6614 *Inorg. Chem.* **1996,** *35,* 6614−6621

Ion-Bearing Propellers: Alkali Metal Complexes of Tris(2-alkoxyphenyl)amine Ionophores

Scott J. Stoudt,*,† Prakash Gopalan,‡ Alexei Bakulin,‡ Bart Kahr,*,‡ and James E. Jackson*,†

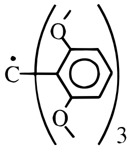
Department of Chemistry and Center for Fundamental Materials Research, Michigan State University,
East Lansing, Michigan 48824-1322, and Department of Chemistry, Purdue University,
West Lafayette, Indiana 47907-1393

Received August 24, 1995[⊗]

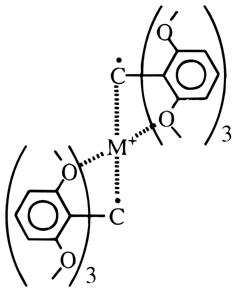
NMR spectroscopic studies reveal that binding of Na^+ by tris(2-methoxyphenyl)amine (**3**) brings two of these tripod ethers together about the metal ion; the related double-tripod-ether ionophore 1,2-bis[2-(bis(2-methoxyphenyl)amino)phenoxy]ethane (**4**), in which two triarylamines are covalently attached, binds LiI, $LiBPh_4$, NaI, $NaBPh_4$, and KB(4-ClPh)$_4$. Dynamic NMR puts lower limits on binding free energies of **4** for Na^+ (71.8 kJ mol^{-1}) and K^+ (66.8 kJ mol^{-1}) ions. X-ray studies of $\mathbf{3}_2\cdot NaBPh_4$, $\mathbf{4}\cdot NaBPh_4$, $\mathbf{4}\cdot$NaB(4-ClPh)$_4$, and $\mathbf{4}\cdot$KB(4-ClPh)$_4\cdot CH_3NO_2$ show eight-coordinate M^+ ions bound between crystallographically independent, homochiral triarylamine tripod ethers in structures reminiscent of alkali metal [2.2.2] cryptates. Complexes crystallize as follows: $\mathbf{3}_2\cdot NaBPh_4$, monoclinic, $P2_1/c$, $Z = 4$, $a = 10.701(3)$ Å, $b = 37.593(3)$ Å, $c = 13.774(2)$ Å, and $\beta = 98.24(2)°$; $\mathbf{4}\cdot NaBPh_4$, triclinic, $P\bar{1}$, $Z = 2$, $a = 12.157(1)$ Å, $b = 14.811(1)$ Å, $c = 15.860(2)$ Å, $\alpha = 105.400(8)°$, $\beta = 91.594(9)°$, and $\gamma = 95.354(8)°$; $\mathbf{4}\cdot$NaB(4-ClPh)$_4$, monoclinic, $P2_1/n$, $Z = 4$, $a = 13.652(5)$ Å, $b = 18.75(1)$ Å, $c = 22.805(5)$ Å, and $\beta = 92.21(5)°$; $\mathbf{4}\cdot$KB(4-ClPh)$_4\cdot CH_3NO_2$, monoclinic, Pn, $Z = 2$, $a = 13.663(4)$ Å, $b = 12.228(3)$ Å, $c = 18.712(8)$ Å, and $\beta = 91.45(3)°$. They show variable N−M−N angles; $\mathbf{3}_2\cdot NaBPh_4$ is surprisingly bent (∠N−Na−N = 154.5°), while the $\mathbf{4}\cdot M^+$ complexes are normal: nearly linear for Na^+ (∠N−Na−N = 178.6, 178.1°) and again bent with the larger K^+ (∠N−K−N = 164.5°). Finally, free **4** is structurally similar to **3**; it crystallizes in the triclinic space group $P\bar{1}$, with $Z = 2$, $a = 8.068(1)$ Å, $b = 14.599(2)$ Å, $c = 16.475(3)$ Å, $\alpha = 115.43(1)°$, $\beta = 92.51(1)°$, and $\gamma = 90.40(1)°$.

Introduction

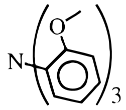
Metal ion complexation by tripod ethers[1] is a new motif for self-assembly of molecular systems.[2] Work from these laboratories has probed the structural,[3] dynamic,[4] and electronic[5] characteristics of tripod ethers and their complexes. Our approach to organic molecular magnetic materials rests on the abilities of paramagnetic tripod ethers (e.g. **1**) to self-assemble by ion binding as in **2**, putting the unpaired electrons into magnetic communication in extended chains. This self-assembly strategy has necessitated a detailed investigation of the ion-binding properties achievable within the tripod ether framework. Here we report NMR and X-ray structural studies of ion binding by tripod ether systems using stable, diamagnetic analogues of **1**.



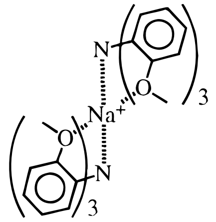
1
$\{C_{25}H_{27}O_6\}$



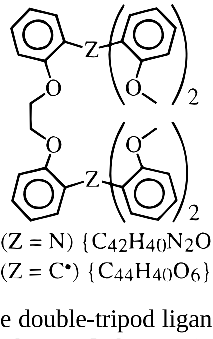
2
$\{C_{50}H_{54}O_{12}M^+\}$



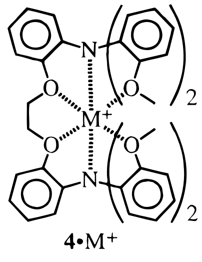
3
$\{C_{21}H_{21}NO_3\}$



$\mathbf{3}_2\cdot Na^+$
$\{C_{42}H_{42}N_2O_6Na^+\}$



4 (Z = N) $\{C_{42}H_{40}N_2O_6\}$
5 (Z = C•) $\{C_{44}H_{40}O_6\}$



$\mathbf{4}\cdot M^+$
$\{C_{42}H_{40}N_2O_6M^+\}$

Tris(2-methoxyphenyl)amine (**3**) is a useful diamagnetic model for **1**; it can offer only one tripod binding site, precluding chain formation, and it crystallizes in a C_3 geometry, placing the three methoxy groups on one face of the propeller.[6] Complex $\mathbf{3}_2\cdot Na^+$ then mimics a radical−metal−radical subunit of **2**. In the double-tripod ligand 1,2-bis[2-(bis(2-methoxyphenyl)amino)phenoxy]ethane (**4**), covalent linkage of two mol-

---

† Michigan State University.

‡ Purdue University.

⊗ Abstract published in *Advance ACS Abstracts*, October 1, 1996.

(1) By analogy to the crown ethers, we propose the name "tripod ether" for the propeller-like tris(*o*-alkoxyaryl)-Z compounds, where Z may be any sp^2 or sp^3 hybridized element.

(2) Jang, S.-H.; Bertsch, R. A.; Jackson, J. E.; Kahr, B. *Mol. Cryst. Liq. Cryst.* **1992**, *211*, 289−303.

(3) Kahr, B.; Jackson, J. E.; Ward, D. L.; Jang, S.-H.; Blount, J. F. *Acta Crystallogr., Sect. B: Struct. Sci.* **1992**, *B48*, 324−329.

(4) Dostal, S.; Stoudt, S. J.; Fanwick, P.; Sereatan, W. F.; Kahr, B.; Jackson, J. E. *Organometallics* **1993**, *12*, 2284−2291.

(5) Jang, S.-H.; Lee, H.-I.; McCracken, J.; Jackson, J. E. *J. Am. Chem. Soc.* **1993**, *115*, 12623−12624.

(6) Müller, E.; Bürgi, H.-B. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1989**, *C45*, 1400−1403. We thank Professor Peter Livant for giving us a sample and prepublication copies of structural data for compound **3** .

S0020-1669(95)01129-3 CCC: $12.00

Table 1. NMR Data for **3**, **4**, and Related Li^+, Na^+, and K^+ Complexes in $CDCl_3$ at 20 °C

species	$\delta(OCH_3)$, ppm	$\delta(OCH_2)$, ppm	$\delta(M^+)$, ppm	k_{ex}, s^{-1}	$\Delta G^{\ddagger}$, kJ mol^{-1}
free ligand **3**	3.54				
3·LiI	4.02		2.11^a	333 (283 K)^b	
3·$LiBPh_4$	3.45		-0.08^a		
$\mathbf{3}_2$·$NaBPh_4$	3.24		-11.9^c		
$\mathbf{3}_2$·$NaB(4\text{-}ClPh)_4$	3.24		-10.3^c		
free ligand **4**	3.51	3.38			
4·2LiI	4.01	4.04	1.85^a		
4·$LiBPh_4$	3.38	3.21	0.15^a		
4·NaI	3.37, 3.06	3.84	*d*	*d*	*d*
4·$NaBPh_4$	3.14, 2.88	3.23, 2.95	-5.5^c	0.96 ± 0.12	71.8 ± 0.3
4·$NaB(4\text{-}ClPh)_4$	3.23, 2.94	3.49, 3.39	-5.3^c	1.02 ± 0.14	71.7 ± 0.3
4·$KB(4\text{-}ClPh)_4$	3.40, 3.13	3.23	7.40 ± 0.40	66.8 ± 0.1	

[a] Referenced to external 0.30 M LiCl in methanol. [b] The coalescence rate constant k_c (coalescence temperature T_c) determined by dynamic NMR; this value is the rate of Li^+ exchange. [c] Referenced to external 3.0 M aqueous NaCl. [d] The low solubility of **4**·NaI in $CDCl_3$ precluded ^{23}Na and dynamic NMR measurements.

ecules of **3** further promotes pairing of tripod sites about a metal cation to form **4**·M^+.

No triarylamine propeller-based complexes have been structurally characterized, to our knowledge. It is by no means obvious that such systems should be effective ligands, with their weakly Lewis basic aromatic amine and ether sites. Vögtle and co-workers have examined related three-armed "open-chain cryptands"[7] and with tris(2-(benzyloxy)phenyl)amine, the closest analogue of **3**, did not obtain crystalline complexes with alkali metal or alkaline earth metal salts.[8] However, the NMR and X-ray studies reported here for **3**, **4**, and related complexes validate the ion-binding strategy for self-assembly of tripod ethers. As detailed below, the ion-binding ability of ligand **4** augurs well for the use of biradical **5** to probe pairwise metal cation-mediated radical–radical coupling.

Results and Discussion

Treatment of $CDCl_3$ solutions of **3** with LiI, $LiBPh_4$, or $NaBPh_4$ in excess leads to stoichiometric uptake of these otherwise insoluble salts, as revealed by ^1H, ^{13}C, and alkali metal (^7Li, ^{23}Na) NMR spectra. Stoichiometries and key NMR data are summarized in Table 1 and the Experimental Section. With LiI and $LiBPh_4$, 1:1 ligand:salt ratios are found; $NaBPh_4$, however, yields *a 2:1 ligand:salt stoichiometry*, our first finding of 2-fold complexation of a metal cation by a tripod ether. No salt uptake is seen in $CDCl_3$ with NaI, KI, $KBPh_4$, $KB(4\text{-}ClPh)_4$, $RbBPh_4$, CsI, or $CsBPh_4$. Analogous studies of **4** show stoichiometric uptake of LiI, $LiBPh_4$, NaI, $NaBPh_4$, and $KB(4\text{-}ClPh)_4$. With LiI, a 1:2 ligand:salt ratio is found; it appears that, as in **3**, one tripod of **4** binds 1 equiv of LiI (vide infra). However, the other salts investigated—$LiBPh_4$, NaI, $NaBPh_4$, and $KB(4\text{-}ClPh)_4$—show 1:1 stoichiometries upon complexation. No complexation of KI, $KBPh_4$, $RbBPh_4$, CsI, or $CsBPh_4$ by ligand **4** was observed in $CDCl_3$.

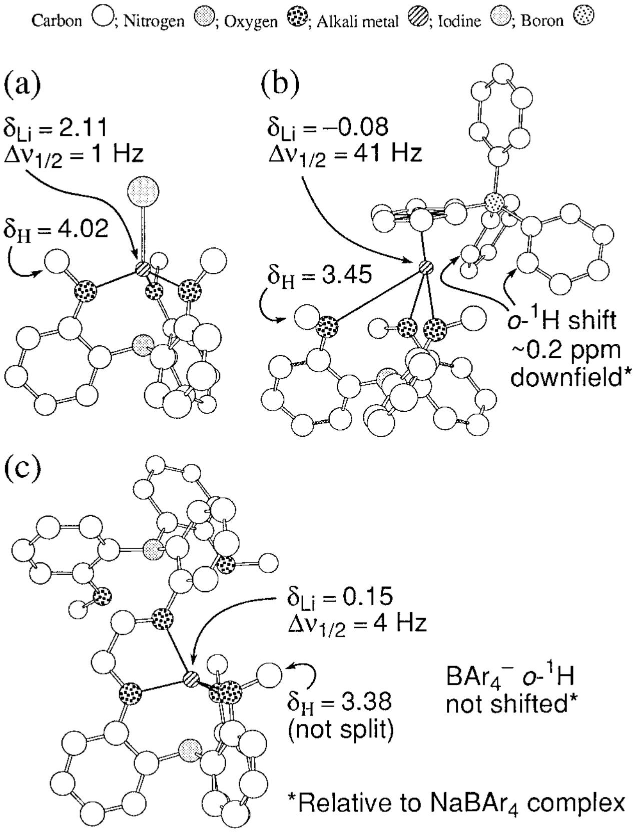


Figure 1. MNDO-calculated structures of Li^+ complexes presented with salient NMR data obtained in $CDCl_3$ solutions: (a) **3**·LiI; (b) **3**·$LiBPh_4$; (c) **4**·Li^+. Hydrogens are omitted for clarity.

Beyond the above simple stoichiometries, solution structures of the complexes may be inferred from detailed analysis of the ^1H, ^{13}C, and alkali metal NMR spectra. For **3**·LiI, time-averaged C_3 symmetric coordination of the Li^+ ion in the ether tripod is indicated by a single methoxy ^1H resonance and seven ^{13}C signals. The narrow ^7Li line width ($\Delta\nu_{1/2} = 1.0$ Hz) suggests a symmetrical environment about Li^+.[9] In a poorly solvating medium like $CDCl_3$, the complex is most likely intimately ion-paired with the I^- counterion,[10] as seen in the recently reported structure of the LiI complex of tris(2-pyridylmethyl)amine;[11] an MNDO-calculated structure of **3**·LiI is presented in Figure 1a. Analogous complexation of 1 equiv of LiI in each tripod moiety of **4** is supported by ^1H, ^{13}C, and ^7Li (δ, $\Delta\nu_{1/2}$) data which are similar to those observed for **3**·LiI. Thus, the methoxy ^1H and ^{13}C shifts for **3** and **4** are nearly identical, both in the free ligands (^1H, 3.54 and 3.51 ppm, respectively; ^{13}C, 55.7 and 55.8 ppm, respectively) and in the

---

(7) (a) Vögtle, F.; Müller, W. M.; Wehner, W.; Buhleier, E. *Angew. Chem.* **1977**, *89*, 564–565; *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 548–549. (b) Vögtle, F.; Müller, W. M.; Buhleier, E.; Wehner, W. *Chem. Ber.* **1979**, *112*, 899–907. (c) Tümmler, B.; Maass, G.; Vögtle, F.; Sieger, H.; Heimann, U.; Weber, E. *J. Am. Chem. Soc.* **1979**, *101*, 2588–2598. For reviews, see: (d) Vögtle, F.; Weber, E. *Angew. Chem.* **1979**, *91*, 813–837; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 753–776. (e) Vogtle, F. *Chimia* **1979**, *33*, 239–251.

(8) Heimann, U.; Herzhoff, M.; Vögtle, F. *Chem. Ber.* **1979**, *112*, 1392–1399.

(9) Green, D. P.; Reich, H. J. *J. Am. Chem. Soc.* **1989**, *111*, 8729–8731.

(10) In acetone, which is a better solvating medium than $CDCl_3$, the ion pair formation constant for LiI is reported to be 145. See: Savedoff, L. G. *J. Am. Chem. Soc.* **1966**, *88*, 664–667.

(11) Brownstein, S. K.; Plouffe, P.-Y.; Bensimon, C.; Tse, J. *Inorg. Chem.* **1994**, *33*, 354–358.

resulting LiI complexes (^{1}H, 4.02 and 4.01 ppm; ^{13}C, 58.3 and 58.3 ppm), while the ^{7}Li shifts are more variant (2.11 and 1.85 ppm).

For **3**·$LiBPh_4$, symmetrical coordination of Li^+ by the three oxygen atoms of the ligand is again suggested by ^{1}H and ^{13}C NMR. However, the methoxy ^{1}H and ^{13}C and the ^{7}Li resonances of this complex are shifted upfield from their counterparts in the spectra of **3**·LiI. Like the latter complex, **3**·$LiBPh_4$ can be envisioned as an intimate ion pair in which the BPh_4^- ion completes the coordination sphere of the tripod-bound Li^+ ion; Figure 1b shows the structure of **3**·$LiBPh_4$ as calculated by MNDO. The upfield chemical shifts above can then be understood as resulting from ring current effects due to the BPh_4^- phenyl groups. This view is strongly supported by two additional findings: the ^{7}Li resonance is much broader for **3**·$LiBPh_4$ than for **3**·LiI ($\Delta\nu_{1/2} = 41$ Hz vs 1 Hz), and the BPh_4^- *ortho* proton signals are shifted roughly 0.2 ppm downfield compared to their chemical shifts for **4**·$LiBPh_4$, **4**·$NaBPh_4$, and $\mathbf{3}_2$·$NaBPh_4$, complexes in which the metal cation is shielded from direct contact with the BPh_4^- counterion (vide infra). Analogous time-averaged interactions between Cs^+ ions and BPh_4^- *ortho* protons have been uncovered by Bauer in ^{133}Cs, ^{1}H HOESY NMR studies of $CsBPh_4$ contact ion pairs in pyridine solution.[12] Unfortunately, our ^{6}Li, ^{1}H HOESY[13] NMR study of **3**·^{6}LiBPh4 in $CDCl_3$ did not reveal any interactions between the complexed Li^+ ion and the BPh_4^- counterion. In related work, however, the ion pair formation constants in 1,2-dichloroethane solution are reported to be 1660 and 7400 M^{-1} for dibenzo-18-crown-6·$LiBPh_4$ and triphenylphosphine oxide·$LiBPh_4$, respectively.[14]

In each of the three Li^+ complexes discussed above, the counterion caps a Li^+ ion bound in an ether tripod. The 1:1 ligand:salt stoichiometry found for complex **4**·$LiBPh_4$ implies a different binding motif, in which the Li^+ ion is sandwiched between the two triether tripods of **4**. Two additional comparisons lend support to this picture: The ^{7}Li line width of **4**·$LiBPh_4$ is narrow ($\Delta\nu_{1/2} = 4$ Hz), indicating a more symmetrical ^{7}Li coordination sphere than that in **3**·$LiBPh_4$; as noted above, the *ortho* protons of the BPh_4^- phenyl rings do not exhibit the downfield shifting seen in **3**·$LiBPh_4$. Thus, the second tripod ether is preferred over the BPh_4^- counterion as a capping ligand when the triarylamine subunits are covalently linked. Consistent with this finding, the ^{7}Li $\Delta\delta$ between **4**·2LiI and **4**·$LiBPh_4$ (+1.70 ppm) is smaller than that between **3**·LiI and **3**·$LiBPh_4$ (+2.19 ppm). The MNDO-calculated structure of **4**·$LiBPh_4$ is shown in Figure 1c.

Although Li^+ displays variable complex stoichiometries, Na^+ is only taken up by *pairs* of tripods. Complexes $\mathbf{3}_2$·$NaBPh_4$ and $\mathbf{3}_2$·NaB(4-ClPh)$_4$ are symmetrical on the NMR time scale, as shown by the simplicity of their ^{1}H and ^{13}C spectra; their methoxy ^{1}H resonances shift upfield relative to that of free ligand, as in the spectra of the complexes of **4** with $NaBPh_4$, NaB(4-ClPh)$_4$, and NaI. For the **4**·Na^+ complexes, the ^{23}Na chemical shifts are independent of the BAr_4^- counterion but are somewhat sensitive to solvent.[15] It is generally observed that ^{23}Na chemical shifts move upfield both with decreased solvent donicity[16] and with lowered Na^+ coordination number by oxygen ligands.[17] Thus, the upfield changes in ^{23}Na chemical shifts from **4**·$NaBPh_4$ and **4**·NaB(4-ClPh)$_4$ to $\mathbf{3}_2$·$NaBPh_4$ and $\mathbf{3}_2$·NaB(4-ClPh)$_4$ and the greater dependence of the latter two on solvent composition[18] imply that **3** is, as expected, the weaker ligand. As will be seen below, X-ray structural data also support these ideas. Competition and extraction experiments also indicate stronger binding of Na^+ by **4** than by **3**. Ligand **4** is competitive with 18-crown-6 for $NaBPh_4$ in dry $CDCl_3$; similarly, a $CDCl_3$ solution of **4** extracts $NaBPh_4$ from D_2O almost quantitatively, as determined by ^{1}H NMR. Unlike **4**, ligand **3** is completely unable to compete with D_2O for $NaBPh_4$. Finally, neither **3** nor **4** is a strong enough ligand to compete with D_2O for LiI and $LiBPh_4$.

For complexes **4**·$NaBPh_4$, **4**·NaB(4-ClPh)$_4$, **4**·NaI, and **4**·KB(4-ClPh)$_4$, the methoxy resonances of **4** split into two equal-intensity peaks; the methylene resonances split into an AB quartet with $NaBPh_4$ and NaB(4-ClPh)$_4$ but only broaden with NaI and KB(4-ClPh)$_4$. These results suggest that Na^+ or K^+ binding locks the triarylamine subunits of **4** into propeller conformations, differentiating the methoxy sites into two sets on the NMR time scale at room temperature. Lower limits on the binding energies of **4** with Na^+ and K^+ were obtained by measuring the rates of methoxy group site exchange (k_{ex}) in **4**·Na^+ and **4**·K^+ using the saturation spin transfer (SST) technique.[19] In $CDCl_3$ at 20 °C, the measured rate constants translate into $\Delta G^{\ddagger}$ values of 71.8 and 66.8 kJ mol^{-1}, respectively (see Table 1). The k_{ex} and $\Delta G^{\ddagger}$ values for complex **4**·Na^+ with BPh_4^- and B(4-ClPh)$_4^-$ counterions are equal within our uncertainties; evidently the site exchange barriers are not differentially affected by these anions. Unfortunately, although the ^{1}H NMR spectrum of **4**·NaI showed the methoxy group splitting characteristic of the other Na^+ complexes, its limited solubility precluded ^{13}C, ^{23}Na, and SST NMR measurements.

In $CDCl_3$ solution, all of the systems discussed here are expected to exist as tight ion pairs.[10,20] However, for the tripod ether complexes of Na^+ and K^+, variations in the counterions have negligible effects on the ^{13}C and ^{23}Na chemical shifts. The ^{13}C spectra for **4**·$NaBPh_4$ and **4**·NaB(4-ClPh)$_4$ show only minuscule differences, as do those for $\mathbf{3}_2$·$NaBPh_4$ and $\mathbf{3}_2$·NaB(4-ClPh)$_4$. As noted above, ^{23}Na spectra of **4**·Na^+ are insensitive to the BAr_4^- counterion, as are the rate constants for methoxy group site exchange. However, the ^{23}Na chemical shifts for the $\mathbf{3}_2$·Na^+ complexes are −11.9 and −10.3 ppm, pointing to ion pairing in these complexes and being consistent with their greater sensitivity to solvent nucleophilicity. Excepting the case

---

(12) Bauer, W. *Magn. Reson. Chem.* **1991**, *29*, 494−499.

(13) (a) Bauer, W.; Schleyer, P. v. R. *Magn. Reson. Chem.* **1988**, *26*, 827−833. (b) Hoffmann, D.; Bauer, W.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1990**, 208−211. (c) Bauer, W.; Lochmann, L. *J. Am. Chem. Soc.* **1992**, *114*, 7482−7489. (d) Hilmersson, G.; Davisson, Ö. *J. Organomet. Chem.* **1995**, *489*, 175−179. (e) Hilmersson, G.; Davisson, Ö. *Organometallics* **1995**, *14*, 912−918.

(14) Gilkerson, W. R.; Jackson, M. D. *J. Am. Chem. Soc.* **1982**, *104*, 1218−1223.

(15) The ^{23}Na chemical shift for 4·$NaBPh_4$ is −5 ppm ($\Delta\nu_{1/2} = 250$ Hz) in $CDCl_3$/acetone-d_6 (7:1, v/v) and −5.9 ppm ($\Delta\nu_{1/2} = 160$ Hz) in $CDCl_3$/acetone-d_6 (1:1, v/v). In the presence of excess $NaBPh_4$, two ^{23}Na signals are observed in $CDCl_3$/acetone-d_6 (7:1, v/v) at −5 ppm (complexed Na^+) and −10 ppm (solvated Na^+). In $CDCl_3$/acetone-d_6 (1:1, v/v), however, only a single, population-averaged signal is observed under these conditions. For comparison, the ^{23}Na chemical shift for 0.03 M $NaBPh_4$ is −10.4 ppm ($\Delta\nu_{1/2} = 76$ Hz) in $CDCl_3$/acetone-d_6 (7:1, v/v) and −7.4 ppm ($\Delta\nu_{1/2} = 14$ Hz) in $CDCl_3$/acetone-d_6 (1:1, v/v).

(16) Erlich, R. H.; Popov, A. I. *J. Am. Chem. Soc.* **1971**, *93*, 5620−5623.

(17) Kintzinger, J. P.; Lehn, J.-M. *J. Am. Chem. Soc.* **1974**, *96*, 3313−3314.

(18) The ^{23}Na chemical shift for 0.03 M 32·$NaBPh_4$ is −8.2 ppm ($\Delta\nu_{1/2} = 107$ Hz) in $CDCl_3$/acetone-d_6 (7:1, v/v) and −7.6 ppm ($\Delta\nu_{1/2} = 14$ Hz) in $CDCl_3$/acetone-d_6 (1:1, v/v). Addition of 1 equiv of $NaBPh_4$ to each of these solutions results in a single, population-averaged signal at −8.4 ppm ($\Delta\nu_{1/2} = 120$ Hz) and at −7.6 ppm ($\Delta\nu_{1/2} = 17$ Hz), respectively.

(19) Dahlquist, F. W.; Longmuir, K. J.; Du Vernet, R. B. *J. Magn. Reson.* **1975**, *17*, 406−410.

(20) In THF, which is a better solvating medium than $CDCl_3$, the ion pair formation constants for $LiBPh_4$ and $NaBPh_4$ at 25 °C are reported to be 1.26×10^4 and 1.23×10^4, respectively. See: Comyn, J.; Dainton, F. S.; Ivin, K. *J. Electrochim. Acta* **1968**, *13*, 1851−1860.

Table 2. Crystallographic Data for **3**$_2$·NaBPh$_4$, **4**·NaBPh$_4$, **4**·NaB(4-ClPh)$_4$, **4**·KB(4-ClPh)$_4$·CH$_3$NO$_2$, and **4**

	3$_2$·NaBPh$_4$	**4**·NaBPh$_4$	**4**·NaB(4-ClPh)$_4$	**4**·KB(4-ClPh)$_4$·CH$_3$NO$_2$	**4**
formula	$C_{66}H_{62}BN_2NaO_6$	$C_{66}H_{60}BN_2NaO_6$	$C_{66}H_{56}BCl_4N_2NaO_6$	$C_{67}H_{59}BCl_4KN_3O_8$	$C_{42}H_{40}N_2O_6$
fw	1013.04	1011.02	1148.80	1225.94	668.80
F(000)	2160	1068	2392	1276	708
space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$	Pn	$P\bar{1}$
crystal system	monoclinic	triclinic	monoclinic	monoclinic	triclinic
Z	4	2	4	2	2
a, Å	10.701(3)	12.157(1)	13.652(5	13.663(4)	8.068(1)
b, Å	37.593(3)	14.811(1)	18.75(1)	12.228(3)	14.599(2)
c, Å	13.774(2)	15.860(2)	22.80(5)	18.712(8)	16.475(3)
α, deg		105.400(8)			115.43(1)
β, deg	98.24(2)	91.594(9)	92.21(5)	91.45(3)	92.51(1)
γ, deg		95.354(8)			90.40(1)
V, Å^3	5483(3)	2737.(1)	5832(10)	3125(3)	1750.1(9)
$D_{c,\ g\ cm^{-3}}$	1.227	1.227	1.308	1.303	1.269
μ(Mo Kα), cm^{-1}	0.79	0.79	2.62	3.10	0.79
$2\theta_{max}$, deg	50.0	55.0	47.4	47.54	55.0
final R[a]	0.056	0.108	0.051	0.055	0.102
final R_w[b]	0.057	0.132	0.056	0.061	0.101

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

Table 3. Selected Distances (Å), Angles (deg), and Torsion Angles (deg) in **3**$_2$·NaBPh$_4$, **4**·NaBPh$_4$, **4**·NaB(4-ClPh)$_4$, **4**·KB(4-ClPh)$_4$·CH$_3$NO$_2$, and **4**

	3$_2$·NaBPh$_4$	**4**·NaBPh$_4$	**4**·NaB(4-ClPh)$_4$	**4**·KB(4-ClPh)$_4$·CH$_3$NO$_2$	**4**
r(N1···N2)	5.25(1)	5.41(1)	5.316(5)	5.82(1)	7.91(1)
r(M−N1)	2.710(6)	2.682(8)	2.677(6)	2.95(1)	
r(M−N2)	2.677(7)	2.726(8)	2.685(6)	2.93(1)	
r(M−O1)	2.543(6)	2.524(8)	2.457(5)	2.654(9)	
r(M−O2)	2.516(6)	2.532(8)	2.428(5)	2.69(1)	
r(M−O3)	2.584(6)	2.490(8)	2.524(5)	2.792(9)	
r(M−O4)	2.521(6)	2.489(8)	2.491(5)	2.712(9)	
r(M−O5)	2.503(6)	2.453(8)	2.466(5)	2.78(1)	
r(M−O6)	2.726(6)	2.458(8)	2.485(5)	2.73(1)	
∠N−M−N	154.5(2)	178.6(3)	178.1(2)	164.5(5)	
τ(O3−C−C−O4)		65.3(9)	62.29(6)	71.23(2)	84(1)
τ(M−N1−C$_N$−C$_{O1}$)[a]	45.9(6)	32.9(5)	33.3(1)	−25.21(1)	−40(1)[b]
τ(M−N1−C$_N$−C$_{O2}$)[a]	28.5(7)	29.4(5)	26.2(1)	−35.11(1)	−53(1)[b]
τ(M−N1−C$_N$−C$_{O3}$)[a]	45.7(6)	48.2(5)	43.6(1)	−52.25(1)	−44(1)[b]
τ(M−N2−C$_N$−C$_{O4}$)[a]	51.0(6)	48.5(5)	50.4(1)	−53.51(1)	47(1)[b]
τ(M−N2−C$_N$−C$_{O5}$)[a]	23.7(7)	33.4(5)	30.0(1)	−33.14(1)	35(1)[b]
τ(M−N2−C$_N$−C$_{O6}$)[a]	44.8(7)	34.2(5)	30.8(1)	−52.19(1)	47(1)[b]

[a] C$_N$ and C$_O$ are the N- and O-linked aryl carbons of interest. [b] For **4**, these values represent torsions relative to the pseudo-3-fold axis of the amine center, defined for each aryl ring as the average of two $\tau(C'_N NC_N C_O)$ angles, where C$_N$ and C$_O$ are the N- and O-linked aryl carbons of interest and C′$_N$ are the two other aryl carbons on the same nitrogen.

of **3**·LiBPh$_4$, evidence for ion interactions is lacking in the ^{1}H and ^{13}C spectra of the tetraarylborate anions, which are essentially unaffected by the nature of the complex cations (i.e.: **3**$_2$·Na$^+$, **4**·Li$^+$, and **4**·Na$^+$ with BPh$_4^-$; **3**$_2$·Na$^+$, **4**·Na$^+$, and **4**·K$^+$ with B(4-ClPh)$_4^-$).

The probes that should be most sensitive to ion pairing are the nuclei that make up the surfaces of groups around the "waist" of the ellipsoidal complex; here an anion can most closely approach the center of positive charge. Indeed, substantial variations are observed in the methoxy and especially the methylene ^{1}H chemical shifts for **4**·NaX (where X = I$^-$, BPh$_4^-$, B(4-ClPh)$_4^-$). However, both 1D NOE and 2D ^{1}H ROESY[21] NMR experiments on **4**·NaBPh$_4$ failed to show interionic NOEs between the BPh$_4^-$ counterion and the **4**·Na$^+$ core.[22] Furthermore, the identical methoxy ^{1}H chemical shift values found for **3**$_2$·NaBPh$_4$ and **3**$_2$·NaB(4-ClPh)$_4$ indicate that such interpretations should be made cautiously.

Crystals of **3**$_2$·NaBPh$_4$, **4**·NaBPh$_4$, **4**·NaB(4-ClPh)$_4$, **4**·KB(4-ClPh)$_4$·CH$_3$NO$_2$, and free **4** have been analyzed by X-ray diffraction. Crystallographic data for these compounds can be found in Table 2, and selected geometrical information is compared in Table 3. Drawings with partial atom-labeling schemes (counterions omitted) for **3**$_2$·NaBPh$_4$, for **4**·NaB(4-ClPh)$_4$ and **4**·KB(4-ClPh)$_4$·CH$_3$NO$_2$, and for **4** are given in Figures 2−4, respectively. Complex **4**·NaBPh$_4$ is not displayed, since its **4**·Na$^+$ core is essentially indistinguishable from that in **4**·NaB(4-ClPh)$_4$.

In **3**$_2$·NaBPh$_4$, the eight-coordinate Na$^+$ ion is sandwiched between two polyether tripods with Na−N distances of 2.677(7) and 2.710(6) Å and six Na−O distances averaging 2.565(6) Å. One Na−O distance is elongated (2.726(6) Å) relative to the other five (2.503(6)−2.583(6) Å; average = 2.533(6) Å), distorting the coordination sphere from an ideal bicapped octahedron. Excluding the long Na−O interaction, these

---

(21) (a) Bothner-By, A. A.; Stephens, R. L.; Lee, J.-M.; Warren, C. D.; Jeanholz, R. W. *J. Am. Chem. Soc.* **1984**, *106*, 811−813. (b) Bax, A.; Davis, D. G. *J. Magn. Reson.* **1985**, *63*, 207−213.

(22) Pochapsky has reported the observation of significant NOEs (1D experiments) in a contact ion pair formed between BH$_4^-$ and the n-Bu$_4$N$^+$ ion in CDCl$_3$ solution. See: (a) Pochapsky, T. C.; Stone, P. M. *J. Am. Chem. Soc.* **1990**, *112*, 6714−6715. (b) Stone, P. M.; Pochapsky, T. C.; Callegari, E. *J. Chem. Soc., Chem. Commun.* **1992**, 178−179. (c) Pochapsky, T. C.; Wang, A.-P.; Stone, P. M. *J. Am. Chem. Soc.* **1993**, *115*, 11084−11091. Furthermore, interionic NOEs have been observed (^{1}H ROESY experiments) for a contact ion pair between BH$_4^-$ and the "benzylquininium" ion in CDCl$_3$ solution: Pochapsky, T. C.; Stone, P. M. *J. Am. Chem. Soc.* **1991**, *113*, 1460−1462. However, our ^{1}H ROESY NMR experiments did not show interionic NOEs between BPh$_4^-$ and the n-Bu$_4$N$^+$ ion in CD$_2$Cl$_2$ solution.

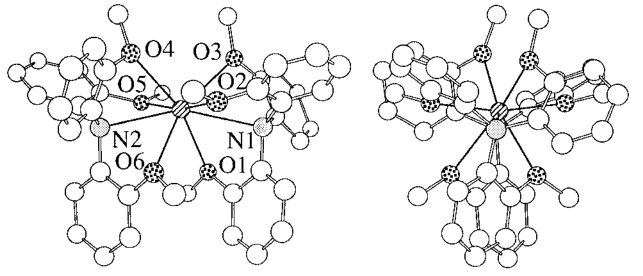


Figure 2. Side and end-on views of the X-ray structure of complex $\mathbf{3}_2$·Na$^+$ (BPh$_4^-$ counterion not shown). See Figure 1 for legend.

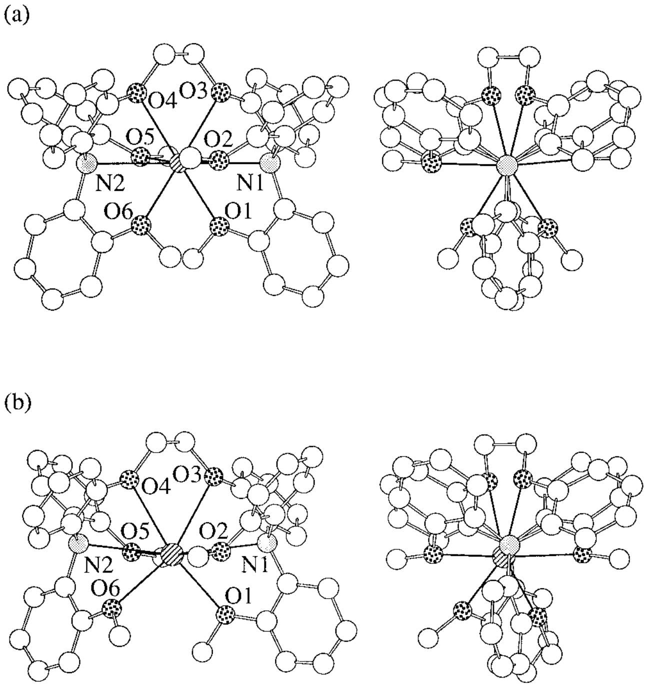


Figure 3. X-ray structures: (a) side and end-on views of **4**·Na$^+$ (B(4-ClPh)$_4^-$ counterion not shown); (b) side and end-on views of **4**·K$^+$(B(4-ClPh)$_4^-$ counterion and CH$_3$NO$_2$ molecule not shown). See Figure 1 for legend.

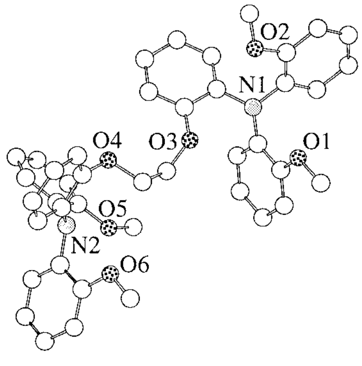


Figure 4. X-ray structure of ligand **4**. See Figure 1 for legend.

distances are comparable to the Na−N (2.682(8) and 2.726(8) Å) and Na−O (2.453(8)−2.524(8) Å; average 2.491(8) Å) lengths found in **4**·NaBPh$_4$, and the Na−N (2.677(6) and 2.685(6) Å) and Na−O (2.428(5)−2.524(5) Å; average 2.475(5) Å) lengths in **4**·NaB(4-ClPh)$_4$. In light of the 3-fold crystallographic axis through the nitrogen atom in free ligand **3**,[6] the nearly linear N−Na−N angles in **4**·NaBPh$_4$ (178.6(3)°) and **4**·NaB(4-ClPh)$_4$ (178.1(2)°), and the NMR data discussed above, the low symmetry and bent (∠N−Na−N = 154.5(2)°) geometry of $\mathbf{3}_2$·NaBPh$_4$ are unexpected. The structures of $\mathbf{3}_2$·NaBPh$_4$, **4**·NaBPh$_4$, and **4**·NaB(4-ClPh)$_4$ are similar in having approximate C_2 symmetry and hence homochiral pitches for the two triarylamine propellers; for **4**·NaBPh$_4$ and **4**·NaB(4-ClPh)$_4$, this geometry is exactly as expected from the solution NMR data described above. The disposition of the basic atoms in $\mathbf{3}_2$·NaBPh$_4$, **4**·NaBPh$_4$, and **4**·NaB(4-ClPh)$_4$ is reminiscent of that seen in [2.2.2] cryptand·Na$^+$ (C222·Na$^+$) structures. For comparison to the above values, the average Na−N and Na−O distances in C222·NaI are 2.75 and 2.57 Å, respectively.[23] The six benzene rings in the tripod ether complexes enforce eclipsed N−C−C−O angles; notably, the analogous torsions in C222·Na$^+$ can be nearly eclipsed,[24] although they are typically skewed.[25]

In contrast to **4**·NaBPh$_4$ and **4**·NaB(4-ClPh)$_4$, the K$^+$ complex of **4** crystallizes as a nitromethane solvate (**4**·KB(4-ClPh)$_4$·CH$_3$NO$_2$) which readily loses solvent on standing. The nitromethane molecule does not appear to interact with the **4**·K$^+$ complex. The eight-coordinate K$^+$ ion is bound between two polyether tripods with K−N distances of 2.93(1) and 2.95(1) Å and six K−O lengths averaging 2.73(1) Å. Relative to the **4**·Na$^+$ complexes, this structure shows an increased O−C−C−O torsion angle (71.23(2)°) and a markedly bent N−K−N angle (164.5(5)°). Such differences are as expected on the basis of the larger size of K$^+$ vs Na$^+$, and hence the longer M$^+$−heteroatom distances in **4**·KB(4-ClPh)$_4$·CH$_3$NO$_2$ compared to those in **4**·NaBPh$_4$ and **4**·NaB(4-ClPh)$_4$. These distances are comparable to the average K−N and K−O lengths of 2.87 and 2.79 Å, respectively, found in C222·KI.[26]

Free ligand **4** may be viewed as two linked molecules of **3** with similar aryl ring twist angles and nitrogen pyramidalization; as in **3**, each propeller's three alkoxy groups are on the same face.[6] Thus, the tripods of **4** represent convergent functionalities poised to encapsulate a suitable guest. Aryl methyl ethers ordinarily prefer a conformation with the methyl group and aryl ring coplanar, as seen for the methoxy groups of **3**,[6] **4**, and related *o*-methoxy-substituted triaryl-Z propellers.[27] In anisole itself, the preference for a coplanar geometry has been estimated at 8−12 kJ mol^{-1}.[28] It is noteworthy, therefore, that the aryl-O bonds in the tether of **4** show large out-of-plane torsions (τ-($\mathrm{C_N{-}C_O{-}O{-}C_{H2}}$) = 73.0, 131.5°) which are relieved in **4**·M$^+$.

Although **4** is formally a podand,[29] it is a surprisingly strong ligand. As an open-chain, 6-fold benzannelated C222 analogue, **4** might be expected to be a feeble ionophore, since bridge cleavage[29] and benzannelation[30] are both generally found to weaken the binding ability of C222.[31] However, scission of two bridges of C222 and benzannelation have opposite effects on the system's conformational flexibility. Two individually

---

(23) Moras, D.; Weiss, R. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1973**, *B29*, 396−399.

(24) Tehan, F. J.; Barnett, B. L.; Dye, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 7203−7208.

(25) (a) Adolphson, D. G.; Corbett, J. D.; Merryman, D. J. *J. Am. Chem. Soc.* **1976**, *98*, 7234−7239; (b) Teller, R. G.; Finke, R. G.; Collman, J. P.; Chin, H. B.; Bau, R. *J. Am. Chem. Soc.* **1977**, *99*, 1104−1111.

(26) Moras, D.; Metz, B.; Weiss, R. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1973**, *B29*, 383−388.

(27) Stoudt, S. J.; Gopalan, P.; Kahr, B.; Jackson, J. E. *Struct. Chem.* **1994**, *5*, 335−340.

(28) The rotational barrier in anisole is a matter of recent debate. Estimates from both theory and experiment are converging on a value of 2−3 kcal mol^{-1} for the perpendicular transition state. See: (a) Spellmeyer, D. C.; Grootenhuis, P. D. J.; Miller, M. D.; Kuyper, L. F.; Kollman, P. A. *J. Phys. Chem.* **1990**, *94*, 4483−4491. (b) Vincent, M. A.; Hillier, I. A. *Chem. Phys.* **1990**, *140*, 35−40.

(29) Weber, E.; Vögtle, F. *Top. Curr. Chem.* **1981**, *98*, 1−41.

(30) (a) Cox, B. G.; Knop, D.; Schneider, H. *J. Phys. Chem.* **1980**, *84*, 320−323; (b) Cox, B. G.; Van Truong, N.; Garcia-Rosas, J.; Schneider, H. *J. Phys. Chem.* **1984**, *88*, 996−1001; (c) Buschmann, H.-J. *Chem. Ber.* **1985**, *118*, 3408−3412.

(31) For a more complete compendium of binding data, see: Izatt, R. M.; Pawlak, K.; Bradshaw, J. S.; Bruening, R. L. *Chem. Rev.* **1991**, *91*, 1721−2085.

deleterious modifications thus offset each other, leaving **4** with substantial complexing ability.

When the bridge in **4** is snipped, the now disconnected tripods **3** become much less effective complexants. These triarylamine propellers are free to rotate[32] to conformations in which the ether tripods are less ideally arranged than they appear in the crystal structure of **3**. Furthermore, the generally weak Lewis basicity of aryl-substituted ethers[33] and amines[34] make the weak complexing ability of **3** unsurprising. What seems out of place is the strength of binding exhibited by **4**, since all of the above criticisms of **3** apply here as well. We can only surmise that, in addition to the binding entropy decrease conferred by the tether, the complexation-induced strain relief suggested by the structures of free **4** and **4**$\cdot$M$^+$ may also enhance binding. In any case, our observations indicate that biradical **5** should be an effective complexant, allowing further work to probe the effects of complexed metal ions on radical−radical interactions.

This report has described the previously unexplored complexation ability of tripod ethers, highlighting structural and energetic aspects of this ion-binding motif. Ongoing studies will probe the limits of binding in **4**, **5**, and analogues and will further explore the self-assembly of triaryl-Z propeller complexants.

Experimental Section

General Methods. Melting points were determined on a Thomas-Hoover apparatus and are uncorrected. The infrared (IR) spectrum was obtained on a Nicolet IR/42 spectrophotometer; the sample was measured as a thin layer prepared by evaporating a $CHCl_3$ solution on a NaCl plate. Routine ^{1}H and ^{13}C{^{1}H} NMR spectra were obtained at 300 and 75.5 MHz, respectively, on Varian GEMINI-300 and VXR-300 spectrometers. ^{7}Li (116.57 MHz) and ^{23}Na (79.35 MHz) spectra were recorded on a Varian VXR-300 spectrometer and referenced to 0.30 M LiCl/MeOH and 3.0 M aqueous NaCl, respectively; no chemical shift corrections were made for bulk diamagnetic susceptibility differences between the sample and reference solvents. Two-dimensional ^{1}H ROESY and ^{6}Li, ^{1}H HOESY NMR experiments were performed on a Varian-VXR 500 spectrometer. The electron impact (EI) mass spectrum was obtained on a Fisons VG Trio-1 mass spectrometer. Fast atom bombardment (FAB) mass spectra were run on a JEOL JMS-HX110 high-resolution double-focusing mass spectrometer; *m*-nitrobenzyl alcohol was used as the FAB matrix. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Geometry optimizations were carried out using standard MNDO[35] procedures as implemented in the SPARTAN computer program (SPARTAN version 3.1, Copyright 1994 Wavefunction, Inc.).

The following salts were obtained from commercial sources and used as received: $NaBPh_4$, CsI (Aldrich); $LiBPh_4\cdot3$(glyme) (Alfa); NaI, KI (Strem). LiI (Aldrich) was twice recrystallized from acetone and dried at 100 °C under high vacuum for 2 days. $LiBPh_4$,[36] $KBPh_4$,[34] $RbBPh_4$,[34] and $CsBPh_4$[37] were prepared by reacting $NaBPh_4$ with the appropriate alkali metal chloride; sodium contamination (%) in the products was determined by metal analysis: $LiBPh_4$ (<0.04%); $KBPh_4$ (0.079%); $RbBPh_4$ (<0.2%); $CsBPh_4$ (0.10%). KB(4-ClPh)$_4$ (Fluka) was used as received; metal analysis gave <0.03% sodium content.

Tris(2-methoxyphenyl)amine (3). The synthesis of this compound has been described by Frye et al.[38] and more recently by Soulié et al.,[39] but neither report gave ^{13}C NMR data. Complete NMR data are as follows: ^{1}H NMR ($CDCl_3$) δ 7.04−6.97 (m, 3 H), 6.85−6.75 (m, 9 H), 3.54 (s, 9 H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 153.1, 137.8, 124.5, 123.7, 120.6, 112.6, 55.7.

1,2-Bis[2-(bis(2-methoxyphenyl)amino)phenoxy]ethane (4). This compound was synthesized using a modified[40] Ullmann coupling procedure. A mixture of 1,2-bis(2-aminophenoxy)ethane[41] (2.01 g, 8.22 mmol), 2-iodoanisole (9.64 g, 41.2 mmol), 18-crown-6 (0.91 g, 3.43 mmol), anhydrous K_2CO_3 (18.3 g, 132 mmol), powdered copper (4.20 g, 66.1 mmol), and 1,2-dichlorobenzene (80 mL) was refluxed under argon for 16 h. After cooling, the mixture was filtered through a thin layer (∼2 cm) of silica gel. The inorganic solids were washed with hot CH_2Cl_2 and the combined filtrates distilled under reduced pressure. After column chromatography (neutral alumina, hexanes/CH_2Cl_2 (3:1)), the product was recrystallized from acetone and dried at ∼60 °C under high vacuum for 24 h, affording **4** (2.24 g, 41%) as an off-white solid: mp 137−137.5 °C; IR (film from $CHCl_3$) 3061, 2934, 2834, 1588, 1497, 1455, 1319, 1267, 1248, 1181, 1119, 1048, 1028 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.08−6.63 (m, 24 H), 3.51 (s, 12 H), 3.38 (s, 4 H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 153.2, 151.6, 137.9, 137.6, 124.8, 124.0, 123.8, 123.1, 120.9, 120.8, 114.3, 112.9, 65.7, 55.8; EIMS *m/z* (relative intensity) 669 (M + 1, 16), 668 (M$^+$, 46), 348 (15), 334 (31), 321 (10), 290 (17), 289 (100), 274 (10), 273 (12), 246 (18), 226 (11), 212 (11), 183 (21), 182 (35); FABHRMS calcd for $C_{42}H_{40}N_2O_6$ 668.2888, found 668.2869. Anal. Calcd for $C_{42}H_{40}N_2O_6$: C, 75.43; H, 6.03; N, 4.19. Found: C, 75.21; H, 6.34; N, 3.96.

Crystals of **4** suitable for X-ray analysis were obtained by treating a suspension of **4** in nitromethane with LiI (2 equiv). The ligand was solubilized after shaking the mixture for ∼10 min. Slow evaporation of the solution at room temperature afforded free **4** as colorless crystals.

Stoichiometry Determinations of LiI Complexes of 3 and 4. For the LiI complexes, stoichiometries were determined using ^{1}H and ^{7}Li NMR. A tube containing a reference sample of $LiBPh_4\cdot3$(glyme) in $CDCl_3$ was coaxially mounted in a 5-mm NMR tube containing **3** and excess LiI (ca. 5 equiv) in $CDCl_3$. LiI is insoluble in $CDCl_3$ (by ^{7}Li NMR) in the absence of added ligand. The **3**$\cdot x$LiI:$LiBPh_4\cdot3$(glyme) ratio was determined from the respective OCH_3 ^{1}H integrals, and a LiI:$LiBPh_4$ ratio was obtained from the respective ^{7}Li integrals. The stoichiometry (x) is the ratio of the ^{7}Li to ^{1}H ratios. The **4**$\cdot x$LiI stoichiometry was similarly determined.

NMR Data for Metal Complexes. Typically, NMR samples were prepared by adding a $CDCl_3$ solution of the ligand (0.03 M) to the appropriate alkali metal salt. After ∼10 min of shaking, the NMR spectra were recorded. Complexes of NaB(4-ClPh)$_4$ were prepared by treating $CDCl_3$ solutions of the respective $NaBPh_4$ complexes with KB(4-ClPh)$_4$. After 10 min of shaking, the $KBPh_4$ precipitate was removed by filtration. The ^{13}C chemical shift assignments for the BAr_4^- counterions are primarily based on known ^{11}B−^{13}C coupling constants.[42]

3$\cdot$LiI: ^{1}H NMR δ 7.23−7.16 (m, 6 H), 7.05−6.9 (m, 6 H), 4.02 (s, 9 H); ^{13}C{^{1}H} NMR δ 152.9, 135.7, 127.3, 126.9, 121.9, 112.1, 58.3; ^{7}Li NMR δ 2.11 ($\Delta\nu_{1/2}$ = 1.0 Hz).

3$\cdot$LiBPh$_4$: ^{1}H NMR δ 7.62−7.51 (m, 8 H), 7.24−7.17 (m, 4 H), 7.11−6.85 (m, 20 H), 3.45 (s, 9 H); ^{13}C{^{1}H} NMR δ 164.0 (q, $^1J_{BC}$ = 49.3 Hz), 152.5, 135.9 ($^2J_{BC}$ unresolved), 135.5, 127.7, 127.2, 126.1 ($^3J_{BC}$ = 2.9 Hz) , 122.7, 122.2 ($^4J_{BC}$ unresolved), 112.4, 56.7; ^{7}Li NMR δ −0.08 ($\Delta\nu_{1/2}$ = 41 Hz).

3$_2\cdot$NaBPh$_4$: ^{1}H NMR δ 7.44−7.36 (m, 8 H), 7.19−7.11 (m, 6 H), 7.04−6.97 (m, 8 H), 6.94−6.85 (m, 16 H), 6.71 (dd, 6 H, J = 8.0, 1.0 Hz), 3.14 (s, 18 H); ^{13}C{^{1}H} NMR δ 163.9 (q, $^1J_{BC}$ = 49.3 Hz), 151.9,

---

[32] Rotational barriers of 12−13 kcal mol^{-1} are found for tri-ortho-substituted triphenylamines related to **3**. See: Hellwinkel, D.; Melan, M.; Degel, C. R. *Tetrahedron* **1973**, *29*, 1895−1907.

[33] As measured by its ability to hydrogen-bond, the anisyl group is an intrinsically poor ligand. See: (a) Arnett, E. M.; Joris, L.; Mitchell, E.; Murty, T. S. S. R.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 2365−2377. (b) Mitsky, J.; Joris, L.; Taft, R. W. *J. Am. Chem. Soc.* **1972**, *94*, 3442−3445.

[34] Triphenylamine itself forms exceedingly unstable adducts with Lewis acids. See: Kemmitt, R. D. W.; Nuttall, R. H.; Sharp, D. W. A. *J. Chem. Soc.* **1960**, 46−50.

[35] MNDO method: (a) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899−4907. (b) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4907−4917.

[36] Bhattacharyya, D. N.; Lee, C. L.; Szwarc, M. *J. Phys. Chem.* **1965**, *69*, 608−611.

[37] DeWitte, W. J.; Liu, L.; Mei, E.; Dye, J. L.; Popov, A. I. *J. Solution Chem.* **1977**, *6*, 337−348.

[38] Frye, C. L.; Vincent, G. A.; Hauschildt, G. L. *J. Am. Chem. Soc.* **1966**, *88*, 2727−2730.

[39] Soulié, C.; Bassoul, P.; Simon, J. *New J. Chem.* **1993**, *17*, 787−791.

[40] Gauthier, S.; Fréchet, J. M. J. *Synthesis* **1987**, 383−385.

[41] Angelici, R. J.; Quick, M. H.; Kraus, G. A.; Plummer, D. T. *Inorg. Chem.* **1982**, *21*, 2178−2184.

[42] (a) Weigert, F. J.; Roberts, J. D. *J. Am. Chem. Soc.* **1969**, *91*, 4940−4941. (b) Odom, J. D.; Hall, L. W.; Ellis, P. D. *Org. Magn. Reson.* **1974**, *6*, 360−361.

137.1, 136.0 (${}^2J_{BC}$ unresolved), 126.1, 125.6 (${}^3J_{BC}$ unresolved), 124.8, 122.3, 121.8 (${}^4J_{BC}$ unresolved), 113.4, 56.3; ^{23}Na NMR δ −11.9 ($\Delta\nu_{1/2}$ = 240 Hz).

3_2·NaB(4-ClPh)$_4$: ^{1}H NMR δ 7.23−7.08 (m, 14 H), 6.96 (d, 8 H, J = 8.4 Hz), 6.91−6.83 (m, 12 H), 6.72 (dd, 6 H, J = 8.1, 1.8 Hz), 3.24 (s, 18 H); ^{13}C{^{1}H} NMR δ 160.9 (q, ${}^1J_{BC}$ = 49.7 Hz), 152.1, 137.3, 137.2 (${}^2J_{BC}$ unresolved), 127.9, 125.6 (${}^3J_{BC}$ unresolved), 124.8, 122.1 (${}^4J_{BC}$ unresolved), 113.3, 56.2 (remaining ^{13}C resonance not observed); ^{23}Na NMR δ −10.3 ($\Delta\nu_{1/2}$ = 200 Hz).

4·2LiI: ^{1}H NMR δ 7.29−6.83 (m, 24 H), 4.04 (s, 4 H), 4.01 (s, 12 H); ^{13}C{^{1}H} NMR δ 152.9, 150.7, 136.7, 135.3, 127.7, 127.2, 127.1, 125.3, 122.6, 122.1, 114.6, 112.4, 64.9, 58.3; ^{7}Li NMR δ 1.85 ($\Delta\nu_{1/2}$ = 2.0 Hz).

4·LiBPh$_4$: ^{1}H NMR δ 7.40−7.32 (m, 8 H), 7.21−7.15 (m, 4 H), 7.10−7.04 (m, 2 H), 6.96−6.77 (m, 28 H), 6.57 (dd, 2 H, J = 7.1, 1.1 Hz), 3.38 (s, 12 H), 3.21 (s, 4 H); ^{13}C{^{1}H} NMR δ 164.2 (q, ${}^1J_{BC}$ = 49.3 Hz), 152.4, 150.8, 137.6, 136.3, 136.2 (${}^2J_{BC}$ unresolved), 126.5, 126.0, 125.6, 125.4 (${}^3J_{BC}$ = 2.4 Hz), 124.4, 122.9, 122.4, 121.5 (${}^4J_{BC}$ unresolved), 114.5, 113.1, 67.8, 56.2; ^{7}Li NMR δ 0.15 ($\Delta\nu_{1/2}$ = 4.0 Hz).

4·NaBPh$_4$: ^{1}H NMR δ 7.40−7.31 (m, 8 H), 7.30−6.63 (m, 34 H), 6.48 (dd, 2 H, J = 8.0, 1.2 Hz), 3.23 (m, 2 H), 3.14 (s, 6 H), 2.95 (m, 2 H), 2.88 (s, 6 H); ^{13}C{^{1}H} NMR δ 164.1 (q, ${}^1J_{BC}$ = 49.4 Hz), 153.1, 151.6, 149.5, 138.3, 136.3, 136.1 (${}^2J_{BC}$ unresolved), 134.3, 128.9, 127.9, 126.7, 126.3, 125.7, 125.4 (${}^3J_{BC}$ = 2.8 Hz), 122.5, 122.2, 122.0, 121.9, 121.5 (${}^4J_{BC}$ unresolved), 112.0, 111.8, 111.7, 65.1, 55.4, 55.2; ^{23}Na NMR δ −5.5 ($\Delta\nu_{1/2}$ = 260 Hz).

4·NaB(4-ClPh)$_4$: ^{1}H NMR δ 7.24−7.07 (m, 14 H), 6.97−6.79 (m, 22 H), 6.70 (dd, 2 H, J = 7.8, 1.5 Hz), 6.61 (dd, 2 H, J = 8.0, 1.2 Hz), 3.47 (s, br, 2 H), 3.39 (s, br, 2 H), 3.23 (s, 6 H), 2.95 (s, 6 H); ^{13}C{^{1}H} NMR δ 160.8 (q, ${}^1J_{BC}$ = 49.8 Hz), 153.0, 151.6, 149.4, 138.4, 137.2 (${}^2J_{BC}$ unresolved), 136.3, 134.2, 128.8, 128.0, 127.9, 126.9, 126.5, 125.8, 125.7 (${}^3J_{BC}$ = 2.7 Hz), 122.7 (${}^4J_{BC}$ unresolved), 122.3, 122.2, 111.9, 111.8, 111.7, 65.0, 55.5, 55.3 (remaining ^{13}C resonance not observed); ^{23}Na NMR δ −5.3 ($\Delta\nu_{1/2}$ = 240 Hz).

4·KB(4-ClPh)$_4$: ^{1}H NMR δ 7.23−7.05 (m, 14 H), 7.00−6.68 (m, 24 H), 6.58 (dd, 2 H, J = 8.0, 1.2 Hz), 3.40 (s, 6 H), 3.13 (s, 6 H), 3.23 (s, 4 H); ^{13}C{^{1}H} NMR δ 160.9 (q, ${}^1J_{BC}$ = 49.6 Hz), 151.7, 149.4, 137.7, 137.2 (${}^2J_{BC}$ unresolved), 136.7, 136.2, 127.9, 126.5, 126.2, 126.0, 125.7 (${}^3J_{BC}$ = 2.7 Hz), 125.5, 125.2, 123.6, 123.3, 123.0, 122.7 (${}^4J_{BC}$ unresolved), 114.7, 114.5, 112.5, 65.7, 56.6, 56.5 (remaining ^{13}C resonance not observed).

Preparation of Crystalline Complexes. 3_2·NaBPh$_4$. A suspension of **3** (107.0 mg, 0.32 mmol) in nitromethane (5 mL) was treated with NaBPh$_4$ (55.5 mg, 0.16 mmol). A clear solution resulted after shaking the mixture for ∼2 min. Slow evaporation of this solution at room temperature afforded $\mathbf{3}_2$·NaBPh$_4$ (101.6 mg, 63%) as colorless crystals: mp 193−194.5 °C dec; ^{1}H NMR (CDCl$_3$) δ 7.44−7.36 (m, 8 H), 7.19−7.11 (m, 6 H), 7.04−6.97 (m, 8 H), 6.94−6.85 (m, 16 H), 6.71 (dd, 6 H, J = 8.0, 1.5 Hz), 3.24 (s, 18 H); FABMS *m/z* 693 (M$^+$). Anal. Calcd for $C_{66}H_{62}BN_2NaO_6$: C, 78.25; H, 6.17; N, 2.76; Na, 2.27. Found: C, 78.47; H, 6.23; N, 2.66; Na, 2.12.

4·NaBPh$_4$. A solution of **4** (100 mg, 0.15 mmol) in CHCl$_3$ (5 mL) was treated with NaBPh$_4$ (513 mg, 1.5 mmol). After 10 min of shaking, the mixture was filtered to remove excess NaBPh$_4$. Evaporation of the filtrate afforded a viscous oil that solidified to white microcystals on trituration with nitromethane. Recrystallization from nitromethane gave **4**·NaBPh$_4$ (64 mg, 42%) as colorless cubes that were suitable for X-ray analysis: mp 231−232 °C; ^{1}H NMR (CDCl$_3$) δ 7.40−7.31 (m, 8 H), 7.30−6.63 (m, 34 H), 6.48 (dd, 2 H, J = 8.0, 1.2 Hz), 3.23 (m, 2 H), 3.14 (s, 6 H), 2.95 (m, 2 H), 2.88 (s, 6 H). Anal. Calcd for $C_{66}H_{60}BN_2NaO_6$: C, 78.41; H, 5.98; N, 2.77; Na, 2.27. Found: C, 78.07; H, 6.33; N, 2.46; Na, 2.31.

4·NaB(4-ClPh)$_4$. A suspension of **4** (32.1 mg, 0.05 mmol) in nitromethane (1 mL) was treated with a solution of NaBPh$_4$ (16.4 mg, 0.05 mmol) in nitromethane (1 mL). After 10 min of shaking, the mixture was filtered through a plug of glass wool into a solution of KB(4-ClPh)$_4$ (23.7 mg, 0.05 mmol) in nitromethane (0.5 mL). The mixture was shaken for 10 min, during which a fine, white solid (KBPh$_4$) precipitated. The resulting suspension was centrifuged, and the supernatant was carefully removed and slowly evaporated at room temperature; **4**·NaB(4-ClPh)$_4$ (26.3 mg, 46%) was obtained as colorless cubes that were suitable for X-ray analysis: mp 179−181 °C; ^{1}H NMR (CDCl$_3$) δ 7.24−7.07 (m, 14 H), 6.97−6.79 (m, 22 H), 6.70 (dd, 2 H, J = 7.8, 1.5 Hz), 6.61 (dd, 2 H, J = 8.0, 1.2 Hz), 3.47 (s, br, 2 H), 3.39 (s, br, 2 H), 3.23 (s, 6 H), 2.95 (s, 6 H). Anal. Calcd for $C_{66}H_{56}BCl_4N_2NaO_6$: C, 69.01; H, 4.91; N, 2.44; Na, 2.00. Found: C, 68.33; H, 4.83; N, 2.33; Na, 2.24.

4·KB(4-ClPh)$_4$·CH$_3$NO$_2$. A solution of **4** (200 mg, 0.30 mmol) in CHCl$_3$ (10 mL) was treated with KB(4-ClPh)$_4$ (345 mg, 0.70 mmol). After 10 min of shaking, the mixture was filtered to remove excess KB(4-ClPh)$_4$. Evaporation of the filtrate afforded a viscous oil that solidified overnight to a waxy residue. Recrystallization of this residue by slowly evaporating a nitromethane solution (∼1.5 mL) at room temperature yielded **4**·KB(4-ClPh)$_4$·CH$_3$NO$_2$ (111 mg, 30%) as colorless crystals that were suitable for X-ray analysis: mp 177−178 °C; ^{1}H NMR (CDCl$_3$) δ 7.23−7.05 (m, 14 H), 7.00−6.68 (m, 24 H), 6.58 (dd, 2 H, J = 8.0, 1.2 Hz), 4.31 (s, CH_3NO$_2$), 3.40 (s, 6 H), 3.13 (s, 6 H), 3.23 (s, 4 H). Anal. Calcd for $C_{66}H_{56}BCl_4N_2KO_6$: C, 68.05; H, 4.85; N, 2.40; K, 3.36. Found: C, 67.26; H, 4.93; N, 2.30; K, 3.52.

X-ray Studies. Crystal data for $\mathbf{3}_2$·NaBPh$_4$, **4**·NaBPh$_4$, **4**·NaB(4-ClPh)$_4$, **4**·KB(4-ClPh)$_4$·CH$_3$NO$_2$, and **4** are presented in Table 2. Intensity data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation. The measured intensities were corrected for Lorentz and polarization effects; in each case, no absorption correction was applied. The structures were solved by direct methods (SHELXS-86[43]) and refined by full-matrix least-squares procedures using the MolEN[44] package of programs. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in the succeeding difference Fourier syntheses and added to the structure factor calculations, but their positions were not refined.

3_2·NaBPh$_4$. A colorless cube of $C_{66}H_{62}BN_2NaO_6$ having approximate dimensions 0.26 × 0.22 × 0.22 mm was mounted on a glass fiber. A total of 9814 reflections ($\pm h,+k,+l$) were collected in the range 4° < 2θ < 50°, with 2577 having $I_o > 3\sigma(I_o)$ being used in the refinement (560 variables). Final R = 0.056 and R_w = 0.057. The maximum and minimum peaks in the final difference Fourier map corresponded to 0.22 and 0.10 e/Å^3, respectively.

4·NaBPh$_4$. A clear needle of $C_{66}H_{60}BN_2NaO_6$ having approximate dimensions 0.30 × 0.25 × 0.20 mm was mounted on a glass fiber. A total of 12 544 reflections ($\pm h,\pm k,+l$) were collected in the range 4° < 2θ < 55°, with 4100 having $I_o > 3\sigma(I_o)$ used in the refinement (560 variables). Final R = 0.108 and R_w = 0.132. The high R values are a consequence of rotational disorder in one phenyl ring of the BPh$_4^-$ counterion. Coordinates of the **4**·Na$^+$ complex core were quickly convergent, and the atomic displacement parameters were ordinary. The maximum and minimum peaks in the final difference Fourier map corresponded to 1.10 and −0.09 e/Å^3, respectively.

4·NaB(4-ClPh)$_4$. A colorless cube of $C_{66}H_{56}BCl_4N_2NaO_6$ having approximate dimensions 0.60 × 0.50 × 0.20 mm was mounted on a glass fiber. A total of 9381 reflections ($\pm h,-k,-l$) were collected in the range 5° < 2θ < 47°, with 3210 having $I_o > 3\sigma(I_o)$ being used in the refinement (586 variables). Final R = 0.051 and R_w = 0.056. The maximum and minimum peaks in the final difference Fourier map corresponded to 0.37 and 0.23 e/Å^3, respectively.

4·KB(4-ClPh)$_4$·CH$_3$NO$_2$. A colorless cube of $C_{67}H_{59}BCl_4KN_3O_8$ having approximate dimensions 0.30 × 0.30 × 0.10 mm was mounted on a glass fiber. A total of 5182 reflections ($\pm h,-k,+l$) were collected in the range 5° < 2θ < 47°, with 2054 having $I_o > 3\sigma(I_o)$ being used in the refinement (430 variables). Final R = 0.055 and R_w = 0.061. The maximum and minimum peaks in the final difference Fourier map corresponded to 0.22 and −0.07 e/Å^3, respectively.

4. A colorless crystal of $C_{42}H_{40}N_2O_6$ having approximate dimensions 0.41 × 0.23 × 0.14 mm was mounted on a glass fiber. A total of 8103 reflections ($\pm h,\pm k,+l$) were collected in the range 4° < 2θ < 55°, with 2068 having $I_o > 2\sigma(I_o)$ being used in the refinement (451 variables). Final R = 0.102 and R_w = 0.101. The maximum and minimum peaks in the final difference Fourier map corresponded to 0.43 and −0.29 e/Å^3, respectively.

---

(43) G. M. Sheldrick, Institut für Anorganische Chemie der Universität Göttingen, Germany, 1986.

(44) MolEN: An Interactive Structure Solution Procedure. Enraf-Nonius, Delft, The Netherlands, 1990.

Acknowledgment. We gratefully acknowledge research support from the National Science Foundation (Grant CHE-9114265) to J.E.J. and B.K., from the AFOSR (Grant F49620-92-J-0523DEF) to J.E.J. (with J. L. Dye and D. Tománek), and from the Center for Fundamental Materials Research at MSU. FAB mass spectral data were obtained at the Michigan State University Mass Spectrometry Facility, which is supported, in part, by a grant (DRR-00480) from the Biotechnology Research Technology Program, National Center for Research Resources, National Institutes of Health. The Max T. Rogers NMR facilty at MSU was equipped in part with instrumentation funds from the NIH (Grant S10-RR04750) and the NSF (Grant CHE 88-00770, 92-13241).

Supporting Information Available: ORTEP drawings, text giving crystallographic procedures, and listings of data collection and refinement parameters, positional parameters, and thermal parameters for **3**$_2$·NaBPh$_4$, **4**·NaBPh$_4$, **4**·NaB(4-ClPh)$_4$, **4**·KB(4-ClPh)$_4$·CH$_3$NO$_2$, and **4** (41 pages). Ordering information is given on any current masthead page.

IC951129Q