Phosphines Functionalized with Crown Ether Groups: Synthesis and Study of Systems Incorporating 1,3-Xylyl-18-Crown-5 Units

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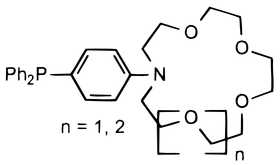
Hybrid phosphine crown ether molecules are obtained from Ph_2PCl, $PhP(OMe)_2$, or $P(OPh)_3$ and the carbanions generated by a lithium/bromine exchange reaction between *n*-butyllithium and 5-bromo-1,3-xylyl-18-crown-5 or 5-bromo-2-methoxy-1,3-xylyl-18-crown-5. With these phosphine systems represented as $Ph_xP(crown)_{3-x}$, the $x = 0-2$ and $1-2$ members are reported for the former and latter crown ethers, respectively. The A_1 $\upsilon(CO)$ stretching frequencies from the $Ni(CO)_3L$ ($L = Ph_xP(crown)_{3-x}$) complexes are within 0.4 cm^{-1} of 2068.9 cm^{-1}, the frequency for $Ni(CO)_3PPh_3$. For both series of ligands, H or OMe in the 2-position, the $\upsilon(CO)$ stretching frequencies are found to decrease with increasing substitution by the crown ether groups (deceasing *x*). The addition of Na^+-Cs^+ (SCN^- salts) to the Ni complexes causes the A_1 bands to shift to higher frequencies and to broaden. The largest shifts are observed with phosphines substituted with larger numbers of crown ether groups and added Na^+ ions. ^{31}P NMR spectral data for the L_2PdCl_2 complexes of these phosphines are reported. For all ligands, the signals from the trans complexes are observed between 22 and 25 ppm, a range considered consistent with cone angles of ca. 145°. The molecular structure, from X- ray crystallographic studies, of the oxide of the phosphine with $x = 2$ and H in the 2-position is reported. The crown ether ring is based on regular gauche and anti arrangements of the carbon−carbon and carbon−oxygen bonds, and the planes defined by the benzene ring and the five oxygen atoms form an angle of 38.4°.

Introduction

Trivalent phosphorus compounds are versatile ligands that form the basis for a range of useful and interesting transition-metal complexes[1] including, for example, the rheumatoid arthritus drug Aurofin[2] and catalysts that promote a variety of organic reactions such as enantioselective hydrogenations[3] or aryl halide aminations.[4] It is not surprising that there continues to be considerable interest in new phosphines that have specific and well-characterized steric, electronic, and solubility properties.

We recently initiated a systematic study of triphenylphosphine-based ligands that have crown ether groups appended to the phenyl rings. Specifically, we have reported the synthesis of **1**, the $\upsilon(CO)$ stretching frequencies of the $Ni(CO)_3L$ complexes of **1** and **2**, and the molecular structure of the oxide of **1**.[5] As will be further discussed, **1** and **2** were found to provide $\upsilon(CO)$ stretching frequencies in the absence of ions of 2066.3 and 2068.3 cm^{-1}, values that are in general consistent with the Hammett parameter constants for the ring substituents.



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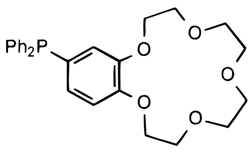

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Several examples of hybrid phosphine crown ether systems have been reported since Shaw and co-workers reported **3** in 1978.[6] Okano and co-workers, who first reported the 12-crown-4 through 21-crown-7 series of type **2** ligands, studied these in conjunction with either [RhCl(1,5-COD)] or $[\eta^3\text{-}C_3H_5\,PdCl]_2$ as catalysts for the

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[1] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotranistion Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

[2] Lippard, S. J.; Berg, J. M. *Principles of Bioorganic Chemistry*; University Science Books: Mill Valley, CA, 1994.

[3] Trabesinger, G.; Albinati, A.; Feiken, N.; Kunz, R. W.; Pregosin, P. S.; Tschoerner, M. *J. Am. Chem. Soc.* **1997**, *119*, 6315.

[4] Marcoux, J.-F.; Wagaw, S.; Buchwald, S. *J. Org. Chem.* **1997**, *62*, 1568.

[5] Muehl, B. S.; Sheu, B.-J.; Burns, S. A.; Fritz, J. E.; Tribbett, D. A.; Weitgenant, J. A.; Storhoff, B. N. *J. Coord. Chem.* **1995**, *35*, 359.

[6] Hyde, E. M.; Shaw, B. L.; Shepherd, I. *J. Chem. Soc., Dalton Trans.* **1978**, 1696.

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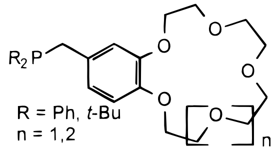

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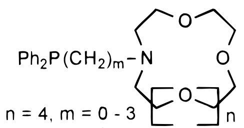
hydrogenation of alkali-metal cinnamates.[7,8] The cinnamates were studied in benzene–water mixtures, and initial hydrogen uptake rates indicated that ligand **2** systems provided Rh(I) catalysts which were up to 50 times more active than catalysts prepared from the same metals, triphenylphosphine, and added 18-crown-6. These enhanced rates were explained as arising from a process in which the transfer of the cinnamate ion from the aqueous to nonaqueous phase was the rate-limiting step.

Ligands of type **4**, with flexible methylene connectors between the phosphine centers and crown ether groups, have been studied in conjunction with Rh(I) and alkali-metal salts, and these mixtures have been reported to be effective catalysts for propylene hydroformylation reactions.[9,10] For example, the rate of hydroformylation by a catalyst system based on **4** ($m = 1$, $n = 2$) was enhanced by a factor of 5 upon the addition of $NaPF_6$. It was proposed that the observed data were consistent with the idea that the complexed cations activate the process by interacting with the coordinated CO oxygen atoms.



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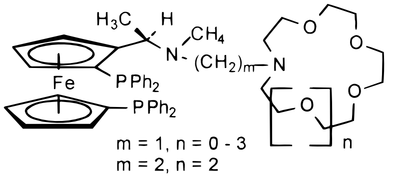
Reported bidentate phosphine crown ligands include **5**–**7**. Palladium catalysts based on **5** have been evaluated for both enantioselectivity and activity for the allylation of substituted β-diketones under biphasic (solid–liquid) conditions involving KF or RbF and dichloromethane or mesitylene as bases and solvents, respectively.[11,12] With a single methylene spacer group between a symmetrical diaza-18-crown-6 and the exocyclic nitrogen, a 65% ee of product was obtained with a 92% yield for the allylation of 2-acetylcylohexanone in the KF/mesitylene mixture, compared to 29% ee and 83% yield from an experiment involving added 18-crown-6 and a ligand with a second methyl group on the exocyclic nitrogen atom. The selectivity observed was attributed to the ability of the catalyst to orient the enolate anion by way of a crown-complexed potassium ion.

Bidentate phosphine **6** was obtained in 83% yield by condensing 4′-aminobenzo-15-crown-5 with aqueous formaldehyde and diphenylphosphine.[13] This ligand was found to form square-planar complexes with Ni(II), Pd(II), and Pt(II).



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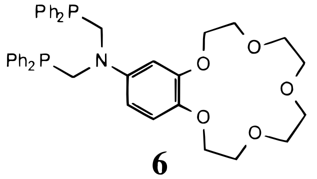

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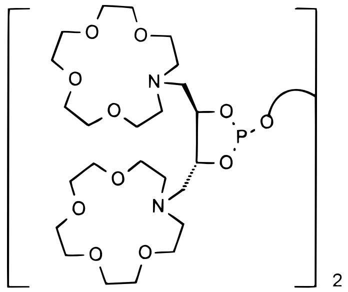

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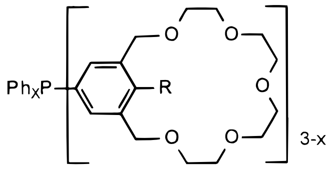
McFarland and Landis used a seven-step procedure starting with tartaric acid to form **7** (bridging neopentyl alcohol or 1,3-propanediol units) with four monoaza-15-crown-5 units in 50% yield.[14] Rh(I) complexes of **7** were studied as hydroformylation catalysts for styrene, 1-buteneamide, and 1-pentenamide. The catalyst activity was found to be similar to catalysts based on related, noncrown-containing tartrate-based phosphites.

To further the understanding of the properties of phosphine crown ligands, we have synthesized phosphine crown systems based on 1,3-xylyl-18-crown-5 systems that are shown as **8**–**12**. Herein, we report the synthetic methods used for these molecules, the X-ray structure of the phosphine oxide of **8**, the ν(CO) stretching frequencies of the corresponding $Ni(CO)_3L$ complexes, and the ^{31}P chemical shifts of the corresponding L_2PdCl_2 complexes.



8-12

#	x	R
8	2	H
9	1	H
10	0	H
11	2	OMe
12	1	OMe

Experimental Section

Reagents and Materials. Chlorodiphenylphosphine, dimethyl phenylphosphonite, triphenyl phosphite, 2,6-dimeth-

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(7) Okano, T.; Iwahara, M.; Konishi, H.; Kiji, J. *J. Organomet. Chem* **1988**, *346*, 267.

(8) Okano, T.; Iwahara, M.; Suzuki, T.; Kiji, J. *Chem. Lett.* **1986**, 1467.

(9) McLain, S. J. *Inorg. Chem.* **1986**, *25*, 3124.

(10) McLain, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 6355.

(11) Sawamura, M.; Nagata, H.; Sakamoto, H.; Ito, Y. *J. Am. Chem. Soc.* **1992**, *114*, 2586.

(12) Sawamura, M.; Nakayama, Y.; Tang, W.-M.; Ito, Y. *J. Org. Chem.* **1996**, *61*, 9090.

(13) Serindag, O. *Synth. React. Inorg. Met.-Org. Chem.* **1995**, *25*, 327.

(14) MacFarland, D. K.; Landis, C. R. *Organometallics* **1996**, *15*, 483.

ylanisole, 5-bromo-*m*-xylene, tetraethylene glycol, benzoyl peroxide, sodium hydride (60% in mineral oil), and *n*-butyllithium (2.5 M in hexane) were obtained from Aldrich Chemical Co., Inc. $Ni(CO)_4$ was purchased from Strem Chemicals, Inc. Prior to use, both tetrahydrofuran (THF, over sodium and benzophenone) and chlorodiphenylphosphine were distilled. 5-Bromo-1,3-bis(bromomethyl)-2-methoxybenzene (4-bromo-2,6-di(bromomethyl)anisole),[15] 5-bromo-1,3-xylyl-18-crown-5,[16] and $(PhCN)_2PdCl_2$[17] (PhCN = C_6H_5CN) were prepared as previously described. The alkali-metal thiocyanates were dried under high vacuum at 60 °C for 24 h prior to use.

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 1,000 and Varian Gemini-200 instruments, respectively. The ^{1}H and ^{31}P NMR spectra 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 υ(CO) stretching band has been reported to be 2068.9 cm^{-1}.[18] 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.

IR and ^{31}P Studies. The $Ni(CO)_3L$ IR[18−20] and L_2PdCl_2 ^{31}P [21,22] studies were carried out in situ as previously described. For the former and latter, deoxygenated dichloromethane (filtered through a column of activated alumina) and $CDCl_3$, respectively, were used as solvents. The IR spectra in the presence of alkali-metal ions were obtained on solutions of $Ni(CO)_3L$ to which an excess of solid MSCN (M = Na^+−Cs^+) had been added; the salt−$Ni(CO)_3L$ mixtures were shaken for 10 min prior to obtaining the spectra.

Preparation of 5-Diphenylphosphino-1,3-xylyl-18-crown-5, 8. 5-Bromo-1,3-xylyl-18-crown-5 (4.00 g, 0.0107 mol) was dissolved in 100 mL of freshly distilled THF and cooled in an ethyl acetate/liquid nitrogen slush. *n*-Butyllithium (4.3 mL, 0.011 mol) in hexane was added via syringe over a period of 10 min to the cooled and stirred solution. After an additional 30 min at this temperature, freshly distilled chlorodiphenylphosphine (1.9 mL, 0.011 mol) was added over a period of 20 min. The mixture was stirred and cooled for an additional 30 min, at which time the cold bath was removed; the mixture was stirred for an additional 12 h. Triethylamine (1 mL) and aqueous ammonium chloride (5 mL, 20%) were added in sequence. Most of the THF was removed using a rotary evaporator, leaving a yellow-colored 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 a yellow-colored residue that was chromatographed on silica gel using ethyl acetate as the mobile phase, providing 1.53 g (30%) of the product. ^{1}H NMR ($CDCl_3$): δ 3.5−3.8 (br, 16 H), 4.6 (s, 4 H), 7.10 (d, *J* = 8 Hz, 2 H), 7.5−7.4 (br, 10 H), 7.8 (s, 1 H). ^{31}P{H} NMR ($CDCl_3$): δ −5.0. Anal. Calcd for $C_{28}H_{33}O_5P{\cdot}0.75H_2O$: C, 68.07; H, 7.04. Found: C, 68.08; H, 6.93.

Preparation of the Oxide of 5-Diphenylphosphino-1,3-xylyl-18-crown-5, 8-Oxide. Phosphine crown **8** (0.48 g, 1.0 mmol) and 0.2 mL of 30% aqueous hydrogen peroxide were stirred in 20 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 solid was crystallized from ethyl acetate by slowly evaporating the solvent at −10 °C. ^{31}P{H} NMR ($CDCl_3$): δ −29.5.

Preparation of 5-Phenylphosphinobis(1,3-xylyl-18-crown-5), 9. 9 was prepared from 5-bromo-1,3-xylyl-18-crown-5 (6.00 g, 0.0160 mol) and dimethyl phenylphosphonite (1.6 mL, 0.010 mol) using the procedure described for **8**. The crude product was chromatographed on a silica gel column using a 4:1 mixture of ethyl acetate and acetone as the mobile phase, providing 2.03 g (36%) of product. ^{1}H NMR ($CDCl_3$): δ 3.5−3.8 (br, 32 H), 4.6 (s, 8 H), 7.1 (d, *J* = 8 Hz, 4 H), 7.4−7.5 (br, 5 H), 7.75 (s, 2 H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −4.4. Anal. Calcd for $C_{38}H_{51}O_{10}P{\cdot}0.50H_2O$: C, 64.48; H, 7.41. Found: C, 64.13; H, 7.11.

Preparation of 5-Phosphinotris-1,3-xylyl-18-crown-5, 10. 10 was prepared from 5-bromo-1,3-xylyl-18-crown-5 (12.00 g, 0.0320 mol) and triphenyl phosphite (2.8 mL, 0.011 mol) using the procedure described for **8**. An analytical sample was obtained by chromatographing 1.34 g of the crude product on a silica gel column using a 1:1 mixture of ethyl acetate and acetone as the mobile phase, providing 0.39 g of pure product. Pure product was also obtained by crystallizing the crude product from ethanol, and a total of 3.52 g (36%) of pure product was obtained. ^{1}H NMR ($CDCl_3$): δ 3.5−3.8 (br, 48 H), 4.6 (s, 12 H), 7.1 (d, *J* = 8 Hz, 6 H), 7.8 (s, 3 H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −4.1. Anal. Calcd for $C_{48}H_{69}O_{10}P{\cdot}H_2O$: C, 61.66; H, 7.65. Found: C, 61.69; H, 7.63.

Preparation of 5-Bromo-2-methoxy-1,3-xylyl-18-crown-5. Sodium hydride emulsion (4.57 g, 0.114 mol) was washed with hexane and added to a 2 L flask containing 1.2 L of THF, fitted with a reflux condenser, mechanical stirrer, and dropping funnel. 4-Bromo-2,6-di(bromomethyl)anisole (20.25 g, 0.0543 mol) and tetraethylene glycol (9.5 mL, 0.055 mol) dissolved in 200 mL of THF were added slowly to the refluxing mixture of THF and sodium hydride. After the addition, the reaction was allowed to reflux an additional 24 h. After the reaction mixture was cooled and filtered, the THF was removed under reduced pressure and the resulting residue was dissolved in dichloromethane and washed with 2 × 50 mL of water. Following separation, the organic layer was dried over anhydrous magnesium sulfate and the dichloromethane was removed under reduced pressure, providing an oil. The product was extracted from this residue with 5 × 100 mL of hot heptane. The fractions were combined and cooled to −5 °C. The white crystalline solid that formed was collected on a filter and dried under high vacuum, providing 10.28 g (47%) of product.

Preparation of 5-Diphenylphosphino-2-methoxy-1,3-xylyl-18-crown-5, 11. 11 was prepared from 5-bromo-2-methoxy-1,3-xylyl-18-crown-5 (7.12 g, 0.0176 mol) and chlorodiphenylphosphine (3.2 mL, 0.018 mol) using the procedure described for **8.** An analytical sample was obtained by chromatographing 1.10 g of crude product using a 6:4 mixture of ethyl acetate and acetone as the mobile phase. The remaining crude compound was crystallized from absolute ethanol (40 mL), providing a product judged to be pure by spectroscopic methods. The overall mass of the pure product was 5.89 g (66%). ^{1}H NMR ($CDCl_3$): δ 3.4−3.7 (br, 16 H), 4.2 (s, 3 H), 4.5 (s, 4 H) 7.2 (d, *J* = 8 Hz, 2 H), 7.3−7.4 (br, 10 H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −5.7. Anal. Calcd for $C_{29}H_{35}O_6P{\cdot}0.5H_2O$: C, 67.04; H, 6.98. Found: C, 67.11; H, 6.79.

Preparation of 5-Phenylphosphinobis(2-methoxy-1,3-xylyl-18-crown-5), 12. 12 was prepared from 5-bromo-2-methoxy-1,3-xylyl-18-crown-5 (12.02 g, 0.0297 mol) and dimethylphenyl phosphonite (2.35 mL, 0.0148 mol) using the procedure described for **8**. The crude product was dissolved in hot absolute ethanol and slowly cooled before being placed

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(15) Tashiro, M.; Mataka, S.; Takezaki, Y.; Takeshita, M.; Arimura, T.; Tsuge, A.; Yamato, T. *J. Org. Chem.* **1989,** *54*, 451.

(16) Moore, S. S.; Tarnowski, T. L.; Newcomb, M.; Cram, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 6398.

(17) Kharasch, M. S.; Seyler, R. C.; Mayo, F. R. *J. Am. Chem. Soc.* **1938**, *60*, 882.

(18) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(19) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2953.

(20) Bartik, T.; Himmler, T.; Schulte, H.-G.; Seevogel, K. *J. Organomet. Chem.* **1984**, *272*, 29.

(21) Mohr, B.; Lynn, D. M.; Grubbs, R. H. *Organometallics* **1996**, *15*, 4317.

(22) Bartik, T.; Himmler, T. *J. Organomet. Chem.* **1985**, *293*, 343.

in a freezer. The white precipitate that formed was collected on a filter and dried under vacuum. The mass of the collected product was 7.09 g (63%). ^{1}H NMR (CDCl$_3$): δ 3.4−3.7 (br, 32 H), 4.2 (s, 6 H), 4.5 (s, 8 H), 7.2 (d, $J = 8$ Hz, 4 H), 7.3−7.4 (br, 5 H). ^{31}P{^{1}H} NMR (CDCl$_3$): δ −6.5. Anal. Calcd for $C_{40}H_{55}O_{12}P{\cdot}H_2O$: C, 61.84; H, 7.40. Found: C, 61.89; H, 7.78.

Single-Crystal X-ray Diffraction Study of 8-Oxide. Single crystals of **8**-oxide were grown by slowly evaporating an ethyl acetate solution at −10 °C. A well-shaped crystal was cleaved from a larger cluster, attached to the tip of a glass fiber with silicone grease, transferred to the goniostat, and cooled to −170 °C. The data were collected by using a moving-crystal, moving-detector technique, with fixed background counts at each extreme of the scan. Data were corrected for Lorentz and polarization effects, and the equivalent data were averaged. The structure was solved by direct methods (Multan78) and Fourier techniques. O9 and C10 and C12 are located on a mirror plane, and P13 exists on either side of this plane. O14 and both phenyl (C_6H_5) groups are disordered, and there is also an apparent 10-membered ring lying on the mirror plane. The hydrogen atoms were included as fixed isotropic contributors in the final cycles of the refinement. The crystallographic data are presented in Table 4.

Results and Discussion

Syntheses. Compounds **8**−**12** have been obtained by nucleophilic attacks on P(III) centers by the crown ether carbanions generated by low-temperature lithium/bromine exchange reactions. Commercially available Ph_2PCl (for **8** and **11**), $PhP(OMe)_2$ (for **9** and **12**), and $P(OPh_3)$ (for **10**) were used as the phosphorus-containing starting materials. Even though the products were obtained in 36−66% yields following purifications, NMR spectra of the crude reaction mixtures were consistent with the conclusion that **8**−**12** were all formed in greater than 70% yields. All were found to be air-stable solids following purification by either chromatography or crystallization from ethanol, and they are very soluble in chlorinated hydrocarbons.

Ni(CO)$_3$L IR Data. The donor/acceptor or electronic characteristics of phosphines have been experimentally evaluated by several methods including calorimetry,[23−25] nonaqueous titrations,[26,27] $E_{1/2}$ measurements,[28−30] and both NMR[31] and IR[18−20] measurements of metal carbonyl complexes ligated with phosphine ligands. In regard to the latter, both the positions of the A$_1$ v(CO) bands and CO group ^{13}C chemical shifts for Ni(CO)$_3$L (L = phosphine) complexes have been used to determine the donor properties of the phosphine ligands. In addition to having been used extensively, Ni(CO)$_3$L complexes have the advantage that experimentally determined values can be compared to those calculated by using substituent contribution calculations such as electrostatic−covalent (E−C)[32,33] or Hammett parameter analyses,[34] thereby providing, for this study, an additional basis for determining if the crown ether substituents in **8**−**12** are comparable to simpler functionalities such as NMe$_2$.

Table 1. A$_1$ v(CO) Stretching Frequencies for Ni(CO)$_3$L Complexes

	added ions			
ligand	none	Na$^+$	K$^+$	Cs$^+$
8	2069.1	2069.5	2069.3	
9	2068.8	2069.7	2069.2	2069.1
10	2068.5	2069.6	2069.2	2068.7
11	2068.9	2069.8	2069.3	2069.4
12	2068.7	2070.1	2069.9	2069.2
1	2066.3	2067.8	2066.2	
2	2068.3	2069.0	2068.5	2068.5
PPh$_3$	2068.9	2068.9		

Table 2. Hammett Substituent Parameters

	position	
group	meta	para
CH$_2$OR	0.02	0.12
OCH$_3$	0.10	−0.28
N(CH$_3$)$_2$	−0.10	−0.63

For **8**−**12**, the A$_1$ v(CO) stretching frequencies of the Ni(CO)$_3$(phosphine) complexes have been recorded and the values, along with those for **1** and **2**, are summarized in Table 1. In the absence of added ions, these frequencies range from 2066.3 (**1**) to 2069.1 cm^{-1} (**8**), values that are approximately midway between those reported[18] for tri-*tert*-butylphosphine, 2056 cm^{-1}, and tris(2-cyanoethyl)phosphine, 2079 cm^{-1}. As summarized, **8**−**12** in the absence of ions provide v(CO) values that are similar to that of triphenylphosphine, 2068.9 ± 0.4; for **8**−**10** as well as **11** and **12**, there is a decrease in the v(CO) values with increasing substitution by the crown ether groups. Considering the entire set of $x = 2$ ligands, the v(CO) values increase **1** $\ll$ **2** $<$ **10** $<$ **12** $<$ **9** $<$ **11** $\approx$ PPh$_3$ $<$ **8**. This order of v(CO) values and the finding that **1** provides a lower v(CO) stretching frequency than **2** or **8**−**12** are in general consistent with the Hammett parameters for the types of substituents found in these ligands (see Table 2[35]). Considering, for example, **1** and **11** with the assumption that the crown ether substituents are similar to NMe$_2$ and OMe, the considerable difference in the Hammett parameters values, −0.63 and −0.28, is consistent with the observation that the v(CO) value for the former phosphine is ca. 2.5 cm^{-1} lower than the latter, indicating that **1** is the better donor. Further, a $\Delta E-\Delta C$ analysis[32,36] of **1** and **11** provides calculated stretching frequencies of 2066.1 and 2068.2 cm^{-1}, respectively, values that are also consistent with those observed. But, the latter value does not include a correction for the meta-positioned −CH$_2$OR groups which could be, as indicated by the Hammett parameters, electron-withdrawing groups. However, a correction factor for this effect can

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[23] Serron, S.; Nolan, S. P. *Organometallics* **1996**, *15*, 4301.

[24] Huang, A.; Marcone, J. E.; Mason, K. L.; Marshall, W. J.; Moloy, K. G.; Serron, S.; Nolan, S. P. *Organometallics* **1997**, *16*, 3377.

[25] Bush, R. C.; Angelici, R. J. *Inorg. Chem.* **1988**, *27*, 681.

[26] Streuli, C. A. *Anal. Chem.* **1959**, *31*, 1652.

[27] Streuli, C. A. *Anal. Chem.* **1960**, *32*, 985.

[28] Woska, D. C.; Bartholomew, J.; Greene, J. E.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* **1993**, *12*, 304.

[29] Woska, D. C.; Wilson, M.; Bartholomew, J.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* **1992**, *11*, 3343.

[30] Panek, J. S.; Prock, A.; Eriks, K.; Giering, W. P. *Organometallics* **1990**, *9*, 2175.

[31] Bodner, G. M.; May, M. P.; McKinney, L. E. *Inorg. Chem.* **1980**, *19*, 1951.

[32] Drago, R. S. *Organometallics* **1995**, *14*, 3408.

[33] Drago, R. S.; Joerg, S. *J. Am. Chem. Soc.* **1996**, *118*, 2654.

[34] Maier, L. *Primary, Secondary and Tertiary Phosphines*; Maier, L., Ed.; John Wiley and Sons: New York, 1972; Vol. 1, pp 1−288.

[35] Exner, O. *Correlation Analysis of Chemical Data*; Plenum Press: New York, 1988.

[36] v(CO) values were calculated using ΔE and ΔC parameters for 4-$C_6H_4NMe_2$ or 4-C_6H_4OMe in conjunction with the following equation from ref 32:

$$\Delta v = [-98.7 \pm 2.9]\Delta E^x + [5.53 \pm 0.70]\Delta C^x + (2071 \pm 1)$$

be estimated from the v(CO) values for **8** and triphenylphosphine. Subtracting the values for triphenylphosphine and **8** provides a difference of 0.2 cm^{-1}, and adding this quantity to the value for **11** provides a new calculated value of 2068.4 cm^{-1}; this correction places both values within 0.5 cm^{-1} of the measured frequencies. The influences exerted by the meta-positioned crown ether groups in **8**−**10** are, however, not simple because the v(CO) values in this series decrease with increasing substitution by crown ether groups. Assuming no other changes, increasing the number of electron-withdrawing groups would be expected to increase, rather than decrease, the v(CO) values. Further, compared to **8** and **9**, **11** and **12** provide values that are lower by ca. 0.1 cm^{-1}. The reported[19] v(CO) values for $Ph_xP(4\text{-}C_6H_4OMe)_{3-x}$ ($x = 2$, 2068.2 cm^{-1}; $x = 0$, 2066.1 cm^{-1}**)** and those determined by a $\Delta E - \Delta C$ analysis incorporating a 0.2 cm^{-1} correction ($x = 2$, 2068.4 cm^{-1}; $x = 0$, 2067.7 cm^{-1}) suggest that the values for **11** and **12** (2068.9 and 2068.7 cm^{-1}, respectively) are ca. 1 cm^{-1} higher than expected. This apparent lack of electron-donating ability by the OMe groups may arise because steric interactions decrease the conjugation of the oxygen lone-pair electrons with the aromatic ring orbitals. Additional insights into the trends and patterns associated with the v(CO) stretching frequencies provided by these ligands should emerge when additional $x = 1$ and 0 examples of these and related phosphine crown ether molecules are synthesized and studied.

Also presented are the v(CO) frequencies obtained after adding solid salts, MSCN, to dichloromethane solutions of the $Ni(CO)_3L$ complexes. For all spectra, the resident "peak picker" was used to determine the peak frequencies. In addition to the A_1 and E bands observed for the samples in the absence of ions, the spectra for all of the complexes with added Na^+ or K^+ ions displayed shoulders on the low-energy sides of the A_1 bands. For example, these appeared at 2060 cm^{-1} for both the Na^+- and K^+-containing samples of **11**. Even though there is uncertainty about the origin of all of the observed spectral features, there are discernible trends in the v(CO) data. First, the shifts observed are in the direction expected, toward longer wavelengths, for an effect caused by crown complexation of ions, which decreases the abilities of the phosphines to donate electrons to the nickel centers. Further, the shifts observed for phosphines with the interannular OCH_3 groups are in general larger than those for the phosphines with a H in the 2-position. This pattern could reflect increased ion binding abilities of the systems with additional oxygen atoms as is known to be the case for the parent crown ethers.[37,38] In addition, as the number of crown ether groups increases, the shift observed increases, a situation that supports the idea that more than one of the crown ether groups is complexing to the ions present. However, the observed shifts do not parallel the well-established relative abilities of the parent crown ethers to bind ions, as established by both extraction and calorimetric methods. For example, calorimetric titration procedures in anhydrous methanol have established the log K values of 2.30, 3.52, and 2.76 for the interactions between Na^+, K^+, and Cs^+, respectively, and the parent crown ether used for **11** and **12**, 2-methoxy-1,3-xylyl-18-crown-5.[38] Clearly, the data presented in Table 1 do not reflect this general trend because Na^+ ion uniformly causes the largest shifts. We have carried out some experiments with LiSCN and $Ca(OAc)_2$, and the preliminary results suggest that the former, but not the latter, can cause significant shifts in the v(CO) bands. For example, the A_1 stretching frequencies for **8**−**10** in the presence of Li^+ ions were observed at 2070.0, 2069.4, and 2070.3 cm^{-1}, respectively. In view of the data from the samples with added Li^+ and Na^+, it is possible that observed shifts in the v(CO) values correlate with the charge-to-radius ratios (polarizing power) of the cations rather than the ion-binding abilities of the crown ether rings. That small, highly charged cations can have significant effects on the physical properties of metal complexes with appended crown ether groups has been demonstrated for both ferrocene (ferrocene/ferrocenium redox couple[39,40]) and [*fac*-(2,2′-bipyridine)(pyridine)Re(CO)$_3$]$^+$ (metal-to-ligand charge-transfer photophysics[41]) functionalized with crown ether groups.

To further establish that the observed shifts in the v(CO) values were the result of complexation of the ions by the crown ether rings, IR spectra of $Ni(CO)_3PPh_3$ samples were recorded in the presence of Na^+ and K^+ ions and the absence and presence of 18-crown-6. In all spectra, the A_1 bands were observed at 2068.9 ± 0.1 cm^{-1}. This outcome along with the previously discussed observations regarding magnitude and direction of the observed shifts provide strong evidence that the observed ion effects are the result of ion complexation by the crown ether rings.

Ligand Steric Properties. The spatial arrangements of the phenyl and crown ether rings are of interest for developing an understanding of both the cone angles of these phosphines and the possibilities for cooperative crown ether effects in the $x = 0$ and 1 molecules. As noted above, the X-ray data from **8**-oxide indicated that the phenyl carbons were disordered, an outcome that rendered those data unreliable for estimating the cone angles for **8** and **11**. However, two additional approaches, the use of CKP models and palladium complexes, have been undertaken to obtain structural information. First, CPK models of **8**−**12** have been constructed and examined. For these, the examination of the models leads to the conclusion that in the absence of ions the cone angles are similar to triphenylphosphine. Further, for **10**, only two of the three crown ether rings could be readily organized into an arrangement consistent with the potential for cooperative behavior between crown-5 units preorganized for ion binding; the cavity formed by the two organized crown groups was estimated to have a diameter of ca. 5 Å.

Phosphines readily form palladium(II) complexes of the stoichiometry L_2PdCl_2, and a linear relationship between the ^{31}P NMR shifts of these complexes and the Tolman cone angles of the phosphines has been dem-

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(37) Newcomb, M.; Moore, S. S.; Cram, D. *J. Am. Chem. Soc.* **1977**, *99*, 6405.

(38) Zanonato, P. L.; Bernardo, P. D.; Cassol, A.; Tomat, G. *Polyhedron* **1987**, *6*, 417.

(39) Beer, P. D.; Chen, Z.; Drew, M. G. B.; Pilgrim, A. J. *Inorg. Chim. Acta* **1994**, *225*, 137.

(40) Beer, P. D. *Adv. Inorg. Chem.* **1992**, *39*, 79.

(41) MacQueen, D. B.; Schanze, K. S. *J. Am. Chem. Soc.* **1991**, *113*, 6108.

Table 3. Experimentally Determined and Calculated ^{31}P Chemical Shifts for L_2PdCl_2 Complexes

	8	9	10	11	12
trans[a]	23.8	24.6	24.6	23.2	22.3
cis[a]	33.6	33.9	34.1	32.7	32.0
trans[b]	23.3	23.7	23.9	22.8	22.3
cis[b]	34.7	35.1	35.4	34.1	34.5

[a] Measured values recorded in $CDCl_3$, referenced to H_3PO_4. [b] Calculated values.

Table 4. Crystallographic Data for the Oxide of 8

formula	$C_{36}H_{25}O_4P\cdot C_xH_yO_z$
space group	$C2/m$
cell dimens, Å, at −170 °C	$a = 22.639(8)$
	$b = 14.425(5)$
	$c = 9.268(3)$
β, deg	111.08(2)
vol., Å^3	2824.15
λ, Å	0.710 69
calcd density, g/cm^3	1.300
Z, molecules/cell	4
μ, cm^{-1}	1.312
max and min 2θ, deg	6−45
no. of unique reflns colld	4675
no. of unique intensities	1932
$R(F)^a$	0.0622
$R_W(F)^b$	0.0525
GOF	1.195

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

onstrated.[21,22] In accord, the phosphines have been reacted with $(PhCN)_2PdCl_2$ and the spectra recorded in situ; the data are summarized in Table 3. As summarized, the trans complexes all provided chemical shifts in the range of 20−25 ppm, values that are consistent with cone angles of ca. 145°.[21,22] There is also an empirical mathematical relationship between the ^{31}P chemical shifts of free ligands and their corresponding trans and cis L_2PdCl_2 complexes.[42] In this relationship, $\Delta = A\delta + B$, Δ is the shift in ppm of the ^{31}P signal of a given isomer from the shift of the free ligand, δ is the chemical shift of the free ligand, and A and B are constants. For the trans and cis isomers, $A = -0.304$ and $B = 26.8$ and $A = -0.212$ and $B = 38.6$, respectively. As shown in Table 3, there is also a good match between the observed and calculated values; this is considered to be another indication that **8**−**12** have cone angles that support the formation of typical palladium(II) complexes. Finally, the conclusion that the cone angles of these ligands are modest is supported by the fact that the sterically unfavored cis isomers were detected for the complexes of **8**−**12**. Only estimates of the relative amounts of trans and cis isomers can be obtained from the ^{31}P NMR experiments carried out. However, $(\mathbf{10})_2$-$PdCl_2$ was found to consist of ca. 30% of the cis isomer, and this ratio did not change upon addition of free ligand.

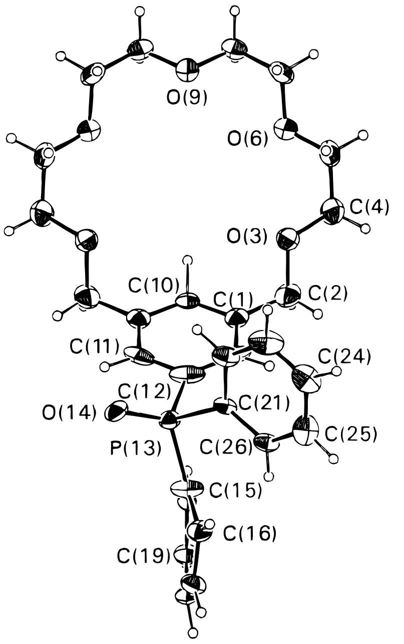

Figure 1. Molecular structure of the oxide of **8**.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for the Oxide of 8

C(1)−C(2)	1.495(3)	O(6)−C(7)	1.425(6)
C(2)−O(3)	1.423(6)	C(7)−C(8)	1.490(3)
O(3)−C(4)	1.415(3)	C(8)−O(9)	1.418(3)
C(4)−C(5)	1.488(8)	C(1)−C(10)	1.396(3)
C(5)−O(6)	1.412(3)	C(1)−C(11)	1.406(6)
C(1)−C(2)−O(3)	107.0(3)	C(7)−C(8)−O(9)	107.8(3)
O(3)−C(4)−C(5)	108.7(3)	C(1)−C(10)−C(1)	122.3(4)
C(4)−C(5)−O(6)	110.2(4)	C(1)−C(11)−C(12)	120.85(26)
O(6)−C(7)−C(8)	109.4(4)		

X-ray Structure. The molecular structure of **8**-oxide is shown in Figure 1, and selected bond distances and angles are presented in Table 5. Even though the phenyl rings were found to be disordered, the outcome clearly supports the general connectivity pattern proposed for **8**−**12**. As shown in Figure 1, a prominent feature of the structure is that the crown ether ring is folded toward a face of the phenyl ring to which it is attached. The angle between the phenyl ring and the mean plane defined by the oxygen atoms is 38.4°. This crown-to-phenyl ring geometric relationship is similar to that found in 1,3-xylyl-18-crown-5 for which this plane angle is 20.6°.[43]

As summarized in Table 5, the bond lengths and bond angles in the crown ether portion of the molecule are unremarkable, with mean ring C−C distances of 1.489(7) Å, C−O distances ranging between 1.412(3) and 1.425 Å, and C−O−C angles ranging between 111.4(3)° and 112.4(3)°. These molecular dimensions are comparable to those reported for other 1,3-xylyl-based crown ethers.[43−47] Further, the crown ether ring is characterized by the expected gauche and anti arrangements. Specifically, the torsion angles for the C−C bonds are 68.0° and −71.1° for O(3)−C(4)−C(5)−O(6) and O(6)−C(7)−C(8)−O(9), respectively, values that reflect approximately gauche arrangements. In contrast, the C(2)−O(3)−C(4)−C(5), C(4)−C(5)−O(6)−C(7), C(5)−

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(42) Verstuyft, A. W.; Nelson, J. H.; Cary, L. W. *Inorg. Nucl. Chem. Lett.* **1976**, *12*, 53.

(43) Smeets, W. J. J.; Spek, A. L.; Markies, P. R.; Akkerman, O. S.; Bickelhaupt, F. *Acta Crystallogr., Sect. C* **1989**, *45*, 443.

(44) Browne, C. M.; Ferguson, G.; McKervey, M. A.; Mulholland, D. L.; O'Conner, T.; Parvez, M. *J. Am. Chem. Soc.* **1985**, *107*, 2703.

(45) Skowronska-Ptasinska, M.; Aarts, V. M. L. J.; Egberink, R. J. M.; van Eerden, J.; Harkema, S.; Reinhoudt, D. N. *J. Org. Chem.* **1988**, *53*, 5484.

(46) Reinhoudt, D. N.; den Hertog, H. J., Jr.; de Jong, F. *Tetrahedron Lett.* **1981**, *22*, 2513.

(47) Weber, E.; Toner, J. L.; Goldberg, I.; Vögtle, F.; Laidler, D.; Stoddard, J. F.; Bartsch, R. A.; Liotta, C. L. *Crown Ethers and Analogues*; John Wiley and Sons: New York, 1989; Chapter 7.

O(6)−C(7)−C(8) and C(7)−C(8)−O(9)−C(8) angles are 178.8°, −179.5°, −179.8°, and 179.8°, respectively, reflecting anti arrangements. This outcome is in contrast to that found for 5-*R*-2-hydroxy-1,3xylyl-18-crown-5 derivatives in which anti and eclipsed O−C−C−O arrangements (R = H) as well as essentially gauche C−O−C−C and C−C−O−C bonds (R = NO_2) are observed, presumably the result of intramolecular hydrogen bonding involving the phenolic hydrogen.[44] The regular gauche and anti relationships observed in **8**-oxide along with the presence of a through-ring mirror plane are also reflected by the across-the-ring distances that are as follows: C(2)−C(2) 4.99 Å, O(3)−O(3) 5.01 Å, C(4)−C(4) 7.22 Å, C(5)−C(5) 7.120 Å, O(6)−O(6) 4.90 Å, and C(7)−C(7) 4.90 Å.

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Supporting Information Available: Tables of atomic coordinates, anisotropic thermal parameters, bond distances, and bond angles for **8**-oxide (11 pages). Ordering information is given on any current masthead page.

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