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Review

Synthesis and coordination chemistry of macrocyclic phosphine ligands

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Contents

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ABSTRACT

Macrocyclic phosphine compounds are sought after as ligands for transition metal complexes because of their strong binding properties. As such, these ligands are particularly useful in applications where robust transition metal–phosphine complexes are employed, as in homogeneous catalysis or in radiopharmaceuticals. This review summarizes the development of macrocyclic phosphine ligands, including their preparation and coordination to transition metals. Synthetic methods for the preparation of phosphine macrocycles are discussed, including methods for controlling ring size and stereochemistry. The coordination chemistry of macrocyclic phosphines is also reviewed. Many phosphine macrocycles are synthesized by template methods, and methods for removing the templating metal from the macrocyclic ligand are reviewed.

1. Introduction

Phosphines (PR_3) are an important class of compound because of their widespread use as ligands for transition–metal complexes. Phosphine ligands are soft, strong σ-donors, and their electronic, steric, and stereochemical properties vary based on the substituents attached to the phosphorus atoms [1–3]. Thus, choosing the correct phosphine ligands for a metal complex allows control over the electronic and steric environment of the complex [4]. Such tunability is most useful for optimizing the activity of homogeneous catalysts, and as such a plethora of phosphine-containing homogeneous catalysts have been developed for a wide variety of organic reactions including hydrogenation, hydroformylation, hydration, hydrolysis, cross-couplings, and carbon-heteroatom

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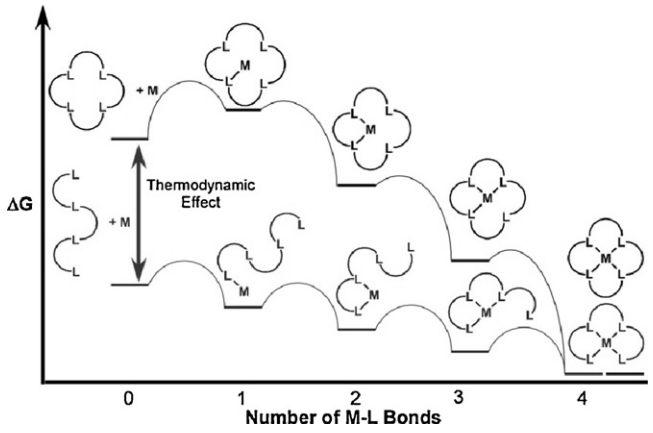


Fig. 1. Origin of the thermodynamic macrocyclic effect.

bond formations [5]. In addition, transition–metal phosphine complexes activate small molecules such as H_2, O_2, N_2, H_2O, and CO_2 [6], which makes them promising candidates for use in hydrogen fuel cells, water-splitting, ambient-pressure ammonia synthesis, and artificial photosynthesis.

Macrocyclic ligands – ligands that form a large, continuous ring around a metal ion – form extremely robust complexes because of the *macrocyclic effect* [7]. This effect has both thermodynamic and kinetic origins. The *thermodynamic macrocyclic effect* refers to the higher binding constant ($\log \beta$) for a macrocyclic ligand compared to an analogous open-chain ligand (Eq. (1)):

$$\text{Macrocyclic effect} = \Delta \log \beta = \log \beta_{\text{macrocycle}} - \log \beta_{\text{open-chain}} \quad (1)$$

Because the macrocyclic ring lacks a "free end," stepwise removal of the donor atoms is exceedingly difficult. This feature results in very slow dissociation rates of macrocyclic ligands from their complexes (the *kinetic macrocyclic effect*).

The energetic basis for the macrocyclic effect can be most easily understood by comparing the relative stabilities of *unbound* macrocyclic ligands to open-chain ligands as illustrated in Figs. 1 and 2 [8–10]. (Note in these figures that the *coordinated* macrocyclic and open-chain complexes have been arbitrarily set at equal energies.) As indicated in the figures, a free macrocyclic ligand in solution is less stable than its open-chain analog because of reduced flexibility and the resulting loss of configurational entropy. Macrocycles also have less solvent-accessible surface area and cannot be as efficiently stabilized by interactions with solvent molecules. This solvent interaction is especially important for nitrogen macrocycles in aqueous solution, where the free open-chain ligand can extend and the nitrogen atoms can accept hydrogen bonds from the solvent. By contrast, macrocyclic nitrogen ligands are conformationally restricted, and the nitrogen atoms are not as accessible for hydrogen bonding, resulting in poor stabilization of the free macrocycle. Because of this, the macrocyclic effect in nitrogen ligands is especially large (up to $\log \beta \sim 10$) [11]. Macrocyclic oxygen ligands (crown ethers), which bind electrostatically to alkali metals and other cations, show smaller macrocyclic effects ($\log \beta \sim 3$–4) [12], which are primarily attributed to enthalpic contributions [13]. Macrocyclic sulfur ligands show an even smaller macrocyclic effect ($\log \beta \sim 2$) [14], although it has been shown that additional functionalization (installation of *gem*-dimethyl groups) can help to further stabilize macrocyclic sulfur complexes [15].

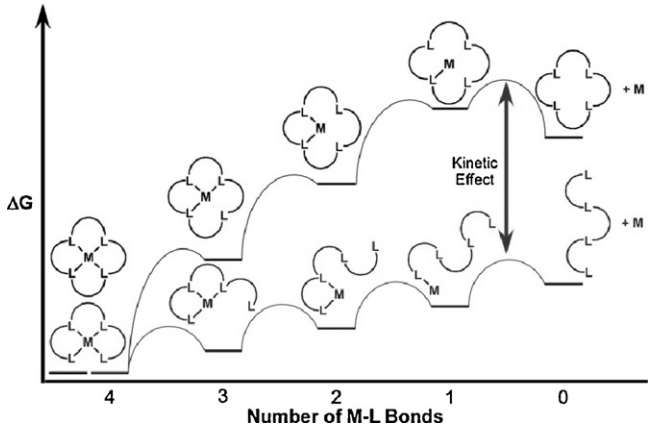


Fig. 2. Origin of the kinetic macrocyclic effect.

Macrocyclic phosphines hold promise as incredibly stable ligands for applications requiring robust complexes, such as radioactive transition metal complexes for use as radiopharmaceuticals [16,17]. Because of this possibility, these ligands and their complexes have been synthetic targets since soon after the macrocyclic effect was discovered. Unfortunately, macrocyclic phosphine ligands have historically been difficult to synthesize in good yield. A general, versatile synthesis of phosphine macrocycles has not yet been developed, for reasons that will be discussed below. Also, the macrocyclic effect has not yet been measured for a phosphine ligand. This is due to the difficulty in synthesizing macrocyclic ligands, as well as open-chain reference ligands, as will be discussed further below.

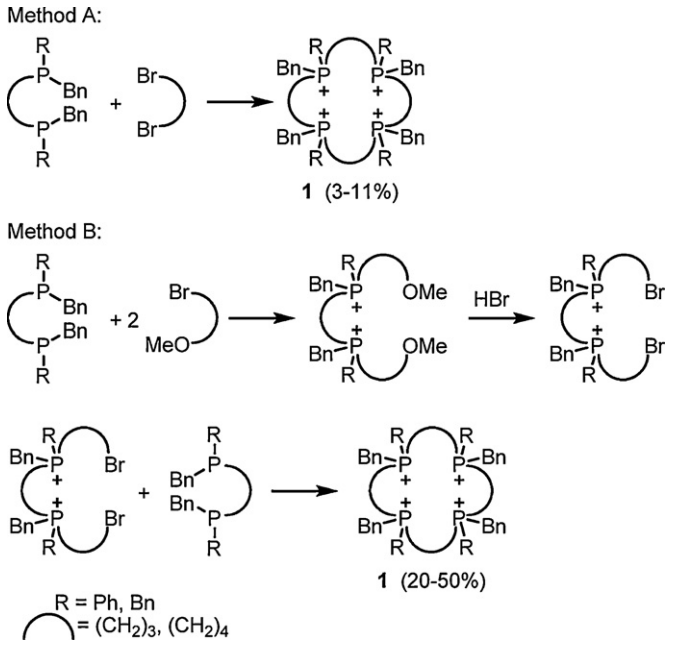
The focus of this review is on advances in both the synthesis and coordination chemistry of macrocyclic phosphine ligands. Several reviews of phosphorus-containing macrocycles have been published [18–21], but none have focused specifically on macrocyclic phosphine ligands. Generally, the term *macrocycle* is used when describing a ring of at least nine covalently bonded atoms, which is not part of a system of fused or bridged smaller rings. This review, then, will only consider macrocycles with at least nine-membered rings. Also, because macrocyclic ligands are generally considered to be polydentate, this review will only cover macrocycles with at least three phosphorus donor atoms as part of the ring. Mixed-donor macrocycles will not be thoroughly reviewed, but will be mentioned in instances when they accompany similar all-phosphorus-donor macrocycles. Finally, this review will also include macrocycles containing functional groups that can be routinely converted to phosphines. For example, phosphine oxides and phosphine sulfides can be converted to phosphines by reduction with $LiAlH_4$ or silanes, and quaternary phenylphosphonium or benzylphosphonium ions can be converted by either reductive cleavage with $LiAlH_4$ or by base hydrolysis to the phosphine oxide, followed by reduction. Because these conversions are possible, the synthesis of macrocycles containing these functional groups can be thought of as *formal* syntheses of phosphine macrocycles; as such, these cases are included in this review.

2. Synthesis of macrocyclic phosphine ligands

2.1. Cyclocondensation reactions

2.1.1. Early syntheses

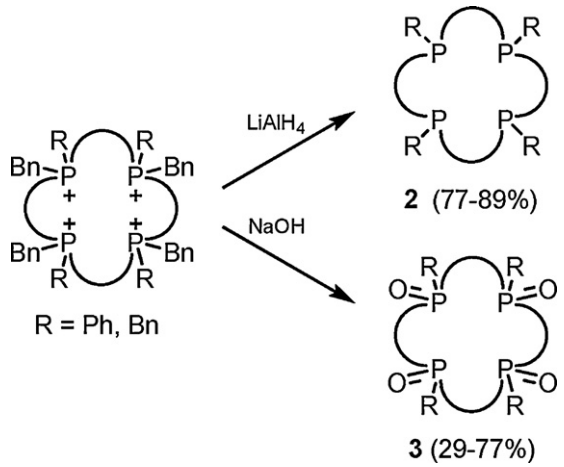
The first macrocyclic phosphine ligands were synthesized in 1975 by Horner et al. [22,23]. These phosphines were generated by the tetramolecular "2:2" reaction of 2 equivalents of α,ω-bis(dibenzyl)phosphines with 2 equivalents of α,ω-dialkyl halides to form 16-, 18-, and 20-membered macrocyclic quaternary benzylphosphonium salts **1** (Scheme 1, Method A). The yields of the phosphonium macrocycles generated by this method were very low (3–11%). In most cases, the bimolecular "1:1" small-ring



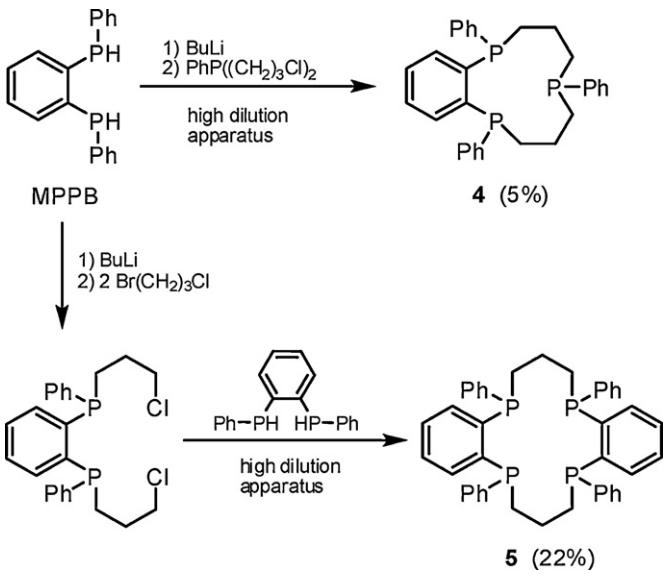
Scheme 1. Summary of Horner's benzylphosphonium macrocycle syntheses [22,23].

compounds were formed in addition to the macrocycles and the mixtures were separated by differential solubility. It should be noted that the 2:2 macrocycles are essentially dimers of the 1:1 small-ring products; thus, their molecular formula is exactly twice that of the small rings, and their elemental ratios are the same. In this case, the macrocycles were characterized by having higher melting points than the small-ring products.

Later syntheses involved stepwise building-up of the macrocyclic ring by first alkylating the phosphine with $MeO(CH_2)_3Br$, followed by conversion of the methoxy groups to bromides, forming an α,ω-brominated bis(phosphonium) compound (Scheme 1, Method B). This compound was then reacted with a second equivalent of bisphosphine to form the tetraphosphonium macrocycle. This stepwise synthesis resulted in higher yields for the macrocyclization step (20–50%). Strangely, the use of high-dilution conditions did not improve the yields of these macrocycles. Reductive cleavage of **1** with $LiAlH_4$ (typically 6–24 h in refluxing THF) gave the corresponding phosphine macrocycles **2** in yields of 77–89% (Scheme 2). Because the synthesis and reductive cleavage



Scheme 2. Reductive and oxidative cleavage of benzylphosphonium macrocycles [22,23].



Scheme 3. Kyba's P_3 and P_4 macrocyles [24].

of these compounds are not stereoselective, multiple isomers of each of the macrocycles were observed. The phosphonium macrocycles could also be converted to phosphine oxides (**3**) by hydrolysis with base. The coordination chemistry of these compounds was not studied.

In 1977, Kyba et al. synthesized 11-membered triphosphine (P_3) macrocycle **4** and 14-membered tetraphosphine (P_4) macrocycle **5** [24] (Scheme 3) using a special high-dilution apparatus (Fig. 3) [25,26]. The apparatus contained reservoirs that pre-diluted each reagent with condensing solvent. These reservoirs then overflowed, combining the pre-diluted reagents into a large volume of refluxing solvent. As the reaction proceeded, small amounts of

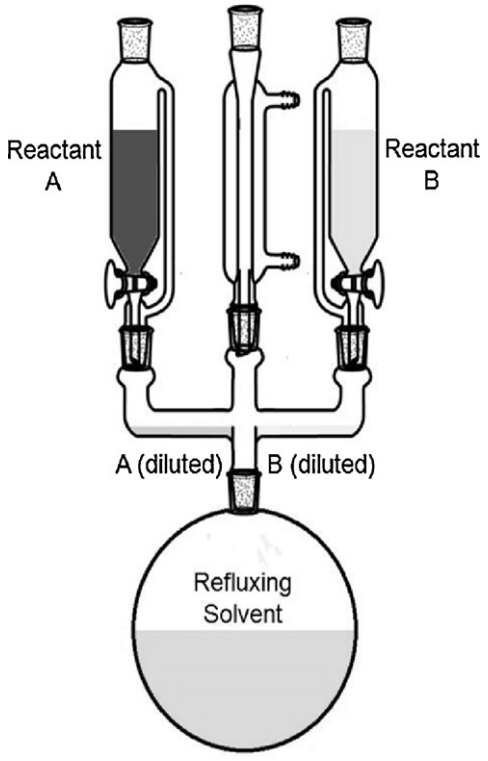
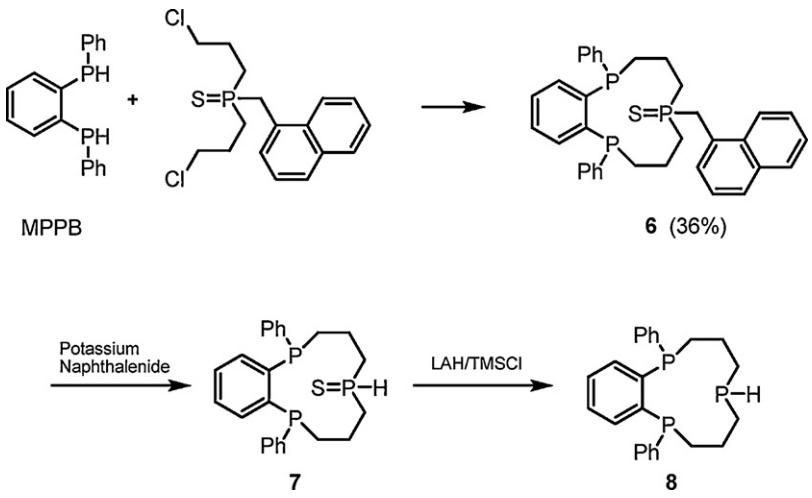


Fig. 3. High-dilution apparatus [25,26].



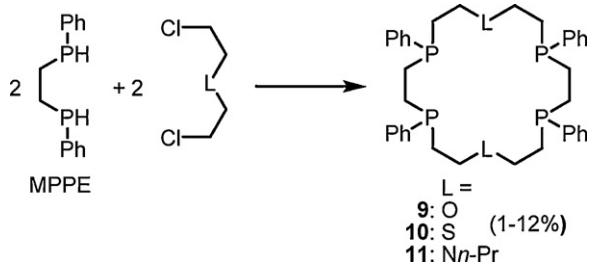
Scheme 4. Synthesis of a secondary triphosphine macrocycle [32].

pre-diluted reactants were slowly added so that the concentration of each reactant at any given time was kept to a minimum to prevent polymerization. Even using such an apparatus, the best yield of a macrocycle was only 22%. The structure of each macrocycle was confirmed by X-ray crystallography and its coordination chemistry investigated (see Section 3.1) [27–29]. Mixed phosphorus/oxygen, phosphorus/nitrogen, and phosphorus/sulfur donor macrocycles were also synthesized by the method in Scheme 3, including a 14-membered P_3S macrocycle in 26% yield [30,31].

Most macrocyclic phosphine ligands consist entirely of tertiary phosphine groups. This often limits the ability to functionalize the phosphine after the macrocyclic ring is formed. The first macrocycle containing a secondary phosphine was synthesized by the 1:1 reaction between 1,2-bis(phenylphosphino)benzene (MPPB) and a chloride-functionalized phosphine sulfide containing a 1-naphthylmethyl group [32]. Following macrocyclization (36% yield), the naphthylmethyl protecting group was cleaved using potassium naphthalenide, followed by reduction of the phosphine sulfide group with $LiAlH_4$ to form **8** (Scheme 4). The coordination chemistry of this macrocycle will be discussed in Section 3.1.

Ciampolini's 18-membered crown ether-type mixed P_4O_2 [33,34], P_4S_2 [35], and P_4N_2 [36] macrocycles were synthesized by 2:2 cyclocondensations between 1,2-bis(phenylphosphino)ethane (MPPE) and $(ClCH_2CH_2)_2L$ (L = O, S, N*n*-Pr), in yields up to 12% (Scheme 5). These ligands showed interesting coordination chemistry with cobalt and nickel, where the ligands could act as tetradentate, pentadentate, or hexadentate ligands depending on the metal, the identity of the non-phosphorus donor, and the presence of other ligands such as chloride or solvent (see Section 3.2).

The low yields of these early syntheses illustrate the inherent difficulties involved in the synthesis of macrocyclic phosphines by cyclocondensation reactions. Control of stoichiometry is often



Scheme 5. Ciampolini's phosphine macrocycles [33–36].

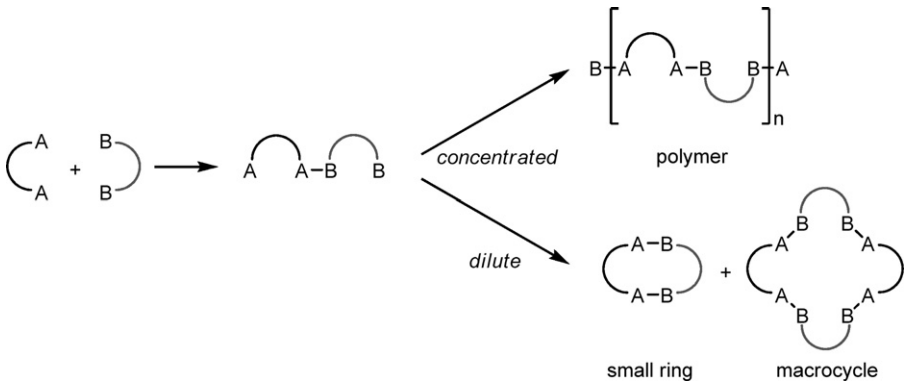
difficult when flexible linkers are used to join phosphine units. In the case of 2:2 cyclocondensations, where two bisphosphine molecules are connected by two difunctional linker molecules, two types of by-products are more favorably generated, depending on the reaction conditions (Scheme 6). After the first coupling between reactants A and B, complementary reactive ends are present on the same molecule. Under concentrated conditions, the reactive ends are more likely to encounter other reactant molecules and form polymers. On the other hand, dilute conditions encourage the formation of small rings because the complementary reactive ends of a single molecule are more likely to find each other than to find another reactant molecule. However, in practice even under "ideal" high-dilution conditions, the macrocyclic products are only formed in small amounts.

Small-ring products can be avoided if a stepwise synthesis is employed in which the linkers are attached first to one phosphine, followed by a 1:1 macrocyclization step with a second phosphine (Scheme 7). For 1:1 macrocyclizations, the macrocycle is the smallest ring possible and is favored over polymeric products if sufficiently dilute reaction conditions are employed. However, the yields are often low even under optimal conditions because of slow kinetics and the entropic penalty of closing a large ring [37]. Also, as more synthetic steps are required, including functional group transformations, the overall yield of the macrocycle from its starting components is still often low.

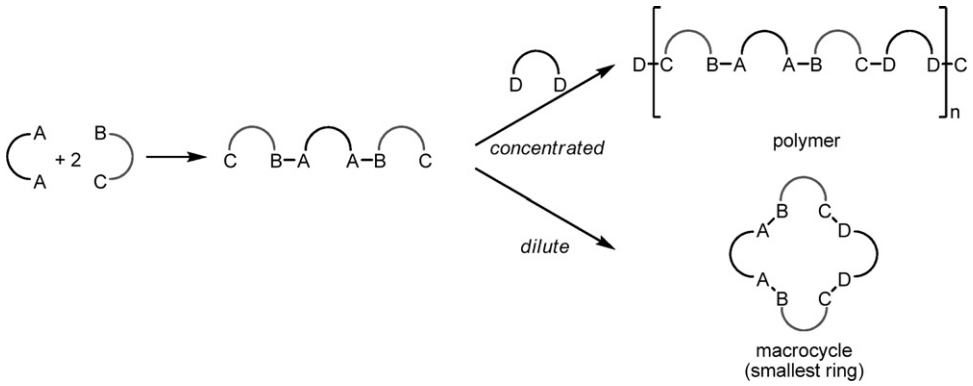
A pair of 15- and 16-membered, mixed phosphine oxide/phosphonium macrocycles **12a** and **12b** was synthesized in a stepwise fashion in 50% and 57% yield, respectively [38]. In the first step, a secondary bisphosphine was alkylated with allyl alcohol, followed by conversion of the hydroxyl groups to bromides using Br_2 (which also oxidized the phosphine groups to phosphine oxides). These steps are then followed by cyclocondensation with 1,3-bis(diphenylphosphino)propane (DPPP) (Scheme 8). The phosphonium groups were hydrolyzed to form the corresponding tetra(phosphine oxide) macrocycles. Reduction to the macrocyclic phosphines was suggested, but not reported.

2.1.2. Cyclocondensations using rigid linkers

Syntheses of macrocycles by cyclocondensation are more successful when rigid linker units are used because rigid linkers favor the conformations necessary for macrocyclization. This point was first realized with tetraphosphonium macrocycles containing *p*-xylene linkers (Scheme 9), which formed in yields up to 98% [39]. Although direct evidence of a macrocycle (molecular weight measurement) was not obtained for this compound,



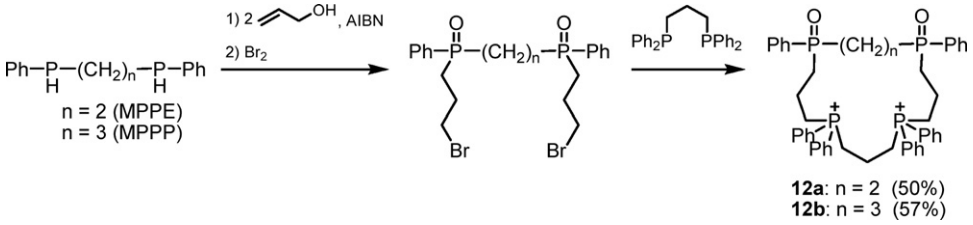
Scheme 6. Macrocyclization via a 2:2 cyclocondensation method.



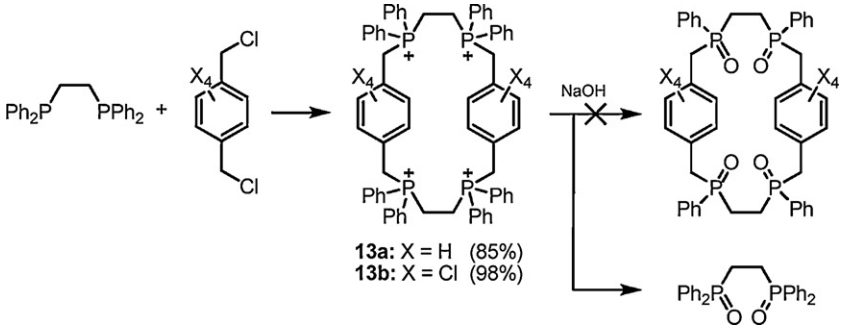
Scheme 7. Macrocycle synthesis by stepwise buildup, followed by 1:1 cyclization.

the open-chain macrocycle precursor $Ph_2P(CH_2)_2P^+PhCH_2(p\text{-}C_6Cl_4)CH_2P^+Ph(CH_2)_2PPh_2$ was isolated when the reaction was stopped before reaching completion. Also, simple molecular modeling revealed that the small-ring product is strained because of the length and rigidity of the *p*-xylene linker and is likely to be disfavored over the macrocyclic product. Unfortunately, base hydrolysis of the tetraphosphonium macrocycle preferentially cleaved the benzylphosphine linkages in the macrocyclic ring as opposed to the phenyl groups, resulting in decomposition of the macrocycle.

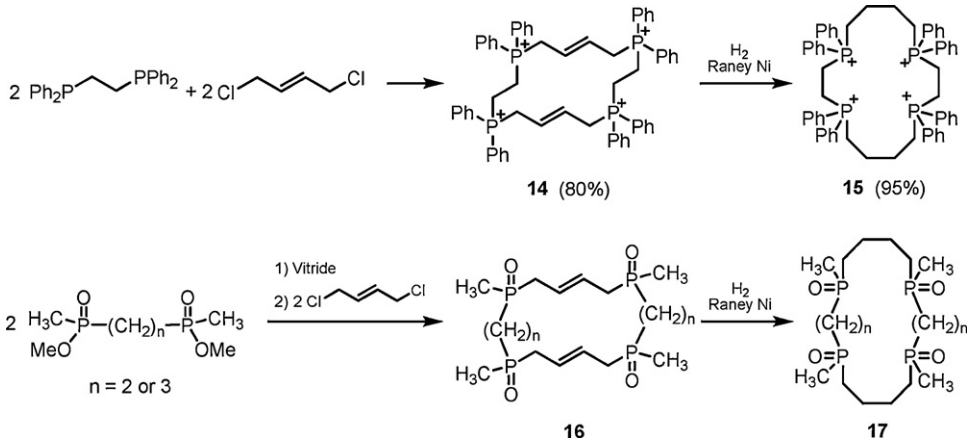
Rigid *trans*-2-butene linkers have been used to synthesize phosphonium and phosphine oxide macrocycles (Scheme 10). Reaction of 1,2-bis(diphenylphosphino)-ethane (DPPE) with *trans*-1,4-dichloro-2-butene gave a 16-membered phosphonium macrocycle in 80% yield [40]. The macrocyclic structure was identified by molecular weight determinations using vapor



Scheme 8. Stepwise synthesis of a mixed phosphonium/phosphine oxide macrocycle [38].



Scheme 9. Macrocyclizations using *p*-xylene linkers [39].



Scheme 10. Macrocyclizations using *trans*-2-butene linkers [40–42].

pressure osmometry. This linker was also used to form 16- and 18-membered phosphine oxide macrocycles [41,42]. The *trans*-butene linkers probably enforce the wrong geometry for chelation to a transition metal, but these molecules could be hydrogenated to generate the saturated, flexible macrocycles.

Interestingly, rigid 2-butene linkers with the *opposite* (*cis*) stereochemistry were also give tetraphosphonium macrocycles in some instances (Scheme 11) [43]. This result suggests that the absolute stereochemistry of the linker is not always important for successful macrocyclization, as long as the linker is generally inflexible. *Ortho*-xylene linkers have also been used, although the yields of macrocycles were very low [44].

2.1.3. Stereochemical control

Another difficulty associated with macrocyclic phosphine synthesis is control of the stereochemistry at the phosphorus atoms. Most macrocyclic phosphine ligands contain asymmetric phosphine groups ($PR^1R^2R^3$), where each substituent attached to the phosphorus is different. Unlike tertiary amines, the inversion barrier of phosphines is sufficiently high (30–35 kcal/mol) that they do not undergo inversion at room temperature [45]. This means that the $PR^1R^2R^3$ groups of macrocyclic phosphines are chiral, resulting in multiple possible stereoisomers for each macrocycle. None of the syntheses described so far have attempted to control the stereochemistry of the phosphine groups. This limits these macrocycles' utility as ligands because the relative orientations of the phosphorus lone pairs will vary in each stereoisomer, and this can affect the coordination behavior of the various stereoisomers.

In an attempt to bypass this problem of stereochemistry, Mathey et al. synthesized a series of phosphole macrocycles (Scheme 12) [46]. Reductive cleavage of the bis(diphosphole) **20** to bis(phospholide) **21** with Na^0, followed by linking with dibromomethane under high-dilution conditions, generated the 10-membered tetraphosphole macrocycle **22a** in moderate yield. In addition, 13- and 16-membered macrocycles **22b** and **22c** could be obtained by stepwise reductive cleavage and reaction with either dibromomethane or 1,4-dibromobutane. These macrocycles were then derivatized to the corresponding phosphine sulfides for complete characterization.

Phosphole groups are not planar but have an inversion barrier of ~16 kcal/mol [47], which allows them to undergo inversion at room temperature. In macrocycles **22a–c**, multiple stereoisomers are still observed, but they readily interconvert so that potentially problematic isomers (i.e. those that may not be the correct geometry for a desired coordination mode) can convert to those better suited for coordination once a metal is introduced.

Another solution to the problem of chiral phosphines is phosphinine (a.k.a. "phosphorine" or "phosphabenzene") macrocycles. P_3 and P_4 phosphinine macrocycles **23** and **24** were successfully synthesized by high-dilution reactions involving bis(1,2-azaphosphinines) and bis(acetylenes) (Scheme 13) [48]. Yields were low (20%), owing to the formation of oligomeric by-products. Fortunately, the macrocycles are less soluble than the by-products, which can simply be rinsed away. Both of these structures were confirmed by X-ray crystallography. Another advantage of phosphinine groups over normal phosphines is that they are air-stable. This synthetic route has also generated mixed phosphinine/furan (**25**), phosphinine/thiophene (**26**), and phosphinine/ether macrocycles **27a–c** (Fig. 4) [49,50].

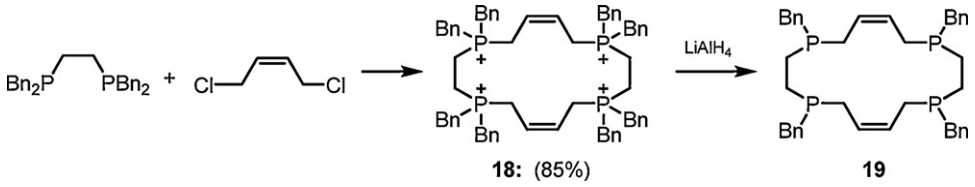
Morisaki recently synthesized a chiral, crown-ether type phosphine–borane macrocycle by stepwise oxidative coupling of chiral methylphosphine–borane oligomers (Scheme 14) [51]. The major product was an 8-phosphorus oligomer; however, macrocycle **28** was also generated and isolated in 15% yield. Its structure was confirmed by X-ray crystallography. This is the only example of a 12-phosphacrown-4 macrocycle. Phosphine–boranes are routinely converted to phosphines by refluxing with excess amine, although this method was not reported for this macrocycle. Although the coordination chemistry of this macrocycle has not been studied, the coordination chemistry of 12-membered N_4 [52–54] and S_4 [55] macrocycles suggests that it would likely not be large enough to fully encircle a transition metal atom.

Recently a nine-membered P_3 macrocycle **30** was synthesized in high yield [56] by reductive cleavage of bis(2-diphenylphosphinoethyl)phenylphosphine (TRIPHOS) to generate the bis(phosphide) **29** [57], followed by the 1:1 cyclocondensation with 1,2-dichloroethane (Scheme 15). Both the *syn-syn* isomer **30a** and the *syn-anti* isomer **30b** were observed by ^{31}P NMR spectroscopy (*syn-syn*:*syn-anti* = 3:7), although these isomers were not separated. See Section 3.1 for a discussion of this ligand's coordination chemistry.

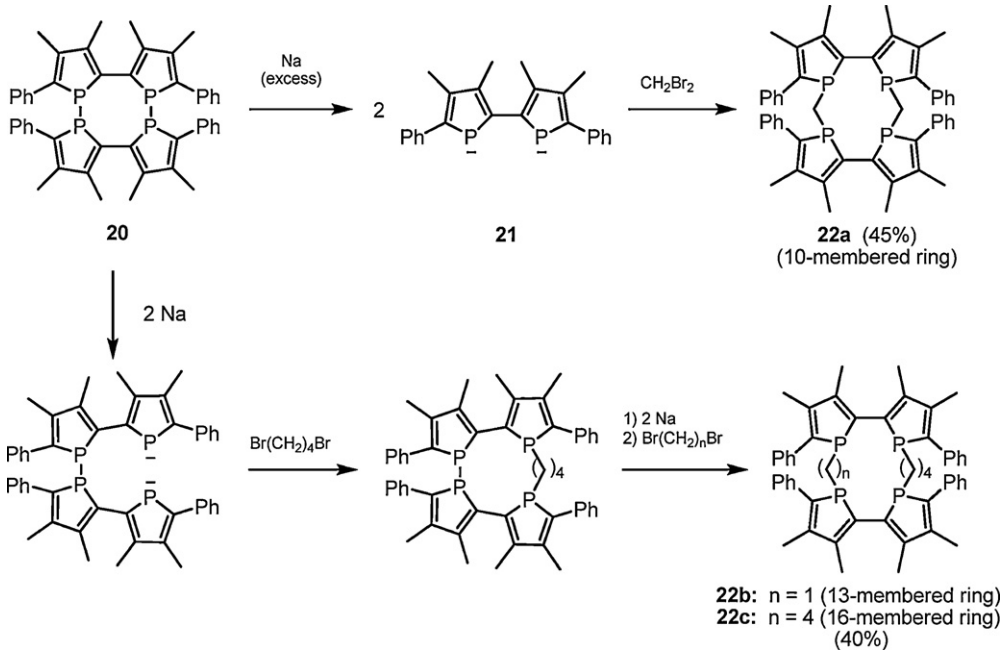
A unique ferrocene-bridged P_3 macrocycle has been isolated, and its crystal structure obtained [58,59]. While synthesizing phosphine-containing poly(ferrocene) **34** by photoinitiated ring-opening polymerization of the strained phosphine-bridged ferrocene **31**, the dimer **32** and macrocyclic trimer **33** were obtained as side-products (Scheme 16). The two isomers all-*syn* **33a** and *syn-anti* **33b** were isolated by conversion to the phosphine sulfide, separated from other oligomers by preparative-scale recycling gel permeation chromatography (GPC), and converted back to the phosphines with MeOTf and $P(NMe_2)_3$. Crystal structures of both **33a** and its phosphine sulfide were obtained.

2.1.4. Self-assembling phosphine macrocycles

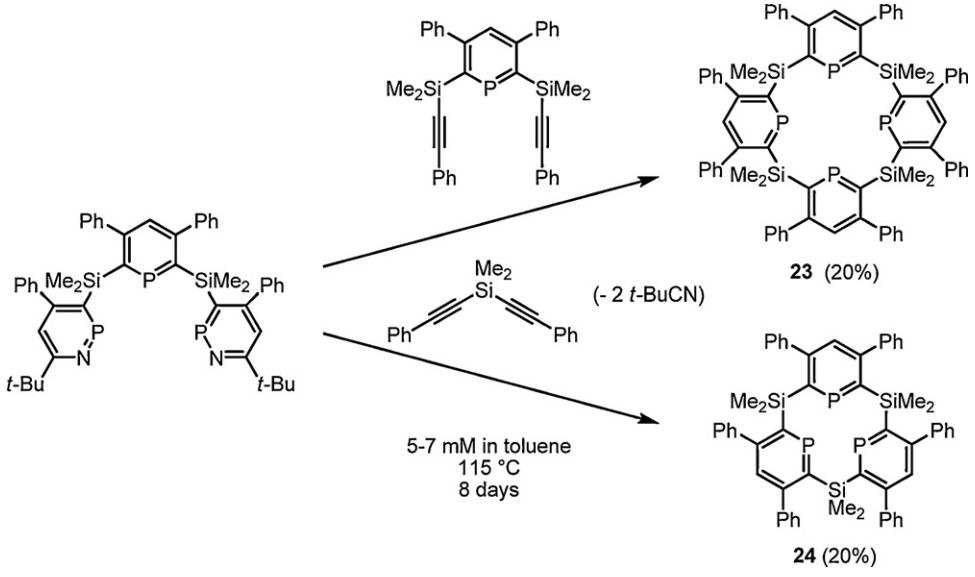
Balueva and colleagues prepared large phosphorus macrocycles that self-assembled by the phosphorus Mannich reaction between hydroxymethylphosphines and NH-functional amines. The first series is the 28-membered P_4 macrocycles **35a–f** (Scheme 17) [60,61], with semi-rigid *p*-diphenyl linkers spanning two 1,5-diaza-3,7-diphosphacyclooctane rings. These macrocycles form under high-dilution conditions in DMF. The phosphorus Mannich reaction is reversible in solution, allowing the six individual components to self-assemble into the thermodynamically favored macrocycles. The self-assembly was observed by monitoring the reactions by ^{31}P NMR spectroscopy, which showed the appearance and dis-



Scheme 11. Phosphine macrocycle synthesis using a *cis*-2-butene linker [43].



Scheme 12. Synthesis of phosphole macrocycles [46].



Scheme 13. Synthesis of phosphinine macrocycles [48].

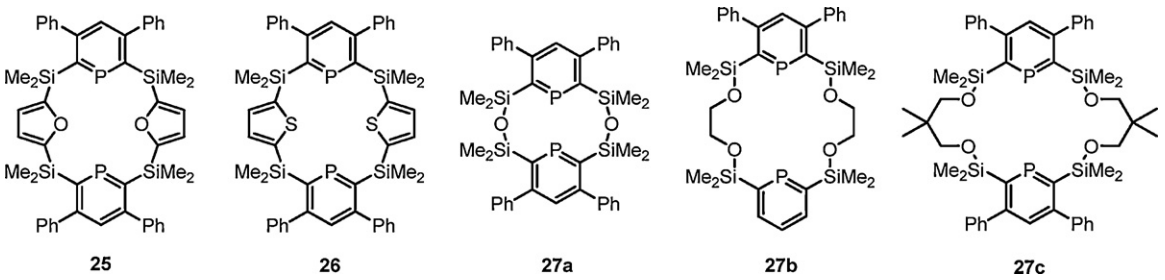
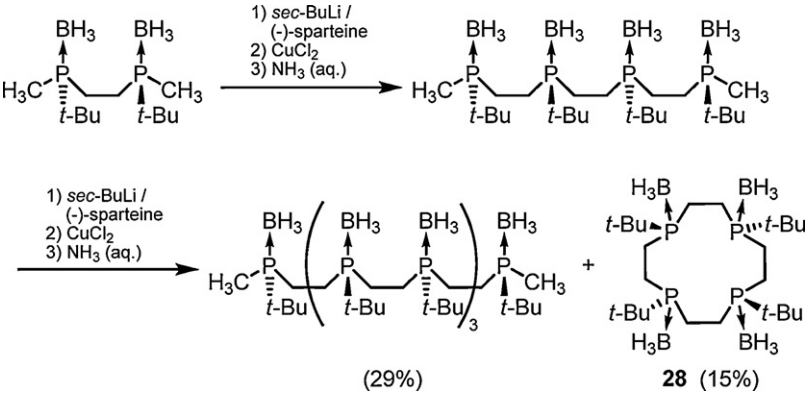


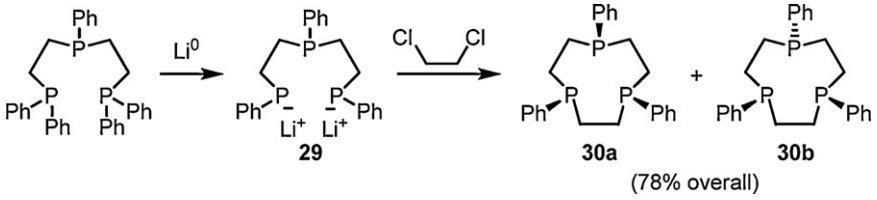
Fig. 4. Mixed phosphinine macrocycles [49,50].

appearance of a variety of intermediates over the course of the reactions and which reached completion between 4 h and 60 h at 110 °C. Four of these macrocycles (**35a**, **d**, **e**, and **f**) were structurally confirmed by XRD, with the others characterized by FAB-MS. The 120° angle between the amine groups on the linking agent is crucial for formation of the macrocycle; for example, using a 3,3′-diaminodiphenylmethane linking agent did not give a discrete product. Even larger macrocycles could be prepared in this manner, including a 36-membered macrocycle (**36**) [62] and two 38-membered macrocyclic cyclophanes **37a** and **37b** [63]. The crystal structure of **37b** reveals that it adopts a helical conformation, with a benzene molecule in the cavity. Solution studies of **37a** and **37b** by 2D NMR as well as computational studies revealed that the molecules are twisted in solution and that the extent of twisting depends on the size of the aryl group attached to the phosphine [64]. NMR also reveals that these molecules encapsulate benzene or toluene in solution.

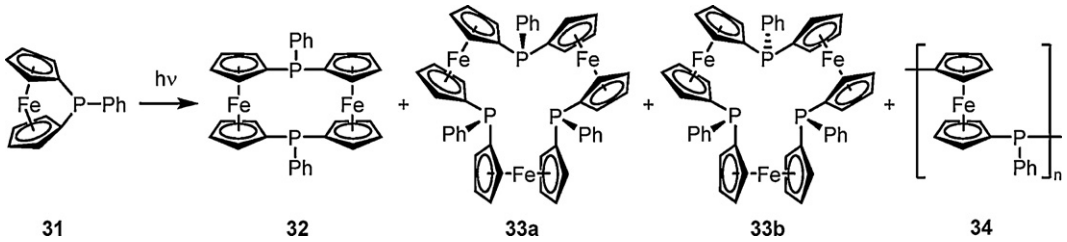
A 16-membered macrocycle was also synthesized by self-assembly using the phosphorus Mannich reaction (Scheme 18) [65]. The bidentate secondary phosphine 1,3-bis(mesitylphosphino)propane reacted with formaldehyde and benzylamine, precipitating macrocycle **38a** in 51% yield after 7 days. In a similar manner, chiral macrocycle **38b** was synthesized using *R*- or *S*-α-methylbenzylamine [66], and cryptand **39** was



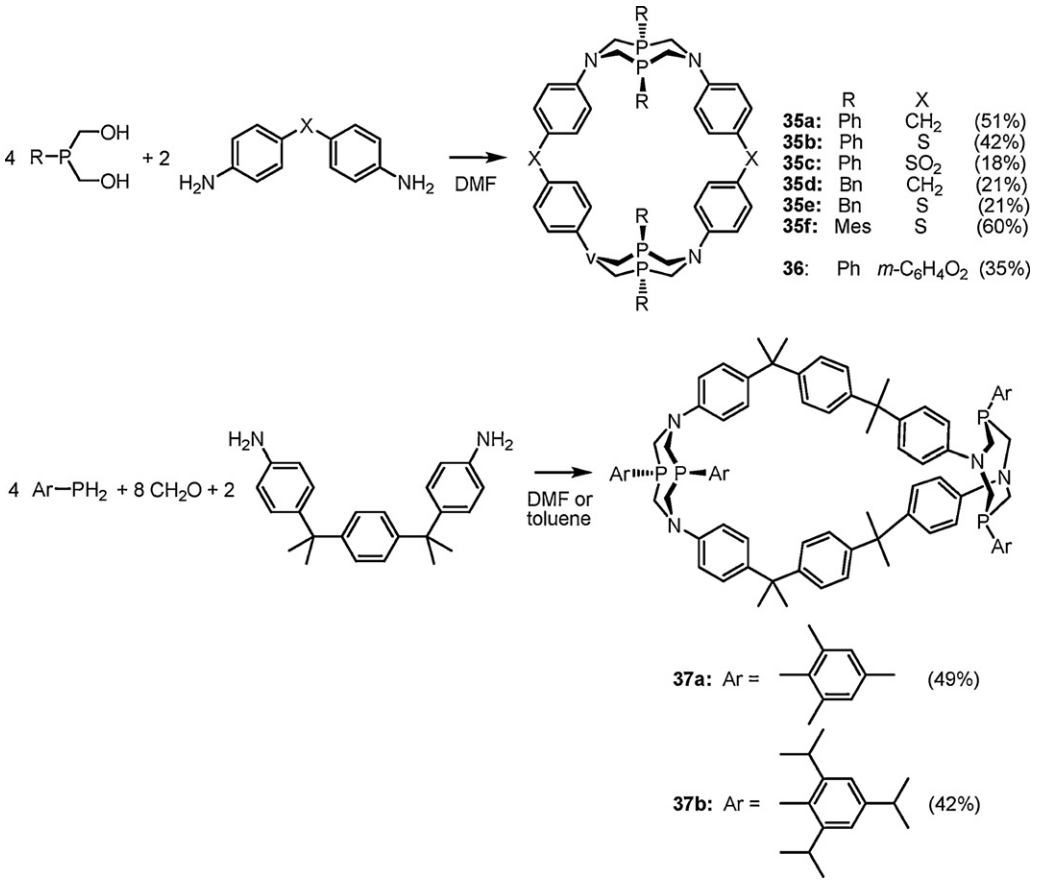
Scheme 14. Synthesis of a borane-protected 12-phosphacrown-4 macrocycle [51].



Scheme 15. Synthesis of a nine-membered P_3 macrocycle by a cyclocondensation method [56].

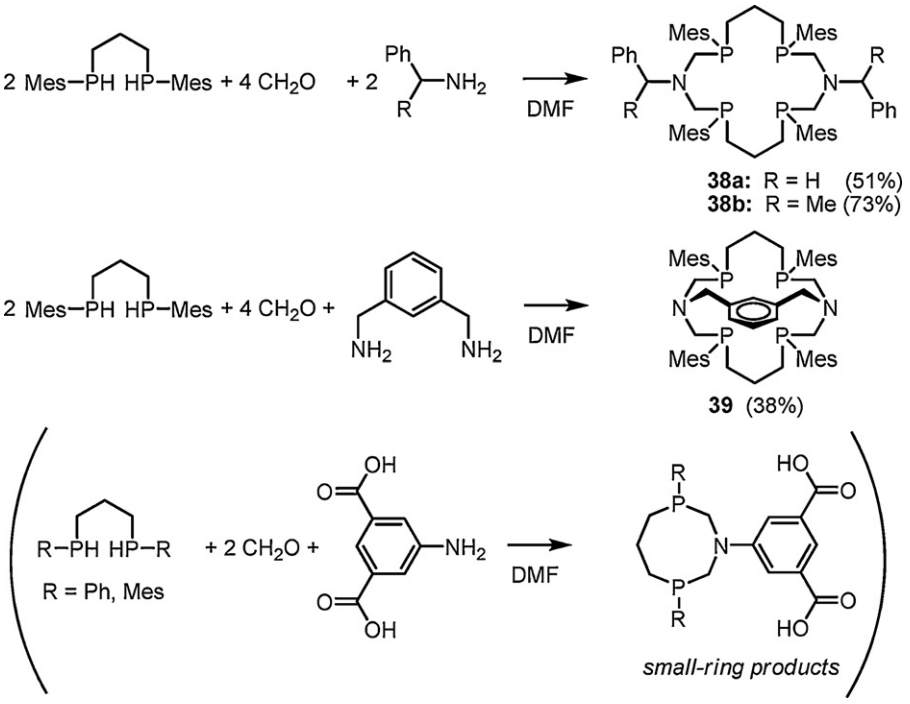


Scheme 16. Synthesis of a ferrocene-bridged P_3 macrocycle [58,59].

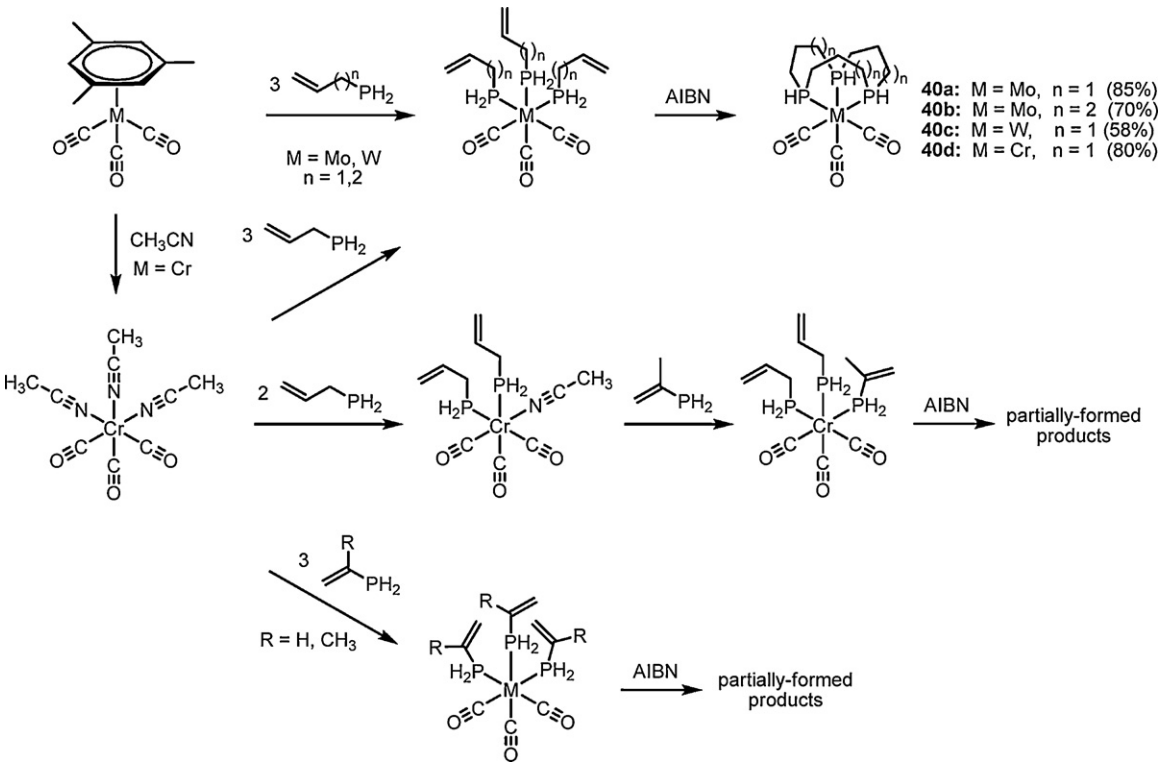


Scheme 17. 28, 36, and 38-membered self-assembled macrocycles [60–63].

generated when *m*-xylylenediamine was used as a tetrafunctional linker [67]. The authors later reported the synthesis of more 16-membered phosphine macrocycles, including water-soluble and chiral versions, by using other amine linkers [68]. However, no experimental data or crystal structures were reported for any of these compounds so this route cannot yet be considered a generalized method for the synthesis of macrocyclic phosphines. Indeed, when aromatic amines were used as linkers, the



Scheme 18. Self-assembly of 16-membered tetraphosphine macrocycles and cryptand [65–69].



Scheme 19. Group 4 metal-templated triphosphorous macrocyclizations [72–75].

eight-membered small-ring products were generated instead of the macrocycles, showing that there are limits to this synthetic strategy [69].

2.1.5. Summary

Cyclocondensation reactions have been employed to synthesize phosphorus macrocycles with varying degrees of success. High-dilution conditions are usually necessary, and as such the reactions often require long reaction times. The 2:2 cyclocondensation method using flexible linkers is the least successful strategy, while rigid linkers and/or self-assembling components can be used to favor macrocycle formation over either 1:1 small-ring products or polymers. Formation of small-ring products can be avoided if a multi-step approach is employed, in which a linear compound is built then cyclized in a 1:1 cyclocondensation reaction. However, formation of the macrocyclic ring still requires high dilution conditions and can suffer from low yields.

2.2. Template syntheses

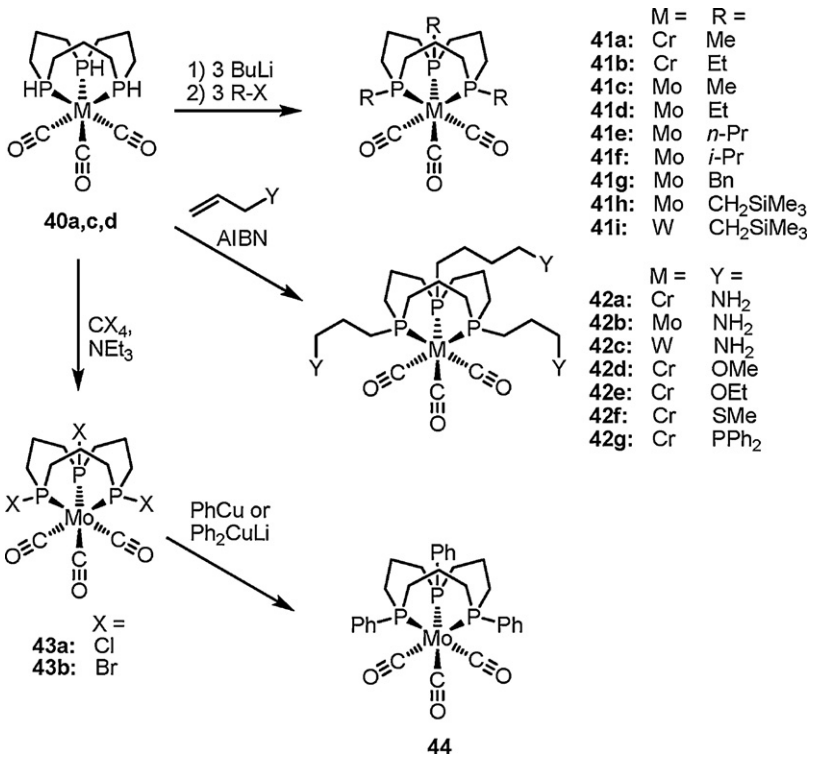
As discussed in the previous section, cyclocondensation reactions often suffer from side-reactions and slow kinetics, resulting in low yields of macrocycles. An alternative strategy is the *template synthesis* [70], where components are coordinated to a transition–metal template before being linked together to form the macrocycle. The metal acts as a collection point, controlling the stoichiometry and increasing the likelihood of the macrocyclization by placing reactive groups in close proximity to each other. In the case of primary and secondary phosphines, the metal may also activate the ligand toward alkylation by increasing the acidity of the P–H bond and the nucleophilicity of the deprotonated phosphido ligand [71].

2.2.1. Triphosphine macrocycles

In 1982, Norman et al. synthesized the 12-membered P_3 macrocycle **40a** from *fac*-Mo(allylphosphine)$(CO)_3$ (Scheme 19) [72]. AIBN-initiated hydrophosphination of the terminal olefins around the Mo template gave the macrocycle in 85% yield. This reaction also worked with 4-phosphino-1-butene, generating the 15-membered P_3 macrocycle **40b** in 70% yield [73]. The progress of the reaction, showing each partially formed intermediate, could be followed by ^{31}P NMR spectroscopy. The Edwards group later synthesized tungsten and chromium analogs **40c** [74] and **40d** [75]. Synthesis of the $W(CO)_3$(allylphosphine)$_3$ template from $W(CO)_3$(mesitylene) was similar to the synthesis of the Mo analog, although heating was required, which resulted in some oligomerization of the allylphosphine as a side-reaction. The $Cr(CO)_3$(allylphosphine)$_3$ template could not be formed from the mesitylene complex but was synthesized instead from $Cr(CO)_3(CH_3CN)_3$. Radical-initiated intramolecular hydrophosphination of each of these templates then led to macrocyclization.

Attempted syntheses of nine-membered macrocycles by template macrocyclizations of vinylphosphine or 2-propenylphosphine were unsuccessful, instead giving oligomeric or polymeric products. Attempts at forming 10- and 11-membered macrocycles using mixed-phosphine templates (formed by first reacting $Cr(CO)_3(CH_3CN)_3$ with two equivalents of a phosphine, followed by one equivalent of a second phosphine) were also unsuccessful. This may be due to unfavorable ring sizes of these smaller macrocycles but is more likely due to inherent differences in reactivity between vinylphosphines and allyl/butenylphosphines.

Derivatives of **40** were synthesized by alkylation of the secondary phosphine groups, either with alkyl halides to form **41a–e** or by radical addition of allyl-functionalized compounds to form **42** (Scheme 20) [75,76]. In addition, the secondary phosphine groups could be converted to halophosphine groups by reaction with CX_4 and NEt_3 [77]. This reaction was significantly



Scheme 20. Alkylated derivatives of P_3 macrocyclic complexes [75–77].

faster than that reported for free secondary phosphines, suggesting that coordination to the metal template activates the ligands toward this reaction. Halophosphines **43a** and **43b** were then converted to arylphosphine **44** by treatment with arylcopper reagents.

As mentioned above, the Group 6 carbonyl templates could not be used to synthesize P_3 macrocycles with rings of fewer than 12 atoms. Instead, Edwards and colleagues used an iron piano stool template to couple 1,2-bis(phosphino)ethane and trivinylphosphine, forming the nine-membered P_3 macrocycle **46** (Scheme 21) [78]. This and other iron piano stool complexes have proven to be the most versatile templates for the synthesis of P_3 macrocycles, with variations in the cyclopentadienyl ring, macrocycle ring size, and substituent groups, generating a myriad of triphosphine macrocycles. A plethora of nine-membered macrocycles **48a**–**j** were synthesized, with the macrocyclizations occurring via Michael-type reactions using KO*t*-Bu instead of radical hydrophosphinations [79]. Nine-membered benzo-fused macrocycles **52** were synthesized by the templated macrocyclization of 1,2-bis(phosphino)benzene (BPB) or 1,2-bis(phosphino)-3-anisole [80], and the dibenzo-fused macrocycle **56** was synthesized by nucleophilic aromatic substitution of $PhPH_2$ on an *o*-fluorophenyl bidentate phosphine [81]. 12-Membered macrocycles **54a**,**b** were synthesized in moderate yield from the templated trimerization of allylphosphine [82]. Strangely, attempted synthesis of an 11-membered macrocycle by the templated coupling of BPE with tri(allyl)phosphine actually generated the 10-membered macrocycle **50** instead [83]. A symmetric 10-membered macrocycle, analogous to **46**, was recently synthesized using the Michael-type addition of trivinylphosphine to 1,3-bis(phosphino)propane [84]. Many derivatives were synthesized by hydrogenation and/or alkylation of these macrocycles.

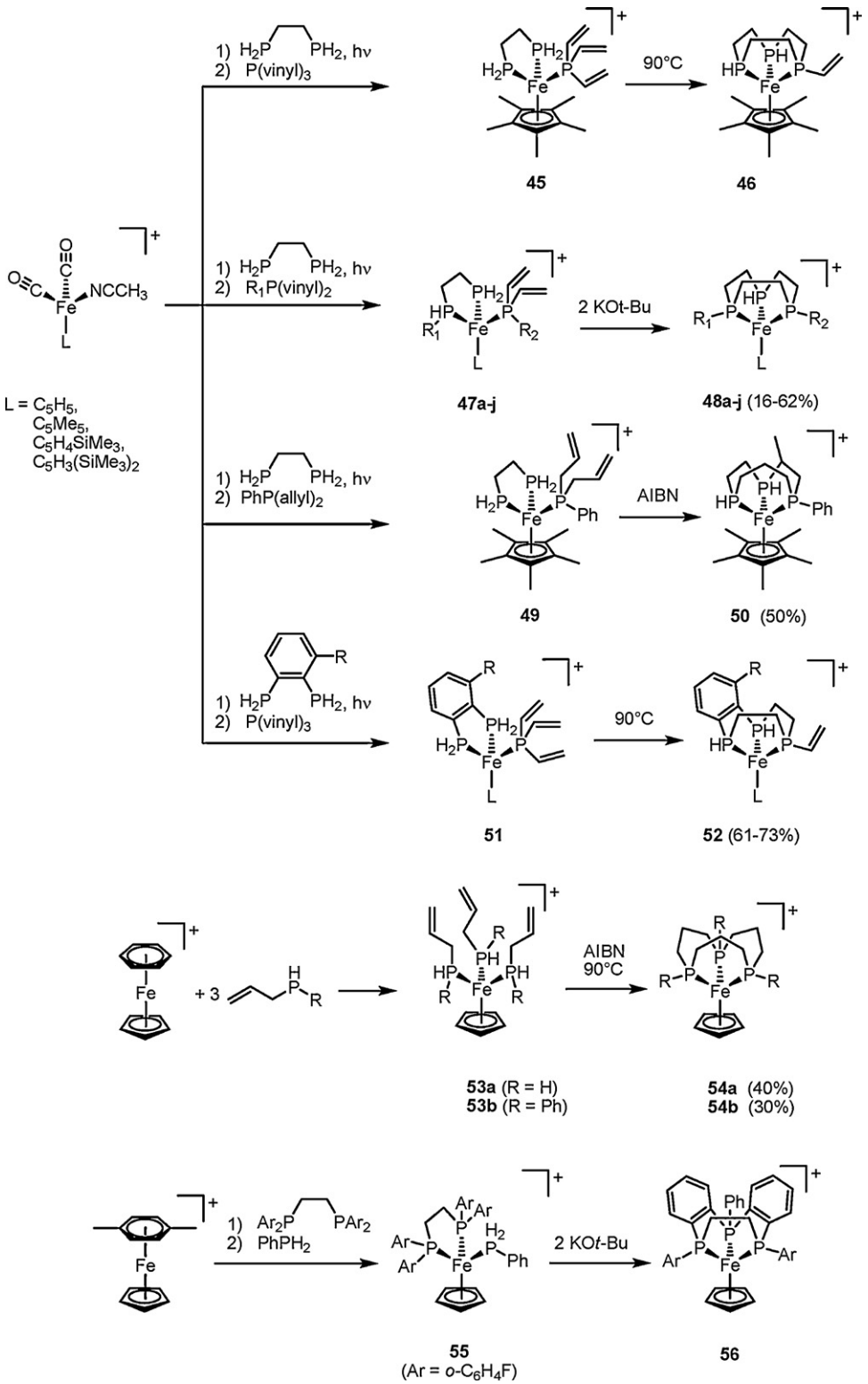
Gladysz et al. synthesized an especially large, 45-membered P_3 macrocycle (**57**) by using ring-closing metathesis of 3 equiv. $PhP((CH_2)_6CH{=}CH_2)_2$ on a *fac*-$W(CO)_3$ template (Scheme 22) [85]. This reaction is an excellent illustration of a template synthesis favoring a macrocycle over polymeric or small-ring products. Such a large macrocycle would be essentially impossible to form in a cyclocondensation reaction. The success of this reaction suggests that ring-closing metathesis might be used to form smaller macrocyclic phosphines; however, this reactivity has not yet been reported.

Although they are not technically within the scope of this review, P_3 and P_6 macrocycles with silicon backbones have been made by a template synthesis (Scheme 23) [86]. The 9-membered P_3 macrocycle **58** was synthesized by coordinating *n*-hexylphosphine on a *fac*-$Mo(CO)_3$ template, followed by treatment with *n*-BuLi, then $Me_2Si_2Cl_2$, and then a second treatment with *n*-BuLi. Similarly, 12-membered P_6 macrocycles **60a**,**b** were synthesized by reacting the cyclic P_3Si_3 compound **59** with CuOTf or AgOTf.

Like phosphines, N-heterocyclic carbenes (NHCs) are strong sigma-donor ligands, and they are commonly used in place of phosphines for this reason. A few mixed phosphine/NHC macrocycles have recently been synthesized via template syntheses, and are shown in Scheme 24. The first was complex **61a**, where an *o*-fluorophenyl-functionalized bidentate phosphine and an NH-functionalized NHC ligand were coordinated to a rhenium template, followed by cyclization by means of an unusual S_n2-type NHC arylation reaction [87]. The resulting complex contains an 11-membered facially coordinating tridentate P_2C^{NHC} macrocycle. The analogous Mn complex **61b** was also synthesized, but attempts at extending this synthesis to a tungsten complex were unsuccessful because of difficulties with forming the template [88]. The macrocyclic ligand was liberated as the bis(phosphine oxide)/imidazolium after exposure to air for weeks. The macrocyclic Ru complex **61c** was synthesized from a RuCp template [89].

2.2.2. Tetraphosphine macrocycles

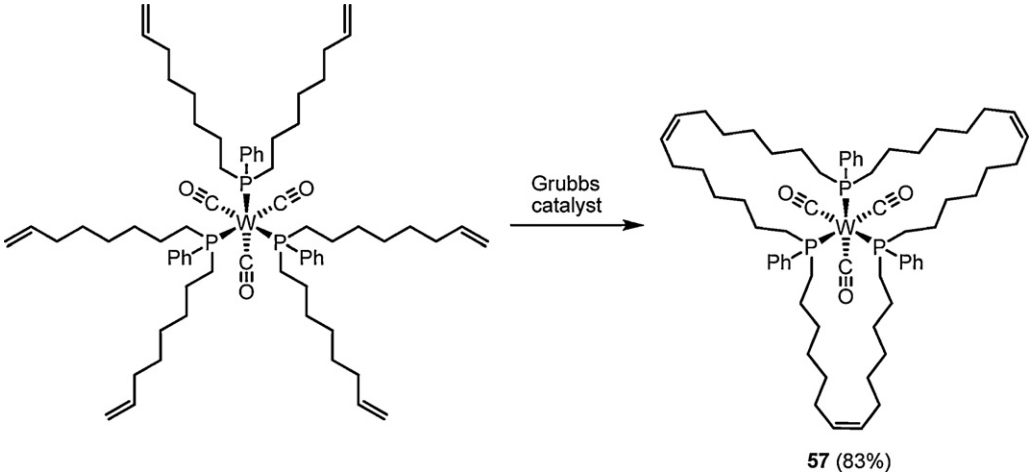
In 1977, only two years after the first phosphine macrocycles were synthesized by cycloaddition, DelDonno and Rosen



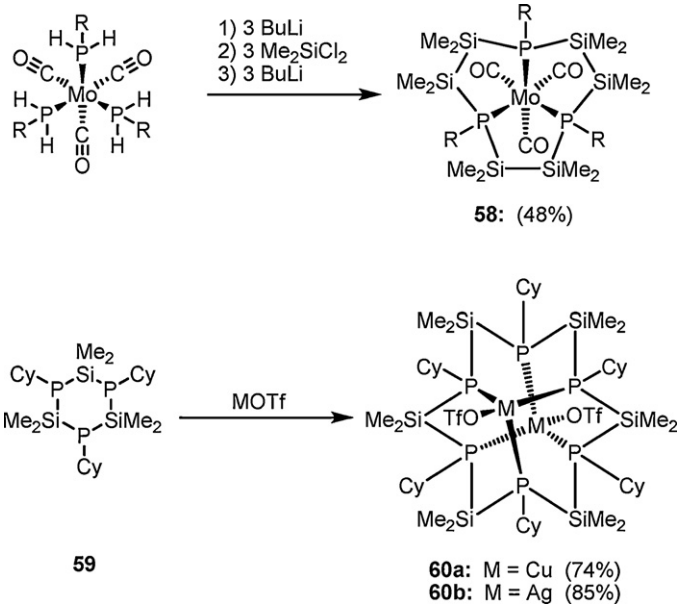
Scheme 21. Synthesis of P_3 macrocycles on iron piano-stool templates [78–84].

synthesized a macrocyclic tetraphosphine ligand around a square-planar nickel(II) template (Scheme 25) [90,91]. They coordinated an open-chain tetraphosphine ligand around Ni(II) and closed the macrocycle with dibromo-*o*-xylene under basic conditions, forming **62** in 52% yield. This macrocyclization did not work with 1,3-dibromopropane, even though methyl iodide alkylates the complex. The failure to react with 1,3-dibromopropane may be because 1,3-dibromopropane has the potential to undergo elimination under basic conditions and may escape as allyl bromide (b.p. 71 °C) over the course of the reaction.

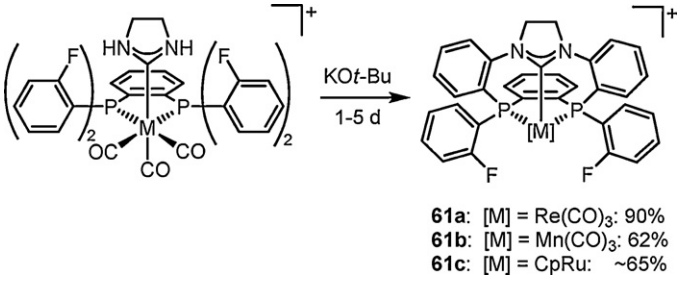
A similar macrocyclization was performed by the Stelzer group, who reacted two equivalents of dichloro-*o*-xylene with $[Pd(MMPE)_2]Cl_2$ to give the 16-membered P_4 macrocycle **63** in 97% yield (Scheme 26) [92]. In contrast to the synthesis of **62**, which



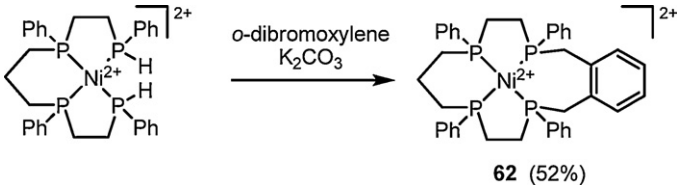
Scheme 22. Synthesis of a 45-membered triphosphorus macrocycle [85].



Scheme 23. Template syntheses of silane-based phosphorus macrocycles [86].



Scheme 24. Template synthesis of mixed phosphine/NHC macrocyclic ligands [87–89].



Scheme 25. DelDonno and Rosen's templated macrocyclization [90,91].

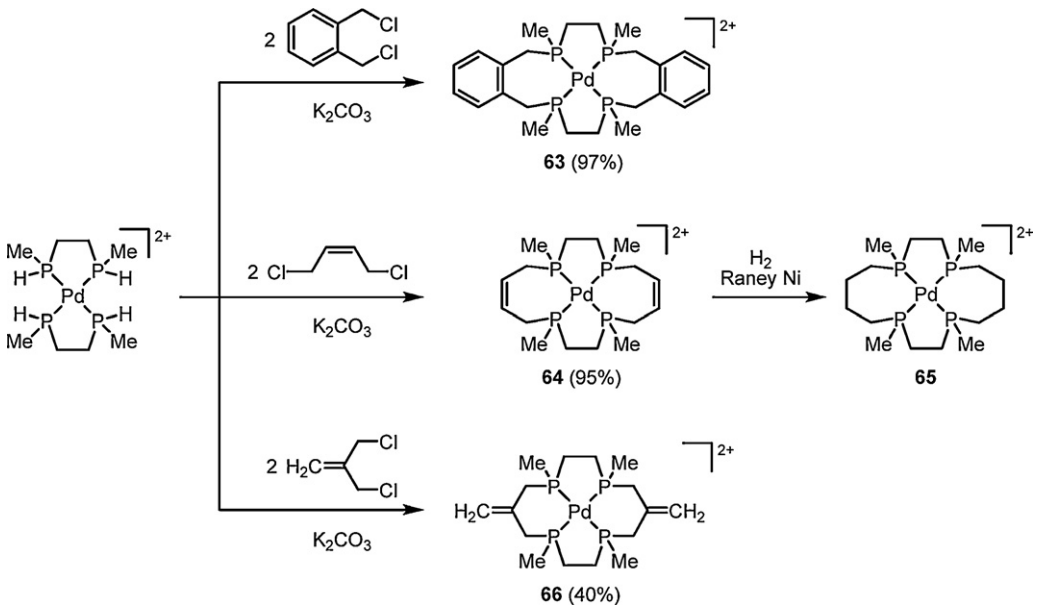
took 48 h to reach completion, formation of **63** was complete after reacting for 1 h at room temperature.[1] The structure of the macrocycle was confirmed by X-ray crystallography. The $[Pd(MMPE)_2]^{2+}$ template was cyclized with *cis*-2-butene and isobutene linkers to form macrocyclic complexes **64** and **66** [16]. Under the same reaction conditions, saturated linkers (1,3-dichloropropane and 1,4-dichlorobutane) did not react. Instead, the saturated macrocycle **65** was obtained by reduction of **64** with H_2 and Raney nickel.

Complexes **64**–**66** were characterized by NMR spectroscopy and FAB mass spectrometry; however, it should be noted that neither of these techniques can conclusively confirm the macrocyclic ligand structure in these complexes. For templated 2:2 macrocyclizations, two possible ring-closing reactions are possible: linking *between* the phosphines to form the macrocycle or linking *across* each phosphine to form two small-ring double-chelate ligands (Scheme 27). Both of these products have the same molecular weight, and there are is no spectroscopic method that can definitively tell one of these possibilities from the other.

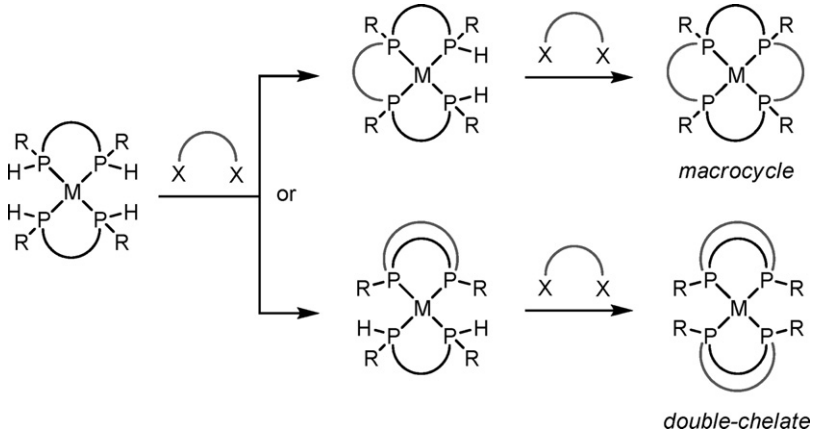
Mizuta et al. formed macrocyclic complexes **67a**,**b** by reacting 1,3-dibromopropane with $[Pd(MMPE)_2]^{2+}$ and $[Pt(MMPE)_2]^{2+}$ (Scheme 28) [94]. The macrocycles were characterized by X-ray diffraction and by ^{31}P NMR spectroscopy, where they displayed sharp singlets indicating highly symmetric macrocycles. However, the reactions took 4 days, yields were very low (10%), and preparative-scale GPC was required in order to separate these complexes from their by-products. The uncharacterized by-products, whose ^{31}P NMR spectra showed multiple unresolved peaks, were speculated to be ill-formed oligomers, but it is also possible they may have been less-symmetric stereoisomers of the macrocycles.

The Stelzer group synthesized hydroxyl-functionalized macrocycles by reacting $[M(MMPE)_2]^{2+}$ (M = Ni or Pd) templates with α,ω-dicarbonyl linkers to form 14-membered P_4 macrocycles **68** and **69** with hydroxyl groups attached to the backbone (Scheme 29) [95,96]. Both acetylacetone and malonaldehyde (added as the bis(dimethyl) acetal) gave macrocycles in high yield. These macrocycles contain hydroxyl groups on C_1 and C_3 of the three-carbon bridge. Macrocycles with vicinal hydroxyl groups on the two-carbon bridge were also synthesized using $[Pd(MMPP)_2]^{2+}$ as a

[1] This synthesis is deceptively appealing due to the small number of steps; however, the starting ligand MMPE is not a commercially available reagent and requires four synthetic steps from commercially available starting materials as well as an air-free fractional vacuum distillation to purify the final ligand [93].



Scheme 26. Palladium-templated tetraphosphine macrocycle syntheses [16,92].



Scheme 27. Possible products from 2:2 cyclizations of templated phosphines.

template and either 2,3-butanedione or benzyl as linking agents. The structures of the macrocyclic complexes were confirmed by X-ray crystallography.

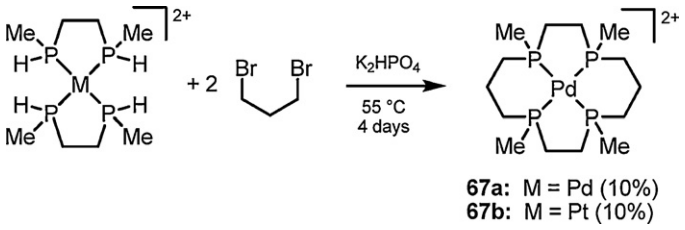
Each of these macrocycles contains eight chiral centers – four chiral phosphorus atoms and four chiral carbons. Interestingly, only a few of the many possible isomers were observed for these complexes. ^{31}P NMR of **68b** and **68c** each displayed peaks for only 2 isomers, while **69a** and **69b** showed peaks for three isomers. Two isomers of **68b** were characterized crystallographically (see Section 3.2).

Whereas alkyl dihalide linkers require basic conditions to undergo cyclization, these reactions occurred under neutral or even acidic conditions. The presence of the four hydroxyl groups makes these ligands some of the few examples of hydrophilic phosphine macrocycles (although water solubility was only reported for **68c**). However, one disadvantage of the hydroxyl groups is that the carbons attached to them are chiral. This creates four chiral carbons in addition to the four chiral phosphorus atoms, and because the synthesis of these macrocycles was not stereochemically controlled, many stereoisomers formed upon macrocyclization.

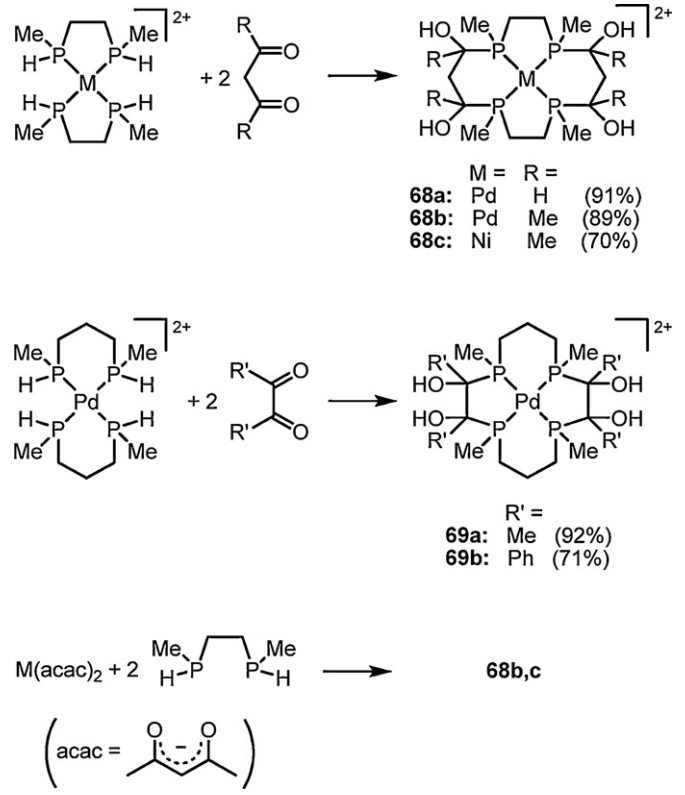
The nickel templates reacted more slowly than the palladium templates (requiring three days to reach completion instead of 12 h). H/D exchange experiments showed that the P–H bonds on the Ni templates are less acidic than those on the Pd templates. This result suggests that the mechanism for alkylation of coordinated phosphines begins by deprotonation of the phosphine, followed by attack of the coordinated phosphido ligand on a carbon electrophile. The metal template not only controls the stoichiometry of the reactants, but also activates the secondary phosphines toward reaction with the electrophilic carbonyl groups.

Macrocycles **68b** and **68c** were also synthesized by reacting free MMPE with M(acac)$_2$ complexes, followed by protonation with dilute HCl. This reaction combines formation of the template and macrocyclization in a single step by introducing the linker reagent as a weak ligand coordinated to the metal, which is displaced by the phosphine to form the template and which then reacts with the template to form the macrocycle.

Twelve-membered and 16-membered macrocycles were inaccessible by this route. This finding suggests that a 14-membered macrocycle may be the ideal ring size to fit around a square-planar transition metal. Although macrocycle size has not yet been systematically studied for phosphine macrocycles, 14-membered macrocyclic amines form more stable Ni(II) complexes than 12- or 16-membered macrocycles [11], which may also hold true for phosphine macrocycles.

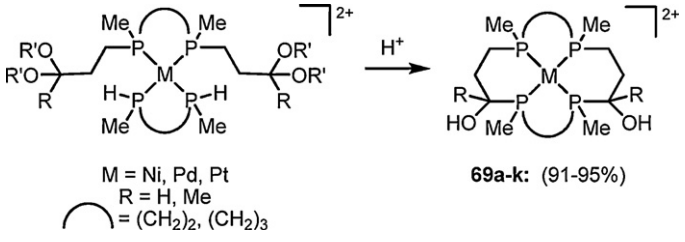


Scheme 28. Mizuta's Pd and Pt-templated P_4 macrocycles [94].

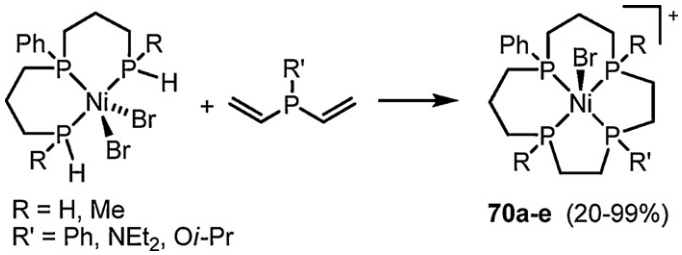


Scheme 29. 14-Membered hydroxyl-functionalized macrocycles [95,96].

The Stelzer group used a 1:1 templated synthesis to make a series of 14-, 15-, and 16-membered macrocyclic complexes, **69a**–**k**, by coordination of one α,ω-acetal-functionalized bisphosphine around a square-planar template then binding this complex to a secondary bisphosphine (MMPE or MMPP) (Scheme 30) [97]. Subsequent deprotection of the acetal with H^+ generates the carbonyl groups *in situ*, which react with the secondary phosphine to form the macrocycle in high yields. This reaction can be considered a 1:1 macrocyclization. Reaction times averaged 70 h and depended on the metal template (Pd and Pt reacted faster than Ni)



Scheme 30. Templated syntheses of 14-, 15-, and 16-membered P_4 macrocycles [97].



Scheme 31. Synthesis of macrocycles with adjacent 5- and 6-membered chelate rings [98,99].

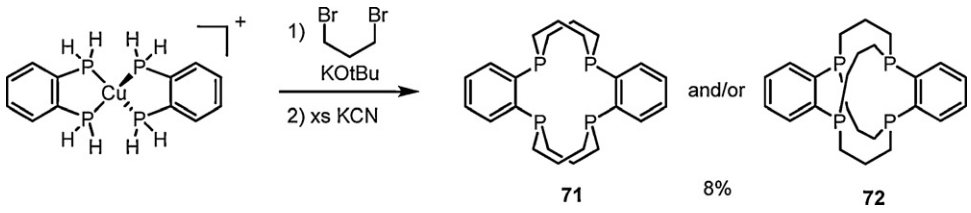
and on the nature of the carbonyl group (aldehydes reacted faster than ketones).

Each of the routes outlined in Schemes 26–30 involve the linking of two bidentate phosphine ligands to form a macrocycle. In 1992, Stelzer et al. synthesized a series of 14-membered macrocyclic complexes, **70a**–**e**, containing adjacent 5- and 6-membered rings by the templated linkage of a tridentate phosphine with divinyl-functionalized monodentate phosphorus ligands (Scheme 31) [98,99]. The reactions occurred within 48 h in refluxing dichloromethane, and resulted in >90% yields for all but one of the macrocycles. Two of these macrocycles, which contain secondary phosphine groups, were further functionalized by hydrophosphination with methyl acrylate.

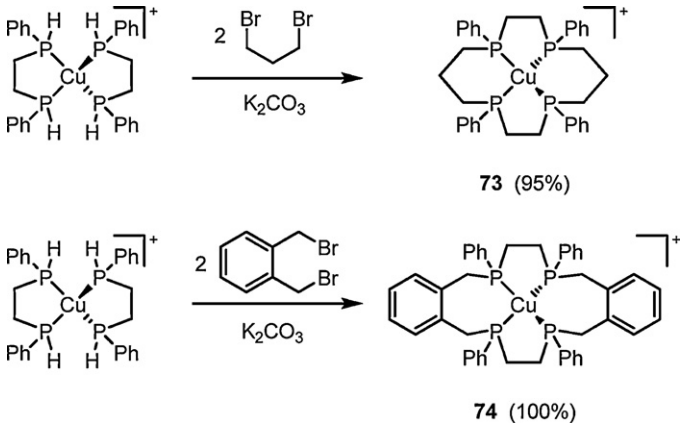
Most template syntheses of tetraphosphine macrocycles occur around d^8 metals such as Ni(II) or Pd(II) because of the preferred square-planar ML_4 or sometimes square-pyramidal ML_4X coordination geometries. Such geometries place the templated precursor ligand in the ideal geometry for macrocyclization, with the reactive phosphines adjacent to each other. However, this geometry is not necessarily required for a macrocyclization template. Two interesting macrocycle structures were synthesized around a copper(I) center (Scheme 32) [100]. Reaction of $Cu(BPB)_2OTf$ (BPB = *o*-bisphosphinobenzene) with 1,3-dibromopropane and KO*t*-Bu, followed by demetallation with excess cyanide, gave a mixture of products that were separated by HPLC. One of the isolated fractions, when analyzed by mass spectrometry, contained a peak corresponding to macrocycles **71** and/or **72** (8% yield). The presence of two signals in the ^{31}P NMR spectrum indicated that both of these isomers were present. These macrocycles may have been generated by linking 1,3-dibromopropane between the two BPB ligands while templated to the copper center, although the authors suggested a bis(phosphetane) intermediate, which then dimerizes to give the macrocyclic products. Although neither of these macrocycles was fully characterized, they are still interesting in that each represents a unique structure type: a doubly bridged "reinforced" macrocycle for **71** and a "cage-type" macrocycle for **72**.

Cu(I) was used in one other case as a template in a phosphine macrocycle synthesis. Reaction of $[Cu(MPPE)_2]^+$ with 1,3-dibromopropane or *o*-dibromoxylene gave macrocyclic complexes **73** and **74** (Scheme 33) [17]. The macrocyclic structures were confirmed by demetallation and characterization of the corresponding macrocyclic phosphine oxides by mass spectrometry. For more details, see Section 4.

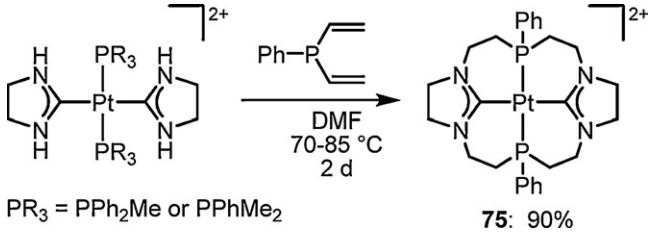
The first example of a tetradentate mixed phosphine/NHC macrocycle was recently reported [101]. Starting with a square-planar Pt(II) template containing alternating phosphine (PMe_2Ph or $PMePh_2$) and NH-functional NHC ligands, substitution of the unreactive phosphines by divinylphenylphosphine allowed templated coupling reactions between the vinylphosphines and NHC ligands, forming complex **75** which features a 16-membered macrocycle with alternating phosphine and NHC donor groups (Scheme 34).



Scheme 32. Wild's Cu(I)-templated phosphine macrocycle synthesis [100].



Scheme 33. Cu(I)-templated phosphine macrocycles [17].



Scheme 34. Template synthesis of a tetradentate phosphine/NHC macrocycle [101].

2.2.3. Larger macrocycles

Although P_3 and P_4 macrocycles have been the primary synthetic targets in phosphine macrocycle syntheses, an impressive 36-membered P_{12} macrocycle was recently reported to result from a hexametallic "golden wheel" template [102]. As shown in Scheme 35, $PhP(vinyl)_2AuCl$ was reacted with benzenehexathiol to generate template **76** in good yield. Molecule **76** then underwent AIBN-initiated hydrophosphination with excess phenylphosphine to generate the macrocyclic complex **77**. This compound was characterized by ^{31}P NMR spectroscopy and ESI-MS, which was reported as a weak signal at +3062 amu. However, the actual molecular mass of **77** is +3078 amu, and there is no reasonable 16 amu fragment that can be lost from this compound. The macrocyclic structure of **77** should therefore be regarded with care.

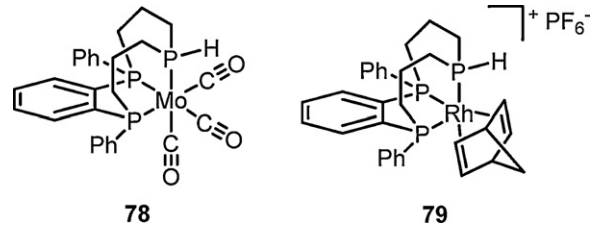
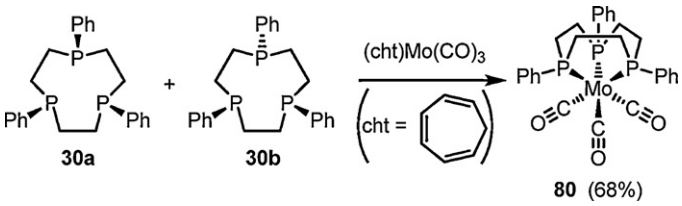


Fig. 5. Facially coordinating triphosphine macrocycles [32].



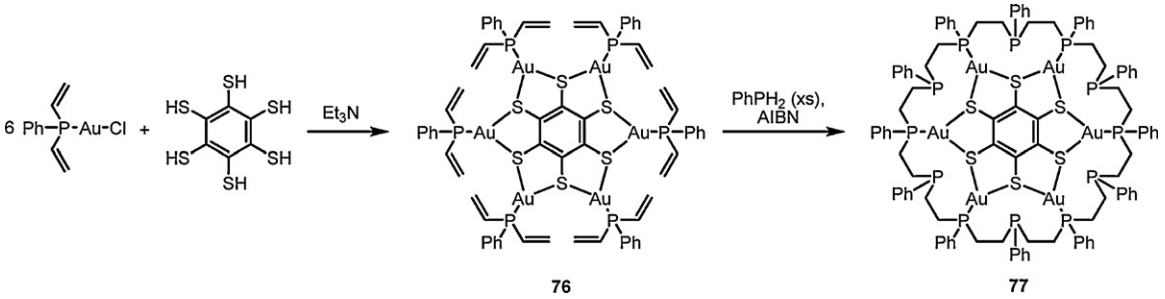
Scheme 36. Coordination of Helm's 9-membered P_3 macrocycle [56].

3. Coordination chemistry of macrocyclic phosphine ligands

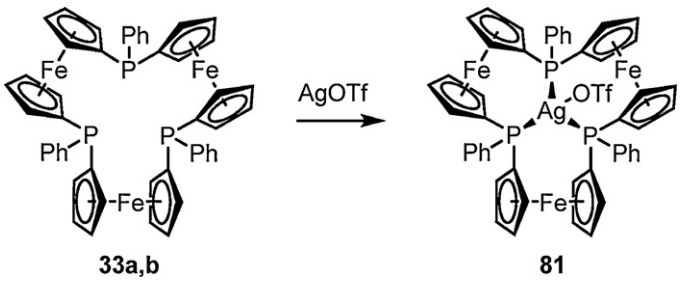
3.1. Triphosphine macrocycles

Most triphosphine macrocycles synthesized to date are 9- to 12-membered, which is too small to fully encircle a transition metal ion. Because of their small size, these ligands act exclusively as facially coordinating tridentate ligands. For example, macrocycle **8** was coordinated to $Mo(CO)_3$ and Rh(norbornadiene) to form complexes **78** and **79**, respectively (Fig. 5) [32].

Helm's nine-membered P_3 macrocycles **30a**,**b** coordinate facially to $Mo(CO)_3$ to form complex **80** (Scheme 36) [56]. The *syn-anti* isomer **30b** is the major isomer of this ligand, which is not geometrically situated to coordinate facially. Surprisingly, though, both the *syn-syn* and *syn-anti* isomers reacted to form **80**, suggesting that isomer **30b** isomerizes to **30a** upon coordination.



Scheme 35. Template synthesis of a 36-membered P_{12} macrocycle [102].



Scheme 37. Coordination chemistry of the ferrocene-bridged P_3 macrocycle [56].

Mizuta's ferrocene-bridged P_3 macrocycle **33** was coordinated to AgOTf to form complex **81** (Scheme 37) and its crystal structure was obtained [56]. In addition to the tridentate ligand, the triflate counterion is also coordinated. Like **34**, both the all-*syn* and *syn-anti* isomers of **33** reacted with Ag^+ to give the same product, suggesting that **33b** (the *syn-anti* isomer) undergoes inversion to form **80**.

In addition to their template syntheses on Cr, Mo, W, and Fe templates, 12-membered P_3 macrocycles have been coordinated to a variety of early transition metal halides ($TiCl_3$, VCl_3, $NbCl_3$ and $NbCl_4$) (Fig. 6) [103], although the Nb complexes were unstable at room temperature. The geometry of the $TiCl_3P_3$ and VCl_3P_3 complexes **82a–c** was confirmed by X-ray crystallography. The complexes in Fig. 6 are excellent (if only qualitative) examples of the macrocyclic effect, as such complexes are usually only stable at low temperature and dissociate a phosphine ligand to form MCl_3P_2 complexes. Also, exposure of a solution of **82b** to air preferentially oxidized the vanadium instead of the phosphine ligand, forming **83a**. This is the first example of an octahedral vanadyl-phosphine complex.

$CrCl_3$ complexes **82d** and **82e** were also synthesized; however, they were formed by oxidation of the Cr^0 complexes **41b** and **42d** with Cl_2. Strangely, attempts to abstract the halides and induce coordination of the ether arms of **82e** were unsuccessful.

Macrocyclic P_3 complexes of Ru(II), Rh(I), Mn(I), Re(III), and Re(I) have also been synthesized [104]. In the case of the Re(I) complex **84c**, the chloro ligand could be replaced by hydride, vinylidene, or cumulene ligands. Mn(I), Re(I), and Ru(II) complexes **84a–c** and **89** were catalysts for ring opening metathesis polymerization (ROMP) when treated with $EtAlCl_2$, with **84b** being especially active.

3.2. Tetraphosphine macrocycles

As reviewed in Section 2, tetraphosphine macrocycles of various sizes have been synthesized by either cyclocondensation reactions or template syntheses. The macrocycles that are formed around metal templates are difficult or even impossible to remove from the metal (see Section 4) so the coordination chemistry of tetraphosphine macrocycles has not been thoroughly studied.

Macrocycle **19** was coordinated to various Mn(II) salts, forming octahedral complexes **91a–d** (Scheme 38) [43]. These complexes contain alternating five and seven-membered chelate rings, with *cis*-alkene groups in the seven-membered rings. It is assumed that these complexes exhibit *trans*-octahedral geometries, although no data are reported to confirm this. These complexes are more air-stable than most MnX_2P_4 complexes because of the macrocyclic effect.

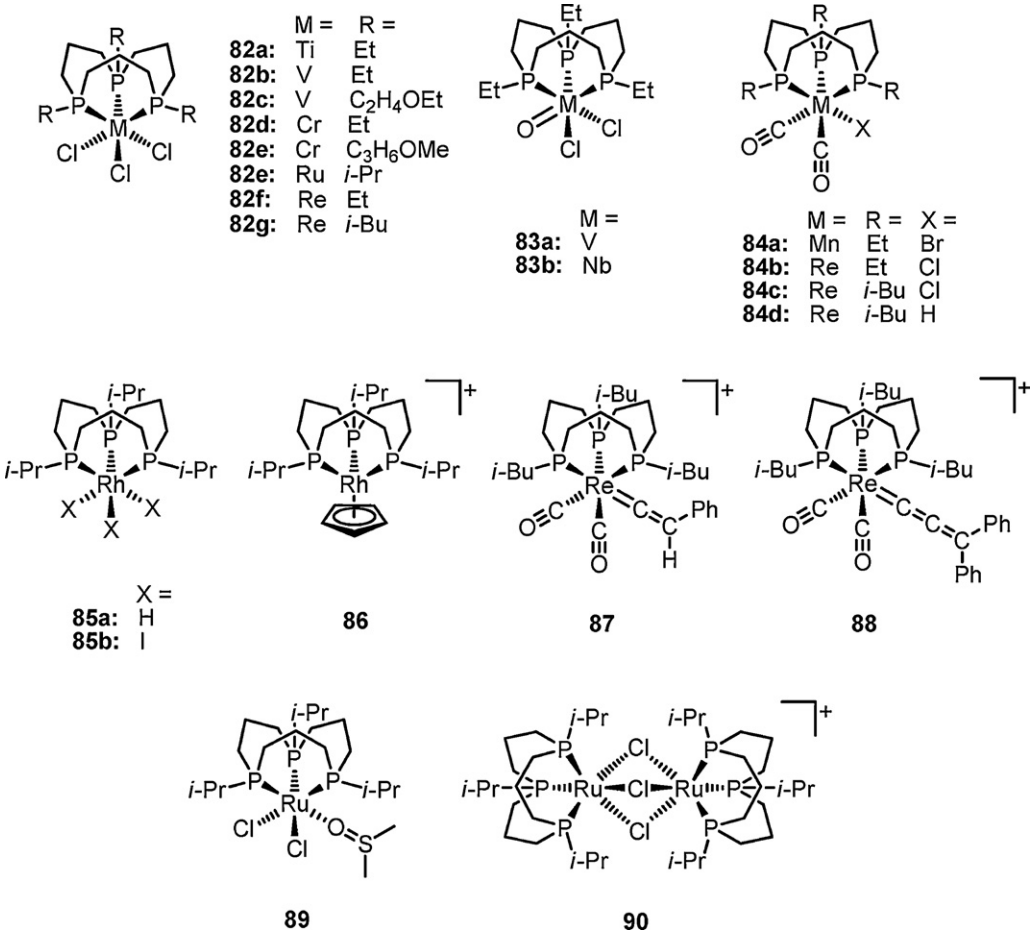


Fig. 6. Complexes of 12-membered P_3 macrocycles [103,104].

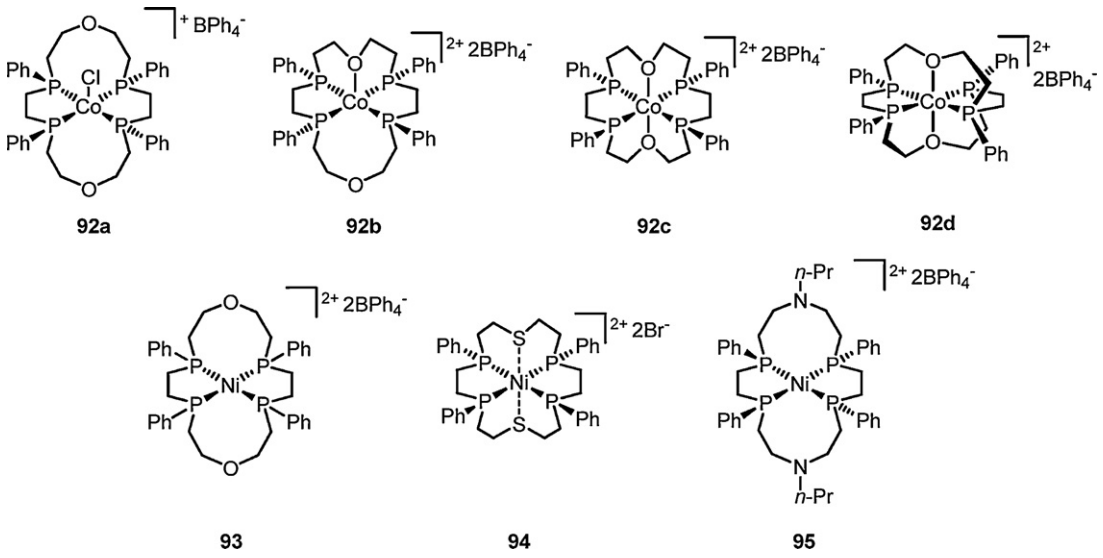


Fig. 7. Coordination complexes of P_4X_2 macrocycles **9–11** [33–36,105].

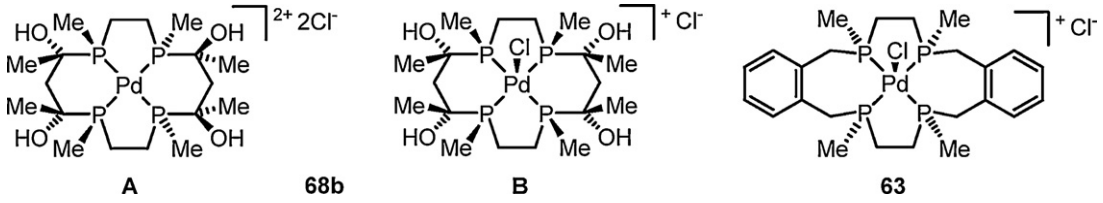
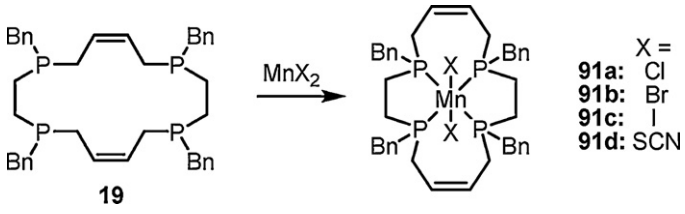


Fig. 8. Solid-state structures of macrocyclic PdP_4 complexes [92,95,96].



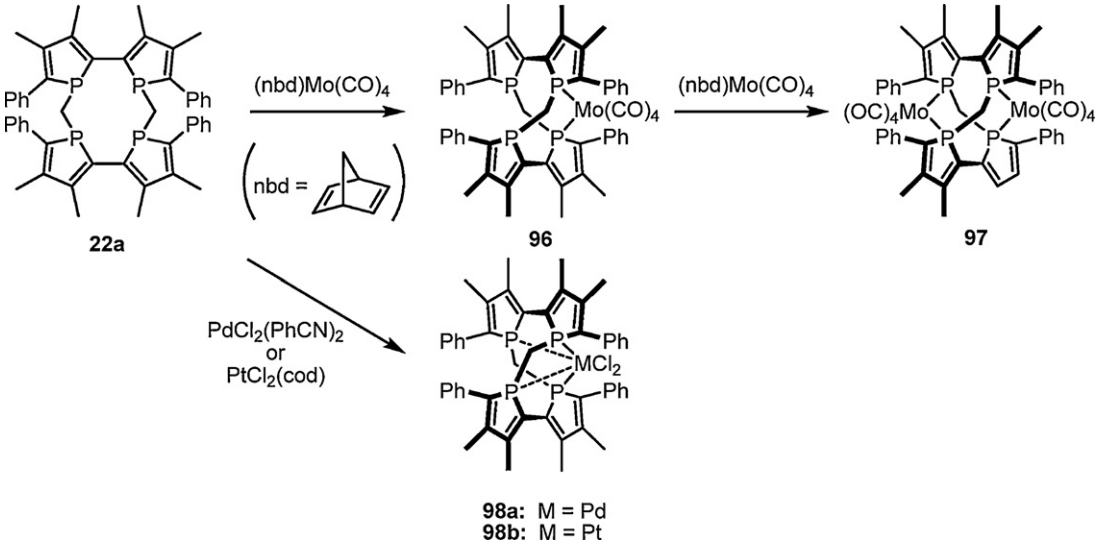
Scheme 38. Manganese complexes of macrocycle **19** [43].

Ciampolini's 18-membered crown ether type mixed-donor macrocycles **9–11** showed interesting coordination chemistry with cobalt and nickel; the complexes acted as tetradentate, pentadentate, or hexadentate ligands depending on the metal, the identity of the non-phosphorus donors, and the presence of auxiliary ligands such as chloride or solvent (Fig. 7) [33–36,105]. Tetradentate and pentadentate Co(II) complexes of **9** were characterized (**92a** and **92b**, respectively), as well as two different hexadentate complexes **92c**,**d**. These examples illustrate that the coordination behavior can vary widely between different stereoisomers of macrocyclic phosphine ligands. As expected, P_4O_2 macrocycles **9** and **11** acted as tetradentate ligands to Ni(II), forming square-planar complex **93**. The P_4S_2 ligand **10** bonded to Ni(II) as a hexacoordinate ligand, forming a highly distorted octahedral complex **94** with the phosphorus donors in the equatorial positions and the sulfur donors in the axial positions. The Ni–S bonds are quite long (2.94 Å), indicating a weak interaction.

Even when the macrocycle contains only phosphorus donors, the stereochemistry of the ligand can influence the coordination behavior of the metal center. Two isomers of Stelzer's α-hydroxyl-functionalized macrocyclic Pd complex **68b** were isolated, and their crystal structures obtained (Fig. 8) [95,96]. Interestingly, isomer **A** (*R*,*S*,*S*,*R*) crystallized as a square planar $[PdP_4]^{2+}$ complex, while isomer **B** (*R*,*S*,*R*,*S*) crystallized as a square-pyramidal $[PdP_4Cl]^+$ complex, with the axial chloro ligand *syn* to the methyl groups. The Pd–Cl bond is especially long (2.831 Å vs. normal bond distances of 2.2–2.4 Å), and dissociates in solution. The authors speculated that the all-*syn* configurations of the methyl substituents (arising from *R*,*S*,*R*,*S* stereochemistries of the phosphines) force the Pd ion slightly out of the macrocyclic plane, allowing access to a fifth coordination site.

The 16-membered *o*-xylene-bridged Pd–P_4 macrocycle **63** also crystallized as a square-pyramidal $[PdP_4Cl]^+$ complex [92]. Again, the macrocyclic phosphine was the (*R*,*S*,*R*,*S*) isomer, with all methyl groups *syn* to each other. However, in this case the chloride ligand coordinated on the *opposite* side of the methyl groups. This suggests that the explanation for the 5-coordinate geometry of complex **68b** does not extend to other systems.

Because no thermodynamic studies of macrocyclic phosphine complexes have been conducted, the ideal ring size for a macrocyclic P_4 ligand is not known. In lieu of thermodynamic data, examination of crystal structures may yield some clues to which ring size will be the best fit. In both isomers of **68b**, the bite angles of the five-membered chelate rings are slightly less than 90° (86.2–87.6°), while the bite angles of the 6-membered rings are slightly more than 90° (92.8–93.2°). This suggests that a P_4 macrocycle with only five-membered chelate rings (a 12-membered ring) would not be large enough to fit around a transition metal ion. Instead, a combination of five and six-membered rings (or perhaps all six-membered rings) should be more ideal for a tetraphosphorus macrocycle. Alternating five- and six-membered chelate rings, formed from phosphines with two- and three-carbon spacers, approximately supplement



Scheme 39. Coordination chemistry of the 10-membered phosphole macrocycle **22a** [46,106].

each other, allowing a planar arrangement of the four phosphorus atoms around the metal center. Complex **63** has a 16-membered macrocycle, with alternating five-membered and seven-membered chelate rings. The five-membered bite angles are about 85°, whereas the seven-membered rings' bite angles are around 95° (thus supplementing each other). However, seven-membered metallacycles are usually less stable than six-membered ones, as will be discussed in Section 4.

The 10-membered tetraphosphole macrocycle **22a** is too small to fully encircle a transition metal ion [46]. Instead, it coordinates to $Mo(CO)_4$ as a bidentate ligand, yielding compound **96** (Scheme 39). The ligand is twisted into a boat-type configuration, with alternating phosphole groups chelating to a single Mo center. The ligand can coordinate to a second Mo center through the other two phosphole groups, generating the bimetallic complex **97**. The structures of both of these complexes were confirmed by X-ray crystallography.

Pd(II) and Pt(II) complexes of ligand **22a** were also synthesized (compounds **98a**,**b**) [106]. As with the Mo complexes, alternating phosphole groups are coordinated to the metal center. X-ray crystallography confirmed the chelation of the metal by alternating phosphole groups and also suggested some degree of interaction between the metal and the non-coordinating phospholes.

A mixture of macrocycle **22a** and $Pd(OAc)_2$ was tested for catalytic activity in the Stille and Heck couplings, where it showed comparable catalytic activity to $Pd(OAc)_2$ + tri(2-furyl)phosphine, but with much longer catalytic lifetimes. In addition, the system did not precipitate Pd^0 over time and remained active when additional reactants were introduced. The extended lifetime of the catalyst is presumably caused by increased stability of the macrocyclic complex. However, because the macrocycle does not actually surround the metal and only acts as a bidentate ligand, this should not be regarded as a true "macrocyclic effect", but more accurately as a reinforced chelate effect. This is the only reported application of a macrocyclic tetraphosphine complex, *ironically as a bidentate ligand*!

Phosphinine macrocycles **23**–**27** were synthesized with the expectation that they would stabilize low oxidation states of metals because phosphinines are good π-acceptor ligands, similar to CO [107]. W, Ir, and Rh complexes **99**, **100a**, and **100b** (Fig. 9) were prepared in high yield and characterized crystallographically [48]. In addition, a rare Au(I) macrocyclic complex (**101**) was synthesized and its redox properties studied [108]. The metal was reduced electrochemically or with sodium naphthalenide. The resulting Au(0) complex was unstable above −20 °C, whereupon it decomposed to free ligand and colloidal gold. Still, this is a rare example of a monomeric Au(0) complex, and it is more stable than Au(0) carbonyl complexes, which are only stable below 77 K [109].

4. Demetallation of macrocyclic phosphine complexes

As described above, template syntheses can result in high-yield macrocyclization steps by coordinating the phosphine precursors around the transition metal, followed by linking these phosphines to form the macrocyclic ligand which is already coordinated to the metal. In order to extend the coordination chemistry of macrocyclic phosphine ligands, it would be useful to be able to replace the template metal with different transition metal ions. This is the

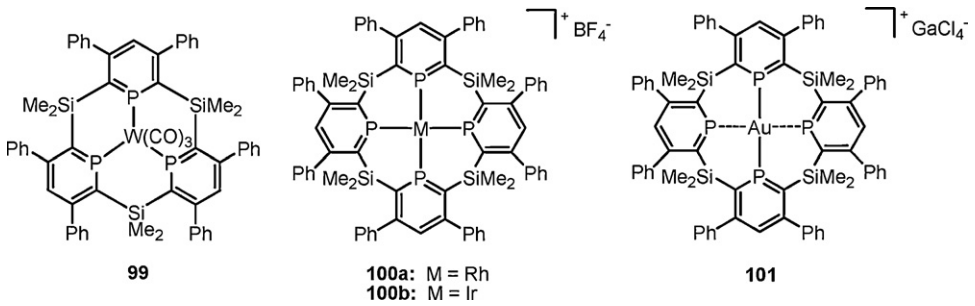
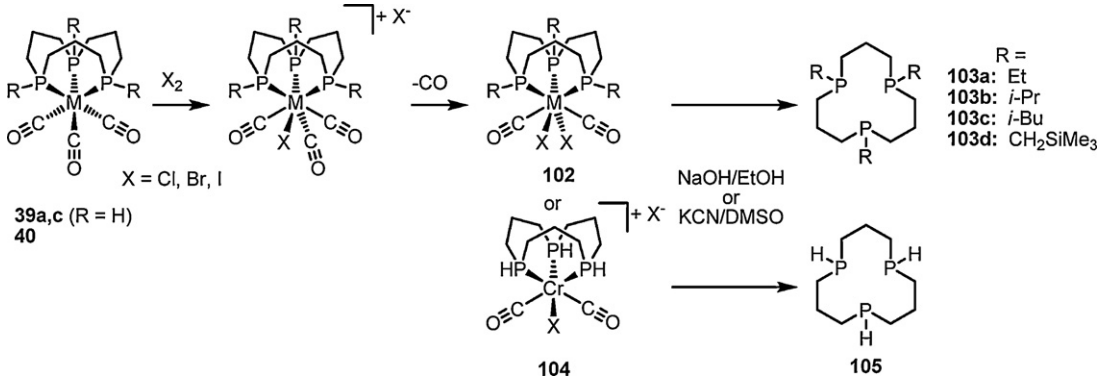


Fig. 9. Phosphinine macrocycle complexes [48,108].



Scheme 40. Demetallation of macrocyclic $MP_3(CO)_3$ complexes [110–112].

major drawback of template syntheses: because of the macrocyclic effect, macrocyclic phosphines are more difficult to remove from their complexes than other ligands. Indeed, it is often difficult or impossible to demetallate macrocyclic phosphine complexes.

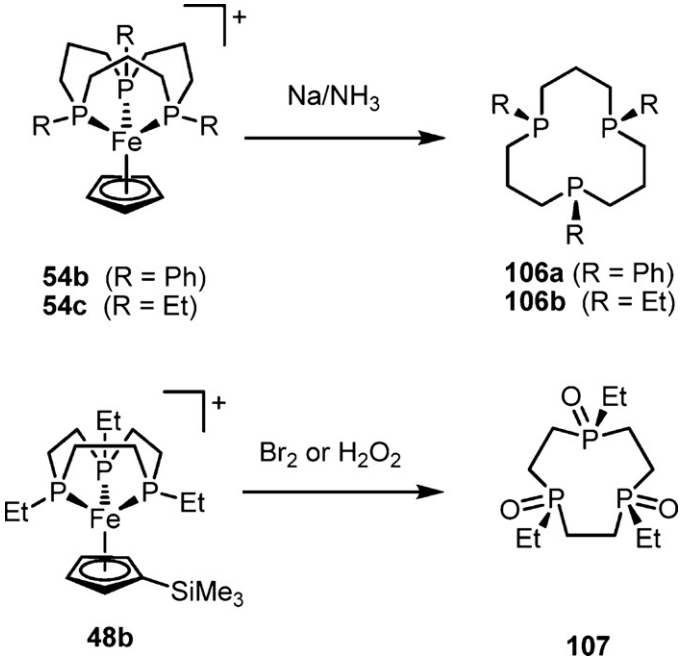
4.1. Triphosphine macrocycles

As discussed in Section 3.1, triphosphine macrocycles do not surround a metal but instead act as facially coordinating ligands. Because the metal is not surrounded by the ligand, stepwise removal of each donor atom should be easier for tridentate macrocycles than for tetradentate macrocycles. Indeed, many P_3 macrocycles can be removed from their complexes, although harsh conditions are often necessary.

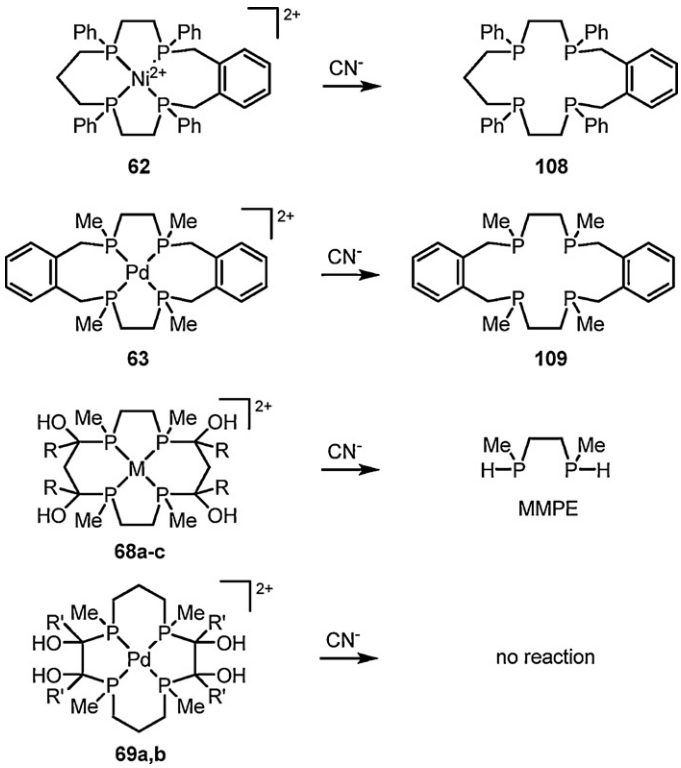
Norman's *fac*-$Mo(CO)P_3$ complexes **40a**–**d** did not demetallate, even upon treatment with cyanide [72,73]. Follow-up studies by the Edwards group showed that these complexes can, however, be converted into complexes that allow dissociation of the phosphine. For example, the W and Mo complexes **40** and **41** undergo oxidative addition with halogens, followed by loss of CO after standing for a few days in dichloromethane (Scheme 40) [110]. Treatment of **99** with NaOH in ethanol liberated the macrocyclic phosphine ligands **103a**–**d**, which were isolated and fully characterized [111,112]. The X-ray crystal structure of **103b** confirmed the all-*syn* stereochemistry (all lone pairs on the same side of the macrocycle), as would be expected for a facially coordinating tridentate ligand. Comparison of this crystal structure to that of its Mo complex showed that the macrocycle contracts upon coordination and might be large enough to facially coordinate much larger metal ions.

Strangely, Mo and W complexes of the secondary triphosphine macrocycle **105** did not liberate the phosphine from the metals. Instead, the analogous Cr complex **104** was prepared, which did liberate the phosphine, although the yields of this demetallation were lower (40% vs. 60–90%).

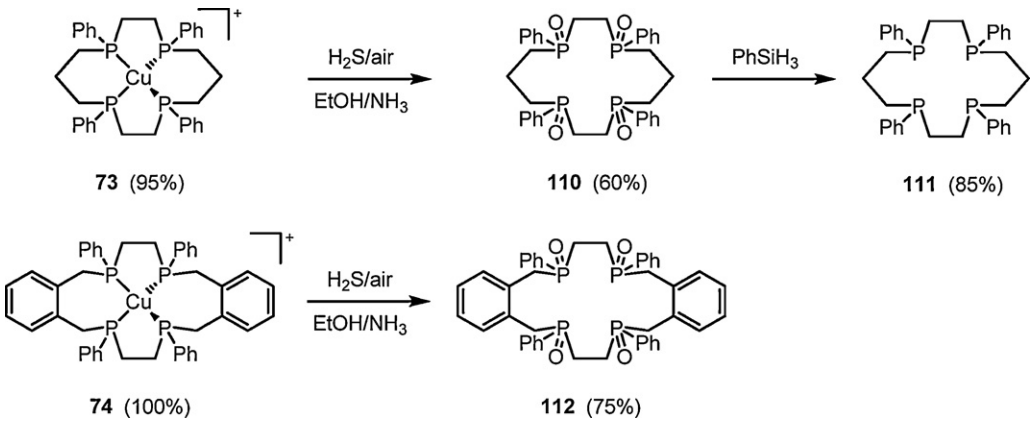
Edwards' macrocyclic piano-stool complexes were demetallated in high yield by digestion of the metal complex with Na/NH_3 to release the free macrocycles **106a**,**b** (Scheme 41) [82]. These free ligands were then coordinated to other first-row transition metals (see Section 3.1) [103]. *These are the only examples where macrocyclic phosphine ligands have been synthesized around one transition metal, demetallated, then transferred to other metals*. The



Scheme 41. Demetallation of macrocyclic iron piano-stool complexes [79,82].



Scheme 42. Demetallation reactions of tetraphosphine macrocycles with cyanide [91,92,96,97].



Scheme 43. Oxidative demetallation of macrocyclic Cu(I) phosphine complexes [17].

9-membered macrocycle on complex **107** (synthesized by alkylation of **48b** (R_1 = H, R_2 = vinyl), followed by hydrogenation of the vinyl group) was oxidatively demetallated with Br_2 or H_2O_2 [79].

4.2. Tetraphosphine macrocycles

The success of demetallations of tetraphosphine macrocycles seems to depend on the size of the chelate rings present on the ligand. Complex **62**, containing five, six, and seven-membered chelate rings, was demetallated by treatment with aqueous NaCN (Scheme 42) [91]. Also, complex **63**, with alternating five and seven-membered metallacycles, was quickly demetallated by heating with excess cyanide [92]. In contrast, complexes **68** and **69**, featuring only five- and six-membered rings, could not be demetallated with cyanide. Instead, the macrocyclic complex either resisted demetallation completely or the macrocycle fell apart, releasing the precursor phosphine MMPE from the template [96,97]. Seven-membered chelate rings are less stable than five- or six-membered rings so it is likely that complexes **62** and **63** are less stable than **68** and **69**, which allows them to be demetallated with cyanide. It is not known whether this result is a thermodynamic or kinetic effect.

Although the 14-membered macrocycles above could not be demetallated, copper(I) complexes of the *reinforced* 14-membered macrocycles **71** and **72** were successfully demetallated by treatment with cyanide (Scheme 32) [100]. In fact, the macrocyclic complexes were not even isolated in this case. Complex **73**, another 14-membered macrocyclic copper complex, was demetallated by treatment with H_2S in basified ethanol and air, which precipitated Cu_2S and oxidized the ligand to phosphine oxide **110**, which was reduced to phosphine **111** by reduction in neat phenylsilane (Scheme 43) [17]. Complex **74** was also demetallated in this manner to release macrocyclic phosphine oxide **112**.

The demetallation of macrocyclic Cu(I) complexes **71–73** contrasts with the inability to successfully demetallate complexes **68** and **69**. This result may be attributable to the differences in the coordination geometries of the metals. The d^8 metals Ni(II), Pd(II), and Pt(II) favor square-planar (or sometimes square-pyramidal) geometries, with P–M–P angles of ~90°. This geometry facilitates coordination of the five- and six-membered chelate rings with minimal ring strain. In contrast, d^{10} Cu(I) favors a tetrahedral geometry, with ideal P–M–P angles of 109°. This geometry strains the chelate rings, resulting in weaker binding to the metal and thus easier demetallation. Unfortunately, for now, this explanation is only hypothetical. Hopefully, further structural studies on macrocyclic copper–phosphine complexes will give data on bond angles and ring strain in these complexes, and the reasons for any instabilities will become clearer.

5. Summary

It has been over 35 years since the first macrocyclic phosphine ligands were synthesized. Because these ligands promise to be strongly coordinating, many strategies have been designed for their synthesis. However, only a handful of synthetic methods have shown broad applicability in terms of the ring sizes, functional groups, and metal complexes that can be obtained. Still fewer of the resulting complexes have found use in their intended applications.

The main challenges in phosphine macrocycle synthesis are: (a) selectivity of the desired ring size over smaller rings or larger oligomers, (b) control over stereochemistry, and (c) characterization, including confirmation that the ligand is indeed macrocyclic. Facially coordinating triphosphorus macrocycles have seen the most success in all of these areas, as well as in their subsequent functionalization, demetallation, and/or coordination to a variety of transition metals. Tetraphosphine macrocycles, on the other hand, are still undeveloped in these respects. Of the handful of synthetic methods that have been developed for tetraphosphine macrocycles, none has allowed for more than a few variations thus far. Only four metals: Ni(II), Pd(II), Pt(II), and Cu(I), have been coordinated to tetradentate phosphine macrocycles, and these have been formed almost exclusively by template syntheses of the macrocycles around that particular metal. Moreover, these ligands bind so strongly to the template metal that their removal from the metal is difficult or even impossible. These difficulties have hampered the development of macrocyclic tetradentate phosphine ligands and have so far prevented their use in applications such as catalysis or radiopharmaceuticals.

Acknowledgments

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