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Seven-coordinated tantalum trichloride complex containing substituted pyrrolyl ligand: synthesis and characterization of $[NC_4H_3(CH_2NMe_2)\text{-}2]_2TaCl_3$

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Abstract

bis[2-(Dimethylaminomethyl)pyrrolyl]tantalum chloride (**1**) was prepared by treatment of the $TaCl_5$ with 2 equiv. of [2-(dimethylaminomethyl)pyrrolyl]lithium. The solid state structure of **1** shows the seven-coordinated tantalum atom, with a geometry corresponding to a pentagonal bipyramidal structure, in which two chlorine atoms occupy the axial position with the angle of 174.8(2)°. Furthermore, variable-temperature ^1H NMR spectra infer the fluxionality of the two chelating pyrrolyl ligands with an estimated energy barrier of 13.8 kcal mol^{-1}. Compound **1** shows no catalytic activity toward ethylene polymerization even activated with MAO.

Keywords: Pyrrolyl; Tantalum chloride; Polymerization

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1. Introduction

Early transition metal complexes have long been interested in their Lewis acidity, of which ancillary ligands are able to fine tune their electronic and steric properties [1]. Recent development of metallocene chemistry for the olefin polymerization is focused on the bis-cyclopentadienyl or mono-cyclopentadienyl ligand systems in cooperating with the metals of Group 4 and 5 [2]. The new types of olefin polymerization catalysts beyond metallocene have been reviewed recently by Gibson et al. [3], where alkoxide [4] and amido [5] ligands, monoanionic bidentate and tridentate aryl amine ligands [6] have been included. 2-(Dimethylaminomethyl) pyrrole [7] has been synthesized in 1947 but only very few examples of complexes containing the bi- and tri-dentate substituted pyrrolyl ligands were reported [8]. In continuing our studies of synthesizing substituted pyrrolyl metal complexes [9], here we report the results of synthesis, characterization, and reactivity of new tantalum complexes containing 2-(dimethylaminomethyl) pyrrole.

2. Results and discussion

The reaction of $TaCl_5$ with 2 equiv. of $Li[NC_4H_3(CH_2NMe_2)\text{-}2]$ in diethyl ether at −78 °C afforded a seven-coordinated tantalum trichloride complex $[NC_4H_3(CH_2NMe_2)\text{-}2]_2TaCl_3$ (**1**) in 83% yield (Scheme 1).

The reaction of $TaCl_5$ with 1 or 3 equiv. of $Li[NC_4H_3(CH_2NMe_2)\text{-}2]$ gives a mixture of unidentified products. ^1H NMR spectrum of complex **1** in $CDCl_3$ at room temperature shows two sharp multiplets for the pyrrolyl protons at δ 6.68 and 5.86. However, two very broad peaks were observed at δ 4.27 and 3.10, corresponding to the resonances of the methylene and

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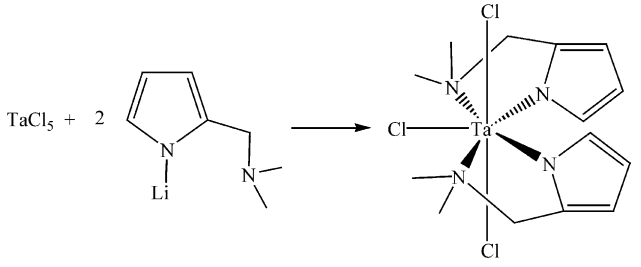

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Scheme 1.

methyl group of CH_2NMe_2, respectively. As expected, complex **1** exhibits similar spectral feature of the ligand in the ^{13}C NMR spectrum at room temperature. However, the methyl group of CH_2NMe_2 is too broad to obtain J_{CH} coupling constant from ^{13}C NMR gated-decoupling experiment. A variable temperature ^1H NMR spectra of complex **1** were recorded between −60 and 50 °C in $CDCl_3$ at 200 MHz NMR spectrometer (Fig. 1). At lower temperature, the methylene and methyl protons of CH_2NMe_2 split into two doublets at δ 4.5 and 4.0 and two singlets at δ 3.5 and 2.7, respectively. On raising the temperature to 300 K, the methylene and methyl resonances coalesce to two broad peaks, and eventually grow into two sharp peaks at δ 4.0 and 2.9, respectively. The phenomena could be resulted from the fluxionation of the two substituted-pyrrolyl ligands, as shown in Scheme 2, and the activation energy is estimated at approximately 13.8 kcal mol^{-1} [10]. However, we are unable to eliminate the possibility of the fluxionality caused by the seven to six-coordinate conversion by dissociation of one NMe_2 from complex **1** in solution.

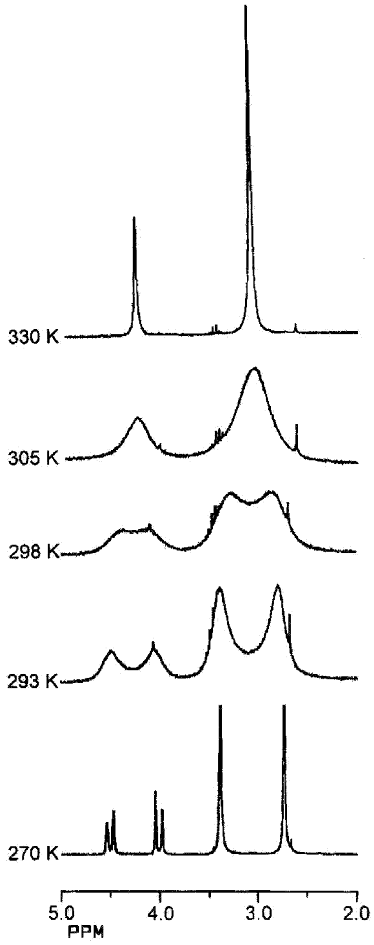
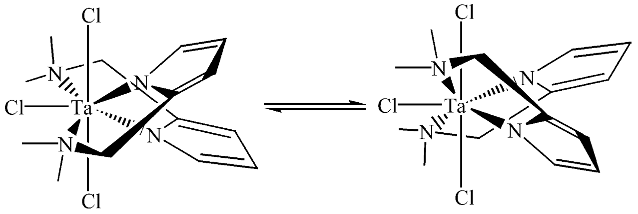


Fig. 1. The variable temperature ^1H NMR spectra of complex **1** in $CDCl_3$ at 200 MHz NMR spectrometer.

Crystals for X-ray diffraction analysis were obtained from a diethyl ether solution of complex **1** at −20 °C. The X-ray crystallographic data are summarized in Table 1 and selected bond distances and angles are listed in Table 2. An ORTEP drawing is depicted in Fig. 2. The solid state structure of **1** contains a seven-coordinate tantalum atom, with a geometry corresponding to a distorted pentagonal bipyramidal structure. Two chlorine atoms occupy the axial positions with Cl(2)–Ta–Cl(3) angle of 174.8(2)° while the four nitrogen atoms of the two substituted pyrrolyl ligands and one chlorine atom compose the pentagonal plane. However, while viewing the structure of **1** along the Ta–Cl(1) axis and placing the Cl(3)–Ta–Cl(1) as a perpendicular axis, the two nitrogen atoms of pyrrolyl are placing on the opposite site of the pentagonal plane with the bond angles of Cl(2)–Ta–N(1) and Cl(2)–Ta–N(3) at 97.8(5) and 83.1(5)°, respectively, and for the two dimethyl amino nitrogen atoms, bond angles of Cl(2)–Ta–N(2) and Cl(2)–Ta–N(4) are 80.1(4) and 102.5(4)°, respectively (Scheme 3).

The bond distances of the equatorial and axial Ta–Cl are in the range of 2.36–2.38 Å, which are comparable with the Ta–Cl bond distances reported in the literature [11,12]. As expected, bond lengths of coordinated Ta–N(dimethylamino) (2.48(2) and 2.4(2) Å) are much longer than those of σ-bonded Ta–N(pyrrolyl) (2.06(2) and 2.04(2) Å). To our knowledge, complex **1** is the first tantalum complex containing a bidentate η^1-pyrrolyl ligand characterized structurally.

A series of metathesis reactions have been carried out in order to synthesize tantalum alkyl or tantalum hydride complexes; unfortunately, the reactions of complex **1** with RMgBr (R = Ph, Me, ^tBu), RLi (R = AlH_4, H, Me, ^nBu, NEt_2), or RNa (R = OMe, N_3) result in inseparable mixture of products. Presumably, the two



Scheme 2.

Table 1
Crystallographic data for complex **1**

Empirical formula	$C_{16}H_{27}Cl_3N_4O_{0.5}Ta$
Formula weight	570.72
Temperature (K)	295(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	8.256(2)
b (Å)	15.098(3)
c (Å)	16.737(3)
β (°)	98.84(2)
V (Å^3)	2061.4(7)
Z	4
D_{calc} (Mg m^{-3})	1.839
Absorption coefficient (mm^{-1})	5.730
F(000)	1116
Crystal size (mm)	0.50 × 0.50 × 0.20
θ Range (°)	1.83–25.00
Reflections collected	3628
Independent reflections	3628 ($R_{int} = 0.0000$)
Absorption correction	semi-empirical from psi-scans
Max/min transmission	0.3581, 0.2472
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	3628/2/213
Goodness-of-fit on F^2	1.061
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0876$, $wR_2 = 0.2180$
R indices (all data)	$R_1 = 0.1617$, $wR_2 = 0.2478$
Extinction coefficient	0.0004(4)
Largest difference peak and hole (e Å^{-3})	4.528 and −5.294

2-(dimethylaminomethyl)pyrrolyl ligands donate electrons toward the tantalum metal decreasing the nucleophilicity of the metal center.

The polymerization reactions catalyzed by complex **1**, activated by MAO and $Al(^{i}Bu)_3$, have been investigated under ethylene (150 psi) and propylene (90 psi) pressure. Surprisingly, no detectable activity was observed for the olefin polymerization reactions. A similar complex, bis(benzylaminopyridinato)trichlorotantalum, published by K. Hakala and M. Polamo et al. shows good activity toward the ethylene polymerization [13]. The reaction procedure and conditions were listed in the supporting information.

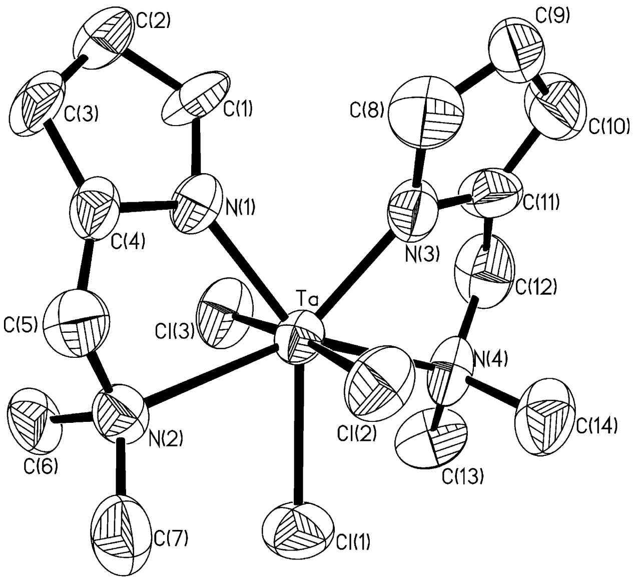
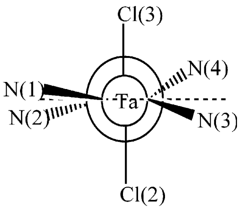


Fig. 2. The ORTEP drawing of complex **1**. The thermal ellipsoids were drawn at the 50% probability level. The hydrogen atoms were omitted for clarity.



Scheme 3.

Table 2
Selected bond distances (Å) and angles (°) for complex **1**

Bond distances					
Ta–N(3)	2.04(2)	Ta–N(1)	2.06(2)	Ta–Cl(3)	2.367(5)
Ta–Cl(2)	2.375(5)	Ta–Cl(1)	2.383(6)	Ta–N(4)	2.46(2)
Ta–N(2)	2.48(2)				
Bond angles					
N(3)–Ta–N(1)	79.3(7)	N(3)–Ta–Cl(3)	102.0(5)		
N(1)–Ta–Cl(3)	84.0(5)	N(3)–Ta–Cl(2)	83.1(5)		
N(1)–Ta–Cl(2)	97.8(5)	Cl(3)–Ta–Cl(2)	174.8(2)		
N(3)–Ta–Cl(1)	138.2(5)	N(1)–Ta–Cl(1)	142.4(5)		
Cl(3)–Ta–Cl(1)	88.7(2)	Cl(2)–Ta–Cl(1)	86.9(2)		
N(3)–Ta–N(4)	68.4(6)	N(1)–Ta–N(4)	139.0(7)		
Cl(3)–Ta–N(4)	79.0(4)	Cl(2)–Ta–N(4)	102.5(4)		
Cl(1)–Ta–N(4)	74.4(5)	N(3)–Ta–N(1)	142.8(6)		
N(1)–Ta–N(2)	70.5(6)	Cl(3)–Ta–N(2)	96.0(4)		
N(4)–Ta–N(2)	147.9(6)				

3. Experimental

All the reactions were performed using standard Schlenk techniques in an atmosphere of high purity nitrogen or in glove box. Ethyl ether was dried over Na–benzophenone ketyl and distilled before use. Methylene chloride was dried over P_2O_5 and distilled prior to use. 2,5-bis(dimethylaminomethyl)pyrrole [7] was prepared according to published literature and corresponding lithium salt was prepared by reacting ^{n}BuLi with the substituted pyrrole ligand. $CDCl_3$ was degassed by using freeze-and-thaw method and dried over 4 Å molecular sieves. ^{1}H and ^{13}C NMR spectra were collected on a Bruker AC200 and elemental analysis was performed on Perkin–Elmer CHN-2400.

3.1. Preparation of $[NC_4H_3(CH_2NMe_2)\text{-}2]_2TaCl_3$ (**1**)

Tantalum chloride (5.0 g, 13.9 mmol) was suspended in 20 ml diethyl ether and cooled to −78 °C. To this suspension was added a solution of $[NC_4H_3(CH_2NMe_2)\text{-}2]Li$ (3.63 g, 28.0 mmol) in 20 ml diethyl ether over a period of 30 min. The reaction mixture was allowed to warm to room temperature (r.t.) and stirred for 12 h. The suspension was filtered through Celite and washed with 15 ml methylene chloride in three times. The combined filtrate was reduced, and recrystallized at −20 °C. Dark crystals were isolated in 83% yield (6.27 g). ^{1}H NMR ($CDCl_3$, r.t.): δ 6.68 (m, 1H, NC_4H_3), 5.86 (m, 2H, NC_4H_3), 4.27 (br, s, 2H, CH_2NMe_2), 3.10 (br, d, 6H, NMe_2). ^{13}C NMR ($CDCl_3$, r.t.): δ 140.5 (s, C_{ipso}, pyrrolyl), 136.5 (d, $J_{CH} = 189$ Hz, CH of pyrrolyl), 111.8 (d, $J_{CH} = 170$ Hz, CH of pyrrolyl), 103.7 (d, $J_{CH} = 169$ Hz, CH of pyrrolyl), 62.4 (t, $J_{CH} = 141$ Hz, CH_2NMe_2), 51.5 (br, CH_2NMe_2). *Anal.* Calc. for $C_{14}H_{22}N_4Cl_3Ta \cdot 0.5Et_2O$: C, 33.67; H, 4.77; N, 9.82. Found: C, 33.14; H, 4.60; N, 10.82%.

3.2. X-ray structure determination of complex **1**

The crystals of $\mathbf{1} \cdot 0.5OEt_2$ were mounted on glass fibers using epoxy resin and transferred to a goniostat. Data were collected on a Nonius CAD4 four-circle diffractometer with graphite-monochromated Mo Kα radiation. A π-scan empirical absorption was applied. Using SHELXTL program on PC computer made the structure analysis. Structure was solved using the direct method and refined by full-matrix least-squares on F^2 values. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed at calculated positions and refined using a riding mode. The crystal data are summarized in Table 1.

4. Supplementary material

Tables of crystallographic data for complex **1** and the olefin polymerization conditions and results (nine pages) are available from the authors on request. The crystallographic data can also be obtained at the Cambridge Structure Database.

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