Supporting Information for:

Structural Elucidation of a Mononuclear Titanium Methylidene

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Experimental Details

General Procedures

Unless otherwise stated, all operations were performed in a M.Braun Lab Master double-dry box under an atmosphere of purified dinitrogen or using high vacuum standard Schlenk techniques under an argon or dinitrogen atmosphere. Anhydrous solvents were purchased from Fisher Scientific or Aldrich. All anhydrous solvents were sparged with argon for 20 minutes and dried by passage through two columns of activated alumina and Q-5 drying agent in a Grubbs-type solvent system. Stabilizer-free Et_2O and THF were purchased from Fisher Scientific and dried by passage through two columns of activated alumina. Deuterated benzene and deuterated toluene were purchased from Cambridge Isotope Laboratories (CIL) and was sparged with argon for 20 minutes, then was dried over 4 Å sieves, and degassed by freeze–pump–thaw cycles. All solvents were transferred into a dry box and were stored over 4 Å sieves. All sieves were heated to 200 °C under vacuum overnight prior to use. Celite used for filtrations was also heated to 200 °C under vacuum overnight prior to use. Solution state magnetic susceptibility was measured by the Evans[1] method in benzene-d_6/tetramethylsilane solution at 298 K. Corrections were applied for diamagnetism calculated for Pascal constants.[2] $(PN)_2TiCl$,[3] the, aryl oxyl radical •OMes* (Mes* = $2,4,6\text{-}^tBu_3C_6H_2$),[4] H_2CPPh_3,[5] and $[FeCp_2][OTf]$[6] were prepared according to published literature procedures. NMR spectra were recorded on a Bruker UNI 400 MHz spectrometer for ^1H and $^{31}P\{^1H\}$ spectra. ^{13}C NMR spectra were recorded on a cryo500. ^1H and ^{13}C NMR chemical shifts are reported referenced to the internal residual proton or carbon resonances of C_6D_6 (δ = 7.16 ppm or 128.06 ppm). ^{19}F and ^{31}P NMR chemical shifts are reported with respect to external CF_3CO_2H (δ −78.5 ppm) and H_3PO_4 (δ 0.0 ppm).

Synthesis of $(PN)_2Ti(CH_3)$ (1)

A dark brown solution of $(PN)_2TiCl$ (294 mg, 0.38 mmol, 1 equiv.) in 5 mL of toluene was cooled to -35 °C for 30 mins in a 20 mL vial. To this solution was added an ethereal solution of 1.6 M $LiCH_3$ (0.24 mL, 0.38 mmol, 1 equiv,) dropwise, over a period of 3 minutes. An immediate color change to dark green was observed during this time. The reaction mixture was stirred at room temperature for 15 minutes, followed by removal of all volatiles. The green residue was then dissolved in 15 mL diethyl ether, filtered through Celite, and the filtrate concentrated to 5 mL. This concentrated solution was then layered with 10 mL *n*-hexanes and stored at -35 °C overnight, resulting in the deposition of a dark green powder. To isolate this material, the solution was rapidly filtered cold and the solid dried *in vacuo*. Total collected was 278 mg (0.37 mmol, 98% yield). In order to grow single crystals suitable for X-ray diffraction studies, half of the powder product from the isolated reaction mixture (140 mg) was dissolved in 10 mL ether, and stored at -35 °C overnight without further filtration to yield green single plates of complex **1**.

^1H NMR (400 MHz, 298 K, benzene-d_6): δ 11.98 (br, $\Delta\nu_{1/2}$ = 5.7 Hz, 2 H, meta-ArH_{Tolyl}), 9.37 (s, 2 H, meta-ArH_{Tolyl}), 8.23 (br, $\Delta\nu_{1/2}$ = 65.2 Hz, 2 H, ortho-ArH_{Tolyl}), 8.14 (s, 4 H, meta-ArH_{Mesityl}), 4.29 (s, 12 H, ortho-C$H_{3\text{Mesityl}}$), 3.31 (s, 6 H, para-C$H_{3\text{Tolyl}}$), 2.80 (s, 6 H para-C$H_{3\text{Mesityl}}$), 2.39 (br, $\Delta\nu_{1/2}$ = 33.2 Hz, 12 H, P-CH-CH_3), 1.37 (s, 3 H, Ti-CH_3) 0.49 (br, 4 H ea, P-CH-CH_3). Some residual solvents such as *n*-hexanes and *n*-pentane are present based on the ^{1}H NMR spectrum. μ_{eff} = 2.03 μ_B, 25 ^{o}C, C_6D_6, Evans' method.

Synthesis of $(PN)_2Ti(CH_3)(OTf)$ (2)

To a dark green solution of **1** in 5 mL THF in a 20 mL vial (224.5 mg, 0.3 mmol, 1 equiv.) was added a 10 mL THF slurry of $[FeCp_2][OTf]$ (101.5 mg, 0.3 mmol, 1 equiv.) at room temperature while stirring. A color change to dark red was observed, whereby all $[FeCp_2][OTf]$ was consumed as it was added, instantaneously resulting in a homogeneous bright red solution. As monitored by ^{1}H NMR spectroscopy, complex **1** is converted quantitatively to complex **2**. Removal of volatiles after stirring at room temperature for 30 minutes provides a pure powder that can be used for NMR characterization. Complex **2** is cleanly formed along with $FeCp_2$ based on the ^{1}H NMR spectrum. Given the clean conversion of **1** to complex **2**, it is possible to conduct *in situ* experiments with the crude material without need for separation from the $FeCp_2$. The details below rely on the use of crude mixture for the synthesis of complex **3**.

^{1}H NMR (400 MHz, 298 K, benzene-*d*6): δ 6.70 (s, 4H, *meta*-Ar$H_{Mesityl}$), 6.55, (br, $\Delta v_{1/2}$ = 3.3 Hz, 2 H, *meta*-ArH_{Tolyl}), 6.53 (s, 2 H, *meta*-ArH_{Tolyl}), 5.48 (dd, $^{3}J_{H\text{-}H}$ = 3.5 Hz, 2H, *ortho*-ArH_{Tolyl}), 3.60 (s, 12 H, ortho-C$H_{3Mesityl}$), 2.82 (sept, $^{3}J_{H\text{-}H}$ = 3.5 Hz, 2 H, P-C*H*-CH$_3$), 2.57 (sept, $^{3}J_{H\text{-}H}$ = 3.3 Hz, 2 H, P-C*H*-CH$_3$), 2.31 (s, 6 H, para-CH_{3Tolyl}), 2.19 (s, 6 H para-C$H_{3Mesityl}$), 1.69 (t, $^{3}J_{H\text{-}H}$ =9.1 Hz, 3 H, Ti-CH_3), 1.54 (m, 3 H, P-CH-CH_3, coupling constant not assignable due to overlapping resonances), 1.48 (m, 3 H, P-CH-CH_3, coupling constant not assignable due to overlapping resonances), 1.26 (m, 3 H, P-CH-CH_3, coupling constant not assignable due to overlapping resonances). ^{31}P{^{1}H} NMR (162 MHz, 298 K, benzene-*d*6): δ 17.45 ppm. ^{19}F NMR (282 MHz, 298 K, benzene-*d*6): δ -76.49 ppm. ^{13}C NMR (125.8 MHz, 298 K, benzene-*d*6): δ 158.45 (Ar-*C*), 145.43 (Ar-*C*), 13, 8.41 (Ar-*C*), 136.47 (Ar-*C*), 136.10 (Ar-*C*), 133.67 (Ar-*C*), 132.40 (Ar-*C*), 130.63 (Ar-*C*), 130.04 (Ar-*C*), 129.27 (Ar-*C*), 113.90 (Ar-*C*), 55.22 (t, $^{1}J_{C\text{-}H}$= 8.1 Hz, Ti-*C*H$_3$), 28.01 (P*C*H(CH$_3$)$_2$, 27.17 (PCH(*C*H$_3$)$_2$), 21.61 (Ar-*C*H$_3$), 21.46 (PCH(*C*H$_3$)$_2$), 21.26 (PCH(*C*H$_3$)$_2$), 20.99 (Ar-*C*H$_3$), 20.66 (Ar-*C*H$_3$), 20.49 (Ar-*C*H$_3$).

Synthesis of $(PN)_2Ti{=}CH_2$ (3)

Route A:

To a dark green solution of complex **1** (224 mg, 0.3 mmol, 1 equiv.) in 5 mL of THF in a 20 mL vial was added a 5 mL slurry of $[FeCp_2][OTf]$ (101.5mg, 0.3 mmol, 1 equiv.) at room temperature while stirring. A color change to a bright red color was observed immediately upon addition. The solution was stirred for another hour at room temperature during which no further color change was observed. All volatiles were taken to dryness under reduced pressure, and the residue redissolved in 5 mL toluene. To this solution was added a stoichiometric amount of H_2CPPh_3 (83.3 mg, 0.3 mmol, 1 equiv.) as a 5 mL toluene solution at room temperature while stirring. A rapid color change from bright red to light orange was observed. The solution was stirred for 5 minutes, and then taken to dryness under reduced pressure, followed by two triturations with *n*-hexanes. The orange residue was then dissolved in 8 mL of *n*-hexanes, and filtered over Celite to remove the colorless precipitate, presumably $[H_3CPPh_3][OTf]$. The filtrate was quickly stored at -35 ^{o}C overnight without further concentration, resulting in the deposition of light orange crystals of complex **3** suitable for x-ray diffraction (168 mg, 0.22 mmol, 75% yield). In solution complex **3** gradually decomposes so it is recommended that manipulation of such a species must be conducted rapidly while maintaining the solution cold.

Route B:

To a dark green stirred solution of complex **1** (75 mg, 0.1 mmol, 1 equiv.) in 5 mL of toluene in a 20 mL vial was added a 5 mL toluene solution of the aryl oxyl radical •OMes* (Mes* = 2,4,6-$^{t}Bu_3C_6H_2$), at room temperature. Within five minutes, the solution began to lighten to an orange color. The reaction does not fully convert to complex **3** as monitored by ^{1}H NMR spectroscopy. The optimized reaction time for conversion to **3** is 15 minutes at room temperature. After this time, the reaction mixture was then taken to dryness under reduced pressure, triturated with *n*-hexanes, and then redissolved in 10 mL *n*-hexanes. The solution was filtered over Celite and the filtrate stored at −35 °C overnight to yield orange crystals of complex **3** (35 mg, 0.05 mmol, 48% yield)

^{1}H NMR (400 MHz, 298 K, benzene-*d*$_6$): *δ* 11.82 ppm (t, $J_{H\text{-}H}$=3.68 Hz, 2 H, Ti=CH_2), 7.04 (s, 4 H, *meta*-ArH_{Mesityl}), 6.85 (br, $\Delta v_{1/2}$ = 4.0 Hz, 2 H, *meta*-ArH_{Tolyl}), (br, $\Delta v_{1/2}$ = 4.0 Hz, 2 H, *meta*-ArH_{Tolyl}), 5.69 (dd, $^{3}J_{H\text{-}H}$ = 4.1 Hz, 2 H, *ortho*-ArH_{Tolyl}), 2.62 (sept, $^{3}J_{H\text{-}H}$ = 6.6 Hz, 2 H, P-C*H*-CH_3), 2.50 (s, 6 H, para-C$H_{3\mathrm{Tolyl}}$), 2.20 (s, 6 H para-C$H_{3\mathrm{Mesityl}}$), 2.08 (s, 12 H, ortho-C$H_{3\mathrm{Mesityl}}$), 1.01 (m, 6 H, P-CH-CH_3, coupling value not assignable), 0.79 (m, 6 H, P-CH-CH_3, coupling value not assignable due to overlapping residual solvent residues), 0.53 (sept, $^{3}J_{H\text{-}H}$ = 6.4 Hz, 2 H, P-C*H*-CH_3). $^{31}P\{^{1}H\}$ NMR (162 MHz, 298 K, benzene-*d*$_6$): δ 23.60 ppm. ^{13}C NMR (125.8 MHz, 298 K, toluene-*d*$_8$): *δ* 291.10 (t, $^{1}J_{C\text{-}H}$=123.5 Hz, $^{2}J_{C\text{-}P}$=12.5 Hz, Ti=CH_2), 170.32 (Ar-*C*), 159.67 (t, Ar-*C*, $^{2}J_{CP}$= 12.3 Hz), 158.17 (Ar-*C*), 145.46 (Ar-*C*), 136.85 (Ar-*C*), 133.78 (Ar-*C*), 133.60 (Ar-*C*), 131.82 (Ar-*C*), 130.27 (Ar-*C*), 129.89 (Ar-*C*), 112.78 (Ar-*C*), 112.12 (t, Ar-*C*, $^{2}J_{C\text{-}P}$= 4.2 Hz), 22.47 (P*C*H$(CH_3)_2$, CP coupling constant not assignable due to overlapping resonances), 21.67 (P*C*H$(CH_3)_2$, 20.86 (PCH(CH_3)$_2$), 20.65 (PCH(CH_3)$_2$), 20.28 (Ar-CH_3), 19.97 (Ar-CH_3), 19.21 (Ar-CH_3).

NMR Spectral Data

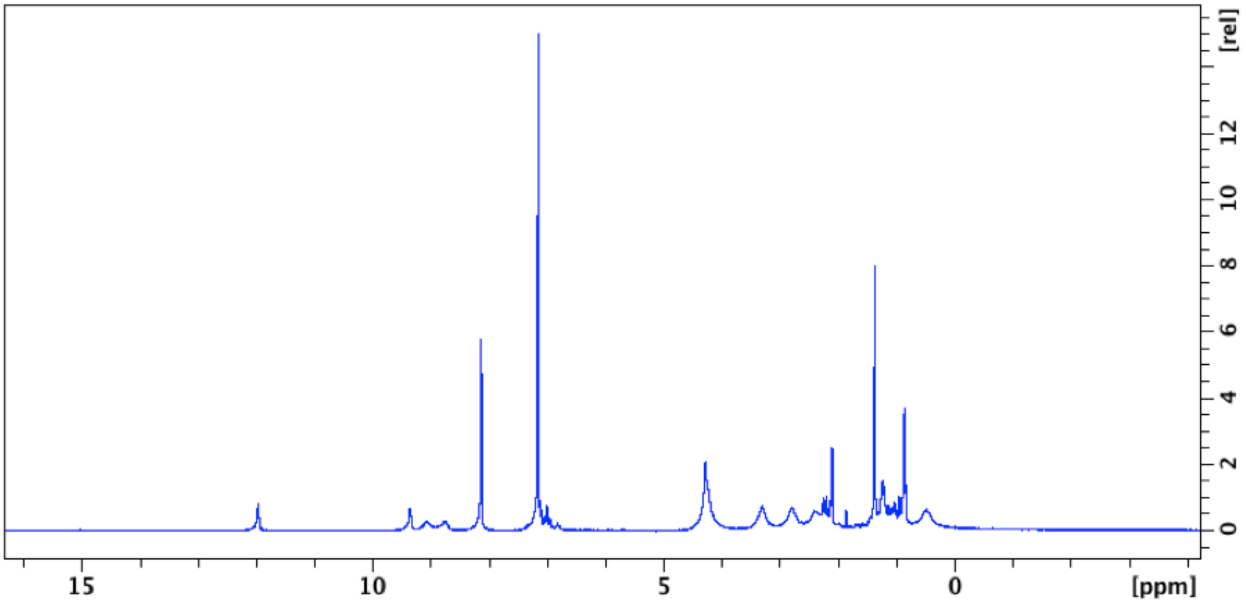

Figure S1: ^{1}H NMR Spectrum of **1** in C_6D_6, 400 MHz, 298 K

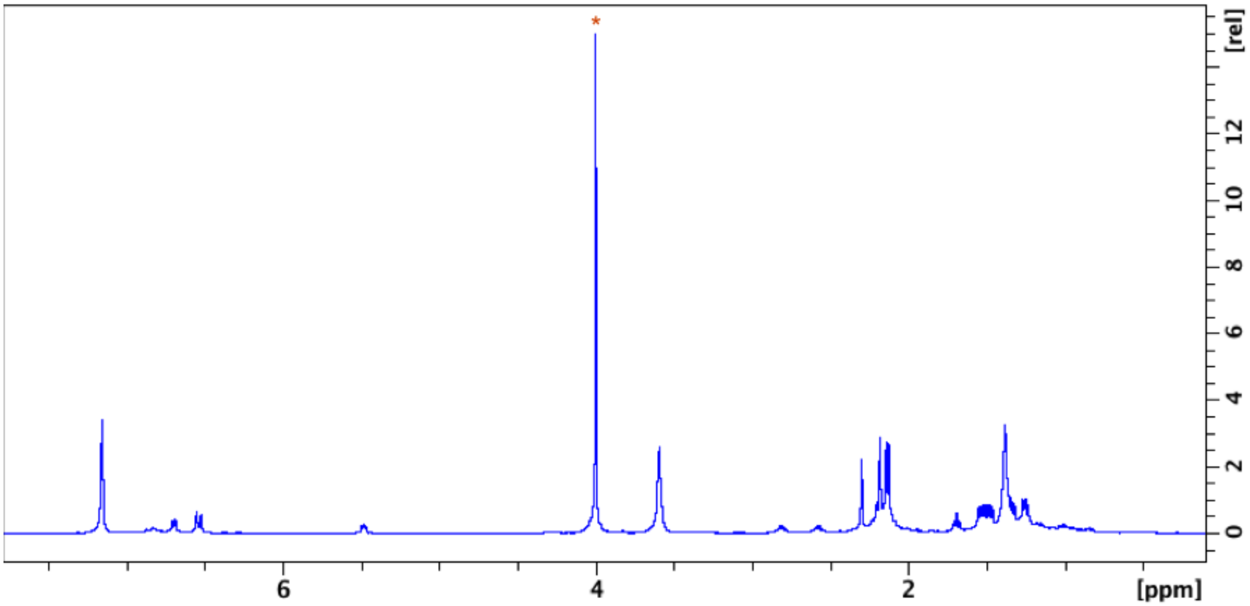

Figure S2: ^{1}H NMR Spectrum of **2** in C_6D_6, 500 MHz, 298 K, *=$FeCp_2$

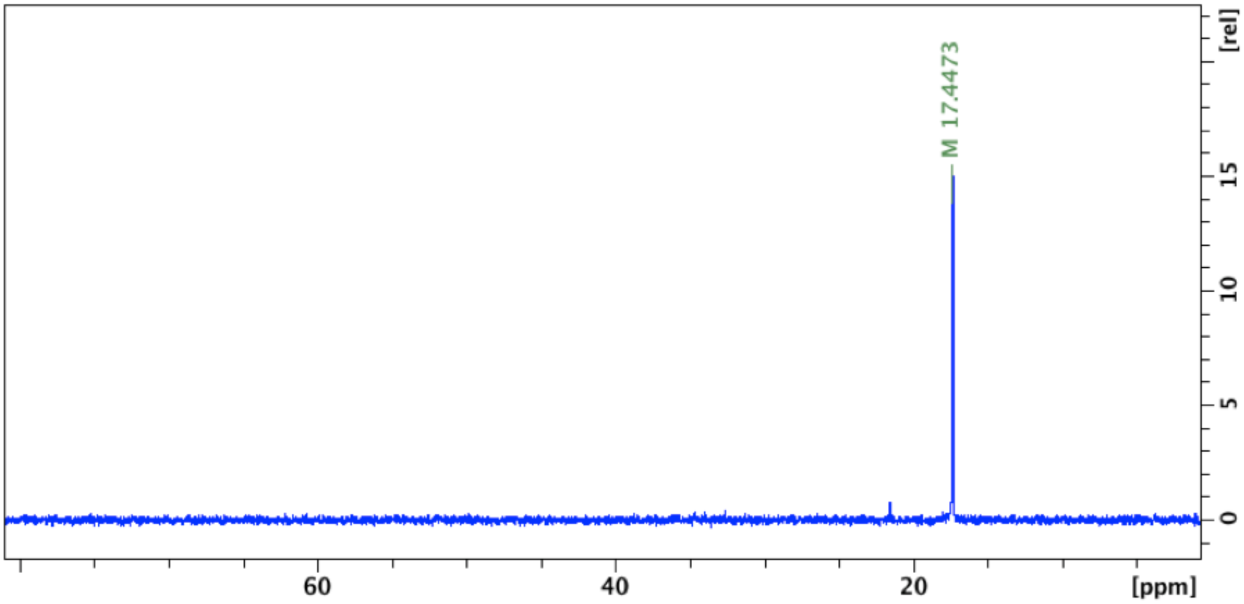

Figure S3: $^{31}P\{^1H\}$ NMR Spectrum of **2** in C_6D_6, 162 MHz, 298 K

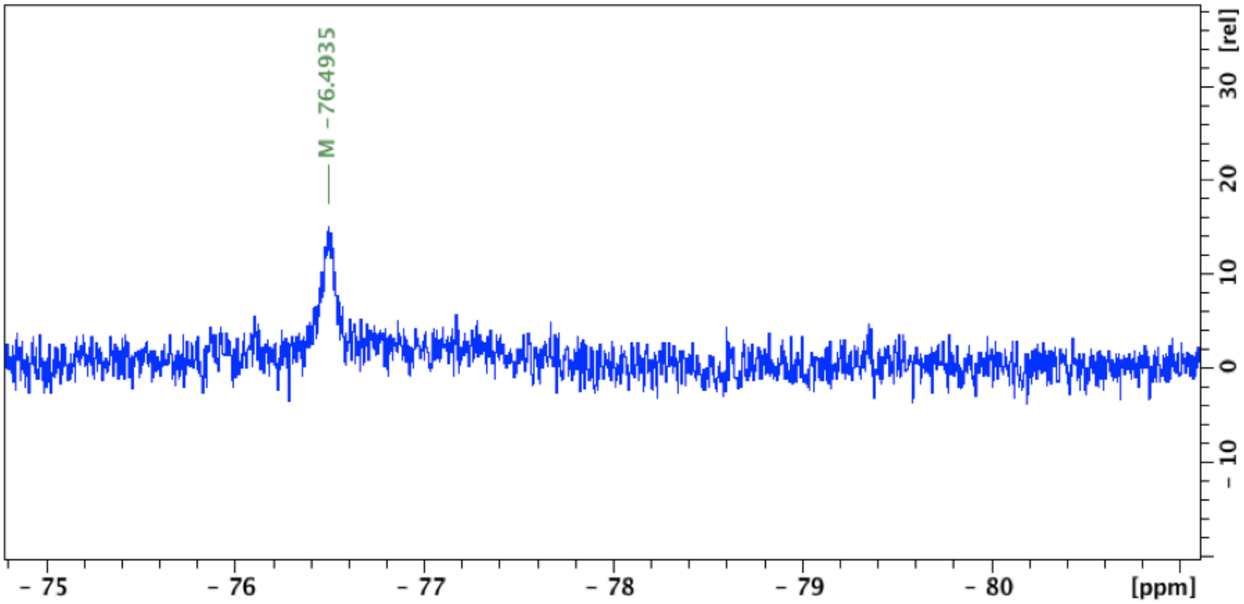

Figure S4: ^{19}F NMR Spectrum of **2** in C_6D_6, 282 MHz, 298 K

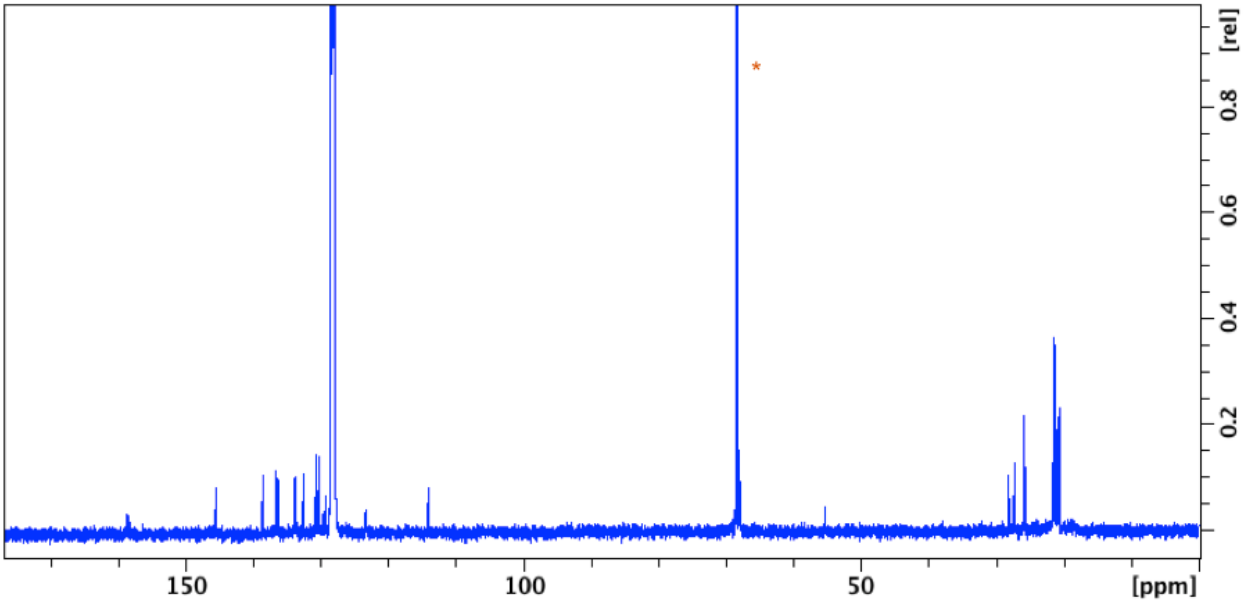

Figure S5: $^{13}C\{^1H\}$ NMR Spectrum of **2** in C_6D_6, 125.8 MHz, 298K, *=$FeCp_2$

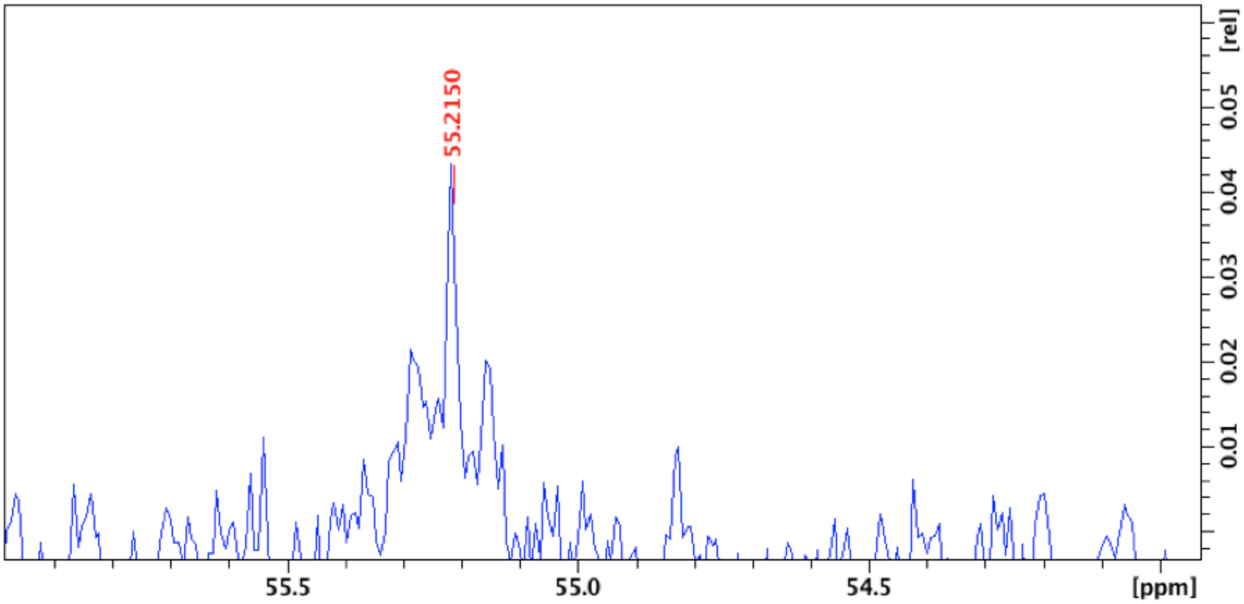

Figure S6: $^{13}C\{^{1}H\}$ NMR Spectrum of **2** in C_6D_6, 125.8 MHz, 298K, feature of Ti-*C*H_3 resonance

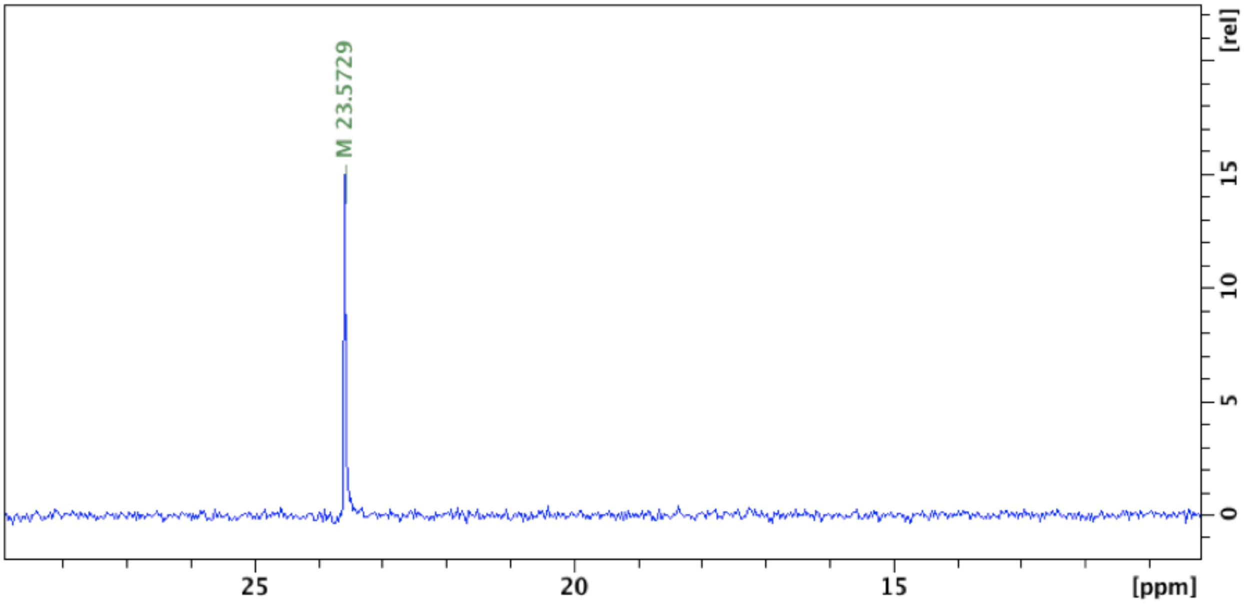

Figure S7: $^{31}P\{^{1}H\}$ NMR Spectrum of **3** in C_6D_6, 162 MHz, 298 K

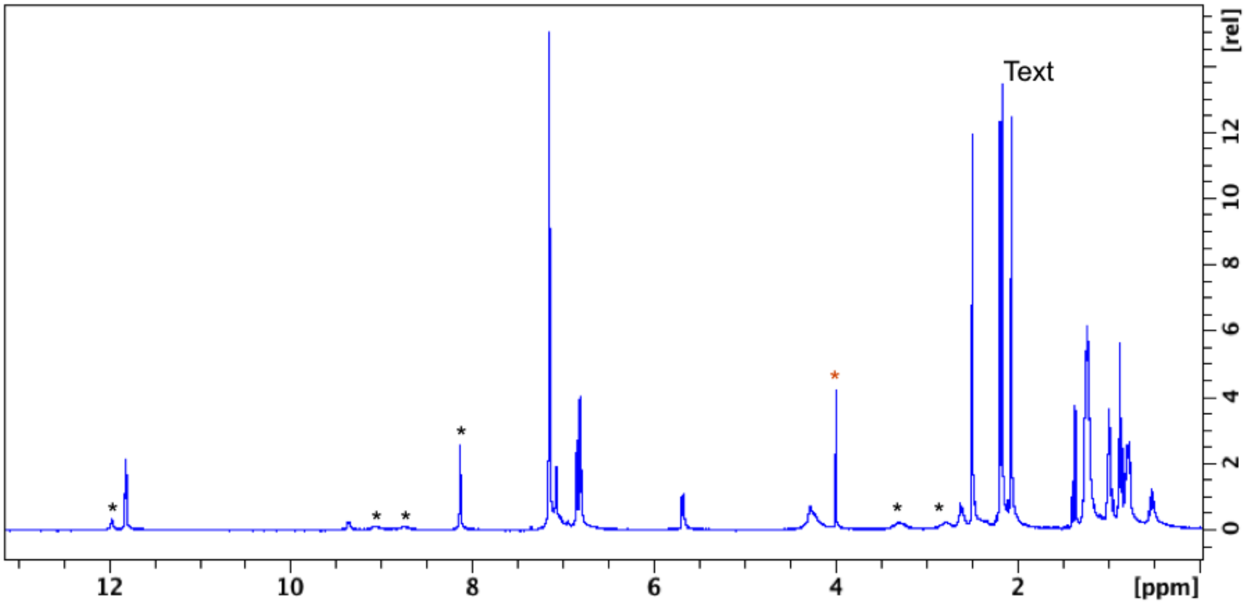

Figure S8: ^{1}H NMR Spectrum of **3** in C_6D_6, 400 MHz, 298 K, *=complex **1**, *=FeCp$_2$

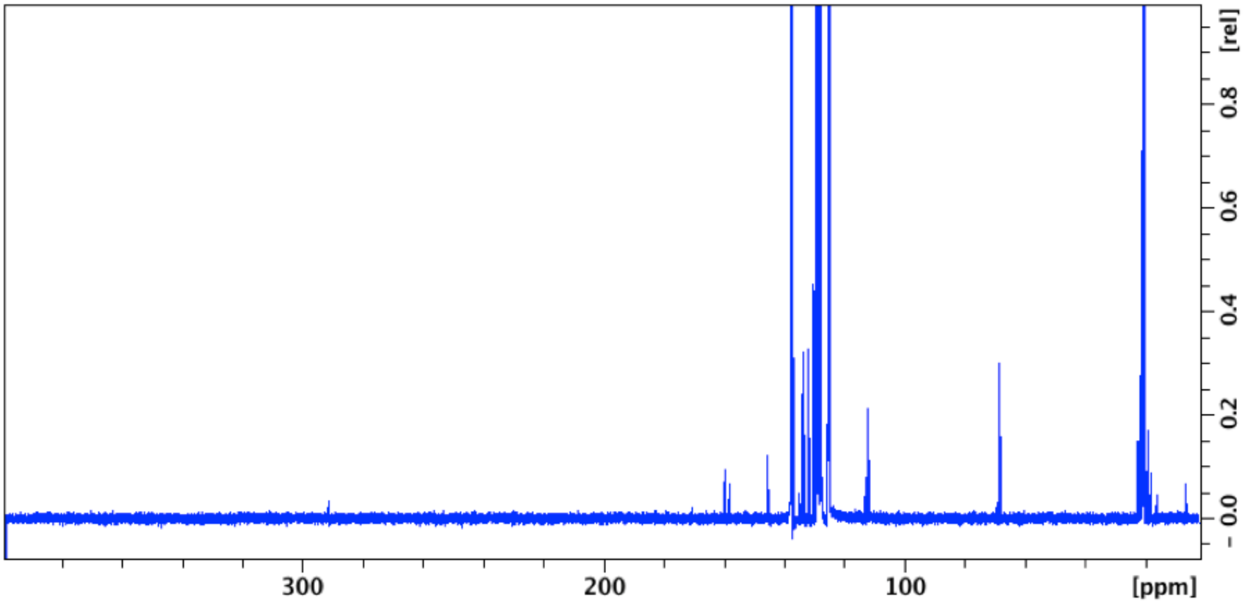

Figure S9: ^{31}P coupled $^{13}C\{^1H\}$ NMR Spectrum of **3** in C_7D_8, 125.8 MHz, 298 K

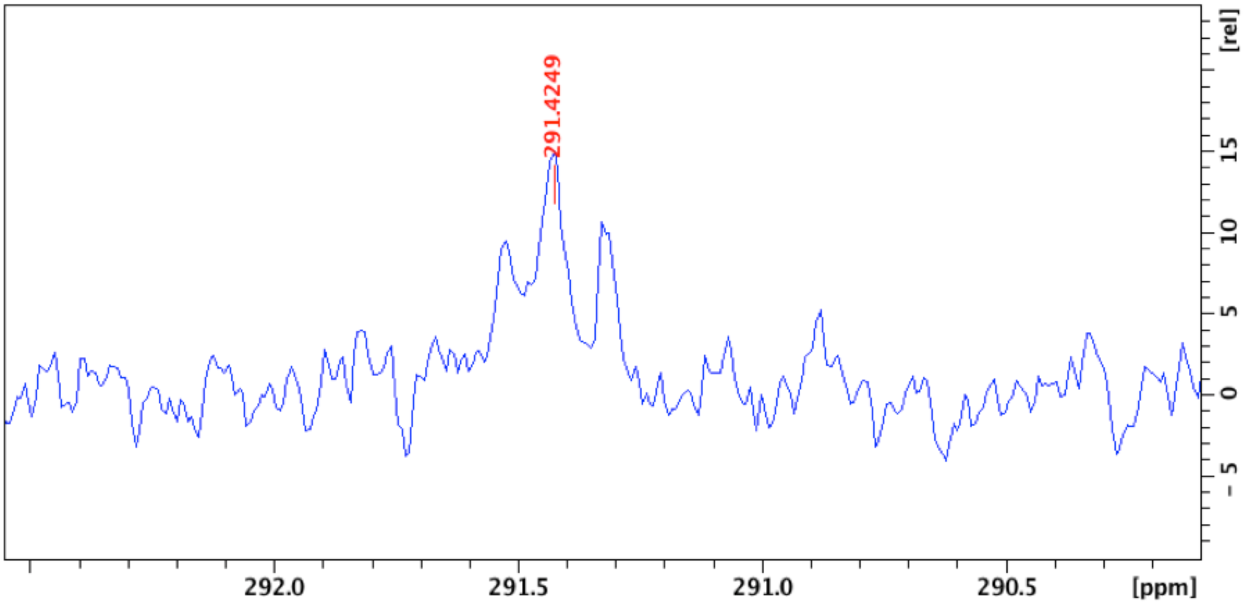

Figure S10: ^{31}P coupled ^{13}C{^{1}H} NMR Spectrum of **3** in C_7D_8, 125.8 MHz, 298 K, feature of Ti=*C*H_2

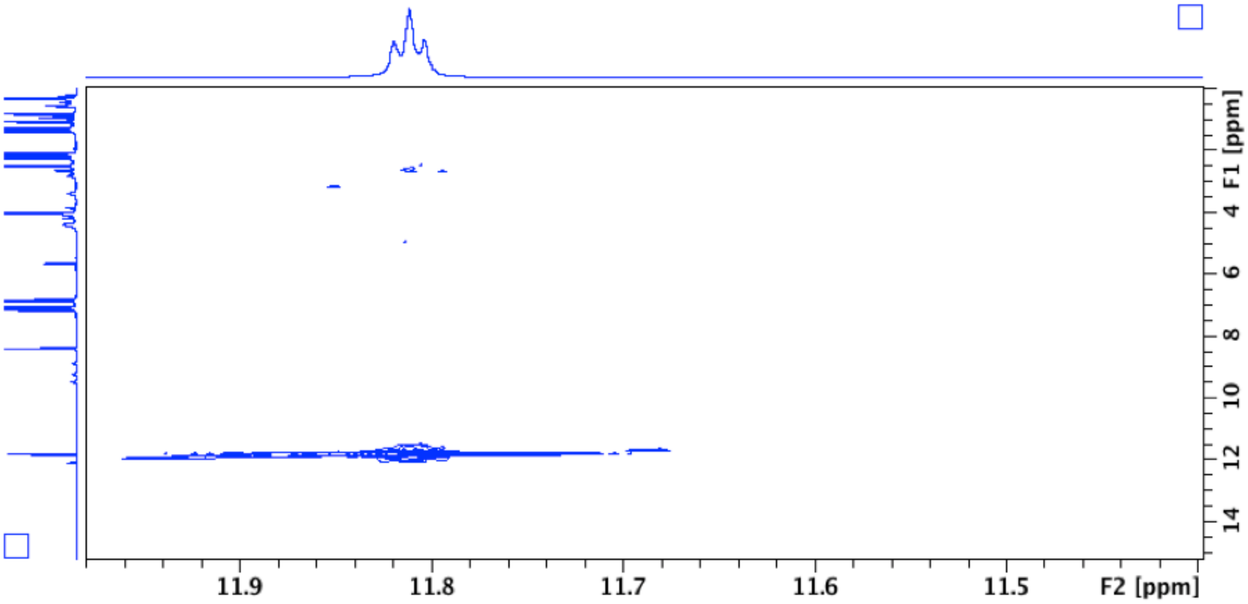

Figure S11: ^{31}P and ^{1}H coupled ^{13}C NMR Spectrum of **3** in C_7D_8, 125.8 MHz, 298 K, feature of Ti=*C*H_2

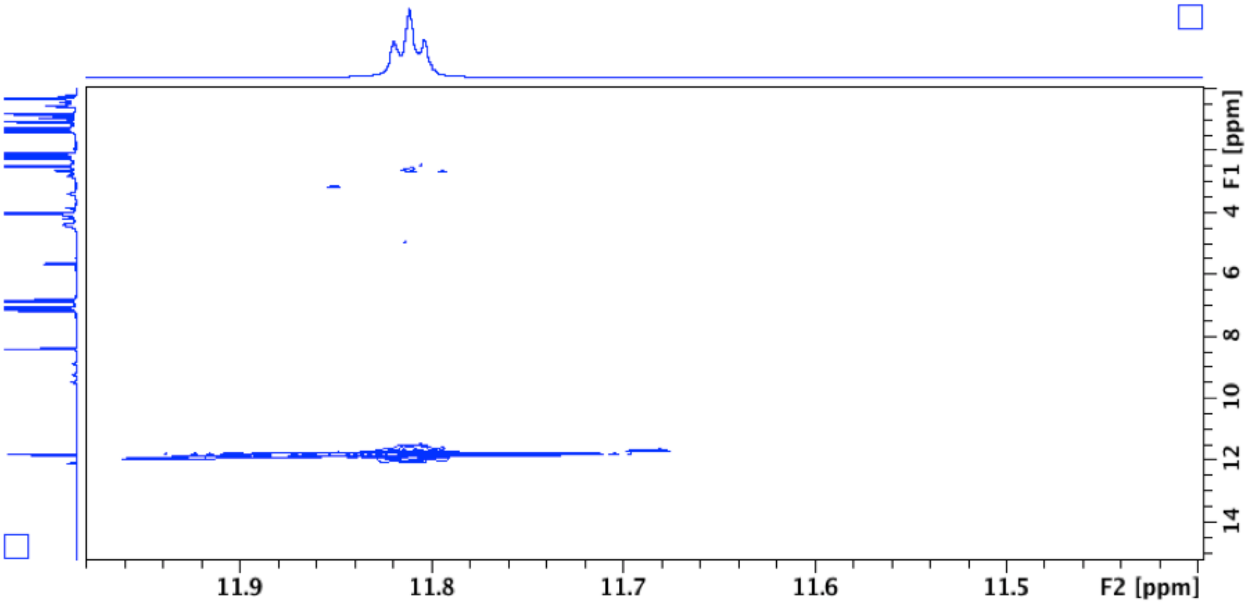

Figure S12: ^{1}H-^{1}H COSY NMR Spectrum of **3** in C_7D_8, 500 MHz, 298 K, feature of Ti=CH_2

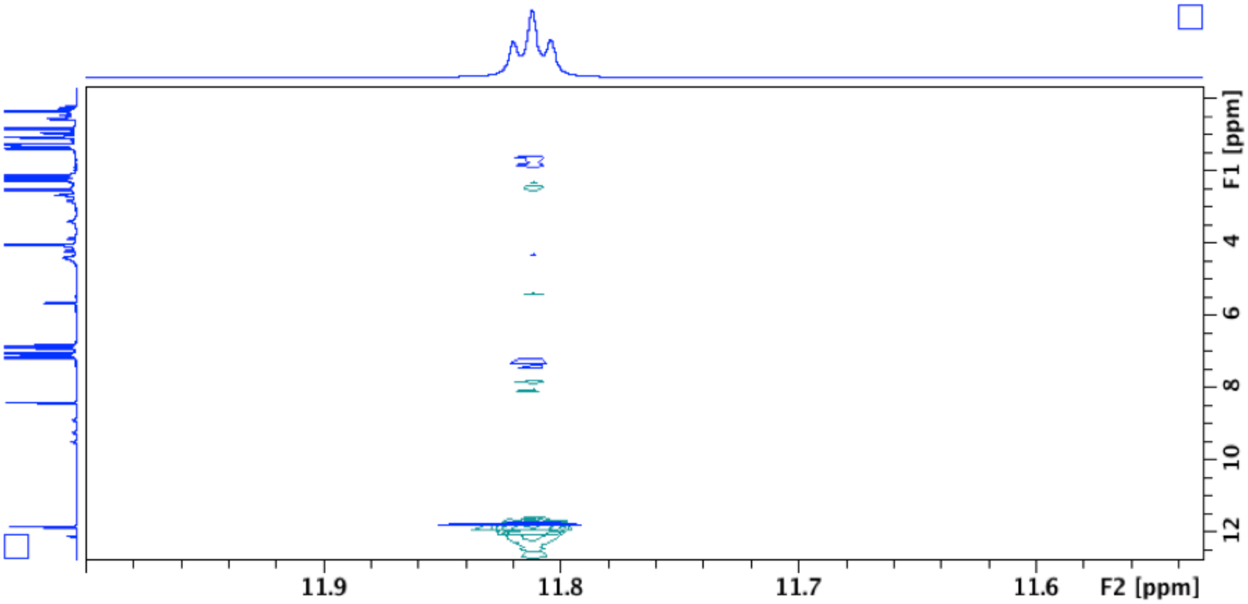

Figure S13: ^{1}H-^{1}H NOESY NMR Spectrum of **3** in C_7D_8, 500 MHz, 298 K, feature of Ti=CH_2

Molecular Structures and Crystallographic Tables

X-ray Crystallography

Crystallographic data for are summarized Table S1 and S2. Suitable single crystals for X-ray analysis of **1** or **3** were placed on the end of a Cryoloop coated in NVH oil. The X-ray intensity data collection was carried out on a Bruker APEXII CCD area detector using graphite-monochromated Mo-K radiation (l = 0.71073 Å) at 100(1) K. Preliminary indexing was performed from a series of thirty-six 0.5° rotation frames with exposures of 10 seconds. Rotation frames were integrated using SAINT,[7] producing a listing of non-averaged F^2 and s(F^2) values which were then passed to the SHELXTL[8] program package for further processing and structure solution. The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS.[9] All calculations were performed using SHELXS[10] and SHELXL.[11] The structures were solved by Patterson and Fourier transform methods. All reflections were used during refinement. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using riding models with exception for methylidene of **3.**

Table S1. Crystallographic Data for Complex 1

Molecular formula	C100 H154 N4 P4 Ti2
Formula weight	815.98
Temperature (K)	100(2)
Crystal system	Triclinic
Space group	P
Cell constants:	
a (Å)	12.3342(3)
b (Å)	14.2207(4)
c (Å)	28.9433(8)
Volume ($Å^3$)	4833.9(2)
Z	4
Density (calcd mg/m3)	1.121
Abs coeff (mm-1)	0.277
F(000)	1772
Wavelength	0.71073
q range for data collection (°)	1.43 to 27.56
# Reflns collected	21616
Refinement method	Full-matrix least-squares on F2
R_1^a	0.0814
wR_2^b	0.0575

Goodness-of-fit on *F2c*	1.044

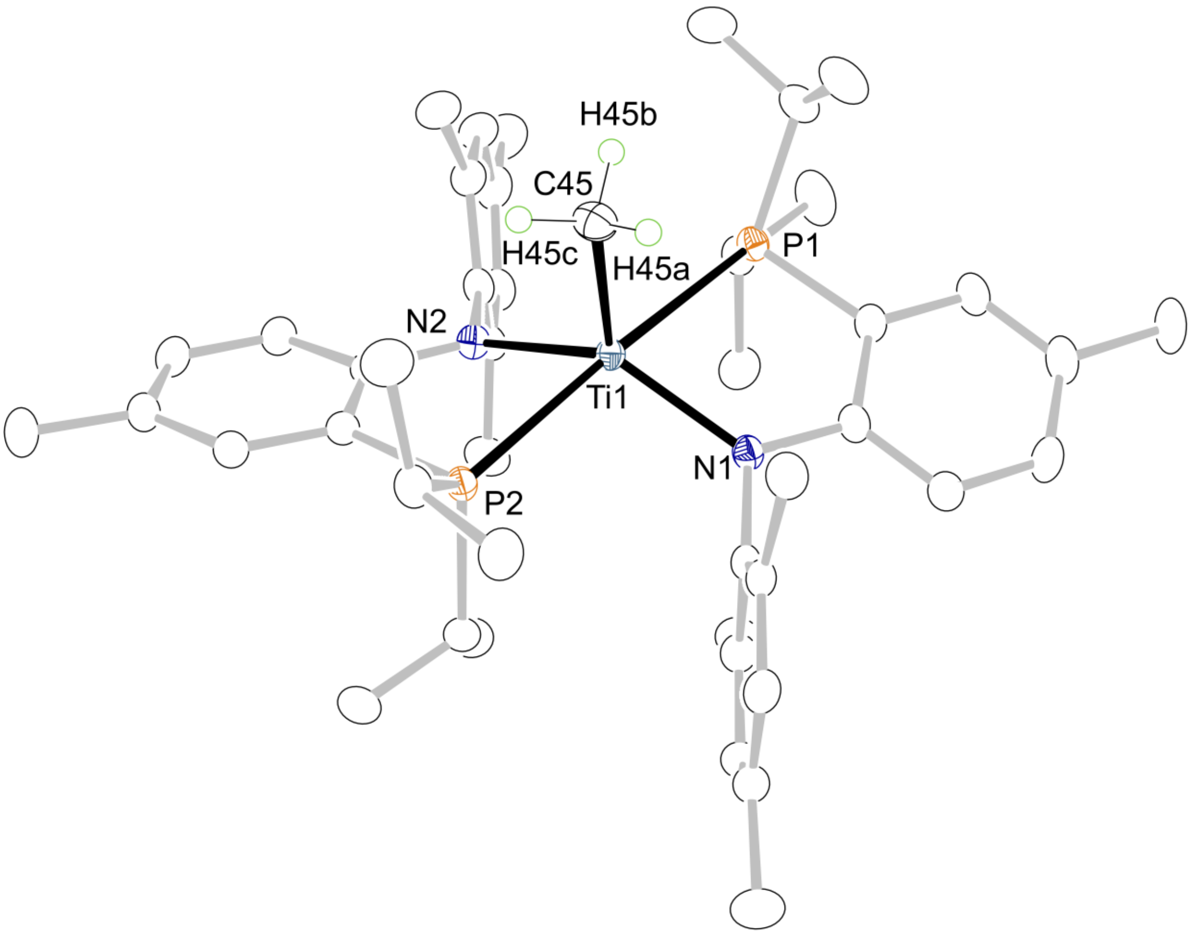

Figure S14. Molecular structure of **1**, showing thermal ellipsoids at 50% probability level. H-atoms, with the exception of those on C45, have been omitted for clarity.

Table S2. Crystallographic Data for 2

Molecular formula	C45 H64 N2 P2 Ti
Formula weight	742.82
Temperature (K)	100(2)
Crystal system	Monoclinic

Space group	C 1 2/c 1
Cell constants:	
a (Å)	15.3286(7)
b (Å)	12.3358(5)
c (Å)	22.4869(11)
Volume (Å^3)	4230.8(3)
Z	4
Density (calcd mg/m3)	1.166
Abs coeff (mm-1)	0.310
F(000)	1600
Wavelength	0.71073
q range for data collection (°)	1.43 to 27.56
# Reflns collected	59618
Refinement method	Full-matrix least-squares on F2
R_1[a]	0.0484
wR_2[b]	0.0374
Goodness-of-fit on *F2c*	1.058

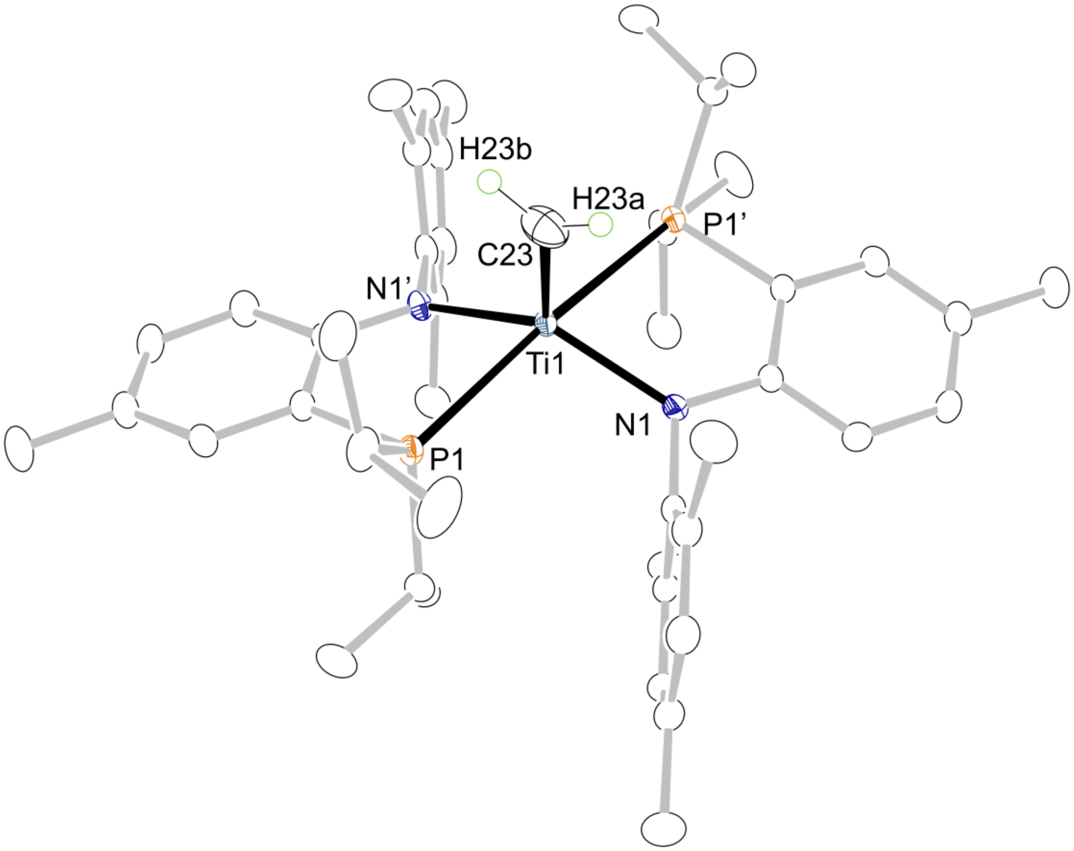

Figure S15. Molecular structure of **1**, showing thermal ellipsoids at 50% probability level. H-atoms, with the exception of those on C23, have been omitted for clarity.

Computational Details

All calculation results were obtained using density functional theory[12] as implemented in the Jaguar 9.1 suite[13] of ab initio quantum chemistry programs. The geometry optimizations were carried out with B3LYP[14–17] functional and 6-31G** basis set. Titanium was represented using the Los Alamos LACVP basis set[18–20] that includes effective core potentials. The energies of the optimized structures were readdressed by single-point calculations using cc-pVTZ(-f)[21] basis set. Titanium used a modified version of LACVP denoted LACV3P. Vibrational frequency calculations were carried out at the B3LYP/6-31G** level of theory. Standard approximation was used to obtain zero-point vibrational energy and entropy corrections. Solvation energies were evaluated by Self-Consistent Reaction field (SCRF)[22–24] calculations with the dielectric constant $\varepsilon = 4.3$ (Ethyl Ether) using the optimized gas phase structures. The natural bond orbital (NBO) analysis was carried out using NBO 6.0 program[25–27] in the Jaguar 9.1 suite. The Gibbs free energy in solution phase was computed as follows[28]:

$$G(\mathrm{Sol}) = G(\mathrm{gas}) + G^{\mathrm{solv}} \tag{1}$$

$$G(\mathrm{gas}) = H(\mathrm{gas}) - TS(\mathrm{gas}) \tag{2}$$

$$H(\mathrm{gas}) = E(\mathrm{SCF}) + ZPE \tag{3}$$

$$\Delta G(\mathrm{Sol}) = \Sigma G(\mathrm{Sol}) \text{ for products} - \Sigma G(\mathrm{Sol}) \text{ for reactants} \tag{4}$$

Cartesian Coordinates of All Computed Structures

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3-Singlet

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Ti	5.980214569	8.332128337	16.777293945
P	7.322321404	8.476039008	19.143521281
N	7.864935571	9.004241905	16.235341647
C	9.032774882	8.939102894	17.012150513
C	10.322553043	9.179381453	16.470400700
H	10.417693252	9.454431158	15.426887182
C	11.474310358	9.060399601	17.235856107
H	12.436221248	9.249990767	16.762109745
C	11.432019652	8.697293442	18.588458309
C	10.166040211	8.490615086	19.137090366
H	10.104042589	8.216342066	20.186561691
C	8.981307752	8.623147333	18.395563386
C	12.693775256	8.553691612	19.407373965
H	13.382380227	7.822731301	18.965854055
H	12.472286072	8.223483924	20.427110657
H	13.240570926	9.502526277	19.479945536
C	7.537446559	7.030357960	20.343671006
H	8.395528358	7.314689515	20.963988049
C	7.895351703	5.728657673	19.614190318
H	7.082867751	5.412607557	18.953921862
H	8.073718740	4.932391147	20.347457505
H	8.798742040	5.839046709	19.007914869
C	6.333907825	6.830106411	21.275570765
H	5.469604252	6.453004327	20.725455150
H	6.030959814	7.748520449	21.786103815
H	6.585593587	6.089146803	22.044450051

C	7.192325833	9.986208244	20.290280708
H	6.145009239	9.976556819	20.611877501
C	7.431671475	11.270875893	19.482846298
H	8.473222992	11.337905390	19.151902913
H	7.217390371	12.149056222	20.103841099
H	6.793156255	11.326323040	18.599576778
C	8.091443873	9.979056157	21.536420184
H	9.151669300	9.998990472	21.265191679
H	7.918451674	9.118137961	22.187714780
H	7.892709874	10.880265376	22.130318297
C	8.087500669	9.460626362	14.889372076
C	8.458955405	8.549638424	13.874819028
C	8.700582092	9.026240210	12.579270376
H	8.986949433	8.314275244	11.807304823
C	8.609659155	10.381832046	12.254274785
C	8.290794740	11.274867437	13.283072702
H	8.248197231	12.341487988	13.067928618
C	8.045775076	10.844301548	14.590720478
C	8.688848777	7.091171543	14.191172997
H	8.918096212	6.527554881	13.282022703
H	7.822456768	6.636720067	14.677171645
H	9.533351278	6.975570592	14.880588099
C	8.862585725	10.876834809	10.848259767
H	9.224743489	10.073515190	10.199960435
H	9.608011660	11.680602267	10.834481601
H	7.949257812	11.281717357	10.394769362
C	7.825143411	11.867043025	15.678598047
H	7.669653736	12.863610357	15.255143318
H	8.693233914	11.915029282	16.346911092
H	6.966434031	11.621969889	16.307115594

C	5.973961148	6.463837612	16.773514302
H	6.847495100	5.846112026	16.536271895
H	5.094507307	5.853055745	17.006931233
P	4.636790350	8.481908776	14.413335255
N	4.097725237	9.007996437	17.322914477
C	2.928709523	8.941275522	16.547578542
C	1.639219045	9.176496205	17.092291460
H	1.545138921	9.446120926	18.137362782
C	0.486873014	9.060310070	16.327193844
H	-0.474660710	9.247493641	16.802538159
C	0.528110430	8.703897144	14.972759206
C	1.793468589	8.497794567	14.422490257
H	1.854918237	8.226660946	13.372102762
C	2.978823747	8.628100759	15.163242929
C	-0.734250292	8.565447032	14.154020269
H	-1.422942382	7.832389480	14.591850928
H	-0.513730694	8.241022203	13.132240708
H	-1.280548151	9.514974797	14.087294721
C	4.426090604	7.036800743	13.213406790
H	3.571814547	7.321248008	12.587635473
C	4.064349327	5.734752171	13.939080811
H	4.875271001	5.415948257	14.599753679
H	3.885899074	4.940757200	13.203484065
H	3.159983679	5.845464823	14.543694779
C	5.637379018	6.838547744	12.290812579
H	6.499677372	6.467929309	12.849064755
H	5.939662763	7.756581735	11.779256608
H	5.395118011	6.093473385	11.522819323
C	4.763701022	9.989276588	13.262450419
H	5.809799147	9.978119957	12.937323213

C	4.528508421	11.276465059	14.066439012
H	3.487413340	11.347565033	14.397788494
H	4.745172379	12.152361278	13.443052289
H	5.167276682	11.332064396	14.949280432
C	3.860195114	9.980109059	12.019467774
H	2.800662126	9.999121304	12.293831084
H	4.032201337	9.119023464	11.368140113
H	4.055961518	10.881160661	11.424279850
C	3.877955806	9.466713628	18.669031515
C	3.530930398	8.552125745	19.688691211
C	3.301362534	9.026625379	20.987412400
H	3.038860373	8.311404386	21.764805462
C	3.372867588	10.384289743	21.308283321
C	3.661318662	11.280849169	20.273523185
H	3.685811700	12.348606551	20.485736675
C	3.899502225	10.851931003	18.964242155
C	3.311362893	7.091735074	19.373950358
H	3.091735393	6.526532177	20.284477460
H	4.177885103	6.643810362	18.882345265
H	2.463527001	6.970011471	18.689684272
C	3.132235369	10.878012400	22.716892020
H	2.798366140	10.069130622	23.373394169
H	2.369785575	11.665415723	22.740628130
H	4.043800331	11.304304515	23.154029411
C	4.092947723	11.876246481	17.873007660
H	4.228908599	12.876931603	18.293454355
H	3.221236412	11.903885875	17.208262810
H	4.954452985	11.648113343	17.241886990

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3-Triplet

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Ti	5.979923075	8.347975707	16.781701496
P	7.361715533	8.344074649	19.146039188
N	7.863009345	9.099189036	16.271993068
C	9.030572117	9.054919196	17.050808957
C	10.308607840	9.394090209	16.528532963
H	10.386280268	9.739664447	15.504511532
C	11.469068273	9.281996833	17.282557133
H	12.418661594	9.549242344	16.821542171
C	11.449658861	8.828659210	18.609120153
C	10.197120844	8.523028490	19.142775377
H	10.151564563	8.175266656	20.172036476
C	9.004291350	8.640097531	18.411502557
C	12.719234852	8.691350165	19.417134897
H	13.436617021	8.015275682	18.935172340
H	12.514854131	8.295049665	20.416979074
H	13.227043731	9.656201498	19.543465994
C	7.623641303	6.844866601	20.263304476
H	8.414902441	7.138881241	20.963423056
C	8.121802202	5.624494383	19.477740574
H	7.365816427	5.280037668	18.765007416
H	8.332854875	4.799597039	20.169374760
H	9.037553437	5.844208823	18.922445610
C	6.367732311	6.502193879	21.078676900
H	5.571527284	6.125801988	20.431023233
H	5.970765472	7.359795645	21.630068992
H	6.601874211	5.716034377	21.807202384
C	7.136556053	9.785792757	20.362663040
H	6.075384285	9.742044636	20.628465662
C	7.395870202	11.113829957	19.635111269

H	8.456941670	11.225830097	19.391251707
H	7.101481372	11.952251153	20.276976430
H	6.827419964	11.195146611	18.706279280
C	7.972381505	9.722015548	21.650114871
H	9.045627153	9.751291474	21.435338275
H	7.765289859	8.833733460	22.253477698
H	7.743417179	10.596748648	22.272118060
C	8.081528736	9.553972037	14.927692969
C	8.448988387	8.641184474	13.912017249
C	8.655962251	9.107891794	12.607501870
H	8.937517240	8.392964596	11.836026543
C	8.541274544	10.460169337	12.274056010
C	8.229346129	11.356568026	13.301582763
H	8.169105073	12.421011140	13.079154662
C	8.013247448	10.933633792	14.617116055
C	8.705055496	7.190317399	14.238078849
H	8.934550842	6.620991603	13.332379570
H	7.848960570	6.726677457	14.734039644
H	9.554878325	7.092460031	14.923901271
C	8.759430438	10.946218142	10.859233429
H	9.148413123	10.149552046	10.217930044
H	9.471088623	11.779569278	10.826949482
H	7.825978422	11.306871517	10.408837055
C	7.790537026	11.959913857	15.701484260
H	7.628943640	12.954363325	15.275049906
H	8.658887838	12.014429912	16.369409881
H	6.933078498	11.712959629	16.332189297
C	5.971236813	6.291339122	16.784440355
H	6.809227224	5.658721703	16.469002081
H	5.126653648	5.668643720	17.102468510

P	4.598834988	8.345357052	14.418664412
N	4.100469430	9.113102301	17.286165684
C	2.930552567	9.058492753	16.510990523
C	1.652172240	9.397244355	17.032834360
H	1.575429081	9.751908058	18.053886381
C	0.490135858	9.272967348	16.282482085
H	-0.459345292	9.539354811	16.744280429
C	0.507362226	8.808869490	14.959361563
C	1.760889958	8.505914209	14.425413253
H	1.806368716	8.151514210	13.398410154
C	2.954967866	8.633843248	15.153237204
C	-0.763938302	8.655505362	14.157296577
H	-1.468256511	7.966385729	14.640195150
H	-0.558548893	8.266198430	13.154922924
H	-1.287204443	9.612845206	14.037631367
C	4.343982908	6.852892842	13.291354628
H	3.525275127	7.133710714	12.617926570
C	3.902302922	5.611236021	14.077596093
H	4.687908220	5.280550673	14.764485904
H	3.693568204	4.787670715	13.383696917
H	2.997791683	5.800146836	14.661886881
C	5.582787655	6.553738008	12.434025060
H	6.410321238	6.195787584	13.052008567
H	5.936155300	7.427246751	11.877980712
H	5.348014694	5.767064363	11.706243189
C	4.817700850	9.794284061	13.210710444
H	5.877077436	9.750114383	12.937995125
C	4.565349632	11.118381566	13.947552849
H	3.506765949	11.228089755	14.203266266
H	4.851525083	11.960658320	13.306938376

H	5.143842976	11.195319744	14.870273431
C	3.972302503	9.738199513	11.929485814
H	2.900943629	9.764374671	12.153881690
H	4.175676249	8.853970212	11.318826959
H	4.195279589	10.617222887	11.311409484
C	3.884434317	9.572138129	18.629234174
C	3.512925805	8.661598864	19.645244482
C	3.300347424	9.130591486	20.947839807
H	3.013850757	8.417228605	21.718955696
C	3.416111465	10.483091756	21.279696737
C	3.738198635	11.377006162	20.252922756
H	3.801717467	12.441328089	20.475048329
C	3.960942498	10.952156798	18.938755324
C	3.260234167	7.209392126	19.321994604
H	3.041456749	6.639401888	20.229867016
H	4.114336002	6.749647237	18.818809015
H	2.404952268	7.107003616	18.643645766
C	3.190214466	10.970639983	22.692839035
H	2.796533281	10.174684239	23.332195768
H	2.479285775	11.804750169	22.720761092
H	4.121410370	11.330209632	23.148722509
C	4.196786466	11.975655518	17.854812391
H	4.330461565	12.974747855	18.280234512
H	3.347094370	12.012171860	17.162398715
H	5.076235388	11.740510047	17.250170175

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