Available online at www.sciencedirect.com
SCIENCE DIRECT®

Journal of Organometallic Chemistry 678 (2003) 134–141

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Synthesis, structural determination, and ethylene polymerization chemistry of mono(salicylaldiminato) complexes of titanium(IV)

David Owiny, Sean Parkin, Folami T. Ladipo *

Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055, USA

Received 20 February 2003; received in revised form 9 May 2003; accepted 15 May 2003

Abstract

Titanium(IV)mono(salicylaldiminato) complexes [$L^1Ti(NMe_2)_3$] (**1**) and [L^1TiCl_3] (**2**) have been synthesized by treatment of $Ti(NMe_2)_4$ or $TiCl_4$ with one equivalent of [4,6-Bu^t_2-2-(CH=NBu^t)C_6H_3OH] (**L^1H**) or [4,6-Bu^t_2-2-(CH=NBu^t)$C_6H_3OSiMe_3$] (**L^1SiMe_3**), respectively. The compounds are monomeric in solution and in the solid-state. Reactions of $TiCl_4$ with one equivalent of [4,6-Bu^t_2-2-(CH=NCH_2Ph)C_6H_3OH] (**L^2H**) and [4,6-Bu^t_2-2-{CH=N(2-C_6H_4OH)}C_6H_3OH] (**L^3H_2**) produced [$L^2TiCl_2(\mu\text{-}Cl)]_2$ (**3**) and [$L^3TiCl_2]_2$ (**4**), respectively. [$L^3TiCl_2(THF)$] (**5**) was also produced in quantitative yield when **4** was stirred in THF for 16 h. The reaction of $TiCl_4$ with **L^3H_2** (Two equivalents) in toluene gave [$(L^3)_2Ti$] (**6**). The molecular structures of **2**–**4** and **6** were established by single-crystal X-ray diffraction studies; and **4** displayed a rare face to face π–π stacking interaction in its structure. Compounds **1** and **2** showed modest ethylene polymerization activities at 25 °C with 900 molar equivalents of methylalumoxane (MAO) as co-catalyst.

Keywords: Titanium(IV) complexes; Olefin polymerization; Salicylaldiminato ligands; Schiff base ligands

1. Introduction

There has been a great deal of interest in the development of well-defined transition metal catalysts for the polymerization of α-olefins since the discovery of highly active Group 4 metallocene catalysts [1]. A wide variety of ligand environments and transition metals have been investigated and olefin polymerization catalysts based on both early- and late transition metals have been developed, some of which show activities superior or comparable to those of Group 4 metallocenes [2]. In fact, Group 4 metal complexes based on chelating di(amido)- 2c2d2e2f, amine-bis(phenolato)- 2n, or bis(salicylaldiminato) 2h2i2j2k ligands have furnished highly active and/or living olefin polymerization catalysts. However, despite extensive investigation of organometallic complexes of salicylaldiminato ligands and the utility of bis(salicylaldiminato)titanium(IV) complexes in olefin polymerization chemistry, few mono(salicylaldiminato)titanium(IV) complexes have been described and their reaction chemistry is poorly developed [3,4]. This is surprising since salicylaldimines ($HOC_6H_4CH{=}NR$, R = alkyl or aryl) are obtained by easy synthetic routes and hence their steric and electronic properties can be readily tuned, via substitution of the aromatic ring or modification of the imino nitrogen substitutent 2h2d2e2f2g2h2k[3]. Herein, we describe the synthesis, X-ray crystallographic characterization, and ethylene polymerization chemistry of mono(salicylaldiminato)titanium(IV) complexes [{4,6-Bu^t_2-2-(CH=NBu^t)C_6H_3O}$TiCl_3$] (**1**) and [{4,6-Bu^t_2-2-(CH=NBu^t)C_6H_3O}$Ti(NMe_2)_3$] (**2**).

2. Experimental

2.1. General

$Ti(NMe_2)_4$ [5], $TiCl_4(THF)_2$ [6], and salicylaldimine compounds, 4,6-bis(*tert*-butyl)-2-{(*tert*-butyl)iminomethyl}phenol [4,6-Bu^t_2-2-(CH=NBu^t)C_6H_3OH] (**L^1H**)

* Corresponding author. Tel.: +1-859-257-7084; fax: +1-859-323-1069.
E-mail address: fladip0@uky.edu (F.T. Ladipo).

0022-328X/03/$ - see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0022-328X(03)00454-6

[7], 4,6-bis(*tert*-butyl)-2-{(benzyl)iminomethyl}phenol [4, 6-Bu^t_2-2-(CH=NCH_2Ph)C_6H_3OH] (**L^2H**) [8], and 4,6-bis(*tert*-butyl)-2-{(2-hydroxyphenyl)iminomethyl}phenol [4, 6-Bu^t_2-2-{CH=N(2-C_6H_4OH)}C_6H_3OH] (**L^3H_2**) [9], were prepared via modifications of literature methods. All other experiments were performed under dry nitrogen atmosphere using standard Schlenk techniques or in a MBraun glovebox. Benzene-d_6, toluene, tetrahydrofuran, pentane, and heptane were distilled from sodium benzophenone ketyl (with 1 ml l^{-1} of teraethyleneglycol dimethyl ether added as a solubilizing agent in the case of pentane and heptane). CD_2Cl_2 and $CDCl_3$ were distilled from calcium hydride. All solvents were stored in the glovebox over 4A molecular sieves that had been dried under vacuum at 150 °C for at least 48 h prior to use. All other chemicals were purchased from Aldrich Chemical Co. and used without further purification (unless otherwise stated). ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian Gemini-200 spectrometer or a Varian VXR-400 spectrometer at ca. 22 °C. ^{1}H- and ^{13}C-chemical shifts were referenced to residual solvent peaks. Infrared spectra were recorded on a Nicolet Magna 560 spectrometer. Mass spectral data were obtained from the University of Kentucky Mass Spectrometry Center on a Thermo Finnigan (San Jose, CA) Polaris Q (quadruple ion trap) spectrometer. Elemental analyses were performed by Complete Analysis Laboratories, Inc., Parsippany, NJ.

2.2. *Synthesis of* [4, 6-Bu^t_2-2-(CH=NBu^t)$C_6H_3OSiMe_3$] (*L^1SiMe_3*)

A Et_2O (5 mL) solution of $KOBu^t$ (257 mg, 2.29 mmol) was added in two portions to a Et_2O (10 ml) solution of 4,6-bis(*tert*-butyl)-2-{(*tert*-butyl)iminomethyl}phenol (**L^1H**, 54.4 mg, 1.88 mmol) at room temperature (r.t.). The reaction mixture was allowed to stir for 0.5 h, after which the yellowish-white precipitate was collected by filtration under N_2 atmosphere. After washing the precipitate several times with Et_2O, it was put back into Et_2O. Me_3SiCl (0.25 ml, 1.97 mmol) was added to the Et_2O suspension and the resulting mixture was stirred for 20 min. The reaction mixture was stripped to dryness under reduced pressure, the residue was extracted with pentane, and the solvent was removed under vacuum to give a yellowish-white crystalline solid. Yield: 0.510 g, 75%. ^{1}H-NMR ($CDCl_3$): δ 8.51 (s, 1H, Bu^tN=C*H*), 7.73 (d, 1H, $J_{HH}=6.0$ Hz, arom CH), 7.41 (d, 1H, $J_{HH}=5.6$ Hz, arom CH), 1.41 (s, 9H, Bu^t), 1.32 (s, 18H, Bu^t, NBu^t), 0.32 (s, 9H, $SiMe_3$). ^{13}C-NMR ($CDCl_3$): δ 153.8 (Bu^tN=*C*H), 152.3, 143.7, 140.2, 128.8, 127.1, 123.1, 57.8 (N*C*Me_3), 34.6 (*C*Me_3), 34.3 (*C*Me_3), 31.6 (C*Me_3*), 30.9 (C*Me_3*), 30.0 (NC*Me_3*), 2.3 ($SiMe_3$).

2.3. *Synthesis of titanium compounds **1–6***

2.3.1. *[$L^1Ti(NMe_2)_3$] (**1**)*

A toluene (15 ml) solution of **L^1H** (0.381 g, 1.32 mmol) was added drop-wise to a stirred toluene (8 ml) solution of [$Ti(NMe_2)_4$] (0.297 g, 1.33 mmol) at r.t. After completion of the addition, the yellow–orange reaction mixture was stirred for 20 min. The solution was stripped under reduced pressure to give a yellow–orange crystalline solid. Yield: 0.538 g, 92%. ^{1}H-NMR (C_6D_6): δ 8.52 (s, 1H, Bu^tN=C*H*), 7.73 (d, 1H, $J_{HH}=2.4$, arom CH), 7.33 (d, 1H, $J_{HH}=2.4$, arom CH), 3.20 (s, 18H, NMe_2), 1.66 (s, 9H, Bu^t), 1.38 (s, 9H, Bu^t), 1.06 (s, 9H, NBu^t). ^{13}C-NMR (C_6D_6): δ 166.5 (Bu^tN=*C*H), 160.9, 140.2, 139.7, 129.3, 128.7, 122.6, 60.6 (N*C*Me_3), 46.7 (NMe_2), 35.9 (*C*Me_3), 34.6 (*C*Me_3), 32.0 (C*Me_3*), 31.2 (C*Me_3*), 30.1 (NC*Me_3*). IR (CH_2Cl_2, cm^{-1}): 1612 ν(C=N). Anal. Calc. for $C_{25}H_{48}N_4OTi$: C, 64.09; H, 10.32; N, 11.96. Found: C, 63.97; H, 10.10; N, 11.67%.

2.3.2. *[L^1TiCl_3] (**2**)*

A toluene (12 ml) solution of **L^1SiMe_3** (1.07 g, 3.27 mmol) was added drop-wise to a stirred toluene (20 ml) solution of $TiCl_4$ (0.830 g, 4.36 mmol) at 0 °C (ice bath). Upon complete addition, the solution was stirred (0–2 °C) for 4 h. The resulting orange–brown precipitate was collected by filtration at r.t., washed once with toluene (10 ml), and dried under vacuum. Yield: 0.830 g, 58%. ^{1}H-NMR ($CDCl_3$): δ 8.59 (s, 1H, Bu^tN=C*H*), 7.66 (d, 1H, $J_{HH}=2.4$, arom CH), 7.44 (d, 1H, $J_{HH}=$ 2.4, arom CH), 1.76 (s, 9H, Bu^t), 1.53 (s, 9H, Bu^t), 1.37 (s, 9H, NBu^t). ^{13}C-NMR ($CDCl_3$): δ 163.7 (Bu^tN=*C*H), 157.9, 144.7, 141.6, 134.1, 127.2, 118.2, 60.9 (N*C*Me_3), 35.4 (*C*Me_3), 35.0 (*C*Me_3), 31.5 (C*Me_3*), 30.1 (C*Me_3*), 28.3 (NC*Me_3*). IR (CH_2Cl_2, cm^{-1}): 1604 ν(C=N). Anal. Calc. for $C_{19}H_{30}Cl_3NOTi$: C, 51.55; H, 6.83. Found C, 51.52; H, 6.82%.

2.3.3. *[$L^2TiCl_2(\mu$-$Cl)]_2$ (**3**)*

A heptane (18 ml) solution of **L^2H** (1.15 g, 3.55 mmol) was added drop-wise to a stirred heptane (30 ml) solution of $TiCl_4$ (0.690 g, 3.64 mmol) at −78 °C. After the addition was complete, the brick-red reaction mixture was allowed to warm gradually up to r.t. and stirred for ~10 h. The resulting red–brown precipitate was collected by filtration, washed with pentane (4 × 15 ml), and dried under vacuum to give an orange–red powder. Yield: 3.01 g, 89%. ^{1}H-NMR ($CDCl_3$): δ 8.22 (s, 1H, $PhCH_2$N=C*H*), 7.65(d, 1H, $J_{HH}=2.0$, arom CH), 7.55–7.34 (m, 5H, *Ph*CH_2), 7.16 (d, 1H, $J_{HH}=$ 2.0, arom CH), 5.36 (s, 2H, PhC*H_2*), 1.54 (s, 9H, Bu^t), 1.30 (s, 9H, Bu^t). ^{13}C-NMR ($CDCl_3$): δ 166.1 ($PhCH_2$N=*C*H), 161.6, 148.4, 136.8, 135.6, 131.3, 130.6, 129.5, 129.1, 129.0, 124.9, 63.2 (Ph*C*H_2), 35.4 (*C*Me_3), 35.1 (*C*Me_3), 31.4 (C*Me_3*), 29.76 (C*Me_3*). MS (EI, 70 eV, *m/z*): 869 [M^+ −Cl]. IR ($CHCl_2$, cm^{-1}):

1613 ν(C=N). Anal. Calc. for $C_{44}H_{56}Cl_6N_2O_2Ti_2$: C, 55.43; H, 5.92. Found: C, 55.26; H, 5.73%.

2.3.4. $[L^3TiCl_2]_2$ (**4**)

A toluene (20 ml) solution of $\mathbf{L^3H_2}$ (0.435 g, 1.33 mmol) was added drop-wise to a stirred toluene (5 ml) solution of $TiCl_4$ (0.259 g, 1.36 mmol) at −78 °C. After the addition was complete, the initially orange–red reaction mixture was allowed to warm gradually up to r.t. and stirred for ~10 h. The resulting brown mixture was filtered and the precipitate was washed with pentane (3 × 15 ml), then dried under vacuum. Yield: 0.923 g, 79%. ^{1}H-NMR ($CDCl_3$): δ 8.82 (s, 2H, N=CH), 7.72 (d, 2H, J_{HH} = 2.4, arom CH), 7.38 (d, 2H, J_{HH} = 2.2 arom CH), 7.34 (d, 2H, J_{HH} = 8.0, arom CH), 7.26 (t, 2H, J_{HH} = 8.0 arom CH), 6.95 (t, 2H, J_{HH} = 8.0, arom C*H*), 6.82 (d, 2H, J_{HH} = 8.0, arom C*H*), 1.55 (s, 18H, Bu^t), 1.37 (s, 18H, Bu^t). ^{13}C-NMR ($CDCl_3$): δ 157.9 (N=*C*H), 146.7, 137.3, 133.6, 131.2, 129.5, 129.3, 128.4, 125.5, 122.5, 115.1, 114.7, 35.5 (*C*Me$_3$), 34.86 (*C*Me$_3$), 31.39 (C*Me*$_3$), 29.92 (C*Me*$_3$). MS (EI, 70 eV, *m/z*): 849 [M^+ −Cl]. IR (CH_2Cl_2, cm^{-1}): 1600 ν(C=N). A sample of **4** was recrystallized from $CHCl_3$ prior to microanalysis and gave $[L^3TiCl_2]_2 \cdot 2CHCl_3$. Anal. Calc. for $C_{44}H_{52}Cl_{10}N_2O_4Ti_2$: C, 47.07; H, 4.64; N, 2.49. Found: C, 47.64; H, 4.99; N, 2.23%.

2.3.5. $[L^3TiCl_2(THF)]$ (**5**)

A toluene (6 ml) solution of $\mathbf{L^3H_2}$ (0.155 g, 0.476 mmol) was added drop-wise to a stirred toluene (5 ml) suspension of $[TiCl_4(THF)_2]$ (0.153 g, 0.459 mmol) at −78 °C. After the addition was complete, the initially orange–red reaction mixture was allowed to warm gradually up to r.t. and stirred for ~16 h. The resulting brown–black mixture was filtered and the precipitate was washed with pentane (2 × 10 ml), then dried under vacuum. Yield: 0.137 g, 58%. ^{1}H-NMR ($CDCl_3$): δ 8.46 (s, 1H, N=CH), 7.55 (d, 1H, J_{HH} = 2.2, arom CH), 7.26 (t, 1H, J_{HH} = 8.0, arom CH), 7.18 (d, 1H, J_{HH} = 2.0, arom CH), 7.09 (t, 1H, J_{HH} = 8.0, arom CH), 6.80 (t, 1H, J_{HH} = 8.0, arom CH), 6.49 (d, 1H, J_{HH} = 8.0, arom CH), 4.20 (m, 4H, THF), 1.93 (m, 4H, THF), 1.47 (s, 9H, Bu^t), 1.33 (s, 9H, Bu^t). ^{13}C-NMR ($CDCl_3$): δ 162.0 (N=CH), 160.6, 156.1, 145.4, 139.0, 136.7, 133.0, 131.2, 129.7, 124.2, 122.0, 114.6, 114.2, 73.2 (THF), 35.3 (*C*Me$_3$), 34.7 (*C*Me$_3$), 31.4 (C*Me*$_3$), 30.0 (C*Me*$_3$), 25.6 (THF). IR (CH_2Cl_2, cm^{-1}): 1604 ν(C=N). Anal. Calc. for $C_{25}H_{33}Cl_2NO_3Ti$: C, 58.39; H, 6.47; N, 2.72. Found: C, 58.34; H, 6.22; N, 2.92%.

2.3.6. $[(L^3)_2Ti]$ (**6**)

A toluene (6 ml) solution of $\mathbf{L^3H_2}$ (0.256 g, 0.786 mmol) was added drop-wise to a stirred toluene (6 ml) solution of $TiCl_4$ (77.0 mg, 0.409 mmol) at −78 °C. After the addition was complete, the initially red reaction mixture was allowed to warm gradually up to r.t. and stirred for ~16 h. The resulting red mixture was filtered and the precipitate was washed with pentane (3 × 15 ml), then dried under vacuum. Yield: 0.202 g, 71%. ^{1}H-NMR ($CDCl_3$): δ 8.86 (s, 2H, N=CH), 7.46 (s, 2H, arom CH), 7.34 (d, 2H, J_{HH} = 8.0, arom CH), 7.32 (s, 2H, arom CH), 7.04 (t, 2H, J_{HH} = 8.0, arom CH), 6.75 (t, 2H, J_{HH} = 8.0, arom CH), 6.56 (d, 2H, J_{HH} = 8.0, arom CH), 1.34 (s, 18H, Bu^t), 1.13 (s, 18H, Bu^t). ^{13}C-NMR ($CDCl_3$): δ 161.5 (N=CH), 158.0, 142.2, 138.7, 136.6, 131.9, 130.1, 128.4, 121.7, 119.4, 115.2, 114.2, 35.0 (*C*Me$_3$), 34.5 (*C*Me$_3$), 31.5 (C*Me*$_3$), 29.4 (C*Me*$_3$). IR (CH_2Cl_2, cm^{-1}): 1604 ν(C=N). MS (EI, 70 eV, *m/z*): 694 [M^+]. A sample of **6** was recrystallized from $CHCl_3$ prior to microanalysis. The resulting crystals contained lattice $CHCl_3$ molecules, ~ one-third of a $CHCl_3$ molecule per titanium. Anal. Calc. for $C_{42}H_{50}N_2O_4Ti \cdot (CHCl_3)_{0.33}$: C, 69.20; H, 6.90; N, 3.81. Found: C, 69.58; H, 6.96; N, 4.03%.

2.4. Ethylene polymerization studies

Toluene (60 ml) was charged into a 250 ml two-necked Schlenk flask under N_2 atmosphere in a glove-box. An excess of MAO (Al/Ti ratio = 900/1) was added and the solution was stirred for several minutes. Next, the catalyst precursor (0.027 mmol of Ti) was added as a solid and the solution was stirred for 30 min. The N_2 atmosphere was replaced with ethylene (passed through a column of BASF catalyst R3-11 and a solution of MAO) and the pressure was maintained at 1 atmosphere by slow bubbling through the solution and controlling the pressure with a bubbler at the outlet. The polymerization was carried out for 10 min. Polymerizations were quenched with MeOH (30 ml) and then 1 M HCl solution (30 ml). The resulting suspension was vigorously stirred until both layers were colorless and clearly separated (~10 min). Polyethylene was filtered off, washed with 1 M HCl, and MeOH then dried at 70 °C for 48 h.

2.5. Crystallographic study

The crystal data for $[L^2TiCl_2(\mu\text{-}Cl)]_2$ (**3**), $[L^3TiCl_2]_2$ (**4**), and $[(L^3)_2Ti]$ (**6**) are collected in Table 1. Further details of the crystallographic study are given in Section 5.

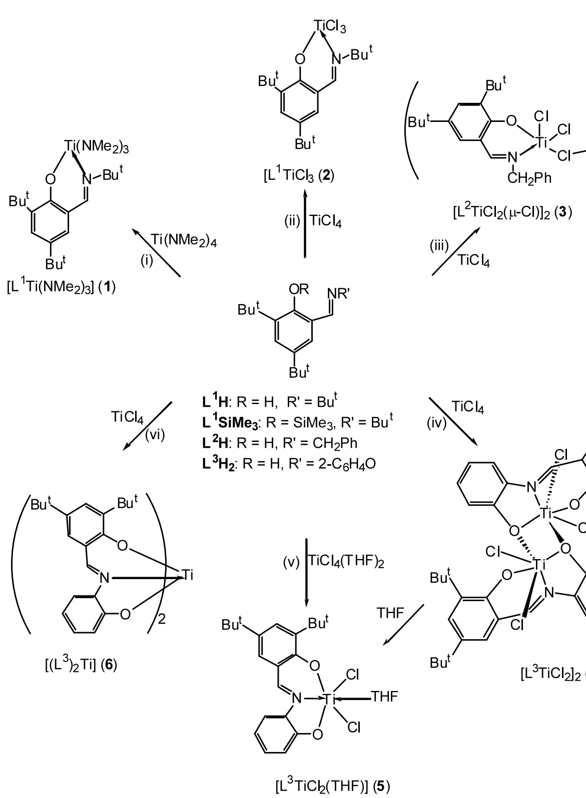
3. Results and discussion

The synthesis of the salicylaldiminato complexes of titanium described in this report is summarized in Scheme 1. The mono(salicylaldiminato)titanium(IV) complex $[L^1Ti(NMe_2)_3]$ (**1**) was isolated in excellent yield from reaction of $Ti(NMe_2)_4$ with one equivalent of $[4,6\text{-}Bu^t_2\text{-}2\text{-}(CH{=}NBu^t)C_6H_3OH]$ ($\mathbf{L^1H}$) in toluene at ~

Table 1
Crystallographic data for $3 \cdot C_5H_{12}$, $4 \cdot CHCl_3$, and $6 \cdot CH_2Cl_2$

	$3 \cdot C_5H_{12}$	$4 \cdot CHCl_3$	$6 \cdot CH_2Cl_2$
Empirical formula	$C_{49}H_{68}Cl_6N_2O_2Ti_2$	$C_{42.50}H_{50.50}Cl_{5.50}N_2O_4Ti_2$	$C_{43}H_{52}Cl_2N_2O_4Ti$
Formula weight	1025.55	944.12	779.67
Temperature (K)	150(2)	90(2)	90(2)
Crystal system	Monoclinic	Tetragonal	Triclinic
Space group	$P2_1/c$	P-421c	$P\bar{1}$
a (Å)	12.4720(5)	15.9770(2)	11.7557(6)
b (Å)	21.1090(8)	15.9770(2)	14.2041(7)
c (Å)	19.7410(7)	17.5674(3)	14.2328(7)
α (°)	90	90	104.837(3)
β (°)	90.6330(18)	90	113.565(3)
γ (°)	90	90	99.152(3)
V (Å^3)	5196.9(3)	4484.33(11)	2012.01(17)
Z	4	4	2
D_{calc} (g cm^{-3})	1.311	1.398	1.287
Final R indices [$I > 2\sigma(I)$]: R_1, wR_2	0.0789, 0.1598	0.0378, 0.0717	0.0892, 0.1456
wR_2, R_1 (all data)	0.1033, 0.1695	0.0470, 0.0741	0.1207, 0.1544

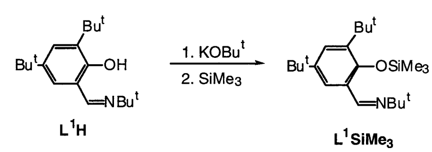
25 °C. The reaction between $TiCl_4$ and $\mathbf{L^1H}$ (one equivalent) in heptane did not cleanly produce mono(salicylaldiminato)titanium trichloride [L^1TiCl_3] (**2**) [10]. Instead, **2** was obtained in excellent yield from the reaction of $TiCl_4$ with one equivalent of [4, 6-Bu^t_2-2-(CH=NBu^t)$C_6H_3OSiMe_3$] ($\mathbf{L^1SiMe_3}$) in toluene at 0 °C. Clean silylation of $\mathbf{L^1H}$ was achieved as



(i) $\mathbf{L^1H}$ (1 equiv); (ii) $\mathbf{L^1SiMe_3}$ (1 equiv); (iii) $\mathbf{L^2H}$ (1 equiv); (iv) $\mathbf{L^3H_2}$ (1 equiv); (v) $\mathbf{L^3H_2}$ (1 equiv); (vi) $\mathbf{L^3H_2}$ (2 equiv).

Scheme 1.

shown in Eq. (1). Reaction of $TiCl_4$ with one equivalent of [4, 6-Bu^t_2-2-(CH=NCH$_2$Ph)C_6H_3OH] ($\mathbf{L^2H}$) or [4, 6-Bu^t_2-2-{CH=N(2-C_6H_4OH)}C_6H_3OH] ($\mathbf{L^3H_2}$) at −78–25 °C produced [$L^2TiCl_2(\mu$-Cl)]$_2$ (**3**) and [L^3TiCl_2]$_2$ (**4**), respectively. The fact that **3** and **4** are dimers likely reflects the reduced steric constraint on titanium by the respective salicylaldiminate ligand in comparison to [4,6-Bu^t_2-2-(CH=NBu^t)$C_6H_3O^-$] ($\mathbf{L^1}$). Consistent with this suggestion, the reaction of $TiCl_4(THF)_2$ with $\mathbf{L^3H_2}$ (one equivalent) in toluene afforded monomeric [L^3TiCl_2(THF)] (**5**), which was also produced in quantitative yield when **4** was dissolved in THF and stirred for 16 h. [$(L^3)_2Ti$] (**6**) was obtained in good yield from the reaction between $TiCl_4$ and $\mathbf{L^3H_2}$ (two equivalents) in toluene at −78–25 °C.



(1)

All of the compounds **1**–**6** are air- and moisture-sensitive, thermally stable red to red–brown solids. They are conveniently stored in the solid-state under N_2 atmosphere at ambient temperature without any observable decomposition. All of the compounds are readily soluble in polar hydrocarbon solvents, such as THF, chloroform, and dichloromethane, and are practically insoluble in aliphatic hydrocarbon solvents, such as pentane and heptane. While **1** is quite soluble in aromatic hydrocarbon solvents, such as benzene and toluene, **2**–**6** are only sparingly soluble in these solvents. The formulations proposed for **1**–**6** were confirmed by microanalysis, ^{1}H-and ^{13}C-NMR, and/or mass spectrometry (see Section 2). The molecular structures of [L^1TiCl_3] (**2**), [$L^2TiCl_2(\mu$-Cl)]$_2$ (**3**), [L^3TiCl_2]$_2$ (**4**), and

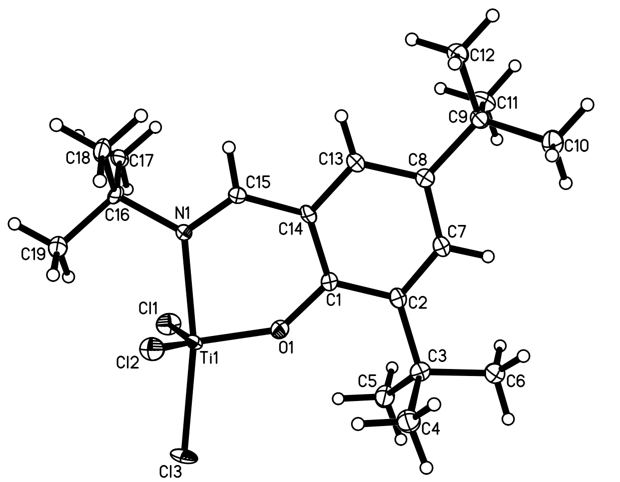


Fig. 1. An ORTEP diagram of the molecular structure of **2** showing 50% thermal ellipsoid probabilities.

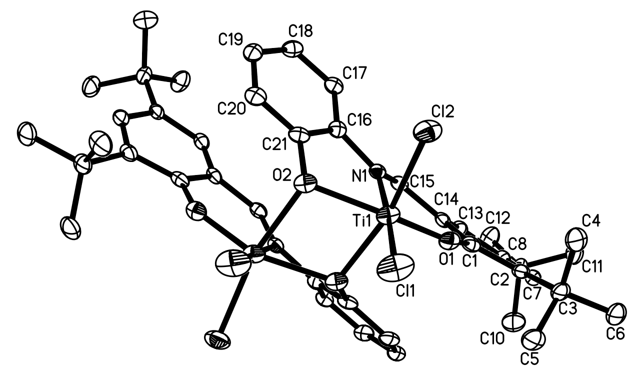


Fig. 3. An ORTEP diagram of the molecular structure of **4** showing 50% thermal ellipsoid probabilities.

$[(L^3)_2Ti]$ (**6**) were also established by single-crystal X-ray diffraction studies (Figs. 1–4). Selected metrical parameters are listed in Tables 2 and 3. Room temperature ^{1}H- and ^{13}C-NMR data for $[L^1Ti(NMe_2)_3]$ (**1**) indicate fast exchange of the NMe_2 ligands on the NMR timescale. For example, a singlet resonance at δ 3.20 ppm (integrating as 18 protons) is observed in the ^{1}H-NMR spectrum of **1** for the NMe_2 groups. We therefore conducted a variable temperature ^{1}H-NMR study of **1** in toluene-d_8 from 298–193 K. The peaks in the NMR spectrum slowly broadened as the temperature was lowered, and the resonance at δ 3.20 ppm split into two broad peaks at δ 3.53 and 2.76 ppm (integrating in 2:1 ratio) at 213 K. The peak at δ 3.53 ppm split further into two broad peaks (at δ 3.59 and 3.48 ppm) at 203 K. Three fairly sharp resonances integrating in 1:1:1 ratio were observed at δ 3.60, 3.47, and 2.70 ppm at 193 K. The NMR data are consistent with a trigonal bipyramidal geometry about Ti with two equitorial NMe_2 ligands, one axial NMe_2, and the bidentate salicylaldiminato ligand (**L**$^{\mathbf{1}}$) coordinated at the remaining axial and equitorial sites. The molecular structure of $[L^1TiCl_3]$ (**2**), shown in Fig. 1, further supports the structural assignment made for $[L^1Ti(NMe_2)_3]$ (**1**). The geometry about the Ti center of **2** is trigonal bipyramidal, with one chloride and the imino nitrogen coordinated at the axial positions, and the remaining two chlorides and the aryloxide group coordinated at the equitorial sites. While the crystal of **2** utilized in the X-ray diffraction study was twinned and the poor crystal quality limits the accuracy of geometrical parameters, the connectivity is unambiguous and bond lengths and angles are within expected ranges 2h2i2j2k[11].

The six-coordinate complexes **3**, **4**, and **6** possess a distorted octahedral geometry about their Ti centers. The molecular structure of $[L^2TiCl_2(\mu\text{-}Cl)]_2$ (**3**), presented in Fig. 2, confirms the C_i symmetry of the molecule in solution (see ^{1}H- and ^{13}C-NMR data) and metrical parameters for **3** (Table 2) are within the range observed for related six-coordinate, chloride-bridged Ti(IV) complexes 4a[11]. While mass spectral data allowed the formulation of $[L^3TiCl_2]_2$ (**4**) as a dimer ($m/z = 849$ for $[M^+ - Cl]$) and NMR data revealed a symmetric salicylaldiminato ligand environment, the molecular structure of **4** was unambiguously established

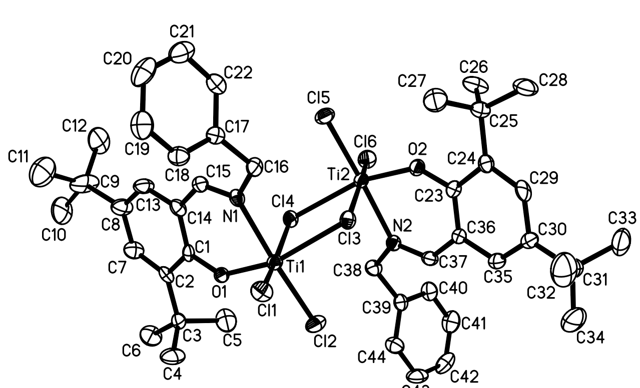


Fig. 2. An ORTEP diagram of the molecular structure of **3** showing 50% thermal ellipsoid probabilities.

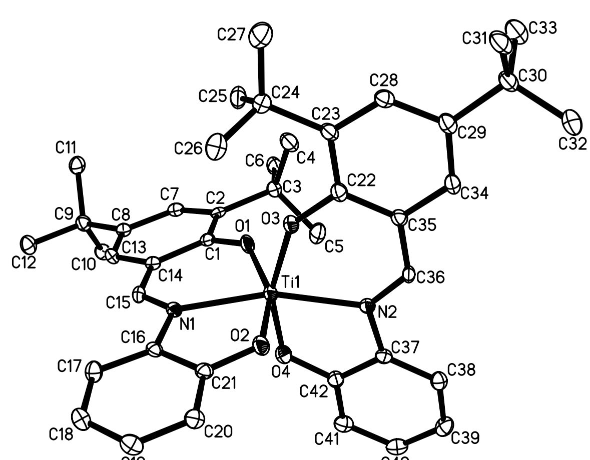


Fig. 4. An ORTEP diagram of the molecular structure of **6** showing 50% thermal ellipsoid probabilities.

Table 2
Selected bond distances (Å) and angles (°) for **3** and **4**

3		**4** [a]	
Bond distance			
Ti(1)–O(1)	1.783(4)	Ti(1)–O(1)	1.7993(17)
Ti(1)–N(1)	2.185(5)	Ti(1)–O(2)	2.0573(16)
Ti(1)–Cl(1)	2.2431(19)	Ti(1)–O(2)#1	2.0934(16)
Ti(1)–Cl(2)	2.2709(19)	Ti(1)–N(1)	2.1697(19)
Ti(1)–Cl(3)	2.4486(18)	Ti(1)–Cl(2)	2.2708(7)
Ti(1)–Cl(4)	2.5434(18)	Ti(1)–Cl(1)	2.2780(7)
Ti(2)–O(2)	1.791(4)	Ti(1)–Ti(1)#1	3.2954(9)
Ti(2)–N(2)	2.194(5)	N(1)–C(15)	1.291(3)
Ti(2)–Cl(6)	2.2518(19)	N(1)–C(16)	1.423(3)
Ti(2)–Cl(5)	2.2681(19)	O(1)–C(1)	1.348(3)
Ti(2)–Cl(4)	2.4379(18)	O(2)–C(21)	1.382(3)
Ti(2)–Cl(3)	2.5193(18)	O(2)–Ti(1)#1	2.0934(16)
Bond angles			
O(1)–Ti(1)–N(1)	83.23(17)	O(1)–Ti(1)–O(2)	151.93(7)
O(1)–Ti(1)–Cl(1)	102.71(14)	O(1)–Ti(1)–O(2)#1	93.82(7)
N(1)–Ti(1)–Cl(1)	87.66(14)	O(2)–Ti(1)–O(2)#1	74.35(6)
O(1)–Ti(1)–Cl(2)	97.98(13)	O(1)–Ti(1)–N(1)	81.03(7)
N(1)–Ti(1)–Cl(2)	175.67(14)	O(2)–Ti(1)–N(1)	74.13(7)
Cl(1)–Ti(1)–Cl(2)	96.10(7)	O(2)#1–Ti(1)–N(1)	91.67(6)
O(1)–Ti(1)–Cl(3)	159.28(14)	O(1)–Ti(1)–Cl(2)	98.77(6)
N(1)–Ti(1)–Cl(3)	86.27(13)	O(2)–Ti(1)–Cl(2)	93.37(5)
Cl(1)–Ti(1)–Cl(3)	94.62(7)	O(2)#1–Ti(1)–Cl(2)	167.23(5)
Cl(2)–Ti(1)–Cl(3)	91.29(7)	N(1)–Ti(1)–Cl(2)	88.21(5)
O(1)–Ti(1)–Cl(4)	83.11(13)	O(1)–Ti(1)–Cl(1)	101.04(6)
N(1)–Ti(1)–Cl(4)	84.25(13)	O(2)–Ti(1)–Cl(1)	103.38(5)
Cl(1)–Ti(1)–Cl(4)	169.42(7)	O(2)#1–Ti(1)–Cl(1)	86.16(5)
Cl(2)–Ti(1)–Cl(4)	91.76(6)	N(1)–Ti(1)–Cl(1)	177.09(6)
Cl(3)–Ti(1)–Cl(4)	78.09(6)	Cl(2)–Ti(1)–Cl(1)	93.48(3)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x+2, 1-y, z$; #2 $y, 1-x, 1-z$; #3 $1-y, x, 1-z$.

Table 3
Selected bond distances (Å) and angles (°) for **6**

Bond distance	
< sp = 1/2 >	
Ti(1)–O(3)	1.862(3)
Ti(1)–O(1)	1.882(3)
Ti(1)–O(4)	1.911(3)
Ti(1)–O(2)	1.925(3)
Ti(1)–N(2)	2.171(4)
Ti(1)–N(1)	2.179(4)
Bond angles	
O(3)–Ti(1)–O(1)	88.44(13)
O(3)–Ti(1)–O(4)	155.76(14)
O(1)–Ti(1)–O(4)	90.34(13)
O(3)–Ti(1)–O(2)	93.04(13)
O(1)–Ti(1)–O(2)	156.97(13)
O(4)–Ti(1)–O(2)	97.42(13)
O(3)–Ti(1)–N(2)	81.29(14)
O(1)–Ti(1)–N(2)	112.58(14)
O(4)–Ti(1)–N(2)	76.86(14)
O(2)–Ti(1)–N(2)	90.34(13)
O(3)–Ti(1)–N(1)	110.24(13)
O(1)–Ti(1)–N(1)	81.29(13)
O(4)–Ti(1)–N(1)	93.47(13)
O(2)–Ti(1)–N(1)	76.64(13)
N(2)–Ti(1)–N(1)	162.78(14)

by X-ray crystallography (Fig. 3) [12]. The Ti centers of **4** are surprisingly bridged by the oxygen atom of the sterically less hindered aryloxide moiety of each salicylaldiminato ligand. Equally interesting, the salicylaldiminato ligands are oriented such that the phenyl ring of the less substituted aryloxide moiety of one ligand is face to face with the phenyl ring of the more substituted aryloxide moiety of the second salicylaldiminato ligand. The distance from plane of the ring labeled C16–C21 to the centroid of the di-*tert*-butyl-substituted ring facing it is 3.293(3) Å, consistent with a π–π stacking interaction [13]. Bond distances and angles of **4** (Table 2) are within the expected ranges although the Ti to terminal aryloxide oxygen bond is somewhat short [Ti(1)–O(1) = 1.7993(17) Å]. This probably reflects increased donation to Ti by this aryloxide oxygen due to its orientation trans to the bridging aryloxide oxygen [Ti(1)–O(2) is much longer at 2.0573(16) Å]. That the bridging aryloxide is weakly-bound is evidenced by the quantitative formation of monomeric [L^3TiCl_2(THF)] (**5**) when **4** was dissolved in THF and stirred for 16 h (vide infra). The molecular structure of [$(L^3)_2$Ti] (**6**) revealed that the tridentate salicylaldiminato ligands are coordinated in a meridional fashion and orthogonal to one another (Fig. 4; selected bond distances and angles are presented in Table 3). In addition, the structure provides support for the molecule being C_2-symmetric in solution, as deduced on the basis of ^{1}H- and ^{13}C-NMR data (see Section 2).

With methylalumoxane (MAO) (900 molar equivalents) as co-catalyst, **1**, and **2** showed ethylene polymerization activities at 25 °C (Table 4) comparable to those reported for several noncyclopentadienyl-based Ti and Zr systems [14]. Thus, **1** and **2** are much less effective catalyst precursors than Cp_2ZrCl_2, which was 28 times more active under identical polymerization conditions, or Group 4 metal complexes based on chelating di(amido)- 2c2d2f], amine-bis(phenolato)- 2n, or bis(salicylaldiminato) 2h2i2j2k ligands. The modest ethylene polymerization activities may be due to several factors, including a low equilibrium concentration of the putative active cationic species, $[LTiMe_2]^+$ (L = $\mathbf{L^1}$ or $\mathbf{L^2}$). We presume that **2** is a somewhat more effective catalyst precursor because the active catalyst species can be more easily generated by chloride substitution. The fact that mono(salicylaldiminato) complexes **1** and **2** are much less effective catalyst precursors than bis(salicylaldiminato)Ti(IV) complexes probably reflects a decreased stability of the active cationic species, which will be more electron deficient and stabilized to a less degree by sterics than the active species generated from bis(salicylaldiminato)Ti(IV) complexes. The stabilization of the cationic species would lead to an increased concentration of the active catalyst and hence to higher activity 2n[14].

Table 4
Ethylene polymerization at 25 °C

Catalyst	mmol of catalyst	Molar excess of MAO	Time (min)	Activity (kg molcat^{-1} h^{-1})
1 [a]	0.028	900	10	14
2 [a]	0.027	900	10	30
Cp_2ZrCl_2 [a]	0.025	900	10	835
2 [b]	0.025	900	10	9

[a] 1 atm C_2H_4 pressure bubbled through toluene mixture of catalyst/MAO, which had been stirred under N_2 atmosphere for 30 min.
[b] 1 atm C_2H_4 pressure bubbled through toluene mixture of catalyst/MAO immediately after mixing.

4. Conclusions

Monomeric mono(salicylaldiminato)Ti(IV) complexes can be prepared through appropriate choice of the salicylaldiminato ligand. With MAO as co-catalyst, Ti(IV) tris(dimethylamide) and -trichloride complexes **1** and **2** showed modest activities in ethylene polymerization. The complexes are much less effective catalyst precursors than previously reported bis(salicylaldiminato) complexes of the Group 4 metals. The design and study of related complexes are currently underway in our laboratory, with the aim of developing highly active olefin polymerization catalysts.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 204405–204408 for **2**, **3**, **4**, and **6**, respectively. Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

Thanks are expressed to the US National Science Foundation (grant number CHE-9984776) for financial support of this work. NMR instruments utilized in this research were funded in part by the CRIF program of the US National Science Foundation (grant number CHE-9974810).

References

[1] See for example:(a) H. Sinn, W. Kaminsky, H. J. Vollmer, R. Woldt, Angew. Chem. Int. Ed. Engl. 19 (1980) 390;
(b) H.H. Brintzinger, D. Fischer, R. Mullhaupt, B. Rieger, R. Waymouth, Angew. Chem. Int. Ed. Engl. 34 (1995) 1143;
(c) G.J.P. Britovsek, V.C. Gibson, D.F. Wass, Angew. Chem. Int. Ed. Engl. 38 (1999) 428;
(d) S.D. Ittel, L.K. Johnson, M. Brookhart, Chem. Rev. 100 (2000) 1169;
(e) S. Matsui, M. Mitani, T. Fujita, Petrotech 24 (2001) 11.
[2] See for example:(a) D.P. Gates, S.A. Sveda, E. Onate, C.M. Killan, L.K. Johnson, P.S. White, M. Brookhart, Macromolecules 33 (2000) 2320;
(b) T.R. Younkin, E.F. Connor, J.I. Henderson, S.K. Friedrich, R.H. Grubbs, Science 287 (2000) 460;
(c) J.D. Scollard, D.H. McConville, J. Am. Chem. Soc. 118 (1996) 10008;
(d) B. Tsuie, D.C. Swenson, R.F. Jordan, Organometallics 16 (1997) 1392;
(e) T.H. Warren, R.R. Schrock, W.M. Davis, Organometallics 17 (1998) 308;
(f) F. Guerin, D.H. McConville, N.C. Payne, Organometallics 15 (1996) 5085;
(g) D.W. Stephan, F. Guerin, R.E.v.H. Spence, L. Koch, X. Gao, S.J. Brown, J.W. Swabey, Q. Wang, W. Xu, P. Zoricak, D.G. Harrison, Organometallics 18 (1999) 2046;
(h) Y. Yoshida, S. Matsui, Y. Takagi, M. Mitani, T. Nakano, H. Tanaka, N. Kashiwa, T. Fujita, Organometallics 20 (2001) 4793;
(i) S.-i. Ishii, J. Saito, M. Mitani, J.-i. Mohri, N. Matsukawa, Y. Tohi, S. Matsui, N. Kashiwa, T. Fujita, J. Mol. Catal. A 179 (2002) 11;
(j) J. Tian, P.D. Hustad, G.W. Coates, J. Am. Chem. Soc. 123 (2001) 5134;
(k) P.D. Hustad, J. Tian, G.W. Coates, J. Am. Chem. Soc. 124 (2002) 3614;
(l) T. Matsugi, S. Matsui, S. Kojoh, Y. Takagi, Y. Inoue, T. Fujita, N. Kashiwa, Chem. Lett. (2001) 566;
(m) V.C. Gibson, B.S. Kimberley, A.J.P. White, D.J. Williams, P. Howard, Chem. Commun. (1998) 313;
(n) E.Y. Tshuva, I. Goldberg, M. Kol, H. Weitman, H.; Z. Goldschmidt, Chem. Commun. (2000) 379;
(o) Y. Yoshida, J. Saito, M. Mitani, Y. Takagi, S. Matsui, S.-i. Ishii, T. Nakano, N. Kashiwa, T. Fujita, Chem. Commun. (2002) 1298.
[3] See for example:(a) A. de Blas, R. Bastida, M.J. Fuentes, Synth. React. Inorg. Met.-Org. Chem. 21 (1991) 1273;
(b) M. Goyal, S. Mishra, A. Singh, Synth. React. Inorg. Met.-Org. Chem. 31 (2001) 1705;
(c) C. Parrado, R. Bastida, A. Marcias, A. Rodriguez, A. Sousa, Synth. React. Inorg. Met.-Org. Chem. 24 (1994) 1613
[4] See for example:(a) J. Strauch, T.H. Warren, G. Erker, R. Frolich, P. Saarenketo, Inorg. Chim. Acta 300–302 (2000) 810;
(b) C. Wang, S.K. Friedrich, T.R. Younkin, R.T. Li, R.H. Grubbs, D.A. Bansleben, M.W. Day, Organometallics 17 (1998) 3149;
(c) P.R. Woodman, N.W. Alcock, I.J. Munslow, C.J. Sanders, P. Scott, J. Chem. Soc. Dalton Trans. 19 (2000) 3340;
(d) S.J. Coles, M.B. Hursthouse, D.G. Kelly, A.J. Toner, Polyhedron 19 (2000) 177;
(e) R. Fleischer, H. Wundelich, M. Braun, Eur. J. Org. Chem. (1998) 1063.
[5] D.C. Bradley, I.M. Thomas, J. Chem. Soc. Sect. A. (1960) 3857.

[6] L.E. Manzer, Inorg. Synth. 21 (1982) 135.
[7] P.A. Cameron, V.C. Gibson, C. Redshaw, J.A. Segal, G.A. Solan, A.J.P. White, D.J. Williams, J. Chem. Soc. Dalton Trans. 9 (2001) 1472.
[8] T. Kawato, H. Hiroyuki, H. Kanatomi, M. Isshiki, J. Photochem. 28 (1985) 103.
[9] V.T. Kasumov, E. Tas, Y. Yakar, F. Koeksal, R. Koeseoglu, Z. Naturforsch. Teil. B: Chem. Sci. 57 (2002) 495.
[10] Although $[L^1TiCl_3]$ (**2**) was formed in good yield, protonation of the imine nitrogen of [4,6-Bu^t_2-2-(CH=NBu^t)C_6H_3OH] also occurred, leading to formation of [{4,6-Bu^t_2-2-(CH=$NHBu^t$)C_6H_3-O}$TiCl_4$] and another unidentified titanium-containing product.
[11] Ranges for Ti–O, Ti–N, and Ti–Cl σ bond distances were estimated using covalent radii taken from the following:(a) W.M. Porterfield, Inorganic Chemistry, Academic Press, San Diego, CA 1993, p. 214;
(b) W.L. Jolly, Modern Inorganic Chemistry, McGraw Hill, Inc., New York, 1984, p. 52.
[12] The crystal lattice contained one $CHCl_3$ molecule per titanium dimer, which posed some problems in refinement. It sits almost but not quite on the 4bar symmetry element. As such, only two peaks were present in the difference map. The best model assigns the peak closest to the 4bar as 0.25C + 0.5Cl and the other peak as 0.25Cl (see Section 5).
[13] This distance is similar to the 3.35 Å interlayer spacing in graphite (A.R. West, Solid-State Chemistry and its Applications, Wiley & Sons, New York, 1984, p. 26). For a discussion of π–π stacking interaction, see for example:(a) S. Brooker, S.S. Iremonger, P.G. Plieger, Polyhedron 22 (2003) 665;
(b) C. Janiak, J. Chem. Soc. Dalton Trans. 21 (2000) 3885.
[14] (a) A. van der Linden, C.J. Schaverien, N. Meijboom, C. Ganter, A.G. Orpen, J. Am. Chem. Soc. 117 (1995) 3008;
(b) S. Fokken, T.P. Spaniol, H.-C. Kang, W. Massa, J. Okuda, Organometallics 15 (1996) 5069;
(c) L. Porri, A. Ripa, P. Colombo, E. Miano, S. Capelli, S.V. Meille, J. Organomet. Chem. 514 (1996) 213.