

Preliminary communication

Novel zirconium complexes derived from C_2 -symmetric diamide ligands; the X-ray crystal structure of $[\text{Zr}(\eta^1\text{-CH}_2\text{Ph})(\eta^2\text{-CH}_2\text{Ph})\{(\text{C}_6\text{H}_3)_2\text{-2,2'-(NCH}_2\text{C}_6\text{H}_4\text{Ph-4)}_2\text{-6,6'-Me}_2\}]$

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

Received 22 August 1995

Abstract

The novel alkene polymerisation cocatalysts $[\text{Zr}(\text{CH}_2\text{Ph})_2(\text{ArDABP})]$ containing the biphenyl-bridged ligands 2,2'-di-(N-benzyl)amino-6,6'-dimethylbiphenyl (ArDABP, Ar = $\text{CH}_2\text{C}_6\text{H}_4\text{-}^t\text{Bu-4}$ or $\text{CH}_2\text{C}_6\text{H}_4\text{-Ph}$) 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

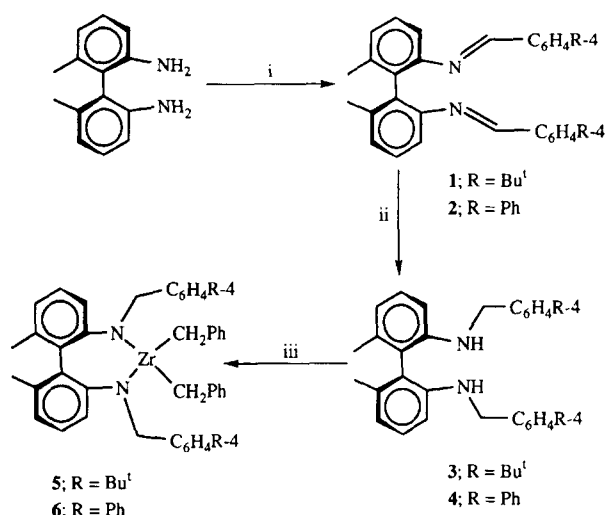
Non-metallocene complexes of Group IV metals have recently attracted considerable attention as possible alternatives for olefin polymerisation catalysts, employing N_4 -macrocycles [1,2], porphyrins [3], tripodal amides [4,5], mixed cyclopentadienyl-amides [6], or -benzamidines [7] and Schiff bases [8] 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 (ArDABPH₂) 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'-dimethylbiphenyl [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 Et₂O were reduced to the benzyl substituted diamines **3** or **4**. The analytical and spectroscopic data for these compounds support their proposed formulation¹. Amines **3** and **4** are sufficiently acidic to undergo protonolysis reactions with $[\text{Zr}(\text{CH}_2\text{Ph})_4]$, resulting in the elimination of toluene and the formation of the air and moisture sensitive dialkyldiamide complexes $[\text{Zr}(\text{CH}_2\text{Ph})_2(\text{ArDABP})]$ (Ar = $\text{CH}_2\text{C}_6\text{H}_4\text{-}^t\text{Bu-4}$ [**5**]; Ar = $\text{CH}_2\text{C}_6\text{H}_4\text{-Ph-4}$ [**6**] respectively) (see Scheme 1)^{1,2}.

The crystal structure of **6** has been determined³ 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

^{*} Corresponding author.



Scheme 1. Reagents and conditions: (i) (CHO)C₆H₄R-4, EtOH, 67°C, 1 h, **1** (R = ^tBu, 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 solution¹, both dibenzyl complexes **5** and **6** show averaged C₂-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 CH₂ carbons 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

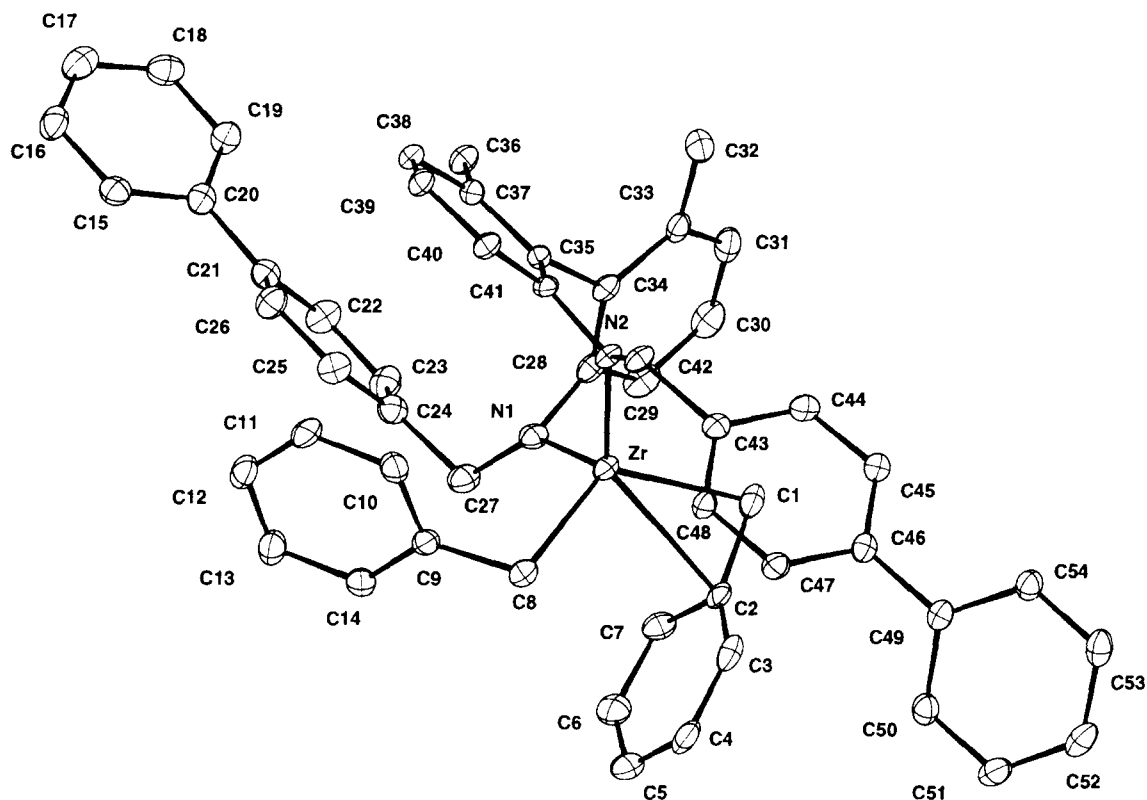


Fig. 1. Molecular structure of [Zr(CH₂Ph)₂(ArDABP)]₆ (Ar = CH₂C₆H₄Ph-4). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Zr–N1 2.031(3), Zr–N2 2.075(3), Zr–C8 2.289(4), Zr–C1 2.296(4), Zr–C2 2.570(4), Zr–C28 2.678(4), N1–Zr–N2 109.36(13), N2–Zr–C8 101.76(14), N2–Zr–C1 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).

¹ Satisfactory analyses have been obtained for all the new compounds described. Selected spectroscopic data: NMR spectra recorded at 360 MHz (¹H) or at 125 MHz (¹³C) and given as δ relative to SiMe₄ with coupling constants in Hz. C_q = quaternary C.

1: ¹H (CDCl₃): 8.20 (s, 2H, N=CH), 7.49 (d, 4H, *J*_{HH} 8.3, ¹BuPh), 7.37 (d, 4H, *J*_{HH} 8.3, ¹BuPh), 7.22 (m, 2H), 7.08 (d, 2H, *J*_{HH} 7.5), 6.80 (d, 2H, *J*_{HH} 7.7, backbone), 2.06 (s, 6H, CH₃), 1.32 (s, 18H, ¹Bu).

2: ¹H (CDCl₃): 8.15 (s, 2H, N=CH), 7.51 (m, 12H, Ph), 7.37 (t, 4H, *J*_{HH} 7.4), 7.30 (d, 2H, *J*_{HH} 7.2), 7.16 (m, 2H), 7.05 (d, 2H, *J*_{HH} 7.6), 6.78 (d, 2H, *J*_{HH} 7.6), 2.02 (s, 6H, CH₃).

3: ¹H (CDCl₃): 7.33 (d, 4H, *J*_{HH} 7.2, ¹BuPh), 7.20 (d, 4H, *J*_{HH} 7.2, ¹BuPh), 7.13 (m, 2H), 6.70 (d, 2H, *J*_{HH} 7.4), 6.55 (d, 2H, *J*_{HH} 7.8, backbone), 4.30 (d, 4H, *J*_{HH} 7.0, N-CH₂), 4.04 (t, 2H, *J*_{HH} 7.0, NH), 1.98 (s, 6H, CH₃), 1.31 (s, 18H, ¹Bu).

4: ¹H (CDCl₃): 7.55 (m, 8H), 7.43 (m, 4H), 7.36 (d, 6H, *J*_{HH} 7.2), 7.17 (t, 2H, *J*_{HH} 7.7), 6.59 (d, 2H, *J*_{HH} 8.2), 4.40 (d, 4H, *J*_{HH} 6.0, N-CH₂), 4.15 (t, 2H, *J*_{HH} 6.0, NH), 2.04 (s, 6H, CH₃).

5: ¹H (C₆D₆): 7.17 (m, 10H), 7.00 (d, 4H, *J*_{HH} 8.0), 6.90 (m, 4H), 6.76 (d, 2H, *J*_{HH} 7.3), 6.60 (d, 4H, *J*_{HH} 7.7, Ph), [4.40, 2H and 4.27, 2H, AB doublets, *J*_{HH} 14.1], [1.92, 2H and 1.50, 2H, AB doublets, *J*_{HH} 9.4], 1.50 (s, 6H, CH₃), 1.21 (s, 18H, CH₃). ¹³C(¹H): 149.8 (s, C_q), 145.2 (s, C_q), 142.0 (s, C_q), 139.0 (s, C_q), 137.5 (s, C_q), 132.6 (s, C_q), 131.0 (s, CH), 129.2 (s, CH), 129.1 (s, CH), 127.0 (s, CH), 125.3 (s, CH), 124.3 (s, CH), 123.2 (s, CH), 118.3 (s, CH), 64.93 (s, Zr-CH₂), 55.29 (s, N-CH₂), 34.40 (s, CMe₃), 31.44 (s, C(CH₃)₃), 20.67 (s, CH₃). ¹³C: 64.93 (t, *J*_{CH} 132), 55.29 (t, *J*_{CH} 134).

6: ¹H (C₆D₆): 7.45 (d, 4H, *J*_{HH} 7.3), 7.34 (d, 4H, *J*_{HH} 8.0), 7.3–7.1 (m, 12H), 7.03 (d, 4H, *J*_{HH} 8.0), 6.87 (m, 4H), 6.71 (d, 2H, *J*_{HH} 7.2), 6.62 (d, 4H, *J*_{HH} 7.4), [4.43, 2H and 4.31, 2H, AB doublets, *J*_{HH} 14.5], [2.03, 2H and 1.54, 2H, AB doublets, *J*_{HH} 9.4], 1.47 (s, 6H, CH₃). ¹³C(¹H) (CD₃C₆D₅): 144.9 (s, C_q), 141.8 (s, C_q), 141.4 (s, C_q), 140.2 (s, C_q), 139.5 (s, C_q), 139.0 (s, C_q), 132.6 (s, C_q), 130.9 (s, CH), 129.4 (s, CH), 129.1 (s, CH), 128.8 (s, CH), 127.2 (s, CH), 127.1 (s, CH), 127.0 (s, CH), 126.9 (s, CH), 124.4 (s, CH), 123.2 (s, CH), 118.4 (s, CH), 64.72 (s, Zr-CH₂), 54.88 (s, N-CH₂), 20.53 (s, CH₃). ¹³C: 64.72 (t, *J*_{CH} 132), 54.88 (t, *J*_{CH} 135).

² A typical preparation was as follows: a mixture of diamine **3** (3.0 g, 0.0059 mol) and [Zr(CH₂Ph)₄] (2.7 g, 0.0059 mol) in pentane (400 cm³) was stirred in the dark at room temperature under argon for 96 h. The solution was then filtered via cannula, and concentration of the filtrate in vacuo and slow cooling to –50°C afforded bright yellow crystals of **5** (yield: 2.64 g, 58%).

³ Crystal data for **6**: C₅₄H₄₈N₂Zr, *M* = 816.2, triclinic, space group P $\bar{1}$ (No. 2), *a* = 10.860(2), *b* = 13.037(6), *c* = 14.677(3) Å, α = 86.96(3), β = 89.60(2), γ = 84.59(3)°, *V* = 2065.8(11) Å³, *Z* = 2, *F*(000) = 852, *D*_c = 1.31 g cm^{–3}, μ = 0.31 mm^{–1}.

Data were collected on an Enraf-Nonius CAD4 diffractometer using a crystal of size 0.40 × 0.20 × 0.20 mm mounted in mineral oil at 173 (2) K. A total of 7260 unique reflections were measured for $4 < 2\theta < 50^\circ$, 5404 reflections with $|F^2| > 2\sigma(F^2)$ being used in the refinement where $\sigma(F^2) = [\sigma^2(I) + (0.041/I)^2]^{0.5}/L_p$. A correction (maximum 1.00, minimum 0.94) was applied for absorption. The structure was solved using SHELXS-86 [17], with all non-H atoms refined anisotropically by full matrix least squares using SHELXL-93 [18]. H atoms were included in the riding mode with *U*_{iso}(H) = 1.2 *U*_{eq}(C). Methyl groups were fixed at idealised geometries but with the torsion angle defining the H atom positions refined and *U*_{iso}(H) = 1.5 *U*_{eq}(C). With a weighting scheme of $\omega = \sigma^2(F)$, the final residuals were *R* = 0.053, *R*' = 0.109 with *S* = 0.912.

Tables of hydrogen atom coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

mol^{–1} h^{–1} bar^{–1}) and propene (Al/Zr = 8370, 5 bar, yield 9.1 g, activity 7×10^4 g mol^{–1} h^{–1} bar^{–1}, *M*_w/*M*_n = 2.55, *M*_w = 5000, atactic). Similar activities for ethene polymerisation are observed when employing [ZrX₂(binaphtholate)] cocatalysts [12]. Studies on the effect of variation of the nitrogen substituents on the tacticity of resultant polyolefins are currently in progress.

Acknowledgements

We thank the E.P.S.R.C. (I.P.S.I.) for financial support (to J.B.L.).

References

- [1] R. Uhrhammer, D.G. Black, T.G. Gardner, J.D. Olsen and R.F. Jordan, *J. Am. Chem. Soc.*, **115** (1993) 8493.
- [2] L. Giannini, E. Solari, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Angew. Chem. Int. Ed. Engl.*, **33** (1993) 2204; C. Floriani, S. Ciurli, A. Chiesi-Villa and C. Guastini, *Angew. Chem. Int. Ed. Engl.*, **26**, (1987) 70.
- [3] H. Brand, J.A. Capriotti and J. Arnold, *Organometallics*, **13** (1994) 4469.
- [4] M. Kol, R.R. Schrock, R. Kempe and W.M. Davies, *J. Am. Chem. Soc.*, **116** (1994) 4382 and references cited therein.
- [5] S. Friedrich, L.H. Gade, A.J. Edwards and M. McPartlin, *Chem. Ber.*, **126** (1993) 1797.
- [6] A.K. Hughes, A. Meetsma and J.H. Teuben, *Organometallics*, **12** (1993) 1936.
- [7] R. Gomez, M.L.H. Green and J.L. Haggitt, *J. Chem. Soc., Chem. Commun.*, (1994) 2607; A.N. Chernega, R. Gomez and M.L.H. Green, *J. Chem. Soc., Chem. Commun.*, (1993) 1415.
- [8] E.B. Tjaden, D.C. Swenson, R.F. Jordan and J.L. Peterson, *Organometallics*, **14** (1995) 371.
- [9] J. Ewan, *J. Am. Chem. Soc.*, **106** (1984) 6355; W. Kaminsky, K. Kulper, H.H. Brintzinger and F. Wild, *Angew. Chem., Int. Ed. Engl.*, **24** (1985) 507; H. Schnutenhaus and H.H. Brintzinger, *Angew. Chem., Int. Ed. Engl.* **18** (1989) 777.
- [10] M.E. Huttenloch, J. Diebold, U. Rief, H.H. Brintzinger, A.M. Gilbert and T.J. Katz, *Organometallics*, **11** (1993) 3600.
- [11] See, for example, S. Kobayashi and H. Ishitani, *J. Am. Chem. Soc.*, **116** (1994) 4083; K. Chibale, N. Greeves, L. Lyford and J.E. Pease, *Tetrahedron: Asym.*, **4** (1993) 2407; M. Terada, K. Mikami and T. Nakai, *J. Chem. Soc., Chem. Commun.*, (1990) 1623.
- [12] A. van der Linden, C.J. Schaverien, N. Meijboom, C. Ganter and A.G. Orpen, *J. Am. Chem. Soc.*, **117** (1995) 3008.
- [13] T.L. Marxen, B.J. Johnson, P.V. Nilsson and L.H. Pignolet, *Inorg. Chem.*, **23** (1984) 4663 and references cited therein.
- [14] D.J. Crowther, S.M. Borkowsky, D. Swenson, T.Y. Meyer and R.F. Jordan, *Organometallics*, **12** (1993) 2897; R.F. Jordan, R.E. LaPointe, N. Baenziger and G.D. Hinch, *Organometallics*, **9** (1990) 1539; R.F. Jordan, R.E. LaPointe, C.S. Bajgur, S.C. Echols and R. Willett, *J. Am. Chem. Soc.*, **109** (1987) 4111.
- [15] C. Pellacchia, A. Grassi and A. Immirzi, *J. Am. Chem. Soc.*, **115** (1993) 1160.
- [16] S.L. Latesky, A.K. McMullen, G.P. Niccolai, I.P. Rothwell and J.C. Huffman, *Organometallics*, **4** (1985) 902.
- [17] G.M. Sheldrick, SHELXS 86, University of Gottingen, 1986.
- [18] G.M. Sheldrick, SHELXL 93, University of Gottingen, 1993.