

Is the metallocene (3-THF-CH₂-Cp)₂ZrCl₂ a better catalyst than the corresponding 2-THF derivative for olefin polymerisation? A molecular modelling study

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Semi-empirical, *ab initio* and density functional calculations performed on the active intermediates (2-THF-CH₂-Cp)₂Zr⁺-CH₃ and (3-THF-CH₂-Cp)₂Zr⁺-CH₃ indicate that the former is more stable as an intra-molecular complex by up to 21.6 kcal mol⁻¹ and is, therefore, a less efficient catalyst for olefin polymerisation.

Incorporating metallocenes onto inorganic supports (TiCl₃ on MgCl₂) for industrial polymerisation of olefins is a major technical challenge. Anchoring traditional Group IV metallic catalysts, *e.g.* Cp₂ZrCl₂, to the support by mono-substitution of each Cp ring with an appropriate 'tethering' group containing a Lewis base is an attractive strategy. Experimentally, in the homogeneous polymerisation of ethylene¹ by (2-THF-CH₂-Cp)₂ZrCl₂ (Fig. 1), the activity was found to be low compared

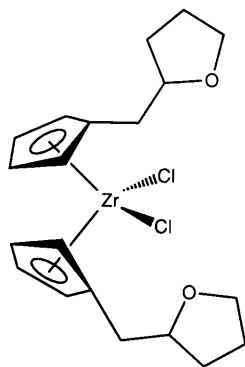


Fig. 1 The structure of (2-THF-CH₂-Cp)₂ZrCl₂

to the parent Kaminsky^{2,3} catalyst. This was rather surprising in view of the fact that any C-substitution in the Cp rings usually gives rise to a marginal increase in the activity of the catalyst. It was, therefore, suspected that the active catalytic site (2-THF-CH₂-Cp)₂Zr⁺-CH₃ (generated by MAO alkylation and Cl⁻ abstraction from the dichloride derivative), could suffer from an intra-molecular complexation of the ether group to the electrophilic Zr centre (see Fig. 2). Ether co-ordination would, of course, compete with ethylene insertion and result in slow polymerisation.

To verify this hypothesis, we have carried out semi-empirical,[†] *ab initio*[‡] and density functional (DFT)[§] calculation on the proposed catalytically active intermediate (Fig. 2). Since the evidence for or against internal complexation is unlikely from the study of a single intermediate, we have carried out these calculations on both the 2-THF and 3-THF (see Fig. 3) complexes. The results on the optimised energies and geometries are shown in Tables 1 and 2 respectively.

Semi-empirical calculations yielded on geometry optimisation an energy difference of only 2.9 kcal mol⁻¹ between the 2-THF and 3-THF complexes. This is too small a difference to preclude the formation of an internal complex by one of the

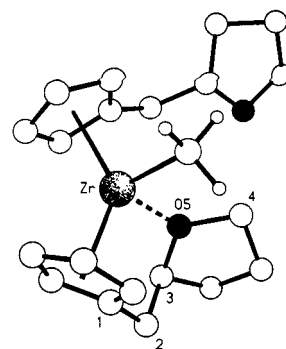


Fig. 2 The structure of the 2-THF cation

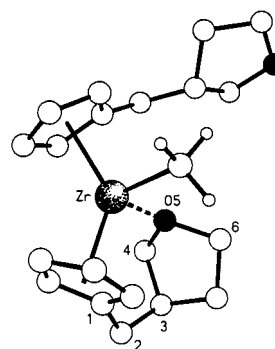


Fig. 3 The structure of the 3-THF cation

Table 1 Energies (kcal mol⁻¹) of the two cations at the semi-empirical (PM3), uncorrelated (HF) and correlated (DFT) levels. The bottom row shows the energy differences

Cation	PM3	HF	DFT
2-THF	-68.5	-629093.9	-677570.5
3-THF	-65.4	-629074.5	-677548.9
ΔE	2.9	19.4	21.6

Table 2 Selected geometry values for the two cations: angles shown in degrees and distances in Å. The figures in brackets refer to the corresponding results from semi-empirical (PM3) calculations. Atom numbering as shown in Fig. 2 and 3

Cation	Zr-O ₅	C ₁ -C ₃ -C ₅	Angle between Zr-O ₅ and plane C ₃ -C ₅ -C ₄ (2-THF), C ₄ -C ₅ -C ₆ (3-THF)
2-THF	2.18 (2.27)	110.5 (112.9)	10.9 (50.8)
3-THF	2.19 (2.29)	117.2 (113.0)	30.8 (65.0)

systems. On the other hand, the *ab initio* HF calculations (with geometry optimisation) carried out gave rise to an energy difference of 19.4 kcal mol⁻¹, clearly indicating that the 3-THF complex cation is less stable and, therefore, should remain an active catalytic site. To examine the effects of electron correlation, non-local single-point DFT calculations were undertaken on the optimised geometries obtained above. These DFT calculations indicated a further increase in the energy difference to 21.6 kcal mol⁻¹ between the two cations. Thus all the above levels of theory and calculations show that the 2-THF cationic complex is more stable than the 3-THF complex—clearly predicting that the (3-THF-CH₂-Cp)₂ZrCl₂ is a better choice between the catalysts. The 3-THF derivative has now been synthesised and its activity for ethylene polymerisation was found to be 9.25 g h⁻¹ compared to zero activity for the 2-THF complex.¹

The results (Table 2) on the optimised geometries reveal the origin of the relative stabilities of the two cationic complexes. In both the systems the Zr and O atoms are within bonding distances of 2.18–2.19 Å. Inspection of the frontier orbitals of both the systems, particularly the LUMO, shows very little difference, indicating the same degree of overlap between the lone pairs of the O and the orbitals of the Zr. We, therefore, conclude that in the 3-THF complex, the increased internal strain is steric in origin and arises from the required distortions in the bond angle between C₁–C₂–C₃ atoms as well as in the angle between the Zr–O bond and the plane of the THF ring.[¶]

In summary, we have successfully rationalised the poorer activity of the (2-THF-CH₂-Cp)₂ZrCl₂ catalyst for ethylene polymerisation compared to the 3-THF variant (not a common experimental choice).

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Notes and References

† Semi-empirical: The MNDO⁴ module provided within SPARTAN⁵ employs PM3 parameters, including PM3TM that incorporates d functions for transition metals. The optimised geometries of several organometallic molecules have reproduced the X-ray structures of zirconocenes to within 0.04–0.05 Å on bond lengths and 3–5° on bond angles around the metal atom. Though the optimum energies are unreliable for the purposes of ligand design, the method does provide a useful starting geometry for subsequent *ab initio*/DFT studies.

‡ *Ab initio*: All *ab initio*/DFT calculations were carried out using the GAUSSIAN94 package.⁶ Geometry optimisations of the two cationic

species were performed at the HF level of theory using the 3-21G basis set.⁷ The LanL2DZ effective core potential⁸ was placed upon the zirconium atom.

§ DFT: Single point DFT calculations using B3LYP^{9,10} were performed with the same basis sets as used for the HF optimisations described above.

¶ It is interesting to note that the crystal structure of the stable tetrahydrofurylcyclopentadienyltitanium trichloride¹¹ (Fig. 4) is in line with our results from the *ab initio*/DFT methods. The results from the semi-empirical calculations are, however, less reliable for predicting the geometries of such cationic complexes.

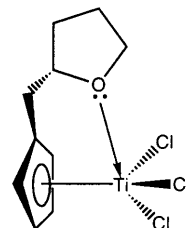


Fig. 4 The structure of tetrahydrofurylcyclopentadienyltitanium trichloride

- 1 BP Patent No: EP 608054. In a laboratory scale experiment it was found that 1.9 mg (4.1×10^{-3} mmol) of the catalyst (2-THF-CH₂-Cp)₂ZrCl₂ in the presence of MAO in toluene (100 ml, 0.41 M) at an ethylene pressure of 4 psig shows no polymerisation activity at room temperature—addition of Cp₂ZrCl₂ to the mixture, however, restored immediate polymerisation activity. In comparison, the catalyst (3-THF-CH₂-Cp)₂ZrCl₂ gave 9.25 g h⁻¹ of the polymer, under similar experimental conditions.
- 2 A. Anderson, H. G. Cordes, J. Herwig, W. Kaminsky, A. Merk, R. Mottweiler, J. H. Sinn and H. J. Vollmer, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 630.
- 3 P. C. Mohring and N. J. Colville, *J. Organomet. Chem.*, 1994, **479**, 1.
- 4 M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 4899.
- 5 SPARTAN version 5.0, Wavefunction Inc., 18401 Von Karman Ave., Suite 370, Irvine, CA 92612, USA.
- 6 GAUSSIAN94 Revision D.3, M. J. Frisch *et al.*, Gaussian Inc., Pittsburgh, PA, 1995.
- 7 J. S. Binkley, J. A. Pople and W. J. Hehre, *J. Am. Chem. Soc.*, 1980, **102**, 939.
- 8 P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270.
- 9 A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098.
- 10 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.
- 11 Y. Qian, G. Li, W. Chen, B. Li and X. Lin, *J. Organomet. Chem.*, 1989, **373**, 185.

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