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η^2-Phosphasilene transition metal complexes – a novel building block for hetero-multimetallic complexes

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Contents

1. General information

Unless otherwise specified, standard Schlenk techniques were used for all syntheses and all sample manipulations. Hexane, pentane, decane and toluene were dried over $CaCl_2$, degassed, kept on *n*BuLi in vacuum and distilled prior to use. THF and Et_2O were degassed and kept on Ph_3CLi under vacuum and distilled prior to use. All commercially available reagents were used without additional purification. In cases where no mass, yields and concentrations were added, the stoichiometry needed was achieved by titration controlled by NMR.

Liquid NMR spectra were recorded at room temperature in hexane, THF, toluene or benzene solutions in tubes equipped with DMSO-d_6 or benzene-d_6 capillary as external standard, unless otherwise specified. For ^{13}C NMR measurement POWGATE (proton decoupling with NOE) program was used. For ^{29}Si NMR the INEPTRD program was routinely used for all the measurements. Bruker Avance 300, Avance 500 and Avance 600 instruments with TopSpin 2.1 acquisition and processing software were used. Chemical shifts are given in ppm relative to TMS. All chemical shifts are given in ppm. ^1H, ^{13}C and ^{29}Si NMR spectra were not given in cases where they were not informative.

Full details of the X-ray crystallography structures are given in CCDC 2110513 (**4**), CCDC 2116257 (**10**), CCDC 2110514 (**12**), CCDC 2110516 (**13a**), CCDC 2110550 (**14**), CCDC 2110515 (**15**). The data can be obtained free of charge from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: ++33-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

2. Synthetic procedures, NMR spectra and X-ray crystallographic data

$Pt(PEt_3)_3$ [S1] and **$(dmpe)Pt(PEt_3)_2$** [S2] **$(TMS_2N)_2Zn$** [S3] **$(TMS_2N)_2Hg$** [S4] and **$(TMS_2N)Ag$** [S4] were prepared according to literature procedures.

Na_3P: Was synthesized by a modified literature procedure [S1]. To a sodium metal cut to small pieces (2 g, 0.087 mol, 12 eq.) a toluene solution of white phosphorus (P_4) (0.9 g, 7.265 mmol, 1 eq.) was added at 0°C. The reaction mixture was heated to 125°C for 4 hours with vigorous stirring, while almost all sodium was consumed and Na_3P in form of black precipitate was formed. Na_3P was stored under vacuum in toluene and was used without further purification.

$(R_3Si)_2Si(F)PH_2$, (1): To a THF suspension of Na_3P (0.56 g, 5.6 mmol, 1.3 eq.) an ether solution of HCl (4.8 mmol, 2.12 eq.) was added at 0°C and reaction mixture was stirred at room temperature for 1 hour. To that mixture a THF solution of $(R_3Si)_2SiF_2$ or $(R_3Si)_2SiFCl$ (1.7 g, 4.3 mmol, 1 eq.) was added at 0°C. The reaction mixture was slowly warmed to room temperature and was stirred overnight. THF was evaporated, and 15ml of dry hexane was added. The mixture was filtered and used without additional purification. (Yield 1.2 g, 61%.)

$^{31}P/^{1}H$ NMR: δ (ppm): -206 (tr of d, $^{2}J(^{31}P,^{19}F)$ = 27 Hz, $^{1}J(^{31}P,^{1}H)$ = 190.8 Hz)

^{29}Si NMR: δ (ppm): 5.2 (dd, 13.3 Hz, 4.9 Hz), 47.1 (dd, 363.6 Hz, 67 Hz)

^{1}H NMR: δ (ppm): 0.26 (s, Me), 1.05, 1.06 (s, tBu), 2.05, 2.06, 2.43, 2.44 (dd, PH, 190.8 Hz)

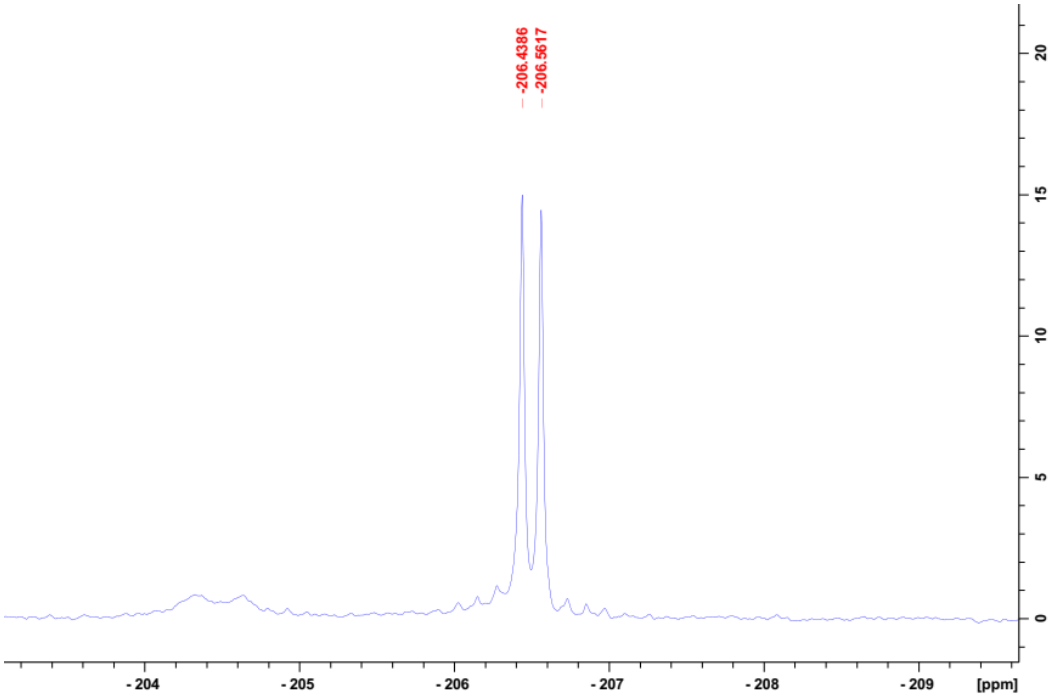


Figure S1. ^{31}P NMR spectrum of **1**

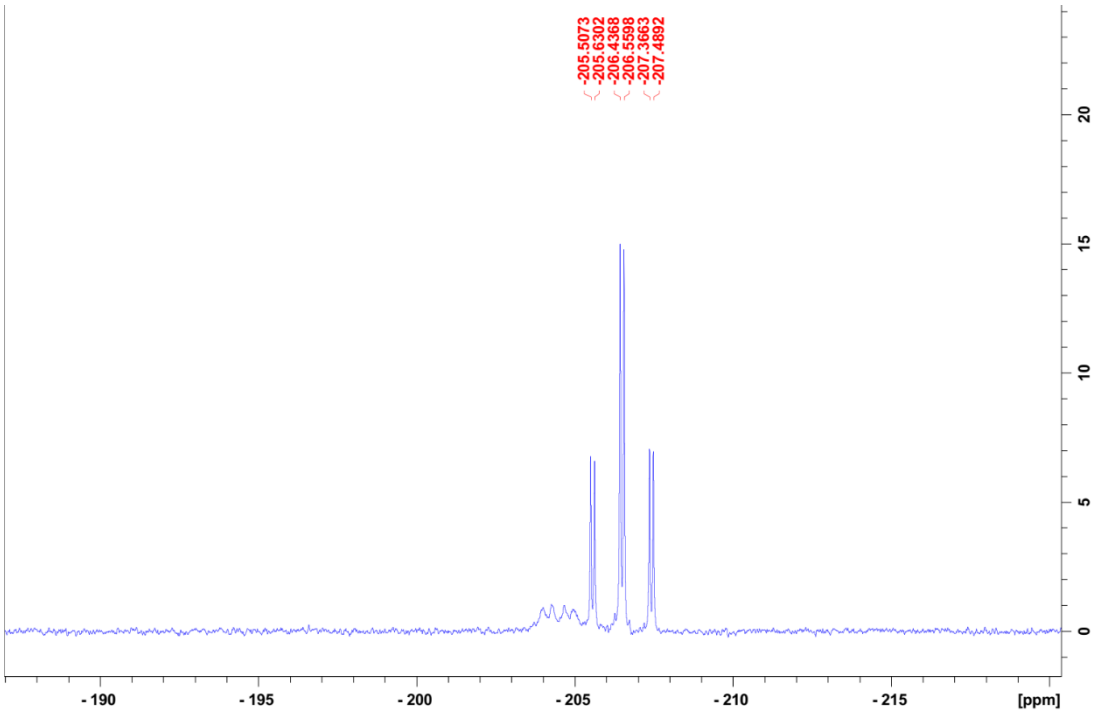


Figure S2. $^{31}P/^{1}H$ NMR spectrum of **1**

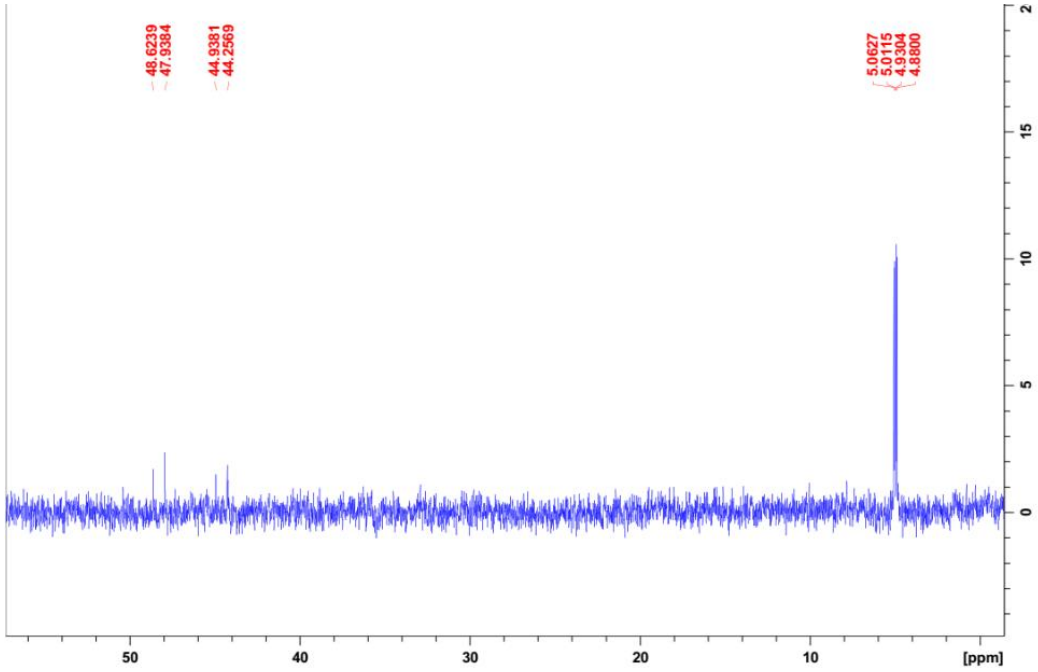


Figure S3. ^{29}Si NMR spectrum of **1**

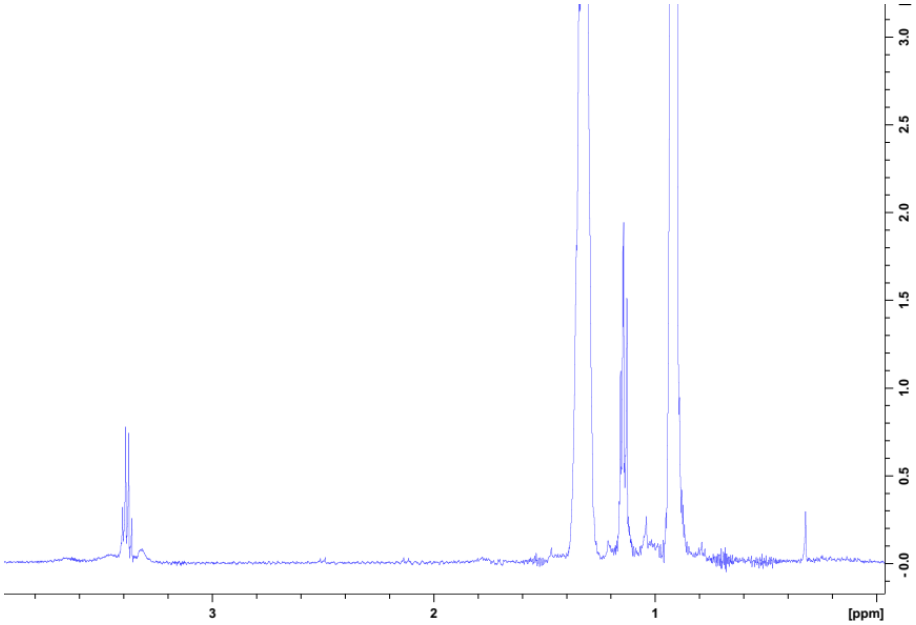


Figure S4. ^{1}H NMR spectrum of **1**

$(R_3Si)_2Si(F)PHLi$, (2): To a THF solution of $(R_3Si)_2Si(F)PH_2$, (**1**) (0.45 mmol, 1 eq.) an ether solution of LDA (0.45 mmol, 1 eq.) was added at 0°C and reaction mixture was stirred at room temperature for 1 hour. The product was identified by ^{29}Si and ^{31}P NMR spectroscopy and was used without additional purification.

^{31}P NMR: δ (ppm): -202.8 (d, $^{2}J(^{31}P,^{19}F)$ = 65 Hz, $^{1}J(^{31}P,^{1}H)$ = 144 Hz)

^{29}Si NMR: δ (ppm): -1.9 (dd, 28 Hz, 11 Hz), 46.4 (dd, 372 Hz, 116.8 Hz)

^{1}H NMR: δ (ppm): -0.26, -0.24, 0.0, 0.02 (dd, PH, 128 Hz), -0.06 (s, Me), 0.85, 0.93 (s, tBu)

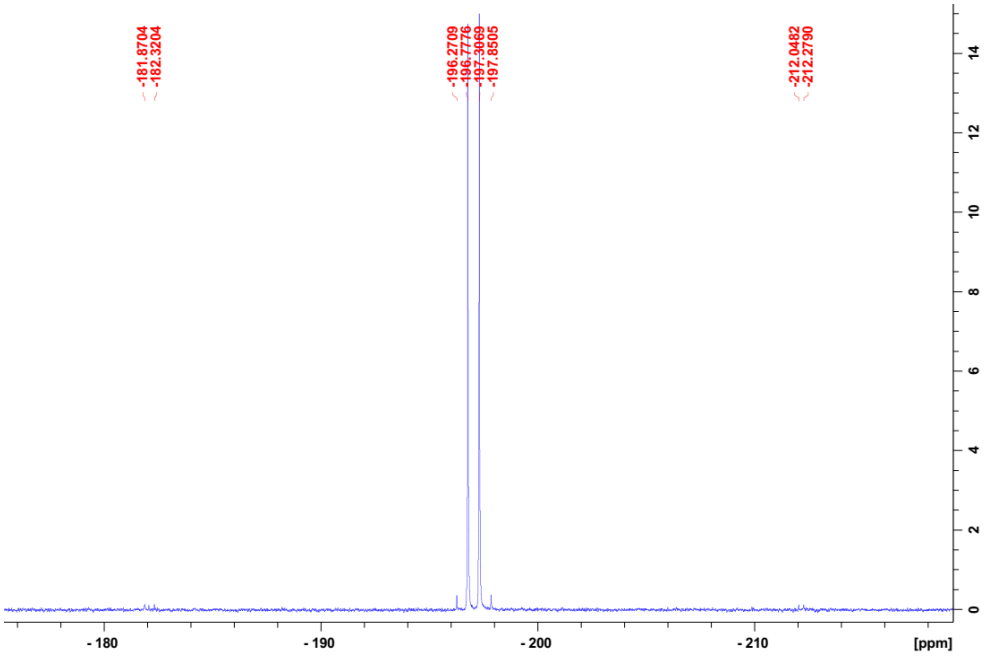


Figure S5. ^{31}P NMR spectrum of **2**

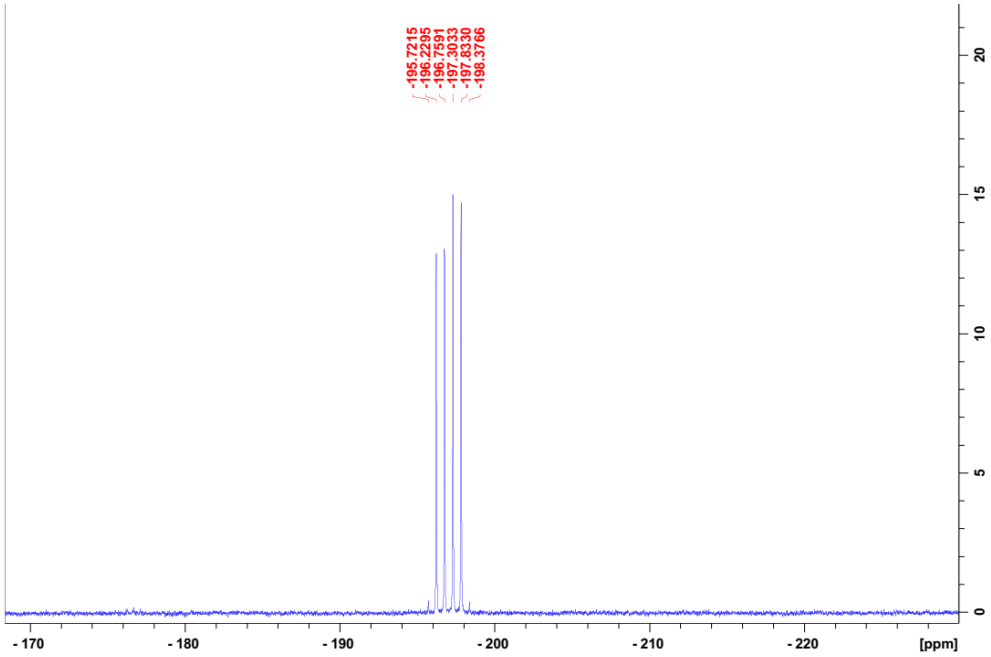


Figure S6. $^{31}P/^{1}H$ NMR spectrum of **2**

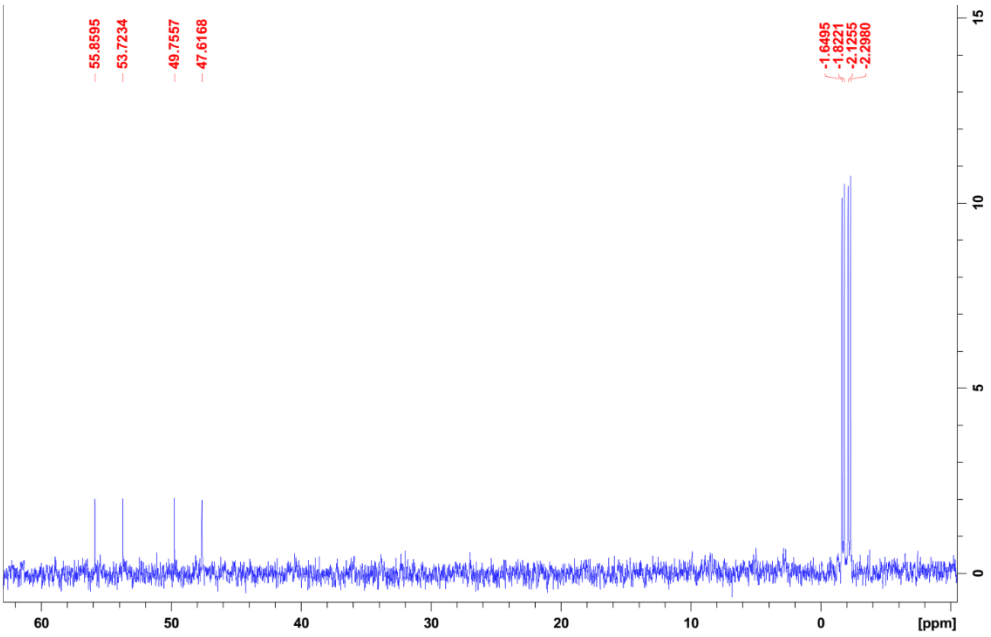


Figure S7. ^{29}Si NMR spectrum of **2**

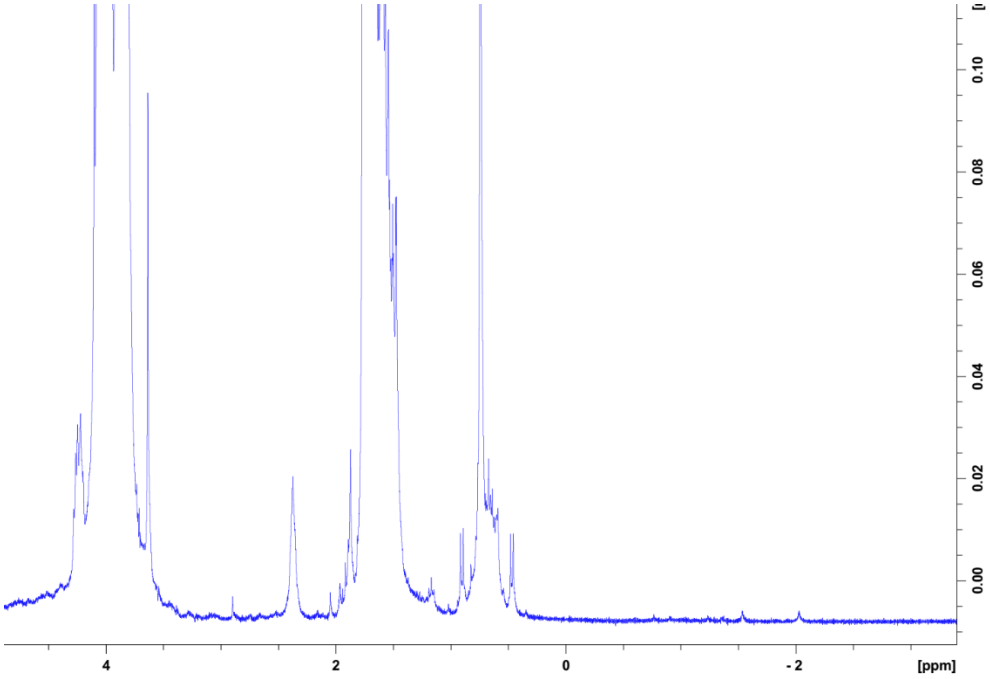
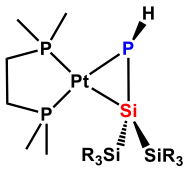


Figure S8. ^{1}H NMR spectrum of **2**

Complex 4: 1) A THF solution of $(R_3Si)_2Si(F)PHLi$ (**2**) (0.1 mmol, 1.7 eq.) was added to a hexane solution of $(dmpe)Pt(Et_3P)_2$ (0.057 mmol, 1 eq.). The reaction mixture was stirred at 65°C for 3 days. The reaction mixture was stirred at 60°C for a week. All volatiles were evaporated, and 10 ml of dry pentane was added. The product crystallizes overnight at -10°C. Mother liquid was decanted, and crystals were washed 2 times with cold pentane (2* 10ml).



2) A hexane solution of $(R_3Si)_2Si(H)PH_2$ (0.21 mmol, 1.2 eq.) was added to a hexane solution of $(dmpe)Pt(Et_3P)_2$ (0.17 mmol, 1 eq.). The reaction mixture was stirred at 60°C for a week. All volatiles were evaporated, and 10 ml of dry pentane was added. The product crystallizes overnight at -10°C. Mother liquid was decanted, and crystals were washed 2 times with cold pentane (2* 10ml). The crystals of **4** were dissolved in hot hexane and this solution was used without additional purification.

^{31}P NMR: δ (ppm): -205.5 (d, (broad), $^{2}J(^{31}P,^{31}P)$ = 49.1 Hz), $^{1}J(^{31}P,^{195}Pt)$ = 65 Hz, $^{1}J(^{31}P,^{1}H)$ = 137.44 Hz), 26.5 (dd, $^{2}J(^{31}P,^{31}P)$ = 41 Hz, 11.6 Hz), $^{1}J(^{31}P,^{195}Pt)$ = 3138 Hz), 35.5 (d, (broad), $^{2}J(^{31}P,^{31}P)$ = 11.6 Hz), $^{1}J(^{31}P,^{195}Pt)$ = 2177 Hz)

^{29}Si NMR: δ (ppm): -54.3 ((up) ddd, $^{1}J(^{29}Si,^{31}P)$ = 121 Hz), $^{2}J(^{29}Si,^{31}P)$ = 97 Hz, 7 Hz), 9 ((up) dd, $^{2}J(^{29}Si,^{31}P)$ = 20.7 Hz), $^{3}J(^{29}Si,^{31}P)$ = 2.1 Hz), 10 ((up) d, $^{2}J(^{29}Si,^{31}P)$ = 83.6 Hz), $^{3}J(^{29}Si,^{31}P)$ = 4.2 Hz)

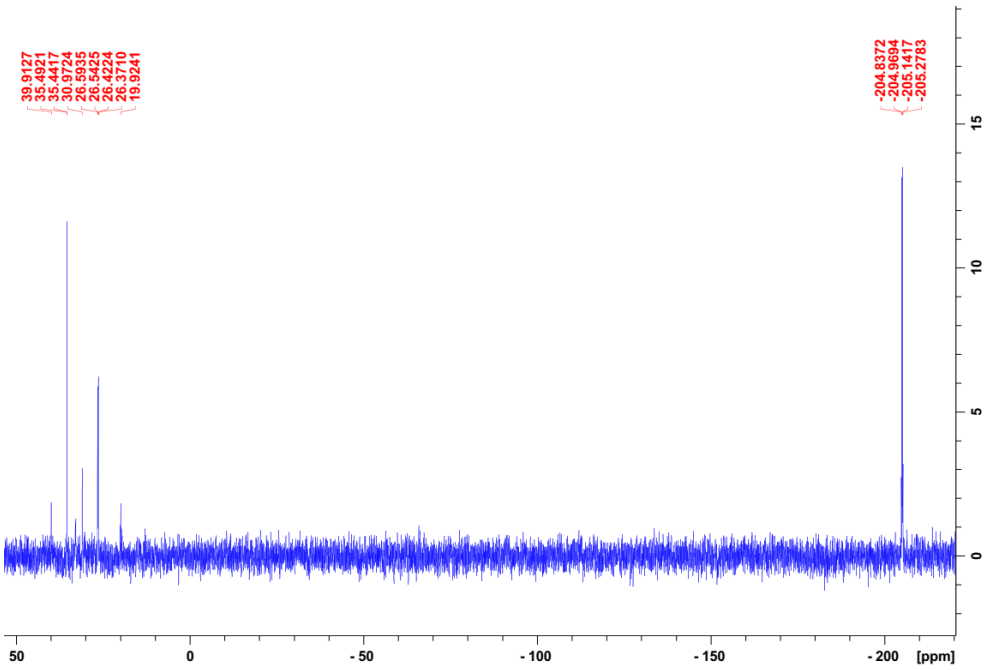


Figure S9. ^{31}P NMR spectrum of **4**

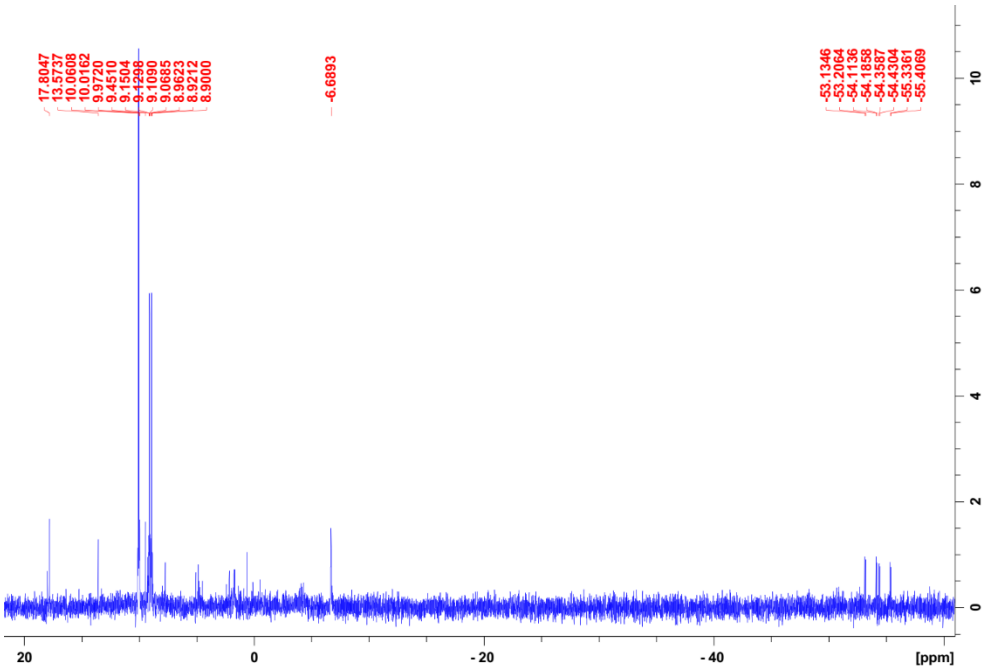


Figure S10. ^{29}Si NMR spectrum of **4**

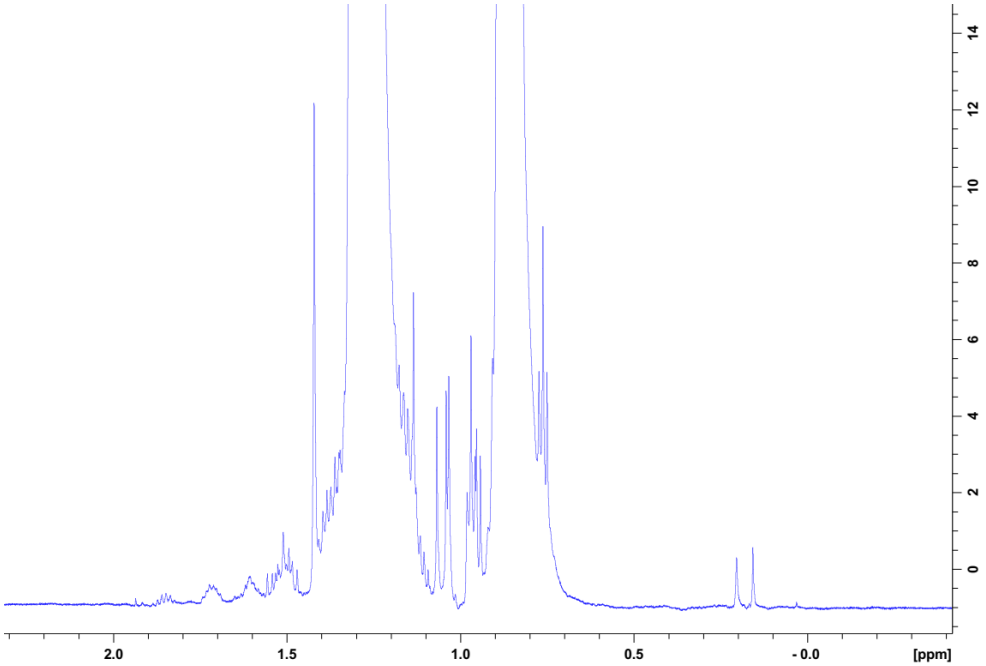


Figure S11. ^{1}H NMR spectrum of **4**

Table S1. Crystal data and structure refinement for **4**

Identification code	Dimitry519
Empirical formula	$C_{24}H_{59}P_3PtSi_3$
Formula weight	719.98
Temperature/K	200(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	17.644(3)
b/Å	11.7330(13)
c/Å	16.971(4)
α/°	90.00
β/°	98.919(7)
γ/°	90.00
Volume/Å^3	3470.8(10)
Z	4
ρ_{calc}g/cm^3	1.378
μ/mm^{-1}	4.296
F(000)	1472.0
Crystal size/mm^3	0.21 × 0.12 × 0.06
Radiation	MoKα (λ = 0.71073)

2Θ range for data collection/°	4.18 to 49.36
Index ranges	-20 ≤ h ≤ 20, -13 ≤ k ≤ 0, 0 ≤ l ≤ 19
Reflections collected	5837
Independent reflections	5837 [R_{int} = 0.0690, R_{sigma} = 0.0473]
Data/restraints/parameters	5837/0/302
Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0371, wR_2 = 0.0722
Final R indexes [all data]	R_1 = 0.0565, wR_2 = 0.0775
Largest diff. peak/hole / e $Å^{-3}$	0.78/-0.91

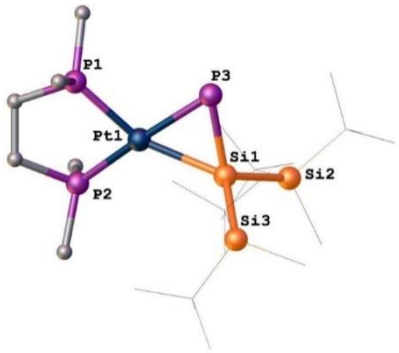


Figure S12. Molecular structures of **4** (Olex drawing). Hydrogen atoms are omitted for clarity. CCDC 2110513

Table S2. Selected bond lengths [Å] and angles [°] for **4**.

Atom 1	Atom 2	bond lengths [Å]		Atom 1	Atom 2	Atom 3	Angle [°]
Pt1	P1	2.2657(16)		P1	Pt1	P3	98.22(6)
Pt1	P2	2.2548(16)		P1	Pt1	Si1	152.66(6)
Pt1	P3	2.3902(16)		P2	Pt1	P1	85.98(7)
Pt1	Si1	2.3955(14)		P2	Pt1	P3	174.35(7)
P3	Si1	2.230(2)		P2	Pt1	Si1	120.77(6)
Si1	Si2	2.377(2)		P3	Pt1	Si1	55.54(5)
Si1	Si3	2.376(2)		Si1	P3	Pt1	62.35(5)
				P3	Si1	Pt1	62.11(5)
				P3	Si1	Si2	113.04(9)
				P3	Si1	Si3	113.68(9)
				Si2	Si1	Pt1	123.69(7)
				Si3	Si1	Pt1	116.85(7)
				Si3	Si1	Si2	115.22(7)
							43.8

$(R_3Si)_2Si(H)PH_2$, (5): To a THF suspension of Na_3P (0.27 g, 2.7 mmol, 1.33 eq.) an ether solution of HCl (5.4 mmol, 2 eq.) was added at 0°C and reaction mixture was stirred at room temperature for 1 h. To the mixture a THF solution of $(R_3Si)_2Si(H)F$ (0.7 g, 2 mmol, 1 eq.) was added at 0°C, and the reaction mixture was stirred overnight at room temperature. All solvents were evaporated, and 20ml of dry hexane was added. The mixture was filtered and used without additional purification.

$^{31}P/^{1}H$ NMR: δ (ppm): -241.1 (tr of d, 12.5 Hz, 182.2 Hz)

^{29}Si NMR: δ (ppm): -98.39 (down, d, 48.2 Hz), 9.9 (up, d, 5.8 Hz)

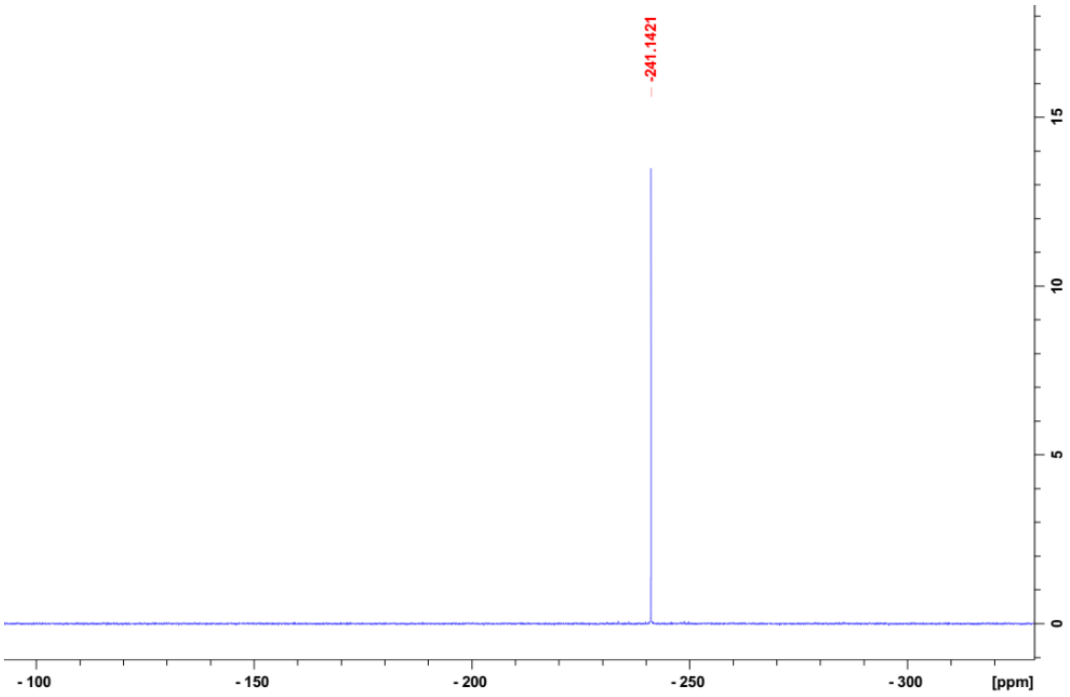


Figure S13. ^{31}P NMR spectrum of **5**

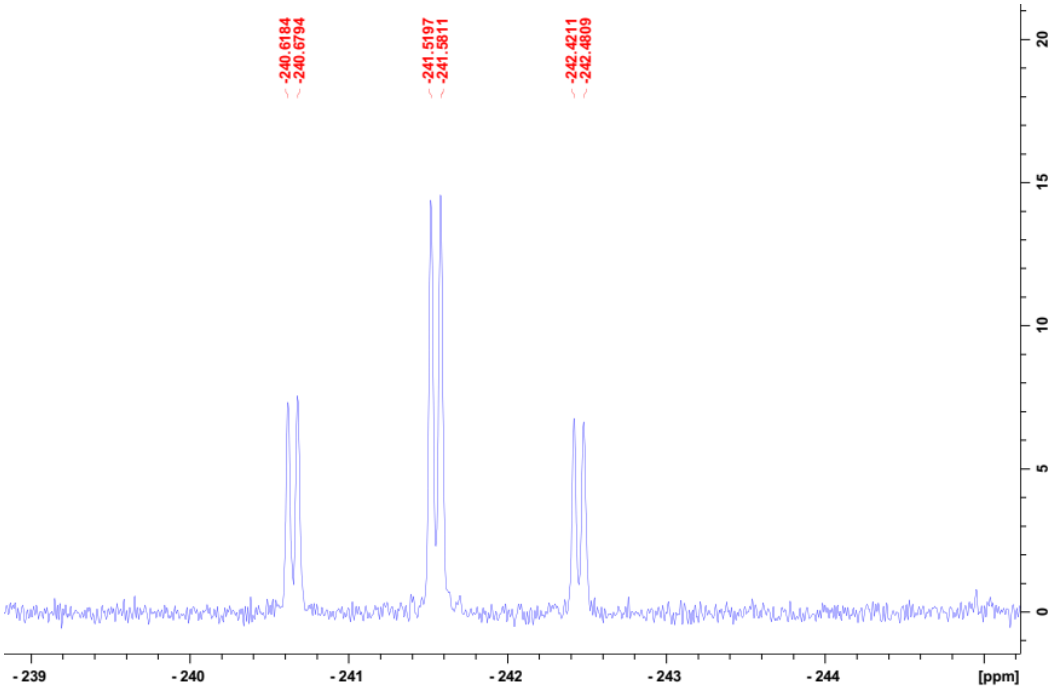


Figure S14. $^{31}P/^{1}H$ NMR spectrum of **5**

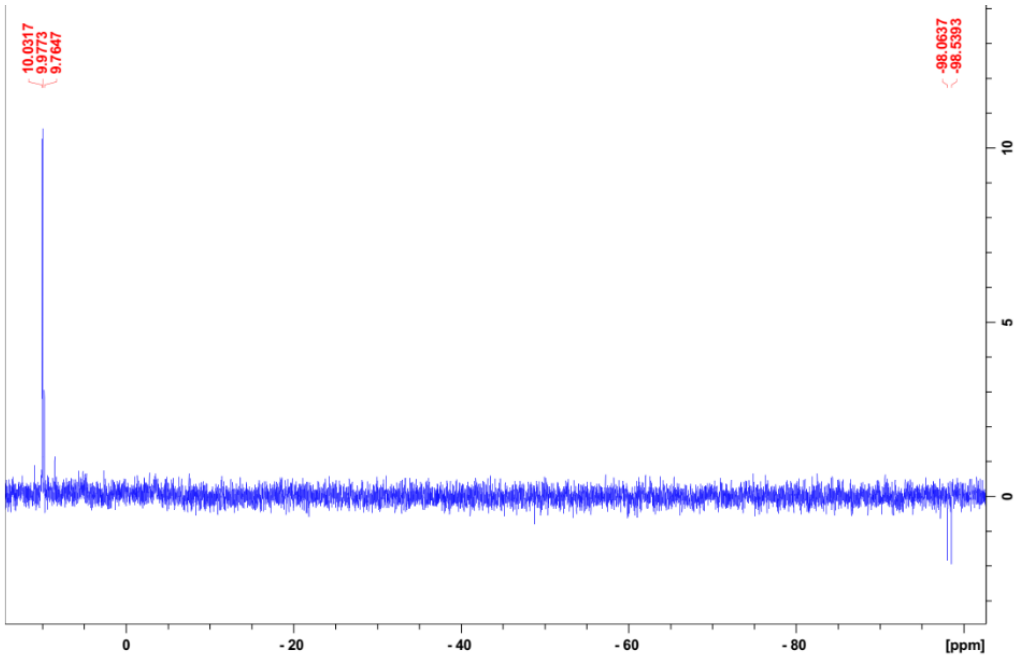
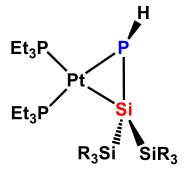


Figure S15. ^{29}Si NMR spectrum of **5**



Complex 7: A THF solution of $(R_3Si)_2Si(F)PHLi$ (**2**) (0.38 mmol, 1.2 eq.) was added to a hexane solution of $(Et_3P)_3Pt$ (0.32 mmol, 1 eq.). The reaction mixture was stirred overnight at room temperature. The product was not isolated and was identified by NMR spectroscopy.

^{31}P NMR: δ (ppm): -177.36 (d, (broad), $^{2}J(^{31}P,^{31}P)$ = 41.7 Hz), $^{1}J(^{31}P,^{195}Pt)$ = 80 Hz, $^{1}J(^{31}P,^{1}H)$ = 137.44 Hz), 16.18 (d, (broad), $^{2}J(^{31}P,^{31}P)$ = 41.7 Hz), $^{1}J(^{31}P,^{195}Pt)$ = 3409 Hz), 17.9 (d, (broad), $^{2}J(^{31}P,^{31}P)$ = 6.7 Hz), $^{1}J(^{31}P,^{195}Pt)$ = 2374 Hz)

^{29}Si NMR: δ (ppm): -50.4 ((up) ddd, $^{1}J(^{29}Si,^{31}P)$ = 118.7 Hz), $^{2}J(^{29}Si,^{31}P)$ = 98.9 Hz, 9.6 Hz), 11.19 ((up) dd, $^{2}J(^{29}Si,^{31}P)$ = 20.6 Hz), $^{3}J(^{29}Si,^{31}P)$ = 5 Hz), 12.14 ((up) d, $^{3}J(^{29}Si,^{31}P)$ = 4 Hz)

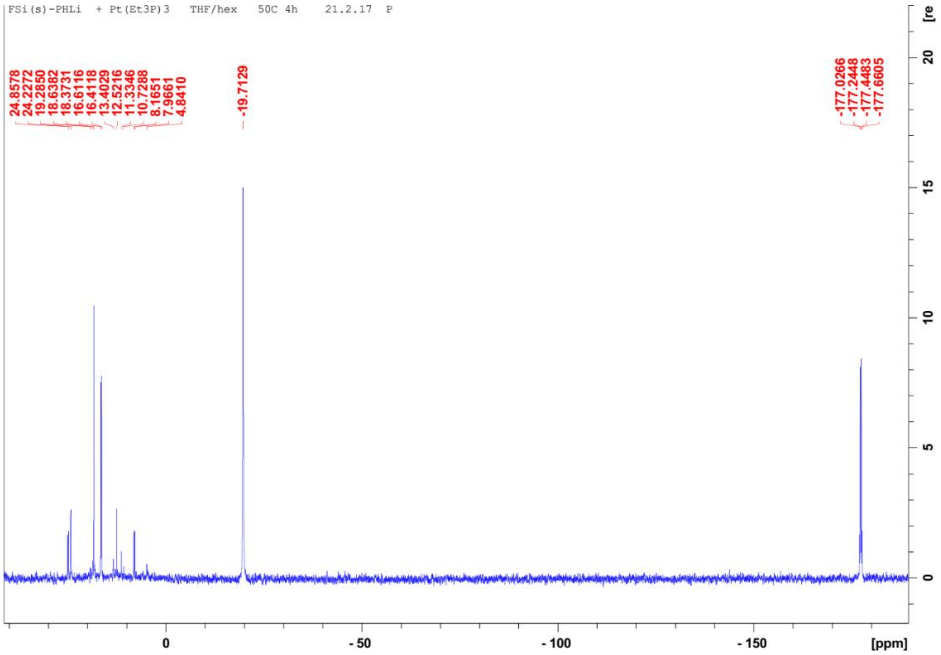


Figure S16. ^{31}P NMR spectrum of **7**

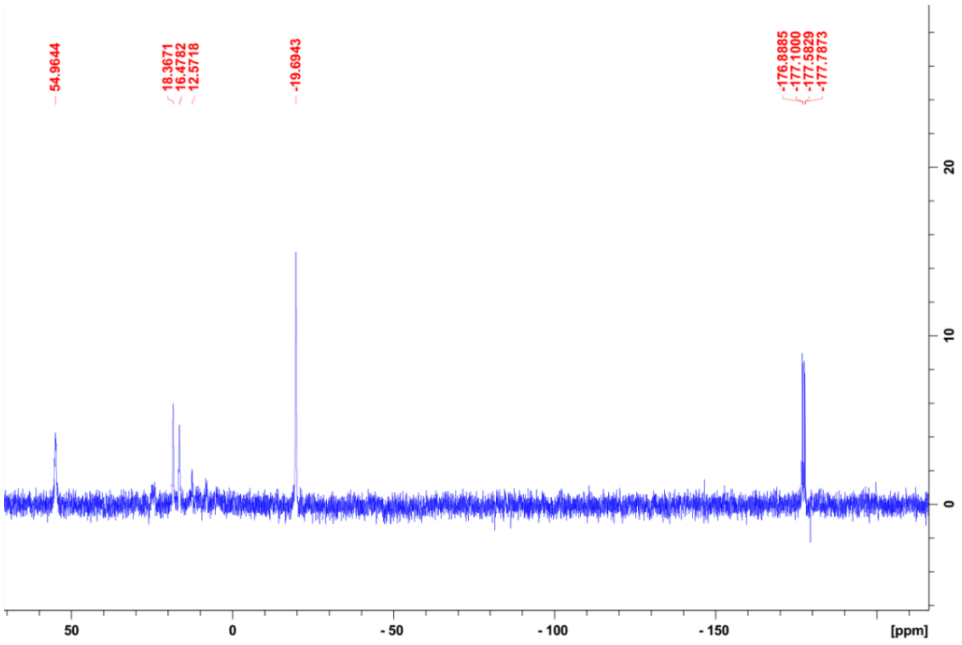


Figure S17. $^{31}P/^{1}H$ NMR spectrum of **7**

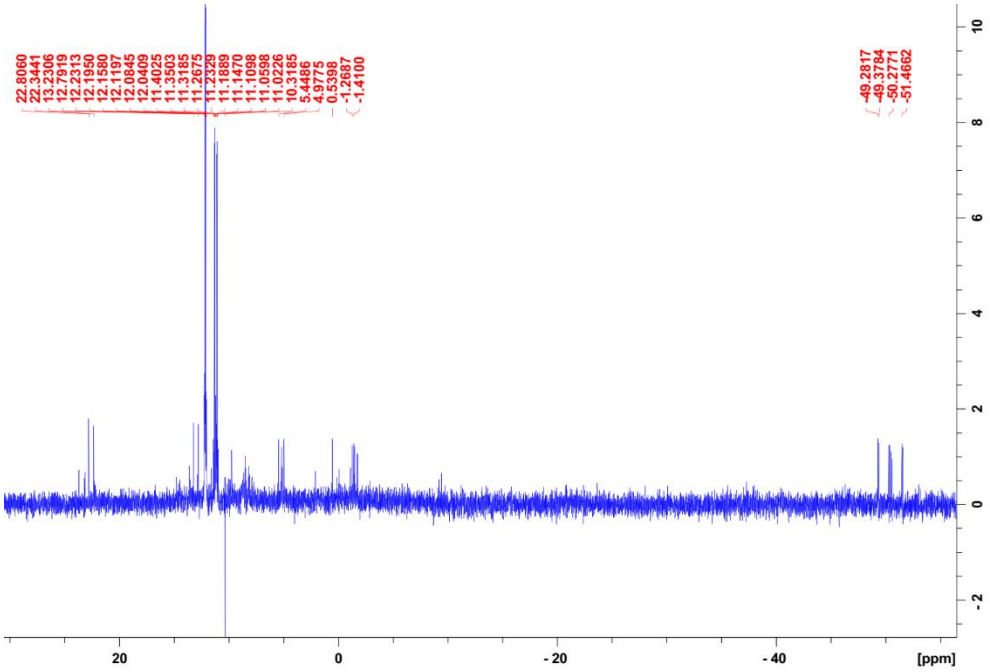
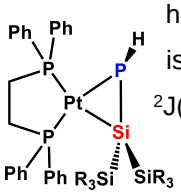


Figure S18. ^{29}Si NMR spectrum of **7**

Complex 8: In NMR tube to a hexane solution of **7** the equimolar amount of dppe was added as a hexane solution. The reaction mixture was heated at 60°C for 3h. The product was not isolated and was identified by NMR spectroscopy. ^{31}P NMR: δ (ppm): -277 (d, (broad), $^{2}J(^{31}P,^{31}P)$ = 54.4 Hz), $^{1}J(^{31}P,^{195}Pt)$ = 53 Hz), 29.1 (dd, $^{2}J(^{31}P,^{31}P)$ = 7 Hz, 11.3 Hz), $^{1}J(^{31}P,^{195}Pt)$ = 2293 Hz), 30.3 (dd, $^{2}J(^{31}P,^{31}P)$ = 54.4 Hz, 11.3 Hz), $^{1}J(^{31}P,^{195}Pt)$ = 3078 Hz)



8

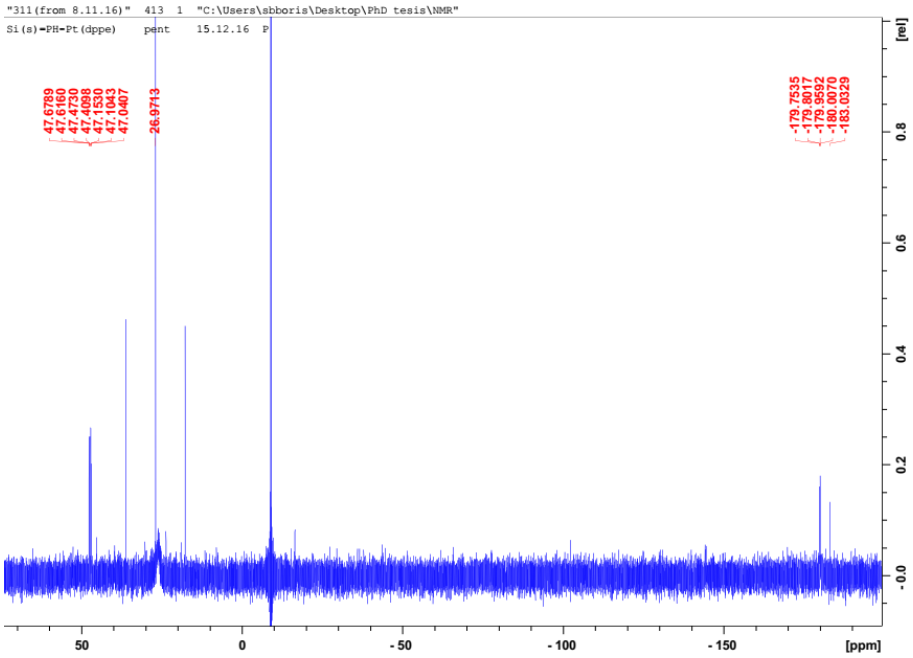
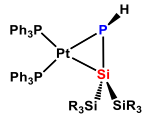


Figure S19. ^{31}P NMR spectrum of **8**

Complex 9: In an NMR tube a hexane solution of **2** was added to an equimolar amount of $(Ph_3P)_3Pt$



and the reaction mixture was stirred at 60°C for 3h. The product was not isolated and was identified by NMR spectroscopy.

^{31}P NMR: δ (ppm): -143.7 (dd, $^{2}J(^{31}P,^{31}P)$ = 80.8 Hz, 29.02 Hz), $^{1}J(^{31}P,^{195}Pt)$ = 277 Hz, $^{1}J(^{31}P,^{1}H)$ = 137.44 Hz), 26 (d, (broad) $^{2}J(^{31}P,^{31}P)$ = 80.8 Hz), $^{1}J(^{31}P,^{195}Pt)$ = 3508 Hz), 32 (d, (broad), $^{2}J(^{31}P,^{31}P)$ = 29.02 Hz), $^{1}J(^{31}P,^{195}Pt)$ = 2323 Hz)

^{29}Si NMR: δ (ppm): -41.5 ((up) ddd, $^{1}J(^{29}Si,^{31}P)$ = 118.7 Hz), $^{2}J(^{29}Si,^{31}P)$ = 98.9 Hz, 9.6 Hz), 11.19 ((up) dd, $^{2}J(^{29}Si,^{31}P)$ = 20.6 Hz), $^{3}J(^{29}Si,^{31}P)$ = 5 Hz), 12.14 ((up) d, $^{3}J(^{29}Si,^{31}P)$ = 4 Hz)

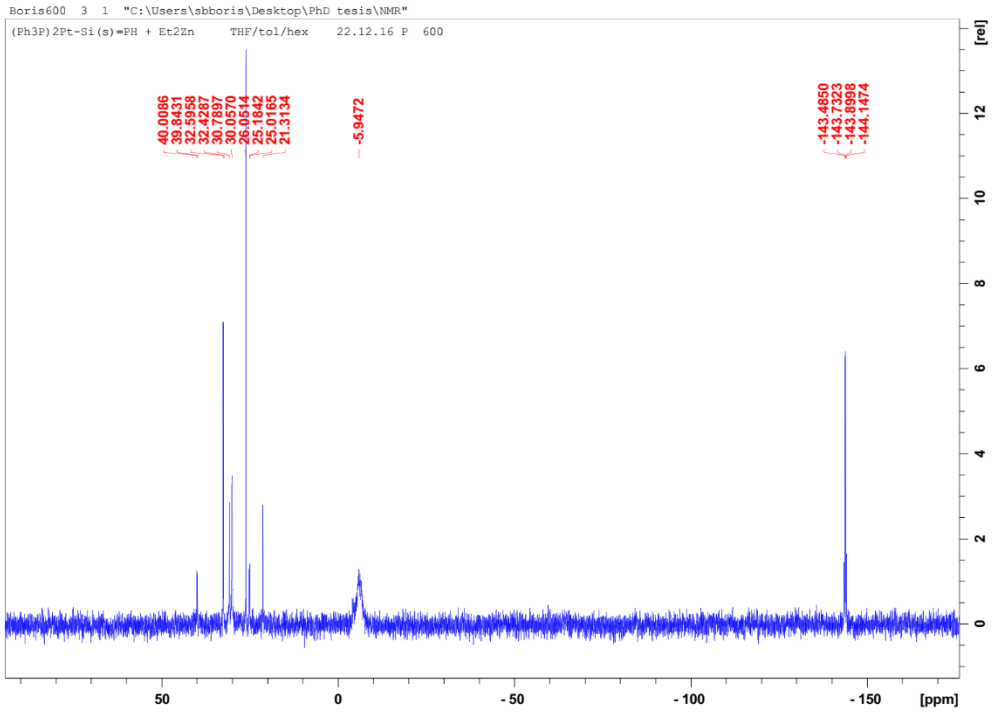


Figure S20. ^{31}P NMR spectrum of **9**

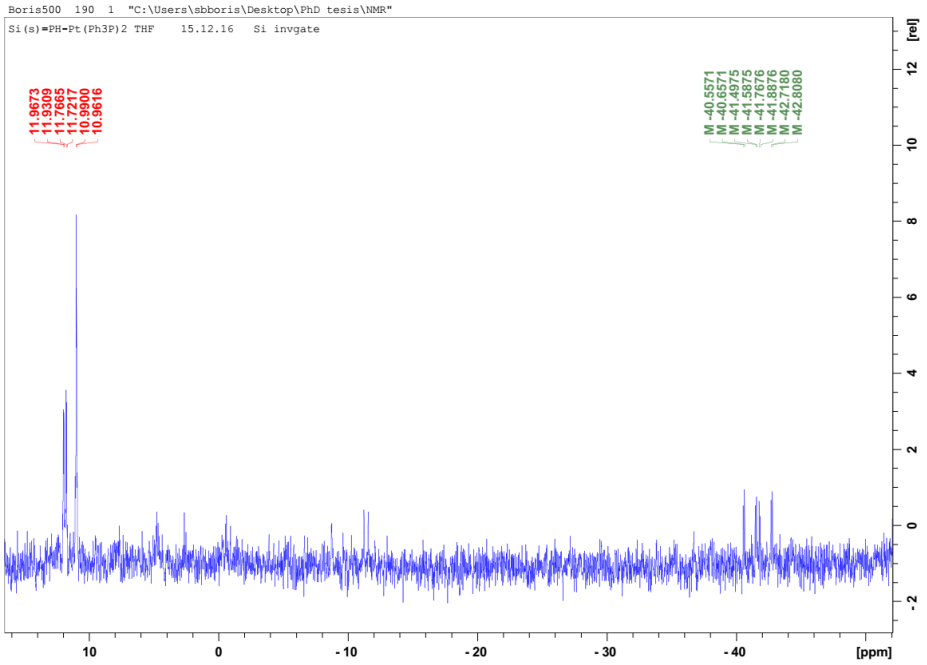
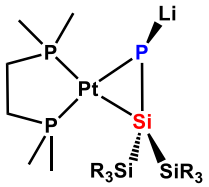


Figure S21. ^{29}Si NMR spectrum of **9**

Complex10: To a hexane solution of **4** (0.019 mmol, 1 eq.) was added a hexane solution of LDA (0.023 mmol, 1.2 eq.). The mixture was stirred at room temperature overnight. All volatiles were evaporated, and 10 ml of dry hexane was added. The volume was reduced to 2ml to obtain the crystal.



^{31}P NMR: δ (ppm): -119 (broad), -117 (broad), 21.6 (dd), 22.5 (broad), 22.8 (dd), 24.85 (d), 25.6 (d), 26.5 (broad)

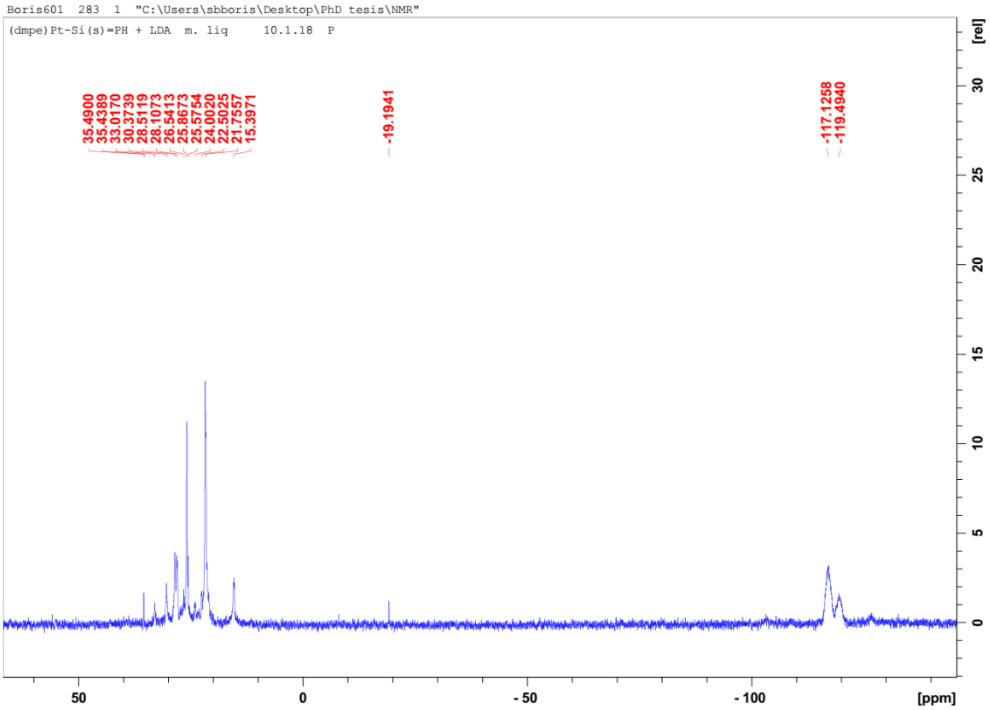


Figure S22. ^{31}P NMR spectrum of **10**

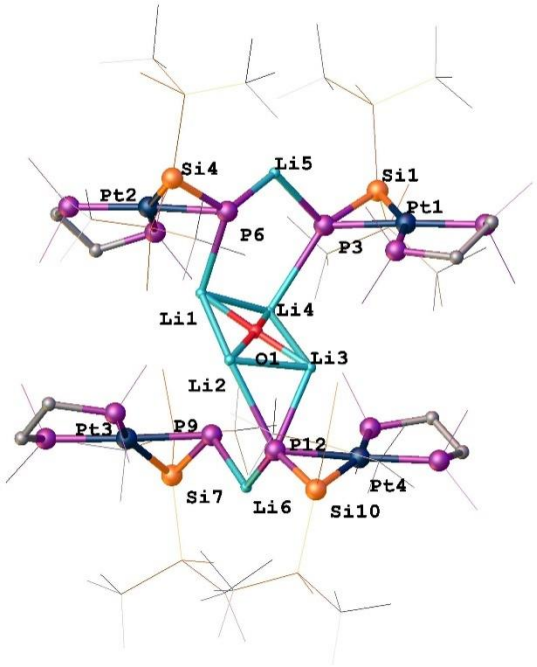


Figure **S23**. X-ray molecular structures of Error! Reference source not found. (Olex drawing). Hydrogen a toms are omitted for clarity

Table S2. Crystal data and structure refinement for **10**.

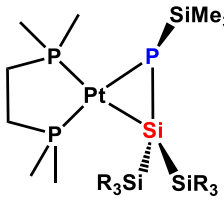
Identification code	PLi
Empirical formula	$C_{96}H_{232}Li_6OP_{12}Pt_4Si_{12}$
Formula weight	2933.52
Temperature/K	200.15
Crystal system	triclinic
Space group	P-1
a/Å	19.140(2)
b/Å	20.004(3)
c/Å	21.225(3)
α/°	69.703(5)
β/°	76.809(6)
γ/°	77.766(7)
Volume/Å^3	7341.7(16)
Z	2
ρ_{calc}g/cm^3	1.327
μ/mm^{-1}	4.063
F(000)	2988.0
Crystal size/mm^3	0.21 × 0.06 × 0.03
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.878 to 47.186
Index ranges	$-20 \le h \le 21$, $-21 \le k \le 22$, $-18 \le l \le 23$

Reflections collected	45972
Independent reflections	13599 [R_{int} = 0.1144, R_{sigma} = 0.3528]
Data/restraints/parameters	13599/1131/1228
Goodness-of-fit on F^2	0.986
Final R indexes [I>=2σ (I)]	R_1 = 0.1165, wR_2 = 0.1920
Final R indexes [all data]	R_1 = 0.2658, wR_2 = 0.2490
Largest diff. peak/hole / e $Å^{-3}$	1.86/-2.17

Table S3. Selected bond lengths [Å] and angles [°] for **10**

Atom 1	Atom 2	bond lengths [Å]		Atom 1	Atom 2	Atom 3	Angle [°]
Pt_1	P_3	2.387(7)		P_3	Pt_1	Si_1	55.0(3)
Pt_1	Si_1	2.420(8)		P_6	Pt_2	Si_4	54.3(3)
Pt_2	P_6	2.369(7)		P_6	Pt_2	Li_1	59.5(10)
Pt_2	Si_4	2.435(8)		Si_4	Pt_2	Li_1	99.8(10)
Pt_2	Li_1	2.82(5)		P_9	Pt_3	Si_7	54.6(2)
Pt_3	P_9	2.376(8)		P_{12}	Pt_4	Si_{10}	53.8(3)
Pt_3	Si_7	2.412(8)		Si1	P3	Pt1	103.84(16)
Pt_4	P_{12}	2.385(9)		Li_1	O_1	Li_2	Li_1
Pt_4	Si_{10}	2.448(9)		Li_1	O_1	Li_3	Li_1
Pt_4	Li_3	2.87(5)		Li_3	O_1	Li_2	Li_3
P_3	Si_1	2.221(11)		Li_4	O_1	Li_1	Li_4
P_3	Li_4	2.87(4)		Li_4	O_1	Li_2	Li_4
P_3	Li_5	2.45(5)		Li_4	O_1	Li_3	Li_4
O_1	Li_1	1.84(5)					
O_1	Li_2	1.89(6)					
O_1	Li_3	1.88(5)					
O_1	Li_4	1.69(5)					
Li_1	Li_2	2.47(7)					
Li_1	Li_4	2.57(7)					
Li_2	Li_3	2.49(8)					
Li_3	Li_4	2.79(7)					

Complex 11: In an NMR tube, to a hexane solution of **10** an excess of Me_3SiCl was added by vacuum transfer. The product was not isolated and was identified by NMR spectroscopy. ^{31}P NMR: δ (ppm): -166.9 (dd, (broad), $^{2}J(^{31}P,^{31}P)$ = 60.5 Hz, 17.7 Hz), $^{1}J(^{31}P,^{195}Pt)$ = 177.8 Hz), 24 (dd, $^{2}J(^{31}P,^{31}P)$ = 60.5 Hz, 11 Hz), $^{1}J(^{31}P,^{195}Pt)$ = 3233 Hz), 26.2 (d, (broad), $^{2}J(^{31}P,^{31}P)$ = 11 Hz, 17.7 Hz), $^{1}J(^{31}P,^{195}Pt)$ = 2230 Hz)



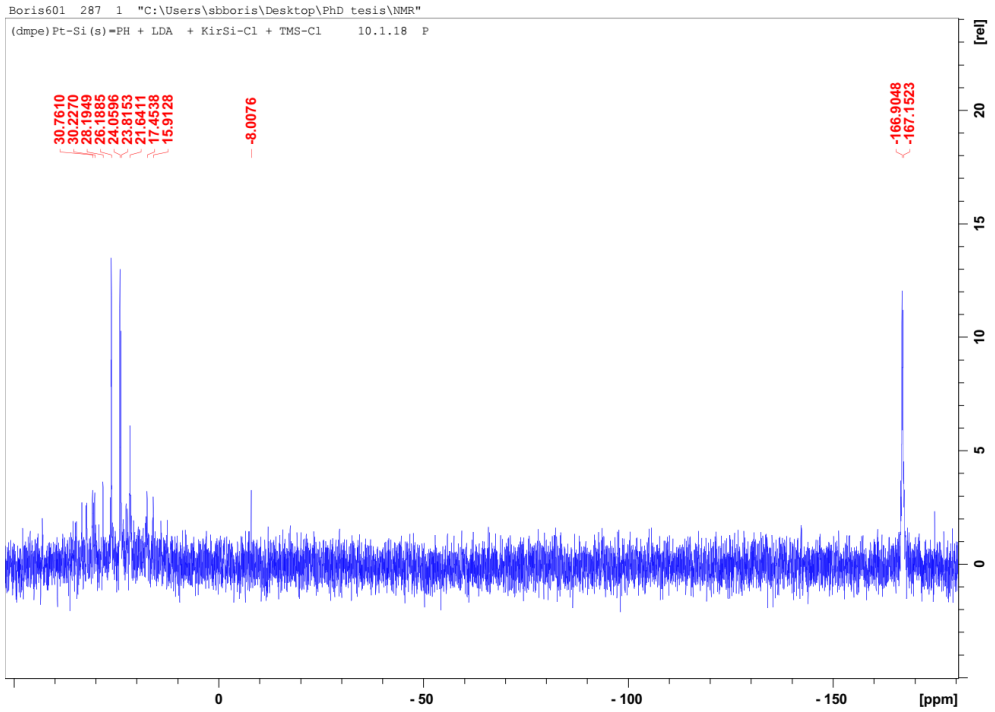


Figure S24. ^{31}P NMR spectrum of **11**

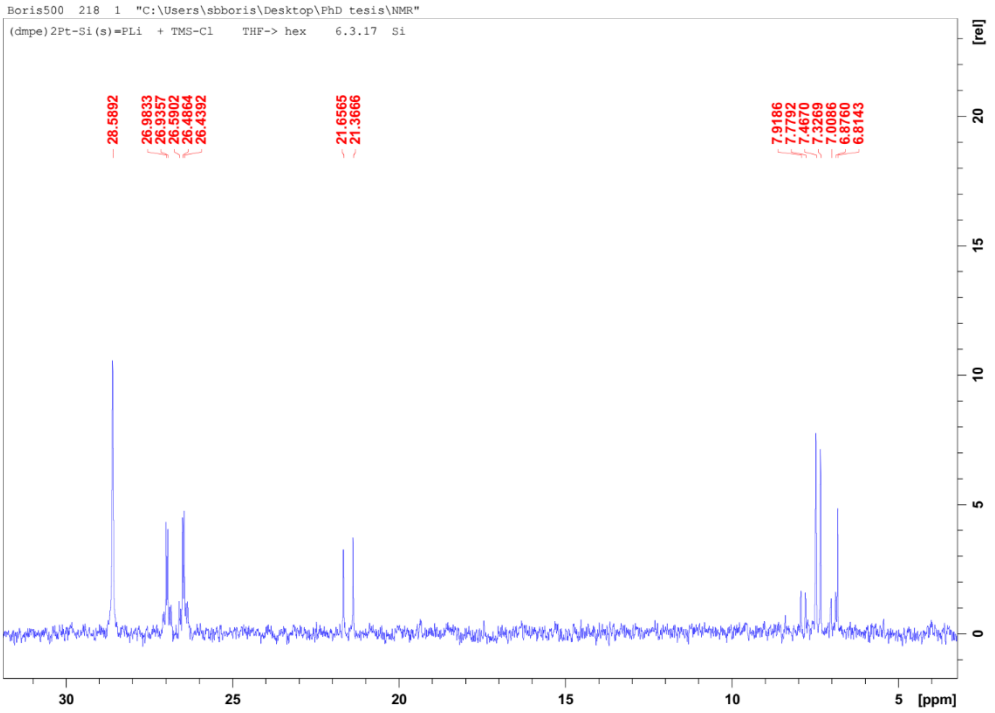
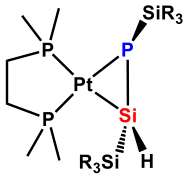


Figure S25. ^{29}Si NMR spectrum of **11**

Complex 12: To a hexane solution of **4** a THF solution of LDA was added. The mixture was stirred at room temperature overnight. All volatiles were evaporated, and 10 ml of dry hexane was added. The solution was filtered, and its volume was reduced to 2 ml yielding light yellow crystals.



^{31}P NMR: δ (ppm): -277 (d, (broad), ^{2}J(^{31}P,^{31}P) = 54.4 Hz), ^{1}J(^{31}P,^{195}Pt) = 53 Hz), 29.1 (dd, ^{2}J(^{31}P,^{31}P) = 7 Hz, 11.3 Hz), ^{1}J(^{31}P,^{195}Pt) = 2293 Hz), 30.3 (dd, ^{2}J(^{31}P,^{31}P) = 54.4 Hz, 11.3 Hz), ^{1}J(^{31}P,^{195}Pt) = 3078 Hz)

^{29}Si NMR: δ (ppm): -39.5 ((down) ddd, ^{1}J(^{29}Si,^{31}P) = 139.5 Hz), ^{2}J(^{29}Si,^{31}P) = 101 Hz, 10 Hz), 1.99 ((up) ddd, ^{2}J(^{29}Si,^{31}P) = 21.4 Hz), ^{3}J(^{29}Si,^{31}P) = 3.3 Hz, 3.8 Hz), 23.5 ((up) dd, ^{1}J(^{29}Si,^{31}P) = 83.6 Hz), ^{3}J(^{29}Si,^{31}P) = 5.4 Hz)

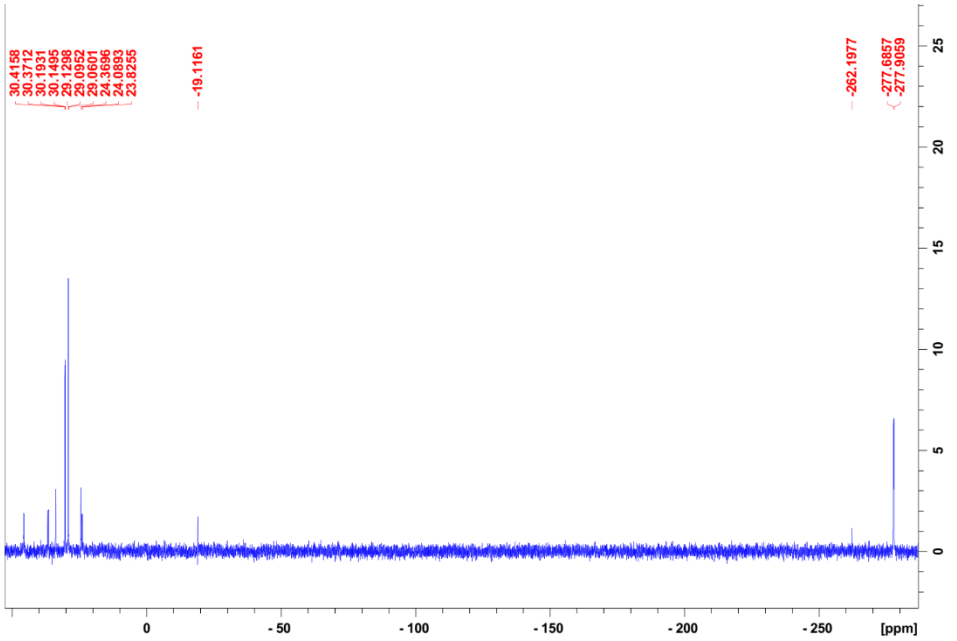


Figure S26. ^{31}P NMR spectrum of **12**

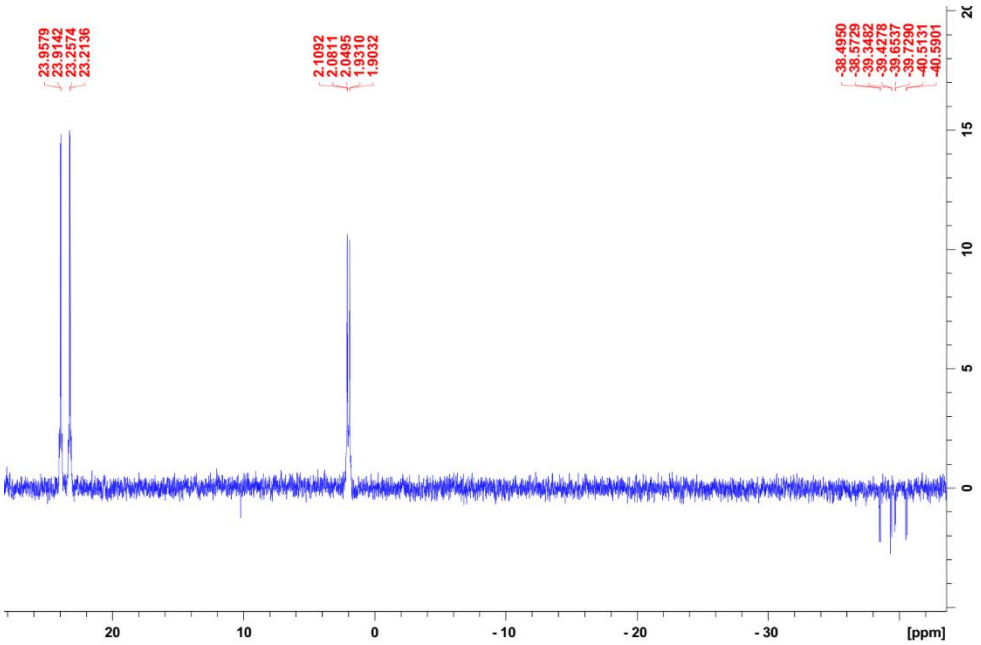


Figure S27. ^{29}Si NMR spectrum of **12**

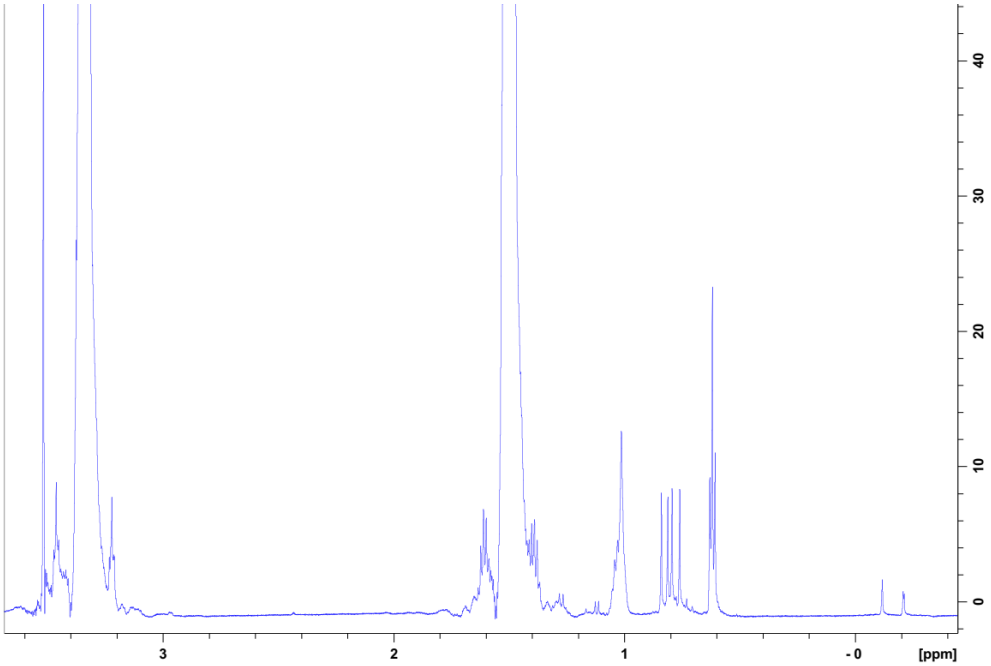


Figure S28. ^{1}H NMR spectrum of **12**

Table S4. Crystal data and structure refinement for **12**.

Identification code	Dimitry533
Empirical formula	$C_{24}H_{59}P_3PtSi_3$
Formula weight	719.98
Temperature/K	200(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.110(8)
b/Å	27.785(9)
c/Å	11.808(4)
α/°	90.00
β/°	118.70(2)
γ/°	90.00
Volume/Å^3	3485(3)
Z	4
ρ_{calc}g/cm^3	1.372
μ/mm^{-1}	4.278
F(000)	1472.0
Crystal size/mm^3	0.06 × 0.06 × 0.03
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.94 to 48.82

Index ranges	$-14 \le h \le 12, -32 \le k \le 0, 0 \le l \le 13$
Reflections collected	5716
Independent reflections	5716 [R_{int} = 0.0800, R_{sigma} = 0.0741]
Data/restraints/parameters	5716/0/298
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0647, wR_2 = 0.1435
Final R indexes [all data]	R_1 = 0.1019, wR_2 = 0.1550
Largest diff. peak/hole / e $Å^{-3}$	2.37/-1.32

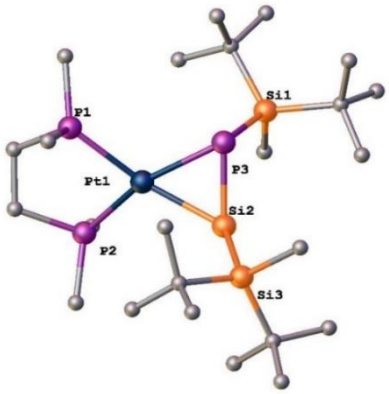
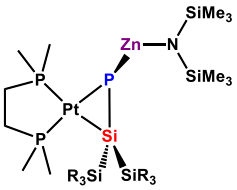


Figure S29. Molecular structures of **12** (Olex drawing). Hydrogen atoms are omitted for clarity. CCDC 2110514

Table S5. Selected bond lengths [Å] and angles [°] for **12**

Atom 1	Atom 2	bond lengths [Å]		Atom 1	Atom 2	Atom 3	Angle [°]
Pt1	P1	2.294(4)		P1	Pt1	P3	109.59(13)
Pt1	P2	2.233(4)		P1	Pt1	Si2	158.98(14)
Pt1	P3	2.413(3)		P2	Pt1	P1	86.48(14)
Pt1	Si2	2.349(4)		P2	Pt1	P3	163.38(13)
P3	Si1	2.256(5)		P2	Pt1	Si2	110.62(14)
P3	Si2	2.193(5)		Si2	Pt1	P3	54.83(13)
Si2	Si3	2.364(6)		Si1	P3	Pt1	103.84(16)
				Si2	P3	Pt1	61.10(13)
				Si2	P3	Si1	99.79(19)
				Pt1	Si2	Si3	123.87(19)
				P3	Si2	Pt1	64.07(14)
				P3	Si2	Si3	111.3(2)
				P1	Pt1	P3	109.59(13)

Complex13a: In an NMR tube, to a hexane solution of **4** an ether solution of $(TMS_2N)_2Zn$ was added.



The mixture was stirred at 75°C for 6 days. All volatiles were evaporated, and 5 ml of dry hexane was added. The volume was reduced to 2 ml yielding light green crystals.

^{31}P NMR: δ (ppm): -199.2 (dd, (broad), $^{2}J(^{31}P,^{31}P)$ = 26.6 Hz, 6.1 Hz), $^{1}J(^{31}P,^{195}Pt)$ = 140 Hz), 25 (dd $^{2}J(^{31}P,^{31}P)$ = 25 Hz, 4.8 Hz), $^{1}J(^{31}P,^{195}Pt)$ = 3272 Hz), 29.3 (d, (broad), $^{2}J(^{31}P,^{31}P)$ = 4.8 Hz, 6.1 Hz), $^{1}J(^{31}P,^{195}Pt)$ = 2094 Hz)

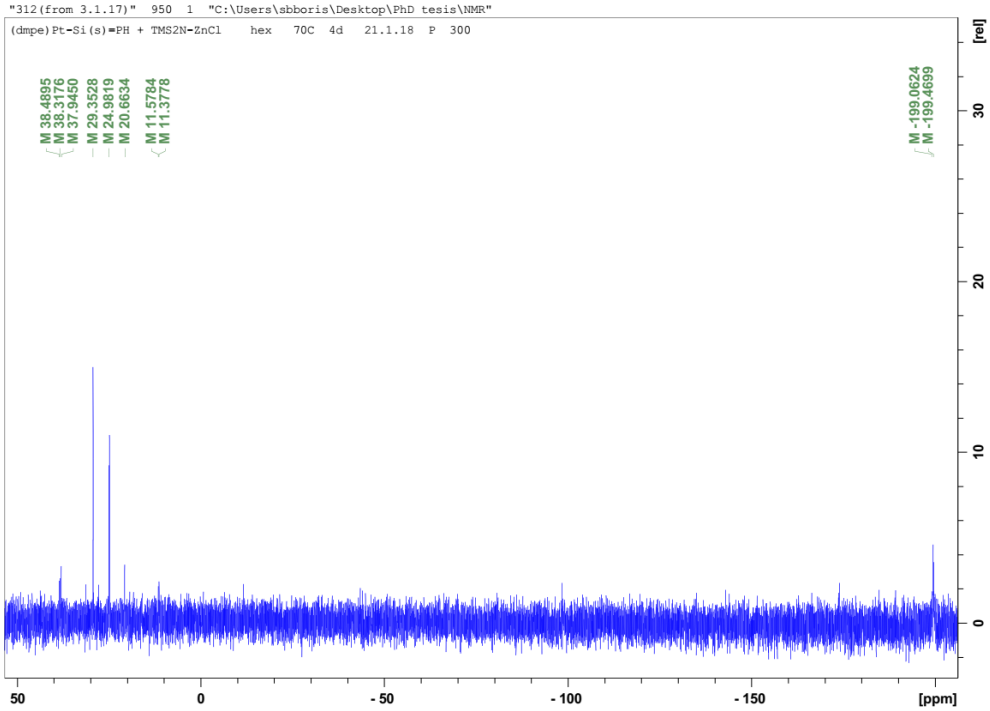


Figure S30. ^{31}P NMR spectrum of **13a**

Table S6. Crystal data and structure refinement for **13a**.

Identification code	Dimitry590b
Empirical formula	$C_{30}H_{76}NP_3PtSi_5Zn$
Formula weight	944.73
Temperature/K	200.15
Crystal system	monoclinic
Space group	$P2_1$
a/Å	12.4026(14)
b/Å	15.6526(19)
c/Å	13.0226(16)
α/°	90
β/°	114.387(2)
γ/°	90
Volume/Å^3	2302.6(5)
Z	2
ρ_{calc} g/cm^3	1.363
μ/mm^{-1}	3.809
F(000)	972.0

Crystal size/mm^3	0.09 × 0.09 × 0.06
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.434 to 50.218
Index ranges	-14 ≤ h ≤ 14, -18 ≤ k ≤ 18, -15 ≤ l ≤ 15
Reflections collected	20968
Independent reflections	8118 [R_{int} = 0.0710, R_{sigma} = 0.1182]
Data/restraints/parameters	8118/1/376
Goodness-of-fit on F^2	0.854
Final R indexes [I>=2σ (I)]	R_1 = 0.0402, wR_2 = 0.0550
Final R indexes [all data]	R_1 = 0.0661, wR_2 = 0.0596
Largest diff. peak/hole / e Å^{-3}	1.09/-0.92
Flack parameter	-0.005(4)

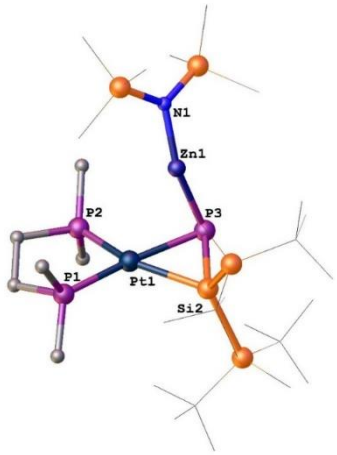
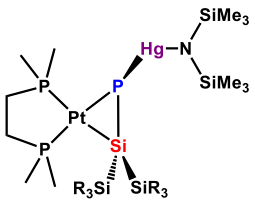


Figure S31. Molecular structures of **13a** (Olex drawing). Hydrogen atoms are omitted for clarity. CCDC 2110516

Table S7. Selected bond lengths [Å] and angles [°] for **13a**

Atom 1	Atom 2	bond lengths [Å]		Atom 1	Atom 2	Atom 3	Angle [°]
P3	Pt1	2.393(3)		Zn1	P3	Si2	103.35(14)
P3	Si2	2.226(4)		P3	Si2	Si1	115.65(16)
P3	Zn1	2.220(3)		P3	Si2	Si3	106.66(16)
Pt1	Si2	2.429(3)					43.8
Pt1	Zn1	2.9262(14)					

Complex 13b: To a hexane solution of **4** (0.019 mmol, 1 eq.) was added a hexane solution of $(TMS_2N)_2Hg$ (0.023 mmol, 1.2 eq.). The mixture was stirred at room temperature overnight. All volatiles were evaporated, and 10 ml of dry hexane was added. The product was not isolated and was identified by NMR spectroscopy.



^{31}P NMR: δ (ppm): -161 (d, (broad), $^{2}J(^{31}P,^{31}P)$ = 35.9 Hz), $^{1}J(^{199}Hg,^{31}P)$ = 1414 Hz), 25.7 (dd, $^{2}J(^{31}P,^{31}P)$ = 33.2 Hz), $^{2}J(^{31}P,^{31}P)$ = 6.5 Hz), $^{1}J(^{31}P,^{195}Pt)$ = 3221 Hz), 31.2 (d, (broad), $^{2}J(^{31}P,^{31}P)$ = 6.5 Hz), $^{1}J(^{31}P,^{195}Pt)$ = 2168 Hz)

^{29}Si NMR: δ (ppm): -10.2, -9.59, -9.47, -9.23, 7.8, 7.9, 8.08, 9.5, 9.9,

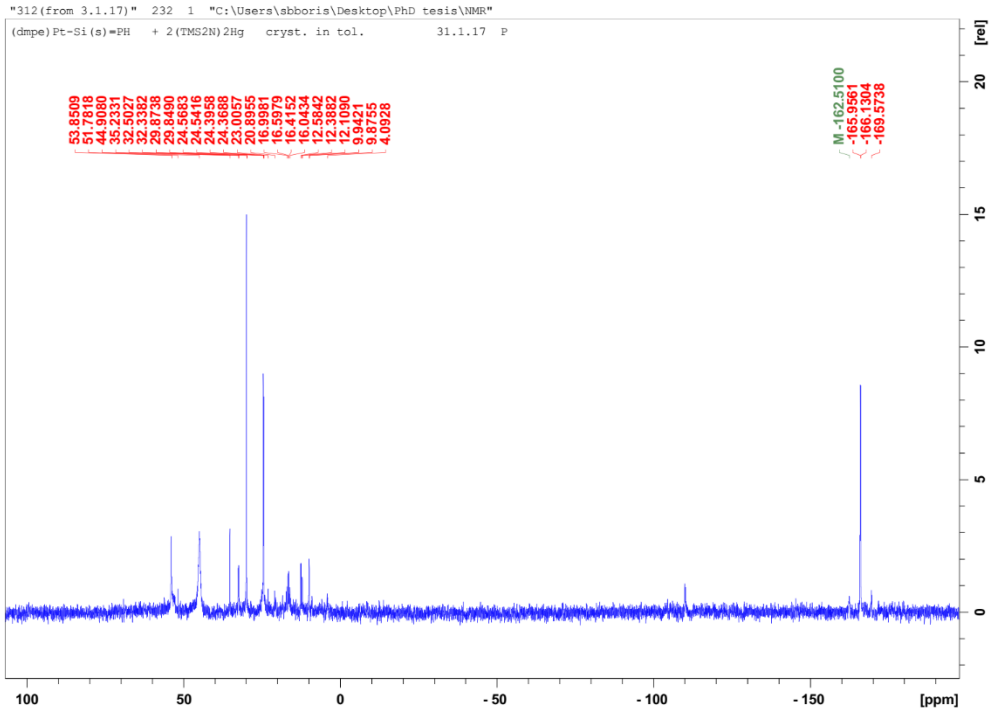


Figure S32. ^{31}P NMR spectrum of **13b**

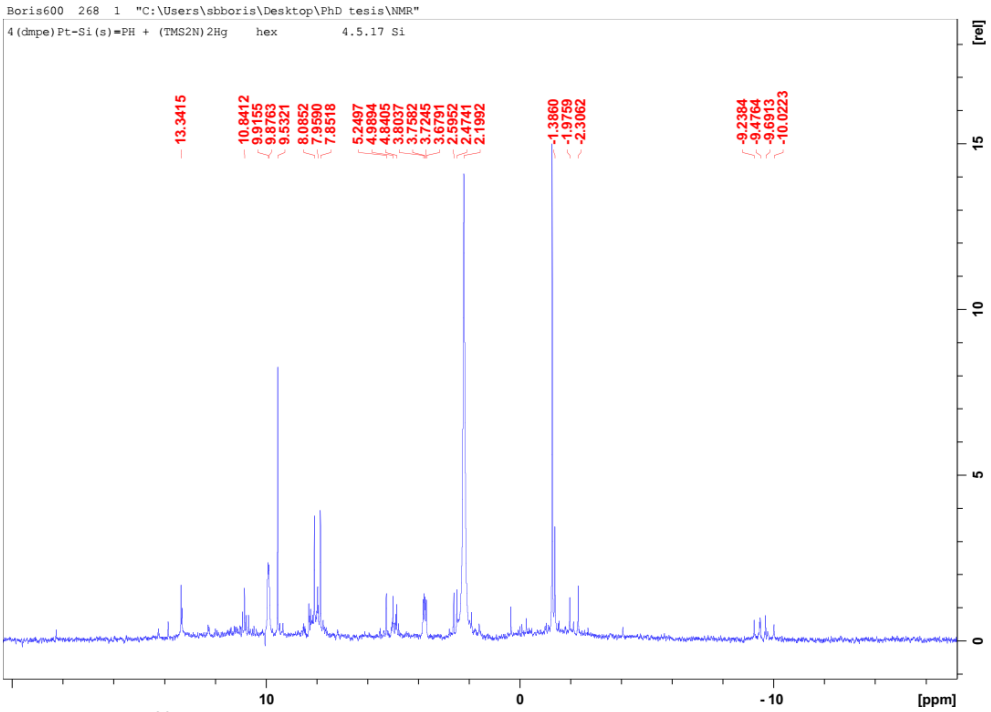


Figure S33. ^{29}Si NMR spectrum of **13b**

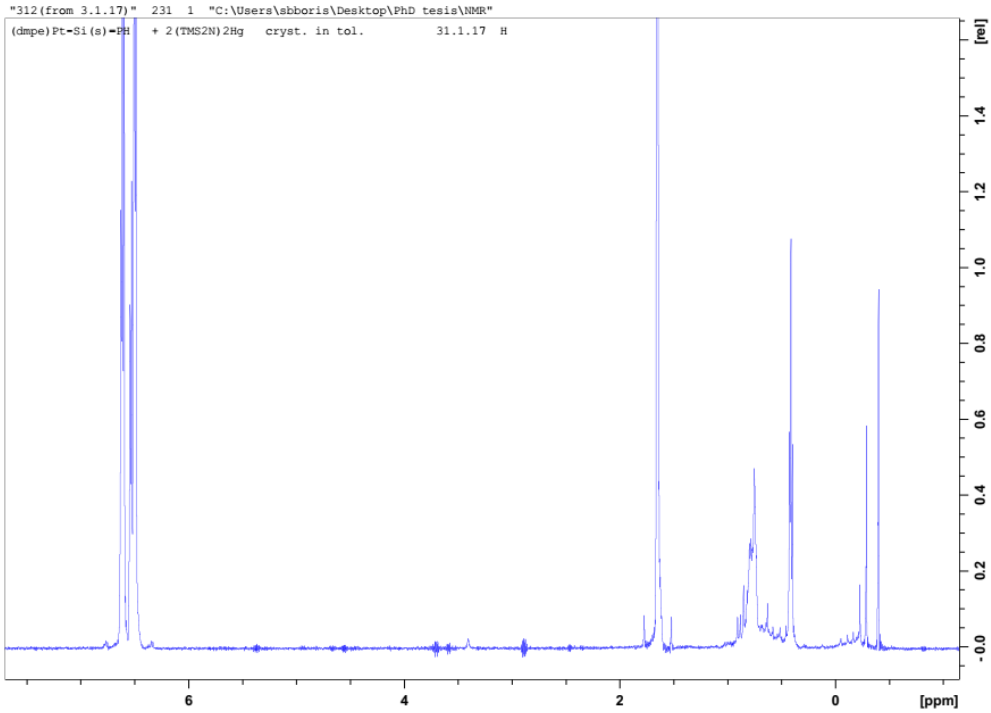
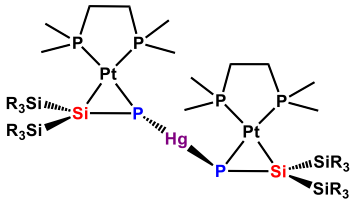


Figure S34. ^{1}H NMR spectrum of **13b**

Complex 14: A hexane solution of **13b** was added to Li metal turnings. The mixture was stirred at room temperature for 3 days. The green crystals precipitated from the reaction mixture were washed with hexane 2 times.



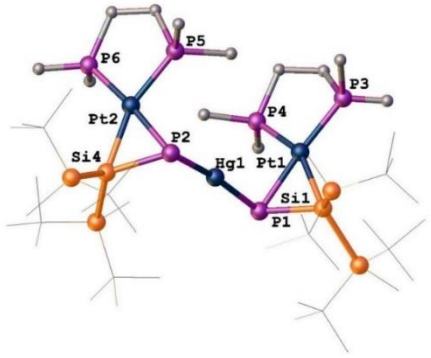


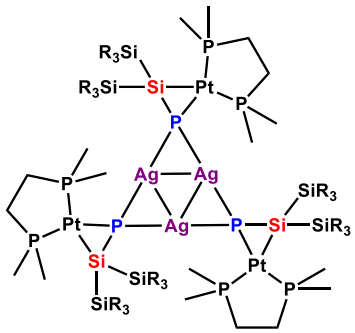
Figure S35. Molecular structures of **14** (Olex drawing). Hydrogen atoms are omitted for clarity. CCDC 2110550

Table S8. Crystal data and structure refinement for **14**.

Identification code	Dimitry551
Empirical formula	$C_{51}H_{116}HgP_6Pt_2Si_6$
Formula weight	1674.56
Temperature/K	296.15
Crystal system	triclinic
Space group	P-1
a/Å	12.345(3)
b/Å	17.313(5)
c/Å	19.497(6)
α/°	112.739(6)
β/°	92.304(6)
γ/°	100.467(6)
Volume/Å^3	3751.1(18)
Z	2
ρ_{calc}g/cm^3	1.483
μ/mm^{-1}	6.013
F(000)	1664.0
Crystal size/mm^3	0.21 × 0.12 × 0.09
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.282 to 51.986
Index ranges	-14 ≤ h ≤ 15, -20 ≤ k ≤ 20, -22 ≤ l ≤ 23
Reflections collected	44822
Independent reflections	13602 [R_{int} = 0.0863, R_{sigma} = 0.1115]
Data/restraints/parameters	13602/221/577
Goodness-of-fit on F^2	1.022
Final R indexes [I>=2σ (I)]	R_1 = 0.1007, wR_2 = 0.2146
Final R indexes [all data]	R_1 = 0.1667, wR_2 = 0.2397
Largest diff. peak/hole / e Å^{-3}	2.84/-2.16

Table S9. Selected bond lengths [Å] and angles [°] for **14**							
Atom 1	Atom 2	bond lengths [Å]		Atom 1	Atom 2	Atom 3	Angle [°]
Hg1	P1	2.402(6)		P1	Pt1	Si1	55.5(2)
Hg1	P2	2.406(6)		P3	Pt1	P1	173.7(3)
P1	Pt1	2.381(6)		P3	Pt1	Si1	118.4(3)
P1	Si1	2.235(8)		P4	Pt1	P1	99.1(2)
P2	Pt2	2.379(6)		P4	Pt1	Si1	154.1(3)
P2	Si4	2.238(9)		P5	Pt2	P2	98.6(2)
Pt1	Si1	2.417(6)		P6	Pt2	P2	174.4(3)
Pt2	Si4	2.420(6)		P6	Pt2	Si4	119.0(3)
Si1	Si2	2.410(10)		P1	Si1	Pt1	61.4(2)
Si1	Si3	2.379(10)		Si2	Si1	Pt1	118.8(3)
Si4	Si5	2.405(10)		P2	Si4	Pt2	61.3(2)
Si4	Si6	2.392(10)		P1	Hg1	P2	171.5(2)
				Pt1	P1	Hg1	96.7(2)
				Si1	P1	Hg1	105.8(3)
				Si1	P1	Pt1	63.1(2)
				Pt2	P2	Hg1	98.2(2)
				Si4	P2	Hg1	106.8(3)
				Si4	P2	Pt2	63.1(2)
				P1	Pt1	Si1	55.5(2)

Complex 15: To a hexane solution of **4** (0.019 mmol, 1 eq.) an ether solution of TMS_2NAg (0.023 mmol, 1.2 eq.) was added. The mixture was stirred overnight at room temperature. All volatiles were evaporated, and 10 ml of dry hexane was added. The volume was reduced to 2 ml yielding bright orange crystals.



^{31}P NMR: δ (ppm): -194.5 (broad, $^{1}J(^{31}P,^{107}Ag)$ = 865.65 Hz), $^{2}J(^{31}P,^{31}P)$=152.7Hz), -185.65 (broad, $^{1}J(^{31}P,^{107}Ag)$ = 882 Hz), $^{2}J(^{31}P,^{31}P)$ = 118 Hz), 23.53 (d, $^{1}J(^{31}P,^{195}Pt)$ = 3053 Hz), $^{2}J(^{31}P,^{31}P)$ = 91.59 Hz), 24.3 (d, $^{1}J(^{31}P,^{195}Pt)$ = 3071 Hz), $^{2}J(^{31}P,^{31}P)$ = 122 Hz), 30.52 (dd, $^{1}J(^{31}P,^{195}Pt)$ = 2314 Hz), $^{2}J(^{31}P,^{31}P)$ = 29 Hz), 31.8 (dd, $^{1}J(^{31}P,^{195}Pt)$ = 2299 Hz), $^{2}J(^{31}P,^{31}P)$ = 24 Hz).

^{29}Si NMR: δ (ppm): 2.78 (broad), 3.31 (broad), 3.99 (broad).

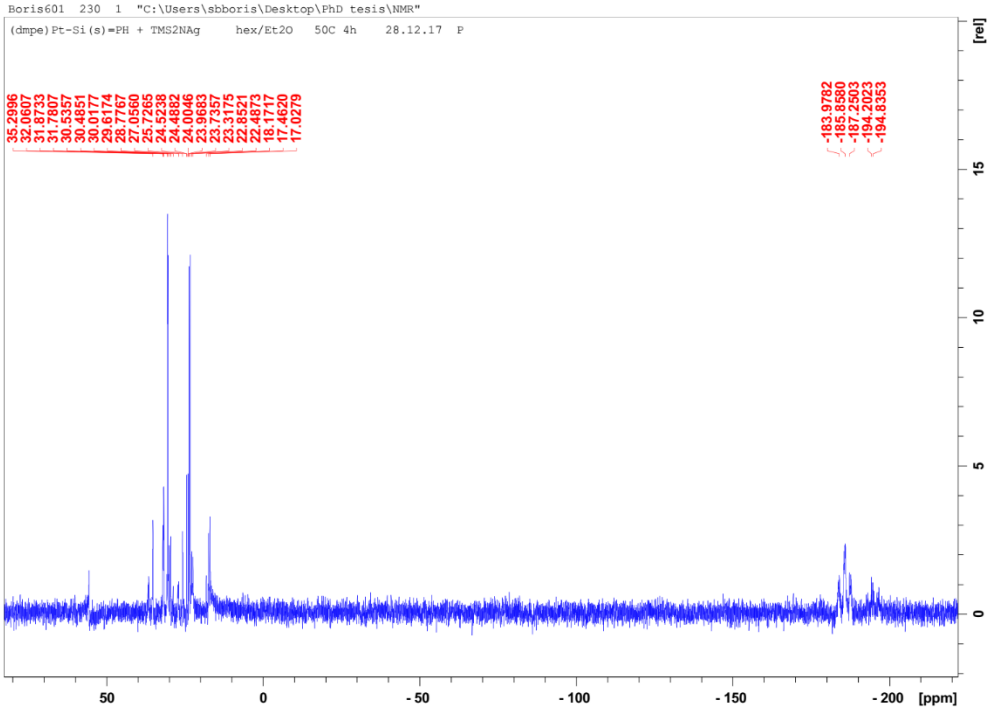


Figure S36. ^{31}P NMR spectrum of **15**

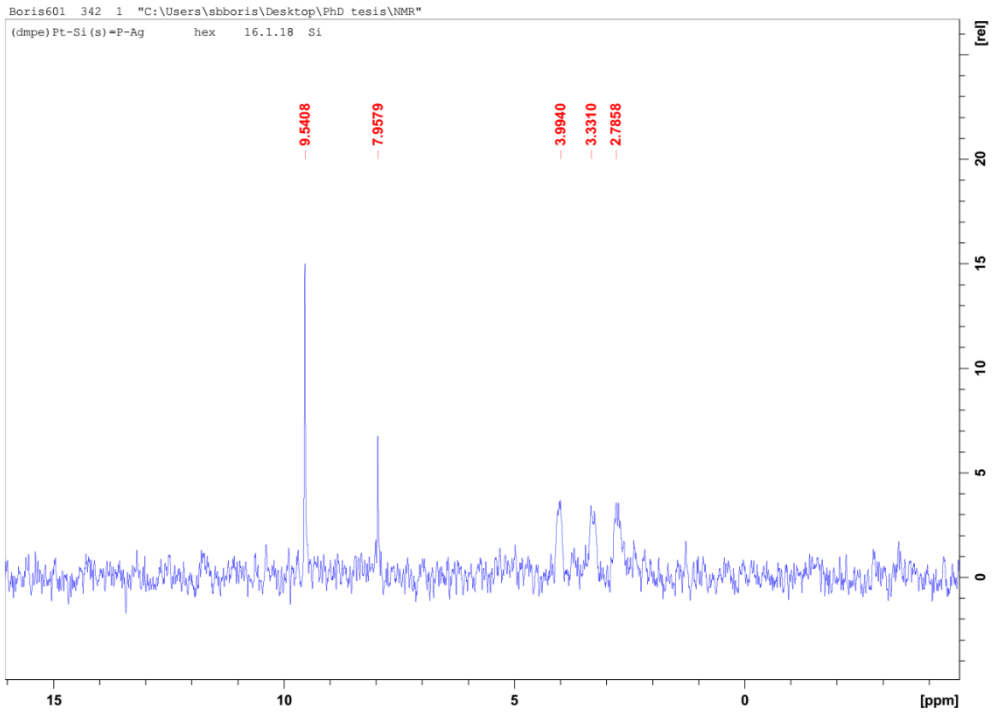


Figure S37. ^{29}Si NMR spectrum of **15**

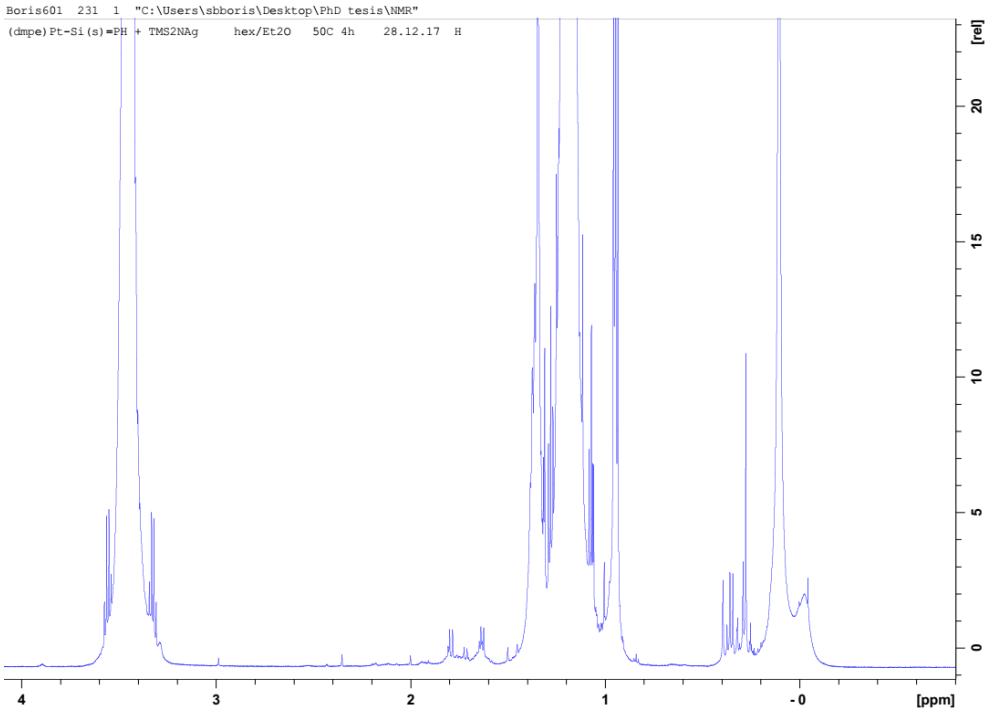


Figure S38. ^{1}H NMR spectrum of **15**

Table S10. Crystal data and structure refinement for **15**.

Identification code	shelxl
Empirical formula	$C_{78}H_{177}Ag_3P_9Pt_3Si_9$
Formula weight	2555.61
Temperature/K	200.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	31.323(11)
b/Å	15.337(7)
c/Å	24.339(3)
α/°	90
β/°	91.746(16)
γ/°	90
Volume/Å^3	11687(7)
Z	4
ρ_{calc}g/cm^3	1.452
μ/mm^{-1}	4.318
F(000)	5124.0
Crystal size/mm^3	0.18 × 0.15 × 0.09
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	1.3 to 49.954
Index ranges	-37 ≤ h ≤ 37, -18 ≤ k ≤ 0, 0 ≤ l ≤ 28
Reflections collected	20496
Independent reflections	20496 [R_{int} = 0.0730, R_{sigma} = 0.0402]
Data/restraints/parameters	20496/329/959
Goodness-of-fit on F^2	1.090
Final R indexes [I>=2σ (I)]	R_1 = 0.0489, wR_2 = 0.1311
Final R indexes [all data]	R_1 = 0.0781, wR_2 = 0.1509
Largest diff. peak/hole / e Å^{-3}	1.67/-2.50

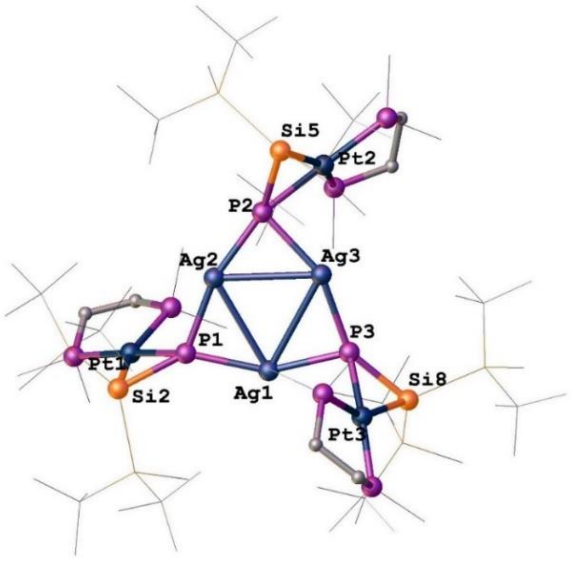


Figure S39. Molecular structures of **15** (Olex drawing). Hydrogen atoms are omitted for clarity. CCDC 2110515

Table S11. Selected bond lengths [Å] and angles [°] for **15**:

Atom 1	Atom 2	bond lengths [Å]		Atom 1	Atom 2	Atom 3	Angle [°]
P1	Si2	2.211(3)		Ag2	Ag1	Ag3	57.02(2)
P2	Si5	2.215(3)		P1	Ag1	Ag2	49.08(6)
P3	Si8	2.222(3)		P1	Ag1	Ag3	106.03(6)
Ag1	Ag2	3.1356(12)		P3	Ag1	Ag2	104.09(6)
Ag1	Ag3	3.3042(14)		P3	Ag1	Ag3	47.07(5)
Ag1	P1	2.410(2)		P3	Ag1	P1	152.90(7)
Ag1	P3	2.405(2)		Ag3	Ag2	Ag1	64.25(3)
Ag2	Ag3	3.0774(11		P1	Ag2	Ag1	49.46(5)
Ag2	P1	2.396(2)		P1	Ag2	Ag3	113.63(5)
Ag2	P2	2.382(2)		P2	Ag2	Ag1	115.15(5)
Ag3	P2	2.445(2)		P2	Ag2	Ag3	51.30(5)
Ag3	P3	2.424(2)		P2	Ag2	P1	164.40(7)
Ag3	Pt2	3.2025(11)		Ag2	Ag3	Ag1	58.73(3)
P1	Pt1	2.366(2)		Ag2	Ag3	Pt2	91.23(4)
P2	Pt2	2.354(2)		P2	Ag3	Ag1	107.87(5)
P3	Pt3	2.373(2)		P2	Ag3	Ag2	49.48(5)
Pt1	Si2	2.427(2)		P2	Ag3	Pt2	46.93(5)
Pt2	Si5	2.455(2)		P3	Ag3	Ag1	46.58(5)
Pt3	Si8	2.428(2)		P3	Ag3	Ag2	105.30(6)
				P3	Ag3	P2	154.10(7)
				P3	Ag3	Pt2	145.75(5)
				Pt2	Ag3	Ag1	137.92(2)

3. Quantum mechanics calculations

Calculations employed Gaussian 09, Revision C.02; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.

All calculations were performed using Density Functional Theory (DFT) [S2]. The calculations were carried out at the B3LYP/6-311+G(d,p) (for H, C, Si, P, O) level [S3-S5], Pt was described with LANL2DZ [S6]. The optimized minima and transition states were verified by harmonic vibrational analysis to have no imaginary frequency and one proper imaginary frequency, respectively. All transition-state structures were confirmed to connect corresponding reactants and products by intrinsic reaction coordinate (IRC) [S7,S8] calculations.

3.1 Optimized Cartesian coordinates for A

Energy: -909773.6779584

Si	-0.00075	0.73304	-0.00043
P	-0.13250	2.89522	-0.00006
Si	-2.06161	-0.47103	0.00000
C	-2.11796	-1.60697	1.55111
C	-3.52737	0.76321	0.02689
C	-2.14275	-1.56828	-1.57762
Si	2.07383	-0.45242	-0.00005
C	2.17112	-1.54584	1.57938
C	2.14903	-1.58515	-1.55274
C	3.52393	0.80117	-0.02613
H	1.30870	3.13366	-0.00115
H	-3.05133	-2.18417	1.55750
H	-1.27916	-2.31241	1.55581
H	-2.07302	-1.01528	2.47206
H	-4.47945	0.21770	0.02935
H	-3.50379	1.41674	-0.85175
H	-3.48794	1.39715	0.91921
H	-1.30323	-2.27189	-1.61378
H	-3.07549	-2.14647	-1.58258
H	-2.11387	-0.95373	-2.48414
H	3.11295	-2.10916	1.58640
H	2.13083	-0.93107	2.48529
H	1.34261	-2.26223	1.61478
H	3.09161	-2.14721	-1.55995
H	2.09399	-0.99358	-2.47321
H	1.32152	-2.30363	-1.55766
H	3.49488	1.45262	0.85416

H	4.48238	0.26694	-0.02942
H	3.47869	1.43464	-0.91877

3.2 Optimized Cartesian coordinates for B

Energy: -2285766.6336588

Pt	-0.17857	-0.66710	-0.06318
P	-0.58667	1.59345	0.10013
P	2.20377	-0.76461	-0.03059
P	-0.57188	-3.13294	-0.29521
Si	-3.35578	-1.99668	1.94351
Si	-2.31782	-1.75261	-0.15707
Si	-3.55877	-1.42617	-2.12434
C	-3.54466	-3.83466	2.36158
C	-5.05902	-0.30731	-1.84536
H	-3.96564	-3.96757	3.36450
H	-4.20365	-4.33637	1.64703
H	-4.75377	0.67214	-1.47263
H	-2.57505	-4.33840	2.32362
H	-5.75052	-0.74116	-1.11754
H	-5.60640	-0.15715	-2.78259
H	-0.47203	-3.16827	-1.72043
C	-4.15569	-3.08994	-2.80914
H	-4.69018	-2.95141	-3.75569
H	-3.31316	-3.76388	-2.98744
H	-4.83446	-3.58560	-2.10879
C	-2.42268	-0.61294	-3.40616
H	-2.19799	0.41617	-3.11553
H	-1.47850	-1.15862	-3.49038
H	-2.89720	-0.59206	-4.39327
C	-2.24582	-1.20995	3.26603
H	-1.25900	-1.68183	3.25587
H	-2.08991	-0.14287	3.09231
H	-2.67439	-1.33605	4.26646
C	-5.07675	-1.20013	1.99745
H	-5.05251	-0.14919	1.70316
H	-5.75894	-1.71600	1.31505
H	-5.49974	-1.26541	3.00583
C	0.36936	2.52697	-1.16984
C	0.98290	3.76286	-0.95446
C	0.43342	1.94849	-2.44563
C	1.62627	4.41951	-2.00237
H	0.98171	4.21090	0.03028
C	1.06284	2.61290	-3.49373
H	-0.01236	0.97514	-2.61260
C	1.65723	3.85505	-3.27509
H	2.11206	5.37111	-1.81807
H	1.09683	2.15525	-4.47615
H	2.15590	4.37142	-4.08773
C	-0.18700	2.31156	1.74798
C	-0.50026	3.63562	2.08566
C	0.39094	1.48268	2.71504
C	-0.19619	4.13047	3.35080
H	-1.00137	4.27465	1.36741
C	0.68790	1.97583	3.98414
H	0.59347	0.44596	2.47398
C	0.40396	3.30249	4.30106
H	-0.43850	5.15767	3.59983
H	1.13190	1.31884	4.72354
H	0.63312	3.68756	5.28849

C	-2.29890	2.24683	-0.14621
C	-2.67876	2.98170	-1.27339
C	-3.25270	1.99233	0.84901
C	-3.98282	3.46503	-1.39475
H	-1.96063	3.19240	-2.05558
C	-4.54605	2.48883	0.73374
H	-2.97764	1.41736	1.72517
C	-4.91639	3.22957	-0.38996
H	-4.26268	4.03052	-2.27659
H	-5.26902	2.29249	1.51731
H	-5.92738	3.60916	-0.48314
C	3.18384	0.79310	-0.16551
C	3.72695	1.21478	-1.38425
C	3.32094	1.62296	0.95626
C	4.40357	2.42969	-1.47322
H	3.62659	0.59558	-2.26692
C	3.99994	2.83383	0.86557
H	2.91015	1.31967	1.90978
C	4.54763	3.24059	-0.35023
H	4.81306	2.74302	-2.42683
H	4.09884	3.45816	1.74679
H	5.07605	4.18459	-0.42293
C	2.85875	-1.78055	-1.41926
C	4.05492	-2.50157	-1.34903
C	2.12075	-1.79635	-2.60886
C	4.50699	-3.22103	-2.45373
H	4.63053	-2.51773	-0.43178
C	2.58107	-2.50374	-3.71663
H	1.17493	-1.26957	-2.65407
C	3.77540	-3.21877	-3.64078
H	5.42978	-3.78644	-2.38512
H	1.99888	-2.50968	-4.63138
H	4.12918	-3.78037	-4.49817
C	2.87623	-1.51837	1.51267
C	2.02347	-2.29297	2.30835
C	4.20489	-1.33329	1.92203
C	2.49114	-2.87490	3.48531
H	0.99893	-2.44776	1.99730
C	4.67000	-1.91659	3.09795
H	4.87379	-0.71818	1.33201
C	3.81345	-2.68871	3.88307
H	1.81861	-3.47341	4.08958
H	5.69953	-1.76425	3.40272
H	4.17550	-3.13992	4.80028

3.3 Optimized Cartesian coordinates for C

Energy: -2044300.6217776

Pt	-0.24953	-0.07712	-0.51585
P	0.36262	0.66268	1.57185
P	-2.47351	-0.03347	0.27498
P	-0.25176	-0.77300	-2.90759
Si	3.01260	1.27480	-2.39198
Si	1.69458	-0.57727	-1.82749
Si	2.79816	-2.54324	-1.18524
C	4.40304	0.80995	-3.59604
C	4.22954	-2.13423	-0.01284
H	5.01312	1.68468	-3.84692
H	5.06431	0.05456	-3.16052
H	3.87642	-1.58457	0.86194

H	3.99724	0.40133	-4.52586
H	4.98467	-1.52062	-0.51369
H	4.72076	-3.04831	0.33827
H	-0.43126	-2.17401	-2.67890
C	3.48942	-3.46221	-2.69220
H	3.99861	-4.38388	-2.38901
H	2.68868	-3.72846	-3.38784
H	4.20874	-2.84227	-3.23562
C	1.56542	-3.67059	-0.28967
H	1.23580	-3.20246	0.64087
H	0.68312	-3.84966	-0.91031
H	2.01844	-4.63790	-0.04673
C	1.93089	2.61152	-3.18512
H	1.47193	2.24084	-4.10567
H	1.12245	2.91122	-2.51395
H	2.52084	3.50163	-3.42942
C	3.80438	1.96559	-0.81094
H	3.03588	2.29029	-0.10555
H	4.41988	1.20956	-0.31432
H	4.44250	2.82667	-1.03804
C	0.64004	2.47144	1.70823
C	0.94544	3.09302	2.92665
C	0.48256	3.25541	0.56081
C	1.10112	4.47491	2.99011
H	1.07678	2.49758	3.82369
C	0.63586	4.63939	0.62603
H	0.24328	2.76956	-0.37817
C	0.94772	5.24981	1.83875
H	1.34439	4.94753	3.93521
H	0.51724	5.23567	-0.27149
H	1.07185	6.32575	1.88984
C	1.73007	-0.13416	2.49595
C	1.56758	-1.45664	2.93369
C	2.96932	0.49099	2.68144
C	2.60836	-2.12454	3.57184
H	0.63219	-1.97798	2.76420
C	4.00984	-0.18132	3.31988
H	3.13072	1.49958	2.32235
C	3.83184	-1.48652	3.77319
H	2.46633	-3.14739	3.90195
H	4.96430	0.31539	3.45284
H	4.64441	-2.00889	4.26470
C	-3.10636	-1.70197	0.72576
C	-4.44588	-1.94060	1.05626
C	-2.18973	-2.75947	0.77795
C	-4.85706	-3.21316	1.44646
H	-5.17347	-1.13897	0.99450
C	-2.60195	-4.02995	1.17586
H	-1.15957	-2.58652	0.48716
C	-3.93508	-4.25861	1.51224
H	-5.89792	-3.39046	1.69394
H	-1.88267	-4.84084	1.20785
H	-4.25840	-5.24868	1.81382
C	-3.83718	0.79748	-0.61824
C	-3.78550	0.78104	-2.01803
C	-4.89974	1.44993	0.02177
C	-4.79308	1.38884	-2.76347
H	-2.94502	0.30929	-2.51576
C	-5.90097	2.06436	-0.72807
H	-4.95273	1.48767	1.10384

C	-5.85174	2.03001	-2.12127
H	-4.74317	1.37016	-3.84630
H	-6.71784	2.56963	-0.22461
H	-6.63156	2.50855	-2.70317
C	-1.12739	0.41877	2.68558
H	-1.00579	0.99533	3.60559
H	-1.16435	-0.63975	2.95509
C	-2.40952	0.81911	1.94217
H	-3.28932	0.56968	2.54049
H	-2.42071	1.89602	1.74899

3.4 Optimized Cartesian coordinates for D

Energy: -1563164.6776869

Pt	-0.84837	0.08877	0.05661
P	-0.88920	-1.81412	-1.23334
P	-3.07524	0.74924	0.49095
P	0.15175	1.89078	1.48598
Si	2.62673	-0.99842	1.74585
Si	1.49507	0.50980	0.35822
Si	2.59159	1.40379	-1.51371
C	0.59346	-2.20099	-2.25372
C	-2.22517	-1.97328	-2.49582
C	-3.49624	0.64636	2.27927
C	4.23865	-0.25727	2.41556
C	3.74635	0.12692	-2.31778
C	-3.41936	2.51559	0.10163
H	0.46345	-3.13613	-2.80649
H	1.46615	-2.27809	-1.60624
H	0.76278	-1.38580	-2.95845
H	-2.12050	-2.89684	-3.07261
H	-2.17801	-1.11824	-3.17286
H	-3.45673	-0.39646	2.59985
H	4.74294	-0.95722	3.09086
H	-4.49121	1.05282	2.48337
H	4.93105	-0.01772	1.60251
H	-3.19625	-1.96686	-2.00103
H	3.21110	-0.78065	-2.60771
H	-2.74337	1.20322	2.83889
H	4.04135	0.66591	2.96763
H	4.54842	-0.16288	-1.63213
H	4.21269	0.54340	-3.21733
H	-4.43732	2.79592	0.38755
H	-3.28250	2.68332	-0.96821
H	-2.70191	3.13689	0.63910
H	0.12153	2.92213	0.49264
C	-1.10103	-3.35906	-0.25241
H	-0.28614	-3.43804	0.46836
H	-2.03938	-3.30167	0.30195
H	-1.10852	-4.24503	-0.89383
C	-4.52778	-0.08489	-0.28992
H	-4.47151	0.02890	-1.37411
H	-4.50862	-1.15043	-0.05144
H	-5.47106	0.34163	0.06412
C	3.63042	2.91684	-1.04503
H	4.11711	3.34601	-1.92788
H	3.00506	3.68954	-0.58959
H	4.40929	2.65237	-0.32381
C	1.27350	1.92881	-2.77005
H	0.66569	1.07452	-3.08023

H	0.59567	2.66164	-2.32394
H	1.72623	2.37519	-3.66221
C	1.48695	-1.44802	3.18910
H	1.21362	-0.55505	3.75794
H	0.56057	-1.89790	2.82032
H	1.96976	-2.15569	3.87175
C	3.06898	-2.59124	0.80561
H	2.17309	-3.14281	0.50676
H	3.65104	-2.37927	-0.09638
H	3.66747	-3.25420	1.44004

3.5 Optimized Cartesian coordinates for E

Energy: -1562905.3425941

Pt	0.72479	-0.15280	-0.27505
P	1.35323	0.66530	1.77636
P	3.01474	-0.35688	-0.77361
P	-0.49193	-0.91829	-2.30923
Si	-2.79813	-1.87785	0.59085
Si	-1.66135	-0.17849	-0.55109
Si	-2.55128	1.98577	-0.60053
C	0.68427	0.05468	3.37507
C	3.18980	0.34002	1.95214
C	1.24164	2.49349	1.96300
C	3.92270	0.51721	0.61115
C	3.70822	-2.06102	-0.73122
C	-4.53457	-2.16398	-0.11604
C	-2.97860	2.52375	1.17326
C	3.76935	0.35947	-2.28859
H	1.23287	0.47174	4.22480
H	0.74770	-1.03425	3.39820
H	-0.36649	0.33774	3.44937
H	3.61910	0.98465	2.72574
H	3.28346	-0.69334	2.30151
H	1.68599	2.82958	2.90422
H	4.95710	0.16608	0.67859
H	0.19305	2.79152	1.92669
H	3.44760	-2.53067	0.21877
H	3.95755	1.57659	0.33677
H	-5.04431	-2.97723	0.41241
H	4.79517	-2.06106	-0.85400
H	-5.15316	-1.26573	-0.02541
H	1.75456	2.97016	1.12619
H	-2.12849	2.38962	1.84834
H	3.24807	-2.64419	-1.53072
H	-4.48433	-2.42700	-1.17634
H	-3.80971	1.93439	1.57211
H	-3.27170	3.57882	1.20493
H	4.85979	0.27174	-2.28449
H	3.48585	1.41049	-2.36471
H	3.36672	-0.16406	-3.15756
H	-0.41766	0.33366	-3.00001
C	-2.97790	-1.43548	2.42957
H	-1.99820	-1.35781	2.90804
H	-3.49426	-0.48042	2.56501
H	-3.55065	-2.20448	2.95946
C	-1.78747	-3.47157	0.44371
H	-0.79612	-3.33486	0.88487
H	-2.28267	-4.30623	0.95186
H	-1.64493	-3.74454	-0.60557

C	-4.11762	2.13890	-1.65572
H	-4.91166	1.48560	-1.28197
H	-4.49664	3.16695	-1.65264
H	-3.91574	1.85525	-2.69248
C	-1.21649	3.14105	-1.28674
H	-0.30553	3.06150	-0.68752
H	-0.95599	2.86033	-2.31102
H	-1.54946	4.18467	-1.28928

4. DFT calculations for the transition state in Figure 4, Figure S40

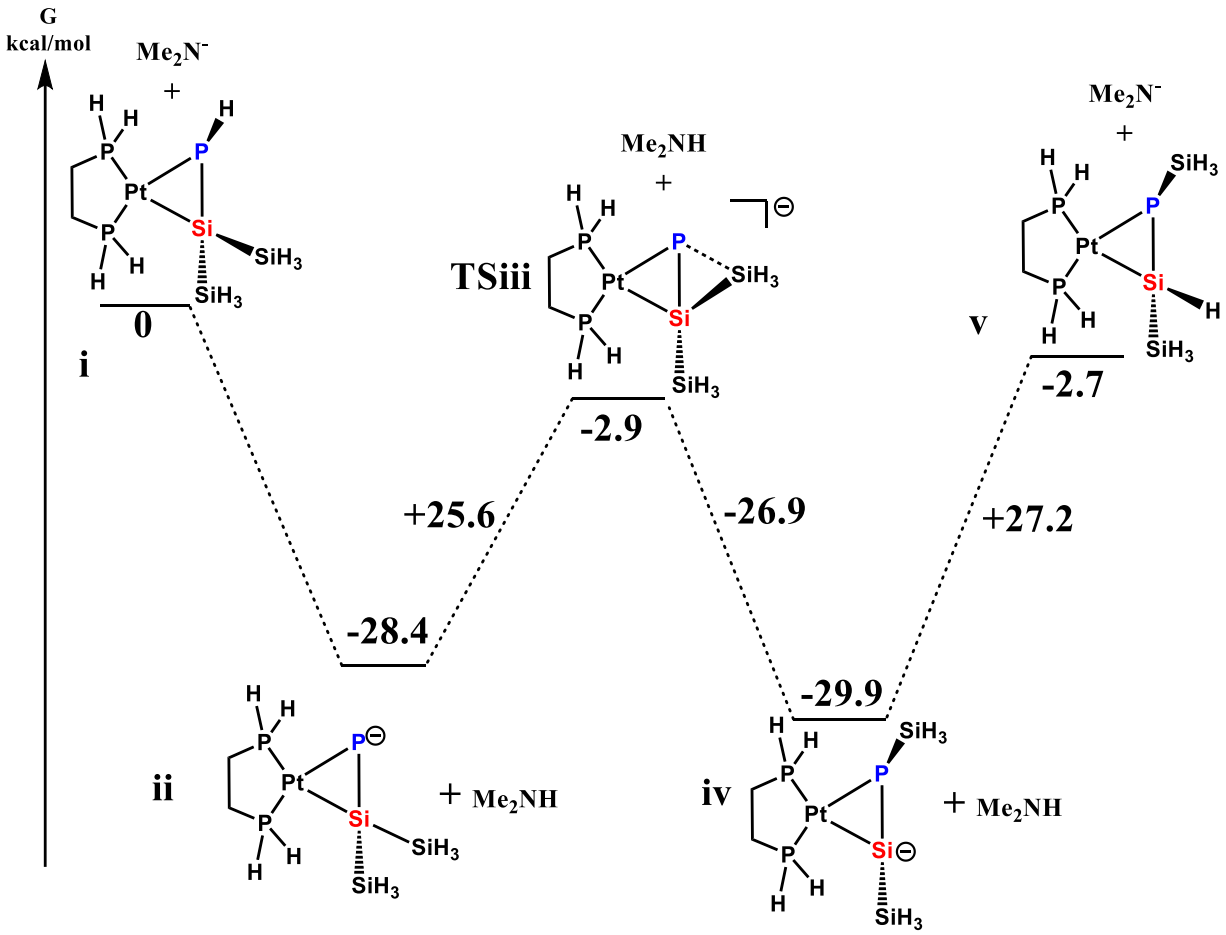


Figure S40. Calculated energies for the rearrangment of (**i**) to (**v**) via transition state TS**iii**. **i, ii, iv and v** are properly charecterized minima.

Optimized Cartesian coordinates for i.

η^2- ((Me$_3$Si)$_2$Si-PH)Pt(dhpe)

Energy: -1316044.6469937

Pt	0.34805	-0.25720	-0.01687
C	3.70701	0.31236	-0.28481
C	3.16200	1.61581	0.32227
Si	-2.01997	-0.04167	0.00561
H	3.76581	0.39466	-1.37354
H	4.71173	0.10627	0.08746
H	3.72767	2.47640	-0.03891
H	3.24705	1.59568	1.41225
Si	-2.94595	0.73423	2.01161
H	-2.71867	2.19990	2.17142
H	-4.41572	0.50391	2.11131
H	-2.29554	0.04532	3.16020
P	2.56676	-1.13099	0.06424
H	3.08283	-2.12801	-0.79119
H	3.05729	-1.62253	1.29509
P	1.34241	1.82939	-0.05125
H	0.97252	2.86998	0.82557
H	1.34544	2.54651	-1.26793

Si	-2.99164	0.78379	-1.95751
H	-2.74284	2.24842	-2.09010
H	-2.38819	0.11259	-3.14207
H	-4.46782	0.58165	-2.02072
P	-1.27675	-2.14571	-0.10531
H	-1.32404	-2.39747	1.30124

Me_2N^-

Energy: -84452.0944982

N	0.00000	0.66317	0.00000
C	1.16093	-0.16994	0.00000
H	2.08452	0.42690	0.00001
H	1.23816	-0.86418	0.88495
H	1.23816	-0.86417	-0.88496
C	-1.16093	-0.16994	0.00000
H	-1.23817	-0.86416	0.88496
H	-2.08452	0.42690	-0.00002
H	-1.23815	-0.86419	-0.88494

Optimized Cartesian coordinates for ii

η^2- $((Me_3Si)_2Si\text{-}P^-)Pt(dhpe)$

Energy: -1315719.1399794

Pt	-0.35356	-0.28171	-0.00155
C	-3.68124	0.39402	0.32420
C	-3.11415	1.69037	-0.27533
P	1.17229	-2.21583	0.01575
Si	2.04598	-0.22588	0.00636
H	-3.71473	0.46342	1.41518
H	-4.69902	0.21765	-0.02941
H	-3.64264	2.56164	0.11704
H	-3.23431	1.69010	-1.36239
Si	3.00100	0.75739	-1.91011
H	2.85989	2.25088	-1.93078
H	4.46818	0.50694	-2.09270
H	2.33992	0.26193	-3.15448
P	-2.57979	-1.07426	-0.06582
H	-3.14496	-2.05722	0.78175
H	-3.14090	-1.53444	-1.28301
P	-1.26997	1.83666	0.04149
H	-0.93244	2.87818	-0.85646
H	-1.24164	2.61048	1.22998
Si	3.01488	0.77739	1.90273
H	2.87380	2.27099	1.90800
H	2.37041	0.29404	3.16039
H	4.48452	0.52953	2.06777

Me_2NH

Energy: -84827.0957426

N	0.00001	0.56784	-0.15145
H	-0.00002	1.33066	0.51777
C	1.21713	-0.22413	0.02013
H	1.27864	-0.97309	-0.77541
H	2.09423	0.42221	-0.05940
H	1.26396	-0.75712	0.98518
C	-1.21713	-0.22414	0.02013
H	-1.26353	-0.75786	0.98479
H	-2.09418	0.42240	-0.05843

H	-1.27916	-0.97246	-0.77597

Optimized Cartesian coordinates for the transition state iii

η^2- ((Me$_3$Si)$_2$Si-P$^-$)Pt(dhpe)

Energy: -1315700.8746409

Pt	0.33276	-0.14985	-0.02945
C	3.72378	-0.43011	0.02299
C	3.50231	1.06655	-0.24546
P	-1.60141	-1.38869	0.77086
Si	-1.93802	0.59986	-0.50431
H	3.85544	-0.97174	-0.91777
H	4.62340	-0.58641	0.62290
H	4.27784	1.45906	-0.90544
H	3.54031	1.63206	0.68978
Si	-2.66083	2.25671	1.04618
H	-2.63012	3.66115	0.49834
H	-4.09128	2.05587	1.45044
H	-1.89384	2.33214	2.33505
P	2.23368	-1.20651	0.85209
H	2.54467	-2.58301	0.73192
H	2.54197	-1.05237	2.22574
P	1.79880	1.38033	-0.96786
H	1.70252	2.78463	-0.83625
H	2.05070	1.32962	-2.35916
Si	-3.30953	-1.36083	-0.95538
H	-4.58738	-0.59143	-1.32002
H	-2.82461	-1.91384	-2.26920
H	-4.02614	-2.51932	-0.25478

Optimized Cartesian coordinates for iv

η^2- ((Me$_3$Si)Si-P(SiMe$_3$)$^-$Pt(dhpe)

Energy: -1315719.1399794

Pt	-0.35356	-0.28171	-0.00155
C	-3.68124	0.39402	0.32420
C	-3.11415	1.69037	-0.27533
P	1.17229	-2.21583	0.01575
Si	2.04598	-0.22588	0.00636
H	-3.71473	0.46342	1.41518
H	-4.69902	0.21765	-0.02941
H	-3.64264	2.56164	0.11704
H	-3.23431	1.69010	-1.36239
Si	3.00100	0.75739	-1.91011
H	2.85989	2.25088	-1.93078
H	4.46818	0.50694	-2.09270
H	2.33992	0.26193	-3.15448
P	-2.57979	-1.07426	-0.06582
H	-3.14496	-2.05722	0.78175
H	-3.14090	-1.53444	-1.28301
P	-1.26997	1.83666	0.04149
H	-0.93244	2.87818	-0.85646
H	-1.24164	2.61048	1.22998
Si	3.01488	0.77739	1.90273
H	2.87380	2.27099	1.90800
H	2.37041	0.29404	3.16039
H	4.48452	0.52953	2.06777

Optimized Cartesian coordinates for v

η^2- ((Me$_3$Si)SiH-P(SiMe$_3$)Pt(dhpe)

Energy: -1316044.6469937

Pt	0.34805	-0.25720	-0.01687
C	3.70701	0.31236	-0.28481
C	3.16200	1.61581	0.32227
Si	-2.01997	-0.04167	0.00561
H	3.76581	0.39466	-1.37354
H	4.71173	0.10627	0.08746
H	3.72767	2.47640	-0.03891
H	3.24705	1.59568	1.41225
Si	-2.94595	0.73423	2.01161
H	-2.71867	2.19990	2.17142
H	-4.41572	0.50391	2.11131
H	-2.29554	0.04532	3.16020
P	2.56676	-1.13099	0.06424
H	3.08283	-2.12801	-0.79119
H	3.05729	-1.62253	1.29509
P	1.34241	1.82939	-0.05125
H	0.97252	2.86998	0.82557
H	1.34544	2.54651	-1.26793
Si	-2.99164	0.78379	-1.95751
H	-2.74284	2.24842	-2.09010
H	-2.38819	0.11259	-3.14207
H	-4.46782	0.58165	-2.02072
P	-1.27675	-2.14571	-0.10531
H	-1.32404	-2.39747	1.30124

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