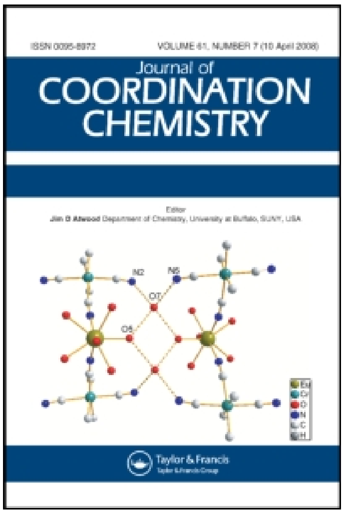

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Xu, Tieqi , Gao, Wei , Mu, Ying and Ye, Ling(2007) 'Synthesis and characterization of a novel η²-iminoacyl monocyclopentadienyl titanium(IV) complex', Journal of Coordination Chemistry, 60: 23, 2533 — 2539, First published on: 22 September 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958970701282580

URL: http://dx.doi.org/10.1080/00958970701282580

Journal of Coordination Chemistry
Vol. 60, No. 23, 1 December 2007, 2533–2539

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Synthesis and characterization of a novel η^2-iminoacyl monocyclopentadienyl titanium(IV) complex

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(*Received 21 December 2006; in final form 5 February 2007*)

An unusual complex, $[CpTi(\eta^2\text{-}(C,N)\text{-}2\text{-}ArNH\text{–}C_6H_4C{=}NAr)Cl_2]$ $(Ar = 2,6\text{-}{}^iPr_2C_6H_3)$ (**1**) has been synthesized and characterized by elemental analysis, NMR spectra, and single crystal X-ray diffraction. The ^{13}C NMR resonance of the imine carbon atom of **1** at δ 221 ppm is consistent with the η^2-(C,N) binding. This was confirmed by single crystal X-ray diffraction study of **1**. In the complex, Ti atom is five-coordinate with a η^2-bound iminoacyl ligand and one Cp ligand occupying the axial position in a distorted square pyramid.

Keywords: Titanium complex; Metallocene complex; Metallacyclic; Iminoacyl ligand

1. Introduction

Organometallic complexes play a significant role in organic synthesis, exhibiting high reactivity, dramatically changing reaction rate [1], activating carbon–hydrogen bonds [2], and adding to carbon–carbon and carbon–heteroatom double and triple bonds [3]. Among the wide variety of organometallic complexes, group 4 transition metal complexes have applications in organic synthesis especially organotitanium [4]. Titanium catalysts or intermediates, such as titanium chlorides, titanium alkoxides, and metallocene titanium derivatives, are especially attractive for practical use, because they are inexpensive and convenient to handle.

Since Breslow *et al.* first discovered the homogeneous metallocene catalytic system (Cp_2TiCl_2/Et_2AlCl), for olefin polymerization [5], intensive research work has focused on developing new metallocene titanium catalysts for the polymerization of alkenes [6]. Consequently, alkenes have been the most extensively studied substrates in reaction with titanocene catalysts. Reaction of imines as substrates with metallocene titanium catalysts has received attention [7]. Imines themselves, or in combination with triple or double bonds, provide a broad variety of substrates. By combination of

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2007 Taylor & Francis
DOI: 10.1080/00958970701282580

different functional groups, a construction set for different substrates becomes available. The η^2-iminoacyl metallocene titanium intermediates play a role in reactions and there is a great deal of interest in model studies with defined and isolable η^2-iminoacyl metallocene titanium complexes [8]. Thus far, two synthetic strategies, oxidative addition of metal reagents to a C=N linkage and insertion of nitriles into metal–carbon bonds, have been reported for the synthesis of such complexes [9]. Furthermore, few η^2-iminoacyl metallocene titanium intermediates have been characterized by single-crystal X-ray structure analysis [10]. Thus, search for new synthetic methods to such complexes represent a challenging issue in organometallic chemistry.

Herein, we report an effective synthesis of a novel η^2-iminoacyl monocyclopentadienyl titanium complex $[\mathrm{CpTi}(\eta^2\text{-(C,N)-2-ArNH–}C_6H_4\mathrm{C{=}NAr})Cl_2]$ ($\mathrm{Ar} = 2,6\text{-}{}^i\mathrm{Pr}_2C_6H_3$) by direct reaction of monocyclopentadienyl titanium trichloride with the lithium salt of an anilido-imine ligand $[2\text{-}(\mathrm{Ar}C_6H_3\mathrm{N{=}CH})C_6H_4\mathrm{N(H)Ar}]$ ($\mathrm{Ar} = 2,6\text{-}{}^i\mathrm{Pr}_2C_6H_3$). To the best of our knowledge, this is the first η^2-iminoacyl monocyclopentadienyl titanium complex synthesized by such a synthetic approach.

2. Experimental

2.1. *General procedures*

Reactions with organometallic reagents were carried out under an argon atmosphere (ultra-high purity) using standard Schlenk techniques [11]. Solvents were dried and distilled prior to use [12]. ^{n}BuLi and $TiCl_4$ were purchased from Aldrich. $[\eta^5\text{-}C_5H_5]TiCl_3$ [13] and $[2\text{-}(2,6\text{-}{}^i\mathrm{Pr}_2C_6H_3\mathrm{N{=}CH})C_6H_4\mathrm{N(H)}(2,6\text{-}{}^i\mathrm{Pr}_2C_6H_3)]$ [14] were prepared according to the literature procedures. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer; NMR spectra were measured using a Varian Mercury-300 NMR spectrometer.

2.2. *Preparation*

A solution of ^{n}BuLi in *n*-hexane (1.6 M, 1.7 mL, 2.72 mmol) was added to a solution of $2\text{-}(2,6\text{-}{}^i\mathrm{Pr}_2C_6H_3\mathrm{N{=}CH})C_6H_4\mathrm{N(H)}(2,6\text{-}{}^i\mathrm{Pr}_2C_6H_3)$ (1.20 g, 2.72 mmol) in *n*-hexane (20 mL) at −78°C. The reaction mixture was warmed to room temperature and stirred for 4 h, producing a yellow suspension. The product was isolated by filtration, washed with *n*-hexane (5 mL) and dried *in vacuo* to yield a yellow air sensitive solid, $2\text{-}(2,6\text{-}{}^i\mathrm{Pr}_2C_6H_3\mathrm{N{=}CH})C_6H_4\mathrm{N(Li)}(2,6\text{-}{}^i\mathrm{Pr}_2C_6H_3)$ (1.01 g, 2.27 mmol). A solution of $2\text{-}(2,6\text{-}{}^i\mathrm{Pr}_2C_6H_3\mathrm{N{=}CH})C_6H_4\mathrm{N(Li)}(2,6\text{-}{}^i\mathrm{Pr}_2C_6H_3)$ (1.01 g, 2.27 mmol) in toluene (10 mL) was added to a solution of $CpTiCl_3$ (0.56 g, 2.57 mmol) in toluene (15 mL) at −78°C, and the reaction mixture was warmed slowly to room temperature, then heated for another 10 h at 80°C. After allowing the mixture to cool to room temperature, the mixture was filtered. The solution was evaporated *in vacuo*, and the resultant solid extracted with *n*-hexane. The extract was concentrated and placed in the freezer; pale yellow microcrystals were collected. Yield 30% (0.42 g, 0.68 mmol). Anal. Calcd for $C_{36}H_{44}Cl_2N_2Ti$ (623.53): C, 69.35; N, 4.49; H, 7.11. Found: C, 69.16; N, 4.61; H, 7.22. ^{1}H NMR ($CDCl_3$, 300 MHz; 298 K): δ 7.65 (s, 1H, NH) 7.17–7.29 (m, 7H, Ph), 6.88

(d, 1H, Ph, $^3J_{HH} = 8.4$ Hz), 6.72 (s, 5H, Cp), 6.44 (t, 1H, Ph, $^3J_{HH} = 8.4$ Hz), 6.25 (d, 1H, Ph, $^3J_{HH} = 8.4$ Hz), 3.27 (sept, 2H, $CHMe_2$, $^3J_{HH} = 6.6$ Hz), 2.64 (sept, 2H, $CHMe_2$, $^3J_{HH} = 6.6$ Hz), 1.27 (d, 6H, Me, $^3J_{HH} = 2.4$ Hz), 1.26 (d, 6H, Me, $^3J_{HH} = 2.7$ Hz), 1.12 (d, 6H, Me, $^3J_{HH} = 6.9$ Hz), 0.99 (d, 6H, Me, $^3J_{HH} = 7.2$ Hz). ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ, ppm: 221.1, 154.1, 148.0, 142.5, 140.6, 137.2, 137.1, 133.4, 128.6, 128.1, 127.2, 124.5, 117.9, 116.8, 114.3, 113.6, 29.2, 29.1, 24.8, 24.3, 23.9, 23.4.

2.3. *X-ray crystallography*

An orange single crystal of **1** with dimensions of 0.34 × 0.32 × 0.15 mm was mounted inside a glass fiber capillary. The data were collected on a Rigaku R-AXIS RAPID IP diffractometer with Mo-Kα ($\lambda = 0.71073$ Å) at 293 K in the range of $3.02 < \theta < 27.48°$. Empirical absorption correction was applied. A total of 32969 (7898 unique, $R_{int} = 0.0343$) reflections were measured ($-22 \le h \le 22$, $-14 \le k \le 14$, $-25 \le l \le 25$).

The structure of **1** was solved by direct methods and refined by the full-matrix least squares on F^2 using the SHELXTL-97 software [15]. All non-hydrogen atoms in **1** were refined anisotropically. Hydrogen atoms attached to carbon and nitrogen were fixed in ideal positions. A summary of the crystallographic data and structural determination for **1** is provided in table 1. Selected bond lengths and angles of **1** are listed in table 2.

CCDC reference number: 631364 for **1**.

Table 1. Crystal data and structure refinement for **1**.

Empirical formula	$C_{36}H_{44}Cl_2N_2Ti$
Formula weight	623.53
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group (Å, °)	$P_2(1)/n$
a	17.278(5)
b	10.874(4)
c	19.708(7)
α	90
β	111.164(2)
γ	90
V (Å^3)	3453(2)
Z	4
ρ_{Calcd} (g cm^{-3})	1.199
Absorption coefficient (mm^{-1})	0.428
F(000)	1320
Crystal size (mm^3)	0.34 × 0.32 × 0.15
θ Range for data collection (°)	3.02–27.48
Limiting indices	$-22 \le h \le 22$, $-14 \le k \le 14$, $-25 \le l \le 25$
Reflections collected	32969
Independent reflections (R_{int})	7898 ($R_{int} = 0.0343$)
Data/restraints/parameters	7898/131/415
Goodness-of-fit on F^2	1.077
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0475$, $wR_2 = 0.1363$
Indices (all data)	$R_1 = 0.0704$, $wR_2 = 0.1497$
Largest difference peak and hole (e Å^{-3})	0.275 and −0.410

3. Results and discussion

3.1. *Complex synthesis*

The titanium complex $CpTiCl_3$ reacts with the lithium salt of the anilido-imine ligand 2-(2,6-$^iPr_2C_6H_3N{=}CH)C_6H_4N(H)$(2,6-$^iPr_2C_6H_3$) to yield [CpTi($\eta^2$-(C,N)-2-2,6-$^iPr_2C_6H_3NH$-$C_6H_4C{=}N$-2,6-$^iPr_2C_6H_3)Cl_2$] (**1**), which was isolated as an air- and moisture-sensitive solid (figure 1).

3.2. *NMR spectroscopy*

The ^{1}H NMR spectrum of **1** exhibits typical resonances at 7.65(s), 6.72(s), 1.12(d) and 0.99(d) ppm which are attributed to the N–H of anilido-imine ligand, the cyclopentadienyl ligand and the methyl groups of the anilido-imine ligand, respectively. The ratio of the integrals is consistent with the proposed structure. The ^{1}H NMR spectrum of **1** indicates that the iminato ligand is η^2-(C,N) bound to the titanium center by comparison with the ^{1}H NMR spectrum of the anilido-imine ligand. Diagnostic features associated with **1** include the following observations: (1) The imino CH proton signal of the free anilido-imine ligand disappears in the ^{1}H NMR spectrum of complex **1**, indicative of formation of a Ti–C bond in this complex. (2) The NH signal shifts about 3 ppm upfield in comparison with the free ligand. (3) One of the two sets

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Ti–C(1)	2.343(3)	Ti–C(2)	2.340(3)
Ti–C(3)	2.342(3)	Ti–C(4)	2.347(3)
Ti–C(5)	2.333(3)	Ti–Cl(1)	2.292(9)
Ti–Cl(2)	2.317(1)	Ti–C(6)	2.071(2)
Ti–N(1)	2.013(2)	C(6)–N(1)	1.267(3)
C(1)–C(2)	1.391(4)	C(2)–C(3)	1.361(4)
C(3)–C(4)	1.325(4)	C(4)–C(5)	1.402(5)
C(1)–C(5)	1.406(4)	Cp(cent)–Ti	2.027
Cp(cent)–Ti–Cl(1)	115.8	Cp(cent)–Ti–Cl(2)	113.8
Cp(cent)–Ti–C(6)	112.0	Cp(cent)–Ti–N(1)	123.8
C(6)–Ti–N(1)	36.10(7)	Cl(1)–Ti–Cl(2)	97.13(4)
C(6)–Ti–Cl(1)	93.23(6)	N(1)–Ti–Cl(2)	88.04(5)

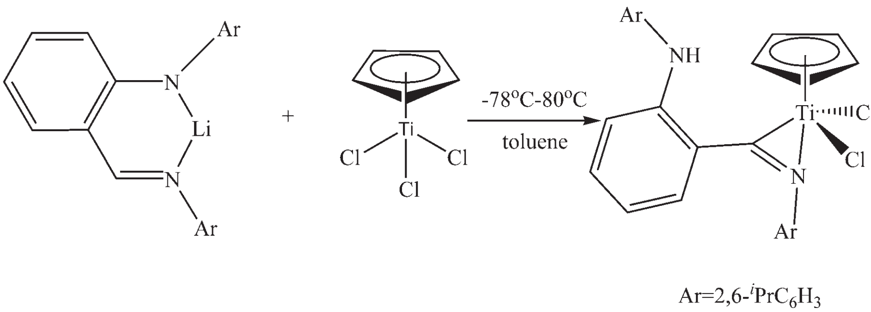
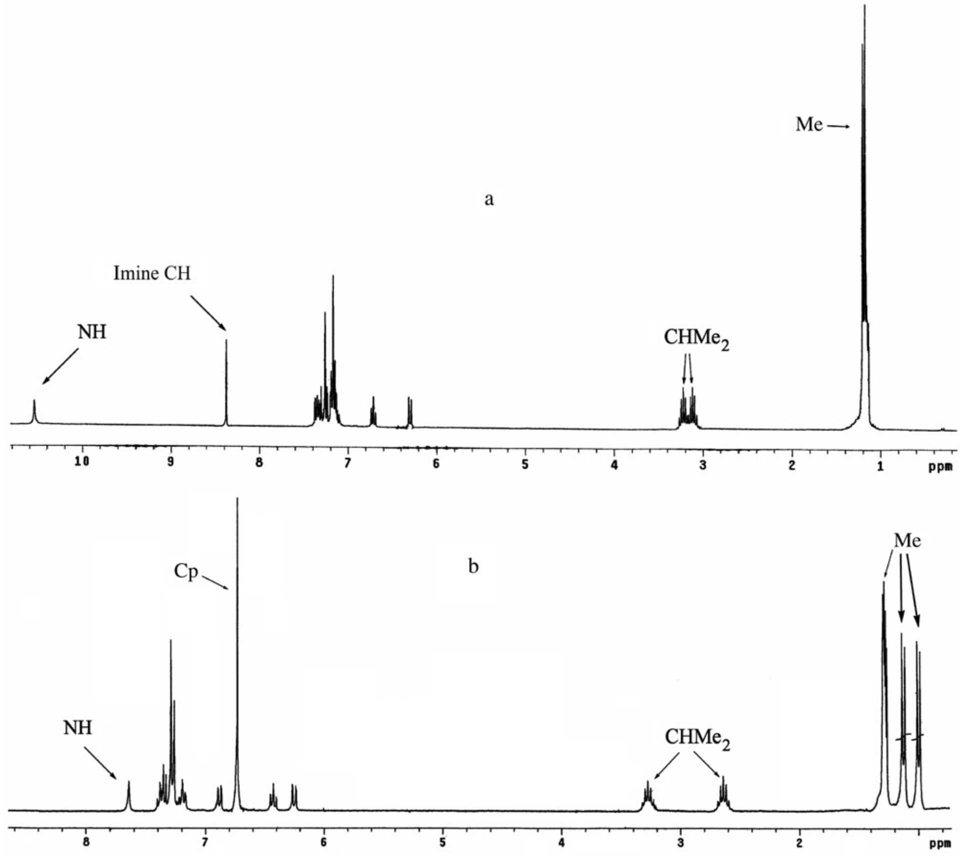
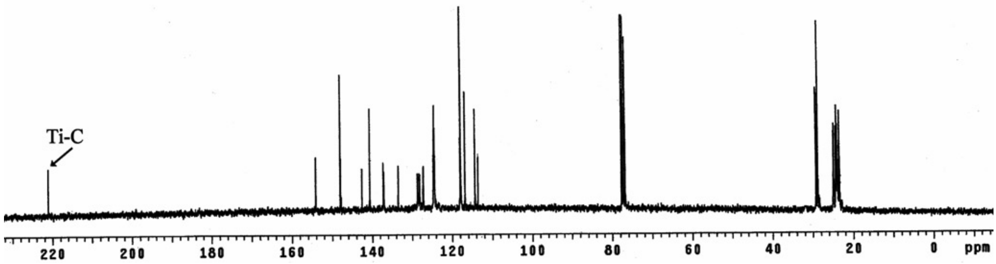


Figure 1. Preparation of the **1**.

of isopropyl CH protons shifts about 0.5 ppm upfield in comparison with the free ligand, indicating formation of a Ti–N bond. In addition, the ^{13}C NMR resonance of the Ti–CN carbon bond is consistent with η^2-(C,N) binding (δ 221.1 ppm) [10]. To further support the connectivity in **1**, single crystals were grown by cooling saturated solutions of **1** in mixed CH_2Cl_2/hexane, and the molecular structure was determined by a single crystal X-ray diffraction.



^{1}H NMR spectra of anilido-imine ligand (a) and the complex **1** (b).



^{13}C.NMR spectra of the complex **1.**

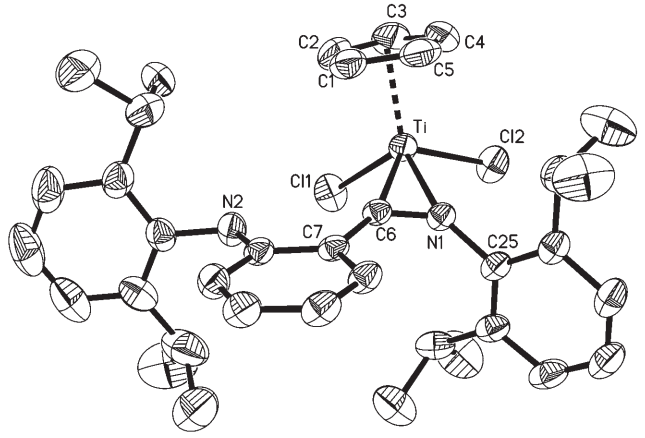


Figure 2. ORTEP drawing of **1** with thermal ellipsoids at 30% probability.

3.3. *Structure description*

The ORTEP drawing of the molecular structure is shown in figure 2. The geometry around titanium in **1** can be described as a distorted square pyramid defined by a Cp ring (assuming Cp to occupy one coordination site), two chlorine atoms, a carbon atom and a nitrogen atom from the η^2-iminoacyl ligand. The Ti–C(6) and Ti–N(1) distances (2.071(2) and 2.013(2) Å, respectively) are comparable to reported Ti–C(sp^2) and Ti–N(sp^2) bond lengths, indicating that the iminoacyl ligand in **1** coordinates to the metal center in a η^2 fashion [16]. The C(6)–N(1) bond distance compares well with that found in other η^2-, η^1-iminoacyl's and is consistent with the presence of a C=N double bond. The Ti–C (Cp ring carbon) bond lengths ranging from 2.333 Å to 2.347 Å, and Ti–Cp distance at 2.027 Å are typical for Ti(IV) Cp complexes [17]. The crystal structure confirms that the Ti–C6–N1 cycle, the ring carbon C7 connected to C6, and the ring carbon C25 connected to N1 are coplanar (max. deviation 0.088 Å). The nitrogen (N1) and carbon (C6) atoms maintain a trigonal-planar environment and are sp^2 hybridized, consistent with the angle sums of 359.9° and 357.6°, respectively. The C6–Ti–N1 angle of 36.10° is comparable to the corresponding C–Ti–N angle reported for organotitanium iminoacyl complexes [9c, 10b]. The dihedral angle between Ti–C6–N1 plane and Cp plane is 34.2°.

4. Conclusions

We have prepared and characterized a novel η^2-iminoacyl monocyclopentadienyl titanium complex by a new synthetic approach. The synthesis of **1** not only represents a remarkable addition to the limited list of η^2-iminoacyl metallocene titanium complexes, but also demonstrates a new simple synthetic approach to these complexes.

Supplementary data

Crystallographic data for **1** have been deposited at Cambridge Crystallographic Data Center (CCDC) as supplementary publication number CCDC 631364. Copies of available material can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Email: deposit@cdc.cam.ac.uk

Acknowledgement

This work was supported by the National Natural Science Foundation of China (Nos 20674024 and 20374023).

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