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ORGANOBORON COMPOUNDS

CCCXCIV *. REACTION OF 1-BORAADAMANTANE WITH CARBONYL COMPOUNDS

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Summary

1-Boraadamantane has been shown to react with aromatic aldehydes, isobutyraldehyde, and acetone forming firstly the 1 : 1 complexes which at 70—80°C form new heterocyclic cage compounds: 5-substituted derivatives of 4-oxa-3-bora-1,1-bihomoadamantane (4-oxa-3-boratricyclo[5.3.1.$1^{3,9}$]dodecane) which exist as dimers. Starting from 4-oxa-5-(4-methoxyphenyl)-3-bora-1,1-bihomoadamantane and 4-oxa-5-(3,4-dimethoxyphenyl)-3-bora-1,1-bihomoadamantane, the corresponding 3-methoxy-7α-(2-methoxy-2-arylethyl)-3-borabicyclo[3.3.1]nonanes were obtained; the latter two compounds eliminate MeOH on heating in vacuum to give 3-methoxy-7α-(2-arylvinyl)-3-borabicyclo[3.3.1]-nonanes, which exist in the double chair conformation, as shown by ^{1}H and ^{13}C NMR spectroscopy.

1-Boraadamantane is a tricyclic analogue of trialkylboranes, but differs from the latter since its boron atom is in the tetrahedral state and not in the trigonal one. This feature of 1-boraadamantane is revealed in its chemical properties: specifically in the high complexing ability. Thus 1-boraadamantane (I) forms adducts with such ligands as ether, THF and ethyl acetate [1,2], whereas trialkylboranes do not give analogous adducts. The 1-boraadamantane complexes are more stable as compared to those of R_3B, since the potential energy of 1-boraadamantane is higher than that of trialkylborane by the amount of the reorganization energy (6—10 kcal/mol) which is consumed on transition of the boron from the trigonal to the tetrahedral configuration [1,3,4].

In the course of a study of the properties of compound I we investigated

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* For part CCCXCIII see ref. 16.

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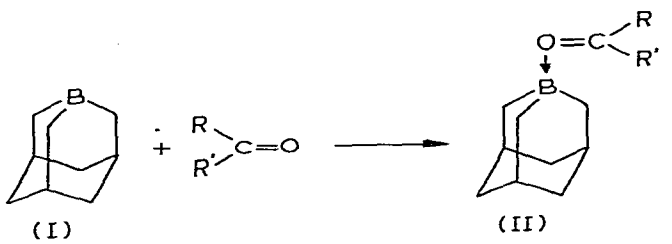
the behaviour of I with respect to benzaldehyde, 4-methoxybenzaldehyde, 3,4-dimethoxybenzaldehyde, isobutyraldehyde and acetone. The interaction of these carbonyl compounds with I in hexane gives the complexes IIa—IIe (1 : 1) (eq. 1).



(I) (II) (1)

(a, R = H ; R' = C_6H_5 ;
b, R = H ; R' = 4-$CH_3OC_6H_4$;
c, R = H ; R' = 3,4$(CH_3O)_2C_6H_3$;
d, R = H ; R' = i-C_3H_7 ;
e, R = R' = CH_3)

The IR spectra of solutions of IIa—IId in CCl_4, recorded in the presence of an excess of I, show absorption bands of the C=O group at lower frequencies (by 70—75 cm^{-1}) in comparison with analogous bands of the free aldehydes. Analogous phenomenon (with a shift of 70—80 cm^{-1}) was observed previously in the case of the complexes of BF_3 with aromatic aldehydes [5]. The low-frequency shift also takes place for IIe as compared with the absorption of C=O in acetone.

The data in Table 1 show that formation of II is accompanied by an upfield shift of the aldehyde proton signal. The same effect was observed in the case of the BF_3 complexes [5]. The ^{11}B NMR spectrum of IIb (in benzene) contains a signal centered at —19.7 ppm.

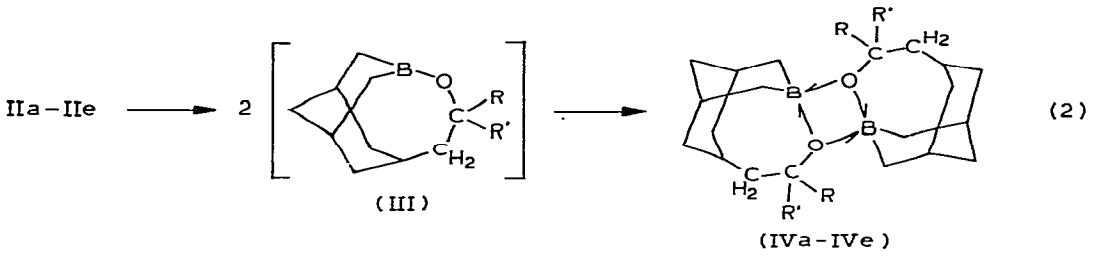
The complexes IIa—IIc are yellow crystalline substances, while IId and IIe are colourless liquids. The compounds IIa—IIe are thermally unstable: on heating in hexane or benzene they undergo a rearrangement to produce 5-substituted derivatives of 4-oxa-3-bora-1,1-bihomoadamantane (III) which exist as dimers (IV) (eq. 2).

TABLE 1

IR AND ^1H NMR SPECTRA OF IIa—IIe AND FREE RCOR' [a]

RCOR'	ν(C=O)II (cm^{-1})	ν(C=O)RCOR' (cm^{-1})	$\Delta\nu$ (cm^{-1})	$\delta(H_{ald.})_{II}$ (ppm)	$\delta(H_{ald.})_{RCOR'}$ (ppm)
a	1635	1710	75	9.76	9.84
b	1630	1705	75	9.58	9.70
c	1623	1695	72	9.08	9.66
d	1670	1740	70	9.09	9.42
e	1669	1719	50	—	—

[a] Solutions in CCl_4.



Thus, the reaction of I with carbonyl compounds proceeds in accordance with the scheme of organometallic synthesis via complex (II) formation. This process can be related to the electrophilic substitution in a series of organometallic compounds and its mechanism, in accord with the Abraham and Hill's classification [6], should be assigned to the S_{EC} type.

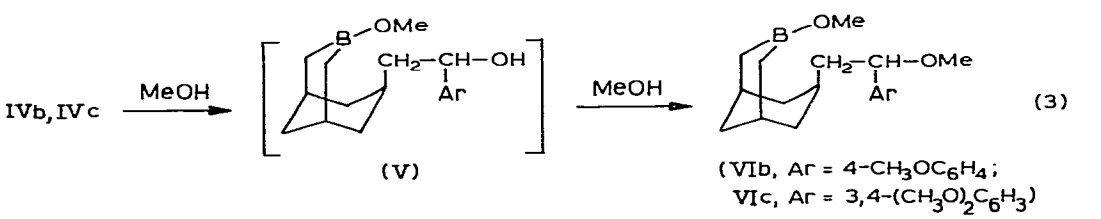
The trialkylboranes, as distinct from I, do not add to carbonyl compounds at the C=O bond, instead they reduce trialkylboranes with olefin elimination at 80—150°C [7,8]. Like the reduction of carbonyl compounds by Grignard reagents, this process proceeds via a six-membered transition state. In contrast, triallylboranes can add at the C=O bond of carbonyl compounds under mild conditions [9]. The reaction occurs according to the six-member mechanism, being accompanied by allylic rearrangement [10].

Compounds IVa—IVe are colourless crystalline substances, stable in air, sparingly soluble in organic solvents. The mass spectra of IVa—IVe contain intense peaks of the molecular ions M^+.

The ^{11}B NMR spectra demonstrate the coordination between the atoms of B and O. For example, the spectrum of dimeric 4-oxa-5-(4-methoxyphenyl)-3-bora-1,1-bihomoadamantane (IVb) reveals one signal centered at 15.5 ppm. The IR spectra of solutions of IVa—IVe in CCl_4 show no intense absorptions in the 1300—1400 cm^{-1} region characteristic of a B(sp^2)—O bond.

The dimer of 4-oxa-3-borahomoadamantane has been previously described [11,12], in which the B and O atoms form the four-membered cycle: the bonds between these atoms being semi-coordinate, as shown by an X-ray analysis [13]. It is clear that the bonds between the B and O atoms in compounds IVa—IVe should be considered as semi-coordinate ones.

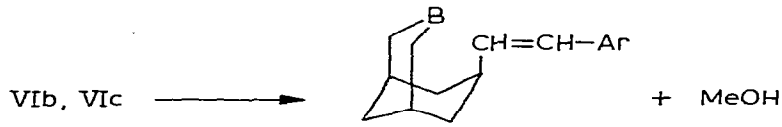
Compounds IVa, IVd and IVe are stable with respect to methanol whereas IVb and IVe react with methanol on heating according to eq. 3. The intermedi-



ate compounds V were not detected as they readily convert to 3-methoxy-7α-(2-methoxy-2-arylethyl)-3-borabicyclo[3.3.1]nonanes (VIb, VIc). The structure of VIb was determined by ^1H and ^{11}B NMR spectroscopy.

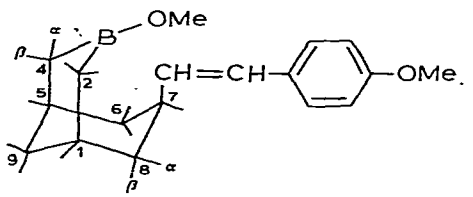
On heating at 100—130°C in vacuum, VIb and VIc eliminate MeOH (1 mol)

to afford 3-methoxy-7α-(2-arylvinyl)-3-borabicyclo[3.3.1]nonanes (VIIb, VIIc) which are colourless crystalline substances, very soluble in organic solvents (eq. 4).



(VIIb, Ar = 4-$CH_3OC_6H_4$;
VIIc, Ar = 3,4-$(CH_3O)_2C_6H_3$)

Based on the results of a conformational analysis of the 3-borabicyclo[3.3.1]-nonane derivatives [14] we managed to determine the conformation of VIIb.

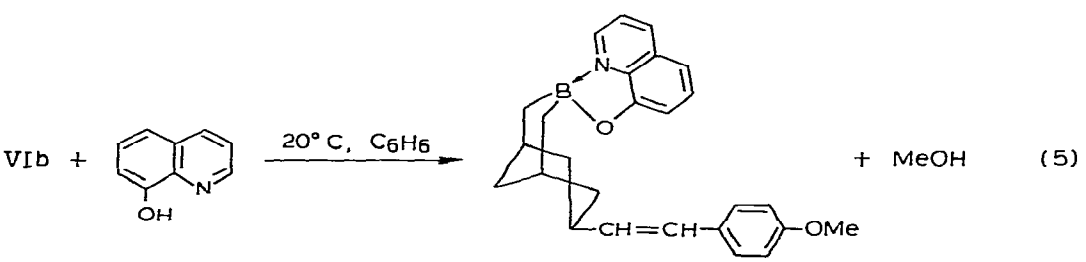


(VIIb)

Because of coincidence of the chemical shifts of the protons H(6,6′) and H(8,8′) in the ^{1}H NMR spectrum, the signal of these protons has the shape of a triplet with broadened components, 1 : 2 : 1, and a coupling constant of ~4 Hz owing to interaction between H(1,5) and H(6,6′,8,8′). The coupling constant between H(6,6′,8,8′) and H(7) apparently does not exceed the width of the triplet, component line (<2.5 Hz). The small coupling constants evidence axial orientation of the substituent in the cycle free of the boron atom as well as a predominant chair conformation.

The ^{13}C NMR spectrum of VIIb confirms this conclusion: the chemical shifts of the C atoms are close to those to the 3-borabicyclo[3.3.1]nonane compounds determined previously.

The compound VIIb reacts with 8-hydroxyquinoline in benzene at 20°C to give 7α-[2-(4-methoxyphenyl)-vinyl]-3-borabicyclo[3.3.1]nonyl-8-hydroxyquinolinate (VIII) as a yellow crystalline compound stable in air (eq. 5).



(VIII)

We have carried out a conformational analysis of VIII. It is known that the 3-borabicyclo[3.3.1]nonane compounds with a 4-coordinated B atom, includ-

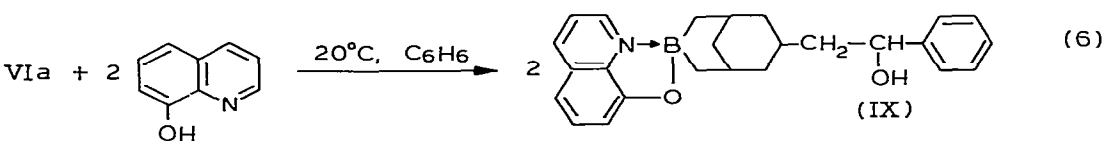
ing VIII, are in the predominating chair-boat conformation, the cyclohexane ring free of the B atom having the boat conformation [14]. It was necessary to bear in mind that some compounds of this type, in which an internal donor-acceptor interaction takes place between the B atom and 7α-substituent, have the chair-chair conformation.

An attempt to elucidate some conclusions about the predominant conformation of the cyclohexane ring with the help of ^{1}H NMR spectroscopy met with failure owing to the poor resolution of the H(6,6',8,8') signals.

The conformation of VIII was determined by ^{13}C NMR spectroscopy. The spectrum of VIII is typical for the compounds of this series having the chair-boat conformation, and the characteristic shift of C(9) is 31.7 ppm, i.e. by ~4 ppm upfield as compared with that of VIIb.

The stereochemistry of the NBO fragment of the chelate ring was not established; however, inspection of the Dreiding models suggests that the structure of VIII shown above is favoured, since in this case the steric hindrances are weaker.

On interaction of 8-hydroxyquinoline and IVa in benzene at 20°C, the 8-membered cycle undergoes cleavage of the B—O bond to give rise to 7α-(2-hydroxy-2-phenylethyl)-3-borabicyclo[3.3.1]-nonyl-8-hydroxyquinolinate (IX) (eq. 6).



(6)

The chelate IX is a yellow crystalline substance, stable in air.

Experimental

All manipulations with organoboron compounds were carried out in an atmosphere of dry argon, the IR spectra were recorded on a UR-20 spectrometer. ^{1}H NMR spectra on a Tesla BS-497 (100 MHz, relative internal TMS), and ^{13}C NMR spectra on a Bruker WP-60 (15.08 MHz, chemical shifts are given on the δ scale) instruments. ^{11}B NMR spectra were recorded on a Bruker WP-80 spectrometer (25.67 MHz for ^{11}B, relative to internal $BF_3 \cdot Et_2O$, chemical shifts are given on the δ scale).

1-Boraadamantane was obtained according to ref. 15.

Preparation of complexes IIa—IIc

0.01 mol of ArCHO was added to a solution of 0.01 mol (1.34 g) of I in 6 ml of hexane. The precipitate was filtered off and washed with cooled hexane to afford IIa—IIc in 84, 80, and 81% yield, respectively. Compounds IIa—IIc are thermally unstable and on heating form IVa—IVc. The main spectral characteristics of IIa—IIc are given in Table 1.

Preparation of complexes IId and IIe

To 0.01 mol(1.34 g) of I in 6 ml of pentane, was added 0.015 mol of $(CH_3)_2CHCHO$ or $(CH_3)_2CO$ at 20°C. The solvent and excess carbonyl com-

TABLE 2

SYNTHESIS CONDITIONS, ELEMENTAL ANALYSIS, AND SPECTRA OF IVa–IVe

Compound	Solvent	Reflux time (h)	Yield (%)	Elemental analysis (%) Found (calcd.)			M.p. (°C)	Mol. weight (Found from mass-spectrum (calcd.)	^{1}H NMR (δ, ppm)
				C	H	B			
IVa	hexane	3.5	77	80.10 (80.02)	8.90 (8.81)	4.62 (4.50)	247–257	480 (480.30)	5.01m (OCH) 7.17s (H–Ph)
IVb	benzene	12	71	75.65 (75.62)	8.65 (8.53)	3.93 (4.01)	186–189	540 (540.32)	3.70s (MeO) 4.93m (OCH)
IVc	benzene	17	75	71.98 (72.01)	8.42 (8.40)	3.55 (3.60)	185–187	600 (600.38)	3.77s and 3.80s (OMe) 4.99m (OCH)
IVd	hexane	3	77	75.72 (75.75)	11.08 (11.25)	5.07 (5.24)	199–205	512 (512.24)	3.90m (OCH)
IVe	hexane	7	82	74.94 (75.02)	10.93 (11.02)	5.49 (5.63)	225–229	384 (384.22)	0.98–2.11 (aliphat. H) 1.15s (CH_3)

pound were carefully removed in vacuo till constant weight of the residue. The compounds IId and IIe are thermally unstable, forming IVd and IVe on heating. Spectral data of IId and IIe are given in Table 1.

Preparation of the dimers IVa—IVe

To 0.05 mol (6.7 g) of I in 30 ml of a solvent (see Table 2) were added 0.05 mol of carbonyl compound at 20°C. The reaction mixture was refluxed (see Table 2), the precipitate formed was filtered and washed with hexane. The spectral data are given in Table 2.

Preparation of 3-methoxy-7α-[2-methoxy-2-(4-methoxyphenyl)ethyl]-3-borabicyclo[3.3.1]nonane (VIb)

A solution of 0.001 mol (0.5 g) of IVb in 10 ml of MeOH was refluxed for 2 h. The low-boiling products were distilled out in vacuo to give the residue, VIb, as a colourless viscous liquid. ^{1}H NMR (δ, ppm, CCl_4): 3.11 s (MeO—B), 3.49s (MeO—C), 3.77s (MeO—Ph), 3.99m (OCH). ^{11}B NMR (CCl_4): 53.3 ppm. On heating at 1 Torr, up to ~100°C, VIb converts to VIIb.

Preparation of 3-methoxy-7α-[2-(4-methoxyphenyl)-vinyl]-3-borabicyclo[3.3.1]-nonane (VIIb)

A solution of 0.01 mol (5.3 g) of IV in 16 ml of MeOH was refluxed for 3 h. The low-boiling substances were distilled out in vacuo. Distillation of the residue afforded 4.39 g (88.5%) of VIIb, b.p. 163—165°C/1 Torr. After crystallisation and recrystallisation from 11 ml of MeOH, 4.16 g (84%) of VIIb were obtained, m.p. 66—68°C. Found: C, 75.70; H, 8.84; B, 3.55. $C_{18}H_{25}BO_2$ (*M* 284.1) calcd.: C, 76.09; H, 8.87; B, 3.81%. Mass spectrum (*m/e*): 284 (M^+).^{1}H NMR (ppm, $CDCl_3$, 20°C): 0.76d.d (2 H, H(2,4), J(2,2′) = 16.5 Hz; J(1,2) = 6.6 Hz), 1.06 d with broadened components (2 H, H(9,9′), J(9,9′) = 12 Hz); 1.86t (4 H, H(6,6′, 8,8′), J(5,6) = 4 Hz; J(6,7) < 2.5 Hz); 2.20m (2 H, H(1,5)); 2.60m (1 H, H(10); J(10,11) = 16.2 Hz; J(10.7) = 3.5 Hz); 6.32 d.d. (1 H, H(11); J(11,7) = 1.8 Hz), 6.76—7.20 AA′—BB′ spectrum (4 H, ph).

^{13}C NMR (ppm, $CDCl_3$, 20°C) ("off-resonance" method):

C(1,5)	C(2,4)	C(6,8)	C(7)	C(9)	BOMe	COMe	C(10)	C(11)
27.75(d)	26.0	36.85(t)	31.75(d)	35.95(t)	52.3(q)	5.50(q)	129.1(d)	135.0(d)

Ar: 113.7, 126.8, 130.5, 158.7.

Preparation of 3-methoxy-7α-[2-(3,4-dimethoxyphenyl)-vinyl]-3-borabicyclo-[3.3.1]nonane (VIIc)

A solution of 0.004 mol (2.07 g) of IVc in 8 ml of MeOH was refluxed for 3 h. After removing the low-boiling products in vacuo at 20°C the residue was kept at 110—130°C in vacuo (1 Torr) for 1.5 h. Crystallization of the product from 10 ml of MeOH gave 2 h (92%) of VIIc, m.p. 52—54°C. Found: C, 72.38; H, 8.62; B, 3.52. $C_{19}H_{27}BO_3$ (*M* 314.22) calcd.: C, 72.62; H, 8.66; B, 3.44%. Mass spectrum (*m/e*): 314 (M^+).

Preparation of 7α-[2-(4-methoxyphenyl)-vinyl]-3-borabicyclo[3.3.1]nonyl-8-hydroxyquinolinate (VIII)

To a solution of 0.004 mol (0.57 g) of 8-hydroxyquinoline in 5 ml of

benzene was added 0.004 mol (1.13 g) of VIIb in 10 ml of benzene. After removing the low-boiling products in vacuo the residue was recrystallized from benzene to yield 1.12 g (68%) of VIII, m.p. 185—188°C. Found: C, 78.95; H, 7.16; B, 3.07. $C_{26}H_{28}BNO_2$ (*M* 397.12) calcd.: C, 78.60; H, 7.10; B, 2.72%. Mass spectrum (*m/e*): 397 (M^+). ^{1}H NMR (ppm, C_6D_6): 0.58 d.d. (2 H, H(2,4); $J(2,2') = 13.5$ Hz; $J(1,2) = 4.9$ Hz); 1.15 d with broadened components (2 H, H(2',4')); 1.46 d with broadend components (1 H, H(9), $J(9,9') = 12.2$ Hz); 2.18m (5 H, H(6,6',8,8',9)); 2.63m (3 H, H(1.5,7)), 3.23s (3 H, OMe); 6.2—7.4m (12 H, H(10,11), Ar).

^{13}C NMR (ppm, CH_2Cl_2) ("off-resonance" method):

C(1,5)	C(2,4)	C(6,8)	C(7)	C(9)	BOMe	C(10)	C(11)
27.0(d)	33.8	35.4(t)	35.2(d)	31.7(t)	55.3(q)	121.7(d)	137.7(d)

Ar: 108.45, 110.9, 114.0, 122.9, 126.4, 128.7, 130.7, 131.5, 136.3, 136.5, 137.6, 158.2, 158.8.

Preparation of 7α-(2-hydroxy-2-phenylethyl)-3-borabicyclo[3.3.1]nonyl-8-hydroxyquinolinate (IX)

A solution of 0.004 mol (0.63 g) of 8-hydroxyquinoline in 5 ml of benzene was added to 0.002 mol (1.05 g) of IVa in 30 ml of benzene. After removing the solvent in vacuo and recrystallization from CH_2Cl_2, 1.62 g (96.5%) of IX were obtained, m.p. 157—160°C (decomp.). Found: C, 77.64; H, 7.53; B, 2.82. $C_{25}H_{28}BNO_2$ calcd.: C, 77.93; H, 7.32; B, 2.81%. IR (ν, cm^{-1}, CH_2Cl_2): 3605 (OH); 1507, 1582, 1619 (aromat.); 3030—3080 (CH aromat.).

References

1 B.M. Mikhailov, Pure and Appl. Chem., 39 (1974) 505.
2 B.M. Mikhailov, V.N. Smirnov and V.A. Kasparov, Izvest. Akad. Nauk SSSR, Ser. Khim., (1976) 2302.
3 B.M. Mikhailov, Pure and Appl. Chem., 52 (1980) 691.
4 B.M. Mikhailov, Soviet Scientific Reviews, Sect. B, Chemistry Reviews, Vol. 2, (1980) 283.
5 A. Grinvald and M. Rabinovitz, J. Chem. Soc. Perkin II (1974) 94.
6 M.H. Abraham and J.H. Hill, J. Organometal. Chem., 7 (1967) 11.
7 B.M. Mikhailov, V.G. Kiselev and Yu.N. Bubnov, Izvest. Akad. Nauk SSSR, Ser. Khim., (1965) 898.
8 B.M. Mikhailov, Yu.N. Bubnov and V.G. Kiselev, Zh. Obshch. Khim., 35 (1966) 62.
9 B.M. Mikhailov and Yu.N. Bubnov, Izvest. Akad. Nauk SSSR, Ser. Khim., (1964) 1874.
10 B.M. Mikhailov and V.F. Pozdnev, Izvest. Akad. SSSR, Ser. Khim., (1967) 1477.
11 B.M. Mikhailov and K.L. Cherkasova, Izvest. Akad. Nauk SSSR, Ser. Khim., (1979) 2729.
12 B.M. Mikhailov, L.S. Vasil'ev and V.V. Veselovsky, Izvest. Akad. Nauk SSSR, Ser. Khim., (1980) 1106.
13 L.G. Vorontsova, O.S. Chizhov, L.S. Vasil'ev, V.V. Veselovsky and B.M. Mikhailov, Izvest. Akad. Nauk SSSR, Ser. Khim., in press.
14 M.E. Gursky, A.S. Shashkov and B.M. Mikhailov, J. Organometal. Chem., 199 (1980) 171.
15 B.M. Mikhailov, T.K. Baryshnikova, V.G. Kiselev and A.S. Shashkov, Izvest. Akad. Nauk SSSR, Ser. Khim., (1979) 2544.
16 B.M. Mikhailov and T.K. Baryshnikova, J. Organometal. Chem., 219 (1981) 295.