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COORDINATION CHEMISTRY AND CATALYSIS WITH HEMILABILE OXYGEN–PHOSPHORUS LIGANDS

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CONTENTS

ABBREVIATIONS

Ac	acetyl
COD	1,5-cyclo-octadiene
COE	cyclo-octene
dmba	*N,N*-dimethylbenzylamine

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Fc	ferrocenyl, $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$
mc	macrocycle
8-mq	8-methylquinoline
$P\sim O$	η^1-bound O,P ligand (through phosphorus)
$\overset{\frown}{P\quad O}$	η^2-bound O,P ligand (through phosphorus and oxygen)
TMF	tetrahydrofuran
TMEDA	tetramethylethylenediamine

A. INTRODUCTION

The complexation of substrates by organotransition metal compounds represents an important step in the course of catalytically operating processes. In this regard, labile solvent complexes are suitable which, by facile elimination of solvent molecules, are transformed into reactive intermediates with an empty coordination site [1,2]. The starting material is thus readily incorporated into the coordination sphere of the catalytically active metal, where it may subsequently undergo further reactions. The solvents in question are usually ethers or ketones. In many syntheses catalyzed by transition metals, tertiary phosphines are used as controlling ligands to increase the selectivity of the desired product.

Polydentate ligands containing pairs of phosphorus and oxygen donor atoms meet both of the requirements mentioned above.

This new type of ligand is currently of considerable interest, in particular with respect to the development of novel homogeneous catalysts. Such O,P chelating ligands exhibit an unusual selectivity enhancing effect in the nickel-catalyzed oligomerization and polymerization of ethene [3] and in the carbonylation and hydrocarbonylation of methanol to oxygen-containing C_2-products such as acetic acid [4,5], acetaldehyde [5,6], ethanol [7], or ethylidene diacetate [8]. Moreover, they have also been used in stereoselective hydrogenations [9], hydrosilylations [10] and hydroformylations [11].

These O,P ligands are provided with tertiary phosphorus atoms, which are responsible for a close contact to the central atom and also with ketonic, alcoholic carboxylic or oxidic oxygen atoms, or oxygen atoms incorporated in open-chain or cyclic ether moieties. These oxygen donors may be regarded as intramolecular solvent molecules forming only weak metal–oxygen bonds which may be cleaved reversibly. As a result of this 'opening and closing mechanism' [12] empty coordination sites are made available when needed in the course of the catalytic cycles without separation of the oxygen donors from the complex fragment. For this reason, O,P ligands are also called hemilabile [13] or hybrid ligands [14]. An additional advantage of O,P ligands is their ability to increase the electron density at the coordination centre by direct metal–oxygen interaction. In this way the oxidative addition of a substrate as well as the reductive elimination of the product is facilitated.

In this review the preparation and properties of hemilabile O,P ligands and some of their complexes with catalytically relevant transition metals are described. Also, their application to important types of catalytic processes, namely the oligomerization of olefins, the carbonylation of methanol and hydrogenations is presented.

B. CLASSIFICATION OF O,P LIGANDS

(i) Ether-phosphines and furylphosphines

Ether-phosphines are one of the most extensively studied class of oxygen-containing functionalized phosphines. A survey of widely used ether-phosphines is given in Table 1.

In many cases the oxygen donors are part of simple acyclic [13,15] or cyclic [7,16] ether moieties such as in **I–III**. Related to these compounds are the various phosphines endowed with a polyether chain [17–25]. These potentially multidentate ligands, e.g. **XI–XIII** have also been shown to provide phase-transfer properties [25].

Of great importance is the appearance of chirality in some ether-phosphines due to asymmetric carbon or phosphorus atoms. Among these are ligands used in enantioselective catalysis [9]. Examples are the *o*-phosphinoanisols PAMP (**VId**), CAMP (**VIe**) [26] and DIPAMP (**X**) [25], as well as some derivatives of 1,3-dioxolane, viz. DIOP (**XVa**) [28], PAMOP (**XVb**) [29] and DIOXOP (**XIV**) [30,31]. Another synthetic approach to chiral ligands is the phosphination of sugars. Such a product is TREDIP (**XVI**), which is obtained from trehalose [32].

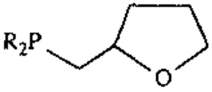
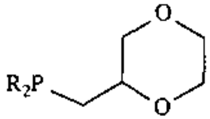
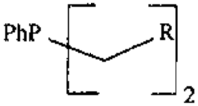
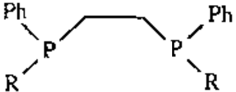
If more than one centre of chirality is present in the molecule, diastereoisomers are formed. In certain cases, such as **IVb,c**, pseudoasymmetry [33] at the phosphorus atom is expected. For this reason **IVb** and **IVc** each form two *meso* configurations and one pair of enantiomers, giving rise to three $^{31}P\{^1H\}$ NMR signals [34].

It is noteworthy that compounds containing dioxolane rings are readily hydrolyzed in acidic solutions and are therefore not applicable under such conditions [4,35].

Lately, O,P-containing macrocycles have been prepared and investigated. Among these are crown-ethers which contain an exocyclic phosphine group [36–40]. Such systems are capable of binding transition metals via the phosphorus atom of the side-arm, as well as alkali metal or alkali-earth cations via the oxygen atoms within the cycle. Due to their Lewis acidity the latter cations are known to accelerate alkyl migration to carbon monoxide

TABLE 1

Structures and syntheses of ether-phosphines and furylphosphines

Basic Structures	Compounds	Syntheses	Ref.
 **I**	R: Ph R': Me **a** Cy Me **b** Cy ^{i}Pr **c** Me Me **d** ^{n}Pr Me **e**	$Ph_2PLi + ClCH_2CH_2OMe \longrightarrow$ **Ia**	15,48
 **II**	R: Ph **a** Cy **b** ^{n}Pr **c** ^{i}Pr **d** Me **e**	$Ph_2PLi + ClCH_2C_4H_7O \longrightarrow$ **IIa**	34
 **III**	R: Ph **a** Mes **b** Cy **c** Me **d**	$Ph_2PLi + ClCH_2C_4H_7O_2 \longrightarrow$ **IIIa**	5,16
 **IV**	R: CH_2OMe **a** C_4H_7O **b** $C_4H_7O_2$ **c**	$PhPLi_2 + 2\ ClCH_2CH_2OMe \longrightarrow$ **IVa**	6, 15
 **V**	R: CH_2CH_2OMe **a** $CH_2C_4H_7O$ **b** $CH_2C_4H_7O_2$ **c**	$PhP(H)CH_2CH_2OMe \xrightarrow[2.\ Cl(CH_2)_2Cl]{1.\ Na\ /\ liq\ NH_3}$ **Va**	6

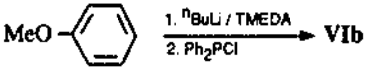
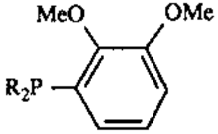
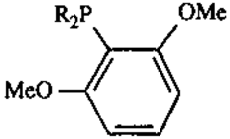
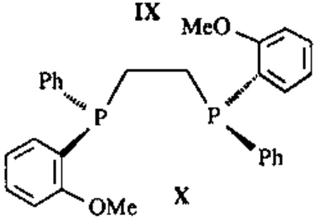
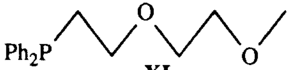
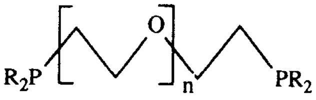
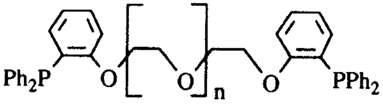
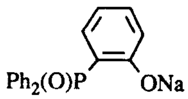
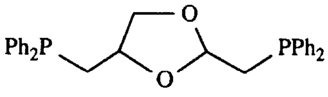
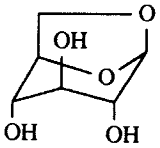
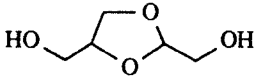
 **VI**	R,R': Me **a** Ph **b** ᵗBu **c** R: Me; R': Ph **d** Me Cy **e**	 $\mathrm{Me(Ph)PCl} \xrightarrow[\text{2. o-(MeO)C}_6\text{H}_4\text{Li}]{\text{1. cinchonine}} \mathbf{VId}$	49-52 53
 **VII**			54, 55
 **VIII**	R: Ph **a** ᵗBu **b**	as above	56
 **IX**	R: Ph **a** ᵗBu **b**	as above	56
 **X**		$\mathrm{Me(Ph)P(O)OH} \xrightarrow[\text{3. sep. of R}_\text{P}\text{ isomer}]{\text{1. SOCl}_2\text{; 2. l-menthol}} \mathrm{Me(Ph)P(O)(O\text{-}men)}$ $\xrightarrow{o\text{-(MeO)C}_6\text{H}_4\text{MgBr}} \mathrm{Me(Ph)P(O)(}o\text{-}\mathrm{MeOC_6H_4)} \xrightarrow[\text{2. HSiCl}_3\text{ / NBu}_3]{\text{1. LiN}^i\text{Pr}_2\text{ / Cu}} \mathbf{X}$	27

TABLE 1 (continued)

Basic Structures	Compounds	Syntheses	Ref.
 **XI**		$HO(CH_2CH_2)_2Me \xrightarrow[2.\ Ph_2PLi]{1.\ MeSO_2Cl}$ **XI**	24
 **XII**	n: 1; R: Ph **a** ^{t}Bu **b** n: 2; R: Ph **c** ^{t}Bu **d**	$ClCH_2CH_2OCH_2CH_2Cl \xrightarrow{2\ Ph_2PLi}$ **XIIa**	17, 19, 22
 **XIII**	n: 1 **a** 2 **b**	 $\xrightarrow[2.\ Si_2Cl_6]{1.\ (TsOCH_2CH_2)_2O}$ **XIIIa**	18
 **XIV**		 $\xrightarrow[2.\ NaBH_4]{1.\ NaIO_4}$  $\xrightarrow[2.\ Ph_2PLi]{1.\ TsCl}$ **XIV**	30, 31, 57

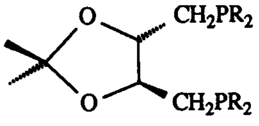
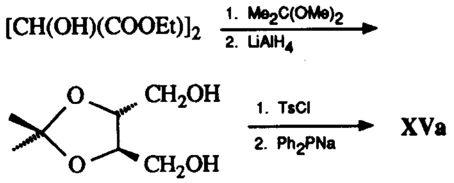
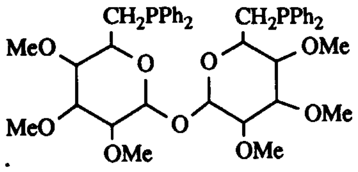
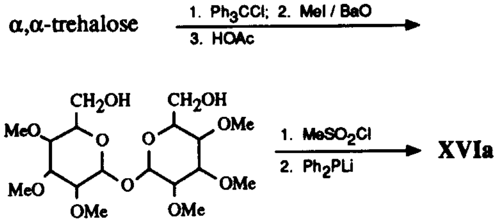
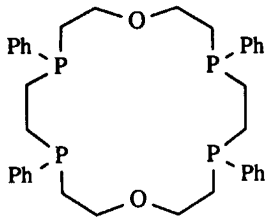
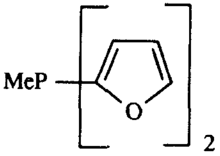
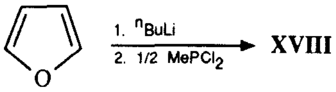
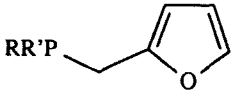
 **XV**	R: Ph (DIOP) **a** *o*-(MeO)C_6H_4 **b**	 	28, 29, 58
 **XVI**	α,α-TREDIP **a** β,β-TREDIP **b**	 	32, 59
 **XVII**		$Li_2[(CH_2PPh)_2]$ + 2 $O(CH_2CH_2Cl)_2$ $\longrightarrow$ **XVII**	42

TABLE 1 (continued)

Basic Structures	Compounds	Syntheses	Ref.
 **XVIII**			34
 **XIX**	R, R': Ph **a** R: Me; R': $CH_2C_4H_3O$ **b**	$Ph_2PSiMe_3 \xrightarrow[2.\ LiAlH_4]{1.\ 2\ BrCH_2C_4H_3O}$ **XIXa**	47

coordinated to the transition metal [38]. Both kinds of metal are thus kept in close proximity for interaction.

A second type of macrocycle consists of oxygen and phosphorus atoms which are both part of the macrocyclic framework [41–46]. This forces O and P contact with the transition metal within the cavity in unusual geometries. As an example, the 18-membered ring **XVII** with two oxygen and four phosphorus atoms connected by C_2H_2 groups is depicted in Table 1. All five possible diastereoisomers, abbreviated as α–ε, are interconvertible and have been isolated [41,42]. They are distinguished by their characteristic set of configurations at the phosphorus atoms and the following assignments have been made:

α-isomer: (4RS, 7RS, 13RS, 16SR),
β-isomer: (4RS, 7RS, 13SR, 16SR),
γ-isomer: (4RS, 7SR, 13SR, 16RS),
δ-isomer: (4RS, 7RS, 13RS, 16RS),
ε-isomer: (4RS, 7SR, 13RS, 16SR).

The furylphosphines **XVIII** and **XIX** represent the group of heteroarylphosphines [34,47]. In this case, the oxygen atom partly contributes one lone pair to the aromatic sextet, leading to a marked reduction of its donor ability.

(ii) β-Ketophosphines (phosphinoenolates) and α-ketoylids

Another way of realizing oxygen donor sites is to provide carbonyl functions in the form of ketones or aldehydes. In the case of β-ketophosphines of the type $R_2PCH_2C(O)R'$ (**XX**), stable five-membered chelate rings can be formed by complexation of a metal species. The structures and syntheses of some β-ketophosphines are outlined in Table 2.

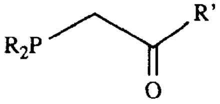
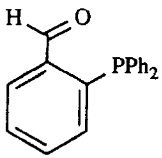
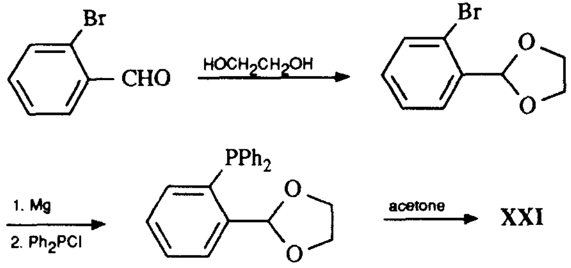
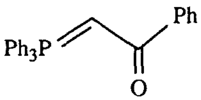
According to expectations, these compounds are capable of enolization promoted by strong electron-withdrawing substituents R′. Deprotonation by a base (e.g. TlOEt [59] or NaH) or reaction with Ni(0) complexes [61] leads to the corresponding phosphinoenolates which act as bidentate O,P ligands. The neutral ketophosphines have been shown to function either as unidentate or as bidentate ligands.

A novel type of ligand is represented by ferrocenyl-substituted ketophosphines [62] such as $Ph_2PCH_2C(O)(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$. They combine O,P chelating and exceptional electron transfer properties, which give rise to interesting applications in coordination chemistry and catalysis.

In contrast to the tervalent phosphorus compounds, α-ketoylids (e.g. **XXII**) must be described as a resonance hybrid involving pentacovalent (phosphorane form) as well as tetracovalent phosphorus [63]:

TABLE 2

Structures and syntheses of β-ketophosphines and α-ketoylids

Basic Structures	Compounds	Syntheses	Ref.
 **XX**	R, R': Ph **a** R: Ph; R': Me **b** Ph Fc **c** ^{t}Bu Ph **d** ^{t}Bu ^{t}Bu **e**	$Ph_2PCl \xrightarrow{LiC\equiv CPh} Ph_2PC\equiv CPh \xrightarrow{H_2O}$ **XXa**	60
		$MeC(O)Ph \xrightarrow[2.\ Ph_2PCl]{1.\ LiN^iPr_2}$ **XXa**	62, 66
		$MeC(O)CH_2Br \xrightarrow[2.\ NaOH]{1.\ Ph_2PSiMe_3}$ **XXb**	67
		$BrCH_2C(O)^tBu \xrightarrow[2.\ NaOAc]{1.\ HP^tBu_2}$ **XXe**	68
 **XXI**		 	69, 70
 **XXII**		$Ph\text{-}C(O)\text{-}CH_2Br \xrightarrow[2.\ Na_2CO_3]{1.\ PPh_3}$ **XXII**	63

$$R_3P{=}CH{-}C(R'){=}O \leftrightarrow R_3\overset{+}{P}{-}\overset{-}{C}H{-}C(R'){=}O \leftrightarrow R_3\overset{+}{P}{-}CH{=}C(R'){-}\overset{-}{O}$$

As there is no lone pair available at the P atom, a direct coordination of the phosphorane is only conceivable via the ylidic carbon atom [64], which is predominantly the site of the HOMO orbital. This can be observed by a strong shift of its ^{13}C NMR signal towards higher field. However, on reaction of $Ph_3P{=}CHC(O)Ph$ with a variety of Ni(0) complexes, a cleavage of one P–Ph bond occurs, leading also to coordination through phosphorus [65].

(iii) Phosphinocarboxylates

Phosphinocarboxylates, summarized in Table 3, are used in the form of carboxylic esters (**XXIII**), including their corresponding carbanions, or in the form of the free acids (**XXIV**) and their salts. In the case of the anions, bidentate behaviour is observed, either in a chelating or bridging mode, whereas the neutral ligands can also act unidentally through the phosphorus atom [71]. Exclusive coordination of the carboxylato group could not be proved to date but might occur in solution.

Characteristic of the free phosphinocarboxylic acids is the dependence of the complexation properties on the conditions for dissociation, mainly on the solvent polarity and on the pH value. The hydrophilicity is increased with the number of carboxylic acid moieties in the ligand molecule. In this way, the investigation of the coordination chemistry of O,P ligands is also feasible in aqueous solution [72].

(iv) Phosphinoalcohols and phosphinophenols

Both phosphinoalcohols and phosphinophenols are easily deprotonated to the respective alkoxides and phenoxides. The acidity of the alcoholic proton in **XXV** depends on the substituents R and R′. Structural features along with synthetic methods of this class of O,P ligand are given in Table 4.

(v) Bisphosphine monoxides and α-phosphinosulphoxides

A number of profound studies, e.g. by McAuliffe et al. and Grim et al., have been carried out concerning the coordination chemistry of unsymmetrically P-substituted diphos ligands [81–84]. In the course of these investigations, many compounds of the type $R_2P(X)CHR''P(Y)R'_2$ have been synthesized, X and Y being an electron pair, oxygen, sulphur, selenium or CH_3^+. In this paper, attention should be drawn to the class of bisphosphine monoxides such as **XXVII** and **XXVIII**.

TABLE 3

Structures and syntheses of phosphinocarboxylates

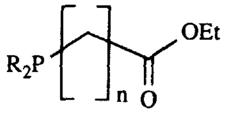
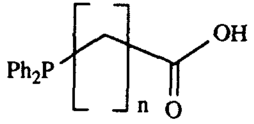
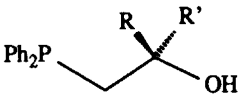
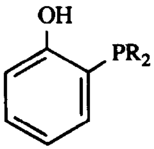
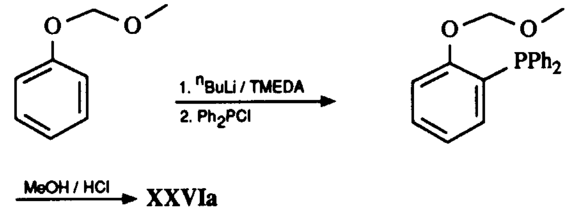
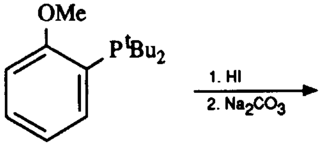
Basic Structures	Compounds	Syntheses	Ref.
 **XXIII**	n: 1; R: Ph **a**	$BrCH_2COOEt + NaPPh_2 \longrightarrow$ **XXIIIa**	73
	^tBu **b**		
	Et **c**	$Ph_2P(O)CH_2COOEt \xrightarrow{PhSiH_3}$ **XXIIIa**	74
	Cy **d**		
	n: 2; R: ^tBu **e**	$BrCH_2COOEt \xrightarrow[2.\ NaOAc]{1.\ ^tBu_2PH}$ **XXIIIb**	75
	n: 3; R: ^tBu **f**		
 **XXIV**	n: 1 **a**	$Ph_2PCH_2COOEt \xrightarrow[2.\ HCl]{1.\ NaOH}$ **XXIVa**	73
	n: 2 **b**		

TABLE 4

Structures and syntheses of phosphinoalcohols and phosphinophenols

Basic Structures	Compounds	Syntheses	Ref.
 **XXV**	R, R': H **a**	$Ph_2PLi + ClCH_2CMe_2OH \longrightarrow$ **XXVb**	76
	Me **b**	$Ph_2PMe \xrightarrow{^{n}BuLi\,/\,TMEDA} Ph_2PCH_2Li \xrightarrow[2.\ H_3O^+]{1.\ (CF_3)_2C{=}O}$ **XXVc**	77, 78
	CF_3 **c**		
	R: Me R': H **d**		
 **XXVI**	R: Ph **a** ^{t}Bu **b**		79
			80

α-Phosphinosulphoxides, which are closely related to the phosphine oxides mentioned above, should also be briefly presented. **XXIX** is a simple representative of this type of ligand, but also optically active compounds containing, for instance, the R-(+)-*p*-tolyl methyl sulphoxide moiety have been prepared [87].

α-Phosphinosulphoxides are prone to isomerization. Thus, $Ph_2PCH_2S(O)Ph$ (**XXIX**) is transformed into the corresponding phosphine oxide $Ph_2P(O)CH_2SPh$ upon treatment with a small amount of iodine.

Both bisphosphine monoxides and α-phosphinosulphoxides are capable of binding to a metal centre in a chelated manner, the oxidic oxygen being only loosely coordinated. The most important examples are given in Table 5.

C. COMPLEXES WITH O,P LIGANDS

An outstanding feature of hemilabile, multidentate O,P ligands is their capability of coordinating to a metal centre in either a η^1-mode through phosphorus, or in a η^2-mode through phosphorus and oxygen. In the following, $P\sim O$ designates the η^1-bound ligand and $P\frown O$ represents the chelating η^2-coordination.

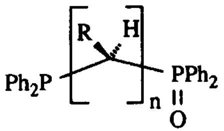
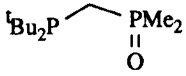
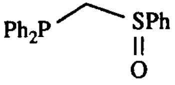
(i) Complexes of the chromium group

Although a large number of chromium, molybdenum and tungsten compounds with oxygen or phosphorus donor ligands have been described [88–90], complexes of these metals containing chelating O,P systems are rare. However, several complexes of Group VIB elements in different oxidation states with hard donor ligands have been synthesized or at least spectroscopically identified. Examples are compounds of the type MCl_3L_3 [91] and $(OC)_5ML$ (M = Cr, Mo, W) with L = amines, nitriles, ethers, ketones and even water [92,93]. $(OC)_5Cr(THF)$ has been isolated as single crystals and its structure established by X-ray crystallography [94]. This clearly demonstrates that O,P ligands will also be expected to form sufficiently stable complexes.

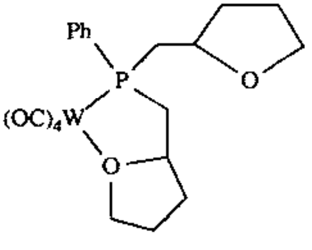
A very effective route to such systems uses complexes with weakly bound ligands, e.g. $(OC)_5M(THF)$ (M = Mo, W) as starting materials, which are easily accessible by UV irradiation of $M(CO)_6$ in THF [95]. Subsequent reaction of $(OC)_5W(THF)$ with the ether-phosphines **Ia–c** [15], **IIa**, **IVb** [7] and **XIXa,b** [96] leads to the respective pentacarbonyl(monophosphine)-tungsten complexes of the type $(OC)_5M(P\sim O)$ (**1**), e.g. $(OC)_5W(P\sim O)$ (**1a**, $P\sim O = Ph_2PCH_2C_4H_7O$, **IIa**). In the same way, $(OC)_5Mo(THF)$ and **IIa** or **IVb** give complexes which are analogous to the corresponding tungsten derivatives [7].

TABLE 5

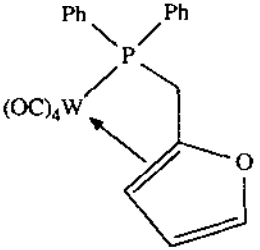
Structures and syntheses of bisphosphine monoxides and α-phosphinosulfoxides

Basic Structures	Compounds	Syntheses	Ref.
 **XXVII**	n: 1; R: H **a** ^{n}Pr **b** n: 2; R: H **c**	$Ph_2P(O)Me \xrightarrow{^{n}BuLi} Ph_2P(O)CH_2Li \xrightarrow{Ph_2PCl}$ **XXVIIa** $Ph_2P(CH_2)_2PPh_2 \xrightarrow[2.\ alkali]{1.\ PhCH_2Br}$ **XXVIIc**	83, 85
 **XXVIII**		as above	86
 **XXIX**		$PhS(O)Me \xrightarrow[2.\ Ph_2PCl]{1.\ MeLi}$ **XXIX**	87

The synthesis of the tetracarbonyl(monophosphine)metal compounds $(OC)_4M(P\frown O)$ (**2**) is performed by the photochemically induced elimination of CO from $(OC)_5M(P\sim O)$ (**1**). In this way, molybdenum and tungsten complexes have been prepared which contain the ligands **Ia–c**, **IIa**, **IVb** and **XIXa,b**. Examples are $(OC)_4W(P\frown O)$ (**2a**, $P\frown O = Ph_2PCH_2C_4H_7O$, **IIa**), $(OC)_4W(P\frown O)$ (**2b**, $P\frown O = PhP(CH_2C_4H_7O)_2$, **IVb**) and $(OC)_4W(P\frown O)$ (**2c**, $P\frown O = Ph_2PCH_2C_4H_3O$, **XIXa**).



2b



2c

2a,b are yellow, fairly air-stable compounds. They can be stored at room temperature for weeks whereas their molybdenum analogues are much more thermolabile. Even in less polar solvents such as chloroform and below −50°C, **2c** decomposes quickly.

The vacant coordination site generated by the elimination of a CO molecule is occupied by a second donor atom of the multidentate O,P ligand. Whereas the ether-phosphines **Ia–c**, **IIa** and **IVb** use their oxygen atom for chelation, **XIXa,b** coordinate in an η^2-mode through the π-system of the furane ring, which is obviously a better ligand than the oxygen atom incorporated in the heteroaromatic system [96].

The bidentate behaviour of the O,P ligand in the resulting complexes $(OC)_4M(P\frown O)$ (**2**) follows from a low-frequency shift of 40–60 cm^{-1} of the antisymmetric C_2O vibration of the ether moiety, which is observed in the IR spectrum if metal oxygen contact is present [7,15]. Along with this observation, further evidence is provided by ^{31}P NMR data. The shift of the ^{31}P resonance towards lower field is about 25–36 ppm greater than expected for exclusive M–P coordination. This effect is attributed to ring formation and strongly indicates the existence of a five-membered M–P–C–C–O heterocycle [97,98].

Due to the high σ-donor property of the bound oxygen atom, the π-backbonding to the remaining CO ligands is increased, which causes a strengthening of the M–C bonds. For this reason, further decarbonylation of **2b** or the related compounds with the formation of a second chelate ring cannot be achieved [7].

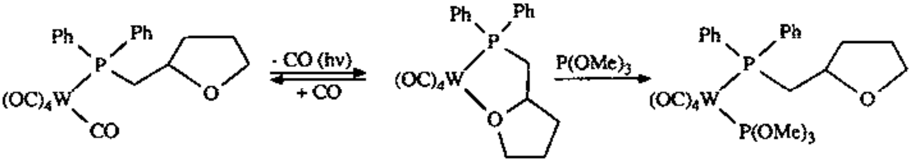
Type **2** bisphosphine monoxide complexes containing ligand **XXVIIb** have been reported [83]. These yellow (Cr, Mo) or orange (W) compounds are made by heating the appropriate metal hexacarbonyl in diethyleneglycol dimethyl ether with **XXVIIb** to 160°C.

The major characteristic of complexes containing hemilabile ligands is their ability to provide unoccupied coordination sites by cleavage of the labile metal–ligand bond. This formerly weakly bound donor atom can thus easily be displaced by a huge number of molecules with a slightly better capability of coordination to the complex fragment. Solvent molecules can also compete for a vacancy.

These substitutions are usually reversible and the leaving group, i.e. the oxygen-bearing side-arm, is still attached to the complex through the phosphorus atom, and therefore the oxygen donor is always in close proximity to the metal centre for re-coordination. This behaviour is designated as the 'opening and closing mechanism', which is typical of hemilabile ligands [12].

There are numerous examples demonstrating the operation of this mechanism in the course of reversible substitutions. Referring to Group VIB chemistry, this is clearly shown by the reactivity of O,P chelates with respect to ring-opening by small molecules such as CO.

As depicted in Scheme 1, the highly reactive molecule **2a** readily takes up carbon monoxide to form the pentacarbonyl species **1a**. This reaction can be reversed photochemically. Similarly, opening of the chelate ring can also be effected by $P(OMe)_3$ [7].



1a **2a**

Scheme 1. Demonstration of the opening and closing mechanism.

If $Mo(CO)_6$, which is known to undergo CO substitution more readily than its chromium or tungsten homologues, is refluxed with one mole of **IIa** in methylcyclohexane, CO is displaced yielding $(OC)_5Mo(P\sim O)$ (**1b**, $P\sim O = Ph_2PCH_2C_4H_7O$, **IIa**) [34]. The application of a 1:2 ratio under the same conditions affords pale yellow *trans*-$(OC)_4Mo(P\sim O)_2$ (**3a**, $P\sim O = Ph_2PCH_2C_4H_7O_2$, **IIa**) [7]. The corresponding *cis*-isomer **3b** can be obtained by displacement of norbornadiene from nor-$C_7H_8Mo(CO)_4$ by two moles of **IIa** at −20°C in diethyl ether. Likewise, nor-$C_7H_8Cr(CO)_4$ reacts with **XVIII** forming *trans*-$(OC)_4Cr(P\sim O)_2$ (**3c**, $P\sim O = MeP(C_4H_3O)_2$, **XVIII**). Its structure has been determined by X-ray crystallography [34] and shows anti-positions of the two methyl groups with respect to the P–Cr–P axis, as well as nearly perpendicular (88°) arrangement of the two furan rings at each phosphorus atom.

Another indication of a participation of the oxygen donor in the course of substitutions is the isomerization of *trans*-$(OC)_4Mo(P\sim O)_2$ (**3a**, $P\sim O = Ph_2PCH_2C_4H_7O$, **IIa**) into its *cis*-isomer (**3b**) which is induced by UV-light [7]. It was proved that $(OC)_4Mo(P\frown O)$ is the intermediate which is formed from **3a** by phosphine dissociation. Re-coordination occurs in the *cis* position by cleavage of the Mo–O bond to give **3b**.

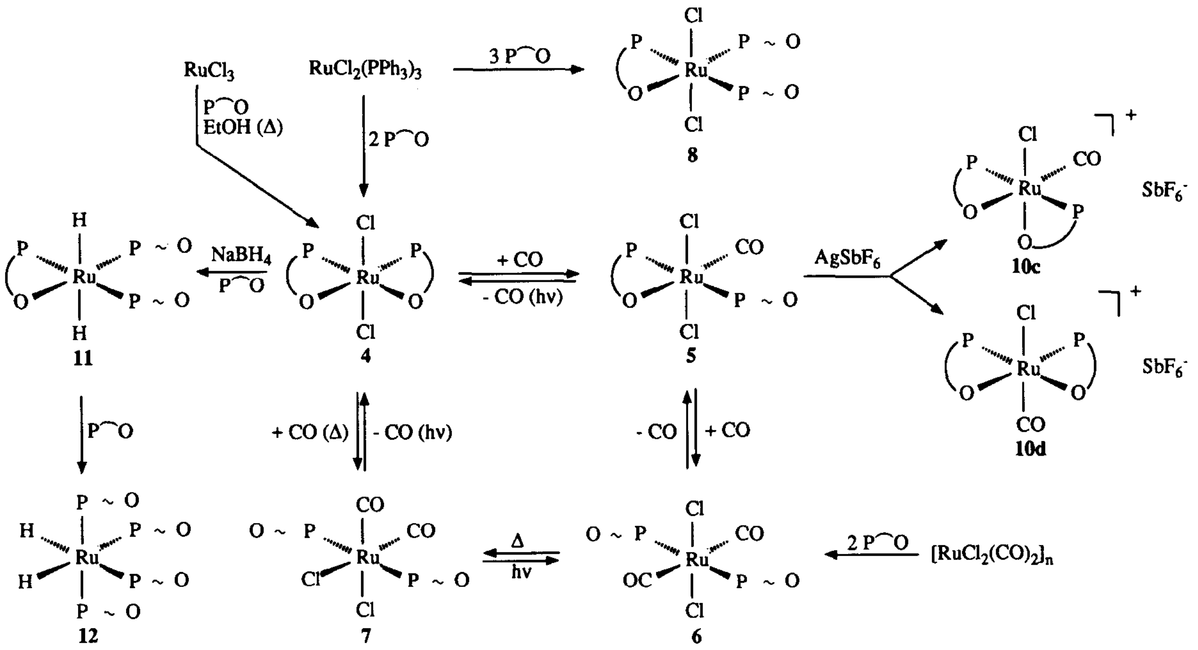
(ii) Ruthenium complexes

Due to the preferred coordination number of six, ruthenium complexes are expected to give rise to a great number of isomeric compounds. Especially if hemilabile, multidentate ligands are present, the stereochemical situation becomes rather complicated. This explains why many different fundamental structural types of ruthenium complexes with O,P ligands are known. Scheme 2 gives a survey of the most important types together with their synthetic relationships.

A convenient synthetic route to compounds of the type *trans,cis*-$RuCl_2(P\frown O)_2$ (**4**) is to reflux a solution of the commercially available $RuCl_3 \cdot 3H_2O$ in ethanol or 2-methoxyethanol with a slight stoichiometric excess of O,P ligand [13,99]. The ligand and the solvent used are crucial factors since at least the latter participates in the reduction of ruthenium(III) to ruthenium(II). In spite of the applicability of this method in conjunction with a variety of ether-phosphines, e.g. **Ia,b**, **IIa,b** [99] and **VIb** [13], and also with diphenylphosphinobenzaldehyde (**XXI**) [100], it fails in the case of the dioxanyl-containing ligand **IIIa** [101] as well as in the case of more basic phosphines such as **Id**, **IIe** and **IIId**. However, the corresponding type **4** compounds are obtained from $RuCl_2(PPh_3)_3$ by substitution of PPh_3 with the desired ligand. The scope of this latter reaction is quite large and can also be extended to the preparation of $RuCl_2(P\frown O)(P\sim O)_2$ (**8**) by using three equivalents of O,P ligand [102].

Complexes of type **4** are remarkably oxygen and heat stable. Their red colour is surprising since most other hexacoordinate Ru(II) phosphine compounds are colourless or yellow. Oxidation of **4b** is performed electrochemically or with $NOBF_4$, yielding red-brown $[RuCl_2(P\frown O)_2]BF_4$ [13].

The structures of **4a,b** are very similar and have been determined by X-ray diffraction [13,99]. The two coplanar chelate rings with bite angles of 83° (**4a**) and 78–79° (**4b**) exhibits *cis* oxygen and phosphorus atoms. The *trans*-configurated chloride ligands are bent towards the coordinated oxygen atoms and away from the phosphorus atoms in order to avoid steric interactions with the phenyl groups. Characteristic of these compounds are



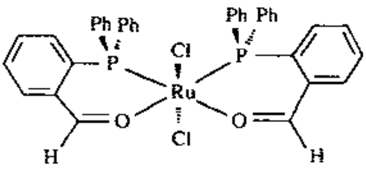
P⌒O	Ia	VIb	IIa	IIb
Complex	a	b	c	d

Scheme 2. Ruthenium(II) complexes and their synthetic relationships.

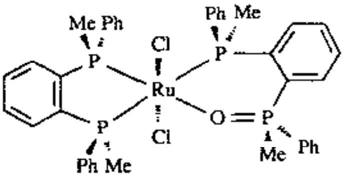
the unusually short Ru–P distances of 221–222 pm. Such a shortening is expected if the ligand *trans* to the phosphorus atom competes only to a minor extent for the electron density available at the ruthenium centre. This would result in an enhancement of the π-backbonding to the phosphorus and therefore in a strengthening of the Ru–P bond. In the present case, this situation is achieved by the very low *trans* influence of the ether oxygen atoms as well as by the distortion of the octahedral geometry. As far as the latter argument is concerned, it should be mentioned that complexes such as $RuH(OAc)(PPh_3)_3$ [103,104] have been regarded as quasi five-coordinate with the chelating acetate ligand occupying only one coordination site. The resulting configuration would then resemble distorted square pyramidal complexes like $RuCl_2(PPh_3)_3$ or $RuHCl(PPh_3)_3$ with comparably short $Ru{-}P_{(apical)}$ distances of 223 and 220 pm, respectively.

The Ru–O distances in **4a** (226.2 and 226.5 pm) and in **4b** (229.9 and 225.7 pm) are longer than the sum of the covalent radii. This indicates a rather weak Ru–O interaction. An extremely long Ru–O bond of 258 pm has been reported for $RuCl(Me)(COD)[P(o\text{-}MeOC_6H_4)_3]_3$ [105].

A bisaldehyde complex (**4e**) is obtained from $RuCl_3$ and **XXI** as deep purple needles [100]. At room temperature, this compound is remarkably inert, and Ru–O bond rupture is not accomplished with CO, dppe or pyridine.



4e



9

The diphos ligand *ortho*-phenylenebis[methyl(phenyl)phosphine] and its coordination chemistry has been extensively studied by Roberts and Wild, especially in the light of stereochemistry [106]. Upon reaction of this ligand with $RuCl_3$ in the presence of formaldehyde, the bisphosphine monoxide complex **9** is obtained as a minor product [107]. In this compound, the Ru–P bond with phosphorus *trans* to oxygen is considerably shorter (222 pm) than the other two Ru–P bonds, which is in keeping with a weak Ru–O contact.

The complexes *trans,cis*-$RuCl_2(P{}^\frown O)_2$ (**4**), except for the above-mentioned aldehyde complex, which is inert at room temperature, take up carbon monoxide to give the respective monocarbonyl species $RuCl_2(CO)(P{}^\frown O)(P\sim O)$ (**5**) and, after prolonged bubbling of CO through the reaction solution, *all-trans*-$RuCl_2(CO)_2(P\sim O)_2$ (**6**) is obtained [13,99], the formation of which is kinetically favoured over the formation of the thermodynamically more stable *cis,cis,trans*-$RuCl_2(CO)_2(P\sim O)_2$ (**7**). Another synthetic route to *all-trans*-$RuCl_2(CO)_2(P\sim O)_2$ (**6**) is the reaction of the desired phosphine with the polymeric ruthenium carbonyl-chloride $[RuCl_2(CO)_2]_n$ at ambient temperature. The latter compound is prepared by passing CO through a refluxing solution of $RuCl_3$ in ethanol or 2-methoxyethanol.

As for the monocarbonyl species **5b**, Jeffrey and Rauchfuss [13] suggested the two phosphines to be mutually *trans*, as corroborated by the X-ray structure of the analogous complex **5a** [99].

Compounds of types **4**–**7** can be mutually interconverted according to the reaction cycle depicted in Scheme 2. It has been demonstrated that, at least in the case of the ether-phosphines **Ia** and **IIa** [99], all steps can be reversed either by passing CO through the reaction solution, by heating, or by irradiation. It is noteworthy that compounds of the type *cis,cis,trans*-$RuCl_2(CO)_2(P\sim O)_2$ (**7**) must be activated photochemically due to their high thermodynamic stability. UV photolysis, however, causes both CO loss with the formation of **4** or **5** and isomerization to the *all-trans* dicarbonyl compounds **6**.

Isomerization processes in ruthenium complexes with conventional alkyl and aryl phosphines have been under investigation [108–110]. It has been pointed out that pentacoordinate intermediates are involved in such rearrangements.

Starting with the monocarbonyl compounds **5**, the ether moiety of the monodentate phosphine binds to the metal if a vacant coordination site is provided, e.g. by chloride abstraction with $AgSbF_6$. The cationic species $[RuCl(CO)(P\frown O)_2]^+$ (**10**), which are obtained in this manner, exhibit ligand-dependent structural features, as has been proved by means of ^{31}P NMR spectroscopy [111]. Thus, in the case of **10d** ($P\frown O = Cy_2PCH_2C_4H_7O$, **IIb**) both in the solid state and in solution, the ether oxygens are coordinated and the phosphorus atoms are in a mutual *cis* position. On the other hand, **10c**, which is formed with $Ph_2PCH_2C_4H_7O$ (**IIa**), contains *trans* phosphorus atoms, and in solution species with only one Ru–O contact could be detected.

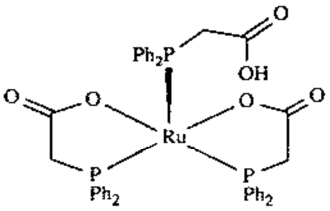
By analogy with CO, ^{t}BuNC reacts with **4b** by successive opening of the two chelate rings, eventually affording yellow *all-trans*-$RuCl_2(^tBuNC)_2(P\sim O)_2$ [13]. This reaction has been monitored by means of ^1H NMR spectroscopy, whereby the intermediate $RuCl_2(^tBuNC)(P\frown O)(P\sim O)$ could be identified. Similarly, **5b** reacts with ^{t}BuNC to give the mixed isocyanide–carbonyl complex *all-trans*-$RuCl_2(^tBuNC)(CO)(P\sim O)_2$.

The cleavage of the Ru–O bond in O,P chelate complexes requires a minimum donor ability of the incoming ligand. It is therefore not surprising that **4b** is unreactive towards SO_2, CS_2, ethene and Et_4NCl, whereas molecules such as MeCN and NO are readily added [13].

$RuCl_2(P^{\frown}O)_2$ (**4**) does not only take up small molecules of this kind, but is also capable of accommodating another O,P ligand to form complexes of the type $RuCl_2(P^{\frown}O)(P{\sim}O)_2$ (**8**) with *trans* chlorides and meridional phosphorus atoms. Complexes of this kind containing the ether-phosphines **Ia,d**, **IIe** and **IIId** [102,112], as well as the phosphinoester **XXIIIa** [113,114], have been thoroughly investigated, especially with respect to their dynamic behaviour. They can be obtained either from $RuCl_3$ and excess O,P ligand in refluxing ethanol or preferably by reaction of $RuCl_2(PPh_3)_3$ with three equivalents of ligand.

Isostructural with these dichloro complexes are the corresponding dihydrido ruthenium compounds *trans*-$RuH_2(P^{\frown}O)(P{\sim}O)_2$ (**11**), which has been reported for $P^{\frown}O = Ph_2PCH_2CH_2OMe$ (**Ia**) [115]. It is obtained as a yellow powder from *trans*-$RuCl_2(P^{\frown}O)_2$ (**4a**) and $NaBH_4$ in the presence of one equivalent of **Ia**. **11a** is unreactive towards molecular hydrogen at ambient conditions, but activation of the Ru–O bond occurs upon addition of a fourth O,P ligand to yield *cis*-$RuH_2(P{\sim}O)_4$ (**12a**) [115]. The *cis* configuration of the two hydrido ligands in this complex is concluded from its $^{31}P\{^1H\}$ NMR spectrum.

Refluxing of diphenylphosphinoacetic acid (**XXIVa**) with $RuCl_2(PPh_3)_3$ in acetone affords diamagnetic complexes of the type $Ru(P^{\frown}O)_2(PPh_3)$ or $Ru(P^{\frown}O)_2(P{\sim}O)$ (**13**), depending on the molar ratios used [116]. In these and the following compounds, the O,P ligand **XXIVa** is present in the form of the free carboxylic acid if η^1-bound and in the form of its anion if η^2-bound.



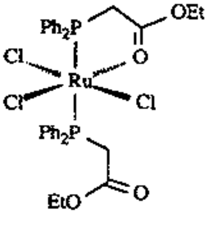
13

The molecular structures of both complexes have been established on the basis of spectroscopic evidence (^{31}P NMR, IR). Thus, five-coordinate square-pyramidal geometries were proposed. These complexes react with CO to give the monocarbonyl species with CO occupying the sixth coordination site. Prolonged purging of CO through a solution of **13** leads to the *all-cis*-dicarbonyl ruthenium complex $Ru(P^{\frown}O)_2(CO)_2$ by substitution of a phosphine ligand rather than by addition after cleavage of an O,P chelate ring. Dimethylsulphoxide reacts in a similar manner. Displacement of Me_2SO in $RuCl_2(Me_2SO)_4$ by **XXIII** provides a synthetic route to $[RuCl(P^\frown O)_2(Me_2SO)]^-$, which exists as a mixture of predominantly two geometrical isomers. Substitution of all four Me_2SO molecules yields fac-$[Ru(P^\frown O)_3]^-$. In contrast with the behaviour of the previously discussed ether-phosphines, the reaction of diphenylphosphinoacetic acid (**XXIVa**) with $RuCl_3$ affords in high yield a paramagnetic green complex with a proposed dimeric structure of the type $[Ru(P^\frown O)_2Cl]_2$ [116].

Reaction of **4a** with different quantities of silver acetate or silver trifluoroacetate in methanol causes ligand exchange of chloride for acetate or trifluoroacetate [112]. In this way, $[Ru(O_2CCF_3)_2(O,P)_2]$, $[RuCl(OAc)(O,P)_2]$ and $[Ru(OAc)_2(O,P)_2]$ could be obtained. The latter complex is capable of accommodating a third O,P ligand, forming fac-$[Ru(OAc)_2(P\sim O)_3]$, which in methanolic solution exists in the ionized form $[Ru(OAc)(P^\frown O)(P\sim O)_2]^+OAc^-$. The cation of this compound contains both $O^\frown O$ and $O^\frown P$ donor sets and exhibits complex fluxional behaviour.

On the basis of NMR investigations, fluxional behaviour has also been observed for some monocarbonyl complexes (**5**) and also for complexes of the type $RuX_2(P^\frown O)(P\sim O)_2$ [X = Cl (**8**), H (**11**)] [102,113,115]. For details on dynamic phenomena, see Sect. C.(v).

Although the overwhelming majority of ruthenium complexes with O,P ligands reported as yet are concerned with ruthenium(II), attention should be drawn to a ruthenium(III) complex containing the ligand Ph_2PCH_2COOEt (**XXIIIa**). Upon reaction of $RuCl_3$ with **XXIIIa** in ethanol/HCl at room temperature, dark-red mer-$RuCl_3(P^\frown O)(P\sim O)$ (**14**) is obtained [114]. The X-ray structure analysis reveals a meridional arrangement of the three chlorides and a *trans*-configuration of the two phosphorus atoms. One of the O,P ligands coordinates in a chelating manner using the carbonyl oxygen of its ester group as a second donor.



14

It is not surprising that ruthenium(III) has a higher affinity for oxygen than has ruthenium(II). Consequently, the Ru–O distance in **14** (214.3 pm) is found to be remarkably short. The high stability of this bond is clearly demonstrated by the behaviour of **14** in cyclic voltammetric experiments.

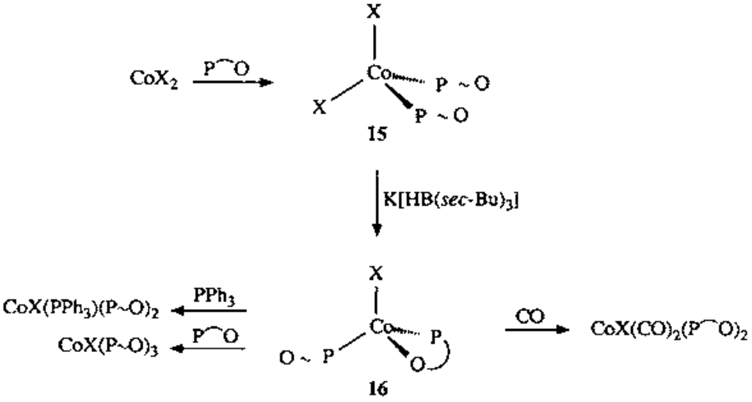
Thus, its electrochemical reduction is not influenced by CO, which is apparently unable to open the O,P chelate ring. This is not necessarily due to an incompatibility of ruthenium(III) and CO since stable complexes such as $RuF_3(CO)_3$ are known [117].

The strong Ru–O bond present in **14** renders a dynamic exchange process at reasonable temperatures unlikely. However, the paramagnetism of ruthenium(III) compounds impedes the recording of conclusive NMR spectra.

(iii) Complexes of the cobalt group

Among all transition metals, those belonging to the cobalt group have attracted great attention. With the goal of finding new organometallic systems which can be successfully used as catalyst precursors, prevailing interest has also been focused on the coordination chemistry of these elements with unsymmetrically chelating O,P ligands. Although the platinum metals play a pivotal role in complex chemistry and catalysis, research work into cobalt complexes of this kind has also been carried out.

According to Scheme 3, the cobalt halides CoX_2 ($X = Cl, Br, I$) have been shown to react with the ether-phosphines **Ia**, **IIa** or **IIIa** to give tetrahedral compounds of the type $CoX_2(P\sim O)_2$ (**15**) [6] which are isostructural with the well-known phosphine complexes $CoX_2(PR_3)_2$ [118].

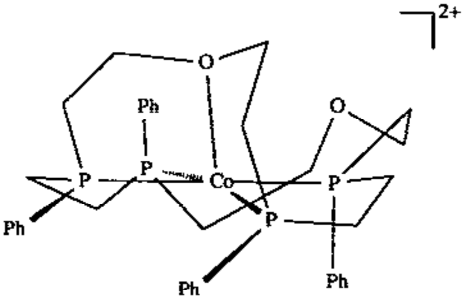


Scheme 3. Cobalt(II) and cobalt(I) complexes with ether-phosphines.

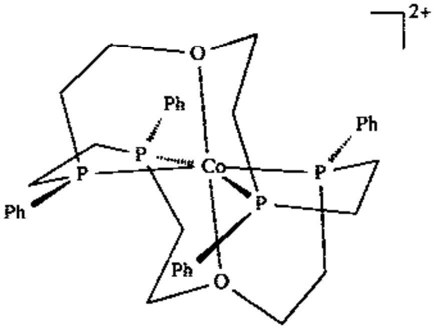
Reduction of **15** can be achieved with $K[HB(sec\text{-}Bu)_3]$ in THF at −40°C, yielding the highly reactive, orange cobalt(I) species $CoX(P\frown O)(P\sim O)$ (**16**), $CoI(P\frown O)(P\sim O)$ ($P\frown O = Ph_2PCH_2C_4H_7O$, **IIa**) has a paramagnetic moment of 3.18 B.M., a value which is in accord with a tetrahedrally coordinated d^8 system [119]. Complexes of type **16** readily react with CO, PPh_3 or another O,P ligand to give $CoX(CO)_2(P{\sim}O)_2$, $CoX(PPh_3)(P{\sim}O)_2$ or $CoX(P{\sim}O)_3$, respectively [6,119].

The fact that $CoX(P^\frown O)(P{\sim}O)$ (**16**) can be isolated from solution may be attributed to the stabilizing effect of internal solvation performed by O,P chelation. On the other hand, the corresponding solvent complexes $CoX(PPh_3)_2\cdot THF$ only exist in the form of their THF solutions and decompose rapidly even upon dilution with diethyl ether [6]. This comparison nicely demonstrates the effect of hemilabile ligands on complex stability.

Considerable interest has been shown in the coordination chemistry of cobalt(II) and O,P-containing macrocycles, which can also be viewed as phosphorus-containing crown ethers. One of those ligands, the 18-membered macrocycle **XVII**, has been extensively investigated by Ciampolini et al. [42,120,121]. It forms low-spin cobalt(II) complexes of the type $[Co(mc)]^{2+}$ (**17**), the counter-ion being $[BPh_4]^-$ or $[BF_4]^-$.



17a



17b

Of the five possible stereoisomers of **XVII** (three meso and two ± pairs), the α- and β-diastereoisomers arise from a 4 RS, 7 RS, 13 RS, 16 RS and from a 4 RS, 7 RS, 13 SR, 16 SR phosphorus configuration, respectively. They behave differently towards a given metal centre such as cobalt(II) or nickel(II). Depending on its configuration, the macrocycle exhibits either a hexadentate, a pentadentate or a tetradentate coordination mode [120]. This can be gleaned unambiguously from the electronic spectra and from the X-ray structures done for several cobalt(II) complexes [42,120,121]. In the case of $[Co(\alpha\text{-mc})]^{2+}$ (**17a**), the four phosphorus atoms lie approximately on the same plane, which is located 120 pm beneath the cobalt centre. One of the two oxygens is coordinated at a rather long Co–O distance of 226 pm. The resulting square-pyramidal geometry is not uncommon for five-coordinate cobalt(I) low-spin systems, in contrast to the hexacoordination in the form of an elongated octahedron, observed in $[Co(\beta\text{-mc})]^{2+}$ (**17b**). In this compound, the structural peculiarities of the macrocycle leads to the coordination of both oxygen donors.

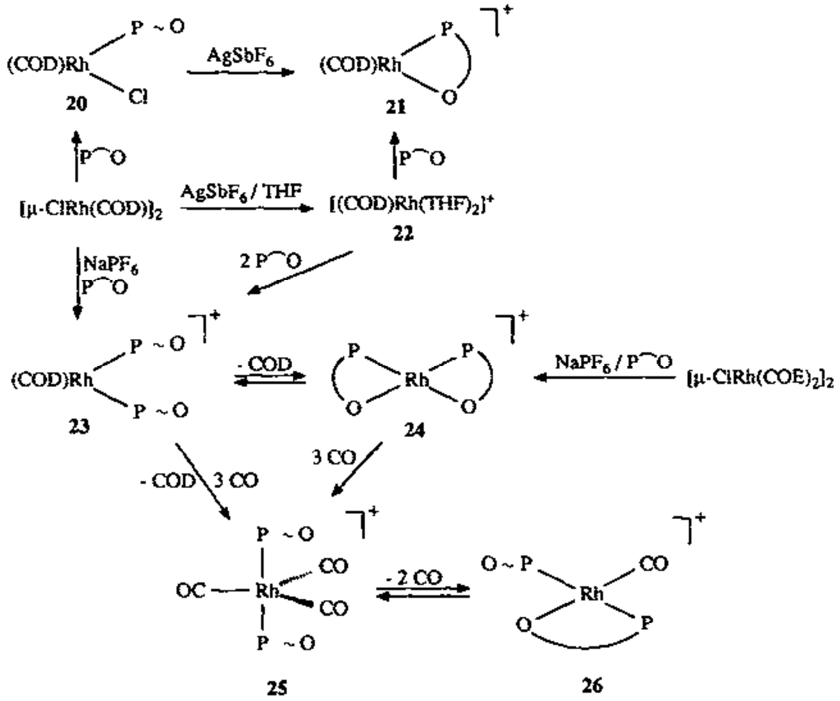
Macrocycles containing the *cis*-1,2-bis(alkylphenylphosphino)benzene moiety have been reported by Kyba et al. Four different types of cobalt complexes have been obtained and described [44].

An interesting compound is made by treatment of (diphenylphosphino) propionic acid ($\mathrm{Ph_2PCH_2CH_2COOH}$, **XXIVb**) in $\mathrm{CH_2Cl_2}$ with Co $\mathrm{(NO_3)_2 \cdot 6H_2O}$ in an aqueous solution of $\mathrm{NaHCO_3}$ [122]. The reaction product, which is extracted into the organic layer of this two-phase system, has the general formula $\mathrm{Co_6(Ph_2PCH_2CH_2CO_2)_{12}}$ (**18**). This compound is obtained as large violet crystals, which are inert towards oxygen. The principal structural basis of **18** is a $\mathrm{Co_6O_6}$ ring in which each cobalt atom is coordinated by five oxygens and one phosphorus atom in an approximately octahedral arrangement. The carboxylato ligands present in this molecule can be compartmentalized into two categories, according to their mode of bonding. Each of the six ligands belonging to the first category bridges two metal centres through the two oxygen donors, the phosphorus atom remaining uncoordinated. The representatives of the other class link three metals in a manner similar to the situation in $\mathrm{Mn(OAc)_2 \cdot 4H_2O}$ [123]. One ligand forms an O,P chelate ring, the oxygen atom of which is also coordinated to the vicinal metal. The second oxygen donor of the carboxylato group is bound to a third metal ion. Nickel(II) forms the same type of complex.

A bis-chelate complex of cobalt(II) is formed with the fluorinated phosphinoalcoholate $[\mathrm{Ph_2PCH_2C(CF_3)_2{-}O}]^-$ derived from ligand **XXVc** [77]. From the reaction of $\mathrm{CoCl_2 \cdot 6H_2O}$ with **XXVc** in ethanol and subsequent deprotonation by KOH, the neutral cobalt(II) complex $\mathrm{Co}(\mathrm{P}\frown\mathrm{O})_2$ (**19**) is obtained. The orange colour of this compound points to a square-planar rather than to a tetrahedral geometry. The two phosphorus atoms most likely occupy *trans* positions due to the low value of the extinction coefficient measured in the UV/VIS region. The assumption of such a molecular configuration is substantiated by the X-ray structure of the nickel analogue [77] and by the fact that, as a rule, planar cobalt(II) complexes are frequently formed in the case of bidentate anionic ligands. In the same way as described above for the cobalt complex **19**, the anionic rhodium(III) compound $\mathrm{K[RhCl_2(P}\frown\mathrm{O)_2]}$ can be made from $\mathrm{RhCl_3}$ and **XXVc** [77].

Olefin complexes of dimeric rhodium(I) compounds such as $[\mu\text{-}\mathrm{ClRh(COD)}]_2$ are suitable, commonly used starting materials for the preparation of other rhodium(I) complexes. In the first step, these binuclear molecules may be cleaved by an incoming ligand to give monomeric (olefin)rhodium(I) compounds, and, in a second step, the olefin itself is also subject to substitution. Scheme 4 gives a survey of (ether-phosphine)rhodium(I) complexes together with their synthetic connections.

If $[\mu\text{-}\mathrm{ClRh(COD)}]_2$ is reacted with two equivalents of ether-phosphine, $\mathrm{RhCl(COD)(P \sim O)}$ (**20**) is obtained [124–128]. Chloride abstraction with



P⌒O	IIa	IIb	IIc	IIe	Ia	Ie
Complexes 20-26	a	b	c	d	e	f

Scheme 4. Rhodium(I) complexes with ether-phosphines.

$AgSbF_6$ in THF transforms **20** into the cationic rhodium(I) complexes $[Rh(COD)(P⌒O)]SbF_6$ (**21**) in which the ether oxygen is now bound to the rhodium centre, occupying the coordination site previously used by the chloride ligand. This reaction can be understood in terms of a $AgSbF_6$-mediated substitution of chloride by the ethereal oxygen donor. As expected, this ring-closure is perceivable by a shift of 30–40 cm^{-1} of the $\nu_{as}(C_2O)$ ether vibration towards lower wavenumbers.

Compound **21** is also accessible by substitution of THF in $[Rh(COD)(THF)_2]SbF_6$ (**22**) by one equivalent of O,P ligand, viz. **Ia,e**, **IIa–c,e** [124–126].

Reaction of $[\mu\text{-}ClRh(COE)_2]_2$ with $NaPF_6$ and the O,P ligands **IIa,b** leads to the formation of the cationic bis(ether-phosphine)rhodium(I) complexes **24a,b** of the type *cis*-$[Rh(P⌒O)_2]^+$ (**24**) [124]. If $[\mu\text{-}ClRh(COD)]_2$, which contains the better coordinating COD compared with COE, is treated with **IIa** and $NaPF_6$ at −40°C, the corresponding olefin complex

$[Rh(COD)(P^\frown O)_2]PF_6$ (**23a**) is obtained. When dissolved in CH_2Cl_2, this compound loses COD to give **24a**. This latter reaction can be reversed by adding a large excess of COD to a solution of **24a**. For steric reasons, arising from the bulky cyclohexyl substituents, **IIb** shows a different behaviour. At −40°C, instead of $[Rh(COD)(P\sim O)_2]^+$ (**23b**), $[Rh(COD)(P^\frown O)]^+$ (**21b**) is formed from the reaction of $[\mu\text{-}ClRh(COD)]_2$ with **IIb** and $NaPF_6$. At room temperature the reaction proceeds directly to *cis*-$[Rh(P^\frown O)_2]^+$ (**24b**), whose O,P chelate rings cannot be opened with COD, in contrast with the corresponding compound **24a** containing **IIa** as O,P ligand. Notably, $[\mu\text{-}ClRh(COD)]_2$ is directly transformed into the cationic complex $[Rh(COD)(P\sim O)_2]^+$ (**23**) without addition of $NaPF_6$ if the reaction is carried out in highly polar solvents such as acetonitrile or acetone [128].

In general it can be anticipated that the O,P chelate confers a considerable increase in stability upon the rhodium(I) species mentioned above. Nevertheless, there is a great propensity, especially of the complexes *cis*-$[Rh(P^\frown O)_2]^+$ (**24**), towards decomposition even at −30°C in the solid state. $[Rh(COD)(P^\frown O)]^+$ (**21**) is more stable due to the presence of the π-acidic COD ligand which is capable of taking up excessive electron density at the rhodium caused by the Rh–O contact [124].

As a centre of reactivity, the Rh–O bond is readily cleaved by CO [121]. Passing of CO through solutions of *cis*-$[Rh(P^\frown O)_2]PF_6$ (**24a,b**) at −40°C affords the corresponding tricarbonylrhodium(I) compounds *trans*-$[Rh(P\sim O)_2(CO)_3]^+$ (**25a,b**) [124], which are also accessible by reacting $[Rh(COD)(P\sim O)_2][SbF_6]$ (**23**) with CO [125,127]. In this way, **25c–f** have been prepared. The proposed trigonal bipyramidal structure (pseudo-D_{3h}) with the two phosphines occupying the axial positions and three equatorial CO ligands follows from its IR [one $\nu(C\equiv O)$ band] and $^{31}P\{^1H\}$ NMR spectrum (quartet due to P–C coupling).

The stability of the tricarbonyl compounds **25** crucially depends on the steric demand of the substituents at the phosphorus atom [125]. Thus, if $Ph_2PCH_2C_4H_7O$ (**IIa**), $Cy_2PCH_2C_4H_7O$ (**IIb**), $^nPr_2PCH_2C_4H_7O$ (**IIc**), $Ph_2PCH_2CH_2OMe$ (**Ia**) or $^nPr_2PCH_2CH_2OMe$ (**Ie**) is used, the respective tricarbonylrhodium complexes **25a–c,e,f** cannot be isolated but only identified in solution and in the presence of CO below 0°C. They quickly undergo reversible decarbonylation by sweeping their THF solutions with an inert gas at −40°C to yield the corresponding monocarbonylrhodium(I) complexes **26**. Under these conditions, no reaction occurs in the case of $Me_2PCH_2C_4H_7O$ (**IIe**), and at higher temperatures decomposition is observed. In all probability, the complexes **26** adopt a square-planar geometry with mutually *trans* phosphorus atoms. In this case, a dynamic exchange of the two ether moieties is expected. Accordingly, the $^{31}P\{^1H\}$ NMR spectra of **26** display a variable temperature dependence [124]. Recently, bis(ether-phosphine)rhodium(I) compounds containing two different O,P ligands have been established [127]. Complexes of this kind are obtained from the reaction of $[Rh(COD)(P^1\frown O)][SbF_6]$ (**21**) with a different ligand $P^2\frown O$ to give $[Rh(COD)(P^1\sim O)(P^2\sim O)][SbF_6]$ (**23**). Further treatment with carbon monoxide yields the corresponding carbonyl derivatives **25** and **26**.

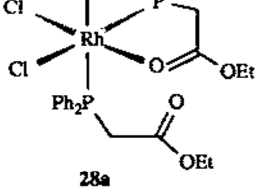
$[\mathit{cis}\text{-}Rh(P\frown O)_2]^+$ (**24b**) adds H_2 or MeI oxidatively. Likewise, $[Rh(CO)(P\frown O)(P\sim O)]^+$ (**26**) readily undergoes oxidative addition of MeI. As outlined later in Sect. E.(ii), the latter reaction represents an important step within a model catalytic cycle which has been established for the carbonylation of methanol.

Complexes of the Vaska-type $IrCl(CO)(P\sim O)_2$ (**27**) have been prepared with the phosphinoanisol **VIa** and its *para* isomer **VII** via the corresponding hydrido complex $IrHCl_2(CO)(P\sim O)_2$ [54]. They are useful compounds for the study of the influence of the methoxy group on oxidative additions. The results of these investigations are discussed in Sect. D.(iii).

The tendency of rhodium(III) and iridium(III) to bind hard oxygen or nitrogen donor ligands is strongly pronounced, as can be concluded from the existence of several stable complexes, such as $[Rh(H_2O)_6]^{3+}$ [129]. Hence, O,P chelates with rhodium(III) and iridium(III) are expected to be readily obtainable.

A range of phosphinocarboxylic esters has been utilized for the synthesis of rhodium and iridium complexes [74,75,113,130]. The most commonly used ligand of this class is Ph_2PCH_2COOEt (**XXIIIa**). Its reaction with $RhCl_3$ in ethanol at ambient conditions affords the orange compound fac-$RhCl_3(P\frown O)(P\sim O)$ (**28a**). The red tribromo derivative (**28b**) is synthesized in a similar way [130].

In order to obtain the related iridium(III) complex fac-$IrCl_3(P\frown O)(P\sim O)$ (**28c**), the ligand **XXIIIa** is reacted with $(NH_4)_2IrCl_6$ in ethylene glycol at elevated temperatures [130]. In all type-**28** compounds, the η^2-bound O,P ligand avails itself of the carbonyl group in order to establish a metal–oxygen interaction.



28a

In contrast with the iridium complex **28c**, the rhodium homologues **28a,b** exhibit stereodynamic behaviour which is discussed in detail in Sect. C.(v).

In general, it is of great interest to investigate the properties of organometallic compounds as a function of the substituents attached to a given ligand framework [131]. In this regard, it is well-known that, due to steric crowding, bulky groups at or in close proximity to the donor atoms often impart salient properties and reactivity to the respective complex, namely with respect to molecular structures, rate and equilibrium constants and NMR chemical shifts and coupling constants.

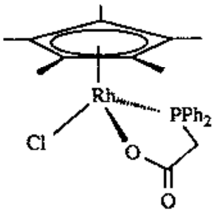
Treatment of $RhCl_3 \cdot 3H_2O$ with $^tBu_2PCH_2COOEt$ (**XXIIIb**) in ethanol yields the cationic complex $[RhCl_2(P\frown O)_2]^+$ (**29a**), which may be isolated in the form of its tetraphenyl boranate salt [75]. The O,P chelate ring of this compound is not planar, and the chlorides are assumed to be in the *trans* position, as follows from its far-IR spectrum.

Unlike the diphenylphosphinoester **XXIIIa**, which forms the neutral monochelate complexes fac-$RhCl_3(P\frown O)(P\sim O)$ (**28a**) [74,130], the *tert*-butyl groups present in ligand **XXIIIb** facilitate the formation of a second O,P chelate ring. To this end, a chloride ion is removed from the complex core as a result of an intramolecular substitution by the oxygen atom of the hitherto η^1-bound O,P ligand.

Chloride abstraction from **28a** is accomplished with $AgPF_6$, yielding $[RhCl_2(P\frown O)_2]^+$ (**29b**). The spectroscopic data are suggestive of a *cis*-arrangement of the chlorides and the phosphorus atoms, as well as of mutually *trans* oxygens [113].

In accordance with the previously mentioned affinity of rhodium(III) towards hard σ-donor ligands, carbon monoxide is not readily coordinated, as demonstrated by its failure to cleave the Rh–O bonds in **28a,b**.

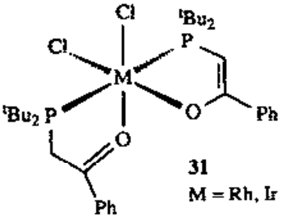
Complexation of anionic phosphinocarboxylates, viz. $[Ph_2PCH_2COO]^-$, which is derived from **XXIVa** upon deprotonation, has also been carried out successfully [132]. In the form of its sodium salt, this ligand is capable of cleaving dimeric $[(\eta^5\text{-}C_5Me_5)RhCl(\mu\text{-}Cl)]_2$ to give orange $[(\eta^5\text{-}C_5Me_5)RhCl(P\frown O)]$ (**30**).



30

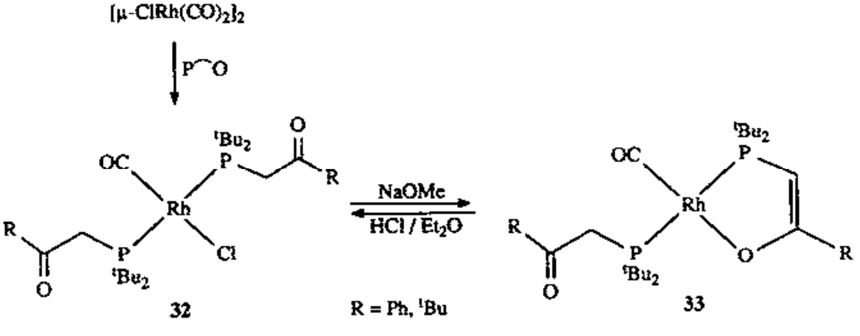
β-Ketophosphines, which are structurally related to the phosphinoesters, show a somewhat different behaviour towards alcoholic solutions of $RhCl_3$

and $IrCl_3$ [133]. Whereas $^tBu_2PCH_2COOEt$ (**XXIIIb**) yields the cationic complex $[RhCl_2(P\frown O)_2]^+$ (**29a**), $^tBu_2PCH_2C(O)Ph$ (**XXd**) gives a neutral orange compound of the type $MCl_2(P\frown O)(P\frown O)'$ [**31**, M = Rh (**31a**), Ir (**31b**)]. $(P\frown O)'$ designates a bidentate phosphinoenolate ligand formed from **XXd** upon deprotonation in the course of the reaction. The other chelating ligand remains in the keto form, using its carbonyl oxygen for occupying the sixth coordination site. The IR spectra of **31a,b** clearly indicate the absence of uncoordinated keto groups, but in addition to the absorptions due to the enolate system [1519 cm^{-1} (**31a**) or 1525 cm^{-1} (**31b**)] the coordinated keto functions give rise to bands at 1581 cm^{-1} (**31a**) or 1538 cm^{-1} (**31b**).



31
M = Rh, Ir

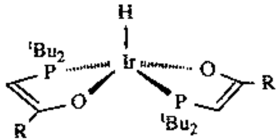
As shown in Scheme 5, cleavage of $[\mu\text{-}ClRh(CO)_2]_2$ with ketophosphines, viz. $^tBu_2PCH_2C(O)Ph$ (**XXd**) or $^tBu_2PCH_2C(O)^tBu$ (**XXe**) in ethanol leads to *trans*-$[RhCl(CO)(P\sim O)_2]$ (**32**) [133]. This universal pathway is also known for other, non-functionalized, phosphines. Compound **32** is quite thermostable, but upon treatment with NaOMe one ketophosphine ligand is transformed into the corresponding enolate, which forms an O,P chelate after elimination of the chloride ligand. In the resulting complex $Rh(CO)(P\frown O)(P\sim O)$ (**33**) this phosphinoenolate is bound in a bidentate manner. Protonation of **33** with HCl in diethyl ether causes ring-opening and coordination of a chloride ion, **32** being re-formed.



Scheme 5. Interconversion of β-ketophosphine and phosphinoenolato rhodium(I) complexes.

Rhodium and iridium form scores of hydrido complexes in both the mono- and trivalent oxidation states. Among those, the iridium(III) compounds are the most stable species.

Penta-coordinate square-pyramidal iridium(III) hydrido complexes of the type *trans*-$[IrH(P⌒O)_2]$ (**34**) have been prepared with various anionic O,P ligands bound in a η^2-mode. The respective compounds containing chelated di-*tert*-butylphosphinoenolates derived from **XXd,e** are readily made by reacting $IrCl_2(P⌒O)(P⌒O)'$ (**31b**) and sodium ethoxide [133].



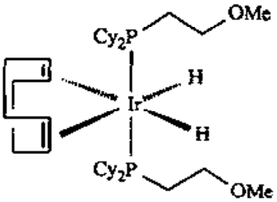
34

R = Ph, ᵗBu

Another synthetic approach to such mono-hydrido complexes is realized by refluxing $IrCl_3$ with ligands, such as the phosphinophenol **XXVIb** [134] or the phosphinoanisol **IXb** [135]. In the latter case, *O*-metallation is observed, a reaction pathway which is discussed in Sect. D.(i). The hydrido complexes **34** rapidly take up small molecules, e.g. carbon monoxide or pyridine, to give the colourless carbonyl hydrides *trans*-$[IrH(CO)(P⌒O)_2]$ (**35**), which in turn lose CO upon heating to 200°C. The bidentate character of the O,P ligands enable the compounds **35** to adopt a six-coordinate geometry. This contrasts with the trigonal bipyramidal structure of carbonyl hydrides $IrH(CO)(PR_3)_3$ formed with common monodentate phosphines.

Cis-dihydrido complexes of rhodium(III) and iridium(III), generally formulated as $[cis\text{-}MH_2L_2S_2]^+$ (L = phosphine ligand, S = solvent molecule) have attracted great interest since they play an important role in hydrogenation and hydrocarbonylation reactions [136]. However, these solvent complexes are rather unstable. The introduction of bidentate O,P ligands, which combine both phosphine moiety and solvent-like side-arm, might be a promising way of overcoming this instability.

Cleavage of dimeric $[\mu\text{-ClIr(COD)}]_2$ with $Cy_2PCH_2CH_2OMe$ (**Ib**) affords (COD)IrCl(P∼O) (**36**). On treatment with $AgBF_4$, **36** is transformed into the cationic O,P-chelated complex $[(COD)Ir(P⌒O)]^+$ (**37**) which is isostructural with its rhodium analogue **21** [137]. Compound **37** is capable of taking up hydrogen and, in the presence of excess ligand, $[cis\text{-}IrH_2(P\sim O)_2\text{-}(COD)]^+$ (**38**) is obtained. Interestingly, the reaction of $[\mu\text{-ClIr(COE)}_2]_2$ with **Ib** proceeds to *trans*-$IrH_2Cl(P⌒O)(P\sim O)$ (**39**, $P⌒O = Cy_2P\text{-}CH_2CH_2OMe$, **Ib**), cyclooctene being the hydrogen source.



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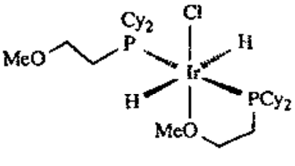
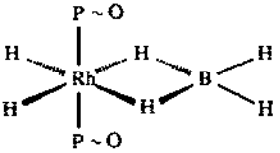


39

In order to synthesize stable *cis*-dihydridorhodium(III) complexes, the use of an appropriate O,P ligand is a crucial factor [128,138,139]. Thus, complexes of the type $[cis\text{-}RhH_2(P^\frown O)_2]^+$ (**40**) are remarkably inert with respect to loss of hydrogen if $^iPr_2PCH_2C_4H_7O$ (**IId**) is used, but cannot be isolated in pure form in the case of $Cy_2PCH_2C_4H_7O$ (**IIb**). This compound undergoes substitution of the hydrogens along with Rh–O bond cleavage upon reaction with carbon monoxide forming $[trans\text{-}Rh(P\sim O)_2(CO)_3]^+$ (**25**). Furthermore, Rh–O bond rupture is also effected by $NaBH_4$, $cis\text{-}RhH_2(\eta^2\text{-}BH_4)(P\sim O)_2$ (**41**) being formed.



41

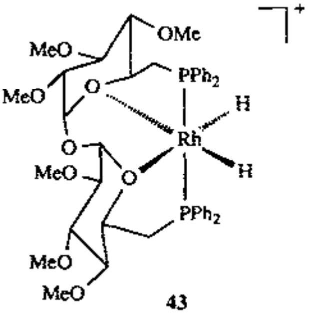
$P^\frown O = Cy_2PCH_2C_4H_7O$ (**IIb**)

Upon treatment with $NaBH_4$, $[RhCl_2(P^\frown O)_2]^+$ (**29a**, $P^\frown O = {}^tBu_2PCH_2COOEt$, **XXIIIb**) is also transformed into the *cis*-dihydrido compound $RhH_2(\eta^2\text{-}BH_4)(P\sim O)_2$ (**41**), which contains *trans*-phosphines and a η^2-bound $[BH_4]^-$ ligand *trans* to the hydrides [75]. The formerly bidentate O,P ligand is now coordinated in a η^1 mode since the $[BH_4]^-$ moiety takes the place of the oxygen atoms in **29a**.

The structure formulated for $RhH_2(\eta^2\text{-}BH_4)(P\sim O)_2$ (**41**) is equivalent to that found for the analogous rhodium and iridium complexes of the type $MH_2(\eta^2\text{-}BH_4)(PR_3)_2$ with common *tert*-butyl phosphines [140].

If more intricate ligands are used to prepare rhodium or iridium *cis*-dihydrido compounds, the stereochemistry of the whole framework becomes very important [59,141]. As an example, the different behaviour of α,α-TREDIP (**XVIa**) and β,β-TREDIP (**XVIb**) should be briefly mentioned [59]. Reaction of $[(nor\text{-}C_7H_8)_2Rh][BF_4]$ with α,α-TREDIP yields orange $[nor\text{-}C_7H_8Rh(P^\frown P)]^+$ (**42a**) with uncoordinated oxygens. Upon agitation under H_2, yellow $[cis\text{-}RhH_2(P^\frown O^\frown O^\frown P)]^+$ (**43**) is formed, regardless of whether methanol or dichloromethane is used as solvent. This latter observation substantiates the assumption of coordinated oxygen atoms.

On the contrary, [nor-$C_7H_8Rh(P\frown P)]^+$ (**42b**) containing β,β-TREDIP (**XVIb**) does not react with H_2 to give a *cis*-dihydrido species analogous to **43**, but *cis*-$[Rh(P\frown O\frown O\frown P)]^+$ (**44**) is formed directly.



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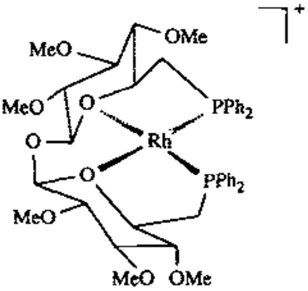
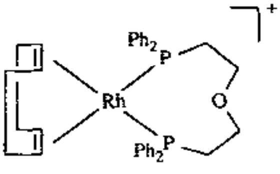


44

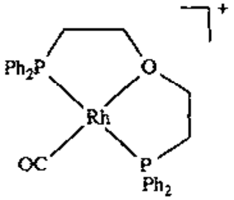
Phosphino polyethers combine the chelating properties exhibited by conventional long-chain diphos ligands with an additional possibility of a weak metal–oxygen interaction. Therefore, complexes are expected to be formed which are similar to those obtained with O,P macrocycles. In both cases, the metal is encapsulated within the cavity provided by the multidentate ligand system.

Rhodium(I) complexes of the type *cis*-$[Rh(COD)(P\frown P)]^+$ (**45**) are accessible by the reaction of Rh(COD)(acac) with a diphenylphosphino polyether of the category **XII** or **XIII** and $HClO_4$ [18,19]. The compounds **45** easily lose COD, which gives rise to a variety of compounds. Among these, a five-coordinate species has been suggested for the complex containing **XIIIb**, all three ether-oxygens being coordinated [18].

Displacement of the olefin can also be achieved by carbon monoxide [18]. Bubbling of CO through a solution of *cis*-$[Rh(COD)(P\frown P)]ClO_4$ (**45a**, $P\frown P$ = **XIIa**) results in the coordination of one CO molecule. In order to preserve the coordination number four, an ether oxygen is expected to interact with the metal centre, thus forming $[Rh(CO)(P\frown O\frown P)]^+$ (**46**). This type of complex is also readily prepared by reaction of $[\mu\text{-}ClRh(CO)_2]_2$ with the appropriate ligand followed by chloride abstraction from *trans*-



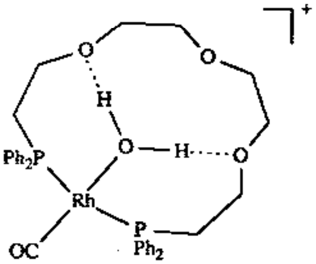
45a



46a

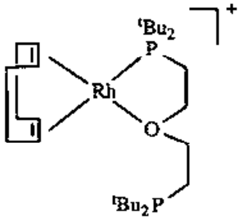
$[\mathrm{Rh}(\mathrm{P}^\frown\mathrm{P})(\mathrm{CO})\mathrm{Cl}]$ formed in the first step. Alcock et al. have unambiguously demonstrated such a metal–oxygen contact for **46a** which contains **XIIa** as ligand [20,21].

It is of great interest to investigate the coordination behaviour of phosphino polyethers as a function of chain length. The preparation of a series of complexes $[\mathrm{Rh}(\mathrm{CO})(\mathrm{P}^\frown\mathrm{O}^\frown\mathrm{P})]^+$ (**46**, $\mathrm{P}^\frown\mathrm{O}^\frown\mathrm{P}$ = type **XII** ligand with $n = 1$–3) and their structural elucidation have revealed that one oxygen atom is bound to the metal in the case of **XIIa,c**. If the chain length becomes longer (viz. ligand **XII**, $n = 3$), the ligand is bidentate only through phosphorus. However, an ethanol or a water molecule, as in **46b**, is readily encapsulated in the cavity owing to a chelate conformation which perfectly meets the requirements of hydrogen bonding [20,21].

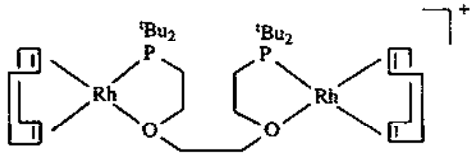


46b

Phosphinopolyethers with bulky groups at the phosphorus atoms [17], e.g. **XIIb,d**, should exhibit unique behaviour due to the steric demand of the *tert*-butyl groups. The cationic rhodium(I) complexes **45b** and **45c** with the ligands **XIIb** and **XIId**, respectively, are made by reacting $[\mathrm{Rh}(\mathrm{COD})(\mathrm{acetone})_2][\mathrm{CF}_3\mathrm{SO}_3]$ with the appropriate phosphine. Due to steric constraint, a *cis* coordination of the two phosphorus atoms is precluded. Instead, the formation of a five-membered O,P chelate (**45b**) or of binuclear species (**45c**) is observed. The structure of **45c** in solution is depicted below. In the solid state, **45c** contains a coordinated and an uncoordinated triflate group and hence one rhodium centre is O,P-chelated to which the triflate-bearing rhodium moiety is linked solely through phosphorus.



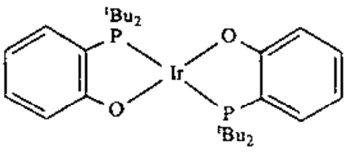
45b



45c (in solution)

A rather striking feature exhibited by O,P chelates is their capability of stabilizing rhodium(II) and iridium(II) species by forming complexes of the type *trans*-$M(P^\frown O)_2$ (**47**, M = Rh, Ir) [142]. This uncommon oxidation state, especially as far as mononuclear complexes are concerned, occurs in the course of oxidative additions [143], but true rhodium(II) and iridium(II) compounds are not at all frequent.

However, upon aerial oxidation, a solution of $Ir(CO)(P^\frown O)(P\sim O)$ (**48**, $P^\frown O = {}^tBu_2PC_6H_4O$) in xylene turns blood red and evolution of carbon dioxide is observed [142]. The reaction product has been identified as *trans*-$Ir(P^\frown O)_2$ (**47a**, $P^\frown O = {}^tBu_2PC_6H_4O$). An X-ray structure of this compound and of a similar one with the O,P ligand derived from **IXb** is available [143]. The latter complex is also accessible by heating $IrCl_3$ and **IXb** in 2-propanol and oxidation by oxygen of the hydride *trans*-$IrH(P^\frown O)_2$ (**34**) formed in the first step. In the same manner, intensely blue *trans*-$Rh(P^\frown O)_2$ (**47b**, $P^\frown O = {}^tBu_2PC_6H_4O$) is made from $RhCl_3$ and **VIc** [144].



47a

The previously discussed divalent rhodium and iridium compounds are paramagnetic, the value of the magnetic moment being approximately 1.73 B.M., as expected for one unpaired electron. They readily take up small ligands, such as carbon monoxide, pyridine or nitrogen monoxide.

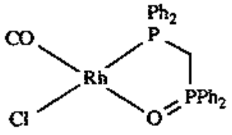
Rhodium(II) and iridium(II) complexes of the type *trans*-$M(P^\frown O)_2$ (**47**) are also known to be formed with phosphinoenolates derived from ligand **XXd** [133]. The intensely blue rhodium compound is obtained unexpectedly from $RhCl_2(P^\frown O)(P\sim O)'$ (**31a**) upon reaction with an alcoholic solution of sodium methoxide.

Interestingly, the product obtained from the reaction of $RhCl_3$ with four equivalents of di-*tert*-butylphosphinocarboxylic esters depends crucially upon the chain length of the respective carboxylic acid moiety [75]. Whereas ${}^tBu_2PCH_2COOEt$ (**XXIIIb**) forms the diamagnetic rhodium(III) compound $[RhCl_2(P^\frown O)_2]^+$ (**29a**), use of the homologues ${}^tBu_2P(CH_2)_2COOEt$ (**XXIIIe**) and ${}^tBu_2P(CH_2)_3COOEt$ (**XXIIIf**) gives rise to the reduction of rhodium(III) to the paramagnetic rhodium(II) complex of the type *trans*-$RhCl_2(P^\frown O)_2$ (**49**). In this connection, the resemblance to analogous compounds obtained with conventional bulky phosphines should be pointed out [145,146].

Recently, Wegman et al. reported rhodium(I) bisphosphine monoxide complexes of the type RhCl(CO)(P⌒O) containing the ligands **XXVIIa** (**50**) or **XXVIIc** (**51**) [147]. Such complexes have been investigated with the object of finding new more efficient carbonylation catalysts [see Sect. E.(ii)]. A crystal structure is available for **50** in the form of its dichloromethane solvate [147].

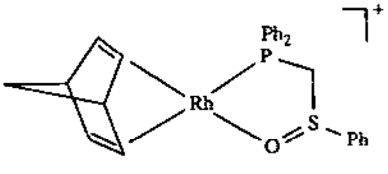
The Rh–O coordination is unambiguously indicated by a shift of the ν(P=O) stretching band of 135 cm^{-1} (**50**) or 40 cm^{-1} (**51**) towards lower wavenumbers. Moreover, in the $^{31}P\{^1H\}$ NMR spectrum of **50** a ^2J(Rh–P) coupling constant of 4.8 Hz is observed due to the complexation of the phosphine oxide end.

The six-membered chelate ring in compound **51** is readily cleaved by carbon monoxide, even at low CO pressures of 1–3 bar, to give *cis*-$RhCl(CO)_2(P\sim O)$ (**52**). As expected, the five-membered O,P chelate in **50** is much more stable with respect to ring opening by carbon monoxide. Hence, no reaction at all is observed at 22°C and 1 bar CO, and at 3 bar only traces of the dicarbonyl complex are formed. The greater reticence of **50** to react with CO is in accord with the $^{31}P\{^1H\}$ NMR and IR data mentioned above, which indicate a stronger Rh–O bond in **50** than in **51**.



50

Recently, Alcock et al. reported on α-phosphinosulfoxide rhodium(I) complexes [87]. They are most successfully synthesized by treatment of nor-$C_7H_8Rh(acac)$ with $Me_3SiOSO_2CF_3$ followed by addition of one equivalent of ligand. Thus, if **XXIX** is used, [nor-$C_7H_8Rh(P⌒O)][CF_3SO_3]$ (**53**) is obtained, whose molecular structure has been established by means of X-ray crystallography [87]. The olefin–rhodium bond *trans* to the oxygen is markedly shorter (209.6 pm) than the one *trans* to the phosphorus atom (224.3 pm). These distortions can be taken as indicative of a difference in magnitude of the *trans* influence exerted by oxygen and phosphorus.



53

Except for preparing a chelate complex by using an O,P ligand as starting material, such an O,P chelate can be generated during a reaction of an ordinary ligand containing a reactive functionality. As a conspicuous example, the attack of the triple bond present in the complexes *trans*-$[\mathrm{MCl(CO)}({}^t\mathrm{Bu_2PC{\equiv}CPh})_2]$ (M = Rh, Ir) by sodium alkoxides is briefly discussed [148]. These starting materials are made from rhodium or iridium carbonylchloride and ${}^t\mathrm{Bu_2PC{\equiv}CPh}$. Upon reaction with sodium propan-2-olate in 2-propanol, type **33** rhodium or iridium enolato complexes are formed (cf. Scheme 5). If sodium methoxide in methanol is used, the η^1-bound phosphine ligand is also attacked. The mechanisms of these reactions are obscure but they probably involve the disintegration of the alkoxy moiety of an initially formed alkoxyvinyl species.

(iv) Complexes of the nickel group

The class of elements at issue in this section comprises nickel, palladium and platinum. Compounds of all three metals have gained outstanding significance in both basic research and catalytic applications.

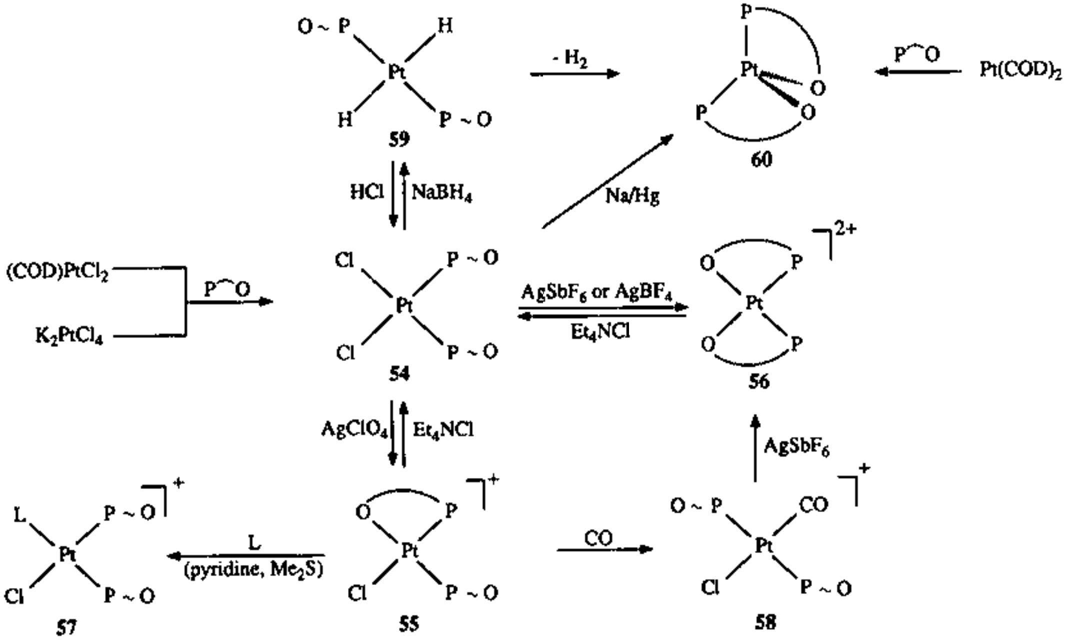
Especially in their divalent oxidation state, palladium and platinum exhibit rather straightforward coordination chemistry and form a wide range of stable complexes. Due to their preferred square-planar geometry, the number of isomers expected for a given complex is much lower than, for instance, in the case of octahedral ruthenium compounds.

As depicted in Scheme 6, (ether-phosphine)platinum complexes and also their palladium analogues are suitable for the demonstration of some fundamental reaction pathways which predominantly involve substitutions.

Entrance into this chemistry is easily gained through $\mathrm{(COD)PtCl_2}$, $\mathrm{(COD)PdCl_2}$, $\mathrm{K_2PtCl_4}$ or $\mathrm{PtCl_2(NC^tBu)_2}$ as starting materials. Upon reaction with two equivalents of an ether-phosphine, e.g. **Ia**, **IIa** and **IIIa**, stable complexes of the type $\mathrm{MCl_2(P{\sim}O)_2}$ (**54**, M = Pd, Pt) are obtained [24,48,149–151]. The stabilities of the *cis* and *trans* isomers of $\mathrm{PtX_2(PR_3)_2}$ and $\mathrm{PdX_2(PR_3)_2}$ are strongly variable, depending on the nature of X and $\mathrm{PR_3}$. The *trans* configuration of the palladium compound of type **54** with ligand **Ia** has been confirmed by an X-ray structure determination [151].

The use of only one equivalent of ligand with respect to $\mathrm{(COD)PdCl_2}$ leads to $\mathrm{PdCl_2}(\overset{\frown}{\mathrm{P\;\;O}})$. An X-ray study reveals that, at least in the solid state, this compound occurs in the form of the loosely associated dimer $[\mu\text{-}\mathrm{ClPdCl(P{\sim}O)}]_2$ with pronounced unsymmetrical chloride bridges and a *trans* arrangement of the two η^1-bound O,P ligands [151]. Conversely, if $\mathrm{(COD)PtCl_2}$ is treated with one equivalent of ether-phosphine, *cis*-$\mathrm{PtCl_2(P{\sim}O)_2}$ (**54a**, $\mathrm{P{\sim}O}$ = **Ia**, **IIa**, **IIIa**) is the only product and 50% of the starting material remains unchanged [48].

Abstraction of one chloride ion from **54a** is effected by a stoichiometric



P⌒O = **Ia**, **IIa**, **IIIa**

Scheme 6. Platinum complexes containing ether-phosphine ligands.

amount of $AgClO_4$ to give the monocation [*cis*-$PtCl(P\frown O)(P\sim O)]^+$ (**55**) [48,149–151]. The molecular structures of two type **55** compounds are known, containing the ligands **Ia** [152] and **IIa** [149]. The lengths of the dative Pt–O bonds are 219.2 and 214.2 pm, respectively. The former seems to be the longest Pt–O bond known as yet. Coordination about the platinum centre is square-planar with a slight tetrahedral distortion.

Two chlorides are removed from **54a** by excess $AgBF_4$ or $AgSbF_6$, whereupon the dicationic bischelate (*cis*-$Pt(P\frown O)_2]^{2+}$ (**56**) is formed [48,149,150]. The analogous palladium complex adopts a *trans* configuration [151].

Oxygen coordination in **55** and **56** is indicated by a shift of approximately $20\,cm^{-1}$ of the $\nu_{as}(C_2O)$ band due to the ether moiety towards lower wavenumbers.

In order to study the chemistry of these cations, attention must be focused on their ability to undergo chelate rupture induced by other ligands. The regeneration of *cis*-$PtCl_2(P\sim O)_2$ (**54a**) from both the monocation **55** and the dication **56** is immediately brought about by adding Et_4NCl [48], which serves as a source of chloride ions. Simple ring opening and subsequent complexation of an incoming ligand L also occurs with **55** upon treatment with pyridine or dimethylsulphide, yielding [*cis*-$Pt(P\sim O)_2(L)Cl]^+$ (**57**) [48]. However, carbon monoxide leads to the formation of [*trans*-$Pt(P\sim O)_2(CO)Cl]^+$ (**58**). The *trans* configuration is most likely due to an isomerization of an initially generated *cis* adduct [48].

Weaker donors such as ethene or methanol do not react at all and also THF is not accommodated. The latter finding may be explained in terms of the chelate effect, which is responsible for a better oxygen coordination of the chelating ether-phosphine ligand compared with that of discrete THF molecules.

Further chloride abstraction from [*trans*-$Pt(P\sim O)_2(CO)Cl]^+$ (**58**) results in the formation of [*cis*-$Pt(P\frown O)_2]^{2+}$ (**56**) [150], CO being eliminated owing to its unfavourable complexation properties [153], especially to dicationic platinum(II) species.

The dihydrido complex *trans*-$[PtH_2(P\sim O)_2]$ (**59**) is readily made from *cis*-$[PtCl_2(P\sim O)_2]$ (**54a**) with $NaBH_4$ in hydrogen saturated ethanol. This reaction may be reversed by acidification with HCl in acetone [150]. Complexes of the type **59** are liable to reductive elimination of H_2, whereupon the yellow bischelate platinum(0) compounds $[Pt(P\frown O)_2]$ (**60**) are formed. They are stable up to 50°C and are also accessible by COD substitution from $Pt(COD)_2$ with two equivalents of ether-phosphine [150].

Phosphinoanisols and their isomers have been prepared in large numbers (see Sect. B.(i), Table 1). Platinum(II) and palladium(II) complexes which contain this type of ligand have been investigated for about two decades, especially by Shaw's group [50,56]. In order to study the properties and reactions (see Sect. D) of these compounds, $[PtCl_2(P\sim O)_2]$ (**54b**, $P\sim O=$ **VI–IX**) are the starting materials of choice. They are readily made by reacting the desired O,P ligand of the types **VI–IX** with K_2PtCl_4 or $PtCl_2(NCPh)_2$. The preferred stereochemistry of the resulting complex **54b** depends on the phosphine employed. Whereas $Me_2PC_6H_4(OMe\text{-}2)$ (**VIa**) leads to colourless *cis*-$PtCl_2(P\sim O)_2$, the more bulky diphenyl or di-*tert*-butyl phosphines **VIb,c** give yellow *trans* complexes [50].

Due to its chiral phosphorus atoms, *trans*-$PtCl_2(P\sim O)_2$ ($P\sim O={}^tBu$-$(Me)PC_6H_4(OMe\text{-}2)$, **VId**) gives rise to stereoisomers (*meso* isomer and racemic mixture), which may be separated by fractional crystallization [50].

The diiodo compounds $PtI_2(P\sim O)_2$ are easily obtained from their dichloro counterparts by metathesis with NaI in acetone [50].

If K_2PtCl_4 or $PdCl_2(NC{}^tBu)_2$ is treated with *o*-diphenylphosphinophenol ($Ph_2PC_6H_4(OH\text{-}2)$, **XXVIa**), *trans*-$PtCl_2(P\sim O)_2$ (**54c**) or *cis*-$PdCl_2(P\sim O)_2$ is obtained [80]. The *cis* configuration of the palladium complex is somewhat unusual since treatment of $PdCl_2(NC{}^tBu)_2$ with many other phosphines under similar conditions affords the *trans* isomer.

Due to the marked acidity of the phenolic protons in type **54** complexes with **XXVIa,b**, such complexes may be easily deprotonated even by weak bases such as sodium acetate. The bis(*o*-phosphinophenolate) complex $[MCl_2(P\sim O)_2]^{2-}$ might be an unstable, not isolable intermediate which rapidly undergoes internal substitution to give neutral *cis*-$[M(\overset{\frown}{P\,O})_2]$ (**61a**, $\overset{\frown}{P\,O}=Ph_2PC_6H_4O$). The use of the more bulky ${}^tBu_2PC_6H_4(OH\text{-}2)$ (**XXVIb**) leads to *trans*-$[M(\overset{\frown}{P\,O})_2]$ (**61b**, M = Ni, Pd, Pt, $\overset{\frown}{P\,O}={}^tBu_2P$-$C_6H_4O$).

Trans-$[Ni(\overset{\frown}{P\,O})_2]$ (**61b**, $\overset{\frown}{P\,O}={}^tBu_2PC_6H_4O$) is green at room temperature and changes its colour to orange upon sublimation at 210°C [80]. Similar phenomena are frequently encountered in nickel(II) chemistry and are often due to small temperature-dependent structural changes.

The complexes **61a,b** are structurally related to the rhodium(II) and iridium(II) compounds **47** described in Sect. C.(iii). However, these latter species are quite reactive in contrast with the extreme stability of the bischelates $[M(\overset{\frown}{P\,O})_2]$ (**61a,b**) formed with nickel, palladium and platinum. **61a,b** are also obtained by *O*-metallation of the *o*-phosphinoanisol complexes $PtCl_2(\overset{\frown}{P\,O})_2$ (**54b**, $\overset{\frown}{P\,O}=$ **VI–IX**) [50,56]. This type of reaction is detailed in Sect. D.(iii).

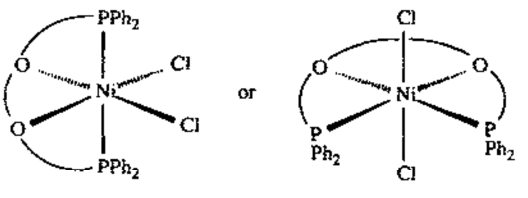
With the intention to study the phenomenon of *trans* chelation, i.e. *trans* bidentate behaviour, various long-chain diphosphines have been investigated with respect to their coordination properties. Moreover, the simple hydrocarbon chains used at the outset of these studies have been endowed with weak oxygen donors. Hence, for example $Ph_2PCH_2CH_2OCH_2CH_2PPh_2$ (**XIIa**)

[154] and $Ph_2P(CH_2CH_2O)_2CH_2CH_2PPh_2$ (**XIIc**) [155] were introduced by Green and Sacconi and their coworkers more than twenty years ago.

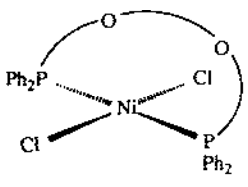
These workers have reported the complexes $NiCl_2(P\frown P)$ (**62a**, $P\frown P$ = **XIIa**) [154] and $NiI_2(P\frown P)$ (**62b**, $P\frown P$ = **XIIc**) [155,156], which are the first representatives of the series of complexes formulated as $NiX_2(P\frown P)$ (**62**). X represents Cl, Br, I or NCS and $P\frown P$ stands for a group **XII** diphosphino polyether ligand. $NiCl_2(P\frown P)$ (**62a**) is pseudo-tetrahedral and therefore paramagnetic [154]. The X-ray structure reveals a large Ni⋯O distance (364 pm), indicating the absence of oxygen coordination. This contrasts with the nickel(II) complexes formed with the sulphur or nitrogen analogues of **XIIa**, which are both five-coordinate square-pyramidal species and thus diamagnetic [157,158]. $NiI_2(P\frown P)$ (**62b**) may be isolated from the reaction of NiI_2 and ligand **XIIc** [155]. Its molecular structure is intermediate between square-planar and tetrahedral, in accord with its diamagnetism. Since the corresponding complex with $Ph_2P(CH_2)_8PPh_2$ is pseudo-tetrahedral and paramagnetic [156], Ni–O interaction in **62b** is supposed to be present at least to a small extent. It might be responsible for a stabilization of the coordination geometry about the nickel centre.

Recently, Hill et al. have completed the $NiX_2(P\frown P)$ (**62**) series using **XIIc** as ligand [22]. In contrast with **62b**, the chloride and bromide analogues are pseudo-tetrahedral as evidenced by means of their IR and electronic spectra as well as by their paramagnetism. The crystal structure determination of square-planar *trans*-$[Ni(NCS)_2(P\frown P)]$ revealed rather large Ni–O distances (306.3 and 319.7 pm), indicating that there is no significant interaction of the two ether oxygens with the nickel atom [22].

The octahedral complex $[NiCl_2(P\frown P)]\cdot 4H_2O$ (**62c**) is readily made from $[Ni(H_2O)_6]Cl_2$ and **XIIc** in ethanol [22]. The shift to lower energy of the $\nu_{as}(C_2O)$ band is strongly suggestive of considerable Ni–O contact in the solid state. However, in dichloromethane solutions, this complex adopts a square-planar geometry with *trans* configuration and uncoordinated oxygens. In contrast with this finding, palladium and platinum complexes of type **62** do not contain metal–oxygen bonds as indicated by IR studies and by X-ray structures of *trans*-$[PdI_2(P\frown P)]$ and *cis*-$[PdCl_2(P\frown P)]$ [23].



62c (solid)



62c (solution)

O,P macrocycles, which strictly speaking fall into the class of ether-phosphine ligands, have been used for the complexation of cobalt(II) and nickel(II). Compounds of cobalt(II), however, are described in Sect. C.(iii).

$NiCl_2$ and $NaBPh_4$ react with the δ isomer of **XVII** (see Sect. B.(i)) to give $[NiCl(\delta\text{-mc})][BPh_4]$ (**63a**) [120]. The electronic spectrum of **63a** shows a broad band at a lower wavenumber (23 000 cm^{-1}) than would be expected for simple square-planar NiP_4 arrangements, which give rise to a lowest energy absorption above 29 000 cm^{-1}. This observation is indicative of considerable Ni–O interaction in the axial direction.

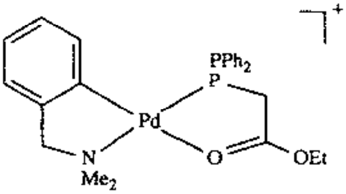
In the compound $[Ni(\varepsilon\text{-mc})_2][BPh_4]$ (**63b**) nickel–oxygen interaction does not occur or is only marginal [120]. Thus, the principal coordination geometry about the nickel centre is square-planar (NiP_4). As expected, the UV/VIS spectra depend on the ability of the solvent to occupy the vacant axial coordination sites. In this respect, acetone is not accommodated but acetonitrile is weakly bound to the nickel atom.

Phosphinoesters (**XXIII**) form palladium and platinum complexes which are similar to those prepared with the aforementioned O,P ligands of the ether-phosphine type. *cis*-$PtCl_2(P\sim O)_2$ and *trans*-$PdCl_2(P\sim O)_2$ ($P\sim O = Ph_2PCH_2COOEt$, **XXIIIa**) are obtained from the reaction of *cis*-$PtCl_2(NCPh)_2$ or *trans*-$PdCl_2(NCPh)_2$ with **XXIIIa** in toluene [130]. Conversion into the corresponding *trans*-diiodides is achieved with NaI in ethanol [75]. *trans*-$PtCl_2(P\sim O)_2$ (**54d**, $P\sim O = {}^tBu_2PCH_2COOEt$, **XXIIIb**) and its palladium analogue, as well as the related compounds with ${}^tBu_2P(CH_2)_2COOEt$ (**XXIIIe**) and ${}^tBu_2P(CH_2)_3COOEt$ (**XXIIIf**), are made in a similar manner [75].

Palladium(II) complexes containing phosphinocarboxylates have been intensively studied by Braunstein et al. In particular, investigation of the chelating and bridging ability of these ligands has been the chief aim of this research work [71,159,160].

As starting materials, the *ortho*-palladated complexes $[(C^\frown N)Pd(\mu\text{-}X)]_2$ have been used. X represents Cl or Br and the C,N chelating ligands are derived from *N,N*-dimethylbenzylamine (dmba) or 8-methylquinoline (8-mq). These chelates may be formally regarded as three-electron donors. They are very resistant to ring-opening and thus only two coordination sites remain available at the palladium centre for the complexation of other ligands. In that way the organometallic systems under investigation are greatly simplified and additionally, the C,N chelates are expected to stabilize species generated in the course of reactions.

Dimeric $[(C^\frown N)Pd(\mu\text{-}X)]_2$ may be cleaved by a phosphinoester, yielding $(C^\frown N)Pd(X)(P\sim O)$ (**64**, $P\sim O = Ph_2PCH_2COOEt$, **XXIIIa**) [159]. Halide abstraction is achieved with $AgPF_6$, leading to O,P-chelated $[(C^\frown N)Pd(P^\frown O)]^+$ (**65**).

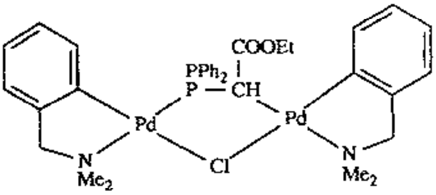


65

Basically, phosphinoesters are capable of displaying various bonding modes in their organometallic compounds. The neutral ligand molecules can be either η^1-bound as in **64** or η^2-bound as in **65**. In the latter case, the carbonyl-oxygen atom is used for coordination.

Moreover, the strong electron-withdrawing property of the ester group leads to CH-acidity of the protons of the adjacent methylene group. Consequently, Ph_2PCH_2COOEt (**XXIIIa**) may be deprotonated with LiNCy^{i}Pr in THF to give $[Ph_2PCHCOOEt]^-$ [159]. This anion, which formally acts as a three-electron donor, is expected to perform interesting coordination chemistry.

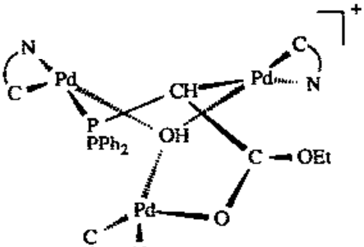
Reaction of $[(C^\frown N)Pd(\mu\text{-}X)]_2$ ($C^\frown N$ = dmba, X = Cl; Cn = 8-mq, X = Br) with $[Ph_2PCHCOOEt]^-$ in a 1:1 molar ratio affords binuclear complexes of the type $(C^\frown N)_2Pd_2(\mu\text{-}X)(\mu\text{-}Ph_2PCHCOOEt)$ (**66**). The molecular structure of **66** ($C^\frown N$ = dmba, X = Cl) has been elucidated by X-ray diffraction [159]. The anionic phosphinoester ligand is encountered in a bridging mode linking the two palladium centres through phosphorus and carbon, the ester group remaining uncoordinated. This complex is quite unusual since it contains two different bridges. The palladium atoms are 388 pm distant from each other and therefore metal–metal interaction can be ruled out.



66

It should be noted that in type **66** compounds the organometallic $(\eta^5\text{-}C_5H_5)Mo(CO)_3$ fragment can take the place of the $[Ph_2PCHCOOEt]^-$ ligand and thus entrance into an interesting chemistry has been found [160].

In the binuclear complexes of type **66**, the halide bridge is indispensable to the maintenance of this unique structure. Abstraction of bromide from $(C^\frown N)_2Pd_2(\mu\text{-}Br)(\mu\text{-}Ph_2PCHCOOEt)$ (**66**, $C^\frown N$ = 8-mq) is achieved with $AgPF_6$ [160]. This reaction causes such a marked destabilization of the complex framework that fragmentation occurs followed by the formation of the trinuclear cationic species **67**. Its interesting structure has been unambiguously established by means of X-ray crystallography [160]. The molecule consists of three Pd(8-mq) units, a μ_3-OH group and the anionic $[Ph_2PCHCOOEt]^-$ ligand in a unique η^3-bridging mode through its P, C and O atoms.



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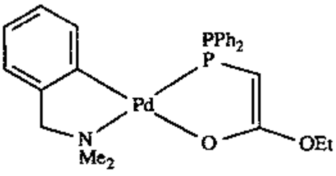
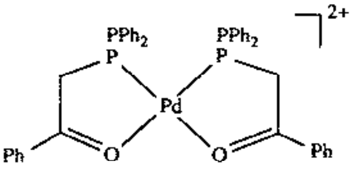


68

If $[(C^\frown N)Pd(\mu\text{-}X)]_2$ is treated with two equivalents of $[Ph_2PCHCOOEt]^-$, mononuclear $[(C^\frown N)Pd(P^\frown O)]$ (**68**) is formed in which the phosphinoester moiety acts as an O,P chelate [159]. An alternative route to such compounds is the deprotonation of the phosphinoester ligand in $[(C^\frown N)Pd(Br)(P{\sim}O)]$ (**64**) with sodium hydride leading to ring closure after internal substitution of the halide by the nucleophilic oxygen atom. Notably, on ring formation five-membered O,P chelates are favoured over three-membered C,P chelates. X-ray structures of **66**–**68** reveal that the phosphorus atoms are always found in the *trans* position with respect to nitrogen. The shortening of the P–C bond in **68** is suggestive of an electron delocalization within the O,P chelate ring.

With regard to their coordination chemistry, β-ketophosphines bear some resemblance to the previously described phosphinocarboxylates. Ligands of both classes are capable of using their carbonyl oxygen atoms as an additional donor function and, due to their CH-acidity, they form anionic species which in turn display ligating properties. Ketophosphine complexes of the type $MX_2(P{\sim}O)_2$ (**69**) are known for nickel, palladium and platinum [61,66,68]. *Trans*-$NiCl_2(P{\sim}O)_2$ (**69a**, $P{\sim}O = Ph_2PCH_2C(O)Ph$, **XXa**) is readily obtained as a violet precipitate from the reaction of $NiCl_2 \cdot 6H_2O$ and **XXa** in ethanol. The X-ray structures of **69a** and of the analogous *trans*-$NiI_2(P{\sim}O)_2$ corroborate the expected square-planar environment of the nickel atom [61]. The absence of oxygen coordination may be concluded from the large Ni–O distances (323 pm). The corresponding palladium compound $PdCl_2(P{\sim}O)_2$ (**69b**, $P{\sim}O = $ **XXa**) is made by treating $PdCl_2(SEt_2)_2$ or $PdCl_2(NCPh)_2$ with two equivalents of **XXa** [61]. Due to a rapid equilibrium, a mixture of the *cis* and *trans* isomers is formed whereas the platinum analogue is obtained as pure *cis*-$PtCl_2(P\sim O)_2$ (**69c**, $P\sim O$ = **XXa**). The use of a 1:1 molar ratio of $PdCl_2(NCPh)_2$ and **XXa** leads to the chloro-bridged dimer $[Pd(P\sim O)Cl(\mu\text{-}Cl)]_2$ (**70**). Removal of both chlorides from $PdCl_2(P\sim O)_2$ (**69b**) with $AgBF_4$ affords [*cis*-$Pd(P^\frown O)_2]^{2+}$ (**71**) with both oxygens coordinated. Deprotonation of type **69** complexes with NaOEt in ethanol or NaH in THF results in the formation of the corresponding phosphinoenolato complexes of the general type $M(P^\frown O)_2$ (**72**). The nickel compound *cis*-$Ni(P^\frown O)_2$ (**72a**, $P^\frown O = Ph_2PCH{=}C(Ph)O$), for which an X-ray structure has been done, has also been prepared in a different way by reacting $Ni(COD)_2$ and the phosphorus ylide $Ph_3P{=}CHC(O)Ph$ (**XXII**) in the presence of $AsPh_3$ [161].



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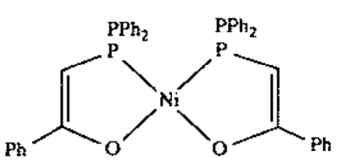


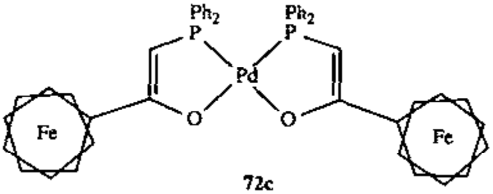
72a

The orange, chloro-bridged palladium complex $[Pd(P^\frown O)(\mu\text{-}Cl)]_2$ (**73**, $P^\frown O = Ph_2PCH{=}C(Ph)O$) is obtained by deprotonation of $[Pd(P\sim O)Cl(\mu\text{-}Cl)]_2$ (**70**) [61]. **73** undergoes bridge-cleavage upon treatment with PPh_3 to give $Pd(P^\frown O)(Cl)PPh_3$ containing the two phosphorus atoms in a *trans* arrangement.

In contrast to $Ph_2PCH_2C(O)Ph$ (**XXa**), the more bulky ketophosphines $^tBu_2PCH_2C(O)R$ (R = Ph (**XXd**), ^{t}Bu (**XXe**)) lead directly to orange-yellow *trans*-$Ni(P^\frown O)_2$ (**72b**, $P^\frown O = {}^tBu_2PCH{=}C(R)O$) upon reaction with $NiCl_2\cdot 6H_2O$ in ethanol [68]. The corresponding palladium and platinum complexes, however, are prepared by treatment of *trans*-$MCl_2(P\sim O)_2$ (**69**, M = Pd, Pt, $P\sim O$ = **XXd,e**) with a strong base, viz. $MeOCH_2CH_2ONa$.

Phosphinoenolato complexes of palladium containing the *ortho*-metallated C,N moiety dmba or 8-mq have been thoroughly investigated by Braunstein and his coworkers [61,66,162–164]. These C,N chelates block two vicinal coordination sites and thus only two sites remain left to be occupied by other ligands. As expected, ketophosphine complexes of the type $(C^\frown N)PdX(P\sim O)$ (**74**) are known which can be transformed into the cationic species $[(C^\frown N)Pd(P^\frown O)]^+$ by halide elimination assisted by $AgCF_3SO_3$ [66]. On the other hand, deprotonation of **74** leads to phosphinoenolato complexes $(C^\frown N)Pd(P^\frown O)$ (**75**, $C^\frown N$ = dmba, $P^\frown O = Ph_2PCH{=}C(Ph)O$).

A most promising field of research deals with the preparation and characterization of polymetallic systems. In recent years, much effort has been made to investigate compounds whose metal atoms are not directly linked by metal–metal bonds but are held at a close distance with the help of an appropriate ligand system. In this regard, substituted metallocenes are expected to display interesting properties and future applications. As described above for the conventional ketophosphines **XXa,d,e**, the ferrocenyl-substituted derivative **XXc** forms complexes of the type **69**, viz. *cis*- and *trans*-$PdCl_2(P{\sim}O)_2$ (**69d**, $P{\sim}O = $ **XXc**) [62]. For the *trans* isomer, a crystal structure determination has been carried out. It shows that the cyclopentadienyl rings are slightly staggered (10.5°) and the structural features are suitable for a conjugation of the keto groups and the aromatic rings. Sodium hydride converts **69d** into the phosphinoenolato complex $Pd(P\frown O)_2$ (**72c**).



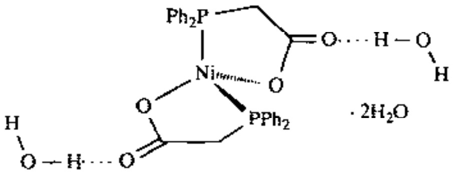
72c

Finally, it should be noted that Taylor and Carty have reported the synthesis of a palladium phosphinoenolato complex by controlled hydrolysis of *cis*-$[PdCl_2(Ph_2PC{\equiv}CCF_3)_2]$. Thus $PdCl(P\frown O)(Ph_2PC{\equiv}CCF_3)$ ($P\frown O = Ph_2PCH{=}C(CF_3)O$) is obtained and its structure has been confirmed by X-ray diffraction [165].

Free phosphinocarboxylic acids are rather versatile ligands [72,166–171]. They are liable to deprotonation and thus acid–base equilibria are established which are strongly dependent on the acidity of the reaction medium and the solvent polarity.

In its undissociated form, Ph_2PCH_2COOH (**XXIVa**) gives rise to a series of complexes of the type $MX_2(P{\sim}O)_2$ (**76**, M = Ni, Pd, Pt; X = Cl, Br, I, SCN). $NiCl_2(P{\sim}O)_2$ is made by reacting an ethanolic solution of $NiCl_2 \cdot 6H_2O$ with **XXIVa** in acetic acid. This diamagnetic, air-stable compound contains two η^1-P bonded ligand molecules in a *trans* square-planar geometry [166]. *trans*-$PdX_2(P{\sim}O)_2$ is made in a similar manner and upon treatment with Na_2PdX_4, dimeric $Pd_2X_4(P{\sim}O)_2$ is generated [167]. For the preparation of *cis*-$PtX_2(P{\sim}O)_2$ from $PtX_2(NCPh)_2$ and **XXIVa**, toluene is used as solvent to avoid dissociation of the COOH group [72].

Under conditions favourable for ligand deprotonation, complexes of the type $M(P\frown O)_2$ ($P\frown O = Ph_2PCH_2COO$) are readily formed. The X-ray structure of the palladium compound $Pd(P\frown O)_2$ reveals a distorted *cis* square-planar environment of the metal centre and almost two coplanar chelate rings [168]. $Ni(P\frown O)_2 \cdot 4H_2O$ (**77**, $P\frown O = Ph_2PCH_2COO$) is paramagnetic ($\mu_{eff} = 3.41$ B.M. at 25°C) and additional supportive evidence for the presumed pseudo-tetrahedral structure is provided by its electronic spectrum [166].



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Phosphinocarboxylato complexes are also obtained from the corresponding compounds containing anionic phosphinoesters as ligands. Thus, (C⌒N)Pd(P⌒O) (**68**, P⌒O = $Ph_2PCHCOOEt$, or $Cy_2PCHCOOEt$, derived from **XXIIId**) is easily hydrolyzed to give (C⌒N)Pd(P⌒O) (**78**, P⌒O = Ph_2PCH_2COO) [132].

The nature of the Pt–O bond has been the subject of a series of papers [172–176]. In the course of these studies, special interest has been devoted to platinum(II) and palladium(II) complexes with alcohols and alkoxides. Thermodynamic reasoning should lead to the assumption that Pt–O and Pd–O bonds are rather weak due to an incompatibility of the 'soft' (class b) metal centre and the 'hard' oxygen donors [177–179]. Indeed, the preparation of late transition metal alkoxides has met with difficulties because of their notorious moisture and thermal sensitivity. However, since Pt–O bond energies are comparable with Pt–C bond energies, this instability must be due to kinetic reasons [180].

Simple alkoxoplatinum complexes, e.g. (dppe)$Pt(OMe)_2$, readily decompose at ambient conditions via β-hydride elimination [175], and it may be anticipated that this reactivity might be overcome if possible decomposition pathways are precluded. In search of model compounds suitable for the study of Pt–O bonds, alkoxo chelate complexes have been found to exhibit a striking kinetic inertness relative to their non-chelated analogues. The chelated glycolate complex (dppe)$Pt(OCH_2CH_2O)$, for example, shows no decomposition even after three days at 120°C whereas (dppe)$Pt(OMe)_2$ readily undergoes thermolysis at 30°C [175].

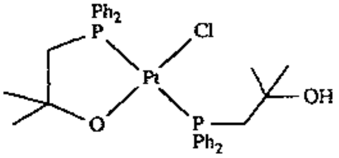
These facts render the potentially O,P-chelating phosphinoalcohols and phosphinoalkoxides to be promising ligands for the examination of Pt–O interactions. Pringle, Payne and Willis and their coworkers have made considerable contributions to this field of research.

Treatment of $PtCl_2(NC^tBu)_2$ with $Ph_2PCH_2CH_2OH$ (**XXVa**), $Ph_2PCH_2CHMeOH$ (**XXVd**) or $Ph_2PCH_2CMe_2OH$ (**XXVb**) yields the complexes **79a**, **79b** and **79c**, respectively, which are all of the type *cis*-$PtCl_2(P{\sim}O)_2$ (**79**) [76,181,182]. **79c** is also obtained from the reaction of (COD)$PtCl_2$ and **XXVb**, whereas the corresponding *trans* isomer

79d is made from Zeise's salt, $\mathrm{K[PtCl_3(C_2H_4)]}$, and **XXVb** in acetone [76].

Although alcohols are rather poor ligands for platinum(II), partial displacement of chloride by an alcohol group occurs in polar solvents to give $\mathrm{[PtCl(P^\frown O)(P{\sim}O)]^+Cl^-}$ (**80**), which forms an equilibrium with $\mathrm{PtCl_2(P{\sim}O)_2}$ (**79**) [182]. This observation points out that the coordination ability towards platinum(II) of ether-phosphines is even less distinct since in this case halide-abstracting reagents must be applied to achieve O,P chelation. Compounds of type **80** exhibit fluxional behaviour [76], details of which are outlined in Sect. C.(v).

Chloride abstraction with $\mathrm{AgClO_4}$ transforms *cis*-$\mathrm{PtCl_2(P{\sim}O)_2}$ (**79**) into the dications *cis*-$\mathrm{[Pt(P^\frown O)_2]^{2+}}$ (**81**). By contrast, *trans*-$\mathrm{PtCl_2(P{\sim}O)_2}$ (**79d**, $\mathrm{P{\sim}O = Ph_2PCH_2CMe_2OH}$, **XXVb**) only gives the monocation [*trans*-$\mathrm{PtCl(P^\frown O)(P{\sim}O)]^+}$ and deprotonation with $\mathrm{NEt_3}$ leads to the monoalkoxo chelate complex *trans*-$\mathrm{PtCl(P^\frown O)(P{\sim}O)}$ (**82**) [76].



82

Upon treatment with the moderately strong base $\mathrm{NEt_3}$, $\mathrm{PtCl_2(P{\sim}O)_2}$ (**79a**, $\mathrm{P{\sim}O = Ph_2PCH_2CH_2OH}$, **XXVa**) is mono-deprotonated. The resulting compound is binuclear in solution and is unique for its unsymmetrical alkoxo bridge [181]. On the other hand, the reaction of **79b,c** with $\mathrm{NEt_3}$ directly proceeds to the bisalkoxo chelates *cis*-$\mathrm{Pt(P^\frown O)_2}$ (**84**).

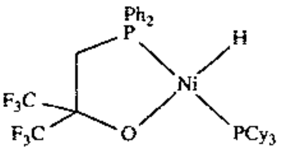
These compounds are extremely stable, including the one formed with $\mathrm{Ph_2PCH_2CH_2OH}$ (**XXVa**). This lends support to the hypothesis that the major contribution to the stability of alkoxo complexes comes from the chelate ring and therefore, the absence of β-hydrogens is not mandatory [181]. An X-ray study made on *cis*-$\mathrm{Pt(P^\frown O)_2}$ (**84a**, $\mathrm{P^\frown O = Ph_2PCH_2CH_2O}$) reveals a Pt–O bond length (202.4 pm) which perfectly agrees with the value expected for a standard single bond [76].

Recently, Platt and Pringle showed that the features of palladium complexes with the aforementioned phosphinoalcohols largely conform to the platinum chemistry discussed above [183].

Payne and coworkers have used the fluorinated phosphinoalcohol $\mathrm{Ph_2PCH_2C(CF)_2OH}$ (**XXVc**) as a ligand which forms complexes similar to those obtained with the related non-fluorinated alcohols of category **XXV** [77,184,185]. The square-planar bischelate $\mathrm{Ni(P^\frown O)_2}$ (**85**, $\mathrm{P^\frown O =}$

$Ph_2PCH_2C(CF_3)_2O$) has attracted great attention [77]. The orange solution of **85** contains a mixture of the *cis* and *trans* isomers. The thermochromic behaviour of the solid complex (25°C: green, 200°C: orange) suggests a specific solid-state interaction. An X-ray structure determination of **85** established the existence of two types of molecule with different ring conformations. In one case, a close approach of the CF_3 groups to the metal centre causes an additional weak Ni–F interaction which leads to a change in the electronic spectrum.

Reaction of $Ni(COD)_2$ with $Ph_2PCH_2C(CF_3)_2OH$ (**XXVc**) in the presence of PCy_3 gives the hydrido complex $NiH(PCy_3)(P\frown O)$ (**86**, $P\frown O = Ph_2PCH_2C(CF_3)_2O$) [186]. Similar, but coordinatively unsaturated, reactive species are most likely to play an important role in the nickel-catalyzed oligomerization of olefins (see Sect. E.(i)). However, the bulky PCy_3 ligand strongly stabilizes this compound.



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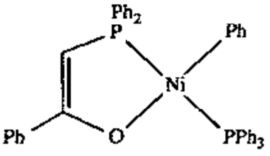
Recently, Shaw and coworkers have used bisphosphine monoxides as ligands for **Pt(II)** and Pd(II) [85]. Reaction of *cis*-$PtCl_2(P{\sim}O)_2$ ($P{\sim}O$ = **XXVIIa,c**) with $AgNO_3$ or $TlPF_6$ affords the dicationic bischelates [*cis*-$Pt(P\frown O)_2]^{2+}$, which contain a five- or six-membered ring. Oxygen coordination failed in the case of bisphosphine monoxides with a longer chain due to the oversize of the expected chelate ring. For the complex [*trans*-$PtCl(PEt_3)(P\frown O)][ClO_4]$ ($P\frown O = {}^tBu_2PCH_2P(O)Me_2$, **XXVIII**) a crystal structure is available [86].

The reaction of phosphorus ylids with zero-valent nickel has proved to be most interesting. Treatment of $Ni(COD)_2$ with $Ph_3P{=}CHC(O)Ph$ (**XXII**) in the presence of a stabilizing ligand L, e.g. PPh_3 or pyridine, leads to an oxidative addition of the ylid via its PPh_3 moiety to give $Ni(Ph)(P\frown O)L$ (**87**, $P\frown O = Ph_2PCHC(Ph)O$) [60,65,161]. Hence, the migration of a phenyl group generates a Ni–Ph bond. The O,P chelate ring represents a phosphinoenolato ligand and considerable electron delocalization within this chelate is evidenced by X-ray studies [161]. By contrast, in the presence of $AsPh_3$, $Ni(COD)_2$ and **XXII** afford *cis*-$[Ni(P\frown O)_2]$ (**72a**, $P\frown O = Ph_2PCHC(Ph)O$) and omission of any stabilizing ligand does not generate a three-coordinate nickel species but dimerization occurs to give $[Ni(Ph)(P\frown O)]_2$ (**88**, $P\frown O = Ph_2PCHC(Ph)O$) [60].



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(v) Dynamic behaviour of hemilabile O,P complexes

Fluxional isomerism [187], also called stereochemical non-rigidity [188], is one of the most outstanding properties of some complexes which contain hemilabile ligands in their coordination sphere. Among these, compounds with both monodentate and chelating O,P ligands are particularly susceptible to fluxionality. This is the case if the structure of the complex is such that it allows the oxygen donor atoms belonging to different O,P ligands to compete for a common coordination site. In this connection, fluxionality may be regarded as an entirely reversible, intramolecular mutual substitution reaction in which donor atoms of the same kind are involved. This is an excellent example of the so-called 'opening and closing mechanism' [12], which clearly demonstrates the lability of the metal–oxygen bond.

Since no major structural changes are necessary to interconvert the corresponding species, the activation enthalpy of such processes is comparatively low. At suitable temperatures, the rate of these dynamic exchanges is slow enough to be monitored by physical methods. NMR spectroscopy, especially ^{31}P NMR, is a very powerful tool for the investigation of such dynamic phenomena.

Among the ruthenium complexes presented in Sect. C.(ii) there are two main types which meet the above-mentioned requirements for fluxionality. These are $\mathrm{RuX_2(P^\frown O)(P\sim O)_2}$ with $\mathrm{X=H}$ (**11**) or Cl (**8**) [101,102,112,115], and the monocarbonyl compounds $\mathrm{RuCl_2(CO)(P^\frown O)(P\sim O)}$ (**5**) [101].

As a representative of the former group, the dynamic behaviour of *trans*-$\mathrm{RuH_2(P^\frown O)(P\sim O)_2}$ (**11**) with $\mathrm{P^\frown O = Ph_2PCH_2CH_2OMe}$ (**Ia**) is discussed here [102,115]. To this end, $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectra of this compound have been recorded between −95 and +35°C. The spectra obtained at different temperatures are plotted in Fig. 1.

In order to interpret these spectra, proposed pathways for this dynamic behaviour are delineated in Scheme 7 using key compounds whose structures are in keeping with the observed spectra.

Below −90°C, a solution of $\mathrm{RuH_2(P^\frown O)(P\sim O)_2}$ (**11**) containing the ether-phosphine **Ia** gives rise to an ABX pattern in the $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum. This is consistent with an octahedral geometry with the two hydride ligands in the *trans* position, one chelating and two monodentate

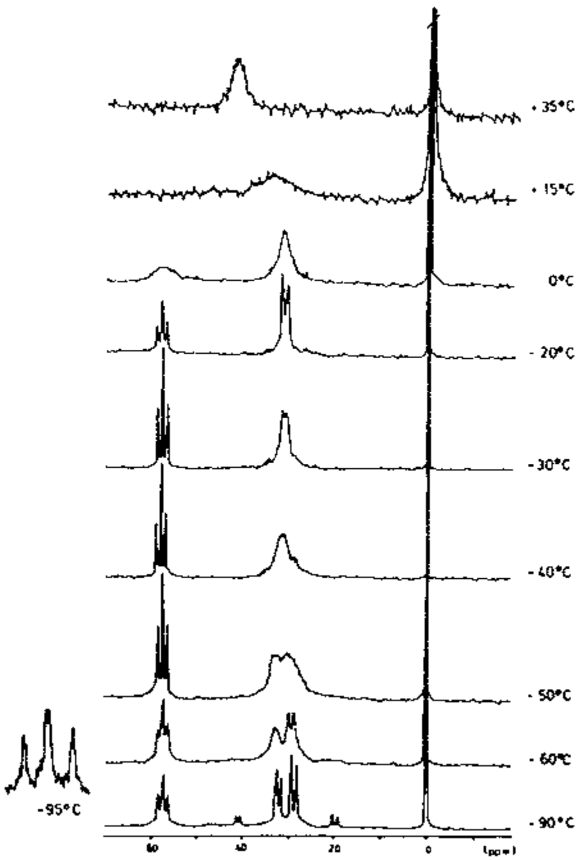
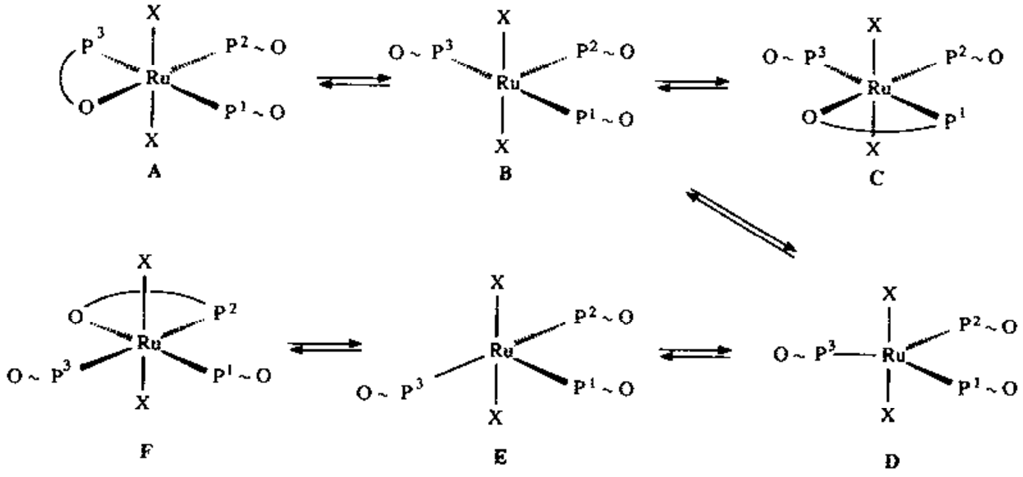


Fig. 1. Variable-temperature $^{31}P\{^{1}H\}$ NMR spectra of $RuH_2(P\frown O)(P\sim O)_2$ (11).



Scheme 7. Dynamic behaviour of ruthenium(II) complexes of the type $RuX_2(P\frown O)(P\sim O)_2$.

O,P ligands, according to the structures A, C and F sketched in Scheme 7. In this arrangement, the pseudo-triplet at 57 ppm, which actually consists of two non-resolved doublets, is caused by the phosphorus atom *trans* to the coordinated oxygen atom (P^2 in structure A), whereas the AB part is due to the mutually trans-positioned phosphines (P^1 and P^3 in structure A). The low-field part of this AB pattern is assigned to the phosphorus atom which is incorporated in the O,P chelate since ring closure is known to cause an additional downfield shift [97,98].

On raising the temperature, rupture of the labile Ru–O bond becomes significant and the oxygen atom of the adjacent O,P ligand can now occupy the vacant coordination site previously formed by cleavage of the chelate ring. In this way, the oxygen atoms of the *trans*-phosphines A and C compete for this common site causing a permanent ring opening and closing of the corresponding O,P ligands.

At −40°C the signals of the AB pattern coincide to give a point of coalescence. This indicates that the interconversion of species A and C has become so fast within the NMR time scale that P^1 and P^3 can no longer be distinguished by this method. The observed A_2X spectrum and the $^2J_{P-P}$ coupling constant of 34 Hz, characteristic of *cis*-phosphines, is consistent with this.

The species **B** more likely adopts a distorted square-pyramidal geometry (C_{4v}) than a trigonal bipyramidal one (D_{3h}), even though these two structures are easily interconverted via the vibrations E' ($D_{3h} \rightarrow C_{4v}$) or B_1 ($C_{4v} \rightarrow D_{3h}$). According to theoretical considerations based upon symmetry arguments, the square-based pyramid is favoured over the trigonal bipyramid in the case of d^5 and d^6 low-spin systems [189]. Moreover, a dynamic exchange process between A and C via a C_{4v}-configurated intermediate or transient B is most likely, since in this case no significant energy-demanding structural changes, e.g. angle distortions, are necessary. This assumption may illustrate the operation of Hine's 'principle of the least motion' [190].

Around room temperature, all three phosphorus atoms appear to be equal in the ^{31}P NMR spectrum, showing only a broad singlet. In order to explain the participation of all phosphines in a dynamic exchange process, an equilibrium between different square pyramidal species is supposed to be established. Thus, as depicted in Scheme 7, B and E can be transformed into each other via a trigonal bipyramidal structure D. The sequence B→D→E is similar to the well-known Berry pseudorotation with the difference that in the case at hand, the five-coordinate species are subject to coordinative saturation by the formation of an O,P chelate ring to give F.

By analogy with the equilibrium between A and F, which averages P^2 and P^3 within the NMR time scale, similar pathways are to be considered to account for the scrambling of all *cis*-phosphines. Due to the greater angle distortions to be performed along these pathways, a higher activation enthalpy and therefore a higher temperature of coalescence is found compared with the corresponding values observed for the exchange of the *trans*-phosphines.

The dichloride compounds $RuCl_2(P\frown O)(P\sim O)_2$ (**8**) exhibit a dynamic behaviour, which is very similar to that of the analogous dihydride discussed above [102,112]. However, depending on the O,P ligand present in the molecule, special features arise which merit further consideration. In the case of the ruthenium complexes with the ether-phosphines **IIe** and **IIId**, which are endowed with a tetrahydrofuran and dioxan ring, respectively, the chirality at the α-carbon atoms of the ether moieties give rise to the formation of diastereoisomers. Due to this fact, additional sets of NMR resonances are observed which make the spectra rather complicated. It is noteworthy that upon coordination to a metal centre, the oxygen atom of an ether-phosphine becomes chiral due to three different substituents in a non-planar arrangement. This would generate further diastereoisomers which are suspected to be responsible for the additional resonances observed below −60°C for the complex $RuCl_2(P\frown O)(P\sim O)_2$ (**8**, $P\frown O = Me_2PCH_2C_4H_7O_2$, **IIId**).

In addition to the common behaviour discussed above, Braunstein et al. have reported a low-energy exchange process for $RuCl_2(P\frown O)(P\sim O)_2$ ($P\frown O = Ph_2PCH_2COOEt$, **XXIIa**), which occurs around −80°C. It was attributed to conformational changes within the ligand framework [113].

The monocarbonylruthenium complexes $RuCl_2(CO)(P\frown O)(P\sim O)$ (**5**) contain two *trans*-phosphines, one of which is monodentate, the other bidentate coordinated. Hence, fluxionality is expected due to a dynamic exchange process of the two ether side arms by analogy with the interconversion of species A and C of Scheme 7 [101]. If the complexes of type **5** contain chiral ether-phosphines, viz. **IIa**, **IIIa**, two diastereoisomers are expected which can be distinguished in the $^{31}P\{^1H\}$ NMR spectrum. Each diastereoisomer gives rise to an AB pattern whose signals become broader and eventually coalesce upon heating the sample.

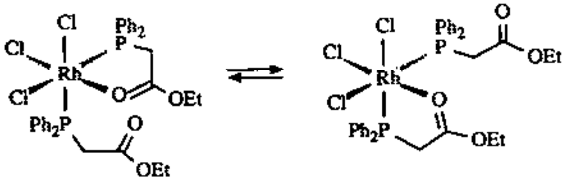
Similar behaviour has been established for [*trans*-$Pd(Cl)(P\frown O)(P\sim O)]^+$ ($P\frown O$ = **Ia**, **IIa**, **IIIa**) [151]. Due to the *trans* arrangement of the phosphorus atoms, the two ether oxygens may compete for a common coordination site. Table 6 compiles temperatures of coalescence and activation enthalpies of some fluxional complexes. These parameters are a measure of the ability of ethereal oxygens to coordinate to a particular metal centre. As expected, they depend on the nature of both the ligand and the metal, but a satisfactory theoretical interpretation of the experimental data has not yet been found. However, the nucleophilicity of the oxygen atom [101] as well as the steric properties of the ligand backbone must be regarded as important factors.

TABLE 6

Coalescence temperatures (T_C) and activation enthalpies of fluxional complexes

Complex	Ligand	T_C (°C)	$\Delta G^{\neq}$ (kJ mol^{-1})
$RuCl_2(P\frown O)(P\sim O)_2$	**Ia**	−15	49.1
		40	56.9
	Id	−15	47
	IIe	15	47
	IIId	−10	48.5
$RuH_2(P\frown O)(P\sim O)_2$	**Ia**	−40	43.7
$RuCl_2(CO)(P\frown O)(P\sim O)$	**Ia**	55	59
	IIa	80	65
	IIIa	10	52
fac-$RhCl_3(P\frown O)(P\sim O)$	**XXIIIa**	52	64.3 (^1H NMR)
		72	67 (^{31}P NMR)
[*trans*-$PdCl(P\frown O)(P\sim O)]^+$	**Ia**	10	53.9
	IIa	−20	48.3
	IIIa	30	58.7

Among the fluxional rhodium compounds, fac-$RhCl_3(P\frown O)(P\sim O)$ (**28a**) with $P\frown O = Ph_2PCH_2COOEt$ (**XXIIIa**) is well-described and is presumably the most prominent example [130]. As depicted in Scheme 8, the ester moieties of the two vicinal phosphinoester ligands in this compound compete for a common coordination site at the rhodium centre using their carbonyl oxygens as donor atoms. The stereodynamic behaviour of **28a** may be monitored both by means of ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. At low temperatures (−2°C), the interconversion $A \rightleftharpoons B$ is slow within the NMR time scale and therefore A and B are discernible in the NMR spectra. Two separate sets of proton resonances are observed which arise from the two unequally bound O,P ligands. Each set of signals consist of a doublet, a quartet and a triplet due to the presence of the $P{-}C\underline{H}_2$, $C\underline{H}_2CH_3$ and



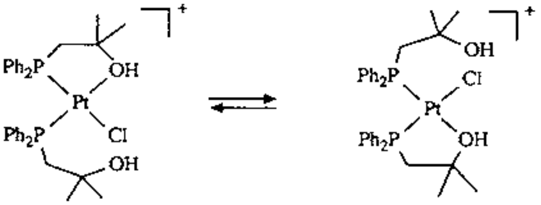
A **B**

Scheme 8. Dynamic behaviour of $RhCl_3(P\frown O)(P\sim O)$ (**28a**).

$CH_2C\underset{\cdot}{H}_3$ hydrogens, respectively. As expected, the $^{31}P\{^1H\}$ NMR spectrum shows eight resonances which stem from the two unisochronous phosphorus atoms, the signals of which are split into doublets of doublets due to Rh–P and P–P coupling. Notably, the small value of $^2J(P–P)$ (23.5 Hz) indicates a *cis* arrangement of the phosphorus atoms. A rise in temperature causes a point of coalescence in both the ^1H and the $^{31}P\{^1H\}$ NMR spectrum due to the averaging of the two O,P ligands. In the former case, coalescence occurs at 52°C, in the latter case at around 72°C. The calculated values of the free activation enthalpy $\Delta G^{\neq}$ are 64.3 and 67 kJ mol^{-1}, respectively. As these values are identical within the experimental error, the same mechanism is assumed to be responsible for the phenomena observed in the ^1H and ^{31}P NMR spectra. As a change in the concentration of **28a** has no effect on the spectral properties, this mechanism is most likely to be intramolecular. Moreover, since a constant Rh–P coupling is maintained throughout the temperature range of the NMR experiments, Rh–P bond rupture can be ruled out.

An example of a fluxional platinum(II) complex has been reported by Pringle and coworkers [76]. In polar solvents, viz. $CDCl_3$ or CD_3OD, *cis*-$PtCl_2(P{\sim}O)_2$ (**79c**, $P{\sim}O = Ph_2PCH_2CMe_2OH$, **XXVb**) occurs in the ionized form [*cis*-PtCl(P$\frown$O)(P$\sim$O)]$^+$Cl$^-$ (**80**). Characteristic of this molecule is an internal exchange process of the two alcohol functions which gives rise to fluxionality. This dynamic behaviour may be monitored in the $^{31}P\{^1H\}$ NMR spectrum. At −40°C it consists of an AX pattern due to one chelated and one non-chelated phosphine ligand. At 25°C a broad singlet with ^{195}Pt satellites indicates coalescence and thus phosphine scrambling. Supportive evidence for the proposed mechanism outlined in Scheme 9 is given by the properties of the cation **80** with PF_6^- as anion and of [$PtCl_2(PMePh_2)(P{\sim}O)$].

With respect to their $^{31}P\{^1H\}$ NMR spectra, the former complex shows striking resemblance to the corresponding chloride salt and the latter is not fluxional owing to the lack of a second O,P ligand required for an exchange process. In methanol, *trans*-$PtCl_2(P{\sim}O)_2$ (**79d**, $P{\sim}O = Ph_2PCH_2CMe_2OH$, **XXVb**) displays a fluxional behaviour similar to that discussed for the *cis*



Scheme 9. Dynamic behaviour of [PtCl(P$\frown$O)(P$\sim$O)]$^+$ (**80**).

isomer **79c**. Accordingly, **79d** occurs in the ionic form [*trans*-$\mathrm{PtCl(P^\frown O)(P\sim O)]^+Cl^-}$ and thus gives rise to an AB pattern at −30°C which is broadened at higher temperatures.

D. REACTIONS OF COMPLEXES CONTAINING HEMILABILE O,P LIGANDS

(i) Oxidative additions

Activation of substrates by organotransition metal compounds has become a most challenging objective for both stoichiometric and catalytic reactions. In this regard, oxidative additions are of outstanding importance because they involve scission of comparatively inert substrate bonds and thus enable further reactions.

An organometallic complex which readily undergoes oxidative additions must fulfil three conditions. First, the metal atom must be able to form at least two oxidation states separated by two units. Secondly, the metal centre must bear a relatively high electron density in order to display the necessary nucleophilicity towards substrate molecules such as methyl iodide. Thirdly, in order to accommodate the two substrate fragments, the parent metal complex must be provided with two vacant coordination sites.

The simultaneous behaviour as both Lewis acid and Lewis base requires an organometallic system which is carefully balanced with respect to electronic and steric factors.

Ligands which increase the electron density at the metal atom should therefore facilitate oxidative additions. In most cases the electronic properties of the metal are influenced by the substituents on the phosphine ligands usually present in such complexes. In this regard, the phosphorus atom acts as a mediator between its substituents and the metal atom which is the centre of reactivity.

However, it could be anticipated that a direct interaction of a strong σ-donor ligand would also significantly increase the electron density at the metal atom and consequently lower the activation barrier of an oxidative addition [54]. This concept is realized by the use of polydentate O,P ligands whose oxygen atoms, if necessary, are capable of performing weak coordinative interaction. An additional oxygen donor is expected to impart great flexibility to the reactive species, e.g. by stabilizing highly polar intermediates or transition states which are frequently involved in many oxidative addition reactions. Moreover, facile displacement of the oxygen-bearing side arm by the incoming substrate regenerates vacant coordination sites. This mechanism has previously been designated as an ‘opening and closing mechanism’. In this section, examples of such chelate-assisted additions will be outlined.

Vaska-type compounds *trans*-IrCl(CO)L_2 have been widely used for the study of oxidative additions. It was found that the rate of addition depends both on the electronic and steric properties of the ligand L. *Para*-substituted arylphosphine ligands, e.g. $Me_2PC_6H_4(OMe\text{-}2)$ (**VII**) presumably differ from their unsubstituted analogues only for electronic reasons. As expected, an electron-donating group Z in such *para*-substituted phenylphosphines increases the rate of oxidative additions significantly in the order $Z = Cl < H < Me < OMe$ [54,191].

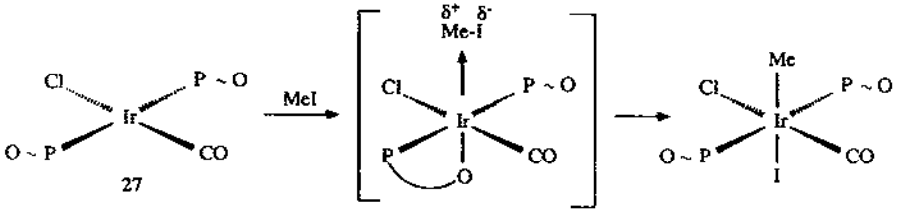
A kinetic study has been carried out for the addition of methyl iodide to Vaska-type compounds *trans*-IrCl(CO)L_2 containing different phosphine ligands [54]. In all cases, the reactions are first-order in both iridium(I) complex and MeI. Table 7 collects the observed values of the rate constants k, $\Delta H^{\neq}$ and $\Delta S^{\neq}$.

TABLE 7

Kinetic data for the oxidative addition of MeI to *trans*-IrCl(CO)L_2 (toluene, 25°C)

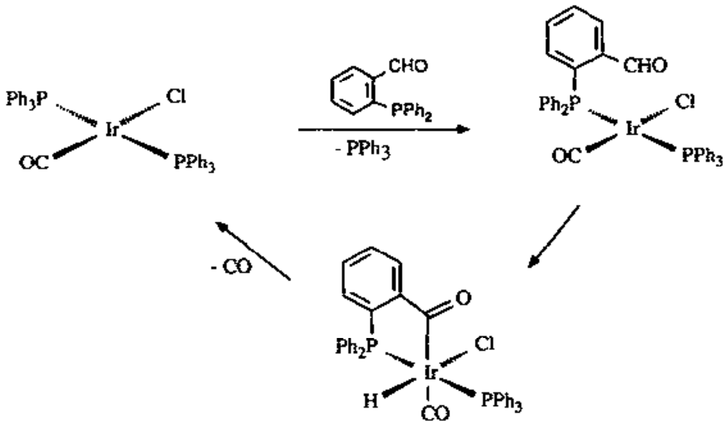
L	$k \times 10^2$ (mol^{-1} s^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J mol^{-1} K^{-1})
Me_2PPh	4.7	46.4	−114
VIa	530	27.6	−133
VII	6.75	38.1	−138

Although the *ortho*-substituted $Me_2PC_6H_4(OMe\text{-}2)$ (**VIa**) should be more sterically hindered than the *para* isomer **VII** its iridium complex reacts about 100 times faster than the other two complexes. These experimental facts may be explained in terms of a direct interaction of the *ortho*-methoxy group with the iridium centre ('anchimeric assistance') as depicted in Scheme 10.



Scheme 10. Direct electronic interaction of an oxygen donor in the course of oxidative additions.

The activation of aldehydes is another striking example of chelate enhancement [100,192]. Simple aldehydes generally show a great reticence to undergo an oxidative addition with the formation of acyl hydrides. However, complexes containing *ortho*-phosphinoaldehydes, viz. phosphinobenzaldehyde (**XXI**), are liable to chelate-assisted oxidative addition of the aldehyde group to the metal centre [100]. The sequence of reactions leading to decarbonylation of the aldehyde is outlined in Scheme 11.



Scheme 11. Chelate-assisted oxidative addition of phosphinoaldehydes to iridium(I).

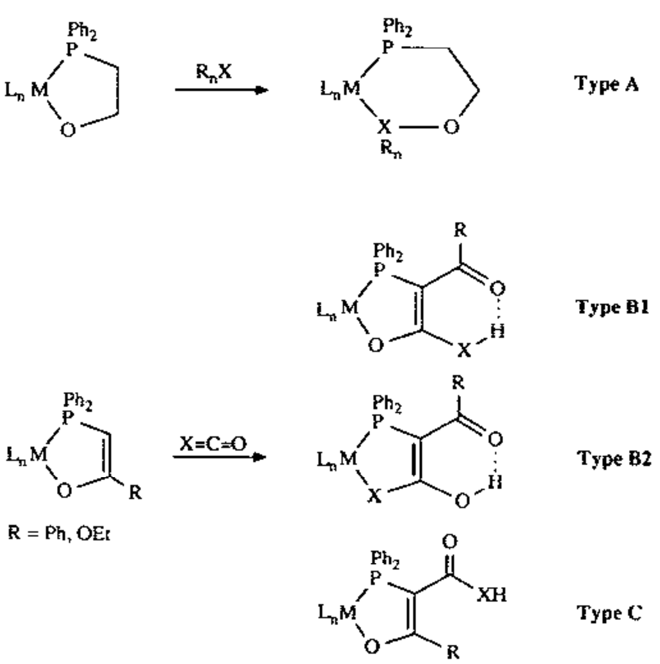
In contrast to the iridium compounds of Scheme 11, thermolysis (250°C) of *cis*-$PtCl_2(P{\sim}O)_2$ ($P{\sim}O = Ph_2PC_6H_4(CHO\text{-}2)$, **XXI**) does not give a hydrido complex but an acyl species, HCl being evolved. On the other hand, $RuCl_2(P\frown O)_2$ (**4e**, $P\frown O = Ph_2PC_6H_4(CHO\text{-}2)$, **XXI**) is transformed into thermodynamically stable *cis,cis,trans*-$RuCl_2(CO)_2(PPh_3)_2$ [100].

(ii) Insertion reactions

Reactions in the course of which a molecule is inserted into a covalent bond, especially into a metal–ligand bond, are an important means of substrate activation. Many reactions of this kind are known but those presented in this section exclusively involve complexes containing O,P ligands. Due to the ease of metal–oxygen bond cleavage often observed in these complexes, this bond should play a pivotal role for such insertions.

According to the type of substrate and its binding mode, different reaction products may be obtained as outlined in Scheme 12.

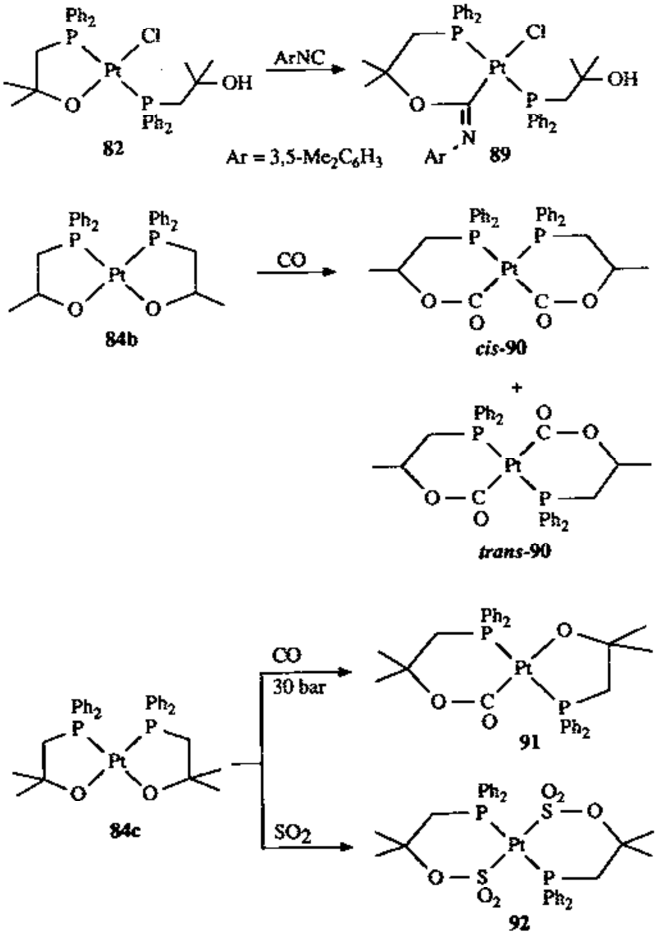
Type A involves molecules which are bound via a single atom X. Type B or C are formed with alkynes or cumulenes X=C=O, B1 and B2 containing M–O or M–X bonds, respectively. Insertions into the C–H bond of the carbon vicinal to phosphorus lead to type C compounds, the O,P chelate ring being preserved.



Scheme 12. Fundamental pathways for insertion reactions.

Simple O,P complexes whose major centre of reactivity is the metal–oxygen bond exclusively form insertion products of type A, irrespective of the substrate used. To demonstrate this behaviour, the Pt–O bond in platinum(II) alkoxides appears to be a suitable object of study. Notably, some results obtained with platinum(II) alkoxo and hydroxo complexes containing common monodentate oxygen donors have recently been reviewed by Bryndza and Tam [193]. Pringle and his coworkers have investigated insertion reactions using phosphinoalkoxo platinum(II) complexes [182,194]. Typical examples are presented in Scheme 13.

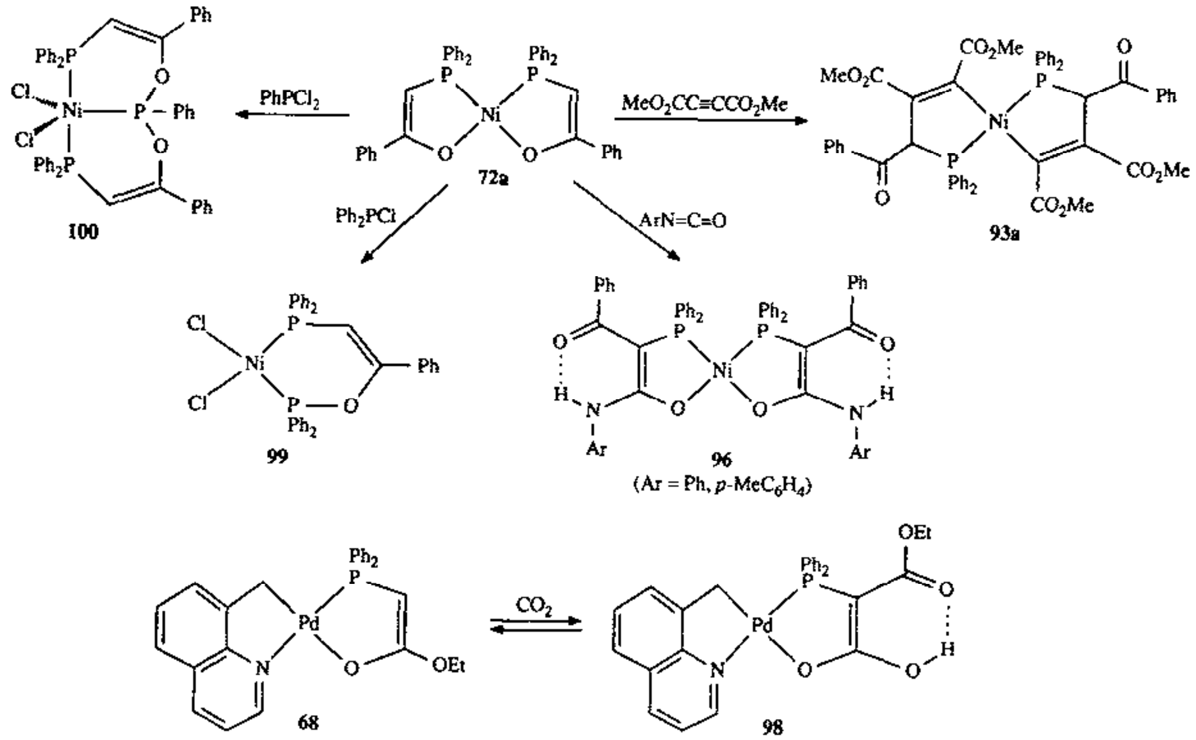
The mono alkoxo chelate compound *trans*-PtCl($P^\frown O$)($P\sim O$) (**82**) readily inserts sulphur dioxide and carbon monoxide under mild conditions (1 bar, 25°C) to give an alkoxysulphonato and alkoxycarbonylato complex, respectively. By analogy, the isocyanide 3,5-$Me_2C_6H_3NC$ leads to an insertion of the terminal carbon atom into the Pt–O bond. The molecular structure of the reaction product **89** has been determined by X-ray crystallography [194]. The environment of the platinum atom is square-planar with mutually *trans*-phosphines, one of them being incorporated in the almost planar six-membered chelate ring. The ring-expansion may also be inferred from the chemical shifts observed in the $^{31}P\{^1H\}$ NMR spectra of the insertion products. They all fall into the range 0–15 ppm relative to H_3PO_4 and thus exclude the presence of five-membered heterocycles.



Scheme 13. Insertion reactions with platinum(II) phosphinoalkoxo complexes.

Upon treatment with carbon monoxide under ambient conditions, the bischelate *cis*-Pt($P\frown O$)$_2$ (**84b**, $P\frown O = Ph_2PCH_2CHMeO$) is converted into the bis insertion product **90**, which is obtained as a mixture of the *cis* and *trans* isomers [194]. The more bulky *cis*-Pt($P\frown O$)$_2$ (**84c**, $P\frown O = Ph_2PCH_2CMe_2O$) is less reactive towards CO under similar conditions and even at higher CO pressures (30 bar) only the mono adduct **91** is formed among other species. The attempt to synthesize the double insertion product also failed in the case of 3,5-$Me_2C_6H_3NC$. In contrast, sulphur dioxide smoothly reacts with **84c** to give **92**. Notably, insertions of SO_2, CO or isocyanides into the Pt–O bonds of type **84** *cis*-bisalkoxo chelate complexes are accompanied, at least to some extent, by a *cis–trans* isomerization.

The rate-determining step is most likely the formation of a five-coordinate



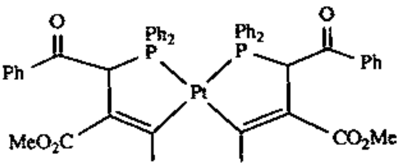
Scheme 14. Insertion reactions with nickel(II) and palladium(II) phosphinoenolato complexes.

species (associative mechanism) since ligands which increase the Lewis acidity of the parent complex facilitate the reaction whereas electron donors such as CH_3 have an inhibiting effect [194].

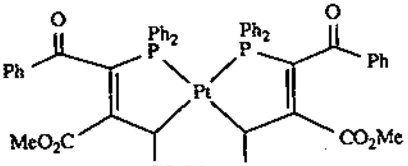
The reaction pathways leading to type B or type C compounds (see Scheme 12) require an O,P chelate complex containing a nucleophilic centre α to the phosphorus atom in addition to a labile M–O bond. This prerequisite of ambidentate behaviour is fulfilled in phosphinoenolato complexes owing to the electron delocalization in such systems. Scheme 14 gives a survey of coupling reactions, illustrating their versatility.

Treatment of *cis*-$Ni(P^\frown O)_2$ (**72a**, $P^\frown O = Ph_2PCH{=}C(Ph)O$) with dimethyl acetylenedicarboxylate, $MeO_2CC{\equiv}CCO_2Me$, affords the stable, orange compound **93a** [162,195]. As a result of the carbon–carbon bond formation, a centre of chirality is generated in each chelate ring, giving rise to diastereoisomers. Interestingly, some other alkynes, e.g. $HC{\equiv}CH$, $PhC{\equiv}CPh$, and $F_3CC{\equiv}CCF_3$, are unreactive towards **72a**. The phosphorus atoms in **93a** are in a mutual *trans* arrangement. By contrast, *cis*-$Pd(P^\frown O)_2$ ($P^\frown O = Ph_2PCH{=}C(Ph)O$) and $MeO_2CC{\equiv}CCO_2Me$ afford the analogous bis insertion product with *cis* phosphorus atoms which may be converted into the thermodynamically more stable *trans* isomer for which an X-ray structure determination has been carried out [195].

cis-$Pt(P^\frown O)_2$ ($P^\frown O = Ph_2PCH{=}C(Ph)O$) is much less reactive towards $MeO_2CC{\equiv}CCO_2Me$ than its nickel and palladium homologues. In refluxing THF, a mixture of the mono and bis insertion product is obtained and even at higher temperatures (boiling toluene) the initially formed bis-alkenyl complex **93b** isomerizes to the bis-η^1-allyl complex **94** as a result of a 1,3-H shift [162,195].



93b



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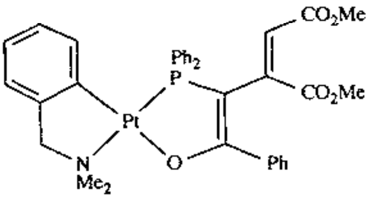
Another kind of rearrangement has been observed on heating the coupling product of $(C^\frown N)Pd(P^\frown O)$ (**75**, $C^\frown N$ = dmba; $P^\frown O = Ph_2PCH{=}C(Ph)O$) and $MeO_2CC{\equiv}CCO_2Me$. Re-formation of the O,P chelated phosphinoenolato ligand leads to an expansion of the conjugated system to give compound **95**, which may formally be regarded as a type C insertion product (see Scheme 12) [195].

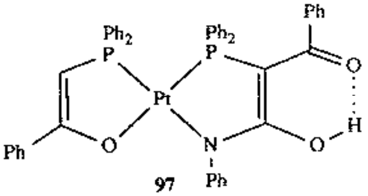


95

Arylisocyanates are rather reactive heterocumulenes [196]. Due to their unsymmetrical structure, different isomeric coupling products are basically expected to be formed.

As depicted in Scheme 14, treatment of *cis*-$\mathrm{Ni(P^\frown O)_2}$ (**72a**, $\mathrm{P^\frown O = Ph_2PCH{=}C(Ph)O}$) with ArN=C=O (Ar = Ph, *p*-$\mathrm{MeC_6H_4}$) yields the bis-insertion product **96**, the *cis* configuration of the phorphorus atoms being retained [163]. Only one isomer (B1, see Scheme 12) is formed, presumably by an attack of the nucleophilic carbon atom of **72a** on the carbon atom of ArNCO and successive 1,3-H shift. In this manner, a phosphine-amide ligand is generated. The NH-proton is connected with the opposite carbonyl group through a hydrogen bond. The six-membered ring thus formed is close to planar as indicated by an X-ray structure determination of **96**.

In contrast, *cis*-$\mathrm{Pt(P^\frown O)_2}$ ($\mathrm{P^\frown O = Ph_2PCH{=}C(Ph)O}$) reacts with PhNCO to give exclusively the mono insertion product **97** which contains an N,P chelate ring (type B2 of Scheme 12) [163]. This latter finding may be explained by the higher affinity of platinum(II) for nitrogen donors than for oxygen.



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The palladium system has been investigated using complexes of the type $\mathrm{(C^\frown N)Pd(P^\frown O)}$ ($\mathrm{C^\frown N}$ = dmba, 8-mq) [163]. Notably, the phosphinocarboxylato complex $\mathrm{(C^\frown N)Pd(P^\frown O)}$ (**68**, $\mathrm{P^\frown O = Ph_2PCHCOOEt}$) reacts with PhNCO to give quantitatively the usual adduct of type B1. However, in the case of the phosphinoenolato complex $\mathrm{(C^\frown N)Pd(P^\frown O)}$ (**75**, $\mathrm{P^\frown O = Ph_2PCH{=}C(Ph)O}$), both the B1 and B2 forms are obtained as a mixture. The interconversion of these species presumably occurs via Pd–O bond rupture followed by a rearrangement of the ligand system.

In view of the outstanding importance of carbon dioxide activation [197], the reactivity of the previously discussed O,P complexes towards CO_2 has been investigated [71,159]. The chief aim is to accomplish carbon–carbon bond formation which might offer a new synthetic route to various organic chemicals. In this regard, (C$^\frown$N)Pd(P$^\frown$O) (**68**, C$^\frown$N = 8-mq; P$^\frown$O = $Ph_2PCHCOOEt$) has proved to be a reversible CO_2-carrier. Thus, **68** readily takes up carbon monoxide at ambient conditions to give **98**, which in turn loses CO_2 upon sweeping with an inert gas (see Scheme 14). The molecular structure of **98** has been confirmed by X-ray diffraction [159].

Finally, we wish to refer to the behaviour of phosphinoenolato complexes towards chlorophosphines [164,198]. As outlined in Scheme 14, treatment of *cis*-Ni(P$^\frown$O)$_2$ (**72a**, P$^\frown$O = $Ph_2PCH{=}C(Ph)O$) with Ph_2PCl yields complex **99**, among other compounds, resulting from an insertion of the phosphorus atom into the Ni–O bond [164]. The second O,P chelate ligand is thereby removed from the complex fragment. The reaction arises from an interaction of the chlorophosphine with the nucleophilic oxygen of **72a** and may be interpreted as an alcoholysis of the P–Cl bond.

Furthermore, the use of difunctional $PhPCl_2$ leads to compound **100** (see Scheme 14) [164,198]. Apparently, both O,P chelates are involved in this reaction and are linked together by the phosphorus atom of the inserted chlorophosphine. Hence this metal-assisted template synthesis provides an interesting route to polyfunctional ligands [198].

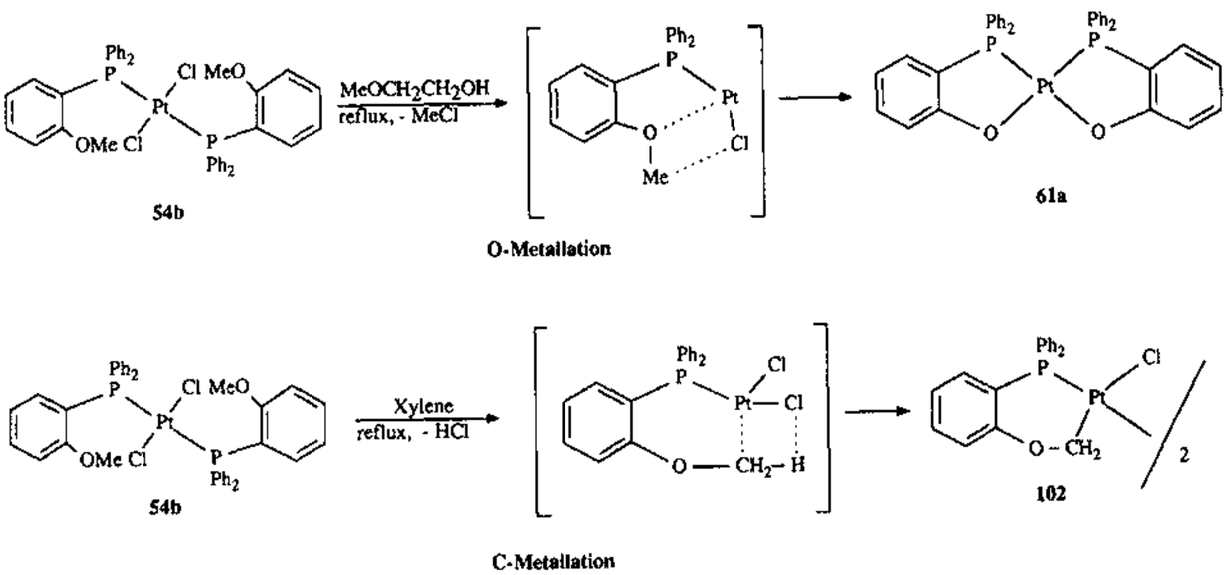
(iii) Metallations

In the preceding sections, many reactions have been presented in the course of which metal–oxygen bonds are reversibly formed and cleaved. In general, it should be anticipated that a ligand which is held in close proximity to the coordination centre is liable to a chemical interaction with the metal atom. These reactions may lead to a crucial change of the ligand molecule, especially with respect to its donor functions. Hence, in these cases the marked reversibility, which is manifested by the opening and closing mechanism and the fluxionality of some complexes, is mostly lost.

Among reactions of this kind, dealkylations have been reported to occur with some platinum [50,56,80], rhodium [144] and iridium [134,135] complexes. Yet quite drastic conditions must be applied in order to promote such metallations. Two principal reaction pathways, *O*- and *C*-metallation, are delineated in Scheme 15.

Platinum(II) complexes of the type $[PtX_2(P\sim O)_2]$ (**54b**) have been intensively studied by Shaw's group, where X designates a halide ion and the O,P ligands used are alkylaryl ethers of the types **VI–IX**, which all contain an alkoxy function in the *ortho* position to the dialkylphosphino group.

Upon heating $[PtCl_2(P\sim O)_2]$ (**54b**, $P\sim O = Ph_2PC_6H_4(OMe\text{-}2)$, **VIb**) to 270°C in the solid state or in boiling 2-methoxyethanol (124°C), chlorometh-



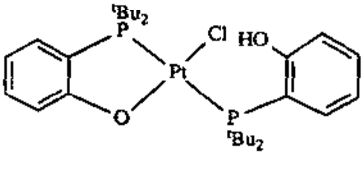
Scheme 15. O- and C-metallation of platinum(II) complexes with *ortho*-phosphinoanisols.

ane is evolved together with the formation of white, very stable *cis*-bis{*o*-(diphenylphosphino)phenoxo}platinum(II) (**61a**) [50,80]. This type of reaction is called *O*-metallation (see Scheme 13). In its course, the ethereal methyl–oxygen bond is cleaved to give chloromethane along with Pt–O bond formation. The oxygen atom used to establish this Pt–O contact is part of the remaining phenolate moiety. Thus, *O*-metallation transforms an ether-phosphine into a phosphinophenolate ligand, the formal oxidation state of the metal centre remaining unchanged.

Such reactions are not restricted to complexes of phosphinoanisols but are also known for multidentate sulphur and selenium compounds such as the Schiff base $Et_2N(CH_2)_2N{=}CHC_6H_4(SMe\text{-}2)$ [199], $Me_2AsC_6H_4(SMe\text{-}2)$ [200] or $Ph_2PC_6H_4(SeMe\text{-}2)$ [201]. Nickel(II), palladium(II) or platinum (II) complexes containing these ligands are readily dealkylated upon heating and M–S or M–Se bonds are formed.

Similar to the reaction of $PtCl_2(P{\sim}O)_2$ (**54b**, $P{\sim}O = Ph_2PC_6H_4(OMe\text{-}2)$, **VIb**), the analogous complex containing $^tBu_2PC_6H_4(OMe\text{-}2)$ (**VIc**) undergoes *O*-metallation to give *trans*-$Pt(P\frown O)_2$ (**61b**, $P\frown O = {}^tBu_2PC_6H_4O$) [50]. The *trans* configuration of this complex is due to the steric bulk of the *tert*-butyl groups. The compounds **61a,b** are thermally very stable and can be heated to above 250°C without decomposition.

Treatment of **61b** with HCl in chloroform/ether causes opening of one O,P chelate ring, presumably via protonation of the corresponding oxygen atom followed by an external attack of the platinum centre by a chloride ion. The resulting complex **101** can be reverted back to **61b** by deprotonation with NaOH in methanol [50].



101

Generally, the iodides $PtI_2(P{\sim}O)_2$ react considerably faster than the chlorides, and also methoxy groups are more reactive than ethoxy groups.

Moreover, it was found that complexes of the type $PtX_2(P{\sim}O)_2$ (**54b**) are *O*-metallated at a higher rate if the phosphorus atoms carry steric demanding substituents.

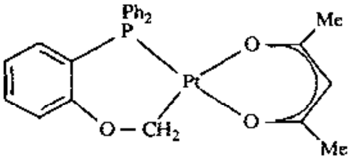
Accordingly, $PtCl_2(P{\sim}O)_2$ (**54b**, $P{\sim}O = Me_2PC_6H_4(OMe\text{-}2)$, **VIa**) is very reluctant to dealkylation and only under harsh conditions, i.e. prolonged heating with a large excess of NaI in boiling 2-methoxyethanol, one of the methoxy groups reacts [50]. However, the corresponding nickel(II) complex is totally unreactive [51].

The use of the very bulky $^{t}Bu_2PC_6H_4(OMe)_2$-2,6 (**IXb**) should be most favourable for the promotion of *O*-metallation [56].

It is well-known that *ortho*-phosphinoanisols with sterically demanding groups at the phosphorus atom exhibit restricted rotation around the phosphorus–aryl bond. In the complexes $MX_2(P\sim O)_2$ this gives rise to two rotamers with different Cl–OMe distances. Irrespective of this ligand conformation in the complex $PtCl_2(P\sim O)_2$ (**54b**, $P\sim O = {}^{t}Bu_2PC_6H_4(OMe)_2$-2,6, **IXb**), one of the methoxy groups is in close proximity to the chloride ligand and therefore predestined to react [56]. As expected, $PtCl_2(P\sim O)_2$ (**54b**) containing $^{t}Bu_2PC_6H_4(OMe)_2$-2,6 (**IX**) is much more reactive than the corresponding compounds with **VIII** or **VI** [56].

In addition to the dealkylations described above, a second pathway, the so-called *C*-metallation, is observed with $PtX_2(P\sim O)_2$ (**54b**) upon heating in non-polar solvents (see Scheme 15). In contrast, on heating in polar solvents such as 2-methoxyethanol, *O*-metallation occurs.

Thus, an equimolar mixture of $PtCl_2(NCPh)_2$ and the O,P ligand **VIb** reacts in boiling xylene to give hydrogen chloride and the insoluble chloride-bridged dimer $(\mu\text{-}ClPt(P^\frown C))_2$ (**102**, $P^\frown C = Ph_2PC_6H_4OCH_2$) which contains a six-membered chelate ring [50]. Similarly, in combination with $PtCl_2(NCPh)_2$ the ligands **VIIIa** and **IXa** undergo *C*-metallation. The platinum–carbon bonds in these species are rather inert and resistant to cleavage by donor molecules. Instead, the chloride-bridges of compound **102** or the related complexes are cleaved with pyridine, several phosphines or Tl(acac) yielding more soluble monomeric products such as **103** which are therefore more amenable to spectroscopic investigations.



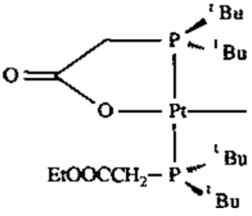
103

The mechanisms of *O*- and *C*-metallations operating in the present systems have not yet been investigated in full detail. However, owing to the fact that the rate of *O*-metallations is only slightly enhanced by added halide ions and only polar solvents are suitable, an intramolecular reaction involving a polar, four-centre transition state is plausible [50]. The same holds true for *C*-metallations as an oxidative addition of a methyl C–H moiety to platinum(II) is unlikely due to a lack of nucleophilicity of a platinum(II) species bearing only one phosphine ligand.

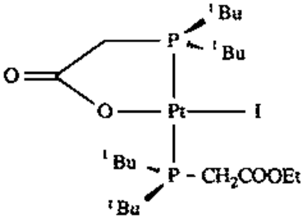
O-metallations of bulky phosphinoesters proceed in a similar manner as already discussed for phosphinoanisols. Notably, in contrast with diphenyl-phosphinoanisol (**VIb**), Ph_2PCH_2COOEt (**XXIIIa**) in the form of $PtI_2(P\sim O)_2$ shows no evidence of *O*-metallation.

Treatment of *trans*-$PtCl_2(P\sim O)_2$ ($P\sim O={}^tBu_2PCH_2COOEt$, **XXIIIb**) with NaI in boiling ethanol results in the loss of one ethyl group and **104** is obtained [75]. Dealkylation of the ester group thus generates a carboxylato function. Further *O*-metallation is promoted by sodium acetate to give the bis-chelate *trans*-$Pt(P\frown O)_2$.

Due to the restricted rotation around the platinum–phosphorus bond, in $CDCl_3$ solutions **104** occurs as a mixture of two rotamers **104a,b** since the *tert*-butyl groups of the η^1-bound phosphine can be either *cis* or *trans* to the iodide [75].

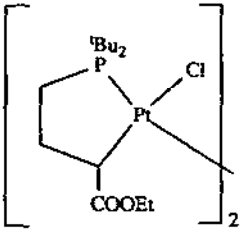


104a



104b

Refluxing of an equimolar mixture of $PtCl_2(NC{}^tBu)_2$ and ${}^tBu_2P$-$(CH_2)_3COOEt$ (**XXIIIf**) in toluene leads to *C*-metallation and **105** is obtained, HCl being liberated. Since the carbon atom bound to the platinum is chiral, several diastereomers of **105** are expected [75].



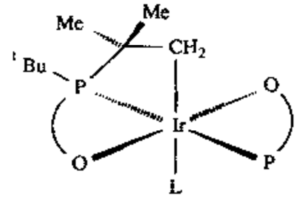
105

In contrast to **XXIIIf**, ${}^tBu_2P(CH_2)_2COOEt$ (**XXIIIe**) could neither be *O*- nor *C*-metallated. Although phosphinoester palladium complexes usually decompose under the conditions of *O*-metallation, a few examples of base-promoted dealkylations are known. In this connection it is worth mentioning that in the presence of ^{n}BuLi $(C\frown N)PdBr(P\sim O)$ ($C\frown N$ = 8-mq, $P\sim O=Ph_2PCH_2COOEt$, **XXIIIa**) undergoes *O*-metallation, $(C\frown N)Pd(P\frown O)$ (**78**, $P\frown O=Ph_2PCH_2COO$) being formed [159].

Dealkylations have also been reported to occur with some rhodium and iridium complexes containing sterically demanding ether-phosphines. *Trans*-[RhCl(CO)$(P \sim O)_2$] ($P \sim O = {}^t\mathrm{Bu_2PC_6H_4(OMe\text{-}2)}$, **VIc**) is *O*-metallated on heating in 2-propanol to give *trans*-[Rh(CO)($P^\frown O$)($P \sim O$)] [144]. This complex shows complicated, temperature-dependent ^{1}H and ^{31}P{^{1}H} NMR spectra, which are probably due to the presence of different conformers. An isostructural iridium complex is obtained from the reaction of **VIc** with iridium carbonylchloride [134].

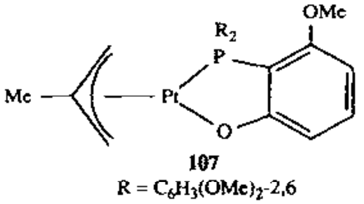
An interesting reaction is the internal *C*-metallation of a *tert*-butyl group in some iridium(II) complexes. In the presence of oxygen, *trans*-Ir$(P^\frown O)_2$ (**47a**, $P^\frown O = {}^t\mathrm{Bu_2PC_6H_4O}$) is slowly oxidized to the iridium(III) complex [Ir($C^\frown P^\frown O$)($P^\frown O$)] [134]. Presumably, an iridium–oxygen species is formed prior to *C*-metallation. The hydrogen is likely to be lost as water or hydrogen peroxide.

The structure of the similar six-coordinate complex *trans*-[Ir(MeNC)($C^\frown P^\frown O$)($P^\frown O$)] (**106**) with **IXb** as O,P ligand has been confirmed by X-ray diffraction [135].



106
L = MeNC

Finally, a ligand-assisted *O*-metallation should be mentioned which has been reported by Kurosawa et al. [202]. These workers have used tris(2,6-dimethoxyphenyl)phosphine as O,P ligand and prepared (η^3-methallyl)PtCl($P \sim O$) which reacts with $\mathrm{AgBF_4}$ to give the O,P chelated cation [(η^3-$\mathrm{C_4H_7}$)Pt($P^\frown O$)]$^+$. This compound is demethylated upon addition of excess phosphine ligand and the neutral complex **107** is obtained. The latter reaction is facilitated by the strong tendency of the free O,P ligand to the formation of phosphonium salts.



107
R = $\mathrm{C_6H_3(OMe)_2}$-2,6

E. CATALYTIC APPLICATIONS OF O,P-CHELATED METAL COMPLEXES

In recent years, the prodigious development of organotransition metal chemistry has revealed, among other things, its great potential in the fields of homogeneous and heterogeneous catalysis. The use of transition metal complexes as catalyst precursors has the advantage of systematic alteration of both the metal and the ligand part. In the first place, 'ligand-tailoring' has become a most promising method on the way to novel, more efficient catalysts. Furthermore, in many instances detailed investigation has given insight into the mechanistic background of such catalytic reactions. Among other systems, those containing unsymmetrical O,P chelate ligands have been scrutinized with respect to their scope of practical application.

In the following sections we wish to present some technically important reactions catalyzed by organometallic complexes which are modified by O,P ligands.

(i) Olefin oligomerization and polymerization

Reactions involving carbon–carbon linkage are of outstanding significance to the preparation of important organic chemicals. Due to their versatility, olefins, especially ethene, have become a major feedstock of industrial processes. In the first place, there is a great demand for oligomerization and polymerization products of lower olefins, which are used for the fabrication of detergents, plasticizers and lubricants.

However, such reactions may lead to compounds with quite similar chemical properties. Owing to this fact, highly selective catalysts are required to obtain the desired products in reasonable yields and purities. As far as olefin oligomerizations and polymerizations are concerned, the average molecular weight of the products is determined by the relative rates of the chain propagation and termination step. Whereas compounds of early transition metals (Groups IV–VI) favour chain propagation and thus polymerization (cf. the Ziegler–Natta process), in the case of Group VIII metal complexes, chain termination (β-elimination) often becomes prevailing and oligomers are preferably obtained.

Since the pioneer works of Reppe and Wilke, various nickel complexes have been discovered as effective catalysts for the formation of carbon frameworks [203]. Improvements of the catalysts have been achieved by variation of the ligand system. This has led to the development of the Shell Higher Olefin Process (SHOP), to which Keim has made eminent contributions [3,65,204,205]. This process has been designed for the manufacture of linear α-olefins and represents one of the most prominent applications of homogeneous catalysis. Several plants are run worldwide with a steadily increasing output which presently amounts to approximately one million tons a year [205]. The combination of oligomerization, isomerization and metathesis confers a great flexibility to the whole process and enables an accurate adaption to the current economic situation [3]. The oligomerization of ethene is the essential reaction and is therefore outlined in the following.

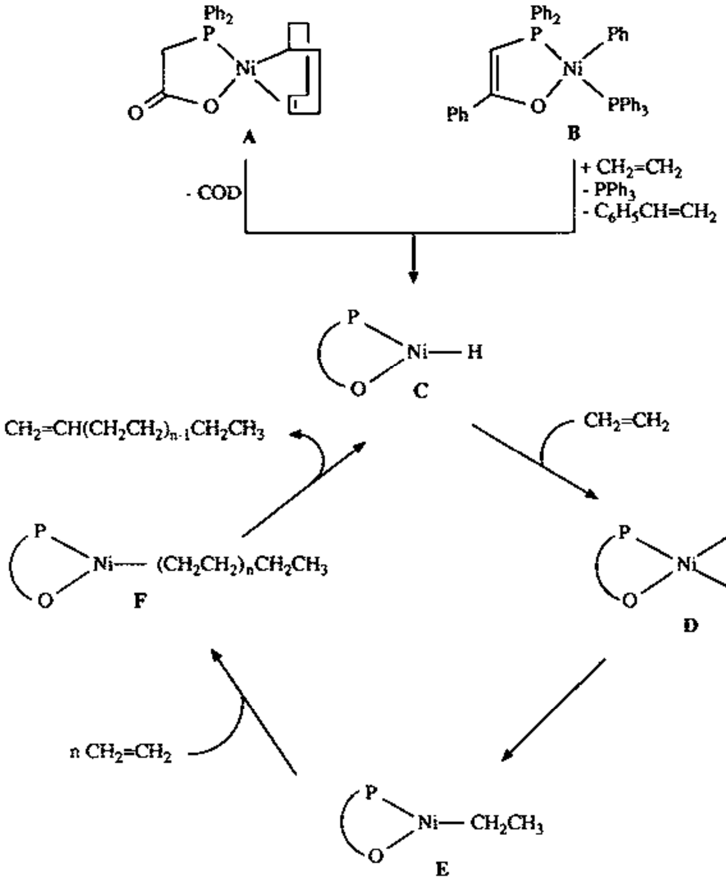
Nickel(II) complexes containing chelating ligands are expected to be suitable catalysts since square-planar systems are favourable for olefin coordination. Detailed studies concerning the influence of ligands on activity and selectivity have revealed that formal three-electron donors are necessary to achieve satisfactory results [204]. Hence, whereas nickel(II) complexes with diphos-ligands $R_2P(CH_2)_nPR_2$ fail to oligomerize ethene, good results are attainable with a variety of three-electron O,P systems.

Detailed studies have revealed that a catalyst precursor suitable for the SHOP reaction can formally be divided into a chelate part and a second organic ligand, both being coordinated to nickel [204,205]. In such precursors, the chelate ligand influences activity and selectivity which is typical of the active species, whereas the second ligand solely stabilizes the catalyst precursor. Depending on the nature of this ancillary ligand, different temperatures are necessary to activate the system during the initiation period [205].

According to Scheme 16, the true catalyst is presumed to be a hydridonickel complex formulated as $\mathrm{Ni(H)(P{\frown}O)}$ (**C**). This species is generated in situ from a variety of precursors such as **A** or **B** depicted in Scheme 16 [3,205–207].

C is capable of coordinating ethene to give the (η^2-ethene)hydridonickel species **D**, which rapidly undergoes an insertion reaction yielding the σ-ethylnickel complex **E**. After several repetitions of these steps, **F** is formed. β-Hydride elimination eventually completes the catalytic loop re-generating $\mathrm{Ni(H)(P{\frown}O)}$ (**C**) and liberating a linear α-olefin. The product mixture follows the geometric Schulz–Flory distribution, which favours C_4–C_{10} α-olefins but is influenced by the ethene-pressure and phosphines added to the reaction solution [208]. If compound **B** is used as precursor, ethene is converted at 50–100 bar and 50°C to oligomers with 99% linearity and $>95\%$ α-olefin content.

Supportive evidence for the proposed mechanism involving nickel hydrides comes from in situ ^1H NMR measurements [186]. Thus, in the reaction medium of $Ni(COD)_2$ and $Ph_2PCH_2(CF_3)_2OH$ (**XXVc**) a hydrido species could be identified by its ^1H NMR signal (-23.8 ppm), which disappears upon bubbling of ethene through the solution. This generates an alkyl-nickel species which in turn has been established by ^1H NMR spectroscopy and in the form of its PCy_3-adduct. Furthermore, reactive hydrides



Scheme 16. Postulated mechanism of the nickel-catalyzed oligomerization of ethene (SHOP process).

have been trapped by admixture of tertiary phosphines to the reaction medium. This has led to the isolation of Ni(H)(P⌒O)(PCy$_3$) (**86**, P⌒O = Ph$_2$PCH$_2$C(CF$_3$)$_2$O) whose structure has been elucidated by X-ray diffraction (see Sect. C.(iv)) [186]. Compound **86** does not catalyze ethene oligomerization, presumably due to a lack of necessary vacant coordination sites [209]. The successful conversion of a nickel hydride with butadiene to give the corresponding η^3-allyl complex Ni(P⌒O)(η^3-C$_4$H$_7$) [P⌒O = Ph$_2$PCH$_2$C(CF$_3$)$_2$O] [205] also adds credence to the hydride mechanism.

The kinetics of the SHOP reaction are consistent with the Michaelis–Menten-type mechanism outlined in Scheme 16. The rate constants and the activation parameters have been determined [206].

Catalysts which are active in the SHOP reaction have also been successfully applied to the cyclization of some α,ω-dienes. This reaction may be regarded as intramolecular dimerization. It has emerged that all cyclic products obtained in this way contain a five-membered ring. Thus Ni(Ph)(PPh_3)($P^{\frown}O$) ($P^{\frown}O = Ph_2PCH{=}C(Ph)O$) as catalyst precursor (compound **B** of Scheme 16) transforms 1,5-hexadiene mainly into methylenecyclopentane, whereas 1,7-cyclooctadiene only undergoes isomerization [210].

As discussed above, compounds of the type Ni(Ph)(L)($P^{\frown}O$) ($P^{\frown}O = Ph_2PCH{=}C(Ph)O$) are used for ethene oligomerization. Klabunde and Ittel found that the molecular weights of the products crucially depend on the donor strength of the ancillary ligand L. Systems containing weakly coordinating donors, e.g. pyridine, or the total absence of such a ligand (compound **88**, see Sect. C.(iv)) lead to polymers due to a decrease in the activation energy for the insertion of ethene [60]. Starzewski and Witte have reported the ylid complex Ni(Ph)(L)($P^{\frown}O$) ($P^{\frown}O = Ph_2PCH{=}C(Ph)O$, $L = CH_2PMe_3$) to be an effective catalyst precursor for the polymerization of ethene. It is prepared from $Ni(COD)_2$, $Ph_3PCHC(O)Ph$ (**XXII**) and $Me_3P{=}CH_2$ [211].

Since Ni(Ph)(L)($P^{\frown}O$) undergoes insertion of carbon dioxide, carbon monoxide and ethene into the nickel-phenyl bond [212,213] copolymerizations of ethene with α-olefins to make linear low-density polyethene or with functionalized olefins have been carried out [60].

After treatment with ethene to accomplish initiation, Ni(Ph)(PEt_3)($P^{\frown}O$) ($P^{\frown}O = Ph_2PCH{=}C(Ph)O$) promotes copolymerization of ethene with carbon monoxide [213].

(ii) Carbonylation of methanol and methyl acetate

For a long time, natural oil and gas have been the prevalent source of hydrocarbon fuels and organic chemicals. In recent years, however, an intense search for alternative raw materials has been undertaken. Due to its unique versatility, synthesis gas derived methanol may in future serve as a basic building block for the manufacture of industrial chemicals [214,215]. Thus, methanol can be converted into acetic acid and methyl acetate by carbonylation with carbon monoxide or into acetaldehyde by hydrocarbonylation with synthesis gas. In all cases, transition-metal based catalysts are indispensable for the successful performance of these reactions. The development of catalysts which are both highly active and highly selective is of paramount importance for the economy of such large-scale processes. Following the concept of ligand tailoring, we have tested a variety of hemilabile ether-phosphines of the types **I–V**. Due to their comparatively low cost, catalysts based on cobalt have been preferred to those containing rhodium. However, Wegman et al. recently reported highly active rhodium catalysts containing the bisphosphine monoxide ligand **XXVIIc** [147].

Catalyst precursors consisting of CoI_2/ligand have proved to be more efficient than the frequently used $Co(OAc)_2$/ligand combination [15].

The potentially bi- or multidentate O,P ligands may stabilize reactive, coordinatively unsaturated species by formation of an O,P chelate ring, i.e. internal solvation. Therefore, weakly coordinating solvents such as THF or dioxane appear to be unnecessary and have thus been omitted.

A host of ether-phosphines has been examined in high-pressure carbonylation and hydrocarbonylation reactions. These experiments have revealed that O,P ligands containing 1,4-dioxanyl groups generally lead to better results than their analogues with other cyclic or open-chained ether moieties [4–6,15]. Moreover, a catalyst precursor consisting of CoI_2, triphenylphosphine and 1,4-dioxane gives only poor selectivities with respect to acetaldehyde and the use of pure CoI_2 results in a marked drop of the maximum conversion achievable [5,216].

A kinetic study of the methanol hydrocarbonylation to acetaldehyde has been carried out using CoI_2 and **Vc** as catalyst precursor [216]. The rate of this reaction can be described by the equation

$$-\frac{\mathrm{d}x_{\mathrm{MeOH}}}{\mathrm{d}t} = 30.8 \exp - \left(5770\frac{K}{T}\right) x^2{}_{\mathrm{MeOH}} x_{\mathrm{Catalyst}} \left(\frac{p}{p_0}\right)^{1.46}$$

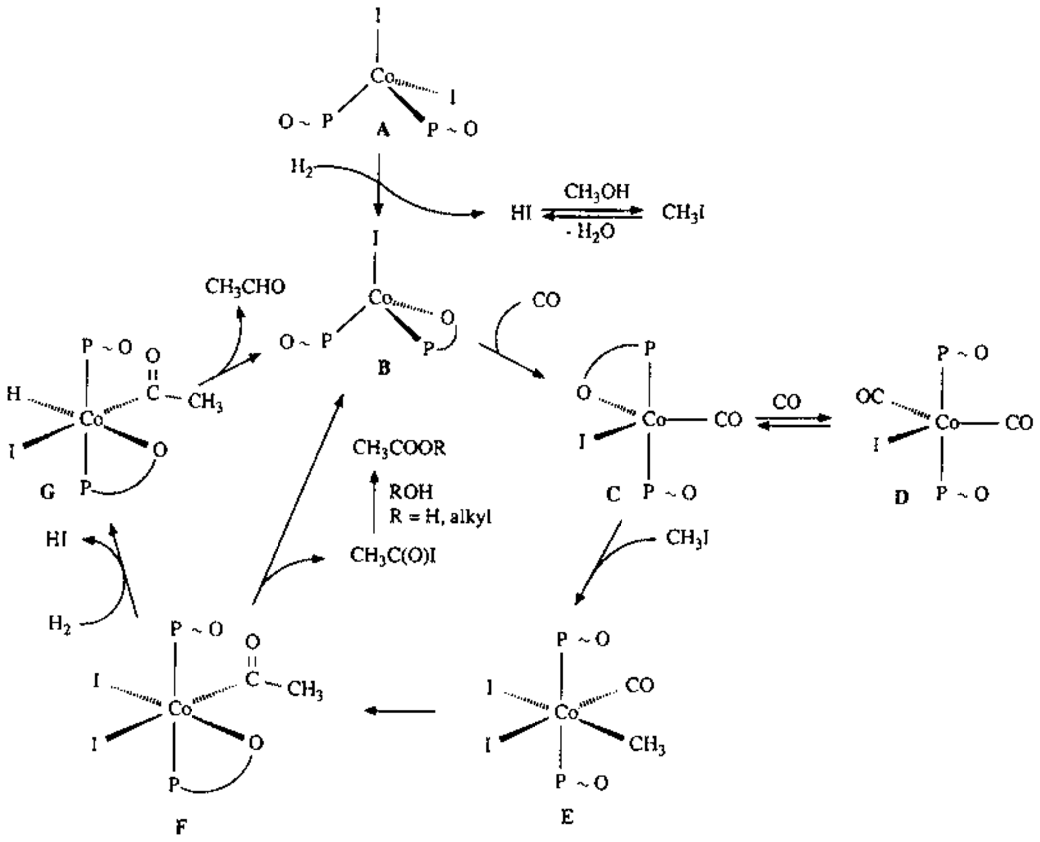
where x = molar fraction and p = pressure.

The activation energy amounts to 48 kJ mol^{-1}, which is somewhat lower than the value reported for the $Co(OAc)_2/PPh_3/MeI$ system (60 kJ mol^{-1}) [217].

With the goal of preparing heterogeneous catalysts, several ether-phosphines have been attached to silica gel by spacers of three and six methylene groups [218,219]. ^{29}Si, ^{31}P and ^{13}C CP/MAS solid-state NMR studies have been performed to gain insight into the bonding mode of the ligands to the support. These heterogeneous systems have been used in the cobalt-catalyzed hydrocarbonylation of methanol [219] and of methyl acetate to ethylene diacetate [220]. The results are comparable with those obtained with the homogeneous counterparts, but the problem of "leaching" has not yet been surmounted.

Detailed studies have been carried out to disclose the mechanism of the methanol carbonylation in the presence of hemilabile O,P ligands. Special attention has been focussed on the operation of the opening and closing mechanism in the course of the catalytic cycle.

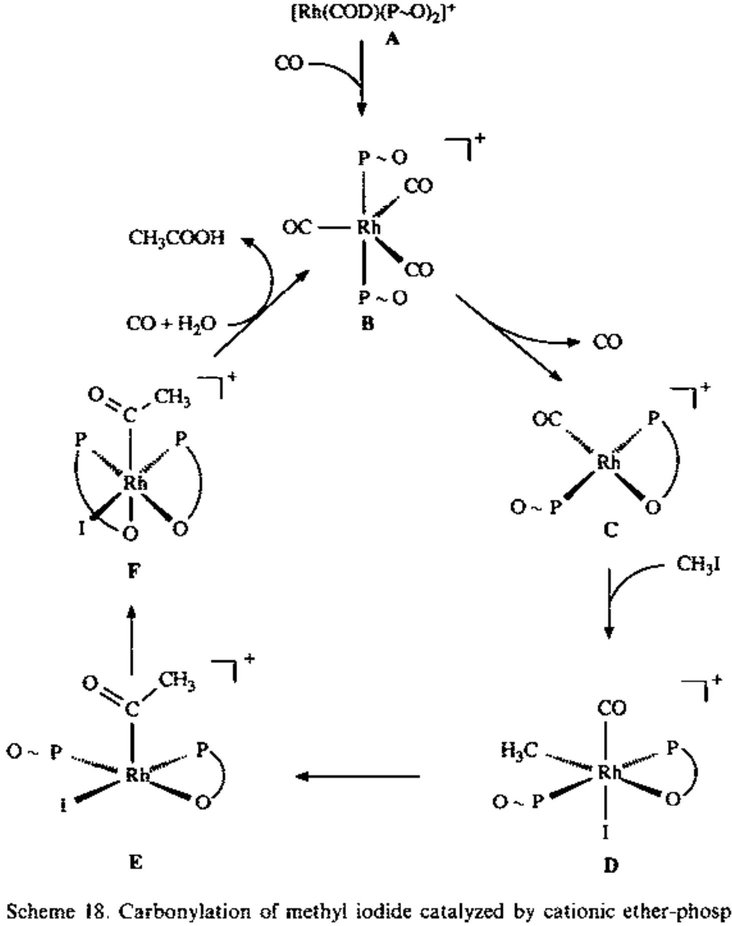
The proposed mechanism for the cobalt-catalysis is delineated in Scheme 17 [5,6]. As previously outlined in Scheme 3 (Sect. C.(iii)), complexes of the type $CoI_2(P{\sim}O)_2$ (**15**, species **A**) serve as catalyst precursors which are subject to reduction yielding $CoI(\overset{\frown}{P\ O})(P{\sim}O)$ (**16**, species **B**). This 16-electron cobalt(I) compound may take up one or two CO molecules



Scheme 17. Proposed mechanism of methanol carbonylation catalyzed by ether-phosphine modified cobalt complexes.

to give **C** or **D**, the former being stabilized by O,P chelation. Oxidative addition of pre-formed methyl iodide to give **C** results in the opening of the O,P chelate since the sixth coordination site is required. Methyl migration regenerates a vacant site which is expected to be occupied by an ether-oxygen (species **F**). Reductive elimination of acetyl iodide from **F** leads back to **B** whereas reaction with hydrogen might give **G** which in turn loses acetaldehyde, thus completing the catalytic loop.

The unrivalled behaviour of O,P ligands in the course of this catalytic reaction has also been demonstrated with rhodium complexes (see Scheme 18) [5,125–127,220,221]. A number of precursor complexes **A** such as $[\mathrm{Rh(COD)(P{\sim}O)_2}]^+$ (**23**) may be converted to $[trans\text{-}\mathrm{Rh(P^{\frown}O)(P{\sim}O)(CO)}]^+$ (**26**, species **C**). **C** readily adds methyl iodide. The resulting complex **D** undergoes methyl migration whereupon **E** (P⌒O = **Ia**) or **F** (P⌒O = **Ie**) is



Scheme 18. Carbonylation of methyl iodide catalyzed by cationic ether-phosphine rhodium complexes.

formed. In the presence of CO, reductive elimination of acetyl iodide, which is hydrolyzed to acetic acid, leads back to **B**.

It is most interesting that analogous complexes with conventional trialkylphosphines behave differently. Thus, $RhCl(CO)(^nBu_3P)_2$ adds MeI but no methyl migration takes place [125]. Similarly, [*trans*-$Rh(^nPr_3P)_2(CO)(THF)]^+$ readily adds MeI but the reaction product also fails to undergo methyl migration. Moreover, [*trans*-$Rh(^nPrPPh_2)_2(CO)(THF)]^+$ decomposes upon treatment with MeI [126,220]. These observations furnish corroborative evidence that the oxidative addition of MeI and the subsequent methyl migration are strongly facilitated by the opening and closing mechanism performed by O,P ligands.

(iii) Hydrogenations

Spurred by the remarkable results achieved in the field of enantioselective hydrogenations of prochiral olefins, much effort has been expended in elucidating the mechanistic background [9,222–224]. This task has turned out to be quite puzzling because the functional groups of the substrate have a considerable bearing on the optical yield. As far as the hydrogenation of α-acetamidocinnamic acid is concerned, continuous improvement has been noted in the following sequence [9]: PhMePPr (28% ee) < PAMP (**VId**, 50–60% ee) < CAMP (**VIe**, 80–88% ee) < DIPAMP (**X**, 95% ee). Notably, DIPAMP has found a very important application in the industrial manufacture of L-Dopa, which is used for the treatment of Parkinson's disease.

Since the best ligands apparently contain an *ortho*-methoxy group, the reason for this effect is of great interest. It seems plausible that the preferred conformation of the aromatic groups is an important factor which determines the stereoselectivity [9]. This may, among other reasons, result from an interaction of the methoxy group with the substrate (e.g. via hydrogen bonds) or with the metal centre [27,223–225].

Horner and Simons have investigated the effect of alkoxyarylphosphines in the course of rhodium-catalyzed hydrogenations of 1-hexene [12]. The H_2-uptake measured for ligands of the type $Ph_2PC_6H_3(OR)_2$-2,5, $Ph_2PC_6H_3(OR)_2$-2,3 (**VIII**) and $Ph_2PC_6H_3(OR)_2$-2,6 (**IX**) depends on the chain length of R. It follows from the comparison with Ph_3P that, with the exception of $Ph_2PC_6H_3(O^iPr)_2$-2,5, the alkoxy substituents retard the reaction.

The higher activity of $Ph_2PC_6H_4(OMe)$-2 (**VIa**) compared with the analogue Ph_2PEt has been attributed to a direct Rh–O interaction ('windscreen-wiper effect', see Scheme 10).

Similar results have been observed in the hydrogenation of 1-hexin catalyzed by *trans*-$PdCl_2(P{\sim}O)_2$ ($P{\sim}O$ = **Ia**, **IIa**, **IIIa**) [151]. After quantitative conversion of the 1-hexin, the selectivities with respect to 1-hexene are almost 100%. In contrast, the analogous complex *trans*-$PdCl_2(Ph_2PPr)_2$ gives 1-hexene with low selectivity (50%). However, the O,P ligand reduces the rate of hydrogenation considerably.

In this review we have presented the chemistry of the major types of O,P ligands. The unique behaviour of many of their transition metal complexes has initiated their successful application in industrial processes and thus further possibilities are to be envisaged.

NOTE ADDED IN PROOF

A crystal structure determination recently done for $RhCl_3(Ph_2PCH_2COOEt)_2$ (**28a**) has revealed a meridional arrangement of the chloride ligands [226] in contrast with the facial geometry proposed on the basis of NMR investigations [130]. In that case the fluxional behaviour of **28a** should also involve the participation of a chloride ligand. However, the molecular structure in the crystalline state may differ from that in solution.

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