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Supplementary Information

"A NHC-phosphinidenyl as synthon for new group 13/15 compounds"

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Content

Experimental Section……S2

Crystal Structure Data……S6

^{1}H NMR spectra of compound **1**……S7

^{1}H NMR spectra of compound **IMesPH**……S8

Density functional treatments of chemical shieldings in detail……S9

Cartesian coordinates of the optimized structures ……S11

References……S25

Experimental Section

General: All working procedures were conducted under rigorous exclusion of oxygen and moisture using a Schlenk line and nitrogen atmosphere. Solvents were dried and freshly distilled before use. NMR spectra were recorded with BRUKERACANCEHD 300, BRUKERDRX400 or with BRUKERAVANCE 500 and were visualized with MestReNova.[1] IR vibrational spectra were gathered with the BRUKER ALPHA ATR-FT-IR. The elemental analysis was performed on a Vario MicroCube. MS spectra were measured with the AccuTOF-GC.

Synthesis of SIMesPH (1)

4.3 g of SIMes·HCl[2] (12.6 mmol) and 3.4 g of [Na(1,4-dioxane)$_{2.5}$PCO][3] (13.36 mmol) were suspended in 600 mL of tetrahydrofuran. The reaction mixture was stirred at 60 °C for 12 h. The solvent was removed in vacuo and, approximately 1 g of active coal and 50 mL of toluene were added to the reddish residue. The suspension was stirred for 30 min and was filtered. The remaining solid was extracted two times with 20 mL of toluene. The solvent of the filtrate was removed in vacuo and the remaining yellow residue was washed three times with 20 mL of *n*-pentane until 1.4 g of a white powder of **1** (4.14 mmol, 34.5 %) was obtained. Elemental analysis for $C_{21}H_{27}N_2P$ [%] calc: C 74.53 %, H 8.04 %, N 8.28 %; found: C 73.95 %, H 7.95 %, N 8.34 %.

^{1}H NMR (C_6D_6): δ/ppm = 2.02 (d, $^1J_{HP}$ = 163 Hz, P**H**, 1H), 2.10 (s, *p*-C**H**$_3$, 3H), 2.11 (s, *p*-C**H**$_3$, 3H), 2.30 (s, *o*-C**H**$_3$, 6H), 2.36 (s, *o*-C**H**$_3$, 6H), 3.26 (s, C**H**$_2$, 4H), 6.79 (s, *m*-C**H**, 4H).
^{13}C{^{1}H} NMR (THF-D8): δ/ppm = 18.17 (s, *o*-**C**H$_3$), 21.30 (s, *p*-**C**H$_3$), 49.09 (s, (N**C**H$_2$), 117.5 (s, *m*-**C**) 129.2 (s, *p*-**C**), 138.3 (s, *o*-**C**), 191,0 ($^1J_{PC}$ = 73.3 Hz, NCN), *i*-C: not observed.
^{31}P NMR (101 MHz, C_6D_6) δ/ppm = -127.2 (d, $^1J_{PH}$ = 163 Hz).
MS (LIFDI+) m/z: 338.1912 [M$^+$] (calc: 338.1912)
IR (ATR-FT) [cm^{-1}]: 2948 (w), 2913 (w), 2873 (w), 2273 (s, PH), 1608 (w), 1479 (m), 1415 (m), 1389 (m), 1341 (m), 1328 (w), 1299 (m), 1268 (s), 1180 (s), 1098 (s), 1029 (m), 935 (w), 886 (s), 853 (m), 801 (w), 762 (w), 737 (vw), 614 (m), 597 (s), 577 (w), 497 (m), 435 (w).

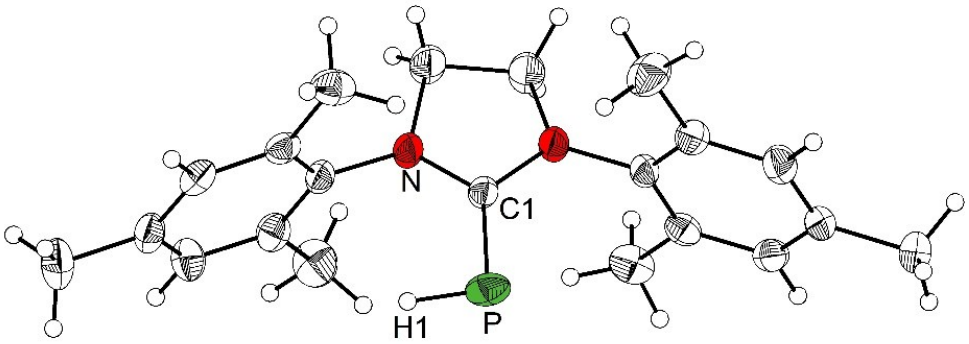


Figure S1. Molecular structure of **1** with thermal displacement parameters drawn at the 70% probability level. Selected bond lengths [pm] and angles [°]: P-C1 174.64(16), C1-N 136.24(13); P-C1-N 126.28(7), N-C1-N 107.45(13).

Synthesis of SIMesPK (2)

500 mg of **1** (1.5 mmol) were solved in 75 mL of toluene and cooled to -75 °C. 181 mg of benzyl potassium[4] (xxx mmol) were slowly added under continuous stirring. The suspension was slowly warmed to room temperature: At -25 °C formation of a yellow precipitate was observed, which vanished at room temperature forming a clear dark red solution. After several minutes an orange precipitate appeared. After additional stirring for 12 hours and subsequent filtration, the precipitate was washed with 5 mL of benzene and 2 times with 5 mL of *n*-pentane. The remaining solid was dried at 10^{-3} mbar yielding 320 mg of **2** (0.96 mmol, 65 %). Elemental analysis for $C_{21}H_{26}N_2PK$ [%]: calc: C 66.99, H 6.96 N 7.44; found: C 66.59, H 7.09, N 7.03

µ-RFA: P: 48.47 %, K: 51.53 %

IR (ATR-FT) [cm^{-1}]: 2954 (w), 2906 (m), 1480 (m), 1362 (m), 1326 (w), 1306 (w), 1294 (w), 1266 (m),1225 (s), 1188 (vs), 1159 (s), 1094 (w), 1032 (w), 1011 (w), 889 (w), 848 (s), 732 (m), 676 (s), 617 (w), 604 (m), 575 (m), 511 (w), 498 (vw), 476 (vw).

Synthesis of [SIMesPGa*t*Bu$_2$]$_2$ (3)

58 mg of Ga*t*Bu$_2$Cl[5] (0.27 mmol) was solved in 3 mL of fluorobenzene and cooled to -40 °C. 100 mg of **2** (0.27 mmol) was slowly added to the solution and the reaction mixture was allowed to warm to room temperature within two hours. Subsequently, the solvent was removed in vacuo and the yellow precipitate was extracted with 10 ml of *n*-pentane. The yellow extract was concentrated to 2 mL and stored at -25 °C to obtain 83 mg of yellow crystals of **3**, suitable for single crystal x-ray diffraction (0.08 mmol, 59.3 %). Elemental analysis for $C_{58}H_{88}N_4P_2Ga_2$ [%]: calc: C 66.81, H 8.51, N 5.37; found: C 66.67, H 8.62, N 5.39.

^{1}H NMR (C_6D_6): δ/ppm = 1.17 (s, GaC(C**H**$_3$)$_3$, 36H), 2.12 (s, *p*-C**H**$_3$, 12H), 2.37 (s, *o*-C**H**$_3$, 24H), 3.21 (s, C**H**$_2$, 8H), 6.80 (s, *m*-C**H**, 8H).
^{13}C{^{1}H} NMR (C_6D_6): δ/ppm = 19.1 (s, *p*-**C**H$_3$), 20.9 (s, *o*-**C**H$_3$), 30.8 (GaC(**C**H$_3$)$_3$),
32.2 (s, Ga**C**(CH$_3$)$_3$), 48.5 (s, **C**H$_2$), 130.5 (s, *m*-**C)**, 137.2 (s, *o*-**C**), 137.4 (s, *p*-**C**), 137.5 (s, *ipso*-**C**), NCN not observed.
^{31}P NMR (C_6D_6): δ/ppm = -113.2 (s).
MS (LIFDI+) m/z: decomposition, observed fragments: 1014.2735 [(SIMesPH)$_2$SIMesP$^+$], 998.2309 [(SIMesP)$_3^+$ -CH$_4$].
IR (ATR-FT) [cm^{-1}]: 2948 (m), 2916 (m), 2863 (m), 2815 (s), 2752 (w), 2692 (w), 2274, (w), 2162 (vw), 2113 (vw), 1608 (w), 1479 (s), 1459 (s), 1371 (s), 1304 (w), 1265 (s), 1234 (s), 1206 (s), 1179 (s), 1117 (m), 1029 (w), 1008 (m), 934 (w), 922 (w), 903 (w), 848 (m), 813 (w), 731 (w), 625 (w), 604 (w), 573 (s), 492 (s),418 (vw), 407 (vw).

Synthesis of SIMesP(Ga*t*Bu$_2$)$_2$Cl (4)

117 mg of Ga*t*Bu$_2$Cl[5] (0.53 mmol) were solved in 3.0 mL of fluorobenzene and added to a suspension of 100 mg of **2** (0.27 mmol) in 5 mL of fluorobenzene at –40 °C. The reaction mixture were slowly warmed to room temperature and stirred for additional 12 h. After filtration, the clear colourless solution was concentrated in vacuo to 4 ml and stored at 6 °C. Within three days 160 mg of colourless crystals of **4** was obtained (0.21 mmol, 78 %). Elemental analysis: $C_{37}H_{62}N_2PGa_2Cl$ [%]: calc: C 59.99, H 8.44 N 3.78; found: 59.82, H 8.55, N 3.80.

^{1}H NMR (C_6D_6): δ/ppm = 1.27 (d, $^4J_{PH}$ = 1.3 Hz, GaC(C**H**$_3$)$_3$, 36H), 2.10 (s, *p*-C**H**$_3$, 6H), 2.28 (s, *o*-C**H**$_3$, 12H), 2.86 (d, $^4J_{PH}$ = 2.0 Hz, C**H**$_2$, 4H), 6.74 (s, *m*-C**H**, 4H).
^{13}C{^{1}H} NMR (C_6D_6): δ/ppm = 19.3 (d, $^5J_{PC}$ = 2.4 Hz, *o*-**C**H$_3$), 21.1 (s, *p*-**C**H$_3$), 29.1 (d, $^2J_{PC}$ = 15 Hz, Ga**C**(CH$_3$)$_3$), 31.9 (s, GaC(**C**H$_3$)$_3$), 50.6 (s, **C**H$_2$), 131.2 (s, *m*-**C**), 136.5 (s, *o*-**C**), 136.6 (s, *p*-**C**), 139.2 (s, *ipso*-**C**), 183.3 (d, $^1J_{CP}$ = 65.7 Hz, N**C**N).
^{31}P NMR (C_6D_6): δ/ppm = -122.6 (s).
IR (ATR-FT) [cm^{-1}]: 2952 (m), 2933 (m), 2867 (m), 2827 (s), 2696 (w), 1608 (w), 1469 (m), 1411 (m), 1378 (m), 1356 (m), 1270 (vs), 1206 (w), 1191 (w), 1170 (w), 1011 (m), 931 (w), 850 (m), 731 (w), 626 (w), 626 (m), 605 (m), 576 (s), 512 (m).

Synthesis of (SIMesP)$_3$Al*t*BuK (5)

50 mg of SIMesPK (0.13 mmol) were suspended in 5 mL of fluorobenzene and cooled to -40 °C. A solution of 16 mg of Al*t*Bu$_2$Cl[5] (0.09 mmol) in 5 ml fluorobenzene was added at -40 °C to the suspension. The reaction mixture was slowly warmed to room temperature and stirred for 12 hours. The solvent was removed in vacuo and the remaining yellow solid was extracted three times with 4 mL of *n*-pentane. The yellow solution was concentrated to half of its former volume and stored at -25 °C. After one week orange crystals of **5** were obtained with a yield of 30 mg, 62%. Elemental analysis: calc. for $C_{67}H_{87}N_6P_3AlK$: C 70.81 %, H 7.81 %, N 7.39 %, found: C 70.85 %, H 7.38 %, N 6.86 %.

^{1}H NMR (C_6D_6): δ/ppm = -0.14 (s, AlC(C**H**$_3$)$_3$, 9H), 2.26 (s, *p*-C**H**$_3$, 18H), 2.49 (s, *o*-C**H**$_3$, 36H), 3.25 (s, C**H**$_2$, 12H), 6.81 (s, *m*-C**H**, 12H).
^{13}C{^{1}H} NMR (C_6D_6): δ/ppm = 19.47 (s, p-**C**H$_3$), 22.74 (s, o-**C**H$_3$), 31.34 (s, Al**C**(CH$_3$)$_3$), 49.29 (s, (**C**H$_2$), 129.6 (s, *m*-**C**), 135.7 (s, *o*-**C**), 138.3 (s, *p*-**C**), 140.6 (s, *ipso*-**C**), NCN not observed.
^{31}P NMR (C_6D_6): δ/ppm = -61.2 (s).
IR (ATR-FT) [cm -1]: 3001 (w), 2956 (w), 2907 (w), 2851 (w), 2747 (m), 1718 (w), 1608, (w), 1479 (m), 1439 (w), 1390 (m), 1390 (m), 1376 (m), 1307 (w), 1292 (w), 1269 (s), 1208 (vs), 1033 (m), 1011 (m), 965 (w), 930 (w), 871 (w), 843 (m), 813 (s), 734 (w), 624 (w), 594 (m), 573 (m), 495 (s), 426 (w).

Synthesis of SIMesPHGa*t*Bu$_2$Cl (6)

100 mg of **1** (0.30 mmol) was solved in 2.0 mL of benzene and a solution of 61 mg of Ga*t*Bu$_2$Cl[5] (0.30 mmol) in 2.0 mL benzene was added. A yellow solution formed immediately. The volume was reduced to 2 mL and the solution stored at 6 °C to obtain 135 mg of colourless crystals of **6** (0.24 mmol, 79.5 %). Elemental analysis: for $C_{29}H_{45}N_2PGaCl$ [%]: calc: C 62.44, H 8.13 N 5.02; found: C 62.37, H 8.16 N 5.08.

^{1}H NMR (C_6D_6): δ/ppm = 1.17 (s, GaC(C**H**$_3$)$_3$, 18H), 2.06 (s, *p*-C**H**$_3$, 6H), 2.37 (s, *o*-C**H**$_3$, 12H), 2.55 (d, $^1J_{HP}$ = 211 Hz, P**H**, 1H), 3.06 (s, C**H**$_2$, 4H), 6.74 (s, *m*-C**H**, 4H).
^{13}C{^{1}H} NMR (C_6D_6): δ/ppm = 18.8 (s, *p*-**C**H$_3$), 20.9 (s, *o*-**C**H$_3$), 26.5 (s, Ga**C**(CH$_3$)$_3$), 30.7 (GaC(**C**H$_3$)$_3$), 49.7 (s, **C**H$_2$), 130.5 (s, *m*-**C)**, 133.9 (s, *o*-**C**), 136.7 (s, *p*-**C**), 139.5 (s, *ipso*-**C**), 183.1 (d, $^1J_{CP}$ = 66.0 Hz, N**C**N).
^{31}P NMR (C_6D_6): δ/ppm = -148.8 (d, $^1J_{HP}$ = 211 Hz).
MS (LIFDI+) m/z: 517.1146 [MH$^+$ -3 CH$_3$], 338.1905 [SIMesPH$^+$], 307.2122 [SIMesH$^+$].
IR (ATR-FT) [cm^{-1}]: 2949 (m), 2912 (m), 2865 (n), 2834 (s), 2698(w), 2340 (w, PH), 1628 (w), 1609 (w), 1491 (s), 1458 (s), 1411 (m), 1378 (w), 1358 (w), 1319 (w), 1301 (s), 1271 (vs), 1171 (w), 1096 (vw), 1011 (m), 933 (w), 915 (w), 858 (m), 813 (m), 733 (w), 631 (w), 596 (w), 578 (m), 530 (w), 502 (w), 478 (mw).

Synthesis of SIMesPHAl(*t*-Bu)$_2$Cl (7)

100 mg of **1** (0.3 mmol) was solved in 2.0 mL of toluene and a solution of 52 mg of Al*t*Bu$_2$Cl[5] (0.3 mmol) in 2.5 mL of toluene was added. A yellow solution was formed immediately and was stored at -25 °C. After two days, 105 mg of white crystals of **7** (0.2 mmol, 66.6 %) was obtained. Elemental analysis for $C_{29}H_{45}N_2PAlCl$ [%]: calc: C 67.64, H 8.81 N 5.44; found: C 67.32, H 8.79 N 5.50.

^{1}H NMR (C_6D_6): δ/ppm = 1.08 (s, AlC(C**H**$_3$)$_3$, 18H), 2.05 (s, *p*-C**H**$_3$, 6H), 2.31 (s, *o*-C**H**$_3$, 12H), 2.54 (d, $^1J_{HP}$ = 215 Hz P**H**, 1H), 3.02 (s, C**H**$_2$, 4H), 6.73 (s, *m*-C**H**, 4H).
^{13}C{^{1}H} NMR (C_6D_6): δ/ppm = 18.6 (s, *p*-**C**H$_3$), 20.9 (s, *o*-**C**H$_3$), 22.7 (s, Al**C**(CH$_3$)$_3$), 30.5 (AlC(**C**H$_3$)$_3$), 49.8 (s, **C**H$_2$), 130.6 (s, *m*-**C)**, 133.6 (s, *o*-**C**), 136.5 (s, *p*-**C**), 139.7 (s, i*pso*-**C**), 187.9 (d, $^1J_{CP}$ = 66 Hz, N**C**N).
^{31}P NMR (C_6D_6): δ/ppm = -151.0 (d, $^1J_{HP}$ = 215 Hz).
MS (LIFDI+) m/z: decomposition, observed fragments: 338.1906 [SIMesPH$^+$], 307.2120 [SIMesH$^+$].
IR[cm-1]: 3294 (m), 2920 (m), 2863 (m), 2810 (s), 2326 (w, PH), 1607 (w), 1549 (w), 1483 (s), 1455 (s), 1412 (m), 1381 (w), 1358 (w), 1355 (w), 1302 (m), 1274 (vs), 1186 (w), 1031 (w), 1007 (q), 936 (w), 899 (w), 862 (m), 848 (m), 812 (s), 637 (vw), 577 (m), 540 (s), 476 (w), 444 (vs).

Crystal Structure Data collection was performed using a BRUKER D8 QUEST diffractometer at 100(2) K with MoK_α radiation and graphite monochromatization (λ = 0.71073). Structure solution was realized by direct methods, refinement with full-matrix-least-squares against F^2 using SHELXL-14 and Olex2 software.[6, 7] The presentation of crystal structures was done with DIAMOND4.2.2.[8]

Table S1. Crystallographic data of **1, 3 – 7**.

Compound	**1**	**3**	**4**	**5**	**6**	**7**
Empirical formula	$C_{21}H_{27}N_2P$	$C_{58}H_{88}Ga_2N_4P_2$	$C_{37}H_{62}ClGaN_2P$	$C_{67}H_{87}AlKN_6P_3$	$C_{29}H_{45}GaClN_2P{\cdot}3.5\ C_6H_6$	$C_{29}H_{45}AlClN_2P$
Crystal system	orthorhombic	triclinic	triclinic	trigonal	triclinic	triclinic
Space group	*Pbcn*	*P*-1	*P*-1	*R*-3	*P*-1	*P*-1
Formula units	4	2	2	2	2	2
Temperature [K]	100	100	100	100	100	100
Unit cell dimensions [pm] [°]	a = 1578.01(8) b = 748.05(4) c = 1618.42(8) α = 90 β = 90 γ = 90	a = 1186.00(6) b = 1297.39(7) c = 2236.82(12) α = 100.545(2) β = 101.098(2) γ = 106.378(2)	a = 970.12(6) b = 988.09(4) c = 2307.92(12) α = 84.726(2) β = 83.754(2) γ = 61.541(2)	a = 1839.40(7) b = 1839.40(7) c = 3395.98(12) α = 90 β = 90 γ = 120	a = 1081.9(5) b = 1362.19(7) c = 1714.42(8) α = 105.26(2) β = 101.977(2) γ = 98.128(2)	a = 960.40(6) b = 1083.06(7) c = 1645.07(10) α = 83.758(2) β = 87.788(2) γ = 68.557(2)
Cell volume [10^6 pm³]	1919.43(17)	3135.8(3)	1931.38(18)	9950,6(8)	2332.5(2)	1583.27(17)
Density [g/cm³]	1.177	1.104	1.274	1,137	1.183	1.080
Absorption coefficient [mm^{-1}]	0.148	0.945	1.532	0.208	0.715	0.217
2Θ range [°]	5.03 – 55.82	4.29 – 54.12	4.64 – 63.88	4.43-63.52°	4.51-55.42°	4.54-55.2°
Reflections measured	23093	78201	81566	36608	47277	32732
Independent reflections	2281 (R_{int} = 0.0265)	13720 (R_{int} = 0.0767)	11774 (R_{int} = 0.0389)	6730 (R_{int} = 0.0777)	10893 (R_{int} = 0.0566)	7290 (R_{int} = 0.0869)
Parameters	117	619	406	253	517	323
$R_1[Fo > 4\sigma(Fo)]$	0.0355	0.0434	0.0327	0.0562	0.0366	0.0610
wR_2 (all data)	0.1012	0.0981	0.0608	0.1171	0.0795	0.1316
GOOF	1.026	1.041	1.028	1.069	1.024	1.033
Residual electron density	0.30/-0.20	0.41/-0.57	0.48/-0.59	0.43/-0.35	0.48/-0.42	0.36/-0.27
CCDC	1537131	1537128	1537133	1537129	1537132	1537130

^{1}H NMR analysis of compound 1

Figure S2. ^{1}H NMR spectrum of compound **1** at 25 °C in Toluene-d8 (Signals with *: remaining hydrogen at the solvent)

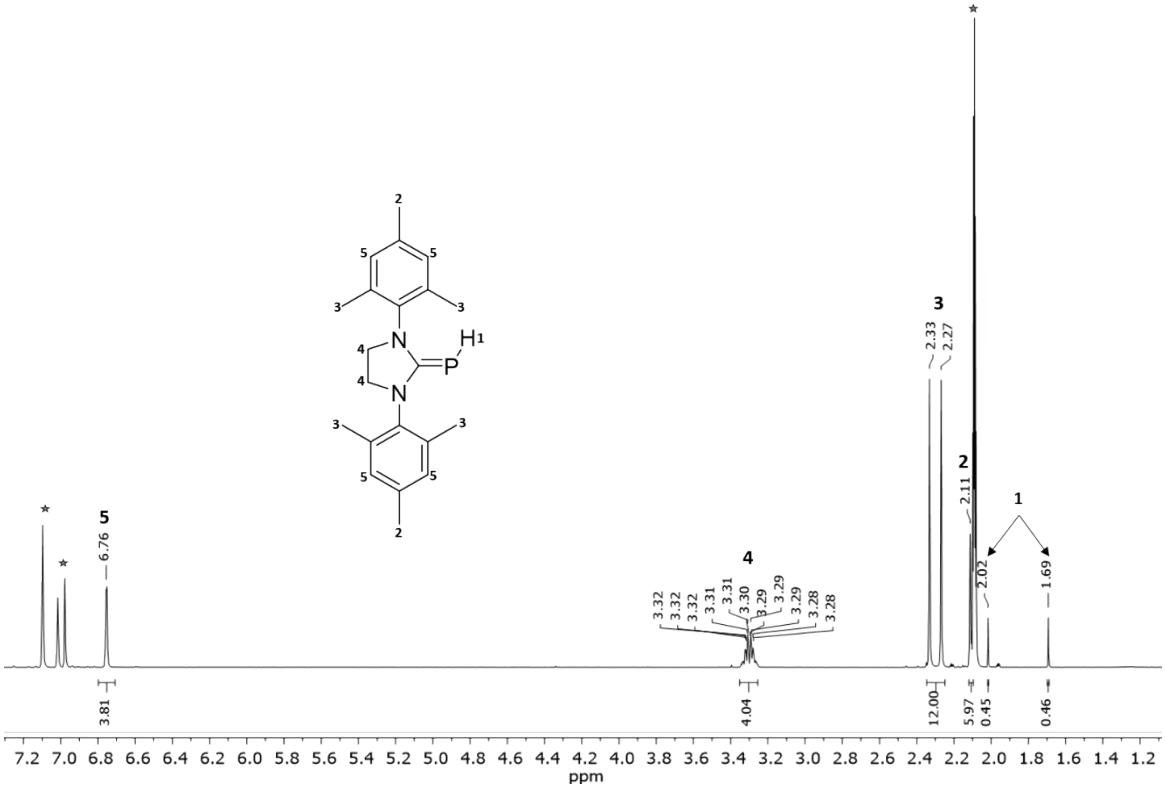
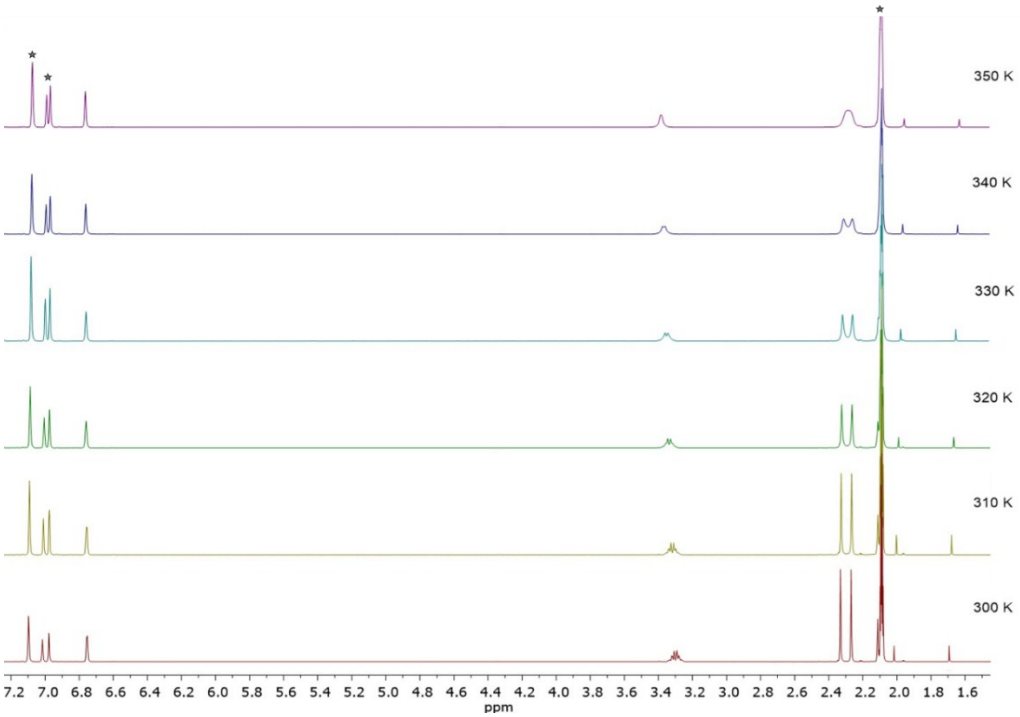


Figure S3. Temperature dependent ^{1}H NMR spectra of compound **1**



^{1}H NMR analysis of IMesPH

Figure S3. ^{1}H NMR spectrum of the compound IMesPH at 25 °C in Toluene-d8 (Signals with *: remaining hydrogen at the solvent)

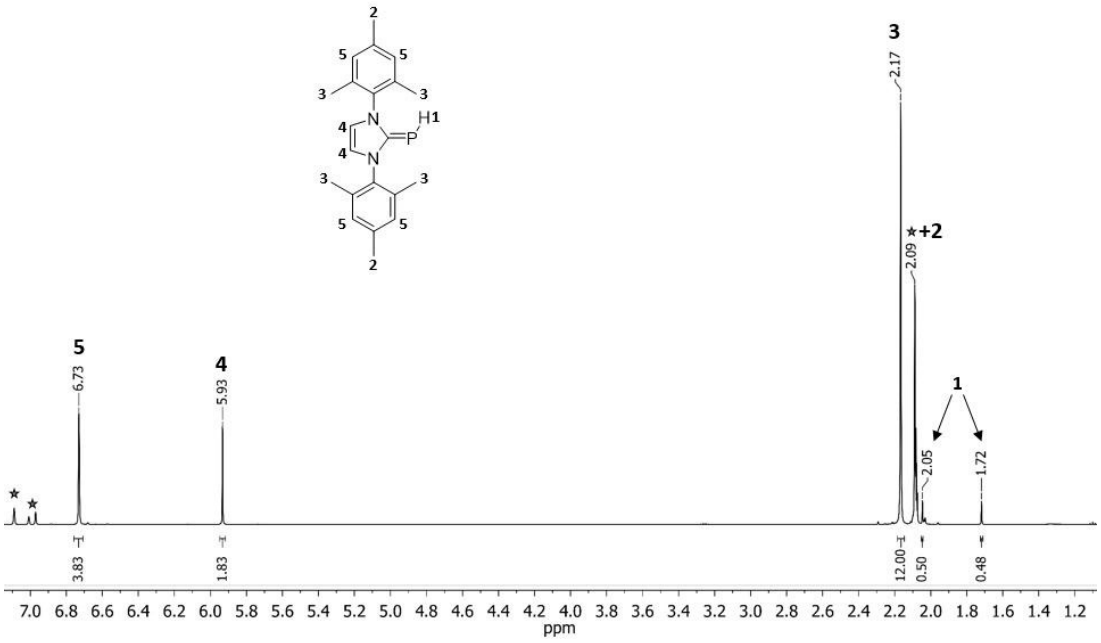
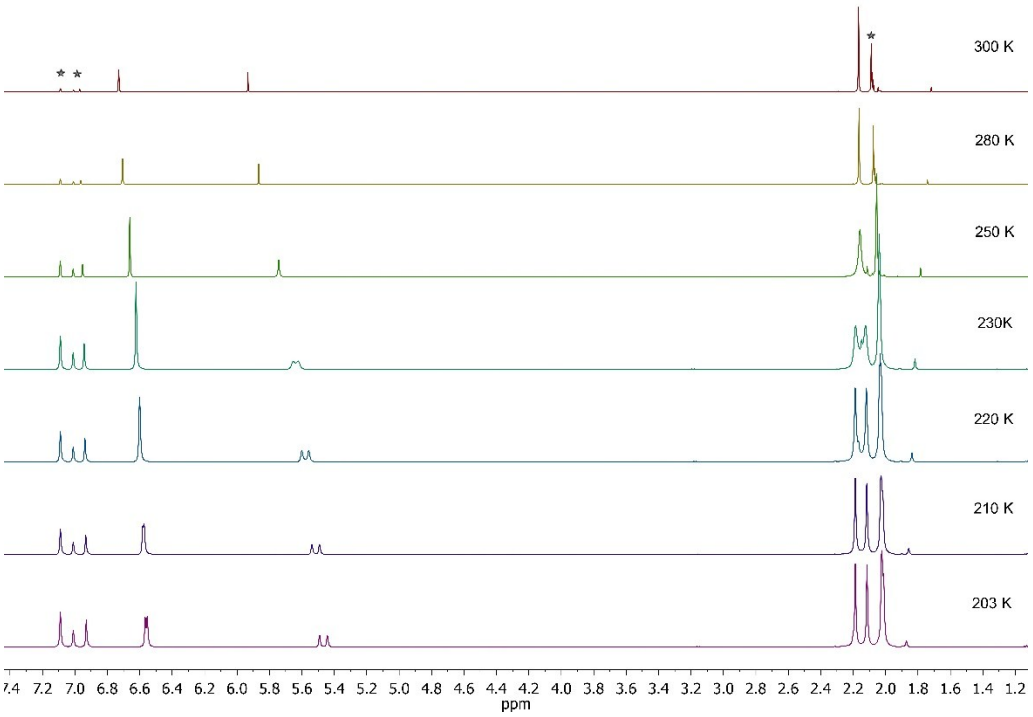


Figure S5. Temperature dependent ^{1}H NMR spectra of IMesPH



Density functional treatments of chemical shieldings in detail

Calculations were done with a local version TURBOMOLE, for which the module for calculating chemical shieldings differs from Version 7.1[9] in the following respects. It allows for the usage of functionals PBE[10] and PBE0[11], the conductor like screening model (COSMO)[12] is supported, and a resolution of the shieldings into orbital contributions[13] as suggested by Wiberg is possible. The PBE functional with D3 dispersion correction.[14] was used for optimization of structure parameters, chemical shieldings were calculated additionally with functionals BP86[15], B3LYP[16] and PBE0 as well as at Hartree-Fock level. Basis sets were of def2-TZVP[17] quality. The conductor-like screening model was employed with a dielectric constant, set to 2.28 (benzene). Calculated and measured ^{31}P and ^{13}C shieldings σ for all compounds are listed in Table S2. For comparability with the experimental data we also list simulated shifts $\delta=\sigma_0 - \sigma$. σ_0 was determined by minimizing the deviation between calculated shieldings σ and measured shifts δ. In this way one obtains an agreement of calculated and measured ^{13}C shifts within 2 ppm, and of ^{31}P shifts within 30 ppm, which is not that much in view of the broad range of ^{31}P shifts. Trends are correctly reproduced by the calculations, in particular the comparably small shift in **5**; this holds largely independent from the chosen functional, see Table S3. Closer investigation shows that the differences mainly stem from the paramagnetic contribution, that is, from the response of the electron density to the magnetic field and not from the electron density itself (diamagnetic contribution). This is evident from the high similarity of calculated numbers for the diamagnetic contribution for all compounds, which range from 960 to 967 ppm. In this case, any rationalization basing on the electron density itself, for instance via comparing electron populations at P, is not really conclusive. The paramagnetic contribution is very sensitive to changes in the geometric and/or the electronic structure. For instance, the ^{31}P shielding of **1** and IMesPH differ by ca. 20 ppm, both due to calculations and measurements, despite very small differences in the composition (one versus two hydrogen atoms per carbon in the NHC. The reason for this are changes in the electronic structure (aromaticity in IMesPH, non-aromaticity in **1**) accompanied by changes in the geometric structure. Similar is observed for the dependence of ^{31}P shifts on the rotation angle of the C-P-bond: for both **1** and IMesPH the ^{31}P shifts for the transition states are higher by ca. 60 ppm than for the respective ground states. The bare electronic influence for the ground states of **1** and IMesPH was estimated by calculating the ^{31}P shift for a hypothetical compound that was obtained by replacing the two H atoms per C in the NHC with one H atom per C in the optimized structure of **1**, without any other changes in structure parameters. Here, a total shielding of 444 ppm was obtained, just in between those for **1** and IMesPH. This is solely to changes in the paramagnetic contribution (the diamagnetic contribution amounts to 962 ppm for all cases). The high sensitivity of the paramagnetic contribution to slight changes in the structure parameters may be the reason for the high discrepancy between calculated and measured shifts in **3**, which differs from **4** only by the replacement of Cl with a

second SIMesP unit. In the calculations, exchanging SiMesP with Cl in **3** without any structure optimization yields a shielding of 336 ppm, very close to that in **3** (333 ppm) and not to that of the optimized structure of **4** (380 ppm. Thus, the calculated difference in the ^{31}P shift of **3** and **4** is a result of changes of the geometric structure, which act on the paramagnetic contribution of the shielding constant. In view of the high sensitivity ^{31}P shifts on slight changes in the geometric structure the measured similarity of shifts in **3** and **4** - despite measured significant differences in the N-C-P-Ga torsion angles - is much more surprising than the (measured and calculated) dissimilarity of the shifts in 5 to those in **3** and **4**. For further investigation the chemical shielding was resolved into orbital contributions, as suggested e.g. by Wiberg et al.[13] We exemplarily show the results for the P atom in **4**, Table S4. The orbitals yielding the largest contributions are displayed in Figure S4. As expected, the diamagnetic part is dominated by inner orbitals of P, first of all the 1s(P), ca. 500 ppm, but also the 2s(P) and 2p(P) orbitals, ca. 100 ppm each. The paramagnetic part receives largest contributions from the C-P π-bond, 180 ppm in sum, but many other orbitals also show contributions larger than 10 ppm.

Table S2. Comparison of selected spectroscopic and structural data of compounds **1**-**7**. For details concerning the calculated absolute shielding constants ("abs.") and the simulated shifts ("sim.") see text.

Compound	**δ^{31}P [ppm]**		**δ^{13}C** (carbene C atom) **[ppm]**		**$^1J_{PC}$ [Hz]**	**d P-C [pm]**	
	measured	**calculated sim./abs.**	**measured**	**calculated sim./abs.**		**x-ray diffraction**	**calculated**
1	-127.2	-157/433	191.0	192/-3	73.3	174.6(2)	175.3
IMesPH [5,6]	-147.3	-178/454	180.0	178/11	93.5	174.7(2)	176.1
3	-113.2	-57/333		182/ 7	-	174.4(2)	175.6
4	-122.6	-104/380	183.3	181/ 8	65.7	175.4(1)	175.3
5	-61.2	-54/330		185/ 4	-	175.3(2)	175.8
6	-148.8	-163/439	188.5	191/-2	68.9	179.8(2)	179.4
7	-151.0	-157/433	187.9	190/-1	65.5	180.1(2)	179.5

Table S3. ^{31}P shifts/shieldings for compounds **1-7** obtained with different functionals. For details concerning the calculated absolute shielding constants ("abs.") and the simulated shifts ("sim.") see text. The column "PBE, opt" contains numbers for optimized structure parameters, the numbers in the subsequent columns were calculated for experimental structure parameters.

compound	**measured**	**PBE, opt**	**PBE**	**BP**	**B3-LYP**	**PBE0**	**HF**
1	-127,2	-157 / 433	-164 / 455	-165 / 450	-163 / 443	-155 / 465	-140 / 491
ImesPH	-147,3	-178 / 454	-137 / 428	-138 / 423	-136 / 416	-133 / 443	-121 / 472
3	-113,2	-57 / 333	-59 / 350	-58 / 343	-61 / 341	-68 / 378	-94 / 445
4	-122,6	-105 / 381	-109 / 400	-107 / 392	-111 / 391	-117 / 427	-137 / 488
5	-61,2	-54 / 330	-77 / 368	-77 / 362	-79 / 359	-83 / 393	-99 / 450
6	-148,8	-163 / 439	-162 / 453	-162 / 447	-162 / 442	-160 / 470	-144 / 495
7	-151	-157 / 433	-163 / 454	-164 / 449	-161 / 441	-158 / 468	-137 / 488

Table S4. Molecular orbital (MO) contributions to ^{31}P shieldings, calculated as suggested in reference 13. Orbitals with contributions of less than 1 ppm to the total shielding are omitted; orbitals with largest contributions are indicated by an "x" in the last column and plotted in Figure S4. The molecule was shifted in a way that P is in the origin, for minimizing problems of gauge invariance.

MO	Energy/eV	diamagnetic part	paramagnetic part	total	
4	-2075.219	517.191836	-0.0045397	517.187296	X
56	-170.577	99.4654758	0.09861722	99.564093	X
59	-122.029	92.6938755	34.7117998	127.405675	X
60	-121.991	95.9498071	-4.87383336	91.0759738	X
61	-121.983	95.8039826	-5.30359114	90.5003915	X
68	-25.662	0.53404716	1.3546215	1.88866866	
69	-23.408	-0.09814514	3.16604807	3.06790293	
70	-21.627	0.01959928	1.78702756	1.80662684	
71	-21.234	0.02197222	1.95831192	1.98028413	
72	-19.775	-0.01793399	2.4592444	2.44131041	
73	-19.633	0.24167534	6.54078556	6.78246089	
74	-19.570	-0.02172001	1.09340645	1.07168644	
76	-19.473	0.09386996	2.11593358	2.20980355	
77	-19.446	0.08714956	1.87050869	1.95765824	
78	-19.368	0.13194102	2.12303904	2.25498006	
79	-19.362	0.49287261	-4.45535897	-3.96248637	
80	-19.357	0.18579217	1.20863043	1.3944226	
81	-19.202	-0.00201103	1.5980115	1.59600048	
93	-17.403	0.01353283	2.14047301	2.15400584	
94	-17.354	-0.01692121	1.55183281	1.53491159	
95	-16.901	-0.01320885	1.1277965	1.11458766	
96	-16.814	0.01229753	1.00358603	1.01588356	
97	-16.764	-0.01172257	1.21713482	1.20541225	
98	-16.437	0.02021503	1.63625805	1.65647307	
99	-16.434	0.06779826	1.45607779	1.52387604	
100	-16.374	0.06596182	1.75989832	1.82586014	
101	-16.303	0.03007284	1.32661045	1.35668329	
102	-16.290	0.01787841	1.52573046	1.54360887	
103	-16.268	0.02568144	1.42316584	1.44884728	
104	-16.195	0.01887398	1.47227302	1.491147	
105	-16.142	0.02095796	1.50018399	1.52114195	
106	-15.952	0.04972872	1.53983104	1.58955976	
107	-15.680	6.94363928	0.69097726	7.63461654	
108	-15.051	3.05882791	2.36501176	5.42383967	
112	-13.518	0.81685183	0.74118574	1.55803757	
113	-13.116	0.16457604	1.78343911	1.94801516	
114	-12.945	1.25055266	-0.04451094	1.20604171	
115	-12.836	0.16214427	-1.90735225	-1.74520798	
116	-12.561	0.1415055	1.15076135	1.29226684	
117	-12.556	3.78081903	5.91381542	9.69463445	
118	-12.483	0.12979966	1.07317233	1.20297198	
119	-12.480	0.32351403	1.25053545	1.57404948	

120	-12.129	0.54584208	1.34398803	1.88983012
121	-11.930	0.09249229	3.24272225	3.33521454
122	-11.276	0.44510731	-16.7759414	-16.3308341
123	-11.273	0.33385082	-9.0936797	-8.75982889
124	-11.139	0.17615005	-1.64865544	-1.47250539
125	-11.108	0.51873119	-5.03044193	-4.51171074
126	-10.787	0.03447635	-1.2173175	-1.18284116
127	-10.726	0.06770143	1.40499911	1.47270054
128	-10.662	0.06156794	2.91941845	2.9809864
134	-10.281	0.04467939	1.25376753	1.29844691
136	-10.209	0.48598321	-9.11261675	-8.62663355
137	-10.185	0.07291205	1.55274159	1.62565365
138	-10.144	0.07830575	1.02481432	1.10312007
141	-10.066	0.1364759	-1.83547857	-1.69900267
143	-9.962	0.18119511	-11.9269724	-11.7457772
145	-9.901	0.54552586	-6.83025033	-6.28472447
146	-9.893	0.01054856	1.15279966	1.16334822
148	-9.795	0.04937586	-1.11751888	-1.06814303
149	-9.771	1.57970367	-35.43946	-33.8597563
150	-9.749	1.05654025	-36.5240686	-35.4675283
151	-9.616	0.14242252	-3.05971013	-2.91728761
152	-9.603	0.54286829	-14.0900846	-13.5472163
154	-9.078	0.45679481	-6.25269617	-5.79590137
155	-9.022	0.30521796	-2.89719583	-2.59197787
157	-8.915	0.3317604	-12.0465755	-11.7148151
158	-8.894	0.03499415	-2.23272019	-2.19772604
159	-8.852	0.12790544	-1.78054627	-1.65264083
160	-8.836	0.11569778	-4.18203675	-4.06633897
161	-8.821	0.22141616	-2.88978294	-2.66836679
163	-8.685	-0.04341331	-1.06858108	-1.11199439
164	-8.613	-0.03929554	-1.37310952	-1.41240506
165	-8.567	0.49516778	-14.9968916	-14.5017238
166	-8.416	0.03588159	-2.28427077	-2.24838919
167	-8.368	0.00248013	-2.06308801	-2.06060789
168	-8.331	0.03514653	-2.25281836	-2.21767183
169	-8.325	0.03804272	-1.083833	-1.04579028
170	-8.287	0.01021177	-2.13399407	-2.1237823
171	-8.262	-0.01101696	-1.80433784	-1.8153548
172	-8.251	0.03656101	-2.5156817	-2.47912069
173	-8.164	0.03218817	-1.9596398	-1.92745163
174	-8.159	0.01339373	-1.20803182	-1.1946381
175	-8.024	0.27091016	-4.46817721	-4.19726705
176	-7.651	0.16272505	-5.41820816	-5.25548311
177	-7.511	0.58622111	-28.1015327	-27.5153116
178	-7.498	0.0600034	-2.75059261	-2.69058921
179	-7.436	0.03258139	-3.8819416	-3.8493602
180	-7.357	0.04926782	-3.68748232	-3.63821451
181	-7.310	1.39166476	-39.4294645	-38.0377997

182	-7.282	0.04584765	-2.46897227	-2.42312462	
183	-7.154	1.64417751	-46.0412125	-44.397035	
184	-7.140	0.81407613	-24.8477059	-24.0336297	
185	-6.995	1.21851146	-33.2754464	-32.056935	
186	-6.930	1.92326147	-41.6456079	-39.7223464	
187	-6.520	0.96541333	2.86932743	3.83474076	
188	-6.399	0.13594597	1.04337865	1.17932463	
189	-6.079	0.38325442	-10.3976843	-10.0144298	
191	-6.027	0.02032565	-3.14864368	-3.12831803	
192	-5.516	0.19730284	-22.6888381	-22.4915353	
193	-5.214	7.32158116	-75.1069516	-67.7853704	X
194	-5.099	6.68651778	4.86354126	11.550059	
195	-4.892	0.15622881	-4.87733749	-4.72110868	
196	-4.434	7.95638357	-117.389691	-109.433307	X
Total		962.655788	-581.846494	380.809294	

Figure S4. Orbitals with largest contributions to the **^{31}P** shielding in **4.** See also Table S4. MO 4 is the 1s of phosphorus, 56 the 2s and 59-61 the 2p orbitals. 193 and 196 are the P-C π orbitals; 196 is the highest occupied MO. Contours are drawn at ±0.05 a.u.

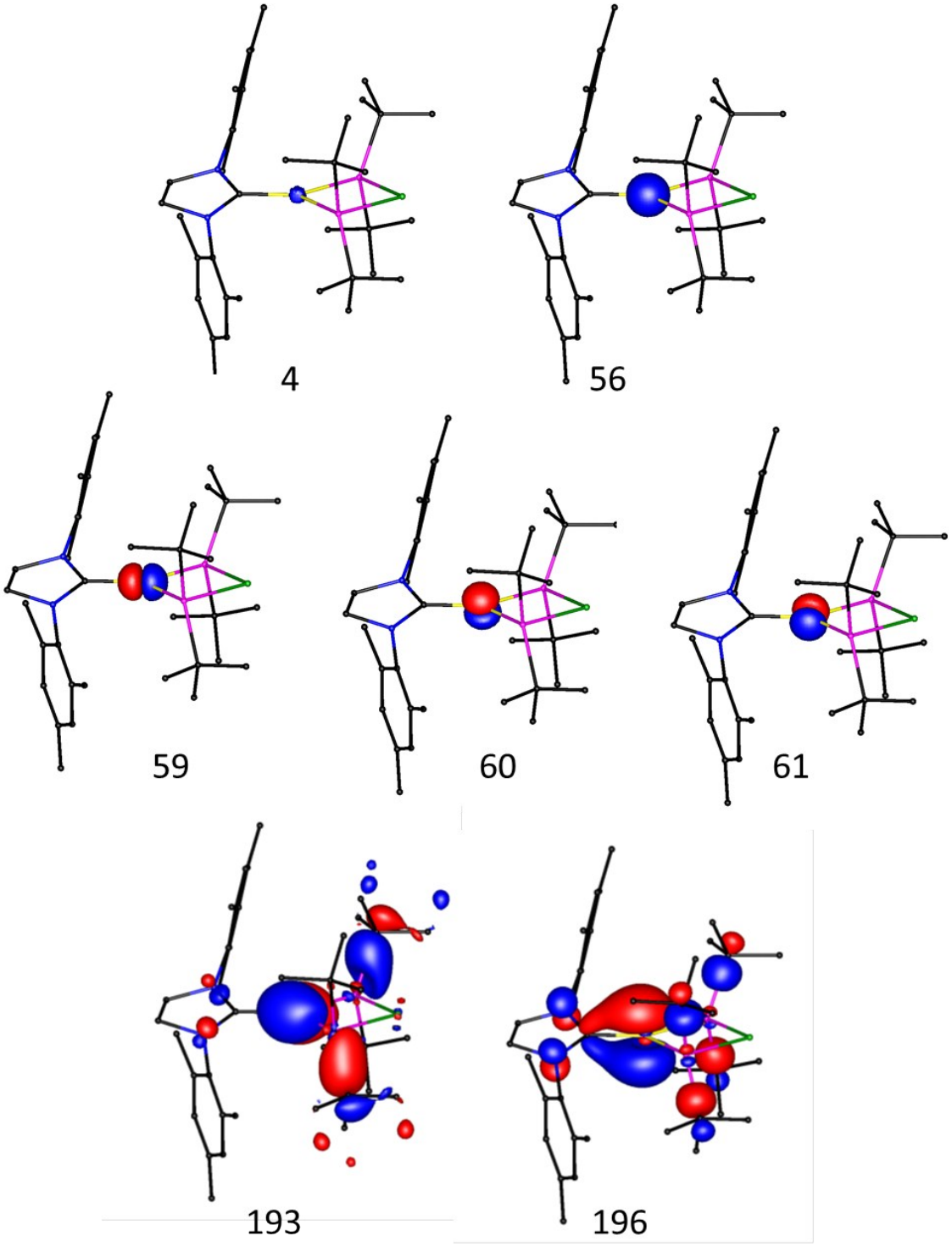


Table S5. Cartesian coordinates of the optimized structures (xyz, in Å).

SIMesPH (**1**)

C	-0.0152253	0.5174412	-5.1124626
C	-1.2092921	0.2191032	-4.4446645
C	-1.2207013	-0.2084255	-3.1134320
C	0.0092642	-0.3433936	-2.4448167
C	1.2274439	-0.0441542	-3.0811408
C	1.1899115	0.3796684	-4.4140181
N	0.0011446	-0.8039352	-1.0951379
C	0.0201833	0.0270812	-0.0039425
N	0.1301257	-0.7634528	1.1121502
C	0.0259872	-2.1892102	0.7790400
C	0.2886595	-2.1928825	-0.7306453
P	-0.0694623	1.7730007	-0.1369521
C	0.0391048	-0.3072609	2.4588876
C	1.2300654	-0.0963039	3.1777294
C	1.1382369	0.3184831	4.5090539
C	-0.0995155	0.5314938	5.1306831
C	-1.2632383	0.3223992	4.3829533
C	-1.2196142	-0.0942492	3.0469582
C	2.5628208	-0.2878182	2.5082879
C	-2.4816687	-0.2762284	2.2498704
C	-0.1687097	0.9957413	6.5613843
C	-2.5108076	-0.4971564	-2.3973896
C	2.5323052	-0.1541683	-2.3409872
C	-0.0306178	1.0118128	-6.5344719
H	2.6394707	0.3444084	1.6105227
H	-0.0688111	1.9442384	1.2852263
H	2.7076949	-1.3286789	2.1796190
H	3.3831162	-0.0290020	3.1898984
H	2.0590274	0.4879531	5.0740374
H	1.3365248	-2.4550713	-0.9624862
H	-0.3684778	-2.8846754	-1.2754303
H	-0.9799423	-2.5761109	1.0216623
H	0.7652179	-2.7769042	1.3406637
H	-2.2370999	0.4953241	4.8489163
H	-2.4483136	0.3303657	1.3311922
H	-3.3591211	0.0247584	2.8361613
H	-2.6251228	-1.3238941	1.9428458
H	0.4446953	0.3605560	7.2175696
H	-1.2004019	0.9823176	6.9367944
H	0.2125494	2.0241172	6.6609350
H	-2.5518860	-1.5360194	-2.0356241
H	-3.3703264	-0.3302012	-3.0590575
H	-2.6148802	0.1546886	-1.5161393
H	-2.1605630	0.3270914	-4.9727726
H	2.1310278	0.6178352	-4.9172334
H	2.4741541	0.3682652	-1.3741395
H	3.3483984	0.2878404	-2.9266586
H	2.7990940	-1.2030590	-2.1357535
H	-0.1356945	2.1083406	-6.5652121
H	-0.8734623	0.5876841	-7.0976342
H	0.9011232	0.7574673	-7.0580467

IMesPH

C	3.6512380	-11.4078487	6.2013959
C	4.7724950	-12.2513738	6.2312481
C	4.7551371	-13.5416898	5.6794611
C	3.5761110	-13.9709760	5.0614269
C	2.4400611	-13.1549258	4.9919926
C	2.4951943	-11.8815889	5.5724772

N	5.9690769	-11.7866076	6.8610302
C	6.2781163	-11.9568287	8.1993613
N	7.5143129	-11.3543816	8.3427093
C	7.9510051	-10.8300691	7.1289582
C	6.9915388	-11.0981236	6.2074346
C	8.2299688	-11.2916011	9.5804497
C	8.0142963	-10.1970243	10.4322038
C	8.7320488	-10.1537974	11.6318252
C	9.6317356	-11.1652328	11.9903131
C	9.8097679	-12.2433164	11.1145150
C	9.1153273	-12.3317069	9.9037147
C	10.3638379	-11.1131283	13.3046882
C	7.0234789	-9.1271083	10.0679889
C	9.2832423	-13.5080952	8.9833737
P	5.3915895	-12.7360976	9.5059661
C	5.9581377	-14.4356938	5.7908225
C	1.1932141	-13.6294009	4.2945488
C	3.6936293	-10.0582291	6.8614334
H	6.2090320	-14.6104476	6.8494127
H	4.3090619	-13.0796996	8.6334306
H	6.8453117	-13.9832204	5.3223365
H	5.7704346	-15.4048132	5.3120592
H	3.5423958	-14.9755913	4.6317724
H	8.9014574	-10.3182666	7.0425172
H	6.9323867	-10.8684027	5.1507416
H	1.6101227	-11.2405780	5.5453697
H	3.9118112	-10.1638149	7.9362771
H	2.7340803	-9.5382423	6.7495474
H	4.4845309	-9.4223829	6.4354295
H	1.2144266	-13.3569957	3.2269354
H	0.2929021	-13.1747609	4.7300585
H	1.0936571	-14.7220185	4.3511509
H	7.2739038	-8.6498643	9.1083924
H	6.9865596	-8.3500375	10.8415871
H	6.0166447	-9.5611630	9.9595177
H	8.5782873	-9.3080308	12.3071016
H	10.5048951	-13.0433581	11.3822790
H	8.3217771	-14.0300089	8.8527223
H	10.0136370	-14.2193001	9.3888072
H	9.6200032	-13.1974135	7.9826888
H	9.7803067	-11.6122099	14.0950328
H	10.5339314	-10.0772232	13.6286306
H	11.3348844	-11.6233885	13.2437569

[SIMesPGa*t*Bu$_2$]$_2$ (**3**)

Ga	1.8695933	0.4257692	0.1403277
P	0.3649189	-1.4396168	-0.4874331
P	-0.3641224	1.4413857	0.4846120
C	2.7744751	0.3628838	1.9772389
C	2.9141519	0.9319138	-1.5477258
Ga	-1.8687801	-0.4246429	-0.1419675
C	0.7744933	-3.0585636	-1.0287276
C	-0.7741697	3.0601245	1.0263049
C	2.8535743	1.8005793	2.4886075
C	4.1853821	-0.2149399	1.8604358
C	1.9488956	-0.4755805	2.9498319
C	3.9060680	2.0559102	-1.2461747
C	1.9591436	1.3654850	-2.6569656
C	3.6767662	-0.3145253	-1.9945142
C	-2.9136612	0.1894096	-1.7936895
C	-2.7722407	-1.4817205	1.3624498
N	1.9637018	-3.7398030	-0.7930377
N	-0.0254892	-3.9127916	-1.7796010
N	0.0244829	4.1950011	0.9388385

N	-1.9618837	3.4608789	1.6283709
H	3.4504974	2.4430863	1.8238223
H	3.3235709	1.8341335	3.4927649
H	1.8518630	2.2480728	2.5764274
H	4.1815198	-1.2378792	1.4636769
H	4.6702880	-0.2524916	2.8577123
H	4.8296288	0.3972362	1.2105849
H	0.9194574	-0.1006354	3.0380025
H	2.4038836	-0.4579368	3.9614971
H	1.8928264	-1.5236974	2.6311303
H	3.4051078	2.9640384	-0.8881075
H	4.4671710	2.3314207	-2.1628792
H	4.6486857	1.7588606	-0.4895819
H	1.2165676	0.5868920	-2.8818155
H	2.5191522	1.5794195	-3.5904557
H	1.4114909	2.2760161	-2.3843151
H	4.3877595	-0.6602864	-1.2290012
H	4.2565284	-0.1094446	-2.9176472
H	2.9889858	-1.1456154	-2.2128783
C	-1.9580181	0.5122297	-2.9395936
C	-3.6774375	1.4527404	-1.3995120
C	-3.9046651	-0.8895793	-2.2316791
C	-2.8523289	-2.9374301	0.9051975
C	-4.1827980	-0.9493919	1.6176755
C	-1.9459611	-1.3982863	2.6433899
C	2.8552389	-3.6495512	0.3152185
C	2.0306761	-4.9652964	-1.6160039
C	-1.0220470	-3.6021879	-2.7499489
C	0.5619175	-5.2679123	-1.8240156
C	1.0172301	4.5324959	-0.0265197
C	-0.5615664	5.3030139	1.7213208
C	-2.8510687	2.7200849	2.4601681
C	-2.0300366	4.9346981	1.7099890
H	-1.2162038	1.2697778	-2.6498700
H	-2.5177540	0.9029555	-3.8141311
H	-1.4092737	-0.3784105	-3.2696375
H	-4.3904740	1.2660323	-0.5823584
H	-4.2551417	1.8462890	-2.2607582
H	-2.9908063	2.2473887	-1.0701469
H	-3.4030889	-1.8298828	-2.4924955
H	-4.4644837	-0.5571075	-3.1301130
H	-4.6484036	-1.1086192	-1.4499964
H	-3.4502812	-3.0499961	-0.0117812
H	-3.3217740	-3.5685803	1.6872762
H	-1.8510264	-3.3480394	0.7048406
H	-4.1782444	0.1060973	1.9172624
H	-4.6679499	-1.5198978	2.4363645
H	-4.8271447	-1.0461736	0.7301881
H	-0.9172713	-1.7528904	2.4879379
H	-2.4017866	-2.0199385	3.4412311
H	-1.8877156	-0.3693243	3.0190881
C	2.3849988	-3.8450113	1.6334773
C	4.2406800	-3.5884143	0.0532067
H	2.5660072	-5.7515364	-1.0717121
H	2.5491469	-4.7713384	-2.5700412
C	-2.2444250	-4.3057283	-2.6990645
C	-0.7129945	-2.7853258	-3.8609876
H	0.3450398	-5.7370888	-2.7904024
H	0.1545702	-5.9006422	-1.0175535
C	2.2409867	5.0641407	0.4333356
C	0.7030775	4.5495886	-1.4042422
H	-0.3472820	6.2597542	1.2316501
H	-0.1509141	5.3229347	2.7448557
C	-2.3780710	2.0826125	3.6293755
C	-4.2370234	2.8271155	2.2163593

H	-2.5626007	5.2337710	2.6199124
H	-2.5519527	5.3541264	0.8334508
C	3.3172315	-3.8703031	2.6753455
C	0.9340695	-4.0877851	1.9254273
C	5.1316705	-3.6395787	1.1310375
C	4.7816476	-3.5274832	-1.3492594
C	-3.1749789	-4.1117744	-3.7260410
C	-2.5463473	-5.2950821	-1.6066802
C	-1.6861614	-2.6114130	-4.8498495
C	0.6415633	-2.1640816	-4.0304931
C	2.5481596	5.1959352	1.9001246
C	3.1678930	5.5282923	-0.5067010
C	-0.6528501	4.1543219	-1.9088027
C	1.6726130	5.0070510	-2.3019415
C	-0.9266106	2.1025853	4.0065354
C	-3.3081065	1.4736963	4.4775779
C	-4.7808290	3.6221955	1.0607914
C	-5.1257631	2.2174378	3.1089055
C	4.6929801	-3.7557331	2.4523402
H	2.9502264	-4.0020561	3.6966889
H	0.3250459	-3.2050876	1.6797459
H	0.7878345	-4.3366904	2.9839412
H	0.5378232	-4.9168748	1.3178620
H	6.2034365	-3.5702268	0.9258338
H	5.7565325	-3.0227521	-1.3668281
H	4.1038930	-2.9940751	-2.0252342
H	4.9313131	-4.5403757	-1.7584636
H	-4.1296951	-4.6420720	-3.6721756
C	-2.9284830	-3.2514663	-4.7988287
H	-2.1845433	-6.3014579	-1.8751881
H	-3.6291614	-5.3723106	-1.4423772
H	-2.0721468	-5.0144942	-0.6594584
H	-1.4528581	-1.9636291	-5.6990466
H	0.8430147	-1.4255357	-3.2402369
H	0.7223431	-1.6704002	-5.0069785
H	1.4393272	-2.9204016	-3.9588821
H	2.1869365	6.1606347	2.2934048
H	3.6316640	5.1595556	2.0737823
H	2.0767259	4.4009362	2.4888092
H	4.1237733	5.9195783	-0.1478306
C	2.9163326	5.4876357	-1.8803184
H	-0.8524369	3.0886620	-1.7219440
H	-0.7377121	4.3480679	-2.9853922
H	-1.4493673	4.7142151	-1.3934038
H	1.4353304	5.0013838	-3.3691100
H	-0.3177991	1.5474029	3.2774722
H	-0.7782423	1.6632000	5.0008716
H	-0.5319513	3.1309717	4.0210804
H	-2.9389643	0.9639817	5.3715129
C	-4.6842876	1.5145861	4.2326758
H	-4.9305346	4.6773092	1.3438536
H	-5.7561187	3.2290766	0.7450085
H	-4.1048157	3.6033927	0.1985390
H	-6.1979474	2.2840802	2.9049956
C	5.6632400	-3.7222453	3.6006680
C	-3.9763321	-2.9925817	-5.8458101
C	3.9603534	5.9119124	-2.8759164
C	-5.6521178	0.7946559	5.1305677
H	6.6531384	-4.0959608	3.3044949
H	5.3036472	-4.3203565	4.4496655
H	5.7956888	-2.6889097	3.9614929
H	-4.6549267	-3.8493151	-5.9589302
H	-3.5239808	-2.7737240	-6.8232179
H	-4.5904988	-2.1204361	-5.5671189
H	3.5044225	6.3231782	-3.7874064

H	4.5754368	5.0485478	-3.1788729
H	4.6386538	6.6661915	-2.4537035
H	-5.7845256	-0.2473409	4.7955619
H	-6.6423988	1.2706263	5.1217561
H	-5.2903086	0.7601012	6.1677461

SIMesP(Ga*t*Bu$_2$)$_2$Cl (**4**)

Ga	7.8393437	3.5922895	3.8862173
Cl	8.0834890	2.0559870	5.8023518
P	7.8785285	5.2196088	5.6920111
C	5.9334954	3.3623308	3.1829709
C	9.4724626	3.1205243	2.7636526
Ga	8.1211182	3.7398991	7.6056093
C	7.7690815	6.9677702	5.6334033
C	5.5471251	4.6785394	2.5025938
C	5.8780308	2.2174096	2.1663018
C	4.9550660	3.0752697	4.3195333
C	10.7718704	3.5278330	3.4548278
C	9.4820049	1.6034496	2.5362493
C	9.3469633	3.8379859	1.4153308
C	10.0388130	3.8015749	8.3117463
C	6.5559479	3.1418887	8.7642893
N	8.0792746	7.7683288	4.5573587
N	7.3570174	7.7920489	6.6563735
H	5.5571710	5.5154311	3.2182160
H	4.5226231	4.6140581	2.0862047
H	6.2230385	4.9368712	1.6722071
H	6.5404742	2.3884258	1.3044590
H	4.8487273	2.1105852	1.7708779
H	6.1548831	1.2528109	2.6184034
H	5.1841700	2.1262379	4.8258443
H	3.9210850	3.0067777	3.9276036
H	4.9720282	3.8677338	5.0812934
H	10.8041388	4.6044882	3.6690464
H	11.6383421	3.2911306	2.8057973
H	10.9088961	2.9881749	4.4016245
H	9.5602046	1.0474738	3.4822350
H	10.3555406	1.3256040	1.9145066
H	8.5825383	1.2519638	2.0099068
H	8.4424190	3.5335179	0.8661089
H	10.2155282	3.5931557	0.7720558
H	9.3221805	4.9300840	1.5275438
C	11.0478025	3.5612287	7.1911513
C	10.2563353	5.1994093	8.8976569
C	10.2347615	2.7453952	9.4043020
C	6.7372800	1.6545156	9.0932076
C	5.2190298	3.3338676	8.0515794
C	6.5824774	3.9583327	10.0609026
C	8.9366797	7.4845966	3.4547564
C	7.6672607	9.1643783	4.8017058
C	6.5287867	7.4776355	7.7728725
C	7.5964561	9.2092742	6.3205390
H	10.9406111	2.5581341	6.7532190
H	12.0814307	3.6503285	7.5798081
H	10.9328904	4.2904506	6.3765447
H	10.1440911	5.9773462	8.1263844
H	11.2798024	5.2916756	9.3113048
H	9.5514596	5.4280680	9.7124857
H	9.5547821	2.8919814	10.2569457
H	11.2687122	2.7947974	9.7988891
H	10.0807411	1.7249531	9.0215544
H	6.7339197	1.0308806	8.1870285
H	5.9031701	1.3109477	9.7359105
H	7.6717040	1.4555703	9.6381015

H	5.0515285	4.3810135	7.7659907
H	4.3860886	3.0327962	8.7176302
H	5.1567968	2.7192293	7.1433724
H	7.5158707	3.8094545	10.6258560
H	5.7492373	3.6482779	10.7225175
H	6.4679932	5.0346277	9.8755217
C	8.4232837	7.6263625	2.1508378
C	10.3136020	7.2607685	3.6731147
H	6.6897433	9.3712477	4.3346866
H	8.4121509	9.8513706	4.3829769
C	5.1929089	7.0693974	7.5663810
C	7.0057077	7.7688887	9.0658577
H	8.5397975	9.5634099	6.7689787
H	6.7718586	9.8259746	6.6971199
C	9.3017929	7.4951548	1.0692792
C	6.9752716	7.9523863	1.9085422
C	11.1450597	7.1222641	2.5581575
C	10.8907323	7.2153823	5.0580289
C	4.6403871	6.8606205	6.1864677
C	4.3730536	6.9016620	8.6859741
C	6.1385594	7.6004858	10.1513566
C	8.3990336	8.2886591	9.2897223
C	10.6623352	7.2300589	1.2488435
H	8.9030411	7.5892709	0.0556684
H	6.3293828	7.5278263	2.6869395
H	6.6462132	7.5637445	0.9361021
H	6.8101398	9.0423344	1.8977731
H	12.2097275	6.9362755	2.7215667
H	10.6191334	8.1132977	5.6352974
H	11.9850093	7.1479572	5.0210441
H	10.5015398	6.3512945	5.6190694
H	4.8077661	7.7434747	5.5494777
H	3.5618962	6.6638752	6.2254861
H	5.1369465	6.0138594	5.6871634
H	3.3417947	6.5733950	8.5324073
C	4.8240310	7.1549850	9.9864227
H	6.5112363	7.8107218	11.1574263
H	9.1022320	7.8936890	8.5462115
H	8.7611772	8.0136576	10.2888275
H	8.4281488	9.3886805	9.2228609
C	11.5734667	7.0192284	0.0715037
C	3.9338043	6.9089514	11.1728759
H	11.2189342	7.5611849	-0.8158103
H	11.6180933	5.9495584	-0.1914672
H	12.5996428	7.3434600	0.2932631
H	4.0259268	5.8635006	11.5103657
H	2.8769237	7.0798883	10.9256978
H	4.2037246	7.5528561	12.0209982

$(SIMesP)_3Al$*t*BuK (**5**)

K	0.0087873	-0.0004556	2.5714536
P	-0.4531231	2.0106294	0.0877756
P	-1.5102469	-1.4031765	0.0913542
P	1.9728520	-0.6092126	0.0860886
Al	0.0011342	-0.0013930	-1.2162952
C	1.5853720	2.6793862	3.4964473
C	-3.0994506	0.0339661	3.4984203
C	1.5156807	-2.7210469	3.4892556
C	1.2226976	2.3550537	4.8110173
C	-2.6371536	-0.1125776	4.8137580
C	1.4042397	-2.2487425	4.8042992
C	2.8708316	2.1712321	2.9045885
C	-3.2987629	1.3985790	2.8994631
C	0.4410197	-3.5834834	2.8875906

H	2.6858009	1.5374097	2.0175912
H	-2.6538844	1.5500423	2.0137822
H	-0.0250567	-3.0960186	2.0109659
C	0.8569082	3.1725739	0.2363003
C	-3.1717409	-0.8507716	0.2434852
C	2.3266778	-2.3243817	0.2360058
C	-0.0040531	-0.0020163	-3.2630202
C	0.6955324	3.4579732	2.7251363
C	-3.3312669	-1.1291430	2.7330111
C	2.6379114	-2.3306899	2.7267672
C	0.0163187	2.7945411	5.3730431
H	1.9031767	1.7424478	5.4083810
C	-2.4163932	-1.3746785	5.3815192
H	-2.4457093	0.7854504	5.4070605
C	2.3782680	-1.4180902	5.3750151
H	0.5311578	-2.5388401	5.3946269
H	3.5241461	2.9938067	2.5770334
H	3.4225767	1.5725532	3.6389912
H	-4.3364059	1.5529572	2.5675063
H	-3.0571038	2.1791345	3.6305972
H	0.8366195	-4.5498431	2.5411990
H	-0.3481362	-3.7837498	3.6219970
N	1.0953867	3.8609055	1.4208109
N	1.7821492	3.6563454	-0.6714756
N	-3.8840253	-0.9898930	1.4296378
N	-4.0559166	-0.2911108	-0.6616931
N	2.7999819	-2.8743228	1.4222027
N	2.2904912	-3.3668669	-0.6726029
C	1.4232574	-0.1298771	-3.7947565
C	-0.6092578	1.2991314	-3.7895152
C	-0.8301952	-1.1755965	-3.7889961
C	-0.5233706	3.9113495	3.2609151
C	-3.1144070	-2.4093461	3.2740038
C	3.6309975	-1.4968066	3.2716629
C	-0.8414249	3.5673125	4.5807695
C	-0.3288105	2.4730734	6.8031235
C	-2.6564921	-2.5073717	4.5937888
C	-1.9701049	-1.5076089	6.8135431
C	3.4795848	-1.0526663	4.5912680
C	2.2592613	-0.9622035	6.8052585
C	2.0676316	4.9444109	1.2532094
C	1.6629044	3.7183915	-2.0865417
C	2.7882905	4.5150438	-0.0196771
C	-5.3088592	-0.6885172	1.2664274
C	-4.0548421	-0.4249690	-2.0767999
C	-5.3009752	0.1504204	-0.0063472
C	3.2595552	-4.2557537	1.2550522
C	2.4033059	-3.2931574	-2.0876669
C	2.5358961	-4.6672107	-0.0220742
H	2.0596897	0.7033483	-3.4725352
H	1.4193830	-0.1285540	-4.9065922
H	1.9005036	-1.0588898	-3.4663367
H	-1.6478526	1.4325786	-3.4628866
H	-0.6128146	1.2976767	-4.9013477
H	-0.0423752	2.1764604	-3.4612867
H	-0.4256554	-2.1424744	-3.4654094
H	-0.8307235	-1.1758788	-4.9008365
H	-1.8723556	-1.1237516	-3.4573558
C	-1.4676285	4.7072821	2.4089273
C	-3.3350616	-3.6283893	2.4275208
C	4.7966432	-1.0691646	2.4293758
H	-1.7892474	3.9147836	5.0015885
H	-1.4155735	2.4713870	6.9661667
H	0.1024337	3.2195341	7.4894785
H	0.0693652	1.4929409	7.1013991

H	-2.4839057	-3.5002277	5.0188325
H	-1.3938775	-2.4295453	6.9742550
H	-2.8365520	-1.5436334	7.4934760
H	-1.3524894	-0.6526885	7.1225966
H	4.2471890	-0.4015022	5.0189866
H	2.7985327	-0.0199759	6.9753155
H	2.6849792	-1.7101525	7.4934668
H	1.2086425	-0.8191407	7.0947666
H	2.7345686	5.0116426	2.1229212
H	1.5556679	5.9181317	1.1360538
C	2.6753959	3.1298509	-2.8671991
C	0.6428053	4.4913211	-2.6818942
H	3.0496003	5.3560886	-0.6736520
H	3.7053490	3.9432562	0.2055063
H	-5.6972139	-0.1443018	2.1374919
H	-5.8972098	-1.6182758	1.1511600
C	-4.0562335	0.7465244	-2.8569588
C	-4.2147114	-1.6948318	-2.6721038
H	-6.1617142	-0.0439758	-0.6580242
H	-5.2640575	1.2305148	0.2186991
H	2.9830399	-4.8693448	2.1226514
H	4.3595415	-4.2936695	1.1433199
C	1.3889982	-3.8781643	-2.8686337
C	3.5812031	-2.7922055	-2.6824680
H	3.1408272	-5.3090127	-0.6744099
H	1.5843223	-5.1820446	0.1972691
H	-0.9953108	5.6278895	2.0344080
H	-2.3711959	4.9826260	2.9683998
H	-1.7512166	4.1093350	1.5254069
H	-4.3708218	-3.6820801	2.0597353
H	-3.1175313	-4.5463313	2.9890455
H	-2.6811056	-3.5778936	1.5397423
H	5.3658976	-1.9349192	2.0588403
H	5.4784899	-0.4207341	2.9949660
H	4.4244871	-0.5261595	1.5432264
C	2.6374721	3.3060120	-4.2545587
C	3.7608336	2.3101442	-2.2246130
C	0.6460625	4.6317074	-4.0730809
C	-0.4239134	5.1498056	-1.8565250
C	-4.1946598	0.6260168	-4.2438838
C	-3.8897028	2.0965232	-2.2144057
C	-4.3432081	-1.7617285	-4.0628418
C	-4.2468124	-2.9482854	-1.8472000
C	1.5606206	-3.9316514	-4.2560393
C	0.1382438	-4.4130360	-2.2262955
C	3.7015200	-2.8639551	-4.0736893
C	4.6826161	-2.1949645	-1.8561095
C	1.6271125	4.0428426	-4.8787804
H	3.4076455	2.8274156	-4.8655020
H	4.5014941	2.9451043	-1.7111730
H	4.2975215	1.7204938	-2.9794562
H	3.3458251	1.6168151	-1.4756740
H	-0.1494572	5.2183201	-4.5412915
H	-1.0588141	4.3871590	-1.3744013
H	-1.0490914	5.8023767	-2.4799777
H	0.0068882	5.7546111	-1.0431714
C	-4.3283283	-0.6173213	-4.8681239
H	-4.1689881	1.5326243	-4.8545224
H	-4.8098964	2.4195136	-1.7002866
H	-3.6489032	2.8564662	-2.9693909
H	-3.0811481	2.0845980	-1.4661633
H	-4.4540774	-2.7439119	-4.5310384
H	-3.2666876	-3.1160310	-1.3692212
H	-4.5011686	-3.8159420	-2.4699772
H	-4.9825344	-2.8786818	-1.0306229

C	2.7026152	-3.4214728	-4.8797601
H	0.7622831	-4.3610783	-4.8673538
H	0.3211416	-5.3718061	-1.7137857
H	-0.6403160	-4.5850496	-2.9810926
H	-0.2569210	-3.7089944	-1.4766521
H	4.6061233	-2.4652911	-4.5416141
H	4.3358829	-1.2661216	-1.3721330
H	5.5594483	-1.9751576	-2.4791783
H	4.9936615	-2.8709364	-1.0441396
C	1.5628141	4.1522850	-6.3782260
C	-4.3968768	-0.7272065	-6.3673670
C	2.8296186	-3.4191812	-6.3792034
H	2.5623547	4.0918538	-6.8309290
H	1.0937512	5.0947919	-6.6943034
H	0.9616471	3.3293923	-6.7987702
H	-4.8481972	0.1678308	-6.8178087
H	-4.9779562	-1.6058248	-6.6813973
H	-3.3851847	-0.8339476	-6.7922151
H	2.2813681	-4.2568955	-6.8323596
H	3.8806791	-3.4792205	-6.6952467
H	2.4132440	-2.4888022	-6.7992508

SIMesPHGa*t*Bu$_2$Cl (**6**)

Ga	6.6426355	2.8415017	7.6661499
P	4.1911808	3.0369881	7.1193648
Cl	7.4488127	4.9915930	7.7589247
C	6.6495620	2.0669212	9.5627158
C	7.5173322	1.8956060	6.0846561
C	8.1024637	1.6981464	9.8896557
C	3.7769979	4.7741680	6.9470919
H	3.7698939	3.0098571	8.4814686
H	5.5733887	6.0932661	9.2858058
C	6.1478279	3.0926487	10.5766559
C	5.7749438	0.8109670	9.6313974
C	7.1145447	2.5639163	4.7728459
C	7.0645268	0.4318435	6.0711522
C	9.0405376	1.9716786	6.2407971
H	8.4937454	0.9188840	9.2176937
H	8.1742838	1.3044466	10.9230475
H	8.7719498	2.5697123	9.8222493
N	3.2645471	5.5882639	7.9033136
N	3.8803654	5.4628269	5.7838526
C	4.9227492	6.5568355	10.0420643
H	6.7450612	4.0160308	10.5518253
H	6.2066264	2.6787977	11.6031590
H	5.0982173	3.3692824	10.3993221
H	4.7168569	1.0300422	9.4171293
H	5.8127139	0.3726347	10.6483407
H	6.1048250	0.0316511	8.9281009
H	6.0260438	2.5436423	4.6113259
H	7.5845995	2.0456175	3.9128395
H	7.4383456	3.6137387	4.7409561
H	7.3782190	-0.1086099	6.9775803
H	7.5054075	-0.1000746	5.2048212
H	5.9696406	0.3401135	5.9855849
H	9.3908273	3.0143541	6.2790108
H	9.5384707	1.4820346	5.3804395
H	9.3930149	1.4664884	7.1526477
C	2.9052772	5.2428845	9.2427213
C	2.8559172	6.8868532	7.3381879
C	4.1621816	4.9257287	4.4899486
C	3.5554208	6.8892461	5.9784496
C	3.6945707	5.7321264	10.3003069
H	5.5026215	6.6803493	10.9652281

H	4.6632661	7.5645557	9.6786376
C	1.7380163	4.4902956	9.4778376
H	3.1834502	7.7088022	7.9858071
H	1.7565437	6.9245885	7.2544817
C	3.2074032	4.0923067	3.8691873
C	5.3399468	5.3135711	3.8214798
H	2.9138171	7.2431169	5.1620411
H	4.4771530	7.4893860	5.9924064
C	3.3093694	5.4143961	11.6068646
C	1.4028374	4.1934937	10.8027140
C	0.8720076	4.0100106	8.3467396
C	3.4993244	3.5912625	2.5964059
C	1.8949051	3.7591747	4.5206285
C	5.5693712	4.8015176	2.5409095
C	6.3449825	6.2347070	4.4532692
H	3.9250245	5.7745223	12.4349266
C	2.1790444	4.6368619	11.8798419
H	0.5031466	3.6036287	10.9964935
H	0.6340836	4.8186089	7.6399816
H	-0.0719008	3.6025750	8.7297633
H	1.3757697	3.2198424	7.7674179
H	2.7698139	2.9360719	2.1131449
C	4.6777349	3.9224109	1.9194014
H	2.0268253	3.0086307	5.3161145
H	1.1912393	3.3575890	3.7805934
H	1.4380272	4.6433159	4.9891577
H	6.4919670	5.0816053	2.0261644
H	6.0233327	7.2868925	4.3878689
H	7.3096609	6.1587542	3.9354210
H	6.5088450	5.9951926	5.5140871
C	1.8220486	4.2654577	13.2934609
C	4.9878366	3.3325744	0.5707212
H	0.7438173	4.0856372	13.4020662
H	2.1188909	5.0506839	14.0021497
H	2.3416285	3.3411880	13.5935212
H	5.5821851	2.4109927	0.6797502
H	5.5738244	4.0269848	-0.0469385
H	4.0708031	3.0687214	0.0263527

SIMesPHAl*t*Bu$_2$Cl (**7**)

Ga	6.6426355	2.8415017	7.6661499
Cl	3.4278206	-11.6716445	6.4244907
Al	5.3181357	-12.8238080	6.3089833
H	1.8810399	-13.2396936	4.8812662
P	4.7572192	-15.2389421	6.6945840
C	6.5374099	-12.2849968	7.8263509
C	6.0088777	-12.8425512	4.4014615
C	1.2501507	-13.7475432	4.1372796
C	2.9939457	-15.4011088	6.9865284
H	4.6188330	-15.5531283	5.3107175
C	5.9060857	-12.6540826	9.1715671
C	7.8886774	-13.0020731	7.7025146
C	6.7636443	-10.7654093	7.7974962
C	4.8678149	-13.0566658	3.4020408
C	7.0686321	-13.9302595	4.1792259
C	6.6451144	-11.4681203	4.1336987
C	1.8325798	-15.0698850	3.7275357
H	0.2492467	-13.8663048	4.5829296
H	1.1474032	-13.0873202	3.2671699
N	2.4140816	-15.2854338	8.2054670
N	2.0476758	-15.7194681	6.0694539
H	4.9423539	-12.1452042	9.3207516
H	6.5685153	-12.3550939	10.0100910
H	5.7291975	-13.7365606	9.2686441

H	7.7769960	-14.0990349	7.7005144
H	8.5463919	-12.7440460	8.5573545
H	8.4269792	-12.7194093	6.7844233
H	7.2603565	-10.4324453	6.8733430
H	7.4077023	-10.4539070	8.6449112
H	5.8157541	-10.2114849	7.8834387
H	4.3919911	-14.0418699	3.5206749
H	5.2490904	-13.0048070	2.3617457
H	4.0810330	-12.2940904	3.5061893
H	7.9313777	-13.8210843	4.8535368
H	7.4570495	-13.8856700	3.1415140
H	6.6611211	-14.9442016	4.3217859
H	5.9326530	-10.6432863	4.2955777
H	6.9915767	-11.4007497	3.0823745
H	7.5214110	-11.2842946	4.7745768
C	2.2428943	-16.0159853	4.6848413
C	1.9999177	-15.3899131	2.3763909
C	3.0800509	-15.1716968	9.4650203
C	0.9456167	-15.4005005	8.1127026
C	0.7440929	-15.9742430	6.7085224
C	2.7739475	-17.2654433	4.3106279
H	1.7006134	-14.6554983	1.6244639
C	2.5559464	-16.6058804	1.9648827
C	3.7961703	-16.2796126	9.9653569
C	2.9312961	-13.9929713	10.2211758
H	0.4798504	-14.4101695	8.2238555
H	0.5704139	-16.0585297	8.9063774
H	0.5395184	-17.0580448	6.7143175
H	-0.0594280	-15.4727196	6.1557662
C	2.9275339	-17.5320709	2.9464862
C	3.1771121	-18.2855958	5.3387279
C	2.7749545	-16.8980640	0.5053787
C	3.8752584	-17.5809360	9.2179725
C	4.4253824	-16.1492004	11.2075364
C	3.5623914	-13.9257846	11.4667871
C	2.1371194	-12.8214885	9.7161625
H	3.3459389	-18.4955905	2.6441100
H	4.0655561	-17.9544498	5.8996948
H	3.4144092	-19.2435710	4.8596074
H	2.3814755	-18.4608526	6.0779086
H	2.0088310	-16.4190255	-0.1195142
H	2.7646452	-17.9781155	0.3053522
H	3.7531606	-16.5117292	0.1766447
H	2.8986358	-17.8718838	8.8036495
H	4.2218360	-18.3832812	9.8813650
H	4.5736824	-17.5077987	8.3692353
C	4.3316388	-14.9794531	11.9690530
H	4.9920118	-16.9985819	11.5979367
H	3.4692328	-13.0054506	12.0488875
H	2.3156019	-12.6384002	8.6471986
H	2.4088401	-11.9110122	10.2653015
H	1.0553088	-12.9769598	9.8588620
C	5.0577464	-14.8489141	13.2799499
H	6.0498944	-14.3942094	13.1273775
H	5.2147770	-15.8281888	13.7523931
H	4.5089255	-14.2057649	13.9815351

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