Preliminary communication

Novel zirconium complexes derived from C_2-symmetric diamide ligands; the X-ray crystal structure of $[Zr(\eta^1\text{-CH}_2\text{Ph})(\eta^2\text{-CH}_2\text{Ph})\{(C_6H_3)_2\text{-}2,2'\text{-}(NCH_2C_6H_4Ph\text{-}4)_2\text{-}6,6'\text{-Me}_2\}]$

F. Geoffrey N. Cloke [*], Tilmann J. Geldbach, Peter B. Hitchcock, Jason B. Love

School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, UK

Abstract

The novel alkene polymerisation cocatalysts $[Zr(CH_2Ph)_2(ArDABP)]$ containing the biphenyl-bridged ligands 2,2'-di-(N-benzyl)amino-6,6'-dimethylbiphenyl (ArDABP, Ar = $CH_2C_6H_4{}^tBu$-4 or $CH_2C_6H_4$-Ph) display averaged C_2-symmetry in solution and an η^2-benzyl coordination mode in the solid state.

Keywords: Zirconium; Diamide ligands; Olefin polymerization; Catalyses; Crystal structure

Non-metallocene complexes of Group IV metals have recently attracted considerable attention as possible alternatives for olefin polymerisation catalysts, employing N_4-macrocycles [1,2], porphyrins [3], tripodal amides [4,5], mixed cyclopentadienyl-amides [6], or -benzamidines [7] and Schiff bases [8] as spectator ligands. Such interest has, in part, stemmed from the principal that the coordination sphere of such catalysts might be more easily tuned by using non-cyclopentadienyl based ligands, leading to systems capable of stereoregular olefin polymerisation in a similar manner to metallocene catalysts that incorporate C_2-symmetric, constrained indenyl [9], or biphenyl-bridged bis(cyclopentadienyl) ligands [10]. In view of the utilisation of hard, chelating ligands as chiral auxiliaries in enantioselective organic synthesis by transition metal complexes [11], it seemed surprising that a similar approach has only recently been employed in order to exert stereochemical control on olefin polymerisation catalysts, using sterically hindered, chelating phenoxides as ancillary ligands [12]. In this communication, we report the synthesis and preliminary results on the catalytic activity of novel zirconium bis(benzyl) complexes that incorporate C_2-symmetric diamide ligands derived from 2,2'-diamino-6,6'-dimethylbiphenyl.

The benzyl-substituted diamine ligands ($ArDABPH_2$) were synthesised in high yield *via* reduction of the imines resulting from the condensation of the parent diamine with aromatic aldehydes, as outlined in Scheme 1. Reaction of the known chelating amine 2,2'-diamino-6,6'-dimethylbipheny [13] with either 4-*tert*-butylbenzaldehyde or 4-phenylbenzaldehyde in EtOH at 70°C resulted in the formation of the diimines 1 or 2 respectively, which upon treatment with LiAlH$_4$ in Et$_2$O were reduced to the benzyl substituted diamines 3 or 4. The analytical and spectroscopic data for these compounds support their proposed formulation [1]. Amines 3 and 4 are sufficiently acidic to undergo protonolysis reactions with $[Zr(CH_2Ph)_4]$, resulting in the elimination of toluene and the formation of the air and moisture sensitive dialkyldiamide complexes $[Zr(CH_2Ph)_2(ArDABP)]$ (Ar = $CH_2C_6H_4{}^tBu$-4 [5]; Ar = $CH_2C_6H_4Ph$-4 [6] respectively) (see Scheme 1) [1,2].

The crystal structure of 6 has been determined [3] and the molecular structure is shown in Fig. 1 together with selected bond distances and angles. The ligand arrangement around the Zr(IV) centre is best described as

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[*] Corresponding author.
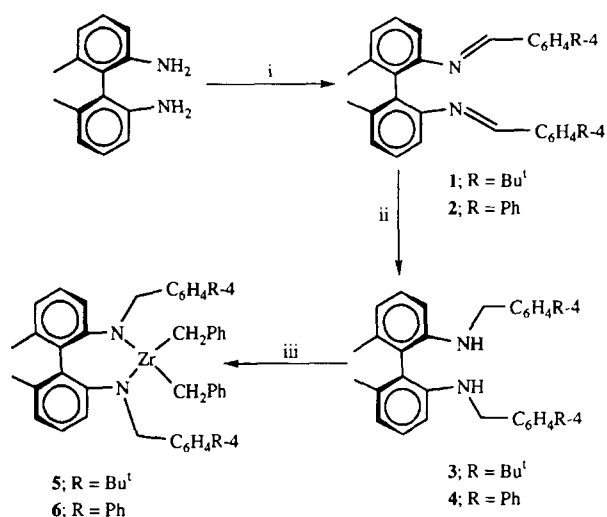
Scheme 1. Reagents and conditions: (i) (CHO)C₆H₄R-4, EtOH, 67°C, 1 h, **1** (R = ¹Bu, 85%), **2** (R = Ph, 89%); (ii) LiAlH₄, Et₂O, 25°C, **3** (83%), **4** (92%); (iii) [Zr(CH₂Ph)₄], **5** petrol (40/60), 96 h, (100% by NMR spectroscopy), **6** toluene, 48 h, (100% by NMR spectroscopy).

distorted tetrahedral, although it is evident that one of the benzyl ligands is coordinated in an η^2-fashion, characterised by an acute Zr–CH₂–C$_{ipso}$ angle [83.4(2)°]

and a short Zr–C$_{ipso}$ contact [2.570(4) Å]. Similar interactions have been observed in structurally characterised benzyl metallocene cations [14], trisbenzyl zwitterions [15], and also neutral benzylalkoxide zirconium complexes [16], and are associated with the presence of a highly electrophilic metal centre. A short Zr–C28 contact [2.678(4) Å] and acute Zr–N1–C28 angle [100.3(2)°] (c.f. > 3 Å and 124.6(2)° respectively for those involving Zr, N2 and C42) are also observed, which might be described as an η^2-amide interaction involving one phenyl ring of the biphenyl backbone.

In solution [1], both dibenzyl complexes **5** and **6** show averaged C_2-symmetry at temperatures between 320 and 180 K, with AB doublets being observed for the diastereotopic N-CH₂ and Zr-CH₂ protons. No evidence for η^2-benzyl coordination was observed by NMR spectroscopy at low temperature. The magnitude of the J_{CH} coupling constants for the benzyl CH₂carbons of ca. 130 Hz are not indicative of any agostic Zr-H-C interactions.

We have made a preliminary study of the catalytic properties of **5** and **6**. For example, a solution of **5** (0.02 mmol) in toluene (200 ml) in the presence of a large excess of methylaluminoxane polymerises ethene (Al/Zr = 3130, 10 bar, yield 3.5 g, activity 1.3 × 10⁴ g
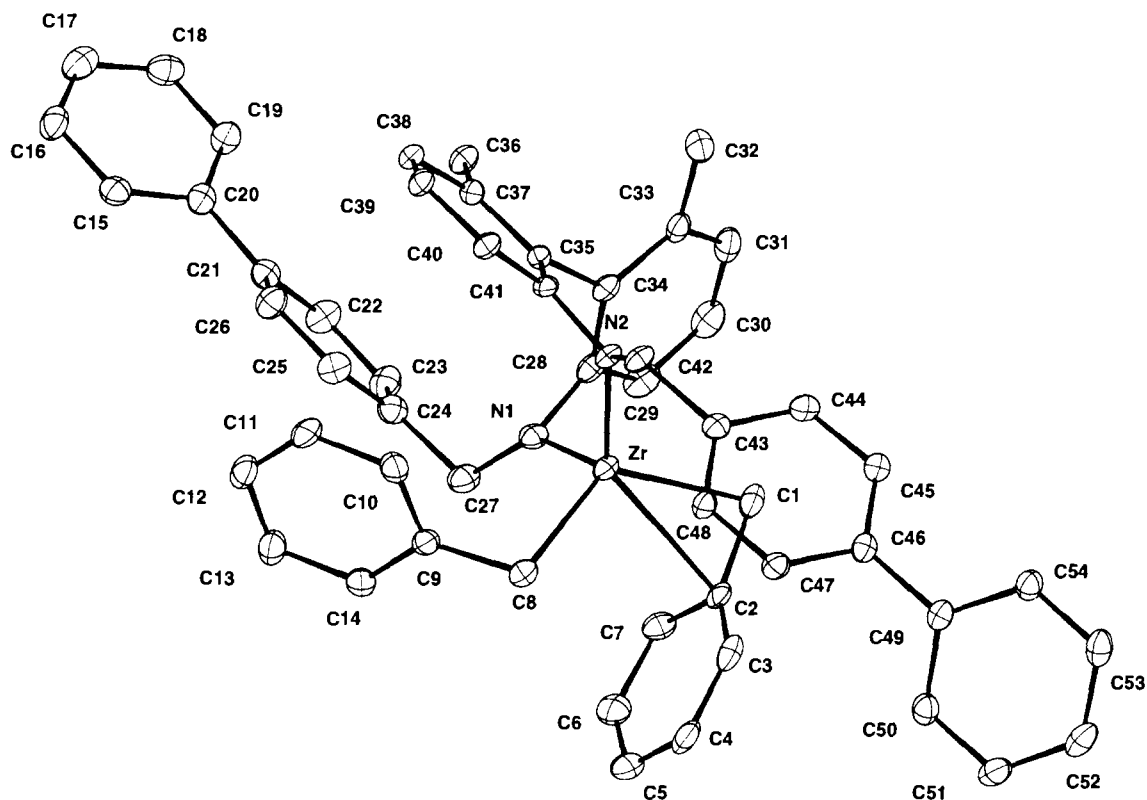
Fig. 1. Molecular structure of [Zr(CH₂Ph)₂(ArDABP)]6(Ar = CH₂C₆H₄Ph-4). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Zr–N1 2.031(3), Zr–N2 2.075(3), Zr–C8 2.289(4), Zr–C1 2.296(4), Zr–C2 2.570(4), Zr–C28 2.678(4), N1–Zr–N2 109.36(13), N2–Zr–C8 101.76(14), N2–Zr–C1 110.31(14), N1–Zr–C8 109.1(2), C1–Zr–C8 121.1(2), C2–C1–Zr 83.4(2), C9–C8–Zr 106.3(3), Zr–N1–C28 100.3(2), Zr–N2–C42 124.6(2).

Acknowledgements

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