Structural Characterization of Bismuth(III) and Antimony(III) Chlorotriflates: Key Intermediates in Catalytic Friedel−Crafts Transformations

Stéphane Mazières,*[a] Christophe Le Roux,*[a] Magali Peyronneau,[a] Heinz Gornitzka,[a] and Nicolas Roques[b]

Keywords: Bismuth / Antimony / Triflate / X-ray diffraction / Friedel−Crafts reactions

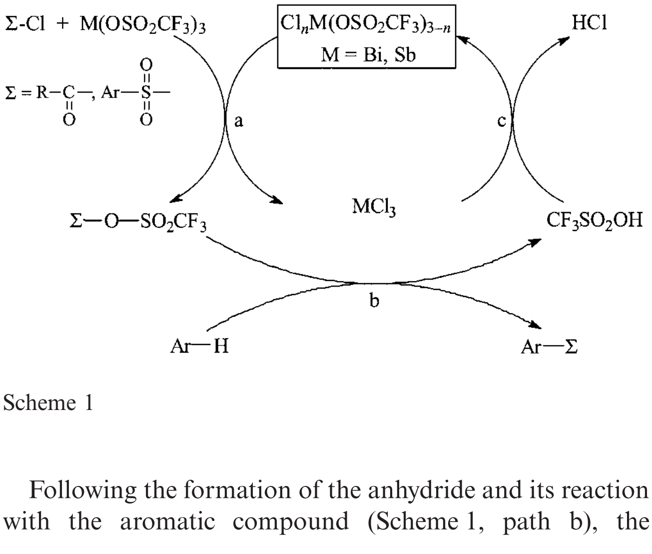
Chlorotriflates of antimony and bismuth $Cl_nM(OSO_2CF_3)_{3-n}$ (n = 1 or 2) are believed to be metallic intermediates of major importance in Friedel–Crafts reactions that use $Bi(OSO_2CF_3)_3$, $Sb(OSO_2CF_3)_3$, the systems $BiCl_3/CF_3SO_2OH$ or $SbCl_3/CF_3SO_2OH$ as catalysts. Unknown until now, the compounds $ClBi(OSO_2CF_3)_2$ (**1**) and $Cl_2Sb(OSO_2CF_3)$ (**2**) have been synthesized by reaction of MCl_3 (M = Bi, Sb) with triflic acid. After crystallization from THF, **1** and **2** were investigated in the solid state by X-ray crystallography. Their use as catalysts in benzoylation of toluene, acylation of *m*-xylene, and sulfonylation of toluene led to conclusive results, thus giving weight to their key role as intermediates in Friedel–Crafts reactions.
(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2004)

Introduction

The number of bismuth compounds structurally characterized by X-ray crystallographic methods has greatly increased over the past decades, showing the growing interest in these structures.[1] For our topic, we will focus on Bi^{III} and also Sb^{III} halides, which are found to be useful in a number of applications;[2] of major interest is the use of bismuth or antimony derivatives in catalysis. For Friedel−Crafts acylations, reactions which are mainly developed on an industrial scale using at least a stoichiometric amount of a Lewis acid such as $AlCl_3$ or $TiCl_4$,[3] $BiCl_3$ and recently bismuth(III) trifluoromethanesulfonate (triflate) appeared to be among the best catalysts for the acylation of aromatic compounds.[4−6] In 1988, Olah had already showed the catalytic activity of boron(III), aluminium(III) and gallium(III) triflates in alkylation and acylation reactions with 50mol % metallic triflates.[7] Later various metallic salts of triflic acid such as rare earth[8−11] and antimony(III) triflates[12,13] were reported. The catalytic efficiency of bismuth(III) triflate was confirmed, especially in the sulfonylation of arenes,[14] a reaction that belongs to the most important group of aromatic electrophilic substitutions.[3,4] In the present work we describe the preparation of mixed chlorotriflates of bismuth and antimony, which are involved in the process of acylation and sulfonylation of aromatic compounds that use Bi^{III} and Sb^{III} triflate based catalysts, and their direct use as catalysts in these reactions.

Results and Discussion

In the mechanism for both acylation and sulfonylation reactions,[6,8−13] it clearly appears that the main electrophilic agent is a mixed anhydride such as trifluoromethanesulfonic carboxylic- or trifluoromethanesulfonic arenesulfonic anhydrides ($RCO-O-SO_2CF_3$ or $ArSO_2-O-SO_2CF_3$), which are known to be strong acylating or sulfonylating reagents.[15] The formation of mixed anhydrides results from ligand exchanges at the metal (Scheme 1, path a).



Scheme 1

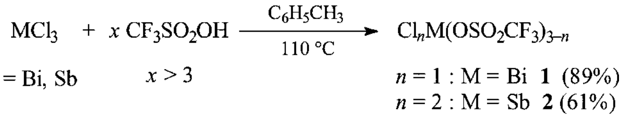
Following the formation of the anhydride and its reaction with the aromatic compound (Scheme 1, path b), the

---

[a] Laboratoire Hétérochimie Fondamentale et Appliquée, UMR 5069,
118 route de Narbonne, 31062 Toulouse Cedex 04, France
Fax: (internat.) +33-5-61-558204
E-mail: mazieres@chimie.ups-tlse.fr
[b] Rhodia Organique Fine, Centre de Recherche de Lyon,
85 rue des frères Perret, 69192 Saint-Fons, France

DOI: 10.1002/ejic.200400281

mechanism involves the reaction of the metal(III) chloride with triflic acid (CF_3SO_2OH), leading to the mixed metallic intermediate (Scheme 1, path c). The metal acts as a shuttle for the triflic acid. Such types of mixed compounds have been previously related with fluorosulfonic acid and result from the reaction of $BiCl_3$ and fluorosulfonic acid; however, they have been poorly characterized.[16] In fact, it appears that these metallic intermediates play a key role with regard to the entire mechanism. Until now their existence was postulated,[8–13] but no real proof was given for their exact structure. One goal was to isolate such mixed metallic chlorotriflates. The reaction between the metal(III) chloride and an excess of triflic acid did not lead to metal tristriflate[17] but to compounds **1** and **2** in appreciable yields (Scheme 2).



$$\underset{M = Bi,\ Sb}{MCl_3} + \underset{x > 3}{x\ CF_3SO_2OH} \xrightarrow[110\ °C]{C_6H_5CH_3} Cl_nM(OSO_2CF_3)_{3-n}$$

$n = 1$: M = Bi **1** (89%)
$n = 2$: M = Sb **2** (61%)

Scheme 2

With bismuth, the only product is the chlorobistriflate **1**, while antimony leads exclusively to the dichlorotriflate **2**. It appears that the trifluoromethanesulfonate ligand exhibits a strong electronic effect, which modifies the strength of the remaining M−Cl bonds. Only one ligand exchange occurred with antimony, while two with bismuth. **1** is stable up to 250 °C,[18] and this thermostability can indicate the strength of the bonds involved.

In the synthesis of these compounds, the use of toluene as solvent proved to be crucial; while $BiCl_3$ is mainly soluble in π-donor solvents, the solvation of $SbCl_3$ with donor solvents can be greatly compromised by strong complexation, which inhibits further reactivity. Indeed, these complexes known as Mentshutkin complexes[19,20] are responsible for the inefficiency of $SbCl_3$ in the catalysis of Friedel- Crafts reactions of activated aromatics.[21] Compounds **1** and **2** are crystalline, and their THF adducts were obtained from a THF/pentane solution. Single crystals suitable for an X-ray structure determination were grown at −20 °C.

The structure analysis of the THF complexes in the solid state shows a monomeric form in the case of the bismuth compound and a dimeric form for the antimony compound (Figure 1 and Figure 2). In both compounds, primary M−Cl bonds (Bi−Cl1 2.465 Å and Sb−Cl1 2.362 Å, Sb−Cl2 2.363 Å) appear shorter than M−Cl bond lengths in MCl_3 or MCl_3 with oxygen donor interactions;[22] this is in accordance with the observed stability of these M−Cl bonds. For the THF adduct of **1**, the chlorine atom, in good approximation, occupies the axial position of a distorted pentagonal bipyramid (Figure 1).

The two triflate ligands are connected to the bismuth atom through oxygen atoms, Bi−O1 2.386 Å and Bi−O4 2.613 Å, the latter bond length is longer, probably due to another weak interaction (Bi−O5 2.879 Å) which destroys the ideal geometry of the bipyramid.

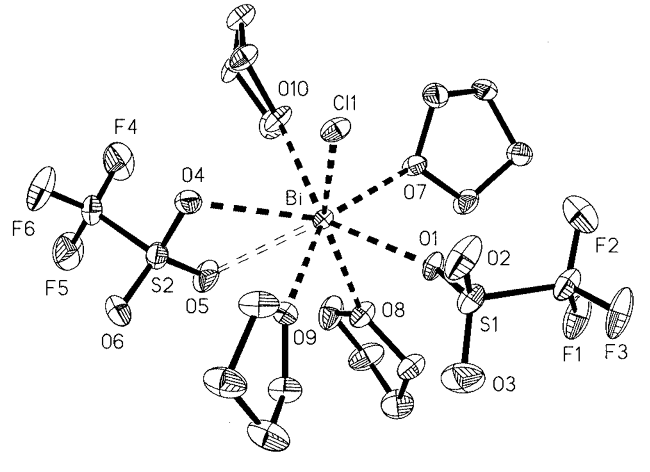


Figure 1. Molecular structure of **1**·4THF in the solid state; selected distances (Å) and angles (°): Bi−Cl1 2.465(4), Bi−O1 2.386(11), Bi−O4 2.613(13), Bi−O5 2.879(15), Cl1−Bi−O8 156.4(3), Cl1−Bi−O4 80.4(3), Cl1−Bi−O5 131.2(3)

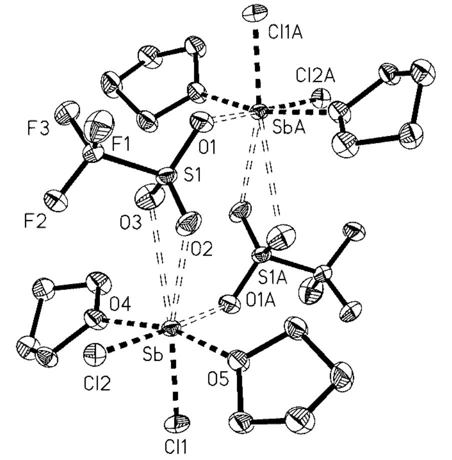


Figure 2. Molecular structure of **2**·2THF in the solid state; selected distances (Å) and angles (°): Sb−Cl1 3.3628(8), Sb−Cl2 2.3629(8), Sb−O1A 2.876(3), Sb−O2 2.911(3), Sb−O3 3.084(3), Cl1−Sb−Cl2 92.75(3), Cl1−Sb−O1A 82.57(5), Cl1−Sb−O2 158.83(5), Cl1−Sb−O3 153.55(5)

The structure of the THF adduct of **2** may be best described as a distorted octahedron in which one SO_2 group occupies an axial position (Figure 2). This structure is associated into dimeric units through two weak coordinations by two triflate ligands of different units thereby bridging the two Sb centers. The antimony atoms are thus seven-coordinate.

These newly synthesized and fully characterized mixed chlorotriflates are believed to be the mixed metallic intermediates involved in the mechanism, but nothing is known about the real mixture in solution during the process. By changing the stoichiometry of the reactants, triflic acid and metal chloride, it was not possible to isolate or even characterize $Cl_2Bi(OSO_2CF_3)$ or $ClSb(OSO_2CF_3)_2$ in solution; this is probably due to their lack of stability. In both cases we only obtained products **1** and **2**.

Finally, experiments were performed in which **1** and **2** were used as catalysts in benzoylation, acylation and sulfon-

Table 1. Catalytic activity of **1** and **2** in benzoylation, acylation and sulfonylation reactions

Entry	Reaction	Catalyst	Mol (%)	Yield (%)	*o*/*m*/*p*
1	benzoylation of toluene	$Bi(OSO_2CF_3)_3$	10	95[6]	22/2/76
2		**1**	10	60	21/2/77
3	acylation of *m*-xylene	$Sb(OSO_2CF_3)_3$	10	77[13]	
4		**2**	30	74	
5	sulfonylation of toluene	**1**	5	99	39/6/55
6		$BiCl_3/CF_3SO_2OH$	5/10	95[23]	39/6/55
7		**2**	5	99	40/6/54
8		$SbCl_3/CF_3SO_2OH$	5/5	99	38/6/56

ylation of aromatic compounds (Table 1). In these catalytic systems, the ratio of triflate ligand, which leads to the mixed anhydride (Scheme 1, path a) is the main factor that influences the efficiency of the catalytic process.

For the benzoylation of toluene (Table 1, entries 1 and 2), the use of $ClBi(OSO_2CF_3)_2$ **1** at 10 mol % led to 60% yield, and gave a similar result to that obtained with $Bi(OSO_2CF_3)_3$.[6] The yield for **1** is lower, but **1** only has two triflate ligands instead of three as is the case for $Bi(OSO_2CF_3)_3$.

$Cl_2Sb(OSO_2CF_3)$ **2** provided identical results (74% yield) for the acylation of *m*-xylene (Table 1, entries 3 and 4) with *n*-pentCOCl to that obtained by the catalytic system described by Kobayashi.[13] For the sulfonylation of toluene (Table 1, entries 5 to 8), where the mixed species play a key role, a 99% yield of tolylphenylsulfones was obtained with **1** [similar to that obtained by the catalytic system $BiCl_3/CF_3SO_2OH$ (5 mol %/10 mol %)],[23] and a 99% yield was also obtained with **2** [the same as that obtained by the catalytic system $SbCl_3/CF_3SO_2OH$ (5 mol %/5 mol %)]. In addition, all the selectivities proved to be similar.

With regard to the yields and the selectivities, the results for the catalytic activity of **1** and **2** are conclusive, and these mixed metallic chlorotriflates are strongly believed to be the key intermediates in these Friedel−Crafts reactions.

Experimental Section

Syntheses of **1** and **2** were performed under a dry and oxygen-free argon atmosphere. Solvents were dried by appropriate methods. Melting points were determined in capillaries sealed under argon and are uncorrected.

$ClBi(OSO_2CF_3)_2$ (1): Triflic acid (10.5 g, 70.0 mmol) was added dropwise at 0 °C to a solution of bismuth(III) chloride (9.1 g, 28.9 mmol) in toluene (60 mL). The reaction mixture was then stirred for 10 min at room temperature and heated to 110 °C for 90 min. After cooling, the mixture was filtered, and the residue was washed twice with dichloromethane (100 mL). Solvents were removed in vacuo, and **1** was obtained as a white powder (14.0 g, 89% yield) and was recrystallized from a THF/pentane solution at −20 °C. M.p. >250 °C. ^{13}C NMR (100.6 MHz, [D$_6$]DMSO, TMS): $\delta = 125.9$ (q, $^1J_{C,F} = 322$ Hz) ppm. ^{19}F NMR (376.4 MHz, CD_3CN, CF_3COOH): $\delta = 0.9$ ppm. IR (CH_3CN): $\tilde{\nu} = 635, 585, 515$ (S−O in OSO_2CF_3), 310 (Bi−Cl) cm^{-1}. RAMAN: $\tilde{\nu} = 307$ (Bi−Cl) cm^{-1}. MS (DCI/CH_4): *m/z* = 543 (4) $[MH]^+$, 507 (5) $[M - Cl]^+$, 393 (8) $[M-Cl-OSO_2CF_3]^+$. $C_2BiClF_6O_6S_2$ (542.57): calcd. C 4.43, Cl 6.53, F 21.01, S 11.82; found C 4.43, Cl 6.05, F 21.09, S 11.87.

$Cl_2Sb(OSO_2CF_3)$ (2): The same procedure was used as for **1**, and the reaction mixture was heated at 110 °C for 5 h. **2** (4.6 g, 61% yield) was recrystallized from a THF/pentane solution at −20 °C. M.p. 61 °C(decomp.). ^{13}C NMR (100.6 MHz, [D$_6$]DMSO, TMS): $\delta = 120.5$ (q, $^1J_{C,F} = 322$ Hz) ppm. ^{19}F NMR (376.4 MHz, [D$_6$]DMSO, CF_3COOH): $\delta = 1.5$ ppm. IR (CH_3CN): $\tilde{\nu} = 588, 515$ (S−O in OSO_2CF_3), 353 (Sb−Cl) cm^{-1}. RAMAN: $\tilde{\nu} = 356$ (Sb−Cl) cm^{-1}. MS (DCI/CH_4): *m/z* = 343 (16) $[MH]^+$, 193 (19) $[M - OSO_2CF_3]^+$. It was not possible to obtain satisfactory elemental data.

Benzoylation of Toluene: PhCOCl (1.97 g, 14 mmol), toluene (2.58 g, 28 mmol), and catalyst (14 mmol) were added together in a 20 mL flask. After 5 h at 110 °C, dichloromethane (20 mL) was added, and the organic layer was extracted with a 6% aqueous HCl (2 × 10 mL), dried ($MgSO_4$), and concentrated. After purification by flash chromatography (silica, pentane/ether, 9:1), methylbenzophenones were isolated. The use of 10 mol % of $Bi(OSO_2CF_3)_3$ led to 95% yield (*o*/*m*/*p*, 22/2/76)[6] and 10 mol % of **1** led to 60% yield (*o*/*m*/*p*, 21/2/77).

Acylation of *m*-Xylene: Following the procedure described by Kobayashi,[13] *n*-pentCOCl (0.20 g, 1.49 mmol), *m*-xylene (4.69 g, 44.2 mmol), and $Sb(OSO_2CF_3)_3$ (83 mg, 1.46 mmol) were added together, and the mixture was heated at 100 °C. After 24 hours, 1-(2,4-dimethylphenyl)hexan-1-one was obtained in 77% yield. With the same procedure, the use of 30 mol % of **2** led to 74% yield.

Sulfonylation of Toluene: (a) **1** as the catalyst: following the procedure described in ref. 23, 99% yield (*o*/*m*/*p*, 39/6/55) was obtained using 5 mol % of **1**, the system $BiCl_3/CF_3SO_2OH$ (5 mol %/10 mol %) provided 95% yield (*o*/*m*/*p*, 39/6/55). (b) **2** as the catalyst: following the typical procedure, $PhSO_2Cl$ (3.25 g, 18.4 mmol), toluene (3.39 g, 36.8 mmol) and catalyst (5 mol %, 0.92 mmol) were heated at 110 °C for 12 hours. Dichloromethane (40 mL) was then added, and the organic layer was extracted with aqueous HCl (40 mL of a 2 N solution), neutralized by saturated $NaHCO_3$ solution (40 mL), and analyzed by GC with tetradecane as external standard.

X-ray Structure Determination for the THF Adducts of 1 and 2: Crystal data were collected at low temperatures [$T = 193(2)$ K] using an oil-coated shock-cooled crystal on a Bruker-AXS CCD 1000 diffractometer with Mo-K_α radiation ($\lambda = 0.71073$ Å). Semiempirical absorption corrections were employed.[24] The structures were solved by direct methods (SHELXS-97)[25] and refined using the least-squares method on F^2.[26] Experimental details are given in Table 2.

Table 2. Crystal Data for **1**·4THF and **2**·2THF

	1·4THF	**2**·2THF
Empirical formula	$C_{18}H_{32}BiClF_6O_{10}S_2$	$C_9H_{16}Cl_2F_3O_5SSb$
Molecular mass	830.99	485.93
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	17.018(2)	8.299(2)
b (Å)	18.394(2)	9.515(2)
c (Å)	8.960(1)	11.395(2)
α (°)		105.791(2)
β (°)	93.232(2)	96.575(2)
γ (°)		106.136(2)
V (Å^3)	2800.3(5)	814.0(3)
Z	4	2
Abs. coeff. (mm^{-1})	6.626	2.196
Crystal size (mm)	0.1 × 0.2 × 0.6	0.3 × 0.5 × 0.6
Max. and min. transmission	0.377188	0.702541
Reflections collected	24516	7073
Independent reflections	3985	4060
R_{int}	0.0870	0.0269
No. of parameters	343	190
$R1$ [$I > 2\sigma(I)$]	0.0646	0.0330
$wR2$ (all data)	0.1631	0.0906
Largest diff. peak (e Å^{-1})	4.498	2.098
CCDC	199266	199267

CCDC-199266 (for **1**·4THF) and -199267 (for **2**·2THF) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

We gratefully acknowledge the Centre National de la Recherche Scientifique (CNRS) and Rhodia Organique Fine for support of this work.

---

[1] C. Silverstru, H. J. Breunig, H. Althaus, *Chem. Rev.* **1999**, *99*, 3277−3327.

[2] [2a] M. N. Leonard, L. C. Wieland, R. S. Mohan, *Tetrahedron* **2002**, *58*, 8373−8397. [2b] N. C. Norman in *Chemistry of Arsenic, Antimony and Bismuth*, Blackie Academic and Professional, London, **1998**. [2c] H. Suzuki, Y. Matano, *Organobismuth Chemistry*, Elsevier, Amsterdam, **2001**.

[3] Reviews about the FC acylation and sulfonylation: [3a] G. A. Olah, *Friedel−Crafts and Related Reactions*, John Wiley & Sons, New York, **1963−1965**, vol. 1−4. [3b]S. B. Mahato, *J. Indian Chem. Soc.* **2000**, *77*, 175−191.

[4] C. Le Roux, J. Dubac, *Synlett* **2002**, 181−200.

[5] J. R. Desmurs, M. Labrouillère, H. Gaspard, A. Laporterie, J. Dubac, *Tetrahedron Lett.* **1997**, *38*, 8871−8874.

[6] S. Répichet, C. Le Roux, J. Dubac, J. R. Desmurs, *Eur. J. Org. Chem.* **1998**, 2743−2746.

[7] G. A. Olah, O. Farook, S. Morteza, F. Farnia, J. A. Olah, *J. Am. Chem. Soc.* **1988**, *110*, 2560−2565.

[8] A. Kawada, S. Mitamura, S. Kobayashi, *J. Chem. Soc., Chem. Commun.* **1993**, 1157−1158.

[9] S. Kobayashi, S. Iwamoto, *Tetrahedron Lett.* **1998**, *39*, 4697−4700.

[10] J. Matsuo, K. Odashima, S. Kobayashi, *Synlett* **2000**, *3*, 403−405.

[11] C. J. Chapman, C. G. Frost, J. P. Hartley, A. J. Whittle, *Tetrahedron Lett.* **2001**, *42*, 773−775.

[12] S. Kobayashi, I. Komoto, *Tetrahedron* **2000**, *56*, 6463−6565.

[13] O. Kobayashi, I. Kawamoto, (Sumitomo Chemical) Jpn. Kokai Tokkyo Koho JP 2001 294.548 (Jp. Appl. 2000/31, 800, 09 Feb. 2000) (*Chem. Abstr.* **2001**, *135*, 30367v).

[14] S. Répichet, C. Le Roux, P. Hernandez, J. Dubac, *J. Org. Chem.* **1999**, *64*, 6479−6482.

[15] [15a] F. Effenberger, G. Epple, *Angew. Chem.* **1972**, *84*, 294−295; *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 299−300. [15b] F. Effenberger, K. Huthmacher, *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 409−410. [15c] F. Effenberger, K. Huthmacher, *Chem. Ber.* **1976**, *109*, 2315−2326.

[16] R. C. Paul, S. Singh, R. C. Kumar, R. D. Sharma, R. D. Verma, *Ind. J. Chem.* **1979**, 273−275.

[17] Preparation of $M(OSO_2CF_3)_3$ (M = Bi or Sb) is known from $M(C_6H_5)_3$ [12,17a] or from the corresponding oxide. [17a] M. Labrouillère, C. Le Roux, H. Gaspard, A. Laporterie, J. Dubac, J.-R. Desmurs, *Tetrahedron Lett.* **1999**, *40*, 285−286. [17b] S. Répichet, A. Zwick, L. Vendier, C. Le Roux, J. Dubac, *Tetrahedron Lett.* **2002**, *43*, 993−995.

[18] DSC analyses have been performed on compound **1**, and no significant decomposition occurred until 250 °C.

[19] H. Schmidbaur, R. Nowak, B. Huber, G. Müller, *Organometallics* **1987**, *6*, 2266−2267 and references cited therein.

[20] See for historical interest, B. Mentshutkin, *Chem. Zentr.* **1910**, *3*, 378−383.

[21] B. Mentshutkin, *Chem. Zentr.* **1912**, *4*, 1436−1439.

[22] [22a] For examples see: J. R. Eveland, K. H. Whitmire, *Inorg. Chim. Acta* **1996**, *249*, 41−46. [22b] E. Hough, D. G. Nicholson, A. K. Vasudevan, *J. Chem. Soc., Dalton Trans.* **1987**, 427−430. [22c] G. R. Wiley, D. R. Aris, W. Errington, *Inorg. Chim. Acta* **2000**, *300*, 1004−1013.

[23] S. Répichet, C. Le Roux, J. Dubac, *Tetrahedron Lett.* **1999**, *40*, 9233−9234.

[24] *SADABS, Program for Absorption Correction*, Bruker AXS.

[25] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467−473.

[26] *SHELXL-97, Program for Crystal Structure Refinement*, G. M. Sheldrick, University of Göttingen, Germany, **1997**.

Received April 5, 2004