Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

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General Considerations

All reactions were carried out under an inert atmosphere of argon or nitrogen with rigorous exclusion of oxygen and moisture using standard glovebox and Schlenk techniques. The glass equipment was stored in an oven at 120 °C and evacuated prior to use. Solvents and liquid educts were dried according to standard procedures and/or freeze-pump-thaw degassed three times prior to use. Solvents were distilled over Na/K alloy and benzophenone or CaH_2 under nitrogen atmosphere. Solid materials were stored and weighed in a glovebox or dried under high vacuum before use. Cp^*TiCl_3 was synthesized according to a literature procedure.[1] The iminophosphane **L1** was synthesized according to a literature procedure.[2]

NMR spectra were recorded on Bruker Avance 300, Bruker Avance 500, and Bruker Avance III 500 spectrometers. ^1H NMR spectra were referenced to the residual solvent resonance as internal standard (benzene-d_6 (C_6D_6): $\delta^1H(C_6D_5H)$ = 7.16 ppm) and $^{13}C\{^1H\}$ spectra were referenced by using the central line of the solvent signal (benzene-d_6 (C_6D_6): $\delta^{13}C\{^1H\}(C_6D_6)$ = 128.06 ppm). $^{31}P\{^1H\}$ NMR were referenced against external standards (H_3PO_3, $\delta(^{31}P\{^1H\})$ H_3PO_4 0.0 ppm). The given chemical shifts of ^{15}N result out of $^{15}N,^1H$ HMBC NMR experiments with nitromethane as external standard (δ = 378.9 vs. NH_3).

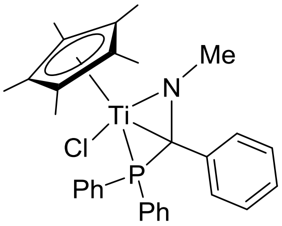
Melting points were determined using a “Mel-Temp” apparatus by Laboratory Devices, Cambridge, U.K..

Infrared spectra were performed on a Bruker Tensor 27 spectrometer with a MKII Reflection Golden Gate Single Diamond ATR system.

Combustion analyses were carried out on a EuroEA 3000 Elemental Analyzer. Satisfactory combustion analyses of **1** could not be obtained due to its high reactivity.

Synthesis and Characterization of the Compounds:

Synthesis of 1 and 2:



1

Cp*TiCl$_3$ (0.935 g, 3.230 mmol), magnesium (0.079 g, 3.230 mmol), and iminophosphane **L1** (0.980 g, 3.230 mmol) were dissolved in 20 mL of tetrahydrofuran and stirred for 16 h at room temperature. The solvent was removed under vacuum, the resulting reddish solid was filtrated with *n*-hexane (4×15 mL). Removal of all volatiles, solving the residue in *n*-hexane and storage at -26 °C for 48 h resulted in the precipitation of red crystals, which were suitable for single-crystal X-ray diffraction. Direct removal of all volatiles under vacuum yielded a red-brown solid, whose NMR spectrum is shown in Figure **S3**. Subsequent removal of all volatiles from the supernatant, solving the residue in toluene, and storage at -26 °C yielded **2** as yellow crystals.

1 is extremely sensitive toward air and moisture, but can be stored for weeks in the glovebox without indication of decomposition. Due to its high air- and moisture sensitivity, elemental analysis failed.

Yield: 0.301 g (0.577 mmol, 18% crystalline yield).

Melting point: 118-120 °C (dec.).

IR (ATR): $\tilde{\nu}$ = 3052, 2977, 2952, 2908, 2855, 1672, 1586, 1483, 1434, 1376, 1288, 1210, 1178, 1161, 1096, 1026, 1000, 977, 891, 789, 759, 742, 692, 618 cm^{-1}.

^{1}H NMR (500 MHz, C_6D_6, 305 K): δ = 2.04 (s, 15H, C_5Me_5), 3.34 (d, $^4J_{P,H}$ = 8.3 Hz, 3H, NCH_3), 6.79-6.82 (m, 1H, *p*-$CH_{Ph}C_qN$), 6.86-6.88 (m, 3H, 2×*o*-$CH_{Ph}C_qN$, *p*-$CH_{Ph}P$), 6.93-6.94 (m, 2H, 2×*o*-$CH_{Ph}P$), 7.01-7.04 (m, 2H, 2×*m*-$CH_{Ph}C_qN$), 7.16-7.21 (m, 3H, 2×*o*-$CH_{Ph}P$, *p*-$CH_{Ph}P$)*, 7.55-7.60 (m, 2H, 2×*m*-$CH_{Ph}P$), 7.87-7.91 (m, 2H, 2×*m*-$CH_{Ph}P$) ppm.

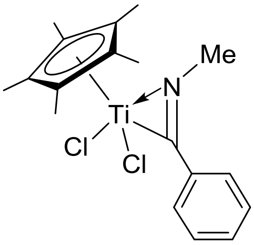
^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 305 K): δ = 12.5 ($C_5\underline{Me}_5$), 43.4 (NCH_3), 69.9 (d, $^1J_{C,P}$ = 30.9 Hz, NC_q), 121.6 ($\underline{C}_5Me_5$), 124.0 (*p*-$\underline{C}H_{Ph}C_qN$), 126.6 (*o*-$\underline{C}H_{Ph}C_qN$), 127.7

(*m*-$\underline{C}H_{Ph}C_{q}N$), 129.0 (d, $^{2}J_{C,P}$ = 10.0 Hz, 2×*o*-$CH_{Ph}P$), 129.2 (d, $^{2}J_{C,P}$ = 9.6 Hz, 2×*o*-$CH_{Ph}P$), 130.0 (*p*-$CH_{Ph}P$), 130.9 (*p*-$CH_{Ph}P$), 132.1 ($\underline{C}_{q,Ph}C_{q}N$), 134.1 (d, $^{3}J_{C,P}$ = 14.1 Hz, 2×*m*-$CH_{Ph}P$), 135.0 (d, $^{3}J_{C,P}$ = 14.0 Hz, 2×*m*-$CH_{Ph}P$), 139.7 (d, $^{1}J_{C,P}$ = 19.7 Hz, 2×$C_{q,Ph}P$) ppm.

* = overlap with C_6D_6 signal

^{31}P{^{1}H} NMR (202 MHz, C_6D_6, 305 K): δ = -44.2 ppm.

^{15}N NMR (202 MHz, C_6D_6, 300 K): δ = 278.6 ppm.



2

Yield: 0.047 g (0.126 mmol, crystalline yield)

Melting point: >250 °C.

IR (ATR): $\tilde{\nu}$ = 3056, 2982, 2909, 2856, 1672, 1614, 1593 (C=N), 1488, 1438, 1373, 1352, 1240, 1175, 1148, 1131, 1101, 1080, 1029, 978, 963, 926, 889, 843, 804, 755, 745, 712, 690, 640, 619, 612 cm^{-1}.

^{1}H NMR (500 MHz, C_6D_6, 305 K): δ = 1.87 (s, 15H, C_5Me_5), 3.23 (s, 3H, NCH_3), 7.07-7.12 (m, 3H, 2×*m*-$CH_{Ph}C_{q}$=N, *p*-$CH_{Ph}C_{q}$=N), 7.56-7.57 (m, 2H, 2×*o*-$CH_{Ph}C_{q}$=N) ppm.

^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 305 K): δ = 12.9 ($C_5\underline{Me}_5$), 37.6 (NCH_3), 126.6 ($\underline{C}_5Me_5$), 129.1 (2×*o*-$\underline{C}H_{Ph}C_{q}$=N), 130.5 (2×*m*-$\underline{C}H_{Ph}C_{q}$=N), 131.1 ($C_{q,Ph}$), 132.2 (*p*-$\underline{C}H_{Ph}C_{q}$=N), 230.5 (N=C_{q}) ppm.

^{15}N NMR (202 MHz, C_6D_6, 300 K): δ = 275.3 ppm.

EA: Anal. calcd. for $C_{18}H_{23}Cl_2NTi$: C, 58.09; H, 6.23; N, 3.76; Found: C, 57.52; H, 6.57; N, 3.44.

Crystallographic Data:

Suitable crystals were selected and measured on a 'Bruker APEX-II CCD' diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The crystal was kept at 100.15 K during data collection. Using Olex2,[3] the structure was solved with the ShelXS[4] structure solution program using Direct Methods and refined with the ShelXL[5] refinement package using Least Squares minimisation.

Table S1: Crystal Structure Data for Compounds **1**, **2**.

	1	**2**
CCDC	1877413	1877412
empirical formula	$C_{30}H_{33}ClNPTi$	$C_{18}H_{23}Cl_2NTi$
fw	521.89	372.17
colour	red	yellow
Habit	plate	block
cryst dimens, mm	0.40 x 0.36 x 0.08	0.20 x 0.14 x 0.06
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1$
a, Å	10.7515(4)	8.9069(8)
b, Å	16.5847(6)	13.7152(12)
c, Å	16.1243(6)	15.0922(13)
α, deg	90	90
β, deg	108.8885(10)	101.607(2)
γ, deg	90	90
V, Å^3	2720.30(17)	1806.0(3)
Z	4	4
D$_{\text{caclcd}}$, g cm^{-3}	1.274	1.369
μ, mm^{-1}	0.490	0.766
T, K	200(2)	100(2)
θ range, deg	1.814 – 32.031	1.377 – 33.724
no. of rflns collected	104120	97555
no. of indep rflns (R(int))	9474 (0.0382)	14412 0.0450
no. of rflns with $I>2\sigma(I)$	7625	13039
abs cor	numerical	numerical
max, min transmission	0.9666 and 0.8445	0.9533 and 0.8715
final R indices [$I>2\sigma(I)$]	R1 = 0.0360 wR2 = 0.0921	R1 = 0.0325 wR2 = 0.0701
R indices (all data)	R1 = 0.0501 wR2 = 0.1010	R1 = 0.0393 wR2 = 0.0732
GOF on F^2	1.044	1.045
largest diff peak / hole (e.Å^{-3})	0.427 / -0.200	0.496 / -0.458

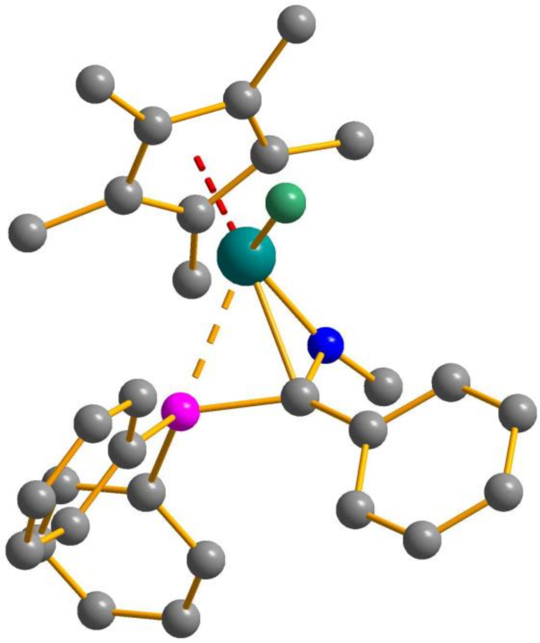


Figure S1: Molecular structure of **1**.

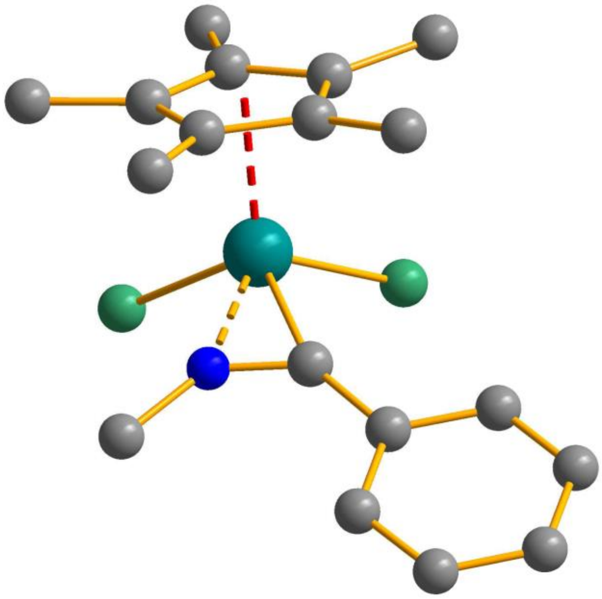


Figure S2: Molecular structure of **2**.

NMR Spectra:

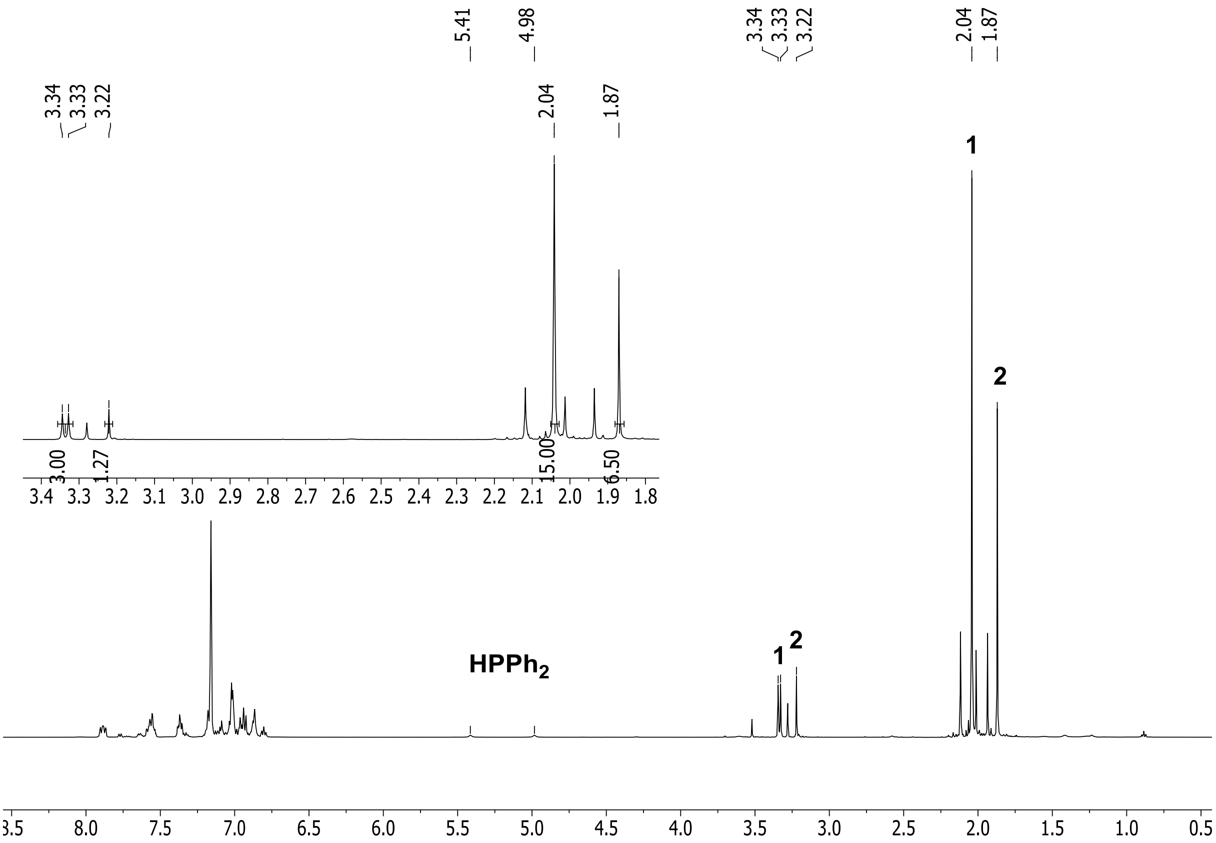


Figure S3: ^{1}H NMR spectrum of the crude product (500 MHz, C_6D_6, rt).

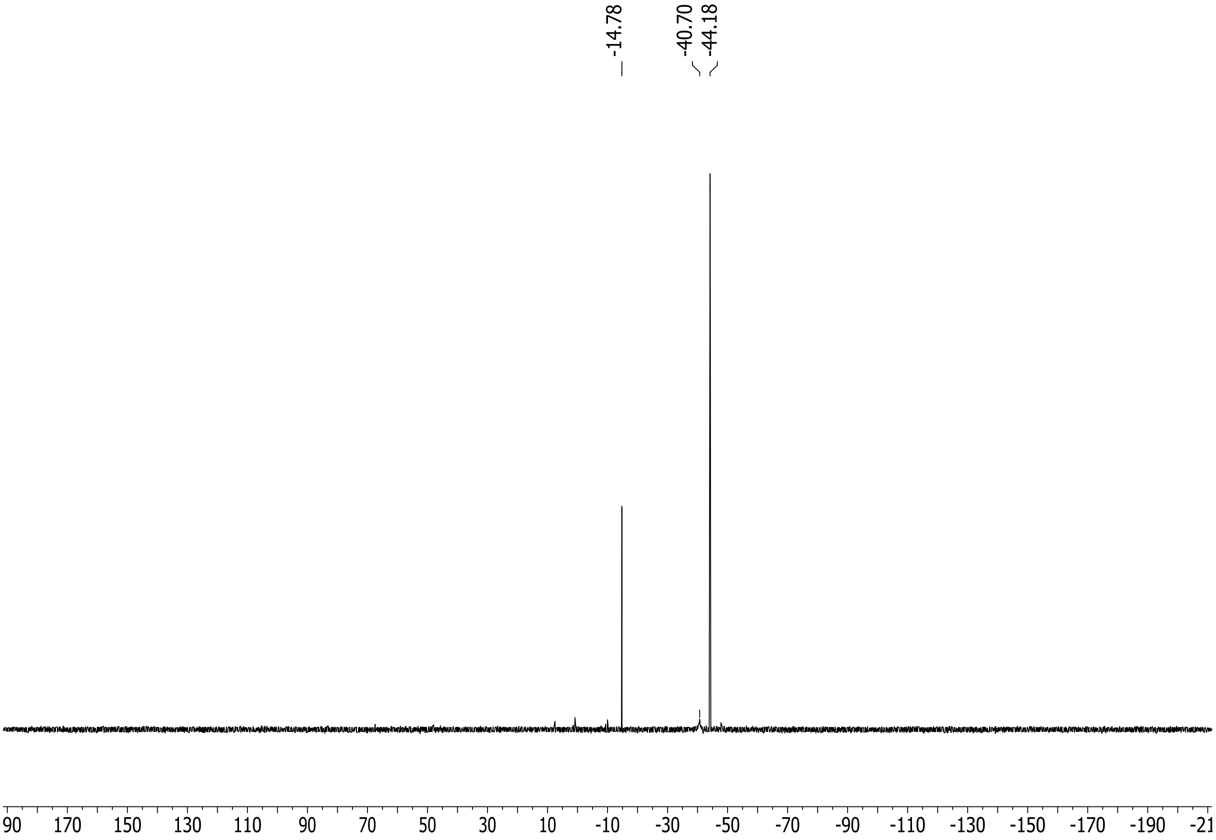


Figure S4: ^{31}P{^{1}H} NMR spectrum of the crude product (202 MHz, C_6D_6, rt).

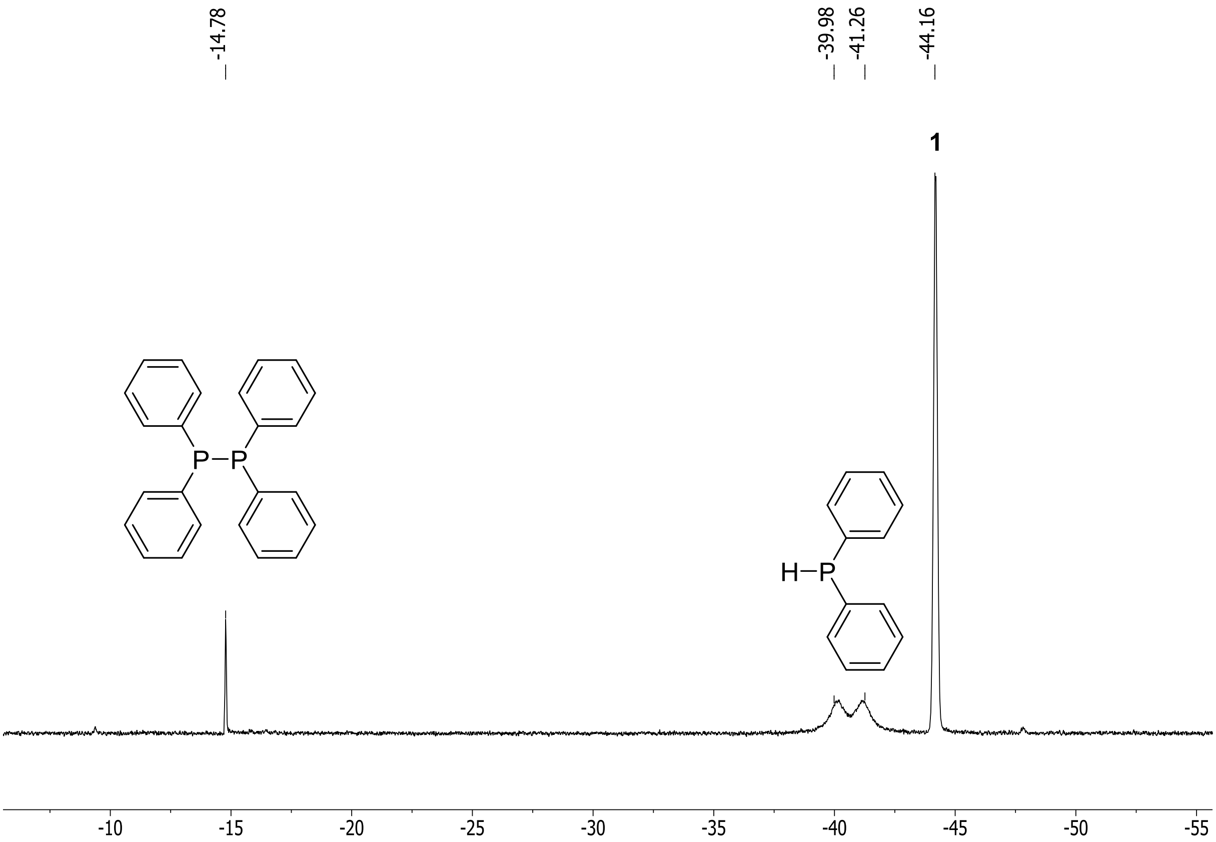


Figure S5: ^{31}P NMR spectrum of the crude product (202 MHz, C_6D_6, rt).

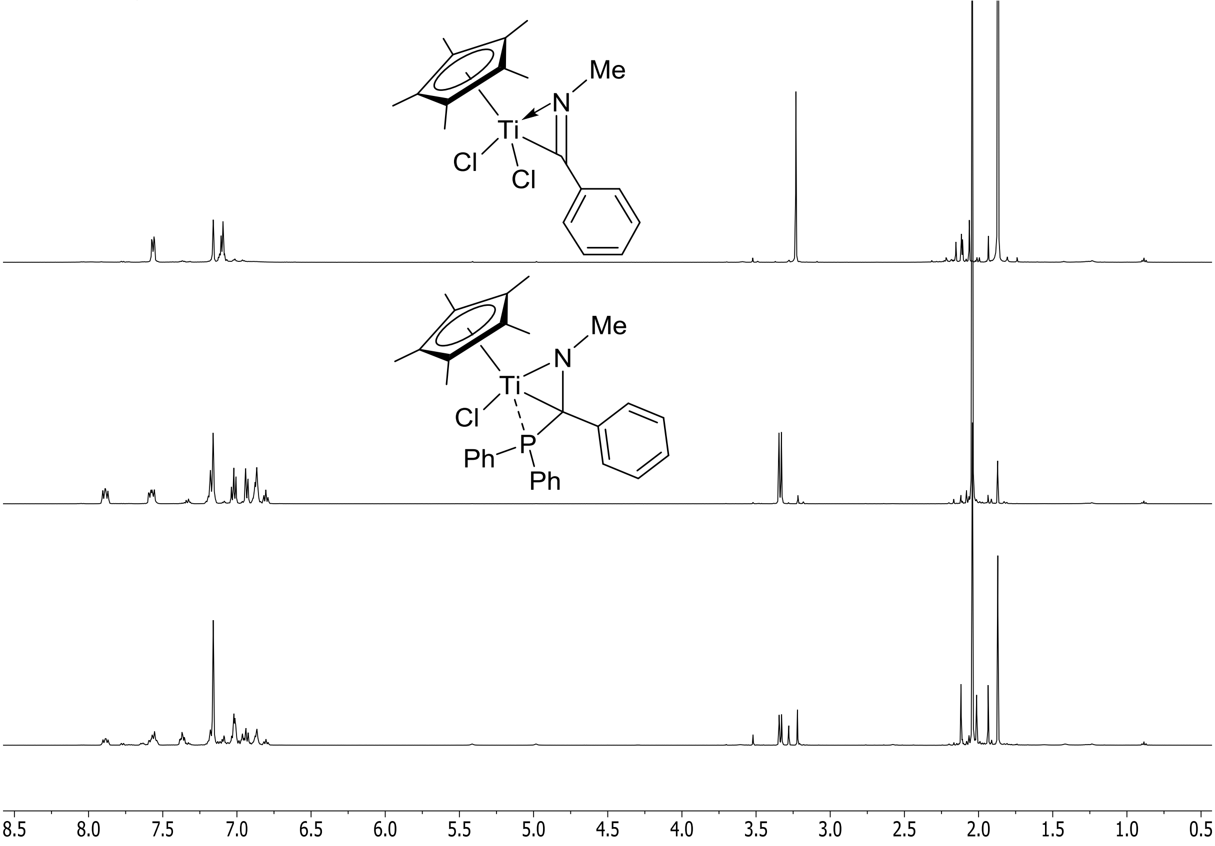


Figure S6: ^{1}H NMR spectrum of the crude product (bottom, 500 MHz, C_6D_6, rt), **1** (middle, 500 MHz, C_6D_6, rt), and **2** (top, 500 MHz, C_6D_6, rt).

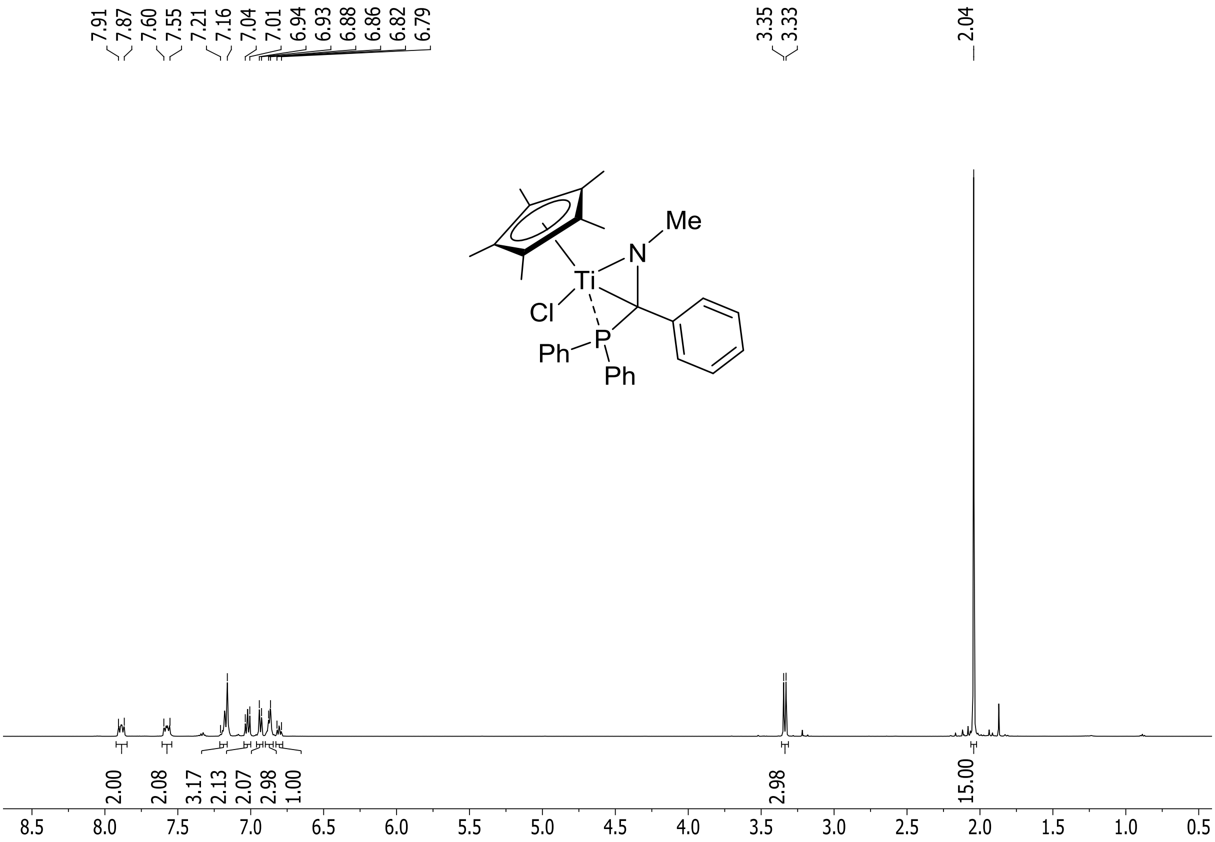


Figure S7: ^{1}H NMR spectrum of **1** (500 MHz, C_6D_6, rt).

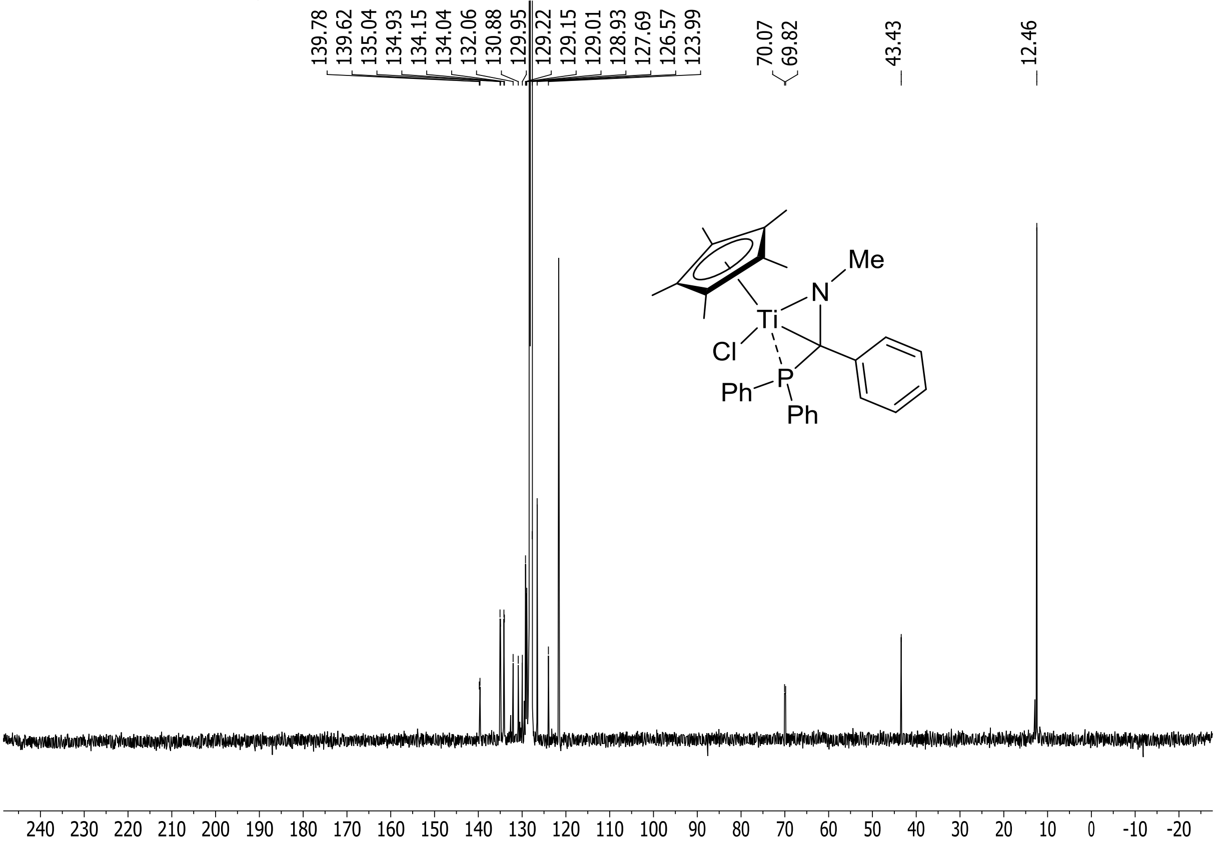


Figure S8: $^{13}C\{^{1}H\}$ NMR spectrum of **1** (126 MHz, C_6D_6, rt).

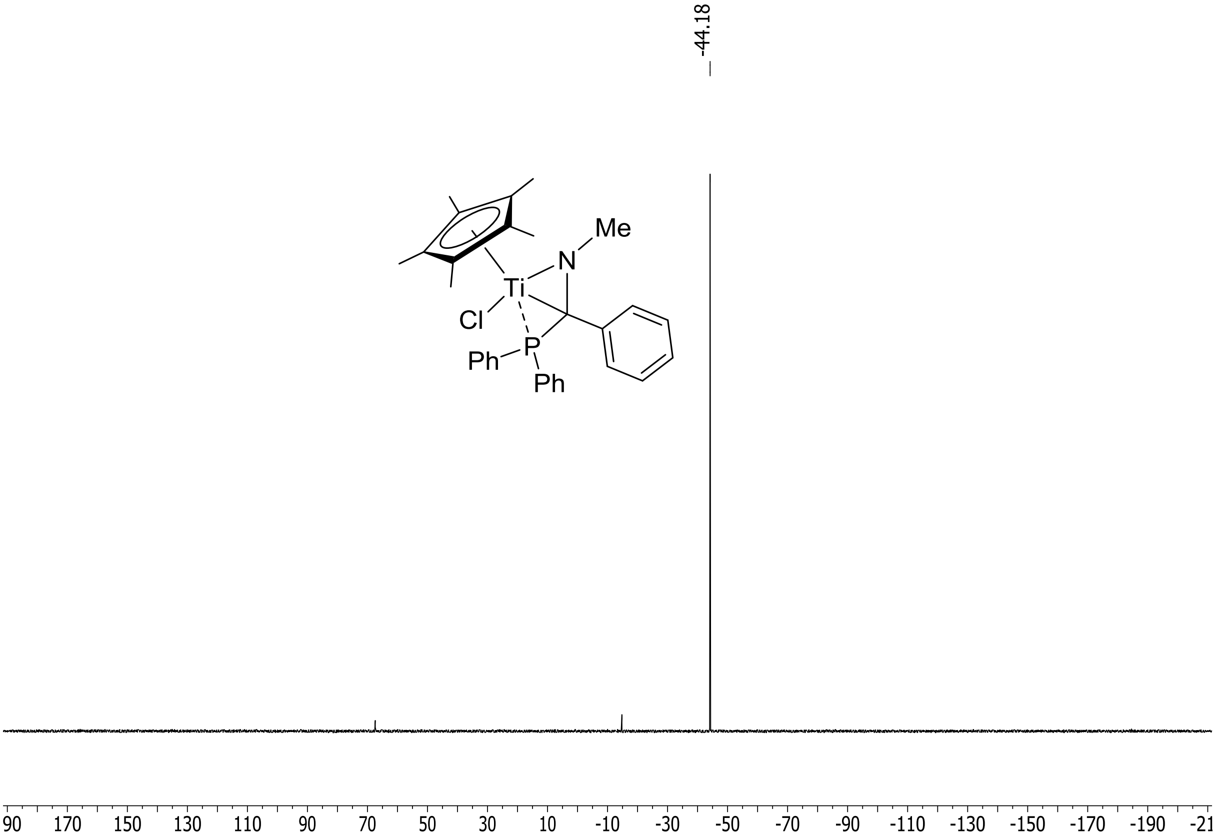


Figure S9: $^{31}P\{^1H\}$ NMR spectrum of **1** (202 MHz, C_6D_6, rt).

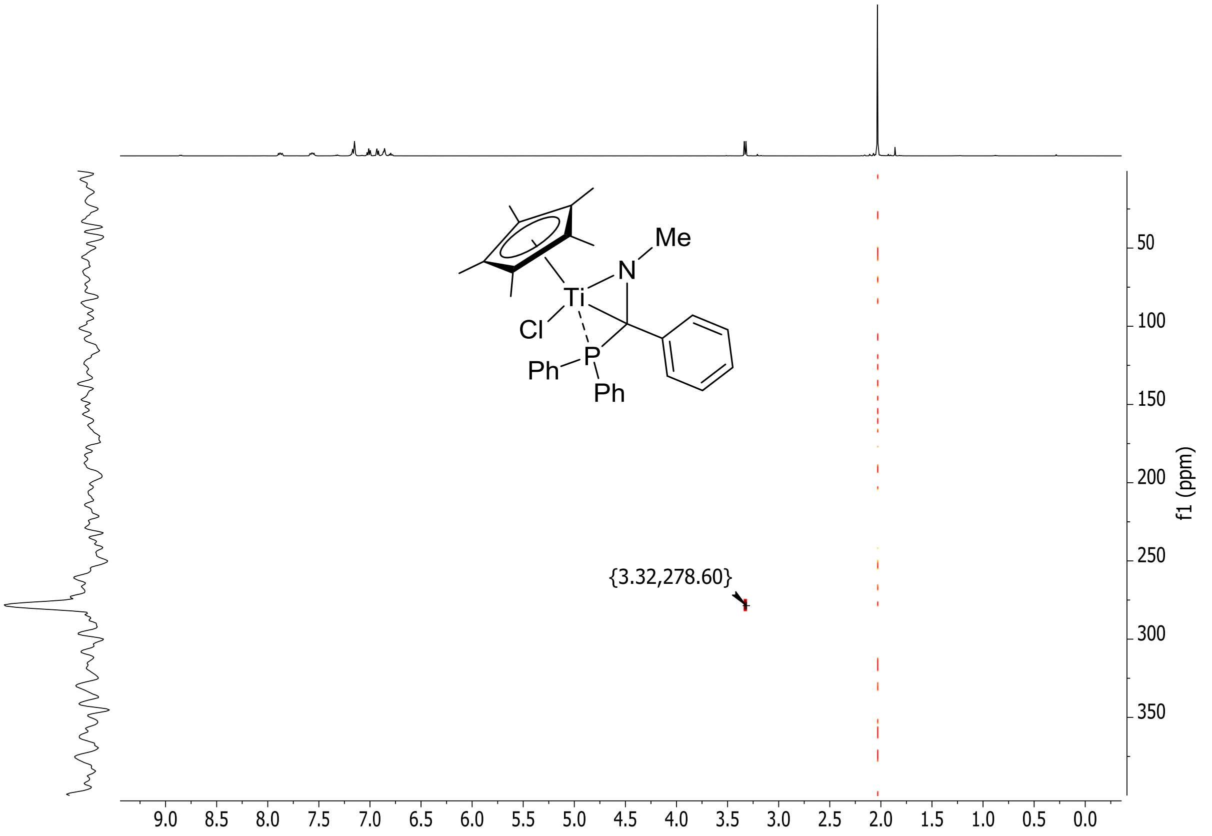


Figure S10: $^1H/^{15}N$ HMBC NMR spectrum of **1** (51 MHz, C_6D_6, rt).

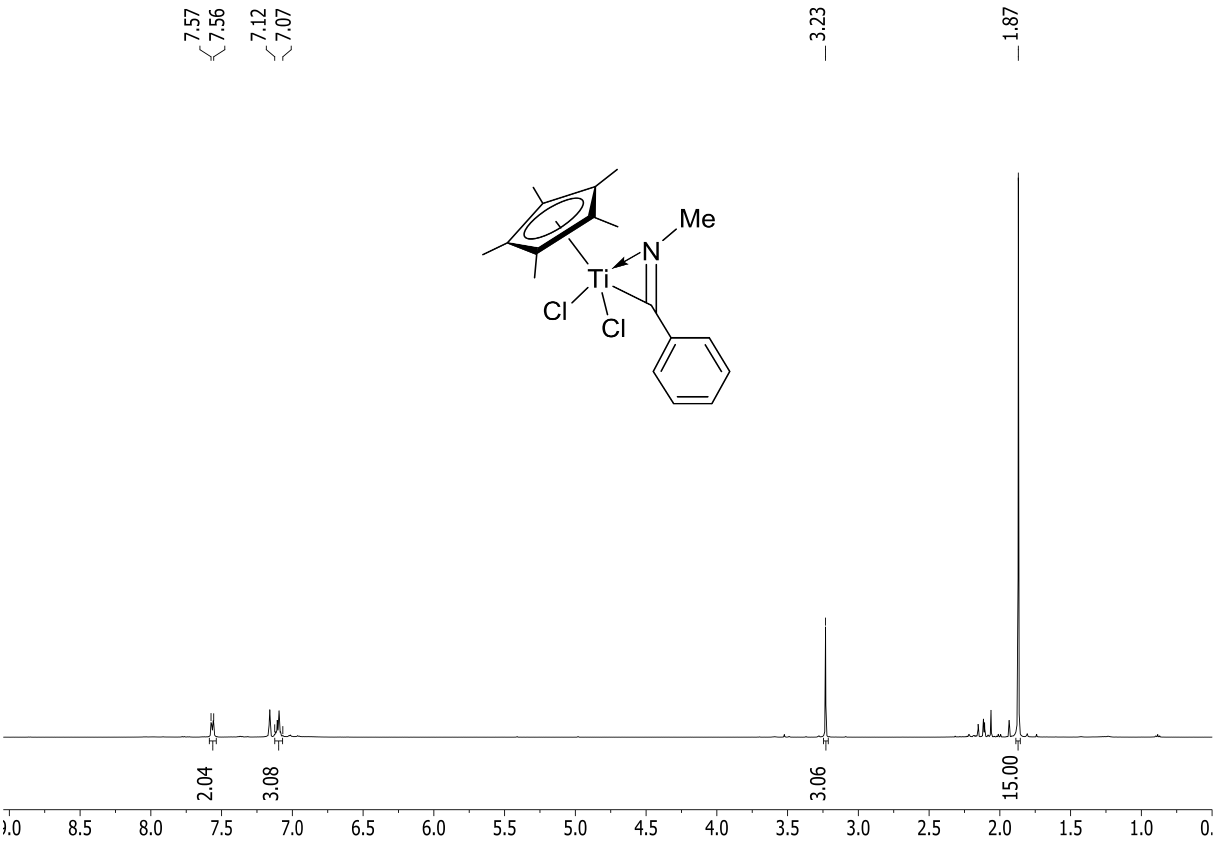


Figure S11: ^{1}H NMR spectrum of **2** (500 MHz, C_6D_6, rt).

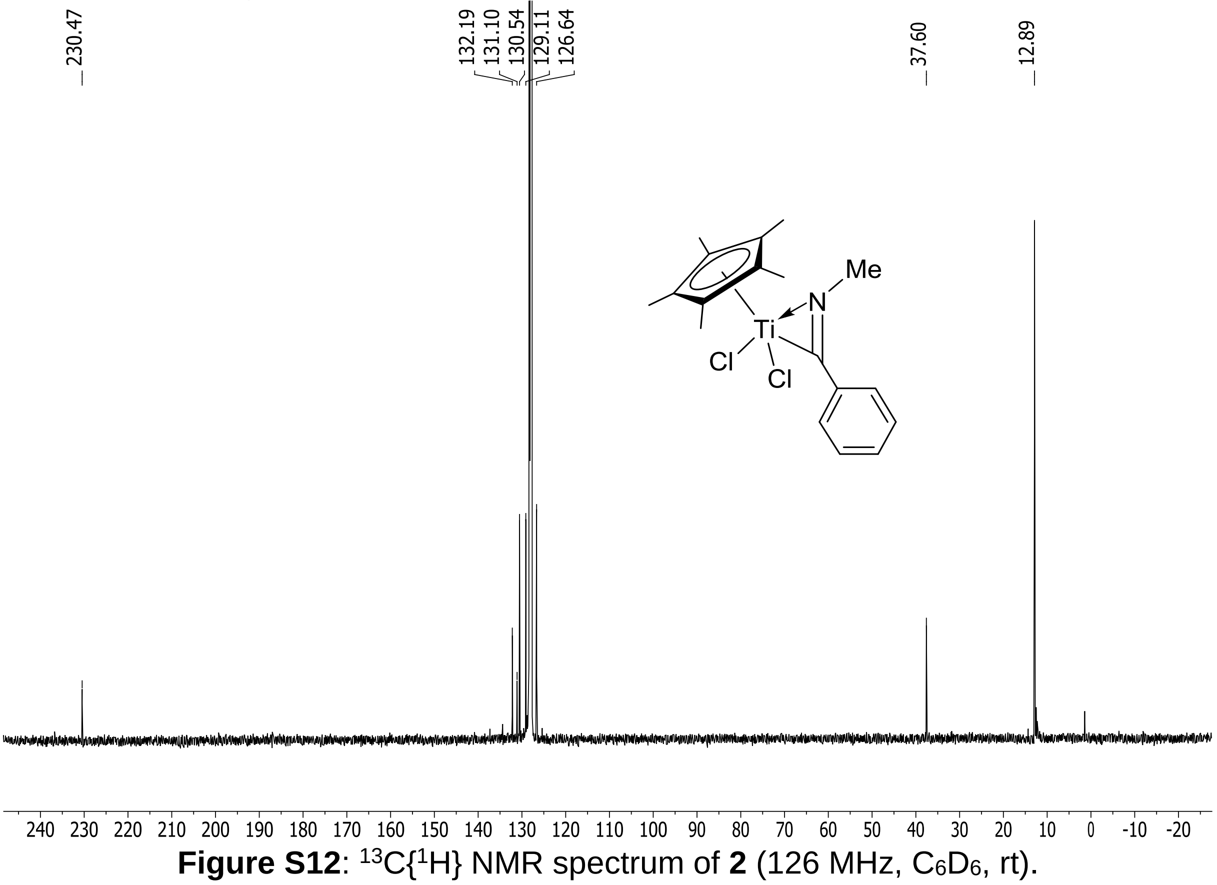


Figure S12: $^{13}C\{^1H\}$ NMR spectrum of **2** (126 MHz, C_6D_6, rt).

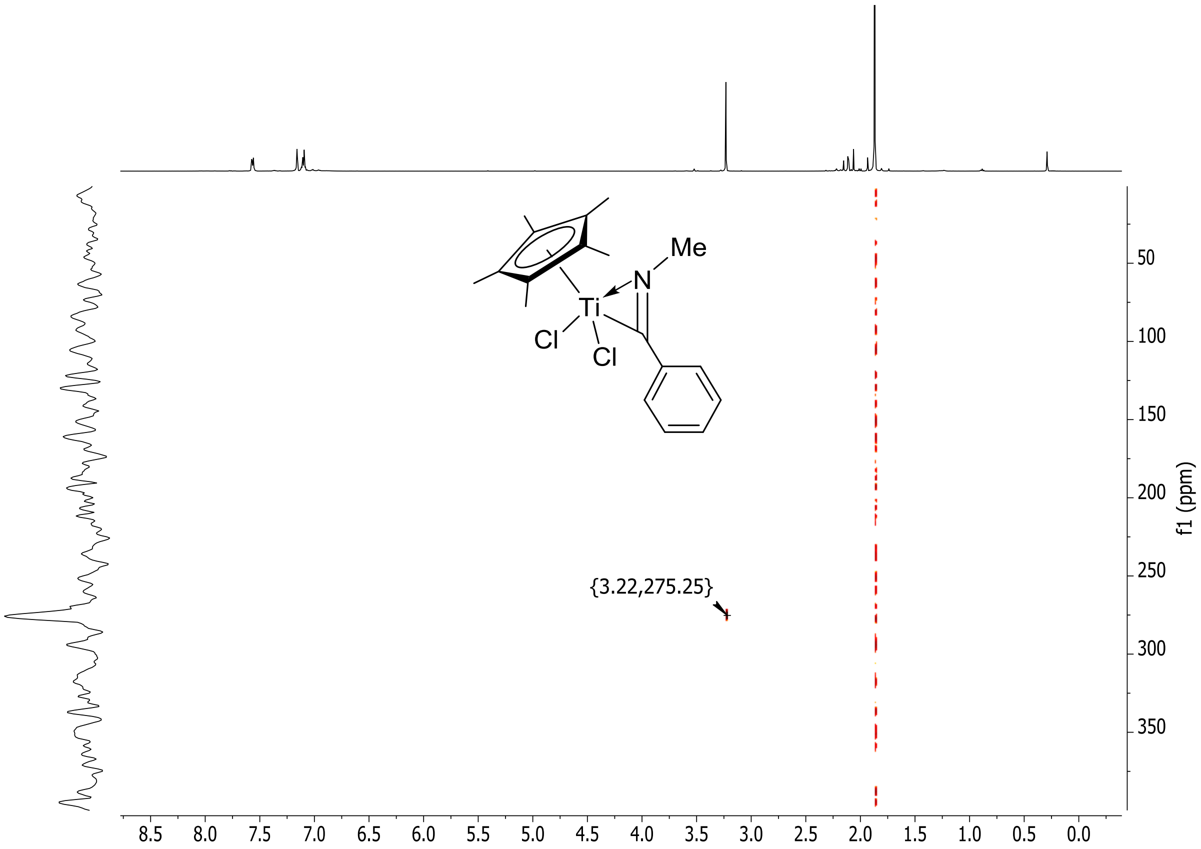


Figure S13: ^{1}H/^{15}N HMBC NMR spectrum of **2** (51 MHz, C_6D_6, rt).

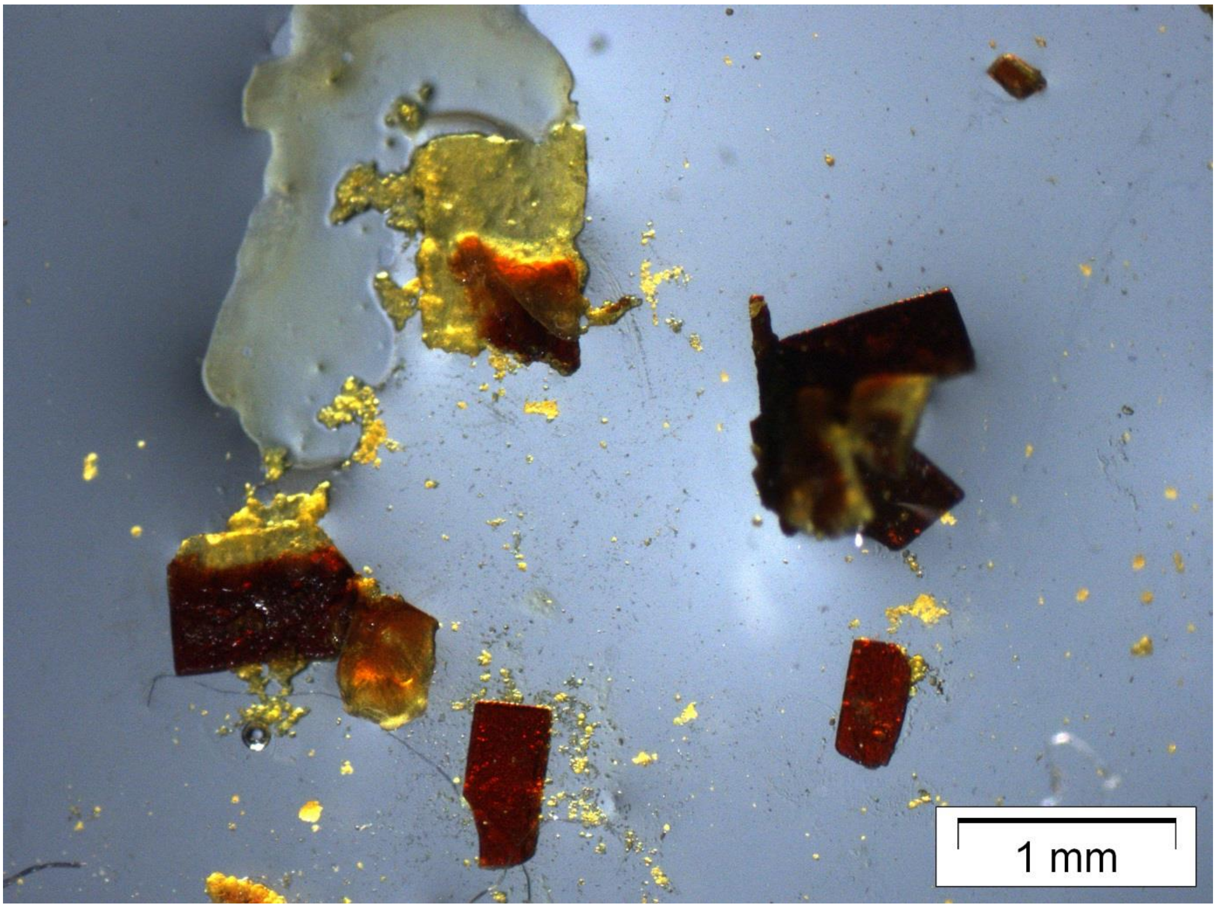


Figure S14: Picture of crystalline **1** (red crystals) taken a few seconds after the transfer to Fomblin YR-1800. The crystals immediately start to decompose to form a yellow oily residue.

References:

[1]	G. H. Llinas, M. Mena, F. Palacios, P. Royo, R. Serrano, *J. Organomet. Chem.* **1988**, *340*, 37-40.
[2]	M. K. Rong, K. van Duin, T. van Dijk, J. J. M. de Pater, B.-J. Deelman, M. Nieger, A. W. Ehlers, J. C. Slootweg, K. Lammertsma, *Organometallics* **2017**, *36*, 1079-1090.
[3]	O.V. Dolomanov , L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339-341.
[4]	G. M. Sheldrick, *Acta Cryst.* ***2008***, *A64*, 112-122.
[5]	G. M. Sheldrick, *Acta Cryst.* **2015**, *C71*, 3-8.