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# ELECTRONIC SUPPLEMENTARY INFORMATION

**Title:** Decamethyltitanocene hydride intermediates in hydrogenation of corresponding titanocene-($\eta^2$-ethene) or ($\eta^2$-alkyne) complexes and effects of bulkier auxiliary ligands

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## HD preparation

HD was prepared by stepwise addition of degassed $D_2O$ (1.4 g, 70 mmol) into suspension of $LiAlH_4$ (1.0 g, 26 mmol) in THF (50 ml). A closed system protected with overpressure valve (overpressure 0.1 bar) was used for the reaction. The evolved HD was purified by consecutive passing through two cold traps (first cooled with solid $CO_2$ and second cooled with liquid nitrogen) and a column filled with molecular sieve 3A. The purified HD was passed into evacuated flasks (identical with those used for hydrogenation experiments). Overall, HD was obtained in a quantity about 1.2 L and purity > 95% (as determined by NMR spectroscopy).

## NMR data for titanocenes

If temperature of measurement is not specified the spectra were taken at 25 °C.

**[Cp*$_2$Ti] (Cp* = $\eta^5$-$C_5Me_5$)**

$^1$H NMR (toluene-$d_8$): 63.8 (br s, 30H, $C_5\mathit{Me}_5$). $^1$H NMR (toluene-$d_8$, −45 °C): 99.6 (br s, 30H, $C_5\mathit{Me}_5$).

**[Cp*($\eta^5$,$\eta^1$-$C_5Me_4(CH_2)$}TiH]** a tucked-in hydride tautomer of the above titanocene (ca 66 mol % with respect to titanocene): $^1$H and $^{13}$C{$^1$H} NMR spectra in toluene-$d_8$ measured at 25 °C spectra see ref.[12]

**[($\eta^5$-$C_5Me_4$tBu)$_2$Ti]**

$^1$H NMR (toluene-$d_8$): 4.0 ($\Delta\nu_{½} \approx$ 60 Hz, 18H, $C\mathit{Me}_3$); 34.0 ($\Delta\nu_{½} \approx$ 70 Hz, 12H, $C_5\mathit{Me}_4$,); 62.2 ($\Delta\nu_{½} \approx$ 110 Hz, 12H, $C_5\mathit{Me}_4$,).

**[($\eta^5$-$C_5Me_4$tBu){$\eta^5$,$\eta^1$-$C_5Me_3$tBu($CH_2$)}TiH]** a tucked-in hydride tautomer of the above titanocene (ca 5 mol % with respect to titanocene): $^1$H NMR (toluene-$d_8$): 2.26, 1.79, 1.57, 1.47 (4 × s, 4 × 3H, $C_5\mathit{Me}_4$); 1.42, 1.40 (2 × s, 2 × 9H, $C\mathit{Me}_3$); 1.36, 1.07, 0.99 (3 × s, 3 × 3H, $C_5\mathit{Me}_4$); 0.61 (d, $^2J_{HH}$ = 5 Hz, 1H, $TiC\mathit{H}_2$); the second $TiC\mathit{H}_2$ proton was not localized.

**[{$C_5Me_4(SiMe_3)$}$_2$Ti]**

$^1$H NMR (toluene-$d_8$): 7.1 ($\Delta\nu_{½} \approx$ 85 Hz, 18H, $Si\mathit{Me}_3$); 26.5 ($\Delta\nu_{½} \approx$ 150 Hz, 12H, $C_5\mathit{Me}_4$,); 77.1 ($\Delta\nu_{½} \approx$ 260 Hz, 12H, $C_5\mathit{Me}_4$,). A tucked-in hydride tautomer was not found.

## $^1$H NMR spectra of hydrogenation products of permethyltitanocene alkyne complexes $Cp^*_2Ti(R_1C{\equiv}CR_2)$ and GC-MS spectra

**$R_1$, $R_2$ = Me:** n-butane (>95%): $^1$H NMR (toluene-$d_8$), $^{13}$C{$^1$H} NMR (toluene-$d_8$), and GC-MS identical with ref.[14].

**$R_1$, $R_2$ = Et:** n-hexane $^1$H NMR (toluene-$d_8$) agreed with the data for n-hexane.[18]

**$R_1$, $R_2$ = Ph:** 1,2-diphenylethane $^1$H NMR (toluene-$d_8$): 2.710 (s, 4H, C*H*$_2$Ph); 6.90-7.18 (m, 10H, CH$_2$*Ph*). A trace of *cis*-stilbene (toluene-$d_8$): 6.428 (s, 2H, C*H*Ph).

**$R_1$ = Ph, $R_2$ = SiMe$_3$:** 1-phenyl-2-(trimethylsilyl)ethane GC-MS, $^1$H NMR (toluene-$d_8$), and $^{13}$C{$^1$H} NMR (toluene-$d_8$) agreed with the data in ref.[14]

**$R_1$ = Me, $R_2$ = SiMe$_3$:** propyltrimethylsilane: $^1$H NMR (toluene-$d_8$): 0.02 (s, 9H, Si*Me*$_3$); 0.39-0.49 (m, 2H, C*H$_2$*SiMe$_3$); 0.96 (t, $^3J_{HH}$ = 7.2 Hz, C*H*$_3$CH$_2$); 1.22-1.37 (m, 2H, CH$_3$C*H$_2$*).

**$R_1$ = $R_2$ = SiMe$_3$:** Final product mixture contained 1,2-bis(trimethylsilyl)ethene ((*E*-) 50%, (*Z*-) 5%) and 1,2-bis(trimethylsilyl)ethane 45%.

(*E*)-SiMe$_3$CH=CHSiMe$_3$ $^1$H NMR (toluene-$d_8$): 0.09 (s, 18H, Si*Me*$_3$); 6.75(s, 2H, C*H*). $^{13}$C {$^1$H}( toluene-$d_8$): –1.49 (Si*Me*$_3$); 151.12 (=*C*H). $^{29}$Si {$^1$H}( toluene-$d_8$): –7.95 (*Si*Me$_3$).

(Z)-SiMe$_3$CH=CHSiMe$_3$ $^1$H NMR (300 MHz, $C_6D_6$, 298 K): 0.15 (s, 18H, Si*Me*$_3$); 6.86 (s, 2H, C*H*). $^{13}$C {$^1$H}($C_6D_6$, 298 K): 0.37 (Si*Me*$_3$); 152.08 (=*C*H). $^{29}$Si {$^1$H}($C_6D_6$): – 10.37 (*Si*Me$_3$).

1,2-bis(trimethylsilyl)ethane $^1$H NMR (toluene-$d_8$): 0.01 (s, 18H, Si*Me*$_3$); 0.41 (s, 4H, C*H*$_2$). $^{13}$C {$^1$H}(toluene-$d_8$): –2.10 (Si*Me*$_3$); 9.09 (*C*H$_2$). $^{29}$Si {$^1$H}( toluene-$d_8$): 2.63 (*Si*Me$_3$).

**REFERENCES** are numbered as in the article.

**Reference 42 in full:**

M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, Ö. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, and D.J. Fox *Gaussian 09*, Revision D.01; Gaussian, Inc., Wallingford CT, 2013

**Figure S1.** $^{1}$H NMR spectra of [$Cp^*_2TiH_2$] (**1**) in toluene-*d*$_8$ measured at −45 °C. (*) denotes solvent signals.

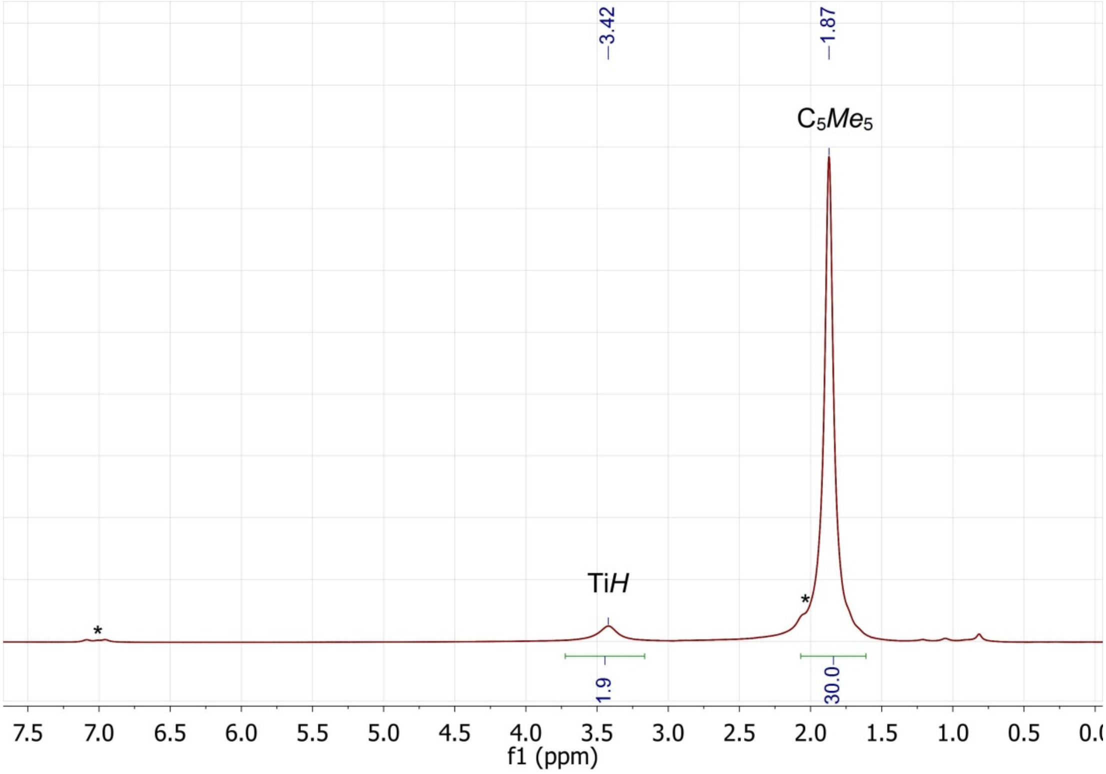
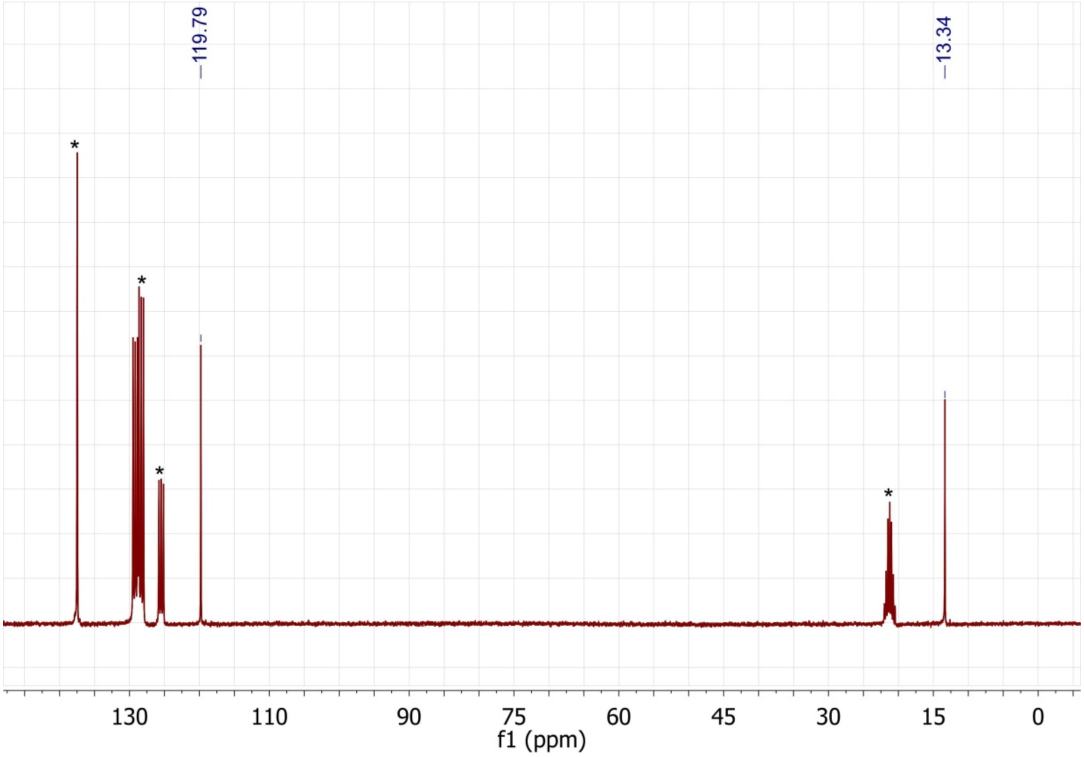


**Figure S2.** $^{13}C\{^{1}H\}$ NMR spectra of [$Cp^*_2TiH_2$] (**1**) in toluene-*d*$_8$ measured at −45 °C. (*) denotes solvent signals.



## Hydrogenations of [$Cp^*_2Ti(C_2H_4)$]

**Figure S3.** An expanded region of $^1H$ NMR spectra of products from hydrogenations of [$Cp^*_2Ti(C_2H_4)$] after: a) 10 min b) 40 min c) 2 h d) 14 days. The following symbols denote [$Cp^*_2TiH_2$] ($); [$Cp^*(C_5Me_4CH_2)TiH$] (#); solvent toluene-$d_8$ signal (*); (i) $Et_2O$. The spectra were normalized to an ethane signal.

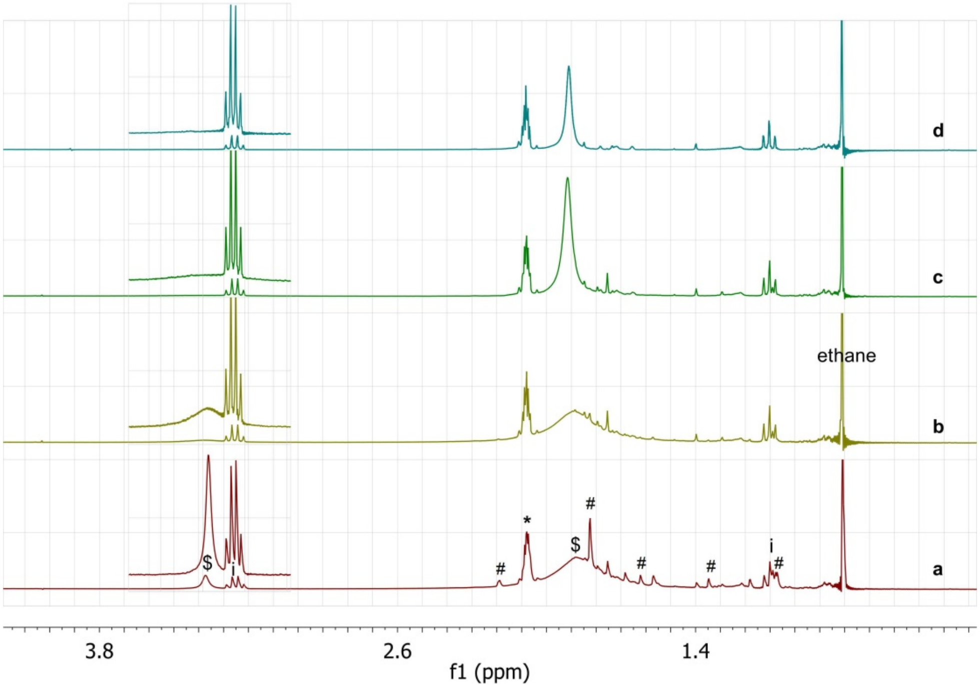
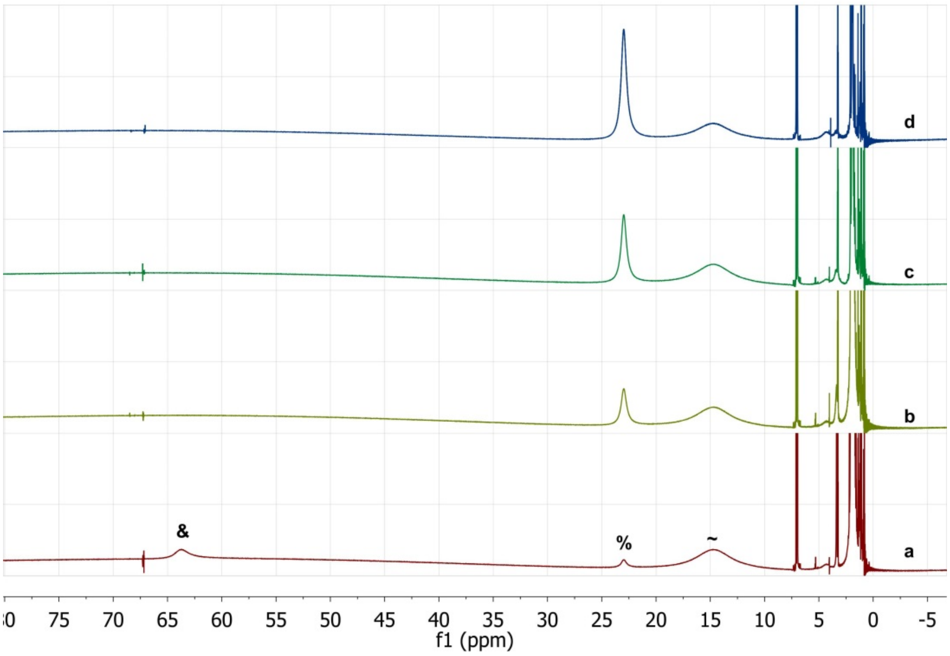


**Figure S4.** Broad range $^1H$ NMR spectra of products from hydrogenation of [$Cp^*_2Ti(C_2H_4)$] after: a) 10 min b) 40 min c) 2 h d) 14 days. The following symbols denote [$Cp^*_2Ti$] (&); [$Cp^*_2TiH$] (%); [$Cp^*_2TiCl$] - an impurity used as an internal intensity standard (~).



## [$Cp^*_2TiH$] + $H_2$ variable temperature

**Figure S5.** Variable temperature $^1H$ NMR spectra of [$Cp^*_2TiH$] (**2**) after addition of hydrogen, measured at: a) −45 °C, b) −35 °C, c) −25 °C, d) −15 °C, e) 5 °C, f) 15 °C, g) 25 °C, h) 35 °C, i) 45 °C, j) 55 °C, k) 65 °C.

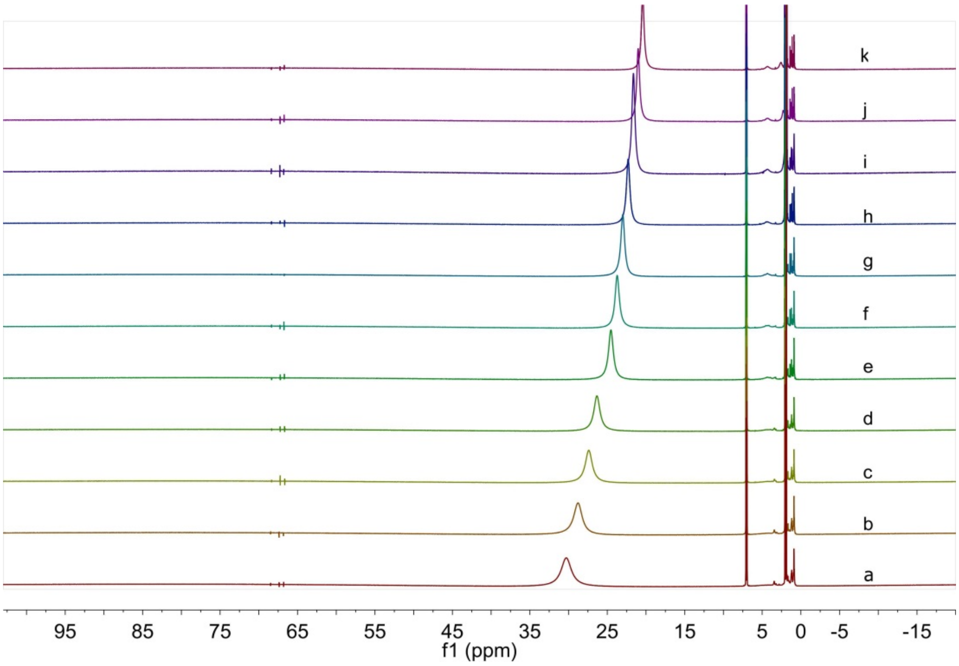
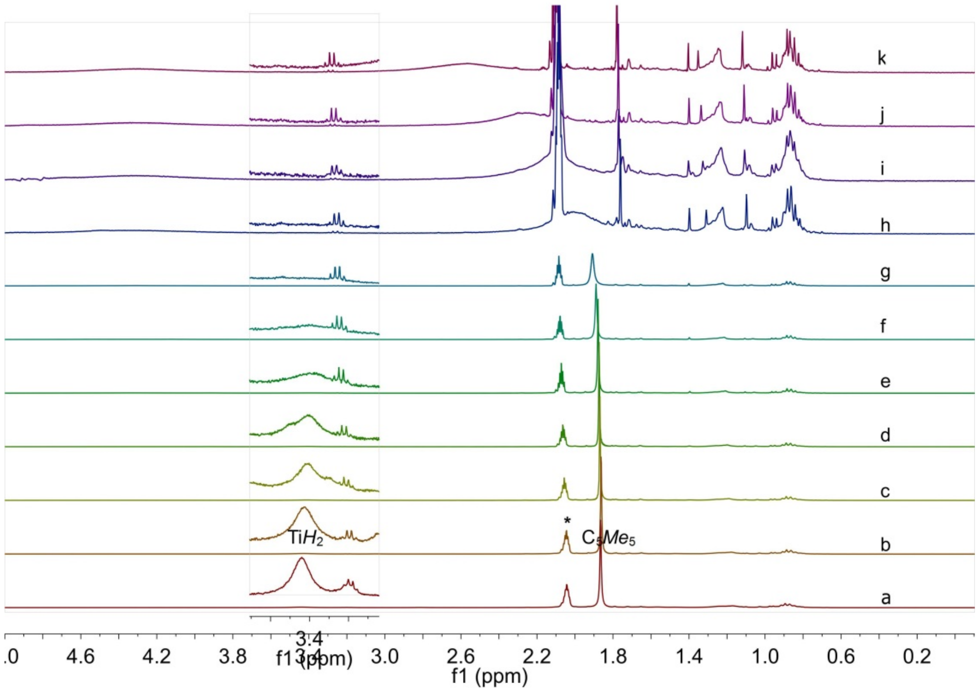


**Figure S6.** Expanded region of variable temperature $^1H$ NMR spectra of [$Cp^*_2TiH_2$] (**1**) after addition of hydrogen to [$Cp^*_2TiH$] (**2**), measured at: a) −45 °C, b) −35 °C, c) −25 °C, d) −15 °C, e) 5 °C, f) 15 °C, g) 25 °C, h) 35 °C, i) 45 °C, j) 55 °C, k) 65 °C. Spectra measured above 25 °C are seven times amplified. Only signals of [$Cp^*_2TiH_2$] are labeled, (*) denotes solvent.



## Reaction of [$Cp^*{}_2Ti(C_2H_4)$] with [$Cp^*{}_2Ti$]

**Figure S7.** $^1$H NMR spectra (expanded region) of two different mixtures of $Cp^*{}_2Ti$ tautomer [$Cp^*(C_5Me_4CH_2)TiH$] (#) and [$Cp^*{}_2Ti(C_2H_4)$] (o) in sealed NMR tubes stored at −30 °C (left side) and 4 °C (right side). The spectrum taken immediately after mixing of reagents (a); reaction mixture after 9 days (b). Only characteristic signals are marked. While the signals of [$Cp^*{}_2Ti(C_2H_4)$] remained unchanged after storing at −30 °C, they disappeared when the sample was stored at 4 °C and the signal of ethane at 0.81 ppm occurred (not depicted).

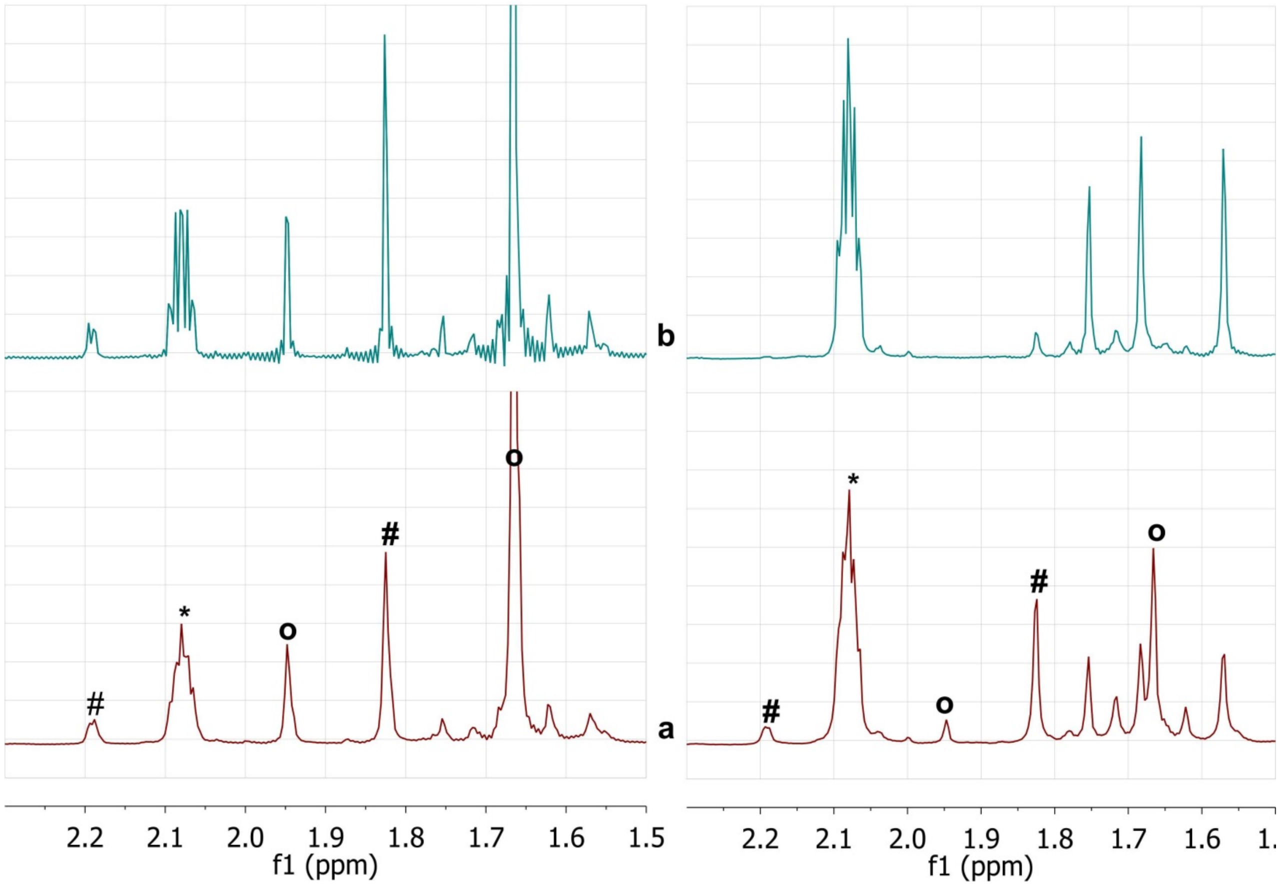
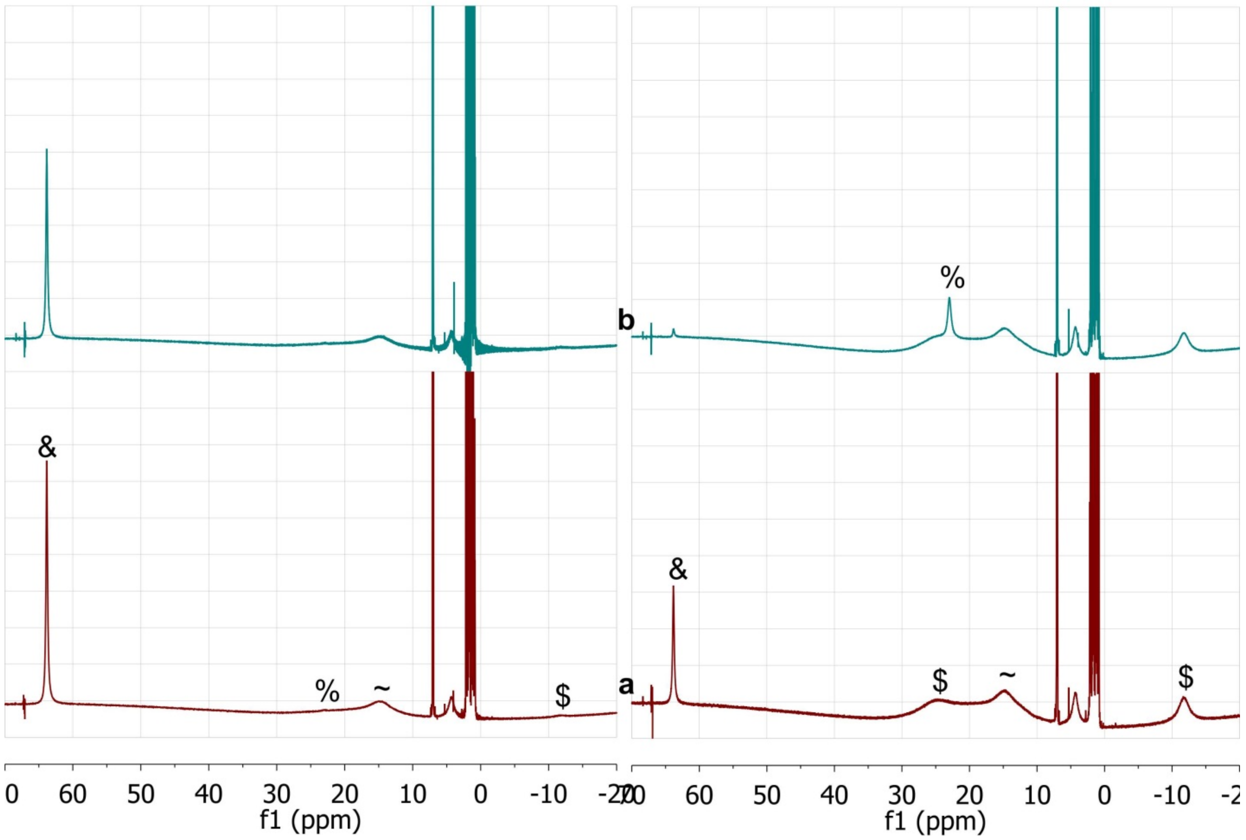


**Figure S8.** Broad range $^1$H NMR spectra corresponding to the above expanded spectra of Figure 7. Compound signals are labeled as follows: [Cp*$_2$Ti] (&); [Cp*(C$_5$Me$_4$CH$_2$)Ti] ($); [Cp*$_2$TiH] (%); [Cp*$_2$TiCl] (~) non-reacting standard. The amount of titanocene with traces of [Cp*$_2$TiH] and [Cp*(C$_5$Me$_4$CH$_2$)Ti] remained unchanged after storing at −30 °C for 9 days (left side). At 4 °C the titanocene (in equilibrium with [Cp*$_2$TiH] and [Cp*(C$_5$Me$_4$CH$_2$)Ti]) reacted at first via [Cp*$_2$TiH] with [Cp*$_2$Ti(C$_2$H$_4$)] (see right side, lower spectrum) to give [Cp*(C$_5$Me$_4$CH$_2$)Ti] and ethane. Only after complete consumption of [Cp*$_2$Ti(C$_2$H$_4$)] the remaining titanocene disproportionated to [Cp*$_2$TiH] and [Cp*(C$_5$Me$_4$CH$_2$)Ti] (right side, upper spectrum).



## [Cp*$_2$TiH] - variable temperature

**Figure S9.** Variable temperature $^1$H NMR spectra of [Cp*$_2$TiH] (**2**) measured at: a) −45 °C, b) −35 °C, c) −25 °C, d) −15 °C, e) −5 °C, f) 5 °C, g) 15 °C, 25 °C (h), 35 °C (i) 45 °C (j). The symbols denote [Cp*$_2$TiH] (%); [Cp*$_2$TiCl] impurity (~).

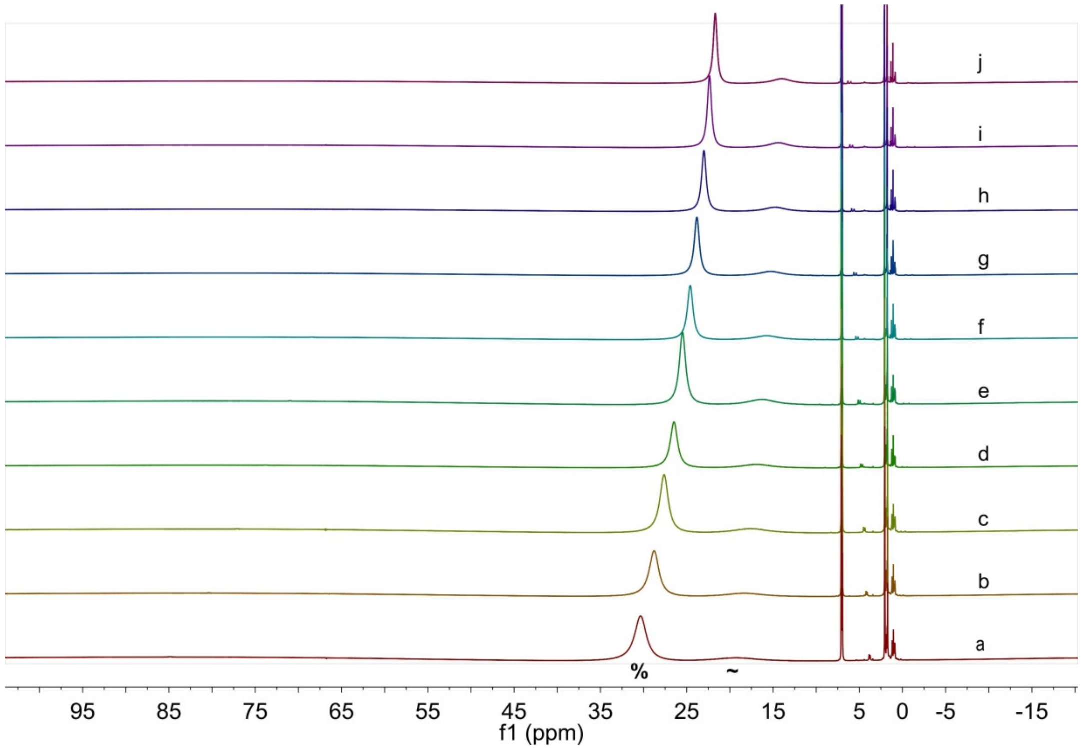
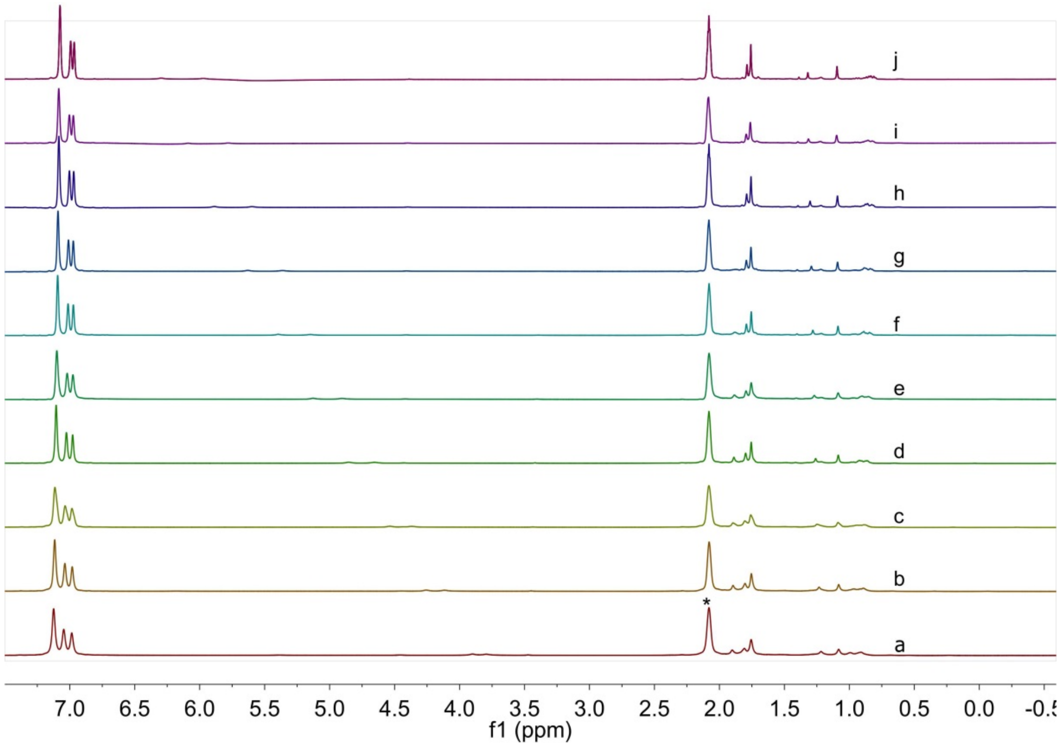


**Figure S10.** An expanded region of variable temperature $^1$H NMR spectra of [Cp*$_2$TiH] (**2**) measured at: a) −45 °C, b) −35 °C, c) −25 °C, d) −15 °C, e) −5 °C, f) 5 °C, g) 15 °C, 25 °C (h), 35 °C (i) 45 °C (j).



**Reaction of [$Cp^*_2Ti(PhCCPh)$] with $H_2$**

**Figure S11.** $^1$H NMR spectra showing the hydrogenation of [$Cp^*_2Ti(PhC{\equiv}CPh)$]: (a) the reagent before hydrogen addition; (b) 1 h after hydrogen addition; (c) after 3 days; (d) after heating to 100 °C for 1 h, measured at 100 °C. The following symbols denote: (@) [$Cp^*_2Ti(PhC{\equiv}CPh)$], ($) [$Cp^*_2TiH_2$], (*) solvent toluene-$d_8$, (i) impurities. The progress in formation of *cis*-stilbene (characteristic olefinic singlet at 6.43 ppm, denoted (I.)) and 1,2-diphenylethane (characteristic singlet of methylene positioned at 2.71 ppm, denoted (II.)) is highlighted with red rectangles. The spectrum (b) demonstrates a concomitant presence of [$Cp^*_2Ti(PhC{\equiv}CPh)$] (highlighted with blue rectangles) and [$Cp^*_2TiH_2$] in early stage of reaction.

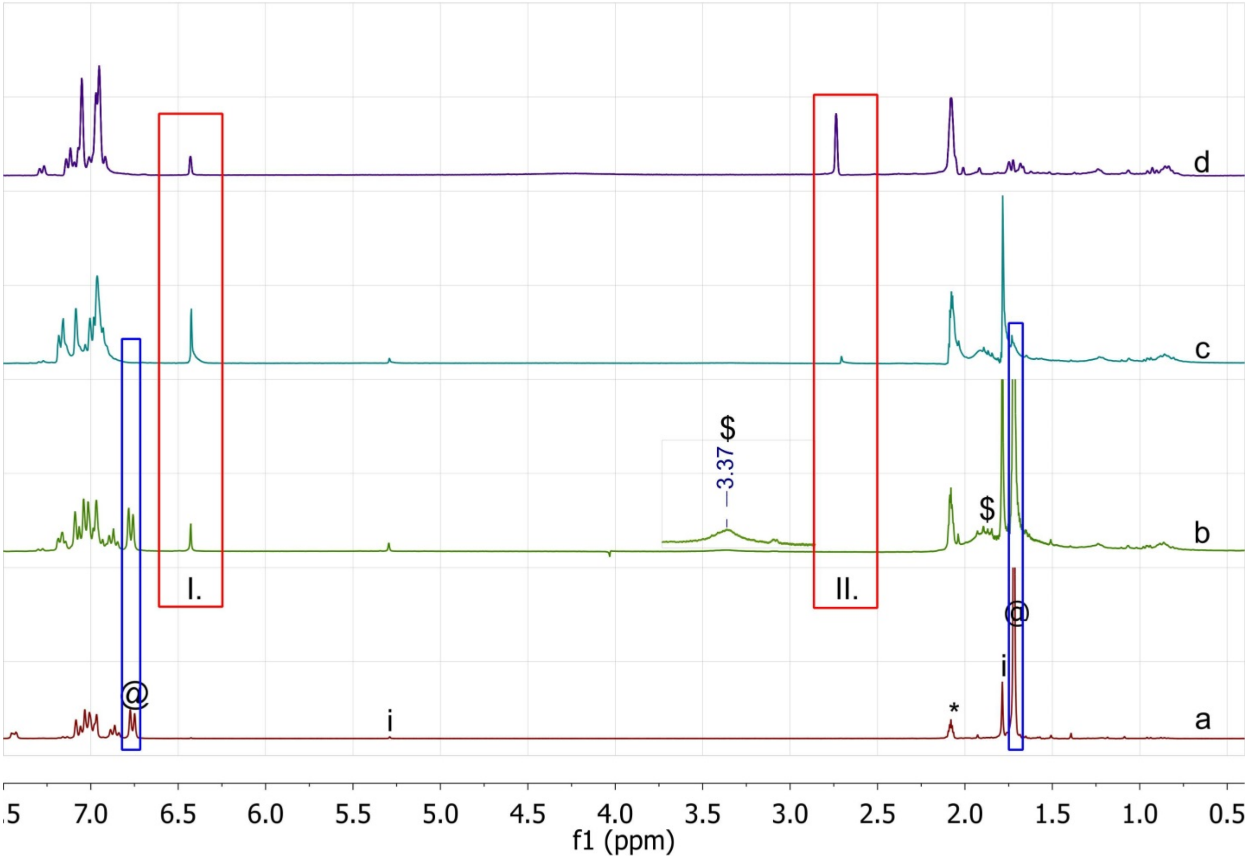


**Figure S12.** Broad range of $^1$H NMR spectra of the above reaction mixture: (a) 1 h after the hydrogen addition; (b) after 3 days; (c) after heating to 100 °C for 1 h in a probe (measured at 100 °C). The following symbols denote: (%) [Cp*$_2$TiH], ($) [Cp*$_2$TiH$_2$] (Ti$H_2$).

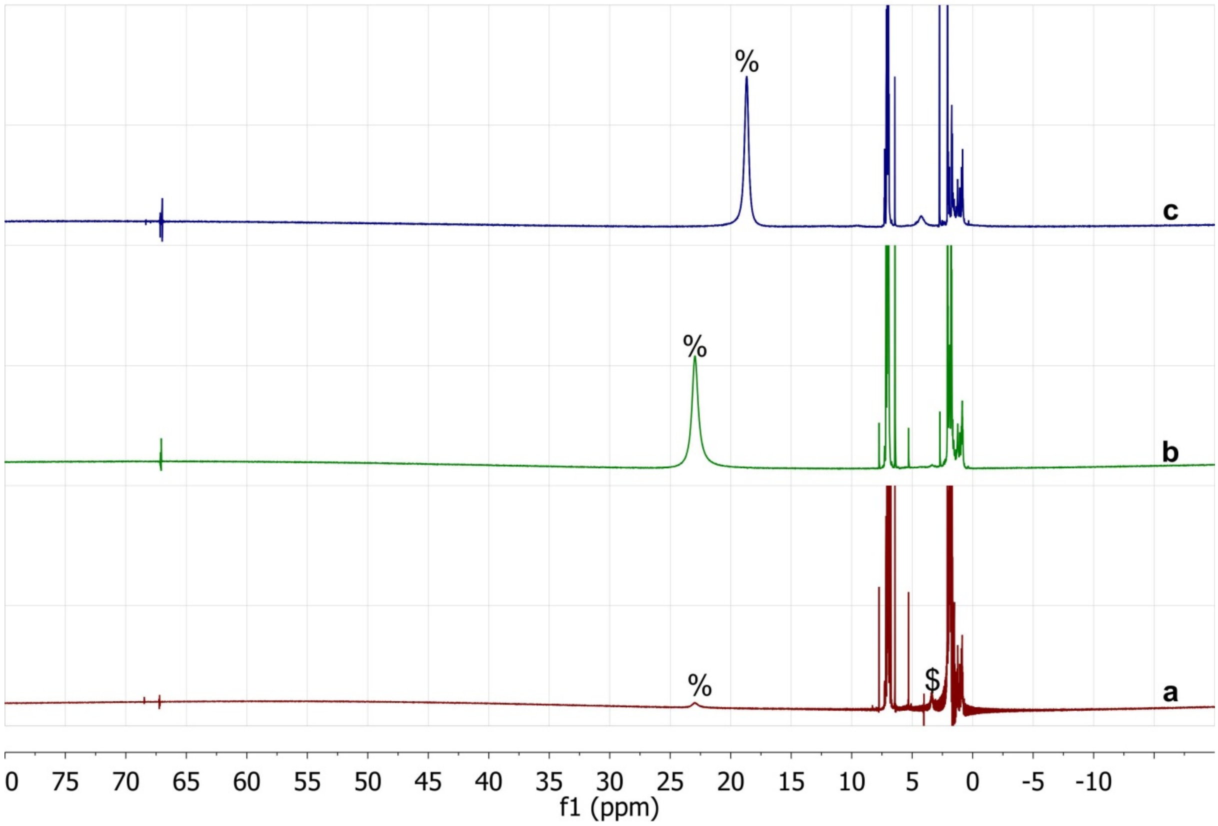


**Figure S13.** An expanded region of $^1$H NMR (brown) and $^1$H{$^2$H}spectra (blue) of the product of deuteration of [Cp*$_2$Ti(PhC≡CPh)]. Spectra were measured at −35 °C in toluene-$d_8$ 30 min after admission of deuterium at room temperature.

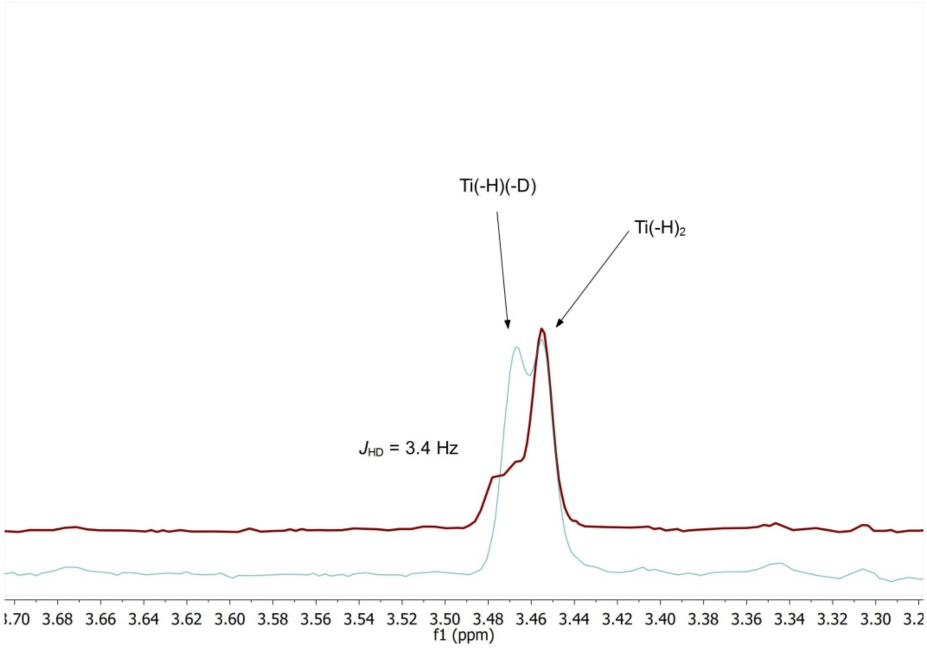
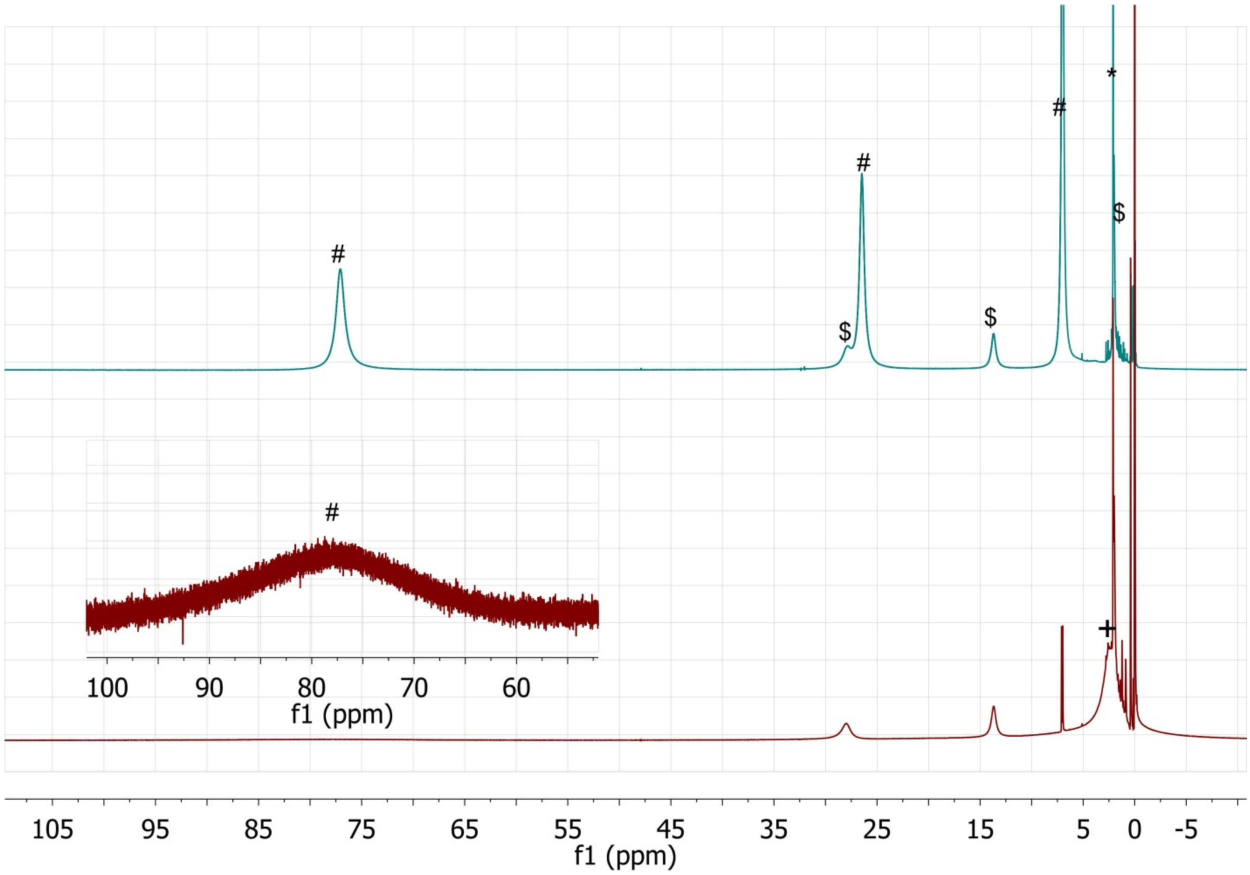


**Figure S14.** $^1$H NMR spectra of a mixture of [($C_5Me_4SiMe_3$)$_2$Ti] (#) and [($C_5Me_4SiMe_3$)$_2$TiH] ($) in toluene-$d_8$ under $H_2$ atmosphere (bottom) and the same mixture after degassing (top spectrum). Both spectra were taken at 25 °C. The insert in the bottom spectrum highlights the presence a broad signal of [($C_5Me_4SiMe_3$)$_2$Ti]. The peak denoted (+) consists of signal of $SiMe_3$ group of [($C_5Me_4SiMe_3$)$_2$TiH] and signals of [($C_5Me_4SiMe_3$)$_2$TiH$_2$].



## Hydrogenation of [$(C_5Me_4SiMe_3)_2Ti$]

Reaction scheme: $[(\eta^5\text{-}C_5Me_4SiMe_3)_2Ti] + H_2 \leftrightarrow [(\eta^5\text{-}C_5Me_4SiMe_3)_2TiH_2]$

**Figure S15.** $^1H$ NMR spectra of [$(C_5Me_4SiMe_3)_2TiH_2$] (**4**) measured in toluene-$d_8$ at −35 °C. (*) denotes solvent signals and (i) is due to an unknown impurity. The broad signal at ca. 3.2 ppm belongs to Si*Me*$_3$ group of [$(C_5Me_4SiMe_3)_2TiH$] (**6**).

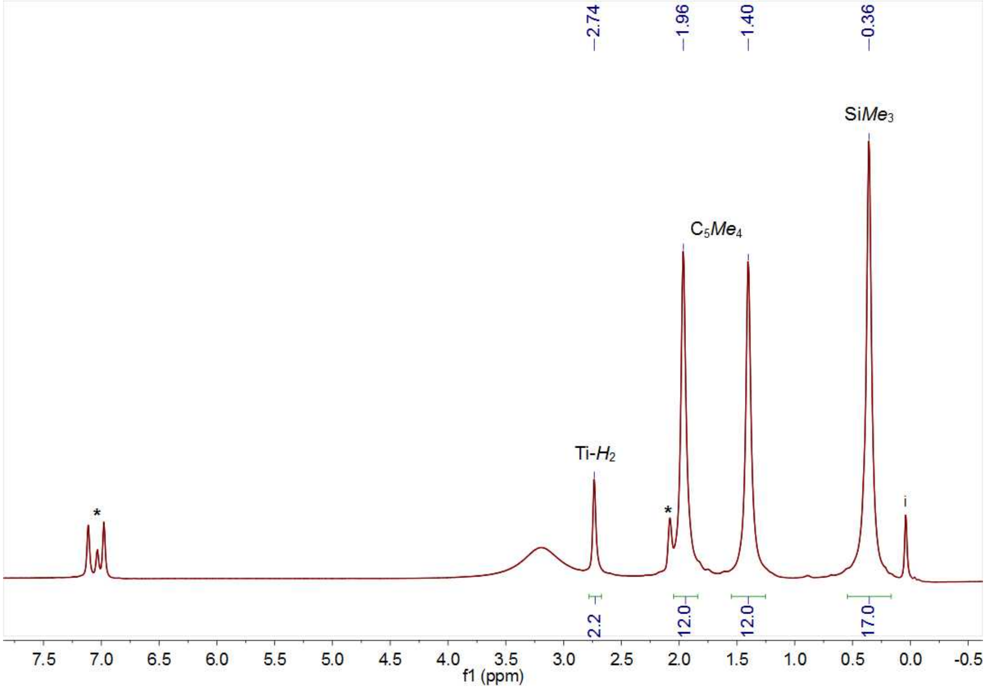


**Figure S16.** $^{13}C\{^1H\}$ NMR spectra of [$(C_5Me_4SiMe_3)_2TiH_2$] (**4**) measured in toluene-$d_8$ at −35 °C. (*) denotes solvent signals.

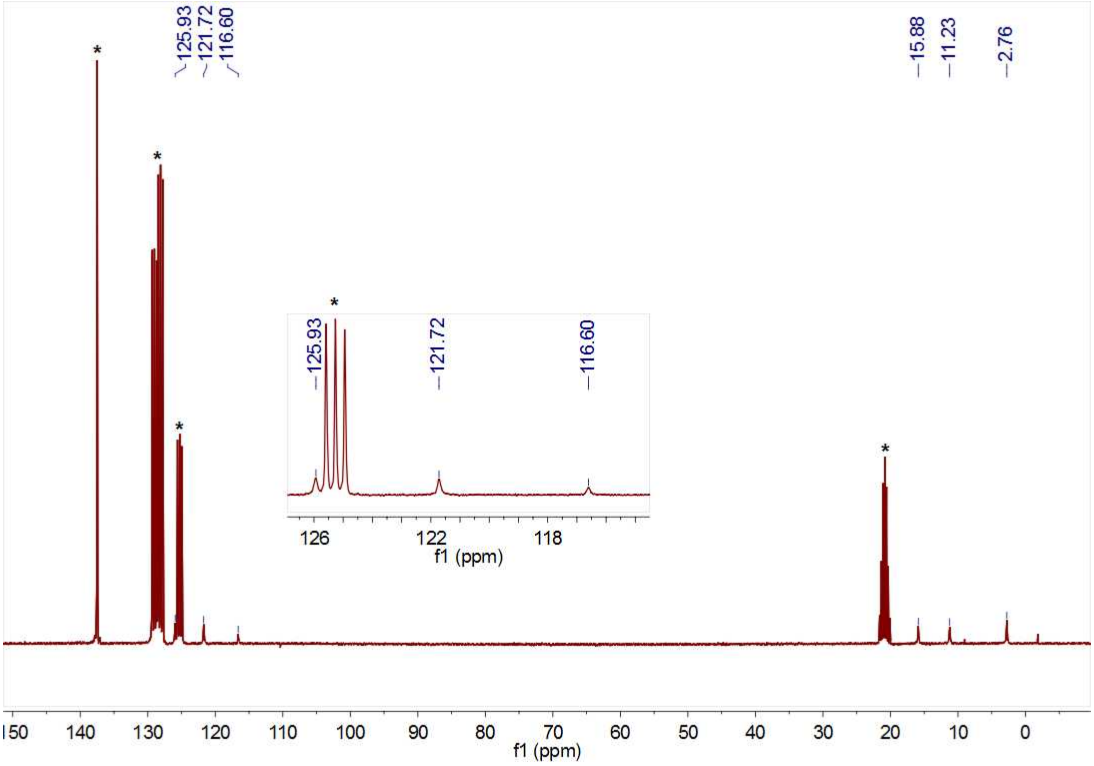


**Figure S17.** $^1$H NMR spectrum of the reaction product of [($C_5Me_4SiMe_3$)$_2$Ti] with HD) in toluene-$d_8$ measured at −45 °C. (*) denotes solvent signals. The hydride signal shows integral intensity of only 1.4 which is consistent with partial isotope exchange. The expanded region displays hydride signals of Ti(-*H*)$_2$ and Ti(-*H*)(-D). The width of the latter signal ca 12 Hz gives an estimated $J_{HD}$ ~ 6 Hz.

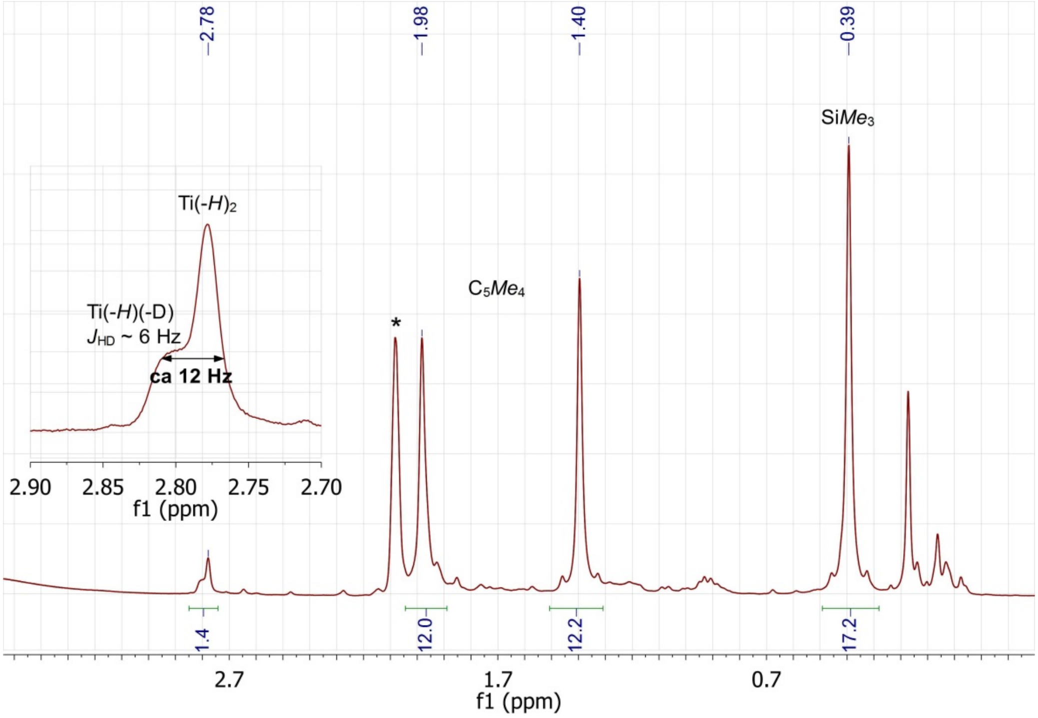


**Figure S18.** $^1$H NMR spectra of the above mixture re-measured after 6 months, taken in toluene-$d_8$ at −45 °C. (*) denotes solvent signals. The hydride integral intensity is restored to an expected value 2.

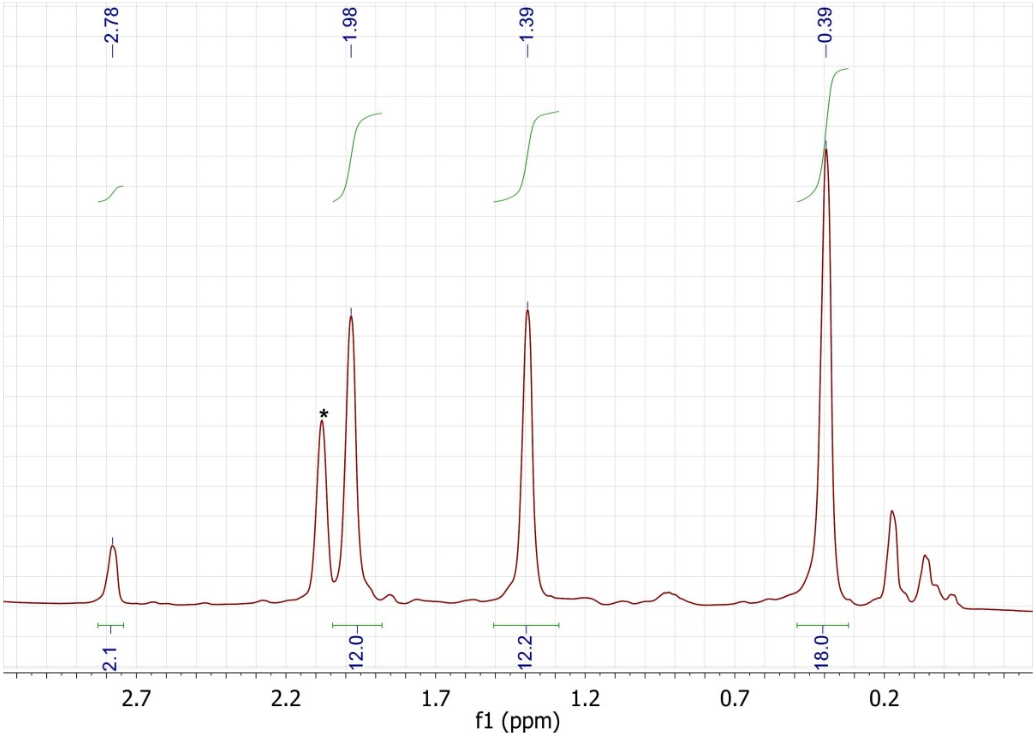


**Figure S19.** $^1$H NMR spectrum of [($C_5Me_4$t-Bu)$_2$TiH] (**5**) in toluene-$d_8$ measured at 25 °C.

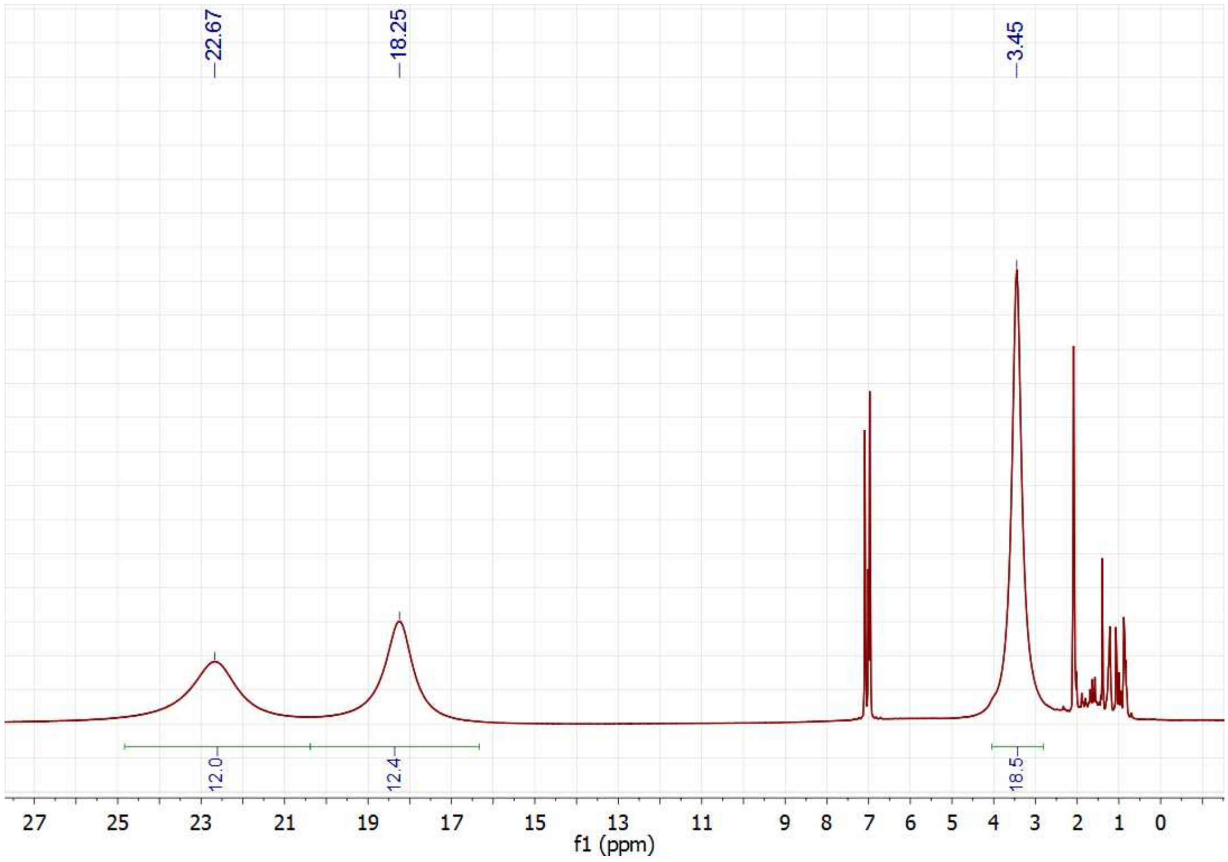


**Figure S20.** $^1$H NMR spectrum of [($C_5Me_4SiMe_3$)$_2$TiH] (**6**) in toluene-$d_8$ measured at 25 °C.

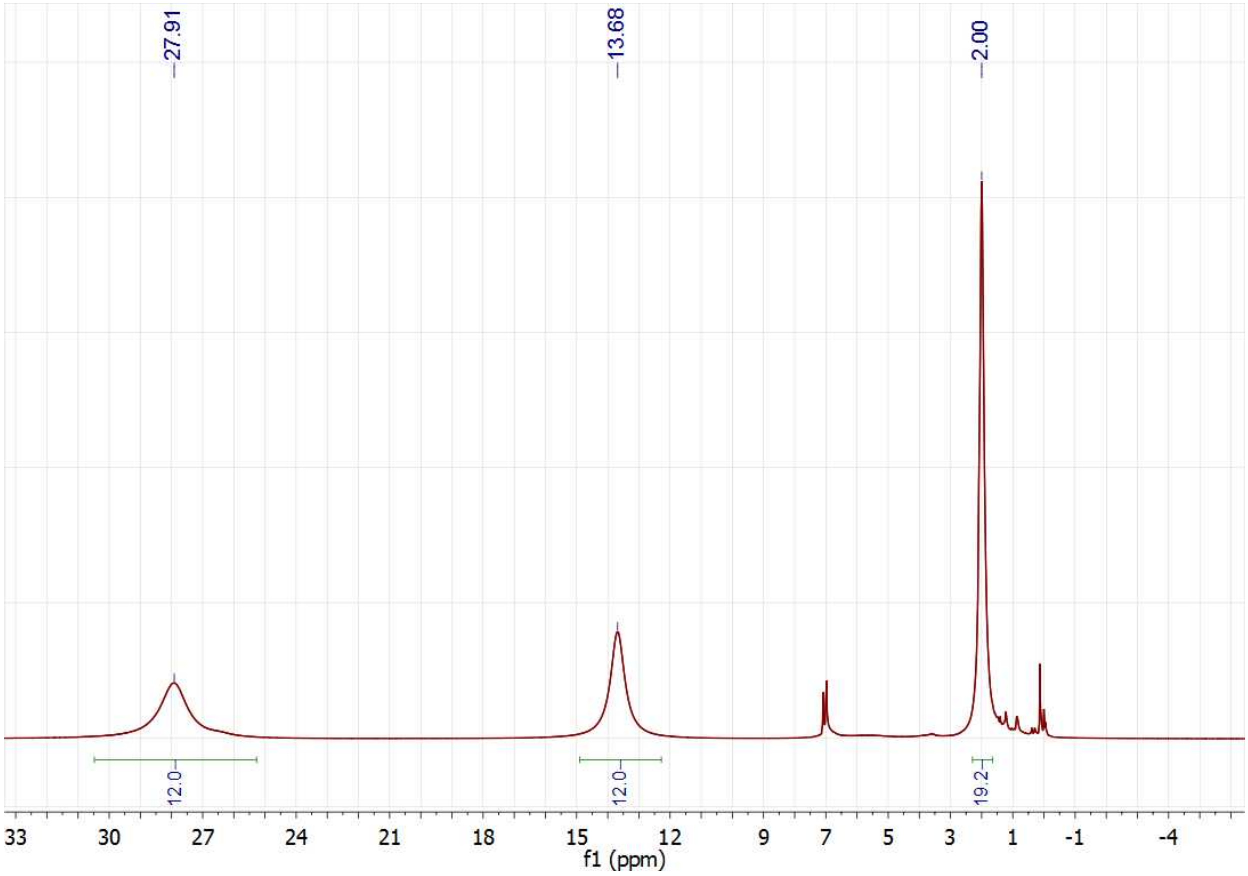


**Figure S21.** $^1$H NMR spectra of a mixture of [($C_5Me_4$t-Bu)$_2$Ti] (#) and [($C_5Me_4$t-Bu)$_2$TiH] ($) (top spectrum); the mixture after addition of 1,3-butadiene (after 24h , the non-reacted butadiene was removed in vacuum) (bottom spectrum). The signals denoted (&) were tentatively attributed to the formed [($C_5Me_4$t-Bu)$_2$Ti(η$^1$-but-2-enyl)].

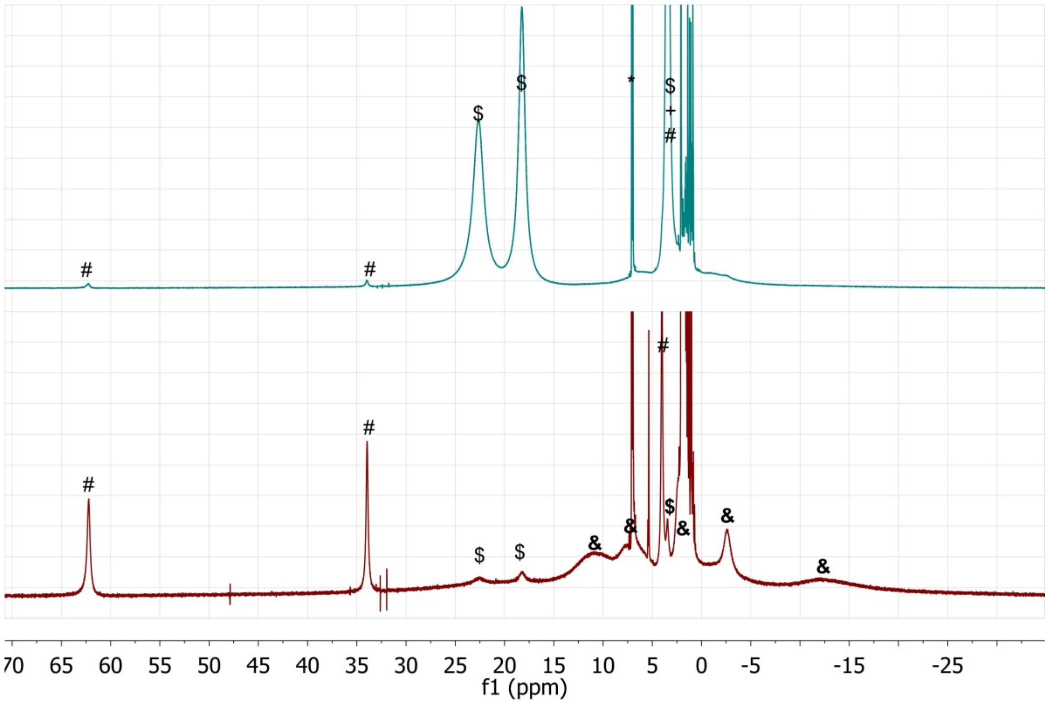
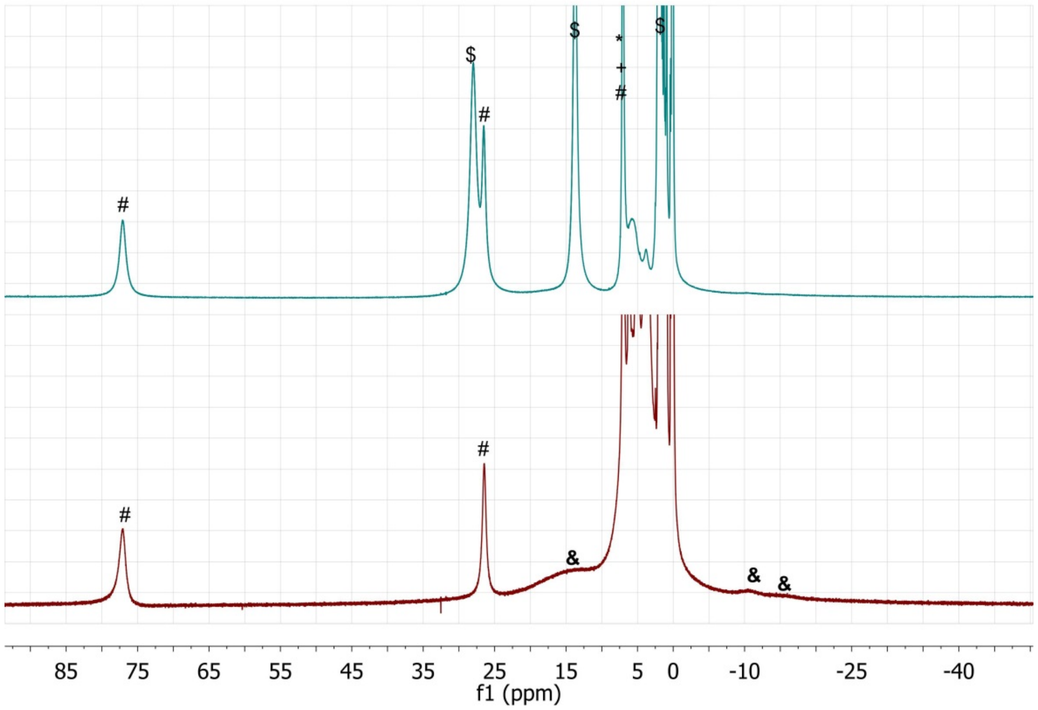
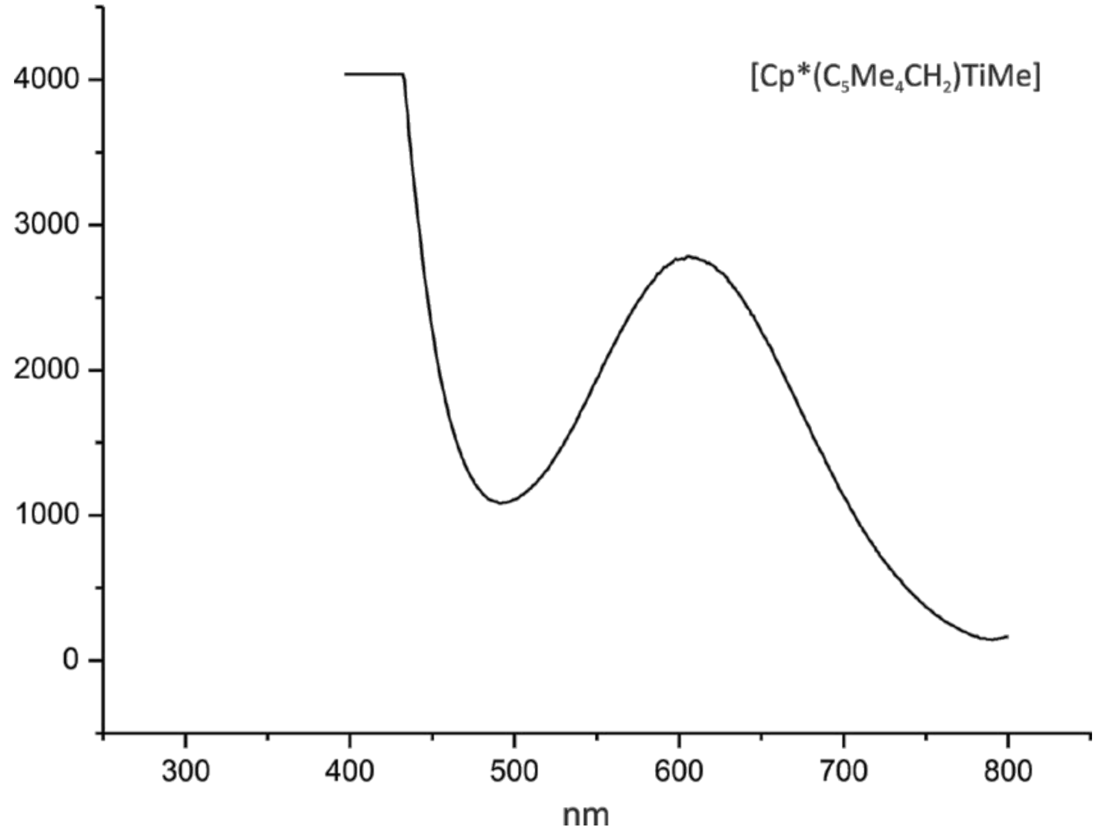


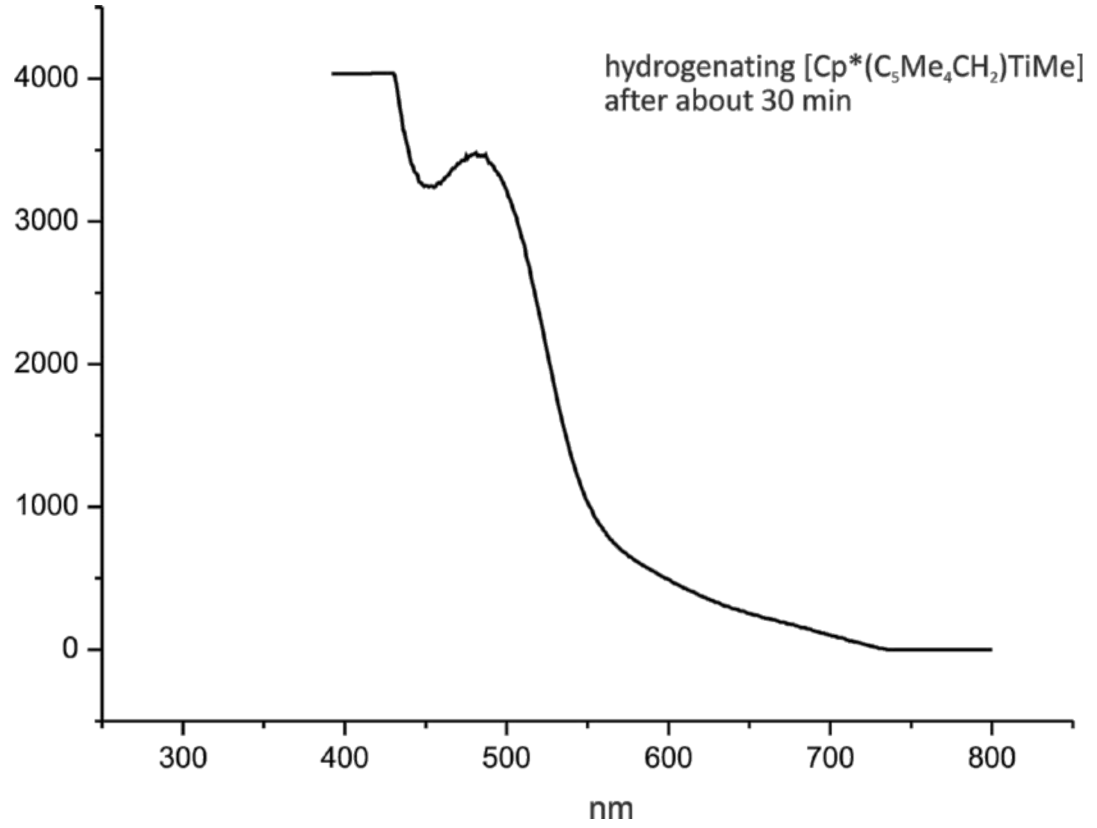
**Figure S22.** $^1$H NMR spectra of a mixture of [($C_5Me_4SiMe_3$)$_2$Ti] (#) and [($C_5Me_4SiMe_3$)$_2$TiH] ($) in toluene-$d_8$ (top spectrum); the mixture after addition of 1,3-butadiene (bottom spectrum). The signals denoted (&) were tentatively assigned to formed [($C_5Me_4SiMe_3$)$_2$Ti(η$^1$-but-2-enyl)].

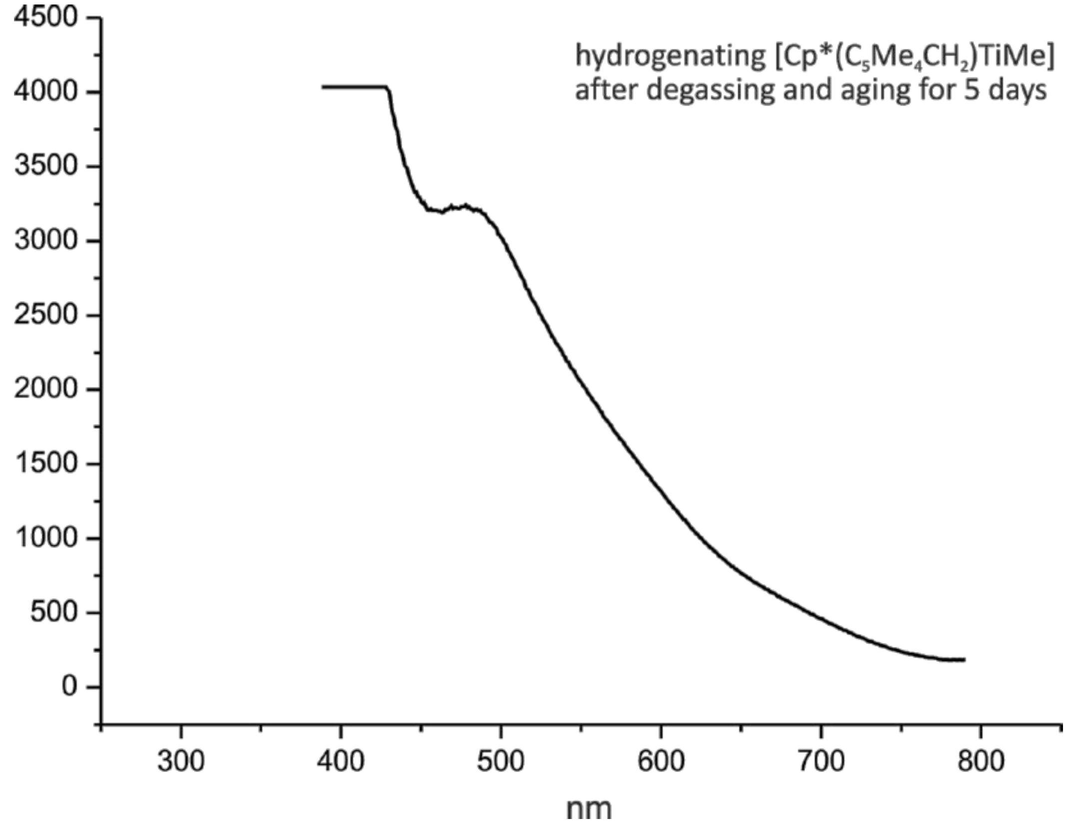


## UV-vis spectra - hydrogenation of [Cp*($C_5Me_4CH_2$)TiMe]

The progress of hydrogenating [Cp*($C_5Me_4CH_2$)TiMe] followed by measuring its electronic absorption spectra in the visible region.

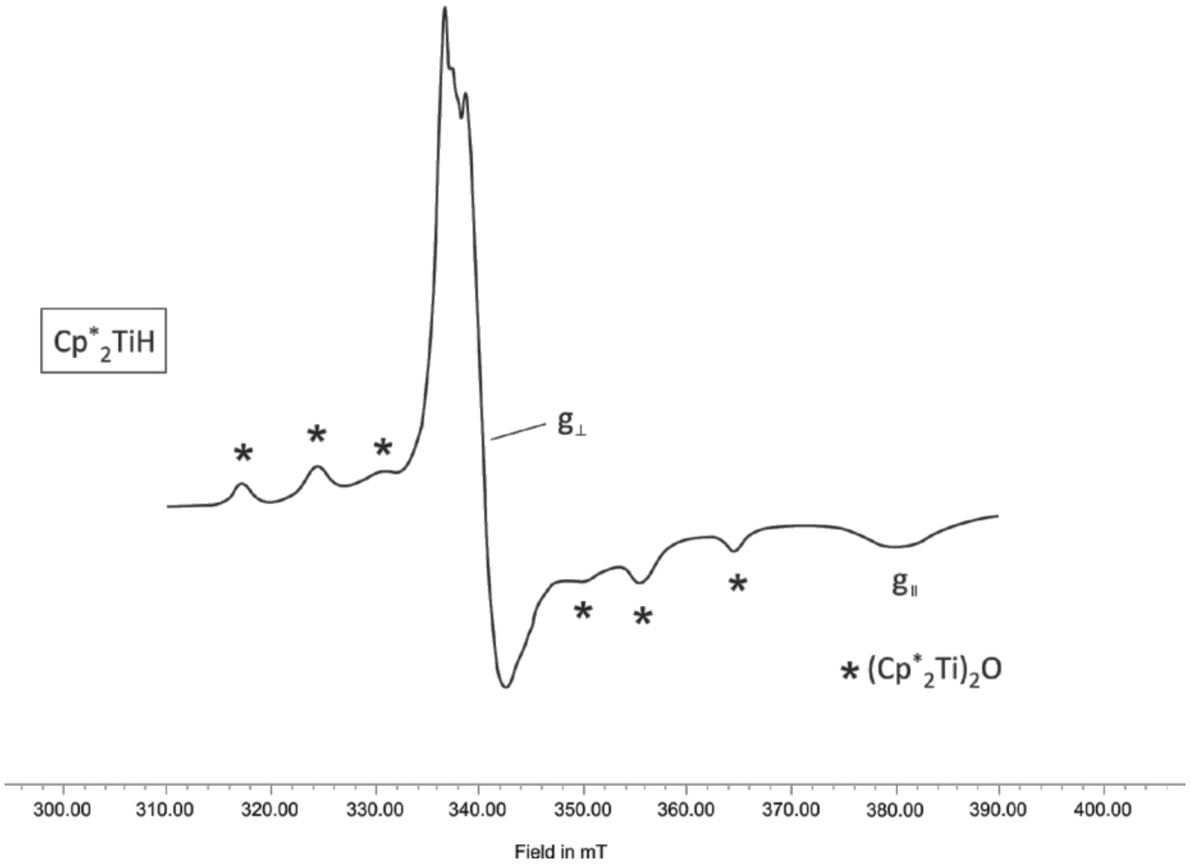


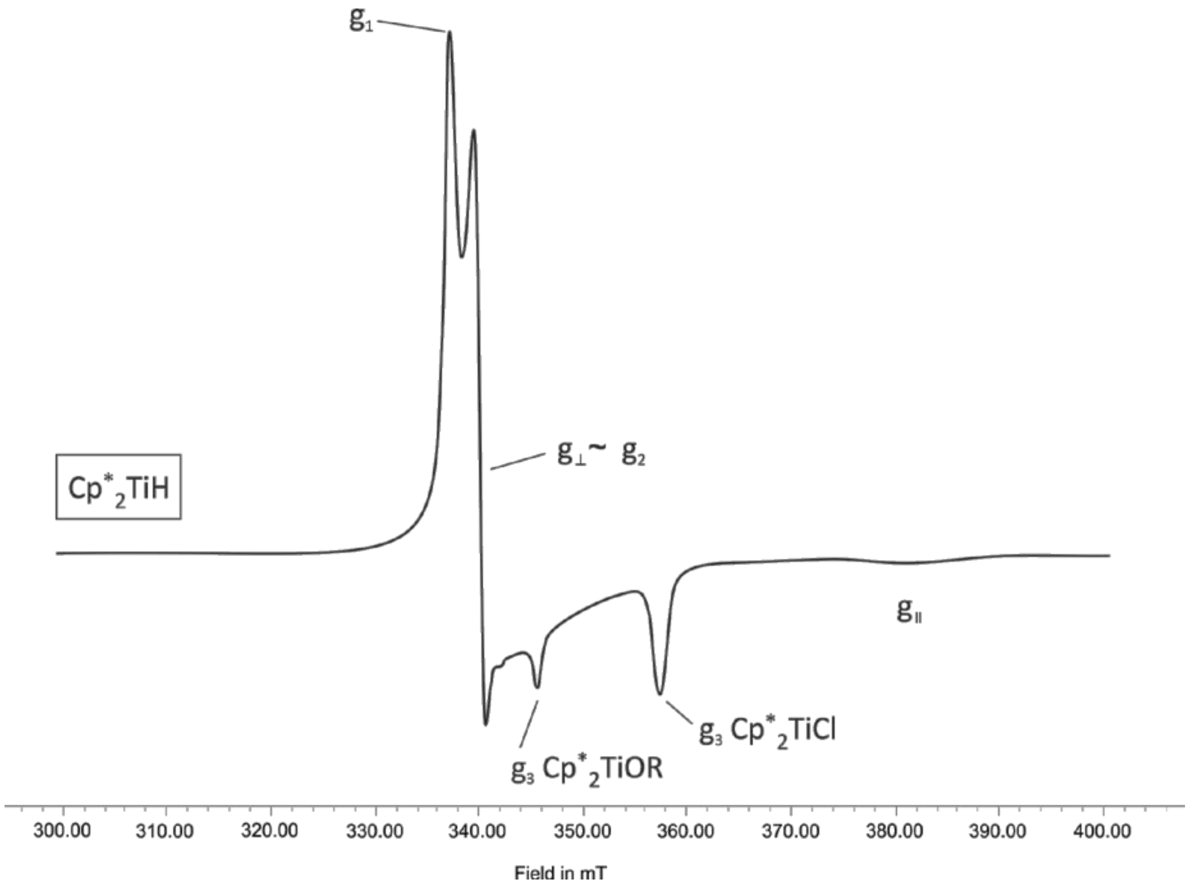



hydrogenating [Cp*(C5Me4CH2)TiMe]
after degassing and aging for 5 days
4500
4000
3500
3000
2500
2000
1500
1000
500
0
300
400
500
600
700
800
nm

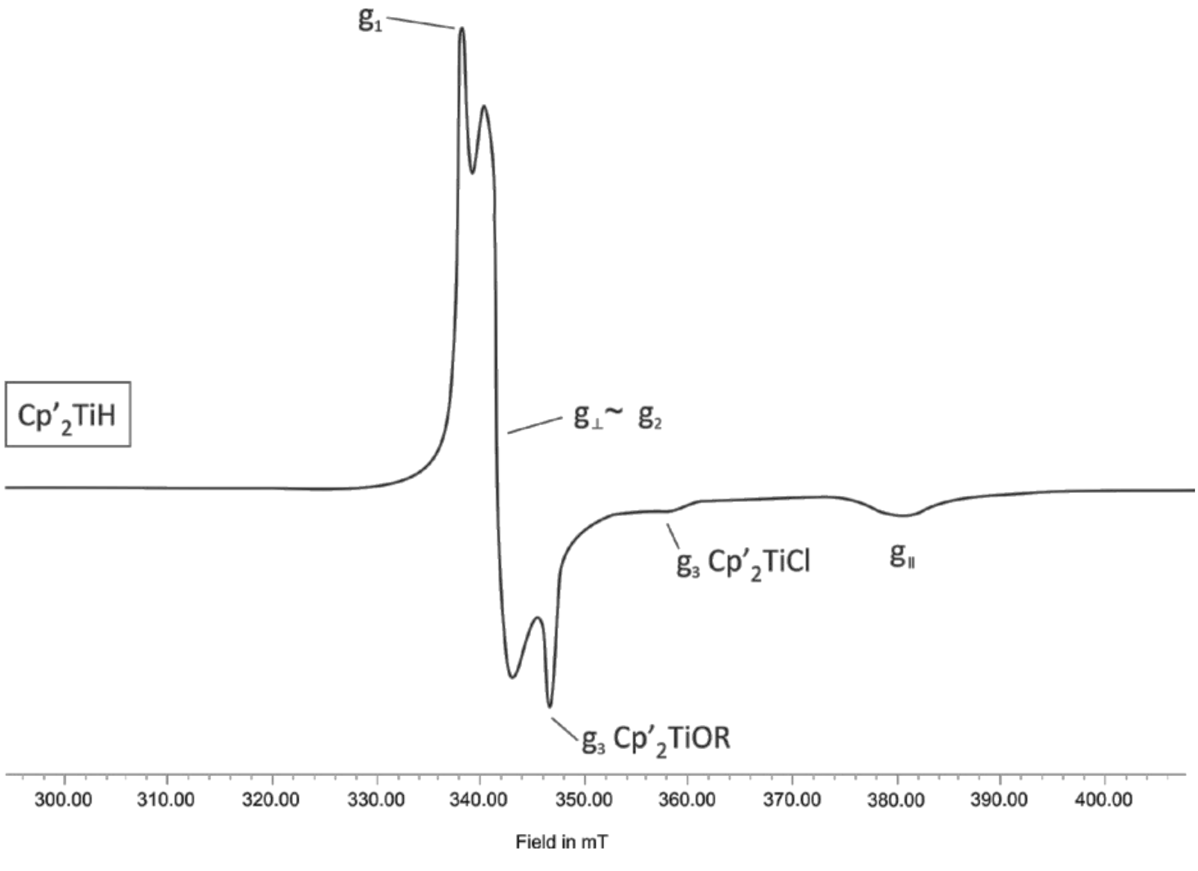
## EPR spectra of $Cp^*_2TiH$ and $Cp'_2TiH$ ($Cp' = C_5Me_4t\text{-}Bu$)

EPR spectra of $Cp^*_2TiH$ and $Cp'_2TiH$ containing various amounts of impurities in toluene-$d_8$ glass at –160 °C. g-Tensor of axial symmetry of the hydrides is denoted by $g_\perp$ and $g_\parallel$; g-tensors of rhombic symmetry for $Cp^*_2TiL$ and $Cp'_2TiL$ (L = OR or Cl) have equal values of $g_1$ and $g_2$; $g_3$ determines the nature of the impurity. $(Cp^*_2Ti)_2O$ forms the electronic triplet state showing the outmost feature $\Delta H_{zz}$ = 473 G, $g_{zz}$ = 1.985 and $\Delta M_S$ = 2 at $g$ ~ 3.970 (for full description see ref.[33]).





$g_1$
$g_\perp \sim g_2$
$Cp^*_2TiH$
$g_3$ $Cp^*_2TiOR$
$g_3$ $Cp^*_2TiCl$
$g_\parallel$
300.00
310.00
320.00
330.00
340.00
350.00
360.00
370.00
380.00
390.00
400.00
Field in mT

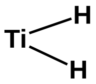
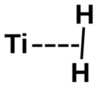


$g_1$
$g_\perp \sim g_2$
$Cp'_2TiH$
$g_3$ $Cp'_2TiCl$
$g_\parallel$
$g_3$ $Cp'_2TiOR$
300.00
310.00
320.00
330.00
340.00
350.00
360.00
370.00
380.00
390.00
400.00
Field in mT

**Crystallographic Data, Data Collection and Structure Refinement for 1B, 1A, 5, and 8**

| | **1B** | **1A** | **5** | **8** |
|---|---|---|---|---|
| Formula | $C_{60}H_{92.50}Cl_{0.75}Ti_3$ | $C_{40}H_{62.50}Cl_{0.25}Ti_2$ | $C_{26}H_{43}Ti$ | $C_{28}H_{49}Si_2Ti$ |
| Mol. Wt. | 984.12 | 648.06 | 403.50 | 489.75 |
| Crystal system | monoclinic | monoclinic | triclinic | monoclinic |
| Space group | *C*2/*c* | *C*2/*c* | *P-1* (No. 2) | $P2_1/n$ (No. 14) |
| $a$ (A) | 31.2307(16) | 38.9059(17) | 8.6546(3) | 12.9701(6) |
| $b$ (A) | 8.4988(4) | 8.4278(3) | 17.0780(5) | 14.6030(7) |
| $c$ (A) | 22.5450(10) | 22.7517(10) | 17.4546(6) | 15.4311(7) |
| $\alpha$ (deg) | 90 | 90 | 66.0210(10) | 90 |
| $\beta$ (deg) | 108.619(2) | 90.247(2) | 88.0080(10) | 102.825(2) |
| $\gamma$ (deg) | 90 | 90 | 88.7080(10) | 90 |
| $V$ ($A^3$) | 5670.8(5) | 7460.0(5) | 2355.67(13) | 2849.8(2) |
| Z | 4 | 8 | 2 | 4 |
| $D_{calcd}$ (g $cm^{-3}$) | 1.153 | 1.154 | 1.138 | 1.141 |
| $\mu$ ($mm^{-1}$) | 0.482 | 0.471 | 0.371 | 0.398 |
| Color | ocher | orange | brown | brown |
| Crystal size ($mm^3$) | 0.627×0.480×0.384 | 0.862×0.309×0.232 | 1.11×0.45×0.45 | 0.787×0.656×0.572 |
| $T$ (K) | 150(2) | 150(2) | 150(2) | 150(2) |
| $\vartheta_{min}$; $\vartheta_{max}$ (deg) | 2.493;27.134 | 2.473;27.498 | 1.31; 27.50 | 1.86; 27.52 |
| Range of $h$ | −40/40 | −50/50 | −11/11 | −16/14 |
| Range of $k$ | −10/10 | −10/10 | −22/20 | −18/18 |
| Range of $l$ | −28/28 | −29/29 | −18/22 | −19/13 |
| No. of diffrns collected | 71667 | 71286 | 21971 | 20593 |
| No. of unique diffrns | 6250 | 8538 | 10747 | 6446 |
| $F(000)$ | 2125 | 2806 | 884 | 1068 |
| No. of params | 317 | 435 | 587 | 305 |
| $R(F)$; $wR(F^2)$ all data (%) | 6.89; 14.93 | 5.25; 10.86 | 5.43; 10.67 | 6.74; 12.06 |
| GooF ($F^2$), all data | 1.082 | 1.052 | 1.026 | 1.033 |
| $R(F)$; $wR(F^2)$ [$I > 2\sigma(I)$] | 5.59; 13.98 | 4.00; 9.97 | 3.94; 10.01 | 4.28;10.90 |
| $\Delta\rho$ (e.$A^{-3}$) | 1.182; −0.890 | 0.368; −0.594 | 0.353; −0.267 | 0.444; −0.345 |

**Table 1 DFT calculations of difference in total energies for titanocene dihydride and titanocene dihydrogen complexes and counterpoise energy for the former ones**

| Titanocene $Cp'_2Ti$ | Total energy of $Cp'_2TiH_2$ $E_1$<br>(hartrees)<br> | Total energy of $Cp'_2Ti(H_2)$ $E_2$<br>(hartrees)<br> | $\Delta H^{\ddagger}=E_1 - E_2$ (kJ/mol) | Counterpoise energy (kJ/mol)<br>$[Cp'_2Ti]/[2H]$ |
|---|---|---|---|---|
| $Cp^*_2Ti$ | -1630.29485294 | -1630.28178644 | 34.31 | -132.70 |
| $(C_5Me_4{}^tBu)_2Ti$ | -1865.95558237 | -1865.94733667 | 21.65 | -121.11 |
| $(C_5Me_4SiMe_3)_2Ti$ | -2368.83159428 | -2368.82507716 | 17.11 | -112.35 |