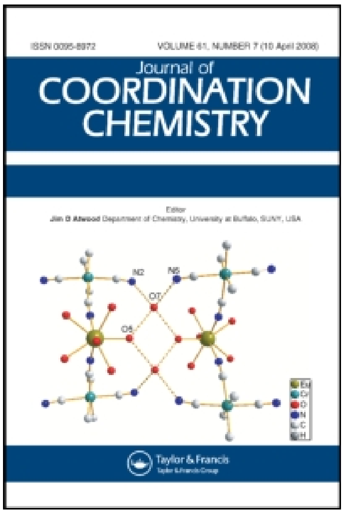

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

HYBRID PHOSPHINE-CROWN ETHER LIGANDS: THE STUDY OF BENZO-15-CROWN-5 AND N-PHENYLAZA-15-CROWN-5 AND -18-CROWN-6 FUNCTIONALIZED WITH Ph_2P-

Brian S. Muehl[a]; Bing-Jahn Sheu[a]; Scot A. Burns[a]; James E. Fritz[a]; David A. Tribbett[a]; Jeremy A. Weitgenant[a]; Bruce N. Storhoff[a]; John C. Huffman[b]
[a] Department of Chemistry, Ball State University, Muncie, IN, USA [b] Molecular Structure Center, Department of Chemistry, Indiana University, Bloomington, IN, USA

To cite this Article Muehl, Brian S. , Sheu, Bing-Jahn , Burns, Scot A. , Fritz, James E. , Tribbett, David A. , Weitgenant, Jeremy A. , Storhoff, Bruce N. and Huffman, John C.(1995) 'HYBRID PHOSPHINE-CROWN ETHER LIGANDS: THE STUDY OF BENZO-15-CROWN-5 AND N-PHENYLAZA-15-CROWN-5 AND -18-CROWN-6 FUNCTIONALIZED WITH Ph_2P-', Journal of Coordination Chemistry, 35: 3, 359 — 370
To link to this Article: DOI: 10.1080/00958979508024048
URL: http://dx.doi.org/10.1080/00958979508024048

J. Coord. Chem., 1995, Vol 35, pp. 359–370
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HYBRID PHOSPHINE-CROWN ETHER LIGANDS: THE STUDY OF BENZO-15-CROWN-5 AND N-PHENYLAZA-15-CROWN-5 AND -18-CROWN-6 FUNCTIONALIZED WITH Ph_2P-

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JAMES E. FRITZ, DAVID A. TRIBBETT, JEREMY A. WEITGENANT,
BRUCE N. STORHOFF*

Department of Chemistry, Ball State University, Muncie, IN 47306, USA

and JOHN C. HUFFMAN

Molecular Structure Center, Department of Chemistry, Indiana University, Bloomington, IN 47405, USA

(Received October 27, 1994; in final form February 13, 1995)

Methods for the preparation of the 4-diphenylphosphino derivatives of N-phenylaza-15-crown-5 and -18-crown-6 are described. The properties of these systems and the 4'-diphenylphosphino derivative of benzo-15-crown-5 have been examined by way of picrate ion extraction abilities and IR spectra of their $Ni(CO)_3L$ (L = these phosphines) complexes. All three have abilities to extract Na^+ and K^+ that are comparable to benzo-15-crown-5. The IR studies (υ_{CO}, A_1 band) indicate that the azacrown systems have better ability than the benzocrown system to increase the electron density on the nickel center. Further, the addition of alkali metal ions, Na^+ and K^+, to the $Ni(CO)_3L$ solutions results in maximum shifts of *ca* 1.5 cm^{-1} for the former systems and 0.7 cm^{-1} for the latter system. A rationale for this observation is presented in terms of Hammett substituent constants. Finally, an X-ray structure of the phosphine oxide of the phenylaza-15-crown-5 derivative is presented. A prominent feature of the structure is that the nitrogen atom is essentially planar with the result that the crown ether ring is large and not preorganized for coordination of spherical ions.

KEYWORDS: crown ether, macrocycle, phosphine ligands, nickel tetracarbonyl

INTRODUCTION

In 1978 Shaw and coworkers reported a series of hybrid phosphine-crown ligands of the general type *A* shown in Figure 1.[1a] Since that report, several additional phosphine-crown systems have been reported including types *B* and *C*. Ligands of type *B* in conjunction with RhCl(1,5-COD) or $[\eta^3C_3H_5PdCl]_2$ have been studied as catalysts in benzene/water mixtures for the hydrogenation of alkali metal cinnamates.[1b] Results from initial hydrogen-uptake rate studies of the Rh(I) systems

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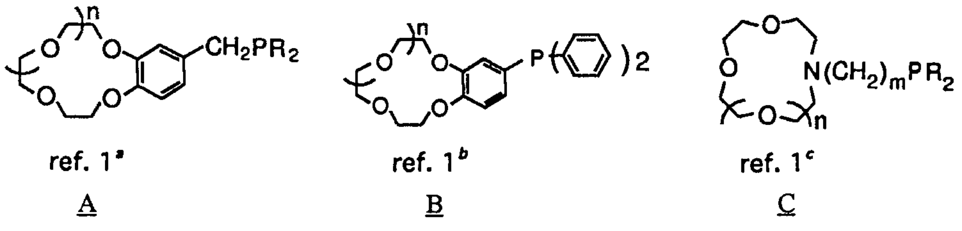
*Author for correspondence.



ref. 1[a] A ref. 1[b] B ref. 1[c] C

Figure 1 Three types of previously reported phosphine-crown ligands.

indicated that the catalysts were up to 50 times more active than catalysts prepared from the same metal complex, PPh_3, and added 18-crown-6. However, the lack of a correlation between crown ring size and the alkali metal ion radius leads to the conclusion that the process was limited by the rate of cinnamate ion transfer from the aqueous to the nonaqueous phase.

Type *C* ligands are the subject of a patent that targets the ability of these ligands to function in conjunction with Co(I) or Rh(I) to promote the hydroformylation of propene.[1c,d] In particular, the study of the diphenylphosphine ligand with m = 1 and n = 2 indicated that the reaction rate was enhanced by a factor of five when carried out in the presence of $NaPF_6$. This outcome is consistent with the idea that a crown-complexed ion might facilitate a hydroformylation process by enhancing the electrophilicity of carbonyl carbons.

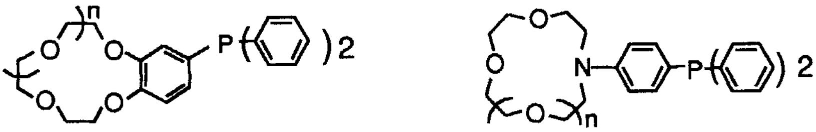
Recently we became interested in how the properties of type *B* ligands compared to those of the azacrown systems shown in Figure 2, with our specific interest being the two crown-5 and the single crown-6 molecules labeled I, II-A and II-B. We questioned, for example, how the donor/acceptor abilities of the phosphorus centers and the cone angles of the two systems, I and II, compared in the presence and absence of crown-complexed guests. Additionally, we questioned to what extent information transfer from the crown, initiated by the complexation of a guest, depended on the nature of the crown-to-phosphorus link and the ion binding abilities of the crown ethers. Herein we report the synthetic methods for crown-5 and crown-6 systems of type II, the structure of the phosphine oxide of the crown-5 system, the results from studies of the phosphorus donor/acceptor abilities and the crown ether ion-binding properties of these systems.

EXPERIMENTAL

Reagents and materials

Tetrabutylammonium tribromide, chlorodiphenylphosphine, picric acid, and n-butyl lithium (2.5 M in hexane) were obtained from Aldrich Chemical Company, Inc. The chlorodiphenylphosphine was distilled prior to use. Nickel carbonyl and potassium tetrachloroplatinate were purchased from Strem Chemicals, Inc. The other reagents and solvents were obtained from departmental supplies. The THF was distilled from sodium benzophenone ketyl prior to use.

4'-(Diphenylphosphino)benzo-15-crown-5 (ligand I)[1b] along with the N-phenylazacrowns (crown-5 and -6)[2] were prepared by the reported methods.



I (crown-5)

II-A (crown-6)

II-B (crown-5)

Figure 2 Phosphine-crown ligands for this study.

Methods and Instruments

Reactions and purifications were carried out under a blanket of argon. IR, NMR and visible region spectra were recorded on Nicolet 5ZDX, Varian Gemini-200, and Hewlett Packard 5193C instruments, respectively. The 5ZDX 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}.[3a] The resident "peak picker" routine was used to determine the peak frequencies. Elemental analyses were carried out by Midwest Microlab Ltd., Indianapolis, IN. The Molecular Structure Center (Indiana University, Bloomington, IN, 47405) carried out the X-ray analysis.

$Ni(CO)_3P(Ph)_2R$ IR studies were carried out as described earlier.[3a-c] Deoxygenated methylene chloride (filtered through a column of activated alumina) was used as the solvent.

Picrate extraction studies were carried out (dichloromethane solvent) as described previously.[4] Benzo-15-crown-5 and 4'-(formyl)benzo-15-crown-5, for which extraction data have been reported,[4b] were used as standards. The values reported in Table 1 were obtained by measuring the absorbance of the dichloromethane layer.

Syntheses

4'-Bromo-N-phenylaza-15-crown-5

N-phenylaza-15-crown-5 (14.05 g, 47.57 mmol) and tetrabutylammonium tribromide (22.94 g, 47.57 mmol) were dissolved in 100 mL of dichloromethane and stirred at ambient conditions for 25 min. During the reaction period the solution became yellow in color. The dichloromethane was washed with 2 x 150 mL of 15% aqueous sodium thiosulfate. The dichloromethane layer was then evaporated to dryness and the resulting oil extracted with 5 x 100 mL of refluxing heptane. Upon cooling, 14.55 g (81.7%) of colorless crystals were obtained.

Table 1 Ion-binding data for the crown ethers, % extracted.

Compound	Na^{+} [a]	K^{+} [a]
II-B	15	28
II-A	14	17
I	18	6

[a] Average from 9 trials, 7.0×10^{-4} molar in crown (CH_2Cl_2), 7×10^{-5} molar picric acid.

4' Bromo-N-phenylaza-18-crown-6

This reaction was carried out as described above for the 15-crown-5 analog. The compound was isolated in 75.5% yield.

Ph_2P-N-phenylaza-18-crown-6, II-A

4'-Bromo-N-phenylaza-18-crown-6 (8.60 g, 20.6 mmol) was dried thoroughly under high vacuum and then dissolved in 160 mL of THF. While under argon, the solution was cooled to -80°C, and n-butyllithium (9.0 mL, 22 mmol) was added *via* syringe over a period of 15 min. The solution was stirred an additional 25 min at this temperature, and chlorodiphenylphosphine (4.41 g, 20.0 mmol) in 30 mL of THF was added over a period of 15 min while maintaining the -80°C. The reaction mixture was warmed to ambient temperature over a period of 3 h. Triethylamine (5.0 mL) and aqueous ammonium chloride (40 mL, 20%) were added in sequence, and the aqueous and nonaqueous layers were separated. The pH of the aqueous layer was adjusted to *ca* 12 with aqueous LiOH, and it was extracted with 3 x 50 mL of dichloromethane. The nonaqueous portions were combined, and the resulting mixture was evaporated to dryness leaving a brown-colored oil. The oil was extracted with 2 x 200 mL portions of boiling heptane. Upon cooling to - 10°C colorless crystals formed that were collected on a filter (6.1 g, 57%). Anal. *Calcd* for $C_{30}H_{38}NO_5P$: C, 68.82%; H, 7.32%; N, 2.68%. Found: C, 68.80%; H, 7.41%, N, 2.78%. Spectroscopic data are presented in Table 2.

Ph_2P-N-phenylaza-15-crown-5, II-B

This compound was prepared and purified by using the methods described above for the crown-6 analog. Spectroscopic data are presented in Table 2. As described below, a Pt(II) complex of this phosphine was prepared by using a standard method,[3d] and this complex was submitted for elemental analysis.

$(II\text{-}B)_2PtCl_2$

Potassium tetrachloroplatinate (0.15 g, 0.36 mmol) was dissolved in 10 mL of 60% aqueous ethanol. II-B (0.40 g 0.83 mmol) was added to the solution, and the mixture was stirred under ambient conditions for 3 h. The solvent was removed *via*

Table 2 P-31 and selected C-13 NMR data[a].

Compound	δP	δC							
		C-16	C-17	C-18	C-19	C-30	C-31	C-32	C-33
II-B[b]	-7.1	148.2 (s)	111.5 (8.2)	135.7 (21.7)	120.5 (3.6)	138.2 (9.3)	133.2 (18.8)	128.2 (9.3)	128.1 (s)
II-A[c]	-7.1	150.0 (s)	113.2 (8.4)	137.0 (21.7)	122.1 (3.5)	139.8 (9.4)	134.5 (18.7)	129.6 (6.2)	129.6 (s)
II-B-oxide[b]	+29.9								
$(II\text{-}B)_2PtCl_2$[b,d]	+12.3								

[a] H_3PO_4 and TMS standards; chemical shifts in ppm, coupling constants, J(PC), in Hz. [b] $CDCl_3$ [c] 50:50 $CDCl_3$-CD_3OD; C-16..C-19 are used to designate the carbons in this phenyl ring with the crown-6 attached even though they would actually be C-19..C-22 if the atom numbering scheme presented in Figure 3 were used. [d] J(PtP) = 3660 Hz.

a rotary evaporator, and the resulting oil was crystalized from a mixture of dichloromethane and 95% ethanol to provide 0.36 g (81%) of colorless crystals. Anal. *Calcd* for $C_{56}H_{68}N_2O_8P_2Cl_2Pt$ $1/8CH_2Cl_2$: C, 54.56%; H, 5.55%; N, 2.27%; Cl, 6.46%. Found: C, 53.97%; H, 5.65%; N, 2.17%; Cl, 6.42%. Spectroscopic data are presented in Table 2.

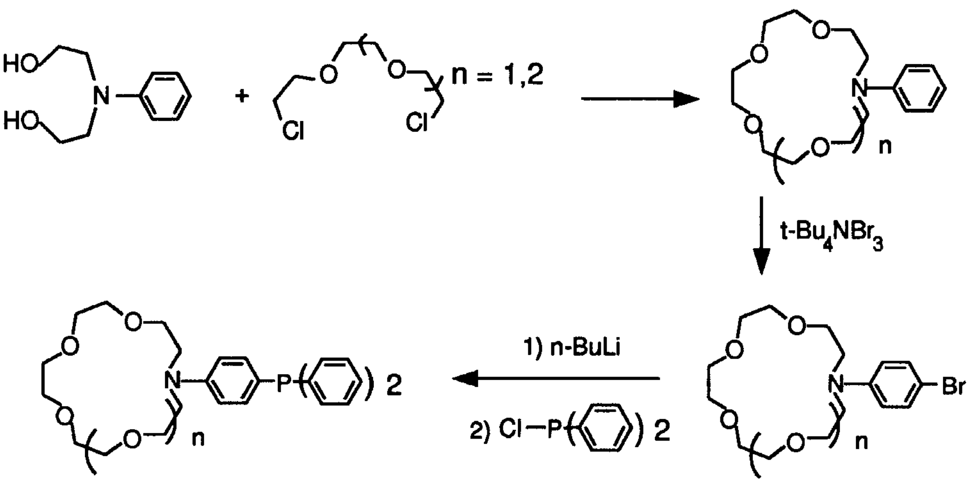
Oxidation of II-B

The phosphine-crown (0.50 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 resulting nonaqueous phase was evaporated to dryness. The oxidized product was crystalized from ethyl acetate to provide the crystal used for the X-ray analysis. Spectroscopic data are presented in Table 2.

RESULTS AND DISCUSSION

Syntheses

Both Ph_2P-N-phenylaza-15-crown-5 and -crown-6 have been prepared in moderate yields *via* the methods summarized in Scheme 1. The Li-Br exchange reaction is particularly facile and readily takes place at temperatures as low as −90 °C. That this is the case is not surprising in view of the fact that Gilman's Color Test 2 which can be used to determine whether a LiR sample contains an alkyl or aryl group makes use of the rapid reaction between 4-bromo-N,N-dimethylaniline and alkyl lithium reagents.[5]



Scheme 1 Synthetic methods for Type II ligands.

X-Ray Structure

Needle-shaped crystals of oxidized II-B were readily obtained by cooling an ethyl acetate solution to − 10°C, and a fragment of one of the needles was analyzed by X-ray methods. Crystallographic data, atomic coordinates, and isotropic thermal parameters are summarized in Tables 3–6. An ORTEP diagram and the atom numbering scheme are shown in Figure 3. The atom numbering scheme reflects the fact that the compound crystallized as a monohydrate with the water oxygen being located 2.89 Å from O(23).

All of the P-C bond angles and distances are in the ranges expected, and all are similar to those reported for $OPPh_3$.[6] As shown in Figure 3, and observed for all related systems, the phenyl rings are in a propeller arrangement.[7] Dunitz has described a method for characterizing to what extent the phenyl rings in $XPPh_3$ species have rotated from a vertical position defined by the P-X bond.[7b] In general, the method involves measuring the torsion angles (φ) from a "dummy" (DU) atom located at the center of a triangle defined by the three ipso carbons. With this convention, larger torsion angles correspond to a greater clockwise rotation around the P-C bond, of the phenyl ring. Torsion angles for the oxide of II-B and $OPPh_3$ were obtained from the X-ray data through the use of the SYBYL[8] calculational package, and the data are presented in Table 7. As summarized, the oxide of II-B provides φ values that are similar to those of $OPPh_3$.

As evident in Figure 3, the nitrogen atom is, as expected, essentially planar. In fact, N-15, C-1, and C-14 are only 0.10, 0.13, and 0.33 Å, respectively, out of the plane defined by the phenyl ring. Previous structural studies of para substituted dialkyl aniline derivatives including the PhS-[9a] and $Me_2P(S)$-[9b] derivatives have also established the planar nature of the nitrogen atoms, and sp^2-C-N bond lengths of *ca* 1.4 Å. The C-N distance of 1.39 Å for the molecule reported here is in agreement with these reported values and indicative of a significant amount of N-C double bond character.

Both crown-cavity diameter and degree of crown-ring preorganization for coordination are factors that influence how effectively a system can complex ions or other guests. In regard to the former, 15-crown-5, for example, is estimated to have a cavity size of 1.7–2.2 Å, a range that matches the 1.9 Å size of Na^+, an ion that is effectively complexes.[10] With an sp^3 hybridized nitrogen atom, a similar cavity size is predicted for II-B. In the solid state however, the presence of the planar

Table 3 Crystal and refinement information.

Formula: $C_{28}H_{36}NO_6P$
Crystal system: monoclinic
Space group: $P2_1/n$
Cell dimensions (Å) at −174 °C: a = 12.718(3),
b = 13.328(4), c = 15.682(5), beta = 94.94(1)
Vol. (Å^3): 2648.31
Calcd density (g/cm^3): 1.288
Z (molecules/cell): 4
Data collection limits; min and max 2-theta (deg): 6–45
No. of reflections collected: 3859
No. of unique intensities: 3460
No. with F_o^2 >2.33 sigma (F_o^2): 2424
Final residuals; R, R_w: 0.0617, 0.0592

Table 4 Coordinates (× 10^4) and isotropic thermal parameters[a] for the oxide of II-B.

Atom	*x*	y	z	Biso
C(1)	2171(4)	2197(4)	4584(3)	22
C(2)	1765(4)	2831(4)	3832(3)	23
O(3)	1147(3)	3608(3)	4176(2)	25
C(4)	950(4)	4436(4)	3625(4)	25
C(5)	176(4)	4257(4)	2868(3)	22
O(6)	683(2)	3764(3)	2202(2)	20
C(7)	-62(4)	3404(4)	1544(3)	21
C(8)	-518(4)	2394(4)	1755(3)	19
O(9)	313(3)	1677(2)	1815(2)	21
C(10)	-35(4)	714(4)	2051(4)	26
C(11)	901(4)	99(4)	2344(4)	28
O(12)	1334(3)	480(3)	3149(2)	27
C(13)	2271(4)	-15(4)	3465(4)	25
C(14)	2603(4)	389(4)	4345(4)	25
N(15)	2932(3)	1436(3)	4376(3)	20
C(16)	3976(4)	1696(4)	4308(3)	17
C(17)	4338(4)	2690(4)	4445(3)	19
C(18)	5393(4)	2927(4)	4421(3)	19
C(19)	6143(4)	2200(4)	4257(3)	17
C(20)	5774(4)	1232(4)	4086(3)	18
C(21)	4723(4)	975(4)	4096(3)	19
P(22)	7530(1)	2453(1)	4247(1)	16
O(23)	8073(2)	1678(2)	3762(2)	19
C(24)	7619(4)	3695(4)	3782(3)	19
C(25)	7306(4)	3796(4)	2915(3)	19
C(26)	7414(4)	4715(4)	2512(3)	22
C(27)	7821(4)	5526(4)	2977(3)	23
C(28)	8122(4)	5432(4)	3843(3)	25
C(29)	8021(4)	4512(4)	4241(3)	21
C(30)	8109(4)	2561(4)	5331(3)	17
C(31)	9181(4)	2333(4)	5487(3)	26
C(32)	9693(4)	2413(4)	6298(3)	27
C(33)	9125(4)	2730(4)	6970(3)	24
C(34)	8071(4)	2958(4)	6828(3)	18
C(35)	7574(4)	2870(4)	6020(3)	18
O(36)	9384(4)	45(4)	4224(3)	63

[a] Estimated standard deviations are given in parentheses. Equivalent isotropic thermal parameters were estimated by using the formula presented by W.C. Hamilton, *Acta Crystallog.* **12,** 609 (1959).

nitrogen atom opens the ring, especially in proximity to that atom. As a result, the O–6 to O–9 distance and O–3 to O–12 distance are 2.88 and 4.48 Å, respectively.

Ion Binding Data

The ion binding data for I and the II series of ligands have been examined by using the two phase (water-dichloromethane) picrate extraction method. Extraction data are presented in Table 1. As shown, all have modest and remarkably similar abilities to extract Na^+ ions into the organic phase. Substitution at the 4' position of benzocrown molecules like I is known to affect the ion binding/extraction abilities of these systems, especially the 15-crown-5 moieties.[11] The measured value of 18% for Na^+ places I between benzo-15-crown-5 and the formyl derivative for which values of 24% and 10%, respectively, have been reported.[4b]

Table 5 Bond distances (Å) for the oxide of II-B.

A	B	Distance
P(22)	O(23)	1.488(3)
P(22)	C(19)	1.796(5)
P(22)	C(24)	1.817(5)
P(22)	C(30)	1.799(5)
O(3)	C(2)	1.434(6)
O(3)	C(4)	1.411(6)
O(6)	C(5)	1.433(6)
O(6)	C(7)	1.423(6)
O(9)	C(8)	1.421(6)
O(9)	C(10)	1.417(6)
O(12)	C(11)	1.426(7)
O(12)	C(13)	1.413(6)
N(15)	C(1)	1.459(7)
N(15)	C(14)	1.456(7)
N(15)	C(16)	1.386(6)
C(1)	C(2)	1.505(7)
C(4)	C(5)	1.495(7)
C(7)	C(8)	1.514(7)
C(10)	C(11)	1.485(8)
C(13)	C(14)	1.507(8)
C(16)	C(17)	1.413(7)
C(16)	C(21)	1.410(7)
C(17)	C(18)	1.383(7)
C(18)	C(19)	1.400(7)
C(19)	C(20)	1.391(7)
C(20)	C(21)	1.382(7)
C(24)	C(25)	1.390(7)
C(24)	C(29)	1.380(7)
C(25)	C(26)	1.390(7)
C(26)	C(27)	1.379(8)
C(27)	C(28)	1.384(7)
C(28)	C(29)	1.385(7)
C(30)	C(31)	1.397(7)
C(30)	C(35)	1.389(7)
C(31)	C(32)	1.382(7)
C(32)	C(33)	1.394(7)
C(33)	C(34)	1.374(7)
C(34)	C(35)	1.371(7)

Donor/Acceptor Properties of the P(III) Centers

The donor/acceptor characteristics of these phosphines have been studied by examining the IR spectra of the corresponding $Ni(CO)_3L$ complexs[3a-b] in the presence and absence of ions. These data, presented in Table 8, lead to the following conclusions. First, in the absence of ions, the series II ligands with υ_{CO} values of 2066.3 are significantly better at increasing the electron density on Ni than ligand I. This is entirely consistent with what is predicted from the Hammett sigma values for OCH_3 (para −0.27, meta +0.12)[2a] and $N(CH_3)_2$ (para −0.83)[12a] if the crown ether ethylene oxy groups are assumed to be similar in effect to methyl substituents. With these Hammett values, I, II-A, and II-B are predicted to have pKa values of *ca* 3, 5 and 5, respectively.[12b,c] We have a preliminary confirmation of this value for I by way of a titration with $HClO_4$ in nitromethane, Streuli's method.[13] For

Table 6 Bond angles (deg) for the oxide of II-B.

A	B	C	Angle
O(23)	P(22)	C(19)	111.96(21)
O(23)	P(22)	C(24)	112.26(21)
O(23)	P(22)	C(30)	111.59(21)
C(19)	P(22)	C(24)	105.65(22)
C(19)	P(22)	C(30)	109.23(22)
C(24)	P(22)	C(30)	105.79(23)
C(2)	O(3)	C(4)	114.1(4)
C(5)	O(6)	C(7)	111.7(4)
C(8)	O(9)	C(10)	112.3(4)
C(11)	O(12)	C(13)	113.3(4)
C(1)	N(15)	C(14)	118.7(4)
C(1)	N(15)	C(16)	120.1(4)
C(14)	N(15)	C(16)	120.8(4)
N(15)	C(1)	C(2)	113.9(4)
O(3)	C(2)	C(1)	105.8(4)
O(3)	C(4)	C(5)	115.5(5)
O(6)	C(5)	C(4)	110.2(4)
O(6)	C(7)	C(8)	112.6(4)
O(9)	C(8)	C(7)	108.4(4)
O(9)	C(10)	C(11)	108.7(4)
O(12)	C(11)	C(10)	108.4(5)
O(12)	C(13)	C(14)	108.5(5)
N(15)	C(14)	C(13)	115.4(5)
N(15)	C(16)	C(17)	121.6(4)
N(15)	C(16)	C(21)	121.1(4)
C(17)	C(16)	C(21)	117.3(4)
C(16)	C(17)	C(18)	121.0(5)
C(17)	C(18)	C(19)	121.7(5)
P(22)	C(19)	C(18)	123.8(4)
P(22)	C(19)	C(20)	119.2(4)
C(18)	C(19)	C(20)	117.0(5)
C(19)	C(20)	C(21)	122.6(5)
C(16)	C(21)	C(20)	120.4(5)
P(22)	C(24)	C(25)	117.3(4)
P(22)	C(24)	C(29)	122.9(4)
C(25)	C(24)	C(29)	119.7(5)
C(24)	C(25)	C(26)	119.9(5)
C(25)	C(26)	C(27)	119.9(5)
C(26)	C(27)	C(28)	120.5(5)
C(27)	C(28)	C(29)	119.5(5)
C(24)	C(29)	C(28)	120.5(5)
P(22)	C(30)	C(31)	117.5(4)
P(22)	C(30)	C(35)	124.8(4)
C(31)	C(30)	C(35)	117.7(4)
C(30)	C(31)	C(32)	121.3(5)
C(31)	C(32)	C(33)	119.0(5)
C(32)	C(33)	C(34)	120.4(5)
C(33)	C(34)	C(35)	119.8(5)
C(30)	C(35)	C(34)	121.8(5)

comparison, it is noted that the pKa value for PPh_3 is 2.83.[13] A second result from the υ_{CO} data is that the crown-5 systems and crown-6 system respond to a greater extent to Na^+ and K^+ ions, respectively. Further, II-B and II-A with υ_{CO} shifts of 1.5 cm^{-1} (Na^+) and 1.4 cm^{-1} (K^+), respectively, are shifted or "tuned" to a greater

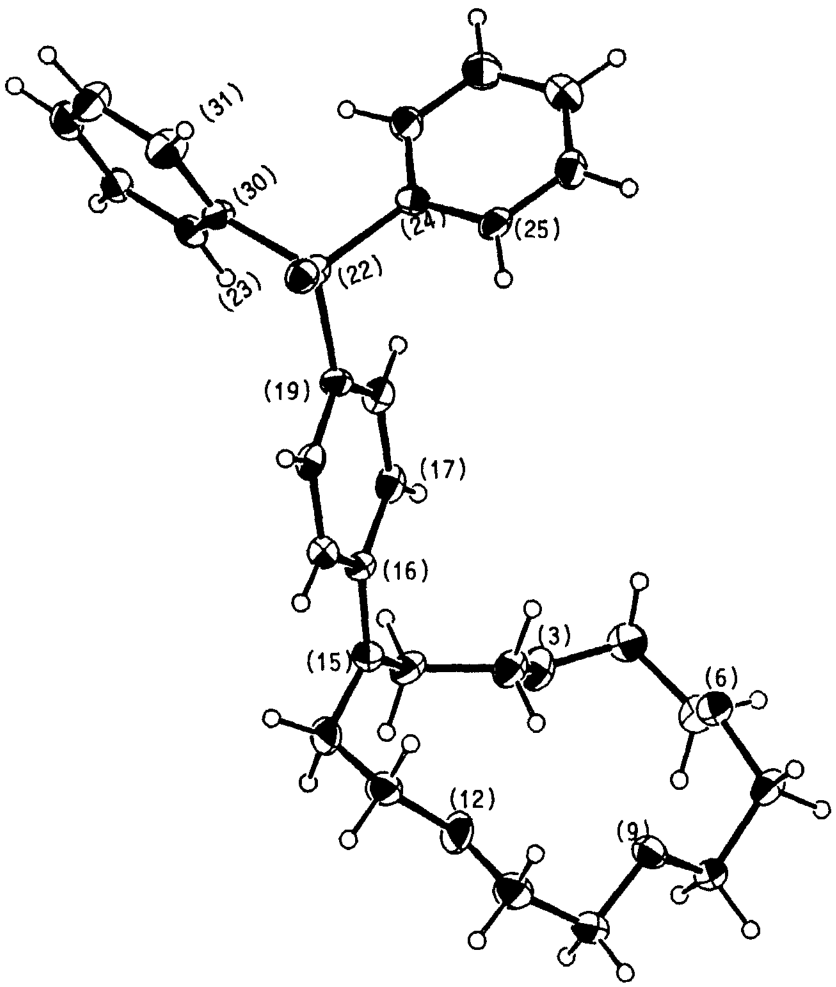


Figure 3 ORTEP Diagram and atom numbering scheme for the oxide of II-B.

extent than I for which the maximum observed shift is 0.7 cm^{-1}. In ligands where the crown ether groups are orbitally coupled to the P(III) atoms, it is possible that the degree to which the P(III) centers can be "tuned" by addition of ions is a function of the overall donor/acceptor abilities of the free ligands compared to

Table 7 Phenyl ring torsion angles.

Compound	Torsion Angles, Degrees		
	φ_1	φ_2	φ_3
$OPPh_3$	58.8	24.4	22.5
O-II-B	53.8	18.3	30.2

Table 8 Ni(CO)$_3$L υ_{CO} studies[a]

Compound	None	Ions Li$^+$	Na$^+$	K$^+$	Cs$^+$
II-B	2066.3	2066.9	2067.8	2066.2	—
II-A	2066.3	—	2066.4	2067.7	2066.3
I	2068.3	2069.4	2069.0	2068.5	2068.5
PPh$_3$	2068.9	—	2068.9	2068.8	—

[a] cm^{-1}, CH$_2$Cl$_2$, excess of MOAc or MSCN.

PPh$_3$. In other words, the larger the pKa (larger sigma effect at P(III)) the larger the possible effect by added ions.

It is also possible that the shifts observed in the υ_{CO} bands upon addition of the salts were the result of effects other than complexation by the crown ether rings. In order to gain insight into these possibilities, IR spectra were recorded of Ni(CO)$_3$PPh$_3$ solutions in the absence and presence of added 18-crown-6 and K$^+$ ions. The observed bands were all within 0.1 cm^{-1}, and it is concluded that the observed shifts were the result of complexation by the crown ether portions of the ligands. In addition it is noted that the shifts observed indicate that the addition of ions reduces the ability of the P(III) centers to donate electrons to the nickel center. It is proposed that this is the effect expected if the crown ether rings complexed a positive ion. Finally, it is noted that the addition of *ca* 5 equivalents of HCl in ether to Ni(CO)$_3$II-B shifts the υ_{CO} band to 2071.5 cm^{-1}.

Acknowledgement

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society along with the Ball State University Faculty Grants Program and the Honors College for support of this Research.

References

1. (a) E.M. Hyde, B.L. Shaw and I. Shepherd, *J. Chem. Soc. Dalton Trans.*, 1696 (1978). (b) T. Okano, M. Iwahara, H. Konishi, and J. Kiji, *J. Organometal. Chem.*, **346**, 267 (1988). (c) S.J. McLain and F.J. Waller, U.S. Patent, 4, 432, 904 (1984). (d) S.J. McLain, *Inorg. Chem.*, **25**, 3124 (1986).
2. J.P. Dix and F. Vögtle, *Chem. Ber.*, **113**, 457 (1980).
3. (a) C.A. Tolman, *J. Am. Chem. Soc.*, **92**, 2953 (1970). (b) C.A. Tolman, *Chem Rev.*, **77**, 313 (1977). (c) G.K. McEwen, C.J. Rix, M.F. Traynor and J.G. Verkade, *Inorg. Chem.* **13**, 2800 (1974) (d) D.M. Roundhill, *Comprehensive Coordination Chemistry*, G. Wilkinson ed. (Pergamon Press, New York, 1987) vol. 5, p. 445.
4. (a) G.J. Pedersen and H.K. Frensdorff, *Angew. Chem. Internat. Edition*, **11**, 16 (1972). (b) A.H. Haines, I. Hodgkisson, and C. Smith, *J. Chem. Soc. Perkin Trans. I*, 311 (1983).
5. H. Gilman and J. Swiss, *J. Am. Chem. Soc.*, **62**, 1847 (1940).
6. G. Bandoli, G. Bortolozzo, D.A. Clemente, U. Croatto and C. Panattoni, *J. Chem. Soc. (A)*, 2778 (1970).
7. (a) J.C. Lockhart, *J. Chem. Soc., Faraday Tans.*, **82**, 1161 (1986). (b) E. Bye, W.B. Schweizer and J.D. Dunitz, *J. Am. Chem. Soc.*, **104**, 5893 (1982).
8. The SYBYL Program set was obtained from TRIPOS associates, St. Louis, MO, USA.

9. (a) G. Bandoli, D.A. Clemente, E. Tondello and A. Dondoni, *J. Chem. Soc. Perkin II,* 157 (1974). (b) V.V. Tkachev, L.O. Atovmyan, A.A. Shvets and O.A. Osipou, *Zh. Strukt. Khim.,* **25,** 161 (1984).
10. C.L. Liotta, *Crown Ethers and Analogs.* E. Weber, J.L. Toner, I. Goldberg, F. Vögtle, D.A. Laidler, J.F. Stoddart, R.A. Bartsch and C.L. Liotta, eds. (John Wiley and Sons, N.Y., 1989) Chapter 2.
11. (a) R. Ungaro, B. El Haj and J. Smid, *J. Am. Chem. Soc.,* **98,** 5198 (1976) (b) S.S. Moore, T.L. Tarnowski, M. Newcomb and D.J. Cram, *J. Am. Chem. Soc.,* **99,** 6398 (1977). (c) F. Vögtle and E. Weber, *Crown Ether and Analogs,* E. Weber, J.L. Toner, I. Goldberg, F. Vögtle, D.A. Laidler, J.F. Stoddart, R.A. Bartsch and C.L. Liotta, eds. (John Wiley and Sons, N.Y., 1989) Chapter 4.
12. (a) R.A.Y. Jones, *Physical and Mechanistic Organic Chemistry,* 2nd ed., (Cambridge Press, N.Y. 1984) p. 39. (b) M.I. Kabachnik and G.A. Balueva, *Izv. Acad. Nauk,* 536 (1962).
13. (a) C.A. Streuli, *Anal. Chem.,* **31,** 1652 (1959). (b) C.A. Streuli, *Anal. Chem.,* **32,** 985 (1960). (c) L. Maier, *Organic Phosphorus Compounds,* G.M. Kosolapoff and L. Maier, eds., (John Wiley and Sons, N.Y., 1972) Vol. I, p. 78.