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Journal of Organometallic Chemistry 640 (2001) 79–84

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Synthesis and structure of *ansa*-cyclopentadienyl pyrrolyl titanium complexes: $[(\eta^5\text{-}C_5H_4)CH_2(2\text{-}C_4H_3N)]Ti(NMe_2)_2$ and $[1,3\text{-}\{CH_2(2\text{-}C_4H_3N)\}_2(\eta^5\text{-}C_5H_3)]Ti(NMe_2)$

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Received 24 May 2001; received in revised form 24 July 2001; accepted 4 August 2001

Abstract

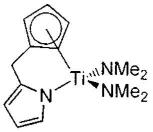
Reaction of *ansa*-cyclopentadienyl pyrrolyl ligand $(C_5H_5)CH_2(2\text{-}C_4H_3NH)$ (**2**) with $Ti(NMe_2)_4$ affords bis(dimethylamido)titanium complex $[(\eta^5\text{-}C_5H_4)CH_2(2\text{-}C_4H_3N)]Ti(NMe_2)_2$ (**3**) via amine elimination. A cyclopentadiene ligand with two pendant pyrrolyl arms, a mixture of 1,3- and 1,4-$\{CH_2(2\text{-}C_4H_3NH)\}_2C_5H_4$ (**4**), undergoes an analogous reaction with $Ti(NMe_2)_4$ to give $[1,3\text{-}\{CH_2(2\text{-}C_4H_3N)\}_2(\eta^5\text{-}C_5H_3)]Ti(NMe_2)$ (**5**). Molecular structures of **3** and **5** have been determined by single crystal X-ray diffraction studies. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Titanium; Cyclopentadienyl; Pyrrolyl; Crystal structures

1. Introduction

The *ansa*-monocyclopentadienyl-amido (CpA) titanium complexes, $[(\eta^5\text{-}C_5R'_4)SiMe_2(NR)]TiX_2$ ($X = Me$, Cl, NR_2; $R =$ alkyl, aryl), have received much attention as olefin polymerization catalysts [1]. In particular, they have shown remarkable activities for copolymerization of ethene with other olefins such as hexene, octene, and cyclic olefins due to the sterically open nature of the catalytic active site [1b,1c,1d]. Since initial introduction of an *ansa*-ligand, $(C_5Me_4H)SiMe_2(HN^tBu)$, by Bercaw and coworkers for scandium olefin polymerization catalysts [2], the ligand components of the CpA titanium catalysts have been systematically varied to achieve a desired catalytic behavior [3–8]. Thus far it appears that $[(\eta^5\text{-}C_5Me_4)SiMe_2(N^tBu)]TiCl_2$ is the best catalyst for ethene polymerization.

In previous work, we reported the synthesis and characterization of various CpA type titanium complexes with a hydrazido ligand such as $[(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^1\text{-}NNMe_2)]Ti(NMe_2)_2$ and $[(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^2\text{-}NNMe_2)]TiCl_2$, which involve η^1- and η^2-hydrazido moieties depending on the electronic nature of the titanium metal center [9]. As an extension of our studies in this area, we employed a CH_2-bridged pyrrolyl moiety as a donor group instead of the Me_2Si-bridged amido ligand in CpA titanium catalysts. Herein we describe the synthesis and structural characterization of *ansa*-cyclopentadienyl pyrrolyl titanium complexes $[(\eta^5\text{-}C_5H_4)CH_2(2\text{-}C_4H_3N)]Ti(NMe_2)_2$ (**3**) and $[1,3\text{-}\{CH_2(2\text{-}C_4H_3N)\}_2(\eta^5\text{-}C_5H_3)]Ti(NMe_2)$ (**5**), which are, to our knowledge, the first examples of CpA titanium complexes with a pyrrolyl donor ligand.



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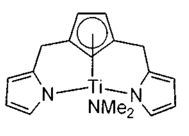

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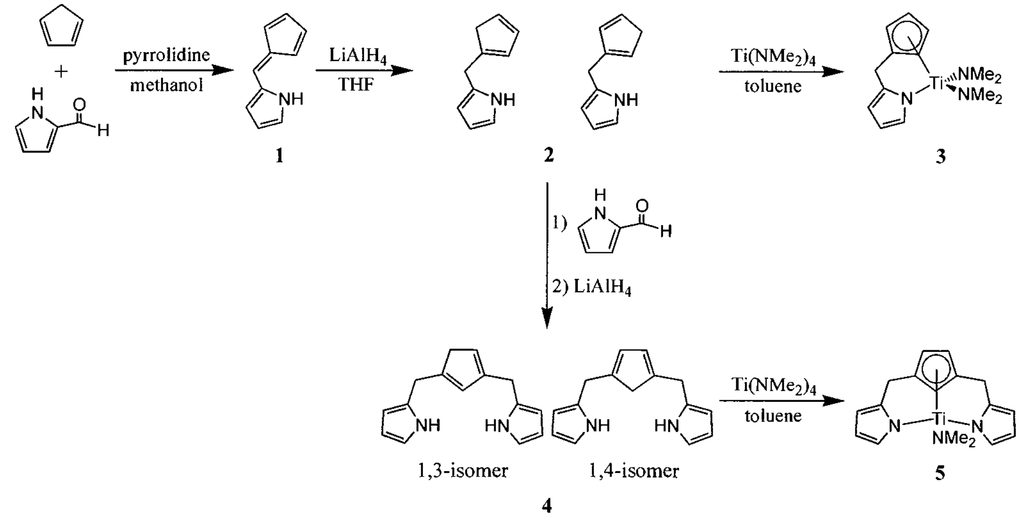
PII: S0022-328X(01)01187-1



Scheme 1.

2. Results and discussion

2.1. Preparation of 3 and 5

Overall synthetic procedures for the pyrrole-substituted *ansa*-ligands **2** and **4** and their metallation products **3** and **5** are summarized in Scheme 1. The reaction of cyclopentadiene (Cp) and pyrrole-2-carboxaldehyde in the presence of pyrrolidine produces pyrrole-substituted fulvene compound **1** (97%) as a red solid after purification by column chromatography. Pyrrolidine is known to be a very effective reagent to promote fulvene formation between cyclopentadiene and a variety of aldehydes and ketones [10]. Compound **1** is reduced by LiAlH$_4$ reagent to produce a methylene bridged *ansa*-ligand (C$_5$H$_4$)CH$_2$(2-C$_4$H$_3$NH) (**2**, 95%) as a colorless oil. ^{1}H-NMR spectrum indicates that **2** exists as two isomers (ca. 2.1:1) of the three possible isomers due to double bond migration in the Cp ring. Treatment of **2** with Ti(NMe$_2$)$_4$ at room temperature affords a bis(dimethylamido)titanium complex [(η^5-C$_5$H$_4$)CH$_2$(2-C$_4$H$_3$N)]Ti(NMe$_2$)$_2$ (**3**) in a high yield (86%) as an orange solid by the well-established amine elimination reaction [11].

In order to introduce two CH$_2$(2-C$_4$H$_3$NH) substituents in the cyclopentadienyl ring, analogous fulvene formation reaction of **2** with pyrrole-2-carboxaldehyde has been carried out. Purification of the crude product by column chromatography gives a broad orange band, which appears to contain a mixture of 1,2- (minor) and 1,3-disubstituted (major) fulvene-type cyclopentadiene compounds with respective *cis* and *trans* isomers based on ^{1}H-NMR spectroscopy. This preference for the formation of the 1,3-disubstituted product is likely to be due to steric reasons. The mixture of fulvene products is reduced with LiAlH$_4$ and purification by column chromatography gives a major yellow band, which comprises two inseparable isomers (1,3- and 1,4- = 1.4:1) of disubstituted cyclopentadiene, {CH$_2$(2-C$_4$H$_3$NH)}$_2$C$_5$H$_4$ (**4**, 39%). The reaction of **4** with Ti(NMe$_2$)$_4$ gives a dimethylamidotitanium complex [1,3-{CH$_2$(2-C$_4$H$_3$N)}$_2$(η^5-C$_5$H$_3$)]Ti(NMe$_2$) (**5**, 78%) as a red solid after recrystallization in dichloromethane.

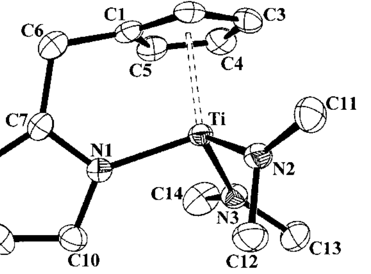


Fig. 1. Molecular structure and atomic labeling scheme of **3**. Thermal ellipsoids are drawn at 30% probability level.

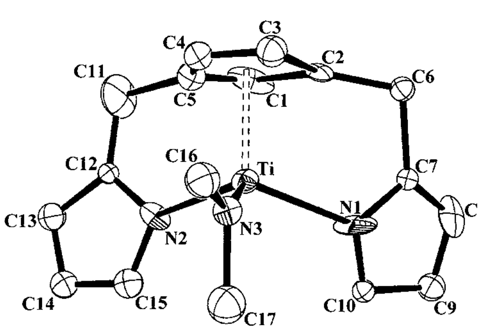


Fig. 2. Molecular structure and atomic labeling scheme of **5**. Thermal ellipsoids are drawn at 30% probability level.

Table 1
Selected bond lengths (Å) and angles (°) with estimated S.D. values for $[(\eta^5\text{-}C_5H_4)CH_2(2\text{-}C_4H_3N)]Ti(NMe_2)_2$ (**3**)

Bond lengths			
Ti–N(1)	2.04(1)	Ti–C(3)	2.35(1)
Ti–N(2)	1.89(1)	Ti–C(4)	2.35(1)
Ti–N(3)	1.90(1)	Ti–C(5)	2.36(1)
Ti–C(1)	2.38(1)	Ti–Cp(Cen [a])	2.04
Ti–C(2)	2.39(1)		
Bond angles			
Cp(Cen)–Ti–N(1)	103	N(2)–Ti–N(3)	103(1)
Cp(Cen)–Ti–N(2)	114	C(1)–C(6)–C(7)	110(1)
Cp(Cen)–Ti–N(3)	124	C(6)–C(7)–N(1)	118(1)
N(1)–Ti–N(2)	108(1)	C(7)–N(1)–Ti	124(1)
N(1)–Ti–N(3)	102(1)		

[a] Cen = ring centroid.

2.2. Crystal structure of **3** and **5**

The overall molecular geometry and the atomic labeling schemes of **3** and **5** are illustrated in Figs. 1 and 2, respectively. Selected bond lengths and angles of **3** and **5** are presented in Tables 1 and 2.

The structure of **3** (see Fig. 1) exhibits a distorted tetrahedral geometry consisting of a bifunctional cyclopentadienyl–pyrrolyl ligand and two terminal dimethylamido groups. General structural features of **3** are similar to those previously reported for $[(\eta^5\text{-}C_5H_4)SiMe_2(N^tBu)]Ti(NMe_2)_2$ [12] and $[(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^1\text{-}NNMe_2)]Ti(NMe_2)_2$ [9]. Complex **3** has a pseudo-C_s symmetry with a mirror plane including the pyrrolyl ring, C(1), C(6), and Ti atoms, and bisecting the $Me_2N\text{–}Ti\text{–}NMe_2$ angle and the Cp ring. The short Ti–N(2) and Ti–N(3) bond lengths (1.89(1) and 1.90(1) Å) and the planar geometry of the N(2) and N(3) nitrogen atoms indicate sp^2 hybridization of the two nitrogen atoms with the out-of-plane lone pairs, giving an $N(p\pi) \rightarrow M(d\pi)$ interactions. The Ti–N(1) bond length (2.04(1) Å) is comparable to that for bis(pyrrolyl-2-aldiminato)titanium complex (av. 2.038(2)) [13] and slightly longer than those for other titaniumdiamido complexes such as $[(\eta^5\text{-}C_5H_4)SiMe_2(N^tBu)]Ti(NMe_2)_2$ (1.972(4) Å) [12] and $[(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^1\text{-}NNMe_2)]Ti(NMe_2)_2$ (1.977(7) Å) [9]. The long Ti–N(1) bond and the aromatic character of the pyrrolyl group imply that the N(1) atom donates one electron to the titanium center. Complex **3**, therefore, can be considered to be a 16-electron species. The Cp(centroid)–Ti–N(1) angle (103°) of **3** is smaller than that (105.5°) of $[(\eta^5\text{-}C_5H_4)SiMe_2(N^tBu)]Ti(NMe_2)_2$ [12].

The coordination geometry of **5** around the titanium atom is pseudo-tetrahedral with two sites being occupied by pyrrolyl nitrogen atoms and the remaining sites by a η^5-cyclopentadienyl and a dimethylamido ligands. Complex **5** also has a pseudo-C_s symmetry with a mirror plane including the Ti, N(3), C(16), and C(17) atoms, and bisecting the Cp ring. The crystallographic

Table 2
Selected bond lengths (Å) and angles (°) with estimated S.D. values for five inequivalent molecules of $[1,3\text{-}\{CH_2(2\text{-}C_4H_3N)\}_2(\eta^5\text{-}C_5H_3)]Ti(NMe_2)$ (**5**)

	5-A	**5**-B	**5**-C	**5**-D	**5**-E
Bond lengths					
Ti–N(1)	2.16(3)	1.91(3)	2.04(2)	1.82(2)	2.02(2)
Ti–N(2)	2.07(3)	2.05(2)	2.13(2)	1.95(2)	2.04(2)
Ti–N(3)	1.89(2)	1.89(2)	1.83(2)	1.79(2)	1.88(2)
Ti–C(1)	2.36(2)	2.37(3)	2.34(3)	2.34(3)	2.26(3)
Ti–C(2)	2.37(3)	2.32(3)	2.37(2)	2.32(3)	2.39(2)
Ti–C(3)	2.31(3)	2.28(3)	2.27(3)	2.33(2)	2.36(2)
Ti–C(4)	2.20(3)	2.31(2)	2.40(3)	2.37(3)	2.27(2)
Ti–C(5)	2.33(3)	2.21(3)	2.32(3)	2.34(3)	2.29(2)
Ti–Cp(Cen [a])	1.99	1.96	2.01	2.01	1.99
Bond angles					
Cp(Cen)–Ti–N(1)	108	106	106	106	103
Cp(Cen)–Ti–N(2)	103	105	106	107	103
Cp(Cen)–Ti–N(3)	113	114	117	118	119
N(1)–Ti–N(2)	114(1)	117(1)	114(1)	111(1)	111(1)
N(1)–Ti–N(3)	109(1)	109(1)	111(1)	108(1)	106(1)
N(2)–Ti–N(3)	108(1)	106(1)	107(1)	109(1)	112(1)
C(2)–C(6)–C(7)	110(2)	111(2)	113(3)	117(2)	115(2)
C(6)–C(7)–N(1)	116(2)	103(4)	116(3)	107(2)	114(2)
C(7)–N(1)–Ti	118(2)	133(2)	124(2)	130(2)	122(2)
C(5)–C(11)–C(12)	113(3)	99(2)	104(2)	106(2)	97(2)
C(11)–C(12)–N(2)	117(3)	126(3)	125(2)	117(3)	138(3)
C(12)–N(2)–Ti	123(2)	121(2)	119(2)	122(2)	114(2)

[a] Cen = ring centroid.

asymmetric unit contains five equivalent molecules (**5**-A, **5**-B, **5**-C, **5**-D and **5**-E), which slightly differ from one another in bond lengths and angles. The average bond lengths of Ti–N(pyrrolyl), Ti–N(3) and Ti–Cp(centroid) are 2.02(2), 1.86(2) and 1.99 Å, respectively, and the average bond angle of Cp(centroid)–Ti–N(pyrrolyl) is 105°. All other bond lengths and angles are within the expected ranges.

3. Experimental

3.1. General comments

All reactions were carried out under an inert atmosphere of Ar by using either standard Schlenk or drybox techniques. Tetrahydrofuran (THF) and toluene were distilled from Na/K alloy under N_2 atmosphere. CH_2Cl_2 was refluxed over CaH_2 and then distilled under N_2 atmosphere.

$Ti(NMe_2)_4$ purchased from Strem was used without further purification. Pyrrolidine (Aldrich) was freshly distilled under nitrogen before use. Silica gel (Merck, 230–400 mesh) was used for column chromatography. ^1H- (400 MHz) and ^{13}C- (100 MHz) NMR spectra were recorded on a Bruker AVANCE-400 spectrometer. Mass spectra (EI) were obtained by the staff of the Korea Basic Science Center using a JEOL JMS-SX-102A mass spectrometer, and all m/z values are referenced to ^{48}Ti. Elemental analyses were provided by the staff of the Energy and Environment Research Center at KAIST.

3.2. Preparation of $(C_5H_4)CH(2\text{-}C_4H_3NH)$ (1)

To a methanol solution (40 ml) of pyrrole-2-carboxaldehyde (3.97 g, 41.8 mmol) and cyclopentadiene (6.90 g, 104.4 mmol) was added pyrrolidine (5.94 g, 83.5 mmol) at 0 °C. The reaction mixture was stirred for 90 min at room temperature (r.t.). Glacial AcOH (5.02 g, 83.5 mmol) was added to the red solution at 0 °C to quench the reaction. The reaction mixture was diluted with ether (50 ml) and water (50 ml). The aqueous portion was extracted with ether (4 × 50 ml). The combined organic portion was washed with water and brine, then dried over anhydrous $MgSO_4$, filtered, and evaporated under reduced pressure. Purification by column chromatography (EtOAc–hexane = 1/8) afforded **1** (5.80 g, 40.5 mmol, 97%) as a red solid. ^1H-NMR ($CDCl_3$, 25 °C): δ 8.62 (br s, 1H, NH), 6.67 (s, 1H, –CH–), 7.02–6.60 (m, 3H, C_4H_3NH), 6.62–6.28 (m, 4H, C_5H_4).

3.3. Preparation of $(C_5H_5)CH_2(2\text{-}C_4H_3NH)$ (2)

A THF solution of $LiAlH_4$ (1.0 M, 40.5 ml, 40.5 mmol) was added to a THF solution (200 ml) of **1** (5.80 g, 40.5 mmol) at 0 °C. The reaction mixture was heated at 40 °C for 10 h and quenched with water. The aqueous layer was extracted with Et_2O (4 × 50 ml). The combined organic layer was washed with water and brine, dried over anhydrous $MgSO_4$, filtered, and evaporated under vacuum. After purification by column chromatography (EtOAc–hexane = 1/8), a colorless oil of **2** (5.59 g, 38.5 mmol, 95%) was obtained as a ca. 2:1 mixture of 1,3- and 1,2-isomers. ^1H-NMR ($CDCl_3$, 25 °C): C_5H_5-olefinic, C_4H_3NH, and NH protons could not be exactly assigned to each isomer: δ 7.88 (br s, NH), 6.67–5.96 (m, C_4H_3NH and C_5H_5-olefinic). 1,2-isomer: δ 3.71 (s, 2H, –CH_2–), 3.00 (m, 2H, C_5H_5-aliphatic). 1,3-isomer: δ 3.75 (s, 2H, –CH_2–), 2.89 (m, 2H, C_5H_5-aliphatic).

3.4. Preparation of $[(\eta^5\text{-}C_5H_4)CH_2(2\text{-}C_4H_3N)]Ti(NMe_2)_2$ (3)

A toluene solution (10 ml) of **2** (0.36 g, 2.49 mmol) was added to a toluene solution (10 ml) of $Ti(NMe_2)_4$ (0.56 g, 2.49 mmol) at 0 °C. The reaction mixture was warmed to r.t. and stirred for 3 h. Evaporation of the solvent and recrystallization in CH_2Cl_2 at −20 °C gave **3** (0.60 g, 2.14 mmol, 86%) as orange crystals. ^1H-NMR ($CDCl_3$, 25 °C): δ 6.90 (m, 1H, C_4H_3N), 6.05 (m, 1H, C_4H_3N), 5.85 (m, 1H, C_4H_3N), 6.19 (m, 2H, C_5H_4), 6.12 (m, 2H, C_5H_4), 3.86 (s, 2H, –CH_2–), 3.21 (s, 12H, $(NMe_2)_2$). MS (70 eV): m/z 279 [M^+]. Anal. Found: C, 60.08; H, 7.63; N, 15.28. Calc. for $C_{14}H_{21}N_3Ti$: C, 60.22; H, 7.58; N, 15.05%.

3.5. Preparation of 1,3- and 1,4-$\{CH_2(2\text{-}C_4H_3NH)\}_2C_5H_4$ (4)

To a MeOH solution (15 ml) of pyrrole-2-carboxaldehyde (1.02 g, 10.7 mmol) and **2** (3.10 g, 21.4 mmol) was added pyrrolidine (1.52 g, 21.4 mmol) at r.t. The reaction mixture was stirred for 3 h. Glacial AcOH (1.28 g, 21.4 mmol) was added to the red solution at 0 °C. The reaction mixture was diluted with ether (30 ml) and water (30 ml). The aqueous portion was extracted with Et_2O (4 × 30 ml) and the combined organic portion was washed with water and brine, dried over anhydrous $MgSO_4$, filtered and evaporated under reduced pressure. Purification by column chromatography (EtOAc–hexane = 1/5) afforded a ca. 1:4 mixture of 1,2- (minor) and 1,3-disubstituted (major) fulvene-type cyclopentadiene compounds (1.17 g, 5.26 mmol, 49%) with respective *cis* and *trans* isomers. To a THF solution (40 ml) of this mixture of fulvene compounds (1.17 g, 5.26 mmol) was added a THF solution of $LiAlH_4$ (1.0 M, 5.26 ml, 5.26 mmol) at 0 °C. The reaction mixture was heated at 40 °C for 10 h and quenched with water. The aqueous layer was extracted

Table 3
Crystallographic data for **3** and **5**

	3	**5**
Empirical formula	$C_{14}H_{21}N_3Ti$	$C_{17}H_{19}N_3Ti$
Formula weight	279.24	313.25
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	7.873(2)	10.346(1)
b (Å)	20.803(4)	11.197(1)
c (Å)	9.241(2)	35.472(5)
α (°)	90	84.21(1)
β (°)	108.65(2)	82.79(1)
γ (°)	90	66.49(1)
V (Å^3)	1434.0(5)	3732.2(8)
Z	4	10 [a]
T (K)	293(2)	293(2)
D_{calc} (g cm^{-3})	1.293	1.394
Crystal size (mm)	$0.56\times0.30\times0.10$	$0.58\times0.54\times0.52$
Radiation	Mo–K$_\alpha$	Mo–K$_\alpha$
λ (Å)	0.7107	0.7107
μ (mm^{-1})	0.581	0.567
Number of unique reflections	2631	15 552
Number of observed reflections ($I>2\sigma(I)$)	1983 ($R_{int}=0.0249$)	13 160 ($R_{int}=0.1067$)
Index ranges	$-8\le h\le 1$, $-1\le k\le 22$, $-9\le l\le 10$	$-1\le h\le 12$, $-12\le k\le 13$, $-42\le l\le 42$
R [b]	0.0363	0.0930
R_w [c]	0.0801	0.2432
Goodness-of-fit [d]	1.025	0.887

[a] An asymmetric unit contains five molecules (A, B, C, D and E).

[b] $R=(\Sigma\|F_o|-|F_c\|)/\Sigma|F_o|$.

[c] $R_w=[\{\Sigma\omega(|F_o|-|F_c|)^2\}/\Sigma\omega|F_o|^2]^{1/2}$.

[d] Goodness-of-fit $=[\{S\omega(|F_o|-|F_c|)^2\}/(N_{observns}-N_{params})]^{1/2}$.

with Et_2O (4 × 30 ml). The combined organic layer was washed with water and brine, dried over anhydrous $MgSO_4$, filtered, and evaporated under reduced pressure. After purification by column chromatography (EtOAc–hexane = 1/4), a pale yellow oil of **4** (0.46 g, 2.05 mmol, 19% based on pyrrole-2-carboxaldehyde) was obtained as a ca. 1.4:1 mixture of 1,3- and 1,4-isomers. ^{1}H-NMR ($CDCl_3$, 25 °C): C_5H_4-olefinic, C_4H_3NH and NH protons could not be exactly assigned to each isomer: δ 7.86 (br s, NH), 6.65–5.91 (m, C_4H_3NH and C_5H_4-olefinic). 1,3-isomer: δ 3.68 (s, 2H, –CH_2–), 3.62 (s, 2H, –CH_2–), 2.89 (m, 2H, C_5H_4-aliphatic). 1,4-isomer: δ 3.64 (s, 4H, –CH_2–), 2.79 (s, 2H, C_5H_4-aliphatic).

3.6. Preparation of [1,3-{$CH_2(2\text{-}C_4H_3N)$}$_2$(η^5-C_5H_3)]Ti(NMe_2) (5)

The reaction of **4** (0.46 g, 2.05 mmol) and $Ti(NMe_2)_4$ (0.46 g, 2.05 mmol) was carried out following a procedure similar to that for **3**. Recrystallization in CH_2Cl_2 gave **5** (0.50 g, 1.60 mmol, 78%) as red crystals. ^{1}H-NMR ($CDCl_3$, 25 °C) δ 7.04 (m, 2H, C_4H_3N), 6.60 (t, 1H, $J=2.35$ Hz, C_5H_3), 6.29 (d, 2H, $J=2.36$ Hz, C_5H_3), 6.00 (m, 2H, C_4H_3N), 5.90 (m, 2H, C_4H_3N), 4.05 (d, 2H, $J=16.0$ Hz, –CH_2–), 3.91 (d, 2H, $J=16.0$ Hz, –CH_2–), 3.30 (s, 6H, NMe_2). MS (70 eV): m/z 313 [M$^+$]. Anal. Found: C, 65.15; H, 6.03; N, 13.39. Calc. for $C_{17}H_{19}N_3Ti$: C, 65.19; H, 6.11; N, 13.42%.

3.7. X-ray data collection and structure determination

Data crystals of **3** and **5** suitable for X-ray structure determination were obtained by slow crystallization in CH_2Cl_2 at −20 °C. The determination of the unit cell parameters and the orientation matrix and the collection of intensity data were made on an Enraf–Nonius CAD-4 diffractometer, employing graphite-monochromated Mo–K$_\alpha$ radiation. Lorentz and polarization corrections were applied to the intensity data. A semi-empirical absorption correction was applied to both **3** and **5**. Relevant crystallographic data are summarized in Table 3. All calculations were performed using the SHELXTL system of computer programs [14]. Scattering factors for all atoms were included in the software package. The structure of **3** was solved using direct method. The position of titanium atom of **5** was obtained from a Patterson map and those of the C and N atoms were taken from difference Fourier maps. Full-matrix least-squares refinement based on F^2 was carried out with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms were placed in calculated positions.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 157424 and 157425 for compounds **3** and **5**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was supported by the Brain Korea 21 Project.

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