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Reactions of methyl-substituted titanocene–bis(trimethylsilyl)acetylene complexes with acetone azine: crystal structures of $(\eta^5:\eta^1\text{-}C_5HMe_3CH_2CMe_2NH)_2Ti$ and $(C_5Me_5)_2Ti(N{=}CMe_2)$

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Dedicated to Professor Stanisław Pasynkiewicz on the occasion of his 70th birthday.

Abstract

The titanocene–bis(trimethylsilyl)acetylene (BTMSA) complexes $Cp'_2Ti[\eta^2\text{-}C_2(SiMe_3)_2]$ ($Cp'{=}C_5H_{5-n}Me_n$; $n = 0$–5) react with acetone azine $Me_2C{=}N{-}N{=}CMe_2$ (AA) in two different ways depending on the number of Me substituents at the Cp′ ligands (n). For $n = 0$–2, BTMSA is replaced by AA, which then undergoes an oxidative addition accompanied by a proton transfer, affording titana-2-isopropyl-4-methyl-2,3-diazacyclopent-3-ene complexes **A0**–**A2**. For $n = 3$–5, replacement of the acetylene is followed by the splitting of AA to give either $(C_5Me_5)_2Ti(III)(N{=}CMe_2)$ (**C5**) or the Ti(IV) $(Cp'A)_2Ti$ complexes **B3** and **B4** for $n = 3$ and 4, respectively. The intramolecularly bridging Cp′A ligand 1-(η^5-2,3,5-trimethylcyclopentadienide)-2-(η^1-amide)-2,2′-dimethylethane arises from a formal insertion of the C=N bond of isopropylidene amide into a C–H bond of one methyl group of the cyclopentadienyl ligands before or after splitting of AA. Crystal structures of **C5** and $(\eta^5:\eta^1\text{-}C_5HMe_3CH_2CMe_2NH)_2Ti(IV)$ (**B4**) were determined. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Titanium; Acetone azine; Titanocene–bis(trimethylsilyl)acetylene complexes; Titanocene–amide complexes; Effect of methyl substituents; Crystal structure

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1. Introduction

The titanocene–bis(trimethylsilyl)acetylene (BTMSA) complexes $Cp'_2Ti[\eta^2\text{-}C_2(SiMe_3)_2]$ ($Cp'{=}C_5H_{5-n}Me_n$; $n = 0$–5) [1] are potential reagents for the clean syntheses of Ti(II), Ti(III), and Ti(IV) titanocene complexes. In these syntheses, entering reagent cleanly replaces the BTMSA ligand on a titanocene moiety, usually affording a product of oxidative addition [2]. The insertion reactions into the Ti–BTMSA bonds are probably hindered by bulky $SiMe_3$ substituents, the only insertion reaction of this type being reported for the addition of one half of an equivalent of CO_2 to $Cp_2Ti{\cdot}BTMSA$ [3]; the product of insertion of acetylene C_2H_2 was also observed, however, an exchange of BTMSA and C_2H_2 could precede the insertion [4]. The formation of a transient titanocene(Ti(II)) species seems to be well established. The thermolysis of the above series of $Cp'_2Ti[\eta^2\text{-}C_2(SiMe_3)_2]$ compounds leads to the elimination of BTMSA, and the titanocene species rearrange to give dimeric titanocenes–(fulvalene)(dihydrido)-bridged cyclopentadienyltitanium(III) compounds for $n = 0$–3

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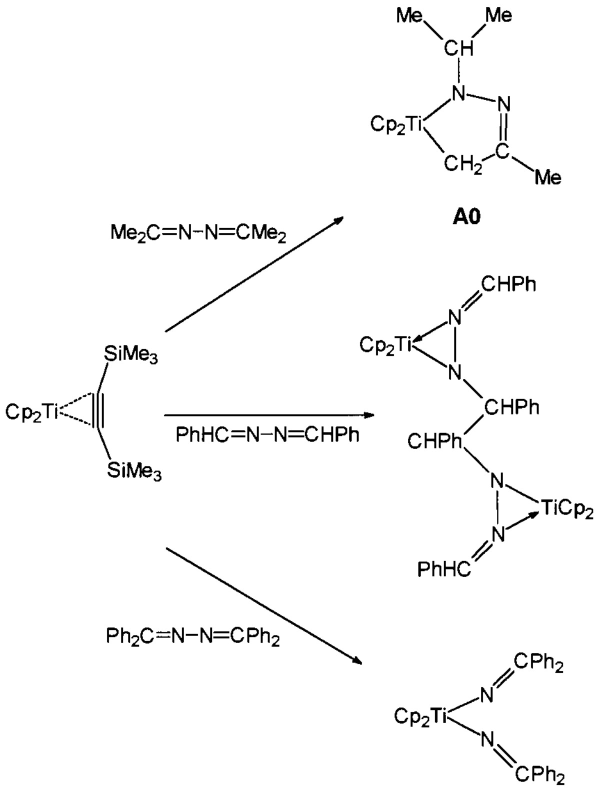
[1a]. Apart from a not-well-understood thermolysis of $(C_5HMe_4)_2Ti[\eta^2\text{-}C_2(SiMe_3)_2]$, BTMSA plays an active role only in the thermolysis of $(C_5Me_5)_2Ti[\eta^2\text{-}C_2(SiMe_3)_2]$. It accepts two protons from the liberated permethyltitanocene, and thus allows the allyl–diene complex $[C_5Me_3(CH_2)_2](C_5Me_5)Ti$ [5] to be obtained in a quantitative yield [1a]. With nitrogen bases like aldimines and ketimines [6a], oxazoles, isooxazoles and thiazoles [6b], siloximes [6c] and 2-vinylpyridine [6d] $(C_5H_5)_2Ti(BTMSA)$ gives Ti(IV) products of oxidative addition and BTMSA is released. On the other hand, in reactions of $Cp'_2Ti(BTMSA)$ complexes with 2,2′-bipyridyl and 4,5-diazafluorene, an electron transfer from a titanocene species gives rise to titanocene Ti(III) complexes with the bipyridyl radical anion [7a,b] and with a release of hydrogen to diazafluorenyltitanocene complexes [7a]. Recently, $(C_5H_5)_2Ti(BTMSA)$ was used to prepare bis(cyclopentadienyl)titana-2,5-diazacyclopent-3-ene complexes from substituted 1,4-diaza-1,3-dienes, and the reactivity of 1,4-substituted 2,3-diaza-1,3-dienes to $Cp_2Ti(BTMSA)$ was also investigated [8]. Unlike in the former case, 1,4-disubstituted 2,3-diazadienes reacted irregularly, giving rise to products whose structure varied depending on the diazadiene substituents (Scheme 1) [8]. Whereas benzophenone azine reacted with the splitting of its N–N bond, benzaldehyde azine coordinated to titanocene by its nitrogens and two such molecules dimerized at sp^2 carbon atoms to give a titanocene–amido dimer (Ti(III)). Most curiously, acetone azine underwent a hydrogen transfer from sp^3- to sp^2-carbon atom to give an asymmetric bis(cyclopentadienyl) titana-2-isopropyl-4-methyl-2,3-diazacyclopent-3-ene (**A0**).



Scheme 1. Reactions of various 1,4-substituted 2,3-diazabuta-1,3-dienes [8b].

Here we report on a remarkable effect of the number of methyl substituents at the cyclopentadienyl ligands on the reactivity of $Cp'_2Ti(BTMSA)$ ($Cp'=C_5H_{5-n}Me_n$; $n = 0–5$) compounds toward acetone azine and structures of reaction products.

2. Experimental

2.1. General data and methods

All operations with Ti complexes were carried out under vacuum in all-sealed devices equipped with magnetically breakable seals. A combined device equipped with a quartz cuvette (2.0 mm) and a quartz tube was used for the UV–NIR and ESR measurements. Crystals for EI MS measurements and melting point determinations were placed in glass capillaries and KBr pellets for IR spectra were prepared in a glovebox Labmaster 130 (mBraun) under purified nitrogen. UV–NIR measurements were performed in the range 340–2000 nm on a Varian Cary 17 D spectrometer using all-sealed quartz cuvettes (Hellma). ESR spectra were measured on an ERS-220 spectrometer (Centre for Production of Scientific Instruments, Academy of Sciences of GDR, Berlin, Germany) operated by a CU-1 unit (Magnettech, Berlin, Germany) in the X-band. g-Values were determined using an Mn^{2+} ($M_I = -1/2$ line) standard at $g = 1.9860$. Concentrations of the paramagnetic compounds were determined by double integration of the first-derivative spectra. A variable-temperature unit STT-3 was used for measurements in the range 102–296 K. Samples in capillaries for mass spectrometry (EI MS) analysis were opened and inserted into the direct inlet of a JEOL D-100 spectrometer under argon. ^1H- and ^{13}C-NMR spectra of organometallic compounds were measured on a Varian VXR-400/INOVA-400 spectrometer (400 and 100 MHz, respectively) in C_6D_6 at 25°C in sealed sample tubes. Chemical shifts (given in the δ scale) were referenced to the solvent signal (δ_H 7.15 ppm, δ_C 128.0 ppm). Infrared spectra of samples in KBr pellets were measured on a Specord 75 IR (Carl Zeiss, Jena, Germany) spectrometer.

2.2. Chemicals

Hexane, toluene and THF were purified by conventional methods, dried by refluxing over $LiALH_4$ and stored as solutions of green dimeric titanocene

(μ-$C_{10}H_8$)[(C_5H_5)Ti(μ-H)]$_2$ [9]. Deuterated benzene was degassed and stored as a solution of dimeric titanocene. Acetone azine (98%, Aldrich) (AA) was degassed and distilled under vacuum. The middle fraction was collected and stored on a vacuum line. (N=CMe$_2$)$_2$. ^{1}H-NMR ($CDCl_3$): 1.77 (s, 6H), 1.82 (s, 6H); ^{13}C-NMR ($CDCl_3$): 17.65 (q, 2C), 25.02 (q, 2C), 160.14 (s, 2C); IR (neat): 2980 (m), 2935 (m), 2908 (m), 2841 (w), 1640 (s), 1428 (s), 1360 (s), 1243 (s), 1072 (w), 1050 (w), 608 (w), 550 (br, w). The titanocene dichlorides ($C_5H_{5-n}Me_n$)$_2$TiCl$_2$ and the ($C_5H_{5-n}Me_n$)$_2$Ti·BTMSA [(1,3-Me$_2$; 1,2,3-Me$_3$), $n = 0$–5; BTMSA = bis(trimethylsilyl)-acetylene] complexes were prepared according to literature procedures [1a].

2.3. Reactions of the ($C_5H_{5-n}Me_n$)$_2$Ti·BTMSA ($n = 0$–5) complexes with acetone azine

Acetone azine (0.7 ml, 5.25 mmol) was distilled into an ampoule attached to a quartz all-sealed cuvette ($d = 0.2$ cm) and the solution of a ($C_5H_{5-n}Me_n$)$_2$Ti·BTMSA complex in hexane (1.0 mmol in 5 ml) was added. After cooling by liquid nitrogen the reaction mixture was sealed off and then kept in a water bath at 60°C. The conversion of yellow ($C_5H_{5-n}Me_n$)$_2$Ti·BTMSA complexes was followed by measuring the intensity of their electronic absorption band in the range 920–1060 nm [1a], where no absorption bands of products interfere. The time of complete conversion was 10 min for $n = 0$, 2 h for $n = 1$, 6 h for $n = 2$, 100 h for $n = 3$ and 4, and 15 h for $n = 5$. Dark-green solutions were obtained for $n = 0$–2 (products denoted **A0**–**A2**), yellow solutions for $n = 3$ and 4 (products **B3** and **B4**), and a red–brown solution for $n = 5$ (product **C5**). The reaction mixtures were evaporated under dynamic vacuum, finally at 60°C for 2 h. The residue was dissolved in a minimum amount of hexane, and the solution was submitted for crystallization at -70°C. Products **A0**–**A2** formed dark-green oily solids which did not crystallize. Attempts to sublime them on a high-vacuum line led to their decomposition, affording dark-blue amorphous residues insoluble in hexane and negligibly soluble in toluene. These thermolytic products did not evaporate in an EI MS spectrometer up to 250°C, and their structure remains unknown. Compounds **A0**–**A2** gave, however, sufficient vapour pressure in the mass spectrometer at a temperature of only 40–70°C. ^{1}H- and ^{13}C-NMR spectra of **A0** were identical to the literature data [8] and the spectra of **A1** and **A2** were assigned accordingly, although unidentified impurities were detected in all the samples. Yellow products **B3** and **B4** were purified by crystallization at -70°C, and crystals of **B4** were suitable for X-ray structure analysis. This revealed the structure of **B4** although the hydrogen atom attached to nitrogen was not localized. This hydrogen atom has been identified in ^{1}H- and ^{13}C-NMR spectra of **B3** and **B4**, which were fully assigned using ^{1}H-, ^{13}C{^{1}H}-, ^{13}C APT, COSY, long-range COSY, HETCOR, TOCSY, 1D TOCSY, HMQC, and HMBC methods. The paramagnetic red–brown compound **C5** crystallized out from a dirty-yellow mother liquor. Its structure was determined by X-ray crystal analysis. The interaction of d^1 electron with the nitrogen nucleus was identified in ESR spectra.

Crude reaction solutions of all the systems contained paramagnetic impurities. EPR (hexane): $g = 1.984$–1.986, $\Delta H = 7.0$ G and $g = 1.976$, $\Delta H = 5.0$–7.0 G of lower intensity. The former signals belong to compounds of the type **C** (**C5** is far the main product). The latter signals, which do not show coupling to ^{47}Ti and ^{49}Ti isotopes, are tentatively assigned to organic radicals generated from AA.

(η^5-C_5H_5)$_2$Ti($C_6N_2H_{12}$) (**A0**) green oily solid. MS (40–50°C; m/z (%)): 290(M$^{+\bullet}$; 5), 234(4), 178([M–AA]$^+$; 100), 152(4), 113(17), 56(10). ^{1}H-NMR (C_6D_6, 23°C): δ 1.23 (d, $^3J_{HH} = 6.1$ Hz, 6H, 2 × Me), 1.37 (s, br, 2H, CH$_2$), 2.36 (s, 3H, Me), 3.84 (septet, $^3J_{HH} = 6.3$ Hz, 1H, CHMe$_2$), 5.26 (s, 10H, 2 × Cp). ^{13}C-NMR (C_6D_6, 23°C): 14.35 (q, 4C), δ 24.5 (q, 2C), 25.8 (q), 55.9 (t,), 60.2 (d), 105.3 (d, 10C), 151.8 (s, C=N). UV–vis (hexane, nm): 370(sh), 450(sh), 620.

(η^5-C_5H_4Me)$_2$Ti($C_6N_2H_{12}$) (**A1**) green oily solid. MS (40–70°C; m/z (%)): 318(M$^{+\bullet}$; 4), 262(2), 206([M–AA]$^+$; 100), 178(2), 127(7), 126(16), 56(10). ^{1}H-NMR (C_6D_6, 23°C): δ 1.27 (m, 2H, CH$_2$), 1.28 (d, $^3J_{HH} = 6.5$ Hz, 6H, 2 × Me), 1.34 (s, br, 2H, CH$_2$), 1.74 (s, 12H, 4 × Me), 2.42 (s, 3H, Me), 3.95 (septet, $^3J_{HH} = 6.5$ Hz, 1H, CHMe$_2$), 5.08–5.14 (m, 8H, Cp) (s, 2H, Cp). ^{13}C-NMR (C_6D_6, 23°C): δ 16.9 (q, 2C) 24.4 (q, 2C), 25.8 (q), 60.2 (t), 60.5 (d), 111.3 (d, 8C), 131.3 (s, 2C) 153.5 (s, C=N). UV–vis (hexane, nm): 370(sh), 450(sh), 615.

(η^5-$C_5H_3Me_2$)$_2$Ti($C_6N_2H_{12}$) (**A2**) green oily solid. MS (40–70°C; m/z (%)): 346(M$^{+\bullet}$; 4), 290(2), 234([M–AA]$^+$; 100), 217(3), 197(3), 140(12), 56(6). ^{1}H-NMR (C_6D_6, 23°C): δ 1.25 (d, $^3J_{HH} = 6.1$ Hz, 6H, 2 × Me), 1.34 (s,br, 2H, CH$_2$), 1.74 (s, 12H, 4 × Me), 2.40 (s, 3H, Me), 3.87 (septet, $^3J_{HH} = 6.1$ Hz, 1H, CHMe$_2$), 5.09 (s, 2H, Cp), 5.29 (s, 4H, Cp). ^{13}C-NMR (C_6D_6, 23°C): δ 15.9 (q, 4C, Me-1,3), 24.5 (q, 4C), 26.1 (q, 2C), 58.1 (t), 60.2 (d), 105.3 (d, 2C), 108.7 (d, 4C), 130.9 (s, 4C, 2 × C-1,3), 152.2 (s, C=N). UV–vis (hexane, nm): 600.

(η^5:η^1-$C_5H_2Me_2CH_2CMe_2NH$)$_2$Ti (**B3**) yellow crystalline solid, yield 0.29 g (77%). MS (70–90°C; m/z (%)): 374(M$^{+\bullet}$; 5), 359(23), 318(46), 317([M–(NH–CMe$_2$)]$^+$; 100), 303(11), 302(12), 268(25), 261(74), 260([M–2(NH–CMe$_2$)]$^+$; 62), 259(18), 211(95), 195(9), 172(9), 154(62), 153(47), 152(33), 151(16), 150(19), 91(17), 42(18). UV–vis (hexane, nm): 375. ^{1}H- and ^{13}C-NMR spectra for four different molecules of **B3** are gathered in Table 1.

Table 1
^{1}H- and ^{13}C-NMR spectra of four isomers of **B3** (δ [ppm]; J [Hz]) [a,b]

Assignment	Ring 1			Ring 2		
	δ_C	δ_H	J	δ_C	δ_H	J
Isomer (*R*-1,2)						
C-1	137.93	–	–	120.48	–	–
C-2	119.44	–	–	135.66	–	–
C-3	120.39	–	–	113.93	–	–
C-4	101.71	5.180	(2.7)	106.43	5.347	(3.2)
C-5	103.64	5.068	(2.7)	103.73	5.074	(3.2)
C-6	40.47	2.616	(12.8)	36.76	2.483	(13.3)
		2.213	(12.8)		2.294	(13.3)
C-7	79.50	–	–	79.20	–	–
1-Me	–	–	–	14.85	2.177	–
2-Me	12.40	2.051	–	–	–	–
3-Me	13.54	1.784	–	14.92	1.733	–
7-Me	35.20	1.232	–	35.78	1.194	–
	36.65	1.187	–	39.11	1.183	–
N–H	–	4.708	–	–	4.233	–
Isomer (*S*-1,2)						
C-1	138.10	–	–	114.03	–	–
C-2	119.02	–	–	135.22	–	–
C-3	111.33	–	–	117.70	–	–
C-4	105.31	4.875	(3.2)	105.50	5.498	(3.2)
C-5	110.11	5.860	(3.2)	106.64	4.875	(3.2)
C-6	36.39	2.431	(13.1,1.0)	39.86	2.493	(13.1)
	–	2.228	(13.1)	–	2.228	(13.1)
C-7	79.35	–	–	77.39	–	–
1-Me	–	–	–	14.92	1.772	–
2-Me	11.14	1.601	–	–	–	–
3-Me	15.02	1.964	–	14.19	1.816	–
7-Me	34.07	1.230	–	36.02	1.204	–
	36.40	1.184	–	36.04	1.329	–
N–H	–	4.922	–	–	4.814	–
	Isomer (1,1)			Isomer (2,2)		
C-1	137.08	–	–	115.15	–	–
C-2	119.85	–	–	136.02	–	–
C-3	117.70	–	–	121.61	–	–
C-4	105.50	5.346	(3.2)	106.64	4.794	(3.2)
C-5	102.05	4.867	(3.2)	108.08	5.171	(3.2)
C-6	40.36	2.583	(12.8, 0.9)	36.84	2.438	(13.1)
		2.214	(12.8)		2.229	(13.1)
C-7	77.39	–	–	79.05	–	–
1-Me	–	–	–	14.44	1.813	–
2-Me	12.33	2.032	–	–	–	–
3-Me	14.19	1.816	–	14.83	2.177	–
7-Me	36.06	1.329	–	34.07	1.232	–
	36.02	1.204	–	36.94	1.209	–
N–H	–	4.814	–	–	4.594	–

[a] Ring 1 bears bridging carbon atom C-6 on C-1, ring 2 on C-2 (see Scheme 3).

[b] Relative abundance of isomers: (*R*-1,2) 48%, (*S*-1,2) 23%, (1,1) 21%, and (2,2) 8%.

(η^5:η^1-$C_5HMe_3CH_2CMe_2NH)_2Ti$ (**B4**) yellow crystals, yield 0.32 g (80%). M.p. 235°C with partial decomposition. MS (90–110°C; *m*/*z* (%)): 402($M^{+\bullet}$; 11), 387(22), 345($[M-(NH-CMe_2)]^+$; 100), 330(11), 290(19), 289(55), 288($[M-2(NH-CMe_2)]^+$; 49), 287(20), 282(30), 241 (12), 225(84), 209(9), 201(4), 186(10), 168(44), 167(26), 166(27), 165(12), 164(12), 105(10). ^{1}H-NMR (C_6D_6, 23°C): δ 1.21 (s, 12H, 2 × CMe_2), 1.79 (s, 6H, 2 × 5-Me), 1.81 (s, 6H, 2 × 3-Me), 2.05 (s, 6H, 2 × 2-Me), 2.27 (d, $J = 13.2$ Hz, 2H), 2.46 (d, $J = 13.2$ Hz, 2H), 4.36 (s, 2H, 2 × N–H), 5.05 (s, 2H, 2 × H-4) (long-range couplings: 2.27 → 1.21, 2.46 → 1.21, 1.81 → 2.05 (i.e. neighbours), 5.05 → 1.79 and 1.81 (i.e. adjacent positions). ^{13}C-NMR (C_6D_6, 23°C): δ 12.8 (q, Me-2), 13.4 (q, Me-3), 14.8 (q, Me-5), 35.8 (q, Me-7), 37.0 (q, Me-7), 37.1 (t, CH$_2$, C-6), 78.7 (s, C-7), 105.3 (d, C-4), 112.8 (s, C-2), 115.8 (s, C-3), 119.8 (s, C-5), 135.4 (s, C-1). UV–vis (hexane, nm): 380. IR (KBr) (cm^{-1}): 3350 (m), 2955 (s), 2930 (vs), 2909 (vs), 2855 (s), 1505 (w), 1491 (w), 1449 (m), 1438 (m), 1373 (s), 1348 (m), 1327 (m), 1287 (w), 1244 (w), 1163 (vs), 1025 (w), 1018 (w), 974 (m), 916 (w), 874 (w), 841 (m), 814 (m), 785 (m), 669 (w), 615 (s), 490 (s), 442 (m).

(η^5-C_5Me_5)$_2$Ti(NCMe$_2$) (**C5**) brown crystals, yield 0.27 g (72%). M.p. 249°C. MS (70–90°C; m/z (%)): 374(M$^{+\bullet}$; 41), 318([M–(N=CMe$_2$)]$^+$; 95), 317([M–(HN=CMe$_2$)]$^+$; 100), 316(34), 315(41), 314(10), 313(14), 182(20), 181(15), 180(21), 179(9), 178(16), 159(24), 158(14), 157(9), 156(10), 119(8), 42(19). UV-NIR (hexane, nm): 490 > 630 (sh) > 750 (sh) > 1150. EPR (toluene, −44°C): $g = 1.9844$, $a_N = 2.7$ G ($\Delta H = 7.4$ G), $a_{Ti} = 8.0$ G; (toluene, −140°C): $g_1 = 2.000$, $g_2 = 1.984$, $g_3 = 1.972$, $g_{av} = 1.985$. IR (KBr) (cm^{-1}): 2984 (s), 2901 (vs), 2855 (s), 1690 (vs), 1489 (w), 1427 (m), 1375 (s), 1343 (m), 1181 (w), 1024 (m), 569 (w), 536 (w), 500 (m), 434 (s).

2.4. Crystal structure analyses of *B4* and *C5*

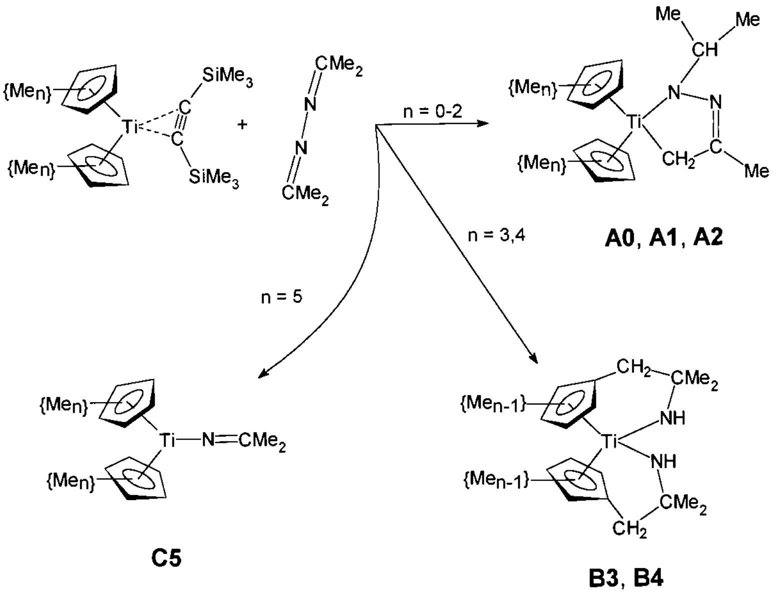
Selected crystal fragments of **B4** and **C5** were mounted into Lindemann glass capillaries under purified nitrogen in a glovebox Labmaster 130 (mBraun) and sealed by wax. All X-ray diffraction measurements were performed at room temperature. Compound **B4** was measured on a STOE IPDS (Imaging Plate Diffraction System) (planar graphite monochromator, Mo–K$_\alpha$ radiation, $\lambda = 071073$ Å). Diffraction data for **C5** were collected on a Philips PW1100 single crystal diffractometer (graphite monochromator, Mo–K$_\alpha$ radiation, $\lambda = 071073$ Å). The intensity data were collected by $\omega/2\theta$ scans. The absorption correction was applied using Ψ-scans. In both structures, the titanium atoms were localized by the Patterson method [10] and all other non-hydrogen atoms by the difference Fourier synthesis. Anisotropic refinement was performed by full-matrix least-squares methods based on F^2 applying variance-based weighting schemes (SHELXL-97 [11]). The cyclopentadienyl hydrogens were included at their calculated positions and the methyl hydrogens were refined using a riding model. Compound **B4** contains three slightly inequivalent molecules in the unit cell. Compound **C5** contains one molecule of toluene of crystallization in the unit cell. The carbon atoms of the toluene molecule were strongly disordered. The crystal, collection and refinement data for **B4** and **C5** are summarized in Table 2. Atomic positional parameters have been deposited at the Cambridge Crystallographic Data Centre.

Table 2
Crystal and structure refinement data for **B4** and **C5**

	B4	**C5**
Chemical formula	$C_{24}H_{38}N_2Ti$	$C_{23}H_{36}NTi$
Molecular weight	402.8	374.4
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$ (no. 14)	$Pnma$ (no. 62)
Unit cell dimensions		
a (Å)	8.9593(10)	14.5438(4)
b (Å)	29.038(4)	14.4252(7)
c (Å)	25.895(4)	10.7512(6)
α (°)	90	90
β (°)	94.169(14)	90
γ (°)	90	90
V (Å^3)	6719(2)	2255.6(2)
Z	12	4
$D_{calc.}$ (g cm^{-3})	1.194	1.103
μ (mm^{-1})	0.393	0.384
F(000)	2616	812
Crystal size (mm^3)	$0.15 \times 0.23 \times 0.92$	$0.8 \times 0.4 \times 0.2$
θ range for data Collection (°)	1.73–24.10	3.14–25.03
Reflections collected	10395	4505
Unique reflections, R_{int}	10395, 0.0000	2078, 0.0537
Data, restraints, parameters	10395, 0, 730	2070, 0, 124
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.0485, 0.1015	0.0690, 0.1630
Final R_1, wR_2 (all data)	0.1139, 0.1134	0.1267, 0.2143
Goodness-of-fit on F^2	0.700	1.138
Largest peak, hole (e Å^{-3})	0.364, −0.255	0.365, −0.219

3. Results and discussion

Acetone azine replaces BTMSA in all the (C_5H_{5-n}-Me$_n$)$_2$Ti·BTMSA ($n = 0$–5) complexes at 60°C; however, the time to accomplish this exchange, as well as the nature of reaction products, vary strongly depending on the number of Me substituents at the cyclopentadienyl ligands (Scheme 2). For $n = 0$–2, dark-green oily products **A0**, **A1**, and **A2** are formed with the reaction time increasing from 10 min for $n = 0$, to 2 h for $n = 1$, and 6 h for $n = 2$. For $n = 3$ and 4, yellow crystalline products denoted **B3** and **B4** were obtained after 100 h at 60°C. For $n = 5$, a brown crystalline compound denoted **C5** was obtained after 15 h only. Compounds **A0**–**A2** belong, apparently, to the same structural type displaying very similar electronic absorption spectra and similar fragmentation in EI-MS spectra. They were identified to be derivatives of titana-2-isopropyl-4-methyl-2,3-diazacyclopent-3-ene on the basis of ^{1}H- and ^{13}C-NMR spectra which were previously interpreted ingeniously by Rosenthal and coworkers for **A0** [8a]. Unfortunately, in our hands all these compounds could be neither purified by crystallization because of their enormous solubility in hydrocarbons and oily appearance nor by sublimation. On heating in vacuum up to 120°C, they afford dark-blue non-volatile (up to 250°C in vacuum of the mass spec-



Scheme 2. Reaction products of the $(C_5H_{5-n}Me_n)_2Ti(BTMSA)$ ($n = 0$–5) complexes and acetone azine.

trometer) thermolytic products that are negligibly soluble in toluene and their structure was not identified. Anyway, the vapour pressure of **A0**–**A2** at 40–70°C is sufficient for EI MS measurement. Their mass spectra show molecular ions $M^{+\bullet}$ and fragment ions $[M\text{-}56]^+$ of a low intensity and titanocene cations as basic peaks. This may indicate that the asymmetric titanacycle rearranges upon electron impact to give a complex with a symmetrically bonded AA, which then easily loses the whole AA ligand and less abundantly one half of AA. Although compounds **A0**–**A2** are far the main products, at least one impurity was observable in NMR spectra and admixtures of paramagnetic compounds $(C_5H_{5-n}Me_n)_2Ti(N{=}CMe_2)$ **C0**–**C2** and one apparently organic radical are observable in EPR spectra. For $n = 3$ and 4, the Ti(IV) compounds of the $(Cp'A)_2Ti$ type **B3** and **B4**, respectively, are far the main products; the paramagnetic compounds **C3** and **C4** were present in crude products as very minor byproducts detected by EPR spectroscopy. The structure of diamagnetic yellow crystalline compounds **B3** and **B4** was identified by combined results of spectroscopic properties and was confirmed by X-ray crystal analysis of **B4** (vide infra). The absence of electronic absorption bands below 400 nm pointed to the presence of a Ti(IV) compound, the absence of IR bands in the range 1500–2600 cm^{-1} proved the absence of $-N{=}C<$ fragment, the presence of a sharp band at 3350 cm^{-1} indicated an N–H bond and the EI MS spectra showed the molecular ions corresponding to the overall composition of $Cp'_2Ti(AA)$. In contrast to **A0**–**A2**, which release most abundantly the whole molecule of AA, **B3** and **B4** fragmented with the subsequent loss of protonated halves of acetone azine. ^{1}H- and ^{13}C-NMR spectra of **B4** revealed that the product consisted of only one resolvable compound containing two magnetically equivalent 1-(η^5-2,3,5-trimethylcyclopentadienide)-2-(η^1-amide)-2,2′-dimethylethane ligands intramolecularly bonded to titanium atom (see Scheme 2 and Fig. 1). The presence of chiral C_2 symmetric racemate was also corroborated by the X-ray crystal structure of **B4** (vide infra).

We suggest that the process of the **B4** formation requires a replacement of BTMSA by AA and its coordination to titanium by its nitrogen atoms. However, this is a necessary prerequisite for a series of further steps whose sequence is not certain. Two scenarios can be considered. In the first, the cleavage of the N–N bond is followed by a Ti–N bond formation and a formal insertion of the N=C bond of isopropylidene amide ligand into the C–H bond of the cyclopentadienyl methyl group accomplishes the (Cp′A) ligand formation. In the second, less favourable, the C=N

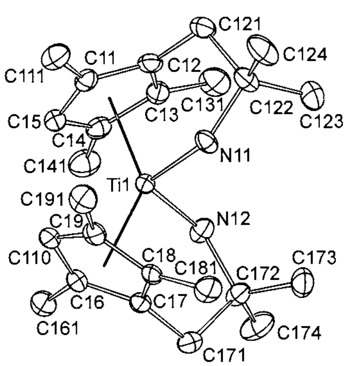
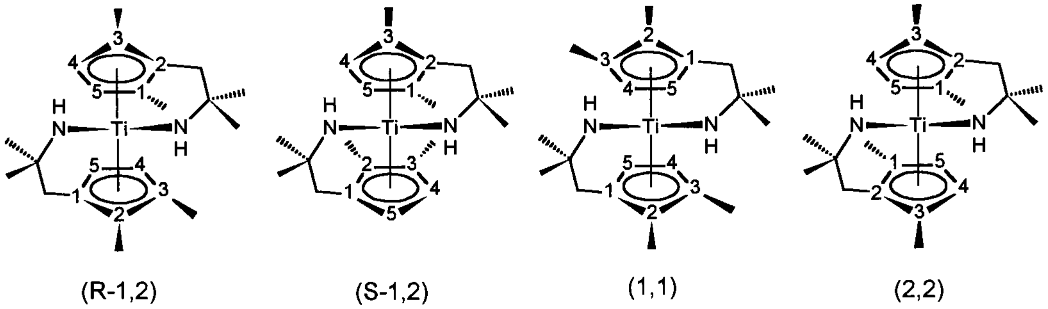


Fig. 1. ORTEP drawing of **B4** with 30% probability ellipsoids and atom numbering scheme for molecule 1.



Scheme 3. Isomers of **B3** resolved by ^{1}H- and ^{13}C-NMR spectroscopy.

bond of the coordinated AA ligand is inserted into the C–H bond, and this induces the N–N bond cleavage followed by the Ti–N bond formation. It has not been possible to obtain evidence for either of the intermediate steps because the monitoring of the reaction between $(C_5HMe_4)_2Ti{\cdot}BTMSA$ and AA by UV–NIR spectra showed that the BTMSA complex decayed slowly, until the reaction went to completion. This means that either the replacement of BTMSA or the first irreversible reaction step is slow.

The formation of **B4** is surprisingly specific because only those methyl groups that are in remote positions with respect to the ring CH group are involved in the bridge ligand formation. The reason may be sought in the hindered rotation of the C_5HMe_4 ligands causing the preferred position of the CH groups in hinge positions (in the solid state [12]) to expose the distant methyl groups to the vicinity of either the amidoisopropylidene group or the coordinated AA ligand for a longer time. However, the induced electronic polarization of the CH bond on the distant Me groups can also contribute.

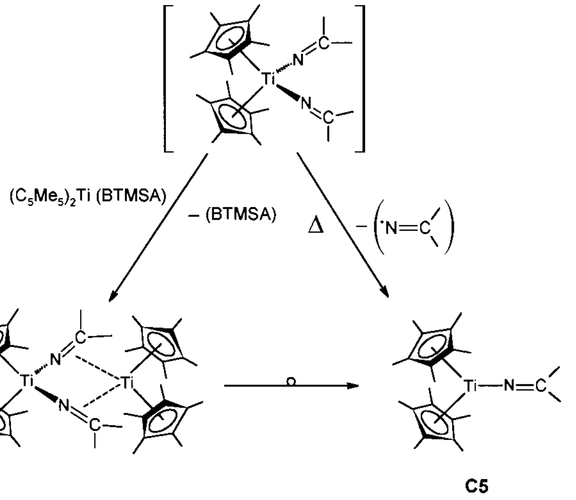
In compound **B3**, containing two vicinal CH groups, two methyl groups and the bridging methylene, the ^{1}H- and ^{13}C-NMR spectra resolved six sets of CpA′ ligands (Table 1), which were assigned to four structures shown in Scheme 3. The attachment of the bridging methylene group to carbon-1 or to carbon-2 of the ring was deduced from HMBC relying on a three-bond coupling between CH_2 and CH_3 and Cp carbons; the former has one Cp carbon coupled to CH_2 and the second to methyl, the latter has both Cp carbons coupled to one Me each. There were three C-1 and three C-2 substituted Cp units. With the major isomer, two pairs of NOEs were found between NH and Cp methyls belonging to two different rings (4.233/2.051 and 4.708/2.177), thus proving that they form one molecule (*R*-1,2). The second isomer (*S*-1,2) was identified on the basis of signal intensity. Both (1,1) and (2,2) gave one set of signals each for symmetry reasons.

The C-1 substituted ligand in (1,2) isomers forms ring-*R* and ring-*S* configurations, which are resolved in NMR spectra. In both the isomers the titanium atom also becomes chiral, since its four ligands are different; however, these isomers are believed to be unresolvable. Of all the chiral isomers (1,1), only one is stable because the bent titanocene geometry strongly prefers the situation with non-substituted carbon atoms at the hinge positions. The achiral (2,2) isomer is the least abundant (8%) whereas the total of (1,2) isomers amounts to 71% and (1,1) to 21%; this roughly reflects the situation in the bent metallocene skeleton exposing to activation randomly C-1 and C-2 methyl groups.

The most interesting feature of the reaction is an unprecedented low temperature of 60°C at which the activation of the cyclopentadienyl methyl groups occurs. The activation of methyl group(s) of the permethylcyclopentadienyl ligand resulting in a hydrogen transfer on a leaving group is well understood. It occurs at the temperature of dissociation of the leaving group, e.g. the alkyl compounds $(C_5Me_5)_2TiR$ eliminate alkanes to give $(C_5Me_5)(C_5Me_4CH_2)Ti$ at temperatures from 90°C for $R = Me$ to 20°C for $R = n$-hexyl [13]. Also, the $(C_5Me_5)_2Ti(BTMSA)$ complex transfers two hydrogen atoms to the leaving BTMSA to give $(C_5Me_5)[C_5Me_3(CH_2)_2]Ti$ at 130°C; however, $(C_5HMe_4)_2Ti(BTMSA)$ requires 200°C and the thermolysis affords a different product of unknown composition [1a]. In the light of this behaviour of $(C_5HMe_4)_2Ti(BTMSA)$, we suggest that AA cooperates in the activation of the methyl groups. It may occur when AA is coordinated to Ti(II) by nitrogen atoms, which polarize its N=C bonds, and titanocene (Ti(II)) tends to lose protons in order to acquire more valence electrons. The titanium atoms in $(C_5HMe_4)_2Ti(AA)$ and $(C_5H_2Me_3)_2Ti(AA)$ complexes should have their Lewis acidity partly saturated by the electron-donating effect of the Me groups at the cyclopentadienyl ligands so that they do not rearrange so very fast into the asymmetric Ti(IV) complexes of type **A**. Instead, the AA ligand and the cyclopentadienyl rings are kept in a position that requires only a low activation energy for insertion of N=C into the C–H bond.

For $n = 5$, the red–brown paramagnetic $(\eta^5\text{-}C_5Me_5)_2Ti(N{=}CMe_2)$ (**C5**) was obtained as the main product. Its molecular structure was determined by X-ray diffraction analysis (vide infra), and the structure (Scheme 2) is fully compatible with the obtained spectroscopic data. The mass spectrum shows an abundant molecular ion and a basic peak of the fragment ion arising from the loss of $[HN{=}CMe_2]^{\bullet}$. The EPR spectrum of a solution of **C5** at $g = 1.9844$ shows a coupling of the unpaired d^1 electron with the nitrogen nucleus ($a_N = 2.7$ G) and a coupling to ^{49}Ti and ^{47}Ti nuclei ($a_{Ti} = 8.0$ G). In frozen toluene solution, the orthorhombic g-tensor is nearly isotropic, which is compatible with a narrow linewidth of the solution signals allowing us to establish the a_N coupling constant. Supposing that the anisotropy of the g-tensor is reversibly proportional to the magnitude of the Ti–N π-bonding [14], compound **C5** exerts a very strong interaction of this type. This is compatible with the occurrence of an absorption band in the NIR region at 1150 nm, assigned to a $1a_1 \rightarrow b_2$ transition [14]. The infrared spectrum of **C5** gives evidence of the N=C bond: a strong absorption band at 1690 cm^{-1} is close to the position of the $\nu(N{=}C)$ vibration in $(C_5Me_5)_2Ti(N{=}C(H)CMe_3)$ 1678 cm^{-1} [15], $(C_5Me_5)(C_2B_9H_{11})Ti(N{=}CMe_2)$ 1678 cm^{-1} [16], $(C_5H_5)_2Ti(NHCHPh_2)(N{=}CPh_2)$ 1647 cm^{-1} [6a], $(C_5H_5)_2Ti[N{\equiv}CR][N{=}C(Me)R]^+\ [BPh_4]^-$ (R = Me, Ph, *t*-Bu and *n*-Pr) and $(ind)_2Ti[N{\equiv}CR][N{=}C(Me)R]^+\ [BPh_4]^-$ (ind = $\eta^5\text{-}C_9H_7$; R = *t*-Bu or Ph) 1645–1662 cm^{-1} [17].

The formation of **C5** can be imagined in two ways as shown in Scheme 4. The cleavage of acetone azine in the intermediate complex $[(C_5Me_5)_2Ti(AA)]$ is either followed by a collision with another $(C_5Me_5)_2Ti(BTMSA)$ molecule producing two molecules of **C5** and leaving BTMSA, or one isopropylidene amide radical is expelled from the crowded intermediate complex, decaying in the solution. Neither of the mechanisms has been proven yet.



Scheme 4. Reaction pathways to **C5**.

3.1. Crystal structure of **B4**

The unit cell of **B4** contains three inequivalent molecules whose bond distances and angles do not differ more than three-fold from the estimated S.D.s. This is seen in Table 3 where minimum and maximum values of selected bond lengths and angles are listed, and for the sake of clarity are denoted by atoms in molecule 1 (Fig. 1). The intramolecular $\eta^5{:}\eta^1$ bonding of ligands does not induce a steric hindrance, at least for the cyclopentadienyl moieties. The deviations of the cyclopentadienyl ring atoms from least-squares planes are smaller than the errors in the determination of their coordinates and the carbon atoms of Me groups deviate only slightly from the least squares plane farther away from the Ti atom (maximum for C(131) and C(181) atoms 0.154–0.182 Å). The hydrogen-bearing carbon atoms of the cyclopentadienyl rings are close to hinge positions of irregularly staggered ligands. Correspondingly, the dihedral angle between the least-squares planes of the cyclopentadienyl rings ($\phi = 47.3$–$48.0°$) is only slightly smaller than in e.g. $(C_5HMe_4)_2Ti(BTMSA)$ complex (50.0°) [12]. The absence of any steric congestion is indicated by a nearly perpendicular dihedral angle between the planes defined by Ti and two N atoms, and Ti and two centroids (CE) of the cyclopentadienyl rings (87.2–87.6°). The Ti–CE distances are only marginally longer (ca. 0.01 Å) and the CE–Ti–CE angles are larger by only ca. 1–2° than those in $(C_5HMe_4)_2Ti(BTMSA)$ [12]. The Ti–N distances 1.961(4)–1.969(4) Å are slightly longer than in similar amide compounds $(C_5Me_5)_2TiN(H)Me$ (1.955(5) Å) [14] or $(C_5Me_5)_2TiNH_2$ (1.944(2) Å) [18] but shorter than in $(C_5Me_5)_2TiN(Ph)Me$ (2.054(2) Å) [19], $(C_5H_5)_2Ti(NHCHPh_2)(N{=}CPh_2)$ 1.980(3) Å [6a] or in the Ti(III) dimeric complex obtained from $(C_5H_5)_2Ti(BTMSA)$ and benzaldehyde azine (Scheme 1) (2.06(2) Å) [8a]. The other bonding distances in the bridging chain are not exceptional, corresponding to single bonds: d(N–C) 1.451(6)–1.469(6) Å, C_{Cp}–$C_{methylene}$ fall into the range of the C_{Cp}–C_{methyl} distances, and only the $C_{methylene}$–$C_{dimethylmethylene}$ distances 1.540(7)–1.564(7) Å are longer than the $C_{dimethylmethylene}$–C_{methyl} distances 1.490(7)–1.522 Å. The geometry of the bridging chain is also not unusual since the Ti–N–C angles 127.3(3)–129.7(3)° do not differ much from the 120° expected for an sp^2-hybridized nitrogen atom, the valence angles on the chain carbon atoms are close to tetrahedral, and the methylene carbon atoms deviate from the least-squares planes of the cyclopentadienyl rings by only 0.13–0.19 Å toward the titanium atom.

Table 3
Selected bond distances (Å) and angles (°) for compound **B4**[a]

Bond distances			
Ti(1)–N(11)	1.96(4)–1.965(4)	Ti(1)–N(12)	1.961(4)–1.969(4)
Ti(1)–CE(11)	2.100(5)–2.118(5)	Ti(1)–CE(12)	2.096(5)–2.118(5)
Ti(1)–C(11)	2.335(5)–2.361(5)	Ti(1)–C(12)	2.394(5)–2.421(5)
Ti(1)–C(13)	2.484(5)–2.502(5)	Ti(1)–C(14)	2.480(5)–2.491(5)
Ti(1)–C(15)	2.373(5)–2.391(5)	Ti(1)–C(16)	2.345(5)–2.359(5)
Ti(1)–C(17)	2.390(5)–2.407(5)	Ti(1)–C(18)	2.477(5)–2.499(5)
Ti(1)–C(19)	2.476(5)–2.497(5)	Ti(1)–C(110)	2.374(5)–2.404(5)
N(11)–C(122)	1.451(6)–1.459(6)	N(12)–C(172)	1.462(6)–1.469(6)
C(12)–C(121)	1.486(7)–1.506(7)	C(17)–C(171)	1.474(7)–1.496(7)
C(121)–C(122)	1.551(7)–1.562(7)	C(171)–C(172)	1.540(7)–1.564(7)
C(122)–C_{Me}	1.515(7)–1.536(7)	C(172)–C_{Me}	1.516(7)–1.543(7)
$(C–C)_{CE(1)}$	1.398(7)–1.435(7)	$(C–C)_{CE(2)}$	1.394(7)–1.414(7)
$(C_{Cp}–C_{Me})_{CE(1)}$	1.490(7)–1.522(7)	$(C_{Cp}–C_{Me})_{CE(2)}$	1.492(7)–1.515(7)
Bond and dihedral angles			
N(11)–Ti(1)–N(12)	106.2(2)–107.0(2)	CE(11)–Ti(1)–CE(12)	136.6(2)–137.2(2)
N(11)–Ti(1)–CE(11)	100.4(2)–100.7(2)	N(12)–Ti(1)–CE(12)	100.6(2)–101.3(2)
N(11)–Ti(1)–CE(12)	104.5(2)–105.2(2)	N(12)–Ti(1)–CE(11)	104.4(2)–104.6(2)
C(122)–N(11)–Ti(1)	129.5(3)–129.7(3)	Ti(1)–N(12)–C(172)	127.3(3)–129.6(3)
N(11)–C(122)–C(121)	106.0(4)–106.5(4)	N(12)–C(172)–C(171)	106.1(4)–106.7(4)
N(11)–C(122)–C_{Me}	109.6(4)–110.7(4)	N(12)–C(172)–C_{Me}	109.7(4)–111.2(4)
C(12)–C(121)–C(122)	111.4(4)–111.5(4)	C(17)–C(171)–C(172)	111.1(4)–111.2(4)
ϕ[b]	47.3–48.0	ω[c]	87.2–87.6

[a] Minimum and maximum values for three inequivalent molecules; atoms denoted for molecule 1 (see Fig. 1).

[b] Dihedral angle between least squares planes of the cyclopentadienyl rings.

[c] Dihedral angle between the planes defined by the Ti and two nitrogen atoms and the Ti and two centroids of cyclopentadienyl rings (CE).

*3.2. Crystal structure of **C5***

The molecule of **C5** is symmetrical with respect to the plane of symmetry containing CE(1), Ti, CE(2), N, C(7), C(11), C(41), etc. (see Fig. 2 and Table 4). The pentamethylcyclopentadienyl ligands are exactly staggered. The carbon atoms of their methyl groups deviate from least-squares planes of the cyclopentadienyl rings, and point away from the Ti atom. This declination is practically the same for C(11) (0.172 Å) pointing to the side of the isopropylidene amide ligand and for C(61) (0.162 Å). The largest declination is observed for C(41) (0.353 Å), which is directed to the top of the dihedral angle between the least-squares planes of the cyclopentadienyl rings (ϕ). This angle amounts to only 33.2(4)°, which is virtually identical with the so far lowest value found in $(C_5Me_5)_2TiF$ [14]. The isopropylidene amide ligand is colinear with the Ti–N bond within the precision of measurement (Ti–N–C(7) 179.7(5)°). The isopropylidene plane, however, is slightly inclined toward the C(11) methyl group (by 1.5°), indicating the absence of steric hindrance toward this methyl group. The amide isopropylidene ligand exerts a shorter Ti–N bond length (1.906(5) Å) than the methyl amide ligand in $(C_5Me_5)_2TiN(H)Me$ (d(Ti–N) 1.955(5) Å) [14] or the amide ligand in $(C_5Me_5)_2TiNH_2$ (1.944(2) Å [18]. It implies that strengthening of the Ti–N bonds which results from involvement of the nitrogen lone electron pair in bonding with $b_2(d_{xz})$ titanium orbital is further enhanced by the N=C bond, although the energy of the $1a_1 \rightarrow b_2$ transition is somewhat higher (8700 cm^{-1} (1150 nm) for **C5** versus 8180 cm^{-1}) for $(C_5Me_5)_2$-TiN(H)Me [14]. The N=C bond length in **C5** is 1.240(8) Å and the plane of the double bond, as indicated by the orientation of isopropylidene group, approximately bisects the angle ϕ. The comparison with the structurally closest compound $(C_5Me_5)(C_2B_9H_{11})Ti(N{=}CMe_2)$ (*d*(Ti–N) 1.85(1) Å, *d*(N=C) 1.27(2) Å) [16] which contains Ti(IV) shows that a higher Lewis acidity of the metal leads to a further shortening of the Ti–N bond but this is compensated by extension of the N=C bond. Similar figures were also obtained for other Ti(IV) alkylidene amido complexes: $(ind)_2Ti[N{\equiv}CPh][N{=}$

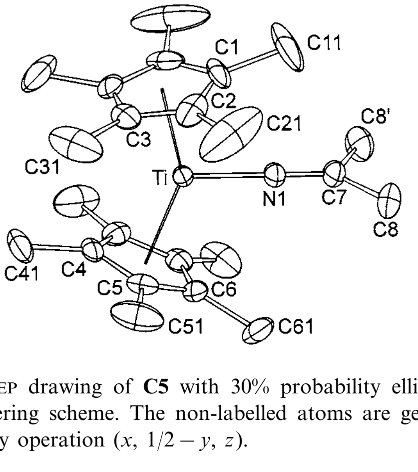


Fig. 2. ORTEP drawing of **C5** with 30% probability ellipsoids and atom numbering scheme. The non-labelled atoms are generated by the symmetry operation (x, $1/2-y$, z).

Table 4
Selected bond distances (Å) and angles for **C5** [a]

Bond distances			
Ti–N	1.906(5)	N–C(7)	1.240(8)
Ti–C(1)	2.353(7)	Ti–C(2)	2.349(5)
Ti–C(3)	2.391(5)	Ti–C(4)	2.381(7)
Ti–C(5)	2.372(5)	Ti–C(6)	2.393(4)
Ti–CE(1)	2.062(5)	Ti–CE(2)	2.069(5)
$(C–C)_{CE(1)}$(av.)	1.37(3)	$(C–C)_{CE(2)}$(av.)	1.39(2)
$(C_{Cp}–C_{Me})$(av.)	1.52(3)	C(7)–C(8)	1.523(6)
Bond and dihedral angles			
N–Ti–CE(1)	108.2(2)	N–Ti–CE(2)	106.2(2)
CE(1)–Ti–CE(2)	145.7(2)	Ti–N–C(7)	179.7(5)
N–C(7)–C(8)	123.4(3)	C(8)–C(7)–C(8′)	113.2(6)
ϕ [b]	33.2	ω [c]	15.2

[a] Symmetry transformation used to generate equivalent positions: x, $1/2-y$, z.

[b] ϕ, dihedral angle between the least squares planes of the cyclopentadienyl rings.

[c] ω, dihedral angle between the least squares plane of the CE(1) cyclopentadienyl ring and the plane defined by the C(7), C(8), and C(8′) atoms.

$C(Me)Ph]^+$ $[BPh_4]^-$ (d(Ti–N) 1.872(7) Å and d(N=C) 1.244(8) Å) [17b], $(C_5H_5)_2Ti(N{=}CPh_2)(NHCHPh_2)$ (d(Ti–N) 1.891(3) Å and d(N=C) 1.277(5) Å) [6a], $(C_5H_5)TiCl_2(N{=}C(n\text{-}Bu)(t\text{-}Bu)$ (1.872(4) Å and 1.267(6) Å) [20], and dimeric $[(C_5H_5)TiCl]_2[\mu\text{-}N{=}C(Bn)\text{-}C(Bn){=}N]_2$ (Bn = benzyl) (1.896(3) and 1.267(6) Å) [21]. On the basis of comparisons with structures of Ti(III) alkyl amide and Ti(IV) alkylidene amide compounds, we can assume that the isopropylidene amide ligand in **C5** is bonded in an allene-like mode (Ti=N=C) [22].

4. Conclusions

It has previously been well demonstrated that the mode of reactions between an in situ formed metallocene of an early transition metal and azines derived from an aldehyde or a ketone is controlled by the substituents at the azines [8,22,23]. Here we have reported examples showing that the reaction pathway of one particular azine strongly depends on the Lewis acidity of the central metal and that this acidity can be finely controlled by methyl substituents at the cyclopentadienyl ligands.

5. Supplementary material

Listings of atomic coordinates, bond lengths and angles and thermal parameters for **B4** and **C5** have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-135675 (**B4**), and CCDC-135674 (**C5**). Copies of the data can be obtained free of charge on application to CCDC, Union Road, Cambridge CD12 1EZ, UK (fax: +44-1223-336033; e-mail:deposit@ccdc.cam.ac.uk). These data, together with lists of observed and calculated structure factors and further details of the structure determination, are available from the authors.

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