Preliminary communication

Unsymmetrical *ansa*-metallocenes of zirconium and hafnium

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Abstract

Tetrakis(dimethylamino)zirconium (**3a**) and -hafnium (**3b**) react with cyclopentadiene-indene ligand precusors to form new $\eta^5 : \eta^5$-metallocenes **1c,d** of the amido-type. A cyclopentadiene-fluorene ligand eliminates only one amide ligand from **3a** to yield a tris(amide) complex **5**, with the fluorenyl ligand not coordinating to the metal.

Keywords: Zirconium; Hafnium; *Ansa*-metallocenes; Metal amides

1. Introduction

Ever since the catalytic power of *ansa*-metallocenes in olefin polymerization was discovered [1], the main interest has concentrated on iso- and syndiospecific polymers [2–7]. However, the scope of metallocene catalysts is not limited to the common commercial "bulk polymers". Recent developments rather focus on new strategies in the polymer and copolymer design [8,9]. Here we report on the synthesis and structural characterization of unsymmetrical *ansa*-metallocenes of zirconium and hafnium of type **A** (Fig. 1), with **1c,d** particularly representing dimethylamide groups. These complexes are possible candidates for catalysis of olefin polymerization.

2. Synthesis

"Bridged metallocenes" of general type **A** combine the essential features required for the catalytic olefin polymerization: a large "aperture gap" and an unsymmetric coordination sphere to generate certain olefins selectivity. The dichloro complexes $[(CH_3)_2C(C_5H_4)$-$(C_9H_6)]MCl_2$ (**1a**: M = Zr; **1b**: M = Hf) are typically

prepared by the standard "salt metathesis" route from the lithiated ligand $Li_2[(CH_3)_2C(C_5H_4)(C_9H_6)]$ and zirconium tetrachloride [4,10–12]. The yields are generally moderate to low (12–35%), entailing a severe loss of ligand.

As recently reported by two independent research groups [13–15], homoleptic metal amides of the early transition metals of type $M(NR_2)_4$ are excellent precursors for the synthesis of *ansa*-metallocenes and bridged half-sandwich complexes. We have found that the iso-propylidene-bridged diprotic ligand $(CH_3)C(C_5H_5)$-(C_9H_7) (**2**) and dimethylamido complexes of zirconium (**3a**) and hafnium (**3b**) give the C_1-symmetric metallocenes **1c** (M = Zr) and **1d** (M = Hf), respectively, in quantitative yields (Scheme 1).

The light-orange, moisture-sensitive complex **1c** is obtained by stirring in toluene at slightly elevated temperatures, whereas for the synthesis of the hafnium congener **1d** higher temperatures and longer reaction times are required (Experimental Section). The progress of the reaction can be monitored by NMR spectroscopy. Each proton of the cyclopentadienyl and indenyl group is different because of the asymmetric ligand sphere. The resonances of the methyl substituents of the iso-propylidene bridge of **1c** are observed at $\delta = 1.56$, 1.89 ppm (1.57, 1.88 ppm for **1d**). The peaks of the amido groups appear at $\delta = 2.46$, 2.81 ppm, which positions are in good agreement with a recent report [15]. Just like the bridge-protons, the peaks of the π-system are moved to higher field ($\Delta\delta = 0.1$–0.8 ppm) as compared

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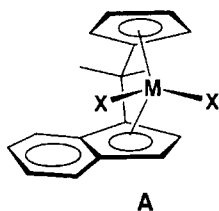
Fig. 1. Unsymmetrical *ansa*-metallocenes of type **A**.

to the dichloro homologue. This tendency is also observed at the dimethylsilicon-bridged metallocene amides and chlorides [15].

The efficiency of the *metal amide strategy* seems mainly to depend on steric effects [16]. Reaction of the fluorene ligand precusor $(CH_3)_2C(C_5H_5)(C_{13}H_9)$ (**4**), which is designed for zirconium complexes as catalysts of syndiospecific polymerization [2], and tetrakis(dimethylamido)zirconium (**3a**) does not lead to the double-substituted *ansa*-metallocene; instead it results in *quantitative* formation of the monocyclopentadienyl complex **5** according to Scheme 1. The zirconium(IV) tris-amide is conclusively characterized by spectroscopic means.

Although the transformation of the metallocene bis-amides to the corresponding dichlorides proved possible by a standard procedure [13], the catalytic performance of these metallocenes shows that the amido derivatives $(X = (CH_3)_2N)$ exhibit the same polymerization behaviour as the standard dichloro complexes $(X = Cl)$.

3. Structure

The unsymmetrical metallocene **1c** crystallizes as an orange–yellow solid from a saturated solution of *n-*
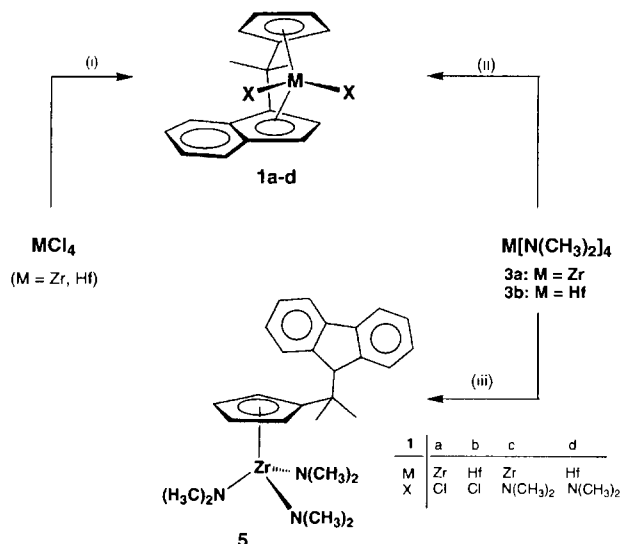
Scheme 1. Reaction conditions: (i) $(CH_3)_2C(C_5H_5)(C_9H_7)$ (**2**), BuLi,-2 LiCl, 12–35% yield. (ii) $(CH_3)_2C(C_5H_5)(C_9H_7)$ (**2**), toluene/xylene,-2(CH_3)_2NH, 99% yield (M = Zr), 95% (M = Hf). (iii) $(CH_3)_2C(C_5H_5)(C_{13}H_9)$ (**4**), toluene,-2(CH_3)_2NH, 99% yield (M = Zr).
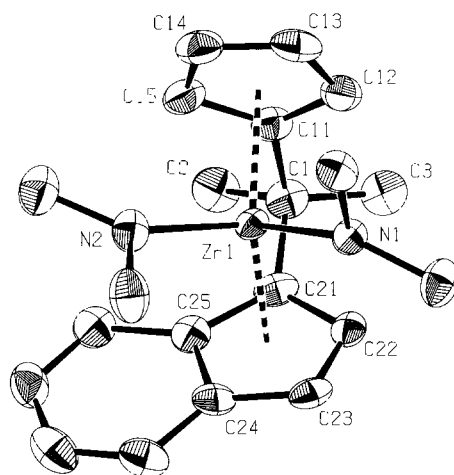

Fig. 2. PLATON drawing with ellipsoids drawn of 50% probability and numbering scheme of the novel zirconocene amide **1c**, see text.

hexane at $-30°C$. A single-crystal X-ray diffraction study revealed a molecular C_1-symmetry (Fig. 2, Table 1) [17]. The four substituents generate a slightly distorted tetrahedral coordination geometry around the zirconium. The lengths of the zirconium–nitrogen bonds amount to 207.4 and 205.6 pm (Table 2). The Zr–N distances of the homoleptic metal amide are 207.1 pm (in the gas phase) [18] and 205.4–210.8 pm in the crystal [19]. The bridging carbon atom also exhibits a distorted tetrahedral symmetry: C(3), C(1), C(2) 107.7°, C(21), C(1), C(11) 100.5°.

The steric consequences of the dimethylamido groups become obvious from a comparison of the distances

Table 1
Atomic coordinates of the metallocene amide $(CH_3)_2C(C_5H_4)-(C_9H_6)Zr[N(CH_3)_2]_2$ (**1c**)

Atom	x/a	y/b	z/c	U(iso)	U(eq) [Å²]
Zr	0.45077(3)	0.68674(3)	0.76986(1)	0.0213	0.0226
C(1)	0.7057(3)	0.8276(3)	0.5970(2)	0.0323	0.0330
C(2)	0.8201(4)	0.7371(4)	0.5160(2)	0.0388	0.0410
C(3)	0.7290(4)	1.0073(4)	0.5823(2)	0.0407	0.0412
C(4)	0.1085(3)	0.7881(3)	0.8989(2)	0.0326	0.0352
C(5)	0.3195(4)	0.94330(3)	0.9316(2)	0.0360	0.0382
C(6)	0.3770(4)	0.3189(4)	0.7535(2)	0.0436	0.0447
C(7)	0.3689(4)	0.4042(4)	0.8998(2)	0.0419	0.0439
C(11)	0.5091(3)	0.8036(3)	0.6093(2)	0.0302	0.0309
C(12)	0.3621(3)	0.9097(3)	0.6563(2)	0.0336	0.0341
C(13)	0.2119(3)	0.8277(4)	0.6761(2)	0.0354	0.0391
C(14)	0.2633(3)	0.6695(4)	0.6432(2)	0.0365	0.0394
C(15)	0.4466(3)	0.6531(3)	0.6032(2)	0.0332	0.0344
C(21)	0.7493(3)	0.7578(3)	0.6886(2)	0.0256	0.0287
C(22)	0.7056(3)	0.8469(3)	0.7689(2)	0.0253	0.0271
C(23)	0.7139(3)	0.7388(3)	0.8443(2)	0.0271	0.0296
C(24)	0.7708(3)	0.5796(3)	0.8140(2)	0.0281	0.0312
C(25)	0.7896(3)	0.5886(3)	0.7178(2)	0.0259	0.0296
C(26)	0.8449(3)	0.4381(3)	0.6716(2)	0.0337	0.0356
C(27)	0.8840(3)	0.2953(3)	0.7201(2)	0.0374	0.0394
C(28)	0.8652(4)	0.2903(4)	0.8153(2)	0.0433	0.0458
C(29)	0.8097(3)	0.4277(3)	0.8623(2)	0.0386	0.0403
N(1)	0.2964(2)	0.8119(2)	0.8792(1)	0.0253	0.0262
N(2)	0.3886(3)	0.4549(2)	0.8052(1)	0.0322	0.0327

Table 2
Selected bond lengths and angles of *ansa*-zirconocene **1c**

Bond lengths [pm]		Bond angles [°]	
Zr–N(1)	207.4(2)	N(2)–Zr–N(1)	99.92(8)
Zr–N(2)	205.6(2)	C(21)–C(1)–C(11)	100.5(2)
Zr–C(11)	252.1(2)	Cp_{zent}–Zr–Ind$_{zent}$	113.6
Zr–C(12)	252.5(3)	C(4)–N(1)–Zr	114.7(2)
Zr–C(13)	260.6(2)	C(5)–N(1)–Zr	135.0(2)
Zr–C(14)	262.9(3)	C(5)–N(1)–C(4)	109.1(2)
Zr–C(15)	255.5(2)	C(6)–N(2)–Zr	133.3(2)
Zr–C(21)	251.4(2)	C(7)–N(2)–Zr	116.9(2)
Zr–C(22)	252.8(2)	C(7)–N(2)–C(6)	109.4(2)
Zr–C(23)	259.9(2)	Cp–Ind	73.5
Zr–C(24)	266.7(2)		
Zr–C(25)	258.2(2)		
Zr–Cp	226.6		
Zr–Ind	227.3		
Zr–Cp$_{cent}$	227.0		
Zr–Ind$_{cent}$	227.9		

C11–C15 = cyclopentadienyl ring; C21–C25 = π-bonded part of the indenyl system; Cp$_{cent}$ or Ind$_{cent}$ = centres of the π-ligands; Cp, Ind defines the ring planes.

between the metal and the π-ligands and the related angles of **1c** (Table 1) with **1a** [10] and related complexes [20–22]. The bonds of **1c** are longer by 3 to 8 pm than in the dichloro complex **1a** (246.3–255.1 Zr–Cp, 242.6–262.6 Zr–Ind) [10], the metal-to-centroid distances also increase (from 218.8/220.9 pm in **1a** to 227.0/227.9 pm in **1c**). The expansion of the coordination core is caused by changes of the characteristic angles; in particular the Cp$_{cent}$–Zr–Ind$_{cent}$ (Table 1) shrinks from 117.1° (**1a**) to 113.6° (**1c**). The angle of the tetramethylcyclopentadienyl derivative amounts to 118.2° [20]. The C(21), C(1), C(11) angle of the metallocene amide **1c** is 100.5°, while that of the dichlorides is at 99.5° and 99.4° [10,20]. Summarizing these results, the "aperture gap" of the π-ligands slightly opens and the metal is placed further away from the chelating η^5 : η^5-ligand sphere.

4. Conclusion

The "amide route" to introduce π-cyclopentadienyl ligands in zirconium(IV) and hafnium(IV) complexes responds in a first approximation on the steric bulk of the (protic) ligand precursors. What has to be explored in the future, is the significance of the steric bulk associated with the amide ligands of the metal as well as the the CH-acidity of the ligand precursors.

5. Experimental section

The ligands were prepared by standard procedures [4,12]. The metal complexes are *extremely air- and moisture-sensitive*, so all reactions and manipulations

must be carried out in an atmosphere of pure and dry argon, using either standard high-vacuum techniques and standard Schlenk procedures or a glove-box. Solvents were pre-dried and freshly distilled or vacuum-transfered from Na/K alloy. ZrCl$_4$ (Aldrich) was sublimed prior to use. The metal amides M(NR$_2$)$_4$ (**3a,b**) were synthesized according to literature procedures [19,23,24], and stored in a glove-box (N$_2$ atmosphere). Taking into account the nitride and carbide formation upon combustion the new organozirconium and -hafnium compounds gave acceptable elemental analyses [25]. IR spectra were recorded as fluid films using a Perkin-Elmer 1650 FTIR Spectrometer. Mass spectra were obtained on a Varian-MAT 90 spectrometer (CI). NMR spectra were performed on a JEOL-JMN-GX 400 spectrometer.

5.1. Bis(dimethylamido)[2-(η^5-cyclopentadienyl)-2-(η^5-indenyl)propane]zirconium (1c)

A solution of Zr[N(CH$_3$)$_2$]$_4$ (**3a**) (416 mg, 1.55 mmol) in 25 ml toluene is cooled to −78°C and (CH$_3$)$_2$C(C$_5$H$_5$)(C$_9$H$_7$) (**2**) (345 mg, 1.55 mmol, dissolved in 10 ml of toluene) is subsequently added. The solution is slowly warmed to room temperature. The clear solution is then stirred at 80°C for 3 h. A yellow color arises first and then changes to orange. The solvent of the clear, orange reaction mixture is removed under reduced pressure. Complex **1c** is obtained as a yellow–orange solid. Yield: 613 mg (1.53 mmol, 99%).

5.1.2. Spectroscopic Data

^{1}H NMR (400 MHz, C$_6$D$_6$, 25°C): [ppm] δ = 1.57, 1.89 (s, 6 H; C(CH$_3$)$_2$), 2.46, 2.81 (s, 12 H; N(CH$_3$)$_2$), 5.29 (q, 1 H, ^3J(H,H) = 2.4 Hz; olefin. CH in C$_5$H$_4$), 5.80 (m, 2 H; olefin. CH in C$_5$H$_4$ and C$_9$H$_7$), 5.99 (q, 1 H, ^3J(H,H) = 2.4 Hz; olefin. CH in C$_5$H$_4$), 6.08 (q, 1 H, ^3J(H,H) = 1.8 Hz; olefin. CH in C$_5$H$_4$), 6.59 (d, 1 H, ^3J(H,H) = 3.0 Hz; olefin. CH in C$_9$H$_7$), 6.69 (dd, 1 H, ^3J(H,H) = 6.7 Hz; olefin. CH in C$_9$H$_7$), 6.87 (dd, 1 H, ^3J(H,H) = 6.7 Hz; olefin. CH in C$_9$H$_7$), 7.49 (d, 1 H ^3J(H,H) = 7.9 Hz; olefin. CH in C$_9$H$_7$), 7.62 (d, 1 H ^3J(H,H) = 7.9 Hz; olefin. CH in C$_9$H$_7$). ^{13}C{^{1}H} NMR (100.5 MHz, C$_6$D$_6$, 25°C): [ppm] δ = 26.2, 26.7 (s; C(CH$_3$)$_2$), 38.1 (s; C(CH$_3$)$_2$), 47.2, 48.3 (s; N(CH$_3$)$_2$), 102.0, 102.2, 102.8, 107.8, 109.6 (s; olefin. CH), 111.8 (s; olefin. C), 114.3 (s; olefin. CH), 118.2 (s; olefin. C), 122.7, 123.2, 123.6, 125.7 (s; aromat. CH). ^{13}C NMR (100.5 MHz, C$_6$D$_6$, 25°C): [ppm] δ = 26.2, 26.7 (q, ^1J(C,H) = 132.0 Hz; C(CH$_3$)$_2$), 38.1 (s; C(CH$_3$)$_2$), 47.2 (q, ^1J(C,H) = 125.9 Hz; N(CH$_3$)$_2$), 48.3 (q, ^1J(C,H) = 125.8 Hz; N(CH$_3$)$_2$), 102.0 (d, ^1J(C,H) = 167.3 Hz; olefin. CH), 102.2 (d, ^1J(C,H) = 176.0 Hz; olefin. CH), 102.8 (d, ^1J(C,H) = 172.5 Hz; olefin. CH), 107.8 (d, ^1J(C,H) = 170.0 Hz; olefin. CH), 109.6 (d,

^1J(C,H) = 164.1 Hz; olefin. CH), 111.8 (s; olefin. C), 114.3 (d, ^1J(C,H) = 170.9 Hz; olefin. CH), 118.2 (s; olefin. C), 122.7 (d, ^1J(C,H) = 166.0 Hz; aromat. CH), 123.2 (d, ^1J(C,H) = 160.0 Hz; aromat. CH), 123.6 (d, ^1J(C,H) = 159.1 Hz; aromat. CH), 125.7 (d, ^1J(C,H) = 162.0 Hz; aromat. CH). MS (CI): m/z (%) = 708 (10) [2M$^+$ − 2 NMe$_2$], 398 (100) [M$^+$], 355 (45) [M$^+$ − NMe$_2$], 311 (21) [M$^+$ − 2 NMe$_2$].

5.2. Bis(dimethylamido)[2-(η^5-cyclopentadienyl)-2-(η^5-indenyl)propane]hafnium (1d)

Using the same procedure as in Section 5.1 833 mg (2.35 mmol) Hf[N(CH$_3$)$_2$]$_4$ (3b) in 30 ml of xylene and 2 (522 mg, 2.35 mmol) in 30 ml of xylene except for a longer reflux time (150°C, 8 h) and recrystallization from n-pentane affords the product in 95% yield: 1.19 g (2.23 mmol, 95%).

5.2.1. Spectroscopic Data

^{1}H NMR (400 MHz, C$_6$D$_6$, 25°C): [ppm] δ = 1.57, 1.88 (s, 6 H; C(CH_3)$_2$), 2.51, 2.85 (s, 12 H; N(CH$_3$)$_2$), 5.29 ("q", 1 H; olefin. CH in C$_5$H$_4$), 5.70–5.80 (m, 2 H; olefin. CH in C$_5$H$_4$ and C$_9$H$_7$), 6.00 (m, 1 H; olefin. CH in C$_5$H$_4$), 6.04 (m, 1 H; olefin. CH in C$_5$H$_4$), 6.53 (d, 1 H, ^3J(H,H) = 3.0 Hz; olefin. CH in C$_9$H$_7$), 6.71 (t, 1 H, ^3J(H,H) = 6.7 Hz; olefin. CH in C$_9$H$_7$), 6.87 (t, 1 H, ^3J(H,H) = 7.0 Hz; olefin. CH in C$_9$H$_7$), 7.49 (d, 1 H ^3J(H,H) = 7.9 Hz; olefin. CH in C$_9$H$_7$), 7.63 (d, 1 H ^3J(H,H) = 8,6 Hz; olefin. CH in C$_9$H$_7$). ^{13}C{^{1}H} NMR (100.5 MHz, C$_6$D$_6$, 25°C): [ppm] δ = 26.3, 26.8 (s; C(CH_3)$_2$), 38.2 (s; C(CH$_3$)$_2$), 47.2, 48.0 (s; N(CH_3)$_2$), 100.6, 101.1, 101.8, 107.2, 108.6 (s; olefin. CH), 111.7 (s; olefin. C) 113.6 (s; olefin. CH), 117.9 (s; olefin. C), 122.7, 123.3, 123.9, 125.7 (s; aromat. CH). MS (CI): m/z (%) = 620 (100), 600 (18), 512 (24), 497 (28), 442 (17), 399 (25), 222 (26), 207 (26), 115 (8), 107 (20).

5.3. Tris(dimethylamido)[2-(η^5-cyclopentadienyl)-2-fluorenylpropane]zirconium (5)

Tetrakis(dimethylamido)zirconium (3a) (267 mg, 1.0 mmol, in 15 ml of toluene) and (CH$_3$)$_2$C(C$_5$H$_5$)(C$_{13}$H$_9$) (8) (272 mg, 1.0 mmol, in 10 ml of toluene) are combined at − 78°C. The reaction mixture is warmed to 25°C and stirred for 2 h. A light yellow solution is being formed during that time. Removal of the solvent in vacuo affords the tris(amido) complex in almost quantitative yield as an off-white solid: 1.19 g (2.23 mmol, 95%).

5.3.1. Spectroscopic data

^{1}H NMR (400 MHz, C$_6$D$_6$, 25°C): [ppm] δ = 1.12 (s, 6 H; C(CH_3)$_2$), 2.90 (s, 16 H; N(CH$_3$)$_2$), 3.96 (s, 1

H; acidic CH in C$_{13}$H$_9$), 5.90 (t, 1 H, ^3J(H,H) = 2.4 Hz; olefin. CH), 6.07 (t, 1 H, ^3J(H,H) = 2.4 Hz; olefin. CH), 6.82 (d, 2 H, ^3J(H,H) = 7.9 Hz; aromat. CH), 7.10 (t, 2 H, ^3J(H,H) = 8.5 Hz; aromat. CH), 7.22 (t, 2 H, ^3J(H,H) = 7.9 Hz; aromat. CH), 7.60 (d, 2 H, ^3J(H,H) = 7.3 Hz; aromat. CH). ^{13}C{^{1}H} NMR (100.5 MHz, C$_6$D$_6$, 25°C): [ppm]δ = 25.1 (s; C(CH_3)$_2$), 39.9 (s; C(CH$_3$)$_2$), 45.2 (s; N(CH_3)$_2$), 61.3 (s; CH), 109.2, 110.2 (s; olefin. CH), 111.4 (s; olefin. C), 119.6, 126.2, 127.0, 127.5 (s; aromat. CH), 140.4, 142.6 (s; aromat. CH). MS (CI): m/z (%) = 493 (1) [M$^+$], 479 (2) [M$^+$ − CH$_3$], 437 (5) [M$^+$ − CH$_3$ − NMe$_2$], 273 (41) [LH$^+$], 221 (20) [Zr(NMe$_2$)$_3^+$], 207 (29) [L$^+$ − C$_5$H$_4$], 165 (60) [C$_{13}$H$_9^+$], 107 (100) [L$^+$ − C$_{13}$H$_9$]. IR (nujol): [cm^{-1}] $\tilde{\nu}$ = 3062 w (ν(=CH)), 2940 vs (ν(C–H)), 2853 vs (ν(C–H)), 1241 m, 1140 m, 940 s, 784 m, 741 s, 535 m.

5.4. Crystal structure determination of 1c

A yellow crystal of 1c was selected in a perfluorinated oil and mounted in a glass capillary on an automatic Four Circle Diffractometer (CAD4, Enraf Nonius). Final lattice parameters were obtained by least squares refinement of 25 high angle reflections (graphite monochromater, λ = 71.073 pm, Mo K$\bar{\alpha}$). Triclinic system, space group P$\bar{1}$ (I.T.-No.: 2), a = 767.2(2) pm, b = 827.6(2) pm, c = 1507.5(3) pm, α = 85.65(1)°, β = 78.80(2)°, γ = 80.86(2)°, V = 926 · 10^6 pm^3, δ_{calc} = 1.434 gcm^{-3}, Z = 2. Data were collected at − 80(± 1)°C, using the omega-scan method, maximal acquisition time 120 sec for a single reflection. Data were corrected for Lorentz and polarization terms. 3388 Data measured, 3065 independent reflections, 106 with negative intensity, 3065 reflections with $I > 0.01 \cdot \sigma(I)$ used for refinement. The structure was solved by direct methods [26] and refined with standard difference Fourier techniques [27]. All hydrogen atoms were located in difference Fourier maps and refined isotropically. 329 Parameters refined, 9.32 data per parameter, weighting scheme according to Tukey and Prince [28] (2 parameters), shift/error < 0.001 in the last cycle of refinement, residual electron density + 0.82 e Å^{-3} 84 pm near Zr, − 0.33 e Å^{-3}, R = 0.027, Rw = 0.026, minimized function was $\Sigma w(|F_o| − |F_c|)^2$.

Supplementary material available

Tables of complete bond distances and angles, anisotropic displacement coefficients, and hydrogen atom coordinates and isotropic displacement coefficients (26 pages). Ordering information is given on any current masthead page.

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