# Synthesis of Heterobimetallic Metal Derivatives: a Carbene Complex as Chelate Ligand

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Dedicated to Professor Heinrich Nöth on the Occasion of his 75th Birthday

Abstract. The carbone complex (4-hydroxybenzoxazol-2-ylidene)pentacarbonyl tungsten (2b) has been synthesized from  $[(CO)_5W-C=N-C_6H_3(OSiMe_3)_2-2,6]$  by Si-O bond cleavage and subsequent intramolecular cyclization. Compared to 2-aminophenol the acidity of the NH/OH protons is inverted in 2b. Consequently, the stepwise monodeprotonation/methylation of 2b yields exclusively the N-alkylated complex 3. A second deprotonation/methylation gives the N- and O-alkylated complex 4. Complex 4 can be obtained directly from 2b by treatment of with two equivalents of base and two equivalents of MeI. In the presents of one equivalent of base **2b** reacts with  $[Cp_2MoCl_2]$  under formation of the heterobimetallic chelate complex  $\mu^2$ -N,O-molybdocene-4-oxobenzoxazol-2-ylidene)-pentacarbonyl tungsten **5**. Complexes **2b**, **3**, **4** and **5** were characterized by X-ray crystallography.

**Keywords:** Isocyanides; 2,6-Bis(trimethylsiloxy)phenyl isocyanide; Carbene complexes; Heterobimetallic complexes; Molybdenum; Tungsten

### Synthese von heterobimetallischen Metallderivaten: Ein Carben-Komplex als Chelat-Ligand

Inhaltsübersicht. Der Carben-Komplex (4-Hydroxybenzoxazol-2yliden)pentacarbonylwolfram (2b) wurde aus  $[(CO)_5W-C=N-C_6H_3(OSiMe_3)_2-2,6]$  durch Si-O-Bindungsspaltung und nachfolgender intramolekularer Zyklisierung erhalten. Die Acidität der NH/OH Protonen in 2b ist im Vergleich zu 2-Aminophenol invertiert. Daher führt die Monodeprotonierung/Methylierung von 2b ausschliesslich zum N-alkylierten Komplex 3. Die zweite Deprotonierung/Methylierung ergibt den N- and O-alkylierten Komplex

#### Introduction

Isocyanides which are coordinated to metal atoms in higher oxidation states may undergo nucleophilic attack at the terminal carbon atom by a variety of reagents [1-3]. In particular with protic nucleophiles, such as alcohols or primary and secondary amines, the reaction yields metal carbene complexes [4]. Whereas the addition of nucleophiles HX to coordinated isocyanides usually leads to the formation of acyclic carbene complexes, the employment of functional isocyanides, which contain both the isocyanide group and the nucleophile in the same molecule, gives access to complexes with heterocyclic carbene ligands through an intramolecular 1,2-addition across the C=N triple bond. For ex-

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Institut für Anorganische und Analytische Chemie Westfälische Wilhelms-Universität Münster Wilhelm-Klemm-Straße 8 D-41849 Münster, Germany Fax: +(49-251) 8333108 E-mail: fehahn@uni-muenster.de 4. Komplex 4 kann direkt durch Reaktion von 2 mit zwei Äquivalenten Base und zwei Äquivalenten MeI erhalten werden. In der Gegenwart von einem Equivalent Base reagiert 2 mit  $[Cp_2MoCl_2]$ unter Bildung des heterobimetallischen Chelatkomplexes  $\mu^2$ -N,O-Molybdocen-4-oxobenzoxazol-2-yliden)pentacarbonylwolfram 5. Die Komplexe 2b, 3, 4 and 5 wurden durch Röntgenbeugung an Einkristallen strukturell gesichert.

ample, *Fehlhammer* et al. have introduced readily available and stable 2-hydroxyalkyl isocyanides such as  $CNCH_2CH_2OH$ , in which the nucleophile and the isocyano group are already linked before coordination to the metal atom. If suitably activated by coordination to transition metals in higher oxidation states these ligands spontaneously cyclize to form oxazolidin-2-ylidenes [5–9] allowing even the isolation of homoleptic tetra [10] and hexacarbene complexes [11].

In  $\beta$ -functional aryl isocyanides the electrophilic isocyanide and the nucleophilic substituent are not only linked, but also suitably oriented in one plane for an intramolecular cycloaddition reaction. This arrangement together with the aromaticity of the resulting carbene ligand leads to an even greater tendency to form heterocyclic ylidenes. Si-O bond cleavage in complexes with the 2-(trimethylsiloxy)phenyl isocyanide ligand **A** gives the complex with the 2-hydroxyphenyl isocyanide ligand **B** which, depending on the electronic situation at the metal atom, exists in an equilibrium with the ylidene complex **C** (Scheme 1) [12]. We have studied the cyclization reaction **B** $\rightarrow$ **C** at various metal atoms like B [13], W [14], Cr [15], Re [16], Pd [17,18], Pt [18],



Scheme 1 Equilibrium between complexes with a 2-hydroxyphenyl isocyanide ligand (B) and a benzimidazol-2-ylidene ligand (C).

and Fe [19]. More recently, the cyclization reaction of 2aminophenyl isocyanide, leading to NH,NH substituted Nheterocyclic carbene ligands has been described [20]. In this contribution we report on the cyclization reaction of tungsten-coordinated 2,6-bis(trimethylsiloxyphenyl) isocyanide after Si-O bond cleavage to give the 4-hydroxybenzoxazol-2-ylidene ligand, on the N- and O-alkylation of this carbene ligand and on the use of the carbene complex as a chelate ligand for the ( $C_5H_5$ )Mo-moiety.

#### **Results and Discussion**

The ligand 2,6-bis(trimethylsiloxy)phenyl isocyanide was obtained as previously described [15]. It can be coordinated to the  $W(CO)_5$  complex fragment to yield the isocyanide complex 1 in good yield (Scheme 2). Cleavage of the Si-O bonds in 1 results in the formation of a product mixture composed of the isocyanide complex 2a and the carbene complex 2b. Both components of the mixture can be identified by <sup>1</sup>H NMR spectroscopy. The phenolic protons of the isocyanide complex 2a are observed at  $\delta = 5.59$ , while the ylidic NH proton in **2b** causes a resonance at  $\delta = 10.46$ (in CD<sub>2</sub>Cl<sub>2</sub>). By integration of these well separated resonances the ratio of 2a:2b was determined to be to be approximately 1:3. The analogous chromium complexes have been prepared previously [15]. Here the equilibrium between the isocyanide and the carbene complex resides on the side of the isocyanide derivative (59%) and the intramolecular cyclization reaction is more strongly hampered by  $(d \rightarrow \pi^*)$ backbonding from the chromium atom.

The main product 2b could be separated from 2a by fractional crystallization. Complex 2b was characterized by single crystal X-ray diffraction (Figure 1). The asymmetric unit contains two essentially similar molecules of 2b, two water molecules and one disordered molecule of DMSO.

The water molecules are hydrogen bonded to the NH and OH protons of the carbene ligand (Figure 1). The bonding parameters of **2b** do not differ significantly from those reported for other benzimidazol-2-ylidene complexes of type C (Scheme 1) with  $ML_x$  equals W(CO)<sub>5</sub> [14].

We reported previously than an equilibrium like the one between **2a** and **2b** can be shifted to either side by a change in the electronic properties of the metal atom [12]. Coordinated hydroxyphenyl isocyanides which do not spontaneous cyclize owing to deactivation of the isocyanide for nucleo-



Scheme 2 Synthesis of the complex mixture 2a/2b.



Figure 1 ORTEP plot of one of the two independent molecules of  $2b \cdot H_2O$  in the asymmetric unit of  $2b \cdot H_2O \cdot 0.5$  DMSO. The disordered DMSO molecule in the asymmetric and the hydrogen atoms are omitted for clarity. Selected bond lengths/Å and bond angles/° for molecule 1 [molecule 2]:

W1-C1 2.183(13) [2.172(13)], O1-C1 1.352(14) [1.354(14)], O1-C7 1.383(14) [1.383(14)], N1-C1 1.346(15) [1.347(15)], N1-C2 1.399(14)[1.372(14)], C2-C7 1.366(17), [1.366(17)], C3-O2 1.368(15) [1.374(17)], O2...O20 2.923(14) [3.122(13)], N1...O20 2.765(15) [2.857(14)], W1-C1-O1 124.5(9) [127.8(10)], W1-C1-N1 129.3(10) [127.6(11), O1-C1-N1 106.2(11) [104.6(11)].

philic attack by backbonding from the metal atom can almost always be converted into ylidenes by deprotonation of the hydroxyl group. This enhances the nucleophilicity of the oxygen atom. The N-alkylation after the cyclization prevents the reopening of the ylidene and the backreaction to the isocyanide.

Complexes of type **2b** have two acidic protons and therefore two sites for an alkylation after cyclization. The acidity for N-H and O-H protons is different and the values for 2-



Scheme 3 Regioselective methylation of 2b.

aminophenol ( $pK_{a1} = 4.74$ ,  $pK_{a2} = 9.87$  [21]) show, that the O-H protons are more acidic. However, the <sup>1</sup>H NMR spectrum indicates, that the acidity of N-H and O-H protons is inverted for **2b** ( $\delta_{OH} = 5.59$ ,  $\delta_{NH} = 10.46$ ) compared to 2-aminophenol. This assumption was confirmed by thechemical behaviour observed. Treatment of a mixture 2a/ 2b - the mixture is reestablished even if crystalline 2b is dissolved - with one equivalent of KOtBu and subsequently with one equivalent of methyliodide leads regioselectively to the N-methylated complex 3 (Scheme 3). The formation of a phenoxymethylether is not observed. In addition, the equilibrium between isocyanide and carbene (2a/ **2b**) shifts completely to the side of the carbene complex **3**. The second deprotonation/alkylation sequence gives the Omethylated complex 4. Complex 4 can also be obtained directly from the mixture 2a/2b and two equivalents base followed by treatment with two equivalents of CH<sub>3</sub>I.

The results of the X-ray structure determination of **3** and **4** are shown in Figure 2. As expected neither N- nor Oalkylation leads to a significant change of bonding parameters obtained for both carbene complexes. Form the crystal structure of **3** and **4** it becomes evident, that the intramolecular carbene formation leads to an inversion of the acidity of N-H and O-H protons compared to 2-aminophenol. The higher acidity and hence better reactivity of the N-H group in **2b** can be explained by the incorporation of the nitrogen atom in the aromatic five-membered ring. Upon deprotonation the delocalized  $\pi$ -system of the five-membered ring allows a much better stabilization of the resulting negative charge, than possible in a non-conjugated system like R-NH<sub>2</sub>.

Due to the facile deprotonation of **2b** and its similarity to 2-aminophenol regarding the arrangement of O- and Ndonors it appeared possible, to utilize the whole complex **2b** as a bidentate chelate ligand. A suitable metal ion could react with fully deprotonated **2b** under formation of a heterobimetallic metal complex, that incorporates a five-membered chelate ring. Our experiments showed that even monodeprotonated **2a/2b** reacts with one equivalent of



Figure 2 ORTEP plots of 3 and 4. Starred atoms represent positions transformed by a crystallographically mirror plane. Hydrogen atoms are omitted for clarity. Selected bond lengths/Å and bond angles/° 3:

W-C1 2.192(7), O1-C1 1.377(8), O1-C7 1.379(8), N-C1 1.333(8), N-C2 1.407(7), N-C8 1.478(8), C2-C7 1.378(9), C3-O2 1.352(9), W-C1-O1 119.1(5), W-C1-N 135.7(5), O1-C1-N 105.2(6), C1-O1-C7 109.9(5), C1-N-C2 112.5(5), C1-N-C8 124.8(6), C2-N-C8 122.7(6); 4: W-C1 2.203(4), O1-C1 1.374(5), O1-C7 1.377(5), N-C1 1.329(5), N-C2 1.405(5), N-C9 1.466(5), C2-C7 1.360(5), C3-O2 1.347(5), C8-O2 1.425(6), W-C1-O1 118.4(3), W-C1-N 135.1(3), O1-C1-N 106.5(3), C1-O1-C7 108.7(3), C1-N-C2 111.0(3), C1-N-C9 124.9(4), C2-N-C9 124.1(3), C3-O2-C8 118.0(4).



Scheme 4 Proposed mechanism for the formation of the heterobimetallic complex 5 from 2b.

 $[Cp_2MoCl_2]$  giving a heterobimetallic complex. As shown in Scheme 4 an intermediate is formed from monodeprotonated **2b** by loss of one equivalent KCl. This intermediate reacts very fast via an internal loss of HCl to form complex **5**. We were not able to isolate the intermediate. Obviously the reaction is driven by the high tendency towards chelatering formation.



Figure 3 ORTEP plot of 5 in 5 CHCl<sub>3</sub>. Hydrogen atoms are omitted for clarity. Selected bond lengths/Å and bond angles/°: W-C1 2.217(5), Mo-O2 2.136(4), Mo-N 2.179(4), O1-C1 1.413(6), O1-C2 1.374(6), N-C1 1.323(6), N-C3 1.395(6), C3-C2 1.344(7), O2-C4 1.327(6), W-C1-O1 115.1(3), W-C1-N 137.2(3), O1-C1-N 107.6(4), C1-O1-C2 108.3(4), Mo-N-C1 145.5(3), Mo-N-C3 106.8(3), C1-N-C3 107.7(4), C4-O2-Mo 113.9(3), O2-Mo-N 79.00(14).

Complex 5 was obtained after column chromatography and recrystallization from chloroform as ruby-red prisms 5. CHCl<sub>3</sub>. The crystal structure analysis of 5 (Figure 3) revealed a (CO)<sub>5</sub>W(carbene) moiety, which is virtually unchanged in comparison to those found in 3 and 4. However, the chelate ring formation leads to a severe distortion of the angles around the nitrogen atom. The carbene complexes 3 and 4 exhibit C-N-C angles within the five-membered ring of 112.5(5)° (3) and 111.0(3)° (4) and C-N-C<sub>Me</sub> angles of 122.7(6)° and 124.8(6)° for 3 and 124.1(3)° and 124.9(4)° for 4. The inner-ring C-N-C angle in complex 5 measures only 107.7(4)°. The angle C1-N-Mo is enlarged to 145.5(3)° while the angle C3-N-Mo shrinked to 106.8(3)°. This distortion is essential to accomodate the molybdenum atom in a chelating fashion. The Mo-O2 and Mo-N distances (2.136(4) Å and 2.179(4) Å) are similar in length. The angle distortion explains, why only metal ions with large ionic radii can be coordinated in a chelating fashion by 2b. Coordination of a metal ion with a smaller ionic radius as molybdenum would lead to even shorter M-O and M-N distances and to an even larger, hence structurally more disadvantageous C1-N-Mo angle. In agreement with this observation we found that 2b does not form a chelate complex with [Cp<sub>2</sub>TiCl<sub>2</sub>].

#### Experimental

All experiments were carried out in an argon atmosphere using standard Schlenk techniques. Solvents were dried by routine procedures and distilled prior to use. Correct elemental analyses were obtained for all reported compounds using a Vario EL elemental analyzer. NMR spectra were recorded at room temperature on Bruker AM 250 and Joel  $\lambda$  400 instruments. Mass spectra were measured with Finnigan MAT 112 and MAT 711 spectrometers.

IR data were obtained with a Perkin Elmer 983 spectrometer. The ligand 2,6-bis(trimethylsiloxy)phenyl isocyanide was synthesized by a described procedure [15].

#### Preparation of the mixture 2,6-dihydroxyphenylisocyanidepentacarbonyl tungsten **2a**/4-hydroxybenzoxazol-2-ylidene)pentacarbonyl tungsten **2b**

To a solution of  $[(THF)W(CO)_5]$ , obtained in an UV reactor [22] from W(CO)<sub>6</sub> (5 g, 14.2 mmol) in THF (150 mL) was added dropwise 2,6-bis(trimethylsiloxy)phenyl isocyanide (3.97 g, 14.2 mmol). The reaction mixture was stirring overnight. Removal of the solvent yielded crude complex 1, which was not further purified. The crude 1 was was taken up in methanol (50 mL) and an aliquot of KF (20 mg) was added. After stirring at room temperature for 3 d the mixture was brought to dryness and the brown residue was purified by column chromatography (Al<sub>2</sub>O<sub>3</sub>, 3 % H<sub>2</sub>O, MeOH/Et<sub>2</sub>O, 1:1, v:v) to give 3.8 g (58 %) of a mixture of **2a/2b** (1:3).

Selected data for crude 1: <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.08 (t, 1 H, Ar-H); 6.49 (d, 2 H, Ar-H); 0.32 (s, 18 H, SiCH<sub>3</sub>). IR (CCl<sub>4</sub>):  $\nu$ (NC) = 2145 cm<sup>-1</sup>.

Data for the mixture **2a/2b**: <sup>1</sup>H NMR (250 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 10.46$  (s, 1 H, N-H of **2b**); 7.16 (d, 2 H, Ar-H of **2b**); 7.05 (t, 1 H, Ar-H of **2a**); 6.74 (t, 1 H, Ar-H of **2b**); 6.48 (d, 2 H, Ar-H of **2a**), 5.59 (s, 3 H, OH of **2a/2b**). <sup>13</sup>C NMR (62.90 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 212.4$  (carbene-C of **2b**); 2018 (trans-CO of **2b**); 197.3 (d, <sup>1</sup>J(W,C) = 126 Hz, cis-CO of **2b**); 196.9 (trans-CO of **2a**), 194.4 (d, <sup>1</sup>J(W,C) = 126 Hz, cis-CO of **2a**); 154.7, 130.6, 108.6 (Ar-C of **2a**); 153.1, 141.3, 126.4, 119.6, 111.9, 104.2 (Ar-C of **2b**); both resonances Ar-C-N=C for **2a** could not be observed. **IR** (KBr):  $\nu$ (OH) 3522 cm<sup>-1</sup> **2a/2b**,  $\nu$ (NH) 3384 cm<sup>-1</sup> **2b**,  $\nu$ (NC) 2131 cm<sup>-1</sup> **2a**. MS (70 eV): m/z = 459 (M<sup>+</sup>, 9.9 %).

#### Preparation of (N-methyl-4-hydroxybenzoxazol-2ylidene)pentacarbonyl tungsten (3)

A sample of mixture 2a/2b (918 mg, 2.0 mmol) was dissolved in DMF (25 mL) at -40 °C. To this was added KOtBU (112 mg, 1.0 mmol) and the reaction mixture was allowed to warm to room temperature. After 3 h stirring at ambient temperature the mixture was treated with MeI (142 mg, 1.0 mmol) and stirred for another 3 h. The DMF was removed in vacuo. Column chromatography (Al<sub>2</sub>O<sub>3</sub> 3 % H<sub>2</sub>O, CHCl<sub>2</sub>/*n*-hexane, 1:2, v:v) yielded 3 (260 mg, 37 %). Recrystallization from CHCl<sub>3</sub> gave 3 as colorless needles.

<sup>1</sup>H NMR (400 MHz,  $D_6$ -acetone):  $\delta$  = 7.25 (t, 1 H, Ar-H); 7.19 (d, 1 H, Ar-H); 6.92 (d, 1 H, Ar-H); 4.32 (s, 3 H, NCH<sub>3</sub>); the OH resonance was not observed. IR (KBr): ν(OH) 3573 cm<sup>-1</sup>. MS (70 eV): m/z = 473 (M<sup>+</sup>, 58 %), 361 (M<sup>+</sup>-4CO, 100 %).

#### Preparation of (N-methyl-4-methoxybenzoxazol-2ylidene)pentacarbonyl tungsten (4)

The double methylation of 2a/2b to yield 4 was carried out as described for the preparation of 3 from 2a/2b using 2 equivalents (4 mmol) of base and MeI. Yield 584 mg (60 %).

<sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta = 7.27$  (t, 1 H, Ar-H); 7.17 (d, 1 H, Ar-H); 6.80 (d, 1 H, Ar-H); 4.23 (s, 3 H, NCH<sub>3</sub>); 3.99 (s, 3 H, OCH<sub>3</sub>). <sup>13</sup>C NMR (62.90 MHz,  $D_6$ -acetone):  $\delta = 212.7$  (carbene-C), 202.1 (*trans*-CO), 197.9 (*cis*-CO), 155.2, 148.0, 127.6, 122.2, 108.4, 104.4 (Ar-C), 56.9 (OCH<sub>3</sub>), 38.7 (NCH<sub>3</sub>). MS (70 eV): m/z = 487 (M<sup>+</sup>, 64 %), 375 (M<sup>+</sup>-4CO, 100 %).

## Preparation of $(\mu^2-N,O\text{-molybdocene-4-} oxobenzoxazol-2-ylidene)$ pentacarbonyl tungsten (5)

A sample of mixture **2a/2b** (918 mg, 2.0 mmol) was dissolved in DMF (20 mL) and KOtBu (225 mg, 2.0 mmol) were added at

	2b·H <sub>2</sub> O·0.5 DMSO	3	4	5·CHCl <sub>3</sub>
crystal size, mm	0.42 x 0.38 x 0.15	0.45 x 0.35 x 0.25	0.62 x 0.32 x 0.28	0.42 x 0.30 x 0.28
formula	C14H13NO8S05W	C <sub>13</sub> H <sub>7</sub> NO <sub>7</sub> W	C14HoNO7W	C23H14Cl3NM0O7W
fw, amu	516.10	473.05	487.07	802.49
a, Å	7.222(5)	9.1310(2)	6.886(2)	10.128(2)
b. Å	15.386(5)	20.536(5)	14.150(3)	10.831(3)
c, Å	16.190(5)	7.650(2)	15.909(5)	11.889(5)
α, deg	106.50(3)	90.0	90.0	82.86(3)
β, deg	91.72(4)	90.0	100.0(2)	86.28(2)
γ.deg	101.23(4)	90.0	90.0	75.65(2)
V, Å <sup>3</sup>	1685.0(14)	1434.6(5)	1526.5(7)	1252.9(7)
$d_{calc}$ , g cm <sup>-1</sup>	2.034	2.190	2.119	2.127
space group	ΡĪ	Pbcm	$P 2_1/n$	ΡĪ
Z	4	4	4	2
$\mu$ , mm <sup>-1</sup>	6.960	8.086	7.603	5.542
unique data	4377	1017	3478	3267
observed data $\{I > 2\sigma(I)\}$	2762	881	2850	3110
R1 (observed data), %	4.14,  wR1 = 7.43	2.04,  wR1 = 4.90	2.80,  wR1 = 6.06	2.27,  wR1 = 5.89
R2 (all data), %	11.34,  wR2 = 8.98	2.69, wR2 = 5.11	4.41,  wR2 = 6.49	2.50,  wR2 = 5.99
GOF (all data)	1.007	1.023	1.077	1.138
no. of variables	445	124	210	332
res. electr. dens., e/Å <sup>3</sup>	0.751 / -0.770	0.419 / -0.448	0.650 / -0.891	0.748 / -0.619

Table 1 Selected Crystal and Data Collection Details for 2b·H<sub>2</sub>O·0.5 DMSO, 3, 4 and 5·CHCl<sub>3</sub>.

-40 °C. The solution was stirred for 3 h while warming to room temperature. A solution of molybdocenedichloride (2.2 mmol in 10 mL of DMF) was added dropwise. The reaction mixture was stirred for 16 h at room temperature and then brought to dryness. Column chromatography (SiO<sub>2</sub>, MeOH) yielded **5** (600 mg, 44 %) as a brown solid. Recrystallization from chloroform gave ruby-red crystals of **5**·CHCl<sub>3</sub>.

<sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  =6.86 (t, 1 H, Ar-H); 6.59 (d, 1 H, Ar-H); 6.26(d, 1 H, Ar-H); 5.64 (s, 10 H, C<sub>5</sub>H<sub>5</sub>). MS (70 eV): m/z = 683 (M<sup>+</sup>, 3.2 %).

#### Crystal structure determinations

Suitable crystals were selected and mounted on a CAD-4 diffractometer equipped with a sealed Mo X-ray tube ( $\lambda = 0.71073$  Å) and a scintillation detector. Diffraction was measured at room temperature in a 2  $\Theta$  range from 2 to 55°. An empirical absorption correction ( $\psi$ -scans) was applied on all data sets. The structures were solved and refined by standard Patterson- and Fourier-techniques [23]. All non hydrogen atoms were refined with anisotropic thermal parameters, hydrogen atoms reside on calculated positions. **2b** crystallizes with two independent molecules, 2 water molecules and one disordered DMSO molecule in the asymmetric unit. Crystals of **5** contain one molecule of CHCl<sub>3</sub> per formula unit. Selected crystal, data collection and refinement details are summarized in Table 1. ORTEP [24] was used for the generation of molecular plots. Thermal ellipsoids represent a 50 % probability level.

**Supplementary Material.** Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplemental publication CCDC-205511 for **2b**, CCDC-205512 for **3**, CCDC-205513 for **4**, and CCDC-205514 for **5**. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code+(1223)336-033; e-mail for inquiry: filserv@ccdc.cam.ac.uk.

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