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ORIGINAL PAPER

Synthesis and characterization of $Cp_2Zr(C_9H_9O)_2$: a new zirconocene derivative catalyzed acetylation of 2-naphtol and benzyl alcohol

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Abstract The new zirconocene compound, $Cp_2Zr(C_9H_9O)_2$, was successfully prepared from the reaction of zirconocene dichloride with 1-indanol in 1:2 molar ratio in dry chloroform at the presence of triethylamine (Et_3N) and in an inert atmosphere. This compound was characterized by (^1H and ^{13}C) NMR, elemental analysis, FT-IR, UV–Vis, TGA and mass spectrum data. The catalytic activity of the synthesized compound for the acetylation of 2-naphtol and benzyl alcohol with acetic anhydride as an acetylating reagent in the solvent free conditions was also investigated. The $Cp_2Zr(C_9H_9O)_2$ as a catalyst affords an efficient and simple method for the acetylation of 2-naphtol and benzyl alcohol.

Keywords Zirconocene dichloride · 1-Indanol · Acetylation · 2-Naphtol · Benzyl alcohol · Catalytic activity

Introduction

The chemistry of compounds containing zirconocene moieties has been of great interest for many years and also has recently attracted considerable attention [1–7]. Such organometallic compounds have been used for investigating their applications either as metal-based anticancer drugs [8, 9] or as catalyst [10–12]. Furthermore, these compounds have found numerous applications as reagents in organic synthesis in order to prepare electronic materials, agrochemicals and pharmaceuticals [13–16]. In order to prepare a suitable catalyst of this kind, a ligand is needed which could bind to the zirconium atom at the center of zirconocene moieties. Most of zirconium catalysts derived from a compound containing zirconium and an oxygen donor ligand with industrial and biological applications [17–21]. Although a number of alcohols are widely used in the synthesis of zirconocene compounds, 1-indanol is also a good intermediate in the synthesis of fine chemicals and a readily available material, has not been reported as a starting material. Among zirconium compounds, zirconocene dichloride is a suitable source of zirconocene moieties and we have previously investigated the reaction of zirconocene dichloride with $(PhNH)_2P(O)H$ [22] and reported two new zirconium complexes [23].

In continuing our research on the ligands containing OH active sites toward organotin(IV) and phosphorous compounds [24, 25], we have now employed 1-indanol as a compound having OH group to investigate its interaction toward zirconocene dichloride. In this view, the new synthesized compound, $Cp_2Zr(C_9H_9O)_2$ is reported here. This compound has been characterized by FT-IR, multinuclear (^1H and ^{13}C) NMR, UV–Vis spectroscopy, TGA, elemental analysis and mass spectrometry. The acetylation is known to be an important process and highly useful reaction in the synthetic medicine intermediate as well as biologically active compounds. Besides zirconocene compounds are reported to be used as catalyst for acetylating of alcohols [26–28]. Therefore in this article we report the use of a new zirconocene compound as an efficient catalyst for acetylation of 2-naphtol and benzyl alcohol with acetic anhydride as an acetylating agent. Our results are reported below.

Experimental

Materials and instrumentation

All the experiments were performed under inert conditions in N_2 atmosphere. The solvents and Et_3N were

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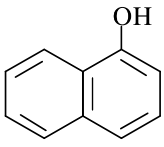
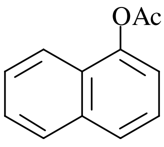
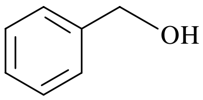
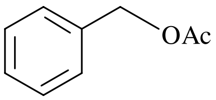
purchased from Acros, Germany and zirconocene dichloride, 1-indanol, 2-naphtol, benzyl alcohol and acetic anhydride were purchased from Merck Company. IR spectra were recorded as KBr disc from 4,000 to 400 cm^{-1} by a Bomen FT-IR spectrophotometer. Multinuclear (^{1}H and ^{13}C) NMR was recorded by a Bruker Avance 400 MHz: ^{1}H NMR (400.13 MHz) and ^{13}C NMR (100.61 MHz) in $CDCl_3$ with TMS as an external reference. The elemental analyses were performed by COSTECH ECS. The mass spectrum of the synthesized compound was obtained on a 5975C/7890S spectrometer. UV–Vis spectrum of the new compound was recorded with a double beam GBC model Cintra 101 spectrophotometer in DMSO. Thermogravimetric analysis (TGA) was performed on a STA503 instrument.

Synthesis of $Cp_2Zr(C_9H_9O)_2$

1-indanol (0.026 g, 0.20 mmol) was dissolved in 20 ml of dry $CHCl_3$. Then Et_3N (0.03 ml, 0.20 mmol) as a base, was added and stirred for 30 min in an ice bath. Zirconocene dichloride (0.030 g, 0.10 mmol) in 15 ml of dry $CHCl_3$ was added dropwise to the mixture, which was then stirred for 60 min in the ice bath. After removing the ice bath, the reaction mixture was stirred for 4 h at reflux temperature under nitrogen in the 45–50 °C. Then the reaction mixture was let to stir for another 1 h at room temperature for completion. After filtration, the remaining $CHCl_3$ was removed on a rotary evaporator and the resulting white solid product was washed with diethyl ether and dried under vacuum.

Yield 78 %, m.p. 250 °C (dec.), Anal. Calcd. for $C_{28}H_{28}O_2Zr$ (%): C, 68.98; H, 5.74; Found (%): C, 68.82; H, 5.65. IR (KBr, cm^{-1}): υ(C=C), 1,425; υ(C–H), 3,077; υ(C–O), 1,356; υ(Zr–O), 830. ^{1}H NMR (δ, ppm, $CDCl_3$): 1.31 (t, 4H), 3.00 (q, 4H) and 5.16 (t, 2H) of 1-indanol protons, 7.14 (S, 8H, aromatic protons of 1-indanol), 7.35 (S, 10H, Cp protons). $^{13}C\{^{1}H\}$ NMR (δ, ppm, $CDCl_3$): 45.8 (Cp carbons), 124.9 (aromatic carbons of 1-indanol, 35.8, 8.6 and 29.8(1-indanol carbons). Ms: *m/z* 51, 64, 77, 90, 91, 92, 94, 96, 107, 115, 133 and 224. UV–Vis (λ_{max}, nm) 253, 255, 264 and 273.

Table 1 Comparison of the results obtained for the acetylation of 2-naphtol and benzyl alcohol under: (a) new catalyst and (b) catalyst free

Entry	Substrate	Product	Yield (%)*	
			a	b
1			92	63
2			95	66

* The isolated yields are based on the starting substrates

Acetylation of 2-naphtol and benzyl alcohol by $Cp_2Zr(C_9H_9–O)_2$ as a catalyst

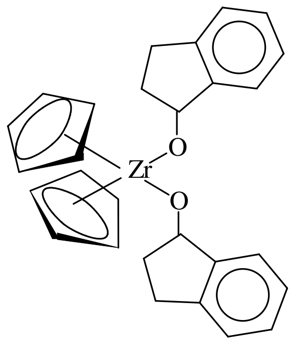
In a solvent free condition, 2-naphtol (0.360 g, 2.5 mmol) was let to react with acetic anhydride (0.24 ml, 2.5 mmol) in the presence of $Cp_2Zr(C_9H_9–O)_2$ (0.014 g, 0.03 mmol) as a catalyst for 8 h at room temperature under stirring. The reaction was monitored by means of TLC and after completion of the reaction; 2-naphthyl acetate was isolated as pure product (0.425 g, 92 % yield). The product was characterized by FT-IR spectroscopy. This reaction was also carried out at the same conditions in the absence of catalyst and the yield was 63 % (Table 1).

In a similar manner benzyl alcohol (0.26 ml, 2.5 mmol) was let to react with acetic anhydride (0.24 ml, 2.5 mmol) in the presence of $Cp_2Zr(C_9H_9–O)_2$ (0.014 g, 0.03 mmol) and the reaction was monitored by TLC. The benzyl acetate was isolated as pure product (0.439 g, 95 % yield) and characterized by FT-IR spectroscopy. This reaction was also carried out at the same conditions in the absence of catalyst and the yield was 66 % (Table 1).

Results and discussion

The reaction of zirconocene dichloride with 1-indanol was carried out in a 1:2 molar ratio. The procedure and proposed structure are shown in Scheme 1. It seems that the

$$Cp_2ZrCl_2 + 2C_9H_9OH \xrightarrow[-\,2\,Et_3NHCl]{+\,2\,Et_3N} Cp_2Zr(C_9H_9O)_2$$



Scheme 1 The synthesis procedure and the proposed structure for the new catalyst $Cp_2Zr(C_9H_9O)_2$

high Lewis acidity of the zirconocenium moiety generated from zirconocene dichloride causes zirconium metal to become susceptible to bind to oxygen atom of 1-indanol and hence facilitates the formation of $Cp_2Zr(C_9H_9{-}O)_2$. The synthesized compound was characterized by FT-IR, multinuclear (^1H and ^{13}C) NMR, elemental analysis, TGA and UV–Vis, as well as mass spectrometry. Attempts to growing single crystal suitable for X-ray crystallography were unsuccessful.

IR spectra

The IR spectrum of 1-indanol as a free ligand showed a wide absorption band centered at 3,234 cm^{-1} typical of O–H bond. This band is disappeared in the synthesized compound indicating the formation of Zr–O bond. However, the absorption bands at 1,356, 1,426, 3,077 and 829 cm^{-1} are seen in the new compound which belong to C–O, $(C{=}C)_{aromatic}$, $(C{-}H)_{aromatic}$ and Zr–O bonds, respectively.

^1H NMR spectra

The signal due to OH proton is disappeared in the ^1H NMR spectrum of the synthesized compound in $CDCl_3$. The signals at δ 1.31–1.34, 3.00–3.05 and 5.16–5.20 ppm are assigned to the protons of methylene part of 1-indanol. The Cp protons are seen at δ 7.35–7.37 ppm and the proton signals of the aromatic part of 1-indanol are appeared at δ 7.14–7.18 ppm.

^{13}C NMR spectra

In the ^{13}C NMR spectrum of this compound in $CDCl_3$, the Cp carbon signals are seen at δ 45.8 ppm. The carbon atom of 1-indanol attached to the zirconocene through oxygen, gives rise to a resonance at 35.8 ppm. Six separate carbon signals are observed in the range of δ 124.9–128.9 ppm for the aromatic part of 1-indanol in the ^{13}C NMR spectrum of this compound. Finally, the signals due to the protons of methylene part of 1-indanol are appeared at δ 8.6 and 29.8 ppm.

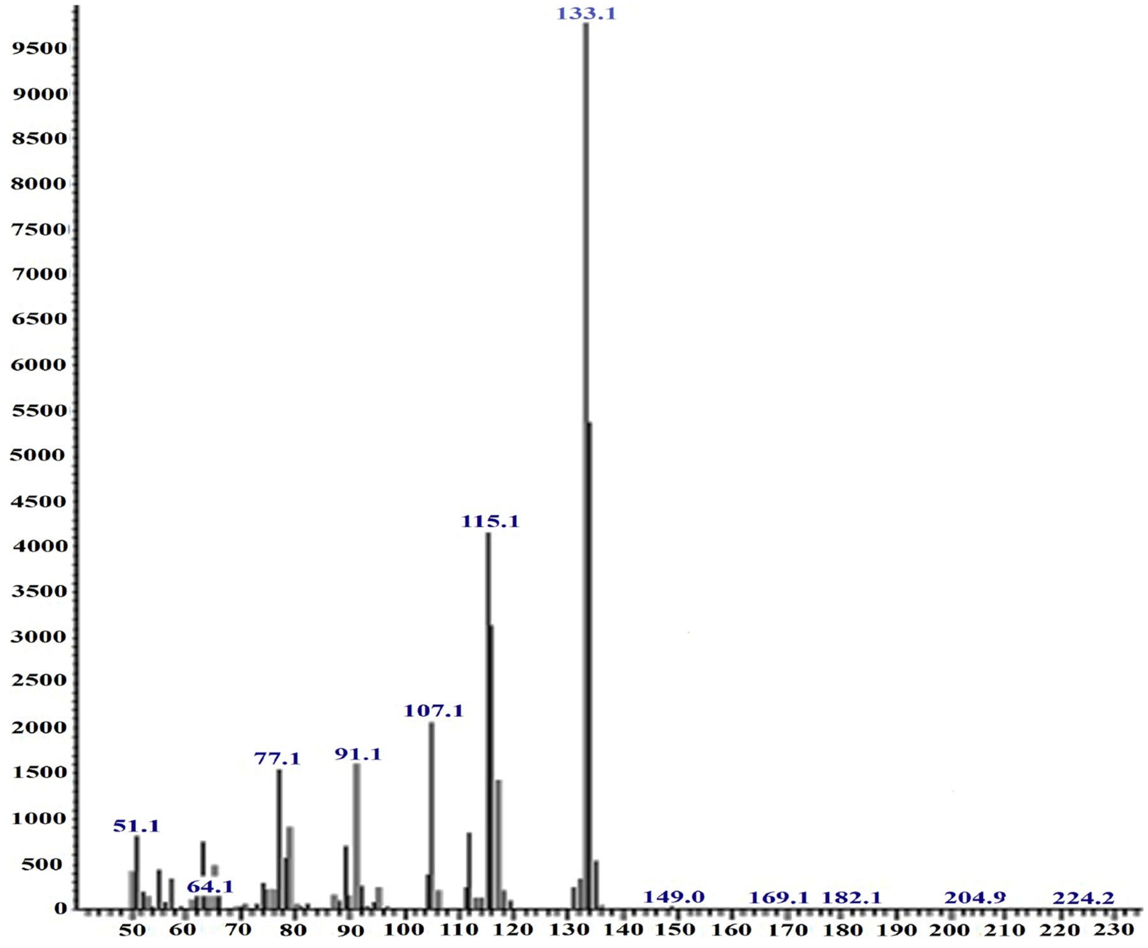


Fig. 1 The mass spectrum of $Cp_2Zr(C_9H_9O)_2$

The UV–Vis spectrum of $Cp_2Zr(C_9H_9O)_2$

Four absorption bands are observed for this compound in UV–Vis spectrum. These are corresponding to $\sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \sigma^*$ and $n \rightarrow \pi^*$ which appear at λ_{max}/nm 231, 253, 263 and 271, respectively. These absorption bands are shifted toward longer wavelengths and are seen at 233, 255, 276 and 283 nm, respectively in the new compound due to the Zr–O bonds formation.

The mass spectrum of $Cp_2Zr(C_9H_9O)_2$

The mass spectrum for the new compound (Fig. 1) is consistent with the proposed structure which suggested on basis of FT-IR, multinuclear NMR and elemental analysis data. The spectrum shows peaks at *m/z* 224, 133, 115, 107, 90, 91, 92, 94, 96, 77, 64 and 51. The peak at *m/z* 224 belongs to $Zr(C_9H_9O)$ moiety. The peak at *m/z* 133 is corresponding to C_9H_9O fragment. The peaks at *m/z* 115 and 107 are related to C_9H_7 and Zr–O fragments, respectively. The peaks at *m/z* 90, 91, 92, 94 and 96 are attributable to zirconium isotopes $^{90}Zr_{40}$, $^{91}Zr_{40}$, $^{92}Zr_{40}$, $^{94}Zr_{40}$ and $^{96}Zr_{40}$ with naturally relative abundance of 54.46, 11.23, 17.11, 17.40 and 2.80 %, respectively. As is generally the case for zirconium compounds, the presence of the isotopic pattern for Zr atom in this spectrum is a strong reason for the existence of zirconium atom in this compound. Finally the mass lines at *m/z* 64, 51 and 77 are related to the cyclopentadienyl ring and the two fragments resulting from the decomposition of the 1-indanol ligand, respectively.

Therogravimetric analysis (TGA) of $Cp_2Zr(C_9H_9–O)_2$

The new compound was heated at a rate of 10 °C/min from ambient temperature to 900 °C. Fig. 2 shows the TGA curve for $Cp_2Zr(C_9H_9–O)_2$. The first weight loss of 1.8 % from 100 to 112 °C may be attributed to the water and volatile materials. The compound is stable up to 205 °C after which a rapid weight loss of 25.2 % at about 205 °C was occurred which belongs to the elimination of a 1-indanol moiety. The TGA curve also indicates a rapid loss of a large mass about 40.9 % at 278 °C which is due to the elimination of the second 1-indanol. This is followed by weight losses of 52.8 and 62.8 % at 310 and 521 °C, respectively which could be assigned to the masses of two cyclopentadienyl rings.

The study of catalytic activity of $Cp_2Zr(C_9H_9–O)_2$

In order to examine the catalytic activity of $Cp_2Zr(C_9H_9–O)_2$, 2-naphtol and benzyl alcohol were acetylated by acetyl anhydride in the presence of this new compound as a catalyst. It was found that a trace of this catalyst is able to promote the acetylation process toward a high yields in

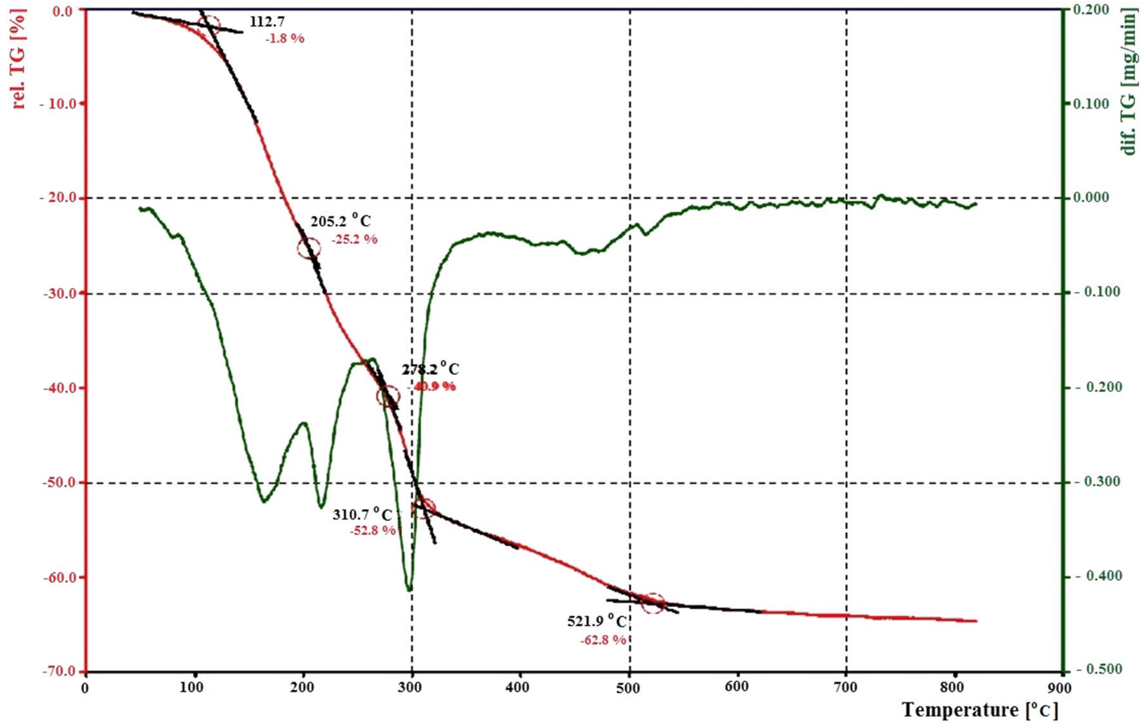


Fig. 2 Thermogravimetric analysis (TGA) curve for $Cp_2Zr(C_9H_9O)_2$

a solvent free conditions. These reactions were monitored by TLC and the products were characterized by spectroscopic techniques. Although Cp_2ZrCl_2 itself has also rarely been employed as a catalyst in organic synthesis [16] due to its weak Lewis acidity [29], it seems that C_9H_9–O species in $Cp_2Zr(C_9H_9\text{–}O)_2$ enhances the Lewis acidity of this new catalyst and therefore, considerably increasing its efficiency.

Conclusion

In conclusion, we have reported the synthesis of $Cp_2Zr(C_9H_9\text{–}O)_2$, a new derivative of zirconocene. This compound was characterized by FT-IR spectrophotometry, elemental analyses, multinuclear (^{1}H and ^{13}C) NMR spectroscopy, UV–Vis spectrophotometry, TGA, as well as Mass spectrometry. We have also demonstrated the catalytic activity of this new compound in acetylation of 2-naphtol and benzyl alcohol using acetic anhydride at room temperature in a simple method. The results indicate that the new compound has the advantages of high thermal stability and catalyst activity in the solvent free condition.

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