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Synthesis, structure and ethylene polymerization of group 4 complexes with phosphinoamide ligands

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Group 4 complexes containing diphosphinoamide ligands $[Ph_2PNR]_2MCl_2$ (3: R = ^tBu, M = Ti; 4: R = ^tBu, M = Zr; 5: R = Ph, M = Ti; 6: R = Ph, M = Zr) were prepared by the reaction of MCl_4 (M = Ti; Zr) with the corresponding lithium phosphinoamides in ether or THF. The structure of $[Ph_2PN^tBu]_2TiCl_2$ (3) was determined by X-ray crystallography. The phosphinoamides functioned as η^2-coordination ligands in the solid state and the Ti–N bond length suggests it is a simple single bond. In the presence of modified methylaluminoxane or *i*-$Bu_3Al/Ph_3BC(C_6F_5)_4$, catalytic activity of up to 59.5 kg PE/mol cat h bar was observed. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: phosphinoamide; group 4 catalyst; cocatalyst; ethylene polymerization

INTRODUCTION

Over the past decade, non-metallocene complexes have attracted extensive research interest in the quest for new olefin polymerization catalysts.[1–3] Within this area, complexes with dinitrogen-based ligands are currently receiving considerably more attention. In 1996, McConville and coworkers reported 1-hexene polymerization using a Ti-diamide catalyst activated with $B(C_6F_5)_3$.[4] After this discovery, many researchers focused on complexes of diamide-based ligands, such as iminopyrolides,[5–7]-diketiminates,[8,9] diamides[10–13] and diamides with additional donors.[14–17]

Recently, Stephan and coworkers[18–21] reported a series of new titanium catalysts containing phosphanimide ligands, most of which showed high activity for olefin polymerization under both laboratory screening and commercially relevant polymerization conditions. To the best of our knowledge, there are no reports on the use of group 4 complexes with diphosphinoamide ligands for ethylene polymerization. Kühl *et al.*[22] reported the homoleptic phosphinoamide complex $Zr(NPhPPh_2)_4$, which showed very low activity for propylene polymerization in liquid propylene.

Phosphinoamines may function as η^2-coordination ligands through the phosphor coordinating with the central metal and forming a three-membered complex. Compared with the diamide ligands, phosphinoamide ligands can satisfy to some extent the electron requirements of the electron-deficient metal center by donating the lone-pair electron of phosphor into a vacant metal orbital, and the three-membered structure will make the complex more electronically flexible, which is very important according to Fujita's FI catalysts.[23] In this paper, we would like to report the synthesis and structural characterization of several group 4 diphosphinoamide complexes and their performance in the polymerization of ethylene in the presence of modified methylaluminoxane (MMAO) and *i*-$Bu_3Al/Ph_3BC(C_6F_5)_4$.

EXPERIMENTAL

All manipulations were performed under dry argon atmosphere using standard Schlenk techniques. Solvents were dried over Na/benzophenone (ether, toluene and hexane) or CaH_2 (CH_2Cl_2) and distilled prior to use. NMR spectra were recorded on a Brucker AM300 instrument at 300 MHz at ambient temperature, C_6D_6 as solvent. Mass spectra were obtained using electron impact (EI-MS)

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and LDI-1700 (Linear Scientific Inc.). Elemental analyses were performed on an elemental Vario EL spectrometer. *n*-BuLi (1.6 M in hexane), Ph_2PCl, *t*-$BuNH_2$ and $PhNH_2$ were purchased from Aldrich and used without further purification. Modified methylaluminoxane (MMAO, 7% aluminum in heptane solution) was purchased from AkzoNobel Chemical Inc. and used as received. The ligands **1**–**2** were synthesized according to the literature.[24,25]

Synthesis of diphosphinoamide complex 3 $[Ph_2PN^tBu]_2TiCl_2$

A 3.3 ml aliquot of *n*-BuLi (1.6 M, 5.28 mmol) was added dropwise to a 20 ml Et_2O solution of ligand **1** (1.35 g, 5.27 mmol) at −78 °C for 10 min. The reaction mixture was warmed slowly to room temperature and was stirred for 3 h. The mixture was then added to a solution of $TiCl_4$ (0.5 g, 2.63 mmol) in ether (20 ml) via a cannula over 10 min at −78 °C. The red solution was allowed to warm to room temperature and stirred overnight. Then the solvent was removed *in vacuo* to give a red solid, and CH_2Cl_2 was added and stirred for 30 min and then the solution was filtered. The filtrate was concentrated to ca. 10 ml, and hexane (40 ml) was added. The product crystallized at −20 °C as red crystals. Yield: 72% (1.2 g). Anal. calcd for $C_{32}H_{38}Cl_2N_2P_2Ti$: C, 60.85; H, 6.02; N, 4.44; found: C, 60.64; H, 6.02; N, 4.51%. ^1H NMR (300 MHz, C_6D_6): δ: 7.73–6.92 (m, 20H, P-Ar-H); 1.17 [s, 18H, -$C(CH_3)$]; MS: $m/z = 631$ (M^+).

Synthesis of complex 4 $[Ph_2PN^tBu]_2ZrCl_2$

The synthesis of **4** was carried out using the same procedure as that for complex **3** except for $ZrCl_4$ in THF in place of $TiCl_4$ in Et_2O. Yield: 83%. Anal. calcd for $C_{32}H_{38}Cl_2N_2P_2Zr$: C, 56.97; H, 5.64; N, 4.15; found: C, 57.08; H, 5.61; N, 4.11%. ^1H NMR (300 MHz, C_6D_6): δ: 7.69–6.94 (m, 20H, P-Ar-H); 1.05 [s, 18H, -$C(CH_3)$]; MS: $m/z = 674$ (M^+).

Synthesis of complex 5 $[Ph_2PNPh]_2TiCl_2$

The synthesis of **5** was carried out using the same procedure as for complex **3** except that ligand **2** was used in place of ligand **1**. Yield: 88%. Anal. calcd for $C_{36}H_{30}Cl_2N_2P_2Ti$: C: 64.38; H: 4.47; N: 4.17; found: C, 64.27; H, 4.50; N, 4.21%. ^1H NMR (300 MHz, C_6D_6): δ: 7.61–7.12 (m, 20H, P-Ar-H); 6.87-6.71 (m, 10H, N-Ar-H). MS: $m/z = 671$ (M^+).

Synthesis of complex 6 $[Ph_2PNPh]_2ZrCl_2$

The synthesis of **6** was carried out using the same procedure as that for complex **4** except for ligand **2** (Ph_2PNHPh) in place of ligand **1**. Yield: 69%. Anal. calcd for $C_{36}H_{30}Cl_2N_2P_2Zr$: C, 60.50; H, 4.20; N, 3.92; found: C, 60.6; H, 4.19; N, 3.91. ^1H NMR (300 MHz, C_6D_6): δ: 7.57–7.07 (m, 20H, P-Ar-H); 6.81–6.64 (m, 10H, N-Ar-H). MS: $m/z = 714$ (M^+).

Typical polymerization procedure

A 250 ml flask was equipped with an ethylene inlet, a mechanical stirrer, and a vacuum line. The typical reaction procedure was as follows. Toluene (50 ml) and MMAO (2 M in heptane) were added into the flask (the flask was previously oven-dried and flame-dried under argon purge stream for three cycles). The toluene solution containing catalyst precursor was then injected into the flask at atmospheric pressure.

In the case of *i*-$Bu_3Al/Ph_3BC(C_6F_5)_4$ as cocatalyst, toluene (50 ml) and *i*-Bu_3Al (one-quarter of the desired content) were added into the dried flask. In a Schlenk flask, a toluene solution of catalyst (2 ml) were mixed with *i*-Bu_3Al (the other three-quarters of the desired content) and stirred for 10 min at room temperature. The resulting solution was added into the reactor with a syringe. The borate in toluene solution was added to initiate polymerization.

After 15 min, the polymerization was terminated with the addition of HCl/EtOH, and the resultant polymer was adequately washed with EtOH, H_2O, and then dried *in vacuo* at 50 °C to a constant weight.

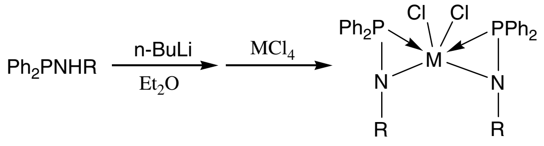
RESULTS AND DISCUSSION

Synthesis and characterization

The synthesis of complexes **3**–**6** is outlined in Scheme 1. The ligands, phosphinoamines, **1** and **2**, can be readily synthesized by reaction of chlorodiphenyl phosphine with 2 equivalents of the corresponding amines in good yields according to the literature.[24,25] After deprotonation by *n*-BuLi in ether at −78 °C, phosphinoamines **1** and **2** react with MCl_4 (M = Ti; Zr) to give the desired complexes **3**–**6**. These complexes can be isolated as red crystals (**3**) or powder (**5**) or white powder (**4, 6**).

The red single crystals of complex **3**, suitable for X-ray analysis, were grown from dichloromethane–hexane (1 : 5) at −20 °C under argon, and a crystal of **3** was sealed under argon in a glass capillary for X-ray analysis. The ORTEP of **3** is shown in Figure 1, and selected bond distances and angles are summarized in Table 1. The data collection and refinement data of the analysis are collected in Table 2.

The Ti–N bond lengths of the complex **3** [1.964(5) and 1.973(5) Å] are longer than those of the diphophinimide Ti complex ($tBu_3PN)TiCl_2$ (1.789(4) Å),[26] and CGC complexes such as $[(C_5Me_5)SiMe_2(NBu^t)]TiCl_2$ [1.907(4) Å].[27] The difference in the Ti–N bond lengths may be caused by a decrease in the relative degree of dπ–pπ bonding between Ti and



1. R = -^{t}Bu;
2. R = -Ph.

3. R = ^{t}Bu, M = Ti;
4. R = ^{t}Bu, M = Zr;
5. R = Ph, M = Ti;
6. R = Ph, M = Zr;

Scheme 1. The synthesis of complexes **3**–**6**.

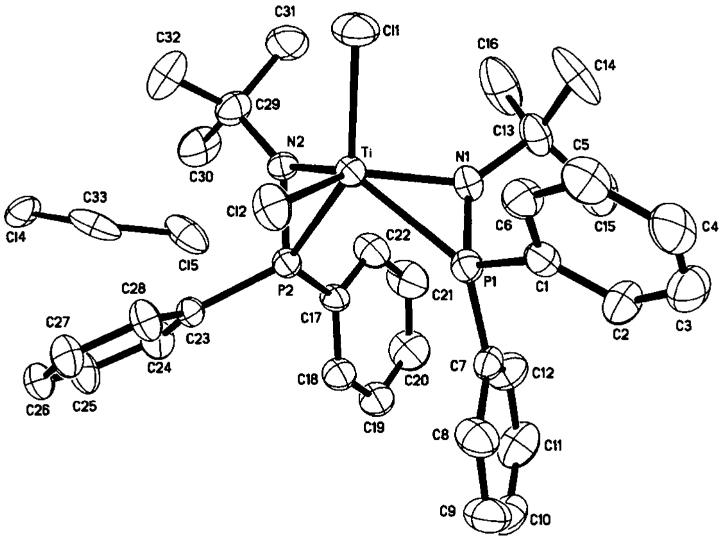


Figure 1. ORTEP drawings of **3**. Thermal ellipsoids at the 30% level are shown. The hydrogen atoms are omitted for clarity.

Table 1. Selected bond distances (Å) and angles(°) for complex **3**

Bond angles	
Ti–N(1)	1.973(5)
Ti–N(2)	1.964(5)
Ti–P(1)	2.425(2)
Ti–P(2)	2.464(2)
N(1)–P(1)	1.633(5)
N(2)–P(2)	1.638(5)
Ti–Cl(1)	2.299(2)
Ti–Cl(2)	2.3162(19)
N(1)–Ti–P(1)	42.06(14)
N(1)–P(1)–Ti	54.00(16)
P(1)–N(1)–Ti	83.95(19)
N(1)–Ti–N(2)	112.09(19)
P(1)–Ti–P(2)	94.66(7)
Cl(1)–Ti–Cl(2)	93.19(8)

N. In fact, the observed values are just a little shorter than the estimated value (2.02 Å) for titanium–nitrogen single bonds according to Pauling's covalent radii.[28] The Ti–P bond lengths [2.425(2) and 2.464(2) Å] suggest that the interaction between Ti and P is somewhat stronger than those of Ti–P found in the literature (ca. 2.63 Å),[29,30] This may be due to the electron-deficient metal center decreasing π interactions between titanium and nitrogen, which leads to more P → Ti π donation into the titanium. The P–N bonds [1.633(5) and 1.638(5) Å] show some double bond character consistent with theoretical calculations.[31] The two Cl atoms are *cis* [Cl–Ti–Cl 93.19(8)°, Ti–Cl 2.299(2) Å], and the N–Ti–N angle [112.09(19)°] is very close to that existing in the diphophinimide complex $(tBu_3PN)_2TiCl_2$ (112.9°).[26]

Table 2. Crystal data and structure refinement for **3**

Empirical formula	$C_{32}H_{38}Cl_2N_2P_2Ti\cdot 0.5CH_2Cl_2$
Formula weight	673.85
Crystal size [mm]	0.50 × 0.42 × 0.36
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	10.927(3)
b (Å)	11.086(3)
c (Å)	17.726(4)
α (deg)	93.61(2)
β (deg)	101.07(2)
γ (deg)	117.58(2)
V (Å^3)	1839.2(9)
Z	2
Density (calcd) (Mg cm^{-3})	1.217
Absorption coefficient (mm^{-1})	0.560
F(000)	702
Wavelength (Å)	0.71073
θ range for data collection (deg)	2.10–25.00
Reflection collected	7598
Data/restrains/parameters	6394/3/394
Independent reflections	6394($R_{int} = 0.0315$)
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0680, wR2 = 0.1607$
R indices (all data)	$R1 = 0.1395, wR2 = 0.1754$
Absorption correction.	Psi-scan
Goodness-of-fit on F^2	1.047
Maximum and minimum transmission	0.7950 and 0.7029
largest peak/hole in final diff. map (e Å^{-3})	0.966 and −0.348

Table 3. Polymerization of ethylene by the complex **3–6**/i-$Bu_3Al/Ph_3CB(C_6F_5)_4$[a]

Entry	Precursor (μmol)	Al : TB: complex	Yield (mg)	Activity[b]	M_v (g/mol)
1	3 (5.4)	200 : 2 : 1	12.1	8.9	—[c]
2	4 (5.7)	200 : 2 : 1	18.3	12.8	—[c]
3	5 (5.0)	200 : 2 : 1	44.2	35.3	791 000
4	6 (6.2)	200 : 2 : 1	92.3	59.5	754 000
5	6 (6.2)	100 : 2 : 1	55.3	35.7	772 000
6	6 (6.2)	400 : 2 : 1	74.6	48.1	812 000

[a] Polymerization condition: 1 atm pressure of ethylene; 20 °C; toluene 50 ml; 15min; Al = i-Bu_3Al; TB = $Ph_3CB(C_6F_5)_4$; [b] activity in kg PE/(mol cat h bar); [c] not available due to low yield of polyethylene.

Polymerization studies

The catalyst precursors **3–6** offer low to moderate activity for ethylene polymerization in combination with MMAO. The highest activity **6** (among **3–6**) was 13.5 kg PE/(mol cat h bar) at 1 atm ethylene and Al:Zr = 2000 : 1. Then, using i-Bu_3Al–$Ph_3CB(C_6F_5)_4$ as cocatalyst, complexes **3–6** were further investigated for ethylene polymerization. All exhibited moderate activity in the sequence **3** < **4** < **5** < **6**. For catalyst **6**, weak effects were observed for changes in the Al : Zr ratio (see entries 4, 5 and 6 in Table 3). Because the obtained polyethylene did not dissolve at 150 °C under the GPC measurement conditions, molecular weights were measured by Ubbelohde viscometer on ~0.08% (w/v) polymer solution in decalin at 135 °C and the following equation was used to estimate the molecular weight:[32] $\eta = 6.2 \times 10^{-4}\ M_\eta{}^{0.7}$. All of the PEs showed high viscosity molecular weights greater than 70×10^4 g/mol.

CONCLUSIONS

Group 4 complexes (**3–6**) with diphosphinoamide ligands were prepared and characterized by X-ray crystallography. Activation with modified methylaluminoxane (MMAO) or i-$Bu_3Al/Ph_3CB(C_6F_5)_4$, **3–6**, exhibited moderate activity for ethylene polymerization with high viscosity molecular weight.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 254441 for complex **3**. 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://ccdc.cam.ac.uk).

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