Supplementary Material

Novel Addition Reactions of 2,2,7,7-Tetramethyl-3,5-octadiyne to the Methyl Groups of an η^5-Pentamethylcyclopentadienyl Ligand.

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Experimental Methods. All manipulations with titanium complexes were performed using all-sealed glass devices equipped with breakable seals on a high-vacuum line.

^{1}H; ^{1}H,^{1}H-COSY-90, ^{13}C{^{1}H}, ^{13}C APT and ^{13}C HMQC NMR spectra were measured on a Varian UNITY Inova 400 instrument (^{1}H, 399.95; ^{13}C, 100.58 MHz) in C_6D_6 at 25°C. Chemical shifts (δ, ppm) are given relative to the solvent signal (δ_H 7.15, δ_C 128.0). Mass spectra were measured on a VG 7070E instrument (EI, 70 eV, direct inlet). UV/vis spectra were recorded on a Varian Cary 17D spectrometer in the range of 280-2000 nm using a pair of all-sealed quartz cells (Hellma; d = 0.1 and 1.0 cm). IR spectra in KBr pellets were measured on a Specord 75 IR spectrometer (Carl Zeiss, Jena, Germany). X-ray data of 3a/3b were collected on a STOE-IPDS/CAD-4 Mach-III four circle diffractometer using graphite-monochromated Mo-K_α radiation. The structures were solved by direct methods (SHELXS 86: Sheldrick, G. M.; *Acta Crystallogr. Sect. A*, **1990**, *46*, 467) and refined by full matrix least square techniques against F^2

(SHELXL 93: Sheldrick, G. M.; University of Göttingen, Germany , **1993**). XP (Siemens Analytical X-ray Instruments, Inc.) was used for the structure representation.

Synthesis of [{η^5-$C_5Me_3(CH_2CH(tBu)CH{=}CHCH(tBu)CH_2)$}{$\eta^3$:$\eta^4$-$C_5Me_3(CH_2)_2$}Ti(II)] (3a). (a) Thermolysis of [(η^5-$C_5Me_5)_2$Ti(η^2-$Me_3SiC{\equiv}CSiMe_3$)]: To a solution of [(η^5-$C_5Me_5)_2$Ti(η^2-$Me_3SiC{\equiv}CSiMe_3$)] (1.0 g, 2.0 mmol) in hexane (20 mL) was added 2,2,7,7-tetramethyl-3,5-octadiyne (0.33 g, 2.0 mmol) and the solvent was replaced by *m*-xylene (10 mL) on a vacuum line. The resulting solution was heated in a sealed ampule to 130°C for 5 h whereupon the mixture turned blue. All volatiles were distilled off in vacuum and the residue was dissolved in 10 mL of hexane. After cooling to -18°C, a blue solid precipated which was separated from a dirty blue mother liquor, washed with hexane and recrystallized from a minimum volume of hexane to give blue crystalline **3a**. Yield 0.81 g (84 %). (b) Thermolysis of [(η^5-C_5Me_5)Ti{η^5-$C_5Me_3(CH_2CH(tBu)$-η^2-C_2-$CH(tBu)CH_2)$}] (**2a**): A solution of **2a** (0.20 g, 0.4 mmol) in *m*-xylene was heated to 130°C for 48 h and the originally green-yellow solution gradually turned blue. All volatiles were distilled off in vacuum and the residue was dissolved in 10 mL of hexane. Cooling to -30°C induced the precipitation of a blue solid which was separated from the blue mother liquor, washed with hexane and recrystallized from a minimum volume of hexane to give blue crystalline **3a**. Yield 0.16 g (80 %).

Mp 109°C. EI-MS (direct inlet, 70 eV, 100°C; *m/z* (relative abundance)): 480 ($M^{+\cdot}$, 48), 465 (2), 423 [M - *t*Bu]$^+$, 100), 422 (17), 421 (17), 419 (8), 366 ([M - 2 *t*Bu]$^{+\cdot}$, 5), 181 (6), 57 (4). ^{1}H NMR (C_6D_6): δ 0.89 (s, 9 H, $(CH_3)_3C$), 0.95 (d, $^2J_{HH}$ = 4.5 Hz, 1 H, =CH_2 A), 0.97 (d, $^2J_{HH}$ =

4.4 Hz, 1 H, =CH_2 B), 0.99 (s, 9 H, $(CH_3)_3C$), 1.00 (d, *J* not read, 1 H, =CH_2 A), 1.01 (d, $^2J_{HH}$ = 4.4 Hz, 1 H, =CH_2 B), 1.16, 1.18, 1.36, 1.75, 1.76, 1.83 (6× s, 3 H, CH_3); 2.31 (ddd, $^3J_{HH}$ = 14, 6.3, 5 Hz, 1 H, CH A), 2.34 (dd, $^3J_{HH}$ = 15.8, 4.4 Hz, 1 H, CH_2 B), 2.43 (dd, $^3J_{HH}$ = 13.8, 4.3 Hz, 1 H, CH_2 A), 2.60 (dd, $^3J_{HH}$ = 15.7, 13.0 Hz, 1 H, CH_2 B), 2.74 (dd, $^3J_{HH}$ = 13.8, 13.8 Hz, 1 H, CH_2 A), 3.05 (ddd, $^3J_{HH}$ = 13.0, 9.6, 4.3 Hz, 1 H, CH B), 5.55 (dd, $^3J_{HH}$ = 9.6, $^2J_{HH}$ = 12.1 Hz, 1 H, -CH= B), 5.63 (dd, $^3J_{HH}$ = 6.4, $^2J_{HH}$ = 12.1 Hz, 1 H, -CH= A). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 10.35 (δ_H 1.16 or 1.18), 10.39 (δ_H 1.16 or 1.18), 10.61 (δ_H 1.36), 11.34 (δ_H 1.76), 12.13 (δ_H 1.75), 12.44 (δ_H 1.83) (6× CH_3); 27.55 (CH_2 A), 27.64 (δ_H 0.89), 28.26 (δ_H 0.99) (2× $C(CH_3)_3$); 30.18 (CH_2 B), 33.11, 34.94 (2× $C(CH_3)_3$); 45.36 (CH B), 53.76 (CH A), 67.44, 67.78 (=CH_2 A and B); 118.87, 119.64, 119.84, 122.64, 122.81, 122.93, 123.63 (7× C_{ipso} cyclopentadienyl and allyldiene); 130.56 (-CH= A), 132.20 (-CH= B), 133.36, 144.78, 144.79 (3× C_{ipso} cyclopentadienyl and allyldiene). The A and B labels used to distinguish between NMR signals of the related groups can be interchanged, however, in the complete series only. UV/vis (hexane, 22°C; nm): 365 (sh) >> 580. IR (KBr, cm^{-1}): 3033 (m), 2995 (s), 2933 (vs,b), 2894 (vs), 2852 (vs), 1622 (vw,b), 1464 (vs,b), 1440 (vs), 1387 (s), 1365 (s), 1358 (vs), 1335 (m), 1281 (w), 1223 (s), 1180 (vw),1109 (vw), 1082 (m), 1073 (sh), 1041 (vw), 1016 (s), 940 (vw), 921 (vw), 874 (m), 822 (vs), 792 (m), 725 (m), 713 (s), 680 (vw), 619 (w), 577 (s), 549 (w), 486 (w), 438 (m). Elemental analysis: Calcd. for $C_{32}H_{48}Ti$ C, 79.97; H, 10.07; found C, 79.68; H, 10.05%.

Synthesis of [{η⁵-$C_5HMe_2(CH_2CH(tBu)CH=CHCH(tBu)CH_2)$}{η³:η⁴-$C_5HMe_2(CH_2)_2$}Ti(II)] (3b). To a solution of [(η⁵-$C_5HMe_4)_2$Ti(η²-$Me_3SiC{\equiv}CSiMe_3$)] (0.28 g, 0.6 mmol) in hexane (5 mL) was added 2,2,7,7-tetramethyl-3,5-octadiyne (0.08 g, 0.5 mmol) and the solvent was replaced by *m*-xylene (5 mL) on a vacuum line. The solution was heated in a

sealed ampule to 140°C for 2 h yielding a brown mixture. Volatiles were distilled off in vacuum and the brown residue was dissolved hexane (5 mL). Upon cooling to -18°C, a blue solid crystallized from the brown mother liquor. The crystals of **3b** were separated, washed with a small amount of hexane and dried in vacuum. The volatiles, contained according to GCMS analysis, *m*-xylene and BTMSA. Yield 22 mg (8%). Mp 104°C. EI-MS (direct inlet, 70 eV, 100°C; *m/z* (relative abundance)): 454 (23), 453 (50), 452 ($M^{+\cdot}$; 96), 451 (26), 450 (20), 397 (20), 395 ([M - tBu]$^+$, 100), 394 (24), 393 (34), 392 (10), 391 (17), 338([M - 2 tBu]$^{+\cdot}$, 12), 168 (11), 167 (15), 166 (12), 57 (14), 41 (14). HR MS analysis: 452.2948, error -2.6×10^{-3} *u* for $C_{30}H_{44}Ti$; 395.2246, error -2.8×10^{-3} *u* for $C_{26}H_{35}Ti$. ^{1}H NMR (C_6D_6): δ 0.89 (d, J not read, 1 H, =CH_2 A), 0.89 (s, 9 H, $(CH_3)_3C$), 0.97 (s, 9 H, $(CH_3)_3C$), 1.08 (d, $^2J_{HH}$ = 4.4 Hz, 1 H, =CH_2 B), 1.10 (d, $^2J_{HH}$ = 4.1 Hz, 1 H, =CH_2 A), 1.11 (s, 3 H, CH_3), 1.19 (d, $^2J_{HH}$ = 4.4 Hz, 1 H, =CH_2 B), 1.38, 1.69, 1.88 (3× s, 3 H, CH_3); 2.24 (dd, $^3J_{HH}$ = 14.2, 5.7 Hz, 1 H, CH_2 A), 2.36 (ddd, $^3J_{HH}$ = 13.2, 6.3, 5.7 Hz, 1 H, CH A), 2.59-2.70 (m, 2 H, CH_2 B), 2.81 (dd, $^3J_{HH,1} \approx {}^3J_{HH,2} \approx$ 13.5 Hz, 1 H, CH_2 A), 3.03 (ddd, $^3J_{HH}$ = 13.0, 9.6, 4.7 Hz, 1 H, CH B), 4.24 (s, 1 H, CH allyldiene), 5.60 (dd, $^3J_{HH}$ = 9.6, $^2J_{HH}$ = 12.2 Hz, 1 H, -CH= B), 5.68 (dd, $^3J_{HH}$ = 6.3, $^2J_{HH}$ = 12.2 Hz, 1 H, -CH= A), 5.78 (s, 1 H, CH cyclopentadienyl). ^{13}C{^{1}H} NMR (C_6D_6): δ 10.44 (δ_H 1.11), 12.39 (δ_H 1.38), 12.52 (δ_H 1.88), 13.62 (δ_H 1.69) (4× CH_3); 27.56 (δ_H 0.89), 28.26 (δ_H 0.97) (2× $C(CH_3)_3$); 30.89 (CH_2 A), 31.19 (CH_2 B), 32.96, 34.47 (2× $C(CH_3)_3$); 45.06 (CH B), 55.53 (CH A), 67.57 (=CH_2 B), 69.52 (=CH_2 A), 109.87 (CH cyclopentadienyl), 115.89 (CH allyldiene), 120.25, 122.08, 124.98, 125.14, 125.33 (5× C_{ipso} cyclopentadienyl and allyldiene); 130.32 (-CH= A), 132.22 (-CH= B), 136.44, 144.36 and 146.84 (3× C_{ipso} cyclopentadienyl and allyldiene). The A and B

labels used to distinguish between NMR signals of the related groups can be interchanged but in the complete series only. IR (KBr, cm^{-1}): 3039 (m), 3021 (m), 3000 (s), 2946 (vs,b), 2900 (vs), 2860 (vs), 1637 (w), 1620 (sh), 1587 (vw), 1467 (s), 1440 (s), 1392 (m), 1378 (m), 1363 (s), 1340 (m), 1316 (vw), 1302 (vw), 1282 (w), 1229 (s), 1167 (w), 1112 (w), 1092 (w), 1023 (m), 985 (w), 962 (w), 927 (w), 920 (w), 874 (m), 834 (s), 823 (s), 795 (s), 739 (m), 719 (m), 677 (w), 657 (w), 629 (vw), 606 (w), 580 (m), 565 (w), 533 (w), 507 (vw), 480 (w), 446 (m). UV/vis (hexane, 22°C; nm): 355 (sh) >> 555.

Supplementary Material

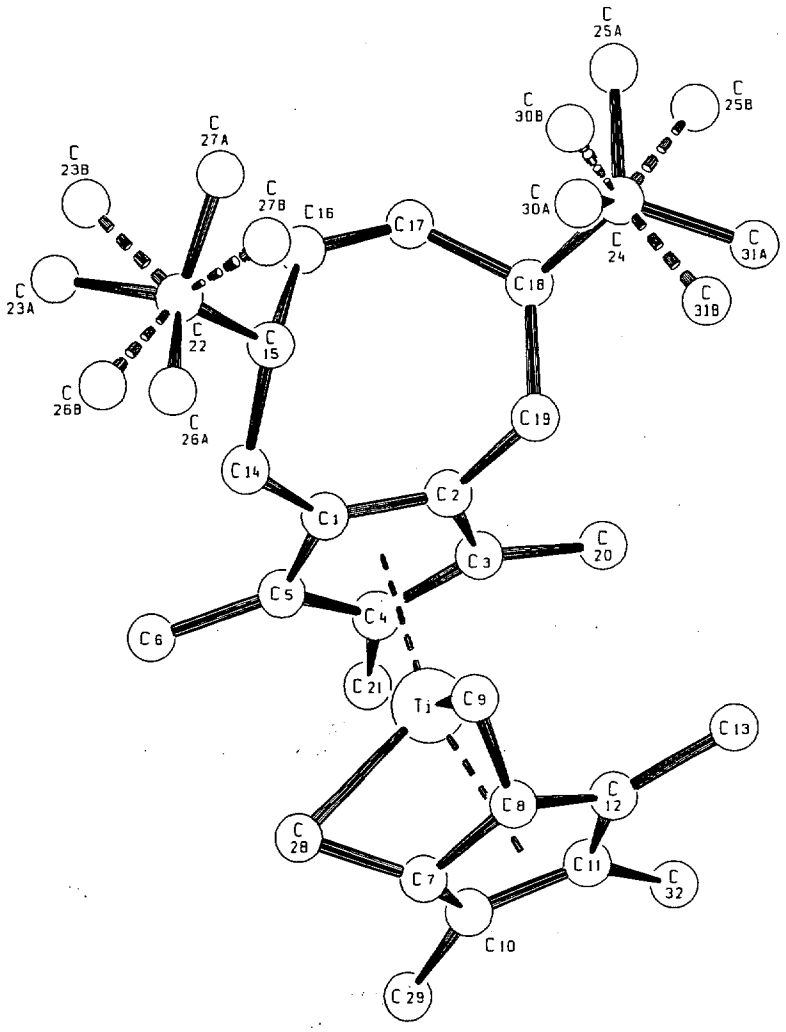

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Figure 1 Molecular structure of 3a.

Contents:

Table 1. Crystal data and structure refinement for 3a.

Identification code	235
Empirical formula	C32 H48 Ti
Formula weight	480.60
Crystal system	TRICLINIC
Space group	P-1
Unit cell dimensions	a= 9.389(2) A alpha= 79.82(3) deg. b= 12.069(2) A beta= 83.11(3) deg. c= 13.328(3) A gamma= 75.82(3) deg.
Temperature for cell	200(2)
Number of reflecions for cell	1660
Theta for cell determination	4 to 20 deg
Volume	1436.5(5) A^3
Z	2
Density (calculated)	1.111 Mg/m^3
Absorption coefficient	0.314 mm^-1
F(000)	524
Crystal colour	BLUE
Crystal description	PRISM
Crystal size	0.2 x 0.1 x 0.1 mm
Temperature	200(2) K
Wavelength	0.71073 A
Radiation type	MoK\a
Radiation source	fine-focus sealed tube
Monochromator	graphite
Measurment device	STOE-IPDS
Scan method	LASER SCANNED IMAGING PLATE
Standards (intensity + orient.)	50-200
Intensity after	360 sec
Theta range for data collection	1.56 to 21.04 deg.

Index ranges	-9<=h<=9, -11<=k<=12, 0<=l<=13
Reflections collected	2929
Independent reflections	2929 [R(int) = 0.0000]
Reflections unique	2929
Reflections observed	1151
Criterion	>2sigma(I)
Absorption correction	MEAN IMAGING PLATE INTENSITY METHOD
Structure solution primary	direct
Structure solution secondary	difmap
Hydrogen positions	geom
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2929 / 30 / 276
Final R indices [I>2sigma(I)]	R1 = 0.0620, wR2 = 0.1015
R indices (all data)	R1 = 0.1573, wR2 = 0.1219
Goodness-of-fit on F^2(all)	0.761
Goodness-of-fit on F^2(obs)	1.095
Shift/esd(max)	0.000
Shift/esd(mean)	0.000

Weighting scheme

calc w=1/[\s^2^(Fo^2^)+(0.0217P)^2^+0.0000P] where P=(Fo^2^+2Fc^2^)/3

Largest diff. peak and hole	0.314 and -0.463 e.A^-3
Diff. density rms	0.052
Data collection	STOE-EXPOSE
Cell refinement	STOE-CELL
Data reduction	STOE-INTEGRATE
Structure solution	SHELXS-86 (Sheldrick, 1990)
Structure refinement	SHELXL-93 (Sheldrick, 1993)
Molecular graphics	SCHAKAL
Publication material	SHELXL-93

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 2a. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(25A)	13941(8)	-484(7)	1919(6)	72(2)
C(30A)	11768(8)	-768(7)	1144(6)	72(2)
C(31A)	12825(10)	981(6)	510(6)	72(2)
C(25B)	14088(8)	222(7)	1410(7)	72(2)
C(30B)	12564(9)	-1155(6)	1428(6)	72(2)
C(31B)	11791(9)	824(7)	480(7)	72(2)
C(1)	8028(8)	1670(6)	3475(6)	29(2)
C(2)	9035(8)	2127(7)	2757(6)	33(2)
C(3)	8951(8)	3267(6)	2916(6)	29(2)
C(4)	7910(8)	3511(7)	3725(7)	38(2)
C(5)	7319(8)	2548(7)	4067(6)	31(2)
C(6)	6201(8)	2444(6)	4990(6)	61(3)
C(7)	4650(9)	3949(9)	1828(8)	52(3)
C(8)	5696(10)	3445(8)	1047(7)	51(3)
C(9)	6336(9)	2250(8)	1220(7)	71(3)
C(10)	4940(12)	4977(9)	1950(9)	63(3)
C(11)	6150(13)	5177(8)	1265(9)	61(3)
C(12)	6618(10)	4235(10)	732(7)	56(3)
C(13)	7892(9)	4095(9)	-99(7)	100(4)
C(14)	7701(7)	488(6)	3658(6)	51(3)
C(15)	8908(8)	-526(6)	3448(6)	42(2)
C(16)	10354(8)	-508(6)	3784(6)	30(2)
C(17)	11386(8)	15(6)	3289(7)	38(2)
C(18)	11414(8)	773(7)	2293(7)	61(3)
C(19)	10013(8)	1520(7)	1925(6)	46(2)
C(20)	9959(8)	4029(6)	2357(7)	70(3)
C(21)	7561(9)	4613(6)	4199(6)	75(3)
C(22)	8536(6)	-1739(6)	3738(5)	44(2)
C(24)	12481(6)	125(5)	1452(4)	56(3)
C(28)	4325(8)	3151(9)	2729(8)	84(3)
C(29)	4073(11)	5834(8)	2658(8)	128(5)
C(32)	6780(11)	6233(8)	1094(8)	116(4)
Ti	6672(2)	3246(1)	2398(1)	38(1)
C(23A)	8218(11)	-2001(9)	4892(6)	40(3)
C(26A)	7211(9)	-1732(9)	3181(9)	47(4)
C(27A)	9835(9)	-2676(8)	3420(9)	48(3)
C(23B)	9099(46)	-2461(32)	4729(18)	116(18)
C(26B)	6961(16)	-1881(33)	3799(32)	88(16)
C(27B)	9281(33)	-2288(27)	2809(17)	60(11)

Table 3. Bond lengths [A] and angles [deg] for 3a.

C(25A)-C(24)	1.535(5)
C(30A)-C(24)	1.535(5)
C(31A)-C(24)	1.534(5)
C(25B)-C(24)	1.535(5)
C(30B)-C(24)	1.534(5)
C(31B)-C(24)	1.535(5)
C(1)-C(2)	1.403(9)
C(1)-C(5)	1.419(9)
C(1)-C(14)	1.504(9)
C(1)-Ti	2.364(7)
C(2)-C(3)	1.411(9)
C(2)-C(19)	1.524(9)
C(2)-Ti	2.352(7)
C(3)-C(4)	1.387(9)
C(3)-C(20)	1.520(9)
C(3)-Ti	2.333(7)
C(4)-C(5)	1.392(9)
C(4)-C(21)	1.519(9)
C(4)-Ti	2.337(8)
C(5)-C(6)	1.527(9)
C(5)-Ti	2.333(8)
C(7)-C(10)	1.373(11)
C(7)-C(8)	1.451(11)
C(7)-C(28)	1.452(11)
C(7)-Ti	2.057(7)
C(8)-C(9)	1.409(10)
C(8)-C(12)	1.418(11)
C(8)-Ti	2.067(8)
C(9)-Ti	2.232(8)
C(10)-C(11)	1.411(12)
C(10)-C(29)	1.541(11)
C(10)-Ti	2.344(8)
C(11)-C(12)	1.399(11)
C(11)-C(32)	1.504(11)
C(11)-Ti	2.515(9)
C(12)-C(13)	1.528(11)
C(12)-Ti	2.327(9)
C(14)-C(15)	1.492(8)
C(15)-C(16)	1.486(8)
C(15)-C(22)	1.559(9)
C(16)-C(17)	1.330(9)
C(17)-C(18)	1.474(10)
C(18)-C(19)	1.484(8)
C(18)-C(24)	1.590(8)
C(22)-C(26B)	1.522(5)
C(22)-C(23A)	1.522(5)
C(22)-C(23B)	1.522(5)
C(22)-C(27B)	1.522(5)
C(22)-C(26A)	1.522(5)
C(22)-C(27A)	1.522(5)
C(28)-Ti	2.222(8)
C(2)-C(1)-C(5)	107.0(6)
C(2)-C(1)-C(14)	130.0(7)
C(5)-C(1)-C(14)	123.1(7)
C(2)-C(1)-Ti	72.2(4)
C(5)-C(1)-Ti	71.2(4)
C(14)-C(1)-Ti	122.5(5)

C(1)-C(2)-C(3)	108.0(7)
C(1)-C(2)-C(19)	126.2(7)
C(3)-C(2)-C(19)	125.8(8)
C(1)-C(2)-Ti	73.2(4)
C(3)-C(2)-Ti	71.8(4)
C(19)-C(2)-Ti	119.3(5)
C(4)-C(3)-C(2)	108.3(7)
C(4)-C(3)-C(20)	126.8(8)
C(2)-C(3)-C(20)	124.6(7)
C(4)-C(3)-Ti	72.9(4)
C(2)-C(3)-Ti	73.2(4)
C(20)-C(3)-Ti	124.7(5)
C(3)-C(4)-C(5)	108.3(7)
C(3)-C(4)-C(21)	125.4(8)
C(5)-C(4)-C(21)	126.1(8)
C(3)-C(4)-Ti	72.6(5)
C(5)-C(4)-Ti	72.5(5)
C(21)-C(4)-Ti	124.0(5)
C(4)-C(5)-C(1)	108.4(7)
C(4)-C(5)-C(6)	124.5(7)
C(1)-C(5)-C(6)	126.9(7)
C(4)-C(5)-Ti	72.8(5)
C(1)-C(5)-Ti	73.6(4)
C(6)-C(5)-Ti	123.8(5)
C(10)-C(7)-C(8)	109.3(9)
C(10)-C(7)-C(28)	119.2(11)
C(8)-C(7)-C(28)	115.9(9)
C(10)-C(7)-Ti	83.7(5)
C(8)-C(7)-Ti	69.8(4)
C(28)-C(7)-Ti	76.4(5)
C(9)-C(8)-C(12)	119.3(9)
C(9)-C(8)-C(7)	118.8(10)
C(12)-C(8)-C(7)	104.6(8)
C(9)-C(8)-Ti	77.3(5)
C(12)-C(8)-Ti	81.5(5)
C(7)-C(8)-Ti	69.0(5)
C(8)-C(9)-Ti	64.7(4)
C(7)-C(10)-C(11)	108.7(9)
C(7)-C(10)-C(29)	127.5(12)
C(11)-C(10)-C(29)	123.7(11)
C(7)-C(10)-Ti	60.7(4)
C(11)-C(10)-Ti	79.9(5)
C(29)-C(10)-Ti	127.7(6)
C(12)-C(11)-C(10)	107.4(9)
C(12)-C(11)-C(32)	125.8(12)
C(10)-C(11)-C(32)	126.7(12)
C(12)-C(11)-Ti	66.0(5)
C(10)-C(11)-Ti	66.6(5)
C(32)-C(11)-Ti	135.2(6)
C(11)-C(12)-C(8)	109.9(9)
C(11)-C(12)-C(13)	125.3(11)
C(8)-C(12)-C(13)	124.7(10)
C(11)-C(12)-Ti	80.7(5)
C(8)-C(12)-Ti	61.5(5)
C(13)-C(12)-Ti	125.6(6)
C(15)-C(14)-C(1)	118.9(6)
C(16)-C(15)-C(14)	114.0(6)
C(16)-C(15)-C(22)	112.6(6)
C(14)-C(15)-C(22)	116.5(6)
C(17)-C(16)-C(15)	128.8(7)
C(16)-C(17)-C(18)	131.1(8)

C(17)-C(18)-C(19)	119.2(7)
C(17)-C(18)-C(24)	111.5(6)
C(19)-C(18)-C(24)	114.8(7)
C(18)-C(19)-C(2)	112.8(6)
C(26B)-C(22)-C(23B)	103(2)
C(26B)-C(22)-C(27B)	104(2)
C(23B)-C(22)-C(27B)	112(2)
C(23A)-C(22)-C(26A)	111.2(7)
C(23A)-C(22)-C(27A)	107.9(7)
C(26A)-C(22)-C(27A)	109.2(7)
C(26B)-C(22)-C(15)	122(2)
C(23A)-C(22)-C(15)	109.7(6)
C(23B)-C(22)-C(15)	116(2)
C(27B)-C(22)-C(15)	100.0(14)
C(26A)-C(22)-C(15)	108.3(7)
C(27A)-C(22)-C(15)	110.5(6)
C(30B)-C(24)-C(25B)	105.3(2)
C(30B)-C(24)-C(31B)	107.59(13)
C(25B)-C(24)-C(31B)	109.30(12)
C(31A)-C(24)-C(30A)	110.37(14)
C(31A)-C(24)-C(25A)	107.65(12)
C(30A)-C(24)-C(25A)	110.00(11)
C(31A)-C(24)-C(18)	111.4(6)
C(30B)-C(24)-C(18)	120.1(6)
C(25B)-C(24)-C(18)	114.1(5)
C(31B)-C(24)-C(18)	99.9(6)
C(30A)-C(24)-C(18)	109.3(5)
C(25A)-C(24)-C(18)	108.1(6)
C(7)-C(28)-Ti	64.1(4)
C(7)-Ti-C(8)	41.2(3)
C(7)-Ti-C(28)	39.5(3)
C(8)-Ti-C(28)	70.0(4)
C(7)-Ti-C(9)	69.9(4)
C(8)-Ti-C(9)	38.0(3)
C(28)-Ti-C(9)	76.8(3)
C(7)-Ti-C(12)	62.0(4)
C(8)-Ti-C(12)	37.1(3)
C(28)-Ti-C(12)	100.3(4)
C(9)-Ti-C(12)	64.7(4)
C(7)-Ti-C(5)	131.1(4)
C(8)-Ti-C(5)	160.8(3)
C(28)-Ti-C(5)	95.4(3)
C(9)-Ti-C(5)	128.3(3)
C(12)-Ti-C(5)	162.0(3)
C(7)-Ti-C(3)	156.0(4)
C(8)-Ti-C(3)	138.2(4)
C(28)-Ti-C(3)	151.8(3)
C(9)-Ti-C(3)	125.3(3)
C(12)-Ti-C(3)	105.2(3)
C(5)-Ti-C(3)	57.7(3)
C(7)-Ti-C(4)	136.2(4)
C(8)-Ti-C(4)	164.2(3)
C(28)-Ti-C(4)	118.0(3)
C(9)-Ti-C(4)	153.0(3)
C(12)-Ti-C(4)	127.9(3)
C(5)-Ti-C(4)	34.7(2)
C(3)-Ti-C(4)	34.5(2)
C(7)-Ti-C(10)	35.6(3)
C(8)-Ti-C(10)	62.6(3)
C(28)-Ti-C(10)	64.5(4)
C(9)-Ti-C(10)	99.5(3)

C(12)-Ti-C(10)	58.0(3)
C(5)-Ti-C(10)	123.2(3)
C(3)-Ti-C(10)	120.7(3)
C(4)-Ti-C(10)	107.2(3)
C(7)-Ti-C(2)	165.8(4)
C(8)-Ti-C(2)	126.1(3)
C(28)-Ti-C(2)	139.6(4)
C(9)-Ti-C(2)	95.9(3)
C(12)-Ti-C(2)	112.4(3)
C(5)-Ti-C(2)	57.9(3)
C(3)-Ti-C(2)	35.0(2)
C(4)-Ti-C(2)	57.8(3)
C(10)-Ti-C(2)	154.5(4)
C(7)-Ti-C(1)	144.2(4)
C(8)-Ti-C(1)	135.3(3)
C(28)-Ti-C(1)	106.0(3)
C(9)-Ti-C(1)	97.3(3)
C(12)-Ti-C(1)	143.5(3)
C(5)-Ti-C(1)	35.2(2)
C(3)-Ti-C(1)	58.0(2)
C(4)-Ti-C(1)	58.0(2)
C(10)-Ti-C(1)	157.9(3)
C(2)-Ti-C(1)	34.6(2)
C(7)-Ti-C(11)	58.3(4)
C(8)-Ti-C(11)	59.5(3)
C(28)-Ti-C(11)	95.3(4)
C(9)-Ti-C(11)	95.0(3)
C(12)-Ti-C(11)	33.3(3)
C(5)-Ti-C(11)	136.7(3)
C(3)-Ti-C(11)	99.4(3)
C(4)-Ti-C(11)	105.2(3)
C(10)-Ti-C(11)	33.5(3)
C(2)-Ti-C(11)	125.1(3)
C(1)-Ti-C(11)	157.3(3)

Symmetry transformations used to generate equivalent atoms:

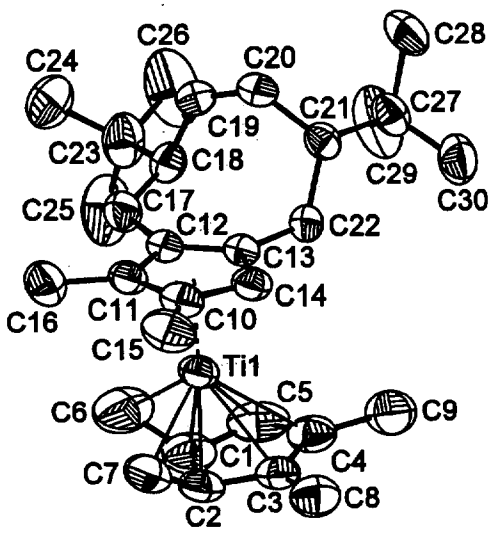
Table 4. Anisotropic displacement parameters (A^2 x 10^3) for 2a.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	28(5)	11(5)	42(6)	8(5)	-5(4)	0(4)
C(2)	32(5)	36(6)	29(7)	5(5)	-10(4)	-6(5)
C(3)	26(5)	21(5)	38(6)	9(5)	-14(4)	-3(4)
C(4)	37(5)	29(6)	43(7)	-10(5)	-2(5)	5(5)
C(5)	38(5)	30(5)	22(6)	6(5)	2(4)	-7(5)
C(6)	49(6)	48(6)	70(8)	3(5)	4(5)	5(5)
C(7)	28(6)	61(8)	64(9)	0(7)	-22(5)	0(5)
C(8)	51(7)	50(7)	51(8)	-12(6)	-21(6)	-1(6)
C(9)	75(7)	54(7)	99(9)	-36(6)	-37(6)	-10(6)
C(10)	65(8)	45(7)	75(9)	-19(7)	-48(7)	23(6)
C(11)	85(9)	40(7)	53(8)	21(6)	-42(6)	-8(7)
C(12)	64(7)	64(8)	33(7)	9(6)	-15(6)	-12(6)
C(13)	70(7)	165(11)	42(8)	32(7)	-7(6)	-13(7)
C(14)	25(5)	50(6)	79(8)	-5(5)	-14(5)	-10(5)
C(15)	27(5)	35(5)	62(7)	-6(5)	2(5)	-8(4)
C(16)	43(6)	19(5)	23(6)	10(4)	-7(4)	-4(4)
C(17)	34(6)	24(5)	46(7)	6(5)	-7(5)	10(4)
C(18)	38(6)	49(6)	70(8)	4(6)	17(5)	22(5)
C(19)	51(6)	52(6)	25(6)	0(5)	7(5)	-2(5)
C(20)	48(6)	50(6)	104(9)	19(6)	1(5)	-19(5)
C(21)	100(7)	42(6)	79(8)	-23(6)	-13(6)	2(5)
C(22)	48(6)	28(5)	55(7)	-9(5)	0(5)	-10(4)
C(24)	39(5)	60(6)	46(6)	11(5)	15(5)	12(4)
C(28)	28(6)	122(9)	94(10)	-10(8)	-3(6)	-8(6)
C(29)	143(10)	92(8)	108(10)	-41(8)	-48(8)	84(8)
C(32)	158(10)	54(7)	146(12)	53(7)	-99(9)	-50(7)
Ti	33(1)	31(1)	46(1)	-2(1)	-5(1)	-1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 3a.

	x	y	z	U(eq)
H(25A)	13759(8)	-1026(7)	2512(6)	108
H(25B)	14378(8)	80(7)	2112(6)	108
H(25C)	14601(8)	-886(7)	1424(6)	108
H(30A)	11558(11)	-1297(9)	1740(8)	108
H(30B)	12430(11)	-1187(8)	662(7)	108
H(30C)	10867(10)	-379(9)	838(8)	108
H(31A)	13271(12)	1534(8)	713(8)	108
H(31B)	11929(12)	1376(8)	202(8)	108
H(31C)	13492(11)	568(9)	25(6)	108
H(25D)	14113(11)	1010(9)	1422(8)	108
H(25E)	14609(9)	-19(9)	791(8)	108
H(25F)	14546(10)	-264(9)	1989(8)	108
H(30D)	11586(11)	-1275(8)	1453(8)	108
H(30E)	13048(12)	-1619(8)	2007(8)	108
H(30F)	13111(11)	-1374(7)	809(7)	108
H(31D)	11725(12)	1632(8)	474(9)	108
H(31E)	10822(10)	698(9)	470(9)	108
H(31F)	12394(12)	579(8)	-111(7)	108
H(6A)	5956(8)	1704(6)	5078(6)	91
H(6B)	5326(8)	3045(6)	4881(6)	91
H(6C)	6617(8)	2517(6)	5592(6)	91
H(9A)	7187(9)	1962(8)	771(7)	85
H(9B)	5673(9)	1732(8)	1417(7)	85
H(13A)	7995(9)	3377(9)	-346(7)	150
H(13B)	8788(9)	4096(9)	181(7)	150
H(13C)	7694(9)	4724(9)	-652(7)	150
H(14A)	7331(7)	337(6)	4368(6)	61
H(14B)	6905(7)	518(6)	3245(6)	61
H(15)	9065(8)	-423(6)	2700(6)	50
H(16)	10567(8)	-918(6)	4429(6)	36
H(17)	12235(8)	-122(6)	3630(7)	46
H(18)	11947(8)	1335(7)	2416(7)	73
H(19A)	9478(8)	1050(7)	1668(6)	55
H(19B)	10235(8)	2097(7)	1362(6)	55
H(20A)	10571(8)	3651(6)	1829(7)	105
H(20B)	10568(8)	4162(6)	2832(7)	105
H(20C)	9374(8)	4755(6)	2057(7)	105
H(21A)	6802(9)	4574(6)	4746(6)	112
H(21B)	7230(9)	5266(6)	3689(6)	112
H(21C)	8432(9)	4695(6)	4462(6)	112
H(28A)	4068(8)	2453(9)	2620(8)	101
H(28B)	3789(8)	3481(9)	3316(8)	101
H(29A)	4525(11)	6479(8)	2586(8)	191
H(29B)	4080(11)	5454(8)	3355(8)	191
H(29C)	3075(11)	6103(8)	2475(8)	191
H(32A)	6267(11)	6751(8)	1557(8)	174
H(32B)	6669(11)	6615(8)	402(8)	174
H(32C)	7807(11)	6008(8)	1212(8)	174
H(23A)	9070(11)	-2000(9)	5224(6)	59
H(23B)	7986(11)	-2747(9)	5068(6)	59
H(23C)	7398(11)	-1422(9)	5110(6)	59
H(26A)	7441(9)	-1565(9)	2456(9)	70
H(26B)	6384(9)	-1151(9)	3388(9)	70

H(26C)	6972(9)	-2476(9)	3346(9)	70
H(27A)	10057(9)	-2529(8)	2694(9)	71
H(27B)	9589(9)	-3416(8)	3605(9)	71
H(27C)	10679(9)	-2675(8)	3761(9)	71
H(23D)	10103(46)	-2429(32)	4766(18)	173
H(23E)	9048(46)	-3249(32)	4745(18)	173
H(23F)	8502(46)	-2161(32)	5300(18)	173
H(26D)	6499(16)	-1451(33)	3199(32)	133
H(26E)	6421(16)	-1597(33)	4396(32)	133
H(26F)	6968(16)	-2684(33)	3840(32)	133
H(27D)	10294(33)	-2236(27)	2713(17)	90
H(27E)	8787(33)	-1888(27)	2214(17)	90
H(27F)	9232(33)	-3086(27)	2915(17)	90



STRUCTURAL DATA

Compound name	[3,6-di-*tert*-butyl-9,10-dimethyl bicyclo[6.3.0]undec-4-en-(η^5-1,8-11-dienyl)][η^3:η^4-1,2-dimethyl-3,4-dimethylenecyclopentenyl] titanium(II)
Chemical formula	$[\eta^3{:}\eta^4\text{-}C_5H(CH_3)_2(CH_2)_2][\eta^5\text{-}C_5H(CH_3)_2\{CH_2CH\{C(CH_3)_3\}CH{=}CHCH\{C(CH_3)_3\}CH_2\}]Ti$
Empirical formula	$C_{30}H_{44}Ti$
Title	Unprecedent Activation of Permethyltitanocene at the Onset of Formation. Addition of 2,2,7,7-Tetramethyl-3,5-octadiyne to the Methyl Groups of η^5-Pentamethylcyclopentadienyl Ligand.
Authors	Michal Horáček, Petr Štěpnička, Róbert Gyepes, Ivana Císařová, Miroslav Polášek and Karel Mach
Journal	J. Am. Chem. Soc.
Formula weight	452.55
Temperature	293(2) K
Wavelength	0.71069 Å (Mo-K_α)
Crystal system	monoclinic
Space group	$P2_1/n$ (No.14)
Unit cell dimensions	a = 12.390(2) Å α = 90° b = 11.8747(8) Å β = 91.790(10)° c = 18.655(2) Å γ = 90°

	S2
Volume	2743.3(6) $Å^3$
Z	4
Density (calculated)	1.096 Mgm^{-3}
Absorption coefficient	0.326 mm^{-1}
F(000)	984
Crystal size	0.5 x 0.46 x 0.36 mm
Theta range for data collection	1.95° to 23.98°
Index ranges	0<=h<=14, 0<=k<=13, -21<=l<=21
Reflections collected	4511
Independent reflections	4300 [R(int) = 0.0141]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4300 / 0 / 336
Goodness-of-fit on F^2	1.032
Final R indices [I>2σ(I)]	R1 = 0.0409, wR2 = 0.1053
R indices (all data)	R1 = 0.0726, wR2 = 0.1175
Largest diff. peak and hole	0.175 and -0.242 $e.Å^{-3}$
Absorption correction	none
Extinction correction	none
Atomic coordinates	table 1, p.3
Neutral atom scattering factors and anomalous dispersion corrections	A.J.C.Wilson, Ed. International Tables for Crystallography,Vol. C; Kluwer Academic Publishers: Dordrecht, The Netherlands
Anisotropic displ. parameters	table 2, p.4
Hydrogen atoms coordinates	table 3, p.5
Bond distances	table 4, p.6
Valence angles	table 5, p.7
Least squares planes	table 6, p.8
Intermolecular contacts	table 7, p.9
Packing diagrams	p.11-13
F_o/F_c-table	table 8, p.14

Supplementary Material

Table 1. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for [3,6-di-*tert*-butyl-9,10-dimethylbicyclo[6.3.0]undec-4-en-(η^5-1,8-11-dienyl)][η^3:η^4-1,2-dimethyl-3,4-dimethylenecyclopentenyl]titanium(II).
U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}
Ti(1)	900(1)	80(1)	2058(1)	49(1)
C(1)	1421(3)	1704(2)	2277(2)	74(1)
C(2)	2131(2)	1166(2)	1783(2)	62(1)
C(3)	2767(2)	361(2)	2189(1)	54(1)
C(4)	2464(2)	401(2)	2908(1)	63(1)
C(5)	1651(3)	1194(3)	2956(2)	79(1)
C(6)	305(3)	1875(3)	2061(4)	107(2)
C(7)	1702(3)	828(3)	1101(2)	78(1)
C(8)	3603(2)	-399(3)	1895(2)	74(1)
C(9)	2950(3)	-274(3)	3509(2)	95(1)
C(10)	335(2)	-1577(2)	1459(1)	51(1)
C(11)	-578(2)	-886(2)	1522(1)	49(1)
C(12)	-796(2)	-756(2)	2262(1)	45(1)
C(13)	5(2)	-1355(2)	2660(1)	43(1)
C(14)	700(2)	-1851(2)	2161(1)	49(1)
C(15)	810(3)	-2002(3)	777(2)	75(1)
C(16)	-1248(2)	-391(3)	913(1)	71(1)
C(17)	-1775(2)	-129(3)	2514(2)	58(1)
C(18)	-2065(2)	-318(2)	3297(1)	50(1)
C(19)	-2351(2)	-1534(2)	3385(1)	54(1)
C(20)	-1733(2)	-2402(2)	3558(1)	53(1)
C(21)	-551(2)	-2478(2)	3755(1)	44(1)
C(22)	155(2)	-1532(2)	3461(1)	45(1)
C(23)	-2961(2)	496(3)	3549(2)	74(1)
C(24)	-3986(2)	430(3)	3068(2)	93(1)
C(25)	-2529(3)	1716(3)	3533(2)	107(1)
C(26)	-3229(4)	191(4)	4319(2)	129(2)
C(27)	-345(2)	-2696(2)	4571(1)	56(1)
C(28)	-1002(3)	-3728(3)	4795(2)	92(1)
C(29)	-677(3)	-1691(3)	5014(2)	106(1)
C(30)	839(2)	-2959(3)	4725(2)	76(1)

Supplementary Material

Table 2. Anisotropic displacement parameters ($Å^2$ x 10^3) for [3,6-di-*tert*-butyl-9,10-dimethylbicyclo[6.3.0]undec-4-en-(η^5-1,8-11-dienyl)][η^3:η^4-1,2-dimethyl-3,4-dimethylenecyclopentenyl]titanium(II). The anisotropic displacement factor exponent takes the form: $-2\pi^2(h^2a^{*2}U_{11}+...+2hka^*b^*U_{12})$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ti(1)	50(1)	42(1)	55(1)	6(1)	6(1)	-8(1)
C(1)	74(2)	39(1)	109(3)	-6(2)	14(2)	-12(1)
C(2)	63(2)	51(2)	72(2)	10(1)	5(1)	-22(1)
C(3)	51(1)	53(1)	59(2)	1(1)	7(1)	-18(1)
C(4)	65(2)	65(2)	57(2)	-10(1)	5(1)	-24(1)
C(5)	86(2)	69(2)	83(2)	-30(2)	29(2)	-27(2)
C(6)	82(3)	55(2)	184(5)	3(3)	13(3)	-2(2)
C(7)	81(2)	81(2)	72(2)	24(2)	0(2)	-28(2)
C(8)	65(2)	80(2)	78(2)	1(2)	16(2)	-5(2)
C(9)	94(2)	130(3)	59(2)	12(2)	-9(2)	-39(2)
C(10)	58(2)	44(1)	51(1)	1(1)	9(1)	-11(1)
C(11)	53(1)	47(1)	45(1)	7(1)	1(1)	-12(1)
C(12)	43(1)	43(1)	51(1)	10(1)	3(1)	-6(1)
C(13)	41(1)	42(1)	47(1)	8(1)	5(1)	-4(1)
C(14)	45(1)	38(1)	64(2)	7(1)	11(1)	-1(1)
C(15)	93(2)	70(2)	64(2)	-5(2)	23(2)	-8(2)
C(16)	80(2)	75(2)	56(2)	14(1)	-6(1)	-9(2)
C(17)	50(2)	59(2)	64(2)	14(1)	6(1)	9(1)
C(18)	42(1)	54(2)	54(1)	-1(1)	-1(1)	7(1)
C(19)	41(1)	61(2)	60(2)	7(1)	5(1)	-5(1)
C(20)	53(2)	46(1)	60(2)	9(1)	5(1)	-10(1)
C(21)	50(1)	37(1)	45(1)	2(1)	6(1)	5(1)
C(22)	41(1)	46(1)	48(1)	7(1)	0(1)	3(1)
C(23)	71(2)	81(2)	69(2)	-2(2)	5(2)	31(2)
C(24)	52(2)	108(3)	119(3)	11(2)	8(2)	29(2)
C(25)	129(3)	73(2)	119(3)	-27(2)	-24(2)	45(2)
C(26)	149(4)	157(4)	84(2)	9(2)	46(3)	94(3)
C(27)	68(2)	58(2)	42(1)	8(1)	10(1)	10(1)
C(28)	90(2)	107(3)	81(2)	52(2)	13(2)	1(2)
C(29)	161(4)	109(3)	49(2)	-10(2)	9(2)	51(3)
C(30)	77(2)	93(2)	57(2)	15(2)	-8(1)	8(2)

Supplementary Material

Table 3. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for [3,6-di-*tert*-butyl-9,10-dimethylbicyclo[6.3.0]undec-4-en-(η^5-1,8-11-dienyl)][η^3:η^4-1,2-dimethyl-3,4-dimethylenecyclopentenyl]titanium(II).

Atom	x	y	z	U_{iso}
H(5)	1250(3)	1320(3)	3348(18)	106(12)
H(61)	160(4)	2240(4)	1540(3)	160(2)
H(62)	-130(4)	2070(4)	2450(2)	139(18)
H(71)	1230(3)	1410(3)	840(18)	109(12)
H(72)	2140(3)	290(3)	831(19)	104(13)
H(81)	4253	21	1824	89
H(82)	3344	-705	1446	89
H(83)	3750	-1001	2228	89
H(91)	3652	21	3638	113
H(92)	3018	-1044	3362	113
H(93)	2495	-232	3916	113
H(14)	1240(2)	-2270(2)	2268(12)	46(7)
H(151)	409	-2645	607	90
H(152)	1550	-2212	868	90
H(153)	775	-1418	420	90
H(161)	-1364	396	1001	85
H(162)	-1932	-771	877	85
H(163)	-877	-482	473	85
H(171)	-2390(2)	-400(2)	2214(13)	61(8)
H(172)	-1710(2)	660(2)	2402(13)	65(8)
H(18)	-1457(19)	-120(18)	3577(12)	45(6)
H(19)	-3030(2)	-1710(2)	3237(13)	59(8)
H(20)	-2081(18)	-3090(2)	3557(12)	50(6)
H(21)	-314(18)	-3150(2)	3527(12)	49(6)
H(221)	54(17)	-830(2)	3725(11)	41(6)
H(222)	880(2)	-1770(2)	3537(12)	55(7)
H(241)	-3814	616	2584	112
H(242)	-4512	952	3237	112
H(243)	-4274	-320	3082	112
H(251)	-2496	1966	3045	129
H(252)	-1819	1740	3754	129
H(253)	-3002	2199	3791	129
H(261)	-2586	235	4618	155
H(262)	-3511	-562	4331	155
H(263)	-3758	707	4491	155
H(281)	-1758	-3553	4762	111
H(282)	-805	-3929	5280	111
H(283)	-853	-4348	4483	111
H(291)	-1430	-1539	4926	127
H(292)	-261	-1045	4884	127
H(293)	-550	-1853	5514	127
H(301)	1051	-3587	4438	91
H(302)	946	-3142	5224	91
H(303)	1269	-2314	4612	91

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Table 4. Bond distances (Å) for [3,6-di-*tert*-butyl-9,10-dimethylbicyclo[6.3.0]undec-4-en-(η^5-1,8-11-dienyl)][η^3:η^4-1,2-dimethyl-3,4-dimethylenecyclopentenyl]titanium(II).

Atoms	d	Atoms	d
Ti(1) - CE(1)	1.915(3)	Ti(1) - CE(2)	2.016(2)
Ti(1) - C(1)	2.071(3)	Ti(1) - C(2)	2.074(2)
Ti(1) - C(3)	2.343(2)	Ti(1) - C(4)	2.495(3)
Ti(1) - C(5)	2.307(3)	Ti(1) - C(6)	2.254(4)
Ti(1) - C(7)	2.253(3)	Ti(1) - C(10)	2.358(2)
Ti(1) - C(11)	2.357(2)	Ti(1) - C(12)	2.366(2)
Ti(1) - C(13)	2.340(2)	Ti(1) - C(14)	2.316(2)
C(1) - C(5)	1.424(5)	C(1) - C(6)	1.442(5)
C(1) - C(2)	1.443(4)	C(2) - C(7)	1.422(4)
C(2) - C(3)	1.440(4)	C(3) - C(4)	1.404(3)
C(3) - C(8)	1.490(4)	C(4) - C(5)	1.385(4)
C(4) - C(9)	1.490(4)	C(10) - C(11)	1.406(3)
C(10) - C(14)	1.409(3)	C(10) - C(15)	1.506(3)
C(11) - C(12)	1.425(3)	C(11) - C(16)	1.505(3)
C(12) - C(13)	1.411(3)	C(12) - C(17)	1.511(3)
C(13) - C(14)	1.417(3)	C(13) - C(22)	1.516(3)
C(17) - C(18)	1.530(4)	C(18) - C(19)	1.498(4)
C(18) - C(23)	1.556(4)	C(19) - C(20)	1.317(4)
C(20) - C(21)	1.502(3)	C(21) - C(22)	1.534(3)
C(21) - C(27)	1.558(3)	C(23) - C(24)	1.535(4)
C(23) - C(25)	1.544(5)	C(23) - C(26)	1.527(5)
C(27) - C(28)	1.537(4)	C(27) - C(29)	1.516(4)
C(27) - C(30)	1.519(4)		

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Table 5. Valence angles (°) for [3,6-di-*tert*-butyl-9,10-dimethylbicyclo[6.3.0]undec-4-en-(η^5-1,8-11-dienyl)][η^3:η^4-1,2-dimethyl-3,4-dimethylenecyclopentenyl]titanium(II).

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
CE(1)	Ti(1)	CE(2)	154.8(1)	CE(2)	Ti(1)	C(1)	159.8(1)
CE(2)	Ti(1)	C(2)	158.5(1)	CE(2)	Ti(1)	C(3)	134.6(1)
CE(2)	Ti(1)	C(5)	135.8(1)	CE(2)	Ti(1)	C(6)	124.5(1)
CE(2)	Ti(1)	C(7)	124.1(1)	C(1)	Ti(1)	C(2)	40.74(11)
C(1)	Ti(1)	C(5)	37.49(12)	C(1)	Ti(1)	C(6)	38.66(14)
C(2)	Ti(1)	C(3)	37.43(10)	C(2)	Ti(1)	C(7)	38.09(11)
C(6)	Ti(1)	C(7)	77.4(2)	C(2)	C(1)	C(5)	105.7(3)
C(2)	C(1)	C(6)	118.8(4)	C(5)	C(1)	C(6)	118.1(4)
C(2)	C(1)	Ti(1)	69.74(14)	C(5)	C(1)	Ti(1)	80.31(17)
C(6)	C(1)	Ti(1)	77.6(2)	C(1)	C(2)	C(3)	107.0(3)
C(1)	C(2)	C(7)	118.6(3)	C(3)	C(2)	C(7)	117.8(3)
C(1)	C(2)	Ti(1)	69.51(15)	C(3)	C(2)	Ti(1)	81.49(14)
C(7)	C(2)	Ti(1)	77.79(16)	C(2)	C(3)	C(4)	108.7(3)
C(2)	C(3)	C(8)	125.7(2)	C(4)	C(3)	C(8)	125.5(3)
C(3)	C(4)	C(5)	107.6(3)	C(3)	C(4)	C(9)	125.9(3)
C(5)	C(4)	C(9)	126.5(3)	C(1)	C(5)	C(4)	111.0(3)
C(1)	C(6)	Ti(1)	63.77(18)	C(2)	C(7)	Ti(1)	64.12(15)
C(11)	C(10)	C(14)	107.1(2)	C(11)	C(10)	C(15)	127.0(2)
C(14)	C(10)	C(15)	125.8(2)	C(10)	C(11)	C(12)	108.7(2)
C(10)	C(11)	C(16)	126.3(2)	C(12)	C(11)	C(16)	125.0(2)
C(11)	C(12)	C(13)	107.7(2)	C(11)	C(12)	C(17)	122.2(2)
C(13)	C(12)	C(17)	130.0(2)	C(12)	C(13)	C(14)	107.2(2)
C(12)	C(13)	C(22)	130.6(2)	C(14)	C(13)	C(22)	122.1(2)
C(10)	C(14)	C(13)	109.3(2)	C(12)	C(17)	C(18)	116.0(2)
C(17)	C(18)	C(19)	108.1(2)	C(17)	C(18)	C(23)	112.9(2)
C(19)	C(18)	C(23)	113.1(2)	C(18)	C(19)	C(20)	130.0(2)
C(19)	C(20)	C(21)	131.5(2)	C(20)	C(21)	C(22)	115.51(19)
C(20)	C(21)	C(27)	112.2(2)	C(22)	C(21)	C(27)	113.1(2)
C(13)	C(22)	C(21)	113.58(19)	C(24)	C(23)	C(25)	108.5(3)
C(24)	C(23)	C(26)	109.7(3)	C(25)	C(23)	C(26)	109.1(3)
C(18)	C(23)	C(24)	112.1(3)	C(18)	C(23)	C(25)	109.0(3)
C(18)	C(23)	C(26)	108.4(2)	C(28)	C(27)	C(29)	108.9(3)
C(28)	C(27)	C(30)	107.5(2)	C(29)	C(27)	C(30)	109.6(3)
C(21)	C(27)	C(28)	109.0(2)	C(21)	C(27)	C(29)	111.3(2)
C(21)	C(27)	C(30)	110.3(2)				

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Table 6. Least-squares planes and atomic deviations therefrom for [3,6-di-*tert*-butyl-9,10-dimethylbicyclo[6.3.0]undec-4-en-(η^5-1,8-11-dienyl)][η^3:η^4-1,2-dimethyl-3,4-dimethylenecyclopentenyl]titanium(II).

Plane №	Formed by atoms	distances (Å) of some atoms from the plane	
1	C(1),C(2),C(3),C(4),C(5)	C(1)	0.0050(17)
		C(2)	-0.0015(16)
		C(3)	-0.0025(16)
		C(4)	0.0058(17)
		C(5)	-0.0068(18)
		C(6)	-0.8690(51)
		C(7)	-0.8674(45)
		C(8)	-0.0217(47)
		C(9)	0.0499(51)
		Ti(1)	-1.8627(14)
2	C(10),C(11),C(12),C(13),C(14)	C(10)	0.0080(14)
		C(11)	-0.0078(14)
		C(12)	0.0046(14)
		C(13)	0.0004(14)
		C(14)	-0.0052(14)
		C(15)	0.0947(44)
		C(16)	0.0081(44)
		C(17)	0.0937(46)
		C(22)	0.0454(40)
		Ti(1)	-2.0155(11)
3	C(1),C(2),C(6),C(7)	C(1)	0.0011(19)
		C(2)	-0.0011(19)
		C(6)	-0.0006(10)
		C(7)	0.0006(10)
		Ti(1)	-1.7221(21)
The angles between the planes are:		1 / 2	12.91(16)
		1 / 3	43.85(15)
		2 / 3	30.96(15)

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Table 7. Important intermolecular contacts for [3,6-di-*tert*-butyl-9,10-dimethylbicyclo[6.3.0]undec-4-en-(η^5-1,8-11-dienyl)][η^3:η^4-1,2-dimethyl-3,4-dimethylenecyclopentenyl]titanium(II).

1.000	0.000	0.000	-1.000		
0.000	1.000	0.000	0.000		
0.000	0.000	1.000	0.000	C(24) - C(8)	3.777(5)
				C(24) - C(9)	3.997(5)
1.000	0.000	0.000	1.000		
0.000	1.000	0.000	0.000		
0.000	0.000	1.000	0.000	C(8) - C(24)	3.777(5)
				C(9) - C(24)	3.997(5)
-1.000	0.000	0.000	0.000		
0.000	-1.000	0.000	-1.000		
0.000	0.000	-1.000	1.000	C(28) - C(28)	3.970(5)
-1.000	0.000	0.000	0.000		
0.000	-1.000	0.000	0.000		
0.000	0.000	-1.000	0.000	C(7) - C(16)	3.816(5)
				C(16) - C(7)	3.816(5)
-1.000	0.000	0.000	-0.500		
0.000	1.000	0.000	-0.500		
0.000	0.000	-1.000	0.500	C(11) - C(25)	3.689(5)
				C(12) - C(25)	3.916(4)
				C(14) - C(24)	3.880(4)
				C(16) - C(25)	3.907(5)
-1.000	0.000	0.000	-0.500		
0.000	1.000	0.000	0.500		
0.000	0.000	-1.000	0.500	C(24) - C(14)	3.880(4)
				C(25) - C(11)	3.689(5)
				C(25) - C(12)	3.916(4)
				C(25) - C(16)	3.907(5)
-1.000	0.000	0.000	0.500		
0.000	1.000	0.000	-0.500		
0.000	0.000	-1.000	0.500	C(8) - C(1)	3.771(4)
				C(8) - C(6)	3.993(6)
				C(9) - C(1)	3.963(5)
				C(14) - C(3)	3.987(4)
				C(14) - C(4)	3.982(4)
				C(30) - C(2)	3.970(4)
				C(30) - C(7)	3.745(5)

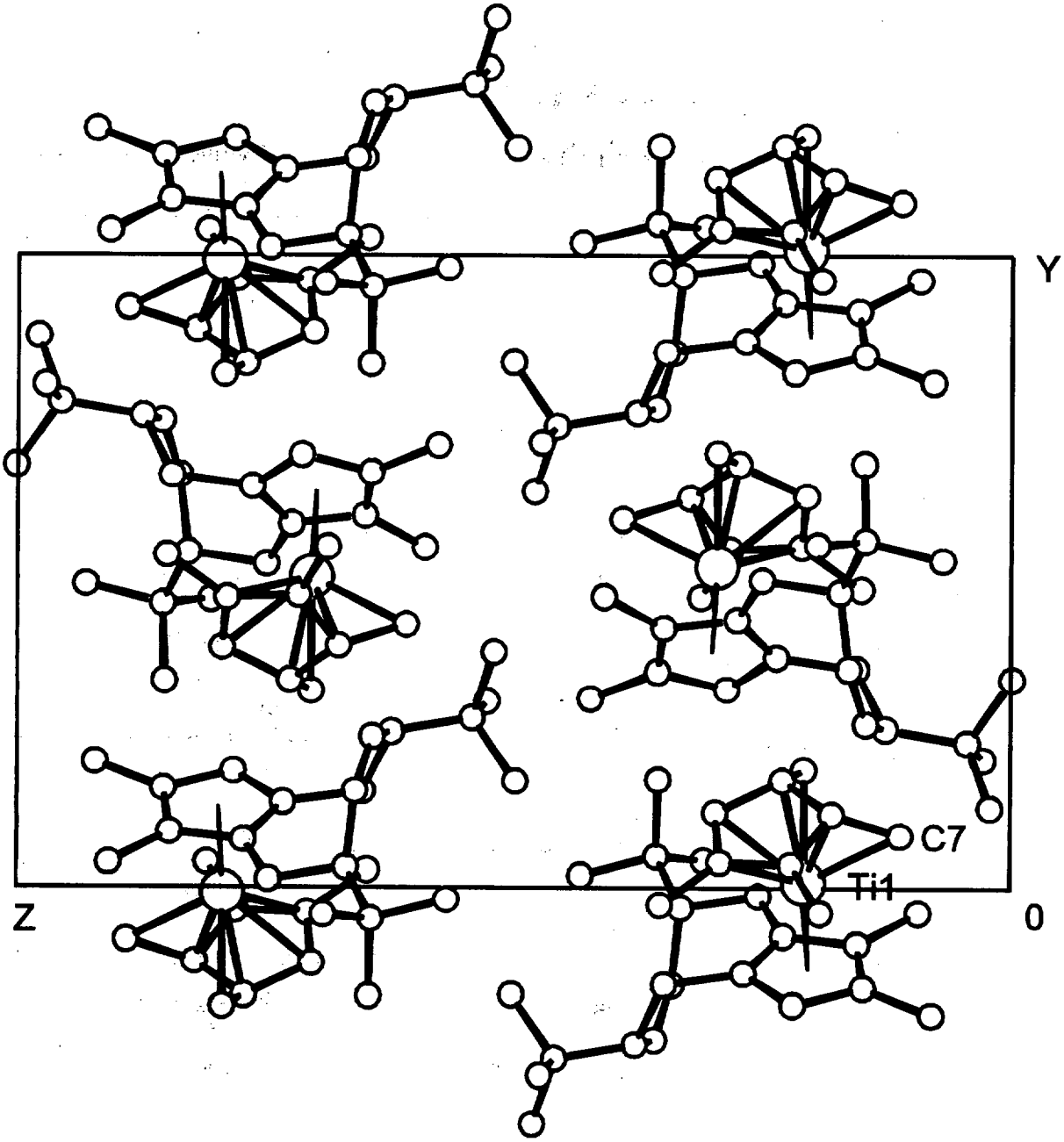
Supplementary Material

Table 7. Important intermolecular contacts for [3,6-di-*tert*-butyl-9,10-dimethylbicyclo[6.3.0]undec-4-en-(η^5-1,8-11-dienyl)][η^3:η^4-1,2-dimethyl-3,4-dimethylenecyclopentenyl]titanium(II). (cont'd)

-1.000	0.000	0.000	0.500			
0.000	1.000	0.000	0.500			
0.000	0.000	-1.000	0.500	C(1)	- C(8)	3.771(4)
				C(1)	- C(9)	3.963(5)
				C(2)	- C(30)	3.970(4)
				C(3)	- C(14)	3.987(4)
				C(4)	- C(14)	3.982(4)
				C(6)	- C(8)	3.993(6)
				C(7)	- C(30)	3.745(5)

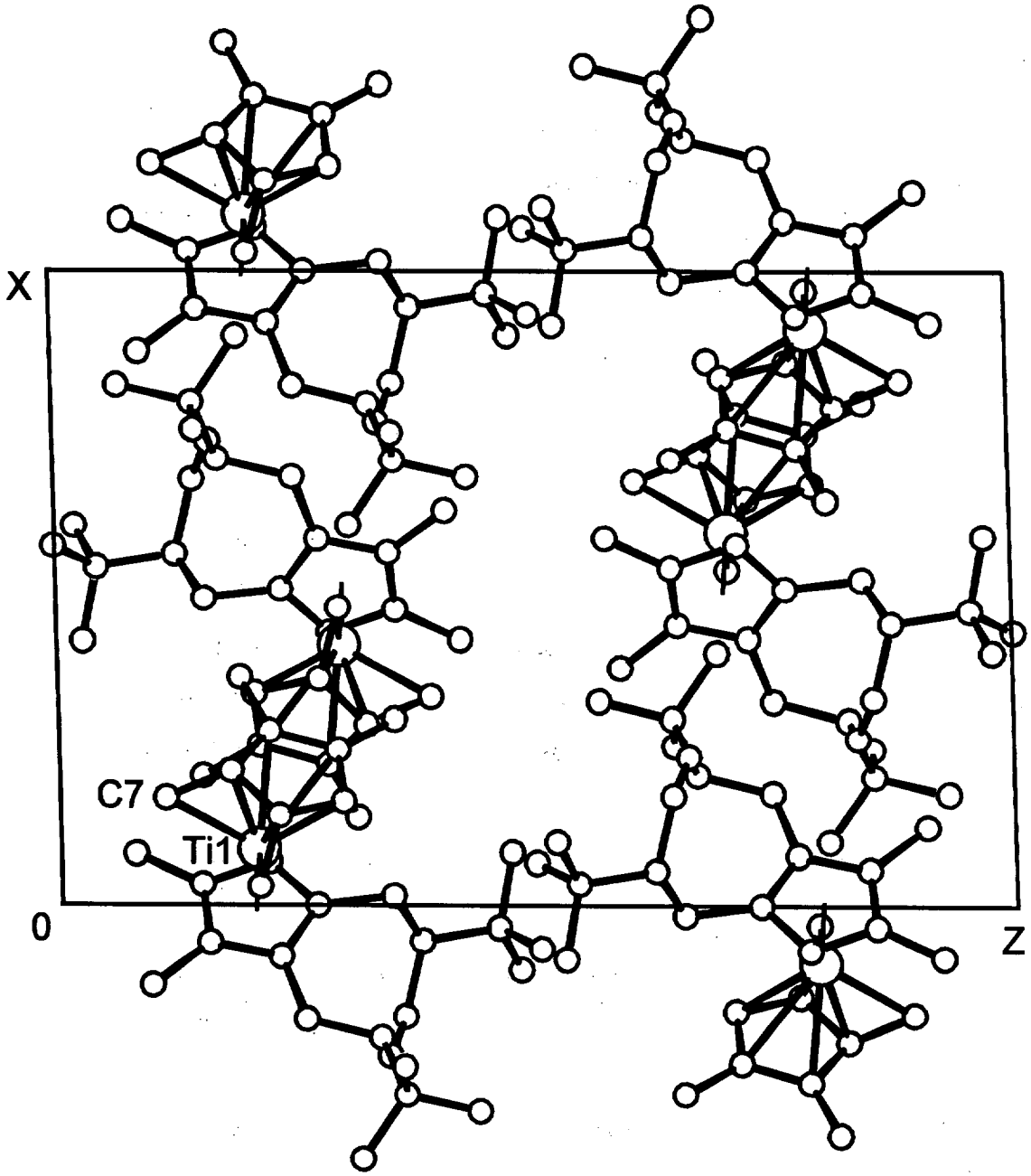
Supplementary Material

Unit cell and packing diagrams for $[\eta^3:\eta^4\text{-}C_5H(CH_3)_2(CH_2)_2][\eta^5\text{-}C_5H(CH_3)_2\{CH_2CH\{C(CH_3)_3\}CH{=}CHCH\{C(CH_3)_3\}CH_2\}]Ti$.



Supplementary Material

Unit cell and packing diagrams for $[\eta^3:\eta^4\text{-}C_5H(CH_3)_2(CH_2)_2][\eta^5\text{-}C_5H(CH_3)_2\{CH_2CH\{C(CH_3)_3\}CH{=}CHCH\{C(CH_3)_3\}CH_2\}]Ti$.



Supplementary Material

Unit cell and packing diagrams for [η^3:η^4-$C_5H(CH_3)_2(CH_2)_2$][η^5-$C_5H(CH_3)_2$ {$CH_2CH\{C(CH_3)_3\}CH=CHCH\{C(CH_3)_3\}CH_2$}]Ti.