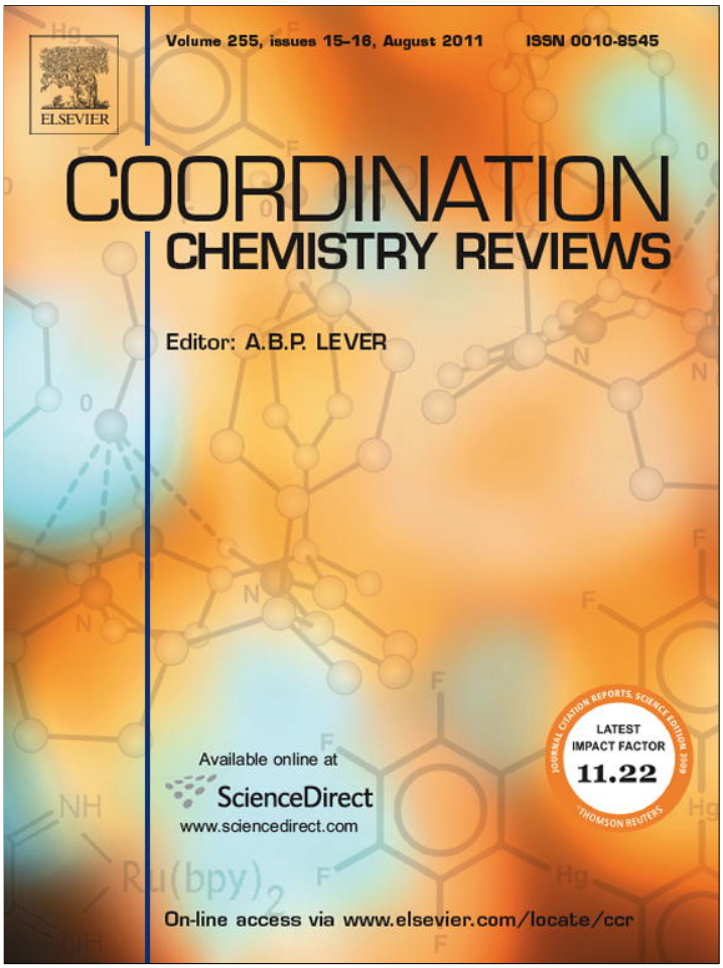


Coordination Chemistry Reviews 255 (2011) 1686–1712

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr

Review

Potential rhodium and ruthenium carbonyl complexes of phosphine-chalcogen (P-O/S/Se) donor ligands and catalytic applications

Dipak Kumar Dutta*, Biswajit Deb

Materials Science Division, Council of Scientific and Industrial Research, North East Institute of Science and Technology, Jorhat 785 006, Assam, India

Contents

Abbreviations: BINAP, 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl; BINAPO(O), 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl monooxide; BPMO, bis-phosphine monooxide; CO, carbon monoxide; COD, 1,5-cyclooctadiene; COE, *cis*-cyclooctene; cot, cyclooctatetraene; DCM, 1,2-dichloro methane; dcpm, bis(di-cyclohexylphosphino)methane; DOPA, 2-amino-3-(3,4-dihydroxyphenyl)propanoic acid; $dpeO_2$, 1,2-bis(diphenylphosphine)ethane dioxide; DPEphos, bis(2-di-phenylphosphanyl-phenyl)ether; DPEphos(O_2), bis(2-di-phenylphosphanyl-phenyl)ether dioxide; DPEphos(S), bis(2-di-phenylphosphanyl-phenyl)ether monosulfide; dippf, 1,1′-bis(diisopropylphosphino)ferrocene; $dpmO_2$, 1,2-bis(diphenylphosphine)methane dioxide; dppeO, 1,2-bis(diphenylphosphine)ethane monoxide; dppf, 1,1′-bis(diphenylphosphino)ferrocene; dppm, 1,2-bis(diphenylphosphine)methane; dppmO, 1,2-bis(diphenylphosphine)methane monooxide; dpppO, 1,2-bis(diphenylphosphine)propane monooxide; ee, enantiomeric excess; F-dppe, 1,2-bis[bis(pentafluorophenyl)phosphino]ethane; Hdpf, 1′-(diphenylphosphino)ferrocenecarboxylic acid; HPIR, high pressure infra red; HPNMR, high pressure nuclear magnetic resonance; ^{i}Pr, Isopropyl; OA, oxidative addition; THF, tetra hydro furan; ^{t}Bu, tertiary butyl; tpp, triphenyl phosphine; TOF, turn over frequency; TON, turn over number; TPPMS, monosulfonated triphenylphosphine; TPPTS, trisulfonated triphenylphosphine; Xantphos, 9,9-dimethyl-4,5-bis(diphenylphosphanyl)xanthene; Xantphos(O_2), 9,9-dimethyl-4,5-bis(diphenylphosphanyl)xanthene dioxide; Xantphos(S), 9,9-dimethyl-4,5-bis(diphenylphosphanyl)xanthene monosulfide.

* Corresponding author. Tel.: +91 376 2370081; fax: +91 376 2370011.
E-mail address: dipakkrdutta@yahoo.com (D.K. Dutta).

0010-8545/$ – see front matter
doi:10.1016/j.ccr.2011.01.025

ARTICLE INFO

Article history:
Received 7 October 2010
Accepted 14 January 2011
Available online 25 January 2011

Keywords:
Rhodium
Ruthenium
Phosphine-chalcogen
Carbonylation
Hydrogenation
Hydroformylation

ABSTRACT

This review reports several types of potential metals (rhodium and ruthenium) carbonyl complexes of functionalized phosphine-chalcogen donors ligands like: P-X (X = O, S, Se) and their catalytic applications particularly in (i) carbonylation of alcohols, (ii) hydrogenation of unsaturated substrates and (iii) hydroformylation of alkenes for industrially important organic molecules.

1. Introduction

1.1. Overview

Platinum metal complexes of unsymmetrical chelating ligands such as functionalized phosphines have aroused much interest in recent time because of their structural novelty, reactivity and catalytic applications [1–14] such as carbonylation [5,6,14], hydrogenation [7–9,11] and hydroformylation [6a,12,13] reactions. Homogeneous catalysis by transition metal complexes has become a major synthetic tool in industrial processes [5–7]. The potential of such catalytic reactions lies in the fact that most of these reactions are highly selective, low energy processes and show high rates of conversion. Among platinum metals, rhodium and ruthenium find special attention due to their versatile catalytic activity and unique character.

1.2. Rhodium

Rhodium is one of the rarest and most expensive precious metals. It has a typical electronic configuration ($[Kr]4d^8 5s^1$) and exhibits mainly the principal oxidation states of 1 and 3. The primary use of this element is in automobiles as a catalyst converter, which converts harmful emission from the engine into less harmful gases [15]. Rhodium(I)-complexes play an important role as industrial homogeneous catalysts such as syntheses of fine chemicals like L-*DOPA* (a drug for curing Parkinson's disease) by an asymmetric hydrogenation of prochiral substrates with rhodium(I)-complexes containing optically active ligands [16], and carbonylation of methanol to produce acetic acid by Monsanto's process [17,18] where $[RhI_2(CO)_2]^-$ is the active catalytic species. Rhodium(I)-complexes are also used for hydroformylation of alkene to synthesize highly selective linear to branch aldehydes [19] and for hydrosilylation crosslinking of silicone rubber [20]. A great variety of rhodium complexes is prepared from $RhCl_3{\cdot}xH_2O$ and the methods for preparation of some selected starting rhodium complexes are shown in Scheme 1.

1.3. Ruthenium

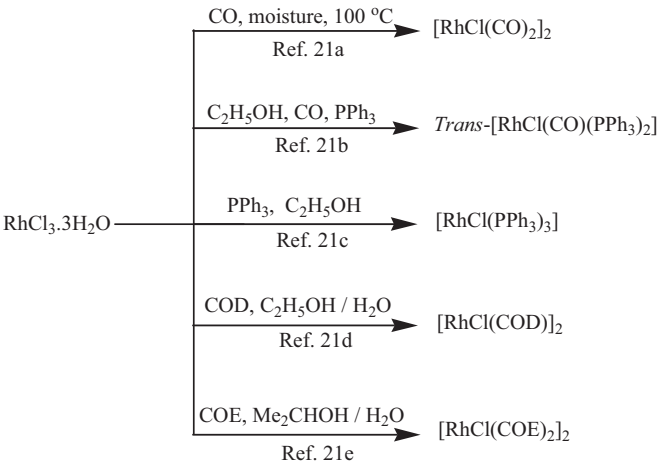
Ruthenium metal atom exhibits a $[Kr]4d^7 5s^1$ electronic configuration and shows a much wider scope of oxidation states e.g. −2, 0, +2, +3, +4, +5, +6 and +8 valence states in $[Ru(CO)_4]^{2-}$, $[Ru(CO)_5]$, $[Ru(H_2O)_6]^{2+}$, $[Ru(NH_3)_6]^{3+}$, $[RuO_2]$, $K[RuF_6]$, $[RuF_6]$ and $[RuO_4]$ respectively and various coordination geometries in each electronic configurations [22]. Due to the variable oxidation states and higher economy of ruthenium compared to the other platinum metals, ruthenium catalysed processes have become the most important and interesting methodologies in organic synthesis [22b,23–25]. In particular, ruthenium complex catalysed hydrogenation reaction is one of the most appealing routes for the reduction of various organic substrates [24]. The development of Noyori's transfer hydrogenation catalysts has attracted the attention of researchers towards the use of ruthenium catalysts in asymmetric hydrogenation reactions [22b,23a,25c,26]. The ruthenium complexes exhibit a variety of suitable characteristics like high Lewis acidity, high electron transfer ability, low redox potentials, stabilities of different reactive species, etc. $RuCl_3{\cdot}xH_2O$ can be utilized for the synthesis of ruthenium complexes of different ligands and the methods for preparation of some selected starting ruthenium complexes are shown in Scheme 2

1.4. Carbon monoxide (CO) ligand

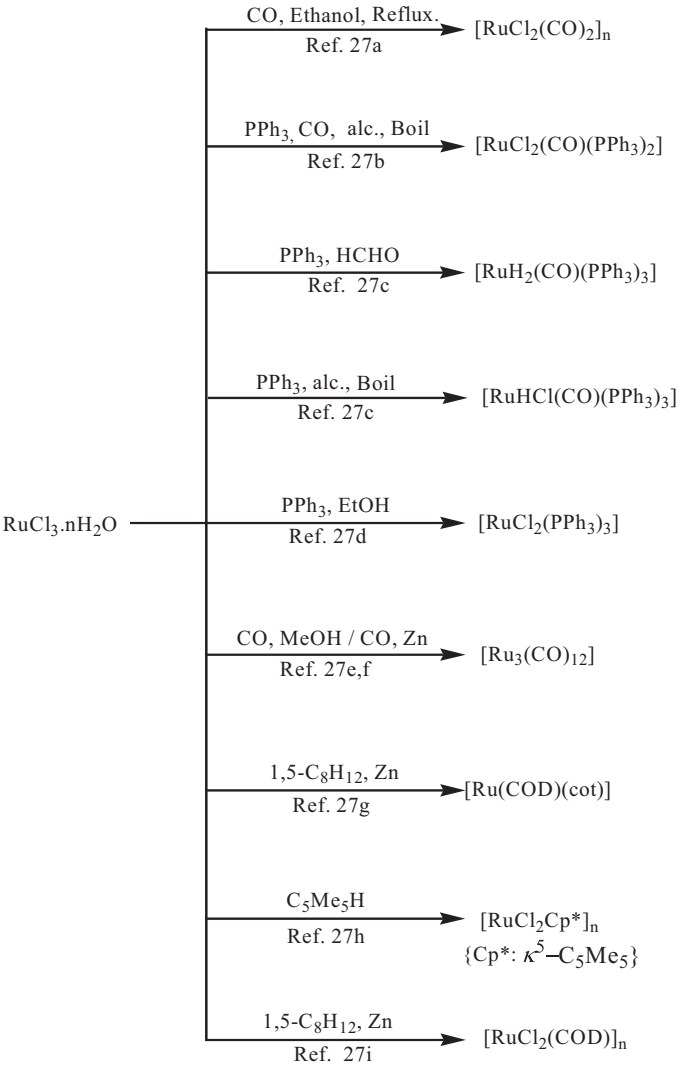
Carbon monoxide is ubiquitous in organometallic and coordination chemistry. It plays a key role in many catalytic processes. Over the last few decades, transition metal carbonyl complexes have become one of the most important families of compounds in organometallic chemistry [28]. Rhodium and iridium carbonyls are very active catalysts for carbonylation and hydroformylation reactions to synthesize industrially important products [5,6,13,29]. Some prominent examples are: (i) Monsanto's process [17,18] for producing acetic acid from methanol, (ii) a recent industrial catalytic process called 'CATIVA' [6b,c] where $[IrI_2(CO)_2]^-$ species with ruthenium-complex activator are used for carbonylation of methanol with high efficiency and (iii) hydroformylation of alkenes to synthesize highly selective linear to branch aldehydes [13,19].

1.5. Functionalized phosphine ligands

Tertiary phosphines functionalized with chalcogen donors like oxygen [30], sulfur [31] and selenium [32] containing 'Soft' phos-

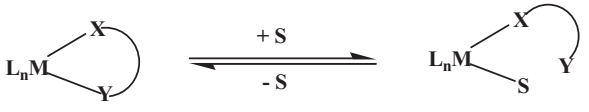


Scheme 1. Some important preparative routes for starting rhodium complexes.



Scheme 2. Some important preparative routes for ruthenium complexes.

phorus and 'Hard' oxygen donors or 'Soft' phosphorus and relatively less 'Softer' sulfur and selenium donor ligands with distinctly different π-acceptor strength [9] form a variety of metal complexes due to their different bonding abilities. Oxygen being a 'Hard' donor is capable of stabilizing metal ions in higher oxidation states which can be ascribed due to the absence of dπ-back bonding. On the other hand, 'Soft' phosphorus donors stabilize metal ions in low oxidation state by dπ-σ* back bonding. The metal-oxygen bond is weak and may dissociate reversibly to generate a vacant site for substrate binding and such ligands are called 'Hemilabile'. The M-S/Se bonds are comparatively labile than the M-P bonds in the chelated complexes of P-S and P-Se donors ligands and thus may permit facile generation of a 'Vacant site' at the metal centre [9,33] and may show interesting dynamic stereo-chemistry. Creation of such vacant coordination site through a reversible 'Opening and Closing' mechanism [33b] is useful for coordination and activation of the small molecules for further reaction with other organic substrates (Scheme 3). These unsymmetrical ligands can also generate chirality and electronic asymmetry at the metal centre, and this may lead to efficient chiral catalysis [34].



M = Metal centre, L_n = Ligand, X = Inert group,
Y = Labile group, S = Solvent,

Scheme 3. Ring "Opening and Closing" mechanism (Hemilabile).

2. Rhodium carbonyl complexes of P-X (X = O, S, Se) donor ligands

Rhodium forms a wide variety of carbonyl complexes of chalcogen functionalized phosphine ligands. Different potential rhodium carbonyl complexes are categorised based on the denticity of the P-X ligands as described below:

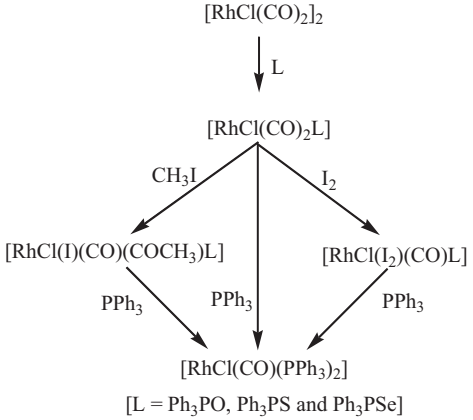
2.1. Complexes of monodentate ligands

Although a large number of rhodium complexes of alkyl or aryl substituted phosphorus donor ligands have been reported [21b,35], complexes containing functionalized P-X (X = chalcogen donors) ligands are quite scanty and only there are a few reports of the rhodium carbonyl complexes of such monodentate ligands.

The reaction of $[RhCl(CO)_2]_2$ with tricyclohexylphosphine oxide (Cy_3PO) (Rh: Cy_3PO mole ratio 1) yields *cis*-$[RhCl(CO)_2(Cy_3PO)]$ which is stable towards loss of carbon monoxide and undergoes subsequent dimerisation [36a]. An interesting complex $[Rh(CO)(PPh_3)_2(SPPh_2)]$, is obtained by the reaction of secondary phosphine sulfide, Ph_2HPS, with $[RhCl(CO)(PPh_3)_2]$ followed by reductive elimination of HCl [36b].

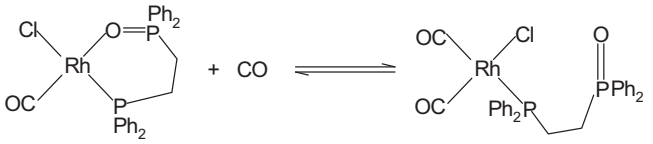
The rhodium(I) carbonyl complexes $[RhCl(CO)_2L]$ of chalcogen functionalised triphenyl phosphine ligands, L = Ph_3PO, Ph_3PS and Ph_3PSe [36c], exhibit ν(CO) frequencies in the order: $Ph_3PO > Ph_3PS > Ph_3PSe$, which may be substantiated by the 'Hard'/'Soft' interactions between the metal centre and chalcogen donor. The complexes undergo OA with electrophiles such as MeI and I_2 to give $[RhClI(CO)(COMe)L]$ and $[RhClI_2(CO)L]$, which react with PPh_3 to generate *trans*-$[RhCl(CO)(PPh_3)_2]$ (Scheme 4).

Some interesting thio-bridged dinuclear complexes $[Rh_2(\mu\text{-}S_2CR_2)(CO)_4]$ (R = alkyl/benzyl) react with P-donor ligands to produce the *trans*-isomer of the disubstituted complexes $[Rh_2(\mu\text{-}S_2CR_2)(CO)_2(PR'_3)_2]$ {R′ = Ph, Cy (cyclohexyl)} and $[Rh_2(\mu\text{-}S_2CBn_2)(CO)_2\{P(OR')_3\}_2]$ (Bn = benzyl, R′ = Me, Ph) [36d]. Similar complexes $[Rh_2(\mu\text{-}S_2CBn_2)(CO)_{4-n}\{P(OR)_3\}_n]$ (n = 1, 4) are also reported [36d].



[L = Ph_3PO, Ph_3PS and Ph_3PSe]

Scheme 4. Rhodium carbonyl complexes of chalcogen functionalised triphenyl phosphine.

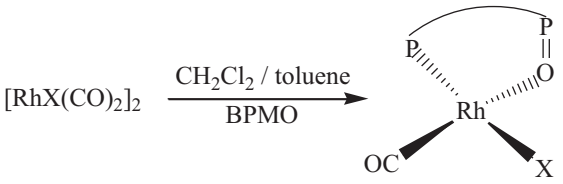


Scheme 5. 'Hemilabile' behaviour of P,O donor ligand.

2.2. Complexes of mono- and di-functionalized bidentate P-X (X = O, S, Se) ligands

During the last two decades, increasing attention has been focussed on the complex chemistry of hemilabile ligands, particularly, bidentate tertiary phosphines functionalized with oxygen [9,33a,37], sulfur [38,39] and selenium [40,41] donors. Reports on catalytic reactions of complexes containing sulfur or selenium donor are scanty because of metal poisoning by sulfur atom [42a] and deselination of selenide under the reaction condition [42b]. However, a few metal complexes containing P-S/P-Se ligands exhibit efficient catalytic activity for carbonylation and hydroformylation reaction under mild reaction conditions (*vide infra*). In this section, rhodium carbonyl complexes of both symmetric and unsymmetric chalcogen functionalized bidentate phosphines are discussed.

The complexes [RhCl(CO)(κ^2-*P,O*-BPMO)] (BPMO = dppmO, dppeO, dpppO, and dppbO), their preparation, and use in catalysis are reported [43a]. These complexes and the iodo dppmO analogue [43b] are prepared by reacting $[RhX(CO)_2]_2$ (X = Cl, I) with corresponding BPMOs (Eq. (1)). The structure of [RhCl(CO)(κ^2-*P,O*-dppmO)] (Cl trans to P), however, is confirmed by X-ray analysis [43a,c] and a similar chelate structure of [RhCl(CO)(κ^2-*P,O*-dppeO)] is also observed in solution [43c]. The formation of Rh–O chelate bond in the complexes [43a] is indicated by the shifting of ν(P=O) stretching band towards lower wave number. The five-membered complex [RhCl(CO){κ^2-*P,O*-$Ph_2PCH_2P(O)Ph_2$}] does not react with CO under low pressure (1 atm.), however, on increasing the pressure to 3 atm., a trace amount of dicarbonyl complex *cis*-[$RhCl(CO)_2${κ^1-*P*-$Ph_2PCH_2P(O)Ph_2$}] is formed [43c]. On the other hand, the six-membered complex [Rh(CO)Cl{κ^2-*P,O*-$Ph_2PCH_2CH_2P(O)Ph_2$}] can be reversibly cleaved by CO even at low pressure (1–3 bar) to give *cis*-[$RhCl(CO)_2${κ^1-*P*-$Ph_2PCH_2CH_2P(O)Ph_2$}] (Scheme 5). The cationic complexes $[Rh(CO)_2(dpmO_2)]ClO_4$ and $[Rh(CO)_2(dpeO_2)]ClO_4$, are prepared from $[Rh(COD)(dpmO_2)]ClO_4$ and $[Rh(COD)(dpeO_2)]ClO_4$ respectively by bubbling CO gas through DCM solutions [43d].



X = Cl; BPMO = dppmO, dppeO, dpppO, dppbO
X = I; BPMO = dppmO (1)

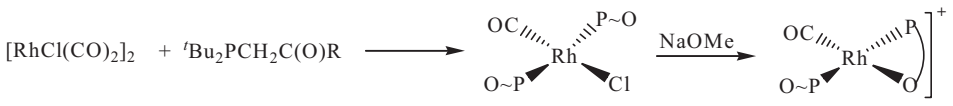
The complex *trans*-[RhCl(CO)(P∼O)$_2$] formed by the reaction of two equivalents of the ligand $^tBu_2PCH_2C(O)R$ with an ethanolic solution of $[RhCl(CO)_2]_2$ [44a], undergoes subsequent reaction with NaOMe to yield a chelate complex *trans*-[Rh(CO)(P∩O)(P∼O)]$^+$ (Scheme 6). The ^{31}P NMR spectra of the complex *trans*-[Rh(CO)(P∩O)(P∼O)]$^+$ display an ABX pattern for two different types of phosphorus and the *trans*-disposition of the two phosphorus atoms is reflected by large $J_{(PP)}$ values.

An interesting complex [RhCl(CO)(BINAP)] synthesized from $[RhCl(COD)]_2$ and BINAP under CO atmosphere [44b], reacts with oxygen to form the square planar [RhClCO{BINAPO(O)}] (Scheme 7) in approximately 50% yield.

The reaction of dimeric complex $[RhCl(CO)_2]_2$ with hemilabile ether phosphine ligands $Ph_2P(CH_2)_nOR$, *n* = 1, 2 and R = Me, Et, produced κ^1-*P* coordinated complexes of the type $[RhCl(CO)_2(P{\sim}O)]$ [44c]. Abstraction of halide from complexes by $AgClO_4$ promote coordination of the ether oxygen atom to yield cationic dicarbonyl complexes $[Rh(CO)_2(P{\cap}O)]ClO_4$ (Scheme 8). The OA of all the complexes with different electrophiles produces rhodium(III) oxidative adducts.

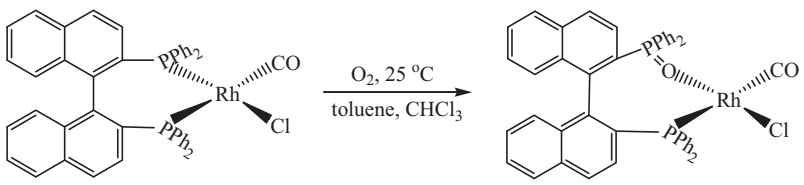
Two complexes of the types [RhCl(CO)(2-$Ph_2PC_6H_4COOMe$)] (κ^2-*P,O* chelate) and *trans*-[RhCl(CO)(2-$Ph_2PC_6H_4COOMe)_2$] (κ^1-*P* coordinated) are reported [14]. The X-ray structure (Fig. 1) of the latter complex indicates the presence of 'Secondary' Rh–O interactions with the ester groups of the phosphines. The complex exhibits ν(CO) at 1949 cm^{-1} indicating the lowest value so far reported of such complexes. The ν(CO) frequencies reflect high electron density at the metal centre in both complexes, which react readily with MeI to give Rh(III) acetyl products, via unstable Rh(III) methyl intermediates.

The complex [RhCl(CO)(κ^2-*P,S*-$Ph_2PCH_2P(S)Ph_2$)] is synthesised by reacting $[RhCl(CO)_2]_2$ with two equivalent of $Ph_2PCH_2P(S)Ph_2$ in methanol [45a]. In the complex, P and S are coordinated to the metal where the M-S bond is more labile than the M-P,

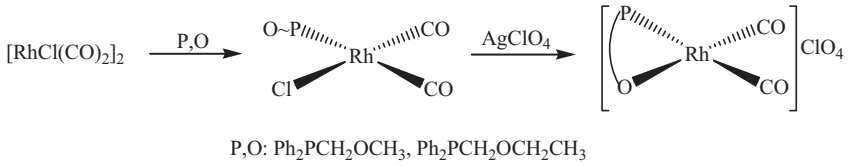


P∼O : κ^1-*P* coordinated $^tBu_2PCH_2C(O)R$
P∩O : κ^2-*P,O* coordinated $^tBu_2PCH_2C(O)R$

Scheme 6. Synthesis of [Rh(CO)(P∼O)(P∩O)]$^+$.



Scheme 7. Synthesis of [RhCl(CO){BINAPO(O)}].



P,O: $Ph_2PCH_2OCH_3$, $Ph_2PCH_2OCH_2CH_3$

Scheme 8. Synthesis of $[Rh(CO)_2(P\cap O)]ClO_4$.

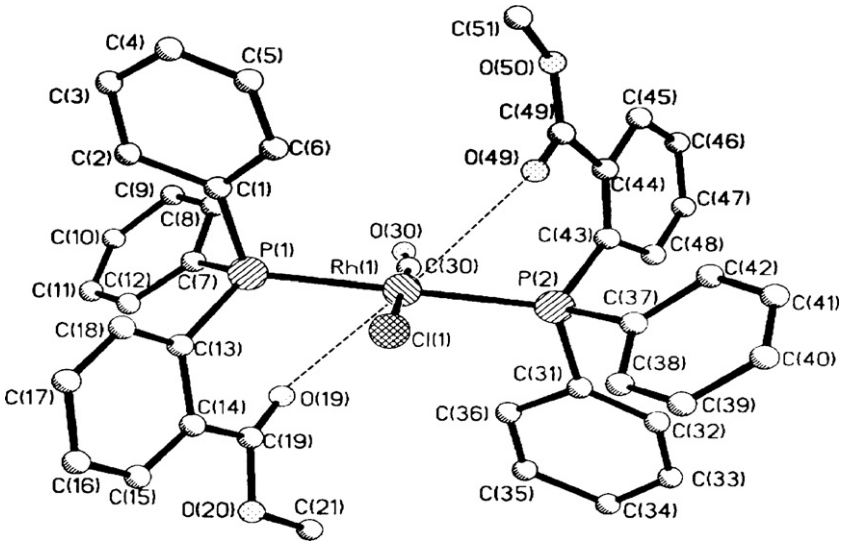
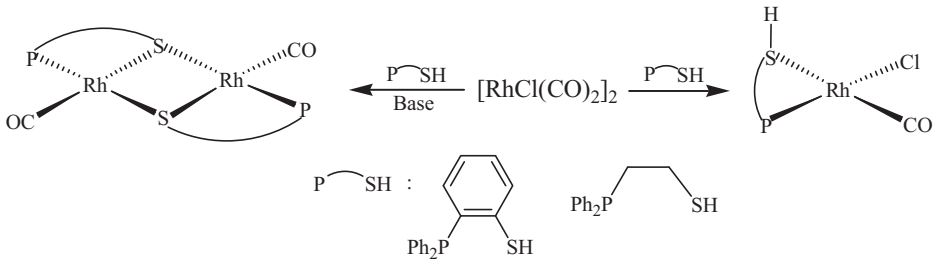


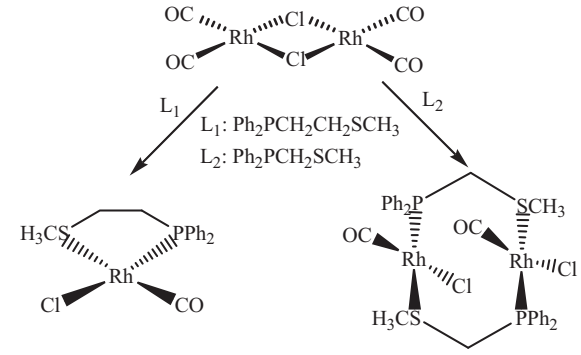
Fig. 1. Crystal structure of the complex *trans*-$[RhCl(CO)(2\text{-}Ph_2PC_6H_4COOCH_3)_2]$ (Ref. [14]).



Scheme 9. Synthesis of rhodium carbonyl complexes of P,S donor ligands.

permitting facile generation of a vacant site at the metal centre. Rhodium(I) also forms dimeric complexes by the reaction of $[RhCl(CO)_2]_2$ with 2-(diphenylphosphino)benzenethiol and 2-(diphenylphosphino)ethanethiol in the presence of base [45b]. However, a simple monomer is obtained [45b] with ligands in appropriate molar ratio without base (Scheme 9).

An interesting feature of P,S ligands is observed as $[RhCl(CO)_2]_2$ reacts with $Ph_2PCH_2SCH_3$ to produce a binuclear complex $[Rh_2Cl_2(CO)_2(\mu\text{-}Ph_2PCH_2SCH_3)_2]$, while with $Ph_2PCH_2CH_2SCH_3$ it yields a mononuclear complex $[RhCl(CO)_2(Ph_2PCH_2CH_2SCH_3)]$ (Scheme 10) [45c]. The complex, *cis*-$[PtCl_2(Ph_2PCH_2SCH_3)_2]$ reacts with $[RhCl(CO)_2]_2$ at ambient temperature to yield *cis*-$[PtCl_2(CO)(Ph_2PCH_2SCH_3)]$ and $[Rh_2Cl_2(CO)_2(\mu\text{-}Ph_2PCH_2SCH_3)_2]$ (Eq. (2)) [45c,d], while $[PdCl_2(Ph_2PCH_2S\text{-}CH_3)_2]$ generates the mixed metal complex $[PdRhCl_3(CO)(\mu\text{-}Ph_2PCH_2SCH_3)_2]$ (Eq. (3)). The structure of this complex (Eqn. (3)) is assigned on the basis of its NMR data, where the $^{31}P\{^1H\}$ NMR spectrum shows a doublet for the P atom coordinated to palladium and a doublet of doublets



Scheme 10. Mono and binuclear rhodium carbonyl complexes of P,S donor ligands.

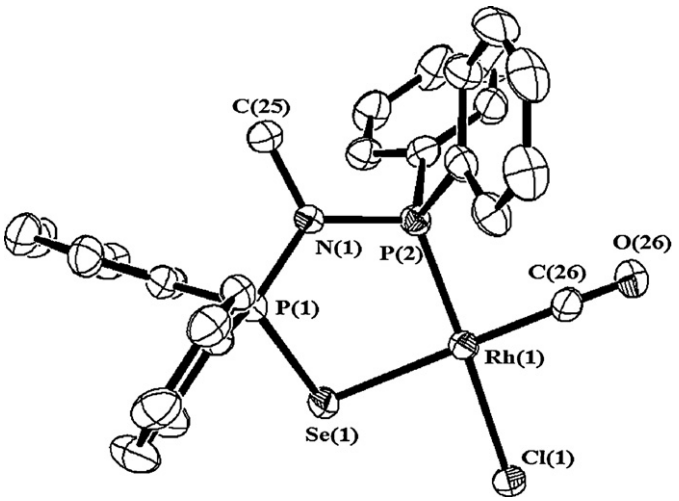


Fig. 2. Molecular structure of [RhCl(CO){κ^2-*P,Se*-$Ph_2PN(CH_3)P(Se)Ph_2$}] showing atomic labelling (Ref. [47a]).

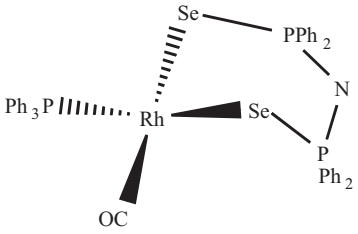
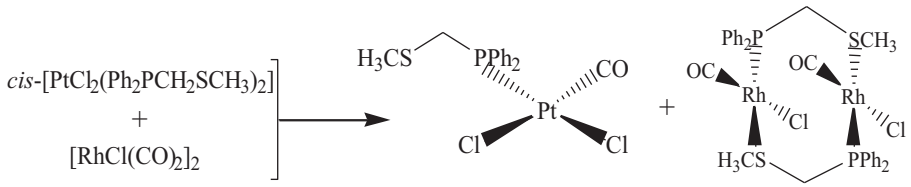


Fig. 3. The molecular structure of [Rh(CO)(PPh_3){κ^2-*Se,Se*′-$Ph_2P(Se)NP(Se)Ph_2$}] (Ref. [48b]).

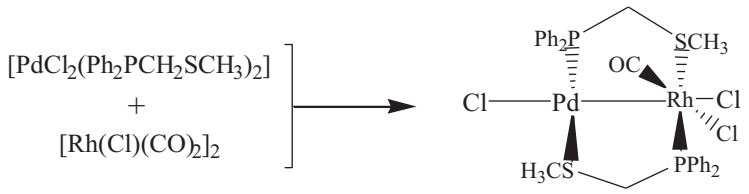
reported [48a] and the molecular structure of which is established by X-ray diffraction studies.

Some interesting complexes [Rh(CO)(PPh_3){κ^2-*P,O*-$Ph_2PNP(O)Ph_2$}], [$Rh(CO)_2$-{κ^2-*Se,Se*′-$Ph_2P(Se)NP(Se)Ph_2$}] and [Rh(CO)(PPh_3){κ^2-*Se,Se*′-$Ph_2P(Se)NP(Se)Ph_2$}], are synthesised by stepwise reactions of CO and PPh_3 with [Rh(COD){κ^2-*P,O*-$Ph_2PNP(O)Ph_2$}] and [Rh(COD){κ^2-*Se,Se*′-$Ph_2P(Se)NP(Se)Ph_2$}] respectively (Scheme 11) [48b]. The structure of the complex

for the P atom attached to rhodium.



(2)



(3)

Another interesting complex [RhCl(CO)(P∩S)] (P∩S = κ^2-*P,S* coordinated $Ph_2PCH_2CH_2SEt$), formed by the bridge splitting reaction of $[RhCl(CO)_2]_2$ with the ligand, undergoes OA with MeI and I_2 to generate [RhCII(COMe)(P∩S)] and [$RhCII_2$(CO)(P∩S)] respectively [46].

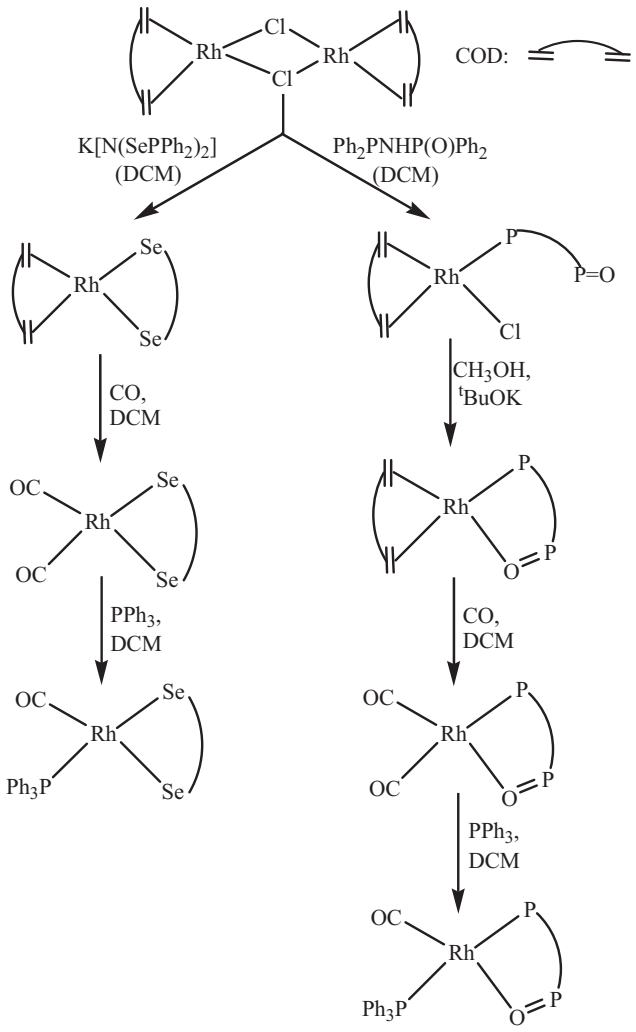
The chelate complexes [RhCl(CO)(κ^2-*P,Se*-$Ph_2PCH_2P(Se)Ph_2$)] and [RhCl(CO)(κ^2-*P,Se*-$Ph_2PN(CH_3)P(Se)Ph_2$)] show lower shift of the ν(P-Se) bands and downfield shift of the ^{31}P {^1H}NMR signals for both P(III) and P(V) atoms in the complexes compared to the corresponding free ligands indicating chelate formation through the selenium donor [47a]. The molecular structure of the latter complex (Fig. 2) shows a stable five-membered heterocyclic (Rh, P, N, P and Se) ring.

A series of unsymmetrical phosphine–phosphine monoselenide ligands react with $[RhCl(CO)_2]_2$ to form non-chelate complexes [$RhCl(CO)_2(Ph_2P(CH_2)_nP(Se)Ph_2)$] {$\kappa^1$-*P* coordinated, n = 2–4}[47b]. The complexes undergo OA with different electrophiles such as CH_3I, C_2H_5I, $C_6H_5CH_2Cl$ and I_2 to produce Rh(III) complexes. The kinetic study of the OA of the complexes with CH_3I and C_2H_5I reveal single stage kinetics. However, CH_3I exhibits reactivities with the different complexes at a rate 10–100 times faster than C_2H_5I.

In addition to the several rhodium carbonyl complexes of unsymmetrical phosphine–phosphine chalcogenides, complexes of symmetrical phosphine–phosphine chalcogenides are also reported [48a]. The preparation of rhodium carbonyl complex [$Rh(CO)_2(dppmS_2)$][ClO_4], where $dppmS_2 = Ph_2P(S)CH_2P(S)Ph_2$ is [Rh(CO)(PPh_3){κ^2-*Se,Se*′: $Ph_2P(Se)NP(Se)Ph_2$}] (Fig. 3) exhibits a slightly distorted boat ring conformation.

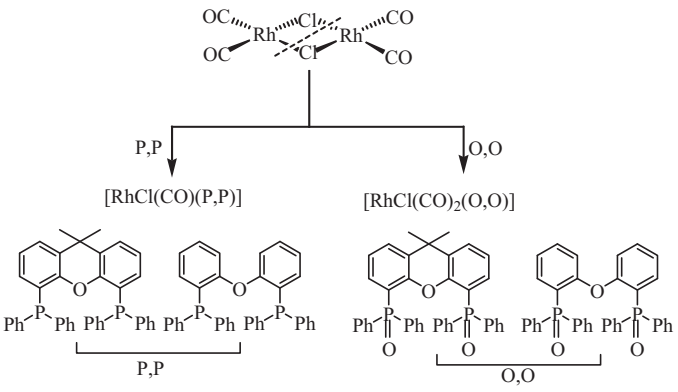
The dimeric rhodium precursor $[Rh(CO)_2Cl]_2$ reacts with two mole equivalent of diphosphine (P,P) [P,P = Xantphos and DPEphos] to produce monocarbonyl complexes of the type [RhCl(CO)(P,P)] [48c] while with diphosphine dioxide (O,O) [O,O = Xantphos(O_2) and DPEphos(O_2)] in stoichiometric quantity affords dicarbonyl complexes [$RhCl(CO)_2$(O,O)] (Scheme 12). The complexes undergo OA with different electrophiles such as CH_3I, C_2H_5I and I_2 to give Rh(III) oxidized products. Kinetic data for the reactions of the complexes with CH_3I indicate a pseudo first order reaction and also exhibit that the rate of OA for the monocarbonyl complexes [RhCl(CO)(P,P)] is slower than those of dicarbonyl complexes [$RhCl(CO)_2$(O,O)]. The reaction of [$RhCl(CO)_2${Xantphos(O_2)}] with CH_3I shows an interesting feature (Fig. 4) and the appearance of two acyl ν(CO) bands of almost equal intensity may be attributed to the formation of equimolar quantities of two acyl Rh(III) complexes in the reaction mixture (Scheme 13).

The S–N–S pincer type rhodium carbonyl complex [Rh(EtSNS)(CO)], EtSNS = $EtNC(S)Ph_2P{=}NPPh_2C(S)NEt^-$ can be prepared by the reaction of HEtSNS with $[RhCl(CO)_2]_2$ in the presence of ^{t}BuOK or by bubbling CO in a solution of the κ^2-*S,S* complex [Rh(EtSNS)(COD)] (Scheme 14) [49]. An unstable κ^2-*S,S* intermediate [Rh(EtSNS)$(CO)_2$] is observed through monitoring the reaction by FTIR (νCO: 2075, 2009 cm^{-1}). The coordination of the nitrogen atom increases the electron density at the metal centre, as



Scheme 11. Preparation of [Rh(CO)(PPh$_3$){κ^2-*Se*,*Se*-Ph$_2$P(Se)NP(Se)Ph$_2$}] and [Rh(CO)(PPh$_3$){κ^2-*P*,*O*-Ph$_2$PNP(O)Ph$_2$}].

inferred from the lower CO stretching frequency of the final complex [νCO (CH_2Cl_2): 1967 cm^{-1}]. The compound [Rh(EtSNS)(CO)] is protonated to produce cationic species like [Rh(HEtSNS)(CO)]$^+$ and [Rh(H_2EtSNS)(CO)]$^{2+}$, in which the protons binds to the nitrogen atoms of the thioamidyl functions (Scheme 15). The complexes react with CH_3I in DCM to yield stable acetyl-Rh(III)-complexes.



Scheme 12. Synthesis of [RhCl(CO)(P,P)] and [RhCl(CO)$_2$(O,O)].

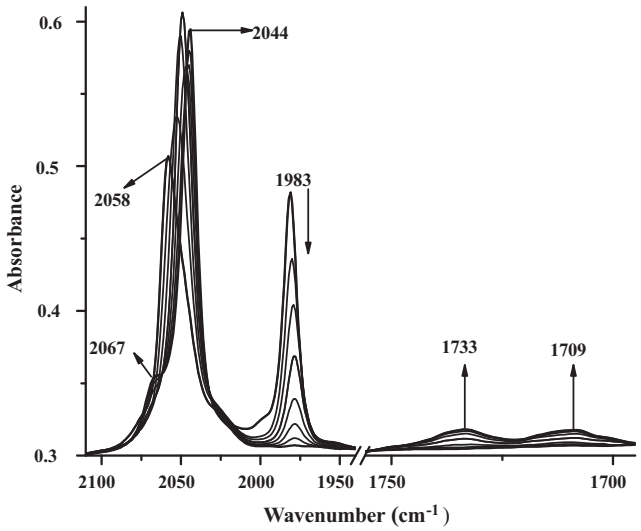


Fig. 4. IR spectra {ν(CO) region} illustrating the reaction of [RhCl(CO)$_2$-{xantphos(O_2)}] with CH_3I at 25 °C (Ref. [48c]).

2.3. Complexes of polyphosphine ligands

Polyphosphines as ligands show several advantages like (i) excellent bonding ability to metal, (ii) create high electron density at the metal centre (high nucleophilicity), (iii) formation of stable metal-complexes, (iv) stabilize different oxidation states of metals, (v) provide structural and bonding information due to the metal–phosphorus and phosphorus–phosphorus coupling constants. Metal complexes of such ligands are thermodynamically more stable than monophosphine analogues. Reviews on stereochemical control of transition metal complexes by polyphosphines [50] elaborate the different aspects of the complexes and their catalytic chemical reactions particularly hydrogenation and hydroformylation.

Tripod, HC(PPh$_2$)$_3$ with least steric constraints forms small rhodium cluster having metal–metal bond (Fig. 5) [51a,b]. The d^8 metal complexes of MeC(CH_2PPh$_2$)$_3$ are much studied [51c,d]. The *fac*-coordinating character of the ligand facilitates the formation of metal–metal bonded complexes but the Rh–Rh bond can be cleaved by suitable reagents to monomeric complexes (Fig. 6). In metal-tripod complex based catalytic reactions like hydroformylation, at least one of the ligand (MeC(CH_2PPh$_2$)$_3$)-metal bonds dissociate to create free coordination site (Fig. 7) for substrate binding [51e]. The polyphosphine ligands are also used in chiral hydrogenation [51e,f]. One of the important chiral complexes of rhodium is highlighted (Fig. 8).

Although, a large number of rhodium complexes of polyphosphine ligands have been reported [51], there are only a few

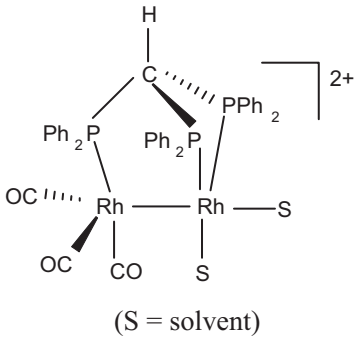
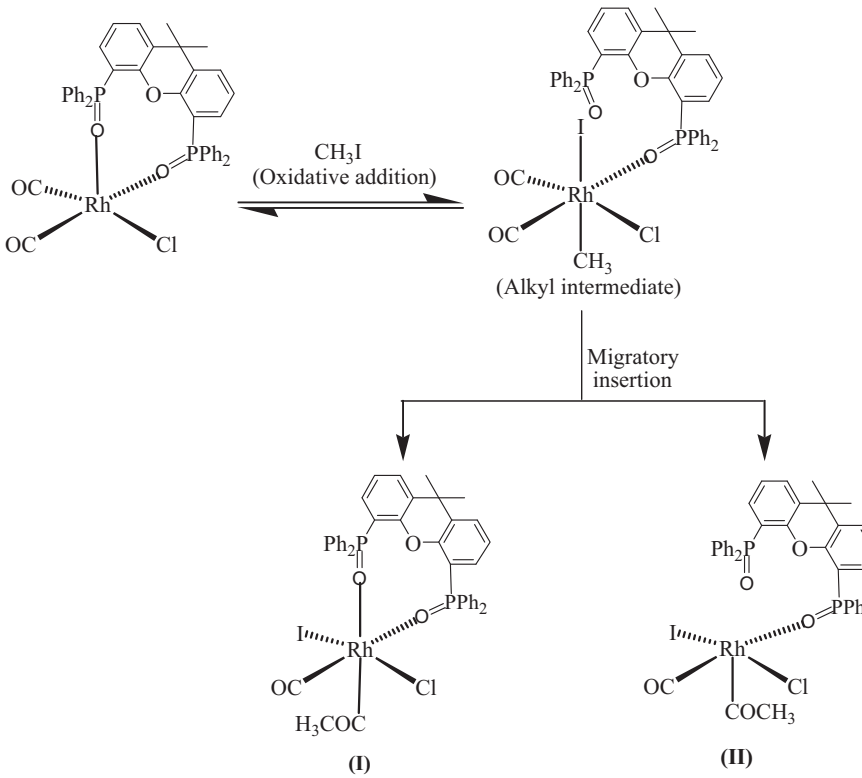
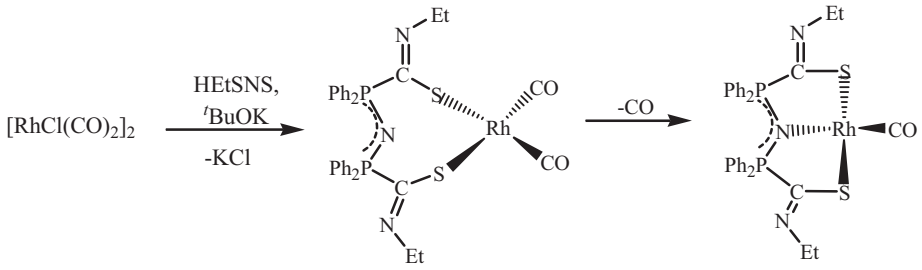


Fig. 5. Rhodium complex of HC(PPh$_2$)$_3$ containing Rh–Rh bond.



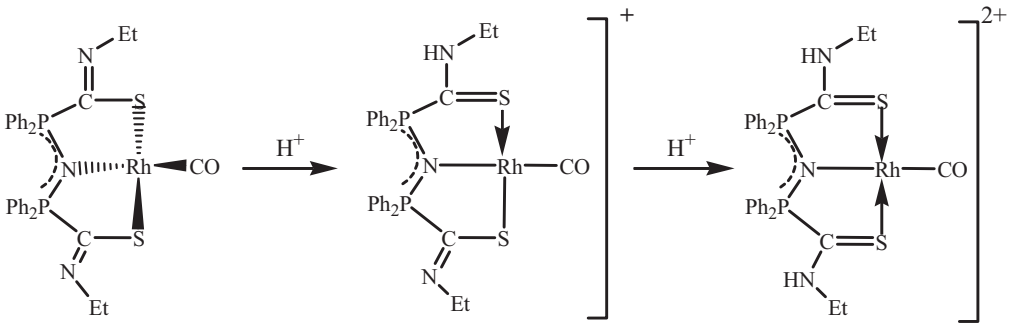
Scheme 13. Plausible Rh(III)-acyl complexes (**I** and **II**) generated after OA of CH_3I to $[RhCl(CO)_2\{Xantphos(O_2)\}]$.



Scheme 14. Preparation of [Rh(EtSNS)(CO)], where EtSNS = $EtNC(S)Ph_2P{=}N\text{-}PPh_2C(S)NEt^-$.

reports of the rhodium complexes of chalcogen functionalized polyphosphine ligands (P-X). The cationic complex $[Rh(COD)\{\kappa^3\text{-}P,S,S\text{-}(CH(PPh_2)(P(S)Ph_2)_2\}]$ is prepared as a fluoroborate salt by the reaction of the ligand $CH(PPh_2)(P(S)Ph_2)_2$ with chlorobridged complex $[Rh_2Cl_2(COD)_2]$ under mild conditions in the presence of $NaBF_4$ [52a]. The structure of the complex is assigned by ^{31}P NMR spectroscopic studies indicating the formation of tripodal κ^3-*P,S,S* coordinated ligand.

The conventional oxidation of triphos with H_2O_2 is nonselective, but the ligand can be mono-oxidized selectively [51c] in the form of its κ^2-*P,P*-triphos metal complex (Eq. (4)). The dicarbonyl rhodium complex that is originally formed, loses a molecule of CO



Scheme 15. Formation of the mono- and the dicationic complexes by protonation of the zwitterionic metalate.

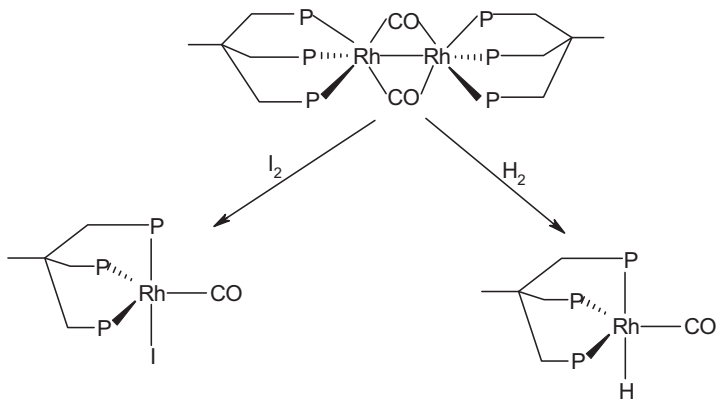
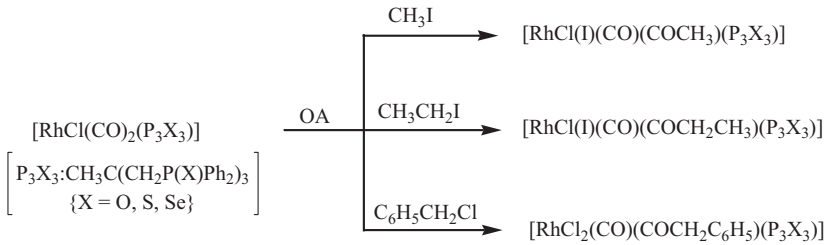


Fig. 6. The cleavage of Rh–Rh bond to form monomeric complexes.



Scheme 16. OA with different electrophiles.

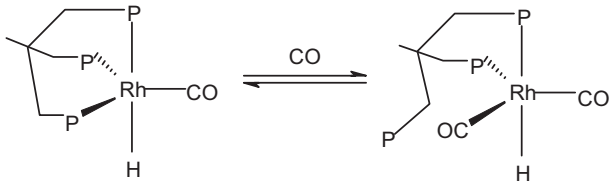


Fig. 7. Reversible dissociation of Rh–P bond (Ref. [51e]).

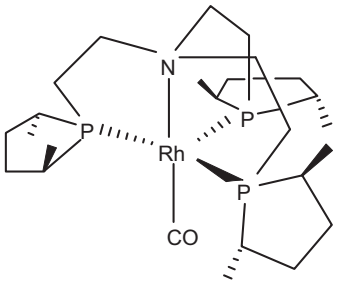
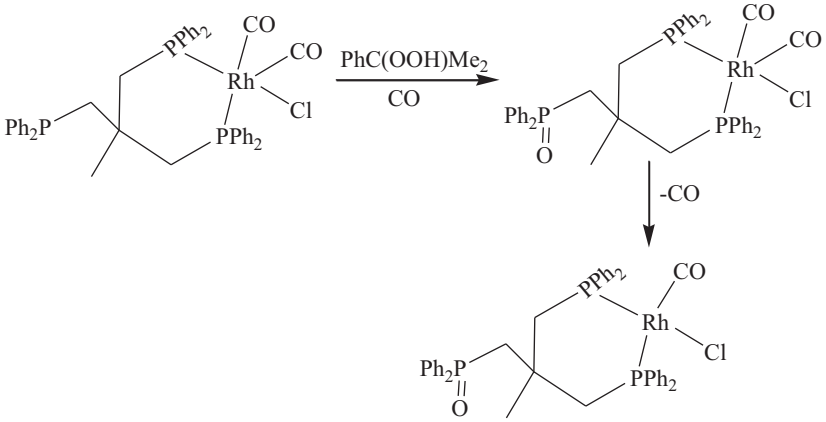


Fig. 8. Rhodium carbonyl complex of nitrogen functionalized polyphosphine (Ref. [51f]).

upon bubbling argon through its solution.



(4)

Recently, the synthesis and catalytic activity of three rhodium carbonyl complexes of 1,1,1-tris(diphenylphosphinomethyl)ethane trichalcogenide ligands, $[CH_3C(CH_2P\text{-}(X)Ph_2)_3]$, where X = O, S and Se are reported [52b]. The complexes are prepared by the reaction of $[RhCl(CO)_2]_2$ in CH_2Cl_2 with two mole equivalent of the ligands (Eq. (5)). Spectroscopic studies of these complexes suggest the formation of a mixture of isomers where P-X groups are coordinated to the metal centre either monodentate and/or bidentate coordination mode. The complexes undergo OA with different electrophiles such as CH_3I, C_2H_5I and $C_6H_5CH_2Cl$ to give Rh(III) acyl complexes (Scheme 16). Kinetic data for the reaction of the complexes with CH_3I indicate a first order reaction, which also demonstrates that the rate of OA depends on the nature of the chalcogen donor ligands at the coordination sphere of the rhodium centre.

$$[RhCl(CO)_2]_2 \xrightarrow[P_3X_3:[CH_3C(CH_2P(X)Ph_2)_3]]{[P_3X_3]} [RhCl(CO)_2(P_3X_3)] \quad X = O, S, Se \tag{5}$$

2.4. Catalytic activities

Although, there is a large number of examples of rhodium complex catalysed organic reactions in the literature [53], it is often very difficult to categorize and thereby appreciate the full impact of this metal. This review highlights three potential catalytic applications; carbonylation, hydrogenation and hydroformylation reactions.

2.4.1. Carbonylation reaction

Carbonylation catalysis has occupied an interesting and important area of chemistry. The majority of carbonylation reactions are carried out in homogeneous phase, because of a lower energy process with higher reaction rates and higher selectivities than heterogeneous systems.

The original $[RhI_2(CO)_2]^-$ catalyst developed at the Monsanto laboratories [17,18] and studied in detail by Forster and co-workers [18a,b], is mainly used for the industrial production of acetic acid and anhydride. However, the conditions used industrially (30–60 bar pressure and 150–200 °C) [18] have spurred the search for new catalysts, which could work in milder conditions [6d,54,55]. The rate determining step of the rhodium based catalytic cycle is the OA of CH_3I and therefore the focus is on the catalyst design for improvement of this reaction. The basic idea was that the ligands which increase the electron density at the metal centre, and consequently its nucleophilicity should promote OA, and subsequently increase the overall rate of the reaction. With this aim, a large number of rhodium complexes have been synthesized in the last few decades, and are shown to be active catalysts of comparable or better performance than the Monsanto catalyst [6d,14,54,55]. In this section, chalcogen functionalized phosphine ligands-promoted rhodium catalysed carbonylation of methanol has been highlighted.

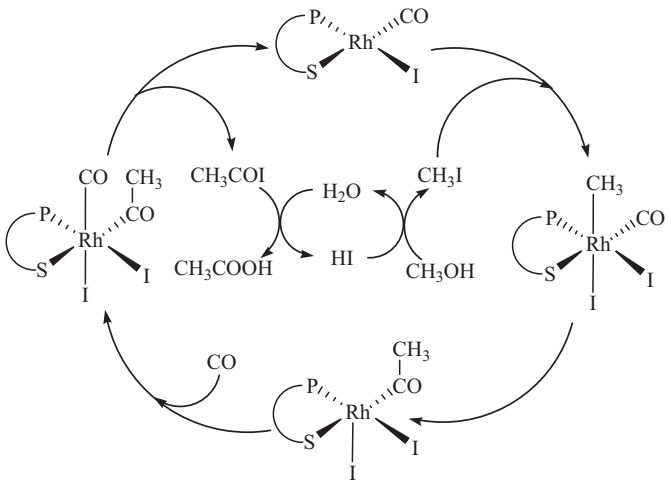
Rhodium carbonyl complexes of chalcogen functionalized monodentate phosphines like $[RhCl(CO)_2L]$ where $L = Ph_3PO$, Ph_3PS and Ph_3PSe [36c] show efficient catalytic activity in carbonylation of methanol. The catalytic reactions are carried out at different temperatures, pressures and time periods and in each case, the complexes exhibit much higher catalytic activity compared to the well-known catalyst precursor $[RhCl(CO)_2]_2$. Among the chalcogenide containing catalyst precursors, $[RhCl(CO)_2(Ph_3PS)]$ shows the highest catalytic activity, however, the factor responsible for such high efficiency could not be substantiated [36c].

Unsymmetrical bidentate ligands such as $PPh_2CH_2P(O)Ph_2$ [43c], $PPh_2CH_2P(NPh)Ph_2$ [56] and $PPh_2CH_2P(S)Ph_2$ [45a] are effective in rhodium-catalysed carbonylation of methanol. The complex, *cis*-$[RhCl(CO)\{Ph_2P(CH_2)_2P(O)Ph_2\}]$ is a very active catalyst for the carbonylation of methanol under mild reaction conditions [43c] and interaction with CO results in the displacement of the rhodium–oxygen bond and the formation of a new species $\{\upsilon(CO)\ 2096 \text{ and } 2012\ cm^{-1}\}$ according to the equilibrium shown in Scheme 5. The ratio of the κ^2- and the κ^1-complexes was determined to be approximatively 1:1 (at 22 °C and 1 bar CO). IR spectroscopic studies carried out under catalytic conditions at 80 °C and 3.5 bar CO (TOF 400 h^{-1}) reveal only the κ^1-coordinated phosphine oxide species.

The diphosphinesulfide $Ph_2PCH_2P(S)Ph_2$ ligand promoted rhodium catalysed carbonylation of methanol allows a substantial rate increase under industrially feasible conditions (185 °C, 70 bar CO) [45a]. The optimum rate enhancement is observed when the discrete complex *cis*-$[RhCl(CO)\{(\kappa^2\text{-}P,S\text{-}Ph_2PCH_2P(S)Ph_2\}]$ is used as precatalyst, but the X-ray structure of the complex shows no unusual features to explain the unexpected stability of the catalyst at high temperatures. Unlike the oxygen analogue, in the complex $[RhI(CO)\{Ph_2PCH_2P(S)Ph_2\}]$, there is no evidence for a hemilabile behaviour of the P-S ligand (Scheme 17), while it is important for catalysis employing mixed-donor ligands [9]. These results show that a discrete rhodium–phosphine complex can give a significant improvement in carbonylation activity over $[RhI_2(CO)_2]^-$ under industrial conditions. The rhodium carbonyl complexes $Rh(CO)(P\cap S)]_2$ and $[RhCl(CO)(P\cap S)]$ synthesized according to Scheme 9 show efficient catalysis in carbonylation of methanol with comparable rate [31e]. A mechanism is proposed similar to the cycle shown in Scheme 17.

Rhodium complexes $[RhCl(CO)_2(Ph_2PCH_2OCH_3)]$, $[RhCl(CO)_2(Ph_2PCH_2CH_2OC_2H_5)]$ [44c], $[RhCl(CO)(Ph_2PCH_2CH_2SC_2H_5)]$ [46], $[RhCl(CO)(2\text{-}Ph_2PC_6H_4COOMe)]$ (κ^2-*P,O* chelate), *trans*-$[RhCl(CO)(2\text{-}Ph_2PC_6H_4COOMe)_2]$ (κ^1-*P* coordinated) complexes [14] show efficient catalysis in carbonylation of methanol compared to well known Monsanto's catalyst. The complex $[RhCl(CO)_2(Ph_2PCH_2CH_2OC_2H_5)]$ exhibits higher TON compared to $[RhCl(CO)_2(Ph_2PCH_2OCH_3)]$ [44c], which may be attributed to the higher stability of the five-membered ring intermediate complex than the four-membered ring (Scheme 18). The catalytic activities of the complexes *cis*-$[RhCl(CO)(2\text{-}Ph_2PC_6H_4COOMe)]$ and *trans*-$[RhCl(CO)(2\text{-}Ph_2PC_6H_4COOMe)_2]$ are higher than the well known complex *trans*-$[RhCl(CO)(Ph_3P)_2]$ [14]. Higher catalytic activity of the functionalized phosphine over the nonfunctionalized one might be due to the higher electron density at the metal centre by the chelate formation through ester oxygen donors of the ligand. From the electronic point of view, *trans*-$[RhCl(CO)(2\text{-}Ph_2PC_6H_4COOMe)_2]$ should show higher catalytic activity than $[RhCl(CO)(2\text{-}Ph_2PC_6H_4COOMe)]$, but in practice, the reverse situation is observed, perhaps because of the steric factor of the two bulky $-COOCH_3$ group on the two phosphine ligands that sterically restrict the path of OA for MeI, which is the rate determining step for carbonylation of methanol [14].

Rhodium complexes of selenium functionalized phosphines like $[RhCl(CO)(Ph_2PCH_2P(Se)Ph_2)]$, $[RhCl(CO)(Ph_2PN(CH_3)P(Se)Ph_2)]$ [47a] and $[RhCl(CO)_2(Ph_2P(CH_2)_nP(Se)Ph_2)]$



Scheme 17. Catalytic cycle of the methanol carbonylation catalysed by the neutral complex $[RhI(CO)\{Ph_2PCH_2P(S)Ph_2\}]$.

Table 1
Results of methanol carbonylation Ref. [48c].

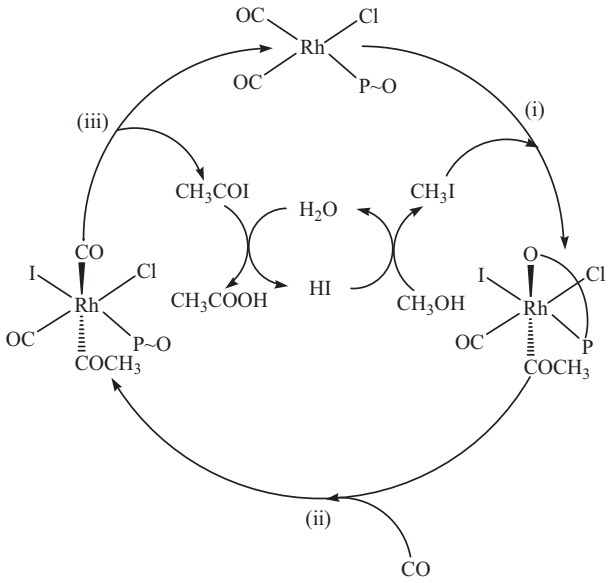
Catalyst precursor	CO pressure at 25 °C (±1 bar)	Total conv. (%)	Acetic acid[a] (%)	Methyl acetate[a]	TON[b]
[RhCl(CO)(Xantphos)]	5	35.3	8.9	26.4	679.0
	10	56.2	24.0	32.2	1081.0
	20	82.4	42.1	40.3	1585.0
[RhCl(CO)(DPEphos)]	5	36.5	7.5	29.0	702.1
	10	66.5	25.3	41.2	1279.2
	20	85.1	48.5	36.6	1637.0
[$RhCl(CO)_2${Xantphos(O_2)}]	5	42.5	12.1	30.4	839.1
	10	66.9	27.8	39.1	1286.9
	20	89.3	49.5	39.8	1717.8
[$RhCl(CO)_2${DPEphos(O_2)}]	5	55.2	12.6	42.6	1061.8
	10	72.4	30.4	42.0	1392.7
	20	91.9	54.4	37.5	1768.4

[a] Yield of methyl acetate and acetic acid were obtained from GC analyses after 1 h reaction time.
[b] TON = [amount of product (mol)]/[amount of catalyst (Rh mol)].

{κ^1-*P* coordinated, n = 2–4} [47b] are stable and efficient catalysts in carbonylation of methanol. All these complexes show better activity compared to well known rhodium precursor $[RhCl(CO)_2]_2$. Among these complexes, [RhCl(CO){κ^1-*P,Se*-$Ph_2PN(CH_3)P(Se)Ph_2$)] exhibits a maximum conversion of 42.4% with the highest TON 901. As expected from higher reactivity in OA of $RhCl(CO)(Ph_2PCH_2P(Se)Ph_2)$] over [$RhCl(CO)(Ph_2PN(CH_3)P(Se)Ph_2)$], the former should act more efficiently over the latter in the carbonylation reaction, but, a reverse trend is observed. This may be substantiated as the higher electron donating ligands make the metal centre more nucleophilic and may lead to the formation of stronger Rh–C (acyl) bond rendering the retardation of the rate of the reductive elimination reaction required for completion of the catalytic cycle [47a].

The rhodium phosphine complexes [RhCl(CO)(P,P)] and $[RhCl(CO)_2(O,O)]$ [48c] show higher catalytic activity in carbonylation of methanol than the well known precursor $[RhI_2(CO)_2]^-$ generated *in situ* from $[RhCl(CO)_2]_2$. The results of carbonylation of methanol to acetic acid and methyl acetate (Table 1) reveal that the complexes $[RhCl(CO)_2(O,O)]$ show higher catalytic activity than [RhCl(CO)(P,P)]. The dicarbonyl complexes undergo OA with MeI with faster rate than those of monocarbonyl complexes and hence the former shows higher TON compared to latter [48c]. The rhodium complexes $[RhCl(CO)_2(P_3X_3)]$ containing tripodal phosphine chalcogenides (Eq. (5)), also show efficient catalytic activity in methanol carbonylation reaction [52b].

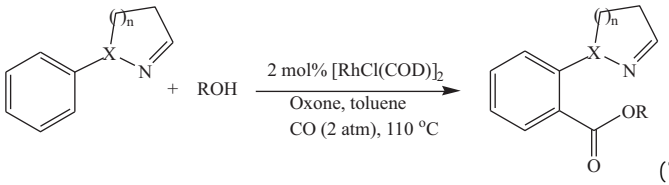
In addition to the methanol carbonylation, other types of carbonylation reactions such as rhodium(I)-catalysed reaction of alkynes with 2-bromophenylboronic acids in the presence of paraformaldehyde result in a CO gas-free carbonylative cyclization, yielding indenone derivatives [56a]. The complexes $[RhCl(BINAP)]_2$ and $[RhCl(COD)]_2$ are responsible for the decarbonylation of the formaldehyde and subsequent carbonylation of alkynes with 2-haloboronic acids, respectively, leading to efficient carbonylation (Eq. (6)).



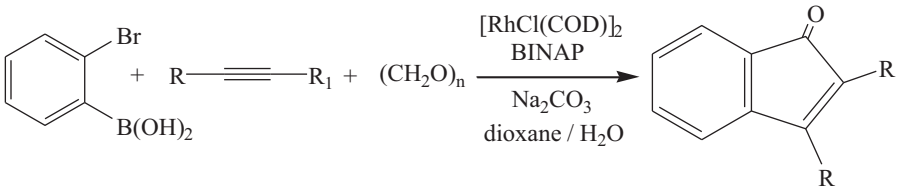
P,O : $Ph_2PCH_2OCH_3$; $Ph_2PCH_2CH_2OCH_2CH_3$
P~O = κ^1-*P* coordinated P,O ; P∩O = κ^2-*P,O* coordinated P,O

Scheme 18. Catalytic cycle for the methanol carbonylation catalysed by [RhCl(CO)-(P∩O)] complexes.

ortho-substituted aryl or heteroaryl carboxylic esters.



(7)

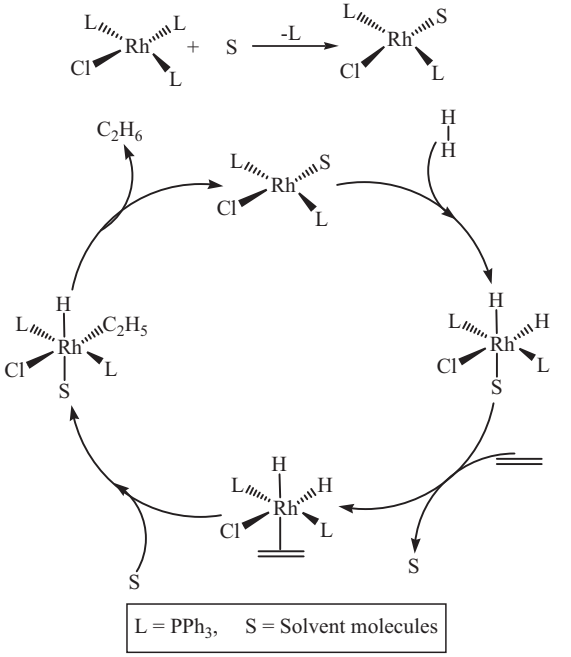


(6)

A general protocol for the rhodium-catalysed oxidative carbonylation of arenes and heteroarenes to form esters in presence of carbon monoxide and alcohols (Eq. (7)) is reported [56b]. Such Rh-catalysed oxidative carbonylation reaction shows high regioselectivity and good functional group tolerance up to 96% yield of

2.4.2. Hydrogenation

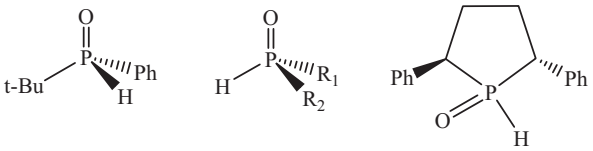
The two important terms 'Hydrogenation' and 'Transfer Hydrogenation' have distinct features i.e. in the former, hydrogen gas (H_2) is involved while in the latter, the hydrogen source must be differ-



Scheme 19. Hydrogenation of ethylene by Wilkinson's catalyst [$RhCl(PPh_3)_3$].

ent from dihydrogen (H_2) i.e. the source of hydrogen atom is from H-donor.

The study of homogeneous hydrogenation reactions catalysed by transition metal complexes has been far more extensive than that of any other catalytic process in solution [57]. One of the most popular homogeneous catalysts for hydrogenation reaction is Wilkinson's catalyst, $RhCl(PPh_3)_3$, discovered in the sixties [21c,58]. The complex [$RhCl(PPh_3)_3$] dissociates one of the PPh_3 ligands in solution to generate solvated [$RhCl(PPh_3)_2(S)$] species (Scheme 19) which undergoes OA with a molecule of hydrogen. An alkene may then coordinate and react with a coordinated hydrogen ligand to form an alkyl group followed by reductive elimination of ethane to complete the cycle. The rate of reductive elimination step can be increased by employing electron withdrawing ligands at the coordination sphere of rhodium. However, if one of the PPh_3 ligands in [$RhCl(PPh_3)_3$] complex is substituted by CO group to form [$RhCl(CO)(PPh_3)_2$] this does not form a rhodium(III) dihydride complex although it is closely related to Wilkinson's species. Substitution of a PPh_3 by CO group (a stronger π-acceptor) lowers the basicity of the metal centre considerably to prevent it from undergoing OA under moderate condition. By changing the halide in the rhodium complexes, the activity and selectivity can be affected remarkably for e.g. [$RhBr(PPh_3)_3$] and [$RhI(PPh_3)_3$] show



R_1: i-Pr, t-Bu, Ph; R_2: Ph, 2-nephthyl, 2-MeO-phenyl etc.

Scheme 21. Enantiopure secondary phosphine oxides.

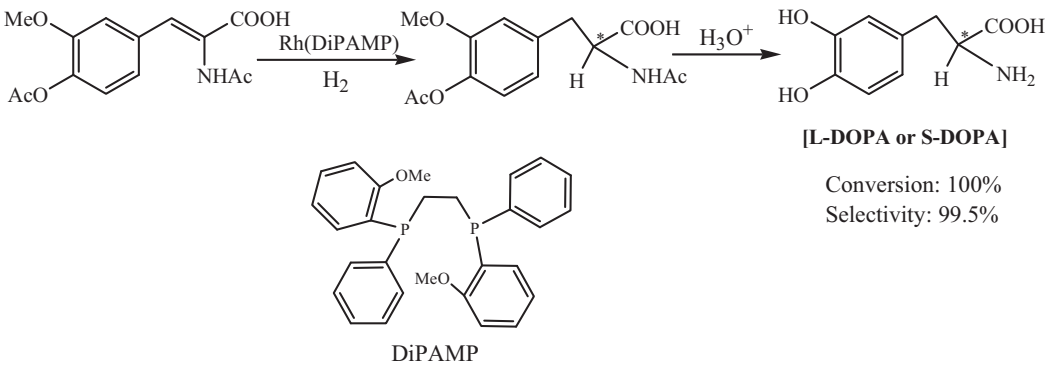
higher catalytic activity in hydrogenation of terminal alkene than [$RhCl(PPh_3)_3$] [59].

A recent survey shows that the use of asymmetric hydrogenation for the production of fine chemicals is limited, but expanding [60]. Two major factors that hamper its use are the cost of the catalysts, and in particular the ligands that are often prepared in a multi-step synthesis. However, the demand for enantiomerically pure compounds with a desired biological activity is growing rapidly in fine-chemical synthesis. An obvious reason for this development is that one of the enantiomers of a chiral pharmaceutical or chemical has at best no activity, or worse, causes side effects. One of the important success stories is the synthesis of fine chemicals like L-*DOPA* (Scheme 20) by an asymmetric hydrogenation of prochiral substrates with rhodium(I)-complexes containing optically active ligand DiPAMP [16]

Though a large number of rhodium complexes of phosphorus and nitrogen donor ligands have been utilised in hydrogenation reaction [61], the use of chalcogen functionalized phosphines as coordinating ligand are very limited. Some interesting hydrogenation reactions catalysed by rhodium complexes of chalcogen functionalized phosphines have been highlighted.

The water-soluble cationic binuclear rhodium complex $[Rh(CO)(Ph_2PCH_2CH_2NMe_3)(\mu\text{-S-}^tBu)]_2[BPh_4]_2$ and the neutral binuclear complex $[Rh(CO)(Ph_2PCH_2CH_2NMe_2)(\mu\text{-S-}^tBu)]_2$ are highly active catalysts for olefin hydrogenation [62a]. Another example of bimetallic water-soluble rhodium complex was prepared [62b] *in situ* from $[RhCl(COD)]_2$ and TPPTS, and is quite an effective catalyst for transfer hydrogenation of aldehydes and ketones with isopropyl alcohol, under basic conditions. The complex $[Rh(\mu\text{-Pz})(CO)(TPPMS)]_2$, where Pz = pyrazolate ligand and $TPPMS = (C_6H_5)_2P(C_6H_4SO_3Na)$, shows catalytic activities in the two phase hydrogenation reaction of olefins to give mainly the expected saturated products [62c].

The enantiopure secondary phosphine oxides (Scheme 21) are evaluated as ligands in the rhodium and iridium-catalysed asymmetric hydrogenation of functionalized olefins [63a]. ^{t}Butylphosphinoyl benzene is a versatile ligand in the iridium-catalysed hydrogenation of β-branched dehydroamino esters and in the rhodium-catalysed hydrogenation of an enol carbamate.



Scheme 20. Synthesis of L-DOPA.

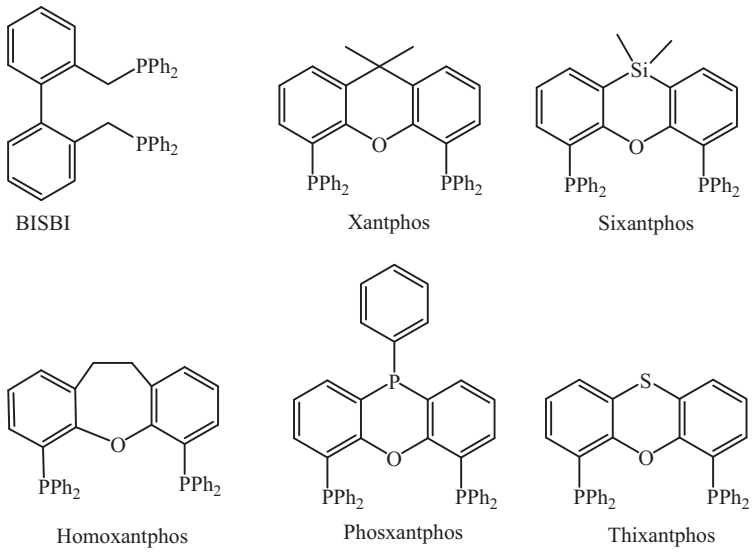


Fig. 9. BISBI and the predecessors of Xantphos family.

The rhodium and iridium-catalysed asymmetric hydrogenation of prochiral olefins in the presence of thioether–phosphinite ligands (P-SR, R = Ph, ^{i}Pr and Me) bearing substituents with different steric demands on the sulfur centre are reported [63b]. High ee (upto 96%) and good activities [TOF upto 860 mol product × (mol catalyst precursor × h)$^{-1}$] are obtained for α-acylaminoacrylates derivatives. The results show that the ee depends strongly on the steric properties of the substituent in the thioether moiety, the metal source and the substrate structure.

The rhodium(I) complexes of urea phosphine ligands that coordinate in a *P,O*-bidentate fashion are effectively used in the asymmetric hydrogenation of cyclic enamides giving high conversions and enantioselectivity [63c].

2.4.3. Hydroformylation

The hydroformylation of olefins, which was discovered as early as 1938 by Otto Roelen, has become one of the largest industrially applied processes and is based on homogeneous catalysis [64]. Since, the first use of phosphines in the cobalt catalysed process, which included preliminary data for the use of rhodium as well [65a], many industries started to apply phosphine ligands in rhodium catalysed processes [65b]. The Rh(I)-PPh_3 complexes are active and highly regioselective hydroformylation catalysts for 1-alkenes, even at ambient conditions [66]. The first rhodium-catalysed, ligand-modified process was introduced in 1974 (Celanese) and more were to follow in 1976 (Union Carbide Corporation) and in 1978 (Mitsubishi Chemical Corporation), all were using triphenylphosphine.

In the late sixties, phosphites have also been considered as ligands for rhodium hydroformylation, but tpp turned out to be the ligand of choice. A renewed interest in phosphites started in the eighties because of peculiar effect of bulky monophosphites giving very high rates [67].

The chelating phosphines show interesting effects on hydroformylation reaction. $R_2P(CH_2)_xPR_2$ (x = 2–4) ligands with alkyl or aryl substituents generally form catalysts that give poor rates and selectivities, as well as extensive alkene isomerization and hydrogenation side reactions. Tridentate tripodal phosphine ligands, such as $MeC(CH_2PPh_2)$, also generate catalysts with very poor rates and regioselectivities [68a]. HPNMR studies have shown that an arm-on, arm-off equilibrium is operational to generate the active unsaturated 16-electron catalyst species [$HRh(CO)\{\kappa^2$-*P,P*-$MeC(CH_2PPh_2)\}$] [68b]. However, certain diphosphines have also become very popular ligands since the late eighties in rhodium hydroformylation. Important breakthroughs were reported with BISBI and the predecessors of Xantphos (Fig. 9) all showing a high regioselectivity for the formation of linear aldehydes [68c]. Propene was hydroformylated by using BISBI under 'Standard' conditions in a vapour stripped reactor. The aldehyde product shows a high linearity (l:b = 30).

Asymmetric hydroformylation of alkenes is potentially an important reaction for the synthesis of chiral aldehydes as intermediates in drug synthesis. The most interesting ligand discovered for asymmetric hydroformylation is undoubtedly BINAPHOS [69a], but certain other diphosphites also give high enantioselectivities [69b–d].

Though a large number of mono and multidentate phosphine based ligands have been nominated for rhodium catalysed hydroformylation [6a,12,13,65–70], in this section only the effectiveness of chalcogen functionalized phosphine ligands in rhodium catalysed hydroformylation reaction will be highlighted.

The chelate cationic rhodium(I) complexes with a hemilabile amino- and sulfur-containing phosphinite ligand (Fig. 10) efficiently catalyze the hydroformylation of styrene [71a]. The chelate rhodium complex with the analogous ligand without the amino group has also been synthesized and evaluated as a catalyst for the same hydroformylation reaction. The reaction rate is higher for the former complex compared to the latter, however, a slightly lower regioselectivity towards the formation of the branched aldehyde is observed.

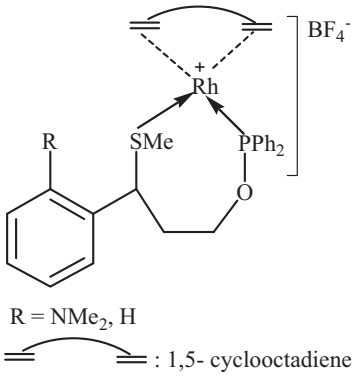


Fig. 10. Rhodium(I) complex of amino- and sulfur-containing phosphinite ligand (Ref. [71a]).

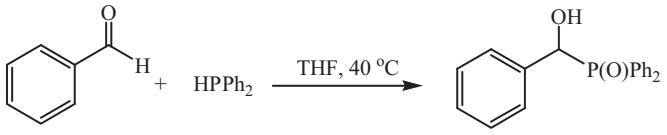


Fig. 11. Synthesis of (diphenylphosphinoyl)phenylmethanol (Ref. [71b]).

The phosphine oxide compound, (diphenylphosphinoyl)phenylmethanol (Fig. 11) in the rhodium-catalysed hydroformylation of alkenes shows good conversions and regioselectivities [71b]. This ligand is partially resolved using an enzyme, and enantioselective hydroformylation is carried out with the addition of a rhodium(I) complex. The cationic complex $[(BINAPO(O))Rh(Diol)]^+$ where (*S*)-BINAPO(O) consistently displays as P,O-chelate ligand, which exhibits active but poorly stereoselective catalysis in hydrogenation, hydroboration, and hydroformylation of alkenes [71c]. Another rhodium complex (Fig. 12) with a nitrogen containing bis(phosphine oxide) ligand is also applied to hydroformylation of styrene. The complex shows a high activity and regioselectivity towards the branched aldehyde, which is higher than those of the tertiary bis(phosphine) analogue [71d].

The gem-dithiolato-bridged rhodium(I) complex $[Rh_2(\mu\text{-}S_2CBn_2)(COD)_2]$ ($Bn_2CS_2^{2-}$ = 1,3-diphenyl-2,2-dithiolatopropane) dissolved in toluene in the presence of monodentate phosphite P-donor ligand $P(OPh)_3$ under CO and H_2 (1:1 syn-gas) atmosphere acts as an effective catalyst for hydroformylation of some olefins (oxo-reactions) [71e]. This innovative method to perform the *in situ* hydroformylation of the olefins would be an important work for future industrial catalytic processes. The dinuclear complexes $[Rh_2(\mu\text{-}S_2Cptn)(COD)_2]$ ($CptnS_2^{2-}$ = 1,1-cyclopent-anedithiolato), $[Rh_2(\mu\text{-}S_2Chxn)(COD)_2]$ ($ChxnS_2^{2-}$ = 1,1-cy-clohexanedithiolato), $[Rh_2(\mu\text{-}S_2CBn_2)(COD)_2]$ ($Bn_2CS_2^{2-}$ = 1,3-diphenyl-2,2-dithiolatopropane) and $[Rh_2(\mu\text{-}S_2C^iPr_2)(COD)_2]$ ($^iPr_2CS_2^{2-}$ = 2,4-dimethyl-2,2-dithiolatopentane) in the presence of monodentate phosphine or phosphite P-donor ligands under CO and H_2 (1:1) atmosphere are efficient catalysts for the hydroformylation of oct-1-ene under mild conditions. Aldehyde selectivities higher than 95% and TOF upto 245 h^{-1} are obtained using $P(OMe)_3$ as modifying ligand [71f]. The compound $[Rh_2(\mu\text{-}S_2Chxn)(COD)_2]$ ($Chxn(SH)_2$ = 1,1-dimercaptocyclohexane) is an active catalyst precursor in the presence of P-donor ligands like $P(OMe)_3$ for the hydroformylation of 1-octene under mild conditions of pressure (100 psi) and temperature (353 K). An aldehyde selectivity of 97%, a regioselectivity towards the linear aldehyde of 81%, and TOF upto 198 h^{-1} are observed [71g].

The complex *trans*-$[Rh(CO)(\kappa^1\text{-}P\text{-}Hdpf)(\kappa^2\text{-}O,P\text{-}dpf)]$ (Hdpf = 1′-(diphenylphosphino)ferrocenecarboxylic acid) acts as an efficient and recyclable catalyst for 1-hexene hydroformylation producing about 80% of aldehydes at 10 atm CO/H_2 and 80 °C [71h]. The complex can be separated from the reaction mixture after reaction and may be reused for three times with the same catalytic activity.

A series of rhodium–phosphine oxide system for the hydroformylation of olefins are reported [72a]. Some of the phosphine oxide ligands of the type $R_2N(CH_2)_nP(O)R'_2$, where R′ = Ph, Cy; *n* = 0–3; R = Me, Et, ^{i}Pr, or NR_2 = 2-pyridyl, are better ligands than the phosphine analogues i.e. $R_2N(CH_2)_nPR'_2$ in the hydroformylation reaction. The detailed examination of the factors controlling the selectivity for aldehydes formation reveals a few characteristics of the reaction: (a) use of ligands having bulkier amino groups decrease the yield of the aldehydes slightly; (b) ligands having amino groups with low basicity decrease the rate of the hydroformylation dramatically; (c) the electronic properties of the phosphine oxide group have no influence on the hydroformylation reaction; (d) uncoordinating solvents of low polarity such as dichloromethane, chloroform and toluene give the best reaction rate and selectivity. In addition to the above, a mixture of phosphine–phosphine oxide ligands are effective in hydroformylation reaction [72b,c].

The first reported rhodium complexes of anionic 2-(bis(2-methoxyphenyl)phosphino)benzenesulfonate (L) ligand shows significant [72d] catalytic activity in homogeneous hydroformylation of 1-hexene. The reaction is carried out in preparative autoclaves and studied under *operando* conditions by means of both HPNMR and HPIR spectroscopy. *Operando* spectroscopic hydroformylation experiments show that the catalyst precursors bearing either COD or triethylamine as ancillary ligand are rapidly converted into di-carbonyl complexes. Mono- and dicarbonyl rhodium(I) complexes show a resting states of the catalytic cycle, most likely due to equilibrium with other species containing either the zwitterionic ligand HL coordinated in the κ^1-*O* bonding mode or exclusively carbonyl ligands.

The *in situ* generated rhodium complex from $[Rh(CO)_2(acac)]$ and $Ph_2P(CH_2)_2S(CH_2)_3Si(OMe)_3$, immobilized in inorganic and hybrid silica matrices via the sol–gel process acts as an effective catalyst in the hydroformylation of 1-hexene and 1-octadecene without any rhodium leaching [72e]. The catalyst can also be used in the absence of a solvent, as observed in the hydroformylation of 1-decene.

The complexes $[Rh(COD)\{\kappa^2\text{-}P,O\text{-}Ph_2PNP(O)Ph_2\}]$, $[Rh(CO)(PPh_3)\{\kappa^2\text{-}P,O\text{-}Ph_2PNP(O)Ph_2\}]$, and $[Rh(CO)(PPh_3)\{\kappa^2\text{-}Se,Se'\text{-}Ph_2P(Se)NP(Se)Ph_2\}]$ show catalytic activity in the hydroformylation of styrene. However, the former two complexes containing chelating P,O-ligands show satisfactory catalytic properties,

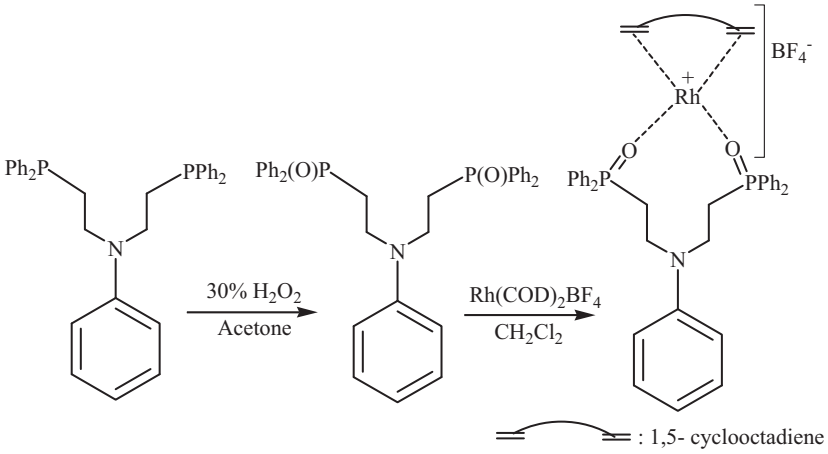
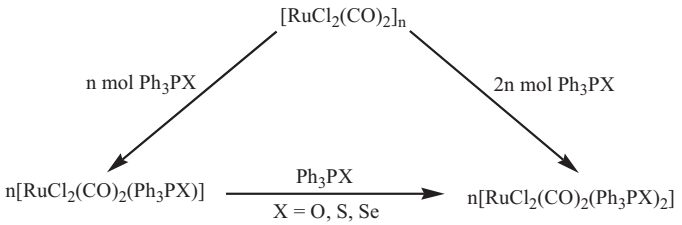


Fig. 12. Rhodium complex of a nitrogen-containing bis(phosphine oxide) ligand (Ref. [71d]).



Scheme 22. The products of reactions between $[RuCl_2(CO)_2]_n$ and Ph_3PX (X = O, S, Se).

whereas the latter complex effectively show no catalytic activity [48b].

3. Ruthenium carbonyl complexes of P-X (X = O, S, Se) donor ligands

Ruthenium forms various types of complexes containing chalcogen functionalized phosphines as coordinating ligands. Different potential ruthenium complexes are categorized based on the denticity of the P-X ligands as described below:

3.1. Complexes of monodentate ligands

Coordination compounds of tertiary phosphine chalcogenides are dedicated to complexes with either the oxygen, sulfur or selenium atom of the ligand acting as a neutral κ^1-donor to the metal centre [73], $Ph_3P=O$ [74] (a 'Hard' donor ligand), $Ph_3P=S$ [74,75] (a 'Soft' donor ligand) and $Ph_3P=Se$ [36c] (a 'Soft' donor ligand).

There are only a few reports on ruthenium complexes [76,77] containing mono-dentate phosphine donor ligands. The polymeric complex $[RuCl_2(CO)_2]_n$ reacts with triphenyl phosphine chalcogenide ligands Ph_3PX; X = O, S and Se [78] in an appropriate Ru: Ligand mole ratio to yield five- and six-coordinated complexes of the types $[RuCl_2(CO)_2(Ph_3PX)]$ and $[RuCl_2(CO)_2(Ph_3PX)_2]$ respectively (Scheme 22) [77]. The υ(CO) frequencies of the complexes, in general, follow the order: $Ph_3PO > Ph_3PS > Ph_3PSe$ which may be ascribed in terms of 'Soft–Hard' (Ru(II)-O) and 'Soft–Soft' (Ru(II)-S/Se) interactions. The ν(PX) bands of the complexes show significantly lower wave number than the corresponding free ligands indicating the formation of Ru–X bonds. The molecular structure of the complex $[RuCl_2(CO)_2(Ph_3PS)_2]$ (Fig. 13) shows a slightly distorted octahedral geometry, two *trans*-*S* atoms of two Ph_3PS ligands, two *cis*-CO groups and two *cis*-chlorides.

The reaction of $[Ru_3(CO)_{12}]$ with Ph_3PS yields $[Ru_3(\mu_3\text{-}S)_2(CO)_{9-n}(PPh_3)_n]$ [n = 1, 2] and $[Ru_3(\mu_3\text{-}S)(\mu_3\text{-}CO)(CO)_7(PPh_3)_2]$ as the major products [79]. Molecular structure of both the complexes show two different classes of compounds to contain square pyramidal Ru_3S_2 and trigonal pyramidal Ru_3S metal cores, respectively, the latter being isostructural to the analogous selenide cluster compound. The clusters $[Ru_3(\mu_3\text{-}E)_2(CO)_{9-n}(PPh_3)_n]$ (E = S, n = 1; E = Se, n = 2) readily undergo ligand displacement reactions with PPh_3 to afford $[Ru_3(\mu_3\text{-}E)_2(CO)_6(PPh_3)_3]$ (E = S/Se). The mixed chalcogenide cluster, $[Ru_3(\mu_3\text{-}S)(\mu_3\text{-}Se)(CO)_7(PPh_3)_2]$ can be prepared by the reaction of $[Ru_3(\mu_3\text{-}S)(\mu_3\text{-}CO)(CO)_7(PPh_3)_2]$ with $SePPh_3$ [79].

An interesting aspect of ruthenium carbonyl cluster is to undergo Se-transfer reactions from tertiary phosphine and diphosphine selenides to the carbonyl clusters $[Ru_3(CO)_{12}]$ to provide a simple, stepwise synthetic route to generate phosphine-substituted mono- and diselenido(carbonyl)ruthenium clusters [80].

The OA of the chalcogenides $[R_2P(E)]_2NH$ (R = Ph or ^{i}Pr, E = S or Se) to the metal carbonyl $[Ru_3(CO)_{12}]$ in the presence of Me_3NO produces substituted tri- and tetranuclear capped sulfido (or selenido) Ru carbonyl complexes [81]. The molecular structures of the three representative complexes $[Ru_4(\mu_4\text{-}Se)_2(\mu\text{-}CO)\text{-}(CO)_8\{(Ph_2P)_2NH\}]$, $[Ru_4(\mu_4\text{-}S)_2(\mu\text{-}CO)(CO)_8\{(^iPr_2P)_2NH\}]$ and $[Ru_3(\mu_3\text{-}S)_2(CO)_7\text{-}\{(Ph_2P)_2NH\}]$ show interesting structural behaviour [81]. Some interesting Ru(II) complexes containing R_3P, R_3PO, R_3PS and R_3PSe (R = tolyl) ligands are reported [82], where the complexes $[RuCl_2(PR_3)_4]$ and $[Ru_2Cl_4(PR_3)_6]$ are assigned as cubic and tetragonal structures respectively.

The reaction of $[Ru_3(CO)_{12}]$ with the chalcogen functionalized phosphines, $(EPR_2)(E'PR'_2)NH$ [E = E′ = S, R = Ph, R′ = Me and E = E′ = Se, R = R′ = Ph], yields the complexes $[Ru_3(\mu_2\text{-}H)(\mu_3\text{-}S)\{\mu_2\text{-}S,S,P'\text{-}(SPPh_2)(PMe_2)N\}(CO)_8]$, $[Ru_3(\mu_2\text{-}H)(\mu_3\text{-}S)\{\mu_2\text{-}S,S,P'\text{-}(SPMe_2)(PPh_2)N\}(CO)_8]$, $[Ru_3(\mu_3\text{-}S)_2\{\mu_2\text{-}P,P'\text{-}(Ph_2P)(PMe_2)NH\}(CO)_7]$, $[Ru_4(\mu_4\text{-}S)_2\{\mu_2\text{-}P,P'\text{-}(Ph_2P)(PMe_2)NH\}(CO)_8(\mu_2\text{-}CO)]$, $[Ru_3(\mu_2\text{-}H)(\mu_3\text{-}Se)\{\mu_2\text{-}Se,Se,P'\text{-}(SePPh_2)(PPh_2)N\}(CO)_8]$, $[Ru_3(\mu_3\text{-}Se)_2\{\mu_2\text{-}P,P'\text{-}(PPh_2)_2NH\}(CO)_7]$, and $[Ru_4(\mu_4\text{-}Se)_2\{\mu_2\text{-}P,P'\text{-}(PPh_2)_2NH\}(CO)_8(\mu_2\text{-}CO)]$. The resulting products of the reaction indicate that the cleavage of the P = E bonds of the ligand is one of the first steps in the reaction, followed by the cleavage of the remaining P = E′ bonds [83].

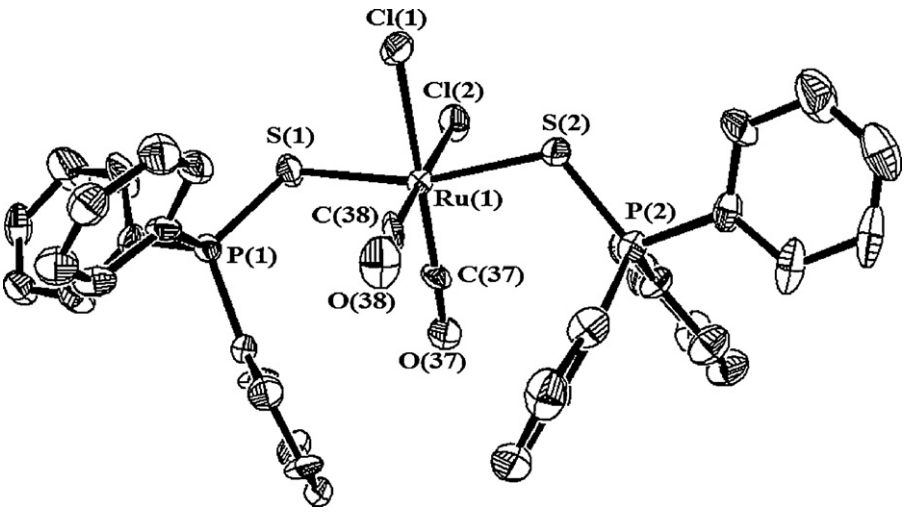


Fig. 13. Molecular structure of $[RuCl_2(CO)_2(Ph_3PS)_2]$ (Ref. [77]).

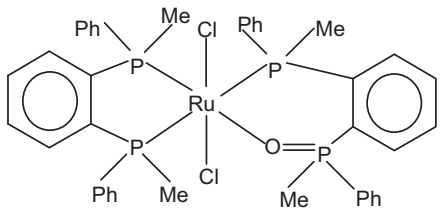


Fig. 14. Ruthenium complexes of P-P and P-O ligands (Ref. [88]).

3.2. Complexes of bidentate ligands

Since the pioneering work of Grim and co-workers in the mid-1970s [84], there has been a continuing interest in the chemistry of mixed tertiary phosphine and monochalcogenide P-X (X = O, S) ligands [85]. These systems, which combine 'Soft' donor (P) and 'Hard' donor (O) binding sites, display unique steric and electronic properties that differ markedly from those of classical bidentate phosphorus ligands. The developments of the potential unsymmetric bidentate ligands, $R_2PCH_2P(Y)R_2$, Y = O, S, Se [86] have paved the ways for synthesizing new and novel metal complexes for applications as catalysts. A few potential ruthenium complexes of chalcogen functionalized phosphine donor ligands are highlighted below.

The reactions of $[\kappa^6\text{-}C_6Me_6)RuCl_2]_2$ and $[(\kappa^5\text{-}C_5Me_5)RhCl_2]_2$ with the ligands L = $Ph_2PCH_2PPh_2$ or $Ph_2PCH_2P(Se)Ph_2$ in benzene yield neutral complexes $[(ring)RuCl_2(\kappa^1\text{-}L)]$, [ring = $(\kappa^6\text{-}C_6Me_6)$ or $(\kappa^5\text{-}C_5Me_5)$] [87]. However, cationic complexes of the type $[(ring)RuCl(\kappa^2\text{-}L)]ClO_4$ can be prepared using acetone as solvent in the presence of $NaClO_4$. The complex $[(\kappa^6\text{-}C_6Me_6)RuCl\{\kappa^2\text{-}S,S\text{-}(SPPh)_2CH_2\}]ClO_4$ reacts with sodium hydride in THF or thallium pyrazolate in DCM, through deprotonation of the coordinated bidentate ligand to produce $[(\kappa^6\text{-}C_6Me_6)Ru\{\kappa^3\text{-}C,S,S\text{-}(SPPh_2)_2CH\}]ClO_4$ [87].

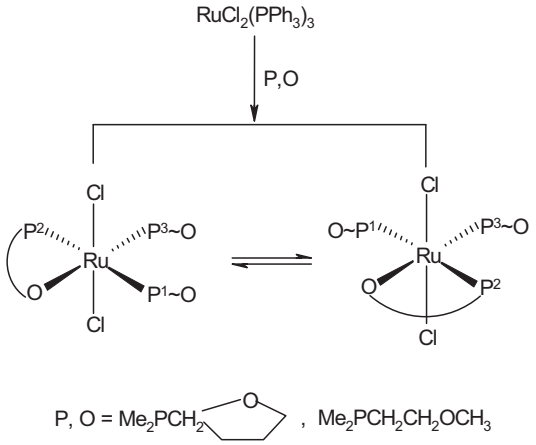
An interesting complex is formed by the reaction of diphosphine, oxygen-functionalized diphosphine ligands and $RuCl_3$ in the presence of formaldehyde (Fig. 14) [88], where the Ru-P bond *trans*- to oxygen is considerably shorter (222 pm) than the other two Ru–P bonds. The complex $[RuCl_2(P\cap O)(P\sim O)_2]$, formed by the reaction between $[RuCl_2(PPh_3)_3]$ and P,O ligands, shows fluxional behaviour (Scheme 23) [89].

Ruthenium complexes are expected to give a large number of isomeric compounds because of its coordination number i.e. six. A considerable amount of work has been done on the ruthenium metal complexes of hemilabile P,O ligands [90,91]. The complex $[RuCl_2(PPh_3)_3]$ reacts with two equivalent of ether–phosphine ligands viz. $Ph_2PCH_2CH_2OCH_3$ and $Ph_2PCH_2C_4H_7O$ in refluxing ethanol to afford a complex of the type *trans,cis*-$[RuCl_2(P\cap O)_2]$ [89], while the use of three equivalent of these ligands give *trans,cis,cis*-$[RuCl_2(P\cap O)(P\sim O)_2]$ (Scheme 24). Further, the reaction of $[RuCl_2(PPh_3)_3]$ with diphenylphosphinoacetic acid (Ph_2PCH_2COOH) in 1:3 mole ratio under refluxing condition produces the complex $[Ru(P\cap O)_2(POH)]$ ($P\cap O = \kappa^2\text{-}P,O$ chelated $Ph_2PCH_2COO^-$; $POH = \kappa^1\text{-}P$ coordinated Ph_2PCH_2COOH) [92] and the structure of the complex has been assigned as five coordinated square pyramidal geometry (Fig. 15) based on IR and $^{31}P\{^1H\}$ NMR spectroscopic studies.

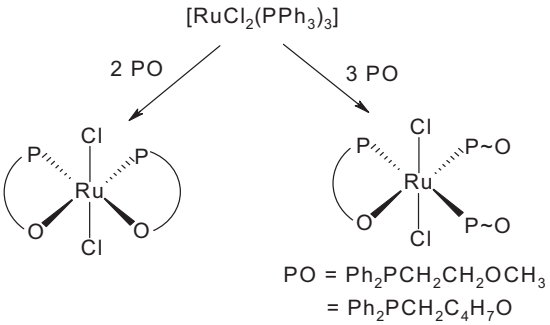
$RuCl_3{\cdot}3H_2O$ can be used as starting material for the synthesis of various metal complexes with hemilabile P,O ligand. $RuCl_3{\cdot}3H_2O$ reacts with Ph_2PCH_2COOEt in 1:3 mole ratio to yield the complex *trans*-$[RuCl_2(P\cap O)(P\sim O)_2]$ [93]. The hemilabile nature of the P,O ligand in the complex is observed (Scheme 25) and the stereodynamic behaviour is indicated by variable temperature $^{31}P\{^1H\}$ NMR spectroscopy. The phosphinoester ligand Ph_2PCH_2COOEt also forms the complex *mer*-$[RuCl_3(P\cap O)(P\sim O)]$ (Fig. 16) [94] by reacting with ethanolic solution of $RuCl_3{\cdot}3H_2O$ in presence of HCl at room temperature.

The ether–phosphine ligands such as $R_2PCH_2CH_2OMe$ and $R_2PCH_2C_4H_7O$ (P,O) (R = Cy, Ph) also react with $RuCl_3{\cdot}3H_2O$ to yield octahedral ruthenium(II) complexes of the type *trans*-$[RuCl_2(P\cap O)_2]$. The bis-chelate complex *trans*-$[RuCl_2(P\cap O)_2]$ reacts with $NaBH_4$ in the presence of excess of P,O ligand to form complexes *trans*-$[RuH_2(P\cap O)(P\sim O)_2]$ (Scheme 26) [9].

The heterobidentate and hemilabile ligands involving P,O-donor chelates produce chiral metal centers when bound to arene–Ru



Scheme 23. Fluxional behaviour of *trans*-, *cis*-, *cis*-$[RuCl_2(P\cap O)(P\sim O)_2]$.



Scheme 24. Synthesis of $[RuCl_2(P\cap O)_2]$ and $[RuCl_2(P\cap O)(P\sim O)_2]$.

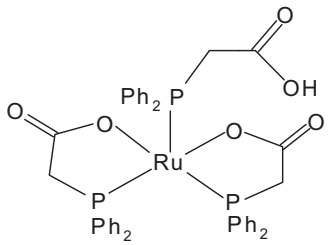
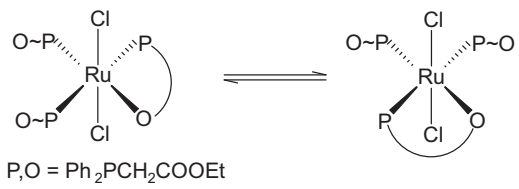


Fig. 15. The $[Ru(P\cap O)_2(POH)]$ ($P\cap O = \kappa^2\text{-}P,O$ chelated $Ph_2PCH_2COO^-$; $POH = \kappa^1\text{-}P$ coordinated Ph_2PCH_2COOH) complex (Ref. [92]).



Scheme 25. Stereodynamic behaviour of *trans*-$[RuCl_2(P\cap O)(P\sim O)_2]$.

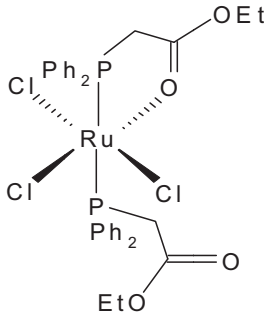


Fig. 16. Ruthenium(III) complex of the type *mer*-[$RuCl_3$(P∩O)(P∼O)] (Ref. [94]).

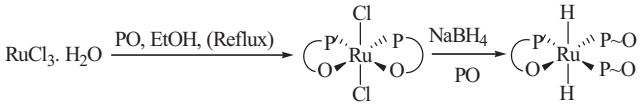
complexes [95]. This chirality in cymene complexes generates diastereotopic CH_3 groups in the ^{i}Pr ligand which serve as a detector of the chirality at the metal. The cationic cymene complexes [(cymene)Ru(κ^2-*P,O*)Cl]$^+$ act as precursors of 16-electron dicationic species, which have potential use in asymmetric catalysis [96]. The 16-electron complexes, however, also provide a pathway with a low energy barrier to epimerization of the metal centre in the intermediates. The dicationic species, [(cymene)Ru{(κ^2-*P,O*)-$Ph_2PCH(Me)CH(Me)P(O)Ph_2$}(solvate)]$^{2+}$ derived from the chloro complex by chloride abstraction with $AgSbF_6$ shows modest ee's (30%) in the Diels–Alder reaction of methacrolein with cyclopentadiene.

The bisphosphine monoxides (*R*)- and (*S*)-BINAPO(O), prepared by the mono-oxidation of (*R*)- and (*S*)-BINAP respectively, form [(*p*-cymene)RuCl{κ^2-*P,O*-BINAPO(O)}]Cl and [(*p*-cymene)Ru{κ^2-*P,O*-BINAPO(O)}]$(SbF_6)_2$ complexes [97]. The BINAPO(O) ligand binds diastereo selectively, and one observes only a single thermodynamically stable diastereomer of the two possible isomers. The compound [(*p*-cymene)Ru{κ^2-*P,O*-BINAPO(O)}]$(SbF_6)_2$ is an efficient catalyst for the Diels–Alder reaction of methacrolein and cyclopentadiene in moderate ee.

The reaction of the dinuclear complex like [(κ^6-*p*-$MeC_6H_4{}^i$Pr)RuCl(μ-Cl)]$_2$ or [(κ^5-C_5Me_5)RhCl(μ-Cl)]$_2$ with K[$Ph_2P(E)NP(E)Ph_2$] (E = S or Se) in THF produces the corresponding bridge cleaved mononuclear compounds [(κ^6-*p*-$MeC_6H_4{}^i$Pr)RuCl-{$Ph_2P(E)NP(E)Ph_2$}] or [(κ^5-C_5Me_5)RhCl{$Ph_2P(E)NP(E)Ph_2$}] in high yields (64–97%) [98].

Two interesting mononuclear ruthenium(II) carbonyl complexes are prepared by the reaction of [$RuCl_2(CO)_2$]$_n$ with ligands, L {L = Xantphos and Xantphos(O_2)}, to yield complexes of the type [$RuCl_2(CO)_2$(L)] [99]. The molecular structures of both the complexes show different coordination environments around the ruthenium centre (Figs. 17 and 18). The complex [$RuCl_2(CO)_2$\{Xantphos(O_2)\}] exhibits an interesting intramolecular O···O interactions (Fig. 18) leading to different electron donicity of the two P=O groups to the metal centre.

The hexa-coordinated chelate complex *cis*-[$RuX_2(CO)_2$(P∩S)] {P∩S = κ^2-*P,S*-coordinated, X = Cl, I} and penta-coordinated non-chelate complexes *cis*-[$RuCl_2(CO)_2$(P∼S)] {P∼S = κ^1-*P*-coordinated} are synthesised [100,101] by the reaction of [$RuX_2(CO)_2$]$_n$ with equimolar quantity of the ligands $Ph_2P(CH_2)_nP(S)Ph_2$ (n = 1–4) at room temperature (Schemes 27 and 28). The bidentate nature of the ligand $Ph_2PCH_2P(S)Ph_2$ in the complex leads to the formation of five-membered chelate ring which confers extra



Scheme 26. Rutheniumhydride complex *trans*-[RuH_2(P∩O)(P∼O)$_2$].

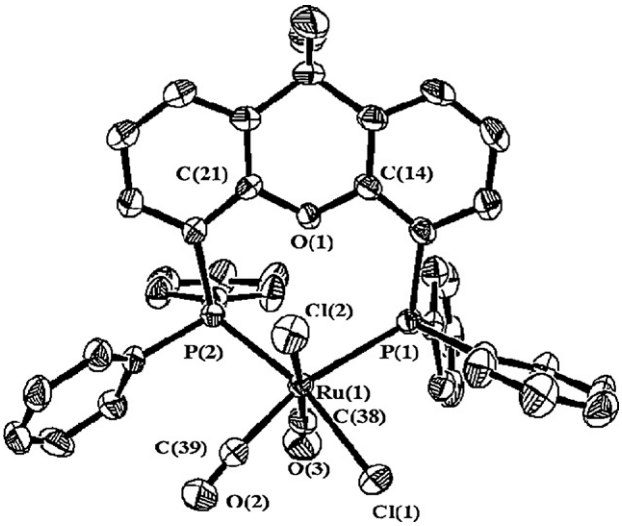


Fig. 17. X-ray crystal structure of [$RuCl_2(CO)_2$(Xantphos)] (Ref. [99a]).

stability to the complex. While, the reaction with 1:2 (Ru:L) mole ratio affords the hexa-coordinated non chelate complexes *cis*-[$RuX_2(CO)_2$(P∼S)$_2$] irrespective of the ligands. The molecular structure of *cis*-[$RuI_2(CO)_2$\{κ^2-*P,S*-$Ph_2PCH_2P(S)Ph_2$\}] (Fig. 19) exhibits a slightly distorted octahedral geometry with two *cis* carbonyl, two *cis* iodides and one *bis*-phosphine sulfide ligand bonding via P and S atom to the ruthenium centre. The complex [$RuCl_2(CO)_2$(P∼S)$_2$] (P∼S = κ^1-*P*-$Ph_2PCH_2P(S)Ph_2$) undergoes partial decarbonylation reaction in CH_2Cl_2–hexane solution to give a chelated complex [RuCl(CO)(P∩S)$_2$]Cl (Scheme 29 and Fig. 20) [101]; but, no such decarbonylation is observed in the complex [$RuI_2(CO)_2$(P∼S)$_2$]. The complex *cis*-[$RuX_2(CO)_2$(P∩S)] does not react with π-donor ligands like Ph_3P, Ph_3As, Ph_3Sb and Ph_3PX'; X′ = O, S and Se, even at vigorous reaction condition indicating that the Ru–S bond is not so labile as expected.

The racemic neutral arene-tethered species [$RuCl_2$(κ^6:κ^1-*P*-$NMe_2C_6H_4C_6H_4PCy_2$)], readily converts to dicationic analogues [Ru(κ^6:κ^1-*P*-$NMe_2C_6H_4C_6H_4$P-Cy_2)(P-S)]$(SbF_6)_2$ (P-S = $Ph_2PCH_2CH_2P(S)Ph_2$, $Ph_2PCH_2P(S)Ph_2$), with the addition of $AgSbF_6$ and the heterobidentate P-S ligands. The binding of P-S ligands introduces metal-centred chirality to the planar chiral parent complex [$RuCl_2$(κ^6:κ^1-*P*-$NMe_2C_6H_4C_6H_4PCy_2$)]. The complexes epimerize very slowly to thermodynamic product ratios,

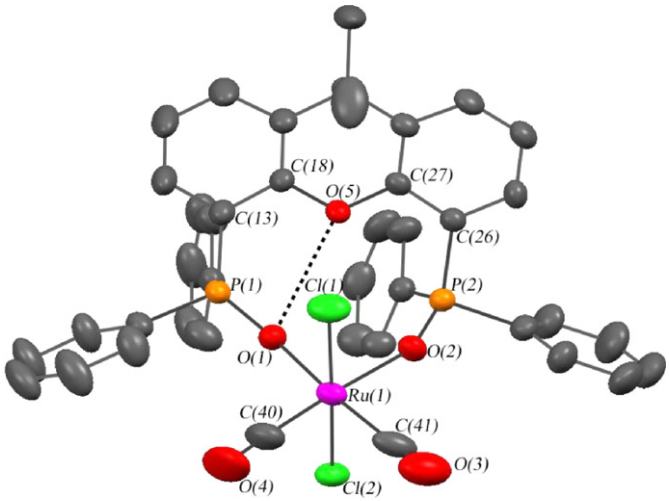
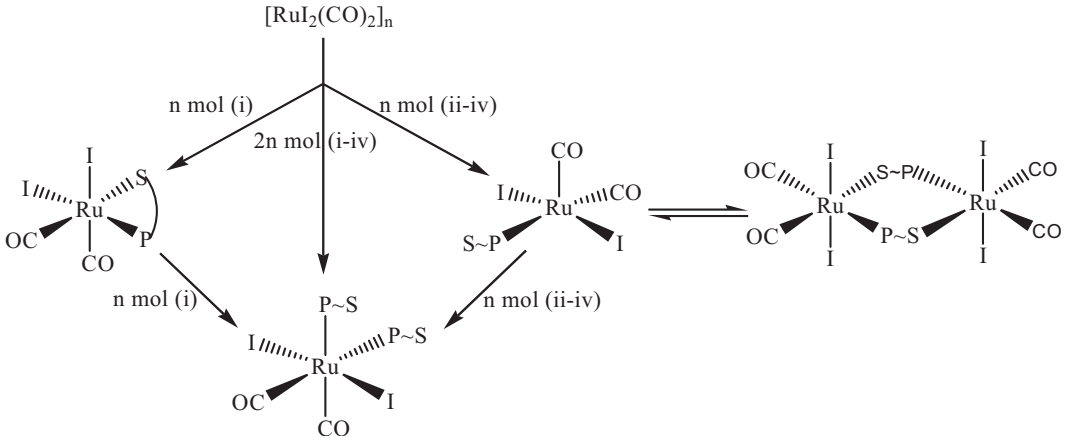


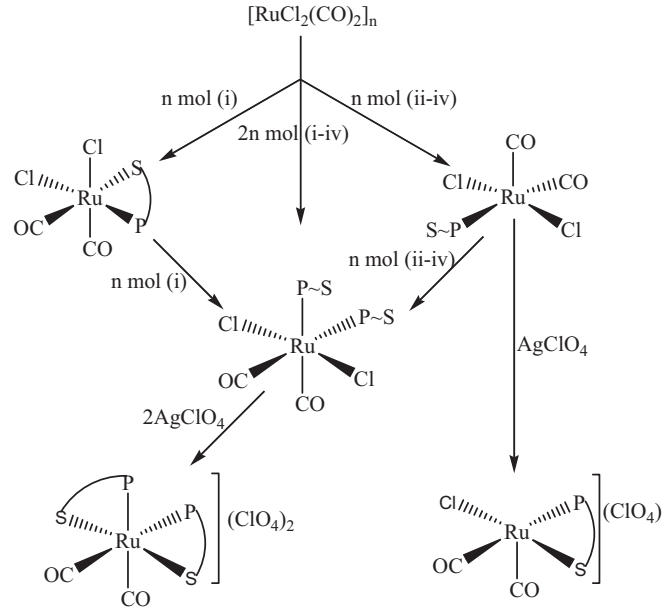
Fig. 18. X-ray crystal structure of [$RuCl_2(CO)_2$\{Xantphos(O_2)\}] (Ref. [99b]).



Scheme 27. Synthesis of iodo-carbonyl ruthenium(II) complexes of P-S ligands.

which are substantially different from the kinetic product ratios [102]. The complexes of general type $[(\kappa^6\text{-MeC}_6\text{H}_4{}^i\text{Pr})\text{RuCl}\{\kappa^2\text{-}E,E'\text{-}(\text{EPPh}_2)_2\text{CHR}\}]\text{BF}_4$ (R = H, E = S, Se; R = Me, E = S are described [103]. The methylene proton of the coordinated dichalcogenide ligand reacts with strong bases in methanol to yield cationic complexes in which the anionic ligand is acting as tridentate chelate with a *C,E,E′*-donor set, $[(\kappa^6\text{-MeC}_6\text{H}_4{}^i\text{Pr})\text{Ru}\{\kappa^3\text{-}C,E,E'\text{-}(\text{EPPh}_2)_2\text{CR}\}]\text{BF}_4$.

The complexes $[\text{Ru}(\text{C}_5\text{H}_4\text{NS})_2(\text{P-X})]$, where P-X: $\text{Ph}_2\text{PCH=CHPPh}_2$ (dppen-P,P), $\text{Ph}_2\text{PCH}_2\text{P(S)Ph}_2$ (dppm-P,S), $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{P(S)Ph}_2$ (dppe-P,S) and $\text{Ph}_2\text{P(S)CH}_2\text{CH}_2\text{P(S)Ph}_2$ (dppe-S,S), are formed [104] by the substitution of PPh_3 in $[\text{Ru}(\text{C}_5\text{H}_4\text{NS})_2(\text{PPh}_3)_2]$ with P-X in the presence of Et_3N base in dry toluene.



Scheme 28. Synthesis of chloro carbonylruthenium(II) complexes of P-S ligands.

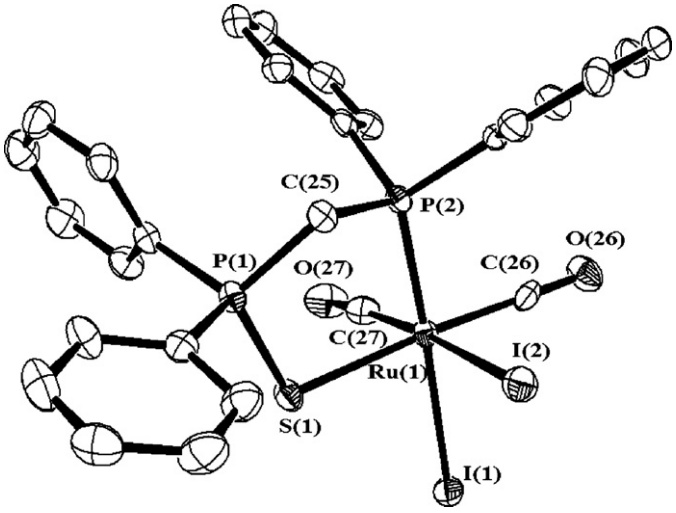
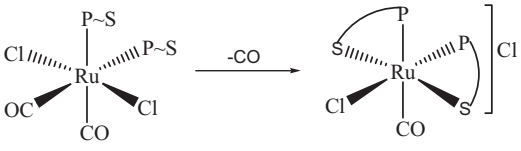


Fig. 19. The structure of $[\text{RuI}_2(\text{CO})_2(\text{Ph}_2\text{PCH}_2\text{P(S)Ph}_2]$ (Ref. [100]).

Interesting complexes $[(\text{Ar})\text{RuCl}_2(\text{P-S})]$ (Ar = C_6H_6, 2-$\text{MeC}_6\text{H}_4({}^i\text{Pr})$ and C_6Me_6), $[\text{RuCl}_2(\kappa^3\text{:}\kappa^3\text{-}\text{C}_{10}\text{H}_{16})(\text{P-S})]$, $[\text{RhCl(COD)(P-S)}]$ and $[(\text{Cp}^*)\text{MCl}_2(\text{P-S})]$, {M = Rh or Ir and P-S = $\text{Ph}_2\text{PNHC}_6\text{H}_4\text{P(S)Ph}_2$}, are synthesized by the reaction of $\text{Ph}_2\text{PNHC}_6\text{H}_4\text{P(S)Ph}_2$ with the appropriate chloride bridged transition metal dimers [105]. In all these complexes, the P-S act as κ^1-*P* coordinated monodentate ligands. Upon chloride abstraction from the representative complexes using $\text{Ag}[\text{ClO}_4]$ yield the cationic compounds $[(o\text{-MeC}_6\text{H}_4\{{}^i\text{Pr}\})\text{RuCl(P-S)}][\text{ClO}_4]$, $[\text{Rh(COD)(P-S)}][\text{ClO}_4]$ and $[(\text{Cp}^*)\text{RhCl(P-S)}][\text{ClO}_4]$ in which P-S act as κ^2-*P,S* coordinated bidentate ligands. The molecular structures of the complexes infer the formation of both monodentate and



Scheme 29. Decarbonylation of $[\text{RuCl}_2(\text{CO})_2(\text{P}\sim\text{S})_2]$ to generate chelate complex $[\text{RuCl(CO)(P}\cap\text{S})_2]\text{Cl}$

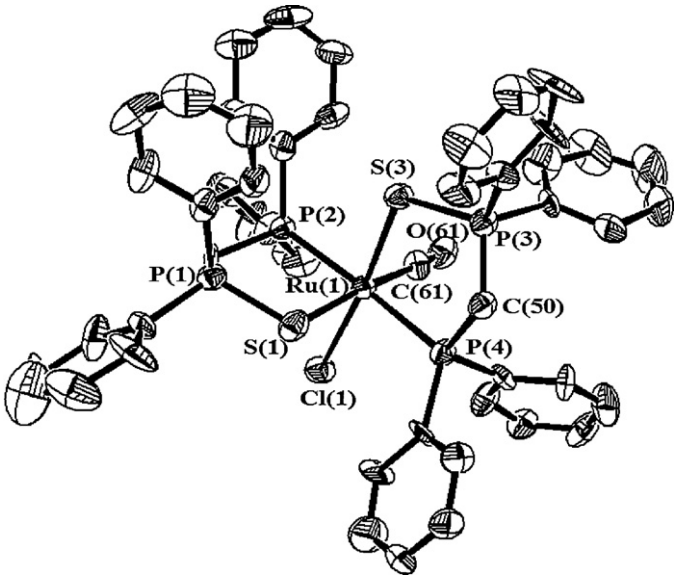


Fig. 20. Crystal structure of $[RuCl(CO)\{Ph_2PCH_2P(S)Ph_2\}2]^+$ (Ref. [101]).

chelate coordination of the ligands. All the κ^1-*P* bonded compounds exhibit intramolecular N···H···S hydrogen bonding [105].

The reactions of $Ru_3(CO)_{12}$ with diphosphazane monoselenides $Ph_2PN(R)P(Se)Ph_2$ [R = (*S*)-*CHMePh (L^1), R = $CHMe_2$ (L^2)] yield mainly the selenium bicapped tetraruthenium clusters $[Ru_4(\mu_4\text{-Se})_2(\mu\text{-CO})(CO)_8\{\mu\text{-}P,P\text{-}Ph_2PN(R)PPh_2\}]$ [106]. The selenium monocapped triruthenium cluster $[Ru_3(\mu_3\text{-Se})(\mu\text{-CO})(CO)_7\{\kappa^2\text{-}P,P\text{-}Ph_2PN\text{-}(S)\text{-}*CHMePh)PPh_2\}]$ is obtained only in the case of L^1. An analogous reaction of the diphosphazane monosulfide $(PhO)_2PN(Me)P(S)(OPh)_2$ (L^3) that bears a strong π-acceptor phosphorus shows a different reactivity pattern to yield the triruthenium clusters, $[Ru_3(\mu_3\text{-S})(\mu_3\text{-CO})(CO)_7\{\mu\text{-}P,P\text{-}(PhO)_2PN(Me)P(OPh)_2\}]$ (single sulfur transfer product) and $[Ru_3(\mu_3\text{-S})_2(CO)_5\{\kappa^2\text{-}P,P\text{-}(PhO)_2PN(Me)P(OPh)_2\}\{\mu\text{-}P,P\text{-}(PhO)_2PN(Me)P(OPh)_2\}]$ (double sulfur transfer product).

The P,S-chelating diphosphine ligands [DPEphos(S)] and [Xantphos(S)] (Fig. 21) with $[RuCl_2(CO)_2]_n$ in 1:1 mole ratio afford the complexes $[RuCl_2(CO)_2(P\cap S)]$ [107]. The ruthenium atom in both the complexes occupies the centre of a slightly distorted octahedral environment formed by a P atom, an S atom, two Cl atoms, and two CO groups (Fig. 22). The ligand DPEphos(S) and its complex

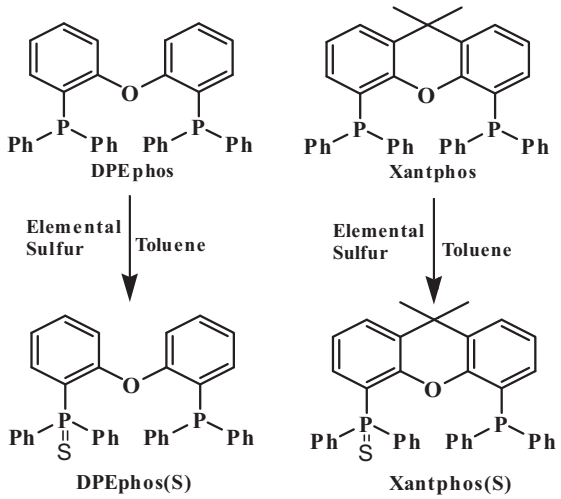


Fig. 21. P,S donor diphosphine ligands (Ref. [107]).

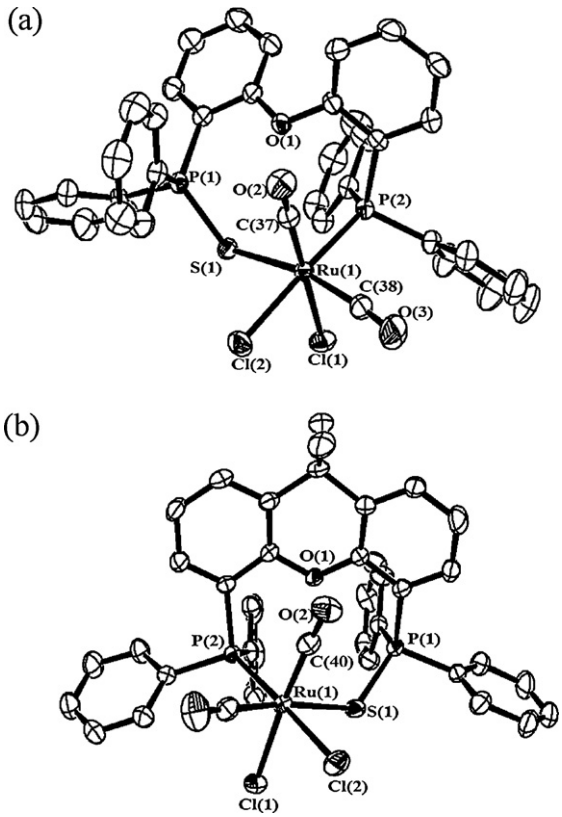


Fig. 22. X-ray crystal structures of (a) $[RuCl_2(CO)_2\{DPEphos(S)\}]$, (b) $[RuCl_2(CO)_2\{Xantphos(S)\}]$ (Ref. [107]).

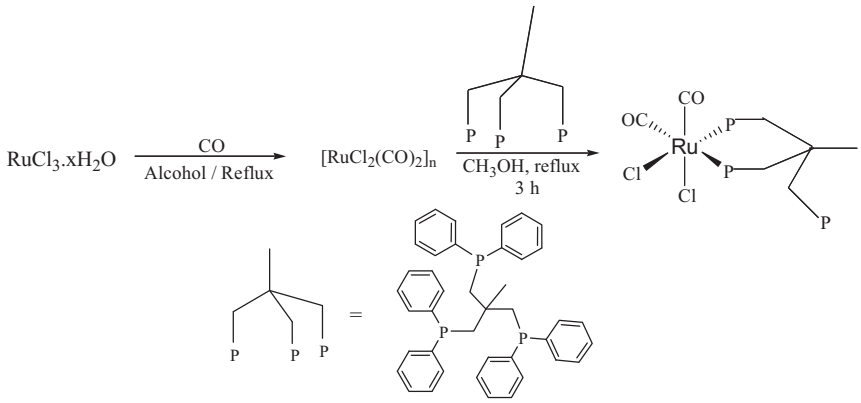
$[RuCl_2(CO)_2\{DPEphos(S)\}]$ show an interesting feature, in which the P(2)–P(1)–S(1) spatial angle (174.7°) in free ligand reduces to around 46° upon complexation indicating a very high flexibility of the angle. $[RuCl_2(CO)_2\{DPEphos(S)\}]$ also exhibits some hemilabile behaviour in solution because of its flexible ligand backbone, while the ligand Xantphos(S) in $[RuCl_2(CO)_2\{Xantphos(S)\}]$ remains rigid in solution [107].

Neutral and cationic half-sandwich complexes of ruthenium, rhodium and iridium with chiral [(*S*)-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethyl]di-^{t}butylphosphine selenide (L) are synthesised and characterized [108]. This ligand L is the first example of a chiral bisphosphine monoselenide prepared by direct monoselenation of a commercially available chiral bisphosphine, which reacts with metal half-sandwich dichlorides to give monodentate neutral complexes $[Cp^*MCl_2(\kappa^1\text{-}P\text{-L})]$ ($Cp^* = \kappa^5\text{-}C_5Me_5$; M = Rh, Ir) and $[(\kappa^6\text{-}p\text{-cymene})RuCl_2(\kappa^1\text{-}P\text{-L})]$. Reaction of these complexes with $NaSbF_6$ yields chelate cationic complexes $[Cp^*MCl(\kappa^2\text{-}P,S\text{-L})]SbF_6$ and $[(\kappa^6\text{-}p\text{-cymene})RuCl((\kappa^2\text{-}P,S\text{-L})]SbF_6$ respectively [108].

3.3. Complexes of tridentate ligands

The cationic complexes $[(arene)RuCl\{\kappa^2\text{-L}\}]A$ are synthesised by the reaction between triphosphine $CH(PPh_2)_3$ or its mono/bichalcogenide derivatives with suitable κ^6-arene–Ru(II) species, where arene = C_6Me_6, *p*-$MeC_6H_4{}^iPr$; L = $CH(PPh_2)_3$, $CH(PPh_2)_2\{P(E)Ph_2\}$ (E = S, Se), $CH(PPh_2)\{P(S)Ph_2\}_2$ and A = PF_6^-, BF_4^- [109]. An interesting complex $[(arene)Ru\{\kappa^3\text{-}S,S,S\text{-}\{P(S)Ph_2\}_3C\}]BF_4$; is prepared by deprotonation of the coordinated ligand $[\{P(S)Ph_2\}_3CH]$, where the ligand is coordinated to the ruthenium centre by tridentate κ^3-*S* mode (Fig. 23).

The polymeric complex $[RuCl_2(CO)_2]_n$ reacts with equimolar quantity of $\{MeC(CH_2PPh_2)_3$(triphos) to afford $[RuCl_2(CO)_2(\kappa^2\text{-}P,P\text{-}$



Scheme 30. Synthesis of $[RuCl_2(CO)_2(\kappa^2\text{-}P,P\text{-triphos})]$.

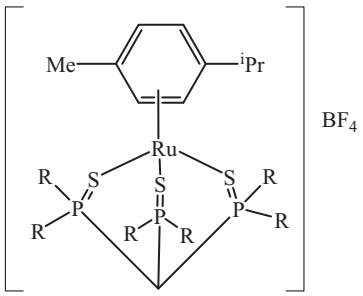
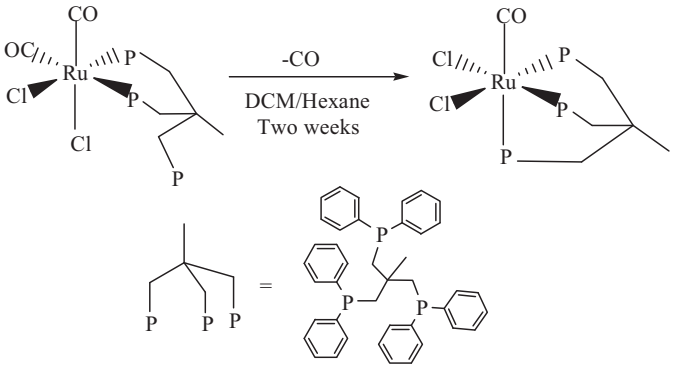


Fig. 23. Synthesis of $[(arene)Ru\{\kappa^3\text{-}S,S,S\text{-}\{P(S)Ph_2\}_3C\}]BF_4$ [arene = *p*-$MeC_6H_4{}^iPr$] (Ref. [109]).



Scheme 31. Decarbonylation of $[RuCl_2(CO)_2(\kappa^2\text{-}P,P\text{-triphos})]$.

triphos)] (Scheme 30), which on setting aside for about two weeks in DCM undergoes decarbonylation to yield a monocarbonyl complex $[RuCl_2(CO)(\kappa^3\text{-}P,P,P\text{-triphos})]$ in good yield (Scheme 31) [110]. The molecular structure of the monocarbonyl complex (Fig. 24) shows the elongation of one of the Ru–P(3) bonds due to the strong

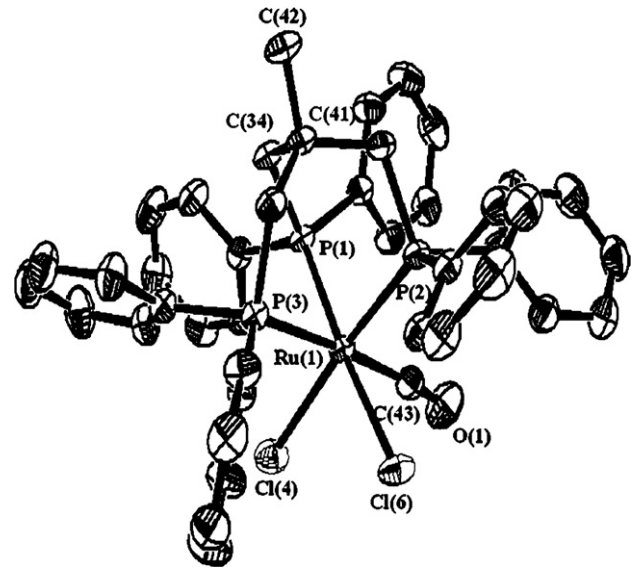


Fig. 24. Single crystal X-ray structure of $[RuCl_2(CO)(\kappa^3\text{-}P,P,P\text{-triphos})]$ (Ref. [110]).

trans-influence of the carbonyl group. The Ru–P bond *trans*- to CO is longer than those *trans*- to Cl by about 0.075 Å. Thus, one of the three M–P bonds is more labile and may show hemilabile behaviour during the course of catalytic reactions. The chalcogen functionalized triphos $[CH_3C(CH_2P(X)Ph_2)_3]$ (P_3X_3), where X = O, S and Se, on the other hand, reacts with $[RuCl_2(CO)_2]_n$ with 1:1 (Ru: ligand) mole ratio to yield only hexa-coordinated bidentate chelate complexes $[RuCl_2(CO)_2\kappa^2\text{-}X,X\text{-}P_3X_3]$ [Fig. 25] [111]. Spectroscopic studies indicate the presence of a dangling P-X bond in all the complexes.

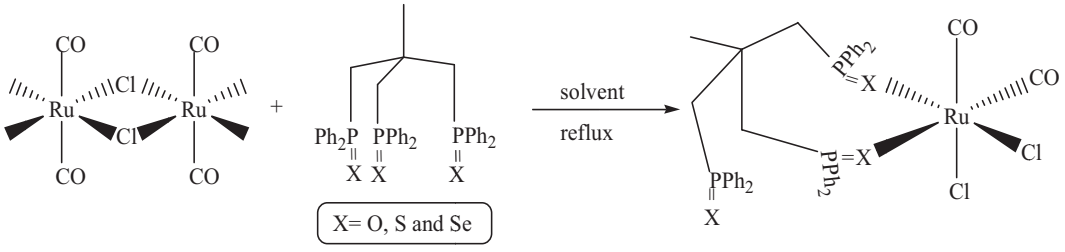


Fig. 25. Synthesis of $\kappa^2\text{-}X,X\text{-}[RuCl_2(CO)_2(P_3X_3)]$ (Ref. [111]).

3.4. Catalytic activities

Ruthenium-catalysed reactions have made a significant contribution to the recent growth of organic synthesis particularly in hydrogenation, oxidation, carbon–carbon bond formation, etc. [22]. In this section, three potential ruthenium catalysed reactions such as carbonylation, hydrogenation and hydroformylation have been reviewed.

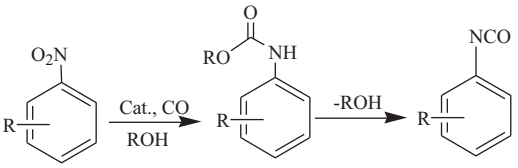
3.4.1. Carbonylation reaction

Carbonylation reactions have a long history and still attract much attention in both academic and industrial fields. Unlike the two well known carbonylation processes, viz. Monsanto [17,18] and 'CATIVA' [6b,c], for industrial production of acetic acid from methanol, ruthenium catalyst does not exhibit such efficient catalytic activity. A few interesting ruthenium catalysed carbonylation reactions with an emphasis on recent progresses are highlighted.

The homogeneous catalytic carbonylation and hydrocarbonylation of alcohols and esters using ruthenium or cobalt–ruthenium mixtures have led to the development of new processes for the carbonylation of alcohols to formates and homologation of higher alcohols [112]. The ruthenium complexes *trans*-/*cis*-$[RuCl_2(CO)_2(PPh_3)_2]$ and $[RuH_2(CO)(PPh_3)_3]$ are active catalysts in carbonylation of methanol to produce acetic acid [113]. Among the complexes, $[RuH_2(CO)(PPh_3)_3]$ shows the higher activity and selectivity as the catalyst precursor. The presence of hydrogen increases the activity and selectivity of both *trans*- and *cis*-$[RuCl_2(CO)_2(PPh_3)_2]$; however, no influence is observed in the case of $[RuH_2(CO)(PPh_3)_3]$.

The complex $[Ru(EDTA\text{-}H)CO]^-$ catalyses the carbonylation of cyclohexene in an alcohol: water mixture of the ratio 80:20 to produce the vinylic aldehyde cyclohexene-1-carboxaldehyde (20%), allylic aldehyde, cyclohexene-3-carboxal-dehyde (20%) and cyclohexane carboxylaldehyde (60%) [114]. The reaction is carried out at 120 °C and 20 atm of CO pressure. The rate of carbonylation exhibits first-order with respect to catalyst, CO pressure and substrate concentration. However, the carbonylations of 1-, 3- and 4-methyl cyclohexenes at 160 °C and 20 atm of CO pressure yield the corresponding alcohols.

The ruthenium-carbonyls are not effective catalysts for the carbonylation of alkynes but can catalyze cyclocarbonylation of allenyl alcohols exclusively to give lactones [115]. The ruthenium-carbonyls also act as efficient catalysts for the reductive carbonylation of nitro aromatics at high temperature and pressure (Eq. (8)) [116,117]. An interesting catalytic activity of $[Ru_3(CO)_{12}]$ is observed in carbonylation of ammonia to transform into urea under mild reaction conditions [118].

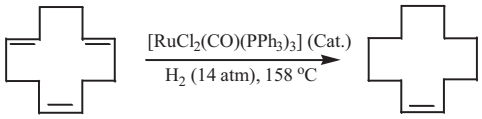


(8)

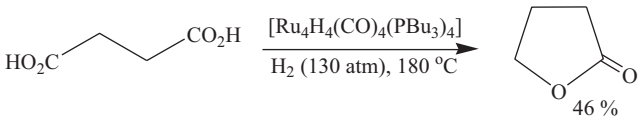
3.4.2. Hydrogenation

A number of homogeneous and heterogeneous ruthenium complexes catalysed hydrogenation of various substrates including functionalized olefins, aldehydes, ketones, other carbonyl compounds, and nitro compounds are reported [7,22,119]. Compared to metal complexes of rhodium, iridium and cobalt, ruthenium complexes generally have less effective catalytic activities for hydrogenation of simple and functionalized alkenes [120], however, low-valent ruthenium complexes are excellent catalysts for the hydrogen transfer reactions [22b] because of their low redox potential and higher affinity towards heteroatom compounds. A variety of substrates such as olefins, α,β-unsaturated ketones, aldehydes, ketones, imines, quinolines, and halogenated compounds undergo hydrogen transfer from alcohols in the presence of low-valent ruthenium complex catalysts [22–24,119,121]. Despite the large number of ruthenium (II) catalysts reported for this particular transformations, the use of ruthenium(II) carbonyl species which are generally considered as sluggish catalysts for hydrogenation reaction [122] are quite limited [99a,107,110,123–127,129]. The hydrogenation reaction catalysed by ruthenium carbonyl complexes of phosphine and chalcogen functionalized phosphine donor ligands are highlighted.

The complex $[RuCl_2(CO)(PPh_3)_3]$ is an efficient catalyst for the selective hydrogenation of 1,5,9-cyclododecatriene to cyclododecene (Eq. (9)), where the catalyst is exceptionally stable under the reaction conditions and is highly productive [124a]. The relative hydrogenation rates of the catalyst for a variety of alkenes and alkadienes in the presence of added PPh_3 follow the order: conjugated dienes > nonconjugated dienes > terminal alkenes > internal alkenes [27b]. In general, polyenes are selectively hydrogenated to monoenes. The lower hydrogenation rate for alkenes is attributed to an equilibrium between $[RuCl(alkyl)(CO)_2]$ and $[RuCl(alkyl)(CO)_2(PPh_3)]$ intermediates in the presence of added PPh_3, which favours the sterically crowded PPh_3 complexed intermediate. $[Ru_4H_4(CO)_8(PBu_3)_4]$ catalyses the hydrogenation of saturated monocarboxylic acids up to C_6 and several bicarboxylic acids to produce the corresponding alcohols or lactones (Eq. (10)) at 100–200 °C under a hydrogen pressure of 100–200 atm [124b].



(9)

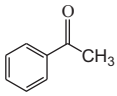
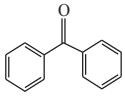


(10)

The ruthenium complexes containing the TPPMS ligand are widely used in two phase and aqueous hydrogenation reactions [125]. The complexes $[RuClH(CO)(TPPMS)_3]$ [126], $[Ru(CO)_3(TPPMS)_2]$ [127], $[RuH_2(CO)(TPPMS)_3]$ [127] and $[RuH(CO)(NCMe)(TPPMS)_3]$ [128] show marginal catalytic activity for the hydrogenation of olefins.

The ruthenium carbonyl dimers $[\{RuX(\mu\text{-}X)(CO)(P\cap P)\}_2]$ (X = Cl, Br; P∩P = 1,1′-bis(diphenylphosphino)ferrocene, 1,1′-bis(diisopropylphosphino)ferrocene) are active catalysts for transfer hydrogenation reactions [129a]. In particular, $[\{RuCl(\mu\text{-}Cl)(CO)(dippf)\}_2]$ is an effective catalyst precursor comparable to the five- or six-coordinated ruthenium(II) complexes like $[RuCl_2(PPh_3)_3]$, $[RuCl_2(PPh_3)(P\cap N)]$ (P∩N: iminophosphines, aminophosphines, oxazolinylferrocenyl phosphine) and many other important species. A series of bis(isocyanide) ruthenium(II) complexes of the type *trans,cis,cis*-$[RuX_2(CNR)_2(dppf)]$ (X = Cl, Br; R = CH_2Ph, Cy, ^tBu, 2,6-$C_6H_3Me_2$, (*S*)-(−)-C(H)MePh) [129b] show efficient catalytic activity in the transfer hydrogenation of acetophenone by propan-2-ol and the most active complex, *trans,cis,cis*-$[RuCl_2(CNCH_2Ph)_2(dppf)]$ is also evaluated as a catalyst in the transfer hydrogenation of a large variety of ketones. The hydride derivatives *cis,cis*-$[RuHCl(CN\text{-}2,6\text{-}C_6H_3Me_2)_2(dppf)]$ and *cis,cis,cis*-$[RuH_2(CN\text{-}2,6\text{-}C_6H_3Me_2)_2(dppf)]$ catalyze the transfer hydrogenation of acetophenone even in the absence of base, however, the reactions proceed about 5 times faster with latter

Table 2
Catalytic transfer hydrogenation of selected substrates by **1**–**4** at 83 °C Refs. [99a,107].

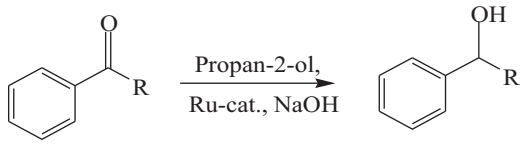
Entry	Substrate	Catalysts	Reaction time (h)	Conv.[a] (%)	TOF (h^{-1})[b]
1		**1**	2	99	200.4
		2	2.5	98	158.6
		3	0.4	99	1001.6
		4	2	98	198.3
2		**1**	18	91	19.8
		2	24	85	13.9
		3	6	99	64.6
		4	24	95	15.5
3		**1**	24	89	14.9
		2	24	72	12.0
		3	6	93	62.1
		4	24	91	15.2

1: $[RuCl_2(CO)_2(DPEphos)]$, **2**: $[RuCl_2(CO)_2(Xantphos)]$, **3**: $[RuCl_2(CO)_2\{DPEphos(S)\}]$, **4**: $[RuCl_2(CO)_2\{Xantphos(S)\}]$.
[a] Conversion of the substrates were obtained from GC analyses
[b] TOF = [amount of product (mol)/amount of catalyst (Ru mol)]/time (h)].

complex than with the former indicating that the real active species are dihydride ruthenium complexes.

A series of carbonyl–isocyanide-ruthenium(II) complexes of the type *cis,cis*-$[RuX_2(CNR)(CO)(P\cap P)]$ (P∩P = dppf, dippf; X = Cl, Br; R = Bn, Cy, ^{t}Bu, 2,6-$C_6H_3Me_2$, (*S*)-(−)-C(H)MePh) and dicarbonyl species *cis,cis,cis*-$[RuX_2(CO)_2(P\cap P)]$ are catalytically active in transfer hydrogenation of acetophenone in presence of propan-2-ol and base [129c]. The carbonyl-isocyanide complexes show efficient catalytic activity with nearly quantitative conversions (yield ≥ 92%) of acetophenone into 1-phenylethanol within 3–24 h. However, the catalytic performance of the carbonyl–isocyanide species is lower than that of the bis(isocyanide) complexes [129b,c].

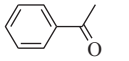
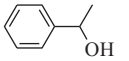
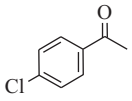
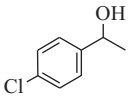
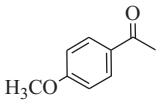
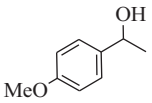
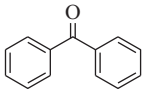
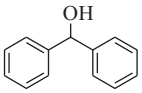
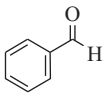
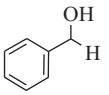
The dicarbonyl ruthenium(II) complexes $[RuCl_2(CO)_2(P\cap P)]$ [99a] and $[RuCl_2(CO)_2(P\cap S)]$ [107], [where P∩P = DPEphos, Xantphos and P∩S = DPEphos(S), Xantphos(S)], are thermally stable up to 300 °C and exhibit high catalytic activity in transfer hydrogenation of aldehyde and ketones to corresponding alcohols (Eq. (11)). All the complexes show much higher catalytic activity for the hydrogenation of aldehyde than ketones (Table 2). The catalytic efficiency of $[RuCl_2(CO)_2\{DPEphos(S)\}]$ is much higher than $[RuCl_2(CO)_2\{Xantphos(S)\}]$, which may be due to the hemilabile behaviour of ligand DPEphos(S) (Fig. 26). The presence of CO and unsymmetric P-X type ligands at the metal centre also provide additional advantage in the catalytic activity of the metal centre, which generate vacant coordination site for substrate binding either through the dissociation of the CO group or by the partial dissociation of the chelate ligand (Fig. 26) [107].



(R = H, CH_3, Ph) (11)

The neutral ruthenium complexes $[(\kappa^6\text{-}p\text{-cymene})RuCl_2(\kappa^1\text{-}P\text{-}PPh_2PCH_2P\{=NP(=S)(OR)_2\}Ph_2)]$, $[(\kappa^3\text{-}C_{10}H_{16})RuCl_2(\kappa^1\text{-}PPh_2PCH_2P\{=NP(=S)(OR)_2\}Ph_2)]$ and cationic species $[(\kappa^6\text{-}p\text{-cymene})RuCl(\kappa^2\text{-}P,S\text{-}Ph_2PCH_2P\{=NP(=S)(OR)_2\}Ph_2)][SbF_6]$ and $[(\kappa^3\text{-}C_{10}H_{16})RuCl(\kappa^2\text{-}P,S\text{-}Ph_2PCH_2P\{=NP(=S)(OR)_2\}Ph_2)][SbF_6]$, where R = Et, Ph, are also efficient catalysts in transfer hydrogenation of ketones [129d]. However, catalytic activity of the complexes is significantly reduced when bulky substituents are present in the ketones.

Table 3
Transfer hydrogenation of carbonyl compounds catalysed by $[RuCl_2(CO)(\kappa^3\text{-}P,P,P\text{-triphos})]$ using 2-propanol and NaOH[a] (Ref. [110]).

Entry	Substrate	Product	Conversion (%)
1			85
2			91
3			75
4			94
5			98
6			100

[a] Conditions: reactions were carried out at 82 °C using 5 mmol of substrate for 24 h. substrate/Ru/NaOH ratio: 100/1/24.

The ruthenium carbonyl complex $[RuCl_2(CO)(\kappa^3\text{-}P,P,P\text{-triphos})]$ containing tridentate phosphine ligand, also act as effective catalyst in the transfer hydrogenation of carbonyl compounds to the corresponding alcohols (Table 3) [110]. The base facilitates the formation of a ruthenium alkoxide by abstracting the proton of the alcohol followed by β-elimination to yield a monohydride ruthenium species (A), which is the active catalyst [110]. The proposed mechanism for this process involves κ^3–κ^2 dissociation of triphos ligand in which one of the labile phosphine coordinating sites (*trans*- to CO) undergoes dissociation (Fig. 27) to create vacant coordination site for the incoming substrate (B).

3.4.3. Hydroformylation

The use of cobalt and rhodium carbonyl complexes in the homogeneous hydroformylation of alkenes has been the subject of several reviews [6a,12,13,130]. However, metal complexes including ruthenium complexes are also reported [131] to be efficient hydroformylation catalysts with high linear/branched product isomer ratio [132].

The main problem associated with the practical application of homogeneous catalysis, is related to the dificulty in separating the products from the catalysts and in the recycling of expensive noble metals. An interesting alternative to solve this problem, which has attracted much attention, is the aqueous-biphasic technology in which the catalyst is immobilized in a water phase that is immiscible with the organic substrates and products. This has been applied with great success in the Ruhrchemie/Rhone-Poulenc process for the hydroformylation of propylene to butyraldehyde in a two-phase medium. The Rh-derived catalyst employed in that process is solubilized in water through the use of triaryl-phosphine ligands modified by introducing highly polar sulfonate groups in the phenyl rings attached to phosphorus, specifically, the sodium salt of tris[(*p*-sulfonato)phenyl]phosphine $P(m\text{-}C_6H_4SO_3Na)_3$ [133].

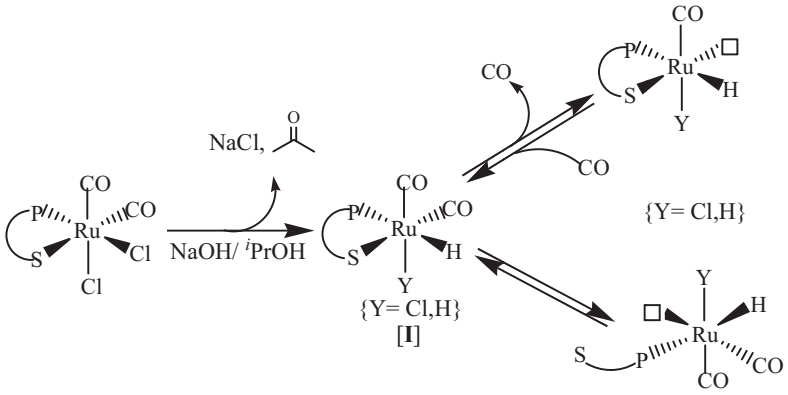


Fig. 26. Generation of vacant (□) coordination sites (Ref. [107]).

The complexes $[Ru(H)_2(CO)_2(PPh_3)_2]$ and other ruthenium complexes [132b,134] show catalytic activity in the homogeneous hydroformylation of alkenes, and although their activity and selectivity are lower than those observed for rhodium-derived catalysts, the much lower price of ruthenium as compared to rhodium makes it worth while further exploring the potential of this metal in hydroformylation.

The interesting complex $[Ru_3(CO)_9(TPPMS)_3]$ is an effective aqueous-biphasic catalyst which catalyses the hydrogenation of acrylic acid and styrene and also the hydroformylation of ethylene and propylene [135]. Water-soluble dihydride ruthenium complex $[RuH_2(CO)(TPPMS)_3]$ shows its catalytic behaviour in the biphasic hydroformylation of 1-hexene, cyclohexene, 2,3-dimethyl-1-butene and their mixtures [136a]. The activity trend for different substrates varies as: 1-hexene > cyclohexene > 2,3-dimethyl-1-butene and the catalyst exhibits its resistance towards the possible sulfur poisoning. Another water soluble complex $[RuH(CO)(CH_3CN)(TPPTS)_3]BF_4$ also acts as efficient catalyst precursor for the aqueous biphasic hydroformylation of several olefins and their mixtures under moderate reaction conditions [$P(H_2/CO)$ = 6288.8 kPa, temperature 353 K, substrate: catalyst = 100 and time 24 h) [136b]. The sulfur tolerance of this complex along with thiophene as a model molecule exhibits that the complex maintains its activity up to the thiophene concentration < 500 ppm.

The diphosphine clusters $[Ru_3(CO)_{10}(dcpm)]$ and $[Ru_3(CO)_{10}$(F-dppe)], as well as the bis(diphosphine) clusters $[Ru_3(CO)_8(dcpm)_2]$ and $[Ru_3(CO)_8$(F-dppe)$_2]$ show catalytic activity in the hydroformylation of ethylene and propylene to yield the corresponding aldehydes [137]. The complex containing F-dppe exhibits higher activities than those observed for $[Ru_3(CO)_{12}]$ and $[Ru_3(CO)_{10}$(dppe)].

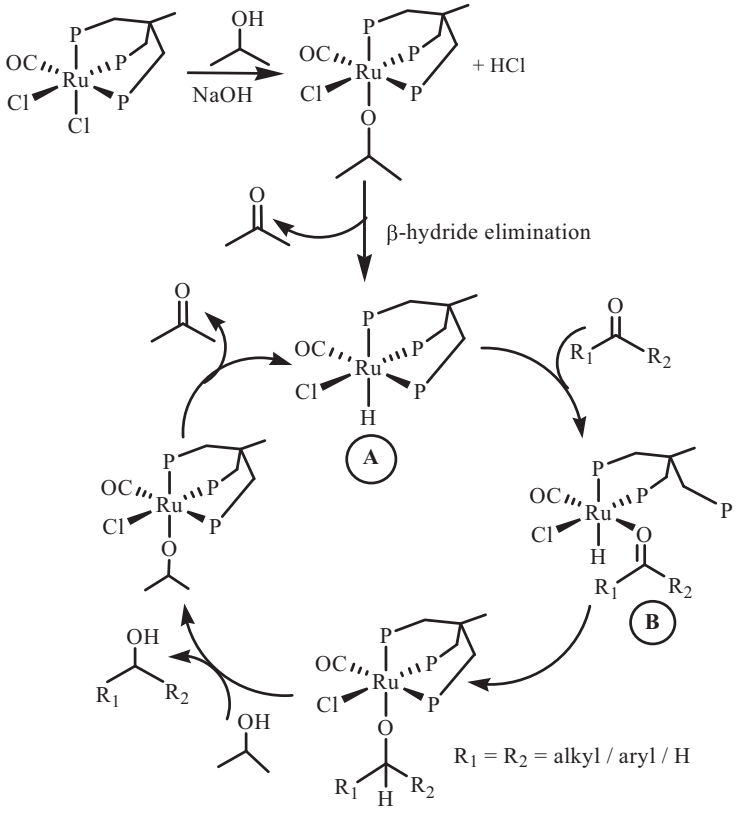


Fig. 27. Proposed mechanism for the transfer hydrogenation of carbonyl compounds by chlorocarbonyl Ru(II) complexes of tripodal phosphine ligand $\{MeC(CH_2PPh_2)_3\}$ (Ref. [110]).

The ruthenium hydride complexes of the type [RuH(CO)(κ^3-OCOR)(PPh_3)$_2$] [R = CH_3, CH_2Cl, C_6H_5 and $CHMe_2$] are efficient and regioselective precatalysts for hydroformylation of 1-hexene under mild reaction conditions (120° C and 15 atm H_2/CO) [138a]. The ruthenium complexes conatining chelating phosphines, [$RuCl_2(CO)_2(\kappa^2$-L)] and [$RuCl_2(CO)(\kappa^2$-L)(L′)], and monodentate phosphines, [$RuCl_2(CO)_2L''_2$] and [Ru(μ-Cl)Cl$(CO)_2L]_2$, also act as catalysts for the hydroformylation of 1-hexene, where L = (2-dimethylaminophenyl)-diphenylphosphine, (2-methylthiophenyl)diphenylphosphine, L′ = (2-methoxyphenyl)diphenylphosphine and, L″ = (2-methylphenyl)diphenylphosphine and (2-ethylphenyl)diphenylphosphine [138b]. The activity of the complexes depends on the binding mode of the phosphine and on the strength of the ruthenium-phosphine interaction. Strongly coordinated chelating ligands (L) show poor activity, while weakly chelated (L′) and nonchelating phosphines (L″) exhibit higher activities.

High-yielding Tandem hydroformylation/hydrogenation of a terminal olefin to produce a linear alcohol using a Rh/Ru dual catalyst system is reported [139]. The combination of Xantphos/[Rh(acac)$(CO)_2$] and Shvo's catalyst shows a highly efficient production of n-alcohol by a simple one-pot process utilizing syn-gas for hydrogenation. Under the optimised conditions, 1-undecanol is prepared from 1-decene showing a yield of 90.1% which is the highest value to date [139].

4. Conclusions

In the present review, we have presented a thorough survey particularly on the synthesis and reactivity of rhodium and ruthenium carbonyl complexes of functionalized mono and multidentate phosphine-chalcogen donors ligands. A few selected catalytic activities like carbonylation, hydrogenation and hydroformylation by ligand promoted rhodium and ruthenium complexes for the synthesis of industrially important organic molecules have been demonstrated. The advantage of hemilability in catalytic reactions has also been highlighted with suitable examples. Phosphine and chalcogen functionalized phosphine donor ligands promoted rhodium, and ruthenium complexes are active catalysts for the synthesis of different value-added organic products. It can be anticipated that these types of ligands will continue to provide new and interesting results in organic synthesis.

4.1. Future scope

Though a large number of metal complexes containing chalcogen functionalized phosphines has been synthesized and evaluated for different catalytic activities, the area is still thirsty and there is a high scope for scientific research in this area. For example, ruthenium catalysed carbonylation and hydroformylation reactions need more attention for the development of efficient processes from the industrial point of view because ruthenium metal is cheaper compared to other precious metals such as rhodium and iridium. The synthesis of new and novel hemilabile metal complexes may lead to important and interesting catalysts for industrial organic transformations.

Acknowledgements

The authors are grateful to Dr. P.G. Rao, Director, North East Institute of Science and Technology, Jorhat-785006, Assam, India, for his encouragement and kind permission to publish the review. The authors thank Dr. P. Sengupta, Head, Materials Science Division, for his encouragement and support. The Department of Science and Technology (DST), New Delhi, India (Grant: SR/S1/IC-05/2006) is also acknowledged for the partial financial grants. The author B. Deb thanks CSIR, New Delhi for providing the Senior Research Fellowship.

References

[1] R.H. Crabtree, The Organometallic Chemistry of the Transition Metals, 2nd ed., John Wiley and Sons, New York, 1994.
[2] F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry. A Comprehensive Text, 4th ed., Interscience, New York, 1980.
[3] G.N. Schrauzer (Ed.), Transition Metals in Homogeneous Catalysis, Marcell Dekker, New York, 1971.
[4] (a) H.-U. Blaser, A. Indolese, A. Schynder, Curr. Sci. 78 (2000) 1336;
(b) B.R. James, F. Lorenzini, Coord. Chem. Rev. 254 (2010) 420.
[5] (a) A. Mullen, Carbonylations catalyzed by metal carbonyls – Reppe reactions, in: J. Falbe (Ed.), New Synthesis with Carbon Monoxide, vol. 11, Springer-Verlag, Heidelberg, New York, 1980, p. 286;
(b) M. Beller (Ed.), Catalytic Carbonylation Reactions, Topics in Organometallic Chemistry, vol. 18, Springer, New York, 2006.
[6] (a) P.W.N.M. van Leeuwen, Homogeneous Catalysis, Kluwer Academic Publishers, 2004;
(b) G.J. Sunley, D.J. Watson, Catal. Today 58 (2000) 293;
(c) J.H. Jones, Platinum Met. Rev. 44 (2000) 94;
(d) C.M. Thomas, G. Süss-Fink, Coord. Chem. Rev. 243 (2003) 125.
[7] B.R. James, Homogeneous Hydrogenation, Wiley, New York, 1973.
[8] (a) W. Baratta, F. Benedetti, A. Del Zotto, L. Fanfoni, F. Felluga, S. Magnolia, E. Putignano, P. Rigo, Organometallics 29 (2010) 3563;
(b) J. Wassenaar, M. Kuil, M. Lutz, A.L. Spek, J.N.H. Reek, Chem. Eur. J. 16 (2010) 6509;
(c) W. Tang, X. Zhang, Chem. Rev. 103 (2003) 3029.
[9] A. Bader, E. Lindner, Coord. Chem. Rev. 108 (1991) 27.
[10] R.A.M. Robertson, A.D. Poole, M.J. Payne, D.J. Cole-Hamilton, Chem. Commun. (2001) 47.
[11] W.S. Knowles, Acc. Chem. Res. 16 (1983) 206.
[12] (a) F. Hebrard, P. Kalck, Chem. Rev. 109 (2009) 4272;
(b) P.C.J. Kamer, A. van Rooy, G.C. Schoemaker, P.W.N.M. van Leeuwen, Coord. Chem. Rev. 248 (2004) 2409;
(c) J. Klosin, C.R. Landis, Acc. Chem. Res. 40 (2007) 1251.
[13] (a) P.W.N.M. van Leeuwen, C. Claver, Rhodium Catalysed Hydroformylation, Kluwar Academic Publishers, Dordrecht, 2000;
(b) H.W. Bohnen, B. Cornils, Adv. Catal. 47 (2002) 1.
[14] D.K. Dutta, J.D. Woollins, A.M.Z. Slawin, D. Konwar, P. Das, M. Sharma, P. Bhattacharyya, S.M. Aucott, Dalton Trans. (2003) 2674.
[15] (a) S. Matsumoto, Catal. Today 90 (2004) 183;
(b) T. Kanazawa, Catal. Today 96 (2004) 171.
[16] W.S. Knowles, J. Chem. Educ. 63 (1986) 222.
[17] F.E. Paulik, J.F. Roth, Chem. Commun. (1968) 1578.
[18] (a) D. Forster, J. Am. Chem. Soc. 98 (1976) 846;
(b) D. Forster, Adv. Organomet. Chem. 17 (1979) 255;
(c) J.F. Roth, J.H. Craddock, A. Hershman, F.E. Paulik, Chem. Technol. (1971) 600.
[19] R.L. Pruett, J.A. Smith, J. Org. Chem. 34 (1969) 327.
[20] M. Heidingsfeldova, M. Capka, J. Appl. Polym. Sci. 30 (1985) 1837.
[21] (a) J.A. McCleverty, G. Wilkinson, Inorg. Synth. 8 (1966) 211;
(b) J. Chatt, B.L. Shaw, J. Chem. Soc. A (1966) 1437;
(c) J.A. Osborn, F.H. Jardine, J.F. Young, G. Wilkinson, J. Chem. Soc. A (1966) 1711;
(d) G. Giordano, R.H. Crabtree, Inorg. Synth. 19 (1979) 218;
(e) A. Van der Ent, A.L. Onderdelinden, Inorg. Synth. 28 (1990) 90.
[22] (a) F.A. Cotton, G. Wilkinson, C.A. Murrillo, M. Bochmann, Advanced Inorganic Chemistry, John Wiley & Sons, New York, US, 2004, p. 1010;
(b) T. Naota, H. Takaya, S.I. Murahashi, Chem. Rev. 98 (1998) 2599;
(c) S.-I. Murahashi (Ed.), Ruthenium in Organic Synthesis, Wiley-VCH, 2004.
[23] (a) R. Noyori, Asymmetric Catalysis in Organic Synthesis, John Wiley & Sons, New York, US, 1994, p. 16;
(b) G. Zassinovich, G. Mestroni, S. Gladiali, Chem. Rev. 92 (1992) 1051.
[24] (a) S.E. Clapham, A. Hadzovic, R.H. Morris, Coord. Chem. Rev. 248 (2004) 2201;
(b) J.S.M. Samec, J.E. Bäckvall, P.G. Andersson, P. Brandt, Chem. Soc. Rev. 35 (2006) 237;
(c) P.J. Fagan, M.H. Voges, R.M. Bullock, Organometallics 29 (2010) 1045;
(d) S. Gladiali, E. Alberico, Chem. Soc. Rev. 35 (2006) 226.
[25] (a) M. Yamakawa, H. Ito, R. Noyori, J. Am. Chem. Soc. 122 (2000) 1466;
(b) R. Noyori, M. Yamakawa, S. Hashiguchi, J. Org. Chem. 66 (2001) 7932;
(c) R.A. Begum, A.A. Farah, H.N. Hunter, A.B.P. Lever, Inorg. Chem. 48 (2009) 2018;
(d) H. Adams, M.J. Morris, A.E. Riddiough, L.J. Yellowlus, A.B.P. Lever, Inorg. Chem. 46 (2007) 9790.
[26] (a) R. Noyori, S. Hashiguchi, Acc. Chem. Res. 30 (1997) 97;
(b) A. Fujii, S. Hashiguchi, N. Uematsu, T. Ikariya, R. Noyori, J. Am. Chem. Soc. 118 (1996) 2521;
(c) I. Yamada, R. Noyori, Org. Lett. 2 (2000) 3425.
[27] (a) M.L. Berch, A. Davison, J. Inorg. Nucl. Chem. 35 (1973) 3763;
(b) D.R. Fahey, J. Org. Chem. 38 (1973) 3343;

(c) N. Ahmad, J.J. Levison, S.D. Robinson, M.F. Uttley, Inorg. Synth. 15 (1974) 45;
(d) P.S. Hallman, T.A. Stephenson, G. Wilkinson, Inorg. Synth. 12 (1970) 237;
(e) A. Mantovani, S. Cenini, Inorg. Synth. 16 (1976) 51;
(f) P. Teulon, J. Roziere, J. Organomet. Chem. 214 (1981) 391;
(g) P. Pertici, G. Vitulli, M. Paci, L. Porri, J. Chem. Soc., Dalton Trans. (1980) 1961;
(h) N. Oshima, H. Suzuki, Y. Moro-oka, Chem. Lett. (1984) 1161;
(i) M.A. Bennett, G. Wilkinson, Chem. Ind. (1959) 1516.

[28] (a) N.N. Greenwood, A. Earnshaw, Chemistry of the Elements, Pergamon, Oxford, UK, 1989;
(b) J.E. Huheey, Inorganic Chemistry: Principles of Structure and Reactivity, 3rd ed., Harper & Row, New York, 1983 (Chapter 13);
(c) F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, 5th ed., Wiley, New York, 1988;
(d) J.P. Collman, L.S. Hegedus, J.R. Norton, R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, CA, 1987;
(e) G.W. Parshall, Organometallics 6 (1987) 697;
(f) A.S. Goldman, K. Krogh-Jespersen, J. Am. Chem. Soc. 118 (1996) 12159;
(g) U. Radius, F.M. Bickelhaupt, A.W. Ehlers, N. Goldberg, R. Hoffmann, Inorg. Chem. 37 (1998) 1080;
(h) R.B. King, T.E. Bitterwolf, Coord. Chem. Rev. 206–207 (2000) 563;
(i) H. Wang, Q. Du, Y. Xie, R.B. King, H.F. Schaefer, J. Organomet. Chem. 695 (2010) 215;
(j) X. Feng, C. Xie, Z. Liu, Y. Xie, R.B. King, H.F. Schaefer, Dalton Trans. (2009) 2599.

[29] P.W.N.M. van Leeuwen, Z. Freixa, in: W.B. Tolman (Ed.), Activation of Small Molecules, Wiley-VCH, Germany, 2006, p. 319.

[30] (a) E. Lindner, K. Gierling, R. Fawzi, M. Steimann, Inorg. Chim. Acta 13 (1998) 269;
(b) L. Gall, P. Laurent, E. Soulier, J.Y. Salaiin, H.D. Abbayes, J. Organomet. Chem. 13 (1998) 567;
(c) P. Braunstein, Y. Chauvin, J. Nahring, A. Decian, J. Fischer, J. Chem. Soc., Dalton Trans. (1995) 863;
(d) P. Braunstein, Y. Chauvin, J. Fischer, H. Oliver, C. Strohmann, D.V. Toranto, New J. Chem. 24 (2000) 437.

[31] (a) G.K. Anderson, R. Kumar, Inorg. Chim. Acta L21 (1985) 97;
(b) S. Kim, J.H. Reibenspies, M.Y. Darensbourg, J. Am. Chem. Soc. 118 (1996) 4115.

[32] T.C. Blagborough, R. Devis, P. Ivison, J. Organomet. Chem. 467 (1994) 85.

[33] (a) E. Lindner, Q. Wang, H.A. Mayer, R. Fawzi, M. Steimann, Organometallics 12 (1993) 1865;
(b) E. Lindner, Q. Wang, H.A. Mayer, A. Bader, H. Kuhbauch, P. Wegner, Organometallics 12 (1993) 3291.

[34] J.W. Faller, B.J. Grimmond, D.G. D'Alliessi, J. Am. Chem. Soc. 123 (2001) 2525.

[35] (a) R.P. Hughes, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 5, Paragon Press, Oxford, New York, 1982, p. 277;
(b) D. Evans, J.A. Osborn, G. Wilkinson, Inorg. Synth. 11 (1968) 99;
(c) D.K. Dutta, M.M. Singh, Trans. Met. Chem. 4 (1980) 244;
(d) J. Rankin, A.D. Poole, A.C. Benyei, D.J. Cole-Hamilton, Chem. Commun. (1997) 1835.

[36] (a) G. Bandoli, D.A. Clemente, G. Deganello, G. Carturan, P. Uguagliati, U. Belluco, J. Organomet. Chem. 71 (1974) 125;
(b) V. Marsala, F. Faraone, P. Piraino, J. Organomet. Chem. 133 (1974) 301;
(c) P. Das, D. Konwar, P. Sengupta, D.K. Dutta, Trans. Met. Chem. 25 (2000) 426;
(d) A.B. Rivas, J.M. Gascon, F.J. Lahoz, A.I. Balana, A.J. Pardey, L.A. Oro, J.J. Perez-Torrente, Inorg. Chem. 47 (2008) 6090.

[37] (a) V.V. Grushin, Chem. Rev. 104 (2004) 1629;
(b) B. Hipler, M. Doring, C. Dubs, H. Gorls, T. Hubler, E.Z. Uhlig, Anrog. Allg. Chem. 624 (1998) 1329;
(c) C.S. Slone, C.A. Mirkin, G.P.A. Yap, I.A. Guzei, A.L. Rheingold, J. Am. Chem. Soc. 119 (1997) 10743;
(d) A.M.Z. Slawin, M.B. Smith, J.D. Woollins, J. Chem. Soc., Dalton Trans. (1996) 1283.

[38] (a) J. Browning, G.W. Bushnell, K.R. Dixon, R.W. Hilts, J. Organomet. Chem. 434 (1992) 241;
(b) J. Browning, G.W. Bushnell, K.R. Dixon, R.W. Hilts, J. Organomet. Chem. 452 (1993) 205;
(c) J. Browning, K.R. Dixon, N.J. Meanwell, F. Wang, J. Organomet. Chem. 460 (1993) 117.

[39] (a) J.W. Faller, S.C. Milheiro, J. Parr, J. Organomet. Chem. 693 (2008) 1478;
(b) J.W. Faller, J.C. Wilt, Organometallics 24 (2005) 5076;
(c) J.R. Dilworth, N. Wheatley, Coord. Chem. Rev. 199 (2000) 89.

[40] D. Cauzzi, C. Graiff, M. Lanfranchi, G. Predieri, A. Tiripicchio, Inorg. Chim. Acta 273 (1998) 320.

[41] (a) M. Valderrama, R. Contreras, P. Munoz, M.P. Lamata, D. Carmona, F.J. Lahoz, S. Elipe, L.A. Oro, J. Organomet. Chem. 633 (2001) 182;
(b) V. Cadierno, J. Diez, J. Garcia-Alverez, J. Gimeno, Dalton Trans. 39 (2010) 941;
(c) B.K. Santra, J.-L. Chen, B. Sarkar, C.W. Liu, Dalton Trans. (2008) 2270.

[42] (a) E. Hauptman, P.J. Fagan, W. Marshall, Organometallics 18 (1999) 2061;
(b) J. Michalski, Z. Skrzypzynski, J. Organomet. Chem. 97 (1975), p. C31.

[43] (a) R.W. Wegman, U.S. Patent 4,563,309, 1986;
(b) L. Gonsalvi, H. Adams, G.J. Sunley, E. Ditzel, A. Haynes, J. Am. Chem. Soc. 124 (2002) 13597;
(c) R.W. Wegman, A.G. Abatjoglou, A.M. Harrison, J. Chem. Soc., Chem. Commun. (1987) 1891;
(d) R. Uson, L.A. Oro, M.A. Ciriano, F.J. Lahoz, J. Organomet. Chem. 240 (1982) 429.

[44] (a) D. Empsall, S. Johanson, B.L. Shaw, J. Chem. Soc., Dalton. Trans. (1980) 302;
(b) K.A. Bunten, D.H. Farrar, A.J. Poe, A. Lough, Organometallics 21 (2002) 3344;
(c) P. Das, M. Sharma, N. Kumari, D. Konwar, D.K. Dutta, Appl. Organomet. Chem. 16 (2002) 302.

[45] (a) M.J. Baker, M.F. Giles, A.G. Orpen, M.J. Taylor, R.J. Watt, J. Chem. Soc., Chem. Commun. (1995) 197;
(b) J.R. Dilworth, J.R. Miller, N. Wheatley, M.J. Baker, J.G. Sunley, J. Chem. Soc., Chem. Commun. (1995) 1579;
(c) G.K. Anderson, R. Kumar, J. Organomet. Chem. 342 (1988) 263;
(d) G.K. Anderson, J. Organomet. Chem. 368 (1989) 385.

[46] P. Das, D. Konwar, D.K. Dutta, Ind. J. Chem. 40A (2001) 626.

[47] (a) D.K. Dutta, J.D. Woollins, A.M.Z. Slawin, D. Konwar, M. Sharma, P. Bhattacharyya, S.M. Aucott, J. Organomet. Chem. 691 (2006) 1229;
(b) P. Chutia, B.J. Sarmah, D.K. Dutta, Appl. Organomet. Chem. 20 (2006) 512.

[48] (a) M.S. Abbassioun, P.A. Chaloner, C. Claver, P.B. Hitchcock, A.M. Masdeu, A. Ruiz, T. Saballs, J. Organomet. Chem. 403 (1991) 229;
(b) K.A. Chatziapostolou, K.A. Vallianatou, A. Grigoropoulos, C.P. Raptopoulou, A. Terzis, I.D. Kostas, P. Kyritsis, G. Pneumatikakis, J. Organomet. Chem. 692 (2007) 4129;
(c) B. Deb, D.K. Dutta, J. Mol. Catal. A 326 (2010) 21.

[49] (a) M. Delferro, M. Tegoni, V. Verdolino, D. Cauzzi, C. Graiff, A. Tiripicchio, Organometallics 28 (2009) 2062;
(b) M. Asti, R. Cammi, D. Cauzzi, C. Graiff, R. Pattacini, G. Predieri, A. Stercoli, A. Tiripicchio, Chem. Eur. J. 11 (2005) 3413;
(c) M. Delferro, D. Cauzzi, R. Pattacini, M. Tegoni, C. Graiff, A. Tiripicchio, Eur. J. Inorg. Chem. (2008) 2302.

[50] (a) H.A. Mayer, W.C. Kaska, Chem. Rev. 94 (1994) 1239;
(b) J.C. Hierso, R. Amardeil, E. Bentabet, R. Broussier, B. Gautheron, P. Meunier, P. Kalk, Coord. Chem. Rev. 236 (2003) 143.

[51] (a) H.E. Amouri, A.A. Bahsoun, J. Fischer, J.A. Osborn, Angew. Chem. Int. Ed. 26 (1987) 1169;
(b) G.F. Holland, D.E. Ellis, D.R. Tylor, H.B. Gray, W.C. Trogler, J. Am. Chem. Soc. 109 (1987) 4276;
(c) W.O. Siegel, S.J. Lapporte, J.D. Collman, Inorg. Chem. 10 (1971) 2158;
(d) T. Horvath, G. Kiss, Organometallics 10 (1991) 3798;
(e) M.J. Burk, R.I. Harlow, Angew. Chem. Int. Ed. 29 (1990) 1467;
(f) T.R. Ward, L.M. Vananzi, F. Lianza, T. Gerfin, V. Gramlich, G.M. Ramos Tomba, Helv. Chim. Acta 74 (1991) 983.

[52] (a) J. Browning, K.R. Dixon, S.F. Wang, J. Organomet. Chem. 474 (1994) 199;
(b) D.K. Dutta, J.D. Woollins, A.M.Z. Slawin, A.L. Fuller, B. Deb, P.P. Sarmah, M.G. Pathak, D. Konwar, J. Mol. Catal. A 313 (2009) 100.

[53] (a) P.A. Evans (Ed.), Modern Rhodium Catalysed Organic Reactions, Wiley-VCH, 2004;
(b) M.C. Simpson, D.J. Cole-Hamilton, Coord. Chem. Rev. 155 (1996) 163.

[54] (a) Q. Qian, F. Li, G. Yuan, Catal. Commun. 6 (2005) 446;
(b) Z. Freixa, P.C.J. Kamer, M. Lutz, A.L. Spek, P.W.N.M. van Leeuwen, Angew. Chem. Int. Ed. 44 (2005) 4385;
(c) S. Burger, B. Therrien, G. Süss-Fink, Helvet. Chim. Acta 88 (2005) 478;
(d) L. Gonsalvi, H. Adams, G.J. Sunley, E. Ditzel, A. Haynes, J. Am. Chem. Soc. 121 (1999) 11233;
(e) A.J. Pardey, C. Longo, Coord. Chem. Rev. 254 (2010) 254.

[55] (a) N. Kumari, B.J. Sarmah, D.K. Dutta, J. Mol. Catal. A 266 (2006) 260;
(b) M. Sharma, N. Kumari, P. Das, P. Chutia, D.K. Dutta, J. Mol. Catal. A 188 (2002) 25;
(c) N. Kumari, M. Sharma, P. Chutia, D.K. Dutta, J. Mol. Catal. A 222 (2004) 53;
(d) B.J. Borah, B. Deb, P.P. Sarmah, D.K. Dutta, J. Mol. Catal. A 319 (2010) 66;
(e) D.K. Dutta, P. Chutia, B.J. Sarmah, B.J. Borah, B. Deb, J.D. Woollins, J. Mol. Catal. A 300 (2009) 29;
(f) B.J. Sarmah, B.J. Borah, B. Deb, D.K. Dutta, J. Mol. Catal. A 289 (2008) 95.

[56] (a) T. Morimoto, K. Yamasaki, A. Hirano, K. Tsutsumi, N. Kagawa, K. Kakiuchi, Y. Harada, Y. Fukumoto, N. Chatani, T. Nishioka, Org. Lett. 11 (2009) 1777;
(b) Z.-H. Guan, Z.-H. Ren, S.M. Spinella, S. Yu, Y.-M. Liang, X. Zhang, J. Am. Chem. Soc. 131 (2009) 729.

[57] B.R. James, G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 8, Pergamon, Oxford, 1982 (Chapter 51).

[58] F.H. Jardine, J.A. Osborn, G. Wilkinson, J.F. Young, Chem. Ind. (London) (1965) 560.

[59] D.N. Lawson, J.A. Osborn, G. Wilkinson, J. Chem. Soc. A (1966) 1733.

[60] (a) H.U. Blaser, F. Spindler, M. Studer, Appl. Catal. A 221 (2001) 119;
(b) I.C. Lennon, P.H. Moran, Curr. Opin. Drug Disc. Dev. 6 (2003) 855.

[61] (a) S. Jimenez, J.A. Lopez, M.A. Ciriano, C. Tejel, A. Martinez, R.A. Sanchez-Delgado, Organometallics 28 (2009) 3193;
(b) D.J. Ager, Platinum Met. Rev. 50 (2006) 54;
(c) X. Wu, C. Wang, J. Xiao, Platinum Met. Rev. 54 (2010) 3;
(d) D.W. Norman, C.A. Carraz, D.J. Hyett, P.G. Pringle, J.B. Sweeney, A.G. Orpen, H. Phetmung, R.L. Wingad, J. Am. Chem. Soc. 130 (2008) 6840;
(e) K.D. Hesp, D. Wechsler, J. Cipot, A. Myers, R. McDonald, M.J. Ferguson, G. Schatte, M. Stradiotto, Organometallics 26 (2007) 5430;

(f) J. Wassenaar, B. de Bruin, M.A. Siegler, A.L. Spek, J.N.H. Reek, J.I. van der Vlugt, Chem. Commun. (2010) 1232;
(g) H. Seino, Y. Misumi, Y. Hojo, Y. Mizobe, Dalton Trans. (2010) 3072.
[62] (a) H. Schumann, H. Hemling, N. Goren, J. Blum, J. Organomet. Chem. 485 (1995) 209;
(b) A.N. Ajjou, J.-L. Pinet, J. Mol. Catal. A 214 (2004) 203;
(c) P.J. Baricelli, T. Ascanio, E. Lujano, L.G. Melean, M. Borusiak, F. López-Linares, L.J. Bastidas, M. Rosales, J. Mol. Catal. A 278 (2007) 107.
[63] (a) X-bin. Jiang, M. van den Berg, A.J. Minnaard, B.L. Feringaa, J.G. de Vries, Tetrahedron: Asymmetry 15 (2004) 2223;
(b) E. Guimet, M. Dieguez, A. Ruiz, C. Claver, Dalton Trans. (2005) 2557;
(c) J. Meeuwissen, R.J. Detz, A.J. Sandee, B. de Bruina, J.N.H. Reek, Dalton Trans. (2010) 1929.
[64] O. Roelen, (Chemische Verwertungsgesellschaft, mbH Ober-hausen). German Patent DE 849,548, 1938/1952, U.S. Patent 2,317,066, 1943 (Chem. Abstr. 38 (1944) 550).
[65] (a) L.H. Slaugh, R.D. Mullineaux, U.S. Pat. 3,239,569 and 3,239,570, 1966 (to Shell); Chem. Abstr. 64 (1964) 15745 and 19420. J. Organomet. Chem. 13 (1968) 469.;
(b) T. Onoda, Chem. Technol. 1993, September 34.
[66] (a) J.F. Young, J.A. Osborn, F.A. Jardine, G. Wilkinson, Chem. Commun. (London) (1965) 131;
(b) D. Evans, J.A. Osborn, G. Wilkinson, J. Chem. Soc. A (1968) 3133;
(c) D. Evans, G. Yagupsky, G. Wilkinson, J. Chem. Soc. A (1968) 2660.
[67] (a) P.W.N.M. van Leeuwen, C.F. Roobeek, J. Organomet. Chem. 258 (1983) 343;
(b) Brit. Patent 2,068,377, US Patent 4,467,116 (to Shell Oil); Chem. Abstr. 101 (1984) 191142;
(c) T. Jongsma, G. Challa, P.W.N.M. van Leeuwen, J. Organomet. Chem. 421 (1991) 121;
(d) A. van Rooy, E.N. Orij, P.C.J. Kamer, P.W.N.M. van Leeuwen, Organometallics 14 (1995) 34.
[68] (a) C. Bianchini, A. Meli, M. Peruzzini, F. Vizza, Organometallics 9 (1990) 226;
(b) G. Kiss, I. Horvath, Organometallics 10 (1991) 3798;
(c) T.A. Herzog, D.L. Zubris, J.E. Bercaw, J. Am. Chem. Soc. 118 (1996) 11988.
[69] (a) N. Sakai, S. Mano, K. Nozaki, H. Takaya, J. Am. Chem. Soc. 115 (1993) 7033;
(b) J.E. Babin, G.T. Whiteker, U.S. Patent 5,360,938, 1994 (to Union Carbide Corp);
(c) G.J.H. Buisman, P.C.J. Kamer, P.W.N.M. van Leeuwen, Tetrahedron: Asymmetry 4 (1993) 1625;
(d) M. Diéguez, O. Pamies, A. Ruiz, S. Castillon, C. Claver, Chem. Eur. J. 7 (2001) 3086.
[70] (a) R. Tudor, M. Ashley, Platinum Met. Rev. 51 (2007) 116;
(b) P. Barbaro, C. Bianchini, G. Giambastiani, S.L. Parisel, Coord. Chem. Rev. 248 (2004) 2131;
(c) E. Zuidema, P.E. Goudriaan, B.H.G. Swennenhuis, P.C.J. Kamer, P.W.N.M. van Leeuwen, M. Lutz, A.L. Spek, Organometallics 29 (2010) 1210;
(d) R. Lazzaroni, R. Settambolo, G. Alagona, C. Ghio, Coord. Chem. Rev. 254 (2010) 696.
[71] (a) I.D. Kostas, B.R. Steele, F.J. Andreadaki, V.A. Potapov, Inorg. Chim. Acta 357 (2004) 2850;
(b) H.J. Clark, R. Wang, H. Alper, J. Org. Chem. 67 (2002) 6224;
(c) S. Gladiali, S. Medici, T. Kegl, L. Kollar, Monatshefte für Chemie 131 (2000) 1351;
(d) E.I. Tolis, K.A. Vallianatou, F.J. Andreadaki, I.D. Kostas, Appl. Organometal. Chem. 20 (2006) 335;
(e) A.J. Pardey, J.D. Suárez, M.C. Ortega, C. Longo, J.J. Pérez-Torrente, L.A. Oro, Open Catal. J. 3 (2010) 44;
(f) A.B. Rivas, J.J. Pérez-Torrente, A.J. Pardey, A.M. Masdeu-Bultó, M. Diéguez, L.A. Oro, J. Mol. Catal. A 300 (2009) 121;
(g) M.A.F. Hernandez-Gruel, G. Gracia-Arruego, A.B. Rivas, I.T. Dobrinovitch, F.J. Lahoz, A.J. Pardey, L.A. Oro, J.J. Pérez-Torrente, Eur. J. Inorg. Chem. (2007) 5677;
(h) A.M. Trzeciak, P. Stepnicka, E. Mieczynska, J.J. Ziolkowski, J. Organomet. Chem. 690 (2005) 3260.
[72] (a) C. Abu-Gnim, I. Amer, J. Organomet. Chem. 516 (1996) 235;
(b) R.M. Gipson, US Patent 3,954,877, 1976 (CA, 85: 77653c).;
(c) S. Arimitsu, K. Shikakura, JP Patent 02174740, 1990 (CA, 113: 39942f);
(d) L. Bettucci, C. Bianchini, A. Meli, W. Oberhauser, J. Mol. Catal. A 291 (2008) 57;
(e) J.D.R. de Campos, R. Buffon, J. Braz. Chem. Soc. 16 (2005) 17.
[73] (a) T.S. Lobana, Prog. Inorg. Chem. 37 (1989) 495;
(b) T.S. Lobana, Coordination chemistry of phosphine chalcogenides and their analytical and catalytic applications, in: The Chemistry of Organophosphorus Compounds, vol. 2, John Wiley and Sons Ltd., 1992.
[74] (a) R. Uson, A. Laguna, J.L. Sanjoaquin, J. Organomet. Chem. 80 (1974) 147;
(b) R. Uson, A. Laguna, M. Laguna, J. Jimenez, M.E. Durana, Inorg. Chim. Acta 168 (1990) 89;
(c) A. Laguna, M. Laguna, J. Jimenez, A.J. Fumanal, J. Organomet. Chem. 396 (1990) 121.
[75] M. Contel, A.J. Edwards, J. Garrido, M.B. Hursthouse, M. Laguna, R. Terroba, J. Organomet. Chem. 607 (2000) 129.
[76] (a) A. Araneo, A. Trovati, Inorg. Chim. Acta 3 (1969) 471;
(b) U.C. Aggarwala, S. Datta, Ind. J. Chem. A 20 (1981) 1153;
(c) U.C. Aggarwala, S. Datta, S.K. Shukla, Ind. J. Chem. A 20 (1981) 985;
(d) W. Hieber, P. John, Chem. Ber. 103 (1970) 2161;
(e) P. John, Chem. Ber. 103 (1970) 2178.
[77] P. Chutia, N. Kumari, M. Sharma, J.D. Woollins, A.M.Z. Slawin, D.K. Dutta, Polyhedron 23 (2004) 1657.
[78] (a) D.H. Williams, R.S. Ward, R.G. Cooks, J. Am. Chem. Soc. 90 (1968) 966;
(b) C. Screttas, A.F. Isbell, J. Org. Chem. 27 (1962) 2573;
(c) G.A. Olah, D. Hehemann, J. Org. Chem. 42 (1977) 2190.
[79] M.G. Humphrey, B. Lockhart-Gillett, M. Samoc, B.W. Skelton, V.-A. Tolhurst, A.H. White, A.J. Wilson, B.F.J. Yates, J. Organomet. Chem. 690 (2005) 1487.
[80] C. Graiff, G. Predieri, A. Tiripicchio, Eur. J. Inorg. Chem. 9 (2003) 1659.
[81] A.M.Z. Slawin, M.B. Smith, J.D. Woollins, J. Chem. Soc., Dalton Trans. 11 (1997) 1877.
[82] M. Negoi, L. Paruta, Rev. Roum. Chim. 39 (1994) 485.
[83] E.V. García-Báez, M.G. Ballinas-López, M.J. Rosales-Hoz, M.A. Leyva, I. Haiduc, C. Silvestru, Polyhedron 28 (2009) 3747.
[84] S.O. Grim, J.D. Mitchell, Synth. React. Met. Org. Chem. 4 (1974) 221.
[85] (a) S.M. Aucott, A.M.Z. Slawin, J.D. Woollins, Eur. J. Inorg. Chem. (2002) 2408;
(b) K.M. Pietrusiewicz, M. Kuznikowski, Heterocycl. Chem. 3 (1991) 37;
(c) T. Mizuta, Y. Imamura, K. Miyoshi, J. Am. Chem. Soc. 125 (2003) 2068;
(d) P. Mastrorilli, C.F. Nobile, G.P. Suranna, F.P. Fanizzi, G. Ciccarella, U. Englert, Q. Li, Eur. J. Inorg. Chem. (2004) 1234.
[86] (a) S.O. Grim, L.C. Satek, C.A. Tolman, J.P. Jesson, Inorg. Chem. 14 (1975) 656;
(b) S.O. Grim, J.D. Mitchell, Inorg. Chem. 16 (1977) 1762;
(c) S.O. Grim, E.D. Walton, Inorg. Chem. 19 (1980) 1982;
(d) S.O. Grim, P.H. Smith, I.J. Colquhoun, W. Mcfarlane, Inorg. Chem. 19 (1980) 3195;
(e) I.J. Colquhoun, S.O. Grim, W. Mcfarlane, J.D. Mitchell, P.H. Smith, Inorg. Chem. 20 (1981) 2516.
[87] M. Valderrama, R. Contreras, M. Bascunan, S. Alegria, D. Boys, Polyhedron 14 (1995) 2239.
[88] S.R. Hall, B.W. Skelton, A.H. White, Aust. J. Chem. 36 (1983) 267.
[89] E. Lindner, B. Karle, Z. Natureforsch 45 (1990) 1108.
[90] (a) J.C. Jeffrey, T.B. Rouchfuss, Inorg. Chem. 18 (1979) 2658;
(b) E. Lindner, M. Haustein, R. Fawzi, M. Steimann, P. Wegner, Organometallics 13 (1994) 5021.
[91] E. Lindner, M. Gepraegs, K. Gierling, R. Fawzi, M. Steimann, Inorg. Chem. 34 (1995) 6106.
[92] M.M. Taqui Khan, M.K. Nazeeruddin, Inorg. Chim. Acta 147 (1988) 33.
[93] P. Braunstein, D. Matt, Y. Dusausoy, Inorg. Chem. 22 (1983) 2043.
[94] P. Braunstein, D. Matt, D. Nobel, S.E. Bouaound, B. Carluer, D. Grandjean, P. Lemoine, J. Chem. Soc., Dalton Trans. (1986) 415.
[95] J.W. Faller, X. Liu, J. Parr, Chirality 12 (2000) 325.
[96] J.W. Faller, J. Parr, Organometallics 19 (2000) 1829.
[97] J.W. Faller, B.P. Patel, M.A. Albrizzio, M. Curtis, Organometallics 18 (1999) 3096.
[98] P. Bhattacharyya, A.M.Z. Slawin, M.B. Smith, J. Chem. Soc., Dalton Trans. (1998) 2467.
[99] (a) B. Deb, B.J. Borah, B.J. Sarmah, B. Das, D.K. Dutta, Inorg. Chem. Commun. 12 (2009) 868;
(b) B. Deb, D.K. Dutta, Polyhedron 28 (2009) 2258.
[100] D.K. Dutta, P. Chutia, J.D. Woollins, A.M.Z. Slawin, Inorg. Chim. Acta 359 (2006) 877.
[101] P. Chutia, M. Sharma, P. Das, N. Kumari, J.D. Woollins, A.M.Z. Slawin, D.K. Dutta, Polyhedron 22 (2003) 2725.
[102] J.W. Faller, P.P. Fontaine, J. Organomet. Chem. 692 (2007) 976.
[103] M. Valderrama, R. Contreras, V. Arancibia, P. Muñoz, Inorg. Chim. Acta 255 (1997) 221.
[104] T.S. Lobana, R. Verma, Ind. J. Chem., Sec. A 42 (2003) 534.
[105] S.M. Aucott, A.M.Z. Slawin, J.D. Woollins, Polyhedron 22 (2003) 361.
[106] T.S. Venkatakrishnan, S.S. Krishnamurthy, M. Nethaji, J. Organomet. Chem. 690 (2005) 4001.
[107] B. Deb, P.P. Sarmah, D.K. Dutta, Eur. J. Inorg. Chem. (2010) 1710.
[108] S. Evans, J.W. Faller, J. Parr, J. Organomet. Chem. 674 (2003) 56.
[109] M. Valderrama, R. Contreras, V. Arancibia, P. Munoz, Bol. Soc. Chil. Quim. 41 (1996) 427.
[110] B.J. Sarmah, D.K. Dutta, J. Organomet. Chem. 695 (2010) 781.
[111] B. Deb, B.J. Sarmah, B.J. Borah, D.K. Dutta, Spectrochim. Acta A 72 (2009) 339.
[112] G. Jenner, Appl. Catal. 50 (1989) 99.
[113] A.A. Kelkar, D.S. Kolhe, R.V. Chaudhari, J. Organomet. Chem. 430 (1992) 111.
[114] M.M. Taqui Khan, S.B. Halligudi, S.H.R. Abdi, S. Shukla, J. Mol. Catal. 61 (1990) 275.
[115] E. Yoneda, S.-W. Zhang, D.-Y. Zhou, K. Onitsuka, S. Takahashi, J. Org. Chem. 68 (2003) 8571.
[116] (a) D.K. Mukherjee, B.K. Palit, C.R. Saha, J. Mol. Catal. 91 (1994) 19;
(b) S. Bhaduri, H. Khwaja, K. Sharma, P.G. Jones, J. Chem. Soc., Chem. Commun. (1989) 515.
[117] A.M. Tafesh, J. Weiguny, Chem. Rev. 96 (1996) 2035.
[118] D.C.D. Butler, D.J. Cole-Hamilton, Inorg. Chem. Commun. 2 (1999) 305.
[119] (a) S. Siegel, in: L.A. Paquette (Ed.), Encyclopedia of Reagents for Organic Synthesis, 6, John Wiley & Sons, Chichester, 1996, p. 4410;
(b) M.A. Bennett, T.W. Matheson, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 4, Pergamon Press, Oxford, 1982, p. 931;
(c) M. Freifelder, Practical Catalytic Hydrogenation, Wiley-InterScience, New York, 1971;
(d) A. Picot, H. Dyer, A. Buchard, A. Auffrant, L. Vendier, P. Le Floch, S. Sabo-Etienne, Inorg. Chem. 49 (2010) 1310.

[120] (a) P.A. Chaloner, M.A. Esteruelas, F. Joo, L.A. Oro, Homogeneous Hydrogenation, Kluwer Academic Publishers, Dordrecht, 1994, p. 119 (Chapter 4);
(b) J. Halpern, J.F. Harrod, B.R. James, J. Am. Chem. Soc. 88 (1966) 5150.
[121] (a) A. Hadzovic, D. Song, C.M. MacLaughlin, R.H. Morris, Organometallics 26 (2007) 5987;
(b) M. Aydemir, N. Meric, A. Baysal, C. Kayan, M. Togrul, B. Gumgum, Appl. Organometal. Chem. 24 (2010) 215;
(c) T. Ikariya, A.J. Blacker, Acc. Chem. Res. 40 (2007) 1300;
(d) A.E.W. Ledger, P.A. Slatford, J.P. Lowe, M.F. Mahon, M.K. Whittlesey, J.M.J. Williams, Dalton Trans. (2009) 716;
(e) M. Zhao, Z. Yu, S. Yan, Y. Li, Tetrahedron Lett. 50 (2009) 4624;
(f) X. Wu, J. Liu, X. Li, A. Zanotti-Garosa, F. Hancock, D. Vinchi, J. Ruan, J. Xiao, Angew. Chem. Int. Ed. 45 (2006) 6718;
(g) W. Jia, X. Chen, R. Guo, C. Sui-Seng, D. Amoroso, A.J. Loughb, K. Abdur-Rashid, Dalton Trans. (2009) 8301;
(h) R. Reguillo, M. Grellier, N. Vautravers, L. Vendier, S. Sabo-Etienne, J. Am. Chem. Soc. 132 (2010) 7854.
[122] S. Rajagopal, J. Mol. Catal. 81 (1993) 185.
[123] (a) Y. Cheng, X.-Y. Lu, H.-J. Xu, Y.-Z. Li, X.-T. Chen, Z.-L. Xue, Inorg. Chim. Acta 363 (2010) 430;
(b) S. Bhaduri, K. Sharma, D. Mukesh, J. Chem. Soc., Dalton Trans. (1993) 1191;
(c) A. Comas-Vives, G. Ujaque, A. Lledos, Organometallics 26 (2007) 4135.
[124] (a) D.R. Fahey, J. Org. Chem. 38 (1973) 80;
(b) M. Bianchi, G. Menchi, F. Francalanci, F. Piacenti, U. Matteoli, P. Frediani, C. Botteghi, J. Organomet. Chem. 188 (1980) 109.
[125] Z. Toth, F. Joo, M.T. Beck, Inorg. Chim. Acta 42 (1980) 153.
[126] (a) A. Andriollo, A. Bolivar, F.A. López, D.E. Páez, Inorg. Chim. Acta 238 (1995) 187;
(b) A. Andriollo, J. Carrasquel, J. Mariño, F.A. López, D.E. Páez, I. Rojas, N. Valencia, J. Mol. Catal. A 116 (1997) 157.
[127] (a) P.J. Baricelli, G. Rodríguez, M. Rodríguez, E. Lujano, F. López-Linares, Appl. Catal. A 239 (2003) 25;
(b) P.J. Baricelli, E. Lujano, M. Rodríguez, A. Fuentes, R.A. Sánchez Delgado, Appl. Catal. A 263 (2004) 187.
[128] P.J. Baricelli, L. Izaguirre, J. López, E. Lujano, F. López-Linares, J. Mol. Catal. A 208 (2004) 67.
[129] (a) V. Cadierno, P. Crochet, J. Diez, S.E. Garcia-Garrido, J. Gimeno, Organometallics 22 (2003) 5226;
(b) V. Cadierno, P. Crochet, J. Diez, S.E. Garcia-Garrido, J. Gimeno, Organometallics 23 (2004) 4836;
(c) J. Albers, V. Cadierno, P. Crochet, S.E. Garcia-Garrido, J. Gimeno, J. Organomet. Chem. 692 (2007) 5234;
(d) V. Cadierno, P. Crochet, J. Díez, J. García-Álvarez, S.E. García-Garrido, S. García-Granda, J. Gimeno, M.A. Rodríguez, Dalton Trans. (2003) 3240.
[130] (a) W.A. Herrmann, B. Cornils, Angew. Chem. Int. Ed. Engl. 36 (1997) 1048;
(b) B. Li, X. Li, K.A. Sami, K. Fujimoto, Chem. Lett. (2002) 836;
(c) S. Rojas, P. Terreros, J.L.G. Fierro, J. Mol. Catal. A 184 (2002) 19;
(d) P.W.N.M. van Leeuwen, A.J. Sandee, J.N.H. Reek, P.C.J. Kamer, J. Mol. Catal. A 182–183 (2002) 107.
[131] (a) L. Alvila, T.A. Pakkanen, T.T. Pakkanen, J. Mol. Catal. 73 (1992) 325;
(b) P. Pino, F. Piacenti, H. Bianchi, R. Lazzaroni, Chim. Ind. 50 (1968) 318.
[132] (a) H. Kang, C.H. Mauldin, T. Cole, W. Slegeir, K. Cann, R. Pettit, J. Am. Chem. Soc. 99 (1977) 8323;
(b) R.A. Sanchez-Delgado, J.S. Bradley, G. Wilkinson, J. Chem. Soc., Dalton Trans. (1976) 399.
[133] (a) B. Cornils, W.A. Herrmann, in: B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, 2nd ed., Wiley-VCH, Weinheim, 2002, p. 603 (Chapter 3.1.1.1);
(b) B. Cornils, W.A. Herrmann (Eds.), Aqueous-phase Organometallic Catalysis. Concepts and Applications, Wiley-VCH, Weinheim, 1998;
(c) C.W. Kohlpaintner, R.W. Fischer, B. Cornils, Appl. Catal. A 221 (2001) 219.
[134] (a) R.A. Sánchez-Delgado, M. Rosales, A. Andriollo, Inorg. Chem. 30 (1991) 1170;
(b) G. Süss-Fink, in: W.R. Moser, D.W. Slocum (Eds.), Homogeneous Transition Metal Catalyzed Reactions, Advanced Chemistry Series, No. 230, American Chemical Society, Washington, 1992;
(c) G. Süss-Fink, G. Meister, Adv. Organomet. Chem. 35 (1993) 41;
(d) C. Erkey, E. Lozano Diz, G. Süss-Fink, X. Dong, Catal. Commun. 3 (2002) 213;
(e) V.K. Srivastava, R.S. Shukla, H.C. Bajaj, R.V. Jasra, J. Mol. Catal. A 202 (2003) 65.
[135] J.-X. Gao, P. Xu, X. Yi, H. Wan, K. Tsai, J. Mol. Catal. 147 (1999) 99.
[136] (a) P.J. Baricelli, E. Lujano, M. Rodriguez, A. Fuentes, R.A. Sánchez-Delgado, Appl. Catal. A 263 (2004) 187;
(b) P.J. Baricelli, K. Segovia, E. Lujano, M. Modrono-Alonso, Fr. Lopez-Linares, R.A. Sanchez-Delgado, J. Mol. Catal. A 252 (2006) 70.
[137] E. Lozano, D.A. Neels, H. Stoeckli-Evans, G. Süss-Fink, Polyhedron 20 (2001) 2771.
[138] (a) R. Merlin, A. Beatriz, A. Federico, D. Carlos, G. Angel, M. Karely, S. Otto, S. Yslamar, Polyhedron 27 (2008) 530;
(b) M.A. Moreno, M. Haukka, S. Jaaskelainen, S. Vuoti, J. Pursiainen, T.A. Pakkanen, J. Organomet. Chem. 690 (2005) 3803.
[139] K. Takahashi, M. Yamashita, T. Ichihara, K. Nakano, K. Nozaki, Angew. Chem. Int. Ed. 49 (2010) 4488.