The synthetic methodology reported, consisting of the use of specific reducing agents on oxochloro complexes, seems to be a good route for the preparation of electron-rich and functionalizable organometallic oxo aggregates.

Acknowledgment. We thank the National Science Foundation (Columbia University Grant CHE-8512660) and Italian C.N.R. (University of Parma) for financial support.

Supplementary Material Available: Crystallographic data (Table I), fractional atomic coordinates (Tables II, III), thermal parameters (Tables IV, V), and bond distances and angles (Tables VI, VII) for complexes **2** and **3** (6 pages). Ordering information is given on any current masthead page.

Enhanced Transport of Li$^+$ through an Organic Model Membrane by an Electrochemically Reduced Anthraquinone Podand

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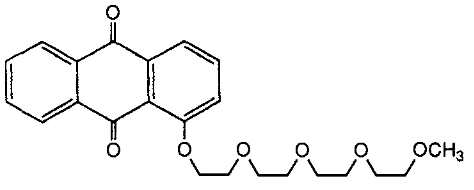
The neutral ligand **1** is unable to transport Li$^+$ to an appreciable extent across a CH_2Cl_2 model membrane system. After electrochemical reduction to the corresponding anion radical $1^{\bullet -}$, a Li$^+$ transport rate of 2.2×10^{-7} mol/h was measured. This constitutes a new method to effect enhanced binding and transport via an electrochemical "switching" mechanism for cations in solution. Direct ESR spectral evidence is presented which shows unequivocally the existence of a strong ion pair between the electrochemically generated $1^{\bullet -}$ and Li$^+$ in the CH_2Cl_2 model membrane phase.



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The idea of binding and transport enhancement of cations by ligands via an external switching mechanism has received considerable attention in recent years.[1] Most notable is the work of Shinkai et al. who have used light-induced isomerization of azo linkages to obtain binding and transport enhancement of metal cations.[1a,b] Izatt and co-workers were able to enhance transport rates via pH gradients using calixarene and pyridone carriers, a process triggered by deprotonation of the ligand in the cation source interphase and reprotonation in the receiving phase.[1c,d] An intermediate anionic carrier species and a neutral cation–ligand complex are involved in this process, a similar situation to that presented in this work. Another recent paper related to this work reported enhanced Na$^+$ transport rates across liquid membranes via an electrochemical "pumping" process.[1e] Our approach to switching and binding enhancement of alkali-metal cations involves electrochemical reduction of ligands which yield relatively stable anion radicals.[2] Nitrobenzene-[2a] and anthraquinone-[2b]substituted lariat ethers and podands have been extensively investigated by using cyclic voltammetry. Cation binding enhancement factors as high as 10^6 for Li$^+$ have been reported.[2a]

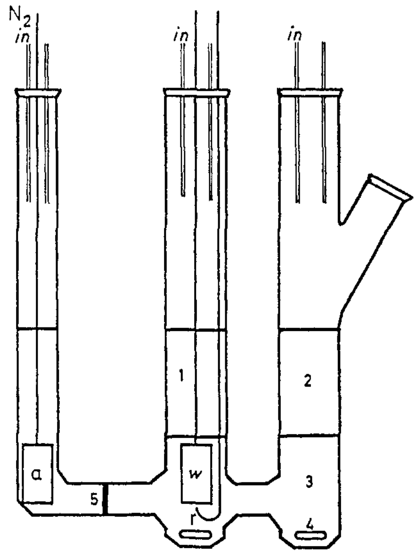

Figure 1. Diagram of transport cell: (1) source phase (1 M $LiClO_4$ in H_2O); (2) receiving phase (deionized water); (3) membrane phase (2 mM **1** and 0.1 M TBAP in CH_2Cl_2); (4) magnetic bar; (5) fine porosity glass filter; (a) Pt auxiliary electrode; (w) Pt working electrode; (r) Ag wire reference electrode.

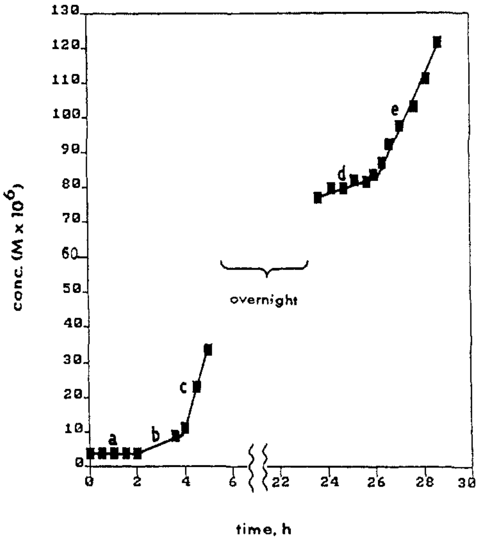

Figure 2. Plot of the Li$^+$ concentration in the receiving phase as a function of time: (a) transport by neutral **1**; (b) and (d) transport during the reduction of **1** to $1^{\bullet -}$; (c) and (e) transport by $1^{\bullet -}$. Note the discontinuity in the time axis during the overnight period. Some transport took place during that time since some $1^{\bullet -}$ was still present.

Figure 1 shows a diagram of the transport cell used. The model membrane, 3 in Figure 1, consisted of a 0.1 M tetra-*n*-butylammonium perchlorate solution containing 2 mM **1** in CH_2Cl_2. The donor water phase, 1 in Figure 1, contained 1 M $LiClO_4$ and the receiving water phase, 2 in Figure 1, was deionized water. Transport of Li$^+$ was monitored by measuring the Li$^+$ concentration in the receiving phase at 20–30-min intervals using atomic absorption spectrophotometry (Perkin-Elmer Model 403). Two magnetic bars, 4 in Figure 1, were used to ensure effective mixing during the course of the experiment.

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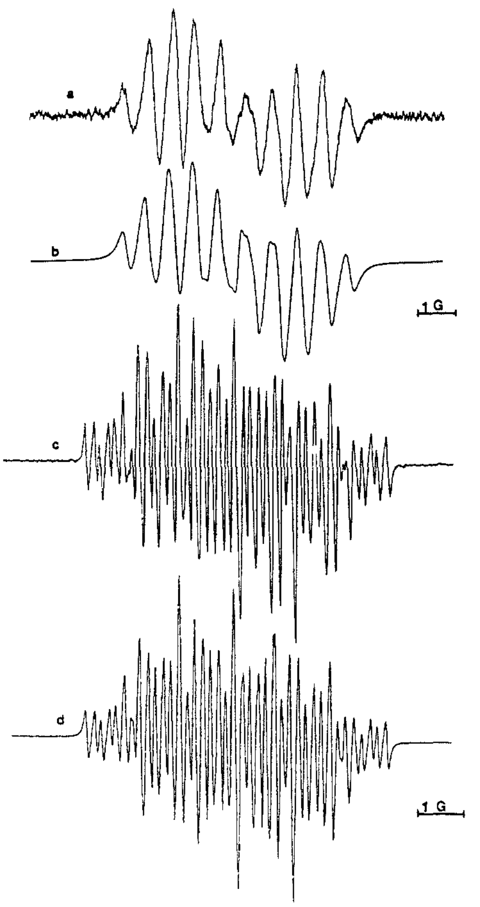

Figure 3. Experimental (a) and simulated (b) ESR spectra for **1**$^{\bullet-}$ in CH_2Cl_2 solution. (c) and (d) are the corresponding experimental and simulated spectra in the presence of a 1 M aqueous $LiClO_4$.

Transport was monitored for the unreduced neutral ligand for a period of 2 h, during which no appreciable Li^+ was detected in the receiving phase, see segment a in Figure 2. At that point a potential of −1.0 V (vs. a Ag wire reference, r in Figure 1) was applied at the working electrode (w) while the auxiliary electrode (a) was kept in the compartment separated by the low-porosity fritted-glass filter (5 in Figure 1). The initial current observed was ≃1 mA and increased as a function of time to ≃1.5 mA, where it remained constant throughout the experiment. During this period reduction at the working electrode resulted in the development of a very intense red color, which was quickly distributed exclusively over the organic phase. Oxidation at the auxiliary electrode did not produce a color change; the pale yellow color of the original solution persisted.

As indicated by segment a in Figure 2, transport by the neutral carrier is negligible in the time interval studied. As the electrolysis progressed and the intensity of the red color increased so did the amount of Li^+ detected until, after 1.5 h, the time dependence was approximately linear, segment c in Figure 2. The calculated transport rate from the slope of this segment is 2.2×10^{-7} mol/h. These results indicate an "all-or-nothing" situation where *no* transport is observed for the neutral ligand and significant transport when reduced.

Some observations deserve mention. If electrolysis is stopped, the red color slowly fades, initially to an intense orange and, eventually, after several hours, to pale yellow. Figure 2 shows a second set of data points (d and e) obtained for the same solution after allowing it to remain overnight in the transport cell without nitrogen or stirring. All the points except the first were obtained during a second electrolysis of the solution during which the intense red color returned to the organic phase. Note again that after an induction period the Li^+ concentration increases until it changes almost linearly with time. The transport rate determined from this limiting slope is 1.8×10^{-7} mol/h. This value coincides well with the previous one, the small difference probably due to some overnight decomposition.

In order to establish if the red and orange colors observed could be identified with the Li^+–**1**$^{\bullet-}$ ion pair, ESR measurements were conducted under identical conditions as those used for the transport experiments. The same CH_2Cl_2 solution used above was placed in an electrolytic ESR cell with Hg as the working electrode. Electrolysis was conducted directly in the ESR cavity as described previously.[3] The resulting spectrum, exhibiting relatively broad lines, is shown in Figure 3a. The simulation shown in Figure 3b was obtained by using the parameters $a_{2H} = 0.53$, $a_{1H} = 0.66$, $a_{1H} = 1.07$, $a_{1H} = 1.19$, and $a_{1H} = 1.40$ G and a line width of 0.22 G. Addition of a 1 M $LiClO_4$ water solution on top of the CH_2Cl_2 phase directly in the ESR cell resulted in the appearance of the spectrum in Figure 3c, with a concomitant color change from red to orange. The simulation for Figure 3c is given as Figure 3d and was obtained using the following parameters: $a_{2H} = 1.19$, $a_{1H} = 0.21$, $a_{1H} = 0.71$, $a_{1H} = 0.87$, $a_{1H} = 1.43$, and $a_{Li^+} = 0.33$ G and a line width of 0.07 G. The observed metal splitting is clear proof of strong ionic association between the anion radical and the cation.

These results indicate that **1**$^{\bullet-}$ is infinitely better as a transporter for Li^+ than **1**, an expected result based on the previously reported binding enhancement factor measured in acetonitrile solution by cyclic voltammetry (10^5).[2c] Estimating a binding constant of ≃10 for **1** with Li^+, binding by the reduced ligand should be in the optimum range for transport as reported by Izatt (≃10^6).[4]

Attempts are currently under way to improve the transport efficiency by not only enhancing the binding strength of the ligand upon reduction at the donor interphase but by returning to the low binding neutral state at the receiving interphase using electrochemical oxidation.

Acknowledgment. We warmly thank the National Institutes of Health, GM 33940, for support of this work.

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Stereospecific Reductive Methylation via a Radical Cyclization–Desilylation Process

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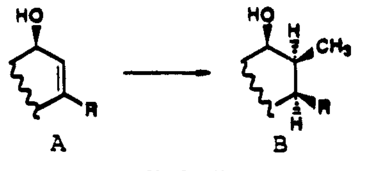
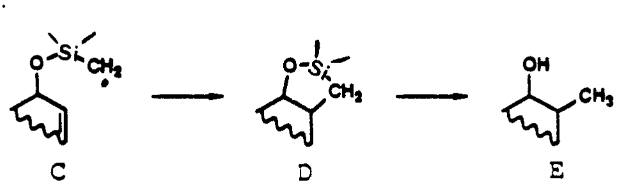
We wish to report a method, schematized in A → B, for the addition of the elements of methane to the double bond of an allyl alcohol.



R= alkyl, H

The importance of the process is that it leads to the introduction of a methyl group regiospecifically next to the allylic hydroxyl and stereospecifically cis to it. This is illustrated by C → D → E.



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