Table 2. ^1H and ^{19}F NMR spectral data for the compounds synthesized

Compound	δ ^1H	δ ^{19}F (*J*/Hz)
5a*	2.40 (s, CH_3); 3.80 (s, OCH_3); 5.70 (s, CH)	2.3 (s, CF_3)
5b	2.60 (s, CH_3); 4.10 (s, OCH_3); 6.10 (s, CH)	6.6 (s, CF_3); 47.5 (s, CF_2)
5c	2.50 (s, CH_3); 3.90 (s, OCH_3); 6.00 (s, CH)	5.2 (t, CF_3); 45.5 (q, CF_2, $J = 9$); 51.0 (s, CF_2)
5d	2.60 (s, CH_3); 4.00 (s, OCH_3); 6.00 (s, CH)	5.8 (t, CF_3, $J = 9$); 44.8 (q, CF_2, $J = 9$); 47.5 (m, CF_2); 50.0 (m, CF_2)
5e	2.30 (s, CH_3); 3.80 (s, OCH_3); 5.80 (s, CH)	6.0 (s, CF_3); 44.7 (m, CF_2); 45.9 (m, CF_2); 46.6 (m, CF_2); 47.1 (m, CF_2); 50.8 (m, CF_2)
5f	2.40 (s, CH_3); 3.80 (s, OCH_3); 5.80 (s, CH)	6.0 (s, CF_3); 44.8 (m, CF_2); 45.6 (m, CF_2); 46.1 (m, 2 CF_2); 46.5 (m, CF_2); 47.0 (m, CF_2); 50.9 (m, CF_2)

* Data from Ref. 1.

Experimental

^1H and ^{19}F NMR spectra were recorded on a Bruker AC-200F spectrometer (200 and 188.4 MHz, respectively) with Me_4Si (^1H) and CF_3COOH (^{19}F) as the external standards. Elemental analysis of the compounds obtained was performed at the Laboratory of Microanalysis of the A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences. The solvents were dried according to the standard procedures.[5]

***C*-Acylation of 2-methoxypropene (1) (general procedure).** An acylating agent **2—4** (1 mol) was added dropwise with vigorous stirring at a temperature indicated in Table 1 to a mixture of ether **1** (1 mol) and a tertiary amine (1 mol) in a dehydrated solvent. The reaction mixture was stirred at the same temperature for ~1 h, allowed to be heated gradually to room temperature, and poured into water. The organic layer was separated off, washed with water, and dried over $CaCl_2$. The solvent was removed, and the corresponding compounds **5a—f** were isolated by distillation (see Table 1). The ^1H and ^{19}F NMR spectral data of the reaction products are given in Table 2.

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Synthesis of new dialkyl α-aminophosphonates and dialkyl α-aminothiophosphonates

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New dialkyl α-aminophosphonates and α-aminothiophosphonates were synthesized by reactions of dialkyl phosphites or *O*,*O*-dialkyl thiophosphites with *N*-benzylidene-2-(vinyloxy)ethylamine or *N*-(4-fluorobenzylidene)-2-(vinyloxy)ethylamine.

Key words: dialkyl phosphites, *O*,*O*-dialkyl thiophosphites, reaction with Schiff bases, dialkyl α-aminophosphonates, dialkyl α-aminothiophosphonates, synthesis.

The Kabachnik—Fields reaction is a classic method for the synthesis of α-aminophosphonates and their numerous functionalized derivatives. Synthetic aspects of this reaction have been well developed and discussed in monographs and reviews.[1—4]

However, despite extended investigations in the field of alkyl α-aminophosphonates, condensation of *N*-benzylidene-2-(vinyloxy)ethylamine or *N*-(4-fluorobenzylidene)-2-(vinyloxy)ethylamine with dialkyl phosphites or *O*,*O*-dialkyl thiophosphites is not reported in the

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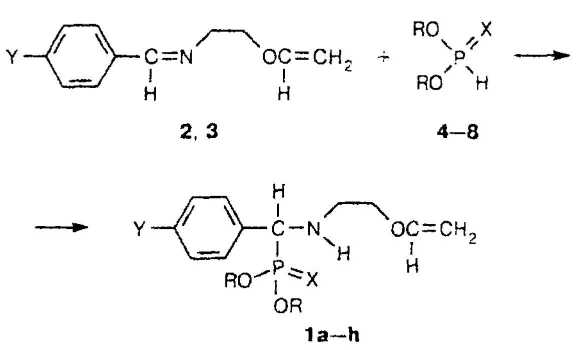
Scheme 1



Y = H (**1a—e**, **2**), F (**1f—h**, **3**);
X = O (**1a,b**, **4**, **5**), S (**1c—h**, **6—8**);
R = Me (**1a,c,f**, **4**, **6**), Et (**1b,d,g**, **5**, **7**), Pr^i (**1e,h**, **8**)

literature, although condensation products may be of interest because of their possible physiological activity.

Dialkyl α-aminophosphonates (**1a,b**) and *O,O*-dialkyl aminothiophosphonates (**1c—h**) were synthesized by reactions of vinyl ethers of Schiff bases (**2**, **3**) with dialkyl phosphites (**4**, **5**) or *O,O*-dialkyl thiophosphites (**6—8**), respectively (Scheme 1).

Schiff bases **2** and **3** were prepared by condensation of 2-aminoethyl vinyl ether with benzaldehyde[5] and 4-fluorobenzaldehyde, respectively. Compound **3** has not been described in the literature.

Dialkyl phosphites or *O,O*-dialkyl thiophosphites react with *N*-benzylidene-2-(vinyloxy)ethylamine (**2**) or *N*-(4-fluorobenzylidene)-2-(vinyloxy)ethylamine (**3**) at room temperature without any catalyst. When the reaction is carried out at a higher temperature or catalyzed by alkali metal alkoxides, the products resinify.

The structures of compounds **1a—h** were determined by ^{31}P NMR and IR spectroscopy, and their compositions were confirmed by elemental analysis (Table 1).

The IR spectra of compounds **1a—h** show absorption bands at 1035—1060 cm^{-1} (P—O—C), 1610—1625 cm^{-1} (C=C), and 3230—3285 cm^{-1} (NH). The IR spectra of phosphonates **1a,b** contain additional bands at 1260—1280 cm^{-1} (P=O), and those of phosphonates **1c—h** contain bands at 635—660 cm^{-1} (P=S).

Experimental

IR spectra were recorded on a UR-20 spectrophotometer (thin film) in the range 500—3600 cm^{-1}. ^{31}P NMR spectra were recorded on a Bruker WP-200 SU instrument (81.01 MHz) in C_6H_6 with 85% H_3PO_4 as the standard.

***N*-(4-Fluorobenzylidene)-2-(vinyloxy)ethylamine (3).** A mixture of 4-fluorobenzaldehyde (12.4 g, 0.1 mol) and 2-aminoethyl vinyl ether (8.7 g, 0.1 mol) in 40 mL of benzene was heated in a flask equipped with a Dean—Stark adapter for 50 min until water ceased to evolve. The solvent was removed, and the residue was distilled *in vacuo* to give Schiff base **3** (17.9 g, 92.7%), b.p. 118—120 °C (2.5 Torr), d_4^{20} 1.1066, n_D^{20} 1.5270. Found (%): C, 68.27; H, 6.09; F, 9.71; N, 7.13. $C_{11}H_{12}FNO$. Calculated (%): C, 68.39; H, 6.22; F, 9.83; N, 7.25.

***O,O*-Dimethyl {α-[(2-vinyloxyethyl)amino]benzyl}thiophosphonate (1c).** *O,O*-Dimethyl thiophosphite (0.60 g, 4.8 mmol) was gradually added to (*N*-benzylidene)-2-(vinyloxy)ethylamine (0.84 g, 4.8 mmol), the reaction being exothermic. Then the reaction mixture was heated at 40—45 °C for 35 min and chromatographed on SiO_2 (elution with hexane—acetone, 2 : 1) to give thiophosphonate **1c** (1.06 g, 73.3%).

***O,O*-dimethyl** and ***O,O*-diethyl {α-[(2-vinyloxyethyl)-amino]benzyl}phosphonates (1a,b)**; ***O,O*-diethyl** and ***O,O*-diisopropyl {α-[2-(vinyloxyethyl)amino]benzyl}thiophosphonates (1d,e)**; and ***O,O*-dimethyl**, ***O,O*-diethyl**, and ***O,O*-diisopropyl {α-[(2-vinyloxyethyl)amino]-4-fluorobenzyl}thiophosphonates (1f—h)** were obtained in a similar way. Their physicochemical and spectral characteristics are presented in Table 1.

Table 1. Physicochemical characteristics of dialkyl α-aminophosphonates and dialkyl α-aminothiophosphonates (**1a—h**)

Compound	R	X	Y	Yield (%)	n_D^{20}	Found/Calculated (%) C	H	N	P	S	F	Molecular formula	^{31}P NMR, δ
1a	Me	O	H	72.6	1.5220	54.24 54.73	6.87 7.06	4.50 4.91	10.67 10.86	—	—	$C_{13}H_{20}NO_4P$	25.99
1b	Et	O	H	74.3	1.5065	57.06 57.50	7.14 7.20	3.98 4.47	9.73 9.88	—	—	$C_{15}H_{24}NO_4P$	23.09
1c	Me	S	H	73.3	1.5405	51.48 51.81	6.35 6.69	4.08 4.65	9.89 10.28	10.14 10.64	—	$C_{13}H_{20}NO_3PS$	98.48
1d	Et	S	H	75.2	1.5345	54.28 54.69	6.87 7.34	3.91 4.25	9.18 9.40	9.40 9.73	—	$C_{15}H_{24}NO_3PS$	93.78
1e	Pr^i	S	H	75.8	1.5235	56.88 57.12	7.60 7.89	3.38 3.92	8.23 8.66	8.43 8.97	—	$C_{17}H_{28}NO_3PS$	90.85
1f	Me	S	F	78.6	1.5310	48.43 48.89	5.63 5.99	4.07 4.38	9.62 9.70	10.73 10.04	5.44 5.95	$C_{13}H_{19}FNO_3PS$	97.52
1g	Et	S	F	83.6	1.5205	51.69 51.86	6.76 6.67	3.93 4.03	8.73 8.91	9.12 9.23	5.32 5.47	$C_{15}H_{23}FNO_3PS$	93.04
1h	Pr^i	S	F	82.3	1.5125	53.97 54.38	6.83 7.25	3.69 3.73	7.89 8.25	8.38 8.54	4.88 5.06	$C_{17}H_{27}FNO_3PS$	90.11

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Synthesis of rhodacarborane halide complexes $[(\eta\text{-}9\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_{10})RhX_2]_2$ (X = Cl, Br, or I)

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The reactions of the complex $(\eta\text{-}9\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_{10})Rh(\eta\text{-cod})$ (cod is 1,5-cyclooctadiene) with HX acids (X = Cl, Br, or I) in acetone afforded rhodacarborane halide complexes $[(\eta\text{-}9\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_{10})RhX_2]_2$, which are carborane analogs of cyclopentadienyl halide rhodium complexes $[(\eta\text{-}C_5R_5)RhX_2]_2$.

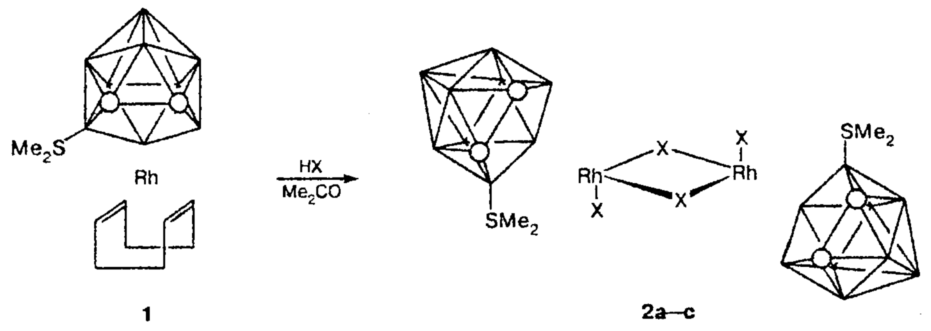
Key words: metallacarboranes, rhodium.

As part of continuing studies[1,2] devoted to the synthesis of transition metal π-complexes with the charge-compensated anion $[9\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_{10}]^-$ isolobal to the cyclopentadienyl anion, we studied the reaction of (cyclooctadiene)rhodacarborane **1**[3] with HX acids (X = Cl, Br, or I). We found that this reaction proceeds readily in acetone at room temperature to form rhodacarborane halide complexes **2a—c** in ~80% yields (Scheme 1).

The rate of the reaction decreases in the order Br > Cl > I. This reaction is analogous to the reactions of HCl with $(\eta\text{-}C_5Me_5)Rh(\eta\text{-chd})$ (chd is 1,3-cyclohexadiene) and (η-arene)Ru(η-cod) to form rhodium and ruthenium compounds, *viz.*, $[(\eta\text{-}C_5Me_5)RhCl_2]_2$ [4] and $[(\eta\text{-arene})RuCl_2]_2$,[5] respectively.

Compounds **2a—c** were characterized by the data of elemental analysis and ^1H and ^{11}B NMR spectroscopy (Table 1). The NMR spectra of these compounds are

Scheme 1



O CH   X = Cl (**a**), Br (**b**), I (**c**)

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