Formation of the Complexes $[Fe(H_2BDI)_3]X_2$ and $[CpCr(H_2BDI)_2]X_2$ (X = OTf) from the Unusual Reactions of Benzil-bis(trimethylsilyl)diimine with $CpML_2Cl$ (M = Fe, L = CO; M = Cr, L = NO)

Nadera Haque, Bernd Neumann, and Ingo-Peter Lorenz

Department of Chemistry and Biochemistry, Ludwig-Maximilians University,
Butenandtstraße 5 – 13 (Building D), 81377 Munich, Germany

Reprint requests to Prof. Dr. I.-P. Lorenz. Fax: +49 89 2180 77867. E-mail: ipl@cup.uni-muenchen.de

Z. Naturforsch. **2010**, *65b,* 101 – 106; received November 13, 2009

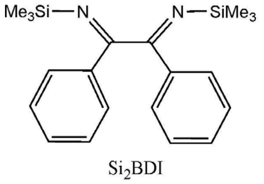
Dedicated to Professor Hubert Schmidbaur on the occasion of his 75th birthday

The reaction of $CpML_2Cl$ (M = Fe, L = CO; M = Cr, L = NO) with benzil diimine (H_2BDI) (**2**) derived from benzil-bis(trimethylsilyl)diimine (Si_2BDI) (**1**) in a 1 : 3 and 1 : 2 molar ratio in the presence of excess AgO_3SCF_3 (= AgOTf) resulted in the formation of the new cationic *tris*- and *bis*-benzildiimine complexes $[Fe(H_2BDI)_3]X_2$ (**3**) and $[CpCr(H_2BDI)_2]X_2$ (X = OTf) (**4**), respectively. The addition of AgO_3SCF_3 is necessary in both cases to abstract chloride. Unusual in the first case is the total replacement of ligands of $CpFe(CO)_2Cl$ and in the second case the oxidation of Cr(0) to Cr(III) leading to the formation of complexes **3** and **4**, respectively, with the neutral bidentate diimine ligand **2**. Complexes **3** and **4** were fully characterized by their IR, mass, ^1H- and ^{13}C-NMR spectra, as well as elemental analyses. The molecular structures determined by X-ray diffraction studies reveal a distorted octahedral tris-chelate configuration in **3** and a *pseudo*-tetragonal pyramidal one in **4**.

Key words: Benzil-bis(trimethylsilyl)diimine, Benzildiimine, Crystal Structures, Iron, Chromium

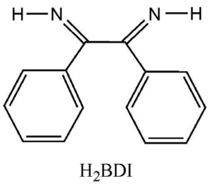
Introduction

Benzil-bis(trimethylsilyl)diimine or 1,2-bis(trimethylsilylimino)-diphenylethane (**1** = Si_2BDI, Fig. 1) was first synthesized and characterized in 1968 [1, 2]. Si_2BDI is an interesting model from the view point of the formation of heterocycles because of its two imino groups in 1,4-relationship and two very labile Me_3Si substituents in the same molecule. Some examples for the organic chemistry of Si_2BDI are given in the literature [3 – 6], but little is known about its coordination chemistry with metal complexes. The reason for this might be the almost *trans*-position of both bulky phenyl and silyl substituents to each other which has been recently derived by us from an X-ray diffraction study [7]. This configuration seems to prevent any coordination to transition metals. Therefore, Si_2BDI very easily loses its very reactive silyl groups against hydrogen in the presence of traces of moisture, especially in chlorinated solvents. This has been recently demonstrated [7] and is also proven in this paper. In the newly prepared complexes $[Fe(H_2BDI)_3]X_2$ (**3**) and $[CpCr(H_2BDI)_2]X_2$ (X = OTf) (**4**), the silyl-free diimine **2** (Fig. 1) is found to be bound to the metal atoms, although starting with the silylated diimine **1**. This is in good agreement with the known *bis*- and *tris*-chelate complexes of general formula $[M(HL)_n](ClO_4)_2$ [HL = benzildiimine, phenanthrenequinonediimine; n = 2, M = Cu; n = 3, M = Fe, Ni] and $[CoL(HL)_2](ClO_4)$ prepared from the corresponding metal salts and alcoholic solutions of the corresponding 1,2-bis(trimethylsilylimino) analog. As metal complexes containing the benzildiimine ligands **1** or **2** are hitherto unknown or relatively rare, respectively, their molecular structures remain unknown (only exception [7]). This inspired us to



Si_2BDI

1

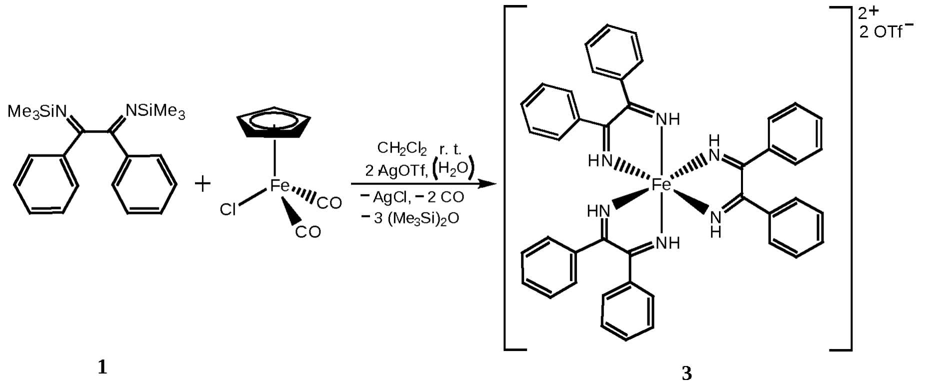


H_2BDI

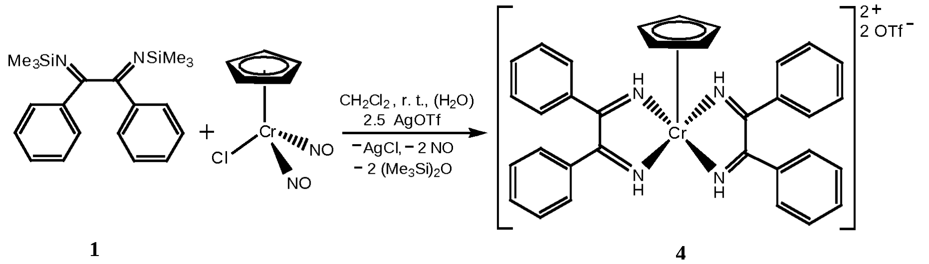
2

Fig. 1. Benzil-bis(trimethylsilyl)diimine (Si_2BDI) (**1**) and benzildiimine (H_2BDI) (**2**).

0932–0776 / 10 / 0200–0101 $ 06.00 © 2010 Verlag der Zeitschrift für Naturforschung, Tübingen · http://znaturforsch.com



Scheme 1. Synthesis of the H_2BDI complex of iron(II) **3**.



Scheme 2. Synthesis of the H_2BDI complex of chromium(III) **4**.

react CpML_2Cl (M = Fe, L = CO; M = Cr, L = NO) with **1** to give the desired complexes CpM(Si_2BDI)X or CpM(H_2BDI)X (X = Cl, OTf). Surprisingly complexes **3** and **4** have been formed instead and were characterized by their IR, mass, ^{1}H- and ^{13}C-{^{1}H}NMR spectra, elemental analyses as well as single crystal X-ray diffraction.

Results and Discussion

Treatment of CpFe(CO)$_2$Cl or CpCr(NO)$_2$Cl with **1** in 1 : 1, 1 : 3 or 1 : 2 molar ratios at r. t. did not lead to any reaction. However, after addition of excess of AgOTf (2 or 2.5 molar) to these reaction mixtures, a reaction takes place which can be monitored by IR spectroscopy (absorption bands ν(CO) (**3**) and ν(NO) (**4**)) and leads to the formation of the complexes **3** and **4** within 1 d (Schemes 1 and 2). The best yield of **3** was achieved by using the molar ratio Fe complex : **1** = 1 : 3 and at least 2 equivalents of AgOTf. In the case of chromium the molar ratio Cr complex : **1** must be at least 1 : 2 and again an excess of AgOTf has to be applied. Surprisingly and despite the mild reaction conditions, all ligands of CpFe(CO)$_2$Cl were found to be replaced, and in the case of CpCr(NO)$_2$Cl only the CpCr moiety remained intact. The metal atoms in the resulting cationic tris- and bis-chelate complexes

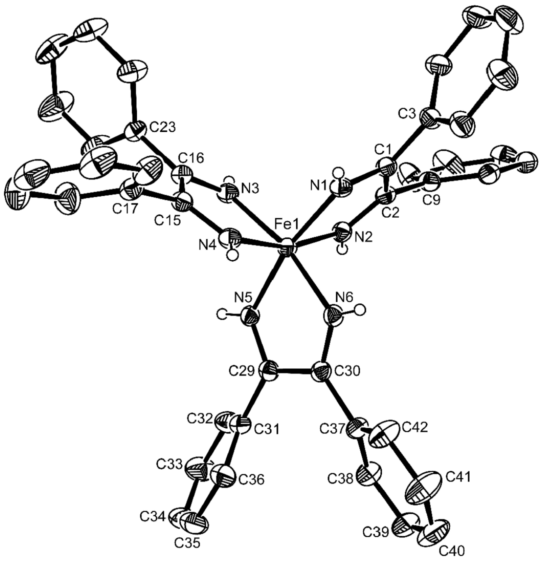


Fig. 2. Molecular structure of **3** in the crystal. The displacement ellipsoids are drawn at the 30 % probability level. C-bound hydrogen atoms and two triflate anions are omitted for clarity.

[Fe(H_2BDI)$_3$](OTf)$_2$ (**3**) and [CpCr(H_2BDI)$_2$](OTf)$_2$ (**4**) are coordinated by three and two H_2BDI ligands, respectively. It is likely that an excess of AgOTf promoted the oxidation of Cr(0) to Cr(III) and the

Table 1. Selected bond lengths (Å) and angles (deg) of **3** and **4**.

3		**4**	
Fe(1)–N(1)	1.903(2)	Cr(1)–N(2)	1.967(4)
Fe(1)–N(2)	1.927(2)	Cr(1)–N(3)	1.978(4)
Fe(1)–N(3)	1.913(2)	Cr(1)–N(1)	1.993(4)
Fe(1)–N(4)	1.912(2)	Cr(1)–N(4)	1.993(4)
Fe(1)–N(5)	1.910(2)	Cr(1)–C(1)	2.221(5)
Fe(1)–N(6)	1.909(2)	N(1)–C(6)	1.307(5)
N(1)–C(1)	1.286(3)	N(2)–C(7)	1.301(6)
N(2)–C(2)	1.288(3)	N(3)–C(20)	1.297(6)
N(3)–C(16)	1.286(3)	N(4)–C(21)	1.297(6)
N(4)–C(15)	1.292(3)	C(6)–C(7)	1.455(6)
N(5)–C(29)	1.291(3)	C(20)–C(21)	1.457(6)
N(6)–C(30)	1.288(3)	N(2)–Cr(1)–N(3)	124.6(2)
C(1)–C(2)	1.483(4)	N(1)–Cr(1)–N(4)	132.7(2)
C(15)–C(16)	1.474(3)	N(2)–Cr(1)–N(1)	74.8(2)
C(29)–C(30)	1.479(4)	N(3)–Cr(1)–N(4)	74.6(2)
N(1)–Fe(1)–N(2)[a]	78.8(1)	N(3)–Cr(1)–N(1)	84.2(2)
N(1)–Fe(1)–N(3)[b]	99.2(1)	N(2)–Cr(1)–N(4)	83.4(2)
N(1)–Fe(1)–N(5)[c]	167.6(1)		
N(6)–Fe(1)–N(2)–C(2)	−88.6(2)		
N(1)–Fe(1)–N(3)–C(16)	−86.6(2)		
N(4)–Fe(1)–N(5)–C(29)	−93.3(2)		
N(6)–Fe(1)–N(1)–C(1)	93.5(2)		

[a] Both other chelate angles: 78.4(1)°; [b] eight further corresponding angles: 89.6(1) – 99.2(1)°; [c] two further axial angles: 164.1(1) and 167.7(1)°.

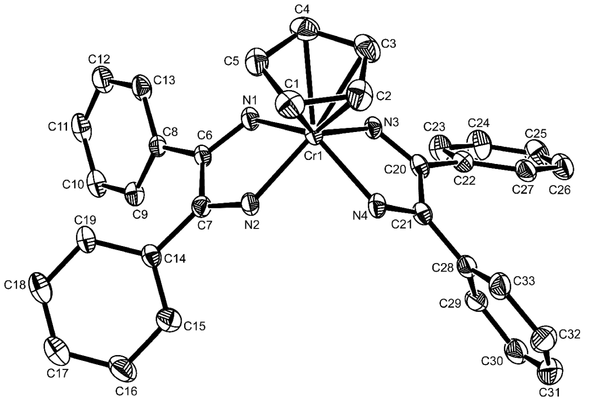


Fig. 3. Molecular structure of **4** in the crystal. The displacement ellipsoids are drawn at the 30 % probability level. Hydrogen atoms, two triflate anions and the CH_2Cl_2 solvate molecules are omitted for clarity.

reductive elimination of NO; the residue in the reaction mixture was always dark-colored. The ink-blue **3** and reddish-brown **4** are air-stable and soluble in solvents of medium polarity (CH_2Cl_2, $CHCl_3$, acetone *etc.*), but insoluble in H_2O, methanol, pentane, hexane *etc.*

Crystals of the complexes suitable for X-ray diffraction were grown by slow isothermic diffusion of *n*-pentane into their solutions in CH_2Cl_2 at r. t. within 2 d. The molecular structures of complexes **3** and **4** are shown in Figs. 2 and 3, respectively, their bond lengths and angles are given in Table 1. The Fe(II) atom in **3** is hexacoordinated by the six N atoms of three bidentate H_2BDI ligands in a rather distorted octahedral arrangement. All ligands are coordinated to Fe(II) *via* the imine N atoms forming five-membered planar metallacycles with bite angles of 78.4 – 78.8(1)°. Therefore, the remaining cisoid (89.6 – 99.2(1)°) and transoid angles N–Fe–N (164.1 – 167.7(1)°) differ from the octahedral geometry. The Fe–N bond lengths (1.903(2) – 1.927(2) Å) are almost equal but slightly shorter than reported Fe–N distances of analogous complexes like [Fe(phen)$_3$](ClO_4)$_2$ · 0.5H_2O and [Fe(dap)$_3$](PF_6)$_2$ [8, 9]. The bond lengths C–C (1.474(4) – 1.483(4) Å) and C=N (1.286(3) – 1.292(3) Å) within the three metallacycles are very similar and comparable to those of reported values [10, 11]. The last ones, however, are shorter because of their double bond character. The two phenyl substituents of each diimine ligand are slightly twisted (torsion angles *e. g.* C3–C1–C2–C9 3.4(4)°, C23–C16–C15–C17 3.2(4)°, C31–C29–C30–C37 6.3(4)°). One H_2BDI ligand plane is nearly orthogonal to both planes of the other two ligands (torsion angles: N1–Fe1–N3–C16 −86.6(2), N4–Fe1–N5–C29 −93.3(2), N6–Fe1–N1–C1 93.5(2), N6–Fe1–N2–C2 −88.6(2)°).

Compound **4** crystallizes with one molecule dichloromethane as solvate. The molecular structure shows a slightly distorted four-legged piano stool configuration at the chromium(III) atom (N2–Cr1–N4 83.4(2), N3–Cr1–N1 84.2(2), N2–Cr1–N3 124.6(2), N1–Cr1–N4 132.7(2)°). The bite angles of the two H_2BDI ligands (N2–Cr1–N1 74.8(2) and N3–Cr1–N4 74.6(2)°) are smaller than those above, but nearly equal. The four Cr–N bond lengths show very similar values between 1.967(4) and 1.993(4) Å which are somewhat longer than the Fe–N bonds in **3** (≈ 1.92 Å). The other bond lengths of the chelate ring are again very similar, but in contrast to those in **3** the C–C bonds are now shorter, and the C=N distances are longer (C–C ≈ 145.6(6) Å; C–N ≈ 1.300(6) Å). All bond lengths and angles, however, lie in the normal range of reported values [12 – 14]. The phenyl rings of each diimine ligand are again twisted to each other with torsion angles of C8–C6–C7–C14 = −1.0(5)°, and C22–C20–C21–C28 = −5.7(5)°.

The H_2BDI ligands in **3** and **4** are connected to the triflate anions by intermolecular N–H ··· O hydrogen

Table 2. Hydrogen bond parameters in **3** and **4** (Å and deg).

D–H ··· A	d(D–H)	d(H ··· A)	d(D ··· A)	<(DHA)
Compound **3**				
N(1)–H(1) ··· O_{OTf}(1)	0.77(3)	2.36(3)	3.105(3)	164(2)
N(2)–H(2) ··· O_{OTf}(4)	0.88(3)	2.42(3)	3.165(3)	143(2)
N(3)–H(3) ··· O_{OTf}(5)	0.72(3)	2.34(3)	3.024(3)	158(3)
N(5)–H(5) ··· O_{OTf}(6)	0.79(3)	2.13(3)	2.906(3)	167(3)
Compound **4**				
N(1)–H(1) ··· O_{OTf}(6)	0.88[a]	2.18[a]	3.030(5)	161.3
N(2)–H(2) ··· O_{OTf}(3)	0.88[a]	2.02[a]	2.869(4)	162.5
N(3)–H(3) ··· O_{OTf}(4)	0.88[a]	2.08[a]	2.958(4)	171.7
N(4)–H(4) ··· O_{OTf}(1)	0.88[a]	2.12[a]	2.990(4)	169.3

[a] H atom positions calculated.

bonds, involving four imine hydrogen atoms and four of the oxygen atoms of the triflates (Table 2).

In the ^{1}H-NMR spectra of **3** and **4**, a characteristic sharp signal at *ca.* 12.1 ppm is assigned to the proton resonance of the N–H group. The phenyl protons are shifted slightly upfield compared to that of the free ligand (7.80 – 7.32 ppm, **1**) and form multiplets in the range of 7.67 – 7.20 ppm. The protons of the Cp ring give a singlet at 5.79 ppm. The ^{13}C-NMR spectrum shows a downfield shift of the resonances for the C=N (178.76 (**3**), 183.10 (**4**) ppm) and an upfield shift for the phenyl C atoms (135.97 – 128.63 ppm) as compared to **1** (^{1}H: 7.80 – 7.32 ppm, ^{13}C: 174.2 ppm (CN), 138.28 – 128.14 (Ph-C) ppm, **1** recorded in CD_2Cl_2). A sharp singlet for the carbon atoms of Cp is found at 103.24 ppm. The IR spectra (in KBr) of the complexes show absorptions for the imine N–H and C–H vibrations in the range of 3224 – 2930 cm^{-1}. It has been further observed that the ν(C=N) bands at 1599 and 1579 cm^{-1} (**3**) and 1596 and 1578 cm^{-1} (**4**) are shifted to lower frequencies as compared to those of the free ligand (1652 and 1646 cm^{-1}) upon metal coordination. The absorptions for $\nu(CF_3)$ and $\nu(SO_3)$ of the OTf anions of **3** and **4** are observed in the typical range of 1259 – 1027 cm^{-1}, those for $\delta(CF_3)$ and $\delta(SO_3)$ between 766 and 516 cm^{-1} [15 – 17]. The FAB$^+$ MS of **3** showed molecular peaks at m/z = 829, 680 and 472 which are formed by gradual loss of the two triflate anions and one H_2BDI ligand. The FAB$^+$ MS of **4** also does not show the parent signal, but the signal for the cation [M–2OTf]$^+$ at m/z = 533 and one for the fragment [M–2OTf–(H_2BDI)]$^+$ at 327.

Experimental Section

General

All reactions were carried out under argon using standard Schlenk and vacuum line techniques. Solvents were purified by standard procedures; dichloromethane was distilled from calcium hydride. The complexes $[CpCr(NO)_2Cl]$ [18], $CpFe(CO)_2Cl$ [19] and Si_2BDI [1, 2] were prepared and purified according to literature procedures. Other reagents were commercially available and used without further purification. NMR spectra were measured with a Jeol Eclipse 270, a Jeol Eclipse 400 or a Jeol EX 400 spectrometer; chemical shifts are given in ppm relative to TMS. Mass spectra were recorded with a Jeol MStation JMS 700, NBA matrix (FAB$^+$). IR spectra were recorded from KBr pellets or in solutions using a Perkin-Elmer Spectrum One FT-IR spectrometer. Elemental analysis was performed by the Microanalytical Laboratory of the Department of Chemistry and Biochemistry, LMU, using a Hereaus Elementar Vario El apparatus.

*General method for the synthesis of the complexes **3** and **4***

A solution of $CpML_2Cl$ (M = Fe, L = CO; M = Cr, L = NO) in CH_2Cl_2 (10 mL) was treated with an excess of AgOTf at r. t. and stirred for 1 h until AgCl had precipitated. After centrifugation and separation of the solution by decantation, **1** was added to the solution. The mixture was stirred at r. t. for 1 d, and the solvent was removed *in vacuo*. The ink-blue (**3**) and reddish-brown (**4**) solid was washed with *n*-pentane and dried *in vacuo* for several hours.

*$[Fe(H_2BDI)_3](OTf)_2$ (**3**)*

Reagents: **1** (105.8 mg, 0.3 mmol); $CpFe(CO)_2Cl$ (21.2 mg, 0.1 mmol); AgOTf (51.3 mg, 0.2 mmol). Yield: 49.9 mg (51 %). M. p. 250 °C. – IR (KBr): ν = 3184 (m), 3064 (vw), 1599 (w), 1579 (w), 1259 (vs), 1166 (s), 1027 (vs), 765 (s), 745 (m), 699 (s), 639 (s), 594 (m), 575 (w), 533 (s), 516 (w) cm^{-1}. – MS ((+)-FAB): m/z (%) = 829 (3.8) [M–OTf]$^{2+}$, 680 (1.2) [M–2OTf]$^{2+}$, 472 (6.9) [M–2OTf–H_2BDI]$^{2+}$. – ^{1}H-NMR (399.78 MHz, CD_2Cl_2): δ = 12.12 (s, 6H, NH), 7.52 – 7.37 (m, 30H, Ph-CH). – ^{13}C-NMR (100.53 MHz, CD_2Cl_2): δ = 178.76 (s, C=N), 134.70, 131.80, 128.77, 128.72 (s, Ph-CH). – $C_{44}H_{36}F_6FeN_6O_6S_2$ (978.76): calcd. C 53.99, H 3.71, N 8.59; found C 53.97, H 3.89, N 7.91.

*$[CpCr(H_2BDI)_2](OTf)_2$ (**4**)*

Reagents: **1** (105.8 mg, 0.3 mmol); $CpCr(NO)_2Cl$ (31.8 mg, 0.15 mmol); AgOTf (96.3 mg, 0.38 mmol). Yield:

Table 3. Crystal data and details of structural refinement for complexes **4** and **5**.

	4	**5**
Empirical formula	$C_{49}H_{48}F_6FeN_6O_6S_2$	$C_{36}H_{31}Cl_2CrF_6N_4O_6S_2$
Formula weight	1050.91	916.679
Temperature, K	200(2)	293(2)
Wavelength, Å	0.71073	0.71073
Crystal size, mm^3	$0.30 \times 0.25 \times 0.19$	$0.16 \times 0.06 \times 0.02$
Crystal system	trigonal	triclinic
Space group	$R\bar{3}$	$P\bar{1}$
a, Å	27.874(4)	12.324(3)
b, Å	27.874(4	13.279(3)
c, Å	32.590(7)	14.257(3)
α, deg	90	83.17(3)
β, deg	90	67.31(3)
γ, deg	120	68.09(3)
V, $Å^3$	21929(6)	1996.3(10)
Z	18	2
$D_{calcd.}$, g cm^{-3}	1.43	1.53
μ, mm^{-1}	0.5	0.6
$F(000)$, e	9792	934
θ range, deg	3.15 to 24.00	3.18 to 24.15
Index ranges h, k, l	$-31 \rightarrow +15, +31, -37 \rightarrow +36$	$\pm 14, \pm 15, \pm 16$
Refl. coll. / indep. / R_{int}	15199 / 7620 / 0.019	11935 / 6356 / 0.025
Completeness to θ_{max}, %	99.6	99.5
Data / restr. / parameters	7620 / 0 / 610	6356 / 0 / 557
$R1/wR2$ $[I \geq 2\sigma(I)]$	0.0427 / 0.1187	0.0500 / 0.1304
$R1/wR2$ (all data)	0.0519 / 0.1265	0.0661 / 0.1399
S on F^2	1.086	1.045
$\Delta\rho_{fin}$ (max. / min.), e $Å^{-3}$	0.73 / −0.50	0.53 / −0.61

40 mg (32 %). M. p. 217 °C (decomp.). – IR (KBr): ν = 3224 (w), 3065 (w), 2930 (w), 1596 (m), 1578 (w), 1544 (w), 1449 (m), 1282 (s), 1244 (vs), 1170 (s), 1029 (vs), 766 (m), 697 (s), 637 (s), 573 (w), 516 (m) cm^{-1}. – MS ((+)-FAB): m/z (%) = 533 (0.7) $[M–2OTf]^+$, 403 (6) $[M–2OTf–C_{10}H_{10}]^+$, 327 (7) $[M–2OTf–(H_2BDI)]^+$. – ^1H-NMR (399.78 MHz, CD_2Cl_2): δ = 12.13 (s, 4H, NH), 7.67 – 7.20 (m, 20H, Ph-CH), 5.79 (s, Cp–CH). – ^{13}C-NMR (100.53 MHz, CD_2Cl_2): δ = 183.10 (s, C=N), 135.97 – 128.63 (m, Ph–CH), 103.24 (s, Cp-CH). – $C_{36}H_{31}Cl_2CrF_6N_4O_6S_2$ (916.68): calcd. C 47.16, H 3.41, N 6.11; found C 46.58, H 3.68, N 6.26.

X-Ray crystal structure determinations

Single crystal X-ray diffraction data were collected on a Nonius Kappa CCD diffractometer using graphite-monochromatized MoK_α radiation. The structures were solved by Direct Methods using the SHELXS software and refined by full-matrix least-squares on F^2 with SHELXL-97 [20]. The crystal data and details of the structure refinement are given in Table 3.

CCDC 745764 (**3**) and 745765 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgement

Financial support from the Bayerische Forschungsstiftung München (N. Haque) and Dr. Klaus-Römer-Stiftung (B. Neumann) are gratefully acknowledged.

---

[1] G. Tuchtenhagen, K. Rühlmann, *Liebigs Ann. Chem.* **1968**, *711*, 174 – 183.

[2] B. N. Diel, T. L. Hubler, W. G. Ambacher, *Heteroatom. Chem.* **1999**, *10*, 423 – 429.

[3] J. Sundermeyer, H. W. Roesky, M. Noltemeyer, *Can. J. Chem.* **1989**, *67*, 1785 – 1787.

[4] N. Weis, H. Pritzkow, W. Siebert, *Eur. J. Inorg. Chem.* **1999**, *1*, 7 – 9.

[5] I. Matsuda, T. Takahashi, Y. Ishii, *Chem. Lett.* **1977**, *12*, 1457 – 1460.

[6] R. Neidlein, D. Knecht, *Helv. Chim. Acta* **1987**, *70*, 1076 – 1078.

[7] N. Haque, B. Neumann, J. N. Roedel, I. -P. Lorenz, *Inorg. Chim. Acta* **2010**, in press.

[8] L. L. Koh, Y. Xu, L. Ji, *Acta Cryst.* **1994**, *50*, 884 – 886.

[9] S. Kammer, H. Müller, N. Grunwald, A. Bellin, A. Kelling, U. Schilde, W. Mickler, C. Dosche, H. J. Holdt, *Eur. J. Inorg. Chem.* **2006**, *8*, 1547 – 1551.

[10] A. K. Das, S. -M. Peng, S. Bhattacharya, *Polyhedron* **2001**, *20*, 327 – 335.

[11] A. M. Pyle, J. P. Rehmann, R. Meshoyrer, C. V. Kumar, N. J. Turro, J. K. Barton, *J. Am. Chem. Soc.* **1989**, *111*, 3051 – 3058.

[12] J. C. Fettinger, S. P. Mattamana, R. Poli, R. D. Rogers, *Organometallics* **1996**, *15*, 4211 – 4222.

[13] A. A. Danopoulos, G. Wilkinson, T. K. N. Sweet, M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.* **1996**, *3*, 271 – 281.

[14] V. W. L. Ng, W. K. Leong, L. L. Koh, G. K. Tan, L. Y. Goh, *J. Organomet. Chem.* **2004**, *689*, 3210 – 3217.

[15] E. L. Varetti, E. L. Fernández, A. Ben Altabef, *Spectrochim. Acta A* **1991**, *47*, 1767 – 1774.

[16] A. S. A. Khiar, R. Puteh, A. K. Arof, *Phys. Status Solidi A* **2006**, *203*, 534 – 543.

[17] C. P. Rhodes, R. Frech, *Solid States Ionics* **2000**, *136 – 137*, 1131 – 1137.

[18] P. Legzdins, J. T. Malito, *Inorg. Chem.* **1975**, *14*, 1875 – 1878.

[19] G. Brauer, *Handbuch der Präparativen Anorganischen Chemie*, 3rd ed., Vol. 3, F. Enke, Stuttgart, **1981**, pp. 1953 – 1955.

[20] G. M. Sheldrick, SHELXS/L-97, Programs for Crystal Structure Determination, University of Göttingen, Göttingen (Germany) **1997**. See also: G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467 – 473; *ibid.* **2008**, *A64*, 112 – 122.