Synthesis and thermal decomposition of derivatives of acyloxytetraphenylantimony

O. K. Sharutina,[a★] *V. V. Sharutin,*[b] *V. A. Senchurin,*[a] *G. K. Fukin,*[c]
L. N. Zakharov,[c] *A. I. Yanovsky,*[d] *and Yu. T. Struchkov*[d†]

[a]*Blagoveshchensk Pedagogical Institute,*
104 ul. Lenina, 675000 Blagoveshchensk, Russian Federation.
[b]*Amur State University,*
21 sh. Ignat'evskoe, 675027 Blagoveshchensk, Russian Federation.
[c]*G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences,*
49 ul. Tropinina, 603600 Nizhnii Novgorod, Russian Federation.
Fax: +7 (831 2) 66 1497
[d]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085

Acyloxy derivatives of tetraphenylantimony of the general formula $Ph_4SbOC(O)R$ (R = Alk or Ar) have been synthesized by the reaction of pentaphenylantimony with carboxylic acids. Thermolysis of the compounds obtained affords phenyl carboxylates and triphenylstibine in quantitative yields. One of these compounds (R = CH=CHPh) has been studied by X-ray structural analysis. In this compound, the Sb atom has a trigonal-bipyramidal coordination. The $Sb—O(Ph)_{eq}$ distances are in the range 2.103(4)—2.140(5) Å; the $Sb—C(Ph)_{ax}$ bond length is 2.167(5) Å. The fragment of the residue of cinnamic acid has a delocalized double bond in the carboxylate group.

Key words: acyloxytetraphenylantimony, thermal decomposition; X-ray structural analysis, molecular structure.

Acyloxy derivatives of tetraphenylantimony were prepared by the reactions of pentaphenylantimony with acids; thermal decomposition of these derivatives at 200 °C affords triphenylstibine and phenyl carboxylates in yields of up to 96 %.

It is known that aryl derivatives of five-coordinate bismuth are used in organic synthesis because of their ability to readily undergo conversions associated with the $Bi^{5+} \rightarrow Bi^{3+}$ transition and to participate in reactions of reductive elimination, for example[1,2]

$$Ph_5Bi + ArOH \rightarrow Ph_3Bi + PhOAr.$$

The yield of diaryl ethers substantially increases if the aromatic nucleus of the phenol contains electron-withdrawing substituents.[2] Aryl derivatives of five-coordinate antimony, the closest analog of bismuth, can also be involved in similar conversions. Thus, when heated to 200 °C, phenoxytetraphenylantimony decomposes according to the analogous scheme to give diphenyl ether and triphenylstibine[3] (quantitative yields).

$$Ph_4SbOPh \xrightarrow{\Delta} Ph_3Sb + PhOPh$$

We have demonstrated that thermal decomposition of tetraphenylantimony carboxylates proceeds in a similar manner and affords triphenylstibine and phenyl carboxylate in a yield up to 96 % (Table 1).

$$Ph_4SbOC(O)R \xrightarrow{\Delta} Ph_3Sb + PhOC(O)R$$

Therefore, thermolysis of aryl derivatives of five-coordinate antimony may be used in organic synthesis for arylation at the O atom of carboxylic acids, phenols, and other ROH compounds, in which electron-withdrawing properties of the R group are more pronounced compared to that of the Ph group. Otherwise, alternative directions of thermolysis of Ph_4SbOR are possible, as, for example, upon thermal decomposition of benzyloxy- or isopropoxytetraphenylantimony.[3,4]

$$Ph_5Sb + PhCH_2OH \longrightarrow Ph_4SbOCH_2Ph \xrightarrow{\Delta}$$
$$\longrightarrow Ph_3Sb + PhH + PhC(O)H$$

The above-mentioned examples provide evidence that the pathways of thermal decomposition of the above-listed derivatives of Sb^{5+} are determined by the

---

[†] Deceased in 1995.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 194—198, January, 1996.

Table 1. Thermolysis products of $Ph_4SbOC(O)R$ compounds (1 h, 200 °C)

R	Yields of products (%)	
	Ph_3Sb	RC(O)OPh (m.p.)
Me	93	94*
Et	90	76*
C_5H_{11}	90	88*
$Me(CH_2)_{14}$	95	92 (45 °C)
$Me(CH_2)_{16}$	96	96 (42 °C)

* Viscous liquid.

nature of the most electronegative ligand at the central atom.

The starting tetraphenylantimony carboxylates were prepared from pentaphenylantimony and carboxylic acid in toluene at room temperature in yields up to 98 %. Generally, the reaction was completed in 0.5—1 h.

$$Ph_5Sb + RCOOH \rightarrow Ph_4SbOC(O)R + PhH$$

All the synthesized compounds form tetraphenylstibonium chloride and carboxylic acid under the action of an aqueous HCl solution in virtually quantitative yields.

The IR spectra of tetraphenylantimony carboxylates show intense bands in the 1520—1700 cm^{-1} region, which characterize stretching vibrations of the carbonyl group. Analogous bands shifted to the near-IR region are observed in the spectra of phenyl carboxylates. The obtained Sb^{5+} compounds are colorless crystalline compounds soluble in a wide range of organic solvents. The data of elemental analysis and IR spectroscopy as well as melting points and yields of compounds of the general formula $Ph_4SbOC(O)R$ are given in Table 2.

The structure of one acyloxy derivative of tetraphenylantimony prepared from pentaphenylantimony and cinnamic acid, $Ph_4SbOC(O)CH{=}CHPh$ (**1**), has been established by X-ray structural analysis (Fig. 1). The Sb atom in molecule **1** has a trigonal-bipyramidal coordination (the sum of the C(Ph)—Sb—C(Ph) angles in the equatorial plane is 357.2°, the axial C(1)—Sb—O(1) angle is 176.4(2)°). The $Sb-C(Ph)_{eq}$ distances in molecule **1** are in the range 2.103(4)—2.140(5) Å; the $Sb-C(Ph)_{ax}$ bond length is 2.167(5) Å.

In the structures of aroxytetraphenyl derivatives of antimony, which we have studied previously,[5] the analogous $Sb-C(Ph)_{eq}$ distances are in the ranges 2.115(4)—2.123(3) and 2.118(4)—2.139(5) Å and the $Sb-C(Ph)_{ax}$ bond distances are 2.181(5) and 2.188(5) Å for 2-nitrophenoxytetraphenylantimony and *p*-formylphenoxytetraphenylantimony, respectively. In these compounds, the value of the Sb—O—C bond angle correlates with the Sb—O bond length. Thus, when the Sb—O—C angle is smallest [122.6(3)°], the Sb—O bond length is maximum

Table 2. Principal physicochemical and spectral parameters of $Ph_4SbOC(O)R$ compounds

R	Yield (%)	M.p. /°C	Found / Calculated (%)		Empirical formula	IR, ν_{max}/cm^{-1}
			C	H		
Et	90	122	64.21 64.41	4.57 4.97	$C_{27}H_{25}O_2Sb$	1520, 1580
CH_2Cl	77	159	59.44 59.60	4.03 4.20	$C_{26}H_{22}ClO_2Sb$	1642
CH_2I	79	159	50.26 50.73	3.42 3.58	$C_{26}H_{22}IO_2Sb$	1645
$Me(CH_2)_4$	69	78	65.87 66.05	5.32 5.69	$C_{30}H_{31}O_2Sb$	1570, 1620
$Me(CH_2)_{14}$	76	72	69.55 70.07	7.18 7.44	$C_{40}H_{51}O_2Sb$	—
$Me(CH_2)_{16}$	78	75	70.44 70.69	7.59 7.71	$C_{42}H_{55}O_2Sb$	1525, 1580
C_6H_4—COOH-*o*	98	186	65.21 64.75	4.10 4.22	$C_{32}H_{25}O_4Sb$	1690, 1560
CH=CHPh	88	166	68.47 68.63	4.45 4.68	$C_{33}H_{27}O_2Sb$	1650, 1610, 1590
Ph	92	165	67.24 67.51	4.32 4.54	$C_{31}H_{25}O_2Sb$	1625, 1586
C_6H_4—OH-*p*	96	210	65.26 65.61	4.17 4.41	$C_{31}H_{25}O_3Sb$	1680, 1610
$(CH_2)_4COOH$	83	161	62.90 62.61	4.87 5.04	$C_{30}H_{29}O_4Sb$	1700, 1640
CH=CHCOOH	82	165	61.07 61.65	4.12 4.22	$C_{28}H_{23}O_4Sb$	1700, 1620

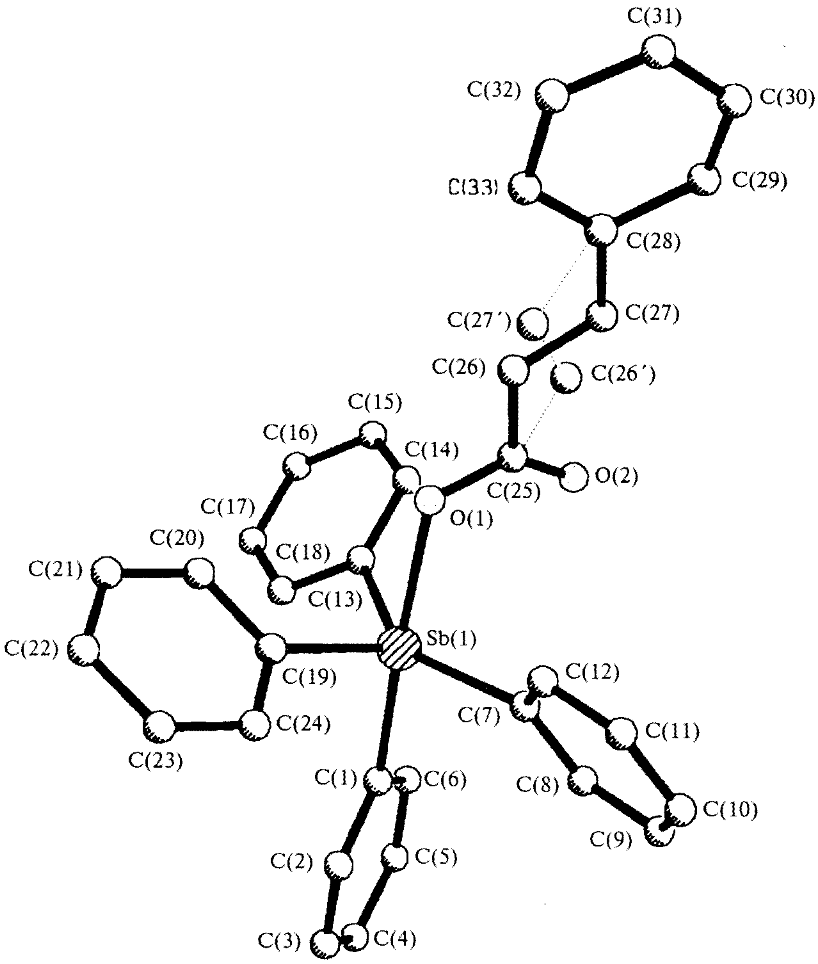

Fig. 1. Structure of molecule **1**.

[2.246(3) Å] (molecule **1**); with the Sb—O—C angle equal to 123.8(3)°, the Sb—O bond length is 2.221(4) Å (2-nitrophenoxytetraphenylantimony); and when the value of the Sb—O—C angle is maximum [129.6(3)°], the Sb—O distance is minimum [2.202(3) Å] (*p*-formylphenoxytetraphenylantimony). Unlike 2-nitrophenoxytetraphenylantimony and *p*-formylphenoxytetraphenylantimony, molecule **1** has an intramolecular contact between the Sb atom and the carbonyl O(2) oxygen atom; the distance between these atoms is 3.300 Å, which is smaller than the sum of van der Waals radii of these atoms (3.70 Å).[6] This may be one of the factors determining the minimum value of the Sb—O—C angle and the maximum length of the Sb—O bond in molecule **1** (compared to 2-nitrophenoxytetraphenylantimony and *p*-formylphenoxytetraphenylantimony).

The C(25)—O(1) and C(25)—O(2) distances are 1.246(7) and 1.219(7) Å, respectively. The C(25)—O(1) bond length is close to that of the delocalized double bond in carboxylate anions[7] (1.250 and 1.255 Å, respectively); the C(25)—O(2) bond length is close to the length of the double bond in carboxylic acids[7] (1.229 and 1.226 Å, respectively). Apparently, this distribution of the C(25)—O(1) and C(25)—O(2) bonds should be interpreted as evidence for the presence of a delocalized double bond.

In the crystal structure of compound **1**, a shortened O(2a)···H(16b) distance is observed (Fig. 2); this distance is 2.493 Å (the O(2a)—H(16b)—C(16b) angle is 162.1°), which is smaller than the sum of van der Waals radii of O and H atoms (2.7 Å).[6]

In the C(26)—C(27) fragment, the C(26) and C(27) atoms are statistically disordered at two sites [C(26′) and C(27′)]. This makes it impossible to adequately explain the large distances C(25)—C(26) [1.61(1) Å] and C(27′)—C(28) [1.59(2) Å]. The distances between the disordered positions C(26)—C(26′) and C(27)—C(27′) are 0.84(2) and 0.98(2) Å, respectively.

The disorder in the C(26)—C(27) fragment should cause disorder of the O(2) atom. The isotropic temperature factor of the O(2) atom [U_{iso} = 0.082(2) Å^2] is substantially larger than that of the O(1) atom [U_{iso} = 0.048(1) Å^2]. This may be associated with the presence of one more position for the O(2) atom as well as with the fact that the O(2) atom is terminal. However, we failed to separate the disordered positions of the O(2) atom.

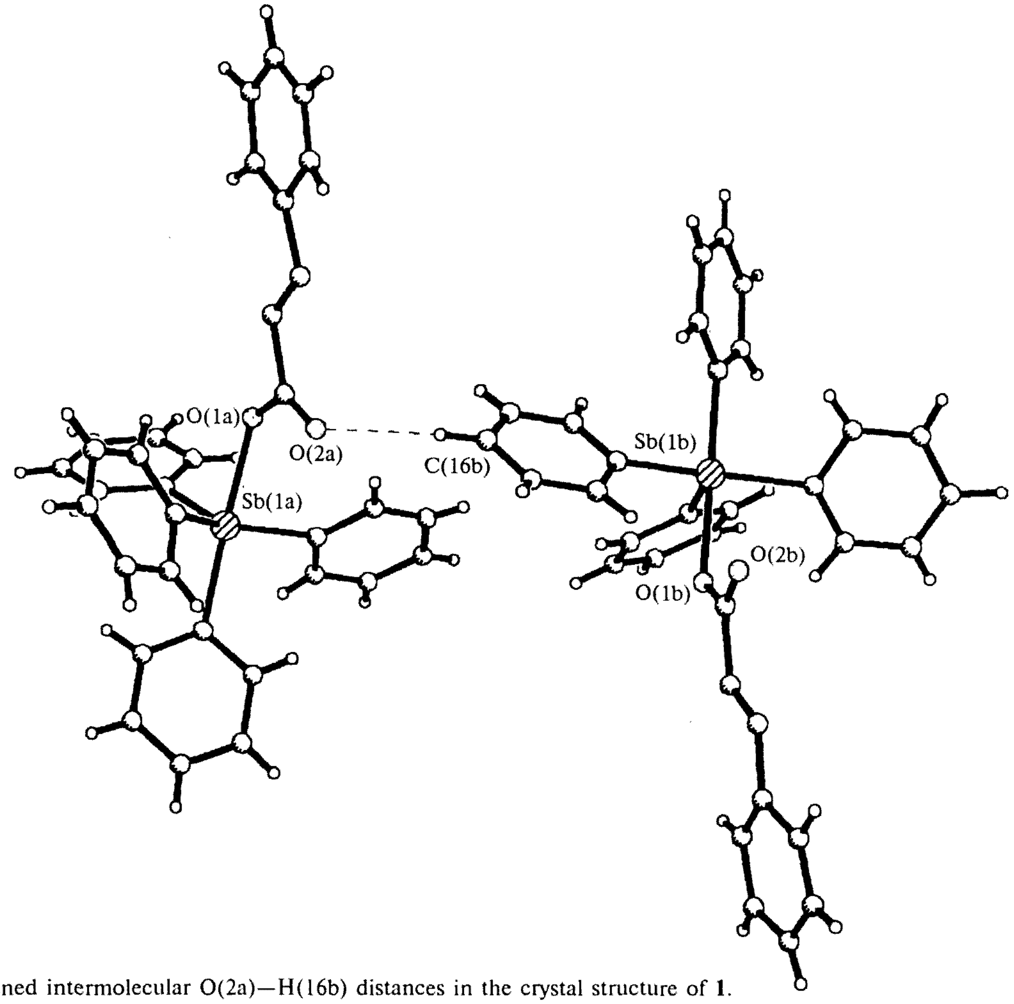

Fig. 2. Shortened intermolecular O(2a)—H(16b) distances in the crystal structure of **1**.

Table 3. Atomic coordinates ($\times 10^4$) and equivalent temperature factors ($U_{eq} \times 10^3$) in molecule **1**

Atom	*x*	*y*	*z*	U_{eq}/Å^2
Sb(1)	526(1)	241(1)	1539(1)	36(1)
O(1)	−1265(3)	−201(4)	1018(1)	48(1)
O(2)	−1378(4)	−2386(5)	1224(2)	82(2)
C(1)	2232(5)	553(5)	2069(2)	42(2)
C(2)	3214(6)	1313(7)	1947(2)	70(2)
C(3)	4276(6)	1511(8)	2305(3)	82(2)
C(4)	4384(6)	899(8)	2777(3)	72(2)
C(5)	3437(7)	95(8)	2907(2)	75(2)
C(6)	2357(6)	−82(6)	2550(2)	59(2)
C(7)	1348(5)	−1188(5)	1059(2)	42(2)
C(8)	2365(5)	−1993(6)	1271(2)	59(2)
C(9)	2996(6)	−2762(7)	944(3)	75(2)
C(10)	2649(6)	−2725(7)	416(3)	67(2)
C(11)	1658(6)	−1945(6)	213(2)	59(2)
C(12)	1008(5)	−1184(5)	530(2)	50(2)
C(13)	−607(5)	382(5)	2152(2)	41(2)
C(14)	−1597(5)	−474(6)	2217(2)	54(2)
C(15)	−2273(6)	−221(7)	2620(3)	69(2)
C(16)	−1970(6)	862(7)	2959(2)	65(2)
C(17)	−1006(6)	1687(6)	2889(2)	59(2)
C(18)	−312(5)	1473(5)	2490(2)	52(2)
C(19)	336(4)	2161(5)	1155(2)	37(1)
C(20)	−665(5)	3002(5)	1220(2)	43(2)
C(21)	−787(5)	4291(6)	991(2)	47(2)
C(22)	80(6)	4750(5)	695(2)	56(2)
C(23)	1059(6)	3908(6)	613(2)	58(2)
C(24)	1187(5)	2609(5)	839(2)	47(2)
C(25)	−1696(5)	−1392(6)	948(2)	49(2)
C(26)	−2680(9)	−1250(9)	428(4)	56(3)
C(26′)	−2555(13)	−2039(15)	561(5)	77(3)
C(27)	−3218(11)	−2437(10)	256(5)	58(3)
C(27′)	−3178(12)	−1448(19)	181(5)	100(3)
C(28)	−4110(6)	−2235(12)	−246(3)	96(2)
C(29)	−4554(9)	−3534(12)	−431(5)	128(3)
C(30)	−5298(9)	−3732(15)	−847(5)	141(3)
C(31)	−5797(7)	−2638(14)	−1132(3)	121(3)
C(32)	−5452(7)	−1341(11)	−985(3)	101(2)
C(33)	−4586(7)	−1124(10)	−542(3)	100(2)

Table 4. Principal bond lengths (*d*) in molecule **1**

Bond	*d*/Å	Bond	*d*/Å
Sb(1)—O(1)	2.246(3)	Sb(1)—C(1)	2.167(5)
Sb(1)—C(7)	2.132(5)	Sb(1)—C(13)	2.140(5)
Sb(1)—C(19)	2.103(4)	O(1)—C(25)	1.246(7)
O(2)—C(25)	1.219(7)	O(2)···Sb(1)	3.300(0)
C(25)—C(26)	1.61(1)	C(25)—C(26′)	1.42(1)
C(26)—C(26′)	0.84(2)	C(27)—C(27′)	0.98(2)
C(26)—C(27)	1.34(1)	C(26′)—C(27′)	1.25(2)
C(27)—C(28)	1.52(1)	C(27′)—C(28)	1.59(2)

Table 5. Principal bond angles (ω) in molecule **1**

Angle	ω/deg
O(1)—Sb(1)—C(1)	176.4(2)
C(1)—Sb(1)—C(7)	94.3(2)
C(1)—Sb(1)—C(13)	92.5(2)
O(1)—Sb(1)—C(19)	82.1(1)
C(7)—Sb(1)—C(19)	108.4(2)
Sb(1)—O(1)—C(25)	122.6(3)
O(1)—C(25)—C(26)	103.6(5)
O(1)—Sb(1)—C(7)	85.4(2)
O(1)—Sb(1)—C(13)	85.8(2)
C(7)—Sb(1)—C(13)	143.3(2)
C(1)—Sb(1)—C(19)	101.4(2)
C(13)—Sb(1)—C(19)	105.5(2)
O(1)—C(25)—O(2)	124.9(5)
O(2)—C(25)—C(26)	131.4(6)

Experimental

The ^{1}H NMR spectra (in acetone-d$_6$) were obtained on a Tesla BS-567A spectrometer (100 MHz); HMDS was used as an internal standard. The IR spectra were recorded on UR-20 and Hitachi spectrometers (Nujol mulls). An analysis of the liquid products was carried out on an LKhM-80 chromatograph (a katharometer was used as a detector, a 2-m-long column, 1.5 % PEG on INZ-600, 130 °C, nitrogen as carrier gas).

X-ray structural analysis of crystals of $Ph_4SbOC(O)CH=CHPh$ (1) was performed on an automated four-circle Siemens P3/PC diffractometer (Mo-Kα radiation, graphite monochromator, θ/2θ scanning technique, $2\theta \le 46°$). Crystals of **1** are monoclinic, at 20 °C a = 10.813(2) Å, b = 9.661(3) Å, c = 25.944(4) Å, β = 97.79(2)°, V = 2685(2) Å^3, d_{calc} = 1.428 g cm^{-3}, μ(Mo-Kα) = 10.58 cm^{-1}, space group $P2(1)/n$, Z = 4. The structure of **1** was solved by the direct method and refined by the block-diagonal least-squares method with anisotropic thermal parameters for all nonhydrogen atoms to R = 0.033, R_w = 0.048, S = 1.33 using 2622 reflections with $I > 3\sigma(I)$. The H atoms of the Ph substituents of molecule **1** were introduced in geometrically calculated positions and refined using the riding model. In the course of refinement of the structure of molecule **1**, the disorder of the C(26) and C(27) atoms at two sites with equal occupancies was found [C(26), C(26′) and C(27), C(27′)]. The H atoms at these atoms were not revealed.

All calculations were performed on an IBM PC/AT computer using the SHELXTL PLUS program package.[8] Atomic coordinates and equivalent temperature factors, principal bond lengths and bond angles in molecule **1** are given in Tables 3—5, respectively.

All reactions were carried out in evacuated glass ampules using the standard procedures (see below).

Tetraphenylantimony propionate. A solution of pentaphenylantimony (5 mmol) and propionic acid (5 mmol) in 10 mL of toluene was kept at room temperature for 1 h. The solvent was removed *in vacuo*, the concentration of benzene was determined by GC (0.36 g, 95 %). The residue was washed with hexane (5 mL) and dried *in vacuo*. The yield of tetraphenylantimony propionate was 2.46 g. IR, ν/cm^{-1}: 1640.

Thermal decomposition of tetraphenylantimony propionate. Tetraphenylantimony propionate (2 mmol) was heated for 1 h at 200 °C in one bend of an evacuated inverted U-tube instrument with simultaneous cooling of another bend. Condensed products were purified chromatographically on Al_2O_3 (hexane as an eluent). Phenylpropionate was obtained in 76 % yield (0.23 g). IR, ν/cm^{-1}: 1690. ^{1}H NMR, δ: 7.15 (m, 5 H, Ph); 2.57 (q, 2 H, CH_2); 1.15 (t, 3 H, CH_3).

Thermal decomposition of other acyloxy derivatives of tetraphenylantimony was carried out in a similar manner.

References

1. G. A. Razuvaev, N. A. Osanova, and V. V. Sharutin, *Dokl. Akad. Nauk SSSR*, 1975, **225**, 581 [*Dokl. Chem.*, 1975, **225** (Engl. Transl.)].
2. D. H. Barton, N. Y. Bhatnagar, J. K. Blazejewski, B. Charpiot, J. P. Finet, D. J. Lester, W. B. Motherwell, P. Barrous, and S. P. Stanforth, *J. Chem. Soc., Perkin Trans. 1*, 1985, 2657.
3. G. A. Razuvaev and N. A. Osanova, *J. Organomet. Chem.*, 1972, **38**, 77.
4. G. A. Razuvaev, N. A. Osanova, T. G. Brilkina, T. I. Zinovjeva, and V. V. Sharutin, *J. Organomet. Chem.*, 1975, **99**, 93.
5. V. V. Sharutin, V. V. Zhidkov, D. V. Muslin, N. Sh. Lyapina, G. K. Fukin, L. N. Zakharov, A. I. Yanovsky, and Yu. T. Struchkov, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 958 [*Russ. Chem. Bull.*, 1995, **44**, 931 (Engl. Transl.)].
6. S. S. Batsanov, *Zh. Neorg. Khim.*, 1991, **36**, 3015 [*Sov. J. Inorg. Chem.*, 1991, **36** (Engl. Transl.)].
7. F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, S1.
8. W. Robinson and G. M. Sheldrick, *SHELX*, in *Crystallographic Computing Techniques and New Technologies*, Eds. N. W. Isaacs and M. R. Taylor, Oxford Univ. Press, Oxford (England), 1988, 366.

Received July 13, 1995