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# *Articles*

# New Fluoride Derivative of a Dinuclear Titanium(III) Fulvalene Complex: Crystal Structure of $[(\eta^5\text{-}C_5H_5)Ti(\mu\text{-}F)]_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)$†

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Reduction of titanocene difluoride ($Cp_2TiF_2$) with 1.5 equiv of potassium in toluene at 60−100 °C affords the dinuclear $\eta^5{:}\eta^5$-fulvalene complex $[(\eta^5\text{-}C_5H_5)Ti(\mu\text{-}F)]_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)$ (**2**). **2** was also obtained *via* reaction of $Me_3SnF$ with the corresponding chloride and hydride compounds $[(\eta^5\text{-}C_5H_5)Ti(\mu\text{-}X)]_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)$ (X = Cl, H). **2** has been characterized by mass spectrometry, IR spectroscopy, and chemical analyses. The molecular structure of **2**, as determined by the X-ray crystal structural analyses, reveals a $Ti_2F_2$ fragment symmetrically folded along the Ti−Ti direction and assuming a butterfly configuration with a dihedral angle of 27.6(2)°. A dihedral angle of 15.3(3)° is observed between the two $C_5H_4$ rings of the folded fulvalene ligand.

## Introduction

In 1956, Wilkinson obtained bis($\eta^5$-cyclopentadienyl)titanium (titanocene) for the first time from the reaction of $TiCl_2$ with cyclopentadienylsodium.[1] Titanocene was later obtained by reduction of $Cp_2TiCl_2$ using sodium naphthalene in THF, sodium metal, $LiAlH_4$ in hydrocarbons, or by hydrogenolysis of $Cp_2TiMe_2$.[2,3] Titanocenes have been implicated as highly reactive intermediates in a wide variety of chemical reactions with olefins, hydrogen, carbon monoxide, and dinitrogen.[4] The chemical properties of titanocene were found, however, to be at variance with the expected chemical behavior of a monomeric titanocene. Though strong evidence for a dimeric structure with one bridging fulvalene ligand and two hydride bridges was given by Brintzinger and Bercaw,[5] it was not until 1992 that the dimeric structure was confirmed by X-ray crystallography.[6] So far, only a few titanocenes with one bridging fulvalene ligand and two $X_1X_2$ bridge atoms ($X_1 = X_2$ = Cl, OH, H; or $X_1$= H, $X_2$ = Cl, $H_2AlEt_2$) (Figure 1) have been synthesized and characterized by X-ray structure determination.[7] All of these complexes exhibit chloro, hydrido, or hydrogen bridging ligands; however, the fluorine-bridged analogue has not been reported to date. Since fluorine atoms demonstrate a considerable tendency to act as bridging ligands,[8] the syntheses of corresponding fluoride-bridged complexes from the titanocene difluoride should be possible. Furthermore, we have found that trimethyltin fluoride, $Me_3SnF$, is an excellent fluorinating reagent. Access to a wide range of cyclopentadienyl-substitued titanium fluorides is possible *via* the reaction of $Me_3SnF$ with the corresponding chloride in suitable solvents.[9,10] We report herein an extension of this fluorination procedure and the properties and solid-state structure of the new titanium fulvalene complex with two fluoride bridges ($X_1 = X_2$ = F).

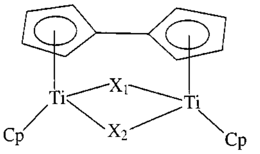

**Figure 1.** Dinuclear titanium fulvalene complexes; $X_1 = X_2$ = F (**2**), Cl (**4**), H (**6**), OH (**7**); $X_1$ = H, $X_2$ = Cl (**3**), $H_2AlEt_2$ (**8**).

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† Dedicated to Professor Gottfried Huttner on the occasion of his 60th birthday.

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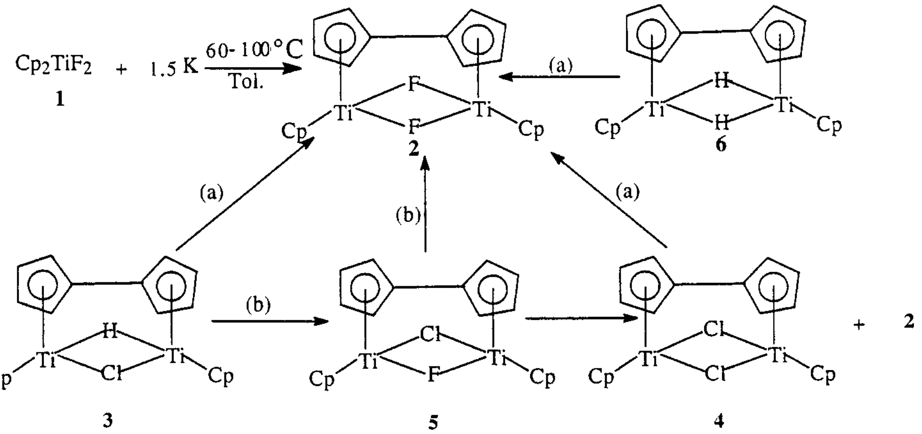
S0276-7333(96)00680-2 CCC: $14.00

**Scheme 1**[a]



[a] Reactions and conditions: (a) $+2Me_3SnF$, $-2Me_3SnCl$/toluene; (b) $+Me_3SnF$, $-Me_3SnCl$/toluene, room temperature.

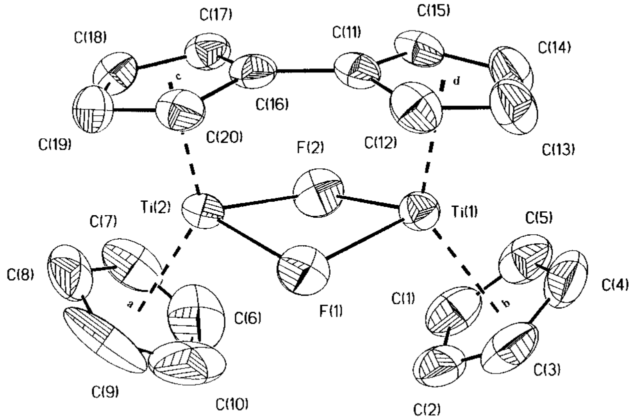


**Figure 2.** Molecular structure of $[(\eta^5\text{-}C_5H_5)Ti(\mu\text{-}F)]_2(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)$.

## Results and Discussion

**Synthesis and Spectra.** Reduction of $Cp_2TiF_2$ (**1**) in toluene with 1.5 molar equiv of potassium at 60–100 °C in toluene gives the dark green crystalline $\mu\text{-}\eta^5\text{:}\eta^5$-fulvalene complex $[(\eta^5\text{-}C_5H_5)Ti(\mu\text{-}F)]_2(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)$ (**2**) in moderate yield (37%). The mass spectrum of **2** confirmed its dinuclear structure [EI-MS: *m/z* 392 ($M^+$)]. In contrast when **1** was reacted with 1 molar equiv of potassium, only the fluorine-bridged compound $[Cp_2Ti(\mu\text{-}F)]_2$[9] was obtained. Attempts to prepare the zirconium analogue by reduction of $Cp_2ZrF_2$ with 1.5 molar equiv of potassium were unsuccessful. In this instance an insoluble solid formed due to the facile polymerization of zirconocene difluoride under reflux. It is interesting to note that under the same conditions reaction of titanocene dichloride ($Cp_2TiCl_2$) with 1.5 molar equiv of potassium proceeds differently, giving a compound with two bridging heteroatoms (H, Cl), $[(\eta^5\text{-}C_5H_5)_2Ti_2(\mu\text{-}H)(\mu\text{-}Cl)](\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)$ (**3**).[7c] The failure to isolate a corresponding fluoride–hydride compound is attributed to the greater bond strength of the Ti–F bond compared with the Ti–Cl bond and the propensity of fluorine to form stable fluorine-bridged compounds.

$Me_3SnF$ is particularly suited for the synthesis of cyclopentadienyl-substitued titanium fluorides. Thus, the (fulvalene)titanium fluoride **2** can be obtained in good yield by reaction of the corresponding chloride $[(\eta^5\text{-}C_5H_5)Ti(\mu\text{-}Cl)]_2(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)$ (**4**) with 2 molar equiv of $Me_3SnF$ (Scheme 1). Moreover, we found that compound **2** can be obtained alternatively by reaction of **3** or $[(\eta^5\text{-}C_5H_5)Ti(\mu\text{-}H)]_2(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)$ (**6**) with 2 equiv of $Me_3SnF$ in toluene in high yield (56%, 75%, respectively), which indicates not only organometallic chlorides but also hydrides may be fluorinated easily using $Me_3SnF$. It is very interesting to note that attempts to prepare the compound with both fluorine and hydrogen bridges $[(\eta^5\text{-}C_5H_5)_2Ti_2(\mu\text{-}H)(\mu\text{-}F)](\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)$ by reaction of compound **3** with $Me_3SnF$ in a molar ratio of 1:1 in toluene were unsuccessful. In this case a mixture of compounds **2**, **4**, and $[(\eta^5\text{-}C_5H_5)_2Ti_2(\mu\text{-}Cl)(\mu\text{-}F)](\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)$ (**5**) was isolated, indicating that a ligand redistribution reaction between Cl and F occurs. This behavior also suggests that replacement of the bridging hydrogen by fluoride occurs prior to that of bridging chloride (Scheme 1).

We also observed a similar redistribution reaction of $(RCp)_2TiCl_2$ (R = H, Me) with $Me_3SnF$ in a molar ratio of 1:1 in toluene, $CH_2Cl_2$, and $CH_3CN$ (eq 1). The reactions between $Cp_2MX_2$ and $Cp_2MR_2$ (M = Ti, Zr; X = F, Cl, Br, I; R = Me, Ph) (eq 2) have been studied in detail by Jordan.[11]

$$2(RCp)_2TiCl_2 + 2Me_3SnF \rightarrow 2(RCp)_2TiClF \rightarrow (RCp)_2TiCl_2 + (RCp)_2TiF_2 \quad (1)$$

$$Cp_2MX_2 + Cp_2MR_2 \rightleftharpoons 2Cp_2MRX \quad (2)$$

The IR spectrum of **2** is similar to those of **4** and **6**,[5b] containing two medium absorptions in the range 1100–1000 cm $^{-1}$ and a strong absorption ca. 780 cm $^{-1}$. Compound **2** is stable up to ca. 300 °C and decomposes without melting on further heating. To our knowledge, it is difficult to record the $^1H$ NMR spectrum of the compounds due to the paramagnetism of titanium(III) compounds.[6,7c,12] It was found in the $^1H$ NMR of compound **2** at room temperature that the cyclopentadienyl ring proton signals are broad and appear at relatively high field [$\delta(H(C_5H_4)$ 5.1 and 7.9 ppm; $\delta(H(C_5H_5)$ 6.7 ppm] as compared with complex **6** [$\delta(H(C_5H_4)$ 5.5 and 8.1 ppm; $\delta(H(C_5H_5)$ 6.9 ppm].[12] In the $^{19}F$ NMR spectrum, however, no signal was observed.

**X-ray Crystal Structure of 2.** The X-ray analysis reveals that the crystal of **2** is composed of discrete

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**Table 1. Selected Bond Distance (Å) and Angles (deg) for Compound 2**

| | | | |
|---|---|---|---|
| Bond Distances | | | |
| Ti(1)−F(2) | 2.046(4) | Ti(1)−F(1) | 2.046(4) |
| Ti(1)−C(11) | 2.333(5) | Ti(1)−C(3) | 2.351(6) |
| Ti(1)−C(4) | 2.357(6) | Ti(1)−C(5) | 2.359(7) |
| Ti(1)−C(15) | 2.369(6) | Ti(1)−C(12) | 2.371(6) |
| Ti(1)−C(14) | 2.388(6) | Ti(1)−C(2) | 2.391(7) |
| Ti(1)−C(13) | 2.397(6) | Ti(1)−C(1) | 2.402(7) |
| Ti(2)−F(2) | 2.044(4) | Ti(2)−F(1) | 2.047(4) |
| Ti(2)−C(16) | 2.336(6) | Ti(2)−C(20) | 2.346(6) |
| T(2)−C(9) | 2.349(7) | Ti(2)−C(7) | 2.349(7) |
| Ti(2)−C(10) | 2.354(8) | Ti(2)−C(17) | 2.361(5) |
| Ti(2)−C(8) | 2.367(6) | Ti(2)−C(6) | 2.372(8) |
| Ti(2)−C(18) | 2.393(6) | Ti(2)−C(19) | 2.396(6) |
| C(11)−C(16) | 1.464(8) | | |
| Angles | | | |
| F(2)−Ti(1)−F(1) | 75.9(2) | F(2)−Ti(2)−F(1) | 75.9(2) |
| Ti(1)−F(1)−Ti(2) | 101.4(2) | Ti(2)−F(2)−Ti(1) | 101.5(2) |

**Table 2. Crystal Data and Structure Refinement for 2**

| | |
|---|---|
| empirical formula | $C_{20}H_{18}F_2Ti_2\cdot C_6H_6$ |
| fw | 470.25 |
| temp, K | 193(2) |
| wavelength, Å | 0.710 73 |
| cryst system | orthorhombic |
| space group | $P2_12_12_1$ |
| $a$, Å | 5.9592(12) |
| $b$, Å | 18.792(4) |
| $c$, Å | 19.989(4) |
| α, deg | 90 |
| $\beta$, deg | 90 |
| $\gamma$, deg | 90 |
| $V$, Å$^3$ | 2238.5(8) |
| $Z$ | 4 |
| $D_{calcd}$, g·cm$^{-3}$ | 1.395 |
| $\mu$, mm$^{-1}$ | 0.739 |
| $F(000)$ | 968 |
| cryst size, mm | 0.8 × 0.4 × 0.3 |
| $\theta$ range, deg | 3.57−22.54 |
| index range | $-6 \le h \le 6$, $-20 \le k \le 20$, $-21 \le l \le 21$ |
| tot. reflcns | 3594 |
| indepdt reflcns | 2946 ($R_{int} = 0.0176$) |
| abs corr | none |
| refinement method | full-matrix least squares on $F^2$ |
| data/restraints/params | 2946/63/271 |
| Flack param | 0.0307 |
| $S$ | 1.003 |
| $R1$, w$R2$ [$I > 2\sigma(I)$] | 0.0496, 0.1311 |
| $R1$, $R2$ (all data) | 0.0543, 0.1370 |
| largest diff peak and hole, e·Å$^{-3}$ | 0.528, −0.420 |

molecules of $[(\eta^5\text{-}C_5H_5)Ti(\mu\text{-}F)]_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)$ (Figure 2), containing two Ti atoms bonded to a bridging fulvalene ligand. The coordination around each Ti atom can be described as a distorted tetrahedron if we consider the Cp ring centroids as each occupying one coordination site around the metal. The fulvalene ligand is folded, forming a dihedral angle (15.3(3)°) between the two ring planes. The inter-ring carbon−carbon bond distance of the fulvalene ligand (C(11)−C(16) 1.464(8) Å) and the distance of the Ti atoms from the fulvalene rings (Ti(1)−Cp$^d$ 2.047(3) Å, Ti(2)−Cp$^c$ 2.041(3) Å) and from the cyclopentadienyl rings (Ti(1)−Cp$^b$ and Ti(2)−Cp$^a$ 2.055(3) Å) have normal values (Table 1), as have the Ti−C distances which average 2.372 and 2.358 Å, respectively, for the fulvalene ligand and 2.372 and 2.358 Å, respectively, for the cyclopentadienyls.[6,7] The Ti−Ti distance (3.167(1) Å) that indicates no formation of a metal−metal bond is shorter than that of compounds **4** (3.638 Å) and **8** (3.374 Å) and similar to that of compounds **3** (3.125 Å) and **7** (3.195 Å) (see Table 3). The Ti−F distances (average 2.046 Å) are comparable with the relative Ti(III) compound $(Cp_2TiF)_3TiF_3$ [Ti−Ti 3.257 Å, Ti−F 1.975 and 2.094 Å, respectively].[13] The angles subtended at the Ti by the centroid of the two staggered individual Cp rings and fulvalene [Cp$^a$−Ti$_1$−Cp$^c$ 136.4(3)°, Cp$^b$−Ti$_2$−Cp$^d$ 138.7(3)°, Cp = ring centroid] are in the region expected for a normal bent $\eta^5$-Cp−metal system.[14] The Ti−F−Ti (101.5, 101.4°) and F−Ti−F (75.9°) angles are comparable to those with bridging bis($\mu$-H), ($\mu$-H)($\mu$-Cl), bis($\mu$-Cl), and bis($\mu$-OH) dititanium fulvalene compounds (see Table 3). Similarly, the plane containing the $Ti_2F_2$ fragment is symmetrically folded along the Ti−Ti direction. The bridging F atoms lie lower than the Ti atoms, farther from the fulvalene ligand and assuming a butterfly configuration with a dihedral angle of (27.6(2)°. All the other bond lengths and angles are as expected.

## Experimental Section

**General Data.** All experimental manipulations were carried out under an atmosphere of dinitrogen rigorously excluding air and moisture. Solvents were purified according to conventional procedures and were freshly distilled prior to use. $Me_3SnF$ and $Cp_2TiF_2$ (**1**),[9] $[(\eta^5\text{-}C_5H_5)_2Ti_2(\mu\text{-}H)(\mu\text{-}Cl)](\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)$ (**3**),[7c] $[(\eta^5\text{-}C_5H_5)Ti(\mu\text{-}Cl)]_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)$ (**4**), and $[(\eta^5\text{-}C_5H_5)Ti(\mu\text{-}H)]_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)$ (**6**)[15] were prepared as previously described. IR spectra were recorded on a Bio-Rad FTS-7 spectrometer. Mass spectra were obtained on Finnigan MAT 8230 and Varian MAT CH5 spectrometers. Elemental analyses were performed at the Analytical Laboratory of the Institute of Inorganic Chemistry of Göttingen University.

**Synthesis of $[(\eta^5\text{-}C_5H_5)Ti(\mu\text{-}F)]_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)$ (2) Method 1.** A suspension of **1** (0.324 g, 1.5 mmol) and potassium (0.088 g, 2.25 mmol) in toluene (40 mL) was vigorously stirred at 60−70 °C for 24 h. Then the reaction mixture was heated to 100 °C for at least 10 h, resulting in a dark green solution. After cooling of the mixture to room temperature and separation of the insoluble solid, partial removal of the solvent, and standing at −20 °C for 1 week, large-size, air-sensitive, dark green crystals of **2** separated in 37% yield (0.11 g). Mass spectrum: $m/z$ 392 (M$^+$), 372 (M$^+$ − 65). IR (Nujol, cm$^{-1}$): 1226 (w),1067 (w), 1019 (m), 787 (s), 722 (m). Anal. Calcd for $C_{20}H_{18}F_2Ti_2$: C, 61.22; H, 4.59; F, 9.69. Found: C, 61.96; H, 4.78; F, 9.12.

**Method 2. Reaction of 4 with $Me_3SnF$.** A mixture of **4** (0.21 g, 0.5 mmol) and $Me_3SnF$ (0.183 g, 1 mmol) in toluene (30 mL) was stirred at room temperature overnight. After filtration of the dark green reaction solution the solvent was removed *in vacuo*, and the solid residue was recrystallized from toluene/hexane (1:2) to give a 61% yield of **2** (0.12 g). Mass spectrum: $m/z$ 392 (M$^+$), 372 (M$^+$ − 65).

**Method 3. Reaction of 6 with $Me_3SnF$.** A suspension of **6** (0.356 g, 1 mmol) and $Me_3SnF$ (0.366 g, 2 mmol) in toluene (30 mL) was stirred at room temperature for 12 h. After filtration, the solvent was evaporated *in vacuo* and the dark green solid obtained washed with hexane to give compound **2** in 75% yield (0.29 g).

**Method 4. Reaction of 3 with $Me_3SnF$ (1:2 Ratio).** A mixture of **3** (0.5 g, 1.28 mmol) and $Me_3SnF$ (0.47 g, 2.56 mmol) in 30 mL of toluene was stirred at ambient temperature overnight. The solution was filtered, and the solvent was removed *in vacuo* from the filtrate. The resulting dark green

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**Table 3. Important Geometrical Parameters in Dititanium Fulvalene $[(C_5H_5)TiX]_2(C_{10}H_8)$ Complexes**

| | | interatomic dist (Å) | | | | | angle (deg)[a] | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| compd | no. | Ti–Ti | Ti–C(fulv) | Ti–C(Cp) | Ti–X | C11–C16 | α | *β* | *θ* | *ω* | refs |
| $Cp_2Ti_2(C_{10}H_8)(F_2)$ | **2** | 3.167 | 2.35–2.37 | 2.37 | 2.04 | 1.46 | 75.9 | 101.5 | 137.7 (136.0) | 15.3 | this work |
| $Cp_2Ti_2(C_{10}H_8)(H)(Cl)$ | **3** | 3.125 | 2.32–2.39 | 2.36 | 2.17 (2.49)[b] | 1.45 | 92 | 93 (77.6)[b] | 137.3 (137.3)[b] | 15.6 | 12 |
| $Cp_2Ti_2(C_{10}H_8)(Cl)_2$ | **4** | 3.638 | 2.37–2.40 | 2.38 | 2.52 | 1.46 | 81.3 | 92.5 | 135.2 | 5.3 | 10 |
| $Cp_2Ti_2(C_{10}H_8)(H)_2$ | **6** | 2.989 | 2.30–2.39 | 2.36 | 1.71 | 1.43 | 57 | 120 | 138.6 | 17.7 | 9 |
| $Cp_2Ti_2(C_{10}H_8)(OH)_2$ | **7** | 3.195 | 2.34–2.39 | 2.41 | 2.07 | 1.43 | 75.4 | 100.7 | 135.1 | 15.1 | 11 |
| $Cp_2Ti_2(C_{10}H_8)H(H_2AlEt_2)$ | **8** | 3.374 | 2.33–2.39 | 2.35 | 1.80 | 1.45 | | 138 | 134.1 | 12.5 | 13 |

[a] α, angle X–Ti–X; *β*, angle Ti–X–Ti; *θ*, dihedral angle between the $C_5H_5$ and $C_5H_4$ planes; *ω*, dihedral angle between the $C_5H_4$ planes. [b] Ti–Cl bond length or Ti–Cl–Ti bond angle.

solid was recrystallized from toluene/hexane (1:2) to give a 56% yield of **2** (0.28 g).

**Reaction of 3 with $Me_3SnF$ (1:1 Ratio).** A mixture of **3** (0.39 g, 1 mmol) and $Me_3SnF$ (0.183 g, 1 mmol) in toluene (30 mL) was stirred at room temperature overnight and filtered. After removal of the solvent, the residue was washed with hexane and dried *in vacuo*. Mass spectrum: *m*/*z* 392 [$M^+$, for compound **2**], 408 [$M^+$, for compound **5**], 424 [$M^+$, for compound **4**].

**X-ray Structure Determination of 2.** Diffraction data were collected on a Siemens-Stoe AED2 four-circle instrument (at −80 °C) using Mo Kα radiation ($\lambda = 0.710\,73$ Å). The structure was solved by direct methods using SHELXS-90,[16] and refinement was made by full-matrix least squares on all $F^2$ values using SHELXL-93.[17] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically calculated positions and refined using a riding model. One molecule of solvent was also found and refined anisotropically using restraints. Other details related to the data collection, structure solution, and refinement are listed in Table 2.

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**Supporting Information Available:** Listings of crystal data, atomic coordinates and equivalent isotropic displacement parameters for all non-hydrogen atoms, hydrogen positional and thermal parameters, anisotropic displacement parameters, and bond distances and angles (7 pages). Ordering information is given on any current masthead page.

OM9606808

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