Synthesis and Structural Behavior of the Tris(η-cyclopentadienyl)zirconium−Betaine Complex $Cp_2[\eta^5\text{-}C_5H_4B(C_6F_5)_3]Zr$

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Received December 4, 2000

Treatment of the reagent $[C_5H_4B(C_6F_5)_3]Na,Li\cdot Et_2O$ (**4**) with zirconocene dichloride gave the neutral tris(cyclopentadienyl)Zr−betaine-type complex $(\eta^5\text{-}Cp)_2[\eta^5\text{-}C_5H_4B(C_6F_5)_3]Zr$ (**1**). In the crystal complex **1** contains the three η-cyclopentadienide ligands in a nearly trigonal-planar coordination around zirconium with a pronounced Zr−F−C(aryl) coordination perpendicular to it. The Zr−F bond length is 2.310(3) Å. The Zr−F−C(aryl) coordination is persistent in solution. The activation energy of the reversible cleavage of the Zr−F linkage of **1** was determined as $\Delta G^{\ddagger}_{(Zr-F)diss}(253\ K) = 10.2 \pm 0.2\ kcal\ mol^{-1}$ by dynamic ^{19}F NMR spectroscopy in toluene-d_8.

Introduction

$[Cp_3Zr^+]$ is a rather unique molecule.[1−4] It contains three η^5-bonded cyclopentadienyl ligands in the crystal as well as in solution, which might formally suggest a coordinatively saturated 18-electron configuration at the metal. However, investigations of its electronic structure have revealed that one electron pair resides in an almost completely Cp_3-ligand-centered molecular orbital,[2−4] which makes $[Cp_3Zr^+]$ electrophilic at the metal similar to the ubiquitous $[Cp_2Zr{-}R^+]$ species, which were so well investigated in conjunction with their role in homogeneous Ziegler−Natta catalysis.[5,6] Consequently, anionic as well as neutral two-electron ligands readily add to the cation $[Cp_3Zr^+]$ to form very stable neutral (e.g., $Cp_3Zr{-}CH_3$) or positively charged adducts, such as $[Cp_3Zr(N{\equiv}C{-}R)^+]$, $[Cp_3Zr(C{\equiv}NR)^+]$, or even $[Cp_3Zr(C{\equiv}O)^+]$.[1,2] One characteristic feature of the $[Cp_2ZrR^+]$ metallocene cations is their ability to form adducts with weak donor ligands, such as the fluorine of C−F bonds. In typical zirconocene cation systems the metal···F−C bond has a bond dissociation energy of ca. 13 ± 5 kcal mol^{-1}.[6−8] Consequently, Zr−F−C(aryl) coordination frequently has been used for the protection of the active catalyst site in homogeneous Ziegler−Natta catalysis in either intramolecular[7−11] or intermolecular situations.[6] We have now used this typical zirconocene cation feature in $[Cp_3Zr^+]$ cation chemistry. This has resulted in the formation of a remarkably structured substituted tris(η^5-cyclopentadienyl)zirconium system, where in a dipolar framework the strongly electrophilic group 4 metal cation is protected by an intramolecular Zr−F−C(aryl) coordination of a $[-B(C_6F_5)_3^-]$ group that is covalently attached to one of the η^5-Cp-rings. The resulting compound, $(\eta^5\text{-}Cp)_2[\eta^5\text{-}C_5H_4B(C_6F_5)_3]Zr$ (**1**), exhibits a pronounced zirconium cation character in an overall neutral organometallic species.

Results and Discussion

The substituted $(\eta^5\text{-}Cp)_2[\eta^5\text{-}C_5H_4B(C_6F_5)_3]Zr$ system (**1**) was prepared by a route similar to the one that we had developed previously for the synthesis of the parent Cp_3M^{IV} complexes.[1,2] The $[C_5H_4B(C_6F_5)_3{}^{2-}]$ ligand system was prepared in analogy with the synthesis of $[C_5H_4B(C_6F_5)_3]Li_2$ published by Bochmann in 1995.[12] Treatment of *sodium* cyclopentadienide (**2**) with $B(C_6F_5)_3$ gave $[C_5H_5B(C_6F_5)_3]Na$ etherate (**3**, obtained as a mixture of isomers), which was subsequently deprotonated

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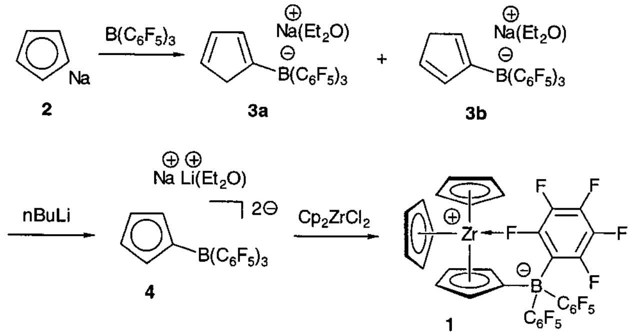
10.1021/om0010316 CCC: $20.00
Publication on Web 04/12/2001

Scheme 1

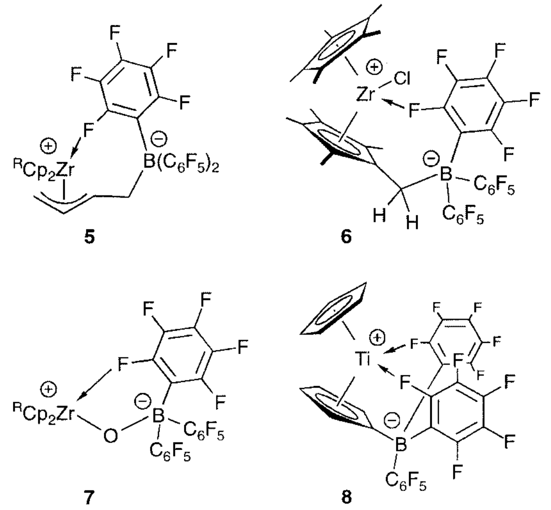


with *n*-butyllithium (in hexane/toluene) to yield $[C_5H_4B(C_6F_5)_3]Na,Li$ (**4**) as an etherate. The reagent **4** was reacted with zirconocene dichloride in ca. 1:1 molar ratio in toluene at ambient temperature to give the neutral betaine system (**1**),[13] which was obtained in ca. 30% yield as a microcrystalline red solid from toluene at −18 °C. Single crystals of **1** suited for the X-ray crystal structure analysis were obtained from dichloromethane solution at −30 °C after several days. All three cyclopentadienyl ligands in complex **1** are η^5-coordinated to the central zirconium atom. The Cp-coordination geometry at the metal is nearly trigonal-planar. The Cp(centroid)−Zr−Cp(centroid) angles are 117.6° (D1−Zr−D2), 118.8° (D2−Zr−D3), and 119.6° (D1−Zr−D3), where D3 denotes the centroid of the substituted Cp-ring. The corresponding D−Zr−D angles in the related cation $Cp_3Zr{-}CO^+$ are 119°.[1] In **1** the zirconium atom is displaced 0.264 Å from the plane determined by the three Cp-centroids ($Cp_3Zr{-}CO^+$ 0.229 Å). The D3−Zr distance (2.240 Å) of the boron-substituted Cp-ring is slightly *smaller* than the D1−Zr (2.301 Å) and D2−Zr (2.280 Å) distances. The two η^5-Cp ligands are uniformly coordinated to zirconium with their Zr−C(Cp) bond lengths found in a narrow range between 2.550(6) and 2.662(6) Å. The η^5-C_5H_4−[B]/Zr coordination is slightly asymmetric, with the distal Zr−C22/Zr−C23 bonds being slightly shorter (2.507(6), 2.472(3) Å) than the proximal Zr−C21/Zr−C24 (2.559(5), 2.549(4) Å) and the ipso-Zr−C25 linkage (2.622(5) Å).

The $-B(C_6F_5)_3$ substituent exhibits a conformation in the crystal that has two of the $-C_6F_5$ groups oriented away from and one $-C_6F_5$ group oriented toward the zirconium atom. The former shows a slightly distorted propeller-like arrangement. The C_5H_4−B linkage (1.644(8) Å) is marginally shorter than the C_6F_5−B bonds (average 1.658 Å). The average C(sp^2)−B−C(sp^2) angle of 109.6° is close to tetrahedral, but the individual angles deviate substantially, ranging from 101.3(4)° (C25−B−C41) to 115.1(4)° (C25−B−C31).

The most remarkable feature of the structure of complex **1** is the internal coordination of one of the ortho aryl C−F bonds to zirconium. The fluorine end of the C36−F36 bond has a significant bonding contact to zirconium. The resulting Zr−F36 distance is 2.310(3) Å, and the C36−F36−Zr bond angle is 138.0(3)°. The (μ)-F36−C36 bond length of 1.384(6) Å is elongated by ca. 0.04 Å relative to the average of 1.344(7) Å for the remaining C(sp^2)−F bonds in complex **1**.

Chart 1



As expected, the Zr−F−C(aryl) bond length of **1** lies between that of a Zr−F σ-bond (Cp_2ZrF_2 1.98(1) Å;[14] $Cp_2Zr(F)C_6F_5$ 1.94(1) Å)[15] and the Zr···F van der Waals interaction of ca. 3.0 Å.[16] Among the systems that exhibit two-coordinate fluorine atoms in intramolecular Zr−(μ-F)−C situations, the *d*(Zr−F) value of 2.310(3) Å found in **1** is at the short end of the bond length range, with only Piers' system **6** exhibiting a shorter Zr−F distance (2.267(5) Å,[17] see Chart 1). The various reported examples of the group 4 metallocene−(conjugated diene)−borate betaine systems **5** have *d*(Zr−F) values between 2.402(3) and 2.423(3) Å for unbridged metallocenes and 2.364(3)−2.483(3) Å for ansa-metallocene derivatives.[7−9] Siedle's oxygen-linked example **7** has a Zr−F distance of 2.346(3) Å,[18] which is shorter than the bridging *d*(Zr−F) values found in Bochmann's systems $Cp^*Zr(C_6F_5)C_4H_5B(C_6F_5)_2$ (2.429(2) Å)[19] and the $[(C_5H_4B(C_6F_5)_3]ZrCl_3$ dimer (2.441(2) and 2.420(2) Å).[20] The titanium−fluorine bonds in the related paramagnetic complex **8**, recently described by Shur et al., are 2.248(2) and 2.223(3) Å.[21]

The strength of the Zr−F dative interaction can be estimated from their dynamic ^{19}F NMR spectra. For the complexes **5** Gibbs activation energies of the (reversible) Zr−F bond cleavage were determined in a range between ca. 8 kcal mol^{-1} (nonbridged metallocene frameworks) and ca. 10 kcal mol^{-1} (silylene-bridged ansa-metallocene systems).[7−9]

The betaine complex **1** exhibits dynamic behavior in solution. At 193 K the dynamic features of **1** are frozen out on the 563.7 MHz ^{19}F NMR time scale in toluene

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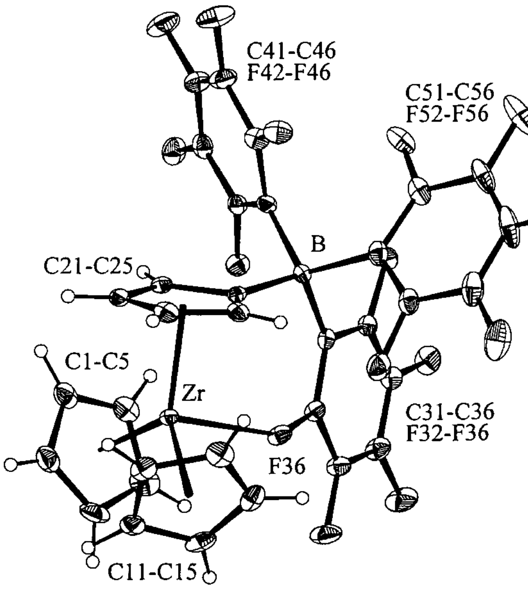

Figure 1. Molecular structure of the betaine complex **1** in the crystal. Selected bond lengths (Å) and angles (deg): Zr−C1 2.662(6), Zr−C2 2.571(6), Zr−C3 2.558(6), Zr−C4 2.563(6), Zr−C5 2.615(6), Zr−C11 2.578(6), Zr−C12 2.554(5), Zr−C13 2.559(5), Zr−C14 2.550(6), Zr−C15 2.615(6), B−C41 1.669(7), B−C51 1.657(8), B−C31 1.649(8), C25−B−C31 115.1(4), C25−B−C51 112.4(5), C31−B−C51 102.7(4), C25−B−C41 101.3(4), C31−B−C41 112.6(5), C51−B−C41 113.3(4); for additional values see the text and the Supporting Information.

solution. All 15 fluorine substituents become inequivalent under these conditions. The most noteworthy feature of the static ^{19}F NMR spectrum at low temperature is the very characteristic splitting of the ortho-fluorine signals into three pairs of diastereotopic resonances, out of which two pairs are found in the region expected for terminal (sp^2)C−F bonds (one pair at δ −126.6 and −131.2, the other at δ −128.9 and −136.3). The third pair of ortho-fluorine resonances has a separation of their chemical shifts by more than 85 ppm: one signal appears in the normal range at δ −128.5, and the other is extremely shifted to negative δ values at δ −213.4 (at 193 K). The latter is very characteristic for the occurrence of a bridging fluorine atom.[13] (Compounds **5** exhibit corresponding [Zr]−(μ-F)−C resonances in a range between δ −213 and −219,[7−9] whereas for complex **7** a ^{19}F NMR signal is observed at δ −190.)[18] This ^{19}F NMR spectral behavior of **1** indicates that the fluorine-bridged structure is retained in solution. Moreover, the presence of sets of diastereotopic pairs of ortho- and meta-F signals of the two remaining −C$_6$F$_5$ groups further indicates the presence of a "frozen" chiral propeller geometry of the borate in solution analogous to that observed in the crystal by X-ray diffraction.

Upon raising the temperature from 193 K, two dynamic processes are observed by temperature-dependent ^{19}F NMR spectroscopy. First we observe a pairwise coalescence of the ortho-fluorine resonances of the two "ordinary" −C$_6$F$_5$ groups, indicating the onset of the B−C(aryl) rotational process on the ^{19}F NMR time scale (see Figure 2).[22,23] From the two pairs of coalescences an averaged Gibbs activation energy of the B−C(aryl) rotational process of $\Delta G^{\ddagger}_{(B-C)rot}(218\ K) = 8.8 \pm 0.3$ kcal mol^{-1} was obtained.[24] The coalescence of the remaining separate ortho-fluorine signals with each other, and consequently with the averaged signal of the other four ortho-fluorine groups, sets in at somewhat higher temperature, as does the coalescence of their corresponding meta-fluorines (δ −156.6 and −162.8) of the −(μF)C$_6$F$_4$ group. From the latter, a Gibbs activation barrier of $\Delta G^{\ddagger}_{(Zr-F)diss}(253\ K) = 10.2 \pm 0.2$ kcal mol^{-1} was deduced, which corresponds to the activation barrier of the (reversible) Zr−F bond cleavage of complex **1**.

This study shows that the complex **1** contains a strongly electrophilic metal center, comparable in its electrophilicity with the [Cp$_2$ZrR$^+$] unit. In complex **1** the zirconium cation interacts with its intramolecularly bound borate anion through a reasonably strong dative Zr−(μ-F)−C interaction, analogously to that found in related metallocene−borate−betaines. The energetics of the Zr−F interaction are similar in the tris(cyclopentadienyl)Zr case **1** and the related metallocene systems. This observed behavior of **1** in the crystal and in solution provides additional experimental evidence of the pronounced coordinatively unsaturated 16-electron-complex behavior of the alleged 18-electron tris(η^5-cyclopentadienyl)Zr cation unit.

Experimental Section

All reactions were carried out in an argon atmosphere using Schlenk-type glassware or in a glovebox. Solvents, including deuterated solvents used for NMR spectroscopy, were dried and distilled under argon prior to use. NMR spectra were measured using a Bruker AC 200P, a Bruker AX 300, or a Varian Unity Plus 600 NMR spectrometer. For additional general information see ref 7.

Preparation of the Ligand System 4. Sodium cyclopentadienide (**2**, 500 mg, 5.7 mmol) was suspended in a mixture of 150 mL of toluene and 10 mL of diethyl ether. A freshly prepared solution of B(C$_6$F$_5$)$_3$[25] (2.9 g, 5.7 mmol) in 60 mL of toluene was added, and the mixture was stirred for 30 min at 60 °C. The product was characterized by taking an aliquot of 3 mL and evaporating it to dryness. The residue was washed twice with pentane, dried in vacuo, and characterized by ^{1}H NMR spectroscopy in benzene-d_6, which revealed the formation of a ca. 1:1 mixture of the adducts **3a** and **3b** [^{1}H NMR (200 MHz, 298 K, benzene-d_6): δ 6.61, 6.12, 6.04, 5.85 (m, each 1H, Cp), 5.96 (m, 2H, Cp), 2.91 (q, 4H, Et$_2$O), 2.76, 2.41 (s, each 2H, CH$_2$ of C$_5$H$_5$), 0.75 (t, 6H, Et$_2$O)]. The remaining solution was treated with *n*-butyllithium (3.88 mL of a 1.61 M solution in hexane; 6.25 mmol) at 0 °C. After 1 h of stirring at room temperature the solvent was removed in vacuo. The residue was washed twice with pentane and dried in vacuo to yield 3.3 g (87%) of **4**: ^{1}H NMR (200 MHz, 298K, benzene-d_6): δ 5.84 (br s, 2H, C$_5$H$_4$), 5.68 (m, 2H, C$_5$H$_4$), 2.71 (q, 4H, Et$_2$O), 0.59 (t, 6H, Et$_2$O). ^{13}C NMR (50.3 MHz, 298 K, benzene-d_6): δ 148.5 (dm, $^1J_{CF}$ = 244 Hz, o-C$_6$F$_5$), 139.2 (dm, $^1J_{CF}$ = 252 Hz, p-C$_6$F$_5$), 137.6 (dm, $^1J_{CF}$ = 261 Hz, m-C$_6$F$_5$), 109.8, 104.6 (CH of C$_5$H$_4$, ipso C of C$_5$H$_4$ not observed), 66.1, 14.0 (Et$_2$O), ipso-C of C$_6$F$_5$ not found. ^{19}F NMR (282.5 MHz, 298 K, benzene-d_6):

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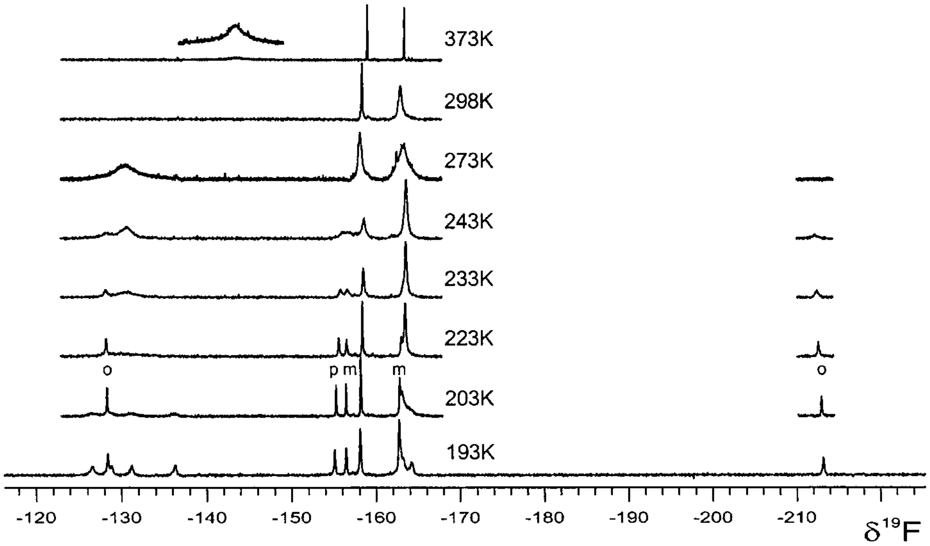

Figure 2. Dynamic ^{19}F NMR spectra (563.7 MHz, in toluene-d_8) of the betaine complex **1**.

δ −134.5 (m, 6F, o-C_6F_5), −161.5 (m, 3F, p-C_6F_5), −164.5 (m, 6F, m-C_6F_5). ^{11}B NMR (64.2 MHz, 298K, benzene-d_6): δ −15.6.

Preparation of 1. Zirconocene dichloride (214 mg, 0.73 mmol) and the reagent **4** (500 mg, 0.73 mmol) were suspended in 10 mL of toluene at room temperature. The mixture was stirred for 3 days at ambient temperature. The red solution was concentrated in vacuo to two-thirds its original volume and the product crystallized at −18 °C to yield 176 mg (30%) of **1**. ^{1}H NMR (599.9 MHz, 298 K, toluene-d_8): δ 5.63 (br m, 2H, α-C*H* of C_5H_4), 5.53 (m, 2H, *β*-C*H* of C_5H_4), 5.37 (s, 10H, Cp). ^{13}C NMR (150.8 MHz, 298 K, toluene-d_8): δ 125.6 (α-*C*H of C_5H_4), 116.8 (*β*-*C*H of C_5H_4), 116.7 (Cp), ipso-C of C_5H_4, and the carbon resonances of C_6F_5 were not observed. ^{11}B NMR (64.2 MHz, 298 K, toluene-d_8): δ −16.5 ($\nu_{1/2} \approx 20$ Hz). ^{19}F NMR (563.7 MHz, toluene-d_8): at 373 K, δ −143 ($\nu_{1/2} \approx 1000$ Hz, 6F, o-C_6F_5), −159.1 (t, $J_{FF} = 20$ Hz, 3F, p-C_6F_5), −163.6 (br, 6F, m−C_6F_5); at 213K, δ −128.4, −212.9 (each 1F, ortho-F of (μ-F)C_6F_4), δ −156.6, −163.1 (each 1F, meta-F of (μ-F)C_6F_4), δ −155.6 (1F, para-F of (μ-F)C_6F_4); δ −158.4 ($\nu_{1/2} \approx 57$ Hz, p-F of C_6F_5), −163.5 ($\nu_{1/2} = 250$ Hz, m-F of C_6F_5), ortho-F of C_6F_5 not observed; at 193 K, δ −128.5, −213.2 (each 1F, o-F of (μ-F)C_6F_4), −156.6, −162.8 (each 2F, m-F of (μ-F)C_6F_4), −155.1 (1F, p-F of (μ-F)C_6F_4), δ −126.6, −128.9, −131.2, −136.3 (each 1F, o-F of C_6F_5), −158.2 (2F), −162.8 (2F), −163.3 (1F), −164.3 (1F, p,m-F of C_6F_5). $\Delta G^{\ddagger}_{(Zr-F)diss}(253\ K) = 10.2 \pm 0.2$ kcal mol^{-1} ($\Delta\nu$, m-F at 213 K = 3640 Hz), $\Delta G^{\ddagger}_{(B-C)rot}(218\ K) = 8.9 \pm 0.3$ kcal mol^{-1} ($\Delta\nu$, o-F (first pair) at 193 K, 2600 Hz), 8.7 ± 0.3 kcal mol^{-1} ($\Delta\nu$, o-F (second pair) at 193 K, 4200 Hz). A sample was recrystallized from dichloromethane to yield single crystals of **1**·CH_2Cl_2, mp 128 °C. Anal. Calcd for $C_{33}H_{14}BF_{15}Zr\cdot CH_2Cl_2$ (882.4): C, 46.24; H, 1.83. Found: C, 46.84; H, 2.48.

X-ray Crystal Structure Analysis of 1·CH_2Cl_2. Single crystals were obtained from dichloromethane at −30 °C: formula $C_{33}H_{14}BF_{15}Zr\cdot CH_2Cl_2$, $M = 882.40$, yellow crystal 0.30 × 0.30 × 0.10 mm, $a = 11.744(1)$, $b = 12.819(1)$, $c = 21.317(1)$ Å, $V = 3209.2(4)$ Å^3, $\rho_{calc} = 1.826$ g cm^{-3}, $\mu = 6.24$ cm^{-1}, empirical absorption correction via SORTAV ($0.835 \le T \le 0.940$), $Z = 4$, orthorhombic, space group $P2_12_12_1$ (No. 19), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 11 238 reflections collected ($\pm h, \pm k, \pm l$), [(sin θ)/λ] = 0.65 Å^{-1}, 6065 independent ($R_{int} = 0.044$) and 5376 observed reflections [$I \ge 2\sigma(I)$], 474 refined parameters, $R = 0.051$, $wR_2 = 0.125$, max. residual electron density 1.16 (−1.03) e Å^{-3} close to the solvate molecule CH_2Cl_2, solvate molecule totally disordered, refined with three different positions for chlorine using restraints for the C−Cl and the Cl−Cl distances and one common isotropic thermal displacement parameter, hydrogens at the solvate molecule not calculated, other hydrogens calculated and refined as riding atoms, Flack parameter indicating a racemic twin with a ratio of 0.76(5) to 0.24(5).

Data set was collected with a Nonius KappaCCD diffractometer, equipped with a rotating anode generator Nonius FR591. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307−326), absorption correction SORTAV (Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33−37; Blessing, R. H. *J. Appl. Crystallogr.* **1997**, *30*, 421−426), structure solution SHELXS-97 (Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473), structure refinement SHELXL-97 (Sheldrick, G. M. Universität Göttingen, 1997), graphics DIAMOND (Brandenburg, K. Universität Bonn, 1997) and SCHAKAL (Keller, E. Universität Freiburg, 1997).

Acknowledgment. Financial support from the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

Supporting Information Available: Details of the X-ray crystal structure analysis of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0010316