Doctoral Dissertations   Student Scholarship

Spring 1995

Reactions of a dimolybdenum cage complex with phosphorus and nitrogen nucleophiles and the synthesis and reactions of heterobimetallic cages

Haiying Yang
University of New Hampshire, Durham

Follow this and additional works at: https://scholars.unh.edu/dissertation

Recommended Citation

Yang, Haiying, "Reactions of a dimolybdenum cage complex with phosphorus and nitrogen nucleophiles and the synthesis and reactions of heterobimetallic cages" (1995). *Doctoral Dissertations*. 1852.
https://scholars.unh.edu/dissertation/1852

INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

UMI

REACTIONS OF A DIMOLYBDENUM CAGE COMPLEX
WITH PHOSPHORUS AND NITROGEN NUCLEOPHILES
AND THE SYNTHESIS AND REACTIONS OF
HETEROBIMETALLIC CAGES

By

HAIYING YANG

B. S., Zhengzhou University, P. R. C., 1982
M. S., Zhengzhou University, P. R. C., 1985

DISSERTATION

Submitted to the University of New Hampshire in Partial
Fulfillment of the Requirements for the Degree of

Doctor of Philosophy
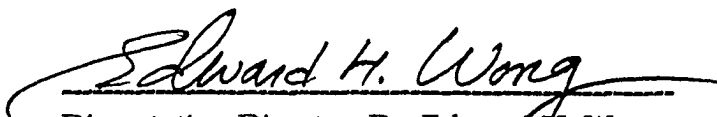in
Chemistry

May, 1995

UMI Number: 9528774

UMI

300 North Zeeb Road
Ann Arbor, MI 48103
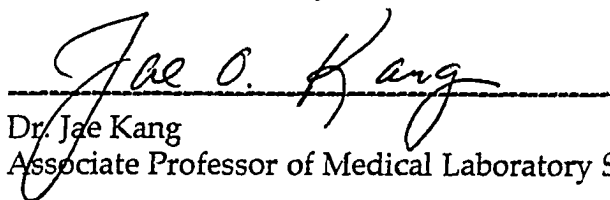
This dissertation has been examined and approved.
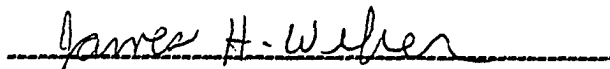
Edward H. Wong

Dissertation Director, Dr. Edward H. Wong,
Professor of Chemistry
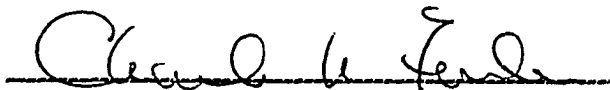
Kenneth K. Andersen

Dr. Kenneth K. Andersen,
Professor of Chemistry

Jae O. Kang
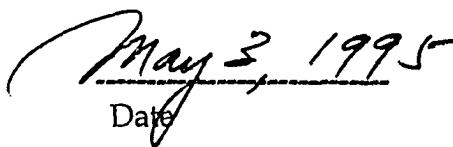
Dr. Jae Kang
Associate Professor of Medical Laboratory Science

James H. Weber

Dr. James H. Weber
Professor of Chemistry

Charles K. Zercher

Dr. Charles K. Zercher
Assistant Professor of Chemistry

May 3, 1995

Date

DEDICATION

To the memory of my grandmother, Shuying Miao, for her love.

To my parents XiuLan and Yongli, my parents-in-law Baizing and Yongshun,

for their love and support.

ACKNOWLEDGEMENTS

I would like to thank Dr. Edward H. Wong, my research advisor, for his guidance, encouragement, patience and help. I must say Dr. Wong is a great professor and research advisor. The help that I received from the former member of the Wong group, X. Y. Sun, is greatly appreciated.

I would like to thank the staff of the Instrumentation Center at UNH for their assistance on this project, especially Ms. Kathleen Gallagher for her instruction in the use of NMR and friendship; Mr. Richard Sweet for fixing the instruments; Deanna Cardin and Nancy Cherim for analyzing countless samples for elemental analysis.

I would also like to thank all the professors and graduate students at the chemistry department, especially Dr. Tomellini for his help with the HPLC.

I would like to thank Jerry P. Jasinski, Roman Y. Pozdniakov, Richard Woudenberg at the Keene State College and A L. Rheingold, B E. Owens-Waltermire, B S. Haggerty at the University of Delaware for their solution of the solid-state x-ray crystal structures for this project.

Finally my deepest thanks go to my husband Rongliang Li, my daughters Yangzi and Kathie for their love and support.

TABLE OF CONTENTS

v

vi

LIST OF TABLES

LIST OF FIGURES

ix

x

ABSTRACT

REACTIONS OF A DIMOLYBDENUM CAGE COMPLEX WITH PHOSPHORUS AND NITROGEN NUCLEOPHILES AND THE SYNTHESIS AND REACTIONS OF HETEROBIMETALLIC CAGES

By

Haiying Yang

University of New Hampshire, May, 1995

The reactions of the dimolybdenum cage complex $Mo(CO)_4$-$[^iPr_2NPO]_4Mo(CO)_4$* with phosphorus and nitrogen nucleophiles were studied. This dimolybdenum cage complex reacted with tertiary phosphines of the type PPh_2R (R=Ph, Me, H) in refluxing toluene. In each case, incorporation of a single phosphine led to the loss of three carbonyls to form orange complexes of the type $Mo(CO)_3[^iPr_2NPO]_4Mo(CO)_2PPh_2R$ (2, 3, 4). The X-ray molecular structure of 2 has been determined. This revealed that a cage P-O-P bond has been cleaved near the substitution site with the resulting phosphinito oxygen replacing a second CO. Additionally, the phosphido group generated displaced a third CO at the other Mo center to bridge the two metals which are now within bonding distance of each other. Under milder conditions, reactions using phosphite yielded both mono- and disubstituted products $Mo(CO)_4[^iPr_2NPO]_4Mo(CO)_3P(OMe)_3$ or $Mo(CO)_3P(OMe)_3$-$[^iPr_2NPO]_4Mo(CO)_3P(OMe)_3$ with the original core structure intact. Both

* See Appendix A for the structure.

products were mixtures of diastereomers and can be transformed to orange $Mo(CO)_3[^iPr_2NPO]_4Mo(CO)_2P(OMe)_3$.

Treatment of the mixed-valent $Mo(CO)_4[^iPr_2NPO]_4Mo(CO)_2I_2$ cage complex with sodium dimethyldithiocarbamate selectively removed the divalent molybdenum vertex to give the metalla-ligand $Mo(CO)_4[^iPr_2NPO]_4$ (14) via an orange intermediate $Mo(CO)_4[^iPr_2NPO]_4$-$Mo(CO)_2(S_2CNMe_2)_2$. The metalla-ligand has been characterized spectrally and by X-ray crystallography. It has been used as a precursor to assemble novel heterobimetallic cage complexes of the type $Mo(CO)_4[^iPr_2NPO]_4ML_n$ where ML_n can be $Cr(CO)_4$, $Fe(CO)_3$, $Cu(MeCN)_2BF_4$, $AgNO_3$, $PtCl_2$, $NiBr_2$ and $PdBr_2$, or the type $Mo(CO)_3[^iPr_2NPO]_5ML_n$ where ML_n can be $PdCl_2$, $PdBr_2$. All these heterobimetallic cage complexes have been characterized by elemental analyses and spectral data. In addition, X-ray structures of the heterobimetallic cage complexes $Mo(CO)_4[^iPr_2NPO]_4MBr_2$ [M=Ni(21), Pd(25)] have been determined. Comparison of the well-resolved A_1 carbonyl stretching frequency and the ^{13}C NMR chemical shift of the cis-$Mo(CO)_4$ moiety in $Mo(CO)_4[^iPr_2NPO]_4ML_n$ and also the X-ray structures of 14, 21, 25 suggest a transmission of the increasing electron demand of the second cage metal to the molybdenum vertex.

xiii

INTRODUCTION

Transition metal complexes with phosphine ligands have proven to be useful and versatile catalysts in homogeneous reactions[1]. Mono-phosphine ligands are used to induce chemistry at metal centers through steric and electronic influences. Chelating phosphines are even more successful in this role, and the use of polyphosphine ligands (i. e., those with several P donor sites) is increasingly important[2].

Recently, binuclear metal complexes, particularly those with bridging phosphine ligands, have begun to attract interest because of their potentially reactive features. The interest in binuclear complexes arose because of anticipation that they can allow for increased versatility in catalyst design[3]. Complexes with two metal atoms can have several advantages over a catalyst containing only a single metal. For example, the presence of two metal atoms may facilitate multielectron redox reactions which could not be handled by only a single metal atom.

The first bimetallic cage complex of 1,3,5,7-tetraoxa-2,4,6,8-tetraphosphorinane [RPO]$_4$ with the familiar adamantane structure common to P$_4$O$_6$ and P$_4$O$_{10}$ was reported in 1983[4]. It contains the novel cyclic tetramer [RNPO]$_4$ in a boat-boat conformation serving as a tetradentate ligand chelating two metals as shown in **Figure 1**:

1
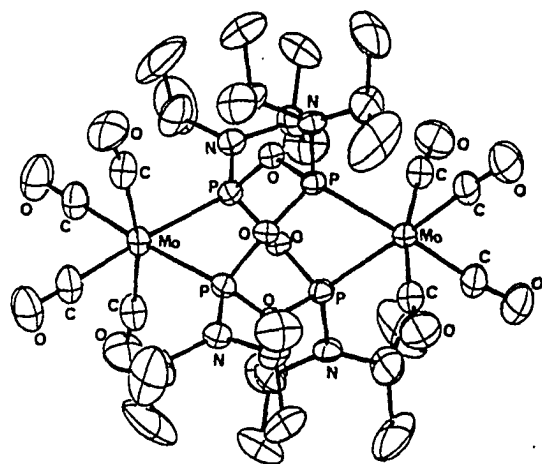
Figure 1. Molecular structure of Cage complex Mo(CO)4[iPr2NPO]4Mo(CO)4

Before this work, the coordination chemistry of the polydentate ligand [RPO]n was not known. The first report of a cyclic phosphoxane [RPO]3 (where R=OEt, OBu, and Et2N) appeared in 1967[5], but the structures of these compounds were not fully identified. In 1980, Niecke[6] isolated and characterized the cyclic trimer [iPr2NPO]3. In 1986, Chasar[7] and co-workers synthesized and identified both [RPO]3 and [RPO]2 where R is 2, 6-di-tert-butyl-4-methylphenoxy. Compared to the familiar cyclic condensed metaphosphates and thiophosphates of phosphorus (V), phosphorus-oxygen heterocycles or cyclophosphoxanes of phosphorus (III) are thus relatively rare. These trivalent phosphorus heterocycles can provide multiple donor sites and should have useful coordination chemistry as polydentate ligands leading to polycyclic and cage complexes.

The dimolybdenum cage complex is the first example of a cyclotetraphosphoxane ligand that chelates two metals. It contains two mutually-orthogonal Mo(CO)4P2 centers which are subjected to considerable steric buttressing due to the rigid polycyclic structure[4]. Complex 1 was

2

synthesized by the reaction of $Mo(CO)_6$ and $(^iPr_2N)_2P(O)H$:

$$2Mo(CO)_6 + 4(^iPr_2N)_2P(O)H \text{-----}>$$

$$Mo(CO)_4[^iPr_2NPO]_4Mo(CO)_4 + 4CO + 4^iPr_2NH \qquad \text{(eq 1)}$$
$$(1)$$
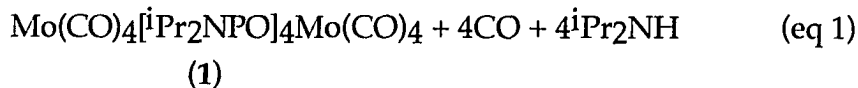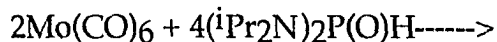
Since the serendipitous synthesis of this $Mo_2P_4O_4$ cage complex 1 in 1983, Wong's group has been studying the mechanism of its formation as well as coming up with alternate methods of preparing other members of this family of compounds. Some reports on the synthesis of phosphoxane complexes have appeared and the reactivity studies of complex 1 were also explored[8-13]. Prior to the work reported here, the reactivity studies of the parent complex have been limited to halogenation and redox investigations. The substitution chemistry at $Mo(CO)_4$ with neutral Group V ligands was unexplored. Only one example of a heterobimetallic cage complex of this type was known[9].

Phosphine substituents at all four cage phosphorus vertices can influence each of the metal sites. For example, the trans CO-Mo-CO angle is compressed to only $167°$[8] due to the diisopropylamino groups on the two remote P's**. Halogenation reactions have already been shown to produce 16-electron trigonal prismatic $MoX_2(CO)_2P_2$ vertices, possibly as a result of this unique cage environment[9].

We are interested in the following aspects of cage chemistry: (I) How does the presence of a very rigid and relatively bulky cage ligand affect the inorganic and organometallic chemistry at the $Mo^0(CO)_4$ centers? (II) Can

** See page 135.

3

heterobimetallic cage complexes be synthesized? (III) Is there any intra-cage "communication" or interaction between the metal centers?

Several interesting aspects of cage halogenation chemistry have already been discovered for the parent cage. This is a two-step process, giving $(CO)_4Mo[^iPr_2NPO]_4Mo(CO)_2X_2$ and then $Mo(CO)_2X_2[^iPr_2NPO]_4Mo(CO)_2X_2$ products (Scheme I):
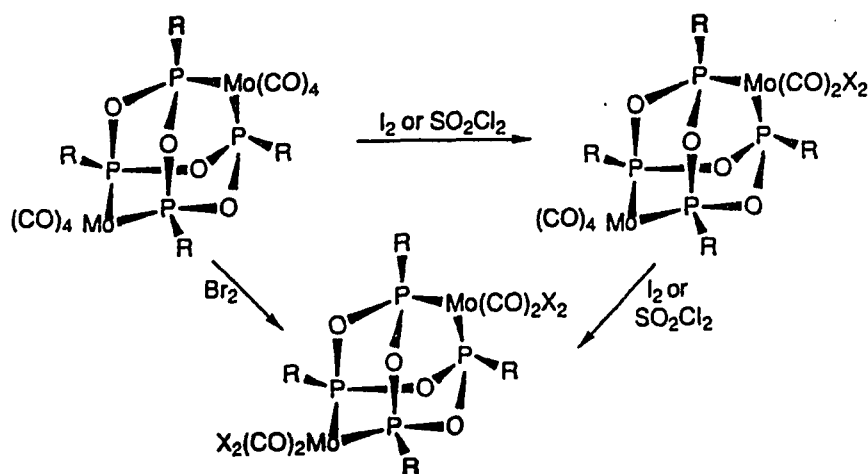
Scheme I

The Mo(II) products are six-coordinate rather the usual seven-coordinate for non-cage analogues. Seven-coordination is expected for the molybdenum-substituted halocarbonyls if we assume that the effective atomic number rule applies to these complexes. By Kepert's calculations[14] there are three possible geometries with lowest energies for seven coordinated complexes: the pentagonal bipyramid, the mono-capped octahedron and the mono-capped trigonal prism. For $M(CO)_3(PR_3)_2X_2$ complexes, often stereochemically nonrigid seven-coordinated complexes are isolated[15]. For example, $Mo(CO)_3I_2(dpm)$ [dpm=bis(diphenylphosphino)-methane] has a mono-capped trigonal prism geometry[16], and

4

$Mo(CO)_3I_2(Ph_2POPPh_2)$ adopted a pentagonal bipyramidal structure[17]. The solution and solid state geometries of the cage halogenation products are unique. In addition, all halogenated cage products are low-spin d^4 and diamagnetic.

The new cage chemistry we shall investigate includes substitution chemistry at $Mo(CO)_4$ with neutral Group V ligands. Nucleophilic substitutions at this center may also generate unusual coordination chemistry due to cage structure constraints. Tertiary phosphines and phosphites can substitute for one or more of the remaining 4 CO's. The types, geometries, distribution of isomeric products, as well as influence of reaction at one cage metal on the other when compared to normal $Mo(CO)_4(diphosphine)$ products will reveal any unique features for the cage reactions. Pyridine, acetonitrile and benzonitrile can potentially substitute CO's also.

While attempted synthesis of heterobimetallic cages from the parent cage failed, we reasoned that the Mo^{II} center in the mixed-valent complex $(CO)_4Mo[^iPr_2NPO]_4Mo(CO)_2I_2$ may provide a potential demetallation site. Dithiocarbamate ion has been found to coordinate to a transition metal both as a bidentate or monodentate ligand[18,19]. It is a potential candidate for use in removing of the Mo^{II} vertex to give the monometallic cage precursor complex $(CO)_4Mo[^iPr_2NPO]_4$. We could then synthesize a series of heterobimetallic cage complexes from this metallo ligand by inserting the second metal into the vacated site.

Since it was known that cage halogenation is a two-step process,

5

oxidation at one metal makes oxidation at the other more difficult. A series of the heterobimetallic cage complexes with rigidly constrained pairs of metal vertices should be especially interesting for the study of intracage metal-metal interactions. Comparison of the spectral properties of the conserved $Mo(CO)4$ moiety in these heterobimetallic cage complexes will give valuable information concerning such interactions.

The first chapter will describe the substitution reactions of the cage complex 1 with phosphine and phosphite ligands, pyridine, acetonitrile and benzonitrile, and the characterization of the products. These results revealed an unusual intramolecular P-O-P bond cleavage with extensive rearrangement of the core structure and formal oxidative addition to both metals, all direct consequences of the replacement of a carbonyl by a single phosphorus or nitrogen donor. Furthermore, the electronic and steric effects of the phosphine ligands were investigated.

In the second chapter, the demetallation of a dimolybdenum cyclotetraphosphoxane cage complex $(CO)_4Mo[^iPr_2NPO]_4Mo(CO)_2I_2$ by reaction with dithiocarbamates to give the metalla-ligand $(CO)_4Mo[^iPr_2NPO]_4$ will be described. The nucleophilic attack by primary alcohols on the precursor and the characterization of the products will be related. The use of this metalla-ligand as a precursor for synthesizing of heterobimetallic cage complexes will also be described. These heterobimetallic cage complexes are among the first examples of a cyclotetraphosphoxane ligand that chelates two different metals. Finally, this chapter will also present a study of the intracage influence between the cage metal sites.

6

CHAPTER I

REACTIONS OF A DIMOLYBDENUM

CYCLO-TETRAPHOSPHOXANE CAGE WITH PHOSPHORUS

AND NITROGEN NUCLEOPHILES

Nucleophilic substitution reactions at Group VI metal carbonyls have been extensively studied[20]. For tetracarbonylmetal diphosphine chelate complexes like Mo(CO)4(diphos), CO substitution reactions with phosphines, phosphites and amines usually yield either axial-substituted *fac* - or equatorial-substituted *mer* -Mo(CO)3L products depending on the ligand used (**Scheme II**)[21]:

fac--   *m e r-*
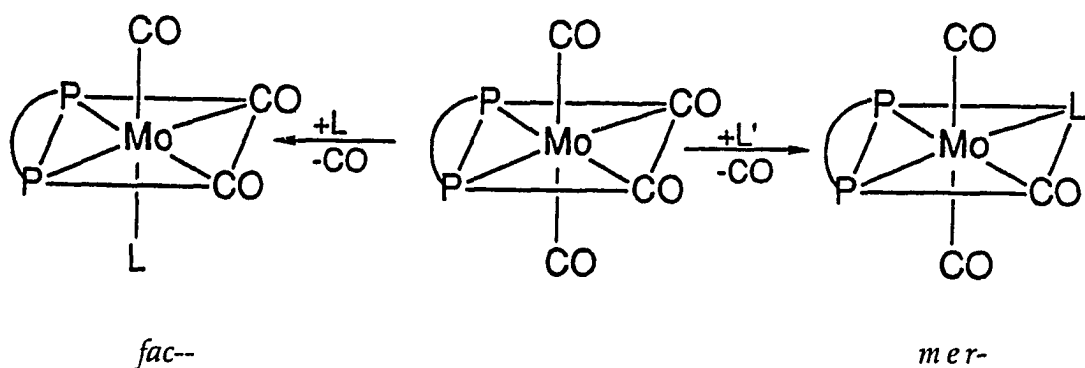
Scheme II

Ligand and carbonyl π-bonding effects are evidently of primary importance for these type of complexes. Thus, the carbonyl group *trans* to the more strongly π-accepting ligand carbonyl is expected to be more labile and more readily replaced, and *fac-* products are anticipated. When considering steric effects, the *mer-* products should be expected because it reduces crowding at a face of the octahedron with the more sterically demanding ligands.

In this chapter, we report the synthesis of the bimetallic cage complexes of the form (CO)4Mo[iPr2NPO]4Mo(CO)3L and (CO)3LMo-[iPr2NPO]4Mo(CO)3L where L is one of several phosphines and the complexes (CO)3Mo[iPr2NPO]4Mo(CO)2L' where L' is a phosphine, pyridine or carbonyl ligand. Spectroscopic characterization of these complexes is

8

reported. Crystallographic investigations of the complexes where L = PPh₃, P(OMe)₃ and CO are also described.

RESULTS AND DISCUSSION

1. Synthesis and Characterization of (CO)₃Mo[^{i}Pr₂NPO]₄Mo(CO)₂PPh₂R (R=Ph, Me, H)

Complexes (CO)₃Mo[^{i}Pr₂NPO]₄Mo(CO)₂PPh₂R(R=Ph, Me, H) were synthesized by the reactions of triphenylphosphine, diphenylmethyl-phosphine, and diphenylphosphine with the dimolybdenum cage complex (CO)₄Mo[^{i}Pr₂NPO]₄Mo(CO)₄ **1** in refluxing toluene. The equation representing the preparations of these complexes is shown below.

$$(CO)_4Mo[^iPr_2NPO]_4Mo(CO)_4 + PR_3 \longrightarrow$$
$$\underline{(\mathbf{1})}$$

$$3CO + (CO)_3Mo[^iPr_2NPO]_4Mo(CO)_2PR_3 \qquad (eq\ 2)$$

$$(\ PR_3 = PPh_3(\mathbf{2}),\ PPh_2Me(\mathbf{3}),\ PPh_2H(\mathbf{4})\ )$$
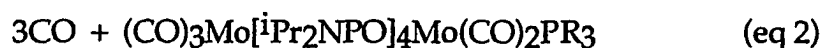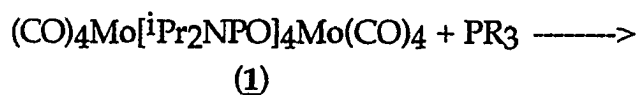
The yields of complexes **2, 3, 4** in the reactions above were 40 (isolated yield from **1**), 80 and 80 percent, respectively.

The reactions were monitored by TLC . In each case, at the beginning there were several spots, but after 24 hours, the starting material was completely gone, and only one orange-colored spot showed as product. The reaction solutions were clear red. By routine column chromatography and recrystallization the pure orange-colored products were isolated. These orange compounds were not very soluble in hexane and so were recrystallized from it. Each of the complexes was characterized by ^{31}P, ^{1}H, ^{13}C

9

NMR , IR and elemental analyses.

^{31}P NMR can serve as an important analytical tool for solution structure determination. In addition, P coupling constants provide important information on the nature of bonding and structure in molecules[22]. Compounds that contain two or more coupled phosphorus atoms exhibit very characteristic coupling patterns in the completely proton-decoupled ^{31}P spectra. When this type of information is used in conjunction with other NMR data, the structures of polyphosphorus compounds are often readily elucidated[23].

Compounds 2, 3, 4 have similar ^{31}P NMR, IR spectra. The one- and two-dimensional ^{31}P and ^{1}H NMR spectra of the product showed that only one attacking phosphine ligand was incorporated even in the presence of excess phosphine and prolonged reaction times. The D_{2d} symmetry of the parent cage is complexly lost upon formation of the orange complexes, since in each case five distinct resonances can be seen(**Figure 2**):
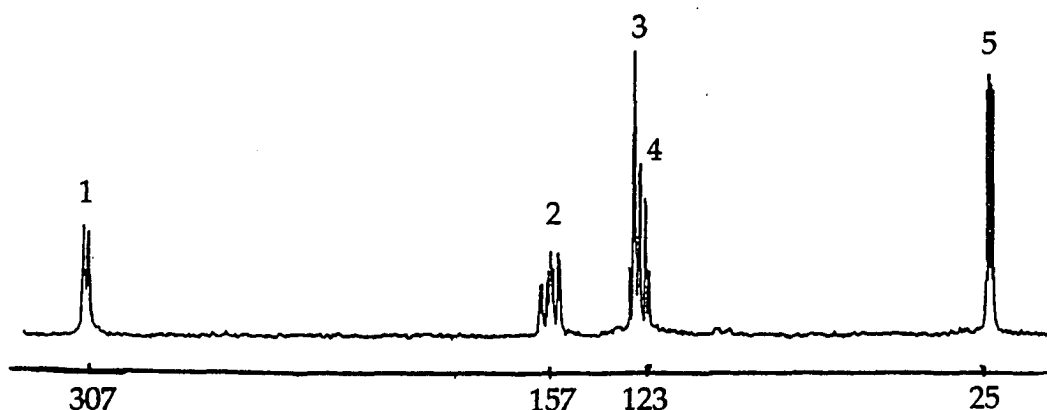
Figure 2. ^{31}P{^{1}H} NMR spectrum of complex **2**

10

Significantly, one phosphorus (P1) has a chemical shift far downfield (305-307 ppm), and its position is essentially independent of the nature of the entering ligand. This chemical shift is not consistent with Mo-coordinated tertiary phosphines or phosphites, but is in the region of phosphenium cations or phosphido ligands[24]. From literature[25], we know that the two-bond phosphorus-phosphorus coupling constant between the *trans* phosphorus atoms, $^2J(P,P)_{trans}$, should be much greater than $^2J(P,P)_{cis}$. Comparing similar coupling constants, $^2J(P,P)$, ranged 25-53 Hz between the entering phosphine ligands and the cage P's in complexes **2, 3, 4** (**Table I**), though it is hard to tell whether an equatorial or axial CO has been substituted. Also, from the IR spectra, we know that the cis-Mo(CO)$_4$P$_2$ coordination sphere at the original cage no longer exists because all of the orange products exhibit metal carbonyl stretches below 2000 cm^{-1}, with four or five well-resolved bands between 1850 and 1980 cm^{-1} that indicate low symmetry of the products (**Table II**):

11

Table I: $^{31}P\{^1H\}$ NMR Data for the Complexes

Complex		Chemical Shift, ppm [J, Hz]
1		150.1(s)
2	AJMNX	307.5, 156.9, 124.3, 123.3, 24.9 [J_{AJ} = J_{AN} = 14.7, J_{AM} = 19.1, J_{AX} = 49.8, J_{JM} = 77.7, J_{JN} = 126.0, J_{JX} = 24.9, J_{MN} = 36.7 Hz]
3	AJMNX	305.5, 156.9, 129.3, 125.4, 15.3 [J_{AJ} = 14.7, J_{AN} = 11.7, J_{AM} = 17.6, J_{AX} = 52.8, J_{JM} = 79.1, J_{JN} = 129.0, J_{JX} = 26.4, J_{MN} = 38.1 Hz]
4	AJMNX	305.9, 154.9, 128.8, 127.1, 23.3 [J_{AJ} = J_{AM} = 14.7, J_{AN} = 11.7, J_{AX} = 52.8, J_{JM} = 90.9, J_{JN} = 129.0, J_{JX} = 29.3, J_{MN} = 38.1 Hz]
7	ALMNX	306.8 156.9, 153.7, 149.8, 123.9 [J_{NX} = 38.1, other J's not obtained]
10	AMXY	295.3, 150.7, 134.7, 128.1 [J_{AM} = 14.7, J_{AX} = 12.2, J_{AY} = 17.1, J_{MX} = 125.7, J_{MY} = 80.6, J_{XY} = 36.6 Hz]
11	AMXY	306.3, 149.8, 131.6, 121.4 [J_{AM} = 15.4, J_{AX} = 24.2, J_{AY} = 11.0, J_{MX} = 101.1, J_{MY} = 127.4, J_{XY} = 37.4 Hz]
5	AMNX$_2$	180.0, 164.0, 155.6, 148.2 [J_{AM}

12

		$= 187.1, J_{AN} = 41.0, J_{MN} = 47.5,$
		$J_{MX} = 10.5, J_{NX} = 6.7$ Hz]
	AM$_2$NX	166.9, 155.0, 151.2, 148.2 [J_{AM}
		$= 45.1, J_{MN} = 10.5, J_{MX} = 6.7, J_{NX} = 48.3$ Hz]
6	AMX	179.3, 159.8, 151.6 [$J_{AM} = 185.5,$
		$J_{AX} = 40.9, J_{MX} = 51.1$ Hz]
	AMNX$_2$Y	178.6, 164.7, 158.8, $\approx$151.1, $\approx$151.1
		[$J_{AN} = 187.1$ Hz, other J's not obtained]
	AMNX$_2$Y	178.1, 163.8, 162.0, $\approx$153.5, $\approx$153.5
		[$J_{AN} = 190.0$ Hz, other J's not obtained]
	AXY	165.8, $\approx$151.6, $\approx$151.6 [J's not obtained]
8	A$_2$M$_2$X	157.1, 149.6, 12.9 [$J_{AM} = 7.0,$
		$J_{AX} = 32.8, J_{MX} = 0$ Hz]
9	A$_2$X	157.3, 13.5 [$J_{AX} = 34.2$ Hz]

a In CDCl$_3$ solution.

Table II. Selected Infrared Absorptions for the Complexes

Complex	CO region, cm^{-1}	POP region, cm^{-1}
1	2015, 1923, 1906, 1887	875, 849, 809
2	1977, 1925, 1904, 1884, 1854	870, 849, 832, 800
3	1975, 1917, 1896, 1853	875, 845, 805
4	1977, 1921, 1895, 1856	874, 856, 826, 805
7	1979, 1925, 1889, 1856	870, 843, 834, 800
10	1973, 1915, 1889, 1874, 1851	875, 839, 800
11	2011, 1983, 1944, 1921, 1917, 1909, 1903, 1893	877, 847, 810
5	2003, 1988, 1975, 1937, 1916, 1900(sh), 1887	866, 845
6	1985, 1965, 1920(sh), 1877(bd), 1860(sh)	867, 846
8	2013, 1962, 1941, 1927, 1905, 1886, 1861	864, 832
9	1952, 1860	864, 833

a KBr pellets, Perkin-Elmer 283B Spectrophotometer.

The species cis-Mo(CO)4P2 has C2v symmetry, so four bands are expected in the CO region of its IR spectrum (**Figure 3**)[26]. These four bands are attributed to the four possible CO vibrations depicted in **Figure 4**:

14
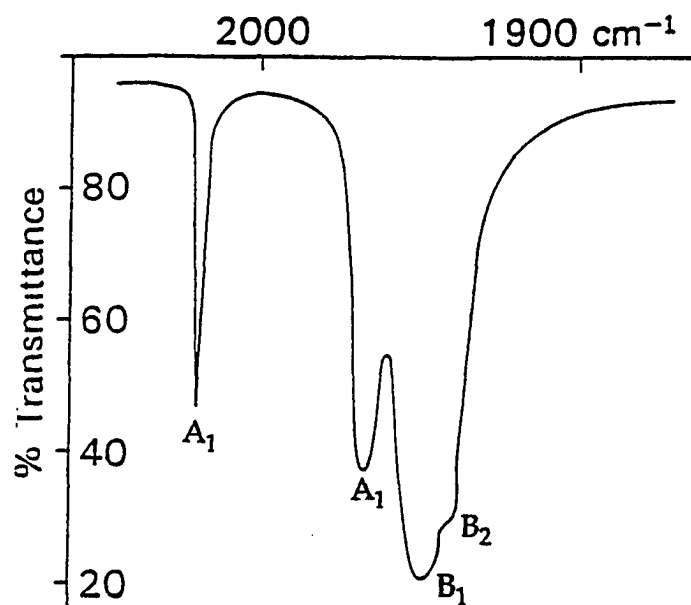
Figure 3. IR spectrum in the ν_{CO} region for cis-(CO)₄Mo[P(OPh)₃]₂

A₁(trans)   B₁   A₁(cis)   B₂
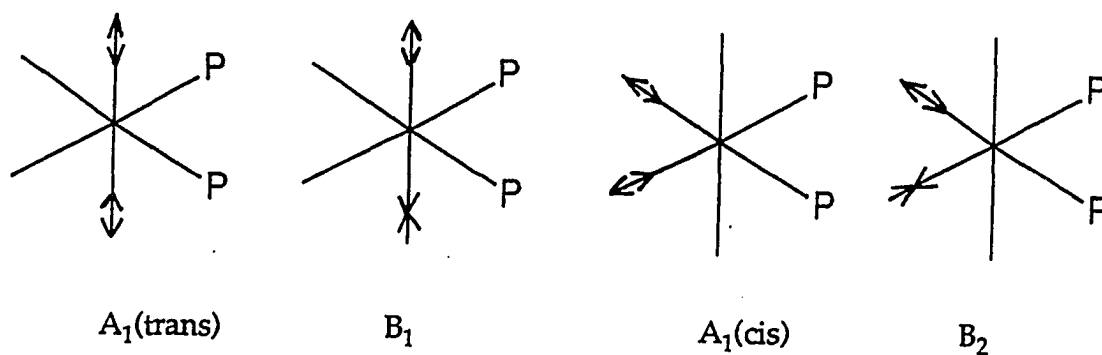
Figure 4. CO Stretches for cis-(CO)₄MoP₂

The band above 2000 cm-1 is due to the A₁(trans) stretch. The bands below 2000 cm-1 are attributed to the B₁, B₂ and A₁(cis) modes. Comparing the IR spectra of the products **2, 3, 4** with the IR spectrum of the original cage **1** (**Figure 5**), it is clear that the A₁ band at 2014 cm⁻¹ had disappeared:

15
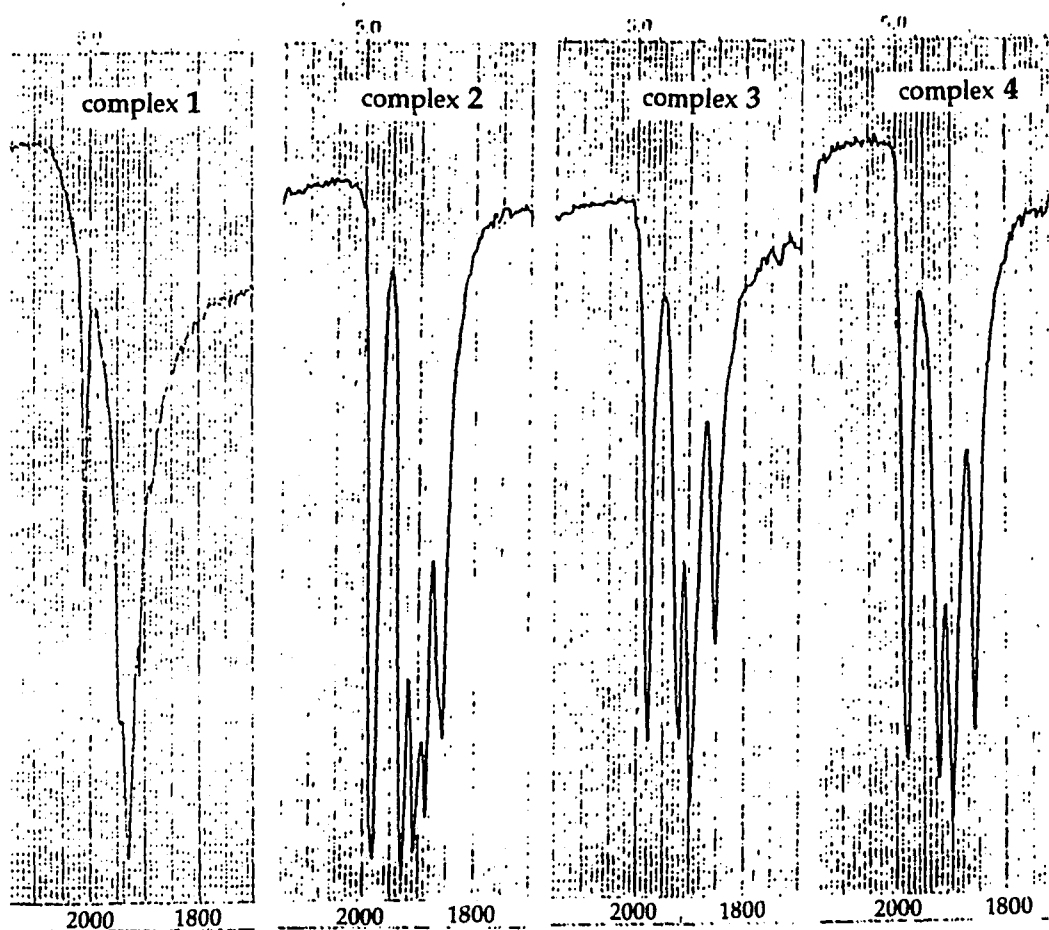
Figure 5. IR spectra in the v_{CO} region for complexes 1, 2, 3 and 4

Thus, both the IR and NMR spectra gave us the first hint that the product may have a novel structure and that the cage structure was disrupted substantially upon CO replacement. Later the X-ray structure of complex 2 confirmed that the cis-Mo(CO)$_4$P$_2$ coordination spheres at <u>both</u> metal sites are changed. The elemental analyses are fully consistent with the structure (**Figures 6 and 7**):

16
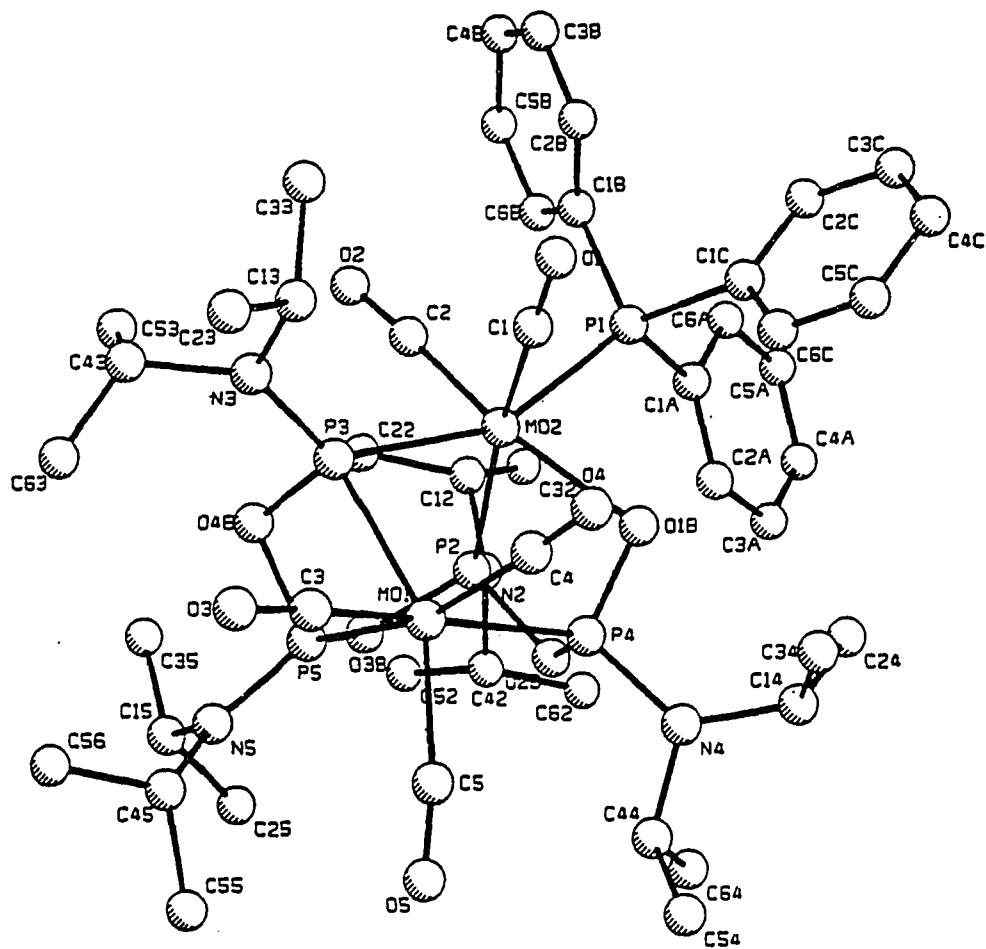
Figure 6. Molecular structure of complex 2

(with hydrogens omitted for clarity)
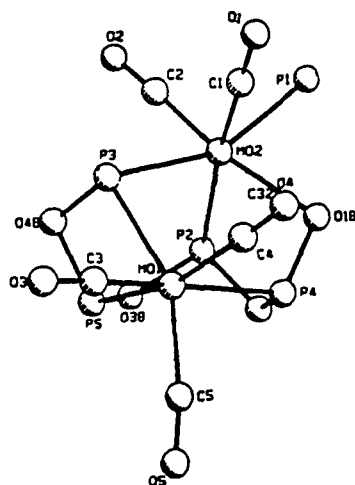
Figure 7. Core geometry of complex 2

17

There are extensive alterations in the metal coordination spheres and cage geometry. Upon the addition of trimethylphosphine, there was a P-O-P bond cleaved near the substitution site with formation of one μ-P-O- and one μ-P- bridge, three carbonyls were lost. The first carbonyl at Mo(2) was replaced by the entering ligand. The phosphinito oxygen (P(4)-O(1B)) replaced a second CO while the μ-P- (P3) displaced a third CO at the other Mo center to bridge the two metals. These are now within bonding distance of each other at 3.186(4) Å, a substantial contraction from the Mo-Mo metal separation (6.001(1) Å) in the original parent cage structure. Mo-Mo single bond distances vary depending on ligand constraints, and 3.186(4) Å is well within the 3.057(6)-3.235(1) Å range of weak single bonds reported for the doubly-bridged molecules $Mo_2(CO)_8(\mu\text{-}PEt_2)_2$[27], $Mo_2(CO)_6(PEt_3)_2(\mu\text{-}PMe_2)_2$[28] and $Cp_2Mo_2(CO)_6$[29], which all contains direct Mo-Mo bonds. If both Mo(1) and Mo(2) are assigned +1 formal oxidation states, electron counting requires the presence of a single Mo-Mo bond to achieve the noble-gas configuration at both metals.

Table III. Selected Bond Distances (Å) and Angles (deg) for Complex 2

Mo(1)-Mo(2)	3.186(4)		
Mo(1)-P(3)	2.464(4)	P(1)-C(1A)	1.87(1)
Mo(1)-P(4)	2.502(4)	P(1)-C(1B)	1.85(1)
Mo(1)-P(5)	2.455(4)	P(1)-C(1C)	1.84(1)
Mo(1)-C(3)	2.00(1)	P(2)-O(2B)	1.635(8)
Mo(1)-C(4)	2.05(1)	P(2)-O(3B)	1.671(8)
Mo(1)-C(5)	2.08(2)	P(3)-O(4B)	1.672(9)
Mo(2)-P(1)	2.563(4)	P(4)-O(1B)	1.540(8)
Mo(2)-P(2)	2.524(4)	P(4)-O(2B)	1.731(9)

18

Mo(2)-P(3)	2.362(4)	P(5)-O(3B)	1.624(8)
Mo(2)-O(1B)	2.222(8)	P(5)-O(4B)	1.677(8)
Mo(2)-C(1)	1.1(1)	C(1)-O(1)	1.18(2)
Mo(2)-C(2)	1.92(1)	C(2)-O(2)	1.17(1)
C(3)-O(3)	1.13(2)	C(4)-O(4)	1.10(2)
C(5)-O(5)	1.12(2)		

P(3)-Mo(1)-P(4)	105.7(1)	P(1)-Mo(2)-P(2)	100.2(1)
P(3)-Mo(1)-P(5)	62.8(1)	P(1)-Mo(2)-P(3)	155.4(1)
P(3)-Mo(1)-C(3)	82.1(4)	P(1)-Mo(2)-O(1B)	81.1(2)
P(3)-Mo(1)-C(4)	101.9(4)	P(1)-Mo(2)-C(1)	82.5(4)
P(3)-Mo(1)-C(5)	153.6(4)	P(1)-Mo(2)-C(2)	83.8(4)
P(4)-Mo(1)-P(5)	94.3(1)	P(2)-Mo(2)-P(3)	90.7(1)
P(4)-Mo(1)-C(3)	168.4(5)	P(2)-Mo(2)-O(1B)	78.5(2)
P(4)-Mo(1)-C(4)	82.7(4)	P(2)-Mo(2)-C(1)	172.1(4)
P(4)-Mo(1)-C(5)	91.9(4)	P(2)-Mo(2)-C(2)	94.9(4)
P(5)-Mo(1)-C(3)	96.9(5)	P(3)-Mo(2)-O(1B)	123.0(2)
P(5)-Mo(1)-C(4)	163.1(3)	P(3)-Mo(2)-C(1)	89.8(4)
P(5)-Mo(1)-C(5)	97.0(4)	P(3)-Mo(2)-C(2)	73.2(4)
C(3)-Mo(1)-C(4)	87.4(6)	O(1B)-Mo(2)-C(1)	94.7(5)
C(3)-Mo(1)-C(5)	83.9(6)	O(1B)-Mo(2)-C(2)	162.1(4)
C(4)-Mo(1)-C(5)	99.7(6)	C(1)-Mo(2)-C(2)	92.8(6)
Mo(1)-P(3)-O(4B)	97.4(3)	Mo(2)-P(1)-C(1A)	121.6(4)
Mo(1)-P(4)-O(1B)	107.6(3)	Mo(2)-P(1)-C(1B)	111.8(4)
Mo(1)-P(4)-O(2B)	110.6(3)	Mo(2)-P(1)-C(1C)	113.2(4)
Mo(1)-P(3)-Mo(2)	82.6(1)	Mo(2)-P(2)-O(2B)	103.3(3)
Mo(1)-P(5)-O(3B)	115.3(3)	Mo(2)-P(2)-O(3B)	115.4(3)
Mo(1)-P(5)-O(4B)	97.5(3)	C(1A)-P(1)-C(1B)	103.9(6)
Mo(2)-P(3)-O(4B)	114.5(3)	C(1A)-P(1)-C(1C)	100.0(6)
Mo(2)-O(1B)-P(4)	100.3(4)	C(1B)-P(1)-C(1C)	104.2(3)
O(2B)-P(2)-O(3B)	100.3(4)	O(1B)-P(4)-O(2B)	103.1(4)
O(3B)-P(5)-O(4B)	98.8(4)	P(2)-O(2B)-P(4)	107.1(5)
P(2)-O(3B)-P(5)	117.8(5)	P(3)-O(4B)-P(5)	99.9(5)

19

Complexes containing metals bridged simultaneously by a phosphido group as well as a P-chalcogen group are known, though they are usually formed by insertion of chalcogens into a metal-phosphido bond[30] (**Scheme III**):

(E = S, Se)
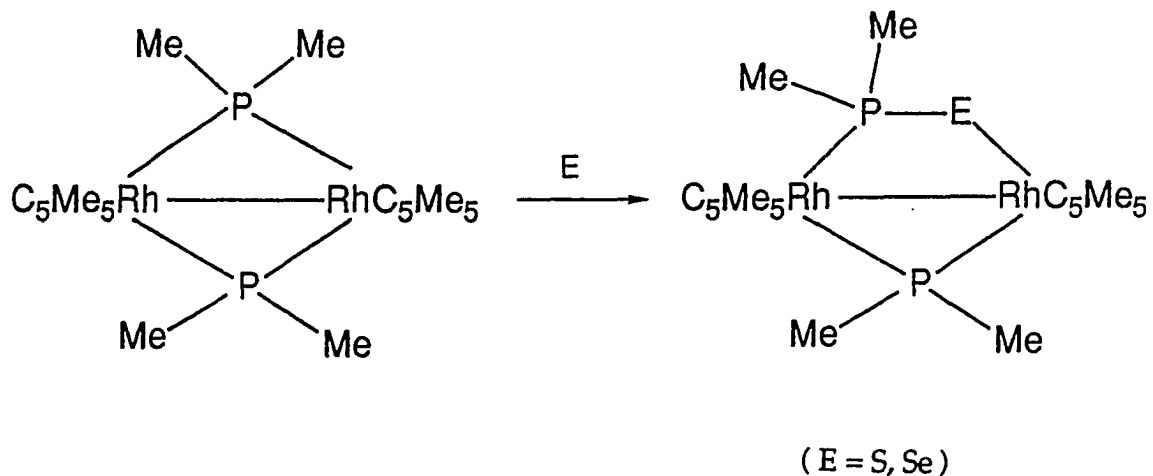
Scheme III

Newton and co-workers have reported a P-N-P cleavage reaction in the photolysis of $CH_3N(PF_2)_2$ with $\{CpFe(CO)_2\}_2$[31]. The structure of the product was found to have a μ-PF_2NMePF_2 and a μ-PF_2 as well as a μ-PNMe bridging ligand (**Figure 8**):
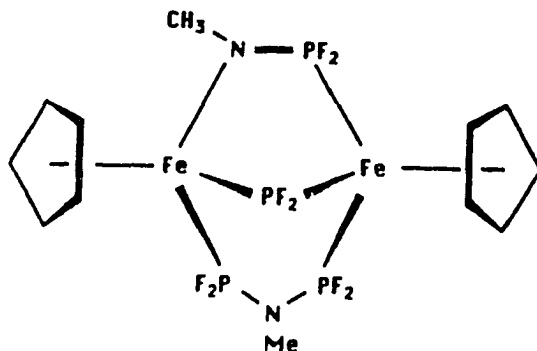
Figure 8. Structure of $[C_5H_5Fe(PF_2)_2NCH_3]_2$ (ref. 39)

20

This triple-bridging by three different ligands is similar to that found in **2**, though there is no accompanying metal-metal bond formation in this case.

A short metal-phosphorus distance of 2.362(4) Å is found for Mo(2)-P3 which is approximately trans to the PPh$_3$ ligand. All other Mo-P bonds are in the 2.46-2.56 Å range, not significantly changed from the value of 2.50 Å in the parent cage complex. The Mo(2)-O(1B) bond length is 2.222(8) Å with the cis-Mo(2)-C(1) and trans-Mo(2)-C(2) bond lengths of 1.91(1) and 1.92(1)Å marginally shorter than all of the other Mo(1)-C bonds (2.00-2.08 Å). Except at P(4), ring P-O distances range from 1.62 to1.67 Å. The two P(4)-O distances are very different with P(4)-O(1B) at 1.540(8) Å and P(4)-O(2B) at 1.731(9) Å. The data reflect the multiple bond character in the former at the expense of the latter. Corbridge summarized bond length data for phosphates and found an average of 1.54 Å for the reported P-O distances[32].

Due to the polycyclic ligand system bridging the two metals, substantial deviations from idealized angles are found for both coordination spheres though each is approximately an octahedron. At Mo(1), the four-membered M-P-O-P chelate ring compresses the P(5)-Mo(1)-P(3) angle to only 62.8(1)°. The five-membered Mo(2)-P(3)-Mo(1)-P(4)-O(1B) heterocycle contains a narrow Mo(2)-P(3)-Mo(1) angle of 82.6(1)° while the P(3)-Mo(2)-O(1B) angle is distended to 123.0(2)°. As a result, the angle closest to linearity at Mo(2) is C(1)-Mo(2)-P(2) at 172.1(4)°. The four equatorial ligand atoms P(3), O(1B), P(1), and C(2) then subtend very distorted angles at Mo(2); P(3)-Mo(2)-O(1B) is 123.0(2)°, O(1B)-Mo(2)-P(1) is 81.1(2)°, P(1)-Mo(2)-C(2) is 83.8(4)°, and C(2)-Mo(2)-P(3) is 73.2(4)°. These equatorial angles sum up to 361°. At Mo(1), C(3) and P(4) are approximately axial as C(3)-Mo(1)-P(4) is 168.4(5)°. The corresponding equatorial angles deviate widely from orthogonality ranging from 62.8° to

21

101.9° but again summing up to 361°.

It is now easy to understand why the ^{31}P NMR spectra of all the orange complexes show one phosphorus chemical shift so far downfield (305-307 ppm). The X-ray structure of 2 (and X-ray structure of 7, 11) explicitly showed that the phosphido ligand is indeed present in the orange complexes. Since the phosphido chemical shift is known to be quite sensitive to the M-P-M angle and the extent of metal-metal interaction[33], the nearly unchanged chemical shift value at around +306 ppm implies that the M-P-M angle as well as the nature of Mo-Mo bonding remain little changed through the series of orange complexes. This is also confirmed by the X-ray structure data of complexes 2, 7, 11 (see Part I-5 for a comparison of the structures). The highest-field resonance in 2, 3, 4 can be readily assigned to the newly-coordinated phosphine ligands by using typical coordination shifts from the free ligand values[34]. That is, there is a linear relationship between the coordination chemical shift, $\Delta \delta = \delta_{complex} - \delta_{free phosphine}$, and the resonance position of the free phosphine. For compound 4, a proton-coupled spectrum clearly identifies the high-field multiplet as the PPh_2H resonance with a $^1J_{P-H}$ of 334 Hz.

In each complex the connectivity between the five resonances can be unambiguously established by ^{31}P COSY (Figure 9):

22
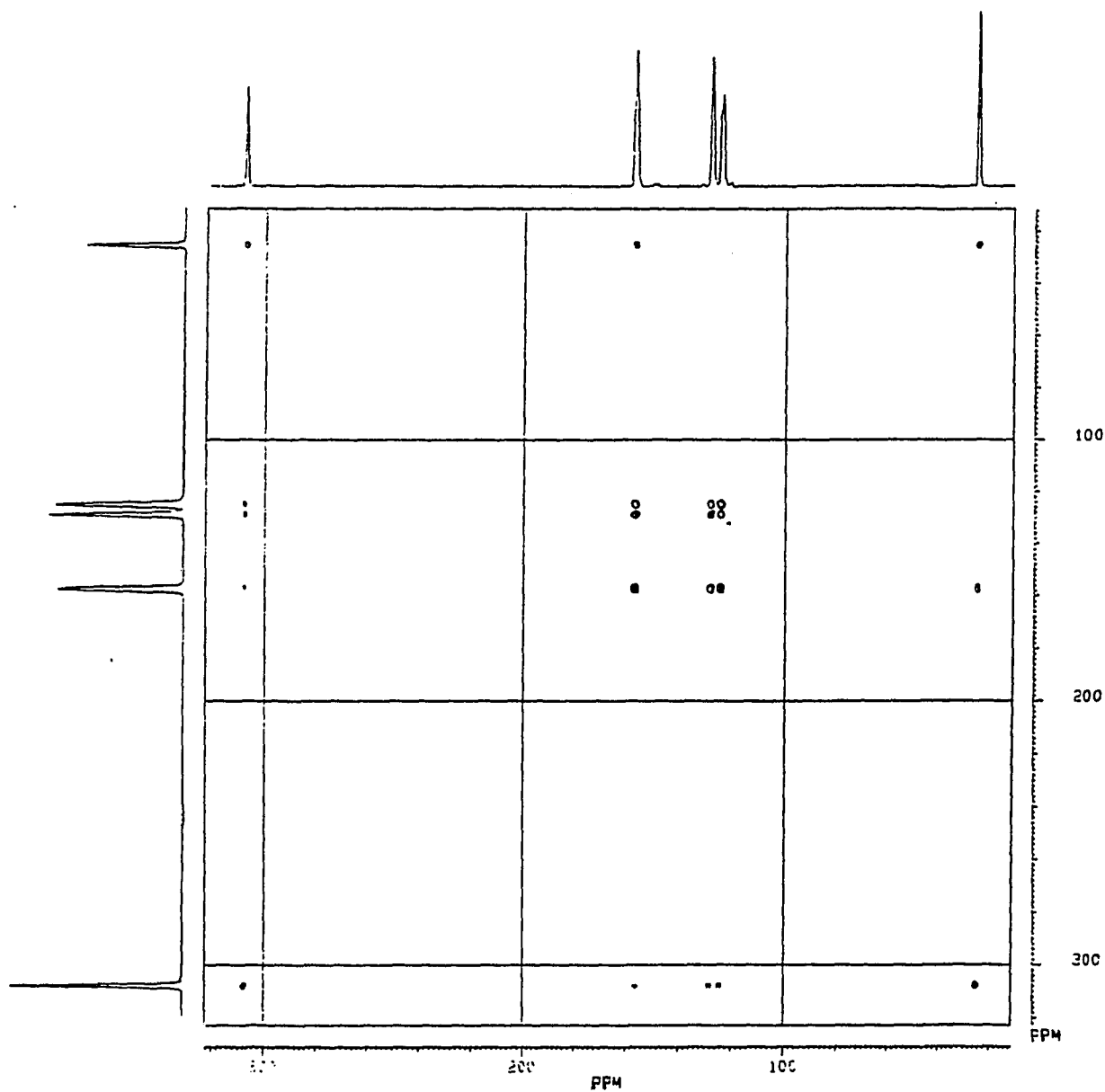
Figure 9. 2D COSY $^{31}P\{^1H\}$ NMR spectrum of complex 2

When CO gas was bubbled through the reaction solutions, the orange compounds did not revert to the original cage but another orange compound 11 formed. This new complex has a similar structure to 2 with the difference that the attacking phosphine was replaced by CO.

23

When compound **2** was first obtained, it was thought that since the attacking ligand was bulky (cone angle of PPh$_3$ =145°), it could only substitute one CO. So the two smaller ligands MeP(C$_6$H$_5$)$_2$ (Θ = 136°) and HP(C$_6$H$_5$)$_2$) (Θ = 126°) were used to react with the cage under the same conditions. The same type of products (**3** and **4**) were obtained. It was therefore thought that a steric threshold might exist for the formation of simple mono- and di- substituted compounds and electronic influences may also play a role for both substitution and rearrangement reactions. In order to verify this, trimethyl phosphite with a smaller cone angle (Θ = 106°) and better π-accepting ability was chosen for reaction with the cage.

2. Synthesis and Characterization of

(CO)$_3$(L)Mo[^{i}Pr$_2$NPO]$_4$Mo(CO)$_3$P(OMe)$_3$ [L=CO, P(OMe)$_3$]

Complexes (CO)$_3$(L)Mo[^{i}Pr$_2$NPO]$_4$Mo(CO)$_3$P(OMe)$_3$ [L=CO (**5**), P(OMe)$_3$ (**6**)] were synthesized by the reaction of trimethylphosphite with the dimolybdenum cage complex (**1**) in refluxing toluene. The equation representing the preparation of these complexes is shown below.

$$2(CO)_4Mo[^iPr_2NPO]_4Mo(CO)_4 + 3P(OMe)_3 \longrightarrow$$
$$(1)$$

$$3CO + (CO)_4Mo[^iPr_2NPO]_4Mo(CO)_3P(OMe)_3$$
$$(5)$$

$$+ (CO)_3P(OMe)_3Mo[^iPr_2NPO]_4Mo(CO)_3P(OMe)_3$$
$$(6) \hspace{4cm} (eq\ 3)$$

24
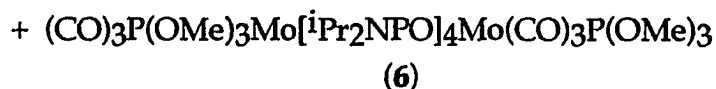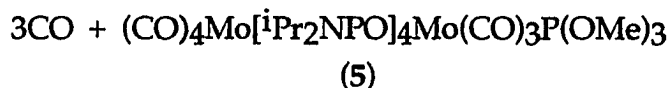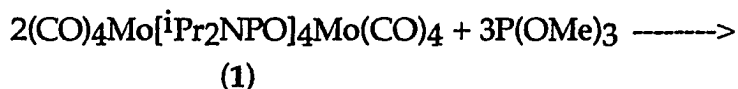
Thus from this ligand, different results were indeed obtained. After only 6 hrs, a clear, very light-yellow solution was formed while the cage was totally consumed. TLC showed only two colorless product spots. By routine column chromatography compound 5 followed by compound 6 were eluted and isolated. The isolated percent yields after chromatography of complexes 5 and 6 were 32 and 50%, respectively.

The products were characterized by ^{31}P, ^{1}H, ^{13}C NMR, IR spectra and elemental analyses. The proton-decoupled 1-D and 2D COSY ^{31}P NMR spectra of 5 and 6 and elemental analytical data showed that 5 is a monosubstituted product and compound 6 is a disubstituted compound with the original cage structure intact. Both of these complexes are mixtures of isomers. For example, in complex 5 only one CO was substituted, but it could be an equatorial or axial CO (**Figure 10**):
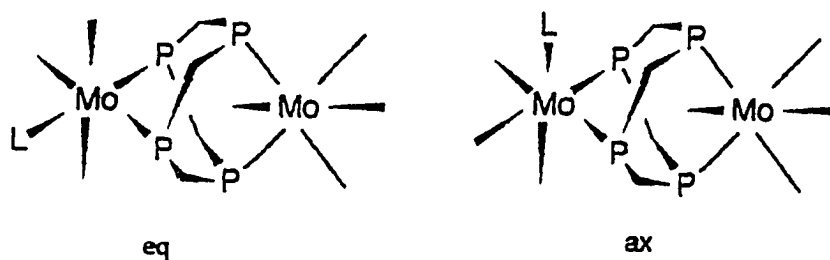
Figure 10. Proposed structures for isomers of complex 5

In order to integrate and calculate the ratio of isomers, we used selective proton decoupling techniques to determine which ^{31}P peaks were phosphite resonances and which were due to the cage phosphorus atoms. If an individual proton resonance is selected and irradiated with sufficient power

to decouple only that proton resonance, it simplifies the spectrum by removing all of the couplings to that proton. For example, if we selectively decouple the trimethyl phosphite protons, the couplings between P and H will disappear. Therefore the decaplets due to the coupling of P with nine H's will be gone and only the P-P couplings will be seen. If the decoupler is set to the center of the proton region and then modulated using a 'noise generator' with a bandwidth wide enough to cover the complete proton region, every proton frequency will be irradiated, resulting in the decoupling of all protons in the molecule[35].

The composition of complex 5 can be easily assigned as 40% axial-substituted and 60% equatorial-substituted $(CO)_4Mo[^iPr_2NPO]_4Mo(CO)_3$-$P(OMe)_3$ by the 2-D COSY ^{31}P NMR spectrum (**Figure 11**) and full-decoupled or selectively-decoupled 1-D ^{31}P NMR spectra (**Figures 12, 13, 14**):

26
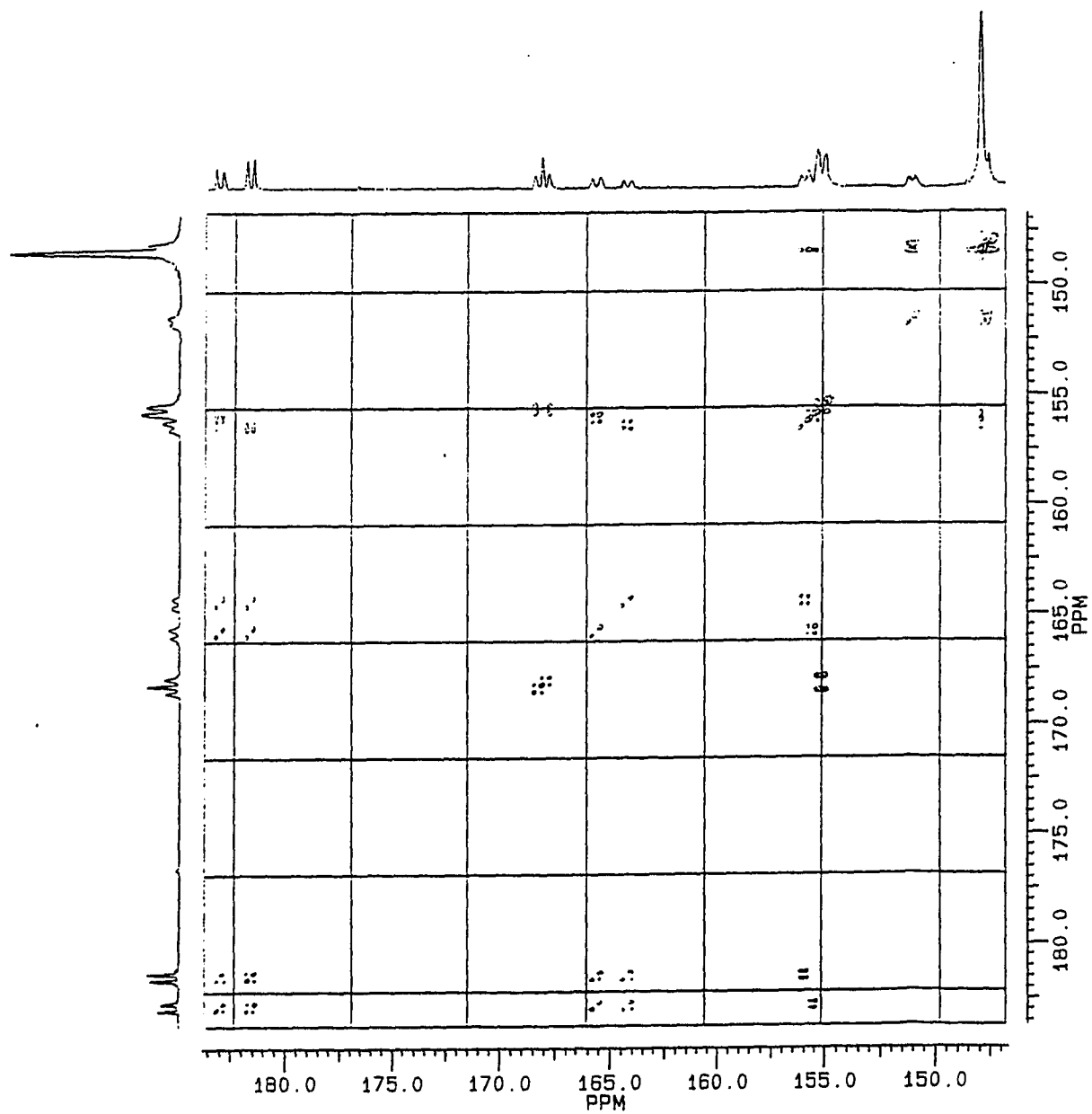
Figure 11. The 2-D COSY $^{31}P\{^1H\}$ NMR spectrum of complex 5

27
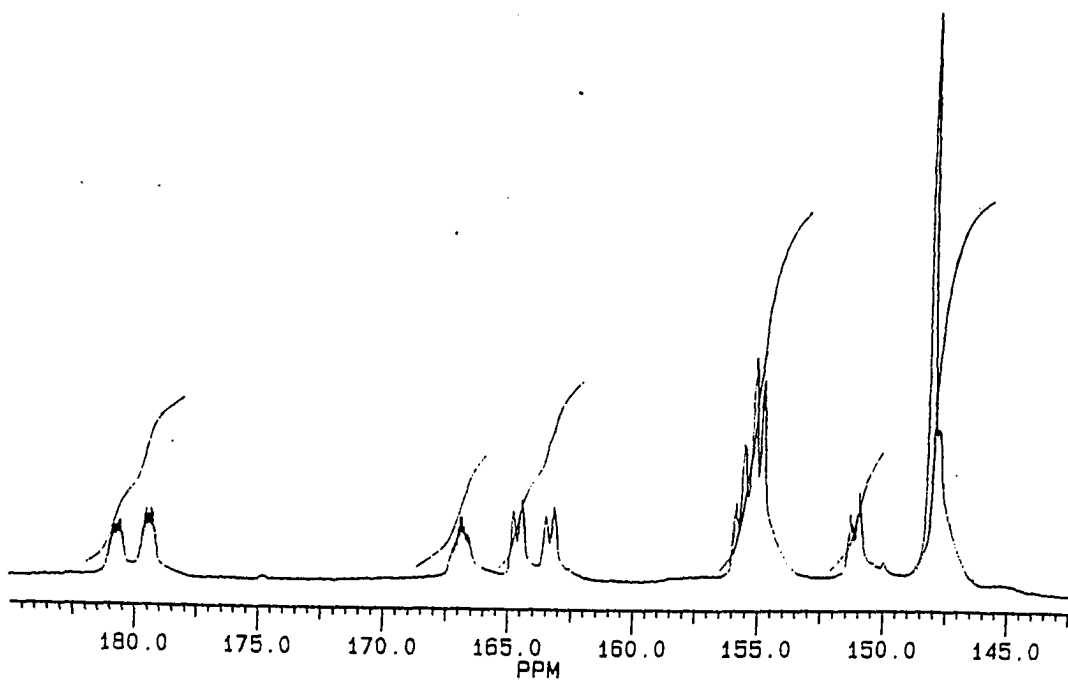
Figure 12. $^{31}P\{^1H\}$ NMR spectrum of complex 5
[Selective methine proton (δ = 4.57-4.38 ppm) decoupled, DP 16L]
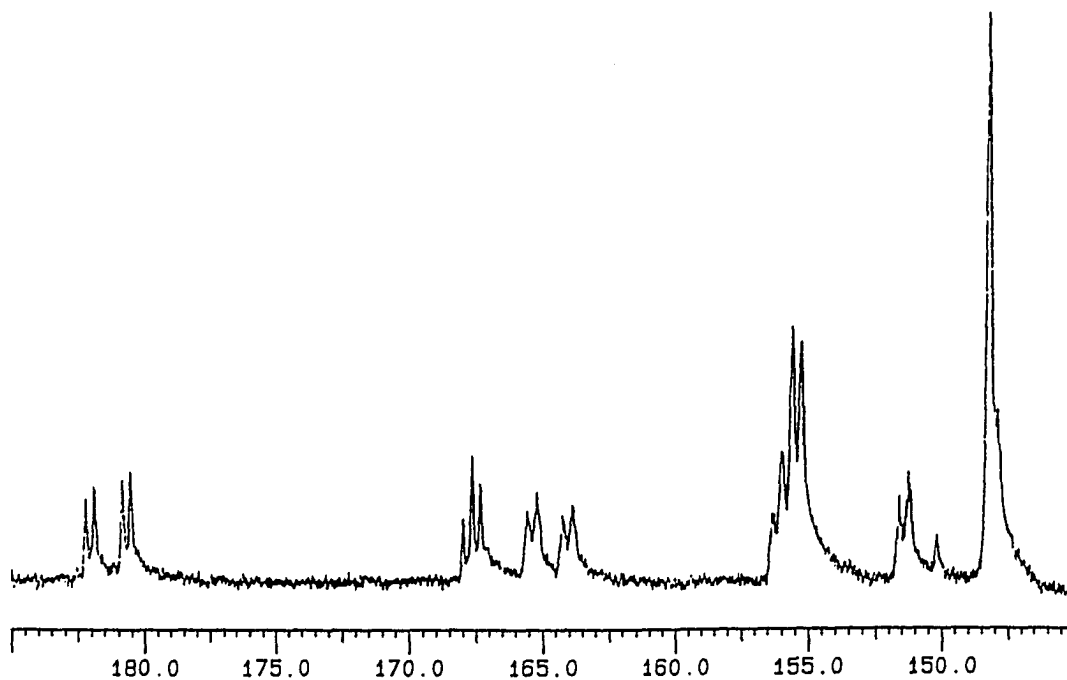
Figure 13. $^{31}P\{^1H\}$ NMR spectrum of complex 5
[Selective trimethyl phosphite proton (δ = 3.61-3.59 ppm) decoupled, DP 24L]

28
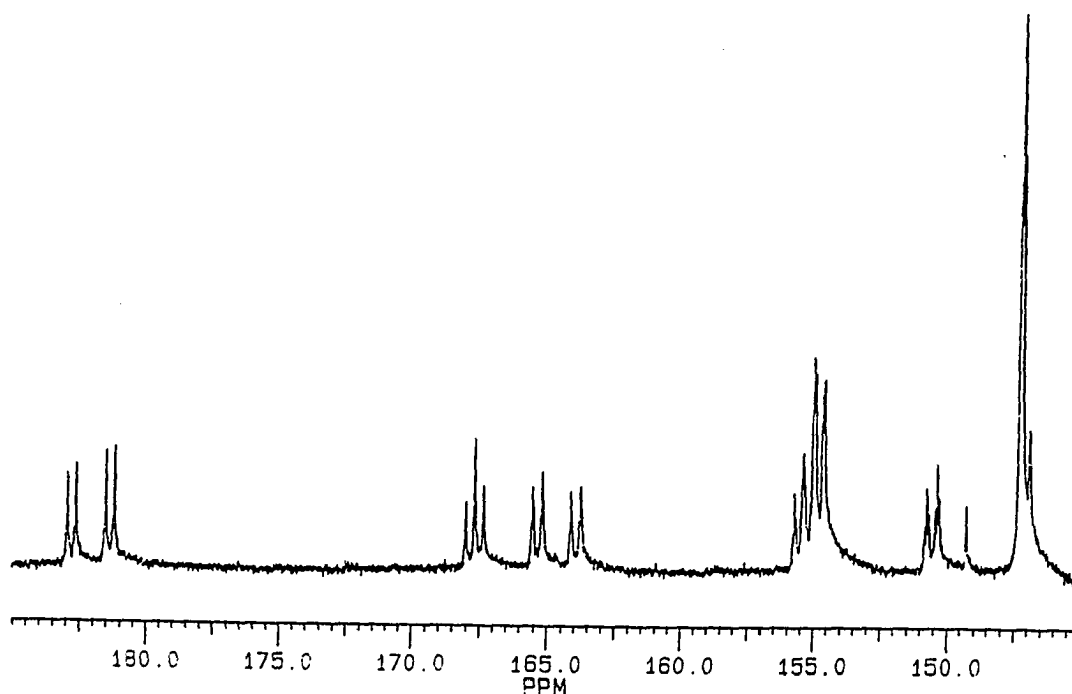
Figure 14. $^{31}P\{^1H\}$ NMR spectrum of complex 5

(Full decoupled, DP 12H)

Complex 6 can have four isomers assuming only monosubstitution at each metal (Figure 15):

eq/eq

eq/ax

eq/ax

ax/ax
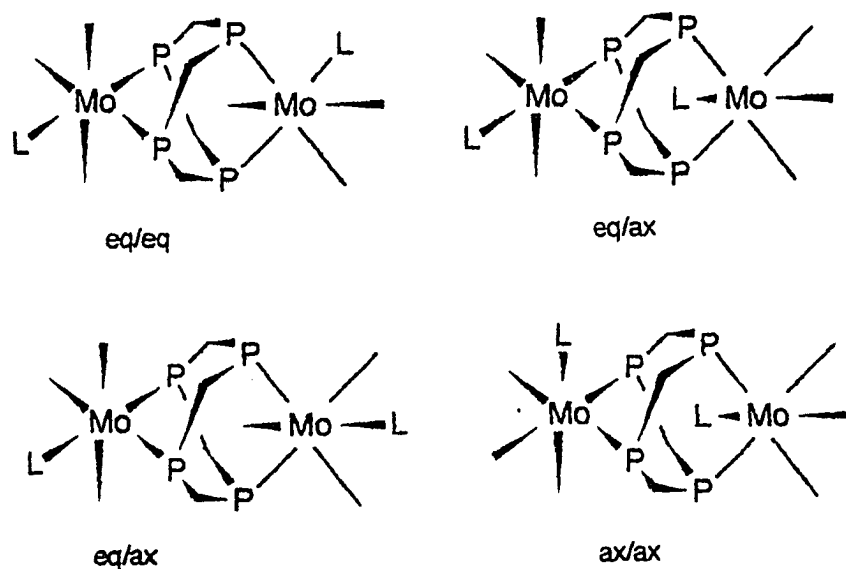
Figure 15. Proposed structures for isomers of complex 6

29

The extremely complex 1-D ^{31}P spectrum of 6 can similarly be satisfactorily resolved into its four diastereomeric components of equatorial/equatorial, equatorial/axial(trans), equatorial/axial(cis), and axial/axial disubstituted $(CO)_3P(OMe)_3Mo[^iPr_2NPO]_4Mo(CO)_3P(OMe)_3$ diastereomers by its 2-D COSY spectrum and the selectively-decoupled 1-D ^{31}P NMR spectrum (Figures 16, 17, 18):
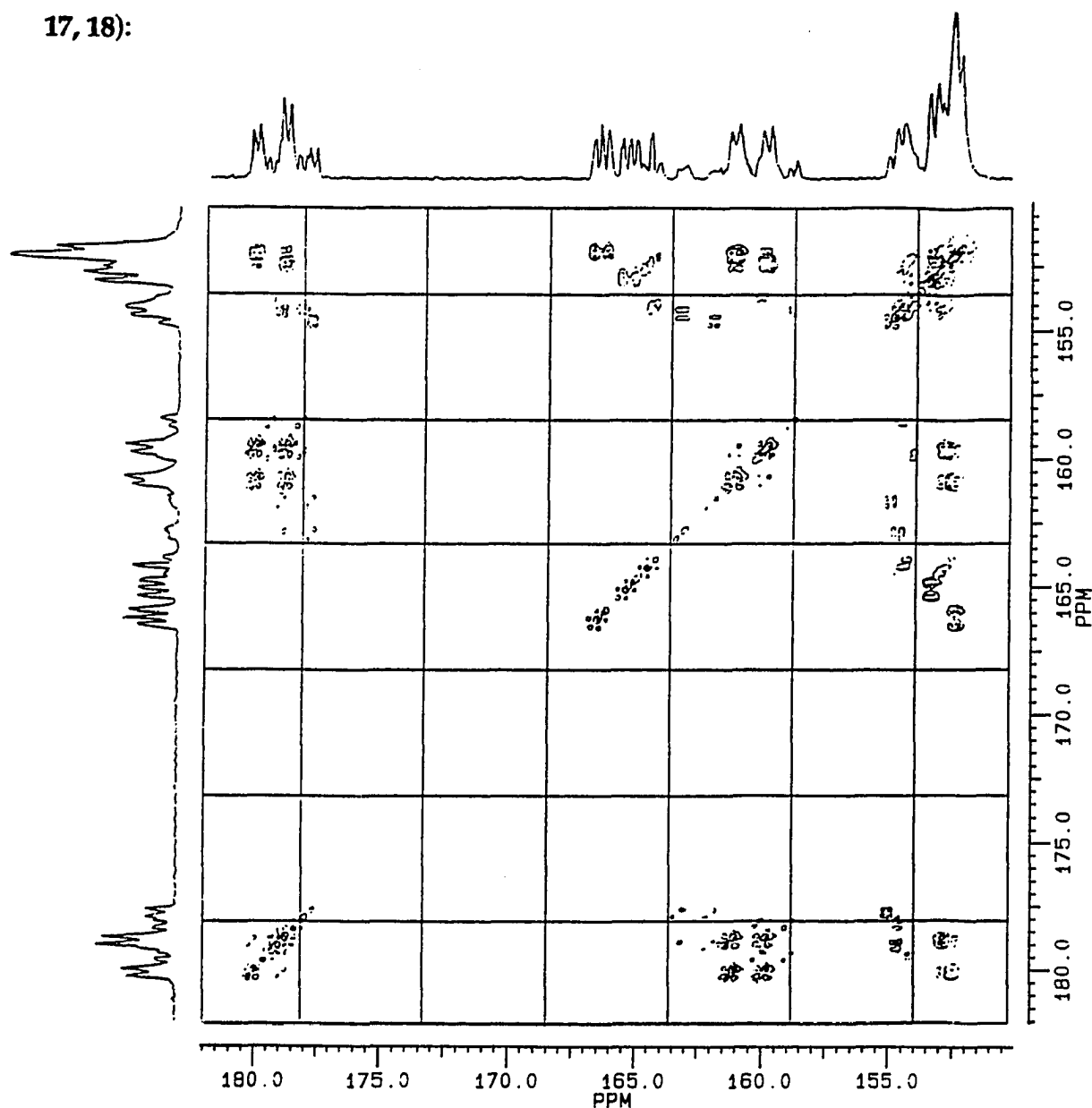
Figure 16. The 2-D COSY $^{31}P\{^1H\}$ NMR spectrum of complex 6

30
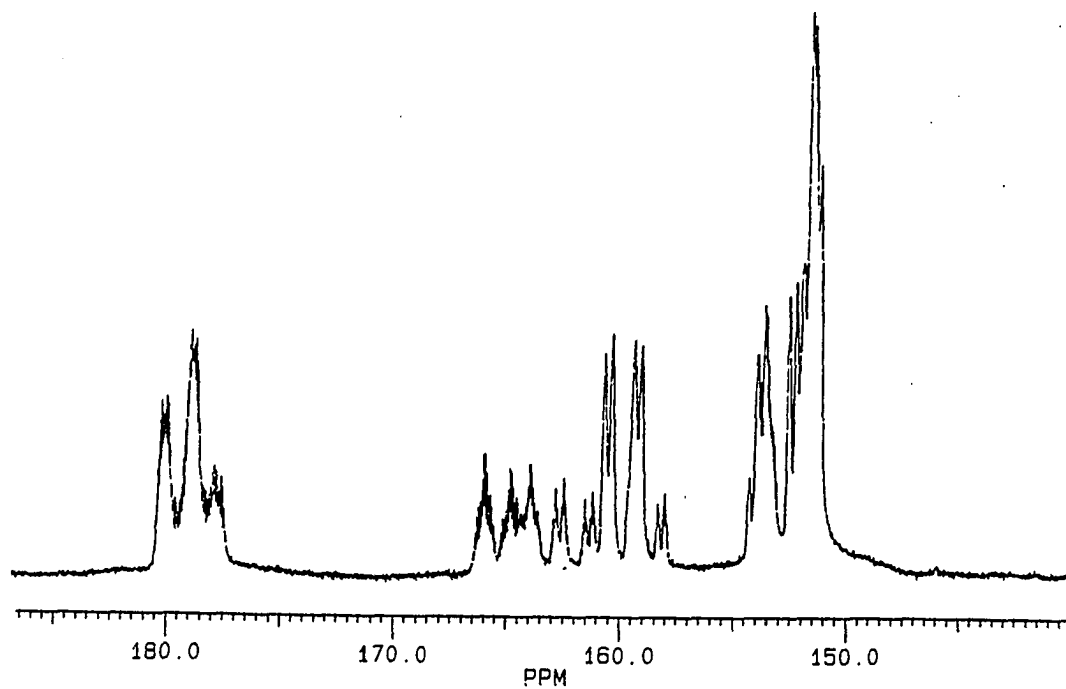
Figure 17. $^{31}P\{^1H\}$ NMR spectrum of complex **6**
[Selective methine proton (δ = 4.66–4.53 ppm) decoupled, DP 16L]
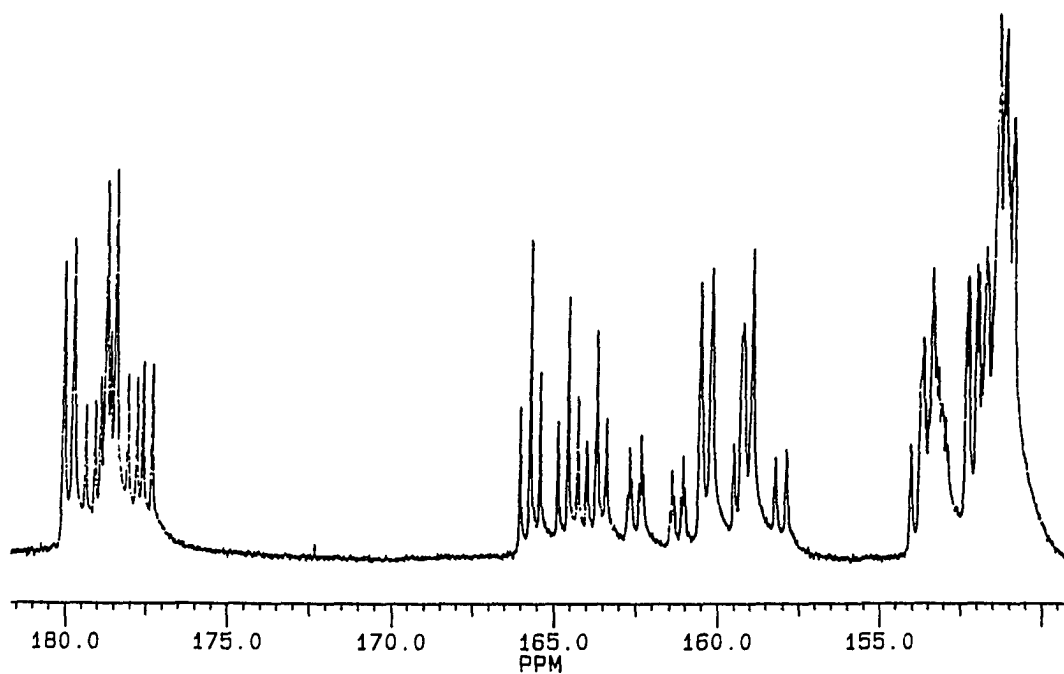
Figure 18. $^{31}P\{^1H\}$ NMR spectrum of complex **6**
(Full decoupled, DP 12H)

31

All of the peaks of these isomers can be assigned. The relative proportions of the isomers are approximately 40 : 24 : 18 : 18, again indicating a preference for equatorial substitution and *mer*- stereochemistry at the Mo atoms. In addition, the presence of all diastereomers in complexes **5** and **6** was confirmed by HPLC (**Figure 19**):

Retention time (min.):
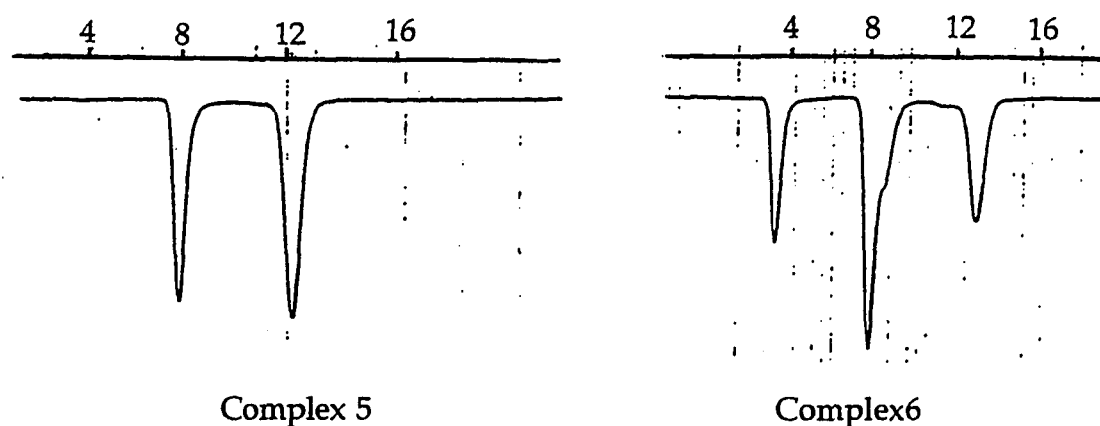
Complex 5   Complex6

Figure 19. HPLC traces for complexes **5** and **6**

Hexane/CH_2Cl_2 (75/25), Al_2O_3 column

Thus, we can see that both complexes **5** and **6** are isomeric mixtures. The HPLC of **5** showed 2 peaks and of **6** showed 3 peaks plus one shoulder. Due to the small capacity of the HPLC column, attempts to separate the diastereometric isomers quantitatively failed.

From the ^{31}P NMR spectra of **5** and **6** we can clearly see that the trans two-bond P-P coupling constants are larger than the cis values ($^2J(P, P)_{trans}$

32

=185 to 189 Hz, $^2J(P,P)_{cis}$ = 41 to 42 Hz). Both products are white solids with no chemical shifts around 307 ppm. Thus, the ^{31}P NMR spectra of compounds **5** and **6** are distinct from those of orange **2, 3,** and **4.** Here we can assign peaks from the phosphorus atoms trans and cis to the entering ligands. The chemical shift differences between these two phosphorus atoms are only about 20 ppm.

Similar reaction conditions using the phosphines resulted in negligible reaction. Under milder conditions, traces of the conventional substitution products similar to **5** and **6** can also be observed in the reactions generating **2, 3,** and **4** (See Part I-4). The bulkier triphenyl phosphite also yielded conventional substitution products similar to **5** and **6** .

3.Synthesis and Characterization of (CO)3Mo[^{i}Pr2NPO]4Mo(CO)2P(OMe)3 (7)

Another interesting result we obtained from the P(OMe)$_3$ reaction was that the compounds **5** and **6** could both thermally rearrange to orange-colored compounds which <u>did</u> show very low-field peaks at around 307 ppm.

Upon refluxing **5** and **6** in toluene for more than 30 hrs, both of these colorless compounds were transformed into orange-red (CO)3Mo[^{i}Pr2NPO]4Mo(CO)2P(OMe)3 (7), which is an analog of complexes **2, 3,** and **4.** Trace amounts of (CO)2P(OMe)3Mo[^{i}Pr2NPO]4Mo(CO)2P(OMe)3 were detected by ^1H NMR.

$$(CO)_4Mo[^iPr_2NPO]_4Mo(CO)_3P(OMe)_3 \longrightarrow$$
$$(5)$$

$$2CO + (CO)_3Mo[^iPr_2NPO]_4Mo(CO)_2P(OMe)_3,$$
$$(7) \qquad\qquad\qquad (eq\ 4)$$

33

$$2(CO)_3P(OMe)_3Mo[^iPr_2NPO]_4Mo(CO)_3P(OMe)_3 \longrightarrow$$

$$(6)$$

$$3CO + P(OMe)_3 + (CO)_3Mo[^iPr_2NPO]_4Mo(CO)_2P(OMe)_3$$

$$(7)$$

$$+ (CO)_2(POMe)_3Mo[^iPr_2NPO]_4Mo(CO)_2P(OMe)_3 \qquad (eq \ 5)$$
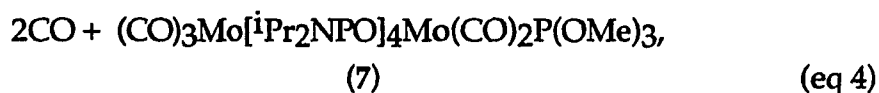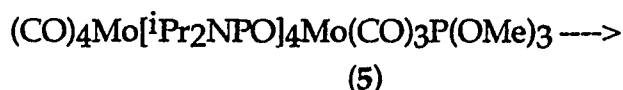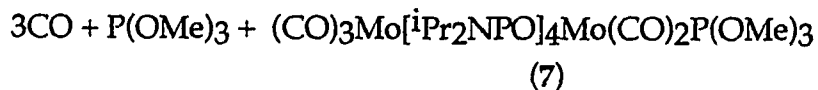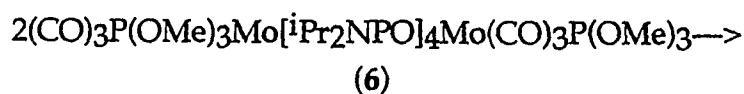
The product complex 7 was characterized by ^{31}P, ^1H, ^{13}C NMR, and IR spectra and by elemental analysis. The X-ray structure of complex 7 has been determined. One is shown in **Figure 20**. Selected bond angles and bond distances are listed in **Table IV**.
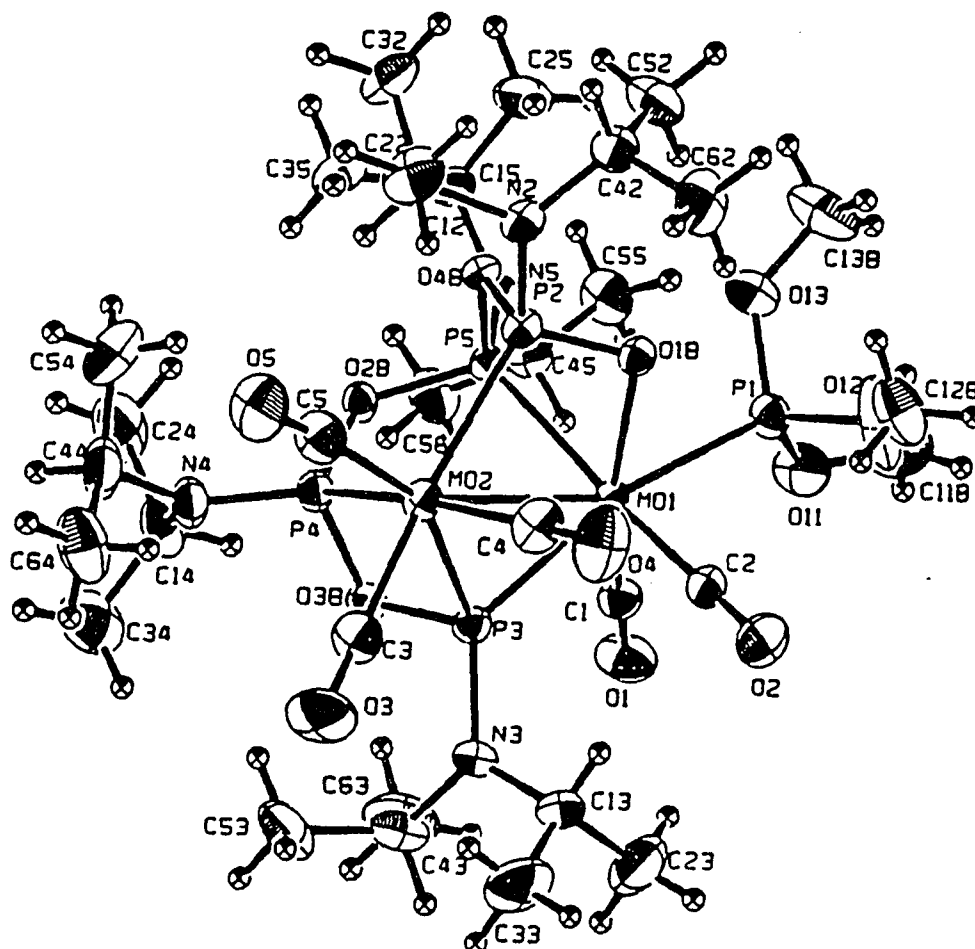
Figure 20. Molecular structure of complex 7

34
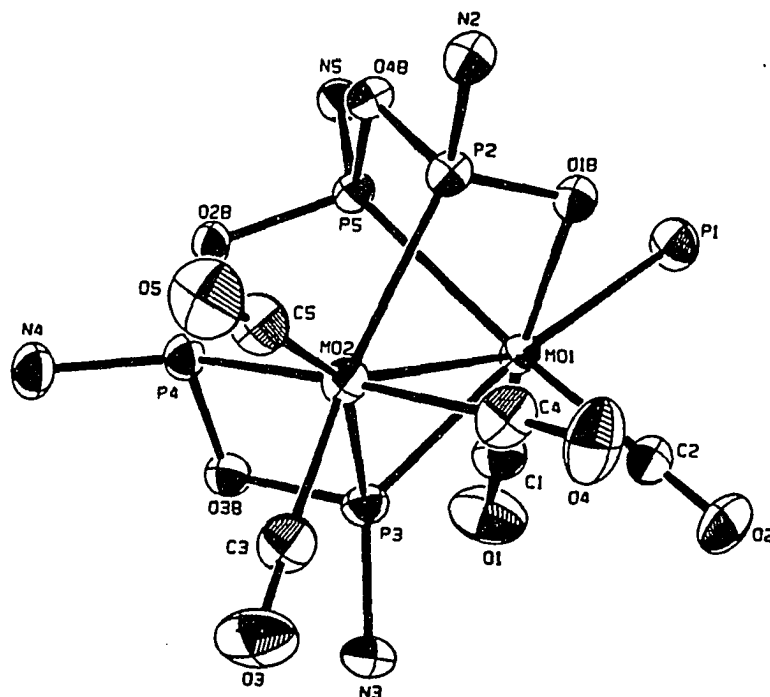
Figure 21. Core geometry of complex 7

Table IV. Selected Bond Distances (Å) and Angles (deg) for Complex 7

Mo(1)-Mo(2)	3.173(1)		
Mo(1)-P(1)	2.465(2)	P(2)-O(1B)	1.537(3)
Mo(1)-P(3)	2.353(2)	P(2)-O(4B)	1.730(3)
Mo(1)-P(5)	2.532(1)	P(3)-O(3B)	1.654(4)
Mo(1)-O(1B)	2.226(3)	P(4)-O(2B)	1.626(3)
Mo(1)-C(1)	1.952(6)	P(3)-O(3B)	1.662(3)
Mo(1)-C(2)	1.969(6)	P(5)-O(2B)	1.670(3)
Mo(2)-P(2)	2.525(2)	P(5)-O(4B)	1.604(3)
Mo(2)-P(3)	2.480(2)	C(1)-O(1)	1.157(6)
Mo(2)-P(4)	2.486(2)	C(2)-O(2)	1.159(6)
Mo(2)-C(3)	1.964(6)	C(3)-O(3)	1.150(7)
Mo(2)-C(4)	2.005(7)	C(4)-O(4)	1.141(7)
Mo(2)-C(5)	1.993(7)	C(5)-O(5)	1.151(7)

35

Mo(2)-Mo(1)-P(1)	48.83(3)	Mo(1)-Mo(2)-P(3)	47.25(3)
Mo(2)-Mo(1)-P(3)	50.73(4)	Mo(1)-Mo(2)-P(4)	81.01(4)
Mo(2)-Mo(1)-P(5)	78.46(3)	Mo(2)-Mo(1)-O(1B)	74.01(9)
P(1)-Mo(1)-P(3)	155.97(5)	P(2)-Mo(2)-P(3)	103.10(5)
P(1)-Mo(1)-P(5)	93.20(5)	P(2)-Mo(2)-P(4)	93.95(5)
P(1)-Mo(1)-O(1B)	79.30(9)	P(2)-Mo(2)-C(3)	171.0(2)
P(1)-Mo(1)-C(1)	83.1(2)	P(2)-Mo(2)-C(4)	84.3(2)
P(1)-Mo(1)-C(2)	88.7(2)	P(2)-Mo(2)-C(5)	96.0(2)
P(3)-Mo(1)-P(5)	91.09(5)	P(3)-Mo(2)-P(4)	62.33(5)
P(3)-Mo(1)-O(1B)	124.71(9)	P(3)-Mo(2)-C(3)	79.1(2)
P(3)-Mo(1)-C(1)	72.9(2)	P(3)-Mo(2)-C(4)	102.6(2)
P(3)-Mo(1)-C(2)	91.7(2)	P(3)-Mo(2)-C(5)	154.1(2)
P(5)-Mo(1)-O(1B)	78.28(9)	P(4)-Mo(2)-C(3)	95.1(2)
P(5)-Mo(1)-C(1)	98.6(2)	P(4)-Mo(2)-C(4)	163.9(2)
P(5)-Mo(1)-C(2)	168.7(2)	P(4)-Mo(2)-C(5)	102.0(2)
O(1B)-Mo(1)-C(1)	161.9(2)	C(3)-Mo(2)-C(4)	87.0(3)
O(1B)-Mo(1)-C(2)	91.1(2)	C(3)-Mo(2)-C(5)	82.2(3)
C(1)-Mo(1)-C(2)	92.7(2)	C(4)-Mo(2)-C(5)	94.1(3)
Mo(1)-P(1)-O(11)	114.2(2)	Mo(2)-P(2)-O(1B)	108.0(1)
Mo(1)-P(1)-O(12)	119.7(2)	Mo(2)-P(2)-O(4B)	110.5(1)
Mo(1)-P(1)-O(13)	111.8(2)	Mo(2)-P(3)-O(3B)	97.0(1)
Mo(1)-P(3)-Mo(2)	82.02(5)	Mo(2)-P(4)-O(2B)	114.1(1)
Mo(1)-P(3)-O(3B)	115.1(1)	Mo(2)-P(4)-O(3B)	96.5(1)
Mo(1)-P(5)-O(2B)	114.0(1)	O(11)-P(1)-O(12)	98.5(3)
Mo(1)-P(5)-O(4B)	102.2(1)	O(11)-P(1)-O(13)	106.0(3)
Mo(1)-O(1B)-P(2)	99.6(2)	O(12)-P(1)-O(13)	105.0(3)
O(1B)-P(2)-O(4B)	101.9(2)	O(2B)-P(5)-O(4B)	100.9(2)
O(2B)-P(4)-O(3B)	98.7(2)	P(4)-O(2B)-P(5)	119.8(2)
P(3)-O(3B)-P(4)	101.7(2)	P(2)-O(4B)-P(5)	108.9(2)

The structure is similar to that for complex 2. With the replacement of PPh$_3$ by P(OMe)$_3$, a few alterations were found in bond angles and lengths.

36

The Mo(1)-Mo(2) separation is now 3.173(1) Å. A metal-phosphorus distance of 2.352(2) Å is observed for Mo(1)-P(3) with a P(OMe)$_3$ instead of the P(Ph)$_3$ ligand approximately trans to it. All other Mo-P bonds are in the range 2.46-2.53 Å. The Mo(1)-O(1B) bond length is 2.226(3) Å and the trans Mo(1)-C(1) bond length is 1.952(6) Å. All other Mo-C bonds are in the range 1.97-2.00 Å. Except at P(2), ring P-O distances range from 1.60 to 1.67 Å. The two disparate P(2)-O distances with P(2)-O(1B) at 1.537 Å and P(2)-O(4B) at 1.730 Å result from the multiple-bond character of the former bond.

Both coordination spheres are similar to those found in 2. At Mo(2), the P(3)-Mo(2)-P(4) angle was compressed by the four-membered M-P-O-P chelate ring to only 62.33(5)°. The five-membered Mo(1)-P(3)-Mo(2)-P(2)-O(1B) heterocycle has a narrow Mo(1)-P(3)-Mo(2) angle of 82.02(5)° while the P(3)-Mo(1)-O(1B) angle is distended to 124.7(1)° . The angle closest to linearity at Mo(1) is C(2)-Mo(1)-P(5) at only 168.7(2)° . The four equatorial ligand atoms P(1), O(1B), P(3), and C(1) subtend very distorted angles at Mo(1): P(3)-Mo(1)-O(1B) is 124.7(1), O(1B)-Mo(1)-P(1) is 79.3(1)°, P(1)-Mo(1)-C(1) is 83.1(2)°, and C(1)-Mo(1)-P(3) is 72.9(2)° . These equatorial angles do sum up to 360°. At Mo(2), the approximately axial angle C(3)-Mo(2)-P(2) is 171.0(2)° . The four equatorial angles ranged from 62.3° to 102.6°, summing up to 361°.

Complex 6 can also form another orange compound. From its ^{1}H NMR spectrum (**Figure 22**), we can see that there are four P(OMe)$_3$ groups (four doublets for the trimethyl phosphite protons) and they are in two sets which means that it is a disubstituted compound as well as an isomeric mixture of (CO)$_2$P(OMe)$_3$Mo[^{i}Pr$_2$NPO]$_4$Mo(CO)$_2$P(OMe)$_3$. Unfortunately, due to the trace amount of the sample available, no satisfactory ^{31}P NMR spectrum was obtained.

37
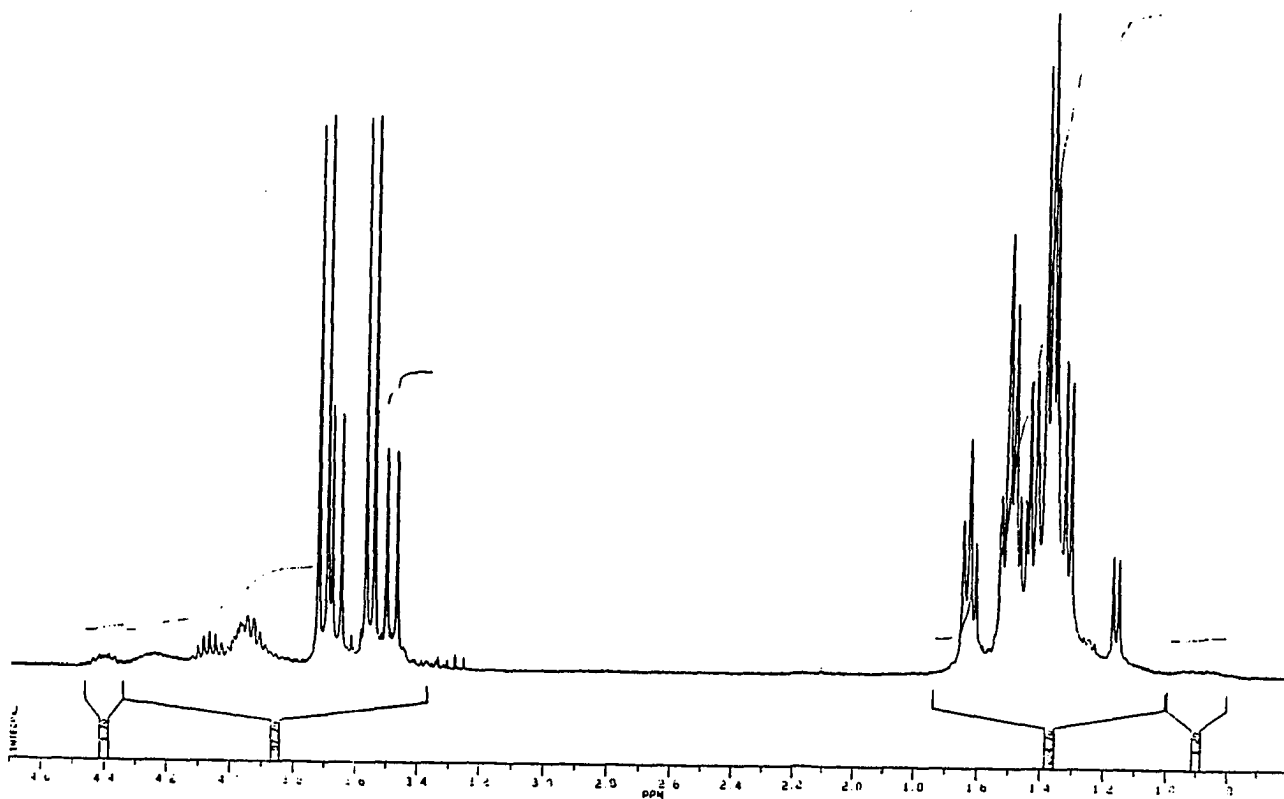
Figure 22. ^{1}H NMR spectrum for

$(CO)_2P(OMe)_3Mo[^iPr_2NPO]_4Mo(CO)_2P(OMe)_3$

4. Synthesis and Characterization of

$(CO)_3(L)Mo[^iPr_2NPO]_4Mo(CO)_3PPh_2H$ (L=CO(8), PPh$_2$H(9))

When the compounds 2, 3, and 4 were obtained, it was thought that only the phosphines with large enough cone angles could   force the cage structural change. Since the trimethyl phosphite ligand with its small cone angle also appeared to give this structure as the thermodynamic product, we realized that reactions described in eq 1 may have also undergone the same initial

38

substitution. These intermediates may be too unstable with the larger phosphine ligands to allow isolation as they quickly transformed to the more stable Mo-Mo bonded structures. Reactions 1, 2 and 3 were repeated under milder conditions (refluxing hexane). At the lower temperature, the reactions were slow. From the TLC and the ^{31}P NMR spectra of the reaction mixtures we noted that indeed each of these gave simple substitution compounds. Because the reactions were far from complete and the products were not stable, we could only isolate two of these intermediates: $(CO)_3(L)Mo[^iPr_2NPO]_4Mo(CO)_3PPh_2H$ (L=CO(8), PPh_2H(9)) were obtained from the reaction mixture by column chromatography.

The complexes $(CO)_3(L)Mo[^iPr_2NPO]_4Mo(CO)_3PPh_2H$ (L=CO (8), PPh_2H (9)) were synthesized by the reaction of diphenylphosphine with the dimolybdenum cage complex $(CO)_4Mo[^iPr_2NPO]_4Mo(CO)_4$ (1) in refluxing hexane. The equation representing the preparation of these complexes is shown below:

$$2(CO)_4Mo[^iPr_2NPO]_4Mo(CO)_4 + 3PPh_2H \longrightarrow$$
$$(1)$$

$$3CO + (CO)_4Mo[^iPr_2NPO]_4Mo(CO)_3PPh_2H$$
$$(8)$$

$$+ (CO)_3(PPh_2H)Mo[^iPr_2NPO]_4Mo(CO)_3PPh_2H$$
$$(9) \qquad\qquad\qquad (eq\ 6)$$
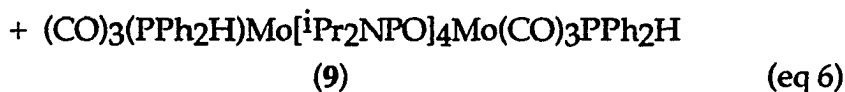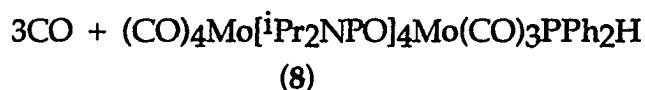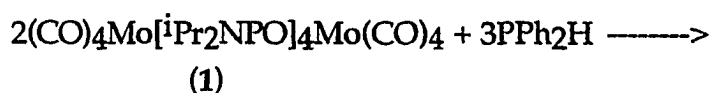
After heating the reaction mixture for 72hrs, a clear light-yellow solution formed. TLC showed four products. The second spot was isolated as

39

compound **8** and the fourth spot as compound **9**. The products were characterized by ^{31}P, ^{1}H, ^{13}C NMR, and IR spectra, and in addition, the structure of compound **8** was confirmed by elemental analysis. The isolated yields of complexes **8** and **9** were only 11 and 4%, respectively.

Both products are cage-like compounds. One is the monosubstituted isomer with one axial CO replaced by the ligand; the other is the diaxial-substituted isomer, (i. e., monosubstitution at each metal, **Figure 23**):

ax   diax
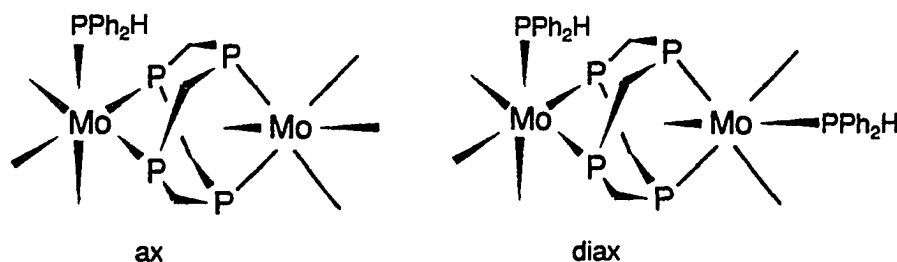
Figure 23. Proposed structures for complex **8** and **9**

Another expected result yet to be proved is that both of these white-colored complexes, **8** and **9**, can also readily transform to the known orange complex **4** in refluxing toluene.

It seems reasonable to postulate that the colorless cage-like products of simple substitution were formed first in each reaction. These compounds were not very stable and readily rearranged to novel orange complexes by breakage of one P-O bond.

5. Synthesis and Characterization of $(CO)_3Mo[^iPr_2NPO]_4Mo(CO)_2(L)$ (L=Py (10), CO (11))

In order to identify whether it was the electronic or steric factor that forced the structural rearrangement, $P(OC_6H_5)_3$ was used for comparison with $HP(C_6H_5)_2$ since they have similar cone angles (128° and 126°) but different π-acceptor abilities. By following the reaction of $P(OC_6H_5)_3$ with cage **1** by TLC and ^{31}P NMR, a similar result was obtained as for $P(OCH_3)_3$. The intermediate substitution product, however, was more stable than that for $HP(C_6H_5)_2$. This suggests that the electronic influence on the rearrangement reaction is more important than the steric influence, and that the stronger π-acceptor ligands can stabilize the simple substitution products.

In order to further verify this observation, a stronger σ-donor ligand, pyridine, was used to react with the cage **1** and to compare with $P(OCH_3)_3$. Pyridine has a cone angle very similar to that of $P(OCH_3)_3$ (Θ=106°). [Cone angle for the phenyl group is 105°[36], pyridine should have essentially the same value.] The reaction of pyridine with the dimolybdenum cage **1** was run in refluxing toluene.

$$(CO)_4Mo[^iPr_2NPO]_4Mo(CO)_4 + Py \longrightarrow$$
$$(1)$$

$$3CO + (CO)_3Mo[^iPr_2NPO]_4Mo(CO)_2Py$$
$$(10) \qquad\qquad (eq\,7)$$
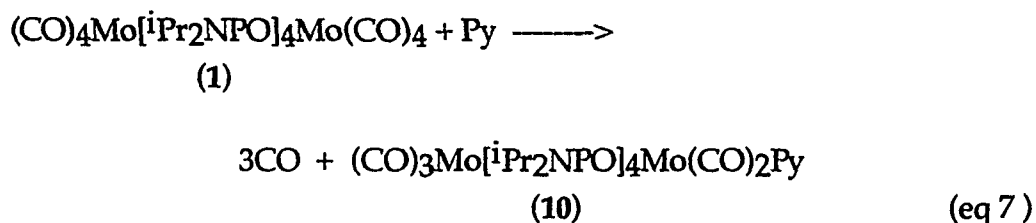
The yield of complex **10** was 76%.

41

Compared to $P(OCH_3)_3$ from which we can get the substitution intermediates, this result was very different. This product was a red-orange compound with structure similar to the orange compounds 2, 3, 4, and 7. No substitution intermediates showed up at all either on TLC or in the ^{31}P NMR spectra taken during the reaction.

This again suggests that strong π-acceptor ligands can stabilize simple substitution intermediates while good σ-donors make the metal electron rich and facilitate the P-O oxidative addition process.

From this reaction we also observed that:

(A) The product 10 is not stable in the NMR solvent $CDCl_3$, since the ^{1}H and ^{31}P NMR spectra showed that it transformed to another orange complex 11 (Figure 23). The ^{1}H NMR spectrum showed that there was no pyridine in the new complex(Figure 25) and its ^{31}P NMR spectrum is similar to that of the complex 2 after reaction with CO .

42
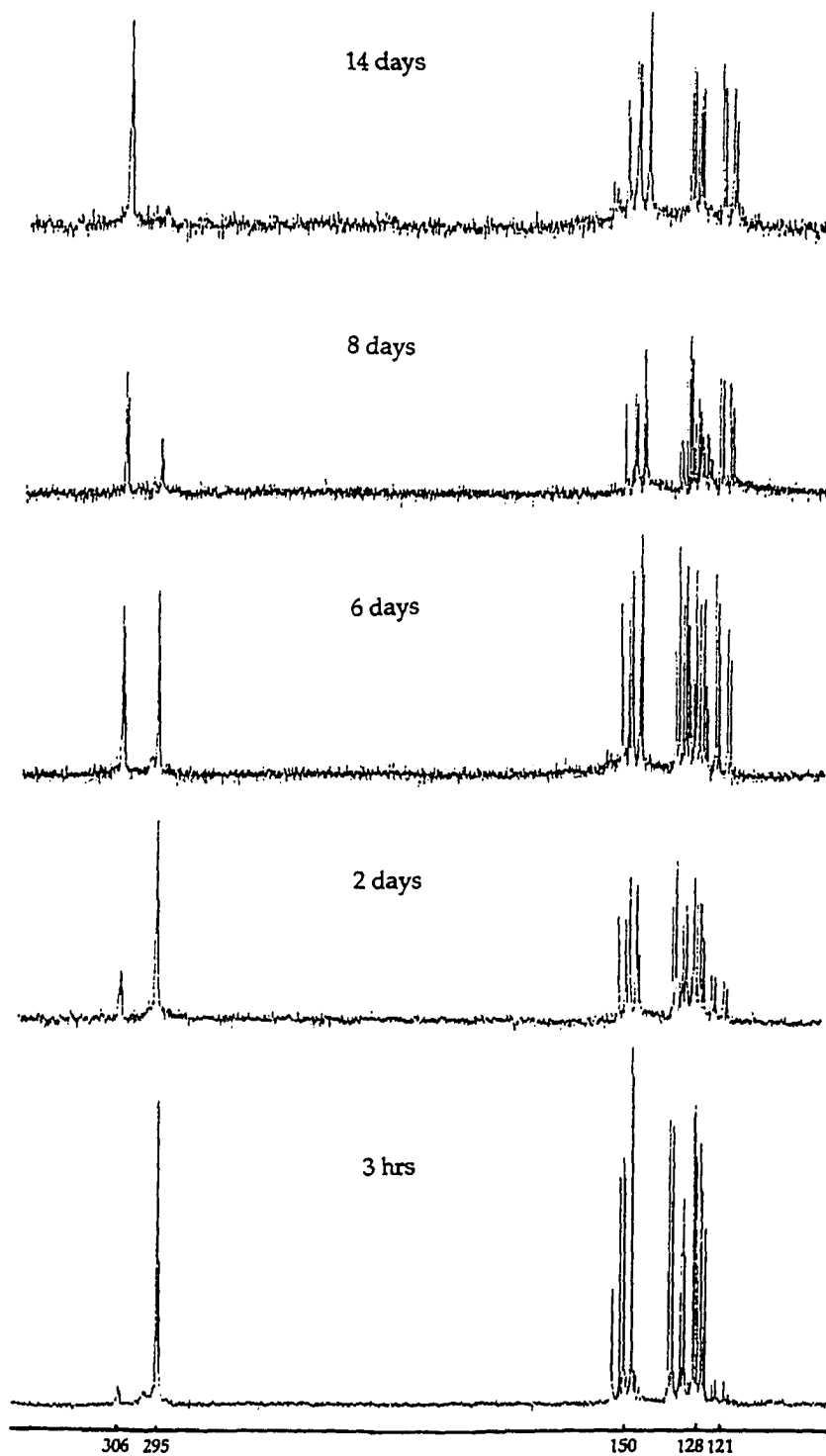
Figure 24. ^{31}P NMR spectra of complex **10** in $CDCl_3$

43

^{1}H NMR Spectrum of $(CO)_3Mo[^iPr_2NPO]_4Mo(CO)_2Py$

^{1}H NMR Spectrum of $(CO)_3Mo[^iPr_2NPO]_4Mo(CO)_3$
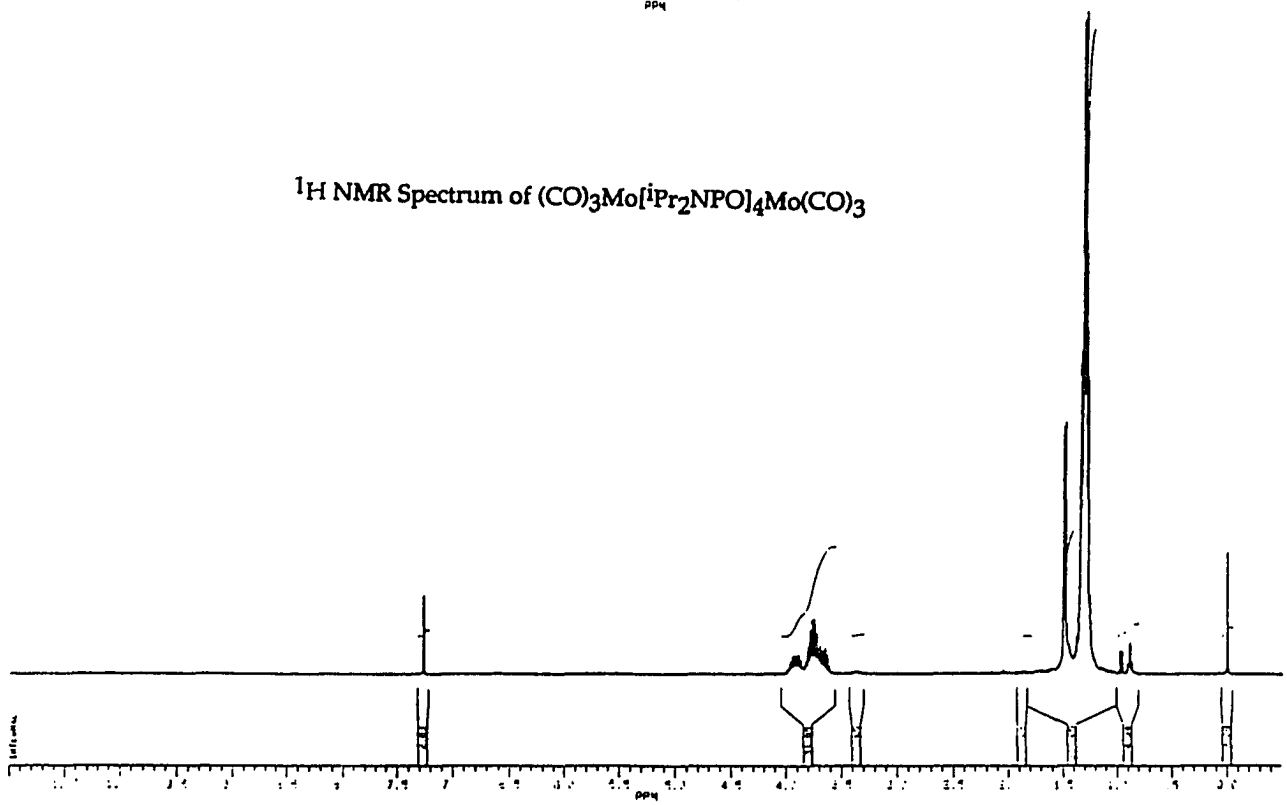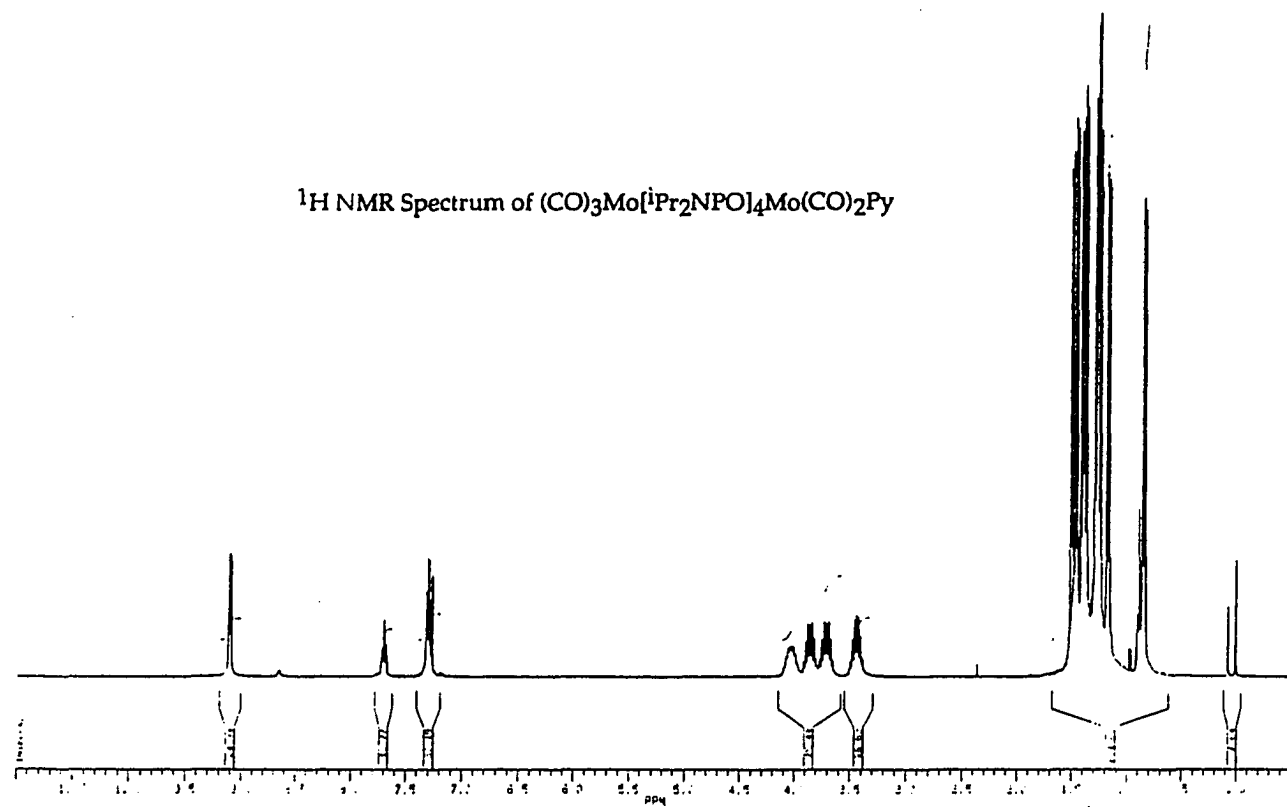
Figure 25. ^{1}H NMR spectra of complex **10** and **11**

44

Thus, liberated CO from decomposition can displace the Py ligand in **10** to form the new orange complex $Mo_2[^iPr_2NPO]_4(CO)_6$. In order to prove this, CO gas was bubbled through a solution of complex **10** at about 60°C. After a few hours, TLC showed that it was completely transformed to orange compound **11**. The new compound showed an orange spot on the top of the spot of complex **10**. ^1H and ^{31}P NMR spectra clearly showed that this new product, $(CO)_3Mo[^iPr_2NPO]_4Mo(CO)_3$ (**11**), is identical to the one obtained from a $CDCl_3$ NMR solution of **10**. The reaction can be written as:

$$(CO)_3Mo[^iPr_2NPO]_4Mo(CO)_2Py + CO \quad \text{---------->}$$
$$(10)$$
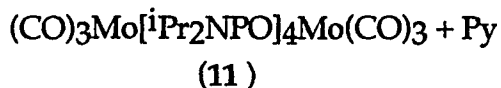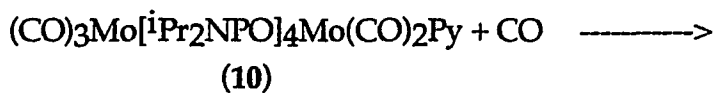
$$(CO)_3Mo[^iPr_2NPO]_4Mo(CO)_3 + Py$$
$$(11) \qquad\qquad\qquad (eq\ 8)$$

(B) Complex **11** is very reactive and easily reacted with pyridine to reform **10**. It can also react with maleic anhydride in warm toluene or refluxing hexane to form a yellow cage-olefin complex . Complex **10** can also react with maleic anhydride in refluxing hexane to form a similar yellow cage-olefin complex. This cage-olefin complex was an inseparable mixture. When complex **10** reacted with $MeP(C_6H_5)_2$ in refluxing toluene, complex **3** was reformed.

Complex **11** was very soluble in warm hexane and hexane solutions under N_2 gave good quality crystals. The X-ray structure of these crystals was determined (**Figure 26**). Selected bond distances and bond angles are listed in **Table V** :

45
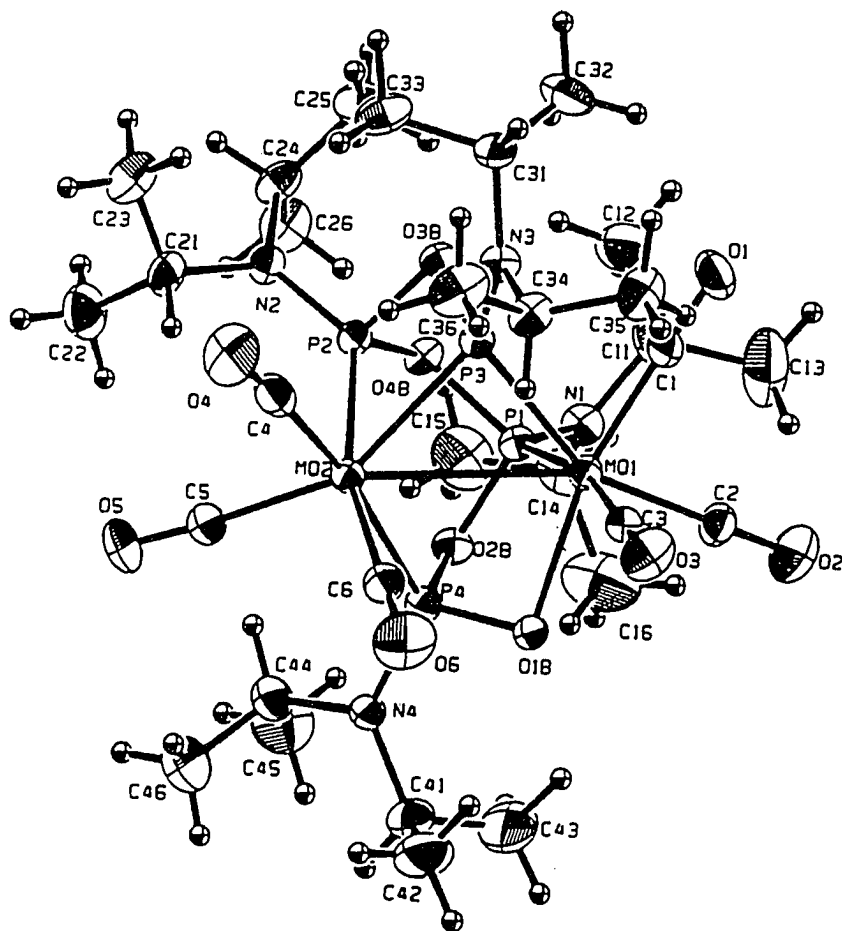
Figure 26. Molecular structure of complex 11
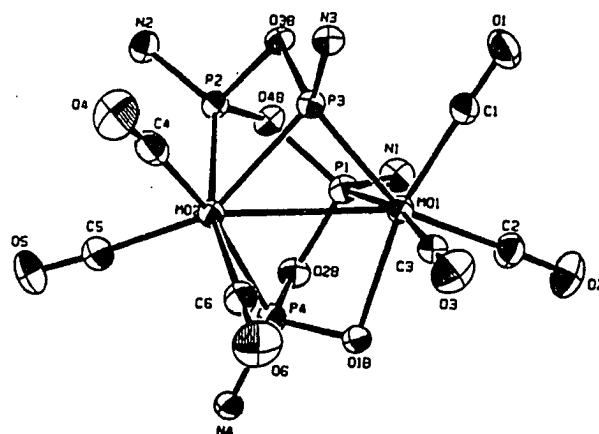
Figure 27. Core geometry of complex 11

46

Table V. Selected Bond Distances (Å) and Angles (deg) for $Mo_2[^iPr_2NPO]_4(CO)_6$ (11)

Mo(1)-Mo(2)	3.143(1)		
Mo(1)-P(1)	2.501(3)	P(2)-O(2B)	1.599(7)
Mo(1)-P(3)	2.403(3)	P(2)-O(4B)	1.676(7)
Mo(1)-O(1B)	2.265(7)	P(2)---P(3)	2.544(4)
Mo(1)-C(1)	1.94(1)	P(2)-O(3B)	1.694(7)
Mo(1)-C(2)	2.04(1)	P(2)-O(4B)	1.621(7)
Mo(1)-C(3)	2.03(1)	P(3)-O(3B)	1.639(7)
Mo(2)-P(2)	2.440(3)	P(4)-O(1B)	1.526(7)
Mo(2)-P(3)	2.443(3)	P(4)-O(2B)	1.742(8)
Mo(2)-P(4)	2.515(3)	C(1)-O(1)	1.16(1)
Mo(2)-C(4)	2.11(2)	C(2)-O(2)	1.13(1)
Mo(2)-C(5)	2.01(1)	C(3)-O(3)	1.13(1)
Mo(2)-C(6)	2.03(1)	C(4)-O(4)	1.10(2)
C(5)-O(5)	1.14(1)	C(6)-O(6)	1.12(1)

Mo(2)-Mo(1)-P(1)	78.42(7)	Mo(1)-Mo(2)-P(2)	81.38(7)
Mo(2)-Mo(1)-P(3)	50.11(7)	Mo(1)-Mo(2)-P(3)	49.00(7)
Mo(2)-Mo(1)-P(4)	49.01(6)	Mo(1)-Mo(2)-P(4)	60.36(7)
Mo(2)-Mo(1)-O(1B)	73.8(2)	Mo(1)-Mo(2)-C(4)	125.2(3)
P(1)-Mo(1)-P(3)	90.6(1)	P(2)-Mo(2)-P(3)	62.8(1)
P(1)-Mo(1)-O(1B)	79.2(2)	P(2)-Mo(2)-P(4)	93.4(1)
P(1)-Mo(1)-C(1)	97.5(4)	P(2)-Mo(2)-C(4)	97.2(1)
P(1)-Mo(1)-C(2)	91.6(4)	P(2)-Mo(2)-C(5)	96.5(4)
P(1)-Mo(1)-C(3)	167.7(3)	P(2)-Mo(2)-C(6)	164.3(4)

47

P(3)-Mo(1)-O(1B)	123.8(2)	P(3)-Mo(2)-P(4)	107.0(1)
P(3)-Mo(1)-C(1)	72.4(3)	P(3)-Mo(2)-C(4)	81.5(3)
P(3)-Mo(1)-C(2)	153.2(4)	P(3)-Mo(2)-C(5)	151.8(4)
P(3)-Mo(1)-C(3)	93.7(3)	P(3)-Mo(2)-C(6)	103.7(4)
O(1B)-Mo(1)-C(1)	163.2(4)	P(4)-Mo(2)-C(4)	168.7(4)
O(1B)-Mo(1)-C(2)	82.7(4)	P(4)-Mo(2)-C(5)	92.4(4)
O(1B)-Mo(1)-C(3)	88.8(4)	P(4)-Mo(2)-C(6)	82.6(4)
C(1)-Mo(1)-C(2)	80.9(5)	C(4)-Mo(2)-C(5)	82.5(5)
C(1)-Mo(1)-C(3)	94.8(5)	C(4)-Mo(2)-C(6)	88.2(5)
C(2)-Mo(1)-C(3)	89.8(5)	C(5)-Mo(2)-C(6)	98.8(5)
Mo(1)-P(1)-O(2B)	103.1(3)	Mo(2)-P(2)-O(3B)	97.2(3)
Mo(1)-P(1)-O(4B)	116.0(3)	Mo(2)-P(2)-O(4B)	116.7(3)
Mo(1)-P(3)-Mo(2)	80.89(9)	Mo(2)-P(3)-O(3B)	98.6(3)
Mo(1)-P(3)-O(3B)	113.1(3)	Mo(2)-P(4)-O(1B)	108.0(3)
Mo(1)-O(1B)-P(4)	97.7(4)	Mo(2)-P(4)-O(2B)	110.5(3)
O(1B)-P(4)-O(2B)	103.3(4)	P(1)-O(2B)-P(4)	107.9(4)
O(2B)-P(1)-O(4B)	100.3(4)	P(1)-O(4B)-P(2)	116.5(4)
P(2)-O(3B)-P(3)	99.5(2)	O(3B)-P(2)-O(4B)	98.0(4)

Complex 11 has a polycyclic structure similar to complexes 2 and 7. Replacing a phosphine or phosphite ligand by a CO ligand only generated relatively few changes in bonding details. The Mo(1)-Mo(2) bond is now at 3.143(1) Å. The Mo(1)-P(3) bond changed from 2.362(4) in 2 and 2.352(2) in 7 to 2.403(3) Å with a CO instead of the PPh$_3$ or P(OCH$_3$)$_3$ *trans* to it. That is because CO ligand is a better π-acceptor ligand, so the π back-bonding between Mo-CO is stronger and the Mo-P bonding is weakened. The Mo(1)-O(1B) bond distance is changed from 2.222(8) in 2 and 2.226(3) in 7 to 2.260(7) Å. The

48

Mo(1)-C(1) bond distance *trans* to the Mo(1)-O(1B) bond is 1.94(1) Å. It is indeed shorter than all of the other Mo-C bonds which are in the range 2.01-2.11 Å. The two disparate P(4)-O distances result in a shorter bond P(4)-O(1B) at 1.526(7) Å and a longer bond P(4)-O(2B) at 1.742(8) Å.

Both bond angles and coordination spheres around Mo(2) are similar to those in **2** or **7**. With the replacement of a phosphine or phosphite by a carbonyl ligand, the four-membered Mo(2)-P(2)-O(3B)-P(3) chelate ring and the five-membered Mo(1)-P(3)-Mo(2)-P(4)-O(1B) heterocycle are essentially unchanged. The Mo(2)-P(3)-Mo(1) angle is slightly decreased to 80.9(1)° due to the smaller Mo-Mo distance. At Mo(1), the angle closest to linearity is C(3)-Mo(1)-P(1) at 167.7(3)° while P(4)-Mo(2)-C(4) is 168.7(4)°. The four equatorial ligand atoms P(3), O(1B), C(1), and C(2) have distorted angles at Mo(1); P(3)-Mo(1)-O(1B) is 123.8(2)°, O(1B)-Mo(1)-C(2) is 82.7(4)°, C(1)-Mo(1)-C(2) is 80.9(5)° and C(1)-Mo(1)-P(3) is 72.4(3)° . These angles sum to 359° . At Mo(2), the corresponding equatorial angles deviate widely from orthogonality ranging from 62.8(1) to 103.7(4)°, summing to 362°. The C(3) at Mo(1) now has reasonably orthogonal angles with O(1B), P(3), C(1), and C(2) ranging from 88.9(4) to 94.8(5)° compared to the corresponding angles in **7** ranging from 79.3(1) to 93.20(5)°.

The overall geometries of the complexes **2, 7,** and **11** are thus quite similar. As mentioned in Part I-2, the phosphido chemical shift is very sensitive to the M-P-M angle and the extent of metal-metal interaction. For the series of orange complexes, the nearly constant phosphido chemical shift at +306 ppm suggests that these geometrical details are very similar in these complexes. A comparison of selected bond details from the X-ray structure of complexes **2, 7, 11,** as depicted in **Figure 28,** demonstrates that the phosphido angle and Mo-

49

Mo bond indeed remain little changed.
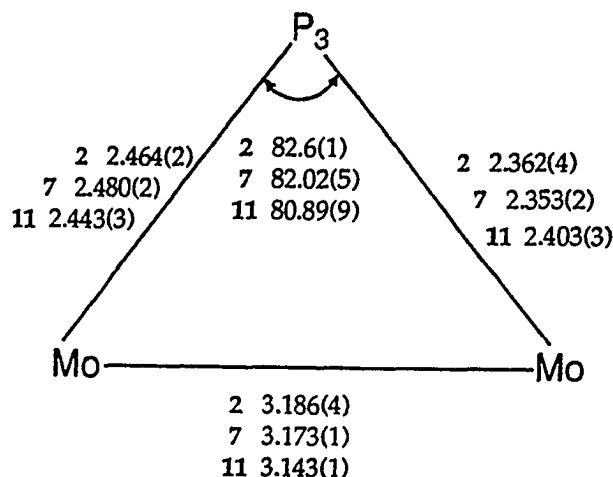
Figure 28. Comparison of the phosphido-bridge
structural data for complex **2, 7, 11**

For the cage reactions of CH_3CN and C_6H_5CN, we deduced from the TLC

and the ^{31}P NMR spectra of the reaction solutions that two orange-colored

products formed. One of these readily rearranged to the other in $CDCl_3$

solvent. By comparing the ^{31}P NMR spectra with that of **10** and **11**, it is clear

that one of the products is $(CO)_3Mo[^iPr_2NPO]_4Mo(CO)_2(RCN)$ and the other

is again complex **11**, $(CO)_3Mo[^iPr_2NPO]_4Mo(CO)_3$. (We tried very hard but

unsuccessfully to isolate the pure products.) Since CH_3CN and C_6H_5CN are

ligands which have very little π-bonding ability[37], the substitution

intermediates are not very stable.

50

For the reaction of pyridine, only one substitution product was formed in a fast reaction, but for secondary amines like piperidine and diisopropylamine, the reactions were slow and the cage was degraded via P-O-P cleavage to give bis (dialkylamino) phosphine oxides:

$$Mo(CO)_4[^iPr_2NPO]_4Mo(CO)_4 + HNC_5H_{10} \text{ (excess)} \longrightarrow$$

$$(^iPr_2N)_2P(O)H + (^iPr_2N)(C_5H_{10}N)P(O)H +$$

$$(C_5H_{10}N)_2P(O)H + Mo(CO)_4(HNC_5H_{10})_2 + etc.$$
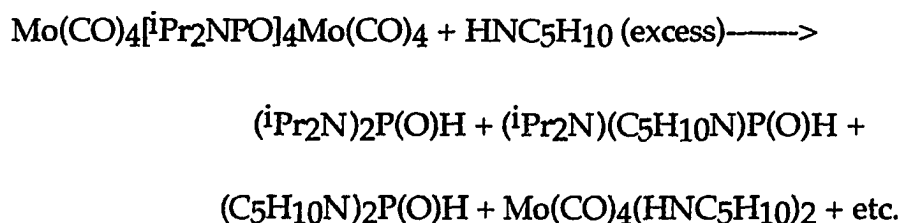
Both transamination and nucleophilic P-O-P cleavage occurred, resulting in essentially a reversal of the cage formation reaction from $Mo(CO)_6$ and $(^iPr_2N)_2P(O)H$[8]. The identities of the products were confirmed by obtaining the proton-decoupled and proton-coupled ^{31}P NMR spectra of the product mixture.

Also, we checked the reactions of the cage compound with tertiary amines such as $[(CH_3)_2CH]_2NC_2H_5$ and $(C_2H_5)_3N$. Because the bonding between the metal and pure σ-donor ligands is very weak, only negligible cage reactions resulted.

6. Relationship of Reaction Rate to Steric and Electronic Factors

It has long been hoped that the stereoelectronic properties of phosphorus(III) ligands can be parameterized into electronic and steric components. Yet, steric effects can have important electronic consequences and vice versa. Thus, the separation of electronic and steric effects into purely

51

steric or electronic factors is difficult. Tolman introduced the cone angle[38] and electronic parameter[39] (x values) of phosphorus (III) ligands for this quantification. A measure of steric effects was proposed based on ligand cone angles (Θ) of space-filling CPK molecular models and the electronic effect was based on A_1 carbonyl stretching frequencies (v) in $Ni(CO)_3L$ complexes. Since then, it has been shown that many chemical and spectroscopic properties of organometallic complexes correlate with the cone angle and the x values, and reflect the collective electronic donor/acceptor properties of the ligands[36] [40]. It is a practical and useful separation.

In order to distinguish the importance of the electronic and steric influences of the phosphorus ligands in these two-step reactions, we compared the reactions of cage complex 1 with $P(C_6H_5)_3$, $MeP(C_6H_5)_2$, $HP(C_6H_5)_2$, $P(OCH_3)_3$, $P(OC_6H_5)_3$ and pyridine under similar conditions. From the ^{31}P NMR spectra of the reaction mixtures we calculated the percent of cage reacted and also the percent of the orange phosphido- compound formed from the substitution intermediates. The results are listed in **Tables VI and VII** along with ligand size and electronic parameters derived by Tolman:

Table VI: Comparison of the Reaction Rates with Ligands Cone Angle

Ligand	Θ	%Cage Reacted(4 h)
$P(C_6H_5)_3$	145	44(2)
$MeP(C_6H_5)_2$	136	56(2)
$P(OC_6H_5)_3$	128	56(5)
$HP(C_6H_5)_2$	126	95(3)
$P(OCH_3)_3$	106	100(1)
pyridine	105	100(1)

(N. B. % is amount of product relative to the Cage Starting Material)

Table VII: Comparison of the Reaction Rates with the Electronic Parameters
of the Ligands

Ligand $PX_1X_2X_3$	$X_1+X_2+X_3$	% orange product formed(4 h)
$P(OC_6H_5)_3$	$9.7 \times 3 = 29.1$	0(1)
$P(OCH_3)_3$	$7.7 \times 3 = 23.1$	~10-20(10)*
$HP(C_6H_5)_2$	$4.3 \times 2 + 8.3 = 16.9$	49(4)
$P(C_6H_5)_3$	$4.3 \times 3 = 12.9$	22(4)
$MeP(C_6H_5)_2$	$4.3 \times 2 + 2.6 = 11.2$	33(1)
pyridine		100(1)

* Estimated from the spectra.

(N. B. % is based on the amount of cage reacted in the reaction mixture.)

53

From the above results, we can see that as the cone angle of the phosphine ligand decreased, the percent of cage reacted increased. As the π-acceptor ability of ligand decreased, the percent of orange phosphido-product increased. In addition, as the reaction progressed, the fraction of the orange complex to the consumed cage increased. So the ligand steric influence upon the initial substitution step is important. For the second rearrangement step, the steric factor is less important than the electronic influence. The smaller the ligand, the easier it can substitute CO's on the cage, while the stronger the π-acceptor ability of the ligand, the more stable these intermediates proved to be.

Why do strong π-acceptor ligands stabilize the cage-structure? It may be because they can decrease the electron density on the metal by increasing the strength of M->P or M->CO π-bonding, whereas stronger σ-donors will make the metal more electron rich and facilitate P-O-P oxidative addition at the metal.

Conclusions and Suggestions for Future Work

Triphenylphosphine, diphenylmethylphosphine, and diphenyl-phosphine or pyridine reacted with the molybdenum cage complex, which resulted in the addition of one ligand and loss of three carbonyls to yield the orange products. One P-O-P intercage linkage has been cleaved and oxidatively added to the two molybdenum vertices to create a μ^2-PO- and a μ^2-P- bridge. In addition, an intercage metal-metal bond has formed (**Scheme IV**).
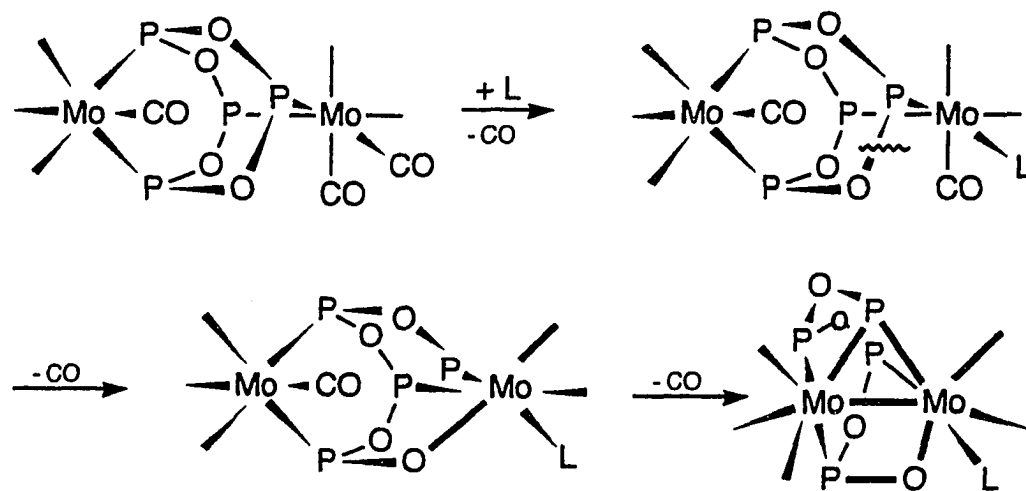
Scheme IV

When trimethylphosphite and triphenylphosphite reacted with the molybdenum cage complex, the simple mono- and disubstituted complexes were obtained. Upon further heating, these substitution products underwent similar P-O-P cleavage and associated transformations to give analogues of the phosphine and pyridine adducts.

When these adducts reacted with CO gas, the attached phosphine was replaced by CO to form complex **11**, $(CO)_3Mo[^iPr_2NPO]_4Mo(CO)_3$. If the weak-

55

bonding ligands acetonitrile or benzonitrile were used to react with the molybdenum cage, complex **11** formed as the major product even though no CO gas was added to the reaction solution.

The facility for the transformation of simple substitution complexes to the orange complexes appeared to depend on the π-acceptor strength of the attacking nucleophile while the initial substitution itself depended on the steric size of the ligands. A smaller ligand with stronger π-acceptor ability can more easily substitute CO's on the cage and form the substitution intermediates, while ligands with more σ-donor ability can more easily form the orange compound. Also, pure σ-donor ligands such as amines have only weak interactions with the zero-valent metal centers.

Future work in this area might involve studies of the reactivities of analogous cage complexes, cage complexes with different substituents on phosphorus atoms, or different-sized cage such as $M_2(CO)_8[DMP-PO]_4$ (M=Cr, Mo), $Ni_2(CO)_4[Cy_2NPO]_4$, $Cr_2(CO)_8[^iPr_2NPO]_4$, and $Cr_2(CO)_6[DMP-PO]_6$. The substitution and oxidation-addition rates, the nature of the products or the distribution of the intermediate isomers of these complexes may prove to be very different, because the different metal centers and the different substituents on the phosphorus atoms and even the polyphosphoxane cage size, may all play important roles in these processes.

Strongly nucleophilic species or noncoordinating acids like HBF_4 and HSO_3CF_3 should be reacted with the cage complex. The former may attack the cage phosphorus atoms, whereas the latter can protonate the cage by attacking the P-N sites.

56

EXPERIMENTAL SECTION

General Procedure: All synthetic procedures were carried out using standard Schlenck technique under an atmosphere of prepurified nitrogen. Chemical reagents were commercial products and were used without further purification. Hexane and methylene chloride were distilled from CaH_2, Toluene was reagent grade and was dried over Na and freshly distilled before use. Triphenylphosphine, diphenylmethylphosphine, diphenylphosphine, trimethyl phosphite were used as purchased from Strem Chemicals. Pyridine, diisopropylamine, piperidine, ethyl acetate, acetonitrile and benzonitrile were reagent grade obtained from Aldrich Chemical Co. Alumina (Aldrich Chemical Co, Brockmann, I, neutral) was used as received. The cage complex $(CO)_4Mo(^iPr_2NPO)_4Mo(CO)_4$ was synthesized as described previously[8]. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on JEOL FX 90Q or Bruker AM360 FT-NMR Spectrometers. For ^1H and ^{13}C, $(CH_3)_4Si$ was used as internal standard, whereas for ^{31}P, the chemical shifts were reported in ppm to high frequency of external 85% H_3PO_4. Spectra were obtained in $CDCl_3$ solution unless otherwise noted. Infrared spectra were recorded on a Perkin-Elmer 283B Spectrometer. Elemental analyses were performed at the University Instrumentation Center using a Perkin-Elmer 240b or Perkin-Elmer Series CHNS/O Analyzer 2400 elemental analyzer.

X-ray crystal structures were determined by Dr. Jerry P. Jasinski, Roman Y. Pozdnizkov, and Richard Woudenberg, Department of Chemistry, Keene

State College, Keene, New Hampshire.

[(CO)$_3$Mo(iPr$_2$NPO)$_4$Mo(CO)$_2$(P(C$_6$H$_5$)$_3$)] (2). A 25 mL, round-bottomed flask was charged with 1.0000 g of the cage complex (CO)$_4$Mo(^{i}Pr$_2$NPO)$_4$Mo(CO)$_4$ and 0.5222 g P(C$_6$H$_5$)$_3$, a magnetic stirbar and evacuated. Toluene 10.0 mL was added into the flask under nitrogen. The mixture was stirred and heated to 110°C. After refluxing for 24 hours (cage completely gone), the clear red-colored reaction solution was evaporated to dryness under reduced pressure. Then 15-mL aliquot of hexane was added to extract the residue. The extract chromatographed on a 1- x 30-cm column of alumina using 2% ethyl acetate in hexane as eluant. Compound **2** was obtained as an orange-red solid in 40% yield (0.4697 g). When **2** was dissolved in hot hexane and the solution cooled, X-ray-quality crystals were obtained. Elemental analyses (calculated/observed for C$_{47}$H$_{71}$Mo$_2$N$_4$O$_9$P$_5$):

C% 47.72/47.79, H% 6.05/6.15, N% 4.74/4.68. ^{1}H NMR: δ 7.86 and 7.24 (m, Ph), 3.86 and 3.68 (m, N-CH), 1.33, 1.32, 1.30, 1.20, 1.19, 1.13, 1.02, 0.87 (d, Me, J=6.7-6.8 Hz). ^{13}C NMR: δ 222.7 and 221.7 (m, CO), 218.4 (dd, CO, J=18.8, 54.2 Hz), 137.0-128.1 (m, Ph), 49.1, 48.6, 46.4, 44.8 (d, N-C, J= 12.4, 7.5, 9.3, 8.6 Hz), 23.3 (m, Me).

[(CO)$_3$Mo(iPr$_2$NPO)$_4$Mo(CO)$_2$(PR$_3$)] (R$_3$= MeP(C$_6$H$_5$)$_2$, HP(C$_6$H$_5$)$_2$. **3, 4).** A 25 mL, round-bottomed flask was charged with 1.0000 g (1.0000 mmol) of the cage complex, a stirbar, 10 mL of toluene and 2.0000 mmol of the respective phosphine. Similar reaction procedures as **2** were used. Because **3** and **4** were not stable on the column, so after running the reactions for 24 hours (cage completely gone), the clear red-colored reaction solutions were

stripped of the toluene under reduced pressure. Upon standing for one day, the resulting viscous oils afforded red crystals of the products. By washing off MeP(C_6H_5)$_2$ or HP(C_6H_5)$_2$) and other impurities with small portions of cold hexane and dried to give 80% yield of **3** or **4**. Elemental analyses (calculated/observed for $C_{42}H_{69}Mo_2N_4O_9P_5$ **3**): C% 45.01/45.18, H% 6.20/6.27, N% 4.60/5.00. Elemental analyses (calculated/observed for $C_{41}H_{67}Mo_2N_4O_9P_5$ **4**): C% 44.49/44.34, H% 6.10/6.48, N% 5.06/4.72. ^{1}H NMR

(for **3**): δ 7.75-7.30 (m, Ph), 3.97 and 3.70 (m, N-CH), 2.02, 1.45, 1.36, 1.28, 1.23, 1.20 (d, Me, J=8.3, 6.7, 6.7, 7.7, 6.9, 6.8 Hz). ^{1}H NMR (for **4**): δ 7.77-7.32 (m, Ph), 6.51 (dd, P-H, J=9, 332 Hz), 4.0-3.55 (m, N-CH), 1.49, 1.32, 1.27, 1.10, 1.00 (d, Me, J=6.7- 6.8 Hz). ^{13}C NMR (for **3**): δ 224.9 and 221.1 (m, CO), 218.6 (dd, CO, J=14.6, 36.4 Hz), 138.0-127.9 (m, Ph), 48.43, 48.38, 46.2, 44.8 (d, N-C, J= 7.5, 10.0, 8.7, 8.7 Hz), 24.5 (s, Me). 23.3 (m, Me), 15.3 (d, Me, J=19.3 Hz). ^{13}C NMR (for **4**): δ 223.2 and 221.2 (m, CO), 218.2 (dd, CO, J=15.2, 51.3 Hz), 134.2-128.7 (m, Ph), 48.5, 47.9, 46.5, 44.5 (d, N-C, J= 8.4, 9.2, 9.2, 8.5 Hz), 24.5 (d, Me, J=7.8 Hz), 22.9 (m, Me).

[(CO)$_4$Mo(iPr$_2$NPO)$_4$Mo(CO)$_3$(HP(C$_6$H$_5$)$_2$)] (8)

[(HP(C$_6$H$_5$)$_2$)(CO)$_3$Mo(iPr$_2$NPO)$_4$Mo(CO)$_3$(HP(C$_6$H$_5$)$_2$)] (9). A 25 mL, round-bottomed flask was charged with a stirbar, 0.2000 g (0.2000 mmol) of the cage complex, 10.0 mL hexane, and 2.000 mmol of the diphenylphosphine. The mixture was stirred and allowed to heat to reflux. After refluxing for three days, TLC gave four spots. The light-yellow reaction solution was evaporated under reduced pressure and the residue chromatographed on an alumina column as described for **2**. The second complex to elute was complex **8**, isolated in 11% yield (0.025 g) , and the fourth was complex **9**, in 4% yield

(0.010 g). Elemental analyses (calculated/observed for $C_{43}H_{67}Mo_2N_4O_{11}P_5$ **8**): C% 44.42/44.19, H% 5.81/5.83, N% 4.82/4.53. Elemental analyses (calculated/observed for $C_{54}H_{78}Mo_2N_4O_{10}P_6$ **9**): C% 49.10/47.36, H% 5.95/6.38, N% 4.38/4.24. Due to the very low yield of **9**, repeated efforts failed to improve on these elemental data. ^{1}H NMR (for **8** in C_6D_6): δ 7.60 and 7.05 (m, Ph), 6.39 (d of t, P-H, J=4.2, 309.7 Hz), 4.78 (septet, N-CH, J=6.4 Hz), 4.55 and 4.11 (m, N-CH), 1.36 (m, Me), 1.04 (d, Me, J=7.0 Hz). ^{13}C NMR (for **8** in C_6D_6): δ 217.7, 217.1, 214.9 (m, CO), 135.0-128.8 (m, Ph), 47.4 (m, N-C), 25.6, 24.3, 23.9 (m, Me). ^{1}H NMR (for **9** in C_6D_6): δ 7.70 and 7.05 (m, Ph), 6.43 (d, P-H, J= 304.9 Hz), 4.93 and 4.54 (m, N-CH), 1.46, 1.45, 1.15, 1.07 (d, Me, J=6.9, 7.0, 7.1, 6.9 Hz). ^{13}C NMR (for **9** in C_6D_6): δ 218.0 (m, CO), 136.1-128.8 (m, Ph), 47.5 (m, N-C), 25.7-24.2 (m, Me).

[(CO)4Mo(iPr2NPO)4Mo(CO)3(P(OMe)3)](5)

[(P(OMe)3)(CO)3Mo(iPr2NPO)4Mo(CO)3(P(OMe)3)](6). A 25 mL round-bottomed flask was charged with 1.0000 g (1.00 mmol) of the cage complex, a stirbar , 0.25 mL (2.10 mmol) of P(OMe)3 and 10.0 mL of toluene. The mixture was stirred and allowed to heat to reflux. After refluxing for six hours, a light-yellow solution formed and two colorless spots due to the products showed on the TLC. The solution was evaporated under reduced pressure and the light-yellow residue chromatographed on an alumina column as for 2. Complex **5** (0.34 g, 0.32 mmol, 32% yield based on the cage) was obtained followed by 0.60 g of complex **6** (0.50 mmol, 50% yield based on the cage). Elemental analyses (calculated/observed for $C_{34}H_{65}Mo_2N_4O_{14}P_5$ **5**): C% 37.10 /36.99, H% 5.95 /6.08, N% 5.09 /4.96. Elemental analyses

60

(calculated/observed for $C_{36}H_{74}Mo_2N_4O_{16}P_6$ **6**): C% 36.13/36.11, H% 6.23/6.12, N% 4.68/4.72. ^1H NMR (for **5**): δ 4.57 and 4.38 (unresolved multiplets, N-CH), 3.61 and 3.59 (d, OMe, J=11.2, 10.4 Hz), 1.3-1.5 (overlapping doublets, Me). ^{13}C NMR (for **5**): δ 217.4, 213.6, 210.3, 206.6 (unresolved multiplets, CO), 50.2, 46.0 (unresolved multiplets, N-C and OMe), 23.5 (unresolved multiplets, Me). ^1H NMR (for **6**): δ 4.66 and 4.53 (unresolved multiplets, N-CH), ~3.6 (unresolved multiplets OMe Hz), ~1.35 (overlapping doublets, Me). ^{13}C NMR (for **6**): δ 219.3, 217.8, 214.3, 211.7 (unresolved multiplets, CO), 51.2 and 46.7 (unresolved multiplets, N-C and OMe), 24.7 (unresolved multiplets, Me).

[(CO)$_3$Mo(iPr$_2$NPO)$_4$Mo(CO)$_2$(P(OMe)$_3$)](7). The same procedure used for the syntheses of complexes as **5** and **6** was followed except that the reaction solution was refluxed for 34 hours. After chromatography, 0.720 g (0.69 mmol, 69% yield) of **7** was obtained. X-ray-quality crystals were obtained by slow evaporation from a hexane solution. Elemental analyses (calculated/observed for $C_{32}H_{65}Mo_2N_4O_{12}P_5$ **7**): C% 36.79 /36.71, H% 6.27/6.58, N% 5.36 /5.00. ^1H NMR (in C_6D_6): δ 4.02, 3.80, 3.65 (m, N-CH), 3.60 (d, OMe, J=10.6 Hz), 1.47 and 1.32 (d, Me, J=6.7 and 6.8 Hz), 1.39 and 1.21 (m, Me). ^{13}C NMR (in C_6D_6): δ 223.2, 221.8, 220.2 (m, CO), 218.6 (dd, J=15.6, 50.6 Hz), 52.2, 48.4, 48.1, 46.5, 44.6 (d, N-C or OMe, J=5.2, 8.4, 10.6, 9.4, 8.4 Hz), 23.0, 22.7, 22.6, 22.3 (m, Me).

[(CO)$_3$Mo(iPr$_2$NPO)$_4$Mo(CO)$_2$(NC5H5)](10). A 25 mL round-bottomed flask was charged with 2.0000 g of the cage complex, 2.00 mL pyridine, a

61

stirbar, 18.0 mL toluene. The mixture was stirred and allowed to heat to reflux, The reaction was followed by TLC. Only one orange-colored spot appeared as the product on the TLC during the reaction. After 9 hours, the cage complex was gone and the reaction mixture was deep red, some brown precipitate formed. A clear deep red solution was obtained after filtering the reaction mixture. The filtrate was evaporated to dryness under reduced pressure and the residue was washed with several portions of hexane to give 1.522 g red compound **10** (1.52 mmol, 76% yield). Elemental analyses (calculated/observed for $C_{34}H_{61}Mo_2N_5O_9P_4$ **10**): C% 40.85/40.87, H% 6.15/6.21, N% 7.01 /6.75. ^1H NMR: δ 9.11-7.29 (m, Py), 4.03, 3.85, 3.71, 3.44 (septets, N-CH, J=6.6, 6.8, 6.9, 6.7 Hz), 1.51, 1.47, 1.41, 1.38, 1.29, 1.26, 1.19 (d, Me, J=6.7, 6.7, 6.8, 6.8, 6.9, 6.9, 6.8 Hz), 1.39 and 1.21 (m, Me). ^{13}C NMR: δ 228.1 (dd, CO, J=12.1, 44.0 Hz), 221.4 218.2 (m, CO), 153.4-124.2 (m, Py), 48.4, 47.5, 46.5, 45.2 (d, N-C, J= 8.4, 10.4, 9.6, 9.2 Hz), 23.5-22.4 (m, Me).

[(CO)3Mo(iPr2NPO)4Mo(CO)3](11). Complex **10** (0.6565 g) was dissolved in 20 mL toluene at 60°C, and CO gas was bubbled through it for 6 hours. Complex **10** was gone, and a new orange-red solution was obtained. The orange red clear solution was evaporated to dryness and an orange residue was obtained. The residue was chromatographed to give 0.3095 g (0.33 mmol, 50% yield) of orange compound **11**. X-ray-quality crystals were obtained by slow evaporation from a hexane solution. Elemental analyses (calculated/observed for $C_{30}H_{56}Mo_2N_4O_{10}P_4$ **11**): C% 37.99/37.57, H% 5.95/6.13, N% 5.91/5.71. ^1H NMR: δ 3.92, 3.72 (m, N-CH), 1.50 and 1.35 (d, Me, J=6.7, 3.0 Hz), 1.31 (m, Me). ^{13}C NMR: δ 220.8, 217.6, 215.6, 208.0 (m, CO), 48.9, 48.2, 47.4, 45.3 (d, N-C, J= 8.9, 10.3, 10.4, 8.6 Hz), 23.0 (m, Me).

62

X-ray Structural Determination of Complex 2. A summary of crystal data, data collection, and structural refinement details is presented in **Table VIII**. The intensities of a 0.6- x 0.2- x 0.8-mm crystal were collected on a Rigaku AFC6S diffractometer. A total of 11267 unique reflections were measured of which 6097 were considered significant at the 3σ level. The structure was solved using direct methods, and the hydrogens were included at calculated positions[41]. Final least squares were performed varying 605 parameters. Final RF=0.074 and Rw=0.120 with a goodness-of-fit (GOF) of 3.81. Selected bond distances and bond angles are listed in **Table III**.

X-ray Structural Determination of Complex 7. A summary of crystal data, data collection, and structural refinement details is presented in **Table VIII**. The intensities of a 0.6- x 0.4- x 0.7-mm crystal were collected to yield a total of 11384 unique reflections were measured of which 6070 were considered significant at the 3σ level. The structure was solved using direct methods, and hydrogens were included at calculated positions. Final least squares were performed varying 497 parameters. Final RF=0.042 and Rw=0.044 with a goodness-of-fit (GOF) of 1.32. Selected bond distances and bond angles are listed in **Table IV**.

Table VIII. Crystal Data for Complexes 2, 7 and 11

	2	7	11
formula	$Mo_2P_5O_9N_4C_{47}H_{71}$	$Mo_2P_5O_{12}N_4C_{32}H_{65}$	$Mo_2P_4O_{10}N_4C_{30}H_{56}$
fw	1182.85	1044.63	948.57
space group	$P2_1/c$	$P2_1/n$	$C2_1/c$
	monoclinic	monoclinic	monoclinic
a, Å	12.684(1)	13.026(3)	36.523(7)
b, Å	13.383(3)	21.054(3)	13.287(5)
c, Å	37.109(4)	18.118(3)	20.348(3)
ß, deg		103.46(2)	109.48(1)
Z	4	4	8
d_{calc}, g cm^{-1}	1.247	1.436	1.353
μ, mm^{-1}	5.58	7.22	7.07
cryst dimens, mm	0.6x0.2x0.8	0.6x0.4x0.7	1.0x1.0x1.0
λ(Mo K radiation), Å	0.71069	0.71069	0.71069
data collcd	$0° < 2\theta < 55.0°$	$0° < 2\theta < 55.0°$	$0° < 2\theta < 55.0°$
scan	ω	ω	ω
no. of unique reflcns	11267	11384	11325
no. of obsd reflcns	6097	6070	4770
F (000)	2448	2160	3904
R_F	0.074	0.042	0.054
R_{WF}	0.121	0.044	0.074
GOF	3.81	1.32	2.00

64

X-ray Structural Determination of Complex 11. A summary of crystal data, data collection, and structural refinement details is presented in **Table VIII.** The intensities of a 1.0- x 1.0- x 1.0-mm crystal were collected to yield a total of 11150 unique reflections were measured of which 4723 were considered significant at the 3σ level. The structure was solved using direct methods, and the hydrogens were included at calculated positions. Final least squares were performed varying 452 parameters. Final Rf=0.054 and Rw=0.074 with a goodness-of-fit (GOF) of 2.00. Selected bond distances and bond angles are listed in **Table V.**

Comparison of the substitution reactions of the cage with different ligands: Each of the six 25 mL round-bottomed Schlenk flasks was charged with the same amount of the cage complex (0.5000 g) and evacuated, and the ligand in toluene was added into the proper flask to make the molar ratio of cage to ligand to be 1 : 2. Then toluene was added to the flasks to make the total volume of solution 5.0 mL. The resulting mixtures were stirred and warmed to dissolve the cage complex. Then 0.5 mL of solution from each of the colorless reaction solutions was removed and added to 0.3 mL of C_6D_6.

The ^{31}P NMR spectrum was obtained. From the integration of the ^{31}P NMR resonances, the beginning molar ratio of the cage to ligand could be calculated . The starting colorless solutions were stirred at reflux for 4 hours. A volume of 3.0 mL reaction solution was removed from each reaction mixture and added to 0.50 mL of C_6D_6 and the ^{31}P NMR spectrum was obtained again.

From the ^{31}P NMR spectra we calculated the % of cage reacted and also the % of the orange compound formed from the intermediates.

65

CHAPTER II

DEMETALLATION OF A DIMOLYBDENUM CYCLO-TETRAPHOSPHOXANE CAGE COMPLEX AND THE SYNTHESIS OF HETEROBIMETALLIC CAGES AND THEIR CHEMICAL REACTIONS

The synthesis and study of heterobimetallic complexes has been the subject of active research over the past decade. Initially studies of complexes containing two different metal atoms from the same or neighboring groups were done[42]. Later, interest developed in complexes that contained widely divergent transition metals[43]. Heterobimetallic complexes are of interest because of the potential to promote unique or sequential interactions.

Bifunctional ligands such as 1-(diphenylphosphino)cyclopentadiene[44] and 2-(diphenylphosphino)pyridine[45] have proven to be particularly useful in constructing heterobimetallic species. Mixed-metal complexes have also been synthesized by using bidentate diphosphines such as bis(diphenylphosphino)methane[46], as well as phosphido ligands[47]. A substantial number of heterobimetallic complexes have now been synthesized. Several typical complexes are shown below:

67
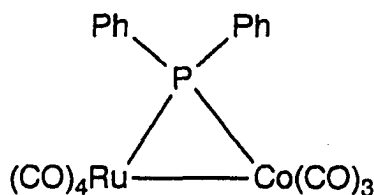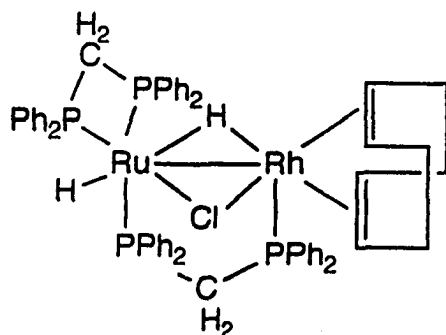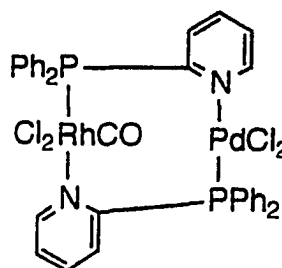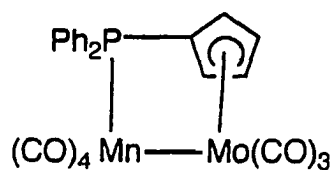
Wong and coworkers have reported results from our laboratory on the synthesis of several bimetallic cage complexes and mixed-valent bimetallic cage complexes as shown below [8,9,13]:
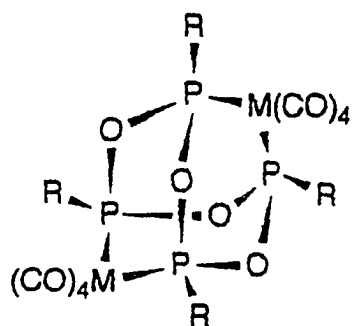
(R=^{i}Pr2N, Ph
M=Mo, Cr)
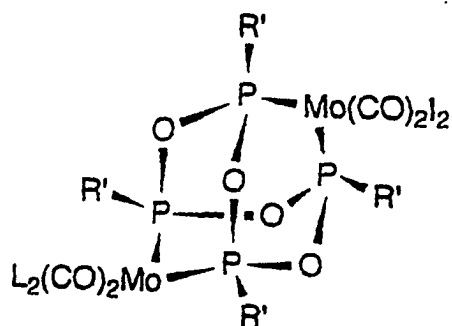
(R'=iPr2N
X=Cl, Br, I.   L=CO, Cl, Br, I)

Before this work, no heterobimetallic cage complexes had been synthesized except (CO)$_4$Cr[PhPO]$_4$Mo(CO)$_4$ which had been detected by ^{31}P NMR spectroscopy of a reaction mixture[48]. Recently, Xiaoyong et al.[49] reported the synthesis of two novel heterobimetallic complexes of the types:
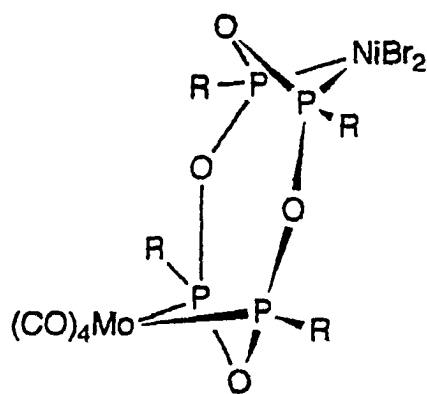
(R=Cy2N)
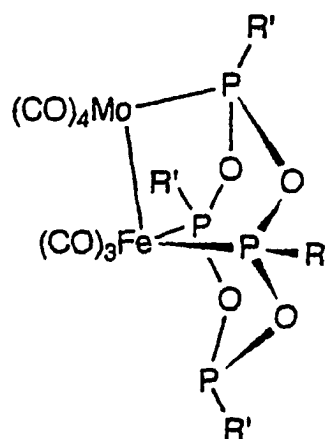
R'=^{i}Pr2N

and a P_5O_5 heterobimetallic cage complex $(CO)_3Mo[Cy_2NPO]_5PdCl_2$. This

Mo^0/Pd^{II} P_5O_5 cage complex was synthesized as shown in eq 9 and eq 10:

$$PdCl_2(C_6H_5CN)_2 + 5/3[Cy_2NPO]_3 \text{-----------}>$$

$$PdCl_2[Cy_2NPO]_5 + 2 C_6H_5CN \qquad (eq\ 9)$$

$$PdCl_2[Cy_2NPO]_5 + (CO)_4Mo(NBD) \text{----------}>$$

$$(CO)_4Mo[Cy_2NPO]_5PdCl_2 + NBD \qquad (eq\ 10)$$
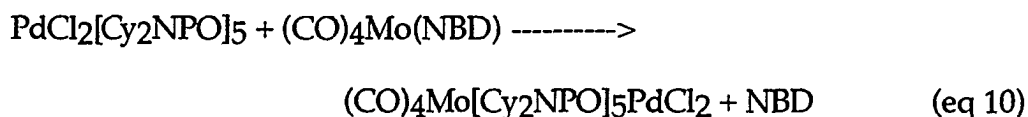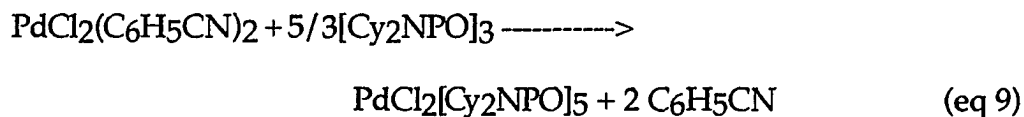
Our research goal was also to study the intracage metal-metal interactions in a series of structurally-related heterobimetallic cage complexes. The parent $(CO)_4Mo[^iPr_2NPO]_4Mo(CO)_4$ cage has been shown to exhibit mixed-valent and intracage oxidative-addition reactions. A series of heterobimetallic complexes of this type with rigidly-constrained pairs of metal vertices should be especially interesting for the study of intracage metal-metal interactions. Substituted cages of this type, however, have been elusive due to lack of rational synthetic routes. Although attempted demetallation of the parent cage complex failed, we note that its mixed-valent derivative $(CO)_4Mo[^iPr_2NPO]_4Mo(CO)_2I_2$ contains one Mo(II) center which does present a potential decomplexation site. Successful demetallation should give the precursor complex $(CO)_4Mo[^iPr_2NPO]_4$[50].

In this chapter, we describe the synthesis, characterization and chemistry of this monometallic cage precursor and its use as a metalla-ligand for the synthesis of a series of heterobimetallic cage complexes of the form $(CO)_4Mo[^iPr_2NPO]_4ML_n$. Possible intracage metal-metal interactions have

69

been investigated. In addition, some reactions of both the precursor and heterobimetallic cage complexes are reported.

RESULTS AND DISCUSSION

1.Synthesis and Characterization of the Monometallic Cage Precursor $(CO)_4Mo[^iPr_2NPO]_4$ (14)

Complex $(CO)_4Mo[^iPr_2NPO]_4$ (14) was synthesized by the reaction of $(CO)_4Mo[^iPr_2NPO]_4Mo(CO)_2I_2$ (12) with two equivalents of sodium dimethyldithiocarbamate in CH_2Cl_2 at room temperature via an orange intermediate $(CO)_4Mo[^iPr_2NPO]_4Mo(CO)_2(S_2CNMe_2)_2$ (13). The reaction sequence representing the preparation of 14 is as follows:

$$(CO)_4Mo[^iPr_2NPO]_4Mo(CO)_2I_2 + 2NaS_2CNMe_2 \longrightarrow$$
$$(12)$$

$$2NaI + (CO)_4Mo[^iPr_2NPO]_4Mo(CO)_2(S_2CNMe_2)_2 \qquad (eq\ 11)$$
$$(13)$$

$$\underline{13} \longrightarrow (CO)_4Mo[^iPr_2NPO]_4 + Mo(CO)_2(S_2CNMe_2)_2 \qquad (eq\ 12)$$
$$(14) \qquad\qquad (15)$$
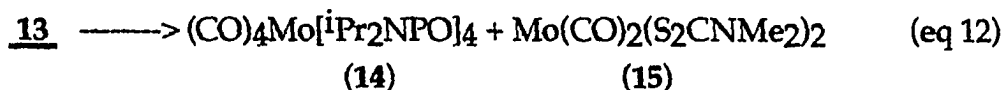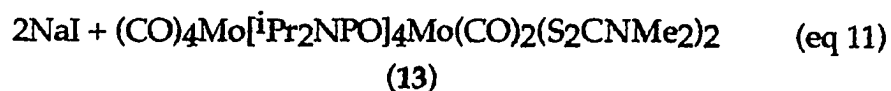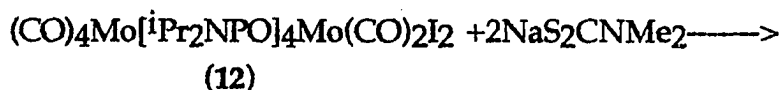
Complex 12 was synthesized by literature methods[9]. At first, a 2:1 CH_2Cl_2/MeOH mixture was chosen as the solvent since 12 is very soluble in CH_2Cl_2 while sodium dimethyldithiocarbamate easily dissolves in MeOH. The following reaction was obtained by using this solvent system at room temperature:

70

$$(CO)_4Mo[^iPr_2NPO]_4Mo(CO)_2I_2 \ +2NaS_2CNMe_2 + MeOH\text{------>}$$
$$(12)$$

$$2NaI + (CO)_4Mo[^iPr_2NPO]_2(^iPr_2NPOMe)\{^iPr_2NP(O)H\}$$
$$(28)$$

$$+ Mo(CO)_2(S_2CNMe_2)_2 \qquad\qquad (eq\ 13)$$
$$(15)$$
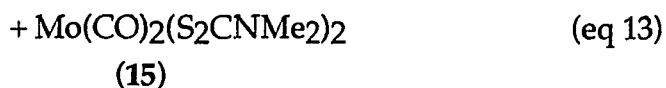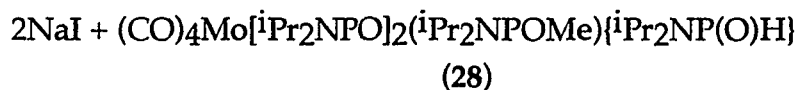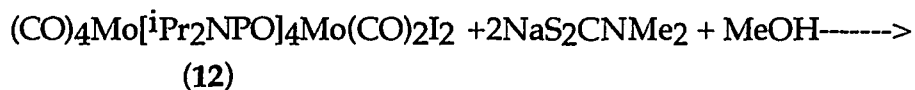
Thus methanol-decomposed <u>14</u> was obtained. Details of this reaction will be discussed in Part II. 5.

When **12** and NaS_2CNMe_2 were mixed with CH_2Cl_2 at room temperature, a suspension was formed. The white solid, NaS_2CNMe_2, was suspended in the deep-red mixture of complex **12**. After stirring for 3 hours, a red suspension was obtained. The red suspension contained complex **15** which could be isolated by filtration of the mixture. Complex **15** gave no ^{31}P NMR signal. Its formula was confirmed by ^1H, ^{13}C NMR, IR and elemental analyses. The two major IR carbonyl bands indicated a *cis* -configuration of the carbonyl groups. The band at $1517cm^{-1}$ was due to the C-N stretching mode[18]. A ^1H NMR spectrum of **15** showed two methyl resonances of unequal intensities. It is likely that this arose from two of isomers[51], (one with an octahedral structure and one with a trigonal prismatic structure similar to that found in the solid state for $Mo(S_2CN^iPr_2)_2(CO)_2$[52].

Dithiocarbamate ligands can act as a bidentate or as a monodentate ligand when coordinated to a transition metal[18][19]:

71

M—S, C—N (structure, bidentate dithiocarbamate)

M—S, C—N (structure, monodentate)
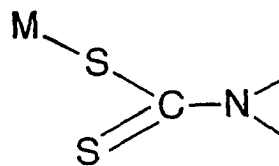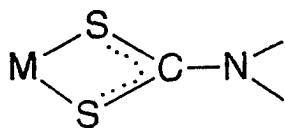
In eq 11, the dithiocarbamate ligand first acted as a monodentate ligand to replace the iodide to give orange **13**. This then rearranged to a bidentate mode and replaced the phosphorus donor atoms, removing the molybdenum from the rest of the cage (eq 12).

TLC and the ^{31}P NMR spectrum of the reaction mixture showed that the orange complex **13** is the major product. Complex **14** gave a colorless TLC spot with a high R_f value. By routine column chromatography, complex **13** was isolated in about 30% yield. This complex was very unstable and it decomposed to white complex **14** and red-purple **15** in solution or in the solid state when left at room temperature for several days. The decomposition products were examined by ^{1}H, ^{31}P NMR and IR spectroscopy. White solid compound **14** was isolated in 59% yield by column chromatography of the decomposition product after one week. Complex **14** has been characterized by ^{1}H, ^{13}C, ^{31}P NMR, IR spectra, elemental analyses and X-ray crystallography. It is an air-stable white solid with four IR carbonyl absorptions at 2010, 1925, 1908, and 1882 cm^{-1} which is consistent with a cis-$Mo(CO)_4P_2$ of C_{2v} symmetry. Its proton-decoupled ^{31}P NMR spectrum exhibited the expected A_2X_2 pattern with one sharp (150.6 ppm, coordinating P's) and one broad (126.0 ppm, uncoordinating P's) triplet with a coupling

72

constant of about 2 Hz (**Figure 29**). The ^{13}C NMR spectrum showed two triplets for carbonyl resonances at 215.8 ppm ($^2Jpc=14$ Hz) and at 209.5 ppm ($^2Jpc=12$ Hz).

Figure 29. $^{31}P\{^1H\}$ NMR spectrum of **14**

The X-ray structure of **14** is shown in **Figure 30** and selected bond distances and bond angles are listed in **Table IX**:

73
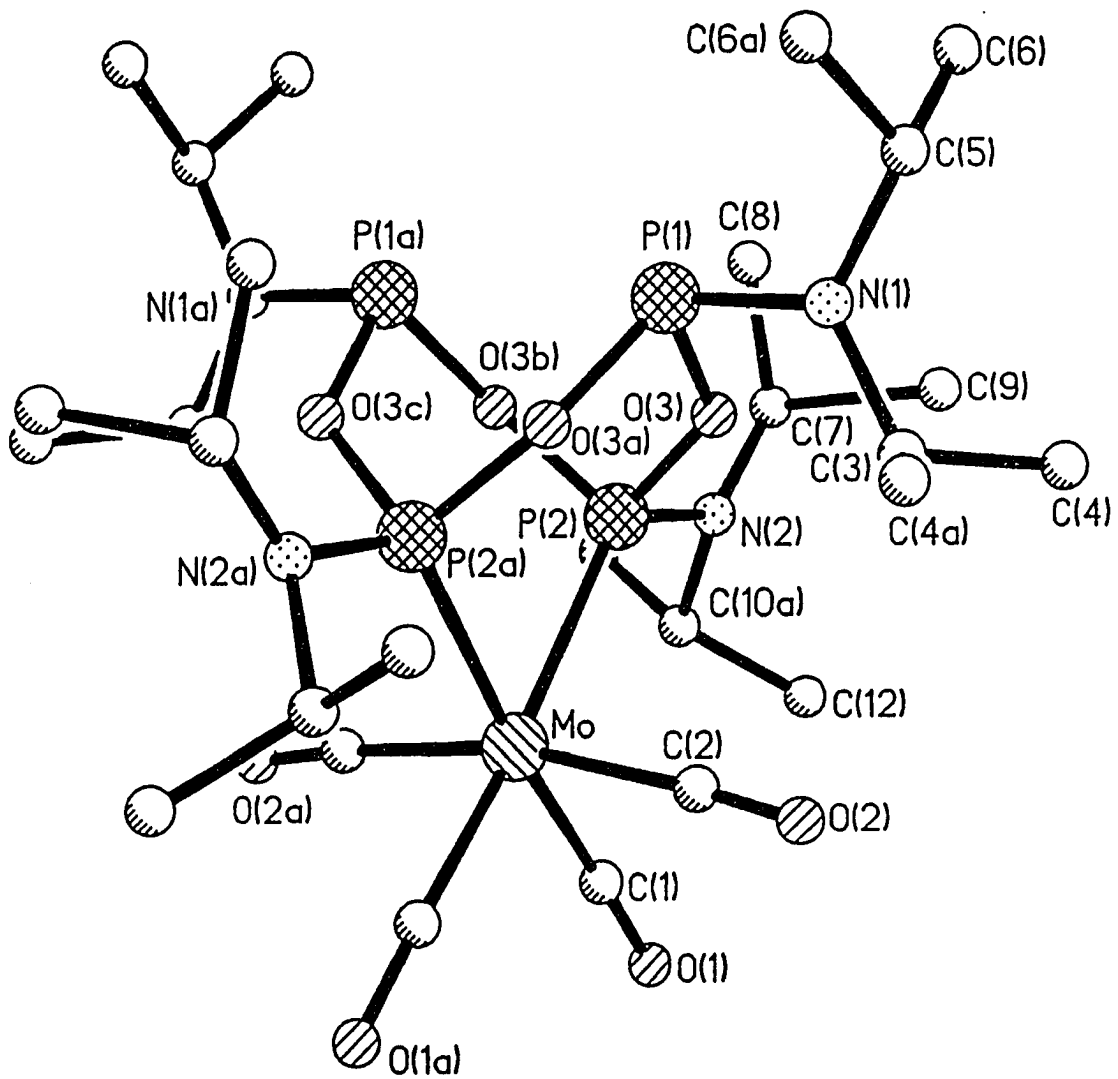
Figure 30. Molecular Structure of **14**

74

Table IX. Selected Bond Distances (Å) and Angles(deg) for $(CO)_4Mo[^iPr_2NPO]_4$

Mo-P(2) = Mo-P(2A)	2.512(2)
Mo-C(2) = Mo-C(2A)	2.027(10)
Mo-C(1) = Mo-C(1A)	1.978(9)
P(1)-O(3) = P(1)-O(3A) = P(1A)-O(3B) = P(1A)-O(3C)	1.671(4)
P(2)-O(3) = P(2)-O(3B) = P(2A)-O(3A) = P(2A)-O(3C)	1.623(4)
P(1)-N(1) = P(1A)-N(1A)	1.655(6)
P(2)-N(2) = P(2A)-N(2A)	1.642(7)
P(2)-Mo-P(2A)	75.1(1)
C(1)-Mo-C(1A)	87.5(5)
C(2)-Mo-C(2A)	169.8(5)
P(2)-Mo-C(1) = P(2A)-Mo-C(1A)	98.7(3)
P(1)-O(3)-P(2) = P(1)-O(3A)-P(2A)	131.6(2)
P(1A)-O(3B)-P(2) = P(1A)-O(3)-P(2A)	131.6(2)
Mo-P(2)-O(3) = Mo-P(2)-O(3B)	112.1(1)
Mo-P(2A)-O(3A) = Mo-P(2A)-O(3C)	112.1(1)
O(3)-P(1)-O(3A) = O(3B)-P(1A)-O(3C)	97.6(3)
O(3)-P(2)-O(3B) = O(3A)-P(2A)-O(3C)	102.1(3)

The molecule has perfect C_{2v} symmetry with the expected vacant metal vertex. Complex 14 retains the parent P_4O_4 boat-boat ring conformation with significant modifications in the phosphorus-oxygen bond lengths. Comparing to the average of 1.646(4) Å found in complex 1, the four coordinated (Mo)-P-

75

O bonds are shortened to 1.623(4) while the uncoordinated phosphorus-oxgen bonds are lengthened to 1.671(4) Å. These data indicate that the P-O -bonding at the coordinated sites are enhanced at the expense of the uncoordinated P-O bonds[53]. This structure represents the third configurational isomer (boat-boat) of the MoP4O4 moiety to be structurally characterized. Previously, chair-boat and chair-chair forms were described but this third geometry has not been accessible by direct synthesis[13]. These three conformations are showed in Figure 31:

| Chair-Chair | Chair-Boat | Boat-Boat |
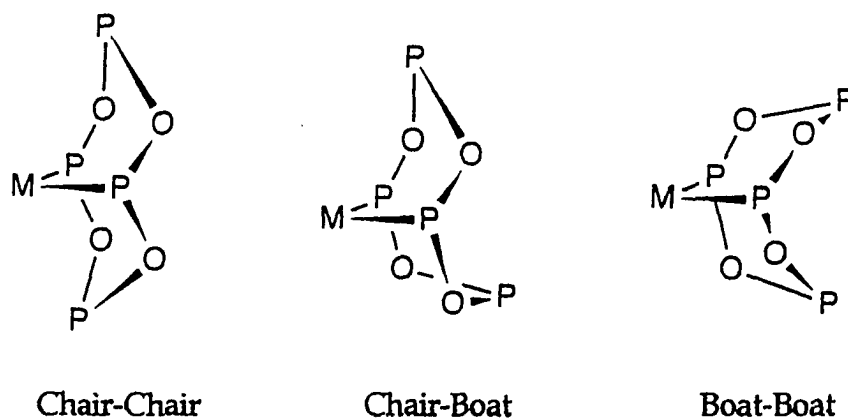
Figure 31. Three Conformations for the MoP4O4 Core

By the temperature-independent NMR spectral behavior of complex 14 up to 110°C and from previous work[13], it can be seen that a substantial barrier to phosphorus inversion exists.

Unlike the MoP4O4 complex with chair-chair or chair-boat forms, complex 14 in the boat-boat form has convergent phosphorus lone pairs that make it a promising metalla-ligand for the formation of novel bimetallic cage complexes.

76

2. Synthesis and Characterization of Heterobimetallic Complexes

In this section, the synthesis and characterization of heterobimetallic cage complexes from complex **14** are described.

2.1. $(CO)_4Mo[^iPr_2NPO]_4Cr(CO)_4(16)$:

Complex **16** was synthesized by the reaction of complex **14** with $Cr(CO)_4NBD$ (NBD = norbornadiene) in refluxing heptane:

$$(CO)_4Mo[^iPr_2NPO]_4 + Cr(CO)_4NBD \text{ --------> }$$
$$\textbf{(14)}$$

$$NBD + (CO)_4Mo[^iPr_2NPO]_4Cr(CO)_4$$
$$\textbf{(16)} \qquad\qquad\qquad\qquad \text{(eq 14)}$$
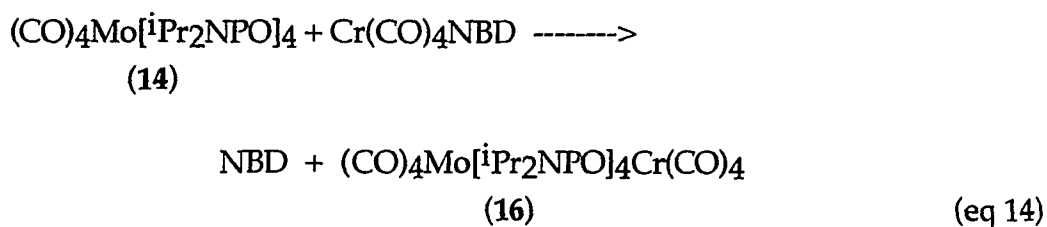
This reaction was monitored by ^{31}P NMR spectroscopy. After one day, the reaction mixture showed that only 32% of complex **16** had formed. When the reaction was run for an additional 3 days, 84% Mo-Cr cage **16** and 9% Mo-Mo cage **1** were found. Because the reaction was slow, some of the precursor decomposed, and some complex **1** formed. By routine column chromatography, pure complex **16** was isolated. The isolated yield of complex **16** was around 35%. This product was identified by ^1H, ^{13}C, ^{31}P NMR, IR spectra and elemental analyses. Its proton-decoupled ^{31}P NMR spectrum exhibits the expected A_2X_2 pattern with two triplets at 175.0 ppm and at 147.9 ppm. The coupling constant is equal to 6 Hz. Both the resonances of the coordinated P's and uncoordinated P's of complex **14** are shifted downfield upon bonding of the chromium. These downfield shifts can be rationalized by the decrease in electron density around the phosphorus atoms coordinated to the chromium.

77

The ^{13}C NMR spectrum of **16** showed four carbonyl resonances with the $Cr(CO)_4P_2$ group at 224.5 ppm (J_{PC}=9 Hz) and 218 ppm (J_{PC}=18 Hz) and the $Mo(CO)_4P_2$ moiety at 214.0 ppm (J_{PC}=16 Hz) and 207.2 ppm (J_{PC}=13Hz). The IR spectrum in the carbonyl stretch region was slightly different from that of complex **14**. Here the cis-$Cr(CO)_4$ group shows a sharp A_1 mode at 2023 cm^{-1}.

The higher energy absorption at 2009 cm^{-1} is assigned to the A_1 mode of cis-$Mo(CO)_4$, because the (Cr)C-O bond is typically stronger than the (Mo)C-O bond[54].

2.2. $(CO)_4Mo[^iPr_2NPO]_4Fe(CO)_3$(17):

Complex **17** was synthesized by the reaction of complex **14** with $Fe_2(CO)_9$ in refluxing hexane as shown below:

$$(CO)_4Mo[^iPr_2NPO]_4 + Fe_2(CO)_9 \text{ --------> }$$
$$\textbf{(14)}$$

$$Fe(CO)_5 + CO + (CO)_4Mo[^iPr_2NPO]_4Fe(CO)_3$$
$$\textbf{(17)} \qquad\qquad \text{(eq15)}$$
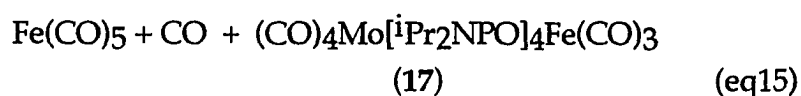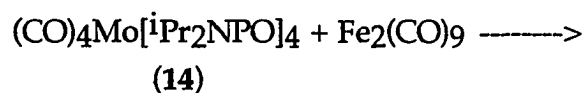
This reaction was monitored by ^{31}P NMR spectroscopy. After one day, ^{31}P NMR spectroscopy of the reaction mixture showed that only 51% of complex **17** had formed while 13% Mo-Mo cage had formed as a side product. When the reaction was allowed to run for an additional 15 hours, ^{31}P NMR spectroscopy showed that 68% of complex **17** had formed. In order to decrease the percentage of the undesired Mo-Mo cage, the reaction was stopped after 39

78

hours. The product was not easy to purify, because both the Mo-Mo cage and green $Fe_3(CO)_{12}$ were hard to remove. By routine column chromatography, a 28% yield of complex **17** was isolated. The product was identified by ^1H, ^{13}C, ^{31}P NMR, and IR spectra and by elemental analyses. The ^{31}P NMR spectrum of the complex showed a familiar A_2X_2 pattern with two triplets at 165.2 ppm and 152.1 ppm (^2J = 14 Hz). In the ^{13}C NMR spectrum, the $Fe(CO)_3$ group shows only one resonance, a triplet at 217.3 ppm with the P-C coupling constant equal to 7 Hz. This is consistent with the well-known fluxional property of the $P_2Fe(CO)_3$ moiety[55]. Carbonyl ligands in a wide variety of ligand-substituted iron pentacarbonyls have been observed with this property, as stereochemical nonrigidity is a very common phenomenon in molecules with five coordination. We also tried the reaction of **14** with $Fe(CO)_5$, but after 5 days in refluxing hexane, only some Mo-Mo cage formed.

2.3 $(CO)_4Mo[^iPr_2NPO]_4Cu(CH_3CN)_2BF_4$ (18):

Complex **18** was synthesized by the reaction of complex **14** with $Cu(CH_3CN)_4BF_4$ in hexane/CH_2Cl_2 (2:1 v:v) solution. The equation representing the preparation of the complex is shown below.

$$(CO)_4Mo[^iPr_2NPO]_4 + Cu(CH_3CN)_4BF_4 \longrightarrow$$
$$\text{(14)}.$$

$$2CH_3CN + (CO)_4Mo[^iPr_2NPO]_4Cu(CH_3CN)_2BF_4$$
$$\text{(18)} \qquad\qquad\qquad \text{(eq 16)}$$
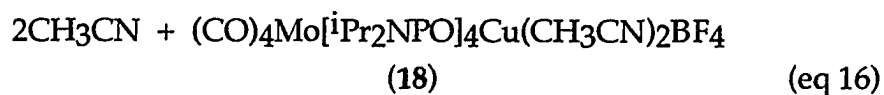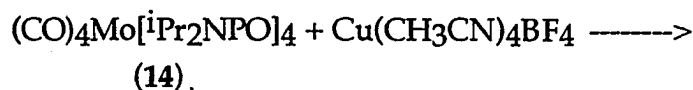
The percent yield of complex **18** in the reaction above was more than

79

95%. This reaction was very fast, being complete after refluxing for one hour. After evaporating the CH_2Cl_2, a white suspension was obtained. After filtration, a few portions of hexane were used to wash the product, and pure complex **18** was obtained. The product was not stable due to the ready loss of CH_3CN ligands. When the product was dried under reduced pressure, it changed color from white to light yellow. A ^1H NMR spectrum of the sample confirmed that some CH_3CN ligand was lost from the sample. Hence, the reaction was run using excess **14** and all of the NMR, IR spectra and CHN analyses had to been done within 24 hours after isolating the pure sample.

Complex **18** was identified by ^1H, ^{13}C, ^{31}P NMR, and IR spectra and by elemental analyses. Its ^{31}P NMR spectrum showed a sharp triplet at 155.6 ppm and a broad triplet at 90.0 ppm with a coupling constant of 10 Hz. The broad resonance was assigned to phosphorus atoms coordinated to copper. Since ^{63}Cu and ^{65}Cu both have spin I=3/2, the nuclear charge distribution around the metal is not symmetrical, thus giving rise to broad peaks due to quadrupolar relaxation[56]. The ^{13}C NMR spectrum showed a singlet resonance at 120.4 for $CH_3\underline{C}N$ and a singlet at 2.2 for $\underline{C}H_3CN$. The ^1H NMR spectrum showed a singlet at 2.35 ppm for the $C\underline{H}_3CN$ group. The IR spectrum showed the usual C_{2v} symmetry in the carbonyl region with one sharp peak at 2019 cm^{-1} and a broad peak at 1905 cm^{-1}. In addition, it also showed peaks in the CN region at 2303 and 2273 cm^{-1} [57].

80

2.4. (CO)₄Mo[^{i}Pr₂NPO]₄AgNO₃(19):

Complex **19** was synthesized by the reaction of complex **14** with NBD(AgNO₃)₂ in hexane at room temperature:

$$(CO)_4Mo[^iPr_2NPO]_4 + NBD(AgNO_3)_2 \text{ ------->}$$
$$\textbf{(14)}$$

$$NBDAgNO_3 + (CO)_4Mo[^iPr_2NPO]_4AgNO_3$$
$$\textbf{(19)} \qquad\qquad\qquad (eq\ 17)$$
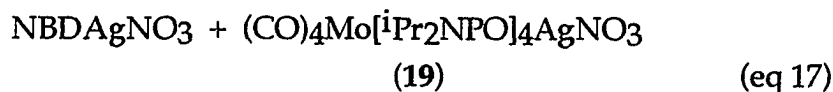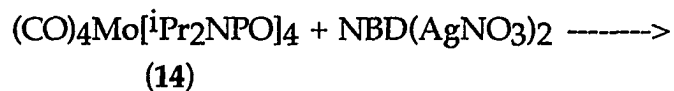
The percent yield of complex **19** in the reaction above was 54%. White solid NBD(AgNO₃)₂ was suspended in hexane. When the reaction was run at room temperature for one hour, the ^{31}P NMR spectrum of the mixture showed that the reaction was already complete. A white suspension was obtained, and after filtration, a white solid resulted. A few portions of hexane were used to wash this product to give pure white solid complex **19**. This product is not stable due to the decomposition of Ag (I). The reaction was therefore run using excess **14** and all of the NMR and IR spectra and CHN analyses were done within a few hours after obtaining a pure sample.

When complex **14** reacted with (AgNO₃)₂NBD, no matter whether the ratio of Mo to Ag was 1:1, 2:1 or 1:2, the same product resulted. Integration of the ^{31}P NMR peaks of starting material and the product reaction mixtures from the different reagent ratios confirmed the 1:1 complex. This cage compound was not stable and changed color to brown even under nitrogen and in the absence of light. It was characterized by ^{31}P, ^1H, ^{13}C NMR and IR spectroscopy, but no satisfactory CHN data were obtained even after repeated

81

attempts.

The ^{31}P NMR spectrum for complex 19 exhibited a unique pattern due to the coupling between phosphorus and silver nuclei. Silver exists as a combination of two isotopes, ^{107}Ag and ^{109}Ag. Both isotopes are NMR-active and have nuclear spins of one half with natural abundances of 51.82% and 48.18%, respectively. In contrast to the quadrupolar copper nuclei discussed for complex 18, the ^{31}P NMR spectrum of 19 clearly displayed Ag-P couplings. It showed a triplet at 154.3 ppm, and a doublet of triplets at both 103.6 ppm and 103.5 ppm [$^2J_{PP} = 13$ Hz, $^1J_{AgP} = 568, 492$ Hz] (Figure 32).

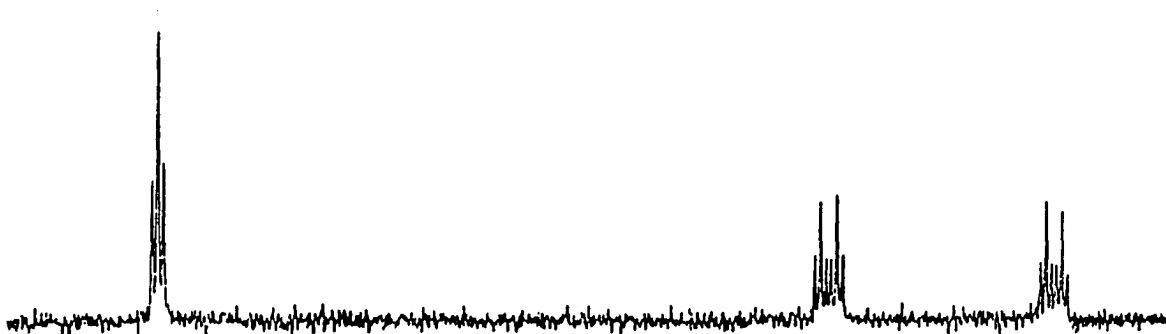Figure 32. $^{31}P\{^1H\}$ NMR spectrum for 19

One-bond coupling between ^{31}P and silver isotopes range from about 210 to more than 1100 Hz[56]. Several groups have reported $^1J_{PAg}$ values for Ag(L2)NO3 complexes of about 500 Hz[58]. The $^1J_{PAg}$ of complex 19 is consistent with these literature values. The IR spectrum of complex 19 indicated the expected C_{2v} symmetry in the carbonyl region.

82

2.5. (CO)$_4$Mo[^{i}Pr$_2$NPO]$_4$PtCl$_2$(20):

Complex **20** was synthesized by the reaction of complex **14** with PtCl$_2$(NBD) in toluene at 60°C:

$$(CO)_4Mo[^iPr_2NPO]_4 + PtCl_2(NBD) \text{ --------> }$$
$$\textbf{(14)}$$

$$NBD + (CO)_4Mo[^iPr_2NPO]_4PtCl_2$$
$$\textbf{(20)} \qquad\qquad (eq\ 18)$$
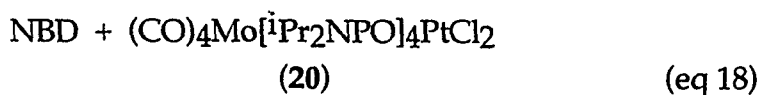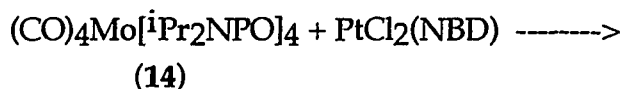
The yield of complex **20** was quantitative. Since PtCl$_2$(NBD) is not very soluble in hot toluene, the white reaction suspension was stirred at 60 °C and monitored by TLC. After 4 hours, this showed that no starting **14** was left. This reaction was fast and clean, and the product (CO)$_4$Mo[^{i}Pr$_2$NPO]$_4$PtCl$_2$ was easily isolated pure by filtration of the suspension to give a white solid. After washing this product with toluene, pure complex **20** was obtained. Complex **20** was identified by ^{1}H, ^{13}C, ^{31}P NMR and IR spectroscopy and elemental analyses. The ^{195}Pt isotope is NMR-active and has a nuclear spin of one half and a natural abundance of 33.8%. Thus the ^{31}P NMR spectrum of this product showed an A$_2$X$_2$ pattern with a triplet at 147.4 ppm and a triplet at 56.6 ppm (Jpp=10 Hz) together with a doublet of triplets of ^{195}Pt satellites (**Figure33**). The value of the coupling between phosphorus and platinum (J$_{195PtP}$=5520 Hz) is typical of phosphorus trans to halogen ligands[59]. Complex **20** shows a similar IR carbonyl spectrum as for complex **14** and **19**.

83
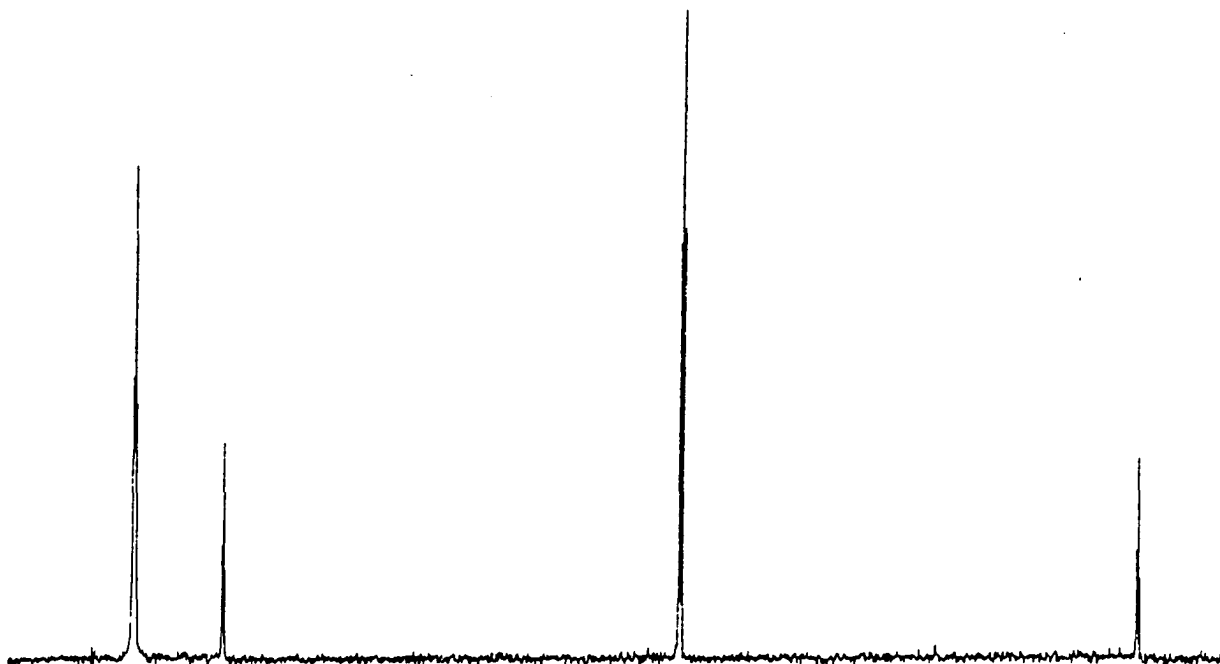
Figure 33. $^{31}P\{^1H\}$ NMR spectrum for **20**

2.6. $(CO)_4Mo[^iPr_2NPO]_4NiBr_2$ (21):

Complex **21** was synthesized by the reaction of complex **14** with $NiBr_2(DME)$ in refluxing hexane for 5 hours:

$$(CO)_4Mo[^iPr_2NPO]_4 + NiBr_2(DME) \text{ -----> }$$
$$(14)$$

$$DME + (CO)_4Mo[^iPr_2NPO]_4NiBr_2$$
$$(21) \qquad\qquad (eq19)$$
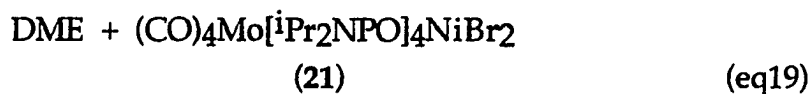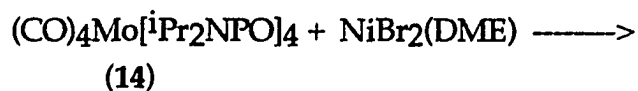
The yield of complex **21** in the reaction above was around 80%. When compound **14** reacted with $NiBr_2(DME)$, the deep-red $Mo-NiBr_2$ cage formed.

This product has no NMR signal and its formulation has been confirmed by X-ray study and IR spectroscopy. The pseudo-tetrahedral coordination geometry around the nickel is consistent with its paramagnetic behavior. The X-ray structure of this complex is shown in **Figure 34** and the selected bond

84

distances and angles are listed in **Table X**:
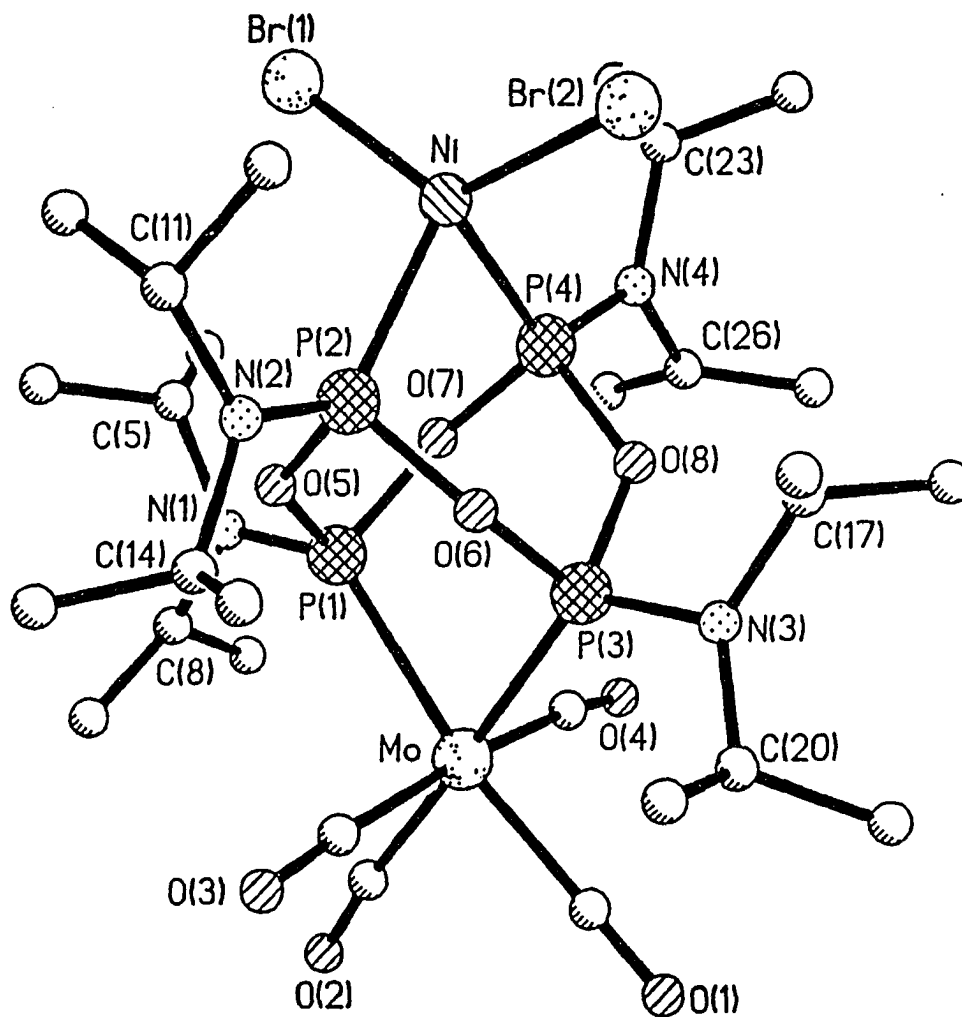
Figure 34. Molecular Structure of **21**

Comparing the X-ray structure of **21** with the precursor **14**, the data clearly show that the eight cage phosphorus-oxygen bonds have readjusted to the new coordination mode: the four (Ni^{II})P-O distances now average 1.633(8)Å while the four (Mo^0)-P-O lengths average to a marginally longer 1.650(9) Å. Again, this shows intracage communication between the two metals. In Part II 3 this structure will be discussed further.

85

This cage compound is not very stable in refluxing hexane, and some of it transformed to a Mo-Ni(CO)$_2$ cage compound by the reduction of Ni(II) and the replacement of Br$^-$ by CO from the decomposition of the parent cage. This was verified by its facilitation by adding a CO source as well as a reducing reagent, Fe(CO)$_5$. (See Part II 2.7 for detail).

Table X. Selected Bond Distances (Å) and Angles(deg) for 21

Mo-P(1)	2.493(4)	Mo-P(3)	2.493(4)
Mo-C(1)	2.004(15)	Mo-C(2)	1.987(17)
Mo-C(3)	2.047(17)	Mo-C(4)	2.019(17)
Ni-Br(1)	2.320(3)	Ni-Br(2)	2.318(3)
Ni-P(2)	2.254(4)	Ni-P(4)	2.266(4)
P(1)-O(5)	1.639(9)	P(1)-O(7)	1.661(9)
P(1)-N(1)	1.587(11)	P(2)-O(5)	1.654(9)
P(2)-O(6)	1.627(8)	P(2)-N(2)	1.614(12)
P(3)-O(6)	1.659(9)	P(3)-O(8)	1.649(9)
P(3)-N(3)	1.660(11)	P(4)-O(7)	1.623(9)
P(4)-O(8)	1.631(8)	P(4)-N(4)	1.609(12)
O(1)-C(1)	1.125(19)	O(2)-C(2)	1.162(21)
O(3)-C(3)	1.140(21)	O(4)-C(4)	1.130(21)
P(1)-Mo-P(3)	77.9(1)	P(1)-Mo-C(1)	171.9(4)
P(3)-Mo-C(1)	96.4(4)	P(1)-Mo-C(2)	100.8(5)
P(3)-Mo-C(2)	177.7(4)	C(1)-Mo-C(2)	85.2(6)
P(1)-Mo-C(3)	94.3(4)	P(3)-Mo-C(3)	92.2(5)
C(1)-Mo-C(3)	91.6(6)	C(2)-Mo-C(3)	85.9(6)
P(1)-Mo-C(4)	89.0(4)	P(3)-Mo-C(4)	94.9(5)
C(1)-Mo-C(4)	85.7(6)	C(2)-Mo-C(4)	87.0(6)
C(3)-Mo-C(4)	172.7(6)	Br(1)-Ni-Br(2)	128.9(1)
Br(1)-Ni-P(2)	110.6(1)	Br(2)-Ni-P(2)	111.3(1)
Br(1)-Ni-P(4)	106.4(1)	Br(2)-Ni-P(4)	104.4(1)
P(2)-Ni-P(4)	85.7(1)	Mo-P(1)-O(5)	112.7(3)
Mo-P(1)-O(7)	108.8(3)	O(5)-P(1)-O(7)	98.9(4)
Ni-P(2)-O(5)	109.3(3)	O(5)-P(2)-O(6)	100.6(4)
Ni-P(2)-O(6)	106.7(3)	O(6)-P(3)-O(8)	98.4(4)
Ni-P(4)-O(7)	110.0(3)	O(7)-P(4)-O(8)	100.7(4)
Ni-P(4)-O(8)	111.3(3)	P(1)-O(5)-P(2)	131.7(5)
Mo-P(3)-O(6)	112.8(3)	P(1)-O(7)-P(4)	132.1(5)
Mo-P(3)-O(8)	111.8(3)	P(2)-O(6)-P(3)	133.6(5)
P(3)-O(8)-P(4)	127.8(5)		

86

2.7. (CO)$_4$Mo[^{i}Pr$_2$NPO]$_4$Ni(CO)$_2$ (22):

Complex **22** was synthesized by the reaction of complex **21** with Fe(CO)$_5$

in refluxing hexane for 1 hour:

(CO)$_4$Mo[^{i}Pr$_2$NPO]$_4$NiBr$_2$ + Fe(CO)$_5$ --------->

(21)

3CO + FeBr$_2$ + (CO)$_4$Mo[^{i}Pr$_2$NPO]$_4$Ni(CO)$_2$

(22)   (eq 20)

The yield of complex **22** in the reaction above was 85%. When the red
reaction suspension was refluxed for one hour, the color disappeared and a
yellow suspension formed. By routine column chromatography, pure white
complex **22** was isolated. The formulation of complex **22** has been confirmed
by NMR and IR spectroscopy and by elemental analyses. A large crystal of **22**
was obtained by recrystallization from hot hexane but unfortunately, this
crystal was twined. It will be very interesting to obtain an X-ray structure of **22**
for comparing with the structure of **21**.

The ^{13}C NMR spectrum of **22** exhibits a triplet (198.4 ppm, $^2J_{PC}$=4 Hz)

resonance associated with the two equivalent carbonyls. This can be compared
with the chemical shift of carbonyl carbons in typical Ni(CO)$_2$P$_2$ complexes at

197.9 ppm for P=P(OMe)$_3$, 198.3 ppm for P=P(OEt)$_3$, and 198.9 ppm for

P=P(O^{i}Pr)$_3$[60]. $^2J_{PC}$ spin-spin couplings are negligible in

Ni(CO)$_2$[(P(OCH$_2$)$_3$CMe]$_2$[61], and only a few Hz in (PR$_3$)$_2$Ni(CO)2 (R=Ph,

Bu, OMe, OPh)[62]. The ^{31}P NMR spectrum of **22** shows an A$_2$X$_2$ pattern

87

with a triplet at 154.5 ppm and a triplet at 128.0 ppm. The P-P coupling

constant is 3 Hz. This small value is consistent with the literature values[62].

2.8. $(CO)_4Mo[^iPr_2NPO]_4NiX_2$ (X=Cl (23), X=I (24)):

Substituted nickel carbonyl complex **22** was oxidized by halogens to give

the corresponding nickel dihalide derivatives. Complexes **23** and **24** were

isolated from the reactions of complex **22** with SO_2Cl_2 in hexane at -78 °C or

with I_2 in CH_2Cl_2 at room temperature, respectively.

$$(CO)_4Mo[^iPr_2NPO]_4Ni(CO)_2 + SO_2Cl_2 \text{------->}$$
$$(22)$$

$$SO_2 + 2CO + (CO)_4Mo[^iPr_2NPO]_4NiCl_2$$
$$(23) \qquad\qquad (eq\ 21)$$

$$(CO)_4Mo[^iPr_2NPO]_4Ni(CO)_2 + I_2 \text{------->}$$
$$(22)$$

$$2CO + (CO)_4Mo[^iPr_2NPO]_4NiI_2$$
$$(24) \qquad\qquad (eq\ 22)$$
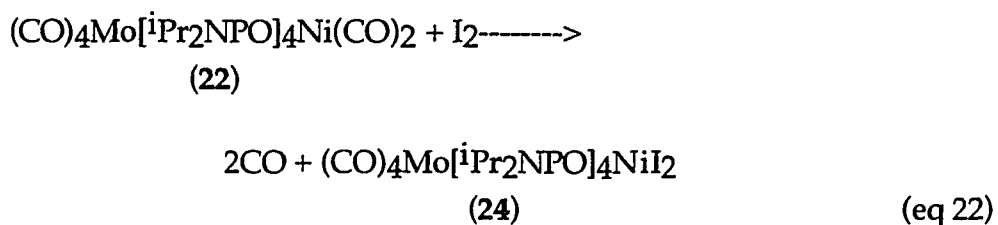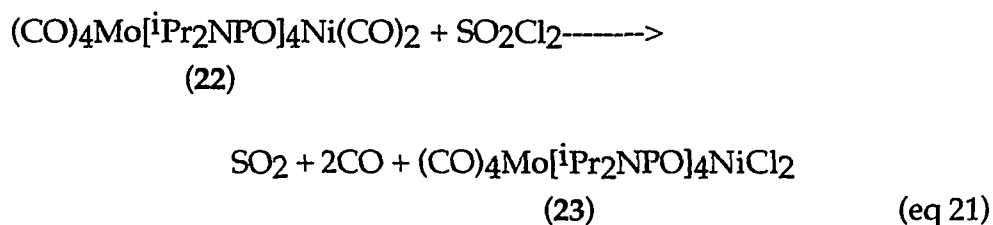
The yields of complexes **23** and **24** in the reactions above were 84% and 76%,

respectively.

When a SO_2Cl_2 solution in CH_2Cl_2 was added to a hexane solution of

$(CO)_4Mo[^iPr_2NPO]_4Ni(CO)_2$, this colorless solution immediately changed to

yellow. After 5 minutes, it became an orange suspension. The TLC of this

solution showed that no complex **21** remained. An orange solid complex **23**

was obtained after work up. This product was identified by its IR spectrum

and elemental analyses. Its IR spectrum showed four carbonyl absorptions

consistent with a C_{2v} symmetry for the cis-$Mo(CO)_4P_2$ moiety.

88

When a CH_2Cl_2 solution of I_2 was added to the colorless solution of complex **22** and stirred at room temperature for 2 hours, a deep-red solution formed. TLC of this solution showed no starting material **22**. The deep-red solution was allowed to dry under reduced pressure to give a deep-red residue. This solid was washed with CH_3CN and vacuum dried, to give complex $(CO)_4Mo[^iPr_2NPO]_4)NiI_2$. It was identified by IR spectroscopy which gave spectra similar to those of complexes **21** and **23**. For the reaction of **22** with I_2, if the excess I_2 was used, the product showed two major carbonyl bands in the IR spectrum, indicating that $(CO)_2I_2Mo[^iPr_2NPO]_4)NiI_2$ had formed. The carbonyl regions of the IR spectra for these Mo/Ni compounds are shown in **Figure 35**:

$(CO)_4Mo/NiCl_2$ $(CO)_4Mo/NiBr_2$ $(CO)_4Mo/NiI_2$ $(CO)_2I_2Mo/NiI_2$

2200 1750 2200 1750 2200 1750 2200 1750
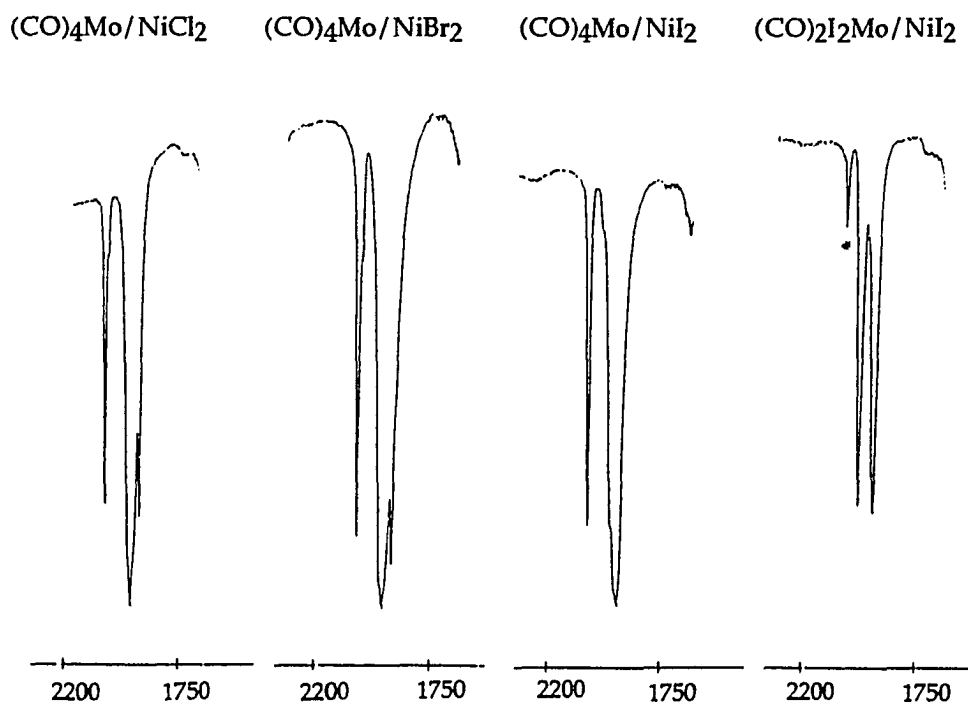
* peak of $(CO)_4Mo/NiI_2$

Figure 35. The carbonyl regions of the IR spectra for Mo/Ni complexes

89

Both complexes **23** and **24** were found to react with $Fe(CO)_5$ to produce complex **22** in 80% yield.

2.9. $(CO)_4Mo[^iPr_2NPO]_4PdBr_2(25)$:

Complex **25** was synthesized by the reaction of complex **14** with $PdBr_2(C_6H_5CN)_2$ in toluene at 70 °C for 16 hours:

$$(CO)_4Mo[^iPr_2NPO]_4 + PdBr_2(C_6H_5CN)_2 \text{------->}$$
$$(14)$$

$$2C_6H_5CN + (CO)_4Mo[^iPr_2NPO]_4PdBr_2$$
$$(25) \hspace{4cm} (eq\ 23)$$
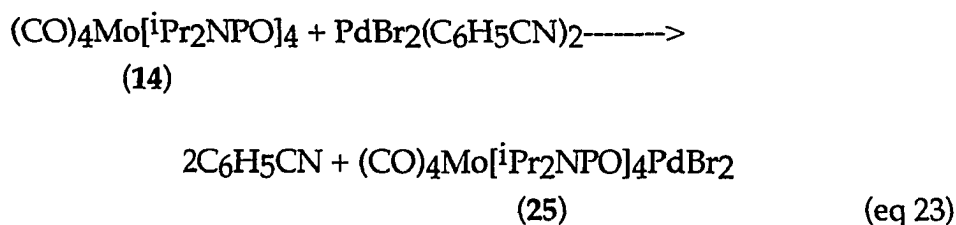
The yield of complex **25** in the reaction above was 83%. ^{31}P NMR spectroscopy was used to monitor the reaction. After 16 hours, there was 95% $Mo^0P_4O_4PdBr_2$ cage and minute amounts of $Mo^0P_4O_4Mo^0$ cage and $Mo^0P_5O_5PdBr_2$ cage, but no starting material. Workup by filtration and purification yielded a yellow solid $(CO)_4Mo[^iPr_2NPO]_4PdCl_2$. Small crystals were formed by recrystallization from hot toluene. This product was identified by ^1H, ^{13}C, ^{31}P NMR, and IR spectroscopy and by elemental analyses. In addition, an X-ray crystal structure determination was completed. The IR spectrum again confirms C_{2v} symmetry for cis-$Mo(CO)_2P_2$ in the carbonyl region with four absorptions at 2045.8 cm^{-1}, 1961.0 cm^{-1}, 1943.0 cm^{-1}, and 1921.8 cm^{-1}. The ^{31}P NMR spectrum of **25** showed a triplet at 147.6 ppm and a triplet at 82.6 ppm ($^2J_{PP} = 6$ Hz). The ^{13}C NMR spectrum in the carbonyl

90

region shows a multiplet at 211.8 ppm and a triplet at 205.1 ppm(J_{pc}=13Hz) in the carbonyl region.

We observed some interesting phosphorus chemical shift changes. For the precursor complex **14**, the coordinated phosphorus atoms resonate at 150.6 ppm and the uncoordinated phosphorus atoms at 126.0 ppm. When the uncoordinated phosphorus atoms coordinated to the second metal in complexes **16, 17, 18, 19, 20, 22** and **25**, large chemical shifts of +26.1 to -69.5 resulted, While the chemical shifts for the phosphorus atoms bound to Mo^0 shifted by +24.4 to -3.2 ppm. Cr(0), Fe(0), Ni(0) moved the phosphorus shifts to lower field in the order: Cr^0>Fe^0>Ni^0 while Cu(I), Ag(I), Pt(II) Pd(II) metals shifted the resonances upfield in the order: Pt(II)>Pd(II)>Cu(I)>Ag(I). These large changes can be explained by the differences between the metals and the ancillary ligands on the metals. The upfield shifts for Cu(I), Ag(I), Pt(II) and Pd(II) metals are consistent with the typical coordination shifts in the phosphine complexes[63]. For example, ^{31}P chemical shifts for free ligands PMe_3 and PPh_3 are at +62 ppm and +6ppm, while in complexes cis-$PtCl_2(PMe_3)_2$, cis-$PdBr_2(PMe_3)_2$, $AgClPPh_3$ and $Cp^*Cu(PMe_3)_3$, ^{31}P chemical shifts are at -24, -17, +3 and -49 ppm[63].

The structure of complex **25** is shown in **Figure 36** and selected bond distances and angles are listed in **Table XI**:
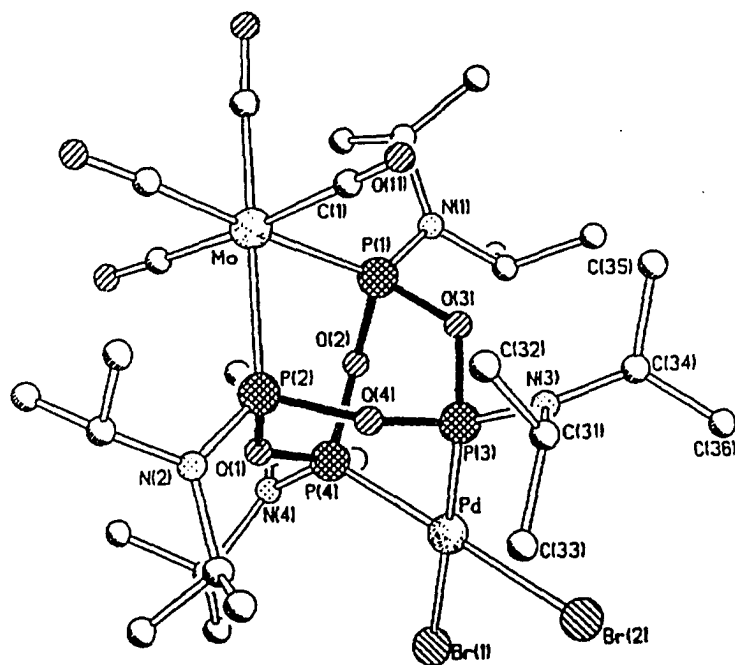
Figure 36. Molecular structure of **25**

In complex **25**, a square-planar geometry has been adopted by the Pd(II) vertex. The energy ordering of the d orbitals in a square-planar ligand field is $d_{x^2-y^2} > d_{xy} > d_{xz}, d_{yz} > d_{z^2}$. Since the pairing energy is less than the difference between the energy of the $d_{x^2-y^2}$ and the d_{xy} orbitals, the eight 4d-electrons in Pd(II) completely fill the four lowest energy orbitals, leaving the $d_{x^2-y^2}$ empty. Thus complex **25** is diamagnetic and gives useful NMR spectra.

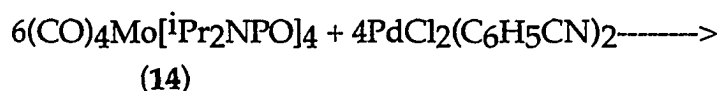From the x-ray structural data, we can see that similar to complex **21**, the eight cage P-O bonds are readjusted to the new coordination mode: the four (Pd^{II})P-O distances now average 1.599(12) (comparing to 1.633(8) Å in **21**) while the four (Mo^0)-P-O lengths average to 1.672(13) (even longer than that of 1.650(9) Å in complex **21**). Once again this suggests intracage transmission of electron density.

92

Table XI. Selected Bond Distances (Å) and Angles(deg) for 25

Mo-P(1)	2.475(5)	Mo-P(2)	2.495(5)
Mo-C(1)	2.026(25)	Mo-C(2)	1.996(26)
Mo-C(3)	2.027(26)	Mo-C(4)	1.970(25)
Pd-Br(1)	2.456(3)	Pd-Br(2)	2.474(5)
Pd-P(3)	2.233(5)	Pd-P(4)	2.233(5)
P(1)-O(2)	1.660(13)	P(1)-O(3)	1.694(12)
P(1)-N(1)	1.631(15)	P(2)-O(1)	1.654(12)
P(2)-O(4)	1.679(12)	P(2)-N(2)	1.642(14)
P(3)-O(3)	1.616(12)	P(3)-O(4)	1.575(11)
P(3)-N(3)	1.625(15)	P(4)-O(1)	1.616(12)
P(4)-O(2)	1.594(12)	P(4)-N(4)	1.627(17)
O(11)-C(1)	1.183(30)	O(22)-C(2)	1.189(31)
O(33)-C(3)	1.152(32)	O(44)-C(4)	1.178(31)
Br(1)-Pd-Br(2)	87.8(1)		
P(1)-Mo-P(2)	80.0(2)	P(1)-Mo-C(1)	89.8(7)
P(2)-Mo-C(1)	92.3(7)	P(1)-Mo-C(2)	99.3(7)
P(2)-Mo-C(2)	178.5(7)	C(1)-Mo-C(2)	89.0(10)
P(1)-Mo-C(3)	92.9(7)	P(2)-Mo-C(3)	90.3(7)
C(1)-Mo-C(3)	176.6(10)	C(2)-Mo-C(3)	88.4(10)
P(1)-Mo-C(4)	177.7(7)	P(2)-Mo-C(4)	100.5(7)
C(1)-Mo-C(4)	87.9(10)	C(2)-Mo-C(4)	80.2(10)
C(3)-Mo-C(4)	89.4(10)	P(3)-Pd-P(4)	85.0(2)
Br(1)-Pd-P(3)	178.5(2)	Br(2)-Pd-P(3)	93.5(2)
Br(1)-Pd-P(4)	93.7(2)	Br(2)-Pd-P(4)	177.4(2)
Mo-P(1)-O(3)	110.2(4)	O(2)-P(1)-O(3)	96.2(6)
Mo-P(2)-O(4)	110.1(4)	O(1)-P(2)-O(4)	98.5(6)
Pd-P(3)-O(3)	109.8(5)	O(3)-P(3)-O(4)	104.7(6)
Pd-P(3)-O(4)	109.5(5)	O(1)-P(4)-O(2)	104.6(6)
Pd-P(4)-O(1)	107.1(3)	P(2)-O(1)-P(4)	132.1(7)
Pd-P(4)-O(2)	110.4(5)	P(1)-O(2)-P(4)	129.7(8)
Mo-P(1)-O(2)	113.7(4)	P(1)-O(3)-P(3)	129.8(7)
Mo-P(2)-O(1)	109.3(5)	P(2)-O(4)-P(3)	129.6(7)

93

2.10. $(CO)_3Mo[^iPr_2NPO]_5PdCl_2$ (26):

Complex **26** was synthesized by the reaction of complex **14** with $PdCl_2(C_6H_5CN)_2$ in toluene at 70 °C for 66 hours.

$$6(CO)_4Mo[^iPr_2NPO]_4 + 4PdCl_2(C_6H_5CN)_2 \text{------->}$$
$$(14)$$

$$8C_6H_5CN + 4(CO)_3Mo[^iPr_2NPO]_5PdCl_2 + 1 \qquad \text{(eq 21)}$$
$$(26)$$

^{31}P NMR spectra were used to monitor the reaction. When the reaction was run for 66 hours, a red-brown suspension formed. Its ^{31}P NMR spectrum showed a mixture of complexes **1** and **26** in about a 1: 2 ratio while the spectrum of the suspended gray yellow solid showed that it was the Mo-PdCl$_2$ P_5O_5 cage complex. Work-up of the solid by recrystallization from chloroform gave pure yellow needle crystals of complex **26**. Evaporating the solution followed by washing the residue with acetone and hexane gave more pure **26**. Acetone removed the brown color and hexane removed complex **1** since complex **26** is not very soluble in either solvent. The combined yield of complex **26** was 52%.
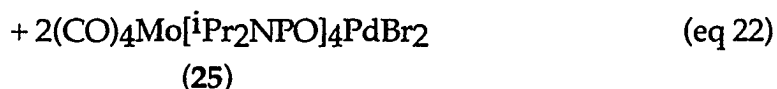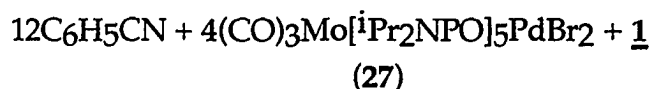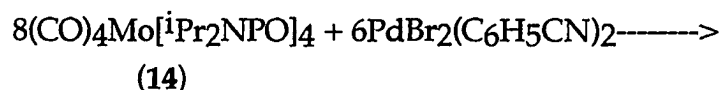
Complex **26** was identified by its ^1H, ^{13}C, ^{31}P NMR, and IR spectra and by elemental analyses. Its spectra are very different from those of complex **25**. The ^{31}P NMR spectrum shows an AM_2X_2 pattern with the three phosphorus atoms coordinated to Mo^0 giving two resonances: a triplet of triplet at 154.7 ppm, and a doublet at 134.9 ppm. The two phosphorus atoms bonded to Pd(II) gave rise to a doublet at 86.0 ppm ($J_{AM}=31$ Hz, $J_{AX}=11$ Hz, $J_{MX}=0$ Hz). The IR spectrum showed three absorptions in the carbonyl region at 1981.6 cm-1,

94

1910.4 cm-1 and 1880.1 cm^{-1} consistent with the fac-Mo(CO)$_3$P$_3$ group. The

^{13}C NMR spectrum in the carbonyl region showed two sets of doublets of

triplets at 218.1 ppm (J$_{PC}$=39, 14 Hz) and 216.1 ppm (J=41, 10 Hz). These data

are consistent with the previously-reported spectra of P$_5$O$_5$ cage

complexes[49].

No trace of the expected Mo-Pd P$_4$O$_4$ cage was detected.

2.11. (CO)$_3$Mo[^{i}Pr$_2$NPO]$_5$PdBr$_2$ (27):

Complex **27** was synthesized by the reaction of complex **14** with

PdBr$_2$(C$_6$H$_5$CN)$_2$ in toluene at 70 °C for 72 hours.

8(CO)$_4$Mo[^{i}Pr$_2$NPO]$_4$ + 6PdBr$_2$(C$_6$H$_5$CN)$_2$------->
(**14**)

12C$_6$H$_5$CN + 4(CO)$_3$Mo[^{i}Pr$_2$NPO]$_5$PdBr$_2$ + <u>1</u>
(**27**)

+ 2(CO)$_4$Mo[^{i}Pr$_2$NPO]$_4$PdBr$_2$ (eq 22)
(**25**)

Again, ^{31}P NMR spectroscopy was used to monitor the reaction. To

optimize the synthesis of the P$_5$O$_5$ cage complex **27**, we used starting

materials in a 5 : 1 ratio of P to Pd. When the reaction was run for 72 hours, a

brown yellow suspension formed. Whose ^{31}P NMR spectrum showed it to

be a mixture of complexes **1**, **25** and **27** in about a 1 : 2 : 4 ratio. The spectrum

of the solid (gray yellow color) showed only the Mo-PdBr$_2$P$_5$O$_5$ cage complex.

Workup of the solid by recrystallization from chloroform gave yellow

95

crystalline solid 27. Work-up of the solution mixture by vacuum drying and washing the residue with acetone followed by hexane yielded more pure complex 27. The combined yield of complex 27 was 48%. Complex 25 is soluble in acetone. Small amounts of complex 1 can be removed by hexane since complex 27 is not very soluble in either solvent.

The product was identified by ^{1}H, ^{13}C, ^{31}P NMR, and IR spectroscopy and by elemental analyses. The spectra of complex 27 are very similar to those of complex 26. These data are listed in Tables XII, XIII, XIV and XV. Selected spectra for 25, 26, and 27 are shown in Figures 37, 38 and 39 for comparison:
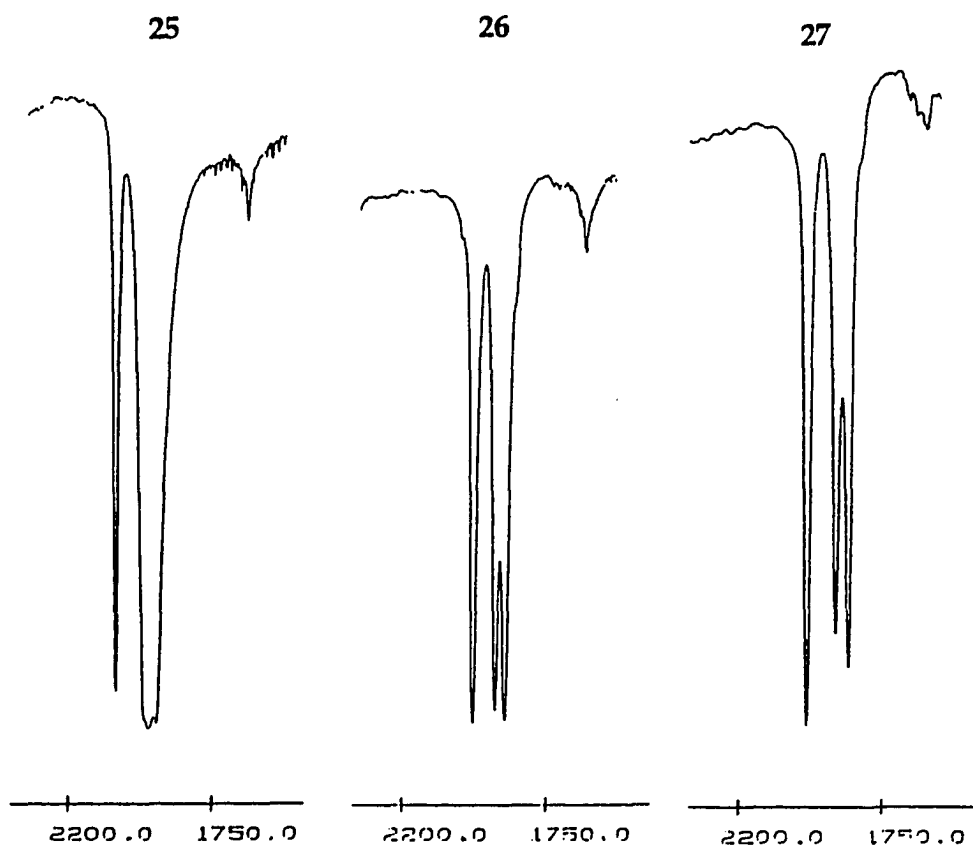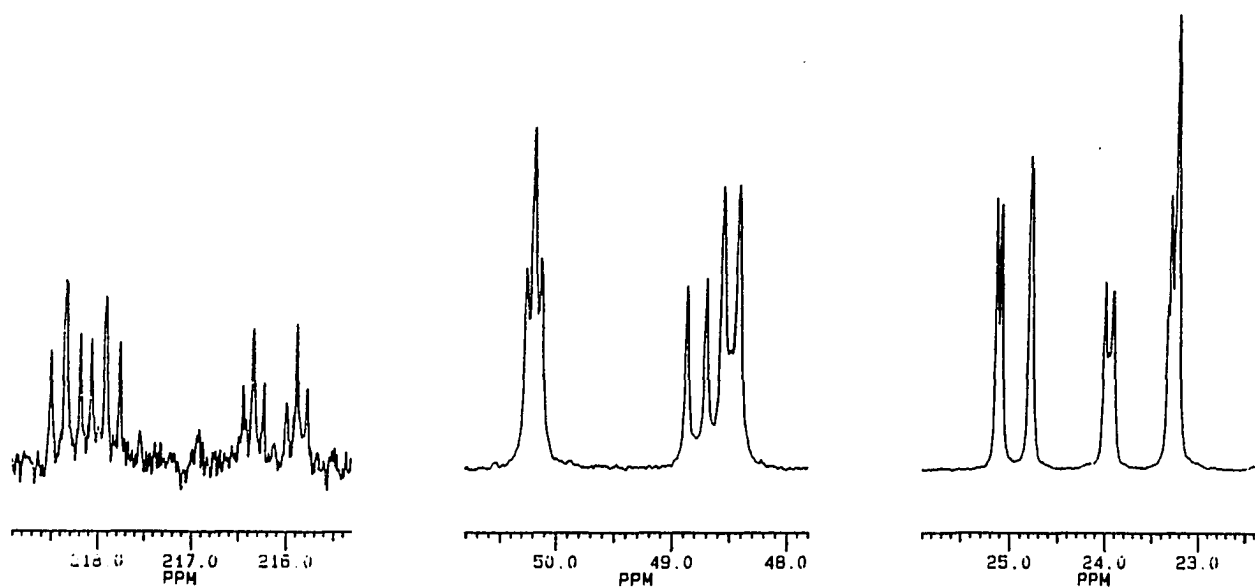

Figure 37. IR spectra of the carbonyl region for 25, 26 and 27
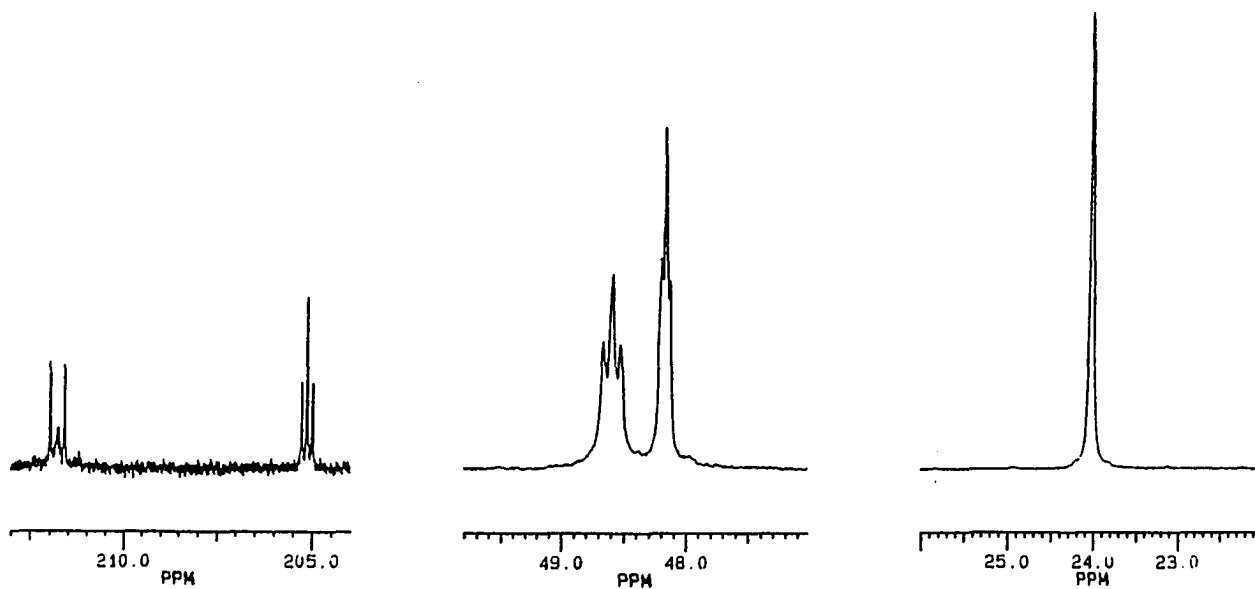
Complex 26

Complex 25

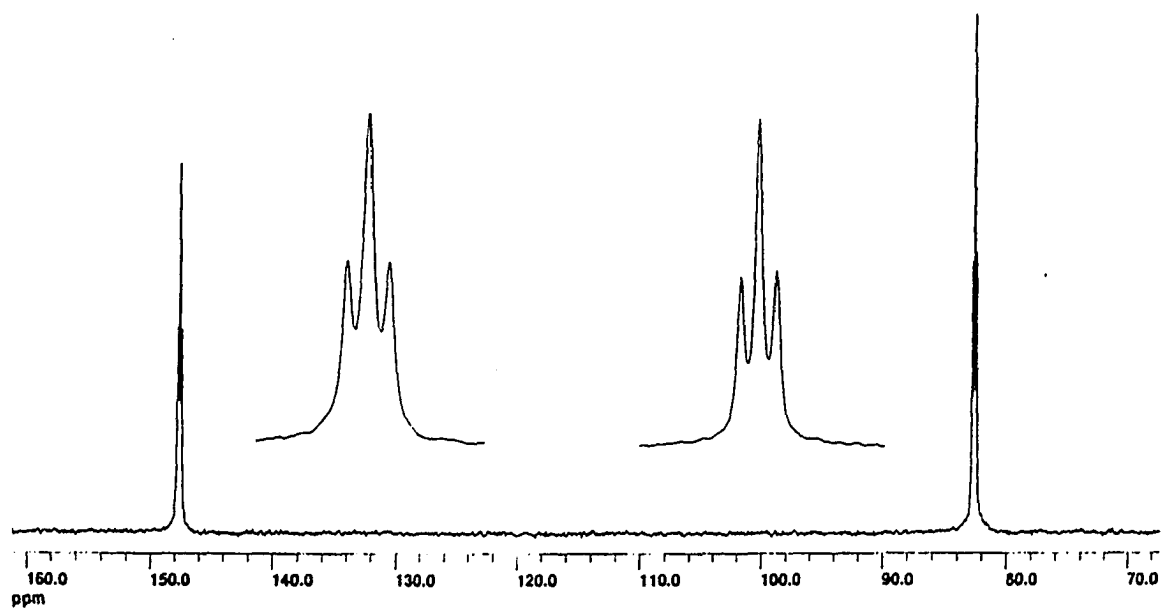**Figure 38.** ^{13}C {^1H}NMR spectra for 25, 26

97
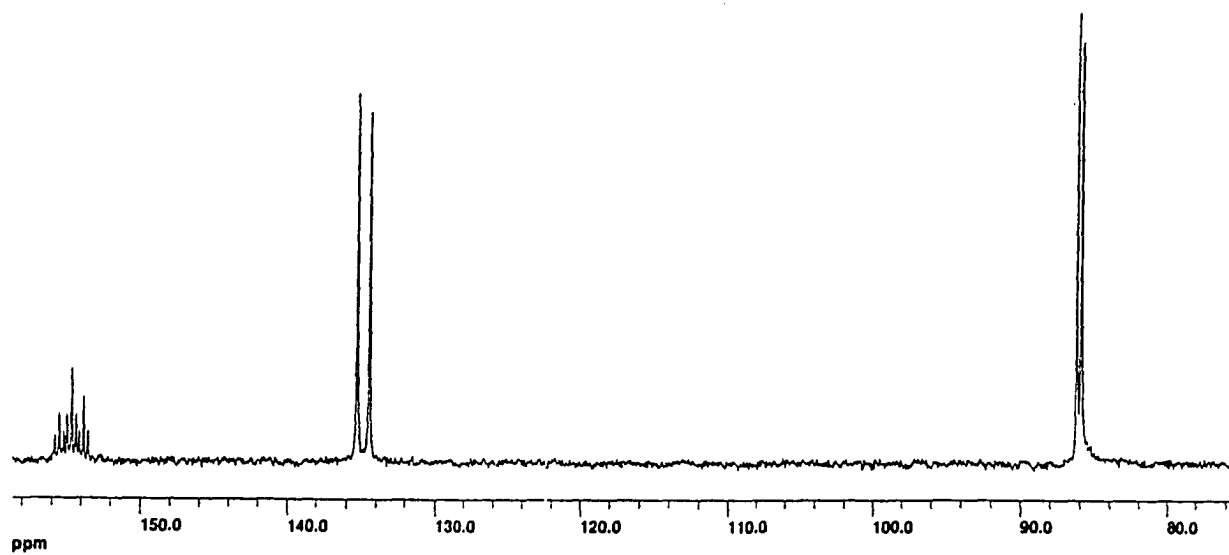
Complex 26

Complex 25

Figure 39. $^{31}P\{^1H\}$ NMR spectra for **25, 26**

98

From the similarity of the spectral data between **26** and **27**, we can see that the influence of the halide ligands is negligible.

The reaction shown by equation 22 is very different from that shown by equation 21. For the reaction of complex **14** with $PdBr_2(C_6H_5CN)_2$, both P_4O_4 and P_5O_5 cage complexes formed. When complex **25** and phosphine oxide $(^iPr_2N)_2P(O)H$ were heated in 70 °C toluene for one day, a ^{31}P NMR spectrum of the reaction mixture showed that the P_4O_4 cage had totally disappeared while the P_5O_5 cage and some complex **14** had formed in about a 4:1 ratio. When only complex **25**, or complex **25** with $PdBr_2(C_6H_5CN)_2$, or complex **14** with phosphine oxide were heated in toluene, no complex **27** formed. This expansion of a P_4O_4 cage to a P_5O_5 cage was discussed in detail in Part II-7.

3. Structure of $(CO)_4Mo[^iPr_2NPO]_4MBr_2$ (M=Ni, Pd).

The X-ray crystal structures of complexes $(CO)_4Mo[^iPr_2NPO]_4NiBr_2$ (**21**) and $(CO)_4Mo[^iPr_2NPO]_4PdBr_2$ (**25**) are shown in **Figures 34** and **36**, and the bond data listed in **Tables IX** and **X**. By comparing the data for these two structures, it can be seen that even though both Ni(II) and Pd(II) are formally of d^8 electronic configuration and both are four-coordinate, there are __major__ differences between their coordination modes. In complex **21**, the four-coordinate nickel(II) center adopts a pseudo-tetrahedral geometry. This geometry is consistent with its paramagnetic behavior[64]. In complex **25**, the Pd(II) center adopts a square-planar geometry which is consistent with its diamagnetism. With few exceptions[65], four-coordinate d^8 Pd(II) complexes

99

form square-planar complexes while four-coordinate Ni(II) complexes can form either tetrahedral D_{2d}, or square-planar complexes. Generally, weak-field ligands such as the halides and bulky ligands tend to form tetrahedral complexes, while strong-field ligands such as phosphines favor the square-planar geometry. In the latter geometry, the metal to phosphorus $d\pi$-$d\pi$ back bonding exists and the alignment of the participating orbitals is better, making the $d\pi$-$d\pi$ back bonding more efficient.

X-ray analysis of complex **21** showed tha deviations from idealized angles are found in both metal coordination spheres though there is approximately a tetrahedral geometry around the Ni vertex and an octahedral geometry at the Mo center. At Mo, the angle closest to linearity is P(3)-Mo-C(2) at 177.7(4)°. The four equatorial ligand atoms P(1), C(1), C(3), and C(4) have angles at Mo from 85.7(6)° to 94.3(4)° which sum up to 361°. The P(1)-Mo-P(3) bond angle is compressed by the chelate ring to 77.9(1)°. The two Mo-P bond distances are similar at 2.493(3) Å which is within the bonding range of the P-Mo(CO)$_n$ bonds[66]. The Mo-C bond distance of the equatorial carbonyls are now at 1.987(17) and 2.004(15) Å, shorter than the Mo-C bond length of the axial carbonyls at 2.019(17) and 2.047(17) Å. This is because the carbonyls trans to the phosphorus (good σ-donor compared to CO) can form better π back-bonding.

The bond angles around nickel deviate widely from 109.5°: the P-Ni-P angle is compressed to only 85.7(1)°. The Br(1)-Ni-Br(2) angle is distorted to 128.9(1)°, and the other angles are in the range of 104.4(1) to 111.3(1)°. The Ni-P bond distances at 2.254 Å and 2.266 Å are consistent with the literature values[66][67].

100

Replacing NiBr$_2$ by PdBr$_2$ in complex **25** generated relatively few changes in bonding data at Mo where the angle closest to linearity is P(2)-Mo-C(2) at 178.5(7)° and in **21** it is at 177.7(4)°. The four equatorial angles range from 87.9(10) to 92.9(7), but sum to 360°. In complex **21** these angles are in the range of 85.7(6)° to 94.3(4)°. The chelate ring compresses the P(1)-Mo-P(2) angle to 80.0(2)° compared with 77.9(1)° in **21**, the Mo-P bond distances are changed from 2.493(3) Å in complex **21** to 2.475(5) Å and 2.495(5) Å. The Mo-C bond distances of the equatorial carbonyls are 1.996(26) and 1.970(25) Å, again, smaller than the Mo-C bond length of the axial carbonyls at 2.026(25) and 2.027(26) Å. The four bond angles around palladium deviate from orthogonality; the P-Pd-P angle is the most distorted one at 85.0°, Br(1)-Pd-Br(2), 87.8(1)°; Br(2)-Pd-P(3), 93.5(2)°; Br(1)-Pd-P(4), 93.7(2)°. These orthogonal angles sum to 360°. The P-Pd bond distances at 2.233 Å are consistent with literature values[66].

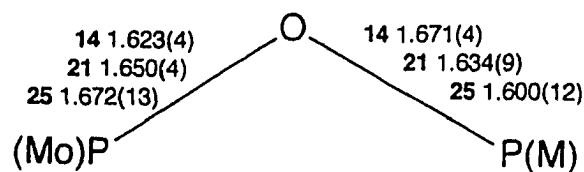The P-O distances of complex **14, 21** and **25** are compared in **Figure 40**:
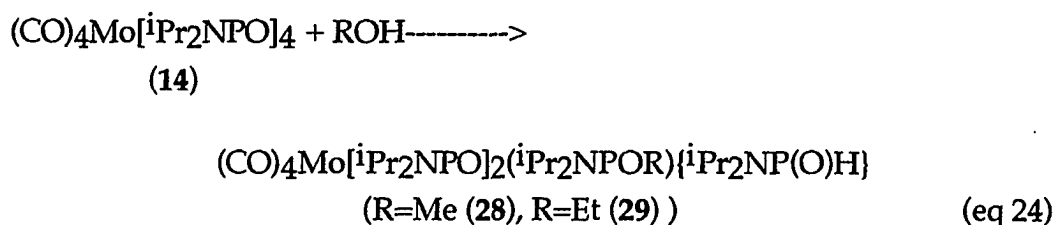

Figure 40. Selected Structural Data for **14, 21** and **25**

The eight cage P-O bond distances in **14, 21, 25** are different; in each case, they are adjusted to the respective coordination needs.

4. Reactions of (CO)$_4$Mo[^{i}Pr$_2$NPO]$_4$ (14) with Alcohols:

In Part II 1, we mentioned the reaction of complex **14** with MeOH; in this section, we will discuss details of this reaction. The reactions of complex **14** with MeOH and EtOH can be written as follows:

$$(CO)_4Mo[^iPr_2NPO]_4 + ROH \text{--------->}$$
$$(14)$$

$$(CO)_4Mo[^iPr_2NPO]_2(^iPr_2NPOR)\{^iPr_2NP(O)H\}$$
$$(R=Me\ (28),\ R=Et\ (29)\ ) \tag{eq 24}$$

The respective yields of complexes **28** and **29** in these reactions were 75 and 72%, respectively. Complex **28** was synthesized by the reaction in refluxing MeOH/hexane solution, and complex **29** was synthesized in refluxing EtOH/hexane solution.

Nucleophilic attack by primary alcohols such as MeOH and EtOH on complex **14** led to cleavage of a single P-O-P bond to give complexes **28** and **29**, (CO)$_4$Mo[^{i}Pr$_2$NPO]$_2$(^{i}Pr$_2$NPOR)\{^{i}Pr$_2$NP(O)H\}. Both **28** and **29** have been identified by ^{1}H, ^{13}C, and ^{31}P NMR and IR spectroscopy and by elemental analyses. In addition, the postulated monocyclic structure of complex **28** has been confirmed by X-ray crystallography. From ^{1}H, ^{13}C, and ^{31}P NMR and IR spectra of compound **28**, we deduced that it was a monomolybdenum compound. The IR spectrum showed a P=O stretching band at 1241 cm^{-1}. The ^{1}H-decoupled ^{31}P NMR spectrum showed an ABMX pattern and the ^{1}H NMR and proton-coupled ^{31}P NMR spectra showed that one phosphorus was bonded directly to a proton to give a -P(H)O group (Chemical shift of P=-1.5

102

ppm, chemical shift of H = 7.56 ppm, J_{PH} = 635.2 Hz) The coupling relationships among the four phosphorus atoms also indicated that one P-OP bond was broken. The ^{1}H NMR showed a P-OCH$_3$ group (3.41 ppm, J_{PH} = 12 Hz). Proton-coupled and decoupled ^{13}C NMR spectra confirmed this, since POCH$_3$ showed a ^{13}C singlet in the proton-decoupled spectrum changing to a quartet in the proton-coupled spectrum (J_{CH} = 145 Hz, the coupling constant between phosphorus and carbon in -POCH$_3$ was not detected). Selected spectra are shown in **Figures 41, 42 and 43.**
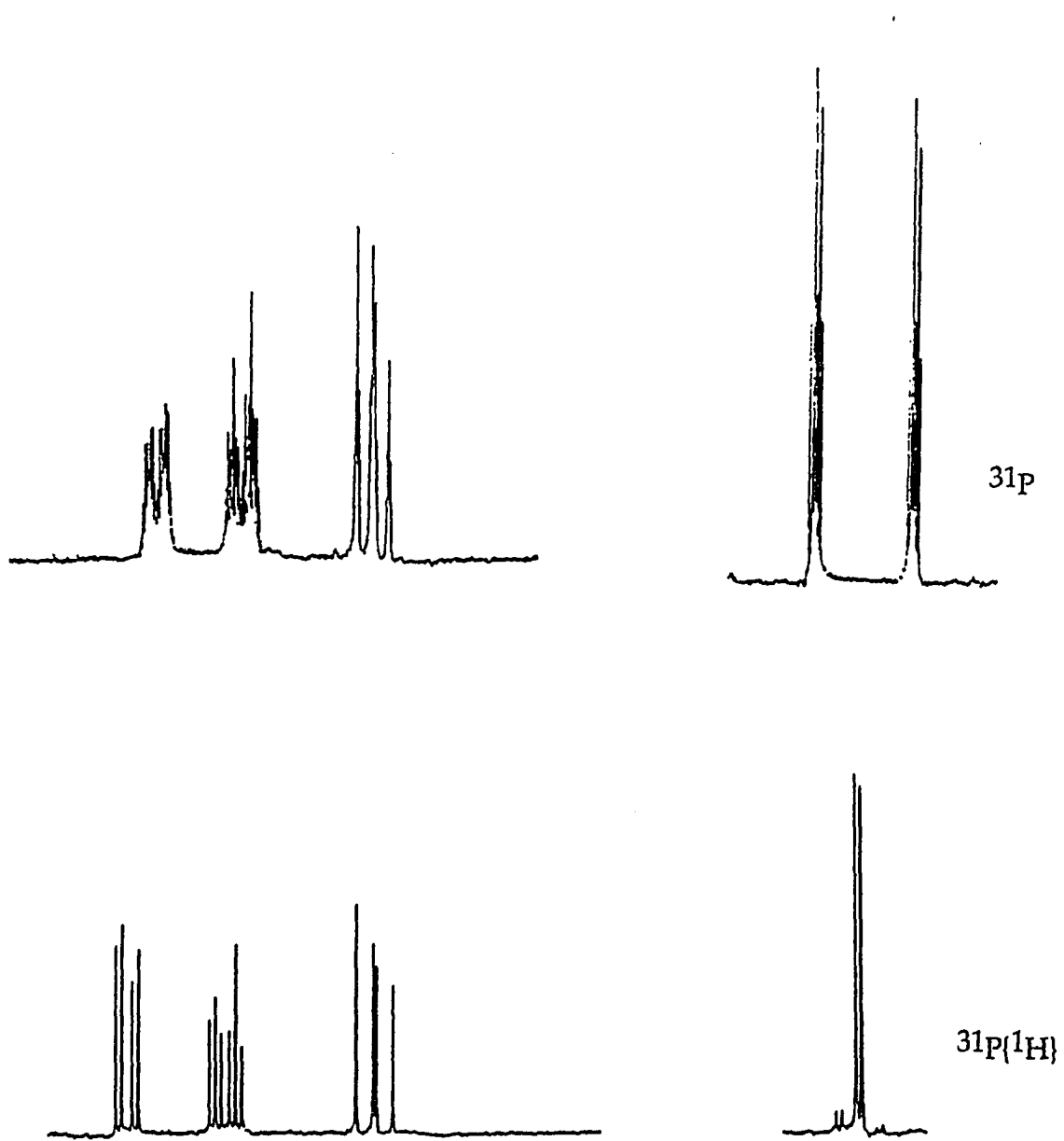
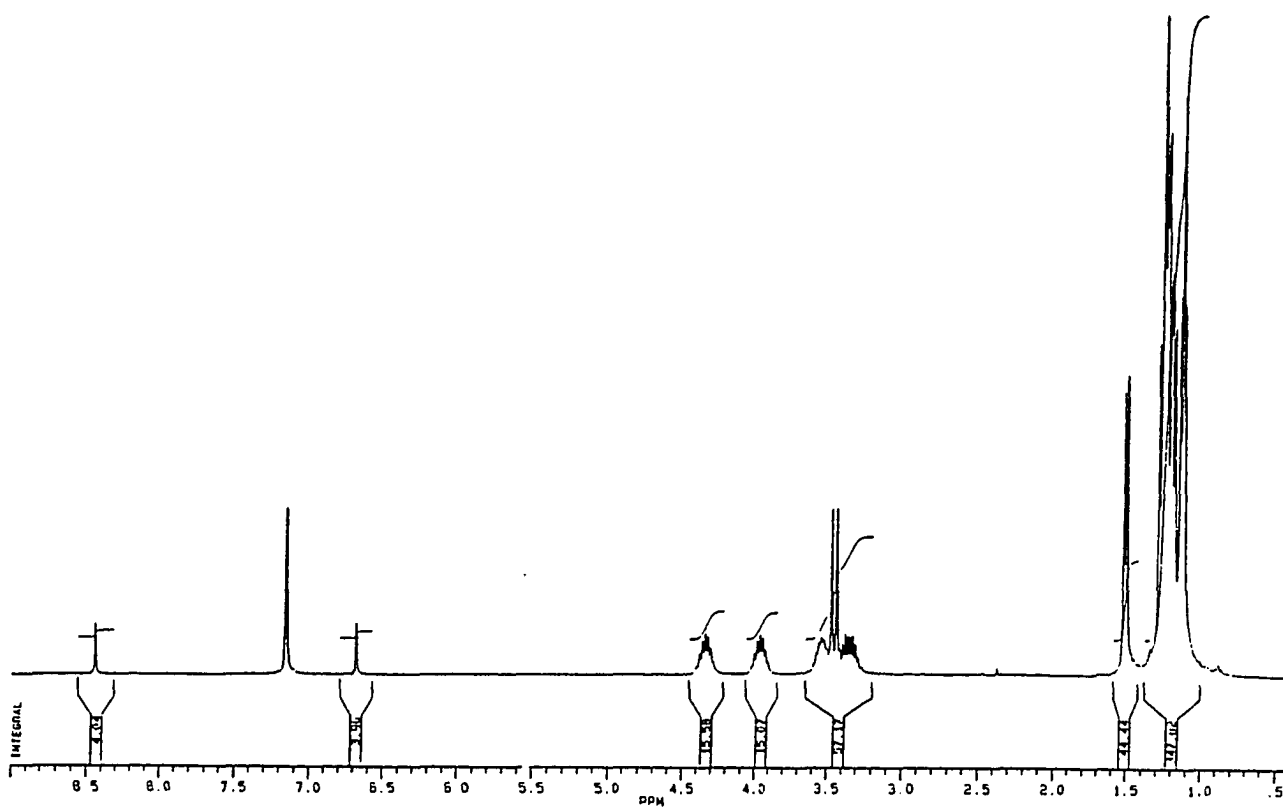**Figure 41.** Proton-coupled and decoupled ^{31}P NMR spectrum for **28**

104

Figure 42. ^{1}H NMR spectrum for **28**
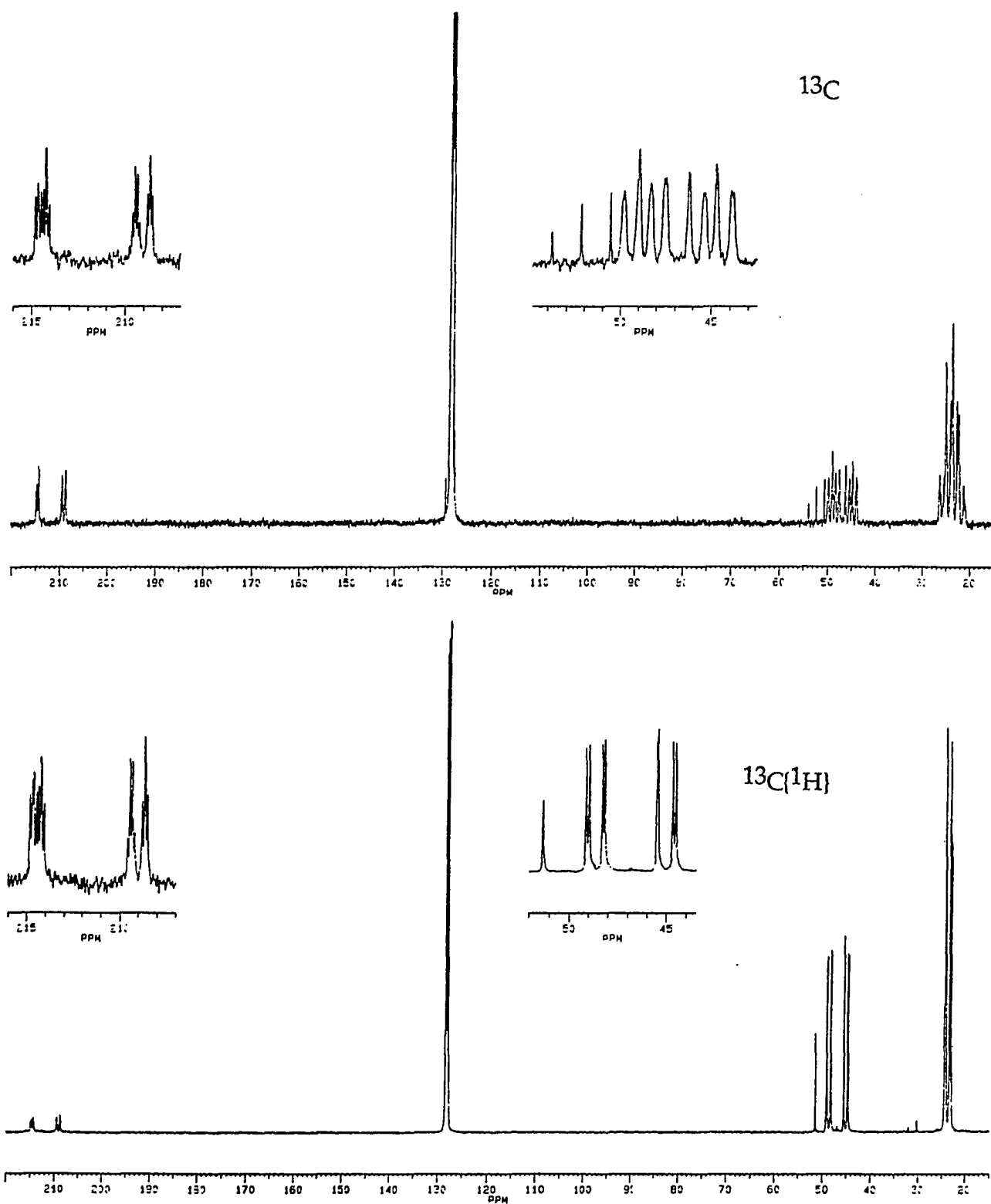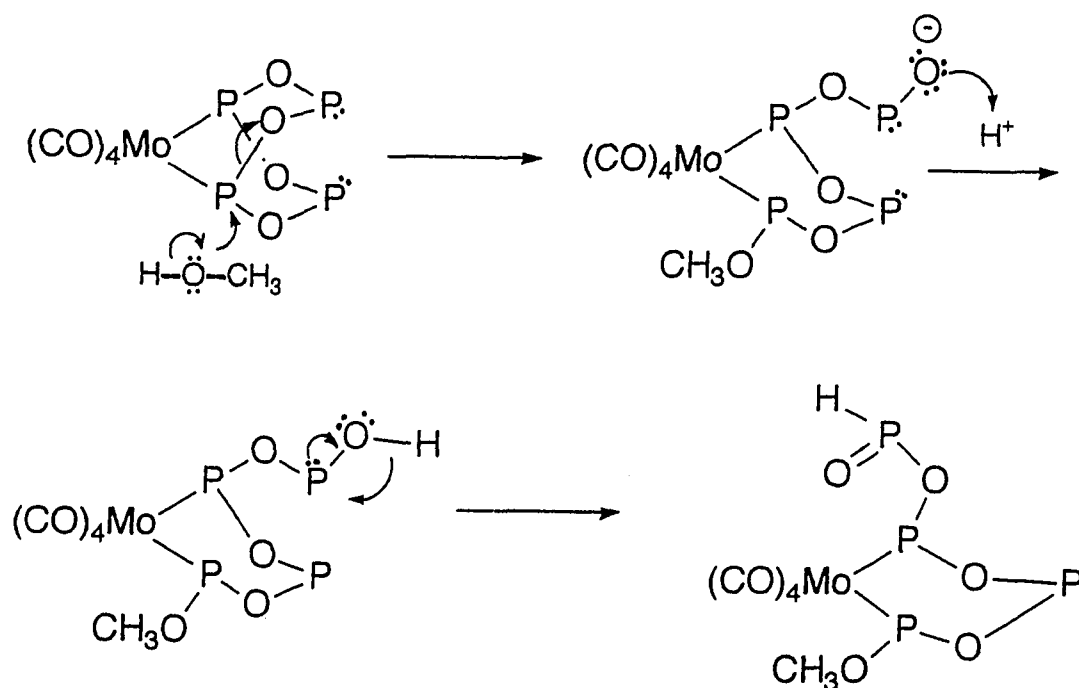
105

Figure 43. Proton-coupled and decoupled ^{13}C NMR spectrum for **28**

106

The bonding relationship of atoms in complex **28** can be deduced by an analysis of all of the spectra. Complex **28** may form following this mechanism (**Scheme V**):

Scheme V

Later, the structure of **28** was determined by X-ray crystallography which confirmed the proposed structure. This X-ray structure is shown in **Figure 44** whth the relevant structural data listed in **Table XII**.
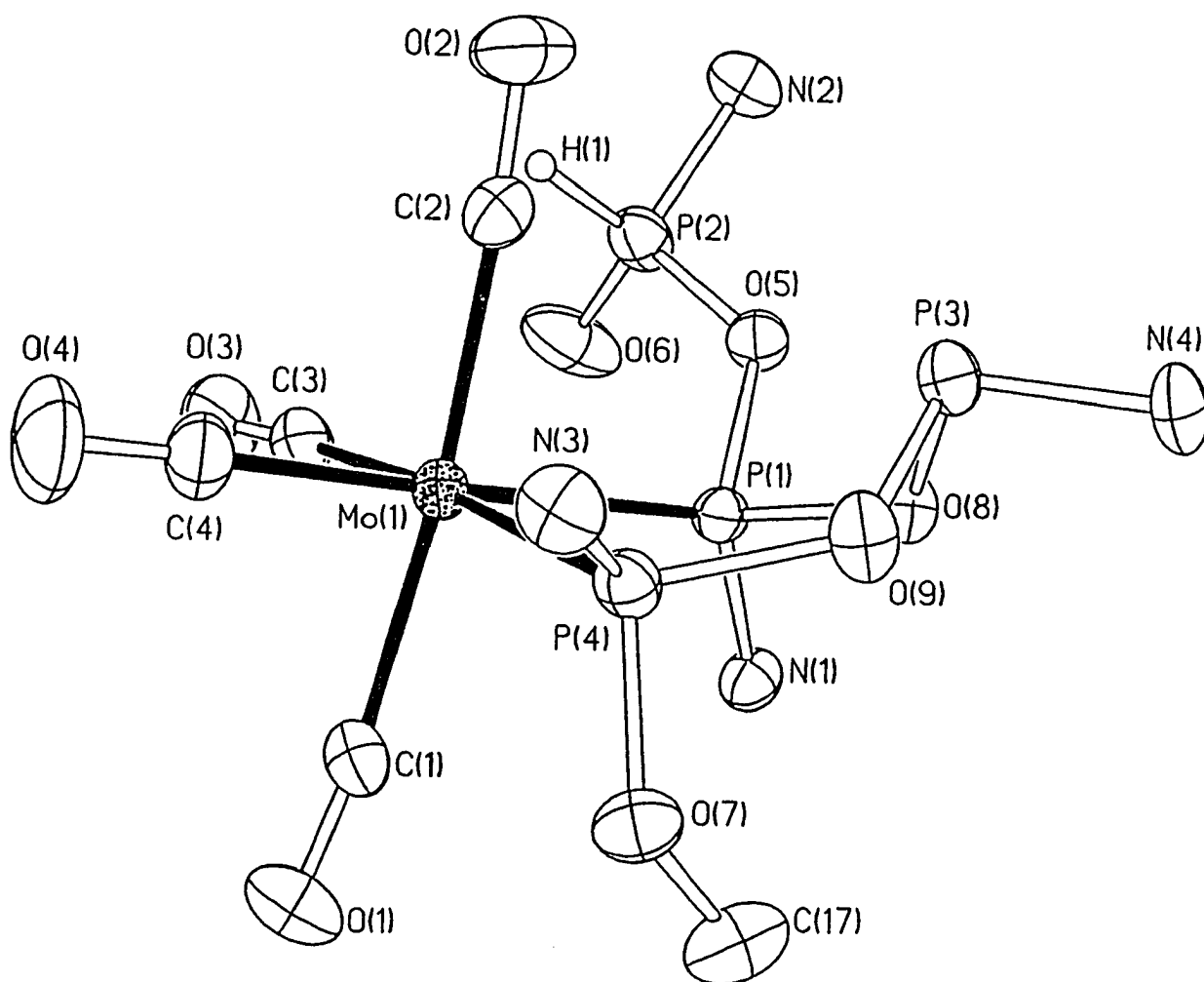
107

Figure 44. Molecular structure of **28**

108

Table XII. Selected Bond Distances (Å) and Angles(deg) for 28

Mo(1)-P(1)	2.521(2)	Mo(1)-P(4)	2.501(2)
Mo(1)-C(1)	2.029(5)	Mo(1)-C(2)	2.030(5)
Mo(1)-C(3)	1.998(5)	Mo(1)-C(4)	1.992(6)
P(1)-O(5)	1.668(3)	P(1)-O(8)	1.616(3)
P(1)-N(1)	1.644(4)	P(2)-O(5)	1.604(3)
P(2)-O(6)	1.452(5)	P(2)-N(2)	1.609(4)
P(3)-O(8)	1.679(3)	P(3)-O(9)	1.649(3)
P(3)-N(4)	1.648(4)	P(4)-O(7)	1.602(3)
P(4)-O(9)	1.644(3)	P(4)-N(3)	1.655(4)
O(1)-C(1)	1.144(7)	O(2)-C(2)	1.145(6)
O(3)-C(3)	1.142(7)	O(4)-C(4)	1.142(7)
O(7)-C(17)	1.422(6)		

P(1)-Mo(1)-P(4)	89.1(1)	P(1)-Mo(1)-C(1)	98.3(2)
P(4)-Mo(1)-C(1)	87.1(2)	P(1)-Mo(1)-C(2)	88.7(1)
P(4)-Mo(1)-C(2)	92.2(1)	C(1)-Mo(1)-C(2)	172.9(2)
P(1)-Mo(1)-C(3)	92.3(2)	P(4)-Mo(1)-C(3)	175.5(1)
C(1)-Mo(1)-C(3)	88.4(2)	C(2)-Mo(1)-C(3)	92.1(2)
P(1)-Mo(1)-C(4)	177.8(2)	P(4)-Mo(1)-C(4)	91.0(2)
C(1)-Mo(1)-C(4)	83.9(2)	C(2)-Mo(1)-C(4)	89.1(2)
C(3)-Mo(1)-C(4)	87.8(2)	Mo(1)-P(1)-O(5)	113.4(1)
Mo(1)-P(1)-O(8)	114.2(1)	O(5)-P(1)-O(8)	95.6(2)
Mo(1)-P(4)-O(7)	115.4(2)	O(5)-P(2)-O(6)	113.5(2)
Mo(1)-P(4)-O(9)	113.9(1)	O(8)-P(3)-O(9)	96.5(2)
P(1)-O(5)-P(2)	131.5(2)	O(7)-P(4)-O(9)	99.0(2)
P(1)-O(8)-P(3)	121.8(2)	P(3)-O(9)-P(4)	125.1(2)
P(4)-O(7)-C(17)	120.7(3)		

This shows that indeed a P-O-P was cleaved. One phosphorus, P(2), has a

109

new P=O double bond, and the other phosphorus, P(4), has a new P-OCH$_3$ bond. The lone remaining chelate ring shows a boat conformation with changes in ring angles and bond distances upon P-O-P cleavage. The P-Mo-P angle opened to 89.1(1)° from 75.1° in **14**. The P-O-P angles in the ring are compressed to 121.8(2)° and 125.1(2))° compared to 131.0° in **14**. This may be due to the repulsion of the two lone pairs flattening the P-O-P bond angles. The O-P-O angle in the ring is 96.5(2)°, similar to the O-P-O angles in **14** (97.7°). The geometry around molybdenum is unexceptional. It is pseudo-octahedral with a compressed axial C-Mo-C angle of 172.9(2) with the axial carbonyls bent away from the bidentate phosphorus ligand. The four equatorial angles are 87.8(2)°, 91.0(2)°, 89.1 (1)° and 92.3(2)°, summing nicely to 360°. The C(3)-Mo-P(4) [175.5(1)°] and C(4)-Mo-P(1) [177.8(2)°] angles are close to orthogonal values. The bonds distances of Mo-P (2.521 and 2.501 Å), P=O (1.452 Å) and P-O (1.602-1.668 Å) are typical literature values[69][69]. The Mo-C bond distances of the two equatorial carbonyls (trans to the phosphorus) are 1.99 Å, shorter than the Mo-C bond lengths of the two axial carbonyls (*cis* to the phosphorus) at 2.03 Å for the previously-discussed reasons (part II. 3).

Complex **29** has ^{1}H, ^{13}C, and ^{31}P NMR and IR spectra very similar to those of **28**. These spectra data are listed in the **Tables XIII, XIV, XV and XVI**. Therefore complexes **29** should has a structure similar to that of complex **28** also.

Table XIII. $^{31}P\{^{1}H\}$ NMR Data for Cage Complexes

Complex		Chemical Shift, ppm [J, Hz]
13	ABXY	201.1(d), 180.52(d) [^2J = 146Hz]
		154.9(d), 151.0(d) [^2J = 39 Hz]
14	A$_2$X$_2$	150.6(t), 126.0(t, bd) [^2J = 2 Hz]
16	A$_2$X$_2$	175.0(t), 147.9(t) [^2J = 6 Hz]
17	A$_2$X$_2$	165.2(t), 152.1(t) [^2J = 14 Hz]
18	A$_2$X$_2$	155.6(t), 90.9(t, bd) [^2J = 10 Hz]
19	A$_2$X$_2$	154.3(t), 103.6 and 103.5(d of t)
		[^2J = 13 Hz, $^1J_{AgP}$ = 568 and 492Hz]
20	A$_2$X$_2$	147.4(t), 132.6(t), 56.5(t) -19.4(t)
		[^2J = 10 Hz, $^1J_{PtP}$ = 5,520Hz]
21		paramagnetic
22	A$_2$X$_2$	154.5(t), 128.0(t) [^2J = 3 Hz]
23		paramagnetic
24		paramagnetic
25	A$_2$X$_2$	147.6(t), 82.6(t) [^2J = 6 Hz]
26	AM$_2$X$_2$	154.7(t of t), 134.9(d), 86.0(d)
		[$^2J_{AM}$ = 30 Hz, $^2J_{AX}$ = 11 Hz]
27	AM$_2$X$_2$	154.0(t of t), 134.7(d), 85.4(d)
		[$^2J_{AM}$ = 30 Hz, $^2J_{AX}$ = 10 Hz]
28	ABMX	169.1(d of d)
		[$^2J_{AB}$ = 34 Hz, $^2J_{AM}$ = 92 Hz]
		154.4(d of d of d) [$^2J_{BX}$ = 32 Hz,
		$^2J_{BA}$ = 34 Hz, $^2J_{BM}$ = 111 Hz]

111

131.3(d of d)

$[^2J_{MA} = 92$ Hz, $^2J_{MB} = 111$ Hz]

-1.50(d) $[^2J_{BX} = 32$ Hz]

29   ABMX   164.4(d of d)

$[^2J_{AB} = 34$ Hz, $^2J_{AM} = 98$ Hz]

153.1(d of d of d) $[^2J_{BX} = 29$ Hz,

$^2J_{BA} = 34$ Hz, $^2J_{BM} = 115$ Hz]

131.2(d of d)

$[^2J_{MA} = 98$ Hz, $^2J_{MB} = 115$ Hz]

-2.86(d) $[^2J_{BX} = 29$ Hz]

-----

a Spectra were run in CDCl3 solutions (d = doublet, t = triplet, bd = broad).

112

Table XIV. ^{13}C NMR Data for Cage Complexes

Complex	Chemical Shift (assignment, J)
13	241.1 (m, S$_2$CNMe$_2$), 215.0 (s, CO), 210.0, 209.1, 207.2 (bs, CO), 48.3, 47.8, 46.9 (bs, NC), 39.4 (bs, S$_2$CN(CH$_3$)$_3$), 24.2 (bs, Me)
14	215.8 (t, CO, $^2J_{PC}$ = 14 Hz), 209.5 (t, CO, $^2J_{PC}$ = 12 Hz), 48.0 (t, NC, $^2J_{PC}$ = 7 Hz), 44.3(t, NC, $^2J_{PC}$ = 8 Hz), 24.2(s, Me), 23.2 (s, Me)
16	224.5(t, CO, $^2J_{PC}$ = 9 Hz), 218.0 (t, CO, $^2J_{PC}$ = 18 Hz), 214.0 (t, CO, $^2J_{PC}$ = 16 Hz), 207.2 (t, CO, $^2J_{PC}$ = 13 Hz), 47.0 (t, NC, $^2J_{PC}$ = 7 Hz), 46.8(t, NC, $^2J_{PC}$ = 5 Hz), 24.3(s, Me), 24.0 (s, Me)
17	217.3(t, CO, $^2J_{PC}$ = 7 Hz), 214.5 (t, CO, $^2J_{PC}$ = 15 Hz), 207.6 (t, CO, $^2J_{PC}$ = 13 Hz), 48.1, 47.7 (t, NC, $^2J_{PC}$ = 6, 7 Hz), 24.1(s, Me), 24.0 (s, Me)
18	213.3(t, CO, $^2J_{PC}$ = 16 Hz), 207.2 (t, CO, $^2J_{PC}$ = 12 Hz), 120.4 (s, CN), 48.3 (t, NC, $^2J_{PC}$ = 6 Hz), 45.3(t, NC, $^2J_{PC}$ = 6 Hz), 23.6 and 23.1 (s, Me's), 2.2 (s, CH$_3$CN)
19	213.2 (t, CO, $^2J_{PC}$ = 16 Hz), 207.5 (t, CO, $^2J_{PC}$ = 12 Hz), 48.6, 45.4 (t, NC, $^2J_{PC}$ = 6, 7 Hz), 23.9(s, Me), 23.1 (s, Me)
20	212.1 (t, CO, $^2J_{PC}$ = 17 Hz), 205.1 (t, CO, $^2J_{PC}$ = 12 Hz), 48.2, 47.3 (t, NC, $^2J_{PC}$ = 6, 3 Hz), 23.9(s, Me), 23.6 (s, Me)
21	paramagnetic

113

22	215.0 (t, CO, $^2J_{PC}$ = 15 Hz), 208.0 (t, CO, $^2J_{PC}$ = 12 Hz), 198.4 (t, CO, $^2J_{PC}$ = 4 Hz), 48.0, 46.3 (t, NC, $^2J_{PC}$ = 6 Hz), 23.7(s, Me), 23.6 (s, Me)
23	paramagnetic
24	paramagnetic
25	211.8 (m, CO), 205.1 (t, CO, $^2J_{PC}$ = 13 Hz), 48.0, 48.2 (t, NC, $^2J_{PC}$ = 6, 3 Hz), 24.0(s, Me)
26	218.1 (d of t, CO, $^2J_{PC}$ = 39, 14 Hz), 216.1 (d of t, CO, $^2J_{PC}$ = 41, 10 Hz), 50.2 (t, NC, $^2J_{PC}$ = 6 Hz), 48.8, 48.5 (d, NC, $^2J_{PC}$ = 15, 12 Hz), 25.1 (d, Me, J = 4 Hz), 24.8 (s, Me), 24,0 (d, J = 7 Hz), 23.3 (t, J = 3Hz), 23.2 (s, Me)
27	218.2 (d of t, CO, $^2J_{PC}$ = 39, 14 Hz), 216.3 (d of t, CO, $^2J_{PC}$ = 41, 10 Hz), 50.2 (t, NC, $^2J_{PC}$ = 5 Hz), 48.7, 48.3 (d, NC, $^2J_{PC}$ = 15, 12 Hz), 25.3 (d, Me, J = 4 Hz), 25.0 (s, Me), 24,0 (d, J = 7 Hz), 23.2 (s, Me), 23.0 (t, J = 3Hz),
28	214.7 (d of d, CO, $^2J_{PC}$ = 12, 18 Hz), 214.3 (t, CO, $^2J_{PC}$ = 14 Hz), 209.4 (m, CO), 208.7 (t, CO, $^2J_{PC}$ = 12 Hz), 51.3(s, POCH₃), 49.0 (d, NC, $^2J_{PC}$ =14 Hz), 48.2, 45.5, 44.6 (d, NC, $^2J_{PC}$ = 14, 11, 6, 15 Hz), 24.3-22.9 (m, Me)
29	214.1 (d of d, CO, $^2J_{PC}$ = 7, 11 Hz), 213.6 (t, CO, $^2J_{PC}$ = 11 Hz), 208.8 (m, CO), 207.9 (t, CO, $^2J_{PC}$ = 12 Hz), 60.4 (s, POCH₂CH₃), 48.7 (d, NC, $^2J_{PC}$ =14 Hz), 47.9, 45.1, 44.3 (d, NC, $^2J_{PC}$ = 14, 11, 6, 14 Hz), 24.1-22.8 (m, Me), 15.7 (d, POCH₂CH₃, J = 9Hz)

a All spectra were run in CDCl₃ solution (t = triplet, d = doublet, s = singlet, bs = broad singlet)

114

Table XV. ^1H NMR Data for the Cage Complexes

Complex	Chemical Shift (multiplicity, assignment, J)
13	4.50 (bd, NCH), 4.30(septet, NCH, J = 7 Hz), 3.40, 3.30 (bd, $S_2CN(CH_3)_3$), 1.30 (bd, Me)
14	4.01(septet, NCH), 3.77 (bd, NCH), 1.30 and 1.12 (d, Me, J = 6.8 Hz)
16	4.47 and 4.14 (septets, NCH), 1.29 (t, Me, J = 7.0 Hz)
17	4.38 and 4.27 (septets, NCH, J = 7 Hz), 1.30 (m, Me)
18	4.03 and 3.83 (septets, NCH), 2.35 (s, MeCN) 1.29 (d, Me, J = 7.1 Hz)
19	3.99 and 3.83 (septets, NCH), 1.28 (d, Me, J = 6.8 Hz)
20	4.30 and 3.69 (septets, NCH), 1.46 and 1.40 (d, Me, J = 6.9 Hz)
21	paramagnetic
22	4.04 and 3.97 (septets, NCH), 1.30, 1.27 (d, Me, J = 7.0 Hz)
23	paramagnetic
24	paramagnetic

115

25	4.29 and 3.79 (septets, NCH, J = 7.3, 6.8 Hz), 1.48 and 1.45 (d, Me, J = 7.2 and 6.8 Hz)
26	4.64, 4.17 and 4.14 (septets, NCH, J = 6.9, 7.2 and 7.1 Hz), 1.43–1.38 (m, Me), 1.32 (d, Me,J = 6.9 Hz)
27	4.68, 4.18 and 4.14 (septets, NCH, J = 6.7, 7.1 and 6.7 Hz), 1.42–1.38 (m, Me), 1.33 (d, Me,J = 6.9 Hz)
28	7.56 (d, P(O)$\underline{H}$, J_{PH} = 635.2 Hz), 4.34, 3.96 and 3.47 (septets, NCH, J = 6.8, 7.1 and 6.4 Hz), 3.41 (d, POCH$_3$, J_{POCH3} = 12.36 Hz), 3.36 and 3.32 (septets, NCH, J = 6.7 Hz), 1.51 (d, Me, J = 6.8 Hz), 1.27–1.12 (m, Me)
29	7.58 (d, P(O)$\underline{H}$, J_{PH} = 634.9 Hz), 4.35 (septet, NCH, J = 6.9 Hz), 3.97 (m, NCH and POC$\underline{H}_2$CH$_3$), 3.54, 3.35 and 3.34 (septets, NCH, J = 5.9, 6.8 and 6.7 Hz), 1.45 (d, Me, J = 6.8 Hz), 1.27 (m, Me and POCH$_2$C$\underline{H}_3$)

116

Table XVI. Infrared Absorptions for the Complexes

Complex	CO region, cm^{-1}	POP region, cm^{-1}
1	2025.8, 1945.0, 1905.3, 1886.5	880.4, 858.5, 820.6[b]
	2015, 1923, 1906, 1887	875, 849, 809[c]
12	2035.1, 1979.3, 1916.2	898.5, 857.7, 824.7[b]
13	2013, 1912	871, 843, 792[c]
14	2022.8, 1925.1, 1908.1, 1982.5	891.5, 873.5, 860.2,838.4[b]
	2010, 1925, 1908, 1882	879, 861, 847, 828[c]
15	2000, 1932, 1869, 1843, 1837	1517(C-N)[c]
16	2035.3, 2020.8, 1930.5,1900.6	879.0, 854.4, 805.3[b]
	2023, 2009, 1925, 1901	869, 843, 786[c]
17	2021, 2014, 2000, 1937, 1907	867, 847, 795[c]
18	2031.3, 1908.0	885.9, 860.0, 814.1[b]
	2019, 1905	874, 850, 795[c]
19	2029.7, 1936.2, 1908.2	887.3, 861.5, 834.6, 815.0[b]
	2015, 1931, 1910	870, 852, 822, 804[c]
20	2045.1, 1958.7, 1948.1, 1917.6	894.1, 873.0, 847.1, 831.0[b]
	2033, 1950, 1940, 1914	879, 861, 835, 818[c]
21	2036.7, 1946.9, 1936.9, 1899.8	861.0, 830.1[b]
	2024, 1949, 1937, 1899	852, 813[c]
22	2022.9, 1968.8, 1931.3, 1919.5, 1905.6	881.3, 854.6, 797.7[b]
	2010, 1968, 1928, 1915, 1903	869, 842, 792[c]
23	2035.7, 1947.4, 1936.3, 1900.0	862.1, 831.8[b]
	2025, 1928,	874, 855[c]
24	2037.4, 1950.5, 1932.2, 1921.0	886.5, 859.7, 823.0[b]
	2025, 1925	875, 850, 815[c]
25	2045.8, 1961.0, 1943.0, 1921.8	871.7, 845.2, 820.9[b]
26	1981.6, 1910.4, 1880.1	888.3, 867.6,858.9, 834.8[b]
27	1981.2, 1910.9, 1880.1	887.1, 866.5, 858.2,833.3[b]
28	2027.2, 1928.0, 1909.8, 1895.8	895.6, 881.7,859.4, 845.5[b]
	2014, 1923, 1907, 1895	884, 871, 850, 834[c]
29	2027.5, 1942.9, 1919.3, 1903.6	896.9,883.2, 859.6, 839.9[b]

[a] KBr pellets, [b] FT-IR: Nicolet MX-1, [c] IR: Perkin-Elmer 283B

117

5. Miscellaneous Reactions:

5.1. Reaction of (CO)$_4$Mo[^{i}Pr$_2$NPO]$_4$ with MeI

Compound (CO)$_4$Mo[^{i}Pr$_2$NPO]$_4$ has two uncoordinated phosphorus atoms each with an available lone pair. We studied its reaction with the alkylating reagent MeI to see if it could be mono-alkylated which might lead to the formation of a bond between these two phosphorus atoms. Di-alkylation products might also form. However, no reaction occurred. At first, we used hexane as a solvent with MeI in large excess. We expected that the alkylation product salt would precipitate easily in this nonpolar solvent. After running the reaction at room temperature for 3 days , the ^{1}H, and ^{31}P NMR spectra of the reaction mixture showed that no reaction had occurred. Next, we tried the more polar solvent THF. In THF, even after three days, again no alkylated products had formed. The ^{1}H NMR spectrum of the reaction mixture showed that some (CO)$_4$Mo[^{i}Pr$_2$NPO]$_4$ had reacted with the THF to form unidentified products. This was confirmed by comparing the ^{1}H NMR spectrum of the control reaction of (CO)$_4$Mo[^{i}Pr$_2$NPO]$_4$ with THF. We also checked the reaction in a 1 : 1 CH$_3$CN/CH$_2$Cl$_2$ solvent mixture (the precursor complex is insoluble in neat CH$_3$CN); again no reaction resulted.

Tertiary phosphines generally react with alkyl halides by an S$_N$2 process to form a phosphonium salt. Displacement at a chiral carbon center occurs with inversion of configuration, consistent with a bimolecular transition state, as shown in the following equation[70]:

118

$$R_3^*P \;+\; \underset{R^1}{\overset{R^3}{\underset{R^2}{\diagup}}}\!\!C\!\!-\!\!X \;\longrightarrow\; R_3^*P\overset{\delta+}{----}\underset{R^2\;\;R^1}{\overset{R^3}{C}}\overset{\delta-}{-----}X \;\longrightarrow\; R_3^*P\!\!-\!\!\underset{R^1}{\overset{R^3}{\overset{+}{C}}}\!\!\!\diagdown_{R^2}\; X^-$$
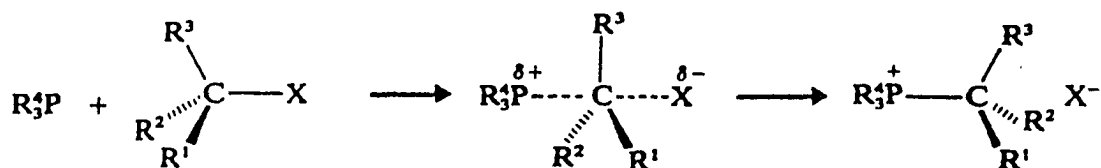
We think the unsuccessful alkylation of these phosphorus atoms may be due to the special structure of the compound (**Scheme VI**). The two electron lone pairs on the phosphorus atoms are convergent, and can not approach the carbon center to form the appropriate transition state; therefore, no alkylation products formed. Also, by its temperature-independent ^{31}P NMR spectral behavior up to 110 °C, we know that the inversion barrier at the phosphorus center is quite high, which prevents the lone pair from becoming accessible in the exo conformation.

$$(CO)_4Mo \cdots \qquad + \qquad \underset{H}{\overset{H}{\underset{\diagup}{\diagdown}}}C\!\!-\!\!X \qquad \longrightarrow \qquad N.\,R.$$
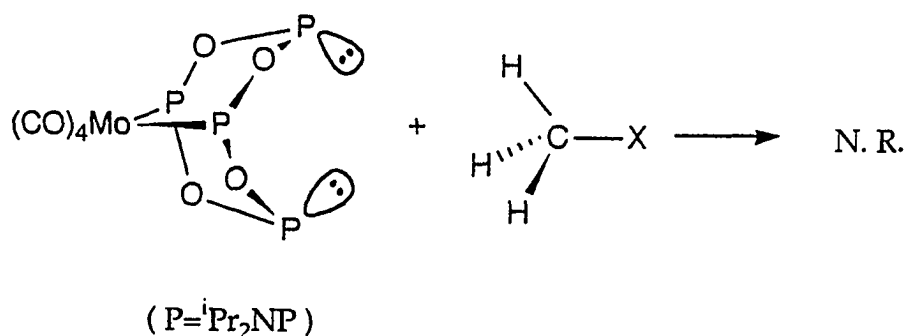
(P=^{i}Pr$_2$NP)

Scheme VI

From this reaction, we recognized that the precursor may only act as a bidentate donor. Thus, only the 1 : 1 Mo-Ag heterobimetallic cage product

119

(CO)4Mo[^{i}Pr2NPO]4AgNO3 formed (**Scheme VII**) regardless of excess Ag$^+$

(See Part II 2.4).
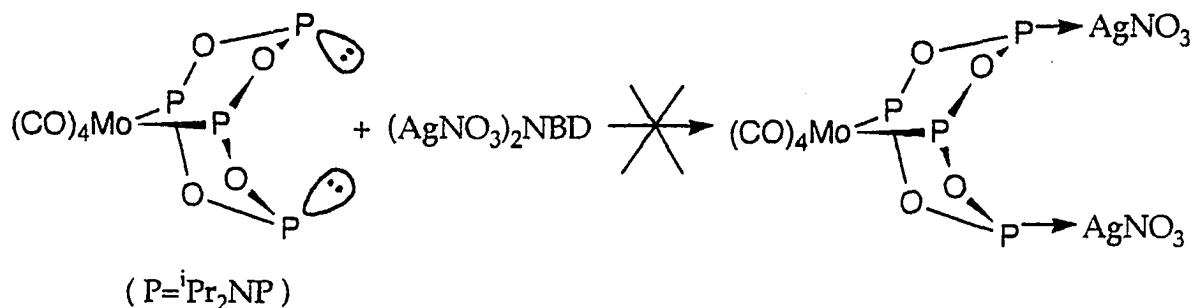
(P=^{i}Pr2NP)

Scheme VII

5.2. The Reaction of (CO)4Mo[^{i}Pr2NPO]4 with Ni(COD)2

We attempted to use (CO)4Mo[^{i}Pr2NPO]4Cu(CH3CN)2BF4 to react with

(CO)4Mo[^{i}Pr2NPO]4 in order to make a trimetallic 2 : 1 (2Mo : Cu) complex.

Unfortunately, the reaction was not clean, and it was hard to tell whether the

major product was (CO)4Mo[^{i}Pr2NPO]4CuBF4 or (CO)4Mo-

[^{i}Pr2NPO]4Cu[^{i}Pr2NPO]4Mo(CO)4BF4, since no pure product was isolated. We

also attempted the reaction of (CO)4Mo[^{i}Pr2NPO]4Ni(CO)2 with

(CO)4Mo[^{i}Pr2NPO]4, but also failed to produce the desired tri-metallic

complex. It may be because the bonds between the carbonyls and Ni are too

strong to be replaced. Hence we synthesized Ni(COD)2 from Ni(py)4Cl2 and

used it as a starting material to react with the Mo precursor, but this reaction

also failed. As the bonding between Ni and COD may be <u>too</u> weak and at the

120

same time the substitution reaction was very slow, after three hours the ^{1}H NMR spectrum of the reaction mixture showed no desired product and the Ni(COD)$_2$ had decomposed. If the reaction was run in refluxing CH$_2$Cl$_2$, a black murky mixture formed in only 20 minutes as the Ni(COD)$_2$ decomposed. Since Ni(COD)$_2$ is very reactive with oxygen and is pyrophoric, we need to find a better nickel compound to use as the starting material.

5.3. Other Reactions of (CO)$_4$Mo[^{i}Pr$_2$NPO]$_4$

Boron trifluoride is a strong Lewis acid and the Mo precursor (14) has several sites (O, N, P) with lone pairs that can act as donors. Thus, we ran the reaction of (CO)$_4$Mo[^{i}Pr$_2$NPO]$_4$ with (CH$_3$CH$_2$)$_2$O·BF$_3$ in CH$_2$Cl$_2$ at room temperature. After 1 hour, ^{1}H and ^{31}P NMR spectra of the reaction mixture showed that the starting complex had decomposed. We also attempted the reaction of 14 with sulfur. ^{31}P NMR spectra showed that the products were mixtures, as one or both of the uncoordinated phosphorus atoms had reacted with S to form mono-P=S or di-P=S compounds. No pure products were obtained.

The reactions of complex 14 with nucleophiles such as ^{i}PrOH, ArCHO, (^{i}Pr$_2$N)$_2$P(O)H, PCl$_3$ or electrophiles such as SnCl$_2$, SnCl$_4$, SnMeCl$_3$ were also attempted; either no reaction was observed or no products were isolated.

Numerous attempts were made to synthesize Mo/Rh and Mo/Ru heterobimetallic cage compounds which would be possible catalysts. For example, Ru(DMSO)$_4$Cl$_2$, [(NBD)RhCl]$_2$, [Rh(NBD)(CH$_3$CN)$_2$]Cl,

121

[Rh(NBD)(PPh$_3$)$_2$]PF$_6$ were all tried, but no desired products were obtained.

6. Evidence for Intracage Influences Due to the Heterometal

The rigidly conserved structures of the heterobimetallic cage complexes provided a useful setting for the study of intracage metal-metal interactions. By examining the variation of the Mo carbonyl ^{13}C NMR shift values and the IR stretching frequencies of the carbonyls of the cis-Mo(CO)$_4$ group in a series of bimetallic cage complexes of the type (CO)$_4$Mo[^{i}Pr$_2$NPO]$_4$ML$_n$(M=Cr(0), Fe(0), Mo(0), Ni(0), Ag(I), Cu(I), Pt(II), Pd(II) and Ni(II)), it has been found that there are two trends. One is the correlation between the well-resolved A$_1$ carbonyl stretching frequencies of the cis-Mo(CO)$_4$ group and the formal charge on the second cage metal M. As the charge of the second metal increases, the A$_1$ carbonyl stretching frequencies for the cis-Mo(CO)$_4$P$_2$ moiety increases. Such a shifting of this carbonyl stretching frequency is in accord with decreasing electron donation to cis-Mo(CO)$_4$.

A second correlation is that the ^{13}C NMR chemical shift of the Mo carbonyl carbon in the heterobimetallic cage compounds moves to higher field with increasing charge on the second cage metal. These observations suggest a transmission of intracage influence from the heterometal. Examination of the X-ray data of several bimetallic cage complexes further supports this conclusion (see Part II 6.3).

6.1. Comparison of the FT-IR Spectral Data of the Mo(CO)$_4$ Moiety.

The infrared stretching frequencies for the carbonyl A$_1$ mode are given in **Table XVII and Scheme VIII.**

122

Table XVII. The Carbonyl Stretching Frequencies (A_1 mode) in $(CO)_4Mo[^iPr_2NPO]_4ML_n$ Heterobimetallic Cage Complexes

compounds	$\nu_{CO(cm-1)}$ (IR)	$\nu_{CO(cm-1)}$ (FT-IR)	metals
14	2010	2022.8	Mo/
22	2010	2022.9	Mo/Ni(0)
1	2015	2025.8	Mo/Mo(0)
16	2009	2020.8	Mo/Cr(0)
19	2015	2029.7	Mo/Ag(I)
18	2019	2031.3	Mo/Cu(I)
12	2025	2035.1	Mo/Mo(II)
23	2025	2035.7	Mo/Ni(II)
21	2024	2036.7	Mo/Ni(II)
24	2025	2037.4	Mo/Ni(II)
20	2033	2045.1	Mo/Pt(II)
25	2034	2045.8	Mo/Pd(II)

IR: Perkin-Elmer 283B (KBr pellet).   FT-IR: Nicolet MX-1 (KBr pellet).

The data in Table XVII suggest that there is indeed a correlation between the carbonyl stretching frequency of the cis-Mo(CO)$_4$P$_2$ group and the charge of the second metal in Mo-M cage complexes.

Mo(0)/M(I)   Mo(0)/M(II)

Mo(0)/M(0)

2020   2025   2030   2035   2040   2045   2050

ν CO(cm-1)

Scheme VIII

123
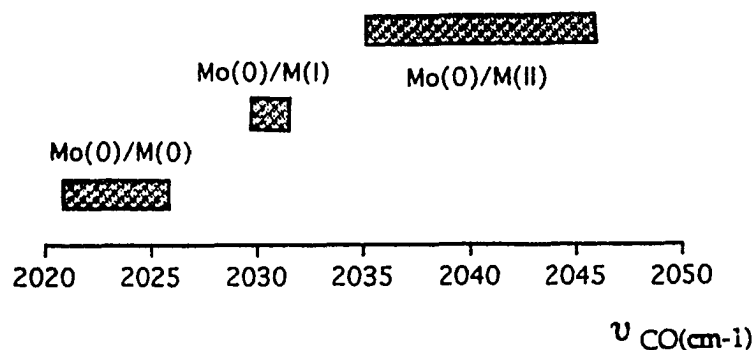
In metal carbonyl complexes, the carbonyl ligand donates its sigma electron density to an empty metal orbital while the metal returns its d electron density to the empty π^* orbital of the carbonyl by π back-bonding (Figure 45)[71].

(a) ligand-to-metal
σ-bonding

(b) Metal to ligand π^* back bonding
(one of a mutually perpendicular
set shown)
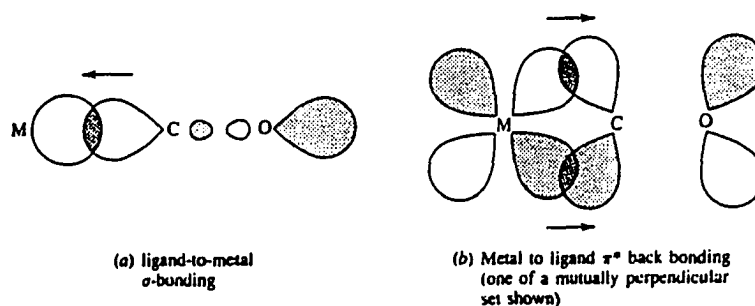
Figure 45. Orbital overlap in M-CO bonding

According to molecular orbital theory, the highest-occupied molecular orbital of CO, which acts as the electron-pair donor to a metal, is slightly antibonding between C and O, donating electron density from this orbital to the metal. This should make the C-O bond slightly stronger and raise ν_{CO}.

However, the back π-bonding by donation of metal d electron density into the CO antibonding π^* orbital should significantly weaken the C-O bond[72]. Thus, the most electron-deficient carbonyl has the strongest C-O bond and gives the highest stretching frequency.

The listed infrared frequencies of these complexes indicate an intracage influence between the two metals: As the second metal increases its electron demand by increasing its formal charge, electron density flows along the

124

(Mo)P-O-P(M) bonds. This makes the phosphorus atoms bonded to Mo^0 less basic, so the P ---> Mo donation decreases, decreasing electron density at the metal Mo^0. As a result, the Mo --> carbonyl π back-donation is also decreased; therefore, the C-O bonds are stronger, and the υ_{CO}'s are raised.

6.2. Comparison of the ^{13}C NMR Chemical Shifts of the Mo(CO)$_4$ Moiety

The ^{13}C NMR chemical shift data for the cis -Mo(CO)$_4$P$_2$ moiety of the complexes are presented in Table XVIII and Scheme IX. The ^{13}C NMR spectra of all of these compounds were run in chloroform. The general trend observed is that ^{13}C resonances of the carbonyl carbons are shifted to a higher field with increasing formal charge at the second cage metal.

Table XVIII. ^{13}C NMR Chemical Shifts for the Carbonyl Resonances of the Complexes

Compounds	$\delta_{CO(ppm)}$ (average)	metals
14	212.7	Mo/
22	211.7	Mo/Ni(0)
17	211.2	Mo/Fe(0)
1	210.7	Mo/Mo(0)
16	210.6	Mo/Cr(0)
19	210.4	Mo/Ag(I)
18	210.3	Mo/Cu(I)
12	209.6	Mo/Mo(II)
20	208.6	Mo/Pt(II)
25	208.5	Mo/Pd(II)

125

Mo(0)/M(II)

Mo(0)/M(I)

Mo(0)/M(0)

-212   -211   -210   -209   -208

$\delta_{^{13}C}$ (ppm)
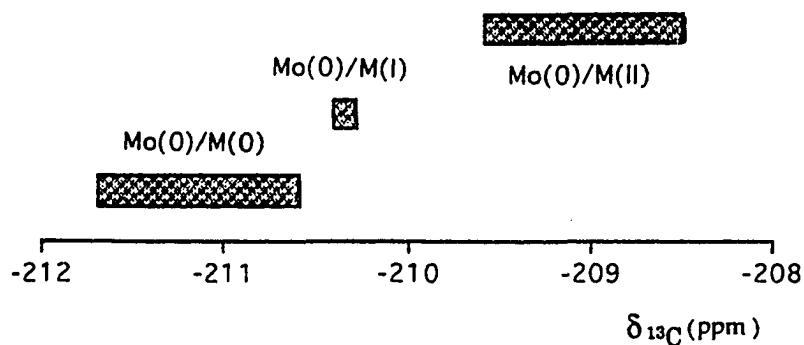
Scheme IX

Examination of the data trend in **Table XVIII** again suggests that there is a transmission of intracage influence between the heterometals. Bodner[73] and Braterman[74] have attributed these shieldings of the carbonyl resonance to a decreasing of electron density at the metal center. They suggest that the variations in the M-CO π back bonding are chiefly responsible for the observed changes. Their hypothesis is supported by Bodner's observation that the carbonyl resonance in $(\eta^5\text{-}C_5H_5)M(CO)_3$ complexes (M=Cr⁻, Mn⁰, Fe⁺) is shielded with increasing positive charge[73].

Not surprisingly, the ^{13}C NMR chemical shifts of these carbonyl carbons go to higher field as their CO stretching frequencies increase. A plot of ^{13}C NMR carbonyl chemical shifts in ppm downfield from TMS versus corresponding infrared stretching frequencies is shown in **Figure 46** for 8 of the 12 known bimetallic complexes (complexes **21, 23** and **24** are paramagnetic, and the υ_{CO} value for $(CO)_4Mo$ group in complex **17** is obscured by the $Fe(CO)_3$ group.).

126
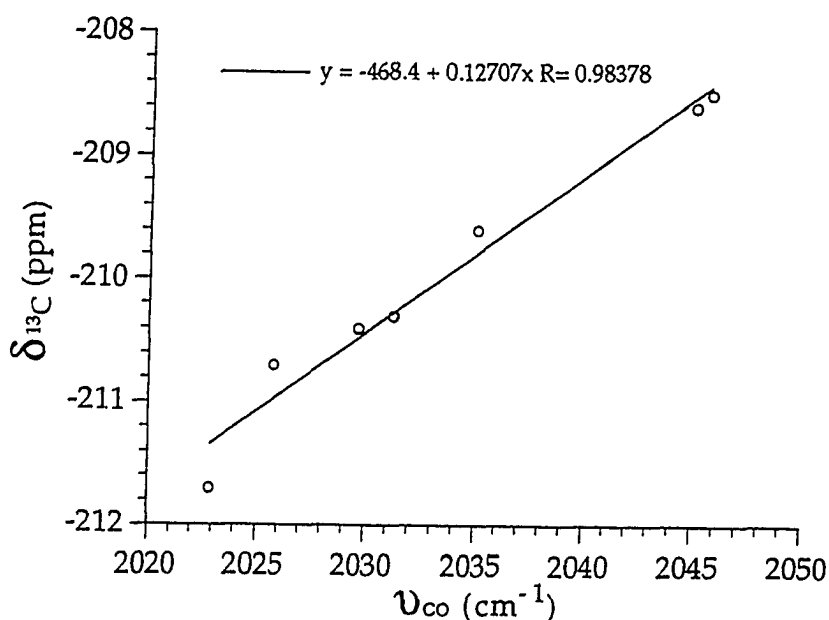
Figure 46. A correlation of the ^{13}C NMR chemical shifts vs the IR frequencies (A1 mode) for the carbonyl groups in cis-(CO)4MoP2

Similar correlations between ^{13}C NMR chemical shifts of carbonyl carbon atoms and their infrared stretching frequencies have been found for LW(CO)5 and π-CpFe(CO)2X derivatives by Gansow and coworkers[75], and for LNi(CO)3, LM(CO)5, M=Cr, and Mo and (C6H5X)Cr(CO)3 by Bodner and coworkers[76].

Although suppositive of intracage effects, the NMR and IR shifts we observe are relatively small and may well be sensitive to steric as well as electronic influences. A broader range of structural and spectral data are still needed to affirm this premise.

6.3. Comparison of the X-ray Structural Data of the Complexes

From the comparison of ^{13}C NMR chemical shifts and the IR stretching

127

frequencies of the *cis* -Mo(CO)$_4$P$_2$ vertices in the bimetallic cage complexes in Part II **6.1** and **6.2**, it appears that there are interactions between the two metals within the cage.

The same conclusion can be reached from a comparison of X-ray crystallographic bond data of the representative complexes. In **Table XVIII** the average bond distances of Mo-P, (Mo^0)P-O and (M) P-O bonds are listed:

Table XIX. Selected Bond Lengths (Å) for Several Complexes

compounds	Mo-P(O)	(Mo^0)P-O	(M)P-O
14 (Mo/)	2.512(2)	1.623(4)	1.671(1)
1 (Mo/Mo(0))	2.501(1)	1.646(4)	1.646(4)
21(Mo/Ni(II))	2.493(4)	1.650(9)	1.633(8)
12(Mo/Mo(II))	2.486(5)	1.66(1)	1.63(1)
25(Mo/Pd(II))	2.485(5)	1.672(13)	1.600(12)

The most interesting differences among the complexes **14, 1, 21, 12** and **25** are the P-O bond lengths. When there is only one metal (molybdenum) in complex **14**, the four coordinated P-O bond are much shorter at 1.623(4) Å than the uncoordinated P-O bonds at 1.671(4) Å. This suggests that the P-O bonding at the coordinated sites is enhanced at the expense of the latter. When a second metal is introduced into the cage, the (M)P-O bonds are significantly modified. For example, the four formerly uncoordinated P-O bonds readjust and decrease from 1.671(4) Å in **14** to 1.646(4) Å, 1.633(8) Å,

128

1.63(1) Å, and 1.600(12) Å in Mo^0-Mo^0, Mo^0-Ni^{II}, Mo^0-Mo^{II} and Mo^0-Pd^{II} cages, respectively. The four P-O bonds that are bonded to the original metal Mo^0 are lengthened at the same time. This changing of bond lengths correlates with the electron demand of the new metals introduced. These data once again support the conclusion that there is a transmission of intracage influence from the heterometal to the Mo center.

7. Expansion of the P_4O_4 Cage to a P_5O_5 Cage

While attempting to synthesize Mo/Pd heterobimetallic cage complexes from $(CO)_4Mo[^iPr_2NPO]_4$ (**14**) and $PdX_2(C_6H_5CN)_2$ (X=Cl, Br), it was found that not only the P_4O_4 cage complex, but also the P_5O_5 cage complex, formed depending on the halide ligand of the starting $PdX_2(C_6H_5CN)_2$. Reaction of $PdCl_2(C_6H_5CN)_2$ with complex **14** only gave a P_5O_5 cage, but $PdBr_2(C_6H_5CN)_2$ formed both P_4O_4 and P_5O_5 cage complexes. The Mo/PdBr$_2$ P_5O_5 cage could be obtained by either thermal reaction of **14** with $PdBr_2(C_6H_5CN)_2$ or by heating the Mo/Pd P_4O_4 cage with phosphine oxide $(^iPr_2N)_2P(O)H$. It was also found that the Mo/Pd P_5O_5 cage always formed in the company of some Mo/Mo P_4O_4 cage. In addition, when pure Mo/PdBr$_2$ P_4O_4 cage was heated alone, no P_5O_5 cage formed. Furthermore, pure **14** did not react with excess phosphine oxide. By the distribution of the product complexes **1** and **26**, or **1** and **27**, it can be noted that their ratios were about 1:4. This number may hint at the mechanism of this cage expansion reaction. The expansion requirs an extra P-O unit, which may come from the added phosphine oxide or come from the decomposition of the MoP_4O_4 precursor.

Clearly, the PdX$_2$ unit plays an important role: it provided the second metal vertex for forming the P$_5$O$_5$ cage and it might also assist in the decomposition of the precursor to generate new P-O units.

Three mechanisms may be involved in this expansion reaction:

Mechanism 1

14

PdBr$_2$(CH$_3$CN)$_2$
- 2CH$_3$CN

25

27

(^{i}Pr$_2$N)$_2$P(O)H
- CO, -^{i}Pr$_2$NH

Mechanism 3

14

PdBr₂(CH₃CN)₂
- 2CH₃CN

25

[ⁱPr₂NPO]
- CO

Mechanism 2

14

1 + 4 [ⁱPr₂NPO]

4 X14 - 4CO

4PdX₂(CH₃CN)₂
- 8CH₃CN

27

X = Cl, Br
P = ⁱPr₂NP

26, 27

Scheme X

131
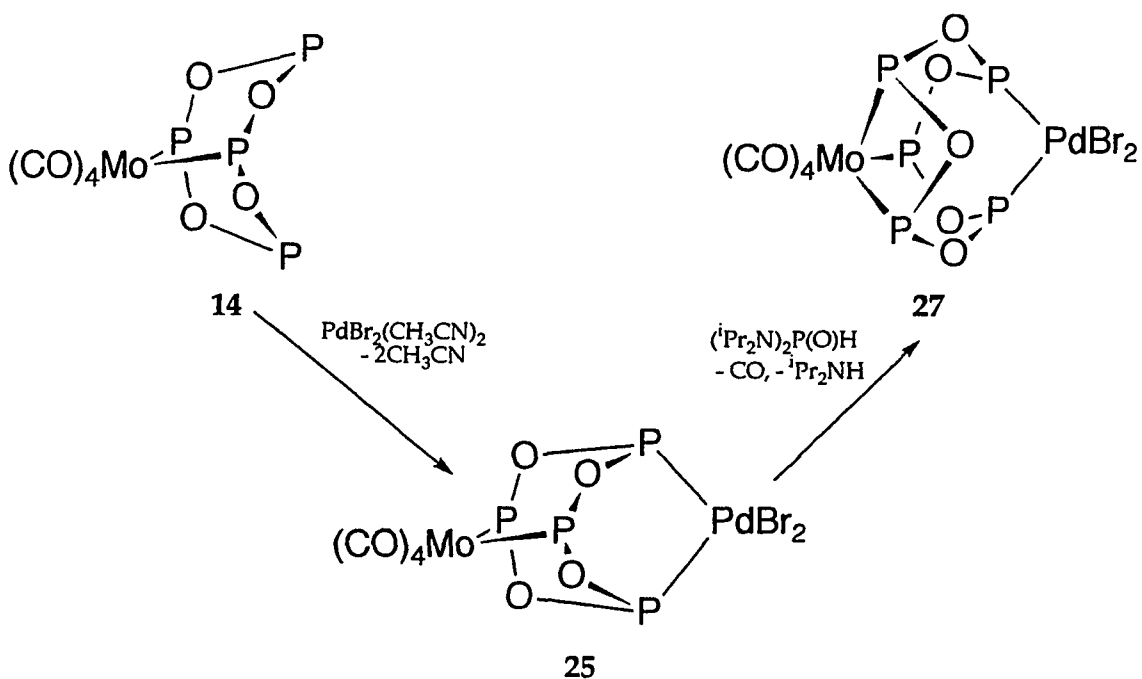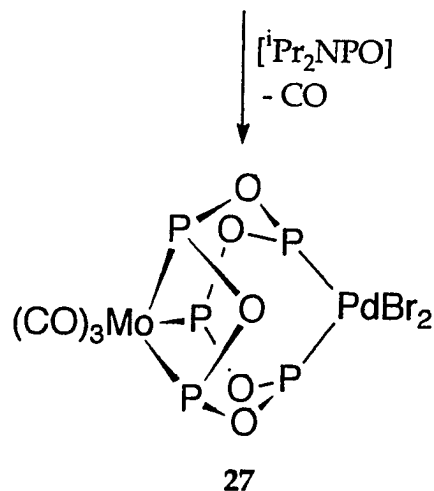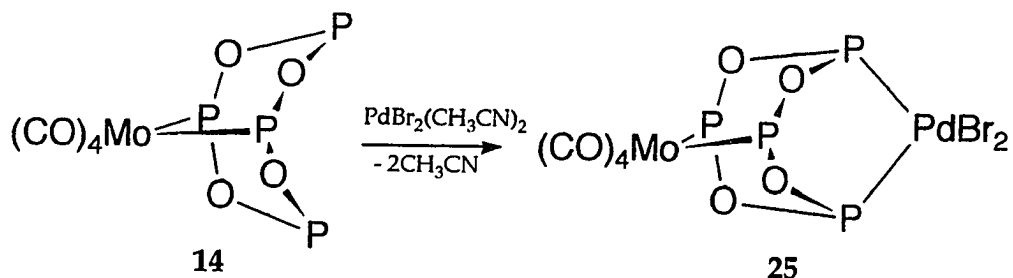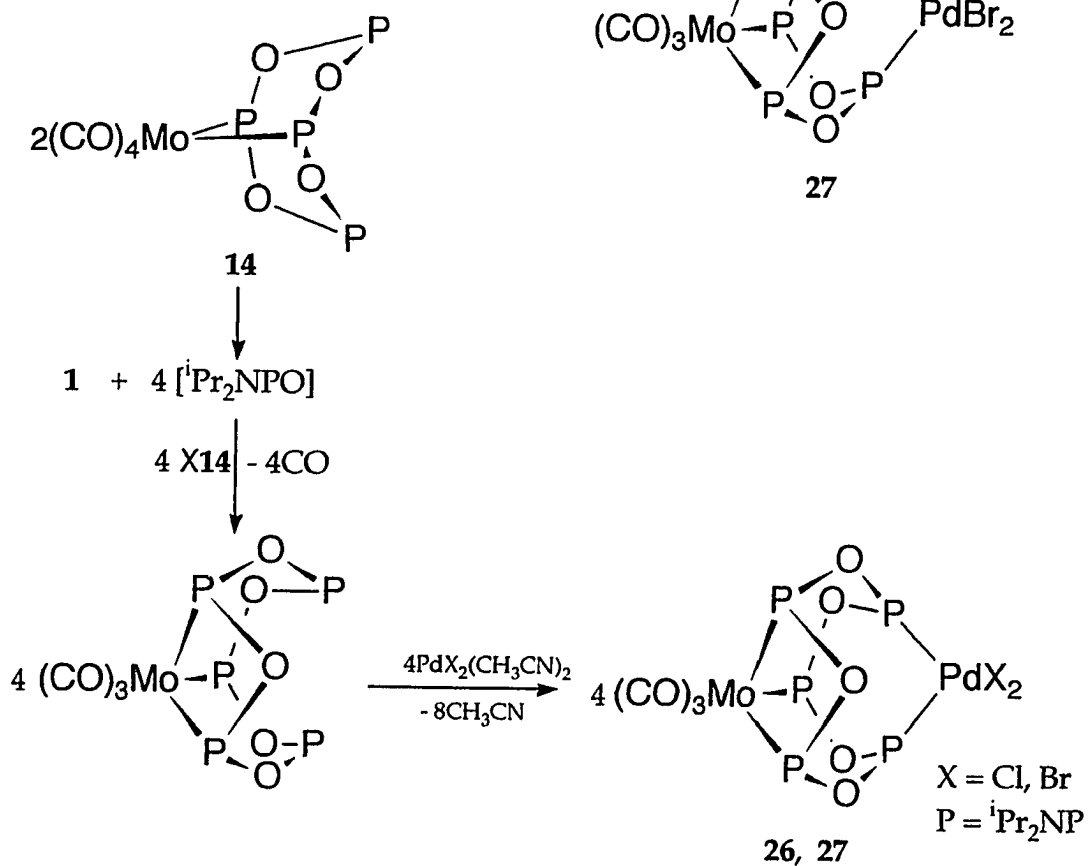
Mechanism 1 involves the direct thermal expansion of the $Mo/PdBr_2$ P_4O_4 cage to a P_5O_5 cage by incorporation of a phosphine oxide unit. Addition of $(^iPr_2N)_2NP(O)H$ to the MoP_4O_4Pd cage and loss of a CO from the cis-$Mo(CO)_4$ moiety and loss of $^iPr_2NH$ from phosphine oxide can lead to a $Mo/PdBr_2$ P_5O_5 cage complex. Mechanism 2 requires the thermal decomposition of $(CO)_4Mo[^iPr_2NPO]_4$ and the formation of a transient $[^iPr_2NPO]$ unit along with the Mo-Mo P_4O_4 cage. Addition of the $[^iPr_2NPO]$ unit to **14** and CO loss from $(CO)_4Mo$ can generate a monometallic P_5O_5 intermediate, $(CO)_3Mo[^iPr_2NPO]_5$. This intermediate can be a ligand and react with $PdX_2(C_6H_5CN)_2$ to form the bimetallic Mo/Pd P_5O_5 cage complex. The P_5O_5 cage may also form from mechanism 3 by reaction of preformed $Mo/PdBr_2$ P_4O_4 cage with the similarly-liberated $[^iPr_2NPO]$ unit. Which of these is the likely mechanism remains to be determined.

132

Conclusions and Suggestions for Future Work

The metalla-ligand complex $(CO)_4Mo[^iPr_2NPO]_4$ (14) has been synthesized by the reaction of the mixed-valent, adamantanoid cage complex $(CO)_4Mo[^iPr_2NPO]_4Mo(CO)_2I_2$ with sodium dimethyldithiocarbamate. X-ray structural data as well as solution NMR spectra of **14** showed that the $[^iPr_2NPO]_4$ ring in this monometallic cage precursor remains in the boat-boat conformation.

This precursor behaved as a bidentate ligand, reacting with suitable metal complexes with labile ligands to provide heterobimetallic cages of the type $(CO)_4Mo[^iPr_2NPO]_4ML_n$ ($ML_n = Cr(CO)_4$, $Fe(CO)_3$, $Cu(CH_3CN)_2BF_4$, $AgNO_3$, $PtCl_2$, $NiBr_2$, $PdBr_2$), and the type $(CO)_3Mo[^iPr_2NPO]_5PdX_2$ (X = Cl, Br). These heterobimetallic products were obtained in moderate to high yields and have been characterized by elemental analyses and spectral data. In addition, the structures of $(CO)_4Mo[^iPr_2NPO]_4NiBr_2$ (21) and $(CO)_4Mo[^iPr_2NPO]_4$-$PdBr_2$ (25) have been determined by X-ray.

X-ray structural data from **14, 21, 25** and complexes **1** and **12** showed that the P_4O_4 core readjusted to the electronic demands of the new metal centers, and comparison of the FT-IR and NMR spectral properties of the conserved cis-$Mo(CO)_4P_2$ moiety also suggested a transmission of intracage influence between the heterometals.

The paramagnetic heterobimetallic cage complex $(CO)_4Mo$-

133

[^{i}Pr$_2$NPO]$_4$NiBr$_2$ reacted with Fe(CO)$_5$, leading to reduction of Ni(II) to Ni(0) and the carbonylation of the nickel vertex to form a diamagnetic cage complex (CO)$_4$Mo[^{i}Pr$_2$NPO]$_4$Ni(CO)$_2$ (**22**). Chlorination and iodination of complex **22** resulted in preferential halogenation at the nickel site.

Primary alcohols reacted with (CO)$_4$Mo[^{i}Pr$_2$NPO]$_4$ by nucleophilic attack, leading to cleavage of a single P-O-P bond and formation of a monocyclic product.

Use of the metallo-ligand (CO)$_4$Mo[^{i}Pr$_2$NPO]$_4$ as a nucleophile towards main group electrophiles like S, SnCl$_2$, SnCl$_4$ have been studied in preliminary work. Although the products could not been isolated at this time, the results were encouraging. Reactions of (CO)$_4$Mo[^{i}Pr$_2$NPO]$_4$ with main group reagents such as SiCl$_4$, MeSiCl$_3$ may also give very interesting results.

Triphenylphosphine and aluminum chlorides reacting together with phosphorus chloride can form a chlorophosphonium and a triphosphenium ion[77]:

PCl$_3$ + 3Ph$_3$P + 2AlCl$_3$ -------> [Ph$_3$P-P-PPh$_3^+$]AlCl$_3^-$ + Ph$_3$PCl$^+$AlCl$_4^-$
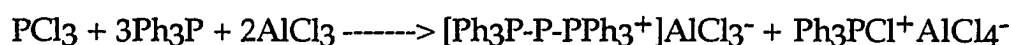
It may be possible to bond the two uncoordinated phosphorus atoms of complex **14** together the same way to form the analogous cage triphosphonium cation. This reaction was tried using anhydrous SnCl$_2$ with PCl$_3$. Though no product was isolated, the spectral results were encouraging.

Heterobimetallic cage products can be used in CO substitution and redox

134

reactions. Reduction using NaBH$_4$/MeOH may give hydride complexes; halogenation of (CO)$_4$Mo[^{i}Pr$_2$NPO]$_4$NiX$_2$ and (CO)$_n$Mo[^{i}Pr$_2$NPO]$_m$PdX$_2$ (n=3, 4; m=4, 5) cages may give Mo(II)/M(II) cage products.

** It is of interest to compare the P-Mo-P chelate bite angles of the cage complexes with other known diphosphine complexes. The bond angles for several cis-Mo(CO)$_4$L$_2$ complexes are presented in the following table:

cage complexes	P-Mo-P (°)	six-membered ring complexes	P-Mo-P (°)
cis-Mo(CO)$_8$[^{i}Pr$_2$NPO]$_4$	76.0 [a]	cis-Mo(CO)$_4$[(Ph$_2$PO)$_2$P(O)Me]	91.5 [b]
cis-Mo(CO)$_8$[PhPO]$_4$	77.7 [a]	cis-Mo(CO)$_4$[(Ph$_2$PO)$_2$P(O)R] (R=C6H4-P-OMe)	91.3 [b]
bis(diphosphino) Complexes	**P-Mo-P (°)**	**Five-membered ring complexes**	**P-Mo-P (°)**
cis-Mo(CO)$_4$(PMe$_3$)$_2$	97.5 [c]	cis-Mo(CO)$_4$[Me$_2$PCHFCF$_2$PMe$_2$]	82.0 [d]
cis-Mo(CO)$_4$(PBu$_3$)$_2$	99.3 [c]	cis-Mo(CO)$_4$(Ph$_2$P-P(O)Ph-OPPh$_2$)	82.3 [e]

As shown in the table, the P-Mo-P bond angles of the cage complexes are constained to be substantially less than the "normal" value of 90°. The angles are significantly smaller than for the monocyclic six-membered chelate ring complexes. They are even smaller than those for the five-membered chelate ring compounds. The effect of the polycyclic cage structure is therefore clearly observed.

a) Wong, E. H.; Turnbull, M. M.; Hutchinson, K. D.; Valdez, C.; Gabe, E. J.; Lee, F.L.; LePage, Y. *J. Am. Chem. Soc.* **1988**, 110, 8422.

b) Gray, G. M.; Zhang, Y. *J. Crystallogr. Spectrosc. Res.* **1993**, 23, 909.

c) Cotton, F. A.; Darensbourg, D. J.; Klein, S. *Inorg. Chem.* **1982**, 21, 2661.

d) Nowell, I. W.; Rettig, S.; Trotter, J. *J. Chem. Soc. Dalton Trans.* **1972**, 2381.

e) Wong, E. H.; Bradley, F. C.; Gabe, E. J. *J. Organomet. Chem.* **1983**, 244, 235.

Experimental section

General Procedure: All manipulations were carried out using standard Schlenck techniques under an atmosphere of prepurified nitrogen. Chemical reagents were commercial products and were used without further purification. Hexane and methylene chloride were distilled from CaH_2. Reagent grade toluene was dried over Na and freshly distilled before use. Norbornadiene, diisopropylamine, ethyl acetate, $CHCl_3$, MeOH, EtOH, $NaS_2CN(Me)_2$, and acetonitrile were purchased from Aldrich Chemical Co. and used without further purification. Alumina (Aldrich Chemical Co., Brockmann, I, neutral) was used as received. The cage complex $(CO)_4Mo(^iPr_2NPO)_4Mo(CO)_4$[8] (1) and $(CO)_4Mo(^iPr_2NPO)_4Mo(CO)_2I_2$[9] (12) were prepared according to previously reported methods. $Cr(CO)_4(NBD)$[78], $(AgNO_3)_2(NBD)$[79], $NiBr_2(DME)$[80] , $PdCl_2(C_6H_5CN)_2$[81], $PdBr_2(C_6H_5CN)_2$[82], $PtCl_2(NBD)$[83] and $Cu(CH_3CN)_4BF_4$[84] $Ni(COD)_2$[85] were prepared according to the literature. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on JEOL FX 90Q or Bruker AM360 FT-NMR spectrometers. ^1H and ^{13}C shifts were referenced to internal TMS, ^{31}P shifts were referenced to external 85% H_3PO_4. Spectra were obtained in $CDCl_3$ solution unless otherwise noted. Infrared spectra were recorded on a Perkin-Elmer 283B or Nicolet MX-1 FT-IR Spectrometer using KBr disks. Elemental analyses were performed at the University Instrumentation Center using a Perkin-Elmer 240b or Perkin-Elmer 2400 elemental analyzer.

136

X-ray crystal structures were determined by Dr. Arnold L. Rheingold and Beth E. Owens-Waltermire, Department of Chemistry, University of Delaware, Newark, Delaware.

(CO)$_4$Mo[^{i}Pr$_2$NPO]$_4$ (14) and (CO)$_4$Mo[^{i}Pr$_2$NPO]$_4$Mo(CO)$_2$(SCNMe$_2$)$_2$ (13): A 250 mL round bottomed flask with a magnetic stirbar was charged with 5.000 g of complex 12 (4.158 mM) and 1.252 g (8.400 mM) of sodium dimethyl-dithiocarbamate. A 100 mL amount of CH$_2$Cl$_2$ was added to dissolve the mixed-valent complex, resulting in a burgundy red suspension. After the mixture had been stirred for three hours at room temperature, a red suspension solution had formed. TLC (15% ethyl acetate in hexane, neutral alumina) revealed a colorless and a yellow component. Filtering yielded a red-purple solid identified as [(CO)$_2$Mo(S$_2$CNMe$_3$)$_2$] (IR, CHN analysis) and a red solution. Evaporation of the filtrate gave a red solid which was allowed to stand at room temperature for one week. This residue was then extracted three times with hexane to give an orange-yellow extract solution. After evaporation, the residue was chromatographed on an alumina column using 15% ethyl acetate in hexane as the eluant. The colorless complex 14 was the first to elute and isolated in 60% yield (1.950 g). Next to elute was the unstable orange complex 13 (0.870 g). Elemental analyses (calculated/observed for C$_{28}$H$_{56}$MoN$_4$O$_8$P$_4$ 14): C% 42.21/42.00 , H% 7.10/7.10, N% 7.03/6.91. Elemental analyses (calculated/observed for C$_{34}$H$_{68}$Mo$_2$N$_6$O$_8$P$_4$S$_2$ 13): C% 36.36/36.37, H% 5.76/6.20, N% 7.10/6.73.

(CO)$_4$Mo[^{i}Pr$_2$NPO]$_4$Cr(CO)$_4$ (16): A 100 mL round bottomed flask with a magnetic stirbar was charged with 1.5210 g of compound 14 (1.9091 mM) and

137

0.9176 g (3.8182 mM) Cr(CO)$_4$(NBD). Hepatane (40 mL) was added to the mixture resulting in a golden-yellow solution. The mixture was refluxed for three days; a yellow suspension was obtained. After evaporation of the volatiles under reduced pressure, a bright yellow residue was obtained. The residue was washed three times with 10 mL hexane to give a light yellow solid. This was chromatographed on alumina using 5% ethyl acetate in hexane as the eluant to give a colorless solution. This solution was evaporated to dryness to give a white solid complex **16** (0.5755 g, 35%). Elemental analyses (calculated/observed for C$_{32}$H$_{56}$MoN$_4$O$_{12}$P$_4$Cr **16**): C% 40.01/40.31, H% 5.88/6.06, N% 5.83/5.74.

(CO)$_4$Mo[^{i}Pr$_2$NPO]$_4$Fe(CO)$_3$(17): A 100 mL round bottomed flask with a magnetic stirbar was charged with 2.83 g of compound **14** (3.55 mM) and 1.75 g (9.59 mM) Fe$_2$(CO)$_9$. Hexane (60 mL) was added and the mixture was stirred under N$_2$ in reflux for 39 hours. A black green residue was obtained when the mixture was dried under reduced pressure. The residue was chromatographed on an alumina column using 2% ethyl acetate in hexane eluant to give 0.9510 g (28%) of **17** as a white solid . Elemental analyses (calculated/observed for C$_{31}$H$_{56}$MoN$_4$O$_{11}$P$_4$Fe C3): C% 39.76/39.50 , H% 6.03/6.30, N% 5.98/6.04.

(CO)$_4$Mo[^{i}Pr$_2$NPO]$_4$Cu(CH$_3$CN)$_2$(BF$_4$) (18): A 50 mL round bottomed flask with a magnetic stirbar was charged with 0.1170 g of compound **14** (0.1468 mM) and 0.0231 g (0.0734 mM) Cu(CH$_3$CN)$_4$(BF$_4$). Hexane (8 mL) and CH$_2$Cl$_2$ (4 mL) were added to the mixture resulting in a colorless solution. The mixture was stirred under N$_2$ in refluxing solvent for one hour. After

138

evaporation of most of the CH_2Cl_2, the reaction suspension was refluxed for another 3 hours. Filtration gave a white solid, which was washed with hexane and dried to give 0.0720 g (95.3% based on Cu) of **18**. Elemental analyses (calculated/observed for $C_{32}H_{62}MoN_6O_8P_4Cu$ C2): C% 37.35/37.10, H% 6.07/6.16, N% 8.16/7.55.

$(CO)_4Mo[^iPr_2NPO]_4AgNO_3$ (19): A 50 mL round bottomed flask with a magnetic stirbar was charged with 0.4400 g of compound **14** (0. 5522 mM) and 0.0592 g $NBD(AgNO_3)_2$ (0.276 mM Ag) and 20 mL hexane. The white suspension solution was stirred at room temperature in the absence of light. After one hour, the white suspension was filtered and the solid washed with hexane and dried to give 0.143 g (54%) of complex **19**. Due to the instability of the product, no satisfactory elemental analyses were obtained.

$(CO)_4Mo[^iPr_2NPO]_4PtCl_2(20)$: A 50 mL round bottomed flask with a stirbar was charged with 0.3059 g of compound **14** (0.3839 mM) and 0.1375 g (0.3839 mM) $PtCl_2(NBD)$. Toluene (10 mL) was added to the mixture resulting in a suspension [$PtCl_2(NBD)$ was not very soluble in toluene]. The suspension was stirred at 60 °C for 4 hours. After cooling and filtration, a white solid and a clear light yellow filtrate were obtained. The solid was washed with toluene, then with hexane, and dried to give 0.3585 g (88%) of complex **20**. Workup of the light yellow solution gave more complex **20** (0.0490 g, 12%). Elemental analyses (calculated/observed for $C_{28}H_{56}Mo-N_4O_8P_4PtCl_2$): C% 31.65/31.94, H% 5.31/5.45, N% 5.27/5.36.

$(CO)_4Mo[^iPr_2NPO]_4NiBr_2(21)$: A 50 mL round bottomed flask with a

139

magnetic stirbar was charged with 1.20 g of compound **14** (1.51 mM) and 0.40 g (1.51 mM) NiBr$_2$(DME). Hexane (10 mL) was added to the mixture. The mixture was refluxed for 5 hours to give a brown-red suspension. This was concentrated to about 5 mL, and the red crystalline precipitate was filtered, washed twice with 5 mL of cold hexane, and dried to give 1.23 g. (80%) of complex **21**. X-ray-quality crystals were grown from a hot hexane solution. Elemental analyses [calculated/observed for C$_{28}$H$_{56}$MoN$_4$O$_8$P$_4$-NiBr$_2$·0.7(hexane)]: C% 35.95/35.92, H% 6.17/6.24, N% 5.21/5.31.

(CO)$_4$Mo[^{i}Pr$_2$NPO]$_4$Ni(CO)$_2$ (**22**): A 50 mL round bottomed flask with a magnetic stirbar was charged with 0.64 g of compound **21** (0.63 mM); 10 mL hexane and 0.5 mL of Fe(CO)$_5$ were added to give a red suspension. This mixture was stirred in refluxing hexane for one hour to give a yellow suspension. Upon cooling the suspension to room temperature, a light yellow clear solution with a yellow precipitate was formed. The top clear solution was removed by pipette to another flask and evaporated to dryness to give a light yellow residue. The residue was chromatographed on alumina using 5% ethyl acetate in hexane to afford a clear colorless solution from which a white complex **22** was obtained (0.49 g, 85%). Elemental analyses (calculated/observed for C$_{30}$H$_{56}$MoN$_4$O$_{10}$P$_4$Ni): C% 39.53/39.40 , H% 6.19/6.23, N% 6.15/6.05.

(CO)$_4$Mo[^{i}Pr$_2$NPO]$_4$NiCl$_2$(**23**): A 50 mL round bottomed flask with a stirbar was charged with 0.320 g of complex **22** (0.3511 mM) and 20.0 mL of hexane. The solution was cooled to -78°C, and a solution of 0.50 mL of SO$_2$Cl$_2$ in 40.0 mL of CH$_2$Cl$_2$ was made; 3.18 mL of this was added dropwise

140

to the hexane solution of **22** (Ni : Cl$_2$ = 1 : 1.1). The colorless solution immediately changed to yellow, and within 5 minutes, an orange suspension then formed. The reaction mixture was concentrated to half its volume. The top clear yellow solution was removed by a pipet, and dried to give 0.2730 g (84%) of complex **23** as an orange solid. Elemental Analyses (calculated/observed for C$_{28}$H$_{56}$N$_4$P$_4$MoNiO$_8$Cl$_2$): C% 36.31/36.54, H% 6.09/6.50, N% 6.05/5.54.

Synthesis of (CO)$_4$Mo[^{i}Pr$_2$NPO]$_4$Ni(CO)$_2$ from (CO)$_4$Mo[^{i}Pr$_2$NPO]$_4$-NiCl$_2$: A 50 mL round bottomed flask with a magnetic stirbar was charged with 0.2040 g of complex **23**, 20.0 mL of hexane and 0.5 mL of Fe(CO)$_5$. The solution was refluxed for 1 hour to give a yellow suspension. After filtration and evaporation of the volatiles from the filtrate, the residue was chromatographed on alumina using 5% ethyl acetate in hexane to give a colorless solution from which white solid complex **22** was obtained (0.1650 g, 80%).

(CO)$_4$Mo[^{i}Pr$_2$NPO]$_4$NiI$_2$(24) : A 25 mL round bottomed flask with a magnetic stirbar was charged with 0.1542 g of complex **22** (0.1691 mM) and 5 mL of CH$_2$Cl$_2$. A solution of 0.472 g (0.186 mM) of iodine in 2.0 mL of CH$_2$Cl$_2$ was added and the mixture was stirred at room temperature for 2 hours to give a deep red solution. This was evaporated to dryness under reduced pressure to give a dark red residue. The solid was washed with 2x1mL of CH$_3$CN and dried to give 0.1425 g (76%) of complex **24**. Satisfactory elemental analyses were not obtained due to its instability.

141

Synthesis of (CO)4Mo[^{i}Pr2NPO]4Ni(CO)2 (22) from (CO)4Mo-[^{i}Pr2NPO]4NiI2 (24): A 25 mL round bottomed flask with a magnetic stirbar was charged with 0.1425 g of complex **24**, 8.0 mL of hexane and 0.5 mL of Fe(CO)5. The mixture was stirred at room temperature for 2 hour to give a yellow suspension. A yellow residue was obtained after filtration and evaporation of the volatiles from the filtrate. The solid was chromatographed on alumina using 5% ethyl acetate in hexane to give a colorless solution from which white solid complex **22** was obtained (0.0935 g, 80%).

(CO)4Mo[^{i}Pr2NPO]4PdBr2 (25): A 50 mL round bottomed flask with a magnetic stirbar was charged with 0.4270 g of complex **14** (0.5359 mM) and 0.2513 g PdBr2(C6H5CN)2 (0.4872 mM, P's : Pd = 4.4 : 1). Toluene (20 mL) was added to the mixture and the resulting solution was stirred at 70°C for 16 hour. After cooling and removal of the volatiles, a yellow-brown residue solid was obtained. This was washed three times with 5 mL hexane to give 0.4490 g of a greenish yellow solid. The solid was dissolve in 5ml of CHCl3 , the solution filtered, and the clear yellow filtrate evaporated to give 0.4320 g of complex **25** (83% based on Pd). X-ray-quality crystals were obtained upon cooling and slow evaporation of a hot toluene solution. Elemental Analyses (calculated/observed for C28H56N4P4MoPdO8Br2): C% 31.64/31.71, H% 5.31/5.32, N% 5.27/5.18.

(CO)3Mo[^{i}Pr2NPO]5PdCl2 (26): A 50 mL round bottomed flask with a stirbar was charged with 0.7120 g of complex **14** (0.8936 mM) and 0.2741 g PdCl2(C6H5CN)2 (P's : Pd = 5 : 1). Toluene (20 mL) was added to the mixture

142

and the resulting solution was stirred at 70 °C for 66 hour. The red-brown suspension was cooled to room temperature and filtered to give a gray yellow solid (0.4210 g) and a red-brown solution. The solid was dissolved in 8 mL of CHCl3, the solution filtered, and the clear yellow filtrate allowed to evaporate slowly. A yellow needle crystalline solid was obtained. The solid was collected by filtration and dried to give 0.3452 g of complex **26**. The red-brown solution was evaporated to dryness and the residue washed three times with 2 mL of acetone to give a yellow solid which was a 2:1 mixture of **26** and complex **1** according to the 31P NMR spectrum. This mixture was washed three times with 1 mL portions of hexane to give additional **26**, for a combined yield of 0.504 g (52% based on Pd). Elemental Analyses (calculated/observed for $C_{33}H_{70}N_5P_5MoPdO_8Cl_2$): C% 36.26/36.27, H% 6.41/6.48, N% 6.46/6.10.

(CO)3Mo[^{i}Pr2NPO]5PdBr2 (**27**): A 50 mL round bottomed flask with a magnetic stirbar was charged with 0.6840 g of complex **14** (0.8585 mM) and 0.3239 g $PdBr_2(C_6H_5CN)_2$ (P's : Pd = 5 : 1). Toluene (20 mL) was added to the mixture and the resulting solution was stirred at 70 °C for 72 hour. The yellow-brown suspension was cooled to room temperature and filtered to give a graynish yellow solid and a clear brown solution. The solid was dissolve in 4 mL of CHCl3, the solution filtered, and the filtrate allowed to evaporate slowly. A yellow crystalline complex **27** formed which was collected and dried (0.3598 g). The brown solution was evaporated to give a brown residue, which was found to be a 1 : 2 : 4 mixture of complexes (CO)4Mo[^{i}Pr2NPO]4MO(CO)4, **25**, and **27** according to the ^{31}P NMR. The residue was washed twice with 5 mL of a 1:1 mixture of acetone and hexane,

143

and the resulting solution was stirred at 70 °C for 66 hour. The red-brown suspension was cooled to room temperature and filtered to give a gray yellow solid (0.4210 g) and a red-brown solution. The solid was dissolved in 8 mL of CHCl3, the solution filtered, and the clear yellow filtrate allowed to evaporate slowly. A yellow needle crystalline solid was obtained. The solid was collected by filtration and dried to give 0.3452 g of complex **26**. The red-brown solution was evaporated to dryness and the residue washed three times with 2 mL of acetone to give a yellow solid which was a 2:1 mixture of **26** and complex **1** according to the 31P NMR spectrum. This mixture was washed three times with 1 mL portions of hexane to give additional **26**, for a combined yield of 0.504 g (52% based on Pd). Elemental Analyses (calculated/observed for $C_{33}H_{70}N_5P_5MoPdO_8Cl_2$): C% 36.26/36.27, H% 6.41/6.48, N% 6.46/6.10.

(CO)3Mo[^{i}Pr2NPO]5PdBr2 (**27**): A 50 mL round bottomed flask with a magnetic stirbar was charged with 0.6840 g of complex **14** (0.8585 mM) and 0.3239 g $PdBr_2(C_6H_5CN)_2$ (P's : Pd = 5 : 1). Toluene (20 mL) was added to the mixture and the resulting solution was stirred at 70 °C for 72 hour. The yellow-brown suspension was cooled to room temperature and filtered to give a graynish yellow solid and a clear brown solution. The solid was dissolve in 4 mL of CHCl3, the solution filtered, and the filtrate allowed to evaporate slowly. A yellow crystalline complex **27** formed which was collected and dried (0.3598 g). The brown solution was evaporated to give a brown residue, which was found to be a 1 : 2 : 4 mixture of complexes (CO)4Mo[^{i}Pr2NPO]4MO(CO)4, **25**, and **27** according to the ^{31}P NMR. The residue was washed twice with 5 mL of a 1:1 mixture of acetone and hexane,

143

followed by 2x2 mL hexane to give 0.1244 g of **27**. The combined yield was 48% based on Pd. Elemental Analyses (calculated/observed for $C_{33}H_{70}N_5P_5MoPdO_8Br_2$): C% 33.53/33.88, H% 5.97/6.33, N% 5.93/5.83.

$(CO)_4Mo[(^iPr_2NPO)_2(^iPr_2NPOMe)\{^iPr_2NP(O)H\}]$ (28):

Method A [From complex **12** $(CO)_4Mo[^iPr_2NPO]_4Mo(CO)_2I_2$]: A 50 mL round bottomed flask with a stirbar was charged with 0.4025 g of complex **12** (0.3347 mM) and 0.0959 g (0.669 mM) sodium dimerhyldithiocarbamate. CH_2Cl_2 (20 mL) was added to dissolve **12**; the ligand was suspended in the burgundy red mixture. Addition of 10 mL of MeOH gave a clear red solution, which was stirred for three hours. The resulted red suspention was filtered to remove $(CO)_2Mo(S_2CNMe_2)_2$ (0.0834 g) and the filtrate was evaporated to give a brown red residue. This was extracted with 20 mL of hexane, and the extract was evaporated to give a white solid complex **28** (0.2104 g, 70%).

Method B [From complex **14** $(CO)_4Mo[iPr2NPO]_4$]: A 50 mL round bottomed flask with a magnetic stirbar was charged with 0.3390 g of complex **14** (0.4255 mM). MeOH (6 mL) and 4 mL of hexane were added into the flask to give a clear colorless solution. Which was stirred under refluxing for 9 hours to give a clear light yellow solution. After evaporation of the solution to dryness, a very light yellow solid was obtained. A white suspension was formed after adding 5 mL of MeOH to the filtrate, which was filtered to give a white solid. This was washed twice with 1 mL portions of cold hexane and dried to yield 0.2644 g (75%) of complex **28**. X-ray quality flake crystals were obtained by recrystallization from hot hexane. Elemental analysis (calculated/observed for $C_{29}H_{60}O_9P_4N_4Mo$): C% 42.02/41.74, H% 7.31/7.62, N% 6.76/6.77.

144

(CO)$_4$Mo[(^{i}Pr$_2$NPO)$_2$(^{i}Pr$_2$NPOEt)$\{^i$Pr$_2$NP(O)H$\}$] **(29):** A 25 mL round bottomed flask with a magnetic stirbar was charged with 0.6950 g of complex **14** (0.8723 mM), 10.0 mL of absolute EtOH and 4.0 mL of hexane. After being refluxed for 24 hours, the light orange solution was cooled and concentrated to about 5 mL to give a suspension which was filtered to give a white solid (0.100 g, identified as unreacted **14**) and a light orange filtrate. Addition of 4 mL of EtOH to the light orange filtrate led to the precipitation of a white solid which was filtered, washed twice with 2 mL portions of EtOH and dried to give 0.4521 g (72% based on reacted **14**) of complex **29**. Elemental Analyses (calculated/observed for C$_{30}$H$_{62}$N$_4$P$_4$MoO$_9$): C% 42.75/42.59, H% 7.41/7.64, N% 6.65/6.51.

LIST OF REFERENCES

[1] See for examples: (a) Ziegler, K.; Holzkamp, H.; Breil, H.; Martin, H. *Angew. Chem.* **1955**, 67, 541. (b) Natta, G.; *Polymer Sci.* **1955**, 16, 143. (c) Young, J. F.; Osborn, J. A.; Jardine, F. H.; Wilkinson, G. *J. Chem. Soc., Chem. Comm.* **1965**, 131. (d) Kagan, H. B.; Dang, T. P. *J. Am. Chem. Soc.* **1972**, 94, 6429.

[2] See for examples: (a) DuBois, D. L.; Meek, D. W. *Inorg. Chim. Acta* **1976**, 19, L29. (b) Niewahner, J.; Meek, D. W. *Inorg. Chim. Acta* **1982**, 64, L123. (c) Letts, J. B.; Mazanec, T. J.; Meek, D. W. *J. Am. Chem. Soc.* **1982**, 104, 3898. (d) Hughes, O. R.; Young, D. A. *J. Am. Chem. Soc.* **1982**, 103, 6636. (e) Jia, G. C.; Meek, D. W. *Inorg. Chem.* **1991**, 30, 1953; *Organometallics*, **1991**, 10, 1444.

[3] Balch, A. L. Homogeneous Catalysis with Metal Phosphine Complexes; Plenum Press: New York, **1983**, p.167.

[4] Wong, E. H.; Turnbull, M. M.; Gabe, E. J.; Lee, F. L.; Le Page, Y. J. *Chem. Soc., Chem. Commun.* **1983**, 776.

[5] Nifant'ev, E. E.; Koroteev, M. P.; Ivanov, N. L.; Gudkova, I. P.; Predvoditelev, D. A. *Dokl. Chem.. (Engl. Transl.)* **1967**, 173, 398.

[6] Niecke, E.; Zorn, H.; Krebs, B.;Henkel, G. *Angew. Chem., Int. Ed. Engl.* **1980**, 19, 709.

[7] Chasar, D. W.; Fackler, J. P.; Mazany, A. M.; Komoroski,R. A.; Kroenke, W. J. *J. Am. Chem. Soc.* **1986**, 108, 5956; *J. Am. Chem. Soc.* **1987**, 109, 5690.

[8] Wong, E. H.; Turnbull, M. M.; Hutchinson, K. D.; Valdez, C.; Gabe, E. J.; Lee, F.L.; LePage, Y. *J. Am. Chem. Soc.* **1988**, 110, 8422.

[9] Turnbull, M. M.; Valdez, C.; Wong, E. H.; Gabe, E. J.; Lee, F. L. *Inorg. Chem.* **1992**, 31, 208.

[10] Wong, E. H.; Prasad, L.; Gabe, E. J.; Bradley, F. C. *J. Organomet. Chem.* **1982**, 236, 321.

[11] Wong, E. H.; Gabe, E. J.; Charland, J. P. *J. Chem. Soc., Chem. Commun.* **1988**, 1632.

[12] Wong, E. H.; Gabe, E. J.; Lee, F. L. *J. Chem. Soc., Chem. Commun.* **1989**, 1236.

[13] Wong, E. H.; Sun, X. Y.; Gabe, E. J.; Lee, F. L.; Charland, J. P.

146

Organometallics, **1991**, 10, 3010.

[14] Kepert, D. L. <u>Inorganic Stereochemistry</u>; Springer Verlag: New York, **1982**, p.130.

[15] Colton, R.; Kevekordes, J. *Aust. J. Chem.* **1982,** 35, 895.

[16] Colton, R. *Coord. Chem. Rev.* **1971,** 6, 269.

[17] Bradley, F. C.; Wong, E. H.; Gabe, E. J.; Lee, F. L.; LePage, Y. *Polyhedron* **1987,** 5, 1103.

[18] Colton, R. *Aust. J. Chem.* **1968,** 21, 15, and **1968,** 21, 1427.

[19] Abrahamson, H. B.; Freeman, M. L.; Hussain, M. B.; Van der Helm, D. *Inorg. Chem.* **1984,** 23, 2286.

[20] See for example: (a) Howell, J. A. S.; Burkinshaw, P. M. *Chem, Rev .* **1983,** 83, 557. (b) Atwood, J. D.; Wovkulich, M. J.; Sonnenberger, D. C. *Acc. Chem. Res .* **1983,** 16, 350. (c) Poliakoff, M.; Weitz, E. *Adv. Organomet. Chem .* **1986,** 25, 277.

[21] See for example: (a) Dobson, G. R.; Houk, L. W. *Inorg. Chim. Acta* **1967,** 1, 287. (b) Faber, G. C.; Dobson, G. R. *Inorg. Chim. Acta* **1968,** 2, 479. (c) Dobson, G. R.; Rettenmaier, A. J. *Inorg. Chim. Acta* **1972,** 6, 507. (d) Dobson, G. R.; Asali, K. A.; Marshell, J. L.; McDaniel, C. R., Jr. *J. Am. Chem. Soc.* **1977,** 99, 8100. (e) Dobson, G. R.; Asali, K. A. *Inorg. Chem..* **1981,** 20, 3563. (f) Isaacs, E. E.; Graham, W. A. G. *Inorg. Chem.* **1975,** 14, 2560. (g) Cohen, M. A.; Brown, T. L. *Inorg. Chem.* **1976,** 15, 1417.

[22] Gorenstein, D. G. <u>P-31 NMR: Principles and applications</u> ; Academic Press: Orlando, **1984,** Chapter 1, Chapter2.

[23] Verkade, J. G.; Quin, L. D. <u>P-31 NMR Spectroscopy in Stereochemical Analysis</u>; VCH: New York, **1987,** Chapter 8.

[24] Verkade, J. G.; Quin, L. D. <u>P-31 NMR Spectroscopy in Stereochemical Analysis</u>; VCH: New York, **1987,** Chapter 16, Chapter 17.

[25] Pregosin, P. S.; Kunz, R. W. <u>31P and 13C NMR of Transition Metal Phosphine Complexes</u>; Springer-Verlag: Berlin, 1979. p. 46, pp 115-123.

[26] (a) Darensbourg, M.Y.; Darensbourg, D.J. *J.Chem. Educ.,* **1970,** 47, 33. (b) Cotton, F. A. <u>Chemical Application of Group Theory</u> , 2nd Edition; Wiley-Interscience: New York, **1971.**

[27] Nassimbeni, L. R. *Inorg. Nucl. Chem. Lett .* **1971,** 7, 909.

147

[28] Mais, R. H. B.; Owston, P. G.; Thompson, D. T. *J. Chem. Soc. A* **1967**, 1735.

[29] Adams, R. D.; Collins, D. M.; Cotton, F. A. *Inorg. Chem.* **1974**, 13, 1086.

[30] Klingert, B.; Werner, H. *J. Organomet. Chem.* **1983**, 252, C47.

[31] Newton, M. G.; King, R. B.; Chang, M.: Gimeno, J. *J. Am. Chem. Soc.* **1978**, 100, 1632.

[32] Corbridge, D. E. C. Phosphorus: An Outline of its Chemistry, Biochemistry, and Technology, 3rd ed.; Elsevier: Amsterdam, **1985**; Chapter1.

[33] Petersen, J. L.; Stewart, R. P. *Inorg. Chem.* **1980**, 19, 186. Carty, A. J.; Maclaughlin, S. A.; Taylor, N. J. *J. Organomet. Chem.* **1981**, 204, C27.

[34] Pregosin, P. S.; Kunz, R. W. 31P and 13C NMR of Transition Metal Phosphine Complexes; Springer-Verlag: Berlin, **1979**, pp 49-50.

[35] Abraham, R. J.; Fisher, J.; Loftus, P. Introduction to NMR Spectroscopy; John Wiley & Sons: New York, **1988**, Chapter 6.

[36] Tolman, C. A. *Chem. Rev.* **1977**, 77, 313.

[37] Cotton, F. A. *Inorg, Chem.* **1964**, 3, 702.

[38] Tolman, C. A. *J. Am. Chem. Soc.* **1970**, 92, 2956.

[39] Tolman, C. A. *J. Am. Chem. Soc.* **1970**, 92, 2953.

[40] Bartik, T.; Himmler, T.; Schulte, H. G.; Seevogel, K. *J. Organomet. Chem.* **1984**, 272, 29.

[41] Gilmore, C. J. *J. Appl. Cryst.* **1984**, 17, 42.

[42] (a) Bruce, M. I. *J. Organomet. Chem.* **1982**, 242, 147. *J. Organomet. Chem.* **1985**, 283, 339. (b) Geoffroy, G. L.; Roberts, D. A. in *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., E. W., Eds.; Pergamon: Oxford, England, **1982**; vol.6, Chapter 40. (c) Rosseenberg, S.; Whittle, R. R.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1984**, 106, 5934.

[43] See for examples: (a) Casey, C. P.; Bullock, R. M.; Nief, F. *J. Am. Chem. Soc.* **1983**, 105, 7574. (b) Casey, C. P.; Jordan, R. F.; Rheingold A. L.*J. Am. Chem. Soc.* **1983**, 105. 665. (c) Casey, C. P.; Palermo, R. E.; Jordan, R. F.; Rheingold A. L. *J. Am. Chem. Soc.* **1985**, 107, 4597. (d) Casey, C. P.; Palermo, R. E. *J. Am. Chem. Soc.* **1986**, 108, 549. (e) Casey, C. P.; Jordan, R. F.; Rheingold A.

L. *Organometallixcs* **1984, 3,** 504. (f) Gelmini, L.; Stephan, D. W. *Inorg. Chem.* **1986, 25,** 1222. (g) Ortiz, J. V. *J. Am. Chem. Soc.* **1986, 108,** 550. (h) Schumann, H.; Albrecht, I.; Hahn, E. *Angew. Chem. , Int. Ed. Engl.* **1985, 11,** 985.

[44] Casey, C. P.; Bullock, R. M.; Nief, F. *J. Am. Chem. Soc.* **1983, 105,** 7574.

[45] Farr, J. P.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **1980. 102,** 6654.

[46] Delavaux, B.; Chaudret, B.; Dahan, F.; Poilblanc, R. *Organometallics* **1985, 4,** 935.

[47] Regragui, R.; Dixneuf, P. H.; Talor, N. J.; Carty, A. J. *Organometallics* **1984, 3,** 814.

[48] Hutchinson, K. D.; M. S. Thesis, University of New Hampshire, Durham, New Hampshire, **1987.**

[49] Sun, X.; Ph. D. Thesis, University of New Hampshire, Durham, New Hampshire, **1993.**

[50] Yang, H. Y.; Wong, E. H.; Rheingold, A. L.; Owens-Waltermire, B. E. *J. Chem. Soc., Chem. Commun.* **1993,** 35.

[51] Broomhead, J. A.; Young, C. G. *Aust. J. Chem.* **1982, 35,** p.277.

[52] Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980, 102,** 6568.

[53] Corbridge, D. E. C. Phosphorus, An Outline of its Chemistry, Biochemistry, and Technology, 3rd edn.; Elsevier: Amsterdam, **1985,** pp.37-40.

[54] Purcell, K. F.; Kotz, J. C. Inorganic chemistry; W. B. Saunders Co.: Philadelphia, **1977,** p.865.

[55] (a) Casey, C. P.; Whiteker, G. T.; Campana, C. F.; Powell, D. R. *Inorg. Chem.* **1990, 29,** 3376. (b) Akhtar, M.; Ellis, P. D.; Macdiarmid, A. G.; Odom, J. D. *Inorg. Chem.* **1972, 11,** 2917.

[56] (a) Verkade, J. G.; Quin, L. D. P-31 NMR Spectroscopy in Sterochemical Analysis; VCH: New York, **1987,** p.441. (b) Johnson, D. K.; Pregosin, P. S.; Venanzi, L. M. *Helv. Chim. Acta.* **1976, 59,** 2691.

[57] Wilkinson, G.; Gillard, R. D.; McCleverty, J. A. Comprehensive Coordination Chemistry; Pergamon Press: New York, **1987,** Vol. 2, p.264.

[58] (a) Mutterties, E. L.; Alegranti, C. W. *J. Am. Chem. Soc.,* **1972, 94,** 6386. (b)Goel, R. G.; Pilon, P. *Inorg. Chem.* **1978, 17,** 2876. (c) Socol, S. M.; Jacobson,

R. A.; Verkade, J. G. *Inorg. Chem.*, **1984**, 23, 88.

[59] Pidcock, A.; Waterhouse, C. R., *J. Chem. Soc. A,* **1970**, 2087.

[60] Bodner, G. M. *Inorg. Chem.*, **1975**, 14, 1932.

[61] Ogilvie, F. B.; Jenkins, J. M.; Verkade J. G. *J. Am. Chem. Soc.,* **1970**, 92, 1916.

[62] Bodner, G. M. Coord. Chem. Rev., 1972, 9, 1. *Inorg. Chem.* **1975**, 14, 1932.

[63]Verkade, J. G.; Quin, L. D. P-31 NMR Spectroscopy in Sterochemical Analysis; VCH: New York,**1987**, Chapter 14.

[64] Cotton, F. A.; Wilkinson, G. Advanced Inorganic Chemistry, 5th edn.; Wiley Interscience: New York, **1988**, pp. 746-748.

[65] Wilkinson, G.; Stone, F. G. A.; Abel, E. W. Comprehensive Organometallic Chemistry; Pergamom Press: New York, **1982**, V. 6, p. 234.

[66] Corbridge, D. E. C. The structural Chemistry of Phosphorus; Elsevier: New York, **1974**, p. 300.

[67] Corbridge, D. E. C. Phosphorus, an outline of its Chemistry, Biochemistry, and Technology, 3rd edn.; Elsevier: Amsterdam, **1985**, p.545.

[68] Corbridge, D. E. C. The Structural Chemistry of Phosphorus; Elsevier: New York, **1974**, p. 65.

[69] Corbridge, D. E. C. The Structural Chemistry of Phosphorus; Elsevier: New York, **1974**, p. 215, p. 301.

[70] Barton, D.; Ollis, W. D. Comprehensive Organic Chemistry, The Synthesis and reactions of Organic Compounds; Pergamon Press: New York, **1979**, p. 1146.

[71] Douglas, B. E.; McDaniel, D. H.; Alexander, J. J. Concepts and models of Inorganic Chemistry, 3rd edn.; John Wiley & Sons: New York, 1994, p. 562.

[72] Douglas, B. E.; McDaniel, D. H.; Alexander, J. J. Concepts and models of Inorganic Chemistry, 3rd edn.; John Wiley & Sons: New York, **1994**, p. 600.

[73] Bodnor, G. M. *Inorg. Chem.* **1974**, 13, 1335.

[74] Braterman, P.S.; Milne, D, W.; Randall, E. W.; Rosenberg, E. *J. Chem. Soc., Dalton* , **1973**, 1027.

[75] Gansow, O. A.; Kimura, B. Y.; Dobson, G. R.; Brown, R. A. *J. Amer. Chem. Soc.*, **1971**, 93, 5922; Gansow, O. A.; Schexnayder, D. A.; Kimura, B. Y. *J. Amer. Chem. Soc.*, **1972**, 94, 3406.

[76] (a) Bodner, G. M.; Todd, L. J. *Inorg. Chem.*, **1974**, 13, 360. (b) Bodner, G. M. *Inorg. Chem.*, **1974**, 13, 2563, (c) Bodner, G. M. *Inorg. Chem.*, **1975**, 14, 1932, and 2694; (d) Bodner, G. M.; May, M. P.; McKinney, L.E. *Inorg. C he m.*, **1980**, 19, 1951.

[77] (a) Schmidpeter A.; Lochschmidt S.; Sheldrick W. S. *Angew. Chem. int. Ed. Engl.* **1985**, 24, 226. (b) Lochschmidt S.; Schmidpeter A. *Z. Naturfor.* **1985**, 40B, 765.

[78] King, R. B. Organometallic Synthesis; Academic Press: New York, **1965**, Vol. 1, p.122.

[79] Abel, E. W.; Bennett, M. A.; Wilkinson, G. J. *J. Chem. Soc.* , **1959**, 3178.

[80] Ward, L. G. L. *Inorg. Synth.* , **1972**, 13, 154.

[81] Doyle, J. R.; Slade, P. E.; Jonassen, H. B., *Inorg. Synth* .,**1960**, 6, 218.

[82] McGindle, R.; Alyea, E. C.; Ferguson, G.; Dias, S. A.; McAlees, J. *J. Chem. Soc.; Dalton Trans* ., **1980**, 1, 137.

[83] Drew, D.; Doyle, J. R. *Inorg. Synth.*, **990**, 28, 346.

[84] Kubas, G. J. *Inorg. Synth.* **1990**, 28, 68.

[85] Belderrain, T. R., Knight, D. A.; Irvine, D. J.; Paneque, M.; Poveda, M. L.; Carmona, E. *J. Chem. Soc. Dalton* , **1992**, 1491.

151

APPENDICES

A. COMPOUND NUMBER ASSIGNMENTS

1 $(CO)_4Mo[^iPr_2NPO]_4Mo(CO)_4$

5 $(CO)_4Mo[^iPr_2NPO]_4Mo(CO)_3P(OMe)_3$

6 $(CO)_3P(OMe)_3Mo[^iPr_2NPO]_4Mo(CO)_3P(OMe)_3$

8 $(CO)_4Mo[^iPr_2NPO]_4Mo(CO)_3(PPh_2H)$

9 $(CO)_3(PPh_2H)Mo[^iPr_2NPO]_4Mo(CO)_3(PPh_2H)$
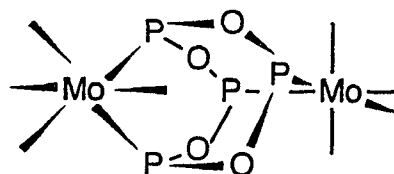
2 $(CO)_3Mo[^iPr_2NPO]_4Mo(CO)_2PPh_3$

3 $(CO)_3Mo[^iPr_2NPO]_4Mo(CO)_2PPh_2Me$

4 $(CO)_3Mo[^iPr_2NPO]_4Mo(CO)_3PPh_2H$

7 $(CO)_3Mo[^iPr_2NPO]_4Mo(CO)_2P(OMe)_3$

10 $(CO)_3Mo[^iPr_2NPO]_4Mo(CO)_2Py$

11 $(CO)_3Mo[^iPr_2NPO]_4Mo(CO)_3$

153

12 $(CO)_4Mo[^iPr_2NPO]_4Mo(CO)_2I_2$

13 $(CO)_4Mo[^iPr_2NPO]_4Mo(CO)_2(S_2CNMe)_2$

14 $(CO)_4Mo[^iPr_2NPO]_4$

16 $(CO)_4Mo[^iPr_2NPO]_4Cr(CO)_4$
17 $(CO)_4Mo[^iPr_2NPO]_4Fe(CO)_3$
18 $(CO)_4Mo[^iPr_2NPO]_4Cu(CH_3CN)_2BF_4$
19 $(CO)_4Mo[^iPr_2NPO]_4AgNO_3$
20 $(CO)_4Mo[^iPr_2NPO]_4PtCl_2$
21 $(CO)_4Mo[^iPr_2NPO]_4NiBr_2$
22 $(CO)_4Mo[^iPr_2NPO]_4Ni(CO)_2$
23 $(CO)_4Mo[^iPr_2NPO]_4NiCl_2$
24 $(CO)_4Mo[^iPr_2NPO]_4NiI_2$
25 $(CO)_4Mo[^iPr_2NPO]_4PdBr_2$

154

26 (CO)$_3$Mo[^{i}Pr$_2$NPO]$_5$PdCl$_2$

27 (CO)$_3$Mo[^{i}Pr$_2$NPO]$_5$PdBr$_2$

28 (CO)$_4$Mo[^{i}Pr$_2$NPO]$_2$(^{i}Pr$_2$NPOMe){^{i}Pr$_2$NP(O)H}

29 (CO)$_4$Mo[^{i}Pr$_2$NPO]$_2$(^{i}Pr$_2$NPOEt){^{i}Pr$_2$NP(O)H}

R=^{i}Pr$_2$N, R'=Me, Et

155

B. SELECTED SPECTRA

IR Spectrum of $(CO)_3Mo[^iPr_2NPO]_4Mo(CO)_2(PPh_3)$

157

IR Spectrum of (CO)$_3$Mo[^{i}Pr$_2$NPO]$_4$Mo(CO)$_2$(PPh$_2$Me)

158

IR Spectrum of (CO)$_3$Mo[iPr$_2$NPO]$_4$Mo(CO)$_2$(PPh$_2$H)

159

IR Spectrum of $(CO)_3Mo[iPr_2NPO]_4Mo(CO)_2[P(OMe)_3]$

160

IR Spectrum of (CO)$_3$ [P(OMe)$_3$] Mo[^{i}Pr$_2$NPO]$_4$Mo(CO)$_3$ [P(OMe)$_3$]

161

IR Spectrum of $(CO)_4Mo[^iPr_2NPO]_4Mo(CO)_3(PPh_2H)$

162

IR Spectrum of $(CO)_3 (PPh_2H) Mo[iPr_2NPO]_4Mo(CO)_3(PPh_2H)$

163

IR Spectrum of (CO)₃Mo[iPr₂NPO]₄Mo(CO)₂Py

164

IR Spectrum of $(CO)_3Mo[iPr_2NPO]_4Mo(CO)_3$

165

^{1}H NMR Spectrum of (CO)$_3$Mo[^{i}Pr$_2$NPO]$_4$Mo(CO)$_2$(PPh$_3$)

166

31P{1H} NMR Spectrum of (CO)₃Mo[iPr₂NPO]₄Mo(CO)₂(PPh₂H)

31P{1H} NMR Spectrum of (CO)₃Mo[iPr₂NPO]₄Mo(CO)₂(PPh₂Me)

167

$^{31}P\{^1H\}$ NMR Spectrum of $(CO)_4Mo[^iPr_2NPO]_4Mo(CO)_3(PPh_2H)$

168

31P[1H] NMR Spectrum of (CO)$_3$(PPh$_2$H)Mo[iPr$_2$NPO]$_4$Mo(CO)$_3$(PPh$_2$H)

169

$^{31}P\{^1H\}$ NMR Spectrum of $(CO)_3Mo[iPr_2NPO]_4Mo(CO)_2P(OMe)_3$

170

$^{31}P\{^1H\}$ NMR Spectrum of $(CO)_3Mo[^iPr_2NPO]_4Mo(CO)_3$

171

IR Spectrum of Mo(CO)$_2$[S$_2$CNMe$_2$]$_2$

172

IR Spectrum of $(CO)_4Mo[^iPr_2NPO]_4Mo(CO)_2(S_2CNMe_2)_2$

173

IR Spectrum of (CO)₄Mo[ⁱPr₂NPO]₄

174

IR Spectrum of (CO)$_4$Mo[^{i}Pr$_2$NPO]$_4$Cr(CO)$_4$

175

IR Spectrum of $(CO)_4Mo[^iPr_2NPO]_4Fe(CO)_3$

176

IR Spectrum of $(CO)_4Mo[^iPr_2NPO]_4Cu(CH_3CN)_2BF_4$

177

IR Spectrum of $(CO)_4Mo[^iPr_2NPO]_4Ag(NO_3)$

178

IR Spectrum of $(CO)_4Mo[iPr_2NPO]_4PtCl_2$

179

IR Spectrum of $(CO)_4Mo[^iPr_2NPO]_4NiBr_2$

180

IR Spectrum of (CO)$_3$Mo[^{i}Pr$_2$NPO]$_5$Ni(CO)$_2$

181

IR Spectrum of (CO)$_4$Mo[^{i}Pr$_2$NPO]$_4$NiCl$_2$

182

IR Spectrum of (CO)$_4$Mo[^{i}Pr$_2$NPO]$_4$NiI$_2$

183

IR Spectrum of (CO)$_2$I$_2$Mo[^{i}Pr$_2$NPO]$_4$NiI$_2$

WAVENUMBER (CM-1)

%TRANSMITTANCE

184

IR Spectrum of (CO)$_4$Mo[iPr$_2$NPO]$_4$PdBr$_2$

185

IR Spectrum of (CO)$_3$Mo[iPr$_2$NPO]$_5$PdCl$_2$

186

IR Spectrum of $(CO)_4Mo[iPr_2NPO]_2(iPr_2NPOMe)(iPr_2NP(O)H)$

187

^{1}H NMR Spectrum of (CO)$_4$Mo[^{i}Pr$_2$NPO]$_4$

$^{13}C\{^{1}H\}$ NMR Spectrum of $(CO)_4Mo[^iPr_2NPO]_4$

189

^1H NMR Spectrum of $(CO)_4Mo[^iPr_2NPO]_4Cu(CH_3CN)_2BF_4$

190

^{13}C NMR Spectrum of $(CO)_4Mo[iPr_2NPO]_4Cu(CH_3CN)_2BF_4$

191

$^{31}P\{^{1}H\}$ NMR Spectrum of $(CO)_4Mo[^iPr_2NPO]_4Cu(CH_3CN)_2BF_4$

192

^{1}H NMR Spectrum of $(CO)_4Mo[iPr_2NPO]_4PtCl_2$

175.24

13.98

14.46

INTEGRAL

193

$^{13}C\{^1H\}$ NMR Spectrum of $(CO)_4Mo[^iPr_2NPO]_4PtCl_2$

194

13C NMR Spectrum of (CO)$_4$Mo[^{i}Pr$_2$NPO]$_4$Ni(CO)$_2$

195

$^{31}P\{^1H\}$ NMR Spectrum of $(CO)_3Mo[^iPr_2NPO]_5Ni(CO)_2$

196

^{1}H NMR Spectrum of (CO)$_4$Mo[iPr$_2$NPO]$_2$(iPr$_2$NPOEt)(iPr$_2$NP(O)H)

197

$^{13}C\{^1H\}$ NMR Spectrum of $(CO)_4Mo[^iPr_2NPO]_2\{^iPr_2NPOEt\}\{^iPr_2NP(O)H\}$

198

$^{31}P\{^1H\}$ NMR Spectrum of $(CO)_4Mo[^iPr_2NPO]_2(^iPr_2NPOEt)(^iPr_2NP(O)H)$

199

31P NMR Spectrum of (CO)$_4$Mo[iPr$_2$NPO]$_2$(iPr$_2$NPOEt)(iPr$_2$NP(O)H]

200