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Crystal structure of 1,1-bis(η^5 -adamantylcyclopentadienyl)-3-phenyl-2-trimethylsilyl-2,3-dihydroisotitanazole, $C_{42}H_{55}NSiTi$

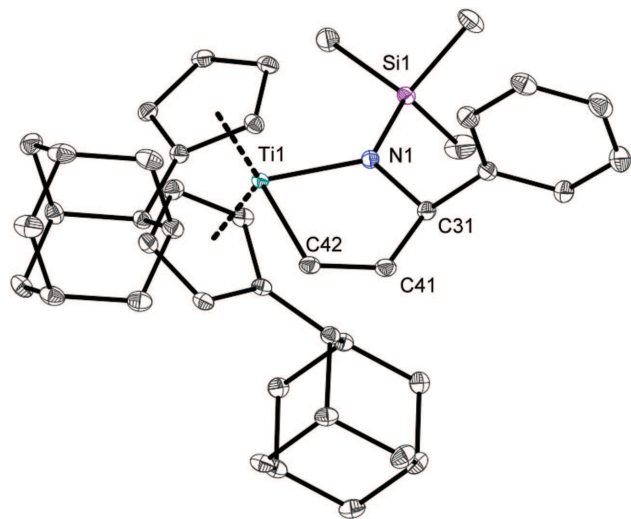


Table 1: Data collection and handling.

Crystal:	Green block
Size:	0.36 × 0.24 × 0.16 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	3.2 cm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$2\theta_{\max}$, completeness:	70°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	32114, 32114
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 28454
$N(\text{param})_{\text{refined}}$:	418
Programs:	Bruker programs [1], SHELX [2]

of the atoms including atomic coordinates and displacement parameters.

Source of material

All reactions were carried out under a dry nitrogen atmosphere using Schlenk-technique. Bis(adamantylidene-pentafulvene)titanium was prepared by procedures reported previously [3, 4]. Bis(adamantylcyclopentadienyl)titanium- η^2 (*N*-benzylidenetrimethylsilylamine) was prepared by reaction of bis(adamantylidenepentafulvene)titanium with *N*-benzyltrimethylsilylamine as described for *N*-methylanilines at 60 °C for 3 d [4]. For the target compound a suspension of bis(adamantylcyclopentadienyl)titanium- η^2 (*N*-benzylidenetrimethylsilylamine) (250 mg, 0.385 mmol) in 10 mL *n*-hexane was stirred under acetylene (1 atm.) for 15 min at room temperature, forming a brown suspension. The brown product was separated, washed with *n*-hexane and dried in vacuum.

Experimental details

The measured crystal was twinned non-merohedrally. The data were processed accordingly and refined against F^2 in the HKLF5 format of the SHELX program [2]. All hydrogen atoms were located in the difference Fourier syntheses, and subsequently fixed to geometric positions using appropriate riding models.

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Abstract

$C_{42}H_{55}NSiTi$, triclinic, $P\bar{1}$ (no. 2), $a = 9.2556(4)$ Å, $b = 12.5048(5)$ Å, $c = 15.7350(7)$ Å, $\alpha = 69.6151(13)^\circ$, $\beta = 85.3502(14)^\circ$, $\gamma = 83.8861(14)^\circ$, $V = 1695.51(13)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0334$, $wR_{\text{ref}}(F^2) = 0.0885$, $T = 100(2)$ K.

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The asymmetric unit of the title crystal structure is shown in the figure. Hydrogen atoms are omitted for clarity. Tables 1 and 2 contain details of the measurement method and a list

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
Ti1	0.35939(2)	0.25596(2)	0.27314(2)	0.00837(3)
Si1	0.62020(3)	0.37181(2)	0.33914(2)	0.01040(5)
N1	0.44596(8)	0.37739(6)	0.30401(5)	0.01022(11)
C1	0.28537(9)	0.24738(7)	0.12846(5)	0.01080(13)
C2	0.39936(9)	0.16056(7)	0.15786(6)	0.01219(14)
H2	0.3919	0.0810	0.1720	0.015*
C3	0.52689(9)	0.21123(8)	0.16296(6)	0.01355(14)
H3	0.6177	0.1716	0.1839	0.016*
C4	0.49456(9)	0.33129(8)	0.13116(6)	0.01312(14)
H4	0.5611	0.3869	0.1243	0.016*
C5	0.34655(9)	0.35377(7)	0.11154(6)	0.01199(14)
H5	0.2955	0.4275	0.0905	0.014*
C6	0.12832(9)	0.23142(7)	0.11884(6)	0.01076(13)
H6	0.0757	0.2215	0.1788	0.013*
C7	0.05216(9)	0.33657(7)	0.04764(6)	0.01313(14)
H7	0.0634	0.4069	0.0622	0.016*
C8	−0.11038(10)	0.31994(8)	0.04948(6)	0.01599(15)
H8A	−0.1553	0.3114	0.1105	0.019*
H8B	−0.1601	0.3880	0.0049	0.019*
C9	−0.12868(10)	0.21289(8)	0.02625(6)	0.01504(15)
H9	−0.2345	0.2021	0.0277	0.018*
C10	−0.05203(10)	0.10865(8)	0.09668(6)	0.01559(15)
H10A	−0.0647	0.0386	0.0833	0.019*
H10B	−0.0962	0.0997	0.1580	0.019*
C11	0.11101(9)	0.12405(7)	0.09462(6)	0.01308(14)
H11	0.1602	0.0552	0.1401	0.016*
C12	0.11990(10)	0.35046(9)	−0.04759(6)	0.01712(16)
H12A	0.2244	0.3623	−0.0497	0.021*
H12B	0.0713	0.4184	−0.0928	0.021*
C13	−0.05990(11)	0.22650(10)	−0.06878(6)	0.01944(18)
H13A	−0.1093	0.2935	−0.1145	0.023*
H13B	−0.0719	0.1576	−0.0839	0.023*
C14	0.17929(10)	0.13840(9)	−0.00047(7)	0.01726(16)
H14A	0.1696	0.0688	−0.0152	0.021*
H14B	0.2842	0.1487	−0.0020	0.021*
C15	0.10269(10)	0.24305(10)	−0.07083(6)	0.01853(17)
H15	0.1475	0.2523	−0.1327	0.022*
C16	0.26417(9)	0.17175(7)	0.43676(5)	0.01074(13)
C17	0.40601(9)	0.12254(7)	0.42704(6)	0.01205(14)
H17	0.4883	0.1289	0.4568	0.014*
C18	0.40638(10)	0.06196(7)	0.36568(6)	0.01368(14)
H18	0.4883	0.0217	0.3468	0.016*
C19	0.26247(10)	0.07250(7)	0.33782(6)	0.01382(14)
H19	0.2296	0.0385	0.2983	0.017*
C20	0.17656(9)	0.14250(7)	0.37912(6)	0.01259(14)
H20	0.0764	0.1663	0.3700	0.015*
C21	0.21769(9)	0.24104(7)	0.49726(6)	0.01104(13)
H21	0.2553	0.3181	0.4678	0.013*
C22	0.05111(9)	0.25946(7)	0.51189(6)	0.01295(14)
H22	0.0059	0.2946	0.4517	0.016*
C23	0.01917(11)	0.34082(8)	0.56658(7)	0.01754(16)
H23A	0.0606	0.4146	0.5330	0.021*
H23B	−0.0873	0.3562	0.5745	0.021*
C24	0.08556(10)	0.28741(8)	0.66007(6)	0.01574(15)
H24	0.0636	0.3408	0.6951	0.019*
C25	0.25063(10)	0.26704(8)	0.64621(6)	0.01523(15)

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
H25A	0.2953	0.2330	0.7059	0.018*
H25B	0.2924	0.3409	0.6133	0.018*
C26	0.28435(9)	0.18613(7)	0.59168(6)	0.01133(13)
H26	0.3921	0.1722	0.5835	0.014*
C27	−0.01438(10)	0.14560(8)	0.56502(6)	0.01439(15)
H27A	−0.1210	0.1593	0.5737	0.017*
H27B	0.0045	0.0925	0.5304	0.017*
C28	0.02163(10)	0.17311(8)	0.71235(6)	0.01608(15)
H28A	−0.0848	0.1861	0.7222	0.019*
H28B	0.0649	0.1383	0.7724	0.019*
C29	0.21932(10)	0.07186(7)	0.64333(6)	0.01286(14)
H29A	0.2408	0.0193	0.6084	0.015*
H29B	0.2640	0.0357	0.7028	0.015*
C30	0.05427(10)	0.09197(8)	0.65778(6)	0.01349(14)
H30	0.0130	0.0173	0.6919	0.016*
C31	0.34483(9)	0.47561(7)	0.30921(6)	0.01141(13)
H31	0.3393	0.4739	0.3734	0.014*
C32	0.38784(9)	0.59398(7)	0.24793(6)	0.01142(13)
C33	0.42535(10)	0.61815(8)	0.15569(6)	0.01477(15)
H33	0.4283	0.5591	0.1304	0.018*
C34	0.45840(10)	0.72734(8)	0.10045(6)	0.01726(16)
H34	0.4855	0.7422	0.0381	0.021*
C35	0.45181(11)	0.81519(8)	0.13659(7)	0.02050(18)
H35	0.4735	0.8901	0.0989	0.025*
C36	0.41346(12)	0.79252(8)	0.22781(7)	0.02068(18)
H36	0.4083	0.8521	0.2526	0.025*
C37	0.38233(10)	0.68227(8)	0.28334(7)	0.01584(15)
H37	0.3571	0.6673	0.3459	0.019*
C38	0.73137(10)	0.23770(8)	0.33748(8)	0.01997(18)
H38A	0.6724	0.1722	0.3633	0.030*
H38B	0.8171	0.2256	0.3735	0.030*
H38C	0.7626	0.2454	0.2748	0.030*
C39	0.73053(11)	0.49011(9)	0.26585(7)	0.02071(18)
H39A	0.7355	0.4910	0.2031	0.031*
H39B	0.8290	0.4777	0.2880	0.031*
H39C	0.6848	0.5636	0.2680	0.031*
C40	0.61472(12)	0.37536(11)	0.45757(7)	0.0241(2)
H40A	0.5626	0.4472	0.4591	0.036*
H40B	0.7142	0.3702	0.4766	0.036*
H40C	0.5644	0.3106	0.4989	0.036*
C41	0.19439(9)	0.46138(7)	0.28591(6)	0.01302(14)
H41	0.1172(15)	0.5245(12)	0.2843(9)	0.018(3)*
C42	0.17073(9)	0.37173(7)	0.26282(6)	0.01207(14)
H42	0.0735(16)	0.3664(13)	0.2483(10)	0.022(4)*

Comment

Titanaaziridines are used in a variety of organic synthesis methods [5, 6]. In this context, the hydroaminoalkylation of alkenes, in which the insertion of the alkene into the Ti–C bond of the titanaaziridine is supposed to be the C–C forming step [7–10], is likely the most important one. To the best of our knowledge, reactions of titanaaziridines and alkynes in the

catalytic hydroaminoalkylation have not been reported until now. However, in stoichiometric reactions there are a few examples of 5-membered ring insertion products [4, 11, 12]. Usually, such products are generated from mono and doubly aryl, alkyl- and trimethylsilyl-substituted alkynes. Here, we present the crystal structure of a dihydroisotitanazole, which was synthesized from bis(adamantylcyclopentadienyl)titanium- η^2 (*N*-benzylidene-trimethylsilylamine) and acetylene. This is the first structurally characterized dihydroisotitanazole employing the smallest possible substituted alkyne acetylene.

The Ti1–N1 (2.0049(7) Å) and the Ti1–C42 (2.1248(9) Å) bonds are in the expected range of dihydroisotitanazoles [4, 12]. The former acetylene C–C triple bond is now elongated to a typical C–C double bond with 1.3363(12) Å between C41–C42 in the insertion product [13]. The newly formed bond C31–C41 (1.5120(12) Å) is in accordance with a single bond [13]. The 5-membered ring (Ti1–N1–C31–C32–C42) is almost planar. Due to the strain of the ring, the angle N1–Ti1–C42 (81.34(3)°) differs significantly from the angle of an ideal pentagon (108°). Consequently, the titanium center has a distorted tetrahedral coordination.

References

1. Bruker. APEX2 and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA (2012).
2. Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr.* **C71** (2015) 3–8.
3. Diekmann, M.; Bockstiegel, G.; Lützen, A.; Friedemann, M.; Haase, D.; Saak, W.; Beckhaus, R.: Chiral bis(η^5 : η^1 -pentafulvene)titanium complexes. *Organometallics* **25** (2006) 339–348.
4. Manßen, M.; Lauterbach, N.; Dörfler, J.; Schmidtman, M.; Saak, W.; Doye, S.; Beckhaus, R.: Efficient access to titanaziridines by C–H activation of *N*-methylanilines at ambient temperatures. *Angew. Chem. Int. Ed.* **54** (2015) 4383–4384.
5. See Ref. 4. and references therein.
6. Loose, F.; Plettenberg, I.; Haase, D.; Saak, W.; Schmidtman, S.; Schäfer, A.; Müller, T.; Beckhaus, R.: Aromatic imines in the titanocene coordination sphere – titanaziridine vs 1-aza-2-titanacyclopent-4-ene structures. *Organometallics* **33** (2014) 6785–6795.
7. Chong, E.; Garcia, P.; Schafer, L. L.: Hydroaminoalkylation: early-transition-metal-catalyzed α -alkylation of amines. *Synthesis* **21** (2014) 2884–2896.
8. Prochnow, I.; Kubiak, R.; Frey, O. N.; Beckhaus, R.: Tetrabenzyltitanium: an improved catalyst for the activation of sp³ C–H bonds adjacent to nitrogen atoms. *ChemCatChem* **1** (2009) 162–172.
9. Prochnow, I.; Zark, P.; Müller, T.; Doye, S.: The mechanism of the titanium-catalyzed hydroaminoalkylation of alkenes. *Angew. Chem. Int. Ed.* **50** (2011) 6401–6405.
10. Roesky, P. W.: Catalytic hydroaminoalkylation. *Angew. Chem. Int. Ed.* **48** (2009) 4892–4894.
11. See Ref. 10. and references therein.
12. Loose, F.; Schmidtman, M.; Saak, W.; Beckhaus, R.: Imines in the titanium coordination sphere: highly reactive titanaziridines and larger titanacycles formed by subsequent C–C coupling reactions. *Eur. J. Inorg. Chem.* **2015** (2015) 5171–5187.
13. March, J.: *Advanced organic chemistry*, 4th ed. Wiley, New York (1992).