Supporting Information

For

CH Bond Activation in Cations of the Type $\{[(2,4,6\text{-}Me_3C_6H_2NCH_2CH_2)_2NMe]ZrR\}^+$ and a Simple Solution that Yields a Catalyst for the Living Polymerization of 1-Hexene

By

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General

All manipulations were performed under an atmosphere of purified N_2 using standard Schlenk or drybox techniques. Toluene and diethyl ether were sparged with N_2 and passed through two columns of activated alumina. THF was distilled from sodium/benzophenone. Pentane was sparged with N_2, then passed through one column of activated alumina, and then through another of activated Q5. Deuterated solvents were sparged with N_2 and stored in the box for 2 days prior to use. All solvents were stored in the glove box over 4 Å molecular sieves. 1-Hexene was refluxed over CaH_2 for four days, distilled, and stored over 4 Å sieves. Molecular sieves and celite were activated *in vacuo* (10^{-3} Torr) for 24 hours at 175 and 125°C, respectively. Chemicals were obtained from commercial sources, and used without further purification (unless indicated otherwise). $^{13}CH_3MgI$ was prepared from $^{13}CH_3I$ and Mg turnings in diethyl ether. $[Ph_3C][B(C_6F_5)_4]$ and $[HNMe_2Ph][B(C_6F_5)_4]$ were provided by Exxon Chemical Corporation. Elemental analyses were performed by H. Kolbe Mikroanalytisches Laboratorium, Höhenweg 17, D-45470 Mülheim an der Ruhr, Germany. NMR spectra were taken at room temperature, unless otherwise indicated, and chemical shifts are reported in ppm downfield from tetramethylsilane.

Preparation of the dimer of 2. $[Ph_3C][B(C_6F_5)_4]$ (88.0 mg, 94.5 μmol) was added to a cold solution (-30°C) of $[N_2NMe]ZrMe_2$ (45.0 mg, 94.5 μmol) in C_6D_5Br (2.0 mL) in a 4 mL vial to yield $\{[(MesNCH_2CH_2)_2NMe]ZrMe\}^+$ (**1**, as its $[B(C_6F_5)_4]^-$ salt) quantitatively according to ^1H NMR. The orange solution was then left at room temperature for two days to give dark orange needles of **2** (105.0 mg, 80.3 μmol) in 85% yield (after decanting C_6D_5Br, washing with pentane, and drying *in vacuo*). The crystals are insoluble in benzene, toluene, bromobenzene, N,N'-dimethylaniline, or a mixture of bromobenzene and N,N'-dimethylaniline.

Kinetic of decomposition of 1. A cold solution (-30°C) of $[Ph_3C][B(C_6F_5)_4]$ (17.6 mg, 19.0 μmol) in C_6D_5Br (250 μL) was added to a cold solution (-30°C) of $[(MesNCH_2CH_2)_2NMe]ZrMe_2$ (9.0 mg, 19.0 μmol) in C_6D_5Br (250 μL) to give a 38.0 mM solution of **1**, which was then transferred to a vial containing Ph_2CH_2 (3.2 mg) as an internal

standard, and finally to an NMR tube. The decomposition was followed by ^{1}H NMR at 20°C and 60°C using the methylene resonances of Ph_2CH_2 as the integration standard. A 19.0 mM solution of **1** in C_6D_5Br containing Ph_2CH_2 was prepared in a similar manner and the decomposition kinetic was followed at 20°C.

Kinetics of 1-hexene polymerization by {[(MesNCH$_2$CH$_2$)$_2$NMe]ZrMe(PhNMe$_2$)}$^+$ (0.25 mM). A 12.6 mM stock solution of {[(MesNCH$_2$CH$_2$)$_2$NMe]ZrMe(PhNMe$_2$)}[B(C_6F_5)$_4$] in C_6D_5Br was prepared by adding [PhNHMe$_2$][B(C_6F_5)$_4$] (10.2 mg, 12.6 μmol) as a solid to a solution of [(MesNCH$_2$CH$_2$)$_2$NMe]ZrMe$_2$ (6.0 mg, 12.6 μmol) in C_6D_5Br (1.0 mL). A stock solution of C_6Me_6 was prepared by dissolving C_6Me_6 (2.0 mg) in C_6D_5Br (1.0 mL). The {[(MesNCH$_2$CH$_2$)$_2$NMe]ZrMe(PhNMe$_2$)}[B(C_6F_5)$_4$] stock solution (20.0 μL) and the C_6Me_6 stock solution (50 μL) were mixed in C_6D_5Br (920 μL) and the solution was cooled down in the freezer (-30°C) for 20 minutes. 1-Hexene (10 μL, 150 equiv) was then added under vigorous stirring and the consumption of olefin was monitored at 0°C by ^{1}H NMR using C_6Me_6 as a standard.

Decomposition of the polymerization intermediates. A solution of [Ph_3C][B(C_6F_5)$_4$] (11.7 mg, 12.6 μmol) in C_6H_5Br (300 μL) was added to a solution of [(MesNCH$_2$CH$_2$)$_2$NMe]ZrMe$_2$ (6.0 mg, 12.6 μmol) in C_6H_5Br (300 μL) to give a solution of **1**, which was cooled down in the freezer (-30°C) for 15 minutes. 1-Hexene (50 μL, 20 equiv) was added while stirring the reaction vigorously and the reaction mixture was allowed to sit at room temperature for 2 days to give dark orange needles of **2** according to X-ray diffraction analysis (unit cell determination).

HN{CH$_2$CH$_2$NH[2,6-$C_6H_3Cl_2$]}$_2$ ($H_2[Ar_{Cl}N_2NH]$). The following reagents were combined in a 100 mL Schlenk tube: toluene (50 mL), 2-bromo-1,3-dichlorobenzene (5.14 g, 22.8 mmol), HN($CH_2CH_2NH_2$)$_2$ (1.17 g, 11.4 mmol), [Pd_2(dba)$_3$] (0.052 g, 0.057 mmol), *rac*-BINAP (0.106 g, 0.170 mmol), and NaO-t-Bu (3.28 g, 0.034 mol). The reaction was stirred in a sealed tube under N_2 in an oil bath heated to 95°C for 5 days. The solvent was removed *in vacuo* at 50°C to leave a dark brown residue. A total of 175 mL of diethyl ether and the same volume of

water were added. The organic layer was separated, washed 3x with a total of 300 mL of a saturated NaCl solution, dried over $MgSO_4$, and filtered (through alumina). The solvents were removed from the filtrate *in vacuo* dryness to give a dark-orange oil which solidified over the course of a fortnight (80%): ^{1}H NMR (300 MHz, C_6D_6) δ 6.96 (d, 4, H_m), 6.24 (t, 2, H_p), 4.76 (br t, 2, ArylNH), 3.23 and 2.36 (m, 4 each, backbone CH_2 groups), 0.48 (br s, 1, NH); FAB-MS: positive ion $(M+H)^+$, measured (calcd) 392.0242 ± 0.0012 (392.0255).

MeN{CH_2CH_2NH[2,6-$C_6H_3Cl_2$]}$_2$ ($H_2[Ar_{Cl}N_2NMe]$). $H_2[Ar_{Cl}N_2NH]$ was dissolved in 100 mL of anhydrous CH_3CN (2.0 g, 5.12 mmol), and to this was added K_2CO_3 (2.59 g, 18.7 mmol). The reaction was sparged with N_2 for 15 min. and MeI was added dropwise *via* syringe with vigorous stirring (0.34 mL, 5.4 mmol). The reaction was stirred overnight during which time a tan suspension formed. All volatile components were removed and the residue was worked up with a mixture of ether and water. The organic layer was separated, washed several times with water, and dried over $MgSO_4$. Removal of solvent *in vacuo* gave a brown-orange semi-solid (61%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (d, 4, H_m), 6.76 (t, 2, H_p), 4.76 (br s, 2, ArylNH), 3.45 and 2.66 (m, 4, backbone CH_2 groups), 2.31 (s, 3, NMe); FAB-MS: positive ion $(M+H)^+$, measured (calcd): 406.0421 ± 0.0012 (406.0411).

This reaction can be scaled up to 5 g (12.8 mmol) of $H_2[Ar_{Cl}N_2NH]$, using 6.5 g of K_2CO_3 and 0.84 mL of MeI in 200 mL of CH_3CN.

$[Ar_{Cl}N_2NMe]Zr(NMe_2)_2$. $H_2[Ar_{Cl}N_2NMe]$ was dissolved in 35 mL of ether (0.98 g, 2.4 mmol), and $Zr(NMe_2)_4$ (0.64 g, 2.4 mmol) was added as a solid all at once. The reaction was allowed to stir overnight and was filtered through a bed of celite. The filtrate was washed with 5 mL of pentane and concentrated *in vacuo* to give a yellow solid (89%): ^{1}H NMR (300 MHz, $C_6D_5CD_3$) δ 7.12 (d, 4, H_m), 6.42 (t, 2, H_p), 3.92, 3.25, 3.05 (m, backbone CH_2 groups), 3.31 and 2.55 (s, 6, NMe_2), 2.31 (s, 3, NMe). *Anal.* Calcd for $ZrCl_4N_5C_{21}H_{29}$: C, 43.15; H, 5.00; N, 11.98; Cl, 24.26. Found: C, 43.02; H, 5.11; N, 11.85; Cl, 24.11.

$[Ar_{Cl}N_2NMe]ZrCl_2$. $[Ar_{Cl}N_2NMe]Zr(NMe_2)_2$ was dissolved in 40 mL of toluene (1.09 g, 1.87 mmol) to give a light yellow solution. To this was added neat TMSCl (0.71 g, 6.54

mmol) at room temperature under N_2 with vigorous stirring. The mixture was allowed to stir overnight. All volatile components were removed *in vacuo* to yield the product as a fine off-white powder (0.97 g, 91%): ^{1}H NMR (300 MHz, C_6D_6) δ 6.95 (d, 4, H_m), 6.32 (t, 2, H_p), 3.74, 3.01, 2.81, 2.33 (m, backbone CH_2 groups), 2.36 (s, 3, NMe).

[$Ar_{Cl}N_2$NMe]ZrMe$_2$. [$Ar_{Cl}N_2$NMe]$ZrCl_2$ was suspended in 20 mL of Et_2O (0.25 g, 0.44 mmol) and the solution was cooled to -20°C. A solution of MeMgBr in Et_2O (0.3 mL of a 3.7 M solution) was added *via* syringe. After 10 min at room temperature 2-3 mL of dioxane were added, which initiated the precipitation of a fine white powder. After an additional 10 min, all volatile components were removed *in vacuo*. The product was extracted into 40 mL of toluene. The solution was filtered through a pad of celite and concentrated to dryness *in vacuo* to yield the compound as a tan-white solid (70%): ^{1}H NMR (300 MHz, C_6D_6) δ 7.12 (d, 4, H_m), 6.42 (t, 2, H_p), 3.70, 3.21, 2.76, and 2.03 (m, each 2, backbone CH_2's), 2.19 (s, 3, NMe), 0.60 (s, 6, CH_3). Zr-bound methyl groups split in the ^{1}H NMR (500 MHz, C_6D_6) δ 0.59 and 0.59 (s, 3). *Anal.* Calcd for $ZrCl_4N_3C_{19}H_{23}$: C, 43.60; H, 4.43; N, 8.03; Cl, 26.75. Found: C, 43.48; H, 4.48; N, 7.94; Cl, 26.66.

[$Ar_{Cl}N_2$NMe]Zr^{13}Me$_2$. [$Ar_{Cl}N_2$NMe]$ZrCl_2$ was suspended in 20 mL of Et_2O (0.32 g, 0.57 mmol) and the solution was set aside to chill, along with a solution of ^{13}MeMgI, at -20°C for 30 min. A solution of ^{13}MeMgI in Et_2O (1.72 mL of a 1.0 M solution) was then added to the [$Ar_{Cl}N_2$NMe]$ZrCl_2$ *via* syringe. After 15 min 2.5 mL of dioxane were added. After an additional 15 min, all volatile components were removed *in vacuo* and the product was extracted into 40 mL of toluene. The solution was filtered through a pad of celite and concentrated to dryness to yield the compound as a pale-white solid (70%): ^{1}H NMR (300 MHz, C_6D_6) δ 7.17 (d, 4, H_m), 6.41 (t, 2, H_p), 3.72, 3,21, 2.75, 2.07 (m, 2, backbone CH_2 groups), 2.20 (s, 3, NMe), 0.61 (d, 6, $^{13}CH_3$, peaks register at 0.81 and 0.42); ^{13}C{^{1}H} NMR (500 MHz, C_6D_5Br) δ 46.18 and 45.44 (s, $^{13}CH_3$); ^{13}C{^{1}H} NMR (500 MHz, C_6D_6) δ 46.96 and 46.03 (s, $^{13}CH_3$). Crystals suitable for X-ray diffraction were obtained overnight from a concentrated THF solution at -20°C.

[{[$Ar_{Cl}N_2NMe$]Zr(^{13}Me)(NMe_2Ph)}][$B(C_6F_5)_4$]. A solution of [$Ar_{Cl}N_2NMe$]$Zr^{13}Me_2$ in 0.5 mL of C_6D_5Br (17.5 mg, 33.21 mmol) and a suspension of [$PhNMe_2H$][$B(C_6F_5)_4$] in 0.5 mL of C_6D_5Br (26.6 mg, 33.18 mmol) were set aside to chill at -20°C for 30 minutes. The Zr solution was added to the activator and the mixture was stirred at room temperature for 20 min to give a yellow solution. An aliquot was placed in an NMR tube. The tube was placed into an ethylene glycol/CO_2 bath before being placed ultimately into an NMR probe sitting at -14°C: ^{1}H NMR (500 MHz, -14°C, C_6D_5Br) δ 7.22 (d, 4, H_m), 6.80 (t, 2, H_p), 6.19, 5.97, 5.78 (br s, 2 each, *Ph*NMe_2), 3.30, 3.02, and 2.87 (m, 2 each, CH_2), 2.61 (s, 6, PhN*Me*$_2$), 2.54 (s, 3, NMe), 0.08 and -0.15 (J_{CH} = 117.5 Hz, d, 3, $^{13}CH_3$); ^{13}C NMR (500 MHz, -14°C, C_6D_5Br) δ 37.80 (s, $^{13}CH_3$). A similar procedure was used to generate the cation for catalytic polymerization runs. However, stock solutions were prepared and the total reaction volume (taking into account that supplied by injecting 1-hexene, activator, and zirconium) was adjusted to 1 mL. All bulk polymerization and kinetic runs were performed at 3mM in zirconium. For kinetic runs the consumption of olefin was monitored at 0°C by ^{1}H NMR using C_6Me_6 as a standard. For bulk polymerizations, reactions were allowed to stir for 60 min. They were quenched by the addition of methanol. All volatile components were removed and the residual poly(1-hexene) was extracted into hexane. The extract was filtered through a plug of silica and the hexane was removed *in vacuo*. Polymers were analyzed in THF by GPC (Wyatt Technology).

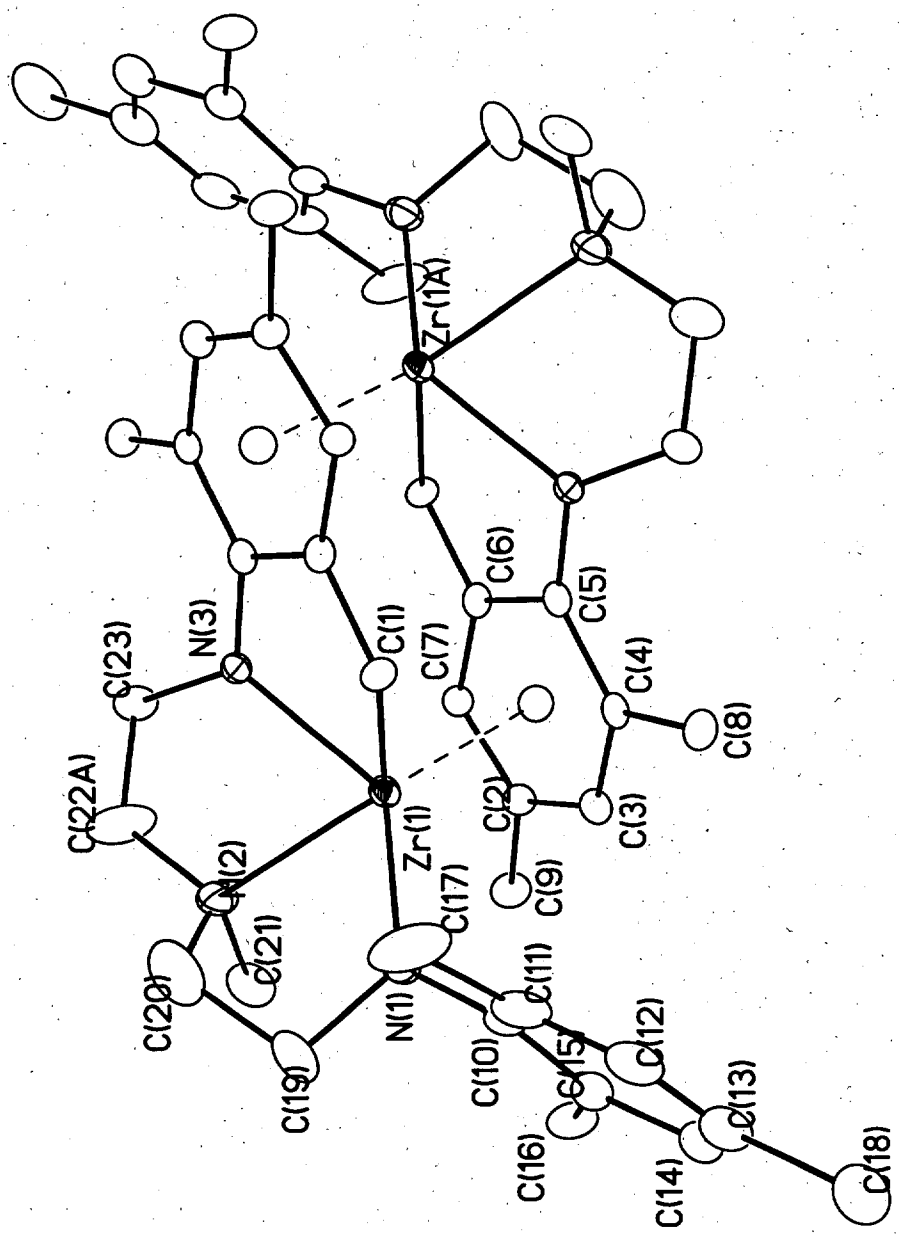
X-Ray Crystallography

Crystals were isolated from mother liquor by using a pipette to deposit a small visible quantity onto a microscope slide. These were then covered with deoxygenated heavy mineral oil (Exxon Paratone N) in order to be manipulated and evaluated under a microscope. A crystal was chosen and mounted on a thin glass fiber with the aid of a mixture of Paratone oil and high-vac silicon grease, and transferred immediately to the cold stream (-90°C) of a Bruker CCD area detector diffractometer (graphite-monochromated MoK_α radiation was provided by a sealed X-

ray tube at 50kV and 40mA). Unit cell parameters were determined using an automatic routine in SMART and refined prior to data collection.

Data collection proceeded by acquisition of 1,270 10 sec frame images using a scan width of 0.3°. These frames were then subjected to scanning for, and integration of data by the SAINT program to obtain a set of integrated reflection intensities.

The resultant data were processed using the SHELXTL-Plus suite of programs. Direct methods routines allowed for solution of the structures. Full-matrix least squares refinements were computed on F^2 values with residuals calculated according to preset formulas. Bond distances and angles of the complexes, anisotropic thermal parameters, atomic coordinates, and ORTEP plots are all provided below.



Fully labeled ORTEP representation of the structure of the dimer of **2.** Hydrogen atoms, $[B(C_6F_5)_4]^-$, and the C_6D_5Br molecule of solvation have been omitted for clarity.

Table 1. Crystal data and structure refinement details for the dimer of **2**.

Temperature	183(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Triclinic, $P\bar{1}$	
Unit cell dimensions	a = 13.2099(14) Å	α = 89.348(2) deg.
	b = 13.8383(14) Å	β = 76.558(2) deg.
	c = 15.1900(15) Å	γ = 81.160(2) deg.
Volume	2667.8(5) $Å^3$	
Z, Calculated density	2, 1.682 g/cm^3	
Absorption coefficient	1.070 mm^{-1}	
F(000)	1335	
Crystal size	0.2 x 0.1 x 0.1 mm^3	
2θ range for data collection	4.02 to 45.0 deg.	
Limiting indices	$-13 \le h \le 14$, $-14 \le k \le 14$, $-16 \le l \le 9$	
Reflections collected / unique	10216 / 6877 [R_{int} = 0.0490]	
Completeness to 2θ = 45.0	98.8 %	
Absorption correction	Empirical	
Max. and min. transmission	0.3737 and 0.2669	
Refinement method	FMLS on F^2	
Data / restraints / parameters	6877 / 0 / 750	
Goodness-of-fit on F^2	1.019	
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0691, wR_2 = 0.1665	
Extinction coefficient	0.0000(6)	
Largest diff. peak and hole	1.616 and -1.107 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for the dimer of **2**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)
Zr(1)	11361(1)	4001(1)	3957(1)	31(1)
Br(1)	5628(2)	6732(2)	2880(1)	139(1)
F(19)	11451(4)	-417(3)	2605(3)	49(1)
F(11)	6793(4)	-621(3)	4295(3)	50(1)
F(20)	9716(3)	901(3)	2741(3)	43(1)
F(10)	8331(4)	2601(3)	2360(3)	48(1)
F(5)	8584(4)	385(3)	4510(3)	49(1)
F(1)	6242(4)	2457(3)	3113(3)	51(1)
F(18)	11344(4)	-2358(3)	2542(3)	50(1)
F(16)	7735(4)	-1669(3)	2712(3)	47(1)
F(15)	5850(4)	1067(4)	1798(3)	55(1)
F(12)	4935(4)	-1234(4)	4688(4)	66(2)
F(8)	8960(7)	2169(5)	-753(4)	112(3)
F(6)	7741(4)	-331(4)	1121(3)	58(1)
F(7)	8383(6)	349(5)	-532(4)	99(2)
C(42)	8617(6)	-304(5)	2779(5)	35(2)
F(2)	5945(4)	3778(4)	4449(4)	70(2)
F(3)	6983(4)	3441(4)	5802(4)	67(2)
C(29)	7933(7)	1225(6)	4432(5)	39(2)
F(17)	9459(4)	-2949(3)	2586(3)	53(1)
C(4)	9413(6)	3950(5)	3666(5)	32(2)
C(5)	9077(6)	4401(5)	4554(5)	31(2)
F(4)	8296(4)	1716(4)	5797(3)	57(1)
C(27)	7138(7)	2774(7)	5131(6)	50(2)
C(39)	4436(7)	-385(6)	3466(7)	48(2)
F(13)	3489(4)	-673(4)	3669(4)	77(2)
F(9)	8921(5)	3255(4)	726(4)	74(2)
F(14)	4010(4)	489(4)	2234(4)	73(2)
C(24)	7472(6)	1358(5)	3703(6)	37(2)
C(34)	8621(7)	2361(6)	820(6)	49(2)
N(3)	11562(5)	4704(4)	5176(4)	34(2)
C(8)	9180(7)	4442(6)	2829(5)	41(2)
C(7)	10103(6)	2991(5)	5120(5)	34(2)
C(46)	10525(6)	-718(6)	2651(5)	35(2)
C(6)	9447(6)	3917(5)	5274(5)	33(2)

C(16)	12069(8)	1855(6)	1824(6)	56(3)
B(1)	7614(7)	598(6)	2839(6)	35(2)
C(17)	12338(10)	5488(7)	1642(7)	94(4)
C(47)	9611(7)	-64(5)	2707(5)	38(2)
C(45)	10467(7)	-1698(6)	2621(5)	38(2)
C(10)	12062(7)	3718(6)	1819(6)	42(2)
C(32)	8349(9)	906(8)	192(6)	64(3)
N(1)	12343(5)	3678(5)	2688(5)	46(2)
C(44)	9517(7)	-1985(5)	2647(5)	39(2)
C(25)	6768(6)	2252(6)	3769(6)	39(2)
C(41)	5690(7)	488(6)	2521(6)	40(2)
C(26)	6601(6)	2934(6)	4443(6)	45(2)
C(15)	11880(7)	2865(6)	1423(6)	47(2)
C(35)	8285(6)	2013(6)	1663(6)	39(2)
C(1)	10906(6)	5619(5)	3807(5)	34(2)
C(30)	7956(6)	1115(5)	1842(5)	33(2)
C(31)	8024(7)	578(6)	1053(6)	43(2)
C(3)	10000(6)	2998(5)	3565(5)	36(2)
C(37)	6119(7)	-344(6)	3741(5)	39(2)
C(36)	6452(7)	222(6)	3003(5)	38(2)
C(28)	7808(7)	1896(7)	5119(5)	44(2)
C(14)	11574(7)	2922(8)	603(6)	61(3)
C(9)	10862(7)	1445(5)	4211(6)	44(2)
C(43)	8615(6)	-1297(6)	2713(5)	36(2)
C(11)	11998(8)	4588(6)	1337(7)	54(3)
C(38)	5159(7)	-661(6)	3973(6)	47(2)
C(33)	8631(8)	1816(8)	81(6)	63(3)
C(2)	10338(6)	2511(5)	4285(5)	33(2)
C(40)	4715(7)	189(6)	2730(7)	53(2)
C(12)	11692(8)	4609(8)	530(7)	64(3)
C(18)	11142(10)	3848(11)	-750(7)	106(5)
C(13)	11466(8)	3805(9)	158(7)	68(3)
C(48)	5222(11)	7507(10)	1975(9)	93(4)
C(49)	5958(11)	7932(11)	1374(11)	94(4)
C(52)	3873(13)	8216(14)	1281(14)	127(6)
C(53)	4174(11)	7666(12)	1937(10)	99(4)
C(50)	5653(15)	8507(13)	710(13)	122(5)
C(51)	4643(19)	8660(13)	626(13)	135(6)
N(2)	13027(6)	3370(6)	4210(5)	62(2)
C(20)	13742(11)	3815(11)	3474(11)	104(4)
C(23)	12375(8)	4293(7)	5637(7)	69(3)
C(19)	13489(9)	3480(12)	2564(8)	104(5)
C(22)	12870(50)	3240(40)	5100(40)	0(15)
C(21A)	13740(40)	4370(40)	4050(40)	10(16)
C(21)	13294(10)	2297(9)	4057(10)	95(6)
C(22A)	13161(18)	3630(20)	5104(15)	209(16)
C(55)	4129(13)	5325(13)	-918(11)	108(5)

C(56)	4102(9)	5952(10)	-822(8)	55(3)
C(57)	3863(8)	6084(9)	-1192(8)	52(3)
C(54)	4515(14)	4375(14)	-279(12)	125(5)
C(58)	3963(7)	6500(7)	-937(6)	40(2)
C(59)	5030(20)	3787(19)	190(17)	198(9)
C(60)	4660(30)	5290(30)	-340(20)	236(12)

Table 3. Bond lengths [Å] and angles [deg] for the dimer of **2**.

Zr(1)-N(1)	2.068(7)
Zr(1)-N(3)	2.190(6)
Zr(1)-C(1)	2.251(7)
Zr(1)-N(2)	2.355(7)
Zr(1)-C(3)	2.608(8)
Zr(1)-C(2)	2.617(7)
Zr(1)-C(7)	2.671(8)
Zr(1)-C(4)	2.722(7)
Zr(1)-C(6)	2.854(8)
Br(1)-C(48)	1.861(14)
F(19)-C(46)	1.338(9)
F(11)-C(37)	1.372(9)
F(20)-C(47)	1.366(8)
F(10)-C(35)	1.361(9)
F(5)-C(29)	1.357(9)
F(1)-C(25)	1.345(9)
F(18)-C(45)	1.343(9)
F(16)-C(43)	1.342(9)
F(15)-C(41)	1.349(9)
F(12)-C(38)	1.341(9)
F(8)-C(33)	1.352(10)
F(6)-C(31)	1.363(9)
F(7)-C(32)	1.339(10)
C(42)-C(43)	1.380(11)
C(42)-C(47)	1.383(11)
C(42)-B(1)	1.661(12)
F(2)-C(26)	1.341(9)
F(3)-C(27)	1.342(9)
C(29)-C(28)	1.369(11)
C(29)-C(24)	1.381(11)
F(17)-C(44)	1.353(8)
C(4)-C(3)	1.413(10)
C(4)-C(5)	1.436(10)
C(4)-C(8)	1.506(10)
C(5)-N(3)#1	1.394(9)
C(5)-C(6)	1.420(10)
F(4)-C(28)	1.339(9)
C(27)-C(28)	1.386(12)
C(27)-C(26)	1.392(12)
C(39)-F(13)	1.339(10)
C(39)-C(38)	1.369(12)
C(39)-C(40)	1.377(13)
F(9)-C(34)	1.352(10)

F(14)-C(40)	1.344(10)
C(24)-C(25)	1.417(11)
C(24)-B(1)	1.649(12)
C(34)-C(33)	1.355(13)
C(34)-C(35)	1.363(11)
N(3)-C(5)#1	1.394(9)
N(3)-C(23)	1.455(10)
C(7)-C(2)	1.387(10)
C(7)-C(6)	1.421(10)
C(46)-C(45)	1.372(11)
C(46)-C(47)	1.380(11)
C(6)-C(1)#1	1.484(10)
C(16)-C(15)	1.527(11)
B(1)-C(36)	1.659(12)
B(1)-C(30)	1.663(12)
C(17)-C(11)	1.499(14)
C(45)-C(44)	1.366(11)
C(10)-C(11)	1.403(11)
C(10)-C(15)	1.409(12)
C(10)-N(1)	1.450(10)
C(32)-C(33)	1.366(13)
C(32)-C(31)	1.372(12)
N(1)-C(19)	1.465(13)
C(44)-C(43)	1.391(11)
C(25)-C(26)	1.357(11)
C(41)-C(40)	1.379(12)
C(41)-C(36)	1.380(11)
C(15)-C(14)	1.394(12)
C(35)-C(30)	1.382(11)
C(1)-C(6)#1	1.484(10)
C(30)-C(31)	1.396(11)
C(3)-C(2)	1.403(10)
C(37)-C(38)	1.372(12)
C(37)-C(36)	1.387(11)
C(14)-C(13)	1.394(14)
C(9)-C(2)	1.523(10)
C(11)-C(12)	1.376(13)
C(12)-C(13)	1.357(14)
C(18)-C(13)	1.533(14)
C(48)-C(49)	1.368(18)
C(48)-C(53)	1.383(17)
C(49)-C(50)	1.37(2)
C(52)-C(53)	1.34(2)
C(52)-C(51)	1.45(2)
C(50)-C(51)	1.35(2)
N(2)-C(22)	1.34(6)
N(2)-C(22A)	1.468(16)

N(2)-C(20)	1.481(16)
N(2)-C(21)	1.481(14)
N(2)-C(21A)	1.77(5)
C(20)-C(21A)	1.16(5)
C(20)-C(19)	1.585(18)
C(23)-C(22A)	1.378(18)
C(23)-C(22)	1.64(6)
C(55)-C(58)	1.608(18)
C(55)-C(54)	1.71(3)
C(56)-C(59)#2	1.74(3)
C(54)-C(59)	1.29(3)
C(54)-C(60)	1.31(3)
C(54)-C(60)#2	1.72(4)
C(58)-C(59)#2	1.94(3)
C(59)-C(60)#2	1.44(4)
C(59)-C(56)#2	1.74(3)
C(59)-C(58)#2	1.94(3)
C(60)-C(59)#2	1.44(4)
C(60)-C(60)#2	1.65(6)
C(60)-C(54)#2	1.72(4)

N(1)-Zr(1)-N(3)	132.8(3)
N(1)-Zr(1)-C(1)	98.6(3)
N(3)-Zr(1)-C(1)	73.9(2)
N(1)-Zr(1)-N(2)	74.2(3)
N(3)-Zr(1)-N(2)	70.8(2)
C(1)-Zr(1)-N(2)	120.4(3)
N(1)-Zr(1)-C(3)	90.6(3)
N(3)-Zr(1)-C(3)	135.9(3)
C(1)-Zr(1)-C(3)	112.2(3)
N(2)-Zr(1)-C(3)	126.7(3)
N(1)-Zr(1)-C(2)	104.0(3)
N(3)-Zr(1)-C(2)	113.9(2)
C(1)-Zr(1)-C(2)	135.1(3)
N(2)-Zr(1)-C(2)	102.9(3)
C(3)-Zr(1)-C(2)	31.2(2)
N(1)-Zr(1)-C(7)	133.5(2)
N(3)-Zr(1)-C(7)	84.6(2)
C(1)-Zr(1)-C(7)	120.9(3)
N(2)-Zr(1)-C(7)	101.7(3)
C(3)-Zr(1)-C(7)	54.0(2)
C(2)-Zr(1)-C(7)	30.4(2)
N(1)-Zr(1)-C(4)	103.0(3)
N(3)-Zr(1)-C(4)	121.3(2)
C(1)-Zr(1)-C(4)	82.5(2)
N(2)-Zr(1)-C(4)	157.0(3)
C(3)-Zr(1)-C(4)	30.6(2)

C(2)-Zr(1)-C(4)	55.0(2)
C(7)-Zr(1)-C(4)	63.1(2)
N(1)-Zr(1)-C(6)	151.9(2)
N(3)-Zr(1)-C(6)	75.2(2)
C(1)-Zr(1)-C(6)	91.3(2)
N(2)-Zr(1)-C(6)	122.6(3)
C(3)-Zr(1)-C(6)	61.3(2)
C(2)-Zr(1)-C(6)	52.9(2)
C(7)-Zr(1)-C(6)	29.6(2)
C(4)-Zr(1)-C(6)	52.2(2)
C(43)-C(42)-C(47)	113.3(7)
C(43)-C(42)-B(1)	128.1(7)
C(47)-C(42)-B(1)	118.3(7)
F(5)-C(29)-C(28)	113.9(7)
F(5)-C(29)-C(24)	120.9(7)
C(28)-C(29)-C(24)	125.3(8)
C(3)-C(4)-C(5)	118.6(7)
C(3)-C(4)-C(8)	117.9(7)
C(5)-C(4)-C(8)	123.5(7)
C(3)-C(4)-Zr(1)	70.2(4)
C(5)-C(4)-Zr(1)	82.5(4)
C(8)-C(4)-Zr(1)	116.5(5)
N(3)#1-C(5)-C(6)	112.9(7)
N(3)#1-C(5)-C(4)	128.6(6)
C(6)-C(5)-C(4)	118.5(7)
F(3)-C(27)-C(28)	121.1(8)
F(3)-C(27)-C(26)	120.6(9)
C(28)-C(27)-C(26)	118.3(8)
F(13)-C(39)-C(38)	121.2(9)
F(13)-C(39)-C(40)	120.6(9)
C(38)-C(39)-C(40)	118.1(8)
C(29)-C(24)-C(25)	112.6(7)
C(29)-C(24)-B(1)	127.8(7)
C(25)-C(24)-B(1)	119.5(7)
F(9)-C(34)-C(33)	120.4(8)
F(9)-C(34)-C(35)	119.9(8)
C(33)-C(34)-C(35)	119.7(9)
C(5)#1-N(3)-C(23)	122.0(6)
C(5)#1-N(3)-Zr(1)	116.4(4)
C(23)-N(3)-Zr(1)	121.5(5)
C(2)-C(7)-C(6)	121.1(7)
C(2)-C(7)-Zr(1)	72.7(4)
C(6)-C(7)-Zr(1)	82.4(4)
F(19)-C(46)-C(45)	120.3(7)
F(19)-C(46)-C(47)	121.7(7)
C(45)-C(46)-C(47)	118.0(8)
C(5)-C(6)-C(7)	120.4(7)

C(5)-C(6)-C(1)#1	118.4(7)
C(7)-C(6)-C(1)#1	121.2(7)
C(5)-C(6)-Zr(1)	77.9(5)
C(7)-C(6)-Zr(1)	68.1(4)
C(1)#1-C(6)-Zr(1)	128.5(5)
C(24)-B(1)-C(36)	103.7(7)
C(24)-B(1)-C(42)	112.4(6)
C(36)-B(1)-C(42)	113.8(6)
C(24)-B(1)-C(30)	113.0(6)
C(36)-B(1)-C(30)	112.8(6)
C(42)-B(1)-C(30)	101.5(6)
F(20)-C(47)-C(46)	115.4(7)
F(20)-C(47)-C(42)	118.7(7)
C(46)-C(47)-C(42)	125.8(7)
F(18)-C(45)-C(44)	121.0(7)
F(18)-C(45)-C(46)	119.8(8)
C(44)-C(45)-C(46)	119.1(7)
C(11)-C(10)-C(15)	118.3(8)
C(11)-C(10)-N(1)	121.5(8)
C(15)-C(10)-N(1)	120.1(7)
F(7)-C(32)-C(33)	120.0(9)
F(7)-C(32)-C(31)	120.9(9)
C(33)-C(32)-C(31)	119.1(9)
C(10)-N(1)-C(19)	110.5(7)
C(10)-N(1)-Zr(1)	128.1(5)
C(19)-N(1)-Zr(1)	121.0(6)
F(17)-C(44)-C(45)	119.6(7)
F(17)-C(44)-C(43)	119.8(8)
C(45)-C(44)-C(43)	120.7(7)
F(1)-C(25)-C(26)	117.0(7)
F(1)-C(25)-C(24)	118.5(7)
C(26)-C(25)-C(24)	124.4(8)
F(15)-C(41)-C(40)	114.5(7)
F(15)-C(41)-C(36)	121.9(7)
C(40)-C(41)-C(36)	123.6(8)
F(2)-C(26)-C(25)	121.3(8)
F(2)-C(26)-C(27)	118.9(8)
C(25)-C(26)-C(27)	119.8(8)
C(14)-C(15)-C(10)	119.4(8)
C(14)-C(15)-C(16)	117.7(8)
C(10)-C(15)-C(16)	122.8(8)
F(10)-C(35)-C(34)	115.3(7)
F(10)-C(35)-C(30)	119.6(7)
C(34)-C(35)-C(30)	125.1(8)
C(6)#1-C(1)-Zr(1)	108.2(5)
C(35)-C(30)-C(31)	112.2(7)
C(35)-C(30)-B(1)	128.4(7)

C(31)-C(30)-B(1)	119.1(7)
F(6)-C(31)-C(32)	116.4(8)
F(6)-C(31)-C(30)	119.1(7)
C(32)-C(31)-C(30)	124.5(8)
C(2)-C(3)-C(4)	122.4(7)
C(2)-C(3)-Zr(1)	74.8(4)
C(4)-C(3)-Zr(1)	79.1(4)
F(11)-C(37)-C(38)	116.2(7)
F(11)-C(37)-C(36)	118.4(7)
C(38)-C(37)-C(36)	125.4(8)
C(41)-C(36)-C(37)	113.0(8)
C(41)-C(36)-B(1)	126.8(7)
C(37)-C(36)-B(1)	119.9(7)
F(4)-C(28)-C(29)	121.6(8)
F(4)-C(28)-C(27)	118.8(8)
C(29)-C(28)-C(27)	119.5(8)
C(13)-C(14)-C(15)	121.2(10)
F(16)-C(43)-C(42)	122.1(7)
F(16)-C(43)-C(44)	115.0(7)
C(42)-C(43)-C(44)	122.9(8)
C(12)-C(11)-C(10)	120.0(9)
C(12)-C(11)-C(17)	118.2(9)
C(10)-C(11)-C(17)	121.6(10)
F(12)-C(38)-C(39)	120.6(8)
F(12)-C(38)-C(37)	120.2(8)
C(39)-C(38)-C(37)	119.2(8)
F(8)-C(33)-C(34)	119.4(10)
F(8)-C(33)-C(32)	121.2(9)
C(34)-C(33)-C(32)	119.4(9)
C(7)-C(2)-C(3)	118.6(7)
C(7)-C(2)-C(9)	118.5(7)
C(3)-C(2)-C(9)	122.7(7)
C(7)-C(2)-Zr(1)	77.0(4)
C(3)-C(2)-Zr(1)	74.1(4)
C(9)-C(2)-Zr(1)	124.3(5)
F(14)-C(40)-C(39)	119.2(8)
F(14)-C(40)-C(41)	120.1(9)
C(39)-C(40)-C(41)	120.6(9)
C(13)-C(12)-C(11)	122.5(9)
C(12)-C(13)-C(14)	118.4(9)
C(12)-C(13)-C(18)	121.2(11)
C(14)-C(13)-C(18)	120.3(12)
C(49)-C(48)-C(53)	121.2(15)
C(49)-C(48)-Br(1)	119.6(12)
C(53)-C(48)-Br(1)	119.2(13)
C(48)-C(49)-C(50)	119.3(14)
C(53)-C(52)-C(51)	120.0(16)

C(52)-C(53)-C(48)	119.8(16)
C(51)-C(50)-C(49)	121.8(18)
C(50)-C(51)-C(52)	117.8(17)
C(22)-N(2)-C(20)	139(2)
C(22A)-N(2)-C(20)	111.6(17)
C(22)-N(2)-C(21)	90(2)
C(22A)-N(2)-C(21)	109.8(14)
C(20)-N(2)-C(21)	106.7(10)
C(22)-N(2)-C(21A)	102(3)
C(22A)-N(2)-C(21A)	74(2)
C(21)-N(2)-C(21A)	135.4(18)
C(22)-N(2)-Zr(1)	106(3)
C(22A)-N(2)-Zr(1)	113.7(8)
C(20)-N(2)-Zr(1)	101.9(6)
C(21)-N(2)-Zr(1)	112.7(7)
C(21A)-N(2)-Zr(1)	105.1(16)
C(21A)-C(20)-N(2)	83(3)
C(21A)-C(20)-C(19)	156(3)
N(2)-C(20)-C(19)	105.4(11)
C(22A)-C(23)-N(3)	113.2(9)
N(3)-C(23)-C(22)	104(2)
N(1)-C(19)-C(20)	107.0(9)
N(2)-C(22)-C(23)	109(3)
C(20)-C(21A)-N(2)	56(2)
C(23)-C(22A)-N(2)	117.6(11)
C(56)-C(55)-C(60)	81(2)
C(57)-C(55)-C(60)	118(2)
C(60)-C(55)-C(58)	93(2)
C(56)-C(55)-C(54)	128.1(19)
C(57)-C(55)-C(54)	165.6(17)
C(60)-C(55)-C(54)	49.4(19)
C(58)-C(55)-C(54)	141.1(14)
C(57)-C(56)-C(58)	59.4(14)
C(57)-C(56)-C(55)	93(2)
C(58)-C(56)-C(55)	152(2)
C(57)-C(56)-C(60)	153(3)
C(58)-C(56)-C(60)	146(3)
C(55)-C(56)-C(60)	61.1(19)
C(57)-C(56)-C(59)#2	147(2)
C(58)-C(56)-C(59)#2	92.6(17)
C(55)-C(56)-C(59)#2	113.4(18)
C(60)-C(56)-C(59)#2	53.5(18)
C(56)-C(57)-C(58)	64.6(15)
C(56)-C(57)-C(55)	49.0(15)
C(58)-C(57)-C(55)	113.6(18)
C(59)-C(54)-C(60)	120(2)
C(59)-C(54)-C(55)	164(2)

C(60)-C(54)-C(55)	46.0(15)
C(59)-C(54)-C(60)#2	55.1(14)
C(60)-C(54)-C(60)#2	65(2)
C(55)-C(54)-C(60)#2	111(2)
C(57)-C(58)-C(56)	56.0(12)
C(57)-C(58)-C(55)	41.4(12)
C(56)-C(58)-C(55)	14.6(13)
C(57)-C(58)-C(59)#2	117.2(16)
C(56)-C(58)-C(59)#2	63.7(15)
C(55)-C(58)-C(59)#2	77.6(10)
C(54)-C(59)-C(60)#2	78(2)
C(54)-C(59)-C(56)#2	128(2)
C(60)#2-C(59)-C(56)#2	50.9(15)
C(54)-C(59)-C(58)#2	152(2)
C(60)#2-C(59)-C(58)#2	74.6(17)
C(55)-C(60)-C(54)	85(3)
C(54)-C(60)-C(56)	122(3)
C(55)-C(60)-C(59)#2	113(3)
C(54)-C(60)-C(59)#2	162(3)
C(56)-C(60)-C(59)#2	76(2)
C(55)-C(60)-C(60)#2	154(5)
C(54)-C(60)-C(60)#2	70(3)
C(56)-C(60)-C(60)#2	168(4)
C(59)#2-C(60)-C(60)#2	93(3)
C(55)-C(60)-C(54)#2	159(3)
C(54)-C(60)-C(54)#2	115(2)
C(56)-C(60)-C(54)#2	123(3)
C(59)#2-C(60)-C(54)#2	47.3(16)
C(60)#2-C(60)-C(54)#2	45.5(18)

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,-y+1,-z+1 #2 -x+1,-y+1,-z

Table 4. Anisotropic displacement parameters ($A^2 \times 10^3$) for the dimer of **2**. The anisotropic displacement factor exponent takes the form:

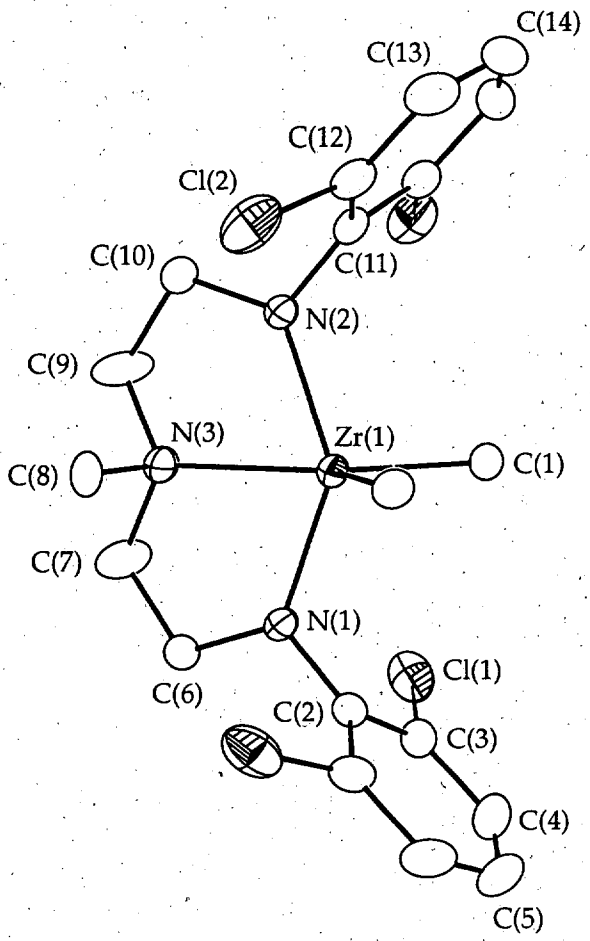
$$-2\pi^2 [h^2 a^{*2} U11 + ... + 2 h k a^* b^* U12]$$

Atom	U11	U22	U33	U23	U13	U12
Zr(1)	27(1)	29(1)	36(1)	0(1)	-10(1)	1(1)
Br(1)	129(2)	193(2)	105(1)	3(1)	-46(1)	-23(1)
F(19)	34(3)	48(3)	65(3)	0(2)	-15(2)	-1(2)
F(11)	53(3)	60(3)	42(3)	15(2)	-12(2)	-19(3)
F(20)	39(3)	33(3)	60(3)	5(2)	-16(2)	-6(2)
F(10)	61(3)	39(3)	45(3)	6(2)	-13(2)	-15(2)
F(5)	59(3)	45(3)	43(3)	8(2)	-21(2)	-1(3)
F(1)	45(3)	46(3)	62(3)	-8(2)	-20(3)	9(2)
F(18)	53(3)	41(3)	55(3)	-7(2)	-22(2)	12(2)
F(16)	43(3)	37(3)	65(3)	-1(2)	-17(2)	-10(2)
F(15)	46(3)	58(3)	64(4)	19(3)	-21(3)	-7(2)
F(12)	68(4)	77(4)	53(3)	11(3)	4(3)	-35(3)
F(8)	172(8)	120(6)	41(4)	21(4)	-3(4)	-51(5)
F(6)	74(4)	57(3)	46(3)	-7(2)	-15(3)	-16(3)
F(7)	149(7)	111(5)	39(4)	-11(3)	-13(4)	-40(5)
C(42)	37(5)	31(5)	37(5)	3(4)	-11(4)	-4(4)
F(2)	60(4)	52(3)	93(4)	-30(3)	-20(3)	15(3)
F(3)	69(4)	68(4)	64(4)	-26(3)	-5(3)	-20(3)
C(29)	41(5)	45(5)	32(5)	10(4)	-11(4)	-9(4)
F(17)	71(4)	34(3)	59(3)	-1(2)	-28(3)	0(2)
C(4)	26(4)	30(4)	42(5)	3(4)	-15(4)	-3(4)
C(5)	24(4)	32(4)	40(5)	4(4)	-11(4)	-4(4)
F(4)	70(4)	78(4)	35(3)	7(3)	-24(3)	-30(3)
C(27)	52(6)	55(6)	41(6)	-18(5)	1(5)	-21(5)
C(39)	35(6)	50(6)	59(6)	-9(5)	-4(5)	-13(5)
F(13)	44(4)	92(4)	96(5)	-2(3)	-5(3)	-32(3)
F(9)	86(4)	64(4)	74(4)	28(3)	-12(3)	-29(3)
F(14)	41(3)	77(4)	111(5)	13(3)	-40(3)	-5(3)
C(24)	32(5)	33(5)	45(5)	4(4)	-4(4)	-6(4)
C(34)	48(6)	49(6)	48(6)	18(5)	-7(5)	-10(5)
N(3)	32(4)	29(3)	41(4)	-2(3)	-18(3)	5(3)
C(8)	41(5)	51(5)	33(5)	1(4)	-15(4)	-4(4)
C(7)	28(5)	31(4)	41(5)	-5(4)	-5(4)	-5(4)
C(46)	30(5)	46(5)	32(5)	4(4)	-12(4)	-1(4)
C(6)	37(5)	24(4)	42(5)	1(4)	-18(4)	-6(4)
C(16)	67(7)	51(6)	44(6)	-8(4)	-5(5)	5(5)
B(1)	37(6)	33(5)	41(6)	4(4)	-14(5)	-8(4)
C(17)	136(12)	50(7)	67(8)	-1(5)	41(7)	-27(7)
C(47)	44(6)	26(5)	42(5)	-1(4)	-9(4)	-6(4)

C(45)	47(6)	33(5)	33(5)	-6(4)	-16(4)	8(4)
C(10)	37(5)	45(5)	36(5)	-3(4)	5(4)	4(4)
C(32)	84(8)	68(7)	37(6)	-8(5)	-7(5)	-14(6)
N(1)	30(4)	49(4)	52(5)	-3(3)	-2(3)	-3(3)
C(44)	59(6)	27(5)	32(5)	-3(3)	-17(4)	-1(4)
C(25)	27(5)	47(5)	43(5)	-4(4)	-5(4)	-12(4)
C(41)	37(5)	35(5)	45(6)	2(4)	-9(4)	-2(4)
C(26)	30(5)	39(5)	58(6)	-9(5)	0(4)	2(4)
C(15)	44(6)	51(6)	40(5)	1(4)	-10(4)	8(4)
C(35)	35(5)	39(5)	40(5)	3(4)	-4(4)	-2(4)
C(1)	42(5)	25(4)	34(5)	-4(3)	-11(4)	-1(4)
C(30)	26(5)	32(5)	39(5)	-1(4)	-8(4)	3(4)
C(31)	48(6)	43(5)	37(6)	1(4)	-6(4)	-6(4)
C(3)	34(5)	27(4)	49(5)	7(4)	-15(4)	-5(4)
C(37)	44(6)	41(5)	33(5)	-1(4)	-10(4)	-9(4)
C(36)	43(5)	35(5)	37(5)	-3(4)	-11(4)	-5(4)
C(28)	58(6)	56(6)	26(5)	6(4)	-11(4)	-28(5)
C(14)	48(6)	79(7)	53(7)	-4(5)	-15(5)	3(5)
C(9)	54(6)	28(4)	47(5)	0(4)	-18(4)	7(4)
C(43)	37(5)	44(5)	29(5)	5(4)	-12(4)	-5(4)
C(11)	54(6)	34(5)	58(7)	3(5)	10(5)	5(4)
C(38)	54(6)	41(5)	43(6)	5(4)	0(5)	-13(5)
C(33)	77(8)	80(8)	31(6)	12(5)	-10(5)	-15(6)
C(2)	38(5)	22(4)	41(5)	2(4)	-12(4)	-5(4)
C(40)	41(6)	43(5)	75(7)	-6(5)	-17(5)	-1(5)
C(12)	50(7)	67(7)	57(7)	21(6)	3(5)	17(5)
C(18)	72(8)	189(14)	47(7)	29(8)	-20(6)	20(9)
C(13)	52(7)	93(9)	50(7)	13(6)	-8(5)	8(6)
C(48)	79(10)	122(11)	79(9)	-33(8)	-14(8)	-25(9)
C(49)	58(9)	113(11)	109(12)	-39(9)	-10(9)	-19(8)
C(52)	72(11)	164(16)	134(16)	-25(13)	-11(11)	-2(11)
C(53)	64(10)	139(13)	94(11)	-31(9)	-21(8)	-6(8)
C(50)	110(15)	118(13)	132(16)	-32(11)	-9(12)	-27(11)
C(51)	143(18)	125(14)	140(17)	-14(11)	-58(15)	13(13)
N(2)	48(5)	75(6)	56(6)	-24(4)	-24(4)	32(4)
C(20)	68(9)	125(12)	120(13)	8(10)	-30(9)	-6(8)
C(23)	61(7)	78(7)	66(7)	-21(6)	-43(6)	42(6)
C(19)	48(7)	189(15)	67(8)	-3(9)	-8(6)	-2(8)
C(21)	60(9)	90(10)	127(13)	-26(9)	-41(8)	43(8)
C(22A)	138(19)	320(30)	155(18)	-180(20)	-127(16)	160(20)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for the dimer of **2**.

Atom	x	y	z	U(eq)
H(8A)	8476	4381	2794	62
H(8B)	9671	4136	2303	62
H(8C)	9245	5122	2858	62
H(16A)	12277	1915	2383	85
H(16B)	12617	1441	1406	85
H(16C)	11433	1572	1934	85
H(17A)	12234	6005	1230	141
H(17B)	13070	5350	1652	141
H(17C)	11926	5685	2238	141
H(14A)	11440	2361	348	73
H(9A)	10331	1030	4362	65
H(9B)	11319	1338	4622	65
H(9C)	11266	1296	3603	65
H(12A)	11637	5197	229	76
H(18A)	11110	4505	-963	159
H(18B)	10463	3648	-670	159
H(18C)	11652	3418	-1184	159
H(49A)	6658	7831	1416	113
H(52A)	3171	8312	1247	152
H(53A)	3679	7393	2364	119
H(50A)	6154	8800	306	147
H(51A)	4448	9038	164	162
H(19A)	13828	3841	2059	125
H(19B)	13744	2787	2443	125
H(21A)	13979	2076	4165	142
H(21B)	13297	2136	3443	142
H(21C)	12780	1982	4463	142



Fully labeled ORTEP representation of the structure of $[Ar_{Cl}N_2NMe]Zr^{13}Me_2$. Hydrogen atoms and the THF molecule of solvation have been omitted for clarity.

Table 1. Crystal data and structure refinement for **3***, $[Ar_{Cl}N_2NMe]Zr(^{13}Me)_2 \cdot THF$.

Temperature	183(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Monoclinic, $P2_1/m$	
Unit cell dimensions	a = 8.186(4) Å b = 12.142(7) Å c = 13.747(6) Å	α = γ = 90 deg. β = 95.17(4) deg.
Volume	1360.9(12) Å^3	
Z, Calculated density	2, 1.449 g/cm^3	
Absorption coefficient	0.816 mm^{-1}	
F(000)	603	
Crystal size	0.3 mm^3	
2θ ange for data collection	5.00 to 44.96 deg.	
Limiting indices	$-4 \le h \le 8$, $-10 \le k \le 8$, $-13 \le l \le 14$	
Reflections collected / unique	2380 / 1568 [R_{int} = 0.0162]	
Completeness to 2θ = 44.96	84.0 %	
Absorption correction	Empirical	
Max. and min. transmission	0.2083 and 0.1537	
Refinement method	FMLS on F^2	
Data / restraints / parameters	1568 / 0 / 170	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2σ(I)]	R_1 = 0.0399, wR_2 = 0.1061	
R indices (all data)	R_1 = 0.0417, wR_2 = 0.1080	
Largest diff. peak and hole	0.508 and -0.519 e·Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for $[Ar_{Cl}N_2NMe]Zr(^{13}Me)_2 \cdot THF$. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)
Zr(1)	7840(1)	7500	7525(1)	37(1)
Cl(2)	7730(2)	5286(1)	5278(1)	82(1)
Cl(1)	7798(2)	9720(1)	9745(1)	83(1)
N(1)	8737(5)	7500	9003(3)	40(1)
N(2)	8683(5)	7500	6131(3)	42(1)
N(3)	10774(5)	7500	7658(3)	52(2)
C(11)	7506(7)	7500	5307(4)	41(2)
O(1)	8428(7)	2500	7983(4)	103(2)
C(12)	6894(5)	6524(4)	4875(3)	52(2)
C(1)	6054(5)	8908(4)	7444(3)	54(1)
C(6)	10454(7)	7500	9407(4)	49(2)
C(10)	10409(7)	7500	5883(4)	53(2)
C(3)	6982(5)	8467(5)	10083(3)	61(2)
C(2)	7589(7)	7500	9714(4)	47(2)
C(13)	5662(6)	6531(7)	4121(3)	81(2)
C(14)	5040(10)	7500	3753(6)	105(5)
C(4)	5762(7)	8483(7)	10720(4)	95(3)
C(5)	5129(11)	7500	11014(6)	113(5)
C(15)	9344(9)	1552(7)	7754(5)	111(3)
C(16)	10541(10)	1897(7)	7113(6)	135(3)
C(8)	11097(10)	8811(10)	7655(6)	48(4)
C(7)	11461(9)	7500	8593(5)	168(7)
C(9)	11425(9)	7500	6806(5)	210(10)

Table 3. Bond lengths [Å] and angles [deg] for $[Ar_{Cl}N_2NMe]Zr(^{13}Me)_2 \cdot THF$.

Zr(1)-N(2)	2.095(4)
Zr(1)-N(1)	2.098(4)
Zr(1)-C(1)#1	2.246(5)
Zr(1)-C(1)	2.246(5)
Zr(1)-N(3)	2.392(5)
Cl(2)-C(12)	1.722(6)
Cl(1)-C(3)	1.742(6)
N(1)-C(2)	1.415(7)
N(1)-C(6)	1.464(7)
N(2)-C(11)	1.419(7)
N(2)-C(10)	1.483(7)
N(3)-C(9)	1.330(9)
N(3)-C(7)	1.356(9)
N(3)-C(8)#1	1.613(12)
N(3)-C(8)	1.613(12)
C(11)-C(12)	1.399(6)
C(11)-C(12)#1	1.399(6)
O(1)-C(15)	1.424(8)
O(1)-C(15)#2	1.424(8)
C(12)-C(13)	1.379(7)
C(6)-C(7)	1.449(9)
C(10)-C(9)	1.453(10)
C(3)-C(4)	1.386(7)
C(3)-C(2)	1.389(6)
C(2)-C(3)#1	1.389(6)
C(13)-C(14)	1.362(7)
C(14)-C(13)#1	1.362(7)
C(4)-C(5)	1.377(8)
C(5)-C(4)#1	1.377(8)
C(15)-C(16)	1.438(9)
C(16)-C(16)#2	1.465(17)
N(2)-Zr(1)-N(1)	140.45(17)
N(2)-Zr(1)-C(1)#1	102.78(13)
N(1)-Zr(1)-C(1)#1	102.56(13)
N(2)-Zr(1)-C(1)	102.78(13)
N(1)-Zr(1)-C(1)	102.56(13)
C(1)#1-Zr(1)-C(1)	99.2(3)
N(2)-Zr(1)-N(3)	70.04(17)
N(1)-Zr(1)-N(3)	70.40(16)
C(1)#1-Zr(1)-N(3)	130.42(13)
C(1)-Zr(1)-N(3)	130.42(13)
C(2)-N(1)-C(6)	114.4(4)
C(2)-N(1)-Zr(1)	118.2(3)

C(6)-N(1)-Zr(1)	127.4(3)
C(11)-N(2)-C(10)	114.2(4)
C(11)-N(2)-Zr(1)	118.3(3)
C(10)-N(2)-Zr(1)	127.6(3)
C(9)-N(3)-C(7)	132.1(6)
C(9)-N(3)-C(8)#1	85.4(4)
C(7)-N(3)-C(8)#1	87.0(4)
C(9)-N(3)-C(8)	85.4(4)
C(7)-N(3)-C(8)	87.0(4)
C(8)#1-N(3)-C(8)	161.1(7)
C(9)-N(3)-Zr(1)	114.3(4)
C(7)-N(3)-Zr(1)	113.6(4)
C(8)#1-N(3)-Zr(1)	99.4(3)
C(8)-N(3)-Zr(1)	99.4(3)
C(12)-C(11)-C(12)#1	115.9(6)
C(12)-C(11)-N(2)	122.1(3)
C(12)#1-C(11)-N(2)	122.1(3)
C(15)-O(1)-C(15)#2	107.8(7)
C(13)-C(12)-C(11)	121.6(6)
C(13)-C(12)-Cl(2)	119.3(5)
C(11)-C(12)-Cl(2)	119.1(4)
C(7)-C(6)-N(1)	107.5(5)
C(9)-C(10)-N(2)	106.4(5)
C(4)-C(3)-C(2)	123.0(6)
C(4)-C(3)-Cl(1)	118.2(5)
C(2)-C(3)-Cl(1)	118.8(4)
C(3)#1-C(2)-C(3)	115.4(6)
C(3)#1-C(2)-N(1)	122.3(3)
C(3)-C(2)-N(1)	122.3(3)
C(14)-C(13)-C(12)	120.5(7)
C(13)-C(14)-C(13)#1	119.6(8)
C(5)-C(4)-C(3)	119.0(8)
C(4)#1-C(5)-C(4)	120.3(9)
O(1)-C(15)-C(16)	107.6(7)
C(15)-C(16)-C(16)#2	106.9(5)
N(3)-C(7)-C(6)	121.1(6)
N(3)-C(9)-C(10)	121.7(6)

Symmetry transformations used to generate equivalent atoms:
#1 x,-y+3/2,z #2 x,-y+1/2,z

Table 4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $[Ar_{Cl}N_2NMe]Zr(^{13}Me)_2 \cdot THF$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Zr(1)	30(1)	47(1)	34(1)	0	5(1)	0
Cl(2)	103(1)	57(1)	90(1)	-18(1)	40(1)	-10(1)
Cl(1)	93(1)	68(1)	84(1)	-27(1)	-15(1)	19(1)
N(1)	36(2)	49(4)	36(2)	0	9(2)	0
N(2)	34(2)	57(4)	35(2)	0	6(2)	0
N(3)	33(3)	80(7)	42(3)	0	5(2)	0
C(11)	38(3)	44(6)	42(3)	0	15(3)	0
O(1)	59(3)	169(8)	85(4)	0	30(3)	0
C(12)	56(3)	53(5)	49(3)	-11(2)	19(2)	-9(2)
C(1)	41(2)	77(4)	44(2)	2(2)	5(2)	9(2)
C(6)	38(3)	66(6)	41(3)	0	0(2)	0
C(10)	39(3)	74(6)	45(3)	0	9(3)	0
C(3)	51(3)	88(5)	41(2)	-12(2)	-1(2)	17(3)
C(2)	36(3)	69(6)	34(3)	0	-3(2)	0
C(13)	58(3)	138(8)	48(3)	-28(3)	10(3)	-32(4)
C(14)	46(5)	225(17)	44(4)	0	1(4)	0
C(4)	60(3)	176(9)	51(3)	-30(4)	3(3)	37(4)
C(5)	50(5)	242(17)	48(5)	0	16(4)	0
C(15)	103(5)	133(8)	98(5)	-3(5)	20(4)	-19(5)
C(16)	135(6)	147(9)	134(6)	-5(5)	78(5)	13(5)
C(8)	37(5)	45(10)	62(6)	2(5)	4(4)	-9(5)
C(7)	30(4)	430(20)	42(4)	0	1(3)	0
C(9)	30(4)	560(30)	39(4)	0	10(3)	0

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for $[Ar_{Cl}N_2NMe]Zr(^{13}Me)_2 \cdot THF$.

Atom	x	y	z	U(eq)
H(1A)	4955	8625	7394	80
H(1B)	6209	9350	6881	80
H(1C)	6236	9350	8023	80
H(6A)	10680	6858	9804	58
H(10A)	10624	8142	5508	63
H(13A)	5254	5868	3862	97
H(14A)	4194	7500	3254	126
H(4A)	5377	9148	10946	115
H(5A)	4270	7500	11414	135
H(15A)	8622	1002	7435	133
H(15B)	9884	1234	8345	133
H(16A)	10257	1619	6458	162
H(16B)	11618	1619	7344	162
H(8A)	12257	8948	7706	72
H(8B)	10627	9141	8200	72
H(8C)	10600	9122	7059	72
H(7A)	12160	8135	8667	202
H(9A)	12124	6865	6803	251