have reinvestigated these compounds in various solvents in order to compare to $VPh_2(salen)\cdot CH_3OH$.

The electrochemistry of VO(salen) was carried out in Me_2SO and in CH_2Cl_2. In Me_2SO there is a reversible oxidation (based on peak height ratio and peak potential separation) at +0.29 V vs. SCE and an irreversible reduction at −1.6 V. In CH_2Cl_2 these processes are observed at +0.64 and −1.6 V, respectively (Figure 4a). The results in Me_2SO are virtually identical with those reported by Kapturkiewicz[37] in DMF, while the oxidation couple is shifted positively about 0.3 V in CH_2Cl_2.

Kapturkiewicz reported a reversible reduction of $VCl_2(salen)$ at −0.450 V vs. SCE in DMF, although the compound was not stable in solution. We also found a transient couple at about −0.5 V in DMF, while in Me_2SO only the reduction peak was present. In both solvents, features corresponding to VO(salen) began to appear on the cyclic voltammograms within a few minutes.

The electrochemistry of $VPh_2(salen)\cdot CH_3OH$ was studied in CH_2Cl_2 (Figure 4b) and was compared to that of VO(salen) in the same solvent (Figure 4a). The cyclic voltammogram of $VPh_2(salen)\cdot CH_3OH$ shows several peaks, although none are distinct. This suggests some decomposition may have taken place, although the solution stayed red-brown for hours, unlike VCl_2(salen), which decomposed quickly. There are two oxidation waves on the initial positive scan, and the first one (0.2 V) could be due to the diphenyl compound. The second oxidation peak (0.6 V) appears at almost the same potential as that for the VO(salen) couple, but its identity is unclear since electrolysis at 0.8 V did not produce the corresponding reduction peak expected for VO(salen)$^+$. The reduction wave at −1.5 V also suggests that some decomposition to VO(salen) may have taken place. Since the absorption spectra indicate that the compound is stable in solution and since quantitative conversion to VO(salen) is not observed, the problem may be that efficient electron transfer between the electrode and the analyte does not occur in this system. To improve the quality of the electrochemical data for this system and others, we are pursuing the use of mediator titrants.

Conclusion

From the stable vanadyl ion, VO^{2+}, we have prepared VCl_2^{2+} by the method of Pasquali and co-workers.[2] This ion can then be used as a precursor for making the VPh_2^{2+} moiety. The compound $VPh_2(salen)\cdot CH_3OH$ is the first organovanadium(IV) species that is stable at room temperature. This reaction pathway is straightforward and should be useful for making other organovanadium compounds such as $VR_2(salen)$, where R = benzyl or *tert*-butyl.

Acknowledgment. Financial support for this work was provided by the Research Corp. and Miami University.

Contribution No. 3830 from the Central Research & Development Department, Experimental Station, E. I. du Pont de Nemours & Company, Wilmington, Delaware 19898

Organometallic Crown Ethers. 2. Syntheses of Phosphino Aza Crown Ether Ligands

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Received October 1, 1985

The syntheses of phosphino aza crown ethers $Ph_2P(CH_2)_m\overline{NCH_2(CH_2OCH_2)_nCH_2}$ (n = 3, m = 0; n = 4, m = 0–3) and $Ph_2PCH_2N(CH_2CH_2OCH_2CH_2O)_2(o\text{-}C_6H_4)$ using simple aza crown ethers $HN\overline{CH_2(CH_2OCH_2)_nCH_2}$ (n = 3, 4) and $HN(CH_2CH_2OCH_2CH_2O)_2(o\text{-}C_6H_4)$ as starting materials are reported. These new ligands can bind to transition metals at phosphorus and alkali-metal ions at the aza crown ether.

Introduction

The migration of a metal alkyl ligand to a coordinated CO to generate a metal acyl is a fundamental reaction of organometallic chemistry[1] and a key step in metal-catalyzed carbonylation reactions.[2] This reaction is promoted by many types of Lewis acids including Li^+,[3] AlX_3,[4] BF_3,[4] $CpFe(CO)_2^+$,[5] $CpMo(CO)_3^+$,[5] $CpW(CO)_3^+$,[5] and amphoteric aluminoaminophosphine ligands.[6]

We recently reported the synthesis of a phosphine-functionalized aza crown ether that is capable of holding Lewis acidic cations close to transition metals.[7] The first phosphine-functionalized crown ethers reported by Shaw and co-workers are rigid, and the positions of the binding sites are not optimum for interaction between a crown-ether-held cation and a phosphine-bound transition metal.[8] Recently a number of more flexible phosphino crown ethers have been reported, particularly by Powell and co-workers.[9] Examples include phosphino aza crown ethers,[9a] chelating bis(phosphinites) with crown-ether-type properties,[9b,c] and crown ethers with phosphorus(III) in the macrocycle ring.[9d,10] As part of a program to study the effect of crown-ether-held cations on the rate of alkyl migration to CO, we have prepared a series of phosphine-functionalized aza crown ethers, $Ph_2P(CH_2)_n\overline{NCH_2(CH_2OCH_2)_4CH_2}$, in which the distance between

(1) Wojcicki, A. *Adv. Organomet. Chem.* **1973**, *11*, 87–145. Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299. Kuhlmann, E. J.; Alexander, J. J. *Coord. Chem. Rev.* **1980**, *33*, 195–225.
(2) Parshall, G. W. *Homogeneous Catalysis*; Wiley: New York, 1980.
(3) Collman, J. P.; Finke, R. G.; Cawse, J. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1978**, *100*, 4766–4772. Nitay, M.; Priester, W.; Rosenblum, M. *J. Am. Chem. Soc.* **1978**, *100*, 3620–3622.
(4) Butts, S. B.; Strauss, S. H.; Holt, E. M.; Stimson, R. E.; Alcock, N. W.; Shriver, D. F. *J. Am. Chem. Soc.* **1980**, *102*, 5093–5100.
(5) La Croce, S. J.; Cutler, A. R. *J. Am. Chem. Soc.* **1982**, *104*, 2312–2314.
(6) Labinger, J. A.; Miller, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 6856–6858. Grimmett, D. I.; Labinger, J. A.; Bonfiglio, J. N.; Masuo, S. T.; Shearin, E.; Miller, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 6858–6859. Labinger, J. A.; Bonfiglio, J. N.; Grimmett, D. L.; Masuo, S. T.; Shearin, E.; Miller, J. S. *Organometallics* **1983**, *2*, 733–740. Grimmett, D. L.; Labinger, J. A.; Bonfiglio, J. N.; Masuo, S. T.; Shearin, E.; Miller, J. S. *Organometallics* **1983**, *2*, 1325–1332.
(7) McLain, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 6355–6357. McLain, S. J.; Waller, F. J. U.S. Patent 4 432 904, 1984.
(8) Hyde, E. M.; Shaw, B. L.; Shepherd, I. *J. Chem. Soc., Dalton Trans.* **1978**, 1696–1705.
(9) (a) Powell, J.; May, C. J. *J. Am. Chem. Soc.* **1982**, *104*, 2636–2637. (b) Powell, J.; Kuksis, A.; May, C. J.; Nyburg, S. C.; Smith, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 5941–5943. (c) Powell, J.; Gregg, M.; Kuksis, A.; Meindl, P. *J. Am. Chem. Soc.* **1983**, *105*, 1064–1065. (d) Powell, J.; Nyburg, S. C.; Smith, S. J. *Inorg. Chim. Acta* **1983**, *76*, L75–L77. (e) Powell, J.; Ng, K. S.; Ng, W. W.; Nyburg, S. C. *J. Organomet. Chem.* **1983**, *243*, C1–C4.
(10) Van Zon, A.; Torny, G. J.; Frijns, J. H. G. *Recl. Trav. Chim. Pays-Bas* **1983**, *102*, 326–330.

0020-1669/86/1325-3124$01.50/0

the phosphorus and the crown ether ring is varied (n = 0–3). This paper describes the details of these syntheses along with the syntheses of some cation adducts and related compounds.

Experimental Section

All operations involving phosphines were done under nitrogen in a Vacuum Atmospheres glovebox, or under argon with use of Schlenk techniques. Diethyl ether, methyl *tert*-butyl ether, and THF were distilled from sodium benzophenone ketyl under argon. Methylene chloride was distilled from calcium hydride under argon. Toluene, benzene, hexane, and pentane were sparged with argon and passed through activity I alumina in the glovebox. Methanol was distilled from $Mg(OCH_3)_2$ under argon and stored over 3A molecular sieves until use. All other solvents were stored over activated 4A molecular sieves until use. Elemental analyses were done by Pascher Microanalytical Laboratory, Bonn, West Germany. The alumina used for column chromatography was Merck aluminum oxide 90, neutral, 70–230 mesh, from Bodman Chemicals, Media, PA. 1,2-(Phenylenedioxy)ethanol was purchased from Parish Chemical Co., Provo, UT. Monoaza crown ethers were prepared by a recently reported one-step method.[11] Before use in our syntheses, they were purified further by recrystallization from pentane at −40 °C. This one-step method was also used to prepare 5,6-benzo-1,4,7,10-tetraoxa-13-azacyclopentadecane (benzomonoaza-15-crown-5). This compound was previously synthesized in low yield by a different route.[12] Lithium diphenylphosphide was prepared by addition of a stoichiometric amount of BuLi to a hexane solution of Ph_2PH. The yellow solid was filtered, washed with hexane, and dried in vacuo. All other starting materials were purchased from standard commercial suppliers, mainly Aldrich Chemical Co., Milwaukee, WI.

$Ph_2PNCH_2(CH_2OCH_2)_3CH_2$ (6). Monoaza-12-crown-4 (0.422 g, 2.41 mmol) and Et_3N (0.293 g, 2.89 mmol) were dissolved in 20 mL of ether. A solution of Ph_2PCl (0.531 g, 2.41 mmol) in 5 mL of ether was added dropwise over a period of 5 min. A white flocculent precipitate of $Et_3NH^+Cl^-$ formed immediately. After being stirred for 30 min, the mixture was filtered and the filtrate was evaporated to an oil. The oil was extracted into pentane, filtered, and evaporated to give 0.861 g of a colorless oil (99%). Anal. Calcd for $C_{20}H_{26}NO_3P$: C, 66.84; H, 7.29; N, 3.90; P, 8.62. Found: C, 67.25; H, 7.14; N, 4.10; P, 9.17. ^1H NMR (δ, C_6D_6, 80 MHz): 3.34 (m, OCH_2CH_2O, NCH_2CH_2O); 3.45 (t, J = 4.0 Hz, NCH_2CH_2O); 7.15, 7.58 (m, Ph). $^{13}C\{^1H\}$ NMR (δ, C_6D_6, 75.49 MHz): 52.90 (d, J_{CP} = 13.9 Hz, OCH_2CH_2N); 70.41, 71.87 (s, OCH_2CH_2O); 72.09 (d, J_{CP} = 2.2 Hz, OCH_2CH_2N); 128.42, 128.49 (*m*-, *p*-C_6H_5); 132.56 (d, J_{CP} = 19.6 Hz, *o*-C_6H_5); 140.57 (d, J_{CP} = 16.6 Hz, *i*-C_6H_5).

$Ph_2PNCH_2(CH_2OCH_2)_3CH_2{\cdot}LiPF_6$ (6·LiPF$_6$). $Ph_2PNCH_2(CH_2OCH_2)_3CH_2$ (0.516 g, 1.44 mmol) and $LiPF_6$ (0.262 g, 1.72 mmol) were combined in 15 mL of CH_2Cl_2, and the mixture was stirred for 90 min. The solution was filtered to remove excess $LiPF_6$ and evaporated to a white crystalline solid, yield 0.728 g (99%). Anal. Calcd for $C_{20}H_{26}F_6LiNO_3P_2$: C, 46.98; H, 5.13; F, 22.29; Li, 1.36; N, 2.74; P, 12.12. Found: C, 47.00; H, 5.23; F, 21.2; Li, 1.22; N, 2.75; P, 12.0.

$Ph_2PNCH_2(CH_2OCH_2)_4CH_2$ (2). A procedure similar to the $Ph_2PNCH_2(CH_2OCH_2)_3CH_2$ preparation starting with 5.00 g (22.8 mmol) of monoaza-15-crown-5 gave 9.01 g (98%) of a colorless oil. Anal. Calcd for $C_{22}H_{30}NO_4P$: C, 65.49; H, 7.50; N, 3.47; P, 7.68. Found: C, 65.15; H, 7.39; N, 3.43; P, 7.57. ^1H NMR (δ, C_6D_6, 360 MHz): 3.33 (s, OCH_2CH_2O); 3.38 (s, OCH_2CH_2O); 3.40 (dt, J_{HH} = 6.5 Hz, J_{PH} = 10.0 Hz, NCH_2CH_2O); 3.55 (t, J = 6.3 Hz, NCH_2CH_2O); 7.12, 7.54 (m, Ph). $^{31}P\{^1H\}$ NMR (δ, C_6D_6, 161.9 MHz): 65.7. $^{13}C\{^1H\}$ NMR (δ, C_6D_6, 100.6 MHz): 50.76 (d, J_{CP} = 14.1 Hz, NCH_2CH_2O); 67.76, 68.10, 69.01, 69.21 (s, NCH_2CH_2O and OCH_2CH_2O); 125.73, 125.77 (*m*-, *p*-C_6H_5); 129.55 (d, J_{CP} = 19.9 Hz, *o*-C_6H_5); 137.96 (d, J_{CP} = 16.3 Hz, *i*-C_6H_5). Mass spectrum (m/e, electron impact): 403.1929 (molecular ion calcd 403.1913); 214.0779 (base peak, $Ph_2PNH(CH_2)^+$).

$Ph_2PCH_2NCH_2(CH_2OCH_2)_4CH_2$ (3). Monoaza-15-crown-5 (11.30 g, 51.5 mmol), aqueous formaldehyde (5.53 g of a 37% solution, 68.2 mmol), and Ph_2PH (9.60 g, 51.5 mmol) were combined in 40 mL of benzene and heated to 60 °C for 5 h under argon. The mixture was evaporated to a yellow oil under high vacuum and dehydrated by refluxing in a Dean-Stark trap with 120 mL of toluene for 3 h. The toluene solution was evaporated to an oil, and the product was extracted into pentane, filtered, and evaporated to a pale yellow oil, 20.98 g (98%). Anal. Calcd for $C_{23}H_{32}NO_4P$: C, 66.17; H, 7.73; N, 3.36; P, 7.42. Found: C, 66.10; H, 7.82; N, 3.36; P, 7.30. ^1H NMR (δ, $CDCl_3$, 80 MHz): 2.97 (t, 4, J = 6 Hz, NCH_2CH_2O); 3.47 (d, J_{PH} = 4.4 Hz, PCH_2N); 3.63 (s, t, J = 6 Hz, OCH_2CH_2O and NCH_2CH_2O); 7.4 (m, 10, C_6H_5). $^{31}P\{^1H\}$ NMR (δ, C_6D_6, 32.206 MHz): −26.4. $^{13}C\{^1H\}$ NMR (δ, C_6D_6, 22.63 MHz): 56.3 (d, J_{CP} = 7.4 Hz, PCH_2N); 60.9 (d, J_{CP} = 2.9 Hz, NCH_2CH_2O); 70.3, 70.5, 70.9, 71.5 (s, NCH_2CH_2O and OCH_2CH_2O); 128.4, 128.5, 128.7 (*m*-, *p*-C_6H_5); 133.4 (d, J_{PC} = 18 Hz, *o*-C_6H_5); 139.4 (d, J_{PC} = 15 Hz, *i*-C_6H_5). Mass spectrum (m/e, electron impact): 232.1551 (base peak, $CH_2{=}NCH_2(CH_2OCH_2)_4CH_2$).

$Ph_2PCH_2NCH_2(CH_2OCH_2)_4CH_2{\cdot}NaPF_6$ (3·NaPF$_6$). $Ph_2PCH_2NCH_2(CH_2OCH_2)_4CH_2$ (3.00 g, 7.21 mmol) was dissolved in 40 mL of CH_2Cl_2, and $NaPF_6$ (1.33 g, 7.93 mmol) was added while the mixture was stirred. Initially, the portions of $NaPF_6$ dissolved, but by the end of the addition there was undissolved white solid. The mixture was stirred overnight, filtered, and evaporated to give a sticky white solid. The product was extracted with 2 × 12 mL of ether, and the ether-insoluble product was filtered to yield a dry white solid, yield 3.95 g (94%). Recrystallization from ~200 mL of toluene/CH_2Cl_2 (9:1) at −78 °C gave 3.23 g of a white solid (two crops, 76%). Anal. Calcd for $C_{23}H_{32}F_6NNaO_4P_2$: C, 47.19; H, 5.51; F, 19.47; N, 2.39; Na, 3.93; P, 10.58. Found: C, 47.29; H, 5.50; F, 19.5; N, 2.47; Na, 3.83; P, 10.6. ^1H NMR (δ, $CDCl_3$, 90 MHz): 2.91 (t, 4, J = 5 Hz, NCH_2CH_2O); 3.40 (t, 4, J = 5 Hz, NCH_2CH_2O); 3.60, 3.65 (s, 12, OCH_2CH_2O); 3.92 (s, 2, NCH_2P); 7.33 (m, 10, C_6H_5). ^1H NMR indicates that the crystals contain toluene, which is removed very slowly by high-vacuum drying at 25 °C.

***o*-$C_6H_4(OCH_2CH_2OTs)_2$.** *o*-$C_6H_4(OCH_2CH_2OH)_2$ was converted to the ditosylate on a 1.25-mol scale.[13] The crude product was dissolved in CH_2Cl_2, and the aqueous layer was separated and discarded. The CH_2Cl_2 layer was dried over Na_2SO_4. Filtration and removal of solvent in vacuo yielded a white solid, yield 56.2 g (90%). This product was used without further purification. ^1H NMR (δ, $CDCl_3$, 90 MHz): 2.42 (s, 6, $CH_3C_6H_4$); 4.23 (m, AA′BB′, 8, OCH_2CH_2O); 6.80 (m, 4, *o*-$C_6H_4O_2$); 7.28, 7.78 (dd, AB, 8, $CH_3C_6H_4$).

5,6-Benzo-1,4,7,10-tetraoxa-13-azacyclopentadecane (Benzomonoaza-15-crown-5). The reaction of *o*-$C_6H_4(OCH_2CH_2OTs)_2$ with $HN(CH_2CH_2OH)_2$ by a literature procedure[11] on a 0.75-mol scale gave a sticky orange solid as the crude product. The short-path distillation step was omitted. Recrystallization from refluxing toluene (cooled to −25 °C) gave pale yellow crystals, 4.21 g (2 crops, 21%). Anal. Calcd for $C_{14}H_{21}NO_4$: C, 62.90; H, 7.92; N, 5.24. Found: C, 61.76; H, 7.77; N, 5.14. ^1H NMR (δ, $CDCl_3$, 360 MHz): 2.61 (s, 1, NH); 2.82 (t, J = 4.7 Hz, 4, NCH_2CH_2O); 3.72 (t, J = 4.7 Hz, 4, NCH_2CH_2O); 3.86 (m, 4, OCH_2CH_2O); 4.10 (m, 4, OCH_2CH_2O); 6.85 (m, AA′BB′, 4, C_6H_4). IR (Nujol mull, cm^{-1}): 3320 (m, NH).

$Ph_2PCH_2N(CH_2CH_2OCH_2CH_2O)_2(o\text{-}C_6H_4)$ (7). Benzomonoaza-15-crown-5 (1.50 g, 5.61 mmol), aqueous formaldehyde (0.59 mL of a 37% solution, 7.29 mmol), and Ph_2PH (1.045 g, 5.61 mmol) were combined in 6 mL of benzene and heated to 60 °C for 19 h in a sealed flask. The mixture was evaporated under high vacuum to an orange oil, which was extracted into ether and evaporated to give a dry white solid. Recrystallization from minimal ether at −40 °C gave a flocculent white solid, yield 2.41 g (two crops, 92%). Anal. Calcd for $C_{27}H_{32}NO_4P$: C, 69.66; H, 6.93; N, 3.01; P, 6.65. Found: C, 70.08; H, 7.02; N, 2.91; P, 6.56. ^1H NMR (δ, C_6D_6, 360 MHz): 3.097 (t, J = 6.0 Hz, 4, NCH_2CH_2O); 3.393 (d, J_{PH} = 5.3 Hz, 2, NCH_2P); 3.505 (t, J = 4.2 Hz, 4, $C_6H_4OCH_2CH_2O$); 3.721 (t, J = 4.2 Hz, $C_6H_4OCH_2CH_2O$); 3.726 (t, J = 6.0 Hz, NCH_2CH_2O); 6.630, 6.830 (m, AA′BB′, 4, C_6H_4); 7.075 (m, 6, *m*-, *p*-C_6H_5); 7.517 (m, 4, *o*-C_6H_5). Mass spectrum (m/e, electron impact): 280.1541 (base peak, $C_{15}H_{22}NO_4$).

$Ph_2PCH_2C(O)NCH_2(CH_2OCH_2)_4CH_2$ (9). A solution of chloroacetyl chloride (1.29 g, 11.4 mmol) in 50 mL of toluene was added dropwise to a stirred mixture of monoaza-15-crown-5 (2.50 g, 11.4 mmol) and powdered K_2CO_3 (2.42 g, 22.8 mmol) in 150 mL of toluene. After it was stirred for 16 h, the mixture was filtered and the filtrate was evaporated to an oil (**8**), yield 3.32 g (98%). ^1H NMR (δ, $CDCl_3$, 300 MHz): 3.5–3.8 (m, NCH_2CH_2O, OCH_2CH_2O); 3.87 (t, J = 6 Hz, NCH_2CH_2O); 4.10 (s, side product); 4.22 (s, $ClCH_2C(O)$). IR (THF solution, cm^{-1}): 1660 (vs, C=O, amide), 1734 (sh, side product), 1754 (m, side product). The crude α-chloro amide was dissolved in 100 mL of THF and filtered. This solution was cooled to −78 °C in a dry ice/acetone bath, and a solution of Ph_2PLi (2.41 g, 12.5 mmol) in 50 mL of THF was added dropwise over a period of 30 min. The mixture was warmed to 25 °C and evaporated to a yellow foam. Degassed H_2O (50

(11) Maeda, H.; Furuyoshi, S.; Nakatsuji, Y.; Okahara, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 212–218.

(12) Hogberg, S. A. G.; Cram, D. J. *J. Org. Chem.* **1975**, *40*, 151–152.

(13) Marvel, C. S.; Sekera, V. C. In *Organic Syntheses*; Collective Volume 3; Horning, E. C., Ed.; Wiley: New York, 1955; Collect. Vol. 3, pp 366–367.

mL) was added, and the mixture was extracted with three 50-mL portions of CH_2Cl_2. The CH_2Cl_2 extracts were transferred by cannula to an argon-filled Schlenk flask containing K_2CO_3. After it was stirred over K_2CO_3 for 30 min, the CH_2Cl_2 solution was filtered and evaporated to a yellow oil, yield 4.35 g. The crude product was purified by chromatography on grade I alumina with 2% MeOH in $CH_3OC(CH_3)_3$ (38 mm × 30 cm column, 50-mL fractions). Fractions were checked by TLC on alumina plates. The desired fractions (R_f 0.25) were evaporated to give a white solid, yield 3.11 g (61% overall). Anal. Calcd for $C_{24}H_{32}NO_5P$: C, 64.71; H, 7.24; N, 3.14; P, 6.95. Found: C, 64.67; H, 7.25; N, 3.29; P, 6.95. ^1H NMR (δ, CD_2Cl_2, 300 MHz): 3.23 (s, 2, $PCH_2C(O)$); 3.4–3.65 (m, 18, NCH_2CH_2O, OCH_2CH_2O); 3.74 (t, J = 7 Hz, 2, NCH_2CH_2O); 7.33, 7.44 (m, m, 10 Ph). $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2, 121.7 MHz): −19.88. $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 75.6 MHz): 35.02 (d, J_{CP} = 15.5 Hz, PCH_2); 49.55 (s, NCH_2CH_2O); 51.40 (d, J_{CP} = 2.7 Hz, NCH_2CH_2O); 69.56, 70.22, 70.30, 70.35, 70.55, 70.89, 71.62 (s, NCH_2CH_2O, OCH_2CH_2O); 128.57, 128.65, 128.91 (s, m-, p-C_6H_5); 132.98 (d, J_{CP} = 19.7 Hz, o-C_6H_5); 138.71 (d, J_{CP} = 15.0 Hz, i-C_6H_5); 170.12 (d, J_{CP} = 8.2 Hz, C(O)N). IR (THF solution, cm^{-1}): 1643 (s, C=O, amide).

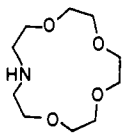
$Ph_2PCH_2CH_2\overline{NCH_2(CH_2OCH_2)_4CH_2}$ (4). A 1.0 M solution of BH_3·THF (35 mL, 35 mmol) was added dropwise to a solution of $Ph_2PCH_2C(O)\overline{NCH_2(CH_2OCH_2)_4CH_2}$ (3.11 g, 6.98 mmol) in 50 mL of THF. The mixture was refluxed for 16 h, and then excess BH_3·THF was destroyed by addition of 6 mL of H_2O. After it was stirred for 30 min, the solution was evaporated to a white solid. A 60-mL portion of 6 N HCl was added, and the mixture was refluxed for 4 h. Evaporation gave a white solid, which was treated with 60 mL of H_2O and 11.7 g of KOH. This mixture was extracted with three 50-mL portions of CH_2Cl_2, and the combined extracts were dried over K_2CO_3. Filtration and evaporation gave a pale red oil, 2.95 g (98%). This crude product is sufficiently pure for most purposes (≥95%). Additional purification can be accomplished by chromatography on activity I alumina using 2% MeOH in $CH_3OC(CH_3)_3$. Anal. Calcd for $C_{24}H_{34}NO_4P$: C, 66.80; H, 7.94; N, 3.25; P, 7.18. Found: C, 67.12; H, 7.86; N, 3.38; P, 7.27. ^1H NMR (δ, CD_2Cl_2, 300 MHz): 2.22 (m, 2, PCH_2CH_2N); 2.60 (m, PCH_2CH_2N); 2.66 (t, J = 6.0 Hz, NCH_2CH_2O); 3.49 (t, J = 6.0 Hz, NCH_2CH_2O); 3.57 (m, OCH_2CH_2O); 7.31, 7.42 (m, 10, Ph). $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2, 121.7 MHz): −19.33. $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 75.6 MHz): 26.20 (d, J_{CP} = 12.7 Hz, PCH_2CH_2N); 53.47 (d, J_{CP} = 23.6 Hz, PCH_2CH_2N); 54.67 (s, NCH_2CH_2O); 70.22, 70.30, 70.47, 71.10 (s, NCH_2CH_2O, OCH_2CH_2O); 128.59, 128.68, 128.72 (s, m-, p-C_6H_5); 132.91 (d, J_{CP} = 18.9 Hz, o-C_6H_5); 139.17 (d, J_{CP} = 13.7 Hz, i-C_6H_5).

$Ph_2PCH_2CH_2C(O)\overline{NCH_2(CH_2OCH_2)_4CH_2}$ (11). A solution of 3-chloropropionyl chloride (1.45 g, 11.4 mmol) in 50 mL of toluene was added dropwise to a stirred mixture of monoaza-15-crown-5 (2.50 g, 11.4 mmol) and powdered K_2CO_3 (2.42 g, 11.4 mmol) in 150 mL of toluene. After it was stirred for 16 h, the mixture was filtered and the filtrate was evaporated to an oil (**10**), yield 3.50 g (99%). ^1H NMR (δ, CD_2Cl_2, 300 MHz): 2.83 (t, J = 8 Hz, 2, $ClCH_2CH_2C(O)$), 3.4–3.7 (m, 18, NCH_2CH_2O, OCH_2CH_2O); 3.75 (m, 2, NCH_2CH_2O); 3.79 (t, J = 8 Hz, 2, $ClCH_2CH_2C(O)$). IR (THF solution, cm^{-1}): 1648 (vs, C=O, amide). The crude β-chloro amide was dissolved in 100 mL of THF and filtered. This solution was cooled to 0 °C, and a solution of Ph_2PLi (2.74 g, 14.3 mmol) in 50 mL of THF was added dropwise until there was a persistent (>1 min) yellow end point. Workup and purification were identical with those in the preparation of $Ph_2PCH_2C(O)\overline{NCH_2(CH_2OCH_2)_4CH_2}$. After chromatography, the product was further purified by recrystallization from methylene chloride/ether at −40 °C to give a white solid, yield 1.76 g (34% overall). Anal. Calcd for $C_{25}H_{34}NO_5P$: C, 65.34; H, 7.46; N, 3.05; P, 6.74. Found: C, 64.99; H, 7.55; N, 3.03; P, 6.55. ^1H NMR (δ, CD_2Cl_2, 300 MHz): 2.36 (m, 4, $PCH_2CH_2C(O)$); 3.35 (t, J = 6 Hz, NCH_2CH_2O); 3.47 (t, J = 6 Hz, NCH_2CH_2O); 3.50–3.70 (m, NCH_2CH_2O, OCH_2CH_2O); 7.31, 7.43 (m, 10, Ph). $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2, 121.7 MHz): −15.05. $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 75.6 MHz): 23.54 (d, J_{CP} = 10.6 Hz, PCH_2CH_2); 29.87 (d, J_{CP} = 20.1 Hz, PCH_2CH_2); 49.60, 50.53 (s, NCH_2CH_2O); 69.73, 69.99, 70.23, 70.40, 70.54, 70.95, 71.52 (s, OCH_2CH_2O, NCH_2CH_2O); 128.67, 128.75, 128.87 (s, m-, p-C_6H_5), 132.96 (d, J_{CP} = 18.6 Hz, o-C_6H_5); 138.91 (d, J_{CP} = 14.4 Hz, i-C_6H_5); 172.47 (d, J_{CP} = 14.3 Hz, C(O)N). IR (THF solution, cm^{-1}): 1649 (vs, C=O, amide).

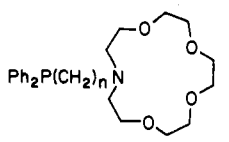
$Ph_2PCH_2CH_2CH_2\overline{NCH_2(CH_2OCH_2)_4CH_2}$ (5). Solid $LiAlH_4$ (0.59 g, 15.7 mmol) was added to a stirred solution of $Ph_2PCH_2CH_2C(O)\overline{NCH_2(CH_2OCH_2)_4CH_2}$ (1.20 g, 2.61 mmol) in 25 mL of THF. The mixture was refluxed for 16 h. Excess $LiAlH_4$ was destroyed by careful addition of Na_2SO_4·$10H_2O$ (5.06 g, 15.7 mmol). After it was stirred for 2 h, the mixture was filtered and the solids were extracted with 4 × 15 mL of THF. The combined filtrates were evaporated to an oil, dissolved in toluene, filtered again, and evaporated to a colorless oil, yield 1.14 g (98%). This crude product is sufficiently pure for most purposes (≥95%). Additional purification can be accomplished by chromatography on activity I alumina using 2% MeOH in $CH_3OC(CH_3)_3$. Anal. Calcd for $C_{25}H_{36}NO_4P$: C, 67.40; H, 8.14; N, 3.14; P, 6.95. Found: C, 67.63; H, 8.24; N, 3.21; P, 6.73. ^1H NMR (δ, CD_2Cl_2, 300 MHz): 1.53 (m, 2, $PCH_2CH_2CH_2$); 2.05 (m, 2, $PCH_2CH_2CH_2N$); 2.56 (t, J = 7.1 Hz, 2, $PCH_2CH_2CH_2N$); 2.62 (t, J = 6.0 Hz, 4, NCH_2CH_2O); 3.52 (t, J = 6.0 Hz, NCH_2CH_2O); 3.56 (m, OCH_2CH_2O); 7.32, 7.41 (m, 10, Ph). $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2, 121.7 MHz): −15.83. $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 75.6 MHz): 24.48 (d, J_{CP} = 16.8 Hz, $PCH_2CH_2CH_2N$); 25.68 (d, J_{CP} = 11.8 Hz, $PCH_2CH_2CH_2N$); 55.21 (s, NCH_2CH_2O); 58.11 (d, J_{CP} = 14.4 Hz, $PCH_2CH_2CH_2N$); 70.41, 70.48, 70.62, 71.22 (s, OCH_2CH_2O, OCH_2CH_2N); 128.57, 128.72 (m-, p-C_6H_5); 132.97 (d, J_{CP} = 18.8 Hz, o-C_6H_5); 139.58 (d, J_{CP} = 14.7 Hz, i-C_6H_5).

Results and Discussion

The aza crown ether **1** (1,4,7,10-tetraoxa-13-azacyclopentadecane, hereafter referred to as monoaza-15-crown-5) can be readily prepared on a large scale by a one-step procedure.[11] Therefore, we chose it as a common starting material for the syntheses of phosphino aza crown ethers **2–5**.

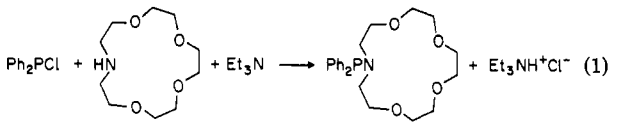


1



2 n = 0
3 n = 1
4 n = 2
5 n = 3

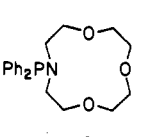
Monoaza-15-crown-5 reacts rapidly with chlorodiphenylphosphine in the presence of triethylamine to give **2** (reaction 1).



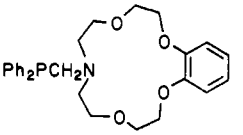
(1)

2

An analogous reaction with monoaza-12-crown-4 yields **6**. Both



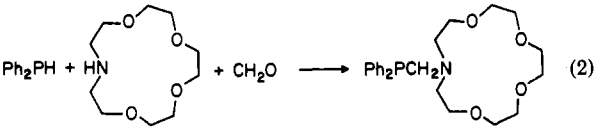
6



7

2 and **6** are viscous air-sensitive oils. They hydrolyze readily and do not survive chromatography.

By use of a modification of the Mannich reaction,[14] the combination of diphenylphosphine and monoaza-15-crown-5 with aqueous formaldehyde produces **3** as a colorless air-sensitive oil (reaction 2). Like compounds **2** and **6**, **3** is sensitive to hydrolysis.



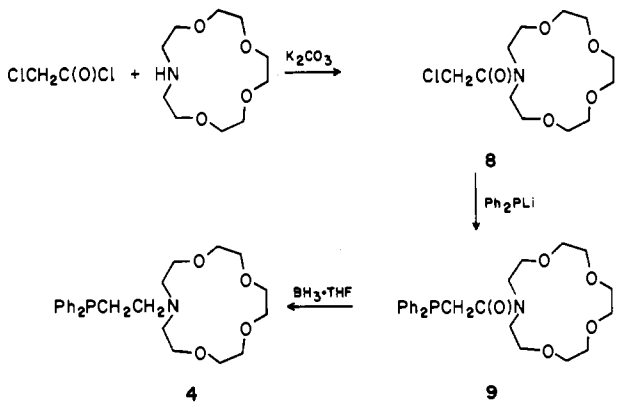
(2)

3

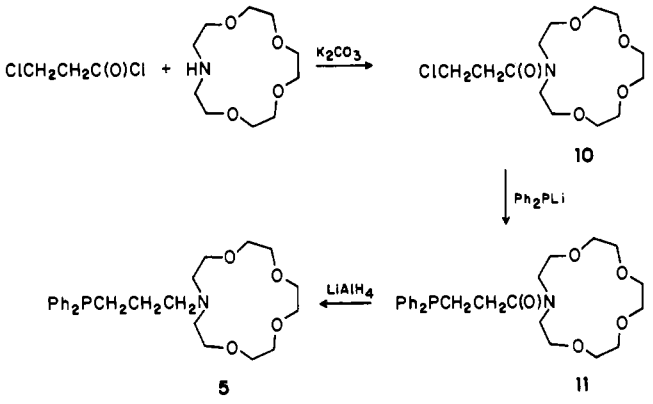
Attempts to chromatograph it on silica gel give high yields of Ph_2PCH_2OH. Diphenylphosphine, formaldehyde, and 5,6-benzo-1,4,7,10-tetraoxa-13-azacyclopentadecane (benzomonoaza-15-crown-5) react similarly to give the benzo phosphino aza crown ether **7**. Compound **7** is a solid and can be purified by recrystallization.

(14) Grim, S. O.; Mateenzo, L. J. *Tetrahedron Lett.* **1973**, 2951–2953.

Scheme I



Scheme II



The synthesis of phosphino aza crown ether **4** is illustrated in Scheme I. The addition of chloroacetyl chloride to a mixture of monoaza-15-crown-5 and potassium carbonate in toluene gives α-chloro amide **8**, which can be isolated as an impure oil and characterized spectroscopically. The addition of lithium diphenylphosphide to **8** gives the phosphine amide **9**, which is isolated as a pure white solid after column chromatography. Phosphine amide **9** can be reduced to **4** with the borane–tetrahydrofuran complex. Product **4** prepared by this method is pure enough for most purposes. It can be purified further by chromatography on alumina.

A similar reaction scheme can be used to synthesize phosphinoazacrown ether **5** (Scheme II). By starting with the appropriate chloroalkyl acid chloride, this method can potentially be used to prepare phosphino aza crown ethers with additional methylene groups between phosphorus and nitrogen.

The phosphino aza crown ethers **2**–**6** are viscous high-boiling oils. All of the syntheses give products of ≥90% purity. In addition to elemental analyses, spectroscopic characterization, particularly ^1H and ^{13}C NMR, was used to confirm the structures and assess the purities of all new compounds.

Alkali-metal ions form solid crystalline 1:1 adducts with the phosphino aza crown ethers. Two examples, **3**·$NaPF_6$ and **6**·$LiPF_6$, are described in the Experimental Section.

All of the phosphino aza crown ethers are pure enough to use as starting materials for the preparation of organometallic derivatives. In many cases the organometallic derivatives are crystalline.[7,15]

Registry No. **2**, 90330-43-1; **3**, 87101-78-8; **3**·$NaPF_6$, 90316-71-5; **4**, 90330-44-2; **5**, 102851-56-9; **6**, 90330-42-0; **6**·$LiPF_6$, 90316-77-1; **7**, 102851-57-0; **8**, 98704-89-3; **9**, 102851-58-1; **10**, 102851-59-2; **11**, 102851-60-5; *o*-$C_6H_4(OCH_2CH_2OTs)_2$, 54535-06-7; *o*-$C_6H_4(OCH_2CH_2OH)_2$, 10234-40-9; $HN(CH_2CH_2OH)_2$, 111-42-2; Ph_2PCl, 1079-66-9; HCHO, 50-00-0; Ph_2PH, 829-85-6; Ph_2PLi, 4541-02-0; monoaza-15-crown-5, 66943-05-3; monoaza-12-crown-4, 41775-76-2; benzomonoaza-15-crown-5, 54533-83-4; chloroacetyl chloride, 79-04-9.

(15) McLain, S. J., to be submitted for publication.