ELSEVIER

Coordination Chemistry Reviews
193–195 (1999) 73–145

COORDINATION CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

Homogeneous catalysis with transition metal complexes containing sulfur ligands

J. Carles Bayón [a,]*, Carmen Claver [b,1],
Anna M. Masdeu-Bultó [b]

[a] *Departament de Química, Universitat Autònoma de Barcelona, 08913 Bellaterra, Spain*
[b] *Departament de Química Física i Inorgànica, Universitat Rovira i Virgili, Pl. Imperial Tarraco 1, 43005 Tarragona, Spain*

Received 25 November 1998; received in revised form 19 April 1999; accepted 25 May 1999

Contents

---

* Corresponding author. Tel.: +34-93-5812889; fax: +34-93-5813101.
E-mail addresses: bayon@cc.uab.es (J.C. Bayón), claver@argo.urv.es (C. Claver)
[1] Also corresponding author.

PII: S0010-8545(99)00169-1

Abstract

Transition metal complexes with sulfur ligands are active catalysts in a considerable number of homogeneous reactions, although they have been less investigated than complexes with other donor atoms. We review the application of complexes containing sulfur ligands in hydrogenation, hydrogen transfer, isomerization, hydrosilylation, carbonylation, hydroformylation, polymerization, Heck reaction, allylic alkylation, Grignard cross-coupling, conjugate addition and oxidation with O_2. The use of different types of sulfur ligands and the characteristics of the coordination complexes are described together with the results of the catalytic reactions. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Homogenous catalysis; Sulfur ligands; Transition metals

Nomenclature

acac	2,4-pentanodionate
bdpp	2,4-bis(diphenylphosphino)pentane
cod	1,5-cycloctadiene
Cp	cyclopentadienyl
Cp′	methylcyclopentadienyl

Cp*	pentamethylcyclopentadienyl
dba	*trans*, *trans*-dibenzylidene acetone
de	diasteroisomeric excess
diop	2,3-*O*-isopropylidene-2,3-dihidroxy-1,4-bis(diphenylphosphino)butane
dmso	dimethylsulfoxide
dppb	1,4-bis(diphenylphosphino)butane
dppm	bis(diphenylphosphino)methane
dppp	1,3-bis(diphenylphosphino)propane
ee	enantiomeric excess
fc	ferrocenyl: $(C_5H_5)Fe(C_5H_4)$
HPIR	high pressure infrared spectroscopy
HPNMR	high pressure nuclear magnetic resonance spectroscopy
MAO	methylaluminium oxide
nbd	norbornadiene
$P(OPh^*)_3$	tris(*o*-tertbutylphenyl)phosphite: $P(O\text{-}o\text{-}^tBuC_6H_4)_3$
PP	diphosphine
pz	pyrazolato
TOF	turnover frequency: (mols of substrate)·(mols of catalyst·time)$^{-1}$
TON	turnover number: (mols of substrate)·(mols of catalyst)$^{-1}$
tppts	$P(m\text{-}NaO_3SC_6H_4)_3$
ttf	tetrathiofulvalene

1. Introduction and scope

Phosphane ligands play a central role in many reactions catalyzed by transition metals [1]. More recently, metal catalysts containing nitrogen [2] or oxygen [3] ligands have been reported to perform very efficiently in a wide range of reactions. The coordination chemistry of sulfur ligands has been extensively studied and has shown a unique variety of structures with most of the transition metals in different oxidation states [4]. However, the use of sulfur ligands in reactions catalyzed by transition metals is still relatively unexplored compared with other ligands [5]. This review deals with reactions catalyzed by metal complexes containing S-donor auxiliary ligands. In this context, an auxiliary ligand means a chemical species which is bonded to the metal, but which is not part of the reagents or products. Thus, reactions involving substrates that contain sulfur are not included, although they often form catalytic intermediates containing M–S bonds. Therefore, HDS [6], and reactions involving thiols [7], thioethers [8], disulfides [9], sulfoxides [10] or H_2S [11] as reagents are not explicitly covered. Metalloenzymes containing sulfur ligands are not included.

The review focuses on catalysts containing monodentate, homo- and hetero-polydentate ligands, in which at least there is a S–M bond. Some ligands containing sulfur atoms, which specific coordination mode has not been unequivocally established (i.e. some sulfoxide ligands), are included as well as molecular immobilized catalysts containing sulfur ligands.

A wide range of catalytic reactions is covered: hydrogenation, hydrogen transfer, isomerization, hydrosilylation, carbonylation, hydroformylation, polymerization, Heck reaction, allylic alkylation, Grignard cross-coupling, conjugate addition and oxidation with O_2. The asymmetric version of the reactions has also been included.

2. Hydrogenation

The hydrogenation of unsaturated substrates using complexes with sulfur-donor ligands has been widely reported in the literature. In this section, catalysts are organized according to the type of sulfur ligands. First the more studied neutral thioethers and sulfoxides are described, then the anionic thiolato and sulfido ligands, and finally the phosphine sulfide ligands. Other less studied compounds such as carbamates and thioureathes are grouped together in a miscellaneous group.

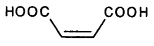
2.1. Thioether and dithioether ligands

The system $[PtCl_2(SPh_2)_2]/SnCl_2$ was one of the first examples of transition metal catalysts containing a thioether ligand used to hydrogenate polyenes to monoenes [12]. Platinum(II) complexes containing thioether ligands are only active in hydrogenation processes in the presence of $SnCl_2$. This system was moderately active at 50 bar of H_2 pressure and 90°C and in 8 h produced 14% of cyclooctene from 1,3-cyclooctadiene in dichloromethane (molar ratio substrate/catalyst = 60). Similarly, low conversions were also reported in the hydrogenation of styrene catalyzed by $[PtCl_2(SMe_2)_2]/SnCl_2$ [13].

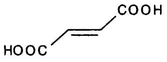
Mononuclear mixed ligand thioether-phosphino platinum(II) complexes of general formula *cis*-$[PtCl_2LL']$ ($L' = SMe_2$, SEt_2 SPh_2 and $S(p\text{-}PhCl)_2$ and $L = P(p\text{-}CH_3OPh)_3$, $P(p\text{-}CH_3Ph)_3$, PPh_3, $P(p\text{-}ClPh)_3$ and $P(p\text{-}FPh)_3$) were used to hydrogenate styrene [13]. Results were best with the *cis*-$[PtCl_2(S(p\text{-}PhCl)_2)(PPh_3)]/SnCl_2$ catalyst precursor at 60°C under 50 bar of H_2 in an acetone solution providing a total turnover frequency (TOF) of 8680 h^{-1} [13a]. The results from the mixed systems and from the corresponding $[PtCl_2L_2]$ and $[PtCl_2L'_2]$ revealed that the ones containing one weak ligand (L′ = thioether) and one strong ligand (L = phosphine) were more effective as catalysts [13a]. The catalytic activity of the complexes $[PtCl_2LL']$ depends on the basicity of the two neutral ligands. In the case of the thioethers, the activity increases as the basicity of the ligand decreases. This suggests that the thioether functions as a weak disociable ligand in this type of catalysts.

Other early work is a patent disclosing the use of the compound $[RuCl_3(SEt_2)_3]$ as a catalyst for the hydrogenation of olefin–acetylene mixtures. The ruthenium complex needs to be activated initially by treatment with $LiAlH_4$ [14].

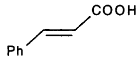
Rhodium thioether and dithioether complexes have been studied as catalyst precursors for the hydrogenation of alkenes. In a pioneering study, James et al. [15] investigated the catalytic activity of rhodium(III) complexes [$RhCl_3(SR_2)_3$] (R = Et and Bz) in the hydrogenation of ethylene, maleic acid (**2.1a**), fumaric acid (**2.1b**) and *trans*-cinnamic acid (**2.2**) in *N*,*N*′-dimethylacetamide solutions at 80°C and 1 bar of H_2 pressure.



2.1a



2.1b

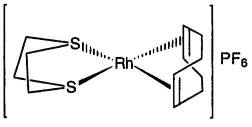


2.2

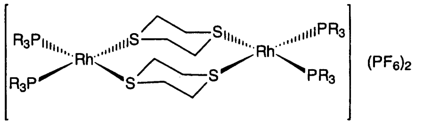
Kinetic and mechanistic studies [15] showed that the reduction of the Rh(III) complex to the Rh(I) species by hydrogen was the initial step in the reaction and the Rh(I) species formed then were stabilized by substrate coordination. The dissociation of one of the sulfur ligands from [$RhCl_3(SR_2)_3$] before reduction with dihydrogen is required to proceed with the catalytic cycle. The subsequent oxidative addition of hydrogen with the d^8 metal complex leads to the saturated product with regeneration of the rhodium(I) catalyst. The kinetic data from [$RhCl_3(SEt_2)_3$] and the rhodium(I) system [$Rh_2(\mu\text{-}Cl)_2(C_8H_{14})_2$]/$SEt_2$ are similar under the same reaction conditions. This confirms that rhodium(I) species are involved in the Rh(III)–SR_2 catalytic systems [15e].

The analogous iridium *mer* and *fac* isomers of complex [$IrCl_3(SEt_2)_3$] and rhodium(III) compounds with a chelate sulfur ligand such as dichlorobis(2,5-dithiahexane)rhodium(III) chloride are inactive for the hydrogenation of maleic acid (**2.1a**) at 1 bar of hydrogen pressure [15b]. The presence of the chelating ligand presumably makes initial dissociation more difficult.

The cationic rhodium(I) complex **2.3** and the binuclear complex **2.4** are active catalysts in the hydrogenation of cyclohexene at 50°C and 50 bar [16]. Results were best (93% conversion in 24 h at substrate/catalyst = 400) with the binuclear system **2.4a**, while **2.3** and **2.4b** gave low yields.



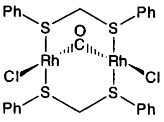
2.3



2.4a (R = Ph), **2.4b** (R = OPh)

A series of iridium(I) mononuclear complexes [$Ir(cod)L_2$]ClO_4 (L = tetrahydrothiophene (tht)) and binuclear [$Ir_2(\mu\text{-}L)_2(cod)_2$]$(ClO_4)_2$ (L = tht, SMe_2) have been prepared from [$Ir_2(\mu\text{-}Cl)_2(cod)_2$] with addition of the thioether in presence of $AgClO_4$ [17]. These mono- and binuclear diolefin complexes and their carbonyl analogs have been used as catalyst precursors in homogeneous hydrogenation of alkenes at 25°C and 1 bar of H_2 [18]. The effect of the different ligands on the catalytic activity has been studied. In this case, the mononuclear complexes behave as active precursors in the hydrogenation of 1-heptene, while related carbonylic binuclear $[Ir_2(\mu\text{-}{}^tBu_2S(CH_2)_2S{}^tBu_2)_2(CO)_4](ClO_4)_2$ complex is inactive [18]. In general, olefin isomerization was observed and in some cases this was the major process. In the case of the mixed complexes $[Ir(cod)(tht)(PR_3)]ClO_4$ ($R = C_6H_5$, $p\text{-}CH_3C_6H_4$, OCH_3, $p\text{-}ClC_6H_4$, OC_6H_4) the activity was determined by a combination of both steric and electronic effects [18]. The presence of PPh_3 enhanced catalytic activity and decreased isomerization.

A-frame systems with dithioethers $PhS(CH_2)_mSPh$ ($m = 1-6$) such as the complex *trans*-$[Rh_2Cl_2(\mu\text{-}CO)(PhSCH_2SPh)_2]$ (**2.5**) and also binuclear complexes *cis*-$[Rh_2Cl_2(CO)_4L]$ ($L = PhS(CH_2)_mSPh$) are active for the hydrogenation of olefins, but they readily decompose to Rh(0) species under hydrogenation conditions . The mononuclear complex $[RhCl(CO)(PhS(CH_2)_2SPh)]$ is inactive at low temperatures and pressures [19a].

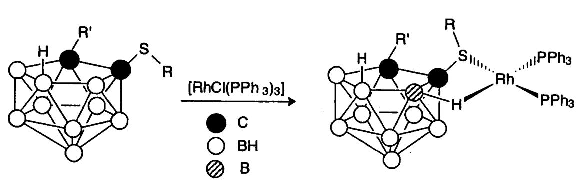


2.5

Catalytic activity of cyclopentadienyl complexes with thioethers has been studied. Rhodium(III) pentamethylcyclopentadienyl derivatives with the empirical formula $[Rh_2Cp^*_2Cl_4L]_n$ ($Cp^* = C_5Me_5$; dinuclear ($n = 1$) for $L = SMe_2$ and polymeric for L = 1,4-dithiane) are active in the hydrogenation of cyclohexene, 1-hexene and styrene at 50°C and 50 bar of H_2 [16]. The related cationic analogous monomer $[RhCp^*(SMe_2)_3](PF_6)_2$ is also active in the hydrogenation of cyclohexene at the same conditions [16].

Polynuclear complexes, like the rhodium aggregate $[Rh_6(CO)_{12}(SMe_2)_4]$, are active in the hydrogenation of 1-hexene in the range of 20–60°C and at 1 bar of hydrogen pressure. The highest rate was 2200 turnovers h^{-1} [20]. Nevertheless, at the end of the reaction a black insoluble solid was recovered. This solid was active in the same reaction, which indicated that the hydrogenation with $[Rh_6(CO)_{12}(SMe_2)_4]$ was heterogeneous in nature.

Recent designs of thioether ligands include a family of carboranes **2.6** with SR functionalities [21]. A series neutral *exo*-*nido*-monothiorhodacarboranes **2.7** have been prepared with these ligands where the rhodium is bonded to the sulfur and takes part in a B–H–Rh three centered, two electron, bond (Scheme 1a). These

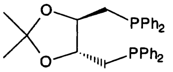


2.6 R = Et, Ph; R' = Me, Ph **2.7**

Scheme 1a.

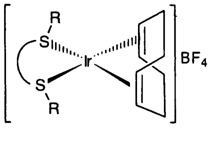
complexes **2.7** are active catalysts for the hydrogenation of 1-hexene under mild conditions. Complex **2.7** with R = Ph and R′ = Me is the most active [21]. It is important to note that this catalysts is more active than both the analogous phosphinorhodacarborane and [RhCl(PPh_3)$_3$] in similar conditions. This was attributed to the unique stereochemistry of these complexes. The catalyst could be recovered when the reaction was finished and there was no sign of deactivation. The hydrogenation of 2-hexenes was much slower than for 1-hexene, but they were eventually hydrogenated at higher pressures.

Chiral sulfur ligands have sometimes been designed taking chiral phosphines as a model. Thus, a series of sulfoxides [22] (discussed in Section 2.2) and dithioethers [23,24] were prepared based on the diop **2.8** skeleton.

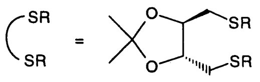


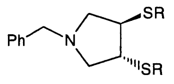
2.8

Iridium(I) cationic complexes [Ir(cod)L]BF_4 (**2.9**), where L are the chiral dithioether diop analogs **2.10**, or the chiral dithioethers **2.11**, have been prepared [23]. These complexes react with H_2 at low temperature to give the corresponding Ir(III) dihydrido species *cis*-[IrH_2(cod)L]BF_4 except for the case of the ligand **2.10** (R = Ph). The cationic complexes **2.9** are active as catalyst precursors in the asymmetric hydrogenation of different prochiral dehydroamino acid derivatives such as *Z*-α-acetamidocinnamic acid (**2.12a**), methyl α-acetamidocinnamate (**2.12b**), α-acetamidoacrylic acid (**2.12c**) and itaconic acid (**2.13**), at room temperature under 1 bar of hydrogen pressure. Results were best with ligand **2.11** (R = Ph). Almost total conversion and ee 68% (*R*) was obtained in 2.5 h in the hydrogenation of itaconic acid [23b].



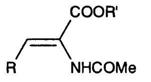
2.9



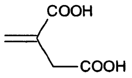


R = Me, ${}^iPr$, Ph

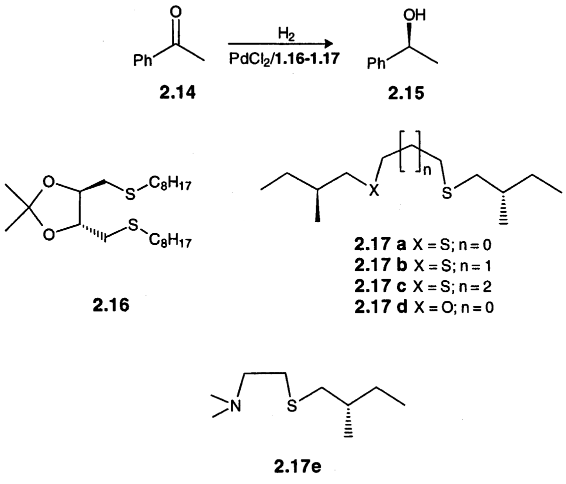
2.10 **2.11**



2.12a R= Ph; R'= H
2.12b R= Ph; R'= Me
2.12c R= R'= H

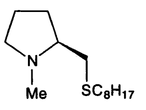


2.13

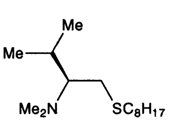


Scheme 1b.

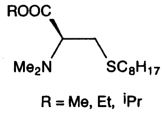
There have also been studies of the asymmetric hydrogenation of acetophenone (**2.14**) to 1-phenylethanol (**2.15**) using $PdCl_2$ with the chiral dithiother ligand **2.16**, the homobidentate ligands **2.17a**–**c** and the heterobidentate ligands **2.17d**–**e** [24] (Scheme 1b). The system containing **2.16** provided a 60% conversion and 16% of ee. The $PdCl_2$ systems with 1,3- and 1,4-dithiothers **2.17b** and **2.17c** were inactive while the system with ligand **2.17a** showed very poor activity (19% after 18 h). Furthermore, the chemioselectivity was low, since ethylbenzene was also formed. There was no optical induction. The low conversions and selectivities were attributed to the poor stabilization of palladium(0) with the thioether ligands, which lead to precipitation of palladium black. Heterobidentate ligands S,O-donor **2.17d** and S,N-donor **2.17e** lead to more active systems, but in the case of the palladium–**2.17d** system, palladium black also precipitated a great deal perhaps because the S,O-ligand is less able to stabilize Pd(0) species. The catalyst system $Pd(OAc)_2$/**2.17e** produced the best conversion (99%) and chemoselectivity (92%), but there was no optical induction. Other palladium complexes with chiral aminoether proline **2.18** and valine **2.19** derivatives were tested and provided just as good conversions as **2.17e** at the same conditions [24]. Cysteine derivatives **2.20** gave rise to lower conversions and ee.



2.18

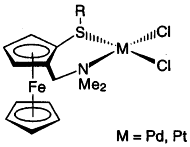


2.19



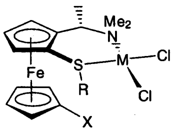
2.20

A number of palladium and platinum complexes of type **2.21** containing heterobidentate ligands and their selenide derivatives, have been synthesized and characterized [25]. Ferrocenylaminothioethers of the Group 10 elements with the structure **2.22** have also been prepared [26]. In the last type (X = SR), the sulfur and nitrogen coordination of the ligands was established by NMR analysis. An X-ray crystal structure (M = Pd; R = Me) confirmed that the metal is coordinated to the S and N atoms of the same cyclopentadienyl ring [27]. Palladium complexes of type **2.21** and **2.22** are active catalysts, at a pressure of 4–8 bar, for the selective hydrogenation of conjugated dienes to monoenes. Results were best with cyclic substrates. 1,3-Cycloctadiene is therefore converted into cyclooctene with excellent activity and selectivity [28]. Other dienes yielded less satisfactory results. Increasing the steric bulkiness on both the amine and the sulfide substituents increased the rate of the reaction while the selectivity was retained. Acetone is the best solvent for the reaction. The solvent is presumably involved in the dissociation of the thioether ligand to create a coordination vacant [29]. So, neither the platinum aminothioether complexes nor the palladium or platinum complexes of the homologous aminoselenide ligands is an active catalysts because the higher energy of the metal–ligand bond prevents the ligand dissociation.



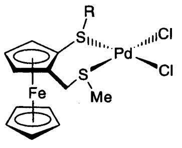
M = Pd, Pt
R = alkyl, aryl

2.21



M = Pd, Pt
X = H, SR

2.22



2.23

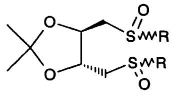
The ferrocenyldithioether palladium complex **2.23** has also been used for the hydrogenation of conjugated dienes. However, the reaction rates were much slower than for the aminothioether catalysts [30].

Other heterobidentate ligands applied in hydrogenation are the thioether phosphine $Ph_2P(CH_2)_nSR$ for $n = 1–3$ and R = Ph, Me and Et [31]. The mononuclear diolefinic complexes $[Rh(nbd)(Ph_2P(CH_2)_nSR)]BF_4$ (nbd = 1,5-norbornadiene) are slightly active in the homogeneous hydrogenation of 1-hexene (6% conversion in 75 min reaction time).

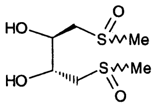
2.2. Sulfoxide ligands

Chiral sulfoxides **2.24** were the first examples of sulfur ligands with the diop backbone used in asymmetric hydrogenation. The **2.24** type ligands are prepared as a mixture of diastereoisomers. Ruthenium(II) complexes with formula $[RuCl_2LL']\cdot 2H_2O$: **2.25** (L = L′ = **2.24a**); **2.26** (L = **2.24a**, L = **2.24c**) and $[RuCl_2(dmso)(H_2O)L]$ **2.27** (L = **2.24c**), have been prepared. IR spectroscopy studies showed that sulfoxide ligands in complexes **2.25** and **2.27** were coordinated through S-atoms, while in complex **2.26** the proposed structure involves a bidentate

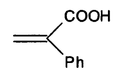
S-bonded ligand **2.24c** and a bidentate ligand **2.24a** coordinated through one sulfur and one oxygen atom. The results from the hydrogenation of itaconic acid (**2.13**) showed that the catalytic activity of these precursors followed the order **2.26** > **2.27** > **2.25**, though the latter is only active in the presence of strong base (1,8-bis-(dimethylamino)naphtalene) [32]. The higher rates with **2.26** were attributed to the greater lability of the O-bonded ligand. The best result for enantioselectivity (25.2% ee in (*R*)-α-methylsuccinic acid) was with **2.26** at 3 bar of H_2 and 55°C. Other substrates, such as atropic acid (**2.28**) and 2-acetamidoacrylic acid (**2.12c**), were also hydrogenated with complex **2.26**, but enantioselectivities were lower. The relevance of the S-bonding to the activity of these catalytic systems is important since some $[Rh(diene)(PPh_3)L]^+$, in which the chiral sulfoxide L was O-bonded, were ineffective and tend to give metal on treatment with H_2. This was said to be because O-bonded sulfoxides are presumably not strong enough π-acceptors to stabilize intermediates [22,33].



2.24a R = Me
2.24b R= Bz

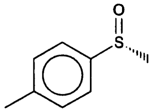


2.24c

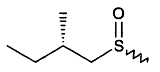


2.28

The asymmetric hydrogenation of 2-acetoamidoacrilic (**2.12c**) and itaconic (**2.13**) acids have been studied with other chiral sulfoxide ruthenium(II) systems [33]. Trimeric complexes $[RuCl_2L_2]_3$, where L = *R*-(+)-methyl-*p*-tolyl sulfoxide (**2.29**) and (*S*,*R*;*S*,*S*)-(+)-2-(methylbutyl)methyl sulfoxide (**2.30**), were prepared by treating $RhCl_3 \cdot 3H_2O$ in methanol with the monodentate sulfoxides under H_2. The optically pure ligand **2.29** was used. However, since the step of formation of the sulfoxide group in **2.30** was nonstereospecific, the ligand was prepared as a mixture of diastereoisomers. The complex with **2.29** clearly showed S-bond evidence, so both trimers were thought to have this type of coordination.



2.29

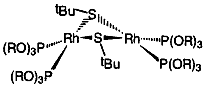


2.30

Enantioselectivity was the highest with the precursor system $[RuCl_2L_2]_3$ (L = **2.30**) in the hydrogenation of itaconic acid (**2.13**) (ee 15% in (*R*)-methylsuccinic acid) at 4 bar and 40°C, in dimethylacetamide as a solvent. Under similar conditions, **2.26** leads to higher optical yields (25.2% (*R*)) than $[RuCl_2L_2]_3$ (L = **2.30**) perhaps because the rigidity of the chelate ligand [33]. The complex $[RuCl_2L_2]_3$ (L = **2.29**), which contains a chiral sulfur center in the ligand, was very active but ruthenium metal formed and there was no stereoselectivity. A kinetic dependence on ruthenium trimer of one third for the hydrogenation of acrylamide suggested complex dissociation of the initial trimer to a monomeric catalyst [33].

2.3. Thiolato ligands

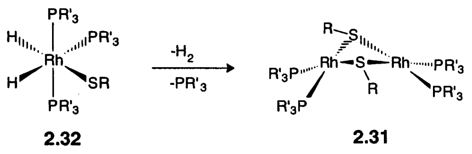
The first example of a thiolato bridged binuclear rhodium complex tested as a catalyst in a hydrogenation process was the inactive compound $[Rh_2(\mu\text{-}SPh)_2(cod)_2]$ [34]. The tetrasubstituted related binuclear complexes of type **2.31**, $[Rh_2(\mu\text{-}S^tBu)_2(P(OR)_3)_2]$ (R = Me (**2.31a**), Ph (**2.31b**), $C_{12}H_{25}$ (**2.31c**)), were very active in the hydrogenation of 1-hexene and cyclohexene [35]. Result were best (100% of 1-hexane in 3 h for a [complex] to [cyclooctane] ratio of 2.8×10^{-4}) with the precursor **2.31a**. Mixed carbonyl–phosphite related complexes $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(PR_3)_2]$ and the series of homo- and heterobridged dimers with the same phosphite ligand $[Rh_2(\mu\text{-}SR)(\mu\text{-}SR')(P(OMe)_3)_4]$ (R = R′ = Ph; R = R′ = Et; R = ^{t}Bu, R′ = Bz) provided moderate yields in the same reaction.



2.31

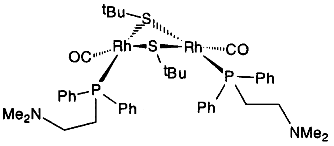
The unstable hydrido thiolato complexes $[Rh(H)_2(SR)(PPh_3)_3]$ (**2.32**) (R = ^{i}Pr, $CH_3(CH_2)_{11}$, Ph), prepared by reacting the corresponding thiol, RSH, with $[RhH(PPh_3)_4]$, are catalysts for the hydrogenation of cyclohexene at room temperature and 1 bar of H_2 [36]. Their catalytic activity is significantly higher than that of the corresponding thiolato bridged complexes $[Rh_2(\mu\text{-}SR)_2(PPh_3)_4]$ into which they are steadily converted during the course of the reaction. The evolution of the alkene conversion during the reaction time using $[RhH(PPh_3)_4]/^iPrSH$ shows an initial phase of high activity after which the rate slows to a much lower value. Comparing these results with the rates for catalyst precursor $[Rh_2(\mu\text{-}S^iPr)_2(PPh_3)_4]/2PPh_3$, it was concluded that monomeric species $[Rh(H)_2(S^iPr)(PPh_3)_3]$ (**2.32**) is responsible for the initial period of high activity and that this evolves during the reaction to the less active binuclear complex $[Rh_2(\mu\text{-}S^iPr)_2(PPh_3)_4]$ (**2.31**) (Scheme 1c) [36]:

Introducing a phosphinoammonium or phosphinoammine ligand to the dinuclear thiolato bridged complexes produced the water-soluble complex $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(Ph_2PCH_2CH_2NMe_3)_2](BPh_4)_2$ (**2.33**) and the analogous neutral $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(Ph_2PCH_2CH_2NMe_2)_2]$ (**2.34**) whose structure was determined by X-ray diffraction methods [37]. In polar solvents (THF and MeOH) and in water, the ionic complex **2.33** was shown to catalyze the hydrogenation of C=C double bonds and nitro groups. The catalyst was recycled without loss of activity. Results were optimal between 70 and 130°C at 25–45 bar of H_2. Allylic alcohol was totally



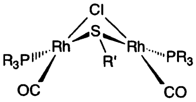
Scheme 1c.

hydrogenated in 2 h at 70°C in water. The rate of hydrogenation of other substrates such as 1-octen-3-ol was higher in THF than in water. Unsaturated carboxylic acids such as maleic (**2.1a**), itaconic (**2.13**) or (acetamino)cinnamic (**2.12a**) were hydrogenated at lower rates than unsaturated alcohols [37]. Styrene or acrolein could not be hydrogenated above 75°C because of the enhanced polymerization at higher temperatures. Nitro groups were reduced smoothly to the corresponding amines. Dinitrobenzene formed selectively phenylenediamine free of any nitroaniline [37]. In THF, complex **2.34** showed similar properties to **2.33** as a catalyst precursor for the hydrogenation of 1-octen-3-ol, but the former was not active in water solutions.



2.34

Related rhodium heterobridged complexes with thiolato/chloro bridge ligands [38] are also active catalysts in the hydrogenation of different unsaturated compounds. Asymmetric hydrogenation of prochiral substrates has been carried out using complexes $[Rh_2(\mu\text{-}Cl)(\mu\text{-}SR')(CO)_2(PR_3)_2]$ (**2.35**) as catalyst precursors. Chiral induction has been obtained by either using a chiral phosphine ligand [39] or by introducing chiral moieties in the bridging SR group [39,40]. In the first case, using the complexes $[Rh_2(\mu\text{-}Cl)(\mu\text{-}SR)(CO)_2(PPh_2R^*)_2]$ (**3.36**) ($PPh_2R^* = (+)$-neomenthyldiphenylphosphine; R = ^{t}Bu (*cis* and *trans* mixture) (**3.36a**), $CH_2CH_2Si(OEt)_3$ (*cis*) (**3.36b**)) at 70 bar of H_2 and 120°C, high ee's (96–97%) were obtained in the hydrogenation of *Z*-methyl α-acetamidocinnamate (**2.12b**) even though the conversions were low (13–15%) [39]. Hydrogenation of other substrates with less steric hindrance than **2.12b**, such as α-acetamidoacrylic acid (**2.12c**) and its methyl ester proceed with better yields (53–100%) but ee in these cases were < 5%. Enantioselectivity was low in these latter cases because the homogeneous catalysts were converted, in part, into metallic rhodium that competes with the residual chiral catalyst to reduce the substrate.

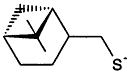


2.35

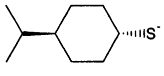
The silicon containing complex **2.36b** was immobilized on silica gel forming a monolayer on the support. The supported catalyst was more active in the hydrogenation of **2.12b** that the homogeneous precursor but enantioselectivity of the former was lower [39].

As far as chiral thiolato bridged complexes concerns, $[Rh_2(\mu\text{-}Cl)(\mu\text{-}SR^*)(CO)_2(P^tBu_3)_2]$ ($SR^* = $ **2.37** and **2.38**) were prepared and applied to the hydrogenation of **2.12b** [40]. At 120°C and 7 bar of hydrogen pressure, the catalyst precursor with the neomenthyl thiolato derivative **2.38** leads to N-acetylphenylalanine methyl ester in 50% ee while precursor with the myrtanyl thiolato **2.37** leads to the racemic product.

Complexes with ligands **2.37** and **2.38** were supported, via phosphine exchange, on various cross-linked diphenylphosphinated polystyrene resins. The immobilization has an opposite effect on the catalytic activity of the two complexes in the asymmetric hydrogenation of **2.12b**. The system with **2.37** induces some ee after immobilization while the supported system with **2.38** loses its chiral induction [40].



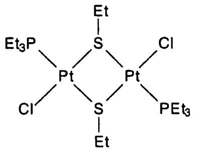
2.37



2.38

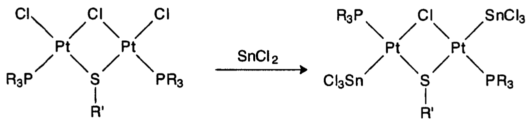
Replacing phosphines with arsines leads to the complex [(+)-*cis*-[$Rh_2(\mu\text{-}Cl)(\mu\text{-}SR^*)(CO)_2(As^tBu_3)_2$] ($R^* =$ **2.38**) [41], which is an active hydrogenation catalyst for unhindered alkenes. Cyclohexene was hydrogenated with this system at similar rate to that of [$RhCl(PPh_3)_3$]. At 120°C and 7 bar of H_2 16% ee was achieved in the asymmetric hydrogenation of substrate **2.12b**. This value was lower than that of the complex with neomenthyldiphenylphosphine **2.36a** [39].

Dinuclear platinum-thiolato homo- [42] and heterobridged [43] complexes are active catalysts in the hydrogenation of styrene in the presence of $SnCl_2$. Dichloromethane solutions of the platinum(II) complex [$Pt_2Cl_2(\mu\text{-}SEt)_2(PEt_3)_2$] (**2.39**) in the presence of five equivalents of $SnCl_2{\cdot}2H_2O$ are active in the hydrogenation of styrene to ehtylbenzene at 60°C and 75 bar of H_2 with a TOF of 94 h^{-1} [42]. This low activity was thought to be due to the stability of the bridging ligand, which does not allow active species to form.



2.39

Mixed chloro-thiolato-bridged binuclear platinum(II) complexes [$Pt_2(\mu\text{-}Cl)(\mu\text{-}SR')Cl_2(PR_3)_2$] ($PR_3 = PEt_3$, P^nPr_3, P^nBu_3, $PPhMe_2$; $R' = Et$, ^iPr) with a *sym-cis* symmetry **2.40a** react with excess $SnCl_2{\cdot}2H_2O$ to give *sym-trans*-[$Pt_2(\mu\text{-}Cl)(\mu\text{-}SR')(SnCl_3)_2(PR_3)_2$] (**2.40b**) (Scheme 1d) [43]. The catalytic activity of [$Pt_2(\mu\text{-}Cl)(\mu\text{-}S^iPr)Cl_2(PR_3)_2$]/$SnCl_2{\cdot}2H_2O$ in the hydrogenation of styrene at 55 bar and 70° is reasonably effective (TOF 1322 h^{-1} for $R = {}^nBu$ and 1221 h^{-1} for $R = {}^iPr$). The highest TOF for [$Pt_2(\mu\text{-}Cl)(\mu\text{-}S^iPr)Cl_2(P^iPr_3)_2$]/$SnCl_2{\cdot}2H_2O$ was at a Sn/Pt ratio of 10. This is far from the ratio of 2 needed to form the corresponding trichlorostannato species. These data suggests that a multicomponent system generates the catalytic cycle [43].



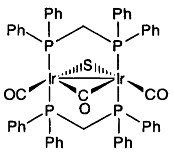
2.40a **2.40b**

Scheme 1d.

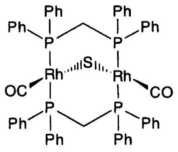
2.4. Sulfido ligands

Catalytic applications of transition-metal complexes with sulfido ligands were extensively reviewed by Rakoski DuBois in 1989 [5]. Some of the examples discussed there and the new examples which have appeared since then are presented here.

The binuclear A-frame complex $[Ir_2(\mu\text{-}S)(CO)_2(dppm)_2]$ (**2.41**) (dppm = 1,2-bis-(diphenyl phosphino)methane) was prepared by reacting $[Ir_2Cl(CO)_4(dppm)_2]^+$ with Na_2S [44]. Complex **2.41** reacts with carbon monoxide to form the A-frame complex $[Ir_2(\mu\text{-}CO)(\mu\text{-}S)(CO)_2(dppm)_2]$ (**2.42**), whose structure was determined by X-ray diffraction methods.



2.42

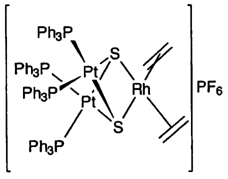


2.43

The oxidative addition of H_2 with complex **2.41** yield a mixture of dihydrido isomers of $[Ir_2(H)_2(\mu\text{-}S)(CO)_2(dpm)_2]$ (**2.44**) [44]. Solutions of the hydrido complex under 0.4 bar of H_2 and equal pressure of acetylene, ethylene or propylene reduce the substrates to the saturated product with TOFs of 1.2, 6.7 and 2.9 h^{-1}, respectively. In all cases, the iridium A-frame complex **2.41** was recovered at the end of the run after heating the solution under nitrogen.

Complex **2.43** did not react with H_2 in solution. However, low catalytic activity was observed in the hydrogenation of ethylene to ethane (TOF = 4–6 day^{-1} at 25°C) [45]. Correlating the catalytic activity of these A-frame complexes with the ability to form carbonyl-bridged species suggests that the catalytic intermediate may also be a carbonyl-bridged complex which is formed by attack of the substrate to the terminal site [19b].

The effectiveness of the heterometallic aggregate complex $[(Ph_3P)_4Pt_2(\mu\text{-}S)_2Rh(C_2H_4)]PF_6$ (**2.45**) to act as a catalyst in the hydrogenation of cyclohexene at 25°C and 1 bar is very low when compared to that of $[RhCl(PPh_3)_3]$ (1:500) [46].

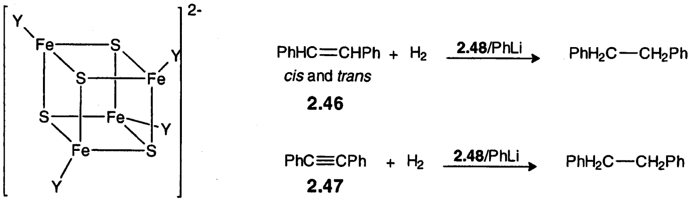


2.45

Clusters derived from the core Fe_4S_4 are model compounds for the active site of the bacterial enzyme hydrogenase [47]. The catalytic activity of **2.48** in the hydrogenation of stilbenes (**2.46**) and diphenylacetylene (**2.47**) (Scheme 1e) has been reported [48]. The catalytic systems were prepared under H_2 from $[Fe_4S_4Y_4](N^nBu_4)_2$ (Y = Cl (**2.48a**) and SPh (**2.48b**)) and addition of PhLi. Results were best with system PhLi–**2.48a**, which contained a labile chloro ligand. The system PhLi–**2.48b** was inactive in the hydrogenation of stilbene. At a molar ratio PhLi/**2.48a** of 12 after 3 h under 1 bar of H_2, the conversion of *cis*-stilbene to 1,2-diphenylethane was 92% with an isomerization to *trans*-stilbene of 8%. The activity in the hydrogenation of *trans*-stilbene was lower (38%). Diphenylacetylene was also hydrogenated with the same system in which the yields of 1,2-diphenylethane and *trans*-stilbene were 77 and 3%, respectively [48].

Related sulfide clusters $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ and $[Mo_2Fe_6S_8(\mu\text{-}SEt)_3(SCH_2\text{-}CH_2OH)_6]^{3-}$ are models for the nitrogenase enzyme. These systems dissolved in MeOH/THF and H_2O are active in the electrochemical reduction of $HOCH_2CH_2N_3$ and CH_3N_3 to ammonia, hydrazine (eight and six electron reduction products) and the corresponding amines and N_2 (two electron reduction products) [49].

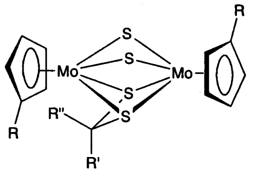
Molybdenum(IV) complexes of composition $[Cp'Mo(\mu\text{-}S)]_2S_2CH_2$ (**2.49a**) and $[Cp'Mo(\mu\text{-}S)(\mu\text{-}SH)]_2$ (**2.50a**) ($Cp' = CH_3C_5H_4$) serve as homogeneous catalysis for the reduction of a series of nitrogen-containing substrates (N=N, C=N and N–O bonds) under 2–3 bars of hydrogen at mild temperatures [50]. Both systems presented similar activities in the reduction of a series of azides RN_3 and azocompounds RN=NR (R = Ph, $EtCO_2$, *p*-NH_2Ph) to the corresponding anilines and hydrazines, respectively. Reduction of nitrobenzenes $ArNO_2$ (Ar = Ph, *p*-BrPh)

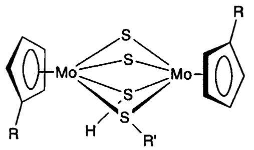


2.48a Y = Cl
2.48b Y = SPh

Scheme 1e.

yielded the anilines but sometimes there were intermediate products, such as hydroxylamine and azoxy derivatives. In the reduction of C=N bonds, methyl and phenyl isocyanate and methylisothiocyanate were hydrogenated slowly in the presence of **2.49a** to produce selectively *N*-methylformamide, formanilide and *N*-methylthioformamide. Mechanistic studies on the reduction of azobenzene pointed out that the activation of hydrogen could take place by forming bridged –SH species [50]. A hydrogen transfer mechanism from these later species to the substrate would yield the reduced product.



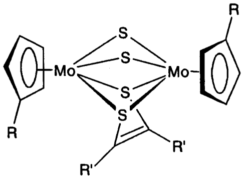


2.49a R = Me; R'= R'' = H
2.49b R = H; R'= CO_2Na; R'' = H
2.49c R = H; R' = R'' = Me

2.50a R= Me; R'= H
2.50b R= H; R'= CH_2CO_2Na

By introduction of a polar group in the sulfur ligand, water-soluble complexes were obtained. The sodium carboxylato derivatives **2.49b** and **2.50b** [51] were prepared and their catalytic activity in hydrogenation of C=N and N = N bonds in two phase systems has been studied. In the catalytic reduction of azobenzene (PhN=NPh) in water/CH_2Cl_2 under 1–2 bar of hydrogen conversions to diphenylhydrazine (PhNHNHPh) using **2.49b** were 15–80%. Reduction of methyl thiocyanate to the thioamide CH_3NHCHS and nitrobenzene to aniline were also performed with this system.

Complex **2.49a** (R = H) and the methylene derivative **2.49c** react with unsaturated substrates such as alkenes, alkynes and cumulenes to form the corresponding unsaturated dithiolate adducts e.g. in the reaction with alkynes the product **2.49d** is formed [52]. These unsaturated species can be hydrogenated under mild conditions to obtain the corresponding saturated substrates and recover the compound **2.49a** or **2.49c**. The reaction does not proceed in a continuous catalytic cycle, apparently because an excess of substrate inhibits hydrogenation.

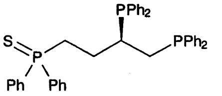


2.49d

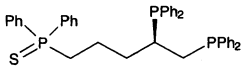
2.5. Phosphine sulfide ligands

Rhodium(I) and iridium(I) diolefinic complexes with phosphine sulfide ligands are catalyst precursors in the homogeneous hydrogenation of olefins [53,54]. Ethanolic solutions of $[Rh(diolefin)(SPPh_3)_2]ClO_4$ (diolefin = cod, nbd) and dichloromethane solutions of [Ir(cod)$(SPPh_3)_2$]ClO_4 behave as moderately active catalyst precursors in the hydrogenation of 1-heptene [53a]. Iridium compounds show higher activities than the corresponding Rh(I) complexes. The complex [Ir(cod)$(SPMe_3)_2$]ClO_4, in dichloromethane at 25°C under 1 bar of hydrogen, was not catalytically active for the hydrogenation of 1-heptene, but in the presence of an excess of $SPMe_3$ ($SPMe_3/Ir = 5/1$), 64% of 1-heptene was converted, and 51% of 1-heptane was obtained in 12 h [53b].

The chiral diphosphino-phosphinosulphide ligands **2.51** and **2.52** have been studied in the hydrogenation of (*Z*)-α-acetamidocinnamic acid (**2.12a**) and itaconic acid (**2.13**) at 30–40°C and 1.1 bar of hydrogen pressure using the in situ catalyst precursor $[Rh_2(\mu\text{-}Cl)_2(cod)_2]/L$ (L = **2.51** and **2.52**) [54]. For the reaction of (*Z*)-α-acetamidocinnamic acid results were best with the system with ligand **2.52** (total conversion in 2 days and 74% (*S*) ee). The enantioselectivity with these diphosphine-phosphinosulfide systems was higher than when analogous triphosphines were used. The ee values observed in the hydrogenation of itaconic acid were 17–23% (*R*).



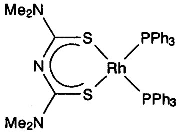
2.51



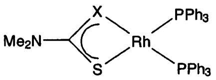
2.52

2.6. Miscellaneous ligands

A series of rhodium(I) complexes [Rh(L–L)$(PPh_3)_2$] (**2.53**–**2.55**) with unsaturated S-donor ligands have been reported [55]. Only complex **2.55** reacts with H_2 to form the *cis*-dihydrido species $[Rh(H)_2(PhNC(S)NMe_2)(PPh_3)_2]$. This dihydrido complex shows an activity in the hydrogenation of cyclohexene (TOF = 8.5×10^{-2} s^{-1}) of about 16% of the activity of $[RhCl(PPh_3)_3]$ in the same conditions.

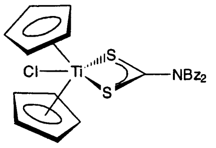


2.53



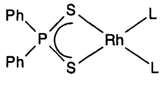
2.54 X= S
2.55 X= NPh

Dithiocarbamates coordinated to rhodium [56] and titanium [57] have also been studied as catalyst precursors in the hydrogenation of olefins. The diene complex $[Rh(S_2CNEt_2)(cod)]$, in which the dithiocarbamate acts as a chelate ligand according to the IR data, did not react with H_2 and is inactive in the hydrogenation of alkenes [56] The titanocene derivative $[TiCp_2(S_2CNBz_2)Cl]$ (**2.56**) with bent metallocene geometry, in the presence of NaH, catalyses the hydrogenation of 1-hexene at 1 bar with a TOF of 1939 s^{-1}, but the activity decays quickly [57]. These values are near to those with system $[TiCp_2Cl_2]$–NaH [58].



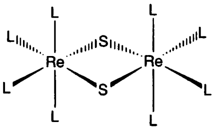
2.56

The rhodium dithiophosphinato derivatives [Rh(S_2PPh_2)L_2] (L_2 = cod (**2.57**); L = CO, PPh_3 (**2.58**)) are not active as catalyst precursors in the hydrogenation of 1-hexene, cod and phenylacetylene at room temperature under 1 bar of H_2 in THF [59]. However, there was some hydrogenation at more severe temperature and pressure (120°C, 20 bar). Part of the complexes decomposed to metallic rhodium under reaction conditions.



2.57 L_2 = COD
2.58 L = CO; L= PPh_3

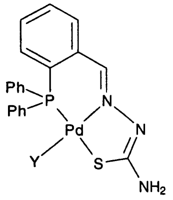
A series of soluble rhenium(V) oxohalide complexes with thiourea type ligands [$ReOX_3L_2$] (where X = Cl, Br; L = thiourea, 2-mercaptobenzothiozole, 2-mercaptobenzoimidazole, 1-methyl-2-mercaptoimidazole) selectively catalyzed the hydrogenation of nitrobenzene and p-nitrotoluene to the corresponding anilines [60]. These homogeneous systems gave results similar to the heterogeneous Re_2S_7 in the hydrogenation of the nitroaromatic substrates. A solid was isolated from the catalytic solution. It was characterized as a mixture of complexes in which the binuclear cluster **2.59** predominates.



L= thiourea, Cl, H_2O

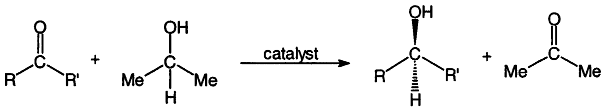
2.59

Palladium(II) complexes **2.60** containing hydrazonic hemilabile ligands with a PNS donor units and analogous PNO ligands have been prepared to compare their catalytic properties [61]. In methanol at 25°C and 1 bar of hydrogen, **2.60** is inactive, while the PNO derivatives are active in the hydrogenation of styrene and phenylacetylene. This was thought to be because the Pd–S bond was stronger than Pd–O and did not allow the formation of a free coordination site.



Y = AcO, Cl, I

2.60



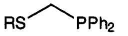
Scheme 2.

3. Hydrogen transfer

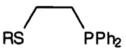
Alcohols, acids, cyclic ethers and other molecules that are fairly readily dehydrogenated can be used as hydrogen sources, instead of H_2, in hydrogenation processes. When the reaction with molecular hydrogen requires high pressures, hydrogen transfer reactions have often the advantage that they take place at ambient pressure. Different substrates can be hydrogenated with appropriate catalysts and hydrogen donors [62]. Considerable effort has been devoted to the study of the asymmetric version of these processes [63], the most widely studied of which is perhaps the asymmetric hydrogenation of ketones with alcohols, normally ^{i}PrOH, as the source of hydrogen (Scheme 2).

In all reported cases of catalysts containing S-donor ligands used in this reaction other heteroatoms are also involved in the coordination of the metal. Some of these reactions are described below.

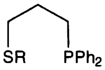
Rhodium complexes [Rh(nbd)L]BF_4, where L are the phosphine-thioether ligands type **3.1**–**3.3**, catalyze the H-transfer from isopropanol to different ketones. The reaction takes place in the presence of an excess of base (KOH). Conversions were best with ligands **3.2** and **3.3** (R = Ph) when acetophenone and cyclohexanone were used as substrates [31].



3.1

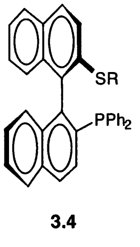


3.2



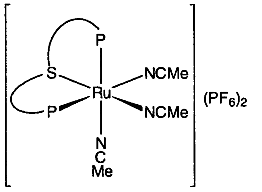
3.3

Rhodium(I) complexes of the atropoisomeric ligands type **3.4** (R = Me, ^{i}Pr) have been prepared in situ by reacting the ligands with $[Rh_2(\mu\text{-}OMe)_2(cod)_2]$ in the presence of KOH. The complexes were used in the asymmetric reduction of ketones with ^{i}PrOH. The catalytic system is quite active for the first 30 min (100 turnovers), and yielded 20% ee in the asymmetric alcohol. However, the reaction rate decreases, as well as the overall ee, as the reaction proceeds [64].

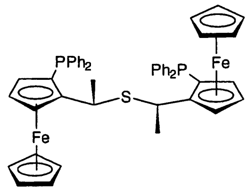


3.4

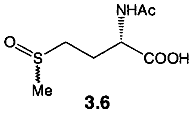
Although the reaction rate is lower than that of related Ru-triphosphine complexes, the cationic complex **3.5** is moderately active in the H-transfer from isopropanol to acetophenone, and yields a 20% ee in 1-phenyethanol [65].



3.5



The H-transfer from isopropanol to ketones has been reported using a catalytic system prepared in situ by reacting different Rh(I)-diene complexes, KOH and the ligand *N*-acetyl-(*S*)-methionine (*R*,*S*)-sulfoxide (**3.6**). Results were best with $[Rh_2(\mu\text{-}Cl)_2(hd)_2]$ (hd = 1,5-hexadiene). The catalytically active complex could not be isolated, although S-bonded sulfoxide and carboxylate are almost certainly the groups coordinated to the metal. Since the sulfoxide center is racemic, the ligand is a mixture of two diastereoisomers. However, enantiomeric excesses were higher than 70% for some substrates, although conversions were relatively low [66].



3.6

4. Isomerization

Isomerization is often a side process in hydrogenation, polymerization, hydroformylation and other reactions catalyzed by metals. We describe here only those reactions in which isomerization is the main process.

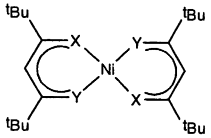
Early work was carried out with $[MX_2(SPh_2)_2]/SnCl_2$ (M = Pd or Pt; X = halide). The bimetallic system is an active catalyst in the isomerization of alkenes. These catalysts hydrogenate polyolefins to monoenes, which, in turn, are only isomerized but not hydrogenated [12]. The same behavior was reported for palladium complexes of ferrocenyl aminothioethers **2.21**–**2.23**. Thus, with the last catalytic systems, 2,3-dimethyl-1,3-butadiene was converted to 2,3-dimethyl-2-butene. In the process, the diene was hydrogenated to the 1-alkene, which was finally isomerized to the internal olefin [27,67].

Binuclear rhodium complexes $[Rh_2(\mu\text{-}Cl)(\mu\text{-}SR')(CO)_2(PR_3)_2]$ **2.35**, and their related arsine derivatives, catalyze the isomerization of olefins, epoxides to ketones, and unsaturated alcohols to ketones. Complete conversions were reached in some cases [68].

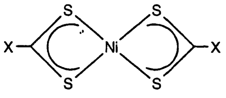
The complex [$PdCl_2(dmso)_2$] under low pressure H_2 (< 1 bar) in dmso catalyzes the isomerization of 1-pentene faster than its hydrogenation. In 15–20 min, the 1-alkene was converted to a 1:1:2.2 mixture of pentane and *cis*- and *trans*-pentene [69]. The palladium complex, as well as the rhodium complex [$RhCl_3(dmso)_3$], can also be activated with $NaBH_4$ instead of H_2, to render an active species, which isomerizes different alkenes. However, the substrates are also partially hydrogenated [70].

Cobalt and nickel complexes [$M(SCN)_2(PR_3)_2$] (M = Co, Ni), promoted by $NaBH_4$, are active catalysts in the isomerization of 1-butene to 2-butene. The reaction conveniently proceeds at a $[H^-]/[M] \leq 2$ and with a slight excess of the phosphine ligand. The cobalt catalyst (R = Ph) is more active than the nickel one. Interestingly, in both cases, the rates achieved by the thiocyanato catalysts are higher than the ones of the corresponding halides [$MX_2(PR_3)_2$] (X = Cl, Br, I), although the former gave a poorer [*cis*-2-butene]/[*trans*-2-butene] selectivity than the halide complexes. Since the selectivity depends on the anionic ligand, complexes of the type [$MHX(PR_3)_2$] (X = SCN, Cl, Br, I) have been proposed to be the active species in these reaction conditions [71].

Nickel complexes of the type **4.1** (X = S, Y = O), in the presence of Et_2AlCl, are very active catalysts for the isomerization of 1-alkenes. In the same conditions, the diketonate complex (X = Y = O) is active in the isomerization and oligomerization of olefins, while the dithiodiketonate complex (X = Y = S) is completely inactive with respect to both oligomerization and isomerization. Also, nickel complexes **4.2** and **4.3** plus Et_2AlCl are active in the isomerization of 1-hexene to a mixture of 2- and 3-hexene [72].

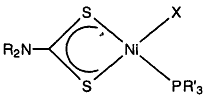


4.1



X= OR, NR_2

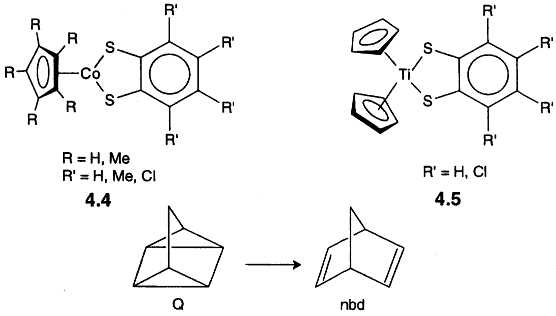
4.2



4.3

Some cobalt complexes **4.4** with dithiolato and cyclopentadienyl ligands are active catalysts in the isomerization of quadricyclane (Q) to norbornadiene (nbd) (Scheme 3). This system has been investigated in the context of solar energy storage and conversion into chemical energy.

Turnover is highest with R′ = Cl and R = H. The reaction may involve a partial bond formation between Q and the metal, initiated by an electron transfer. The catalytic reaction is hampered by the formation of non-reactive adducts, with S–C and Co–C bonds. One of these adducts has been characterized. The titanium complexes **4.5** are inactive [73].



R = H, Me
R' = H, Me, Cl
4.4

R' = H, Cl
4.5

Scheme 3.

5. Hydrosilylation

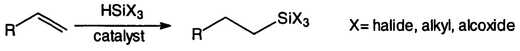
Since the discovery of the catalytic activity of $H_2[PtCl_6]$ in the addition of silicon hydrides to olefins, many platinum group metal complexes have been assayed as catalysts for the hydrosilylation of unsaturated substrates, such as alkenes, alkynes, ketones and imines. Sulfur ligands form a broad family of complexes with these metals, and therefore they have been widely investigated in this context. Beside these second and third series transition metal complexes, some nickel species, which contain sulfur ligands, have also been shown to catalyze this reaction.

5.1. Thiolato and thioether ligands

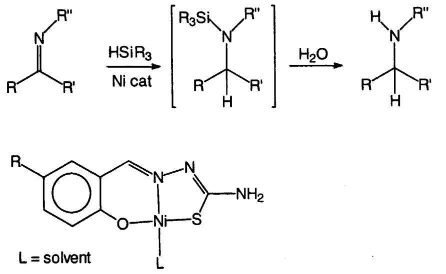
Simple thioether platinum complexes, *cis*- and *trans*-$[PtX_2(SR_2)_2]$ (X = Cl, Br; R = alkyl), are active catalysts, at moderate temperature, for the addition of $HSiCl_2Me$ to 1-alkenes, to yield the linear silyl derivative (Scheme 4a).

The rate of the reaction is only slightly dependent on the substituents of the thioether ligands and the stereochemistry of the complexes, but the chloro derivatives are significantly more active than the bromo ones [74]. Similarly, the rhodium thioether complex $[RhCl_3(EtSCH_2SiMe_3)_3]$ efficiently catalyzes the addition of $HSi(OR)_2Me$ to 1-alkenes [75].

More sophisticated thioether ligands have also been used as auxiliary ligands. For instance, platinum(II) complexes $[PtCl_2L]$, where L = calix[4]-1,3-dithioether **5.1** [76], or calix[4]dithiacrowns **5.2** [77,78], have proved to be active catalysts for the homogeneous hydrosilylation of 1-alkenes with $HSi(OEt)_3$. Most of the alkenes yielded the linear silyl derivatives as the major reaction products, but styrene produced predominantly the branched isomer. The platinum catalysts were characterized by elemental analysis and MS-FAB. The mercury test [79] corroborated that the active components were homogenous in nature.

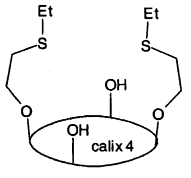


Scheme 4a.

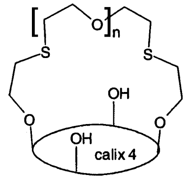


5.3

Scheme 4b.



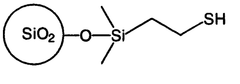
5.1



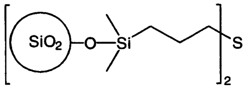
5.2 (n=1, 2)

Nickel complexes of aromatic thiosemicarbazones derived from salicylaldehyde **5.3** are active catalysts in the hydrosilylation of imines with $HSiEt_3$ (Scheme 4b). The silyl derivatives obtained can be hydrolized to render amines in excellent yields [80].

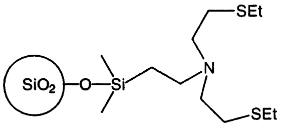
A considerable number of reports have appeared in the last years dealing with the hydrosilylation of olefins and acetylene catalyzed by immobilized platinum group metal complexes which contain S-donor ligands. These ligands include simple thiols and thioethers, as well as heteropolydentate ligands. Some examples are **5.4**–**5.8**:



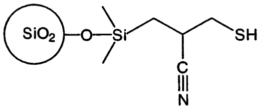
5.4



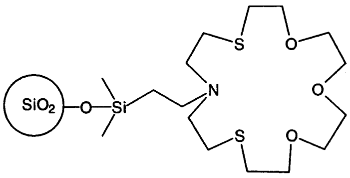
5.5



5.6



5.7



5.8

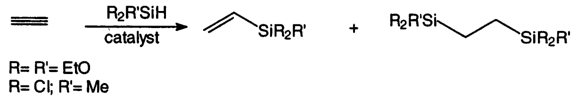
The reaction which has been studied most is the addition of $HSi(OEt)_3$ to 1-alkenes to yield the linear silyl derivative. Of the catalysts reported, the one with the simplest structure is the supported metal complex prepared by reacting metal chlorides with the thiol anchored to silica **5.4**. Thus, $H_2[PtCl_6]\cdot 6H_2O$, $PdCl_2\cdot 2H_2O$ or $RhCl_3\cdot 3H_2O$ reacted with **5.4** in ethanol at different ligand to metal ratios. The best results were obtained with the platinum complex at $S/Pt = 4$. In this case, an XPS analysis was carried out to characterize the supported complex. Results were not conclusive, although the shift in the Pt(4f) binding energy was significant with respect to $H_2[PtCl_6]\cdot 6H_2O$. This could be associated to a reduction of the metal upon coordination. A sample of this catalyst was reused 20 times (total TON 10 000) in the hydrosilylation of 1-hexene with $HSi(OEt)_3$, with no appreciable loss in the catalytic activity [81]. The same type of platinum supported complexes catalyze the selective hydrosilylation of 1,5-hexadiene with $HSiMeCl_2$, with no significant isomerization of the double bond, in contrast with $H_2[PtCl_6]$ homogenous catalyst, which renders more than 30% of internal alkenes [82].

The complexes formed by reacting $K_2[PtCl_4]$ with silica-supported heteropolydentate ligands **5.6** [83], **5.7** [84], and **5.8** [85], were also assayed as catalysts for the hydrosilylation of 1-alkenes. The results are similar to those of **5.4**. XPS analysis did not determine conclusively whether the N or O atoms were involved in the metal coordination.

Hydrosilylation of olefins with dichloromethylsilane has also been studied with the immobilized platinum complex of the simple dithioether **5.5** (atomic ratio $S/Pt = 2$). The reaction takes place at 60–70°C in a few minutes with complete regioselectivity in the case of simple 1-alkenes, although the results were less satisfactory with functionalized olefins. TONs were in the range 1000–2000 [86].

The hydrosilylation of acetylene catalyzed by silica-anchored platinum complexes yields the vinylsilyl derivative, which can further react to produce the 1,2-disilylethane product (Scheme 4c). The composition of the final mixture depends on the catalyst and reaction conditions used.

At 80°C, the reaction of $HSi(OEt)_3$ with acetylene, catalyzed by the platinum complex of ligand **5.4**, is fast, but it renders a 1:1 mixture of the two products. Lower temperatures slightly increase the yield of the vinylic product, although there is a significant decrease in the activity [81]. Results were similar in the reaction of $HSiMeCl_2$ with acetylene, catalyzed by a complex which was formed by reacting $H_2[PtCl_6]\cdot 6H_2O$ with thioether **5.5** ($S/Pt = 2$). In this complex, the XPS binding energies for Pt(4f) and S(2p) are similar to the ones reported for the thiol complex **5.4**. The supported catalyst can also be reused up to eight times with no appreciable decrease in the catalytic activity [87].



Scheme 4c.

In addition to the silica bound platinum complexes described above, other strategies have been used to immobilize hydrosilylation catalysts. Insoluble cross-linked polystyrene, functionalized with aryl-CH_2SH groups, has been used as support for a platinum complex. This immobilized species is active in the hydrosilylation of different substrates [88]. The platinum complexes of silicone polymeric materials which contain thiol and amine functionalities have also been successfully assayed in the hydrosilylation of glycidyl ether with $HSi(OMe)_3$. These systems can be reused with no significant metal leaching [89].

5.2. Sulfoxide and other ligands

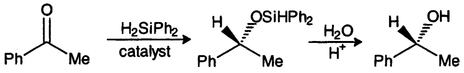
Platinum(II)-sulfoxide complexes have been investigated as catalysts for the reaction of $HSiCl_2Me$ with 1-alkenes. *Cis*- and *trans*-$[PtX_2(R_2SO)_2]$ ($X = Cl, Br$; $R =$ alkyl), at 55°C, are active catalysts for this reaction. The reaction rate depends on the halide ($Cl = Br$) and the substituents on the sulfoxide ligands ($Me \approx Et < Pr < {}^iPr$). Similar rates were observed for *cis* and *trans* complexes, probably because of the rapid *trans*/*cis* isomerization of these species [74]. *Cis*- and *trans*-$[PtX_2(R_2SO)L]$ ($X = Cl, Br$; $R =$ alkyl; $L =$ pyridine, picoline and 2,6-lutidine) have also been studied as catalysts for this reaction. These species are again active at moderate temperatures, but their reaction rate is somewhat lower than that of the one of the bis(sulfoxide) complexes. The rate of reactions catalyzed by mixed sulfoxide–pyridine complexes, unlike bis(sulfoxide) complexes, does not depend on the nature of the halide ligand. Furthermore, the *cis* isomer was considerably more active than the *trans* isomer. This result is consistent with the stability of both isomeric forms in the organic media of the reaction [90].

Nickel complexes, generated in situ by reacting $NiCl_2$ with tetraalkyldiphosphine disulfide ligands $R_2P(S)P(S)R_2$ (1:1 molar ratio), are moderately active catalysts for the addition of dichloromethylsilane to 1-alkenes [91].

5.3. Asymmetric hydrosilylation of ketones

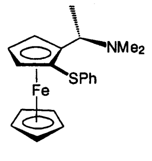
Asymmetric hydrosilylation has been an active field of research in the last 20 years [92]. The most studied reaction has probably been the hydrosilylation of acetophenone to yield the corresponding silyl ether, which when hydrolized gives the enantiomerically enriched 1-phenylethanol (Scheme 4d). Diphenylsilane is commonly used as the reagent for this reaction.

A number of rhodium complexes prepared by reacting the chiral thioether ligands **2.10** ($R = Ph$) and **5.9**–**5.11**, and the disulfide-sulfoxide ligand **5.12** with $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$ or $[Rh(cod)_2]BF_4$ have been investigated as catalysts for the

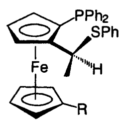


Scheme 4d.

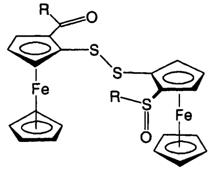
hydrosilylation of acetophenone with H_2SiPh_2. The structure of the complexes was not investigated. They all show moderate to good activity. The best ee (31%) was with **5.10**. Ligands **5.9, 5.11** and **5.12** yielded meaningless enantiomeric discrimination [93].



5.9

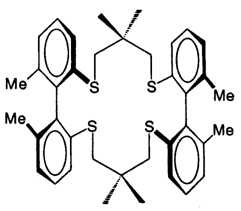


5.10 R = H
5.11 R = Ph

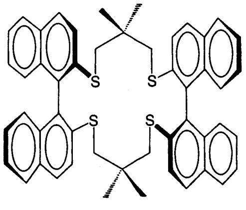


R= *p*-tolyl
5.12

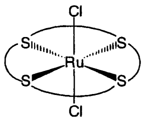
Chiral thioether macrocyclic ligands, containing atropoisomeric biphenyl and binaphthyl fragments, have been synthesized and tested as auxiliary ligands for this metal catalyzed reaction:



5.13



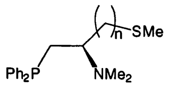
5.14



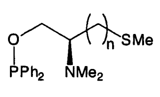
5.15

By reacting $[Rh_2(\mu\text{-}Cl)_2(C_8H_{14})_4]$ with ligand **5.13** (1:2 molar ratio) a catalytic system was generated, which, after hydrolysis, rendered a 35% yield of 1-phenylethanol from 10 mmols of acetophenone in 20 h. The enantiomeric excess was 57% [94]. In the same reaction conditions, ligand **5.14** yielded 68% of (*S*)-1-phenylethanol [95]. On reaction of $K_2[RuCl_5(H_2O)]$ with ligand **5.13**, the Ru(II) complex **5.15** was synthesized, and characterized by X-ray diffraction. When applied to the hydrosilylation of acetophenone, the system yielded 1-phenylethanol with 57% ee [96].

The catalytic systems formed by reacting $[M_2(\mu\text{-}Cl)_2(\text{diene})_2]$ (M = Rh, Ir; diene = cod or nbd) and ligand **5.16** ($n = 1$) achieved 63% ee in 1-phenylethanol. Ligands with a longer thioether arm yielded much lower enantiomeric discrimination. Since the sulfur coordination is favored in the latter cases, it seems that this coordination has a negative effect on the selectivity. The iridium complex (M = Ir, diene = cod) of ligand **5.16** ($n = 1$) yields lower ee (32%) than the rhodium complex. Interestingly, opposite configurations of the secondary alcohol were obtained with the rhodium and iridium complexes of the same ligand. The hydrosilylation of benzylacetone and α-tetralone catalyzed by the rhodium complex of ligand **5.16** ($n = 1$) yielded ee in the range 50–60% [97].



5.16 n = 1, 2

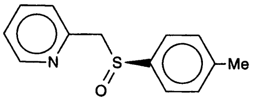


5.17 n = 1, 2

Rhodium complexes prepared in situ from chiral pyridinethiazolidine ligands **5.18** and $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$ yield one of best selectivities for this process (ee = 80%) [98]. These thiazolidines are prepared by reacting cysteine or its esters with pyridine functionalized at the 2-position. During the synthesis a new chiral center is generated at the C2 carbon (Scheme 4e).

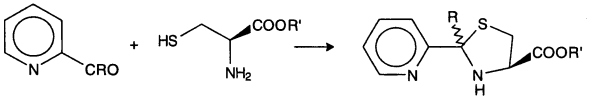
The structure of the rhodium complexes of these ligands has yet to be explored, although the ligand is assumed to coordinate through the two nitrogen atoms. The fact that related Rh-oxazoline catalysts yield only slightly lower selectivity than pyridinethiazolidines supports this hypothesis [99]. However, it is interesting to notice that the enantiomeric excess was nearly the same with a 1:1 diastereoisomeric mixture of type **5.18** ligands than with optically pure species. In the presence of the metal, the racemization at the C2 carbon takes place in a few minutes, so, a mixture of diastereoisomers catalyzes the reaction, even when the optically pure ligands are used [100]. Probably, the racemization of the ligands involves the opening of the thiazolidine ring. The role of the sulfur atom in the last process and in the catalytic reaction has not been investigated.

The rhodium complex of the chiral pyridine-sulfoxide ligand **5.19** has also been investigated as a catalyst for this reaction.



5.19

In complexes with ligand **5.19**, the coordination mode of the sulfoxide fragment depends on the ancillary ligands which complete the coordination sphere of the metal. Thus, whereas in $[RhL(CO)(PPh_3)]PF_6$ (L = **5.19**), the ligand acts as a N,O chelate, in $[RhL(cod)]PF_6$ and $[RhL(cod)(PPh_3)]PF_6$ the ligand coordinates through the N and S atoms. Only the two complexes containing PPh_3 are active catalysts for the hydrosilylation of acetophenone, but the enantiomeric excess was 0 in both cases [101].



5.18

Scheme 4e.

$$CH_3OH + CO \xrightarrow{\text{catalyst}} CH_3COOH$$

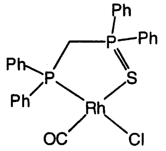
Scheme 5a.

6. Carbonylation

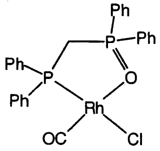
The carbonylation of methanol is a process of great industrial importance (Scheme 5a). Currently, about 60% of the estimated acetic acid production is based on this technology, which uses the so-called Monsanto catalyst [102]. This is a mixture of $[RhI_2(CO)_2]^-$ and MeI, which operates in industry at temperatures of about 180°C and pressures of nearly 30 bar. A recent development for this reaction is the new BP process based on an iridium/iodide catalyst [103].

Early work in the carbonylation of methanol with rhodium catalysts was carried out with systems formed by reacting C_6Cl_5SH or C_6F_5SH with $[RhCl(PPh_3)_3]$ in a homogeneous phase [104] or incorporating the arylthiol into a cross-linked polystyrene matrix [105]. In both cases, the catalysts were less efficient than the Rh–MeI system. Furthermore, the anchored catalyst suffered severe metal leaching during the reaction. Related to this work, a recent patent revealed that a mixture of $HS(CH_2)_3Si(OMe)_3$, $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ and $NaBPh_4$ can be used as catalyst for this reaction [106].

In 1995, two new efficient catalytic systems were published for carbonylation of methanol, both of which were based on rhodium complexes containing S-donor ligands. Hence, rhodium complexes of type **6.1** catalyzed this reaction, with a rate eight times higher than that of the classical Monsanto catalyst, under industrially feasible conditions. The reaction takes place with MeI as co-catalyst, 70 bar of CO and 185°C [107]. Interestingly, the homologous phosphine oxide complex **6.2** is active even at low pressures (4 bar of CO), although the absolute rates achieved are not appropriate for industrial application [108].

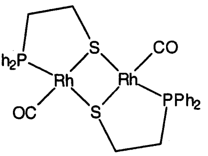


6.1

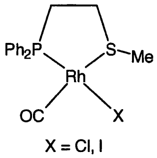


6.2

The second catalytic systems recently reported consist on rhodium complexes with phosphine-thiolato **6.3** and phosphine-thioether **6.4** ligands plus MeI as co-catalyst. Typical reaction conditions for these systems are 185°C and 70 bar. In these conditions, they are almost four times more active in the carbonylation of methanol than the currently used industrial rhodium catalyst [109].

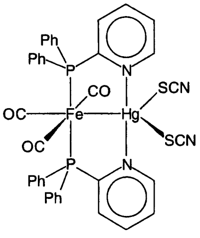


6.3



6.4

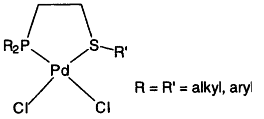
The heteronuclear complex [$(CO)_3Fe(\mu\text{-}Ph_2Ppy)_2Hg(SCN)_2$] (**6.5**) has been structurally characterized by X-ray diffraction. At 35 bar and 220°C, this, and other related [$(CO)_3Fe(\mu\text{-}Ph_2Ppy)_2ML_n$] complexes, are active catalysts in the presence of EtI for the carbonylation of ethanol to ethyl propionate. The selectivity of the reaction strongly depends on the ML_n fragment. The complex **6.5** yielded 27% selectivity in the ester [110].



6.5

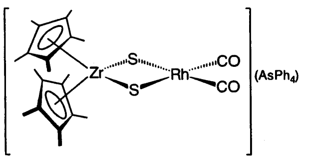
A catalytic system for the synthesis of C4 products from MeOH has been disclosed. The active species is believed to be a cobalt carbonyl or carbonyl hydride with the ligand $Et_2P(S)P(S)Et_2$, and requires the use of I_2 as promoter. The catalyst is prepared by reacting $Co(acac)_3$ with iodine and the diphosphine disulfide ligand under *syn*-gas. Thus, by reacting methanol under CO and H_2 pressure, at 200°C and in the presence of the catalyst, a mixture of *n*-butanol and *n*-butanal was obtained with 27% selectivity [111].

Palladium thioether-phosphine complexes **6.6** have been used in the photochemical carbonylation of benzene to yield benzaldehyde at room temperature and 1 bar of CO pressure. A 70 W mercury lamp was used ($\lambda = 320$ nm). The activity of the catalysts depends significantly on the substituents on the S and P atoms. Results were best for the ligand $R = R' = Et$, which reaches a TON of 350. A mechanism involving a labile coordination of the sulfur is proposed for the reaction [112].

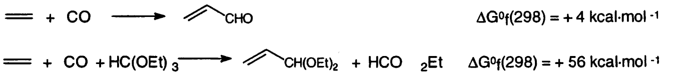


6.6

The carbonylation of ethene to acrolein is catalyzed by the heterobimetallic complex $(AsPh_4)[(Cp^*)_2Zr(\mu\text{-}S)_2Rh(CO)_2]$ (**6.7**), at 20 bar of CO/C_2H_4 and 140°C, and in the presence of 5-fold excess of PPh_3. The reaction requires the presence of stoichiometric $HC(OEt)_3$ to form the diethyl acetal (**6.8**) (Scheme 5b), since this step is the driving force of the reaction The TON was only 2 after 16 h reaction [113].



6.7



6.8

Scheme 5b.

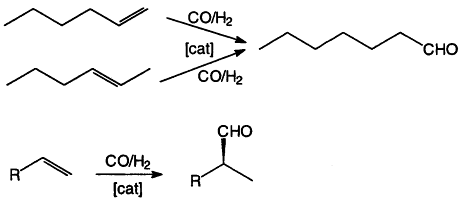
7. Hydroformylation

Hydroformylation is one of the most studied reactions in homogeneous catalysis. In recent years several reviews have discussed this process [114] which is used for the large-scale preparation of butanol, 2-ethylhexanol and detergent alcohols [115].

The regioselective formation of linear aldehydes from 1-alkenes or internal alkenes and the regio- and enantioselective synthesis of the optically pure branched aldehydes, in the case of functionalized olefins, are important challenges for this reaction (Scheme 6a).

Several metal complexes catalyze this reaction. However Rh, Co and to a lesser extent Pt/Sn are the metals that have most been investigated. Various phosphorus ligands, such as phosphines, phosphites, chiral diphosphines and diphosphites, diphosphinites and phoshine-phosphite, have been used with these and other metals to improve the performance of the catalysts [116].

The mechanism for the [RhH(CO)(PPh$_3$)$_2$] catalyst is nowadays quite well established, and some of the catalytic intermediates have been characterized [117]. Recent investigations on different diphosphanes have demonstrated that the selectivity can be controlled by appropriate modifications on these ligands [118].



Scheme 6a.

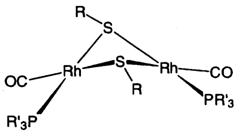
7.1. Cobalt catalysts

An early study reported the use of Co catalysts modified with thioether ligands in the hydroformylation of alkenes. A considerable excess of Me_2S was reacted with $[Co_2(CO)_8]$ and $[Co_4(CO)_{12}]$ and the resulting compound $[Co_4(CO)_{11}(SMe_2)]$ was characterized by infrared spectra. The formation of $[Co_4(CO)_{11}(SMe_2)]$ is probably due to the partial decomposition of the primary product $[Co_2(CO)_7(SMe_2)]$. The effect of SBu_2 on this system is small, and mainly reduces the rate of the hydroformylation reaction with respect to the non-modified catalyst; an increase in the CO pressure can compensate this retarding effect of the thioether [119].

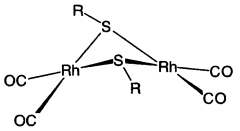
7.2. Binuclear rhodium thiolato bridged complexes

In 1983 binuclear rhodium thiolato bridge complexes $[Rh_2(\mu\text{-SR})_2(CO)_2(PR'_3)_2]$ (**7.1**) were discovered to be effective catalysts in the hydroformylation of olefins at low pressures and temperatures [120]. One of the advantages of these systems is that they can be chemically modified both at the thiolato bridge and at the phosphorous ligand. The use of binuclear bridged thiolato rhodium complexes **7.1** as catalyst precursors in the hydroformylation of olefins has been studied by Kalck et al. during the last decade. The effect of solvent and the nature of the thiolato bridge and phosphorous ligand have been investigated. The complex $[Rh_2(\mu\text{-S}^t\text{Bu})_2(CO)_2(P(OMe)_3)_2]$ is highly active at low pressure in the 1-hexene hydroformylation. For instance, at 5 bar pressure ($H_2/CO = 1/1$) and 80°C, the TOF is 32 min^{-1}. A phosphorous ligand is required to obtain catalytic activity since the corresponding carbonyl complexes $[Rh_2(\mu\text{-SR})_2(CO)_4]$ (**7.2**) are inactive in these conditions [121].

For the precursor complexes $[Rh_2(\mu\text{-}^t\text{BuS})_2(CO)_2(PPh_3)_2]$ conversion rates were initially low. This was attributed to the formation of the carbonyl complex **7.2**, which was detected at the end of the reaction. In this case, the phosphorus to rhodium molar ratio has considerable influence on the rate of the reaction. For instance, when the P/Rh molar ratio was 6, activity was reasonably good (TOF = 23 min^{-1}) and selectivity towards linear aldehyde was 76% [121].



7.1



7.2

Kinetic studies have shown that the reaction was inhibited by both CO pressure and high H_2/CO ratios [122]. The addition of the ^{t}BuSH to $[RhH(CO)(PPh_3)_3]$, either under nitrogen or under CO/H_2 pressure, generates the binuclear species $[Rh_2(\mu\text{-S}^t\text{Bu})_2(CO)_2(PPh_3)_2]$ [123].

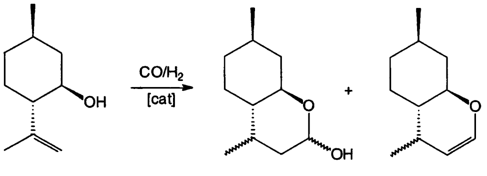
A catalytic cycle, based on spectroscopic evidence and theoretical calculations, in which the binuclear framework is retained for all steps has been proposed for

$[Rh_2(\mu\text{-}SR)_2(CO)_2(PR_3)_2]$ precursors [121,124]. The binuclear nature of all intermediates has, however, been questioned and whether there is a cooperative effect between the two metal centers is still controversial. Kinetic studies, and an investigation of catalyst cross-over reactions in the case of a mixture of two complexes $[Rh_2(SR)_2(CO)_2(P(OMe)_3)_2]$ in which R = ^{t}Bu and Ph, suggested the presence of mononuclear species [125]. Nevertheless, a complete kinetic study of these systems has never been reported probably because the existence of different species in equilibrium hampers a mechanistic proposal based on kinetic data.

Water-soluble binuclear complexes $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(tppts)_2]$ (tppts = P(*m*-$NaO_3SC_6H_4)_3$) were used in the biphasic hydroformylation of 1-alkenes. Selectivities in the linear aldehyde were > 95% and a metal complex could be recovered at the end of the reaction in the aqueous phase. Furthermore, in this case the CO/H_2 or CO/H_2O pairs can be used as feedstocks, since the system is also active in the WGS reaction [126]. Addition of ethanol as a co-solvent dramatically improved the yields, but the high regioselectivity in lineal aldehyde observed in the water system decreased to 83%. It was shown that the binuclear framework is not maintained and the mononuclear complex $[RhH(CO)(tppts)_3]$ is formed in the aqueous phase [127].

The catalytic precursors $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(PR_3)_2]$ have been applied in the low pressure hydroformylation of different substrates such as styrene, 2-vinyl furan [128], formaldehyde [129] and monoterpenes [130]. In particular, **7.1** ($PR'_3 = PPh_3$, $P(OMe)_3$ and $P(OPh)_3$) have been used to carbonylate limonene, isopulegol and isopulegyl acetate at 5 bar and 85°C [131]. Recently, optically-pure di- or trifunctionalized cyclic monoterpenes were hydroformylated at low pressure using the binuclear rhodium complexes **7.1** (PR_3 = phosphine or phosphite). The exocyclic ethylenic double bonds of (*R*)-limonene, (*S*)-carvone, (*S*)-perillyl alcohol, or (1*R*,4*R*)-isolimonene were selectively hydroformylated. The hydroformylation, which was followed by the cyclization of (1*R*, 2*S*, 5*R*)-isopulegol (**7.3**), yielded the lactol **7.4** as the major product with 64% de. The dehydrated benzopyran **7.5** was obtained as a minor product (Scheme 6b).

This reaction does not require chiral phosphorus ligands, since the asymmetric induction is directed by the substrate configuration. (−)-β-Pinene and (−)-camphene were selectively hydroformylated and ee values ranged from 26 to 85% when **7.1** containing classical phosphite or diphosphine ligands was used as precursor. At high pressure (100 bar CO/H_2), hydroformylation of (−)-α-pinene and (−)-



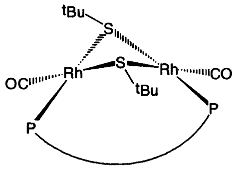
7.3 **7.4** **7.5**

Scheme 6b.

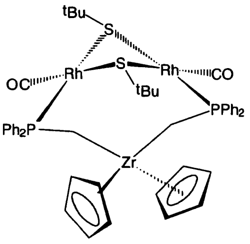
myrtenol into 10-formylpinane and myrtenal, respectively, gave moderate yields and selectivities, but ee were as high as 100% [131].

The addition of Ph_2PXPPh_2 ($X = (CH_2)_3$, $(CH_2)_4$, 1,1′-ferrocenyl and 1,1′-ruthenocenyl) to a solution of $[Rh_2(\mu\text{-}S^tBu)_2(CO)_4]$ gave the complexes $[Rh_2(\mu\text{-}S^tBu)_2(\mu\text{-}Ph_2PXPPh_2)(CO)_2]$ (**7.6**) [132]. The crystal structures of complexes with $X = (CH_2)_4$, and 1,1′-ferrocenyl were determined [132b].

The d^0-d^8 heterobimetallic complex **7.7** obtained by coordination of a zirconium(IV) diphosphine to a binuclear rhodium(I) moiety has been also prepared and characterized [132a]. The catalytic activity of precursors **7.6** and **7.7** in the hydroformylation of 1-hexene has been investigated and the results show that the Zr–Rh bimetallic complex is more active than complexes type **7.6**. It is suggested that the tetrahedral geometry around the zirconium maintains the rhodium atoms in short contact [132,133].



7.6



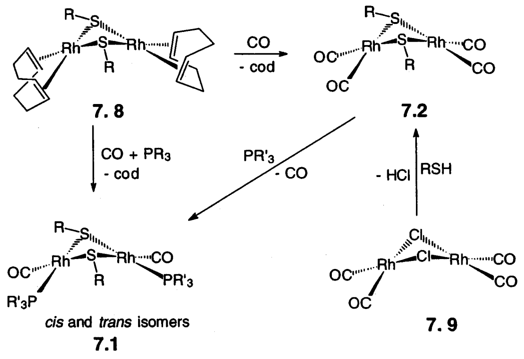
7.7

7.3. *Modified thiolato bridge and heterobridged binuclear rhodium complexes*

Catalytic systems based on binuclear thiolato bridged rhodium complexes have generally been prepared by reacting the carbonyl derivatives $[Rh_2(\mu\text{-}SR)_2(CO)_4]$ (**7.2**) with phosphorus ligands, or $[Rh_2(\mu\text{-}SR)_2(cod)_2]$ (**7.8**), with a suitable phosphorous ligand under the hydroformylation reaction. Carbonyl complexes $[Rh_2(\mu\text{-}SR)_2(CO)_4]$ were obtained either from the cyclooctadiene complexes [134–136] or from $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ (**7.9**) [124,137]. The tetracarbonyl complexes react with phosphines or phosphites PR_3 and in most cases afford mixed carbonyl-phosphine complexes $[Rh_2(\mu\text{-}SR)_2(CO)_2(PR_3)_2]$ (**7.1**) (Scheme 6c).

Heterobridged complexes which contain only one thiolato ligand have been prepared and characterized [38b,68,137]. When one of the two chloro bridges in the complex $[Rh_2(\mu\text{-}Cl)_2(CO)_2(PR_3)_2]$ is replaced by a thiolato ligand, complexes of the type $[Rh_2(\mu\text{-}Cl)(\mu\text{-}SR)(CO)_2(PR_3)_2]$ (**2.35**) are produced [38]. The complexes $[Rh_2(\mu\text{-}Cl)(\mu\text{-}SR)(CO)_2(As^tBu)_3]$ were prepared by treating $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ with As^tBu_3 and Me_3SiSR. These species are effective catalysts in hydroformylation of olefins, but pressures need to be higher than the ones used for bis(thiolato) complexes [38b,138].

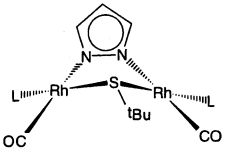
Complexes $[Rh_2(\mu\text{-}pz)(\mu\text{-}S^tBu)(CO)_2L_2]$ (pz = pyrazolato, L = CO, $P(OMe)_3$, $P(OPh)_3$, PPh_3) (**7.10**) have been prepared while the crystal and molecular structure of *cis*-$[Rh_2(\mu\text{-}pz)(\mu\text{-}S^tBu)(CO)_2(P(OEt)_3)_2]$ **7.10** was determined by X-ray diffraction.



Scheme 6c.

The heterobridged complex $[Rh_2(\mu\text{-pz})(\mu\text{-S}^t\text{Bu})(CO)_2(P(OMe_3)_2]$ is an active catalyst precursor for 1-hexene hydroformylation in mild conditions. The conversions and regioselectivities afforded were similar to the ones obtained with the related complex $[Rh_2(\mu\text{-S}^t\text{Bu})_2(CO)_2(P(OMe_3)_2]$ [137].

The tetracarbonyl complex **7.10** has also been used, in the presence of triphenylphosphine and chiral diphosphines, for the hydroformylation of styrene. The effect of pressure and the dependence on the P/Rh ratio has been reported. Low pressures and temperatures provide total conversions in aldehydes and regioselectivities up to 90% in 2-phenylpropanal when triphenylphosphine is used. When the chiral diphosphines diop (**2.8**) and 2,4-bis(diphenylphosphino)pentane (bdpp) are used in a P/ Rh ratio of 2 regioselectivities are high and ee between 12–50% in 2-phenylpropanal [139].



L = CO, PR3, P(OR)3
7.10

Fluorothiolato-bridged $[Rh_2(\mu\text{-SR})_2(CO)_4]$ ($SR = SC_6F_5$, p-SC_6HF_4, p-SC_6H_4F) were obtained by reacting **7.9** and $Pb(SR)_2$ [134a][134a]. The catalytic system generated with $[Rh_2(\mu\text{-SCF}_3)_2(CO)_4]$ and several phosphorous ligands were studied as catalyst precursors for the hydroformylation of 1-hexene in CH_2Cl_2 at 5 bar and 30°C. The extent of aldehyde conversion is 5–94%, with a linear/branched aldehyde ratio in the range 3–3.5 [134b]. The binuclear complexes $[Rh_2(\mu\text{-SC}_6F_5)_2(cod)_2]$ and $[Rh_2(\mu\text{-SC}_6F_5)_2(CO)_4]$ react with PPh_3 to give mono- and binuclear complexes. The product formed depends on the PR_3/Rh ratio and the reaction conditions. The binuclear species showed higher selectivity in the linear aldehyde than the corresponding mononuclear complexes [140].

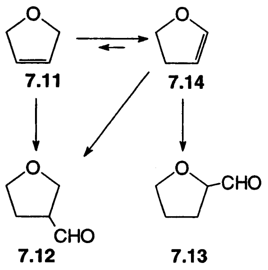
The precursor system formed by the [$Rh_2(\mu\text{-}S(CH_2)_3NMe_2)_2(cod)_2$] complex with the addition of PPh_3 catalyses the hydroformylation of 1-hexene into heptanals under mild conditions with high yields and selectivities. Owing to the presence of the amine group in the thiolate bridge ligand, the rhodium catalyst can be quantitatively recovered from the reaction mixture by adding dilute H_2SO_4, and reused without loss of activity [135]. A study has been carried out on the hydroformylation of 1-hexene with the addition of different phosphorous ligands to the aminothiolate system. HPIR experiments under hydroformylation conditions showed the formation of mononuclear rhodium hydrido carbonyl species. The hydroformylation results obtained with this system are the same as that with [$Rh(acac)(CO)_2$]/PPh_3. This revealed that the mononuclear hydrido species formed are the responsible for catalytic activity [141]. Deuteroformylation studies agree with a mechanism involving mononuclear species.

The complex [$Rh_2(\mu\text{-}S(CH_2)_3NMe_2)(cod)_2$] in presence of P-donor ligands is also an effective catalyst precursor for the hydroformylation of vinyl and allyl cyclic ethers. Mononuclear species were observed at the end of the reaction when $P(\textit{O-o-}{}^{t}BuC_6H_4)_3$ ($P(OPh^*)_3$) was used. A systematic study has been made of the regioselective hydroformylation of dihydrofurans and dihydropyrans and a model for the mechanism has been proposed [136]. This study rationalized the selectivity observed and optimized the yields and regioselectivities. When PPh_3 was used as auxiliary ligand at 5 bar and 80°C, 2,5-dihydrofuran (**7.11**) afforded the expected aldehyde **7.12**, and also variable amounts of **7.13** which was formed through an isomerization-hydroformylation of the substrate (Scheme 6d).

When the reaction parameters were modified, **7.12** was obtained in quantitative yields from 2,5-dihydrofuran, and tetrahydrofuran-2-carbaldehyde was prepared by either 2,3-dihydrofuran or 2,5-dihydrofuran in a yield of approximately 75%.

The 3,4-dihydro-2H-pyran and 2,3-dihydrofuran can be considered as simple glucal models. Although 2,3-dihydrofuran was easily hydroformylated under mild conditions, in the presence of PPh_3, 3,4-dihydro-2H-pyran was hydroformylated in very low yields even in more drastic conditions and only when $P(OPh^*)_3$ was used as auxiliary ligand [136].

Glucal derivatives have been hydroformylated in good yields and selectivities with [$Rh_2(\mu\text{-}S(CH_2)_3NMe_2)(cod)_2$] as catalytic precursor and $P(OPh^*)_3$ as auxiliary



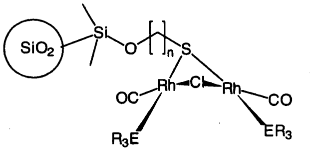
Scheme 6d.

ligand. The regioselectivity observed seems to be related to the polarization of the alkene and the steric hindrance of the protective group at the 3 position of the sugar ring, which results in the preferential introduction of an equatorial formyl group at the 2 position [142]. The isolation of *trans*-[RhCl(CO)((P(OPh*)$_3$)$_2$] species at the end of the reaction, when chlorinated solvents were used [136], and the fact that the same results were obtained with a classical catalytic precursor without a sulfur ligand, indicates that the thiolato complex is cleaved during the reaction [143].

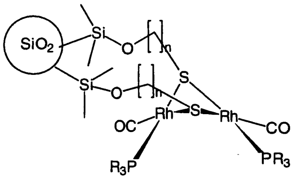
7.4. Immobilized thiolato rhodium catalysts

Recovery of the homogenous hydroformylation catalysts is one off the main research topics for this reaction. Regarding catalysts containing sulfur ligands two main approaches have been used: anchoring the catalyst through the sulfur ligand or through the ancillary P-donor ligand. They are described separately.

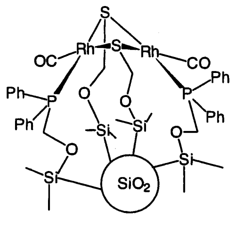
The following scheme represents some of the immobilized catalysts bonded to the support through the sulfur ligand:



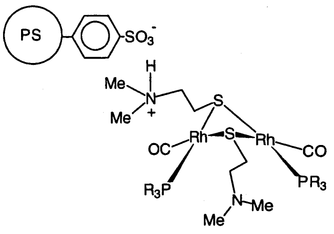
7.15



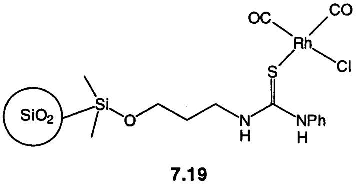
7.16



7.17



7.18



7.19

Rhodium complexes [Rh$_2$(μ-Cl)(μ-SR)(CO)$_2$(ER$_3$)$_2$] (ER$_3$ = phosphine or arsine) which were functionalized at the thiolato ligand (R = (CH$_2$)$_n$Si(OEt)$_3$) were anchored to silica (**7.15**) or alumina. The supported species proved to be active for the hydroformylation of olefins at 80 bar of *syn*-gas and 120°C. The catalysts were recycled more than 10 times with no change in their performance [38c].

More recently, the same strategy was used to anchor $[Rh_2(\mu\text{-}SR)_2(CO)_2(PR_3)_2]$ to silica through the thiolato (**7.16**) or, both through the thiolato and the phosphine ligands (**7.17**). These systems are active precursors in the hydroformylation of 1-octene at 1 bar of *syn*-gas, and they remain active for several cycles. In the case of **7.16**, the selectivity and activity are markedly affected by the nature of the phosphine donor. It has been suggested that part of the binuclear complex generates mononuclear thiolato species under reaction conditions [144].

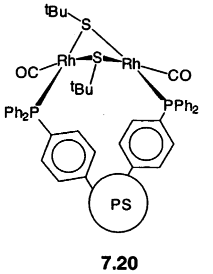
Finally, binuclear aminothiolato complexes $[Rh_2(\mu\text{-}S(CH_2)_2NMe_2)_2(CO)_2(PR_3)_2]$ have been prepared. They were anchored to a sulfonic exchange resin (**7.18**). These species were tested in the hydroformylation of styrene. The supported catalyst is active at 8 bar and 80°C, with selectivity identical to that of the structurally comparable homogenous catalysts $[Rh_2(\mu\text{-}S(CH_2)_2NHMe_2)_2(CO)_2(PR_3)_2](TsO)_2$, the activity of which, however, is 20 times higher than that of the immobilized catalyst [145].

Thioether containing polymers were synthesized by partially substituting the chlorine atoms in the poly(vinyl chloride) by SR groups (R = Pr, n-hexyl, benzyl, *p*-tolyl). The rhodium complexes of these thioether-containing polymeric ligands are highly active catalysts for the hydroformylation of olefins. The effects on the activity of the temperature, pressure, H_2/CO ratio, S/Rh ratio, catalyst concentration and reaction time were studied [146].

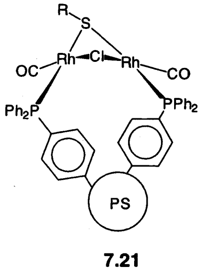
Thiourea-functionalized siloxane materials react with Rh(I) species to give supported complexes such as **7.19**. These complexes are very active and recoverable catalysts for the hydroformylation of styrene. The regioselectivity of some of these materials varies when they are used in consecutive catalytic runs. Furthermore, the non-siloxanized thioureas PhNHC(S)NHPh and $p\text{-}(PrNHC(S)NH)_2C_6H_4$, which give discrete molecular Rh(I) complexes, were studied as models for the surface bond species. The structure of [RhCl(cod){PhNHC(S)NHPh}] has been determined by X-ray diffraction methods [147].

Some sulfur-containing ligand catalysts, bonded to the support exclusively through the P-donor ligand, have also been reported. In all cases, phosphinated cross-linked polystyrene was used as insoluble matrix.

The immobilized rhodium thiolate catalyst prepared from phosphinated cross-linked polystyrene and $[Rh_2(\mu\text{-}S^tBu)_2(CO)_4]$ (**7.20**) was used to catalyze the hydroformylation of olefins at 80°C and 5 bar [148]. The nature of the related supported catalyst which was prepared by reacting $[Rh_2(\mu\text{-}SC_6F_5)_2(CO)_4]$ with phosphinated polystyrene has been investigated with XPS and SEM-EDX [149]. Finally, the behavior of catalyst type **7.21** in the hydroformylation of cyclohexene has been reported. The activity of the catalyst which was supported in 20% cross-linked matrix was higher than that of the flexible 2% cross-linked polymer [38c].



7.20



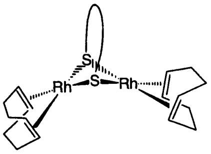
7.21

7.5. Binuclear bridged dithiolato rhodium complexes

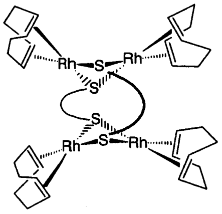
Binuclear dithiolato-bridged rhodium complexes have been the focus of considerable interest during the last decade. Dithiolato complexes could provide a more rigid structure than thiolato-bridged complexes and this should decrease the conformational mobility of the intermediates, which could give a better steric control. Furthermore, in the case of asymmetric hydroformylation, chiral information can be introduced in both the dithiolato and the phosphorous ligands.

The achiral dithiolate complexes $[Rh_2(\mu\text{-}S(CH_2)_nS)(cod)_2]_x$ ($n = 2$, 3 and 4; $x = 1$ and 2) were studied as a model for chiral dithiolates. They were prepared by adding the corresponding dithiol to solutions of the complex $[Rh_2(\mu\text{-}OMe)_2(cod)_2]$. The nuclearity of the diolefinic complexes depends on the number of methylenic units between the two sulfur atoms. For $n = 2$ or 3 it is binuclear (**7.22a**) and for the 1,4-butanodithiolato bridge ligand it is tetranuclear $[Rh_2(\mu\text{-}S(CH_2)_4S)(cod)_2]_2$ (**7.22b**) [150]. The reactivity of these cyclooctadiene complexes towards carbon monoxide and carbon monoxide/PR_3 ($R = C_6H_5$, C_6H_{11}, $O\text{-}o\text{-}{}^tBuC_6H_4$) has also been studied. Only binuclear carbonyl complexes were obtained $[Rh_2(\mu\text{-}S(CH_2)_nS)(CO)_4]$ by cod substitution [151].

The rhodium complexes **7.22** have been used as catalyst precursors in presence of triphenylphosphine for the hydroformylation of 1-hexene. When $n = 2$ or 3 $[Rh_2(\mu\text{-}S(CH_2)_nS)(cod)_2]/PR_3$ ($P/Rh = 2$) no conversion was detected at 5 bar and complete conversion required 30 bar [151] However, the complex $[Rh_2(\mu\text{-}S(CH_2)_4S)(cod)_2]_2$ is active at 5 bar when $PPh_3/Rh = 2$ is used. The infrared spectrum recorded at the end of the catalytic reaction shows only one $\nu(CO)$ frequency corresponding to the mixed binuclear $[Rh_2(\mu\text{-}S(CH_2)_4S)(CO)_2(PR_3)_2]$ complex which was independently characterized. This species and also the pentacoordinated $[Rh_2(\mu\text{-}S(CH_2)_4S)(CO)_4(PR_3)_2]$ are observed by HPIR under hydroformylation conditions [141]. In the case of ethanodithiolate and propanodithiolate, which are not active at 5 bar, CO frequencies corresponding to other carbonyl species were observed at the end of the catalytic reaction [151].

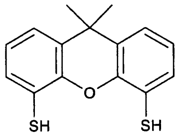


7.22a



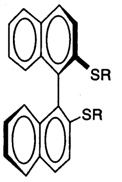
7.22b

The system $[Rh_4(\mu\text{-}xantoss)_2(cod)_4]/PPh_3$ (xantoss = **7.23**) is very active in the hydroformylation of 1-octene. Nevertheless, HPIR studies under CO/H_2 of this precursor showed that this system evolves to the mononuclear complex $[RhH(PPh_3)(CO)_2]$ which is the main species under hydroformylation conditions [141].

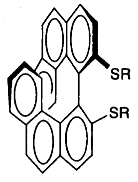


7.23

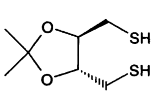
Chiral dithiolate ligands such as binasH_2 (1,1′-binaphtalene-2,2′-dithiol) (**7.24**) [152], biphesH_2 (4,4′-biphenanthrene-3,3′-dithiol) (**7.25**) [153], 2,3-*O*-isopropylidene-1,4-dithio-L-threitol (**7.26**) [154], bcosH_2 ((+)-*trans*-2,3-bis(mercaptomethyl)-bicyclo[2.2.2]octane) (**7.27**) [155], containing four carbon atoms between the sulfur atoms, as the most active of the achiral dithiolate, have been used to prepare binuclear or tetranuclear rhodium complexes to be used as catalytic precursors in olefin hydroformylation.



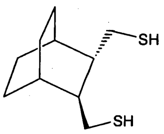
7.24a R = H
7.24b R = Me, ^{i}Pr



7.25a R = H
7.25b R = Me, ^{i}Pr

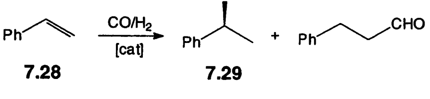


7.26



7.27

The first report on the use of chiral sulfur ligands in rhodium catalyzed asymmetric hydroformylation appeared in 1993. Enantiopure binasH_2 (**7.24a**) was used as the bridging ligand and the complex $[Rh_2(\mu\text{-binas})(cod)_2]$ was found to have good catalytic activity in the hydroformylation of styrene (**7.28**) in the presence of two moles of PPh_3 [152] (Scheme 6e). At 30 bars of pressure, the branched aldehyde **7.29** was obtained in a high chemical yield and with a regioselectivity of more than 90%. The ee, however, was less than 10%. In the absence of PPh_3, the complex still



Scheme 6e.

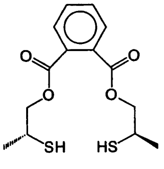
maintains its catalytic activity and provides a slightly higher stereoselectivity, but is less active and regioselective.

Results with the binuclear complexes $[Rh_2(\mu\text{-}L)(cod)_2]$ (L = **7.25a, 7.26**) are similar. In the absence of a phosphorous ligand at 30 bar and 65°C, styrene has been completely converted into aldehydes. Regioselectivities, however, were low. At 80 bar and 30°C, the regioselectivity increases (up to 96%) but the ee did not improve. The activity and the regioselectivity in 2-phenylpropanal (**7.29**) increased when the catalytic system was formed by adding PPh_3 to the rhodium precursor, but enantioselectivity remained very low [152–154]. In the case of the complex with ligand **7.26** the reaction was also carried out in triethyl orthoformate. The activity and the selectivity of the catalyst was maintained and the corresponding diethyl acetals were obtained with the same poor ee [154]. These results indicate that the low optical yield is not due to the racemization of the aldehyde.

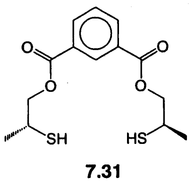
Lower CO/H_2 pressures have been used for the $[Rh_2(\mu\text{-bcos})(cod)_2]_2$ precursor (5–10 bar, 65°C) but results were similar (regioselectivities up to 90% and ee up to 10%) [155].

The results of using both achiral and chiral dithiolate precursor systems without phosphorous ligands in the hydroformylation reaction, and in particular the low regioselectivities in styrene hydroformylation, suggest cleavage of the binuclear complex. The displacement of the dithiolato bridge ligand may lead to the formation of active rhodium hydride carbonyl complexes, which have low regioselectivities in these conditions [156].

In a preliminary communication, enantioselectivity was reported to be fairly good with binuclear rhodium complexes containing long-chain chiral dithiolato ligands [157]. These results, however, were not subsequently corroborated A number of chiral dithiolato ligands containing 12–13 atoms between the two S-donor atoms have been synthesized, and their rhodium complexes assayed in asymmetric hydroformylation. These ligands were designed with the aim of creating a chiral cavity above the open faces of the two metals in the folded binuclear structure, mimicking the role of long-chain chiral diphosphine ligands in some asymmetric catalytic reactions [158]. The long-chain dithiolato ligands should also provide flexibility to the bimetallic frame, which allows the reaction to proceed at low pressure. Thus, the thioacetate of ligands **7.30** and **7.31** react with $[Rh_2(\mu\text{-OMe})_2(cod)_2]$ to form a mixture of oligomeric dithiolato complexes $[Rh_2L(cod)_2]_n$ and in the case of ligand **7.30** the binuclear complex is the major component of the mixture. These cyclooctadiene complexes, in the presence of PPh_3, were used as catalyst precursors for the hydroformylation of styrene. Neither the oligomeric mixtures nor the binuclear complexes yielded significant ee ($< 5\%$), although the systems were quite active, even at 6 bar, and the regioselectivity reached 85% in the branched aldehyde [159].



7.30



7.31

In summary, although a wide variety of chiral dithiolato ligands have been assayed in rhodium asymmetric hydroformylation, the ee's achieved so far have been very low.

Chiral diphosphines have also been used as auxiliary phosphorous ligand in combination with binuclear dithiolate bridged rhodium systems. It has been shown that bdpp (**7.32**) provides higher ee than other diphosphines [154,155,160].

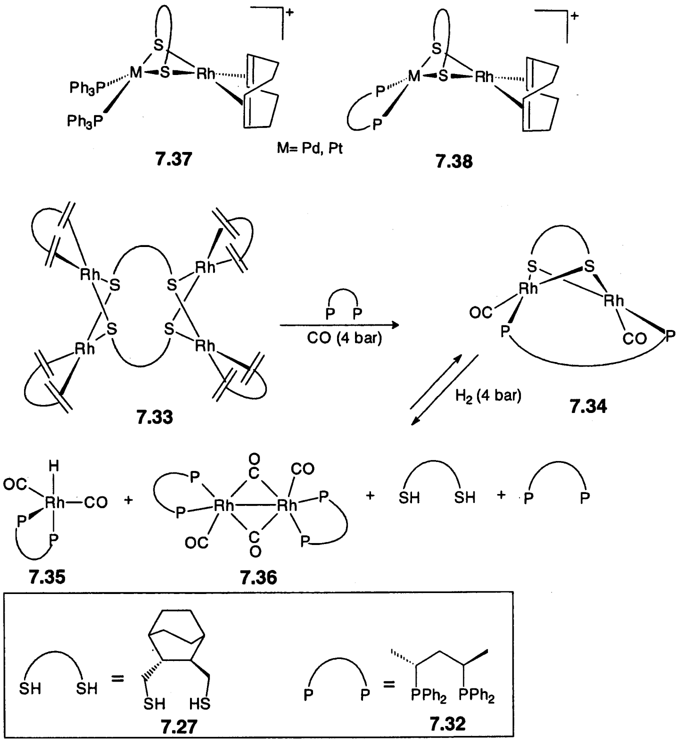
The influence of the binuclear framework of the rhodium thiolato precursor has also been reported. The addition of (+)-bdpp (**7.32**) to the binuclear thiolato rhodium complex $[Rh_2(\mu\text{-S}^t\text{Bu})_2(CO)_4]$ provides total conversion into aldehydes with a regioselectivity in 2-phenylpropanal (**7.29**) of 90%, but the ee was 10% (*R*) [160]. In the case of the achiral binuclear dithiolate complexes $[Rh_2(\mu\text{-S}(CH_2)_4S)(cod)_2]$, the addition of (+)-bdpp increased the enantioselectivity and enantiomeric excess to 42% (*S*) at 30 bar and 65°C and P/Rh molar ratio of 2. Conversion into aldehydes was complete and regioselectivity was as high as 94% in 2-phenylpropanal. Of the four possible combinations with the binuclear precursor $[Rh_2(\mu\text{-L})(cod)_2]$ (L = **7.25**), results were best with the couple (−)-**7.25** and (+)-bdpp which produced (*S*)-2-phenylpropanal in 43% ee [154]. This is almost identical to the value recorded for the achiral bridge complex $[Rh_2(\mu\text{-S}(CH_2)_4S)(cod)_2]$/bdpp system, which contains an achiral bridging dithiolate ligand [160]. The system $[Rh_2(\mu\text{-bcos})(cod)_2]_2$/bdpp provided the best results, giving ee up to 55% and regioselectivity of 96% in 2-phenylpropanal [155].

An achiral rhodium precursor system $[Rh_2(\mu\text{-OMe})(cod)]_2$, which leads to the rhodium hydride carbonyl phosphorous species in hydroformylation conditions [161], was used in the same conditions. The $[Rh_2(\mu\text{-OMe})(cod)]_2$/(+)-bdpp system provides a lower ee (12%) than the system based on dinuclear bridged dithiolate $[Rh_2(\mu\text{-dithiolate})(cod)_2]_2$/bdpp when the P/Rh ratio = 2. It has been concluded that the asymmetric induction of a given enantiopure phosphorous ligand can be improved by changing the starting organometallic complex [160]. However, when the P/Rh ratio = 4, for the $[Rh_2(\mu\text{-OMe})(cod)]_2$/(+)-bdpp and the $[Rh_2(\mu\text{-dithiolate})(cod)_2]_2$/bdpp systems, the ee obtained were the same for both systems (55%). This study on dithiolate-bridged rhodium precursors in combination with diphosphines has shown that precursors based on available rhodium systems such as $[Rh(\mu\text{-OMe})(cod)]_2$ or $[Rh(acac)(CO)_2]$ using the structurally simple diphosphine bdpp provided a regioselectivity in 2-phenylpropanal of 95% with an ee as high as 60% at 40°C. The ee obtained depends heavily on the excess of diphosphine, the appropiate P/Rh ratio being 4 in this case [162].

The reactivity of tetracarbonyl rhodium complexes $[Rh_2(\mu\text{-dithiolato})(CO)_4]$ (dithiolato = $S(CH_2)_4S$, bcos) with achiral diphosphines such as dppe and dppp has been studied to investigate the species formed under catalytic conditions. The reaction of dinuclear dithiolato-bridged Rh(I) complexes with a stoichiometric amount of diphosphine yields a mixture of a dinuclear complex which maintains the dithiolato ligand bridging the two rhodium atoms, $[Rh_2(\mu\text{-bcos})(dppp)_2]$, and the unexpected ionic complexes $[Rh(dppp)_2]^+[Rh(dithiolato)(CO)_2]^-$ and $[Rh(CO)(dppp)_2]^+$ $[Rh(dithiolato)(CO)_2]^-$. In the presence of an excess of diphosphine, only those ionic complexes which have the dithiolato in the anionic fragment are observed [163].

The structures in solution of the dominant species present during the styrene hydroformylation using as precursor the dithiolato bridged complex $[Rh_2(\mu\text{-bcos})(cod)_2]_2$ (**7.33**) in presence of bdpp have been determined. High pressure spectroscopic techniques (HPNMR and HPIR) studies revealed that the mononuclear complex $[RhH(bdpp)(CO)_2]$ (**7.35**) was the predominant species during the hydroformylation process in equilibrium with the dimeric species $[Rh(bdpp)(CO)_2]_2$ (**7.36**). However, species containing the dithiolato bridge ligand, proposed as dinuclear $[Rh_2(\mu\text{-bcos})(\mu\text{-bdpp})(CO)]_2$ (**7.34**) stable under hydroformylation conditions, have also been observed [164] (Scheme 6f).

Heterodinuclear Pt–Rh and Pd–Rh complexes of general formula $[(PPh_3)_2M(\mu\text{-L})Rh(cod)]ClO_4$ (**7.37**) or $[(PP)M(\mu\text{-L})Rh(cod)]ClO_4$ (**7.38**) (M = Pt, Pd; L = $S(CH_2)_nS$, $n = 2, 3, 4$; PP = dppp and dppb) have been prepared and structurally characterized through X-ray diffraction methods [165]. These complexes were used as catalyst precursors in the hydroformylation of styrene. However, the results of the hydroformylation reaction, together with a preliminary HPNMR study under hydroformylation conditions, suggested the formation of Rh-diphosphine species that were the responsible for the catalytic activity [166].



Scheme 6f.

7.6. Rhodium complexes with chiral dithioether ligands

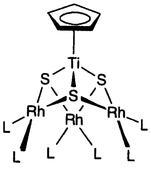
Chiral dithioethers have been synthesized and used as ligands for preparing cationic rhodium complexes $[Rh(cod)(dithioether)]^+$, dithioether = $diosR_2$ (R = Me, ^{i}Pr, Ph) (**2.10**) [167], $binasR_2$ (**7.24b**) [152] and $biphesR_2$ (R = Me, ^{i}Pr) (**7.25b**) [153]. These complexes were used as catalyst precursors in the hydroformylation of styrene. In the case of $binasR_2$ systems (**7.24b**), the addition of phosphorous ligands was not required to obtain efficient activity and regioselectivity. One of the advantages of neutral thioethers with respect to the thiolato ligands is that the ligand/Rh molar ratio can be tuned to improve the performance of the catalytic system, without affect the charge balance. The regioselectivity in 2-phenylpropanal increases with the excess of ligand and reaches 96% in the branched aldehyde **7.29**, when **7.24**/Rh = 3. The enantiomeric excesses obtained were, however, low. The best results have been reported for $[Rh(cod)(binasR_2)]^+$ which achieve 15% for R = Me and 20% ee for R = ^{i}Pr in **7.29** [152,153]. However, the regioselectivity achieved with other chiral dithioethers assayed is nearly identical to that of the unmodified system (i.e. $RhH(CO)_4$) and no significant ee's were observed [166].

Regarding the use of chiral dithioether ligands in asymmetric reactions, it should be noticed that the coordination of the sulfur to the metal generates a new stereogenic center. In this context, the Rh(I) and also the Pd(II) and Pt (II) complexes of the dithioether ligands derived from binas **7.24b** were studied by variable temperature NMR. The results showed that all the complexes are fluxional in solution at room temperature and that the different diasteroisomers can not be observed. Interconversion between the stereoisomers can take place by equilibrating the conformation of the chelate ring and/or inverting the configuration at the sulfur stereogenic center [168].

7.7. Early-late sulfido complexes

Early-late metal complexes of formula $[CpTi(\mu\text{-}S)_3\{Rh(L_2)\}_3]$ (L = olefin, CO) (**7.39**) have been recently reported [169].

The carbonyl species reacts with P-donor ligands giving tetranuclear complexes, where different numbers of CO are substituted. Complexes **7.39**, in the presence of phosphorus ligands, have been tested as catalysts for the hydroformylation of olefins at 5–30 bar. Interestingly, when PPh_3 was used, the styrene was hydroformylated at lower rates than 1-hexene. The ^{31}P-NMR registered at the end of the catalytic reaction and a HPNMR study under CO/H_2 pressure showed that the heteronuclear framework is maintained under hydroformylation conditions [170].



L= CO, olefin
7.39

7.8. Platinum catalysts

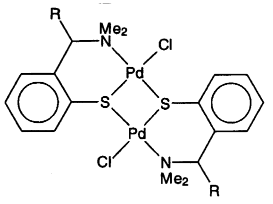
The catalytic activity of Pt/$SnCl_2$ systems containing sulfur ligands has hardly been studied. First reports deal with the study of the reactivity of the thiolato-bridged dimers $[Pt_2(\mu\text{-}SR)_2Cl_2L_2]$ (L = PEt_3, PPr_3, P^tBu_3, PMe_2Ph, PBu_3; R = Et, $CHMe_2$) and the thioether complex $[PtH(SnCl_3)(SMe_2)(PPh_3)]$ under hydroformylation conditions [13b,42].

The synthesis and characterization of [PtL(PP)] complexes (L = 1,4-butanedithiolato, **7.24a** and **7.26**; PP = dppp, dppb) have been reported. These complexes, in the presence of $SnCl_2$, are active in the hydroformylation of styrene at 100 bar and 125°C (yields ca. 80%). Best results were with the precursor [Pt(binas)(dppp)]; the regioselectivity was 42% in 2-phenylpropanal and the ee was 14% [171].

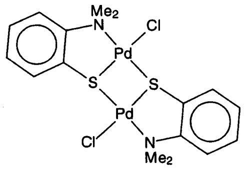
7.9. Related reactions

The hydrocarboxylation of olefins is a powerful synthetic tool for the preparation of carboxylic acids from readily available reagents. Various catalytic systems have been used for this process. One of the reported cases is the reaction of the olefin with oxalic acid, under CO pressure and catalyzed by palladium complexes [172] (Scheme 6g).

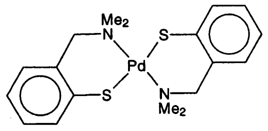
Complexes **7.40**–**7.43**, in the presence of PPh_3 (PPh_3/Pd = 4), are active catalysts for the hydrocarboxylation of styrene with $H_2C_2O_4$, at 100°C and 30 bar pressure of CO.



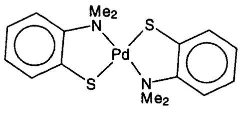
7.40 R = H, Me



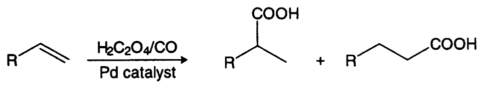
7.41



7.42



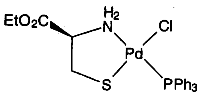
7.43



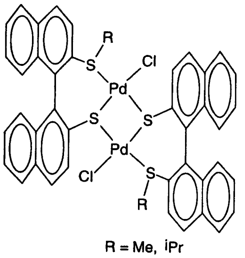
Scheme 6g.

The reaction provided conversions of 34–98% in acids and regioselectivities of 83–100% in the 2-phenylpropanoic acid. The conversion decreased when the PPh_3/Pd ratio was lowered, although in these conditions selectivity in the branched derivative was complete in some cases. The asymmetric reaction was assayed with the optically pure ligand **7.40** (R = Me), but the ee was only 4% [173].

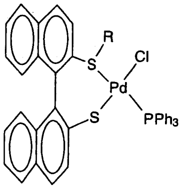
The same reaction was investigated with the Pd-cysteine catalyst **7.44**. In this case, no further PPh_3 was added. Conversions were similar to the previous case, but the regioselectivities in the branched acid were always > 96%. This acid was racemic in all the reaction conditions used [174].



7.44



R = Me, iPr
7.45



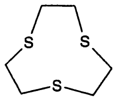
R = Me, iPr
7.46

The palladium complexes **7.45** and **7.46**, which contain the racemic mixture of the atropoisomeric S-donor ligands, have also been tested in the hydrocarboxylation of styrene with oxalic acid. Triphenylphosphine (P/Pd = 4) was added in the case of the binuclear complexes **7.45**. Conversions were higher than 90%, and selectivities in the branched aldehyde ranged between 74–89%. The mononuclear complexes **7.46** rendered significantly lower conversions, although the regioselectivity in the 2-phenylpropanoic acid was > 95% [175].

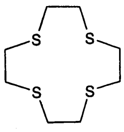
Finally, palladium(II) complexes $[Pd(S(CH_2)_nS)(PP)]$ ($n = 2, 3, 4$; PP = dppp, dppb) are also shown to be active in the hydrocarboxylation of styrene with oxalic acid to form the corresponding carboxylic acids at 150°C and 30 bar pressure of CO [176]. Best conversions (53–60% yield) were with the dppb complexes. Regioselectivities in the linear acid were ca. 85%. Similar results were reported for palladium-diphosphine systems without dithiolato ligands [172b]. Conversions were higher (87%) with the binuclear complex $[Pd_2(S(CH_2)_2S)_2(PPh_3)_2]$ and the regioselectivity shifted to the branched aldehyde (66%).

8. Polymerization

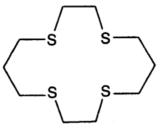
Since the discovery of the very high catalytic activity of Group 4 metallocenes in the presence of MAO (methylaluminium oxide) for olefin polymerization [177], the development of new catalysts for this reaction has been an active field of research. Macrocyclic ligands may act as a protecting group for the metal, paralleling the role of the cyclopentadienyl ring in classical metallocenes. Tri- and tetradentate sulfur macrocyclic ligands **8.1**–**8.4** readily coordinate platinum group metals to form stable complexes, which have been assayed in the polymerization of ethylene. Results were best with ligand **8.1**, which reacts with MCl_3 (M = Fe, Ru, Rh, and Ir) to form the *fac*-octahedral complexes $[MLCl_3]$. The ligand also forms the platinum complexes $[PtLCl_4]$ and $[PtLCl_2]$. The Rh(III) and the Pt(IV) complexes, in the presence of MAO co-catalyst ($Al/m = 500$), are not very active in the polymerization of ethylene, at room temperature and 1 bar. However, their activity dramatically increases with pressure and temperature. Thus, at 70°C and 10 bar of olefin, the platinum catalyst produced 120 kg of polyethylene·(mol of catalyst·h)$^{-1}$. The polymer had a molecular weight of 900 000 with a narrow molecular weight distribution [178].



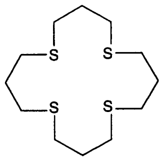
8.1



8.2

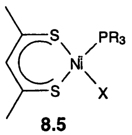


8.3



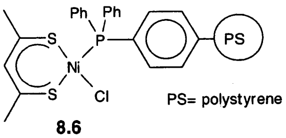
8.4

The nickel complex **8.5** and the polystyrene supported analog **8.6** were studied as catalysts for the polymerization of olefins. With both catalysts, and in the presence of $AlEtCl_2$, the dimerization of 1-hexene was quite selective, although some amount of the isomerization products of the alkene was also formed. Results were similar when related complexes of dithiocarbamate and xanthate ligands were used [72,179]. The complex **8.5** was also tested in the oligomerization of propene [180].



8.5

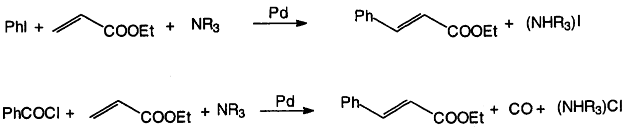
X= Cl, Br
R= aryl, alkyl



8.6

9. Heck reaction

The oxidative addition/olefin insertion sequences, which enable olefins to be arylated in the presence of a palladium catalyst were developed by Heck and coworkers [181]. There are many examples of the use of the Heck reaction in organic syntheses [182]. However, compared with other transition metal catalyzed reactions, the effect of the ligands has been less investigated [183]. Most of these reactions have been carried out homogeneously, often using palladium phosphine complexes. This type of complexes, anchored to a polymer matrix, has been used as catalysts for the reaction [184], but they suffer severe metal leaching under reaction conditions [185].

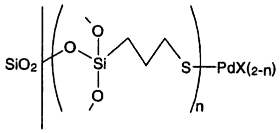


Scheme 7.

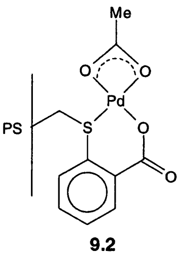
Two works have been reported dealing with the Heck reaction catalyzed by palladium complexes which contain sulfur ligands. In both cases, the catalyst was immobilized in a insoluble matrix. The reactions investigated were the arylation of ethyl acrylate with iodobenzene or benzoyl chloride (Scheme 7).

The thiolato complexes supported on silica **9.1**, the thioether-carboxylate complex immobilized in cross-linked polystyrene **9.2**, or the homologous thioether-amino complex, were used as catalysts for the reaction of iodobenzene with ethyl acetate. Best results were with catalyst **9.1a**, at 100°C and using NBu_3 as base. The catalyst was reused three times (total TON = 2000), with only a slight decrease in the activity. However, some palladium was leached from the solid catalyst [185].

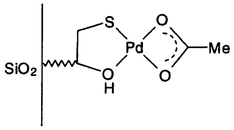
A macromolecular thiolato-hydroxyl bidentate ligand has been used to prepare an immobilized palladium catalyst for the Heck reaction [186]. The ligand was synthesized by reacting an epoxy–phenolic oligomer with H_2S. Palladium acetate was incorporated into the macromolecular ligand and then the complex was absorbed onto silica. Complexes like **9.3** are proposed to be the catalytically active species. This silica-supported palladium complex was investigated in the arylation of ethyl acrylate. Iodobenzene and benzoyl chloride were used as reactants. The activity of this system depends on the sulfur to palladium molar ratio used. Thus, an active catalyst was obtained at a S:Pd ratio of 2, but the system was inactive at ratios higher than 6. Best results were obtained at 85°C in dioxane and NBu_3 as base, when PhI was the reagent. In the case of PhCOCl, the same base was used, the solvent was xylene and the reaction temperature ranged between 85 and 130°C. In both reactions, the activity of the supported catalyst was comparable to the one of $Pd(AcO)_2$, at the same substrate/Pd molar ratio. The supported catalyst can be recycled rendering a total TON of 13 000. Low metal leaching was observed.



9.1a X = AcO
9.1b X = Cl



9.2



9.3

10. Allylic alkylation

Considerable efforts have been devoted to the study of the reaction between allylic substrates and nucleophiles catalyzed by palladium complexes. The chemo-, regio-, diastereo- and enantioselectivities of this process have been widely analyzed and the results applied to the synthesis of target molecules [187].

The reaction is often modeled using 1,3-diphenylallyl acetate (**10.1**) as substrate and the sodium salt of dialkylmalonate (**10.2**) as nucleophile (Scheme 8).

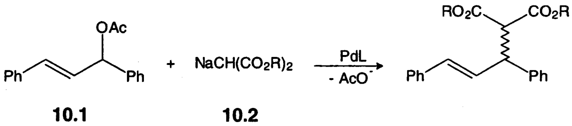
In particular, the enantioselective allylic alkylation reaction catalyzed by Pd has been of great interest in recent years. Many chiral auxiliary ligands have been used allowing for ees higher than 90%. Catalysts often consist of a Pd complex containing a chiral chelate ligand, but they can also be generated in situ from $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_3H_5)_2]$ or $[Pd_2(dba)_3]$ and a suitable number of equivalents of the chiral auxiliary. Several different donor combinations within the chelating chiral auxiliary have been studied (e.g. P,P- [188], P,N- [189], P,O- [189d] and *N*,*N*-donor ligands [189e,190]).

The mechanism of this Pd mediated allylic reaction is reasonably well understood [191,192]. A chiral Pd(0) olefin complex oxidatively adds the prochiral allylic acetate to afford an isolable η^3-allylic cationic compound, which is then attacked by the nucleophile.

Although in this reaction the most widely investigated sulfur ligands have been the N,S-donor type, often derived from a chiral oxazoline moiety, other combinations of donor atoms have been also explored. Most part of the catalytic results reported concern the reaction described above between **10.1** and **10.2**, and especially to the enantioselectivity of the process. Thus, this reaction will be used here to compare the performance of the different type of sulfur ligands.

10.1. Oxazoline N,S-ligands

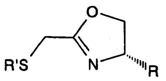
Chiral oxazoline type ligands have been successfully used in the asymmetric allylic alkylation catalyzed by palladium [189c,193]. Oxazolines have several advantages as sources of chirality, the main one being that they are readily accessible from homochiral amino alcohols and have proved to be effective catalysts in a variety of reactions [194]. Furthermore, these ligands are easily modifiable and can incorporate different donor atoms in the side chains of the heterocyclic ring. Thus, oxazoline ligands, with a secondary donor atom have proven to be most successful ligands in palladium-catalyzed allylic alkylation [195]. Different types of oxazolines ligands containing a S-donor atom have been designed to be tested in allylic alkylation. Some of them are shown in Scheme 8.



Scheme 8.

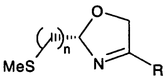
Thioethers tethered to an oxazoline function **10.3**–**10.5** are effective ligands for palladium catalyzed allylic alkylation of **10.1** with the sodium salt of the dimethyl malonate **10.2**. They afford good to excellent levels of enantioselectivity (56–90%). Both the length of the tether between the nitrogen and sulfur atoms and the nature of the thioether affect the performance of these catalysts [196].

Chiral oxazolines tethered to aryl thioethers **10.5** are prepared in one step from commercially available 2-(methylthiobenzonitrile) and enantiomerically pure amino alcohols [196b]. Asymmetric inductions of 40–80% ee and yields of 78–90% were achieved. The results indicate that, in general, aryl thioethers provide higher levels of enantioselectivity than alkyl thioethers. This may be due to steric effects, but also to electronic effects, since the aromatic thioethers are better π-acceptors than the aliphatic ones (see below). The influence of the S-aryl substituents was also analyzed because it could affect the stereochemistry of the sulfur atom. Thus, by changing the aryl group the ee can be raised from 81 to 93%. Oxazolines tethered to sulfoxides were prepared in unoptimized yields. Since the thioether ligands afford levels of enantioselectivity which are similar to the best diastereomeric sulfoxide ligands (96% ee), it is proposed that the stereochemistry of the sulfur atom can switch readily to the preferred configuration after binding to the palladium [195a].



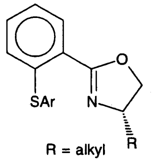
R = alkyl
R' = alkyl, aryl

10.3



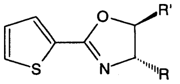
n = 1,2
R = alkyl

10.4



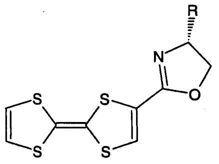
R = alkyl

10.5

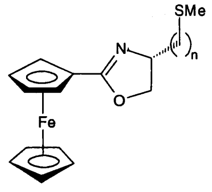


R = alkyl
R' = H, alkyl

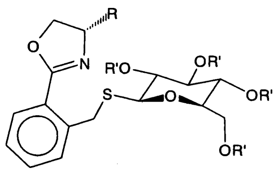
10.6



10.7

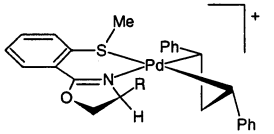


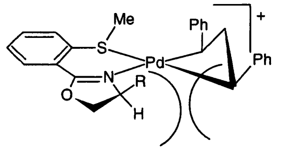
10.8 n =1
10.9 n =2



10.10

Since palladium catalyzed allylic alkylation reactions proceed via π-allyl complexes, there are two possible diastereomeric intermediates for these species:



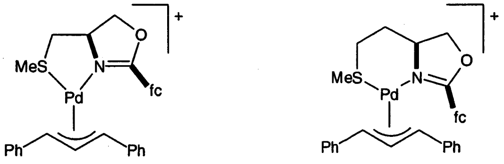


It is assumed that the nucleophilic substitution takes place in the *trans* position to the better π-acceptor, the sulfur in this case. However, the equilibrium rate between both diastereomeric intermediates seems also to be relevant for the enantioselectivity of the process [195c,196b].

Chiral oxazolines tethered to thiophene **10.6** were also used as ligands for enantioselective Pd-catalyzed allylic alkylation. Again, the Pd catalysts containing these ligands afford good levels of asymmetric induction (up to 81% ee with R = ^{i}Pr), but catalysts with ligands **10.6** (R = Ph, ^{t}Bu) showed no activity [197]. In the active systems, both the yield and the enantioselectivity of the reaction, depend on the ligand/Pd molar ratio [195c,197].

Chiral oxazolines linked to tetrathiafulvalene (ttf) (**10.7**) have been also synthesized and applied to asymmetric Pd catalyzed allylic alkylation. In this case the sulfur in the ttf fragment act as a secondary donor atom [198]. The ee's obtained with these systems are lower than the ones reported for ligands **10.3**–**10.6**. The difference can be explained considering that in the case of the thioether ligands the sulfur acts as π-acceptor and the nucleophilic attack occurs *trans* to the sulfur atom (*cis* to the N), as it has been described above. This is in contrast to the 1,3-dithiole sulfur atoms of the ttf unit, which are strong π-donors and then the reaction occurs *trans* to the N, far from the chiral group of the oxazoline ring. In summary, the stereochemical outcome of the reaction with the N,S-donor auxiliary ligands is controlled by their steric and electronic properties.

Chiral ferrocenyl-oxazolines **10.8** and **10.9**, which incorporate thioether units, have been synthesized and they have been used as auxiliary ligands for the palladium catalyzed asymmetric allylic alkylation. The ligand **10.9** is more effective than **10.8** in transferring chirality in this reaction. This is because the tether length between the donor atoms which coordinate palladium in **10.9** increases and brings the asymmetric environment closer to the allyl species during the reaction, as can be seen from the transition states [199]:

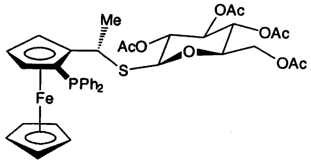


fc = ferrocenyl

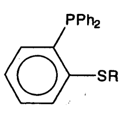
Bidentate ligands containing both chiral oxazoline and thiosugar elements (**10.10**) and their corresponding 1,3-diphenylallyl palladium (II) complexes have been prepared. The sugar is based on a 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranose moiety. These N,S-donor ligands afford ee's between 90–97% in the enantioselective allylic alkylation of **10.1**. This result is one of the best ee's obtained for an N,S-donor ligand in this reaction. The ee's in the case of the related S-cyclohexyl ligand were lower (ca. 75%), indicating that the sugar moiety plays a role in the selectivity of the reaction. ^{1}H- and ^{13}C-NMR spectra of the palladium complexes show that they exist in solution as a mixture of (*syn*–*syn*) *exo* and *endo* diastereomeric complexes, the former being the major product. It is proposed that the dimethyl malonate nucleophile (**10.2**) attacks the allylic position *trans* to the thioether donor because the π-acceptor character of the thioether and that the reaction takes place with the endo diastereisomer isomer for steric reasons. Thus, the product substitution may be formed by preferential reaction of the minor component of the mixture of palladium complexes [200].

10.2. P,S-donor ligands

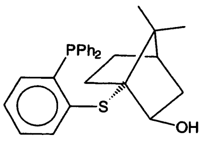
Different types of P,S chelating ligands have been synthesized and characterized. The corresponding Pd-π-allyl complexes have also been prepared to be used as catalysts in allylic alkylation affording high ee's in some cases. [201–203].



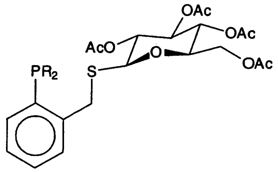
10.11



10.12 R = Et
10.13 R = Cy



10.14



10.15 R = Ph
10.16 R = Cy

NMR studies and solid-state structures of the intermediate have also been reported for these P,S ligands, providing important contributions for the understanding of the mechanism of the catalytic reaction.

The ferrocenylphosphino thiosugar bidentate ligand **10.11** afforded an ee of 88% in the Pd allylic alkylation of **10.1**. The X-ray structure of the allyl cationic complex [Pd(η^3-Ph(CH)$_3$Ph)L]CF$_3$SO$_3$ (L = **10.11**) revealed that the allyl moiety is strongly rotated with respect to the P–Pd–S coordination plane. This structural distortion was also observed in solution (NOE experiments) and it seems to be related to the outcome of the substitution. Thus, it is possible to predict the site of the attack and therefore the configuration of the organic product on the basis of the structure of the complex [201].

Neutral and cationic Pd(II) complexes [PdCl$_2$L], [Pd(η^3-C$_3$H$_5$)L]CF$_3$SO$_3$ and [Pd(η^3-PhCHCHCHPh)(L)]BF$_4$ (L = **10.14)** and complexes of ligands **10.12** and **10.13** with cyclohexyl or ethyl substituents were prepared. The solid-state structure of [Pd(η^3-C$_3$H$_5$)L]CF$_3$SO$_3$ (L = **10.14**) was determined by X-ray diffraction. Complex [Pd(η^3-PhCHCHCHPh)L]$^+$ (L = **10.14**) has been used as catalyst for both allylic alkylation and the allylic amination reactions. Although the yields were high, the reactions were very slow and the ee's poor (ca. 22%) [202].

Bidentate P,S-ligands **10.15** and **10.16** based on β-D-thioglucose tetracetate, as well as their (1,3-diphenylallyl)palladium(II) cationic complexes, were prepared. The solid-state structure (L = **10.16**) shows that the S-sugar substituent and one of the P–Ph rings are on the same side of the P–Pd–S coordination plane in pseudo axial positions [203].

10.3. Other N,S-donor ligands

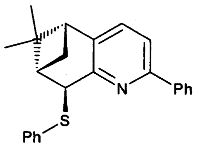
Several reports deal with the use of N,S-donor ligands, other than the oxazoline type described in Section 10.1, for palladium catalyzed asymmetric allylic alkylation. These ligands include pyridine thioethers [204,205], imine-thioethers [206] and optically active sulfoximines [207].

Enantioselective palladium-catalyzed allylic alkylation of **10.1** with the pyridine ligand **10.17** yielded ees up to 83% [204].

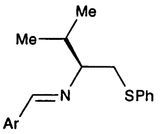
Chiral 2-(1-*p*-tolylsulfinyl)alkylpyridines and the corresponding thioether-pyridines were also prepared and applied to the enantioselective palladium catalyzed allylic alkylation [205].

A series of chiral thioether-imine ligands, like **10.18**, were prepared in two steps from commercially available (*S*)-valinol. The palladium complexes of these ligands render ee's up to 94% in the allylic alkylation of **10.1** [206].

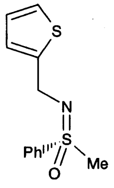
The only N,S-bidentate chiral sulfoximine ligand reported in the context of the allylic alkylation reaction is **10.19**, but its palladium complex is not active in the reported conditions. However, *N*,*N*-donor sulfoximine chiral ligand systems efficiently catalyze this reaction [207].



10.17



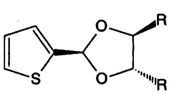
10.18



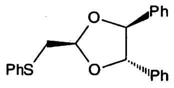
10.19

10.4. S,O-donor ligands

The enantiomerically pure acetals **10.20–10.22,** derived from C_2 chiral diols, have been prepared and used as ligands for palladium catalyzed allylic alkylation.



10.20 R = Me
10.21 R = Ph

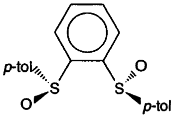


10.22

Best results were with ligand **10.22**, which afforded good yields in palladium catalyzed allylic alkylation of **10.1**. The ee's were ca. 82% [208].

10.5. Chiral bis-sulfoxide ligands

A chiral bis-sulfoxide ligand (*S*,*S*)-1,2-bis(*p*-tolylsulfinyl)benzene (**10.23**), which has *S*,*S*-bidentate chelating donor atoms on an aromatic ring, was synthesized and characterized spectroscopically. The Pd, Rh and Ru complexes were also synthesized.



10.23

The crystal structure of $[PdCl_2L]\cdot 2(C_6H_6)$ (L = **10.23** racemic) showed that the ligand has C_2-symmetry and S-coordination. The Pd complex of the optically pure ligand rendered low yields (40%) and moderate asymmetric induction (64% ee) [209].

11. Grignard cross-coupling

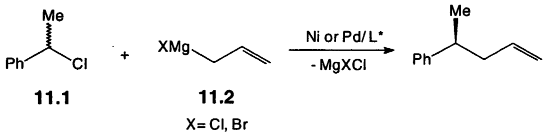
Palladium and nickel complexes with N- and P-donor ligands have been used as catalysts for the coupling of a variety of Grignard reagents with organic halides [210]. The asymmetric Grignard cross-coupling reactions is a valuable tool in organic syntheses because it allows the formation of asymmetric carbon–carbon bonds. Hayashi introduced the chiral ferrocenylphosphine ligands and used their palladium and nickel complexes in this enantioselective reaction [211].

Complexes of Ni, Pd, Pt and Cu, which contain several types of S-donor ligands, have been used in regioselective and enantioselective Grignard cross-coupling reactions. These ligands can be divided in four groups: ferrocenylamine thioethers, macrocyclic thioethers, aminoacid derivatives and aminothiolato ligands. The three first types were used to prepare Group 10 metal catalysts, while the last group was applied to Cu(I) catalyzed reactions.

11.1. Ferrocenylamine thioether ligands

The chiral ferrocenylamine thioether palladium complexes **2.22** (X = H) are effective Grignard cross-coupling catalysts for the reaction of 1-chloro-1-phenylethane (**11.1**) with allylmagnesium halides **11.2**. Yields are higher than 95% of the (1-methyl-3-butenyl)benzene and the ee's of the product range between 16–26% [26,27] (Scheme 9a).

Platinum complexes **2.22** (X = SR) and related in situ prepared nickel complexes were also used as catalysts for the previous reaction. These catalysts are interesting not only because they are air-stable and possess both center and planar chirality, but also because they render high catalytic activity and selectivity. The nickel and platinum complexes give chemical yields between 92–97% and enantiomeric excesses up to 45% [212].



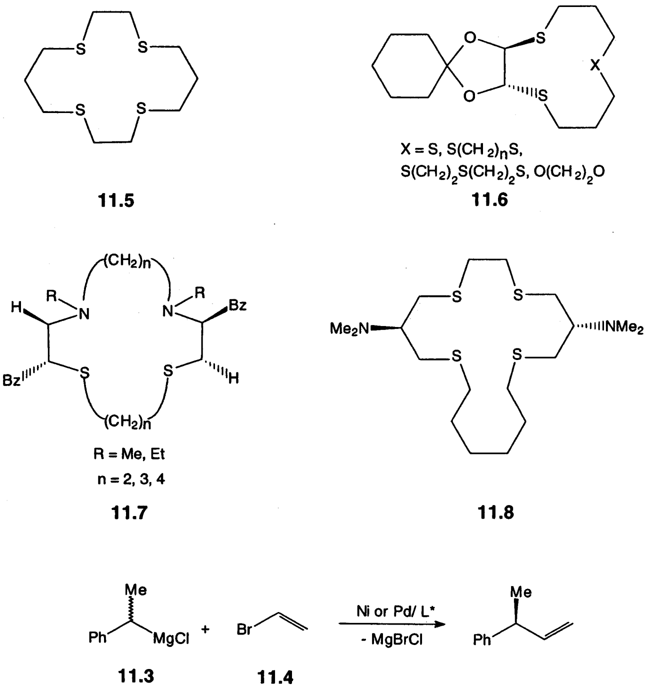
Scheme 9a.

11.2. Macrocyclic thioether ligands

Nickel complexes of macrocyclic thioether and thioether-alkylamino ligands such as **11.5**–**11.8** have been used as catalysts for the cross-coupling of the Grignard reagent of 1-phenyl-1-chloroethane **11.3** with vinyl bromide **11.4** to provide (1-methyl-2-propenyl)benzene [213] (Scheme 9b).

The achiral macrocyclic thioether 1, 4, 8, 11-tetrathiatetradecane (**11.5**) was as good as PPh_3 for this reaction, since the yields with both ligands were nearly quantitative [213a].

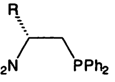
When chiral macrocycles **11.6** and **11.7** were used, yields of (1-methyl-2-propenyl)benzene were excellent in most cases but ees were poor (< 17%). On the basis of these results, ligands of the type **11.8** were prepared from L-cysteine. With the ligand **11.8** reaction TON was about 200 and the ee was 46%. An open-chain analog of **11.8** provided only a 8% ee.



Scheme 9b.

11.3. Amino acid derivative ligands (P,N-donor)

Ligands type **11.9** derived from the amino acids cystein, lysine, methionine, methionine sulfoxide, homomethionine and D-penicillamine have been prepared by alkylation of the thiol and the amine groups, the reduction of the carboxyl group and the subsequent phosphination of the alcohol [214].



11.9

R = $-CH_2SMe$
$-(CH_2)_2SMe$
$-(CH_2)SOMe$
$-(CH_2)_3SMe$

R = $-CH_2S^iPr$
$-CMe_2SMe$
$-NMe(CH_2)S^iPr$

These ligands are effective in promoting the Ni or Pd catalyzed cross coupling of the Grignard reagent of 1-chloro-1-phenylethane (**11.3**) with vinyl bromide (**11.4**). The ee's found for the coupling product ranged between 20–88%, depending on the R substituent.

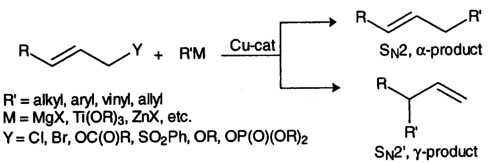
By systematically modifying the structurally variable part of the ligands a relationship between their structure and catalytic properties was established. X-ray diffraction studies of the palladium complexes [$PdLCl_2$] (L = **11.9**; R = $-(CH_2)_2SCH_3$; R = $-(CH_2)_3SCH_3$) confirm the expected coordination of the Pd by the phosphino and amino centers and reveal that there is not coordination through the thioether group. However, the nature of the side chain has a significant effect in the catalytic process, since the steric bulk of this substituent influences the enantioselectivity. On the other hand, the coordination of the sulfur atom during the catalytic has also been considered [214b].

The course of the reaction is not only affected by heteroatoms in the side chain but also by the presence of other metal cations in solution [214b]. When $ZnBr_2$ is added to the Grignard reagent, the rate of Ni or Pd catalyzed coupling with vinyl bromide increases and the direction of the enantioselection is reversed. Similar effects are observed with ZnI_2, but $ZnCl_2$ has a pronounced inhibitory effect on the cross coupling [214b].

The cross coupling of vinyl bromide to the Grignard reagent of 2-octyl chloride was also examined and enantiomeric excesses of 3-methyl-1-nonene of up to 18% were obtained [214a].

11.4. Cu catalyzed cross-coupling reactions

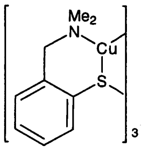
The copper catalyzed cross-coupling reaction of allylic substrates has been of considerable interest in recent years [215]. An important aspect of the cross-coupling reaction between an allylic substrate and a Grignard reagent is the regioselectivity of the carbon–carbon bond formation, that is,whether the organometallic attacks α (S_N2) or γ(S_N2') to the leaving group (Scheme 9c).



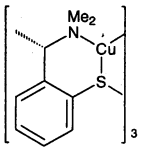
Scheme 9c.

The mechanism of these copper catalyzed cross-coupling reactions has been analyzed in several reports [215,216]. It is commonly accepted that the process involves π-allyl intermediates and the formation of allylcopper(III) species. It is also assumed that the stereo- and regioselectivity of the product is determined in different steps of the catalytic process.

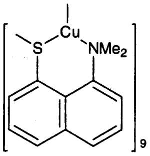
Arenethiolatecopper(I) and related catalysts have been used for the regio and stereoselective alkylation of acyclic and cyclic allylic acetates with ^{n}BuMgI [217]. These arenethiolato copper(I) catalysts have different flexibility of the hydrocarbon skeleton which connects the S- and N-donor atoms and different donor abilities of the S- and N-binding sites.



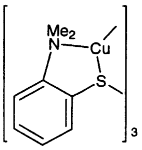
11.10



11.11

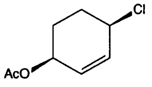


11.12

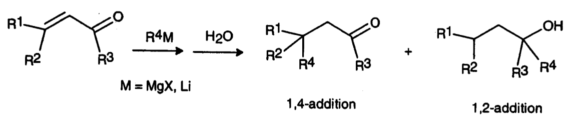


11.13

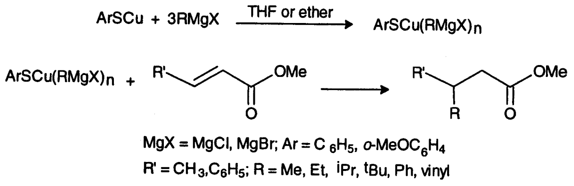
A full and interesting account of the arenethiolato copper(I) catalyzed cross-coupling reaction has been reported, which includes a discussion of the mechanism involved in this reaction and its application to a cyclic allylic substrate **11.14** [217b]. In this substrate the allylic acetoxy group can be made more reactive than the allylic chloro group using the arenethiolato copper(I) **11.10**. It has been concluded that the regioselectivity depends on the leaving group, the solvent, the temperature and the addition time of the Grignard reagent. Excellent γ-selectivity is obtained with the copper arenethiolato catalysts in Et_2O, which is attributed to the bidentate coordination of the allylic acetate to the copper(I) arenethiolato catalyst. It has also been observed that γ-selectivity is high when the reactivity of the leaving group is also high.



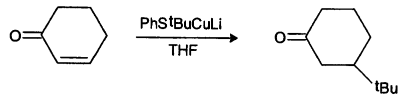
11.14



Scheme 10a.



Scheme 10b.



12.1 **12.2**

Scheme 10c.

12. Conjugate addition

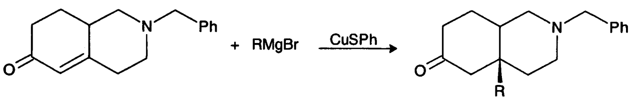
Copper(I) compounds with arenethiolato ligands are used as catalyst in the conjugate addition of Grignard or organolithium reagents to α,β-unsaturated ketones or esters (Scheme 10a). This reaction produces the 1,2- or 1,4-addition product [218].

Copper arenethiolato complexes [Cu(SAr)] (Ar = Ph, *p*-$MeOC_6H_4$) were reported to be more efficient than other copper(I) species in the addition of organocuprates $ArSCu(RMgX)_n$ to α,β-unsaturated esters such as cinnamates and crotonates (Scheme 10b) [219]. In this case the [Cu(SAr)] is not used in catalytic amounts, since the cuprate is formed stoichiometrically before the ester is added. However, the copper complex is recovered at the end of the reaction.

Copper(I) thiophenolate was first used in the conjugate addition in the case of the reaction of ^{t}BuLi towards 2-cyclohexen-1-one (**12.1**) to obtain 3-*tert*-buthyl-cyclohexanone (Scheme 10c) [220]. The yields obtained were 27–86% when a stoichiometric amount of copper reagent was used.

Conjugate addition of organomagnesianes to other cyclic ketones such as α,β-unsaturated octahydroisoquinolinones has been studied [221]. The 1,4-addition of different RMgBr reagents to 2-benzyl-6-oxo-octahydroisoquinoline **12.3** using [CuSPh] as catalyst (molar ratio **12.3**/[CuSPh] = 3/1) leads to the corresponding substituted decahydroisoquinolinones **12.4** in yields of 30–80% (Scheme 10d).

The enantioselective version of the 1,4-addition of Grignard reagents to α,β-unsaturated carbonyl compounds has been studied using different mono- and biden-

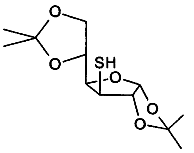


12.3 R = alkyl, alkenyl, aryl **12.4**

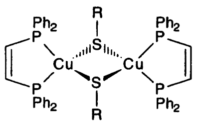
Scheme 10d.

tate chiral ligands such as monodentate thiosugars [222], heterobidentate S,N-donor ligands [223,224], oxazoline arenethiolates [225], S,O-donor ligands [226] and S,P-ligands [227]. The high efficiency of the heterobidentate ligands has been attributed to the different nature of the donor atoms since S, a soft base, creates more stable interactions with copper, and N- or O-preferentially interact with magnesium or lithium.

Reaction of the lithium salt of the monodentate thiosugar HL = **12.5** with $[Cu(CH_3CN)_4]PF_4$ gave a compound with formula [CuL] [222]. The complex could not be characterized structurally, but a diphosphine derivative $[Cu(Ph_2PCH=CHPPh_2)L]$ (**12.6**; HL = **12.5**) was characterized by X-ray diffraction. The catalytic system which was prepared in situ by adding **12.5** to Cu(I) salts in the presence of BuLi was active in the conjugate addition of Grignard reagents to 1-cyclohexen-1-one (**12.1**). In all cases, chemical yields were high (> 90%) and regioselectivities in the 1,4- product (> 98%) were excellent. The ee's ranged from 50 to 60%. This catalyst gives lower regioselectivities with other substrates such as PhCH = CHCHO or PhCH = $CHCOCH_3$. No reaction was observed with PhCH = $CHCO_2CH_3$.



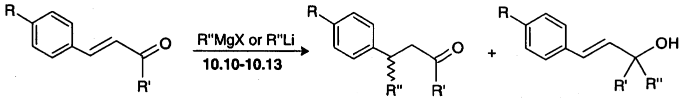
12.5



12.6

Copper(I) aminothiolato complexes (**11.10–11.13**) were prepared by van Koten and co-workers. They were used in the asymmetric conjugate addition of organo-lithium and organo-magnesium compounds to benzylideneacetone derivatives (**12.7**) to obtain the products of 1,4-addition (**12.8**) or 1,2-addition (**12.9**) (Scheme 10e) [223]. The *o*-aminoarenethiolato ligands have shown excellent properties as a non-transferable group for obtaining high chemo- and regioselectivity in this reaction.

The study of the influence of the MeLi/catalyst ratio on the distribution of the 1,2- or 1,4-addition products and the isolation of species [CuLiMeL] (L = amino-



12.7 R = H, Me, OMe, Cl, CN **12.8** **12.9**
R' = Me, iPr, tBu, Ph
R" = Me, iPr, nBu

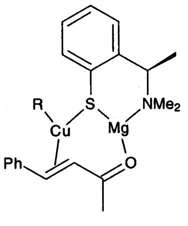
Scheme 10e.

thiolato) shows that the ligand group strongly binds to Cu(I) even in the presence of an excess of MeLi [223a]. The 1,4-addition product was almost exclusively formed at MeLi/catalyst molar ratios between 1/1–2/1.

Despite differences in the flexibility and donor properties of the ligands in complexes **11.10**, **11.12** and **11.13**, they all gave high chemoselectivities in the 1,4-reaction product [223b]. The addition of MeMgI to **12.7** ($X = H$, $R = Me$) catalyzed by the chiral complex **11.11** (9% molar ratio) yielded 97% of the 1,4-product with a 76% ee in the S enantiomer [223b].

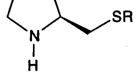
The results of the addition of RMgX reagents to the different enones **12.7** showed that the electronic and steric properties of the *para* substituent R has little effect on the chemo- and enantioselectivity of the reaction. On the other hand, in the R' substituent, the electronic effects have probably more influence on the output of the reaction than the steric effects [223b].

A synthetic study of the reactivity of the chiral aminothiolatocopper(I) complexes **11.11** with RMgX reagents showed that they form cuprate aggregates which are real precatalytic species with well defined structure [228]. It has been proposed that in these species, the thiolato group is bonded as a bridge to the copper and magnesium or lithium atoms. This interaction can be stabilized by additional *N*-coordination. Thus, the high chemo- and enantioselectivity afforded with catalyst **11.11** was explained through the formation of a key intermediate, which contains an active unit such as the one in **12.10**. The enone anchors to the Cu–Mg arenethiolato unit in a bidentate fashion with the double bond coordinated to the Cu(I) center and the oxygen coordinated to Mg(II). So, the alkyl group of the Grignard is oriented selectively towards the 4-position of the enone [223b].



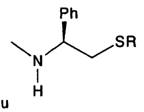
12.10

Other chiral N,S-donor ligands used in the copper catalyzed conjugate addition of MeLi to 2-cyclohexe-1-one **(12.1)** to obtain 3-methylcyclohexanone are the L-proline derivatives **12.11** and the (*S*)-phenylglycine derivatives **12.12** [229].



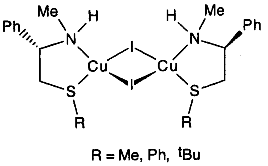
R = Me, Ph, ᵗBu

12.11



12.12

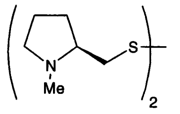
Copper(I) halides, in the presence of chiral ligands **12.11** and **12.12**, rendered isolated yields up to 46% in the 1,4-addition product. The higher ee (64% in the S isomer) was obtained with ligand **12.11** ($R = {}^{t}Bu$). With ligand **12.12** binuclear complexes **12.13** were isolated and the end of the reaction and characterized by X-ray diffraction.



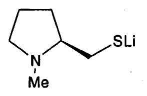
12.13

The β-aminodisulfide **12.14** and the β-aminothiolato **12.15** ligands were used in the nickel(II) catalyzed addition of diethylzinc(II) to calchone **12.7** (X = H, R = Ph) to obtain **12.16** (Scheme 10f). Results of conversion and enantioselectivity were best with the aminothiolato **12.15** (85% conversion and 50% ee).

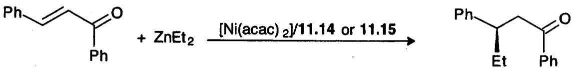
The copper(I) complexes **12.17** containing heterobidentate chiral oxazolinearenethiolato ligands **12.18** were prepared by Pfaltz and co-workers (Scheme 10g). These complexes were found to be efficient catalysts for the enantioselective conjugate addition of Grignard reagents to cyclic enones **12.19** to yield the corresponding 3-alkylketones **12.20** [225]. The methyl and isopropyl derivatives of **12.17** (R^1 = Me, ^{i}Pr; R^2 = H) are the most effective catalysts whereas the complex **12.17** (R^1 = ^{t}Bu; R^2 = H) gave markedly lower enantioselectivity. Regarding the nature of the substrate, it was noticed that ee increased with the ring size of the cycloalkenone. So, the lowest enantioselectivity was for cyclopentenone and the highest (87% ee) were for cycloheptenone.



12.14

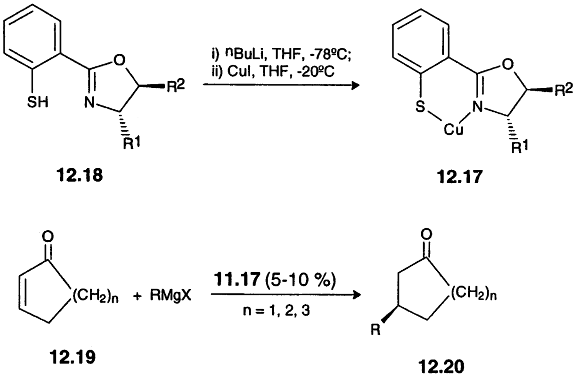


12.15



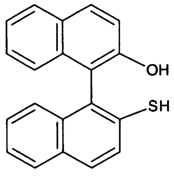
12.7 **12.16**

Scheme 10f.



Scheme 10g.

The atropoisomeric disymmetric racemic S,O-donor ligand **12.21** has been used in the copper(I) catalyzed conjugate addition of ^{n}BuLi to 2-cyclohexen-1-one **(12.1)** to obtain the 1,4-addition product **12.2** [226].



12.21

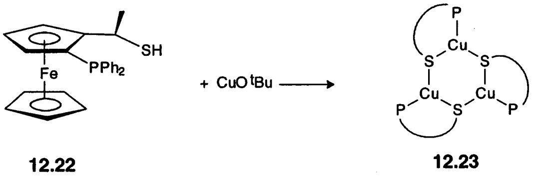
In the presence of $[Cu(MeCN)_4]BF_4$ (10%) and ^{n}BuLi, ligand **12.21** provides an active catalyst at a ligand/Cu(I) molar ratio of 12/10. In THF and 0°C, this catalyst yields 86% of the 1,4-addition product and 3% of the 1,2-addition product.

The chiral P,S-donor ferrocenyl derivative ligand **12.22** reacts with CuO^{t}Bu to form the trinuclear complex **12.23** (Scheme 10h), which structure was determined by X-ray diffraction [227]. Despite the low reactivity and high stability of this complex, it catalyses the 1,4-addition of Grignard reagents to cyclohexanone. No asymmetric induction was observed, however.

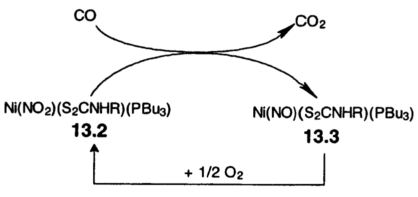
13. Oxidation with O_2

Catalytic oxidation is a field of particular interest for homogeneous catalysis. This field has been very active in the last 20 years and therefore important contributions have been made to the development of new processes for organic synthesis [230].

The activation of molecular oxygen and the homogeneous oxidation of organic substrates by transition metal complexes have been widely investigated. The main objectives in this area have been to increase the rates and selectivity of these reactions and to determine their mechanism. Several types of metal transition complexes have been investigated.

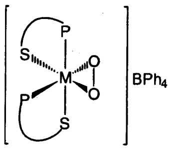


Scheme 10h.



Scheme 11a.

Cationic square–planar rhodium and iridium complexes $[ML_2]^+$, where L is a thioether-phosphine ligand $Ph_2P(CH_2)_2SR$ (**2.2**) (R = Me, Et or Ph) have been synthesized and characterized. The dioxygen adducts $[MO_2L_2]BPh_4$ (**13.1**) have been prepared by reacting the Rh(I) and Ir(I) complexes with O_2 [231]. The rhodium complexes are effective in the catalytic oxidation of terminal olefins to methyl ketones under mild conditions (25–70°C, 0.2–1 bar O_2) in acidic alcoholic media. Stoichiometric oxygen transfer takes place with no acid addition but it is required for the oxidation to become catalytic. Some mechanistic aspects of the reaction involving these and other diphosphine cationic complexes of Rh(I) have been reported [232].

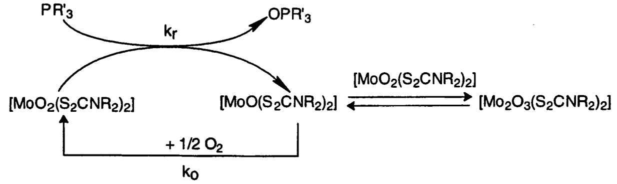


M= Rh, Ir

13.1

Four-coordinated nickel-nitro complexes containing alkyldithiocarbamate ligands have been reported to transfer O-atom to CO yielding nickel-nitrosyl complexes and CO_2. The $[Ni(NO_2)(S_2CNHR)(PBu_3)]$ (**13.2**) complexes (R = Me, Et, ^{i}Pr, ^{t}Bu) were prepared by adding $[Ni(S_2CNHR)_2]$ to $[Ni(NO_2)_2(PBu_3)_2]$ in acetone at room temperature. When CO is bubbled through C_6H_6 solutions containing **13.2**, the corresponding nitrosyl complexes $[Ni(NO)(S_2CNHR)(PBu_3)]$ (**13.3**) were obtained. This O-transfer reaction can be represented by the following scheme (Scheme 11a).

Due to the facile conversion of the nitro and nitrosyl nickel complexes, the $Ni(NO_2)$–Ni(NO) redox couple effects the homogenous oxidation of CO by O_2. The changes observed in the electronic spectra clearly indicate the interconversion of the nitro-nitrosyl complexes during the catalytic oxidation of CO by O_2 in CH_2Cl_2. The structures of the two nickel complexes were established by spectroscopic methods and susceptibility measurements. The results are consistent with a bidentate coordination mode of the dithiocarbamate ligand. Square-planar coordination around the metal is proposed for **13.2** and pseudo-tetrahedral for **13.3** [233].



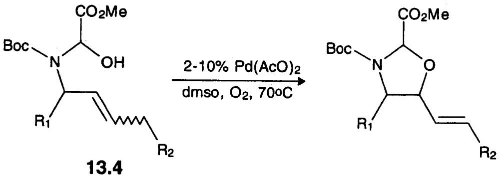
Scheme 11b.

Diethyldithiocarbamates also form molybdenum(VI) oxo complexes, which lead to the selective catalytic oxidation of tertiary phosphines by molecular oxygen. Thus, PPh_3 is oxidized by dioxo complexes $[MoO_2(S_2CNR_2)_2]$ ($R = C2$-4 alkyl) to give $OPPh_3$ and $[MoO(S_2CNR_2)_2]$. This reacts with further $[MoO_2(S_2CNR_2)_2]$ to yield the Mo(V) complexes $[Mo_2O_3(S_2CNR_2)_4]$ which serve as well as oxidant in the reaction. At 1 bar of O_2, the rate limiting step is the oxidation of the Mo(IV) to Mo(VI) ($k_r > k_o$). The following scheme has been proposed for the catalytic oxidation [234] (Scheme 11b).

Some dmso-stabilized palladium clusters have been investigated as catalysts for homogeneous oxidation. Thus, the catalytic system $Pd(OAc)_2$/dmso/O_2 is quite versatile for oxidative reactions. The giant palladium clusters stabilized by the sulfoxide solvent are efficient catalysts for the oxidative cyclization of allylic *N*-hydroxymethyl carbamates (**13.4**). The dmso plays an essential role in this process, since the palladium catalyst can interact with either the harder O-donor or the softer S-donor sites of the ligand during the catalytic cycle. The Pd(0) species formed after the reduction of Pd(II) intermediate by oxidative cyclization is assumed to be stabilized by the S-dmso ligand and reoxidized by molecular oxygen to catalyze further cyclizations [235] (Scheme 11c).

The presence of large palladium clusters with more or less uniform size distribution was shown by electron microscopy techniques. The infrared spectrum of these materials indicates the presence of two different types of coordinated Me_2SO through the O or S atom [236].

Nickel complexes with sterically restricted dithiolate ligands activate O_2. These adducts oxidize sulfur containing substrates, including the coordinated ligand.



13.4

Scheme 11c.

Although the reaction is stoichiometric, it could have significant catalytic implications [237].

14. Summary

Thioethers are the most widely used sulfur ligands in catalysis. However, rhodium complexes of thioethers or dithioethers have hardly been used in hydrogenation, because their catalytic activity is lower than that of other rhodium catalysts. On the other hand, iridium complexes containing thioether ligands are active catalysts in the hydrogenation of different substrates, even at low pressures. Furthermore, recent works have shown that chiral dithioether-iridium complexes render fair ee's in the hydrogenation of prochiral acrylic acids. Platinum complexes with thioether ligands in the presence of a $SnCl_2$ co-catalyst, as well as palladium complexes with thioether-amine ligands, are active in the selective hydrogenation of polyenes to monoenes, at moderate pressures (4–50 bar). Both catalytic systems are also active in the isomerization of alkenes.

A broad family of platinum-thioeter catalysts has been assayed in the hydrosilylation of alkenes and alkynes. These catalysts include simple thioethers and more elaborate heteropolydentate ligands, which contain the thioether group. They are selective in the formation of the linear silyl product, when the substrate is an unfunctionalized 1-alkene. Cationic rhodium(I) and ruthenium(II) catalysts which contain atropoisomeric macrocyclic S_4-thioethers are active in the hydrosilylation of prochiral ketones with Ph_2SiH_2. Optical yields (ca. 50% ee) have been moderate with these systems. Rh(III) and Pt(II) complexes of S_3-macrocyclic thioethers, in the presence of MAO, are active in the polymerization of ethylene.

Rhodium complexes of bidentate thioether-phosphine ligands, in the presence of a basic co-catalyst (KOH), are moderately active in the hydrogen transfer from alcohols to ketones. Chiral ligands of this type afforded low ee's in the reduction of acetophenone with ^{i}PrOH. Rhodium thioether-phosphine complexes, under CO pressure and in the presence of MeI, are very active catalysts for the carbonylation of methanol to yield acetic acid.

Palladium complexes of heterobidentate ligands, oxazoline-thioether, phosphinothioether and ether-thioether render excellent yields and ee's in the asymmetric alkylation of allylic acetates with dialkylmalonate.

Palladium and nickel complexes of chiral amino-thioether ligands catalyze the Grignard cross-coupling between allylmagnesium bromide and 1-chloro-1-phenylethane. Chemical and optical yields are good with these catalysts. Nickel complexes of macrocyclic thioethers are also active in cross-coupling reactions between halides and secondary Grignard reagents. The ee's of related chiral macrocyclic thioether nickel catalysts reach ca. 50%.

Mononuclear dihydrido Rh(III) and binuclear Rh(I) thiolato complexes, both of which have P-donor ancillary ligands, have been used in the hydrogenation of olefins. The mononuclear species are more active than the dimers, but the former evolve to the latter under reaction conditions.

Heterobridged binuclear species $[Rh_2(\mu\text{-}Cl)(\mu\text{-}SR)(CO)_2(PR_3)_2]$ are active catalysts in the hydrogenation of different substrates at moderate pressures. Species of this type, which contain either chiral thiolato or chiral P-donor ligands, yield fair to good ee's in the hydrogenation of acrylic acids, although the conversions are not always satisfactory.

Thiolato bridged binuclear platinum(II) complexes, in the presence of $SnCl_2$, are also active in the hydrogenation of olefins, although pressures need to be higher than 50 bar of H_2 to carry out the reaction.

Considerable efforts have been devoted to the study of rhodium binuclear thiolato complexes as hydroformylation catalysts. They have been applied to different substrates. Furthermore, a number of chiral dithiolato ligands have been synthesized in an attempt to increase the enantioselectivy of the process. Nevertheless, the ee's were always very low and, in some cases, the regioselectivities were not far from the ones obtained using rhodium systems without dithiolato ligands in the same conditions. Mechanistic studies have been carried out in some of these systems, although the kinetic studies were not conclusive. When the characterization of the species under reaction conditions has been investigated through HP-NMR and HPIR, partial cleavage of the binuclear species has been observed with the subsequent formation of $[RhH(CO)_2P_2]$ and related species. These are, at least in part, responsible for the catalytic activity of these systems.

Copper(I) thiolato and amino-thiolato species active catalysts for the 1,4-addition of RMgX or RLi to α,β-unsaturated ketones, giving good ee's in some cases.

A limited number of efficient transition metal catalysts, which contain S-donor ligands other than thioether or thiolato type, have been reported. These include the ruthenium complexes of chiral bidentate sulfoxide ligands, which were applied to the asymmetric hydrogenation of acrylic acids; a palladium complex of this family of ligands, which was used in allylic alkylation; and a hydrogen transfer Rh(I) catalyst containing a methionine sulfoxide ligand. It has also been reported that dmso is a good ligand–solvent for palladium-catalyzed oxidation.

Finally, high reaction rates were reported in the carbonylation of methanol, with a rhodium catalyst of a bidentate phosphine-phosphine sulfide ligand, promoted by MeI.

Acknowledgements

We thank DGR and CAICYT (project QFN95-4725-C03) for financial support and our colleagues for allowing their results to be used in this review. Part of the work described in this review was carried out in the frame of the COST Chemistry D2 project ('Stereoselective reactions promoted by metal complexes with chiral ligands containing sulfur donors') of the EU.

References

[1] (a) L.H. Pignolet (Ed.), Homogeneous Catalysis with Metal Phosphine Complexes, Plenum Press, New York, 1983. (b) M.C. Simpson, D.J. Cole-Hamilton, Coord. Chem. Rev. 155 (1996) 163. (c) B. Cornils, W.H. Herrmann (Eds.), Applied Homogenous Catalysis with Organometallic Compounds, VCH, Weinheim, 1996.

[2] (a) A. Togni, L.M. Venanzi, Angew. Chem. Int. Ed. Eng. 33 (1994) 497. (b) A.K. Gosh, P. Mathiavanan, J. Cappiello, Tetrahedron Asymmetry 9 (1998) 1. (c) A.M.d'A. Rocha Gonsalves, M.M. Pereira, J. Mol. Catal. 113 (1996) 209.

[3] (a) R.A. Johnson, K.B. Sharpless, Catalytic Asymmetric Synthesis I. Ojima (Ed.), VCH, New York, 1993. (b) M. Bougauchi, S. Watanabe, T. Arai, H. Sasai, M. Shibashaki, J. Am. Chem. Soc. 119 (1997) 2329.

[4] (a) S.E. Livingstone, Q. Rev. Chem. Soc. 19 (1965) 386. (b) S.G. Murray, F.R. Hartley, Chem. Rev. 81 (1981) 365. (c) E.W. Abel, S.K. Barghava, K.G. Orrell, in: S.L. Lippard (Ed.), Progres in Inorganic Chemistry, Wiley, New York, 1984, p. 1. (d) G. Dance, Polyhedron 5 (1986) 1037. (e) K.G. Orrell, Coord. Chem. Rev. 96 (1989) 1. (f) P.J. Blower, J.R. Dilworth, Coord. Chem. Rev. 76 (1987) 121. (g) J.R. Dilworth, J. Hu, Adv. Inorg. Chem. 40 (1993) 411. (h) I. Dance, K. Fisher, Prog. Inorg. Chem. 41 (1994) 637.

[5] M. Rakowski DuBois, Chem. Rev. 89 (1989) 1.

[6] (a) C. Bianchini, A. Meli, in: B. Cornils, W.H. Herrmann (Eds.), Applied Homogenous Catalysis with Organometallic Compounds, VCH, Weinheim, Germany, 1996, p. 969. (b) R.J. Angelici, Coord. Chem. Rev. 105 (1990) 61. (c) R.A. Sanchez-Delgado, J. Mol. Catal. 86 (1994) 287. (d) T.B. Rauchfuss, Prog. Inorg. Chem. 39 (1991) 259.

[7] W.J. Xiao, H. Alper, J. Org. Chem. 62 (1997) 3422.

[8] (a) H.B. Kagan, in: I. Ojima (Ed.), Catalytic Asymmetric Synthesis VCH, New York, 1993, p. 203–226. (b) T. Nanno, N. Sakai, K. Nozaki, H. Takaya, Tetrahedron Asymmetry 6 (1995) 2583.

[9] A. Ogawa, H. Kuniyasu, N. Sonoda, T. Hirao, J. Org. Chem. 62 (1997) 8361.

[10] (a) R.K. Bhatia, G.N. Rao, Synth. React. Inorg. Met. Org. Chem. 25 (1995) 781. (b) R.K. Bhatia, G.N. Rao, J. Mol. Catal. 93 (1994) 29.

[11] (a) H. Alper, F. Sibtain, J. Org. Chem. 53 (1988) 3306. (b) B.R. James, Pure Appl. Chem. 69 (1997) 2213.

[12] H.A. Tayim, J.C. Bailar Jr., J. Am. Chem. Soc. 89 (1967) 4330.

[13] (a) H.C. Clark, C. Billard, C.S. Wong, J. Organomet. Chem. 190 (1980) C105. (b) G.K. Anderson, C. Billard, H.C. Clark, J.A. Davies, C.S. Wong, Inorg. Chem. 22 (1983) 439.

[14] F.P. 1.538.700 (Chem. Abs. 71 (1969) 317).

[15] (a) B.R. James, Coord. Chem. Rev. 1 (1966) 505. (b) B.R. James, F.T.T. Ng, G.L. Rempel, Inorg. Nucl. Chem. Lett. 4 (1968) 197. (c) B.R. James, F.T.T. Ng, J. Chem. Soc. (A) (1972) 355. (d) B.R. James, F.T.T. Ng, J. Chem. Soc. (A) (1972) 1321. (e) B.R. James, F.T.T. Ng, Can. J. Chem. 53 (1975) 797.

[16] M.J.H. Russell, C. White, A. Yates, P.M. Maitlis, J. Chem. Soc. Dalton Trans. (1978) 849.

[17] C. Claver, J.C. Rodnguez, A. Ruiz, J. Organomet. Chem. 251 (1983) 369.

[18] J. Sole, C. Bo, C. Claver, A. Ruiz, J. Mol. Catal. 61 (1990) 163.

[19] (a) A.R. Sanger, C.G. Lobe, J.R. Weiner-Fedorak, Inorg. Chim. Acta, 53 (1981) L123. (b) A.R. Sanger, Can. J. Chem. 60 (1982) 1363.

[20] S. Rossi, K. Kallinen, J. Pursiainen, T.T. Pakkanen, T.A. Pakkanen, J. Organomet. Chem. 419 (1991) 219.

[21] C. Vinas, M.A. Flores, R. Nunez, F. Teixidor, R. Kivekas, R. Sillanpaa, Organometallics 17 (1998) 2278.

[22] B.R. James, R.H. Morris, K.J. Reimer, Can. J. Chem. 55 (1977) 2353.

[23] (a) M. Diéguez, A. Orejón, A.M. Masdeu-Bulto, R. Echarri, S. Castillon, C. Claver, A. Ruiz, J. Chem. Soc. Dalton Trans. (1997) 4611. (b) M. Diéguez, A. Ruiz, C. Claver, M.M. Pereira, A.M.d'A. Rocha Gonsalves, J. Chem. Soc. Dalton Trans. (1998) 3517.

[24] F. Fache, P. Gamez, F. Nour, M. Lemaire, J. Mol. Catal. 85 (1993) 131.

[25] M.O. Okoroafor, L.H. Shen, R.V. Honeychuck, C.H. Brubaker Jr., Organometallics 7 (1988) 1297.
[26] R.V. Honeychuck, M.O. Okoroafor, L.H. Shen, C.H. Brubaker Jr., Organometallics 5 (1986) 482.
[27] A.A. Naiini, C.K. Lai, D.L. Ward, C.H. Brubaker Jr., J. Organomet. Chem. 390 (1990) 73.
[28] C.K. Lai, A.A. Naiini, C.H. Brubaker Jr., Inorg. Chim. Acta 164 (1989) 205.
[29] A.A. Naiini, M.O. Okoroafor, C.H. Brubaker Jr., J. Mol. Catal. 54 (1989) L27.
[30] C.H. Wang, C.H. Brubaker Jr., J. Mol. Catal. 75 (1992) 221.
[31] M. Bressan, C. Bonuzzi, F. Morandini, A. Morvillo, Inorg. Chim. Acta 182 (1991) 153.
[32] B.R. James, R.S. McMillan, Can. J. Chem. 55 (1977) 3927.
[33] B.R. James, R.S. McMillan, R.H. Morris, D.K.W. Wang, Adv. Chem. Ser. 167 (1978) 122.
[34] R.H. Crabtree, A. Gautier, G. Giordano, T. Khan, J. Organomet. Chem. 141 (1977) 113.
[35] Ph. Kalck, R. Poilblanc, R.-P. Martin, A. Rovera, A. Gaset, J. Organomet. Chem. 195 (1980) C9.
[36] L. Carlton, Phosphorus Sulfur Silicon 59 (1991) 231.
[37] H. Schumann, H. Hemling, N. Goren, J. Blum, J. Organomet. Chem. 485 (1995) 209.
[38] (a) H. Schumann, G. Cielusek, J. Pickardt, Agnew. Chem. Int. Ed. Eng. 19 (1984) 70. (b) M. Eisen, J. Blum, H. Schumann, J. Mol. Catal. 31 (1985) 317. (c) M. Eisen, T. Bernstein, J. Blum, H. Schumann, J. Mol. Catal. 43 (1987) 199.
[39] M. Eisen, J. Blum, H. Schumann, B. Gorella, J. Mol. Catal. 56 (1989) 329.
[40] M. Eisen, P. Weitz, S. Shtelzer, J. Blum, H. Schumann, B. Gorella, F.H. Gorlitz, Inorg. Chim. Acta 188 (1991) 167.
[41] H. Schumann, B. Gorella, M. Eisen, J. Blum, J. Organomet. Chem. 412 (1991) 251.
[42] H.C. Clark, V.K. Jain, G.S. Rao, J. Organomet. Chem. 279 (1985) 181.
[43] V.K. Jain, G.S. Rao, Inorg. Chim. Acta 127 (1987) 161.
[44] C.P. Kubiak, C. Woodcock, R. Eisenberg, Inorg. Chem. 19 (1980) 2733.
[45] C.P. Kubiak, R. Eisenberg, Inorg. Chem. 19 (1980) 2726.
[46] D.I. Gilmour, M.A. Luke, D.M.P. Mingos, J. Chem. Soc. Dalton Trans. (1987) 335.
[47] R.H. Holm, Acc. Chem. Res. 10 (1977) 427.
[48] H. Inoue, M. Suzuki, J. Chem. Soc. Chem. Commun. (1980) 817.
[49] S. Kuwabata, K. Tanaka, T. Tanaka, Inorg. Chem. 25 (1986) 1691.
[50] C.J. Casewit, D.E. Coons, L.L. Wright, W.K. Miller, M. Rakowski DuBois, Organometallics 5 (1986) 951.
[51] L.L. Lopez, J. Gabay, R.C. Haltiwanger, K. Green, J. Allshouse, C.J. Casewit, M. Rakowski DuBois, Organometallics 12 (1993) 4764.
[52] M. Mckenna, L.L. Wright, D.J. Miller, L. Tanner, R.C. Haltiwanger, M. Rakowski DuBois, J. Am. Chem. Soc. 105 (1983) 5329.
[53] (a) C. Claver, F. Gili, J. Vinas, A. Ruiz, Polyhedron 6 (1987) 1329. (b) C. Claver, A. Ruiz, A.M. Masdeu, J. Vinas, T. Saballs, F.J. Lahoz, F.J. Plou, J. Organomet. Chem. 373 (1989) 2665.
[54] H. Brunner, H.-J. Lautenschlager, W.A. Koning, R. Krebber, Chem. Ber. 123 (1990) 847.
[55] A.W. Gal, F.H.A. Bolder, J. Organomet. Chem. 142 (1977) 375.
[56] R.H. Crabtree, A. Gautier, G. Giordano, T. Khan, J. Organomet. Chem. 141 (1977) 113.
[57] Z.-Q. Wang, S.-W. Lu, H.-F. Guo, N.H. Hu, Polyhedron 11 (1992) 1131.
[58] Y. Zhang, S. Liao, Y. Xu, S. Chen, J. Organomet. Chem. 382 (1990) 69.
[59] J.A. Cabeza, V. Riera, M.A. Villa-Garcia, L. Ouahab, S. Triki, J. Organomet. Chem. 441 (1992) 323.
[60] V.M. Belousov, T.A. Palchevskaya, L.V. Bogutskaya, L.A. Zyuzya, J. Mol. Catal. 60 (1990) 165.
[61] A. Bacchi, M. Carcelli, M. Costa, A. Leporati, E. Leporati, P. Pelagatti, C. Pelizzi, G. Pelizzi, J. Organomet. Chem. 535 (1997) 107.
[62] R.A.W. Johnstone, A.H. Wilby, I.D. Entwistle, Chem. Rev. 85 (1985) 129.
[63] G. Zassinovich, G. Mestroni, S. Gladiali, Chem. Rev. 92 (1992) 1051.
[64] S. Gladiali, A. Dore, D. Fabri, Tetrahedron Asymmetry 5 (1994) 1143.
[65] P. Barbaro, C. Bianchini, A. Togni, Organometallics 16 (1997) 3004.
[66] P. Kvintovics, B.R. James, B. Heil, J. Chem. Soc. Chem. Commun. (1986) 1810.

[67] A.A. Naiini, H.M. Ali, C.H. Brubaker Jr., J. Mol. Catal. 67 (1991) 47.
[68] (a) H. Schumann, G. Cielusek, S. Jurgis, E. Hahn, J. Pickardt, J. Blum, Y. Sasson, A. Zoran, Chem. Ber. 117 (1984) 2825. (b) H. Schumann, S. Jurgis, H. Stanislaw; P. Ekkehardt, J. Blum, M. Eisen, Chem. Ber. 118 (1985) 2738.
[69] L.Kh. Freidlin, N.M. Nazarova, Y.A. Kopyttsev, Izv. Akad. Nauk. SSSR, Ser. Khim. (1972) 201.
[70] Y.A. Kopyttsev, L.Kh. Freidlin, N.M. Nazarova, I.P. Yakovlev, Izv. Akad. Nauk. SSSR, Ser. Khim. (1975) 997.
[71] H. Kanai, S. Sakaki, T. Sakatani, Bull. Chem. Soc. Jpn. 60 (1987) 1589.
[72] S.J. Brown, L.M. Clutterbuck, C. Hinton, G.B. Humphreys, A.F. Masters, J.I. Sachinidis, P.A. Tregloan, Prepr. Am. Chem. Soc. Div. Pet. Chem. 36 (1991) 569.
[73] M. Kajitani, T. Fujita, T. Okumachi, M. Yokoyama, H. Hatano, H. Ushijima, T. Akayama, A. Sugimori, J. Mol. Catal. 77 (1992) L1.
[74] A.E. Tromifov, V.N. Spevak, V.I. Lobadyuk, N.K. Skvortsov, V.O. Reikhsfeltd, Zh. Obshch. Khim. 59 (1989) 2048.
[75] G. Chandra, British patent 73-5962 730207 for Dow Corning Ltd. (1973), CA 86:72861.
[76] X. Hu, Z. Tian, X. Lu, Y.Y. Chen, Chin. J. Catal. 18 (1997) 187.
[77] Y.Y. Chen, Y.S. Zhou, X.H. Tong, Q. Liu, Z.L. Zhong, Chem. Res. Chin. Univ. 14 (1998) 101.
[78] Y.Y. Chen, Z.L. Zhong, Y.S. Zhou, B.L. Zhang, X.R. Lu, Chin. Chem. Lett. 8 (1997) 213.
[79] L.N. Lewis, N. Lewis, J. Am. Chem. Soc. 108 (1986) 7228.
[80] A.H. Vetter, A. Berkessel, Synthesis (1995) 419.
[81] L.Z. Wang, Y.Y. Jiang, J. Organomet. Chem. 251 (1983) 39.
[82] R.A. Drake, B.J. Griffiths, D.R. Randall, Eur. Pat. Appl. for Dow Corning Corp. UK, EP 546716 (1993), CA 119:160553.
[83] Y.Y. Chen, L. Meng, L. Li, X.R. Lu, Chin. J. React. Polym. 1 (1992) 182.
[84] M.Z. Cai, C.S. Song, J.M. Chen, Yingyong Huaxue (CA :248503) 14 127 (1997) 37.
[85] Y.Y. Chen, L. Meng, L. Li, X. Lu, Chin. J. React. Polym. 1 (1992) 152.
[86] C.Y. Hu, X.M. Han, Y.Y. Jiang, Kexue Tongbao 33 (1988) 843.
[87] C.Y. Hu, X.M. Han, Y.Y. Jiang, J. Mol. Catal. 35 (1986) 329.
[88] C.Y. Kan, Q Yuan, A. Luo, X.Z. Kong, Polym. Adv. Technol. 7 (1996) 76.
[89] K. Matsumura, S. Ichinohe, Jpn. Kokai Tokkyo Koho for Shinetsu Chem. Ind. Co. JP 08127584 (1996) CA 125:168926.
[90] A.E. Tromifov, N.K. Skvortsov, V.N. Spevak, V.I. Lobadyuk, V.Y. Komarov, V.O. Reikhsfeld, Zh. Obshch. Khim. 60 (1990) 276.
[91] A.V. Kalinin, A.E. Tromifov, N.K. Skvortsov, Russ. J. Gen. Chem. 67 (1997) 820.
[92] H. Brunner, H. Nishiyama, K. Itoh, in: I. Ojima (Ed.), Catalytic Asymmetric Synthesis, VCH, New York, 1993, pp. 303–322.
[93] Y. Nishibayashi, K. Segawa, J.D. Singh, S. Fukuzawa, K. Ohe, S. Uemura, Organometallics 15 (1996) 370.
[94] H. Yoshida, T. Ueda, Jpn. Kokai Tokkyo Koho for Takasago Perfumery, JP 08134064 (1996) CA 125:195700.
[95] H. Yoshida, T. Ueda, Jpn. Kokai Tokkyo Koho for Takasago Perfumery, JP 08217775 (1996) CA 125:301032.
[96] T. Ueda, T. Adachi, K. Sumiya, T. Yoshida, J. Chem. Soc. Chem. Commun. (1995) 935.
[97] J.W. Faller, K.J. Chase, Organometallics 13 (1994) 989.
[98] (a) H. Brunner, G. Riepl, H. Weitzer, Agnew. Chem. Int. Ed. Engl. 22 (1983) 331. (b) H. Brunner, R. Becker, G. Riepl, Organometallics 3 (1984) 1354.
[99] G. Balavoine, J.C. Clinet, I. Lellouche, Tetrahedron Lett. 30 (1989) 5141.
[100] H. Li, J. Yao, B. He, Sci. China, Ser. B Chem. 40 (1997) 485.
[101] A.V. Iretskii, G.B. Kagan, Russ. J. Gen. Chem. 67 (1997) 331.
[102] M. Gaup, A. Seidel, P. Torrence, P. Heymanns, in: B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, VCH, Weinheim, 1996, pp. 106–115.
[103] J.M. Pearson, A. Haynes, G.E. Morris, G.J. Sunley, P.M. Maitlis, J. Chem. Soc. Chem. Commun. (1995) 1045.

[104] K.M. Weber, B.C. Gates, W. Drenth, J. Catal. 47 (1977) 269.

[105] K.M. Weber, B.C. Gates, W. Drenth, J. Mol. Catal. 3 (1977) 1.

[106] Z.Y. Liu, P.L. Pan, M.K. Huang, Faming Zhuanli Shenqing Gongkai Shnomingshu CN 95 1105604 (1995), CA 124:90933.

[107] M.J. Baker, M.F. Giles, A.G. Orpen, M.J. Taylor, R.J. Watt, J. Chem. Soc. Chem. Commun. (1995) 197.

[108] (a) R.W. Wegman, A.G. Abatjoglou, A.M. Harrison, J. Chem. Soc. Chem. Commun. (1987) 1891.

[109] J.R. Dilworth, J.R. Miller, N. Wheatley, M.J. Baker, J.G. Sunley, J. Chem. Soc. Chem. Commun. (1995) 1579.

[110] Z. Zhang, H. Xi, W. Zhao, K. Jiang, R. Wang, H. Wang, Y. Wu, J. Organomet. Chem. 454 (1993) 221.

[111] W.R. Pretzer, T.P Kobylinski, J.E. Bozik, US patent for Gulf 80-215554 801211, CA 97181717.

[112] L. Zhang, J. Yang, D. Huang, G. Li, Sci. China Ser. B 36 (1993) 513.

[113] Ph. Kalck, C. Serra, C. Machet, R. Broussier, B. Gautheron, G. Delmas, G. Trouve, M. Kubicki, Organometallics 12 (1993) 1021.

[114] (a) M. Beller, B. Cornils, C.D. Frohning, C.W. Kohlpaintner, J. Mol. Catal. A, 104 (1995) 17. (b) C.D. Frohhning, C.W Kohlpaintner, in: B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, Springer Verlag, Weinheim, 1996, p. 29–90.

[115] P.W.N.M van Leeuwen, in: J.A. Moulijn, P.W.N.M van Leeuwen, R.A. van Santen (Eds.), Surface Science and Catalysis, Elsevier, Amsterdam, 1993 (Chapter. 6.2).

[116] (a) S. Gladiali, J.C. Bayon, C. Claver, Tetrahedron Asymmetry 6 (1995) 145. (b) F. Agbossou, J.F. Carpentier, A. Mortreux, Chem. Rev. 95 (1995) 2485.

[117] J.M. Brown, A. Kent, J. Chem. Soc. Perkins Trans. (1987) 1597.

[118] (a) N. Sakai, S. Mano, K. Nozaki, H. Takaya, J. Am. Chem. Soc. 115 (1993) 7033. (b) T. Horiuchi, T. Ohta, E. Shirakawa, K. Nozaki, H. Takaya, J. Org. Chem. 62 (1997) 4285. (c) C.P. Casey, G.T. Whiteker, M.G. Melville, L.M. Petrovich, J.A. Gavney Jr., D.R. Powell, J. Am. Chem. Soc. 114 (1992) 5535. (d) G.J.H. Buisman, E.J. Vos, P.C.J. Kamer, P.W.N.M. van Leenwen, J. Chem. Soc. Dalton Trans. (1995) 409. (e) G.J.H. Buisman, L.A. van der Veen, P.C.J. Kamer, P.W.N.M. van Leenwen, Organometallics 16 (1997) 5681.

[119] L. Marko, Acta Chim. 59 (1969) 367.

[120] (a) Ph. Kalck, J.M. Frances, P.M. Pfister, T.G. Southern, A. Thorez, J. Chem. Soc. Chem. Commun. (1983) 510. (b) J.M. Frances, A. Thorez, Ph. Kalck, C, Mol. Chem. 1 (1985) 213.

[121] (a) Ph. Kalck, in: A. de Meijere, H. Tom Dick (Eds.), Organometallics in Organic Syntheses, Springer Verlag, Weinheim, 1987, p. 297. (b) Ph. Kalck, Polyhedron 7 (1988) 2441.

[122] Ph. Kalck, Y. Peres, R. Queau, J. Molinier, P. Escaffre, E. Leandro, B. Peyrille, J. Organomet. Chem. 426 (1992) C16.

[123] P. Escaffre, A. Thorez, Ph. Kalck, B. Besson, R. Perron, Y. Colleuille, J. Organomet. Chem. 302 (1986) C17.

[124] A. Dedieu, P. Escaffre, J.M. Frances, Ph. Kalck, Nouv. J. Chim. 10 (1986) 631.

[125] R. Davis, J.W. Epton, T.G. Southern, J. Mol. Catal. 77 (1992) 159.

[126] (a) Ph. Kalck, P. Escaffre, F. Serein-Spirau, A. Thorez, B. Besson, Y. Coleuille, R. Perron, New J. Chem. 12 (1988) 687. (b) Ph. Kalck, Pure Appl. Chem. 61 (1989) 967.

[127] F. Monteil, R. Queau, Ph. Kalck, J. Organomet. Chem. 480 (1994) 177.

[128] Ph. Kalck, F. Serein-Spirau, New J. Chem. 13 (1989) 515.

[129] C. Claver, J. Fis, Ph. Kalck, C. Bourgeois, C. Demay, C_1 Mol. Chem. 2 (1987) 25.

[130] (a) J.M. Frances, A. Thorez, Ph. Kalck, New J. Chem. 8 (1984) 213. (b) I. C^iPres, Ph. Kalck, D.C. Park, F. Serein Spirau, J. Mol. Catal. 66 (1991) 399.

[131] S. Sirol, Ph. Kalck, New J. Chem. 21 (1997) 1129.

[132] (a) F. Senocq, C. Randrianalimanana, A. Thorez, Ph. Kalck, R. Choukroun, D. Gervais, J. Chem. Soc. Chem. Commun. 20 (1984) 1376. (b) Ph. Kalck, C. Randrianalimanana, M. Ridmy, A. Thorez, H. tom Dieck, J. Ehlers, New J. Chem. 12 (1988) 679. (c) R. Choukroun, F. Dahan,

D. Gervais, Ch. Rifa, Organometallics 9 (1990) 1982. (d) F. Senocq, C. Randrialimanana, A. Thorez, Ph. Kalck, J. Mol. Catal. 35 (1986) 35.

[133] R. Choukroun, D. Gervais, J. Jaud, Ph. Kalck, F. Senocq, Organometallics 5 (1986) 67.

[134] (a) D. Cruz-Garritz, B. Rodriguez, H. Torrens, J. Leal, Transition Met. Chem. 9 (1984) 284. (b) C. Claver, A.M. Masdeu, N. Ruiz, C. Foces-Foces, F. Cano, C. Apreda, L.A. Oro, J. Garcia Alejandre, H. Torrens, J. Organomet. Chem. 398 (1990) 177.

[135] J.C. Bayon, J. Real, C. Claver, A. Polo, A. Ruiz, J. Chem. Soc. Chem. Commun. (1989) 1056.

[136] A. Polo, C. Claver, S. Castillón, A. Ruiz, J.C. Bayon, J.C. Real, J. Mealli, D. Masi, Organometallics 11 (1992) 3525.

[137] C. Claver, Ph. Kalck. M. Ridmy, A. Thorez, L.A. Oro, M.T. Pinillos, M.C. Apreda, F. Cano, C, Foces-Foces, J. Chem. Soc. Dalton Trans. (1988) 1523.

[138] H. Schumann, S. Jurgis, E. Hahn, J. Pickardt, J. Blum, M. Eisen, Chem. Ber. 118 (1985) 2738.

[139] A. Orejon, C. Claver, L.A. Oro, A. Elduque, M.T. Pinillos, J. Mol. Catal. 136 (1998) 279.

[140] J.L.G. Fierro, M. Martinez-Ripoll, M. Merchan, A. Rodriguez, P. Terreros, H. Torrens, M.A. Vivar-Cerrato, J. Organomet. Chem. 544 (1997) 243.

[141] M. Dieguez, C. Claver, A.M. Masdeu-Bultó, A. Ruiz, P.W.N.M. van Leeuwen, G. Schoemaker, Organometallics 18 (1999) 2107.

[142] A. Polo, E. Fernandez, C. Claver, S. Castillón, J. Chem. Soc. Chem. Commun. (1992) 642.

[143] E. Fernandez, A. Ruiz, C. Claver, S. Castilldn, A. Polo, J.F. Piniella, A. AlvarezLarena, Organometallics 17 (1998) 2857.

[144] R.H. Gao, R.J. Angelici, Organometallics 17 (1998) 3063.

[145] J. Balue, J.C. Bayón, J. Mol. Catal. A 137 (1999) 193.

[146] H.J. Zong, X.Y. Guo, Q. Tang, Y. Jin, Y.J. Li, Y.Y. Jiang, Macromol. Sci. Chem. 24 (1987) 277.

[147] D. Cauzzi, M. Costa, L. Gonsalvi, M.A. Pellinghelli, G. Predieri, A. Tiripicchio, R. Zanoni, J. Organomet. Chem. 541 (1997) 377.

[148] Ph. Kalck, E.L. de Oliveira, R. Queau, B. Peyrille, J. Molinier, J. Organomet. Chem. 433 (1992) C4.

[149] P. Terreros, E. Pastor, J.M. Palacios, J.L.G. Fierro, Surf. Interf. Anal. 15 (1990) 279.

[150] A.M. Masdeu, C. Claver, S. Castillón, A. Ruiz, C. B6, J.M. Poblet, P. Sarasa, P. Chaloner, P.J. Hitchcock, J. Chem. Soc. Dalton Trans. (1993) 2689.

[151] A. Aaliti, A.M. Masdeu, A. Ruiz, C. Claver, J. Organomet. Chem. 489 (1995) 101.

[152] C. Claver, S. Castillón, N. Ruiz, G. Delogu, D. Fabbri, S. Gladiali, J. Chem. Soc. Chem. Commun. (1993) 1833.

[153] N. Ruiz, S. Castillón, A. Ruiz, C. Claver, A. Aaliti, A. Alvarez-Larena, F. Piniella, G. Germain, J. Chem. Soc. Dalton Trans. (1996) 969.

[154] A.M. Masdeu, A. Orejon, A. Ruiz, S. Castillón, C. Claver, J. Mol. Catal. 94 (1994) 149.

[155] A. Castellanos-Paez, S. Castillón, C. Claver, J. Organomet. Chem. 539 (1997) 1.

[156] R. Lazzaroni, A. Rafaelli, R. Settambolo, S. Bertozzi, G. Vitulli, J. Mol. Catal. 50 (1989) 1.

[157] J.A. Pinilla, E. Martin, J.C. Bayón, Proceedings of the 9th International Symposium of Homogenous Catalysis, Jerusalem (1994), p. 114.

[158] L. David, D.L. van Vranken, B.M. Trost, Chem. Rev. 96 (1996) 395.

[159] Z. Freixa, E. Martin, J.C. Bayón, S. Gladiali, J. Organomet. Chem., accepted for publication.

[160] A.M. Masdeu-Bultó, A. Orejón, S. Castillón, C. Claver, Tetrahedron Asymmetry 6 (1995) 1885.

[161] C. Claver, A. Ruiz, A.M. Masdeu, N. Ruiz, Inorg. Chim. Acta 175 (1990) 77.

[162] A.M. Masdeu-Bultó, A. Orejón, A. Castellanos, S. Castillón, C Claver, Tetrahedron Asymmetry 7 (1996) 1829.

[163] A. Castellanos-Paez, J. Thayaparan, S. Castillón, C. Claver, J. Organomet. Chem. 551 (1998) 375.

[164] A. Castellanos-Paez, S. Castill6n, C. Claver, P.W.N.M. van Leeuwen, W.G.J. de Lange, Organometallics 17 (1998) 2543.

[165] J. Fornies-Camer, A.M. Masdeu-Bultó, C. Claver, C. Cardin, Inorg. Chem. 37 (1998) 2626.

[166] J. Fornies-Camer, A.M. Masdeu-Bultó, C. Claver, unpublished results.

[167] A. Orejón, A.M. Masdeu-Bultó, R. Echarri, J. Fornies-Camer, M. Dieguez, C. Claver, C. Cardin, J. Organometal. Chem. 559 (1998) 23.
[168] S. Gladiali, D. Fabri, L. Kollar, C. Claver, N. Ruiz, A. Alvarez Larena, J.F. Piniella, Eur. J. Inorg. Chem. (1998) 113.
[169] R. Atencio, M.A. Casado, M.A. Ciriano, F.J. Lahoz, J. Perez Torrente, A. Tiripicchio, L.A. Oro, J. Organomet. Chem. 514 (1996) 103.
[170] A. Orejón, M.A. Casado, J. Perez Torrente, M.A. Ciriano, C. Claver, L.A. Oro, Organometallics, in press.
[171] J. Fornies-Camer, A. Aaliti, N. Ruiz, A.M. Masdeu-Bultó, C. Claver, C. Cardin, J. Organomet. Chem. 530 (1997) 199.
[172] (a) D. Zargarian, H. Alper, Organometallics 12 (1993) 712. (b) B. El Ali, H. Alper, J. Mol. Catal. 80 (1993) 377.
[173] D. Kruis, N. Ruiz, M.D. Janssen, J. Boersma, C. Claver, G. van Koten, Inorg. Chem. Commun. 1 (1998) 295.
[174] J. Real, M. Pages, A. Polo, J.F. Piniella, A. Alvarez-Larena, Chem. Commun. (1999) 277.
[175] N. Ruiz, I. del Río, J.L. Jimenez, C. Claver, J. Fornies-Camer, C.J. Cardin, S. Gladiali, J. Mol. Catal., in press.
[176] J. Fornies-Camer, A.M. Masdeu-Bultó, C. Claver, unpublished results.
[177] H. Sinn, W. Kaminsky, Adv. Organomet. Chem. 18 (1980) 99.
[178] S. Timonen, T.T. Pakkanen, T.A. Pakkanen, J. Mol. Catal. 11 (1996) 267.
[179] A.M.A. Bennett, G.A. Foulds, D.A. Thornton, Polyhedron 9 (1990) 2823.
[180] K.J. Cavell, A.F. Masters, J. Chem. Res. Symp. (1983) 72.
[181] R.F. Heck, J.P. Nolly, J. Org. Chem. 37 (1972) 2320.
[182] L.S. Hegedus, Transition Metals in the Synthesis of Complex Organic Molecules, University Science Books, Mill Valley, USA, 1994.
[183] W. Cabri, I. Candiani, Acc. Chem. Res. 28 (1995) 2.
[184] M. Teresawa, K. Kaneda, T Imanake, S. Teranishi, J. Organomet. Chem. 162 (1978) 403.
[185] X. Li, H. Liu, Y. Jiang, J. Mol. Catal. 39 (1987) 55.
[186] Y.L. Wang, H. Liu, J. Mol. Catal. 45 (1988) 127.
[187] (a) B.M. Trost, T.R. Verhoeven, in: G. Wilkinson (Ed.), Comprehensive Organometallic Chemistry, Pergamon Press, Oxford, UK, 1982, p. 799. (b) S.A. Godleski, in: M. Trost (Ed.), Comprehensive Organic Syntheses, Pergamon Press, Oxford, 1994, p. 585. (c) G. Consiglio, R. Waymouth, Chem. Rev. 89 (1989) 257. (d) C.G. Frost, J. Howarth, J.M.J. Williams, Tetrahedron Asymmetry 3 (1992) 1089.
[188] (a) A. Togni, C. Breutel, A. Schinder, F. Splinder, H. Lander, A. Tijani, J. Am. Chem. Soc. 116 (1994) 4062. (b) T. Hayhasi, A. Yamamoto, Tetrahedron Lett. 29 (1988) 669. (c) B.M. Trost, B. Breit, S. Peukert, J. Zambrano, J.W. Ziller, Agnew. Chem. Int. Ed. Engl. 34 (1995) 2386.
[189] (a) J.M. Brown, D.I. Hulmes, P.J. Guiry, Tetrahedron 50 (1994) 4493. (b) J. Sprinz, M. Kiefer, J. Helmchen, M. Reggeleein, M. Huttner, L. Zsolnai, Tetrahedron Lett. 35 (1994) 1523. (c) J. Sprinz, J. Helmchen, Tetrahedron Lett. 34 (1993) 1769. (d) G. Knuhl, P. Sennhenn, G. Helmchen, J. Chem. Soc. Chem. Commun. (1995) 1845. (e) M.P.T. Sjogren, S. Hansson, B. Akemark, A. Vitagliano, Organometallics 13 (1994) 1963.
[190] (a) A. Pfaltz, Acc. Chem. Res. 32 (1993) 566. (b) P. Gamez, B. Dunjic, F. Fache, M. Lemaire, J. Chem. Soc. Chem. Commun. (1994) 1417. (c) P.G. Anderson, A. Harden, D. Tanner, P.O. Norrby, Chem. Eur. J. 1 (1995) 12. (d) P. von Matt, J.C. Lloyd-Jones, A.B. Minidis, A. Pfaltz, L. Macko, M. Neuburger, M. Zehnedr, H. Ruegegr, P.S. Pregosin, Helv. Chim. Acta 78 (1995) 265.
[191] P.B. Mackenzie, J. Whelan, B. Bosnich, J. Am. Chem. Soc. 107 (1985) 2046.
[192] K.L. Granberg, J.E. Backwall, J. Am. Chem. Soc. 114 (1992) 6858.
[193] (a) G.J. Dawson, C.G. Frost, J.M.J. Williams, S.J. Coote, Tetrahedron Lett. 34 (1993) 3149. (b) P. von Matt, A. Pflatz, Agnew. Chem. Int. Ed. Engl. 32 (1993) 556.
[194] (a) A. Togni, L. Venanzi, Agnew. Chem. Int. Ed. Engl. 33 (1993) 497. (b) A. Pfaltz, Acc. Chem. Res. 26 (1993) 239. (c) A.Y Meyers, M. Reuman, Tetrahedron 41 (1985) 837.

[195] (a) J.V. Allen, J.F. Bower, J.M.J. Williams, Tetrahedron Asymmetry 5 (1994) 1895. (b) J.V. Allen, S.J. Coote, G.J. Dawson, C.G. Frost, C.J. Martin, J.M.J. Williams, J. Chem. Soc. Perkin Trans. (1994) 2065. (c) J.V. Allen, G.J. Dawson, C.G. Frost, J.M.J. Williams, S.J. Coote, Tetrahedron 50 (1994) 799.
[196] (a) G.J. Dawson, C.G. Frost, C.J. Martin, J.M.J. Williams, S.J. Coote, Tetrahedron Lett. 34 (1993) 7793. (b) C.G. Frost, J.M. Williams, Tetrahedron Asymmetry 4 (1993) 1785.
[197] C.G. Frost, G. Christopher, J.M.J. Williams, Tetrahedron Lett. 34 (1993) 2015.
[198] A. Chesney, M.R Bryce, Tetrahedron Asymmetry 7 (1996) 3247.
[199] A. Chesney, M.R. Bryce, R.W.J. Chubb, A.S. Batsanov, J.A.K. Howard, Tetrahedron Asymmetry 8 (1997) 2337.
[200] K.W. Wick, P.S. Pregosin, G. Trabesinger, Organometallics 17 (1998) 3254.
[201] A. Albinati, P.S. Pregosin, K. Wick, Organometallics 15 (1996) 2419.
[202] J. Herrmann, P.S. Pregosin, R. Salzmann, A. Albinati, Organometallics 14 (1995) 3311.
[203] P. Barbaro, A. Currao, J. Herrmann, R. Nesper, P.S. Pregosin, R. Salzman, Organometallics 15 (1996) 1879.
[204] G. Chelucci, M.A. Cabras, Tetrahedron Asymmetry 7 (1996) 965.
[205] G. Chelucci, D. Berta, Tetrahedron 53 (1997) 3843.
[206] J.C. Anderson, C. James, S. Daniel, J.P. Mathias, Tetrahedron Asymmetry 9 (1998) 753.
[207] C. Bolm, D. Kaufmann, M. Zehnder, M. Neuburger, Tetrahedron Lett. 37 (1996) 3985.
[208] C.G. Frost, J.M.J. Williams, Synlett 7 (1994) 551.
[209] R. Tokunoh, M. Sodeoka, K. Aoe, M. Shibasaki, Tetrahedron Lett. 36 (1995) 8035.
[210] (a) T. Hayashi, K. Mitsuo, M. Fukusihima, T. Mise, M. Kagotani, M. Tajika, M. Kumada, J. Am. Chem. Soc. 104 (1982) 180. (b) T. Hayashi, M. Fukusihima, M. Konishi, M. Kumada, Tetrahedron Lett. 21 (1980) 79. (c) T. Hayashi, Y. Okamoto, M. Kumada, Tetrahedron Lett. 24 (1983) 807. (d) T. Hayashi, M. Konishi, Y. Kobori, M. Kumada, J. Am. Chem. Soc. 106 (1984) 158.
[211] T. Hayashi, M. Konishi, Y. Okamoto, K. Kebeta, M. Kumada, J. Org. Chem. 51 (1986) 3772.
[212] H.A. Ali, C.H. Brubaker Jr., J. Mol. Catal. 60 (1990) 331.
[213] (a) B.K. Vriesema, M. Lemaire, J. Buter, R.M. Kellogg, J. Org. Chem. 51 (1986) 5169. (b) M. Lemaire, B.K. Vriesma, R.M. Kellogg, Tetrahedron Lett. 26 (1985) 3499.
[214] (a) J.H. Griffin, R.M. Kellogg, J. Org. Chem. 50 (1985) 3261. (b) G. Cross, B.K. Vriesema, G. Boven, R.M. Kellogg, F. van Bolhuis, J. Organomet. Chem. 370 (1989) 357. (c) B.K. Vriesma, R.M. Kellogg, Tetrahedron Lett. 27 (1986) 2049.
[215] (a) H.L. Goering, T.L. Underiner, J. Org. Chem. 56 (1991) 2563. (b) M. Arai, B.H. Lipshutz, E. Nakamura, Tetrahedron 48 (1992) 5709.
[216] (a) J.E. Backwall, M. Sellen, B. Grant, J. Am. Chem. Soc. 112 (1990) 6615. (b) J.E. Backwall, E.S.M. Persson, A. Bombrun, J. Org. Chem. 59 (1994) 4126. (c) E. Keinan, E. Bosch, J. Org. Chem. 51 (1986) 4006.
[217] (a) M. van Klaveren, E.S.M. Persson, D.M. Grove, J.E. Backwall, G. van Koten, Tetrahedron Lett. 35 (1994) 5931. (b) E.S.M. Persson, M. van Klaveren, D.M. Grove, J.E. Backwall, G. van Koten, Chem. Eur. J. 6 (1995) 351.
[218] R.J.K. Taylor (Ed.), Organocopper Reagents, Oxford University Press, Oxford, UK, 1994.
[219] M. Behforonz, T.T. Curran, J.L. Bolan, Tetrahedron Lett. 27 (1986) 3107.
[220] G.H. Posner, C.E. Whitten, J.J. Sterling, J. Am. Chem. Soc. 95 (1973) 7788.
[221] W. Bartmann, E. Guntrum, H. Urbach, J. Wunner, Synth. Commun. 18 (1988) 711.
[222] M. Spescha, G. Rihs, Helv. Chim. Acta 76 (1993) 1219.
[223] (a) F. Lambert, D.M. Knotter, M.D. Janssen, M. van Klaveren, J. Boersma, G. van Koten, Tetrahedron Asymmetry 2 (1991) 1097. (b) M. van Klaveren, F. Lambert, D.J.F.M. Eijkelkamp, D.M. Grove, G. van Koten, Tetrahedron Lett. 35 (1994) 6135.
[224] C.L. Gibson, Tetrahedron Asymmetry 7 (1996) 3357.
[225] Q. Zhou, A. Pfaltz, Tetrahedron Lett. 34 (1993) 7725.
[226] J. Green, S. Woodward, Synlett (1995) 155.
[227] A. Togni, G. Rihs, R.E. Blumer, Organometallics 11 (1992) 613.

[228] G. van Koten, Pure Appl. Chem. 66 (1994) 1455.

[229] G.A. Cran, C.L. Gibson, S. Handa, A.R. Kennedy, Tetrahedron Asymmetry 7 (1996) 2511.

[230] (a) G. Strukul (Ed.), Catalytic Oxidations with Hydrogen Peroxide as Oxidant, Kluwer Academic, Dordrecht, The Netherlands, 1992. (b) K. Weissermel, H.J. Harpe (Eds.), Indrustielel Organische Chemie, VCH, Weinheim, 1988.

[231] M. Bressan, F. Morandini, P.L. Rigo, Inorg. Chim. Acta 77 (1983) L139.

[232] M. Bressan, F. Morandini, A. Morvillo, P.L. Rigo, J. Organomet. Chem. 280 (1985) 139.

[233] C.A. Tsipis, D.P. Kessissoglou, G.E. Manoussakis, Inorg. Chim. Acta 65 (1982) L137.

[234] R. Barral, C. Bocard, I. Seree de Roch, L. Sajus, Tetrahedron Lett. 17 (1972) 1693.

[235] (a) R.A.T.M. van Benthem, H. Hiemstra, E.N. Speckam, J. Org. Chem. 57 (1992) 6083. (b) R.A.T.M. van Benthem, H. Hiemstra, J.J. Michels, W.N. Speckam, J. Chem. Soc. Chem. Commun. (1994) 357.

[236] R.A.T.M. van Benthem, H. Hiemstra, P.W.N.M. van Leeuven, J.W. Geus, W.N. Speckam, Agnew. Chem. Int. Ed. Engl. 4 (1995) 457.

[237] C.A. Grapperhaus end, M.Y. Darensbourg, Acc. Chem. Res. 31 (1998) 451.