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Review

Asymmetric catalysis induced by the substrate itself

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Abstract

This review presents the main potentialities provided by a substrate bearing at least one chiral carbon atom which is the source of stereodifferentiation when a catalytic functionalization is performed. This chirality control introduced by the substrate itself is an alternative to the classical strategy of introducing chiral ligands in the coordination sphere of a metal, although the level of diastereoselectivity is lower in the former system. We describe how the substrate can induce asymmetry; several catalytic mechanisms are detailed. This relatively unexplored concept could have potential as abundant bidentate non-chiral ligands can be used to tune the stereocontrol of the substrate functionalization.

Keywords: Asymmetric induction; Catalysis; Chiral substrate; Stereodifferentiation

1. Introduction

Chirality takes a special place in organic synthesis since it has been recognized that two enantiomers possess generally different biological properties. The terminology "dissymmetry" was initially used by Pasteur [1] who discovered in 1848 that an enzyme could selectively transform the (d)-stereomer of racemic mixtures of ammonium tartrate and thus proceeded to the first kinetic resolution. For many years the aim of chemists was to find the most efficient way to synthesize chiral compounds. Asymmetric catalysis is a young scientific part of such an objective and became popular when Knowles and his group, in 1975, prepared a cationic rhodium complex containing the dipamp chiral phosphine to produce the (*S*)-dihydroxyphenylalanine (L-DOPA) on an industrial scale [2]. Since this early stage, the tenet is to synthesize the most appropriate chiral ligand for a given reaction and to design the correct coordination sphere of the metal in order to have the convenient chiral catalyst [3]. High stereoselectivities have been obtained and a recent comprehensive analysis has been published in

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which many organic reactions reach an enantiomeric excess greater than 99% [4].

A myriad of chiral ligands has been synthesized and used in almost all catalytic asymmetric reactions. Chirality can be located on the coordinating atoms (nitrogen, phosphorus, arsenic mainly) of the ligand. Bidentate ligands have been shown to be the most efficient ones, and generally they contain adjacent chiral functionalities; the ligand can be of C2 symmetry, the prototype being BINAP designed by Noyori and his research group in 1980 [5]. Many ligands are displayed in Ojima's book [6], but reviews appear regularly to relate new observations in asymmetric catalysis [7].

Moreover, it has been observed that a combination of a chiral substrate and an asymmetric catalyst could dramatically improve performance so that "double stereodifferentiation" is often the way to gain high stereoselectivities [8].

This strategy can be extended to substrates bearing one or more asymmetric centers which react with an achiral reagent in the presence of an achiral catalyst [9]. Indeed, use of monoterpenes containing one or more stereogenic centers provides an alternative to the use of chiral ligands in the coordination sphere of the metal. Thus, during our studies on the carbonylation of representative monoterpenes we observed that interesting diastereoselectivities can be reached, but also that subsequent complete stereodifferentiations could be engaged. We were interested in the generality of the strategy by which one chiral center present or introduced in the substrate can produce such stereodifferentiation.

This review analyses the literature related to this approach and is essentially focused on the intimate understanding of the mechanism by which the substrate approaches the metal to induce enantioselectivity of the functionalization of its prochiral carbon atom(s).

2. Asymmetric functionalization of monoterpenes

2.1. Tandem carbonylations

From our own experience, isopulegol **1**, a monoterpene which contains three chiral carbon atoms and an exocyclic carbon–carbon double bond is representative of a substrate whose functionalization can be influenced by the presence of two stereogenic centers (C_1 and C_2 of Fig. 1).

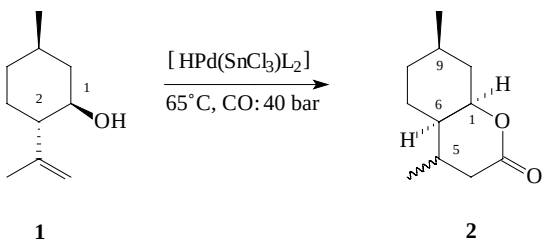
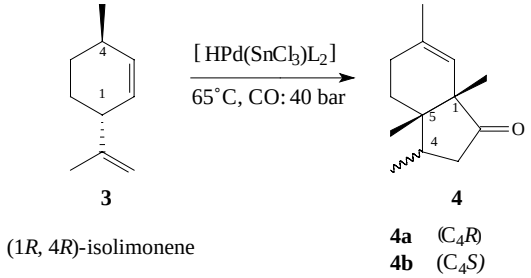


Fig. 1. Cyclocarbonylation of (1*R*, 2*S*, 5*R*)-isopulegol into **2a** (1*R*, 2S, 6*S*, 9*R*)- or **2b** (1*R*, 2*S*, 6*S*, 9*R*)-5,9-dimethyl-2-oxabicyclo [4.4.0] decan-3-on.



(1*R*, 4*R*)-isolimonene

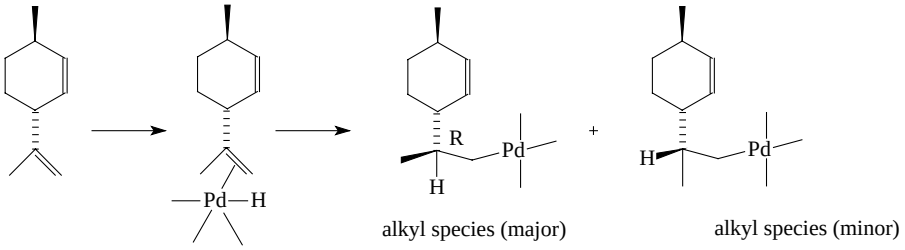
4a (C_4R)
4b (C_4S)

Fig. 2. Cyclocarbonylation reaction of (1*R*, 4*R*)-isolimonene.

Indeed, the cyclocarbonylation reaction of **1** [9] is efficiently catalyzed by palladium(II) precursors containing the non-chiral ligands 1,4-bis(diphenylphosphino)butane (dppb), or 1,1′-bis(diphenylphosphino)ferrocene (dppf). It produces the two lactones drawn in Fig. 1, with **2a** having a 5*R* and **2b** a 5*S* configuration (nomenclature of **1** is that of terpenes whereas those of **2a** and **b** are IUPAC ones). The enantioselectivity on carbon C_5 reaches 60% with dppb, and 44% with dppf. Interestingly, the use of (−)- or (+)-DIOP as L_2 gives rise to the same **2a**/**2b** ratio (81/19)indicating that chirality of the DIOP ligand does not play any role in the course of the enantio- and diastereoselectivities. These two bidentate (+)- and (−)-DIOP ligands appear to influence the reaction only through their chelating effect and their steric hindrance. Even with the monodentate PPh_3 ligand, an enantioselectivity of 24% (**2a**/**2b** = 62/38) has been observed. Thus, as the catalytic cycle involves coordination of the carbon–carbon double bond to a palladium-hydride active species, the only possibility to have diastereoselectivity should result from interactions, or even coordination, of the hydroxyl oxygen atom to the palladium center. Therefore, a diasterodifferentiation process takes place in which only the substrate is involved whatever the nature of the L_2 ligand.

Further investigation into this phenomenon led us to consider the cyclocarbonylation of (1*R*, 4*R*)-isolimonene **3** (Fig. 2) in which the stereogenic center C_4 is far from C_1 that bears the isopropenyl group which is first functionalized [10]. Coordination of the exocyclic carbon–carbon double bond followed by the hydride transfer to give the corresponding alkyl species (see Scheme 1) is the source of the enantioselectivity of 82/18 on carbon C_4 for the two cyclopentanones **4a**/**4b** (when L_2 = dppb).

Introducing (+)-DIOP or (−)-DIOP as L_2 in the Pd coordination sphere results in the same **4a**/**4b** ratio as with dppb. Thus, coordination of the C=C bond determines the enantiodiscrimination, and Fig. 3 shows the *re* and *si* faces that lead to the major and minor *R* and *S* configurations. It can be clearly seen that due to steric hindrance the diphosphine L_2 ligand interacts more strongly with the cyclohexenyl ring in the *si* situation. Such a steric constraint should be significantly released with the monodentate PPh_3 ligand, as indicated with the assumed [$HPd(SnCl_3)(PPh_3)_2$] complex, as the diastereoselectivity is reduced to **4a**/**4b** = 56/44 [10].



Scheme 1.

Using the dppb ligand, diastereoselectivity for substrate **1** compares quite well with substrate **3** and reaches 60% for **2a**/**2b** and 64% for **4a**/**4b**. In fact, examination of the molecular model of **1** shows that palladium can approach the *re* face without any significant assistance of the hydroxyl group which occupies the axial position on C_1 atom (Fig. 1). Thus, the cyclohexyl group in **1**, or cyclohexenyl moiety in **3**, exerts such a steric effect that palladium is preferentially coordinated by the propenyl double bond through the *re* face. Additionally, the hydroxyl group in **3** does not favour the approach through the *si* face. However, this OH substituent likely interacts with palladium as soon as the acyl species is formed so that lactone **2** is produced even in the presence of methanol. Similarly, the distances involved and the flexibility of the acyl intermediate formed from **3** allow the coordination of the endocyclic carbon–carbon double bond to palladium [9,11] (Fig. 3).

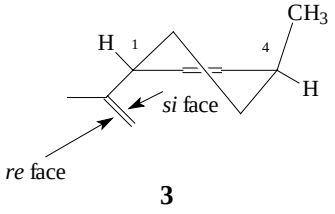


Fig. 3. The *re* and *si* faces approach on (1*R*, 4*R*)-isolimonene.

Another example of tandem cyclocarbonylation has been described by Gusevskaya and her group when they studied the hydroformylation of (*R*)-limonene. In the presence of the $[PtCl_2L_2] + SnCl_2$ precursor, the substrate is transformed, via the assumed active hydrido species $[PtH(SnCl_3)L_2]$, into the alcohol **6** namely 4,8-dimethyl-bicyclo[3.3.1] non-7-en-2-ol, (Fig. 4) [12].

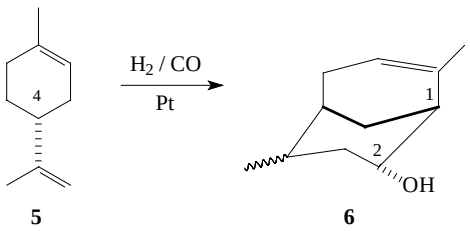
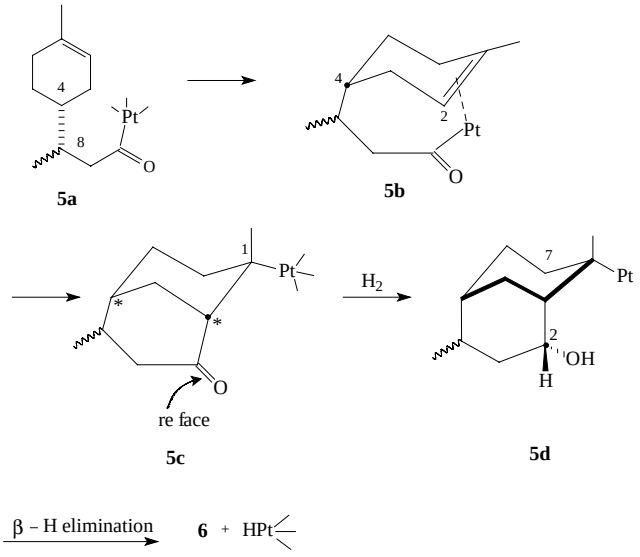


Fig. 4. Tandem cyclocarbonylation of (*R*)-limonene.

By careful examination of the successive steps in the catalytic cycle, we suggest that reaction is under the control of the C_4 stereochemistry. Indeed, when the alkyl species is formed by hydride transfer from platinum, a subsequent migratory CO insertion step produces the acyl species **5a**, as shown in Scheme 2. Platinum, with no stereodifferentiation on C_8, can be coordinated by the endocyclic carbon–carbon double bond, but only in the endo mode as represented for **5b**. The exo mode should induce too large a steric constraint and thus too high an energy level to exist. Thus the C_2/C=O coupling arises to generate only the *R* configuration with simultaneous σ-bonding between C_1 and platinum. The authors found that, in **6**, the configuration of carbon C_2 (new numbering scheme in the bicyclic compound) is exclusively *R*, so hydrogenation of the carbonyl function occurs in **5c**, through the *re* face, the platinum atom preventing the approach of the *si* face. Then, a classical β-H elimination of a hydrogen atom on the C_7 of **5d** restores the platinum hydride active species and produces **6**, in which the initial carbon–carbon double bond present in **5** has been shifted.

2.2. Hydroformylation of β-pinene

Hydroformylation of (1*S*, 5*S*)-(−)- and (1*R*, 5*R*)-(+)-β-pinene, in the presence of a rhodium or a cobalt–rhodium



Scheme 2.

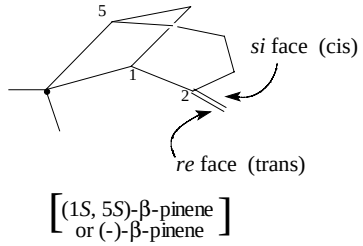


Fig. 5. The *re*-face and *si*-face of (1*S*, 5*S*)-β-pinene.

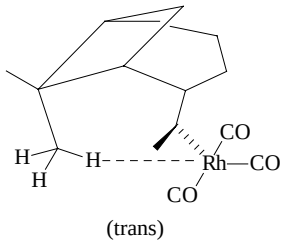


Fig. 6. Agostic interaction between the methyl group and the rhodium center.

carbonyl precursor, sometimes with an excess of ligand, has been carried out by Azzaroni et al. [13]. Most of the results deal with $[Co_2(CO)_8]$ and $[Rh_4(CO)_{12}]$ in a 2:1 molar ratio and the major products of catalysis are (1*S*, 2*R*, 5*S*)-(−)-10-formylpinane starting from (1*S*, 5*S*)-(−)-β-pinene and (1*R*, 2*R*, 5*R*)-(+)-10-formylpinane from (1*R*, 5*R*)-(+)-β-pinene. As shown in Fig. 5, the attack of the catalytic species proceeds through the *re* face which provides the *R* configuration at the C_2 carbon atom, i.e. the more hindered face. As the active species is presumably $[HRh(CO)_3]$ containing weakly donating ligands [14], coordination of the C=C double bond of β-pinene in the *re*-mode should provide a stabilization over the *si*-mode. We suggest that an agostic interaction between one of the two methyls and the rhodium center compensates sufficiently in energy for the steric hindrance of the substrate. Presumably this interaction takes place after the hydride transfer generates the alkyl species (Fig. 6).

The same unexpected observation has been reported by Gusevskaya and her group [15] for the (−)-β-pinene hydroformylation catalyzed by the putative $[PtH(SnCl_3)L_2]$, in which L is PPh_3 or L_2 is a diphosphine ligand. *Trans*-10-formylpinane was obtained with a diastereomeric excess as high as 98%. Platinum(II) is known to have significant electrophilic character so that it can relatively easily accommodate an agostic interaction with a methyl substituent. NMR data should be an elegant way to validate this hypothesis. Moreover, Barros et al. [16] describe that the more basic the ligands, the higher is the *cis/trans* ratio. Such an observation is consistent with the absence of any agostic interaction when the electron density on the metal center is too high.

The use of $[Rh_2(\mu\text{-}StBu)_2(CO)_2L_2]$ dinuclear complexes bearing bulky ligands and a relatively high electron density on rhodium, affords large *cis*/*trans* ratios, so that the same general tendency is obeyed [17]. Camphene, and α-pinene can also be functionalized and in this case too, the chirality present on the substrate is responsible for an enantiotopic discrimination [17].

2.3. Dihydroxylation of terpineol

The epoxidation of terpinen-4-ol, which belongs to the family of homoallylic alcohols, has been performed in a catalytic asymmetric way by using H_2O_2 as oxidant in the presence of V_2O_5. Interestingly, high yields and selectivities in *trans*-dihydroxylation are observed starting from a single enantiomer. Thus (4*S*)-terpen-4-ol produces (1*S*, 2*S*, 4*S*)-*p*-menthane-1,2,4-triol very easily with a diastereomeric excess (de) as high as 94%. A similar observation is repeated with (4*R*)-terpinen-4-ol which gives (1*R*, 2*R*, 4*R*)-*p*-menthane-1,2,4-triol [18]. Not only does the stereochemistry at the C_4 carbon atom influence the approach of the metal center to the C=C double bond, but the authors also propose that the transition state involves the simultaneous interaction of an oxygen atom of the coordinated hydroperoxo group with the C=C bond and a hydrogen-bond between this same group and the alcohol function of terpineol, as shown in Fig. 7.

Conversely, protection of the OH group by a tosylate function introduces large steric hindrance so that the attack or transfer of the oxygen atom proceeds through the least hindered enantiotopic face. Thus, the (4*S*) enantiomer gives diastereomer (1*R*, 2*R*, 4*S*) with a 60% de [18].

3. Functionalization of steroids

In order to modulate biological properties of various steroids with some flexibility, there is a growing interest in

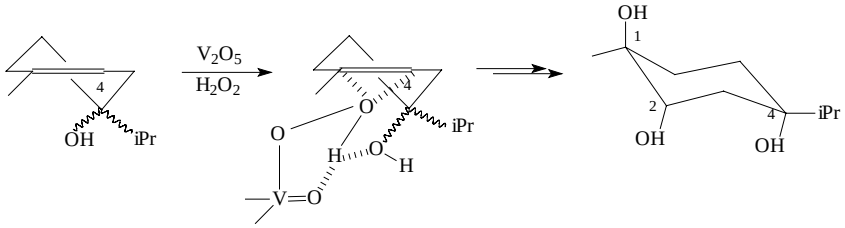


Fig. 7. *Trans*-dihydroxylation of (4*R*)- or (4*S*)-terpinen-4-ol by V_2O_5/H_2O_2.

introducing functional groups into specific positions [19]. We selected two different representative strategies that are detailed below.

When studying several steroidal dehydroamino acid esters, Skoda-Földes et al. [20] found that those bearing an acetamidoacrylate moiety in the 17-position can be efficiently hydrogenated in the presence of a rhodium/triphenylphosphine precursor at 80–110 bar.

Diastereomeric ratios reaching 75/25 were explained by the relative proximity of the two stereogenic centers C_{13} and C_{14} (Fig. 8).

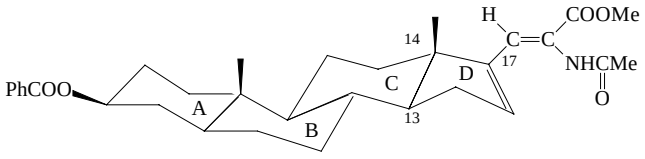


Fig. 8. Methyl α-acetamino-β-(3β-benzoyloxy-androsta-16-en-17-yl) acrylate.

Moreover, the authors suspect that the 3-benzoate moiety on C_3 plays a significant role in the diastereoselectivity, although it is far from the reaction center. Surprisingly, we note that this induction also seems to be correlated with the presence of a phenyl group in the C_3 substituent.

Concerning the hydroformylation of steroids, Freixa et al. [21] succeeded recently in the carbonylation within the β-face of the backbone whereas until this time, only the α-face was functionalyzed [22]. The rhodium catalyst $[HRh(CO)\{P(O^tBu)_3\}_n]$ generated in situ has no chiral ligand and the asymmetric induction is driven by the configurations at C_{10} and C_3 as shown in Fig. 9. The resulting aldehyde is obtained with 68% diastereoselectivity and has been fully characterized by an X-ray crystal structure and 2D-NMR studies.

4. Tandem allylic alkylation and annulation reactions

In order to prepare bicyclic cyclopentenones in a one-pot reaction, Evans and Robinson developed a strategy that combines the introduction of an acetylenic substituent by an allylic alkylation followed by its carbonylation and cyclization through a Pauson–Khand annulation reaction. The same catalyst is used for the two steps, i.e. [RhCl(CO)(dppe)] or its congeners with dppp or dppb diphosphine ligands (dppe being 1,2-bis(diphenylphosphino)ethane and dppp 1,3-bis(diphenylphosphino)propane) [23]. The authors observed for the first time a regio- and diastereoselective rhodium-catalyzed tandem reaction. Alkylation of the chiral allylic carbonate **7** with an acetylenic containing malonate anion by rhodium complexes, in which the diphosphine ligands are dppe, dppp, and dppb, provides under mild conditions the intermediate **8a** which is heated to give mainly the diastereomer **9a** (Fig. 10).

This diastereoselectivity is largely governed by the nature of the substituent on C_2 as defined in the resulting product **9a**.

This reaction has been extended to allylic amination followed by the similar annulation reaction to give a bicyclic azacyclopentenone [23]; in this case a diastereoisomeric excess of 98% was noted.

5. Diastereoselectivity promoted by chiral auxiliaries or directing groups

Beyond asymmetric induction provided only by the substrate, we have considered that introduction of a chiral substituent on a given substrate could provide a similar heuristic approach. Indeed, such a powerful strategy can lead to high diastereoselectivities and in many cases the substituent is removed after the reaction. Such a strategy can be improved by the design of a substrate-bound directing group which produces efficient control of facial stereoselectivity.

5.1. Chiral auxiliaries

Incorporation of a chiral aminoacid on a substrate, especially on an aromatic ring, allows for subsequent hydrogenation to be diastereoselective. Heterogeneous catalysis has been used exclusively for such a strategy. A representative example concerns the reaction of *o*-toluidine with Boc-(*S*)-proline to create in **10** a chiral amide bond which after deprotection of the proline moiety and hydro-

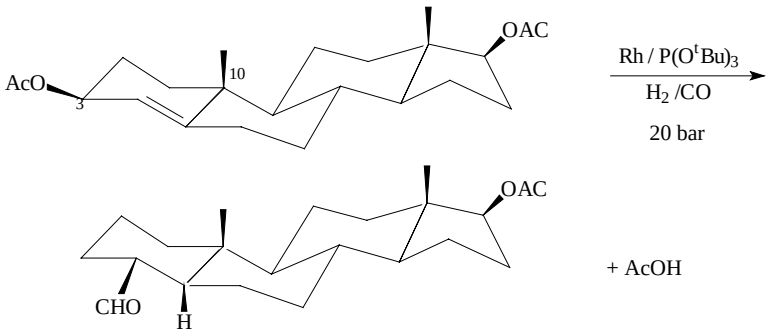


Fig. 9. Hydroformylation of 3β, 17β-diacetoxyandrost-4-ene.

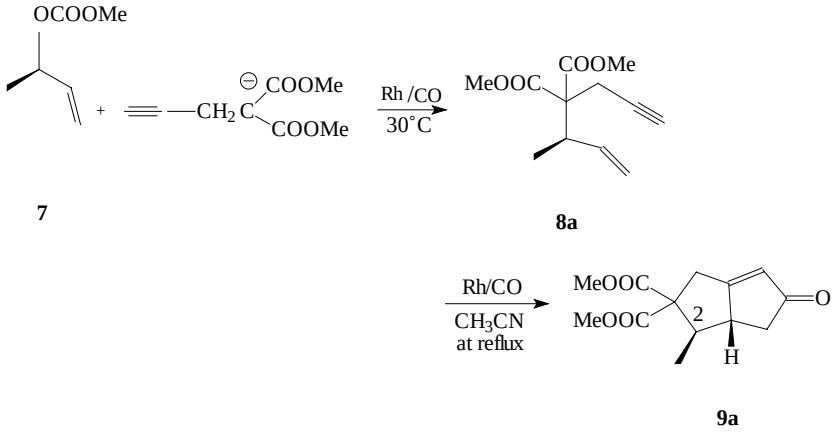


Fig. 10. Tandem rhodium-catalyzed allylic alkylation/Pauson–Khand annulation reaction (and minor amounts of the two *trans* diastereomers).

genation of the aromatic ring over Rh/C or Rh/Al_2O_3 or Rh/TiO_2 at 40 bar [24], as shown in Fig. 11, gives both **11a** and **11b** isomers of *cis*-(*S*)-proline-2-methylcyclohexyl amide.

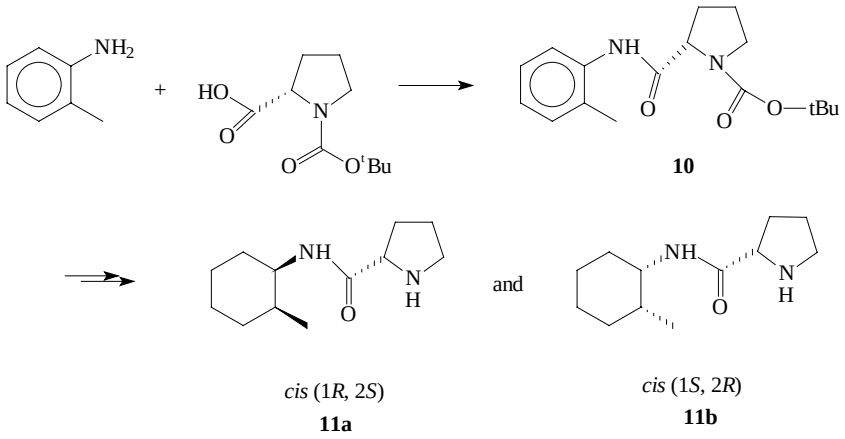
An excess of one *cis* diastereomer over the other *cis* one is observed. Starting from (*S*)-proline affords *cis*-(1*R*, 2*S*) with a 55% de and the reverse is seen on using (*R*)-proline to generate *cis*-(1*S*, 2*R*). The authors provide evidence that the proline moiety is responsible for the asymmetric induction, presumably through strong adsorption of the nitrogen atom on the catalyst surface. Such a phenomenon favours the approach of only one of the two faces of the aromatic ring. This diastereoselective strategy has been illustrated by other examples on supported metal catalysts [25].

Similarly pyridine rings have been diastereoselectively hydrogenated with the assistance of (*S*)-methylproline, and de values as high as 90% at 50 bar have been obtained [26].

A recent paper shows that pyrazine rings can be hydrogenated in two successive steps: the first one gives a tricyclic α, β-dehydrodipeptide by intramolecular cyclization, the second step providing a satisfactory de of 71–83% on Pd, Rh or Ru/C [27].

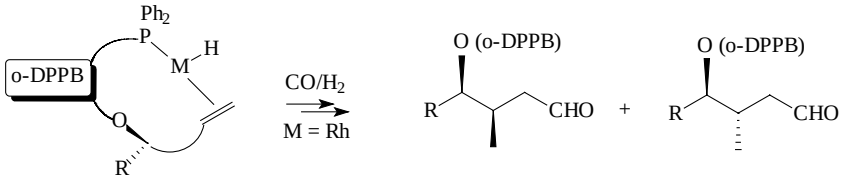
Interestingly, the Heck reaction has been assisted in a diastereoselective version by attaching a chiral sulfinyl group on a cyclopentene function. In the presence of palladium acetate, the addition of iodoarene produces (*S*)-1-phenylcyclopentene (ee = 90%) and, by a double Heck reaction, (*S*)-1,3-diphenylcyclopentene (ee = 94%), after the removal of the chiral auxiliary [28]. In our opinion and consistent with previous related observations [29], the sulfur atom likely coordinates to palladium and orients the enantiofacial discrimination of the vicinal endocyclic C=C bond.

Finally, steroids represent potentially useful chiral auxiliaries since preliminary results have appeared on the cyclopropanation of cinnamic acid or cinnamic aldehyde derivatives of steroids [30]. Yields higher than 80% and stereoselectivities reaching 90% have been reported, the reaction of diazomethane being simply catalyzed by $Pd(OAc)_2$.



(and minor amounts of the two *trans* diastereomers)

Fig. 11. Chiral hydrogenation of *o*-toluidine bearing a chiral proline auxiliary.



Scheme 3.

5.2. Directing groups

Breit and his group have designed the utilization of substrate-bound metal center directing groups to assist an asymmetric induction in the hydroformylation of alkenes. Indeed, recently they used *o*-diphenylphosphinobenzoic acid (*o*-DPPB) as a ligand to induce an interaction with a chiral group already present on the substrate and to amplify the stereofacial transfer of the hydride ligand to the C=C double bond as represented in Scheme 3 [31–33]. Such a strategy recalls the protection of OH groups.

Starting from methallylic or homomethallylic alcohols, *syn*-aldehydes are obtained with high diastereoselectivities up to 96:4. This route has been extended, as a key step, to give an efficient construction of stereotriads which represent building block precursors for polyketide chain extensions [34] and an access to the *anti*-aldol retron with mono-or di-substituted allylic alcohols [35].

The efficiency of a directing group for stereoselective catalysis, such as *o*-DPPB, should obey the following requirements: (i) reversible coordination of the directing ligand to the metal center under hydroformylation reaction conditions, (ii) easy introduction and removal from the substrate (like a protecting group), and (iii) adapted geometry to allow the most efficient coordination of the double bond through one face [36].

6. Heterogeneous catalysis and stereoselectivity

The introduction of a chiral modifier on the surface of heterogeneous catalysts has been largely developed and used in asymmetric catalysis [37]. This method has been reviewed and hydrogenation is the core of production of chiral products, including those of industrial interest [38].

However, chiral substrates have been introduced in heterogeneous catalysis in the absence of modifiers. This is surprising since a priori, one would expect to have both diastereomers in a rigorous 50/50 ratio. In fact some reports show that significant to good diastereomeric excesses can be reached [39–43]. In the absence of any clear explanation of the phenomenon, we can tentatively assume that the substrate is adsorbed on the surface preferentially by one face, and that a reconstruction of the local sites of the heterogeneous catalyst (adatoms, edges, corners) occurs in such a way that one diastereomer is favoured over the other, as in a kinetic resolution process. Then this favoured diastereomer acts as a modifier on the active metal center or aggregate and so asymmetric induction occurs. It would be interesting to try to quench the first stages of catalysis and reveal by appropriate analyses the sacrificial transformation of small amounts of the substrate into the modifier.

Several examples from the literature display that new chiral carbon atoms can be produced under the influence of a pre-existing stereogenic center on the substrate, which drives its preferential approach to the catalysts surface. The chiral center can be already present on the backbone [39–43], or a chiral auxiliary can be introduced [44]. The evident preferential adsorption via the unhindered side of the molecule has been proposed. In another review on supported palladium catalysts [45], the diastereoselective reduction of an alkene is shown to give an interesting *trans*/*cis* 95/5 ratio (Fig. 12). Such an asymmetric catalysis needs further investigation to allow a deeper understanding of the mechanism. It cannot be excluded that autocatalytic phenomena take some part, and that, as shown recently, an inhibition is indispensable to observe an asymmetric amplification [46].

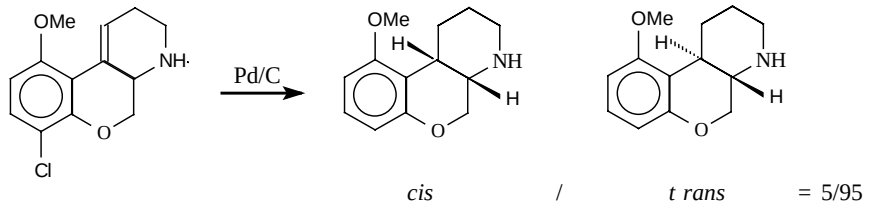


Fig. 12. Diastereoselective hydrogenation in a tricyclic alkene.

7. Conclusion

This article gives an insight into stereodifferentiation which can be provided by a chiral substituent, pre-existing or introduced on the substrate, when a prochiral group is catalytically functionalized. Usually, sophisticated chiral complexes are designed for a given reaction, but in a few cases, chiral substrates can self promote an asymmetric induction. In most cases, diastereomeric excess remains modest and do not compete with the largely explored asymmetric catalysis using chiral ligands. However, the concept is heuristic and we can quote R. Noyori in his Nobel lecture: "*the recent exceptional advances in [asymmetric catalysis] attest to a range of conceptual breakthroughs in chemical sciences*" [47].

We hope this review might contribute to the definition of such a concept.

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