Phosphorus-containing podands

10.* An improved method for synthesizing oligo(ethylene glycol) bis[2-(diphenylphosphinoyl)ethyl] ethers and their complex-forming properties with respect to alkali-metal-cations in anhydrous acetonitrile

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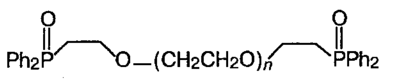
An improved preparative method for the synthesis of oligo(ethylene glycol) bis[2-(diphenylphosphinoyl)ethyl] ethers has been developed. The complex-forming ability of these ligands toward alkali-metal cations has been studied by conductometry in anhydrous MeCN at 25°C. Ligands of this type have been shown to be highly efficient and selective complexing agents with respect to the Li^+ cation. The stability series of the complexes M^+L has the form Li > Na > K > Rb in all cases. The complexing properties and selectivity displayed by these new monopodands in MeCN have been compared with those in the $THF—CHCl_3$ (4:1) system studied previously.

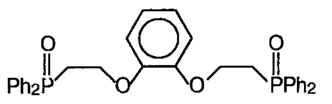
Key words: phosphorus-containing monopodands; synthesis; complex formation, conductometry.

Phosphorus-containing monopodands with 2-(diphenylphosphinoyl)ethyl terminal groups **1a—f** and **2** exhibit some interesting properties.



1a—f

n = 0 (**a**), 1 (**b**), 2 (**c**), 3 (**d**), 4 (**e**), 5 (**f**)



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It was found that these compounds have a high complex-forming ability toward cations of alkali and alkaline-earth metals. The stability constants of the complexes of these ligands with alkali-metal cations (M^+L) were determined by conductometry in a mixed $THF—CHCl_3$ solvent (4:1, v/v), and it was shown that monopodand **1a** has high Li/Na-selectivity and an efficiency in binding Li^+ cation scarcely falling short of that for such a strong complexing agent as 18-crown-6.[1] A calometric study of the complexing ability of ligand **1e** toward salts of alkali and alkaline-earth metal in anhydrous MeCN also showed that its selectivity with respect to the Li^+ cation is significantly higher than that of crown ethers.[2] In addition, the extraction of alkali metal and alkaline-earth metal picrates from neutral aqueous solutions by compounds **1a—d** in $CHCl_3$ and CH_2Cl_2 has been examined, and it was found that these ligands can compete with crown ethers in some cases.[3]

However, monopodands of type **1** are not easily accessible compounds. The synthetic methods proposed earlier[1] on the basis of the addition of oligo(ethylene glycols) to diphenylvinylphosphine oxide requires the use of ethylene oxide,[4] which severely limits the possibilities of this method. The synthesis of monopodands **1a** described in the literature by the alkylation of lithium diphenylphosphide with diethylene glycol ditosylate followed by oxidation[5] likewise does not solve the accessibility problem. The use of the Michaelis—Becker reaction for the synthesis of podands with alkoxy substituents at the phosphorus atom is known.[6] However, this method can hardly be applied to the synthesis of podands of the phosphine oxide type, since it has been shown for β-substituted phosphines oxides that an alkoxy or hydroxy group in the β-position is readily replaced by various nucleophilic groups in the presence of bases.[7—9] The reaction apparently proceeds with the intermediate formation of the corresponding vinyl oxide. Accordingly, the interaction of sodium diphenylphosphinite with 1,5-dichloro-3-oxapentane in EtOH or dioxane gives a

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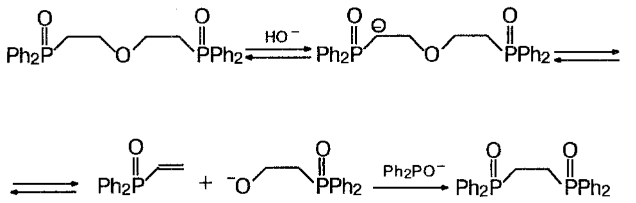
*For a preliminary communication, see Ref.1.

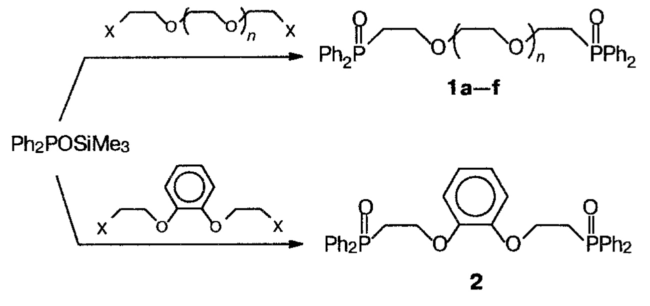
Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 3, pp. 518—522, March, 1993.

1066-5285/93/4203-0472$12.50

mixture of three major products (as shown by ^{31}P NMR), from which tetraphenylethylenediphosphine dioxide is easily isolated. The use of anhydrous K_2CO_3 as a base gives the same result. Monopodand **1a** is stable under alkaline conditions (heating for 5 h in aqueous—alcoholic KOH at 80°C, monitoring by ^{31}P NMR), but in the presence of diphenylphosphinous acid and a basic reagent (NaOH, EtONa, NaH, K_2CO_3) at >30°C, **1a** very rapidly forms tetraphenylethylenediphosphine dioxide in a nearly quantitative yield. In the absence of substances which bind the hypothetical intermediate diphenylvinylphosphine oxide, the equilibrium is shifted completely to the left. When diphenylphosphinous acid is added, the latter readily reacts with diphenylvinylphosphine oxide.



As was shown in this work, the rearrangement of trimethylsilyl diphenylphosphinite under the action of dihalogenated derivatives or ditosylates of oligo(ethylene glycols) is a convenient method for the synthesis of monopodands **1**. The ester was obtained by reacting diphenylphosphinous acid with hexamethyldisilazane[4] and was usually used without isolation.



The rearrangement proceeds at 140—150°C for the bromides and tosylates, but the chlorides require more severe conditions (180—200°C). We note that monopodand **2** with a pyrocatechol fragment in the polyether chain cannot be prepared by the method described earlier,[1] i.e., by reacting diphenylvinylphosphine oxide with pyrocatechol. It should also be emphasized that monopodands **1c** and **1d** with *n* = 2 and 3, respectively, which we characterized as oils,[1] were obtained in the crystalline state in this work.

We previously[1] studied the complexing ability of monopodands **1** (*n* = 0—5) with respect to alkali-metal cations in a mixed THF—$CHCl_3$ (4:1, v/v) solvent. In the present work the values of the logarithms (lg*K*) of the stability constants of the complexes M^+L were determined for the same compounds by conductometry[10] in anhydrous MeCN at 25°C, and the results obtained for these two solvents, which differ in polarity and donor activity, were compared.

Experimental

The ^{1}H and ^{31}P NMR spectra were recorded on a Bruker-CXP-200 spectrometer relative to tetramethylsilane and 85 % H_3PO_4. The melting points were measured on a Boetius PHMK-05 instrument.

1,5-Bis(diphenylphosphinoyl)-3-oxapentane (1a). A mixture of diphenylphosphinous acid (57.0 g, 0.28 mol) and hexamethyldisilazane (32.2 g, 0.20 mol) was heated with stirring under argon to 120°C and held for 1 h, and then 1,5-dichloro-3-oxapentane (23.3 g, 0.13 mol) was added dropwise. The mixture was stirred for 3 h at 180—200°C and trimethylchlorosilane was distilled off. After cooling to 20°C, 50 mL of ethanol and 5 mL of 30 % H_2O_2 were added, and the solution was stirred for 1 h at 80°C and poured into 200 mL of water. The mixture was extracted with $CHCl_3$ (three 50-mL portions), and the extract was washed first with a 20 % Na_2CO_3 solution (three 40-mL portions)* and then with water (three 50-ml portions) and concentrated in vacuum. The residue was

Table 1. Logarithms of the stability constants (lg*K*) of the complexes of alkali-metal cations M^+L with monopodands **1** and several crown ethers in anhydrous CH_3CN at 25°C

Ligand (*n*)	Li^+	Na^+	K^+	Rb^+	Cs^+
1a (0)	5.15±0.10	—	—	—	—
1b (1)	5.50±0.14	3.44±0.06	2.80±0.09	~2	—
1c (2)	5.65±0.12	3.91±0.06	2.95±0.04	~2	—
1d (3)	5.75±0.15	4.77±0.07	3.39±0.07	2.77±0.06	—
1e (4)	5.48±0.08	4.54±0.09	3.36±0.06	2.81±0.04	2.45±0.04
1f (5)	4.92±0.05	4.22±0.07	3.67±0.08	3.32±0.07	—
15-Crown-5 [22]	5.34	5.38	3.98	3.42	3.14
16-Crown-5 [22]	4.48	5.39	3.57	2.94	2.38
18-Crown-6	3.73[23]	4.55[24]	5.70[24]	—	—

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*A large-scale synthesis requires washing the extract with an acidified solution of Mohr's salt or $FeSO_4$ to remove the residual H_2O_2.

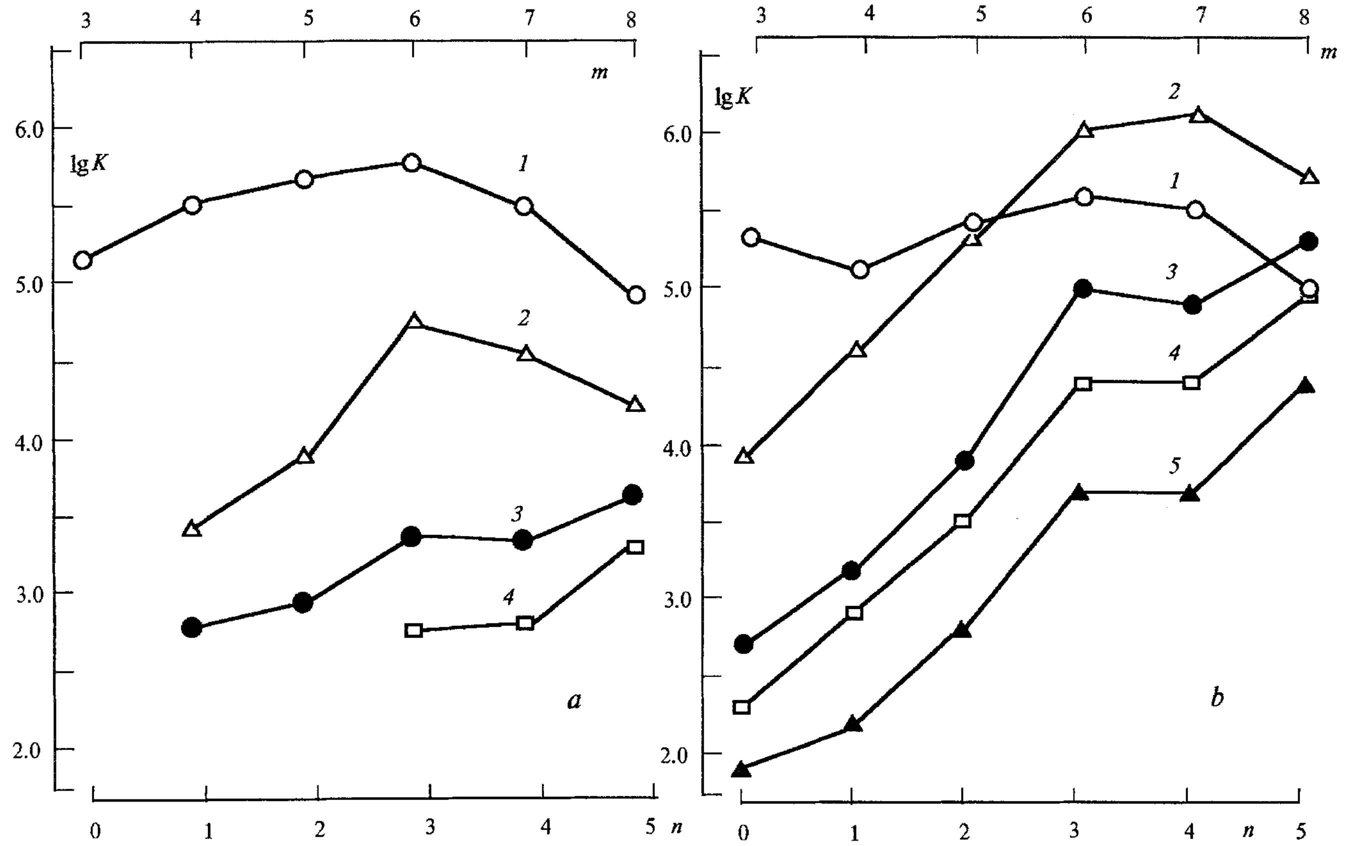

Fig. 1. Logarithms of the stability constants of complexes of oligo(ethylene glycol) bis[2-(diphenylphosphinoyl)ethyl] ethers **1a—f** with alkali-metal cations as a function of the length of the polyether chain (*n*) and the number of donor centers (*m*) in anhydrous CH_3CN (*a*) and in a mixed THF—$CHCl_3$ solvent (4:1, v/v)[1] (*b*): *1*, Li^+; *2*, Na^+; *3*, K^+; *4*, Rb^+; *5*, Cs^+.

chromatographed in a column with silica gel L (the eluent was $CHCl_3$) to give 53.0 g of **1a** (82 %), mp 134—136°C (benzene—hexane). Monohydrate of **1a**: mp 81—82°C (see Ref.[5]).

Compounds **1b—f** were prepared as was **1a** from diphenylphosphinous acid and dichloro derivatives of the corresponding glycols. The yields were 79—82 %. Their constants, analytical data, and ^1H and ^{31}P NMR spectra correspond to those reported earlier.[1] **1c**: mp 79—82°C (ether—acetone, hygroscopic); **1d**: mp 52—55°C (ether—acetone, hygroscopic).

1,2-Bis(β-diphenylphosphinoylethoxy)benzene (2). Compound **2** was prepared from trimethylsilyl diphenylphosphinite[4] (13.7 g, 0.05 mol) and 1,2-bis(2-tosyloxyethoxy)benzene (10.0 g, 0.02 mol) at 150°C as was **1a**. The yield of **2** was 6.3 g (55 %), mp 145—147°C (benzene—hexane). ^1H NMR spectrum ($CDCl_3$), δ: 2.88 (m, 4 H, CH_2—P); 4.36 (m, 4 H, OCH_2); 6.46—7.85 (m, 24 H, arom.). ^{31}P NMR spectrum ($CDCl_3$), δ: 29.35. Found (%): C, 72.1, 72.2; H, 5.80, 5.70; P, 11.2, 11.3. $C_{34}H_{32}O_4P_2$. Calculated (%): C, 72.1; H, 5.70; P, 10.9.

The procedure for the conductometric measurements in anhydrous CH_3CN was described elsewhere.[11] The random error (±2σ, where σ is the standard deviation of the arithmetic mean) in determination of lg*K* of the complexes M^+L was calculated from the results of at least three independent measurements. The concentration of ionogenic impurities in the ligands was monitored conductometrically and taken into account in the calculations of lg*K*. Lithium perchlorate and tetraphenylborates of other alkali metals which remain unassociated in CH_3CN were used as supporting electrolytes.

Results and Discussion

Table 1 presents the data on the complexing properties of ligands **1a—f**. Figure 1*a* presents plots of the dependence of lg*K* of the complexes of the alkali-metal cations M^+L on the number of CH_2CH_2O units in the polyether chain (*n*) and the total number of donor centers in the ligand (*m*). For comparison, the analogous plots which we previously[1] obtained for the same ligands in a mixed THF—$CHCl_3$ solvent are presented in Fig. 1*b*.

It is easily seen that monopodands **1** are efficient complex-forming agents in MeCN, especially toward the Li^+ cation. As in the case of the mixed solvent THF—$CHCl_3$, the plots of the dependence of lg*K* on *n* for Li^+ and Na^+ cations in CH_3CN do not have pronounced minima for Li^+ and Na^+, which are observed for the closely related monopodands with *o*-(diphenylphosphinoyl)[12] and *o*-(diethoxyphosphinoyl)phenyl[13] terminal groups. Recently,[1] we discussed this behavior in detail for the THF—$CHCl_3$ system and interpreted it as a consequence of an increase in the conformational mobility of the terminal phosphinoylethyl groups in monopodands **1** as compared to that of the terminal phosphoryl-containing groups. The efficiency of mono-

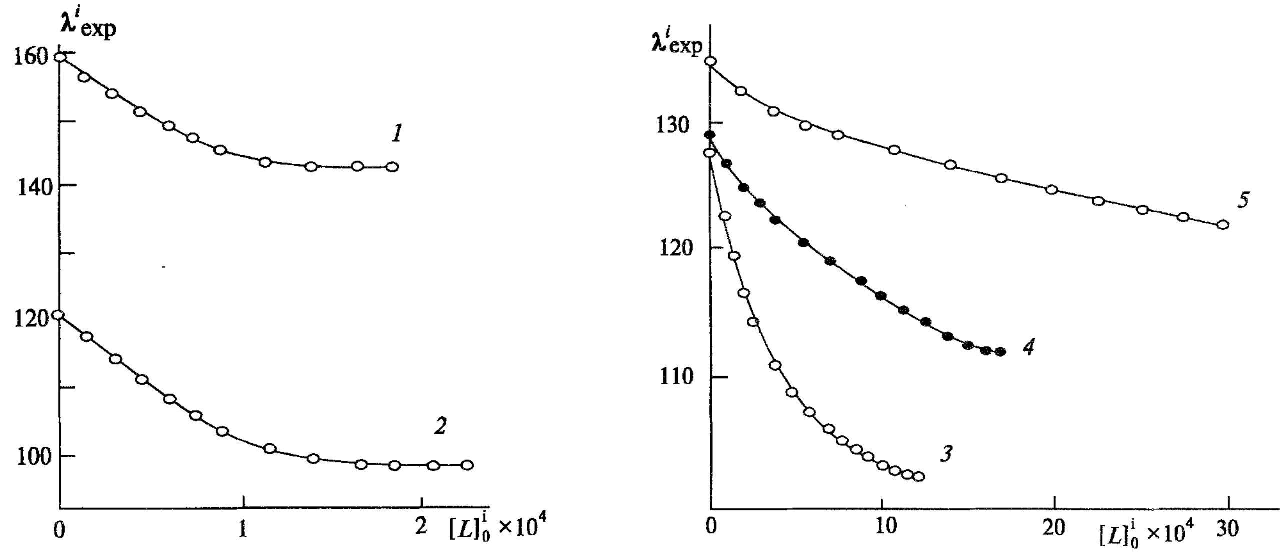

Fig. 2. Equivalent electroconductivity λ^i_{exp} (Ohm^{-1} cm^2 mol^{-1}) of 1.0 · 10^{-4} *M* solutions of alkali-metal salts as a function of the concentration of monopodand **1e**, $[L]^i_0$ (*M*), in anhydrous CH_3CN: *1*, $LiClO_4$; *2*, $NaBPh_4$; *3*, $KBPh_4$; *4*, $RbBPh_4$; *5*, $CsBPh_4$.

podands **1** with respect to the large K^+, Rb^+, and Cs^+ cations monotonically increases, as a rule, with increases in *n* and *m* in both solvents (Fig. 1). These facts have been noted and discussed repeatedly in the literature.[13–15] They were usually attributed to an increase in a degree of cooperativity of ion—dipole interactions of the donor ligand centers on complex formation with M^+.*

As follows from the comparison of Figs. 1*a* and 1*b*, the stability of the complexes M^+L decreases along the series Li > Na > K > Rb. In the THF—$CHCl_3$ system this sequence holds completely only for «short» monopodands **1a—c** (n = 0÷2), while in the case of monopodands **1d—f** (n = 3÷5) it is not valid for the Li^+ cation due to the «underestimated» (in comparison with those expected from the data on CH_3CN) values of log*K* for the corresponding Li complexes. Indeed, while the appreciable decrease in the values of lg*K* for the complexes with the Na^+, K^+, and Rb^+ cations in CH_3CN (ε = 37.5) as compared with THF—$CHCl_3$ (ε = 7.6 and 4.8) may be attributed to the larger dielectric constant of CH_3CN, the lg*K* values for Li^+ complexes are almost identical, regardless of the dielectric constant of the medium. It should also be emphasized that the differences between the values of lg*K* for the Li^+ and Na^+ complexes with **1b**, **1c**, and, evidently, **1a** measured in CH_3CN are much greater than those in the THF—$CHCl_3$ solutions, i.e., the Li/Na selectivity of these ligands increases in CH_3CN. Such a «lithium anomaly» is evidently related mainly to the different solvating abilities of THF* and CH_3CN toward each specific alkali-metal cation M^+. As we demonstrated[11] by analyzing data on the free energies of transfer of M^+ ΔG^0_{tr} (M^+, $H_2O \rightarrow Solv$) from water to an organic solvent,[17] the solvating ability of CH_3CN decreases markedly as the radius of the alkali-metal cation decreases, while the solvatability of M^+, in contrast, increases dramatically in THF. This fact is reflected in the values of ΔG^0_{tr} (M^+, THF$\rightarrow CH_3CN$). The value for Li^+ is close to 12 kcal mol^{-1}, which is much higher than the corresponding values for other M^+ (ΔG^0_{tr} = 6 kcal mol^{-1}, −0.5 kcal mol^{-1}, −4.5 kcal mol^{-1}, and −5 kcal mol^{-1} for Na^+, K^+, Rb^+, and Cs^+ cations, respectively). Thus, in THF Li^+ is solvated more strongly than the other akali-metal cations, while in MeCN, in contrast, it is solvated least strongly. In our opinion, it is the increased solvation of the Li^+ cation by THF molecules that can explain the «abnormal lowering» of the value of lg*K* for Li complexes with monopodands **1** in THF—$CHCl_3$, as well as the more pronounced Li/Na selectivity of ligands **1** in CH_3CN as compared with THF—$CHCl_3$. Similar laws governing the behavior of monopodands having *o*-(diethoxyphosphinoyl)phenyl terminal groups were discussed in greater detail in an earlier publication of ours.[11]

We should dwell some more on the results of the determination of lg*K* for the complexes of monopodands **1e** (n = 4) with Li^+, Na^+, and K^+ cations, obtained by conductometry (this work) and by calorimetric titration[2]

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*It is noteworthy that the monotonic increase in the values of lg*K* for K^+, Rb^+, and Cs^+ cations parallels the continuous variation of the coordination numbers of these cations from 6 to 12 (Ref.[16]).

*According to our data for monopodands **1**, the values of lg*K* for M^+L in THF and the THF—$CHCl_3$ system are practically the same (see also Ref.[11]).

in CH_3CN. As we know,[10,11] the calculation of $\lg K$ for M^+L from conductometric data is based on the assumption that only 1:1 complexes exist in the systems under study, and the use of unassociated salts under conditions of high dilution is mandatory. The calculations of $\lg K$ and the thermodynamic parameters were carried out[18] from the calorimetric data with statistical selection of the sum of the equilibria in the solution which best fits the experimental data, i.e., with consideration of the possibility of the formation of complexes with 1:1, 1:2, 2:1, and other compositions in various combinations. Hence, calorimetric titrations permit only indirect estimation of the compositions of the complexes that are actually formed in the solution. An appreciable discrepancy between the data from the two methods obtained with consideration of only 1:1 complexes by ligand **1e** is discovered for the Na^+ cation ($\lg K_{cond}$ = 4.54 for the unassociated salt $NaBPh_4$ and $\lg K_{cal}$ = 3.82 for NaNCS*) and, in our opinion, is due to the participation of the thiocyanate anion in complex formation. The discrepancy is also revealed by comparing the values of $\lg K_{cal}$ for unassociated ($LiClO_4$ and $KBPh_4$) and associated (LiNCS and KNCS)** salts. The calorimetric titrations for the two lithium salts indicate[2] that two types of complexes having 1:1 (M^+L) and 2:1 (M^+_2L) compositions and the values $\lg K^1{}_{cal}$ = 3.5 and $\lg K^2{}_{cal}$ = 2.5 for the associated salt (LiNCS) and $\lg K^1{}_{cal}$ = 4.36 and $\lg K^2{}_{cal}$ = 2.70 for the unassociated salt ($LiClO_4$), respectively, form in CH_3CN. Therefore, direct comparison of the results of two methods seems to be virtually impossible. It should be stressed that the conductometric method provides indirect evidence in favor of the formation of a 1:1 complex in CH_3CN, specifically for the lithium complexes of monopodand **1e** and its isodentate analog with *o*-(diethoxyphosphinoyl)phenyl terminal groups. The latter are characterized by high values of $\lg K_{cond}$ (5.48 and 5.73, respectively[11]). As follows from Fig. 2 (curves *1* and *2*), the plots of the dependence of the experimental equivalent conductivity λ^i_{exp} of a solution of $LiClO_4$ ($1.0 \cdot 10^{-4}$ *M*) in MeCN on the total concentration of the ligand $[L]^i_0$ in the solution are nonlinear, and the curves reach a plateau at a concentration ratio $M^+:L \approx 1:1$. Similar plots of the dependence of λ^i_{exp} on $[L]^i_0$ were also observed for the cation Na^+ at high values of $\lg K$ (≥ 5). We note that in the case of the formation of 1:1 complex at $K = \infty$, these plots should theoretically be strictly linear up to $M^+:L$ = 1:1 and should then reach a plateau abruptly. For moderate values of $\lg K$, the plots of the dependence of λ^i_{exp} on $[L]^i_0$ do not reach a plateau and thus do not allow even indirect estimation of the composition of the complex formed in the solution (Fig. 2, curves *3—5*).

Thus, the complexing ability of monopodands **1** toward alkali-metal cations in CH_3CN is at least equal or even superior to that of the most effective crown ethers (Table 1). At the same time, they have high Li/Na selectivity, which is not typical of either crown ethers[18,21] or glymes.[11]

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*We were unable to find quantitative data on the association of NaNCS in MeCN. The association constants of LiNCS and KNCS are equal to 1730—1800 L mol^{-1} (Ref.[19]) and 38.2 L mol^{-1} (Ref.[20]), respectively. Apparently, the use of similar salts, e.g., alkali-metal thiocyanates, does not permit the complete exclusion of the effect of the anion of the salt on complexation due to the differences in the association constants of salts with the same anion.

**We note that differences of 0.4 of a unit between the values of $\lg K$ for complexes obtained by different authors using the same experimental methods for similar systems are not rare, let alone the discrepancies between the values of $\lg K$ obtained by different authors using different methods.[21]

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Received April 3, 1992