

Stereochemical Control of Transition Metal Complexes by Polyphosphine Ligands[†]

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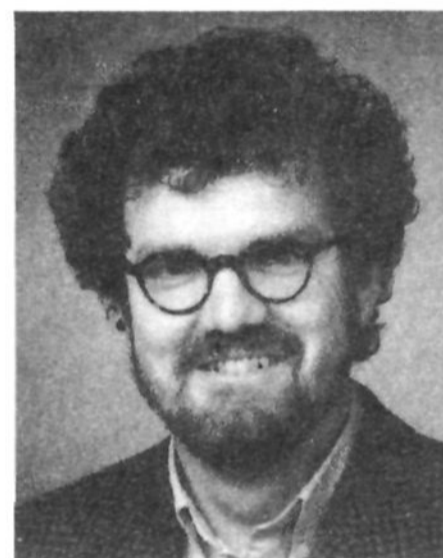
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I. Introduction and Scope of the Review

Tertiary phosphines are excellent ligating agents to metal ions and transition metals in a variety of oxidation states and, thus, are important constituents of compounds for catalysis, structure-bonding relationships, and spectroscopic studies. The compability of phosphorus ligands with other organic functional groups has extended their importance and synthetic scope. New technologies such as thin-film electronic device manufacture and surface preparation have benefited from the use of complexes with chelating phosphine ligands. Chemical bonding with the chalcogenides, halogens, and oxygen as additional functional groups can enhance this coordinating ability so that the ligands used for example as extractants for rare earths, uranium, and transuranium elements.

[†] Dedicated to Professor Dr. E. Lindner, University of Tübingen, on the occasion of his 60th birthday.



Hermann A. Mayer was born in Heidelberg, Germany, and received his Diplom in Chemistry in 1982 and his Ph.D. in 1986 both at the University of Tübingen with Professor E. Lindner. After two years of postdoctoral work with Professor William C. Kaska at the University of California, Santa Barbara, he returned to the University of Tübingen where he presently is preparing his Habilitation. His research interest include the design of polyphosphine ligands, transition metal chemistry, and the application of multinuclear NMR spectroscopy to organometallic chemistry in solution and in the solid state.



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The ligand effect and coordinating ability of phosphines was not always appreciated even though the

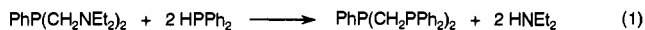
first observations of compound formation were recorded in the middle 1800s.¹ F. G. Mann in England and K. Jensen in Denmark initiated the revitalization and promoted the renaissance of phosphine coordination chemistry in the 1930s. This beginning was subsequently expanded by J. Chatt^{2,3} and others.⁴⁻¹⁰ Their research fortuitously came at the time of rapid development of organometallic chemistry, especially with the stabilization of multivalent metal oxidation states and coordinated ligand reactivity. Further growth in polyphosphine chemistry results from their use in catalysis,¹¹⁻¹³ organic synthesis,¹⁴ and solid-state materials.¹⁵

This current review will specifically cover the reaction chemistry of polydentate tertiary phosphine complexes with the exclusion of bidentate compounds. Also excluded will be catenated phosphorus compounds, macrocyclic derivatives, and compounds that lack direct phosphorus-metal bonds. Excellent reviews of bidentate phosphine complexes and structural aspects of polydentate compounds currently exist.¹⁶⁻²⁴ A compilation of polyphosphine ligands and their physicochemical properties is displayed in ref 19 along with their coordination possibilities.

II. Stereochemistry and Synthesis

A. Basic Methods

The traditional methods of polyphosphine synthesis have been carefully documented²¹ and only specific aspects will be noted here. One such process that held considerable promise involved the cleavage of carbon-nitrogen bonds (eq 1).²⁵ Although the process was potentially versatile and broad in scope, carbon-nitrogen bond cleavage was not always observed.



Another variation of a traditional method which is not completely appreciated is the substitution of fluoride from aromatic ring systems. Since the synthetic potential of placing fluorine atoms as substituents on aromatic rings is under continual development, the use of these materials in phosphine synthesis can be expanded.²⁶⁻²⁸

Some of the first polydentate phosphines were reported in 1962 using metathesis reactions with alkali metal phosphides and alkali halides.²⁹ However, the most dramatic advance in synthesis came with the work of R. B. King and the use of two methods: base-catalyzed and the free radical-catalyzed addition of P-H bonds across the double bond of vinyl phosphines.^{30,31}

One of the main incentives behind the synthesis of inorganic complexes is the interest in promoting factors that control structure and bonding. The polydentate phosphines are becoming more important because they are chelating systems or podands^{32,33} for many types of metals. Thus their properties can be altered to favor different kinds of reactions. Moreover, they can be precursors to other types of polydentate phosphines.²¹

The polyphosphine advantage which is the favorable behavior of polyphosphines over their comparable monodentate phosphines has been developed by Meek³⁴ and expanded by Bianchini³⁵ and co-workers. Polyphosphines exhibit (i) excellent bonding ability to

metals, (ii) an increased basicity (or nucleophilicity) at the metal, (iv) strong *trans* influence, (v) formation of stable complexes in a variety of metal oxidation states, and (vi) detailed structural and bonding information due to the metal-phosphorus and phosphorus-phosphorus coupling constants. Thus polyphosphine-metal complexes are thermodynamically more stable than comparable monophosphine analogs which lead to the isolation and characterization of many reactive intermediates normally not observed. In addition the reactivity of the participative coligands is generally preserved.

The factors which can control ligand size and ligand design and thereby determine the structure of a complex is a rapidly evolving theme.^{36,37} Brown and Lee³⁸ have summarized the important aspects of phosphine ligand steric effects for monodentate compounds of phosphorus. Similar work with polyphosphines will greatly enhance the directions of this category of compounds in synthesis. The stereochemistry of many polydentate complexes can be accurately described in an elegant series of studies by Keppert and White.³⁹⁻⁴² They have used structural data in the form of graphs and diagrams to help in the predictions of stereochemistry. A valuable emerging aspect of this theme is the concept of preorganization introduced by Cram.⁴³⁻⁴⁸ According to this concept the stereochemical arrangement of the free ligand can be synthetically prearranged by a knowledge of the donor-acceptor complex. Application of this concept is inherent in the development of the chelate effect.⁴⁹ Further progress along these lines will promote the role of organophosphorus chelates in enantiomeric synthesis and catalysis.

B. Aspects of Bonding

The structure and bonding in organophosphorus(III) compounds was reviewed by Gilheany,⁵⁰ while the bonding in transition metal-phosphine complexes was briefly discussed by Levason.¹⁸ The relationship between steric and electronic effects is of preeminent concern in phosphine ligand design. The concept of a cone angle and the ancillary electronic effects associated with this idea on phosphines were introduced by Tolman.^{51,52} More recently in a series of papers Giering^{49,53-55} has developed equations that will separate σ - and π -effects in the reactivity of phosphine ligand complexes. Although the relationship between monodentate and polydentate ligands is not complete, the influence of π -bonding is less important on the reactivity of metal phosphine complexes than σ -bonding and steric effects.

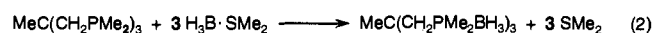
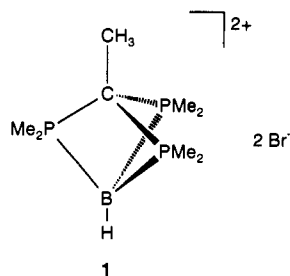
III. Reactions of Complexes

A. Non-Transition Metals

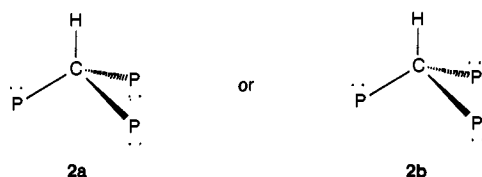
1. Boron

The podand $\text{MeC}(\text{CH}_2\text{PMe}_2)_3$ interacts with $\text{Br}_2\text{-HB-SMe}_2$ to give a quinuclidine type structure, with facile nucleophilic substitution of the bromide ions and SMe_2 . Coordinated SMe_2 is easily displaced when the phosphine is treated with 3 equiv of $\text{H}_3\text{B-SMe}_2$ (eq 2).⁵⁶

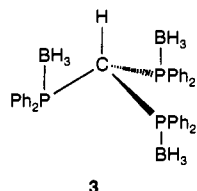
The first X-ray molecular structure of the simple podand $\text{HC}(\text{PPh}_2)_3$ shows that the free molecule has



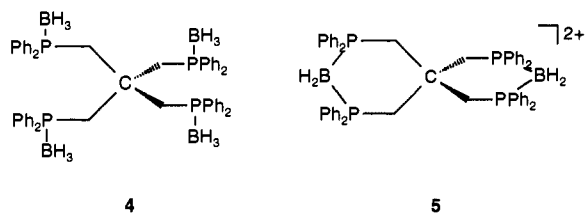
the phosphorus atom lone pairs in a *trans* orientation (2a,b).⁵⁷



The tris(borane) adduct **3** also reflect this stereochemical arrangement and the consequences of this will be apparent with corresponding transition metal complexes of this ligand.⁵⁷⁻⁵⁹

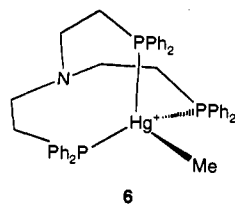


The tripod ligand $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$ (tdpme) because of its larger bite angle will complex three BH_3 molecules. It is more stable thermally than the $\text{HC}(\text{PPh}_2\text{BH}_3)_3$ analog. Tetradentate tetrakis[(diphenylphosphino)methyl]methane will complex four BH_3 groups (**4**) and form chelates as in **5**.⁶⁰



2. Mercury

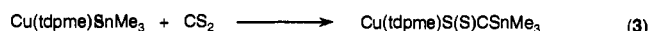
Chelate geometry and specificity have been instrumental in using phosphorus podal ligands to complex non-transition metal ions. Thus the coordination sphere of mercury can be increased. This renders the HgMe^+ cation insoluble in water and forces a tetrahedral geometry around the mercury ion (**6**).^{61,62}



3. Copper, Silver, and Gold

Polyphosphine complexes of the coinage metals have been only modestly developed. Two examples of direct

copper complexes have been made and at least one reaction (eq 3) has been studied.⁶³



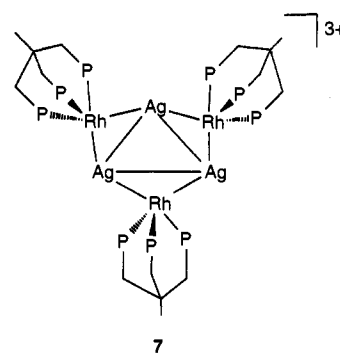
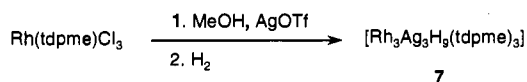
Ghilardi⁶⁴ has synthesized some polynuclear phosphinecopper-containing complexes, $[\{(\text{tdpme})\text{CoP}_3\}_3(\text{CuBr}_6)]$ and $[\{(\text{tdpme})\text{IrP}_3\}_3(\text{Cu}_5\text{Br}_4)]$, whose structures were determined by X-ray diffraction.

Complexes with silver and gold are usually of two types: one type involves direct combination of the coinage metal with the polyphosphine and the other involves a remote complexation.

Reaction of $\text{HC}(\text{PPh}_2)_3$ with silver carboxylates give $[\{(\text{Ph}_2\text{P})_3\text{CH}\}\text{Ag}_3(\text{O}_2\text{CR})_3]$ ($\text{R} = \text{Me}, \text{Et}, \text{Pr}, \text{Ph}$). From multinuclear NMR spectroscopic studies it was concluded that each silver atom is coordinated to one phosphorus atom and that the carboxylate groups bind to the silver atoms either as chelating or as bridging ligands. This requires that the silver atoms must be at the same side of the ligand.⁶⁵

Because the polyphosphine ligands promote the concentration of electron density on the metal atom they facilitate cluster and H bridge formation. Complex **7** (Scheme 1) is stable in acid solution, but it decomposes

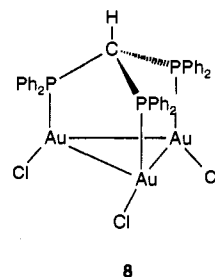
Scheme 1



The hydrides are omitted for clarity.

in neutral or basic solution with the formation of silver, although no precipitate of AgCl occurs.⁶⁶

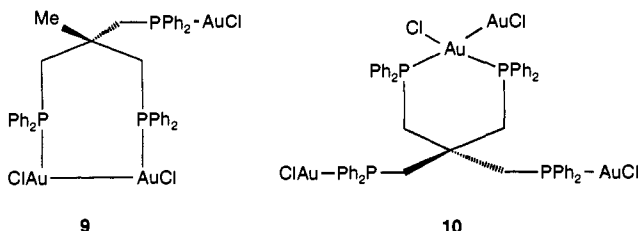
Schmidbaur⁶⁷ has used the specific geometry of the podands to emphasize the phenomenon of aurophilicity. Aurophilicity is a largely based relativistic effect⁶⁸ which leads to additional bonding between heavy metal atoms like gold. Thus $\text{HC}(\text{PPh}_2)_3$ interacts with 3 equiv of Me_2SAuCl to form **8**, with an *all-cis* arrangement of the AuCl units.



In contrast, $\text{MeC}(\text{CH}_2\text{PMe}_2)_3$ interacts with Me_2SAuCl to form a layer structured compound shown in eq 4 where the auriphilic effect is intramolecularly directed to only two gold atoms; the third gold atom interacts in an intermolecular chain effect. Presumably

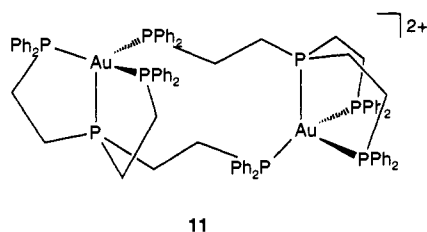


the stereochemical flexibility of the $\text{MeC}(\text{CH}_2\text{PMe}_2)_3$ podand compared to $\text{HC}(\text{PPh}_2)_3$ is the reason for the different structure.⁶⁹ Earlier studies showed that the polyphosphine $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$ (tdpme) gold complex has structure 9.^{70,71} Even though the Au–Au pairing energy is on the order of 7 kcal/mol only two gold atoms in the complex 10 form intramolecular pairs.⁷²



Other attempts to obtain clusters of gold atoms were not successful (11, Scheme 2). Complex 11 showed no

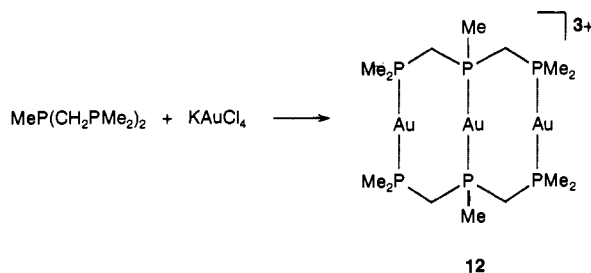
Scheme 2



reaction with nucleophiles such as azide or thiocyanate, but it did interact with Me_2AuCl to give $\text{Au}_4\text{Cl}_4(\mu\text{-L}_3)$.⁷³

The so-called linear phosphine, $\text{MeP}(\text{CH}_2\text{PMe}_2)_2$, does interact with KAuCl_4 to form a linear array of gold atoms (12, Scheme 3).⁷⁴

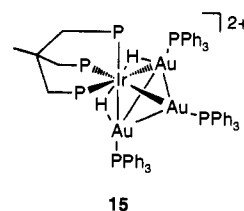
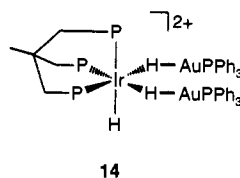
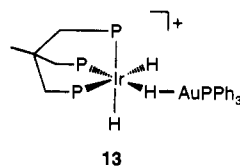
Scheme 3



Since $\text{IrH}_3(\text{PPh}_3)_3$ could be isolated in *fac* and *mer* forms, similar studies were performed to determine stereochemical control of the polyphosphine ligand $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$. This ligand can stereochemically control the isolation of the *fac* isomer which can be used to promote cluster growth shown in Scheme 4 with Ph_3PAuCl .⁷⁵

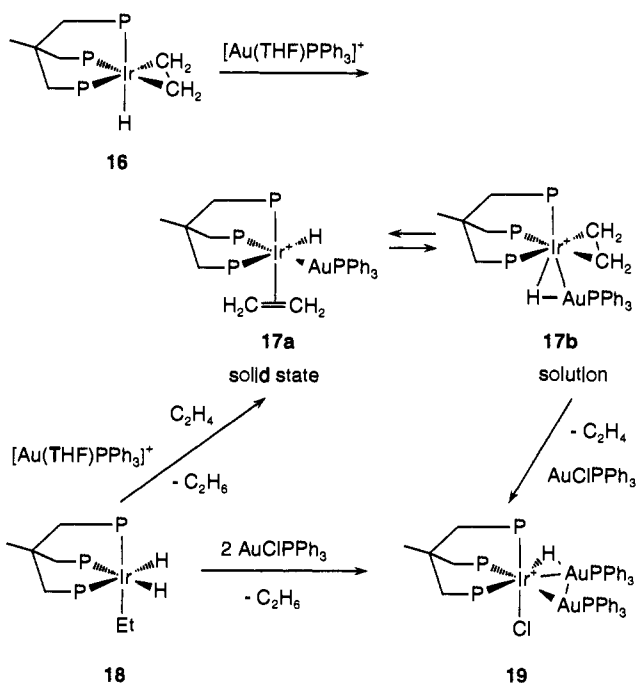
Bianchini used stereochemical control of tdpme to prepare gold cluster compounds in anticipation of using

Scheme 4

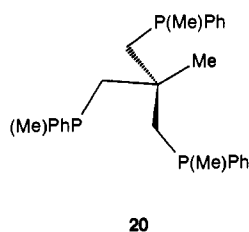


the isolobal relationship between “ $\text{Au}(\text{PPh}_3)$ ” and hydrogen to synthesize mixed gold polyhydride complexes (Scheme 5).⁷⁶ For example the $(\eta^3\text{-H})\text{Au}(\text{PPh}_3)\text{-Au}(\text{PPh}_3)$ ligand in 19 is isolobal to trihydrogen.

Scheme 5

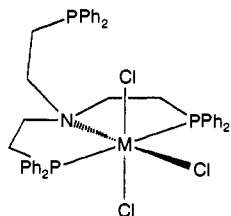


Venanzi described an achiral rhodium complex⁷⁷ which has the same structure as 15 by using the isolobal analogy of Ph_3PAuCl for hydrogen and the stereochemical control of $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$ (tdpme) to force an octahedral coordination on the rhodium atom. The molecular details of 15 can be elaborated by using chiral 20 to prepare a chiral rhodium complex with remotely bonded gold atoms.



an analog to 27 but $[\text{CpMo}(\text{CO})_3]_2$ results in $[\text{CpMo}(\text{CO})_2\{\eta^2\text{-HC}(\text{PPh}_2)_3\}][\text{CpMo}(\text{CO})_3]$.

More recently it was shown that $\text{N}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$ (np_3) and $\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$ (pp_3) both interact with chromium and molybdenum to give *mer*-distorted octahedral complexes⁹⁰ like 29.

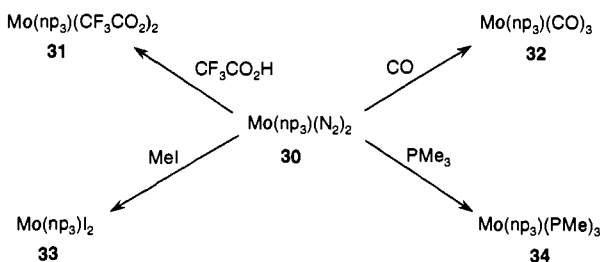


29 M = Cr, Mo, W

The choice of *mer* geometry is electronic in origin, i.e. decreasing electrostatic repulsions between X^- ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$). A *fac* geometry is common for neutral ligands.⁹¹

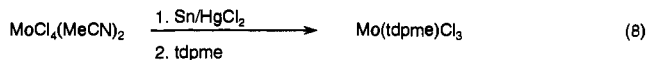
When the molybdenum complex is reduced, the *cis*- $\text{Mo}[\text{N}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3](\text{N}_2)_2$ (30) is formed. The $\text{Mo}[\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3]\text{Cl}_3$ gives the *trans* nitrogen complex.⁹² The larger apical phosphorus atom probably allows a larger bite angle so that all the donor atoms do not need to bond to the central metal. Hence stereochemical control of the complex is governed simply by the apical atom of the tripod. The *cis* complex undergoes the reactions shown in Scheme 8.

Scheme 8



The tetradentate $\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$ forms *mer* octahedral complexes; one phosphorus atom is not connected. The branched ligand $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$ coordinates in a *facial* way because of steric constraints. Also observed was the fact that CrF_3 or hydrated CrF_3 would react with the phosphines.⁹³⁻⁹⁵

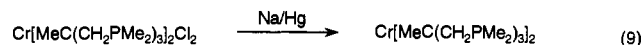
Huttner synthesized the first *fac* trihalide coordination complex of molybdenum with all phosphorus atoms bound to the metal.⁹⁶ The X-ray molecular structure of the *fac* molybdenum trihalide complex shows a great deal of steric congestion from the six phenyl groups. In order to isolate this isomer, the mode of synthesis is important. Thus the synthesis begins with a high-valent metal halide to insure complexation of the sterically rigid phosphine (eq 8). Concurrent reduction with a



mild reducing agent then lowers the oxidation to the observed product. When this discovery is joined with the facile synthesis of chiral $\text{MeC}[\text{CH}_2\text{P}(\text{Ph})(\text{R})_3]$ and tripod ligands with three different donor groups $[\text{MeC}(\text{CH}_2\text{PR}_2)(\text{CH}_2\text{PR}'_2)(\text{CH}_2\text{PR}''_2)]$, chiral com-

plexes of the type *fac*- $\text{Mo}\{\text{MeC}[\text{CH}_2\text{P}(\text{Ph})(\text{R})_3](\text{CO})_3$ and $\text{Mo}\{\text{MeC}(\text{CH}_2\text{PR}_2)(\text{CH}_2\text{PR}'_2)(\text{CH}_2\text{PR}''_2)\}(\text{CO})_3$ can be generated, respectively.^{97,98}

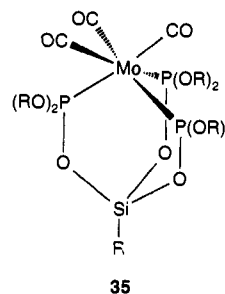
The podal ligand (1,1,1-tris(dimethylphosphino)methyl)ethane $[\text{MeC}(\text{CH}_2\text{PMe}_2)_3]$ forms *fac* complexes with chromium halides. In addition one is able to isolate $\text{Cr}[\text{MeC}(\text{CH}_2\text{PMe}_2)_3]_2$ (eq 9). This species is thermo-



chromic and changes from yellow to orange when it is heated.⁹⁹

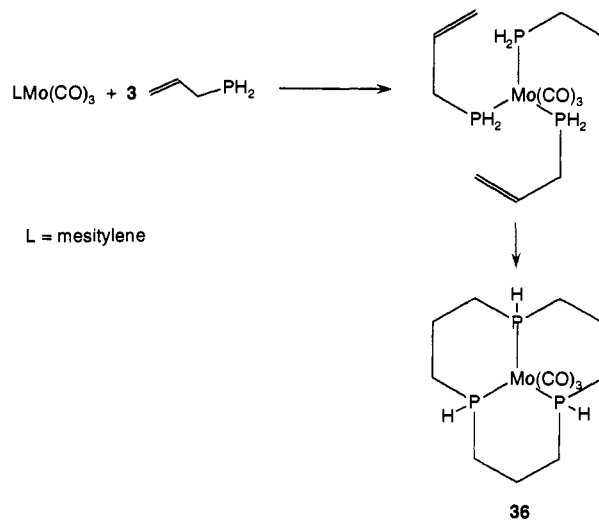
Although no reactions were studied, treatment of $\text{Cr}[\text{MeC}(\text{CH}_2\text{PMe}_2)_3]\text{Cl}_3$ with LiHBEt_3 gives $\{\text{HCr}[\text{MeC}(\text{CH}_2\text{PMe}_2)_3]_2\}\text{BEt}_4$. The actual structure is between a regular trigonal antiprism and trigonal prismatic which allows the hydrogen atom to be easily deprotonated to give $\text{Cr}[\text{MeC}(\text{CH}_2\text{PMe}_2)_3]_2$. The reverse protonation of $\text{Cr}[\text{MeC}(\text{CH}_2\text{PMe}_2)_3]_2$ was not possible.¹⁰⁰

Since phosphites have been used in some homogeneous catalytic systems, their introduction as podand ligands has generated considerable interest. The phosphite systems tend to be less electron donating than the phosphine analogs. The stereoelectronic control has generated *fac* isomer 35.¹⁰¹



Norman used a template approach to make the *fac*-polyphosphinemolybdenum complex 36 (Scheme 9).¹⁰²

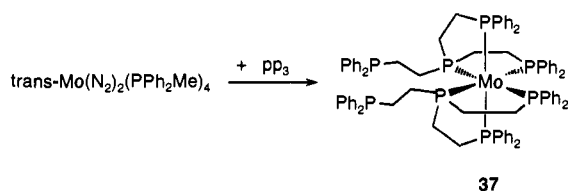
Scheme 9



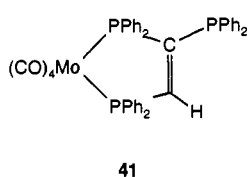
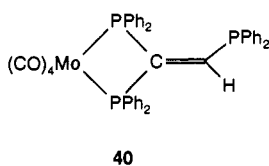
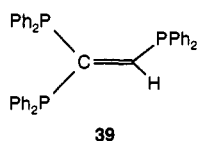
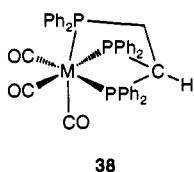
Here the central metal atom holds the ligands in place for *fac* coordination, although the 12-membered ring is large enough to encapsulate the metal atom. A long

sought after six-coordinated polyphosphine complex (37) was recently prepared as an air stable solid (Scheme 10).¹⁰³

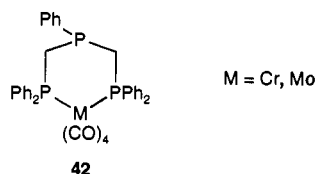
Scheme 10



Polyphosphines related to bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe), and 1,1,2-tris(diphenylphosphino)ethane (tppe) have been introduced by McFarlane.^{104,105} They form complexes with chromium, molybdenum, and tungsten in five different bonding modes. The tridentate example is shown below (38). The analog 1,1,2-tris(diphenylphosphino)ethene (tppee) (39) forms only bidentate complexes.



Balch also observed that bis[(diphenylphosphino)methyl]phenylphosphine [$\text{PhP}(\text{CH}_2\text{PPh}_2)_2$] only forms a bidentate boat chelate structure to a single metal atom represented in 42; the unoccupied phosphorus orbital can then coordinate to other metals.⁸⁸ A similar observation was made in the cases of 24 and 25.

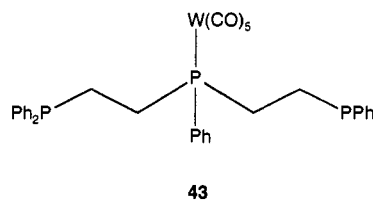
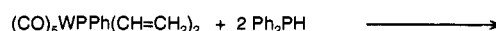


The potentially tridentate ligand bis[(di-*tert*-butylphosphino)methyl]methylphosphine [$\text{MeP}(\text{CH}_2\text{P}^t\text{Bu}_2)_2$] also acts only bipodal when treated with $\text{Mo}(\text{CO})_4(\text{NBD})$ (NBD = norbornadiene) or $\text{Mo}(\text{CO})_3(\text{C}_7\text{H}_8)$ (C_7H_8 = cycloheptatriene) to give $\text{Mo}[\text{MeP}(\text{CH}_2\text{P}^t\text{Bu}_2)_2](\text{CO})_4$. In contrast to 42, the central phosphorus atom coordinates to the metal resulting in four-membered rings with one $^t\text{Bu}_2\text{P}$ -unit dangling.¹⁰⁶

Stepwise addition of diphenylphosphine to a coordinated phenyldivinylphosphine was used by Keiter¹⁰⁷ to obtain monodentate complexes of potentially polydentate phosphine ligands¹⁰⁸ (Scheme 11).

Angelici¹⁰⁹ has investigated the heats of protonation to quantify the basicities of monodentate and of tridentate phosphine tungsten carbonyl complexes.

Scheme 11

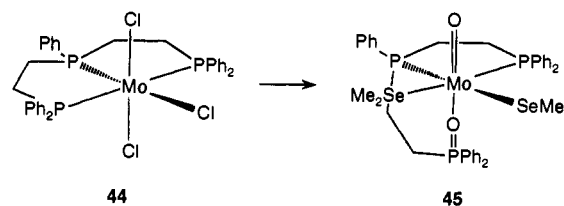


There is a remarkable decrease in basicity in the *fac* complex $\text{W}(\text{tdpme})(\text{CO})_3$ compared to *fac*- $\text{W}(\text{etp})(\text{CO})_3$ ¹¹⁰ because the protonated $\text{W}(\text{tdpme})(\text{CO})_3$ structure is forced to adopt an unstable geometry by the restrictive tdpme. Thus the flexible tridentate etp is more basic than tdpme. Monodentate phosphines^{111,112} are less basic than the flexible polyphosphine etp but more basic than tdpme, at least where protonation reactions are involved. A comparison with cone angles suggests that steric effects also contribute to basicity. These physicochemical results will set the stage for the better design of ligands that will influence the electron density on the metal atom.

Polyhydride complexes of tungsten can be synthesized by reacting $\text{WCl}_4(\text{PPh}_3)_2 \cdot \text{CH}_2\text{Cl}_2$ with $\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$, $\text{PhP}(\text{C}_6\text{H}_4\text{-o-PPh}_2)_2$ and tdpme to give WCl_4L . Treatment with LiAlH_4 results in WH_6L 's which are classical polyhydrides with no $\eta^2\text{-H}_2$ ligands. With triphenylsilane $\text{WH}_6\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$ can be converted into the silyl pentahydride complex $\text{WH}_5(\text{SiPh}_3)\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$. However, protonation of WH_6L with HBF_4 gave $[\text{WH}_{7-2x}(\eta^2\text{-H}_2)_x\text{L}]^+$.¹¹³

When $\text{Mo}[\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2]\text{Cl}_3$ is treated with $\text{NaSeC}_6\text{H}_2\text{Mes}_3\text{-2,4,6}$ in the presence of oxygen, a molybdenum(IV) oxo-selenolato complex is obtained 45¹¹⁴ (Scheme 12). Although the reaction starts out as

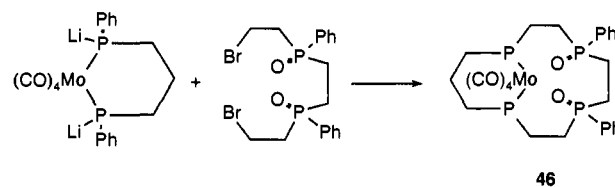
Scheme 12



a *mer* complex, the "steric pressure" of the podand keeps the coordination geometry virtually intact so that there is a reaction site for adventitious oxygen to give the final product.

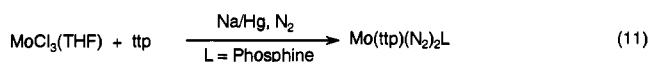
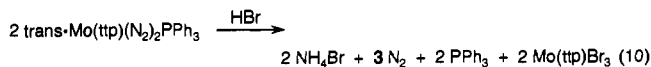
Polyphosphine complexes of molybdenum were synthetically explored by King,^{80,81,115,116} but very little reaction chemistry was performed. Stelzer, on the other hand used a stepwise approach to prepare 45 and 46 (Scheme 13).^{117,118} The metal behaved like a template

Scheme 13



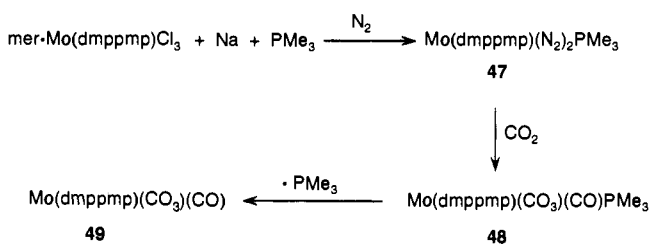
so that the ligand could be synthesized in an organized fashion around the metal.

In early investigations George observed that reactions (eq 10) could be performed on the N_2 ligands that were coordinated to a polyphosphine complex.¹¹⁹ Later

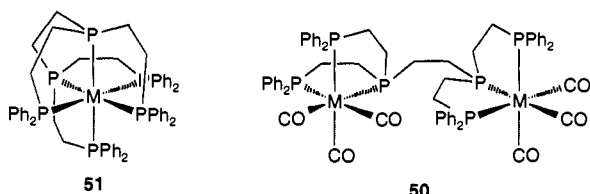


Dahlenburg^{120,121} used metal reduction methods to prepare similar polyphosphine molybdenum complexes (12). The polyphosphine complex was determined to be *mer* and the two nitrogen ligands occupy *trans* positions. A trisnitrogen species could not be isolated. Dahlenburg¹²² and Pietsch prepared the molybdenum complex (47) and illustrated its reactivity with carbon dioxide (Scheme 14).

Scheme 14

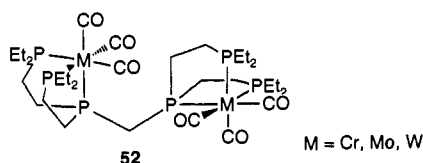


King's classic papers on the synthesis of podal ligands expanded the scope of polyphosphine-metal complex chemistry.^{81,115,116} The hexatertiary phosphine 1,1,4,4-tetrakis[2-(diphenylphosphino)ethyl]-1,4-diphosphabutane $\{[(\text{Ph})_2\text{PCH}_2\text{CH}_2]_2\text{PCH}_2\text{CH}_2\text{P}[\text{CH}_2\text{CH}_2\text{P}(\text{Ph})_2]_2\}$ readily forms carbonyl complexes **50**. No complexes were observed where the ligand acted as a hexadentate monometallic species as in **51**. The $\text{CH}_2\text{-CH}_2$ bridge atoms are too short to allow bonding to a single metal atom. No reactions of the complex were studied.



M = Cr, Mo, W

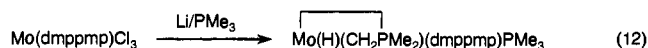
Stanley¹²³ has taken the hexaphosphine system, $(\text{Et}_2\text{-PCH}_2\text{CH}_2)_2\text{PCH}_2\text{P}(\text{CH}_2\text{CH}_2\text{PEt}_2)_2$ (eHTP) and treated it with $\text{M}(\text{CO})_6$ (M = Cr, Mo, W). Complex **52** is structurally comparable to those observed by King with ethylene bridges between the phosphorus atoms.



M = Cr, Mo, W

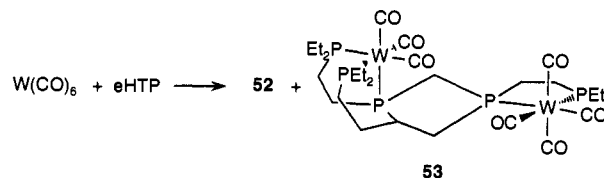
In contrast to similar chromium complexes, Dahlenburg¹²⁴ observed that $\text{MoCl}_3[\text{MeP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{-}$

$\text{PMe}_2)_2]$ when treated with Li underwent C-H intramolecular insertion in the presence of Me_3P (eq 12).

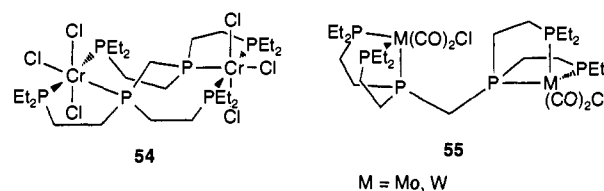


A related type of reaction was reported by Stanley.¹²⁵ When tungsten carbonyl is heated with (eHTP) one of the (diethylphosphino)ethyl arms is lost to form a pentaphosphine ligand (**53**). In addition an intramolecular C-H metalation takes place (Scheme 15).

Scheme 15



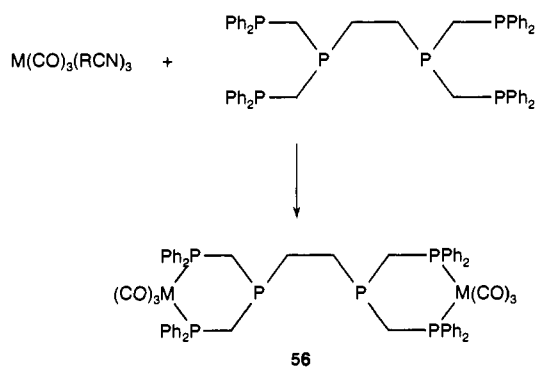
The photochemical reactivity of the eHTP complexes varies from $\text{Cr}_2(\text{eHTP})(\text{CO})_{10}$ to $\text{Mo}_2/\text{W}_2(\text{eHTP})(\text{CO})_6$.¹²⁶ Photolysis of the chromium complex in CH_2Cl_2 gives air stable, *mer*- $\text{Cr}_2(\text{eHTP})\text{Cl}_6$ (**54**) while the tungsten and molybdenum carbonyl produces a chlorinated carbonyl (**55**).



M = Mo, W

The stereochemistry of the tetraphosphine $[\text{CH}_2\text{P}(\text{CH}_2\text{PPh}_2)_2]_2$ is governed by the ethylene bridge which does not allow all four phosphine groups to be coordinated to one metal center. In cases where binuclear complexes are formed the metal atoms are not juxtaposed (Scheme 16).¹²⁷

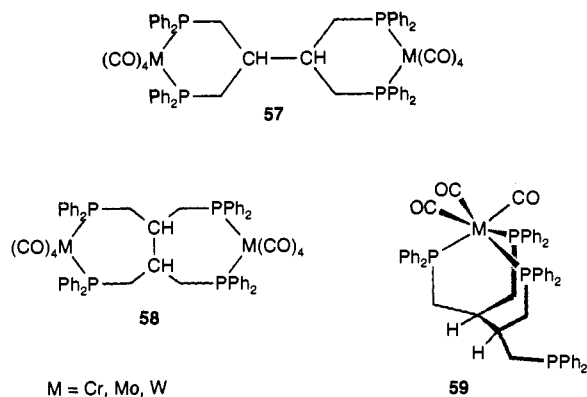
Scheme 16



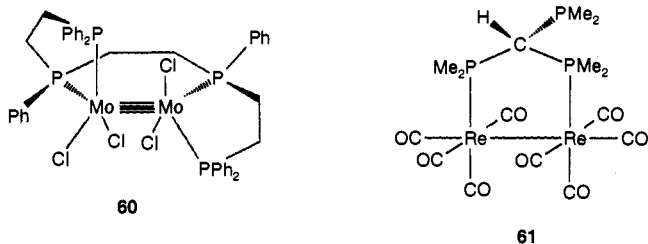
The new tetratertiary phosphine ligand $[\text{CH}(\text{CH}_2\text{-PPh}_2)_2]_2$ has been synthesized but there is little stereochemical control over the formation of **57** or **58** type complexes.¹²⁸ Most derivatives with the early transition metals are of type **57** although type **59** are obtained with an uncoordinated donor atom (Scheme 17). Presumably the small number of methylene groups in the chains offer little structural flexibility.

For the $\text{Mo}_2\text{X}_2\text{L}_2$ system (X = e.g. Cl) up to 13 isomers are possible. When the ligands L are four separate monophosphines only the isomer where the bulky

Scheme 17

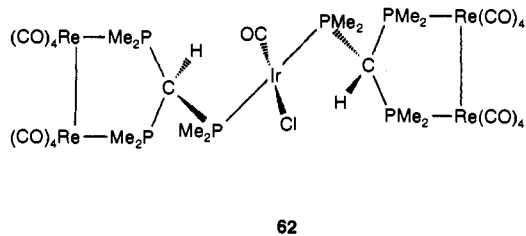


phosphine groups are far from each other has been found. The stereochemistry of the linear tetraphosphine $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{P}(\text{Ph})\text{CH}_2\text{CH}_2\text{P}(\text{Ph})\text{CH}_2\text{CH}_2\text{PPh}_2$ is rearranged to coordinate molybdenum in such a way that another of the 13 isomers can be isolated.¹²⁹⁻¹³¹ Here the short separation between donor atoms most likely influences metal-metal bond formation.



4. Manganese, Technetium, and Rhenium

Heterobimetallic clusters have been synthesized by taking advantage of the small steric constraints of the ligand $\text{HC}(\text{PMe}_2)_3$. When $\text{Re}_2(\text{CO})_{10}(\mu\text{-H})(\mu\text{-C}_6\text{H}_{10})$ was treated with this ligand the binuclear rhenium complex 61 was obtained in good yields. Further reaction of this material with $[\text{IrCl}(\text{COD})]_2$ (COD = cyclooctadiene) gave 62 and not a polynuclear cluster as intended.¹³²

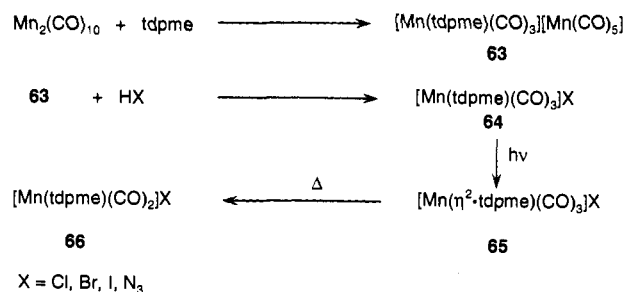


Obviously there is much more to be studied about the stereochemical control exerted by small podal phosphines to generate metal cluster compounds from monomeric units.

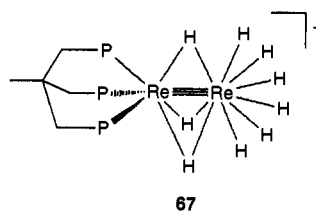
Ellermann^{133,134} has shown that $\text{Mn}_2(\text{CO})_{10}$ and tdpme undergo a disproportionation to give the products shown in Scheme 18, which basically amount to "cluster" fragmentation.

On the other hand a new complex with the ligand tdpme was synthesized with a rhenium atom coordinated to six terminal hydrogen atoms and linked to a second rhenium atom by three hydride bridges.^{135,136} The rigid stereochemical control of the ligand and small

Scheme 18

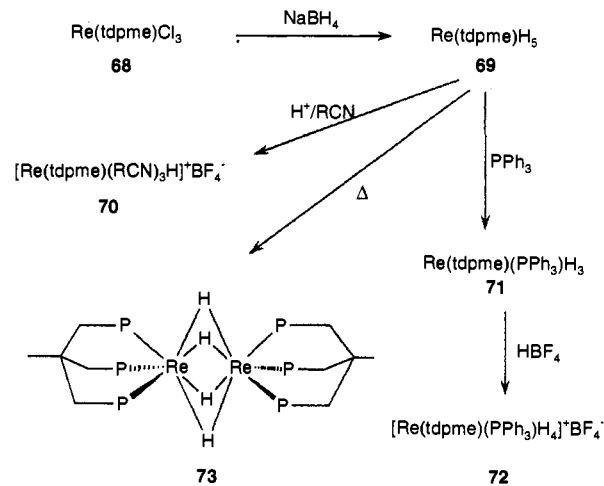


hydrogen atoms probably influence the polyhydride composition of complex 67. All of the H atoms are fluxional.



The ligand tdpme can be used to make a *fac*- $\text{Re}(\text{tdpme})\text{X}_3$ complex, which can be converted to the polyhydride, $\text{Re}(\text{tdpme})\text{H}_5$ ¹³⁷⁻¹³⁸ (Scheme 19). When

Scheme 19



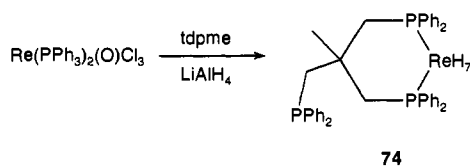
this is heated a hydride-bridged cluster 73 is formed.

The easier deprotonation of the tetrahydridorhenium cation $[\text{Re}(\text{tdpme})(\text{H})_4\text{L}]^+$ (L = MeCN, ^tBuNC, xylylNC) compared to their monophosphine analogs indicates a nonclassical structure of the hydride ligands. This is also consistent with the easy conversion of $\text{Re}(\text{tdpme})\text{H}_5$ to the hydrido species $\text{Re}(\text{tdpme})\text{H}_3$ which in the absence of a ligand L forms the dirhenium polyhydride $\text{Re}_2(\text{tdpme})_2\text{H}_4$.¹³⁷

Complex 69 shows enhanced thermal reactivity, which is a function of the *fac* stereochemical control of the ligand. Thus the hydrogen atoms in the rhenium dimer are readily *fac* coordinated like the ligand.

The more powerful hydriding agent LiAlH_4 forms the optimum $\text{Re}(\text{tdpme})\text{H}_7$ complex 74 (Scheme 20). The seven "soft" hydride ligands coordinated to the rhenium atom create a "soft" metal center which competes with the "soft" donor phosphine ligand. Thus

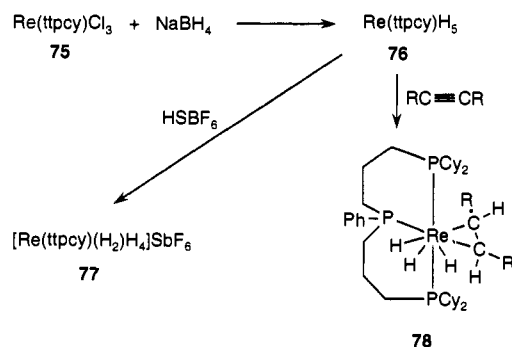
Scheme 20



one of the "soft" donor phosphines of the tripod ligand is readily replaced.¹³⁹

Linear polyphosphines like $\text{PhP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PCy}_2)_2$ (ttpcy) can be used to synthesize molecular hydrogen complexes **77** by protonation of $\text{Re}(\text{ttpcy})\text{H}_5$ ¹⁴⁰ (Scheme 21). The complex shows a meridional coordination of of

Scheme 21

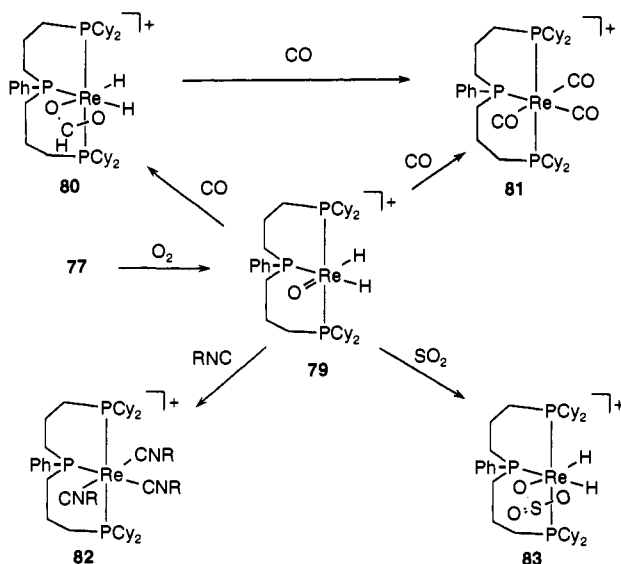


the phosphine but no substitution reactions readily occur presumably because of the unusually long H-H bond distance of the $\eta^2\text{-H}_2$ ligand. Similar results were reported for the hexahydridorhenium complex stabilized by etp¹⁴¹ which makes the unusual properties of these hydride complexes independent of the substituents on the phosphorus atoms.

Reactions of $\text{Re}(\text{ttpcy})\text{H}_5$ and $\text{Re}(\text{ttp})\text{H}_5$ [ttp = $\text{PhP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2$] are known with respect to acetylene (Scheme 21) (**78**).¹⁴²

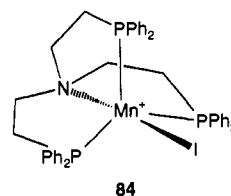
Polyphosphines have enabled Wojcicki¹⁴³ to prepare hydrido oxo complexes as potential model systems for catalyzed reactions of H_2O , O_2 , and peroxides. Examples of reactions of $[\text{Re}(\text{ttpcy})(\eta^2\text{-H}_2)\text{H}_4]\text{SbF}_6$ (**77**) with CO, SO_2 , and isocyanides are summarized in Scheme 22. The *mer* coordinating action of the

Scheme 22



polyphosphine serves to increase electron density on the metal atom, and the stereocontrol of the ligand offers coordination sites for chemical reactivity. The reactions with CO are particularly interesting because a CO_2 adduct could be part of the reaction scheme.

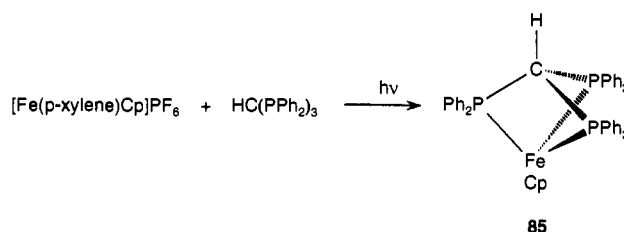
The tripodal tetradentate np_3 interacts with MnI_2 to form **84**, which is moderately stable in air. The structure is half-way between a trigonal bipyramid and a tetrahedron.¹⁴⁴



5. Iron, Ruthenium, and Osmium

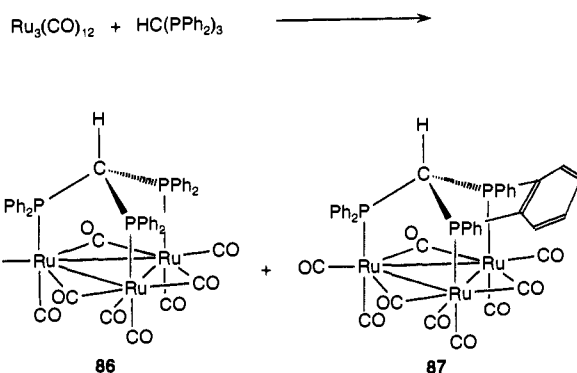
Generally tris(diphenylphosphino)methane [$\text{HC}(\text{PPh}_2)_3$] promotes the spontaneous assembly of transition metals as clusters, or it will stabilize already formed clusters, but with iron it coordinates to a single transition metal (**85**, Scheme 23).^{86,145} When the

Scheme 23



sterically constrained $\text{HC}(\text{PPh}_2)_3$ ligand is treated with preformed metal clusters, the cluster bonds remain intact since all the metal atoms are within the donor influence of the phosphorus atoms.¹⁴⁶ Two of the many products **86** and **87** are shown in Scheme 24.

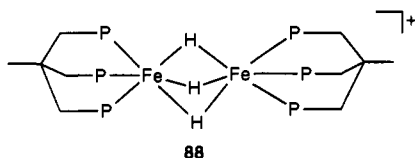
Scheme 24



More recently $\text{Ru}_3(\text{CO})_{12}$ has been treated with the sterically smaller $\text{HC}(\text{PMe}_2)_3$ to give a capped cluster $\text{Ru}_3\{\eta^3\text{-HC}(\text{PMe}_2)_3\}(\text{CO})_6(\mu\text{-CO})_3$ comparable to $\text{Ru}_3(\text{CO})_6(\mu\text{-CO})_3\{\text{MeSi}(\text{P}^n\text{Bu})_2\}_3$. The product however is not reactive to substitution or addition reactions with phosphines, olefins, or isocyanides. Even thermal or photochemical interaction with hydrogen failed. The ruthenium cluster did interact with hexafluorophosphoric acid and $[\text{Au}(\text{Ph}_3\text{P})]\text{O}_3\text{SCF}_3$. The major reason

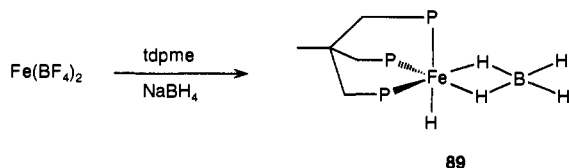
for this lack of reactivity is the envelope effect that the ligand has on the metal coordination sphere.⁸⁹

When the ligand spatial groups are extended by the introduction of methylene groups, the steric requirements are still rigid and there is some distortion in the *fac* complexes. This forces other co-ligands to occupy additional coordination sites. Such is the case for low-valent iron which forms a hydrido-bridged dimer **88**.^{22,147,148}



The course of the reaction is sometimes dependent upon the steric requirements of the groups attached to phosphorus and to the particular anion which is used (Scheme 25). For example with $\text{Fe}(\text{BF}_4)_2$ the borohy-

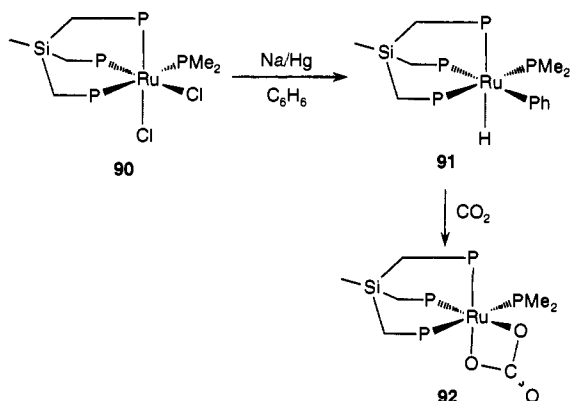
Scheme 25



dride fragment remains attached to the iron. One could envision that BH_3 simply takes the place of an iron tdpme moiety in **88**.

When the apical carbon atom in these podands is replaced by the larger silicon atom as in $\text{MeSi}(\text{CH}_2\text{-PMe}_2)_3$, the resultant metal complexes can metalate certain substrates.¹⁴⁹ The larger stereochemical control of the ligand and the added electron density on the metal atom, contribute to electron rich coordination sites for the type of intermolecular metalation (Scheme 26). The formation of the carbonate complex **92** is

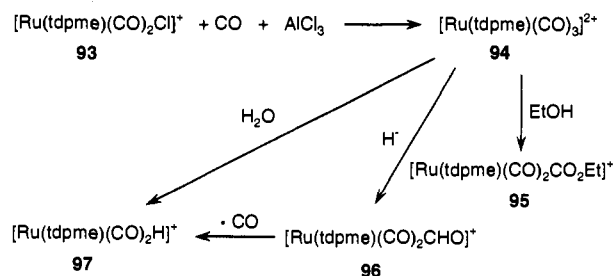
Scheme 26



unusual and only occurs under pressure. Adventitious moisture and oxygen under pressure is the most likely source of the extra oxygen atom.

The rigid steric requirements, small apical carbon atom, and increased electron density of tdpme complexed to ruthenium also promote extranuclear attack on coordinated carbon monoxide¹⁵⁰ (Scheme 27). The high values of the CO stretching frequencies suggest that coordinated CO is attacked nucleophilically by water.

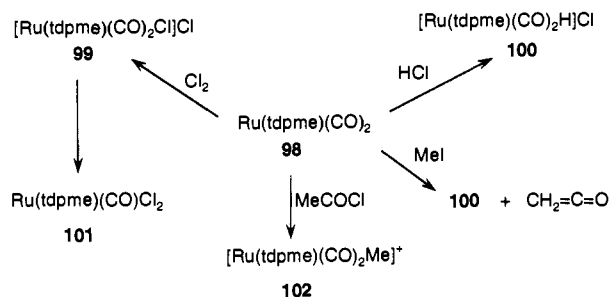
Scheme 27



The intermediate in the reaction is $[\text{Ru}(\text{CO}_2\text{H})(\text{CO})_2\text{-}(\text{tdpme})]^+$, a coordinated carboxylic acid which loses CO_2 . A similar reaction occurs with hydride ion, but the intermediate here is a metalloformate.

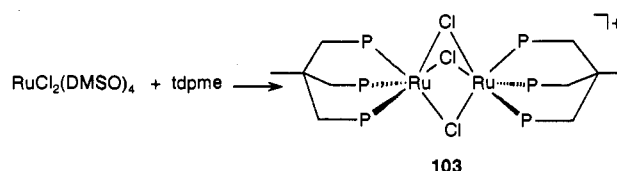
X-ray molecular structures of the complexes with tdpme show that this phosphine has three 90° bite angles and caps a triangular face of the octahedron with a *fac* stereochemistry; recall that $\text{PhP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{-PPh}_2)_2$ is *mer*. All three of the remaining coordination sites of a *facial*, octahedral MP_3 are *trans* to phosphorus, while only one remaining site is *trans* to phosphorus in the *mer* structure. Since the phosphorus atoms have a high *trans* influence, there is greater reactivity in the *fac* series.¹⁵¹ This is illustrated in Scheme 28.

Scheme 28



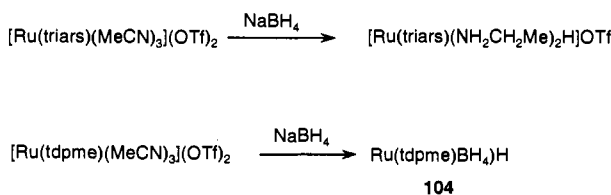
Solvento complexes and mixed solvent species of tripod ligands can be made by Cl^- abstraction with Ag^+ . Reactions of the solvento species with H^- are not the same as those with Cl^- .^{152,153} (Scheme 29).

Scheme 29



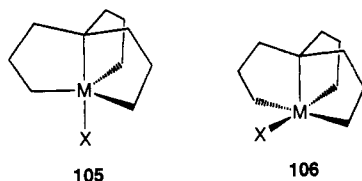
Polyarsine complexes of ruthenium with coordinated acetonitrile are reduced by borohydrides to give a bisamine hydride complex. In contrast $[\text{Ru}(\text{tdpme})\text{-}(\text{MeCN})_3]^{2+}$ is only reduced to the ruthenium hydride borohydride ion; no reduction of the coordinated nitrile occurs (Scheme 30).¹⁵⁴ The different chemical reactivity

Scheme 30

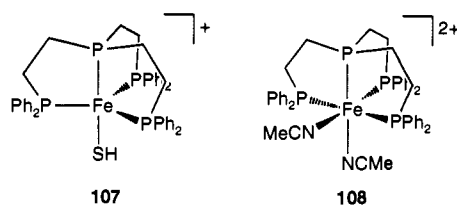


in the two compounds is related to the differences in the *trans* effect of the two tripodal ligands.

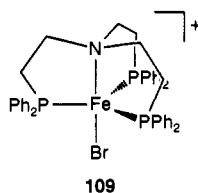
The tripodal ligand $N(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$ (np_3) is potentially tetradentate and forms complexes of the type 105 and 106. The donor atoms nominally can occupy



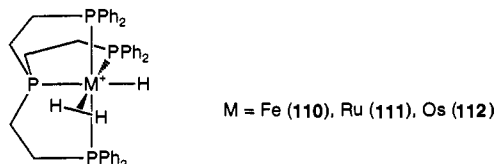
four sites on the metal atom but the stereochemical control is such that the coordination sphere can be expanded by one other ligand site. This gives a trigonal-bipyramidal or square-pyramidal form. The metal ion electronic configuration can sometimes override the stereochemistry influence. Thus Fe(II) can exhibit tetradentate^{23,155,156} trigonal-bipyramidal derivatives or hexadentate ones (107 and 108, respectively).



Complexes of $N(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$ (np_3) have been studied extensively by Sacconi, but few reactions were recorded.^{22,157-161} Complex $[\text{Fe}(\text{np}_3)\text{Br}]\text{PF}_6$ (109) which is a typical example of this series, is five coordinate from X-ray molecular structural data:



The series of M(II) *cis*-hydride- η^2 -dihydrogen compounds with the formula $[\text{M}(\text{pp}_3)(\eta^2\text{-H}_2)\text{H}]\text{BPh}_4$ (M = Fe,¹⁶² Ru,¹⁶³ Os¹⁶⁴) display a similar trend in their properties down the iron group triad compared to the *trans*-hydride- η^2 -dihydrogen complexes $[\text{ML}_2(\eta^2\text{-H}_2)\text{H}]^+$ [L = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (dppe), $\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2$ (depe)].¹⁶⁵ Thus the metal-dihydrogen bond strength increases in the order Ru < Fe < Os while the H-H interaction decreases.



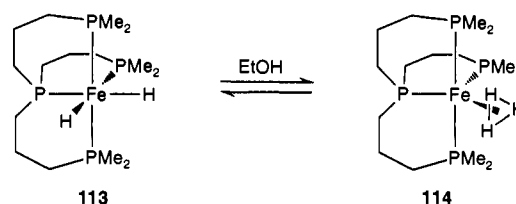
However, the pp_3 complexes are more stable than the corresponding dppe and depe compounds. Due to the stereochemistry of the polyphosphine pp_3 , the η^2 -dihydrogen and hydride ligands are forced in mutual *cis* positions which experience a stabilizing overlap between the filled M-H σ -orbital and the empty $\sigma^*_{\text{H-H}}$

(attractive "cis effect").^{166,167} This is also in agreement with a higher fluxionality found for the pp_3 complexes compared to the dppe and depe derivatives. Inelastic neutron scattering experiments reveal that $d_r(\text{M})-\sigma^*(\text{H}_2)$ back-donation is stronger in the iron complex than in the ruthenium derivative.¹⁸⁸ The different metal-dihydrogen bond interactions in 110-112 is reflected in their behavior as catalyst precursors (see below).

The neutral dihydride complex $\text{Ru}(\text{etp})(\text{L})\text{H}_2$ (L = PMe_2Ph , $\text{P}(\text{OCH}_2)_3\text{CEt}$) which adopts an octahedral structure with the triphosphine coordinated in a *fac* way changes to *mer* upon protonation. This makes it possible for the η^2 -dihydrogen ligand to occupy a *trans* position to the high *trans*-influence terminal hydride.¹⁶⁹

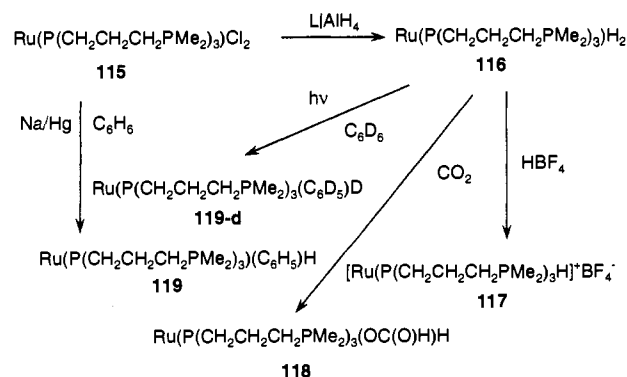
As in the iron complex shown in Scheme 31 the increased electron density allows polyhydrogen compound 114 to form.¹⁷⁰

Scheme 31



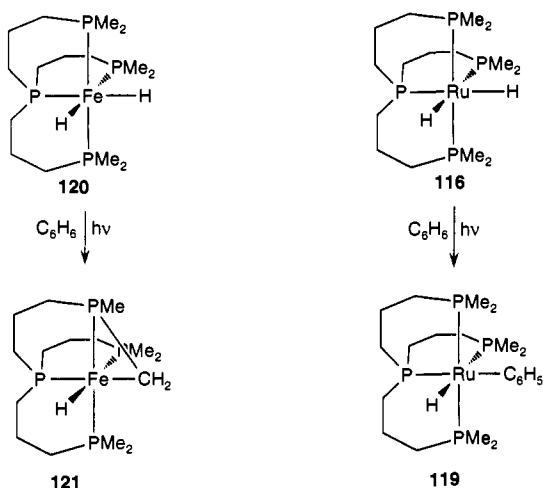
Since Dahlenburg has shown that the ruthenium tdpme complex will metalate hydrocarbons, the more electron-rich tetradentate compounds should behave similarly.¹⁷¹ The X-ray molecular structure of *cis*- $\text{Ru}(\text{Me}_3\text{P})_4\text{H}_2$ and $\text{Ru}\{\text{P}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PMe}_2)_3\}\text{H}_2$ was determined in order to understand the differences and relationships between monodentate and chelating phosphines with respect to stereochemical control of hydrocarbon metalation reactions. Thus the steric encumbrance in the trimethylphosphine complex is greater than in the triphos complex. This is perhaps a deciding factor in making *cis*- $(\text{Me}_3\text{P})_4\text{Ru}^0$ undergo spontaneous cyclometalation.¹⁷² Scheme 32 summarizes these reactions with a tetraphosphine ligand.

Scheme 32



In a similar comparative study, Dahlenburg^{173,174} has noted the interesting differences between ruthenium and iron in the hydrocarbon metalation reaction with *fac* stereochemical control of the metal geometry in Scheme 33. The larger ruthenium atom does not undergo intramolecular cyclometalation of the coordinated phosphine ligand. Although no structural data

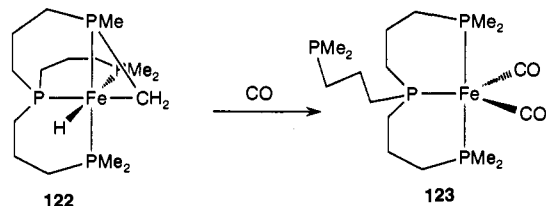
Scheme 33



specifically exists, there is less steric congestion around the ruthenium atom. This normally tends to disfavor intramolecular metalation.¹⁷⁵ When the iron compound 120 is treated with CO₂, the carbonate Fe(O₂CO)[P(CH₂-CH₂-CH₂-PMe₂)₃] is formed along with CO and hydrogen.

One of the donor groups is released when 122 (Scheme 34) is treated with a donor ligand. This can be the

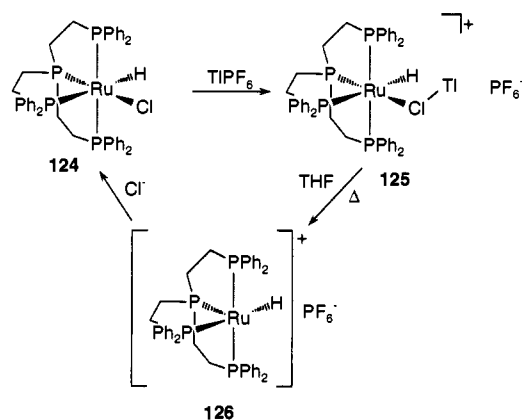
Scheme 34



result of stereochemical control or most likely from electronic influences of the new ligand. It can allow for synthetic and reaction flexibility.¹⁷⁶⁻¹⁷⁹

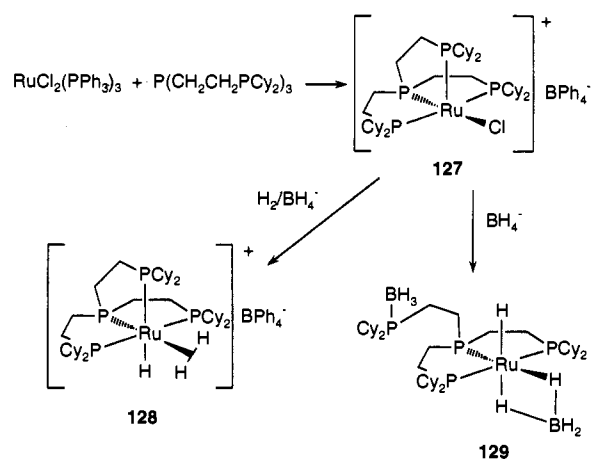
Since most of the polyphosphines enhance the electron density on the metal atom, supplemental bonding to a main group metal system can be observed. One of the first examples of this is illustrated in Scheme 35.¹⁸⁰ Morris¹⁸¹ expanded the chemistry of polyphos-

Scheme 35



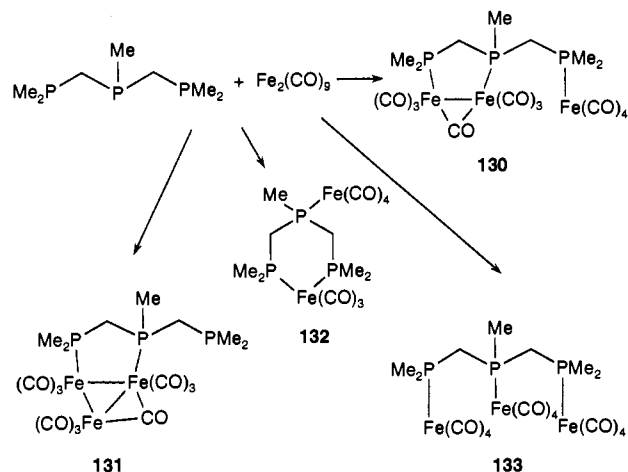
phine-stabilized ruthenium complexes and synthesized the hydrogen complex 128 (Scheme 36). The reaction with BH₄⁻ must be done under hydrogen gas or the borohydride adduct 129 will be obtained.

Scheme 36



The *mer* stereochemical control of the linear tridentate MeP(CH₂PMe₂)₂ on metal carbonyl complexes like Fe₂(CO)₉¹⁸² is directed toward compounds that reflect cluster building products and linear adducts (Scheme 37). The more sterically hindered ligand MeP(CH₂Pt-

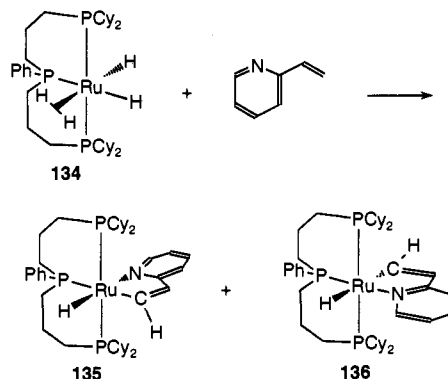
Scheme 37



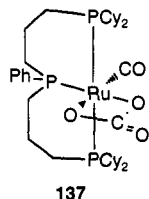
Bu₂)₂ does not react with Fe₂(CO)₉ under the same reaction conditions.¹⁰⁶

Meek attempted to compare the chemistry of chelating ruthenium hydrides with their monophosphine analogs. He found that Ru(ttpcy)H₄ and Ru(ttpcy)-(H)Cl are similar to Ru(PPh₃)₃H₄ and Ru(PPh₃)₄H₂ in their reactions with olefins. However, 2-vinylpyridine formed an interesting vinyl metalated complex with Ru(ttpcy)H₄¹⁸³ (Scheme 38).

Scheme 38

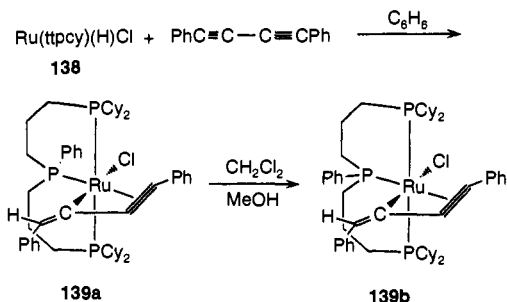


Meek¹⁸⁴ used stereochemical control of the linear polyphosphine ttpcy to obtain the dihydrogen complex 134. The hydrogen atoms interact with substrates as a dihydrogen complex and as a metal hydride. Thus carbon dioxide insertion occurs to form a bidentate formate ligand. Carbon monoxide reacts irreversibly to form a six-coordinate dihydride and dihydrogen can be displaced by nitrogen to form a nitrogen dihydride complex. The carbonyl groups in Ru(ttpcy)(CO)₂ are oxidized by oxygen and the carbonate complex 137 is formed. When Ru(ttp)(CO)₂ is treated with oxygen an uncharacterizable material is obtained.¹⁸⁵

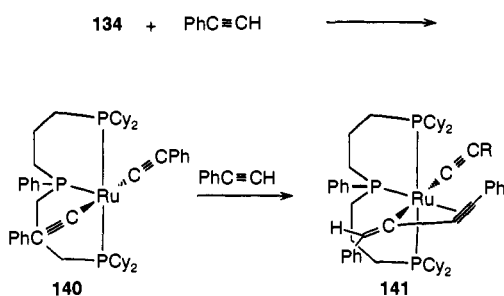


The stereochemical control exhibited by ttpcy in earlier reactions prompted the investigation of forming carbon-carbon bonds with acetylenic reagents shown in Schemes 39 and 40.¹⁸⁶ For example Ru(ttpcy)(H)Cl

Scheme 39



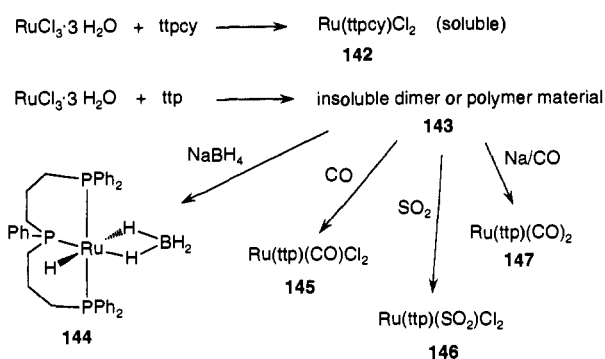
Scheme 40



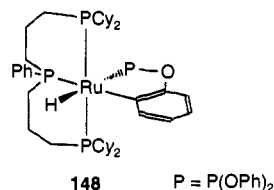
reacts with 1,4-diphenylbutadiyne to give the *syn,cis* insertion product 139a. This dissolves in polar solvents to give the *anti,mer* isomer 139b.¹⁸⁷ Most of the reactions are typical of metal-coordinated ligands except for Ru(ttpcy)H₄ (134) which interacts with two molecules of phenylacetylene to form a coordinated ligand.

A more detailed description of the less hindered ttp ruthenium chemistry is depicted in Scheme 41. For example the more hindered ttpcy ligand gives soluble ruthenium dichloride complexes, whereas the less hindered ttp ligand forms an insoluble material. An attempt to make a dihydrogen complex like 134 by using NaBH₄ gave a borohydride adduct (144) (Scheme 41). This is often the case when hydrogen is not used in the reaction. An attempt to displace BH₃ from 144 with

Scheme 41

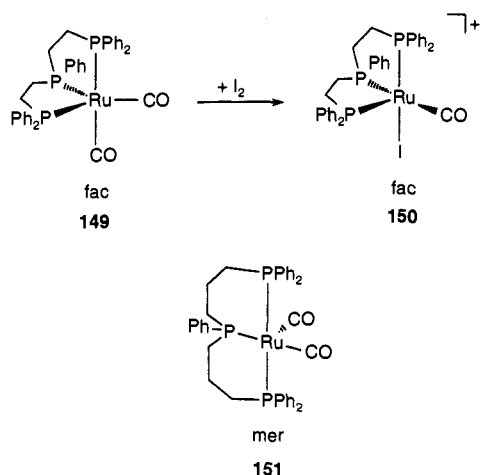


the Lewis base donor P(OPh)₃ resulted in a substitution reaction followed by orthometalation of the phosphite 148.¹⁸⁸



Complexes of the Ru(CO)₂ moiety with PhP(CH₂CH₂PPh₂)₂ and PhP(CH₂CH₂PPh₂)₂ interact the same way with many substrates but the final stereochemistry is different. The ligands PhP(CH₂CH₂CH₂PPh₂)₂ prefer *mer* arrangements, while PhP(CH₂CH₂PPh₂)₂ prefers a *fac*-coordinated octahedral complex. This is undoubtedly because of the smaller bite angle in the latter ligand.^{185,189} The reactions shown in Scheme 42 exhibit these differences.

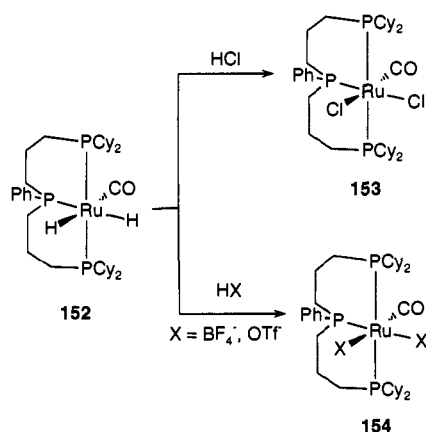
Scheme 42



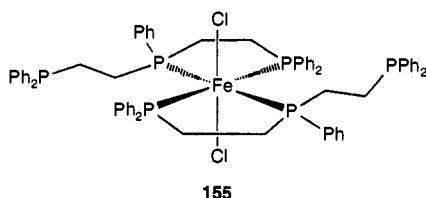
Some oxidative addition reactions with PhP(CH₂CH₂PCy₂)₂ are displayed in Scheme 43. The *mer* stereochemistry predominates in the final product. These air-stable complexes are labile low-spin d⁶ materials.^{153,190}

Meek^{189,191} has reported that the structure of the complex Ru(ttpcy)Cl₂ is dependent on the polarity and coordinating ability of the solvent. In nonpolar solvents i.e. C₆H₆ the *mer* and *fac* are present but in halogenated solvents the *fac* form predominates. In contrast to the ttpcy ligand with its sterically encumbered cyclohexyl groups, the polyphosphine PhP(CH₂CH₂PPh₂)₂ (etp)

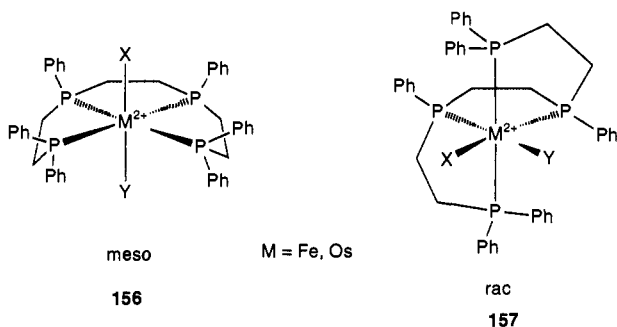
Scheme 43



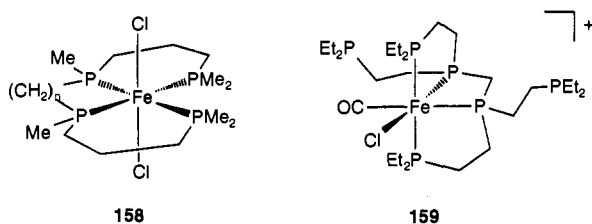
with one less methylene group and thus less flexibility acts as a bidentate ligand in 155 with one phosphorus atom of each ligand uncoordinated.^{192,193}



meso- and *rac*-tetraphos iron and osmium complexes 156 and 157 allowed Morris to probe the stereochemical control of hydrogen atom exchange with dihydrogen. Thus the *meso* complex holds the H and H₂ ligands far apart and prevents exchange. Stereocontrol in the *rac* complex forces the H and H₂ ligands in the *cis* position and encourages exchange.¹⁹⁴

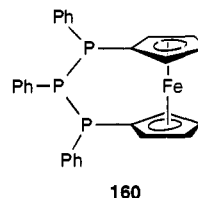


The linear tetraphosphaalkane Me₂P[CH₂]₃PMe-[CH₂]₇PMe[CH₂]₃PMe₂ forms diamagnetic complexes,¹⁹⁵ e.g. 158, by stereochemically coordinating to the metal in a *mer* fashion. In contrast the hexaphosphine (Et₂PCH₂CH₂)₂PCH₂P(CH₂CH₂PEt₂)₂ (eHTP) gives the binuclear complex [Fe₂Cl₂(eHTP)]²⁺ which is cleaved by CO, and an iron chloride moiety is released to form mononuclear 159 with dangling phosphorus donor ligands.¹⁹⁶



A mixture of *fac* and *mer* isomers arise from the ligand PhP(CH₂CH₂PPh₂)₂, because of the relatively short methylene chain. When the total chain length is increased, structural data on Ph₂PC₂H₄P(Ph)C₂H₄P(Ph)C₂H₄PPh₂ iron complexes show that all four phosphorus atoms can coordinate to the metal atom under special conditions.¹⁹⁷

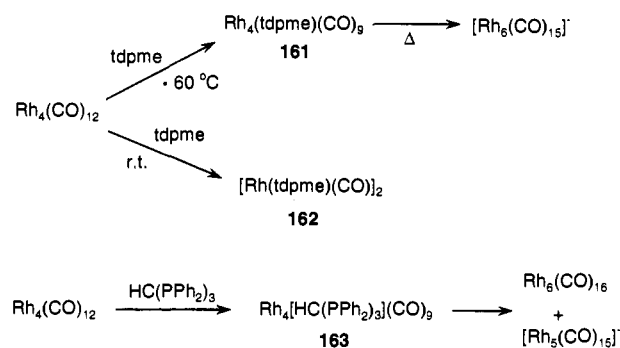
An interesting polyphosphine of ferrocene 160 has been synthesized but no reactions have been reported.¹⁹⁸



6. Cobalt, Rhodium, and Iridium

The metal carbonyl compounds of group 9 portray examples of the cluster-forming potential and stereochemical control by sterically small polyphosphine podands. Scheme 44 illustrates that the initial reactions

Scheme 44

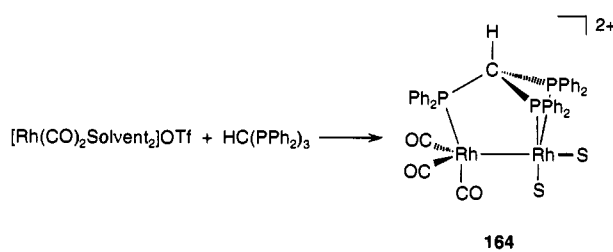


of Rh₄(CO)₁₂ with tdpme are face capping or fragmentation at different temperatures. The sterically larger ligand tdpme exhibits less control in reactions with Rh₄(CO)₁₂. At -60 °C face capping of the rhodium tetrahedron occurs followed by heating to isolate the uncoordinated hexarhodium species. However, at room temperature fragmentation of the tetramer is observed with tdpme. Only at low temperatures the tetrahedral cluster is maintained (Scheme 44). The clusters can be reversibly protonated without decomposition.¹⁹⁹ The tripod ligand HC(PPh₂)₃ only exhibits face capping.²⁰⁰

Tripod, HC(PPh₂)₃, with the least steric constraints interacts with rhodium and iridium clusters to give M₄(CO)₉HC(PPh₂)₃ compounds which do not decompose at 120 °C in toluene. These can be eventually converted into polyhedral compounds.

In Scheme 45 the construction of a small cluster with HC(PPh₂)₃ is displayed albeit with the formation of a

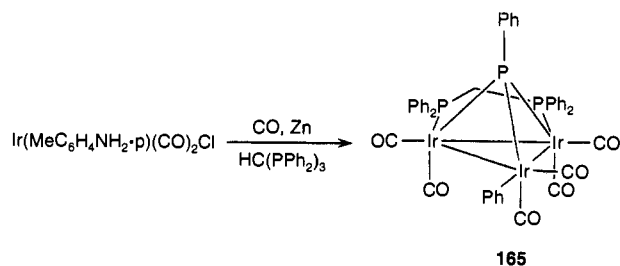
Scheme 45



single metal-metal bond.²⁰¹⁻²⁰³ Thus treatment of a rhodium dicarbonyl compound with $\text{HC}(\text{PPh}_2)_3$ gives a partially constructed cluster. Addition of further rhodium fragments to increase the size of the cluster was not reported.

Fragmentation of the polyphosphine ligand can occur under certain conditions. When $\text{IrCl}(\text{CO})_2(p\text{-CH}_3\text{C}_6\text{H}_4\text{-NH}_2)$ is used instead of $\text{Ir}_4(\text{CO})_{12}$, a cluster is formed but part of the polyphosphine is cleaved in the process (Scheme 46).²⁰⁴ The tridentate phosphine ligand

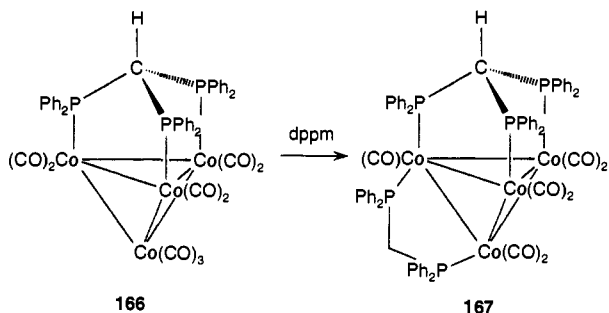
Scheme 46



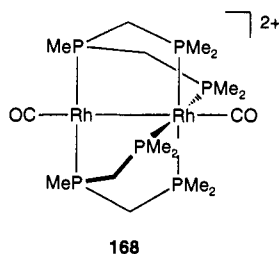
underwent HC-PPh_2 bond cleavage followed by protonation to give dppm ($\text{Ph}_2\text{PCH}_2\text{PPh}_2$) and PPh_2 . The PPh_2 moiety underwent P-Ph bond cleavage leading to $\mu_3\text{-PPh}$ and formation of a Ir-Ph bond. The different reaction products in terms of stereocontrol by the polyphosphine are not understood.

Dicobalt octacarbonyl interacts with the tripod ligand $\text{HC}(\text{PPh}_2)_3$ to give the cluster $\text{Co}_4(\text{CO})_9\text{HC}(\text{PPh}_2)_3$ ²⁰⁵ (166). This is the same type of behavior observed with 163. The prominent electron-donating character of tripod with its stereocontrol allows the addition of another cobalt carbonyl fragment to the initial $\text{Co}_2(\text{CO})_8$. Thus the tripod retards metal-metal bond cleavage without breaking down the cluster, and simultaneously it promotes carbonyl displacement from the apical position (167, Scheme 47).

Scheme 47



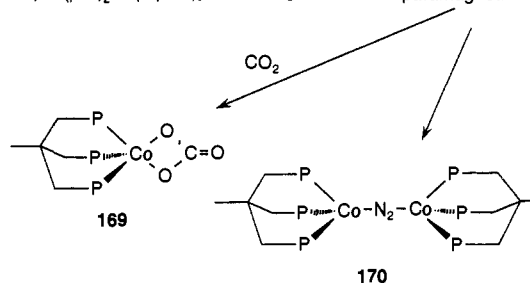
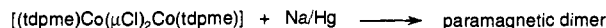
Another example of "cluster" formation by sterically small polyphosphine podands is 168,²⁰⁶ although this reaction is not completely general and often depends



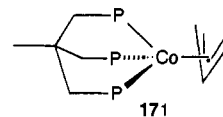
upon the metal coordination sphere and reaction conditions.

A highly reactive paramagnetic dimer 170 can be obtained by reduction of a tdpme cobalt complex²⁰⁷⁻²⁰⁹ (Scheme 48). This will form a paramagnetic carbonate

Scheme 48

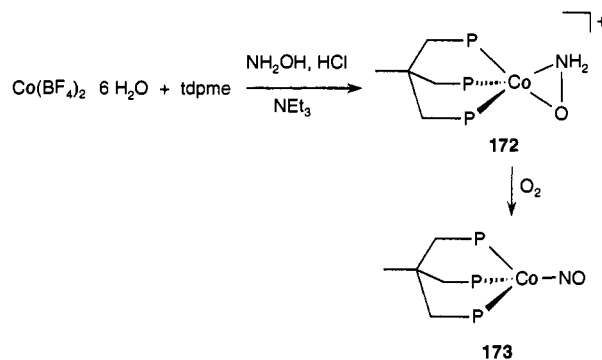


derivative 169 and a paramagnetic 17-electron allyl complex 171 which is effective in catalytic allylic alkylations.²¹⁰



The stereochemical control of tdpme allows three coordination sites on cobalt to interact with hydroxyl amine to give an $(\eta^2\text{-oxo})$ amine 172 which can be oxidized with oxygen to the cobalt nitrosyl 173 (Scheme 49). The stereochemical control imposed by tdpme is

Scheme 49

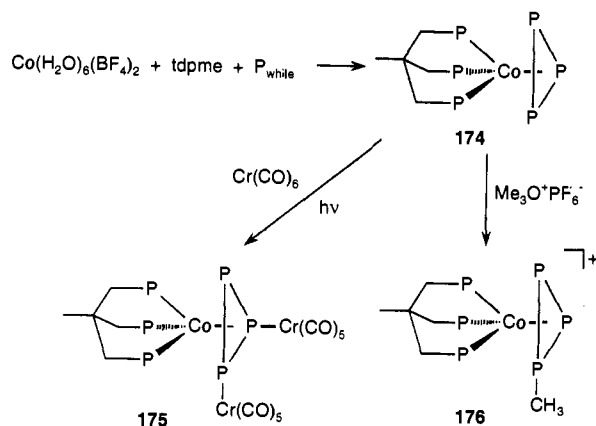


tetrahedral around the metal so the nitrosyl group is linear instead of bent. These reactions indicate the forceful stereochemical control by the tdpme ligand which guarantees that open coordination sites will be available for coordinated ligand reactivity.

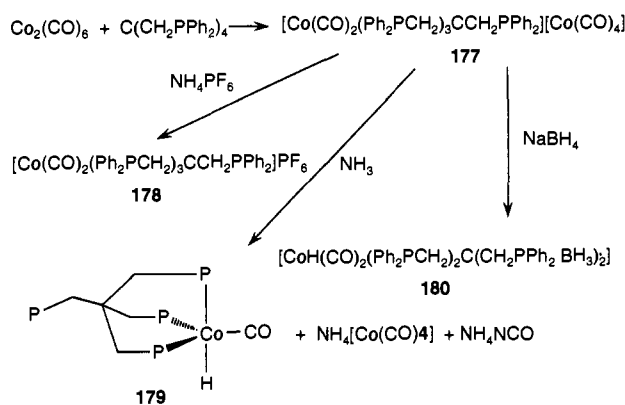
An additional example of such ligand reactivity that is promoted by a polyphosphine is the aqueous cobalt system and tdpme which interacts with white phosphorus by replacing one of the phosphorus tetrahedra with the stereocontrolled face of the cobalt complex. The lone pair electrons on the phosphorus atoms can be coordinated to transition metal carbonyls 175 or alkylated as in 176^{211,212} (Scheme 50). Treatment of $\text{Co}(\text{tdpme})\text{P}_3$ with $\text{CF}_3\text{SO}_3\text{H}$ gives $[\text{Co}(\text{tdpme})\text{P}_3\text{H}](\text{CF}_3\text{SO}_3)_2 \cdot (\text{H}_5\text{O}_2)$.²¹³ The product consists of a H^+ -bridged Co-P edge, H_3O^+ , and a molecule of water.

A spiro type of polyphosphine ligand gives a podal complex 179 (Scheme 51) with one dangling donor

Scheme 50



Scheme 51



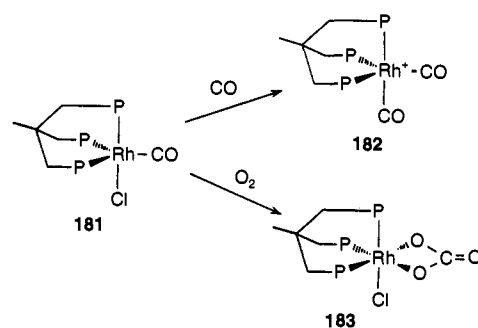
arm^{214} by using cobalt octacarbonyl as the starting material. Note that the sterically larger podand does not stabilize cluster formation but rather forms *facially* directed compounds.

The three equivalent *cis* positions which are generated when the *facial* tripod ligand tdpme is coordinated to an octahedral metal center has made tdpme one of the most popular polyphosphines. Especially with the d^8 metals rhodium and iridium, a rich chemistry which is relevant to several areas in organometallic chemistry exists. The $[\text{M}(\text{tdpme})]$ fragment ($\text{M} = \text{Rh}, \text{Ir}$) is able to coordinate important reactive ligands such as acyl groups, alkyls, aryls, carbon monoxide, hydrides, and olefins in a stable way and in a large variety of different arrangements and bonding modes. Thus by using tdpme instead of three monophosphines, some reaction intermediates such as the alkyl carbonyl $\text{Rh}(\text{tdpme})(\text{CO})\text{R}$,^{35,215} the carbonyl acyl $\text{Rh}(\text{tdpme})(\text{CO})(\text{COR})$,^{35,215} ($\text{R} = \text{Me}, \text{Et}, \text{Ph}$), the dihydride carbonyl $[\text{Rh}(\text{tdpme})(\text{H})_2(\text{CO})]\text{BPh}_4$,³⁵ the ethylene ethyl $\text{Rh}(\text{tdpme})(\text{C}_2\text{H}_4)\text{C}_2\text{H}_5$,^{35,216} the dihydride alkyl $[\text{Ir}(\text{tdpme})(\text{H})_2\text{C}_2\text{H}_5]$,²¹⁷ and ethylene dihydride $[\text{Ir}(\text{tdpme})(\text{H})_2\text{C}_2\text{H}_4]\text{BPh}_4$,²¹⁷ and the hydride alkyl carbonyl $[\text{Ir}(\text{tdpme})(\text{CO})(\text{C}_2\text{H}_5)\text{H}]\text{BPh}_4$ ²¹⁷ could be isolated and characterized.

One of the earliest studies on the complex chemistry of d^8 metals with the tripod ligand $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$ was Collman's report.^{218,219} Here the chloro group could be substituted with a variety of anions including azide, and the iridium and rhodium carbonato complexes could be made by oxidation of the coordinated CO ligand (Scheme 52).

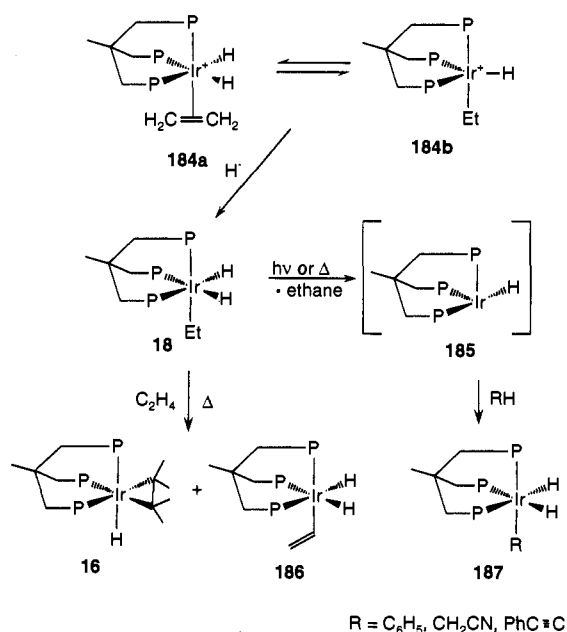
More recent examples show that the dihydride $[\text{Ir}(\text{tdpme})(\text{H})_2\text{C}_2\text{H}_4]^+$ (184a) is in a fast equilibrium

Scheme 52



with its $[\text{Ir}(\text{tdpme})(\text{C}_2\text{H}_5)\text{H}]^+$ (184b) isomer via a hydride migration/ β -H elimination process (Scheme 53). The reduction of $[\text{Ir}(\text{tdpme})(\text{H})_2\text{C}_2\text{H}_4]^+$ with

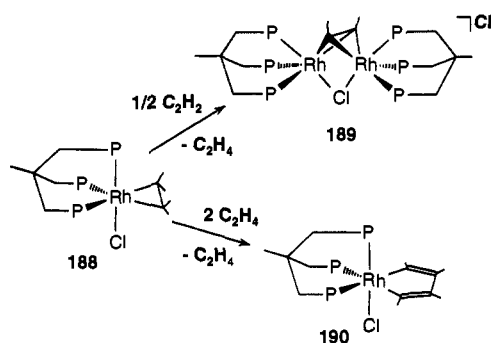
Scheme 53



NaBH_4 or LiHBEt_3 leads to the dihydride ethyl complex $\text{Ir}(\text{tdpme})(\text{H})_2(\text{C}_2\text{H}_5)$ (18). Ethane but no hydrogen or β -H elimination occurs to form the reactive intermediate $[\text{Ir}(\text{tdpme})\text{H}]$ (185) upon thermolysis or photolysis of $\text{Ir}(\text{tdpme})(\text{H})_2(\text{C}_2\text{H}_5)$ (18). The geometry which tdpme imposes on the $[\text{Ir}(\text{tdpme})\text{H}]$ (185) fragment forces frontier orbitals with the appropriate symmetry and energy for insertion into sp^3 , sp^2 , and sp C-H bonds to be generated. This has been used by Bianchini et al. to study the intermolecular C-H activation reaction at iridium.²²⁰ The π -olefin complex 16 and the vinyl dihydride 186 are observed upon thermolysis of 18 in the presence of ethene. It was concluded that the two products form via different transition states which is in agreement with studies performed on the isoelectronic fragment $[(\eta^5\text{-C}_5\text{H}_5)\text{IrPMe}_3]$.²²¹

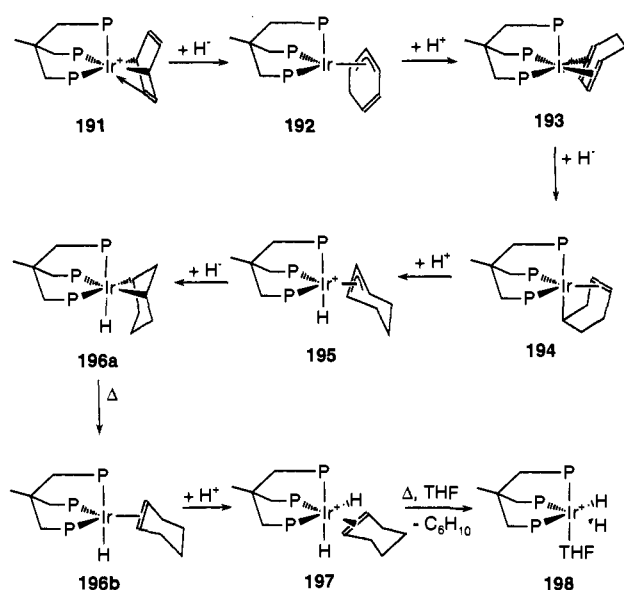
Reaction of $\text{Rh}(\text{tdpme})(\text{C}_2\text{H}_4)\text{Cl}$ (188) with ethyne in a 1:1 ratio forms $[(\text{tdpme})\text{Rh}(\mu\text{-Cl})(\mu\text{-}\eta^2\text{-}\eta^2\text{-C}_2\text{H}_4)\text{Rh}(\text{tdpme})]$ (189) as brick red crystals while with a metal/ethyne ratio of 1:2 off-white crystals of $\text{Rh}(\text{tdpme})(\eta^2\text{-C}_4\text{H}_4)\text{Cl}$ (190) are obtained (Scheme 54).²²² This species is an active catalyst for acetylene cyclo-trimerization and functionalization.²²³ The η^4 -benzene complex $[\text{Ir}(\text{tdpme})(\eta^4\text{-C}_6\text{H}_6)]^+$ (191) could be isolated when rhodium is replaced by iridium.²²⁴ This species

Scheme 54



has allowed one to study the stepwise reduction of the η^4 -coordinated benzene to cyclohexene.²²⁵ The use of tdpme as ligand has enabled the authors to characterize the η^3 -cyclohexadienyl (192), η^4 -cyclohexadiene (193), cyclohex-1-ene-4-yl (194), η^3 -allyl (195), and the 1,3-diyl (196a) and its isomer 196b as intermediates (Scheme 55).

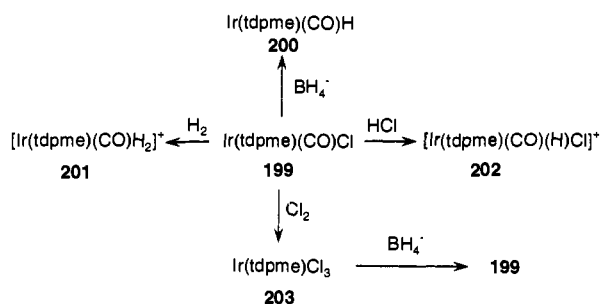
Scheme 55



Triphos $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$ can confer some extra stability on the multiple hydrides of rhodium and iridium. For example $\text{IrH}_3(\text{PPh}_3)$ as the *fac* and *mer* complex is stable but the corresponding rhodium complex is not. By using tdpme the rhodium complex is stabilized and interacts with CO to give $\text{Rh}(\text{tdpme})(\text{CO})\text{H}$ (209).²²⁶

Some additional examples of reactions with iridium complexes are shown in Scheme 56.²²⁷ The pentaco-

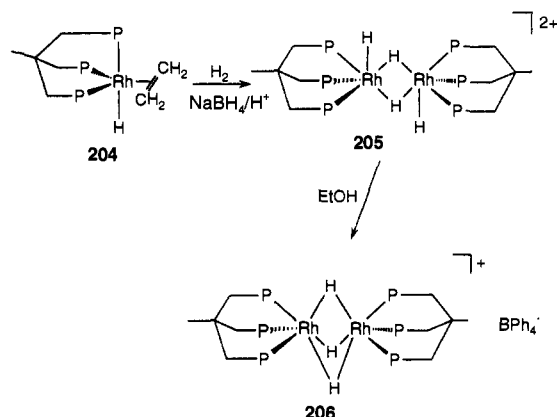
Scheme 56



ordinate complexes in Scheme 56 are trigonal bipyramidal with two phosphorus atoms at the equatorial and one at the axial position. Due to the better π -bonding ability of CO, this group is equatorial and the halogen occupies the apical site.²²⁸

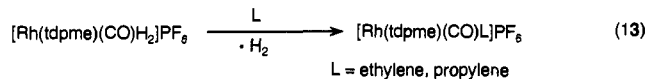
The purpose of the ethylene in 204 is most likely to protect the rhodium site for hydrogen addition to give a trihydride which reacts with acid; hydrogen is released to give 205. The bridged trihydride 206 forms from EtOH and completes the reaction (Scheme 57).^{229,230}

Scheme 57



There is no report on whether ethylene is reduced or not to ethane. Compound 206 is paramagnetic although there is very little temperature variation in its magnetic susceptibility.

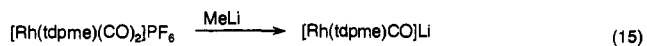
Baird²³¹ observed that some complexes with specific ligands could not be made by substitution of CO from $[\text{Rh}(\text{tdpme})(\text{CO})_2]\text{PF}_6$. Complexes of PPh_3 , ethylene, and propylene have to be prepared by displacement of hydrogen:



A route to the trimethylrhodium complex is described in eq 14. $\text{Rh}(\text{tdpme})\text{Me}_3$ reacts with CO to the acyl CO adduct $\text{Rh}(\text{tdpme})(\text{CO})\text{CMe}_3$.²¹⁵ No ethane but acetone is observed during the reaction. This implies that a phosphine arm of tdpme is decoordinates during the course of the reaction.



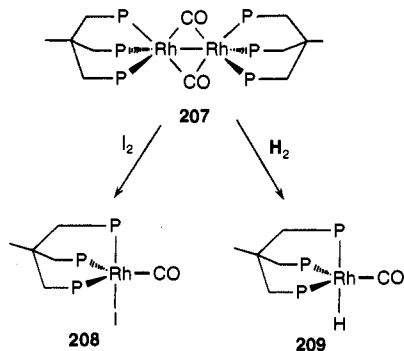
When $[\text{Rh}(\text{tdpme})(\text{CO})_2]\text{PF}_6$ is treated with MeLi, the nucleophile attacks the CO group to give the acyl product which eliminates acetone after a second attack by MeLi to result in the final product anion²³² (eq 15). The vibration of the stretching frequency of CO is often an indicator of substitution of CO or addition.



Interestingly the complex $\text{Rh}(\text{tdpme})(\text{CO})\text{Me}$ is inert to MeI, but in the presence of Me_3P it reacts with MeI to form $[\text{Rh}(\text{tdpme})(\text{CO})(\text{PMe}_3)]^+$ and methane, but no ethane. The formation of $\text{Rh}(\eta^2\text{-tdpme})(\text{CO})(\text{PMe}_3)\text{Me}$ was detected but the exact nature of the reaction is still unclear.²³³

The *fac*-coordinating character of $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$ is instrumental in influencing the formation of metal-metal-bonded compounds,²³⁴ although the rhodium-rhodium bond in the following can be cleaved by specific reagents (Scheme 58). This is similar to the

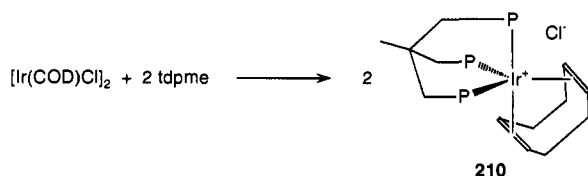
Scheme 58



cluster-forming capabilities of the smaller podal ligands.

The COD iridium complex **210** was recently prepared and characterized²³⁵ (Scheme 59). The barrier to

Scheme 59



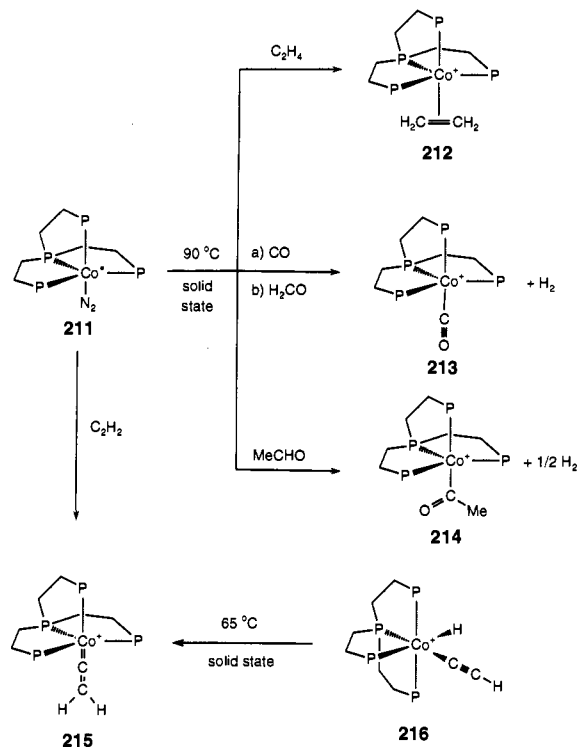
pseudorotation is significantly lower than that observed for $[\text{Ir}(\text{PMe}_3)_3(\text{COD})]\text{Cl}$. The chelating *tdpme* is responsible for the fast turnstile mechanism in contrast to the Berry pseudorotation which accounts for the high fluxionality of the monodentate counterparts. The structure of $[\text{Ir}(\text{tdpme})(\text{COD})]^+$ in the solid state is best described as a distorted trigonal bipyramid, while $[\text{Ir}(\text{PMe}_3)_3(\text{COD})]^+$ is best represented as square pyramidal with the COD ligand and two PMe_3 groups occupying the basal sites.

Note the different chemistry presented by the COD ligand in this complex compared to the tetradentate one described later by Bianchini (Scheme 66).

The observation that the off-white or pale yellow *cis*-hydride alkynyl complexes $[\text{Co}(\text{PP}_3)(\text{H})(\text{CCR})]^+$ ($\text{R} = \text{H}, \text{Ph}, \text{SiMe}_3, \text{CMe}_3$) transform into the corresponding red vinylidene derivatives when a solid sample is heated²³⁶ has led Bianchini and co-workers to develop a molecular solid-gas organometallic chemistry. In the solid-vapor reactions of $[\text{Co}(\text{PP}_3)(\text{N}_2)]\text{BPh}_4$ (**211**) with small organic molecules (C_2H_2 , C_2H_4 , CH_2O , MeCHO , and CO), N_2 is evolved and 1:1 complexes involving the reagents are formed²³⁷ in high yields (Scheme 60). The stereochemical control of the ligand indicates that all metal centers are accessible to the organic substrate. Fragmentation of the crystals of the precursors is not observed.

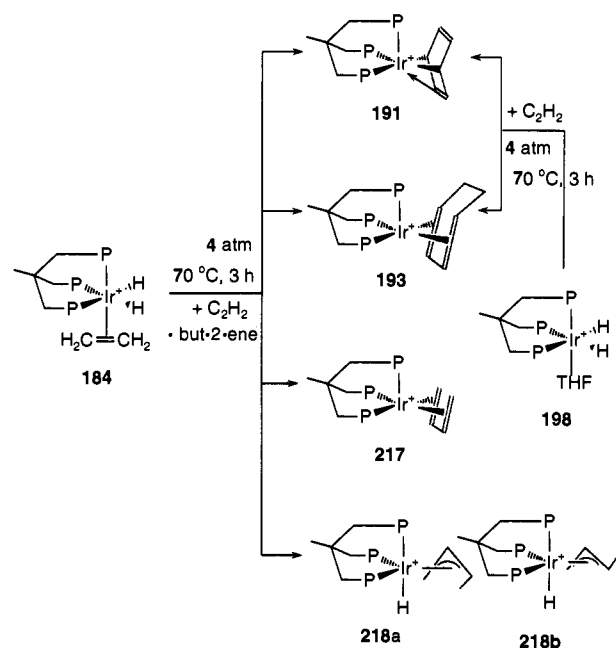
The reaction between solid metal complexes and gaseous molecules may be controlled by the restrictive environment of the reactant crystal lattice which leads to a different product distribution compared to the reaction in solution. This has been shown by the treatment of ethyne with the crystals of the η^2 -ethene

Scheme 60



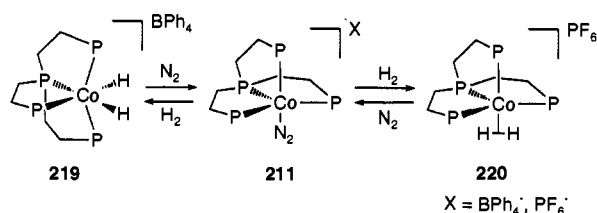
dihydride $[\text{Ir}(\text{tdpme})(\text{H})_2(\text{C}_2\text{H}_4)]\text{BPh}_4$ (**184**) which when carried out in solution yields the η^4 -benzene complex (**191**) and the η^4 -buta-1,3-diene complex **217** while in the solid-gas reaction the products shown in Scheme 61 are observed.²³⁸

Scheme 61



A reversible exchange of the H_2 and N_2 above 65°C takes place when a stream of H_2 or N_2 gas is passed over crystals of $[\text{Co}(\text{PP}_3)(\text{N}_2)]^+$ and $[\text{Co}(\text{PP}_3)(\text{H}_2)]^+$, respectively.²³⁹ X-ray studies reveal that the colorless classical dihydride **219** or the pink-red nonclassical dihydrogen complex **220** is formed depending on the nature of the counterion (Scheme 62). When **219** is

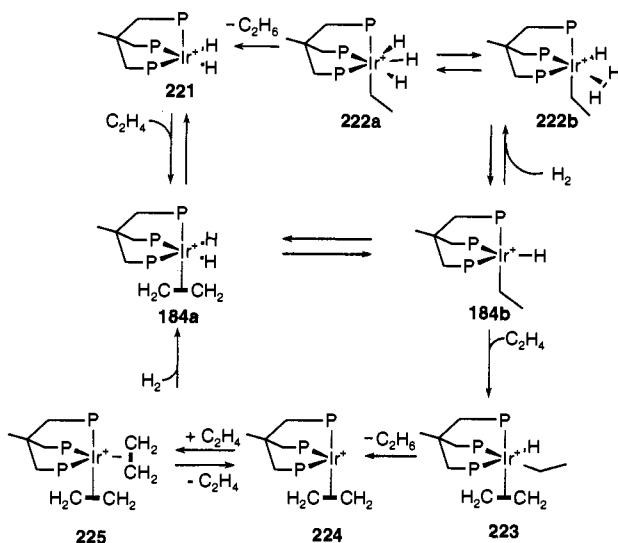
Scheme 62



dissolved the colorless classical dihydride tautomerizes into the pink-red η^2 -dihydrogen complex. The structural difference between the [Co(PP₃)] fragments in the BPh₄⁻ and PF₆⁻ salts were traced back to the opening of the *trans*-P-Co-P angles.

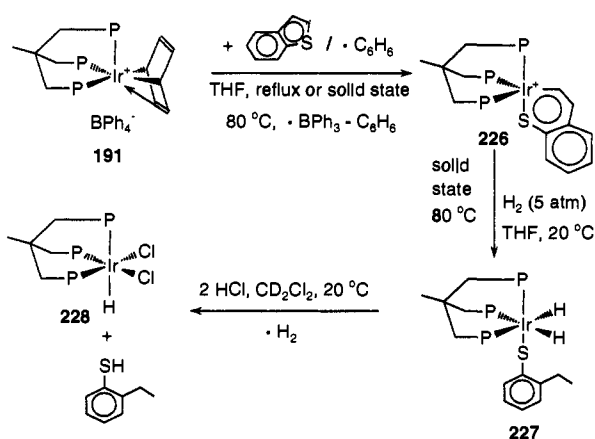
With the ethylene dihydride complex [Ir(tdpme)(C₂H₂)(H)₂]BPh₄ (184) as the precursor the solid-gas hydrogenation of ethylene can be performed catalytically.²⁴⁰ A steady-state condition at 60 °C could be maintained for several days. On the basis of experimental evidence a mechanism has been proposed which is shown in Scheme 63.

Scheme 63



The reaction of benzo[*b*]thiophene with the η^4 -benzene complex [Ir(tdpme)(C₆H₆)]BPh₄ (191) leads to the dissociation of benzene followed by the insertion of the [Ir(tdpme)]⁺ fragment into the C-S bond of benzo[*b*]thiophene forming [Ir(tdpme)(η^2 -C,S-C₈H₆S)]BPh₄ (226) (Scheme 64).²⁴¹ The yields of 90% can be

Scheme 64

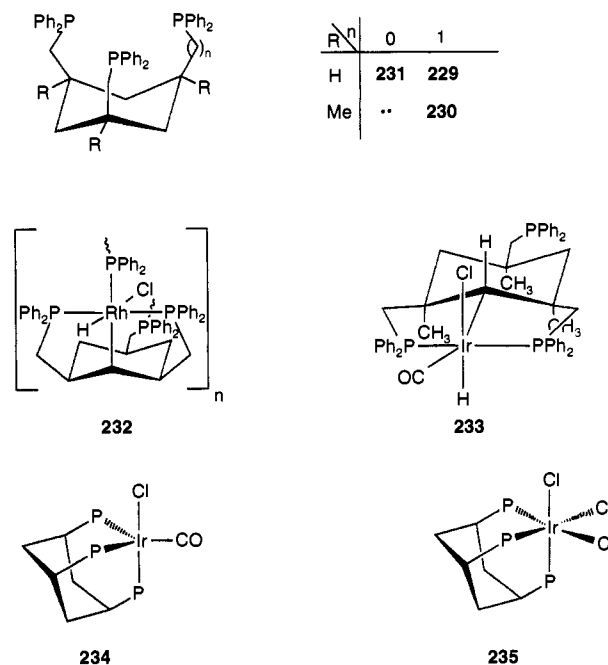


improved to 100% when the reaction components are heated as a solid-solid mixture instead of refluxing a THF solution. Treatment of 226 with H₂ in either the solid state or THF quantitatively affords Ir(tdpme)(H)₂(*o*-S(C₆H₅)C₂H₅) (227) which is completely converted to Ir(tdpme)(H)Cl₂ (228) and 2-ethylbenzenethiol by the protonolysis with an excess of gaseous HCl in CD₂Cl₂.

The solid-gas chemistry outlined above demonstrates the ability of organometallic fragments which are stabilized by tripodal phosphine ligands to assist in heterogeneous reactions. It was found that in certain cases the nature of the counterion is important for the activity of the metal complexes.

Recently the cyclohexane frame was introduced as a backbone in tripodal phosphine ligands (Scheme 65).

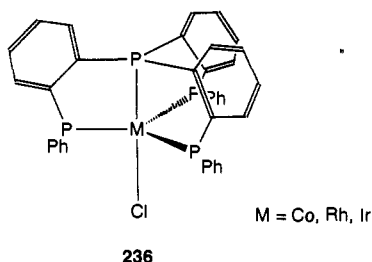
Scheme 65



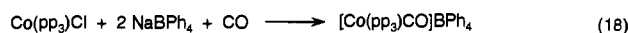
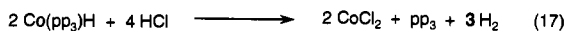
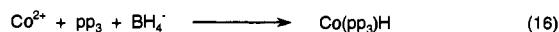
The complexation behavior of these ligands is not only a function of the bite angle but also depends on the flexibility of the cyclohexane ring and the specific *cis,cis* arrangement of the phosphine functional groups. The complexation of 229 to the Rh-Cl fragment resulted in an octahedral environment at the metal.²⁴²

In solution the compound forms an oligomer (232). In spite of the higher flexibility of 230 only two phosphine groups are coordinated to the metal center in 233, while the third remains noncoordinated.²⁴³ In both complexes an intramolecular C-H metalation takes place resulting in the oxidative addition of a ring methylene C-H bond to the metal. In contrast the tripodal ligand 231 is able to coordinate all three phosphine groups to one metal center resulting in either trigonal bipyramidal or octahedral adamantane-type structures 234 and 235.²⁴⁴ The steric constraint of the ligand (tdppcy) does not allow the dissociation of one phosphine arm while the other two remain bonded to the metal. This might be important in developing catalytic systems. The barrier to pseudorotation in tdppcy-stabilized pentacoordinated complexes is lower than in comparable complexes stabilized by tdpme.^{215,244,245}

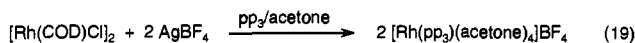
Complexes of cobalt, rhodium, and iridium have played an important role in understanding the stereochemical control of polyphosphine complexes because the coordination stereochemistry was defined by using factors such as chelate, bite angle, and sterically demanding groups. One of the first such ligands was that of Venanzi²⁴⁶ with the following structure:



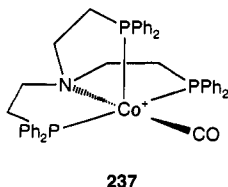
The central phosphorus atom forms a complex with the metal so that a trigonal bipyramidal coordination is found.^{247,248} Soon afterward other ligands like the linear polyphosphines $\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$ and $\text{PhP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2$ and tripodal ligands $\text{N}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$ for example illustrated that one can vary the ring size and bite angle just by changing the number of CH_2 groups.²⁴⁹ Cobalt complexes of the rare $\text{Sb}(\text{CH}_2\text{CH}_2\text{CH}_2\text{AsMe}_2)_3$ were prepared as ionic salts, i.e. $[\text{Co}\{\text{Sb}(\text{CH}_2\text{CH}_2\text{CH}_2\text{AsMe}_2)_3\}]\text{ClO}_4$.²⁵⁰ The ligand $\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$ more commonly forms trigonal-bipyramidal complexes and less commonly square-pyramidal compounds. It can function as a bidentate or tridentate ligand to one metal or bridge two or more other metals.²⁵¹⁻²⁵⁴ Examples and reactions are shown in eqs 16-18.



Complexes with the ligand tris(2-diphenylphosphino)ethylphosphine and rhodium (pp_3) can be made as follows:²⁵⁵



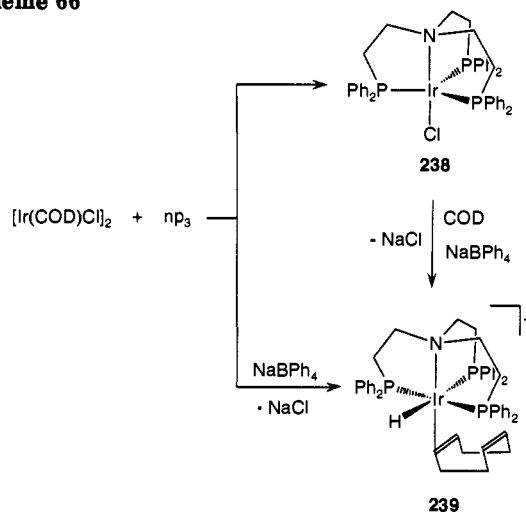
A common podal system which contains nitrogen forms complex 237. In reactions with aquo cations of cobalt, the medium is important since two different series of products hydroxo and aquo are obtained depending on whether EtOH, THF or acetone are used.^{256,257}



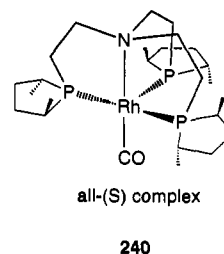
Bianchini²⁵⁸ has observed the intermolecular metalation of the COD ligand by 238. In contrast the corresponding rhodium complex orthometalates a C-H bond of the np_3 ligand even in the presence of COD. The tripodal ligands certainly confer considerable elec-

tron density on the metal for oxidative addition reactions. However the stereochemical control of the ligand must be subtle enough for distinctions to be made between rhodium and iridium (Scheme 66).

Scheme 66

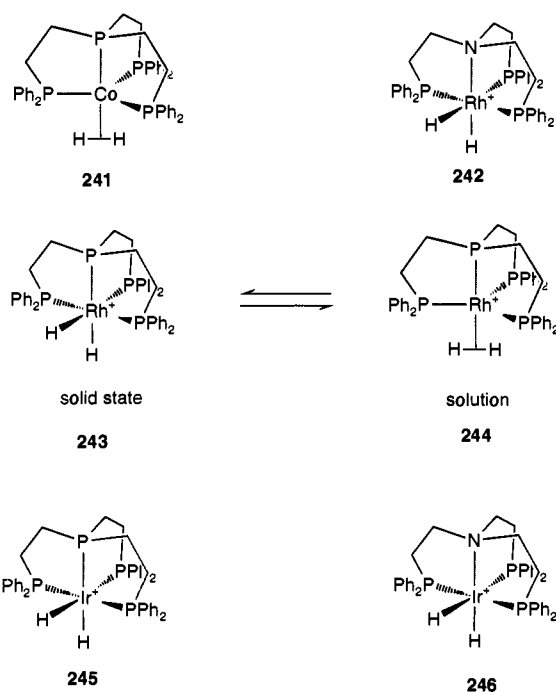


A current use of polyphosphine ligands is in chiral hydrogenation.^{259,260} Such a successful chiral complex of rhodium is 240.



The importance of the interplay between the stereochemical control of the polyphosphine and the nature of the metal center is demonstrated by the *cis*-dihydride and η^2 -dihydrogen complexes of the Co, Rh, and Ir triad with the tripodal ligands pp_3 and np_3 (Scheme 67). While the pp_3Co fragment forms a η^2 -dihydrogen complex of C_{3v} symmetry in solution and in the solid state,²⁶¹ the rhodium derivative exists as a *cis*-dihydride complex with pseudo octahedral C_{2v} symmetry in the solid state and in solution below 183 K. At higher temperature the compound rearranges to a trigonal bipyramid of C_{3v} symmetry with a η^2 -dihydrogen ligand.²⁶² The iridium complex maintains the octahedral geometry with the classical dihydride structure in solution and in the solid state.²⁶³ From theoretical studies it was concluded that if a $d^8 \text{ML}_4$ complex adopts a C_{3v} symmetry, H_2 will be nonclassically coordinated as η^2 , otherwise the classical dihydride structure is more stable.²⁶⁴ This is due to the better back-donation from an occupied metal π -orbital to the $\text{H}_2 \sigma^*$ orbital in the latter case. In general the C_{3v} symmetry of $d^8 \text{ML}_4$ complexes is unstable with respect to the octahedral C_{2v} structure. However, the tripodal ligands pp_3 and np_3 are able to compensate for the instability of the C_{3v} symmetry by their strong steric requirements which makes the η^2 coordination of H_2 possible. The increase in π -back-donation on going from cobalt to iridium favors the classical bonding mode and thus only

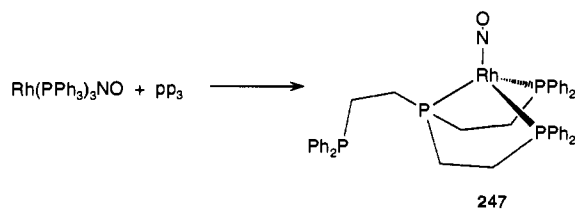
Scheme 67



octahedral dihydride complexes exist. When the central P atom in pp_3 is replaced by a N atom, which delivers more electron density to the metal, the better $M-H_2$ (σ^*) back-donation results exclusively in octahedral dihydride complexes.²⁶⁵ A direct consequence of the different binding modes of H_2 in the pp_3MH_2 ($M = Co, Rh, Ir$) series is their different behavior toward olefins. The cobalt derivative quantitatively isomerizes dimethyl maleate to dimethyl fumarate while the rhodium complex hydrogenates the C-C double bond. The iridium complex does not react with dimethyl maleate at all.

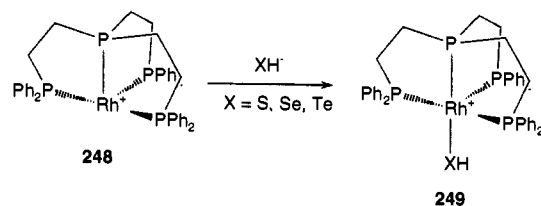
Polyphosphine ligands which impose a square-planar geometry on a d^8 metal can potentially control metal nitrosyl complexes to adopt bent nitrosyl geometry.^{266,267} Complex 247, however, remains tetrahedral with one of the donor atoms dangling²⁶⁸ and the nitrosyl group is linear (Scheme 68). Most likely the NO group with

Scheme 68



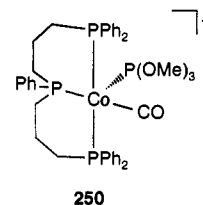
its three electrons overrides the stereochemical control of the polyphosphine.

Scheme 69



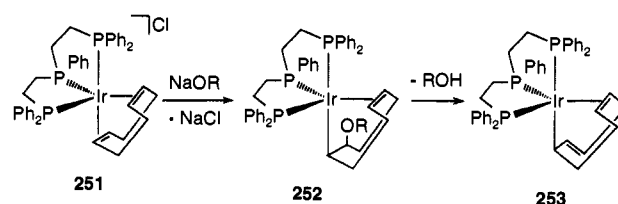
When groups other than nitrosyl are used, as shown in Scheme 69 the vacant trigonal-bipyramidal site is readily substituted.²⁶⁹

Linear polyphosphines form a broad spectrum of complexes with group VIII metals. For example, the linear ligand $PhP(CH_2CH_2PPh_2)_2$ (etp) constitutes trigonal-bipyramidal complexes with cobalt $[Co(etp)L(CO)]X$ and $[Co(etp)(CO)_2]X$ while the ligand $PhP(CH_2CH_2CH_2PPh_2)_2$ (ttp) prefers the square pyramidal geometry in the complex $[Co(ttp)(CO)P(OMe)_3]^+$.^{270,271}



More recently Kubiak²⁷² has shown that the coordinated COD in 251 (Scheme 70) can interact with bases

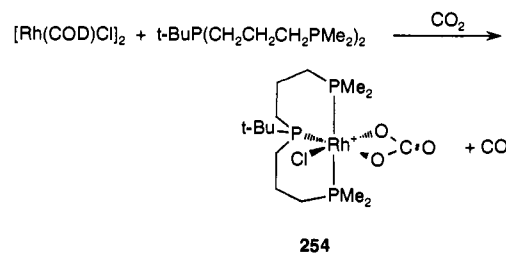
Scheme 70



in two different ways. When bases like alkoxides are used the mechanism goes through a *mer* intermediate to form 253, when bases like pyridine are used the *mer* intermediate is not observed. The etp ligand has enough stereochemical control to prevent a Michael-type adduct in the mechanism of forming 253 with bases like pyridine.

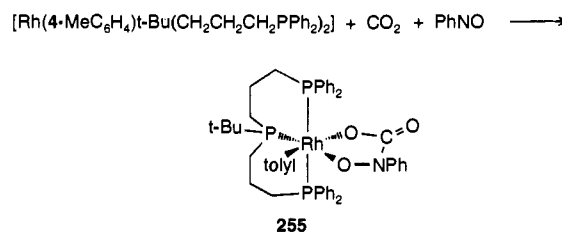
Linear polyphosphine coordination complexes will disproportionate carbon dioxide (Scheme 71),^{273,274}

Scheme 71



although with bulky groups placed on the ring next to the metal atom the carbon dioxide adducts can undergo insertion reactions²⁷⁵ (Scheme 72).

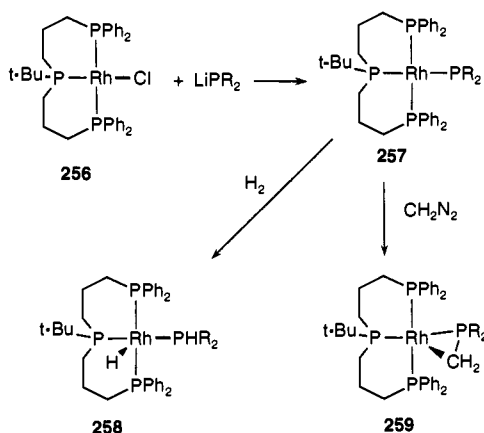
Scheme 72



Complex 256 readily undergoes substitution with phosphides which in turn can be converted with

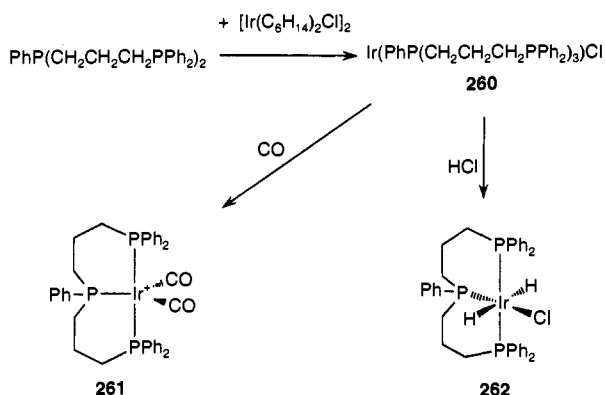
hydrogen (258) and diazomethane (259) into two types of coordinated phosphines^{276,277} (Scheme 73).

Scheme 73

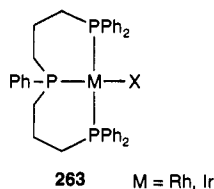


Dahlenburg also showed that the iridium complex 260 was easily prepared²⁷⁸ and underwent reactions with CO to give 261 and with HCl to give 262. Dahlenburg also observed that ortho-metalated iridium complexes will form chelates²⁷⁹⁻²⁸² (Scheme 74).

Scheme 74



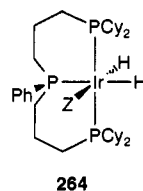
The electron-rich chelating triphosphine ligand $\text{PhP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2$ occupies three of four coordination sites in square-planar rhodium and iridium complexes (263).²⁸³ By variation of the fourth coordination position with different anionic ligands, the *cis* and *trans* influences have been studied.^{284,285}



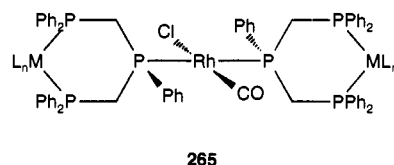
With the more hindered podand, $\text{PhP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{-PCy}_2)_2$, only oils could be isolated. The meridional stereochemistry of the ligands and electron-releasing character of the phosphines make the OH group basic enough to interact with a variety of organic acids and SO_2 .

Some of the stereochemical aspects of these rhodium complexes are discussed in the ref 268. Iridium also forms *mer* octahedral complexes, and because the

phenyl group on the apical carbon is *syn* or *anti* to the chloride ligand, diastereomers can be obtained.²⁸⁶⁻²⁸⁸



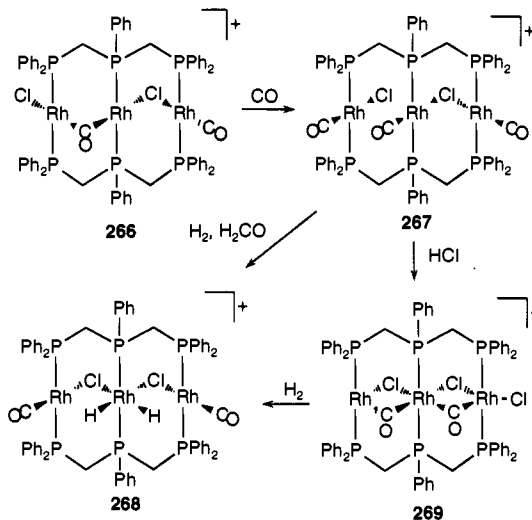
Linear polyphosphines with small bite angles like $\text{PhP}(\text{CH}_2\text{PPh}_2)_2$ form 265⁸⁸ although polynuclear metal derivatives are known.²⁸⁹⁻²⁹¹



Carbonyl complexes of rhodium with the same ligand bis(diphenylphosphinomethyl)phenylphosphine (dpmp) are structure sensitive to the anion present. Thus $[\text{Rh}_3(\mu\text{-dpmp})_2(\text{CO})_3\text{X}_2][\text{BPh}_4]$ loses CO to give $[\text{Rh}_3(\mu\text{-dpmp})_2(\mu\text{-CO})(\text{CO})(\mu\text{-X})\text{X}][\text{BPh}_4]$.²⁹²

The reactions of the metal carbonyls are typical oxidative addition reactions²⁹³ in which cooperativity between the metal atoms is promoted by the stereochemical control of the linear tridentate ligand (Scheme 75). The dihydride 268 is stable in the solid state and in air.

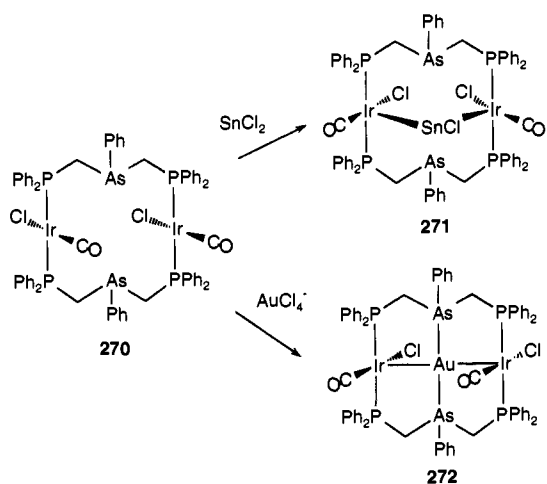
Scheme 75



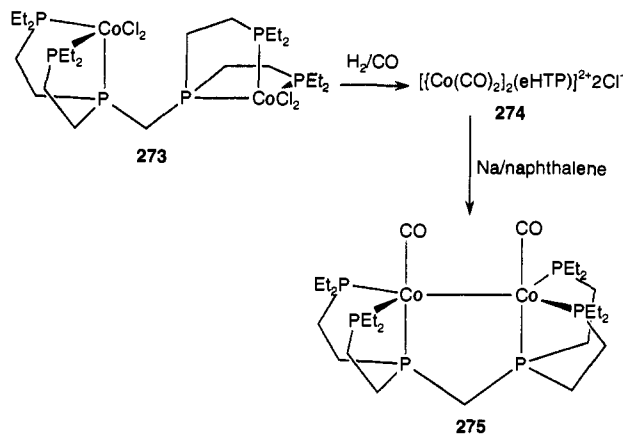
When the apical atom is replaced by arsenic, a series of mixed metal complexes can be made (271 and 272, Scheme 76). Some are photoluminescent.²⁹⁴

Stanley²⁹⁵ has expanded on the chemistry of the hexatertiary polyphosphine $(\text{Et}_2\text{PCH}_2\text{CH}_2)_2\text{PCH}_2\text{CH}_2\text{P}(\text{CH}_2\text{CH}_2\text{PET}_2)_2$ (eHTP). With CoCl_2 it gives Co_2Cl_4 (eHTP) 273 which forms a metal carbonyl complex (Scheme 77). The ligand in 273 can undergo trigonal bipyramidal-square planar changes about the cobalt center. When the cation is reduced with sodium naphthalene the closed mode configuration is formed (275).²⁹⁶

Scheme 76

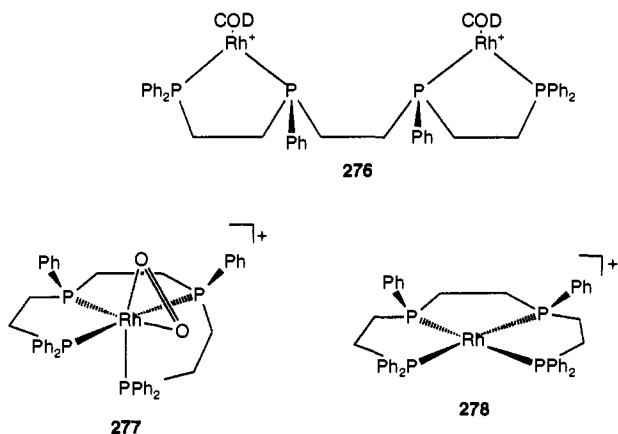


Scheme 77



The commercial linear tetraphosphine ligand $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{P}(\text{Ph})\text{CH}_2\text{CH}_2\text{P}(\text{Ph})\text{CH}_2\text{CH}_2\text{PPh}_2$ exists as a stereoisomeric mixture. It forms *meso* and *rac* mixtures of iron compounds 156 and 157. An extension of this chemistry to group VIII was attempted in order to prepare bimetallic compounds. Thus when *meso* tetraphos is treated with $(\text{COD})\text{Rh}(\text{acac})$ and HBF_4 , complex 276 is generated (Scheme 78). Hydrogenation

Scheme 78



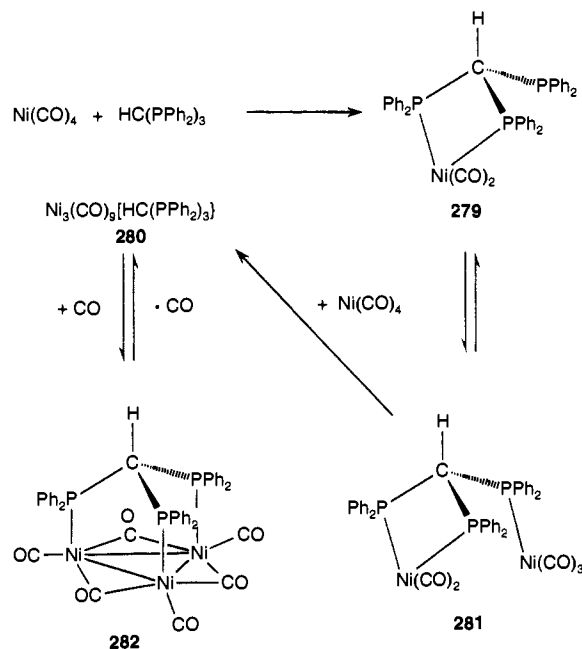
of 276 gives 278 which interacts with oxygen to give 277. The corresponding *dl* isomer to 278 also reacts with oxygen but much faster. Thus stereochemical control governs the kind of isomer that forms from either

the starting *meso* or *dl* tetraphos. This control is reflected in the type of $\text{Ph}-\text{Ph}$ interactions which occur and demonstrates that small changes in ligand geometry can have profound effects on the coordination chemistry of the complex.²⁹⁷

7. Nickel, Palladium, and Platinum

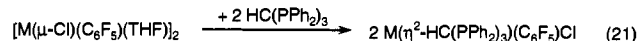
Small bite angle podal polyphosphines interact with nickel carbonyl compounds in much the same way as octacarbonyldicobalt compounds to form clusters and monometallic derivatives²⁹⁸ (Scheme 79). Thus ster-

Scheme 79



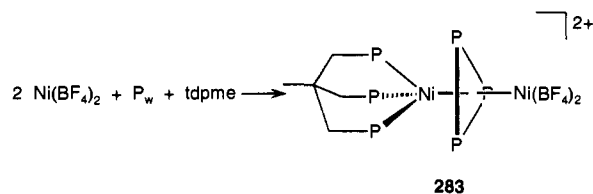
eochemical control of metal synthesis is similar to other metals that have been studied, although attempts to carry the synthesis further to heterometallic complexes by using $\text{HC}(\text{PMe}_2)_3$ and platinum were not successful.²⁹⁹

Specific studies with platinum and palladium have just recently been initiated, and the major effects of polyphosphines stereochemical control with small bite angles like in $\text{HC}(\text{PPh}_2)_3$ are not completely clear.³⁰⁰



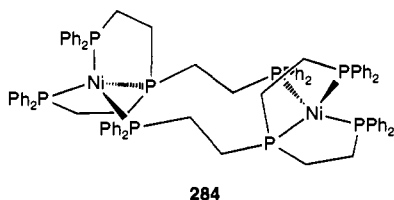
The $[\text{Ni}(\text{tdpme})]^{2+}$ fragment is basic enough to cleave white phosphorus and replace one of the phosphorus atoms in the tetrahedral phosphorus cluster (Scheme 80).³⁰¹

Scheme 80



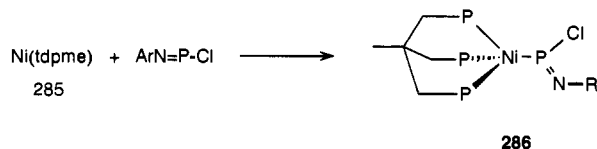
The specific ligand $N(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$ does not effectively neutralize the positive charge on nickel(II) so that a sterically unhindered target for nucleophilic attack is still present. Thus BH_4^- reduces the nickel atom to Ni^0 . The phenyl groups make somewhat of a cage around the metal atom and thus stereochemically control the chemistry.^{155,209,254,256,302}

A nickel(0) complex with an unusual dimeric structure (284) has been reported with $\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$ as the ligand.³⁰³



The stereochemical rigidity of $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$ with Ni^0 was used to make a complex of the following haloiminophosphine ($\text{ArN}=\text{P}-\text{X}$, $\text{X} = \text{Cl}, \text{Br}$) (Scheme 81). The tripod ligand conferred an extra degree of

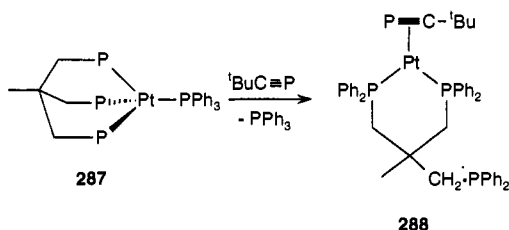
Scheme 81



thermal sensitivity to the complex, which was not experienced by other phosphine complexes of the haloiminophosphine.³⁰⁴

The ease with which some of the phosphorus donor atoms in a platinum tdpme complex can be replaced is illustrated in Scheme 82.³⁰⁵ Although one of the podal

Scheme 82



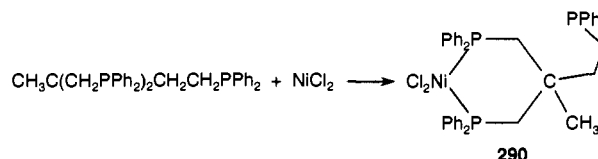
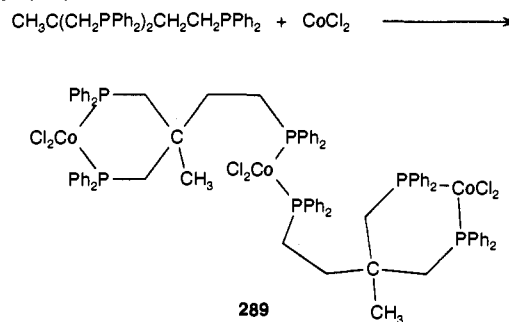
donating arms is removed in the reaction, stereochemical control over the entire complex is still maintained. This again is a decided advantage in forming complexes with the podal polyphosphines.

By careful addition of the reagents, mixed-metal tricoordinate phosphines can be obtained with a tripod phosphine ligand that has different methylene chain lengths³⁰⁶ (Scheme 83).

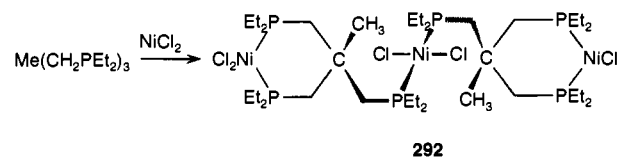
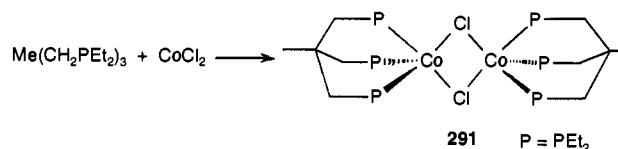
The more symmetrical podal phosphine ligand forms the different derivatives shown in Scheme 84.

The complexes $\text{Ni}\{\text{N}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3\}$, $[\text{Ni}\{\text{N}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3\}\text{H}]\text{BF}_4$, and $[\text{Co}\{\text{N}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3\}]\text{BF}_4$ are rare examples of trigonal-bipyramidal complexes which are stereochemically generated by these podal ligands. Their synthesis is very interesting and is displayed in Scheme 85 with pp_3 that has an apical phosphorus atom.³⁰⁷

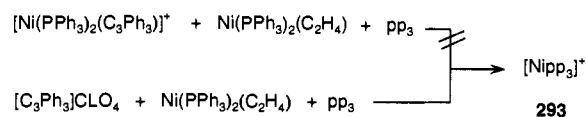
Scheme 83



Scheme 84



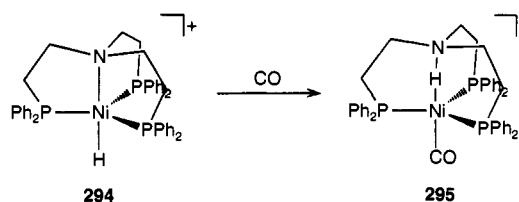
Scheme 85



Note that the cyclopropane derivative cannot be initially complexed to the nickel atom, or the reaction will not give the desired product. The only pathway to the podal complex is to introduce a different olefin complex, cyclopropenium ion and polyphosphine.

A solid-state reaction occurs with the nickel podal 294 and CO. The metal hydride has a $\nu(\text{MH})$ of 1855 cm^{-1} which is characteristic of a metal that is electron rich from the tripod ligand.^{251,252,257,308} When CO is added to the material, the hydrogen atom "tunnels" to form a metal-hydrogen bridge bond³⁰⁹ (Scheme 86).

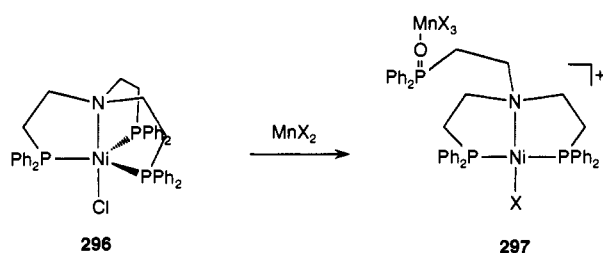
Scheme 86



The hydrogen atom in the complex above can be replaced by alkyl groups like CH_3 , Et , and CH_2Ph , but movement of these groups was not reported. These compounds are very stable to reaction because there is

kinetic shielding around the metal atom by the substituents on the phosphorus atom.^{310,311} The same nickel complex interacts with MnI_2 in the manner shown in Scheme 87.³¹²

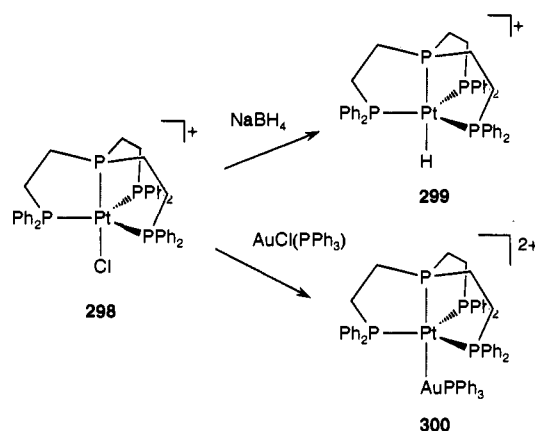
Scheme 87



Early work with platinum centered on the use of tdpme as a ligand. Specifically Pt⁰ complexes showed that only four phosphorus atoms of six were coordinated to platinum. With Pt(II) derivatives, the chelate ring adopts a flexible twist boat configuration.³¹³⁻³¹⁵

Complexes with tdpme, ttp, ttpcy, etp, and PhP(CH₂-CH₂PMe₂)₂ as ligands are all bidentate at room temperature, although coordination of the central phosphorus atoms is possible.^{316,317} Later structural work showed that platinum(II) forms complexes in much the same way as nickel. Substitution of the halogen atom in 298 for hydrogen (Scheme 88) occurs

Scheme 88



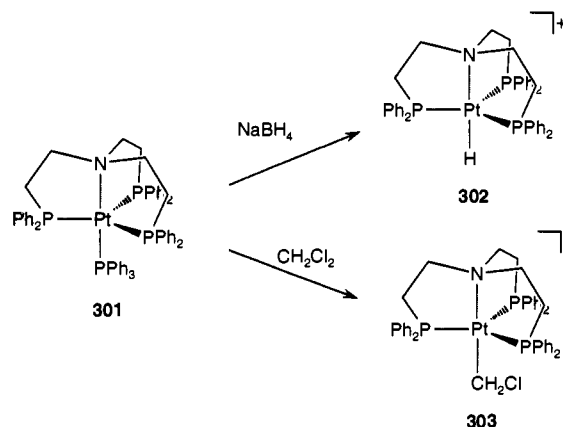
readily.^{318,319} The hydride in 299 is readily replaced with the isolobal AuL⁺ moiety.³²⁰

Attempts to prepare the Pt⁰ complex with three phosphorus donor atoms was not successful, but the H could be replaced with SnCl_3^- and phosphides after deprotonation of the corresponding secondary phosphine adduct.³²¹⁻³²⁴ Similar results have been obtained with nitrogen as the apical atom³²⁵ (Scheme 89).

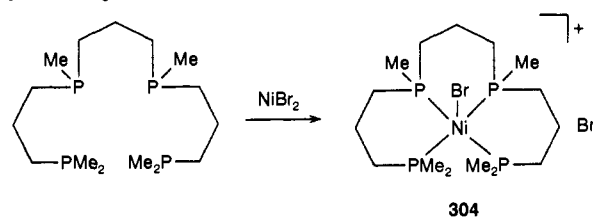
Nickel, palladium, and platinum complexes of the linear polyphosphine PhP(CH₂CH₂CH₂PPh₂)₂ are known.³²⁶ Stelzer observed that the tetraphos derivative formed square-pyramidal complexes with nickel (304)³²⁷ (Scheme 90).

When nickel(II) is used as a template, macrocycle 306 can be made^{328,329} (Scheme 91). Some of the macrocycles which have alkyl substituents on the phosphorus atoms have such high ligand fields that the nickel atom cannot be removed with concentrated KCN at 80 °C. However, when phenyl substituents are used the metal can be removed from the complex.³³⁰

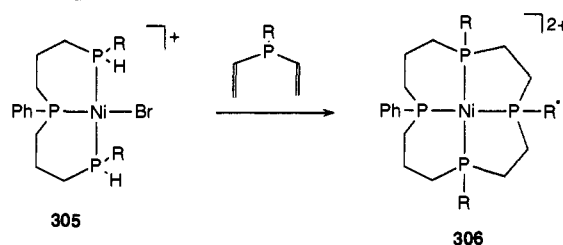
Scheme 89



Scheme 90

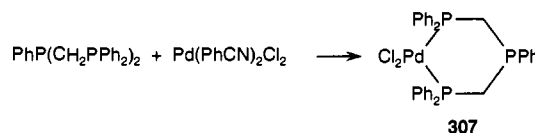


Scheme 91

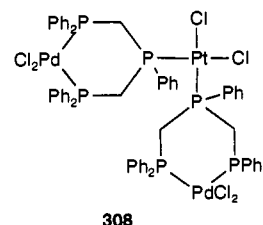


Early research on the polyphosphine complexes of palladium showed that compounds of the type $\text{M}\{\text{MeC}(\text{CH}_2\text{PPh}_2)_3\}_2$ (M = Pd, Pt) could exist. The complexes exhibited various types of isomerism.³³¹ Later results revealed that not all of the phosphorus atoms necessarily coordinate to the metal atom (Scheme 92).^{290,332}

Scheme 92



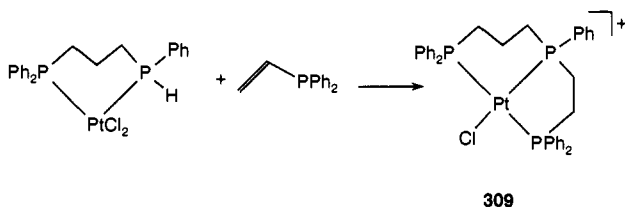
All of these polyphosphines leave a dangling phosphorus atom when they behave as bidentate ligands, but these in turn can form bonds to other metals.⁸⁸



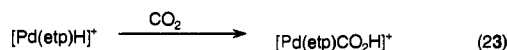
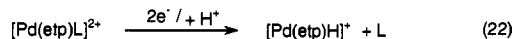
When the methylene chain is lengthened, the boat-type coordination with a dangling phosphorus group

still predominates. This is particularly the case with the ligands $\text{PhP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph})_2$, $\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$, and $\text{PhP}(\text{CH}_2\text{CH}_2\text{PMe}_2)_2$. They all form square-planar complexes with Pt(II) and a dangling phosphine which also exchanges with the bound phosphines.³³³ Mixed-chain complexes can be made with platinum as a template.^{334,335} Thus stereochemical control can be introduced into the complex by varying the number of methylene groups (Scheme 93).

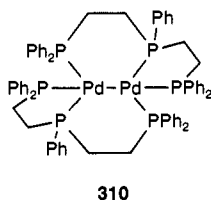
Scheme 93



Linear polyphosphine complexes of palladium will promote electrochemical reduction reactions with carbon dioxide.³³⁶ The nature of the ligand is very important and influences the rate of the reaction. No increase in the rate is found when bulky substituents on the terminal phosphorus atoms are used. It was



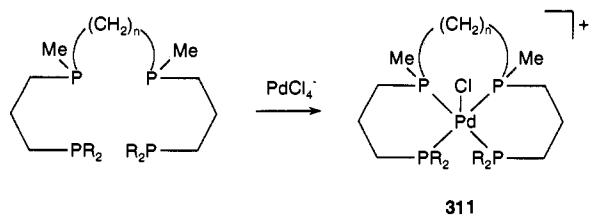
observed that an increase in the steric bulk on the central phosphorus atom is more important than electronic effects. The bite size of the chelate ring has some impact on the reaction as well. Complexes with donor atoms other than phosphorus are not catalytically active. Certain side reactions produce a bimetallic compound of interest.³³⁷



Interestingly, the same type of complexes with Pt as the central metal atom are not effective catalysts.

Multidonor linear phosphines generate square-pyramidal complexes with palladium³³⁸ (Scheme 94).

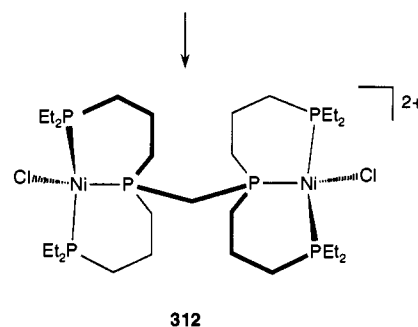
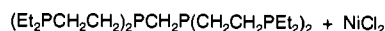
Scheme 94



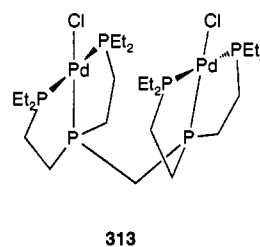
Linear polytetraphosphines form similar square-planar complexes with nickel as observed with cobalt; *meso* and *rac* forms of 312 are also possible³³⁹ (Scheme

95). These tetradentate materials designed to juxtapose metal atoms have been prepared by Stanley. Although

Scheme 95

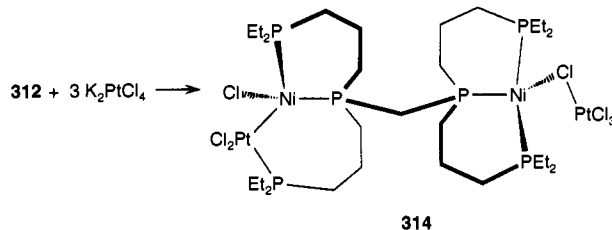


these compounds do not have intact metal-metal bonds, the ligands coordinate the metals in a "closed" mode (313).³⁴⁰ Stereochemical design is important here especially with the appended groups on the phosphorus atoms.

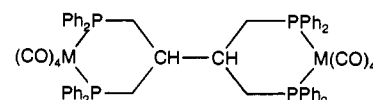
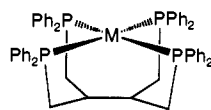


Stanley has synthesized an interesting mixed-metal complex by using the stoichiometry shown in Scheme 96.^{341,342}

Scheme 96



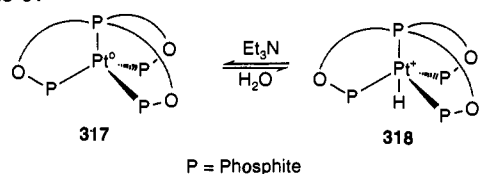
In an attempt to exert stereochemical control on the synthesis of planar Ni^0 , Pd^0 , and Pt^0 complexes, Verkade introduced the tetratertiary phosphine ligand $[\text{CH}(\text{CH}_2\text{PPh}_2)_2]_2$. However, there are not enough backbone carbon atoms to enable the ligand to bind all four phosphorus atoms to one metal center (315). The bimetallic complex 316 is obtained instead. Since the basic stereochemical control has been shown to be operative, these results offer the opportunity to form future heterobimetallic derivatives.³⁴³



The possibility that tetradentate complexes can be used as optically active catalysts has suggested the

synthesis of the derivative in Scheme 97 by using more manageable phosphite derivatives.³⁴⁴ In this case

Scheme 97



stereochemical control of the internal groups allows the synthesis of a rare polyphosphite Pt⁰ complex.

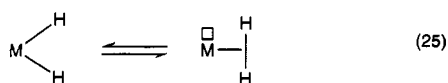
IV. Catalytic Chemical Reactions

The goal in catalysis to produce pure products in high yields requires the rigorous stereochemical control of the catalytic reactions. Thus the idea to use polyphosphine-stabilized metal complexes as catalysts has emerged early. However, the nondissociative character of the chelating polyphosphines is a disadvantage in catalytic processes which require open sites at the metal center. This seems to limit the application of polyphosphines in catalysis to processes which do not need many available positions at the metal center. Several elegant examples have been reported to circumvent this drawback.

In square-planar d⁸ metal complexes with chelating tridentate phosphine ligands the catalytic cycle does not need the dissociation of a phosphine group if the fourth position is a participative ligand during the reaction sequence.^{11,345}

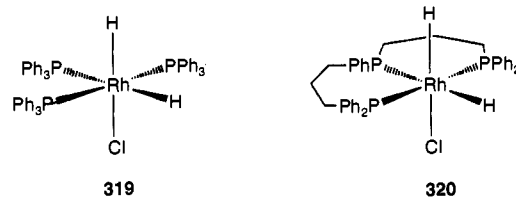
Hydride polydentate ligands which contain phosphorus and nitrogen donors are able to supply free coordination sites at the metal by dissociation of either a phosphine or a nitrogen donor.^{13,346-349}

A free coordination site can be created by the tautomerization of a dihydride to a dihydrogen complex:²⁶¹



A. Hydrogenation

While Rh(PPh₃)₃Cl is an efficient hydrogenation catalyst under mild conditions³⁵⁰ the comparable complex Rh(ttp)Cl adds irreversibly hydrogen under the same conditions and is inactive. The proposed hydrogenation mechanism³⁵¹ suggests the dissociation of the PPh₃ group *trans* to hydride leaving a free coordination site for binding the olefin molecule. However, in Rh(ttp)(H)₂Cl the dissociation of the phosphorus *trans* to the hydride ligand is not possible without breaking the two chelate rings. There is no low-energy pathway to create a free coordination site. The situation changes when the chlorine in the d⁸ square planar complex Rh(ttp)Cl is replaced by a ligand which is involved in the catalytic cycle. Thus Rh(ttp)H and Co(ttp)H (generated *in situ*) hydrogenate 1-octene under mild conditions (room temperature and 1 atm H₂).³⁴⁵ When in these complexes a fifth coordination



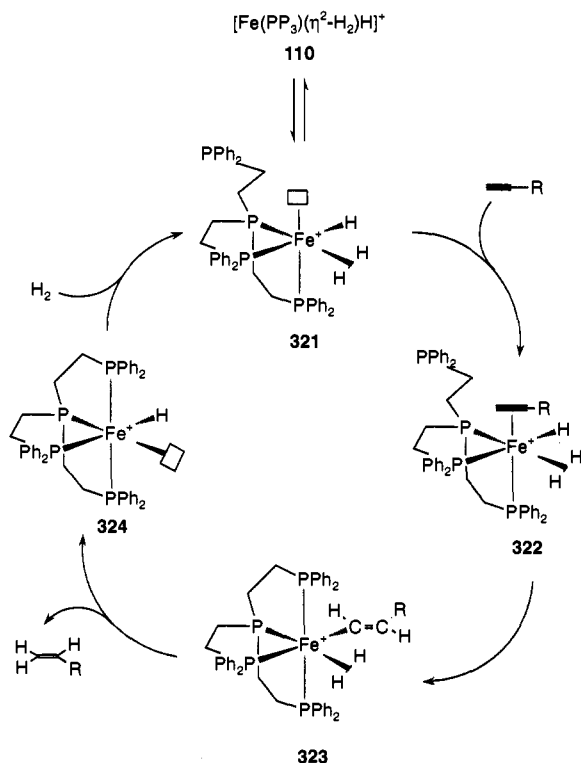
site is occupied by a nondissociating ligand (CO, phosphine) no hydrogenation of 1-octene under the same conditions is observed. This shows that the catalytic cycle for the hydrogenation of 1-octene with M(ttp)H (M = Rh, Co) does not require the dissociation of a phosphorus group of the triphosphine ligand. The catalytic cycle can simply be described as the coordination of an olefin, hydride transfer to produce a metal alkyl, oxidative addition of H₂, a second hydride transfer, elimination of the alkane, and regeneration of the catalyst.³⁴⁵

Since AlEt₃ and AlEt₂Cl have been used to generate the metal hydride via β-elimination, Rh(ttp)Cl acts in the presence of either AlEt₃ or AlEt₂Cl as an effective catalyst for homogeneous hydrogenation of terminal olefins and 1-octyne.^{352,353} Under comparable conditions (20 °C, 750 Torr H₂) this system is 25 times faster than Rh(PPh₃)₃Cl. Careful ³¹P and ¹H NMR spectroscopy showed that Rh(ttp)H is formed instantaneously and that the addition of terminal olefins results in very rapid conversion of Rh(ttp)H to Rh(ttp)R. Although the exact nature of the active species is not known, NMR data suggest that one AlEt₃ molecule is bonded directly to the rhodium atom while a second species is bridged via the Rh-H linkage.

Hydrogen of 1-octene with Ru(ttp)(H)BH₄ as a catalyst has only been obtained when a base or an acid was added.¹⁸⁸ An equivalent amount of added acid generated a catalyst to selectively hydrogenate 1-octene to *n*-octane at a rate 0.75 times of Rh(PPh₃)₃Cl. In the presence of a large excess of NEt₃ a quantitative reaction with a comparable rate to that of Rh(PPh₃)₃Cl is obtained. While Ru(ttp)(H)₂ is thought to be the active catalyst in the presence of a base, the cationic complex [Ru(solvans)_x(ttp)H]⁺ might be the active species produced by the acid.

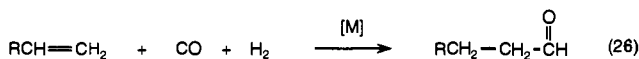
In spite of the weakly bound dihydrogen ligand in η²-H₂ complexes, experimental evidence suggests that when [Fe(pp₃)(η²-H₂)H]BPH₄ (110) is used as a homogeneous hydrogenation catalyst, a free coordination site for substrate binding is provided by the dissociation of a phosphine arm, rather than loss of H₂ coordination^{354,355} (Scheme 98). No H₂ evolution at any stage of the reaction was observed which is in agreement with the independence of the reaction rate of the H₂ precursor. The transformation of 1-alkynes to alkenes is highly selective. After the 1-alkyne insertion across the Fe-H bond, a proton transfer from the acidic dihydrogen ligand to the σ-vinyl group liberates the alkene. It is worth mentioning that according to this mechanism the hydrogen does not need to be oxidatively added to the metal in order to react with the olefin. In contrast in the selective hydrogenation of phenylacetylene to styrene where [Ru(pp₃)(η²-H₂)H]⁺ (111) acts as a catalyst precursor, a free site for the incoming molecule is generated by the dissociation of the η²-H₂ ligand and not by unfastening of a phosphine arm.³⁵⁶

Scheme 98



B. Hydroformylation

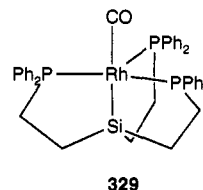
Hydroformylation is the condensation of 1-alkenes, H_2 , and CO to give aldehydes from a complex which has rhodium or cobalt as the typical metal center. It is



one of the most important homogeneous catalytic processes which is industrially used to exploit the production of aldehydes which are then converted to important basic chemicals like alcohols. Extensive mechanistic investigations on RhPPh_3 -catalyzed systems reveal that a large excess of PPh_3 is required to maintain a high selectivity toward linear aldehydes.^{357,358} The large excess was thought to be necessary because at least two phosphine ligands must be coordinated to the metal center during the selectivity step of the reaction. Although this has been known for many years it was not until recently that polyphosphines have successfully been employed in hydroformylation reactions.

A series of polyphosphines of the type $(\text{CH}_3)_{4-n}\text{Si}(\text{CH}_2\text{CH}_2\text{PPh}_2)_n$ ($n = 1-4$) (325-328) have been tested in rhodium-catalyzed hydroformylation.³⁵⁹ The objection was to design the ligands in a way that chelation was prevented, but at the same time supply a high concentration of phosphines in the area around the rhodium center. The bridge length connecting two phosphorus atoms was chosen so that eight-membered rings would be formed upon chelation which is known to be an unfavorable ring size.³⁶⁰ Kinetic studies are consistent with the nonchelating character of these ligands. Comparison reactions with 325-328 and PPh_3 at the same ligand/rhodium ratio of 12 showed that the rate with PPh_3 as ligand is much faster, the selectivity to *n*-propanal of 59% is much lower compared to 83%

obtained with 327 and 328, respectively. It has been observed that under continuous reaction conditions for 5 days, the activity decreased steadily to zero. A metal complex could be isolated and characterized in which the starting ligand $(\text{CH}_3)\text{Si}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$ underwent a carbon-silicon bond cleavage. After removing the methyl group the undercoordinated silicon atom is then able to intramolecularly add to the rhodium metal:



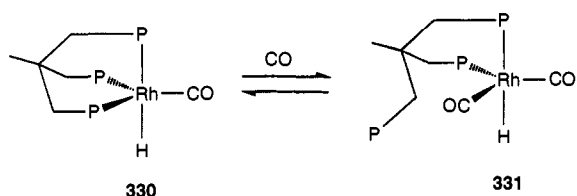
Complex 329 contains a rare $\text{Rh}(\text{I})\text{-Si}$ bond.^{360,361} It was stated that the lack of a hydride ligand at the metal center of 329 is responsible for its inactivity in the hydroformylation process.

Replacement of three comparable monophosphines by the tripodal ligand tdpme has supported the isolation and the characterization of the carbonyl acyl $\text{Rh}(\text{tdpme})(\text{CO})\text{COR}$ ^{35,215} and the alkyl carbonyl $\text{Rh}(\text{tdpme})(\text{CO})\text{R}$ ($\text{R} = \text{Me}, \text{Et}, \text{Ph}$)^{35,215} which are believed to be reaction intermediates in the hydroformylation process. This and the observation that $\text{Rh}(\text{tdpme})(\text{CO})\text{COMe}$ was easily hydrogenated to acetaldehyde and that the carbonyl hydride $\text{Rh}(\text{tdpme})(\text{CO})\text{H}$ (209) reacts with excess ethylene has inspired these authors to investigate the hydroformylation based on $[\text{Rh}(\text{tdpme})]$ ^{35,215,362} The ethylene hydride complex $\text{Rh}(\text{tdpme})(\text{C}_2\text{H}_4)\text{H}$ (204) and the carbonyl hydrido complex $\text{Rh}(\text{tdpme})(\text{CO})\text{H}$ (209) were successfully employed as precursors in the hydroformylation of 1-hexene. Under mild conditions (100 °C, 30 atm H_2/CO ; 67 °C, 900 psi H_2/CO) both catalysts precursors convert 1-hexene to *n*-heptanal and 2-methylhexanal quantitatively, with only little isomerization to 2-hexene. A more detailed study of the $\text{Rh}(\text{tdpme})(\text{C}_2\text{H}_4)\text{H}$ (204) system unveiled that $[\text{Rh}(\text{tdpme})\text{H}]$ is the active catalyst. Increasing the catalyst to substrate ratio increases the selectivity but reduces the activity of the catalyst. Under hydroformylation conditions the catalyst forms dimers which display less activity. The carbonyl hydride is ca. 10% less active than ethylene hydride; both create comparable isomeric compositions. At lower temperatures $\text{Rh}(\text{tdpme})(\text{CO})\text{H}$ (209) produces a linear to branched ratio close to the commercially applied catalyst $\text{Rh}(\text{PPh}_3)_2(\text{CO})\text{H}/\text{excess PPh}_3$ which demonstrates that polyphosphines are able to imitate the redundancy of PPh_3 .

When $[\text{Rh}(\text{tdpme})(\text{CO})\text{C}_2\text{H}_4]^+$ and $[\text{Rh}(\text{tdpme})(\text{CO})\text{H}]^+$ are used as catalyst precursors, the 14-electron fragment $[\text{Rh}(\text{tdpme})]^+$ was identified as the active catalyst species. $[\text{Rh}(\text{tdpme})]^+$ is less active with an increase in selectivity when the temperature is raised.³⁵

The catalytic cycle of the hydroformylation demands that at least in one step tdpme has to become bidentate to avoid a 20-electron species as intermediate. Recently it has been shown that under hydroformylation conditions one of the three phosphine arms dissociates to create a free coordination site for substrate binding³⁶³ (Scheme 99).

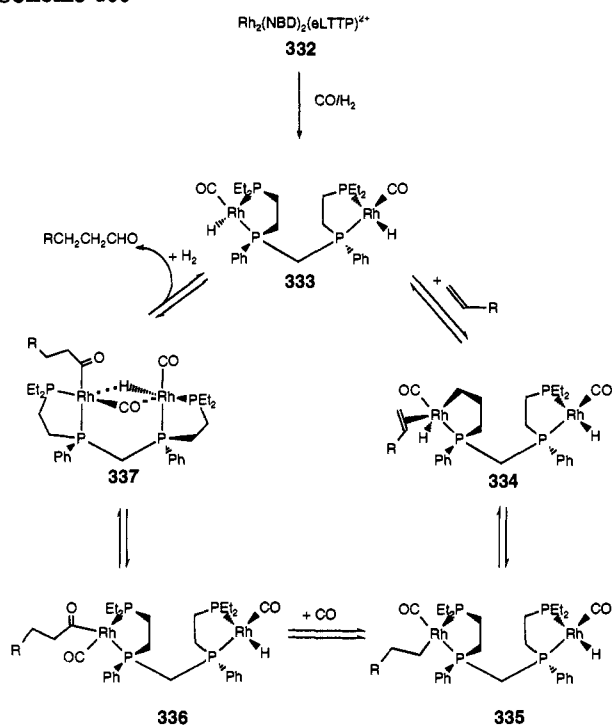
Scheme 99



There have been numerous examples of reactions involving tdpme as tripodal ligand which can only be explained on the basis of an "arm-off" process during the course of the reaction which demonstrates the kinetic lability in contrast to the thermodynamic stability of the M–P bond in chelating polyphosphine complexes.^{218,226,231,233,364–366}

It is still of some controversy, whether the aldehyde is formed by reaction of H₂ with the acyl complex or if a hydrido complex transfers the hydride to the acyl moiety.^{12,367} In the case of Rh(tdpme)(CO)H (209) evidence has been given for the reaction pathway with hydrogen, while the use of a binucleating tetraphosphine ligand system (Et₂PC₂H₄PPh)₂CH₂ (eLTTP) favors the hydride transfer from one metal to another. This tetraphosphine ligand is able to bridge and bichelate two transition metal centers and forms a highly flexible binuclear metal complex. Rh₂(NBD)₂(eLTTP)²⁺ (332, NBD = norbornadiene) (Scheme 100) is a remarkably

Scheme 100



good hydroformylation catalyst with a selectivity higher and an activity only slower by a factor of 2 compared to commercially available Rh(PPh₃)₂(CO)H/excess PPh₃. Until the acyl intermediate is formed, [Rh₂(eLTTP)] behaves like a common monometallic hydroformylation catalyst. At this stage the conformational flexibility of the ligand allows the two rhodium atoms to approach one another generating a bridged species for a facile hydride transfer. The observation that high concentrations of 1-hexene inhibit the hy-

droformylation catalysis is consistent with the bimetallic cooperativity in the proposed mechanism.

C. Miscellaneous

Bianchini et al. have reviewed the stoichiometric and catalytic transformations of alkynes, α,β -unsaturated ketones to allylic alcohols, of 1-alkynes and carboxylic acids to enol esters, and of the dimerization of 1-alkynes to *Z*-butenyne with tripodal phosphine metal complexes.^{13,388} They developed the *tripodal polyphosphine control element* which due to the stereochemical constraints the ligand imposes on the metal complexes, only one specifically favored reaction pathway is left open for high chemo-, regio-, and/or stereoselectivity.

The nonclassical hydrides M(pp₃)(η^2 -H₂)H [M = Fe (110), Ru (111), Os (112)] represent catalyst precursors for the chemoselective reduction of α,β -unsaturated ketones to allylic alcohols, with secondary alcohols as hydrogen sources.³⁶⁹ The free coordination site for substrate binding is generated by the release of H₂ which, due to the different metal–dihydrogen bond strengths in 110–112 results in different activities. When M = Ru and the substrates are acyclic ketones a disproportionation of the acyclic ketones to carboxylate ions and ethers was reported as side reactions.³⁷⁰

The use of the Rh(III) complexes [Rh(tdpme)Cl_x(MeCN)_{3-x}](CF₃SO₃)_{3-x} (x = 1–3) as catalyst precursors for various acetalization and *trans*-acetalizations was reported by Venanzi and coworkers.^{371,372} A high turnover rate together with high stereoselectivity was observed under mild reaction conditions. The *facial* chelating tripodal phosphine (tdpme) provides three equivalent *cis* positions activated by a *trans* phosphine at any time. These prerequisites are important to weakly coordinate an alcohol and carbonyl molecule in mutual *cis* positions for simultaneous activation.

Crabtree et al. showed that the tripodal phosphine-stabilized base metal polyhydride [W(PhP(CH₂CH₂-PPh₂)₂)₆] displays catalytic activity in alkane dehydrogenation in contrast to the monophosphine analogs which form catalytically inactive WH₄L₄ by disproportionation of WH₆L₃ (L = monophosphine).³⁷³

V. Conclusions

The reaction chemistry that has been described in this review portrays polyphosphine ligand complexes as major aspects of modern coordination chemical interactions. Catalysis, reactions of coordinated ligands, organometallic transformations, and structure and bonding can be represented with new perspectives because of polyphosphine ligands. Novel complexes of small molecules, like hydrogen, nitrogen, carbon dioxide, and alkanes along with important catalytic reactions can be used to develop molecular organization effects and stereochemistry needed for the synthesis of new polyphosphine ligands. Coupled with new synthetic methods that are specific for phosphorus, the union of steric effects and size and shape of ligands³⁷⁴ will contribute to the development of this chemistry.

VI. Abbreviations

acac	acetylaceton
COD	1,5-cyclooctadiene
Cp	cyclopentadiene
Cy	cyclohexyl

depe	1,2-bis(diethylphosphino)ethane (Et ₂ PCH ₂ CH ₂ -PEt ₂)
dpmp	bis[(diphenylphosphino)methyl]phenylphosphine [(Ph ₂ PCH ₂) ₂ PPh]
dppe	1,2-bis(diphenylphosphino)ethane (Ph ₂ PCH ₂ -CH ₂ PPh ₂)
dppm	bis(diphenylphosphino)methane (Ph ₂ PCH ₂ PPh ₂)
eHTP	ethyl-substituted hexatertiary phosphine [(Et ₂ -PCH ₂ CH ₂) ₂ PCH ₂ CH ₂ P(CH ₂ CH ₂ PEt ₂) ₂]
eLTTP	ethyl-substituted linear tetratertiary phosphine [(Et ₂ PC ₂ H ₄ PPh) ₂ CH ₂]
etp	bis[2-(diphenylphosphino)ethyl]phenylphosphine [PhP(CH ₂ CH ₂ PPh ₂) ₂]
NBD	norbornadiene
np ₃	tris[2-(diphenylphosphino)ethyl]amine [N(CH ₂ -CH ₂ PPh ₂) ₃]
P	PPh ₂ unless otherwise stated
pip	pipridine
pp ₃	tris[2-(diphenylphosphino)ethyl]phosphine [P(CH ₂ CH ₂ PPh ₂) ₃]
THF	tetrahydrofuran (solvent)
tdmme	bis[3-(dimethylphosphino)propyl]methylphosphine
tdpme	1,1,1-tris[(diphenylphosphino)methyl]ethane [MeC(CH ₂ PPh ₂) ₃]
tdppcy	cis,cis-1,3,5-tris(diphenylphosphino)cyclohexan [1,3,5-C ₆ H ₉ (PPh ₂) ₃]
tpepe	1,1,2-tris(diphenylphosphino)ethane [(Ph ₂ P) ₂ -CCHPPh ₂]
tpee	1,1,2-tris(diphenylphosphino)ethene [(Ph ₂ P) ₂ -CHCH ₂ PPh ₂]
trimpis	tert-butyltris[(dimethylphosphino)methyl]silane [tBuSi(CH ₂ PMe ₂) ₃]
ttp	bis[3-(diphenylphosphino)propyl]phenylphosphine [PhP(CH ₂ CH ₂ CH ₂ PPh ₂) ₂]
ttpcy	bis[3-(dicyclohexylphosphino)propyl]phenylphosphine [PhP(CH ₂ CH ₂ CH ₂ PCy ₂) ₂]

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