4
Palladium and Platinum

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4.1
Introduction

Studies of homogeneous hydrogenation catalyzed by soluble palladium (Pd) or platinum (Pt) catalysts first began when the process of heterogeneous hydrogenation was already known. The reduction of $[Pt(C_2H_4)Cl_2]_2$ with H_2 to produce Pt(0), C_2H_6 and HCl was first reported in 1954, and can be considered as one of the events to have opened up the field of homogeneous hydrogenation [1]. The homogeneity of the reaction appeared to be dependent upon the temperature and on the amount of hydrogen employed [2]. The discovery that H_2 could be homogeneously activated by Pd(II) was first observed by Halpern's group in the 1950s and 1960s, as part of a series of hydrometallurgical investigations involving the precipitation of metals from solution with H_2 [3]. The first reports relating to homogeneous catalysts appeared in the literature during the 1960s, their aim being mainly to identify the reaction mechanisms of heterogeneous hydrogenations [2]. The use of Pd(II) as a hydrogenation catalyst was retarded by its instability under H_2 atmosphere, as demonstrated during alkene isomerization reactions [4, 5], in favor of the more stable catalyst, Pt(II). However, interest towards Pd- and Pt-catalyzed homogeneous reductions of unsaturated functions was renewed when it was found that the selectivities were usually higher than those obtained under heterogeneous conditions [6]. Today, the use of soluble Pd and Pt hydrogenating catalysts remains the subject of intense academic and industrial research, as evidenced by the numerous publications on the subject, and the many deposited patents.

An analysis of the most significant homogeneous catalytic systems reported in the literature reveals a structural variety for Pd which is not found for Pt. In fact, although in most cases Pd is incorporated into the (pre)catalyst as divalent ion, active Pd(0)-catalysts have also been reported. By contrast, Pt(0)-catalysts are a rarity. Moreover, Pd complexes containing mono-, di-, tri-, and even tetradentate ligands have found application as hydrogenation catalysts, and often their activity and selectivity is governed by the steric and electronic features of

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the chelating systems. The most thoroughly studied Pt-catalysts are instead simple phosphine-containing Pt(II) complexes, usually activated with stannous chloride, $SnCl_2$. Tin(II) salts have instead found scarce application with Pd, and in some cases have turned out to be poisons of the catalytic processes. Another important aspect which differentiates the two metals has practical consequences: the well-known higher reactivity of Pd with respect to Pt [7] allows the Pd-promoted hydrogenations to be carried out under much milder conditions (room temperature and atmospheric pressure of H_2) than those usually required for activating Pt-catalysts. However, Pd-based catalysts are usually more subject to decomposition than are Pt-based catalysts.

As unsaturated C–C bonds have certainly been the most thoroughly investigated substrates, this chapter focuses on the hydrogenation of alkenes and alkynes, and the hydrogenation of other functional groups such as nitro, nitrile, and carbonyl will be excluded. Particular emphasis will be given to those catalytic systems for which a mechanistic study has been carried out. Where possible, a brief discussion of the homogeneous character of the catalytic processes will be given.

4.2 Palladium

4.2.1 Phosphorus-Containing Catalysts

In 1963, in a report which focused mainly on the use of first-row transition-metal catalysts combined with organoaluminum compounds, the hydrogenating activity of the catalytic system $[PdCl_2(Pn\text{-}Bu_3)_2/Al(i\text{-}Bu)_3]$ towards 1-hexene under mild conditions (heptane, 25 °C, 3.5–3.7 atm of H_2 pressure, Pd : alkene ratio ~1 : 80) was briefly addressed [8]. After 19 h of reaction, a 25.5% conversion to hexane was obtained (TOF ~1.1 h^{-1}). In 1967, several Pd(II) complexes of the general formula $[PdX_2(Ph_3Q)_2]$ (Q = P or As, X = Cl or CN) were used to homogeneously hydrogenate soybean oil Me-ester in the presence or absence of co-catalysts, such as $SnCl_2$ or $GeCl_2$ [9]. *Cis-trans* double-bond isomerization, migration of isolated double bonds to conjugated dienes, and selective hydrogenation of polyenes to monoenes without further reduction were observed. The most active system was found to be $PdCl_2(PPh_3)_2/SnCl_2 \cdot 2\,H_2O$ which, after 3 h, converted both linoleate and linolenate to monoenes almost completely, but not at all to stearate (benzene/methanol, 90 °C, 39.1 atm H_2 pressure); Me-oleate was selectively converted to the corresponding monoene under the same experimental conditions and reaction time. In both cases high catalyst loadings were applied. Traces of Pd black were observed at the end of the reaction. Lowering of the temperature precluded the formation of Pd black, but slowed down the hydrogenations.

By the end of the 1970s, $PdCl_2(PPh_3)_2$ was being used to hydrogenate 1,5-cyclooctadiene [10]. The substrate isomerization to 1,3-cyclooctadiene preceded its

reduction to cyclooctene. For example, after 5 h of reaction (CH_2Cl_2/MeOH, 90 °C, 51 atm H_2 pressure, alkene : Pd ratio = 1 : 15) the products distribution was 4% of 1,3-cyclooctadiene, 93% of cyclooctene, and 3% of cyclooctane. The reactivity and selectivity remained quite high up to an alkene : Pd ratio of 250. However, under the same experimental conditions, $SnCl_2$ proved to be a poison of the reaction. The π-allylic reaction intermediate [PdCl(π-cyclooctenyl)(PPh_3)] was isolated from the reactant solutions and resulted in a much more active catalyst than its precursor $PdCl_2(PPh_3)_2$, although it was less selective. After 3 h of reaction, under 34 atm H_2 pressure, the product distribution was 10% of 1,3-cyclooctadiene, 83% of cyclooctene, and 6% of cyclooctane. During the same period, other π-allyl-Pd(II) complexes that were effective in the selective hydrogenation of allene to propene (THF, 15 °C, 1 atm total pressure) were reported [11]. Turnover numbers (TONs) ranging from 18 to 75 were obtained with [(η^3-allyl)-PdCl(PR_3)] (allyl = C_3H_5, 1-Me-C_3H_4, 2-Me-C_3H_4; R = PPh_3, PPh_2Me, Pt-Bu_3) or [Pd(η^3-C_3H_5)$_2$] ([Pd(η^3-C_3H_5)$_2$] was used at 0 °C). The TOFs ranged from 0.19 to 75 h^{-1}, the highest being obtained with the bis-allene complex [Pd(C_3H_5)$_2$], though this was significantly decomposed. Since the stability of the complexes under H_2 atmosphere were shown to differ, a comparison of the catalytic results was possible only for the strictly similar allyl-complexes [(η^3-C_3H_5)PdCl(PPh_3)], [(η^3-1-Me-C_3H_4)PdCl(PPh_3)] and [(η^3-2-Me-C_3H_4)PdCl(PPh_3)]. These showed similar turnover frequency (TOF) values of 0.21, 0.23, and 0.19 h^{-1}, respectively, and comparable stability. The same complexes slowly catalyzed the selective hydrogenation of 1,5-cyclooctadiene and 1,3-cyclooctadiene to the corresponding monoenes (Pd : diene ratio = 1 : 31) [12]; 1,5-cyclooctadiene was first isomerized to 1,3-cyclooctadiene and then hydrogenated to cyclooctene. In several cases, however, Pd-black was detected at the end of the catalytic reactions.

The catalytic activity of other Pd-complexes containing mono- or chelating phosphines was studied by Stern and Maples [13]. In the hydrogenation of butadiene (toluene, r.t., 6.8 atm H_2 pressure), the dinuclear Pd(0) complex $Pd_2(dppm)_3$ showed the highest TOF (0.25 h^{-1}), leading to an excess of 1-butene with respect to *cis*- or *trans*-2-butene. (Since the complex was handled in plain air, caution must be taken about its nature.) The Pd(II) complexes [$PdCl_2$(dppm)], [$PdCl_2$(1,1-dppe)] and [$PdCl_2$(dppe)], although not completely soluble in toluene, also promoted the hydrogenation, albeit with lower TOF values and selectivities. $PdCl_2(PhCN)_2$ was practically inactive. The hydrogenating activity of $Pd_2(dppm)_3$ towards a variety of other unsaturated substrates (alkenes, dienes, trienes, and acetylenes) was reported in the same work. The nature of the substrate appeared to regulate the catalyst activity, in the sense that complexing substrates led to faster reactions. For example, the TOFs varied in the following order: 0.012 h^{-1} (1,9-decadiene), 0.014 h^{-1} (1,5-hexadiene), 0.16 h^{-1} (1,4-pentadiene), 0.25 h^{-1} (butadiene), 0.44 h^{-1} (*cis*-1,3-pentadiene), 0.58 h^{-1} (1,3-cyclohexadiene), 0.80 h^{-1} (*trans*-1,3-pentadiene), and 1.3 h^{-1} (norbornadiene). Studies on the catalyst pretreatment showed that a dissociation equilibrium in solution is necessary in order to enable a coordinatively unsaturated species to bind the substrate, according to Eqs. (1) and (2) (L = ligand, S = solvent, ol = alkene).

$$PdL_4 + S \leftrightarrow PdL_3S + L \quad (1)$$

$$PdL_3S + ol \leftrightarrow PdL_3ol + S \quad (2)$$

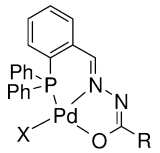
Treatment of the precatalytic solutions with oxygen brought about a remarkable enhancement of the catalysis, and an improved selectivity. The effect of oxygen was tentatively rationalized in terms of oxidation of a phosphine ligand with subsequent dissociation of the so-formed phosphine oxide or, alternatively, with formation of oxygen complexes able to promote the substrate/hydrogen activation via hydroperoxide intermediates or the formation of either hydrogen or substrate complexes. The effect of the activating oxygen pretreatment was, at least partially, clarified by Alper et al. for the dinuclear Pd(II) complex $[\{(t\text{-Bu})_2HP\}PdP(t\text{-Bu})_2]_2$. This alone was a completely inactive hydrogenating catalyst towards *α,β*-unsaturated compounds. Once exposed to oxygen for some minutes, it transformed into the mononuclear species $[Pd\{O_2P(t\text{-Bu})_2\}\{OP(t\text{-Bu})_2\}\{OHP(t\text{-Bu})_2\}]$ [14] containing a η^2-phosphinate ligand. This species was an active pre-catalyst for the selective reduction of the double C–C bond of several *α,β*-unsaturated ketones and aldehydes under mild conditions (THF, r.t., 1 atm H_2 pressure, 1–2% catalyst loading) [15]. A TOF $\approx 5\ h^{-1}$ was achieved in the hydrogenation of 3-nonen-2-one. The same system was applied in the chemoselective hydrogenation of several substrates, such as *α,β*-unsaturated sulfones and phosphonates [16], simple and functionalized conjugated dienes [17], and vinyl epoxides [18]. In all cases good catalytic activities and selectivities were obtained (TOFs up to $100\ h^{-1}$).

In recent years, a number of other polynuclear complexes have been investigated in addition to $[Pd_2(dppm)_3]$. In 1989, Eisenberg reported that the reaction between $Pd_2Cl_2(dppm)_2$ with an excess of $NaBH_4$ led to the formation of a palladium hydride species of approximate stoichiometry $[Pd_2H_x(dppm)_2]$ [19]. This hydride was effective in small-scale hydrogenations of alkynes and alkenes. Parahydrogen-induced polarization was observed in styrene formed during the hydrogenation of phenylacetylene, indicating that the transfer of hydrogen to the substrate occurred pairwise and rapidly relative to proton relaxation. In 1998, the structure of $[Pd_2H_x(dppm)_2]$ was inferred by using a variety of spectroscopic tools [20], and revealed to be a cluster of formula $[Pd_4(dppm)_4(H_2)]^{2+}$. The hydrogenating capability of this material was further investigated quite recently [21]. The $[Pd_4(dppm)_4(H_2)](BPh_4)_2$ cluster catalyzed the homogeneous hydrogenation of phenylacetylene, diphenylethyne and 1-phenyl-1-propyne (THF, 20 °C, 1 atm H_2 pressure), with TOFs of 500, 200, and $500\ h^{-1}$, respectively. The products distribution was seen to be time-dependent; after 3 h the *cis*-alkenes were in the range 75–90%, whereas after 24 h the over-reduced products were predominant, at least with phenylacetylene and diphenylethyne. Strongly coordinating solvents such as dimethylformamide (DMF) led to high TOFs (up to $1800\ h^{-1}$ under 41 atm H_2 pressure), while less-coordinating solvents such as tetrahydrofuran (THF), acetone (Me_2CO), and acetonitrile (MeCN) led to lower TOF values (1240, 1130, and $1060\ h^{-1}$, respectively, under the same pressure); pyridine inhibited the reaction (TOF = $660\ h^{-1}$), most likely due to the presence

of reactivity with $[Pd_4(dppm)_4(H_2)]^{2+}$. The polymeric low-valent complex $[Pd_5(PPh_2)]_n$ ($n \approx 4$) was also reported to be a highly active catalyst in the semi-hydrogenation of phenylacetylene and 1,3-pentadiene, as well as in the hydrogenation of 1- and 2-pentene (DMF, 20 °C, 1 atm H_2 pressure) [22]. The TOFs reached with the different substrates were 7200, 60 000, and 6000 (for both simple alkenes) h^{-1}, respectively.

Palladium(II) complexes containing tridentate PNP ligands first appeared during the late 1980s. A complex of general formula [Pd(PNP)Cl]Cl containing the pincer ligand N,N′-bis(diphenylphosphino)-2,6-diaminopyridine was briefly mentioned in 1987 as a catalyst for styrene hydrogenation (ethanol, 60 °C, 10 atm H_2 pressure) [23]; the platinum version was also active. In 1988, a kinetic analysis of the hydrogenation of cyclohexene catalyzed by different [Pd(PNP)Cl]Cl complexes (PNP = bis-2-(diphenylphosphino)ethyl benzylamine [24], bis-2-(diphenylphosphino)ethyl amine [25] or tris-2-(diphenylphosphino)ethyl amine [25]) under mild conditions (ethanol, 10–40 °C, 0.1–1 atm H_2 pressure) was reported (see Section 4.2.4).

During the 1990s, [Pd(PNO)X] (X = OAc, Cl, I) complexes derived from protic HPNO acyl-hydrazones (**1** in Scheme 4.1) were reported to be effective in the homogeneous hydrogenation of styrene and phenylacetylene under mild conditions (MeOH, r.t. or 40 °C, 1 atm H_2 pressure, 1% catalyst loading) [26–28]. With styrene, the acetate-complexes showed appreciable activity (TOFs up to 67 h^{-1}), the chloride-complexes reacted sluggishly (complete conversion after 48 h), and the iodide-complexes were completely inactive. With phenylacetylene as the substrate, the hydrogenations catalyzed by the chloride-complexes proceeded slowly (conversions not complete after 24 h), although with good selectivity to styrene, whilst the iodide complexes were, again, not active. With the acetate complexes, hydrogenation of the alkyne was poisoned by the precipitation of phenylethynyl palladium(II) complexes of the type [Pd(PNO)(C≡C–Ph)], which formed by the elimination of acetic acid. The formation of these organometallic species is independent of the catalytic conditions, as shown by the possibility of synthesizing them by reaction between the acetate complexes [Pd(PNO)(OAc)] and an excess of alkyne in methanol. Catalytic hydrogenations promoted by the phenylethynyl palladium(II) complexes in solvents in which these are completely soluble (CH_2Cl_2 or THF), led to much lower conversions than those reached with the acetate precursors, which exemplifies the pollutant nature of this *in-situ*-formed species.



X = OAc, Cl, I

R = Me, C_6H_5, *p*-Me-C_6H_4
p-Br-C_6H_4, *p*-NO_2-C_6H_4, py

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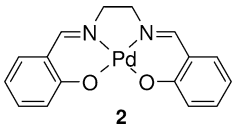
Scheme 4.1 The Pd(II) complexes containing acyl-hydrazone ligands, Pd(PNO)X.



2 **Scheme 4.2** The Pd-Salen complex.

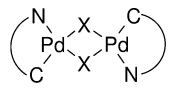
4.2.2
Nitrogen-Containing Catalysts

Nitrogen ligand-containing complexes were first reported in the literature during the 1970s. Pd-Salen (**2** in Scheme 4.2) was reported as being a suitable catalyst for the hydrogenation of 1-hexene, and a good enzyme hydrogenase model [29, 30]. The complex was active in heterogeneous as well as homogeneous conditions, depending on the solvent employed (ethanol or DMF, respectively). Modified versions of the present catalyst appeared later in the literature [31, 32]; low reactivities and selectivities were observed in the hydrogenations of 1-hexene and phenylacetylene.

Ferrocenyl sulfide palladium(II) complexes of formula $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3\text{-}1\text{-}CHRNR'_2\text{-}2\text{-}SR'')PdCl_2]$ or $[(R''S)(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_3\text{-}1\text{-}CHRNR'_2\text{-}2\text{-}SR'')PdCl_2]$ were employed in the selective hydrogenation of conjugated dienes to monoenes and in the hydrogenation of styrene derivatives [33–38]. The speed and selectivity were governed mainly by the nature of the R'' group, with 4-Cl-C_6H_4 leading to the best results in both series of complexes (TOFs up to 722 h^{-1} and almost complete selectivity to cyclooctene were achieved in the hydrogenation of 1,3-cyclooctadiene conducted at r.t. under 7 atm H_2 pressure). The solvent of choice was acetone, while dichloromethane, THF, and DMF led to much poorer results. Replacement of the Pd–S bond with a Pd–Se bond, or substitution of Pd with Pt, led to inactive systems. On the basis of these observations the authors argued that rupture of the Pd–S bond was a necessary prerequisite to form the active species. Nevertheless, induction times observed in some catalytic reactions (up to 49.7 h) cannot completely rule out – at least in those cases – a heterogeneous contribution to the reaction. Systems containing two sulfide moieties were almost inactive under the same experimental conditions [38].

Orthometallated dimer palladium(II) complexes $[Pd(NC)X]_2$ (**3** in Scheme 4.3) were reported by Saha as effective catalysts for the hydrogenation of alkenes and alkynes under mild conditions (25 °C, 1 atm H_2 pressure) [39, 40]. The reactions were efficient in either DMF or DMSO, reaching initial TOFs higher than 10 000 h^{-1} in the case of styrene, while in less-coordinating or non-coordinating solvents no activity was observed. Selectivity was never obtained, and the over-reduced products (or a mixture of different isomers) were always obtained. This, and the fact that the authors reported for a set of experiments that "... the yellow DMF solution of the catalyst turned deep greenish brown within 10 min on stirring under hydrogen at 20 °C" before the addition of the substrate [40], cast serious doubt on the homogeneous character of the reaction.

In 1991, Elsevier reported other nitrogen ligand-containing complexes as active hydrogenating catalysts. Palladium(0) complexes containing the Ar-bian bis-imine



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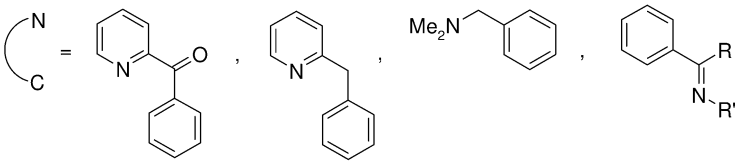
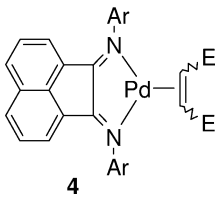


X = OAc or Cl; R = H or Me; R' = Me or aryl

Scheme 4.3 The orthometallated Pd(II) complexes, $[Pd(NC)_2X]_2$.

Ar = C_6H_5, *p*-Me-C_6H_4, *p*-MeO-C_6H_4
E = CO_2Me, CN, C(O)–O–C(O)



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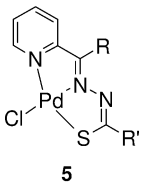
Scheme 4.4 The [Pd(Ar-bian)(dmf)] complexes.

ligand bis(arylimino)acenaphthene (**4** in Scheme 4.4), were successful in the reduction of electron-deficient alkenes [41]. The hydrogenations proceed under mild conditions (THF, 20 °C, 1–1.5 atm H_2 pressure, 1% catalyst loading, complete conversion within 8–16 h), with high chemoselectivity for C=C double bonds. Thus, nitro and cyano groups were not reduced to the corresponding amines, and the alkene functions of unsaturated esters, ketones and anhydrides were selectively hydrogenated. High selectivity (up to 90%) was also observed in the hydrogenation of *α,β*-unsaturated aldehydes. In the case of alkenes not containing electron-withdrawing substituents, the hydrogenations began only after an induction period, and for these instances a heterogeneous contribution was evidenced. [Pd(Ar-bian)(dmf)] (dmf = dimethylfumarate) complexes were also efficient in the highly selective hydrogenation of alkynes to the corresponding *Z*-alkenes [42]. The complex with Ar = *p*-Me-C_6H_4 was able to hydrogenate several linear and cyclic alkynes with selectivity up to 99% to the corresponding alkenes, and with high tolerance towards different functional groups. Substitution of the Ar-bian ligand with other nitrogen (bipy or dab = *p*-anisyldiazabutadiene) or phosphine (dppe) ligands led to poorer catalysts. More recently, other bis-imine ligands containing Pd(0) complexes of the general formula 6-R″-C_5H_3N-(C(R′)=NR)-2 (R″ = H, Me; R′ = H, Me; R = alkyl, aryl) were used in the stereoselective hydrogenation of 1-phenyl-1-propyne to *Z*-1-phenyl-1-propene [43]. The experimental conditions were identical to those applied with the [Pd(Ar-bian)(dmf)] complexes. The stability and behavior of the complexes under H_2 atmosphere were strongly dependent on the substitu-



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R = Me or Ph
R' = NH_2 or Ph

Scheme 4.5 The Pd(II) complexes with thiosemicarbazone or thiobenzoylhydrazone ligands, Pd(NN′S)Cl.

ents R, R′, and R″. Moderately bulky, σ-donating substituents were necessary in order to have hydrogenating activity without loss of palladium. The best compromise was reached with R″ = H, R′ = H and R = *i*-Pr, which led to complete consumption of the alkyne within 2 h of reaction, and with the following products distribution: 87% *Z*-alkene, 3% *E*-alkene, and 10% alkane. Water-soluble bis-imine Pd(0) complexes of the general formula 6-R′-C_5H_3N-(C(H)=NR)-2 (R′ = H, Me; R = 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranose residue) were used to hydrogenate unsaturated nitriles in water (r.t., 1 atm H_2 pressure, Pd : substrate ratio = 1 : 50) [44]. The complexes displayed high activity in distilled water, but the reactions were substantially heterogeneous. In 0.1 M KOH solution, the hydrogenations of acrylonitrile, methacrylonitrile, and crotonitrile were homogeneous and proceeded fairly rapidly (after 2 h the yields of the saturated products were 70, 50, and 50%, respectively); however, undesired side reactions also occurred. In 0.25 M KOH solution only the hydrogenation of acrylonitrile was homogeneous and complete within 2 h. No enantioselectivity was observed in the hydrogenation of α-ethylacrylonitrile.

High chemoselectivities (up to 96%) were reached in the hydrogenation of phenylacetylene to styrene (DMF, 30 °C, 1 atm H_2 pressure, 1% catalyst loading, TOFs up to 4.2 h^{-1}) catalyzed by chloride Pd(II) complexes [Pd(NN′S)Cl] containing thiosemicarbazone or thiobenzoylhydrazone ligands (**5** in Scheme 4.5) [45]. Instead, minor reactivities and selectivities were obtained with NN′N″ pyridyl-hydrazone-containing Pd(II) complexes in the hydrogenation of phenylacetylene [46].

4.2.3
Other Catalysts

$Pd(acac)_2$ has been reported to be an active catalyst in soybean oil hydrogenation [47]. The reactions were conducted in bulk with low catalyst loadings (1–60 ppm) and without any co-catalyst. Under 10 atm H_2 pressure and at 80–120 °C, optimum linolenate selectivity and high *trans*-isomers content were obtained. Decomposition of the catalyst occurred at temperatures above 120 °C.

Simple inorganic salts, such as $PdCl_2$, were also studied. $PdCl_2/SnCl_2 \cdot 2H_2O$ and $K_2PdCl_4/SnCl_2 \cdot 2H_2O$ turned out to be completely inactive in the hydrogenation of soybean oil methylester [9], while $PdCl_2$ in DMF was active towards conjugated dienes and alkynes (DMF, 25 °C, 25 atm H_2 pressure, 0.31–0.5% cat-

alyst loading) [48]. 1-Heptyne and 2-pentyne were selectively reduced to the corresponding alkenes within 25 minutes, while the hydrogenation of dienes was slower. $PdCl_2$ dissolved in a CH_2Cl_2-polyethylene glycol (PEG) mixture was employed in the hydrogenation of diphenylacetylene (10 °C, 1 atm H_2 pressure, Pd : substrate ratio $\approx 1:10$) [49]. The rate and selectivity of the reaction were dependent on the PEG molecular weight; with PEG-400, 90% conversion was achieved after 80 minutes, with 80% of *cis*-stilbene.

4.2.4 Mechanistic Aspects

Reaction mechanisms based on kinetic studies have been proposed for most of the aforementioned catalytic hydrogenations. For the Pd(II)-catalysts, the heterolytic activation of molecular hydrogen results generally favored compared to oxidative addition which, in contrast, is common for low-valent Pd-catalysts. For example, a molecular orbital analysis of the hydrogenation of styrene catalyzed by the $[PdCl_4]^{2-}$ anion [50] showed that H_2 was activated by heterolytic splitting (in these experiments the catalyst was supported on a solid, but no profound differences were believed to exist between the homogeneous and heterogeneous cases). The four successive steps depicted in Eqs. (3) to (6) were defined as:

- Splitting of H_2 with formation of the palladium hydride $[HPdCl_3]^{2-}$ and HCl (Eq. (3)).
- π-coordination of styrene through a pentacoordinate intermediate (Eq. (4)).
- Alkene insertion into the Pd–H bond with formation of an alkyl intermediate (Eq. (5)).
- Reaction with HCl to eliminate ethylbenzene and re-form the anion $[PdCl_4]^{2-}$ (Eq. (6)).

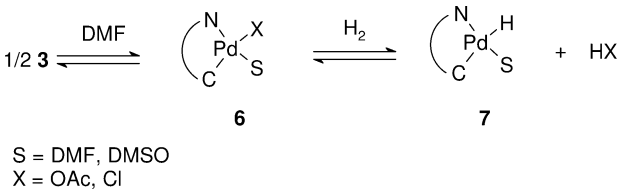
$$[PdCl_4]^{2-} + H_2 \leftrightarrow [HPdCl_3]^{2-} + HCl \tag{3}$$

$$[HPdCl_3]^{2-} + C_6H_5\text{-}CH = CH_2 \leftrightarrow [HPdCl_3(C_6H_5\text{-}CH = CH_2)]^{2-} \tag{4}$$

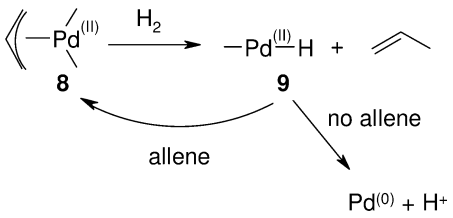
$$[HPdCl_3(C_6H_5\text{-}CH = CH_2)]^{2-} \leftrightarrow [(C_6H_5\text{-}CH_2\text{-}CH_2)PdCl_3]^{2-} \tag{5}$$

$$[(C_6H_5\text{-}CH_2\text{-}CH_2)PdCl_3]^{2-} + HCl \rightarrow [PdCl_4]^{2-} + C_6H_5CH_2CH_3 \tag{6}$$

The elimination of HCl was proposed to occur also during the H_2 activation with the [Pd(PNP)Cl]Cl complexes (PNP = bis-2-(diphenylphosphino)ethyl benzylamine, bis-2-(diphenylphosphino)ethyl amine or tris-2-(diphenylphosphino)ethyl amine) [24, 25]. Based on the findings of $^{31}P\{^1H\}$- and ^1H-NMR investigations, the hydride [HPd(PNP)]Cl was detected under H_2 atmosphere. The alternative mechanism which involves the oxidative addition of H_2 with formation of a Pd(IV)-dihydride intermediate, appeared less likely on the basis of thermodynamic considerations.



Scheme 4.6 Heterolytic splitting of H_2 with $[Pd(NC)_2X]_2$ complexes.



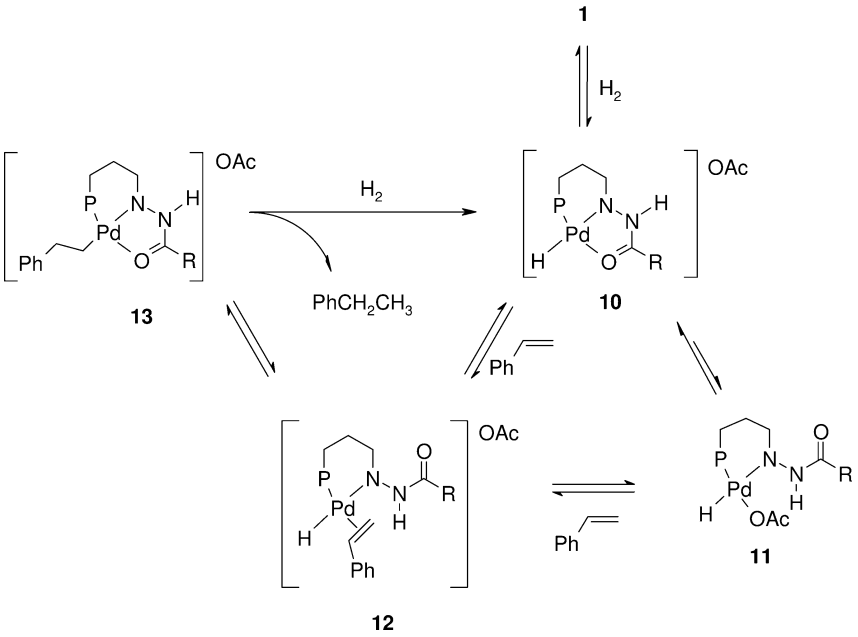
Scheme 4.7 Hydrogenation of allene catalyzed by $[(\eta^3\text{-allyl})Pd(PR_3)Cl]$ complexes.

The efficiency of the orthometallated Pd(II) complexes $[Pd(NC)X]_2$ [39, 40] (**3** in Scheme 4.3) in coordinating solvents such as DMF or DMSO was considered to be in favor of the initial dissociation of the dimers **3** into the mononuclear species **6** (Scheme 4.6). The heterolytic splitting of H_2 leads to the formation of the hydride **7** plus HCl or AcOH. The solvato-hydride intermediate **7** was characterized spectroscopically and its elemental analysis furnished [39]; regrettably, no data regarding its catalytic activity were reported.

The dissociation of a coordinated allene by hydrogen was evidenced for $[(\eta^3\text{-allyl})Pd(PR_3)Cl]$ complexes [11]. The hydrogenation of allene to propene was then invoked to follow the pathway depicted in Scheme 4.7:

- H_2 activation by protonation of the coordinated allene in **8** with formation of the palladium hydride intermediate **9** and propene.
- Insertion of an allene molecule into the Pd–H bond, with regeneration of the starting allene complex **8** which then re-enters the catalytic cycle. In the absence of allene, extensive Pd black formation was observed.

In the hydrogenation of styrene catalyzed by the [Pd(PNO)(OAc)] complexes (**1** in Scheme 4.1) [26–28], a clear correlation between the activity of the complexes and the basicity of the hydrazonic ligand, in turn governed by the nature of the R group, was established [28]. Indeed, the higher the ligand basicity, the faster the hydrogenation reactions. This result, combined with a kinetic analysis, led to the mechanism depicted in Scheme 4.8. The first step is the heterolytic activation of H_2 with protonation of the hydrazonic arm in **1** and formation of the hydride intermediate **10**; **10** can be considered at equilibrium with **11**, where the acetate anion re-enters in the coordination sphere by displacement of the C=O amide group of the ligand. By rupture of the Pd-O(amide) (**10**) or Pd-O-

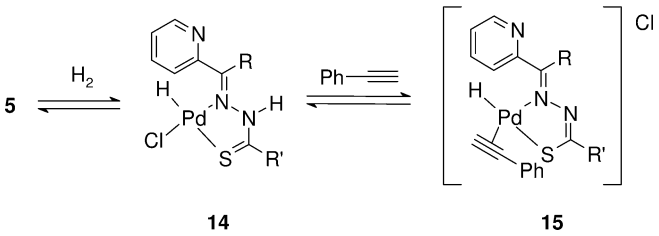


Scheme 4.8 Proposed pathway for the hydrogenation of styrene catalyzed by Pd(PNO)(OAc) complexes.

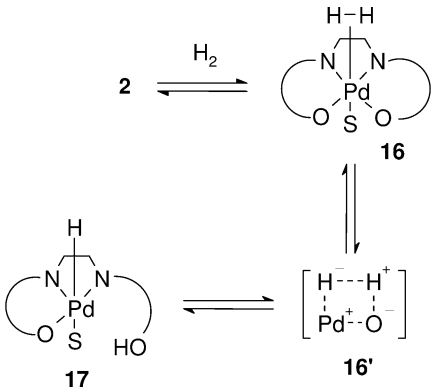
(acetate) (**11**) bond, a styrene molecule coordinates to palladium with formation of **12**, and after the alkene insertion into the Pd–H bond the alkyl-intermediate **13** forms. The involvement of **10** in the catalytic cycle appeared more likely than that of **11**, on the basis of the inertness shown by the acetate complex [Pd(PNS)(OAc)] (PNS = 2-(diphenylphosphino)benzaldehyde thiosemicarbazone), where the two soft donors P and S make the complex too stable [27]. The cycle closes with the intervention of a H_2 molecule, which leads to the restoration of **10** (or alternatively **11**) and elimination of ethylbenzene.

A similar H_2 activation mechanism was proposed for the [Pd(NN′S)Cl] complexes (**5** in Scheme 4.5) in the semi-hydrogenation of phenylacetylene [45]; after formation of the hydride **14** (Scheme 4.9), coordination of the alkyne occurs by displacement of the chloride ligand from Pd (**15**). The observed chemoselectivity (up to 96% to styrene) was indeed ascribed to the chloride anion, which can be removed from the coordination sphere by phenylacetylene, but not by the poorer coordinating styrene. This was substantiated by the lower chemoselectivities observed in the presence of halogen scavengers, or in the hydrogenations catalyzed by acetate complexes of formula [Pd(NN′S)(OAc)]. Here, the acetate anion can be easily removed by either phenylacetylene or styrene.

A net heterolytic H_2 cleavage was evidenced for [Pd(Salen)] (**2** in Scheme 4.2) [29, 30]. Its catalytic activity was pH-dependent; namely, it was inhibited by acids and enhanced by bases. A kinetic study of the hydrogenation of 1-hexene in DMF led to the definition of the following mechanism (Scheme 4.10):



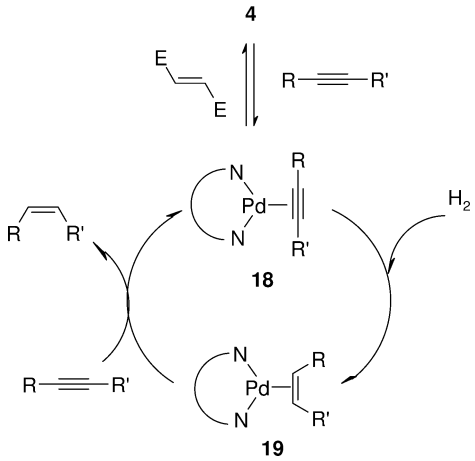
Scheme 4.9 Heterolytic splitting of H_2 and coordination of phenylacetylene in Pd(NN′S)Cl complexes.



Scheme 4.10 Heterolytic H_2 splitting promoted by Pd–Salen complex; S = DMF.

- solvent-assisted hydrogen coordination to the metal (**16**);
- heterolytic activation of the molecular hydrogen through a highly polarized, four-center transition state (**16′**) which involves a coordinate phenolate group. The so-formed OH group leaves a vacant coordination site on the metal (**17**), which can now accommodate the entering alkene, the subsequent alkene insertion into the Pd–H bond forming an alkyl intermediate. Finally, hydrogen transfer from the OH group of the ligand to the coordinated alkyl group gives the final alkane, with restoration of **2**.

Oxidative addition of molecular hydrogen was considered to be involved in the alkyne hydrogenations catalyzed by [Pd(Ar-bian)(dmf)] complexes (**4** in Scheme 4.4) [41, 42]. Although the mechanism was not completely addressed, **4** was considered to be the pre-catalyst, the real catalyst most likely being the [Pd(Ar-bian)(alkyne)] complex **18** in Scheme 4.11. Alkyne complex **18** was then invoked to undergo oxidative addition of H_2 followed by insertion/elimination or pairwise transfer of hydrogen atoms, giving rise to the alkene-complex **19**.



Scheme 4.11 Proposed catalytic cycle for the hydrogenation of alkynes promoted by Pd(Ar-bian)(dmf) complexes.

Displacement of the alkene by an incoming alkyne molecule leads to the elimination of the product and restoration of **18** (see also chapter 14).

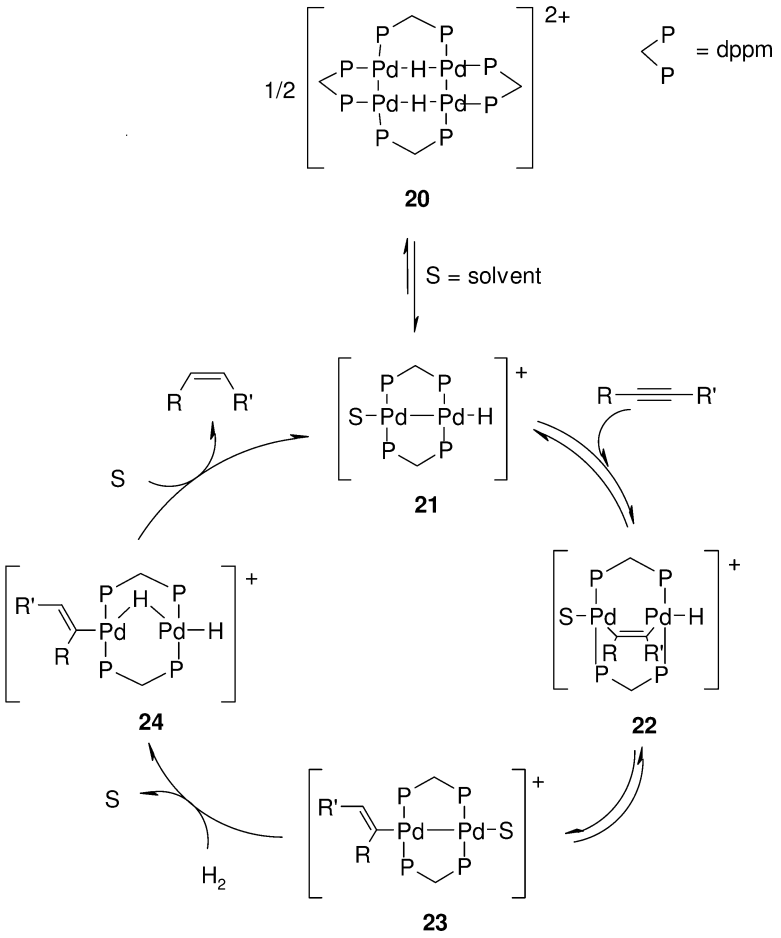
The higher catalytic activity of the cluster compound $[Pd_4(dppm)_4(H_2)](BPh_4)_2$ [21] (**20** in Scheme 4.12) in DMF with respect to less coordinating solvents (e.g., THF, acetone, acetonitrile), combined with a kinetic analysis, led to the mechanism depicted in Scheme 4.12. Initially, **20** dissociates into the less sterically demanding d^9-d^9 solvento-dimer **21**, which is the active catalyst. An alkyne molecule then inserts into the Pd–Pd bond to yield **22** and, after migratory insertion into the Pd–H bond, the d^9-d^9 intermediate **23** forms. Now, H_2 can oxidatively add to **23** giving rise to **24** which, upon reductive elimination, results in the formation of the alkene and regenerates **21**.

The high activity of the polymeric compound $[Pd_5(PPh_2)]_n$ ($n \approx 4$) [22] in the hydrogenation of alkenes and alkynes was ascribed to the initial DMF-assisted dissociation of the polymer (Eq. (7)); the resulting $[Pd_5(PPh)_2]$ species forms an adduct with the substrate molecule (Sub) (Eq. (8)) which, after reaction with H_2, leads to the hydrogenation product and gives back $[Pd_5(PPh)_2]$ (Eq. (9)), which re-enters the catalytic cycle.

$$[Pd_5(PPh)_2]_n \leftrightarrow n[Pd_5(PPh)_2] \tag{7}$$

$$[Pd_5(PPh)_2] + Sub \leftrightarrow [Pd_5(PPh)_2](Sub) \tag{8}$$

$$[Pd_5(PPh)_2](Sub) + H_2 \leftrightarrow [Pd_5(PPh)_2] + SubH_2 \tag{9}$$



Scheme 4.12 Proposed mechanism for the hydrogenation of alkynes catalyzed by $[Pd_4(dppm)_4(H_2)]^{2+}$.

4.3 Platinum

4.3.1 Platinum Complexes Activated with Sn(II) Salts

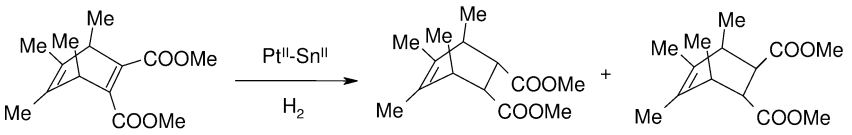
4.3.1.1 Phosphorus-Containing Catalysts

The catalytic activity of $[PtX_2(QPh_3)_2]/SnCl_2$ complexes (Q = P or As, X = halogen or pseudo-halogen) was intensively studied, starting during the late 1960s. Such catalytic systems promoted the isomerization and hydrogenation of methyl oleate [51], methyl linolenate [52], and polyenes [53], as well as short-chain alkenes

[54]. The Pt:substrate ratios ranged from 1:10 to 1:180. The formation of conjugated isomers which were slowly hydrogenated to the corresponding monoene was observed (see Section 4.3.3). *Cis*-$[PtCl_2L(PR_3)]/SnCl_2$ complexes (L=SR'_2, p-X-$C_6H_4NH_2$; R=aryl) also showed activity in the hydrogenation of alkenes, such as styrene (acetone, 60 °C, 41 atm H_2 pressure) [55]. TOF values up to 4400 h^{-1} were reached, depending on the nature of ligands L and PR_3. These complexes resulted in more active catalysts than the parent complexes *cis*-$[PtCl_2L_2]/SnCl_2$ or *cis*-$[PtCl_2(PR_3)_2]/SnCl_2$, which brought about a maximum TOF of 910 h^{-1}. Rationalization of the results, in terms of a plausible reaction mechanism, was far from straightforward because of the contemporary presence, under catalytic conditions, of several Pt and Pt-Sn species, both neutral and ionic, all of which played a catalytic role. Indeed, the authors reported that the multicomponent system was necessary to establish the catalytic cycle, as evidenced by catalytic runs involving isolated species. Dimeric versions of the aforementioned complexes of the type $[Pt_2(\mu\text{-}Cl)_2(PR_3)_2]/SnCl_2$ [55] or *cis*-$[Pt_2(\mu\text{-}SR')(\mu\text{-}Cl)Cl_2(PR_3)_2]$ [56] led to reactivities similar to those observed with the mononuclear parents, thus indicating the necessity of dimer dissociation to bring about the formation of active mononuclear species.

4.3.1.2 **Other Catalysts**

In 1963, the hydrogenation of ethylene and acetylene under mild conditions (methanol, r.t., 1 atm total pressure) was readily carried out with the catalytic system $H_2PtCl_6/SnCl_2$ (Pt/Sn ratio=1:10) [57]. With higher Pt/Sn ratios and higher alcohols, the hydrogenation of higher alkenes became feasible. For example, the hydrogenation of cyclohexene in *i*-PrOH proceeded with a TOF of 5 h^{-1} [58]. The addition of chloride or bromide ions and water strongly increased the hydrogenation rate (TOFs up to 94 h^{-1}). Carboxylic acids or esters also turned out to be suitable solvents: with a Pt/Sn ratio of 1:5, the hydrogenation of 1-hexene in glacial acetic acid led, after 2 h of reaction, to a mixture of hexane (≈50%), 2-*trans*-hexene (≈25%), 3-*trans*-hexene (≈5%), traces of 2-*cis*- and 3-*cis*-hexene, and unreacted 1-hexene [59]. As expected, the hydrogenation of 2-hexene proceeded somewhat sluggishly, whilst in the hydrogenation of soybean oil a remarkable preference for the reduction of linoleic acid was observed. Again, $H_2PtCl_6/SnCl_2$ was employed in the hydrogenation of Dewar-benzene derivatives, such as dimethyl tetramethylbicyclo[2.2.0]hexa-2,5-diene-2,3-dicarboxylate (**25** in Scheme 4.13) and its di-*tert*-Bu-ester under mild conditions (*i*-PrOH, 25 °C, 1 atm H_2 pressure, Pt:substrate ratio 1:10) [60]. Contrary to heterogeneous systems, the hydrogenation of **25** was restricted to the ester-substituted double bond, giving rise to dimethyl tetramethylbicyclo[2.2.0]hex-5-ene-2-endo, 3-endo-dicarboxylate (**26**); the exo,endo hydrogenation (**27**) was involved for 16%. In 1972, Parshall showed that $PtCl_2$ could be used as hydrogenation catalyst for alkenes in molten $[R_4N][SnCl_3]$ [61]. With $PtCl_2/[Et_4N][SnCl_3]$, a 50% conversion was obtained in the hydrogenation of ethylene after 5 h of reaction (100 °C, 1.7 atm total pressure, Pt:ethylene ratio 1:13). At higher temperatures



25 **26**(84%) **27**(16%)

Scheme 4.13 Hydrogenation of Dewar-benzene derivatives.

and pressures, 1,5,9-cyclododecatriene was hydrogenated to cyclododecene with considerable selectivity: 87% monoene, 10% diene, 2% of unreacted triene, and traces of over-reduced product were obtained at 160 °C and 100 atm H_2 pressure after 8 h of reaction (Pt : substrate ratio = 1 : 15).

4.3.2
Platinum Complexes not Activated with Sn(II) Salts

Platinum complexes that display hydrogenating activity without the addition of Sn(II) salts are scarce in the literature. The dihydride Pt(II) complex [PtH_2{(*t*-Bu)$_2$PCH$_2$CH$_2$P(*t*-Bu)$_2$}] hydrogenated cyclohexene to cyclohexane only under drastic conditions (benzene, 100 °C, 77.4 atm H_2 pressure, 1% catalyst loading), with a TOF of 0.26 h^{-1} [62]. The chloro-bridged complex [$PtCl_2$(2,4,6-Me_3-pyridine)]$_2$ was active at r.t. and 1 atm H_2 pressure toward mono- and dienes (a TOF of 270 h^{-1} was obtained with styrene) [63]; however, when racemization was possible all the isomers were detected in the final solutions. The hydride complex *trans*-[$PtH(NO_3)(PEt_3)_2$] [64] was active towards both internal and terminal alkenes, but was inactive toward alkenes bearing electron-withdrawing substituents. The hydrogenation rate was dependent on the solvent employed, with methanol leading to the highest TOF values. With styrene as substrate, a TOF of 115 h^{-1} was reached at 60 °C and 41 atm H_2 pressure. The methoxide intermediate $PtH(OMe)(PEt_3)_2$ was considered to be involved in the reaction mechanism. The activity towards internal alkenes was slower.

Pt(0) complexes of the type [Pt(P-P)(C_2H_4)] (P-P = dppb, 1,2-bis[(diphenylphosphino)methyl]benzene (dpmb) and (+)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane ((+)-diop)) were used in the hydrogenation of several alkenes in combination with CH_3SO_3H (toluene, 80 °C, 50 atm H_2 pressure, Pt : substrate ratio 1 : 320) [65]. With the dppb-containing complex, the reduction of terminal alkenes was accompanied by extensive isomerization, and the resulting internal alkenes underwent very little hydrogenation (1-hexene led to 29.3% yield of hexane and 68.8% yield of hexenes after 22 h). Alkenes bearing electron-withdrawing substituents were hydrogenated much more easily (3-buten-2-one and 2-cyclohexen-1-one were reduced to the corresponding saturated ketones with TOFs of 68 and 282 h^{-1}, respectively). The activity of [Pt(dppb)(C_2H_4)] was usually higher than that of [Pt(dpmb)(C_2H_4)], both with simple olefins (styrene, TOFs of 6.2 and 3.7 h^{-1}, respectively) and unsaturated ketones (2-cyclohexen-1-one, TOFs of 80 and 48 h^{-1}, respectively). Poor chiral in-

duction (8% *ee*, *R*-isomer) was observed in the hydrogenation of *α*-ethylstyrene catalyzed by [Pt((+)-diop)(C_2H_4)].

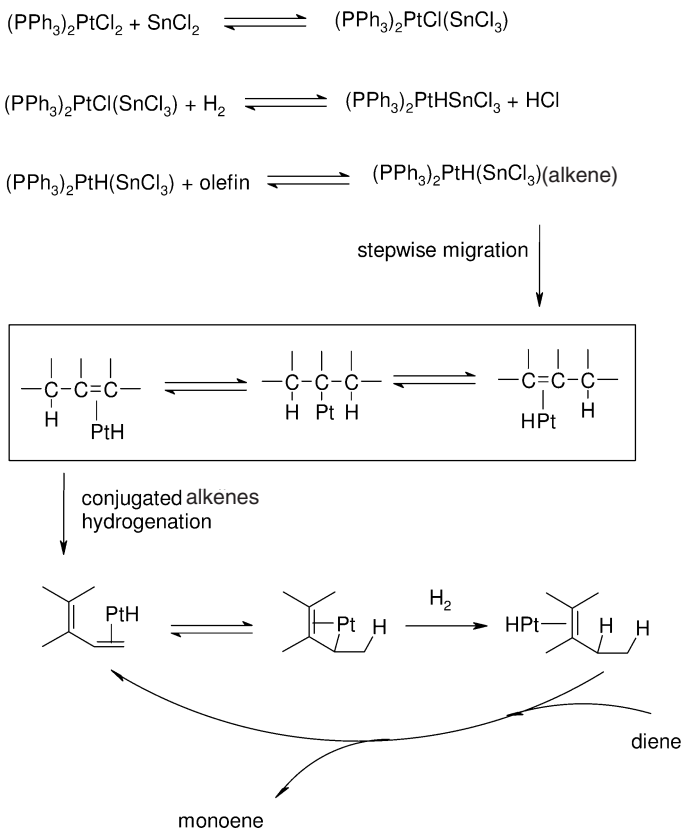
Finally, the only example of a polynuclear homogeneous catalyst is the dinuclear complex $[Pt_2(P_2O_5H_2)_4]^{4-}$ [66], which catalyzed the hydrogenation of styrene, phenylacetylene, 1-octyne, and 1-hexyne (*i*-PrOH, 60 °C, 20.7 atm H_2 pressure, Pd : substrate ratio 1 : 1800) to the corresponding alkanes within 10 h of reaction.

4.3.3 Mechanistic Aspects

Because of its industrial importance, many studies have conducted in order to establish the mechanism which regulates the hydrogenation of polyunsaturated fatty acid derivatives catalyzed by the $[PtX_2(QPh_3)_2]/SnCl_2$ complexes (Q = P or As, X = halogen or pseudo-halogen) [51, 52]. The following observations were made:

- Initial, rapid step-wise migration of double bonds takes place to give a conjugated isomer [67], which is then reduced more slowly to the corresponding monoene. The necessary formation of conjugated isomers was highlighted by the inertness of polyenes where the double bonds are separated by several methylene groups [52]. Isomerization occurred before, as well as after, the hydrogenation. *Cis-trans* isomerization also occurred. High H_2 pressures (usually higher than 30 atm) were required, otherwise only isomerization was observed.
- Hydride formation was a fundamental step in the mechanism, and indeed $PtHCl(PPh_3)_2$ species were isolated from the reactant solutions. However, their formation was not the rate-determining step, since the same rate of hydrogenation was observed with either $PtCl_2(PPh_3)_2$ or $PtHCl(PPh_3)_2$ complexes.
- Metal–alkene complex formation was also necessary, but again was not rate-determining.
- The formation of hydride-Pt(II)-alkene complexes was thought to be the rate-determining step, as evidenced by the isolation of a number of such species.
- The addition of an excess of $SnCl_2$ (a Pt : Sn ratio of 1 : 5 was found to be the best) was necessary as co-catalyst; $SnCl_2$ reacts with chloride ions to give the poor *σ*-donor and strong *π*-acceptor $SnCl_3^-$ ligand [68] that, decreasing the electron density on Pt, favors the formation of Pt–H or Pt–alkene bonds.
- Triphenylphosphine and related ligands stabilized the hydride intermediate once formed, besides rendering Pt soluble in non-polar organic solvents. These observations have been condensed in the mechanism depicted in Scheme 4.14.

Penta-coordinate Pt–Sn anions of the type $[Pt(SnCl_3)_5]^{3-}$ [69] appeared also to be involved in the hydrogenations catalyzed by the phosphine-free $H_2PtCl_6/SnCl_2$ [57] and $PtCl_2/[R_4N][SnCl_3]$ [61] systems. The anion $[Pt(SnCl_3)_5]^{3-}$ transforms into the active species $[PtH(SnCl_3)_3]^{2-}$ upon heterolytic hydrogen activation and loss of two $SnCl_3^-$ ligands (Eqs. (10) to (12)).



Scheme 4.14 Pathway for the selective hydrogenation of polyenes to monoenes catalyzed by $PtX_2(QPh_3)_2/SnCl_2$; Q = P or As, X = halogen or pseudo-halogen.

$$[Pt(SnCl_3)_5]^{3-} \leftrightarrow [Pt(SnCl_3)_4]^{2-} + SnCl_3^- \quad (10)$$

$$[Pt(SnCl_3)_4]^{2-} + H_2 \leftrightarrow [PtH(SnCl_3)_4]^{3-} + H^+ \quad (11)$$

$$[PtH(SnCl_3)_4]^{3-} \leftrightarrow [PtH(SnCl_3)_3]^{2-} + SnCl_3^- \quad (12)$$

In the case of ethylene hydrogenation, the mechanism proposed by Parshall [61] involves the coordination of an alkene molecule through a five-coordinate intermediate (Eq. (13)); the subsequent alkene insertion into the Pt–H bond (Eq. (14)) and intervention of a second molecule of H_2 (Eq. (15)) leads to the elimination of ethane and restoration of the catalytic active species $[PtH(SnCl_3)]^{2-}$. However, in 1976 Yasumori and coworkers reported a kinetic analysis conducted on the hydrogenation of ethylene catalyzed by the Pt–Sn complex $[(Me)_4N]_3[Pt(SnCl_3)_5]$ [70], under much milder conditions than those

applied by Parshall (acetone, 0–15 °C, partial H_2 pressure up to 0.13 atm). The collected data were in agreement with the formation of Pt_n clusters of different sizes (n = 1 to 6, depending on Pt concentration), which were invoked as being responsible for the observed catalytic activity. The possibility that the catalyses described by Parshall might have a heterogeneous character is further supported by the well-known ability of tetraalkylammonium salts to stabilize metal-clusters, and by the harsh experimental conditions applied [71].

$$[PtH(SnCl_3)_3]^{2-} + C_2H_4 \leftrightarrow [PtH(C_2H_4)(SnCl_3)_3]^{2-} \quad (13)$$

$$[PtH(C_2H_4)(SnCl_3)_3]^{2-} \leftrightarrow [Pt(C_2H_5)(SnCl_3)_3]^{2-} \quad (14)$$

$$[Pt(C_2H_5)(SnCl_3)_3]^{2-} + H_2 \rightarrow [PtH(SnCl_3)_3]^{2-} + C_2H_6 \quad (15)$$

A kinetic analysis of the styrene hydrogenation catalyzed by $[Pt_2(P_2O_5H_2)_4]^{4-}$ [66] was indicative of the fact that the dinuclear core of the catalyst was maintained during hydrogenation. However, three speculative mechanisms were in agreement with the kinetic data, which mainly differ in the H_2 activation step. This in fact can occur through the formation of two Pt–monohydrides, still connected by a Pt–Pt bond, or through the formation of two independent Pt–monohydrides. The third mechanism involves the dissociation of a phosphine from one Pt center, with subsequent oxidative addition of H_2 to produce a Pt–dihydride intermediate.

Abbreviations

dmf	dimethylfumarate
DMF	dimethylformamide
DMSO	dimethylsulfoxide
PEG	polyethylene glycol
THF	tetrahydrofuran
TOF	turnover frequency
TON	turnover number

References

1 J. H. Flynn, H. M. Hulburt, *J. Am. Chem. Soc.* **1954**, *76*, 3393.
2 A. S. Gow, H. Heinemann, *J. Phys. Chem.* **1960**, *64*, 1574.
3 J. Halpern, *J. Organomet. Chem.* **1980**, *200*, 133.
4 J. F. Harrod, A. J. Chalk, *J. Am. Chem. Soc.* **1964**, *86*, 1776.
5 R. Cramer, R. V. Lindsey, *J. Am. Chem. Soc.* **1966**, *88*, 3534.
6 B. R. James, *Homogeneous Hydrogenation*, Wiley, New York, **1975**.
7 F. Basolo, H. B. Gary, R. G. Pearson, *J. Am. Chem. Soc.* **1960**, *82*, 4200.
8 M. F. Sloan, A. S. Matlack, D. S. Breslow, *J. Am. Chem. Soc.* **1963**, *85*, 4014.

9 H. Itatani, J.C. Bailar Jr., *J. Am. Oil Chemists' Soc.* **1967**, *44*, 147.
10 Y. Fujii, J.C. Bailar Jr., *J. Catal.* **1978**, *55*, 146.
11 G. Carturan, G. Strukul, *J. Organomet. Chem.* **1978**, *157*, 475.
12 G. Strukul, G. Carturan, *Inorg. Chim. Acta* **1979**, *35*, 99.
13 E.W. Stern, P.K. Maples, *J. Catal.* **1972**, *27*, 120.
14 P. Leoni, F. Marchetti, M. Pasquali, *J. Organomet. Chem.* **1993**, *451*, C25.
15 M. Sommovigo, H. Alper, *Tetrahedron Lett.* **1993**, *34*, 59.
16 I.S. Cho, H. Alper, *J. Org. Chem.* **1994**, *59*, 4027.
17 I.S. Cho, H. Alper, *Tetrahedron Lett.* **1995**, *36*, 5673.
18 I.S. Cho, B. Lee, H. Alper, *Tetrahedron Lett.* **1995**, *36*, 6009.
19 R.U. Kirss, R. Eisenberg, *Inorg. Chem.* **1989**, *28*, 3372.
20 I. Gauthron, J. Gagnon, T. Zhang, D. Rivard, D. Lucas, Y. Mugnier, P.D. Harvey, *Inorg. Chem.* **1998**, *37*, 1112.
21 D. Evrard, K. Groison, Y. Mugnier, P.D. Harvey, *Inorg. Chem.* **2004**, *43*, 790.
22 I.I. Moiseev, M.N. Vargaftic, *New J. Chem.* **1998**, 1217.
23 W. Schirmer, U. Flörke, H.-J. Haupt, *Z. Anorg. Allg. Chem.* **1987**, *545*, 83.
24 V.V.S. Reddy, *J. Mol. Catal.* **1988**, *45*, 73.
25 M.M. Taqui Khan, B. Taqui Khan, S. Begum, *J. Mol. Catal.* **1988**, *45*, 305.
26 A. Bacchi, M. Carcelli, M. Costa, P. Pelagatti, C. Pelizzi, G. Pelizzi, *Gazz. Chim. Ital.* **1994**, *124*, 429.
27 A. Bacchi, M. Carcelli, M. Costa, A. Leporati, E. Leporati, P. Pelagatti, C. Pelizzi, G. Pelizzi, *J. Organomet. Chem.* **1997**, *535*, 107.
28 P. Pelagatti, A. Bacchi, M. Carcelli, M. Costa, A. Fochi, P. Ghidini, E. Leporati, M. Masi, C. Pelizzi, G. Pelizzi, *J. Organomet. Chem.* **1999**, *583*, 94.
29 G.H. Olivé, S. Olivé, *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 549.
30 G.H. Olivé, S. Olivé, *J. Mol. Catal.* **1975/76**, *1*, 121.
31 A. El-M.M. Ramadan, *Transition Met. Chem.* **1996**, *21*, 536.
32 A. Bacchi, M. Carcelli, L. Gabba, S. Ianelli, P. Pelagatti, G. Pelizzi, D. Rogolino, *Inorg. Chim. Acta* **2003**, *342*, 229.
33 R.V. Honeychuck, M.O. Okoroafor, L.-H. Shen, C.H. Brubaker, Jr., *Organometallics* **1986**, *5*, 482.
34 M.O. Okoroafor, L.-H. Shen, R.V. Honeychuck, C.H. Brubaker, Jr., *Organometallics* **1988**, *7*, 1297.
35 C.-K. Lai, A.A. Naiini, C.H. Brubaker, Jr., *Inorg. Chim. Acta* **1989**, *164*, 205.
36 A.A. Naiini, C.-K. Lai, D.L. Ward, C.H. Brubaker, Jr., *J. Organomet. Chem.* **1990**, *390*, 73.
37 A.A. Naiini, H.M. Ali, C.H. Brubaker, Jr., *J. Mol. Catal.* **1991**, *67*, 47.
38 C.-H. Wang, C.H. Brubaker, Jr., *J. Mol. Catal.* **1992**, *75*, 221.
39 A. Bose, C.R. Saha, *Indian J. Chem.* **1990**, *29A*, 461.
40 D.K. Mukherjee, B.K. Palit, C.R. Saha, *Indian J. Chem.* **1992**, *31A*, 243.
41 R. van Asselt, C.J. Elsevier, *J. Mol. Catal.* **1991**, *65*, L13.
42 M.W. van Laren, C.J. Elsevier, *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 3715.
43 M.W. van Laren, M.A. Duin, C. Klerk, M. Naglia, D. Rogolino, P. Pelagatti, A. Bacchi, C. Pelizzi, C.J. Elsevier, *Organometallics* **2002**, *21*, 1546.
44 C. Borriello, M.L. Ferrara, I. Orabona, A. Panunzi, F. Ruffo, *J. Chem. Soc., Dalton Trans.* **2000**, 2545.
45 P. Pelagatti, A. Venturini, A. Leporati, M. Carcelli, M. Costa, A. Bacchi, G. Pelizzi, C. Pelizzi, *J. Chem. Soc., Dalton Trans.* **1998**, 2715.
46 M. Costa, P. Pelagatti, C. Pelizzi, D. Rogolino, *J. Mol. Catal. A: Chem.* **2002**, *178*, 21.
47 S. Koritala, *J. Am. Oil Chemist's Soc.* **1985**, *62*, 517.
48 A. Sisak, F. Ungváry, *Chem. Ber.* **1976**, *109*, 531.
49 N. Suzuki, Y. Ayaguchi, Y. Izawa, *Chem. Ind.* **1983**, *4*, 166.
50 D.R. Armstrong, O. Novaro, M.E. Ruiz-Vizcaya, R. Linarte, *J. Catal.* **1977**, *48*, 8.
51 J.C. Bailar, Jr., H. Itatani, *J. Am. Chem. Soc.* **1967**, *89*, 1592.
52 E.N. Frankel, E.A. Emken, H. Itatani, J.C. Bailar, Jr., *J. Org. Chem.* **1967**, *32*, 1447.
53 H.A. Tayim, J.C. Bailar, Jr., *J. Am. Chem. Soc.* **1967**, *89*, 4330.
54 R.W. Adams, G.E. Batley, J.C. Bailar, Jr., *J. Am. Chem. Soc.* **1968**, *90*, 6051.

55 G. K. Anderson, C. Billard, H. C. Clark, J. A. Davies, C. S. Wong, *Inorg. Chem.* **1983**, *22*, 439.

56 V. K. Jain, G. S. Rao, *Inorg. Chim. Acta* **1987**, *127*, 161.

57 R. D. Cramer, E. L. Jenner, R. V. Lindsey, Jr., U. G. Stolberg, *J. Am. Chem. Soc.* **1963**, *85*, 1691.

58 H. van Bekkum, J. van Gogh, G. van Minnen-Pathuis, *J. Catal.* **1967**, *7*, 292.

59 L. P. van 't Hoff, B. G. Linsen, *J. Catal.* **1967**, *7*, 295.

60 F. van Rantwijk, G. J. Timmermans, H. van Bekkum, *Recl. Trav. Chim. Pays-Bas* **1976**, *95*, 39.

61 G. W. Parshall, *J. Am. Chem. Soc.* **1972**, *94*, 8716.

62 T. Yoshida, T. Yamagata, T. H. Tulip, J. A. Ibers, S. Otsuka, *J. Am. Chem. Soc.* **1978**, *100*, 2063.

63 R. Rumin, *J. Organomet. Chem.* **1983**, *247*, 351.

64 H. C. Clark, C. Billard, C. S. Wong, *J. Organomet. Chem.* **1979**, *173*, 341.

65 S. Paganelli, U. Matteoli, A. Scrivanti, C. Botteghi, *J. Organomet. Chem.* **1990**, *397*, 375.

66 J. Lin, C. U. Pittman, Jr., *J. Organomet. Chem.* **1996**, *512*, 69.

67 H. A. Tayim, J. C. Bailar, Jr., *J. Am. Chem. Soc.* **1967**, *89*, 3420.

68 G. W. Parshall, *J. Am. Chem. Soc.* **1966**, *88*, 704.

69 R. D. Cramer, R. V. Lindsey, Jr., C. T. Prewitt, U. G. Stolberg, *J. Am. Chem. Soc.* **1965**, *87*, 658.

70 H. Nowatary, K. Hirabayashi, I. Yasumori, *J. Chem. Soc., Faraday Trans.* **1976**, *72*, 2785.

71 J. A. Widegren, R. G. Finke, *J. Mol. Catal. A: Chem.* **2003**, *198*, 317.