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Tridentate phosphine ligands bearing aza-crown ether lariats

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ABSTRACT

Crown ethers are useful macrocycles that act as size-selective binding sites for alkali metals. These frameworks have been incorporated into a number of macromolecular assemblies that use simple cations as reporters and/or activity triggers. Incorporating crown ethers into secondary coordination sphere ligand frameworks for transition metal chemistry will lead to new potential methods for controlling bond formation steps, and routes that couple traditional ligand frameworks with these moieties are highly desirable. Herein we report the syntheses of a family of tridentate phosphine complexes bearing tethered aza-crown ethers (lariats) designed to modularize the variation of aza-crown size, lariat length, and distal phosphine substituents, followed by the synthesis and solid-state structures of Mo(III) complexes bearing cations in the pendent crown ethers.

1. Introduction

Since their discovery by Pedersen [1], crown ethers have proved to be extremely useful binding sites for alkali metals cations. One of the most important properties of crown ether chemistry is the size-dependence of cation binding, largely dictated by the inner size of the macrocycle. In addition to alkali metals, these host molecules are able to bind a wide range of ionic and neutral species [2–5], and have been utilized as chemical modulators in a wide range of ion-selective applications [2,4,6–10]. In transition metal (TM) chemistry, secondary coordination sphere modifications have become an important way of modulating stoichiometric and catalytic activity [11–14]. Secondary coordination sphere modifications of TMs involving control of simple cations and their interactions with TM-bound substrates are a relatively underexplored area. McLain was among the first to investigate such systems, reporting studies of alkyl insertion promoted by tethered alkali metals [15,16], and systematic studies of cation-substrate interactions have had renewed interest [17,18]. Our laboratory has been developing multidentate lariat-ether phosphine ligands in order to further investigate the secondary coordination effects of tethered cations on catalytic and stoichiometric reactions of both polar and non-polar substrates. Herein we report the modular synthesis of a family of such phosphines bearing aza-crown ethers.

Our overall goal was to develop a modular synthetic pathway to tridentate phosphine ligands tethered to aza-crown ethers (lariats). A critical aspect of our synthetic strategy was that key features of the ligand framework could be tuned, such as the size of the crown ether, lariat length, and distal phosphine substituents. A key intermediate in this approach is an aza-crown tethered phosphonate, wherein the $-(CH_2)_n-$ tether is established directly between aza-crown ether and phosphonate precursors. Several examples of such compounds have been prepared, most notably by Keglevich ($n = 2–5$) [19–21]; the chemistry we present here has focused on just two lariat lengths ($-CH_2-$ and $-CH_2CH_2-$), but can be readily extended to these longer-lariat precursors.

2. Results and discussion

2.1. Synthesis of lariat primary phosphines

Entry into the target framework (Scheme 1) began with aza-macrocycles 1-aza-15-crown-5 (**1a**) and 1-aza-18-crown-6 (**1b**) [22], where control of the linker length between N and P atoms is readily accomplished via various nucleophilic addition strategies.

Routes toward amine-tethered phosphonates and phosphonate esters have been previously reported [16,20–26], however reduction to the primary phosphines and further homologation has (to our knowledge) not been reported.

A single CH_2 linker can be installed by the Kabachnick-Fields reaction as outlined by the Keglevich group [27–29]. The aza-crown ether **1a** condenses with formaldehyde and diethylphosphonate under microwave conditions to form **2a**. At this stage, the pure phosphonate can be isolated after extraction with triethylamine, which can be reduced to the primary phosphine **3a** with $LiAlH_4$ in Et_2O. The primary phosphine is highly reactive; the N–

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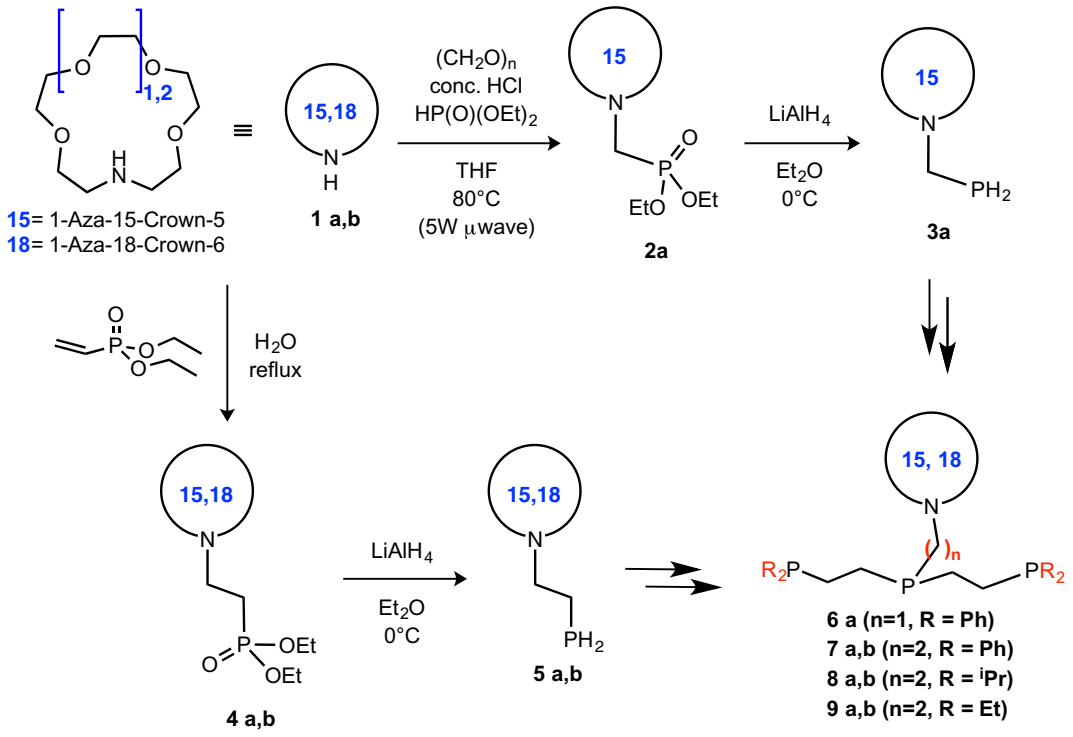


Scheme 1. Synthesis of primary phosphines synthons **3** and **5** used for the synthesis of tridentate lariat phosphines **6**–**9**.

CH_2–P linkage is prone to hydrolytic and/or radical cleavage (see below), severely limiting the possible purification/derivatization steps.

Ligands and ligand precursors based on the ethylene spacer are far more robust and offer a wider variety of synthetic approaches. The ethylene-linked aza-crown phosphonates **4a** and **4b** were prepared via Michael addition to diethylvinylphosphonate in refluxing water using a modification of published procedures [20,21], Reduction to the primary phosphine proceeded in the same manner as with **2a**, by the action of $LiAlH_4$ in Et_2O. Although the reduction ultimately produces good yields of these aza-crown tethered primary phosphines, the work-up is somewhat cumbersome. Following a published $LiAlH_4$ quenching procedure [30], a prescribed portion of water, LiOH solution, and a second portion of water are slowly added to the cooled reaction solution. No matter how slowly the quenching steps are performed, quenching is very uneven and prone to rapid heating and boiling of the ether solvent. Intramolecular binding of intermediate Li^+- or AlX^{n+}-phosphides to the crown is possible [31], leading to precipitation and subsequent irregular hydrolysis kinetics.

The single-carbon spacing between the phosphine and nitrogen in **3a** leads to a significant upfield shift of the ^{31}P resonance relative to the longer **5a** and **5b** (Fig. 1). Moreover, in contrast to the expected trends, the $^2J_{PH}$ and $^3J_{PH}$ couplings between the primary phosphine and methylene protons in **5a** and **5b** are essentially the same magnitude (5 Hz), leading to a triplet of pentets in the proton-coupled ^{31}P NMR spectrum.

We have exclusively used Li^+ salts when it has been necessary to expose intermediates to cationic reagents. Crown ethers are designed to carry cations into organic solutions, an obvious potential problem for our future studies if the preparation of non-metalated crown intermediates were impossible. Li^+ usually has lower binding affinity in the larger unsubstituted macrocycles (e.g. aza-15-crown-5 and aza-18-crown-6) when compared to other cations [20,21], and thus the complications from cation binding are minimized.

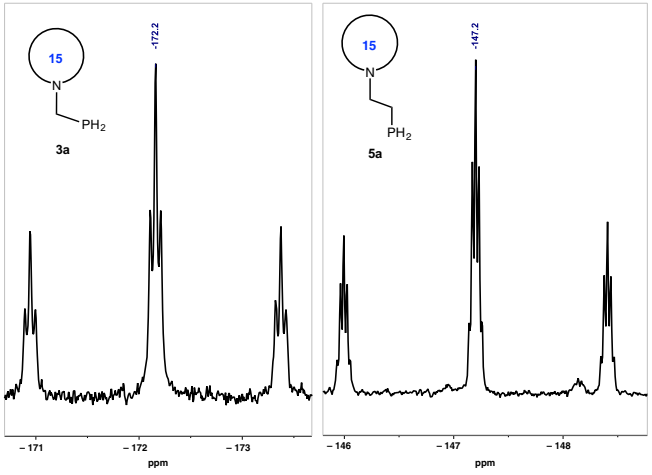


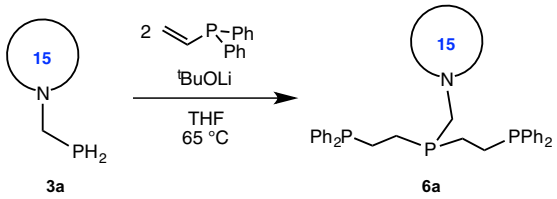
Fig. 1. ^{31}P NMR spectra of **3a** and **5a**, highlighting the primary, secondary and tertiary P–H couplings.

2.2. Assembling the tridentate TM-binding environment

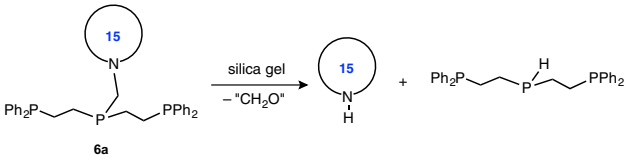
The overall objective is to design a scalable and modular synthesis of these frameworks so that we could systematically investigate the impacts of substituents and linker length on alkali metal-substrate interactions in TM complexes. To that end, we initially focused on using primary phosphine synthons and rely on addition of the P-H bonds across the C=C bonds in vinylphosphines and vinylphosphonates [32,33]. We investigated both radical-initiated and anion-catalyzed variations of these reactions.

Although the radical-initiated approach works well for the more robust **5a** and **5b** (see below), the single-methylene linked **3a** did not survive radical coupling conditions without significant byproducts. Instead we have found that **3a** is readily amenable to anionic

coupling conditions with diphenylvinylphosphine to synthesize **6a** in 87% yield.



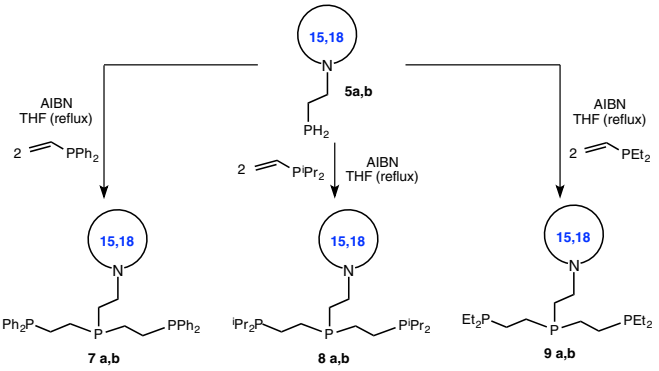
The product **6a** can be prepared very cleanly; excess diphenylvinylphosphine can be removed via hexane extraction of a methanolic solution of **6a**. Attempts to purify **6a** via silica gel chromatography led to hydrolysis of the methylene spacer and isolation of only the deformylated secondary phosphine.



Due to these difficulties in purification, **6a** was the only methylene-separated derivative that we could isolate in analytically pure form. Other derivatives of this ligand framework can nonetheless be prepared via this method and used (unpurified) for the formation of metal complexes; work in this area is still ongoing.

Although assembly of the tridentate framework from ethylene-linked **5a** and **5b** worked rather well under anionic conditions, we found it synthetically expedient to rely instead on radical-initiated couplings (Scheme 2).

All six derivatives of this framework (R = Ph, ^{i}Pr, Et for the aza-15-crown-5 and aza-18-crown-6 macrocycles) can be synthesized in consistently good yields. The phenyl-derivatives **7a**/**7b** were prepared from radical-initiated coupling of primary phosphines **5a**/**5b** with diphenylvinylphosphine for 18 h in refluxing THF. Depending on the cleanliness of the radical reaction, the resulting viscous, pale yellow oils can sometimes be used without purification, otherwise they are purified by distributing over a silica pad and washing with hexane to remove excess diphenylvinylphosphine. The silica was then washed with THF and the solvent was removed from the filtrate under reduced pressure to yield the products as viscous oils in yields of 89–94% (over a dozen synthetic trials). Similarly, the isopropyl derivatives **8a**/**8b** and ethyl derivatives **9a**/**9b** could be synthesized by radical coupling with their respective vinylphosphine precursors for 6 h. In all cases, only our products and residual vinylphosphine are observable in crude reaction mixtures by ^{31}P NMR spectroscopy if the reaction is run for the prescribed time. In the case of R = ^{i}Pr (**8a** and **8b**) reactions that ran for more than a day led to significant amounts (24%) of a side product that was consistent with a compound consisting of multiple P–P bonds (Fig. S24). After coupling and removal of excess vinylphosphine *in vacuo*, **8a** and **8b** are sufficiently free of impurities to be isolated as-is, whereas crude **9a** and **9b** require purification steps similar to those for **7a**/**7b**. The viscous and oily crude products are layered on a silica pad and washed with hexane, followed by a 1:1 mixture of dichloromethane and hexane (these washings contain byproducts and are discarded). The silica is then washed with dichloromethane and the clean products **9a** and **9b** are isolated as light yellow oils (in 90% and 89% yields, respectively).



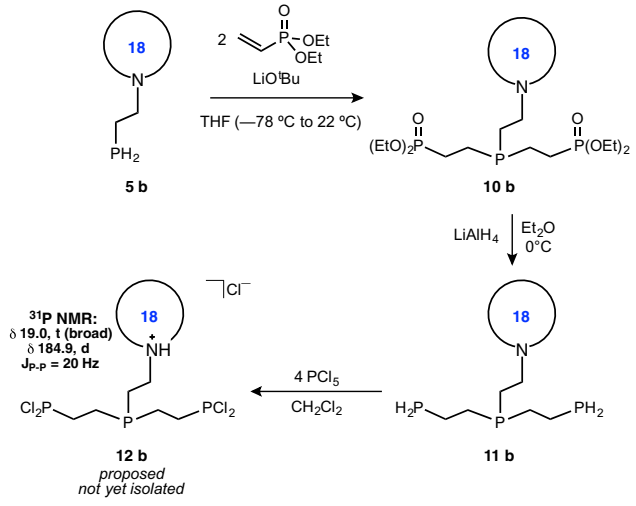
Scheme 2. Assembly of the tridentate scaffold from primary phosphines **5a** and **5b**.

2.3. Attempted alternative strategies and side products

We had initially hoped that we would be able to access a wider range of R-group substitutions on the distal phosphines via the route highlighted in Scheme 3.

Primary phosphine **5b** reacted with diethylvinylphosphonate under anionic conditions (a solution was cooled to −78 °C and a LiO^{t}Bu in THF was added dropwise over 5 min) to yield diphosphonate **10b**, which was reduced to the triphosphine **11b** with $LiAlH_4$ in 77% yield.

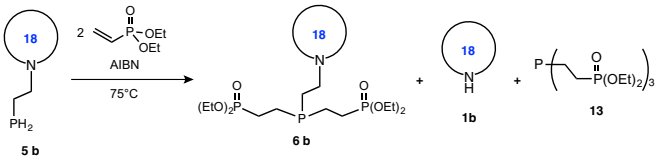
The initial (perhaps overly optimistic) hope was to chlorinate the distal phosphine arms of **11b** so that we might be able to alkylate or arylate with a variety of nucleophilic reagents [34], however we were unable to find chlorination conditions that reliably made isolable amounts of the proposed tetrachloride **12b**. We were unable to cleanly synthesize **12b** despite thirty-five distinct chlorination conditions with different chlorine sources (PCl_5, PCl_3, phosgene, and C_2Cl_6). On one occasion we were able to observe conversion to a new compound consistent with the proposed **12b** in roughly quantitative yield on NMR scale (30 mg) with PCl_5 (Figs. S37–S39), but due to irreproducibility and its high reactivity we were unable to optimize this reaction nor isolate the product. The ^{31}P NMR resonance associated with the central phosphine of **12b** is quite broad, implying chemical exchange, and sharpens somewhat upon application of broadband ^{1}H-decoupling. We hypothesize this species is protonated at the aza-crown nitrogen and engages in reversible binding with the central phosphine.



Scheme 3. Synthesis of triphosphine **11b** from **5b** (via **10b**) and its proposed chlorination.

Indeed, it seems likely the amine moiety of the aza-crown is responsible for complicating chlorination reactions.

We have also noticed that the ethylene-bridged primary phosphine **5b** and/or its alkylation products may not be sufficiently stable to radical coupling conditions when using electron-poor alkenes. During the course of our studies we discovered that although **10b** formed under radical coupling conditions with diethylvinylphosphonate, it formed in a roughly 1:1 ratio with a new ^{31}P-containing species consistent with tetraphosphine **13** (with concomitant formation of aza-crown **1b**).

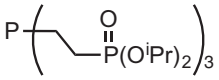


Since it is a relatively electron-poor alkene, it is plausible that diethylvinylphosphonate reacts with phosphinyl radicals rather slowly and P–C bond cleavage (and subsequent fragmentation) of intermediate radicals is competitive with alkene addition. Although we have not independently synthesized **13**, the ^{31}P NMR spectrum of **13** is nearly identical to that observed for the previously reported isopropyl variant P(CH_2CH_2(PO(O^iPr)$_2$)$_2$)$_3$ (Fig. 2) [35].

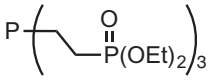
2.4. Molybdenum phosphine complexes bearing tethered cations

We have begun to explore the coordination chemistry of these lariat phosphine ligands in Mo systems, giving particular attention to the nature of the binding of simple alkali metal cations in the crown ether moieties. Of the lariat phosphines prepared above, only two of the ligands (**8a** and **8b**) have thus far resulted in the eventual formation of crystalline Mo-based products. The lack of crystallinity might be expected for compounds with large conformational flexibility (the pure ligands themselves all manifest as liquids under ambient conditions), but we anticipated that locking the crown ether *via* cation binding would assist in the isolation of crystalline products.

As with related Mo(III) phosphine complexes, substitution of the THF ligands of $MoCl_3(THF)_3$ is facile and rapid (Scheme 4), and substitution is evident by the conversion of the pale orange suspension of $MoCl_3(THF)_3$ to dark brown solutions of (**8a**/**8b**)$MoCl_3$ complexes within 2–3 min. These complexes, highly soluble in halogenated solvents, are isolable as pale orange powders upon precipitation with ether. We screened a variety of alkali and alkaline earth salts (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}) of non-coordinating anions (OTf^-, NTf_2^-, $B(C_6F_5)_4^-$) in an effort to see evidence of cation capture and potential interactions with metal-bound ligands. Thus although the parent compounds (**8a**/**8b**)$MoCl_3$ do not manifest as

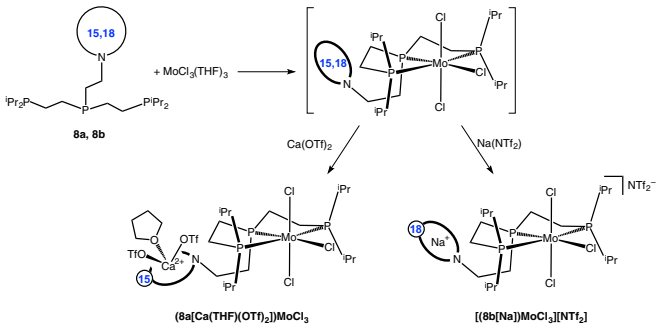


δ **–19.1, q (J_{P-P} = 49.6 Hz), 1P**
δ **29.4, d (J_{P-P} = 49.6 Hz), 3P**
ref 34



δ **–18.8, q (J_{P-P} = 51 Hz), 1P**
δ **30.4, d (J_{P-P} = 51 Hz), 3P**
this work

Fig. 2. Comparison of ^{31}P NMR spectral data of proposed **13** and known compound P(CH_2CH_2(PO(O^iPr)$_2$)$_2$)$_3$.



Scheme 4. Metallation of **8a** and **8b** with $MoCl_3(THF)_3$ and complexation with Ca$(OTf)_2$ and Na(NTf_2), respectively.

crystalline materials, we were able to crystallize two 'salted' derivatives.

Treatment of solutions of intermediates **(8a)MoCl$_3$** or **(8b)MoCl$_3$** with a variety of simple salts led to significant changes in the ^{1}H NMR spectra, but the latent paramagnetism and high spectral complexity prevented determining binding metal coefficients. We were able to crystallize new products in two cases, **(8a)MoCl$_3$** with Ca$(OTf)_2$ and **(8b)MoCl$_3$** with Na(NTf_2), by addition of 1.2 equivalents of metal salt to solutions of the Mo(III) precursors (in ether/THF/toluene 1:1:1). (Figs. 3 and 4). The $(P_3)MoCl_3$ cores in (**8a**[Ca$(OTf)_2$(THF)])$MoCl_3$ and [(**8b**[Na])$MoCl_3$][NTf_2] are nearly isostructural and are similar to other (*mer*-triphosphine)$MoCl_3$ complexes [36–39], where the Mo–Cl distances are all between 2.38 and 2.44 Å and the Mo–P distances are between 2.46 and 2.47 Å for the central phosphine and 2.55–2.57 Å for the distal phosphine arms (see Table 1). The calcium complex (**8a**[Ca$(OTf)_2$(-THF)])$MoCl_3$ bears an eight-coordinate calcium atom (best described as a square-faced bicapped trigonal prism) that binds both triflate anions and a THF molecule, a coordination geometry that appears to be common for Ca^{2+} complexes of 15-crown-5 derivatives [3,40–42]. The cation/crown size mismatch of the Ca^{2+} complex is notable, as engineering such "destabilized" systems may prove critical for the type of secondary coordination sphere interactions we are investigating. In contrast to the overall neutral [Ca^{2+}]/Mo complex, the sodium complex [(**8b**[Na])$MoCl_3$][NTf_2] manifests as a salt in the solid state, with the distorted pentagonal bipyramidal Na^+ ion preferring to interact with the chloride of an adjacent complex and forming a 1D-chain coordination polymer (d(Mo–Cl···Na) = 2.8478(8) Å). The Mo–Cl bond *trans* to the trialkylphosphine in [(**8b**[Na])$MoCl_3$]$^+$ is marginally longer than that in (**8a**[Ca$(OTf)_2$(THF)])$MoCl_3$ (2.4478(5) Å versus 2.439 (2) Å, respectively), thus there is a slight perturbation from the Mo–Cl···Na interaction on the ground state structure of the Mo (III) core. Unlike triflate, interactions between the triflimide anion with other alkali and alkaline earth metals are relatively rare outside of the parent salts [43–46]. The sodium is thus rendered sufficiently electrophilic to distort the crown (moving the nitrogen of the aza-crown to a pseudoaxial position) and interact with the Mo-bound chloride.

We found the use of ethereal solvents to be necessary for adequate solvation of the alkali and alkaline earth metal salts, but crown ether capture of Ca^{2+} (by **8a**) and Na^+ (by **8b**) is sufficiently reversible under these conditions that bulk products contained co-crystallized Ca$(OTf)_2$ or Na(NTf_2). Thus although crystals of highly-soluble (**8a**[Ca$(OTf)_2$(THF)])$MoCl_3$ and (**8b**[Na])$MoCl_3$ were isolable (in low yields, 5–10%), they were both found to be mixed with crystals of Ca$(OTf)_2$ or Na(NTf_2) [47], respectively, and as a result could not be isolated in bulk crystalline form.

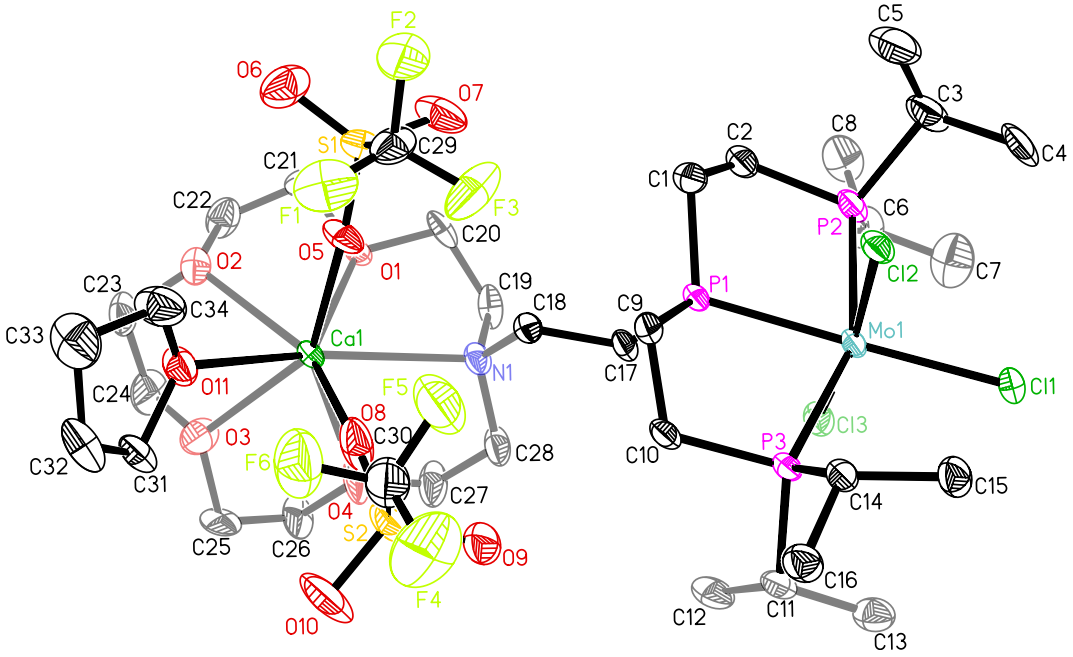


Fig. 3. Solid-state structure of (**8a**[Ca(OTf)$_2$(THF)])MoCl$_3$. Crystallization solvent (THF) and hydrogen atoms have been omitted for clarity.

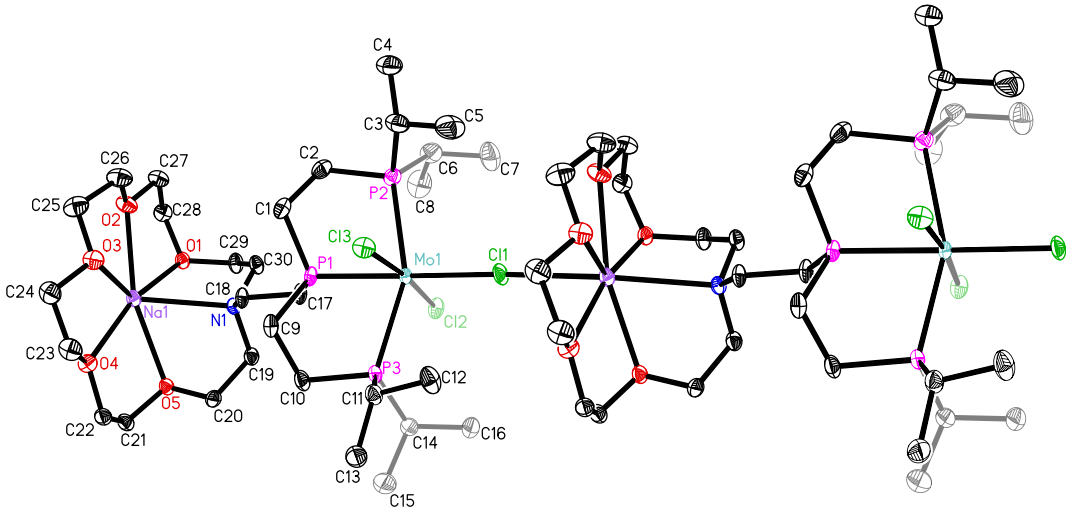


Fig. 4. Solid-state structure of (**8b**[Na])MoCl$_3$ with two adjacent asymmetric units shown to highlight intermolecular Mo–Cl···Na interactions. Hydrogen atoms and the triflimide anions ((CF$_3$SO$_2$)$_2$N$^-$, one per Na) have been omitted for clarity.

Table 1
Comparison of selected solid-state structure metrics of (**8a**[Ca(OTf)$_2$(THF)])MoCl$_3$ and of [(**8b**[Na])MoCl$_3$[NTf$_2$].The data for [(**8b**[Na])MoCl$_3$[NTf$_2$] refer to the majority disorder component (85%).

	(**8a**[Ca(OTf)$_2$(THF)])MoCl$_3$	[(**8b**[Na])MoCl$_3$][NTf$_2$]
d(Mo–Cl1), Å	2.439(2)	2.4478(5)
d(Mo–Cl2), Å	2.444(2)	2.3814(8)
d(Mo–Cl3), Å	2.390(2)	2.4416(8)
d(Mo–P1), Å	2.461(2)	2.4689(5)
d(Mo–P2), Å	2.553(1)	2.5741(7)
d(Mo–P3), Å	2.572(2)	2.5613(8)
∠(Cl1–Mo–Cl2), °	92.96(5)	90.59(3)
∠(Cl1–Mo–Cl3), °	92.88(5)	93.73(2)
∠(Cl2–Mo–Cl3), °	173.72(5)	174.05(3)
∠(P1–Mo–P2), °	78.84(5)	78.07(2)
∠(P1–Mo–P3), °	77.54(5)	78.59(2)
∠(P2–Mo–P3), °	156.21(5)	156.03(3)

3. Conclusion

A general method for the preparation of tridentate phosphine ligands bearing lariat crown-ethers has been developed. In addition to the systems outlined here, the overall approach is likely to be general for polydentate phosphine aza-crown lariats of essentially any lariat length. Such variations could help to tune the interactions between encapsulated alkali metals and TM-bound substrates, which is our particular interest, but may also find use in a host of other applications. We have begun to develop a family of Mo-based systems based on this ligand architecture and presented two examples of crystallographically-characterized Mo(III) complexes bearing pendent cations. The reduction chemistry of complexes of this type are currently under exploration and will be the subject of a future publication.

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4. Experimental section

All manipulations were conducted under N_2, Ar or using high-vacuum line and glovebox techniques unless otherwise noted. All ambient-pressure chemistry was carried out under a pressure of approximately 590 torr (elevation ~7220 ft) and a temperature of 22 ± 3 °C unless otherwise stated; a table of pressure-corrected boiling points for the solvents used in this manuscript are reported in the Supplementary Material. All solvents were dried using an Innovative Technologies PureSolv Solvent Purification System. Deuterated solvents used in NMR studies were dried over activated 3 Å molecular sieves. NMR spectra were obtained with a Bruker DRX-400 or Bruker DRX-600 instruments using 5 mm NMR tubes fitted with re-sealable Teflon valves; reported spectral data were acquired at 400 MHz unless otherwise noted. ^{1}H and ^{13}C NMR spectra were referenced internally to either tetramethylsilane or residual protic solvent peaks. ^{31}P NMR spectra were referenced to an 85% H_3PO_4 external standard. Reagents were purchased from Sigma–Aldrich and used without further purification. High-resolution mass spectroscopy (HRMS) data were obtained on an AB Sciex 5800 MALDI-TOF mass spectrometer. Calibration were performed internally by Poly(ethylene glycol) 600 and 2,5-dihydroxybenzoic acid was used as a matrix. Air sensitive samples were prepared in a glove box and were carried to the mass spectrometer in a sealed container. The same loading procedure was used for all samples and the exposure to O_2 while loading was limited to 10–15 s followed by a 25 s pump down time. Diethylvinylphosphonate, diethylphosphonyl chloride, diphenylphosphonyl chloride, diisopropyl phosphonyl chloride, and $MoCl_5$ were purchased and used as received. The phosphine starting materials **2a** [20], **4a** [20], diethylvinyl phosphine [48], diphenylvinyl phosphine [49], and diisopropylvinyl phosphine [50] were synthesized according to a modification of literature procedures (details in Supporting Information). Representative syntheses for **3a**, **5a** and **8a** are presented here; synthetic and analytical details for the other compounds discussed in this report are available in the Supplementary Material.

4.1. 13-(2-Phosphanylmethyl)-1,4,7,10-tetraoxa-13-azacyclopentadecane) (*3a*)

A 100 mL Schlenk flask was charged with 1-aza-15-crown-5-methyl-phosphonate (1.00 g, 2.707 mmol), a magnetic stir bar and Et_2O (10 mL) under N_2 atmosphere. The system was sealed with a rubber septum and taken out of the glovebox, placed under Ar atmosphere, and cooled down to 0 °C. A suspension of $LiAlH_4$ (463 mg, 12.1 mmol) in 10 mL Et_2O was prepared and loaded into a syringe with a large-gauge needle (all in the glovebox) and was added slowly, over the course of 10 min to the solution of **2a**. Note: Gas generation upon addition of $LiAlH_4$ is substantial and requires sufficient ventilation to prevent over pressurizing. After addition, the reaction was allowed warm up to room temperature. Solvent was evaporated and 15 mL deoxygenated DI H_2O was added to the solid material, followed by 15 mL 10% aqueous LiOH, and then another 10 mL DI H_2O (all dropwise) over the course of 1 h to quench the excess $LiAlH_4$. Note: It is crucial to perform the quenching slowly! Fast addition of water can result in dark/black side products. After quenching, the water was evaporated under high-vacuum at 50 °C. The resulting solid white powder was taken into the glovebox, extracted with THF (5 × 15 mL) and filtered through a Celite pad. Solvent was removed *in vacuo* and the resulting colorless, pale yellow oil was used without any further purification (521 mg, 72%). ^{1}H NMR ($CDCl_3$): δ 2.48 ppm (m, 2H, H_2PCH_2N), δ 2.77 ppm (t, 4H, $^{3}J_{H\text{-}H}$ = 5.95 Hz, OCH_2CH_2N); δ 3.63 ppm (m, 16H, OCH_2CH_2O); δ 3.71 ppm (dt, 2H, $^{1}J_{H\text{-}P}$ = 196.2 Hz, $^{3}J_{H\text{-}H}$ = 8.4 Hz, NCH_2PH_2). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 27.5 ppm (d, 1C, $^{1}J_{C\text{-}P}$ = 5.7 Hz, PH_2CH_2N), δ 53.9 ppm (s, 2C, NCH_2CH_2O), δ 69.7 ppm (s, 2C, OCH_2CH_2N), δ 70.2 ppm (s, 2C, OCH_2CH_2O), δ 70.5 ppm (s, 2C, OCH_2CH_2O), δ 71.0 ppm (s, 2C, OCH_2CH_2O). ^{31}P NMR ($CDCl_3$): δ −172.2 ppm (tt, 1P, $^{1}J_{P\text{-}H}$ = 196.2 Hz, $^{3}J_{P\text{-}H}$ = 8.4 Hz, PH_2); HRMS (MALDI-TOF): MLi^+, found 272.16585. $C_{11}H_{24}NO_4PLi^+$ requires 272.15975.

4.2. 13-(2-Phosphanylethyl)-1,4,7,10-tetraoxa-13-azacyclopentadecane) (*5a*)

A 100 mL Schlenk flask was charged with **4a** (3.92 g, 10.2 mmol), a stir bar and 10 mL Et_2O under N_2 atmosphere. The system was sealed with a rubber septum and taken out of the glovebox, placed under Ar atmosphere, and cooled down to 0 °C. A suspension of $LiAlH_4$ (1.4 g, 37 mmol) in 10 mL Et_2O was prepared and loaded into a syringe with a large-gauge needle (all in the glovebox) and was added slowly, over the course of 10 min to the solution of **4a**. Note: Gas generation upon addition of $LiAlH_4$ is substantial and requires sufficient ventilation to prevent over pressurizing. After addition, the reaction was allowed warm up to room temperature. Solvent was evaporated and 15 mL deoxygenated DI H_2O was added, followed by 15 mL 10% aqueous LiOH, and then another 10 mL DI H_2O were slowly added to the solid material (all dropwise) over the course of 1 h to quench the excess $LiAlH_4$. Note: It is crucial to perform the quenching slowly! Fast addition of water can result in dark/black side products. After quenching, the water was evaporated under high-vacuum at 50 °C. The resulting solid white powder was taken into the glovebox, extracted with THF (5 × 10 mL) and filtered through a Celite pad. Solvent was removed *in vacuo* and the resulting colorless, pale yellow oil was used without any further purification (2.29 g, 80%). ^{1}H NMR ($CDCl_3$): δ 1.65 ppm (m, 2H, PCH_2CH_2N), δ 2.61 ppm (dtt, 2H, $^{1}J_{H\text{-}P}$ = 195.70 Hz, $^{2}J_{H\text{-}H}$ = 7.26 Hz, $^{4}J_{H\text{-}H}$ = 6.00 Hz, $NCH_2CH_2PH_2$), δ 2.71 ppm (m, 2H, PCH_2CH_2N), δ 2.77 ppm (t, 4H, $^{3}J_{H\text{-}H}$ = 6.0 Hz, OCH_2CH_2N), δ 3.59 ppm (m, 16H, OCH_2CH_2O and OCH_2CH_2N). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 11.8 ppm (d, $^{1}J_{C\text{-}P}$ = 9.5 Hz, PCH_2CH_2N), δ 27.5 ppm (d, $^{1}J_{C\text{-}P}$ = 4.3 Hz, NCH_2CH_2P), δ 53.7 ppm (s, NCH_2CH_2O), δ 70.1 ppm (s, NCH_2CH_2O), δ 70.5 ppm (s, OCH_2CH_2N), δ 70.8 ppm (s, OCH_2CH_2O), δ 70.9 ppm (s, OCH_2CH_2O). ^{31}P NMR ($CDCl_3$): δ −147.2 ppm (ttt, $^{1}J_{P\text{-}H}$ = 195.7 Hz, $^{2}J_{P\text{-}H}$ = 5.0 Hz, $^{3}J_{P\text{-}H}$ = 4.1 Hz); HRMS (MALDI-TOF): MH^+, found 280.17163. $C_{12}H_{26}NO_4PH^+$ requires 280.16722.

4.3. 13-(2-(Bis(2-(diphenylphosphanyl)ethyl)phosphanyl) ethyl)-1,4,7,10-tetraoxa-13-azacyclopentadecane) (*7a*)

A 50 mL Schlenk flask was charged with **5a** (2.285 g, 8.179 mmol), a magnetic stir bar, diphenylvinylphosphine (3.476 g, 16.38 mmol), AIBN (88 mg, 0.5359 mmol) and 15 mL THF under N_2 atmosphere. The sealed system was taken out of the glovebox and heated to reflux for 18 h under Ar atmosphere. Upon cooling the solvent was removed *in vacuo* yielding a light-yellow oil which was used without any further purification (5.431 g, 94%). ^{1}H NMR ($CDCl_3$): δ 1.46 ppm (m, 4H, $Ph_2PCH_2CH_2P$), δ 1.55 ppm (m, 2H, PCH_2CH_2N), δ 2.02 ppm (m, 4H, $Ph_2PCH_2CH_2P$), δ 2.58 ppm (m, 2H, PCH_2CH_2N), δ 2.72 ppm (m, 4H, $^{3}J_{H\text{-}H}$ = 6.29 Hz, NCH_2CH_2O), δ 3.66 ppm (m, 16H, OCH_2CH_2O and OCH_2CH_2N), δ 7.32 ppm (m, 12H, $^{m,p}Ph$), δ 7.39 ppm (m, 8H, ^{o}Ph). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 22.0 ppm (t, 2C, $^{1}J_{C\text{-}P}$ = 15.5 Hz, ($PCH_2CH_2PPh_2$), δ 23.7 ppm (t, 2C, $^{1}J_{C\text{-}P}$ = 13.4 Hz, $Ph_2PCH_2CH_2P$), δ 24.1 ppm (d, 1C, $^{1}J_{C\text{-}P}$ = 16.95 Hz, PCH_2CH_2N), δ 53.4 ppm (d, 1C, $^{2}J_{C\text{-}P}$ = 17.1 Hz, NCH_2CH_2P), δ 54.1 ppm (s, 2C, NCH_2CH_2O), δ 70.0 ppm (s, 2C, NCH_2CH_2O), δ 70.2 ppm (s, 2C, OCH_2CH_2O), δ 70.4 ppm (s, 2C, OCH_2CH_2O), δ 71.0 ppm (s, 2C, OCH_2CH_2O), δ 128.5 ppm (d, 4C, $^{3}J_{C\text{-}P}$ = 6.5 Hz, $^{m}Ph_A$ + $^{m}Ph_B$), δ 128.6 ppm (s, 2C, $^{4}J_{C\text{-}P}$ = 2.8 Hz, $^{p}Ph_A$), δ 128.7 ppm (s, 2C, $^{4}J_{C\text{-}P}$ = 2.8 Hz, $^{p}Ph_B$), δ 132.6 ppm (d, 4C, $^{2}J_{C\text{-}P}$ = 18.2 Hz, $J_{C\text{-}P}$ = 4.4 Hz, $^{o}Ph_A$), δ 132.8 ppm (d, 4C, $^{2}J_{C\text{-}P}$ = 18.2 Hz, $J_{C\text{-}P}$ = 4.4 Hz, $^{o}Ph_B$), δ 138.2 ppm (d, 2C, $^{i}Ph_A$),

δ 138.4 ppm (d, 2C, $^{i}Ph_B$). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ −12.7 ppm (d, $^{3}J_{P\text{-}P}$ = 26.7 Hz), δ −23.7 ppm (t, $^{3}J_{P\text{-}P}$ = 26.7 Hz). HRMS (MALDI-TOF): MH^+, found 704.32629. $C_{40}H_{52}NO_4P_3H^+$ requires 704.31820.

4.4. X-ray crystallography

The X-ray diffraction data for (**8a**[Ca(OTf)$_2$(THF)])$MoCl_3$ and [(**8b**[Na])$MoCl_3$][NTf_2] were measured at 100 K on a Bruker SMART APEX II CCD area detector system equipped with a graphite monochromator and a Mo Kα fine-focus sealed tube operated at 1.5 kW power (50 kV, 30 mA). The crystals were mounted on MiTeGen micromounts using Paratone N oil and the detector was placed at a distance of 5.13 cm from the crystal during the data collection. A series of narrow frames of data were collected for each of the crystals with a scan width of 0.5° in ω or ϕ and an exposure time of 10 s per frame. The frames were integrated with the Bruker SAINT Software package using a narrow-frame integration algorithm [51]. The data were corrected for absorption effects by the multi-scan method (SADABS) [52]. Crystallographic data collection parameters and refinement data are collected below in Table 1. The structure was solved by the direct methods using SHELXTL as implemented in the Bruker APEX2 (V. 6.14) Software Package [53,54]. All non-hydrogen atoms were located in successive Fourier maps and refined anisotropically. Complete crystallographic details are available in the Supplementary Material (Table S2).

Compound (**8a**[Ca(OTf)$_2$(THF)])$MoCl_3$ crystallizes in the monoclinic system belonging to the $P2_1/n$ space group. The yellow rectangular plates were grown from THF solutions. The crystals are air sensitive and diffracted poorly (R1 = 7.31%; R_{int} = 23.5%) – we suspect the Ca^{2+} in renders the complex highly hygroscopic. The asymmetric unit contains one complex molecule and one solvated THF molecule. All non-hydrogen atoms except those of the THF solvate are located in successive Fourier maps and refined anisotropically. All H atoms were placed in calculated positions and refined isotropically adopting a riding model with fixed positional parameters. One of the ethylene linkages in the clathrate is disordered and the disorder is modeled by assigning two sets of positions for the associated C and H atoms. The Ca^{2+} cation is coordinated to the clathrate oxygen atoms, two triflate anions and a THF molecule. Although the calcium-bound THF is well ordered, the solvated THF is highly disordered and refinements did not satisfactorily converge on a reasonable solution. The data were therefore corrected by the SQUEEZE/PLATON program considering the solvate as a diffused contribution [55].

Compound [(**8b**[Na])$MoCl_3$][NTf_2] crystallizes in the centrosymmetric monoclinic space group *C2/c*. The asymmetric unit contains a complex cation and a bistriflimide anion. Both ions are well separated and reasonably well ordered except for one of the mono-hapto chloride ligands. The disordered Cl atom is refined by assigning two site occupancies of 0.85 and 0.15. All H atoms were placed in calculated positions and refined isotropically adopting a riding model with fixed positional parameters. All atoms of the two ions are located on general positions, but one of the chloride ligands which interacts with a neighboring complex cation with the associated Cl···Na distance of 2.8477(9) Å, leading to a chain of polymeric cation units.

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Appendix A. Supplementary data

CCDC 1578149 and 1578148 contains the supplementary crystallographic data for **8a**[Ca(OTf)$_2$(THF)]$MoCl_3$ and [(**8b**[Na])$MoCl_3$][NTf_2]. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.poly.2017.11.012.

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