# *Communications to the Editor*

## The Lipophilic Macrocyclic Polyether 2,3,9,10-Dibenzo-1,4,8,11-tetraoxacyclotetradeca-2,9-diene (Dibenzo-14-crown-4): A Selective Ionophore for Lithium Ions

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Electrically neutral lipophilic ligands containing the appropriate number of binding sites of high solvating ability can behave as ionophores for alkali and alkaline earth cations.[1-5] The macrocyclic polyethers ("crown"-ethers) have cavities that can take up alkali and alkaline earth cations.[6-8] Complexation occurs between the cations and the ethereal oxygens of the crown ether,[8] and the resulting complexes are highly stable and selective.[7-9] These lipophilic ethers, when incorporated into membranes, behave as ionophores selective for alkali and alkaline earth cations.[10-12]

Preferential complexation of lithium by small 12-, 13-, and 14-member ring crown ethers has been reported.[6,7,9,13-15] Since monitoring of $Li^+$ activities in biological systems is important,[16-18] the 12-, 13-, and 14-member ring crown ethers have been synthesized[6,15] and tested as ion-selective components in solvent-polymeric membrane electrodes. The crown ether 2,3,9,10-dibenzo-1,4,8,11-tetraoxacyclotetradeca-2,9-diene (dibenzo-14-crown-4) (see Figure 1) is most selective for $Li^+$ as determined by the electromotive force measurements. We report here on the characteristics of this neutral carrier sensor for lithium.

The solvent-polymeric membranes were prepared with 2 wt % ligand, 33 wt % poly(vinyl chloride) (SDP, hochmolekular, Lonza AG, CH-3930 Visp), and 65 wt % *o*-nitrophenyl octyl ether (*o*-NPOE) or dioctyl sebacate (DOS). The membrane preparation and the measuring technique have been described.[19] The EMF measurements were performed at 25 °C with a standard deviation of <0.1 mV for a single determination.[20]

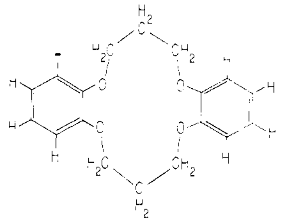

**Figure 1.** Dibenzo-14-crown-4.

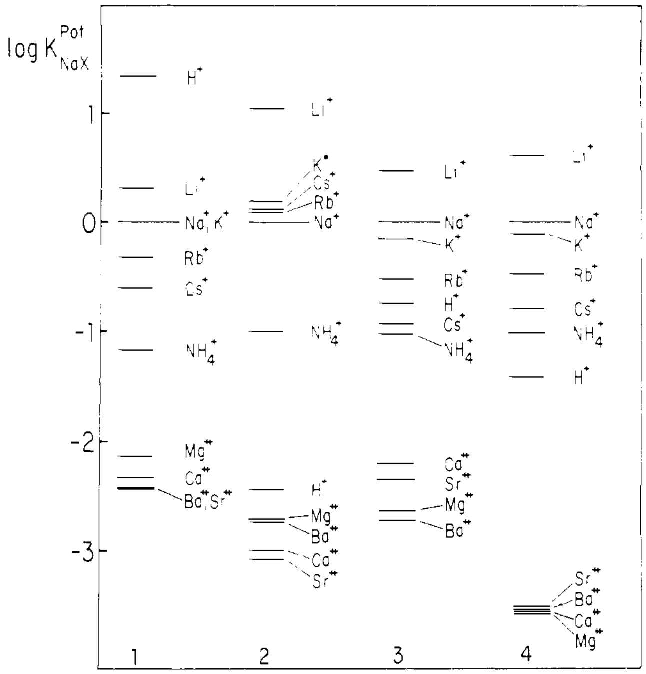

**Figure 2.** Selectivity factors log $K_{NaX}^{Pot}$ for solvent polymeric membranes with (1) *o*-nitrophenyl octyl ether (*o*-NPOE) as membrane solvent, (2) *o*-nitrophenyl octyl ether (*o*-NPOE) as membrane solvent and incorporated lipophilic anionic sites (potassium tetra(*p*-chlorophenyl)borate (KTpClPB)), (3) dioctyl sebacate (DOS) as membrane solvent, (4) dioctyl sebacate (DOS) as membrane solvent and incorporated lipophilic anionic sites (potassium tetra(*p*-chlorophenyl)borate (KTpClPB)).

The potentiometrically determined selectivity factors induced in solvent-polymeric membranes by dibenzo-14-crown-4 are presented in Figure 2. The selectivity factors given as $K_{NaX}^{Pot}$ represent the membranes' preference for ion X relative to $Na^+$. The data show that among the alkali and alkaline earth metal cations tested, lithium is the preferred ion for dibenzo-14-crown-4. Comparing column 1 with 2, and column 3 with 4 (in Figure 2), demonstrates that incorporation of lipophilic anions (potassium salt of tetra(*p*-chlorophenyl)borate (KTpClPB)), the sole difference in the experimental conditions, into the membranes of the type discussed leads to an increase in lithium selectivity.

In water and other highly solvating media, the charged complex and the anion are separately solvated, and no anion effect on complex stability is expected. However, in poorly solvating media such as the solvent polymeric membranes, pronounced ion pairing occurs, and complexed ion pairs or ligand-separated ion pairs are formed.

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The electrostatic cation–anion interactions will depend on the properties of the anion: its charge, size, shape, and polarizability. The solubility properties of the anion, i.e., its lipophilicity, are extremely important for the dissolution of the complex in solvents of low polarity.

Our data (see Figure 2) indicate the crucial importance of the counterion. This study, along with a more comprehensive experiment currently underway,[21] shows that bulky, spherical, polarizable, monovalent anions enable the cation to interact more effectively with the ligand-binding sites, generating a more selective and specific system.[22] In some cases (Figure 2, column 4) divalent cations are strongly rejected,[23] an important factor in the design of lithium-selective membranes for industrial and medical purposes.[24,25]

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**Registry No.** $Li^+$, 17341-24-1; dibenzo-14-crown-4, 14174-06-2.

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# Direct Observation of Substitution Reactions of Tricarbonylbis(phosphine)manganese(0) Radicals[1]

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It has become evident during the past few years that reaction pathways involving metal-centered radicals, with 17 electrons in the valence orbitals of the metal, are important in many organometallic systems.[2] The radicals most widely studied to date are those involving only CO groups as ligands or CO and other groups such as $\eta^5$-$C_5H_5$. Since the initial observation of a radical chain pathway for substitution,[3] the substitution lability of metal carbonyl radicals has been recognized as an important aspect of their chemical behavior.[4,5] In addition to the evidence based on radical chain substitution reactions, other indications of lability in the radicals exist: (a) The quantum yields for photochemical substitution, e.g., in $Mn_2(CO)_{10}$, are nearly 1.[6,7] Because the rate of recombination of $Mn(CO)_5\cdot$ radicals approaches the diffusion-controlled limit,[8,9] substitution of the radical must be very rapid. (b) Formation of $(\eta^5\text{-}C_5H_5)_2M_2(CO)_4$ (M = Cr, Mo, W) on irradiation or heating of $(\eta^5\text{-}C_5H_5)M_2(CO)_6$ suggests CO loss from the radicals formed via metal–metal homolysis.[10] (c) Various photochemical reactions of metal carbonyl compounds, e.g., of $Re_2(CO)_{10}$ with $H_2$[4] or of various dinuclear carbonyl compounds with hydrides,[11] are most readily accounted for in terms of a high lability of the radical formed via metal–metal bond homolysis.

The results of these studies suggest simple mononuclear carbonyl radicals such as $Mn(CO)_5\cdot$, $Re(CO)_5\cdot$, or $Co(CO)_4\cdot$ may react via a rate-determining dissociative loss of CO, followed by rapid uptake of L or by an oxidative addition step. On the other hand, Poë has recently provided convincing evidence that substitutions of $Re(CO)_5\cdot$ by phosphines can also occur via an associative pathway.[12] In substituted metal carbonyl radicals, replacement of one ligand L by another, or possibly substitution of CO to yield a more highly substituted radical, is relatively slower and may occur via an associative pathway.[13,14]

We have earlier reported the formation of persistent zerovalent manganese radicals, $Mn(CO)_3L_2\cdot$ (L = phosphorus donor ligand).[13] The steric requirements of L preclude recombination of the radicals to form a stable dinuclear species. We have recently carried out additional physical and chemical studies of such radicals.[15] We report here the first direct observations of the kinetics of substitution at the metal center in a substituted metal carbonyl radical.[16]

A reaction of particular interest is that with CO as delineated in eq 1 and 2. The reaction is readily followed by mixing hexane

$$Mn(CO)_3L_2\cdot + CO \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Mn(CO)_4L\cdot + L \tag{1}$$

$$2Mn(CO)_4L\cdot \xrightarrow{k_3} Mn_2(CO)_8L_2 \tag{2}$$

solutions of $Mn(CO)_3L_2\cdot$ and CO and observing the time dependence of the IR bands due to $Mn(CO)_3L_2\cdot$ in the region of CO stretching modes. Neither $Mn_2(CO)_9L$ nor $Mn_2(CO)_{10}$ are observed as products. All of the reactions studied exhibit good first-order kinetics through at least 3 half-lives. Observed pseudo-first-order rate constants, pertaining mainly to the case L = $P(i\text{-}Bu)_3$, for reaction at 20 °C are given in Table I. (This particular phosphine was chosen for detailed study because in preparation of the radical it is possible to achieve low ambient concentrations of the phosphine.)

The important observations are these: The observed pseudo-first-order rate constant is approximately proportional to [CO], and added $P(i\text{-}Bu)_3$ at a concentration level on the order of that of CO or greater has no effect on the observed reaction rate.

The dependence of the pseudo-first-order rate constant on [CO] suggests strongly that the reaction is associative in character. This conclusion is reinforced by the comparative rate constants for reaction of CO with $Mn(CO)_3[P(i\text{-}Bu)_3]_2\cdot$ and $Mn(CO)_3[P(n\text{-}Bu)_3]_2\cdot$. Reaction is faster when the phosphine is less bulky, consistent with an associative transition state. The second-order rate constants for reactions of $Mn(CO)_3[P(i\text{-}Bu)_3]_2\cdot$ and $Mn(CO)_3[P(n\text{-}Bu)_3]_2\cdot$ with CO at 20 °C are 0.32 and 42 $M^{-1}\ s^{-1}$, respectively.

The fact that the pseudo-first-order rate constant is unaffected by addition of $P(i\text{-}Bu)_3$ suggests that the reverse reaction in 1 is relatively slow in relation to reaction 2.

The present observations for the first time directly establish the lability of the 17-electron metal carbonyl radicals toward thermal substitution.[16] Results for these highly substituted radicals

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