Preparation, Properties, and Reactions of Metal-Containing Heterocycles, XCVII[◇]

Differently Substituted Benzomolybdacrown Ethers and Their Capability of Including Alkali Metal Cations☆

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The reaction of the diphosphanes **2a−f** with $(OC)_4Mo(nbd)$ under high dilution conditions affords the mononuclear benzomolybdacrown ethers *cis*-$(OC)_4Mo\{1,2\text{-}, 1,3\text{-}, 1,4\text{-}[Ph_2PCH_2(CH_2OCH_2)_nCH_2]_2C_6H_4\text{-}P,P'\}$ (**3a−f**) (n = 1, 2). On the basis of the ^{31}P nucleus the inclusion behavior of the molybdacycles **3a−f** toward the alkali metal salts $LiBF_4$ and $NaBPh_4$ was investigated with the aid of a NMR titration technique by using the program EQNMR. Only **3d** shows an interaction with the alkali metal cation Na^+ forming a 1:1 and 2:1 complex (**3d**/cation) while no interaction with Li^+ could be detected. The molecular structures of **3a** and **3d** were elucidated by X-ray structural analyses. Complexes **3a** and **3d** crystallize in the monoclinic space groups $P2_1/c$ and $P2_1/n$ with Z = 8 and 4, respectively.

Introduction

Cyclophosphane chemistry is undergoing a rapid development and has created a multitude of architecturally impressive molecules with features related to structure and functionalization, that are able to embed guests[1][2]. The introduction of transition metal fragments leads to a remarkable influence on the structure of the resulting metallacyclophanes[3] because of their steric requirement. Simultaneously, a new reactive center is obtained that is capable of inserting carbon monoxide into M−C σ bonds[3][4]. The specific incorporation of heteroatoms like oxygen into the cyclophane framework would allow to extend the complexation qualities of metallacyclophanes to include also alkali metal cations as guests. However, the hitherto successfully applied bis(triflate) method[3][5] for the concomitant formation of several metal−carbon σ bonds − a variant of the cationic alkylation − failed when polyether moieties were present in the cyclophane backbone. A suitable alternative for the synthesis of metallacyclophanes with ether building blocks, which can be also denoted as benzometallacrown ethers, is the employment of adequate phosphane ligands which form stable metal−phosphorus bonds within the cyclophane ring. Herein the sythesis and their behavior toward alkali metal cations is studied. Because of their rigid nature it is anticipated that both the aromatic part and the transition metal fragment provide a higher preorganization of these cycles compared to aliphatic systems. The size of the cavity of these benzometallacrown ethers can be adjusted by the substitution pattern of the aromatic ring and by the number of C_2H_4O units in the polyether chain. One of the most basic and important processes in supramolecular chemistry is the formation of host/guest complexes between two or more chemical species[6]. An appropriate parameter to describe the thermodynamic features of such an inclusion is supplied by the stability constants which are determined by the method of NMR titrations[7]. The advantage of applying NMR spectroscopy is that misinterpretations caused by minor impurities, which are sometimes serious in other optical methods[7], are avoided.

As the benzomolybdacrown ethers being under consideration in this article may be regarded as a connecting link between benzocrown[8] and metallacrown ethers[9−23] it is reasonable to discuss and to compare the inclusion behavior of these related host molecules.

Results and Discussion

Phosphane Ligands and Benzomolybdacrown Ethers

For the access to the benzomolybdacrown ethers **3a−f** the corresponding diphosphane ligands **2a−f** are necessary as starting materials. They are synthesized by reaction of the dichlorides 1,2-, 1,3-, and 1,4-$[ClCH_2(CH_2OCH_2)_nCH_2O]_2C_6H_4$ (**1a−f**) (n = 1, 2) with $LiPPh_2$ in a THF/n-hexane mixture at 0°C (Scheme 1). After purification by column chromatography **2a−f** are obtained as colorless viscous oils which are sensitive to air and dissolve readily in dichloromethane and tetrahydrofuran. The molecular composition of the diphosphanes **2a−f** was corroborated by their FD or EI mass spectra, displaying the molecular peak in each a case. In the $^{31}P\{^1H\}$-NMR spectra of **2a−f** each one signal around $\delta = -20$ is observed which is located in the same region as that of related diphosphanes with an aliphatic backbone[17].

In a following step the diphosphanes **2a−f** are reacted with one equivalent of the molybdenum complex $(OC)_4$-

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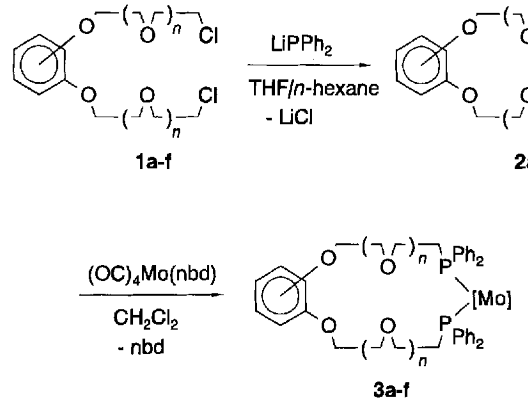
Scheme 1



nbd = norbornadiene
[Mo] = Mo(CO)$_4$

n	ortho	meta	para
1	**a**	**b**	**c**
2	**d**	**e**	**f**

Mo(nbd) in CH_2Cl_2 at ambient temperatures as described in the literature[17] to afford the benzomolybdacrown ethers *cis*-(OC)$_4$Mo{1,2-, 1,3-, 1,4-[$Ph_2PCH_2(CH_2OCH_2)_nCH_2$-O]$_2C_6H_4$-*P,P'*} (**3a–f**) (*n* = 1, 2) as colorless solids (Scheme 1 and Figure 1). To suppress the formation of oligo- or polymeric products the application of the high dilution method is necessary. Nevertheless in the $^{31}P\{^1H\}$-NMR spectra of the *para* compounds **3c** and **3f** with a stretched OC_6H_4O arrangement traces of impurities are detectable pointing to oligomeric species. The complexes **3a–f** are somewhat sensitive to air and soluble in polar organic solvents like tetrahydrofuran, acetonitrile, or dichloromethane. Nor in the FD mass spectra neither with the electro spray technique other masses than those for the mononuclear species could be observed.

In the 5-μm region of the IR spectra of **3a–f** four intensive absorptions occur which is consistent with a *cis*-Mo(CO)$_4$ geometry. Compared to the phosphanes **2a–f** the $^{31}P\{^1H\}$-NMR spectra of **3a–f** reveal one signal which is shifted to lower fields. This finding is in agreement with the results of Gray et al. who reported about comparable aliphatic systems[17]. In the low field part of the $^{13}C\{^1H\}$-NMR spectra of **3a–f** two signal groups are discernible. The first one represents an AXX′ spin system being assigned to the carbon atoms of the carbonyls arranged *trans* to the phosphorus atoms. The second resonance has the shape of a triplet and can be ascribed to the carbonyls arranged cis to the phosphorus atoms. The carbon atoms of the methylene groups in the α- and β-positions to the phosphorus atom are responsible of the A parts of AXX′ patterns.

The cyclization reaction to give the benzomolybdacrown ethers **3a–f** has to be performed under exclusion of light to avoid a *cis/trans* isomerization. When a solution of **3f** in CH_2Cl_2 is subjected to an UV irradiation for several minutes, the $^{31}P\{^1H\}$-NMR spectrum shows an additional singlet at δ = 30.3 caused by a *cis/trans* rearrangement of the phosphanes. Beside the four CO bands in the 5-μm region of the IR spectrum of **3f** an additional CO absorption occurs for the Mo(CO)$_4$ fragment. A similar observation recently was made in the case of the molybdacrown ether *cis*-(OC)$_4$Mo[$Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2$-*P,P'*] in the presence of $HgCl_2$ or under UV irradiation[22].

Structures of 3a and 3d

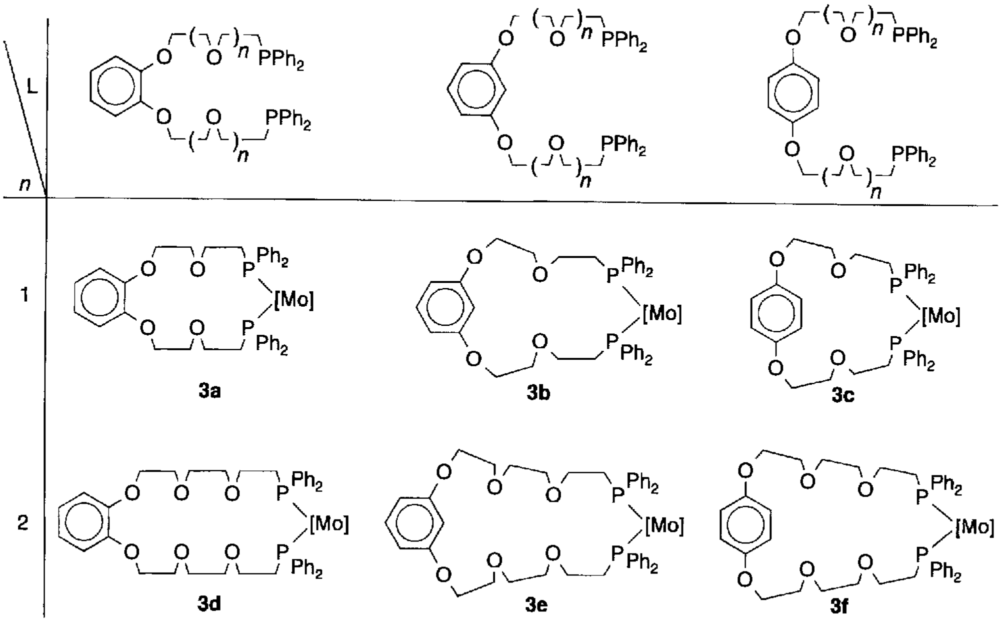
Concerning the possibility of the formation of benzomolybdacrown ether/guest complexes the structures of **3a,d** were elucidated by X-ray structural analyses. **3a** crystallizes with two independent molecules (**A** and **B**) in the asymmetric unit having nearly the same conformation, one of which (**A**) is depicted at the top of Figure 2. The dioxophenylene unit (C9–C14, O6, O7) and the adjacent carbon atoms (C8 and C15) of **3a** are located in the aromatic ring plane while the remaining part of the molecule is folded over this plane. The four oxygen atoms of the polyether backbone are oriented in another least-square plane forming an angle of 42.2° to the aromatic ring with the deviations of −0.016 Å for O5, 0.036 Å for O6, −0.034 Å for O7, and 0.014 Å for O8. The torsional angles C5–P1–Mo1–P2 (28.4°) and P1–Mo1–P2–C18 (−100.6°) at the transition metal center reflect a relatively unsymmetric structure of **3a**. Figure 2 (bottom) displays the space-filling model of **3a** in which the phenyl groups were omitted for clarity. The distance between Mo1 and the phenylene unit is 7.0 Å while the ether oxygen atoms have the following distances for both independent molecules **A** and **B**: O5–O6 (3.0, 3.0 Å), O5–O7 (5.0, 5.0 Å), O5–O8 (5.8, 6.2 Å), O6–O7 (2.6, 2.6 Å), O6–O8 (4.8, 4.9 Å), and O7–O8 (3.0, 3.0 Å).

Although the crystal structure of **3d** (Figure 3, top) shows a disorder, nevertheless it can be used for a very brief discussion. One disordered acetonitrile molecule is located out of the center of the cavity, the C47 atom being nearer than the N1 atom (O5–N1 4.4, O10–N1 4.5, O6–C47 3.0, and O9–C47 3.4 Å). In contrast to **3a** the aliphatic skeleton is not folded. The ether oxygen atoms have the following distances: O5–O6 (6.1 Å), O6–O9 (5.8 Å), O6–O10 (7.3 Å), O5–O9 (6.1 Å). The space-filling model of **3d** (Figure 3, bottom) shows a larger cavity compared to **3a** in the solid state.

Examination of the Inclusion Characteristic of the Benzomolydacrown Ethers 3a–f

Since the discovery of crown ethers by Pederson in 1967[24] an amazing number of macrocyclic ligands with heteroatoms have been reported[8][25]. The properties of these cycles, in particular their inclusion behavior depend on factors as cavity size, the number and the nature of the heteroatoms, the kind of substituents in the periphery of

Figure 1. Benzomolybdacrown ethers **3a–f** obtained by the reaction between the diphosphanes **2a–f** and $Mo(CO)_4(nbd)$

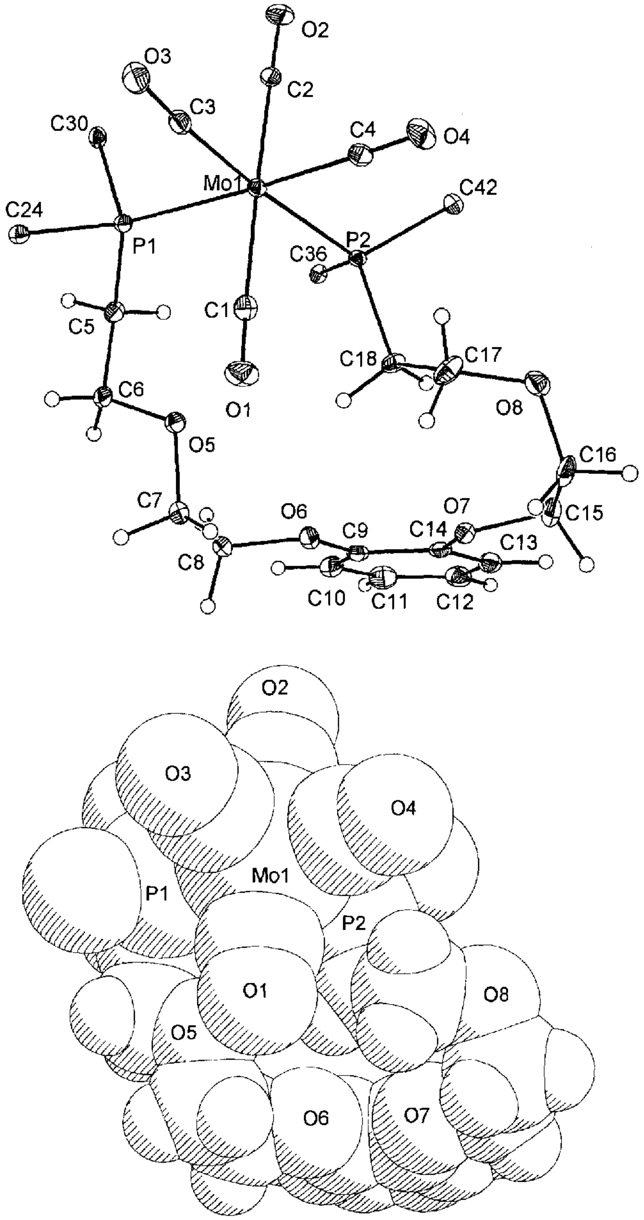


the ligands, the properties of the solvent[26], and the possibility of preorganization[27]. Compared to aliphatic crown ethers benzocrown ethers implicate two additional effects. The aromatic unit represents a sterically defined building block in the otherwise completely flexible system. Furthermore the aromatic π-system is able to participate in the complexation of alkali metal cations as was shown by studies in the gas-phase and in an aqueous medium[28][29]. The incorporation of transition metal fragments into the crown ether framework, leading to metallacrown ethers, offers the possibility to combine a hard cation and a soft transition metal center[30]. Such an arrangement is capable to activate carbon monoxide in the coordination sphere of a transition metal[14][15][16][18][22][30]. Moreover the latter exerts a steric influence on the cyclophane which is expected to change the inclusion properties. Benzomolybdacrown ethers are regarded as the combination of benzocrown and metallacrown ethers. Therefore it is of special interest to compare the stability constants of these systems if alkali metal cations are included.

The NMR spectroscopy is an often applied method for studying the reaction of alkali metal cations with macrocyclic crown ethers, because of the possibility of measuring different nuclei for the independent evaluation of stability constants. Generally envisaged nuclei for the NMR titration procedure are ^{1}H[8], ^{13}C[8], and different metal nuclei[8][31]and recently also the ^{31}P nucleus[23] was employed. Compared to the ^{1}H-NMR spectroscopy the ^{31}P nucleus provides a larger chemical shift dispersion, therefore the determination of the stability constants is more reliable. Unfortunately the quadrupole moments of ^{7}Li, ^{23}Na lead to a serious line broadening, hence the determination of small changes of the chemical shifts becomes difficult. In particular this is the case if the symmetry of the environment of the nucleus is less than T_d as in the present study[32]. Measuring the ^{31}P-chemical shifts affords a higher sensitivity compared to ^{13}C, which is necessary because of the *p*-value originally defined by Weber as the "probability of binding"[33]. This important parameter to consider in choosing the conditions for a titration is the ratio (concentration of the inclusion complex)/(maximum possible concentration of the inclusion complex)[34]. Most informations are obtained if the *p*-value is between 0.2–0.8[34].

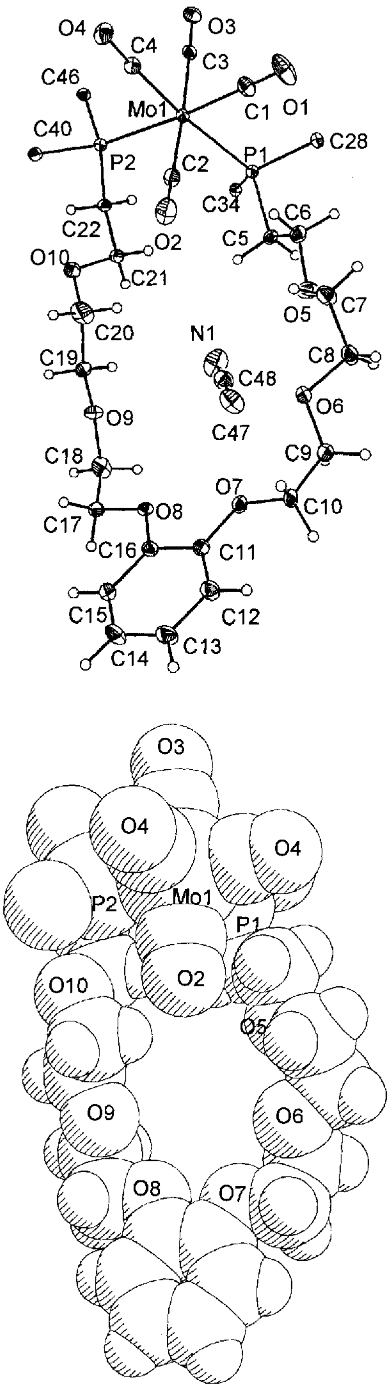
The complexation between the benzomolybdacrown ethers **3a–f** and the alkali metal salts $LiBF_4$ and $NaBPh_4$ was carried out in CD_2Cl_2/CD_3CN (1:1) and the course of the reaction was monitored $^{31}P\{^{1}H\}$-NMR spectroscopically. This combination of solvents turned out to be favorable, because both educts (**3a–f** and the alkali salts) are soluble in such a mixture and the solvent components have only a low donating capability[35]. In Figure 4 the changes of the ^{31}P chemical shifts are plotted versus the molar ratio cation/**3d**. Figure 5 displays the agreement of the calculated[36] with those of the experimental data assuming that both 1:1 and 2:1 (**3d**/Na^+) complexes are formed[31c]. The application of the 1:1 binding model only did not lead to a satisfying result[37] which was proved by comparison of the calculated with the experimental data (Figure 6). A plot of residuals[36] is also depicted in each case (bottom of Figures 5 and 6) indicating that there is no systematic error in the measurements if the proper model is selected. The stability constants for the 1:1 ($\log K_1 = 4.12$) and 2:1 ($\log K_2 = 2.88$) inclusion complexes were determined as described in the Experimental Section applying the non-linear least-squares program EQNMR[38]. The *R*-factor [1.18% in the case of 1:1 beside 2:1 complex (**3d**/Na^+)] is a quantitative comparison of the fits using the "merit function"[38]. As already mentioned the *p*-value represents a standard of valuation for the reliability of a NMR titration. While the *p*-values for the 1:1 complex (**3d**/Na^+) are indeed in the range be-

Figure 2. Top: ORTEP plot of the independent molecule **A** of compound **3a**. – Bottom: Space-filling representation of compound **3a**. In both cases the phenyl groups at the phosphorus atoms are omitted for clarity[a]



[a] Selected bond lengths [Å] and angles [°]: Mo1–P1 2.566(9), Mo1–P2 2.537(8), Mo1–C1 2.062(4), Mo1–C2 2.020(3), Mo1–C3 1.982(3), Mo1–C4 1.984(3), P1–C5 1.850(3), P2–C18 1.826(3), O5–C6 1.425(4), O5–C7 1.424(4), O6–C8 1.432(4), O6–C9 1.373(4), O7–C14 1.362(4), O7–C15 1.431(4), O8–C16 1.417(5), O8–C17 1.410(5); P1–Mo1–P2 95.86(3), C1–Mo1–P1 90.85(10), C2–Mo1–P1 90.33(9), C3–Mo1–P1 89.05(10), C4–Mo1–P1 174.42(10), C1–Mo1–P2 90.23(9), C2–Mo1–P2 88.58(9), C3–Mo1–P2 174.96(10), C4–Mo1–P2 89.62(10), C5–P1–Mo1 125.52(11), C18–P2–Mo1 113.54(12), C6–O5–C7 111.7(3), C8–O6–C9 117.8(8), C14–O7–C15 117.4(3), C16–O8–C17 115.9(3).

Figure 3. Top: ORTEP plot of the molecular structure of compound **3d**. – Bottom: Space-filling representation of compound **3d**. In both cases the phenyl groups at the phosphorus atoms are omitted for clarity[a]

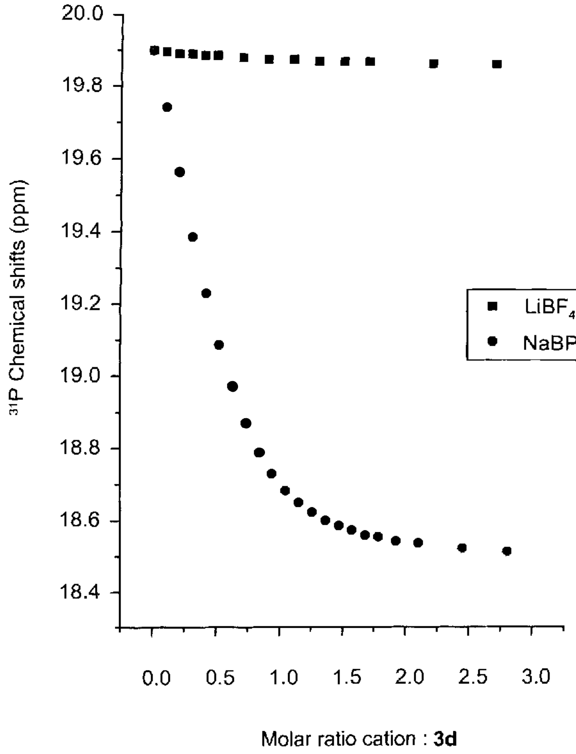


[a] Selected bond lengths [Å] and angles [°]: Mo1–P1 2.552(8), Mo1–P2 2.556(7), Mo1–C1 1.990(3), Mo1–C2 2.026(3), Mo1–C3 1.984(3), Mo1–C4 2.032(3), P1–C5 1.844(3), P2–C22 1.850(3); P1–Mo1–P2 98.26(2), C1–Mo1–P1 85.58(12), C2–Mo1–P1 91.32(10), C3–Mo1–P1 173.90(9), C4–Mo1–P1 93.16(8), C1–Mo1–P2 176.02(12), C2–Mo1–P2 92.68(10), C3–Mo1–P2 87.83(9), C4–Mo1–P2 87.75(8), C5–P1–Mo1 114.72(10), C22–P2–Mo1 120.16(9).

tween 0.2 and 0.8 for all measured points, in the case of the 2:1 complexes this is only valid for one third of about twenty data points.

A conspicuous finding is the fact that only **3d** interacts with Na^+ but not with Li^+, while no changes in the ^{31}P-chemical shifts in the cases of the meta and para crown ethers **3e** and **3f**, and the smaller cycles (n = 1) **3a–c** indi-

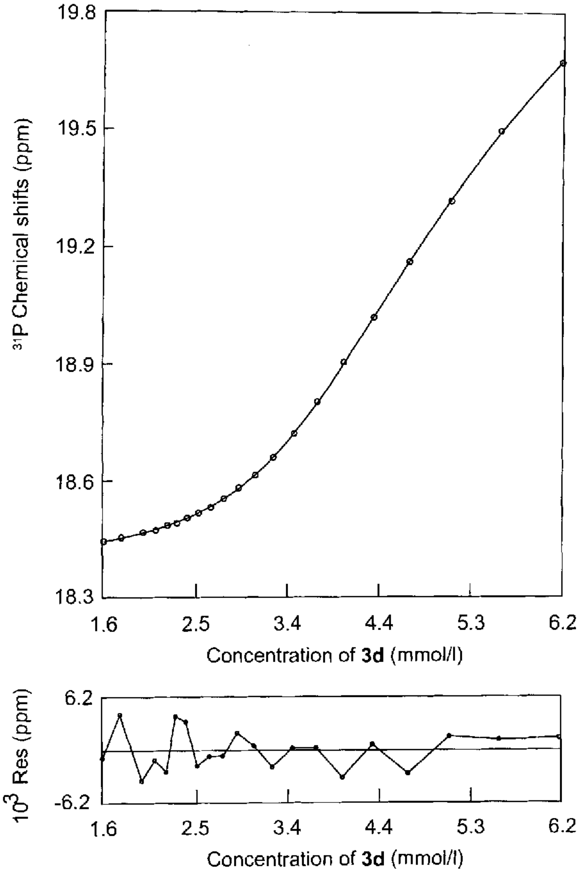
Figure 4. ^{31}P-chemical shifts vs the molar ratio cation/**3d** in a mixture of CD_2Cl_2/CD_3CN (1:1). Used alkali metal salts were $LiBF_4$, and $NaBPh_4$. The ligand (**3d**) concentrations were in the range between 0.01 M and 0.001 M



cate that no inclusion compounds are formed whith the alkali metal cations. With regard to the related benzo-12-crown-4[8] and the molybdacrown ethers *cis*-$(OC)_4Mo[Ph_2PCH_2(CH_2OCH_2)_nCH_2PPh_2$-*P,P'*] ($n$ = 4, 5) examined by Gray et al. this result is in marked contrast.

As reflected in Figure 4 the ^{31}P-chemical shift moves upfield in the case of the inclusion of Na^+. No effect is established if $LiBF_4$ reacts with **3d**. Thus **3d** is able to discriminate between Na^+ and Li^+ which is in contrast to the related benzo-18-crown-6 where the stability constants of lithium and sodium are in the same range[8]. A direct comparison of both systems is inappropriate, because the anions (BF_4^- and BPh_4^- vs picrate) and the employed solvents (CD_2Cl_2/CD_3CN vs $CDCl_3$) are different. Gray et al.[23] reported on the inclusion of Li^+ ($LiBF_4$) and Na^+ ($NaBPh_4$) into the aliphatic molybdacrown ethers *cis*-$(OC)_4Mo[PPh_2CH_2(CH_2OCH_2)_nCH_2PPh_2$-*P,P'*] ($n$ = 4, 5) in a 1:1 solvent mixture of CD_3CN and CCl_4. In contrast to **3d** both metallacrown ethers form 1:1 complexes with Li^+. On the other hand the sodium complex of **3d** shows a stability constant which is one or two orders of magnitude higher than those for the molybdacrown ethers with n = 4, 5. Compared to the systems of Gray[23] this behavior indicates that the number of oxygen atoms in the ring framework and the cavity of the crown ether in **3d** are responsible for the discrimination between Li^+ and Na^+. Another difference between aliphatic and aromatic molybdacrown ethers is the fact that the latter form 2:1 (**3d**/Na^+) along with 1:1 complexes while the first mentioned type forms only 1:1 complexes.

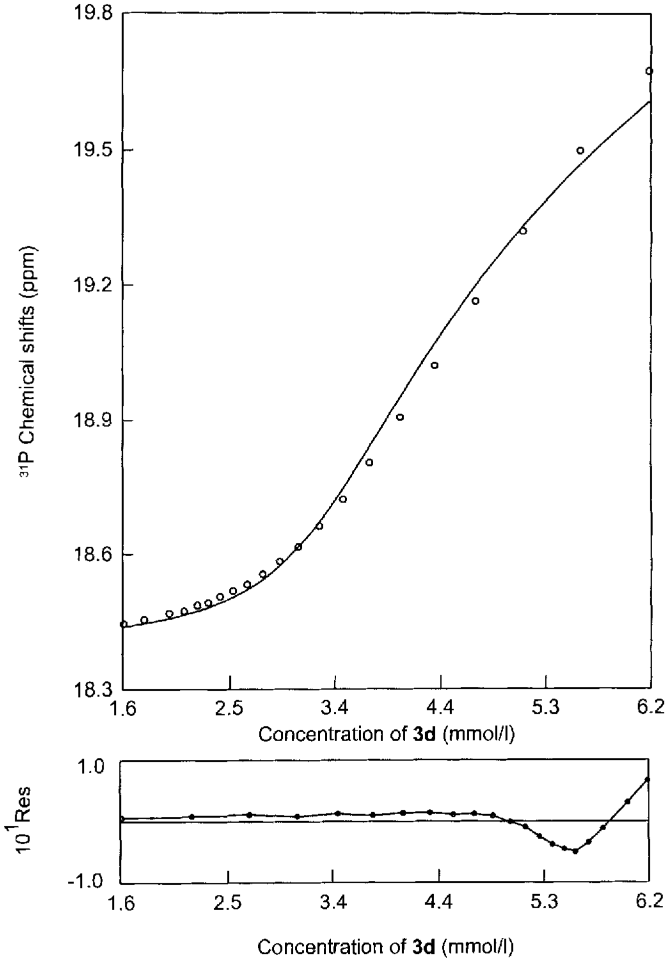
Figure 5. Top: Plot of the δ^{31}P-chemical shifts vs the concentration of **3d** (CD_2Cl_2/CD_3CN = 1:1) assuming that 2:1 and 1:1 (**3d**/Na^+) complexes are formed. Open circles (○) represent experimental data, the graph (—) represents shifts calculated using the "best-fit" parameters. Bottom: Residuals plot



Conclusion

Benzometallacrown ethers take an intermediate position between benzo- and metallacrown ethers. In addition to their polyether chain they consist of an aromatic building block and a transition metal center. Both constituents control the inclusion characteristics and are responsible for a defined geometry. Compared to crown ethers with an aliphatic framework benzometallacrown ethers are less flexible. Dependent on the number of CH_2CH_2O units and the substitution pattern at the benzene ring the benzomolybdacrown ethers **3a**–**f** offer different cavities. The well known cyclic ethers 1,2-benzo-12-crown-4 and 1,2-benzo-18-crown-6 are capable to include Li^+, Na^+, and K^+ and Li^+, Na^+, K^+, Rb^+, and Cs^+, respectively[8]. Gray et al. determined the stability constants of the related aliphatic molybdacrown ethers *cis*-$(OC)_4Mo[PPh_2CH_2(CH_2OCH_2)_n$-$CH_2PPh_2$-*P,P'*] ($n$ = 4, 5) which are able to complex Li^+ and Na^+[23]. Unlike to both systems, the benzomolybdacrown ether **3d** shows an interaction with Na^+ forming a 1:1 and 2:1 (**3d**/cation) complex, while no effect could be observed with Li^+. Thus **3d** discriminates strongly between

Figure 6. Top: Plot of the δ^{31}P-chemical shifts vs the concentration of **3d** (CD_2Cl_2/CD_3CN = 1:1) assuming that only a 1:1 (**3d**/Na^+) complex is formed. Open circles (○) represent experimental data, the graph (—) represents shifts calculated using the "best-fit" parameters. Bottom: Residuals plot



Li^+ and Na^+. However, all other benzomolybdacrown ethers **3a–c** and **3e, f** are not able to incorporate any alkali metal cation. The same behavior show the 1,3-substituted benzo-19-crown-6 and benzo-13-crown-4 related to **3b,e** and the 1,4-substituted benzo-20-crown-6, related to **3f**[8].

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Experimental Section

General: All manipulations were carried out under an atmosphere of argon by using standard Schlenk techniques. For the synthesis of the benzomolybdacrown ethers **3a–f** brown glass tubes were used to protect the reaction mixture from light. The dichlorides **1a–f** were synthezised following the literature procedure[39]. Solvents were dried with appropriate reagents and stored under argon. –Column chromatography: Activated silica gel, 0.063–0.2 mm (Merck), diameter/length of the column 2.5/30 cm. – Elemental analyses: Carlo Erba 1106. – AAS: Perkin-Elmer model 4000. – FD-MS: Finnigan MAT 711A (8 kV) modified by AMD. – EI-MS Finnigan TSQ 70 (200°C). – ESI spectra were recorded on a triple-quadrupole mass spectrometer API III (Sciex, Thornhill, Canada) equipped with a nebulizer-assisted electrospray source. – IR: Bruker IFS 48 FT-IR. – ^{1}H, ^{13}C, and ^{31}P NMR: Bruker DRX 250 spectrometer at 250.13, 62.90, and 101.25 MHz, at 25°C. ^{1}H and ^{13}C chemical shifts were recorded relative to partially deuterated solvent peaks which are reported relative to TMS. ^{31}P-chemical shifts were measured relative to 85% H_3PO_4 (δ = 0). – $Mo(CO)_4(nbd)$ was obtained according to literature methods[40]. Lithium tetrafluoroborate (Merck) and sodium tetraphenylborate (Merck) were dried in vacuo at 70°C for 3 d.

NMR Titration Procedure: The titration experiments as described in the literature[23] were performed in a NMR tube (diameter/length = 5/160 mm) containing a solution of **3d** in a 1:1 mixture of CD_2Cl_2/CD_3CN at 25°C. The molar starting concentration of **3d** were $6.2\cdot10^{-3}$ for the titration of Na^+ as BPh_4^- salt. To this were added stepwise in 30 µl (Na^+) portions stock solution of $NaBPh_4$ ($1.51\cdot10^{-2}$ M) in CD_3CN. To maintain the 1:1 proportion of CD_2Cl_2/CD_3CN the same amount of CD_2Cl_2 was added after each step. The procedure was finished when a **3d**/cation ratio of ca. 1:3 was achieved.

Calculational Methods

The program EQNMR[38] is used to evaluate equilibrium constants and chemical shifts in systems where all the species are in rapid equilibrium under the experimental conditions and where the NMR-chemical shift of a nucleus varies with the degree of complex formation. Equation (1) shows a reaction type in which M is the corresponding alkali metal cation and L is the employed complexing agent, the chemical shift of which is monitored by NMR spectroscopy.

$$m\mathrm{M} + n\mathrm{L} \rightleftharpoons \mathrm{M}_m\mathrm{L}_n \tag{1}$$

The chemical shift of this signal is demonstrated by equation (2) where δ_{calc} is the weighted average of the chemical shifts of the various L-containing species present, L represents the uncomplexed form of the ligand L, M represents the alkali metal cation, and *i* and *j* represent the maximum values of *m* and *n*, respectively.

$$\delta_{calc} = \sum_{m=0}^{m=i}\sum_{n=1}^{n=j} \frac{\delta_{mn}\cdot n\cdot[\mathrm{M}_m\mathrm{L}_n]}{[\mathrm{L}]_{total}} \tag{2}$$

If M_mL_n in equation (2) is substituted by (3), equation (4) is obtained. The problem consists in a determination of the optimum values for the various δ_{mn} and β_{mn} which best fit the experimental chemical shift data, where β_{mn} represents the stability constant.

$$[\mathrm{M}_m\mathrm{L}_n] = \beta_{mn}\cdot[\mathrm{M}]^m\cdot[\mathrm{L}]^n \tag{3}$$

$$\delta_{calc} = \sum_{m=0}^{m=i}\sum_{n=1}^{n=j} \frac{\delta_{mn}\cdot\beta_{mn}\cdot n\cdot[\mathrm{M}]^m\cdot[\mathrm{L}]^n}{[\mathrm{L}]_{total}} \tag{4}$$

The program EQNMR is suitable to calculate the concentrations of all species present in solution on the basis of an initial estimate of the stability constants. By using equation (4) the program subsequently calculates the chemical shifts δ_{calc}, in consideration of the complexed and umcomplexed species contributing to the overall chemical shift of the nucleus being monitored. This procedure is followed by the non-linear least-squares subroutines which are responsible for the refinement of the various parameters. The ob-

Table 1. Crystal data and refinement details for compounds **3a** and **3d**

	3a	**3d**
formula	$C_{42}H_{40}MoO_8P_2$	$C_{48}H_{51}MoNO_{10}P_2$
M_r	830.62	959.78
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
a [Å]	18.674(2)	9.812(2)
b [Å]	17.867(2)	44.436(7)
c [Å]	23.492(3)	10.592(2)
β [°]	90.42(1)	95.10(1)
V [Å^3]	7838(2)	4600(1)
$\rho_{calcd.}$[g·cm^{-3}]	1.408	1.386
Z	8	4
F(000) [e]	3424	1992
T [°C]	−100	−100
μ(Mo-K_α)[mm^{-1}]	0.468	0.411
scan mode	ω	ω
hkl range	4/−22, 0/−21, ±27	±12, ±57, ±13
2θ limits [°]	4−50	4−50
measured refl.	17240	42142
observed refl. $I > 2\sigma(I)$	8774	7458
refined parameters	956	706
S	0.90	1.73
$R1$	0.03	0.04
$wR2$	0.076	0.091

tained data were employed for the calculation of the refined stability constants. The next iteration step of the whole procedure follows until a minimum of the R-factor is achieved.

General Procedure for the Preparation of the Diphosphanes **2a−f**

A solution of $LiPPh_2$ in 50 ml of THF/n-hexane (5:1) was added dropwise to a stirred solution of the dichlorides **1a−f** in 50 ml of THF at 0 °C until the color of the reaction mixture remained red. The solution was stirred for 12 h at 20°C. Subsequently it was hydrolyzed with a 40-ml portion of saturated aqueous NH_4Cl. The organic layer was separated and after removing the solvent in vacuo the remainder was purified by column chromatography (CH_2Cl_2/Et_2O/silica gel/30 cm) yielding colorless viscous oils.

O,O-Bis(5-diphenylphosphanyl-3-oxapentyl)catechol (**2a**): Starting materials: 2.22 g (6.81 mmol) of **1a** and 2.62 g (13.62 mmol) of $LiPPh_2$. Yield 3.52 g (82.9%) of **2a**. − ^1H NMR ($CDCl_3$): δ = 2.34 (m, 4 H, CH_2P), 3.60 (m, 4 H, CH_2CH_2P), 3.67 (m, 4 H, $C_6H_4OCH_2CH_2$), 4.03 (m, 4 H, $C_6H_4OCH_2$), 6.84 (m, 4 H, C_6H_4), 7.2−7.4 (m, 20 H, Ph). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 28.8 (d, $^1J_{PC}$ = 13.4 Hz, CH_2P), 68.6 (d, $^2J_{PC}$ = 24.2 Hz, CH_2CH_2P), 68.8, 69.2 ($C_6H_4OCH_2CH_2$), 115.1, 121.6, 149.0 (C_6H_4), 128.4, 128.5,132.6 (*o*-, *m*-, *p*-Ph), 138.2 (*ipso*-Ph). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −21.1 (s). − MS (FD, 35°C), *m/z*: 622.4 [M^+]. − $C_{38}H_{40}O_4P_2$ (622.67): calcd. C 73.30, H 6.48; found C 73.06, H 6.49.

O,O-Bis(5-diphenylphosphanyl-3-oxapentyl)resorcinol (**2b**): Starting materials: 3.98 g (12.38 mmol) of **1b** and 4.75 g (24.76 mmol) of $LiPPh_2$. Yield 6.28 g (81.5%) of **2b**. − ^1H NMR ($CDCl_3$): δ = 2.36 (m, 4 H, CH_2P), 3.59 (m, 4 H, CH_2CH_2P), 3.67 (m, 4 H, $C_6H_4OCH_2CH_2$), 3.96 (m, 4 H, $C_6H_4OCH_2$), 6.37−6.45 (m, 4 H, C_6H_4), 7.20−7.41 (m, 20 H, Ph). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 28.8 (d, $^1J_{PC}$ = 12.8 Hz, CH_2P), 68.7 (d, $^2J_{PC}$ = 24.93 Hz, CH_2CH_2P), 67.3, 69.1 ($C_6H_4OCH_2CH_2O$), 101.7, 107.1, 129.7, 159.9 (C_6H_4), 128.5, 128.6, 132.7 (*o*-, *m*-, *p*-Ph) , 138.16 (*ipso*-Ph). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −21.1 (s). − MS (EI, 70 eV), *m/z*: 622.2 [M^+]. − $C_{38}H_{40}O_4P_2$ (622.67): calcd. C 73.30, H 6.48; found C 73.42, H 6.61.

O,O-Bis(5-diphenylphosphanyl-3-oxypentyl)hydroquinone (**2c**): Starting materials: 3.84 g (11.87 mmol) of **1c** and 4.57 g (23.74 mmol) of $LiPPh_2$. Yield 6.80 g (92.0%) of **2c**. − ^1H NMR ($CDCl_3$): δ = 2.38 (m, 4 H, CH_2P), 3.56−3.69 (m, 8 H, $CH_2OCH_2CH_2P$), 3.95 (m, 4 H, $C_6H_4OCH_2$), 6.75 (m, 4 H, C_6H_4), 7.25−7.41 (m, 20 H, Ph). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 28.7 (d, $^1J_{PC}$ = 13.3 Hz, CH_2P), 68.7 (d, $^2J_{PC}$ = 25.5 Hz, CH_2CH_2P), 67.9, 69.2 ($C_6H_4OCH_2CH_2$), 115.5, 153.0 (C_6H_4), 128.4, 128.6, 132.7 (*o*-, *m*-, *p*-Ph) , 138.2 (*ipso*-Ph). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −21.1 (s). − MS (FD, 35°C), *m/z*: 622.4 [M^+]. − $C_{38}H_{40}O_4P_2$ (622.67): calcd. C 73.30, H 6.48; found C 73.25, H 6.40.

O,O-Bis(8-diphenylphosphanyl-3,6-dioxaoctyl)catechol (**2d**): Starting materials: 4.12 g (10.03 mmol) of **1d** and 3.85 g (20.04 mmol) of $LiPPh_2$. Yield 6.29 g (88.3%) of **2d**. − ^1H NMR ($CDCl_3$): δ = 2.36 (m, 4 H, CH_2P), 3.44−3.66 (m, 12 H, $CH_2CH_2OCH_2CH_2P$), 3.77 (m, 4 H, $C_6H_4OCH_2CH_2$), 4.09 (m, 4 H, $C_6H_4OCH_2$), 6.85 (m, 4 H, C_6H_4), 7.31−7.44 (m, 20 H, Ph). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 28.6 (d, $^1J_{PC}$ = 12.8 Hz, CH_2P), 68.4 (d, $^2J_{PC}$ = 25.6 Hz, CH_2CH_2P), 68.7, 69.6, 70.0, 70.6 ($C_6H_4OCH_2$-$CH_2OCH_2CH_2O$), 114.7, 121.5, 148.8 (C_6H_4), 128.3, 128.5, 132.5 (*o*-, *m*-, *p*-Ph) , 138.1 (*ipso*-Ph). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −21.1 (s). − MS (FD, 35°C), *m/z*: 710.5 [M^+]. − $C_{42}H_{48}O_6P_2$ (710.76): calcd. C 70.98, H 6.81; found C 71.03, H 6.87.

O,O-Bis(8-diphenylphosphanyl-3,6-dioxaoctyl)resorcinol (**2e**): Starting materials: 3.85 g (9.36 mmol) of **1e** and 3.60 g (18.72 mmol) of $LiPPh_2$. Yield 6.62 g (99.5%) of **2e**. − ^1H NMR ($CDCl_3$): δ = 2.37 (m, 4 H, CH_2P), 3.48−3.65 (m, 12 H, OCH_2CH_2-OCH_2CH_2P), 3.75 (m, 4 H, $C_6H_4OCH_2CH_2$), 4.02 (m, 4 H, $C_6H_4OCH_2$), 6.41−6.50, 7.04−7.14 (m, 4 H, C_6H_4), 7.22−7.43 (m, 20 H, Ph). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 28.6 (d, $^1J_{PC}$ = 13.5 Hz, CH_2P), 68.4 (d, $^2J_{PC}$ = 25.6 Hz, CH_2CH_2P), 67.2, 69.6, 70.0, 70.6 ($C_6H_4OCH_2CH_2OCH_2CH_2$), 101.6, 106.9, 129.6, 159.8 (C_6H_4), 128.3, 128.4, 132.5 (*o*-, *m*-, *p*-Ph), 138.1 (*ipso*-Ph). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −21.0 (s). − MS (EI, 70 eV), *m/z*: 710.4 [M^+]. − $C_{42}H_{48}O_6P_2$ (710.76): calcd. C 70.98, H 6.81; found C 70.99, H 6.78.

O,O-Bis(8-diphenylphosphanyl-3,6-dioxaoctyl)hydrochinone (**2f**): Starting materials: 4.17 g (10.15 mmol) of **1f** and 3.91 g (20.3 mmol) of $LiPPh_2$. Yield 6.25 g (86.6%) of **2f**. − ^1H NMR ($CDCl_3$): δ = 2.36 (m, 4 H, CH_2P), 3.50−3.62 [m, 12 H, OCH_2CH_2-OCH_2CH_2P), 3.73 (m, 4 H, $C_6H_4OCH_2CH_2$), 3.98 (m, 4 H, $C_6H_4OCH_2$), 6.76 (m, 4 H, C_6H_4), 7.24−7.40 (m, 20 H, Ph). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 28.7 (d, $^1J_{PC}$ = 13.2 Hz, CH_2P), 68.5 (d, $^2J_{PC}$ = 25.4 Hz, CH_2CH_2P), 67.9, 69.8, 70.1, 70.7 ($C_6H_4OCH_2$-$CH_2OCH_2CH_2$), 115.4, 153.0 (C_6H_4), 128.4, 128.6, 132.7 (*o*-, *m*-, *p*-Ph) , 138.2 (*ipso*-Ph). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −21.0 (s). − MS (EI, 70 eV), *m/z*: 710.2 [M^+]. − $C_{42}H_{48}O_6P_2$ (710.76): calcd. C 70.98, H 6.81; found C 70.63, H 6.89.

General Procedure for the Formation of the Molybdacycles **3a−f**[17]

To 500 ml of CH_2Cl_2 were added simultaneously equimolar solutions of $(OC)_4Mo(nbd)$ and **2a−f** dissolved in 50 ml of CH_2Cl_2 at 20°C. After stirring overnight, the solvent was removed under vacuum and the residue was purified by column chromatography (silica gel, column length 30 cm, with a linear gradient of diethylether/CH_2Cl_2 starting with pure CH_2Cl_2 and finishing with a volume ratio of 1:3). The complexes were dissolved in 20 ml of CH_3CN and the products were precepitated by degassed water providing an almost colorless powder which was dried under vacuum for several days.

9,9,9,9-Tetracarbonyl-8,8,10,10-tetraphenyl-2,5,13,16-tetraoxa-9-molybda-8,10-diphosphabicyclo[15.4.0^{1,17}]henicosa-1(21),17,19-

triene (**3a**): Starting material: 470 mg (0.75 mmol) of **2a** and 223 mg (0.74 mmol) of $(OC)_4Mo(nbd)$. Yield 372 mg (59.4%) of **3a**. – ^1H NMR (CD_2CL_2): δ = 2.42 (m, 4 H, CH_2P), 3.44 (m, 4 H, $C\mathit{H}_2CH_2P$), 3.71 (m, 4 H, $C_6H_4OCH_2C\mathit{H}_2$), 4.08 (m, 4 H, $C_6H_4OC\mathit{H}_2$), 6.91 (m, 4 H, C_6H_4), 7.29–7.41 (m, 20 H, Ph). – $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 31.8 (vt[41], N = 16.4 Hz, CH_2P), 67.5, 69.1, 70.0 ($C_6H_4O\mathit{C}H_2\mathit{C}H_2O\mathit{C}H_2$), 114.7, 121.9, 149.6 ($C_6H_4$), 128.8, 129.9, 132.7 (*o*-, *m*-, *p*-Ph), 137.3 (m[41], N = 34.9 Hz, *ipso*-Ph), 210.3 (t, $^2J_{PC}$ = 9.2 Hz, axial CO), 215.8 (m[41], N = 15.3 Hz, equatorial CO). – $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 21.5 (s). – m.p. > 145°C (dec.). – IR (KBr): $\tilde{\nu}$ = 2018 cm^{-1}, 1918, 1895, 1861 (CO). – MS (FD, 30°C), *m/z*: 832.2 [M^+]. – $C_{42}H_{40}MoO_8P_2$ (830.63): calcd. C 60.73, H 4.85, Mo 11.55; found C 60.61, H 4.78, Mo 11.61.

9,9,9,9-Tetracarbonyl-8,8,10,10-tetraphenyl-2,5,13,16-tetraoxa-9-molybda-8,10-diphosphabicyclo[15.3.1$^{1.17}$]henicosa-1(21),17,19-triene (**3b**): Starting material: 415 mg (0.67 mmol) of **2b** and 202 mg (0.67 mmol) of $(OC)_4Mo(nbd)$. Yield 285 mg (51.2%) of **3b**. – ^1H NMR (CD_2Cl_2): δ = 2.14–2.24 (m, 4 H, CH_2P), 3.37–3.46 (m, 4 H, $C\mathit{H}_2CH_2P$), 3.60–3.67 (m, 4 H, $C_6H_4OCH_2C\mathit{H}_2$), 4.17–4.23 (m, 4 H, $C_6H_4OC\mathit{H}_2$), 6.58, 7.00, 7.22 (4 H, C_6H_4), 7.32–7.41 (m, 20 H, Ph). – $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 31.1 (vt[41], N = 17.9 Hz, CH_2P), 67.2 (m, $\mathit{C}H_2CH_2P$), 68.1, 70.0 ($C_6H_4O\mathit{C}H_2\mathit{C}H_2$), 104.0, 108.3, 160.3 ($C_6H_4$), 128.4, 129.8, 132.2 (*o*-, *m*-, *p*-Ph), 137.1 (m[41], N = 33.7 Hz, *ipso*-Ph), 210.0 [t, $^2J_{PC}$ = 9.4 Hz, axial CO], 215.5 (m[41], N = 15.2 Hz, equatorial CO). – $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 19.7 (s). – m.p. > 140°C (dec.). – IR (KBr): $\tilde{\nu}$ = 2023 cm^{-1}, 1927, 1895, 1866 (CO). – MS (FD, 30°C), *m/z*: 832.2 [M^+]. – $C_{42}H_{40}MoO_8P_2$ (830.63): calcd. C 60.73, H 4.85, Mo 11.55; found C 60.41, H 4.92, Mo 11.78.

9,9,9,9-Tetracarbonyl-8,8,10,10-tetraphenyl-2,5,13,16-tetraoxa-9-molybda-8,10-diphosphabicyclo[15.2.2$^{1.17}$]henicosa-1(20),17,18-triene (**3c**): Starting material: 532 mg (0.85 mmol) of **2c** and 256 mg (0.85 mmol) of $(OC)_4Mo(nbd)$. Yield 230 mg (32.4%) of **3c**. – ^1H NMR (CD_2Cl_2): δ = 1.83–1.94 (m, 4 H, CH_2P), 3.03–3.13 (m, 4 H, $C\mathit{H}_2CH_2P$), 3.47–3.53 (m, 4 H, $C_6H_4OCH_2C\mathit{H}_2$), 4.15–4.22 (m, 4 H, $C_6H_4OC\mathit{H}_2$), 7.01 (s, 4 H), 7.21–7.39 (m, 20 H, Ph). – $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 30.6 (vt[41], N = 17.1 Hz, CH_2P), 66.7 (m, $\mathit{C}H_2CH_2P$), 67.9, 69.8 ($C_6H_4O\mathit{C}H_2\mathit{C}H_2$), 117.1, 152.8 ($C_6H_4$), 128.4, 129.4, 132.1 (*o*-, *m*-, *p*-Ph), 136.6 (m[41], N = 33.4 Hz, *ipso*-Ph), 210.0 (t, $^2J_{PC}$ = 9.6 Hz, axial CO), 215.5 (m[41], N = 14.9 Hz, equatorial CO). – $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 19.9 (s). – IR (KBr): $\tilde{\nu}$ = 2019 cm^{-1}, 1914, 1893, 1876 (CO). – MS (FD, 30°C), *m/z*: 832.0 [M^+]. – $C_{42}H_{40}MoO_8P_2$ (830.63): calcd. C 60.73, H 4.85, Mo 11.55; found C 61.00, H 5.12, Mo 11.76.

12,12,12,12-Tetracarbonyl-11,11,13,13-tetraphenyl-2,5,8,16,19,22-hexaoxa-12-molybda-11,13-diphosphabicyclo[21.4.0$^{1.23}$]heptacosa-1(27),23,25-triene (**3d**): Starting material: 454 mg (0.64 mmol) of **2d** and 0.192 g (0.64 mmol) of $(OC)_4$-Mo(nbd). Yield 196 mg (33.4%) of **3d**. – ^1H NMR ($CDCl_3$): δ = 2.28–2.40 (m, 4 H, CH_2P), 3.31–3.43 (m, 4 H, $C\mathit{H}_2CH_2P$), 3.46–3.53, 3.69–3.76 (m, 4 H, m, 4 H, $C\mathit{H}_2C\mathit{H}_2OCH_2CH_2P$), 3.87 (m, 4 H, $C_6H_4OCH_2C\mathit{H}_2$), 4.17 (m, 4 H, $C_6H_4OC\mathit{H}_2$), 6.90 (m, 4 H, C_6H_4), 7.27–7.42 (m, 20 H, Ph). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 31.1 (vt[41], N = 17.0 Hz, CH_2P), 67.1 (m, $\mathit{C}H_2CH_2P$), 69.2, 69.8, 70.4, 70.7 ($C_6H_4O\mathit{C}H_2\mathit{C}H_2O\mathit{C}H_2\mathit{C}H_2$), 114.5, 121.5, 148.9 ($C_6H_4$), 128.3, 129.3, 132.1 (*o*-, *m*-, *p*-Ph) , 137.2 (m[41], N = 34.4 Hz, *ipso*-Ph), 209.8 (t, $^2J_{PC}$ = 9.4 Hz, axial CO), 215.1 (m[41], N = 15.5 Hz, equatorial CO). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 20.4 (s). – m.p. > 130°C (dec.). – IR (KBr): $\tilde{\nu}$ = 2019 cm^{-1}, 1932, 1888, 1870 (CO). – MS (FD, 30°C), *m/z*: 919.5 [M^+]. – $C_{46}H_{48}MoO_{10}P_2$ (918.73): calcd. C 60.14, H 5.27, Mo 10.44; found C 60.34, H 5.30, Mo 10.38.

12,12,12,12-Tetracarbonyl-11,11,13,13-tetraphenyl-2,5,8,16,19,22-hexaoxa-12-molybda-11,13-diphosphabicyclo[21.3.1$^{1.23}$]heptacosa-1(27),23,25-triene (**3e**): Starting material: 294 mg (0.41 mmol) of **2e** and 124 mg (0.41 mmol) of $(OC)_4$-Mo(nbd). Yield 246 mg (64.7%) of **3e**. – ^1H NMR (CD_2Cl_2): δ = 2.13–2.25 (m, 4 H, CH_2P), 3.09–3.20 (m, 4 H, $C\mathit{H}_2CH_2P$), 3.21–3.28, 3.39–3.45, 3.60–3.66, 3.94–4.00 (m, 16 H, C_6H_4O-$C\mathit{H}_2C\mathit{H}_2OC\mathit{H}_2C\mathit{H}_2$), 6.40, 6.45, 7.07 (4 H, C_6H_4), 7.19–7.33 (m, 20 H, Ph). – $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 31.6 (vt[41], N = 19.2 Hz, CH_2P), 66.9 (m, $\mathit{C}H_2CH_2P$), 67.8, 69.5, 70.2, 70.8 ($C_6H_4O\mathit{C}H_2\mathit{C}H_2O\mathit{C}H_2\mathit{C}H_2$), 102.3, 107.1, 160.2 ($C_6H_4$), 128.4, 129.8, 132.2 (*o*-, *m*-, *p*-Ph), 136.6 (m[41], N = 32.7 Hz, *ipso*-Ph), 209.9 (t, $^2J_{PC}$ = 9.6 Hz, axial CO), 215.6 (m[41], N = 15.7 Hz, equatorial CO). – $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 20.9 (s). – m.p. > 135°C (dec.). – IR (KBr): $\tilde{\nu}$= 2019 cm^{-1}, 1917, 1897, 1877 (CO). – MS (FD, 30°C), *m/z*: 919.6 [M^+]. – $C_{46}H_{48}MoO_{10}P_2$ (918.73): calcd. C 60.14, H 5.23, Mo 10.44; found C 60.46, H 5.40, Mo 10.71.

12,12,12,12-Tetracarbonyl-11,11,13,13-tetraphenyl-2,5,8,16,19,22-hexaoxa-12-molybda-11,13-diphosphabicyclo[21.2.2$^{1.23}$]heptacosa-1(26),23,24-triene (**3f**): Starting material: 410 mg (0.58 mmol) of **2f** and 173 mg (0.58 mmol) of $(OC)_4$-Mo(nbd). Yield 305 mg (58.3%) of **3f**. – ^1H NMR (CD_2Cl_2): δ = 2.18–2.32 (m, 4 H, CH_2P), 3.17–3.37, 3.48–3.55, 3.69–3.76 (m, 16 H, $C_6H_4OCH_2C\mathit{H}_2OC\mathit{H}_2C\mathit{H}_2OC\mathit{H}_2$), 4.09–4.16 (m, 4 H, $C_6H_4OC\mathit{H}_2$), 6.91 (s, 4 H, C_6H_4), 7.26–7.41 (m, 20 H, Ph). – $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 31.6 (vt[41], N = 19.5 Hz, CH_2P), 66.7 (m, $\mathit{C}H_2CH_2P$), 68.6, 69.8, 70.2, 70.5 ($C_6H_4O\mathit{C}H_2\mathit{C}H_2$-$O\mathit{C}H_2\mathit{C}H_2$), 116.1, 153.1 ($C_6H_4$), 128.2, 129.3, 131.9 (*o*-, *m*-, *p*-Ph), 136.4 (m[41], N = 32.3 Hz, *ipso*-Ph), 209.6 (t, $^2J_{PC}$ = 9.4 Hz, axial CO), 215.3 (m[41], N = 14.8 Hz, equatorial CO). – $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 20.8 (s). – IR (KBr): $\tilde{\nu}$ = 2018 cm^{-1}, 1915, 1899, 1874 (CO). – MS (FD, 30°C), *m/z*: 919.6 [M^+]. – $C_{46}H_{48}MoO_{10}P_2$ (918.73): calcd. C 60.14, H 5.23, Mo 10.44; found C 60.06, H 5.45, Mo 10.11.

Crystal Structure Determination: Single crystals of **3a** and **3d** were obtained from *n*-hexane/dichloromethane and acetonitrile/H_2O, respectively. Crystals were mounted on a glass fibre and transferred to a P4 Siemens diffractometer by taking rotation photographs to find a suitable reduced cell (graphite-monochromated Mo-K_α radiation). The final cell parameters and specific data collection parameters for **3a** and **3d**, respectively, are compiled in Table 1. The lattice constants were determined with 25 precisely centered high-angle reflections and refined by least-squares methods. The presence of two molecules in the asymmetric unit of **3a** and the β angle of near 90° suggest that the crystal could belong to an orthorhombic crystal system. A search for higher metric symmetry led to a R(int) = 0.47 for an orthorhombic P-Lattice in contrast to R(int) = 0.03 for a monoclinic P-Lattice. There is no acceptable orthorhombic space group. The R(int) value of **3d** is 0.075. Minor decay corrections were applied to both crystals. All structures were solved by Patterson methods[42] and refined with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included in calculated positions (riding model). An absorption correction (ψ scan) was applied to compound **3d** with maximum and minimum transmission 0.494 and 0.445. Maximum and minimum peaks in the final difference synthesis were 0.300 and −0.354 and 0.977 and −0.508 $e\text{Å}^{-3}$, respectively. In an early refinement stage the phenyl group C11–C16 proved to be disordered. The disorder had to be extended to the atoms C10–C19 and the acetonitrile molecule. The disorder was treated with split positions leading to separate occupation factors of 0.55 for the atoms C10–C19 and 0.59 for the acetonitrile molecule. The final combined occupation factor is 0.55. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100442. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code +44(0)1223/336-033, e-mail: deposit@chemcrys.cam.ac.uk].

☆ Dedicated to Professor *Achim Müller* on the occasion of his 60th birthday.

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