

# Mixed Phosphine–Phosphine Oxide Ligands

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Received July 15, 2003

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Vladimir Grushin, a native of Moscow, Russia, obtained his education and Ph.D. degree in organometallic/organic chemistry (1984) from Moscow State University. He then spent several years doing research at the Institute of Organo-Element Compounds of the USSR Academy of Sciences and at the University of Ottawa before joining the faculty at Wilfrid Laurier University, Ontario, Canada. Since his move to the United States in 1997, he has been a principal investigator with DuPont Central Research in Wilmington, Delaware. His research interests are in the areas of organometallic chemistry, catalysis with metal complexes, activation of inert bonds, and aromatic nucleophilic substitution. He has over 100 publications to his credit.

somewhat like a fine art, requiring an individual, often intuitive approach for each catalytic system. There are certain families of ligands, however, that seem to hold special promise for a wide variety of reactions, catalyzed by late transition metals. Among those are so-called hemilabile ligands,<sup>1–4</sup> with both soft and hard nucleophilic centers within one molecule. Bis-phosphine monoxides (BPMPs) of the general formula R<sup>1</sup>R<sup>2</sup>P–Y–P(O)R<sup>3</sup>R<sup>4</sup>, where Y is a divalent spacer, constitute an important class of hemilabile ligands. Due to the presence of both the soft (P) and hard (O) Lewis base centers on one molecule, BPMPs can stabilize various transition metals in low and high oxidation states. Also, BPMPs often form labile metal chelates which can easily generate reactive, coordinatively unsaturated species (see section 4.1.1 for more detail). Consequently, the weak BPMP chelation provides low activation energy paths to various transformations at the metal center, such as ligand exchange, isomerization, oxidative addition, migratory insertion, reductive elimination, and so forth. As a result, transition metal–BPMP complexes are often capable of catalyzing various reactions under uncommonly mild conditions with very high selectivities. As will be shown in section 4.1, some BPMP complexes of Rh and Pd exhibit exceptionally high catalytic activities and/or superior

## 1. Introduction

The right choice of a ligand for a metal-catalyzed homogeneous reaction can be as critical as the choice of the metal itself. In general, ligand design is

<sup>†</sup> Contribution No. 8428.

selectivities in such important processes as methanol carbonylation (the Monsanto acetic acid process) and olefin hydroformylation and hydrocarboxylation. A number of BPMOs have also proven usefulness in synthesis, analytical chemistry, and the chemistry of materials, and in cancer and AIDS research. Due to the practical importance of BPMOs, a substantial share of information on their synthesis and applications can be found in the patent rather than the open literature.

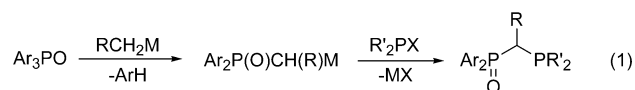
The birth of the chemistry of BPMOs dates back to the 1960s, when a few reports<sup>5–7</sup> appeared describing the first members of the family of BPMOs, in which the P(III) and P(V) centers are separated by a C<sub>1</sub><sup>5,7</sup> or a C<sub>2</sub><sup>6</sup> spacer. Since then the field has advanced considerably. New synthetic methods have been developed and exciting applications found for a variety of BPMOs with different linkers between the phosphine and phosphinyl functionalities. In 1991, Bader and Lindner<sup>1</sup> published a survey of P,O-ligands, and more recently Slone, Weinberger, and Mirkin<sup>2</sup> reviewed various classes of hemilabile ligands. However, no reviews have appeared in the literature focusing specifically on the chemistry of BPMOs. In this article, we provide a detailed overview of mixed phosphine–phosphine oxide compounds, with the literature covered up to mid-2003. More recent progress is briefly summarized in section 5. Mono-oxides of polycyclic, P-bridgehead diphosphines<sup>8</sup> and BPMO analogues with the two P centers separated by a nitrogen atom (recently reviewed by Ly and Woollins<sup>9</sup>) are beyond the scope of this article.

## 2. Synthesis

Two general synthetic strategies are known for the preparation of BPMOs. One involves two P<sub>1</sub> units coming together to form a BPMO molecule. The other approach is based on selective oxidation of one P atom in readily available bidentate tertiary organic phosphines.

### 2.1. Assembling BPMO Molecules from Two P<sub>1</sub> Fragments

As early as 1960, Issleib and Baldauf<sup>5</sup> reported the formation of Ph<sub>2</sub>PCH<sub>2</sub>P(O)Ph<sub>2</sub> (dppmO) in the reaction of Ph<sub>2</sub>PCL with moist solutions of CH<sub>2</sub>N<sub>2</sub>. Soon after that, Seyferth<sup>7</sup> developed the first general method for the preparation of BPMOs of the general formula Ar<sub>2</sub>PCH(R)P(O)Ar'<sub>2</sub>, as shown in eq 1.



M = Li, MgX; X = Cl, Br

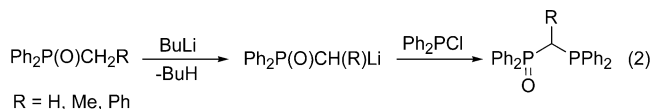
Ar = Ph, 1-C<sub>10</sub>H<sub>7</sub>, 2-BuOC<sub>6</sub>H<sub>4</sub>, 3-PhC<sub>6</sub>H<sub>4</sub>

R = H, Me, Et, Pr, Bu

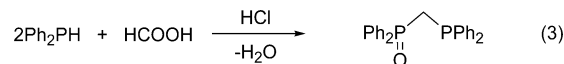
R' = Ph, HC=CMe<sub>2</sub>, 2,4,6-C<sub>6</sub>H<sub>2</sub>Cl<sub>3</sub>, CHCl<sub>2</sub>, p-dioxanyl, Cy, Me, 2-C<sub>10</sub>H<sub>7</sub>, N-morpholinyl

Modifications of this method have been reported by several groups.<sup>10–14</sup> Grim's work<sup>10</sup> communicates improved yields of Ph<sub>2</sub>PCH(R)P(O)Ph<sub>2</sub> (R = H, Me, and Pr) from the inverse addition procedure, i.e.,

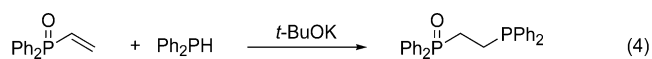
when the phosphinylalkyllithium is added to Ph<sub>2</sub>PCL. Also, a different route has been used to generate the reactive nucleophilic building block Ph<sub>2</sub>P(O)CH(R)Li via deprotonation of Ph<sub>2</sub>P(O)CH<sub>2</sub>R with BuLi (eq 2).<sup>11–14</sup>



Rudomino and Tsvetkov<sup>15</sup> have reported the synthesis of dppmO from Ph<sub>2</sub>PH and formic acid in the presence of HCl (eq 3). However, Bu<sub>2</sub>PH or Ph(Bu)PH remained unreactive under similar conditions.

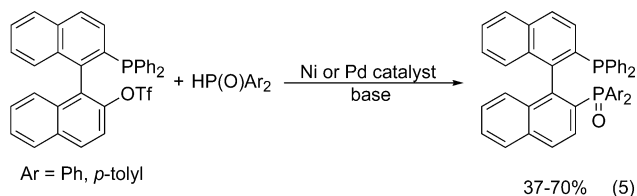


The mono-oxide of 1,2-bis(diphenylphosphino)ethane (dppeO) was first isolated from the reaction of 1,2-bis(diphenylphosphino)ethylene with HBr in AcOH followed by hydrolysis<sup>6a</sup> and from alkaline hydrolysis of 1,1,4,4-tetraphenyl-1,4-diphosphoniacyclohexane dibromide,<sup>6b</sup> in unspecified yield. The reaction of Ph<sub>2</sub>PH with Ph<sub>2</sub>P(O)CH=CH<sub>2</sub> (eq 4)<sup>16</sup> or Ph<sub>2</sub>P(O)CH<sub>2</sub>CH<sub>2</sub>OR (R = H, Et)<sup>17</sup> afforded dppeO in 89 and 91% yield, respectively. The same molecule has also been obtained in 41% isolated yield from the photochemical addition of Ph<sub>2</sub>P(O)H to Ph<sub>2</sub>PCH=CH<sub>2</sub> in *i*-PrOH.<sup>18</sup>



The backbone isomer of dppeO, 1,1-bis(diphenylphosphino)ethane monoxide, has been prepared, in unspecified yield, via hydrosilylation of diphenyl(vinyl)phosphine oxide, followed by the treatment with Ph<sub>2</sub>PCL.<sup>19</sup>

Butler and Davies<sup>20</sup> have reported the synthesis of 1,1'-bis(diphenylphosphino)ferrocene monoxide (dp-pfcO), by reacting 1-(diphenylphosphino)-1'-lithioferrocene with Ph<sub>2</sub>P(O)Cl or, alternatively, 1-(diphenylphosphinyl)-1'-lithioferrocene with Ph<sub>2</sub>PCL. A somewhat similar strategy has been employed for the preparation of BINAP monoxide (BINAP(O))<sup>21–24</sup> and its 5,5',6,6',7,7',8,8'-octahydro derivative<sup>21</sup> via the Ni- or Pd-catalyzed phosphinylation of the phosphino triflates (eq 5). The triflates, in turn, are synthesized in several steps from the corresponding binaphthol. The racemic BINAP(O) prepared this way<sup>23</sup> has been resolved with an optically active C,N-cyclopalladated complex. Treatment of the less soluble diastereomer with ethylenediamine released (*S*)-BINAP(O).<sup>23</sup>



A series of tri-P-substituted methanes of the type (Ph<sub>2</sub>P(X))(Ph<sub>2</sub>P(Y))(Ph<sub>2</sub>P(Z))CH, where X, Y, Z = an electron pair, O, S, or Se in various combinations

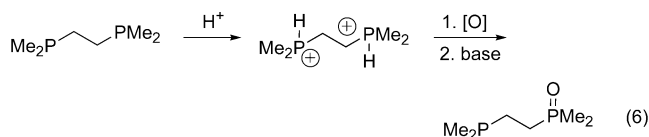
have been prepared.<sup>25–28</sup> For instance, deprotonation of  $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{P}(\text{S})\text{Ph}_2$  with  $\text{BuLi}$ , followed by treatment with  $\text{Ph}_2\text{PCl}$ , produced  $(\text{Ph}_2\text{P})(\text{Ph}_2\text{P}(\text{O}))(\text{Ph}_2\text{P}(\text{S}))\text{CH}$ .<sup>28</sup>

## 2.2. Selective Oxidation of Polyphosphines

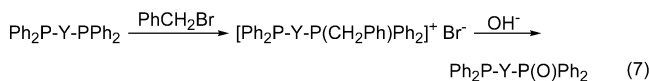
Numerous bidentate phosphines are easily accessible and/or commercially available. Clearly, direct mono-oxidation of organic tertiary diphosphines is the most attractive approach to BPMOs. However, oxidation of one of the two P(III) atoms in a diphosphine molecule to P(V) does not diminish substantially the reducing ability of the remaining P(III) center. As a result, direct oxidation of bidentate phosphines with conventional oxidants (e.g.,  $\text{O}_2$ ,  $\text{H}_2\text{O}_2$ ,  $\text{Br}_2/\text{H}_2\text{O}$ ) is nonselective, leading to mixtures of the unreacted diphosphine, its monoxide, and its dioxide.<sup>29–39</sup> Tedious column separations of such mixtures and poor yields (10–30%) are inevitable when conventional diphosphine oxidations are employed to prepare BPMOs. Exceptions are rare. Thus,  $\text{Ph}_2\text{PNHPPH}_2$  has been reported to undergo oxidation with  $\text{H}_2\text{O}_2$  to the corresponding mono-oxide, which was isolated in ca. 50% yield (crude form).<sup>40</sup> Triphos has been air-oxidized in the presence of a cobalt catalyst to triphosO in 30–45% yield or to triphos $\text{O}_2$  in 80–95% yield.<sup>41</sup> The Co-catalyzed air oxidation of *dppm* and *dppe* in the presence of excess sacrificial 3-methylbutanal has been claimed to produce *dppm*O and *dppe*O in ca. 55% yield at 88–100% conversion (GC data; no product isolation described).<sup>42</sup> Similarly, the Rh-catalyzed oxidation of BINAP with  $\text{O}_2$  in the presence of CO has been reported<sup>43</sup> to produce mixtures of  $\text{BINAP}(\text{O})_2$  and  $\text{BINAP}(\text{O})$ , with the selectivity for the desired mono-oxide being only ca. 30–50%, as determined by NMR. No attempts have been made to isolate  $\text{BINAP}(\text{O})$  from these Rh-catalyzed oxidations.<sup>43</sup> The Staudinger-type reaction of 1,2-bis(diphenylphosphino)benzene with  $\text{Me}_3\text{SiN}_3$  has been found to result in the exclusive formation of the corresponding mono-iminophosphorane,<sup>44a</sup> which may be hydrolyzed to the oxide. This selectivity is rather exceptional, as diphosphines with a flexible backbone, such as *dppm*, often react with azides nonselectively, unless special conditions (e.g., high temperature, solvent-free) are applied.<sup>44b</sup> Although a few more examples of selective mono-amination of bidentate phosphines are known,<sup>45,46</sup> hydrolysis of such phosphine–iminophosphoranes to the desired BPMO often occurs in low yield.<sup>47</sup> Remarkably, the electrochemical oxidation of *dppfc* under thoroughly optimized conditions has been shown to produce *dppfc*O in 66% isolated yield.<sup>36</sup> Since the difference in the  $E^\circ$  values of *dppfc* and *dppfc*O is only 0.1 V, careful optimization of the working potential is critical in order to avoid further oxidation of the electrochemically produced *dppfc*O to *dppfcO}\_2.<sup>36</sup>*

Mäding and Scheller<sup>33</sup> have found an elegant solution to the problem of low selectivity of polyphosphine oxidation. They have demonstrated that protonated forms of bidentate phosphines containing basic dialkylphosphino groups (e.g., *dmpe*) can be selectively mono-oxidized (eq 6).<sup>33,48</sup> Unfortunately, this “protection via protonation followed by oxidation”

method (eq 6)<sup>33</sup> is not applicable to the most readily available and attractive diarylphosphino substrates due to their insufficient basicity.

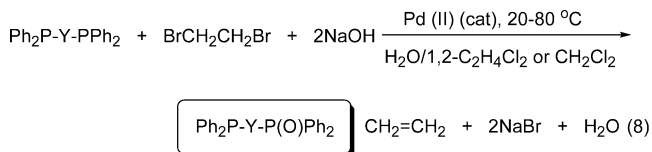


Abatjoglou and Kapicak<sup>49</sup> have developed a general two-step method for the synthesis of BPMOs via monobenylation of a bidentate phosphine with benzylic halides, followed by alkaline hydrolysis of the phosphonium salt (eq 7). The first step of the Abatjoglou–Kapicak process<sup>49</sup> is run in a low-polarity medium, such as toluene. This way the monophosphonium salt precipitates from the reaction mixture as the reaction occurs, and thus benzylation of the second P atom is avoided. The phosphonium salt is then isolated and treated with aqueous NaOH to produce the desired mono-oxide. Overall yields of 52–81% for the two steps have been claimed<sup>49</sup> for the purified products  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{P}(\text{O})\text{PPh}_2$  ( $n = 1–6$ ). This two-step method has also been successfully used by others.<sup>12,51–54</sup> Although difficulties in preparing  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{P}(\text{O})\text{PPh}_2$  ( $n = 1^{12}$  and  $3^{55}$ ) via the Abatjoglou–Kapicak process have been mentioned, Alajarin and co-workers<sup>54</sup> have recently reconfirmed the yield of 56% for *dppm*O ( $n = 1$ ) in reaction 7.



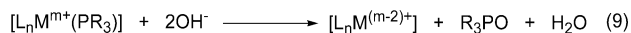
Y =  $(\text{CH}_2)_n$ ,  $n = 1–6$ ;  
*cis*-CH=CH; *trans*-CH=CH

The first general, one-step method has been recently developed for catalytic mono-oxidation of diphosphines.<sup>56–58</sup> This anaerobic oxidation readily occurs under biphasic conditions in the presence of a palladium catalyst and 1,2-dibromoethane as the oxidant (eq 8) to afford various BPMOs in 50–90% isolated yield. More recently, Tol-BINAP(O) was prepared in the same manner.<sup>59</sup>



$\text{Ph}_2\text{P}-\text{Y}-\text{PPh}_2 = \text{dppm}, \text{dppe}, \text{dppp}, \text{dppb}, \text{dppbz}, \text{dppfc}$ ,  
(*S*)-BINAP, (*R*)-BINAP, rac-BINAP

The catalytic mono-oxidation is based on the ability of some hard ligands, such as  $\text{O}^{2-}$ ,  $\text{F}^-$ ,  $\text{OH}^-$ ,  $\text{AcO}^-$ , and (in certain cases)  $\text{H}_2\text{O}$ , to promote the remarkably clean inner-sphere redox transformation of phosphine complexes of certain late transition metals, such as Cu, Ni, Rh, Ir, Pd, and Pt (eq 9).<sup>60–87</sup>



Reaction 9 is most characteristic of Pd(II) complexes.<sup>65–72,74–78,80,81,83–85,87</sup> Coordination of a hard anion  $\text{X}^-$  to the metal center, followed by P–X



**Table 1. Preparative Methods for the Synthesis of BPMOs**

BPMO	acronym	method of synthesis	isolated yield, %	<sup>31</sup> P NMR, δ, ppm (J <sub>P-P</sub> , Hz)	ref
	dmpmO	Protonation of dmpm, followed by oxidation with H <sub>2</sub> O <sub>2</sub> and alkaline hydrolysis	63.5	MeOH: -47.0; +50.2 (37.7) THF: -47.8; +36.4 (36.3)	33
	dppmO	Reaction of Ph <sub>3</sub> PO with MeLi, followed by Ph <sub>2</sub> PCl	ns <sup>a</sup> 60	-28.4; +27.7 (50)	7 10
		Reaction of Ph <sub>2</sub> P(O)Me with BuLi, followed by Ph <sub>2</sub> PCl	64 57.6		12 13
		Mono-benylation of dppm with PhCH <sub>2</sub> Br, followed by alkaline hydrolysis of the phosphonium salt	ns 52.5 56	-27.9; +29.4 (53)	14 49 54
		Reaction of Ph <sub>2</sub> PH with formic acid in the presence of HCl	76	-28.7; +27.2 (49.5)	15
		Pd-catalyzed anaerobic mono-oxidation of dppm	70–84	-26.4; +27.9 (50.5)	56–58
	dtolpmO	Reaction of Ph <sub>2</sub> PH with formic acid in the presence of HCl	71	-28.5; +28.0 (47.8)	15
		Mono-benylation of Tol <sub>2</sub> PCH <sub>2</sub> CH <sub>2</sub> PTol <sub>2</sub> with PhCH <sub>2</sub> Br, followed by alkaline hydrolysis of the phosphonium salt	ns	-29.7; +29.9 (48)	52, 167
		Reaction of Ph <sub>3</sub> PO with EtLi, followed by Ph <sub>2</sub> PCl	25	-12.3; +33.6 (62)	10
		Reaction of Ph <sub>2</sub> P(O)Me with BuLi, followed by Ph <sub>2</sub> PCl	ns	-12.6; +36.1 (65)	14
		Hydrozirconation of diphenyl(vinyl)phosphine oxide, followed by treatment with Ph <sub>2</sub> PCl	ns	-10.1; +31.4 (64.4)	19
		Reaction of Ph <sub>3</sub> PO with BuLi, followed by Ph <sub>2</sub> PCl	48 46.5 ns	-9.5; +32.7 (65)	10 13 14
		Reaction of Ph <sub>2</sub> P(O)CH <sub>2</sub> Ph with BuLi, followed by Ph <sub>2</sub> PCl	61 ns	-6.8; +30.0 (56)	11 14
	dppeO	Reaction of Ph <sub>2</sub> PH with CH <sub>2</sub> =CHP(O)Ph <sub>2</sub> in the presence of <i>t</i> -BuOK	89	-13.2; +34.7 (50)	16
		Reaction of Ph <sub>2</sub> PH with HOCH <sub>2</sub> CH <sub>2</sub> P(O)Ph <sub>2</sub> in the presence of KOH	91	-11.9; +31.6 (51.2)	17
		Mono-benylation of dppe with PhCH <sub>2</sub> Br, followed by alkaline hydrolysis of the phosphonium salt	81	-12.4; +31.7 (48.3)	49
		Photochemical addition of Ph <sub>2</sub> P(O)H to Ph <sub>2</sub> PCH=CH <sub>2</sub>	41		18
		Pd-catalyzed anaerobic mono-oxidation of dppe	78–87	-11.5; +32.3 (48.0)	56–58
	dpppO	Mono-benylation of dppp with PhCH <sub>2</sub> Br, followed by alkaline hydrolysis of the phosphonium salt	76	-18.6; +29.8	49
		Pd-catalyzed anaerobic mono-oxidation of dppp	73–76	-17.2; +32.0	56–58
	dppbO	Mono-benylation of dppb with PhCH <sub>2</sub> Br, followed by alkaline hydrolysis of the phosphonium salt	75.5	-17.0; +30.1	49
		Pd-catalyzed anaerobic mono-oxidation of dppb	80–83	-16.5; +32.2	56–58
		Mono-benylation of 1,5-bis(diphenylphosphino)pentane with PhCH <sub>2</sub> Br, followed by alkaline hydrolysis of the phosphonium salt	69	-16.3; +31.3	49
		Mono-benylation of 1,6-bis(diphenylphosphino)hexane with PhCH <sub>2</sub> Br, followed by alkaline hydrolysis of the phosphonium salt	60	-16.6; +30.7	49
		Mono-benylation of <i>cis</i> -1,2-bis(diphenylphosphino)ethylene with PhCH <sub>2</sub> Br, followed by alkaline hydrolysis of the phosphonium salt	ns	-18.9; +34.0 (24.4)	49

**Table 1 (Continued)**

BPMO	acronym	method of synthesis	isolated yield, %	<sup>31</sup> P NMR, δ, ppm ( <i>J</i> <sub>P-P</sub> , Hz)	ref
		Mono-benylation of <i>trans</i> -1,2-bis(diphenylphosphino)ethylene with PhCH <sub>2</sub> Br, followed by alkaline hydrolysis of the phosphonium salt	ns	-5.8; +21.4 (19.6)	49
	dppbzO	Pd-catalyzed anaerobic mono-oxidation of dppbz	81–83	-12.8; +30.7 (14.8)	58
		Mono-benylation of dppbz with PhCH <sub>2</sub> Br, followed by alkaline hydrolysis of the phosphonium salt	ns		167
	dppfcO	Reaction of (C <sub>5</sub> H <sub>4</sub> Br)Fe(C <sub>5</sub> H <sub>4</sub> PPh <sub>2</sub> ) with BuLi followed by Ph <sub>2</sub> P(O)Cl, or of (C <sub>5</sub> H <sub>4</sub> Br)Fe-(C <sub>5</sub> H <sub>4</sub> P(O)Ph <sub>2</sub> ) with BuLi followed by Ph <sub>2</sub> PCl	72–95		20
		Electrochemical oxidation of dppfc	66	-17.4; +28.5	36
		Pd-catalyzed anaerobic mono-oxidation of dppfc	40–65	-16.7; +28.5	56–58
	(±)-BINAP(O)	Multistep synthesis starting with BINOL <sup>b</sup>	70	-14.7; +27.7	23
		Pd-catalyzed anaerobic mono-oxidation of (±)-BINAP	71	-16.7; +27.9	58
	( <i>S</i> )-BINAP(O)	Resolution of (±)-BINAP(O) with an optically active C,N-cyclopalladated complex, followed by treatment of the less soluble diastereomer with ethylenediamine	100	-14.7; +27.7	23
		Pd-catalyzed anaerobic mono-oxidation of ( <i>S</i> )-BINAP	80–83	-16.7; +27.9	56–58
	( <i>R</i> )-BINAP(O)	Pd-catalyzed anaerobic mono-oxidation of ( <i>R</i> )-BINAP	80–81	-16.7; +27.9	56–58
	( <i>S</i> )-Tol-BINAP(O)	Pd-catalyzed anaerobic mono-oxidation of ( <i>S</i> )-Tol-BINAP	ns		59
	triphosO	Co-catalyzed air oxidation of triphos	30–45	-24.1; +29.1	41
	triphosO <sub>2</sub>	Co-catalyzed air oxidation of triphos	80–95	-23.7; +30.2	41
		Reaction of Ph <sub>2</sub> PH with (CH <sub>2</sub> =CH) <sub>2</sub> P(O)Ph in the presence of <i>t</i> -BuOK	72.5	-13.1; +42.8 (46.0)	16
		Reaction of PhPH <sub>2</sub> with CH <sub>2</sub> =CHP(O)Ph <sub>2</sub> in the presence of <i>t</i> -BuOK	90	-17.0; +34.3 (43.5)	16

<sup>a</sup> ns, not specified. <sup>b</sup> The yield in the next column is for the final step, the Pd- or Ni-catalyzed reaction of Ph<sub>2</sub>P(O)H with 2-diphenylphosphino-2'-triflato-1,1'-binaphthyl.

### 3. Metal Complexes Containing BPMOs

Due to their unique coordination properties, BPMOs find numerous applications in catalysis with metal complexes (see section 4.1). Understanding the modes of binding of BPMOs to various metals is therefore important in order to design new, efficient catalytic systems for various organic reactions. In

connection with this, an overview of the coordination chemistry of BPMOs will be presented in this section, to precede the description of organic reactions catalyzed by phosphine–phosphine oxide metal complexes further below.

As mentioned above (section 2), oxidation of one phosphino group in a bidentate phosphine to phos-

phanyl does not influence significantly the electron-donating ability of the remaining P(III) atom. As a result, phosphino groups of BPMP molecules readily undergo oxidation (see above) and quaternization with alkyl halides<sup>10,112</sup> and aryl halides in the presence of a metal complex catalyst. Thus, quaternization of dppmO with PhBr readily occurs in acetonitrile in the presence of a Ni catalyst to produce  $[\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{PPh}_3]^+\text{Br}^-$ .<sup>113</sup> The phosphinyl group of a BPMP also exhibits the expected properties. For instance, Wittig–Horner-type reactions of dppmO with various aldehydes RCHO in the presence of *t*-BuOK have been reported<sup>114</sup> to afford  $\text{Ph}_2\text{PCH}=\text{CHR}$  in 48–69% yield (see section 4.2). It is not surprising, therefore, that both the P (phosphine) and O (phosphinyl) nucleophilic centers on BPMP molecules can form complexes with various metal ions.

Both <sup>31</sup>P NMR and IR spectral methods are most helpful in determining the coordination modes of BPMPs. When coordinated to a metal, the phosphino and phosphinyl groups display <sup>31</sup>P NMR signals that are shifted (usually downfield for diamagnetic species) from those of the free ligand (Table 1). In IR spectra, the P=O band (commonly 1170–1200  $\text{cm}^{-1}$  for free  $\text{R}_3\text{PO}$ ) undergoes a noticeable shift to lower frequencies upon coordination of the oxygen to a metal center. Only on a rare occasion is the shift  $\Delta\nu_{\text{P=O}}$  not very well-pronounced, e.g., for some  $\text{Hg}^{2+}$ – and  $\text{Cd}^{2+}$ –BPMP complexes (see section 3.1.7).

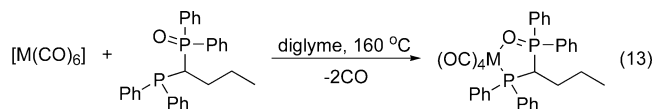
Simple considerations in terms of the hard and soft acid and base principle predict that the soft P center of BPMPs would prefer to bind to softer metals in low oxidation states, such as  $\text{Hg}^{2+}$ ,  $\text{Pd}^0$ ,  $\text{Pd}^{2+}$ ,  $\text{Pt}^{2+}$ , and the like, whereas the hard O donor should have a higher affinity for hard Lewis acids, e.g., the lanthanides in the high oxidation state of +3. However, the presence of two basic centers on a BPMP molecule allows, in many cases, for the binding of both the P and O atoms to one metal center to form a chelate. Such chelates are expected to be weak. Indeed, for the softer metals it is the M–O bond that would dissociate more readily, whereas for the harder metals it is the soft phosphine group that would be prone to come off with ease. As will be shown below, in this section and in section 4, it is the weakness of the chelates (hemilability) that makes the coordination chemistry of BPMPs very rich and most relevant to homogeneous catalysis.

### 3.1. Mononuclear and Homopolymetallic Complexes

#### 3.1.1. Chromium, Molybdenum, and Tungsten

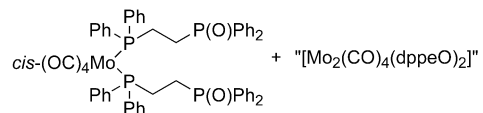
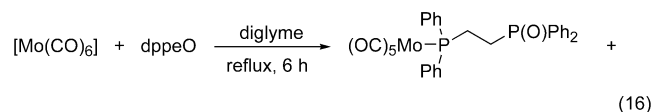
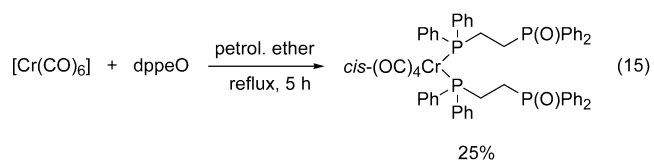
The original 1975 report from Grim et al.<sup>10</sup> describes the high-temperature displacement of two carbonyls in  $[\text{M}(\text{CO})_6]$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ) with  $\text{Ph}_2\text{PCH}(\text{n-Pr})\text{P}(\text{O})\text{Ph}_2$  to give the corresponding five-membered chelates (eq 13). Unfortunately, yields and selectivities for reaction 13 have not been specified. The chelate structures were assigned on the basis of analytical, IR, and <sup>31</sup>P NMR data. The chemical shifts from those of the free ligand, indicating coordination of both the P and O centers. Furthermore, the

characteristic  $\nu_{\text{P=O}}$  frequency in the complexes was lower by 35–42  $\text{cm}^{-1}$  than the value of the free ligand (1170  $\text{cm}^{-1}$ ), confirming metal binding to the phosphinyl group.



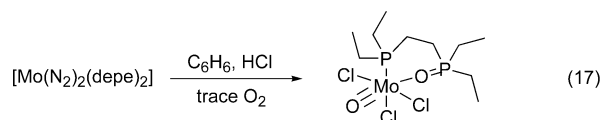
$\text{M} = \text{Cr}, \text{Mo}, \text{W}$

In sharp contrast, similar reactions of  $[\text{M}(\text{CO})_6]$  ( $\text{M} = \text{Cr}, \text{Mo}$ ) with dppmO and dppeO resulted in isolation of only unilaterally P-bound species (eqs 14–16).<sup>50</sup> In all cases, complex reaction mixtures were obtained, as indicated by TLC (although preparative separation by column chromatography failed). Two Cr complexes (eqs 14 and 15) were isolated by recrystallization. The Mo complexes (eq 16) were identified by FABMS and IR analysis of micro-scale quantities of the components absorbed on an analytical TLC plate after the separation. Disubstituted complexes  $[(\text{dppeO}-\kappa^1\text{-P})_2\text{M}(\text{CO})_4]$  ( $\text{M} = \text{Cr}, \text{Mo}$ ) were found to possess the *cis* geometry. The dinuclear complex  $[\text{Mo}_2(\text{CO})_4(\text{dppeO})_2]$  was proposed to have a macrocyclic structure, in which each Mo is coordinated to two carbonyls, one P, and an  $\eta^6\text{-Ph}$  of the phosphinyl group.<sup>50</sup>



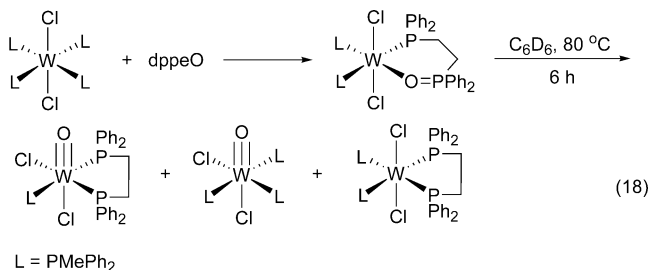
The markedly different coordination modes of  $\text{Ph}_2\text{PCH}(\text{n-Pr})\text{P}(\text{O})\text{Ph}_2$  and dppmO or dppeO to the soft, zerovalent Cr, Mo, and W may be rationalized in terms of the softer character of the P=O oxygen on the former ligand bearing an electron-donating *n*-propyl group.

An interesting reaction occurred upon oxidation of  $[(\text{depe})_2\text{Mo}(\text{N}_2)_2]$  with adventitious oxygen in anhydrous  $\text{C}_6\text{H}_6/\text{HCl}$  to produce the P,O-chelate  $[\text{MoOCl}_3(\text{depeO}-\kappa^2\text{-P,O})]$ , as established by X-ray diffraction (eq 17).<sup>91</sup>

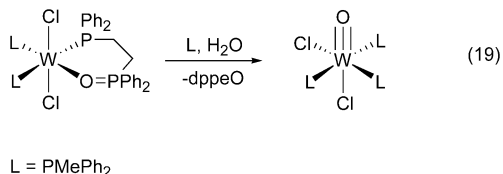


Oxidation of  $[\text{W}(\text{CO})_3(\text{I})_2(\text{dppfc})]$  with  $\text{H}_2\text{O}_2$  gave  $[\text{W}(\text{CO})_3(\text{I})_2(\text{dppfcO}-\kappa^2-P,O)]$ , in which the 1,1'-bis-(diphenylphosphino)ferrocene monoxide is P,O-bonded to the tungsten atom.<sup>97</sup> Likewise, oxidation of the dangling  $\text{PPh}_2$  group in  $[\text{M}(\text{CO})_3(\text{dppm}-\kappa^2-P,P)(\text{dppm}-\kappa^1-P)]$  ( $\text{M} = \text{W}^{90}$  and  $\text{Mo}^{115}$ ) with adventitious oxygen has been reported to produce P-bonded dppmO complexes  $[\text{M}(\text{CO})_3(\text{dppm}-\kappa^2-P,P)(\text{dppmO}-\kappa^1-P)]$  ( $\text{M} = \text{W}$  and  $\text{Mo}$ ), both of which have been structurally characterized.<sup>90,115</sup>

Brock and Mayer have reported<sup>34</sup> oxygen transfer from dppeO to W(II), one of the most exciting findings in the field of BPMP–metal complexes. It has been shown that the heating of  $[(\text{Ph}_2\text{MeP})_4\text{WCl}_2]$  with dppeO in  $\text{C}_6\text{D}_6$  results in the formation of three products, of which two are oxo–tungsten species (eq 18). Both the stoichiometry and labeling experiments with dppe- $^{18}\text{O}$  provided unambiguous evidence for oxygen transfer from the dppeO. Remarkably, this is the first example of oxygen abstraction from a tertiary phosphine oxide by a metal, resulting in the cleavage of the very strong P=O bond (ca. 130 kcal mol<sup>-1</sup>).



The intermediate dppeO chelate (eq 18) has been isolated and fully characterized. It has also been shown that the dppeO ligand in  $[(\text{Ph}_2\text{MeP})_2\text{WCl}_2(\text{dppeO}-\kappa^2-P,O)]$  is readily displaced by dppe. The dppeO ligand can also be displaced by  $\text{Ph}_2\text{MeP}$ , although in this case the reaction is reversible, the equilibrium being shifted toward the chelate. However, in the presence of both  $\text{Ph}_2\text{MeP}$  and water, the metal is oxidized to release dppeO irreversibly (eq 19). Reaction 18 also occurs for more strongly binding  $\text{L} = \text{PMe}_3$ , albeit more sluggishly, with no dppeO intermediate being observed.<sup>34</sup>

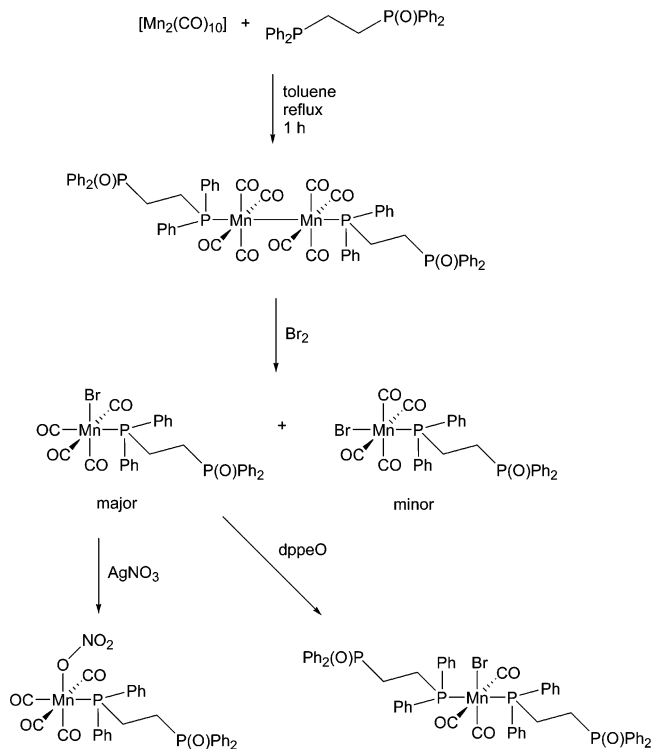


### 3.1.2. Manganese, Technetium, and Rhenium

Blagborough, Davis, and Ivison have reported<sup>50</sup> the formation of  $[\text{Mn}_2(\text{CO})_8(\text{dppeO}-\kappa^1-P)_2]$  in 52% yield upon treatment of  $[\text{Mn}_2(\text{CO})_{10}]$  with 2 equiv of dppeO in toluene under reflux. Bromination of the resulting dppeO complex produced a mixture of trans (minor) and cis (major) isomers of  $[\text{MnBr}(\text{CO})_3(\text{dppeO}-\kappa^1-P)]$ . Treatment of the latter with  $\text{AgNO}_3$  did not produce the expected cationic P,O-chelate  $[\text{Mn}(\text{CO})_4(\text{dppeO}-$

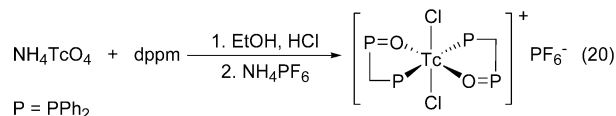
$\kappa^2-P,O)^+$  but rather gave  $[\text{Mn}(\text{NO}_3)(\text{CO})_4(\text{dppeO}-\kappa^1-P)]$  instead. All these transformations are shown in Scheme 3, along with the formation of *mer-trans-*

### Scheme 3



$[\text{MnBr}(\text{CO})_3(\text{dppeO}-\kappa^1-P)_2]$ , which can also be prepared directly from  $[\text{MnBr}(\text{CO})_5]$  and 2 equiv of dppeO. In contrast, the reaction of  $[\text{Mn}_2(\text{CO})_{10}]$  with dppmO was found to be poorly selective, resulting in a complex mixture of unidentified products.<sup>50</sup>

The formation of cationic bis-P,O-chelate,  $[\text{TcCl}_2(\text{dppmO}-\kappa^2-P,O)_2]^+$ , in the reaction of  $\text{NH}_4\text{TcO}_4$  with dppm has been recently reported by the Davison group (eq 20).<sup>109</sup> The all-trans structure of the dppmO complex, isolated in 33% yield as  $[\text{TcCl}_2(\text{dppmO}-\kappa^2-P,O)_2]^+\text{PF}_6^-$ , has been established by X-ray diffraction.

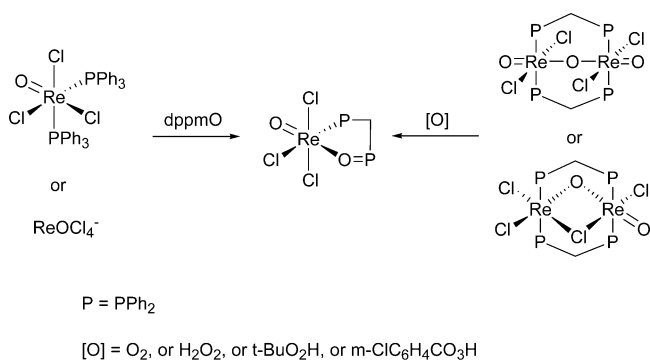


Katti and Barnes<sup>116</sup> have synthesized P,O-chelated  $[\text{Re}(\text{O})\text{Cl}_2(\text{X})(\text{dppmO}-\kappa^2-P,O)]$  ( $\text{X} = \text{Cl}, \text{OEt}$ ) by reacting dppmO with  $[\text{Re}(\text{O})\text{Cl}_3(\text{PPh}_3)_2]$  or  $[\text{ReOCl}_4]^-$  generated from  $\text{NH}_4\text{ReO}_4$  and  $\text{HCl}$ . Alternatively,  $[\text{Re}(\text{O})\text{Cl}_3(\text{dppmO}-\kappa^2-P,O)]$  can be prepared by oxidation of  $[\text{Re}_2(\mu\text{-O})(\text{O})_2\text{Cl}_4(\mu\text{-dppm})_2]$  or  $[\text{Re}_2(\mu\text{-O})(\mu\text{-Cl})(\text{O})\text{Cl}_3(\mu\text{-dppm})_2]$ .<sup>96</sup> Scheme 4 summarizes these synthetic routes to  $[\text{Re}(\text{O})\text{Cl}_2(\text{X})(\text{dppmO}-\kappa^2-P,O)]$ , whose structure has been established by X-ray analysis carried out by both groups.<sup>96,116</sup>

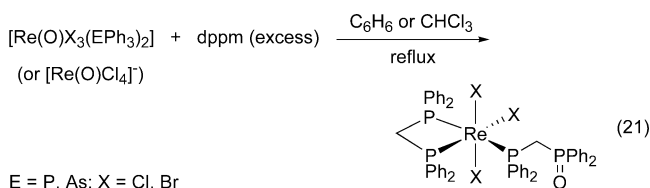
Interestingly, reactions of  $[\text{Re}(\text{O})\text{X}_3(\text{EPh}_3)_2]$  ( $\text{E} = \text{P}, \text{As}$ )<sup>117,118</sup> or  $[\text{Ph}_4\text{As}][\text{ReOCl}_4]$ <sup>118</sup> with excess dppm in hot benzene<sup>117</sup> or chloroform<sup>118</sup> resulted in deoxygenation of Re and the formation of  $[\text{ReX}_3(\text{dppm})-$



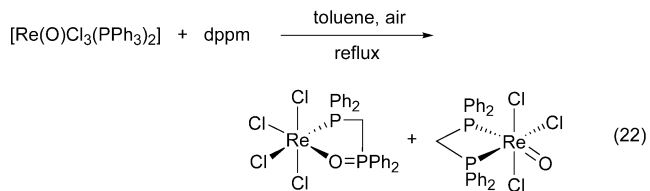
## Scheme 4



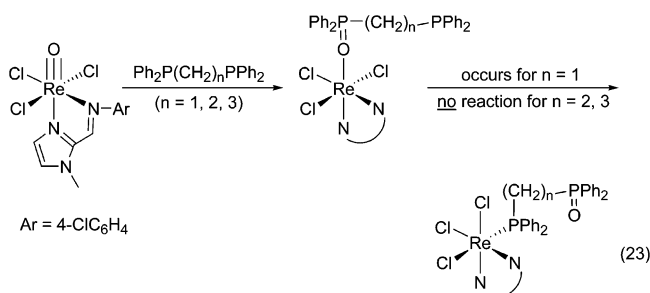
(dppmO- $\kappa^1$ -P)], in which the dppmO ligand is P-bonded to the metal (eq 21). When [Re(O)Cl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>]



was reacted with dppm at a higher temperature (boiling toluene) in air, a poorly soluble green precipitate formed, consisting of *mer*-[Re(O)Cl<sub>3</sub>(dppm)] and some paramagnetic Re species (NMR).<sup>118</sup> X-ray analysis of a single crystal from the green solid revealed the structure of one paramagnetic component of the mixture, the Re(IV) P,O-chelate [ReCl<sub>4</sub>(dppmO- $\kappa^2$ -P,O)] (eq 22).



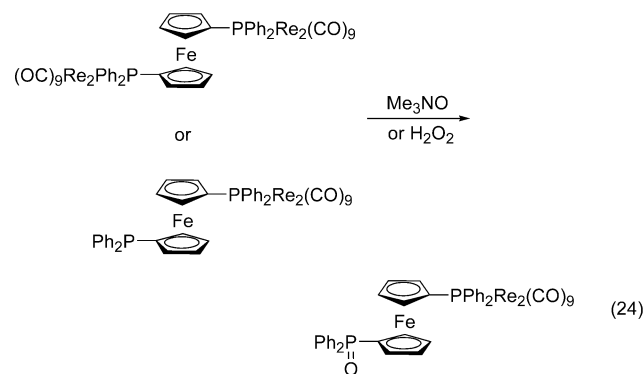
Chakravorty and co-workers<sup>119</sup> have recently reported some observations that are of special interest and importance to the coordination chemistry of BPMOs. It was demonstrated that oxygen atom transfer from a Re(V)–oxo complex to dppm, dppe, and dppp occurred to produce the corresponding meridional Re(III) species containing dppmO, dppeO, and dpppO that are O-bonded to the metal (eq 23).



While the dppeO and dpppO complexes were stable, the dppmO analogue readily rearranged to the P-bonded, facial isomer. Activation energy parameters for the “*mer*,O-dppmO” to “*fac*,P-dppmO” isomerization ( $\Delta H^\ddagger = 12.3$  kcal mol<sup>-1</sup>;  $\Delta S^\ddagger = -38.2$  cal K<sup>-1</sup>

mol<sup>-1</sup>) pointed to an intramolecular, strongly associative mechanism. Conformational analysis (based on the X-ray data) indicated that the dangling PPh<sub>2</sub> group of the O-bonded dppmO can easily access a reactive site in the coordination sphere of Re. On the contrary, the anti conformation of the PCH<sub>2</sub>CH<sub>2</sub>P fragment appeared to prevent the gauche conformation needed for the isomerization to occur, due to the cumbersome PPh<sub>2</sub> group. The geometry of the dppeO complex was ideally suited for oxygen transfer to the PPh<sub>2</sub> group from another molecule of the oxo complex, to give dinuclear *mer,mer*-[(NN)<sub>2</sub>Re<sub>2</sub>(Cl)<sub>6</sub>( $\mu$ -dppeO<sub>2</sub>)]. In contrast, no dinucleation but only oxidation was observed for the analogous reaction of the dppmO species.<sup>119</sup>

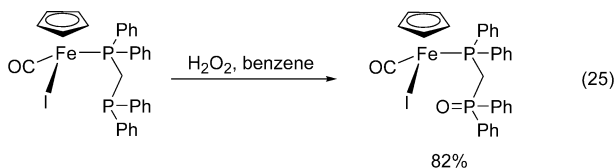
The dangling free PPh<sub>2</sub> group in [(CO)<sub>2</sub>ReBr(dppm- $\kappa^2$ -P,P)(dppmO- $\kappa^1$ -P)] has been oxidized upon bubbling air through a xylene solution of the complex at ambient temperature for 12 days to produce [(CO)<sub>2</sub>-ReBr(dppm- $\kappa^2$ -P,P)(dppmO- $\kappa^1$ -P)] (X-ray) in 75% yield.<sup>120</sup> Likewise, the PPh<sub>2</sub> groups of Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>n</sub>-PPh<sub>2</sub>- $\kappa^1$ -P (n = 1–5), hanging off the [Re<sub>6</sub>Se<sub>8</sub>] core, have been found to undergo facile air oxidation to P(O)Ph<sub>2</sub>.<sup>121</sup> A minor product of the reaction of Re<sub>2</sub>(CO)<sub>10</sub> with triphos has been isolated and found (X-ray) to be *fac*-[Re(CO)<sub>3</sub>Cl(triphosO- $\kappa^2$ -P,P)], with the triphosO being  $\kappa^2$ -P,P-coordinated to the metal.<sup>122</sup> Oxidation of [Re<sub>2</sub>(CO)<sub>9</sub>(dppfc- $\kappa^1$ -P)] or [Re<sub>2</sub>(CO)<sub>9</sub>( $\mu$ -dppfc)Re<sub>2</sub>(CO)<sub>9</sub>] with Me<sub>3</sub>NO or H<sub>2</sub>O<sub>2</sub> has been reported<sup>93</sup> to furnish [Re<sub>2</sub>(CO)<sub>9</sub>(dppfcO- $\kappa^1$ -P)] in 33–50% yield (eq 24). The structure of [Re<sub>2</sub>(CO)<sub>9</sub>(dppfcO- $\kappa^1$ -P)] as a monohydrate has been determined by X-ray diffraction.



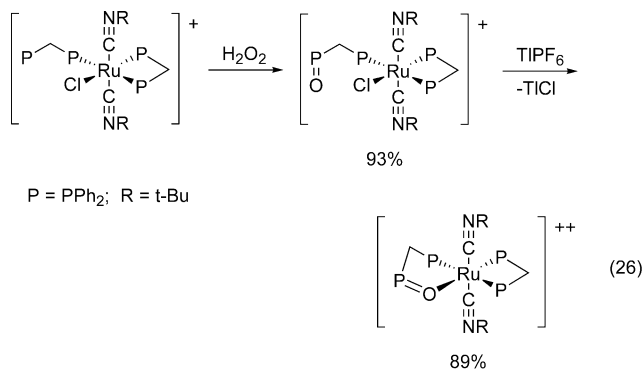
Kinetic and mechanistic studies of sulfur transfer from [(ArN)<sub>4</sub>Re<sub>2</sub>(Me)<sub>2</sub>( $\mu$ -S)<sub>2</sub>] (Ar = 2,6-diisopropylphenyl) to dmpeO (to give Me<sub>2</sub>P(S)CH<sub>2</sub>P(O)Me<sub>2</sub>) have been conducted to indicate P-coordination of two dmpeO molecules, one to a metal center and one to a sulfur bridge of the dinuclear complex.<sup>123</sup>

## 3.1.3. Iron, Ruthenium, and Osmium

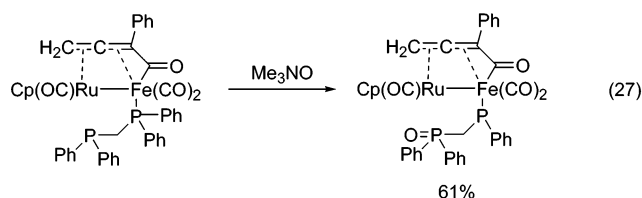
There have been a number of papers describing the formation of BPMO–Fe and –Ru complexes upon oxidation of their bis-phosphine precursors with various oxidants. Thus, oxidation of the dangling phosphine group in [CpFe(CO)I(dppm- $\kappa^1$ -P)] with H<sub>2</sub>O<sub>2</sub> has been reported<sup>124</sup> to produce the corresponding dppmO complex in 82% yield (eq 25). The same complex has been obtained, albeit in low yield, upon treatment of [Cp<sub>2</sub>Fe<sub>2</sub>( $\mu$ -CO)<sub>2</sub>( $\mu$ -dppm)] with iodine.<sup>124</sup>



Similarly, the noncoordinated phosphino group in  $[(t\text{-BuNC})_2\text{RuCl}(\text{dppm-}\kappa^1\text{-}P)(\text{dppm-}\kappa^2\text{-}P,P)]$  has been oxidized with  $\text{H}_2\text{O}_2$  to give the structurally similar dppmO complex.<sup>98</sup> Cyclization to the corresponding P,O-chelate was induced by Cl abstraction with  $\text{TIPF}_6$  (eq 26).<sup>98</sup> Oxidation of the dangling phosphine function in the dppm- $\kappa^1$ -PRu-Fe complex (eq 27) was as straightforward.<sup>125</sup>

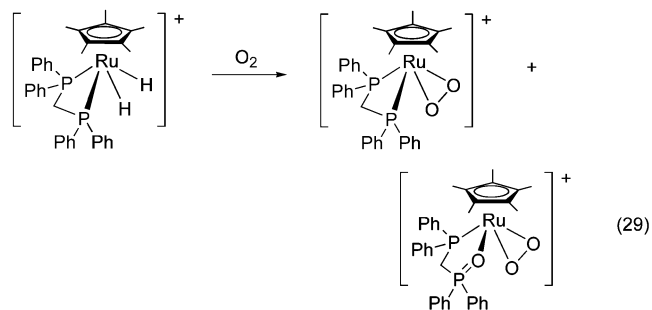
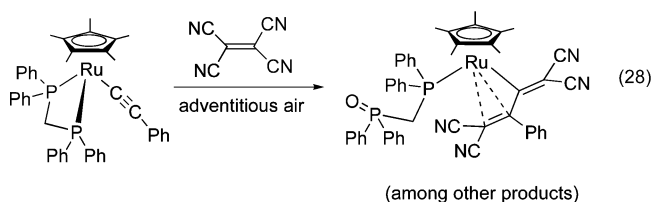


P = PPh<sub>2</sub>; R = t-Bu

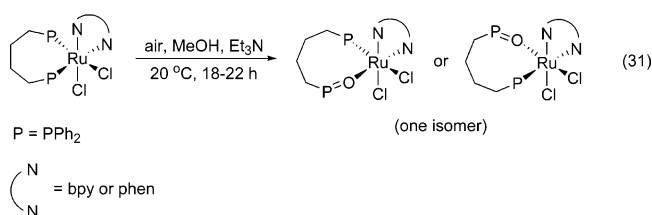
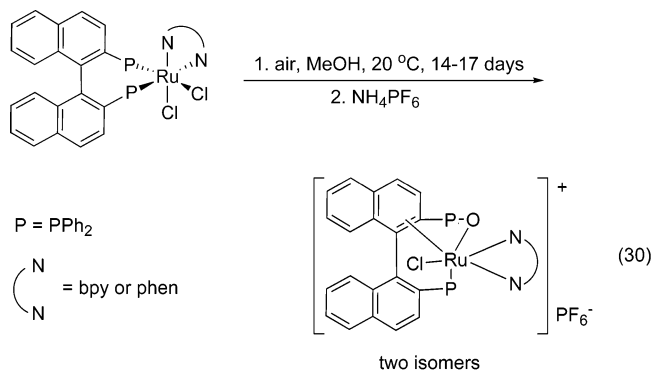


Oxidation of one P-center in dppm Ru chelates has also been reported,<sup>106,126</sup> though these reactions are often not as selective, commonly producing side products (eqs 28 and 29). It has also been found that the yield of the resulting dppmO complexes strongly depends on the solvent used. Thus, the reaction with tetracyanoethylene in the presence of adventitious air (eq 28) gave the dppmO complex in 31% and 2% yield when carried out in THF and benzene, respectively.<sup>106</sup>

Jia and co-workers<sup>126</sup> have observed the formation of a mixture of the dppm- $\kappa^2$ -P,P and dppmO- $\kappa^2$ -P,O Ru dioxygen complexes, as shown in eq 29. The product ratio varied in a broad range depending on solvent used (acetone or methanol). Remarkably, the dppm dioxygen complex is unlikely to be an intermediate in this reaction, as it did not react further with air to give the dppmO chelate. Similar transformations have also been observed with the corresponding dppe Ru dihydride, although the resulting dppe and dppeO dioxygen complexes were not isolated but rather were characterized in situ.<sup>126</sup> Because  $[\text{Cp}^*\text{Ru}(\text{H})_2(\text{dppe})]$  is a classical hydride, unlike its dppm counterpart that exists as a 1:2 mixture of the Ru(H)<sub>2</sub> and Ru(H) forms, it can be concluded that the oxidation involves the (dppm)Ru(H)<sub>2</sub> isomer<sup>126</sup> shown in eq 29. Nonetheless, the lack of reactivity of the nonclassical hydride toward oxygen cannot be ruled out.

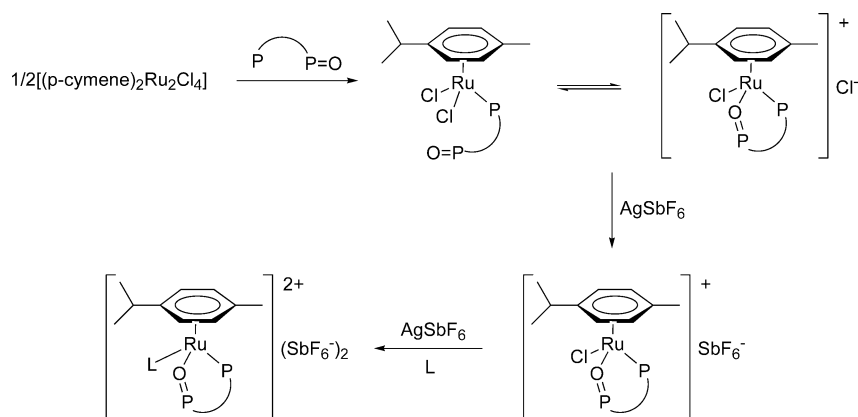


In contrast with reactions 28 and 29, air oxidation of complexes of the type  $[(\text{N}-\text{N})\text{RuCl}_2(\text{P}-\text{P})]$  (N-N = bpy or phen; P-P = (R)-BINAP or dppe) has been reported<sup>108</sup> to occur selectively, affording the corresponding P,O-chelates  $[(\text{N}-\text{N})\text{RuCl}(\text{BINAP}(\text{O})-\kappa^2\text{-}P,O)]^+$  and  $[(\text{N}-\text{N})\text{RuCl}_2(\text{dppeO}-\kappa^2\text{-}P,O)]$  in 73–88% isolated yield (eqs 30 and 31). A remarkable coordination mode was observed (X-ray) for the BINAP(O) ligand, involving both the P and O basic centers, as well as the  $\eta^2$ -bonded aromatic C=C moiety next to the phosphinyl group. The cationic BINAP(O) complexes are formed as a mixture of two isomers. For both the bpy and phen derivatives, the major isomers (Cl trans to C=C) were structurally characterized by X-ray diffraction.<sup>108</sup> It was also found that, unlike the kinetically inert major isomers, the minor isomers (Cl trans to N) are reactive toward donor molecules (CO, MeCN) addition with concomitant dissociation of the  $\pi$ -coordinated C=C moiety from Ru. In the resulting cationic octahedral P,O-chelates  $[(\text{N}-\text{N})\text{RuCl}(\text{L})(\text{BINAP}(\text{O})-\kappa^2\text{-}P,O)]$  (L = CO, MeCN), the ligand L is likely trans to P(III).



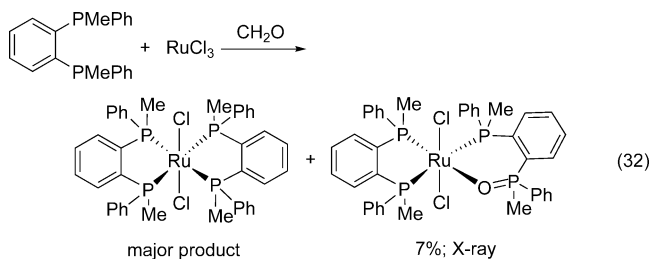
The oxidation reaction of  $[(\text{N}-\text{N})\text{RuCl}_2(\text{dppb-}\kappa^2\text{-}P,P)]$  was slow but could be accelerated by base

## Scheme 5

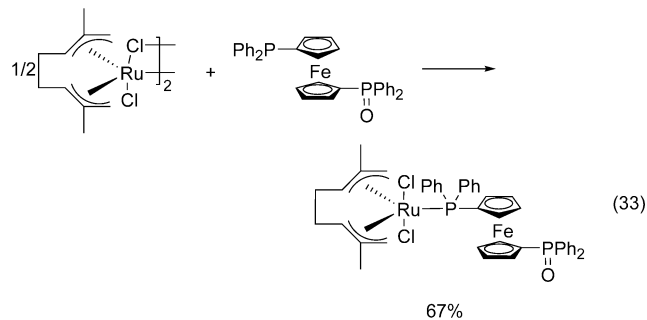


(Et<sub>3</sub>N). Only one isomer was detected, which can have one of the two structures shown in eq 31. Unlike their cationic BINAP(O) counterparts, the [(N–N)RuCl<sub>2</sub>–(dppbO–κ<sup>2</sup>-P,O)] complexes were unreactive toward MeCN and CO.<sup>108</sup>

A crystallographic study of one minor (7%) byproduct of the reaction of RuCl<sub>3</sub>·*n*H<sub>2</sub>O with 1,2-bis-(methyl(phenyl)phosphino)benzene in the presence of formaldehyde (eq 32) revealed the P,O-chelate structure.<sup>127</sup>



Several BPMO complexes of Ru have been prepared using presynthesized phosphine–phosphine oxide ligands. Gimeno and co-workers have reported the synthesis of a series of bis-allyl Ru(IV) species containing dppfcO,<sup>128</sup> dppmO,<sup>129</sup> dppeO,<sup>129</sup> dpppO,<sup>129</sup> and dppbO.<sup>129</sup> All these reactions led to the formation of the P-bonded nonchelates, as exemplified for dppfcO (eq 33). The treatment of the analogous



dppmO and dppeO complexes with 1 equiv of AgBF<sub>4</sub> brought about cyclization via chloride abstraction and coordination of the dangling phosphinyl to the metal, to produce cationic P,O-chelates [(η<sup>3</sup>:η<sup>3</sup>-C<sub>10</sub>H<sub>16</sub>)Ru–(BPMO–κ<sup>2</sup>-P,O)Cl]<sup>+</sup>BF<sub>4</sub><sup>–</sup>.<sup>129</sup> The larger and hence less stable dpppO and dppbO P,O-chelates failed to form under similar conditions. These results<sup>129</sup> are in accord with the previously observed dechlorination–

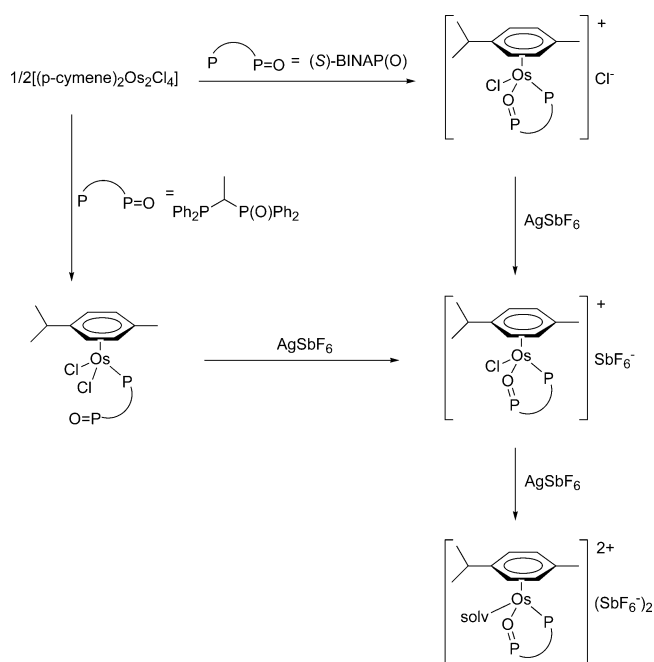
cyclization trends in complexes of the type [(BPMO–κ<sup>1</sup>-P)<sub>2</sub>PdCl<sub>2</sub>] (BPMO = dppmO, dppeO, dpppO, dppbO, and dppfcO; see section 3.1.5. below).

Faller's group have reported the synthesis of a series of chiral Ru<sup>14,59,130–133</sup> and Os<sup>134,135</sup> BPMO complexes and their successful use as catalysts for asymmetric Diels–Alder reactions. Dinuclear complexes [(η<sup>6</sup>-*p*-cymene)<sub>2</sub>M<sub>2</sub>Cl<sub>2</sub>(μ-Cl)<sub>2</sub>] (M = Ru, Os) readily reacted with various phosphine–phosphine oxide ligands to produce mononuclear species. The outcome of the reaction for Ru was found to be strongly dependent on the nature of the BPMO ligand used (Scheme 5). The reaction with dppmO<sup>14</sup> or chiraphos(O)<sup>130</sup> produced only the P-bonded BPMO–κ<sup>1</sup>-P Ru species. Under similar conditions, the dppmO derivative methylated at the central carbon was found to exist in equilibrium with the corresponding cationic P,O-chelate in a 1:1 ratio.<sup>14</sup> Such equilibria, however, were shifted entirely toward the corresponding chelates for BINAP(O) and TolBINAP(O)<sup>131</sup> as well as for the derivatives of dppmO containing Ph or Pr at the central C atom, Ph<sub>2</sub>PCH(*i*-Pr)P(O)Ph<sub>2</sub> and Ph<sub>2</sub>PCH(Ph)P(O)Ph<sub>2</sub>.<sup>14</sup> Regardless of the position of the equilibrium, treatment with AgSbF<sub>6</sub> (1 equiv) resulted in the clean formation of [(η<sup>6</sup>-*p*-cymene)RuCl(BPMO–κ<sup>2</sup>-P,O)]<sup>+</sup>SbF<sub>6</sub><sup>–</sup> in high yield (Scheme 5). The high-yield synthesis of [(η<sup>6</sup>-*p*-cymene)–RuCl(BPMO–κ<sup>2</sup>-P,O)]<sup>+</sup>SbF<sub>6</sub><sup>–</sup> can also be carried out as a one-pot reaction of [(η<sup>6</sup>-*p*-cymene)<sub>2</sub>Ru<sub>2</sub>Cl<sub>4</sub>] with 2 equiv of a BPMO and 2 equiv of AgSbF<sub>6</sub><sup>129–132</sup> or NaSbF<sub>6</sub>.<sup>59</sup>

Treatment of the monocationic monochlorides [(η<sup>6</sup>-*p*-cymene)RuCl(BPMO–κ<sup>2</sup>-P,O)]<sup>+</sup>SbF<sub>6</sub><sup>–</sup> with one more equivalent of AgSbF<sub>6</sub> resulted in chloride abstraction and generation of a Lewis acid center on the metal. The vacant coordination site can be occupied, often in a stereoselective fashion, by a variety of other ligands L (Scheme 5), such as aldehydes,<sup>14,130,133</sup> sulfoxides,<sup>14,133</sup> water,<sup>130</sup> acetonitrile,<sup>130</sup> pyridines,<sup>132</sup> and a solvent.<sup>14,59,130–133</sup>

A similar strategy has been employed for the synthesis of analogous osmium complexes containing Ph<sub>2</sub>PCH(Me)P(O)Ph<sub>2</sub><sup>134</sup> and (*S*)-BINAP(O)<sup>135</sup> (Scheme 6). Interestingly, the reaction of [(η<sup>6</sup>-*p*-cymene)<sub>2</sub>Os<sub>2</sub>Cl<sub>2</sub>(μ-Cl)<sub>2</sub>] with Ph<sub>2</sub>PCH(Me)P(O)Ph<sub>2</sub> produced only the P-bonded nonchelate [(η<sup>6</sup>-*p*-cymene)OsCl<sub>2</sub>(Ph<sub>2</sub>PCH(Me)P(O)Ph<sub>2</sub>–κ<sup>1</sup>-P)<sub>2</sub>]<sup>134</sup> which, unlike its Ru analogue,<sup>14</sup> is not prone to chelate formation via disso-

Scheme 6



ciation of one of the chloro ligands (see above). The cyclization was induced by the reaction with 1 equiv of  $\text{AgSbF}_6$ .

For chiral BPMOs, complexes of the type  $[(\eta^6\text{-}p\text{-cymene})\text{MCl}(\text{BPMO-}\kappa^2\text{-}P,\text{O})]^+$ , where  $\text{M} = \text{Ru}, \text{Os}$  (Schemes 5 and 6), are diastereomeric due to the chiral center on the ligand and on the metal. Only one diastereomer was observed by  $^{31}\text{P}$  NMR for  $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}(\text{BPMO-}\kappa^2\text{-}P,\text{O})]^+$ , where  $\text{BPMO} = \text{Ph}_2\text{PCH}(\text{R})\text{P}(\text{O})\text{Ph}_2$  ( $\text{R} = \text{Me}, \text{Pr}, \text{Ph}$ ).<sup>14</sup> X-ray analysis of  $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}(\text{Ph}_2\text{PCH}(\text{Pr})\text{P}(\text{O})\text{Ph}_2\text{-}\kappa^2\text{-}P,\text{O})]^+\text{SbF}_6^-$  and  $[(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{PhCHO})(\text{Ph}_2\text{PCH}(\text{Pr})\text{P}(\text{O})\text{Ph}_2\text{-}\kappa^2\text{-}P,\text{O})]^{2+}(\text{SbF}_6^-)_2$  indicated that the propyl group on the central carbon is endo, tilting from the Cl or PhCHO ligands and thus minimizing steric strain in the complexes. The dicationic complex  $[(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{L})(\text{dppmO-}\kappa^2\text{-}P,\text{O})]^{2+}$  (Scheme 5) racemized at Ru, whereas its analogues with the chiral BPMOs underwent epimerization to adopt the least sterically hindered configuration. Upon addition of sulfoxides or (1*R*)-(-)-myrtenal to  $[(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{L})(\text{BPMO-}\kappa^2\text{-}P,\text{O})]^{2+}$  ( $\text{BPMO} = \text{dppmO}, \text{Ph}_2\text{PCH}(\text{Me})\text{P}(\text{O})\text{Ph}_2$ ), the weakly bound L was displaced by the oxygen atom of the incoming sulfoxide or aldehyde with 2–40 diastereomeric excess.<sup>14</sup>

Similar studies have been carried out<sup>134</sup> with analogous osmium complexes  $[(\eta^6\text{-}p\text{-cymene})\text{OsCl}(\text{Ph}_2\text{PCH}(\text{Me})\text{P}(\text{O})\text{Ph}_2\text{-}\kappa^2\text{-}P,\text{O})]^+\text{SbF}_6^-$  and  $[(\eta^6\text{-}p\text{-cymene})\text{Os}(\text{L})(\text{Ph}_2\text{PCH}(\text{Me})\text{P}(\text{O})\text{Ph}_2\text{-}\kappa^2\text{-}P,\text{O})]^{2+}(\text{SbF}_6^-)_2$ . Unlike its Ru analogue,  $[(\eta^6\text{-}p\text{-cymene})\text{OsCl}(\text{Ph}_2\text{PCH}(\text{Me})\text{P}(\text{O})\text{Ph}_2\text{-}\kappa^2\text{-}P,\text{O})]^+$  was found to exist in solution as two sets of enantiomeric diastereoisomers in a 3.8:1 ratio that did not change after 3 days. This indicates that the more inert Os complex epimerizes more slowly than the Ru analogue. Remarkably, even the dication  $[(\eta^6\text{-}p\text{-cymene})\text{Os}(\text{L})(\text{Ph}_2\text{PCH}(\text{Me})\text{P}(\text{O})\text{Ph}_2\text{-}\kappa^2\text{-}P,\text{O})]^{2+}$  (Scheme 6) existed as a 1.4:1 mixture of diastereomers, to which unsaturated aldehydes (*trans*-cinnamaldehyde, methacrolein, and crotonaldehyde) coordinated exclusively via the car-

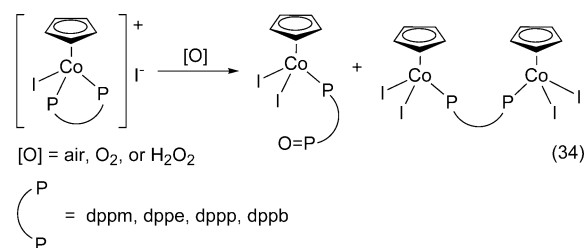
bonyl oxygen upon dissociation of L. The more stable diastereomers of the mono- and dicationic Os complexes are the ones in which the methyl group of the BPMO is distal to the monodentate ligand. The slow epimerization rates for the Os complexes allowed for detection of isomers that could not be observed for the Ru counterparts.

The formation of  $[(\eta^6\text{-}p\text{-cymene})\text{MCl}((S)\text{-BINAP}(\text{O})\text{-}\kappa^2\text{-}P,\text{O})]^+\text{SbF}_6^-$  ( $\text{M} = \text{Ru}^{59,131}$  and  $\text{Os}^{135}$ ) occurred diastereoselectively, i.e., only one isomer was observed. In contrast, mixtures of diastereomers in different ratios were produced for the Ru (*R,R*)-chiraphos(O) analogue in solution.<sup>130</sup> Regardless of the initial ratio, the chiraphos(O) complex always crystallized in a 1:1 diastereomeric ratio. The use of the chiral BPMO–Ru and –Os complexes as catalysts is discussed in section 4.1.9. below.

### 3.1.4. Cobalt, Rhodium, and Iridium

It has been demonstrated that BPMO–Rh complexes can efficiently and selectively catalyze a number of reactions, including some industrially important processes (section 4.1). Therefore, coordination and reactivity studies of BPMO complexes of Rh and its lighter and heavier analogues, Co and Ir, can bear important implications for catalysis.

The formation of a series of cobalt complexes of the type  $[\text{CpCoI}_2(\text{BPMO})]$  has been found<sup>89</sup> to occur upon oxidation of the corresponding diphosphine chelates with air or 30%  $\text{H}_2\text{O}_2$  (eq 34). Reaction 34 is not highly selective, as approximately one-third of the bis-phosphine ligand was lost from the metal during the oxidation, in the form of the corresponding monoxide and dioxide. One of the BPMO complexes,  $[\text{CpCoI}_2(\text{dppmO-}\kappa^1\text{-}P)]$ , was studied by X-ray diffraction to confirm the P-bonded, nonchelate structure. The dppeO analogue was also synthesized independently from  $[\text{CpCoI}_2(\text{CO})]$  and dppeO.



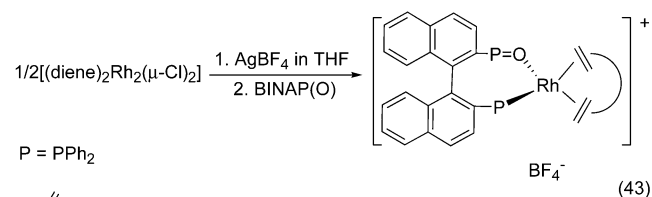
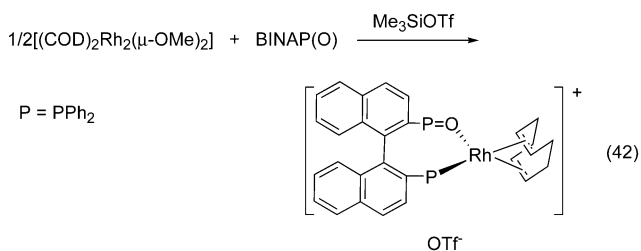
Several important observations were made during the studies of reaction 34. First, the reactivity toward oxidation was strongly dependent on the length of the linker in the diphosphine ligand,  $\text{dppb} \gg \text{dppm} \gg \text{dppp} \cong \text{dppe}$ , the reverse of the trend in chelate strength. That indicated that chelate opening was required for the oxidation to occur. This conclusion was supported by the fact that  $\text{O}_2$  pressure up to 3.4 atm had little effect on the rate of oxidation. Reaction 34 occurred more readily in solvents of low polarity ( $\text{CH}_2\text{Cl}_2, \text{CHCl}_3$ ) than in methanol and was promoted by the room light.<sup>89</sup>

Remarkably, the most easily oxidizable cationic complex,  $[\text{CpCoI}(\text{dppb-}\kappa^2\text{-}P,\text{P})]^+\text{I}^-$ , turned out to be completely unreactive upon replacement of the iodide counterion with  $\text{BF}_4^-$  or  $\text{PF}_6^-$ . However, the addition

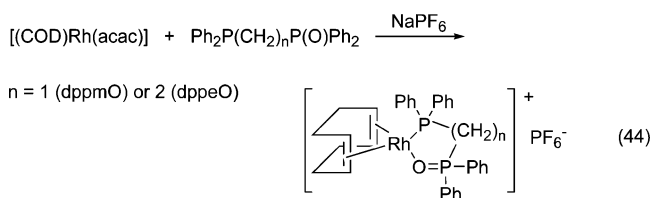




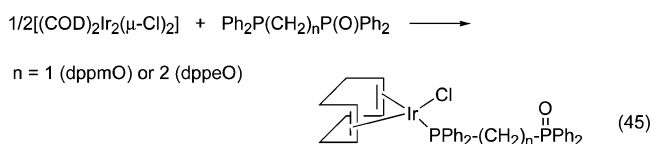
NMR studies of the cationic complexes indicated fluxionality, probably due to diene mobility rather than BINAP(O) chelate ring-opening. It is noteworthy that the NBD derivative appeared more fluxional than the COD counterpart.<sup>144</sup>



The necessity to employ weakly coordinating anions in order to obtain P,O-dppmO and -dppeO Rh chelates was established before Gladiali's report,<sup>144</sup> by Blagborough, Davis, and Ivison.<sup>50</sup> They found that [(COD)Rh(acac)] reacted with 2 equiv of dppmO or dppeO to give a material that was tentatively formulated as [(COD)Rh(BPMO-κ<sup>1</sup>-P)<sub>2</sub>]<sup>+</sup>[acac]<sup>-</sup> (BPMO = dppmO or dppeO). Treatment with NaPF<sub>6</sub> gave rise to cationic P,O-chelates [(COD)Rh(dppmO-κ<sup>2</sup>-P,O)]<sup>+</sup>PF<sub>6</sub><sup>-</sup> and [(COD)Rh(dppeO-κ<sup>2</sup>-P,O)]<sup>+</sup>PF<sub>6</sub><sup>-</sup> in 75% and 67% yield, respectively (eq 44).<sup>50</sup>



The reaction of [(COD)<sub>2</sub>Ir<sub>2</sub>(μ-Cl)<sub>2</sub>] with dppmO or dppeO has been reported<sup>50</sup> to cleanly produce P-bound nonchelates in 87% yield (eq 45). The P,O- (eq 44) and P- (eq 45) coordination modes have been reliably established on the basis of the NMR and IR spectral data.<sup>50</sup>

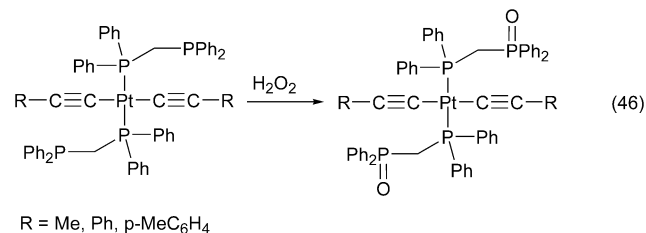


### 3.1.5. Nickel, Palladium, and Platinum

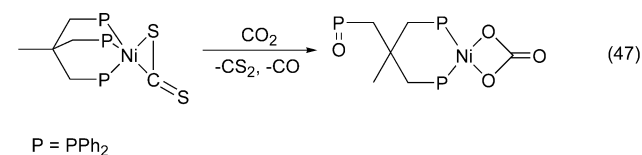
The number of BPMO complexes of Ni, Pd, and Pt reported in the literature exceeds that for any other group of elements in the Periodic Table. Considering the importance of the Ni group metals and BPMOs in catalysis, this is not surprising. First we will review BPMO complexes obtained by oxidation of Ni,

Pd, and Pt derivatives of various polydentate phosphines. Then we will move on to the syntheses with premade BPMOs.

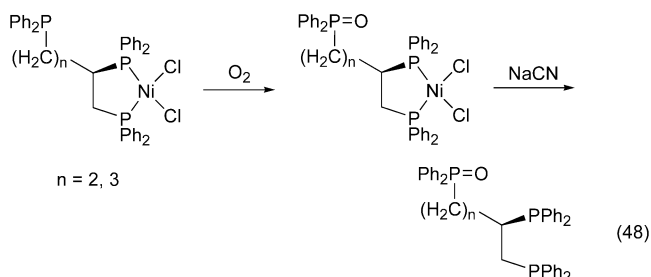
In 1983, Langrick, McEwen, Pringle, and Shaw reported<sup>88</sup> the clean, high-yield oxidation of the dangling PPh<sub>2</sub> groups in a series of Pt complexes (eq 46). Mealli and co-workers described,<sup>145</sup> also in 1983, the slow air oxidation of [(η<sup>3</sup>-C<sub>3</sub>Ph<sub>3</sub>)Ni((Ph<sub>2</sub>PCH<sub>2</sub>-CH<sub>2</sub>)<sub>3</sub>P)]<sup>+</sup>BPh<sub>4</sub><sup>-</sup> to [(η<sup>3</sup>-C<sub>3</sub>Ph<sub>3</sub>)Ni((Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>PCH<sub>2</sub>-CH<sub>2</sub>P(O)Ph<sub>2</sub>-κ<sup>3</sup>-P,P,P)]<sup>+</sup>BPh<sub>4</sub><sup>-</sup>, in which all three P(III) centers are bonded to Ni (X-ray). Since then, this approach has been used for the preparation of a number of Ni,<sup>92,100,104,146–148</sup> Pd,<sup>94,99,101,102,110,149,150</sup> and Pt<sup>86,107,151–153</sup> complexes containing BPMOs.



Bianchini and co-workers have reported the remarkable oxidation of [(triphos)Ni(η<sup>2</sup>-CS<sub>2</sub>)] with CO<sub>2</sub> to produce [(triphosO-κ<sup>2</sup>-P,P)Ni(CO<sub>3</sub>)] (X-ray) with concomitant release of CO (eq 47).<sup>146</sup> When the reaction was repeated with air, pure O<sub>2</sub>, or KO<sub>2</sub> as oxidants, the structurally similar (X-ray) *S,S*-dithiocarbonate complex [(triphosO-κ<sup>2</sup>-P,P)Ni(S<sub>2</sub>CO)] was isolated in good yield.<sup>147</sup> Likewise, the reaction of [(triphos)Ni(S<sub>2</sub>CS)] with PhNO gave rise to [(triphosO-κ<sup>2</sup>-P,P)Ni(S<sub>2</sub>CS)] in 80% yield.<sup>147</sup> Air oxidation of the 1,3-dithiol-2-ylidene-Ni(0) complex [(triphos)-Ni(CS<sub>2</sub>C<sub>2</sub>(CF<sub>3</sub>)<sub>2</sub>)] resulted in the formation of a mixture of dithiolene derivatives of triphos-κ<sup>2</sup>-P,P and triphosO-κ<sup>2</sup>-P,P, [(triphosO-κ<sup>2</sup>-P,P)Ni(SC(CF<sub>3</sub>)<sub>2</sub>=C(CF<sub>3</sub>)-CS)], in 27% and 18% yield, respectively.<sup>148</sup>

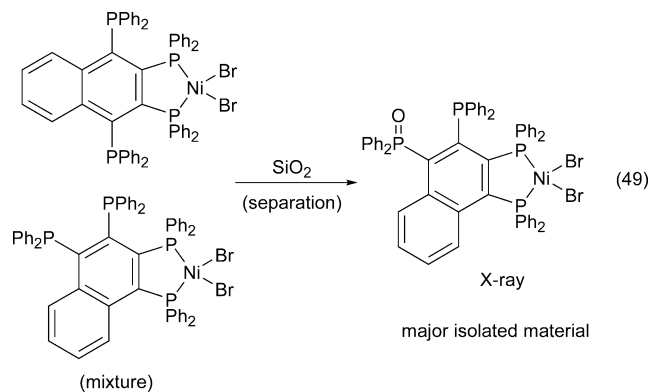


Brunner et al.<sup>92</sup> have reported the highly selective oxidation of the sidearm PPh<sub>2</sub> groups in tridentate phosphine–Ni(II) complexes with O<sub>2</sub>, followed by release of the optically active mono-oxidized ligands from the Ni center by NaCN (eq 48).

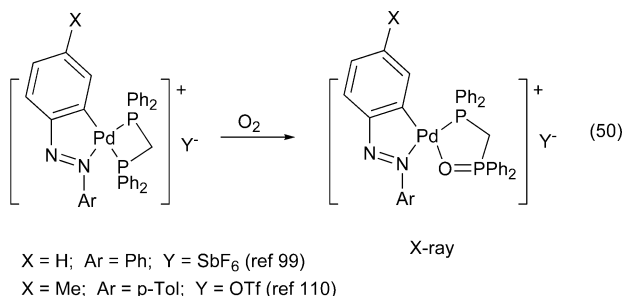


A series of interesting oxidation reactions of naphthalene-based polyphosphine–Ni complexes have been recently reported<sup>100,104</sup> by Bennett and co-

workers (e.g., eq 49).<sup>104</sup> Separation of the mixture of the two isomeric tetraphosphine complexes on degassed silica gel resulted in the isolation of the mono-oxidized product (X-ray, see eq 49),<sup>104</sup> presumably due to residual oxygen in the system. Reaction 49 is somewhat relevant to the air oxidation of 1,2,3,4-tetrakis(diphenylphosphino)benzene,<sup>154</sup> which has been stated<sup>104,154</sup> to be monoselective toward one of the two external PPh<sub>2</sub> groups.

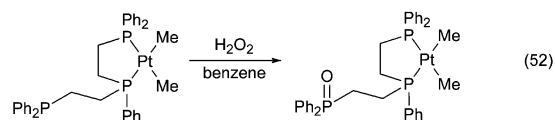
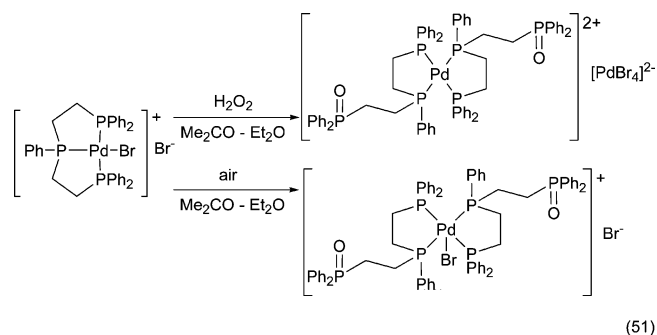


Air oxidation of [Pd<sub>2</sub>Cl<sub>2</sub>(dmpm)<sub>2</sub>] has been reported<sup>94</sup> to produce, in unspecified yield, *cis*-[(dmpmO-κ<sup>1</sup>-P)<sub>2</sub>PdCl<sub>2</sub>], in which the dmpmO ligands are P-bonded to Pd (X-ray). Some cyclopalladated dppmO complexes have been synthesized via air oxidation of the corresponding dppm species, either isolated (e.g., eq 50)<sup>99,110,150</sup> or generated in situ.<sup>101</sup>

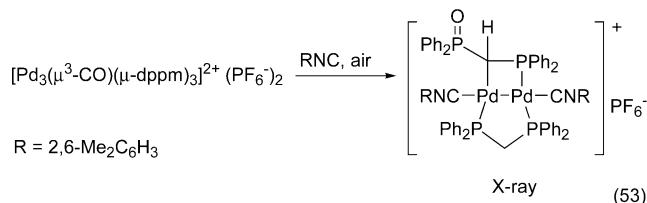


Interestingly, oxidation of the tridentate phosphine in the P,P,P-Pd bromide complex (eq 51) can produce either the four-coordinate or five-coordinate product, depending on the oxidant used.<sup>102</sup> The structure of the pentacoordinate complex has been established by X-ray analysis, and the tetracoordinate dicationic species has been characterized by NMR spectroscopic data and elemental analysis.<sup>102</sup> A closely related oxidation reaction of the same ligand on platinum with H<sub>2</sub>O<sub>2</sub> selectively produced only one complex in 79% yield (eq 52).<sup>107</sup>

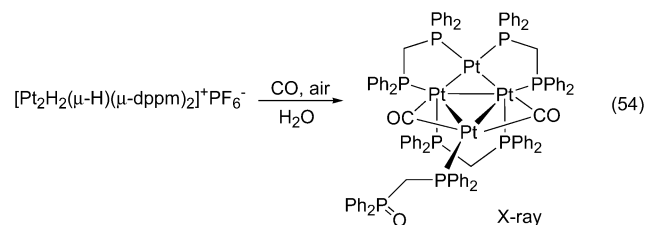
Rashidi, Vittal, and Puddephatt<sup>149</sup> have reported the remarkable reaction of [Pd<sub>3</sub>(μ<sup>3</sup>-CO)(μ-dppm)<sub>3</sub>]<sup>2+</sup>(PF<sub>6</sub><sup>-</sup>)<sub>2</sub> with 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC to produce a dinuclear Pd complex containing deprotonated dppmO in the rare C,P-coordination mode (X-ray), as shown in eq 53. The formation of the unusual product is believed<sup>149</sup> to involve a series of sequential transformations to produce [(RNC)<sub>2</sub>Pd<sub>2</sub>(μ-dppm)<sub>2</sub>]<sup>+</sup>, which then



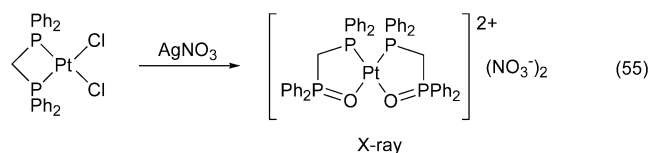
undergoes deprotonation and oxidation of a dppm ligand.



Another interesting report from Puddephatt's group describes the formation of a dppmO tetraplatinum complex from [Pt<sub>2</sub>H<sub>2</sub>(μ-H)(μ-dppm)<sub>2</sub>]<sup>+</sup>PF<sub>6</sub><sup>-</sup> during catalysis of the water gas shift reaction (eq 54).<sup>151</sup>



The dicationic dppmO-κ<sup>2</sup>-P,O bis-chelate (eq 55) has been reported to form as an unexpected byproduct upon treatment of [(dppm)PtCl<sub>2</sub>] with AgNO<sub>3</sub> in air. The *cis* geometry of this dication in the form of [(dppmO-κ<sup>2</sup>-P,O)<sub>2</sub>Pt]<sup>2+</sup>(NO<sub>3</sub><sup>-</sup>)<sub>2</sub>·2H<sub>2</sub>O has been determined by X-ray analysis.<sup>152</sup> Inadvertent oxidation has been reported<sup>153</sup> to occur during the reaction of *t*-Bu<sub>2</sub>PCH<sub>2</sub>PMe<sub>2</sub> with [(Et<sub>3</sub>P)<sub>2</sub>PtCl<sub>4</sub>] in the presence of NaClO<sub>4</sub>. The reaction gave cationic *trans*-[(Et<sub>3</sub>P)PtCl(*t*-Bu<sub>2</sub>PCH<sub>2</sub>P(O)Me<sub>2</sub>-κ<sup>2</sup>-P,O)]<sup>+</sup>ClO<sub>4</sub><sup>-</sup>, in which the P,O binding mode and *trans* geometry were established by X-ray analysis.<sup>153</sup>



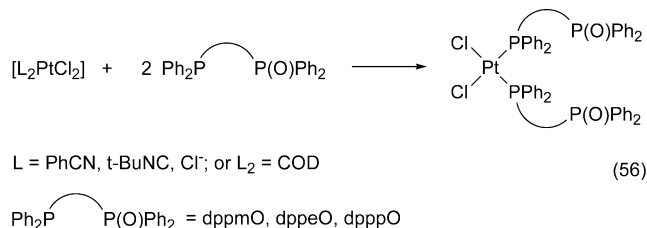
A Pt(II)/P(III)-to-Pt(0)/P(V) redox reaction occurred upon treatment of [(dppp)<sub>2</sub>Pt(μ-O)<sub>2</sub>] with ethylene in



the presence of water or catalytic amounts of [(dppp)-Pt(OH)<sub>2</sub>] to furnish the P-bonded Pt(0) nonchelate [(CH<sub>2</sub>=CH<sub>2</sub>)<sub>2</sub>Pt(dpppO-κ<sup>1</sup>-P)].<sup>86</sup> The complex was isolated as an oil and characterized in solution. Like numerous similar processes<sup>65–85</sup> involving tertiary phosphine Pd(II) or Pt(II) complexes (section 2.2), this reaction likely involves P–OH reductive elimination from the Pt(II) center.

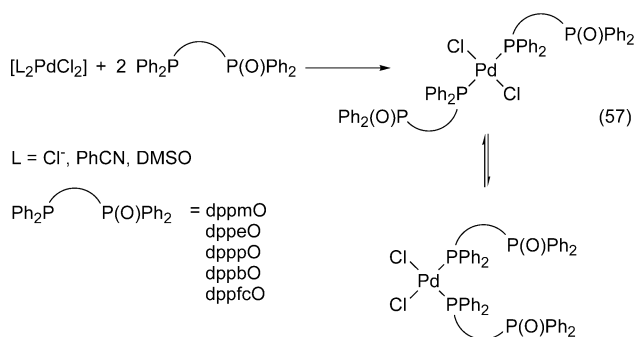
Presynthesized BPMOs have been used to prepare various complexes of Ni, Pd, and Pt, both inorganic and organometallic. Simple inorganic BPMO complexes will be reviewed first, followed by BPMO organometallics containing Ni–C, Pd–C, and Pt–C bonds.

The simplest complexes of the type [(BPMO-κ<sup>1</sup>-P)<sub>2</sub>-PtCl<sub>2</sub>] have been synthesized and isolated in 57–83% yield from the reaction of various chloro Pt(II) starting materials [(COD)PtCl<sub>2</sub>], [(PhCN)<sub>2</sub>PtCl<sub>2</sub>], [(*t*-BuNC)<sub>2</sub>PtCl<sub>2</sub>], and K<sub>2</sub>PtCl<sub>4</sub>) with 2 equiv of the corresponding BPMO = dppmO,<sup>12,155</sup> dppeO,<sup>12,155</sup> and dpppO<sup>12</sup> (eq 56). The bromo and iodo analogues [(dppmO-κ<sup>1</sup>-P)<sub>2</sub>PtX<sub>2</sub>] (X = Br, I) can be prepared by running reaction 56 in the presence of LiBr and LiI, respectively.<sup>12</sup> In all these complexes, the monodentate P-bound BPMO ligands are cis in the solid state and in solution. The only exception is the iodo complex [(dppmO-κ<sup>1</sup>-P)<sub>2</sub>PtI<sub>2</sub>], which was isolated as the cis isomer but in CDCl<sub>3</sub> slowly (3 h at 20 °C) isomerized to a 3:7 mixture of the cis and trans species.<sup>12</sup>



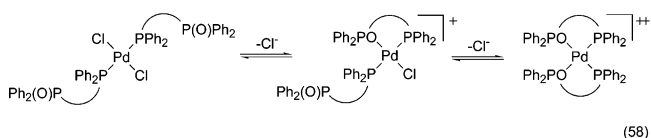
Palladium chloro complexes [(BPMO-κ<sup>1</sup>-P)<sub>2</sub>PdCl<sub>2</sub>] have been prepared similarly for BPMO = dppmO,<sup>12,13,156</sup> dppeO,<sup>156,157</sup> dpppO,<sup>156</sup> dppbO,<sup>156</sup> and dp-pfcO<sup>156</sup> (eq 57). The earliest report<sup>16</sup> on the synthesis of some chloro dppeO Pd(II) complexes lacks sufficient data to support the proposed structures/formulas, some of which might look implausible to a coordination chemist. Like the Pt analogues, complexes of the type [(BPMO-κ<sup>1</sup>-P)<sub>2</sub>PdCl<sub>2</sub>] exhibit only unilateral P-coordination to the metal. Single-crystal X-ray diffraction studies indicated that [(dppeO-κ<sup>1</sup>-P)<sub>2</sub>PdCl<sub>2</sub>]<sup>158</sup> and [(dppfco-κ<sup>1</sup>-P)<sub>2</sub>PdCl<sub>2</sub>]<sup>156</sup> are trans, unlike the BPMO–Pt chloro species. Furthermore, in sharp contrast with the Pt analogues, the Pd complexes undergo remarkably facile cis–trans isomerization in solution.<sup>156</sup>

The position of the equilibrium between the cis and trans isomers (eq 57) strongly depends on the medium. A detailed <sup>31</sup>P NMR study of cis–trans isomerization of [(BPMO-κ<sup>1</sup>-P)<sub>2</sub>PdCl<sub>2</sub>] (BPMO = dppmO, dppeO, dpppO, dppbO, and dppfco) in benzene, chloroform, dichloromethane, and methanol has been reported.<sup>156</sup> As anticipated,<sup>159</sup> an increase in polarity



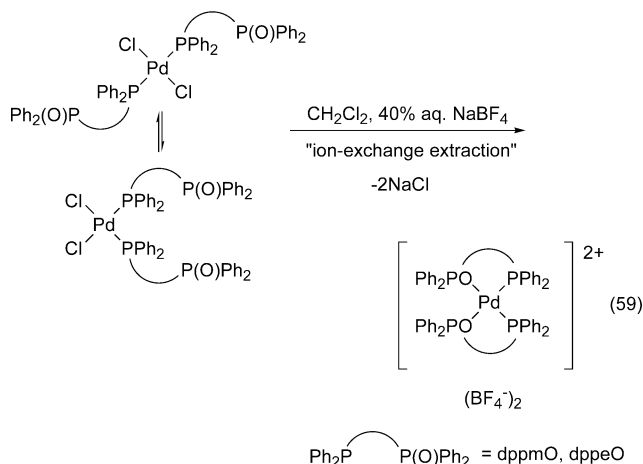
of the medium favored the more polar cis isomers. Thus, in benzene, [(dppmO-κ<sup>1</sup>-P)<sub>2</sub>PdCl<sub>2</sub>] and [(dppeO-κ<sup>1</sup>-P)<sub>2</sub>PdCl<sub>2</sub>] were exclusively trans, whereas in methanol the cis-to-trans ratios for the two complexes were 95:5 and 40:60, respectively.<sup>156</sup> The only exception was [(dppfco-κ<sup>1</sup>-P)<sub>2</sub>PdCl<sub>2</sub>], which was always trans, likely due to the cumbersome ferrocene-containing BPMO ligand.<sup>156</sup>

Cis–trans isomerization has been found<sup>156</sup> to be remarkably more facile for the complexes [(BPMO-κ<sup>1</sup>-P)<sub>2</sub>PdCl<sub>2</sub>] (seconds at room temperature) than for most common [L<sub>2</sub>PdCl<sub>2</sub>], where L is a conventional monodentate tertiary phosphine.<sup>159</sup> This effect has been attributed<sup>156</sup> to the presence of the phosphinyl groups that are capable of intramolecularly coordinating to the Pd center, thus mimicking the well-known<sup>159</sup> catalysis of the cis–trans isomerization in [(R<sub>3</sub>P)<sub>2</sub>MCl<sub>2</sub>] (M = Pd, Pt) with free R<sub>3</sub>P. Although such intramolecular P=O–Pd interactions have not been observed directly for the complexes [(BPMO-κ<sup>1</sup>-P)<sub>2</sub>PdCl<sub>2</sub>] and [(BPMO-κ<sup>1</sup>-P)<sub>2</sub>PtCl<sub>2</sub>], firm indirect evidence for equilibrium 58 has been obtained.<sup>156</sup>

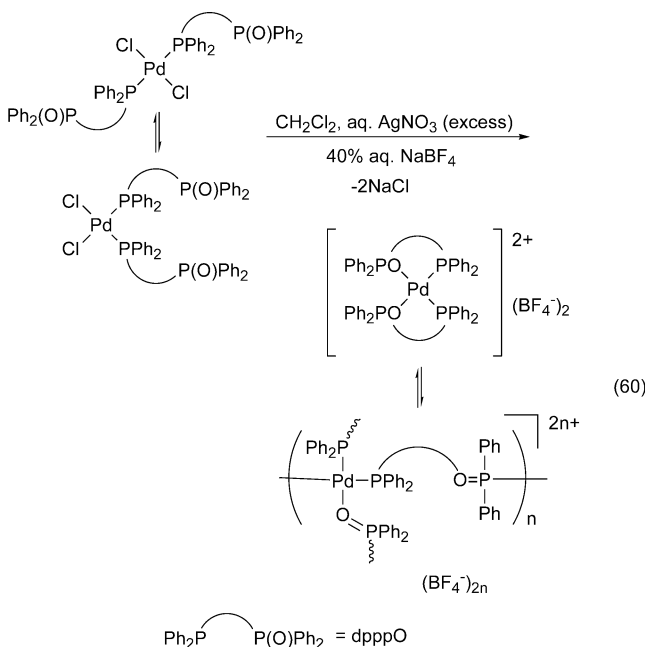


It was found<sup>156</sup> that bis-P,O-chelates *cis*-[(dppmO-κ<sup>2</sup>-P,O)<sub>2</sub>Pd]<sup>2+</sup>(BF<sub>4</sub><sup>-</sup>)<sub>2</sub> and *cis*-[(dppeO-κ<sup>2</sup>-P,O)<sub>2</sub>Pd]<sup>2+</sup>(BF<sub>4</sub><sup>-</sup>)<sub>2</sub> form quantitatively upon ion-exchange extraction of dichloromethane solutions of [(dppmO-κ<sup>1</sup>-P)<sub>2</sub>PdCl<sub>2</sub>] and [(dppeO-κ<sup>1</sup>-P)<sub>2</sub>PdCl<sub>2</sub>] with 40% aqueous NaBF<sub>4</sub><sup>-</sup> (eq 59). The structure of *cis*-[(dppeO-κ<sup>2</sup>-P,O)<sub>2</sub>Pd]<sup>2+</sup>(BF<sub>4</sub><sup>-</sup>)<sub>2</sub> was established by X-ray analysis.<sup>156</sup> Bis-P,O-chelates of the type [(dppmO-κ<sup>2</sup>-P,O)<sub>2</sub>M]<sup>2+</sup> (M = Pd, Pt) and [(dppeO-κ<sup>2</sup>-P,O)<sub>2</sub>Pt]<sup>2+</sup> were first synthesized by treatment of the corresponding complexes [(BPMO-κ<sup>1</sup>-P)<sub>2</sub>MCl<sub>2</sub>] (M = Pt, Pd) with 2 equiv of AgNO<sub>3</sub> and (optionally) addition of NH<sub>4</sub>PF<sub>6</sub>.<sup>12</sup> However, due to the strong ability of Ag<sup>+</sup> to scavenge chloride, the silver nitrate reaction with [(BPMO-κ<sup>1</sup>-P)<sub>2</sub>MCl<sub>2</sub>] (M = Pt, Pd) may not be regarded as firm evidence for equilibrium 58.

The ion-exchange extraction technique did not produce satisfactory results with [(dpppO-κ<sup>1</sup>-P)<sub>2</sub>PdCl<sub>2</sub>]. Treatment of the latter with excess AgNO<sub>3</sub> and NaBF<sub>4</sub> produced a material that was shown to be a mixture of polymeric/oligomeric species



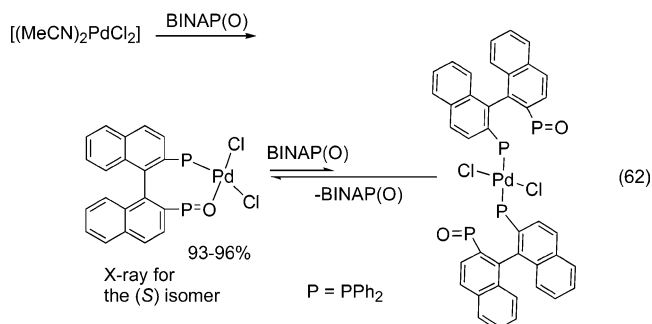
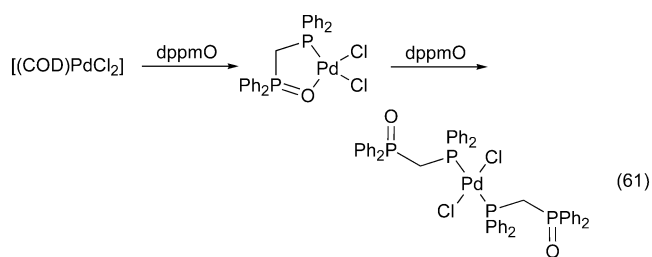
$\{[(\text{dpppO})_2\text{Pd}]^{2+}\}_n(\text{BF}_4^-)_{2n}$  on the basis of the solubility and spectroscopic (NMR and IR) data (eq 60).<sup>156</sup>



In very dilute solutions, however,  $\{[(\text{dpppO})_2\text{Pd}]^{2+}\}_n(\text{BF}_4^-)_{2n}$  underwent slow depolymerization to  $[(\text{dpppO}-\kappa^2-P,O)_2\text{Pd}]^{2+}(\text{BF}_4^-)_2$ , which exhibited (<sup>31</sup>P NMR) two sharp doublets for the P(III) and P(V) nuclei with  $J_{\text{P-P}} = 7$  Hz. The <sup>31</sup>P NMR signals from the polymer  $\{[(\text{dpppO})_2\text{Pd}]^{2+}\}_n(\text{BF}_4^-)_{2n}$  had the same chemical shifts (30 and 55 ppm) but appeared as broad, unresolved singlets with  $\Delta\nu = 40$ –100 Hz, largely exceeding the value of 7 Hz for the P–P coupling in the monomer. Attempted preparation of  $[(\text{dppbO}-\kappa^2-P,O)_2\text{Pd}]^{2+}(\text{BF}_4^-)_2$  and  $[(\text{dppfcO}-\kappa^2-P,O)_2\text{Pd}]^{2+}(\text{BF}_4^-)_2$  using the ion extraction and  $\text{AgNO}_3/\text{NaBF}_4$  methods was unsuccessful, giving rise to complex mixtures of unidentified materials.<sup>156</sup> Therefore, the study<sup>156</sup> of the dechlorination reactions of  $[(\text{BPMO}-\kappa^1-P)_2\text{PdCl}_2]$  has clearly demonstrated that the resulting P,O-chelates  $[(\text{BPMO}-\kappa^2-P,O)_2\text{Pd}]^{2+}$  are stable for BPMO = dppmO (five-membered ring) and dppeO (six-membered ring). The larger rings (dpppO, dppbO, and dppfcO) are unstable toward polymerization. The smallest of the three (dpppO, seven-membered chelate ring) can be observed but only at high dilution, which disfavors its ring-opening oligomerization.

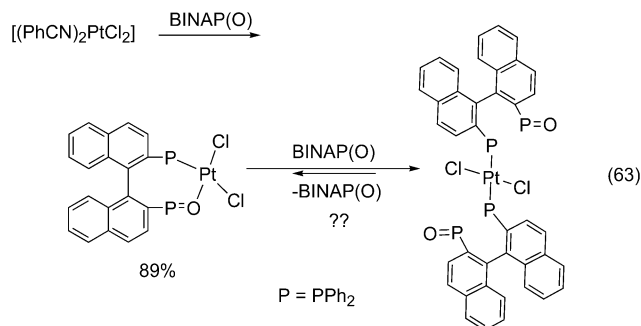
It is apparent that dppmO forms the most stable five-membered P,O-chelate rings. In accord with this, treatment of  $[(\text{Et}_3\text{P})_2\text{Pt}_2\text{Cl}_4]$  with dppmO in acetone– $\text{CH}_2\text{Cl}_2$ , in the presence or absence of  $\text{NaClO}_4$ , has been reported<sup>153</sup> to initially produce *trans*- $[(\text{Et}_3\text{P})\text{PtCl}_2(\text{dppmO}-\kappa^1-P)]$ , which can isomerize to the *cis* isomer. In the presence of  $\text{NaClO}_4$ , however, one chloride dissociated and the stable P,O-chelate  $[(\text{Et}_3\text{P})\text{PtCl}(\text{dppmO}-\kappa^2-P,O)]^+\text{ClO}_4^-$  is readily formed.<sup>153</sup> At the same time, dppmO coordinates to  $[\text{Pt}(\text{Ph}_2\text{P}(\text{CH}_2)_2)_2\text{PPh}]^{2+}$  only via the P center to give square-planar  $[(\text{dppmO}-\kappa^1-P)\text{Pt}(\text{Ph}_2\text{P}(\text{CH}_2)_2)_2\text{PPh}]^{2+}$ , whereas dppmS and dppmSe, with softer chalcogens, form pentacoordinate complexes with Pt–S and Pt–Se bonds under similar conditions.<sup>160</sup> Treatment of  $[\text{L}_2\text{M}]$  (M = Pd, Pt; L = 5-phenyl-1,3,4-oxadiazole-2-thione) with 2 equiv of dppeO gave rise to  $[(\text{dppeO}-\kappa^1-P)_2\text{-ML}_2]$ , in which the BPMO ligand is bonded to the metal only through the phosphine end.<sup>161</sup> However, the coordination mode for L (S vs N) in the  $[(\text{dppeO}-\kappa^1-P)_2\text{ML}_2]$  was not entirely clear.

Equations 56–60 indicate that, in general, Pd and Pt are prone to coordinate to two BPMO ligands in the P,O-chelating or P-unilateral fashion. This, however, is not necessarily true for all BPMOs. It has been shown<sup>52</sup> that  $[(\text{COD})\text{PdCl}_2]$  reacts with 1 equiv of dppmO to produce a P,O-chelate,  $[(\text{dppmO}-\kappa^2-P,O)\text{PdCl}_2]$ . Similarly,  $[(\text{MeCN})_2\text{PdCl}_2]$  has been converted to  $[(\text{BINAP}(\text{O})-\kappa^2-P,O)\text{PdCl}_2]$  upon treatment with 1 equiv of (*R*)- or (*S*)-BINAP(O).<sup>162</sup> While it is apparent (eq 57)<sup>12,13,156</sup> that addition of one more equivalent of dppmO to  $[(\text{dppmO}-\kappa^2-P,O)\text{PdCl}_2]$  would result in the clean formation of  $[(\text{dppmO}-\kappa^1-P)_2\text{PdCl}_2]$  (eq 61), the analogous reaction of  $[(\text{BINAP}(\text{O})-\kappa^2-P,O)\text{PdCl}_2]$  with BINAP(O) produced a mixture of the starting materials and a complex formulated as  $[(\text{BINAP}(\text{O})-\kappa^1-P)_2\text{PdCl}_2]$  (eq 62).<sup>162</sup> The three species (eq 62) were found to be in equilibrium which was strongly shifted toward the starting P,O-chelate.



Gladiali et al. have reported<sup>163</sup> the synthesis of  $[(\text{BINAP}(\text{O})-\kappa^2-P,O)\text{PtCl}_2]$  in 89% yield and mentioned the formation of  $[(\text{BINAP}(\text{O})-\kappa^1-P)_2\text{PtCl}_2]$  (eq

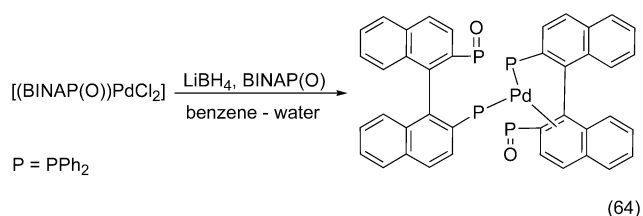
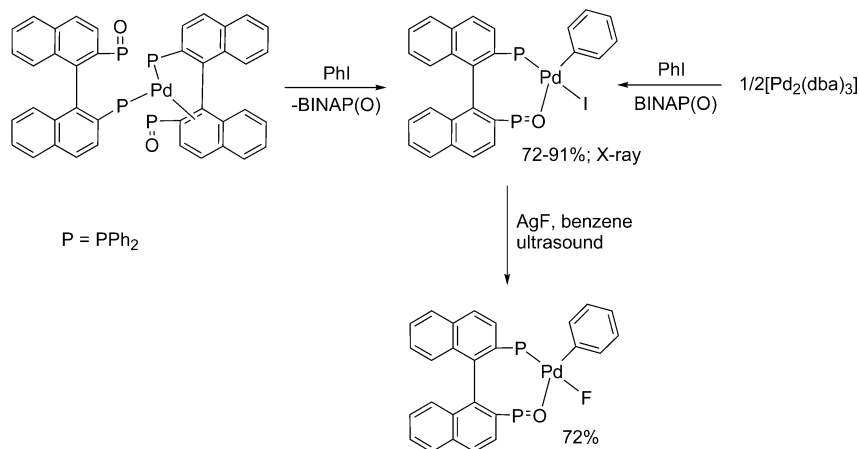
63). Isolation of the latter was not described,<sup>163</sup> and considering the analogous Pd chemistry,<sup>162</sup> it remains unclear whether the two Pt complexes equilibrate. The P,O-chelate [(BINAP(O)- $\kappa^2$ -P,O)PtCl<sub>2</sub>] was found<sup>163</sup> to open up easily upon phosphinyl displacement with CO and DMSO. The insertion of SnCl<sub>2</sub> into the Pt–Cl bond of [(BINAP(O)- $\kappa^2$ -P,O)PtCl<sub>2</sub>] trans to the P=O ligand gave poorly soluble [(BINAP(O)- $\kappa^2$ -P,O)-PtCl(SnCl<sub>3</sub>)], which was used as a catalyst for hydroformylation of styrene (section 4.1.5).<sup>163</sup> Equations 61–63 serve as another reminder of the fact that BPMP binding trends can be strongly dependent on the linker between the two P centers and on the metal.



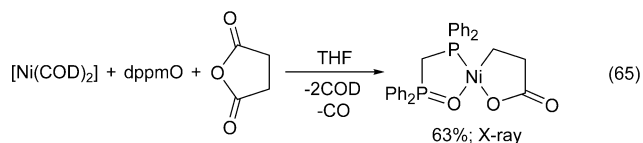
The only homoleptic BPMP complex of M(0) (M = Ni, Pd, Pt) reported is [(BINAP(O))<sub>2</sub>Pd], which has been prepared for both (*R*) and (*S*) isomers of BINAP(O) (eq 64).<sup>162</sup> As revealed by X-ray analysis, both BINAP(O) molecules are coordinated to the Pd through the phosphine groups. In addition, one of the two BINAP(O) ligands is  $\pi$ -bonded to the metal via the aromatic C=C bond bearing the naphthyl and phosphinyl substituents, as schematically shown in eq 64. No sign has been detected of any interactions between the soft Pd(0) and the hard phosphinyl groups.<sup>162</sup>

A variety of organometallic BPMP complexes of Ni, Pd, and Pt have been reported. Three general synthetic strategies have been developed for these BPMP organometallics: (i) oxidative addition to isolated or in situ-generated BPMP complexes of zerovalent Ni and Pd; (ii) alkylation and arylation reactions of inorganic BPMP complexes; and (iii) ligand exchange involving a BPMP ligand and a non-BPMP organometallic complex.

#### Scheme 8



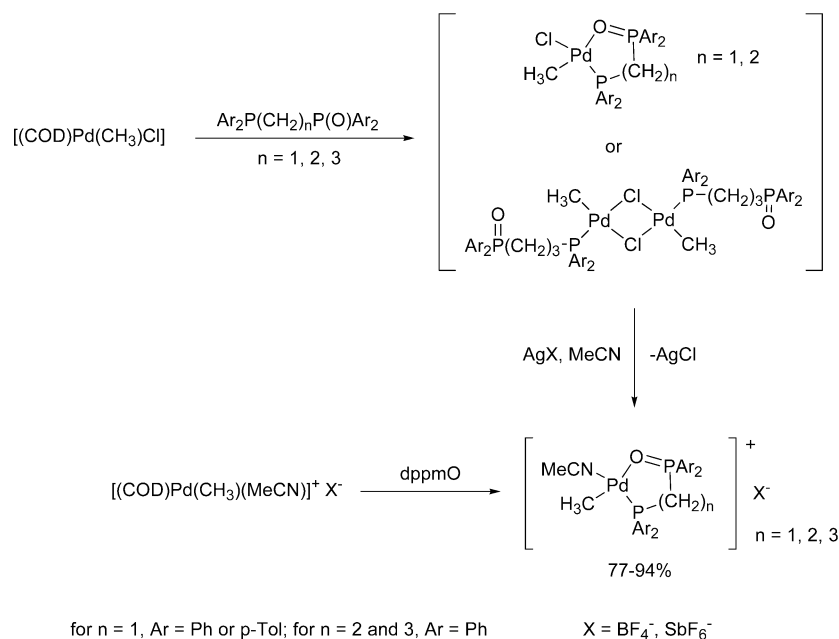
Succinic anhydride has been shown<sup>164</sup> to undergo clean oxidative addition, accompanied by decarbonylation, to a Ni(0) complex generated in situ from [Ni(COD)<sub>2</sub>] and dppmO (eq 65). The structure of the



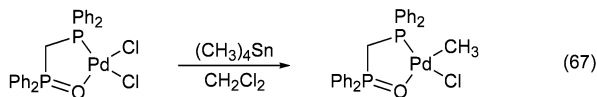
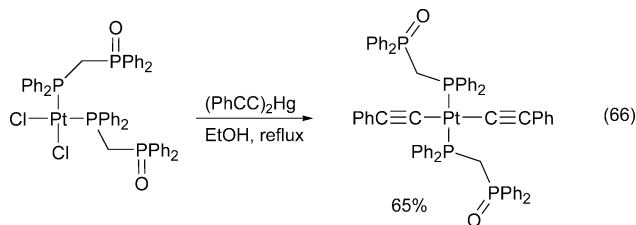
resulting nickelacycle has been confirmed by X-ray analysis.<sup>164</sup> The zerovalent Pd complex [(BINAP(O))<sub>2</sub>Pd] (prepared as shown in eq 64) has been reacted with iodobenzene to give [(BINAP(O)- $\kappa^2$ -P,O)-Pd(Ph)I] (Scheme 8).<sup>162</sup> Although this reaction also gave an equimolar amount of free BINAP(O), the latter exhibited no sign of interaction with the P,O-chelate produced. Alternatively, [(BINAP(O)- $\kappa^2$ -P,O)-Pd(Ph)I] has been prepared from [Pd<sub>2</sub>(dba)<sub>3</sub>], BINAP(O), and iodobenzene.<sup>162</sup> When dppmO was used instead of BINAP(O) under similar conditions, the corresponding dppmO P,O-chelate, [(dppmO)- $\kappa^2$ -P,O)-Pd(Ph)I], was formed.<sup>165</sup> The ultrasound-promoted I/F ligand exchange between [(BINAP(O)- $\kappa^2$ -P,O)Pd(Ph)I] and AgF cleanly afforded [(BINAP(O)- $\kappa^2$ -P,O)Pd(Ph)F] (Scheme 8),<sup>162</sup> the only reported member of the organopalladium fluoride family,<sup>166</sup> in which the terminal F ligand is trans to a phosphine. Nonetheless, the thermal decomposition of [(BINAP(O)- $\kappa^2$ -P,O)Pd(Ph)F] was governed by P–F and P–C rather than C–F reductive elimination processes.<sup>162</sup>

Some inorganic Pd and Pt complexes bearing BPMP ligands have been converted to the corresponding organometallics using standard techniques, e.g., alkylation of a M–Cl bond with organomercury (eq 66)<sup>12</sup> and organotin (eq 67)<sup>52</sup> compounds. Interestingly, the resulting alkynyl complex (eq 66) ap-

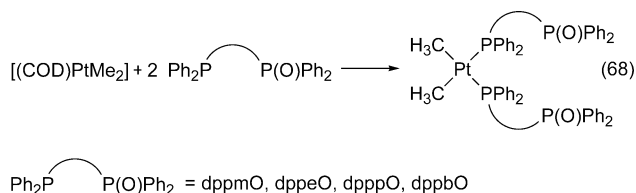
## Scheme 9



peared to be trans, whereas the starting material had the cis geometry.<sup>12</sup>



The largest number of organometallic BPMO complexes of Pd and Pt have been prepared via ligand-exchange reactions involving complexes with a Pd–C or a Pt–C bond and BPMO ligands. The reaction of [(COD)PtMe<sub>2</sub>] with various BPMOs produced *cis*-[(BPMO- $\kappa^1$ -P)<sub>2</sub>PtMe<sub>2</sub>] in 48–87% yield (eq 68).<sup>12</sup> The dppmO derivative, *cis*-[(dppmO- $\kappa^1$ -P)<sub>2</sub>PtMe<sub>2</sub>], was converted to *trans*-[(dppmO- $\kappa^1$ -P)<sub>2</sub>Pt(Cl)Me] in 81% yield upon electrophilic cleavage of one of the Pt–Me bonds with HCl in MeOH.<sup>12</sup> No oxidative addition of MeI to *cis*-[(dppmO- $\kappa^1$ -P)<sub>2</sub>PtMe<sub>2</sub>] was observed after 2 weeks at room temperature.<sup>12</sup>

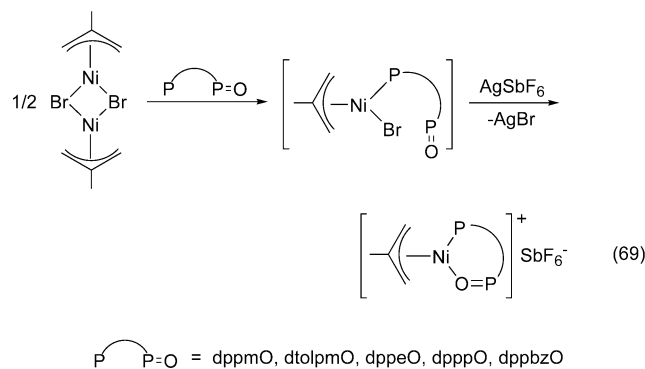


A series of cationic P,O-chelates of the type [(BPMO- $\kappa^2$ -P,O)Pd(Me)(MeCN)]<sup>+</sup>X<sup>-</sup> (BPMO = dppmO, dtolpmO, dppeO, and dppbO; X = BF<sub>4</sub> or SbF<sub>6</sub>) have been synthesized in 77–94% yield, as shown in Scheme 9.<sup>167</sup> Two important facts about this synthetic scheme

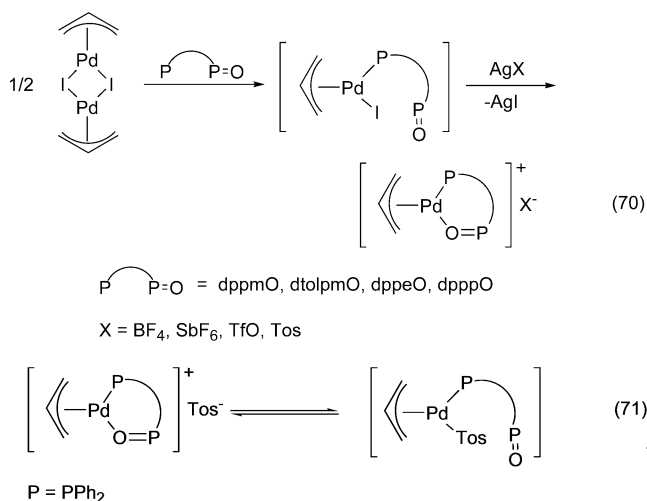
are worth emphasis. First, one neutral intermediate, [(dppmO- $\kappa^2$ -P,O)Pd(Me)Cl], has been isolated, found identical with the samples prepared by other means (eqs 61 and 67), and structurally characterized.<sup>52</sup> Second, the reaction of [(COD)Pd(Me)Cl] with dpppO did not produce the P,O-chelate but rather gave rise to a complex with unilateral P-coordination of the dpppO to the metal, formulated as a dinuclear species, [(dpppO- $\kappa^1$ -P)<sub>2</sub>Pd<sub>2</sub>(Me)<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>].<sup>52,167</sup> This result is in accord with the previously shown<sup>156</sup> poor stability of the seven-membered P,O-dpppO Pd chelates. However, treatment of the dinuclear complex with 1 equiv of AgBF<sub>4</sub> in MeCN did yield a complex which exhibited P=O coordination to Pd. No firm evidence for a *monomeric* structure of [(dpppO- $\kappa^2$ -P,O)Pd(Me)(MeCN)]<sup>+</sup>BF<sub>4</sub><sup>-</sup> was presented (see Scheme 9 vs eq 60 and its discussion above).

A similar strategy has been employed for the preparation of a large number of  $\eta^3$ -allyl complexes of Ni and Pd bearing BPMOs.<sup>51,52,167</sup> The bridging Ni–Br bonds in [( $\eta^3$ -methallyl)<sub>2</sub>Ni<sub>2</sub>Br<sub>2</sub>] were easily cleaved with dppmO,<sup>52,167</sup> dtolpmO,<sup>52</sup> dppeO,<sup>52,167</sup> dpppO,<sup>52,167</sup> and dppbO<sup>167</sup> to produce the neutral P-bonded BPMO complexes [( $\eta^3$ -methallyl)Ni(BPMO- $\kappa^1$ -P)Br] (not isolated), which produced the corresponding cationic P,O-chelates [( $\eta^3$ -methallyl)Ni(BPMO- $\kappa^2$ -P,O)]<sup>+</sup>SbF<sub>6</sub><sup>-</sup> (70–91%) upon treatment with AgSbF<sub>6</sub> (eq 69). Both steps of the synthesis were carried out in CH<sub>2</sub>Cl<sub>2</sub> at –20 °C in order to avoid side reactions leading to contamination with paramagnetic species. Alternatively, the dppmO cationic complex [( $\eta^3$ -methallyl)Ni(dppmO- $\kappa^2$ -P,O)]<sup>+</sup>SbF<sub>6</sub><sup>-</sup> has been prepared by reacting [( $\eta^3$ -methallyl)Ni(COD)]<sup>+</sup>SbF<sub>6</sub><sup>-</sup> with dppmO.<sup>52</sup>

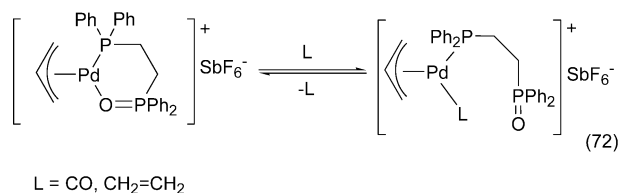
Several  $\eta^3$ -allyl palladium–BPMO complexes have been synthesized as shown in eq 70.<sup>51,52,167</sup> Unlike their nickel analogues (eq 69), the neutral Pd intermediates have been isolated for dppmO, dtolpmO, and dppeO.<sup>52</sup> For X = SbF<sub>6</sub> and BF<sub>4</sub>, the complexes are certainly cationic P,O-chelates, whereas the tosylates and, in some cases, triflates can equilibrate



with the neutral species bearing the BPMO that is unilaterally P-bound to the metal (eq 71).

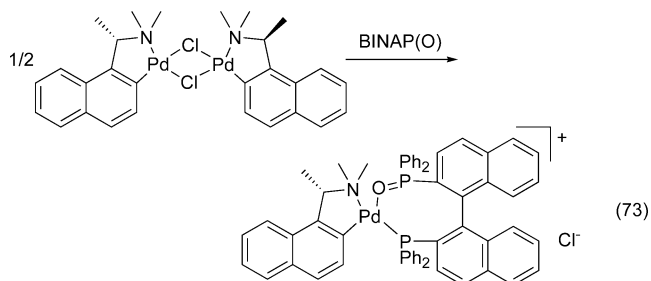


In accord with considerations of the chelate size/strength relationship, equilibrium 71 was shifted entirely toward the neutral complex for the least stable dpppO chelate, whereas both species were present for the dppeO and dppmO species. In the latter two cases, the proportion of the neutral complex was higher for the derivative of dppeO due to the larger size and lower stability of the Pd-dppeO- $\kappa^2$ -P,O ring (eq 71).<sup>52</sup> The phosphinyl group in the P,O-chelate [(dppeO- $\kappa^2$ -P,O)Pd( $\eta^3$ -allyl)]<sup>+</sup>SbF<sub>6</sub><sup>-</sup> was readily and completely displaced with *t*-BuNC.<sup>51</sup> In the presence of CO or ethylene, however, only reversible chelate ring-opening took place, the equilibrium (eq 72) being strongly temperature dependent; i.e., the Pd–L adduct was favored at lower temperatures.<sup>51</sup>



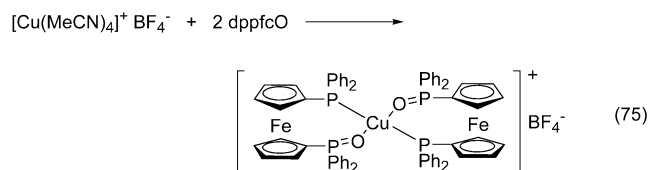
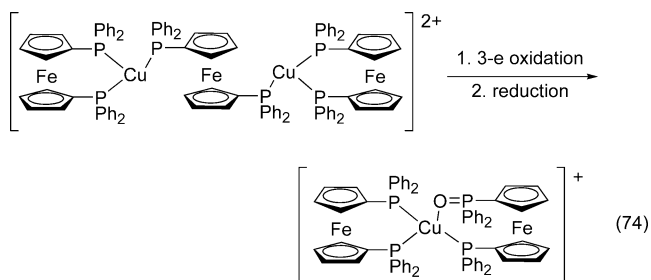
Racemic BINAP(O) has been reacted with the enantiopure cyclometalated Pd dichloro dimer (eq 73) to give a mixture of two diastereomers.<sup>23</sup> After anion exchange with PF<sub>6</sub><sup>-</sup>, one crystallization from CH<sub>2</sub>-Cl<sub>2</sub>-petroleum ether afforded the pure, least soluble diastereomer, which was structurally characterized

and then used to release enantiopure (*S*)-BINAP(O) upon reaction with ethylenediamine (see section 2.1 above).<sup>23</sup>



### 3.1.6. Copper and Gold

Pilloni and Longato<sup>95</sup> have carried out the electrochemical synthesis of [Cu(dppfc- $\kappa^2$ -P,P)<sub>2</sub>(dppfcO- $\kappa^2$ -P,O)]<sup>+</sup>PF<sub>6</sub><sup>-</sup> from [Cu(dppfc)<sub>2</sub>( $\mu$ -dppfc)]<sup>2+</sup>(BF<sub>4</sub><sup>-</sup>)<sub>2</sub> via three-electron oxidation, followed by reduction (eq 74). Another report<sup>168</sup> from Pilloni's group describes the preparation of [Cu(dppfcO- $\kappa^2$ -P,O)<sub>2</sub>]<sup>+</sup>BF<sub>4</sub><sup>-</sup> by reacting [Cu(MeCN)<sub>4</sub>]<sup>+</sup>BF<sub>4</sub><sup>-</sup> with 2 equiv of dppfcO (eq 75).

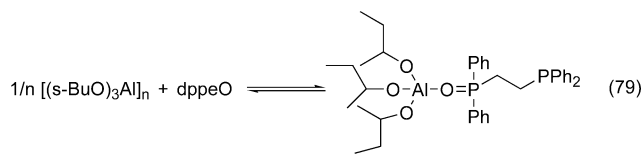


Both [Cu(dppfc- $\kappa^2$ -P,P)<sub>2</sub>(dppfcO- $\kappa^2$ -P,O)]<sup>+</sup>PF<sub>6</sub><sup>-</sup> and [Cu(dppfcO- $\kappa^2$ -P,O)<sub>2</sub>]<sup>+</sup>BF<sub>4</sub><sup>-</sup> have been found to exhibit fluxional behavior in solution, likely due to chelate ring-opening.<sup>95,168</sup> More recently, the similar complexes [Cu(dppeO- $\kappa^2$ -P,O)<sub>2</sub>]<sup>+</sup>ClO<sub>4</sub><sup>-</sup> and [Cu(dppmO- $\kappa^2$ -P,O)<sub>2</sub>]<sup>+</sup>ClO<sub>4</sub><sup>-</sup> were synthesized (Scheme 10) and also found to be labile in solution.<sup>169</sup> X-ray analysis of [Cu(dppeO- $\kappa^2$ -P,O)<sub>2</sub>]<sup>+</sup>ClO<sub>4</sub><sup>-</sup> revealed a bis-chelate, strongly distorted tetrahedral structure. It was also demonstrated that the Cu<sup>+</sup> center has a higher affinity for the softer P rather than the harder O terminus of the BPMO ligands, and that the Cu–OP bond could be easily cleaved with some donor molecules (Scheme 10). Electrochemical studies indicated<sup>169</sup> that [Cu(dppeO- $\kappa^2$ -P,O)<sub>2</sub>]<sup>+</sup>ClO<sub>4</sub><sup>-</sup> and [Cu(dppmO- $\kappa^2$ -P,O)<sub>2</sub>]<sup>+</sup>ClO<sub>4</sub><sup>-</sup> undergo oxidation more readily than [Cu(dppe- $\kappa^2$ -P,P)<sub>2</sub>]<sup>+</sup>ClO<sub>4</sub><sup>-</sup>.

The reaction of [( $\mu$ -dppm)<sub>2</sub>Cu<sub>2</sub>(MeCN)<sub>2</sub>]<sup>2+</sup>(PF<sub>6</sub><sup>-</sup>)<sub>2</sub> with K<sub>2</sub>S<sub>2</sub>CC(CN)P(O)(OEt)<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> has been reported to lead to a mixture of copper cluster complexes, the main product (47%) being (X-ray) a tetranuclear cluster bearing one P-bonded



values were obtained for  $n = 1, 2, 3,$  and  $4$  at various concentrations. The best fit occurred with  $n = 2$ .

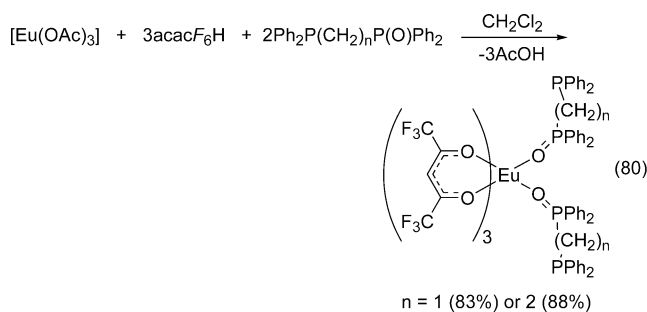


Having been established within a few hours, equilibrium 79 remained unchanged for months.<sup>53</sup> For Al: dppeO = 1, the ratio of uncoordinated to coordinated P=O groups in the system varied in the range of ca. 4–13, depending on concentration, as determined by <sup>31</sup>P NMR. Variable-temperature studies led to calculation of  $\Delta H = 10.5 \pm 0.5 \text{ kJ mol}^{-1}$  and  $\Delta S = 38 \pm 2 \text{ J K}^{-1} \text{ mol}^{-1}$  for reaction 79 at  $n = 2$ .

### 3.1.8. The Lanthanides

Being hard Lewis acids, the lanthanide 3+ ions are prone to coordinate to BPMOs exclusively via the hard oxygen. Visseaux, Dormond, and Baudry<sup>13</sup> have demonstrated that  $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$  readily reacts with  $\text{Ph}_2\text{PCH}(\text{Pr})\text{P}(\text{O})\text{Ph}_2$  in ethanol to give a complex formulated as  $[\text{NdCl}_3(\text{Ph}_2\text{PCH}(\text{Pr})\text{P}(\text{O})\text{Ph}_2-\kappa^1-\text{O})_2]$ . Also,  $[(t\text{-BuC}_5\text{H}_4)_4\text{Nd}_2(\mu\text{-Cl})_2]$  has been shown to react with dpmmO to give  $[(t\text{-BuC}_5\text{H}_4)_2\text{Nd}(\text{Cl})(\text{dpmmO}-\kappa^1-\text{O})]$ , which seems to equilibrate with  $[(t\text{-BuC}_5\text{H}_4)_4\text{Nd}_2(\mu\text{-Cl})(\text{Cl})(\text{dpmmO}-\kappa^1-\text{O})] + \text{dpmmO}$ .<sup>13</sup>

The recently reported<sup>176</sup> series of Eu, Tb, and Tm hexa- and heptafluoroacetylacetonate tertiary phosphine oxide complexes contains two BPMO derivatives,  $[(\text{acac-F}_6)_3\text{Eu}(\text{dpmmO}-\kappa^1-\text{O})_2]$  (83% yield) and  $[(\text{acac-F}_6)_3\text{Eu}(\text{dppeO}-\kappa^1-\text{O})_2]$  (88% yield), which can be prepared in one step from anhydrous  $\text{Eu}(\text{OAc})_3$ ,  $\text{acacH-F}_6$ , and dpmmO or dppeO, respectively (eq 80). A similar Er complex,  $[(\text{acac-F}_6)_3\text{Er}(\text{dppeO}-\kappa^1-\text{O})_2]$ , has been prepared using the same synthetic method and structurally characterized (X-ray) to confirm the unilateral O-binding mode of both dppeO ligands.<sup>177</sup> Due to the presence of two dangling PPh<sub>2</sub> groups, these BPMO complexes of the lanthanides can be regarded as the most exotic bidentate phosphine ligands.<sup>176</sup>

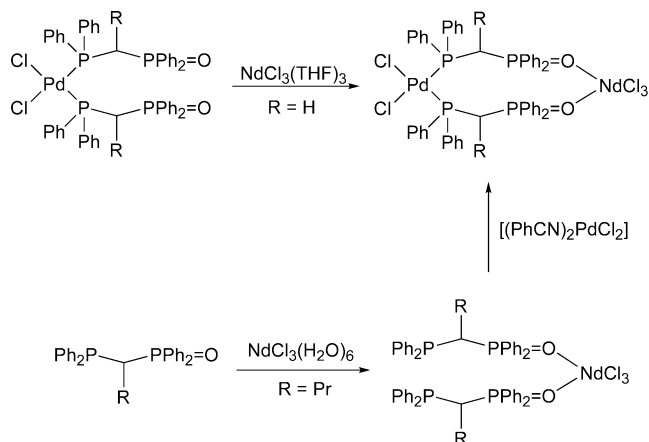


### 3.2. Heteropolymetallic Complexes

In 1993–1994, Visseaux, Dormond, and Baudry<sup>13,178</sup> and the Al-Jibori group<sup>155</sup> published independently and almost simultaneously the first examples of heterobimetallic complexes, in which a BPMO ligand bridged a soft metal ion and a hard metal ion via the phosphine and phosphinyl functions, respectively.

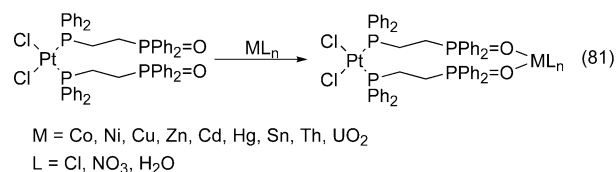
Visseaux, Dormond, and Baudry<sup>13</sup> prepared Pd–Nd heterobimetallics according to Scheme 11. Al-

#### Scheme 11



though the two materials did not analyze well for carbon and were not structurally characterized, the P–Pd and PO–Nd coordination within one scaffold was established unambiguously by the IR and <sup>31</sup>P NMR data. Evidence was also obtained for the formation of a trinuclear  $\text{Mo}_2\text{Nd}$  complex,  $cis\text{-}[(\text{COT})\text{Nd}(\text{Cl})(\mu\text{-dpmmO})_2\text{Mo}(\text{CO})_4]$ , from the reaction of  $[\text{Mo}(\text{CO})_4(\text{NBD})]$  with a solution generated by treatment of  $[(\text{COT})\text{NdCl}(\text{THF})_2]$  with dpmmO.<sup>13,178</sup>

Al-Jibori, Kalay, and Al-Allaf<sup>155</sup> made a large series of derivatives by the reaction of  $cis\text{-}[(\text{dppeO}-\kappa^1\text{-P})_2\text{PtCl}_2]$  with  $\text{MCl}_2 \cdot n\text{H}_2\text{O}$  ( $\text{M} = \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}, \text{Cd}, \text{Hg}$ ),  $\text{Me}_2\text{SnCl}_2$ ,  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{Th}(\text{NO}_3)_4 \cdot n\text{H}_2\text{O}$ , and  $\text{UO}_2 \cdot (\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (eq 81). All products were characterized by satisfactory microanalysis (C, H) and IR spectroscopic data. Magnetic susceptibility and TGA data were also obtained for selected products. Unfortunately, the authors<sup>155</sup> were not able to obtain any structural data on the new heterobimetallics, and therefore they carefully proposed the cyclic structure shown in eq 81. Attempts to synthesize similar dpmmO complexes appeared unsuccessful.<sup>155</sup>

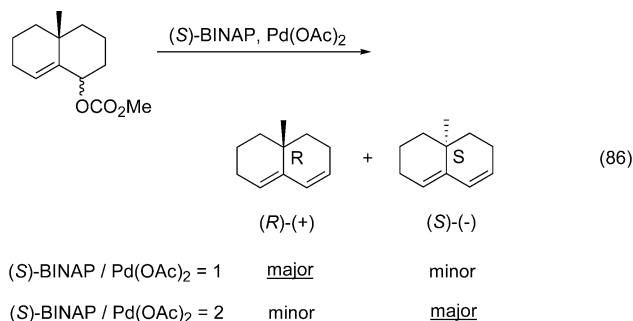


Very recently, Al-Jibori and co-workers described a series of heterobimetallic compounds prepared using the same methodology from  $[(\text{dppeO}-\kappa^1\text{-P})_2\text{PdCl}_2]$  and  $\text{MCl}_2 \cdot n\text{H}_2\text{O}$  ( $\text{M} = \text{Mn}, \text{Co}, \text{Cu}, \text{Zn}, \text{Hg}$ ),  $\text{Me}_2\text{SnCl}_2$ ,  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{UO}_2 \cdot (\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ .<sup>157</sup> Like in the preceding work on the analogous Pt complexes,<sup>155</sup> no structural determination of the Pd-derived heterobimetallics was carried out.<sup>157</sup> On the basis of the IR data, the geometry around Pd was concluded to be trans. Considering that and the large size of the Pt–M (eq 81) and Pd–M rings, it is conceivable that the products might in fact be oligomeric or polymeric species. The most recently described Pd–Eu dppeO material was indeed formulated as a polymer (eq 82).<sup>176</sup>





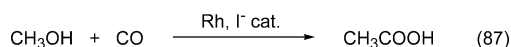
the most popular combination of a bidentate phosphine and  $\text{Pd}(\text{OAc})_2$  is used as added catalyst, the formation of BPMO–Pd species is virtually guaranteed,<sup>58,69,83,84,86,87</sup> unless a reducing agent is present, which reduces the Pd(II) to Pd(0) faster than the Pd(II)/P(III)-to-Pd(0)/P(V) redox process can occur. This point is nicely illustrated by the work of Shimizu et al.<sup>184</sup> reporting chirality reversal depending on the ratio of  $\text{Pd}(\text{OAc})_2$  to (*S*)-BINAP used as added catalyst for reaction 86. It was clearly demonstrated<sup>184</sup> by independent experiments that the effect was due to the oxidation of the (*S*)-BINAP to (*S*)-BINAP(O) with the Pd(II) (eq 11).<sup>69</sup> Therefore, at the (*S*)-BINAP-to- $\text{Pd}(\text{OAc})_2$  ratio of 1, the active zerovalent Pd catalyst generated in situ is expected to be a Pd(0)–(*S*)-BINAP(O) rather than a Pd(0)–(*S*)-BINAP species. When the ratio of (*S*)-BINAP to  $\text{Pd}(\text{OAc})_2$  equals 2, the resulting complex will have a totally different composition, being a blend of 1 equiv of Pd(0), 1 equiv of (*S*)-BINAP(O), and 1 equiv of unreacted (*S*)-BINAP. As compared to BINAP, its monoxide, BINAP(O), exhibits vastly different coordination modes with Pd(0) and Pd(II).<sup>162</sup> This explains the chirality reversal effect (eq 86)<sup>184</sup> and points to the importance of formation of BPMOs in situ from mixtures of a divalent Pd or Pt precursor and a bidentate phosphine as added catalyst. Equally important is the fact that the use of a BPMO instead of a diphosphine under similar conditions will likely result in oxidation of the BPMO to the corresponding dioxide with a very low ability to coordinate and stabilize a soft metal center.



(III) Some BPMOs exhibit unusual reactivity patterns when coordinated to a metal center. For instance,  $\text{dppmO}$  coordinated to Pd(II) has been reported<sup>156</sup> to undergo facile H/D exchange at the  $\text{CH}_2$  group with  $\text{CD}_3\text{OD}$ , even at ambient temperature. The aliphatic C–H acidity of coordinated  $\text{dppmO}$  is likely responsible for the facile palladation (eq 53)<sup>149</sup> and auration (eq 77)<sup>173</sup> reactions described above.

#### 4.1.2. Carbonylation of Alcohols to Carboxylic Acids and Esters

The Monsanto acetic acid process (eq 87) for methanol carbonylation is one of the few most important industrial processes catalyzed by soluble metal complexes. This highly efficient and selective methanol carbonylation reaction presently accounts for ca. 55% of all acetic acid produced worldwide.<sup>185</sup>



Wegman, Abatjoglou, and co-workers at Union Carbide have found<sup>143,186</sup> that  $\text{dppeO}$  complexes of rhodium are highly efficient catalysts for the Monsanto process. Thus,  $[(\text{dppeO}-\kappa^2\text{-}P,O)\text{Rh}(\text{CO})\text{Cl}]$  (pre-formed or generated in situ) catalyzes methanol carbonylation at 80 °C and 3.5 atm of CO with a turnover frequency (TOF) number of ca. 400  $\text{h}^{-1}$ .<sup>143</sup> These are exceedingly mild conditions in comparison with those of the standard process, employing 200 °C and 35 atm of CO to reach the  $\text{TOF} = 200\text{--}600 \text{ h}^{-1}$  in the presence of the industrial rhodium–iodine catalyst. A detailed study<sup>186</sup> of methanol carbonylation, catalyzed by Rh–BPMO complexes, revealed the following important features. First, the reaction was 45–150 times slower in the absence of  $\text{dppeO}$  or upon replacement of the latter with  $\text{PPh}_3$ ,  $\text{MePPH}_2$ , or  $\text{dppeO}_2$ . No reaction occurred in the presence of  $\text{dppe}$ . Second, an increase in the  $\text{dppeO}/\text{Rh}$  ratio from 1 to 2 slowed the process by a factor of 5. Third, the Rh– $\text{dpppO}$  and – $\text{dppbO}$  catalytic systems were ca. 40% less active than the  $\text{dppeO}$ –Rh catalyst, whereas  $\text{dppmO}$  formed a catalytically inactive complex.<sup>186</sup> Ethanol can also be carbonylated to propionic acid in the presence of the  $\text{dppeO}$ –Rh catalyst, albeit at a slower rate.<sup>186</sup>

Mechanistic studies of the Rh– $\text{dppeO}$ -catalyzed carbonylation of MeOH to AcOH nicely demonstrate the idea of hemilability in catalysis.<sup>143</sup> The reaction of  $[\text{Rh}_2(\text{CO})_4(\mu\text{-Cl})_2]$  with  $\text{dppeO}$  gives rise to  $[(\text{dppeO}-\kappa^2\text{-}P,O)\text{Rh}(\text{CO})\text{Cl}]$  which, in the presence of CO, exists in equilibrium with  $[(\text{dppeO}-\kappa^1\text{-}P)\text{Rh}(\text{CO})_2\text{Cl}]$  (eq 40). At room temperature and 1 atm of CO, the ratio of the two complexes is ca. 1:1. Treatment of the dicarbonyl  $\text{dppeO}-\kappa^1\text{-}P$  complex with MeI resulted in the instantaneous formation of acetyl iodide and the initial  $\text{dppeO}-\kappa^2\text{-}P,O$  Rh monocarbonyl (eq 41). The reaction occurs via oxidative addition of MeI to Rh, followed by migratory CO insertion and subsequent reductive elimination of  $\text{CH}_3\text{C}(\text{O})\text{I}$ . Under the catalytic process conditions, the acetyl iodide reacts with MeOH to give AcOH and MeI that is needed to commence another catalytic turnover. In the analogous  $[(\text{dppmO}-\kappa^2\text{-}P,O)\text{Rh}(\text{CO})\text{Cl}]$  (characterized by X-ray diffraction),<sup>143</sup> the  $\text{dppmO}$  ligand forms a much more stable five-membered chelate. As a result, the  $\text{dppmO}$  complex is much less reactive toward CO and MeI. This accounts for  $\text{dppmO}$  being a catalytic poison for the process.

While being exceptionally active in MeOH carbonylation under very mild conditions, the Rh– $\text{dppeO}$  catalytic system provided only a slight rate improvement under the “ligandless” harsh conditions currently adopted by the industry.<sup>187</sup> This is not surprising, as at high temperatures the Rh–O bond of the P,O- $\text{dppeO}$  chelate becomes too weak to retain its hemilabile properties, i.e., the ability to protect the vacant coordination site needed for efficient catalysis to occur. As a result, the  $\text{dppeO}$  on the rhodium at a high enough temperature behaves essentially as a conventional monodentate phosphine. In contrast, the P,S-chelate complex  $[(\text{dppmS}-\kappa^2\text{-}P,S)\text{Rh}(\text{CO})\text{X}]$  (X = Cl or I)<sup>187</sup> fails to catalyze the Monsanto process under mild conditions due to poor hemilability, i.e., the high stability of the five-

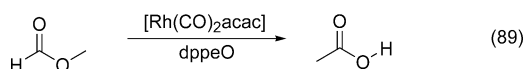


**Table 2.** [Rh(CO)<sub>2</sub>(acac)]-Catalyzed Hydroformylation of 1-Hexene (Eq 90, R = *n*-C<sub>4</sub>H<sub>9</sub>) in the Presence of BP MO or Mono-phosphine Ligands (40 mol equiv per Rh) in 1,2-Diethoxyethane–1,4-Butanediol (2:1) at 80 °C and 8.2 atm of CO/H<sub>2</sub> (1:1)<sup>193</sup>

ligand	reaction rate, mol L <sup>-1</sup> h <sup>-1</sup>	linear:branched ratio at 10–20% conversion
Ph <sub>2</sub> PCH <sub>2</sub> P(O)Ph <sub>2</sub> (dppmO)	0.61	9.4
Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> P(O)Ph <sub>2</sub> (dppeO)	0.53	33.8
Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>3</sub> P(O)Ph <sub>2</sub> (dpppO)	1.03	22.9
Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>4</sub> P(O)Ph <sub>2</sub> (dppbO)	0.96	25.8
Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>5</sub> P(O)Ph <sub>2</sub>	2.23	15.5
Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>6</sub> P(O)Ph <sub>2</sub>	1.46	9.1
<i>cis</i> -Ph <sub>2</sub> PCH=CHP(O)Ph <sub>2</sub>	0.45	5.1
<i>trans</i> -Ph <sub>2</sub> PCH=CHP(O)Ph <sub>2</sub>	1.27	3.2
Ph <sub>3</sub> P	2.70	19.6
Ph <sub>2</sub> (Pr)P	1.67	10.9

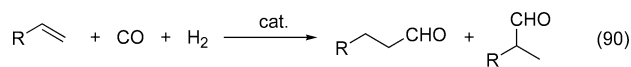
#### 4.1.4. Isomerization of Methyl Formate to Acetic Acid

While formally being an isomerization process, this reaction (eq 89) is run under CO. In the presence of a Rh–dppeO catalyst and an iodide promoter, such as MeI, HI, LiI, or SrI<sub>2</sub>, the reaction readily occurred at 80–115 °C to give acetic acid in >95% selectivity at up to 63% conversion.<sup>192</sup> The use of AcOH as a solvent resulted in more efficient catalysis.



#### 4.1.5. Hydroformylation of Olefins

Like the Monsanto acetic acid process, olefin hydroformylation to aldehydes (eq 90) belongs to the limited number of homogeneously catalyzed reactions of exceptional industrial importance.<sup>185</sup> The first olefin hydroformylation reaction catalyzed by a BP MO complex was patented more than 20 years ago.<sup>18</sup> The reaction of 1-butene with CO/H<sub>2</sub> in the presence of a dppeO Rh catalyst was reported<sup>18</sup> to proceed to 80% conversion after 17 min at 145 °C and 26 atm. Although a molar ratio of the linear to branched aldehyde of 7.3 was reported, the actual absolute yields of the two isomeric products were not specified.



In the 1980s, Abatjoglou, Billing, and Bryant of Union Carbide were granted a number of patents<sup>193,194</sup> for their invention of advantageous use of BP MOs as ligands for hydroformylation of various olefins. More recently, a patent was issued to the Union Carbide group on a process for separation and recovery of catalysts, BP MO–Rh catalysts included, from hydroformylation reactions.<sup>195</sup>

It has been found by Abatjoglou and Billing<sup>193</sup> that the use of certain BP MOs for Rh-catalyzed olefin hydroformylation provides a number of clear advantages to the common process employing monophosphine Rh catalysts. Most importantly, olefin hydroformylation reactions catalyzed by Rh–BP MO complexes occur with unusually high selectivities to the desired<sup>185</sup> linear products (Table 2).<sup>193</sup> As can be seen from Table 2, the dppeO–Rh catalyst provided the highest regioselectivity (>97%) to *n*-heptanal, the linear product of interest. This catalytic system was

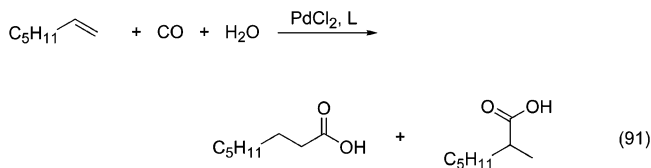
also found to possess high thermal stability and ability to catalyze hydroformylation of other substrates, such as propylene, 1,5-hexadiene, and allyl alcohol with superior chemo- and regioselectivity. The already excellent catalyst lifetime can be further improved by the addition of a conventional tertiary organophosphine, such as (*p*-XC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>P (X = H, Me, MeO), to the Rh–dppeO catalyst.<sup>194</sup> Remarkably, the Rh/dppeO/R<sub>3</sub>P catalytic systems were more thermally stable than Rh/R<sub>3</sub>P and Rh/dppeO.

The catalytic activity of Rh–phosphine oxide systems in the hydroformylation of styrene has been studied.<sup>196</sup> Of over a dozen different phosphine oxides, dppmO (the only BP MO used in this study) and Ph<sub>2</sub>P(O)CH<sub>2</sub>NR<sub>2</sub> exhibited by far the highest activity (95–100% yield) and selectivity (93–97%) toward the branched aldehyde, 2-phenylpropanal. However, the high activity is exhibited by the dppmO–Rh catalytic system only in the presence of a base, Et<sub>3</sub>N. The latter is probably needed to promote reductive elimination of HCl<sup>197</sup> from the intermediate [(dppmO-κ<sup>2</sup>-*P,O*)Rh(H)<sub>2</sub>(CO)Cl] to give catalytically active [(dppmO-κ<sup>2</sup>-*P,O*)Rh(H)(CO)].<sup>196</sup> Interestingly, the Rh–dppmO<sub>2</sub> system was inactive in the hydroformylation of styrene under the same conditions,<sup>196</sup> whereas dppbO<sub>2</sub> was later reported to promote the Rh-catalyzed hydroformylation of mixed octenes more efficiently than dppbO and dppb.<sup>198</sup> Among other P-ligands, dppeO has been reported<sup>199</sup> to promote Rh-catalyzed hydroformylation of dihydromyrcenol.

Gladiali and co-workers have recently reported hydroformylation of styrene with BINAP(O) Rh<sup>144</sup> and Pt–Sn<sup>163</sup> catalysts. The Rh-catalyzed hydroformylation of styrene with 1:1 CO/H<sub>2</sub> and a 4000:1 substrate-to-catalyst ratio easily occurred to 36–99% conversion at 40–100 °C and an initial CO pressure of 79 atm. Although the process was up to 96% chemo- and regioselective toward the formation of the branched aldehyde, very low ee values (4–6%; *R*) were observed when (*S*)-BINAP(O) was used.<sup>144</sup> A much better but still insufficiently high ee (28–30%; *R*) was obtained for the Pt–Sn–(*S*)-BINAP(O)-catalyzed hydroformylation of styrene to the branched aldehyde that was formed with high chemoselectivity but only 40–60% positional selectivity.<sup>163</sup>

#### 4.1.6. Hydrocarboxylation of Olefins

The Pd-catalyzed hydrocarboxylation reactions of 1-heptene (eq 91) at 120 °C and 19.7 atm of CO in the presence of various ligands L have been studied by Terekhova et al.<sup>200</sup>



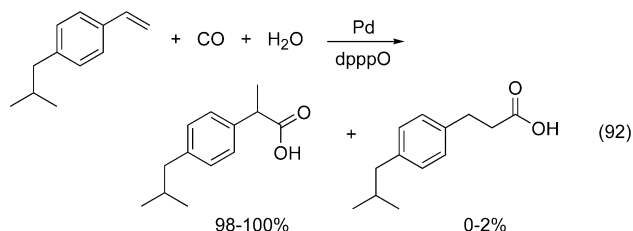
L = dppe, dppeO, dppeS, dppmO, Ph<sub>3</sub>P, Ph<sub>2</sub>PET

Among all ligands examined (eq 91), dppeO was the one that resulted in the highest molar ratio of the linear to branched acid. Depending on the solvent, Pd-to-dppeO ratio, and CO pressure, the selec-

tivity for the desired linear acid was 80–91%, an uncommonly high number for this type of transformation. Palladium catalysts based on dppe and dppeS were inefficient, whereas the Pd–dppmO system exhibited both very poor stability and selectivity under identical conditions. Monodentate PPh<sub>3</sub> formed a very active but poorly selective catalyst. In contrast, Ph<sub>2</sub>PEt provided good selectivity to the linear product (83%), albeit at a low rate.

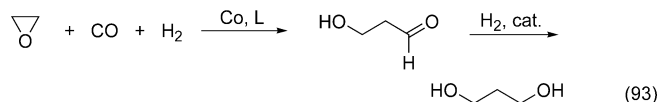
The regioselectivity and rate of reaction 91, catalyzed by the dppeO–Pd system, were affected by the medium. Thus, in acetonitrile the process was slow, producing only 62% of the linear acid, whereas in benzene, dioxane, or their mixtures the reaction occurred ca. 4–27 times faster and with higher selectivities (74–89%). Also, it was established that an increase in CO pressure in the range of 5–30 atm leads to faster rates but lower selectivities. On the basis of this very well-done work, it was concluded<sup>200</sup> that the excellent catalytic properties of the dppeO–Pd catalyst are likely due to optimum hemilability of the dppeO ligand. The Pd–dppeO-catalyzed hydrocarboxylations of propylene, 1-decene, and styrene were also found to occur with a high selectivity to the linear acids, 70% for the aliphatic and 50% for the aromatic derivatives.<sup>200</sup>

Wu has patented,<sup>201</sup> among other findings, the very successful use of dpppO in the Pd-catalyzed hydrocarboxylation of 4-isobutylstyrene to ibuprofen at 50–80 °C and 34 atm of CO (eq 92). In sharp contrast, the use of dppp or monodentate tertiary phosphines resulted in a very sluggish and poorly selective reaction. Excellent results were also obtained when the Pd catalyst was promoted with mixtures of R<sub>3</sub>P, R<sub>3</sub>PO, and, optionally, CuCl<sub>2</sub> in the presence of HCl.<sup>201</sup>



#### 4.1.7. Hydroformylation of Epoxides

The metal-catalyzed hydroformylation of epoxides furnishes  $\beta$ -hydroxyaldehydes which can be hydrogenated to 1,3-diols, important and promising monomers (eq 93). Weber et al.<sup>138,202</sup> have reported the first use of BPMOs in the [Co<sub>2</sub>(CO)<sub>8</sub>]-catalyzed ring-opening of epoxides with CO and H<sub>2</sub> (99 atm at 100 °C, 3 h), followed by hydrogenation to the diol.



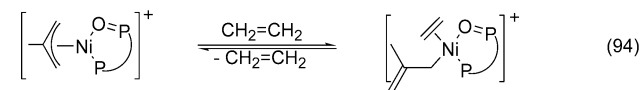
Of the ligands tested (dppmO, dppeO, dpppO, dppm, dppe, dppp, dppb, PPh<sub>3</sub>, and PPh<sub>3</sub>/Ph<sub>2</sub>MePO), the highest selectivity to the hydroxyaldehyde (up to 90%) was observed for dppmO. All other bidentate ligands exhibited activity, except for dppm which, like PPh<sub>3</sub> and Ph<sub>3</sub>P/Ph<sub>2</sub>MePO, was inactive. It was there-

fore concluded that chelate formation is important for the catalysis which occurs most efficiently with ligands that are capable of forming five-membered chelates, hemilabile dppmO being the best. Interestingly, a stable complex, [Co<sub>2</sub>(CO)<sub>6</sub>(dppmO- $\kappa^1$ -P)<sub>2</sub>], that was isolated and found to be catalytically active (90% conversion to the hydroxyaldehyde) exhibited a nonchelate but rather P-unilateral binding mode for the dppmO ligand on each metal (see section 3.1.4). It was proposed that, under the reaction conditions, i.e., upon exposure to CO/H<sub>2</sub>, the complex [Co<sub>2</sub>(CO)<sub>6</sub>(dppmO- $\kappa^1$ -P)<sub>2</sub>] was converted to [HCo(CO)<sub>2</sub>(dppmO- $\kappa^2$ -P,O)], an actual catalytically active species. The best overall yield of the diol for the two steps (eq 93) was 54% (GC).<sup>138</sup> Other epoxides have also been used in the two-step sequential hydroformylation–hydrogenation process, catalyzed by [Co<sub>2</sub>(CO)<sub>8</sub>]/dppmO. Propylene oxide, *trans*-2,3-butene oxide, cyclohexene oxide, and styrene oxide gave the corresponding aldehydes with 75, 79, 52, and 4% selectivity and then the diols in 30, 66, 39, and 7% GC yield, respectively.<sup>138</sup>

#### 4.1.8. Oligomerization of Ethylene and Copolymerization of Ethylene and CO

These processes are of great commercial interest as industrially feasible routes to  $\alpha$ -olefins and polyketones. BPMOs have been successfully used in the Ni- and Pd-catalyzed oligomerization of ethylene<sup>167</sup> and alternating copolymerization<sup>167</sup> and co-oligomerization<sup>203,204</sup> of ethylene and CO with Pd<sup>167,203</sup> and Rh<sup>204</sup> catalysts.

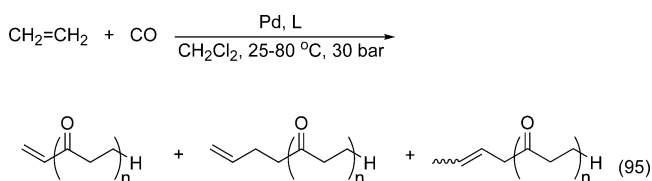
Nickel catalysts of the type [( $\eta^3$ -methylallyl)Ni(BPMO- $\kappa^2$ -P,O)]<sup>+</sup>SbF<sub>6</sub><sup>−</sup>, both presynthesized and generated in situ, have been shown<sup>167</sup> to exhibit excellent activity in ethylene oligomerization with high selectivities toward linear products (87–96%) with the terminal C=C bond (up to 89%). These results are the best ever reported for ethylene oligomerization with cationic P,O-chelated nickel catalysts. The high selectivities were ascribed to the inert Ni–O bond in the P,O-chelate ring that does not open during the catalytic process, similar to the industrial Shell catalysts.<sup>167</sup> Instead, the  $\eta^3$ -methylallyl ligand on the metal reversibly changes hapticity to  $\eta^1$ , thus creating a vacant coordination site that is occupied by CH<sub>2</sub>=CH<sub>2</sub> (eq 94).



The nature of BPMO strongly influences the reaction outcome. Thus, the most stable, five-membered dppmO chelate produced heavier oligomers, up to C<sub>16</sub>, whereas the dpppO analogue catalyzed the formation of only short-chained alkenes. The highest molecular weight oligomers (up to C<sub>34</sub>) were obtained, however, when [( $\eta^3$ -methylallyl)Ni(dppbzO- $\kappa^2$ -P,O)]<sup>+</sup>SbF<sub>6</sub><sup>−</sup> was used, due to the rigidity of the dppbzO backbone that disfavors  $\beta$ -elimination. Analogous palladium–BPMO complexes also catalyzed ethylene oligomerization but mostly to butanes (65–86%). Decenes and dodecenes were produced in trace quantities, if at all.<sup>167</sup>

Of the Pd complexes of the type  $[(\eta^3\text{-allyl})\text{Pd}(\text{BPMO}-\kappa^2\text{-P},\text{O})]^+\text{X}^-$  (BPMO = dppmO, dppeO, dpppO; X = TosO, TfO,  $\text{BF}_4^-$ ) tested for catalytic activity in ethylene/CO copolymerization, the highest efficiency was observed for BPMO = dppmO and X =  $\text{BF}_4^-$ . The analogous dppeO and dpppO catalysts were less stable, undergoing reduction to Pd(0). Therefore, reaction conditions were optimized for the most catalytically active complex,  $[(\eta^3\text{-allyl})\text{Pd}(\text{dppmO}-\kappa^2\text{-P},\text{O})]^+\text{BF}_4^-$ , and its methyl analogue,  $[(\text{MeCN})\text{Pd}(\text{Me})(\text{dppmO}-\kappa^2\text{-P},\text{O})]^+\text{BF}_4^-$ , at the upper limit of their thermal stability (80 °C). The allyl and methyl complexes exhibited similar catalytic activity. Although high CO conversions of up to 96% and TON of up to ca. 4500 were observed in dichloromethane after 15 min under 30 atm of CO + 30 atm of  $\text{C}_2\text{H}_4$ , the catalytic activity was lower than that of the Shell catalysts.<sup>167</sup>

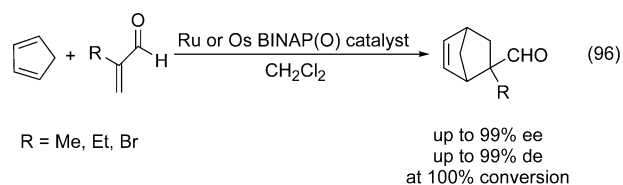
It has also been found<sup>203</sup> that a series of cationic Pd complexes containing P,O and P,S hemilabile ligands catalyze the formation of unsaturated polyketones from CO and ethylene, as long as the latter is used in a large (e.g., 10-fold) excess (eq 95). The only



BPMO used as a ligand for reaction 95 was dppeO employed in the form of  $[(\eta^3\text{-allyl})\text{Pd}(\text{dppeO}-\kappa^2\text{-P},\text{O})]^+\text{SbF}_6^-$ . This catalyst resulted in the production of the highest molecular weight unsaturated polyketones at 98% conversion of CO. All other P,O and P,S ligands used, i.e., phosphino esters, phosphino thiophenes, and phosphino sulfoxides, produced catalysts which catalyzed the formation of mostly short-chained products with  $n = 1, 2$ , and  $\geq 3$ , with the selectivity to ethyl vinyl ketone ( $n = 1$ ) being 2–10%.<sup>203</sup> Co-oligomerization of CO and ethylene in the presence of Rh complexes stabilized with various hemilabile ligands has been reported<sup>204</sup> to produce mixtures of methyl acrylate, methyl propionate, ethyl vinyl ketone, diethyl ketone, 1-methoxypentan-3-one, methyl 4-oxohexanoate, octan-3,6-dione, and other products with  $\geq 7$  atoms in the backbone. The only BPMO ligand employed in this study,<sup>204</sup> dmpmO, exhibited good efficiency, although it did not produce results that one would consider distinct in terms of reaction rate, lifetime, or selectivity toward any particular component of the product mixture.

#### 4.1.9. Asymmetric Cycloaddition

Over the past 4 years, Faller and co-workers have published a series of papers<sup>14,59,130–135</sup> describing the synthesis of chiral BPMO-derived Ru and Os complexes and their use as Lewis acid catalysts in asymmetric Diels–Alder reaction of cyclopentadiene with substituted acroleins (eq 96). The cycloadduct resulting from reaction 96 might be useful for prostaglandin synthesis.<sup>59</sup>



The catalysts used by the Faller group for reaction 96 were Ru<sup>59,130,131,133</sup> and Os<sup>135</sup> chiral Lewis acids of the type  $[(\eta^6\text{-}p\text{-cymene})\text{M}(\text{L})(\text{BPMO}-\kappa^2\text{-P},\text{O})]^{2+}(\text{SbF}_6^-)_2$ , where BPMO = (*R,R*)-chiraphos(O) or (*S*)-BINAP(O). The exact structure of the catalyst is unknown. It is believed<sup>14,59,130–135</sup> that the Lewis acidic center on the metal is stabilized via coordination of a weakly bound solvent molecule L, a counterion, or through some agostic interactions. Various Lewis bases, such as aldehydes, pyridines, sulfoxides, water, and  $\text{Cl}^-$ , readily coordinate to the metal in these complexes, as mentioned above in section 3.1.3.

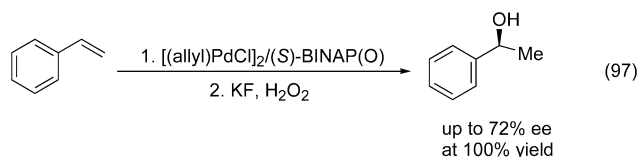
When the more easily epimerizing chiraphos(O) Ru complex was used as a catalyst (10%) for reaction 96 (R = Me, –25 °C), the ee was modest (30%).<sup>130</sup> Slightly better ee values of up to 50% at a 9.9:1 exo/endo ratio were obtained in the initial experiments with the more stereochemically rigid BINAP(O) Ru complex in the presence of lutidine.<sup>131</sup> After some optimization, however, remarkably high enantioselectivities of up to 99% ((*S*)-(+)) for R = Me) and diastereoselectivities (exo) also up to 99% were obtained for reaction 96 in the presence of Ru catalysts stabilized with optically pure (*S*)-BINAP(O) and (*S*)-TolBINAP(O).<sup>59</sup> To reach the high enantio- and diastereoselectivity, reaction 96 was run in the absence of lutidine at a low temperature (–24 to –78 °C) with 1–10% of the catalyst. The latter was generated in situ from  $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}(\text{BPMO}-\kappa^2\text{-P},\text{O})]^+\text{SbF}_6^-$  and slightly less than 1 equiv of  $\text{AgSbF}_6$ , to avoid the presence of  $\text{Ag}^+$  which might act as a nonchiral catalyst. Remarkably, the cycloaddition reaction exhibited high tolerance for water and air. After full conversion was reached, the catalyst was found to be in the aqua form  $[(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{H}_2\text{O})(\text{BINAP}(\text{O})-\kappa^2\text{-P},\text{O})]^{2+}(\text{SbF}_6^-)_2$ , which can be recycled. When analogous Os–BINAP(O) catalysts were employed for reaction 96, the cycloadducts were formed with good diastereoselectivity but lower enantioselectivity (ee = 8–93%).<sup>135</sup> The chiral poisoning strategy has been employed for reaction 96, catalyzed by the Ru Lewis acid derived from racemic BINAP(O).<sup>133</sup> Although high diastereoselectivity was observed with various chiral additives, only a modest ee of <60% was obtained with L-proline and L-prolinamide, the most efficient chiral poisons.

For the chiral induction, no hemilabile behavior is needed from the BINAP(O)- $\kappa^2\text{-P},\text{O}$  ligand on Ru and Os in the catalytically active species. Moreover, experimental data and mechanistic considerations strongly suggest<sup>59,135</sup> that *electronic asymmetry* in the  $C_1$ -symmetric BINAP(O) ligand is likely a very important reason for the high induction of chirality. In fact, the use of BINAP, a closely related  $C_2$ -symmetric, *non-oxidized* bisphosphine ligand, instead of BINAP(O) for reaction 96 under identical conditions resulted in an abrupt decrease in ee from 93–99% to 19–50% for the opposite enantiomer.<sup>59</sup> This

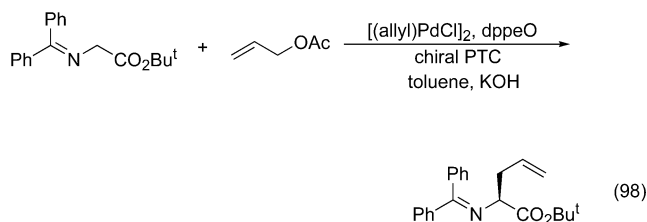
result clearly indicates the importance of the stereogenic metal center for the chiral induction.

#### 4.1.10. Miscellaneous Catalytic Reactions

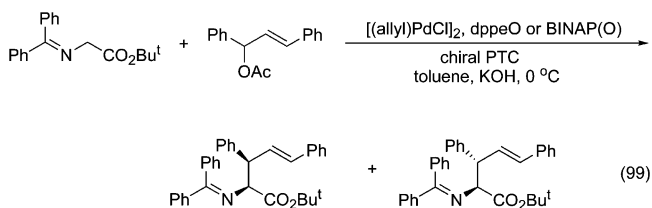
Styrene has been hydrosilylated with a Pd–BINAP(O) catalyst at a substrate-to-Pd ratio of 1000 to produce exclusively the branched product, which was converted to the corresponding alcohol (eq 97).<sup>23</sup> Importantly, (*S*)-1-phenylethanol was obtained in only 18% ee when the reaction was performed in neat styrene. However, the use of benzene as a solvent for reaction 97 brought the ee up considerably, to 72%.



Very recently, an interesting example was reported<sup>205</sup> of Pd-catalyzed asymmetric allylic alkylation of a glycine imino ester in the presence of cinchonidinium salts as a chiral phase-transfer catalyst and some P-ligands, including dppeO (eq 98). Of the several P-ligands examined in reaction 98 (dppe, Ph<sub>3</sub>P, Bu<sub>3</sub>P, (EtO)<sub>3</sub>P, (PhO)<sub>3</sub>P, and dppeO), the ones that led to the highest yield (>80%) and ee (93–94%) were dppeO and triphenyl phosphite. Although both the yield and ee were comparable for (PhO)<sub>3</sub>P and dppeO, the latter is much more stable toward the strong alkali used than the phosphite.



Dual asymmetric induction was achieved in the same work<sup>205</sup> by using a chiral phase-transfer catalyst and dppeO or BINAP(O) (eq 99). The use of dppeO yielded the product in 76% yield with the best stereoselectivities (de = 70% and ee = 51%), whereas (*R*)- and (*S*)-BINAP(O) produced better enantioselectivity (up to 77%) but lower yield (33–61%) and a diastereoselectivity of slightly above 30%.

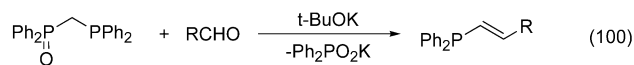


A very important, educational example of asymmetric catalysis with an unintentionally in situ-generated BINAP(O)–Pd species (eq 86) is briefly discussed above. A few cases have been reported where the use of BPMOs in catalysis failed or was only modestly successful. The C=C bond in acetamidoacrylate has been efficiently hydrogenated in the presence of [(NBD)Rh((*S*)-BINAP(O)-κ<sup>2</sup>-P,O)]<sup>+</sup>

BF<sub>4</sub><sup>−</sup>, albeit with negligible enantioselectivity of 4%.<sup>144</sup> The same catalyst has been applied for hydroboration of styrene with catecholborate, followed by oxidative alkaline cleavage to give the branched alcohol in 73% regioselectivity with only 40% ee at 22% conversion.<sup>144</sup> An attempt to enhance the efficiency of a Ru-catalyzed hydrogenation reaction with a 1:1 mixture of [NdCl<sub>3</sub>(THF)<sub>3</sub>] and dppeO has been reported<sup>206</sup> to result in the loss of catalytic activity. Likewise, a BINAP(O)–Ni complex was inactive in the hydrovinylation reaction of 2-methoxy-6-vinylnaphthalene.<sup>207</sup> The Pd–(*R*)-BINAP(O)-catalyzed asymmetric Suzuki coupling reaction of 1-iodo-2-methoxynaphthalene with 2-methoxy-1-naphthylboronic acid was sluggish, resulting in only 22–31% yield and very low enantioselectivity (ee = 14–24%).<sup>208</sup>

## 4.2. Use in Synthesis and Miscellaneous Applications

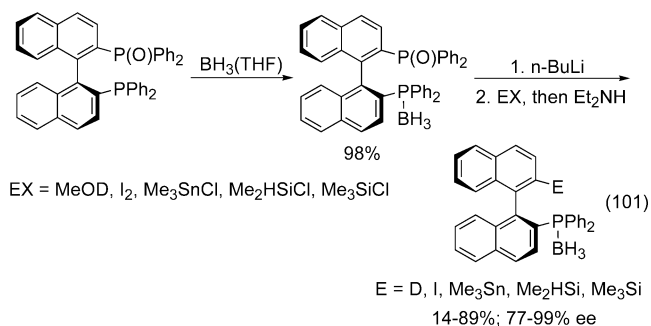
The Wittig–Horner-type reaction of dppeO with a variety of aldehydes has been reported<sup>114</sup> to give vinylphosphines in 48–69% yield (eq 100).



R = 4-XC<sub>6</sub>H<sub>4</sub> (X = H, Me, Me<sub>2</sub>N, Cl, CN, NO<sub>2</sub>), 2-MeOC<sub>6</sub>H<sub>4</sub>, PhCH=CH, 2-thienyl, 2-pyridyl

Hayashi et al.<sup>209</sup> have used BINAP(O) for the synthesis of optically active 2'-substituted 2-diphenylphosphino-1,1'-binaphthyls, as outlined in eq 101. The BINAP(O) starting material should be used in the form of its BH<sub>3</sub> complex, or otherwise complete racemization would occur. For instance, the reaction of (*S*)-BINAP(O) with *n*-BuLi, followed by quenching with MeOD, produced 2-deuterio-2'-diphenylphosphino-1,1'-binaphthyl in 87% yield and 0% ee. In contrast, when the experiment was repeated using (*S*)-BINAP(O)·BH<sub>3</sub>, the reaction occurred with retention of the axial chirality to produce the same deuterated phosphine in 89% yield and >99% ee.<sup>209</sup>

Sekar and Nishiyama<sup>210</sup> have used BINAP(O) to



obtain valuable mechanistic information on their nonenzymatic kinetic resolution of secondary alcohols using *N*-chlorosuccinimide in the presence of BINAP. It has been reported that dppeO and (Ph<sub>2</sub>PCH<sub>2</sub>-CH<sub>2</sub>)<sub>2</sub>P(O)Ph can be useful in spectrophotometric determination of Pd and Rh in the presence of Pt, Ir, Cu, Ni, and Co.<sup>211</sup> Interestingly, dppeO was among

the 16 compounds (selected from a database of 20 000 organic molecules) that provided the best fit for docking into the hydrophobic pocket of the HIV-1 envelope glycoprotein gp-41 core.<sup>212</sup> Experiments with the 16 candidates identified only two compounds (neither one was dppeO) which did exhibit inhibitory activity toward HIV-1 infection due to changes caused in the structure of the gp-41 core.

### 5. Most Recent Progress

Since completion of our work on this article (summer 2003), a number of interesting reports on BPMOs have appeared. A brief summary of these most recent publications is presented below.

Thomas and Süß-Fink<sup>213</sup> have reviewed ligand effects in the Monsanto acetic acid process, emphasizing the exceptional catalytic activity of the Rh–dppeO system (see section 4.1.2.). In their very recent review article on chiral poisoning and asymmetric activation, Faller, Lavoie, and Parr<sup>214</sup> discuss, among other aspects, the enantioselective Diels–Alder reactions catalyzed by the chiral Ru–BINAP(O) complexes (section 4.1.9.).

The low yield of BINAP(O) (21%) from the oxidation of BINAP with an oxaziridine<sup>215</sup> once again confirmed the fact that conventional oxidations of bidentate phosphines cannot be selective toward the mono-oxides, even when conducted at a low temperature. Both the Pt- and Mo-mediated oxidations of dppe<sup>216</sup> and dppm,<sup>217</sup> respectively, appeared to be poorly selective, giving rise to the corresponding BPMOs in low yield. The molecular and crystal structure of dppbO has been determined.<sup>218</sup> A novel P-chiral BPMO has been synthesized via the Pd-promoted cycloaddition reaction of 1-phenyl-3,4-dimethylphosphole with diphenyl(vinyl)phosphine oxide.<sup>219</sup> The ligand, 5-diphenylphosphinyl-2,3-dimethyl-7-phenyl-7-phospha-bicyclo[2.2.1]hept-2-ene, was liberated from its structurally characterized palladium complex in an enantiomerically pure (*R*<sub>p</sub>) form. It reacted with [Me<sub>2</sub>SAuCl] to produce a gold complex, whose structure was established by X-ray diffraction.<sup>219</sup> Another new gold complex, [AuBr(dppmO-κ<sup>1</sup>-P)], has been prepared from dppmO and [Bu<sub>4</sub>N]<sup>+</sup>[AuBr<sub>2</sub>]<sup>−</sup> and structurally characterized (X-ray) as a 1:1 MeCN solvate.<sup>220</sup>

One more example<sup>221</sup> has been described recently of the stoichiometric Pd(II)/P(III) → Pd(0)/P(V) redox process (see section 2.2.) leading to dppeO from Pd(OAc)<sub>2</sub> and dppe. Complexes of the type [M(CH<sub>3</sub>)(DPPEPM-*P,P,P*)]<sup>+</sup>Cl<sup>−</sup>, where M = Pd, Pt and DPPEPM = bis[(diphenylphosphinoethyl)phenylphosphino]methane, have been found to undergo air oxidation of the only uncoordinated P atom.<sup>222</sup> The structure of the products, [M(CH<sub>3</sub>)(DPPEPM(O)-*P,P,P*)]<sup>+</sup>Cl<sup>−</sup>, was established by X-ray analysis for the platinum derivative. An interesting complex, [(η<sup>6</sup>:η<sup>1</sup>-L-*P*)Ru(dppmO-κ<sup>2</sup>-*P,O*)]<sup>2+</sup>(SbF<sub>6</sub><sup>−</sup>)<sub>2</sub> has been prepared for L = 2-dicyclohexylphosphino-2'-(*N,N*-dimethylamino)biphenyl from [(η<sup>6</sup>:η<sup>1</sup>-L-*P*)RuCl<sub>2</sub>], dppmO, and AgSbF<sub>6</sub> and isolated as one diastereomer.<sup>223</sup>

Cacatian and Fuchs<sup>224</sup> have recently developed an efficient method for the synthesis of allylphosphine oxides and boranes, based on the Horner reaction of

dppeO with various aldehydes. This work demonstrates a novel, efficient approach to the preparation of allylphosphine oxides, important precursors to conjugated polyenes.<sup>224</sup>

Most recently, Charette and co-workers<sup>225</sup> reported the synthesis of a new chiral BPMO–Me-DuPHOS monoxide, via the reaction of Me-DuPHOS with 1 equiv of Me<sub>2</sub>S·BH<sub>3</sub>, followed by oxidation with H<sub>2</sub>O<sub>2</sub> and deprotection with DABCO. The new chiral BPMO was successfully used for the highly enantioselective Cu(OTf)<sub>2</sub>-catalyzed addition of R<sub>2</sub>Zn to *N*-phosphinoylimines in up to 98% yield and 98% ee. The resulting α-chiral amines are important syntheses for the preparation of chiral drugs.<sup>225</sup>

### 6. Outlook

As can be seen from the above, BPMO ligands have demonstrated very interesting and often unique coordination properties, as well as the ability to form remarkably efficient and selective metal–complex catalysts. These exciting findings have resulted from the great effort of the few industrial and academic research groups that took pains to prepare the then hardly accessible BPMOs in order to study them. Meanwhile, a larger group of researchers kept observing the formation, sometimes targeted but more often accidental (section 3), of various BPMO–transition metal complexes emerging from oxidation of coordinated bidentate phosphines. As a result, sufficient information was accrued by the mid-1990s to recognize the value of BPMOs and realize their potential in catalysis and inorganic/materials synthesis. However, progress in the field remained sluggish due to the lack of efficient, high-yield synthetic routes to BPMO ligands. Now that a solution to this problem was recently found (section 2.2) and several BPMOs are commercially available,<sup>226</sup> one might expect the field to gain momentum, the first signs of which have begun to emerge.

Today, chemical research is strongly oriented toward the development of marketable products. This is true not only for the industrial institutions that are to generate revenue by definition but also for modern academia, where basic research is (alas) often dominated by profit-driven, applied science. Considering this current trend and the already realized potential of BPMOs, these compounds can be attractive for both industrial and academic research with high probability for practical outcome. Hence, it is conceivable that the field may be developing quite rapidly in the near future, though making predictions should be left to a fortuneteller rather than to a scientist.

### 7. Abbreviations

Ac	acetyl
acac	acetylacetonate
acac-F <sub>6</sub>	1,1,1,5,5,5-hexafluoroacetylacetonate
acacH-F <sub>6</sub>	1,1,1,5,5,5-hexafluoroacetylacetone
Ar	aryl
BINAP	2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
BINAP(O)	2,2'-bis(diphenylphosphino)-1,1'-binaphthyl mono-oxide

BPMO	bis-phosphine mono-oxide
bpy	2,2'-bipyridyl
Bu	butyl
chiraphos	2,3-bis(diphenylphosphino)butane
chiraphos(O)	2,3-bis(diphenylphosphino)butane mono-oxide
COD	1,5-cyclooctadiene
COT	1,3,5,7-cyclooctatetraene
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
dba	dibenzylideneacetone
depe	1,2-bis(diethylphosphino)ethane
depeO	1,2-bis(diethylphosphino)ethane mono-oxide
dmpe	1,2-bis(dimethylphosphino)ethane
dpmeO	1,2-bis(dimethylphosphino)ethane mono-oxide
dmpm	bis(dimethylphosphino)methane
dmpmO	bis(dimethylphosphino)methane mono-oxide
dppb	1,4-bis(diphenylphosphino)butane
dppbO	1,4-bis(diphenylphosphino)butane mono-oxide
dppbz	1,2-bis(diphenylphosphino)benzene
dppbzO	1,2-bis(diphenylphosphino)benzene mono-oxide
dppe	1,2-bis(diphenylphosphino)ethane
dppeO	1,2-bis(diphenylphosphino)ethane mono-oxide
dppeS	1,2-bis(diphenylphosphino)ethane mono-sulfide
dppfc	1,1'-bis(diphenylphosphino)ferrocene
dppfcO	1,1'-bis(diphenylphosphino)ferrocene mono-oxide
dppm	bis(diphenylphosphino)methane
dppmO	bis(diphenylphosphino)methane mono-oxide
dppmS	bis(diphenylphosphino)methane mono-sulfide
dppmSe	bis(diphenylphosphino)methane mono-selenide
dppp	1,3-bis(diphenylphosphino)propane
dpppO	1,3-bis(diphenylphosphino)propane mono-oxide
dtolpmO	bis( <i>p</i> -tolylphosphino)methane mono-oxide
Et	ethyl
Me	methyl
Me-DuPHOS	1,2-bis(2,5-dimethylphospholano)benzene
NBD	norbornadiene
Ph	phenyl
phen	1,10-phenanthroline
Pr	propyl
Tol	<i>p</i> -tolyl
Tol-BINAP	2,2'-bis( <i>p</i> -tolylphosphino)-1,1'-binaphthyl
Tol-BINAP(O)	2,2'-bis( <i>p</i> -tolylphosphino)-1,1'-binaphthyl mono-oxide
TfO	triflate (trifluoromethanesulfonate)
TosO	tosylate ( <i>p</i> -toluenesulfonate)
THF	tetrahydrofuran
triphos	1,1,1-tris(diphenylphosphinomethyl)-ethane
triphosO	1,1,1-tris(diphenylphosphinomethyl)-ethane mono-oxide
triphosO <sub>2</sub>	1,1,1-tris(diphenylphosphinomethyl)-ethane dioxide

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