BF_3-Stabilized Metalated Sulfinylimides and Sulfurdiimides of the Type $Cp(NO)_2CrNSE·BF_3$ (E = O, $NSiMe_3$)

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Dedicated to Professor Kurt Dehnicke on the occasion of his 70th birthday

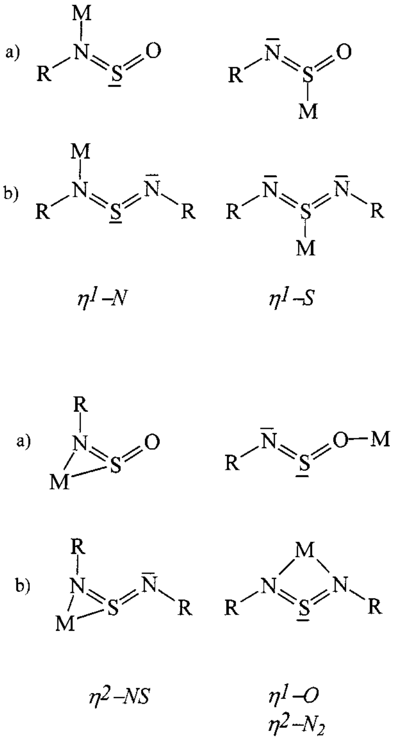
Keywords: Chromium / Metalation / Sulfur / N ligands / Lewis acids / Structure elucidation

The coordination behavior of the imido derivatives of sulfur Me_3SiNSE (E = O, $NSiMe_3$) towards the 16-electron complex $[CpCr(NO)_2]BF_4$ has been studied. In both cases coordination through an η^1-*N* linkage occurs as well as elimination of Me_3SiF to afford the metalated derivatives $Cp(NO)_2CrNSE$, which as N-nucleophiles are additionally bound to the also-formed electrophilic BF_3 molecule (**1**, **2**). Neither the possible addition products $[Cp(NO)_2Cr\{N(SiMe_3)SE\}]BF_4$ as intermediates in the synthesis of **1**, **2** nor the BF_3-free derivatives $Cp(NO)_2CrNSE$ as elimination products of **1**, **2** could be stabilized or generated. The molecular structures of **1**, **2** have been determined by single crystal X-ray analyses. Both compounds contain a distorted tetrahedrally configured chromium center and an almost planar zig-zag conformation of their sulfinyl imido (F_3BNSO) and sulfur diimido ligand ($F_3BNSNSiMe_3$), respectively.

Introduction

In contrast to SO_2 the isoelectronic molecules sulfinylimide HNSO and sulfurdiimide $S(NH)_2$ are not monomeric, are unstable and are difficult to generate and handle.[1] Thus, they more closely resemble the also isoelectronic methylenesulfine CH_2SO. The N-substituted derivatives RNSO and $S(NR)_2$, however, especially with R = aryl are easily accessible, more stable and have proven useful as synthons in organic synthesis.[2] Because of their heterocumulene structure their manifold coordination chemistry has been investigated.[3] They coordinate above all by η^2-*N*=*S*,[4,5] η^1-*S*[4a,6,7] or η^1-*N*[8,9] binding to various electrophilic complex fragments. There are two further ligand functions known. Whereas RNSO additionally undergoes the η^1-*O* linkage,[10] $S(NR)_2$ can also bind as a chelate ligand through both the N atoms (η^2-N_2;[11] see Scheme 1).

Recently we have been able to prepare some new sulfinylimide complexes of the type $CpMn(CO)_2\{S(O)NR\}$ (Cp = C_5H_5, $C_5H_4CH_3$; R = C_6H_5, $SiMe_3$) with η^1-*S* coordination.[12] In the beginning, and with respect to the silyl derivatives, our aim was to generate and stabilize the basic molecule HNSO within the coordination sphere of the transition metal by directed substitution reactions of, for example, Me_3SiX (X = OH, F, Cl). Our attempts, however, were not successful.[12] Hitherto, no HNSO complex has been structurally characterized, although some have been mentioned in the literature.[13−15] Here we report on further attempts at the synthesis of sulfinylimide (RNSO: R = $SiMe_3$, H) and, analogously, sulfurdiimide complexes [$S(NR)_2$: R = $SiMe_3$, H]. We have chosen the cation $[CpCr(NO)_2]^+$, which is isoelectronic with the neutral $CpMn(CO)_2$ used earlier[12] and which seemed to be a suitable complex fragment.



Scheme 1. The most important ligand functions of sulfinylimides (a) and sulfurdiimides (b)

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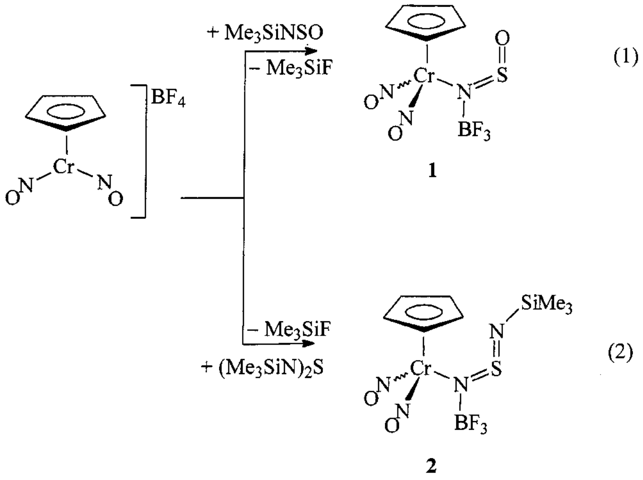
Results and Discussion

The 16-electron species $[CpCr(NO)_2]BF_4$ was generated from the chloride $CpCr(NO)_2Cl$ by dehalogenation with $AgBF_4$ and then reacted with the sulfinylimide Me_3SiNSO in CH_2Cl_2 to afford very surprisingly the neutral BF_3-containing complex $Cp(NO)_2Cr\{N(BF_3)SO\}$ (**1**) [Equation (1)]. The simultaneous elimination of Me_3SiF has been proved by ^1H NMR spectroscopy. Normally, and analogously,[12] we would have expected the formation of the addition compound $[Cp(NO)_2Cr\{N(SiMe_3)SO\}]BF_4$, although with an η^1-*N* linkage because of the strong electrophilicity of $CpCr(NO)_2^+$. The fragment $CpMn(CO)_2$ is amphoteric, has a soft center and forms an Mn−S bond to the same ligand Me_3SiNSO.[12]



The same reaction occurred when the salt $[CpCr(NO)_2]BF_4$ was reacted with the sulfurdiimide $S(NSiMe_3)_2$, and the neutral BF_3-containing product $Cp(NO)_2Cr\{N(BF_3)SNSiMe_3\}$ (**2**) was obtained [Equation (2)]. Both compounds are dark-green solids which are air stable, but sensitive towards moisture. They dissolve only moderately in $CDCl_3$ and decompose very easily in acetone. In both cases a Cr−N bond has been formed and one $SiMe_3$ group of the sulfinylimide or the sulfurdiimide has been substituted for the isolobal organometallic fragment $CpCr(NO)_2$. The reaction pathway, however, seems to be more complicated.

Despite many efforts, including the use of low reaction temperatures, we could not find any hint of the addition compound mentioned above as a possible intermediate for **1** or **2**. In separate experiments $AgBF_4$ reacts with the molecules Me_3SiNSO and $S(NSiMe_3)_2$ to eliminate Me_3SiF, although no further product could be identified or isolated. Therefore, we assume for the reaction mechanism that, after separation of AgCl, the silyl derivatives are attacked by the BF_4^- anion to give Me_3SiF and the corresponding anions NSO^- and $NSNSiMe_3^-$, respectively. These anions coordinate to the chromium center through the nucleophilic nitrogen, which has been proved previously as their preferred linkage mode.[14,16,17] The resulting metalated sulfinylimide **1** and sulfurdiimide **2** are finally stabilized by the remaining electrophile BF_3 molecule as Lewis acid−base adducts. On the other hand, BF_3 could already bind to the generated anions mentioned above. The presence of BF_4^- and BF_3 is obviously necessary. When $AgCF_3SO_3$ was used for dehalogenation of $CpCr(NO)_2Cl$ to form $[CpCr(NO)_2]CF_3SO_3$, no elimination of Me_3SiX and no coordination of the imides was observed.

The IR, ^1H, ^{11}B, $^{13}C\{^1H\}$, and ^{19}F NMR and mass spectra of compounds **1**, **2** were measured. The IR spectra of **1**, **2** exhibit two ν(NO) bands at about 1815 and 1710 cm^{-1} (in KBr). The frequency range is the same, although the frequency difference of both is less than in the starting material $CpCr(NO)_2Cl$ [IR (KBr): ν(NO) = 1824; 1707/1689 cm^{-1}]. The absorptions for ν(SO) and ν(SN) of **1** are assigned at 1245 and 1123 cm^{-1}, and ν(BF) is found at 1084 cm^{-1} as a broad unresolved absorption. Compound **2** shows two ν(SN) absorptions at 1246 and 1132 cm^{-1} and one broad ν(BF) absorption again at 1096 cm^{-1}.

In the ^1H NMR spectra of **1**, **2** the protons of the Cp ring give singlets at $\delta = 5.75$ and 5.67, respectively. The protons of the $SiMe_3$ group in **2** absorb at $\delta = 0.30$. In the $^{13}C\{^1H\}$ NMR spectrum of **2** singlets are found at $\delta = 0.9$ ($SiMe_3$) and 102 (Cp).

Due to the low solubility of **1** in $CDCl_3$, the expected quadruplet signals in both the ^{11}B and ^{19}F NMR spectra of **1** only appear as unresolved broad signals at $\delta = 0.98$ and 138.7, respectively. Compound **2**, however, dissolves better in $CDCl_3$ and does show, therefore, two quadruplets at $\delta = 1.0$ ($^1J_{BF} = 21.2$ Hz) and 139.5 ($^1J_{BF} = 18.8$ Hz). In both the spectra the broadness of the signals and the values of the chemical shifts are similar, indicating that the influence of SO (in **1**) and $NSiMe_3$ (in **2**) on the coordinating N atom seems to be identical.

No mass spectrum of **1** could be recorded; that of **2** does not show the parent signal, but fragments at $m/z = 310$, 280, 250 $[M^+ - BF_3 - nNO]$ ($n = 0-2$) and 207 $[CpCr(NO)SN_2^+]$, confirming the molecular structure.

X-ray Structure Analyses of 1 and 2

Single crystals of **1** and **2** suitable for X-ray diffraction analysis were obtained by covering their CH_2Cl_2 solutions with a layer of *n*-hexane and cooling to −20 °C. The results of the structural determinations are summarized in Table 1 and the molecular structures of **1** and **2** with the most important bonding parameters are given in Figure 1 and 2, respectively.

The analysis of **1** confirms the pseudo-tetrahedral coordination of Cr(1), the trigonal planar environment of N(3) [sum of angles at N(3) = 359.9°], the almost linear NO ligands [Cr(1)−N−O ≈ 172°] and the Cr(1)−N(3) bond length of 2.049(2) Å (η^1-*N*), indicating a typical Cr−N single bond. The bond lengths S(1)−N(3) [1.526(2) Å] and S(1)−O(3) [1.441(2) Å], typical for double bond character, are not very different to free sulfinylimides.[18] The distance N(3)−B(1) [1.662(4) Å] is also typical for borane imino adducts;[19] the B(1)−F_n bonds have an average value of 1.37 Å.

Table 1. Crystallographic data of **1** and **2**

	1	**2**
Empirical formula	$C_5H_5BCrF_3N_3O_3S$	$C_8H_{14}BCrF_3N_4O_2SSi$
Mol. wt.	306.99	378.19
Size	0.10 × 0.10 × 0.10 mm	0.30 × 0.30 × 0.10 mm
Color and habit	Green prism	Colorless prism
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
Unit cell dimensions		
a [Å]	7.8842(5)	6.5180(4)
b [Å]	10.8873(7)	13.3477(8)
c [Å]	12.1251(8)	17.772(1)
β [°]	102.613(1)	93.079(1)
V [Å]^3	1015.7(1)	1543.97
Z	4	4
$D_{calcd.}$ (g/cm^3)	2.008	1.627
Absorption coefficient [mm^1]	1.374	0.992
F(000)	608	768
Diffractometer	Siemens P4 CCD area detector	Siemens P4 CCD area detector
Radiation	Mo-K_α (λ = 0.71073 Å)	Mo-K_α (λ = 0.71073 Å)
Scan type	Hemisphere	Hemisphere
Temperature [K]	193(2)	193(2)
2θ range	5.08 to 57.62°	3.82 to 57.28°
Index ranges	$-8 \le h \le 10$	$-5 \le h \le 8$
	$-13 \le k \le 14$	$-16 \le k \le 16$
	$-15 \le l \le 15$	$-22 \le l \le 22$
Reflections collected	5722	8592
Independent reflections	1928 (R_{int} = 0.0192)	2757 (R_{int} = 0.0207)
Observed reflections	1747 [$F > 4\sigma(F)$]	2455 [$F > 4\sigma(F)$]
Absorption correction	SADABS	SADABS
Max./min. transmission	0.962/0.822	0.942/0.706
System	SHELXS−97	SHELXS−97
Solution	Direct methods	Direct methods
Refinement	Full-matrix least squares	Full−matrix least squares
Hydrogen atoms	Riding	Riding
Weighting scheme, x, y	0.05310	0.04220
	1.99650	0.93480
Data/restraints/parameters	1928/0/154	2757/0/193
Data-to-parameter-ratio	12.5:1 {11.3:1 [$F > 4\sigma(F)$]}	14.3:1 {12.7:1 [$F > 4\sigma(F)$]}
R index [$F > 4F(F)$][a]	$R1$ = 0.0361, $wR2$ = 0.0962	$R1$ = 0.0294, $wR2$ = 0.0761
R index (all data)	$R1$ = 0.0401, $wR2$ = 0.1000	$R1$ = 0.0341, $wR2$ = 0.0793
GOOF	1.020	1.057

[a] $w^{-1} = \sigma^2 F_o^2 + (xP)^2 + yP$, where $P = (F_o^2 + 2F_c^2)/3$.

The angles at Cr(1) differ significantly. The angle N(1)−Cr(1)−N(2) [90.7(1)°] is the smallest of the three Cr-containing angles, the other two are 100.0(1)° for N(1)−Cr(1)−N(3) and 96.2(1)° for N(2)−Cr(1)−N(3). The same characteristic is found for the angles of N(3). Whereas the angle Cr(1)−N(3)−B(1) is exactly 120.2(2)°, those of Cr(1)−N(3)−S(1) and S(1)−N(3)−B(1) are 123.5(1)° and 116.2(2)°, respectively. The angle N(3)−S(1)−O(3) [115.4(1)°] of **1** is smaller than the analogous angle in $[Cp(CO)_2MnS(O)NSiMe_3]$ [118.8(3)°][12] due to the free electron pair on sulfur demanding more space. The angles N(3)−B(1)−F_n ≈ 108° are almost tetrahedral, the angles F_n−B(1)−F_n average 111°. The dihedral angle defined by O−S−N−B/Cr connectivity is only 1.4° so that the electron delocalization is almost perfect.

Compound **2** possesses structural configurations and parameters very similar to those found for **1**: pseudo-tetrahedral configuration at Cr(1), trigonal planar N(3) (sum of angles at N(3) = 360°), linear NO ligands (≈ 172°) and an almost identical Cr(1)−N(3) bond of 2.043(2) Å. The double-bond containing distances S(1)−N(4) [1.505(2) Å] and S(1)−N(3) [1.546(2) Å] differ due to the different substituents on N(4) and N(3). The distance N(3)−B(1) of 1.593(3) Å is a little bit smaller than that found in **1**.

The angle between both the NO ligands in **2** is, as in **1**, the smallest [N(1)−Cr(1)−N(2) = 95.8(3)°] of the three Cr(1)-containing angles, but it does not differ so much from the others as in **1**. The angles N(1)−Cr(1)−N(3) [98.90(8)°] and N(2)−Cr(1)−N(3) [97.05(8)°] differ only slightly. The angles around N(3) behave as in **1**: the angle Cr(1)−N(3)−S(1) is again 120.5(1)°, whereas the other two are Cr(1)−N(3)−S(1) = 123.0(1)° and S(1)−N(3)−B(1) = 116.5(1)°. The angle 112.0(1)° for N(3)−S(1)−N(4) is comparable to the analogous O(3)−S(1)−N(3) of the metalated

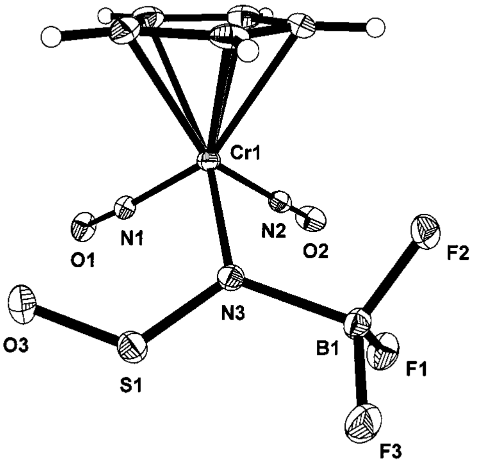


Figure 1. Molecular structure of **1**; selected bond lengths [Å] and angles [°]: Cr(1)−N(1) 1.718(3), Cr(1)−N(2) 1.720(3), Cr(1)−N(3) 2.049(2), N(3)−B(1) 1.622(4), N(3)−S(1) 1.526(2), S(1)−O(3) 1.441(2), B(1)−F$_n$ 1.37; Cr(1)−N−O 172.5, N(1)−Cr(1)−N(2) 90.7(1), N(1)−Cr(1)−N(3) 100.0(1), N(2)−Cr(1)−N(3) 96.2(1), Cr(1)−N(3)−B(1) 120.2(2), Cr(1)−N(3)−S(1) 123.5(1), B(1)−N(3)−S(1) 116.2(2), N(3)−S(1)−O(3) 115.4(1), O(3)−S(1)−N(3)−B(1) 1.4 (dihedral)

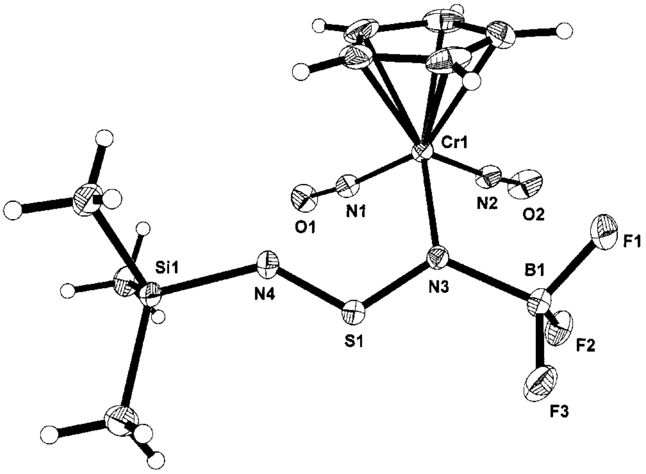


Figure 2. Molecular structure of **2**; selected bond lengths [Å] and angles [°]: Cr(1)−N(1) 1.722(2), Cr(1)−N(2) 1.708(2), Cr(1)−N(3) 2.044(2), N(3)−B(1) 1.593(3), N(3)−S(1) 1.546(2), S(1)−N(4) 1.505(2), N(4)−Si(1) 1.750(2), B(1)−F$_n$ 1.375; Cr(1)−N−O 172.3, N(1)−Cr(1)−N(2) 95.83(8), N(1)−Cr(1)−N(3) 98.90(8), N(2)−Cr(1)−N(3) 97.05(8), Cr(1)−N(3)−B(1) 120.5(1), Cr(1)−N(3)−S(1) 123.0(1), B(1)−N(3)−S(1) 4116.5(1), N(3)−S(1)−N(4) 112.0(1), S(1)−N(4)−Si(1) 130.5(1), Si(1)−N(4)−S(1)−N(3) 2.5 (dihedral)

sulfinylimide **1**, but surprisingly much smaller than that in the free ligand $S(NSiMe_3)_2$ (129.5°) which was measured, however, by electron diffraction in the gas phase.[20] The bond angles with respect to the Lewis acid−base adduct part of **2** are very similar to those in **1** [N(3)−B(1)−F$_n$ ≈ 108°; F$_n$−B(1)−F$_n$ ≈ 110°].

Experimental Section

All operations were carried out under an argon atmosphere in dry, argon-saturated solvents. $CpCr(NO)_2Cl$,[21] Me_3SiNSO[22] and $S(NSiMe_3)_2$ [23] were prepared according to literature procedures. − IR: Nicolet 520 FT-IR (KBr). − NMR: Jeol EX-400 (^{1}H: 399.784 MHz; ^{11}B: 128.3 MHz; ^{13}C: 100.5 MHz; ^{19}F: 376.1 MHz). − MS: Jeol MS 700 (EI). − X-ray: Siemens P4 CCD area detector.

{*N*-η^5-Cyclopentadienyldinitrosylchromio}sulfinylimide·Trifluoroborane (1): A solution of $CpCr(NO)_2Cl$ (0.1 g, 0.47 mmol) in CH_2Cl_2 (5 mL) was stirred with $AgBF_4$ (0.1 mg, 0.48 mmol) until AgCl precipitated. After 10 min. Me_3SiNSO (0.08 mL, 0.5 mmol) was added to the filtered solution, which was then stirred for at least 20 min. The resulting yellow-green solution was covered with a layer of *n*-hexane and cooled to −20 °C. After one week green crystals of **1** separated, which were filtered off, washed with *n*-hexane and dried in vacuum. Yield: 0.035 g (25%), m.p. 132 °C (dec.). − IR (KBr): $\tilde{\nu}$ = 3143, 3114 (C−H; Cp), 1816, 1705/1696 (N≡O), 1429, 1402 (C=C; Cp), 1298 (S=O), 1245, 1123 (S=N), 1084 (BF) cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 5.74 (s, Cp). − ^{11}B NMR ($CDCl_3$): δ = 0.98 (br. m). − ^{19}F NMR ($CDCl_3$): δ = 138.7 (br. m). − Neither a ^{13}C NMR nor an ms spectrum of **1** could be recorded due to its low solubility in $CDCl_3$ and its instability in solution. − $C_5H_5BCrF_3N_3O_3S$ (306.97): calcd. C 19.45, H 1.63, N 13.68; found C 20.10, H 2.03, N 12.78.

{*N*-η^5-Cyclopentadienyldinitrosylchromio}(*N*′-trimethylsilyl)-sulfurdiimide·Trifluoroborane (2): The dehalogenation of $CpCr(NO)_2Cl$ (0.1 g, 0.47 mmol) with $AgBF_4$ (0.1 mg, 0.48 mmol) was carried out as described above for **1**. $S(NSiMe_3)_2$ (0.12 mL, 0.48 mmol) was added to the resulting solution. After stirring for 30 min. a yellow-green solution was formed, which was layered with *n*-hexane and stored at −20 °C for crystallization. After one week green crystals of **2** separated, which were filtered off, washed with *n*-hexane and dried in vacuum. Yield: 0.05 g (40%), m.p. 160 °C (dec.). − IR (KBr): $\tilde{\nu}$ = 3118 (C−H; Cp), 2967, 2902 (C−H), $SiMe_3$), 1818, 1727/1696 (N≡O), 1432, 1417 (C=C; Cp), 1246, 1132 (S=N), 1096 (B−F) cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 5.67 (s, Cp), 0.30 (s, $SiMe_3$). − ^{11}B NMR ($CDCl_3$): δ = 1.0 (q, $^1J_{BF}$ = 21.2 Hz, BF_3). − ^{19}F NMR ($CDCl_3$): δ =139.5 (q, $^1J_{BF}$ = 18.8 Hz). − ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 102.2 (s, Cp), 0.9 (s, $SiMe_3$). − EI-MS: *m*/*z* = 310, 280, 250 [M$^+$ − BF_3 − *n*NO] (*n* = 0−2), 207 [CpCr(NO)NSNF]. Despite repeated attempts no reliable elemental analyses were obtained.

X-ray Crystallography: Single crystals were selected and mounted with perfluoroether oil on the tip of a glass fiber. For all measurements a Siemens P4 diffractometer equipped with a CCD area detector and a low-temperature device LT2 was used with Mo-K_α radiation and a graphite monochromator. Preliminary dimensions of the unit cell were calculated from a strong reflection collected on four different sets of 15 frames. Data collection was performed by the hemisphere method and the data collected on 1360 frames by changing θ by 0.3° increments at two different χ settings. The data were reduced by the program SAINT followed by absorption correction with the program SADABS. The structures were solved by direct methods (SHELXS-97). All non-hydrogen atoms are given in anisotropic description. H atoms were put in calculated positions and included in the final cycles of refinement as riding on the respective C atoms with $U_i = 1.2U_c$. Relevant crystallographic data are summarized in Table 1.

Crystallographic data (excluding structure factors) for the structure(s) included in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-148949 (**1**) and -148948 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; Email: deposit@ccdc.cam.ac.uk].

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