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Journal of Organometallic Chemistry 491 (1995) 153–158

Journal of Organometallic Chemistry

Mono-η-cyclopentadienyl-benzamidinato chloro compounds of titanium, zirconium and hafnium

Rafael Gómez [a,1], Robbert Duchateau [b], Alexander N. Chernega [a], Jan H. Teuben [b], Frank T. Edelmann [c], Malcolm L.H. Green [a,*]

[a] *Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, UK*
[b] *Department of Chemistry, University of Groningen, Nijenborgh 4 9747 AG Groningen, Netherlands*
[c] *Institut fur Anorganische Chemie der Universitat Göttingen, Tammannst. 4, D-37077 Göttingen, Germany*

Received 12 August 1994

Abstract

The new compounds {M(η-C_5R_5)[η-CPh($NSiMe_3$)$_2$]]Cl_2} (where R = H, M = Ti, Zr, Hf or R = Me, M = Ti or Zr), are described. The crystal structures of {M(η-C_5R_5)([η-CPh($NSiMe_3$)$_2$]Cl_2} (R = H, M = Zr or Hf) have been determined. The compound {Zr(η-C_5H_5)[η-CPh($NSiMe_3$)$_2$]Cl_2} acts as a co-catalyst for the polymerisation of ethylene and propene.

Keywords: Titanium; Zirconium; Hafnium; η-Cyclopentadieryl; Benzamidinato; Ziegler-Natta

1. Introduction

There is considerable interest in new homogeneous Ziegler-Natta catalysts for the polymerisation of olefins which are based on d^0 bis-η-cyclopentadienyl metal compounds, especially for the metals Ti, Zr and Hf [1–5]. Also, related mono-cyclopentadienyl compounds of the class [Zr(η-C_5R_4Si(Me_2)NR')Me][B(C_6F_5)$_4$] have been found to be active as Ziegler-Natta catalysts [6]. The N,N'-bis(alkyl)benzamidinato ligands η-RNCR'NR have been shown to bond to transition metals through coordination of the central NCN system, which acts as a formal three-electron donating group [7]. We therefore decided to prepare complexes of the class [M(η-C_5R_5)(η-R'NCR"NR')X_2], where M = Ti, Zr or Hf and X = Cl, and to explore their ability to act as co-catalysts towards olefin polymerisation, as described below. During the course of this work we became aware that the synthesis and crystal structure of the compound {Ti(η-C_5R_5)[η-CPh(NSiMe$_3$)$_2$]Cl_2} had been reported [8,9]. It was noted that the [η-CPh(NSiMe$_3$)$_2$] ligand has some steric similarities to the η-cyclopentadienyl ligand [7]. Also, during the course of this work the compound {Ti(η-C_5Me_5)[(TMS)NC(p-C_6H_4OMe)N(TMS)]F_2} was reported [10]. The related formamidinato compound, [V(η-C_5R_5)(*N,N'*-di-*p*-tolylformamidine)$_2$] has also been described [11]. Part of the work described below has been the subject of a preliminary communication [12].

2. Results and discussion.

The compounds [M(η-C_5R_5)(TCT)Cl_2], where TCT = [CPh($NSiMe_3$)$_2$], R = H and M = Ti **1**, or Zr **2**, or Hf**3**, and R = Me and M = Ti **4**, or Zr **5**, were prepared from the corresponding [M(η-C_5R_5)Cl_3] and the lithium salt Li[TCT] [7]. The compounds **1**–**5** are all highly sensitive to oxygen and water, are stable at room temperature, and are slightly soluble in petroleum ether and soluble in toluene.

The analytical and spectroscopic data for compounds **1**–**5** are given in Table 1, and are not further discussed. The crystal structures of **2** and **3** [12] have been determined. A perspective view of **2** with the atom numbering scheme is shown in Fig. 1. Selected intramolecular distances and angles are listed in Table 2, and fractional atomic coordinates in Table 3. The

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[*] Corresponding author.

[1] Present address: Department of Inorganic Chemistry, Universidad of Alcala de Henares, Alcala de Henares, Madrid, Spain.

SSDI 0022-328X(94)05237-9

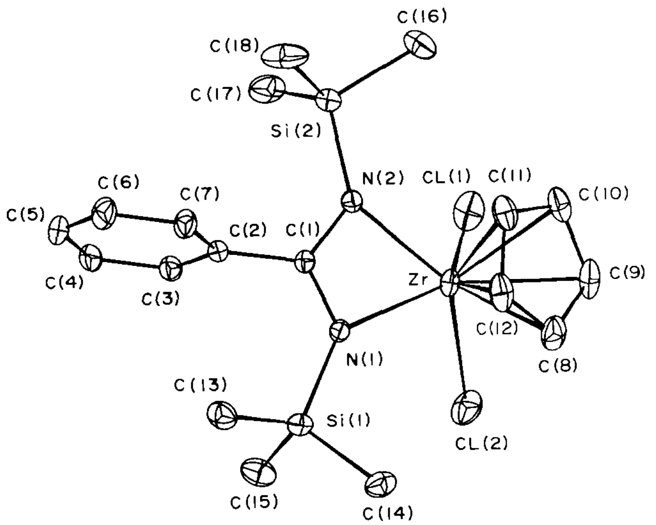


Fig. 1. Molecular structure of $[Zr(\eta-C_5H_5)(TCT)Cl_2]$ **2**. Hydrogen atoms are omitted for clarity.

crystal structure determination shows that **2** is monomeric in the solid state with no intermolecular contacts closer than the sum of the appropriate van der Waals radii. The Zr–Cl bond lengths of 2.4212(9) Å and 2.422(1) Å in **2** lie at the lowest end of the range of values previously reported for Zr–Cl bond, and may be compared with the value of 2.429(2) Å in $[Zr(\eta-C_5Me_5)(\eta-C_3H_5)Cl_2]$ [13] 2.426(4) Å in $[Zr\{\eta-C_5H_3-(SiMe_3)_2\}_2Cl_2]$ [14], 2.428(1) Å in $[Zr(\eta-C_5Me_5)_2(CH_2PPh_2)Cl]$ [15] and 2.423(3) Å in $[Zr(\eta-C_5H_3Bu_2)_2Cl_2]$ [16]. The Zr–N 2.204(2) Å and 2.212(2) Å in **2** are comparable with the related values of 2.22(2) Å in $[Zr(\eta^5-C_5H_5)_2(\eta^1-NC_4H_2Me_2)_2]$ [17] and 2.21(1) Å in $[Zr_2Cl_3O(NC_4H_4)_2(\eta-C_5Me_5)_2]$ $[Li(C_4H_{10}O_2)_3]$ [18].

The four-membered ring ZrN_2C of **2** is not exactly planar (the deviations from least-square plane average 0.073 Å) but slightly puckered. The dihedral angle between the N(1)–Zr–N(2) and N(1)–C(1)–N(2) planes is 12.3°. Both nitrogen atoms N(1) and N(2) as well as atom C(1) have trigonal-planar bond configuration; the sums of the bond angles are 359.2(5)°, 358.5(5)° and 359.9(6)° respectively. The C(1)–N(1) and C(1)–N(2) bond lengths 1.323(3) Å and 1.329(3) Å, are the same within the estimated errors limit and correspond to a bond order of 1.5 [19], indicating electron delocalization in the N(1)–C(1)–N(2) group. The orthogonal orientation of the C(2)–C(7) phenyl ring relative to the N(1)C(1)N(2) plane excludes the possibility of π-conjugation between these systems, and the C(1)–C(2) bond length 1.493(3) Å, corresponds to that of a pure single $C(sp^2)-C(sp^2)$ bond [20]. Because of the steric repulsion between the bulky substituents, both Zr–N(1)–Si(1) and Zr–N(2)–Si(2) bond angles are opened to 138.2(1)°. The structural features of the compound **2** are similar to those for the Hf-analogue, $\{Hf(\eta-C_5H_5)[(\eta-C(Ph)(NTMS)_2]Cl_2\}$**3** [12].

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 cm^3) in the presence of a large

Table 1
Analytical and spectroscopic data [a]

Compound	Colour	NMR [b]
1 C: 49.0 (48.3) H: 6.4 (6.3) N: 6.1 (6.3)	Red	^1H: 6.96, 6.73 (5H, m, C_6H_5), 6.48 (5H, s, C_5H_5), 0.04 (2 × 9H, s, $SiMe_3$). ^{13}C: 173.5 [*C*(Ph)($NSiMe_3)_2$], 136.6 (C_{ipso}, C_6H_5), 129.4 $(C_6H_5)^c$, 120.2 (C_5H_5), 2.4 ($SiMe_3$).
2 C: 44.2 (44.1) H: 5.4 (5.7) N: 5.5 (5.7)	Cream	^1H: 6.85, 6.73 (5H, m, C_6H_5), 6.41 (5H, s, C_5H_5), −0.09 (2 × 9H, s, $SiMe_3$). ^{13}C: 179.6 [*C*(Ph)($NSiMe_3)_2$], 137.9 (C_{ipso}, C_6H_5), 129.3 (C_6H_5), 126.8 $(C_6H_5)^c$, 115.7 (C_5H_5), 2.2 ($SiMe_3$).
3 C: 37.3 (37.4) H: 5.0 (4.8) N: 4.9 (4.8)	White	^1H: 6.86, 6.72 (5H, m, C_6H_5), 6.35 (5H, s, C_5H_5), −0.02 (2 × 9H, s, $SiMe_3$). ^{13}C: 179.4 [*C*(Ph)($NSiMe_3)_2$], 138.2 (C_{ipso}, C_6H_5), 129.3 (C_6H_5), 126.8 $(C_6H_5)^c$ 114.3 (C_5H_5), 2.2 ($SiMe_3$).
4 C: 53.75 (53.4) H: 7.5 (7.35) N: 5.2 (5.4)	Red-orange	^1H: 7.14, 6.85 (5H, m, C_6H_5), 2.15 (15H, s, C_5Me_5), 0.08 (2 × 9H, s, $SiMe_3$). ^{13}C: 177.3 [*C*(Ph)($NSiMe_3)_2$], 137.7 (C_{ipso}, C_6H_5), 133.4 (C_5Me_5), 129.3 (C_6H_5), 127.8 (C_6H_5), 127.2 (C_6H_5), 14.6 ($C_5\mathit{Me}_5$), 4.0 ($SiMe_3$).
5 C: 48.85 (49.3) H: 6.9 (6.8) N: 5.0 (5.0)	Pale yellow	^1H: 7.01, 6.60 (5H, m, C_6H_5), 2.12 (15H, s, C_5Me_5), 0.02 (2 × 9H, s, $SiMe_3$). ^{13}C: 182.2 [*C*(Ph)($NSiMe_3)_2$], 138.2 (C_{ipso}, C_6H_5), 129.3 (C_6H_5), 126.7 $(C_6H_5)^c$, 126.1 (C_5Me_5), 13.0 ($C_5\mathit{Me}_5$), 3.3 ($SiMe_3$).

[a] Unless otherwise stated: ^1H at 300 MHz, ^{13}C at 75 MHz. Analytical data given as: found (calculated) %. Mass spectral data (e.i.): **1**, 446 (P^+), 411 ($P^+ - Cl$), 381 ($P^+ - C_5H_5$); **2**, 489 (P^+), 424 ($P^+ - C_5H_5$)); **3**, 511 ($P^+ - C_5H_5$)); **4**, 516 (P^+), 481 ($P^+ - Cl$), 381. ($P^+ - C_5H_5$); **5**, 559 (P^+), 425 ($P^+ - C_5Me_5$). [b] In $[^2H_6]$benzene. [c] Other signals are overlapping.

Table 2
Selected interatomic distances (Å) and angles (°) for compound **2**

Zr–Cl (1)	2.4212 (9)
Zr–Cl (2)	2.422 (1)
Zr–N (1)	2.204 (2)
Zr–N (2)	2.212 (2)
Zr–C (8)	2.482 (4)
Zr–C (9)	2.474 (3)
Zr–C (10)	2.491 (4)
Zr–C (11)	2.498 (4)
Zr–C (12)	2.481 (3)
Zr–CEN	2.186
Si (1)–N (1)	1.764 (2)
Si (2)–N (2)	1.762 (2)
N (1)–C (1)	1.323 (3)
N (2)–C (1)	1.329 (3)
C (1)–C (2)	1.493 (3)
Zr....C (1)	2.599 (2)
Cl (1)–Zr–Cl (2)	90.95 (4)
Cl (1)–Zr–N (1)	128.23 (6)
Cl (2)–Zr–N (1)	87.54 (6)
Cl (1)–Zr–N (2)	87.39 (6)
Cl (2)–Zr–N (2)	136.85 (6)
N (1)–Zr–N (2)	61.04 (8)
Cl (1)–Zr–CEN	114.3
Cl (2)–Zr–CEN	111.2
N (1)–Zr–CEN	114.3
N (2)–Zr–CEN	108.6
Zr (1)–N (1)–Si (1)	138.2 (1)
Zr (1)–N (1)–C (1)	91.4 (2)
Si (1)–N (1)–C (1)	129.6 (2)
Zr (1)–N (2)–Si (2)	138.2 (1)
Zr (1)–N (2)–C (1)	90.9 (2)
Si (2)–N (2)–C (1)	129.4 (2)
N (1)–C (1)–N (2)	115.4 (2)
N (1)–C (1)–C (2)	122.9 (2)
N (2)–C (1)–C (2)	121.6 (2)

CEN denotes the centroid of the cyclopentadienyl ring C(8)–C(12).

excess of methylaluminoxane (MAO, Al/M = 839)) at room temperature causes polymerisation of ethylene (at 2 bar, activity 1.23×10^5) and slow polymerisation of propene (at 2 bar, activity, 1.14×10^5, yield 3.3 g after 1 h) giving an atactic polymer. The data are shown in Table 4.

The presence of the benzamidinato unit in the catalyst is supported by the observation that the system **2**/MAO exhibited lower polymerization activities and gave polymers of lower molecular weight than did the systems Cp_2ZrCl_2/MAO or $CpZrCl_3$/MAO [21,22]. The higher rate constant for chain transfer in **2** may reflect a greater Lewis acidity at the zirconium atom induced by the benzamidinato ligand [23].

The reactions and structures suggested for **1**–**5** are shown in Scheme 1.

3. Experimental details

All manipulations of air- and moisture- sensitive materials were performed either (i) by use of standard Schlenk-line techniques under argon that had been purified by passage over BASF catalyst and 4 Å molecular sieves, or (ii) in an inert-atmosphere dry box containing dinitrogen unless stated otherwise. Solvents were dried by standing over 4 Å molecular sieves, and then distilled under dinitrogen from phosphorus pentoxide (dichloromethane), sodium (toluene, benzene), potassium-benzophenone (THF), or sodium-potassium alloy (1 : 3 w/w) [light petroleum (b.p. 40–60°C), diethyl ether, pentane]. Deuteriated solvents for NMR studies were stored in Young' ampoules under dinitrogen over sodium-potassium alloy ($[^2H_6]$ benzene). Proton and ^{13}C NMR spectra were recorded on a Brüker AM 300 spectrometer (^1H 300 MHz, ^{13}C 75.5 MHz), with residual protio solvent (^1H) or solvent (^{13}C) reso-

Table 3
Fractional atomic coordinates and equivalent isotropic temperature factors ($Å^2$) for compound **2**.

Atom	x	y	z	U_{eq}
Zr	0.39878 (4)	0.57719 (2)	0.77882 (2)	0.0450
Cl (1)	0.6559 (1)	0.6338 (1)	0.84176 (8)	0.0816
Cl (2)	0.6381 (1)	0.5230 (1)	0.66611 (7)	0.0829
Si (1)	0.1952 (1)	0.71623 (8)	0.59111 (5)	0.0515
Si (2)	0.1809 (1)	0.84651 (8)	0.89331 (5)	0.0531
N (1)	0.2293 (3)	0.7064 (2)	0.6914 (1)	0.0429
N (2)	0.2195 (3)	0.7571 (2)	0.8133 (1)	0.0449
C (1)	0.1783 (3)	0.7958 (2)	0.7392 (1)	0.0382
C (2)	0.0902 (4)	0.9335 (2)	0.7116 (2)	0.0432
C (3)	0.2113 (5)	1.0279 (3)	0.6688 (2)	0.0540
C (4)	0.1344 (7)	1.1560 (3)	0.6447 (2)	0.0647
C (5)	−0.0632 (8)	1.1897 (4)	0.6619 (2)	0.0734
C (6)	−0.1859 (7)	1.0980 (4)	0.7035 (3)	0.0776
C (7)	−0.1088 (5)	0.9675 (3)	0.7282 (2)	0.0607
C (8)	0.3008 (7)	0.3512 (4)	0.7862 (3)	0.0757
C (9)	0.4119 (7)	0.3427 (4)	0.8471 (3)	0.0735
C (10)	0.3077 (6)	0.4153 (4)	0.9034 (3)	0.0717
C (11)	0.1306 (6)	0.4715 (4)	0.8777 (3)	0.0683
C (12)	0.1272 (6)	0.4318 (4)	0.8051 (3)	0.0674
C (13)	−0.0450 (6)	0.8091 (5)	0.5723 (3)	0.0719
C (14)	0.1953 (8)	0.5435 (4)	0.5749 (3)	0.0765
C (15)	0.3964 (8)	0.7980 (6)	0.5211 (3)	0.0790
C (16)	0.257 (2)	0.7347 (7)	0.9822 (3)	0.0988
C (17)	0.332 (1)	0.9864 (6)	0.8684 (3)	0.0858
C (18)	−0.0851 (8)	0.8945 (9)	0.9226 (4)	0.0974

Table 4
Ethene and propene polymerisation using compound 2 with MAO [a]

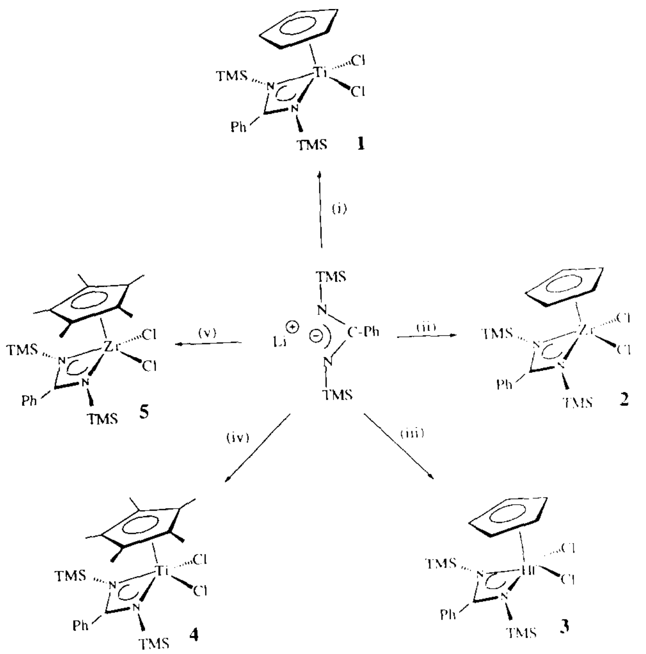
Catalyst	Monomer	Yield (g)	Activity [b] $\times 10^6$	Tacticity
2 [c]	ethene	2.9	0.12	–
2 [d]	propene	3.3	0.11	atactic

[a] Polymerisation condition: monomer pressure 2 bars, solvent 250 ml of toluene, time 1 h, temperature 30 °C, Al/Zr = 839. Preliminary molecular weight determination show the molecular weight to be above 20,000 (in chloroform, on the polystyrene scale).

[b] Activity = g of polymer per mol Zr per h.

[c] $[Zr] = 2.44 \times 10^{-5}$ mol.

[d] $[Zr] = 2.89 \times 10^{-5}$ mol.



Scheme 1. Reagents and conditions: (i) [Ti(η-C_5H_5)Cl_3], toluene, room temperature, 12 h, yield 58%; (ii) [Zr(η-C_5H_5)Cl_3]. DME, toluene, room temperature 12 h, yield 85%; (iii) [Hf(η-C_5H_5)Cl_3]. 2THF, toluene, room temperature, 12 h, yield 72%; (iv) [Ti(η-C_5Me_5)Cl_3], toluene, at room temperature for 12 h, at 80°C for 5 h, yield 51%; (v) [Zr(η-C_5Me_5)Cl_3]. 2THF, toluene, at room temperature for 12 h, at 80°C for 5 h, yield 77%.

nances as internal references. Low resolution mass spectra were obtained on an AEI MS 302 mass spectrometer, updated by addition of a data handling system supplied by Mass Spectra Services LTD. Elemental analyses were performed by the analytical department of this laboratory. The compounds Li[PhC(NSiMe$_3$)$_2$] and methylaluminoxanme (MAO) were prepared as described previously [1,7].

3.1. Preparation of [Ti(η-C_5H_5)(TCT)Cl_2] 1.

A solution of [Ti(η-C_5H_5)Cl_3] (0 45 g, 2.05 mmol) in toluene (50 cm^3) was treated with one of Li[PhC(NSiMe$_3$)$_2$] (0.57 g, 2.10 mmol) in toluene (10 cm^3) and the mixture was stirred for 12 h at room temperature. The resulting red-orange solution was filtered, and the solvent removed under reduced pressure. The red solid was washed with petroleum ether (40–60°C:30 cm^3) and dried. Recrystalization from toluene at −40°C, afforded bright red crystals of compound **1**. Yield: 0.53 g (58%).

3.2. Preparation of [Zr(η-C_5H_5)(TCT)Cl_2] 2.

A solution of [Zr(η-C_5H_5)Cl_3].DME (0.38 g, 1.08 mmol) in toluene (50 cm^3) was treated with one of Li[PhC(NSiMe$_3$)$_2$] (0.31 g, 1.15 mmol) in toluene (10 cm^3) and the mixture was stirred for 12 h at room temperature. The resulting pale-yellow solution was filtered and reduced in volume to ca. 5 cm^3 then kept at −80°C to afford **2** as white cream crystals. Yield: 0.45 g (85%). Recrystallization from toluene yielded white crystals suitable for an X-ray study.

3.3. Preparation of [Hf(η-C_5H_5)(TCT)Cl_2] 3.

A solution of [Hf(η-C_5H_5)Cl_3].THF (0.4 g, 0.81 mmol) in toluene (50 cm^3) was treated with one of Li[PhC(NSiMe$_3$)$_2$] (0.24 g, 0.89 mmol) in toluene (10 cm^3) and the mixture was stirred for 12 h at room temperature. The resulting pale yellow solution was filtered and reduced in volume in ca. 5 cm^3 then kept at −80°C to afford **3** as white crystals. Yield: 0.34 g (72%).

3.4. Preparation of [Ti(η-C_5Me_5)(TCT)Cl_2] 4.

A solution of [Ti(η-C_5H_5)Cl_3] (0.5 g, 1.73 mmol) in toluene (50 cm^3) was treated with one of Li[PhC(NSiMe$_3$)$_2$] (0.47 g, 1.74 mmol) in toluene (10 cm^3). The mixture was stirred for 12 h at room temperature and then for 3 h at 80°C. The resulting red-orange solution was filtered and the solvent removed under reduced pressure. The sticky red crystals were extracted with light petroleum (40–60°C: 2 × 15 cm^3) and the extract filtered. The red filtrate was reduced in volume in ca. 5 cm^3 and kept at −80°C to afford **4** as bright red-orange crystals. Yield: 0.46 g (51%).

3.5. Preparation of [Zr(η-C_5Me_5)(TCT)Cl_2] 5.

A solution of [Zr(η-C_5H_5)Cl_3].2THF (0.4 g, 0.84 mmol) in toluene (50 cm^3) was treated with one of Li[PhC(NSiMe$_3$)$_2$] (0.23 g, 0.85 mmol) in toluene (10 cm^3). The mixture was stirred for 12 h at room temperature and then for 4 h at 80°C. The resulting pale-yellow solution was filtered and the solvent removed under reduced pressure. The sticky crystals were extracted with diethyl ether (60 cm^3) and the extract filtered. The pale filtrate was reduced in volume in ca. 5 cm^3 and kept at −80°C to afford **5** as pale-yellow crystals. Yield: 0.36 g (77%).

3.6. Polymerisation studies.

Ethene and propene were dried by passage over potassium supported on glass wool and then over 4 Å molecular sieves. Polymerisation were performed in a 500 cm^3 Fischer-Porter apparatus equipped with a thermocouple and a Teflon stirrer bar.

3.6.1. Ethene polymerisation

Toluene (200 cm^3) and MAO (0.98 g) were placed in the Fischer-Porter apparatus. The mixture was stirred at 30°C and saturated with ethene at a pressure of 2 bar. A seperate solution of MAO (0.20 g) and **2** (2.44×10^{-5} mol) in toluene (10 cm^3) was prepared, and was allowed to react for 15 min and then introduced through a cannula to the solution in the Fischer-Porter apparatus. After 1 h the polymerisation was quenched by adding a few drops of ethanol, and dinitrogen was passed through the solution to remove the excess of ethene. The mixture was then poured into an acidified ethanol solution and stirred overnight. The product polyethylene was filtered off, washed with water and ethanol, and dried at 60°C to constant weight.

3.6.2. Propene polymerisation

In a similar procedure toluene (200 cm^3) and MAO (1.17 g) were placed in the Fischer-Porter apparatus. The mixture was stirred at 30°C and saturated with propene at a pressure of 2 bar. MAO (0.23 g) and **2** (2.89×10^{-5} mol) were dissolved in toluene (10 cm^3) and after a 15 min preactivation, the mixture was introduced through a cannula to the Fischer-Porter apparatus. After 1 h the polymerisation was quenched by adding a few drops of ethanol and passing dinitrogen to remove the excess of ethene. The product mixture was then poured into an acidified ethanol solution and stirred overnight. The toluene solution was dried over anhydrous $MgSO_4$ for 12 h and then the solvent removed to leave a waxy polypropylene material.

3.7. Crystal Structure Determination of Compound 2.

$C_{18}H_{28}Cl_2N_2Si_2Zr$, $M = 490.73$, triclinic, $a = 6.923(2)$ Å, $b = 10.300(4)$ Å, $c = 17.198(7)$ Å, $\alpha = 79.03(3)°$, $\beta = 79.95(4)°$, $\gamma = 82.56(4)°$, $U = 1184(1)$ $Å^{-3}$ (by the least-squares refinement of the setting angles for 24 automatically centered reflections), space group $P\bar{1}$, $Z = 2$, $D_c = 1.38$ g cm^{-3}, $F(000) = 504$, $\mu = 7.91$ cm^{-1}. Crystal dimensions ca. $0.19 \times 0.34 \times 0.40$ mm. Data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer (ω-2Θ mode with the ω scan width = 0.75 + 0.34 tan Θ, ω scan speed 1.4–10.1° min^{-1}, the ratio of the scanning rates $\omega/\Theta = 1.2$, graphite-monochromated Mo–Kα radiation, $\lambda = 0.71069$ Å). 4027 reflections were measured ($1.0 < \Theta < 24°$, $-h, h, -k, k, 0, 1$), 3673 unique (merging $R = 0.018$). No significant crystal decay or movement was noted. The structure was solved by direct methods and refined by full-matrix least-squares technique with all non-hydrogen atoms in the anisotropic approximation (2853 reflections with $I > 3\sigma(I)$, 338 variables, observations/variables = 8.4). All hydrogen atoms were located in the difference Fourier maps and refined isotropically. Chebyshev weighting scheme [24] with parameters 4.08, −1.49, 3.13 was applied. Corrections for Lorentz and polarization effects as well as empirical correction for absorption [25] based on azimuthal scan data were applied. Anomalous-dispersion contributions were included in the calculated structure factors. Final R and R' values are 0.027 and 0.031. Maximum and minimum peaks in the final difference synthesis are 1.23 e $Å^{-3}$ and −1.22 e $Å^{-3}$. Crystallographic calculations were carried out using the CRYSTALS [26] program package on a MicroVAX 3800 computer.

Neutral atom scattering factors were taken from the usual sources [27]. Fractional coordinates of non-hydrogen atoms are listed in the Table 2. Tables of H-atom coordinates and thermal parameters and a full list of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. The determination of the structure of 3 was reported earlier [12].

Acknowledgements

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

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