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STUDIES OF POLYMER-BOUND MACROCYCLIC POLYTERTIARY
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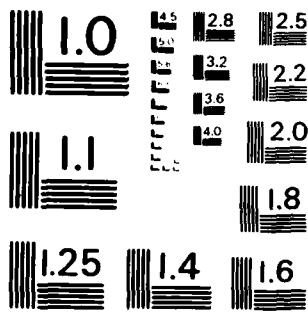
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The goals of this research were to incorporate macrocyclic polyphosphines (MPP) into polymer supports and to study the properties of such polymer-bound species. Synthetic efforts were successful in the preparation of functionalized intermediates which could be elaborated into functionalized MPP, capable of incorporation into polymers. A Diels-Alder route to 1,2-bis(phosphoryl)-4-X-benzene, where X = CH ₂ OAc has been developed. The photochemical Arbusov reaction of 1,2-dichlorobenzene and 3,4-dichlorotoluene has been studied, and gives access to 1,2-diphosphorylbenzenes and 3,4-diphosphoryltoluenes, respectively. The		

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latter compound, as well as the Diels-Alder product can be used as precursors to functionalized MPP. Very recently an efficient method for the reduction of 1,2-diphosphorylbenzenes to 1,2-diphosphinobenzenes has been developed, which involves a reagent produced from the reaction of trimethylsilyl chloride and lithium aluminum hydride. Three MPP have been incorporated into polystyrene supports: *cis*-2,17-diphenyl-2,17-diphospha-6,13-dioxatricyclo[16.4.0.0^{7,12}]-docosa-7(12),8,10,1(18),19,21-hexaene (14-P₂O₂); *cis*-2,10-diphenyl-6-phenyl-6-aza-2,10-diphosphabicyclo[9.4.0]pentadeca-11(1),12,14-triene (11-P₂NPh); and *cis*-2,10-diphenyl-6-aza-2,10-diphosphabicyclo[9.4.0]pentadeca-11(1), 12,14-triene (11-P₂NH). The polymer attachment of the 14-P₂O₂ was on the dioxabenzene side, 11-P₂NPh via the N-Ph group, and the 11-P₂NH, via the nitrogen atom. The polymers used were 1% crosslinked polystyrene resins. The ability of polymer-bound (PB) MPP to coordinate transition metals was probed using Co(II). The PB-14-P₂O₂ and 11-P₂NPh have complexes which had the stoichiometry (PB-MPP)₂CoX₂, by comparison of solid state UV spectra with those from non-PB-MPP Co(II) complexes. In one case the (MPP)₂CoX₂ structure was confirmed by a single crystal x-ray structure determination. Thus the polydentate MPP were acting as bidentate ligands and two such ligands were attached to each metal center, using 1% cross-linked polymer, *i.e.* site-site isolation is not achieved. Preliminary studies of the more highly cross-linked polymers indicated that site-site isolation is achievable. The PB-11-P₂NH behaves as a tridentate ligand towards Co(II) giving complexes of the type (PB-11-P₂N)CoL₂, by comparison of spectral properties with those of well-characterized non-PB-MPP complexes. Several approaches to precursors of optically active PB-MPP and related compounds have been investigated.

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Studies of Polymer-Bound Macrocyclic

Polytertiary Phosphines

2/1/79 - 7/31/83

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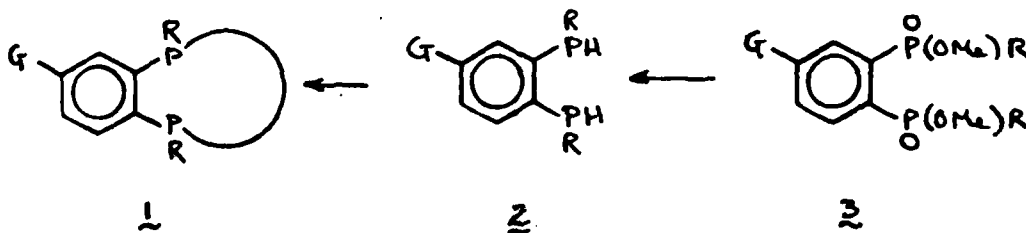
I. Research Objectives

→ The research objectives of this work were to synthesize functionalized macrocyclic polyphosphines (MPP) and to use the functional group to attach the MPP to a functionalized polymer support (PS). The PS-MPP species were to be studied for their ability to coordinate transition metals, and to compare the behavior of PS-MPP-metal complexes with that of non-PS-MPP analogs. ←

II. Synthesis

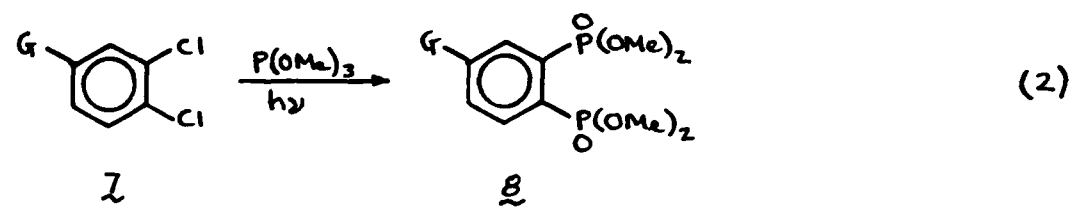
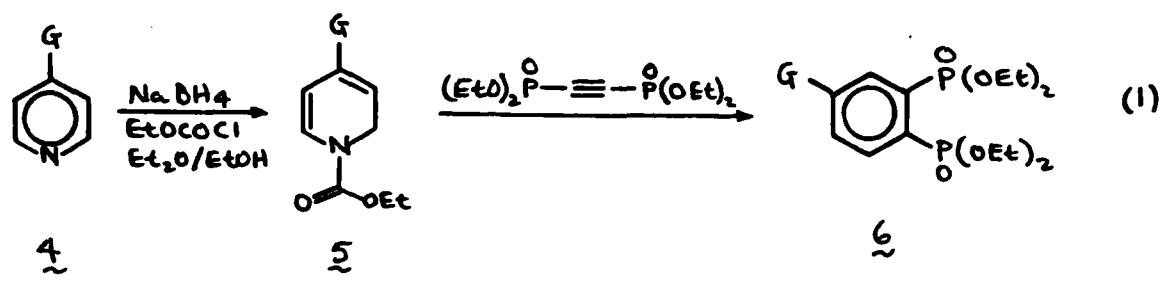
A. The 4-X-1,2-Diphosphoryl Moiety

In order to have a generalized approach to functionalized MPP (1) it is necessary to have routes to species 2, which could be derived from the diphosphoryl compound 3. We have developed two different routes to 3, as shown in



eq. 1 and 2. The chemistry shown in eq. 1 with G = H has been published,¹ but that with G = CH₂OAc has not.² Similarly, the reaction shown in eq. 2 and subsequent reduction chemistry (vide infra) with G = H is to be published³ but

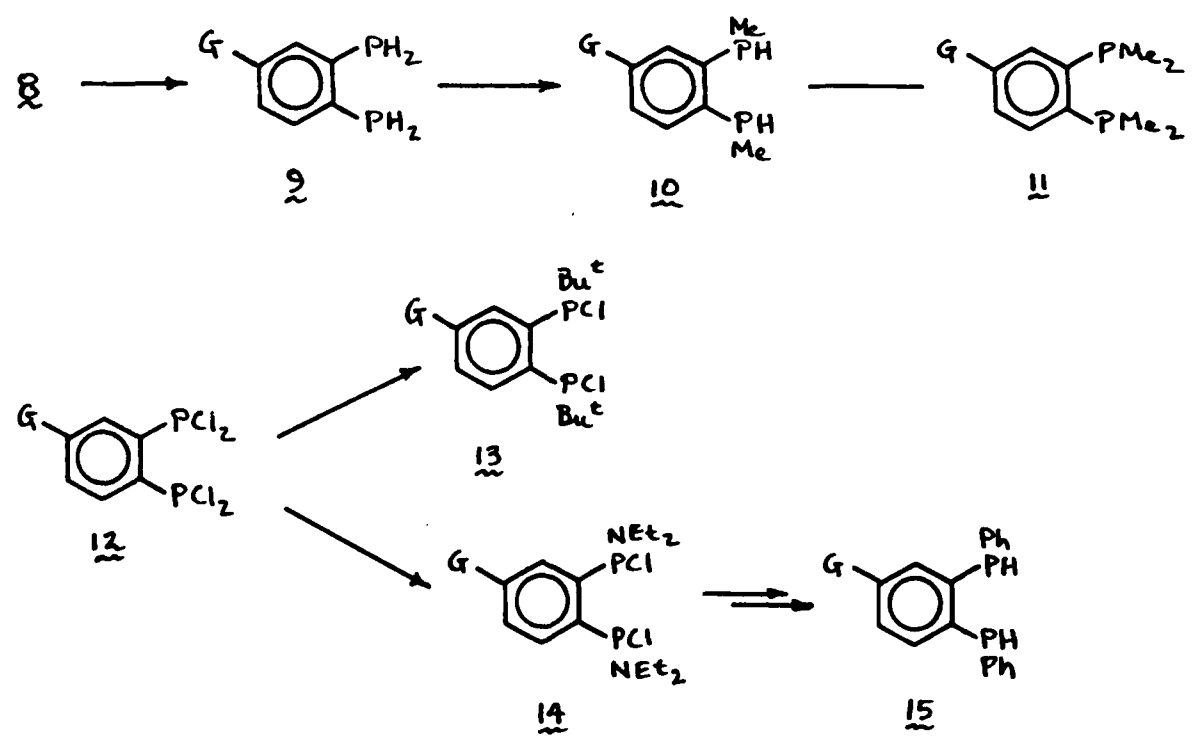
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that with G = Me has not been communicated.⁴

B. Reduction of the 1,2-Diphosphorylbenzenes and Further Transformations

The transformation of 8 to 9 (G = H) (Scheme 1) has challenged us for over a year, with no reducing agent giving a yield better than ca. 20%. Very recently,

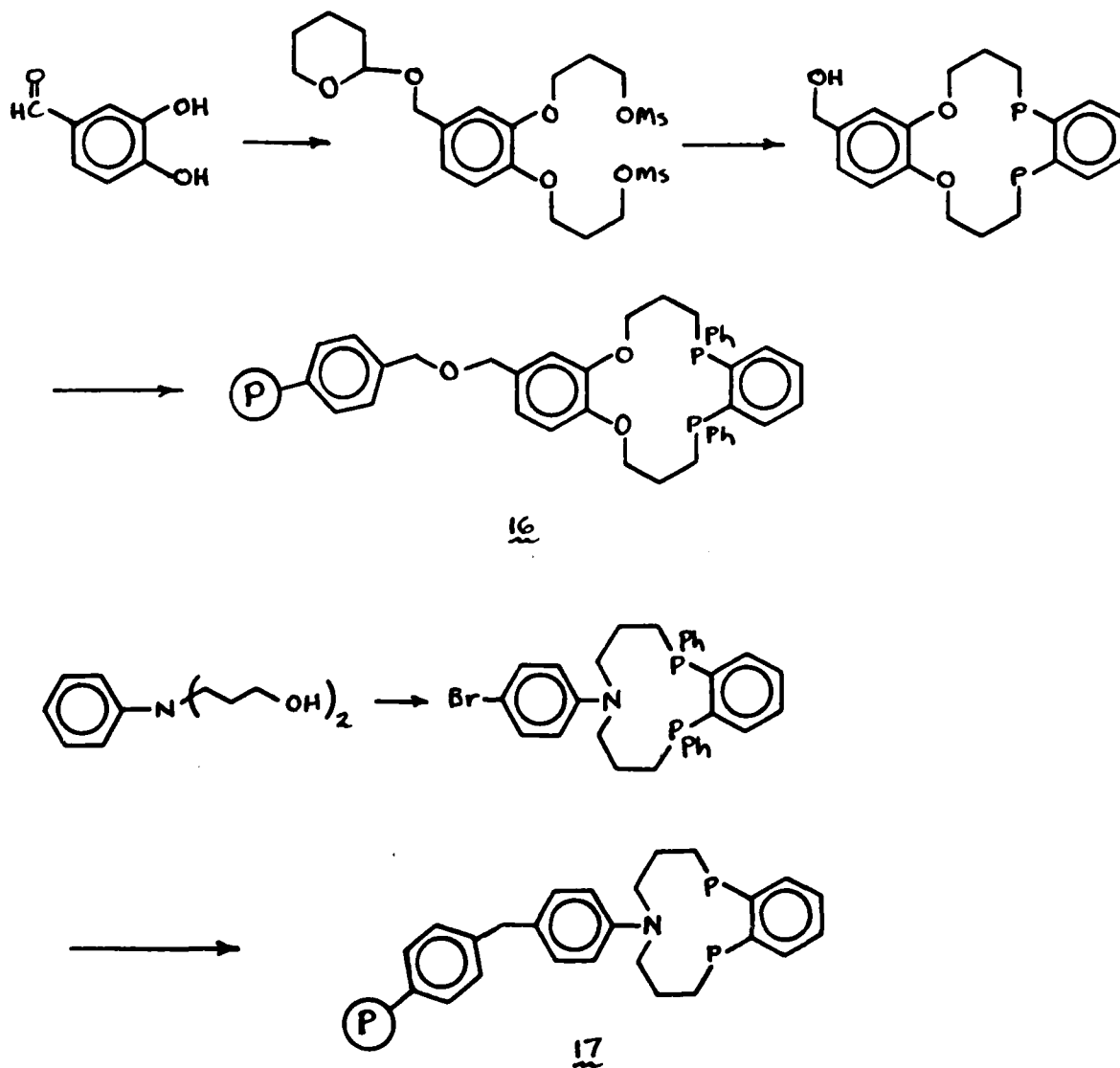


Scheme 1

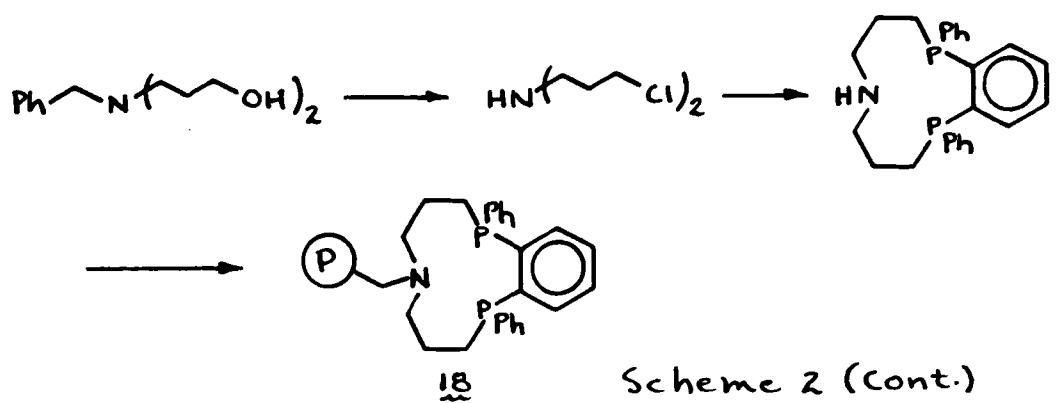
however, we have discovered a reagent derived from trimethylsilyl chloride and lithium aluminum hydride which gives $8 \rightarrow 9$ ($G = H$) in 85% distilled yield. This has allowed the synthesis of species $10 - 15$.³⁻⁵ Unfortunately, this breakthrough came essentially at the end of the grant period so that compounds 10 , 13 , 14 and 15 were unavailable for macrocycle synthesis.

C. Synthesis of Functionalized MPP

Three different PS-MPP were prepared as shown in Scheme 2. These involved a specific procedure for each MPP, because we had not been able to develop a general procedure (now available, *vide supra*) in time. The synthetic manipulations



Scheme 2



summarized in Scheme 2 are relatively straightforward, although not necessarily without pitfalls that required significant amounts of time to solve. We have used commercially available 1% crosslinked Merrifield's resin with 0.70 meq/g chloromethylation for most of our work so far but we also have done preliminary work on the more rigid macroreticular resins. Regardless of the mode of introduction of the ligand onto the polymer [ether formation (1), C-C bond formation (3)], only about 50% of the chloromethylated sites are substituted, as determined by elemental analysis and also titration using Co(II) (*vide infra*). Apparently the rest of the sites are sterically inaccessible. This work will be published.⁶

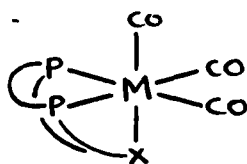
D. Other Synthetic Efforts

A series of 11- and 14-membered t-arsinomacrocycles were synthesized and described fully in three publications,⁷⁻⁹ as well as three macrocycles which contain secondary-phosphino sites (*i.e.* capable of polymer attachment).¹⁰

III. Metal Complexation of Non-PS-MPP and Other Ligands

A. Metal Carbonyls

In anticipation of comparison of properties of PS-MPP-transition metal complexes with those of the non-PS-MPP analogs we have studied the electrochemistry of a series of tricoordinating MCC complexes of group VI metal tricarbonyls of the type 19. The oxidation potential was found to vary by ca. 0.42 - 0.45 V as a



19, X = PhP, S, MeN
M = Cr, Mo, W

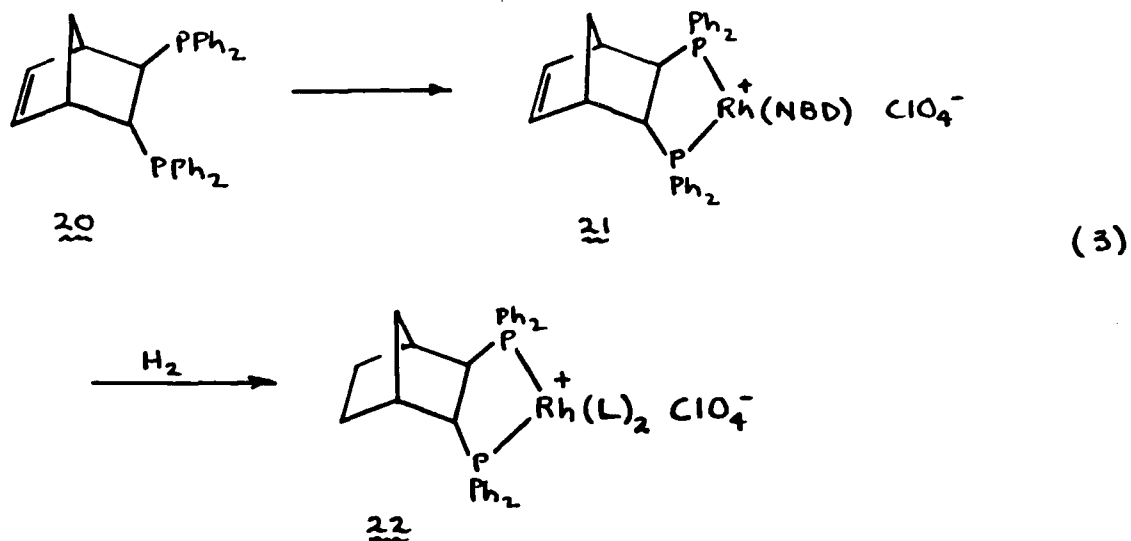
function of X, indicating considerable potential in fine-tuning the redox potential by judicious ligand design.¹¹

B. Cobalt(II) Complexes

An extensive study of the Co(II) complexation by MPP which had combinations of t-phosphino and hard (O,NPh) coordination sites revealed rather complicated behavior, and four types of complexes were found to be interconvertible. This has been fully described in a recent report.¹²

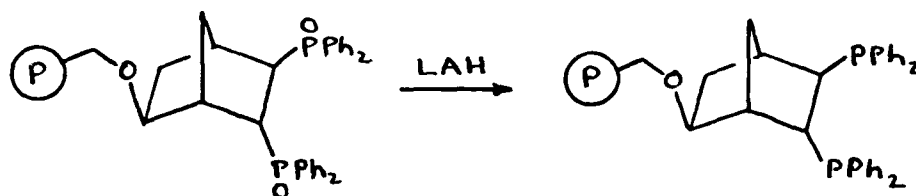
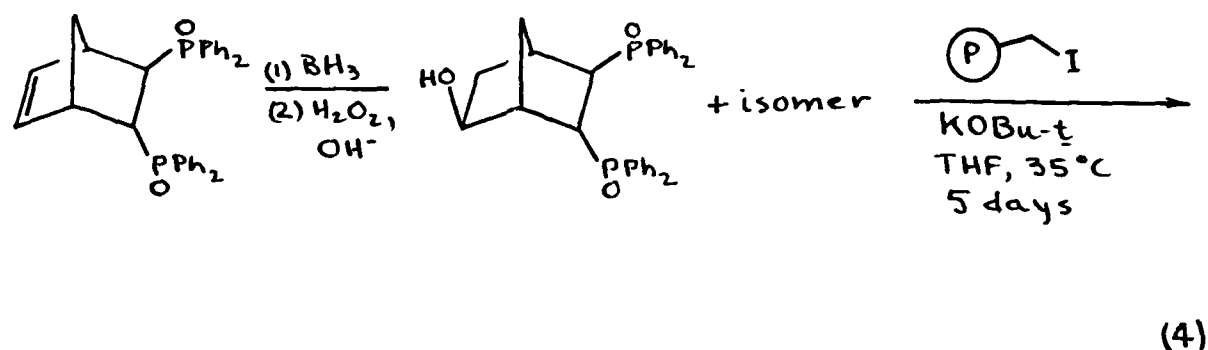
C. Chiral Diphosphines

The chiral diphosphine 20 was transformed into the Rh(I) complex 21 (eq. 3) and the structure was determined by x-ray crystallography, the point of interest



being the way in which the [2.2.1] skeleton accommodates the considerable strain upon chelation of the Rh(I) center. It was also established that under catalytic hydrogenation conditions, 21 is transformed into 22 (L = HOME), which is the operating catalyst in asymmetric hydrogenations of enamides.¹³ More recently we have described the structure of the penultimate catalyst precursor 22 (L = NBD).¹⁴

Preliminary work has resulted in the polymer attachment of 20 as shown in eq. 4.¹⁵ The polymer used was a 2% divinylbenzene crosslinked polystyrene which had been chloromethylated, followed by substitution by I⁻.



In conjunction with these studies we developed the first NMR spectroscopic method for determination of enantiomeric purity of chiral, chelating diphosphines, utilizing a chiral Pd(II) complex.¹⁶

IV. Cobalt(II) Complexes of PS-MPP

The CoX₂ (X = Cl, Br, I, SCN, NO₂) uptake by 16 - 18 was used as a measure of the ligand loading on the polymer after it was established that with 16 and 17

the complex stoichiometry was $(\text{PS-MCC})_2\text{CoX}_2$. This was done by comparison of solid state UV spectra of the PS-complexes with those of the non-PS analogs. The agreement between this spectroscopic and combustion analytical method for the ligand loading was very good.^{6,17} The complex stoichiometry indicated that site-site isolation did not occur with the 1% DVB crosslinked polystyrene. Not only is the polymer support quite flexible, but also the length of attachment is considerable. We did show in one case, however, that the use of a highly rigid, macroreticular resin of type 17 gave rise to complexes of the type $(\text{PS-MCC})\text{CoCl}_2$ which was blue, indicating a tetrahedral environment about Co(II). Thus site-site isolation was achievable with the more highly rigid macroreticular PS.

The coordination behavior of 18 paralleled that of the non-PS analog, 11- P_2NMe . Thus 18 gave a purple complex with CoCl_2 , as opposed to the green complexes obtained with 16 and 17.

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