

active site of $\text{Hg}^{11}\text{HCAB}$. Therefore the order of ligand binding strengths observed to date is $\text{CN}^- > \text{Br}^- > \text{Cl}^- > \text{en} \approx \text{HCO}_3^- \approx \text{CH}_3\text{CO}_2^-$ in the active site of $\text{Hg}^{11}\text{HCAB}$.

Longitudinal relaxation times, T_1 , for ^{199}Hg in $^{199}\text{Hg}^{11}\text{HCAB}$ are ~ 2 s, based on optimization of the flip angle. The use of broad-band proton decoupling, which was impractical with the homemade probe used herein, should lead to line narrowing and, hence, to improve signal-to-noise ratios in future experiments.

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Preparation of Polymer-Bound Bipyridine and Some of Its Transition Metal Complexes

Sir:

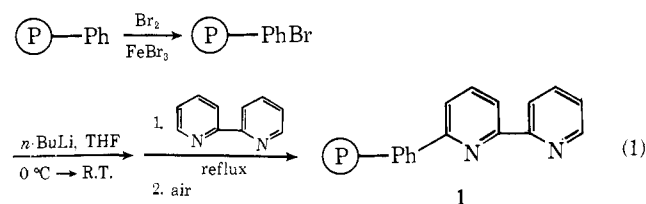
Anchoring reagents to insoluble supports has come to be known as solid-phase synthesis. Based on the pioneering efforts

of Merrifield in polypeptide synthesis,¹ rapid developments now not only make polypeptide synthesis on polymer supports routine, but immobilized enzymes, immobilized photosensitizers, immobilized organic reagents, and immobilized transition metal catalysts are also frequently reported.²

The immobilized transition metal catalyst offers, potentially, a plethora of practical advantages. Significant examples, generally employing phosphine ligands, have been reported by Grubbs,³ Pittman,⁴ Whitehurst,⁵ and others.^{6,7} Unfortunately, polymeric phosphine transition metal complexes are occasionally so labile that heterogeneous catalysis is not observed⁸ or leaching of the metal from the polymer limits catalyst reusability.⁹ In addition, potential applications exist in analysis, in single reactions, in photoprocesses, and in other aspects of synthesis which make these polymer-based reagents of great general potential.

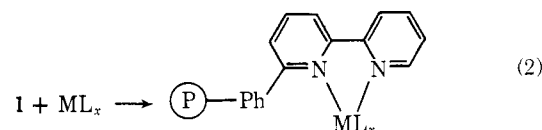
To increase the general availability of immobilized transition metal catalysts, we undertook the synthesis and study of polymer-based chelating ligands.¹⁰ We report herein the facile synthesis of a remarkably general polymer-bound chelating ligand and demonstrate its versatility by the many transition metal complexes prepared from it.

Bipyridine is attached to phenyl residues of polystyrene-2% divinylbenzene copolymer beads through the reaction sequence shown in eq 1. Ring bromination and lithiation are commonly



used in the preparation of polystyrene derivatives.¹⁶ In our system the stoichiometry of the ring bromination is controlled so that $< 25\%$ of the phenyl residues are brominated. Solid bipyridine is added to a tetrahydrofuran suspension of the lithiated polymer and the resulting solution is brought to reflux. After a few hours, the solution is allowed to cool to room temperature and air is bubbled through the solution until a color change from dark purple to yellow-gold is observed. The polymer is separated by filtration and washed with copious amounts of various solvents. The yellow-gold polymer, characterized by its infrared spectral data,¹⁷ swells less than the original copolymer in standard solvents and is stable to large quantities of these solvents. Elemental analysis is quantitatively unreliable¹⁸ but suggests ca. one bipyridine per nine styrene units.

Complexation of metal salts with **1** is strikingly facile. In a typical procedure, **1** is added to an $\sim 10^{-3}$ M tetrahydrofuran solution of ferric chloride, or other metal salt. The resulting



solution is shaken for several minutes and the polymer is filtered off and washed with copious amounts of various solvents. The amount of metal bound to the polymer can be determined from the quantitative analysis of the visible spectra of the metal ion solutions before and after exposure to the polymer. The variety of metal salts and the amount of metal incorporated, as determined by this method, are presented in Table I. These data illustrate the generality of this method with respect to metal, oxidation state, and counterion.

The infrared spectra of the metal complexes are very similar to each other and differ from that of **1** by the addition of a

Table I. The Amounts of Various Metal Salts Which Become Bound to Polymer **1** in Tetrahydrofuran

Metal salt	Quantity bound (mequiv of metal/g of polymer)
Cr(NO ₃) ₃	0.22
MnI ₂	0.14
FeCl ₃	0.83
RuCl ₃	Not determined
CoCl ₂	0.35
Ni(NO ₃) ₂	0.70
Pd(O ₂ CCH ₃) ₂	0.73 ^a
CuBr ₂	0.34 and 0.37 ^b
AgNO ₃	Not determined

^a Determined by elemental analysis for Pd (Spang Microanalytical Laboratory). ^b Two different batches of polymer were used.

Table II. Effect of Solvent on the Quantity of FeCl₃ Bound to **1**

Solvent	Swelling factor ^a	Quantity bound (mequiv/g)
Methanol	1.0	0.002
Acetonitrile	1.4	0.25
Tetrahydrofuran	2.2	0.83
Ethyl acetate	2.4	1.2
Ethyl acetate-Benzene (1:1)	3.2	1.2

^a The ratio of volume of swollen to nonswollen polymer **1**.

weak, broad band at ~1700 cm⁻¹ and by an increased intensity of the bands at 1100 and 905 relative to the intensity of those at 700 and 755 cm⁻¹.

The data in Table II show that the amount of iron bound to the polymer can be controlled, at least in part, by proper choice of the solvent system. Only binding to surface bipyridyl groups should occur in methanol. The amount of iron binding increases as the swelling factor increases, to a maximum at ethyl acetate. The lack of further increase in the extent of iron incorporation may indicate that all the bipyridyl sites are now complexed.

The potential applications of **1** and its metal complexes should be obvious and the catalytic and analytical properties of these materials are currently under vigorous study.

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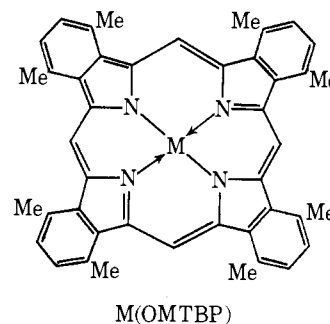
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Conductive Molecular Crystals. Partially Oxidized Octamethyltetraazaporphyrins

Sir:

The study of the quasi-one-dimensional electrical and magnetic properties of stacked molecular crystals is currently of great experimental and theoretical interest,¹ but the range of materials with high conductivities remain limited. It appears that two necessary conditions for obtaining high electrical conductivity are a structure containing infinite stacks of closely packed planar molecules and the occurrence of a nonintegral formal oxidation of the constituents. Guided by these requirements we have embarked on a program of synthesizing nonintegral oxidation-state crystals through substoichiometric oxidation of planar macrocyclic transition ion complexes (ML).

The I₂ oxidation of the metallophthalocyanines (M(Pc)) has recently been shown to yield highly conductive materials.² As part of the program to explore metal-macrocycle systems, we have prepared a variety of transition-metal complexes of 1,4,5,8,9,12,13,16-octamethyltetraazaporphyrin



(M(OMTBP)) and have subjected them to I₂ oxidation forming the partially oxidized M(OMTBP)(I)_x. In this communication we discuss the oxidation products of Ni(OMTBP), for which single crystals of suitable quality for characterization have been obtained. A particularly important result is the isolation of conductive single crystals with two distinct degrees of partial oxidation, both of which exhibit metal-like conductivity.

The condensation reaction³ of 1,3,4,7-tetramethylisindole⁴ and nickel acetate tetrahydrate directly gives Ni(OMTBP), which was purified by recrystallization from 1,2,4-trichloro-