Synthesis and Study of Triphenylphosphines Functionalized at the 4-Positions through the Nitrogen Atoms in 1,4,7,10-Tetraoxa-13-azacyclopentadecane and the X-ray Structure of the Oxide of the Molecule Substituted at All Three Positions

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Hybrid phosphine crown ether ligands have been obtained from PhP(OMe)$_2$ and P(OPh)$_3$ and carbanions generated by low-temperature Li/Br exchange reactions involving 4′-bromo-*N*-phenylaza-15-crown-5 and *n*-butyllithium. The A$_1$ ν(CO) values for the Ni(CO)$_3$L complexes of these phosphines have been found to be 2063.7 and 2060.8 cm^{-1}, for the bis (**1b**) and tris (**1c**) crown species, respectively, indicating the significant electron-donating abilities of the nitrogen atoms. Addition of NaSCN salts in dichloromethane causes these frequencies to increase by 2.40 (**1b**) and 3.70 cm^{-1} (**1c**), indicating that the P(III) centers detect the presence of crown-coordinated ions. The oxide of **1c** has been prepared and the X-ray structure obtained. A prominent feature of that structure, $R\bar{3}$ symmetry, is that the nitrogen atoms are nearly planar and the ring carbon-to-nitrogen distances are 1.375 Å, features that are also consistent with a significant amount of sp^2 C–N double-bond character. The phenyl rings are arranged in a typical propeller shape with torsion angles of 132.4°.

Introduction

Phosphines continue to be of considerable interest as ligands that are used in conjunction with transition metals for a variety of applications.[1–3] For example, it has recently been reported that palladium complexes in the presence of bulky phosphines provide active catalysts for a range of coupling reactions.[4–6] In addition, the sulfonate group in $^-$O$_3$S(C$_6$H$_4$)CH$_2$C(CH$_2$PPh$_2$)$_3$ has been shown to be an effective site for immobilizing the ligand and its complexes on partially dehydroxylated silica, providing selective hydrogenation catalysts.[7] Finally, P(iPr)$_3$- or P(Cy)$_3$-ligated Ru complexes have been reported which have both a dihydrogen ligand and agostic interactions, providing additional examples of the diverse nature of phosphine complexes.[8] Given the wide range of properties and uses for phosphine complexes, there continues to be considerable interest in new ligands with specific and characterized electronic, steric, and solubility properties.

We have been interested in synthesizing and characterizing new types of phosphines of the types shown in **1**–**3**.[9,10] For the systems studied to date, the donor abilities of the P(III) centers, assessed by ν(CO) frequencies of the Ni(CO)$_3$L complexes, decreased in the order 2066.3 (**1a**) > 2068.3 (**2**[11]) > 2068.5 (**3c**) > 2068.7 (**3e**) > 2068.8 (**3b**) > 2068.9 (**3d**) > 2069.1 cm^{-1} (**3a**) (Table 1). That **1a** is a significantly better donor than any of the other ligands is apparently the result of two major factors: first, the nitrogen atom in the oxide of **1a** has been shown to be planar,[9] indicating that, as expected,[12] the lone pair is conjugated with the benzene ring, and second, the methoxy groups in **3d,e** are likely hindered from adopting a conformation where a significant degree of conjugation can take place. The latter conclusion stems from our recently reported X-ray structure of the model compound **4**, which shows the OCH$_3$ groups to be perpendicular to the phenyl ring

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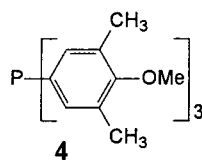
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1a

1b, c

2

3
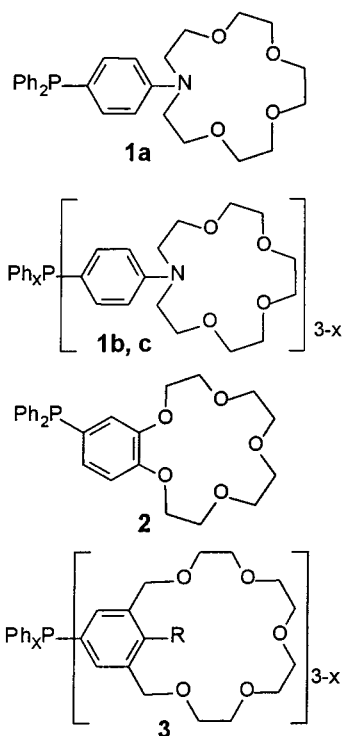
#	X	R
3a	2	H
3b	1	H
3c	0	H
3d	2	OMe
3e	1	OMe

faces[13] rather than in the same plane, as reported for unhindered anisoles,[14,15] including $P(4\text{-}C_6H_4OCH_3)_3$.[16,17]

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Given these IR and X-ray data, it appeared that **1b,c** would be significantly better donors than any of the phosphine–crown molecules previously reported. Further, the IR data for the $Ni(CO)_3L$ complexes reported thus far were consistent with the preliminary conclusions that alkali-metal ions added to the complexes caused the largest shifts in the $\nu(CO)$ values for complexes based on phosphines with both the largest number of crown ether groups and the best donor abilities (lowest $\nu(CO)$ values). In light of these considerations, we elected to prepare **1b,c** and study their properties in the presence and absence of ions. Herein

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Table 1. Crystallographic Data for 1d

formula	$C_{48}H_{72}PO_{13}N_3\cdot3CH_2Cl_2$
space group	$R\overline{3}$
cell dimens at −170 °C	
$\quad a = b$, Å	20.297(1)
$\quad c$, Å	25.004(2)
$\quad \alpha = \beta$, deg	90
$\quad \gamma$, deg	120
V, Å^3	8921.34
λ, Å	0.710 69
calcd density, g/cm^3	1.323
Z, molecules/cell	6
μ, cm^{-1}	3.740
max and min 2θ, deg	45, 6
no. of unique rflns collected	5362
no. of rflns with $F > 0.0$	2221
no. of rflns with $F > 2.33\sigma(F)$	1751
no. of unique intensities	2384
final residuals	
$R(F)^a$	0.0585
$R_w(F)^b$	0.0608
goodness of fit for last cycle	2.286
max Δ/σ for last cycle	0.05

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w = 1/\sigma^2(|F_o|)$.

we report the results from those investigations along with the preparation and X-ray structure of the oxide of **1c** and **1d**.

Experimental Section

Reagents and Materials. Triphenyl phosphite, dimethyl phenylphosphonite, and *n*-butyllithium (2.5 molar in hexane) were obtained from Aldrich Chemical Co., Inc. $Ni(CO)_4$ was purchased from Strem Chemicals, Inc. Tetrahydrofuran was distilled immediately prior to use from sodium benzophenone ketyl. The alkali-metal thiocyanides were dried under high vacuum at 60 °C for 24 h prior to use. 13-Phenyl-1,4,7,10-tetraoxa-13-azacyclopentadecane[18] (*N*-phenylaza-15-crown-5) and the 4′-bromo derivative[9] were prepared as described previously from reagents purchased from Aldrich Chemical Co., Inc.

Methods and Instruments. Reactions and purifications were carried out under a blanket of argon. Chromatographic separations were carried out by using 40–63 μm silica gel cartridges fixed in a Biotage apparatus. IR and NMR spectra were recorded on Perkin-Elmer Spectrum 1000 and JEOL Eclipse or Varian Gemini instruments, respectively. The ^1H and ^{31}P NMR spectra were recorded in $CDCl_3$, and they are referenced to TMS (internal) and 85% phosphoric acid (external). The IR instrument was calibrated with solutions of $Ni(CO)_3PPh_3$, for which the A_1 $\nu(CO)$ stretching band has been reported to be 2068.9 cm^{-1}.[19] Elemental analyses were carried out by Midwest Microlab Ltd., Indianapolis, IN. The X-ray analysis was carried out by the Molecular Structure Center, Indiana University, Bloomington, IN 47405.

IR Studies. The $Ni(CO)_3L$ IR studies were carried out in situ as previously described.[19–21]

PhP(4-*N*-phenylaza-15-crown-5)$_2$ (1b). 4′-Bromo-*N*-phenylaza-15-crown-5 (7.22 g, 1.93×10^{-2} mol) was added to 150

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mL of THF contained in a three-necked flask fitted with a magnetic stir bar, gas inlet, and two rubber septa. The flask was cooled in a liquid-nitrogen/ethyl acetate slush. *n*-Butyl-lithium (7.7 mL, 1.9×10^{-2} mol) was added via syringe over a period of 25 min, and the solution was stirred for an additional 25 min at this temperature. Dimethyl phenylphosphonite (1.5 mL, 1.0×10^{-3} mol) in 8 mL of THF was then added over a period of 25 min. The mixture was stirred and cooled for an additional 25 min, at which time the cold bath was removed; the mixture was stirred for an additional 12 h. Triethylamine (2 mL) and aqueous ammonium chloride (30 mL, 20%) were added in sequence. Most of the THF was removed by using a rotary evaporator, leaving a yellow oil that was dissolved in 100 mL of dichloromethane, and this solution was shaken with 50 mL of water. The nonaqueous phase was collected and dried over magnesium sulfate. The solvent was removed, providing 4.37 g of a yellow residue. A 1.5 g aliquot of this crude material was chromatographed by using a mixture of 75% ethyl acetate and 25% acetone, providing 0.85 g of solid compound. Anal. Calcd for $C_{38}H_{53}N_2O_8P \cdot 0.67H_2O$: C, 64.39; H, 7.73; N, 3.95. Found: C, 64.31; H, 7.62; N, 3.84. $^{31}P\{^1H\}$ NMR: δ -9.4. ^{13}C-$\{^1H\}$ NMR: δ 52.7, 68.5, 70.1, 70.3, 71.3 (s, CH_2); δ 111.0 (d, J_{PC} = 12.2 Hz, C_6H_5); δ 111.6 (d, J_{PC} = 5.4 Hz, C_6H_5); δ 127.7 (s, C_6H_5); δ 128.1 (d, J_{PC} = 6.1 Hz, C_6H_5); δ 132.9 (d, J_{PC} = 17.6 Hz, C_6H_5); δ 133.7 (d, J_{PC} = 11.5 Hz, C_6H_5); δ 135.3 (d, J_{PC} = 20.7 Hz, C_6H_5); δ 148.0 (s, C_6H_5).

P(4′-*N*-phenylaza-15-crown-5)₃ (1c). **1c** was prepared from 4′-bromo-*N*-phenylaza-15-crown-5 (7.22 g, 1.93×10^{-2} mol) and triphenyl phosphite (1.6 mL, 6.4×10^{-3} mol) using the procedure described for **1b**. A tan oil (3.0 g) was isolated, which was judged to be ca. 80% **1c** ($^{31}P\{^1H\}$ NMR: δ -11.9 (s)) and 10% **1d**, the oxide (δ 30.0 (s)), along with impurites which gave ^{31}P signals at δ -21.4 and 25.6. An aliquot of this mixture (1.5 g) was chromatographed by using a mixture of 70% ethyl acetate, 29% acetone, and 1% triethylamine, providing 0.8 g of compound which solidified into a colorless solid upon removal of the solvent. Spectroscopic studies in degassed $CDCl_3$ indicated that the sample was ca. 95% **1c** and 5% **1d**.

Preparation of the Oxide of 4′-Phosphinotris(*N*-phenylaza-15-crown-5) (1d). A 1.0 g aliquot of the crude oil **1c** and 0.5 mL of 30% aqueous hydrogen peroxide were stirred in 30 mL of dichloromethane for 30 min at ambient temperature. The mixture was treated with 5 drops of 10% aqueous sodium thiosulfate, and the nonaqueous phase was evaporated to dryness. The resulting oil was crystallized from a mixture of dichloromethane and heptane by allowing the solvent to slowly evaporate at -10 °C, providing 0.3 g of colorless and transparent crystals. A few of the crystals were harvested and stored with a few drops of the mother liquor for the X-ray analysis (vide infra), and the rest were dried under high vacuum, providing 0.26 g of product. Anal. Calcd for $C_{48}H_{72}N_3O_{13}P \cdot 3H_2O$: C, 58.58; H, 7.99; N, 4.27. Found: C, 58.71; H, 7.72; N, 4.36. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -30.0. ^{13}C-$\{^1H\}$ NMR: δ 52.6, 68.4, 70.2, 70.3, 71.4 (s, CH_2); δ 110.8 (d, J_{PC} = 6.4 Hz, C_6H_5); δ 119.4 (d, J_{PC} = 114.6 Hz C_6H_5); δ 133.6 (d, J_{PC} = 11.2 Hz, C_6H_5); δ 149.7 (s, C_6H_5).

Single-Crystal X-ray Diffraction Study of 1d. As indicated above, crystals of **1d** were obtained from a mixture of dichloromethane and heptane. A well-shaped crystal was cleaved to form a nearly equidimensional fragment, which was attached to the tip of a glass fiber with silicone grease and transferred to a goniostat and cooled to -170 °C. Data were corrected for Lorentz and polarization effects, and the equivalent data were averaged. The structure was readily solved by direct methods, SHELXTL-PC, and Fourier techniques. Many of the hydrogens were located in the difference Fourier maps, and all were placed in idealized positions as fixed atom contributors for the least squares treatment. A solvent molecule, CH_2Cl_2, was also located in the cell. The crystallographic data are presented in Table 1.

Table 2. A₁ ν(CO) Bands (cm⁻¹) for Ni(CO)₃L Complexes

	added ions[a]			
	none[a] (Δ^b)	Li⁺	Na⁺	K⁺	Cs⁺
1a	2066.3 (2.6)	2066.9	2067.8	2066.2	
1b	2063.7 (5.2)		2066.1	2063.6	
1c	2060.8 (8.1)	2063.7	2064.5	2061.1	2060.8
PPh₃	2068.9 (0.0)		2068.9	2068.8	

[a] MSCN salts, CH_2Cl_2 solutions. *[b]* Observed ν(CO) 2068.9 cm⁻¹.

Results and Discussion

Syntheses. Compounds **1b,c** have been obtained by nucleophilic attacks on P(III) centers by the crown ether carbanions generated from 4′-bromo-*N*-phenylaza-15-crown-5 by low-temperature lithium−bromine exchange reactions. Commercially available PhP(OMe)₂ (**1b**) and P(OPh)₃ (**1c**) were used as the phosphorus-containing starting materials. Even though the estimated yields following purifications were less than 20%, NMR spectra of the crude reaction mixtures were consistent with the conclusion that both **1b** and **1c** were formed in about 60% yields. Compound **1c** proved to be very difficult to purify completely because it readily forms the oxide, and satisfactory elemental analyses were not obtained. That **1c** is very readily oxidized is signaled by the ν(CO) data presented in Table 2 and discussed in the following section, Ni(CO)₃L Studies. In view of this difficulty, **1d**, the oxide, was prepared and thoroughly analyzed to provide a basis for the spectroscopic identification of **1c**.

The $^{31}P\{^1H\}$ spectra of **1a**−**c** shift upfield as the number of crown ether groups increases from -7.1 to -9.4 to -11.9. Similar upfield shifts with decreasing numbers of unsubstituted phenyl rings have also been observed for **3d,e**[10] and the noncrown analogues[12] Ph_xP-$(3,5\text{-Me}_2\text{-4-OCH}_3C_6H_2)_{3-x}$ (see **4**), but not for **3a**−**c**, which shift downfield.[10]

Ni(CO)₃L Studies. A wide variety of experimental methods have been used to quantify the donor/acceptor properties of phosphines, including calorimetry,[22,23] nonaqueous titrations,[24,25] and electrochemical methods[26−28] along with NMR[29] and IR[19−21] studies of Ni(CO)₃L complexes. The latter method was selected for this study so that the data could be directly compared to previous reports from related molecules including **1b**.[9,10]

The A₁ ν(CO) bands for **1b,c** along with that from **1a** are summarized in Table 2. In the absence of ions there is a regular decrease in the stretching frequencies with an increase in the number of crown ether groups. This trend is expected because alkyl-substituted nitrogen atoms in the para positions are well-established to be good donor groups, and in fact, the Hammett substituent parameter for N(CH₃)₂ is -0.63.[12] The ν(CO) fre-

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quencies obtained for **1a**−**c** are very similar to those from P(CH$_2$C$_6$H$_5$)$_3$ (2066.4 cm^{-1}), PhP(C$_2$H$_5$)$_2$ (2066.7 cm^{-1}), and P(C$_4$H$_9$)$_3$ (2060.3 cm^{-1}),[19] a comparison which serves to emphasize both the substantial effects caused by the aza crown nitrogen atoms and the conclusion that the effects are additive.

As shown in Table 2, additions of alkali-metal ions shift the ν(CO) bands to higher frequencies, the trend that is expected if the P(III) centers can detect the presence of positively charged ions complexed by the crown ether rings. The fact that the Na$^+$ ion causes the largest shift is consistent with the well-established size match between this ion, 1.9 Å, and preorganized crown-5 ring diameters, which range from 1.7 to 2.2 Å.[30] Even though the shifts caused by Na$^+$ ions are not strictly linear with increasing numbers of crown ether groups, there are clearly larger shifts with increasing number of crowns. The magnitude of the shifts observed for the aza crowns discussed herein are significantly larger than those observed for the series **3** ligands. For example, Na$^+$ ions caused shifts of 0.9 and 1.40 cm^{-1}, respectively, for **3b**,**e**. There are several factors that might affect the magnitude of the observed shifts. First, the K_{eq} values are expected to be a primary factor, since many physical properties of crown ether complexes depend on the strength of the binding. In the presence of ions, for example, the electrochemical properties displayed by crown ethers depend on the binding constants.[31] The difference between R = H and R = OCH$_3$ in **3** likely reflects the increased ability of the latter to bind ions.[32] Second, electrostatic effects are a potential factor for systems with two or more crown ether rings. If the crown ether groups are close together, repulsion terms could arise that would decrease the ion binding abilities of the crown ether rings. As will be discussed later, this does not appear to be the situation for **1c**. An additional consideration might arise from the Hammett parameters. It could be that the largest shifts upon the addition of ions are possible with systems containing the substituents like those found in **1**, because added ions have the potential to substantially reduce the conjugation of the nitrogen lone pair with the phenyl ring. Our previous report that the addition of HCl in ether to the complex of **1a** caused a shift to 2071.5 cm^{-1} provides additional support for this latter conclusion.[9]

Finally, it has been reported that small, highly charged cations can sometimes cause larger effects than might be predicted from K_{eq} data. Specifically, both Li$^+$ and Ca^{2+} have been shown to have significant effects on metal-to-ligand charge-transfer photophysics for the *fac*-(2,2′-bipyridine)(pyridine)Re(CO)$_3^+$ complex functionalized with a crown ether of the type used in **1**.[33] For the systems described here, the strongest binding is expected for Na$^+$ ion, but the limited Li$^+$-based data presented here suggest that perhaps Na$^+$ has the mix of radius and polarizability characteristics necessary to effect the largest shifts.

Table 3. Selected Bond Lengths (Å) for 1d

P(2)−O(1)	1.483(6)	N(9)−C(23)	1.464(6)
P(2)−C(3)	1.801(5)	C(3)−C(4)	1.389(7)
O(12)−C(11)	1.416(6)	C(3)−C(8)	1.384(7)
O(12)−C(13)	1.424(6)	C(4)−C(5)	1.385(7)
O(15)−C(14)	1.412(8)	C(5)−C(6)	1.409(7)
O(15)−C(16)	1.437(8)	C(6)−C(7)	1.411(7)
O(18)−C(17)	1.410(9)	C(7)−C(8)	1.383(7)
O(18)−C(19)	1.405(8)	C(10)−C(11)	1.503(8)
O(21)−C(20)	1.420(8)	C(13)−C(14)	1.494(9)
O(21)−C(22)	1.424(6)	C(16)−C(17)	1.435(10)
N(9)−C(6)	1.375(6)	C(19)−C(20)	1.498(10)
N(9)−C(10)	1.453(7)	C(22)−C(23)	1.509(7)

Table 4. Selected Bond Angles (deg) for 1d

O(1)−P(2)−C(3)	113.40(18)	N(9)−C(6)−C(7)	121.4(5)
C(3)−P(2)−C(3)	105.27(20)	C(5)−C(6)−C(7)	116.9(4)
C(11)−O(12)−C(13)	112.0(4)	C(6)−C(7)−C(8)	120.6(5)
C(14)−O(15)−C(16)	115.9(5)	C(3)−C(8)−C(7)	122.2(4)
C(17)−O(18)−C(19)	109.5(6)	N(9)−C(10)−C(11)	113.9(4)
C(20)−O(21)−C(22)	114.6(4)	O(12)−C(11)−C(10)	109.0(4)
C(6)−N(9)−C(10)	120.4(4)	O(12)−C(13)−C(14)	109.6(5)
C(6)−N(9)−C(23)	120.7(4)	O(15)−C(14)−C(13)	110.1(5)
C(10)−N(9)−C(23)	118.5(4)	O(15)−C(16)−C(17)	114.0(5)
P(2)−C(3)−C(4)	119.3(4)	O(18)−C(17)−C(16)	108.7(6)
P(2)−C(3)−C(8)	123.1(4)	O(18)−C(19)−C(20)	110.0(5)
C(4)−C(3)−C(8)	117.7(4)	O(21)−C(20)−C(19)	113.8(6)
C(3)−C(4)−C(5)	121.4(5)	O(21)−C(22)−C(23)	104.9(4)
C(4)−C(5)−C(6)	121.2(4)	N(9)−C(23)−C(22)	114.6(4)
N(9)−C(6)−C(5)	121.6(4)		

Predicting the properties of ligands by way of $\Delta E - \Delta C$ analysis[34,35] not only provides a convenient approach for predicting the donor abilities of newly designed systems but also, for ligands of the type reported here, for determining whether the structurally more complex crown ether groups might have the same effects as related but simpler functional groups. In accord with this, the Ni(CO)$_3$L A$_1$ ν(CO) stretching frequencies have been calculated for **1** by using the reported ΔE and ΔC values for C$_6$H$_5$ and 4-C$_6$H$_5$N(CH$_3$)$_2$,[34] and the values are 2066, 2063, and 2061 cm^{-1} for **1a**−**c**, respectively. The close match between the calculated and measured frequencies are another indication that the crown ether groups in **1a**−**c** are similar in effect to N(CH$_3$)$_2$ groups.

X-ray Structure of 1d. Crystallographic data are summarized in Table 1, and bond angles and distances are presented in Tables 3 and 4. All the bond distances and angles are unremarkable and similar to those of the oxide of **1a**[9] and OPPh$_3$.[36] As evident in the ORTEP plot (Figure 1) the phenyl rings are in the typical propeller arrangement observed for triarylphosphines and their oxides and metal complexes. The torsion angles from the centroid of the three ipso carbons through the phosphorus to C3 and C4 or C8 are 132 and −47.2°, respectively. Using the method described by Dunitz,[36] this corresponds to a torsion angle of 132.4° and hexagonal coordinates of 0, 0, and 132.4 for *x*, *y*, and *z*, respectively. The comparable torsion angles for the structure of the oxide of **1a** are, $\phi(1-3) = 53.8$, 18.3, and 30.2°, respectively, which correspond to hexagonal coordinates of 19.7° (*x*), 3.9° (*y*) and 34.1° (*z*). These values for the oxides of **1a** and **1c** are completely in line with the values reported for triphenylphosphine oxide[36] and related molecules, many of which are known to have

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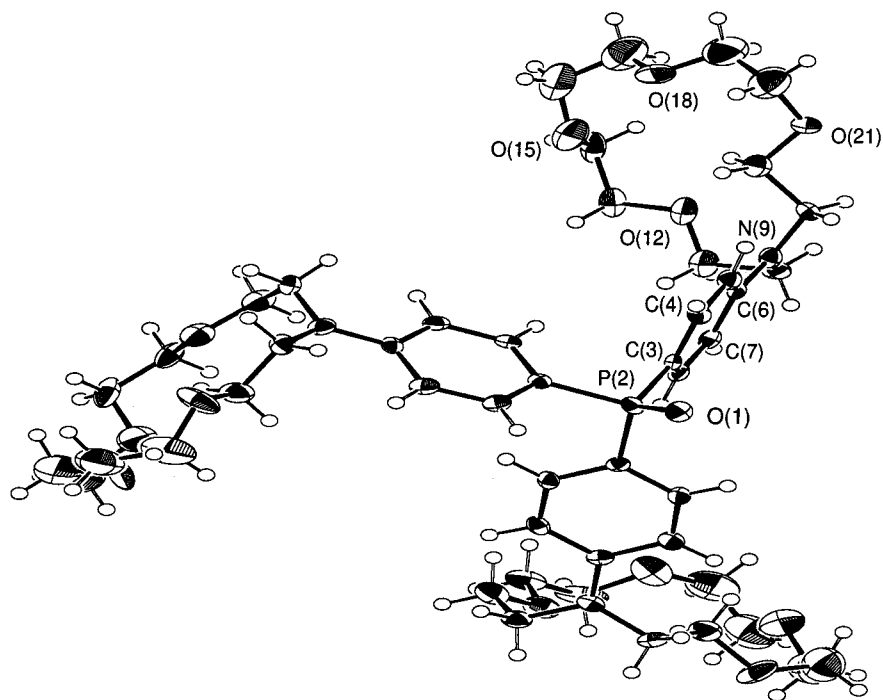(36) Bandoli, G.; Bortolozzo, G.; Clemente, D. A.; Croatto, U.; Panattoni, C. *J. Chem. Soc. A* **1970**, 2778.

Figure 1. Molecular structure of **1d**.

structures that provide *z* hexagonal angles of ca. 40°.[37] A major difference, however, in the structures of the oxides of **1a**,**c** is that they correspond to propellers with opposite pitches.

As shown in Figure 1, the irregularly shaped crown ether rings are folded toward the faces of the phenyl rings so that the planes defined by the phenyl ring and the five heteroatoms intersect at an angle of 103.3°. Further, the C(3)−N(9)−O(18) angle is 112.5°.

As observed for the structure of the oxide of **1a**,[9] the nitrogen atoms in **1d** are essentially planar with N(9), C(10), and C(23) being 0.06, 0.05, and 0.3 Å, respectively, above the plane defined by the phenyl ring carbons. In addition, the C(sp^3)−N−C(sp^2) angles average 119.6°. As expected for planar nitrogen atoms, the C(6) to N(9) bond length is 1.375(6) Å, indicating a significant amount of CN double-bond character. Overall, the planar nitrogen atoms result in a crown ether ring that is large in diameter and not preorganized for ion binding with the interatom distances shown in Table 5. As shown, the result is a crown ether with oxygen-to-oxygen across-ring distances of ca. 4.5 Å with a longest heteroatom-to-heteroatom distance, N(9)−O(18), of 5.24 Å.

The distance between two of the crown ether groups has been estimated by measuring the distance between the centroids defined by the four oxygen atoms in each

Table 5. Interatomic Distances (Å) for 1d

N(9)−O(18)	5.24	O(12)−O(21)	4.48
N(9)−O(15)	4.98	O(12)−O(18)	4.45
N(9)−O(21)	3.67	O(18)−O(21)	3.06
N(9)−O(12)	2.92	O(15)−O(18)	2.82
O(15)−O(21)	4.84		

of two of the rings in **1d**, and that distance was found to be 12.7 Å. Since this distance is over 6 times the diameter of a Na$^+$ ion, it is unlikely that ions in neighboring crown ether rings would experience substantial repulsive forces. It is likely that an intercrown distance of this magnitude would also be present in **1b**,**c**, because the C−P−C bond angles in phosphines with three aryl groups are usually about[13,16,17] 100−105°, which is only a few degrees less than those of phosphine oxides such as **1d**, the oxide of **1a**[9] (average 106.9°), and triphenyl phosphine oxide[32] (average 107.1°).

Supporting Information Available: Tables giving all crystallographic data, bond lengths, and bond angles for **1d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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