Reactions of (Ph)*t*BuP-P(SiMe$_3$)Li·3THF with [(PNP)TiCl$_2$] and [^{Me}NacNacTiCl$_2$·THF]. Synthesis of first PNP titanium(IV) complex with phosphanylphosphinidene ligand [(PNP)Ti(Cl){η^2-P-P(Ph)*t*Bu}]

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Supporting information

PART A. X-ray crystallographic analysis

Diffraction data of **1**, **2** and **3** were collected an a diffractometer equipped with a STOE image plate detector system IPDS2T using Cu- *K*α (λ = 1.54178 Å) for **2** and Mo-*K*α (λ = 0.71073 Å) for **1** and **3** radiation with graphite monochromatization. The experiment diffraction data of **4** were collected with a KM4CCD kappa-geometry diffractometer equipped with a Sapphire2 CCD detector. An enhanced X-ray Mo-*K*α radiation source with a graphite monochromator was used. Good quality single-crystal specimens of **1**, **2**, **3** and **4** were selected for the X-ray diffraction experiments at 120 K for **1**, **3**, **4** and at 150 K for **2**. The structures were solved by direct methods and refined against F^2 using the Shelxs-97 and Shelxl-97 programs[1] run under WinGX.[2] Non-hydrogen atoms were refined with anisotropic displacement parameters: hydrogen atoms were usually refined using the isotropic model with U_{iso}(H) values fixed at 1.5 U_{eq} of the C atoms for CH_3 and 1.2 U_{eq} for CH, CH_2 and aromatic H.

Crystallographic data for the structures of **1**, **2**, **3** and **4** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 1818921-1818924. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223-336-033; E mail: deposit@ccdc.cam.ac.uk).

Table S1. Crystallographic data for **1**, **2** , **3** and **4**.

	1	**2**	**3**	**4**
Empirical formula	$C_{25}H_{47}LiO_3P_2Si$	$C_{42}H_{64}ClN_2P_2SiTi$	$C_{39}H_{55}ClN_2P_2Ti$	$C_{36}H_{54}ClNP_4Ti$
Formula weight	492.59	770.33	697.14	708.03
Crystallographic System	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*Cc*	$P2_1/n$	$P2_1/c$	$P2_1/n$
a [Å]	10.0158(6)	10.5863(8)	17.6073(5)	11.9613(8)
b [Å]	15.7842(12)	20.8521(16)	16.8138(5)	15.7093(13)
c [Å]	18.8280(12)	19.6293(12)	13.4071(8)	20.8473(15)
α [°]	90	90	90	90
β [°]	96.404(5)	95.244(6)	104.874(3)	99.206(7)
γ [°]	90	90	90	90
V [Å^3]	2958.0(3)	4315.0(5)	3836.1(3)	3866.8(5)
Z	4	4	4	4
Calculated Density [g·cm^{-1}]	1.106	1.186	1.207	1.216
T [K]	120(2)	150(2)	120(2)	120(2)
μ [mm^{-1}]	0.209	3.433	0.405	0.481
Final R indices	R_1 = 0.0898	R_1 = 0.0581	R_1 = 0.0468	R_1 = 0.0726
[*I*>2σ(I)]	*w*R_2 = 0.1735	*w*R_2 = 0.1425	*w*R_2 = 0.1324	*w*R_2 = 0.177
R indices (all data)	R_1 = 0.2226	R_1 = 0.0850	R_1 = 0.0584	R_1= 0.1175
	wR_2 = 0.2268	*w*R_2 = 0.1719	*w*R_2 = 0.1497	*w*R_2 = 0.2219
CCDC	1818923	1818921	1818922	1818924

PART B. NMR Spectrum

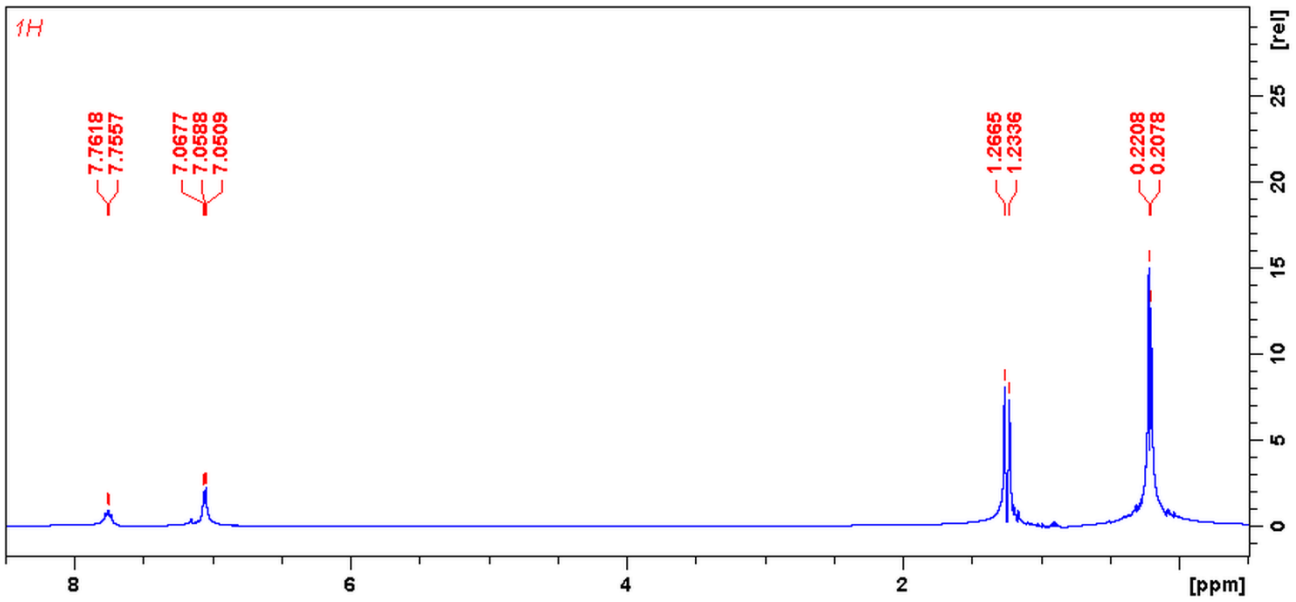

Figure S1. ^{1}H NMR Spectrum of (Ph)*t*BuP-P(SiMe$_3$)$_2$.

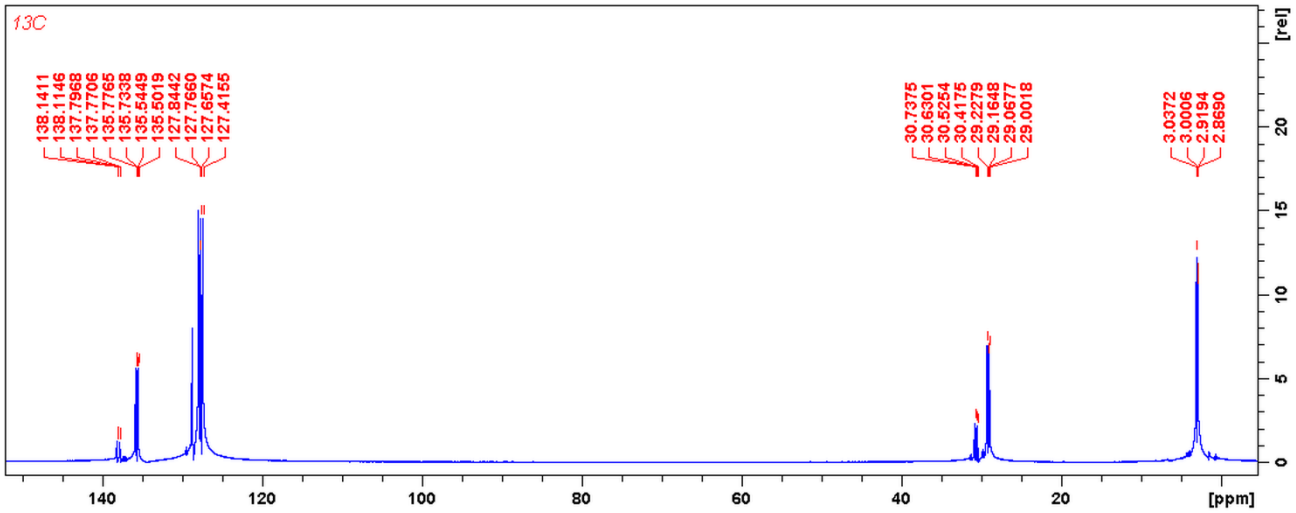

Figure S2. ^{13}C NMR Spectrum of (Ph)*t*BuP-P(SiMe$_3$)$_2$.

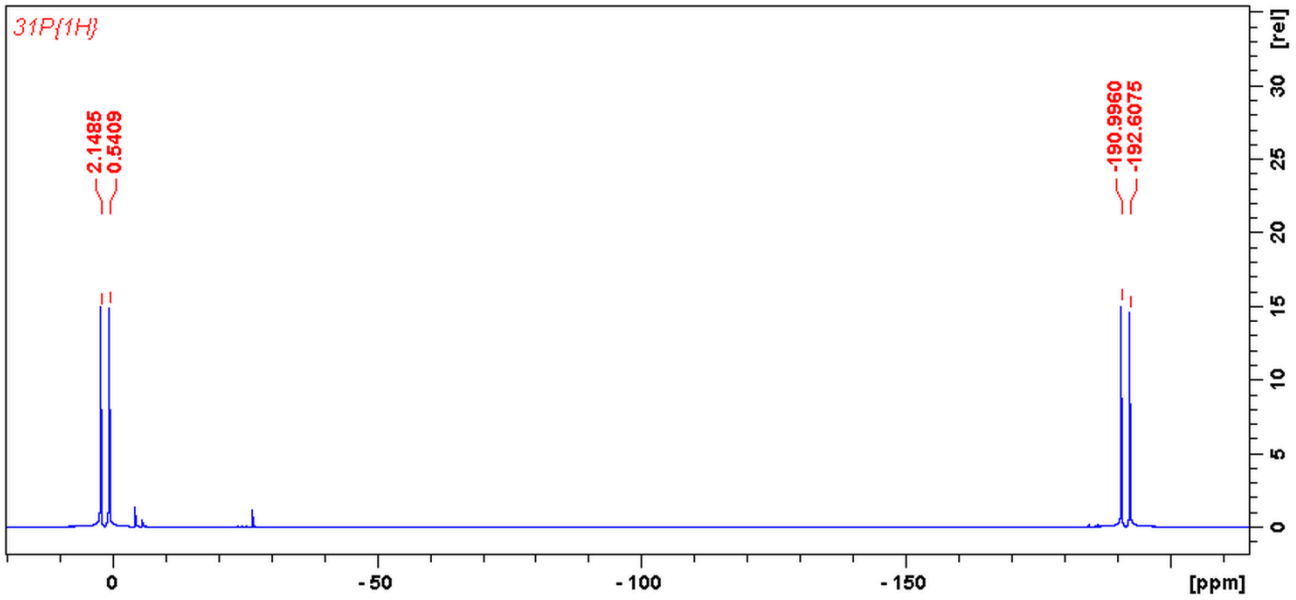

Figure S3. $^{31}P\{H\}$ NMR Spectrum of (Ph)*t*BuP-P($SiMe_3$)$_2$.

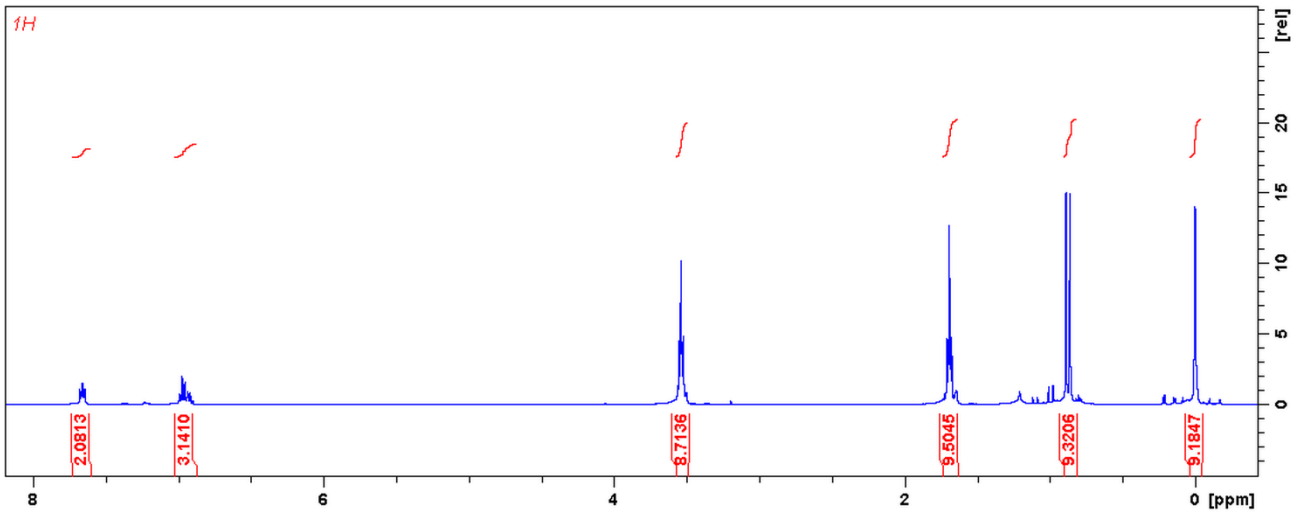

Figure S4. ^{1}H NMR spectrum of (Ph)*t*BuP-P($SiMe_3$)Li·2.2THF **(1)**.

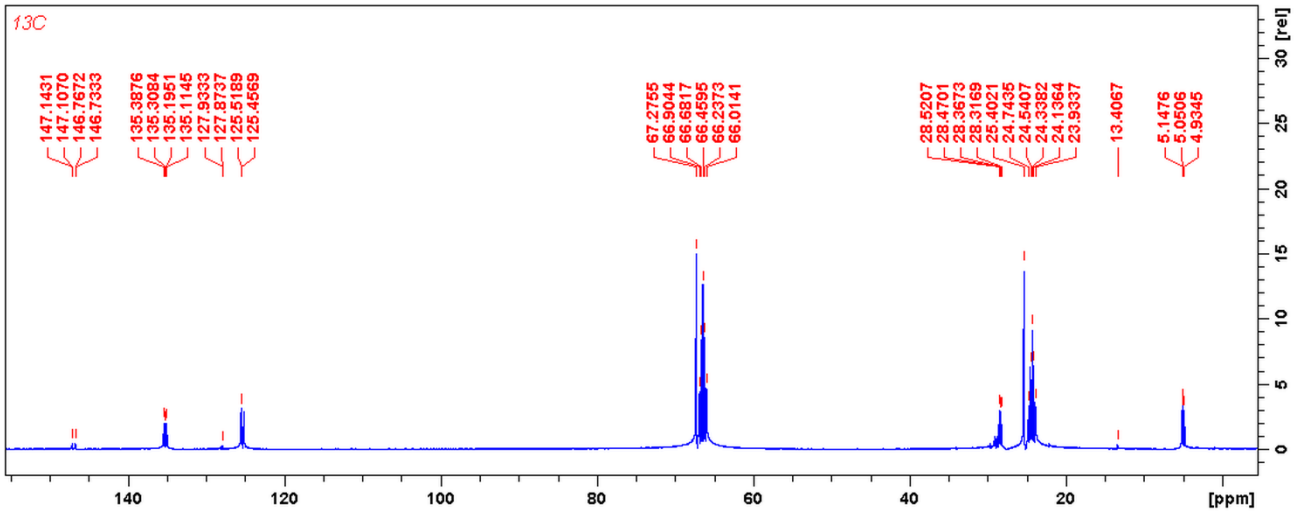

Figure S5. ^{13}C NMR spectrum of (Ph)*t*BuP-P($SiMe_3$)Li·2.2THF **(1)**.

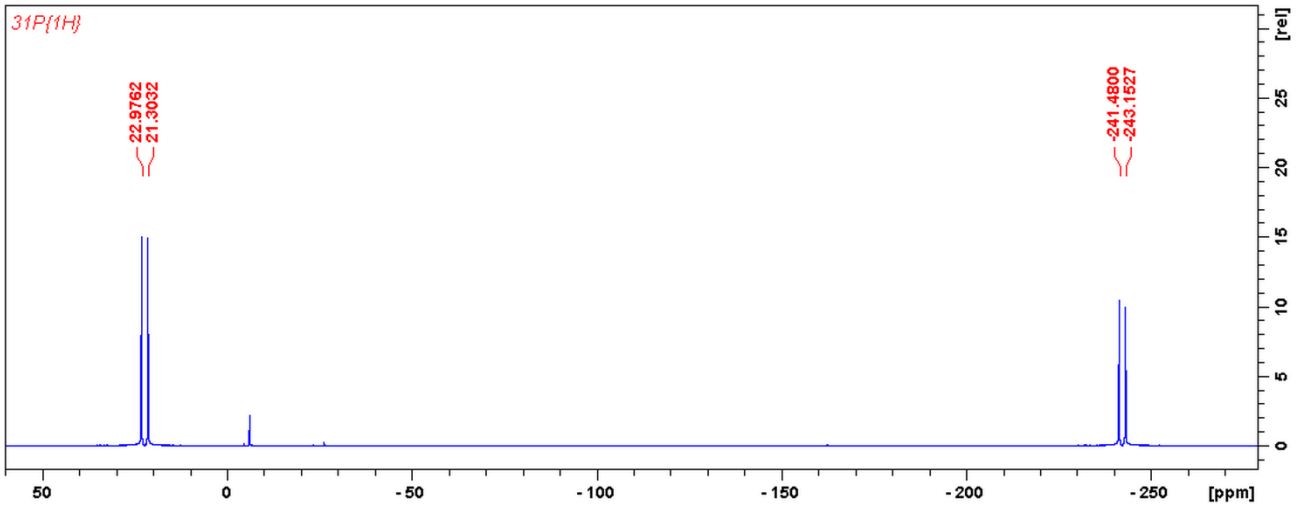

Figure S6. $^{31}P\{H\}$ NMR spectrum of (Ph)*t*BuP-P($SiMe_3$)Li·2.2THF **(1)**.

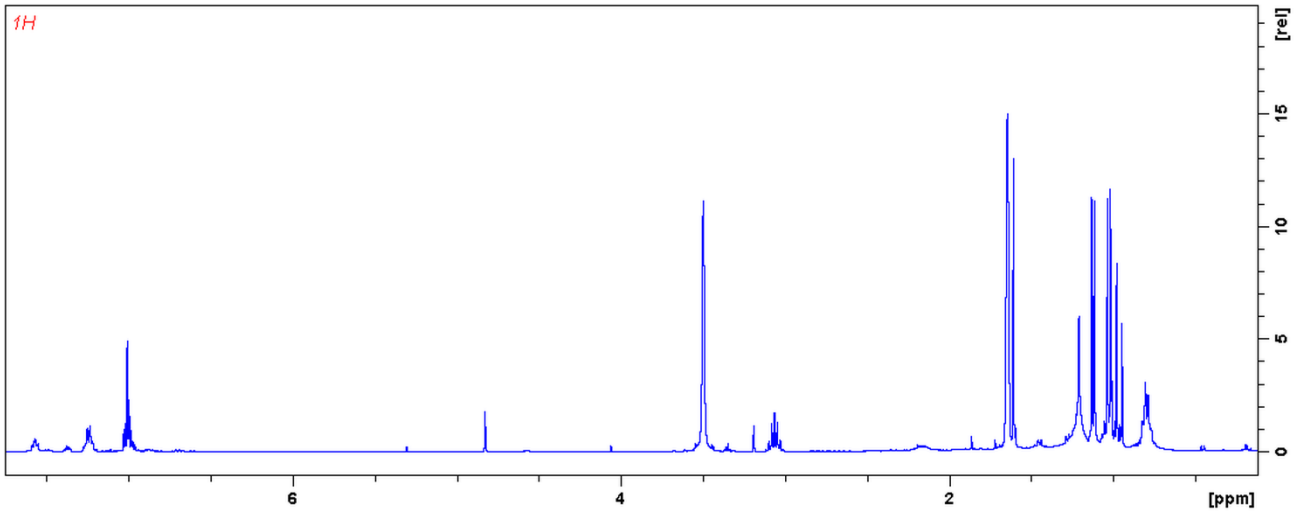

Figure S7. ^{1}H NMR spectrum of **3** (from crystals).

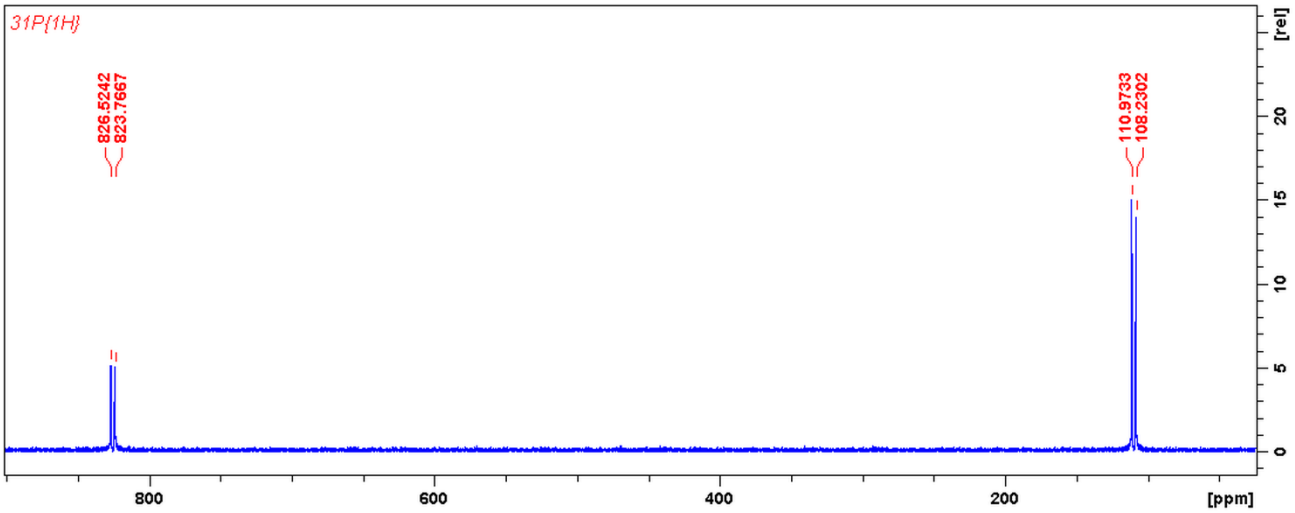

Figure S8. ^{31}P{H} NMR spectrum from crystals of **3**.

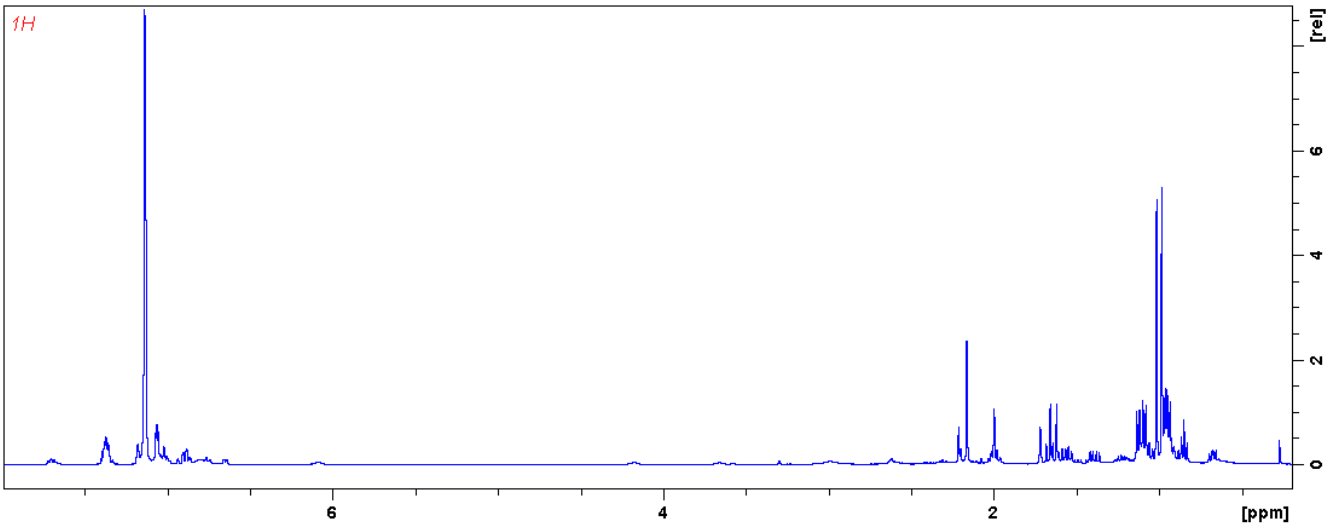

Figure S9. ^{1}H NMR spectrum of **4** (from crystals).

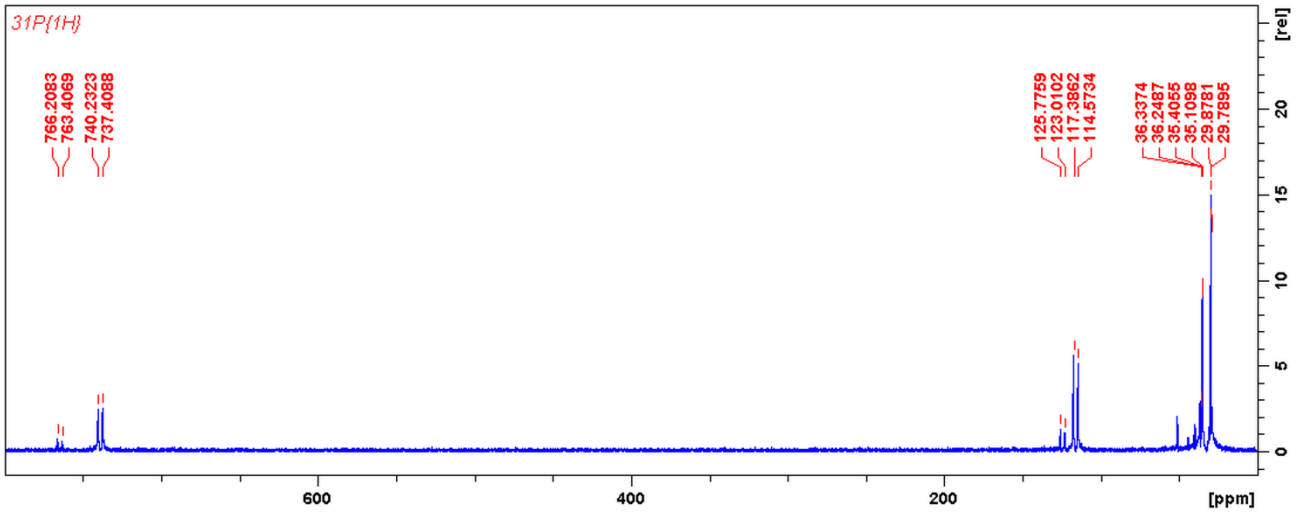

Figure S10. ^{31}P{H} NMR spectrum from crystals of **4**.

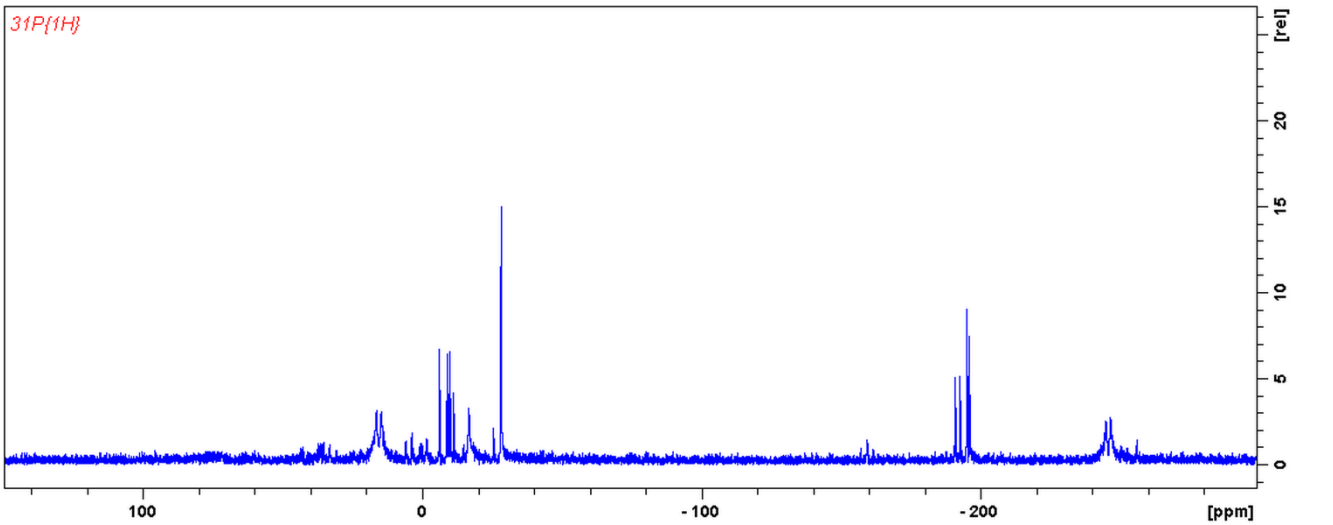

Figure S11. ^{31}P{H} NMR spectrum of **4** at 248 K in the range from 125 to -300 ppm.

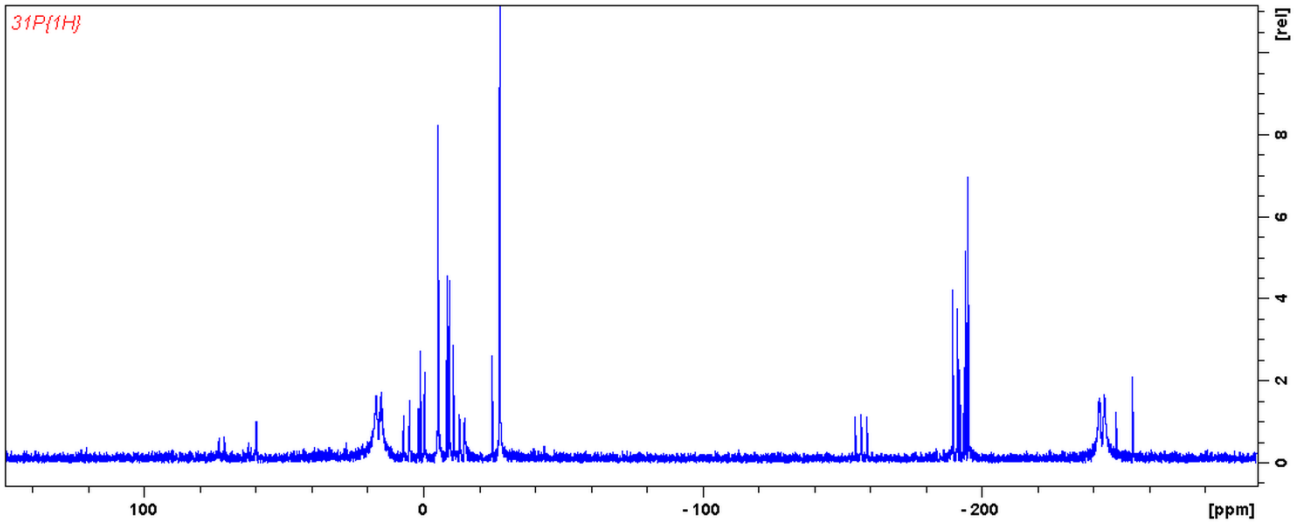

Figure S12. $^{31}P\{H\}$ NMR spectrum of **4** at 273 K in the range from 125 to -300 ppm.

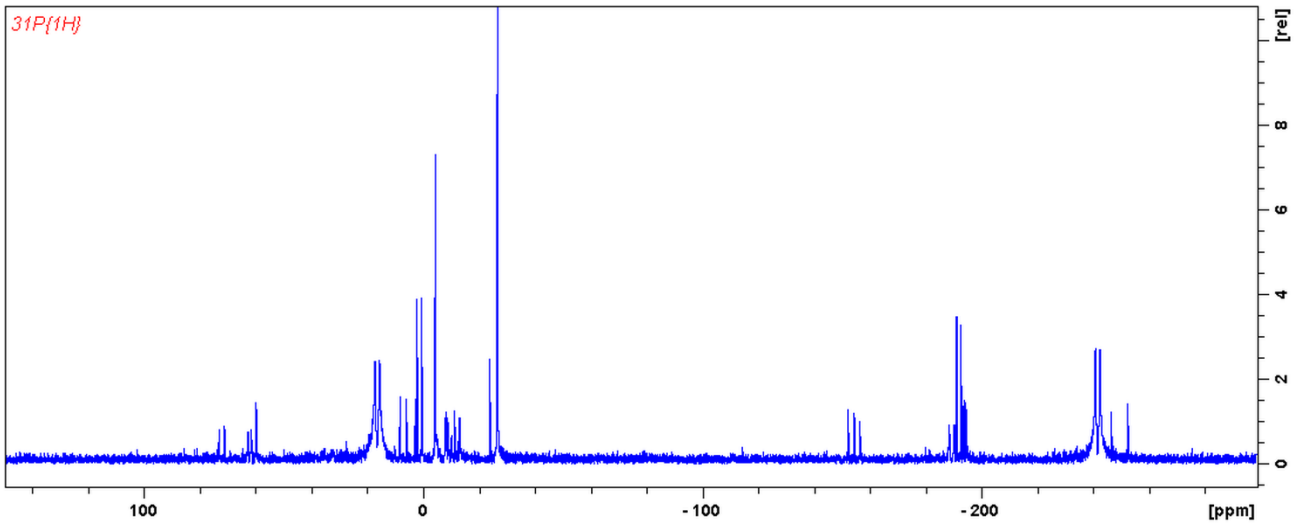

Figure S13. $^{31}P\{H\}$ NMR spectrum of **4** at 298 K in the range from 125 to -300 ppm.

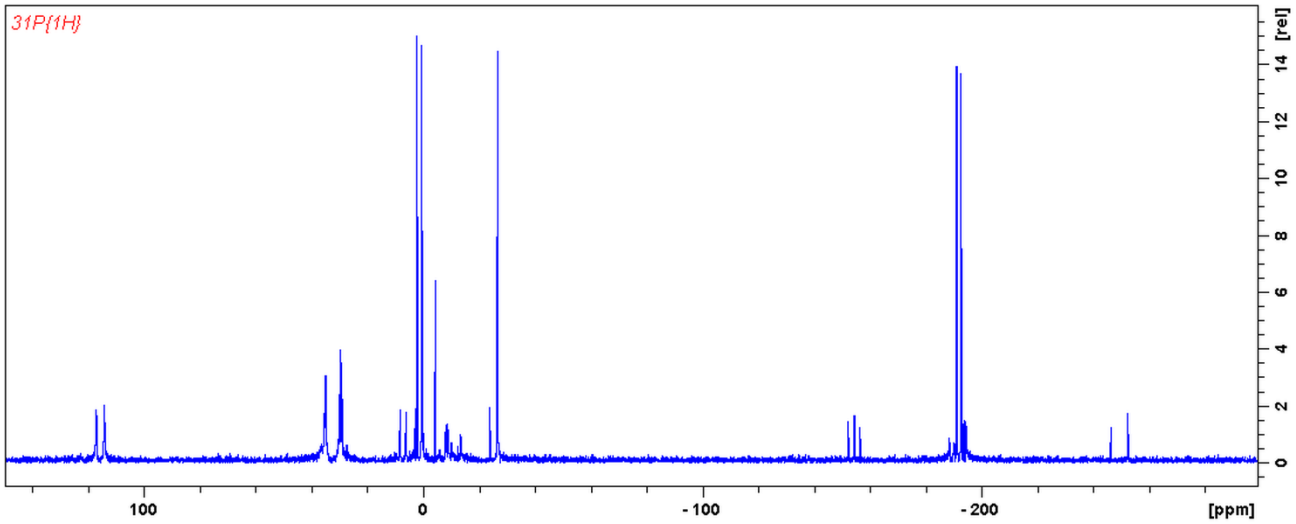

Figure S14. $^{31}P\{H\}$ NMR spectrum of **4** at 298 K (after 1h) in the range from 125 to -300 ppm.

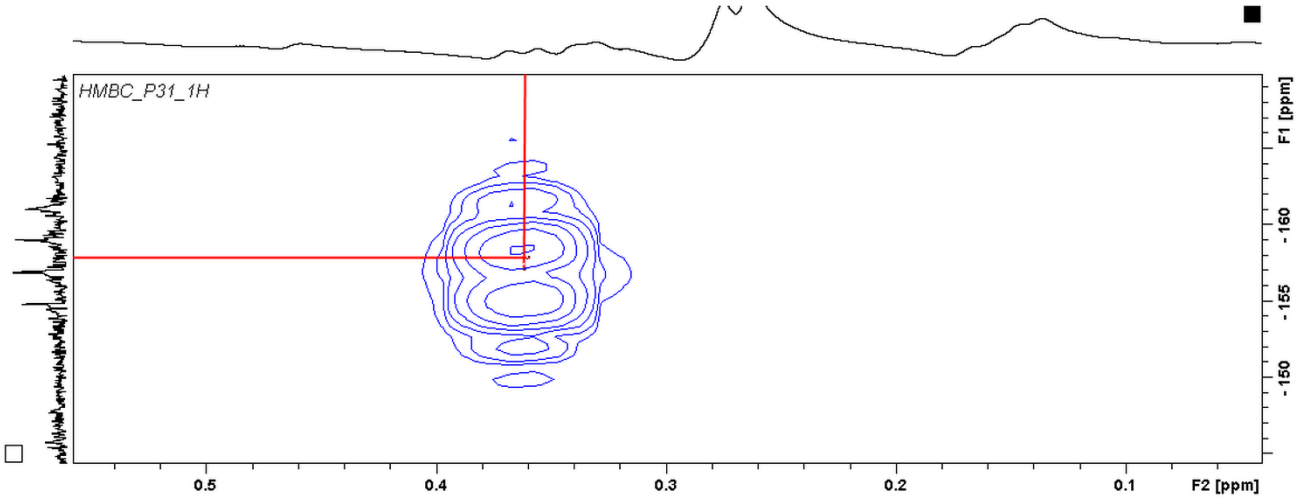

Figure S15. ^{1}H-coupled ^{31}P HMBC NMR spectrum. The correlation of phosphorus atom with the proton of $-SiMe_3$ group in the triphosphorus moiety (Ph)*t*BuP-P($SiMe_3$)-P(Ph)*t*Bu.

PART C. DFT Results

The geometries of all anions RR'P-P($SiMe_3$) and their RR'P-P($SiMe_3$)Li lithiated derivatives (R= *t*Bu, Ph; R' = *t*Bu, Ph) discussed in this paper were optimized using density functional theory at the ωB97XD functional by Head-Gordon [3] with 6-311G+(d,p) basis set. The ωB97XD exchange-correlation functional has been chosen, as it has good overall performance for the description of main-group element compounds, and it also accounts well for long-range and dispersion interactions between $SiMe_3P$ and PR_2 fragments. Molecular geometries were first energy optimized using the solid-state structures as starting points, and the nature of the final geometries as local minima on the potential energy surface was then validated by frequency calculations at the same level of theory. Condensed Fukui functions [4] were calculated using partial charges derived via both, natural and Hirshfeld population analysis.
Single point calculations on [^{Me}NaNacTi(Cl){η^2-P($SiMe_3$)-P*t*Bu_2}], [^{Me}NaNacTi(Cl){η^2-P($SiMe_3$)-P*i*Pr_2}], [(PNP)Ti(Cl){η^1-P($SiMe_3$)-P*t*Bu_2}], [(PNP)Ti(Cl){η^2-P($SiMe_3$)-P*i*Pr_2}], [^{Me}NaNacTi(Cl){η^2-P($SiMe_3$)-P(Ph)*t*Bu}], [^{Me}NaNacTi(Cl){η^2-P-P(Ph)*t*Bu}] and [(PNP)Ti(Cl){η^2-P-P(Ph)*t*Bu}] complexes (for *N*, *N-1* and both, singlet and triplet *N+1* electron states) carried out at the ωB97XD/6-31G+(d) for non-metals and ωB97XD/Lanl2DZ for Ti atom levels were done without previous optimization and vibrational analysis of used solid-state structures. For [(PNP)Ti(Cl){η^2-P($SiMe_3$)-P(Ph)*t*Bu}] that X-ray structure was not determined, molecular geometry was built up based on its analogues, optimized and used to Fukui function calculations. In the present work, we intend to focus on the trends of calculated condensed Fukui functions as well as on identifying the influencing factors. For that purpose we think the present approach is fairly adequate.
All calculations presented in the paper were performed using the Gaussian 09 [5] program package. Multiwfn 3.3.9 program [6] was used for visualization of Fukui functions [4] and dual descriptors [7] as well as computation of HPA atomic charges.[8]

a) Fukui functions of the phosphorus ligands.

Computational data (Table S5, Figure S16) for lithium derivatives of diphosphanes and respective RR'P-P$SiMe_3$ anions are almost identical, therefore, our considerations rely on the anionic forms.

Table S2. Values of condensed nucleophilic f^- and electrophilic f^+ Fukui functions and the Δf dual descriptor calculated based on HPA. In the case of f^+ and f^- the more positive value of function, the more electrophilic/nucleophilic character of an atom.

$PSiMe_3$			
	f^+	f^-	Δf
Ph_2P-P$SiMe_3$	0.006	0.376	-0.370
(Ph)*t*BuP-P$SiMe_3$	0.028	0.385	-0.357
tBu_2P-P$SiMe_3$	0.024	0.376	-0.352
PRR'			
Ph_2P-P$SiMe_3$	0.004	0.075	-0.071
(Ph)*t*BuP-P$SiMe_3$	0.025	0.053	-0.028
tBu_2P-P$SiMe_3$	-0.002	0.046	-0.049
Si			
Ph_2P-P$SiMe_3$	0.009	0.045	-0.036
(Ph)*t*BuP-P$SiMe_3$	-0.048	-0.017	-0.031
tBu_2P-P$SiMe_3$	0.036	0.047	-0.011

Based on the data contained in Table S2, we found that in each case, the **P***SiMe*$_3$ phosphorus atom is unambiguously the most favorable position for electrophilic attack. Moreover, as follows from figures A-C (Figure S16), isosurfaces of dual descriptors in these region have characteristic d-orbital shapes. Hence, we may notice that the HOMO orbital of the anion is mainly localized on the P$SiMe_3$ d-orbital (as Fukui functions describe the electron density in frontier orbitals). In the case of *RR'***P** atoms, values of f^-, f^+ and Δf are virtually zero and suggest that this atoms are rather inert. Nevertheless, in comparison with P$SiMe_3$, the RR'P group might be regarded as an electrophilic region of the system.

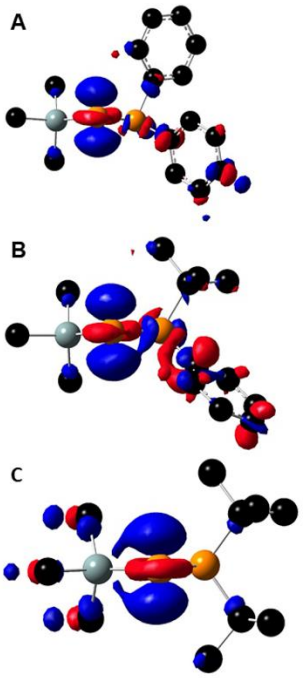

Figure S16. Visualization of isosurfaces of the dual descriptor for Ph_2P-$PSiMe_3$ (A), (Ph)*t*BuP-$PSiMe_3$ (B), and tBu_2P-$PSiMe_3$ (C). Blue area corresponds to a decrease ($\Delta f < 0$) and red one to an increase ($\Delta f > 0$) of electron density along the reaction pathway, showing fragments involved in the reaction with electrophile (blue) and these more favorable for nucleophilic attack (red), respectively.

Although only slight differences between the values of respective f^- parameters are noticed, a tendency to increase in nucleophilicity of the $PSiMe_3$ moiety with simultaneous decrease of electron density at RR'P may be observed when Ph groups are replaced with *t*Bu. Hence, even though in the RR'P$PSiMe_3$ systems negative charge is mainly localized on the *d*-orbital of **P*SiMe*$_3$** atoms, phenyl groups attached to neighboring phosphorus may cause charge delocalization over a molecule.

Table S3. Values of condensed to atom Fukui functions and dual descriptors of titanium(III) atom in selected complexes. Parameters obtained for singlet state at *N+1* electron system.

	Ti(III)			**P**$SiMe_3$			**P**RR'			**Si**		
Ligands	f^+	f	Δf	f^+	f	Δf	f^+	f	Δf	f^+	f	Δf
[^{Me}NaNacTi(Cl){η^2-P($SiMe_3$)-P*t*$Bu_2$4]	0.163	0.131	0.032	0.043	0.077	-0.034	0.023	0.031	-0.009	0.027	0.025	0.002
[(PNP)Ti(Cl){η^1-P($SiMe_3$)-P*t*Bu_2}]	0.149	0.105	0.043	0.061	0.083	-0.022	0.049	0.038	0.010	0.018	0.014	0.004
[^{Me}NaNacTi(Cl){η^2-P($SiMe_3$)-P*i*Pr_2}]	0.157	0.134	0.024	0.048	0.092	-0.044	0.030	0.032	-0.002	0.025	0.020	0.005
[(PNP)Ti(Cl){η^2-P($SiMe_3$)-P*i*Pr_2}]	0.146	0.113	0.032	0.059	0.072	-0.013	0.026	0.023	0.003	0.027	0.019	0.007
[^{Me}NaNacTi(Cl){η^2-P-P(Ph)*t*Bu}]	0.155	0.132	0.023	0.049	0.079	-0.031	0.029	0.030	-0.001	0.032	0.028	0.004
[(PNP)Ti(Cl){η^2-P-P(Ph)*t*Bu}]	0.012	-0.013	0.025	0.207	-0.076	0.283	0.037	0.039	-0.002	0.019	0.012	0.007

Table S4. Values of condensed to atom Fukui functions and dual descriptors of titanium(IV) atom in selected complexes.

	Ti(IV)		
Ligands	f^+	f^-	Δf
[^{Me}NaNacTi(Cl){η^2-P-P(Ph)*t*Bu}]	0.144	0.065	0.078
[(PNP)Ti(Cl){η^2-P-P(Ph)*t*Bu}]	0.132	0.051	0.081

Table S5. Values of condensed to atoms Fukui functions and dual descriptors for RR'P-P($SiMe_3$)Li· 3THF salts calculated using partial charges derived via natural (NPA) and Hirshfeld (HPA) population analysis.

	P*SiMe$_3$*			P*RR'*			Si		
NPA	f^+	f^-	Δf	f^+	f^-	Δf	f^+	f^-	Δf
Ph_2P-P($SiMe_3$)Li	0.092	0.541	-0.449	0.019	0.018	0.002	0.009	-0.086	0.095
(Ph)*t*BuP-P($SiMe_3$)Li	-0.017	0.675	-0.692	0.011	-0.016	0.027	0.002	-0.087	0.088
***t*Bu_2P-P($SiMe_3$)Li**	-0.015	0.676	-0.691	0.009	-0.012	0.021	0.001	-0.083	0.085
HPA	f^+	f^-	Δf	f^+	f^-	Δf	f^+	f^-	Δf
Ph_2P-P($SiMe_3$)Li	-0.008	0.277	-0.285	0.008	0.054	-0.046	0.001	0.029	-0.028
(Ph)*t*BuP-P($SiMe_3$)Li	-0.008	0.333	-0.341	0.008	0.050	-0.043	0.001	0.034	-0.033
***t*Bu_2P-P($SiMe_3$)Li**	-0.009	0.338	-0.347	0.006	0.044	-0.039	0.001	0.036	-0.035

Table S6. Values of total energy E_{tot}, HOMO (E_{HOMO}), LUMO (E_{LUMO}) orbital energies and HOMO-LUMO gap of considered compounds.

Compound	E_{tot} [a. u.]	E_{HOMO} [eV]	E_{LUMO} [eV]	ΔE_{H-L} [eV]
Anions				
Ph_2P-P$SiMe_3$	-1555.30	-2.66	3.78	6.43
(Ph)*t*BuP-P$SiMe_3$	-1481.52	-2.62	3.81	6.43
tBu_2P-P$SiMe_3$	-1407.74	-2.46	3.88	6.34
Lithium derivatives				
Ph_2P-P($SiMe_3$)Li	-2260.25	-6.06	0.29	6.35
(Ph)*t*BuP-P($SiMe_3$)Li	-2186.46	-5.96	0.25	6.21
tBu_2P-P($SiMe_3$)Li	-2112.68	-5.85	0.24	6.09
Complexes of Ti				
[^{Me}NaNacTi(Cl){η^2-P($SiMe_3$)-P*t*Bu_2}]	-3164.63	-6.83	0.30	7.13
[(PNP)Ti(Cl){η^1-P($SiMe_3$)-P*t*Bu_2}]	-3677.72	-6.60	0.12	6.72
[^{Me}NaNacTi(Cl){η^2-P($SiMe_3$)-P*i*Pr_2}]	-3086.07	-6.70	0.19	6.89
[(PNP)Ti(Cl){η^2-P($SiMe_3$)-P*i*Pr_2}]	-3599.11	-6.44	0.33	6.77
[^{Me}NaNacTi(Cl){η^2-P-P(Ph)*t*Bu}]	-3238.43	-6.84	0.22	7.07
[(PNP)Ti(Cl){η^2-P-P(Ph)*t*Bu}]	-4019.46	-6.81	0.67	7.49
[^{Me}NaNacTi(Cl){η^2-P-P(Ph)*t*Bu}]	-2829.25	-7.04	-0.25	6.79
[(PNP)Ti(Cl){η^2-P-P(Ph)*t*Bu}]	-3342.32	-6.72	0.04	6.76

b) Hirshfeld atomic charges and output coordinates.

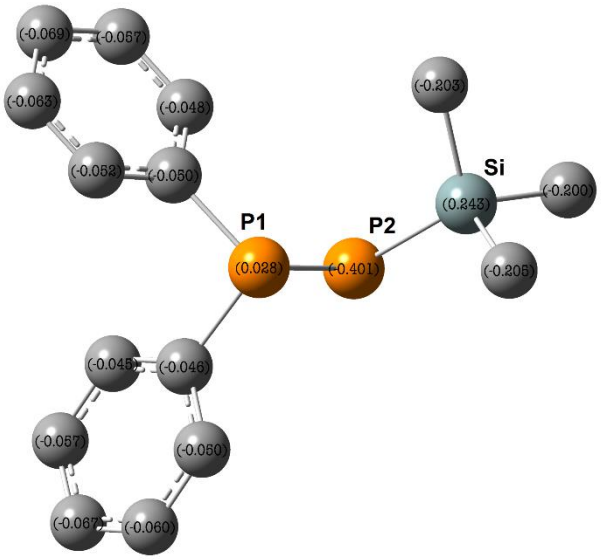

Figure S17. Hirshfeld charges for main atoms in the diphosphorus anion Ph_2P-$PSiMe_3$**.**

Below are presented xyz coordinates for optimized geometry of Ph_2P-$PSiMe_3$ anion.

C	1.60913900	-1.17733300	-0.15642500
C	1.83751900	-2.39596100	-0.80175400
H	1.10662800	-2.75368600	-1.52077700
C	2.97304000	-3.15132400	-0.53291600
H	3.12651900	-4.09609900	-1.04568300
C	3.91269700	-2.69737200	0.38720700
H	4.80308000	-3.28218000	0.59604300
C	3.69895800	-1.48680300	1.03802500
H	4.42132300	-1.12589400	1.76399800
C	2.55841800	-0.73833000	0.77082800
H	2.39947200	0.20101600	1.28947900
C	-3.41256300	1.20481800	-0.66777200
H	-2.61683600	1.49287000	-1.36295700
H	-3.41263800	1.93344800	0.14927400
H	-4.37143400	1.27606900	-1.19687100
C	-3.30898200	-1.69123800	-1.49982300
H	-2.49801400	-1.51856800	-2.21426100
H	-4.26432400	-1.52039400	-2.01202100
H	-3.26156100	-2.73969800	-1.18933900
C	-4.55306100	-0.93173500	1.16797800
H	-4.47614600	-1.95174700	1.55788100
H	-5.51382400	-0.83428500	0.64861300
H	-4.55580900	-0.24728600	2.02228200
Si	-3.10388000	-0.54744400	0.00196200
P	0.04837200	-0.25390900	-0.54094400
P	-1.22380600	-0.79732100	1.13919000
C	0.68689500	1.47398400	-0.25282800
C	1.69871100	1.96816000	-1.08503700
C	0.14737200	2.32977300	0.70512500
C	2.17315300	3.26525300	-0.94846300
H	2.12575000	1.31678600	-1.84315200
C	0.61211400	3.63627500	0.83876700
H	-0.63484300	1.94219200	1.35384500
C	1.62801900	4.10947900	0.01723200
H	2.96605100	3.62286000	-1.59880100
H	0.18039600	4.28527100	1.59526000
H	1.99347000	5.12613100	0.12515600

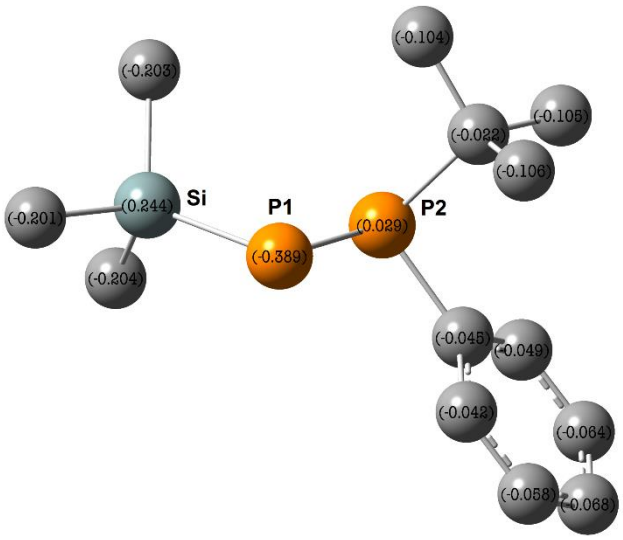

Figure S18. Hirshfeld charges for main atoms in the diphosphorus anion (Ph)*t*BuP-PSiMe$_3$**.**

Below are presented xyz coordinates for optimized geometry of (Ph)*t*BuP-PSiMe$_3$ anion.

C	1.75574100	-0.54389700	-0.19639200
C	2.09052700	-1.26119200	0.95484000
H	1.35807000	-1.32449300	1.75428300
C	3.31955500	-1.90051100	1.07182900
H	3.55617200	-2.44687200	1.98022900
C	4.24251200	-1.84795500	0.03167800
H	5.20105400	-2.34971400	0.12221200
C	3.91757700	-1.15778500	-1.13095800
H	4.62104600	-1.12337200	-1.95770800
C	2.68470500	-0.52240400	-1.24188700
H	2.43045100	-0.00260000	-2.16103200
C	0.68945500	2.10428900	0.12518200
C	1.27411300	2.13851200	1.53806600
H	2.20008200	1.55842800	1.60105700
H	0.55985600	1.72786100	2.25793400
H	1.50287600	3.17352400	1.82971200
C	1.71646200	2.65482500	-0.87058300
H	1.34142500	2.59697700	-1.89812700
H	2.66291600	2.10963600	-0.82015300
H	1.92781700	3.70916100	-0.64549300
C	-0.56668800	2.98147300	0.07489500
H	-1.00639900	2.98773400	-0.92828400
H	-0.31387300	4.01579500	0.34503500
H	-1.32317500	2.61004800	0.77121000
C	-3.55071700	0.83256800	-1.00995500
H	-2.78995000	1.22539600	-1.69215700
H	-3.79171300	1.62103300	-0.28987000
H	-4.45209300	0.60441500	-1.59310900
C	-2.65594000	-2.00469300	-1.48352700
H	-1.85182100	-1.69498800	-2.15847900
H	-3.57123500	-2.14005200	-2.07399200
H	-2.37379800	-2.96913800	-1.04991200
C	-4.32012200	-1.33534000	0.96730700
H	-4.04526800	-2.26612900	1.47376400
H	-5.21601700	-1.52565700	0.36416300

H	-4.57585100	-0.59948700	1.73633800
Si	-2.88862400	-0.70883500	-0.11442900
P	0.13319300	0.34641900	-0.41787700
P	-1.14605500	-0.37316300	1.19463800

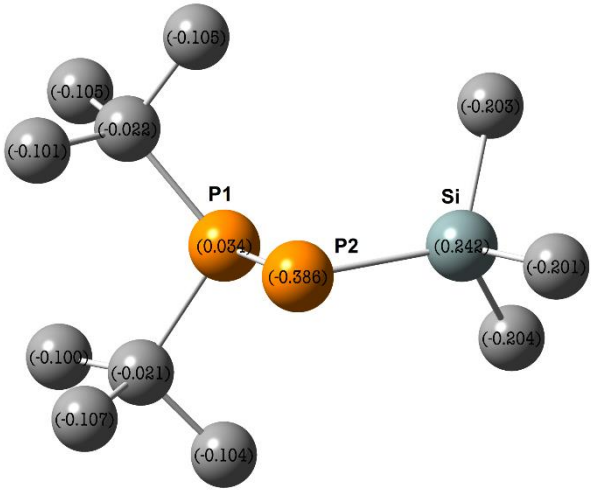

Figure S19. Hirshfeld charges for main atoms in the diphosphorus anion *t*Bu_2P-P$SiMe_3$**.**

Below are presented xyz coordinates for optimized geometry of *t*Bu_2P-P$SiMe_3$ anion.

Si	2.58887300	-0.01921900	-0.04283200
P	0.82370600	-0.11421400	1.26969500
P	-0.62213000	-0.00216600	-0.37403700
C	2.74887100	-1.43771700	-1.29893100
H	3.65158200	-1.33629000	-1.91499500
H	1.87704400	-1.44698200	-1.96089600
H	2.78639000	-2.40257900	-0.78277700
C	4.14474700	-0.11106100	1.04710400
H	5.05764100	-0.06336300	0.44112600
H	4.16076100	-1.04630700	1.61618300
H	4.16622300	0.71543900	1.76475300
C	2.78087800	1.56040800	-1.08556100
H	3.72664800	1.56162200	-1.64268000
H	2.74894900	2.45097100	-0.44972700
H	1.95917800	1.63318300	-1.80543000
C	-1.66066600	1.57817000	-0.02799600
C	-2.44750400	1.57103600	1.28417700
H	-2.87012500	2.56707600	1.48010400
H	-1.79647000	1.30447700	2.12218900
H	-3.28028700	0.86322200	1.25115000
C	-0.64877800	2.73335600	0.01673700
H	-1.18370100	3.68735100	0.12266100
H	-0.05469400	2.77424500	-0.90221700
H	0.04486200	2.61245400	0.85164200
C	-2.60785300	1.85573100	-1.20598000
H	-3.07615000	2.84241300	-1.08219100
H	-3.40981800	1.12067700	-1.28656600
H	-2.05860200	1.85746400	-2.15257800
C	-1.74886800	-1.53003000	-0.06077600
C	-0.92278400	-2.70367800	-0.61442400
H	-1.47164800	-3.64585800	-0.47853100
H	0.03459900	-2.78021500	-0.09171400

H	-0.71735300	-2.57319900	-1.68169900
C	-2.07188700	-1.83137200	1.40690200
H	-2.58339000	-2.80188200	1.48337100
H	-2.72469900	-1.07674000	1.85035000
H	-1.15305500	-1.87562000	1.99734400
C	-3.05383900	-1.45069000	-0.86067300
H	-3.54780400	-2.43214400	-0.86206300
H	-2.87128300	-1.16378800	-1.90149600
H	-3.75655200	-0.73577900	-0.42401100

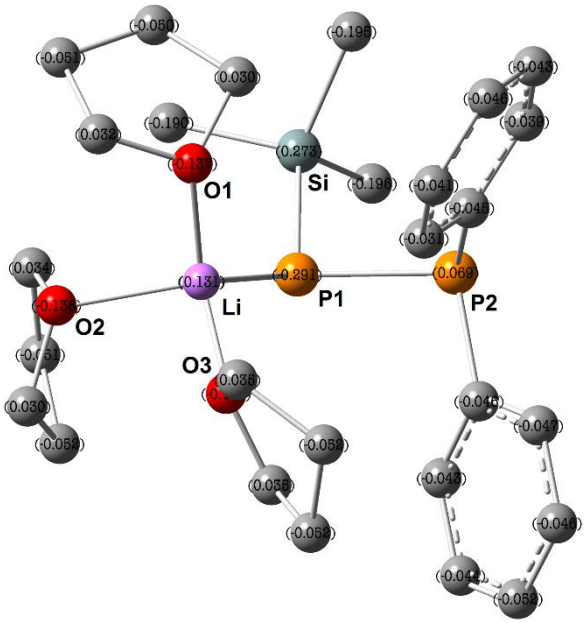

Figure S20. Hirshfeld charges for main atoms in the lithium derivative of diphosphane Ph_2P-$P(SiMe_3)Li{\cdot}3THF$.

Below are presented xyz coordinates for optimized geometry of Ph_2P-$P(SiMe_3)Li{\cdot}3THF$.

C	-2.44130100	-1.30633000	-1.21617000
C	-2.55151700	-0.70765600	-2.47705200
H	-1.67969400	-0.67760100	-3.12232400
C	-3.74071900	-0.12104500	-2.89030200
H	-3.79746200	0.34234600	-3.86977900
C	-4.85288500	-0.11839400	-2.05382900
H	-5.77951600	0.34566100	-2.37380700
C	-4.76485100	-0.72924600	-0.80853500
H	-5.62669900	-0.74790900	-0.14905400
C	-3.57627400	-1.32413500	-0.39822000
H	-3.53303400	-1.79672400	0.57652200
C	2.71661100	-3.15464900	-0.13567400
H	1.86011000	-3.77489500	0.14449800
H	2.99777300	-2.56314000	0.74011300
H	3.55026300	-3.82548100	-0.37316100
C	1.92792100	-3.22771200	-3.05986600
H	0.98440200	-3.75384300	-2.88878900
H	2.72033700	-3.97507900	-3.17938000
H	1.83358300	-2.67066300	-3.99653500
C	3.88314500	-1.11920500	-2.05999300
H	3.72208000	-0.39368700	-2.86273900
H	4.64114000	-1.83056800	-2.40533200

H	4.30611100	-0.59019700	-1.20033000
C	2.81861900	2.27593700	-1.23178700
H	3.00515100	1.25022400	-0.91643400
H	3.72705500	2.87181300	-1.08450100
C	2.29365800	2.37941300	-2.67679300
H	3.00335700	2.91840000	-3.30752900
H	2.12571300	1.39184700	-3.10619900
C	0.96467900	3.14554500	-2.53200200
H	0.13198700	2.43762300	-2.53618900
H	0.80570900	3.88234700	-3.32103000
C	1.09275600	3.77999500	-1.15382200
H	1.68986900	4.70187900	-1.18562300
H	0.14712200	3.97863400	-0.65133000
C	-2.18447500	2.25554600	-0.37043900
H	-2.26660200	1.24249200	-0.76488400
H	-1.94122400	2.93396000	-1.19221400
C	-3.43027400	2.67762900	0.40570800
H	-4.31496100	2.15166300	0.04717700
H	-3.60182200	3.75362800	0.30941100
C	-3.06548100	2.32454600	1.85051100
H	-3.62423300	2.90284000	2.58781900
H	-3.23960300	1.26185000	2.03882100
C	-1.57511700	2.63275200	1.87958400
H	-1.39178200	3.70100600	2.05156500
H	-1.00257700	2.05209900	2.60472600
C	2.27300300	2.02446500	2.63407300
H	2.13069400	2.11984900	3.71806900
H	2.03339400	2.97006900	2.14928500
C	3.67725000	1.49940800	2.29763800
H	4.37040900	1.66949800	3.12320200
H	4.07744000	2.00447100	1.41725200
C	3.45156100	-0.00439600	2.01782800
H	3.60681300	-0.22838500	0.96051300
H	4.11385200	-0.64919200	2.59713200
C	1.98355800	-0.22724700	2.37344900
H	1.48081800	-0.95928200	1.74376700
H	1.84729300	-0.49410100	3.42849400
Li	0.60647000	1.29214300	0.32927700
O	1.78279000	2.79502300	-0.38707800
O	-1.09579100	2.27711800	0.57801100
O	1.36726300	1.04362400	2.13509400
Si	2.29648800	-2.06201600	-1.62408300
P	-0.85600100	-2.13568200	-0.74525000
P	0.63046600	-0.62302200	-1.29584000
C	-0.96402900	-2.06396500	1.10581600
C	-0.63945100	-3.21131300	1.82867200
C	-1.28808900	-0.90756700	1.81928400
C	-0.62881900	-3.20272900	3.22214300
H	-0.38950300	-4.12224000	1.29382800
C	-1.30203000	-0.89683900	3.20526800
H	-1.52141000	-0.00347400	1.27022600
C	-0.96552400	-2.04750700	3.91454600
H	-0.36602800	-4.10484400	3.76423100
H	-1.56195200	0.01238600	3.73853700
H	-0.96721800	-2.04085100	4.99922600

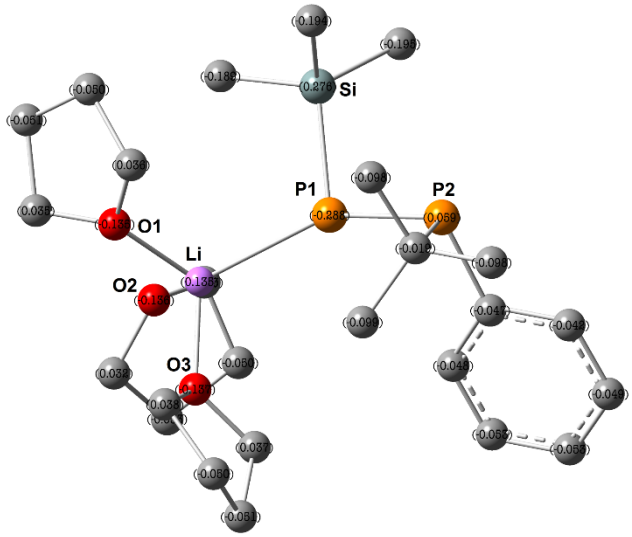

Figure S21. Hirshfeld charges for main atoms in the lithium derivative of diphosphane (Ph)*t*BuP-P(SiMe$_3$)Li·3THF**.**

Below are presented xyz coordinates for optimized geometry of Ph*t*BuP-P(SiMe$_3$)Li·3THF.

C	3.26669300	-0.45775900	0.59268200
C	2.90547400	0.76895200	1.15279400
H	1.85148500	0.97544800	1.30828100
C	3.86551100	1.69427200	1.54624900
H	3.55630300	2.63912200	1.98294600
C	5.21732200	1.40810200	1.39558600
H	5.96832300	2.12725700	1.70411300
C	5.59709000	0.17829300	0.86960300
H	6.64883800	-0.06873300	0.77011500
C	4.63203900	-0.74527500	0.48472500
H	4.94512300	-1.71230300	0.10474500
C	2.10454200	-1.46826500	-1.86319300
C	1.75895400	-0.03854600	-2.27346900
H	2.49402600	0.67356600	-1.88435700
H	0.77113400	0.23661600	-1.89238100
H	1.74705900	0.05257400	-3.36813000
C	3.49400600	-1.83102800	-2.39974600
H	3.80592600	-2.82525900	-2.06465900
H	4.25075800	-1.10837300	-2.08666400
H	3.47587800	-1.83712800	-3.49647100
C	1.07917700	-2.43515300	-2.46395600
H	1.33055600	-3.47504600	-2.23482000
H	1.05121800	-2.32442600	-3.55476000
H	0.08062800	-2.23858600	-2.06756000
C	-1.16403200	-4.06947000	-0.06526900
H	-0.19643000	-4.44562900	-0.41116500
H	-1.68048400	-3.65386400	-0.93517600
H	-1.74509700	-4.92291800	0.30262800
C	-0.06301100	-3.70124400	2.72025600
H	0.95209900	-3.98896100	2.43042400
H	-0.60964100	-4.60946100	2.99809600
H	0.01449600	-3.05904600	3.60226800
C	-2.61520200	-2.21317100	1.90161500
H	-2.54971900	-1.79490100	2.91082800
H	-3.33119700	-3.04166200	1.93148800
H	-3.02220400	-1.43409400	1.24931600

C	-1.81630400	1.34524500	2.75176800
H	-1.33178000	0.37251700	2.67614000
H	-2.65733300	1.30127000	3.45629500
C	-0.85712700	2.47739400	3.07839400
H	-0.66471300	2.57518400	4.14737900
H	0.09456200	2.28611700	2.57508900
C	-1.56998800	3.70387800	2.48230300
H	-0.87015900	4.41921200	2.04693100
H	-2.14237900	4.23230400	3.24753800
C	-2.51643200	3.09943700	1.42329300
H	-3.56627200	3.30836200	1.65906100
H	-2.30629300	3.43317100	0.40649200
C	0.49767600	2.96222200	-0.68256700
H	1.26693900	2.19915300	-0.54018700
H	0.29888700	3.44634300	0.27570100
C	0.86232600	3.92763400	-1.79949400
H	1.93106700	4.14349100	-1.82174800
H	0.32023900	4.87124900	-1.68660100
C	0.37856100	3.16780500	-3.03773300
H	0.17710400	3.81802800	-3.89003000
H	1.12096400	2.42545900	-3.33706900
C	-0.88526700	2.47616900	-2.53157700
H	-1.78292300	3.07914800	-2.70378000
H	-1.03800600	1.48718500	-2.96873500
C	-4.31908000	0.51738500	-0.99773400
H	-4.70122700	1.03942200	-1.88524500
H	-4.36999700	1.18355300	-0.13663800
C	-5.02775500	-0.82554200	-0.79242000
H	-6.02957500	-0.81583000	-1.22451400
H	-5.12341300	-1.04737000	0.27149100
C	-4.09515400	-1.85033400	-1.47865800
H	-3.76330100	-2.60537200	-0.76587800
H	-4.58105300	-2.36406200	-2.30941700
C	-2.90795200	-1.01119000	-1.96663400
H	-1.93506100	-1.46822500	-1.78568400
H	-3.00407500	-0.76049900	-3.03108700
Li	-1.43354400	0.78738000	-0.11797500
O	-2.30488700	1.68540500	1.44960600
O	-0.71590800	2.32810300	-1.11364000
O	-2.94915400	0.19239300	-1.20087900
Si	-0.90526600	-2.78624800	1.30308200
P	2.04505200	-1.74281100	0.03509900
P	0.13163200	-0.93750700	0.68320500

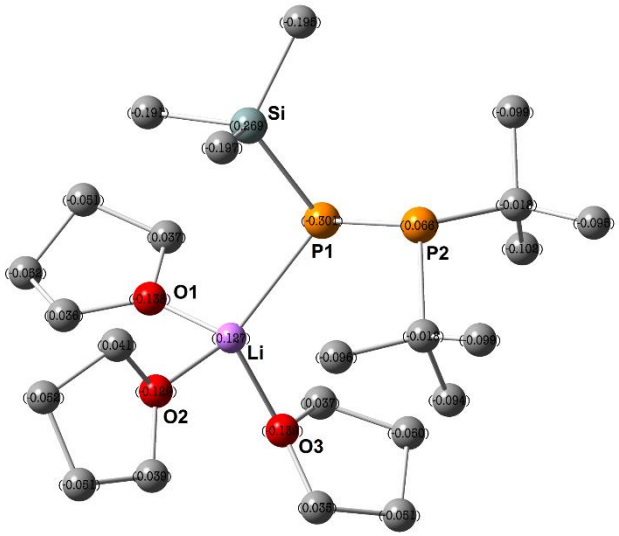

Figure S22. Hirshfeld charges for main atoms in the lithium derivative of diphosphane *t*Bu_2P-P($SiMe_3$)Li·3THF**.**

Below are presented xyz coordinates for optimized geometry of *t*Bu_2P-P($SiMe_3$)Li·3THF.

Li	1.24387600	0.52171100	-0.24598300
Si	-0.30170900	-2.89136500	0.36444800
P	-0.73813700	-0.92051000	-0.54815100
P	-2.61877500	-0.60949500	0.53981200
O	2.68873500	-0.27328700	-1.34543900
O	1.11407500	2.34073100	-1.03305600
O	2.23508800	0.79017000	1.42627400
C	-0.31987400	-2.95375200	2.25736200
H	-0.12432500	-3.97185300	2.61304800
H	-1.30377000	-2.64903900	2.62570400
H	0.42512800	-2.28931400	2.70186600
C	1.43118400	-3.43782700	-0.19129600
H	1.73229700	-4.35771200	0.32114700
H	2.18470300	-2.67048600	0.01411700
H	1.44425800	-3.63816400	-1.26734300
C	-1.49803200	-4.24192300	-0.19479600
H	-1.24978900	-5.21083900	0.25321400
H	-1.48247600	-4.34915600	-1.28360100
H	-2.51993900	-3.98386400	0.09878900
C	-3.87512400	-0.30433000	-0.87322200
C	-3.40809900	0.60314500	-2.01613300
H	-4.13771000	0.57041200	-2.83538700
H	-2.44308500	0.26816400	-2.40643100
H	-3.31865200	1.64502700	-1.70302900
C	-4.11848300	-1.70880200	-1.45286100
H	-4.85830200	-1.65258100	-2.26068600
H	-4.49817300	-2.39394300	-0.68924000
H	-3.19540400	-2.12991300	-1.85978800
C	-5.20389200	0.22245200	-0.31860500
H	-5.97883700	0.15128600	-1.09149200
H	-5.13623200	1.27343900	-0.02647700
H	-5.53961400	-0.35663400	0.54697700
C	-2.41333300	1.01581600	1.53403500
C	-1.14991200	0.85043200	2.39114900
H	-1.08318600	1.67870000	3.10899700
H	-0.25229800	0.84469000	1.77046500

H	-1.16705100	-0.08816600	2.95420900
C	-2.25917300	2.28239100	0.69301000
H	-1.97375100	3.13189100	1.32973500
H	-3.18872400	2.55326700	0.18750400
H	-1.48239900	2.14034400	-0.06233100
C	-3.59934700	1.16271100	2.50072600
H	-3.43699000	2.02545700	3.15965400
H	-3.70140600	0.27250000	3.12751700
H	-4.54731100	1.31783900	1.98539800
C	4.03353500	-0.44217900	-0.89181400
H	4.02859400	-1.09010300	-0.00698900
H	4.42738000	0.53473900	-0.60433800
C	4.78131300	-1.09510900	-2.04907800
H	5.16331400	-0.33340200	-2.73514500
H	5.62137300	-1.70208200	-1.70873100
C	3.67401300	-1.91194800	-2.72030000
H	3.50630200	-2.84648200	-2.17970100
H	3.88512800	-2.14782200	-3.76410600
C	2.47047100	-0.99215300	-2.56997700
H	2.41894800	-0.26669000	-3.39081500
H	1.51071200	-1.50490900	-2.48810400
C	0.79119600	3.63685600	-0.52800000
H	1.70895800	4.23089000	-0.45178100
H	0.37465100	3.50039500	0.47131000
C	-0.21363100	4.26200400	-1.51378800
H	-1.13392300	4.56157900	-1.01112600
H	0.21606900	5.14810000	-1.98578500
C	0.77197600	2.27725600	-2.41833100
H	0.58679500	1.22877700	-2.65724500
H	1.61053300	2.65230500	-3.02010300
C	2.34867800	-0.26365200	2.37982400
H	2.44733400	-1.20046400	1.83124400
H	1.43735200	-0.30914300	2.98817300
C	2.53546100	2.02075400	2.08572400
H	3.05471700	2.65423600	1.36475800
H	1.59901100	2.50930300	2.37645100
C	-0.46469900	3.15175000	-2.54783900
H	-1.34820300	2.56828400	-2.28651700
H	-0.59731000	3.53947700	-3.55885500
C	3.56043600	0.13153700	3.20714800
H	3.58742500	-0.36425900	4.17802500
H	4.47657000	-0.11964400	2.66614000
C	3.38971500	1.65617300	3.31724900
H	2.86181400	1.91889100	4.23601100
H	4.34600300	2.18022500	3.32210900

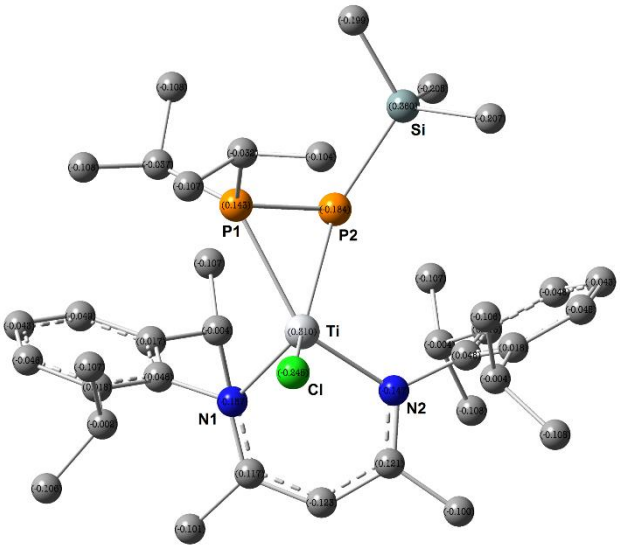

Figure S23. Hirshfeld charges for main atoms in [^{Me}NaNacTi(Cl){η^2-P(SiMe$_3$)-P*i*Pr$_2$}].

Below are presented xyz coordinates for optimized geometry of [^{Me}NaNacTi(Cl){η^2-P(SiMe$_3$)-P*i*Pr$_2$}].

Ti	5.87300000	6.63800000	5.19800000
Cl	8.01100000	7.40000000	5.43700000
P	4.78000000	4.48700000	5.75700000
P	6.29300000	4.27500000	4.29200000
N	5.12900000	7.75400000	3.64000000
N	4.77300000	7.82200000	6.53400000
C	5.03300000	7.18400000	2.30900000
C	3.84600000	6.50800000	1.96600000
C	3.74700000	5.93600000	0.69600000
H	2.95300000	5.47900000	0.45100000
C	4.78700000	6.02600000	-0.21000000
H	4.70300000	5.63700000	-1.07300000
C	5.94300000	6.68200000	0.14600000
H	6.65700000	6.73000000	-0.47800000
C	6.09400000	7.28100000	1.40300000
C	2.68700000	6.40300000	2.94500000
H	3.07700000	6.32500000	3.86300000
C	1.83500000	7.67800000	2.91300000
H	1.09800000	7.59300000	3.55200000
H	1.47300000	7.80600000	2.01200000
H	2.39100000	8.44700000	3.15500000
C	1.81500000	5.17400000	2.71600000
H	1.09000000	5.16100000	3.37500000
H	2.35900000	4.36600000	2.81300000
H	1.43700000	5.20600000	1.81200000
C	7.40200000	7.98200000	1.72800000
H	7.30400000	8.43600000	2.61300000
C	7.75800000	9.04400000	0.67900000
H	8.60500000	9.47000000	0.92000000
H	7.04900000	9.72000000	0.64500000
H	7.84500000	8.61800000	-0.20000000
C	8.52300000	6.96100000	1.83700000
H	9.36400000	7.41800000	2.04700000
H	8.61500000	6.48300000	0.98400000
H	8.31400000	6.32000000	2.54700000
C	4.35000000	7.30600000	7.82300000

C	5.26400000	7.26900000	8.89900000
C	4.81400000	6.69400000	10.09900000
H	5.40800000	6.64100000	10.83800000
C	3.55000000	6.20900000	10.22900000
H	3.27800000	5.81200000	11.04800000
C	2.65400000	6.29200000	9.17000000
H	1.76900000	5.96400000	9.27900000
C	3.03600000	6.84900000	7.95300000
C	6.65700000	7.82500000	8.82700000
H	6.77700000	8.23500000	7.92200000
C	7.69700000	6.72200000	8.98100000
H	8.59500000	7.11200000	8.92900000
H	7.58300000	6.06600000	8.26200000
H	7.58000000	6.28200000	9.84700000
C	6.89200000	8.93200000	9.88100000
H	7.81100000	9.26700000	9.80400000
H	6.75100000	8.56600000	10.77800000
H	6.26400000	9.66800000	9.72800000
C	2.00800000	7.02000000	6.83600000
H	2.51000000	7.20600000	5.99200000
C	1.11600000	8.23600000	7.11300000
H	1.67600000	9.02500000	7.26700000
H	0.56800000	8.06500000	7.90700000
H	0.53200000	8.39600000	6.34200000
C	1.14500000	5.80300000	6.59200000
H	0.51600000	5.98900000	5.86500000
H	0.64700000	5.58600000	7.40700000
H	1.71500000	5.04500000	6.34700000
C	4.72800000	9.94800000	2.56400000
H	4.84100000	9.40800000	1.75200000
H	5.40700000	10.65300000	2.58400000
H	3.83600000	10.35200000	2.56600000
C	4.88400000	9.06200000	3.78400000
C	4.75000000	9.70100000	5.02100000
C	4.61700000	9.11400000	6.29800000
C	4.27500000	10.08300000	7.41400000
H	4.20000000	9.59400000	8.26000000
H	3.42400000	10.52400000	7.21300000
H	4.98200000	10.75700000	7.48900000
C	7.84200000	3.38700000	4.83900000
H	7.74100000	2.40800000	4.65800000
C	8.11200000	3.59600000	6.32800000
H	7.35200000	3.26100000	6.84900000
H	8.23600000	4.55200000	6.50700000
H	8.92400000	3.10900000	6.58500000
C	9.03700000	3.91700000	4.05800000
H	8.88400000	3.78800000	3.09900000
H	9.84500000	3.43100000	4.32800000
H	9.15200000	4.87200000	4.24400000
C	5.63000000	3.40300000	2.78200000
H	4.87000000	3.96500000	2.45700000
C	6.62000000	3.34800000	1.63400000
H	6.98200000	4.24300000	1.47200000
H	6.16700000	3.02800000	0.82600000
H	7.35100000	2.73700000	1.86400000
C	5.04600000	2.02900000	3.03600000
H	4.40600000	2.08000000	3.77700000
H	5.76600000	1.40700000	3.27000000
H	4.59000000	1.71300000	2.22800000

Si	4.42100000	2.75100000	7.09800000
C	5.17900000	1.14900000	6.50100000
H	4.84800000	0.94600000	5.60100000
H	4.93400000	0.42500000	7.11300000
H	6.15600000	1.24000000	6.47600000
C	2.59400000	2.44900000	7.26500000
H	2.15800000	3.26100000	7.59400000
H	2.44100000	1.71500000	7.89700000
H	2.22100000	2.20800000	6.39200000
C	5.05600000	3.13400000	8.81100000
H	4.66200000	3.97400000	9.12400000
H	6.03200000	3.22000000	8.78700000
H	4.80700000	2.40800000	9.42100000
H	4.65700000	10.62900000	4.98300000

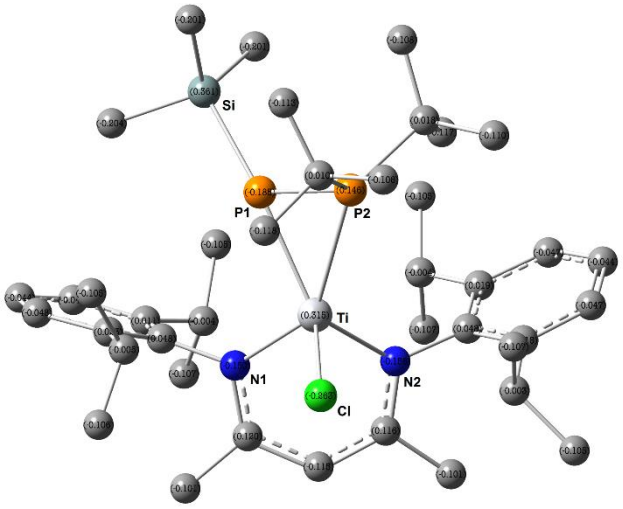

Figure S24. Hirshfeld charges for main atoms in [^{Me}NaNacTi(Cl){η^2-P(SiMe$_3$)-P*t*Bu$_2$}].

Below are presented xyz coordinates for optimized geometry of [^{Me}NaNacTi(Cl){η^2-P(SiMe$_3$)-P*t*Bu$_2$}].

Ti	7.28600000	8.47800000	5.85800000
Cl	9.40000000	8.19000000	6.74000000
P	6.53100000	10.12900000	4.22100000
P	7.93400000	8.83400000	3.28700000
Si	5.19800000	11.54300000	3.11500000
N	6.45900000	6.64900000	6.36300000
N	6.28500000	9.33200000	7.48000000
C	5.76100000	10.68200000	7.58700000
C	6.64300000	11.79200000	7.59400000
C	6.07800000	13.04500000	7.83700000
H	6.64800000	13.80300000	7.89500000
C	4.75200000	13.21600000	7.99300000
H	4.40700000	14.08400000	8.16600000
C	3.88100000	12.13900000	7.90500000
H	2.94500000	12.28100000	7.98300000
C	4.37800000	10.84600000	7.70300000
C	8.13300000	11.65400000	7.45800000
H	8.31400000	10.75800000	7.05200000
C	8.81300000	11.69100000	8.77700000
H	9.78000000	11.59900000	8.64900000
H	8.48600000	10.95400000	9.33500000
H	8.62300000	12.54500000	9.22000000

C	8.71700000	12.69800000	6.53000000
H	9.68700000	12.57300000	6.46600000
H	8.52600000	13.59200000	6.88300000
H	8.31600000	12.60600000	5.64000000
C	3.40500000	9.68800000	7.57700000
H	3.93900000	8.85000000	7.45600000
C	2.49400000	9.83800000	6.36800000
H	1.88600000	9.07000000	6.32000000
H	3.03500000	9.87800000	5.55200000
H	1.97100000	10.66300000	6.45400000
C	2.52700000	9.51000000	8.83000000
H	1.92100000	8.75100000	8.69800000
H	2.00400000	10.32500000	8.98000000
H	3.09900000	9.34100000	9.60700000
C	6.22100000	5.59600000	5.39500000
C	4.91900000	5.46900000	4.86900000
C	4.70600000	4.47400000	3.91100000
H	3.83800000	4.36300000	3.54200000
C	5.72600000	3.65600000	3.49300000
H	5.56200000	3.00200000	2.82300000
C	6.97600000	3.77400000	4.03500000
H	7.66400000	3.18800000	3.74600000
C	7.26400000	4.73900000	5.00500000
C	3.78700000	6.37400000	5.27900000
H	4.19400000	7.22800000	5.60100000
C	2.82300000	6.73100000	4.16500000
H	2.12500000	7.32300000	4.51500000
H	2.41400000	5.91400000	3.81400000
H	3.31000000	7.18800000	3.44800000
C	3.00300000	5.78200000	6.44200000
H	2.28100000	6.39500000	6.69500000
H	3.60300000	5.65200000	7.20600000
H	2.62200000	4.92000000	6.17600000
C	8.64400000	4.77800000	5.62000000
H	8.62100000	5.43300000	6.37600000
C	9.69800000	5.27300000	4.60400000
H	10.57900000	5.29600000	5.03200000
H	9.45900000	6.17300000	4.29700000
H	9.72400000	4.66200000	3.83700000
C	9.08500000	3.41900000	6.19600000
H	9.97700000	3.50300000	6.58800000
H	9.10600000	2.75300000	5.47700000
H	8.45000000	3.13400000	6.88500000
C	6.20600000	9.32900000	9.97000000
H	6.12100000	10.29600000	9.83400000
H	7.00100000	9.14500000	10.51200000
H	5.41000000	8.99500000	10.43500000
C	6.33600000	8.64100000	8.63200000
C	6.46800000	7.24400000	8.69400000
H	6.63800000	6.88200000	9.55700000
C	6.38400000	6.32700000	7.66200000
C	6.17600000	4.87600000	8.06800000
H	6.12800000	4.31600000	7.26600000
H	5.34000000	4.79600000	8.57400000
H	6.92600000	4.58300000	8.62800000
C	4.70300000	12.82600000	4.36700000
H	4.23400000	12.39300000	5.11000000
H	4.10900000	13.48300000	3.94600000
H	5.50300000	13.27900000	4.70500000

C	3.67000000	10.72700000	2.36800000
H	3.94700000	10.05300000	1.71400000
H	3.12000000	11.40700000	1.92500000
H	3.14900000	10.29700000	3.07900000
C	6.07600000	12.42300000	1.73100000
H	6.35000000	11.77100000	1.05100000
H	6.86800000	12.87900000	2.08500000
H	5.47300000	13.08100000	1.32700000
C	7.27500000	7.93100000	1.75200000
C	5.94300000	7.33000000	2.17000000
H	5.32500000	8.04700000	2.42300000
H	6.07900000	6.73100000	2.93400000
H	5.56600000	6.82200000	1.42200000
C	8.21500000	6.79700000	1.36400000
H	9.08000000	7.16900000	1.09200000
H	7.82600000	6.29100000	0.62000000
H	8.34400000	6.20200000	2.13300000
C	7.00900000	8.82000000	0.54400000
H	6.39000000	9.53700000	0.79700000
H	6.61300000	8.28400000	-0.17500000
H	7.85200000	9.21000000	0.23300000
C	9.54300000	9.74300000	2.84600000
C	10.06200000	10.38500000	4.03500000
H	10.19300000	9.71500000	4.73800000
H	9.42600000	11.06300000	4.34400000
H	10.91900000	10.81200000	3.82700000
C	9.39300000	10.81800000	1.82800000
H	8.97200000	10.44900000	1.02400000
H	10.27600000	11.17700000	1.60100000
H	8.83200000	11.53500000	2.19100000
C	10.55600000	8.78800000	2.28100000
H	10.21400000	8.40500000	1.44700000
H	10.72400000	8.07000000	2.92600000
H	11.39200000	9.26700000	2.10000000

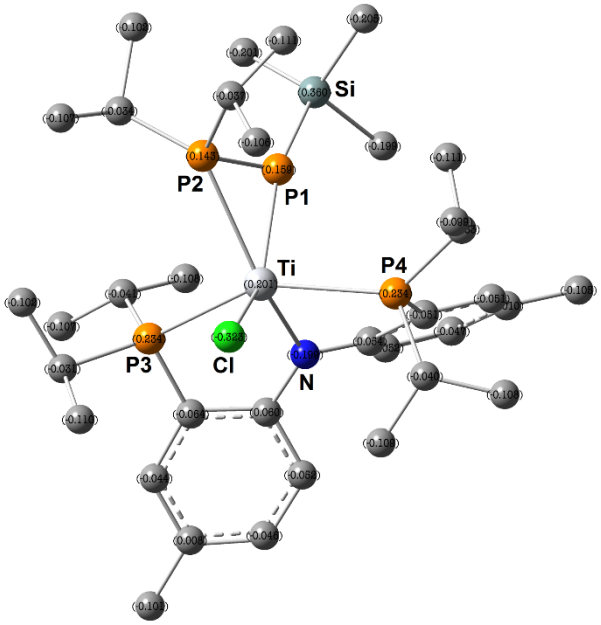

Figure S25. Hirshfeld charges for main atoms in [(PNP)Ti(Cl){η^2-P(SiMe$_3$)-P*i*Pr$_2$}].

Below are presented xyz coordinates for optimized geometry of [(PNP)Ti(Cl){η^2-P(SiMe$_3$)-P*i*Pr$_2$}].

Ti	8.39300000	20.13600000	4.23200000
Cl	10.64600000	20.19700000	5.08800000
N	8.00300000	21.59200000	2.88400000
Si	4.13000000	18.89900000	4.64900000
P	7.82700000	22.27200000	5.59900000
P	9.14800000	19.05500000	1.98100000
P	6.28000000	19.16200000	4.73300000
P	7.73000000	17.85000000	5.47400000
C	6.90300000	22.44100000	2.99700000
C	6.69500000	22.96100000	4.27400000
C	5.61800000	23.81800000	4.52400000
H	5.51400000	24.18700000	5.39400000
C	4.68700000	24.14400000	3.53000000
C	4.90400000	23.59900000	2.27800000
H	4.29800000	23.80900000	1.57700000
C	5.95600000	22.77200000	2.00900000
H	6.05000000	22.41200000	1.13500000
C	3.54100000	25.07700000	3.76600000
H	3.02600000	25.17800000	2.93800000
H	3.88400000	25.95100000	4.04500000
H	2.96300000	24.71400000	4.46800000
C	8.60300000	21.64600000	1.60100000
C	9.26400000	20.51500000	1.06300000
C	10.08700000	20.67000000	-0.08100000
H	10.53300000	19.90700000	-0.42600000
C	10.27100000	21.88900000	-0.71900000
C	9.59200000	22.96400000	-0.15500000
H	9.68900000	23.81500000	-0.56500000
C	8.79200000	22.87400000	0.95400000
H	8.36300000	23.65300000	1.28700000
C	11.02900000	22.00800000	-2.03200000
H	11.02800000	22.94300000	-2.32600000
H	10.59600000	21.45000000	-2.71000000
H	11.95400000	21.70700000	-1.90300000
C	6.99200000	22.56700000	7.22500000
H	6.64300000	23.50400000	7.25300000
C	7.95800000	22.35100000	8.39400000
H	8.69200000	22.99800000	8.33400000
H	8.31800000	21.44100000	8.35700000
H	7.47900000	22.47900000	9.24000000
C	5.82300000	21.58500000	7.31300000
H	5.20700000	21.74500000	6.56900000
H	5.35100000	21.71600000	8.16200000
H	6.16300000	20.66800000	7.26700000
C	9.11100000	23.60400000	5.65400000
H	9.71900000	23.33100000	6.40000000
C	8.65700000	25.01400000	6.02900000
H	8.11500000	24.97800000	6.84500000
H	8.12300000	25.39000000	5.29800000
H	9.44200000	25.58200000	6.18500000
C	10.02100000	23.66700000	4.42500000
H	10.35300000	22.76800000	4.21700000
H	10.77800000	24.25900000	4.60900000
H	9.51300000	24.01100000	3.66000000
C	7.80800000	18.19000000	1.04500000
H	7.57500000	17.39200000	1.60100000
C	6.50800000	18.98700000	0.93100000
H	6.21500000	19.26200000	1.82500000
H	5.81700000	18.43100000	0.51700000

H	6.66000000	19.78500000	0.38000000
C	8.15200000	17.62700000	-0.33500000
H	9.00400000	17.14400000	-0.28900000
H	8.22500000	18.36100000	-0.97900000
H	7.44400000	17.01200000	-0.62200000
C	10.65400000	18.05500000	1.59100000
H	10.72400000	17.90100000	0.60500000
C	11.85900000	18.85400000	2.09100000
H	11.90100000	19.71300000	1.62100000
H	12.68100000	18.34800000	1.92100000
H	11.76900000	19.01400000	3.05400000
C	10.54100000	16.72100000	2.33200000
H	9.74300000	16.24300000	2.02300000
H	10.46600000	16.89000000	3.29600000
H	11.33700000	16.18000000	2.15600000
C	3.57500000	17.41300000	3.76400000
H	3.94900000	17.41500000	2.85800000
H	2.59700000	17.41000000	3.71300000
H	3.88200000	16.61500000	4.24300000
C	3.40800000	18.84500000	6.35600000
H	3.74900000	19.60000000	6.88000000
H	3.66300000	18.00500000	6.79100000
H	2.43200000	18.90200000	6.30000000
C	3.54900000	20.53700000	3.87000000
H	4.00100000	21.28800000	4.31100000
H	2.58000000	20.62700000	3.98400000
H	3.76800000	20.54000000	2.91500000
C	7.71700000	17.60200000	7.32800000
H	7.97700000	16.65100000	7.49600000
C	6.40300000	17.80200000	7.96200000
H	5.73900000	17.23000000	7.52700000
H	6.13600000	18.74200000	7.86900000
H	6.46000000	17.57300000	8.91300000
C	8.81500000	18.47400000	7.93500000
H	9.66400000	18.29300000	7.47900000
H	8.90600000	18.26900000	8.88900000
H	8.58000000	19.42000000	7.82400000
C	7.49400000	16.11000000	4.86500000
H	7.39100000	16.14900000	3.87000000
C	6.13400000	15.41900000	5.47600000
H	5.35800000	15.97500000	5.25500000
H	6.21600000	15.34400000	6.44900000
H	6.01800000	14.52700000	5.08900000
C	8.74500000	15.27900000	5.16800000
H	9.53300000	15.72500000	4.79600000
H	8.65200000	14.38900000	4.76400000
H	8.84800000	15.18700000	6.13800000

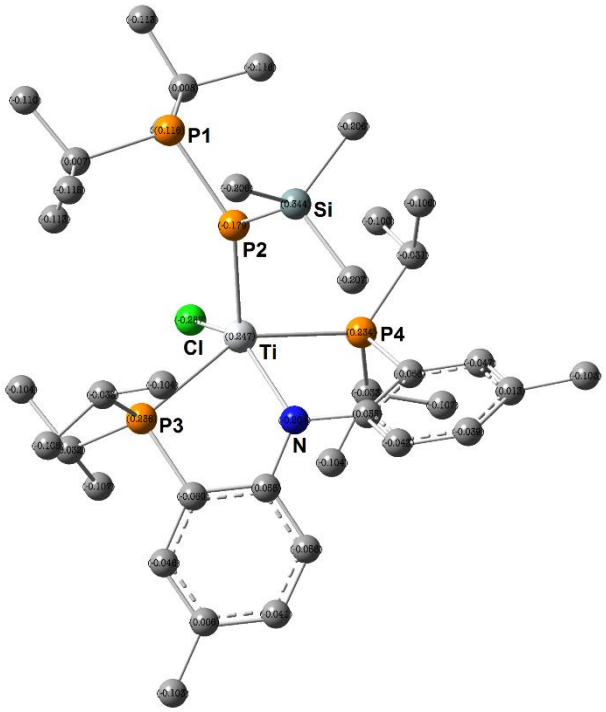

Figure S26. Hirshfeld charges for main atoms in [(PNP)Ti(Cl){η^1-P(SiMe$_3$)-P*t*Bu$_2$}].

Below are presented xyz coordinates for optimized geometry of [(PNP)Ti(Cl){η^1-P(SiMe$_3$)-P*t*Bu$_2$}].

C	8.55300000	10.76100000	4.90800000
C	7.40500000	11.50400000	5.21400000
C	7.38200000	12.34600000	6.32400000
H	6.59500000	12.84500000	6.51400000
C	8.48100000	12.47000000	7.15800000
C	9.62200000	11.74800000	6.83300000
H	10.39500000	11.83800000	7.37800000
C	9.66500000	10.90100000	5.73800000
H	10.45700000	10.41100000	5.55200000
C	8.41700000	13.32500000	8.39700000
H	8.33700000	12.75000000	9.18600000
H	7.63900000	13.91900000	8.34400000
H	9.23400000	13.86200000	8.46600000
C	9.68900000	9.82700000	3.01300000
C	10.61600000	10.87000000	2.96200000
H	10.46200000	11.65100000	3.48200000
C	11.75200000	10.79700000	2.17200000
H	12.36700000	11.52100000	2.18000000
C	12.01700000	9.69400000	1.37000000
C	11.08100000	8.68900000	1.36000000
H	11.22300000	7.93700000	0.79700000
C	9.92000000	8.73300000	2.15200000
C	13.27300000	9.62400000	0.53700000
H	14.05600000	9.62500000	1.12700000
H	13.31200000	10.40000000	-0.06000000
H	13.26700000	8.80200000	0.00500000
C	4.47800000	11.55100000	5.11200000
H	4.53800000	12.51600000	5.36200000
C	4.37400000	10.73000000	6.39100000
H	3.52700000	10.93400000	6.84200000
H	5.12100000	10.95300000	6.98500000

H	4.40400000	9.77500000	6.17100000
C	3.23900000	11.36000000	4.22800000
H	3.20700000	10.43500000	3.90800000
H	3.28700000	11.97100000	3.46200000
H	2.43300000	11.55400000	4.75100000
C	6.02700000	12.33500000	2.76300000
H	5.24300000	12.13400000	2.17500000
C	5.88300000	13.78300000	3.22500000
H	6.60100000	13.99900000	3.85600000
H	5.01600000	13.90100000	3.66500000
H	5.94000000	14.38000000	2.44900000
C	7.28200000	12.18000000	1.91000000
H	7.23900000	12.79600000	1.14900000
H	7.34200000	11.25800000	1.58200000
H	8.07200000	12.38600000	2.45100000
C	8.45400000	7.17300000	0.23700000
H	9.31500000	6.76300000	-0.06900000
C	8.24300000	8.47300000	-0.53400000
H	8.19800000	8.28100000	-1.49300000
H	8.99100000	9.08200000	-0.35800000
H	7.40600000	8.89300000	-0.24400000
C	7.33400000	6.17700000	-0.02600000
H	6.48500000	6.54900000	0.29000000
H	7.52100000	5.34200000	0.44900000
H	7.27500000	6.00000000	-0.98800000
C	9.23200000	5.98400000	2.84800000
H	8.47000000	5.34000000	2.91500000
C	9.65300000	6.34000000	4.27000000
H	9.96600000	5.53200000	4.73000000
H	8.88700000	6.71500000	4.75300000
H	10.37500000	7.00100000	4.24100000
C	10.35300000	5.28500000	2.09200000
H	11.11900000	5.88900000	2.01100000
H	10.03800000	5.03500000	1.19900000
H	10.62300000	4.47900000	2.58000000
C	7.27300000	5.48700000	7.57600000
H	7.99700000	5.27400000	6.95100000
H	6.55800000	4.82400000	7.48400000
H	7.61700000	5.47200000	8.49300000
C	5.24200000	7.58800000	8.40500000
H	5.57700000	7.47600000	9.31900000
H	4.48400000	6.98400000	8.25900000
H	4.95200000	8.51500000	8.27400000
C	7.95900000	8.42200000	7.44000000
H	8.29500000	8.35900000	8.35900000
H	7.61100000	9.32500000	7.28300000
H	8.68900000	8.23900000	6.81200000
C	2.75300000	6.30900000	4.63800000
C	2.39700000	7.31300000	5.72200000
H	2.99500000	8.08700000	5.65900000
H	2.50000000	6.89300000	6.60100000
H	1.47000000	7.60400000	5.60500000
C	2.66500000	6.93700000	3.28300000
H	2.83900000	6.26000000	2.59700000
H	3.32900000	7.65500000	3.21300000
H	1.76700000	7.31000000	3.15400000
C	1.72200000	5.18800000	4.75000000
H	0.82300000	5.57400000	4.79700000
H	1.89500000	4.66500000	5.56000000

H	1.78700000	4.60500000	3.96500000
C	5.04700000	4.35800000	3.90400000
C	6.34700000	3.79600000	4.48600000
H	6.69400000	3.09600000	3.89400000
H	6.17000000	3.41600000	5.37300000
H	7.00700000	4.51700000	4.56400000
C	5.35400000	4.91900000	2.52700000
H	5.76400000	4.22100000	1.97400000
H	5.97300000	5.67300000	2.61200000
H	4.52300000	5.22300000	2.10600000
C	4.07200000	3.19300000	3.78000000
H	3.28100000	3.48000000	3.27600000
H	3.79800000	2.89900000	4.67400000
H	4.50600000	2.44900000	3.31200000
N	8.51500000	9.84700000	3.81600000
Si	6.60100000	7.18300000	7.19100000
P	5.99300000	11.10900000	4.15100000
P	8.58900000	7.52100000	2.04900000
P	5.83800000	7.29100000	5.09300000
P	4.42900000	5.61000000	5.18100000
Cl	5.28700000	8.92100000	1.61500000
Ti	6.78200000	8.79200000	3.39800000

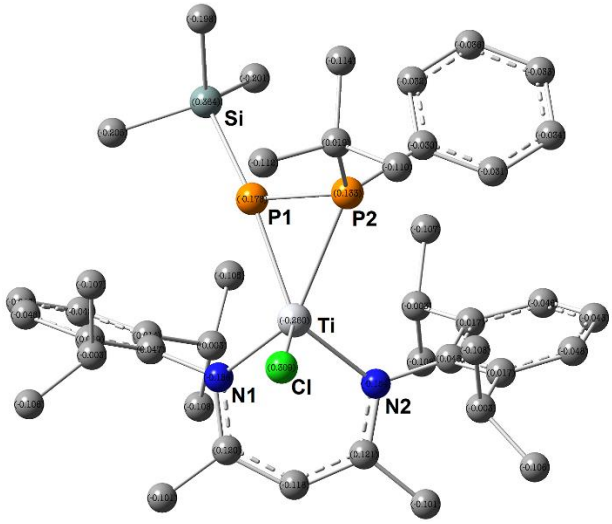

Figure S27. Hirshfeld charges for main atoms in [^{Me}NaNacTi(Cl){η^2-P(SiMe$_3$)-P(Ph)*t*Bu}].

Below are presented xyz coordinates for optimized geometry of [^{Me}NaNacTi(Cl){η^2-P(SiMe$_3$)-P(Ph)*t*Bu}].

Ti	9.08100000	5.31700000	1.98300000
Cl	11.18900000	5.25400000	2.89100000
P	8.61100000	6.18100000	-0.25900000
P	9.52900000	4.27800000	-0.35200000
Si	7.69500000	7.17700000	-2.06400000
N	8.15800000	6.85600000	3.02000000
N	8.02300000	3.94900000	3.12900000
C	7.81900000	8.17000000	2.50200000
C	6.46500000	8.43100000	2.21700000
C	6.11900000	9.71700000	1.77300000
H	5.20900000	9.91500000	1.58100000
C	7.07200000	10.69100000	1.61500000
H	6.81700000	11.55800000	1.32500000
C	8.40100000	10.41400000	1.87500000

H	9.05000000	11.09300000	1.74000000
C	8.81200000	9.15700000	2.33200000
C	5.36800000	7.38200000	2.37900000
H	5.80100000	6.51600000	2.62900000
C	4.38100000	7.75500000	3.48500000
H	3.69200000	7.06300000	3.55600000
H	3.96000000	8.61400000	3.27000000
H	4.85900000	7.83000000	4.33800000
C	4.60100000	7.16700000	1.07700000
H	3.90100000	6.49500000	1.21800000
H	5.21800000	6.85600000	0.38300000
H	4.19200000	8.01100000	0.79800000
C	10.27400000	8.91200000	2.64900000
H	10.34300000	8.03600000	3.12400000
C	10.84700000	9.99400000	3.56900000
H	11.79100000	9.80500000	3.74900000
H	10.34900000	10.00300000	4.41200000
H	10.76800000	10.87000000	3.13300000
C	11.10100000	8.81600000	1.36600000
H	12.04100000	8.65200000	1.59500000
H	11.03000000	9.65700000	0.86800000
H	10.76600000	8.07800000	0.81500000
C	7.69000000	2.61400000	2.66000000
C	6.47800000	2.41900000	1.97000000
C	6.13700000	1.11600000	1.60300000
H	5.31800000	0.96100000	1.14500000
C	6.96500000	0.04800000	1.88800000
H	6.70700000	-0.83400000	1.64800000
C	8.17000000	0.26700000	2.52700000
H	8.74700000	-0.46900000	2.69400000
C	8.56200000	1.54900000	2.93400000
C	5.51400000	3.55700000	1.65000000
H	6.02800000	4.41400000	1.72200000
C	4.97300000	3.47000000	0.22700000
H	5.72100000	3.45100000	-0.40700000
H	4.40900000	4.25200000	0.04300000
H	4.44200000	2.65200000	0.12900000
C	4.39600000	3.61600000	2.65800000
H	3.79000000	4.35200000	2.43200000
H	4.76900000	3.76200000	3.55200000
H	3.90200000	2.76900000	2.64700000
C	9.91400000	1.72700000	3.60800000
H	9.93200000	2.63200000	4.03500000
C	11.01500000	1.67900000	2.56300000
H	11.88500000	1.79500000	2.99900000
H	10.87700000	2.39800000	1.91000000
H	10.99200000	0.81300000	2.10300000
C	10.16400000	0.68400000	4.70100000
H	11.04000000	0.84200000	5.11200000
H	10.14600000	-0.21500000	4.30800000
H	9.46500000	0.75300000	5.38500000
C	7.92700000	7.92900000	5.23300000
H	8.01000000	8.73500000	4.68300000
H	8.64200000	7.91500000	5.90300000
H	7.05700000	7.92800000	5.68200000
C	8.04000000	6.71200000	4.35700000
C	7.95200000	5.47100000	4.99200000
C	7.76300000	4.20200000	4.42500000
C	7.23800000	3.12600000	5.32900000

H	7.15900000	2.28700000	4.82800000
H	6.35700000	3.38600000	5.67100000
H	7.85600000	2.99900000	6.07900000
C	6.02000000	6.50800000	-2.53300000
H	6.11300000	5.58200000	-2.83800000
H	5.64000000	7.05400000	-3.25300000
H	5.42700000	6.53700000	-1.75300000
C	8.80400000	7.10800000	-3.57100000
H	9.69200000	7.45300000	-3.33900000
H	8.41900000	7.65700000	-4.28700000
H	8.88300000	6.18100000	-3.87800000
C	7.54600000	8.93700000	-1.49500000
H	8.43100000	9.27700000	-1.25100000
H	6.95200000	8.97900000	-0.71700000
H	7.17400000	9.48400000	-2.21900000
C	8.54500000	3.02400000	-1.25300000
C	8.50100000	1.72200000	-0.77200000
H	8.96200000	1.49500000	0.02700000
C	7.78500000	0.75300000	-1.45800000
H	7.74400000	-0.13100000	-1.11000000
C	7.12800000	1.04900000	-2.63900000
H	6.64600000	0.37500000	-3.10600000
C	7.18200000	2.35200000	-3.13500000
H	6.73700000	2.57100000	-3.94500000
C	7.87900000	3.32200000	-2.44700000
H	7.90900000	4.20800000	-2.79100000
C	11.20300000	4.25600000	-1.24900000
C	11.95700000	3.01100000	-0.78600000
H	11.45500000	2.21000000	-1.04000000
H	12.06200000	3.03600000	0.19000000
H	12.84200000	2.99000000	-1.20800000
C	11.98300000	5.49700000	-0.86000000
H	11.49800000	6.29300000	-1.15700000
H	12.86600000	5.47400000	-1.28600000
H	12.09100000	5.52400000	0.11300000
C	11.01700000	4.20400000	-2.76400000
H	10.51100000	3.39900000	-3.00200000
H	11.89400000	4.18100000	-3.20000000
H	10.52500000	4.99600000	-3.06100000
H	7.87400000	5.50700000	5.90300000

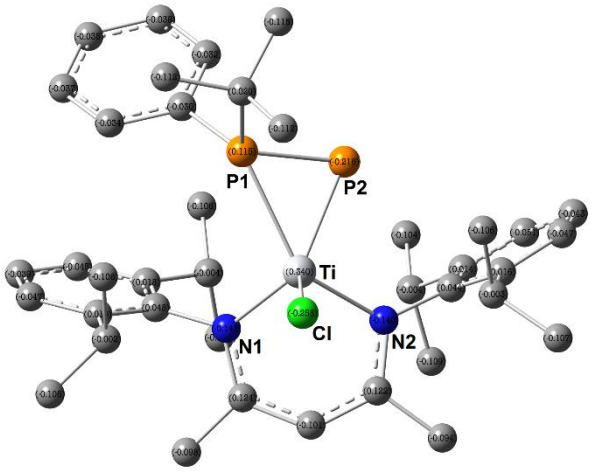

Figure S28. Hirshfeld charges for main atoms in [^{Me}NaNacTi(Cl){η^2-P-P(Ph)*t*Bu}].

Below are presented xyz coordinates for optimized geometry of [^{Me}NaNacTi(Cl){η^2-P-P(Ph)*t*Bu}].

C	9.51900000	9.18800000	4.75900000
C	8.89800000	10.43500000	4.94200000
C	8.60800000	10.84200000	6.24200000
H	8.21400000	11.69400000	6.39100000
C	8.88700000	10.02000000	7.32200000
H	8.69300000	10.31400000	8.20500000
C	9.44500000	8.77300000	7.11500000
H	9.60400000	8.20500000	7.85900000
C	9.78100000	8.33400000	5.84100000
C	8.52800000	11.36000000	3.79900000
H	8.71600000	10.88200000	2.94100000
C	7.02500000	11.69200000	3.83900000
H	6.80200000	12.28800000	3.09300000
H	6.81100000	12.13500000	4.68700000
H	6.50700000	10.86500000	3.76300000
C	9.35400000	12.64800000	3.81500000
H	9.08500000	13.21700000	3.06300000
H	10.30500000	12.42700000	3.73300000
H	9.20100000	13.12500000	4.65700000
C	10.37800000	6.95400000	5.64600000
H	10.91900000	6.96900000	4.80500000
C	9.27300000	5.92000000	5.47300000
H	9.67100000	5.03400000	5.34600000
H	8.73100000	6.14900000	4.68900000
H	8.70500000	5.91200000	6.27200000
C	11.29400000	6.52200000	6.78300000
H	11.64500000	5.62600000	6.59800000
H	10.78800000	6.50900000	7.62300000
H	12.03900000	7.15600000	6.86000000
C	13.34600000	7.06300000	1.29200000
C	13.97800000	6.17900000	2.18200000
C	15.17100000	5.58500000	1.78500000
H	15.59800000	4.96700000	2.36700000
C	15.75300000	5.87200000	0.56000000
H	16.56300000	5.44900000	0.30100000
C	15.13800000	6.78600000	-0.28400000
H	15.55000000	7.00100000	-1.11200000
C	13.93300000	7.39500000	0.05200000
C	13.37400000	5.85200000	3.53700000
H	12.77100000	6.61100000	3.78500000
C	12.52500000	4.60900000	3.48300000
H	12.14900000	4.43000000	4.36900000
H	13.07700000	3.84900000	3.20300000
H	11.79800000	4.73800000	2.83900000
C	14.43000000	5.74000000	4.62900000
H	14.96300000	6.56100000	4.65200000
H	15.01400000	4.97500000	4.44100000
H	13.99100000	5.61100000	5.49500000
C	13.30200000	8.38300000	-0.92200000
H	12.34700000	8.51300000	-0.65300000
C	13.32000000	7.85900000	-2.35800000
H	12.90700000	8.52000000	-2.95200000
H	12.81800000	7.01800000	-2.40500000
H	14.24600000	7.70100000	-2.63700000
C	13.99900000	9.74900000	-0.86700000

H	13.57100000	10.35900000	-1.50300000
H	14.94400000	9.64300000	-1.10300000
H	13.92600000	10.11700000	0.03900000
C	7.67500000	8.08600000	2.85800000
H	7.46600000	8.60200000	3.66400000
H	7.37600000	7.16100000	2.97600000
H	7.21500000	8.48300000	2.08900000
C	9.16900000	8.10700000	2.62000000
C	9.64200000	7.40900000	1.49800000
C	10.95600000	7.06400000	1.13100000
C	11.07900000	5.96100000	0.10700000
H	12.02600000	5.79200000	-0.07900000
H	10.62500000	6.23000000	-0.71900000
H	10.66300000	5.14300000	0.45600000
C	15.46600000	9.51000000	3.37600000
C	15.91200000	9.42100000	4.69600000
H	15.38800000	9.80100000	5.39200000
C	17.10000000	8.78900000	5.00700000
H	17.39200000	8.74700000	5.91000000
C	17.86700000	8.21400000	4.00400000
H	18.68300000	7.77600000	4.21800000
C	17.43700000	8.28300000	2.68600000
H	17.95600000	7.88900000	1.99600000
C	16.24900000	8.92800000	2.38000000
H	15.96300000	8.97400000	1.47600000
C	14.47000000	12.18100000	2.72100000
C	15.63700000	12.23600000	1.72900000
H	15.35400000	11.86400000	0.86800000
H	16.38900000	11.71400000	2.08000000
H	15.91700000	13.16700000	1.60500000
C	14.90100000	12.75500000	4.06000000
H	15.65600000	12.23700000	4.41000000
H	14.15300000	12.71000000	4.69200000
H	15.17100000	13.69000000	3.94300000
C	13.28500000	12.98300000	2.17800000
H	13.00800000	12.61200000	1.31500000
H	13.55100000	13.91800000	2.06200000
H	12.53800000	12.93100000	2.81200000
N	9.98100000	8.76900000	3.45400000
N	12.05700000	7.62200000	1.65400000
P	12.50100000	10.19800000	4.50500000
P	13.91300000	10.38500000	2.95600000
Cl	10.76800000	10.82900000	0.88000000
Ti	11.63200000	9.44200000	2.48700000
H	8.91500000	7.01600000	0.97200000

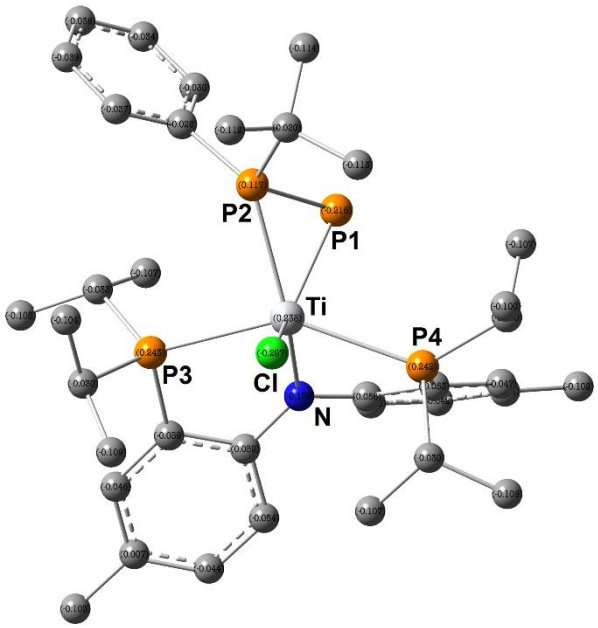

Figure S29. Hirshfeld charges for main atoms in [(PNP)Ti(Cl){η^2-P-P(Ph)*t*Bu}].

Below are presented xyz coordinates for optimized geometry of [(PNP)Ti(Cl){η^2-P-P(Ph)*t*Bu}].

C	5.20200000	12.31900000	7.10600000
C	3.93500000	12.82400000	6.69000000
C	3.52400000	14.09600000	7.11600000
H	2.67700000	14.42100000	6.83400000
C	4.32000000	14.90300000	7.93900000
C	5.56900000	14.39000000	8.32000000
H	6.13600000	14.91600000	8.87200000
C	6.00000000	13.13100000	7.91300000
H	6.85300000	12.82000000	8.18800000
C	3.86600000	16.30000000	8.34900000
H	4.54700000	16.71000000	8.92100000
H	3.02000000	16.23700000	8.83900000
H	3.74000000	16.85000000	7.54600000
C	6.27800000	10.18900000	7.55400000
C	6.03300000	10.25000000	8.95600000
H	5.42100000	10.88800000	9.30000000
C	6.68900000	9.37400000	9.82800000
H	6.49800000	9.42600000	10.75700000
C	7.61000000	8.43100000	9.38600000
C	7.83000000	8.35100000	8.00100000
H	8.44300000	7.70500000	7.67000000
C	7.17800000	9.18700000	7.09800000
C	8.35600000	7.53400000	10.36300000
H	8.96100000	6.94400000	9.86800000
H	7.71300000	6.99400000	10.86800000
H	8.87600000	8.08700000	10.98300000
C	1.92800000	10.66000000	6.47200000
H	1.49000000	10.03700000	5.82400000
C	2.71600000	9.80400000	7.45400000
H	3.42200000	9.32300000	6.97400000
H	2.11400000	9.16000000	7.88400000
H	3.12000000	10.37900000	8.13900000
C	0.78800000	11.42900000	7.21300000

H	0.28100000	11.96400000	6.56700000
H	1.17900000	12.01900000	7.89000000
H	0.18900000	10.78600000	7.64700000
C	1.90300000	12.90400000	4.58300000
H	1.30500000	13.31200000	5.27000000
C	1.00400000	12.06900000	3.64200000
H	0.58700000	11.34100000	4.14900000
H	1.54700000	11.69400000	2.91800000
H	0.30600000	12.64300000	3.26400000
C	2.58200000	14.06100000	3.83600000
H	3.13200000	14.57500000	4.46100000
H	1.89700000	14.64400000	3.44700000
H	3.14800000	13.70200000	3.12200000
C	7.14200000	7.17400000	5.02100000
H	7.97300000	6.75800000	5.39000000
C	5.93600000	6.57400000	5.76600000
H	6.00400000	6.78500000	6.72100000
H	5.92900000	5.60200000	5.64500000
H	5.10800000	6.95500000	5.40600000
C	7.07700000	6.85600000	3.50700000
H	7.85700000	7.24400000	3.05800000
H	6.25800000	7.23900000	3.12800000
H	7.07300000	5.88500000	3.37700000
C	8.98700000	9.48100000	4.78700000
H	9.01200000	9.47300000	3.78600000
C	9.24000000	10.93400000	5.22700000
H	8.51700000	11.50700000	4.89600000
H	10.09600000	11.24200000	4.86100000
H	9.27000000	10.97800000	6.20700000
C	10.09100000	8.54400000	5.26200000
H	9.89800000	7.63200000	4.96200000
H	10.13500000	8.56200000	6.23900000
H	10.94900000	8.83500000	4.89000000
C	7.84400000	10.91300000	1.59500000
C	8.64200000	12.05500000	1.65000000
H	8.33100000	12.82200000	2.11800000
C	9.90000000	12.08800000	1.02300000
H	10.44400000	12.86400000	1.08700000
C	10.34100000	10.98900000	0.31500000
H	11.17800000	11.01400000	-0.13400000
C	9.55500000	9.84200000	0.26100000
H	9.85800000	9.08500000	-0.22600000
C	8.33900000	9.79500000	0.91200000
H	7.83100000	8.99200000	0.89500000
C	5.06000000	10.90400000	0.70800000
C	5.53300000	11.97400000	-0.29200000
H	6.45300000	11.77700000	-0.56800000
H	5.49900000	12.85500000	0.13200000
H	4.94700000	11.96600000	-1.07800000
C	5.06400000	9.50300000	0.08600000
H	4.76000000	8.84900000	0.75100000
H	5.97200000	9.27500000	-0.20400000
H	4.46100000	9.48500000	-0.68700000
C	3.61300000	11.21000000	1.14200000
H	3.31300000	10.53000000	1.78000000
H	3.02700000	11.20400000	0.35800000
H	3.57900000	12.09300000	1.56800000
Cl	3.76700000	8.77500000	3.98600000
Ti	5.24000000	10.60000000	4.63700000

P	3.06600000	11.78100000	5.47900000
P	7.24700000	9.01000000	5.28800000
P	5.80200000	12.59500000	3.52200000
P	6.12300000	10.89700000	2.27900000
N	5.61400000	11.03300000	6.61700000

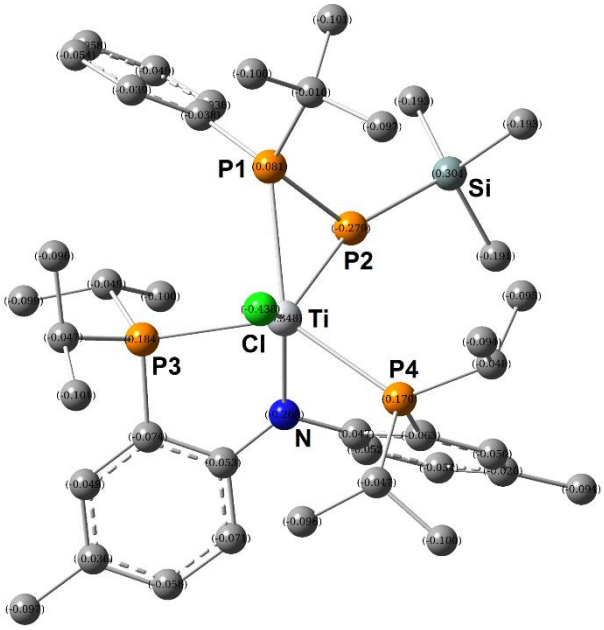

Figure S30. Hirshfeld charges for main atoms in [(PNP)Ti(Cl){η^2-P(SiMe$_3$)-P(Ph)*t*Bu}].

Below are presented xyz coordinates for optimized geometry of [(PNP)Ti(Cl){η^2-P(SiMe$_3$)-P(Ph)*t*Bu}].

Ti	-0.14985400	0.07834700	0.76085000
Cl	0.05793000	0.28306100	3.16172900
N	-1.64788900	0.79522100	-0.48854000
Si	1.15110700	-3.45563400	-1.84671900
P	-2.27258500	-1.25399400	1.34469800
P	0.51352000	2.53907600	0.22483300
P	0.90035000	-1.54600000	-0.68992200
P	2.39909900	-0.71886500	0.56238900
C	-2.42981400	-0.19737000	-1.12212200
C	-2.93099300	-1.26535900	-0.35093000
C	-3.70088800	-2.26461600	-0.94288700
H	-4.07928500	-3.08479600	-0.33426600
C	-3.98516800	-2.25390200	-2.31102600
C	-3.45960300	-1.20668700	-3.07224100
H	-3.64096500	-1.18387400	-4.14499400
C	-2.69314000	-0.19824500	-2.49663800
H	-2.29027200	0.59924100	-3.11482800
C	-4.79371600	-3.36214700	-2.93911700
H	-4.99581300	-3.15757500	-3.99523900
H	-5.75732400	-3.49188000	-2.43287600
H	-4.26279600	-4.32051800	-2.88316000
C	-1.98945000	2.12792300	-0.73726000
C	-1.07030800	3.14615500	-0.40861900
C	-1.39447300	4.49279600	-0.58195600
H	-0.66945500	5.25339100	-0.29692300
C	-2.62699900	4.89630500	-1.09037300

C	-3.53850100	3.88479300	-1.41207700
H	-4.52077900	4.15559000	-1.79576600
C	-3.24065400	2.54015100	-1.24126400
H	-3.99488200	1.79974100	-1.48653900
C	-2.95935400	6.35233800	-1.30334300
H	-4.00545100	6.56358000	-1.05509300
H	-2.80538500	6.64762900	-2.34901300
H	-2.33062300	6.99915200	-0.68214000
C	-2.36378100	-3.00865600	1.95171700
H	-3.39767700	-3.35390300	1.82069800
C	-2.00958300	-3.07475900	3.44387400
H	-2.74686200	-2.56504300	4.07182700
H	-1.03266300	-2.61851900	3.63811300
H	-1.96839100	-4.12241200	3.76531700
C	-1.44251400	-3.92259000	1.14428900
H	-1.64347000	-3.87101200	0.06995700
H	-1.57375100	-4.96318500	1.46659600
H	-0.39837600	-3.64227700	1.30230800
C	-3.50366300	-0.36327900	2.42388700
H	-3.05692900	-0.42806200	3.42412300
C	-4.88728500	-1.01941900	2.43267600
H	-4.86906200	-2.03810300	2.83436800
H	-5.31119400	-1.05620700	1.42176600
H	-5.57090400	-0.43373700	3.05926700
C	-3.60319400	1.12061400	2.06129500
H	-2.63066900	1.61877300	2.10907700
H	-4.27473100	1.62270000	2.76839600
H	-4.01008000	1.26235700	1.05502600
C	1.70667000	2.80294500	-1.18984900
H	2.63174300	2.31526800	-0.86871100
C	1.19218700	2.07736000	-2.43849200
H	0.97845700	1.02200700	-2.24220600
H	1.95202000	2.12961100	-3.22743000
H	0.27558000	2.54848000	-2.81324200
C	2.02203600	4.26700800	-1.50453300
H	2.48144100	4.78945800	-0.65896700
H	1.12317800	4.81513700	-1.80927600
H	2.73398800	4.30857900	-2.33785300
C	1.03173700	3.73473400	1.54431600
H	1.15792400	4.71301600	1.06308500
C	-0.03619600	3.87251400	2.63483700
H	-0.99143700	4.21614900	2.22469500
H	0.29732100	4.60760400	3.37769400
H	-0.19967400	2.92030300	3.14734800
C	2.38061300	3.29423000	2.12384000
H	3.16244300	3.26297200	1.35638100
H	2.29634800	2.30078100	2.57914600
H	2.70179200	3.99944800	2.89982500
C	2.61276800	-3.31989000	-3.03261400
H	2.47291800	-2.50366600	-3.75049800
H	2.71229300	-4.25366900	-3.60141700
H	3.55760600	-3.15084500	-2.50322800
C	1.40259300	-5.01804000	-0.81870500
H	0.59358800	-5.18540000	-0.10155700
H	2.34883700	-5.00380000	-0.26734500
H	1.43053900	-5.88003900	-1.49886400
C	-0.45352900	-3.58426300	-2.82625600
H	-1.33562900	-3.54282500	-2.17742100
H	-0.48698200	-4.52577300	-3.38959800

H	-0.54296600	-2.75573000	-3.53787300
C	3.26247700	-1.95007200	1.70621300
C	4.31871400	-2.75638600	0.94145600
C	3.91866900	-1.18405400	2.86721600
C	2.19527900	-2.88850000	2.28212800
H	3.87582500	-3.29175900	0.09404300
H	5.11683900	-2.11390600	0.55403600
H	4.77533900	-3.49910000	1.60964100
H	3.19380200	-0.54294300	3.38092300
H	4.31484500	-1.90343200	3.59620600
H	4.76125200	-0.57246100	2.53024600
H	2.66315200	-3.55999600	3.01384200
H	1.40025600	-2.32992300	2.78826900
H	1.74216800	-3.50418200	1.50111100
C	3.74760600	0.09020200	-0.38600300
C	4.59758300	0.99479000	0.26693700
C	3.89422900	-0.08251700	-1.76472600
C	5.57521900	1.69264000	-0.43717200
H	4.47323000	1.18565000	1.32838000
C	4.86549200	0.62129700	-2.47405500
H	3.22053900	-0.75053800	-2.29151800
C	5.71085200	1.50982500	-1.81291000
H	6.21953200	2.39274800	0.08775600
H	4.95837600	0.47611200	-3.54698200
H	6.46571100	2.06177100	-2.36593100

c) Electrophilic Fukui functions of Ti complexes

Red area corresponds with positive value ($f^+ > 0$) of electrophilic Fukui functions, the most favorable for nucleophilic attack site of a molecule. Hydrogen atoms were omitted for clarity.

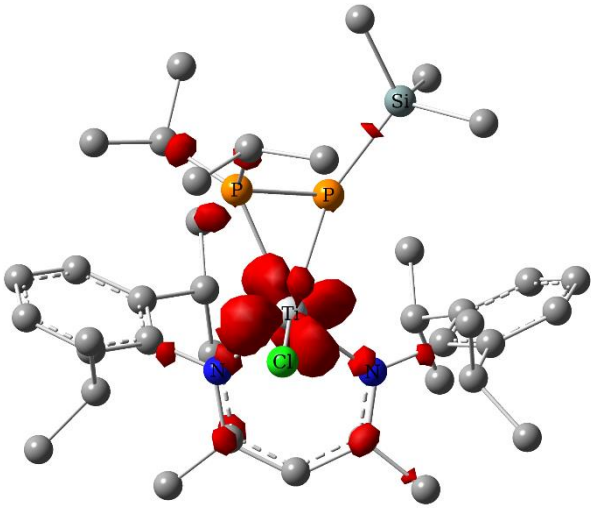

Figure S31. Electrophilic Fukui function obtained using solid-state (experimental) structure of [^{Me}NaNacTi(Cl){η^2-P(SiMe$_3$)-P*i*Pr$_2$}] complex.

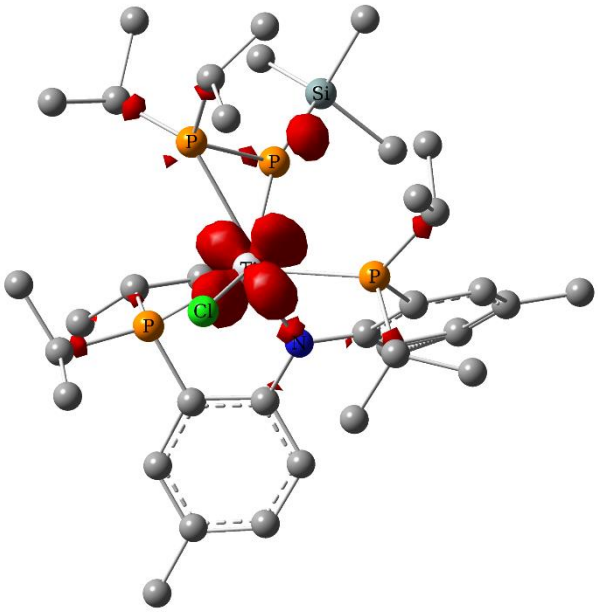

Figure S32. Electrophilic Fukui function obtained using solid-state (experimental) structure of [(PNP)Ti(Cl){η^2-P(SiMe$_3$)-P*i*Pr$_2$}] complex.

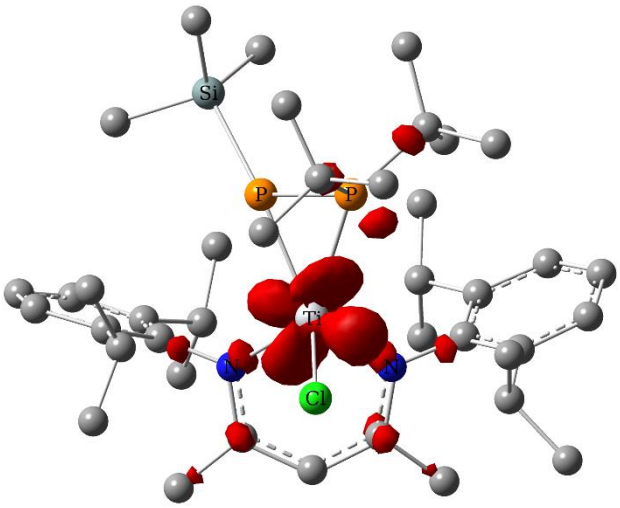

Figure S33. Electrophilic Fukui function obtained using solid-state (experimental) structure of [^{Me}NaNacTi(Cl){η^2-P(SiMe$_3$)-P*t*Bu$_2$}] complex

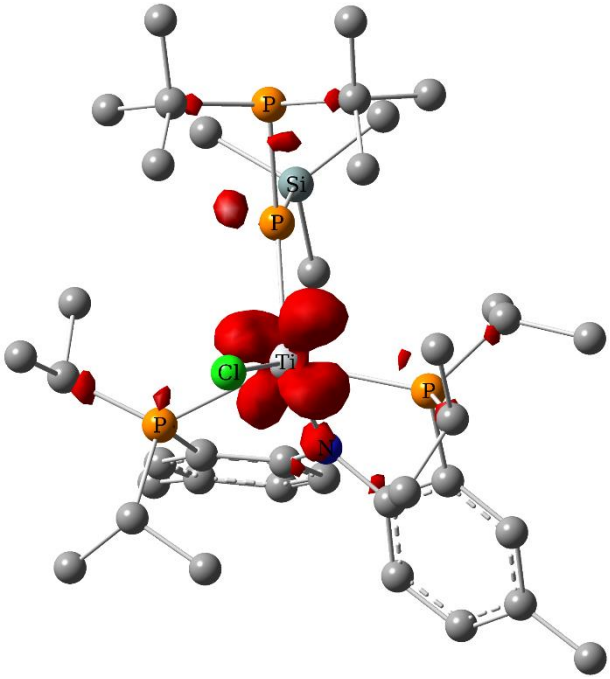

Figure S34. Electrophilic Fukui function obtained using solid-state (experimental) structure of [(PNP)Ti(Cl){η^1-P(SiMe$_3$)-P*t*Bu$_2$}] complex.

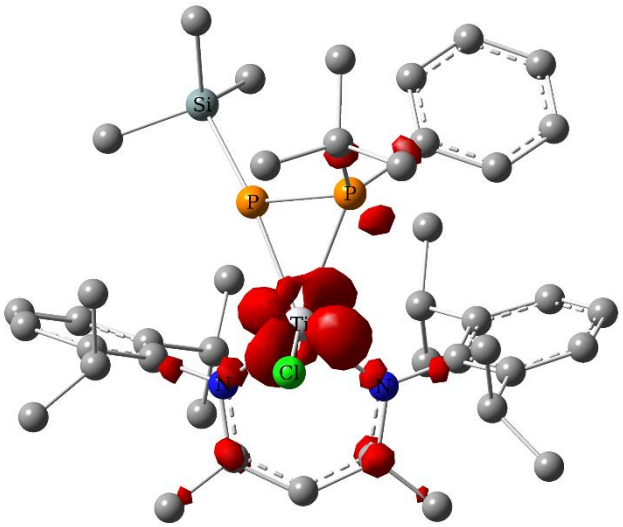

Figure S35. Electrophilic Fukui function obtained using solid-state (experimental) structure of [^{Me}NaNacTi(Cl){η^2-P(SiMe$_3$)-P(Ph)*t*Bu}] complex.

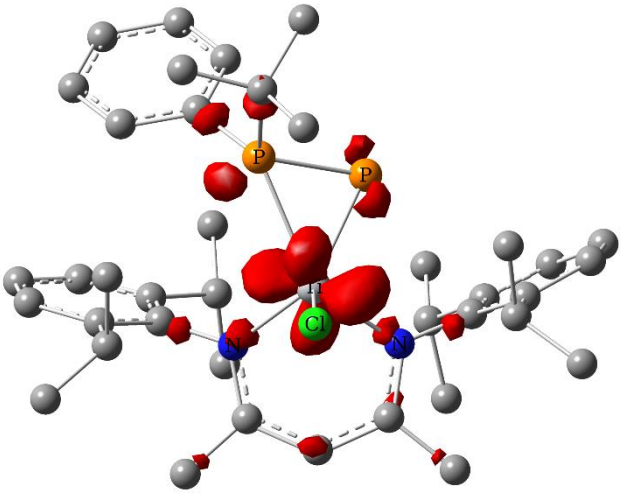

Figure S36. Electrophilic Fukui function obtained using solid-state (experimental) structure of [^{Me}NaNacTi(Cl){η^2-P-P(Ph)*t*Bu}] complex.

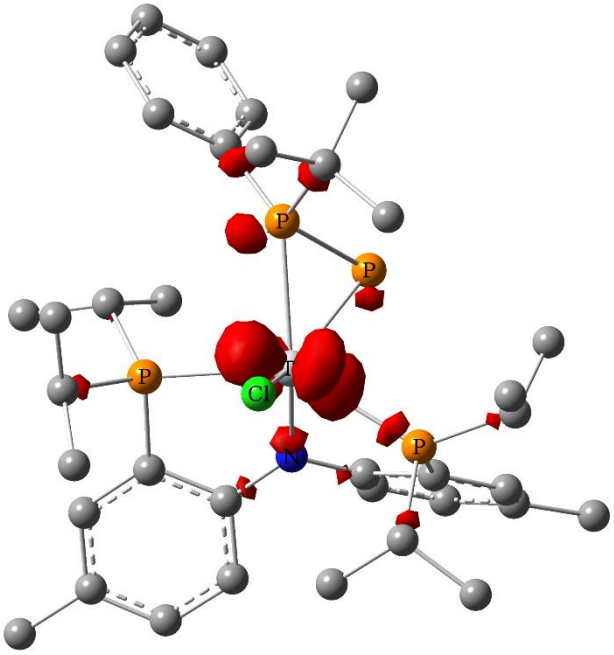

Figure S37. Electrophilic Fukui function obtained using solid-state (experimental) structure of [(PNP)Ti(Cl){η^2-P-P(Ph)*t*Bu}] complex.

PART D. References

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