4.63732	-3.15322	-1.02335
C	2.19095	-3.58593	-0.75203
C	5.40462	-0.70377	3.12019
C	2.96022	-0.81809	3.67640
C	3.08222	2.57626	-2.83721
C	4.62733	3.16796	-1.03833
H	4.76168	-4.10791	-1.54576
H	2.34638	-4.57764	-1.19193
H	4.82279	-3.33734	0.03720
H	3.42863	-3.51913	-3.23927
H	5.40803	-2.46474	-1.38410
H	2.26795	-3.68342	0.33539
H	-1.95788	-4.60930	0.22008
H	1.16942	-3.27350	-0.99091
H	-0.57137	-3.53806	2.02102
H	-2.72911	-4.03681	2.52356
H	5.40278	-1.73041	2.74184
H	3.75595	-1.78312	-3.26696



```
H          2.09078       -2.38667       -3.19020
H          3.78128       -2.10620        1.21895
H         -1.63781       -3.35037       -0.98704
H         -3.29913       -3.73199       -0.52874
H          5.66297       -0.74154        4.18448
H         -0.01391       -2.38849        0.81761
H          2.89090       -1.84778        3.31310
H         -4.14387       -3.22741        1.84953
H          6.19454       -0.15532        2.59697
H         -3.09236       -2.36077        2.97540
H         -0.68996       -1.80480        2.34686
H          3.18888       -0.85528        4.74757
H         -4.66766       -2.09366        0.23378
H          1.97700       -0.35362        3.55002
H         -6.10086       -1.81520       -1.52740
H         -6.77095       -1.70690        0.96451
H          4.33060        1.30150        4.61133
H          4.90573        1.98450        3.08899
H          3.72298        1.80577       -3.27826
H          5.39296        2.48035       -1.41149
H          3.76008        2.13772        1.21351
H         -7.51467       -0.82471       -1.91513
H          3.16480        1.91744        3.43294
H         -8.16214       -0.70311        0.53484
H         -5.89839       -0.31655       -2.44229
H         -6.99292       -0.13393        1.74180
H          2.06060        2.41537       -3.18569
H          4.82379        3.34469        0.02143
H         -0.67126        1.77290        2.38674
H          3.40250        3.54265       -3.24179
H          4.74790        4.12547       -1.55648
H          0.02142        2.35592        0.86481
H          1.15932        3.29251       -0.97444
H          2.27080        3.70365        0.34071
H         -3.06486        2.35101        3.01073
H         -7.90512        1.33989       -0.84736
H         -4.63341        2.14931        0.26748
H         -0.52134        3.50679        2.07428
H         -6.31359        1.95161       -1.31585
H         -6.82984        2.00774        0.38248
H          2.33460        4.59621       -1.18788
H         -1.58171        3.37312       -0.93286
H         -4.09824        3.25119        1.89421
H         -2.67240        4.02696        2.58383
H         -3.24016        3.76925       -0.47679
H         -1.89131        4.61964        0.28944
```

6.3.2 Optimized structure (PBE0/aug-cc-pVDZ)

Atom	x	y	z
C	-4.10579	1.20529	0.29551
C	-4.81204	0.03041	0.05905
C	-4.11792	-1.16124	0.27465
C	-2.74849	-1.21369	0.54564
C	-2.01087	0.00642	0.50639
C	-2.73069	1.23103	0.56909
C	-2.20812	-2.59294	0.99936
C	-3.10213	-3.06982	2.16468
P	-0.17180	0.00100	0.05892
P	-0.32382	1.10945	-1.90308
P	1.49200	0.00786	-2.62671
P	-0.32489	-1.09581	-1.90864
C	-6.29235	0.00448	-0.32721
C	-6.85649	1.40956	-0.54821
C	-2.17314	2.59672	1.04153
C	-2.23340	3.65216	-0.07175
C	-2.28431	-3.63210	-0.12814
C	-0.78745	-2.56177	1.57014
C	-6.45461	-0.78951	-1.63264
C	-7.10344	-0.67294	0.78841
C	-0.75439	2.53956	1.61510
C	-3.06327	3.06947	2.21167
C	2.71895	0.00935	-1.21100
C	3.12203	-1.21689	-0.60738
C	3.55172	-1.17269	0.72051
C	3.68866	0.01452	1.44197
C	3.54583	1.19692	0.72291
C	3.11671	1.23390	-0.61093
C	3.22316	-2.59610	-1.30831
C	3.12969	-2.54492	-2.83844
C	4.04893	-0.02286	2.92854
C	4.12952	1.37788	3.53939
C	3.21348	2.61435	-1.30949
C	2.17266	3.59842	-0.75922
C	4.62464	-3.17144	-1.00962
C	2.17214	-3.57774	-0.77361
C	5.40978	-0.71140	3.11631
C	2.96714	-0.81378	3.68128
C	3.10276	2.57198	-2.83865
C	4.62162	3.18081	-1.02391
H	4.74862	-4.12773	-1.54196
H	2.31718	-4.57350	-1.22331
H	4.79139	-3.36933	0.05794
H	3.44877	-3.51586	-3.24852
H	5.41364	-2.48446	-1.35253
H	2.24015	-3.68757	0.31943
H	-1.95860	-4.61820	0.24078
H	1.15098	-3.24639	-1.01647
H	-0.56484	-3.53569	2.03410
H	-2.72719	-4.03308	2.54634
H	5.40217	-1.74467	2.73806
H	3.79063	-1.77203	-3.26037
H	2.11216	-2.36517	-3.20840
H	3.78618	-2.11407	1.21896
H	-1.64285	-3.35680	-0.97820
H	-3.31120	-3.74083	-0.50900



```
H          5.67552       -0.74940        4.18524
H         -0.01480       -2.38600        0.81165
H          2.89019       -1.84909        3.31662
H         -4.14931       -3.21785        1.86722
H          6.20484       -0.16503        2.58541
H         -3.08667       -2.34471        2.99310
H         -0.68359       -1.79034        2.34917
H          3.19948       -0.85310        4.75791
H         -4.67174       -2.10096        0.23922
H          1.97982       -0.34209        3.55767
H         -6.09728       -1.82495       -1.52861
H         -6.77591       -1.70926        0.96148
H          4.35658        1.30144        4.61389
H          4.92471        1.98382        3.07813
H          3.75405        1.79747       -3.27240
H          5.40249        2.49315       -1.38389
H          3.76839        2.14159        1.21600
H         -7.51559       -0.82888       -1.92849
H          3.17829        1.92285        3.43736
H         -8.17292       -0.70064        0.52344
H         -5.88717       -0.32062       -2.45142
H         -6.99992       -0.12544        1.73819
H          2.08008        2.40140       -3.19835
H          4.80323        3.36713        0.04322
H         -0.66519        1.75987        2.38778
H          3.42413        3.54314       -3.24647
H          4.74326        4.14124       -1.54932
H          0.01765        2.35758        0.85728
H          1.14767        3.27130       -0.99156
H          2.25334        3.70550        0.33316
H         -3.06034        2.33212        3.02936
H         -7.90902        1.34068       -0.86342
H         -4.63972        2.15425        0.27281
H         -0.51829        3.50629        2.08737
H         -6.30745        1.95066       -1.33419
H         -6.82833        2.01459        0.37118
H          2.31622        4.59483       -1.20792
H         -1.59078        3.38211       -0.92256
H         -4.10729        3.23725        1.91389
H         -2.67520        4.02142        2.60821
H         -3.25729        3.77682       -0.45569
H         -1.89891        4.62953        0.31226
```

6.3.3 Thermodynamic data

```
 Absolute energy=-2770.0667691
 T = 298 K
 Zero-point correction=                          0.858708 (Hartree/Particle)
 Thermal correction to Energy=                   0.907460
 Thermal correction to Enthalpy=                 0.908404
 Thermal correction to Gibbs Free Energy=        0.778030
 Sum of electronic and zero-point Energies=          -2769.208061
 Sum of electronic and thermal Energies=             -2769.159309
 Sum of electronic and thermal Enthalpies=           -2769.158365
 Sum of electronic and thermal Free Energies=        -2769.288739
 T = 348 K
 Zero-point correction=                          0.858708 (Hartree/Particle)
 Thermal correction to Energy=                   0.923595
```

```
 Thermal correction to Enthalpy=                 0.924697
 Thermal correction to Gibbs Free Energy=        0.754968
 Sum of electronic and zero-point Energies=          -2769.208061
 Sum of electronic and thermal Energies=             -2769.143174
 Sum of electronic and thermal Enthalpies=           -2769.142072
 Sum of electronic and thermal Free Energies=        -2769.311801
```

6.3.4 NBO analysis (excerpt)

```
                                     Natural Population
              Natural    -----------------------------------------------
 Atom No      Charge         Core      Valence    Rydberg      Total
-------------------------------------------------------------------------
   C  1   -0.24633      1.99895     4.23485    0.01253     6.24633
   C  2   -0.00714      1.99896     3.98864    0.01954     6.00714
   C  3   -0.24130      1.99895     4.22983    0.01252     6.24130
   C  4   -0.01051      1.99892     3.99017    0.02141     6.01051
   C  5   -0.34830      1.99881     4.33038    0.01911     6.34830
   C  6   -0.00825      1.99893     3.98799    0.02133     6.00825
   C  7   -0.07362      1.99910     4.06265    0.01188     6.07362
   C  8   -0.70209      1.99939     4.69178    0.01093     6.70209
   P  9    0.26620      9.99880     4.68624    0.04876    14.73380
   P 10    0.00278      9.99899     4.95029    0.04793    14.99722
   P 11    0.27339      9.99877     4.67666    0.05118    14.72661
   P 12    0.00216      9.99899     4.95086    0.04799    14.99784
   C 13   -0.07038      1.99909     4.05987    0.01141     6.07038
   C 14   -0.71958      1.99940     4.70904    0.01114     6.71958
   C 15   -0.07388      1.99910     4.06289    0.01189     6.07388
   C 16   -0.70212      1.99937     4.69182    0.01094     6.70212
   C 17   -0.70202      1.99937     4.69172    0.01093     6.70202
   C 18   -0.71810      1.99938     4.70586    0.01287     6.71810
   C 19   -0.70595      1.99938     4.69578    0.01078     6.70595
   C 20   -0.70437      1.99938     4.69445    0.01054     6.70437
   C 21   -0.71818      1.99938     4.70593    0.01288     6.71818
   C 22   -0.70243      1.99939     4.69210    0.01094     6.70243
   C 23   -0.35559      1.99880     4.33754    0.01924     6.35559
   C 24   -0.00190      1.99892     3.98126    0.02172     6.00190
   C 25   -0.24258      1.99895     4.23112    0.01251     6.24258
   C 26   -0.00263      1.99896     3.98401    0.01966     6.00263
   C 27   -0.24797      1.99895     4.23647    0.01255     6.24797
   C 28    0.00048      1.99892     3.97895    0.02165     5.99952
   C 29   -0.07428      1.99910     4.06322    0.01197     6.07428
   C 30   -0.72057      1.99938     4.70875    0.01243     6.72057
   C 31   -0.07017      1.99909     4.05962    0.01147     6.07017
   C 32   -0.71953      1.99940     4.70898    0.01115     6.71953
   C 33   -0.07463      1.99910     4.06354    0.01199     6.07463
   C 34   -0.69940      1.99936     4.68910    0.01094     6.69940
   C 35   -0.70308      1.99939     4.69282    0.01086     6.70308
   C 36   -0.69902      1.99936     4.68872    0.01094     6.69902
   C 37   -0.70478      1.99938     4.69473    0.01067     6.70478
   C 38   -0.70472      1.99938     4.69466    0.01067     6.70472
   C 39   -0.72078      1.99938     4.70894    0.01245     6.72078
   C 40   -0.70306      1.99939     4.69282    0.01085     6.70306
   H 41    0.24569      0.00000     0.75292    0.00139     0.75431
   H 42    0.24667      0.00000     0.75187    0.00146     0.75333
   H 43    0.24156      0.00000     0.75726    0.00118     0.75844
   H 44    0.25289      0.00000     0.74564    0.00147     0.74711
   H 45    0.25353      0.00000     0.74516    0.00131     0.74647
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   H 46    0.24521      0.00000     0.75353    0.00126     0.75479
   H 47    0.24374      0.00000     0.75481    0.00145     0.75626
   H 48    0.24256      0.00000     0.75524    0.00220     0.75744
   H 49    0.25227      0.00000     0.74627    0.00145     0.74773
   H 50    0.24481      0.00000     0.75379    0.00140     0.75519
   H 51    0.24325      0.00000     0.75553    0.00122     0.75675
   H 52    0.25402      0.00000     0.74427    0.00171     0.74598
   H 53    0.25178      0.00000     0.74538    0.00284     0.74822
   H 54    0.23910      0.00000     0.75936    0.00153     0.76090
   H 55    0.25025      0.00000     0.74730    0.00245     0.74975
   H 56    0.24438      0.00000     0.75440    0.00122     0.75562
   H 57    0.24463      0.00000     0.75393    0.00145     0.75537
   H 58    0.24859      0.00000     0.74806    0.00335     0.75141
   H 59    0.24473      0.00000     0.75405    0.00122     0.75527
   H 60    0.24269      0.00000     0.75613    0.00118     0.75731
   H 61    0.25026      0.00000     0.74841    0.00133     0.74974
   H 62    0.25209      0.00000     0.74659    0.00132     0.74791
   H 63    0.25222      0.00000     0.74592    0.00186     0.74778
   H 64    0.24346      0.00000     0.75510    0.00144     0.75654
   H 65    0.23945      0.00000     0.75905    0.00151     0.76055
   H 66    0.25292      0.00000     0.74568    0.00141     0.74708
   H 67    0.24499      0.00000     0.75381    0.00120     0.75501
   H 68    0.24312      0.00000     0.75566    0.00122     0.75688
   H 69    0.25173      0.00000     0.74696    0.00131     0.74827
   H 70    0.24545      0.00000     0.75315    0.00140     0.75455
   H 71    0.25405      0.00000     0.74421    0.00173     0.74595
   H 72    0.25325      0.00000     0.74543    0.00132     0.74675
   H 73    0.24460      0.00000     0.75373    0.00167     0.75540
   H 74    0.24389      0.00000     0.75469    0.00141     0.75611
   H 75    0.25022      0.00000     0.74834    0.00144     0.74978
   H 76    0.24463      0.00000     0.75391    0.00145     0.75537
   H 77    0.25371      0.00000     0.74500    0.00129     0.74629
   H 78    0.24998      0.00000     0.74868    0.00134     0.75002
   H 79    0.25187      0.00000     0.74531    0.00282     0.74813
   H 80    0.24232      0.00000     0.75647    0.00120     0.75768
   H 81    0.25172      0.00000     0.74640    0.00188     0.74828
   H 82    0.25291      0.00000     0.74562    0.00147     0.74709
   H 83    0.24562      0.00000     0.75299    0.00138     0.75438
   H 84    0.24906      0.00000     0.74758    0.00336     0.75094
   H 85    0.24271      0.00000     0.75511    0.00218     0.75729
   H 86    0.24538      0.00000     0.75336    0.00126     0.75462
   H 87    0.25192      0.00000     0.74675    0.00133     0.74808
   H 88    0.25187      0.00000     0.74682    0.00131     0.74813
   H 89    0.24486      0.00000     0.75349    0.00165     0.75514
   H 90    0.25211      0.00000     0.74644    0.00146     0.74789
   H 91    0.25080      0.00000     0.74781    0.00139     0.74920
   H 92    0.24506      0.00000     0.75353    0.00141     0.75494
   H 93    0.24676      0.00000     0.75178    0.00146     0.75324
   H 94    0.24980      0.00000     0.74780    0.00240     0.75020
   H 95    0.24326      0.00000     0.75554    0.00120     0.75674
   H 96    0.24493      0.00000     0.75368    0.00139     0.75507
   H 97    0.24510      0.00000     0.75368    0.00122     0.75490
   H 98    0.24378      0.00000     0.75478    0.00145     0.75622
 ===============================================================
 * Total *  0.00000    111.96602   221.25924    0.77474   334.00000
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    (Occupancy)   Bond orbital / Coefficients / Hybrids
 ------------------ Lewis ----------------------------------------------------
 [...]
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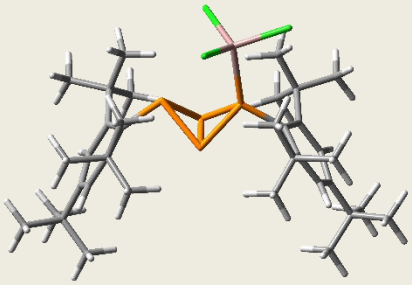
```
 82. (1.95825) BD ( 1) P  9- P 10
             ( 49.28%)   0.7020* P  9 s(  7.86%)p11.63( 91.40%)d 0.09(  0.74%)
                                       0.0000  0.0000  0.2802  0.0085 -0.0020
                                       0.0000 -0.0710  0.0087  0.0000  0.7053
                                      -0.0104  0.0000 -0.6413 -0.0074 -0.0114
                                       0.0129 -0.0673 -0.0141  0.0486
             ( 50.72%)   0.7122* P 10 s(  9.63%)p 9.30( 89.58%)d 0.08(  0.79%)
                                       0.0000  0.0000  0.3104  0.0007 -0.0020
                                       0.0000  0.1157 -0.0177  0.0000 -0.1801
                                       0.0041  0.0000  0.9217  0.0125 -0.0044
                                       0.0176 -0.0685 -0.0155  0.0514
 83. (1.95824) BD ( 1) P  9- P 12
             ( 49.29%)   0.7020* P  9 s(  7.87%)p11.61( 91.39%)d 0.09(  0.74%)
                                       0.0000  0.0000  0.2804  0.0079 -0.0020
                                       0.0000 -0.0732  0.0093  0.0000 -0.7021
                                       0.0111  0.0000 -0.6444 -0.0065  0.0114
                                       0.0131  0.0670 -0.0137  0.0491
             ( 50.71%)   0.7121* P 12 s(  9.65%)p 9.28( 89.56%)d 0.08(  0.79%)
                                       0.0000  0.0000  0.3106  0.0007 -0.0020
                                       0.0000  0.1138 -0.0176  0.0000  0.1772
                                      -0.0039  0.0000  0.9224  0.0126  0.0042
                                       0.0174  0.0682 -0.0152  0.0519
 84. (1.94954) BD ( 1) P 10- P 11
             ( 50.24%)   0.7088* P 10 s(  9.96%)p 8.95( 89.18%)d 0.09(  0.85%)
                                       0.0000  0.0000  0.3156 -0.0030 -0.0024
                                       0.0000  0.8934 -0.0048  0.0000 -0.1758
                                       0.0191  0.0000 -0.2478 -0.0317 -0.0652
                                      -0.0236  0.0215  0.0383 -0.0423
             ( 49.76%)   0.7054* P 11 s(  9.96%)p 8.96( 89.25%)d 0.08(  0.79%)
                                       0.0000  0.0000  0.3153  0.0134 -0.0020
                                       0.0000 -0.5368 -0.0283  0.0000  0.7032
                                      -0.0102  0.0000  0.3286 -0.0320 -0.0560
                                      -0.0509  0.0394  0.0197 -0.0144
 85. (1.94481) BD ( 1) P 10- P 12
             ( 49.98%)   0.7070* P 10 s(  7.28%)p12.63( 91.88%)d 0.12(  0.85%)
                                       0.0000  0.0000  0.2696 -0.0077 -0.0041
                                       0.0000 -0.3269 -0.0226  0.0000 -0.8735
                                       0.0036  0.0000 -0.2195 -0.0128  0.0054
                                      -0.0093  0.0056 -0.0835 -0.0369
             ( 50.02%)   0.7073* P 12 s(  7.28%)p12.62( 91.87%)d 0.12(  0.85%)
                                       0.0000  0.0000  0.2697 -0.0077 -0.0041
                                       0.0000 -0.3268 -0.0228  0.0000  0.8741
                                      -0.0034  0.0000 -0.2174 -0.0129 -0.0054
                                      -0.0094 -0.0051 -0.0834 -0.0369
 86. (1.94907) BD ( 1) P 11- P 12
             ( 49.74%)   0.7052* P 11 s(  9.95%)p 8.98( 89.27%)d 0.08(  0.78%)
                                       0.0000  0.0000  0.3151  0.0134 -0.0020
                                       0.0000 -0.5354 -0.0284  0.0000 -0.7042
                                       0.0098  0.0000  0.3289 -0.0321  0.0561
                                      -0.0507 -0.0394  0.0193 -0.0144
             ( 50.26%)   0.7090* P 12 s(  9.96%)p 8.95( 89.18%)d 0.09(  0.85%)
                                       0.0000  0.0000  0.3156 -0.0029 -0.0024
                                       0.0000  0.8938 -0.0051  0.0000  0.1768
                                      -0.0195  0.0000 -0.2456 -0.0319  0.0653
                                      -0.0230 -0.0213  0.0382 -0.0425
```

6.4 *exo-exo*-Mes*P_4Mes*·$GaCl_3$ (5a·$GaCl_3$)

6.4.1 Optimized structure (PBE0/6-31g(d,p))

Atom	x	y	z
C	-2.94806	0.25480	3.65962
C	2.30490	1.07680	3.64594
C	-5.05343	-0.96305	3.07795
C	-6.13438	3.60925	1.42131
C	-3.61566	-0.64455	2.60852
C	4.60466	0.21817	3.12837
C	4.83621	4.87650	1.43565
C	3.13827	0.26627	2.64096
C	-2.89693	-1.99832	2.57158
C	-4.59521	1.18164	1.21402
C	2.66303	-1.18870	2.66128
C	-5.83155	3.08599	0.01461
C	-7.16712	2.79233	-0.68804
C	-3.74146	0.07223	1.24083
C	3.77280	2.20805	1.22311
C	-4.97309	1.82083	0.03939
C	-5.07897	4.18348	-0.75543
C	3.15516	0.95293	1.25299
C	4.63290	4.30997	0.02834
C	3.68822	5.24989	-0.73861
C	4.02715	2.90595	0.04994
C	5.99817	4.26811	-0.67772
C	-3.17600	-0.35501	0.01125
C	-4.58822	1.21168	-1.15446
C	2.71197	0.41488	0.01495
C	-3.73921	0.10668	-1.21210
C	3.76202	2.24101	-1.14533
C	3.14619	0.99259	-1.21331
C	-3.61493	-0.57943	-2.59615
C	-5.05284	-0.88380	-3.07364
C	-2.89916	-1.93508	-2.58871
C	3.12045	0.34723	-2.62119
C	-2.94426	0.34184	-3.62590
C	4.58258	0.31467	-3.12174
C	2.64580	-1.10718	-2.68138
C	2.27837	1.18655	-3.59471
H	-2.94387	-0.24832	4.63263
H	2.35408	0.60412	4.63272
H	-3.47760	1.20519	3.77684
H	-5.01403	-1.49683	4.03344
H	-6.72706	2.89625	2.00411
H	2.66845	2.10338	3.75002
H	-5.66197	-0.06771	3.22597
H	-5.21814	3.83310	1.97774
H	-6.71396	4.53517	1.35151
H	-1.91080	0.48143	3.39602
H	4.64381	-0.27000	4.10782
H	1.25296	1.12374	3.34772
H	-4.97603	1.55272	2.15813
H	5.05276	1.20879	3.23489
H	-3.04958	-2.50596	3.53001
H	3.89445	4.93076	1.99175



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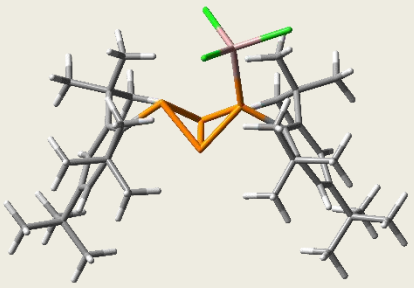
H          5.54791        4.28141        2.01749
H          5.23903        5.89182        1.36646
H         -5.56657       -1.60260        2.35291
H          2.90343       -1.62051        3.63828
H         -7.78805        3.69472       -0.71302
H          4.06395        2.65062        2.16751
H         -1.81577       -1.93387        2.43398
H          5.22349       -0.36152        2.43655
H          1.58393       -1.30462        2.54902
H         -7.72309        2.01042       -0.16099
H         -5.67784        5.10027       -0.79100
H         -3.30505       -2.65298        1.79405
H          2.71211        5.31135       -0.24706
H          3.18216       -1.79998        1.91612
H         -4.12550        4.41731       -0.27120
H          4.11286        6.25880       -0.78162
H         -7.02183        2.46172       -1.72085
H          6.68921        3.59885       -0.15554
H          6.44268        5.26916       -0.69829
H         -4.86590        3.88395       -1.78588
H          3.52443        4.91330       -1.76667
H          5.91334        3.92141       -1.71191
H         -4.97226        1.61143       -2.08795
H          4.05313        2.71575       -2.07629
H         -5.56836       -1.53781       -2.36337
H         -5.65915        0.01618       -3.20185
H         -3.31073       -2.60679       -1.82770
H         -3.47075        1.29646       -3.72056
H         -1.81837       -1.87574       -2.44643
H          3.16806       -1.73944       -1.95609
H          5.20743       -0.28470       -2.45249
H          5.02977        1.30825       -3.20240
H          1.22911        1.22462       -3.28593
H          2.64090        2.21599       -3.67121
H         -1.90633        0.55913       -3.35733
H          1.56711       -1.22687       -2.56871
H         -5.01457       -1.39611       -4.04088
H         -3.04968       -2.42024       -3.55906
H         -2.94174       -0.13817       -4.61052
H          2.88287       -1.51066       -3.67119
H          4.61404       -0.14410       -4.11556
H          2.31900        0.74366       -4.59561
P         -0.33897        0.23794        1.11688
P         -1.55285       -1.27264       -0.00134
P          1.28707       -0.73745        0.00240
P         -0.34213        0.27167       -1.07613
Cl         0.40037       -3.90303        1.77861
Cl         3.46136       -3.63898       -0.04766
Cl         0.39739       -3.84799       -1.87259
Ga         1.33116       -3.15998       -0.03681
```

6.4.2 Optimized structure (PBE0/aug-cc-pVDZ)



Atom	x	y	z
C	-2.96489	0.21670	3.66632
C	2.28695	1.12604	3.65765
C	-5.05231	-1.02255	3.06255
C	-6.11072	3.57088	1.41420
C	-3.61268	-0.69182	2.61124
C	4.61393	0.36987	3.10618
C	4.51572	5.06630	1.42847
C	3.14066	0.35140	2.64223
C	-2.87646	-2.03539	2.58783
C	-4.58215	1.13650	1.21180
C	2.72555	-1.12077	2.66988
C	-5.81293	3.04478	0.00835
C	-7.14975	2.75327	-0.69115
C	-3.73110	0.02239	1.24108
C	3.64653	2.32852	1.22056
C	-4.95859	1.77591	0.03463
C	-5.05647	4.13644	-0.76460
C	3.10925	1.03459	1.25262
C	4.37221	4.48097	0.02215
C	3.37965	5.35145	-0.76453
C	3.85934	3.03967	0.04484
C	5.74694	4.52304	-0.66358
C	-3.16776	-0.41025	0.01075
C	-4.57661	1.16072	-1.15920
C	2.70327	0.46498	0.01434
C	-3.72992	0.05120	-1.21487
C	3.64233	2.35297	-1.14999
C	3.10488	1.06617	-1.21541
C	-3.61360	-0.63860	-2.59828
C	-5.05355	-0.95763	-3.05614
C	-2.88039	-1.98393	-2.59830
C	3.12996	0.41585	-2.62118
C	-2.96289	0.28718	-3.63621
C	4.59958	0.44642	-3.09516
C	2.71574	-1.05584	-2.68067
C	2.26831	1.21325	-3.61194
H	-2.95495	-0.28931	4.64483
H	2.36422	0.65191	4.64882
H	-3.51235	1.16375	3.78524
H	-5.02214	-1.55127	4.02828
H	-6.70423	2.85612	2.00497
H	2.61122	2.17198	3.76279
H	-5.67615	-0.12750	3.19317
H	-5.18827	3.79712	1.97105
H	-6.69373	4.50191	1.34519
H	-1.92460	0.46243	3.40475
H	4.69207	-0.11508	4.09180
H	1.22490	1.13225	3.36826
H	-4.96619	1.51050	2.15970
H	5.02006	1.38644	3.20063
H	-3.05040	-2.55370	3.54356
H	3.55923	5.06021	1.97348
H	5.25950	4.52032	2.02909
H	4.85354	6.11156	1.36038
H	-5.55044	-1.67752	2.33104
H	3.00563	-1.55033	3.64377

```
H         -7.77268        3.66182       -0.71910
H          3.90980        2.79221        2.16935
H         -1.78740       -1.94910        2.47962
H          5.25117       -0.18698        2.40213
H          1.64416       -1.28008        2.57301
H         -7.71117        1.97007       -0.15847
H         -5.65180        5.06300       -0.80008
H         -3.25127       -2.69626        1.79046
H          2.38601        5.34509       -0.29019
H          3.24957       -1.71381        1.90471
H         -4.09401        4.36561       -0.28124
H          3.73439        6.39383       -0.80251
H         -7.00668        2.41707       -1.72911
H          6.47627        3.89863       -0.12472
H          6.13034        5.55584       -0.68537
H         -4.84710        3.83355       -1.80146
H          3.25910        5.00214       -1.80099
H          5.69932        4.16386       -1.70248
H         -4.96429        1.55898       -2.09815
H          3.91031        2.84246       -2.08677
H         -5.55415       -1.62354       -2.33631
H         -5.67510       -0.05881       -3.17157
H         -3.25830       -2.65860       -1.81403
H         -3.50715        1.23823       -3.73688
H         -1.79141       -1.90186       -2.48621
H          3.24391       -1.66609       -1.93197
H          5.24256       -0.12554       -2.40871
H          5.00465        1.46516       -3.16948
H          1.20867        1.21353       -3.31372
H          2.59223        2.26130       -3.69560
H         -1.92172        0.52455       -3.37062
H          1.63487       -1.21833       -2.58267
H         -5.02464       -1.46959       -4.03091
H         -3.05320       -2.48434       -3.56374
H         -2.95508       -0.20013       -4.62419
H          2.99127       -1.46269       -3.66555
H          4.67118       -0.01560       -4.09223
H          2.33733        0.76201       -4.61437
P         -0.32529        0.19234        1.12606
P         -1.53891       -1.34177       -0.00051
P          1.32987       -0.77220        0.00275
P         -0.32816        0.22146       -1.09016
Cl         0.48570       -3.95971        1.80088
Cl         3.61088       -3.64355       -0.03767
Cl         0.48609       -3.91262       -1.88231
Ga         1.44925       -3.25906       -0.03184
```

6.4.3 Thermodynamic data

```
 Absolute energy=-4409.883553
 Zero-point correction=                           0.864348 (Hartree/Particle)
 Thermal correction to Energy=                    0.920582
 Thermal correction to Enthalpy=                  0.921526
 Thermal correction to Gibbs Free Energy=         0.773328
 Sum of electronic and zero-point Energies=          -4409.019205
 Sum of electronic and thermal Energies=             -4408.962971
 Sum of electronic and thermal Enthalpies=           -4408.962027
 Sum of electronic and thermal Free Energies=        -4409.110225
```

6.4.4 NBO analysis (excerpt)

		Natural Population			
Atom No	Natural Charge	Core	Valence	Rydberg	Total
C 1	-0.70069	1.99937	4.69040	0.01093	6.70069
C 2	-0.70175	1.99937	4.69149	0.01089	6.70175
C 3	-0.70243	1.99939	4.69203	0.01101	6.70243
C 4	-0.72099	1.99940	4.71021	0.01139	6.72099
C 5	-0.07891	1.99910	4.06751	0.01230	6.07891
C 6	-0.70289	1.99939	4.69245	0.01106	6.70289
C 7	-0.72162	1.99940	4.71085	0.01137	6.72162
C 8	-0.07862	1.99910	4.06715	0.01236	6.07862
C 9	-0.72756	1.99938	4.71424	0.01394	6.72756
C 10	-0.24258	1.99897	4.23145	0.01217	6.24258
C 11	-0.73416	1.99937	4.72000	0.01479	6.73416
C 12	-0.07353	1.99910	4.06275	0.01167	6.07353
C 13	-0.70559	1.99938	4.69540	0.01081	6.70559
C 14	-0.00153	1.99893	3.98125	0.02135	6.00153
C 15	-0.24309	1.99896	4.23179	0.01234	6.24309
C 16	0.00137	1.99898	3.97936	0.02030	5.99863
C 17	-0.70586	1.99938	4.69574	0.01075	6.70586
C 18	0.02131	1.99893	3.95886	0.02091	5.97869
C 19	-0.07343	1.99910	4.06280	0.01153	6.07343
C 20	-0.70608	1.99938	4.69600	0.01070	6.70608
C 21	0.01250	1.99897	3.96862	0.01991	5.98750
C 22	-0.70604	1.99938	4.69583	0.01083	6.70604
C 23	-0.36116	1.99881	4.34259	0.01976	6.36116
C 24	-0.23733	1.99897	4.22618	0.01219	6.23733
C 25	-0.36959	1.99877	4.34713	0.02369	6.36959
C 26	-0.00449	1.99893	3.98416	0.02141	6.00449
C 27	-0.23739	1.99896	4.22611	0.01232	6.23739
C 28	0.01691	1.99892	3.96318	0.02099	5.98309
C 29	-0.07859	1.99910	4.06719	0.01230	6.07859
C 30	-0.70223	1.99939	4.69182	0.01102	6.70223
C 31	-0.72761	1.99938	4.71428	0.01395	6.72761
C 32	-0.07825	1.99910	4.06678	0.01236	6.07825
C 33	-0.70044	1.99937	4.69015	0.01093	6.70044
C 34	-0.70266	1.99939	4.69221	0.01106	6.70266
C 35	-0.73405	1.99937	4.71990	0.01478	6.73405
C 36	-0.70146	1.99937	4.69120	0.01089	6.70146
H 37	0.24980	0.00000	0.74880	0.00140	0.75020
H 38	0.25103	0.00000	0.74759	0.00138	0.74897
H 39	0.24436	0.00000	0.75442	0.00122	0.75564
H 40	0.24893	0.00000	0.74973	0.00134	0.75107
H 41	0.24690	0.00000	0.75171	0.00138	0.75310
H 42	0.24345	0.00000	0.75533	0.00122	0.75655
H 43	0.24303	0.00000	0.75578	0.00119	0.75697
H 44	0.24986	0.00000	0.74873	0.00140	0.75014
H 45	0.25411	0.00000	0.74463	0.00127	0.74589
H 46	0.24474	0.00000	0.75280	0.00245	0.75526
H 47	0.25047	0.00000	0.74822	0.00131	0.74953
H 48	0.24677	0.00000	0.75077	0.00246	0.75323
H 49	0.24786	0.00000	0.75049	0.00165	0.75214
H 50	0.24188	0.00000	0.75693	0.00119	0.75812
H 51	0.26205	0.00000	0.73656	0.00139	0.73795
H 52	0.25005	0.00000	0.74856	0.00139	0.74995
H 53	0.24781	0.00000	0.75082	0.00137	0.75219

```
    H 54    0.25536      0.00000     0.74338    0.00127     0.74464
    H 55    0.25435      0.00000     0.74437    0.00128     0.74565
    H 56    0.26776      0.00000     0.73094    0.00130     0.73224
    H 57    0.24701      0.00000     0.75162    0.00138     0.75299
    H 58    0.25010      0.00000     0.74825    0.00165     0.74990
    H 59    0.25520      0.00000     0.74137    0.00343     0.74480
    H 60    0.25918      0.00000     0.73958    0.00123     0.74082
    H 61    0.24734      0.00000     0.74953    0.00314     0.75266
    H 62    0.25173      0.00000     0.74696    0.00131     0.74827
    H 63    0.24650      0.00000     0.75212    0.00137     0.75350
    H 64    0.25631      0.00000     0.74164    0.00205     0.74369
    H 65    0.25271      0.00000     0.74598    0.00130     0.74729
    H 66    0.26438      0.00000     0.73330    0.00232     0.73562
    H 67    0.25220      0.00000     0.74649    0.00131     0.74780
    H 68    0.24784      0.00000     0.75079    0.00137     0.75216
    H 69    0.24366      0.00000     0.75512    0.00122     0.75634
    H 70    0.25301      0.00000     0.74571    0.00129     0.74699
    H 71    0.24820      0.00000     0.75043    0.00137     0.75180
    H 72    0.24520      0.00000     0.75358    0.00122     0.75480
    H 73    0.24552      0.00000     0.75327    0.00120     0.75448
    H 74    0.24427      0.00000     0.75452    0.00121     0.75573
    H 75    0.24243      0.00000     0.75606    0.00151     0.75757
    H 76    0.24457      0.00000     0.75393    0.00150     0.75543
    H 77    0.25450      0.00000     0.74423    0.00128     0.74550
    H 78    0.24251      0.00000     0.75632    0.00117     0.75749
    H 79    0.25622      0.00000     0.74173    0.00205     0.74378
    H 80    0.24382      0.00000     0.75497    0.00121     0.75618
    H 81    0.25533      0.00000     0.74124    0.00344     0.74467
    H 82    0.26421      0.00000     0.73348    0.00231     0.73579
    H 83    0.25930      0.00000     0.73946    0.00123     0.74070
    H 84    0.24126      0.00000     0.75757    0.00117     0.75874
    H 85    0.24681      0.00000     0.75072    0.00248     0.75319
    H 86    0.24287      0.00000     0.75592    0.00121     0.75713
    H 87    0.24484      0.00000     0.75272    0.00245     0.75516
    H 88    0.24738      0.00000     0.74950    0.00312     0.75262
    H 89    0.24883      0.00000     0.74982    0.00135     0.75117
    H 90    0.26217      0.00000     0.73644    0.00139     0.73783
    H 91    0.24981      0.00000     0.74879    0.00140     0.75019
    H 92    0.26775      0.00000     0.73095    0.00130     0.73225
    H 93    0.25030      0.00000     0.74838    0.00132     0.74970
    H 94    0.25098      0.00000     0.74764    0.00138     0.74902
    P 95    0.08298      9.99888     4.86851    0.04963    14.91702
    P 96    0.33417      9.99862     4.61575    0.05145    14.66583
    P 97    0.24575      9.99781     4.69394    0.06251    14.75425
    P 98    0.08315      9.99888     4.86835    0.04962    14.91685
  Cl 99    -0.47831      9.99974     7.47237    0.00621    17.47831
  Cl100    -0.48441      9.99975     7.47844    0.00622    17.48441
  Cl101    -0.47841      9.99974     7.47247    0.00620    17.47841
  Ga102     1.07877     27.99118     1.87570    0.05435    29.92123
 ===============================================================
 * Total *  0.00000    169.95513   245.16524    0.87962   416.00000
```

```
     (Occupancy)   Bond orbital / Coefficients / Hybrids
 ------------------ Lewis ----------------------------------------------------
 [...]
  86. (1.97973) LP ( 1) P 95           s( 74.10%)p 0.35( 25.85%)d 0.00(  0.05%)
                                        0.0000  0.0000  0.8608  0.0026  0.0014
                                        0.0000 -0.0470 -0.0014  0.0000  0.3077
                                       -0.0064  0.0000  0.4016 -0.0171  0.0022
```

```
                                      0.0032 -0.0179  0.0069 -0.0089
  87. (1.94805) LP ( 1) P 96         s( 70.11%)p 0.43( 29.85%)d 0.00(  0.04%)
                                      0.0000  0.0000  0.8373  0.0047  0.0005
                                      0.0000  0.1372 -0.0195  0.0000 -0.5283
                                      0.0079  0.0000 -0.0079  0.0002  0.0083
                                      0.0001 -0.0005  0.0127  0.0138
  88. (1.65818) LP ( 1) P 97         s( 60.12%)p 0.66( 39.85%)d 0.00(  0.03%)
                                      0.0000  0.0000  0.7752  0.0153  0.0015
                                      0.0000  0.0055  0.0103  0.0000 -0.6301
                                      0.0360  0.0000 -0.0093  0.0005 -0.0028
                                      0.0000  0.0005 -0.0168 -0.0071
  89. (1.97970) LP ( 1) P 98         s( 74.10%)p 0.35( 25.85%)d 0.00(  0.05%)
                                      0.0000  0.0000  0.8608  0.0026  0.0014
                                      0.0000 -0.0484 -0.0015  0.0000  0.3198
                                     -0.0068  0.0000 -0.3918  0.0170  0.0024
                                     -0.0032  0.0181  0.0075 -0.0079
 [...]
201. (1.94993) BD ( 1) P 95- P 96
               ( 52.03%)   0.7213* P 95 s(  9.67%)p 9.26( 89.51%)d 0.09(  0.82%)
                                      0.0000  0.0000  0.3109  0.0038 -0.0027
                                      0.0000 -0.5875 -0.0074  0.0000 -0.7187
                                      0.0044  0.0000 -0.1818  0.0170  0.0509
                                      0.0435  0.0555 -0.0242 -0.0091
               ( 47.97%)   0.6926* P 96 s(  7.44%)p12.33( 91.71%)d 0.11(  0.85%)
                                      0.0000  0.0000  0.2723  0.0150 -0.0020
                                      0.0000  0.3775  0.0113  0.0000  0.5187
                                      0.0031  0.0000  0.7109 -0.0079  0.0513
                                      0.0395  0.0623 -0.0163 -0.0125
 202. (1.94990) BD ( 1) P 95- P 97
               ( 44.60%)   0.6678* P 95 s(  9.34%)p 9.60( 89.68%)d 0.10(  0.97%)
                                      0.0000  0.0000  0.3051 -0.0180 -0.0024
                                      0.0000  0.7955  0.0243  0.0000 -0.4746
                                      0.0094  0.0000 -0.1942  0.0194 -0.0613
                                     -0.0625  0.0389  0.0189 -0.0137
               ( 55.40%)   0.7443* P 97 s( 10.15%)p 8.78( 89.19%)d 0.06(  0.65%)
                                      0.0000  0.0000  0.3186  0.0013 -0.0030
                                      0.0000 -0.4943 -0.0115  0.0000  0.3763
                                     -0.0038  0.0000  0.7112  0.0058 -0.0431
                                     -0.0525  0.0338  0.0274  0.0003
 203. (1.95956) BD ( 1) P 95- P 98
               ( 49.99%)   0.7071* P 95 s(  6.89%)p13.40( 92.24%)d 0.13(  0.88%)
                                      0.0000  0.0000  0.2624  0.0004 -0.0035
                                      0.0000 -0.0759 -0.0066  0.0000  0.3949
                                      0.0318  0.0000 -0.8715  0.0081  0.0069
                                     -0.0008 -0.0078  0.0076  0.0928
               ( 50.01%)   0.7071* P 98 s(  6.89%)p13.39( 92.23%)d 0.13(  0.88%)
                                      0.0000  0.0000  0.2624  0.0004 -0.0035
                                      0.0000 -0.0734 -0.0065  0.0000  0.3679
                                      0.0320  0.0000  0.8835 -0.0073  0.0068
                                      0.0015  0.0026  0.0077  0.0931
 204. (1.94958) BD ( 1) P 96- P 98
               ( 47.98%)   0.6927* P 96 s(  7.43%)p12.34( 91.72%)d 0.11(  0.85%)
                                      0.0000  0.0000  0.2722  0.0153 -0.0020
                                      0.0000  0.3770  0.0112  0.0000  0.5395
                                      0.0032  0.0000 -0.6956  0.0080  0.0523
                                     -0.0379 -0.0612 -0.0183 -0.0155
               ( 52.02%)   0.7213* P 98 s(  9.66%)p 9.27( 89.52%)d 0.09(  0.82%)
                                      0.0000  0.0000  0.3108  0.0038 -0.0027
                                      0.0000 -0.5869 -0.0073  0.0000 -0.7241
                                      0.0049  0.0000  0.1614 -0.0171  0.0520
```

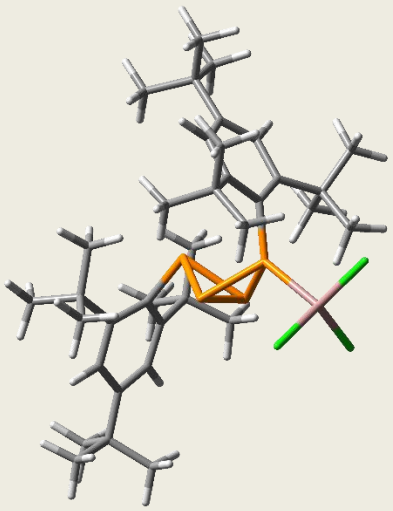
```
                                       -0.0418 -0.0543 -0.0261 -0.0118
 205. (1.94989) BD ( 1) P 97- P 98
              ( 55.39%)   0.7442* P 97 s( 10.15%)p 8.79( 89.20%)d 0.06(  0.65%)
                                        0.0000  0.0000  0.3186  0.0013 -0.0030
                                        0.0000 -0.4978 -0.0113  0.0000  0.3971
                                       -0.0035  0.0000 -0.6974 -0.0058 -0.0449
                                        0.0511 -0.0345  0.0265 -0.0018
              ( 44.61%)   0.6679* P 98 s(  9.35%)p 9.59( 89.67%)d 0.10(  0.97%)
                                        0.0000  0.0000  0.3053 -0.0181 -0.0024
                                        0.0000  0.7961  0.0243  0.0000 -0.4802
                                        0.0097  0.0000  0.1771 -0.0189 -0.0634
                                        0.0605 -0.0385  0.0179 -0.0162
 [...]
 ---------------- non-Lewis ----------------------------------------------------
 209. (0.39762) LV ( 1)Ga102           s(  5.28%)p17.92( 94.64%)d 0.01(  0.08%)
                                        0.0000  0.0000  0.0000  0.2270  0.0226
                                       -0.0277  0.0013 -0.0002  0.0000  0.0000
                                       -0.0628  0.0108  0.0000  0.0000  0.9706
                                       -0.0066  0.0000  0.0000  0.0151 -0.0001
                                        0.0000 -0.0060  0.0000 -0.0001  0.0000
                                        0.0008  0.0000 -0.0205  0.0000 -0.0174
```

```
NLMO / Occupancy / Percent from Parent NBO / Atomic Hybrid Contributions
 ---------------------------------------------------------------------------
 [...]
  88. (2.00000)  81.5777% LP ( 1) P 97
                          0.023%  C 11 s( 11.97%)p 7.16( 85.71%)d 0.19(  2.31%)
                          0.054%  C 18 s( 16.81%)p 4.90( 82.44%)d 0.04(  0.75%)
                          0.018%  C 21 s(  4.20%)p22.79( 95.79%)d 0.00(  0.01%)
                          0.116%  C 23 s( 27.75%)p 2.60( 72.16%)d 0.00(  0.09%)
                          0.206%  C 25 s(  7.22%)p12.75( 92.06%)d 0.10(  0.72%)
                          0.049%  C 28 s( 19.14%)p 4.18( 80.04%)d 0.04(  0.82%)
                          0.023%  C 35 s( 11.97%)p 7.16( 85.74%)d 0.19(  2.29%)
                          0.011%  H 56 s( 99.84%)p 0.00(  0.16%)
                          0.011%  H 61 s( 98.02%)p 0.02(  1.98%)
                          0.011%  H 88 s( 98.04%)p 0.02(  1.96%)
                          0.010%  H 92 s( 99.85%)p 0.00(  0.15%)
                          0.124%  P 95 s(  2.17%)p38.25( 83.17%)d 6.74( 14.65%)
                          0.212%  P 96 s( 14.43%)p 5.50( 79.31%)d 0.43(  6.26%)
                         81.692%  P 97 s( 56.47%)p 0.77( 43.47%)d 0.00(  0.06%)
                          0.126%  P 98 s(  2.03%)p41.09( 83.41%)d 7.18( 14.56%)
                          0.262% Cl 99 s( 25.39%)p 2.89( 73.43%)d 0.05(  1.18%)
                          0.285% Cl100 s( 25.81%)p 2.83( 72.98%)d 0.05(  1.21%)
                          0.262% Cl101 s( 25.31%)p 2.90( 73.51%)d 0.05(  1.18%)
                         16.446% Ga102 s( 39.70%)p 1.51( 60.05%)d 0.01(  0.24%)
```

6.5 *endo-exo*-Mes*P_4Mes*·$GaCl_3$ (5b·$GaCl_3$)

6.5.1 Optimized structure (PBE0/6-31g(d,p))

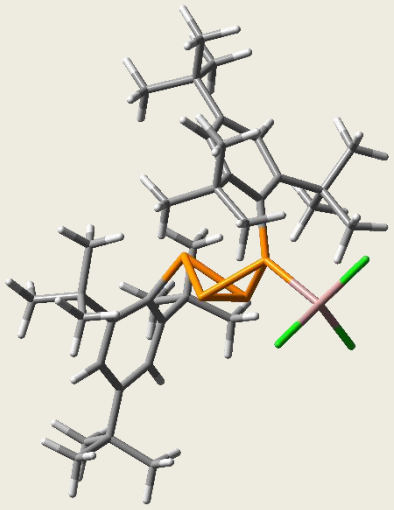
Atom	x	y	z
C	4.53962	4.97320	0.66421
C	3.20654	5.23149	-1.41980
C	2.04504	5.23827	0.77880
C	3.20691	4.62001	-0.01630
C	3.03284	3.10136	-0.04473
C	2.97425	2.36781	-1.22338
C	2.99318	2.38022	1.14802
C	-1.69279	2.40286	-2.54475
C	4.23823	0.76088	-3.22301
C	-4.09436	2.43716	-3.00466
C	-1.67199	2.40176	2.57197
C	4.28876	0.80939	3.15698
C	-4.07124	2.44115	3.04470
C	2.72718	0.99186	-1.25680
C	2.74874	1.01021	1.20758
C	1.76508	0.73735	-3.59930
C	-2.93675	1.50776	-2.57455
C	2.88134	0.30923	-2.63655
C	1.82122	0.77091	3.56469
C	-2.91749	1.50922	2.60906
C	2.92839	0.34252	2.59198
C	2.45346	0.35189	-0.01978
C	-2.62272	1.05223	0.01814
C	-3.33835	0.90572	-1.20492
C	-3.32856	0.90876	1.24211
C	-2.75697	0.42525	-3.64889
C	-2.73434	0.42711	3.68335
C	-4.58521	0.28213	-1.15809
C	2.94925	-1.22043	-2.59437
C	-4.58066	0.28260	1.20834
C	3.00660	-1.18687	2.56109
C	-7.59659	-0.03811	-0.68578
C	-5.19571	-0.12054	0.02915
C	-6.51446	-0.89308	-0.00620
C	-7.00518	-1.26530	1.39551
C	-6.31048	-2.19055	-0.80550
H	4.67205	6.06027	0.69352
H	3.29425	6.31979	-1.34418
H	2.15285	6.32774	0.81937
H	4.58309	4.60554	1.69373
H	5.38452	4.54165	0.11829
H	4.05038	4.87688	-2.02096
H	2.27974	5.01062	-1.95974
H	2.01296	4.86779	1.80768
H	1.08350	5.00605	0.30981
H	3.12005	2.87988	-2.16613
H	3.15857	2.91047	2.07981
H	4.28816	1.83496	-3.41635
H	-1.75711	3.15627	-1.75222
H	-1.61822	2.93650	-3.49857
H	4.33266	1.88546	3.34096
H	-4.25911	3.22399	-2.26170



```
H         -1.73873        3.15496        1.77945
H         -3.84637        2.91454       -3.95900
H         -4.23843        3.22779        2.30205
H         -1.59092        2.93584        3.52499
H          1.69684        1.82618       -3.68713
H         -3.81672        2.91874        3.99718
H          5.06068        0.49825       -2.55070
H          1.74680        1.86006        3.64369
H          4.40474        0.25071       -4.17736
H          5.10475        0.54788        2.47648
H         -0.75786        1.85232       -2.42369
H         -0.73905        1.84905        2.44635
H          4.47152        0.30894        4.11349
H         -5.03683        1.90156       -3.13911
H          1.95594        0.32862       -4.59735
H         -5.01376        1.90719        3.18497
H          2.02619        0.37183        4.56385
H         -2.54235        0.89077       -4.61712
H          0.79000        0.36228       -3.27248
H          0.84509        0.38680        3.25188
H         -2.51365        0.89330        4.64988
H         -7.75648        0.89798       -0.14103
H         -1.93218       -0.25208       -3.40988
H         -5.10655        0.10709       -2.09431
H          3.27696       -1.58722       -3.57261
H         -3.65891       -0.18259       -3.76498
H         -7.32994        0.21447       -1.71649
H          3.67730       -1.57856       -1.85975
H         -5.08832        0.10769        2.14982
H          3.72542       -1.54627        1.81811
H         -1.91187       -0.25172        3.44063
H          3.35097       -1.54391        3.53721
H         -3.63676       -0.17885        3.80504
H          1.98403       -1.70006       -2.41914
H          2.04175       -1.67346        2.40384
H         -8.54647       -0.58333       -0.71351
H         -7.22949       -0.37981        1.99986
H         -5.99217       -1.98988       -1.83285
H         -6.27139       -1.87465        1.93325
H         -7.92755       -1.84936        1.31773
H         -5.54993       -2.82370       -0.33812
H         -7.24636       -2.75822       -0.85117
P         -0.74671        1.08014        0.00780
P          1.36791       -1.12171       -0.00057
P         -0.52578       -0.86486       -1.08648
P         -0.50552       -0.85320        1.11794
Cl         4.07174       -3.68959       -0.00961
Cl         0.94106       -4.24865       -1.76867
Cl         0.97527       -4.22618        1.81549
Ga         1.91353       -3.46478        0.00942
```

6.5.2 Optimized structure (PBE0/aug-cc-pVDZ)

Atom	x	y	z
C	4.54670	4.98650	0.67597
C	3.22986	5.24145	-1.41777
C	2.05106	5.24710	0.77131
C	3.22027	4.63205	-0.01422
C	3.04894	3.11224	-0.04303
C	2.99013	2.37782	-1.22309
C	3.01120	2.38843	1.15010
C	-1.67731	2.43344	-2.53439
C	4.26102	0.76832	-3.21955
C	-4.07984	2.48066	-2.99316
C	-1.65998	2.42092	2.57332
C	4.31370	0.81373	3.15420
C	-4.06131	2.47346	3.03905
C	2.74636	0.99888	-1.25745
C	2.76962	1.01555	1.20890
C	1.78753	0.75442	-3.59978
C	-2.92519	1.54574	-2.57125
C	2.90209	0.31974	-2.63903
C	1.84589	0.78083	3.56540
C	-2.91007	1.53664	2.61138
C	2.95206	0.34933	2.59394
C	2.47594	0.35579	-0.01977
C	-2.61260	1.08187	0.02030
C	-3.32714	0.93641	-1.20511
C	-3.31902	0.93415	1.24491
C	-2.75063	0.46896	-3.65138
C	-2.73568	0.45633	3.68815
C	-4.57451	0.30951	-1.16065
C	2.96142	-1.20934	-2.59830
C	-4.57140	0.30438	1.20893
C	3.02378	-1.17944	2.56150
C	-7.58572	-0.02528	-0.68648
C	-5.18493	-0.09984	0.02684
C	-6.50101	-0.87832	-0.01031
C	-6.98811	-1.25629	1.39028
C	-6.29030	-2.17168	-0.81309
H	4.68058	6.07968	0.70592
H	3.32183	6.33565	-1.34382
H	2.15445	6.34321	0.81351
H	4.58297	4.61851	1.71227
H	5.40129	4.55189	0.13473
H	4.07936	4.88105	-2.01817
H	2.30088	5.02315	-1.96696
H	2.01142	4.87460	1.80588
H	1.08792	5.01040	0.29268
H	3.13706	2.89199	-2.17072
H	3.17859	2.91932	2.08745
H	4.31796	1.85022	-3.40175
H	-1.73842	3.18566	-1.73209
H	-1.59588	2.97556	-3.48949
H	4.36303	1.89714	3.32989
H	-4.24272	3.26724	-2.24015
H	-1.72160	3.17653	1.77427
H	-3.83101	2.96758	-3.94957
H	-4.22381	3.26282	2.28885
H	-1.57329	2.95919	3.53012



```
H          1.73203        1.84922       -3.69777
H         -3.80838        2.95673        3.99622
H          5.08608        0.49240       -2.54518
H          1.78296        1.87585        3.65686
H          4.42737        0.26404       -4.18412
H          5.13287        0.54177        2.47112
H         -0.74207        1.87249       -2.41023
H         -0.72688        1.85781        2.44369
H          4.49695        0.31696        4.11958
H         -5.02929        1.94525       -3.13011
H          1.96750        0.33306       -4.60142
H         -5.01162        1.93986        3.17688
H          2.04041        0.36699        4.56747
H         -2.53369        0.93990       -4.62350
H          0.80416        0.39465       -3.26053
H          0.86173        0.41148        3.23901
H         -2.51544        0.92438        4.66091
H         -7.74960        0.91445       -0.13634
H         -1.92339       -0.21677       -3.41577
H         -5.09835        0.13776       -2.10239
H          3.31342       -1.58207       -3.57222
H         -3.65989       -0.13853       -3.77137
H         -7.31937        0.23299       -1.72252
H          3.66790       -1.57766       -1.83893
H         -5.08334        0.12886        2.15425
H          3.71991       -1.54684        1.79225
H         -1.91027       -0.23036        3.44884
H          3.39454       -1.54372        3.53163
H         -3.64594       -0.14944        3.80885
H          1.98480       -1.68599       -2.44021
H          2.04810       -1.66399        2.42247
H         -8.53999       -0.57539       -0.71640
H         -7.21432       -0.36954        2.00257
H         -5.97148       -1.96563       -1.84586
H         -6.24868       -1.86909        1.92853
H         -7.91450       -1.84549        1.31292
H         -5.52138       -2.80572       -0.34534
H         -7.22756       -2.74891       -0.86130
P         -0.72599        1.09775        0.01100
P          1.38905       -1.13558       -0.00076
P         -0.51958       -0.86368       -1.09752
P         -0.49789       -0.85442        1.13156
Cl         4.03963       -3.81203       -0.01366
Cl         0.85040       -4.25372       -1.79646
Cl         0.88821       -4.23536        1.83846
Ga         1.87204       -3.54910        0.00705
```

6.5.3 Thermodynamic data

```
Absolute energy=-4409.8809576
 Zero-point correction=                           0.864337 (Hartree/Particle)
 Thermal correction to Energy=                    0.920504
 Thermal correction to Enthalpy=                  0.921448
 Thermal correction to Gibbs Free Energy=         0.773793
 Sum of electronic and zero-point Energies=          -4409.016621
 Sum of electronic and thermal Energies=             -4408.960454
 Sum of electronic and thermal Enthalpies=           -4408.959510
 Sum of electronic and thermal Free Energies=        -4409.107165
```

6.5.4 NBO analysis (excerpt)

		Natural Population			
Atom No	Natural Charge	Core	Valence	Rydberg	Total
C 1	-0.70586	1.99938	4.69573	0.01075	6.70586
C 2	-0.72132	1.99940	4.71068	0.01125	6.72132
C 3	-0.70559	1.99938	4.69549	0.01072	6.70559
C 4	-0.07201	1.99909	4.06157	0.01134	6.07201
C 5	0.01530	1.99897	3.96640	0.01933	5.98470
C 6	-0.24640	1.99894	4.23471	0.01275	6.24640
C 7	-0.24053	1.99895	4.22887	0.01272	6.24053
C 8	-0.72082	1.99938	4.70839	0.01306	6.72082
C 9	-0.70389	1.99939	4.69341	0.01109	6.70389
C 10	-0.70204	1.99939	4.69156	0.01109	6.70204
C 11	-0.72056	1.99938	4.70812	0.01306	6.72056
C 12	-0.70380	1.99939	4.69330	0.01111	6.70380
C 13	-0.70217	1.99939	4.69170	0.01108	6.70217
C 14	0.02303	1.99892	3.95655	0.02150	5.97697
C 15	0.01900	1.99891	3.96049	0.02160	5.98100
C 16	-0.69819	1.99936	4.68785	0.01098	6.69819
C 17	-0.07608	1.99910	4.06475	0.01224	6.07608
C 18	-0.07763	1.99909	4.06649	0.01205	6.07763
C 19	-0.69765	1.99936	4.68731	0.01098	6.69765
C 20	-0.07642	1.99910	4.06509	0.01224	6.07642
C 21	-0.07725	1.99909	4.06612	0.01204	6.07725
C 22	-0.37394	1.99876	4.35333	0.02185	6.37394
C 23	-0.36081	1.99881	4.34242	0.01958	6.36081
C 24	-0.01263	1.99893	3.99216	0.02155	6.01263
C 25	-0.00967	1.99893	3.98926	0.02148	6.00967
C 26	-0.70246	1.99937	4.69192	0.01117	6.70246
C 27	-0.70269	1.99937	4.69215	0.01117	6.70269
C 28	-0.23598	1.99896	4.22471	0.01232	6.23598
C 29	-0.73305	1.99938	4.71933	0.01435	6.73305
C 30	-0.24145	1.99896	4.23018	0.01230	6.24145
C 31	-0.73266	1.99938	4.71896	0.01433	6.73266
C 32	-0.70499	1.99938	4.69498	0.01063	6.70499
C 33	0.00349	1.99897	3.97735	0.02018	5.99651
C 34	-0.07371	1.99910	4.06301	0.01160	6.07371
C 35	-0.72125	1.99940	4.71047	0.01139	6.72125
C 36	-0.70705	1.99938	4.69671	0.01096	6.70705
H 37	0.24824	0.00000	0.75037	0.00140	0.75176
H 38	0.25524	0.00000	0.74348	0.00128	0.74476
H 39	0.24749	0.00000	0.75112	0.00139	0.75251
H 40	0.24438	0.00000	0.75443	0.00120	0.75562
H 41	0.25269	0.00000	0.74602	0.00129	0.74731
H 42	0.24764	0.00000	0.75100	0.00136	0.75236
H 43	0.25007	0.00000	0.74854	0.00139	0.74993
H 44	0.24526	0.00000	0.75354	0.00120	0.75474
H 45	0.25273	0.00000	0.74590	0.00137	0.74727
H 46	0.25077	0.00000	0.74761	0.00162	0.74923
H 47	0.24529	0.00000	0.75322	0.00149	0.75471
H 48	0.24123	0.00000	0.75757	0.00120	0.75877
H 49	0.25202	0.00000	0.74591	0.00207	0.74798
H 50	0.25738	0.00000	0.74120	0.00142	0.74262
H 51	0.24047	0.00000	0.75835	0.00118	0.75953
H 52	0.25283	0.00000	0.74586	0.00130	0.74717
H 53	0.25221	0.00000	0.74573	0.00207	0.74779

```
    H 54    0.24701      0.00000     0.75163    0.00136     0.75299
    H 55    0.25265      0.00000     0.74604    0.00130     0.74735
    H 56    0.25743      0.00000     0.74115    0.00142     0.74257
    H 57    0.24556      0.00000     0.75319    0.00126     0.75444
    H 58    0.24717      0.00000     0.75148    0.00135     0.75283
    H 59    0.25791      0.00000     0.74085    0.00124     0.74209
    H 60    0.24524      0.00000     0.75350    0.00125     0.75476
    H 61    0.25175      0.00000     0.74694    0.00131     0.74825
    H 62    0.25805      0.00000     0.74071    0.00124     0.74195
    H 63    0.24599      0.00000     0.75087    0.00314     0.75401
    H 64    0.24561      0.00000     0.75125    0.00314     0.75439
    H 65    0.25170      0.00000     0.74699    0.00131     0.74830
    H 66    0.24559      0.00000     0.75326    0.00115     0.75441
    H 67    0.25363      0.00000     0.74498    0.00139     0.74637
    H 68    0.24601      0.00000     0.75282    0.00117     0.75399
    H 69    0.25357      0.00000     0.74503    0.00139     0.74643
    H 70    0.24781      0.00000     0.75079    0.00140     0.75219
    H 71    0.23805      0.00000     0.75968    0.00228     0.76195
    H 72    0.23772      0.00000     0.75995    0.00233     0.76228
    H 73    0.24781      0.00000     0.75079    0.00140     0.75219
    H 74    0.25018      0.00000     0.74849    0.00133     0.74982
    H 75    0.24825      0.00000     0.74926    0.00249     0.75175
    H 76    0.24323      0.00000     0.75528    0.00149     0.75677
    H 77    0.26705      0.00000     0.73166    0.00129     0.73295
    H 78    0.24759      0.00000     0.75124    0.00117     0.75241
    H 79    0.24286      0.00000     0.75592    0.00122     0.75714
    H 80    0.26544      0.00000     0.73250    0.00207     0.73456
    H 81    0.24867      0.00000     0.74970    0.00162     0.75133
    H 82    0.26557      0.00000     0.73238    0.00205     0.73443
    H 83    0.24833      0.00000     0.74915    0.00252     0.75167
    H 84    0.26701      0.00000     0.73169    0.00129     0.73299
    H 85    0.24799      0.00000     0.75084    0.00117     0.75201
    H 86    0.24810      0.00000     0.74880    0.00310     0.75190
    H 87    0.24771      0.00000     0.74918    0.00311     0.75229
    H 88    0.24767      0.00000     0.75093    0.00139     0.75233
    H 89    0.24482      0.00000     0.75378    0.00140     0.75518
    H 90    0.24516      0.00000     0.75364    0.00120     0.75484
    H 91    0.25238      0.00000     0.74625    0.00137     0.74762
    H 92    0.25483      0.00000     0.74392    0.00126     0.74517
    H 93    0.25650      0.00000     0.74224    0.00126     0.74350
    H 94    0.24703      0.00000     0.75163    0.00135     0.75297
    P 95    0.29158      9.99878     4.66242    0.04722    14.70842
    P 96    0.22941      9.99785     4.70668    0.06606    14.77059
    P 97    0.10876      9.99894     4.84380    0.04850    14.89124
    P 98    0.10784      9.99894     4.84469    0.04854    14.89216
  Cl 99    -0.47779      9.99976     7.47183    0.00620    17.47779
  Cl100    -0.47522      9.99976     7.46927    0.00619    17.47522
  Cl101    -0.47524      9.99976     7.46929    0.00619    17.47524
  Ga102     1.09184     27.99106     1.86782    0.04928    29.90816
=======================================================================
* Total *  0.00000    169.95526   245.17752    0.86722   416.00000
```

```
     (Occupancy)   Bond orbital / Coefficients / Hybrids
------------------ Lewis ----------------------------------------------------
[...]
 86. (1.97901) LP ( 1) P 95           s( 70.16%)p 0.42( 29.80%)d 0.00(  0.04%)
                                       0.0000  0.0000  0.8376  0.0031  0.0006
                                       0.0000  0.3712 -0.0118  0.0000  0.4001
                                      -0.0013  0.0000 -0.0048  0.0003 -0.0141
```

```
                                      0.0002  0.0002 -0.0016  0.0149
  87. (1.64435) LP ( 1) P 96           s( 56.67%)p 0.76( 43.29%)d 0.00(  0.04%)
                                       0.0000  0.0000  0.7526  0.0140  0.0019
                                       0.0000  0.2019  0.0002  0.0000 -0.6249
                                       0.0409  0.0000  0.0016 -0.0003 -0.0089
                                       0.0001 -0.0001 -0.0181 -0.0059
  88. (1.97628) LP ( 1) P 97           s( 74.64%)p 0.34( 25.32%)d 0.00(  0.05%)
                                       0.0000  0.0000  0.8639  0.0026  0.0012
                                       0.0000 -0.2263  0.0065  0.0000 -0.2113
                                      -0.0014  0.0000 -0.3963  0.0151 -0.0067
                                      -0.0133 -0.0136 -0.0002 -0.0075
  89. (1.97612) LP ( 1) P 98           s( 74.64%)p 0.34( 25.31%)d 0.00(  0.05%)
                                       0.0000  0.0000  0.8640  0.0026  0.0012
                                       0.0000 -0.2189  0.0064  0.0000 -0.2075
                                      -0.0015  0.0000  0.4023 -0.0152 -0.0063
                                       0.0130  0.0136 -0.0001 -0.0081
 [...]
201. (1.95340) BD ( 1) P 95- P 97
               ( 48.73%)   0.6981* P 95 s(  7.66%)p11.95( 91.53%)d 0.11(  0.81%)
                                       0.0000  0.0000  0.2763  0.0150 -0.0022
                                       0.0000  0.0657  0.0096  0.0000 -0.6477
                                      -0.0015  0.0000 -0.7009  0.0089 -0.0081
                                      -0.0022  0.0704 -0.0537 -0.0145
               ( 51.27%)   0.7160* P 97 s(  8.72%)p10.37( 90.44%)d 0.10(  0.84%)
                                       0.0000  0.0000  0.2952  0.0052 -0.0021
                                       0.0000 -0.0635 -0.0126  0.0000  0.9314
                                       0.0034  0.0000  0.1809 -0.0032  0.0020
                                      -0.0071  0.0702 -0.0573 -0.0123
 202. (1.95371) BD ( 1) P 95- P 98
               ( 48.72%)   0.6980* P 95 s(  7.68%)p11.92( 91.51%)d 0.11(  0.81%)
                                       0.0000  0.0000  0.2767  0.0145 -0.0022
                                       0.0000  0.0759  0.0096  0.0000 -0.6408
                                      -0.0010  0.0000  0.7060 -0.0094 -0.0093
                                       0.0028 -0.0711 -0.0529 -0.0135
               ( 51.28%)   0.7161* P 98 s(  8.73%)p10.36( 90.43%)d 0.10(  0.84%)
                                       0.0000  0.0000  0.2953  0.0052 -0.0021
                                       0.0000 -0.0676 -0.0128  0.0000  0.9293
                                       0.0036  0.0000 -0.1896  0.0031  0.0007
                                       0.0078 -0.0710 -0.0563 -0.0113
 203. (1.95268) BD ( 1) P 96- P 97
               ( 55.57%)   0.7454* P 96 s( 11.62%)p 7.55( 87.73%)d 0.06(  0.64%)
                                       0.0000  0.0000  0.3409  0.0046 -0.0027
                                       0.0000 -0.5812 -0.0230  0.0000  0.2179
                                      -0.0350  0.0000 -0.7002 -0.0074 -0.0240
                                       0.0592 -0.0165  0.0454 -0.0013
               ( 44.43%)   0.6666* P 97 s(  9.62%)p 9.29( 89.39%)d 0.10(  0.99%)
                                       0.0000  0.0000  0.3096 -0.0181 -0.0023
                                       0.0000  0.9260  0.0091  0.0000 -0.0645
                                      -0.0121  0.0000  0.1779 -0.0219  0.0004
                                       0.0724 -0.0065  0.0658 -0.0166
 204. (1.95265) BD ( 1) P 96- P 98
               ( 55.56%)   0.7454* P 96 s( 11.63%)p 7.55( 87.73%)d 0.05(  0.64%)
                                       0.0000  0.0000  0.3409  0.0047 -0.0026
                                       0.0000 -0.5680 -0.0228  0.0000  0.2258
                                      -0.0349  0.0000  0.7084  0.0082 -0.0243
                                      -0.0597  0.0175  0.0439  0.0003
               ( 44.44%)   0.6666* P 98 s(  9.62%)p 9.29( 89.39%)d 0.10(  0.99%)
                                       0.0000  0.0000  0.3096 -0.0180 -0.0022
                                       0.0000  0.9226  0.0092  0.0000 -0.0658
                                      -0.0122  0.0000 -0.1943  0.0219 -0.0001
```

```
                                       -0.0740  0.0069  0.0643 -0.0144
205. (1.93035) BD ( 1) P 97- P 98
              ( 49.99%)   0.7070* P 97 s(  7.03%)p13.10( 92.05%)d 0.13(  0.92%)
                                        0.0000  0.0000  0.2651 -0.0003 -0.0039
                                        0.0000 -0.2743 -0.0217  0.0000 -0.2722
                                       -0.0139  0.0000  0.8778 -0.0062 -0.0119
                                       -0.0005 -0.0044 -0.0051  0.0949
              ( 50.01%)   0.7072* P 98 s(  7.01%)p13.13( 92.07%)d 0.13(  0.92%)
                                        0.0000  0.0000  0.2648 -0.0004 -0.0039
                                        0.0000 -0.2902 -0.0218  0.0000 -0.2817
                                       -0.0138  0.0000 -0.8697  0.0067 -0.0118
                                        0.0037  0.0063 -0.0052  0.0947
[...]
---------------- non-Lewis ----------------------------------------------------
209. (0.39109) LV ( 1)Ga102           s(  5.25%)p18.05( 94.67%)d 0.02(  0.09%)
                                        0.0000  0.0000  0.0000  0.2270  0.0061
                                       -0.0300  0.0017  0.0000  0.0000  0.0000
                                       -0.1809  0.0134  0.0000  0.0000  0.9558
                                       -0.0106  0.0000  0.0000 -0.0044 -0.0001
                                        0.0000 -0.0139  0.0000  0.0001  0.0000
                                       -0.0001  0.0000 -0.0242  0.0000 -0.0097
```

```
NLMO / Occupancy / Percent from Parent NBO / Atomic Hybrid Contributions
--------------------------------------------------------------------------------
[...]
 87. (2.00000)  80.9303% LP ( 1) P 96
                          0.026%  C  5 s(  3.20%)p30.23( 96.79%)d 0.00(  0.00%)
                          0.069%  C 14 s( 12.57%)p 6.90( 86.74%)d 0.06(  0.70%)
                          0.062%  C 15 s( 14.91%)p 5.65( 84.31%)d 0.05(  0.78%)
                          0.213%  C 22 s(  4.38%)p21.67( 94.83%)d 0.18(  0.80%)
                          0.039%  C 23 s( 18.86%)p 4.27( 80.56%)d 0.03(  0.58%)
                          0.014%  C 25 s(  0.48%)p99.99( 99.22%)d 0.61(  0.30%)
                          0.030%  C 29 s( 13.29%)p 6.40( 85.01%)d 0.13(  1.71%)
                          0.031%  C 31 s( 13.59%)p 6.24( 84.77%)d 0.12(  1.64%)
                          0.010%  H 77 s( 99.80%)p 0.00(  0.20%)
                          0.014%  H 80 s( 99.42%)p 0.01(  0.58%)
                          0.013%  H 82 s( 99.46%)p 0.01(  0.54%)
                          0.010%  H 84 s( 99.80%)p 0.00(  0.20%)
                          0.015%  H 86 s( 96.92%)p 0.03(  3.08%)
                          0.016%  H 87 s( 96.96%)p 0.03(  3.04%)
                          0.179%  P 95 s( 24.46%)p 2.84( 69.51%)d 0.25(  6.03%)
                         81.066%  P 96 s( 52.63%)p 0.90( 47.30%)d 0.00(  0.07%)
                          0.217%  P 97 s(  1.58%)p53.51( 84.67%)d 8.69( 13.75%)
                          0.220%  P 98 s(  1.60%)p53.13( 84.80%)d 8.53( 13.61%)
                          0.279% Cl 99 s( 24.30%)p 3.06( 74.42%)d 0.05(  1.28%)
                          0.292% Cl100 s( 22.95%)p 3.30( 75.76%)d 0.06(  1.29%)
                          0.292% Cl101 s( 22.96%)p 3.30( 75.75%)d 0.06(  1.29%)
                         16.832% Ga102 s( 39.51%)p 1.52( 60.20%)d 0.01(  0.29%)
```

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