Silicon—nitrogen bond cleavage in *N*-(dimethylimidosilylmethyl)imides and dimethyl(lactamomethyl)aminosilanes with BF_3 etherate as an alternative route to *N*-(dimethylfluorosilylmethyl)imides and related compounds

A. G. Shipov,[a] E. P. Kramarova,[a] T. P. Murasheva,[a] O. B. Artamkina,[a] Vad. V. Negrebetskii,[a] Yu. I. Baukov,[a] S. A. Pogozhikh,[b] Yu. E. Ovchinnikov,[b] M. G. Voronkov,[c] A. R. Bassindale,[d] and P. G. Taylor[d]*

[a]*Russian State Medical University*
1 ul. Ostrovityanova, 117997 Moscow, Russian Federation.
Fax: +7 (495) 434 0329. E-mail: baukov.rgmu@mtu-net.ru
[b]*Novosibirsk State Pedagogical University,*
28 ul. Vilyuiskaya, 630126 Novosibirsk, Russian Federation.
E-mail: ovchin@hotmail.ru
[c]*A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences,*
1 ul. Favorskogo, 664033 Irkutsk, Russian Federation.
E-mail: voronkov@irioch.irk.ru
[d]*Chemistry Department, Open University, Walton Hall, Milton Keynes, MK7 6AA UK.*
E-mail: a.bassindale@open.ac.uk

N-(Dimethylfluorosilylmethyl)succinimide (**2a**) and *N*-(dimethylfluorosilylmethyl)phthalimide (**2b**) were synthesized by the Si—N bond cleavage in readily accessible *N*-(dimethylimidosilylmethyl)imides with BF_3 etherate. Analogously, (O→Si)-chelated 1-(dimethylfluorosilylmethyl)-2-pyrrolidone was prepared from 1-(dimethylmorpholinosilylmethyl)-2-pyrrolidone. X-ray diffraction study demonstrated that the silicon atom in the crystals of **2b** is pentacoordinated.

Key words: boron trifluoride etherate, Si—N bond cleavage, pentacoordinate silicon compounds, intramolecular coordination, X-ray diffraction study.

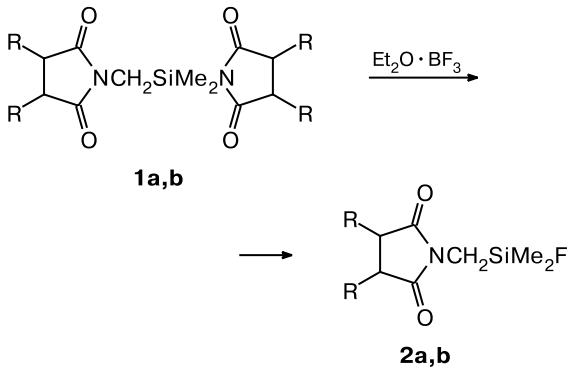
The influence of the structure of the amidomethyl and lactamomethyl ligands and the nature of substituents at the silicon atom on the degree of intramolecular O→Si coordination as well as on the reactivity and stereochemical nonrigidity of *N*-(silylmethyl)amides and *N*-(silylmethyl)lactams has been studied in detail.[1—3] By contrast, their analogs, for example, *N*-(halodimethylsilylmethyl)imides, have received less attention (see, for example, Refs 4—6 and references therein). Nevertheless, these studies revealed substantial differences in the structure and chemical behavior of *N*-(dimethylchlorosilylmethyl)imides containing the five- and six-membered imide rings.[6b] For example, no intramolecular O→Si coordination was observed by spectroscopic methods in a solution of *N*-(dimethylchlorosilylmethyl)succinimide, whereas this coordination in *N*-(dimethylchlorosilylmethyl)glutarimide was established by ^{29}Si NMR spectroscopy and X-ray diffraction. Moreover, succinimide and glutarimide give different types of products in reactions with a mixture of hexamethyldisilazane and dimethyl(chloromethyl)chlorosilane. The former reaction affords *N*-(dimethylsuccinimidosilylmethyl)succinimide (**1a**), whereas the latter reaction gives *N*-(dimethylchlorosilylmethyl)glutarimide.

Taking into account that *N*-(dimethylimidosilylmethyl)imides **1a,b** containing five-membered imide rings are readily formed and can easily be isolated, we examined the Si—N bond cleavage in these compounds with BF_3 etherate with the aim of preparing the corresponding *N*-dimethylfluorosilylmethyl derivatives. The H_3SiF and Me_3SiF compounds have previously been generated by the Si—N bond cleavage in $(H_3Si)_3N$,[7] Me_3SiNMe_2,[8a,8b] and $(Me_3Si)_2NH$,[8a] respectively, with BF_3.

We found that the reaction of silylmethylimides **1a,b** with an excess of BF_3 etherate in CH_2Cl_2 affords the corresponding *N*-(dimethylfluorosilylmethyl)imides **2a,b** in good yields.

Using 1-(dimethylmorpholinosilylmethyl)-2-pyrrolidone (**3**) as an example, we demonstrated that the above method can be applied also to the synthesis of 1-(fluorodimethylsilylmethyl)-2-pyrrolidone (**4**) described earlier.[9] The latter is one of the known *N*-(fluoro-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 3, pp. 558—561, March, 2006.



R = H (**a**), RCHCHR = *o*-C_6H_4 (**b**)

dimethylsilylmethyl)lactams containing the pentacoordinate silicon atom.

It should be noted that the common procedure for the synthesis of (O→Si)-chelated *N*-(fluorosilylmethyl)lactams, *N*-(fluorosilylmethyl)imides, and related compounds involves the reaction of alkoxysilanes or siloxanes with BF_3 etherate.[2,4,10,11]

The structures of compounds **1b** and **2a,b** were confirmed by IR and NMR spectroscopic data. The signals for the $SiMe_2$ and NCH_2 protons in the spectra of fluorides **2a,b** appear as doublets due to the spin-spin coupling with the fluorine atom. In the NMR spectra of many related compounds, in particular, of *N*-(trifluorosilylmethyl)succinimide,[4a] no splitting of the signal caused by such a spin-spin coupling is observed. This is attributed to fast HF-initiated exchange of the fluorine atoms bound to the silicon atom. Traces of HF are generated through hydrolysis of fluorosilane with glass-adsorbed water or surface hydroxy groups.

The ^{13}C NMR spectra of fluorides **2a,b** also show the $N^{13}CH_2$—Si—^{19}F and $^{13}CH_3$—Si—^{19}F spin-spin coupling constants (see the Experimental section). The signal for the carbon atoms of the carbonyl groups are observed as one narrow singlet. This is indicative of the equivalence of both C=O groups, and is, apparently, evidence for the absence of the intramolecular O→Si coordination bond in these compounds.

In solutions of fluorides **2a,b** and *N*-(dimethylchlorosilylmethyl)succinimide,[6b] this coupling was also not observed by ^{29}Si NMR spectroscopy. This is more reliably evidenced by the parameters of the ^{19}F and ^{29}Si NMR spectra. The chemical shifts of the ^{29}Si signal in the spectra of **2a**,**b** (δ_{Si} 26.8 and 28.05, respectively) correspond to the tetrahedrally coordinated silicon atom.[12] For example, the chemical shifts of the silicon nuclei in the NMR spectra of $ClCH_2SiMe_2F$ [1] and Me_3SiF [13] are 23.1 and 30.5, respectively.

In turn, the position of the signal in the ^{19}F NMR spectrum of fluoride **2b** (δ_F −158.2) is virtually identical to that in the spectrum of Me_3SiF (δ_F −158.0).[14]

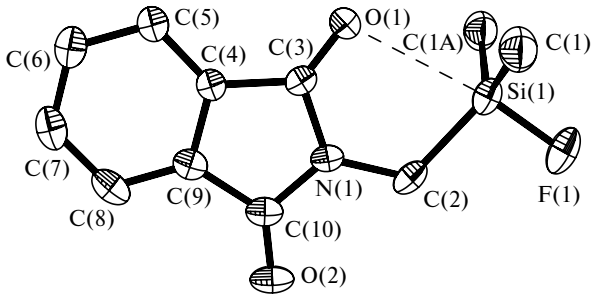


Fig. 1. Crystal structure of *N*-(dimethylfluorosilylmethyl)phthalimide (**2b**). The H atoms are omitted.

Table 1. Selected bond lengths and bond angles in molecule **2b**

Bond	*d*/Å	Angle	ω/deg
Si(1)—F(1)	1.630(2)	O(1)—Si(1)—F(1)	172.1(1)
Si(1)—O(1)	2.706(2)	O(1)—Si(1)—C(2)	74.3(1)
Si(1)—C(1A)*	1.843(3)	C(3)—O(1)—Si(1)	100.3(1)
Si(1)—C(1)	1.843(3)	C(1A)*—Si(1)—C(1)	116.3(2)
Si(1)—C(2)	1.882(4)	C(1A)*—Si(1)—C(2)	116.1(1)
O(1)—C(3)	1.199(4)	C(1)—Si(1)—C(2)	116.1(1)
N(1)—C(3)	1.392(4)	C(3)—N(1)—C(2)	122.3(3)
		N(1)—C(2)—Si(1)	119.1(2)
		O(1)—C(3)—N(1)	123.9(3)

* The atom is generated by the symmetry operation $-x, y, z$.

X-ray diffraction study revealed the intramolecular O→Si coordination bond in the crystals of fluoride **2b** (Fig. 1, Table 1).

In molecule **2b**, the Si atom is pentacoordinated and has a distorted trigonal-bipyramidal geometry formed by the axial O and F atoms and the equatorial carbon atoms. Generally, the Si—F bond lengths in the $CH_2Si(F)Me_2$ moieties of tetrahedral silicon compounds are in the range of 1.602—1.610 Å (see, for example, Refs 15a and 15b). In known structures of pentacoordinate silicon compounds,[9,15a,16] the Si—F bond lengths are in the range of 1.650—1.675 Å. In compound **2b**, this bond is shorter (1.630(2) Å). Correspondingly, the interatomic O(1)...Si distance is 2.706(2) Å. This is indicative of a very weak O→Si interaction. The Si atom deviates from the plane passing through the equatorial substituents by 0.368 Å toward the F atom. All three rings lie in the crystallographic mirror plane perpendicular to the crystallographic axis *a*.

Such a pronounced asymmetry of the components of the hypervalent bond is a result of the influence of the second oxygen atom, O(2), in the nearest valence environment of the silicon atom on the donor properties of the coordinated O(1) atom. A similar effect has been observed earlier.[17]

In conclusion, our results complement the procedures known for the synthesis of pentacoordinate silicon compounds containing the weak O→Si coordination bond.

Experimental

The IR spectra of solutions were measured in KBr cells on a double-beam Specord IR-75 spectrometer. The ^1H, ^{13}C, ^{19}F, and ^{29}Si NMR spectra were recorded in $CDCl_3$ on Varian XL-400 and Jeol JNM-EX400 spectrometers operating at 400.0, 100.6, 396, and 79.5 MHz, respectively. The ^1H, ^{13}C, and ^{29}Si NMR spectra were measured with Me_4Si as the internal standard. The ^{19}F NMR spectra were recorded with $CFCl_3$ as the external standard.

***N*-(Dimethylphthalimidosilylmethyl)phthalimide (1b).** A mixture of phthalimide (8.2 g, 0.056 mol), hexamethyldisilazane (7.7 g, 0.048 mol), and chloromethyldimethylchlorosilane (8.02 g, 0.056 mol) in benzene (80 mL) was refluxed with stirring for 2 h and kept for 16 h. The salt was separated, the solvent was removed from the filtrate, and hexane (70 mL) was added to the residue. The crystals that formed were filtered off. Compound **1b** was obtained in a yield of 5 g (49%), m.p. 133—135 °C (hexane—benzene, 9 : 1). Found (%): C, 62.42; H, 4.48; N, 7.66. $C_{19}H_{16}N_2O_4Si$. Calculated (%): C, 62.62; H, 4.43; N, 7.69. IR ($CHCl_3$), ν/cm^{-1}: 1780 w, 1740 s, 1610 v.w (NCO, Ar). ^1H NMR ($CDCl_3$), δ: 0.62 (s, 6 H, $SiMe_2$); 3.63 (s, 2 H, NCH_2); 7.70—7.96 (m, 8 H, Ar).

***N*-(Dimethylfluorosilylmethyl)succinimide (2a).** Boron trifluoride etherate (2.13 g, 0.015 mol) was added to a suspension of *N*-(dimethylsuccinimidosilylmethyl)succinimide[6b] (**1a**) (5.3 g, 0.02 mol) in CH_2Cl_2 (3 mL). The reaction mixture was heated in a distillation flask at 100—120 °C until the solvent and diethyl ether (~4 mL) were removed. Fractionation of the residue afforded fluoride **2a** in a yield of 3.6 g (80%), b.p. 121—124 °C (7 Torr), n_D^{20} 1.4634. Found (%): C, 44.30; H, 6.39; N, 7.10. $C_7H_{12}FNO_2Si$. Calculated (%): C, 44.42; H, 6.39; N, 7.40. IR ($CHCl_3$), ν/cm^{-1}: 1780 w, 1720 s (NCO). ^1H NMR ($CDCl_3$), δ: 0.36 (d, 6 H, $SiMe_2$, $^3J_{H,F}$ = 3 Hz); 2.80 (d, 4 H, CH_2CH_2, $^3J_{H,F}$ = 2 Hz); 3.04 (s, 2 H, NCH_2). ^{29}Si NMR ($CDCl_3$), δ: 26.8 (d, $^1J_{Si,F}$ = 282.1 Hz).

***N*-(Dimethylfluorosilylmethyl)phthalimide (2b).** Boron trifluoride etherate (0.53 g, 0.004 mol) was added to a suspension of compound **1b** (1.82 g, 0.005 mol) in CH_2Cl_2 (4 mL). The reaction mixture was refluxed for 1 h, and diethyl ether (15 mL) was added. The resulting suspension was filtered off. The mother liquor was concentrated. Fluoride **2b** was obtained in a yield of 1.0 g (84%), m.p. 73—75 °C (hexane). Found (%): C, 55.54; H, 5.17; N, 5.89. $C_{11}H_{12}NO_2SiF$. Calculated (%): C, 55.67; H, 5.11; N, 5.90. IR ($CHCl_3$), ν/cm^{-1}: 1780 w, 1715 s, 1610 v.w (NCO, Ar). ^1H NMR ($CDCl_3$), δ: 0.32 (d, 6 H, $SiMe_2$, $^3J_{H,F}$ = 7.5 Hz); 3.14 (d, 2 H, NCH_2, $^3J_{H,F}$ = 4.2 Hz); 7.71 and 7.62 (both m, 4 H, C_6H_4). ^{13}C NMR ($CDCl_3$), δ: −1.72 (d, $SiMe_2$, $^2J_{C,F}$ = 14.7 Hz); 27.52 (d, NCH_2, $^2J_{C,F}$ = 21 Hz); 133.98 (C(4), C(7)), 132.20 (C(3), C(8)), 123.26 (C(5), C(6)), 168.56 (C=O). ^{19}F NMR ($CDCl_3$), δ: −158.22. ^{29}Si NMR ($CDCl_3$), δ: 28.05 (d, $^1J_{Si,F}$ = 281.7 Hz).

1-(Dimethylmorpholinosilylmethyl)-2-pyrrolidone (3) was prepared by heating 1-(dimethylchlorosilylmethyl)-2-pyrrolidone and *N*-trimethylsilylmorpholine in 58% yield, b.p. 180—186 °C (12 Torr), n_D^{20} 1.4937. Found (%): C, 54.26; H, 9.21; Si, 11.91. $C_{11}H_{22}N_2O_2Si$. Calculated (%): C, 54.51; H, 9.15; Si, 11.59. IR ($CHCl_3$), ν/cm^{-1}: 1685 (C=O).

1-(Dimethylfluorosilylmethyl)-2-pyrrolidone (4). A mixture of compound **3** (2.5 g, 0.01 mol) and $BF_3 \cdot Et_2O$ (1.14 g, 0.008 mol) was warmed in a distillation flask at 30—50 °C until diethyl ether (0.5 mL) was removed. Fractionation of the residue afforded fluoride **4** in a yield of 1 g (57%), b.p. 120—121 °C (20 Torr), n_D^{20} 1.4560 (*cf.* lit. data[9]: b.p. 103—104 °C (10 Torr), n_D^{20} 1.4560).

X-ray diffraction study of compound 2b. Crystals suitable for X-ray diffraction study were grown by recrystallization from hexane. X-ray diffraction data for the structure of **2b** were collected on an automated SMART CCD diffractometer. Colorless crystals, a = 7.006(2) Å, b = 13.933(2) Å, c = 23.433(5) Å, space group *Cmca*, Z = 8, d_{calc} = 1.285 g cm^{-3}, at 120 K, 1633 independent reflections were measured (R_{int} = 0.049, $2\theta_{max}$ = 60°). The structure was solved by direct methods. The H atoms were located from difference electron density maps. The structure was refined with anisotropic displacement parameters for nonhydrogen atoms. The H atoms were refined isotropically. The final R factors were R_1 = 0.060 for 895 reflections with $I > 2\sigma(I)$, wR_2 = 0.163 for all reflections. All calculations were carried out using the SHELXTL program package (version 5.0)[18] on IBM PC.

The atomic coordinates, bond lengths, bond angles, and torsion angles were deposited with the Cambridge Structural Database. The X-ray diffraction study was carried out in the Center of X-ray Diffraction Studies (A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences).

This study was financially supported by the Russian Foundation for Basic Research (Project No. 04-03-32557) and the International Association for the Promotion of Cooperation with Scientists from the Independent States of the Former Soviet Union (INTAS, Project No. 03-51-4164).

References

1. M. G. Voronkov, V. A. Pestunovich, and Yu. I. Baukov, *Metalloorg. Khim.,* 1991, **4**, 1210 [*Organomet. Chem. USSR*, 1991, **4**, 593 (Engl. Transl.)].
2. D. Kost and I. Kalikhman, in *The Chemistry of Organic Silicon Compound*, Eds Z. Rappoport and Y. Apeloig, J. Wiley and Sons, Chichester, 1998, Vol. **2**, 1339.
3. Vad. V. Negrebetskii and Yu. I. Baukov, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 997 [*Russ. Chem. Bull.*, 1998, **47**, 967 (Engl. Transl.)].
4. (a) M. G. Voronkov, E. A. Zel´bst, Yu. V. Katkevich, A. A. Kashaev, V. S. Fundamenskii, Yu. I. Bolgova, O. M. Trofimova, N. F. Chernov, A. I. Albanov, Yu. I. Baukov, and V. A. Pestunovich, *Dokl. Akad. Nauk*, 2005, **402**, 344 [*Dokl. Chem.*, 2005 (Engl. Transl.)]; (b) T. N. Aksamentova, M. G. Voronkov, O. M. Trofimova, N. N. Chipanina, Yu. I. Bolgova, N. F. Chernov, E. A. Zel´bst, and V. K. Turchaninov, *Zh. Strukt. Khim.,* 2005, **46**, 257 [*Russ. J. Struct. Chem.*, 2005, **46** (Engl. Transl.)].
5. (a) M. G. Voronkov, N. N. Chipanina, B. A. Shainyan, Yu. I. Bolgova, O. M. Trofimova, N. F. Chernov, T. N. Aksamentova, and V. K. Turchaninov, *Dokl. Akad. Nauk*, 2004, **394**, 203 [*Dokl. Chem.*, 2004 (Engl. Transl.)]; (b) M. G. Voronkov, E. A. Zel´bst, A. A. Kashaev, Yu. V. Katkevich,

V. S. Fundamenskii, Yu. I. Bolgova, O. M. Trofimova, A. I. Albanov, N. F. Chernov, and V. A. Pestunovich, *Dokl. Akad. Nauk*, 2003, **393**, 493 [*Dokl. Chem.*, 2003 (Engl. Transl.)]; (c) S. G. Shevchenko, Yu. L. Frolov, A. V. Abramov, and M. G. Voronkov, *J. Organomet. Chem.*, 2005, **690**, 2922.

6. (a) I. D. Kalikhman, O. B. Bannikova, L. I. Belousova, B. A. Gostevskii, E. Liepin´sh, O. A. Vyazankina, N. S. Vyazankin, and V. A. Pestunovich, *Metalloorg. Khim.,* 1988, **1**, 683 [*Organomet. Chem. USSR*, 1988, **1** (Engl. Transl.)]; (b) S. A. Pogozhikh, Yu. E. Ovchinnikov, E. P. Kramarova, Vad. V. Negrebetskii, A. G. Shipov, A. I. Albanov, M. G. Voronkov, V. A. Pestunovich, and Yu. I. Baukov, *Zh. Obshch. Khim.*, 2004, **74**, 1617 [*Russ. J. Gen. Chem.*, 2004, **74** (Engl. Transl.)].
7. S. Sujishi and S. Witz, *J. Am. Chem. Soc.*, 1957, **79**, 2447.
8. (a) H. Grosse-Ruyken, *Angew. Chem.*, 1954, **66**, 754; (b) E. A. W. Ebsworth and H. J. Emeleus, *J. Chem. Soc.*, 1958, 2150.
9. A. A. Macharashvili, V. E. Shklover, N. Yu. Chernikova, M. Yu. Antipin, Yu. T. Struchkov, Yu. I. Baukov, G. I. Oleneva, E. P. Kramarova, and A. G. Shipov, *J. Organomet. Chem.*, 1989, **359**, 13.
10. M. G. Voronkov, V. P. Mileshkevich, and Yu. A. Yuzhelevskii, *The Siloxane Bond*, Consultants Bureau, New York—London, 1978, 493 p..
11. (a) O. B. Artamkina, A. G. Shipov, and Yu. I. Baukov, *Zh. Obshch. Khim.*, 1995, **65**, 2005 [*Russ. J. Gen. Chem.*, 1995, **65** (Engl. Transl.)]; (b) Yu. I. Baukov, O. A. Zamyshlyaeva, S. A. Pogozhikh, E. P. Kramarova, A. G. Shipov, Vad. V. Negrebetskii, and Yu. E. Ovchinnikov, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 1820 [*Russ. Chem. Bull.*, 1999, **48**, 1796 (Engl. Transl.)]; (c) E. P. Kramarova, A. G. Shipov, Vad. V. Negrebetskii, and Yu. I. Baukov, *Zh. Obshch. Khim.*, 1997, **67**, 1403 [*Russ. J. Gen. Chem.*, 1997, **67** (Engl. Transl.)].
12. Y. Takeuchi and T. Takayama, in *The Chemistry of Organic Silicon Compounds*, Eds Z. Rappoport and Y. Apeloig, J. Wiley and Sons, Chichester, 1998, Vol. **2**, 267.
13. H. Marsmann, *NMR-17 Bas. Princip. Prog.*, 1981, **17**, 64.
14. A. R. Bassindale, Yu. I. Baukov, M. Borbaruah, S. J. Glynn, Vad. V. Negrebetsky, D. J. Parker, P. G. Taylor, and R. Turtle, *J. Organomet. Chem.*, 2003, **669**, 154.
15. (a) Yu. I. Baukov, Yu. E. Ovchinnikov, A. G. Shipov, E. P. Kramarova, Vad. V. Negrebetsky, and Yu. T. Struchkov, *J. Organomet. Chem.*, 1997, **536**, 399; (b) J. Grobe, R. Martin, B. Krebs, and G. Henkel, *Z. Anorg. Allg. Chem.*, 1992, **607**, 79.
16. (a) A. G. Shipov, E. P. Kramarova, E. A. Mamaeva, O. A. Zamyshlyaeva, Vad. V. Negrebetsky, Yu. E. Ovchinnikov, S. A. Pogozhikh, A. R. Bassindale, P. G. Taylor, and Yu. I. Baukov, *J. Organomet. Chem.*, 2001, **620**, 139; (b) O. A. Zamyshlyaeva, A. G. Shipov, E. P. Kramarova, Vad. V. Negrebetskii, A. N. Shumskii, S. N. Tandura, S. Yu. Bylikin, Yu. E. Ovchinnikov, S. A. Pogozhikh, and Yu. I. Baukov, *Khim. Geterotsikl. Soedin.*, 2002, 127 [*Chem. Heterocycl. Compd.*, 2002 (Engl. Transl.)]; (c) A. R. Bassindale, D. J. Parker, P. G. Taylor, N. Auner, and B. Herrschaft, *J. Organomet. Chem.*, 2003, **667**, 66.
17. Yu. E. Ovchinnikov, A. O. Mozzhukhin, M. Yu. Antipin, Yu. T. Struchkov, V. P. Baryshok, N. F. Lazareva, and M. G. Voronkov, *Zh. Strukt. Khim.,* 1993, **34** (6), 66 [*Russ. J. Struct. Chem.*, 1993 (Engl. Transl.)].
18. G. M. Sheldrick, *SHELXTL PC Version 5.0*, Siemens Analytical X-Ray Instruments, Inc., Madison (WI), 1994.

Received December 16, 2005;
in revised form March 29, 2006