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Atropochiral C,X- and C,C-Chelating Carbon Ligands

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In the realm of atropochiral ligands initiated by the BINOL and BINAP paradigms and extended by modifications of the 1,1′-binaphthyl backbone and the coordinating heteroatoms (O, P, N, S,..), the emerging domain of the carbon versions serving as spectator ligands in catalysis is reviewed. These atropochiral C,X-chelating ligands are classified according to their coordinating mode (monodentate or bidentate), to the nature of the auxiliary donor X (a heteroatom or a carbon atom), to the overall charge of the coordinating carbon function (neutral or anionic C-ligands), and to the hapticity of the coordinating carbon function (η^1 for NHCs and ylides, or η^2 for alkenes). Emphasis is put on both synthetic aspects and applications in catalysis, and especially in asymmetric catalysis. This survey suggests that the "carbon ligands" should continue to provide surprises not only in coordination chemistry and in stereoselective synthesis and catalysis, but also in fundamental molecular chemistry by pushing farther the stability limits of the metal–ligand interactions, thus reconciliating further the fields of organic and inorganic chemistry.

Introduction

Atropisomerism is a particular case of stereoisomerism caused by restricted rotation about a single bond that is not constrained in a ring.[1] It mainly refers to sp^2X–sp^2Y single bonds (X, Y = C, N), and gives rise to a stereogenic unit which is also a chirality element, namely a chirality axis (or helicoidal axis) defined by a chemical topography on a VSEPR-idealized achiral D_{2d} skeleton. The configuration of such chirality axes is currently assigned by the value of the *R*/*S* CIP descriptor using specific conventions.[2] In the absence of any improper symmetry element, the chiral molecule is said atropo-chiral. In standard conditions, the atropisomers do not interconvert due to a high rotation barrier of steric origin.[3] The word "atropisomer" is derived from the Greek *a* which means *not*, and *tropos* which translates as *turn* or *direction*. It was coined by Kuhn in 1933,[4] but atropisomerism was first detected in the 6,6′-dinitro-2,2′-diphenic acid by Cristie in 1922.[5] However, since the discovery of racemic BINOL in 1873,[6] and the determination of the absolute configurations of its enantiomers one century later,[7] (+)-, (–)- and (±)-BINOL have been widely used as precursors of atropochiral molecules. The current interest in the design of new atropochiral ligands for transi-

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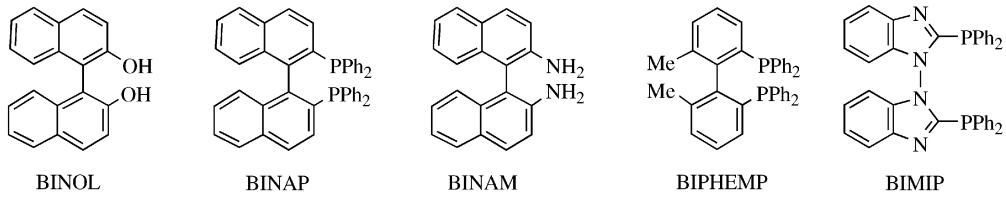
Yves Canac obtained his PhD degree in 1996 under the supervision of Prof. Guy Bertrand in Toulouse (France). After a postdoctoral fellow with Prof. Andrea Vasella at the ETH-Zürich (Switzerland), he entered the CNRS in 1998 at the University of Paris XI (Orsay). In 2001, he moved to the University of California-Riverside (UCR), taking part in the foundation of the joint Research Chemistry Laboratory UCR/CNRS. In 2006, he came back to Toulouse at the CNRS Laboratory of Coordination Chemistry. His research activities are mainly focused on the design, the coordination chemistry and the catalytic properties of novel chiral electron-rich carbon ligands (NHCs, ylides) and electron-poor cationic phosphorus ligands (amidiniophosphanes).

Remi Chauvin received his Ph.D. in 1988 under the supervision of Prof. H. Kagan in Orsay (France). He pursued as a post-doctoral fellow with K. B. Sharpless at MIT (USA), and then with A. Vasella in Zürich (Switzerland). Back to France, he first worked at the Roussel Uclaf company in Romainville. In 1993 he came back to the academic research at the CNRS in Toulouse, and in 1998 was appointed as a Professor at the Paul Sabatier University. Today he is interested in four aspects of molecular chemistry: theoretical analysis (molecular modeling, aromaticity), acetylenic synthesis (ring carbo-mers), coordination chemistry and catalysis (chiral carbon–phosphorus ligands), and synthesis of biologically active products (natural polyyne-polyols. and analogues).



Scheme 1. Ideally C_2-symmetric ligands based on a biaryl or bis-heteroaryl backbone.[9]

tion metals catalysts has thus been originally conditioned by the advent of Noyori–Takaya's 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl (BINAP) in 1980, which was prepared in four steps from BINOL.[8] The academic and industrial successes of BINAP then inspired the design of numerous axially chiral ligands based on the 1,1′-binaphthyl skeleton,[9] and especially of C_2-symmetric representatives complying to the "quadrant rule" in d^8 metal complexes (Scheme 1).[10]

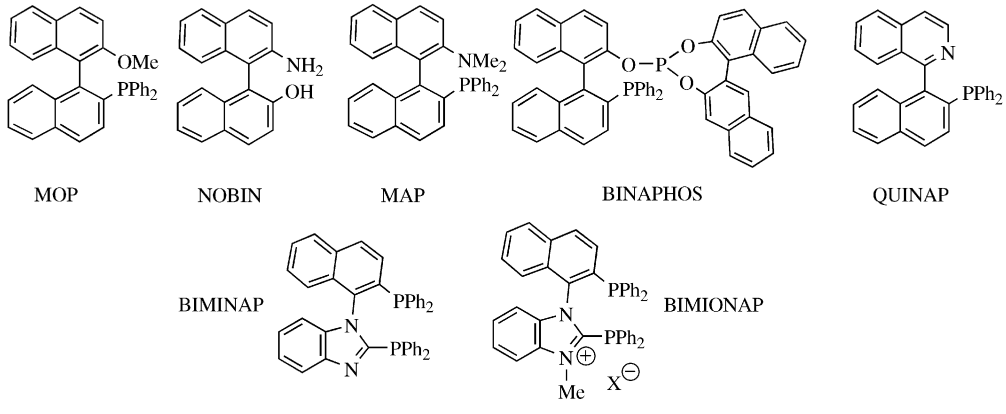
The remakable efficiency of the 1,1′-binaphthyl skeleton in asymmetric catalysis, can be ascribed to a subtle combination of overall rigidity and residual flexibility, allowing respectively for a high control of chirality transfer (enantioselectivity), and for steric adapatation to all the steps of the catalytic cycle (activity). Similar requirements can also be achieved with alternative atropo-chiral C_2-symmetric backbones, such as bis-alkylaryl bridges (e.g. in BIPHEMP)[8] or bis-heteroaryl bridges.[11]

As compared to their biaryl analogues, bis-heteroaryl backbones are generally more accessible and more diversified due to the heterocycle manifold, both in terms of heteroatoms and aromatic ring sizes. They thus allow for a large variation of ligand electronic properties, in particular by influencing the coordinating ability of soft phosphorus atom lone pairs in diphosphane ligands. As a relevant example, the 2,2′-bis(diphenylphosphanyl)-1,1′-bibenzimidazole (BIMIP) ligand was reported by Sannicolò et al. as the most electron-poor ligand of the five-membered bis-heteroaromatic diphosphanes, and as the first atropisomeric diphosphane possessing a hindered rotation about an N–N bond (Scheme 1).[12]

Beyond C_2-symmetric homo-bidentate ligands, C_1-symmetric versions proved valuable for specific applications in enantioselective catalysis.[13] Atropo-chiral hetero-bidentate ligands were thus designed by either anchoring two different coordinating groups at a given C_2-symmetric backbone (e.g. 1,1′-binaphthyl, in MOP,[14] NOBIN,[15] MAP,[16] BINAPHOS[17]) (Scheme 2), or bridging two identical or different coordinating groups by a C_1-symmetric atropo-chiral backbone (e.g. in QUINAP, an aza-binaphthyl analogue of BINAP).[18] The second approach is refined by the hybridization method of known C_2-symmetric ligands, such as BINAP and BIMIP in the BIMINAP ligand (Scheme 2).[19]

The functional nature of the 1,1′-naphthyl-benzimidazole core of neutral BIMINAP allowed for further desymmetrization by quaternization of a nitrogen atom in the cationic BIMIONAP ligand (Scheme 2).[19]

Whereas the simplest ligand scheme consists in a coordinating heteroatom (P: or N: or S:) bonded to a hydrocarbon backbone, it has been illustrated above that introducing heteroatoms in the backbone is a valuable source of variability. What about replacing the heteroatom by a coordinating carbon atom? The so-called "carbon ligands" are actually of topical interest for tuning the performance of transition metal catalysts. They are essentially represented by the cyclic diaminocarbenes (NHCs),[20] but anionic or other neutral carbon ligands like ylides and cumulenylidenes can also be considered as alternatives to the classical P:, N: or S: ligands.[21] The structural diversity of phosphorus and nitrogen ligands is however far beyond that of carbon ligands. Nevertheless, although the number of reports about atropo-



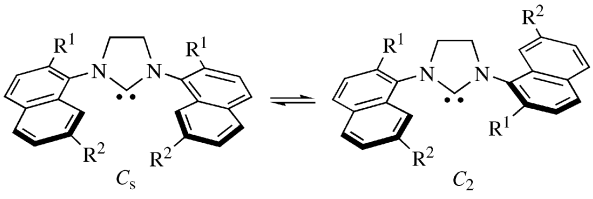
Scheme 2. C_1-symmetric ligands based on symmetric or dissymmetric atropo-chiral bridges.

chiral carbon ligands remains anecdotal as compared to their phosphorus versions, several atropostereogenic chelating carbon ligands have been described and can lend themselves to comparison. Selected aspects of their preparation, characterization, and complexation to transition metal centers are hereafter reviewed.

Three levels of "atropochirality" are here distinguished, depending on the environment and the generating circumstances of the sp^2–sp^2 "atropo-stereogenic" axis: (a) non-endocyclic to any ring before complexation (atropo-chirality of the "free" carbon ligand); (b) endocyclic to a "large" ring before complexation; (c) endocyclic to a metalacycle after complexation. The last two cases are obviously less interesting, and the first case (a) will be treated in more detail.

I. Monodentate Carbon Ligands

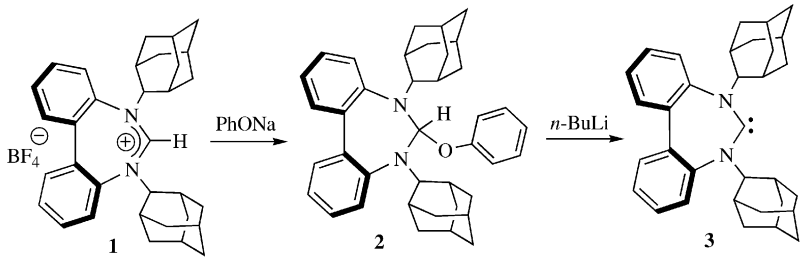
Although most atropo-chiral phosphorus ligands have been devised as bidentate, monodentate versions have also attracted interest due to their paradoxical performance in asymmetric catalysis.[22] The cases of phosphoramidites,[23] phosphonites,[24] and phosphites[25] are eloquent with this respect. In a similar manner, atropo-chiral carbon ligands are mainly exemplified in the *bidentate* version, but few *monodentate* analogues deserve to be mentioned. They are all of the NHC type. Bulky monodentate aryl-substituted imidazol-2-ylidenes, namely 2,4,6-mesityl-substituted IMes and 2,6-isopropylphenyl-substituted IPr and their saturated imidazolin-2-ylidene counterparts (SIMes and SIPr) have been reported to act as efficient ligands in transition metal catalysts.[20] A rationale for this efficiency is based on the orthogonal arrangement of the aryl side chains and the steric hindrance of the aromatic rings. Along this line, Dorta et al. showed that the introduction of two substituted naphthyl groups at the NHC core generates enantiomeric C_2-symmetric atropisomers (in the *rac* series, with an *anti* orientation of the substituents) and an achiral C_s-symmetric atropisomer (*meso*, with a *syn* orientation of the substituents) (Scheme 3).[26]



Scheme 3. Atropoisomerism of imidazolin-2-ylidenes substituted by hindered naphthyl groups. Only one enantiomer of the ideally C_2-symmetric isomers is depicted.

Experimental and computational analyses indicated that the rotation about the C–N bond becomes forbidden when the carbenic carbon is protonated or coordinated to a metallic center. In the case of the free carbenes, DFT calculations showed that their behaviour is directly correlated with the nature of the R^2 substituent. If R^2 = H, the rotation about the C–N bond is free, and dimerization to the corresponding enetetramine is observed. If R^2 = Me, the rotation presents a moderate barrier (12.9 kcal/mol). If R^2 = *i*Pr, the rotation is frozen at room temperature (with a barrier of about 16.7 kcal/mol) and dimerization is not observed. For catalytic purposes, these ligands were shown to compete with the most widely used NHCs (IMes/SIMes and IPr/SIPr). Satisfactory results were indeed obtained directly with the salts for the organocatalytic ring-opening alkylation of epoxides.[26] Palladium and ruthenium complexes of these atropo-stereogenic NHC ligands also proved to be efficient for the catalysis of C–C or C–N cross-coupling reactions and ring-closing metathesis.[26] By introducing a C_2-symmetric chiral diamine to the heterocyclic backbone of the NHC, the formation of three diastereoisomers was logically observed, and their palladium complexes (NHC)-Pd(cin)Cl (cin = cinnamyl) were isolated in a pure form by fractional crystallization.[27] When employed in the asymmetric intramolecular α-arylation of amides, they led to the enantioselective formation of oxindoles with high yields and *ee* up to 89%.

Another way to induce atropochirality is to incorporate the ligand itself inside an appropriate cyclic structure. Thus, Stahl et al. have designed a new class of atropochiral NHCs featuring an axially chiral seven-membered heterocyclic framework.[28] Starting from the 2,2′-dinitrobiphenyl, the reduction of both nitro groups followed by the introduction of bulky adamantyl substituents and cyclization in presence of triethylorthoformate led to the C_2-symmetric amidinium salt **1**. As the classical deprotonation method failed to generate the free carbene **3**, an alternative method involving a base-induced α-elimination process was devised from the phenol adduct **2** (Scheme 4).[28d] An X-ray diffraction analysis indicated that the value of the torsional angle between the two phenyl rings of the amidinium salt **1**



Scheme 4. Synthesis of an axially chiral free NHC **3** embedded in a seven-membered ring.

[ca. 46.1(8)°] is similar to the corresponding values measured in the free carbene **3** [45.2(3)°] and in related palladium(II) complexes [41.9(5)–46.4(8)°].[28a]

An enantiopur chiral version of **3** was later prepared from enantiomerically pure 2,2′-diamino-6,6′-dimethylbiphenyl.[29] The preparation of the starting amidinium salt (homologous to **1**) was reported by a synthetic sequence consisting successively of an *ortho*-arylation, an *N*-alkylation and a cyclization reaction. A palladium(II) complex of this enantiopur atropo-chiral NHC ligand was then employed as a catalyst for an aerobic oxidative cyclizing amination reaction of alkenes, affording ee's up to 63%, higher than those obtained with Pd-catalysts bearing a chiral five-membered NHC ligand (*ee* ≤ 7% *ee*).[29]

II. Bidentate Carbon Ligands C,X (X ≠ C)

Two kinds of chelating C,X carbon ligands are distinguished, depending on the hapticity of the coordinating carbon function, one (η^1-carbyls) or two (η^2-alkenes).

1. η^1-C Coordination

a. Anionic η^1-C Coordination

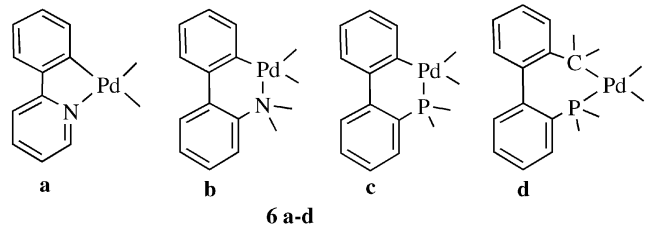
A class of complexes where the metallic center is involved in a strong σ bond with an anionic carbon ligand (an X-type ligand in the Green formalism) is constituted by the *ortho*-metallacycles. In this category, the palladacyles turned out as attractive organometallic catalysts.[30]

A non-resolved racemic atropochiral palladacycle **5a** has been obtained through a P–C bond cleavage from the BINAP complex **4** (Scheme 5). The phosphane-aryl complex **5a** displays a small dihedral angle of 51° and severe deviation from ideal square-planar geometry at the metallic center.[31]

As the complex **4** is obtained by oxidative addition of phenyl bromide to the $(Binap)_2Pd^0$ precursor, it becomes envisageable that palladacycles similar to **5a** could be generated during a catalytic process in which the life time of the intermediate aryl halide complex is sufficient.

A resolved version **5b** has been prepared from (*S*)-H-MOP by Hou et al. and was found to be an efficient catalyst for the ring-opening of oxabicyclic alkenes with arylboronic acids in high yields and *ee* up to 83% (Scheme 5).[32]

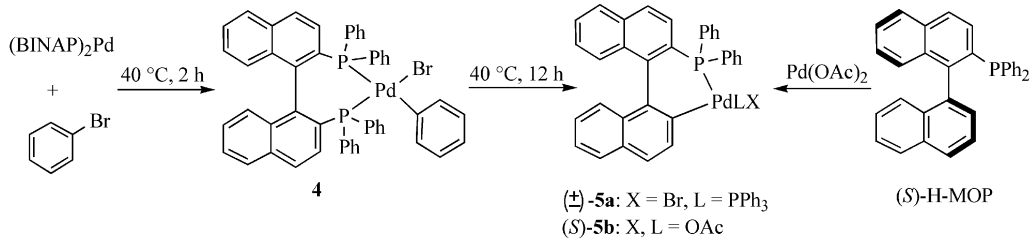
Other palladacyles with different backbones **6a**–**d** have been reported in the literature showing high catalytic activities (Scheme 6).[33]



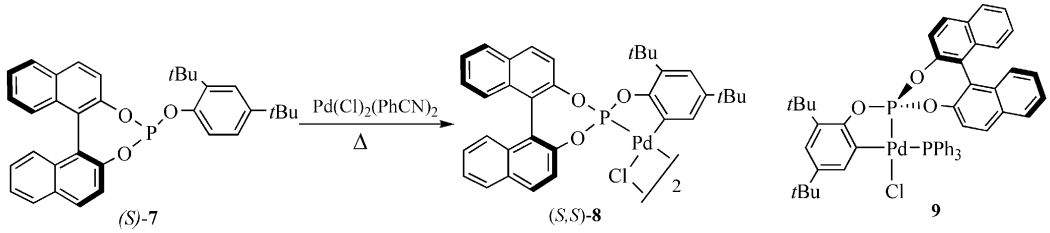
Scheme 6. Known structures of atropochiral palladacycles **6a**–**d**.

Although these palladacycles can be considered as atropochiral at the (c) level (see introduction), there is no doubt about the conformational instability of the free protonated ligands, due to the absence of sterically hindered substituents preventing the free rotation about the aryl–aryl bond.

Examples of resolved complexes containing an anionic C-ligand and an atropochiral ligand are also constituted by complexes in which the element of axially chirality belongs to a monodendate co-ligand independent from the C-metallated ligand. As representative example, the optically active phosphapalladacycle **8** was recently reported (Scheme 7).[34]



Scheme 5. Formation of palladacycles **5a**,**b** from respectively (±)-BINAP and (*S*)-H-MOP.

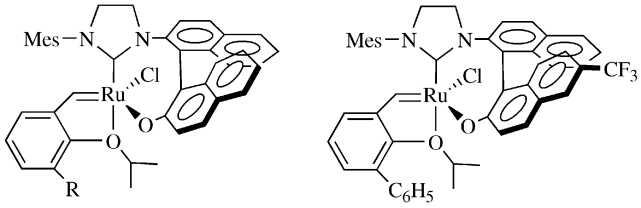


Scheme 7. Resolved atropochiral palladium complexes with an independent *ortho*-C-metallated ligand.

The dimeric cyclopalladated complex (*S*,*S*)-[Pd(η^2-L)(μ-Cl)]$_2$ **8** was obtained by thermally induced C–H activation of the (*S*)-BINOL-derived phosphite **7** with complete retention of enantiopurity. The chiral triaryl phosphite complex **9** resulting from complex **8** upon addition of triphenylphosphane, was tested for its catalytic properties in 1,4-conjugate addition of phenylboronic acid to cyclohexen-2-one and allylation of benzaldehyde with allyltributyltin. Despite the high activity observed, the weak chiral induction (*ee* ≤ 15%) can be attributed to the large distance of the chiral BINOL moiety from the catalytic active site.

b. Neutral η^1-C Coordination

NHC-Type Ligands: Amongst mono-NHC representatives, an atropochiral C,O-chelating ligand featuring simultaneously a NHC and a naphthoxy donor group was designed by Hoveyda et al. in 2002.[35] The complexation of this ligand derived from pure (*S*)-2-amino-2′-hydroxy-1,1′-binaphthalene (NOBIN, see Scheme 2) in the ruthenium complex **10** (Scheme 8) was accomplished by reaction of the Hoveyda's metathesis catalyst precursor with the corresponding in situ-generated silver carbene. Similar ligands were successfully employed in asymmetric ruthenium-catalyzed ring opening metathesis (AROM/CM)[36] and copper-catalyzed allylic substitution,[37] affording respectively *ee* up to 91% and 98%. Following the initial report, different steric and electronic modifications of the parent catalytic system were achieved for tuning the catalytic activities.[38] For example, substitution of the C,X ligand backbone of **11** by a CF_3 group induces a weaker donation of the naphtholate moiety in the ruthenium complex **12** (Scheme 8) and results in improved AROM/CM catalytic efficiency.[36]

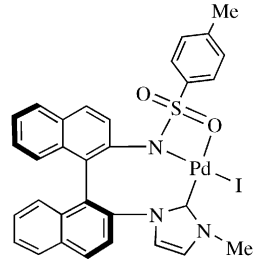


10: R = H
11: R = C_6H_5
12

Scheme 8. Hoveyda's catalytic precursors with atropochiral C,O-chelating ligands.

Replacement of the alcoholate donor by a phosphanyl group leads to the atropochiral NHC ligand **13**. This carbene precursor was obtained by coupling a chiral NHC derived from (*S*,*S*)-1,2-diphenyl-ethylen-1,2-diamine with diphenylnaphthyphosphane. Transmetallation of a silver-carbene complex of ligand **13** with [Rh(cod)Cl]$_2$ afforded two diastereoisomers of the rhodium complex **14** in a 1:2 ratio.[39] It was assumed that these isomers are actually atropisomers with respect to the *i*PrC_6H_4–N bond. The mixture of atropoisomers of **14** was found effective in the asymmetric hydrogenation of α,β-unsaturated esters giving up to 99% *ee*, and in the conjugate addition of aryl boronic acids to enones and α,β-unsaturated esters with up to 98% yield and 99% *ee* (Scheme 9).[40]

An original O,N,C-tridentate atropochiral NHC–Pd^{II} complex **15**, where the metallic center adopts a quasi square-planar geometry and is simultaneously bonded to the carbenic center and the nitrogen and oxygen atoms of the sulfonamide moiety (Scheme 10) has been described by Shi et al. This complex was found effective as catalyst for Suzuki–Miyaura and Heck cross-coupling reactions.[41]



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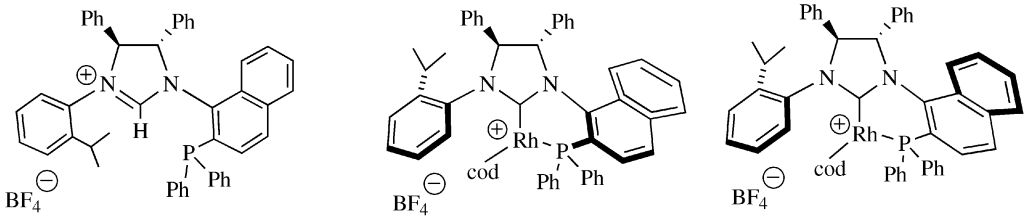
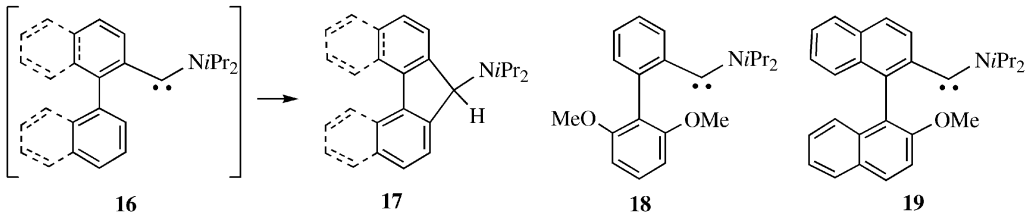
Scheme 10. O,N,C-tridentate atropochiral NHC-type Pd^{II} complex derived from BINAM (see Scheme 1).

Bertand et al. described atropochiral carbon ligands containing an acyclic aminocarbene in both the biphenyl and binaphthyl series.[42] The biphenyl and binaphthyl diisopropylaminocarbenes **16** were found to be only transient species rearranging to the corresponding aminofluorenes **17**. DFT calculations confirmed that the insertion reaction of aminocarbenes into the proximal aromatic C–H bonds requires only a moderate energy barrier (biphenyl serie: 17 kcal/mol; binaphthyl serie: 27.5 kcal/mol). From these calculations, a concerted asynchronous mechanism dominated by a $C_{arom} \rightarrow C_{carbene}$ proton transfer was proposed by the authors. However the introduction of a methoxy group on the second biraryl moiety allowed for a NMR characterization of the free carbenes (MACs) **18** and **19** (Scheme 11).[42]



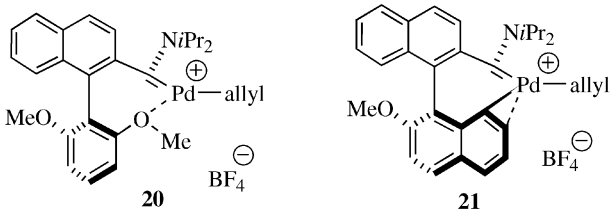
(*S*,*S*)-**13**
(a*R*,*S*,*S*,a*R*)-**14**
(a*R*,*S*,*S*,a*S*)-**14**

Scheme 9. Atropochiral NHC-type P,C-chelating ligand and its atropoisomeric rhodium complexes.



Scheme 11. Atropochiral acyclic amino-carbenes **16**, **18** and **19** and insertion product **17**.

In the solid state, cationic palladium complexes **20** and **21** of the respective amino-carbenes **18** and **19** exhibit palladium-oxygen and palladium-arene interactions (Scheme 12).[43]



Scheme 12. Cationic palladium(II) complexes of the C,O- and C,C_2-chelating atropochiral amino-carbenes **18** and **19** (see Scheme 11).

The neutral version of the palladium complex **20** was evaluated as a catalyst for the α-arylation of propiophenone with aryl bromides and was found to compete in terms of activity with the most efficient phosphane-based catalysts reported to date.[43]

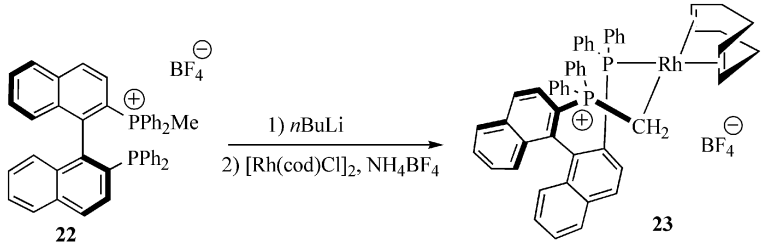
Ylide-Type Ligands: Beyond their ubiquitous role in organic synthesis as in the Wittig-type olefination of carbonyl compounds, phosphonium ylides, are fascinating ligands of transition metals acting as stable Csp^3 carbyl ligands. These ylides are now attracting a renewed interest from the standpoints of stereochemistry and catalysis.[44]

In 1998, one of the present authors proposed the study of complexes where a "proximal" cationic charge would embed the metal into a chiral electrostatic field. The aim was to identify catalytic transformations of polar substrates whose stereoselectivity would be governed by dative-electrostatic interactions. Preliminary results with the flexible methyl diopium ligand suggested that the chelating character of the ligand is required to perform enantioselective reactions as hydrogenation or hydrogen transfer.[45] A natural prolongation was the synthesis of a hybrid ligand, containing both a η^1-phosphane terminus and a η^1-C non-stabilized phosphonium ylide terminus. It was achieved by the study of the ylide derivative namely "YLIPHOS" of the more rigid methylBINAPIUM ligand.[46] The chiral phosphane-phosphonium precursor namely methylBINAPIUM **22** was obtained by mono-quaternization of the (*R*)-BINAP enantiomer. The corresponding ylide, generated in situ by addition of butyllithium, was converted into the atropochiral phosphane-phosphonium ylide complex **23** by reaction with [Rh(cod)Cl]$_2$ (Scheme 13).

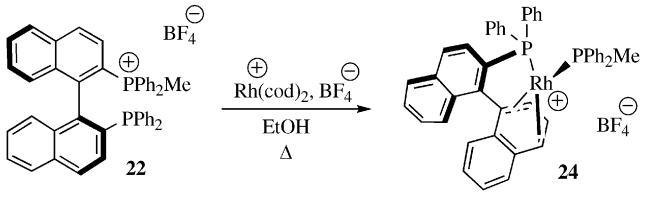
DFT calculation of a model complex indicated the extreme kinetic flexibility of the chiral eight-membered rhodacycle of **23**.[47] More precisely, the flip-flop process was attributed to the interconversion between the *M* and *P* configurations of the local chirality element involving the rhodium center, namely the P–Rh–C–P^+ helicoidal axis. And indeed, the flexible chiral configuration in the vicinity of the metal center accounted for the low enantioselectivity ($ee \leq 15\%$) obtained with **23** in catalytic hydrosilylation of ketones, despite significant activity. Simultaneously, Ohta et al. claimed that Pd- or Pt-stabilized YLIPHOS complexes catalyze allylic substitution in high yields and high enantioselectivities (up to 90%).[48] Later on, more rigid chiral six membered pallada- and rhoda-cycles involving P,C-chelating ligands based on the *ortho* 1,2-diphenylphosphanylbenzene backbone were reported. In these complexes, the chirality element is centered at the metallated ylidic carbon.[49]

During the study of the coordination chemistry of methylBINAPIUM, an atropochiral mixed bis(monophosphane)rhodium(I) complex [Rh(η^5-H-MOP)($MePh_2P$)][BF_4] **24** was isolated when methylBINAPIUM **22** was treated with the cationic rhodium(I) precursor [Rh(cod)$_2$][BF_4] in ethanol (Scheme 14).[50]

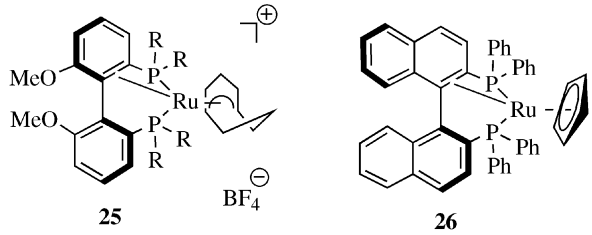
This peculiar hetero-chelating behaviour resulting from a selective reductive P^+–C bond cleavage in the Rh^I series is related to the coordination modes reported by Pregosin et



Scheme 13. Preparation of an atropochiral resolved phosphane-phosphonium ylide rhodium(I) complex **23**.



Scheme 14. Preparation of an atropochiral mixed bis(monophosphane)rhodium(I) complex [Rh(η^5-H-MOP)($MePh_2P$)][BF_4] **24**.



R = (3,5-di-*t*butylphenyl)

Scheme 15. Pregosin's ruthenium complexes of atropochiral P,C ligands involving a η^2-chelated alkene moiety.

al. in the coordination sphere of Ru^{II} (this specific aspect will be developed in the next section). The selective hydrolytic P–C bond cleavage observed in this specific case has already been observed in BINAP and MeO-BIPHEP–ruthenium complexes leading to H-MOP analogues. It is noteworthy that complex **24** is a catalytic precursor for the hydrogenation of (*Z*)-α-acetamidocinnamic acid (95% yield), albeit without significant enantioselectivity ($ee \leq 2\%$). The lack of chiral induction was theoretically explained by the conformational lability of the original atropoisomeric C–C axis after hydrogenation of the coordinated double bonds of **24**.[50]

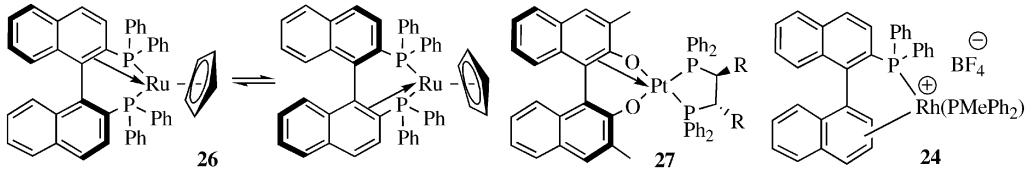
2. η^2-C Coordination

Alkene-Type Ligands: In the previous neutral carbon complexes, the atropochiral NHC or phosphonium ylide ligands act by strong η^1-C coordination. However P,C and N,C bidentate ligands involving an η^2-olefin donor can also present stable atropochiral configuration. This is the case for the atropoisomeric chelating ligands BINAP, MeO-BIPHEP, MOP, MAP and phosphoramidite-type ligands which can use their aromatic moieties as donors to stabilize unsaturated 14 or 16 electron centers.[51]

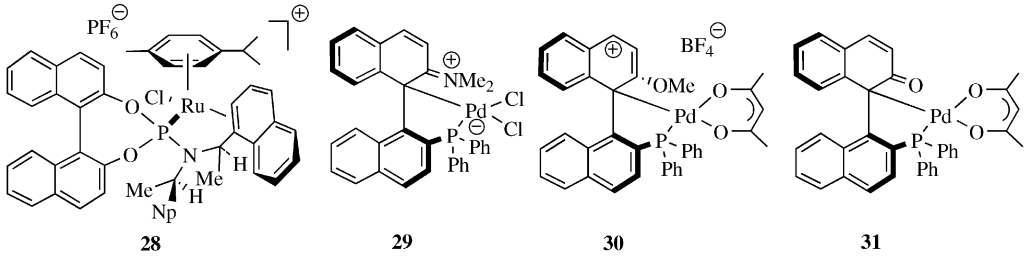
The first example of such coordination was described by Pregosin et al. with the report of the ruthenium complexes **25** and **26** based on the MeO-BIPHEP and BINAP ligands (Scheme 15).[52]

In these complexes, the MeO-BIPHEP and the BINAP ligands act as six-electron donors rather than classically as four-electrons donors. The two strategies used for the preparation of such complexes consist in creating a vacant site at the metallic center by either protonation of a labile ligand (e.g. an acetate) or abstraction of a halogen atom from the ruthenium atom with a silver salt. In spite of the biaryl skeleton distortion observed in the solid state, the η^2-alkene interaction remains fairly weak. The direct consequence is an equilibrium in solution (observed by NMR) where a double bond of one of the aryl moieties is substituted by a double bond of the second aryl moiety (Scheme 16). This peculiar type of bonding is not inherent to the ruthenium case, and has been observed at other metallic centers like in the platinum complex **27**[53] or in the previously described rhodium complex **24**[50] (Scheme 16, and Scheme 14).

In the ruthenium complex **28** of a naphthyl phosphoramidite ligand, the η^2-coordinated alkene comes from the *N*-naphthyl substituent rather than from the atropochiral BINOL core (Scheme 17).[54] In the MAP and MOP complexes **29**,[55] **30**,[56] and **31**,[56] the interaction between the arene and the metal could occur through η^1-coordination of one of the bridge head carbon atoms of the atropochiral binaphthyl backbone (Scheme 17). While the positive charge of **29** is located at the iminium fragment, the positive



Scheme 16. Ruthenium, platinum and rhodium complexes of C,P- or C,O-chelating ligands coordinated by an alkene bond of the binaphthyl backbone.



Scheme 17. C,X-chelated complexes of atropochiral phosphoramidite (**28**), MAP (**29**) and MOP (**30** and **31**) neutral ligands.

charge of **30** is delocalized throughout the naphthyl moiety. The carbon atom σ-bonded to the metallic center presents a tetrahedral environment thus suggesting an alkyl η^1-C zwitter-anionic character. These complexes are therefore "haptomerically" related to the above-discussed category of η^1-C-coordinated neutral C,X ligands.[57]

In contrast to the NHC or ylide complexes (see above), the η^1, η^2 or η^4 bonding of the arene moiety to the metallic center evidenced both in the solid and solution states, can not be considered as a strongly localized σ- or π-carbon–metal bonds, but only as "weak interactions".[51] These interactions could thus be anticipated to play a role in catalytic processes requiring hemilabile ligands.

III. Bidentate Ligands C,C

1. η^1-C Coordination

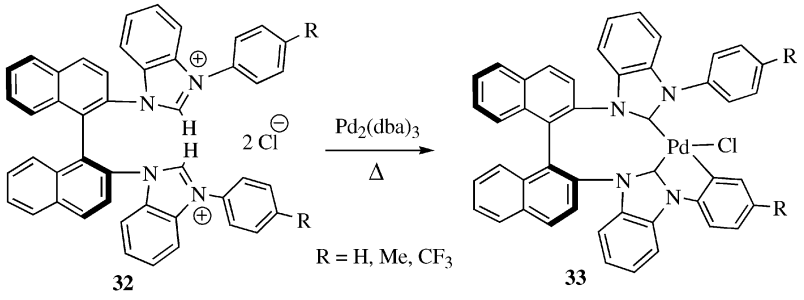
a. Anionic η^1-C Coordination

Cyclometalated *cis*-chelated bis-NHC ligands derived from BINAM have been reported in palladium complexes **33** resulting from a thermal treatment of bis(benzymidazolium) salts **32** in the presence of a Pd^0 precursor (Scheme 18).[58] The triple carbon coordination results from a metal insertion into the *ortho* sp^2-C–H bond of the neighbouring phenyl ring. The palladium(II) center, presenting a slightly distorted square-planar geometry in an atropochiral environment, is thus bonded to three sp^2-carbon atoms coming from two neutral NHCs and one anionic aryl moiety (it must be however emphasized that the anionic carbon ligand does not belong to the atropochiral backbone). Catalytic activities of these complexes have been evidenced in the Suzuki–Miyaura and Friedel–Crafts reactions. Stereocontrol has been achieved for the asymmetric Fiedel–Crafts reaction of indole with *N*-tosylarylimines, by the adjustement of the R group on the benzene rings of the NHC–Pd^{II} complexes **33**, affording *ee* up to 74%.[59]

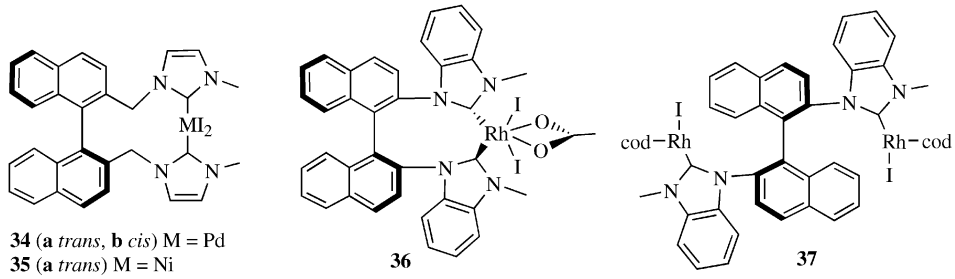
b. Neutral Double η^1-C Coordination

NHC-Type Ligands: The first isolation of an atropochiral carbene derivative was reported in 2000 by Rajanbabu et al. with the preparation of the bidentate bis-NHC palladium(II) and nickel(II) complexes **34** and **35**, respectively.[60] The bis-imidazolium salt precursor of these complexes was obtained from pure (*S*)-1,1′-bi-2-naphthol-bis(trifluoromethanesulfonate) in four steps in 66% overall yield. The linkage of the two imidazolium rings to the biaryl unit in the 2- and 2′-positions is established through methylene bridges. It was shown that depending on the nature of the metal (Pd or Ni), the complexes can adopt either a *trans* and/or a *cis*-square-planar geometry. In the palladium series, catalytic activity has been evidenced for the Heck coupling of ethyl acrylate with bromo- and iodobenzene in 79% and 95% yields, respectively (Scheme 19). A rationale for the *cis*-*trans* coordination is provided by the high flexibility of the bis-carbene framework and by the important size of the final metallacycle. This is likely the reason why these complexes were not employed in asymmetric catalysis.

In order to circumvent this drawback, a more rigid axially chiral NHC–rhodium(III) complex **36** derived from enantiomerically pure (*S*)-1,1′-binaphthalenyl-2,2′-diamine (BINAM) was designed by Shi et al.[61] The two benzimidazolium moieties are here directly connected to the binaphthyl skeleton. During the complexation process, a second dinuclear derivative **37** was produced, featuring two



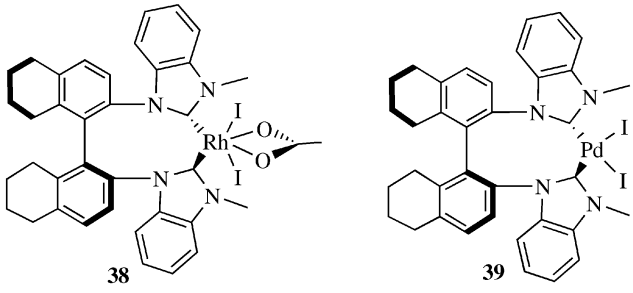
Scheme 18. Atropochiral C,C palladacyles **33** with a coordinated anionic carbon center derived from bis-iminiums **32**.



Scheme 19. First complexes of C,C-chelated atropochiral bis-NHC ligands.

rhodium(I) centers (Scheme 19). The rhodium(III) complex **36** was used in enantioselective catalytic hydrosilylation of alkyl aryl ketones, showing high activities (82–96% yield) and chiral induction of 67–98% *ee*.

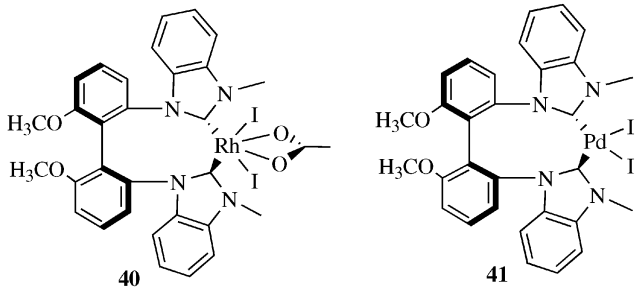
Shi et al. extended the preparation of atropochiral NHC ligands from optically active BINAM to its partially saturated H_8-BINAM version. The related rhodium(III) complex **38** was employed in the enantioselective hydrosilylation of methyl and ethyl esters of 3-oxo-3-arylpropionic acid giving good yields (65–88%) and good to excellent enantioselectivities (80–99%) under mild conditions.[62] The related Pd^{II} complex **39** was also found to catalyze oxidative kinetic resolution of secondary alcohols (Scheme 20).[63]



38 **39**

Scheme 20. Atropochiral rhodium and palladium complexes of the C,C-chelated H_8-BINAM ligand.

Other palladium(II) analogues containing the 1,1′-binaphthyl backbone, or its hydrogenated form, have been described by the same authors, and were studied in different catalytic processes such as: addition of arylboronic acids to cyclic enones,[64] arylation of *N*-tosylimines with arylboronic acids,[65] allylation of aldehydes,[66] and Suzuki and Heck-type cross-coupling reactions.[67] Recently, the more "flexible" chiral bis-NHC rhodium(III) and palladium(II) complexes **40** and **41**, respectively, have been synthetized from optically active 6,6′-dimethoxybiphenyl-2,2′-diamine (Scheme 21).[68] The rhodium complex (*R*)-**40**, was applied in the asymmetric hydrosilylation of ketones, affording good catalytic activities and *ee* up to 98%. With the palladium complex (*R*)-**41**, moderate conversion (48–68%) and high enantioselectivities (53–94% *ee*) were also obtained in the oxidative kinetic resolution of secondary alcohols.

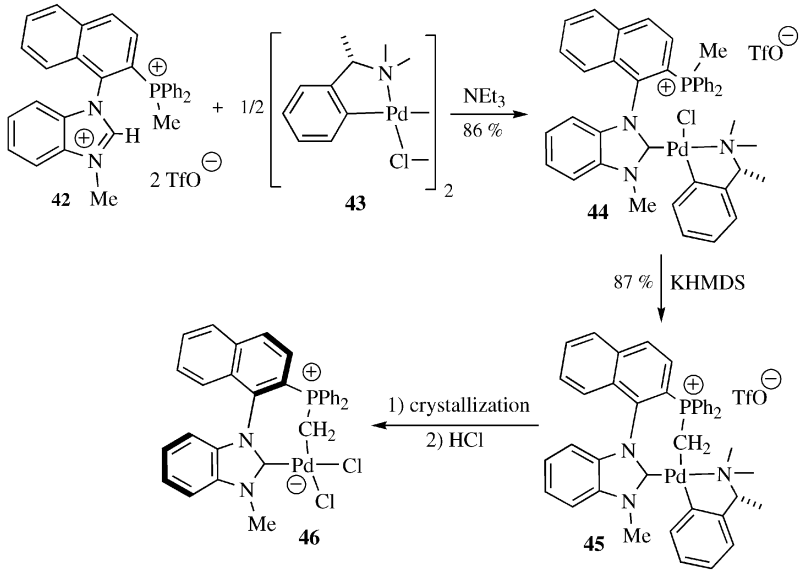


40 **41**

Scheme 21. Rhodium and palladium complexes of an atropochiral bis-NHC ligand based on a " flexible" 1,1′-biphenyl backbone.

The selected examples illustrate the definite potential of atropochiral bis-carbene ligands in asymmetric catalysis.[69] Their combined values are the electron-richness of the NHC ligands and the atropochirality of BINAP.

Ylide-Type Ligands: Considering the original report of P,C-chelated phosphane-phosphonium ylide complexes[46,47] and the above-mentioned value of bis-NHC ligands, the preparation of hybrid C,C-chelating ligands for transition metals, namely the NHC-phosphonium ylide ligands, has been recently targeted. For this purpose, the initial strategy developed in the achiral imidazolyl-phenyl case was transposed in the benzimidazolyl-naphthyl series.[70] The enantiomerically pure *ortho*-palladated (*S*)-dimethyl(1-phenylethyl)amine co-ligand **43** was used as a chiral resolving agent for the separation of two diastereoisomeric NHC-ylide complexes **45** derived from the racemic amidinium-phosphonium precursor **42**. A selective pre complexation of the carbenic center allowed to isolate the NHC-phospho-



42 **43** **44** **45** **46**

Scheme 22. Synthesis and resolution of atropochiral NHC-phosphonium ylide palladium complexes.

nium complexes **44**, which then underwent intramolecular coordination of the appending phosphonium ylidic carbon atom under basic conditions. After separation by fractional crystallization, hydrochloric treatment of each diastereoisomer was found to keep intact the two carbon–palladium bonds, affording the two β-zwitterionic NHC-ylide palladate enantiomers (*R*)-**46** and (*S*)-**46**,[71] where the phosphonium positive charge is compensated by a palladate negative charge (Scheme 22). According to X-ray diffraction analyses, these complexes exhibit a classical square-planar geometry and a low dihedral angle value of the atropochiral ligand (64.10°).

These ligands and complexes now deserve to be tested in catalytic processes requiring electron-rich ligands, like oxidative additions of non-reactive bonds. Submitted to the condition of atropochiral configuration stability, the isolation of the "free" atropochiral NHC-ylide ligand precursor **42** is a challenging perspective.

Conclusions

Asymmetric catalysis is the most attractive way to prepare chiral molecules with "high value added". Atropoisomerism was originally considered as an academic form of chirality, but it has proved over the years to provide one of the most effective tools for achieving high stereocontrol, including in industrial processes. BINAP represents the prototype of atropostereogenic chelating ligands, combining both the steric and electronic requirements for the design of efficient transition metal catalysts. By modifying the 1,1′-binaphthyl backbone, chemists have been able to tune the ligand properties to achieve high activity and enantioselectivity in many types of catalytic transformations. By contrast to these atropochiral ligands based on heteroatom donors (P, N, S, ...), their carbon congeners have received little attention until recently, mainly because of synthetic and stability problems. Recent advances have shown that these problems can be overcome, and a promising future can be foreseen for the "spectator" carbon ligands, in particular in the atropochiral series.

Acknowledgments

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