APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2006; **20**: 70–73 **Materials, Nanoscience and Catalysis** AOC
DOI:10.1002/aoc.1019

Titanium and zirconium complexes with aminoiminophosphorane ligands

Changhe Qi[1] **and Suobo Zhang**[2]*

[1]State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun 130022, People's Republic of China
[2]Graduate School of the Chinese Academy of Sciences, People's Republic of China

Received 10 July 2005; Revised 10 October 2005; Accepted 10 October 2005

A series of titanium and zirconium complexes based on aminoiminophosphorane ligands $[Ph_2P(Nt\text{-}Bu)(NR)]_2MCl_2$ (4, M = Ti, R = Ph; 5, M = Zr, R = Ph; 6, M = Ti, R = $SiMe_3$; 7, M = Zr, R = $SiMe_3$) have been synthesized by the reaction of the ligands with $TiCl_4$ and $ZrCl_4$. The structure of complex 4 has been determined by X-ray crystallography. The observed very weak interaction between Ti and P suggests partial π-electron delocalization through both Ti and P. The complexes 4–7 are inactive for ethylene polymerization in the presence of modified methylaluminoxane (MMAO) or $i\text{-}Bu_3Al{-}Ph_3CB(C_6F_5)_4$ under atmospheric pressure, and is probably the result of low monomer ethylene concentration and steric congestion around the central metal. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: titanium; zirconium; aminoiminophosphorane; complex

INTRODUCTION

During the past decade, more and more research groups in the field of olefin polymerizations have focused on non-metallocene catalysts, including early and late transition metals,[1–4] in order to obtain ever greater control over the properties of the resultant polymers. Some complexes have been found to be effective olefin polymerization catalysts and even living polymerizations have been observed with early transition metal complexes based on phenoxy-imines,[5–7] pyrrolide-imines[8,9] and β-enaminoketonates,[10] and late transition metal complexes based on bis(imino)pyridines,[11,12] α-dimines[13] and related ligands.

In 1999, Stephan and coworkers[14,15] reported a series of titanium phosphinimide complexes that displayed high activity for ethylene polymerization under both laboratory screening and commercially relevant polymerization conditions.

Almost at the same time, Collins *et al.*[16,17] prepared a series of group 4 iminophosphonamide complexes by reaction of iminophosphonamidinium salts $R_2P({=}NR')NHR' \cdot HCl$ with $M(NMe_2)_4$ (M = Ti or Zr), and moderate to high activity for ethylene polymerization was observed for these complexes. However, the synthesis of the salts was wasteful of primary amine (for absorbing HX), and the same substituents R′ on the two N atoms were always used.

Recently, we reported a series of group 4 complexes containing bis(phosphinoamide) ligands, and moderate ethylene polymerization activity was observed.[18] Herein, we report the synthesis, structure and preliminary ethylene polymerization behavior of a series of group 4 complexes based on aminoiminophosphorane ligands prepared by Staudinger reaction[19] of phosphinoamines with azides. These synthesis methods are more economical and the substituents on the two N atoms can be adjusted by reaction of different phosphinoamines with different azides.

EXPERIMENTAL

Materials and measurements

All manipulations were performed under an atmosphere of dry, oxygen-free argon employing standard Schlenk techniques. Solvents were distilled under argon from sodium-benzophenone (THF, Et_2O, toluene and *n*-hexane) or CaH_2 (CH_2Cl_2).

---

*Correspondence to: Suobo Zhang, State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun 130022, People's Republic of China.
E-mail: sbzhang@ciac.jl.cn
Contract/grant sponsor: National Natural Science Foundation of China; Contract/grant number: 20334030.

NMR data for ligands and complexes were obtained on a Brucker AM300 instrument at 300 MHz and ambient temperature, C_6D_6 or $CDCl_3$ as solvent with tetramethylsilane as internal standard. Mass spectra were obtained using electron impact (EI-MS) and LDI-1700 (Linear Scientific Inc.). Elemental analyses were recorded on an elemental Vario EL spectrometer.

Materials

Ph_2PCl, *t*-$BuNH_2$, *n*-BuLi (1.6 M in hexane) were obtained from Aldrich and used without purification. Modified methylaluminoxane (MMAO, 7% aluminum in heptane solution) was purchased from AkzoNobel Chemical Inc. Phosphinoamine, **1**, was synthesized according to the literature.[20]

Synthesis of ligand 2

In a 250 ml Schlenk flask, a solution of phenyl azide (4.7 g, 39.5 mmol) in Et_2O (50 ml) was added dropwise to a solution of phosphinoamine **1** (10.2 g, 39.5 mmol) in Et_2O (100 ml) at 0 °C and stirred for 8 h at room temperature. The solvents were evaporated and yielded a crude product. Pure white crystals were obtained after recrystallization from Et_2O and dried *in vacuo*. Yield: 12.23 g (89%). Anal. calcd for $C_{22}H_{25}N_2P$: C, 75.86; H, 7.18; N, 8.05%; found: C, 76.02; H, 7.11; N, 7.94%; ^1H NMR (300MHz, $CDCl_3$): 8.04–7.98 (m, 4H, Ar–H), 7.44 (m, 6H, Ar–H), 7.13–7.08 (m, 2H, Ar–H), 6.96–6.93 (m, 2H, Ar–H), 6.73–6.69 (m, 1H, Ar–H), 3.01 (b, 1H, N–H), 1.21 (s, 9H, CMe_3); MS: $m/z = 348$ (M^+).

Synthesis of ligand 3

In a 50 ml Schlenk flask, trimethylsilyl azide (3.4 ml, 25.4 mmol) was injected into phosphinoamine, **1** (6.4 g, 24.9 mmol), by syringe under argon and with magnetic stirring, and stirred for 6 h at 110 °C. The evolution of gas could be observed. Pure product was obtained after recrystallization from CH_3CN and washing with hexane and drying *in vacuo*. Yield: 7.97 g (93%). Anal. calcd for $C_{19}H_{29}N_2PSi$: C, 66.28; H, 8.43; N, 8.14%; found: C, 66.76; H, 8.37; N, 8.05%; ^1H NMR (300MHz, $CDCl_3$): 8.01–7.94 (m, 1H, Ar–H), 7.86–7.80 (m, 3H, Ar–H), 7.51–7.48 (m, 1H, Ar–H), 7.30 (m, 5H, Ar–H), 2.46 (b, 1H, N–H), 1.31 (s, 9H, CMe_3); 0.04 (s, 9H, $SiMe_3$); MS: $m/z = 344$ (M^+).

Synthesis of complex 4

In a 50 ml Schlenk flask, *n*-BuLi (1.6 M in hexane, 2.44 ml, 3.9 mmol) was syringed dropwise into a solution of ligand **2** (1.36 g, 3.9 mmol) in THF at −78 °C with magnetic stirring. The reaction mixture was warmed slowly to room temperature and stirred for 3 h. The resulting red solution was transferred by cannula to a solution of $TiCl_4$ (0.37 g, 1.95 mmol) in Et_2O at −78 °C and stirred overnight at room temperature. The solvent was removed under vaccum to give the crude product, and then 40 ml of CH_2Cl_2 were added, and the mixture was stirred for 30 min and filtered. The filtrate was concentrated to ca. 10 ml, and hexane (30 ml) was added. The product crystallized at −20 C as red crystals, and pure red crystals could be obtained after washing with hexane and drying *in vacuo*. Yield: 78% (1.25 g). Anal. calcd for $C_{44}H_{48}Cl_2N_4P_2Ti$: C, 64.94; H, 5.90; N, 6.89%; found: C, 65.11; H, 5.82; N, 6.78%; ^1H NMR (300 MHz, C_6D_6): 7.18 (b, 10H, Ar–H), 6.97 (b, 20H, Ar–H), 1.76 (s, 18H, CMe_3); MS: $m/z = 813$ (M^+).

Synthesis of complex 5

The synthesis of **5** was carried out using the same procedure as that for complex **4** except that $ZrCl_4$ in THF was used in place of $TiCl_4$ in Et_2O. Yield: 65%. Anal. calcd for $C_{44}H_{48}Cl_2N_4P_2Zr$: C, 61.68; H, 5.61; N, 6.54%; found: C, 62.04; H, 5.70; N, 6.42%; ^1H NMR (300MHz, C_6D_6): 7.26 (b, 6H, Ar–H), 7.06 (b, 10H, Ar–H), 6.84 (b, 14H, Ar–H), 1.68 (s, 18H, CMe_3); MS: $m/z = 856$ (M^+).

Synthesis of complex 6

The synthesis of **6** was carried out using the same procedure as that for complex **4** except that ligand **3** was used in place of ligand **2**. Yield: 83%. Anal. calcd for $C_{38}H_{56}Cl_2N_4P_2SiTi$: C, 58.76; H, 7.22; N, 7.22%; found: C, 59.12; H, 7.09; N, 7.13%; ^1H NMR (300MHz, C_6D_6): 7.20–7.14 (b, 12H, Ar–H), 6.96–6.89 (b, 8H, Ar–H), 1.72 (s, 18H, CMe_3); 0.37 (s, 18H, $SiMe_3$); MS: $m/z = 776$ (M^+).

Synthesis of complex 7

The synthesis of **7** was carried out using the same procedure as that for complex **6** except that $ZrCl_4$ in THF was used in place of $TiCl_4$ in Et_2O. Yield: 71%. Anal. calcd for $C_{38}H_{56}Cl_2N_4P_2SiZr$: C, 55.61; H, 6.83; N, 6.83%; found: C, 56.08; H, 6.77; N, 6.92%; ^1H NMR (300MHz, C_6D_6): 7.27–7.22 (b, 8H, Ar–H), 7.18–7.10 (b, 4H, Ar–H), 7.05–6.93 (b, 8H, Ar–H), 1.70 (s, 18H, CMe_3); 0.29 (s, 18H, $SiMe_3$); MS: $m/z = 820$ (M^+).

RESULTS AND DISCUSSION

The syntheses of the ligands **2–3** and complexes **4–7** are outlined in Scheme 1. Phosphinoamine, **1**, was prepared according to literature.[20] After oxidation of **1** with phenyl azide of trimethylsilyl azide, the aminoiminophosphoranes, **2** and **3**, were obtained in good yields (89–93%). These ligands could be readily deprotonated by *n*-BuLi; after treatment with $TiCl_4$ or $ZrCl_4$ in Et_2O or THF, the complexes **4–7** could be isolated as red crystals or white solids in yields of 65–83%.

Single crystals of complex **4** suitable for the X-ray analysis were grown from CH_2Cl_2/*n*-hexane at −20 °C under argon. The ORTEP diagram of **4** is shown in Fig. 1, and selected bond distances and bond angles are listed in Table 1 [similar data of complex $(Ph_2PNt\text{-}Bu)_2TiCl_2$[18] are also listed for comparison]; crystal data are summarized in Table 2. As shown in Fig. 1, complex **4** adopted a distorted-octahedral geometry and having approximate C_2-symmetry.

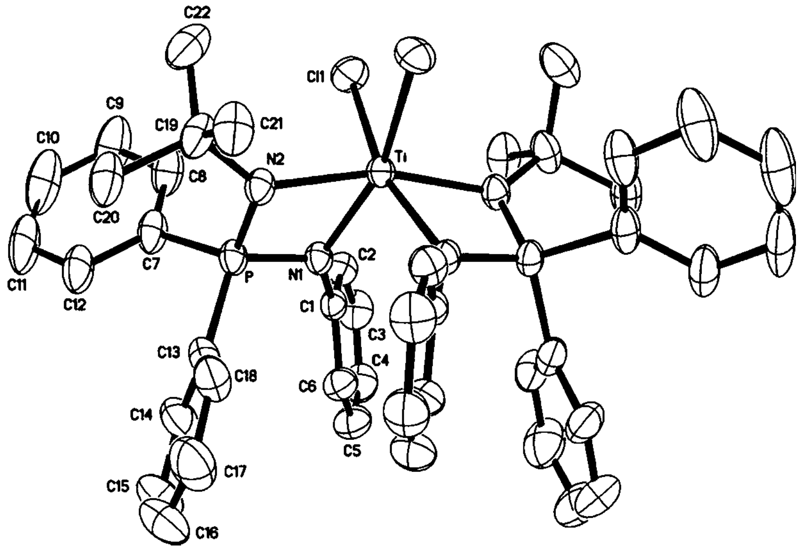
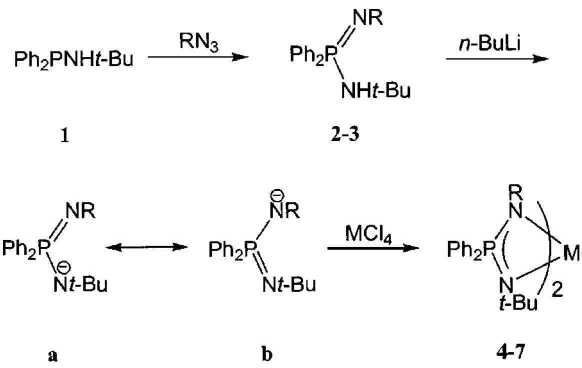


Figure 1. ORTEP drawings of **4**. Thermal ellipsoids at the 30% level are shown. The hydrogen atoms are omitted for clarity.



2: R = Ph; **3**: R = SiMe$_3$;
4: M = Ti, R = Ph; **5**: M = Zr, R = Ph;
6: M = Ti, R = SiMe$_3$; **7**: M = Zr, R = SiMe$_3$.

Scheme 1. The synthesis of complexes **4–7**.

The Ti–N bond distances of complex **4** were found to be 2.044(2) [Ti-N(Ph)] and 2.105(3) [Ti-N(*t*-Bu)] Å, and showed single bond character [slightly longer than the estimated value (~2.02 Å) for Ti–N single bonds according to Pauling's covalent radii].[21] The P–N bond lengths [P–N(Ph), 1.621(3); P–N(*t*-Bu), 1.616(3) Å] indicate that these bonds have some double bond character. The observed very weak interaction between Ti and P [Ti–P bond 2.7841(8) and 2.7842(8) Å] suggest partial π-electron delocalization through both Ti and P. From the differences of Ti–N and P–N [Ti–N(Ph) < Ti–N(*t*-Bu), P–N(Ph) > P–N(*t*-Bu)] bond distances, the anion should mainly function as b (in Scheme 1) between the two mesomeric structures (possibly caused by the difference in electron-donating ability of *t*-Bu vs electron-withdrawing of Ph), although the negative charge appears to be delocalized among N, P and N.

Table 1. Selected bond distances (Å) and angles( ) for complex **4**

Bond lengths	Complex **4**	(Ph$_2$PN*t*-Bu)$_2$TiCl$_2$
Ti–N(Ph)(1)	2.044(2)	—
Ti–N(*t*-Bu)(2)	2.105(3)	1.973(5)
Ti–P(1)	2.7841(8)	2.425(2)
Ti–P(2)	2.7842(8)	2.464(2)
P(1)–N(Ph)(1)	1.621(3)	—
P(1)–N(*t*-Bu)(2)	1.616(3)	1.638(5)
Ti–Cl(1)	2.3640(9)	2.299(2)
Ti–Cl(2)	2.3640(9)	2.3162(19)
Bond angles		
N(Ph)(1)–Ti–N(Ph)(2)	93.78(14)	—
N(t-Bu)(1)–Ti–N(*t*-Bu)(2)	164.19(15)	112.09(19)
P(1)–Ti–P(2)	119.76(4)	94.66(7)
Cl(1)–Ti–Cl(2)	86.90(5)	93.19(8)

The two N(*t*-Bu) atoms are situated in *trans* positions [N(*t*-Bu)(1)–Ti–N(*t*-Bu)(2)] 164.19(15)°, while the two N(Ph) atoms and the two Cl atoms are oriented *cis* to each other at the central metal [N(Ph)(1)–Ti–N(Ph)(2) 93.78(14)° and Cl(1)–Ti–Cl(2) 86.90(5)°]. Compared with the complex [Ph$_2$PN*t*-Bu]$_2$TiCl$_2$, the Cl–Ti–Cl bond angle of complex **4** decreased by ca. 7°, possibly due to the introduction of the imine group (=NPh).

Preliminary evaluation of complexes **4–7** as ethylene polymerization catalysts was performed in the presence of MMAO and *i*-Bu$_3$Al–Ph$_3$BC(C$_6$F$_5$)$_4$ at 20 °C and 1 atm, but only traces of polymer were obtained. It should be noted that the high polymerization activities reported by Collins were all performed at 75 psi (ca. 0.5 MPa). Similar pressure effects for polymerization activity for

Table 2. Crystal data and structure refinement for **4**

Empirical formula	$C_{44}H_{48}Cl_2N_4P_2Ti \cdot 0.5CH_2Cl_2$
Formula weight	856.07
Crystal size (mm)	0.44 × 0.42 × 0.06
Crystal system	monoclinic
Space group	C2/c
a (Å)	22.0331(12)
b (Å)	14.0272(7)
c (Å)	16.9042(9)
α (deg)	90
β (deg)	103.1150(10)
γ (deg)	90
V (Å^3)	5088.2(5)
Z	4
Density (calcd; mg cm^{-3})	1.118
Absorption coefficient (mm^{-1})	0.419
F(000)	1788
θ range for data collection [deg]	1.90-26.02
Reflection collected	13 675
Data/restrains/parameters	4936/6/263
Independent reflections	4936($R_{int} = 0.0177$)
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0701, wR2 = 0.1962
R indices (all data)	R1 = 0.0890, wR2 = 0.2318
Absorption correction.	Semi-empirical from equivalents
Goodness-of-fit on F^2	0.988
Maximum and minimum transmission	0.9753 and 0.8376
largest peak/hole in final diff map (e Å^{-3})	1.052 and −0.405

phosphinimide complexes were also observed by Stephan and coworkers.[22,23]

We have also reported a series of titanium and zirconium phenoxy-phosphinimide complexes,[24] and these complexes were inactive for ethylene polymerization at atmospheric pressure, but were highly active under ca. 0.6 MPa ethylene pressure.[25] The low activity observed appears to be caused mainly by high steric congestion around the central metal.

For complexes **4–7**, the olefin monomers will coordinate with difficulty at atmospheric pressure (lower monomer concentration), where the active species would be prone to deactivation. At higher monomer concentrations, however, coordination between the active species and the monomers will be more effective and the steric congestion could be negligible.

Ethylene polymerization and copolymerization with α-olefin by these complexes under high ethylene pressure will be reported in a subsequent paper.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 255 502 for complex **4**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336 033; e-mail: deposit@ccdc.cam.ac.uk or http://ccdc.cam.ac.uk)

Acknowledgement

The authors are grateful for financial supported by the National Natural Science Foundation of China and SINOPEC (no. 20334030).

REFERENCES

1. Britovsek GP, Gibson VC, Wass DF. *Angew. Chem. Int. Edn* 1999; **38**: 428.
2. Gibson VC, Spitzmesser SK. *Chem. Rev.* 2003; **103**: 283.
3. Ittel SD, Johnson LK, Brookhart M. *Chem. Rev.* 2000; **100**: 1169.
4. Boffa LS, Novak BM. *Chem. Rev.* 2000; **100**: 1479.
5. Matsui S, Mitani M, Saito J, Tohi Y, Makio H, Tanaka H, Fujita T. *Chem. Lett.* 1999; 1263.
6. Mitani M, Furuyama R, Mohri J, Saito J, Ishii S, Terao H, Nakano T, Tanaka H, Fujita T. *J. Am. Chem. Soc.* 2003; **125**: 4293.
7. Furuyama R, Mitani M, Mohri J, Mori R, Tanaka H, Fujita T. *Macromolecules* 2005; **38**: 1546.
8. Yoshida Y, Matsui S, Takagi Y, Mitani M, Nakano T, Tanaka H, Kashiwa N, Fujita T. *Organometallics* 2001; **20**: 4793.
9. Yoshida Y, Saito J, Mitani M, Takagi Y, Matsui S, Ishii S, Nakano T, Kashiwa N, Fujita T. *Chem. Commun.* 2002; **12**: 1298.
10. Li XF, Dai K, Ye WP, Pan L, Li YS. *Organometallics* 2004; **23**: 1223.
11. Small BL, Brookhart M, Bennett AMA. *J. Am. Chem. Soc.* 1998; **120**: 4049.
12. Britovsek GJP, Gibson VC, Kimberley BS, Maddox PJ, McTavish SJ, Solan GA, White AJP, Williams DJ. *Chem. Commun.* 1998; 849.
13. Johnson LK, Killian CM, Brookhart M. *J. Am. Chem. Soc.* 1995; **117**: 6414.
14. Stephan DW, Guérin F, Spence REvH, Koch L, Gao X, Brown SJ, Swabey JW, Wang Q, Xu W, Zoricak P, Harrison DG. *Organometallics* 1999; **18**: 2046.
15. Guérin F, Stewart JC, Beddie C, Stephan DW. *Organometallics* 2000; **19**: 2994.
16. Vollmerhaus R, Shao P, Taylor NJ, Collins S. *Organometallics* 1999; **18**: 2731.
17. Vollmerhaus R, Tomaszewski R, Shao P, Taylor NJ, Wiacek KJ, Lewis PS, Al-Humydi A, Collins S. *Organometallics* 2005; **24**: 494.
18. Qi C, Zhang S, Sun J. *Appl. Organomet. Chem.* (in press DOI:10.1002/aoc.1029).
19. Staudinger H, Meyer J. *Helv. Chim. Acta* 1919; **2**: 635.
20. Cross RJ, Green TH, Keat R. *J. Chem. Soc. Dalton* 1976; 1424.
21. Pauling L. *The Nature of the Chemical Bond*, 3rd edn. Cornell University Press: Ithaca, NY, 1960.
22. Yue N, Hollink E, Guerin F, Stephan DW. *Organometallics* 2001; **20**: 4424.
23. Hollink E, Wei P, Stephan DW. *Organometallics* 2004; **23**: 1562.
24. Qi C, Zhang S, Sun J. *J. Organomet. Chem.* 2005; **690**: 3946.
25. Hanaoka H, Azumai T. Japanese patent no. JP2003-327 594.