Peter J. Bonitatibus, Jr.* and Guido J. Reiss

Preparation and crystal structure of a cationic olefin polymerization precatalyst: (1,7-bis(2,6-dichlorophenyl)-1,7-di-aza-4-oxo-heptan-1,4,7-triyl)dimethyl zirconium(IV), $C_{18}H_{20}Cl_4N_2OZr$

Table 1: Data collection and handling.

Crystal:	Colorless plate
Size:	0.50 × 0.30 × 0.10 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.04 mm ⁻¹
Diffractometer, scan mode:	Siemens P4, ω
$\theta_{\max}$, completeness:	23.0°, 94%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	3537, 1404, 0.048
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1174
$N(\text{param})_{\text{refined}}$:	139
Programs:	XSCANS [1], SHELX [2–4], Diamond [5]

The molecular structure is shown in the Figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

Synthesis of the title complex $[\text{NON}^{\text{Cl}}]\text{ZrMe}_2$, was carried out by reaction of the tridentate $\text{H}_2[\text{NON}^{\text{Cl}}]$ ligand $[(2,6\text{-Cl}_2\text{C}_6\text{H}_3\text{NHCH}_2\text{CH}_2)_2\text{O}]$ with tetrakis(dimethylamide) zirconium(IV) to form $[\text{NON}^{\text{Cl}}]\text{Zr}(\text{NMe}_2)_2$ initially, followed by stepwise conversion from $[\text{NON}^{\text{Cl}}]\text{Zr}(\text{NMe}_2)_2$ to $[\text{NON}^{\text{Cl}}]\text{ZrCl}_2$ with subsequent methylation to form $[\text{NON}^{\text{Cl}}]\text{ZrMe}_2$ (structure pictured in the Figure). Synthesis of the ligand involved reaction of the lithium anilide (protected with a trimethylsilyl group) [6] with commercially available diethylene glycol di(*p*-toluenesulfonate) in THF, followed by hydrolysis with aqueous HCl. Synthesis of all compounds required to produce $[\text{NON}^{\text{Cl}}]\text{ZrMe}_2$ are described below.

2,6-Dichloro(trimethylsilyl)aniline: 5.0 g (30.86 mmol) of 2,6-dichloroaniline was dissolved in 100 mL of a 70:30 mixture of THF:Et₂O. Potassium hydride (1.24 g, 30.92 mmol) was added in small portions at room temperature under N₂ with stirring, so as to keep bubbling to a

<https://doi.org/10.1515/ncrs-2020-0464>

Received September 18, 2020; accepted October 12, 2020;
published online November 6, 2020

Abstract

$C_{18}H_{20}Cl_4N_2OZr$, monoclinic, *Pnma* (no. 62), $a = 12.457(3)$ Å, $b = 22.806(8)$ Å, $c = 7.398(2)$ Å, $V = 2101.7(11)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0291$, $wR_{\text{ref}}(F^2) = 0.0685$, $T = 110$ K.

CCDC no.: 2036254

*Corresponding author: Peter J. Bonitatibus, Jr., Department of Chemistry and Chemical Biology, Rensselaer Polytechnic Institute Cogswell Laboratory, 110 8th Street, Troy, NY 12180-3590, USA, E-mail: bonitp2@rpi.edu. <https://orcid.org/0000-0002-6650-9059>
Guido J. Reiss, Institut für Anorganische Chemie und Strukturchemie Lehrstuhl II: Material- und Strukturforchung, Heinrich-Heine-Universität Düsseldorf Universitätsstrasse 1, D-40225 Düsseldorf, Germany

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Zr	0.74304 (4)	0.750000	0.68161 (7)	0.0302 (2)
Cl1	0.63067 (8)	0.61740 (4)	0.99885 (14)	0.0474 (3)
Cl2	0.85483 (9)	0.61215 (5)	0.37369 (14)	0.0529 (3)
O	0.5856 (3)	0.750000	0.5144 (4)	0.0312 (8)
N	0.6935 (2)	0.66376 (11)	0.6302 (4)	0.0318 (7)
C1	0.7687 (6)	0.750000	0.9815 (9)	0.0440 (15)
H11	0.805 (3)	0.7816 (12)	1.013 (5)	0.064 (14)*
H12	0.705 (3)	0.750000	1.037 (9)	0.09 (3)*
C2	0.9116 (5)	0.750000	0.5820 (11)	0.0499 (16)
H21	0.948 (3)	0.7160 (11)	0.605 (5)	0.060 (13)*
H22	0.914 (5)	0.750000	0.461 (3)	0.08 (3)*
C3	0.5669 (3)	0.69755 (14)	0.4115 (5)	0.0394 (9)
H3A	0.612280	0.696770	0.304961	0.047*
H3B	0.492496	0.695285	0.373711	0.047*
C4	0.5940 (3)	0.64784 (15)	0.5352 (5)	0.0400 (10)
H4A	0.536413	0.641547	0.621226	0.048*
H4B	0.604383	0.612078	0.466423	0.048*
C5	0.7530 (3)	0.61610 (13)	0.6965 (5)	0.0309 (8)
C6	0.7366 (3)	0.59144 (14)	0.8692 (5)	0.0332 (9)
C7	0.7987 (3)	0.54664 (14)	0.9378 (6)	0.0414 (10)
H7	0.785559	0.531923	1.052918	0.050*
C8	0.8802 (3)	0.52399 (15)	0.8342 (6)	0.0475 (11)
H8	0.923621	0.494371	0.880285	0.057*
C9	0.8979 (3)	0.54501 (15)	0.6619 (6)	0.0444 (11)
H9	0.952312	0.529165	0.591022	0.053*
C10	0.8348 (3)	0.58951 (14)	0.5956 (5)	0.0343 (9)

minimum. With each addition of solid KH bubbling occurred, and more KH was added only when the solution homogenized. After 2 h of stirring, the resulting light orange-yellow solution of anilide was treated with chlorotrimethylsilane (3.35 g, 30.84 mmol). Upon addition, the color was discharged to originate a cloudy white suspension. After 2 h, all volatiles were removed and the product was extracted with 60 mL of pentane and filtered through a pad of celite. A light-yellow/colorless oil-liquid was isolated (80.6%) upon removal of pentane. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.20 (d, 2, H_m), 6.65 (t, 1, H_p), 4.01 (br s, 1, NH), 0.318 (s, 9, $\text{Si}(\text{CH}_3)_3$).

$\text{H}_2[\text{NON}^{\text{Cl}}]$ ligand $[(2,6\text{-Cl}_2\text{C}_6\text{H}_3\text{NHCH}_2\text{CH}_2)_2\text{O}]$: 2.22 g (9.48 mmol) of 2,6-dichloro(trimethylsilyl)aniline was dissolved in 100 mL of THF. This was set to chill for 90 min at -20°C . *n*-BuLi (3.80 mL, 9.5 mmol) was added dropwise as a 2.5 M solution in hexanes over 10 min with stirring under N_2 . This was allowed to stir for hours originating a deep-orange homogeneous solution of lithium anilide at room temperature. The reaction was again set to chill for 45 min at -20°C , and then treated with solid diethylene glycol di(*p*-toluenesulfonate) over a 7-min period in small

portions (4.74 mmol). This reaction was allowed to stir for 3 days. Next, the homogeneous mixture was taken to dryness, and the resulting orange microcrystalline solid was stirred for 60 min in 100 mL of pentane. A very light-yellow solution was obtained upon filtration through a celite pad. All volatiles were removed to obtain an almost colorless oil which completely solidified to a white solid. The white solid was treated with 40 mL of a 3 N HCl solution after dissolution with 100 mL of Et_2O . Hydrolysis proceeded overnight with stirring at 40°C . The reaction was then quenched with 60 mL of 3 N KOH (until slightly basic). The organic phase was separated and the aqueous layer extracted with another 50 mL of Et_2O . The organics were combined, washed twice with distilled water (until neutral), dried over MgSO_4 , and filtered. This compound was isolated as a light-orange oil (80%), which solidified over the course of a fortnight upon Et_2O removal. **FAB-MS**: positive ion ($\text{M}+\text{H}$) $^+$, measured (**calc'd**): 393.0106 $\pm$ 0.0012 (393.009499), $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.23 (d, 4, H_m), 6.79 (t, 2, H_p), 4.51 (br s, 2, NH), 3.61 (t, 4, OCH_2), 3.55 (t, 4, NHCH_2).

$[\text{NON}^{\text{Cl}}]\text{Zr}(\text{NMe}_2)_2 \cdot \text{H}_2[\text{NON}^{\text{Cl}}]$ was dissolved in 15 mL of pentane (0.48 g, 1.22 mmol). To this was added as a 5 mL pentane solution, $\text{Zr}(\text{NMe}_2)_4$ (0.33 g, 1.22 mmol). This was allowed to stir overnight, filtered through a bed of celite, and concentrated *in vacuo* to a yellow solid (0.61 g, 88%). This reaction has been scaled up to 1.5 g of $\text{H}_2[\text{NON}^{\text{Cl}}]$. $^1\text{H NMR}$ (300 MHz, C_6D_6): δ 7.11 (d, 4, H_m), 6.316 (t, 2, H_p), 3.55 (t, 4, OCH_2), 3.48 (t, 4, NCH_2), 2.88 (s, 12, NMe_2).

$[\text{NON}^{\text{Cl}}]\text{ZrCl}_2 \cdot [\text{NON}^{\text{Cl}}]\text{Zr}(\text{NMe}_2)_2$ was dissolved in 40 mL of Et_2O (0.61 g, 1.07 mmol) to originate a light-yellow solution. To this was added neat chlorotrimethylsilane (2.31 g, 21.26 mmol) at room temperature under N_2 with vigorous stirring. After 60 min, the reaction was only slightly turbid, so the mixture was allowed to stir overnight. All volatiles were removed *in vacuo* to yield the compound as a fine off-white powder (0.53 g, 90%). In some cases, the product was washed with pentane. $^1\text{H NMR}$ (300 MHz, C_6D_6): δ 6.93 (d, 4, H_m), 6.28 (t, 2, H_p), 3.57 (t, 4, OCH_2), 3.38 (t, 4, NCH_2); $^1\text{H NMR}$ (300 MHz, toluene- d^8): δ 6.90 (d, 4, H_m), 6.28 (t, 2, H_p), 3.62 (t, 4, OCH_2), 3.37 (t, 4, NCH_2).

$[\text{NON}^{\text{Cl}}]\text{ZrMe}_2 \cdot [\text{NON}^{\text{Cl}}]\text{ZrCl}_2$ was suspended in 20 mL of Et_2O (0.50 g, 0.91 mmol). This was set to chill at -20°C for 30 min after which 0.5 mL of a 3.7 M solution of MeMgBr in Et_2O (also at -20°C) was added *via* syringe. The white suspension appeared to homogenize to a light-yellow solution upon addition of the Grignard reagent. This was set to stir at room temperature for 10 min until the reaction gave deposition of brown solids. At this point, 5 mL of dioxane were added which initiated the precipitation of a

fine white powder. After stirring for an additional 20 min, all volatiles were removed in vacuo. The product was extracted using 40 mL of toluene, filtered through a pad of celite, and concentrated to dryness to yield the compound as a pale-white solid (0.326 g, 70%). Crystals suitable for X-ray diffraction were obtained overnight from a concentrated toluene solution sitting at -20°C . **Anal.**: found (calc'd.): C: 41.96 (42.11)%, H: 4.04 (3.93)%, N: 5.37 (5.46)%, Cl: 27.69 (27.62)%; $^1\text{H NMR}$ (300 MHz, C_6D_6): δ 7.081 (d, 4, H_m), 6.371 (t, 2, H_p), 3.479 (t, 4, OCH_2), 3.35 (t, 4, NCH_2), 0.67 (s, 6, CH_3).

Experimental details

Coordinates of hydrogen atoms of the methyl groups were refined with a restrained C–H distance and individually refined U_{iso} parameters. All other H atoms were included using the standard riding models of the SHELX system [3] with constrained U_{iso} parameters ($U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$). The data collection which dates back many years was accidentally interrupted. Thus, the completeness is only 94% in the chosen Ewald sphere, but we still achieved a data to parameter ratio of 10:1.

Comparing the title structure containing the 2,6-dichlorophenyl moiety with the structure of the analogous literature known 2,6-dimethylphenyl derivative, an isomorphous structural relation (same space group type, and indeed almost the same coordinates) is present, if the methyl group is seen as a pseudo atom.

Furthermore in contrast to the literature known 2,6-dimethylphenyl derivative [6], for the title structure, we were able to show that the two methyl groups exactly fulfill the crystallographically imposed mirror symmetry (see the Figure) of the space group $Pnma$.

Comment

The title complex, $[\text{NON}^{\text{Cl}}]\text{ZrMe}_2$, was obtained in 70% colorless crystalline yield from toluene and thoroughly characterized by means of X-ray diffraction and bulk analyses. The asymmetric unit of the title structure contains one half of the title complex (see the Figure), located on a mirror plane. Thus, the atoms Zr, O, C1, and C2 and one hydrogen atom of each methyl group (C1, C2) occupy the 4c Wyckoff site (transparent, red plane in the Figure). This X-ray study confirmed that the structure contains axial amido groups and a highly distorted trigonal

bipyramidal geometry of zirconium(IV) with a N–Zr–N' angle of $139.5(2)^{\circ}$ (see the Figure). The Zr–C1 and Zr–C2 bond lengths, 2.225(7) and 2.242(6) Å respectively, are very close to being statistically equivalent, while the O–Zr–C1 and O–Zr–C2 angles, $130.4(2)^{\circ}$ and $128.4(2)^{\circ}$ respectively, are statistically distinct. On the NMR time scale (solution NMR), no structure lower than C_{2v} symmetry was detected.

A Cambridge Structural Database [7] search shows closely related examples, namely the bis(2,6-dimethylphenyl) derivative, $[\text{NON}^{\text{Me}}]\text{ZrMe}_2$, [6] as well as the N,N -bis(2-(2,6-dichloroanilino)ethyl)- N -methylamine- N,N',N'' derivative, $[\text{NNN}^{\text{Cl}}]\text{ZrMe}_2$ [8]. While all three dimethylzirconium(IV) complexes are structurally very similar (near identical), they display different reactivity. Both $[\text{NON}^{\text{Me}}]\text{ZrMe}_2$ and $[\text{NON}^{\text{Cl}}]\text{ZrMe}_2$ can be activated with one equivalent of $[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$ to form $[(\text{NON}^E)\text{Zr}(\text{Me})(\text{NMe}_2\text{Ph})][\text{B}(\text{C}_6\text{F}_5)_4]$ where $E = \text{Me}$ or Cl , however the former is substitutionally inert (with respect to NMe_2Ph exchange) relative to the latter title complex [6]. Activation of $[\text{NON}^{\text{Cl}}]\text{ZrMe}_2$ in bromobenzene at 0°C generated a catalyst for the cationic polymerization of 1-hexene to poly(1-hexene) and shows some semblance to the rather highly active and more stable catalyst $[\text{NNN}^{\text{Cl}}]\text{ZrMe}_2$ reported previously [8].

Author contribution: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: None declared.

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. SCANS Siemens. XSCANS; Siemens Analytical X-ray Instruments Inc.: Madison, Wisconsin, USA, 1994.
2. Sheldrick G. M. SHELXT – integrated space-group and crystal-structure determination. *Acta Crystallogr.* 2015, *A71*, 3–8.
3. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
4. Hübschle C. B., Sheldrick G. M., Dittrich B. ShelXle: a Qt graphical user interface for SHELXL. *J. Appl. Crystallogr.* 2011, *44*, 1281–1284.
5. Brandenburg K. DIAMOND. Visual Crystal Structure Information System. Ver. 4.0; Crystal Impact: Bonn, Germany, 2015.
6. Aizenberg M., Turculet L., Davis W. M., Schattenmann F., Schrock R. R. Synthesis of group 4 complexes that contain the tridentate diamido/donor ligands $[(\text{Ary}(\text{NCH}_2\text{CH}_2)_2\text{O})_2]^-$ and zirconium complexes that contain $[(\text{ary}(\text{NCH}_2\text{CH}_2)_2\text{S})_2]^-$ and an

- evaluation of their activity for the polymerization of 1-hexene. *Organometallics* 1998, 17, 4795–4812. CSD Identifier NECRIW01.
7. Groom C. R., Allen F. H. The Cambridge Structural Database (CSD) in retrospect and prospect. *Angew. Chem. Int. Ed.* 2014, 53, 662–671.
8. Schrock R. R., Bonitatibus P. J. Jr., Schrodi Y. CH bond activation in cations of the type $\{[(2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{NCH}_2\text{CH}_2)_2\text{NMe}]\text{ZrR}\}^+$ and a simple solution that yields a catalyst for the living polymerization of 1-hexene. *Organometallics* 2001, 20, 1056–1058. CSD Identifier XIDFOF.