Silicon–carbon bridged bis(fluorenyl) and bis(octahydrofluorenyl) ansa-zirconocenes: synthesis, characterization and ethylene polymerization catalysis

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Abstract

The synthesis and characterization of two new silicon–carbon bridged ansa-bis(fluorenyl) and ansa-bis(octahydrofluorenyl) zirconocene complexes, (Flu–CH$_2$–SiMe$_2$–Flu)ZrCl$_2$ (3) and (FluH$_8$–CH$_2$–SiMe$_2$–FluH$_8$)ZrCl$_2$ (4) is reported. Complex 3, in combination with methylaluminoxane (MAO), forms an active catalyst system for homogeneous polymerization of ethylene. The molecular structure of 4 reveals a large Centroid–Zr–Centroid angle (131.9°) and an unusually small Cl–Zr–Cl angle (93.2°). The Zr–C bond distances range from 2.48 to 2.64 Å. © 1997 Elsevier Science S.A.

1. Introduction

Chiral C_2-symmetric bis(indenyl) ansa-zirconocenes have received considerable interest in isospecific polymerization of propylene (for recent reviews, see [1]). Recently, it has been shown, especially by Alt and coworkers [2–4], but also by others [5–10], that C_{2v} symmetric bis(fluorenyl) ansa-metallocenes are potential catalyst precursors for the preparation of high-molecular-weight polyethylene and atactic polypropylene. We report here the synthesis and characterization of two new silicon-carbon bridged bis(fluorenyl) and bis(octahydrofluorenyl) ansa-zirconocenes, [dimethyl(9-fluorenyl)(9-fluorenylmethyl)silane]zirco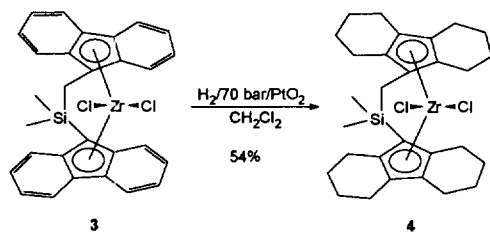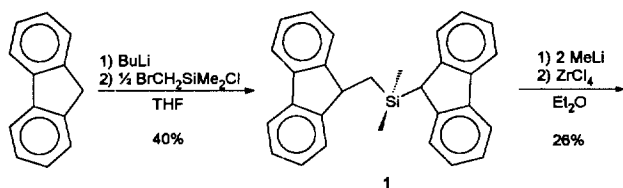nium dichloride (3) and [dimethyl(octahydro-9-fluorenyl)(octahydro-9-fluorenylmethyl)silane]zirconium dichloride (4), and their application in polymerization of ethylene.
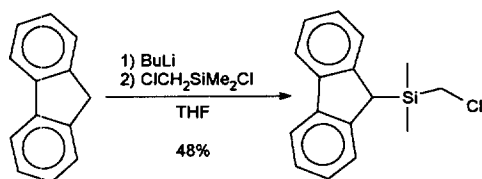
2. Results and discussion

Dimethyl(9-fluorenyl)(9-fluorenylmethyl)silane (1) was prepared in 40% yield by reacting bromomethyldimethylchlorosilane with two equivalents of fluorenyllithium (Scheme 1). Considerable amounts of the spiro compound 2 were formed along with 1 when the corresponding dichloride was used. [1] Reaction of one equivalent of fluorenyllithium with chloromethyldimethylchlorosilane gave 9-(chloromethyldimethylsilyl)fluorene (5) (Scheme 2; structure of 2 in Scheme 3). Double deprotonation of 1 with MeLi and the subsequent reaction of the dianion with ZrCl$_4$ in diethyl ether

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[1] Separation of 2 from 1 is troublesome. An analytical sample was obtained by recrystallization from THF. ^{1}H-NMR (CDCl$_3$, δ): 7.90–7.86 (m, 8H); 7.47–7.37 (m, 8H); 1.75 (s, 4H); −0.26 (s, 12H). ^{13}C-NMR (CDCl$_3$, δ): 151.84; 139.26; 126.22; 125.66; 124.62; 119.90; 45.18; 21.46; −0.04.
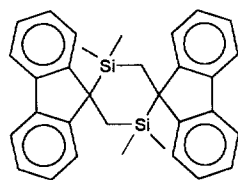
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Scheme 1.

Scheme 2.

2

Scheme 3.

Fig. 1. Molecular structure of 4. Thermal ellipsoids are drawn at 20% probability.

the expected bent metallocene structure. The two methyl groups and the methylene protons of the bridge are non-equivalent in the crystal. However, only single absorbances are observed in the ^{1}H- and ^{13}C-NMR

Table 1
Crystal data and structure refinement for 4

Formula	$C_{29}H_{40}SiZrCl_2$
Formula weight	578.85
Color, habit	yellow, prism
Crystal size (mm)	0.200 × 0.200 × 0.200
Crystal system	monoclinic
Space group	Cc
a (Å)	16.825(2)
b (Å)	10.746(3)
c (Å)	16.848(2)
β (deg)	118.341(6)
V (Å^3)	2681.2(8)
Z	4
D_c (g cm^{-3})	1.434
$F(000)$	1208
Temperature (K)	294
Diffractometer	Rigaku AFC5S
Radiation	Mo K_a ($\lambda = 0.71069$ Å)
Scan type	omega-2
Scan rate (min^{-1})	8.0 (in omega, 2 rescans)
Scan width	(1.47 + 0.30 tan)
Reflections collected	2594
Unique reflections	2500 [R(int) = 0.021]
Number of observations [$I > 3.00 \sigma(I)$]	2107
Refinement method	full-matrix least-squares
Goodness of fit	1.34
Final R indices	$R = 0.028$, $wR_2 = 0.025$

gave after work-up and crystallization the bis(fluorenyl) *ansa*-zirconocene 3 in 26% yield. [2] Hydrogenation of 3 gave the octahydrofluorenyl complex 4 in 54% yield.

Complex 3 is poorly soluble and quite unstable in common organic solvents. The crystals are stable in dry air but extremely sensitive to moisture. The hydrogenated analogue 4 is air-stable and soluble in hexane, cyclohexane, diethyl ether, toluene and methylenechloride. The molecular structure of 4 is displayed in Fig. 1. The crystallographic data and parameters are presented in Table 1 with selected bond distances and angles in Table 2. Table 3 shows a comparison of selected bonding parameters for different bis(fluorenyl) and bis(octahydrofluorenyl) *ansa*-zirconocenes. Complex 4 adopts

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[2] The hafnocene analogue of 3 was prepared in 20% yield from the dianion of the ligand and HfCl$_4$ and was identified by its EIMS mass spectrum. Its catalytic activity, upon activation with MAO, is considerably lower compared with 3/MAO (1300 vs. 5300 kg PE/mol M/h, for polymerization details see Table 4).
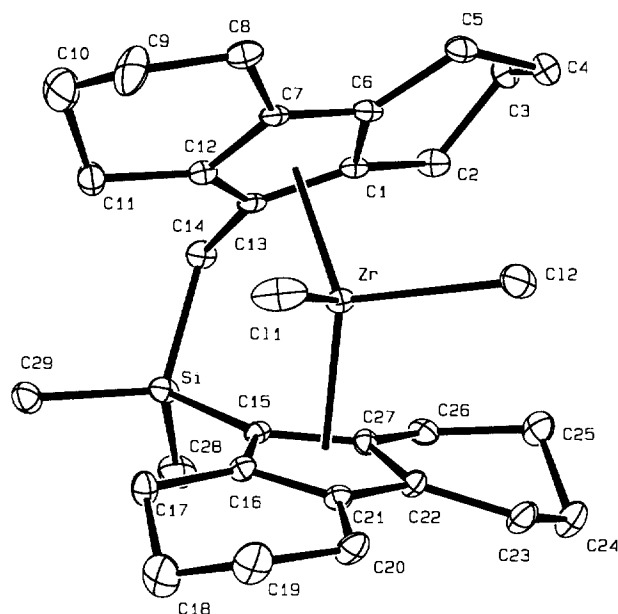
Table 2
Selected interatomic distances (Å) and angles (deg) for **4**[a]

Interatomic distances			
Zr–Cl(1)	2.430(2)	Zr–C(21)	2.635(5)
Zr–Cl(2)	2.436(2)	Zr–C(22)	2.633(5)
Zr–C(13)	2.551(4)	Zr–C(27)	2.518(5)
Zr–C(1)	2.539(5)	C(13)–C(14)	1.514(6)
Zr–C(6)	2.583(6)	Si–C(14)	1.888(5)
Zr–C(7)	2.562(5)	Si–C(15)	1.881(5)
Zr–C(12)	2.536(5)	Zr–Cen(1)	2.2497(3)
Zr–C(15)	2.484(5)	Zr–Cen(2)	2.2615(5)
Zr–C(16)	2.562(5)		

Interatomic and torsion angles			
Cl(1)–Zr–Cl(2)	93.17(7)	C(13)–C(14)–Si	113.2(3)
Cen(1)–Zr–Cen(2)	131.87(1)	C(14)–Si–C(15)	103.8(2)
Cp(1)–Cp(2)[b]	53.84	C(13)–C(14)–Si–C(15)	−27.4(4)

[a] Cen(1) refers to the centroid of the C(13)–C(1)–C(6)–C(7)–C(12) ring and Cen(2) to the centroid of the C(15)–C(16)–C(21)–C(22)–C(27) ring.
[b] Angle between the cyclopentadienyl planes.

spectra. Apparently a rapid λ–δ conformational fluctuation of the metallacycle takes place in solution resulting in averaging of the NMR signals. The Zr–C bond distances of the $Me_2Si–C_5$ ring show distortion toward η^3 bonding varying from 2.48 to 2.64 Å. The corresponding Zr–C bond distances of the $CH_2–C_5$ ring range from 2.54 to 2.58 Å. The Centroid–Zr–Centroid angle of **4** (131.9°) is larger than those of cyclohexylethylenebis(octahydro-9-fluorenyl)zirconium dichloride (126.1°) [10] and ethylenebis(9-

fluorenyl)zirconium dichloride (129.0°) [2]. Similar Cen–Zr–Cen angles have been observed previously for the racemic disiloxane bridged bis(indenyl) [11,12] and bis(tetrahydroindenyl) [11] zirconocene dichlorides (130.1° resp. 131.5°), and the dimethylsilylene bridged bis(9-fluorenyl)zirconocene dimethyl (130.3°) [9]. The Cl–Zr–Cl angle of **4** is unusually small (93.2°) compared with the corresponding bond angles of $CyhexEt(FluH_8)_2ZrCl_2$ (96.1°) [10], $Et(Flu)_2ZrCl_2$ (96.9°) [2] and $Et(2-EtFlu)_2ZrCl_2$ (96.8°) [8]. Racemic ethylene and silicon bridged bis(indenyl) and bis(tetrahydroindenyl) zirconium dichlorides have Cl–Zr–Cl angles ranging from 97.3° to 99.4° [13].

Complexes **3** and **4** were activated with methylaluminoxane (MAO) for homogeneous polymerization of ethylene. Selected polymerization results obtained with **3**/MAO, **4**/MAO and four different zirconocene/MAO catalyst systems [14,15] under similar conditions are presented in Table 4. The lower catalytic activity of **3**/MAO compared with the bis(indenyl) and bis(tetrahydroindenyl) *ansa*-zirconocene/MAO and Cp_2ZrCl_2/MAO catalyst systems is apparently due to steric reasons. In general, *ansa*-zirconocene catalysts with one-membered silicon bridges and two-membered carbon bridges show high polymerization activities [1,13]. Previous reports on *ansa*-metallocenes with two-membered silicon–carbon bridges have not appeared. Lengthening of the bridge in **3** should increase the Cen–Zr–Cen angle and decrease the angle between the cyclopentadienyl planes, as observed in the molecular structure of **4**. The resulting narrowing of the coordi-

Table 3
Comparison of bonding parameters for different bis(fluorenyl) and bis(octahydrofluorenyl) *ansa*-zirconocenes[a]

ansa-Zirconocene	Zr–Cen (av) (Å)	X–Zr–X (deg)	Cen–Zr–Cen (deg)
$(FluH_8CH_2SiMe_2FluH_8)ZrCl_2$ (**4**)	2.256	93.2	131.9
$CyhexEt(FluH_8)_2ZrCl_2$[b]	2.233	96.1	126.1
$Et(Flu)_2ZrCl_2$[c]	2.269	96.9	129.0
$Et(2-EtFlu)_2ZrCl_2$[d]	2.257	96.8	129.6
$Me_2Si(Flu)_2ZrMe_2$[e]	2.298	94.9	130.3

[a] Cen refers to the centroid of the C_5 ring; (av), average; X = Cl or Me.
[b] Ref. [10]; [c] Ref. [2]; [d] Ref. [8]; [e] Ref. [9].

Table 4
Selected ethylene polymerization results obtained with different zirconocene/MAO catalyst systems under similar conditions[a]

Metallocene	Activity (kg PE/mol Zr/h)	M_w^b (g/mol)	M_w/M_n	T_m (°C)
Cp_2ZrCl_2[c]	9300	59300	2.5	132
$Et[(2-t-BuMe_2SiO)Ind]_2ZrCl_2$[d]	6900	14700	3.8	126
$Me_2Si(IndH_4)_2ZrCl_2$[d]	6400	55800	2.0	134
$Et(IndH_4)_2ZrCl_2$[c]	6000	74300	2.3	134
$(FluCH_2SiMe_2Flu)ZrCl_2$ (**3**)	5300	29400	2.7	129
$(FluH_8CH_2SiMe_2FluH_8)ZrCl_2$ (**4**)	100	125000	3.0	129

[a] $T_p = 80$°C; $P(C_2H_4) = 1.6$ bar; polymerization time = 20 min; [metallocene] = 11 μmol/200 ml of toluene; [Al]:[Zr] = 3000:1.
[b] By GPC vs. polystyrene standards.
[c] Ref. [14]; [d] Ref. [15].

nation gap-aperture increases the steric hindrance to monomer coordination at the Zr atom.[3] An even more pronounced effect is observed for **4**/MAO, where the combined influence of the large Cen–Zr–Cen angle and the exceptionally small Cl–Zr–Cl angle apparently causes the almost complete inactivity toward ethylene. Increased steric hindrance results from the hydrogenated six-membered rings.

3. Experimental section

3.1. General comments

All operations were carried out in an argon or nitrogen atmosphere using standard Schlenk, vacuum or glove box techniques. Solvents were dried and distilled under argon prior to use. Bromomethyldimethylchlorosilane was purchased from ABCR GmbH & Co. and used as received. Cp_2ZrCl_2 was purchased from Aldrich. rac-Et[IndH$_4$]ZrCl$_2$ was prepared according to the literature procedure [16]. Methylaluminoxane (MAO 29.3% w/w toluene solution) was obtained from Witco and used as received. The ^{1}H- and ^{13}C-NMR spectra were recorded in $CDCl_3$ or CD_2Cl_2 solutions using a JEOL JNM-LA400 or JEOL JNM-A500 NMR spectrometer and referenced against tetramethylsilane or the residual protons of the deuterated solvents. Direct inlet electron ionization mass spectra (EIMS) were obtained on a Varian VG-7070E or a Varian-8000 mass spectrometer.

3.2. Polymerization procedure and polymer characterization

The polymerizations were performed in a 0.5-l Büchi glass autoclave in 200 ml of toluene. In a typical run half of the MAO/toluene solution was added to the reactor and stirred for 5 min in order to reduce any impurities in the reactor. In a parallel procedure 10–15 μmol of the metallocene was dissolved in the remaining half of the MAO/toluene solution and preactivated at 25°C for 5 min. The catalyst/activator mixture was charged into the reactor and the polymerization was started by introducing the monomer. The polymerization was interrupted after 20 min by the addition of methanol. The polymer was analyzed after being washed with methanol/HCl.

The melting temperatures and enthalpies of the polymers were determined using a Perkin Elmer DSC IV instrument. The samples were heated twice (heating rate 10°C/min) and the second heating curve was analyzed. Molecular weights and molecular weight distributions were determined by gel permeation chromatography on a Waters high-temperature GPC instrument equipped with TOSOH mixed-bed columns (exclusion limits for polystyrene 4×10^8 Å) or Waters Styragel HT-columns (exclusion limits 10^3 Å, 10^4 Å and 10^6 Å) in 1,2,4-trichlorobenzene (flow rate 1 ml/min).

3.3. Dimethyl-9-fluorenyl-(9-fluorenylmethyl)silane (1)

To a solution of fluorene (16.62 g, 100.0 mmol) in THF (100 ml) at 0°C was added dropwise n-BuLi (40.0 ml of a 2.5 M solution in hexane, 100.0 mmol), and the reaction mixture was stirred overnight at room temperature. The resulting solution was then added dropwise to a solution of bromomethyldimethylchlorosilane (9.38 g, 50.0 mmol) in THF (50 ml) at 0°C. After completed addition the reaction mixture was stirred overnight and washed with saturated ammonium chloride solution (300 ml). The solvents were evaporated, and the product was dissolved in CH_2Cl_2 (250 ml), washed with water (2 × 200 ml) and dried over sodium sulfate. Evaporation of the solvent left a white solid that was stirred overnight with Et_2O (100 ml). Filtration of the resulting suspension gave 8.13 g (40.4%) of **1** as a white powder. EIMS (calculated/found): 402.1804/402.1789. ^{1}H-NMR ($CDCl_3$, δ): 8.05 (m, 2H); 7.55–7.41 (m, 8H); 7.35 (td, $^3J = 7.4$ Hz, $^4J = 1.1$ Hz, 2H); 7.25 (d, $^3J = 7.6$ Hz, 2H); 4.06 (t, $^3J = 5.6$ Hz, 1H); 3.82 (s, 1H); 1.12 (d, $^3J = 5.6$ Hz, 2H); −0.33 (s, 6H). ^{13}C-NMR ($CDCl_3$, δ): 148.34; 145.49; 140.58; 140.44; 126.85; 126.76; 126.02; 125.25; 124.42; 124.12; 119.87; 119.64; 43.25; 42.97; 14.15; −2.27.

3.4. [Dimethyl-(η^5-9-fluorenyl)-((η^5-9-fluorenyl)methyl)silane]zirconium dichloride (3)

To a suspension of **1** (4.03 g, 10.0 mmol) in Et_2O (350 ml) at 0°C was added dropwise MeLi (12.5 ml of a 1.6 M solution in Et_2O, 20.0 mmol). The dark red solution was stirred for 2 h at room temperature and treated portionwise with $ZrCl_4$ (2.33 g, 10.0 mmol). The resulting suspension was stirred for 2 h and the solvent was removed in vacuo. The crude product was extracted with CH_2Cl_2 (200 ml) and filtered through Celite to remove lithium chloride. Concentration and cooling to −30°C gave 1.48 g (26.3%) of **3** as a dark purple microcrystalline solid. In the EIMS mass spectrum of **3** parent ions of composition (Flu–SiMe$_2$–CH$_2$–Flu)ZrCl$_2^+$ were observed at $m/e = 560$–569 in the appropriate isotope ratios. The base peak at $m/e = 179$ corresponds to FluCH$_2^+$. ^{1}H-NMR ($CDCl_3$, δ):

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[3] According to previous reports the silicon bridged and ethylene bridged bis(fluorenyl) zirconocene/MAO catalyst systems may exhibit high activities in polymerization of propylene (see e.g., [8] and [9]). However, the activity of **3**/MAO toward propylene is very low. As expected the produced polypropylene is almost completely atactic.

7.81–7.69 (m, 8H); 7.39–7.14 (m, 8H); 3.37 (s, 2H); 1.06 (s, 6H).

3.5. [Dimethyl-(η⁵-1,2,3,4,5,6,7,8-octahydro-9-fluorenyl)-((η⁵-1,2,3,4,5,6,7,8-octahydro-9-fluorenyl)methyl)silane]zirconium dichloride (4)

A suspension of 2 (0.40 g, 0.72 mmol) and PtO_2 (20 mg) in CH_2Cl_2 (150 ml) was hydrogenated at 70 bar in a stirred reactor for 16 h. The light-green suspension was filtered through Celite and the solvent was evaporated. The yellow/green residue was dissolved in hexane (50 ml) and cooled to 0°C to provide 0.22 g (53.5%) of 4 as a light-green crystalline solid. In the EIMS mass spectrum of 4, parent ions of composition $(FluH_8-SiMe_2-CH_2-FluH_8)ZrCl_2^+$ were observed at $m/e = 576-584$ in the appropriate isotope ratios. ^{1}H-NMR ($CDCl_3$, δ): 2.91–2.76 (m, 4H); 2.62–2.18 (m, 11H); 2.26 (s, 2H); 2.01–1.32 (m, 17H); 0.54 (s, 6H). ^{13}C-NMR ($CDCl_3$, δ): 135.11; 130.23; 127.48; 120.27; 115.15; 26.71; 24.15; 23.26; 23.20; 22.28; 22.17; 22.10; 21.95; 16.65; 2.45.

3.6. 9-((Chloromethyl)dimethylsilyl)fluorene (5)

To a solution of fluorene (12.47 g, 75.0 mmol) in THF (75 ml) at 0°C was added dropwise n-BuLi (30.3 ml of a 2.5 M solution in hexane, 75.8 mmol), and the reaction mixture was stirred overnight at room temperature. The resulting solution was then added dropwise at −50°C to a solution of chloromethyldimethylchlorosilane (10.73 g, 75.0 mmol) in THF (75 ml). After completed addition the reaction mixture was stirred overnight and the solvents were evaporated. The crude product was extracted with Et_2O (100 ml) and filtered through Celite to remove lithium chloride. The solvent was evaporated and the product was dissolved in pentane (80 ml). Cooling to 0°C gave 9.8 g (47.9%) of 5 as yellow crystals. Mp: 62–64°C. EIMS (calcd/found): 272.0788/272.0763. ^{1}H-NMR ($CDCl_3$): δ 7.89 (d, ^3J = 7.2 Hz, 2H); 7.55 (dd, ^3J = 7.4 Hz, ^4J = 0.5 Hz, 2H); 7.42–7.32 (m, 4H); 4.14 (s, 1H); 2.79 (s, 2H); 0.00 (s, 6H). ^{13}C-NMR ($CDCl_3$): δ 144.45; 140.51; 126.34; 125.67; 123.91; 120.12; 39.95; 29.11; −5.97.

3.7. Crystal structure determination

Single crystals of 4 were obtained by recrystallization from a 1:5 toluene/hexane solution at ambient temperature. The structure was solved by direct methods and refined by least-squares techniques. Heavy atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions with fixed displacement parameters (1.2 × that of the host atom). All refinements were performed using SHELXL93 software [17]. Figures were plotted

Table 5
Atomic coordinates and isotropic displacement parameters for 4

Atom	x	y	z	B_{eq}
Zr	0.9997	0.2358O(4)	0.9990	2.15(2)
Cl(1)	0.8717(1)	0.1988(2)	0.8511(1)	5.40(8)
Cl(2)	0.9216(1)	0.3985(2)	1.0356(2)	5.3(1)
Si	1.1899(1)	0.0047(1)	1.0958(1)	2.44(5)
C(1)	1.1421(3)	0.3656(5)	1.0529(3)	2.2(2)
C(2)	1.1948(4)	0.4301(5)	1.1435(4)	2.9(2)
C(3)	1.1847(4)	0.5713(5)	1.1317(4)	3.2(2)
C(4)	1.0887(4)	0.6103(5)	1.0758(4)	3.5(2)
C(5)	1.0490(4)	0.5629(5)	0.9786(4)	3.0(2)
C(6)	1.0756(4)	0.4309(5)	0.9753(4)	2.4(2)
C(7)	1.0528(3)	0.3535(5)	0.9004(4)	2.4(2)
C(8)	0.9960(4)	0.3884(6)	0.8012(4)	3.6(2)
C(9)	0.9949(5)	0.2841(9)	0.7389(4)	5.7(4)
C(10)	1.0743(6)	0.2080(7)	0.7711(5)	5.8(4)
C(11)	1.1042(4)	0.1483(5)	0.8629(4)	3.3(2)
C(12)	1.1039(3)	0.2422(5)	0.9291(3)	2.3(2)
C(13)	1.1613(3)	0.2503(5)	1.0239(3)	2.2(2)
C(14)	1.2349(3)	0.1596(5)	1.0820(3)	2.5(2)
C(15)	1.0752(3)	0.0435(5)	1.0826(3)	2.0(2)
C(16)	0.9860(3)	0.0019(5)	1.0190(3)	2.3(2)
C(17)	0.9566(3)	−0.0927(5)	0.9441(4)	3.1(2)
C(18)	0.8708(5)	−0.1564(7)	0.9310(5)	5.1(3)
C(19)	0.7973(4)	−0.0701(7)	0.9203(5)	5.0(3)
C(20)	0.8236(4)	0.0218(6)	0.9968(4)	3.5(2)
C(21)	0.9227(3)	0.0535(5)	1.0423(3)	2.4(2)
C(22)	0.9707(3)	0.1244(5)	1.1220(3)	2.3(2)
C(23)	0.9343(4)	0.1811(6)	1.1790(4)	3.6(3)
C(24)	1.0090(4)	0.2151(7)	1.2728(4)	3.8(3)
C(25)	1.0915(4)	0.2697(6)	1.2708(3)	3.5(2)
C(26)	1.1341(3)	0.1734(5)	1.2355(3)	2.6(2)
C(27)	1.0644(3)	0.1210(4)	1.1469(3)	2.0(2)
C(28)	1.2633(4)	−0.0633(5)	1.2098(4)	4.0(3)
C(29)	1.1877(4)	−0.1106(5)	1.0123(4)	3.3(2)

on ORTEPII [18]. The atomic coordinates of 4 are collected in Table 5. Additional data including front and top views of 4, complete listings of the interatomic distances and angles and torsion angles are recorded as supplementary material and can be obtained from the authors upon request.

Acknowledgements

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