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The Synthesis and Complex Forming Capacity of Phosphorus-containing Macrocycles

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The review considers questions concerning the synthesis and complex-forming capacity of macrocyclic compounds containing in the ring phosphorus atoms with different degrees of coordination (from three to five) as well as macroheterocycles with phosphorus-containing side chains (lariat compounds). The introduction of the phosphoryl group into the macrocycle lowers the stability of the complexes of the macrocyclic compounds with alkali metals and reduces the selectivity compared with the analogous crown-ethers. Only the lithium cation in the case of macrocyclic phosphine oxides is an exception. Lariat macrocycles are promising: the phosphorus fragment ensures the effective additional binding of the cation imparting a high stability to the complex.
The bibliography includes 191 references.

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I. INTRODUCTION

The discovery by Pedersen[1] in 1967 of the complex forming properties of macrocyclic polyethers (crown-ethers) in relation to alkali and alkaline earth metal cations has had a revolutionary influence on organic synthesis, which may be compared only with the influence by another major event in organic chemistry—the discovery of the method of synthesis in two-phase systems using phase transfer catalysts.[2] The discovery of crown-ethers gave rise to a powerful wave of studies not only on the use of the complex forming phenomenon in various branches of chemistry but also on the synthesis of new macrocyclic complex forming agents. Despite the fact that the principle of the macrocyclic binding of a metal was known before the discovery of crown-ethers both in the field of natural products (porphyrin and corrin complexes,[3-7] cyclic peptides, cyclic depsipeptides[8]) and among synthetic complex forming agents (phthalocyanine dyes,[9,10] certain other nitrogen-containing macrocycles[11]), only the discovery of crown-ethers has made this principle a guiding light in the search for new complex forming compounds. The "chelation" principle, which until recently predominated in the construction of new complex forming agents, became of secondary importance.

A large field of the synthesis of macrocyclic complex forming substances, which embraces increasing numbers of new elements, including phosphorus, has arisen on the basis of the new approach. The first studies on the specific synthesis of phosphorus-containing macrocyclic compounds were published in 1974 in France and in the USA. Soviet investigations on this problem began to be published since 1976. From the very beginning, two almost independent aspects arose in studies on the synthesis and properties of phosphorus containing macrocycles: (1) the preparation of macrocyclic compounds of tervalent phosphorus, mainly phosphines, and (2) the synthesis of phosphoryl macrocycles. The first aspect is related genetically to the chemistry of ligands for transition metals (phosphines and polyphosphines) and the second to the chemistry of phosphoryl extractants.

The data in the review are described in accordance with this subdivision into two aspects: the macrocyclic compounds with a tervalent phosphorus atom are described initially and this is followed by a description of the phosphoryl and thiophosphoryl macrocycles—compounds of pentacoordinate phosphorus: in conclusion, data are presented on the complex forming capacity of phosphorus-containing macrocycles.

In contrast to the reviews already published, devoted to the synthesis of phosphorus-containing macrocycles[12] and the complex forming compounds of some of them,[13] the aim of the present communication is an exhaustive description of the literature and analysis of the likely usefulness of individual aspects of the field of phosphorus-containing macrocyclic compounds.

II. MACROCYCLIC COMPOUNDS OF TRICOORDINATE PHOSPHORUS

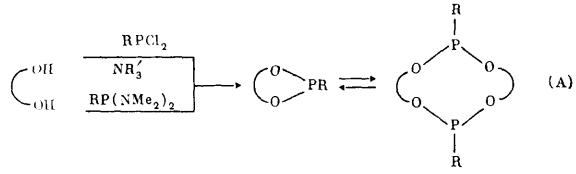
Despite the fact that the first ten-membered phosphorus-containing macrocycles of the phosphite type (acid and neutral) were obtained as early as the end of the 1940's,[14] i.e. long before the discovery of crown-ethers, specific research in this field was not begun until the 1970's. The majority of the macrocyclic tervalent phosphorus acid esters are phosphonites. These compounds have not acquired independent importance because of their instability, although they have come to be used as the starting materials for the synthesis of macrocyclic phosphonates and especially phosphonothioates, which are stable.

1. Macrocyclic Phosphonites

The principal method of synthesis of macrocyclic phosphonites [method (A)] is the dimerisation or oligomerisation of cyclic phosphonites (ring size ranging from five to eight atoms). The capacity of such compounds for oligomerisation has been frequently

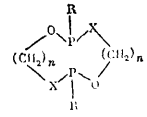
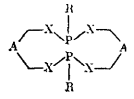
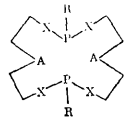
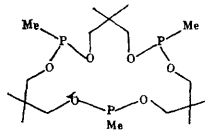
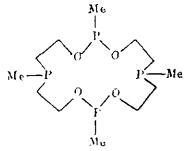
noted in the literature,[15-18] but a detailed investigation of the oligomerisation of cyclic phosphonites and their derivatives as a method of synthesis of phosphorus-containing macrocycles has been undertaken only recently.[19-29]

The cyclic phosphonites, obtained by the interaction of a diol with alkyldichlorophosphine or an alkyl phosphonodiamidite in ether, dimerise spontaneously and oligomerise:



The oligomerisation is reversible. The equilibrium shifts towards the initial compound on heating (distillation) or dilution of the solution. The macrocyclic phosphonites (I), (IIa–c), (IIIa–g), (IV), and (V), listed in Table 1, were therefore investigated mainly by NMR. The products of the addition of sulphur—the corresponding phosphonothionates—are stable compounds (they will be examined in Section III).

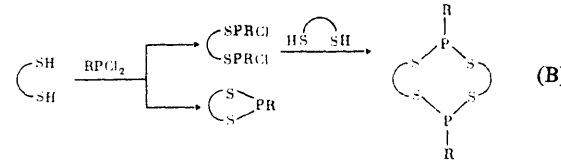
Table 1. Macrocyclic phosphonites.

Compound	Formula	Substituents	Refs.
(Ia–f)		$n = 2$, X = O, R = Me (a), Ph (b) cyclohexyl (c), t-Bu (d) X = NMe, R = Ph (e) $n = 4$, X = O, R = t-Bu (f)	[19,20] [20] [21] [25]
(IIa–e)		A = CMe_2, X = O, R = Me (a) Et (b), iso-Pr (c) A = CH_2, X = S, R = Me (d) t-Bu (e)	[22] [23] [23] [24]
(IIIa–i)		A = CH_2, X = O, R = Me (a) A = CMe_2, X = O, R = Me (b) A = S, X = O, R = Me (c) A = O, X = O, R = Me (d), Ph (e) A = NMe, X = O, R = Me (f) A = N-Bu-t, X = O, R = Ph (g) A = S, X = S, R = Me (h), t-Bu (i)	[29] [23,29] [23,29] [23,26] [29] [30] [26,27]
(IV)		—	[22]
(V)		—	[28]

The rate of dimerisation depends on the structure of the phosphonite. Dioxaphospholans dimerise fastest and are followed in this respect by dioxaphosphorinanes and dioxaphosphepans.[25] It has been shown that the oligomerisation of dioxaphosphorinanes is accelerated in the presence of the following series of substituents at the phosphorus atom:[25]

$$Ph \ll Me < Et < iso\text{-}Pr < t\text{-}Bu.$$

Dimerisation does not occur in those cases[23] where the substituent of this kind is an electronegative atom or a group of atoms with unshared electron pairs (F, Cl, OMe, OPh, NMe_2). Dithia- and diaza-phospholans and dithia- and diazaphosphorinanes do not oligomerise either.[21,23,24]† Oxazaphospholans do oligomerise;[21] the process evidently proceeds via the dissociation of the P–O bond. Despite the fact that dithiaphospholans do not dimerise, the interaction of alkyldichlorophosphine with dithiole leads not only to cyclic phosphonodithioites but also to their dimers.[23,24,27] It has been shown that the latter are formed via intermediate metastable bischlorides:



The macrocycles (IId, e) and (IIIh, i) have been obtained in this way [method (B)]. The replacement of the endocyclic oxygen atoms by sulphur stabilises the dimers so much that it is possible to isolate their *cis*- and *trans*-isomers by column chromatography [compounds (IIe) and (IIIh, i)]. Heating and/or dilution of a solution of one of the isomers of the dimer leads to the formation of the second isomer and the monomer.

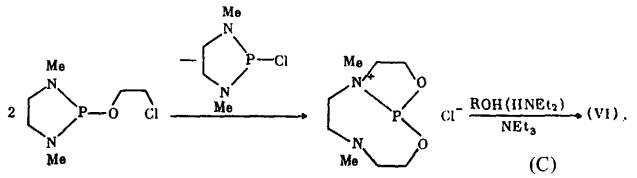
The ratio of the diastereoisomers of the 10- and 12-membered macrocycles is determined by the size of the substituent at the phosphorus atom: the macrocycle (Id), for example, is formed only as the *trans*-isomer. For the 16-membered macrocycles (IIIh, i), the ratio of the isomers becomes statistical. In the oligomerisation of 2,5,5-trimethyl-1,3,2-dioxaphosphorinane in concentrated solutions (~50%),[22] the corresponding *cis*- and *trans*-trimers (IV) were isolated together with the dimers (IIa). One should note that in all cases of oligomerisation polymeric compounds of a known structure (cyclic or linear) are also formed. Their molecular weight varies from 2000 to 15 000 (established after the addition of sulphur).

2. Macrocyclic Phosphites

A sufficiently general method of synthesis of macrocyclic phosphites has not been devised. There exist only individual examples of the preparation of particular macrocycles. Thus diazaphospholans, which are incapable of oligomerising as already mentioned above, can nevertheless be used[32] for the preparation of macrocyclic phosphites in the presence of the β-chloroethoxy-group in the molecule [method (C)]. Such a diazaphospholan is converted quantitatively and spontaneously into an ammonium salt, the exchange of the chlorine atom in which by an alkoxy-group[32,33] or amino-group[34]

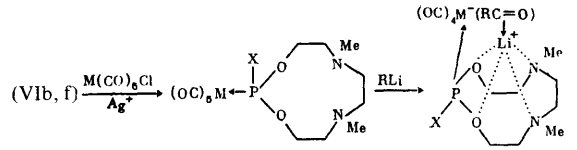
†The effect of the structure of cyclic compounds on their tendency to dimerise has been examined[31] from the standpoint of the concept of antibonding orbitals.

leads to the formation of 11-membered macrocycles (VI) (Table 2):



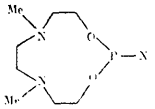
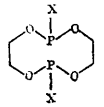
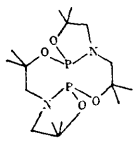
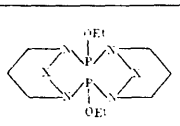
(C)

The quaternisation is accelerated in polar solvents (acetonitrile). The complexes of the macrocycle (VI) with molybdenum or tungsten pentacarbonyls readily interact with aryl- or alkyl-lithium reagents,[34] forming lithium benzoylate or acylate complexes, which are stable by virtue of their macrocyclic nature:



The rhodium complexes obtained from the macrocyclces (VIa–e), having the composition RhCl(CO).L and $RhCl(C_2H_4).L$, are promising catalysts of the hydroformylation of olefins.[33]

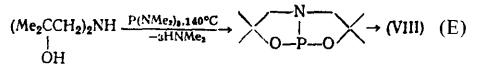
Table 2. Macrocyclic phosphites.

Compound	Formula	X	Refs.
(VIa–f)		OMe (a), OEt (b), OCH(Me)Et (c)	[32,33]
		OCH(Me)Pr (d), O–  (e)	[33]
		NEt_2 (f)	[34]
(VII)		OCH_2CH_2Cl	[35]
(VIII)		—	[36]
(IXa, b)		CH_2CH_2 (a), o-C_6H_4 (b)	[37]

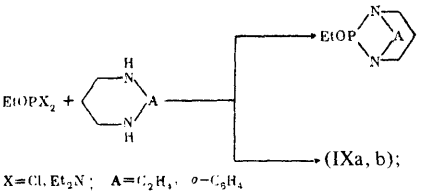
Another method of synthesis [method (D)] of macrocyclic phosphites involves the condensation of two molecules of tri(β-chloroethyl) phosphite with liberation of dichlorethane and the formation of the dimeric phosphite (VII) (Table 2), which is entirely stable.[35]

$$2\,(ClCH_2CH_2O)_3P \xrightarrow[-2ClCH_2CH_2Cl]{\Delta} \text{(VII)} \quad \text{(D)}$$
20%

In contrast to the monocyclic phosphoromonoamidites, which do not dimerise,[23] the bicyclic dialkyl phosphoramidite, obtained[36] from di(β-hydroxyalkyl)-amine and phosphorous tris(*NN*-dimethyl)triamide, is converted irreversibly and stereoselectively on heating into the dimer (VIII) [method (E)] (Table 2), whose structure has been established by X-ray diffraction:



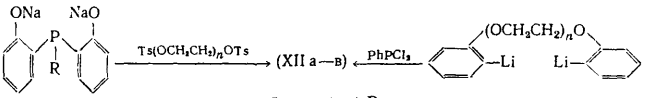
The interaction of ethyl phosphordichloridite or ethyl phosphorodi-imidite with cyclic diamines probably leads not to the expected product but to the dimer (IX) for the same reason:[37]



3. Macrocyclic Phosphines

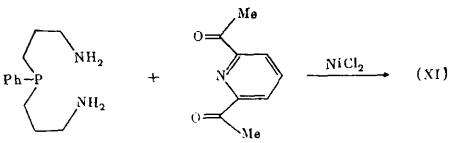
The field of macrocyclic phosphines and polyphosphines is probably the most thoroughly developed branch of the chemistry of phosphorus-containing macrocycles. More than 40 free macrocyclic ligands of the phosphine type, containing between one and four phosphorus atoms, frequently together with other heteroatoms (nitrogen, oxygen, sulphur, and arsenic), are now known. A series of macrocyclic phosphines have been obtained only in the form of transition metal complexes. Unusual catalytic properties are to be expected from complexes of this type. The stabilising capacity of macrocyclic phosphines in relation to the lowest valence states of transition metals is of interest.

The crown-ethers (Xa–c) (Table 3) containing one phosphorus atom have been obtained both by alkylating the diphenoxides of phosphorus-containing bisphenols with ditosylates of oligo(ethylene glycols) and by the interaction of dichlorophenylphosphine with organic dilithio-derivatives of polyethers:[38]



$n = 4, 5$; R=Ph, t-Bu.

A whole series of macrocycles in the form of metal complexes have been synthesised by the interaction of diketones with phosphine-containing diamines. Thus compound (XI) (Table 3) has been obtained from diacetylpyridine in the presence of $NiCl_2$:[39]



Its reduction with sodium tetrahydroborate yielded the macrocycle (XII) (Table 3). The complexes of the pentadentate macrocycle (XIII) have been synthesised analogously from diaminodiphosphines and diacetylpyridine in the presence of $Cd(ClO_4)_2$ or $AgClO_4$,[40] while the tetradentate complexes (XIVa, b) have been obtained[41,42]

Table 3. Macrocyclic phosphines.

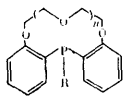
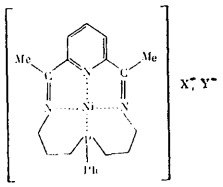
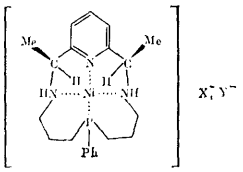
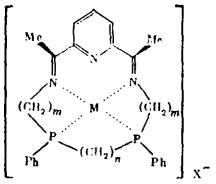
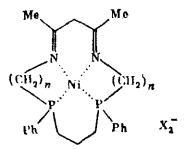
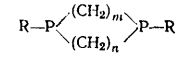
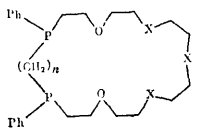
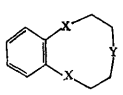
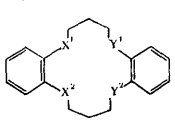
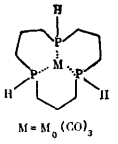
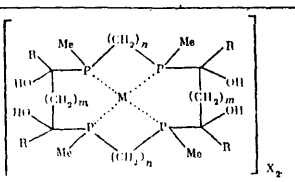
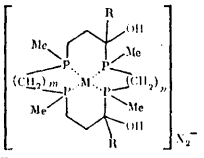
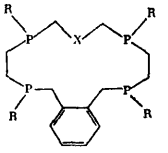
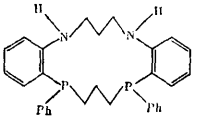
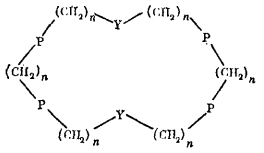
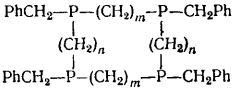
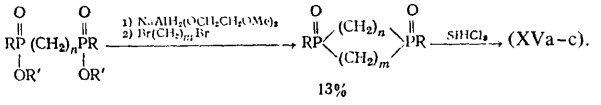
Compound	Formula	M, R, X, Y, *m*, *n*	Yields, %	Refs.
(Xa–c)		*n* = 3, R = Ph (a) *n* = 4, R = Ph (b) *n* = 3, R = t-Bu (c)	11 11 29	[38] [38] [38]
(XIa–c)		X = Br, Y = PF_6 (a) X = I, Y = PF_6 (b) X = Y = PF_6 (c)	— — —	[39] [39] [39]
(XIIa, b)		X = Y = PF_6 (a) X = I, Y = PF_6 (b)	— —	[39] [39]
(XIIIa–e)		M = Ag, *m* = 3, *n* = 2, X = ClO_4, BPh_4 (a) M = Ag, *m* = *n* = 3, X = ClO_4, BPh_4 (b) M = Cd, *m* = 3, *n* = 2, X = $(ClO_4)_2$, $(BPh_4)_2$ (c) M = Cd, *m* = *n* = 3, X = $(ClO_4)_2$, $(BPh_4)_2$ (d)	10—15 50—70 15—25 20—30	[40] [40] [40] [40]
(XIVa, b)		X = PF_6, *n* = 2 (a), *n* = 3 (b)	30, —	[41 42]
(XVa–h)		R = iso-Pr, *m* = *n* = 8 (a) *m* = *n* = 10 (b) *m* = 10, *n* = 12 (c) R = CH_2Ph, *m* = 3, *n* = 4 (d) *m* = 2, *n* = 5 (e) *m* = 4, *n* = 4 (f) *m* = 4, *n* = 5 (g) R = Ph, *m* = 4, *n* = 4 (h)	65, 81 83, 80 75, 92 78 83 80 90 89	[43] [43] [43] [79, 80] [79, 80] [79, 80] [79, 80] [79, 80]
(XVIa–c)		*n* = 3, X = NTs (a) X = NH (b) *n* = 2, X = O (c)	68 — —	[44] [44] [44]
(XVIIa–l)		X = Y = PPh (a) X = PPh, Y = S (b) X = PPh, Y = O (c) X = PPh, Y = NPh (d) X = PPh, Y = NMe (e) X = PPh, Y = CH_2 (f) X = S, Y = PPh (g) X = AsMe, Y = PPh (h) X = PPh, Y = AsPh (i) X = PH, Y = S (k) X = PH, Y = NMe (l)	34 51 32 56 42 33	[45, 47] [45, 47] [45, 47] [45, 47] [45, 47] [45, 47] [45, 47] [48, 52] [48, 52] [53] [53]
(XVIIIa–h)		$X^1 = X^2 = Y^1 = Y^2$ = PPh (a) $X^1 = X^2$ = PPh, $Y^1 = Y^2$ = S (b) $X^1 = X^2$ = PPh, $Y^1 = Y^2$ = NMe (c) $X^1 = X^2$ = PPh, $Y^1 = Y^2$ = O (d) $X^1 = X^2$ = PPh, $Y^1 = Y^2$ = AsMe (e) $X^1 = Y^1$ = PPh, $X^2 = Y^2$ = S (f) $X^1 = Y^2$ = PPh, $X^2 = Y^1$ = S (g) $X^1 = Y^1 = Y^2$ = PPh, X^2 = S (h)	11, 25 45 18 38 20 — — —	[45, 46, 51] [45, 46, 51] [45, 46, 51] [45, 46, 51] [52] [52] [52] [52]

Table 3 (contd.).

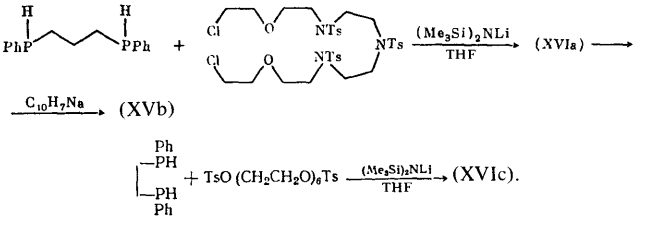
Compound	Formula	M, R, X, Y, *m*, *n*	Yields, %	Refs.
(XIX)	 M = $Mo(CO)_3$	—	85	[58]
(XXa–e)		*m* = 1, *n* = 2, R = H, M = Pd, X = Cl (a) R = Me, M = Ni, X = Br (b) R = Me, M = Pd, X = Cl (c) *m* = 0, *n* = 3, R = Me, M = Pd, X = Cl (d) R = Ph, M = Pd, X = Cl (e)	91 89 20.70 92 71	[59,60] [59,60] [59,60] [59,60] [59,60]
(XXIa–f)		X = Cl, R = H, *m* = 2, *n* = 2, M = Ni, Pd (a) *n* = 3, M = Ni, Pd (b) X = Cl, R = Me, *m* = 2, *n* = 2, M = Pd, Pt (c) *m* = 2, *n* = 3, M = Ni, Pd, Pt (d) X = Cl, R = Me, *m* = 3, *n* = 2, M = Pd (e) *m* = 3, *n* = 3, M = Pd (f)	91—95 91—95 91—95 91—95 91—95 91—95	[61] [61] [61] [61] [61] [61]
(XXIIa, b)		X = CH_2, R = Ph (a) X = *o*-C_6H_4, R = Me (b)	50 27	[62,63] [64]
(XXIII)		— —	—	[66]
(XXIVa–d)		*n* = 2, Y = O (a) Y = S (b) Y = NPr (c) *n* = 3, Y = S (d)	12 14 — 13	[67,69] [68,72] [71] [78]
(XXVa–c)		*m* = 3, *n* = 3 (a) *m* = 3, *n* = 4 (b) *m* = 4, *n* = 4 (c)	85 77 89	[79,80] [79,80] [79,80]

from acetylacetone in the presence of $NiCl_2$ (Table 3). The macrocycle (XIVb) has been shown to have a *meso*-structure by X-ray diffraction.

Macrocyclic bisoxides of bisphosphines have been synthesised by reducing polymethylenebisphosphinates with sodium bis(2-methoxyethoxy)aluminium hydride followed by their alkylation (without isolation) by dibromoalkanes under the conditions of high dilution (10^{-3} M).[43] Their reduction gave rise to the corresponding bisphosphines (XIVa–c), isolated in the form of *cis*- and *trans*-isomers (Table 3):

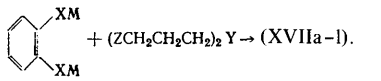


The phosphinocrown-ethers (XVIa–c) have been obtained by alkylating, under the conditions of high dilution, lithium 1,2-ethylene- and 1,3-propylenediphosphides, generated in solution, with αω-dichloro-derivatives of polyaminoethers and the ditosylates of polyether diols (Table 3):[44]



The *syn*- and *anti*-isomers of the macrocycle (XVIa) have been isolated via their complexes with $NiCl_2$. Their detosylation with sodionaphthalene takes place without isomerisation. The complex $PdCl_2.L$ has been obtained from the *anti*-isomer (XVIb), while the macrocycle (XVIc) gave rise to the complexes $NiCl_2(BF_4)_2.L$ and $Ni(NCS)_2(NCS)_2.L$.[44]

A series of 11-membered macrocyclic phosphines (XVIIa–l) (Table 3), containing between one and three phosphorus atoms in the ring together with other heteroatoms, have also been synthesised under the conditions of high dilution:[45–53]

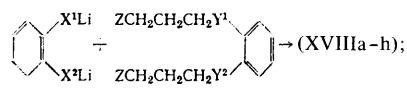


$$+ (ZCH_2CH_2CH_2)_2Y \rightarrow (XVIIa\text{–}l).$$

M = H, Li; X, Y = PH, PPh, AsPh, AsMe,NPh, NMe, S, O, CH_2; Z = Cl, Br, OSO_2Me

The study of the steric structures of compounds (XVIIa, d, e, g) established the *cis*-orientation of the phenyl substituents at the phosphorus atoms. The isomers with the *trans*-configuration were not detected even after heating under conditions promoting the inversion of the tertiary phosphines (xylene, 135 °C, 1 h). Carbonyl-containing complexes with a series of transition metals (Cr, Mo, and W)[49,50,54] and complexes with $NiCl_2$ and CuCl [50,54] have been obtained from the macrocycles (XVIIa, d, e) and the structures of some of them have been determined.[50,54] The electrochemical properties of the carbonyl complexes of the macrocycles (XVIIa, e) have been investigated.[55] Three geometrical isomers are possible for the macrocycles (XVIIh, i), but compound (XVIIh) exists only in two isomeric *meso*-forms and only one isomer has been isolated for the macrocycle (XVIIi).

The tetradentate macrocycles (XVIIIa–h) (Table 3), containing phosphorus, nitrogen, arsenic, oxygen, and sulphur atoms in the ring, have also been synthesised under the conditions of high dilution:[46,51,56]

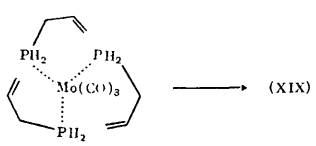


$$\rightarrow (XVIIIa\text{–}h);$$

X=PPh, S; Y=PPh, S, NMe, O, AsMe; Z=Cl, OH, OSO_2Me

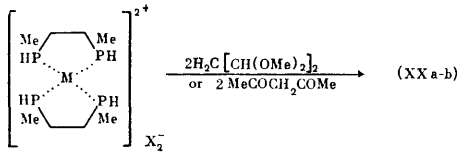
The starting compound in the synthesis of compounds (XVIIIf–h) (Table 3) was 2-(phenylphosphino)thiophenol.[56] The *cis*- and *trans*-isomers of the macrocycles (XVIIIa, f–h) have been isolated and for compounds (XVIIIf–h) the structures have also been established.[56] Four different types of complexes are formed by 11- and 14-membered ligands with cobalt halides depending on the reaction conditions and the structure of the macrocycle.[57]

A series of polyphosphine macrocycles have been obtained in the form of complexes or as free ligands by the matrix cyclisation method, i.e. by the cyclisation of phosphine ligands already bound in complexes. Thus a molybdenum tricarbonyl complex, containing three allylphosphine molecules, gives rise to a high yield of the complex (XIX) with a triphosphine macrocycle (Table 3) as a result of the intermolecular interligand free-radical addition of phosphino-groups to the double bonds:[58]



(XIX)

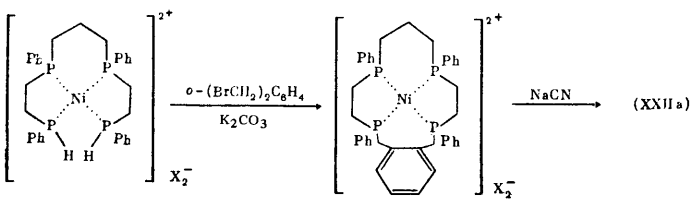
The tetradentate 14-membered cyclic adducts (XXa–c) (Table 3) have been obtained analogously by the interaction of diphosphine complexes of nickel(II) and palladium(II) with malonic dialdehyde or with acetylacetone:[59,60]



(XXa-b)

The macrocyclic complexes (XXb, c) were then obtained in the form of two isomers. The complexes (XXd, e) [59,60] and (XXIa–f) (Table 3)[61] have also been synthesised by a similar method.

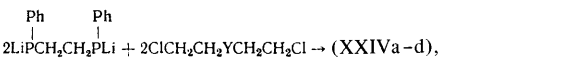
Alkylation of the nickel complex of a tetraphosphine ligand with *o*-xylylene dibromide in the presence of K_2CO_3 led to the synthesis of a macrocyclic complex, from which the macrocyclic tetraphosphine (XXIIa) (Table 3) was isolated by treatment with NaCN:[62,63]



(XXIIa)

The macrocycle (XXIIb) was obtained analogously from 1,4-di-(methylphosphino)-ethane and *o*-xylylene dichloride using K_2PdCl_4 as the matrix.[64] Complexes having the compositions $PdCl_2.L$ and $NiBr_2.L$ were synthesised from this compound.[64] Alkylation of the amino-group of the nickel *meso*-complex of 1,3-di[(*o*-aminophenyl)-phenylphosphino]propane[65] made it possible to obtain the tetradentate ligand (XXIII) (Table 3).[66] The cyclic nature and *meso*-configuration of the ligand have been demonstrated by X-ray diffraction.

The 18-membered macrocyclic phosphines (XXIVa–g) (Table 3) have been synthesised by alkylating the dilithio-derivative of 1,2-di-(phenylphosphino)ethane with the corresponding dihalides containing the oxygen or sulphur atoms or the propylimino-group as the heterofragment Y:[67–75]



$$2LiPCH_2CH_2PLi + 2ClCH_2CH_2YCH_2CH_2Cl \rightarrow (XXIVa\text{–}d),$$

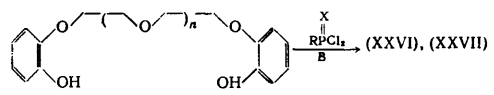
All five possible isomers have been isolated by the ion-exchange chromatography and fractional crystallisation of the metal complexes of the macrocycles. The diastereoisomers obtained show different numbers of binding sites (from 4 to 6). Their structure has been established by the X-ray diffraction analysis of the complexes of the tetraphosphines (XXIV) with the Co^{2+}, Ni^{2+}, and Fe^{2+} cations.[69–78]

A method of synthesis of the oligophosphacycloalkanes (XVd–h) and (XXVa–c) (Table 3), containing two or four phosphorus atoms, based on the reduction of the macrocyclic benzylphosphonium salts of lithium tetrahydroaluminate, has been proposed in Horner's studies.[79,80] The synthesis of the phosphonium salts themselves is examined in Section IV.

III. MACROCYCLIC COMPOUNDS OF TETRACOORDINATE PHOSPHORUS

1. Macrocyclic Phosphonates, Phosphonothioates, Phosphonimidates, and Phosphates

(a) *Macrocycles with a single phosphorus atom.* Studies on the specific synthesis and the physicochemical properties of macrocycles containing one phosphorus atom were first initiated in the USSR. The results of these investigations have been published since 1976. Macrocyclic compounds (Table 4) have been obtained by the reaction of phosphorus acid dichlorides with polyether-bisphenols:[81-90]

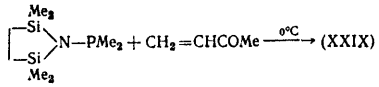


X=O, S, NSO_2Ph; $n = 1, 2$

Methyl di(β-chloroethyl)phosphonate was used as the phosphorus component in the synthesis of single phosphorus atom (Table 4), the corresponding dimers were also isolated in a number of instances (3–18%) [Table 5, compounds (XXVIIa–e)], their formation being promoted by the use of an aprotic solvent (acetonitrile).[82] The employment of the corresponding bisphenoxides instead of triethylamine increases the yield by ~10%.[83] The macrocycles (XXVIg) and (XXVIII) can be obtained only by the latter method because of the low reactivity of the phosphorus-containing fragment.[91,92] $LiClO_4$ was added as the matrix in the synthesis of compounds (XXVIc, d). The use of potassium bisphenoxide ($n = 1$) rather than sodium bisphenoxide ($n = 2$) in the reaction with methyl phosphonodichloridothioate alters the direction of the process—a mixture of the isomeric dimers (XXXVIIe) is obtained instead of the monomeric product (XXVIf) (Table 5).[83] The macrocycles (XXVIIa, b, e) have been synthesised by the high dilution method. It is of interest to note that, when lithium and potassium bisphenoxides are used in the synthesis of compound (XXVIII) instead of sodium bisphenoxide, the yield is reduced from 40 to 3–5%, which the authors believe to be associated with the matrix effect of the Na^+ cation.

The macrocycle (XXVIe) is a mixture of three polymorphic modifications, having different melting points. Their structure was investigated by IR spectroscopy.[87] The macrocycles (XXVIa, c) have been investigated by field desorption method mass spectrometry.[93]

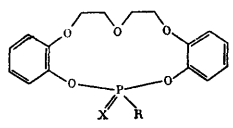
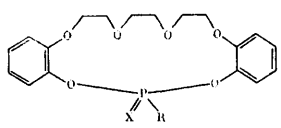
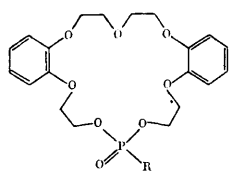
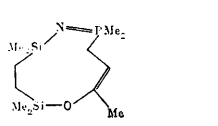
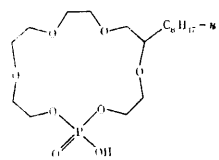
The 10-membered macrocycle (XXIX) (Table 4) has been obtained by adding methyl vinyl ketone to the cyclic phosphinic *NN*-disilylamide:[94]



The slow addition of methyl vinyl ketone to the reaction medium leads mainly to the formation of the (*Z*)-isomer, which is in its turn slowly converted into the (*E*)-isomer.

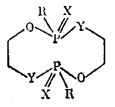
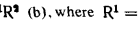
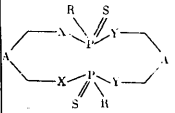
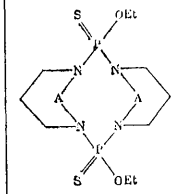
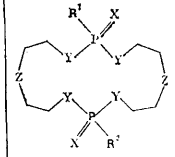
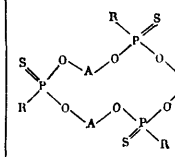
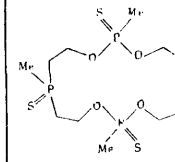
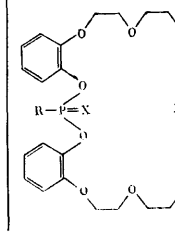
(b) *Macrocycles with two and more phosphorus atoms.* The 10-membered cyclic acid bisphosphite and the dihydrobisphosphonate (XXXIa) (Table 5) were obtained long before interest was aroused in macrocyclic complex-forming agents and an attempt was made to synthesise the acid ethylene phosphite. Later it was shown[95] that, like the cyclic phosphonites, the acid cyclic phosphites oligomerise, the process slowing down on passing from the unsubstituted acid ethylene phosphite to a substituted derivative and further to acid trimethyl phosphite. The reaction is accelerated in the presence of acids and bases. This is evidently why the interaction of phosphorus trichloride with ethylene glycol leads[14] not to the expected ethylene phosphite but to its dimer (XXXIa), which has also been obtained[35] by the condensation of two molecules of di(β-hydroxyethyl) phosphite [analogously to the method (D) for the synthesis of the macrocyclic phosphite (XII) (Table 2)]. The interaction of the diphosphite (XXXIa) with αβ-unsaturated compounds made it possible to obtain the macrocycles (XXXIb) with different side chains (Table 5), which have found applications as antipyrenes for synthetic resins:[96]

Table 4. Macrocycles with a single tetracoordinate phosphorus atom.

Compound	Formula	X, R	Yields, %	Refs.
(XXVIa–i)		X = O, R = Me (a) R = iso-Bu (b) R = Ph (c) R = OPh (d) R = N = PPh_3 (e) X = S, R = Me (f) R = Ph (g) X = NSO_2Ph, R = Ph (h) X = NSO_2Ph, R = N = PPh_3 (i)	17 5 5 7 22 53 17 32 12	[81,82,84] [83] [84] [84] [86,87] [84,85] [85] [86] [86]
(XXVIIa–g)		X = O, R = Me (a) R = Et (b) R = Ph (c) R = OPh (d) R = adamantyl (e) X = S, R = Me (f) R = Ph (g)	52 51 12 14 — 46 24	[90] [90] [88] [88] [89] [88] [88]
(XXVIII)		R=Me	40	[84,91]
(XXIX)		—	—	[94]
(XXX)		—	—	[168]

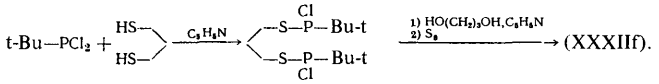
The principal method of synthesis of macrocyclic phosphonates and phosphonothioates with two and more phosphorus atoms in the ring is the oxidation of the corresponding phosphonites or the addition of sulphur to the latter. As already mentioned in the previous Section, macrocycles with tervalent phosphorus are unstable and are

Table 5. Macrocycle with two and more tetracoordinate phosphorus atoms.

Compound	Formula of macrocycle	X, Y, R, A	Refs.
(XXXIa-g)		X=O, Y=O, R=H (a) X=O, Y=O, R=$CH_2CH^1R^2$ (b), where R^1 = COOAlk, CN, $CONH_2$,  R^2=H, Alk X = S, Y = O, R = Me (c), cyclohexyl (d) R = Ph (e), t-Bu (f) X = S, Y = NMe, R = Ph (g)	[14,35] [96] [20] [19,20] [21]
(XXXIIa-h)		X = Y = O, A = CMe_2, Re = Me (a) Et (b), iso-Pr (c) X = Y = S, A = CH_2, R = Me (d), t-Bu (e) X = S, Y = O, A = CH_2, R = t-Bu (f) X = Y = O, A = CH_2, R = t-Bu (g) X = Y = O, A = CH_2, CMe_2CH_2, R = Me (h)	[22,23] [23,24] [24] [25] [23]
(XXXIIIa, b)		A = CH_2CH_2 (a), o-C_6H_4 (b)	[37]
(XXXIVa-k)		X = Z = S, Y = O, R^1 = R^2 = Me (a), Ph (b) X = S, Y = Z = O, R^1 = R^2 = Me (c), Ph (d) X = O, Y = Z = S, R^1 = R^2 = Me (e), t-Bu (f) X = Y = Z = S, R^1 = R^2 = Me (g), t-Bu (h) X = S, Y = O, Z-NMe, R^1 = R^2 = Me (i) X = S, Y = Z = O, R^1Me, R^2 = Ph (k)	[23] [23,26] [27,97] [27,97] [29] [29]
(XXXVa, b)		A=$CH_2CMe_2CH_2$, R=Me (a) A=$CH_2CH_2OCH_2CH_2$, R = Me (b)	[22] [23,29]
(XXXVI)		—	[28]
(XXXVIIa-e)		X=O, R=Me (a) X = O, R = Et (b), OEt (c) X = O, R = OPh (d) X = S, R = Me (e)	[82-84] [83] [84,93] [83,93]

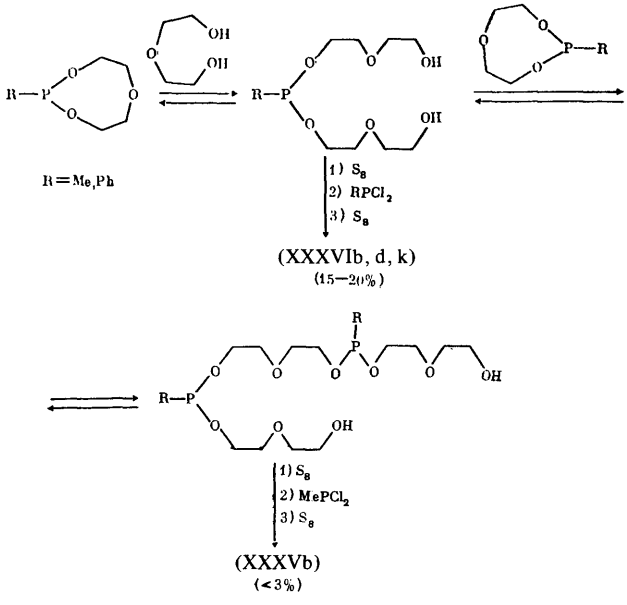
almost always isolated as phosphonates or phosphonothioates. The macrocycles (XXXIc–g), (XXXII)–(XXXIV), (XXXVa), and (XXXVI) (Table 5) have been synthesised in this way.

The stability of the bischloride, formed in the course of the synthesis of macrocyclic phosphonites [method (B)] made it possible to introduce it into the reaction with a diol and to obtain after oxidation the mixed type dimer (XXXIIf):[24]



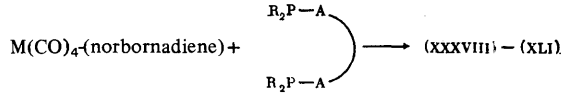
The ease of the opening of the phosphonite ring already mentioned has been used for the synthesis of the macrocyclic phosphonothioates (XXXIVc, d, k) and (XXXVb). The interaction of

diethylene glycol with an eight-membered cyclic phosphonite leads to the intermediate diol, which is capable of reacting with the next phosphonite molecule. The oxidation of phosphorus-containing polyglycols with sulphur, the subsequent interaction with alkyl- or aryl-dichlorophosphine, and the repeated addition of sulphur made it possible to obtain macrocycles containing 2–3 phosphorus atoms:[23,29]



Compounds (XXXIId, e) and (XXXIVe–h) have been studied in detail by NMR.[97] The structure of the *cis*-isomers of the macrocycles (XXXIIa) and (XXXIVh) has been confirmed by X-ray diffraction.[98,99] The complex forming properties of compounds (XXXIVe, f) in relation to uranyl nitrate and $SnCl_4$ have been investigated.[27] Among the macrocyclic dimers (XXXVIIa–e) (Table 5), compound (XXXVIIa) has been studied in greatest detail. Three isomers of this macrocycle have been isolated. The authors believe that one of the factors determining the isomerism is the steric directionality of the phosphoryl groups in relation to the polyether ring. Compound (XXVIIa) has been studied by mass spectrometry[93] and ^1H NMR using lanthanide shift reagents.[100]

The heteronuclear macrocycles (XXXVIII)–(XLI), containing a transition metal atom in the ring (Table 6), have been obtained from the polyether bisphosphites, bisphosphinates, and bisphosphinamidites by reaction with the norbornadiene complexes of molybdenum, chromium, and tungsten tetracarbonyls under high dilution conditions (in 5–70% yields):[101-103]



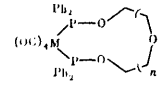
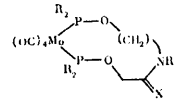
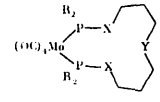
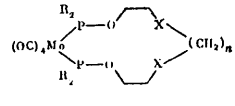
M = Mo, Cr, W; A = O, NH, NMe; R = Alk, Ar; O–Alk, OAr, NR_2

The macrocycles obtained interact effectively with alkali metal cations and form stable products of the reaction with organolithium compounds via the intermolecular coordination of lithium to the polyether ring. On hydrolysis, the latter are capable of giving rise to stable hydroxycarbenes.[104]

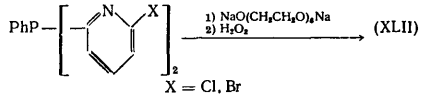
2. Macrocyclic Phosphine Oxides and Their Analogues

Among phosphoryl-containing complex forming agents, phosphine oxides are some of the most effective.[105] This is precisely why macrocyclic phosphine oxides containing, together with phosphorus,

Table 6. Phosphorus-containing macrocycles based on metal tetracarbonyls.

Compound	Formula	M, *n*, X, R	Refs.
(XXXVIIIa–c)		M=Mo, Cr, W; *n*=1 (a), 3 (b), 4 (c)	[101]
(XXXIXa, b)		*n*=2, X=H_2, R=CH_2CH_2OMe (a) *n*=3, X=O, R = H (b)	[102] [103]
(XLa–h)		X = Y = O, R = Et (a), Ph (b), R_2 = OCH_2CH_2O (c) 1,2-OC_6H_4O (d), $NMeCH_2CH_2NMe$ (e) X = Y = NMe, R = Et (f), Ph (g) X = NH, Y = NMe, R = Ph (h)	[101,103] [101,103] [101,103] [103]
(XLIa–f)		X = O, *n* = 2, R = Ph (a); R_2 = OCH_2CH_2O (b) 1,2-OC_6H_4O (c), $NMeCH_2CH_2NMe$ (d) X = NMe, *n* = 2 (e), 3 (f)	[103] [101]

other heteroatoms (O, N) have attracted special attention. Thus the phosphine oxide (XLII) (Table 7) has been synthesised by the reaction of di(halogenopyridyl)phosphine with sodium polyglycolate and subsequent oxidation of the resulting macrocyclic phosphine:[106]



Under conditions analogous to those in the synthesis of the phosphonate macrocycle (XXVIII) (Table 4), the macrocycle (XLIII) (Table 7) was obtained from sodium bisphenoxide di(chloromethyl)-methylphosphine:[107]

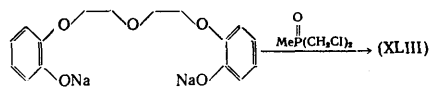
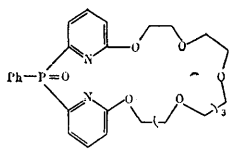
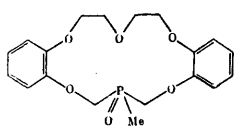
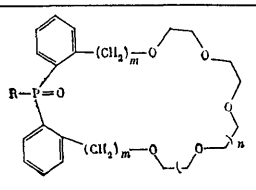
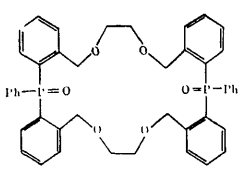
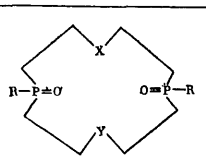
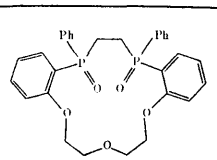
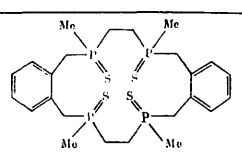
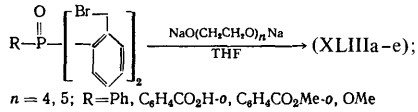


Table 7. Macrocyclic phosphine oxides and their analogues.

Compound	Formula	R, X, Y, *m*, *n*	Yield, %	Refs.
(XLII)		—	47	[106]
(XLIII)		—	15	[107]
(XLIVa-h)		*m*=0, *n*=2, R=Ph (a) *n* = 3, R = t-Bu (c), Ph (b) *m* = 1, *n* = 1, R = Ph (d) *n* = 2, R = Ph (e) *n* = 1, R = $C_6H_4CO_2H$-*o* (f) *n* = 1, R = $C_6H_4CO_2Me$-*o* (g) *n* = 1, R = OMe (h)	— — 69 67 18 — 23	[38] [38] [108] [108] [108] [108] [108]
(XLV)		—	19,22	[108]
(XLVIa-g)		R = Ph, X = Y-absent (a) R—iso-Pr, X = Y = $(CH_2)_4$ (b) X = Y = $(CH_2)_6$ (c) X = $(CH_2)_6$, Y = $(CH_2)_8$ (d) R = Ph, X = Y = CH_2OCH_2 (e) X = Y = *p*-$(CH_2O)_2C_6H_4$ (f) X = CH_2OCH_2, Y = *p*-$(CH_2O)_2C_6H_4$ (g)	— 13 13 13 — — —	[109] [43] [43] [43] [110,111] [110,111] [110,111]
(XLVII)		—	44	[112]
(XLVIII)		—	47	[64]

The phosphine oxides (XLIVa–c) (Table 7) have been synthesised by oxidising the corresponding macrocyclic phosphines (XIIa–c) (Table 3).

The interaction of di(*o*-bromomethylphenyl)-substituted phosphine oxides and phosphinic acids with sodium polyglycolates under high dilution conditions led to the formation of the macrocycles (XLIVd–h) (Table 7):[108]

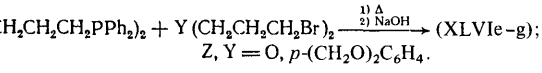


$n = 4, 5$; R=Ph, $C_6H_4CO_2H$-*o*, $C_6H_4CO_2Me$-*o*, OMe

Using ethylene glycol, the bisphosphine bisoxide (XLV) (Table 7) has been synthesised under the same conditions in the form of two isomers (apparently *syn*- and *anti*-). The above study[108] has played a major role in the elucidation of the effect of the phosphoryl group on the complex forming capacity of the macrocycles compared with other coordination centres.

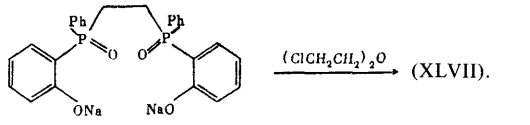
The synthesis of the bisphosphine bisoxides (XLVIb–d) (Table 7),[43] the reduction of which yielded the bisphosphines (XVa–c) (Table 3), was described in the same Section. The pairs of isomers of each macrocycle isolated after the reaction have apparently the *cis*- and *trans*-configurations.

The *trans*-isomer (XLVIa) proved to be the first phosphorus-containing macrocycle whose X-ray diffraction analysis has been carried out.[109] The macrocycles (XLVIe–g) with a more complex structure have been synthesised from an acyclic bisphosphine and the corresponding dibromide via cyclic bis-phosphonium salts (see Section IV) with the aid of the alkaline cleavage of the latter:[110,111]



Z, Y = O, *p*-$(CH_2O)_2C_6H_4$.

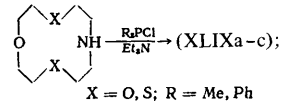
The macrocyclic bisphosphine bisoxide (XLVII) (Table 7) has been synthesised by alkylating the disodium salt of di[phenyl(*o*-hydroxyphenyl)phosphinyl]ethane with chlorex:[112]



The macrocycle (XLVIII) (Table 7) has been obtained by adding sulphur to the tetraphosphine (XXIIb) (Table 3).[64]

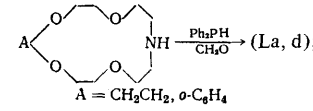
3. Macrocycles with Exocyclic Phosphorus-Containing Groups

Much attention has been devoted recently to the study of crown-ethers modified with various complex forming side groups. Macrocycles containing additional polyether groups have been called lariat (or lasso-like) ethers.[113] Similar phosphorus-containing compounds (Table 8) are obtained by modifying the usual crown-ethers. Thus the macrocyclic phosphinamidites (XLIXa–c) have been synthesised by the reaction of azacrown-ethers with dialkyl- and diaryl-chlorophosphines:[114,115]



X = O, S; R = Me, Ph

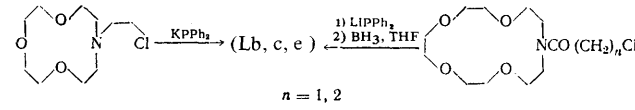
The macrocycles (La, d) (Table 8)[115,116] with phosphinomethyl side groups have been obtained in high yields by a modified Mannich reaction:



A = CH_2CH_2, *o*-C_6H_4

The macrocycle (LI) (Table 8) with four lariat phosphine groups has been obtained analogously from 1,4,8,11-tetra-azacyclotetra-decane.[117] Lariat phosphine ligands form complexes with both transition and alkali metals: complexes of the macrocycles (XLIXa, b) and (La) with Pd, Rh, Ir, Fe(0), and Cu(I) compounds and those of the ligands (XLIXc) and (Ia) with $LiPF_6$ and $NaPF_6$ respectively have been obtained.

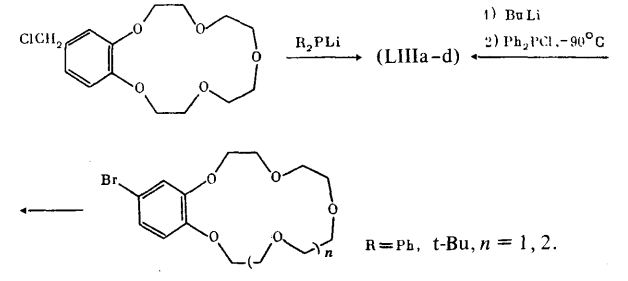
The macrocycles (Lb, c, e), in which the phosphine groups are separated from the polyether ring by 2–3 methylene units, have been synthesised by alkylating lithium (potassium) diphenylphosphite with ω-chloroalkyl derivatives of azacrown-ethers:[115,118]



$n = 1, 2$

The macrocycles (LIIa–e) (Table 8) have been synthesised similarly by the reaction of *NN'*-di(ω-chloroalkyl) derivatives of diaza-crown-ethers and diazathiacrown-ethers with potassium diphenylphosphide generated in solution from PPh_3 and potassium.[118,119] Compounds (LIIa–d) are capable of interacting with both "hard" cations of alkali and alkaline earth metals and with "soft" cations of transition metals via the phosphine. The primary coordination of the cation to the polyether ring and the oxygen atoms in the lariat groups then ensures the *cis*-configuration of the bisphosphine section in the secondary coordination to the transition metal cation. Thus a heteronuclear complex of the macrocycle (LIId) with $CaCl_2$ and $PdCl_2(PhCN)_2$ and the complex of the macrocycle (LIIb) with $Zn(ClO_4)_2$ and $Rh(nbd)_2^+ ClO_4^-$, where nbd = bicyclo[2.2.1]hepta-2,5-diene, have been obtained.[119]

The macrocycles (LIIIa–d) (Table 8)—benzocrown-ethers containing a phosphino-group in the benzene ring—have been synthesised from the corresponding chloromethyl and bromo-derivatives:[120,121]



R=Ph, t-Bu, $n = 1, 2$.

The complexes of these macrocycles with a series of rhodium, iridium, palladium, and tungsten salts have been obtained. The complexes *trans*-$PdCl_2.L_2$ and *trans*-$PdBr_2.L_2$ of the ligands (LIIIc, d) have been shown[121] to be not only reaction catalysts but also to

Table 8. Macrocycles with exocyclic phosphorus-containg groups.

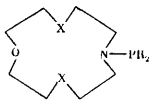
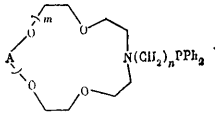
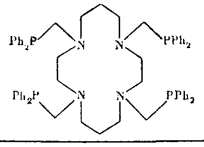
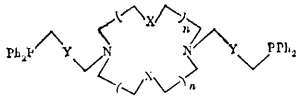
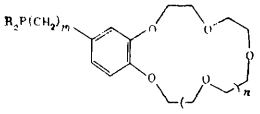
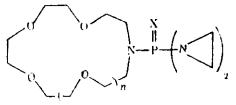
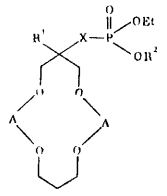
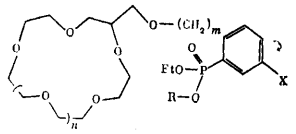
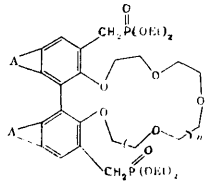
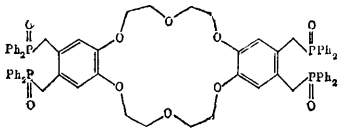
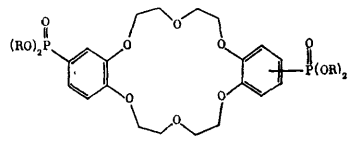
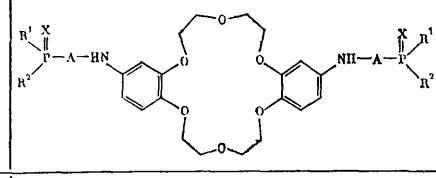
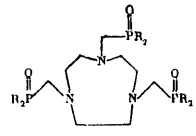
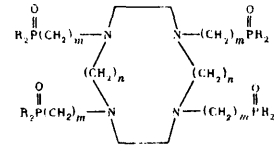
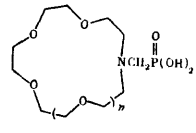
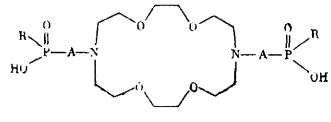
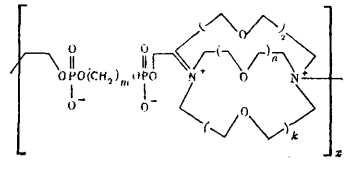
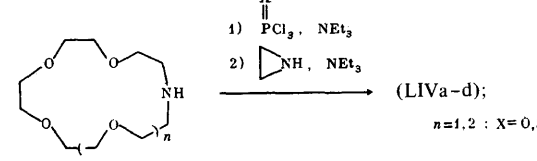
Compound	Formula	A, X, Y, R, *m*, *n*	Yield (after introduction of phosphorus)	Refs.
(XLIXa–c)		X = S, R = Me (a), Ph (b) X = O, R = Ph (c)	— 99	[114] [115]
(La–d)		*m* = 1, A = CH_2CH_2, *n* = 1 (a) *n* = 2 (b) *n* = 3 (c) *m* = 1, A = *o*-C_6H_4, *n* = 1 (d) *m* = 0, *n* = 2 (e)	98 61 34 92 41	[115,116] [115] [115] [115] [118]
(LI)		—	70	[117]
(LIIa–e)		X = S, *n* = 1, Y—absent (a) Y = CH_2OCH_2 (b) X = O, *n* = 1, Y—absent (c) Y = CH_2OCH_2 (d) X = O, *n* = 2, Y = CH_2 (e)	63 75 44 45 45	[118,119] [118,119] [118,119] [118,119] [118,119]
(LIIIa–d)		*m* = 1, *n* = 1, R = Ph (a) R = t-Bu (b) *m* = 0, R = Ph, *n* = 1 (c) *n* = 2 (d)	75 — 92 76	[120] [120] [121] [121]
(LIVa–d)		*n* = 0, X = O (a) *n* = 1, X = O (b) *n* = 0, X = S (c) *n* = 1, X = S (d)	44 63 41 18	[122] [122] [122] [122]
(LVa–e)		A = CH_2CH_2, X = CH_2CH_2O, R^1 = $C_{12}H_{25}$, R^2 = Et (a) A = *o*-C_6H_3(Bu-t), R^1 = H, X = $O(CH_2)_n$, R^2 = H, Et, *n* = 1 (b) *n* = 2 (c) *n* = 3 (d) *n* = 4 (e)	16 42 87 61 77	[123] [124] [124] [124] [124]
(LVIa–e)		*m* = 1, *n* = 1, X = t-Bu, R = H (a) *m* = 0, X = $C_{10}H_{21}$; R = H, Et, *n* = 1 (b) *n* = 2 (c) *n* = 3 (d) *n* = 4 (e)	36 71 61 61 69	[126] [125] [125] [125] [125]
(LVIIa–c)		A = $(CH_2)_4$, *n* = 1 (a) A = CH=CH—CH=CH, *n* = 2 (b) *n* = 3 (c)	84 90 97	[127] [127] [127]
(LVIII)		—	54	[128]

Table 8 (contd.).

Compound	Formula	A, X, Y, R, *m*, *n*	Yield (after introduction of phosphorus)	Refs.
(LIXa-c)		R=Et (a) R = Pr (b) R = iso-Pr (c)	67 80 71	[129] [129] [129]
(LXa-e)		A=CONH, X=O, R^1=R^2=OH (a) A—absent, X = O, R^1 = R^2 = OEt (b) R^1 = R^2 = OBu (c) R^1 = R^2 = OPh (d) X = S, R^1 = Me, R^2 = Ph (e)	— 71,24 85 53,30 72	[161] [130] [130] [130] [130]
(LXIa, b)		R=Ph (a) R = OH (b)	— 58	[131] [132, 133]
(LXIIa-c)		R=Ph, *m*=2, *n*=2 (a) R=OH, *m*=1, *n* = 2 (b) *n* = 3 (c)	63 65 85	[138] [134] [135]
(LXIIIa, b)		*n*=1 (a) *n* = 2 (b)	— 74	[136] [136]
(LXIVa-d)		A=CH_2, R=OH (a) R = H (b) A = CH_2CH_2, R = OH (c) A = CH_2CH_2O, R = OH (d)	84 74 75 69	[136,137] [137] [137] [137]
(LXVa-c)		*m*=2, 4, 6, 8, 10; *n*=*k*=2 (a); *n* = 2, *k* = 1 (b); *n* = *k* = 1 (c)	—	[139]

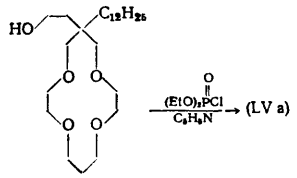
fulfill the role of phase transfer catalysts in the two-phase reduction of chloromethylnaphthalene by formic acid salts. In this case the HCO_2K complex of the ligand (LIIId) (an analogue of 18-crown-6-ether) is more active.

The macrocyclic triamides of phosphoric and phosphorithoic acids (LIVa–d) (Table 8), which exhibit antitumour activity, have been synthesised by phosphorylating monoazacrown-ethers with $POCl_3$ (or $PSCl_3$), this being followed by treatment with aziridine:[122]

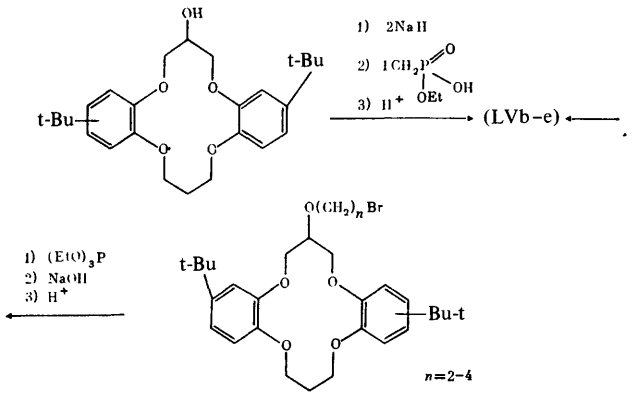


Crystalline complexes with $NaBPh_4$ have been isolated for all the complexes (LIVa–d) and have been investigated by ^{23}Na NMR.

In order to increase the lithium selectivity of 14-crown-4-ethers, its various lariat derivatives have been obtained,[123] including the macrocycle (LVa) (Table 8):

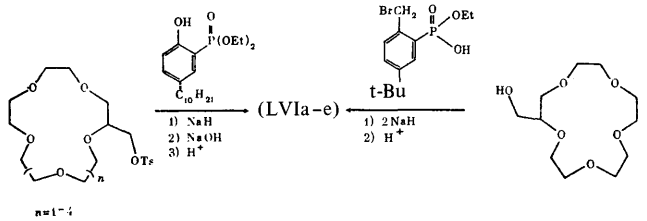


The monoethyl esters of crown-ether-substituted phosphonic acids (LVb–e) have been synthesised[124] as extractants for alkali metals from di(t-butylbenzo)-14-crown-4-ether by alkylating its hydroxy-derivative with $ICH_2PO(OEt)ONa$ [compound (LVb)] or by the reaction of the ω-bromoalkoxy-derivative of the crown-ether with triethyl phosphite [compound (LVc–e)]:



Compound (LVc) could not be obtained by alkylation [by analogy with compound (LVb)] with the aid of $BrCH_2CH_2PO(OEt)_2$ or by the addition of diethyl vinyl phosphonate.

The macrocyclic extractants (LVIa–e) (Table 8), containing the lipophilic phosphite groups, have been synthesised from the hydroxymethyl derivative of the corresponding crown-ether and the esters of *o*-bromomethyl- and *o*-hydroxyarylphophonic acids:[125,126]



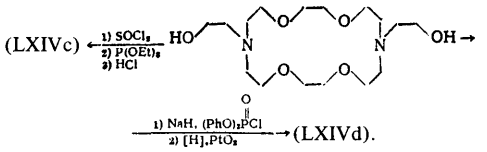
The macrocycles (LVIIa–c) (Table 8) have been synthesised by the reactions of the di(chloromethyl) derivatives of octahydrobinaphthyl-17-crown-5-ether, binaphthyl-20-crown-6-ether, and binaphthyl-23-crown-7-ether with triethyl phosphite.[127] The macrocycle (LVIII) (Table 8) has been synthesised analogously from bis-[4,5-di(bromoethyl)benzo]-18-crown-6-ether,[128] while the bisphosphonates (LIXa–c) (Table 8) have been obtained from dibromobenzo-18-crown-6-ether in the presence of nickel halides.[129]

The macrocyclic bisamides (LXa–e) (Table 8) have been obtained by phosphorylating the 4,4′-diaminodibenzo-18-crown-6-ether[130] and two polymorphic modifications of compound (LXb, c) have been isolated.

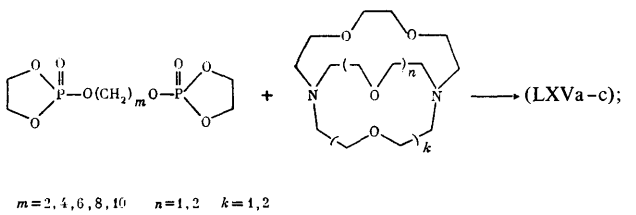
A whole series of azacrown-ethers and cyclans have been converted by reaction with paraformaldehyde (formaldehyde) and phosphorous acid or its analogues into lariat derivatives with neutral and acid phosphinylmethyl groups—the macrocycles (LXIa, b),[131–133] (LXIIb, c),[134,135] (LXa, b),[136] and (LXIVa, b).[136,137]

The octadentate ligand (LXIIa) has been synthesised by the addition of diphenylvinylphosphine oxide to 1,4,7,10-tetra-azacyclododecane.[138]

Macrocycles with acid phosphonate [compound (LXIVc)] and phosphate [compound (LXIVd)] groups have been obtained from the *NN′*-di(β-hydroxyethyl) derivative of diaza-18-crown-6-ether:[137]



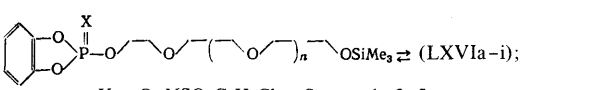
The oligomers (LXVa–c) (Table 8), capable of extracting alkali metal cations into the organic phase, have been obtained by the reaction of cyclic bisethylene phosphates with various cryptands:[139]



Their selectivity is determined by the size of the cryptand and their efficiency increases with increase in the length of the alkylene unit (*m*).

IV. MACROCYCLIC COMPOUNDS OF PENTACOORDINATE PHOSPHORUS

A series of macrocyclic pentacoordinate phosphorus compounds have been synthesised (Table 9). Here the phosphorus atom plays merely the role of a structural unit, determining in many instances the conformation of the polyether ring. Compounds of this kind have been obtained with the aid of reversible intermolecular cyclisation of *o*-phenylene phosphates or their analogues containing a poly(ethylene glycol) chain with the trimethylsilyl group in the ring:[140,141]

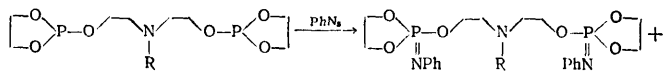


The macrocycles (LXVIIa–c) (Table 9) have been obtained in an analogous way.

The cyclisation equilibrium, investigated by NMR, shifts towards the macrocyclic spirophosphorane with increase in temperature or with increase in solvent polarity. In particular the addition of pyridine stabilises the macrocyclic molecule, which the authors believe to be the result of the coordination to the phosphorus atom. However, such coordination does not cause an appreciable upfield shift of the signal in the ^{31}P NMR spectrum.[141] The tendency towards cycli-sation diminishes with increase in the length of the polyether chain and also on decrease of its conformational flexibility (after the intro-duction of the cyclohexane or benzene ring). As a

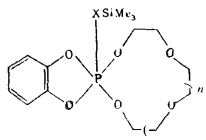
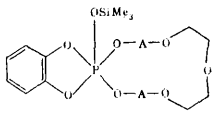
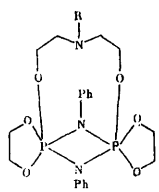
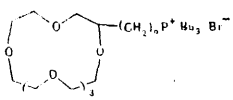
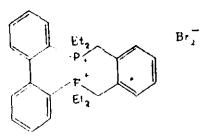
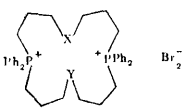
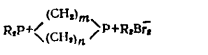
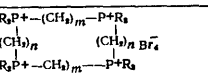
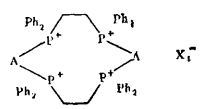
consequence of the lower affinity of silicon for nitrogen compared with oxygen, the equilibrium involving the *N*-trimethylsilyl derivatives (LXVIc, f, i) is greatly displaced towards the linear form. In the case of the thio-phosphoranes (LXVIb, e, h), the slow cyclisation is followed by the reversible dissociation of the P–OC bond in the macrocycle. The equilibrium in this process is displaced towards the quasi-phospho-nium structure. The authors believe that, according to ^{31}P NMR data, the equilibrium mixture contains also dimeric linear and cyclic phosphoranes in an amount of 1–5%.

The addition of phenyl azide to the bisdioxaphospholan phosphite entails not only the formation of a bisiminophosphoryl compound but also of its cyclisation product (LXVIIIa, b) (Table 9) as a result of the formation of the diazadiphosphetidine fragment:[142,143]



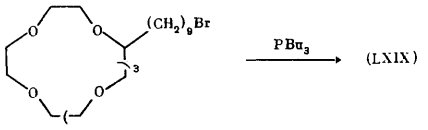
+ (LXVIIIa, b);
R = Me, t-Bu.

Table 9. Macrocycles containing a pentacoordinate phosphorus atom.

Compound	Formula	A, X, Y, R, *m*, *n*	Yield, %	Refs.
(LXVIa-i)		$n = 1$, X = O (a), S (b), $NSO_2C_6H_4Cl$-*p* (c) $n = 3$, X = O (d), S (e), $NSO_2C_6H_4Cl$-*p* (f) $n = 5$, X = O (g), S (h), $NSO_2C_6H_4Cl$-*p* (i)	— — —	[140, 141] [140, 141] [140, 141]
(LXVIIa-c)		A = CH_2CH_2 (a), *o*-C_6H_4 (b),  (c)	—	[141]
(LXVIIIa, b)		R = Me (a) R = t-Bu (b)	— 23	[142] [143]
(LXIX)		—	60	[144]
(LXX)		—	—	[145]
(LXXIa-c)		X=Y=O (a) X = Y = *p*-$O_2C_6H_4$ (b) X = O, Y = *p*-$O_2C_6H_4$ (c)	40 16 35	[110, 111] [110, 111] [110, 111]
(LXXIIa-e)		R = Ph, *m* = 3, *n* = 4 (a) *m* = 2, *n* = 5 (b) *m* = 4, *n* = 4 (c) *m* = 4, *n* = 5 (d) R = CH_2Ph, *m* = 4, *n* = 4 (e)	31 29 28 10 12	[79,80] [79,80] [79,80] [79,80] [79,80]
(LXXIIIa-d)		R = Ph, *m* = *n* = 3 (a) *m* = 3, *n* = 4 (b) *m* = *n* = 4 (c) R = CH_2Ph, *m* = *n* = 3 (d)	9 11 20 3	[79,80] [79,80] [79,80] [79,80]
(LXXIVa-d)		X = Cl, A = CH=CH (a) A = CH_2CH_2 (b) X = Cl, PF_6, A = *p*-C_6H_4 (c) A = *p*-C_6Cl_4 (d)	80 95 85 98	[147] [147] [146] [146]

This Section presents data not only on pentacoordinate phosphorus compounds but also on phosphonium salt. Some of them have already been discussed in Sections II and III.

The macrocycle (LXIX) (Table 9), which has an exocyclic phosphonium group, has been obtained by the reaction of ω-bromononyl-18-crown-6-ether with tributylphosphine:[144]



Compound (LXIX) can effect phase transfer catalysis both in a liquid–liquid system via the phosphonium fragment and also solid–liquid phase transfer catalysis by virtue of the crown-ether fragment. However, both catalytic centres (in the reaction involving the exchange of a halogen or the cyano-group) act indpendently without synergism.[144]

The macrocyclic bisphosphonium salts (LXX) [145] and (LXXIa–c) [110,111] (Table 9) have been obtained by alkylating bisphosphine by the corresponding dibromide under the conditions of high dilution.

The bis- and tetrakis-phosphonium salts (LXXIIa–e) and (LXXIIIa–d) (Table 9) have been synthesised by the reactions of αω-alkylenebisphosphines with αω-dihalogenoalkanes and by the reactions of di(ωω′-halogenoalkyl)bisphosphonium salts with alkylenediphosphines respectively.[79,80] The use of high dilution does not increase the yield of macrocycles.

The macrycyclic phosphonium salts (LXXIVa, c, d) (Table 9) have been synthesised in an unusually high yield (80–98%) from bis(diphenylphosphino)ethane and *p*-di(chloromethyl)arenes[146] or 1,4-dichlorobut-2-ene[147] under the conditions of high dilution (10^{-2} M) on prolonged refluxing in toluene (96 h):

$$Ph_2PCH_2CH_2PPh_2 + ClCH_2{-}A{-}CH_2Cl \rightarrow (LXXIVa, c, d);$$
$$A = CH{=}CH,\ p\text{-}C_6H_4,\ p\text{-}C_6Cl_4.$$

Compound (LXXIVa) apparently the (*E*)-isomer, is formed regardless of whether the *cis*- or the *trans*-isomer of the dichlorobutene is used in the reaction. Its catalytic hydrogenation yielded the macrocycle (LXXIVb).

V. COMPLEX FORMING PROPERTIES OF PHOSPHORUS-CONTAINING MACROCYCLES

Mainly the complex-forming properties in relation to alkali and alkaline earth metal cations are considered in this Section. Data on the formation of complexes by phosphine macrocycles with transition metals are described above together with studies on their synthesis.

1. The Complex Forming Properties of Macrocycles Containing a Tervalent Phosphorus Atom

The polyether macrocycles containing a tervalent phosphorus atom, which is incapable of interacting effectively with alkali metal cations, resemble in their complex forming properties the crown-ethers having a macrocyclic ring of the same size. The stability constant and the selectivities of substances of these types are similar. For example, compounds (VIa, b) (Table 2) interact effectively with Li^+: K_s > 300 litre mol^{-1} (acetonitrile), whereas in the case of Na^+ and K^+ the stability constants fall to 8 and 5 litre mol^{-1} respectively.[148] Similarly unstable complexes with Na^+ and K^+ are formed by the macrocycles (Xa) (Table 3) and (XLIa) (Table 6). However, compound (Xc) (Table 3), differing from compound (Xa) by the substituent at the phosphorus atom (t-butyl instead of phenyl), is capable of interacting with $NaPF_6$.

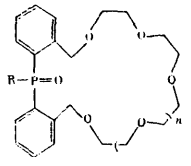
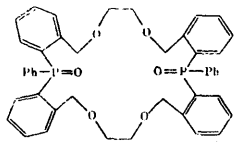
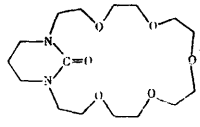
2. The Complex Forming Properties of Macrocycles Containing a Tetracoordinate Phosphorus Atom

The synthesis of phosphoryl-containing macrocycles was dictated by the endeavour to increase the efficiency of macrocyclic ligands by introducing into the ring the phosphoryl group, which possesses a high complex forming capacity. The effect of the introduction of phosphorus-containing fragments has been studied in greatest detail by Cram and co-workers.[108] Their data (Table 10) show that the introduction of the phosphoryl fragment lowers the stability of the complexes of macrocycles with Na^+, K^+, Rb^+, and Cs^+ and also the selectivity relative to the analogous crown-ethers. Only lithium is an exception in the case of the phosphine oxides (XLIVd–g) and (XLV). A decrease in the efficiency of the ligand after the introduction of the phosphorus-containing fragment into the ring can apparently be explained by the characteristics of the conformational structure of the macrocycle which prevents the cooperative interaction of all the oxygen atoms with a metal cation—the phosphoryl group is oriented away from the polyether fragment. On the other hand, the introduction of lariat carboxy-groups in the *o*-position relative to the phosphoryl group [compounds (XLIVf, g)] stabilises the complex formed. It is of interest to note that the use of the urea residue in the polyether ring [the macrocycle (LXXV), (Table 10)] leads, as in the case of the phosphoryl group, to a decrease in selectivity and in the stability constants.

The results of the study of the formation of complexes by the macrocycles (XXVI), (XXVIII), (XLVII), and (XXXVIIa) (Table 11), obtained by Yatsimirskii and Kabachnik and co-workers,[149,152] agree with the features demonstrated by Cram.[108] The compounds enumerated as well as the macrocyclic phosphine oxide (XLIII) (Table 11) [107] are inferior to crown-ethers as regards the efficiency and selectivity of their interaction with alkali metals. The "macrocyclic effect" for Li^+ is in this case insignificant, in contrast to the other cations, as can be seen from the comparison of the ligand (XLVII) with its acyclic analogue (LXXVII). The low efficiency of the phosphorus-containing crown-ethers is due to the unfavourable orientation of the phosphoryl (or thiophosphoryl) group away from the polyether ring. This conformation is energetically most favourable for the macrocycles (XXVIa),[153,154] (XXVIII),[155] and (XXVIf) (Table 4).[156]

The phosphoryl groups make the main contribution to the stability of the complex. Their decisive role in complex formation has been demonstrated by NMR for compounds (XXVIII) [152,153] and (XLIII) [157] and by IR and Raman spectroscopy for the ligands (XXVIa) [89,158] and (XXVIIe) (Table 4).[89,159] Together with the phosphoryl group, in compounds (XLIII) and (XXVIII) the oxygen atom on the opposite side of the macrocycle participates in the coordination of the cation. This conclusion is based on the chemical shift differences in the ^1H NMR spectra in the presence of lithium dinitrophenoxide for compound (XLIII) [157] and $NaClO_4$ for compound (XXVIII) [152] and also on interaction with shift reagents.

Table 10. Stability constants (10^3 K_s, M) of complexes of phosphorus-containing crown-ethers of the neutral type and their analogues with alkali metal picrates in $CDCl_3$ (24–26 °C).[108]11.

Compound	Formula	R, n	Cations				
			Li	Na	K	Rb	Cs
(XLIVd–h)		R = Ph, n = 1 (d) R = Ph, n = 2 (e) R = $C_6H_4CO_2H$-o, n = 1 (f) R = $C_6H_4CO_2Me$-o, n = 1 (g) R = OMe, n = 1 (h)	25.6 41 75 38 10	189 117 599 466 63.9	815 961 1500 3100 233	109 1040 372 461 64.6	32.3 1900 113 882 18
(XLV)		—	80	103	50	15	7,5
(LXXV)		—	71	67	240	220	150
(LXXVI)	2,3-naphtho-18-crown-6-ether	—	22.5	1220	85 990	11 300	1250

The increase by approximately an order of magnitude in lg β for Na^+ (Table 11) corresponds to the increase in the size of the cavity in the macrocycle on passing from the ligand (XLIII) to (XXVIII) for the same number of active donor centres. Compounds (XXVIIa–g) (Table 4) also interact more effectively with Na^+ than with Li^+ and K^+.[90] On the other hand, the study of the ionophoric properties of the ligand (XXVIIe) on double layer lipid membranes[89] revealed its high K^+/Na^+ selectivity. It has been suggested that a stable complex of the sandwich type analogous to the 2:1 calcium complex, in which the two phosphoryl and four (anisole) oxygen atoms are coordinated to the cation, is formed in this case.[159,160] The calculated radius of the cavity formed then corresponds to the crystallographic radius of the K^+ ion.[89] In contrast to the ligand (XXVIIe), compounds (XXVIa) and (XXVIII) form 1:1 and 1:2 calcium complexes respectively,[160] in which the cation is not shielded, as a consequence of which they do not possess an ionophoric activity.[89,161]

The stability constants of the complexes of the ligands (XLVII) [162] and (XXVIIa–g) [90] with calcium and magnesium salts have been determined by the solubility method. The thiophosphoryl macrocycles (XXVIIf, g) are weaker complex forming agents in relation to alkali and alkaline earth metals than their phosphoryl analogues (XXVIIa, c) but, like compounds (XXVIf, g), they form stable complexes with Ag^+ [85] and are effective agents for the transfer of silver picrate through a liquid dichloroethane membrane.[163]

The macrocycles (XXVIa, f),[158] (XXXVIIa),[164] and (XLVII) [165] are capable of interacting effectively with transition metal (Fe^{3+}, Cu^{2+}, Ni^{2+}, and Co^{2+}) salts and also of transporting them through a liquid membrane, which is done, for example, by the macrocycle (XXVIa) (transport of $FeCl^3$ through dichloroethane).[166]

The macrocycle (XXX) (Table 4) is an ionophore of the acid type which at pH 1.5 effectively transfers K^+ and (in the opposite direction) H^+.[167]

3. The Complex Forming Properties of Macrocycles Containing Lariat Phosphoryl Groups.

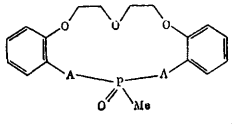
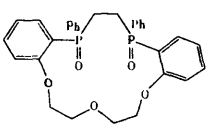
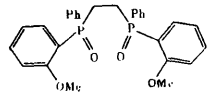
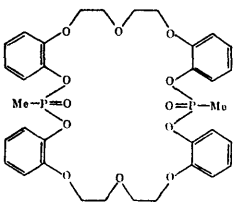
The most promising of the phosphorus-containing macrocycles at the present time are apparently crown-ethers or their analogues with phosphoryl groups in the side chain (lariat compounds). The phosphorus-containing fragment does not significantly distort the conformation of the macrocycle in this instance and hence does not disturb the effect of the cooperative interaction of the donor ring atoms with the cation. At the same time, the phosphoryl group is capable of ensuring additional binding of the cation, imparting a high stability to the complex. Thus the introduction of two phosphonate groups into the dinaphthyl residue of the crown-ether significantly increases the binding constants, as can be seen from the comparison of compounds (LVIIb, c) with compound (LXXIX) (Table 12). The values $\Delta G = -12.4$ kcal mol^{-1} for the binding of the ligand (LVIIb) to Na^+ and $\Delta G = -12.2$ kcal mol^{-1} for the formation of the complex between compound (LVIIc) and Rb^+ correspond to this kind of jump in K_s.[127] It must be emphasised that the macrocycle (LVIIb) forms the most stable complex with K^+ among the crown-ethers containing the 1,1'-binaphthyl residue.[168] X-Ray diffraction analysis has shown[169] that, in the potassium complex of the macrocycle (LVIIb) having the composition L.KSCN.$CHCl_3$, the cation is located at the centre of the polyether ring and the two oxygen atoms of the P=O groups are coordinated to it, being located on the axis

perpendicular to the plane of the polyether ring and passing through its centre. The $O_{eth}...K^+$ and $O_{P=O}...K^+$ distances are respectively 2.76 and 2.70 Å, while in most crown-ether complexes the distance exceeds somewhat 2.8 Å.[169]

In contrast to compounds (LVIIb, c), the macrocycle (LVIIa), which should be an ideal complex forming agent for Na^+ according to theoretical calculations, interacts only weakly with alkali metal cations (Table 12), although it does exhibit a very pronounced selectivity. The introduction of four diphenylphosphinylmethyl groups in the *meta*-position relative to the polyether ring in dibenzo-18-crown-6-ether [compound (LVIII, Table 13)] lowers the selectivity in relation to K^+ (cf. Table 11). However, the four additional centres, which differ from the ether oxygen atoms in the macrocycle, make it possible to obtain dimetallic complexes, such as, for example, $(CoCl_2)_2.KCl.L$,[170] in which the potassium cation is in the plane of the macrocycle and the phosphoryl groups are coordinated to the cobalt atoms.

For the lariat compound (LXIa), constructed from triazacyclononane and carrying phosphine oxide side chains (Table 13), highly stable complexes have been obtained with magnesium and calcium iodides, namely $(MgI_2)_3L_2.3H_2O$ and $CaLI_2.3H_2O$,[171] which do not decompose on heating at 100°C. Analysis of the ^1H NMR spectra of the complexes led to the conclusion that all the nitrogen atoms of the ligand in the Mg^{2+} complex are involved in coordination to the metal, whereas in the Ca^{2+} complex only one nitrogen atom interacts with the cation. The different stabilities of the complexes are indicated also by the values of $\lg K$ for MgI_2 and CaI_2—2.8 and 2.4 respectively (1:1 acetonitrile–$CHCl_3$ mixture).[171] The study of complex formation with alkali metals showed that the macrocycle (LXIa) forms a highly stable complex with Li^+: $\lg\beta = 5.6$ (4:1 THF–$CHCl_3$ mixture).[131] The higher selectivity of the compound with respect to lithium compared with the simplest analogues, for example, compound (LXXX) (Table 13) is caused, according to the authors, by the flexibility of the lariat molecule, which enables it to

Table 11. The logarithms of the stability constants ($\lg\beta$) of complexes of phosphorus-containing crown-ethers with alkali metal cations.

Compound	Formula	A	Cations				Anion	Solvent	Refs.
			Li	Na	K	Cs			
(XXVI a)		O	1.2	—	—	—	Cl	MeCN	[149]
(XXVIII)		OCH_2CH_2O	2.25	2.36	—	—	ClO_4	acetone	[152]
(XXVIII)		OCH_2CH_2O	3.36	4.23	—	—	picrate	THF/DCE	[151]
(XLIII)		CH_2O	3.26	3.29	3.29	2.56	2,4-dinitrophenoxide	THF/$CHCl_3$	[107]
(XLVII)		—	2.30	2.13	2.04	2.02	acetate	EtOH/$CHCl_3$	[150]
		—	2.70	—	—	—	Cl	MeCN	[150]
		—	2.81	3.42	2.85	2.26	I	MeCN	[150]
		—	3.12	2.64	1.78	—	ClO_4	MeCN	[150]
(LXXVII)		—	1.64	1.59	1.56	1.51	acetate	EtOH/$CHCl_3$	[150]
			3.08	2.46	1.88	0.4	I	MeCN/$CHCl_3$	[150]
			3.18	2.01	0.3	—	ClO_4	MeCN/$CHCl_3$	[150]
(XXXVII a)		—	1.9	1.7	1.0	0.3	acetate	EtOH/$CHCl_3$	[149]
			3.0	—	—	—	Cl	MeCN/$CHCl_3$	[149]
			2.7	—	—	—	I	MeCN/$CHCl_3$	[149]
(LXXVIII)	Dibenzo-18-crown-6-ether	—	3.48	3.97	4.51	3.47	Cl	EtOH/$CHCl_3$	[170]
			4.06	5.60	4.66	3.3	2,4-dinitrophenoxide	THF/$CHCl_3$	[138]

assume the energetically most favourable conformation. The linearity of the relation between $\lg\beta$ and $1/r$ (where r is the ionic radius of the cation) indicates the ion–dipole character of the interaction, i.e. the electrostatic interaction of the cation with the polar groups of the ligand makes the main contribution to the free energy change.[131]

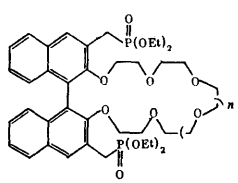
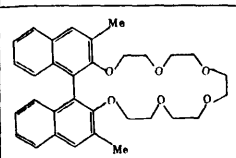
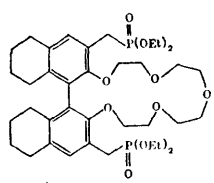
In contrast to the macrocycle (LXIa), the phosphinylethylated tetra-azacyclododecane (LXIIa) (Table 13) interacts preferentially with Na^+ and is significantly superior to dibenzo-18-crown-6-ether (Table 11) as regards efficiency and Na^+/K^+ selectivity.[138] Complexes with cobalt salts have been obtained for both compound (LXIa) [172,173] and the macrocycle (LXIIa).[173]

The acid analogue of compound (LXIa) [the macrocycle (LXIb), Table 8)] does not form stable complexes with alkali metal cations in water but it does interact effectively and selectively with doubly charged cations having a small radius.[132,133] Thus the difference between the stability constants of the complexes with Mg^{2+} and Ca^{2+} is by about 5 orders of magnitude (the $\lg K$ for the complexes ML are respectively 11.01 and 6.38). A high selectivity is observed also in the series of Group II B transition metals: the complex with Zn^{2+} (r = 0.74 Å) formed by the ligand is the most stable among all those known for zinc ($\lg K$ = 24.9 for the complex ML). The stability constant for Cd^{2+} (r = 0.97 Å) is lower by five orders of magnitude. A very stable complex is also formed with the Fe^{3+} ion (r = 0.64 Å): $\lg K$ = 29.6 for the complex ML. According to X-ray diffraction data,[174] the Fe^{3+} cation in the complex is located in the inner cavity of the ligand, formed by the side groups, and interacts with all its donor centres. The "twisted basket" conformation produced under these conditions differs in energy from the conformation in the free state by only ~5 kJ mol^{-1}.[175]

The tetraphosphinic acid (LXIIb) (Table 8), whose ring has been increased by one aminoethyl unit, has a completely different spectrum of interaction with cations:[134] whereas complexes of the ligand (LXIb) are more stable for cations with an ionic radius ≤0.7 Å, cations with a radius >0.8 Å form more stable complexes with the ligand (LXIIb). For example, the macrocycle (LXIIb) forms a more stable complex with Ca^{2+} than with Mg^{2+} (the $\lg K$ for the complexes ML are 10.3 and 7.3 respectively). The ligand (LXIIb) is a selective complex forming agent for Cd^{2+} and Pb^{2+}, but, in relation to a whole series of cations, including alkaline earth metals, it is greatly inferior to the carboxyl-containing analogue 1,4,7,10-tetrakis-(carboxymethyl)-1,4,7,10-tetra-azacyclododecane, and also to the macrocycle (LXIb), and is close to the relatively weakly selective complexone EDTA. Atom–atom potential function calculations have shown[175,176] that the low selectivity of compound (LXIIb) can be explained by the adequate conformational possibilities for the formation of six- and five-coordinated complexes with various cations. The maximum number of binding sites (eight) is not utilised owing to the mutual repulsion of the phosphenyl group. Like compound (LXIb), the macrocycle (LXIIb) forms relatively unstable complexes with the alkali metal cations, the stability decreasing in the sequence $Li^+ > Na^+ > K^+$. For the K^+ cation, $\lg K < 1$.[134]

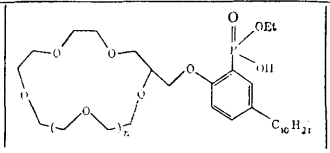
The "expansion" of the ring in the ligand (LXIIb) by two methylene units [to give compound (LXIIc), Table 8] and hence the increase in its conformational mobility lead to a sharp decrease (by 6–8 orders of magnitude) of the stability of the complexes with all cations.[135] For example, $\lg K < 2$ for alkaline earth metal cations (for the ML complexes). The carbonyl-containing analogue of compound (LXIIc)—1,5,8,12-tetrakis(carboxymethyl)-1,5,8,12-tetra-azacyclotetradecane—is only slightly inferior to it as regards efficiency, but the difference between the values of $\lg K$ for the two ligands in the case of Cu^{2+} reaches 8 orders of magnitude. The high selectivity of compound (LXIIc) with respect to the Cu^{2+} ion ($\lg K$ = 26.6 Cu^{2+} and $\lg K$ = 15.6 for Ni^{2+}) is probably favoured by the

Table 12. Stability constants (10^{-3} K_s, M) of complexes of phosphonate lariats of the neutral type with alkali metal picrates in $CDCl_3$.[127]

Compound	Formula	n	Cations				
			Li	Na	K	Rb	Cs
(LVIIb)		1	136	$1.16\cdot10^6$	$8.39\cdot10^5$	19500	2520
(LVIIc)		2	320	830	$5.8\cdot10^5$	$1.1\cdot10^6$	23200
(LXXIX)		—	228	1730	$4.28\cdot10^4$	4700	576
(LXIIa)		—	33	620	12	4.5	2.75

stable conformation, found by the method of atom–atom potential functions. The nitrogen atoms in it form a planar square and the phosphono-groups in the apical positions can additionally stabilise the complex.

Table 14. The competitive extraction of alkali metal chlorides from 0.25 M aqueous solutions into a 0.05 M ligand solution in $CHCl_3$ (in %) at pH 9.[125]

Compound	Formula	n	LiCl	NaCl	KCl	RbCl	CsCl
(LVIb)		1	5	50	21	14	5
(LVIc)		2	—	—	57	24	5
(LVId)		3	10	12	17	31	30
(LVIe)		4	11	22	23	18	20

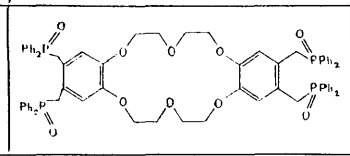
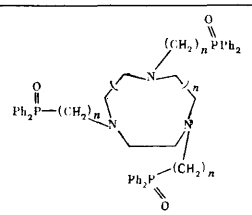
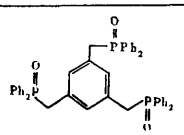
In contrast to the ligands (LXIb) and (LXIIb, c), the *N*-dihydroxyphosphinylmethylated azacrown-ethers (LXIIIa, b) and (LXIVa) (Table 8) form more stable complexes with Na^+: $K_{NaL} = 20-40$.[136] The presence of at least one phosphonate group is essential for the formation of stable complexes, since unsubstituted monoaza- and diaza-crown-ethers do not interact with Na^+. Macrocycles with five heteroatoms in the ring [compound (LXIIIa)] are the most effective, which is particularly characteristic of the carboxy-analogues of compound (LXIVa).

The macrocycle (LXIVa) and its analogues with carboxy- and phosphonite groups [compound (LXIVb), Table 8] proved to be promising solubilising agents for barium sulphate.[137] Their efficiency in relation to the [2.2.2]cryptand is 65, 65, and 19% respectively. The use of longer phosphonoalkyl and carboxyalkyl chains or other polar groups (SO_3H, OPO_3H_2, OSO_3H) lowers sharply the solubility of the Ba^{2+} complexes.

The introduction of a lariat phosphoryl-containing group [the macrocycle (LVa), Table 8] or of the amino-group into 14-crown-4-ether increases its selectivity with respect to lithium.[123] The selectivity coefficients in a polymer membrane then reach 182 (Li^+/Na^+) and 288 (Li^+/K^+). On the other hand, ester and 8-hydroxyquinoline groups impair the selective properties of the crown-ether.

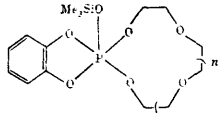
A whole series of crown-ether-substituted phosphonic acids have been investigated as extractants of alkali metal cations.[124–126] Thus, among phosphinylalkoxy-derivatives of di(t-butylbenzo)-14-crown-4-ether (LVb–e) (Table 8), a highly selective extractant for Na^+ has been found, namely the ligand (LVc).[124] A further increase in the length of the alkyl chain between the polyether ring and the charged phosphonate group leads to the loss of selectivity and to a decrease in the efficiency of the extractant [compounds (LVd, e)]. As shown on models, the length of the lariat group in compounds (LVc) is optimum from the additional stabilisation of the sodium complex. The macrocycles (LVIb–e) (Table 14),[125] containing the lipophilic

Table 13. Logarithms of the stability constants ($\lg\beta$) of complexes of phosphorus-containing lariats of the neutral type and their analogues with alkali metal cations.

Compound	Formula	n	Cations				Anion	Solvent	Refs.
			Li	Na	K	Cs			
(LVIII)		—	3.09	3.86	3.95	3.47	Cl	EtOH/$CHCl_3$	[170]
(LXIa)		1	5.6	4.5	3.2	2.2	2,4-dinitrophenoxide	THF/$CHCl_3$	[131]
(LXIIa)		2	5.91	6.29	5.04	3.6	2,4-dinitrophenoxide	THF/$CHCl_3$	[138]
(LXXX)		—	5.1	4.4	4.0	3.3	2,4-dinitrophenoxide	THF/$CHCl_3$	[131]

phosphonate group, extract cations in conformity with the size of their polyether ring. For example, the macrocycle (LVIb), constructed from 15-crown-5-ether, extracts Na^+ preferentially. Compound (LVIa) (Table 8) behaves analogously. The formation of its highly stable sodium complex has been demonstrated by ^1H NMR.[126] The principal advantage of the phosphorus-containing extractants investigated compared with their carboxy-analogues is their higher efficiency and also their ability to extract cations at low pH (down to pH 2).

Table 15. The solubilities of alkali metal chlorides (mole % relative to the ligand) in 0.1 M solutions of the macrocycles in dichloroethane (20 °C).[141]

Compound	Formula	n	LiCl	NaCl	KCl	RbCl	CsCl
(LXVIa)		1	25.2	1.9	0.1	—	—
(LXVIIa)		2	34.4	0.6	0.5	—	—
(LXVId)		3	43.9	0.6	0.5	—	—
(LXVIg)		5	52.1	3.4	3.3	3.7	1.7
(LXXXI)	18-crown-6-ether		2.7	2.7	17.3	—	—

4. The Complex Forming Properties of Macrocycles Containing a Pentacoordinate Phosphorus Atom

The formation of complexes by the macrocycles (LXVIa, d, g) and (LXVIIa) (Table 15), containing the phosphoranyl group, with alkali metal chloride has been investigated by the solubility method.[141] In contrast to compound (LXVI) (n = 0), which does not possess complex forming properties because of its small ring size, the macrocycles (LXVIa, d, g) and (LXVIIa) interact selectively and effectively with Li^+, being greatly superior in this respect to 18-crown-6-ether. With increase in ring size and in the number of ether oxygen atoms on passing from compound (LXVIa) to (LXVIg), the efficiency of the complex formation with LiCl also increases. On the other hand, the interaction with cations having larger radii (Na^+, K^+, Rb^+, Cs^+) is weaker, even for the 23-membered macrocycle. The authors explain the selectivity with respect to Li^+, especially for compounds (LXVIa, d) and (LXVIIa), by the fact that the trigonal-bipyrimidal configuration of the phosphorus atom imparts to the conformationally labile ring a geometry in which the donor oxygen atoms are not in a single plane and the size of the cavity formed by them corresponds only to the lithium cation. The disadvantage of the phosphorane macrocycles is their hydrolytic instability.

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During the preparation of the manuscript for the press, new studies on the synthesis and complex-forming properties of phosphorus-containing macrocycles were published. Thus macrocycles with phosphorus(III) have been obtained by the transamidation of the amide $PhP(NMe_2)_2$ or $P(NMe_2)_3$ with polyetherbisamines containing *o*-aminophenol or 3-amino-2-methoxybenzyl alcohol fragments as the end group. They were converted by oxidation or the addition of sulphur into the corresponding macrocycles with phosphorus(IV).[177] A tetraphosphorus(III) macrocycle has been synthsised in a high yield in the form of the nickle complex by the matrix cyclisation method from the phosphine complex $PhP[(CH_2)_3PhMe]_2.NiBr_2$ and the amide $Et_2NP(CH=CH_2)_2$ [cf. the ligand (XIX) (Table 3)] in a high yield. The nickel complex was then oxidised to the phosphorus(IV) derivative.[178] A 22-membered bisphosphonate macrocycle has been obtaind[179] in 6–8% yield from *OO'*-di(β-hydroxyethyl)-catechol and $MeP(O)Cl_2$ by the same method as compound (XXXVIIa–e) (Table 5). The stability of its complexes with alkali metals varies in the sequence Na > Li ≫ K. The complex-forming properties of the macrocycles (XXVIa, c), (XXVIIa, c), (XXVIII), and (XXXVIIa) in relation to the lithium, sodium, potassium, magnesium, and calcium cations have been investigated by a modified solubility method in the CH_2Cl_2 + 2% MeCN mixture.[180] The extraction of sodium, potassium, magnesium, calcium, strontium, barium, and other metals by chloroform solutions of the macrocycles (XXVIa, f), (XXVIIIa, e, f), and (XXXVIIe) has been studied.[181] In contrast to the phosphonate crown-ethers, which possess no extracting properties, the phosphonothionates (XXVIf), (XXVIIf), and (XXXVIIe) extract to a slight extent silver, mercury, and palladium at pH 1–5 and extract them quantitatively from concentrated acid solutions. Phosphate ionophores of the acid type—compound (XXX) (Table 4) and five of its analogues—have been obtained by the interaction of oligo(ethylene glycols) with $POCl_3$ under high dilution conditions (5×10^{-2} M) with subsequent hydrolysis of the resulting cyclic phosphoromonochloridate[182] [demonstrated in relation to compound (XXX)]:

$$HOCH_2CH_2OCH(CH_2OCH_2)_3CH_2OH \xrightarrow[2)\ H_2O,15^\circ C]{1)\ POCl_3,\ -70^\circ C} (XXX)$$
$$\quad\quad\quad

Methods of synthesis have been developed for phosphorane macrocycles. Such compounds with two and more phosphorus atoms can be obtained by the reaction of the disilyl ethers of alkane-αω-diols with $PhPF_4$ [189] or of the diols themselves with Ph_3P in the presence of di-isopropyl azodicarboxylate.[190,191]

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