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Synthesis and characterization of some new organometallic complexes obtained by the reaction of bis(anilino)phosphine oxide with $TiCl_4$ and Cp_2ZrCl_2

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Abstract The bis(anilino)phosphine oxide (PhNH)₂P(O)H as a ligand reacts directly with zirconocene dichloride CP_2ZrCl_2 to afford H(PhNH)P[(NPh)OZr(Cp)_2Cl] (1), while in the presence of triethylamine as a base the ligand is deprotonated and H(O)P[(NPh)_2Zr(Cp)_2] (2) is isolated in a very good yield. When the ligand is treated with TiCl₄, however, the diligand complex $Cl_3TiO(NPh)PH(NPh)$ -PHO(Nph)TiCl₃ (3) is separated in high yield. These new compounds have been fully characterized by FT-IR, UV–Vis spectrophotometry and multi-nuclear (¹H, ³¹P) NMR spectroscopy and elemental analysis as well as XRF analysis of SEM images.

Keywords Aminophosphine · Zirconocene dichloride · Bis(anilino)phosphine oxide · Coordination chemistry

Introduction

Phosph(III/V)azane derivatives are now being widely employed as ligands in the synthesis of metallic complexes of early-transition metals [1, 2]. Such ligands usually bear N, O and P active sites as hard and soft centers and N–H bonds' functionality. Therefore, they are very useful starting materials in forming various coordination complexes with some main groups and transition metals in which they act as a monodentate or bidentate ligand [3–6]. In most synthetic routes, the Phosph(III/V)azanes act as an anionic ligand, in the presence of *n*-BuLi or a base such as triethylamine, which abstracts hydrogen from N–H bonds. However, in some cases the reaction could be carried out straightforward even in the absence of a base [7-9]. Up to date, a considerable number of organometallic compounds have been prepared using these ligands such as bis(anillino)phosphine oxide [10] and many of them have been considered as potential catalyst precursors for olefin polymerization [1, 8]. The synthesis and X-ray structural determination of selected (amino)-or (anilino)phosphine molybdenum carbonyls have also been extensively studied [11–13]. Recently, group IVB metal complexes with bis(amido)cyclodiphosph(V)azane ligands have attracted special attention as a modern generation of early-transition metal-based-polymerization catalyst. Therefore, in this research work, the synthesis of organometallic compounds $H(PhNH)P[(NPh)OZr(Cp)_2Cl]$ (1), $H(O)P[(NPh)_2Zr(Cp)_2]$ (2) and $Cl_3TiO(NPh)PH$ (NPh) $PHO(NPh)TiCl_3$ (3) are reported, which are prepared from the reaction of bis(anilino)phosphine oxide as a ligand with TiCl₄ or Cp₂ZrCl₂ at different experimental conditions. Although a variety of phosphazane systems are known, the linked Zr-Cp complexes are among the few and rare examples of commercially exploited catalysts [14]. The coordination behavior of this ligand with silicon, tin, zinc and titanocene dichloride derivatives has already been reported by this research group [15–18]. The present investigation has expanded and developed the coordination chemistry of group IVB metals phosphazane complexes.

Experimental

Apparatus and materials

All experiments were performed under nitrogen using standard Schlenk techniques. Tetrahydrofuran was treated with KOH and freshly distilled twice from sodium before use.

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Toluene and *n*-hexane were treated with calcium chloride and distilled over sodium before use. Aniline was dried over magnesium sulfate, distilled at reduced pressure and stored over it. Triethylamine was distilled over magnesium sulfate and stored over it. Phosphorus trichloride and titanium tetrachloride were used as purchased from Merck Co. The bis(anillino)phosphine oxide was prepared by previously reported procedures [10, 15]. NMR spectra were recorded on a Bruker Avance 500 and 400 MHz at ambient temperature. ¹H NMR (500.13 and 400.13 MHz) spectra were recorded using DMSO as a solvent and TMS as an external standard. ³¹P NMR spectra (202.45 and 161.97 MHz) were recorded using DMSO as a solvent and referenced to external H₃PO₄ (85 %). IR spectra were measured on a Bomen FT-IR spectrophotometer. Elemental analysis(C, H, N) was performed by the Department of Chemistry, College of Sciences Shiraz University, Shiraz, Iran. The Zr and Ti contents were determined by XRF analysis of SEM images for compounds (1), (2) and (3), respectively, and was performed by Scanning Electron Microscopy (SEM) model LEO 1455-VP in Central Laboratory, Shahid Chamran University, Ahvaz, Iran. The chloride contents for (1) and (3) were measured by potentiometric titration (argentometry).

Synthesis of H(PhNH)P[(NPh)OZr(Cp)₂Cl] (1)

In a 100-mL two-necked flask, equipped with stir bar, inlet and dropping funnel which containing 30 mL of dry toluene, Cp₂ZrCl₂ (0.292 g, 1 mmol) was dissolved at 25 °C under N₂ atmosphere. Then, (PhNH)₂P(O)H (0.232 g, 1 mmol) which was dissolved in 50 mL of dry toluene was dropwisely added. The reaction mixture was stirred at 75 °C for 24 h, then cooled to 0 °C and filtered through a medium-porosity frit. The bright-yellow filtrate was concentrated in vacuo and kept at -12 °C for 3 days. The obtained orange solid product was washed with cold toluene and dried in vacuo for 24-h yield 75 %, m.p. 128–130 °C (dec). IR (KBr, cm⁻¹): 3,331 (C–H, Ph), 2,289 (P-H), 1,219 (P=O), 3,098-2,904 (P-N), 1,494-1,596 (C=C, Ph), 1,077-1,015 (C-H, Ph). UV-Vis (DMSO, nm) λ_{max} 485. ¹H NMR (25 °C, DMSO-d₆, ppm): 7.40-7.06 (m, 20H, Ph and Cp), 9.88 (br, N-H), 7.40 (d, ${}^{1}J_{PH} = 503.5$ Hz, 1H, P–H). ${}^{31}P \{{}^{1}H\}NMR$ (25 °C, DMSO-d₆, ppm): 1.2 (singlet).

Anal. calcd. for $C_{22}H_{22}N_2OPClZr$ (%): C, 54.11; H, 4.55; N,5.74. Found (%): C, 53.84; H, 4.46; N, 5.53. Anal. calcd. (%) for $C_{22}H_{22}N_2OPClZr$: Zr, 18.69; P, 6.35; O, 3.28; Cl, 7.28. Found (XRF analysis of SEM Images) (%): Zr, 18.75; P, 6.57; O, 3.33; Cl, 7.47.

Synthesis of H(O)P[(NPh)₂ Zr(Cp)₂] (2)

In a 100-mL two-necked flask, equipped with stir bar, inlet and dropping funnel containing Et_3N (0.3 mL, 2 mmol), the

zirconium compound Cp₂ZrCl₂ (0.292 g, 1 mmol) which was already dissolved in 30 mL of dry toluene was slowly added. Then (PhNH)₂P(O)H (0.232 g, 1 mmol) in 50 mL of dry toluene was dropwisely added into the flask. The reaction was carried out under N₂ at room temperature. The brightvellow reaction mixture was stirred at 75 °C for 1 day, then cooled to 0 °C and filtered through a medium porosity frit to remove triethylammonium hydrochloride. The resulting bright-yellow filtrate was concentrated in vacuo and kept at -12 °C for several days until to afford a solid product. The product was washed with cold toluene and dried under vacuum for 24-h yield 75 % m.p. 140-142 °C (dec). IR (KBr, cm⁻¹): 2,354 (P–H), 1,172 (P=O), 3,422 (C–H in Cp), 1,277 (C-N), 909.5 (P-N), 1,444 (C-C in Cp). UV-Vis (DMSO, nm) λ_{max} 478. ¹H NMR (25 °C, DMSO-d₆, ppm): 7.11–6.34 (m, 20H, Ph and Cp) and 6.75 (d, $J_{PH} = 498.7$ Hz, 1H, P–H). ${}^{31}p$ { ${}^{1}H$ } NMR (25 °C, DMSO-d₆, ppm): -4.7 (singlet). Anal. Calcd. for C₂₂H₂₁PON₂Zr (%): C, 58.48; H, 4.7; N, 6.21. Found (%): C, 58.20; H, 4.86; N, 5.59. Anal. cald. for C₂₂H₂₁PON₂Zr (%): Zr, 20.22; P, 6.87; O, 3.55. Found (XRF analysis of SEM Images) (%): Zr, 20.81; P, 6.83; O, 3.49.

Synthesis of Cl₃TiO(NPh)PH(NPh)PHO(NPh)TiCl₃ (3)

A two-neck 100-mL round bottom flask, equipped with inlet, stir bar and dropping funnel under N2 at RT was charged with THF (30 mL), n-hexane (10 mL), Et₃N (2 mmol, 0.3 mL) and TiCl₄ (1.03 mL from a stock solution). To the cooled (0 °C) flask was added dropwise a solution of (PhNH)₂P(O)H (0.232 g, 1 mmol) dissolved in 20 mL mixture of THF: n-hexane. The obtained darkbrown suspension gradually changed to orange. This mixture was allowed to warm slowly up to room temperature and stirred for 12 h. Then, it was filtered through a medium porosity frit and the resulting orange filtrate was concentrated in vacuo until an orange product was obtained yield 78 %, m.p. 214–218 °C (dec). IR (KBr, cm^{-1}): 2,358 (P-H), 3,402 (C-H, Ph), 1,172 (P=O), 744-682 (Ph), 925 (P–N), cm⁻¹. UV–Vis (DMSO, nm) λ_{max} 487. ¹H NMR (25 °C, DMSO-d₆, ppm): 7.18(d, $J_{PH} = 571.6$ Hz, 2H, P-H) 7.05-7.41 (m, 15H, Ph). ³¹p {¹H} NMR (25 °C, DMSO-d₆, ppm): 12.9 (singlet). Anal. Calcd. for C₁₈H₁₇P₂O₂N₃Ti₂Cl₆ (%): C, 31.86; H, 2.53; N, 6.20. Found (%): C, 31.58; H, 2.67; N, 6.31. Anal. Calcd. for C₁₈H₁₇P₂O₂N₃Ti₂Cl₆ (%): Ti, 14.13; P, 9.14; O, 4.72; Cl, 31.42. Found (XRF analysis of SEM Images) (%): Ti, 14.29; P, 9.08; O, 4.57; Cl, 31.68.

Results and discussion

The bis(anilino)phosphine oxide (PhNH)₂P(O)H was prepared according to the previously reported procedures



Scheme 1 The bis(anilino) phosphine oxide ligand

[10, 15] and fully characterized before use as a phosphazane ligand (Scheme 1).

On treating of the ligand with zirconocene dichloride in 1:1 molar ratio in dry toluene, a new orange solid $H(PhNH)P[(NPh)OZr(Cp)_2Cl]$ (1) was obtained in very good yield (65 %). In this reaction, 1 mol of HCl was eliminated and (O-Zr-N) bonds were formed. In a similar manner, the reaction of the ligand with zirconocene dichloride in the presence of triethylamine in (1:1:2 molar ratio) and in dry toluene yielded the new zirconium complex $H(O)P[(NPh)_2Zr(Cp)_2]$ (2) as a pale-yellow powder (75 %). Triethylamine acts as a base and HCl acceptor and the reaction was proceeded via the elimination of 2 mol of triethylammonium hydrochloride to form N-Zr bonds. The reaction of the ligand with TiCl₄ in the presence of Et₃N in 1:2:2 molar ratio, respectively, in the mixture of dry solvents (THF-*n*-hexane 1:1) afforded an orange powder, organometallic compound formulated as Cl₃TiO(NPh)PH (NPh)PHO(NPh)TiCl₃ (3) (yield 78 %) (Scheme 2).

The reaction was proceeded via the precipitation of 2 mol of Et_3NHCl and then dimerization was occurred together with the elimination of 1 mol of aniline. The newly obtained compounds were fully characterized by



Scheme 2 The structures of the new compound (1–3)

elemental analysis, multi-nuclear (¹H, ³¹P) NMR, FT-IR spectroscopy as well as XRF analysis of SEM images and UV–Vis spectrophotometry. Reliable mass data were not obtained for these complexes.

The IR spectroscopic data show that the ligand in compounds (1) and (2) is bonded to Zr atoms through (O, N) and (N, N), respectively, and in compound (3) is bonded to Ti atoms through (O, N), and there was no indication of the presence of N–H bond in compounds (2) and (3). The P=O stretching band of ligand in compound (1) shifted to the higher frequency by almost 47 cm⁻¹, due to π -delocalization of electrons in the ring formed upon coordination to zirconium [2, 10], but this band in compound (2) was almost without variation, which indicates that this bond is not participated in the coordination. The P–H stretching band of the ligand in compound (1) is shifted 80 cm⁻¹ to the lower frequency, due to participation of P in the O–P–N moiety which is chelated to Zr(IV) center through O and N. This band is almost without change for new compounds (2) and (3).

In the ¹H NMR spectrum of compound (1), N–H and P–H resonances are observed with the appropriate relative intensities at δ 9.8 ppm (br, 1H) and δ 7.40 ppm (d, 1H) for N–H and P–H, respectively. The aromatic protons are appeared in the region of δ 7.40–7.06 ppm (m, 20H) with $J_{\rm PH} = 503.5$ Hz. The ¹HNMR spectra of (2) and (3) show P–H protons at δ 6.75 ppm (d, 1H) and at 7.18 ppm (d, 2H), for (2) and (3), respectively. $J_{\rm PH} = 498.7$ Hz for (2) and 571.6 Hz for (3) are characteristic coupling constants for these kind of compounds [4, 10, 18]. Aromatic protons of (2) and (3) appear at δ 7.1–6.34 ppm (m, 20H) and at δ 7.41–7.05 ppm (m, 15H), respectively.

In the ${}^{31}P{}^{1}H{}NMR$ of (1), (2) and (3), only one signal as a singlet is detected which proves the existence of just one type of phosphorous atom and is consistent with the proposed structures. These signals are slightly shifted to the up field with respect to the free ligand (-4.87 ppm) [10], which indicates that the ligand is coordinated to the metal.

Conclusion

In the present investigation, three new titanium and zirconium complexes (1-3) are synthesized from the reaction of bis(anilino)phosphine oxide with TiCl₄ and Cp₂ZrCl₂ at various experimental conditions and fully characterized. The results indicate that the phosphazene ligand shows different coordination preferences with Ti and Zr in the formation of monomeric or dimeric structures. Finally, it seems that the unique feature of these compounds causes them to be applicable in the field of commercial catalysis, material research and medicine which are practically unexplored to date. Studies of these applications could be an interesting subject for future investigations. Acknowledgments The authors wish to thank Shahid Chamran University Research Council, Ahvaz, Iran for financial support of this project (Grant 1391).

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