Supporting Information

Reaction of a Bis(pentafulvene)titanium Complex with an *N*-heterocyclic Olefin: C–H-Activation Leads to Resonance Between a Titanium Vinyl and Titanium Alkylidene Complex

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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 unless stated otherwise. The glass equipment was stored in an oven at 120 °C prior to use. Solvents and liquid starting materials were dried according to standard procedures. Solvent were distilled over Na/K alloy and benzophenone or CaH_2 under nitrogen atmosphere. Solid materials were stored and weighted in a glovebox and dried under high vacuum prior to use. The bispentafulvene titanium complexes **1a,b** were synthesized according to literature procedures.[1a,b] 1,3,4,5-Tetramethyl-2-methyleneimidazoline (**2**) was synthesized according to literature procedures.[2a-c]

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

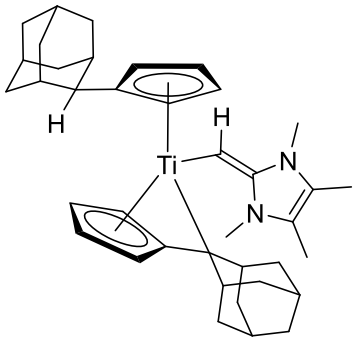
Infrared spectra were performed on a Bruker Tensor 27 spectrometer with a MKII Reflection Golden Gate Single Diamond ATR system.

Elemental analyses were carried out on a EuroEA 3000 Elemental Analyzer.

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

Synthesis and characterization of compounds

Synthesis of 3:



Complex **1a** (0.500 g, 1.125 mmol) and 1,3,4,5-Tetramethyl-2-methyleneimidazoline (0.155 g, 1.125 mmol) were dissolved in 15 mL of *n*-hexane. The color of the reaction mixture changes from dark blue to magenta. The reaction mixture was stirred for 16 h at room temperature. All volatile components were removed under vacuum to yield complex **3** as a magenta solid. No further purification steps are required.

Crystals suitable for single-crystal X-ray diffraction were obtained from a saturated *n*-hexane/toluene solution of **3** at -26 °C.

Yield: 0.618 g (1.061 mmol, 94%).

Melting point: >250 °C.

IR (ATR): $\tilde{\nu}$ = 2898, 2846, 1644, 1601, 1538, 1489, 1448, 1410, 1388, 1352, 1339, 1259, 1209, 1096, 1059, 1032, 948, 933, 896, 862, 791, 774, 756, 708, 675, 627 cm^{-1}.

^{1}H NMR (500 MHz, C_6D_6, 305 K): δ = 1.45 (s, 6H, 2×C_qCH_3), 1.48-2.60 (m, 28H, CH_{Ad}/$CH_{2,Ad}$), 2.81 (s, 6H, 2×NCH_3), 3.02 (s, 1H, CH_{exo}), 4.30-4.31 (m, 1H, C_5H_4), 5.01-5.02 (m, 1H, C_5H_4), 5.29-5.30 (m, 1H, C_5H_4), 5.38-5.39 (m, 1H, C_5H_4), 5.59-5.60 (m, 1H, C_5H_4), 6.27-6.30 (m, 2H, 2×C_5H_4), 6.46-6.47 (m, 1H, C_5H_4), 7.17 (s, $^{1}J_{C,H}$ = 118.5 Hz, 1H, TiCH) ppm.

^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 305 K): δ = 8.8 (2×$C_q\underline{C}H_3$), 28.5 (CH_{Ad}), 28.6 (CH_{Ad}), 29.5 (CH_{Ad}), 30.0 (CH_{Ad}), 32.3 (2×NCH_3), 32.6 ($CH_{2,Ad}$), 32.7 ($CH_{2,Ad}$), 32.8 (CH_{Ad}), 33.1 (CH_{Ad}), 36.2 (CH_{Ad}), 37.5 ($CH_{2,Ad}$), 38.6 ($CH_{2,Ad}$), 39.0 (CH_{Ad}), 39.1 ($CH_{2,Ad}$), 39.47 ($CH_{2,Ad}$), 39.49 ($CH_{2,Ad}$), 40.0 ($CH_{2,Ad}$), 44.2 ($CH_{2,Ad}$), 45.0 ($CH_{2,Ad}$), 45.6 (CH_{exo}), 100.7 (C_5H_4), 103.6 (C_5H_4), 105.1 (C_5H_4), 106.0 (C_5H_4), 108.3 (C_5H_4), 109.4 (C_5H_4), 110.4 (C_5H_4), 111.1 ($C_{q,exo}$), 112.1 (C_5H_4), 117.6 (2×$\underline{C}_qCH_3$), 123.7 ($C_{q,ipso}$), 124.7 ($C_{q,ipso}$), 160.4 ($\underline{C}_q$=CH), 166.7 (TiCH) ppm.

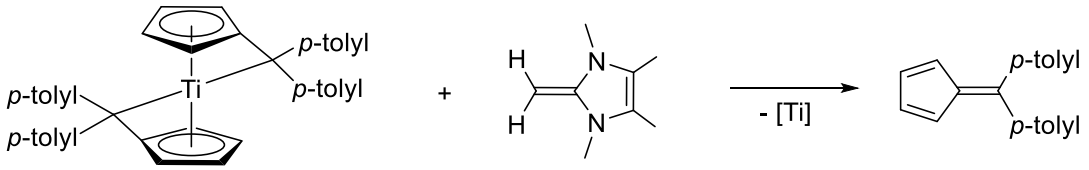
^{13}C Gated Decoupling NMR (126 MHz, C_6D_6, 305 K): δ = 166.7 (d, $^1J_{C,H}$ = 117.4 Hz, TiCH) ppm.

^{15}N NMR (51 MHz, C_6D_6, 305 K): δ = 123.4 ppm.

EA: Anal. calcd. for $C_{38}H_{50}N_2Ti$: C, 78.33; H, 8.65; N, 4.81; Found: C, 78.67; H, 8.73; N, 4.87.

Figure S1. Magenta colored solution of **3** in *n*-hexane after 15 minutes of vigorous stirring of the reaction mixture.

Reaction of 1b with 2:



1b **2**

Complex **1b** (0.100 g, 0.177 mmol) and 1,3,4,5-Tetramethyl-2-methyleneimidazoline (0.024 g, 0.177 mmol) were dissolved in 8 mL of *n*-hexane. The color of the reaction mixture changed from a deep green to yellow-green. The reaction mixture was stirred for 16 h at room temperature. All volatile components were removed under vacuum and the residue was analyzed by ^{1}H-NMR spectroscopy, which verified the release of di-*p*-tolylpentafulvene. Same results were obtained by reacting **1b** with **2** in different solvents (toluene, tetrahydrofuran) and/or starting the reaction at -80 °C. Figure S7 shows the ^{1}H NMR spectrum of the di-*p*-tolylpentafulvene and a representative ^{1}H NMR spectrum of the abovementioned reaction.

NMR-Spectra

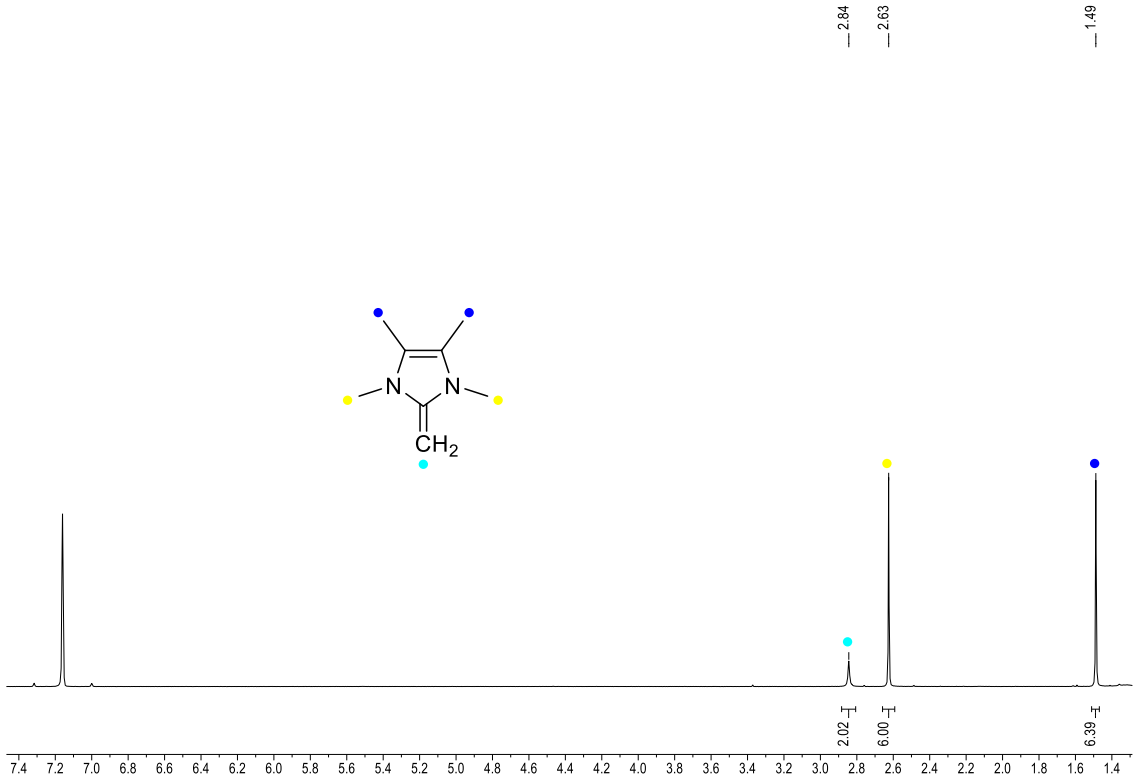


Figure S2: ^{1}H NMR spectrum of **2** (500 MHz, C_6D_6, rt).

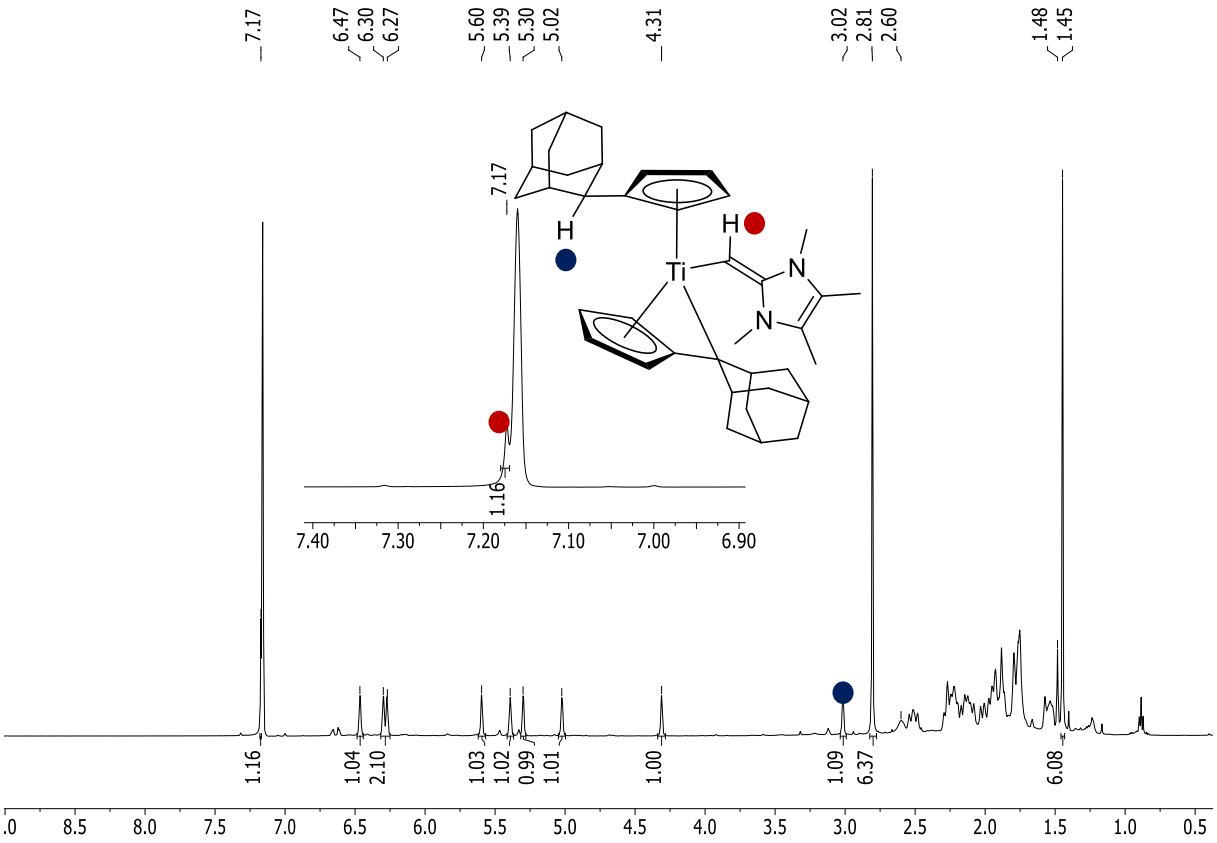


Figure S3: ^{1}H NMR spectrum of **3** (500 MHz, C_6D_6, rt).

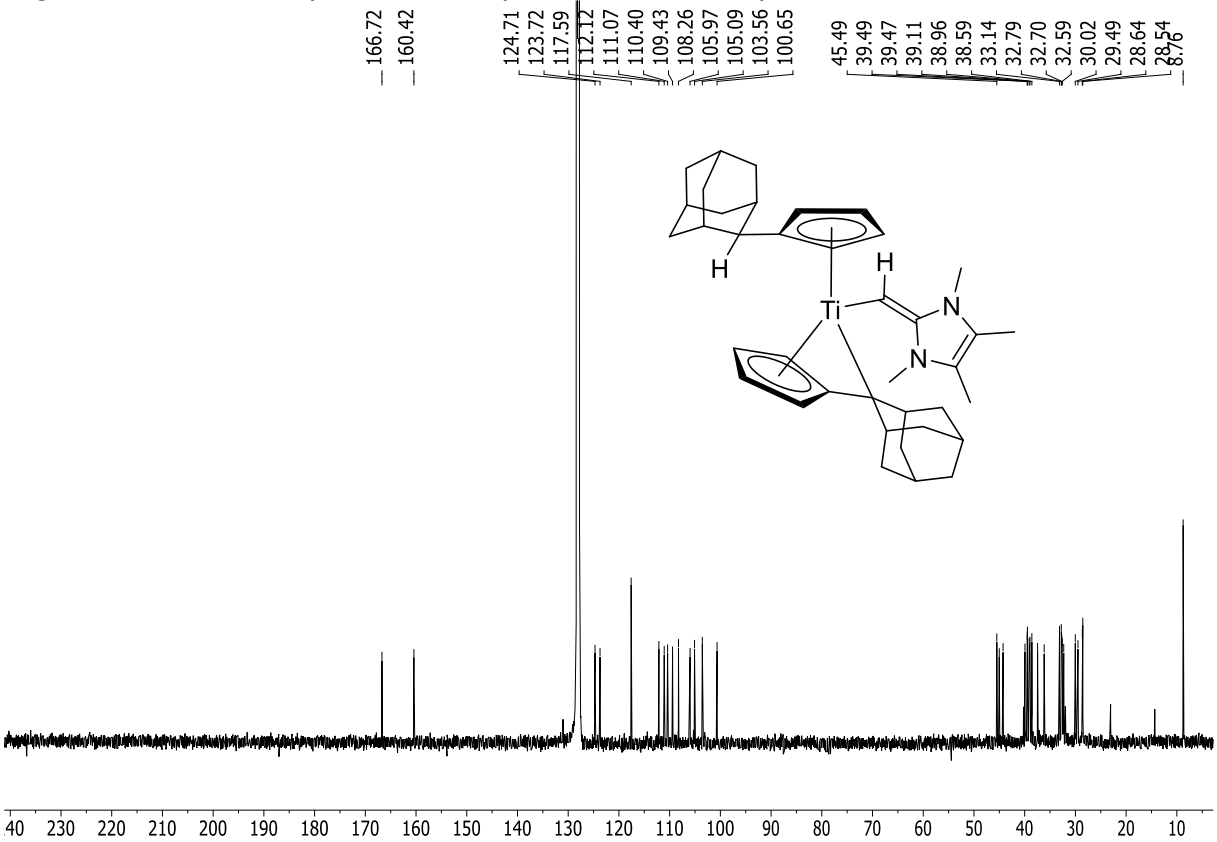


Figure S4: $^{13}C\{^{1}H\}$ NMR spectrum of **3** (126 MHz, C_6D_6, rt).

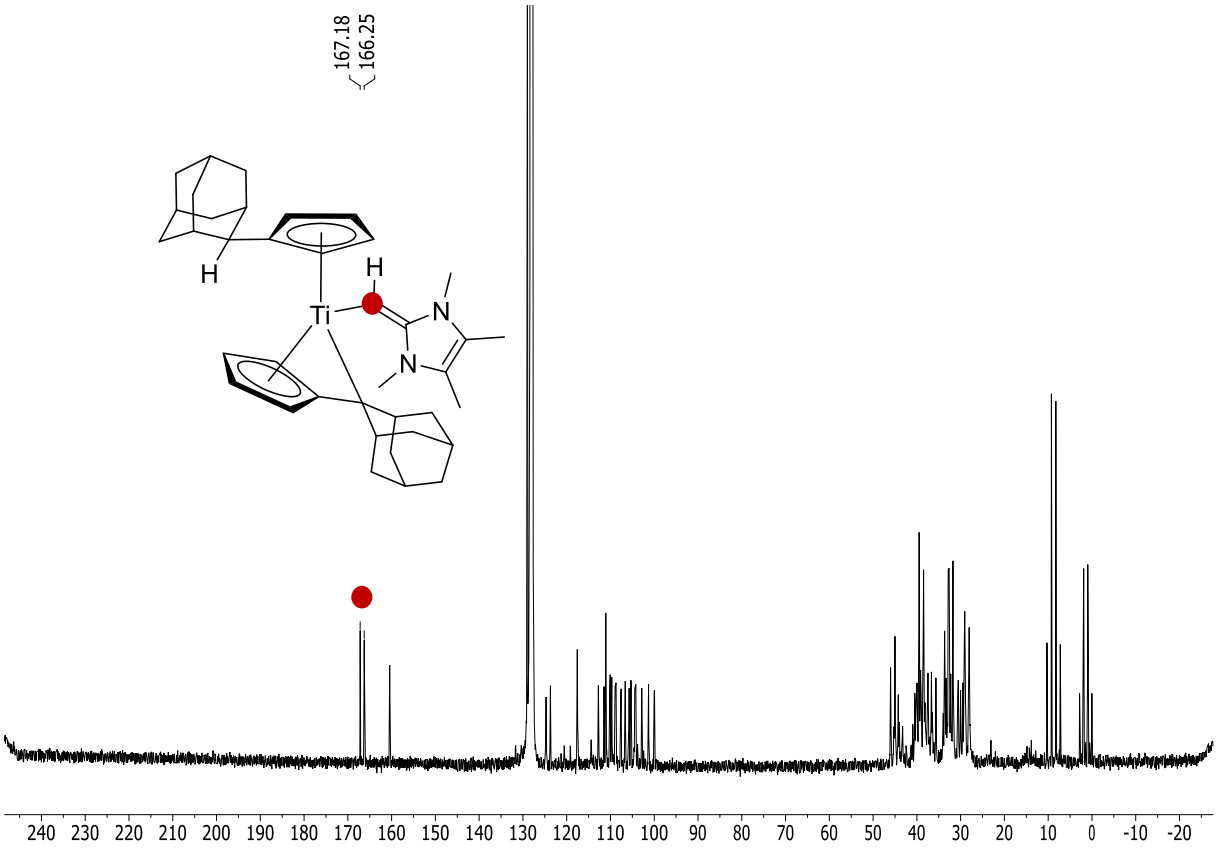


Figure S5: ^{13}C gated decoupling NMR spectrum of **3** (126 MHz, C_6D_6, rt).

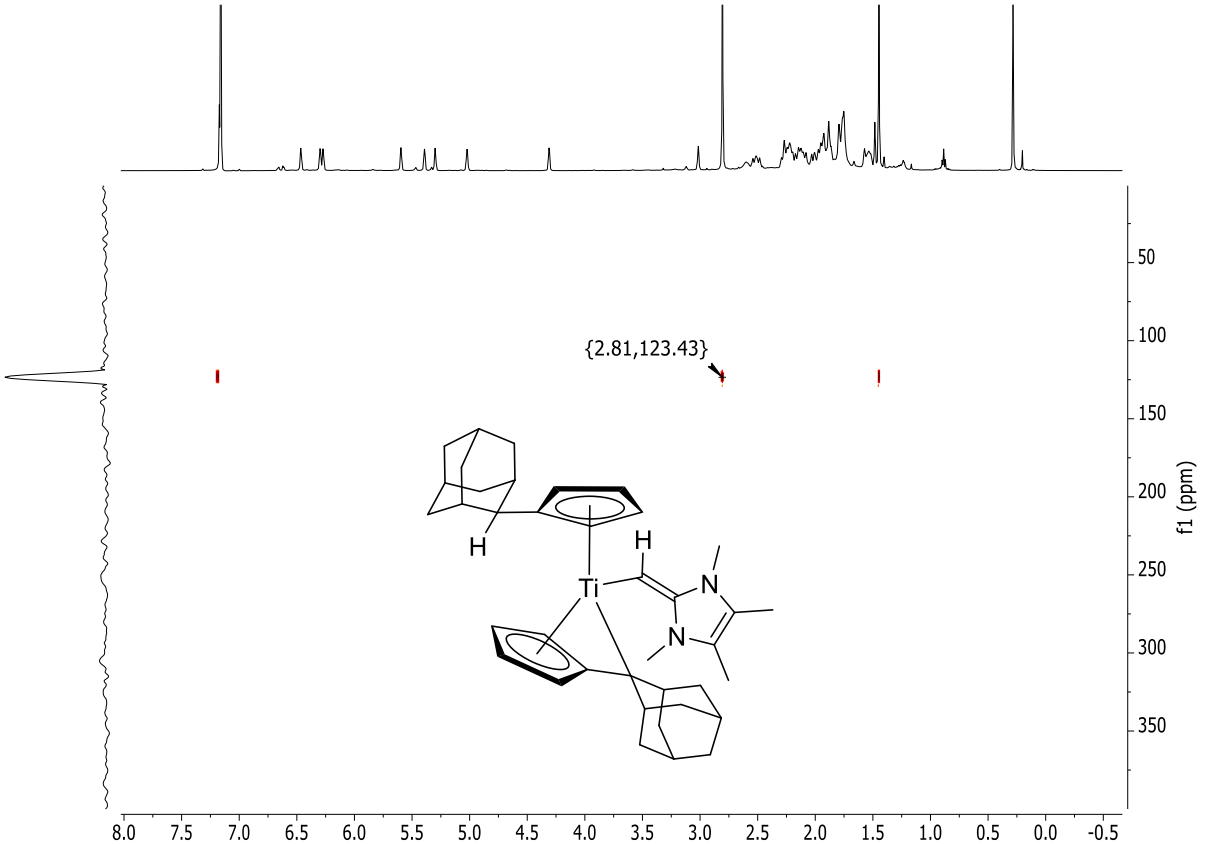


Figure S6: $^{15}N/^{1}H$ HMBC NMR spectrum of **3** (51 MHz, C_6D_6, rt).

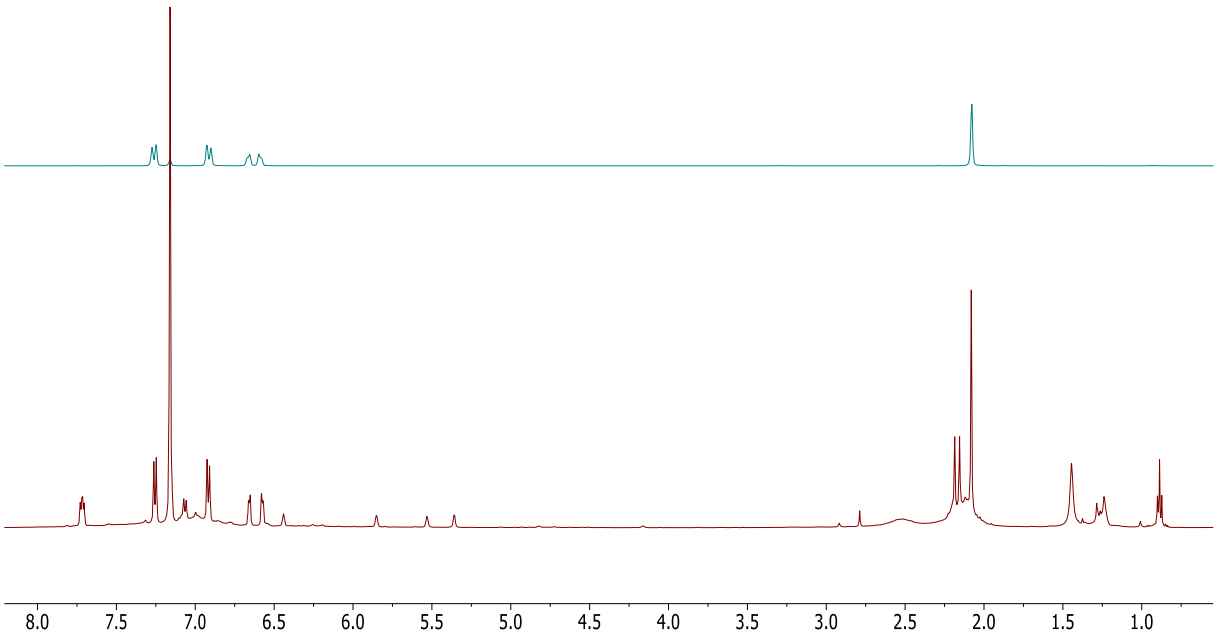


Figure S7: ^{1}H NMR spectrum of the reaction of **1b** with the NHO **2** (bottom) (500 MHz, C_6D_6, rt), and ^{1}H NMR spectrum of di-*p*-tolylpentafulvene (top) (300 MHz, C_6D_6, rt).

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 Compound **3**.

	3
CCDC	2126498
empirical formula	$C_{38}H_{50}N_2Ti$
fw	582.70
colour	Violet
Habit	block
cryst dimens, mm	0.40 x 0.25 x 0.10
cryst syst	orthorhombic
space group	*Pccn*
a, Å	14.7397(7)
b, Å	18.1959(9)
c, Å	22.9425(11)
α, deg	90
β, deg	90
γ, deg	90
V, Å^3	6153.2(5)
Z	8
D_{caclcd}, g cm^{-3}	1.258
μ, mm^{-1}	0.308
T, K	100(2)
θ range, deg	1.775 – 33.141
no. of rflns collected	278457
no. of indep rflns	11725
(R(int))	(0.0539)
no. of rflns with I>2σ(I)	9450
abs cor	semi-empirical
max, min transmission	1.0000 and 0.9614
final R indices	R1 = 0.0497
[I>2σ(I)]	wR2 = 0.1301
R indices (all data)	R1 = 0.0642 wR2 = 0.1417
GOF on F^2	1.028
largest diff peak / hole (e.Å^{-3})	2.007 / -0.795

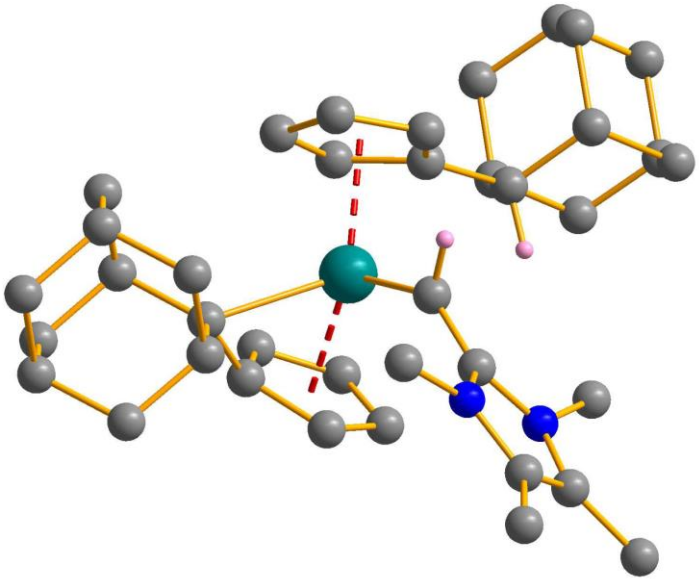


Figure S8: Molecular structure of **3**.

Computational Details

Energy (E) = -2437.03189758 a.u.

Enthalpy (H) = -2436.184091 a.u.

Free Energy (G) = -2436.284575 a.u.

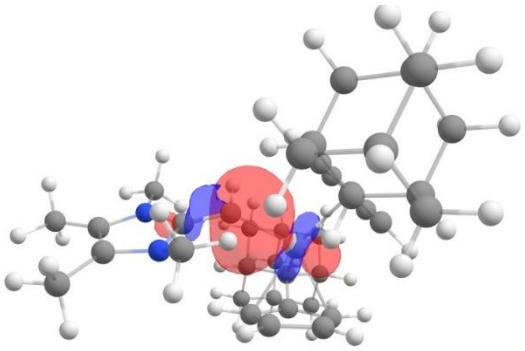
Cartesian coordinates of the optimized geometry

Ti	-0.32960200	-0.71720600	0.27713500
C	-1.89027900	-0.83992800	1.75128900
C	-1.37513600	0.48150600	1.97202500
H	-1.85436300	1.39914300	1.67702200
C	-0.08488200	0.38614000	2.51088600
H	0.54994300	1.21205800	2.78387500
C	0.22391900	-0.97804400	2.68228200
H	1.14753600	-1.37048800	3.08091400
C	-0.88195500	-1.72997400	2.26283600
H	-0.91999000	-2.80609400	2.21046100
C	-2.57482500	-1.16386900	0.52096800
C	-3.15894700	-2.56673200	0.37529400
H	-2.46610700	-3.31512900	0.76410000
C	-3.47405800	-2.87572600	-1.09383400
H	-2.55920400	-2.85898600	-1.68839000
H	-3.90193500	-3.88001600	-1.17417900
C	-4.46630100	-1.84357600	-1.63901700
H	-4.67783400	-2.05838100	-2.68968000
C	-3.85305200	-0.44495200	-1.51163400
H	-2.92669300	-0.38497900	-2.09181900
H	-4.54767200	0.30085700	-1.91353100
C	-3.55575500	-0.13685000	-0.03893900
H	-3.13055400	0.86483300	0.03851200
C	-4.46970900	-2.64079100	1.18410400
H	-4.89546400	-3.64683900	1.10958100
H	-4.25862200	-2.44680100	2.23915600
C	-5.76611200	-1.90909700	-0.82793400
H	-6.21607500	-2.90174400	-0.92607600
H	-6.48748800	-1.18431400	-1.21783500

C	-4.86824500	-0.20535900	0.76402200
H	-4.66735000	0.03445600	1.81185200
H	-5.57810500	0.53703500	0.38389300
C	-5.46995900	-1.61013300	0.64688200
H	-6.39606400	-1.66350700	1.22498300
C	1.82815400	-1.52962700	-0.42198600
C	1.13820000	-1.13348200	-1.59500800
H	1.39732400	-0.29584800	-2.21891300
C	0.01696700	-1.96409000	-1.76906900
H	-0.70491700	-1.89355400	-2.56731200
C	0.00997900	-2.90471600	-0.71386100
H	-0.71795700	-3.68527500	-0.56163200
C	1.13014600	-2.64702000	0.09758500
H	1.38581100	-3.18275900	0.99885500
C	3.04267300	-0.87297700	0.19296500
H	2.71986300	-0.36887600	1.11386500
C	4.13038200	-1.88565100	0.60656800
H	3.67815800	-2.66561300	1.22466800
C	5.20401300	-1.15051900	1.41712300
H	4.75873400	-0.71412400	2.31672500
H	5.97229800	-1.85724100	1.74438200
C	5.83943400	-0.05095800	0.55781900
H	6.59863200	0.47736900	1.13983500
C	4.75545100	0.93784600	0.10815800
H	4.29953800	1.41514500	0.98232100
H	5.20300800	1.73076900	-0.49865600
C	3.68269200	0.20218100	-0.70507600
H	2.90962500	0.90996400	-1.01923300
C	4.76641900	-2.51825400	-0.63630200
H	5.51480600	-3.25550300	-0.33092600
H	4.00432300	-3.04560800	-1.21700800
C	6.48683500	-0.69227400	-0.67552900
H	7.26884900	-1.39123500	-0.36370000
H	6.96387100	0.07686800	-1.29045200
C	4.34160200	-0.43300000	-1.93794400

H	3.59955800	-0.94739900	-2.55100900
H	4.78717500	0.35307900	-2.55523800
C	5.41972000	-1.42747400	-1.49448500
H	5.88125300	-1.88231600	-2.37424200
C	-0.39406400	1.08568600	-0.71344000
H	-0.76350400	0.86092000	-1.71851900
N	0.17443300	3.14479600	0.55293400
N	-1.30947500	3.34671100	-1.04931500
C	-0.50192000	2.41966000	-0.42313000
C	-1.10786700	4.61911700	-0.51098700
C	-0.19389300	4.49907200	0.46727900
C	-2.19120700	2.99605300	-2.13001600
H	-2.87251100	3.82002700	-2.32732000
H	-2.76785700	2.10920800	-1.86168800
H	-1.63030300	2.77254500	-3.04242200
C	-1.87973800	5.79922700	-0.97790700
H	-1.72060500	5.98373500	-2.04255400
H	-1.56915100	6.68796300	-0.43323800
H	-2.95291700	5.66573200	-0.82019400
C	0.37633200	5.50482100	1.40057500
H	1.45928900	5.59534000	1.28843800
H	0.17418900	5.23281500	2.43957500
H	-0.06003700	6.48431100	1.21644300
C	1.52393100	2.79358300	0.95310700
H	1.66172700	1.72695200	0.80620200
H	1.69321300	3.03922000	2.00188700
H	2.25740400	3.33135800	0.34192000

Table S2: Selected NBOs of the Ti1–C31–C32 unit in **3**.

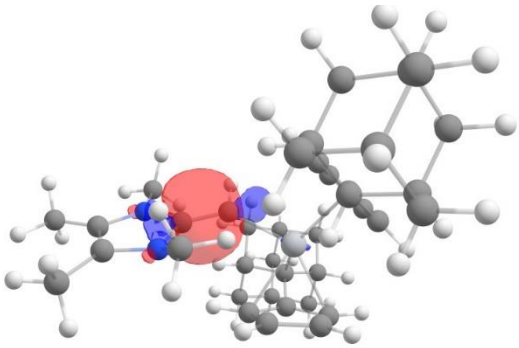


NBO 2 (Ti1-C31)

Occupancy: 1.92975 e

26% Ti1 [**s** (11.26%), **p** (16.79%), **d** (71.91%)]

74% C31 [**s** (44.90%), **p** (55.03%)]

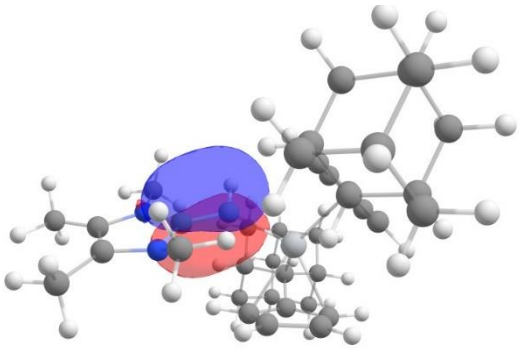


NBO 81 (C31-C32)

Occupancy: 1.96940 e

46% C31 [**s** (31.46%), **p** (68.35%)]

54% C32 [**s** (45.30%), **p** (54.66%)]



NBO 82 (C31-C32)

Occupancy: 1.79427 e

61% C31 [**s** (0.22%), **p** (99.69%)]

39% C32 [**s** (0.08%), **p** (99.83%)]

References

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