Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

One-Step Methylation of Phosphabenzenes: Synthesis and Crystallographic Characterization of a 1-Methyl-Phosphininium Salt

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Table of Contents

1. DFT Calculations

DFT calculations for Figure 4 and Figure S21:

DFT calculations were carried out with the ORCA 4.2.0 program suite.[1] Initial molecular structures were created in the program Avogadro[2] or were based on crystal structures, if available. Geometry optimizations were then performed with the PBEh-3c method developed by Grimme and co-workers.[3] PBEh-3c is a reparametrized version of PBE0 (with 42 % HF exchange) with a valence-double-zeta Gaussian AO basis set (def2-mSVP) and with Basis set superposition errors and London dispersion effects accounted for by the gCP and D3 schemes. Numerical Frequency calculations were carried out to confirm the nature of stationary points found by geometry optimizations. The absence of imaginary vibrational frequencies indicated that the optimized structure is at a local minimum. Final single point calculations on the optimized structures were conducted with the B3LYP functional.[4] Additionally, for all calculations, the empirical Van der Waals Correction (D3) was used.[5]. Standardized convergence criteria were used for the geometry optimization (OPT) and the addition "tight" for SCF-calculations ("TIGHTSCF"). A Triple-ζ-valence-basis set (def2-TZVP) was applied for all atoms (single point calculation).[6] Singe point calculations with the B3LYP-functional were done with the RIJCOSX-approximation[7] and solvent effects were taken into account with the Conductor-like-Polarizable-Continuum-Model (CPCM)[8] for n-pentane with ε=1.8371. Intrinsic bond orbital (IBO) analysis[9] was carried out with the IBO module implemented in the ORCA program suite. Molecular orbitals and IBOs were visualized via the freely available programs Avogadro or IBOView v20150427[10].

Gas phase basicity:

The gas phase basicities were calculated as previously reported.[11]

Methyl ion affinity and lone pair energy:

DFT calculations with the B3LYP functional, applying the resolution of identity (RI) approximation[12], were performed with the Turbomole program[13]. For all atoms, the def2-TZVPP basis set[14] was used. Gibbs free energies including thermal corrections at 298.15 K as well as simulated IR-/Raman-Spectra were calculated from normal mode analyses with harmonic approximation. The methyl ion affinity was calculated in the gas phase. Lone pair energies were calculated using the solvent model COSMO[15] (ε_R n-pentane).

2. Experimental Procedures

General Remarks

All reactions were performed under argon in oven-dried glassware using modified Schlenk techniques unless otherwise stated. All solvents and chemicals were commercially available and were used without further purification, except for drying and degassing. All dry or deoxygenated solvents were prepared using standard techniques or were used from an MBraun solvent purification system. *n*-Pentane was additionally dried over molecular sieve (4 Å). 2-Trimethylsilylphosphinine (**5**)[16], 2,3,5,6-tetrakis-(trimethylsilyl)phosphinine (**7**)[17], and dimehtylchloronium tetrakis((pentafluorotellaneyl)oxy)-aluminate[18] were prepared according to literature procedures. The ^{1}H, $^{13}C\{^{1}H\}$, ^{19}F NMR, ^{27}Al NMR, $^{29}Si\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra were recorded on a JEOL ECX400 (400 MHz) spectrometer and all chemical shifts are reported relative to the residual resonance in the deuterated solvents. The ESI-TOF-Mass spectrometry measurements were performed on an Agilent 6210 ESI-TOF, *Agilent Technologies*, Santa Clara, CA, USA.

Phosphinine (5)

5 was prepared using a modified literature procedure.[19] $HCl{\cdot}Et_2O$ (1 M, 15 ml, 15 mmol, 1.7 eq.) was added to 2-trimethylsilylphosphinine (**6**) (1.52 g, 9.02 mmol, 1 eq.) in diethyl ether (30 ml) and was stirred for 7 days at T = 60 °C. The solvent, trimethylsilylchloride and the excess HCl were carefully removed by distillation at p = 300 mbar. The product **5** was isolated as a colorless liquid (236 mg, 2.46 mmol, 27%) with minor impurities by condensation from the residue.

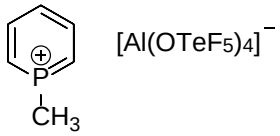
^{1}H NMR (401 MHz, Dichlormethane-d_2): δ = 8.87 – 8.68 (m, 2 H, *ortho*-H), 7.96 – 7.83 (m, 2 H, *meta*-H), 7.63 – 7.52 (m, 1 H, *para*-H) ppm.

^{31}P NMR (162 MHz, Dichlormethane-d_2): δ = 206.4 ppm.

General method: direct electrophilic methylation of phosphinines

All steps were performed at low temperature. The corresponding phosphinines were dissolved in *n*-pentane (1 ml) and transferred to $[(CH_3)_2Cl][Al(OTeF_5)_4]$ in chloromethane (1 ml). The reaction mixture was stirred for about 20 minutes until the solution turned orange or, depending on the concentration, an orange phase separated from the reaction solvent. After removal of all volatile compounds the products were isolated as beige powders and stored at low temperature.

A) 1-methylphosphinine tetrakis((pentafluorotellaneyl)oxy)aluminate (5-CH_3)



Phosphinine (**5**, 13 mg, 0.14 mmol, 1 eq.), $[(CH_3)_2Cl][Al(OTeF_5)_4]$ (149 mg, 0.14 mmol, 1 eq.), *T* = -80 °C, Product (**5-CH_3**, 153 mg, 0.14 mmol, quant.), product only stable at low temperature, NMR spectra were collected at *T* = -70 °C, .NMR spectra show small amounts of decomposition products due to very high sensitivity of the product.

^{1}H NMR (401 MHz, Dichlormethane-*d_2*): δ = 8.66 – 7.93 (m, 5 H), 3.16 (d, $^{2}J_{P,H}$ = 22.2 Hz, 3 H, -CH_3) ppm.

^{13}C{^{1}H} NMR (101 MHz, Dichlormethane-*d_2*): δ = 143.7 (d, *J* = 16.7 Hz), 132.8 (d, *J* = 49.5 Hz), 127.4 (d, *J* = 90.4 Hz), 6.9 (d, *J* = 50.5 Hz, -CH_3) ppm.

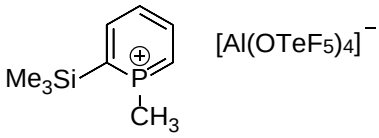
^{19}F NMR (377 MHz, Dichlormethane-*d_2*): δ = -36.79 – -39.30 (m, 1 F), -44.20 – -46.11 (m, 4 F) ppm.

^{27}Al NMR (104 MHz, Dichlormethane-*d_2*): δ = 47.7 ppm.

^{31}P NMR (162 MHz, Dichlormethane-*d_2*): δ = 136.6 ppm.

ESI-TOF$^+$ (m/z): calculated for $C_6H_8P^+$ [M^+]: 111.0358; found: 111.0374.

B) 1-methyl-2-trimethylsilylphosphinine tetrakis((pentafluorotellaneyl)oxy)aluminate (6-CH_3)



2-Trimethylsilylphosphinine (**6**, 23 mg, 0.14 mmol, 1 eq.), $[(CH_3)_2Cl][Al(OTeF_5)_4]$ (149 mg, 0.14 mmol, 1 eq.), *T* = -80 °C, Product (**6-CH_3**, 163 mg, 0.14 mmol, quant.), at room temperature as a CD_2Cl_2 solution **6-CH_3** starts to decompose after around one hour and is fully decomposed after two days.

^{1}H NMR (401 MHz, Dichlormethane-*d_2*): δ = 8.63 – 8.35 (m, 3 H), 8.09 – 7.98 (m, 1 H), 3.10 (d, $^{2}J_{P,H}$ = 21.8 Hz, 3 H, -CH_3), 0.53 (s, 9 H, -$SiMe_3$) ppm.

^{19}F NMR (377 MHz, Dichlormethane-*d_2*): δ = -36.90 – -39.69 (m, 1 F), -44.46 – -46.97 (m, 4 F) ppm.

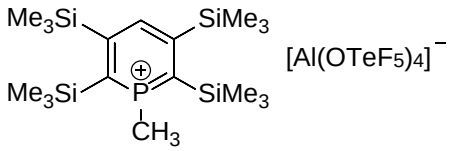
^{27}Al NMR (104 MHz, Dichlormethane-*d_2*): δ = 46.9 ppm.

^{29}Si{^{1}H} NMR (80 MHz, Dichlormethane-*d_2*): δ = 4.59 (d, $^{2}J_{P,Si}$ = 8.3 Hz) ppm.

^{31}P{^{1}H} NMR (162 MHz, Dichlormethane-*d*$_2$): δ = 142.4 ppm.

ESI-TOF$^+$ (m/z): calculated for $C_9H_{16}PSi^+$ [M^+]: 183.0753; found: 183.0809.

C) 1-methyl-2,3,5,6-tetrakis(trimethylsilyl)phosphinine tetrakis((pentafluorotellaneyl)oxy)aluminate (7-CH$_3$)



2,3,5,6-Tetrakis(trimethylsilyl)phosphinine (**7**, 10 mg, 0.026 mmol, 1 eq.), $[(CH_3)_2Cl][Al(OTeF_5)_4]$ (27 mg, 0.026 mmol, 1 eq.), *T* = -110 °C, after addition slowly warmed up to *T* = -80 °C, Product (**7-CH$_3$**, 36 mg, 0.026 mmol, quant.), at room temperature as a CD_2Cl_2 solution **7-CH$_3$** starts to decompose after around five hours and is fully decomposed after four days.

^{1}H NMR (401 MHz, Dichlormethane-*d*$_2$): δ = 8.39 (d, $^4J_{P,H}$ = 10.1 Hz, 1 H, *para*-H), 3.02 (d, $^2J_{P,H}$ = 19.9 Hz, 3 H, -CH_3), 0.61 (s, 18 H, *ortho*-$SiMe_3$), 0.49 (s, 18 H, *meta*-$SiMe_3$) ppm.

^{19}F NMR (377 MHz, Dichlormethane-*d*$_2$): δ = -37.23 – -39.96 (m, 1 F), -44.98 – -46.43 (m, 4 F) ppm.

^{27}Al NMR (104 MHz, Dichlormethane-*d*$_2$): δ = 46.8 ppm.

^{29}Si{^{1}H} NMR (80 MHz, Dichlormethane-*d*$_2$): δ = 5.75 (d, $^2J_{P,Si}$ = 21.1 Hz, *ortho*-$SiMe_3$), 0.85 (d, $^3J_{P,Si}$ = 10.3 Hz, *meta*-$SiMe_3$) ppm.

^{31}P NMR (162 MHz, Dichlormethane-*d*$_2$): δ = 157.63 (qd, *J* = 20.0, 10.1 Hz) ppm.

ESI-TOF$^+$ (m/z): calculated for $C_{18}H_{40}PSi_4^+$ [M^+]: 399.1939; found: 399.1888.

3. NMR Spectra

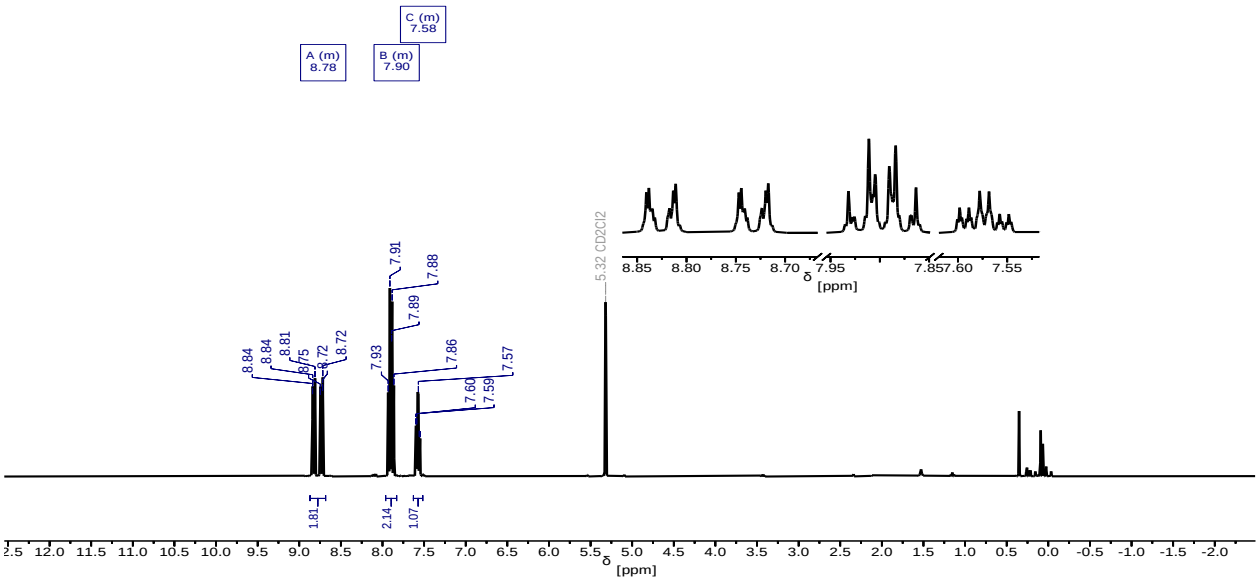


Figure S1: ^{1}H NMR spectra of phosphinine (**5**) in CD_2Cl_2.

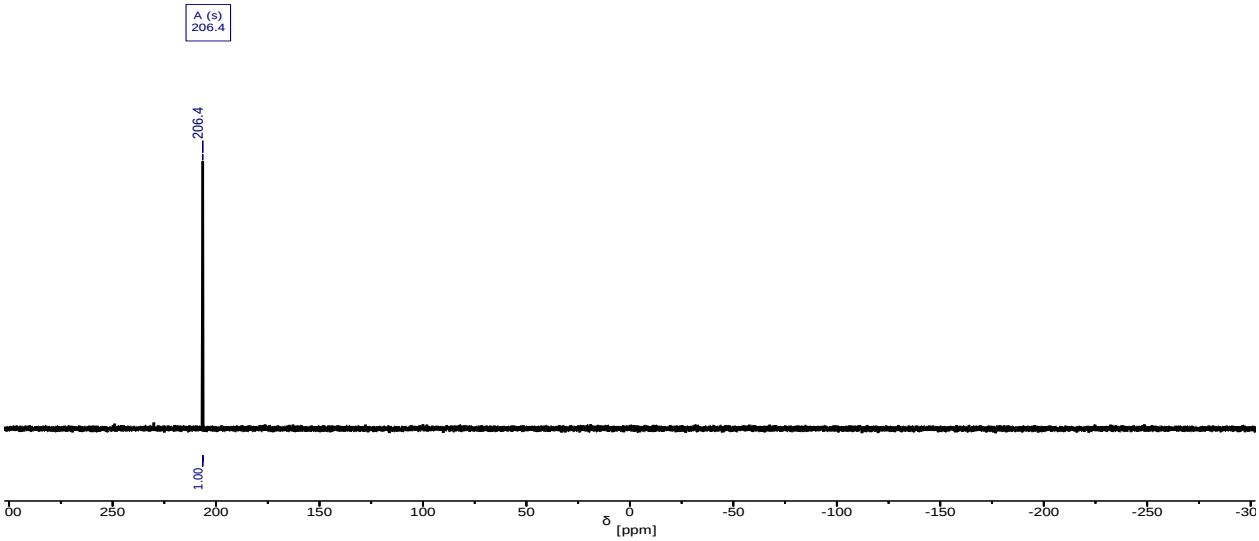


Figure S2: $^{31}P\{^{1}H\}$ NMR spectra of phosphinine (**5**) in CD_2Cl_2.

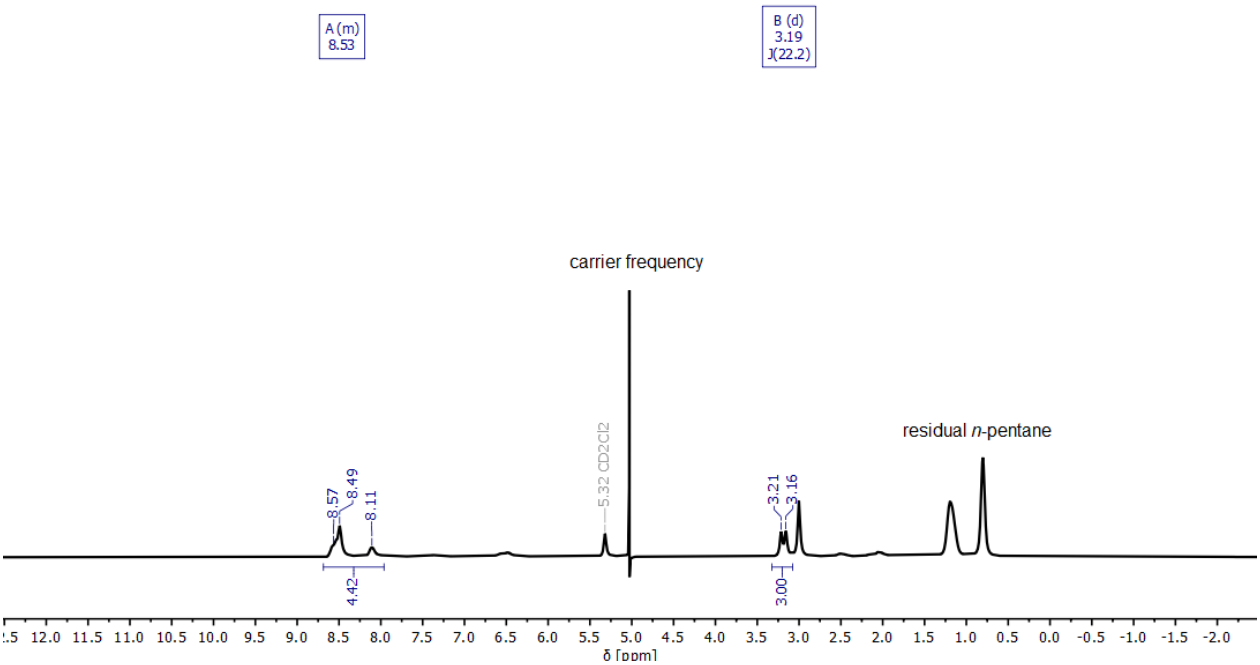


Figure S3: ^{1}H NMR spectra of 1-methylphosphinine tetrakis((pentafluorotellaneyl)oxy)aluminate (**5-CH$_3$**) in CD_2Cl_2 at T = -70 °C.

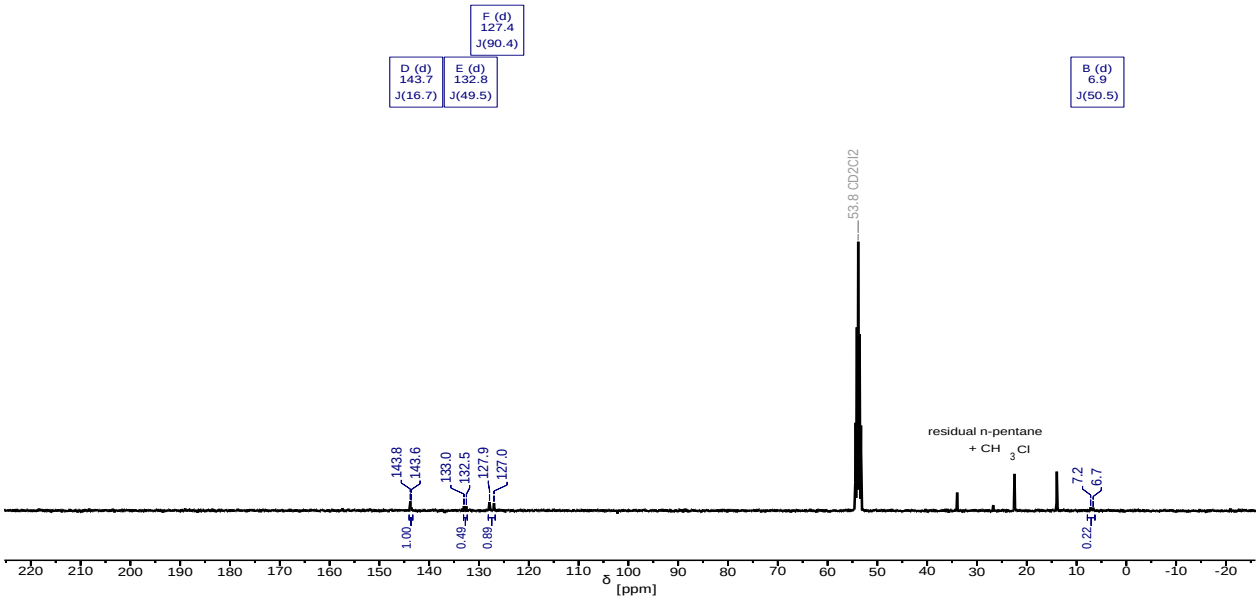


Figure S4: ^{13}C{^{1}H} NMR spectra of 1-methylphosphinine tetrakis((pentafluorotellaneyl)oxy)aluminate (**5-CH$_3$**) in CD_2Cl_2 at T = -70 °C.

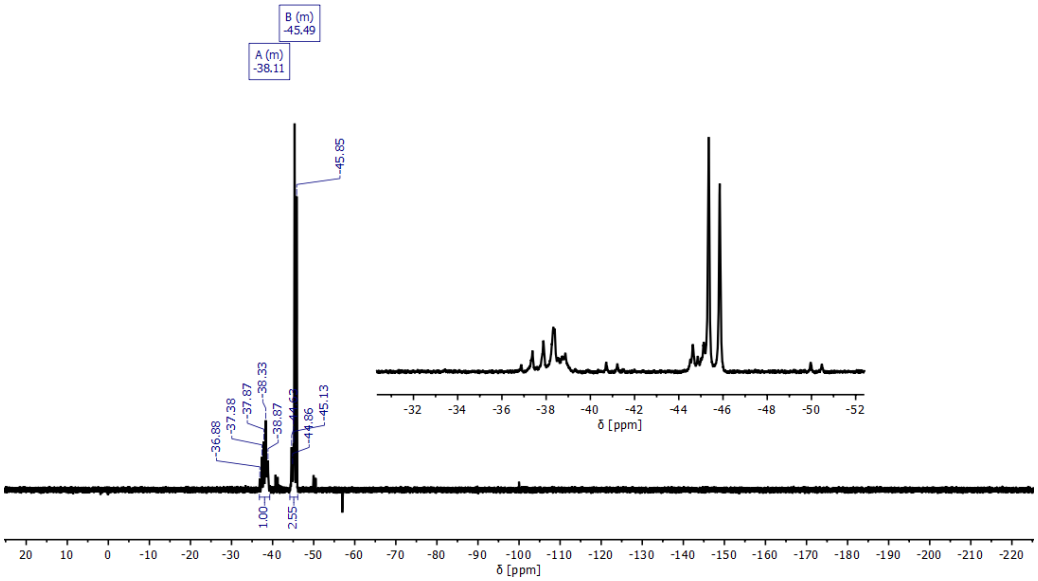


Figure S5: ^{19}F NMR spectra of 1-methylphosphinine tetrakis((pentafluorotellaneyl)oxy)aluminate (**5-CH$_3$**) in CD_2Cl_2 at T = -70 °C.

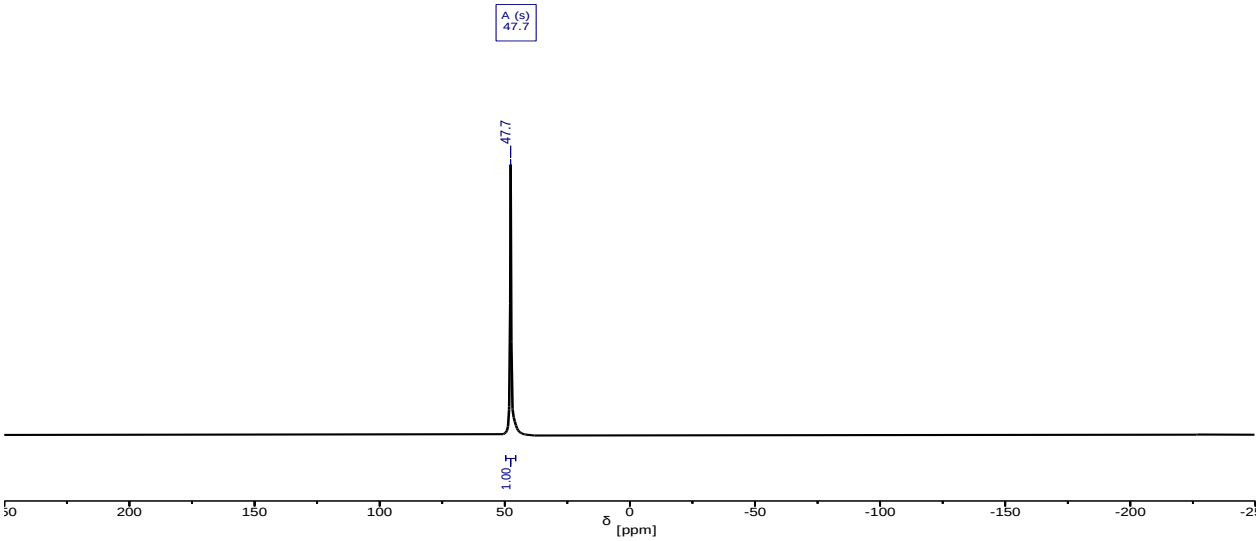


Figure S6: ^{27}Al NMR spectra of 1-methylphosphinine tetrakis((pentafluorotellaneyl)oxy)aluminate (**5-CH$_3$**) in CD_2Cl_2 at T = -70 °C.

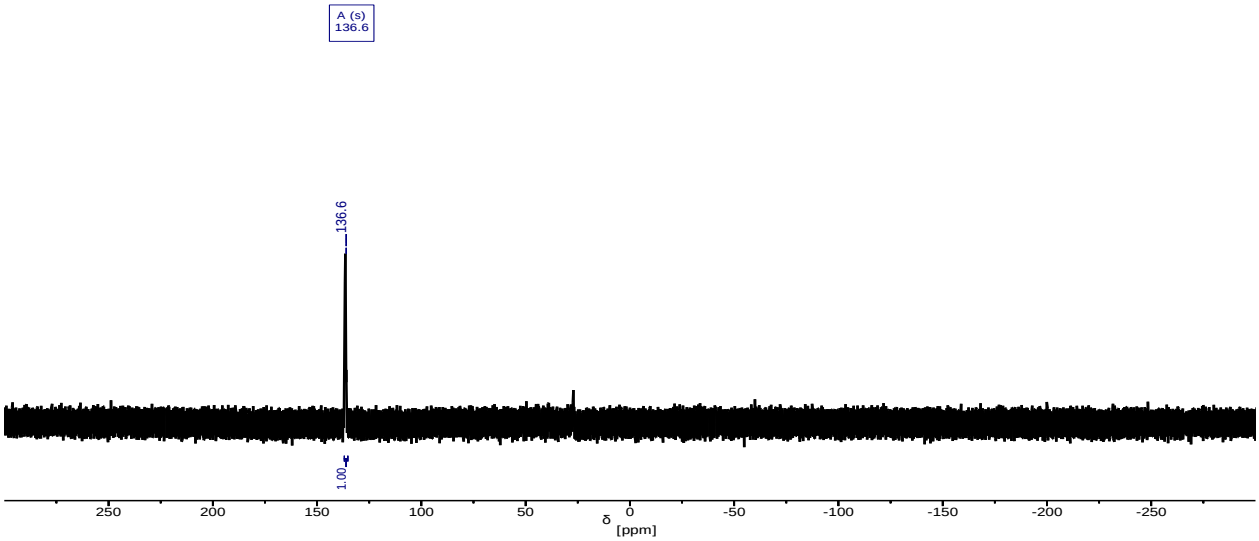


Figure S7: ^{31}P NMR spectra of 1-methylphosphinine tetrakis((pentafluorotellaneyl)oxy)aluminate (**5-CH$_3$**) in CD_2Cl_2 at T = -70 °C.

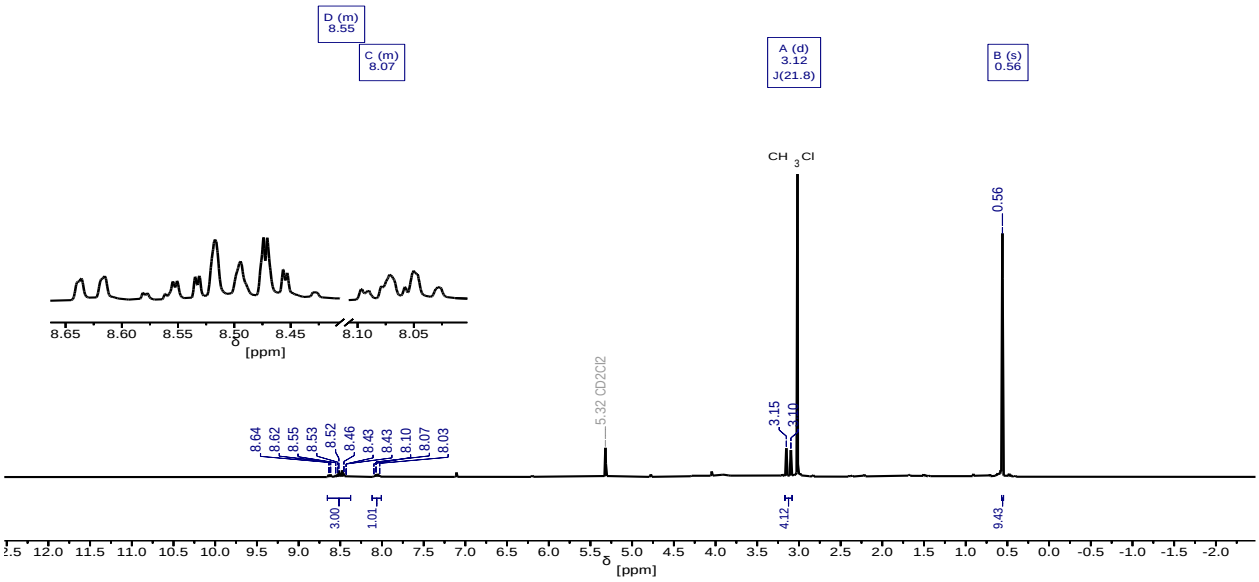


Figure S8: ^{1}H NMR spectra of 1-methyl-2-trimethylsilylphosphinine tetrakis((pentafluorotellaneyl)oxy)aluminate (**6-CH$_3$**) in CD_2Cl_2.

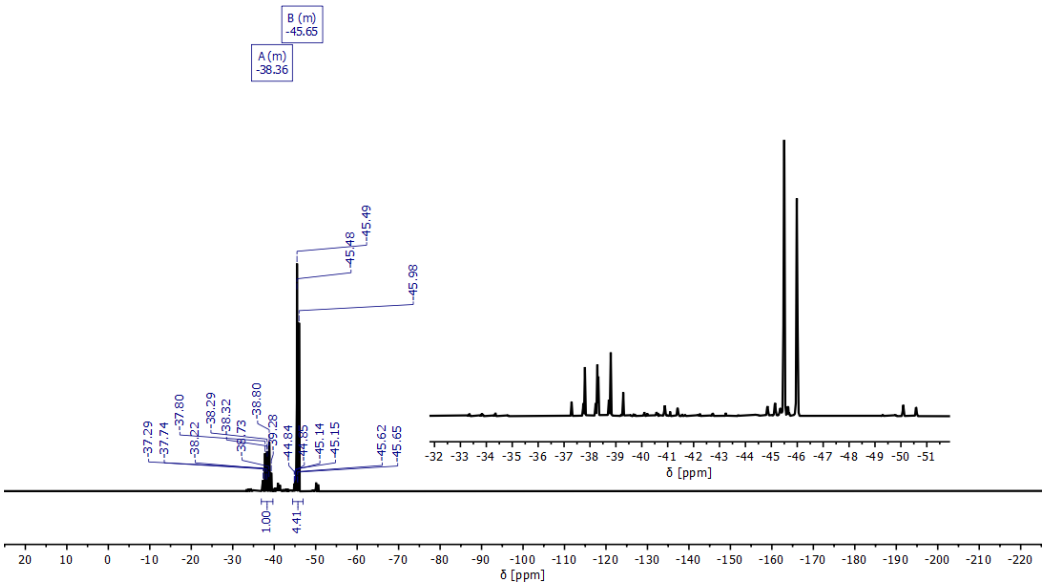


Figure S9: ^{19}F NMR spectra of 1-methyl-2-trimethylsilylphosphinine tetrakis((pentafluorotellaneyl)oxy)aluminate (**6-CH$_3$**) in CD_2Cl_2.

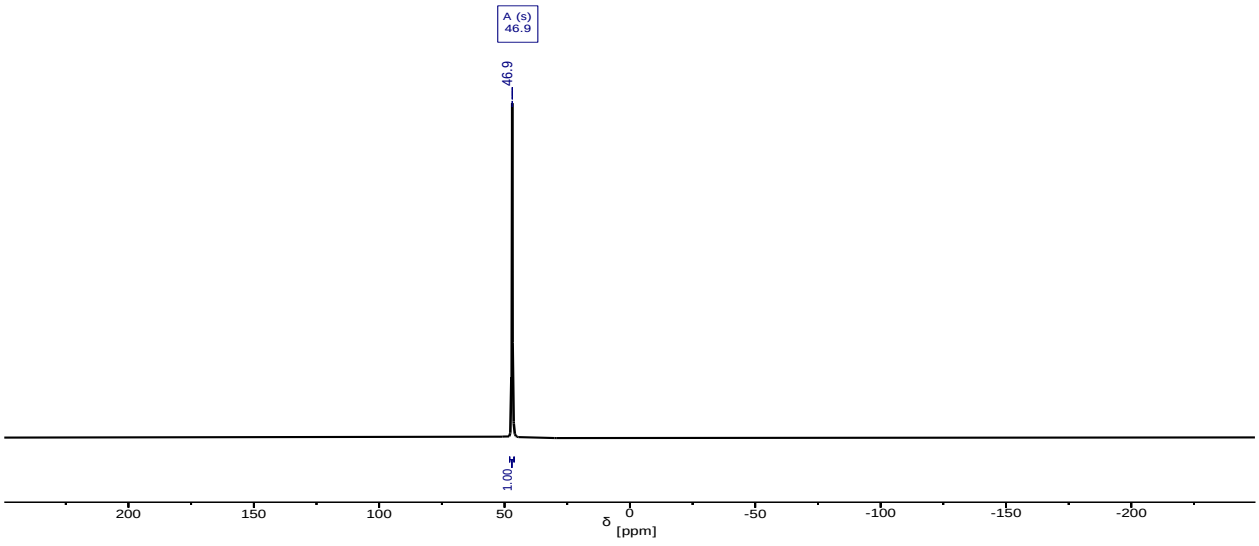


Figure S10: ^{27}Al NMR spectra of 1-methyl-2-trimethylsilylphosphinine tetrakis((pentafluorotellaneyl)oxy)aluminate (**6-CH$_3$**) in CD_2Cl_2.

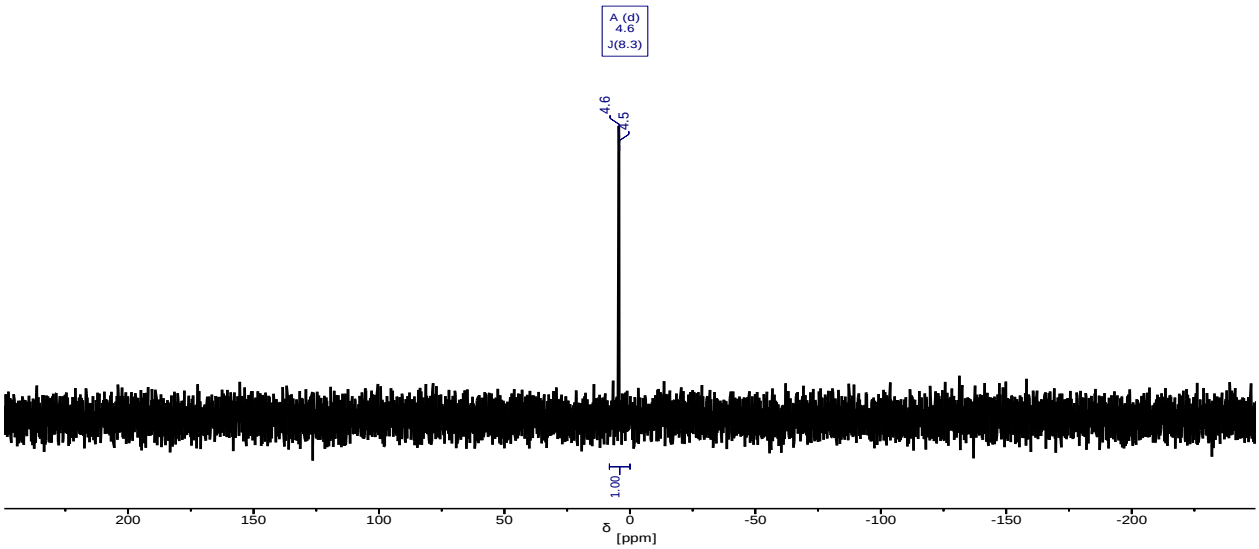


Figure S11: $^{29}Si\{^{1}H\}$ NMR spectra of 1-methyl-2-trimethylsilylphosphinine tetrakis((pentafluorotellaneyl)oxy)aluminate (**6-CH$_3$**) in CD_2Cl_2.

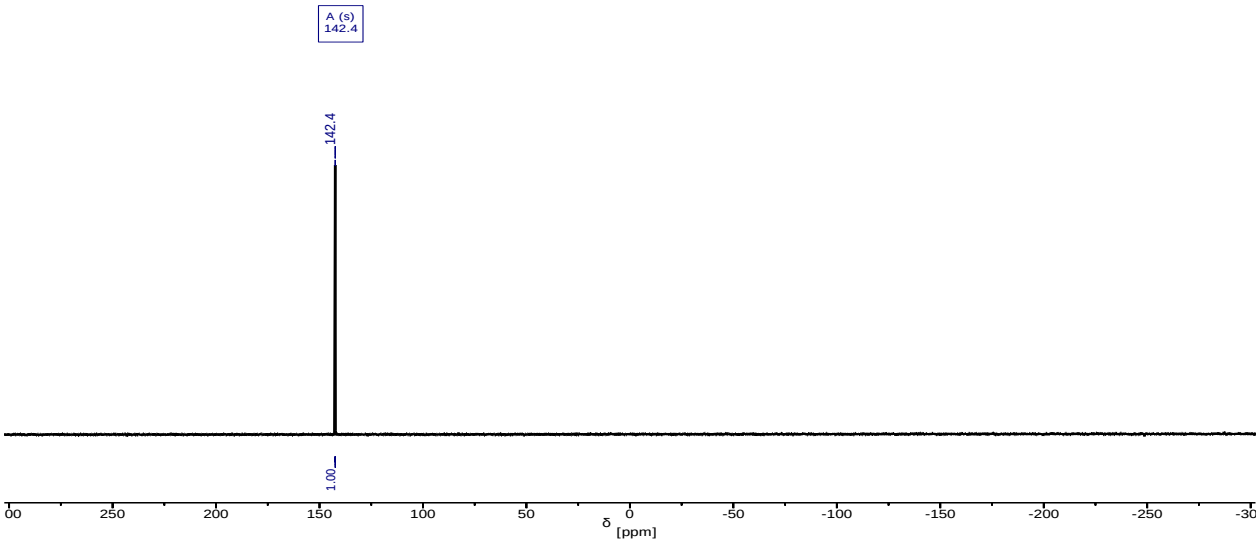


Figure S12: $^{31}P\{^{1}H\}$ NMR spectra of 1-methyl-2-trimethylsilylphosphinine tetrakis((pentafluorotellaneyl)oxy)aluminate (**6-CH$_3$**) in CD_2Cl_2.

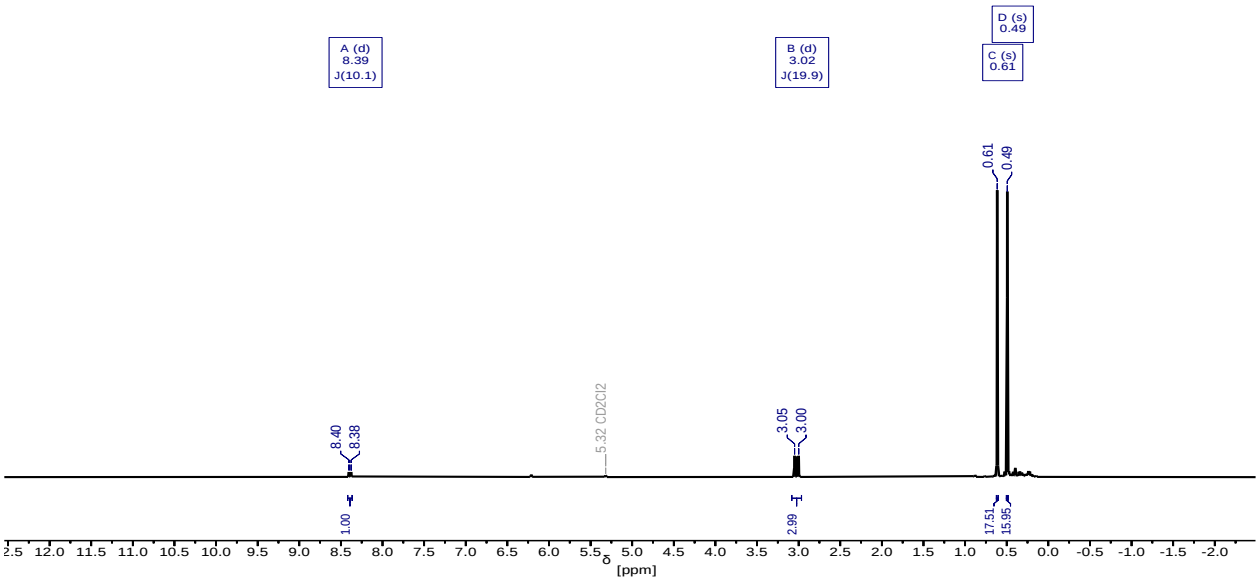


Figure S13: ^{1}H NMR spectra of 1-methyl-2,3,5,6-tetrakis(trimethylsilyl)phosphinine tetrakis((pentafluorotellaneyl)oxy)aluminate (**7-CH$_3$**) in CD_2Cl_2.

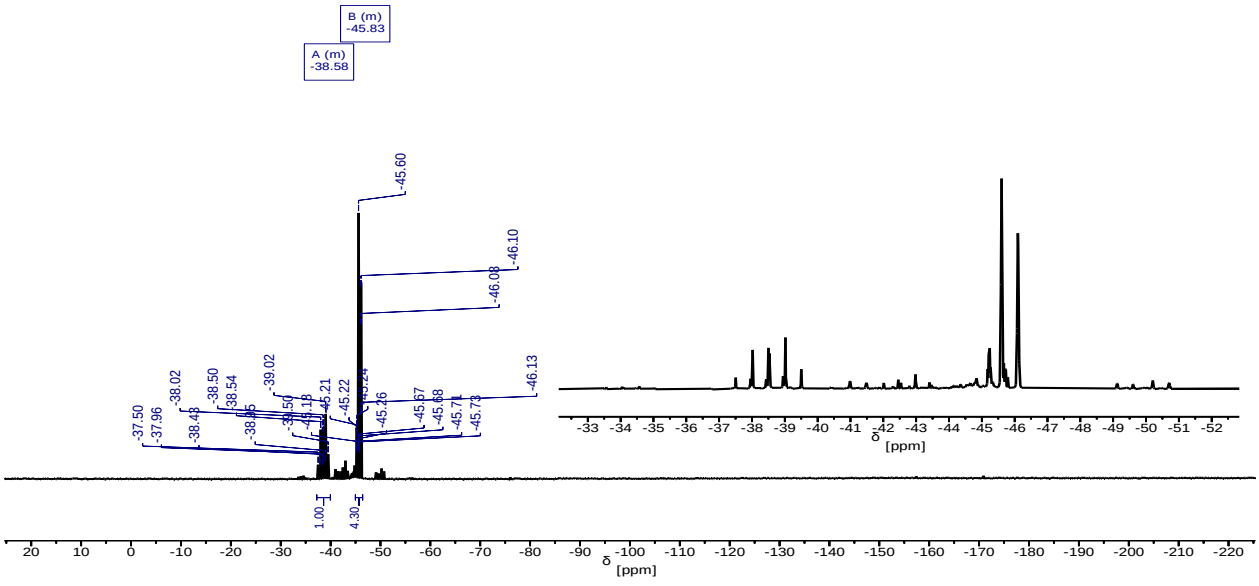


Figure S14: ^{19}F NMR spectra of 1-methyl-2,3,5,6-tetrakis(trimethylsilyl)phosphinine tetrakis((pentafluorotellaneyl)oxy)aluminate (**7-CH$_3$**) in CD_2Cl_2.

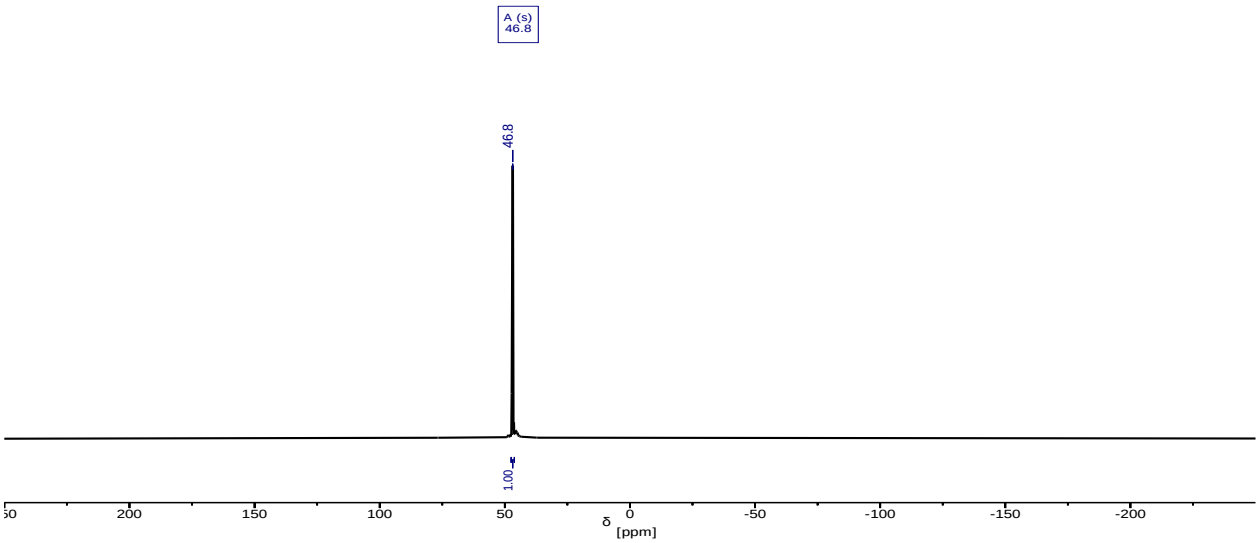


Figure S15: ^{27}Al NMR spectra of 1-methyl-2,3,5,6-tetrakis(trimethylsilyl)phosphinine tetrakis((pentafluorotellaneyl)oxy)aluminate (**7-CH$_3$**) in CD_2Cl_2.

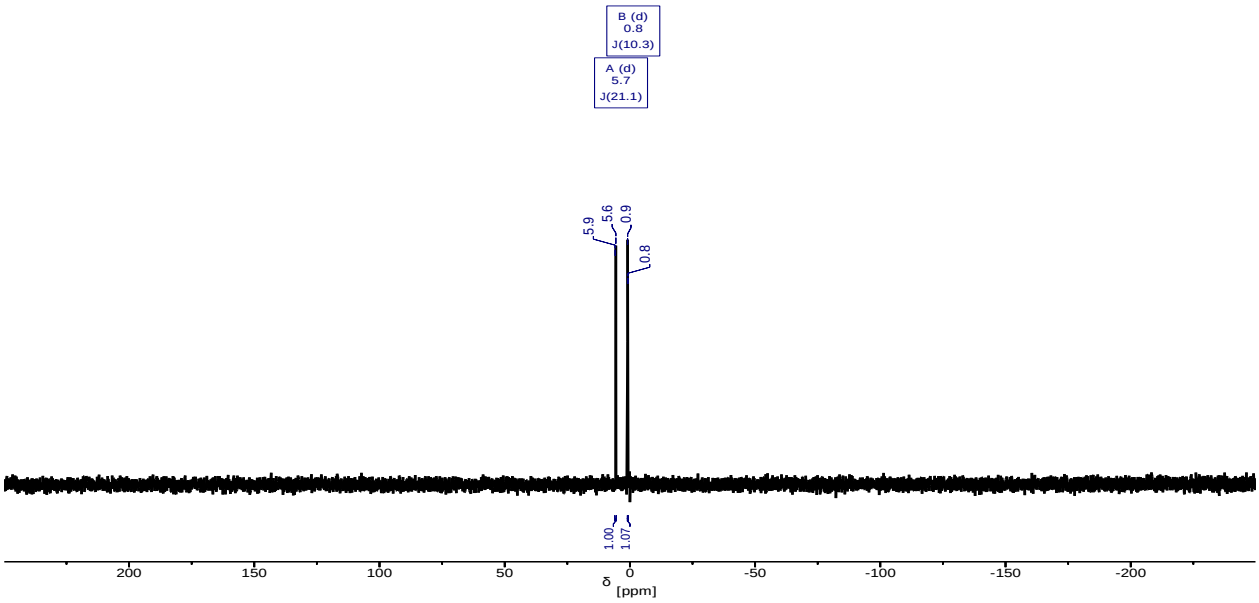


Figure S16: ^{29}Si{^{1}H} NMR spectra of 1-methyl-2,3,5,6-tetrakis(trimethylsilyl)phosphinine tetrakis((pentafluorotellaneyl)oxy)aluminate (**7-CH$_3$**) in CD_2Cl_2.

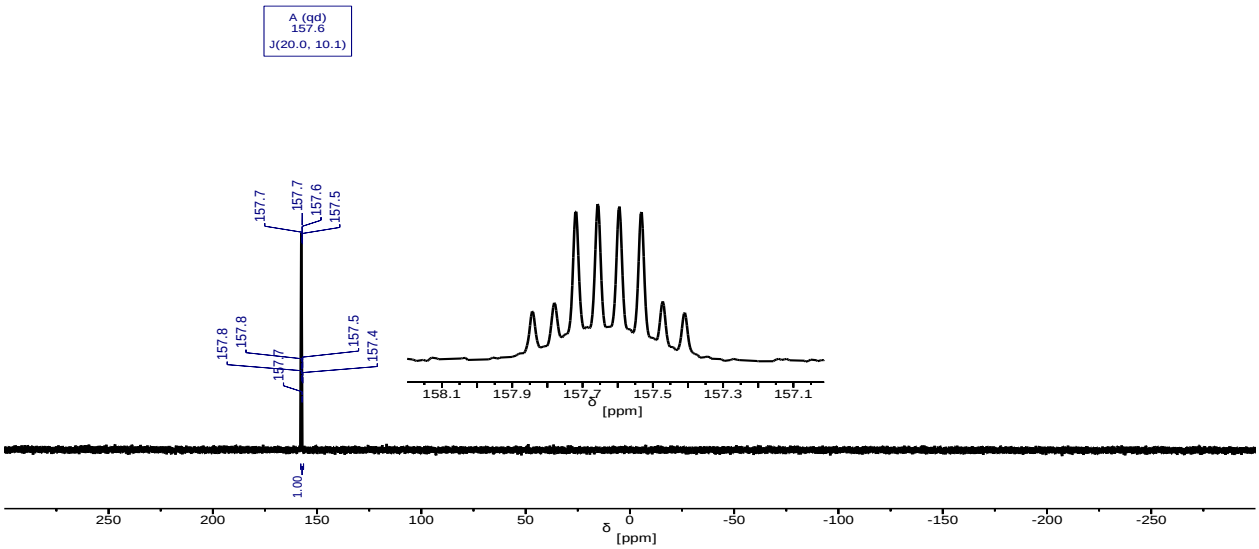


Figure S17: ^{31}P NMR spectra of 1-methyl-2,3,5,6-tetrakis(trimethylsilyl)phosphinine tetrakis((pentafluorotellaneyl)oxy)aluminate (**7-CH$_3$**) in CD_2Cl_2.

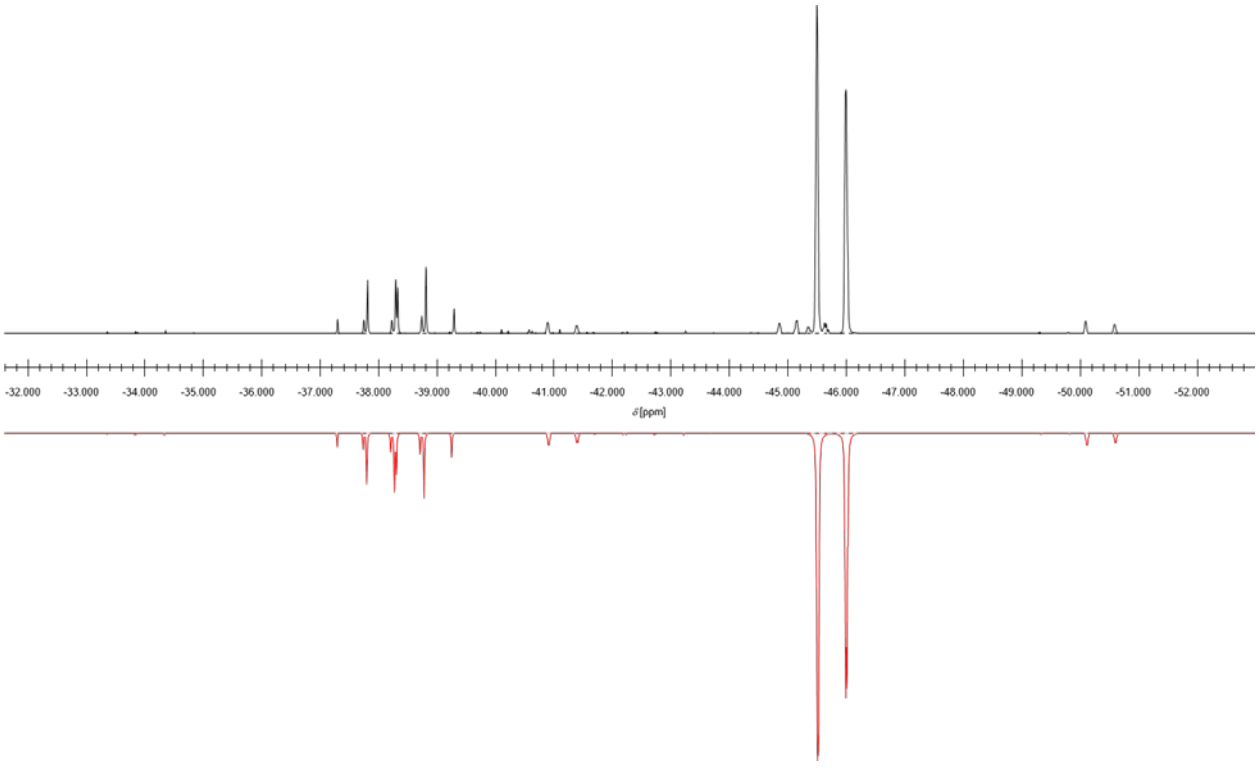


Figure S18: Experimental (top) and simulated (bottom) ^{19}F NMR spectra of 1-methyl-2-trimethylsilylphosphinine tetrakis((pentafluorotellaneyl)oxy)aluminate (**6-CH$_3$**) in CD_2Cl_2.

Table S1. NMR and MS data of **1-CH$_3$**-phosphininium salts

	5-CH$_3$[a]	**6-CH$_3$**	**7-CH$_3$**
$\delta(^{31}P)$ [ppm]	136.6 (206.4)[b]	142.4 (230.7)[b]	157.6 (268.0)[b]
$\delta(^{1}H)_{Me}$ [ppm]	3.16	3.12	2.99
$^{2}J_{(P,H)}$ [Hz]	23.0	21.0	20.0
$\delta(^{1}H)_{aromatic}$ [ppm]	8.0 - 8.7	8.0 - 8.4	8.36
$\delta(^{1}H)_{SiMe3}$ [ppm]	-	0.56	0.59; 0.47
$\delta(^{27}Al)$ [ppm]	47.7	46.9	46.8
$\delta(^{19}F)$ [ppm]	-37.9; -45.6	-38.4; -45.7	-38.5; -45.9
$\delta(^{29}Si)$ [ppm]	-	4.6	5.7; 0.9
$m/z_{(measured)}$, $[M^+]$	111.0374	183.0809	399.1888
$m/z_{(calculated)}$, $[M^+]$	111.0358	183.0753	399.1939

[a] NMR spectra recorded at T = -70 °C. [b] $^{31}P\{^{1}H\}$ chemical shift of the corresponding phosphinines **5**, **6** and **7**.

4. Crystallographic Data

Low-temperature x-ray diffraction data was collected on a Bruker-AXS X8 Kappa Duo diffractometer coupled to a Photon 2 detector. The data collection was executed with Mo K_α radiation (λ = 0.71073 Å) from an $I\mu S$ micro-source, performing ϕ- and ω-scans. The structure was solved by dual-space methods using SHELXT[20] and refined against F^2 on all data by full-matrix least squares with SHELXL-2017[21] following established refinement strategies[22]. The program Olex2[7] was also used to aid in the refinement of the structures.[23] All non-hydrogen atoms were refined anisotropically, all hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups). Selected crystallographic data for **7** and **7-CH$_3$** can be found in **Table S1** below.

The supplementary crystallographic data for **7** and **7-CH$_3$** can be found in the CCDC with the following deposit numbers CCDC 2062243-2062244. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Table S2. Selected crystallographic data

	7	**7-CH_3**
CCDC number	2062244	2062243
Empirical formula	$C_{17}H_{37}PSi_4$	$C_{18}H_{40}AlF_{20}O_4PSi_4Te_4$
Formula weight	384.79	1381.21
Temperature/K	100.0	100.0
Crystal system	orthorhombic	monoclinic
Space group	Pbca	Cc
a/Å	11.0213(5)	12.0027(4)
b/Å	11.8221(5)	16.9978(5)
c/Å	18.3959(7)	21.5539(7)
α/°	90	90
β/°	90	90.5900(10)
γ/°	90	90
Volume/$Å^3$	2396.89(17)	4397.2(2)
Z	4	4
Reflections collected	187764	189889
Independent reflections (R_{int})	3375 (0.0503)	13410 (0.0296)
wR_2 (all data)	0.0849	0.0421

Additional refinement details for 2,3,5,6-tetrakis(trimethylsilyl)phosphinine (7):

The structure was found to be disordered across a special position. RIGU restraints were required for the phosphinine core (P1, C1-C5) to produce a stable model. SADI restraints were also used for all Si-C distances. Without these restraints C2-Si2 was found to be 2.00 Å (1.98 Å with restraint) and C5-Si4 was found to be ~1.7 Å (1.82 Å with restraint). These are closer to the bond lengths observed for the remaining Si-C_{ring} bonds (1.90-1.91 Å), which are typical for Si-C_{ring} of this type of species.

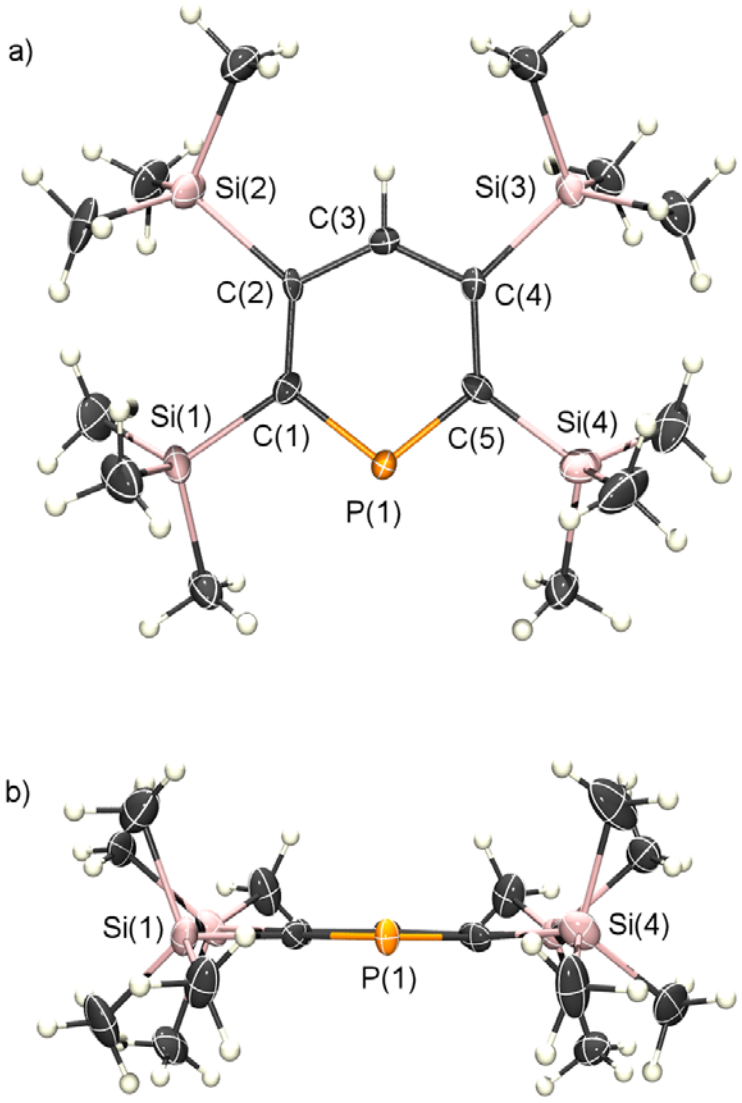


Figure S19. Molecular structure of **7** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): P(1)-C(1): 1.745(11); P(1)-C(5): 1.707(11); C(1)-C(2): 1.406(9); C(2)-C(3): 1.449(9); C(3)-C(4): 1.421(11); C(4)-C(5): 1.417(10). C(1)-P(1)-C(5): 106.0(4); C(2)-C(3)-C(4): 131.1(5).

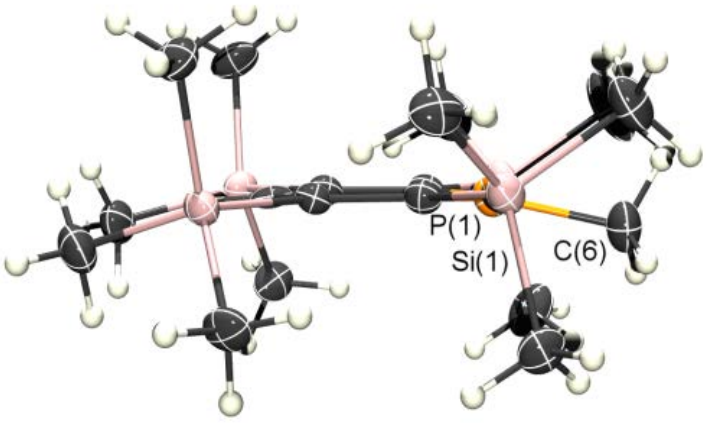


Figure S20. Molecular structure of **7-CH$_3$** in the crystal. Only the cation is illustrated in a side view. Displacement ellipsoids are shown at the 50% probability level.

5. Calculated structures

DFT calculations for Figure 4 and Figure S21, coordinates in Ångström [Å]:

5-CH$_3$

C	5.35376158687973	-0.86283511310896	0.72347652622314
C	4.02452055482778	-1.26538417663744	0.73367878466697
C	2.95477429109902	-0.43236611179612	1.04477388426075
C	4.28319307497381	1.59472476204638	1.45885989847672
C	3.07678634363176	0.91155760743743	1.38499784599266
H	1.96100145728742	-0.85752559226262	1.01972189900522
P	5.69412058870549	0.74273030726653	1.10541702926622
H	2.17507275167520	1.46734244213564	1.60810066935512
H	4.31604851627453	2.64174847748094	1.72874405331804
C	7.34670995448802	1.43817230331182	1.18019319995695
H	8.01999151747321	0.81764517616328	0.59068870708887
H	7.70077597206935	1.47498165936176	2.20925804656576
H	7.34118886957887	2.44302809352521	0.76091886754160
H	3.81459851187944	-2.29699503217780	0.48179326164966
H	6.14469549554435	-1.55677370851205	0.47249443253631

7-CH$_3$

C	6.52244650745755	-3.01932477100843	-1.43076072337978
C	3.03916226496959	-3.37061331031474	-1.39554718529429
C	8.15148589175086	-0.62943945295324	-0.81686690238547
C	6.09998196497021	4.08297509007274	0.62262621565350
C	5.41805992811378	-0.88366487244563	0.62508072040919
C	0.52066499446256	2.42818529037717	0.38047092701709
C	4.06893629691324	-1.29196652087570	0.69119823086643
C	7.31137680566773	1.30222388430537	1.55568507685604

C	3.20509619665168	4.60963380701510	0.90569249172332
C	7.79097215056423	-2.69556678831229	1.43624506870189
C	4.55651260173852	-4.36748248229723	1.21467242246274
C	1.79162916269092	-3.25434498645911	1.36498312299399
C	3.04794388743078	-0.40246211622481	1.06590626257439
C	4.30137246572433	1.68411144217702	1.41140066554619
C	3.08709779205731	0.96576944129403	1.38281544922818
C	0.29226631249760	0.19797059409719	2.42558545412190
C	4.91646276979489	3.92045384533769	3.45983563479046
C	1.45711410119434	2.76655094919498	3.40004499685972
H	6.08069557078515	-2.46831520126852	-2.26210742608149
H	8.77551542115498	-1.18563896386213	-1.51939895134577
H	3.87490125336689	-3.19930933900907	-2.06934808372357
H	7.46306138181413	-3.43727637380075	-1.79769333780667
H	2.69265513585800	-4.39304521986662	-1.55751496444807
H	7.65012078140742	0.14214176188299	-1.40461633857930
H	2.22987502030645	-2.70814549188968	-1.70776137393941
H	5.87553056388825	-3.85921624955225	-1.19965060089267
H	8.84013626090675	-0.14502572874699	-0.12746317205846
H	6.14618077264717	3.59086978383524	-0.35094204126306
H	6.01690256238656	5.15206927364815	0.41675415389691
H	7.85950339005910	1.78638292318297	0.75344479556083
H	1.09857810596851	3.20555215544217	-0.11300418866762
H	3.09563574464481	4.40192628254324	-0.15961074769567
H	0.31676273311596	1.65509919019882	-0.36255877501419
H	7.05768180656993	3.95040123782611	1.12199462715434
H	4.05800955564481	-5.33855655949700	1.17969189069692
H	8.65326273086970	-3.27322289666320	1.09837085218962
H	0.96406467040882	-2.70279418596177	0.91754953440427
H	-0.44130978339784	2.86236640521493	0.65897858668731
H	1.49486635966101	-4.30533642714339	1.36005564136497
H	5.53396796961899	-4.50404966754227	0.76078372468591
H	3.50910669787448	5.65583230051590	0.98990877415882
H	7.87457993021533	0.44221524801069	1.91113464942014
H	2.06490577660314	-0.84621956025278	1.11910597047622
H	7.19852886650422	1.99492633079755	2.38668151564000
H	8.16308310068798	-1.96894491924499	2.16106046631384
H	2.22664850425707	4.52929991014163	1.36784103893779
H	7.13330397667663	-3.37569157473112	1.97489610225504
H	-0.00887556863493	-0.46117369438484	1.61071992313204
H	4.70825530752992	-4.13373244325641	2.27011658976132
H	1.87061213178142	-2.95486019344409	2.41106427815272
H	-0.63128301995871	0.58616321012632	2.86032752662719
H	0.76952878811237	-0.41173319014431	3.19418699769688
H	5.06482229191059	4.98935567214397	3.62373184552651

H	5.82104015574231	3.41971004424518	3.81034233348254
H	1.95369843420683	3.72511039900084	3.27818676500587
H	0.44021929731907	2.98296544975189	3.73447448935226
H	4.10306809796214	3.60050356482861	4.10885478558799
H	1.94797784866801	2.23774629909750	4.21914846116586
P	5.66830455262586	0.74130744219610	1.05241431696818
Si	6.95706270178229	-1.85970573506555	-0.02231461865283
Si	3.41669620100711	-3.09715824935011	0.42419915884226
Si	4.59015271798881	3.58228447977398	1.64290485242809
Si	1.34840310680193	1.66074345729296	1.88222204385061

Methyl ion affinity, coordinates in Bohr [a_0]:

$[CH_3]^+$

C	-0.00000000000112	-0.00000000289526	-0.00003242021457
H	0.00000000000042	0.00000000096511	-2.06197538334113
H	-1.78574512123733	0.00000000096507	1.03100390177791
H	1.78574512123802	0.00000000096507	1.03100390177781

5

C	-2.51678191008340	0.00000000000000	-1.70596235679524
C	-2.30841503426824	0.00000000000000	0.90770302143356
C	0.00000000000000	0.00000000000000	2.16963309625464
C	2.30841503426824	0.00000000000000	0.90770302143356
C	2.51678191008340	0.00000000000000	-1.70596235679524
H	-4.39627671411148	0.00000000000000	-2.52261781778365
H	-4.02221807701247	0.00000000000000	2.03221943884841
H	0.00000000000000	0.00000000000000	4.21532841170741
H	4.02221807701247	0.00000000000000	2.03221943884841
H	4.39627671411148	0.00000000000000	-2.52261781778365
P	0.00000000000000	0.00000000000000	-3.80764607936833

5-CH_3

C	0.76669064002812	1.45116786735497	-0.02539970079560
C	3.38058485020842	6.41376805893781	0.03908581996073
C	0.76646573765707	6.11296492973481	0.01739626588186
C	-0.46216964620764	3.78182364196311	-0.01501048301599
H	-0.37564579185506	-0.24636321156352	-0.04758583415774
H	4.23558048839256	8.26961140961626	0.06761559727928
H	-0.37655859547059	7.81017348729775	0.02632059247593
H	-2.50557172303249	3.78188006163714	-0.03028615627337
P	5.18701008172367	3.78209575380836	0.05063610222929
C	3.38134392996800	1.15109172954088	-0.00918853951544
H	4.23723027882261	-0.70450880494347	-0.01473675011930
C	8.58459755627476	3.78063726666150	-0.01636264211224
H	9.25770459209640	3.92780857961736	-1.95640696524254
H	9.27585300655186	5.37565124175842	1.08648605047662

H	9.25887908531353	2.02645119681326	0.82417610945881

6

C	-1.62595713709201	2.16484179766833	0.09528914466922
C	2.96712925384555	4.43456641849094	0.02229985073081
C	1.53015372431733	6.64467185962546	-0.10586331341905
C	-1.10144622097489	6.73669407764994	-0.13661875074054
C	-2.61334900075154	4.58931645880928	-0.04057212924586
H	-2.93069108790017	0.58588411987720	0.16657258297942
H	2.50606101196415	8.44768774607235	-0.18631214742209
H	-2.00807361551045	8.56873137319050	-0.23907528864133
H	-4.64866351764366	4.83260252406646	-0.07203712458120
P	1.56749891384807	1.44738356103040	0.16672964784426
Si	6.55380016183150	4.57867869859932	0.00498209785731
C	7.62902059238192	7.96173753113191	0.28157389945786
H	6.94905928431772	8.84825172131099	2.01611126973340
H	9.69217196744682	8.03495779211904	0.31715558765728
H	7.00377715001431	9.11546037246654	-1.31074918457300
C	7.82925466027757	2.70545869423192	2.74706507253986
H	7.22714382224564	0.73481880493935	2.65679168409218
H	9.89371516256833	2.73282718813835	2.75448907389452
H	7.17943138896683	3.47539975382921	4.54742099868401
C	7.76400557748737	3.20100223794991	-3.04532772416480
H	7.05659793949766	4.25246727648786	-4.67374814323064
H	9.82712021725795	3.24874351759131	-3.10840557242880
H	7.17129157460463	1.23726548972724	-3.26474527603417

6-CH_3

C	-2.84288438750407	0.97608909731599	-0.02051346239704
C	1.92963556727946	3.41088768513643	-0.01890746283231
C	0.35322294834813	5.54804495359748	-0.10441436064655
C	-2.28343310480132	5.57152066028806	-0.14384556668320
C	-3.80158382238459	3.42173755634479	-0.10614838124934
H	-4.07539023606505	-0.65373952863428	0.00497988320979
H	1.27855561474396	7.37357315924342	-0.14104832378224
H	-3.21055788208866	7.39230598969325	-0.20963608788064
H	-5.83391975937041	3.65557698512481	-0.14505347720260
P	0.33245795361438	0.63552817406607	0.02702460851098
C	1.73989020748570	-2.45816333310948	0.19604416691075
H	3.26875754728299	-2.61341448405873	-1.17077497515879
H	2.46146833788156	-2.81698247160117	2.08932205078285
H	0.28332743628117	-3.84082405797914	-0.25614476523780
Si	5.58304560406734	3.72070221572176	-0.00120980158793
C	6.32197732146622	7.16670947322487	0.22156236052066
H	5.57242586300819	8.02918770861755	1.93804534497894

H	8.37268685597207	7.39932581371869	0.27113615536232
H	5.63519351810820	8.23545028712812	-1.40289201930311
C	6.80517096431444	1.96276869315267	2.82001260631513
H	6.47524535543994	-0.07061428893996	2.71731451241294
H	8.84828404793576	2.22597201975308	2.95478791562097
H	5.97829221556235	2.66050049981793	4.57568066254353
C	6.77586945285057	2.34156557383063	-3.03704559269789
H	8.82740854328695	2.55168849738960	-3.12915051395671
H	6.36958550521621	0.32852979876238	-3.23122412089736
H	5.98057492751853	3.30857615089384	-4.67565795626282

7

C	0.25600686604322	3.17686077501896	2.65478149991201
C	4.73791638409084	4.54835242782878	0.13413470181354
C	3.35984801729540	3.99216812949382	-2.08372706225717
C	0.78574713036470	3.33670540056824	-1.93428538211302
C	-0.76980711739835	2.99442356680173	0.19669083372703
H	-0.13816247136198	3.05280297359990	-3.73147851485685
P	3.38320131963383	4.13475860612678	3.11826623953857
Si	4.53060061323851	4.09516941718243	-5.52682246137430
Si	8.16619943145605	5.66468250572588	0.49989080094861
Si	-4.19397963007220	2.20030328122853	-0.74251482069541
Si	-1.33467689729826	2.62576654309282	5.86406598998875
C	8.61046157529108	7.20665214031410	3.68515734535474
H	10.54085951880694	7.93873373775107	3.78183673491387
H	7.32491599593977	8.79448410813228	3.96688746321528
H	8.34918620351983	5.90529472504206	5.25785089534792
C	10.38473927054537	2.87531475652041	0.39172954397501
H	10.25269708191993	1.78787861138194	-1.34956891881571
H	12.34065892660415	3.50501775685060	0.60098088049841
H	9.96942721864000	1.59835410204747	1.95896717076699
C	1.13764364223948	1.97968465042627	8.35231810072611
H	2.31950733245265	0.35921160904574	7.87211660230825
H	2.38340697851444	3.58234259963117	8.69105234390238
H	0.16796510811911	1.54443101853093	10.12489442303620
C	-3.08093604418910	5.56063785272470	6.88941019356411
H	-4.52707635507624	6.16354915573466	5.55621923424712
H	-3.99078596246785	5.25295096917177	8.71792574501015
H	-1.74641505356684	7.11927471953101	7.11104277997921
C	-4.65918788803269	-1.33361604215271	-0.78334955735572
H	-3.37698525538544	-2.19775377723979	-2.15067140697990
H	-4.31027576209092	-2.21819110577693	1.04106304960722
H	-6.58771032015906	-1.80006531550842	-1.35661325659755
C	-6.67366125182233	3.81817341550532	1.24204513407999
H	-6.42614336973636	5.86606120242013	1.18632774648673

H	-8.52342986542082	3.40161268669259	0.42218446154841
H	-6.73255065715046	3.24229393380325	3.21220308028629
C	4.32535120821377	7.42386497355178	-6.78549770249754
H	5.46751619315769	8.76460895835909	-5.72228943746137
H	4.94041236922141	7.48827770379168	-8.75601980010559
H	2.37014650524809	8.08221029557990	-6.72172136054330
C	9.12955698650938	8.18388435867170	-1.83797798268440
H	7.85936274956574	9.80581239705282	-1.71917055542265
H	11.01679724012487	8.84566792600386	-1.31997130685995
H	9.20805668527031	7.58259060878531	-3.80049309974200
C	7.78060662969888	2.71542339770370	-6.01460661286120
H	9.31324569082632	3.74280008174945	-5.11354233202630
H	7.84795302772406	0.76305472584721	-5.34987392504627
H	8.16700405503359	2.68596964818050	-8.04367953984089
C	2.40450519104021	2.08237364692670	-7.57634812306022
H	2.21357156832852	0.16009781411372	-6.85240064581595
H	0.51362262259244	2.86654854676098	-7.81492022500509
H	3.24599980274676	1.95332806075142	-9.45814667918074
C	-3.45089775919608	-0.24691806818131	5.96093270815363
H	-2.40341531182654	-1.93723810373331	5.40971695125509
H	-4.06691153747695	-0.51878768218264	7.91404858027985
H	-5.13870877207961	-0.13879144024647	4.79517490167672
C	-4.82729237320457	3.36507810198356	-4.06130424412277
H	-6.84020860916208	3.13088811696775	-4.46042784075233
H	-4.38258013011181	5.36714990513080	-4.28432139315409
H	-3.80065864022925	2.31698343272229	-5.50861596557204

7-CH_3

C	0.46319235031120	1.09855673626616	-0.36270365502897
C	5.26241112615418	3.86723595937117	-0.04550133489531
C	3.63473677112686	5.99413428386024	0.10170372816193
C	0.98271984667913	5.72023945917715	0.04862119820163
C	-0.57596303463963	3.56182169885202	-0.06580931145647
H	-0.03732648839071	7.48253752390996	0.12169533580526
P	3.68777209156128	1.07975011680573	-0.45813373011240
C	5.36194557824096	-1.58359986190264	-1.81973206323855
H	7.01255670684383	-0.85549075126230	-2.80107969455253
H	5.94287039049149	-2.95830323550565	-0.41326448119981
H	4.12711059866427	-2.48064996033856	-3.19455942845730
Si	-4.15902459956682	4.45240937213433	0.08109116597554
Si	-1.24686035927744	-2.17036005921470	-0.44049105652346
Si	4.62589949027810	9.55310442414629	0.18280919738096
Si	8.89749453737864	3.67453364405833	0.54170633946013
C	-5.31109651111628	4.06772075014834	3.41773759966564
H	-7.31726554934949	4.54656333267170	3.51438323687895

H	-5.07983410892182	2.17964022438262	4.19333109636846
H	-4.30908826720365	5.38138390320088	4.65459404710994
C	-4.01229105806050	-2.30424661802192	1.77146324410352
H	-3.40727498734996	-1.99936713747270	3.71914640626505
H	-5.57004458656685	-1.03552533243014	1.37016947300690
H	-4.74696740882437	-4.23238766009392	1.66314573201962
C	-4.51733072543877	7.89091147602013	-0.75582964651289
H	-3.68604364519482	8.37640130267087	-2.57876237451210
H	-6.54128947925287	8.27965674836557	-0.89060152090229
H	-3.76391859910998	9.17574945944691	0.66803451262948
C	-6.08031702971012	2.72489867925587	-2.35915749093577
H	-6.22319695387121	0.69003587722197	-2.13896794781718
H	-8.00156203785564	3.47945267098250	-2.29043532930951
H	-5.34957362691718	3.11469379270952	-4.24950445038427
C	-2.09813852755985	-2.89684672809200	-3.80504039111465
H	-3.34501814400953	-1.48868643408766	-4.63913979445053
H	-0.42105788703574	-3.02679526274687	-5.00045820973011
H	-3.05715924065013	-4.72262990465949	-3.89877148329380
C	0.91937955490572	-4.71527039057619	0.80813879980422
H	2.26101777505324	-5.46108407486538	-0.55891768728435
H	1.94895993421334	-4.14581560173305	2.50321998742357
H	-0.28895403227768	-6.29516287988795	1.36123407168323
C	4.90127175539128	10.61975889852476	3.55680159081388
H	5.37851131504257	12.62786845330550	3.60879900672991
H	3.09261183923795	10.39453751592341	4.52460802828578
H	6.32283281171338	9.60984562433561	4.64579804467221
C	2.02948188206882	11.43328416612984	-1.36116508448834
H	0.30345620673891	11.56008756704248	-0.24543636294282
H	2.72280609237504	13.36335691125503	-1.60373122760399
H	1.53809328528280	10.72498777858243	-3.23457089238035
C	7.50986106589390	10.22477035334233	-1.78008435197008
H	9.27710107349298	9.42579681531742	-1.11010254896559
H	7.22139021455521	9.61054518422741	-3.72880262545568
H	7.75364402006967	12.27514517337422	-1.82829768764686
C	9.91066887337836	5.98568397492843	3.02964443327167
H	8.90280991712188	5.64668984302378	4.79682659735724
H	11.91185471364819	5.62618973805373	3.39522764100933
H	9.72598625592553	7.96993548325203	2.55043083584684
C	9.69395210556008	0.50114140456786	1.96199505368148
H	8.39097433347493	-0.05923411805938	3.46076397283291
H	9.84671818852061	-1.04211373991706	0.61236491286303
H	11.55249515178645	0.69299082449584	2.84071269479699
C	10.62279162574075	4.04499398476951	-2.53313985633808
H	12.65703274909083	3.93566672349463	-2.19781168419889
H	10.14472829136322	2.53917246194368	-3.86060028254452

H	10.23593856296553	5.83784151214656	-3.46405690722125

Pyridine

C	-1.43115678107010	-4.42821497599381	-0.01323149727069
C	-0.02927099499355	-2.20461347388019	-0.01415343024844
C	-1.31239540053638	0.08477816631413	-0.01616365516096
C	-3.93656187432724	0.05174817726855	-0.01687698947923
C	-5.16121037517340	-2.27416130850221	-0.01579735363189
H	-0.48604733293418	-6.24735241924785	-0.01173196321934
H	2.01370349334279	-2.27551756087699	-0.01340173874930
H	-0.28906042743032	1.85584938188114	-0.01709472569057
H	-5.01986145552476	1.78537858468053	-0.01831088489989
H	-7.20911559004342	-2.36499061828356	-0.01634527013625
N	-3.95043873742956	-4.48425468028711	-0.01416294187128

1-Methylpyridinium

C	-1.19666217567416	-4.14722775619215	-0.72155008570930
C	0.08088464417617	-2.03490366439693	0.11099739218606
C	-1.25360052349146	0.18812087187871	0.53955501003241
C	-3.84708138252900	0.22929369866056	0.11741318894669
C	-5.03681600076814	-1.93386173630130	-0.71520283475068
H	-0.26878139607722	-5.92752725403858	-1.08648172977162
H	2.09512089506938	-2.14799481580537	0.42048647336743
H	-0.28663245118587	1.86363876589493	1.19787008227922
H	-4.95395730205487	1.91504193906627	0.43191519261211
H	-7.04310443161499	-2.02300120134997	-1.07492712888795
N	-3.71421222057568	-4.07568530705882	-1.12038329034598
C	-5.02681223265409	-6.35167251268110	-2.08851813318945
H	-4.06386881742865	-8.02640199059740	-1.39781578089904
H	-6.96336719764649	-6.34800629754452	-1.41193398289143
H	-5.00211539330585	-6.32585117844575	-4.14497465442474

Triphenylphosphine

C	-8.08976800163164	0.11615568044321	2.89078139332265
C	-6.60608353579749	-1.94223470894101	3.58153094663310
C	-4.00801093139899	-1.87182082122269	3.21320953090833
C	-2.84625929445014	0.23504628752331	2.11224781065154
C	-4.35697350258288	2.29096620417526	1.43260985947461
C	-6.95710667274343	2.23270669925125	1.82448355418561
H	-10.11181986332607	0.07436995851316	3.19471765204232
H	-7.46861026897110	-3.59270177891265	4.42801403994015
H	-2.86215644547671	-3.46641464688499	3.79372659482430
H	-3.50537078454191	3.95131228350526	0.59903136673260
H	-8.09678205621107	3.84584833241371	1.29097369132333
C	1.45103018352578	3.42183587966630	1.05107897795674

C	1.71005420120988	4.41940626534802	-1.38000116004527
C	1.92162691382454	5.00461610632029	3.11827531489958
C	2.39991083748465	6.93241644868908	-1.73279183184616
H	1.38010013988629	3.23174302676673	-3.01015675103601
C	2.58539041033947	7.52021097627243	2.76843863721810
H	1.77427688116422	4.25320681456793	5.01722156234175
C	2.83108595620916	8.49114658777552	0.33729141705676
H	2.59743193720201	7.67042107774965	-3.63068401759608
H	2.93325468985828	8.71508907009603	4.39186756604218
H	3.36830721717224	10.44505012073084	0.05993813947460
C	1.03572749831353	-1.47349545405739	-1.31224732220215
C	-0.88702031143576	-1.85632784166397	-3.08085080135657
C	3.45014092842868	-2.40984133632645	-1.85376292007906
C	-0.40362591501210	-3.12181755223168	-5.33484091247465
H	-2.77455882673350	-1.17170317094957	-2.69938492504740
C	3.94067759261778	-3.65091115133257	-4.11439047153299
H	4.95429234469478	-2.17015532608158	-0.48531324013329
C	2.01026137514444	-4.01412743605459	-5.86219649548149
H	-1.91810332169386	-3.40591765984739	-6.68086231321180
H	5.82242232927464	-4.35351474912311	-4.50122747756826
H	2.38304775640799	-4.99785758332463	-7.61613502977421
P	0.62035265081205	0.11181976184896	1.76487880847985

Methyltriphenylphosphonium

C	-7.48043360824464	-6.81834129221482	1.17440366356862
C	-4.94062276408944	-6.73420312786625	0.51141062522982
C	-3.65216806580323	-4.44554938480247	0.51318141540470
C	-4.91556572829665	-2.22478290753315	1.18552760454357
C	-7.47409404728157	-2.32029022481146	1.86311954282015
C	-8.74522874194126	-4.61246782824353	1.85148626194525
H	-8.47947925362772	-8.60150506426841	1.16320803037145
H	-3.95750825469104	-8.44665166780992	-0.01431394866529
H	-1.68023062885661	-4.39624533641804	-0.01642176658535
H	-8.48078308398701	-0.62633089695570	2.40920998859394
H	-10.72095868031708	-4.67744872373376	2.36861027285345
P	-3.27405974189116	0.75708930382459	1.22377722379131
C	-5.21755992912748	3.08590689995758	-0.36462168215386
H	-6.99596108674937	3.31131651683947	0.64406349063525
H	-4.23983706733064	4.89461816544073	-0.42007758509478
H	-5.60973795570979	2.47120989314388	-2.28792864989924
C	-0.31212127259673	0.50234579291668	-0.43361110734969
C	-0.29301174460827	0.36246201774718	-3.07800135954874
C	1.96538894968440	0.40101997543127	0.90200499782932
C	1.98286028560156	0.13628656019272	-4.35895531162884
H	-2.03467598957830	0.41930739907492	-4.14711306418177

C	4.23569789445933	0.16933578305914	-0.39745576146850
H	1.97589524673106	0.51352248786752	2.94149669113212
C	4.24611931245830	0.04076269499415	-3.02078737193925
H	1.99023703217377	0.03641716109860	-6.39983266592455
H	5.99268946202206	0.09635749414957	0.64329274907571
H	6.01666636825266	-0.13174715445682	-4.02734561578859
C	-2.75210901088143	1.78351266722551	4.42706659760775
C	-2.06241360079910	4.29619248347882	4.90065284933216
C	-2.98882885886937	0.08638549865999	6.43821892717405
C	-1.62979985977576	5.09222928388825	7.36025298481530
H	-1.84969239303197	5.63483712465626	3.36963931503488
C	-2.54761913232018	0.90061661483751	8.89581923172840
H	-3.52375707295503	-1.85558960339255	6.09841208537159
C	-1.87343707308734	3.39649364310897	9.35731744757440
H	-1.10404259401860	7.03413219386109	7.71842484089857
H	-2.73745708523976	-0.41689830208258	10.44611683377637
H	-1.53808903726909	4.02543665026357	11.27287506827987

Table S3. Calculated Energies (E_{tot}) and Zero Point Energies (ZPE) of selected molecules.

	E_{tot} [H]	**ZPE [kJ/mol]**
$[CH_3]^+$	-39.46703085729	81.21
5	-534.7974510734	219.2
5-CH_3	-574.4474845479	318.2
6	-943.4069787243	481.7
6-CH_3	-983.0693665864	581.8
7	-2169.196150478	1273.0
7-CH_3	-2208.868860466	1376.0
Pyridine	-248.2266226497	230.7
1-Methylpyridinium	-287.8968663244	338.6
Triphenylphosphine	-1036.078532706	711.0
Methyltriphenylphosphonium	-1075.784295534	815.1

Optimized Structures of the cations 7-CH_3 and 5-CH_3.

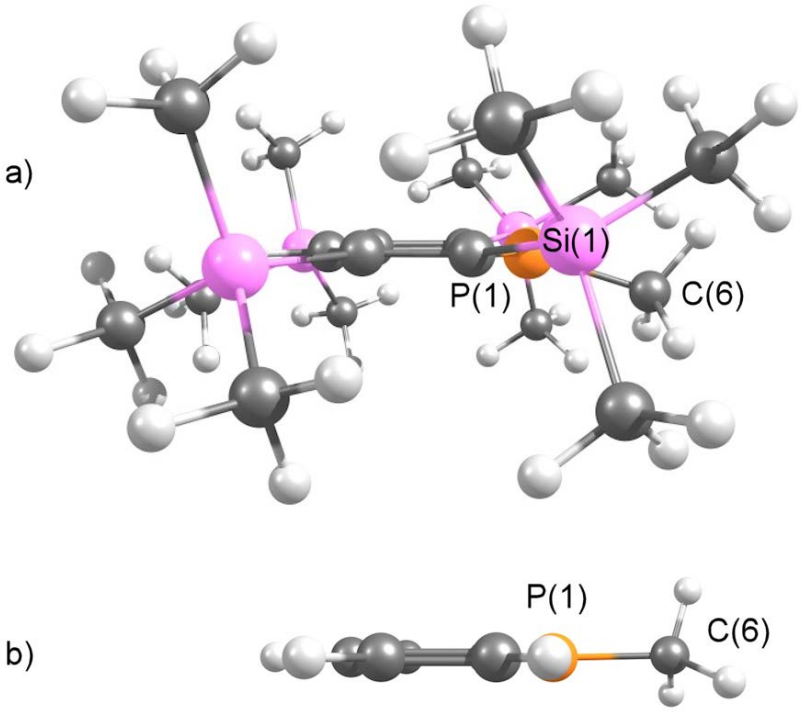


Figure S21. Optimized structures of the cations of 7-CH_3 (a) and 5-CH_3 (b). Calculated bond lengths and angles: 7-CH_3^+: P(1)-C(6): 1.8077; P(1)-C(1): 1.6988, P(1)-C(5): 1.6989; C(1)-P(1)-C(5): 117.71; C(3)-(P1)-C(6): 17.085. 5-CH_3^+: P(1)-C(1): 1.6851; P(1)-C(6): 1.795; P(1)-C(5): 1.6857; C(1)-P(1)-C(5): 111.103; C(3)-P(1)-C(6): 178.72.

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