Reactivity of [$Cp_2Ti(CO)_2$] towards Nitrile and Water Adducts of $B(C_6F_5)_3$: Formation of [$Cp_2Ti(\eta^2\text{-}F_3CC_6H_4CN)\cdot B(C_6F_5)_3$] and [$Cp_2Ti$][$HOB(C_6F_5)_3$] with a Ti···F Interaction

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The reaction of [$Cp_2Ti(CO)_2$] with borane adducts $CF_3C_6H_4CN\cdot B(C_6F_5)_3$ and [$H_2O\cdot B(C_6F_5)_3$] has afforded the titanaazirine [$Cp_2Ti(\eta^2\text{-}C,N\text{-}F_3CC_6H_4CN)\cdot B(C_6F_5)_3$] (**1**) and the Ti^{III} salt [Cp_2Ti][$HOB(C_6F_5)_3$] (**2**), respectively. In both cases, a Ti···F interaction between the titanium centre and an *ortho*-fluorine atom of the tris(perfluorophenyl)borane is observed in the X-ray structure determination.

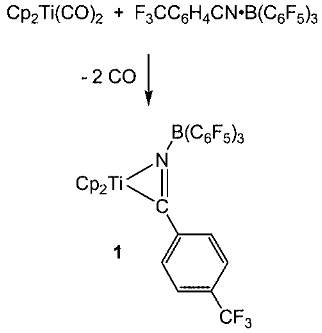
Introduction

The reactivity of the Lewis acid $B(C_6F_5)_3$ with organometallic complexes has been the subject of much literature, mainly concerning Ziegler−Natta catalysts in relation to the cationic group-4 complexes.[1−3] Novel aspects of the reactivity of $B(C_6F_5)_3$ recently investigated by our group on the vanadium(V) complex [$VO(OCH_2CF_3)_3$][4] and the titanocene [$Cp_2Ti(CO)_2$][5] led to the unexpected formation of the organometallic complex [$VO(C_6F_5)(\mu\text{-}OCH_2CF_3)(OCH_2CF_3)$]$_2$ and to the acylborane [$Cp_2Ti(CO)\{\eta^2\text{-}OCB(C_6F_5)_3\}$], respectively. Addition of a Lewis acid to a nitrile allows the activation of the C−N nitrile bond; reaction with the vanadocene [VCp_2] gives the vanada(IV)azirine complex [$Cp_2V\{\eta^2\text{-}RC{=}N\cdot B(C_6F_5)_3\}$] (R = CH_3, $CF_3C_6H_4$).[6]

To prepare the titanium analogue to the vanada(IV)azirine series, we extended our findings on the reactivity of a nitrile bond activated with the Lewis acid $B(C_6F_5)_3$ toward the vanadocene[6] to the titanocene [$Cp_2Ti(CO)_2$]. In addition, a titanium(III) complex has been obtained by a controlled hydrolytic reaction with the [$H_2O\cdot B(C_6F_5)_3$] adduct.

Results and Discussion

[$Cp_2Ti(CO)_2$] reacts with a stoichiometric mixture of $CF_3C_6H_4CN$ and $B(C_6F_5)_3$ at 50 °C in toluene to give a red-orange crystalline complex of the titanaazirine [$Cp_2Ti(\eta^2\text{-}C,N\text{-}F_3CC_6H_4CN)\cdot B(C_6F_5)_3$] (**1**), which has been isolated and characterized by an X-ray structure determination (Scheme 1, Figure 1).



Scheme 1. Synthesis of [$Cp_2Ti(\eta^2\text{-}C,N\text{-}F_3CC_6H_4CN\cdot B(C_6F_5)_3$] (**1**)

This is reminiscent of our recent work based on the vanadocene [VCp_2] and the so-called "activated" nitrile $RCN\cdot B(C_6F_5)_3$.[6] The well-known formation of adducts between nitrile and a Lewis acid is associated with an increase in the ν(CN) frequency in the IR spectrum and an increase of the electron density on the C≡N triple bond.[3a,7]

The C−N nitrile bond is attached to the titanium atom through two σ-type Ti−C and Ti−N bonds of 2.075(2) and 2.0940(18) Å. These values are expected for such bonds, by comparison with those of the iminoacyl complex [$Ti(OAr\text{-}2,6\text{-}i Pr_2)_2(\eta^2\text{-}t BuNCCH_2Ph)(CH_2Ph)$] [Ti−C 2.086(6), Ti−N 2.025(5) Å] and [$Cp_2Ti(\eta^2\text{-x,yNCPh})$] [xy = 2,6-$(CH_3)_2C_6H_3$] [Ti−C 2.096(4), Ti−N 2.149(4) Å].[8] The carbon−nitrogen distance [1.243(3) Å] is typical of a carbon−nitrogen double bond. There are small differences between the distances and angles in the organic framework $F_3CC_6H_4CN\cdot B(C_6F_5)_3$ of **1** and those in the previously published vanadium(IV) analogue complex [$Cp_2V(\eta^2\text{-}C,N\text{-}F_3CC_6H_4CN)\cdot B(C_6F_5)_3$].[6] The molecular geometry of **1** is

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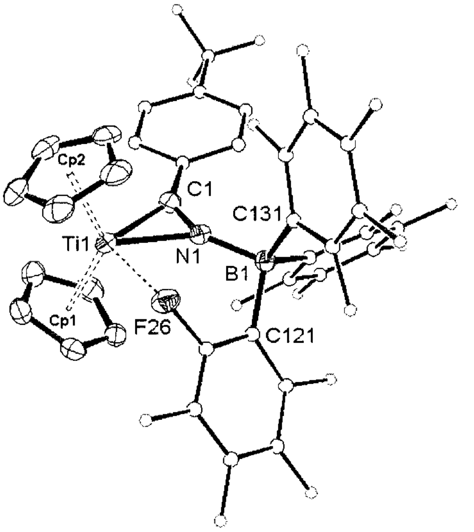
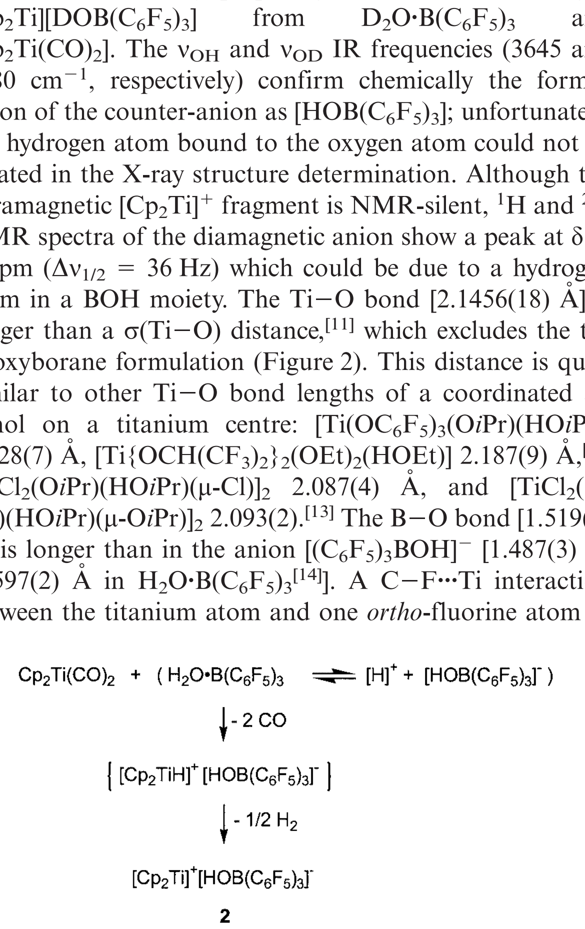


Figure 1. Molecular structure of **1**; hydrogen atoms and some labeled atoms are omitted for clarity; selected bond lengths [Å] and angles [°]: Ti(1)−C(1) 2.075(2), Ti(1)−N(1) 2.0940(18), C(1)−N(1) 1.243(3), N(1)−B(1) 1.575(3), C(1)−Ti(1)−N(1) 34.69(3), C(1)−N(1)−B(1) 147.19(9), Ti(1)−N(1)−C(1) 140.84(14)

similar to vanadium(IV) except for a C−F···Ti interaction in the solid state between an *ortho*-fluorine atom of the borane adduct and the titanium atom. The Ti···F distance (2.453 Å) is notably less than the sum of the Ti and F van der Walls radii (1.45 and 1.47 Å, respectively). This is similar to that found in $[(C_5Me_5)Ti\{C_5Me_4CH_2B(C_6F_5)_3\}]$ [Ti−*ortho*-fluorine atom = 2.406(3) Å].[9] A small but significant lengthening of the C−F(···Ti) bond [1.378(2) Å] relative to other C−F bonds (average 1.346 Å) of the perfluorophenyl groups of the borane is observed. In the ^{13}C NMR spectrum, the characteristic carbon resonance at δ = 225.6 ppm of the η^2-*C,N* carbon atom is found and the corresponding ν(C=N) band appears in the IR spectrum at 1725 cm^{-1}. ^{19}F NMR obtained in $[D_8]THF$ (the only solvent in which **3** is soluble) does not show a peak attributable to a Ti···F interaction at room temperature, but at 233 K the five fluorine substituents of one pentafluorophenyl group become inequivalent. This splitting exhibits a high-field ^{19}F resonance at δ = −128.1 ppm, which is characteristic for a bridging fluorine atom, in agreement with the fluorine-bridged solid-state structure. The C−F···V interaction was not observed in the vanadium analogue in the solid state but is demonstrated in solution by EPR.[6] Complex **1** can also be obtained directly by addition of a toluene solution of $CF_3C_6H_4CN$ on insoluble $[Cp_2Ti(CO)\{\eta^2\text{-}OCB(C_6F_5)_3\}]$[5] in toluene with evolution of CO.

Additionally, accidental hydrolysis during the crystallization procedure of **1** yielded a few large crystals of a blue complex. This hydrolysis was confirmed by treating the $[H_2O{\cdot}B(C_6F_5)_3]$ adduct, prepared in situ,[10] with $[Cp_2Ti(CO)_2]$ in pentane, which gave a blue complex after at least 4 d. Although an X-ray structure determination allowed us to characterize this product as the titanoxyborane $[Cp_2TiOB(C_6F_5)_3]$, careful investigation of the crystals by IR and NMR spectroscopy revealed the salt structure $[Cp_2Ti][HOB(C_6F_5)_3]$ (**2**) for the blue Ti^{III} paramagnetic crystals (vide infra) (Scheme 2). This ambiguous situation has been clarified by preparing the deuterated analogue $[Cp_2Ti][DOB(C_6F_5)_3]$ from $D_2O{\cdot}B(C_6F_5)_3$ and $[Cp_2Ti(CO)_2]$. The ν_{OH} and ν_{OD} IR frequencies (3645 and 2680 cm^{-1}, respectively) confirm chemically the formulation of the counter-anion as $[HOB(C_6F_5)_3]$; unfortunately, the hydrogen atom bound to the oxygen atom could not be located in the X-ray structure determination. Although the paramagnetic $[Cp_2Ti]^+$ fragment is NMR-silent, ^1H and ^2H NMR spectra of the diamagnetic anion show a peak at δ = 3 ppm ($\Delta\nu_{1/2}$ = 36 Hz) which could be due to a hydrogen atom in a BOH moiety. The Ti−O bond [2.1456(18) Å] is longer than a σ(Ti−O) distance,[11] which excludes the titanoxyborane formulation (Figure 2). This distance is quite similar to other Ti−O bond lengths of a coordinated alcohol on a titanium centre: $[Ti(OC_6F_5)_3(O\textit{i}Pr)(HO\textit{i}Pr)]$ 2.128(7) Å, $[Ti\{OCH(CF_3)_2\}_2(OEt)_2(HOEt)]$ 2.187(9) Å,[12] $[TiCl_2(O\textit{i}Pr)(HO\textit{i}Pr)(\mu\text{-}Cl)]_2$ 2.087(4) Å, and $[TiCl_2(O\textit{i}Pr)(HO\textit{i}Pr)(\mu\text{-}O\textit{i}Pr)]_2$ 2.093(2).[13] The B−O bond [1.519(3) Å] is longer than in the anion $[(C_6F_5)_3BOH]^-$ [1.487(3) Å] [1.597(2) Å in $H_2O{\cdot}B(C_6F_5)_3$[14]]. A C−F···Ti interaction between the titanium atom and one *ortho*-fluorine atom of



Scheme 2. Suggested hydrolytic pathway leading to $[Cp_2Ti][HOB(C_6F_5)_3]$ (**2**)

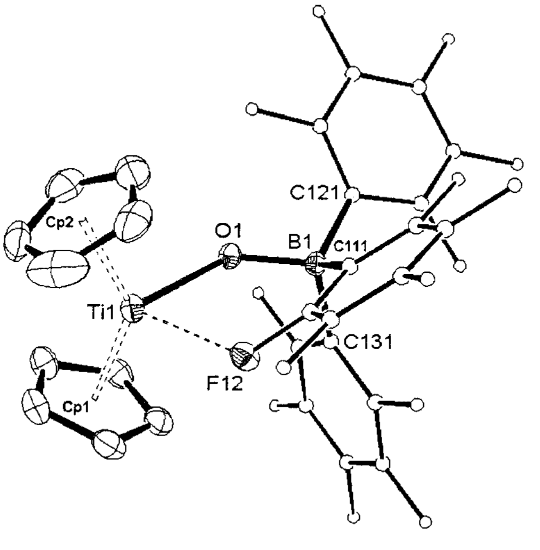


Figure 2. Molecular structure of **2**; hydrogen atoms and some labeled atoms are omitted for clarity; selected bond lengths [Å] and angles [°]: Ti(1)−O(1) 2.1456(18), O(1)−B(1) 1.519(3), Ti(1)−F(12) 2.2841(17); Ti(1)−O(1)−B(1) 137.78(14), O(1)−Ti(1)−F(12) 73.37(6)

the $B(C_6F_5)_3$ moiety occurs in the solid-state structure. The Ti···F distance [2.2841(17) Å] is still shorter than in complex **1** and there is a lengthening of the C−F(···Ti) bond [1.375(3) Å] relative to other C−F bonds (average 1.340 Å) of the perfluorophenyl groups of the borane. A similar Ti^{III} complex as [*rac*-(ebthi)Ti][$HOB(C_6F_5)_3$] [ebthi = 1,2-ethylene-1,1′-bis(η^5-tetrahydroindenyl)], formed due to adventitious water, has been recently fully characterized by an X-ray structure analysis; the hydrogen atom attached to the oxygen atom could not be localized [d(Ti−O) = 2.097(3) Å; d(B−O) = 1.482(4) Å; d(Ti···F) = 2.365(2) Å].[15] Similar Ti···F distances between the titanium centre and *ortho*-fluorine atoms in zwitterionic Ti^{III} structures have also been observed {[CpTi{$C_5H_4B(C_6F_5)_3$}]: 2.248(2), 2.223(3) Å; [(iPrC_5H_4)Ti{iPr$C_5H_3B(C_6F_5)_3$}]: 2.64(2), 2.256(2) Å}.[16,17]

Our result differs slightly from those of Green and colleagues with [MCp_2] (M = Cr, Fe, Co) yielding cationic [MCp_2]$^+$ with a counter-anion such as [$(C_6F_5)_3B(\mu\text{-}OH)B(C_6F_5)_3$]$^-$ or [$(C_6F_5)_3BOH\cdots H_2OB(C_6F_5)_3$]$^-$.[14] In their case the observed difference in the anion part is due to their synthetic procedure {2 equiv. of $H_2O\cdot B(C_6F_5)_3$ or an equimolecular mixture of $H_2O\cdot B(C_6F_5)_3/B(C_6F_5)_3$ are implied in the reaction with [MCp_2]}. Their proposed pathway contains the suggested intermediate [Cp_2M][$HOB(C_6F_5)_3$], which is corroborated here {Scheme 2; the first intermediate [Cp_2TiH][$HOB(C_6F_5)_3$] is assumed only}. Complex **2** is blue, and its magnetic susceptibility (1.76 µB) and EPR spectrum in THF (g = 1.974) confirm that it is a paramagnetic Ti^{III} complex. The single line in the EPR spectrum implies that there is no interaction between the Ti atom and the *ortho*-fluorine atom (I = 1/2) in THF solution, suggesting that the solvent occupies a coordination position on the metal atom, thus releasing the Ti···F interaction. The EPR solution spectrum is unchanged at −100 °C.

In conclusion, the reactivity of the borane adducts [$RCN\cdot B(C_6F_5)_3$] and [$H_2O\cdot B(C_6F_5)_3$] is described with [$Cp_2Ti(CO)_2$]. As expected, the formation of the titana(IV)-azirine complex **1** confirms the role of the tris(perfluorophenyl)borane in activating a nitrile bond, as already observed in the vanadium chemistry. The formation of **2** can be controlled and derives from an hydrolytic decomposition pathway.

Experimental Section

General: All manipulations were carried out using standard Schlenk line or dry-box techniques under argon. Solvents were boiled under reflux, dried with appropriate agents under argon, collected by distillation, and then stored in a dry-box over activated molecular sieves (4 Å). Deuterated solvents were degassed and dried over activated molecular sieves (4 Å). NMR spectroscopic data were recorded using Bruker AMX-400, DPX-300, and AC-200 spectrometers, and referenced internally to residual protio solvent (^{1}H) resonances, and are reported relative to tetramethylsilane (δ = 0 ppm). ^{19}F NMR (188.298 MHz) spectra were recorded with a Bruker AC-200 spectrometer (reference CF_3CO_2H). EPR spectra were obtained by using a Bruker ESP300E spectrometer. Elemental analyses (C, H, N) were performed at the Laboratoire de Chimie de Coordination (Toulouse, France). $B(C_6F_5)_3$ was prepared according to the literature.[18]

[$Cp_2Ti(\eta^2\text{-}F_3CC_6H_4CN)\cdot B(C_6F_5)_3$] (1): A freshly prepared toluene (3 mL) solution of $B(C_6F_5)_3$ (51 mg, 0.01 mmol) and $CF_3C_6H_4CN$ (17 mg, 0.01 mmol) was added to [$Cp_2Ti(CO)_2$] (23 mg, 0.01 mmol) in toluene (3 mL). The resulting red solution was heated to 50 °C for 12 h. Red crystals of **1** were formed at room temperature (15 mg). The filtrate was left for 2 d to give a further crop of microcrystalline **1** (35 mg). Yield: 58%. $C_{36}H_{14}BF_{18}NTi$ (861.19): calcd. C 50.21, H 1.64, N 1.63; found: C 50.3, H 1.58, N 1.61. IR: $\tilde{\nu}$ = 1725 [ν(C≡N)] cm^{-1}. ^{1}H NMR ([D$_8$]THF): δ = 6.18 (s, Cp), 7.85, 7.21 (d, $^1J_{C,H}$ = 8.3 Hz, C_6H_4) ppm. ^{11}B NMR ([D$_8$]THF): δ = −9.60 ppm. ^{13}C NMR ([D$_8$]THF): δ = 114.3 (d, $^1J_{C,H}$ = 174 Hz, Cp), 121 [br., $\Delta\nu_{1/2}$ = 190 Hz, *ipso*-C, $B(C_6F_5)$], 125.2 (q, $^1J_{C,F}$ = 253 Hz, CF_3), 126.8 (d, $^1J_{C,H}$ = 168 Hz, C_6H_4), 133.7, (d, $^1J_{C,H}$ = 164 Hz, C_6H_4), 134.2 (q, $^3J_{C,F}$ = 33 Hz, CCF_3), 136.1 (s, *ipso*-C, C_6H_4), 138.8 (d, $^1J_{C,F}$ = 253 Hz, C_6F_5), 141.3 (d, $^1J_{C,F}$ = 250 Hz, C_6F_5), 150.0 (d, $^1J_{C,F}$ = 237 Hz, C_6F_5), 225.6 (s, C=N) ppm. ^{19}F NMR (376.41 MHz, 298 K, [D$_8$]THF): δ = 13.3 (s, CF_3), −56.9 (br., 6 *o*-F, C_6F_5), −82.5 (t, 3 *p*-F, C_6F_5), −88.6 (br., 6 *m*-F, C_6F_5); (233 K): δ = 12.7 (s, CF_3), −56.8 (d, 1 *o*-F, C_6F_5), −57.2 (d, 4 *o*-F, C_6F_5), −82.2 (t, 1 *p*-F, C_6F_5), −87.5 (t, 4 *p*-F C_6F_5), −85.4 (t, 1 *m*-F, C_6F_5), −87.9 (1 *m*-F, C_6F_5), −88.5 (t, 4 *m*-F, C_6F_5), −128.1 (d, 1 *o*-F, C_6F_5) ppm.

[Cp_2Ti][$HOB(C_6F_5)_3$] (2): [$Cp_2Ti(CO)_2$] (23 mg, 0.01 mmol) in pentane (3 mL) was added to a pentane suspension of $B(C_6F_5)_3$ (51 mg, 0.01 mmol) in the presence of H_2O (or D_2O) (1.8 µmol). After leaving the resultant red solution for one week, blue crystalline **2** was obtained in 35% yield (25 mg). Another synthesis from a mixture of [$Cp_2Ti(CO)_2$] (23 mg, 0.01 mmol) and $B(C_6F_5)_3$ (51 mg, 0.01 mmol) in pentane (5 mL), passed several times through undried deoxygenated Celite and left for one week, afforded large blue crystals of **2** that were suitable for X-ray analysis. $C_{28}H_{10}BF_{15}OTi$ (706.07): calcd. C 47.63, H 1.43; found: C 47.24, H 1.33. EPR: g = 1.974, a(^{49}Ti) = 11.0 G (a single line with low intensity satellites due to the interaction of d^1 electron with ^{49}Ti and ^{47}Ti isotopes (5.51% abundant, I = 7/2 and 7.75% abundant, I = 5/2, respectively), the six inner components of the ^{49}Ti octuplet exactly superimpose on the sextuplet from ^{47}Ti). μ_{eff} = 1.76 µB. ^{1}H NMR ([D$_8$]THF): δ = 3 (br., $\Delta\nu_{1/2}$ = 36 Hz, BOH) ppm.

Crystallographic Data for 1 and 2: For structures **1** and **2** (Table 1) data were collected using a Stoe Imaging Plate Diffraction System (IPDS). The final unit cell parameters were obtained by least-squares refinement of a set of 5000 reflections, and crystal decay was monitored by measuring 200 reflections by image. No fluctuations of the intensity were observed over the course of the data collection. A semiempirical absorption correction[19] was applied to the data. The structure was solved by direct methods using SIR92[20] and refined by least-squares procedures on F^2 with the aid of SHELXL-97[21] which is included in WinGX (version 1.63).[22] The atomic scattering factors were taken from International Tables for X-ray crystallography.[23] All hydrogen atoms were located on a difference Fourier map. All the remaining non-hydrogen atoms were anisotropically refined and in the last refinement cycles a weighting scheme was used where weights were calculated from $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$. The molecules were drawn using the program ORTEP32.[24] The criteria for a satisfactory complete analysis were the ratio of rms shift to standard deviation being less than 0.1 and no significant features in final difference maps. CCDC-212614 (**1**) and -212615 (**2**) contain the supplementary crystallographic data for this paper.

Table 1. Summary of crystal data, data collection, and structure refinement parameters

	1	**2**
Empirical formula	$C_{36}H_{14}BF_{18}NTi$	$C_{28}H_{10}BF_{15}OTi$
Formula mass	861.19	706.07
Temperature [K]	160	160
Wavelength [Å]	0.71073	0.71073
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12_1$	*Cc*
a [Å]	9.106(5)	9.189(2)
b [Å]	18.720(5)	17.390(3)
c [Å]	19.499(5)	16.173(3)
β [°]	90.000(5)	97.63(3)
V [$Å^3$]	3324(2)	2561.5(9)
Z, density [g cm^{-3}]	4, 1.721	4, 1.831
F(000)	1704	1392
Absorption coefficient [mm^{-1}]	0.389	0.468
Crystal description	prismatic	prismatic
Crystal size [mm]	0.4 × 0.32 × 0.27	0.45 × 0.40 × 0.22
Collection method	rotation	rotation
2θ range for data collection [°]	3.3−52.1	3.3−52.1
No. reflections collected/unique	26272/6508 [*R*(int) = 0.0437]	6541/4260 [*R*(int) = 0.0386]
Completeness to 2θ [%]	98.4	79.8
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2
Data/restraints/parameters	6508/0/514	4260/2/416
GOF on F^2	1.026	1.046
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0314$, $wR2 = 0.0719$	$R1 = 0.0442$, $wR2 = 0.1157$
R indices (total)	$R1 = 0.0404$, $wR2 = 0.0753$	$R1 = 0.0425$, $wR2 = 0.1157$
Largest difference peak and hole [e·$Å^{-3}$]	0.255 and −0.192 e·$Å^{-3}$	0.313 and −0.286 e·$Å^{-3}$

These data can be obtained free of charge at www.ccdc.ac.uk/conts/retrieving.html [or from the Cambridge Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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