

Mono- η -cyclopentadienyl-benzamidinato Compounds of Titanium, Zirconium and Hafnium

Alexandrov N. Chernega, Rafael Gómez and Malcolm L. H. Green

Inorganic Chemistry Laboratory, South Parks Road, Oxford, UK OX1 3QR

The new compounds $[M(\eta\text{-C}_5\text{R}_5)\{\eta\text{-R}'\text{NC}(\text{Ph})\text{NR}'\}\text{Cl}_2]$ [where $\text{R}' = \text{Me}_3\text{Si}(\text{TMS})$, and $\text{R} = \text{H}$, $\text{M} = \text{Ti}$, Zr , Hf or $\text{R} = \text{Me}$, $\text{M} = \text{Ti}$ or Zr], $[\text{Zr}(\eta\text{-C}_5\text{R}_5)\{\eta\text{-R}'\text{NC}(\text{Ph})\text{NR}'\}(\text{CH}_2\text{Ph})\text{Cl}]$ ($\text{R} = \text{H}$, Me), and $[\text{Zr}(\eta\text{-C}_5\text{R}_5)\{\eta\text{-R}'\text{NC}(\text{Ph})\text{NR}'\}(\text{CH}_2\text{Ph})_2]$ ($\text{R} = \text{H}$, Me) are described; the compound $[\text{Zr}(\eta\text{-C}_5\text{H}_5)\{\eta\text{-R}'\text{C}(\text{Ph})\text{R}'\}\text{Cl}_2]$ acts as a cocatalyst for the polymerisation of ethylene and propene.

There is considerable interest in new homogeneous Ziegler-Natta catalysts for the polymerisation of olefins which are based on d^0 bis- η -cyclopentadienylmetal compounds, especially for the metals Ti, Zr and Hf.¹⁻⁵ Also, related monocyclopentadienyl compounds in the class $[\text{Zr}\{\eta\text{-C}_5\text{R}_4\text{Si}(\text{Me}_2)\text{NR}'\}\text{Me}][\text{B}(\text{C}_6\text{F}_5)_4]$ have been found to be active as Ziegler-Natta catalysts.⁶ The N,N' -bis(alkyl)benzamidinato ligands $\eta\text{-RNCR}'\text{NR}$ have been shown to bond to transition metals

via coordination of the central NCN system which acts as a formal three-electron donating group.⁷ We, therefore, decided to prepare complexes in the class $[\text{M}(\eta\text{-C}_5\text{R}_5)(\eta\text{-R}'\text{NCR}'\text{NR}')\text{X}_2]$, where $\text{M} = \text{Ti}$, Zr or Hf and $\text{X} = \text{Cl}$ or alkyl, and to explore their ability to act as cocatalysts towards olefin polymerisation, as described below. A related formamidinato compound, $[\text{V}(\eta\text{-C}_5\text{H}_5)(N,N'\text{-di-}i\text{-p-tolylformidene})_2]$, has also been described⁸ and during the course of this work the

compound $\{\text{Ti}(\eta\text{-C}_5\text{Me}_5)[(\text{TMS})\text{NC}(p\text{-C}_6\text{H}_4\text{OMe})\text{N}(\text{TMS})]\text{-F}_2\}$ was reported.⁹

Treatment of $[\text{Hf}(\eta\text{-C}_5\text{H}_5)\text{Cl}_3]$ in toluene with a solution of the lithium salt $\text{Li}[(\text{TMS})\text{NC}(\text{Ph})\text{N}(\text{TMS})]$,⁷ designated hereafter as $\text{Li}[\text{TCT}]$, in toluene at room temp. gave air-sensitive white crystals of the compound $[\text{Hf}(\eta\text{-C}_5\text{H}_5)(\eta\text{-TCT})\text{Cl}_2]$ **1** in ca. 70% yield. The analytical and spectroscopic data† support the proposed formulation for **1**. The crystal structure of **1** has been determined‡ and the molecular structure is shown in Fig.

† Satisfactory analyses have been obtained for all the new compounds described. *Selected spectroscopic data*: NMR data recorded at 300 MHz (¹H) or at 75 MHz (¹³C{¹H}) and given as δ relative to SiMe₄, relative intensity, multiplicity, coupling constant, (in Hz) and assignment. [²H₆]benzene was used as solvent in all the NMR experiments. Mass spectra (MS) measured using electron-impact techniques. NMR and MS data: ^a Bands overlapping with those of deuterated solvents. ^b Bonds overlapping with η-C₅Me₅ band.

1: ¹H: 6.86, 6.72 (5H, m, C₆H₅), 6.35 (5H, s, C₅H₅), -0.02 (2 × 9H, s, SiMe₃). ¹³C: 179.4 [-C(Ph)(NSiMe₃)₂], 138.2 (C_{ipso}, C₆H₅), 129.3 (C₆H₅), 126.8 (C₆H₅)^a 114.3 (C₅H₅), 2.2 (SiMe₃). MS: 511 (M⁺ - Cp).

2: ¹H: 6.96, 6.73 (5H, m, C₆H₅), 6.48 (5H, s, C₅H₅), 0.04 (2 × 9H, s, SiMe₃). ¹³C: 173.5 [-C(Ph)(NSiMe₃)₂], 136.6 (C_{ipso}, C₆H₅), 129.4 (C₆H₅), 129.4 (C₆H₅)^a 120.2 (C₅H₅), 2.4 (SiMe₃). MS: 446 (M⁺), 411 (M⁺ - Cl), 381 (M⁺ - Cp).

3: ¹H: 6.85, 6.73 (5H, m, C₆H₅), 6.41 (5H, s, C₅H₅), -0.09 (2 × 9H, s, SiMe₃). ¹³C: 179.6 [-C(Ph)(NSiMe₃)₂], 137.9 (C_{ipso}, C₆H₅), 129.3 (C₆H₅), 126.8 (C₆H₅)^a 115.7 (C₅H₅), 2.2 (SiMe₃). MS: 489 (M⁺), 424 (M⁺ - Cp).

4: ¹H: 7.14, 6.85 (5H, m, C₆H₅), 2.15 (15H, s, C₅Me₅), 0.08 (2 × 9H, s, SiMe₃). ¹³C: 177.3 [-C(Ph)(NSiMe₃)₂], 137.7 (C_{ipso}, C₆H₅), 133.4 (C₅Me₅), 129.3 (C₆H₅), 127.8 (C₆H₅), 127.2 (C₆H₅), 14.6 (C₅Me₅), 4.0 (SiMe₃). MS: 516 (M⁺), 481 (M⁺ - Cl), 3.81. (M⁺ - C₅Me₅).

5: ¹H: 7.01, 6.60 (5H, m, C₆H₅), 2.12 (15H, s, C₅Me₅), 0.02 (2 × 9H, s, SiMe₃). ¹³C: 182.2 [-C(Ph)(NSiMe₃)₂], 138.2 (C_{ipso}, C₆H₅), 129.3 (C₆H₅), 126.7 (C₆H₅)^a 126.1 (C₅Me₅), 13.0 (C₅Me₅), 3.3 (SiMe₃). MS: 559 (M⁺), 425 (M⁺ - C₅Me₅).

6: ¹H: 7.42 (2H, d, *J*_{HH} 7.8 Hz, *o*-CH₂C₆H₅), 7.25 (2H, t, *J*_{HH} 7.6 Hz, *m*-CH₂C₆H₅), 6.95-6.73 (6H, m, C₆H₅), 6.32 (5H, s, C₅H₅), 2.49 (1H, d, *J*_{HH} 11.1 Hz, CH₂), 2.31 (1H, d, *J*_{HH} 11.1 Hz, CH₂), -0.08 (2 × 9H, s, SiMe₃).

7: ¹H: 7.31-6.98 (15H, m, C₆H₅), 6.11 (5H, s, C₅H₅), 2.41 (2H, d, *J*_{HH} 11.3 Hz, CH₂), 2.26 (2H, d, *J*_{HH} 11.3 Hz, CH₂), -0.12 (2 × 9H, s, SiMe₃).

8: ¹H: 7.56 (2H, d, *J*_{HH} 7.7 Hz, *o*-CH₂C₆H₅), 7.30 (2H, t, *J*_{HH} 7.6 Hz, *m*-CH₂C₆H₅), 7.20-6.60 (6H, m, C₆H₅), 2.46 (1H, d, *J*_{HH} 11.6 Hz, CH₂),^b 2.06 (15H, s, C₅Me₅), -0.02 (9H, s, SiMe₃), -0.07 (9H, s, SiMe₃).

9: ¹H: 7.41 (4H, d, *J*_{HH} 7.8 Hz, *o*-CH₂C₆H₅), 7.25 (4H, t, *J*_{HH} 7.7 Hz, *m*-CH₂C₆H₅), 7.05-6.87 (7H, m, C₆H₅), 2.59 (2H, d, *J*_{HH} 12.2 Hz, CH₂),^b 1.98 (15H, s, C₅Me₅), -0.14 (2 × 9H, s, SiMe₃).

‡ *Crystal data* for **1**: C₁₈H₂₈Cl₂HfN₂Si₂, *M* = 577.99 triclinic, spacegroup P1, *a* = 6.903(5), *b* = 10.265(5), *c* = 17.138(7) Å, α = 79.10(4), β = 79.95(5), γ = 82.57(5)°, *V* = 1169.6 Å³, *Z* = 2, *F*(000) = 568, *D*_c = 1.64 g cm⁻³, μ = 47.57 cm⁻¹, crystal size ca. 0.12 × 0.34 × 0.56 mm.

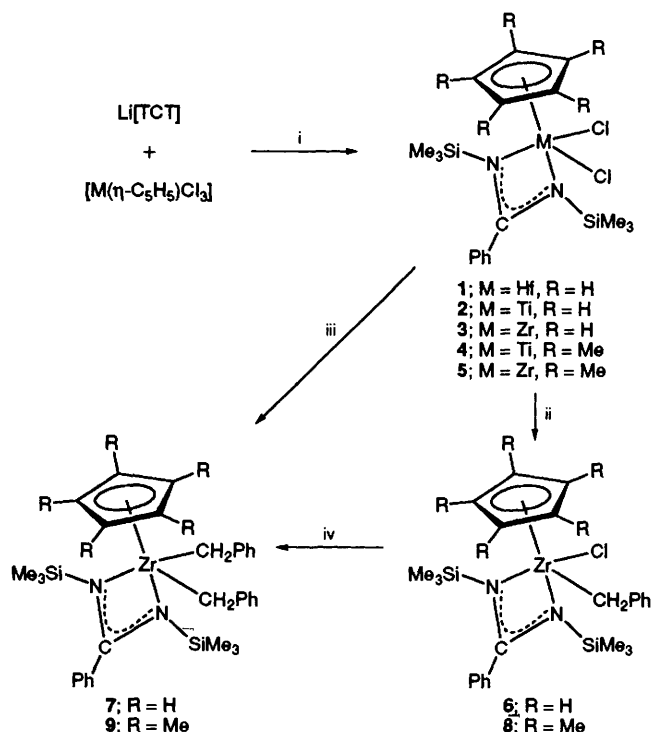
A total of 3730 (3365 independent) reflections were collected at room temperature on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα-radiation (λ = 0.71069 μ, ω-2θ scan mode, the ratio of the scanning rates ω/θ = 1.2, θ_{max} = 24°).

The structure was solved by direct methods and refined by the full-matrix least-squares technique in the anisotropic approximation [2906 reflections with *I* > 3σ(*I*), 226 variables, observations/variables 12.9, Chebyshev weighting scheme with parameters 7.40, -2.33, 6.03]. All hydrogen atoms were located in the difference Fourier maps and included in the final refinement with fixed positional and thermal parameters. Correction for Lorentz and polarization effects as well as empirical correction for absorption were applied.¹⁰ Convergence was obtained at *R* = 0.033, *R*_w = 0.039, a maximum peak in the final Fourier difference synthesis 0.82 e Å⁻³.

Crystallographic calculations were carried out using the CRYSTALS¹¹ program package on a MicroVAX3800 computer. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

1 together with selected distances and angles. The four-membered ring HfN₂C is slightly puckered and the dihedral angle between N(1)-Hf(1)-N(2) and N(1)-C(1)-N(2) is 11.5°.

The compounds $[\text{M}(\eta\text{-C}_5\text{R}_5)(\eta\text{-TCT})\text{X}_2]$, where R = H and M = Ti **2**, or Zr **3**, and R = Me and M = Ti **4** or Zr **5**, have been prepared from the corresponding $[\text{M}(\eta\text{-C}_5\text{R}_5)\text{Cl}_3]$ and $\text{Li}[\text{TCT}]$. The crystal structure of **2** has been determined and is closely similar to that of **1**. The compounds **1-5** are all highly sensitive to oxygen and water. They are stable at room



Scheme 1 Reagents and conditions: i, In toluene for 12 h, **1** (72%), **2** (58%), **3** (85%), **4** (51%), **5** (77%); ii, PhCH₂MgCl, in Et₂O for 2 h, **6** (56%), **8** (51%); iii, KCH₂Ph, in C₆H₆ for 12 h, **7** (83%), **9** (73%); iv, PhCH₂MgCl, in Et₂O for 2 h, **7** (76%), KCH₂Ph, in C₆H₆ for 12 h, **9** (64%)

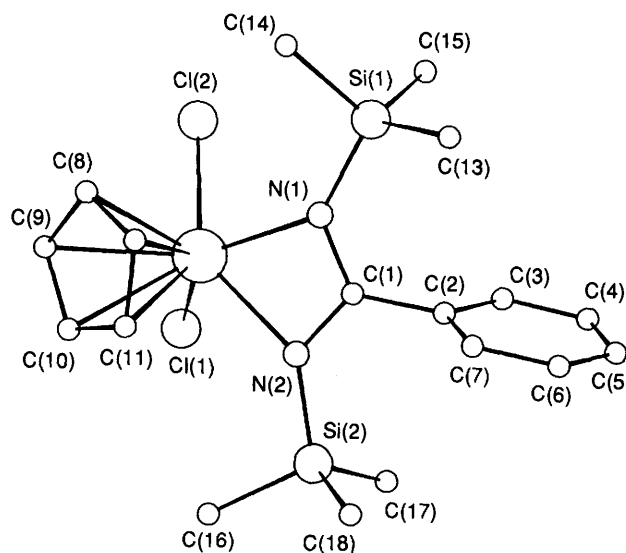


Fig. 1 Molecular structure of $[\text{Hf}(\eta\text{-C}_5\text{H}_5)(\eta\text{-TMSN})_2\text{C}(\text{Ph})\text{Cl}_2]$ **1**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Hf(1)-Cl(1) 2.399(2), Hf(1)-N(1) 2.182(4), Hf(1)-N(2) 2.204(5), Hf(1)-C(1) 2.589(5), Hf(1)-C(8) 2.447(7), Hf(1)-Cp_{cent} 2.163; Cl(1)-Hf-Cl(2) 89.96(9), N(1)-Hf(1)-N(2) 61.7(1), N(1)-C(1)-N(2) 115.0(5), Hf(1)-N(1)-C(1) 91.6(3), Hf(1)-N(2)-C(1) 90.6(3), Cp_{cent}-Hf(1)-C(1) 118.8, where Cp_{cent} refers to the computed η-C₅H₅ centroid.

temperature and are slightly soluble in light petroleum and soluble in toluene.

Treatment of **3** with one mole of benzylmagnesium chloride in Et₂O gave the orange, microcrystalline mono-η¹-benzyl derivative [Zr(η-C₅H₅)(η-TCT)(CH₂Ph)Cl] **6**. Further reaction between **6** and an additional mole of PhCH₂MgCl caused replacement of the chloro group giving the orange bis-η¹-benzyl derivative [Zr(η-C₅H₅)(η-TCT)(CH₂Ph)₂] **7**. The compound **7** can be prepared directly from **3** using two moles of PhCH₂MgCl or K(CH₂Ph).

The related pentamethyl compound [Zr(η-C₅Me₅)(η-TCT)(CH₂Ph)Cl] **8** was prepared in a similar manner starting from **5** and one mole of PhCH₂MgCl in diethyl ether. The bis-η¹-benzyl derivative [Zr(η-C₅Me₅)(η-TCT)(CH₂Ph)₂] **9** was prepared from **8** using one mole of potassiumbenzyl or from **5** and two moles of KCH₂Ph. Selected spectroscopic data for **6-9**† support the proposed structures, which are given in Scheme 1.

We have made a preliminary study of the catalytic properties of **2**. Typically, a solution of **2** (2.44 × 10⁻⁵ mol) in toluene (250 cm³) in the presence of a large excess of methylaluminoxane (MAO, M/Al = 839) at room temp. causes polymerisation of ethylene (at 2 bar, activity 1.23 × 10⁵) and slow polymerisation of propene (at 2 bar, activity, 1.14 × 10⁵, yield 3.3 g after 1 h) giving atactic polymer.

In conclusion, the compounds in the class [M(η-C₅R₅)-

(η-R'NCR'NR')X₂] show promise as Ziegler-Natta catalyst precursors and further investigations are in progress.

We thank the Science and Educational Ministry of Spain for financial support (to R. G. R.).

Received, 12th May 1993; Com. 3/02695G

References

- 1 W. Kaminsky, R. Engehausen, K. Zoumis, W. Spalek and J. Rohrmann, *Makromol. Chem.*, 1992, **193**, 1643.
- 2 J. A. Ewen, M. J. Elder, R. L. Jones, Haspesslagh, J. L. Atwood, S. G. Bott and K. Robinson, *Makromol. Chem., Makromol. Symp.*, 1989, **48/49**, 253.
- 3 K. Hortmann and H.-H. Brintzinger, *New J. Chem.*, 1992, **16**, 51.
- 4 T. J. Marks, *Acc. Chem. Res.*, 1992, **25**, 57.
- 5 R. F. Jordan, *Adv. Organomet. Chem.*, 1991, **32**, 325.
- 6 J. M. Canich, G. G. Hlatky and H. W. Turner, Int. Pat. No.: WO 92/00333.
- 7 M. Wedler, F. Knosel, T. T. Edelmann and U. Behrens, *Chem. Ber.*, 1992, **125**, 1313, and references therein.
- 8 F. A. Cotton and R. Poli, *Inorg. Chim. Acta.*, 1988, **141**, 91.
- 9 M. Sotoodeh, I. Leichtweis, H. W. Roesky, M. Noltemeyer and H.-G. Schmidt, *Chem. Ber.*, 1993, **126**, 913.
- 10 N. Walker and D. Stuart, *Acta Crystallogr. Sect. A*, 1983, **39**, 158.
- 11 D. J. Watkins, R. Carruthers and P. W. Betteridge, CRYSTALS user guide, Chemical Crystallography Laboratory, University of Oxford, 1985.