Novel zirconium complexes of amine bis(phenolate) ligands. Remarkable reactivity in polymerization of hex-1-ene due to an extra donor arm†

Edit Y. Tshuva,[a] Israel Goldberg,[a] Moshe Kol,*[a] Hana Weitman[b] and Zeev Goldschmidt*[b]

[a] *School of Chemistry, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel Aviv University, Tel Aviv 69978, Israel. E-mail: moshekol@post.tau.ac.il*

[b] *Department of Chemistry, Bar-Ilan University, Ramat-Gan 52900, Israel. E-mail: goldz@mail.biu.ac.il*

Received (in Cambridge, UK) 11th January 2000, Accepted 2nd February 2000

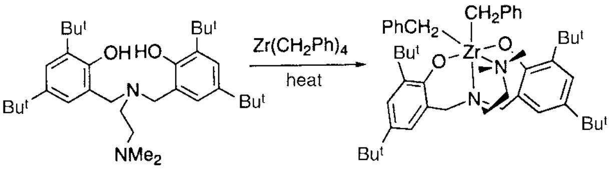
Zirconium complexes of two dianionic amine bis(phenolate) ligands have been synthesized, their X-ray structures solved, and their activity as hex-1-ene polymerization catalysts studied; upon treatment with $B(C_6F_5)_3$, an octahedral $[ONNO]Zr(CH_2Ph)_2$ complex, having an extra N-donor group on a side arm, shows exceptionally high polymerization activity and yields a high molecular weight poly(hex-1-ene), whereas a related pentacoordinate $[ONO]Zr(CH_2Ph)_2$ complex, having no extra donor group, shows only poor activity as a polymerization catalyst.

The increased interest in development of novel catalysts for polymerization of α-olefins has resulted in the introduction of a variety of non-metallocene group 4 metal complexes.[1] Most interest was drawn to pre-catalysts based on chelating di(amido) ligands,[2] while di(alkoxo) based pre-catalysts have attracted more limited attention.[3] Recently, we introduced the amine bis(phenolate) family of ligands to group 4 transition metal chemistry.[4] Here, we report on the synthesis, structure and hex-1-ene polymerization activity of two zirconium dibenzyl complexes of related amine bis(phenolate) ligands: a tetradentate $[ONNO]^{2-}$ ligand and a tridentate $[ONO]^{2-}$ ligand.

The ligand precursor $[ONNO]H_2$ **1** reacted cleanly with 1 mol equiv. of tetrabenzylzirconium at 65 °C yielding the dibenzyl complex $[ONNO]Zr(CH_2Ph)_2$ **2**, quantitatively, as a yellow crystalline solid (Scheme 1).† The spectral data of **2** indicate the formation of a rigid C_s symmetrical complex having symmetry related phenolate rings and two different benzyl groups.

The X-ray structure of **2** (Fig. 1)‡ features a complex having a slightly distorted octahedral geometry, in which the two oxygen atoms of the phenolate rings are in a *trans* configuration. Most importantly, the *cis* configuration of the two benzyl groups, expected from the arrangement of the donor atoms in this $[ONNO]^{2-}$ tetradentate ligand, is evident from the narrow C–Zr–C angle of 93.7°. A narrow angle between the active positions may facilitate the formation of a metallacyclobutane, in the rate determining step of the polymerization of α-olefins.[5]

The tridentate ligand precursor $[ONO]H_2$ **3**, having identical phenolate groups but lacking the extra donor group on the side arm, also reacted cleanly with 1 mol equiv. of tetrabenzylzirconium at 65 °C yielding the formally penta-coordinate dibenzyl complex $[ONO]Zr(CH_2Ph)_2$ **4**, quantitatively, as a yellow crystalline solid (Scheme 2).†



$[ONNO]H_2$ **1** $[ONNO]Zr(CH_2Ph)_2$ **2**

Scheme 1

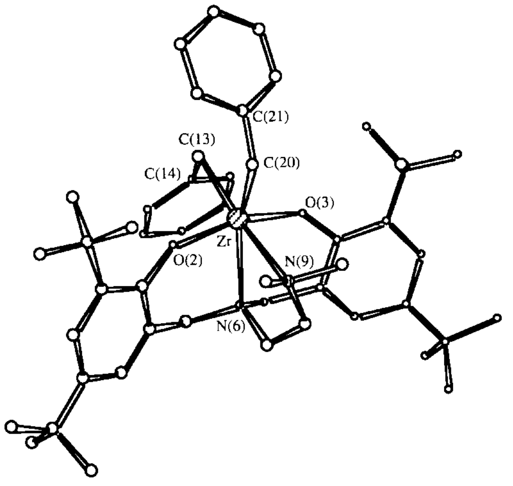
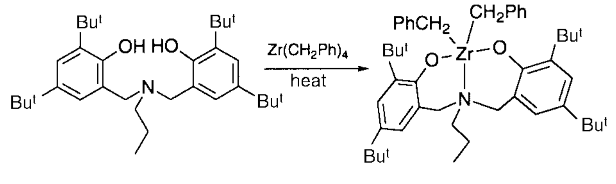


Fig. 1 Molecular structure of **2**. Selected bond lengths (Å) and angles (°): Zr–O(2) 1.995(5), Zr–O(3) 1.994(5), Zr–N(6) 2.446(6), Zr–N(9) 2.594(6), Zr–C(13) 2.305(7), Zr–C(20) 2.250(6); O(2)–Zr–O(3) 160.3 (2), N(6)–Zr–N(9) 69.7(2), C(13)–Zr–C(20) 93.7(2), Zr–C(13)–C(14) 104.9(5), Zr–C(20)–C(21) 115.8(5).

Interestingly, a homoleptic complex of the type $[ONO]_2Zr$, was not formed, apparently due to the steric effect of the *tert*-butyl groups in the *ortho* position of the phenolate rings.[4] In analogy to **2**, the spectral data of **4** also indicated the formation of a rigid C_s symmetrical complex having symmetry related phenolate rings and two different benzyl groups. However, the X-ray crystal structure of **4** indicated several differences between it and **2** (Fig. 2).‡

The structure features a complex having a pseudo-trigonal bipyramidal geometry, with axial O atoms and equatorial N, C, C atoms, as evident from an O–Zr–O angle of 157.3°, and sum of angles between the equatorial substituents around the zirconium of 360°. The angle between the two benzyl groups in **4** is much wider than in **2**, at 117.4°. An acute $Zr–CH_2–C(Ar)$ angle of 89.4° as well as a short Zr–C(Ar) distance of 2.71 Å, for one of the benzyl groups, indicate that the π-system interacts with the metal, *i.e.* there is a non-classical η^2 binding of this group to the Zr atom.[6] The η^2 binding in **4** may reflect the



$[ONO]H_2$ **3** $[ONO]Zr(CH_2Ph)_2$ **4**

Scheme 2

---

† Electronic supplementary information (ESI) available: selected spectroscopic data. See http://www.rsc.org/suppdata/cc/b0/b000396o/

DOI: 10.1039/b000396o

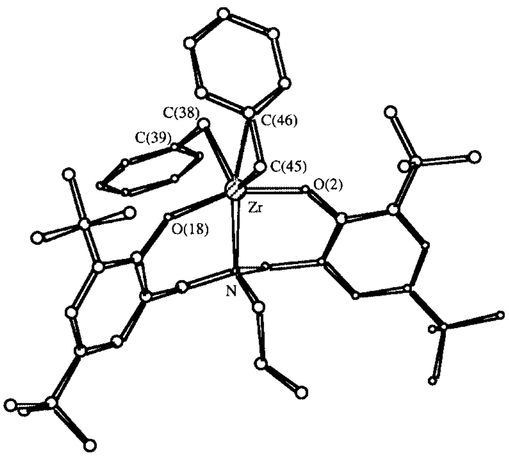


Fig. 2 Molecular structure of **4**. Selected bond lengths (Å) and angles (°): Zr–O(2) 2.002(2), Zr–O(18) 2.000(2), Zr–N 2.378(2), Zr–C(38) 2.272(2), Zr–C(45) 2.292(2), Zr–C(46) 2.714(2); O(2)–Zr–O(18) 157.33(6), C(45)–Zr–C(38) 117.39(9), Zr–C(45)–C(46) 89.4(1), Zr–C(38)–C(30) 108.7(2).

electron deficiency of this complex relative to **2**, or may simply result from the lower crowding around the metal, allowing the bending of one of the benzyl groups. It is noteworthy that the central nitrogen and the two phenolate rings bind very similarly in **2** and **4**, despite the additional donor in **2**, and difference in benzyl hapticities.

Which of these systems is expected to lead to a better catalyst for polymerization of α-olefins? Since additional donor groups have been reported to increase the reactivity in certain systems[7] and reduce the reactivity in other systems,[8] this prediction is not straightforward. **2** proved to be an extremely reactive catalyst in the presence of tris(pentafluorophenyl)borane: adding 0.01 mmol of **2** and 1 mol equiv. of $B(C_6F_5)_3$ to 10 mL of neat hex-1-ene at room temperature, initiated a fast polymerization reaction accompanied by heat release, causing boiling of the hex-1-ene.§ The monomer reacted almost completely within 2 min giving an activity of 15 500 g $mmol_{cat}^{-1}$ h^{-1}. To the best of our knowledge, this is the highest reactivity reported for polymerization of hex-1-ene under such mild conditions, namely a dibenzyl complex[9] activated by the mild Lewis acid tris(pentafluorophenyl)borane.[2a,10] In order to restrain the polymerization, the monomer was diluted in an inert solvent, and the quantity of catalyst was reduced. Thus, adding 0.005 mmol of **2** and 1 mol equiv. of $B(C_6F_5)_3$ to 3 mL of hex-1-ene in 7 mL of heptane resulted in a slower evolution of heat, and linear consumption of the monomer for 8 min, after which time 80% had reacted. The polymer obtained had a molecular weight of M_w = 170 000 and PDI M_w/M_n = 2.2, indicating that the catalytic system is homogeneous.

In contrast, **4** yielded a poor hex-1-ene polymerization catalyst: adding 0.01 mmol of **4** and 1 mol equiv. of $B(C_6F_5)_3$ to 2 mL of neat hex-1-ene at room temperature, yielded only oligo(hex-1-ene) chains (30 mg), giving a low activity of 23 g $mmol_{cat}^{-1}$ h^{-1}. Olefinic termination groups were observed in the ^{1}H NMR spectra, integration of which indicated an average of < 20 units of monomer per chain.

In summary, of the two amine bis(phenolate) zirconium complexes that were introduced, that having an extra donor arm was about three orders of magnitude more reactive than its counterpart. We therefore propose that the side arm nitrogen of the $[ONNO]^{2-}$ ligand remains attached to the metal in the reactive catalyst. Since the extra donor is supposed to *lower* the electrophilicity of the zirconium complex, it seems that, at least for these systems, electrophilicity does not play a major role in determining the polymerization activity.[11] The extreme reactivity of the catalyst derived from the $[ONNO]^{2-}$ ligand may result from steric effects, *e.g.* a narrow angle between the growing polymer chain and a coordinated olefin, as well as electronic effects induced by the N-donors being *trans* to the active positions. The synthesis of related systems and their application as polymerization catalysts is currently under way.

This research was supported in part by the Israel Science Foundation founded by the Israel Academy of Sciences and Humanities. We thank Sima Alfi (BIU) for technical assistance.

Notes and references

‡ *Crystal data*: for **2**: $C_{53}H_{80}N_2O_2Zr{\cdot}C_5H_{12}$, M = 868.41, orthorhombic, space group *Pbca*, a = 18.4520(10), b = 19.1310(19), c = 28.2390(10) Å, U = 9968.5(8) Å^3, Z = 8, D_c = 1.157 g cm^{-3}, μ(Mo-Kα) = 0.260 mm^{-1}, T = 117 K, Enraf-Nonius Kappa-CCD, 9375 reflections were measured (R_{int} = 0.000). The structure was solved by direct methods and refined by full-matrix least-squares on F^2. In the crystal, the dimethylamino(ethyl) arm was found to be disordered. The unit cell contains one molecule of disordered pentane, which could not be modelled precisely. When its contribution to the structure factors was substracted by the 'Bypass' procedure,[12] the final refinement converged at R_1 = 0.1028 and wR_2 = 0.2636 for observations with $[I > 2\sigma(I)]$ and R_1 = 0.1480 and wR_2 = 0.2853 for all data. For **4**: $C_{54}H_{81}NO_2Zr{\cdot}C_7H_{16}$, M = 867.42, monoclinic, space group $P2_1/c$, a = 10.4840(1), b = 19.2970(4), c = 24.5940(5) Å, β = 91.048(1)°, U = 4974.77(15) Å^3, Z = 4, D_c = 1.158 g cm^{-3}, μ(Mo-Kα) = 0.259 mm^{-1}, T = 116 K, Enraf-Nonius Kappa-CCD, 12508 reflections were measured. The structure was solved by direct methods and refined by full-matrix least squares on F^2. In the crystal, one of the Bu^t groups was found to be disordered. The unit cell contains one molecule of disordered heptane. The final refinement converged at R_1 = 0.0493 and wR_2 = 0.1295 for observations with $[I > 2\sigma(I)]$ and R_1 = 0.0624 and wR_2 = 0.1377 for all data. CCDC 182/1535. See http://www.rsc.org/suppdata/cc/b0/b000396o/for crystallographic files in .cif format.

§ The extreme reactivity of this catalytic system was even more pronounced in the polymerization of oct-1-ene: adding 0.01 mmol of **2** and 1 mol equiv. of $B(C_6F_5)_3$ to 2 mL of neat oct-1-ene at r.t. caused boiling of the oct-1-ene (bp = 123 °C), which was almost completely consumed within 2 min.

1 G. J. P. Britovsek, V. C. Gibson and D. F. Wass, *Angew. Chem., Int. Ed.*, 1999, **38**, 428.

2 (*a*) J. D. Scollard, D. H. McConville, N. C. Payne and J. J. Vittal, *Macromolecules*, 1996, **29**, 5241; (*b*) J. D. Scollard and D. H. McConville, *J. Am. Chem. Soc.*, 1996, **118**, 10 008; (*c*) R. Baumann, W. M. Davis and R. R. Schrock, *J. Am. Chem. Soc.*, 1997, **119**, 3830; (*d*) M. Aizenberg, L. Turculet, W. M. Davis, F. Schattenmann and R. R. Schrock, *Organometallics*, 1998, **17**, 4795; (*e*) L.-C. Liang, R. R. Schrock, W. M. Davis and D. H. McConville, *J. Am. Chem. Soc.*, 1999, **121**, 5797; (*f*) S. Tinkler, R. J. Deeth, D. J. Duncalf and A. McCamley, *Chem. Commun.*, 1996, 2623; (*g*) Y.-M. Jeon, S. J. Park, J. Heo and K. Kim, *Organometallics*, 1998, **17**, 3161; (*h*) V. C. Gibson, V. S. Kimberley, A. J. P. White, D. J. Williams and P. Howard, *Chem. Commun.*, 1998, 313.

3 A. van der Linden, C. J. Schaverien, N. Meijboom, C. Ganter and A. G. Orpen, *J. Am. Chem. Soc.*, 1995, **117**, 3008; E. B. Tjaden, D. C. Swenson, R. F. Jordan and J. L. Petersen, *Organometallics*, 1995, **14**, 371; S. Fokken, T. P. Spaniol, J. Okuda, F. G. Sernetz and R. Mülhaupt, *Organometallics*, 1997, **16**, 4240; L. Matilainen, M. Klinga and M. Leskalä, *J. Chem. Soc., Dalton Trans.*, 1996, 219.

4 E. Y. Tshuva, M. Versano, I. Goldberg, M. Kol, H. Weitman and Z. Goldschmidt, *Inorg. Chem. Commun.*, 1999, **2**, 371.

5 N. A. H. Male, M. Thornton-Pett and M. Bochmann, *J. Chem. Soc., Dalton Trans.*, 1997, 2487.

6 F. G. N. Cloke, T. J. Geldbach, P. B. Hitchcock and J. B. Love, *J. Organomet. Chem.*, 1996, **506**, 343.

7 L. Porri, A. Ripa, P. Colombo, E. Miano, S. Capelli and S. V. Meille, *J. Organomet. Chem.*, 1996, **514**, 213; F. G. Sernetz, R. Mülhaupt, S. Fokken and J. Okuda, *Macromolecules*, 1997, **30**, 1562.

8 F. J. Schattenmann, R. R. Schrock and W. M. Davis, *Organometallics*, 1998, **17**, 989.

9 A. D. Horton and J. de With, *Organometallics*, 1997, **16**, 5424.

10 Y.-X. Chen, P. F. Fu, C. L. Stern and T. J. Marks, *Organometallics*, 1997, **16**, 5958.

11 T. H. Warren, R. R. Schrock and W. M. Davis, *Organometallics*, 1998, **17**, 308.

12 P. Van der Sluis and A. L. Spek, *Acta Crystallogr., Sect. A*, 1990, **46**, 194.

Communication b000396o