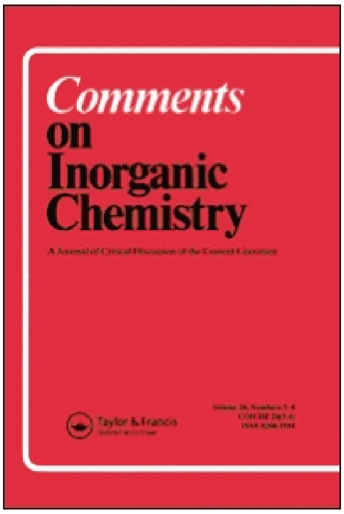

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Coordination Chemistry of Eight-Membered Polyphosphorus Heterocycles

Edward H. Wong[a]
[a] Department of Chemistry, University of New Hampshire, Durham, New Hampshire

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Coordination Chemistry of Eight-Membered Polyphosphorus Heterocycles

EDWARD H. WONG
Department of Chemistry,
University of New Hampshire,
Durham, New Hampshire 03824

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The coordination and reaction chemistry of eight-membered polyphosphorus heterocycles is outlined with particular focus on a versatile tetraphosphoxane P_4O_4 ring system. This ligand's coordination modes includes an *exo*-ditopic form which has been used to prepare a mixed-valent family of heterobimetallic complexes with conserved cage structures suitable for the study of metal-metal interactions.

Key Words: *polyphosphorus heterocycle, heterobimetallic complexes, eight-membered rings, mixed-valent complexes, cage complexes*

A. INTRODUCTION

Eight-membered rings containing two or more donor atoms occupy a useful position between macrocycles which can serve as multidentate ligands to envelope one or more metal centers and smaller heterocycles which have limited chelating ability.[1] Since incorporation of donor atoms into cyclic and polycyclic structures endows specific and rigid

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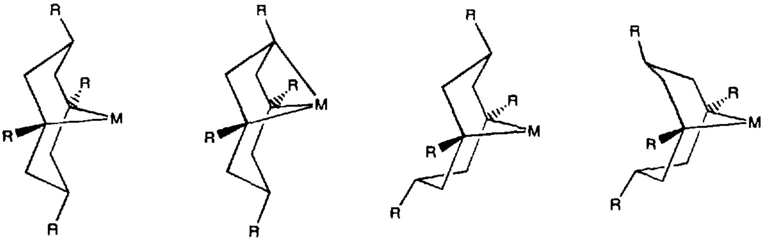


FIGURE 1

steric constraints on the coordinated metal center (Fig. 1), chelation by 8-membered rings should have major ramifications on its catalytic and stereospecific reactivities.

A particularly attractive aspect of a tetradentate 8-membered ring lies in its ability to act as an *exo*-ditopic receptor for two metals.[2] To attain this mode of binding, the heterocycle must adopt a *boat/boat* conformation such that two lone pairs (from donor atoms D) are convergent at *each* of the two potential coordination sites (Fig. 2). Assuming general synthetic routes, heterobimetallic complexes can be systematically prepared and studied. Also, depending on the extent of through-bond and (or) through-space intramolecular metal–metal interaction, a variety of mixed-valence behavior can occur. Such molecular units may be of interest, for example, for the construction of molecular wires.

An additional feature of interest in 8-membered heterocycles is the possibility of 1,5-transannular interactions which has been explored for tetrasulfur tetranitride, dithia-, diphospha-, and related ring systems (Fig. 3).[3]

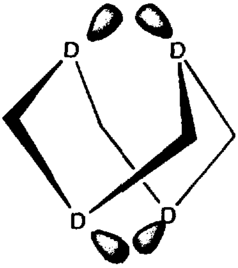


FIGURE 2

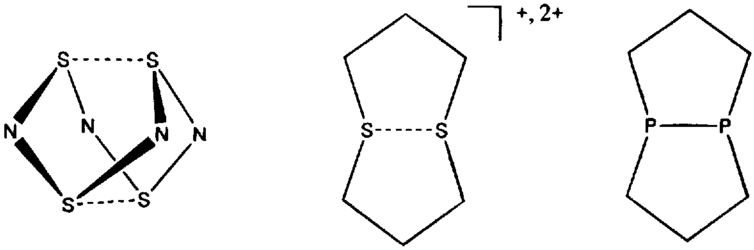


FIGURE 3

Several families of 8-membered heterocycles containing two or more trivalent phosphorus atoms are already known. These include the 1,5-diphosphocines, the 1,5-diaza-3,7-diphosphocines, the 1,3,5,7-tetraphosphazanes, and 1,2,5,6-tetraphosphocine (Fig. 4).[4] To varying extents, the coordination chemistry of most of these have been reported with monometallic chelation appearing to be the most prevalent complexation mode (Fig. 5).[4,5]

We have been interested in heterocycles containing alternating phosphorus and oxygen atoms called *cyclo*-phosphoxanes and have found the P_4O_4 ring (tetraphosphoxane or 1,3,5,7-tetraoxa-2,4,6,8-tetraphosphocine, Fig. 6) to be especially versatile in its metal-coordinating chemistry.[6–10] In this article, we will summarize the synthetic, structural and reaction chemistry of this unique 8-membered ring system.

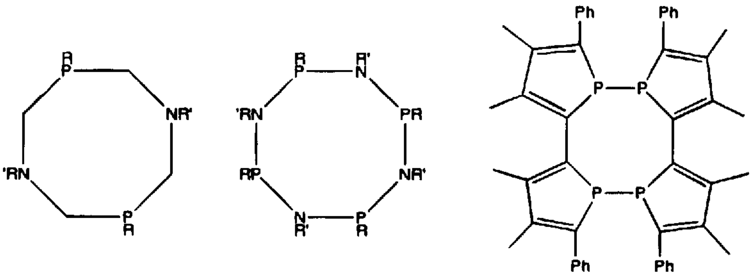


FIGURE 4

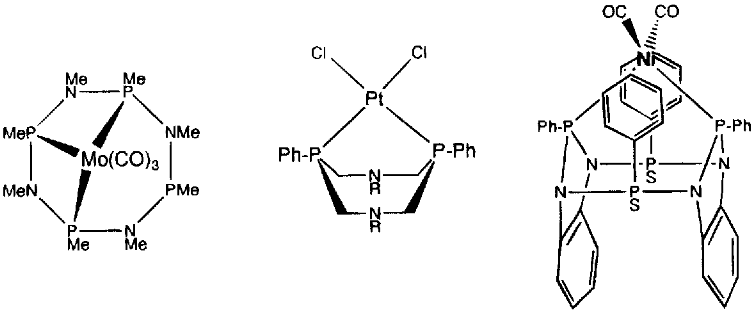


FIGURE 5

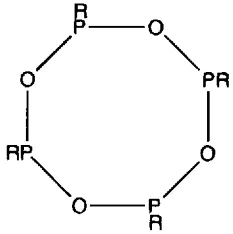


FIGURE 6

B. SYNTHESES, STRUCTURES, AND PROPERTIES OF TETRAPHOSPHOXANE COMPLEXES

1. Synthesis

Heterocycles with alternating trivalent phosphorus and oxygen atoms (phosphoxanes) are only known for the P_2O_2 and P_3O_3 rings with dialkylamino- or aryloxy-substituents.[11] In 1988, we reported the assembly of the first tetraphosphoxane in coordinated form by a serendipitous synthesis from $Mo(CO)_6$ and $({}^iPr_2N)_2P(O)H$.[6] The bimetallic product $Mo(CO)_4[{}^iPr_2NPO]_4Mo(CO)_4$,

$$2Mo(CO)_6 + 4({}^iPr_2N)_2P(O)H \rightarrow Mo(CO)_4[{}^iPr_2NPO]_4Mo(CO)_4 + 4CO + 4\,{}^iPr_2NH,$$

formally a result of diisopropylamine elimination from the phosphine oxide and carbonyl substitution at molybdenum, has a unique adamantanoid cage structure (Figure 7) with the P_4O_4 heterocycle in a *boat/boat* conformation as an *exo*-ditopic receptor for the two $Mo(CO)_4$ metal fragments. Metal-templating is a critical factor in the formation of this and related products since, in its absence, only intractable polymeric material formed. A monometallic intermediate was isolated under milder reaction conditions and found to be the triphosphoxane complex $Mo(CO)_5[^iPr_2NPO]_3$ (Fig. 8).[12] This quantitatively transformed into the bimetallic cage complex upon further heating.

This particular synthetic route was rather limited in scope since only phosphine oxides with secondary dialkylamino-groups like dicyclohexylamine and dimethylpiperidine (DMP) led to similar cage complexes. Furthermore, changing the metal precursor to $Cr(CO)_6$ or $W(CO)_6$ resulted in formation of very different products while metal halides like $PdCl_2$ and $NiCl_2$ did not yield any stable complexes. This problem was alleviated when triphosphoxanes were used as starting materials in ring expansion reactions. Using a combination of these routes, a variety of tetra- as well as penta- and even hexa-phosphoxane complexes were subsequently prepared (Schemes I and II).[7,8]

An interesting coproduct was provided by the reaction of $[^iPr_2NPO]_3$ with $Fe_2(CO)_9$ which yielded a complex with the formula

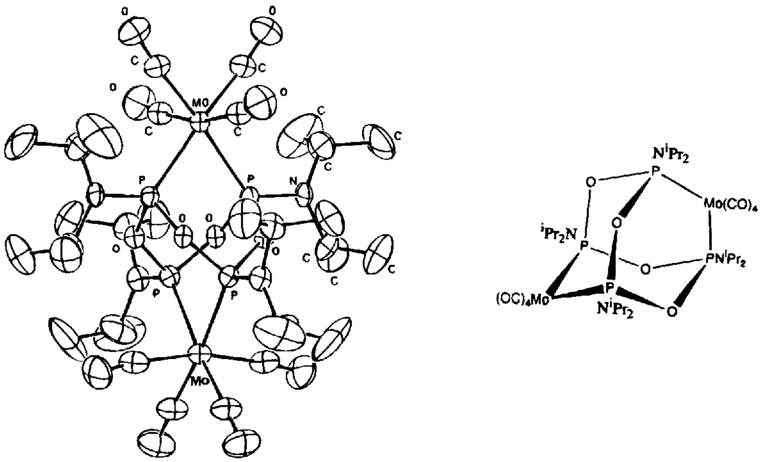


FIGURE 7 Molecular and schematic structures of $Mo(CO)_4[^iPr_2NPO]_4Mo(CO)_4$.

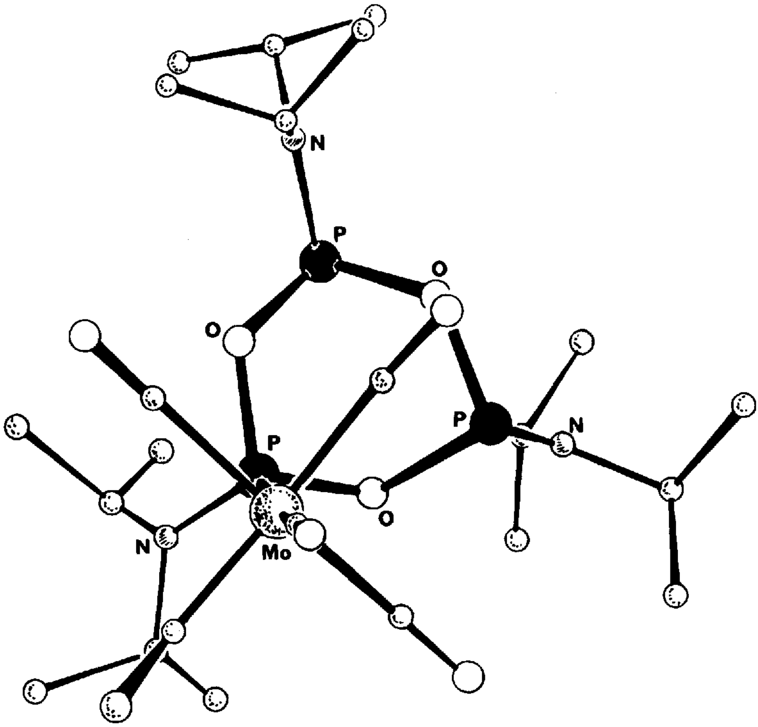
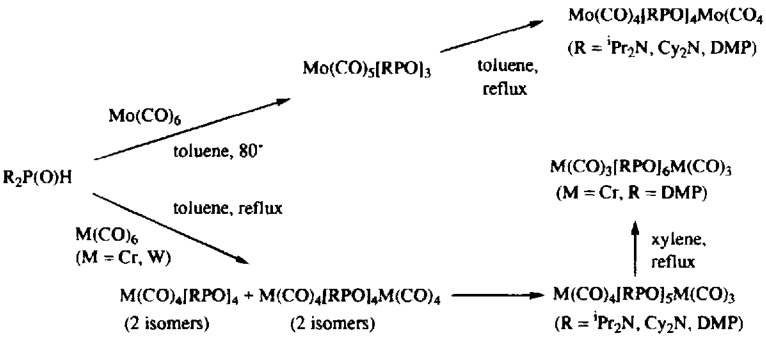
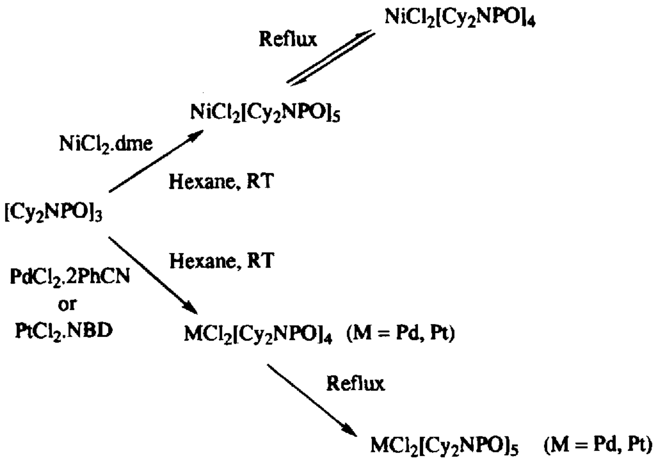


FIGURE 8 Molecular structure of $Mo(CO)_5[^iPr_2NPO]_3$.



SCHEME I



SCHEME II

$Fe(CO)_4[^iPr_2NPO]_4$ as well as the expected $Fe(CO)_3[^iPr_2NPO]_4$ in approximately equal amounts.[8] The molecular structural determination of this revealed a monodentate tetraphosphoxane ring which has undergone a double P–O–P to P–P=O rearrangement to generate a six-membered [P–O–P(=O)–P–P(=O)–O] heterocycle (Fig. 9, Scheme III).

A key breakthrough in the synthesis of P_4O_4 cage complexes was made through the preparation of a monometallic complex, $Mo(CO)_4[^iPr_2NPO]_4$, by the selective demetallation of $Mo(CO)_4[^iPr_2NPO]_4Mo(CO)_2I_2$ (*vide infra*). Reaction of this metalla-ligand with convergent lone pairs and a variety of metal reagents led to a family of heterobimetallic complexes with similar cage structures (Scheme IV).[10]

During the preparation of Mo/Pd cage complexes, it was found that novel $MoP_5O_5PdX_2$ cages formed as thermodynamically favored products.[10]

$$Mo(CO)_4[^iPr_2NPO]_4 + PdX_2.2PhCN \rightarrow Mo(CO)_4[^iPr_2NPO]_4PdX_2,$$

$$Mo(CO)_4[^iPr_2NPO]_4PdX_2 \rightarrow Mo(CO)_3[^iPr_2NPO]_5PdX_2.$$

These interesting compounds are proposed to have the structure shown in Fig. 10. The expected $MoP_4O_4PdBr_2$ cage complex can be isolated after brief reaction times.

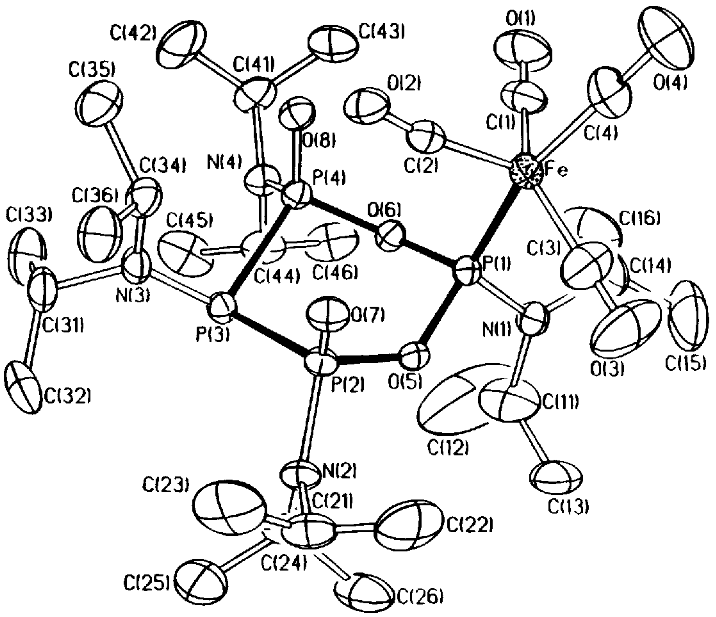
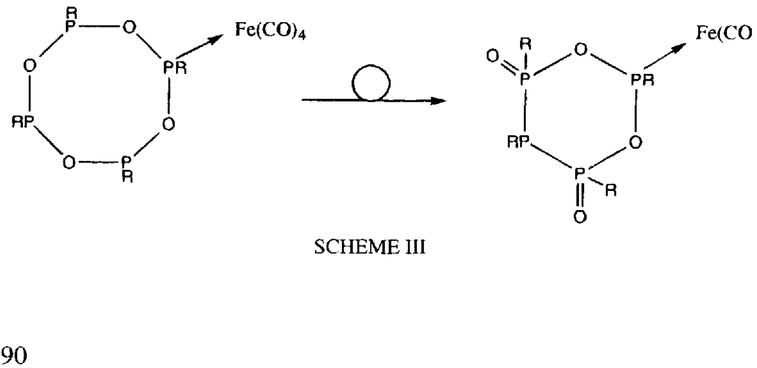


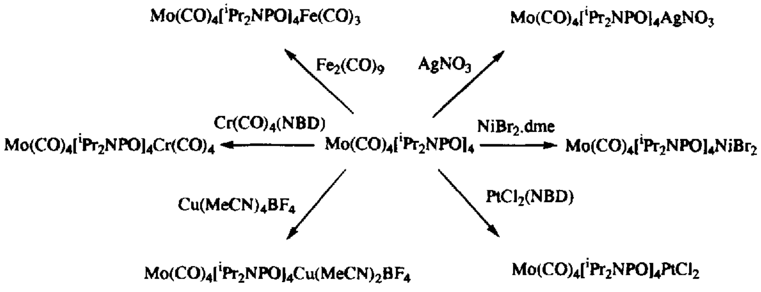
FIGURE 9 Molecular structure of $Fe(CO)_4[^iPr_2NPO]_4$.

An attractive alternate approach to form bimetallic P_4O_4 cage complexes directly from two separate monometallic halves was realized for the $M[PhPO]_4M$ family (where M = Cr, Mo):

$$cis-M(CO)_4(PPhCl_2)_2 + Na_4[cis-M(CO)_4(PPhO_2)_2] \rightarrow 4NaCl + M(CO)_4[PhPO]_4M(CO)_4.$$



SCHEME III



SCHEME IV

Though the yields were moderate at best, potentially this remains a viable route to heterobimetallics as well as cage complexes with a broader variety of phosphorus substituents.[6,13]

2. Structural and Spectral Aspects

The flexibility and versatility of tetraphosphoxane as a ligand has been amply confirmed. It can form monometallic complexes as a bidentate chelator with the P_4O_4 ring in either *boat/chair, chair/chair, boat/boat,* or long *chair* conformations (Fig. 11a–d). It can chelate two metals in either the *boat/boat* (cage) or long *chair* form (Fig. 11e,f). Additionally, it can bridge two metals as found in the Mo/Fe complex (Fig. 11g). One example of an iron tetracarbonyl complex with a rearranged P_4O_4 ring has already been described (Fig. 11h).[8] X-ray structural determinations of all these coordination modes have been completed. Furthermore, the relatively high inversion barrier of 30–35 kcal/mol at the phosphorus centers means that solid-state X-ray configurations are usually main-

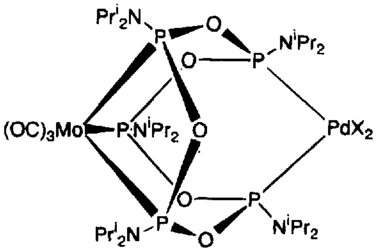


FIGURE 10

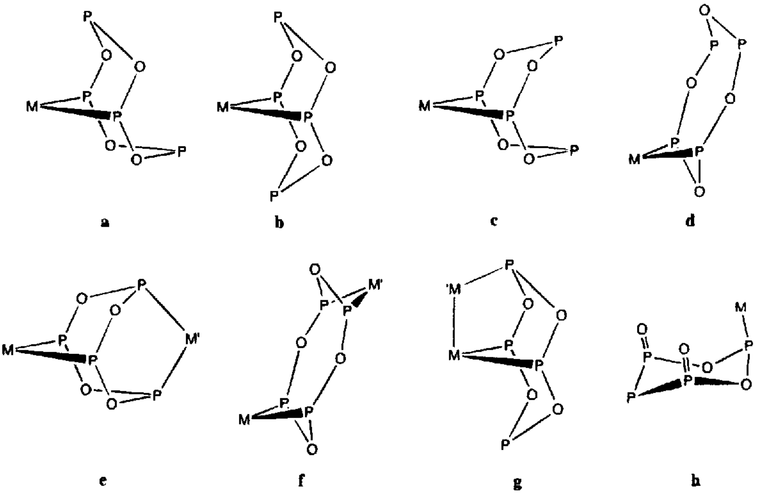


FIGURE 11

tained in solution. This has been confirmed by variable-temperature solution ^{31}P NMR studies.

A survey of the structural data reveals subtle but significant variations in ring P–O distances in accord with the presence and type of coordinated metal centers. Typically, coordinated P–O distances are between 1.60 and 1.65 Å, while uncoordinated P–O bond lengths are longer, between 1.67 and 1.70 Å. Since the P—P separation of every individual phosphoxane P–O–P linkage remains almost invariant at around 3.3 Å (Fig. 12),[14] the oxygen atom appears to serve as an effective relay for transmission of electronic effects upon metal coordination.

Intracage metal–metal separations of the adamantanoid MP_4O_4M complexes depend critically on the P-substituent. For example, the $Mo(CO)_4[^iPr_2NPO]_4Mo(CO)_4$ cage metals are 6.00 Å apart, while the $Mo(CO)_4[PhPO]_4Mo(CO)_4$ separation has narrowed to only 4.53 Å.[6]

Availability of the series of heterobimetallic cage complexes allows a direct comparison of intracage metal/metal interactions. The conserved $Mo(CO)_4$ moiety has a number of sensitive probes to gauge such effects, including carbonyl IR stretching frequencies and ^{13}C NMR chemical shifts.[15] A schematic plot of the data (Scheme V) shows a correlation of these properties to the formal oxidation state of the heterometal across

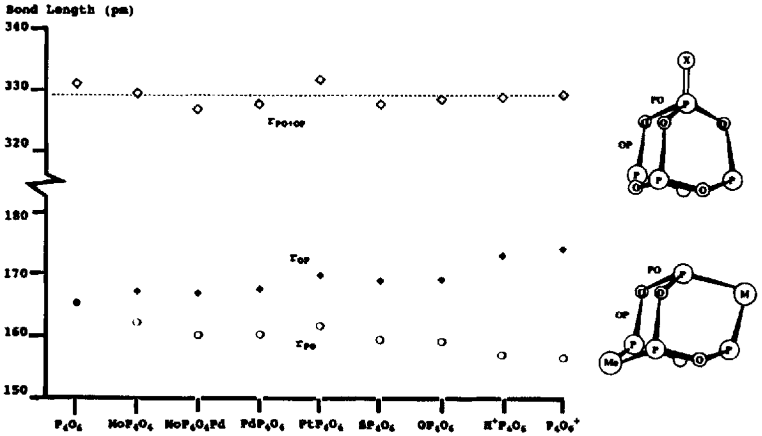
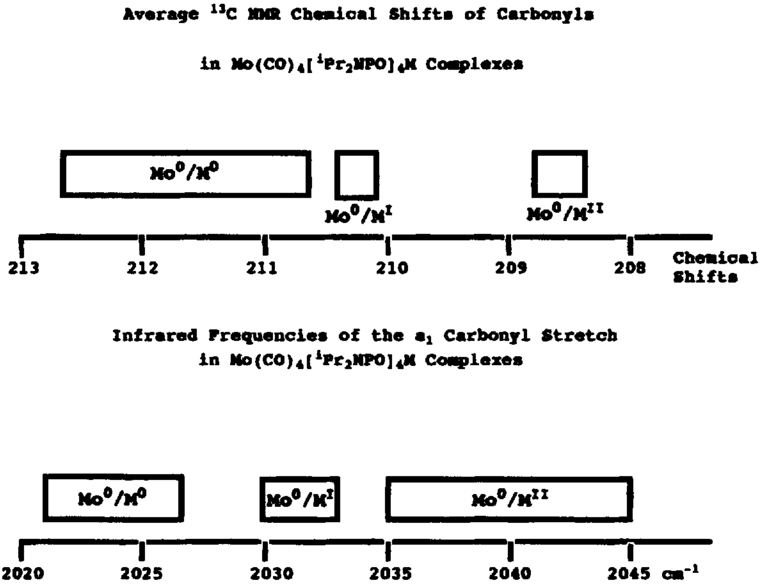


FIGURE 12 Relationship between P–O shortening and O–P lengthening in P_4O_6, its derivatives, and P_4O_4 complexes.



SCHEME V

the cage, consistent with decreasing electron density at $Mo(CO)_4$ due to increasing positive charge.

The use of ^{31}P NMR spectroscopy to aid in establishing solution structures and stereochemistry is well documented.[16] We have made abundant use of this technique to assign solution geometries of phosphoxane complexes. For example, the mixed-valent $Mo(CO)_4[^iPr_2NPO]_4Mo(CO)_2I_2$ spectrum consists of an AMX_2 pattern with clearly resolved $^2J_{PP}$ couplings of 2, 12, and 40 Hz. These required the assignment of a non-octahedral geometry (trigonal prismatic) at the $Mo(CO)_2I_2$ vertex (Fig. 13) which was later confirmed by an X-ray diffraction study.[17]

The unusually low-field signals (+305 to +307 ppm) observed for the phosphine substitution products of $Mo(CO)_4[^iPr_2NPO]_4Mo(CO)_4$ such as $Mo(CO)_3[^iPr_2NPO]_4Mo(CO)_2PPh_3$ immediately revealed a possible phosphido-bridged bimetallic species.[9] Complete P---P connectivity can then be assigned using a two-dimensional COSY experiment wherein only two-bond P–P couplings are observed as off-diagonal peaks (Fig. 14).[18] The well-known ring contribution (Δ_R) for four- and six-membered phosphine chelates has now been ascribed to the shift tensor component normal to the chelate plane.[19,20] This proved very useful for distinguishing four-membered MPOP chelate rings in our compounds from the usual six-membered ones. For example, the two configurational isomers of $Cr(CO)_4[DMP\text{-}PO]_4Cr(CO)_4$ can be structurally assigned based on their ^{31}P chemical shifts of 171.1(singlet) and 155.4(singlet) ppm.[8] The former has the adamantanoid cage structure with all six-membered chelate rings while the latter has the long-chair geometry (Fig. 11e and f, respectively) featuring two Cr–P–O–P chelate rings with an associated upfield Δ_R of −15.7 ppm.

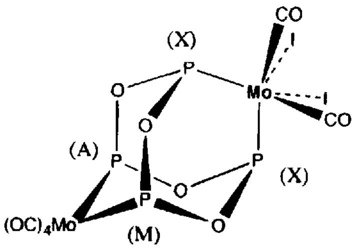


FIGURE 13

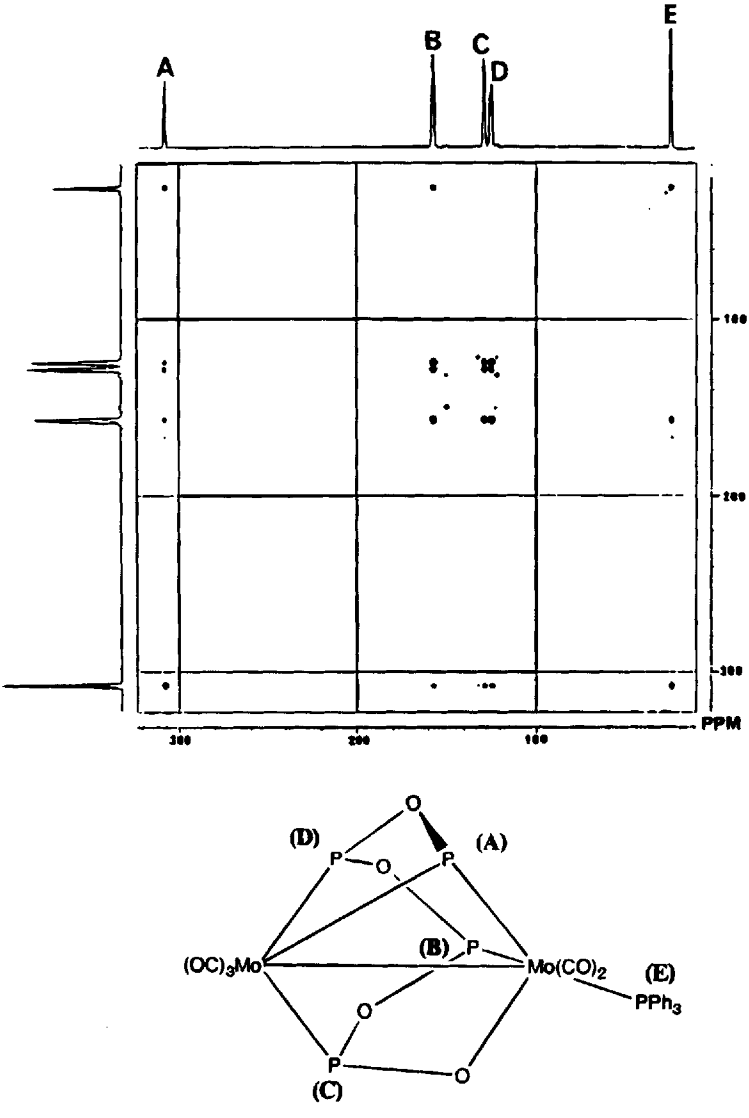

A
B
C
D
E
100
200
300
PPM
300
200
100
O
(D)
(A)
P
O
P
(B)
P
(OC)$_3$Mo
Mo(CO)$_2$
(E)
PPh$_3$
O
P
O
(C)

FIGURE 14

Established dependence of ${}^2J_{PP}$ on lone pair orientation also proved to be useful for stereochemical assignments.[18] We observed ${}^2J_{POP}$ values from less than 1 to over 60 Hz, with the larger magnitudes corresponding to phosphorus lone pairs *syn* to the metal-coordination bond. For example, in the *chair/boat* and *chair/chair* forms of MP_4O_4 (Fig. 11a,b; M = Cr, Mo, W, Fe, Pd, Pt), the *syn* ${}^2J$ values range from 38 to 59 Hz, while the *anti* couplings are at 1–13 Hz. This helped in the assignment of the $PdCl_2P_5O_5$ structure since it has an AA′MXX′ spectrum with ${}^2J_{AX}$ and ${}^2J_{MX}$ of 11–19 Hz and ${}^4J_{AM \text{ and } A'M}$ can actually be observed to be 3 Hz. Thus all phosphorus lone pairs must be positioned *anti* to the coordinated palladium (Fig. 15).

C. REACTIONS OF TETRAPHOSPHOXANE COMPLEXES

1. Monometallic Complexes

The $Mo(CO)_4[{}^iPr_2NPO]_4$ complex reacted readily with protic nucleophiles like alcohols and primary or secondary amines to give P–O–P cleavage products. Ethanol and methanol gave single P–O–P alcoholysis products of the type $Mo(CO)_4[{}^iPr_2NPO]_2({}^iPr_2NPOR)\{{}^iPr_2NP(O)H\}$ which were isolated and fully characterized (Scheme VI).[10] Reactions of amines, however, led to complete destruction of the cage complex to give amino-phosphine oxides in a reversal of the cage formation reaction.

The convergent lone pairs in this complex were inert to electrophiles like methyl iodide, benzyl bromide, and benzaldehyde even after prolonged reaction times. This can be attributed to geometrical factors. Both the constrained O–P–O angles (97°) and the orientations of the lone pairs

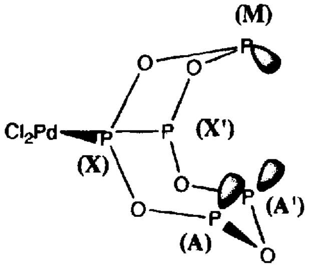
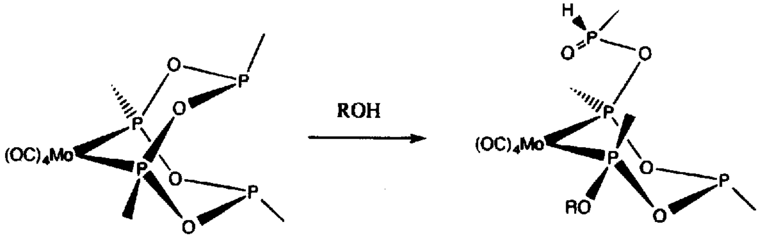


FIGURE 15



SCHEME VI

discourage nucleophilic attacks at an sp^3 C center. The suitability of this metalla-ligand as a precursor to heterobimetallic cage complexes has already been described.

Dihalo-nickel tetraphosphoxane complexes can also serve as metalla-ligands. For example:

$$NiBr_2[Cy_2NPO]_4 + (Norbornadiene)Mo(CO)_4 \rightarrow NiBr_2[Cy_2NPO]_4Mo(CO)_4.$$

Similarly, $Fe(CO)_3[{}^iPr_2NPO]_4$ led to the bimetallic $Fe(CO)_3[{}^iPr_2NPO]_4Mo(CO)_4$ product. This isomer of the Mo/Fe cage complex has been shown to have a tridentate P_4O_4 ring bridging the metals in a *syn* fashion. An Fe → Mo dative bond formally completes the EAN electron count (Fig. 16).[8]

Reaction of $NiBr_2[Cy_2NPO]_4$ with iron pentacarbonyl did not yield the desired bimetallic product. Instead a redox reaction gave the unexpected $Ni(CO)_2[Cy_2NPO]_4Ni(CO)_2$ cage complex.[8]

Instead of forming bimetallics, this same nickel tetraphosphoxane complex underwent ring transfer reactions with palladium and platinum dihalides:

$$NiBr_2[Cy_2NPO]_4 + PdBr_2.2PhCN \rightarrow PdBr_2[Cy_2NPO]_4 + NiBr_2,$$

$$NiBr_2[Cy_2NPO]_4 + PtCl_2(norbornadiene) \rightarrow PtCl_2[Cy_2NPO]_4NiBr_2,$$
$$PtCl_2[Cy_2NPO]_4NiBr_2 \rightarrow PtCl_2[Cy_2NPO]_4 + NiBr_2.$$

At low temperature, the transient bimetallic PtP_4O_4Ni intermediate can be observed by ^{31}P and ^1H NMR spectroscopy.[7,8]

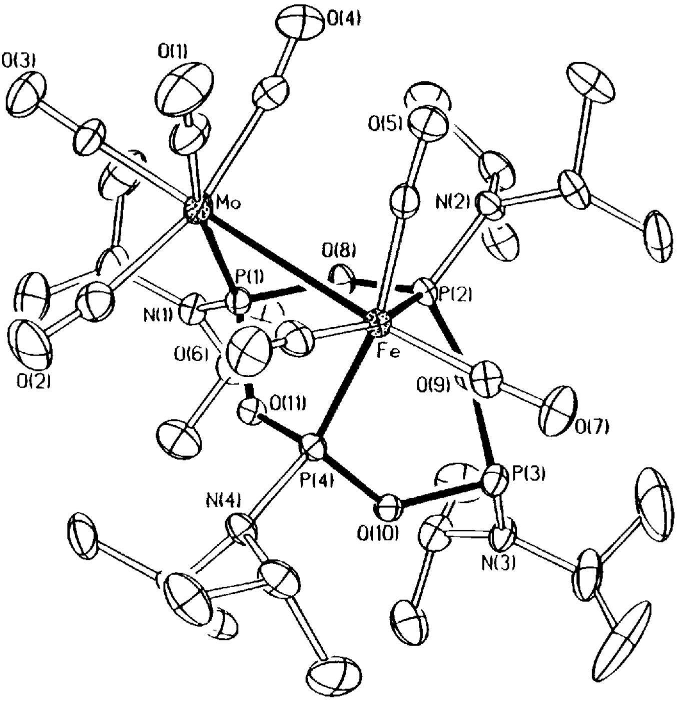


FIGURE 16

Possible release of the novel tetraphosphoxane ligand from this precursor was also explored.[7] At low temperature, in chloroform solution, excess pyridine readily displaced the heterocycle from $NiBr_2$. ^{31}P and ^{1}H NMR spectral characterization of this suggested actual or averaged C_4 symmetry. However, warming to room temperature resulted in disappearance of the tetraphosphoxane signal and emergence of the known triphosphoxane $[Cy_2NPO]_3$ resonances:

$$NiBr_2[Cy_2NPO]_4 + \text{Pyridine} \rightarrow [Cy_2NPO]_4 + NiBr_2(\text{Pyridine})_4,$$

$$3[Cy_2NPO]_4 \rightarrow 4[Cy_2NPO]_3.$$

2. The Bimetallic $Mo(CO)_4[{}^iPr_2NPO]_4Mo(CO)_4$ Complex

Cyclic voltammetry of this MoP_4O_4Mo cage complex in methylene chloride gave two irreversible one-electron oxidation waves at 1.15 and 1.52

V (vs Ag/AgCl) which suggested possible mixed-valent chemistry.[6] Chemically, it can indeed be halogenated using elemental iodine or sulfuryl chloride to give, initially,[17] the mixed-valent Mo^0/Mo^{II} complexes $Mo(CO)_4[^iPr_2NPO]_4Mo(CO)_2X_2$ and eventually the Mo^{II}/Mo^{II} tetrahalo derivatives $Mo(CO)_2X_2[^iPr_2NPO]_4Mo(CO)_2X_2$. For example:

$$Mo(CO)_4[^iPr_2NPO]_4Mo(CO)_4 + I_2 \rightarrow Mo(CO)_4[^iPr_2NPO]_4Mo(CO)_2I_2 + 2\,CO,$$

$$Mo(CO)_4[^iPr_2NPO]_4Mo(CO)_2I_2 + I_2 \rightarrow Mo(CO)_2I_2[^iPr_2NPO]_4Mo(CO)_2I_2 + 2\,CO.$$

Spectral studies of both types of products revealed dynamical aspects, suggesting hindered rotation of the diisopropylamino groups about the P–N bond at low temperature.[21] The solid-state molecular structure of the diiodo derivative (Fig. 13) features a trigonal prismatic Mo(II) coordination sphere.[17] This formally 16-electron center only binds CO and donor solvents like THF, acetone, and acetonitrile reversibly in accord with its attenuated Lewis acidity due to iodide π-bonding.[22]

Useful synthetically, the mixed-valent complex $Mo(CO)_4[^iPr_2NPO]_4 Mo(CO)_2I_2$ can be selectively demetallated by reaction with sodium dithiocarbamate to give the monometallic cage precursor $Mo(CO)_4 [^iPr_2NPO]_4$:

$$Mo(CO)_4[^iPr_2NPO]_4Mo(CO)_2I_2 + 2\,NaS_2CNMe_2 \rightarrow 2NaI + Mo(CO)_4[^iPr_2NPO]_4Mo(CO)_2(\eta^1 - S_2CNMe_2)_2,$$

$$Mo(CO)_4[^iPr_2NPO]_4Mo(CO)_2(\eta^1 - S_2CNMe_2)_2 \rightarrow Mo(CO)_2(\eta^2 - S_2CNMe_2)_2 + Mo(CO)_4[^iPr_2NPO]_4.$$

The isolable orange-red intermediate with monodentate dithiocarbamate ligands has been characterized by spectral data. It slowly demetallated to form the monometallic species in both solution and solid states. The metalla-ligand product is a colorless solid with a reasonable stability to both air and moisture and is a convenient reagent for the formation of heterobimetallic P_4O_4 cage complexes (Fig. 17 and Scheme IV).[10]

The mixed-valent $Mo(CO)_4[^iPr_2NPO]_4NiBr_2$ product spontaneously decomposed to the zero-valent $Mo(CO)_4[^iPr_2NPO]_4Ni(CO)_2$ upon stand-

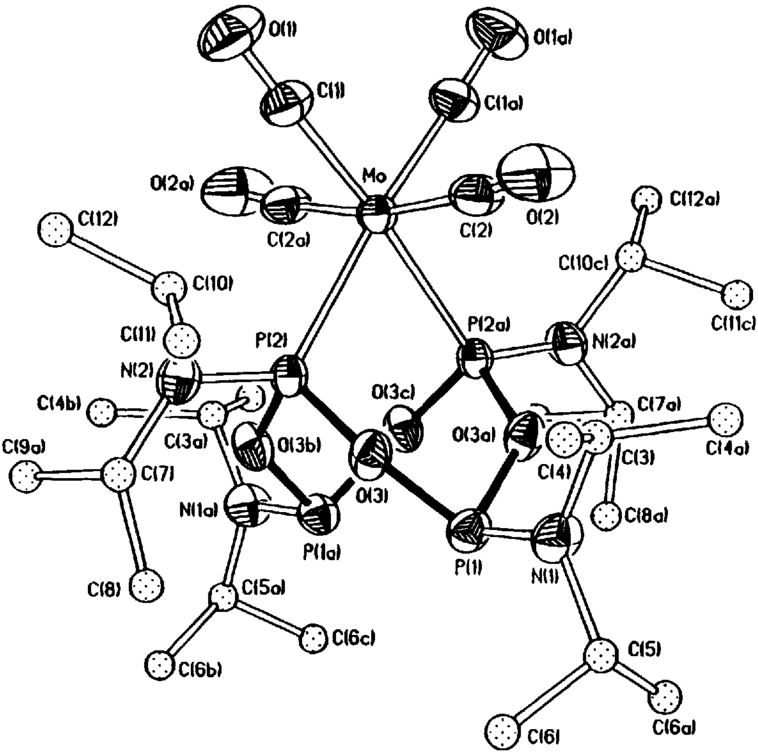


FIGURE 17

ing in hexane solution.[10] This carbonylation can also be effected by reaction with $Fe(CO)_5$:

$$Mo(CO)_4[{}^iPr_2NPO]_4NiBr_2 + Fe(CO)_5 \rightarrow Mo(CO)_4[{}^iPr_2NPO]_4Ni(CO)_2 + FeBr_2 + 3CO.$$

Nucleophilic substitution at the molybdenum centers of the $Mo(CO)_4[{}^iPr_2NPO]_4Mo(CO)_4$ cage complex led to unexpected results. Reactions with trialkylphosphites and phosphines yielded orange or orange-red products in which one ligand has replaced three CO's.[9] Infrared and ^{31}P NMR data indicated low symmetry as five inequivalent phosphorus nuclei were observed (Fig. 14). X-ray structural determination confirmed a major disruption of the parent cage framework due to P–O bond cleavage and formation of an intracage metal–metal bond bridged by both phosphide and P–O groups (Fig. 18). Additional studies revealed the formation of simple carbonyl substitution products before the P–O–P oxidative addition when the relatively π-acidic phosphites (Nu) were used. Further heating converted these to the observed products (Scheme VII). This type of intermediate was not observed for nucleophiles with less π-accepting ability like arylphosphines and pyridines as the substituted metal center was sufficiently electron-rich to undergo facile P–O–P oxidative addition.

D. SUMMARY AND PROSPECTS

We have presented the synthetic, structural, spectral, and reaction chemistry of a unique family of tetraphosphoxane complexes. The polyphosphorus rings found are unusually versatile donors capable of chelating either one or two metals in a variety of configurations. The *boat/boat exo*-ditopic coordination mode is especially interesting since intracage metal–metal interactions may be systematically studied. Preliminary

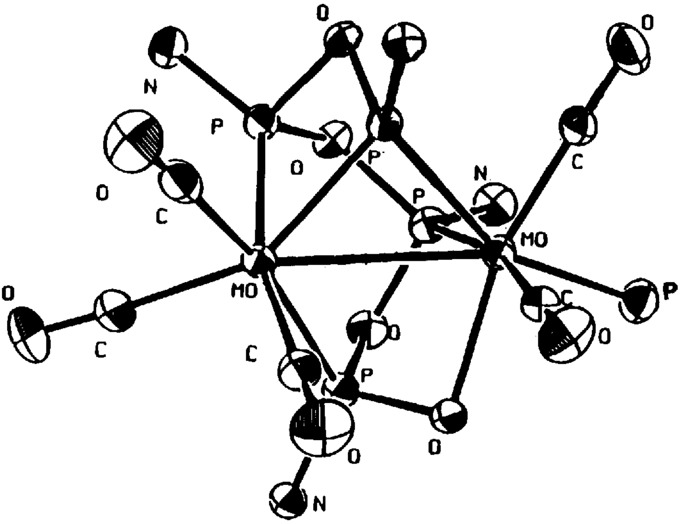
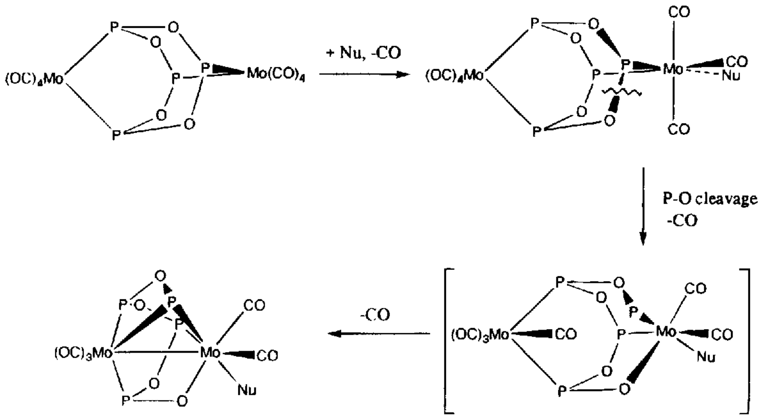


FIGURE 18



SCHEME VII

data suggest the existence of such effects. Both halogenation and nucleophilic substitution chemistry of cage complexes led to novel products. Selective demetallation from these derivatives has enhanced our ability to fashion a wider variety of polyphosphoxane complexes and should be further exploited. The chemistry of penta- and hexa-phosphoxane analogues remains to be explored. Incorporation of catalytically active metal vertices like rhodium and ruthenium into these rigid polycyclic structures holds additional promise.

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