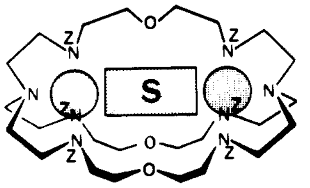
right sides of the molecule are different; this agrees with structure **1**-M (Figure 1) for this species and shows that the side to side exchange of the cation inside the molecular cavity is slow. The data also indicate that the cation exchange between the free ligand **1** and **1**-M is slow, but no firm indication about the rate of cation exchange between **1**-M and **1**-M_2 has been obtained. The processes involved are represented in Figure 1. The ^1H and ^{13}C spectra of the zinc complexes display broad signals which may be due to the coexistence of several isomers as noted above.

The electronic spectrum of the blue $[2Cu^{2+} \subset \mathbf{1a}]\cdot 4ClO_4^-$ cryptate in acetonitrile shows bands at 765 nm (ϵ 350), 640 (sh) (275), 350 (5000), 283 (5600). In the same conditions tren-$Cu(ClO_4)_2$ has bands at 800 nm (ϵ 183) and 275 (4400). The 350-nm band is characteristic of the bis-tren complex and may undergo marked changes (see below).[13] A green bis-$Cu(ClO_4)_2$ complex of **1a** has also been obtained with absorptions at 743, 634 (sh), 351, and 285 nm.

The powder ESR spectrum of the blue $[2Cu^{2+} \subset \mathbf{1a}]$ complex displays a pattern indicating an environment of axial symmetry for the copper ions,[14] in agreement with structure **1**-M_2 ($g_{\|} = 2.0766$ and $g_{\perp} = 2.2176$). A weak $\Delta m_s \pm 2$ transition is observed at $g = 4.7$ consistent with the presence of Cu(II) dimers.[15,16] In acetonitrile solution the ESR spectrum is a symmetric band and μ_{eff} is $\sim 2.0\ \mu_B$ per copper at 294 K.

We have proposed earlier[1,3] that binuclear cryptates might form *cascade complexes* by insertion of a substrate of compatible size between the metal cations. This involves two successive complexation processes: selection of the metal cations by the ligand and selection of the substrate controlled by the nature and the arrangement of the complexed cations.

Like the cylindrical macrotricyclic cryptands,[1,3] the present bis-tren ligands should be suitable systems. Indeed, in the **1**-M_2 species, the fifth coordination axis of each cation is directed toward the other one so that insertion of a substrate S may be possible leading to a species of type **1**-M_2S, provided that the intercationic distance is compatible. Some preliminary indications about the interaction with substrates will be briefly mentioned here. Addition of water to the $[2Cu^{2+} \subset \mathbf{1a}]\cdot 4ClO_4^-$ complex in acetonitrile leads to a strong decrease in the intensity of the EPR signal which becomes markedly asymmetric; simultaneously the intensity of the 350-nm UV band doubles. Addition of cyanide leads to a change in shape of the EPR signal and to the complete disappearance of the 350-nm UV band. This band also disappears on azide addition while two bands appear at 670 and 380 nm. These results may indicate the formation of species of type **1**-M_2S containing H_2O, CN^-, and N_3^- as substrates. However the estimated distance between the two Cu(II) cations in **1**-M_2 (see above) is probably too short for end to end bridging by a substrate especially for azide (which might involve bridging by a terminal nitrogen).[16,17] Both cyanide[18] and azide[16] bridging has been observed in dimeric tren-Cu(II) complexes; in the latter case an electronic absorption band is present at 670 nm similar to that observed above.



1-M$_2$S

Cation complexation, intercationic distance, and substrate inclusion in systems of the bis-tren type may be regulated via the length of the bridges linking the tripodal subunits and the nature of the heteroatoms (e.g., NZ = S, PZ in **1**). Cascade complexes like **1**-M_2S, as well as the corresponding species derived from cylindrical macrotricycles A,[2,3] may lead to selective *fixation* and *transport* of a given substrate as well as to the development of new *bi(or poly)nuclear catalysts* for multicenter-multielectronic processes (condensation of two or more included substrates held in proximity, O_2 and N_2 reduction, water splitting,[19] etc.) and of models for polynuclear metalloproteins (hemocyanin, hemerythrin, oxygenases, etc.).[20,21]

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Preparation of [3,3-$(Ph_3P)_2$-3-H-4-(polystyrylmethyl)-3,1,2-$RhC_2B_9H_{10}$]. A Polymer-Bound Metallocarborane Catalyst

Sir:

Considerable interest has recently developed in the attachment of homogeneous transition metal catalysts to insoluble supports in order to aid in product isolation and in catalyst retrieval.[1-5] This concept of supporting active catalytic molecules was initially developed[6,7] by biochemists who utilized bound enzymes as their catalysts. Inorganic approaches to this area have centered on anchoring transition metal catalysts to

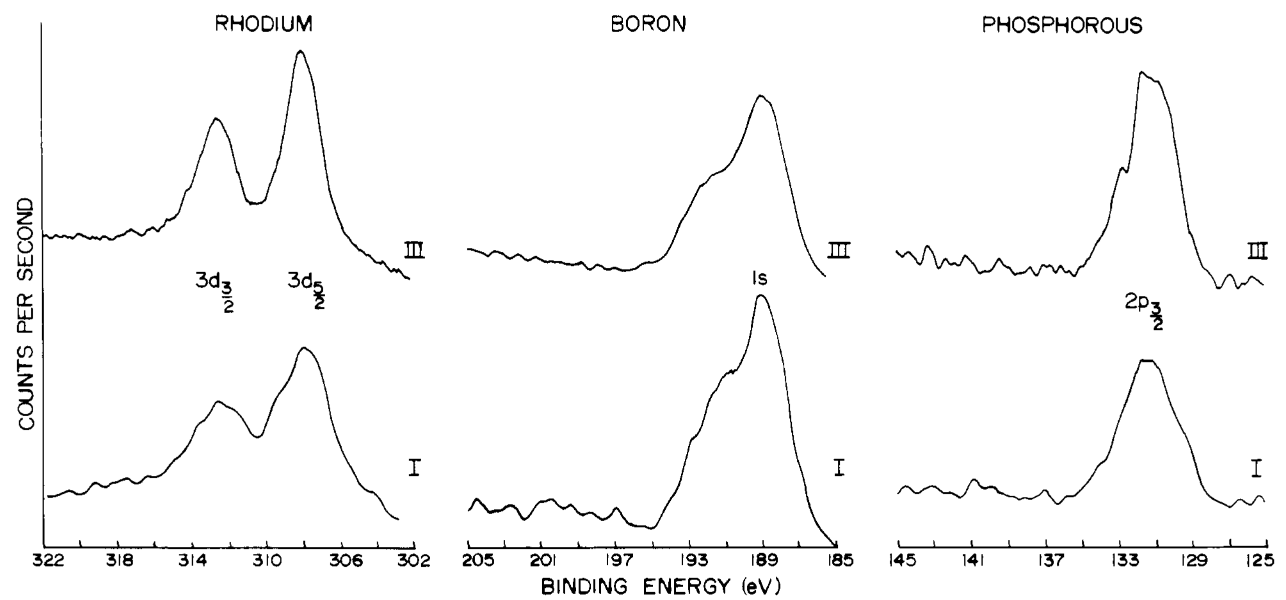


Figure 1. X-ray photoelectron spectra (ESCA) of $[3,3\text{-}(Ph_3P)_2\text{-}3\text{-}H\text{-}3,1,2\text{-}RhC_2B_9H_{11}]$ (III) and $[3,3\text{-}(Ph_3P)_2\text{-}3\text{-}H\text{-}4\text{-}(polystyrylmethyl)\text{-}3,1,2\text{-}RhC_2B_9H_{10}]$ (I).

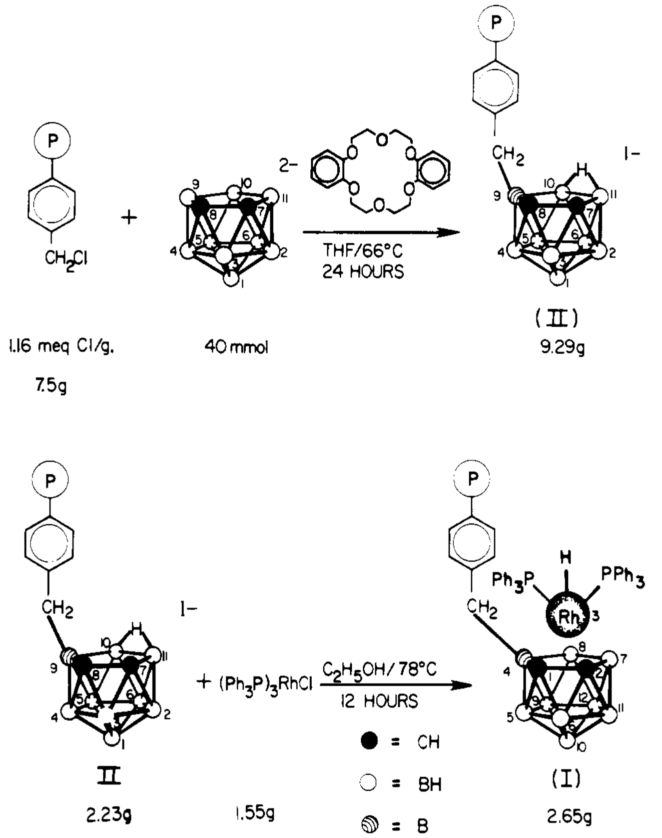
both polar supports[8,9] such as silica and to nonpolar supports[10-14] such as functionalized organic polymers either directly or via bound ligands.[10-13,15-20]

We wish to report the synthesis and characterization of $[3,3\text{-}(Ph_3P)_2\text{-}3\text{-}H\text{-}4\text{-}(polystyrylmethyl)\text{-}3,1,2\text{-}RhC_2B_9H_{10}]$ (I), the first supported metallocarborane catalyst (polymer bound by a carbon–boron bond), and an analogue of the previously reported[21] homogeneous hydrogenation catalyst $[3,3\text{-}(Ph_3P)_2\text{-}3\text{-}H\text{-}3,1,2\text{-}RhC_2B_9H_{11}]$ (III). The preparation of polymer catalyst I outlined in Scheme I involved the intermediate preparation of $M^+[9(polystyrylmethyl)\text{-}7,8\text{-}C_2B_9H_{11}]^-$ (II, M = Na, K) by reaction of dicarbollide dianion[22,23] with chloromethylated polystyrene polymer[24] (Merrifield's peptide resin) in the presence of dibenzo-18-crown-6. The crown ether was used as a catalyst to aid in the transfer of dianion into the lipophilic polymer. Reaction of the carborane-substituted polymer II with $[(Ph_3P)_3RhCl]$ yielded the rhodacarborane polymer-bound catalyst I.

Supported metallocarborane catalysts exhibit a distinctive advantage not found in previously explored polymer-bound catalysts. Systems in which a triaryl phosphine ligand is attached to the polymer and serves as the metal–polymer linkage[12,13,17,25] require reversible phosphine dissociation in the catalysis mechanism and may be susceptible to eventual loss of metal content. The strong metal–carborane bond should be retained and the catalytic metal center rendered immobile.

The alkylation of $(7,8\text{-}C_2B_9H_{11})^{2-}$ with alkyl halides had been found previously to occur at the boron atom adjacent to the carbon in the open pentagonal face (positions 9 and 11) and to a lesser extent at the boron atom in between and below the two carbon atoms (position 3).[26] Heating the 9 isomer (R = Me, and Et) at 65 °C for short periods completely isomerizes it to the 3 isomer.[26] Alkylation of $(7,8\text{-}C_2B_9H_{11})^{2-}$ with benzyl chloride under identical reaction conditions with which the polymer is made yielded a 4:1 mixture of the 9-benzyl- and 3-benzyl-substituted cage. Based on these findings, we believe that the carborane in I and II is predominantly bound to the polymeric benzyl groups at the 9 position, and to a somewhat lesser extent at the 3 position.

Scheme I. Synthesis of $[3,3\text{-}(Ph_3P)_2\text{-}3\text{-}H\text{-}4\text{-}(polystyrylmethyl)\text{-}3,1,2\text{-}RhC_2B_9H_{10}]$.



The infrared spectrum (KBr) of $(9\text{-}(polystyrylmethyl)\text{-}7,8\text{-}C_2B_9H_{11})^-$ (II) exhibits a strong ν_{BH} stretch centered at 2058 cm^{-1}. Compound II is a white solid which is stable in air for extended periods. However, II was handled under an inert atmosphere whenever possible to prevent contamination with water as $K(C_2B_9H_{12})$ is quite hygroscopic.[23] Elemental analysis of II demonstrated the incorporation of 6.72% boron (C, 79.24; H, 8.11; K, 1.30; Na, 0.69; Cl, 0.00). These data suggests quantitative cage incorporation into the chloromethylated polystyrene matrix.

The infrared spectrum (KBr pellet) of I contains a B–H stretching absorption at 2560 cm^{-1} and a weak ν_{RhH} stretch at 2080 cm^{-1}. No other characteristic bands were observed owing to the low concentration of embedded complex and also to the obscuration of several spectral regions by the polymer backbone. Complex I is a bright yellow air-stable material with a color identical with that of its homogeneous analogue III. Elemental analyses of several preparations of the polymer-bound complex I were determined and are typified by the following figures: C, 76.76; H, 6.88; B, 4.90; Rh, 4.42; P, 2.33; Cl, 0.62.[27] This analysis established ratios of cage/Cl of 2.9,[27] Rh/cage of 0.85, and P/Rh of 1.8.[28] The residual percentage of the compound not found in the analysis was 4.09, presumably due to the presence of oxygen along with some sodium or potassium.[27] Other determinations of I established cage/Cl ratios of 0.37–5.2,[27] Rh/cage ratios of 0.27–0.85, Rh/P ratios of 1.75–2.7, and residual percentage of undetermined elements of 2.9–5.4.[27,28]

The diffuse visible reflectance spectra of both I and III were measured (relative to MgO). Both spectra are identical in shape and exhibited broad absorption with a maxima at 444.5 nm. Measurement of the visible and UV spectrum of III (C_6H_6) reveals two absorptions at 415 nm (ϵ 930 L/mol cm) and 325 nm (ϵ 9500 L/mol cm), the latter of which appears as a shoulder on an intense charge-transfer band. The two bands arise[29] from transitions from $^1A_1$ ground state to $^1T_1$ and $^1T_2$ upper states. The extinction coefficient of the absorption at 325 nm is increased by intensity stealing from the charge-transfer band.

The x-ray photoelectron spectra (ESCA)[30] of both I and III were measured for the phosphorus $2p_{3/2}$, boron 1s, and rhodium $3d_{5/2}$ and $3d_{3/2}$ levels. The phosphorus and boron signals in III and I are broad but of nearly the same shape and have the following maxima: boron at 188.7 and 188.9 and phosphorus at 131.4 and 131.4 eV, respectively. The following rhodium levels for III and i were found: $3d_{3/2}$ at 312.4 and 312.5 and $3d_{5/2}$ at 307.8 and 307.9, respectively. This data is shown graphically in Figure 1.

In general, valence electron binding energy levels as measured by the x-ray photoelectron spectroscopy do not change much with an oxidation state change.[31,32] Rhodium foil exhibits its $3d_{3/2}$ and $3d_{5/2}$ levels at 311.8 and 307.0 eV, respectively. However, small differences in the core 3d levels are significant[31] and the close agreement between the maxima for the rhodium levels in I and III suggest that the majority of the rhodium atoms incorporated into the polymer beads (at least at the surface) have an identical chemical environment with that of rhodium atoms in [3,3-$(Ph_3P)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$]. These measurements are only indicative of the surface environments. However, with a highly porous polymer considerably more surface area may be exposed than with a normal crystal. Measurement of the UV photoelectron spectra (UV PES) may yield a more definitive comparison as UV PES measures valence levels and is therefore more sensitive to oxidation-state changes.[32]

The beads (I) in an amount equivalent to a 10^{-4} M solution of III in benzene isomerize 1-octene (0.3 M) within 24 h at 40 °C to a mixture of 1-octene (14%), *trans*-2-octene (65%), and *cis*-2-octene (20%). Reaction of I with deuterium gas at 300 psi and 45 °C for 2 days yielded tan beads with a considerable amount of cage-deuterium incorporation as shown in the infrared.[33]

The compound [3,3-$(Ph_3P)_2$-3-H-4-(polystrylmethyl)-3,1,2-$RhC_2B_9H_{10}$] (I) was found to be an efficient catalyst for the reduction of (blocked) alkenes to alkanes as has been demonstrated[21,34] for its homogeneous analogue [3,3-$(Ph_3P)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$] (III). Kinetic runs of I were made in a flask containing a vortex plug with a hole through the center so that polymer beads would remain suspended in the solution (and not be deposited on the walls of the flask above the solution level), and with a stir bar rotating at maximum speed. The rate of reduction may be diffusion controlled and a more efficient stirring system might increase the rate somewhat. Hydrogenation of 3,3-dimethyl-1-butene (0.39 M) using the bead catalyst I proceeded at a rate of 2.45×10^{-3} mL of H_2 (1 atm)/min × mg of I (or 9.52×10^{-5} mol/min × g of I) at 40.0 °C in *o*-dichlorobenzene solution, and ethyl acrylate reduction in *o*-dichlorobenzene with I (at 0.67 M ethyl acrylate) occurred at an initial rate of 3.79×10^{-3} mL of H_2 (1 atm)/min × mg of I (or 4.7×10^{-5} mol/min × g of I).

Under a hydrogen atmosphere and in the presence of alkene solutions, bead catalyst I is yellow. Upon consumption of the olefin the beads change to a brown color. The homogeneous catalyst III shows no such color change in the absence of oxygen. Elaborate measures to exclude oxygen failed to prevent the color change in hydrogenation reactions of I. However, with 3,3-dimethyl-1-butene the supported catalyst I has been observed to go over 250 turnovers (per Rh atom) without changing color, and to continue hydrogenating 3,3-dimethyl-1-butene roughly 20% slower for an additional 280 turnovers (the length of the experiment) after becoming brown. No color change has been observed over a period of several weeks for I in air either as a solid or in solution. Attempts to induce the color change by reaction of I with air either in the presence of 3,3-dimethyl-1-butene or in its absence left the beads an unchanged yellow color after several days. The reason for the color change after hydrogenation is not known at this time.

In addition to the method we have demonstrated for the attachment of carborane cages to polymers, a variety of new routes and extensions to polymeric metallocarboranes may easily be envisaged. Considerable derivative chemistry of carboranes exists which would allow not only the attachment of the polymer to cages in various locations, but also homo- and copolymerizations of monomers already containing boron cages.[35,36]

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Effect of Lectin-Induced Agglutination on Carbon-13 Nuclear Magnetic Resonance Line Width in Sonicated Phospholipid/Glycolipid Vesicles

Sir:

Sonication of aqueous dispersions of phosphatidylcholine results in the formation of small spherical unilamellar vesicles ~250 Å in diameter.[1] Structural similarities and differences between these sonicated vesicles and unsonicated multilamellar liposomes are of biological interest because these systems can serve as models of natural membranes with widely different radii of curvature.[2] Sonication of phosphatidylcholine dispersions causes narrowing of NMR resonance peaks assigned to the protons and carbons of phosphatidylcholine,[3-12] and the reasons for this have been debated. Some have argued that the line narrowing is due to increased disorder in the packing of the phospholipid molecules in the sonicated vesicles relative to that in unsonicated dispersions.[3-6] Others believe that the observed decrease in line width is not related to any structural difference between phospholipids in sonicated vesicles and in unsonicated dispersions, but is related to motional narrowing resulting from the faster tumbling rate of the small sonicated vesicles.[7-9] Chan et al.[4] and Horwitz et al.[6] attempted to eliminate tumbling as an agent of motional narrowing by showing that the ^{1}H NMR line widths of the phospholipid protons in sonicated vesicles are independent of solution viscosity. This interpretation has been questioned, however, because of the possibility that hydration layers at the vesicle surface could render vesicle tumbling insensitive to bulk solution viscosity.[9]

Since a variety of other physical techniques such as dilatometry,[3] differential scanning calorimetry,[13,14] electron spin resonance,[15] and fluorescence depolarization[13] have shown differences in the physical properties of sonicated and unsonicated phospholipid dispersions, it is of interest to determine whether the NMR spectral differences between sonicated and unsonicated dispersions are due, in fact, to a difference in tumbling rate or to real differences in phospholipid motion and packing. To answer this question, we have prepared phospholipid/glycolipid vesicles which can be quantitatively agglutinated by a plant lectin (carbohydrate-binding protein). These vesicle–lectin aggregates are large visible precipitates whose tumbling rate is similar to that of unsonicated dispersions. Using tri[*N-methyl*-^{13}C]choline labeled phosphatidylcholine (^{13}C-PC),[16,17] we studied the effect of lectin-induced agglutination on the line width of the [*N-methyl*-^{13}C]choline resonance of the sonicated vesicles.

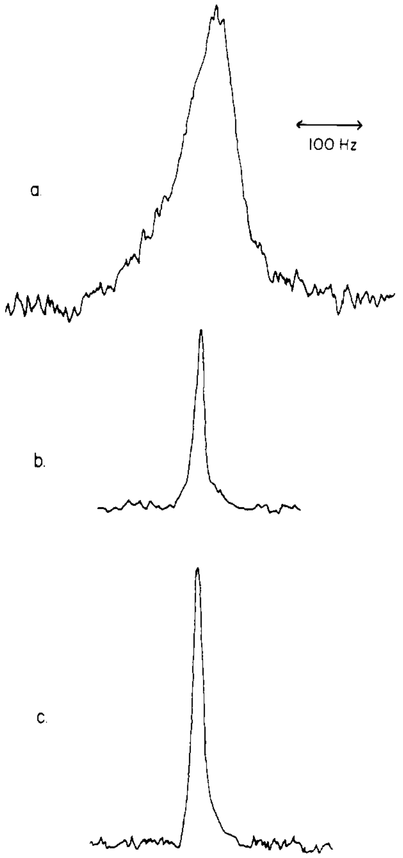

Figure 1. ^{13}C NMR spectra of ^{13}C-PC/LC mixtures obtained at 27 °C using a Bruker HX-270 Fourier transform spectrometer operating at 67.9 MHz with 3 W of decoupling power: (a) unsonicated ^{13}C-PC/LC (10:1, m/m) dispersion (7000 accumulations); (b) sonicated ^{13}C-PC/LC (10:1, m/m) vesicles (1000 accumulations); (c) lectin-agglutinated sonicated ^{13}C-PC/LC (10:1 m/m) vesicles (1500 accumulations). 8 K data points and a recycle time of 0.8 s were used to obtain the spectra.

An unsonicated dispersion of ^{13}C-PC/LC (10:1, mol/mol) exhibits the ^{13}C NMR spectrum shown in Figure 1a at 27 °C. The single *N*-methyl carbon resonance is broad ($\Delta\nu_{1/2}$ = 86 Hz) and asymmetric, indicative of restricted anisotropic motion of the phosphatidylcholine polar head group. This spectrum has the same line width and spectral appearance as that of unsonicated ^{13}C-PC alone. Sonicated vesicles of ^{13}C-PC/LC (10:1, mol/mol), on the other hand, exhibit a single sharp resonance ($\Delta\nu_{1/2}$ = 14 Hz), as shown in Figure 1b. This line width is slightly larger than that observed for ^{13}C-PC vesicles ($\Delta\nu_{1/2}$ = 12 Hz).

Addition of 400 μl of a solution of *R. communis* lectin[22] (4.88 mg/mL) to 1.2 mL of the clear sonicated ^{13}C-PC/LC (10:1, m/m) vesicle solution (3 μmol of ^{13}C-PC/mL) results in the formation of a flocculent white precipitate. The ^{13}C NMR spectrum of the redispersed lectin–vesicle aggregate, shown in Figure 1c, is similar to that of the unagglutinated ^{13}C-PC/LC vesicles (Figure 1b) although the line width for the aggregate is slightly larger ($\Delta\nu_{1/2}$ = 16 Hz). To ensure that the ^{13}C-PC/LC vesicles were quantitatively agglutinated by the quantity of lectin added, the agglutination was repeated under exactly the same conditions, using sonicated ^{14}C-PC/LC (10:1, mol/mol). After addition of lectin, the suspension was centrifuged at 12 000 × *g* for 20 min at 4 °C, resulting in sedimentation of >97% of the radioactive ^{14}C-PC, and thus