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Azobenzenes and catalysis

Estelle Léonard,[a] Floriane Mangin,[a] Carole Villette,[a] Muriel Billamboz[a] and Christophe Len[a,b*]

[a]Sorbonne Universités, Université de Technologie de Compiègne, Ecole Supérieure de Chimie Organique et Minérale, EA4297 Transformations Chimiques de la Matière Renouvelable, Centre de Recherche Royallieu, CS 60319, F-60203 Compiègne cedex, France.
[b]Department of Chemistry, University of Hull, Hull, HU6 7RX, England

Abstract

Azobenzene is the most extensively used class of chromophores in a large variety of applications. Recently, the use of azobenzene derivatives was developed in catalysis especially as promoter. This paper aims to provide a global overview of the main access to the diazo compounds from 2010, as well as their use as a reactant or a promoter in organometallic catalysis.

1. Introduction

Amongst the class of photo-reversible molecules, and the large variety of applications in photoregulation, azobenzene is the most intensively used, and azopolymers[1] can be considered as useful materials for photo-mechanical applications.[2] We propose here in a first part to complete and update the synthetic pathways to azobenzenes. In a second part, the various catalytic transformations of azobenzenes as reactant will be discussed, and finally, the use of diazo compounds as catalytic promoter will be presented.

There are three spectroscopic classes in the diazo compounds: azobenzene (R_1 and R_2 are H, alkynes, alkenes etc…), aminoazobenzene (R_1 or R_2 is NH_2), pseudo-stillbene (R_1 = EWG, R_2 = EDG) (Fig. 1a).[3] For the isomerization step, there is two major ways of light-induced switching from *trans* to *cis* isomer: N=N torsion (rotamers) *vs* *N*-inversion (invertomers).[4–10] However, according to the literature reviewed by Bandara and Burdette,[11] as an experimental result, if *trans*-azobenzene isomerization always occurs in the S1 state by an inversion process, regardless of the initial excitement, some theoretical studies predict isomerization of *trans*-azobenzene to be multi-dimensional or dominated by rotation. For *cis*-to-*trans* fast thermal isomerization, regarding to the azobenzene substituents, two structural features should be present: push–pull electronic distribution; a hydroxy group that allows the keto–enol equilibrium. These two factors permit the azo-dye to

proceed through the rotation pathway, and, consequently, the thermodynamically stable *trans* form of the azo-dye can be restored very quickly.[12] If we focus on the azobenzene class, a simplified state model for azobenzene isomerization can be described, leading to the energy that the system needs or release during the transformations (Fig. 1b)[3] with however a strong dependence of both photoisomerization and thermal isomerization rates on the polarity but not on the viscosity of the solvent.[13] It is noticeable that a dark-switch can occur when using gold nanoparticles.[14]
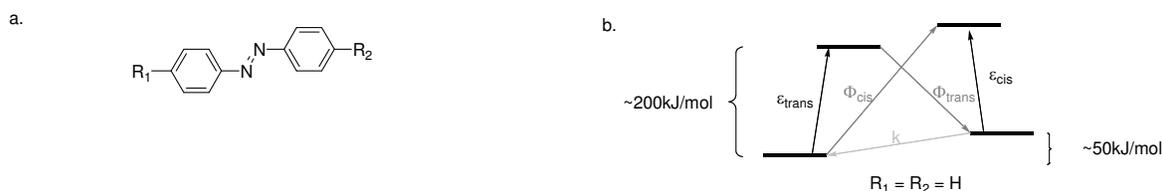
Fig. 1 a General classes of diazo compounds. **Fig. 1b** Simplified state model for azobenzene. ε = extinction coefficients, Φ = quantum yields for the photoisomerization, k = rate of thermal relaxation.

Concerning the azo syntheses, there are several ways to envision the formation and the functionalization of azobenzenes (Fig. 2).[15]
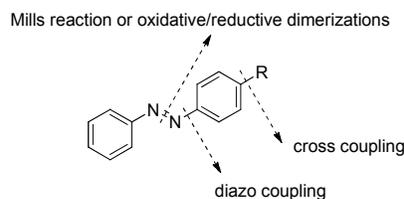
Fig. 2 General pathways to azobenzene formation or functionalization.[15]

Mills reaction or oxidative/reductive dimerizations can form the N=N bond from their corresponding aniline/nitrobenzene derivatives, whereas diazo coupling are of the best known methods to form the C-N bond. Transpositions can also occur, leading to an azo compound. Finally, cross couplings can modify pre-formed azobenzenes. Some of these reactions, published from 2010, will be discussed here.

2. General synthetic pathways

Very few recent reviews dealt with the syntheses of azobenzenes.[16–18] Part from the reviews, the azobenzenes syntheses are still extensively described. The present review does not aim to list all the occurrences in literature, but to provide a

global overview of the main synthetic pathways from 2010, as well as the catalysis, as a tool for their functionalization, or as an application.
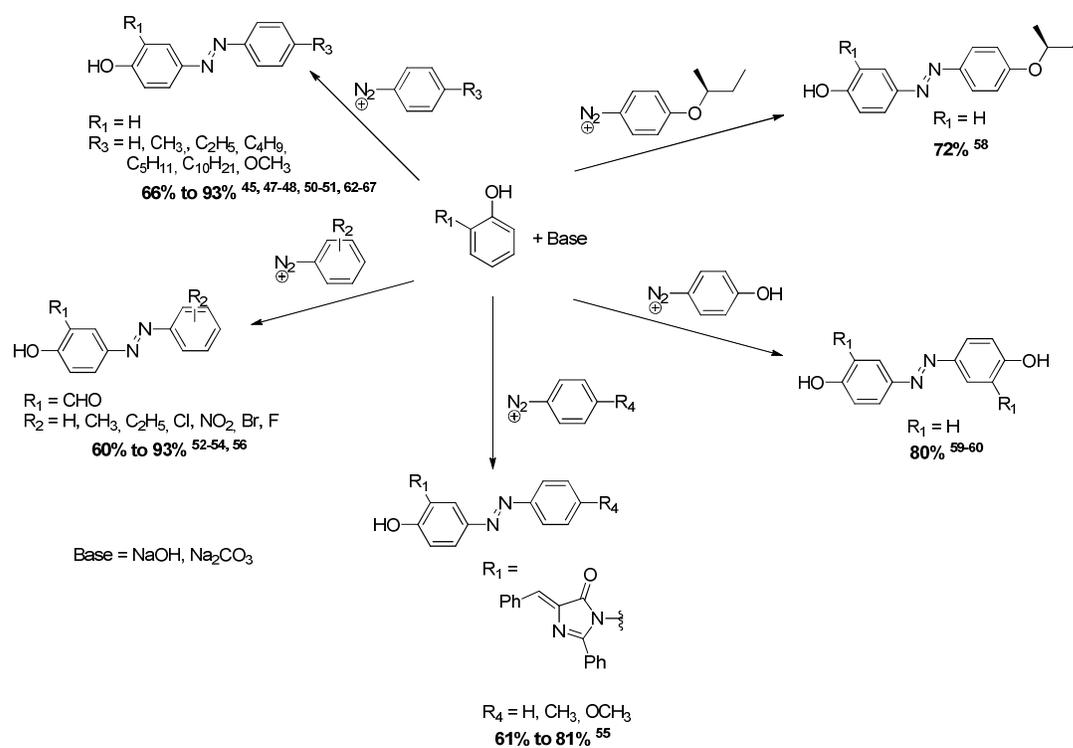
2.1. Diazo coupling

Diazo coupling, as an exetensively used method to perform azobenzene syntheses with huge application area,[19–37] implies a two steps process: (i) formation of a diazonium salt starting from aniline derivative with or without isolation of the salt and (ii) formation of the target azobenzene by coupling the diazonium salt and an electron-rich aromatic core such as phenol or aniline derivatives (Scheme 1).

EDG: Electro-donating group
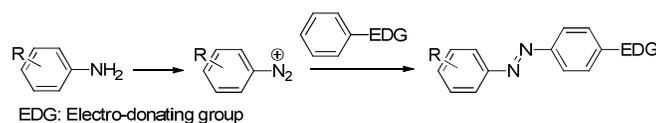
Scheme 1 General scheme of diazo coupling.

Concerning the first step, the main methodologies were the synthesis of diazonium salt in presence of *in-situ* HNO_2[38–41] or its nitrosylsulfuric acid derivative.[42] However, depending of the starting materials, other reagents were described for the production of diazonium salts such as a mixture of acetic acid/hydrochloric acid/isoamyl nitrite[43] or a modified montmorillonite K-10 clay coupled with sodium nitrite.[44] Concerning the addition of aromatic core, phenol[45–51] or its derivatives[52–56] are central molecules (Scheme 2), because of their easiest way of reaction with diazonium salts free in solution or blocked on backbone polymer.[57] This strategy permitted the synthesis of achiral, chiral[58] target azobenzenes but also symmetrical [59] [60] and unsymmetrical[61] [62–65] [66] [67] ones.

Scheme 2 Examples of various diazo couplings using phenol or its derivatives as substrate.

2.2. Reductive and oxidative dimerization

To build up azobenzenes, oxidations of primary aromatic amines or reductions of nitroaryl compounds are well described.

2.2.1. Reduction of nitrobenzene derivatives

To reduce selectively nitro moiety for the production of azobenzene, zinc dust or lead are one of the main reagent used (Scheme 3).
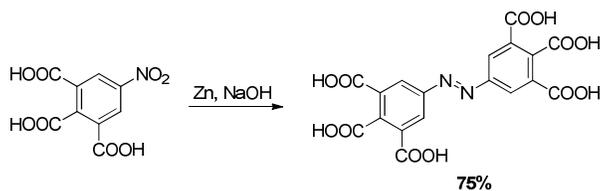
Scheme 3 Example of chemioselective reduction of nitroarene to arylhydroxylamine.[68]

However, other reagents were described for the reduction of nitroaromatic derivatives. For example, Nanjundaswamy and co-workers studied the effectiveness of triethylammonium formate (TEAF) in the presence of magnesium for the formation of azo compounds by the reductive coupling of nitroaromatics (Scheme 4).[69]

R = H, Me, OMe, OEt, Cl
80% to 93%

Scheme 4 Synthetic pathway for reductive dimerization of nitrobenzenes derivatives.[69]
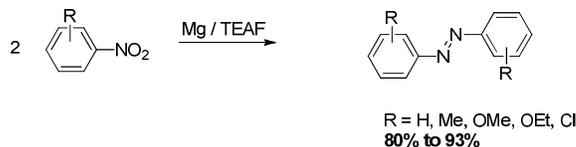
Hydrogenations can also lead to azobenzene formation using unsupported ultra-thin platinum nanowires as catalysts for the nitrobenzene hydrogenation under mild conditions (Scheme 5a).[70] If the yields are great (with KOH as a base, 89% of azobenzene was obtained), the reaction is not fully selective (under these conditions, 10% of aniline was obtained). Corma's group described reductive dimerization with gold supported on nanocrystalline cerium oxide.[71] The azobenzene adsorption on the catalyst surface seemed to be much weaker than the azoxybenzene one. Consequently, the non-desired hydrogenation of the azobenzene to the aniline only occurred when the azoxybenzene has been completely hydrogenated. However, if conversions are full (excluding nitrophenol and nitroaniline as starting material), selectivities seemed to be strongly dependant on substituents (Scheme 5b).

a.

90%

b.

R_1 = H or C_2H_5
R_2 = CH_3, Cl, OCH_3, $C(O)CH_3$, NH_2, OH

conv. = 60% to 100%
**selec. = 0% to 95%**
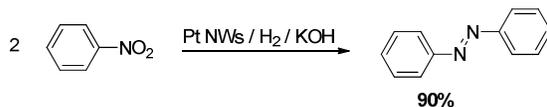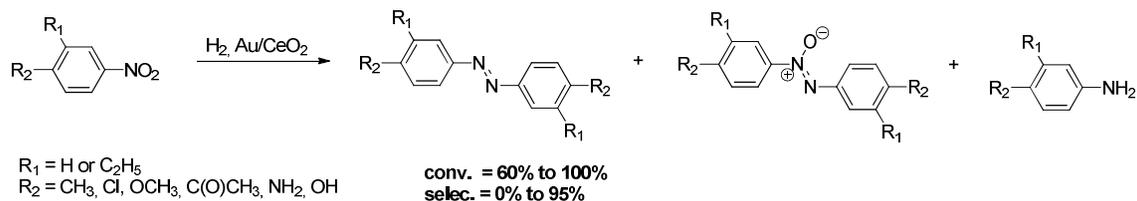
Scheme 5 Reductive dimerizations by hydrogenation.[70,71]

Part from metallic reductions, symmetrical 4,4'-dihydroxyazobenzene was obtained in 40% yield through the self-condensation of 4-nitrophenol in the presence of potassium hydroxide at high temperature (Scheme 6).[72] However, to the best of our knowledge, the mechanistic aspect of the reaction is still not elucidated.
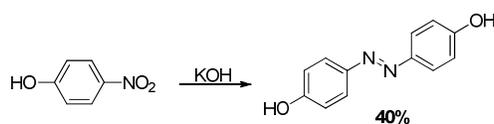
Scheme 6 Reductive dimerization at high temperature.[72]

Complex hydrids such as LiAlH$_4$ might reduce and dimerize nitroaniline derivatives.[73] These hydrids were also used to perform intramolecular reductive dimerization (Scheme 7).[74]

n = 2 or 3
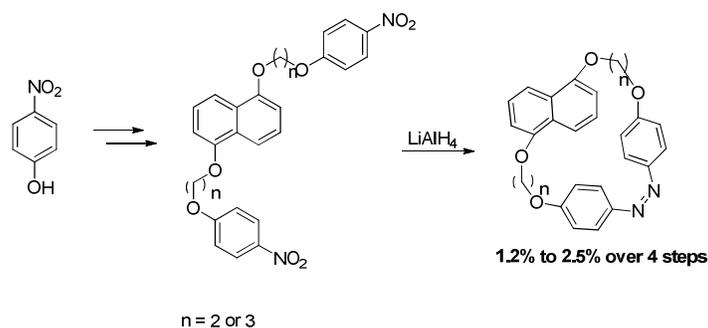
Scheme 7 Intramolecular reductive dimerization.[74]

Sakai and co-workers demonstrated how a reduction step with a system comprised of In(OTf)$_3$ and Et$_3$SiH allowed the reductive dimerization of nitrobenzene derivatives to the corresponding azobenzene.[75] The possible pathway was also described (Scheme 8).

In = In(OTf)$_3$
Si-H = Et$_3$SiH
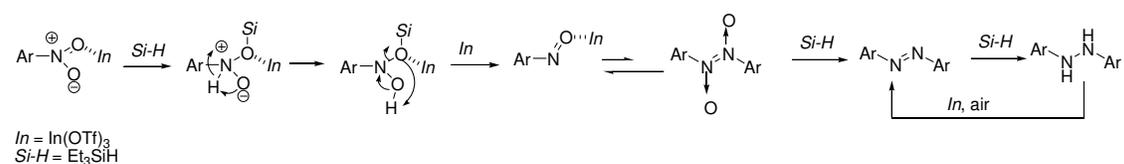
Scheme 8 Plausible pathway for the formation of azobenzene.[75]

2.2.2. Oxidation of aniline derivatives

Oxidative coupling of aniline is usually performed using KMnO$_4$/CuSO$_4$ in good yield (Scheme 9).[76,77]
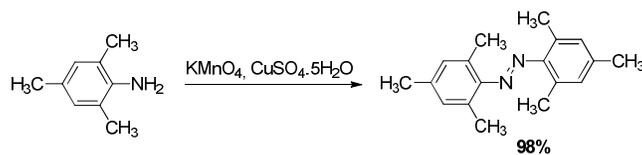
Scheme 9 Oxidative coupling of aniline.[76,77]

It was noticeable that symmetrical ortho-thioether substituted azobenzenes were obtained in only 2% yield when iron sulfate was used instead of copper sulfate.[78] MnO_2, a weaker oxidative agent than $KMnO_4$, allowed also the formation of azobenzenes in 87% (Scheme 10).[79]

Br — [2-F-aniline] —NH₂ → MnO₂ → Br—[aryl]—N=N—[aryl]—Br (with F substituents) **87%**
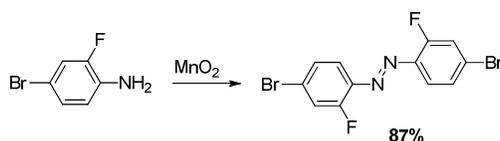
Scheme 10 Oxidative dimerization with MnO_2.[79]

A simplest way of oxidative dimerization consists in the use of air or dioxygen.[80,81] Recently, Commins and Garcia-Garibay synthesized a photochromic molecular gyroscope using this method of copper-catalysed air-oxidative dimerization of aminotoluene into its corresponding azobenzene (Scheme 11).[82] Red copper was also successfully used with dioxygen to afford symmetrical azobenzenes from aniline.[83]

[methylaniline]—NH₂ → CuBr, DMAP, air → [tolyl]—N=N—[tolyl] **85%**
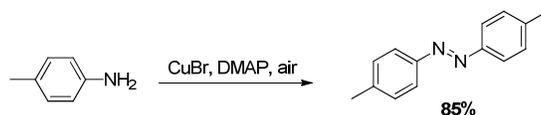
Scheme 11 Copper-catalysed air-oxidative dimerization of methylaniline.[82]

An oxidative one-pot route to *N*-substituted sulfonamidic azobenzene derivatives as protected aniline was recently reported.[84] A part from CF_3 substituent which did not afford the desired product, the method gave yields from 19 to 75% (Scheme 12).

[dihydrobenzothiadiazine structure] → *m*-CPBA → [azobenzene sulfonamide product] **19% to 75%**

R_1 = Me, Et, n-Pr, Ph, 3-ClC$_6$H$_4$, 2-MeOC$_6$H$_4$, 4-HOC$_6$H$_4$
R_2 = H or Cl
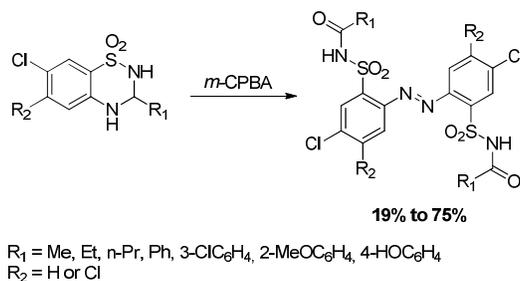
Scheme 12 mCPBA oxidation of dihydrobenzothiadiazines.[84]

After the formation of several lanthanide complexes of Pr(III), Sm(III), Gd(III), Tb(III), Er(III) and Yb(III) with the sodium

salt of the Schiff base, the Gd(III) complex formed was applied to the oxidative dimerization of anilines with yields between

12 and 88% (Scheme 13).[85]

X = H, CH$_3$, Cl, NO$_2$, OCH$_3$, COOH, NH$_2$*   **12% to 88%**

* oxidized to NO$_2$ during the operation
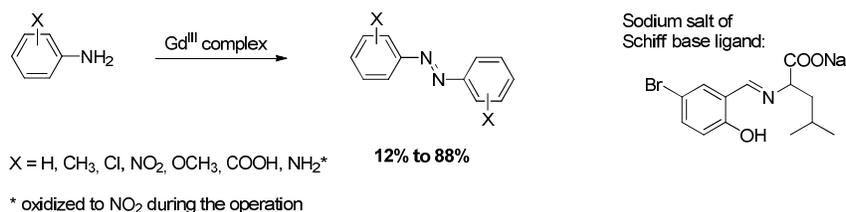
Scheme 13 Lanthanide complexes applied to oxidative dimerization of aniline.[85]

Usually, the *trans*-azobenzene is the major isomer obtained during its formation. But surprisingly, by an oxidative

dimerization of 4-bromo-2,3,5,6-tetrafluoroaniline to its corresponding azobenzene, Friščić and co-workers[86] managed to

isolate *cis* form as major isomer after flash silica column (Scheme 14). However, the long half-lives of *cis*-azobenzenes are in

agreement with the literature as *o*-fluorinated azobenzenes can exhibit significantly separated *trans*- and *cis*-form n–π*

absorption maxima leading to long *cis*-isomer half-lives.[87]

cis-4,4'-dibromooctafluoroazobenzene

30%   *trans*-4,4'-dibromooctafluoroazobenzene

                                   13%
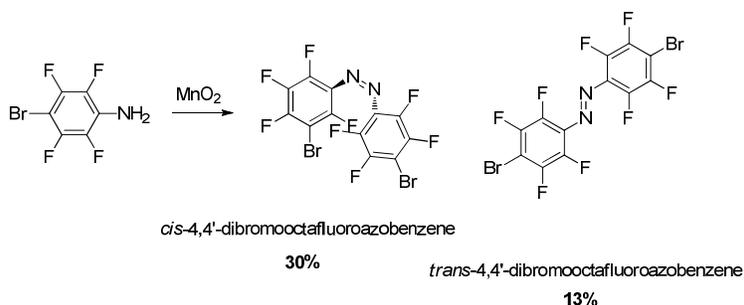
Scheme 14 *Cis* and *trans* azobenzene formation.[86]

2.3. Mills reaction

Equivalent to oxidative dimerization mechanistically speaking, Mills reaction differs in leading to the possibility to obtain

unsymmetrical products . However, only few oxidants were recently reported for the formation of nitroso compounds from

their corresponding anilines: Oxone (2KHSO$_5$.KHSO$_4$.K$_2$SO$_4$, Scheme 15),[88–92] or *m*-CPBA.[93]
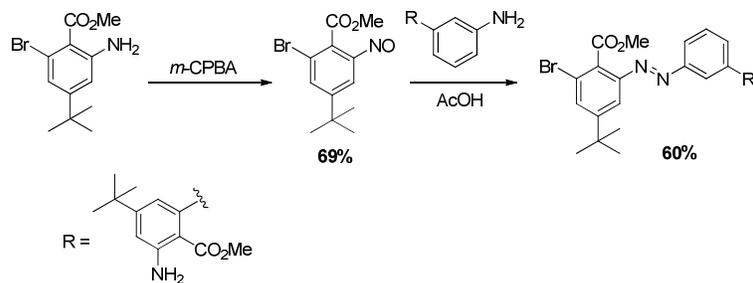
Scheme 15 Example of Mills reaction with *m*-CPBA.[93]

2.4. Rearrangements

As triazene rearrangement is one of the intramolecular possibilities to obtain azobenzenes from triazene, there are other rearrangements published recently, such as urea or Wallach ones.

Triazene rearrangement is an intramolecular reaction performed in acidic conditions, and leads to two products (para position as major one) in three steps.[94,95] However, when another electron-rich arene is present in the media, its coupling with the ionic[96] or radical[97] rearrangement of triazene (leading to the diazonium salt/radical formed) allowed the formation of the corresponding azobenzene (Scheme 16).

ionic pathway

R = H
R₁ = H, Cl
R₂ = H, CH₃, F, Cl, Br

Yields = 50 - 62%

1

2

R = R₁ = R₂ = H
ratio 1/₂ = 7.3

3

4

R = CH₃, R₁ = R₂ = H
ratio 3/₄ = 2.5 with DMA in equimolar conditions

radical pathway

R = CH₃
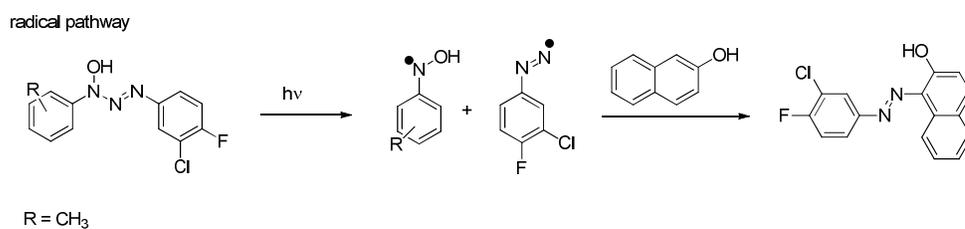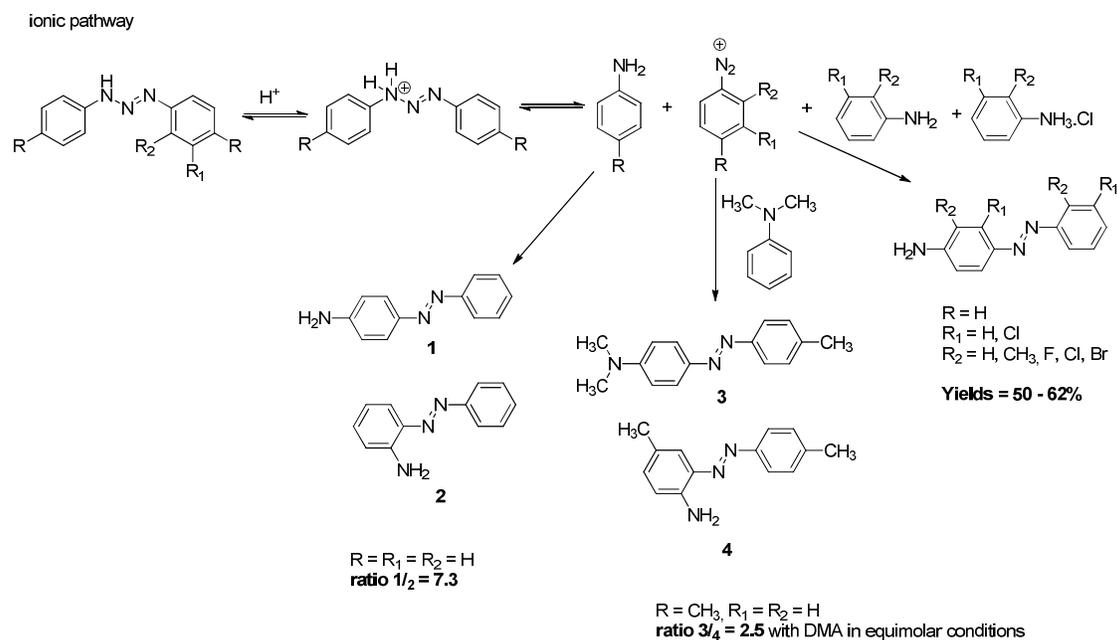
Scheme 16 Triazene rearrangement or decomposition for the formation of azobenzene.[94-97]

Another important rearrangement in azobenzene formation is the Wallach transformation. For example, in 2013, Wallach rearrangement permitted the preparation of *p*-hydroxyazobenzocrown ethers starting from different azoxybenzocrowns as substrates with yields between 30% and 78% (Scheme 17).[98]

n = 1, 2
R₁ = H, C₂H₅, C₁₅H₃₁
R₂ = R₃ = H, C₈H₁₇, C₁₂H₂₅, C₆H₅

30% to 78%
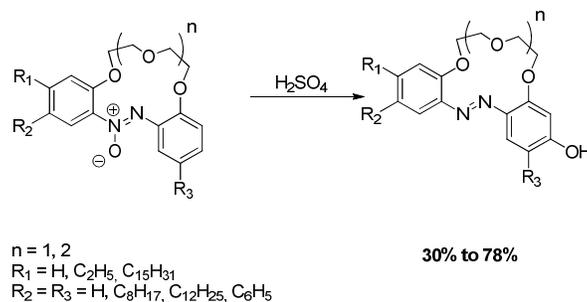
Scheme 17 Wallach rearrangement on various azoxybenzocrowns.[98]

3. Catalytic transformations involving azobenzene as reactant

3.1. Metal complexation using azobenzene

Azobenzene with its two aromatic rings and its two nitrogen atoms can undergo a complexation with a metal (Scheme 18). For example, pallado-complexes syntheses were already reviewed by Ghedini and co-workers,[99] centered on five-membered "(C,N)Pd" metallacycle and some representative examples of complexes featuring a useful set of physical properties. They were selected and divided into different classes (depending on the nature of the ligands). Some recent interesting examples of metallo complexes of azobenzenes bearing palladium, nickel or rhodium are presented.

Examples of azobenzene metallacycles can be found on diazo compounds bearing various heteroatoms, such as sulphur,[100,101] nitrogen[102] and/or oxygen.[103,104] In the case of sulfur atom, the reliability of auxiliary C-H---S synthons is investigated in dictating the crystal packing of the synthesized molecules. In the case of nitrogen and/or oxygen atoms, an unexpected migration or elimination of the ortho moiety beard by the azo compound was studied. It is also noticeable that keto/enol isomerization of azonaphtols can lead to isomer palladacycles (Scheme 18).
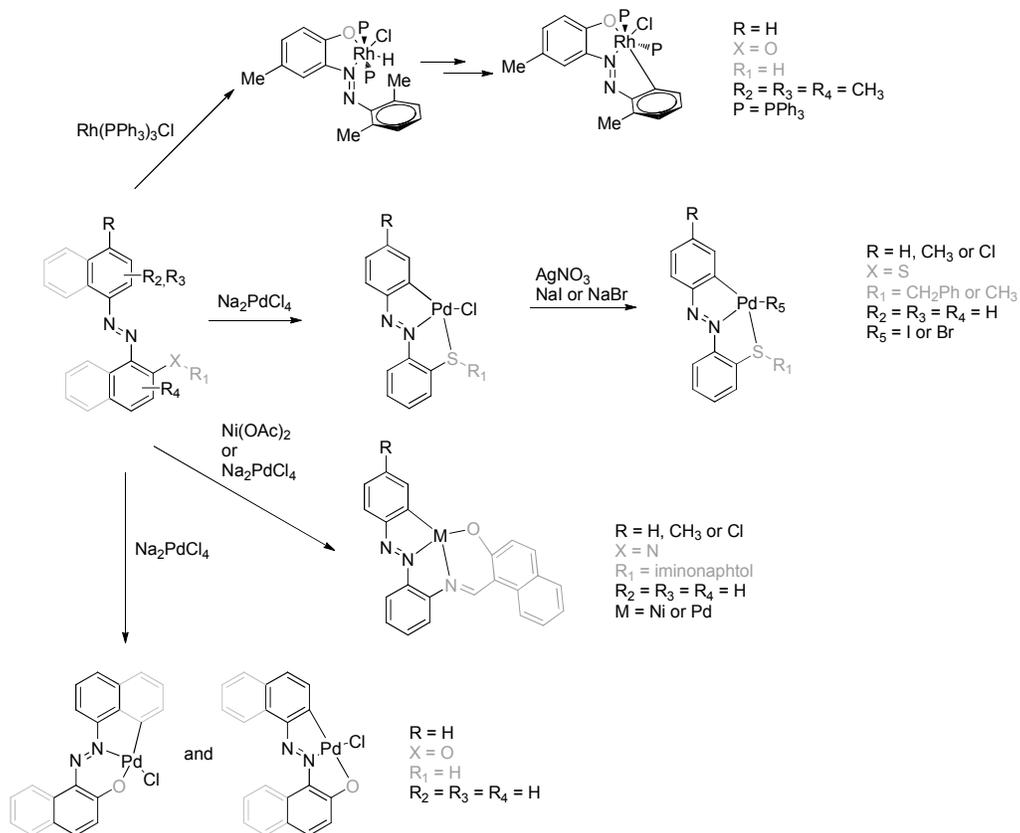
Scheme 18 Azobenzene complexations.[100-104]

It is however important to notice that when competing 3d metals(II) such as Ni, Co, Mn, with palladium(II), 3d-metals

turned to be inactive in ortho-metallation and transform into the corresponding M(II) acetates, although nickel(II) is known

to be a historical good metallating agent for azobenzene.[105] Another point is that heterometallic complexes react with azo

compound much easier than homometallic ones (Scheme 19).[106]
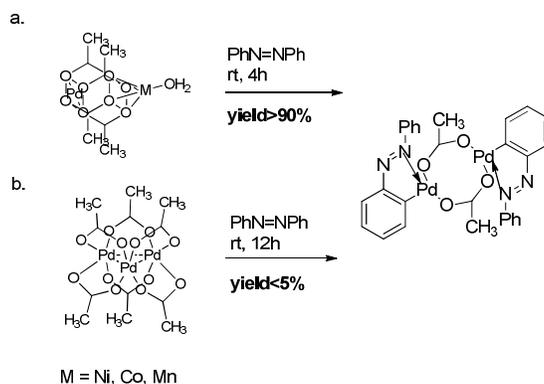
Scheme 19 Homo- *vs* heterometallic complexes reaction with azobenzene.[106]

Other ortho C-H activations were also related with for example *C,N*-chelated stannylene[107] or *N*-heterocyclic chlorosilylene[108] with azobenzene. Recently, Rh(III)-catalyzed formation of cinnolines and cinnolinium salts,[109] or selenylation of arenes including azobenzenes was decribed.[110] Moreover, with push-pull (and so dissymmetrical) azobenzenes, mechanochemistry with liquid-assisted grinding played an important role in regioselective ortho C-H activation.[111] Then, direct ortho-hydroxylation with dioxane as source of hydroxyl radical was published.[112]
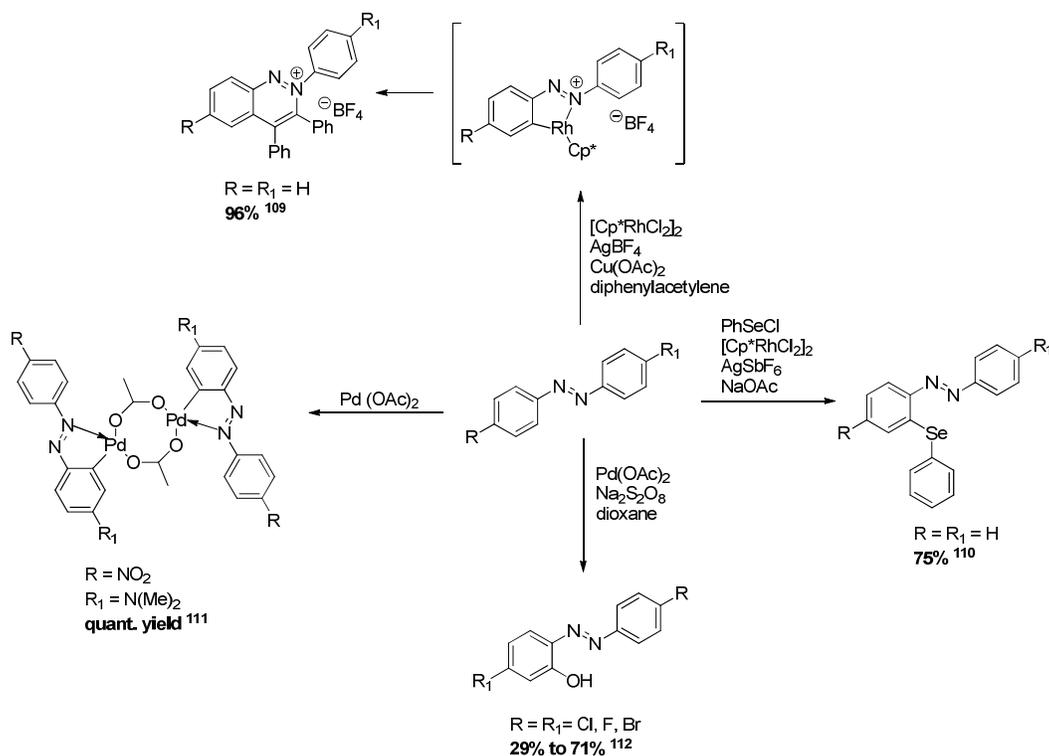
Scheme 20 Recent ortho C-H activations

When azobenzene is transformed into its anion radical with potassium graphite previously to the complexation, the treatment with a stable Ni complex can afford a substitution in 84% overall yield (Scheme 21).[113]

13
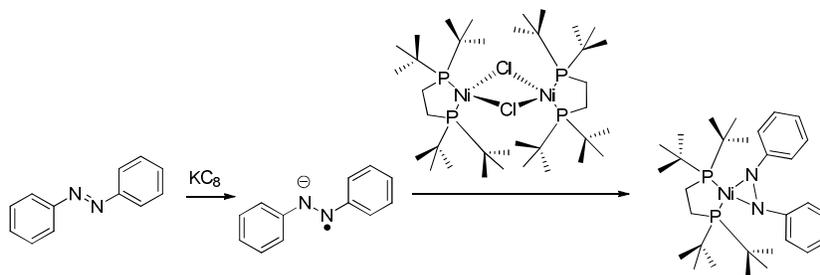
Scheme 21 Ni-complex formation.[113]

3.2. Palladium catalysis

In literature, palladium-catalyzed reaction and complexations involving azobenzenes are the most important. In 2013, acylation of azobenzenes at the 2-position through a Pd-catalyzed C-H functionalization was performed in yields from 54 to 86% with various benzaldehydes (Scheme 22a).[114] They also performed these acylation with α-oxocarboxylic acids (Scheme 22b).[115]
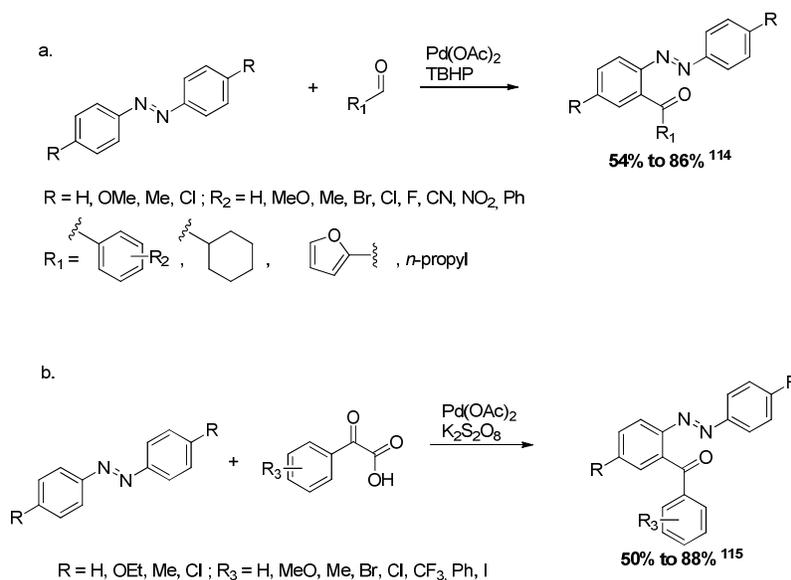
Scheme 22 Direct access to acylated azobenzenes via Pd-Catalyzed C-H functionalization.

A procedure to afford mono- and diacylazobenzene *via* Pd-catalyzed oxidative C–H bond activation from toluene was reported and permitted to control mono- and diacylated products by the oxidant loading *tert*-butylhydroperoxide (TBHP) (Scheme 23).[116] Indeed, adding 4 equivalents of oxidant led to the mono functionalization, whereas 15 equivalents allowed the bis-coupling to occur.
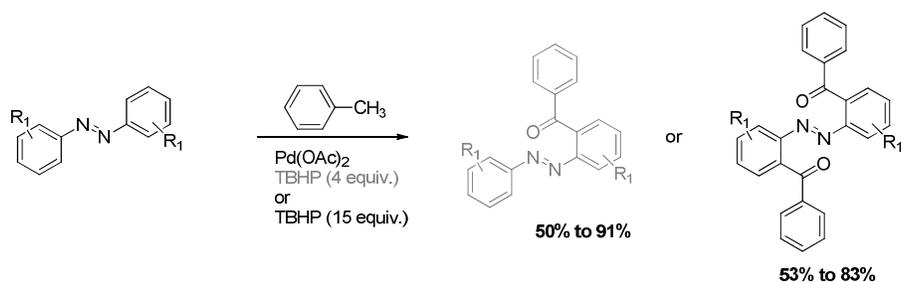
Scheme 23 Oxidative C-H bond activation of azobenzene.[116]

With the rediscovery of the Staudinger reaction as a mild and highly selective method for bioconjugation, Saxon and Bertozzi led access to various applications in chemical biology.[117] Feringa's group studied the possibility of using the Staudinger–Bertozzi ligation, making the aromatic moiety used in this reaction a part of the chromophore system of the molecular photoswitch ligation.[118] The reactant was synthesized by diazo coupling followed by the bromo-PEG3 substitution on the aromatic ring, and finally the palladed phosphination was performed (Scheme 24).
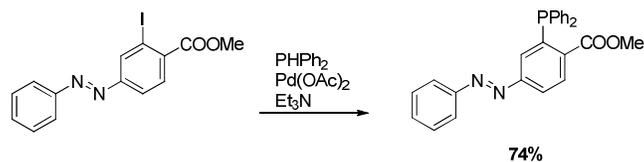
Scheme 24 Reactant synthesis for Staudinger-Bertozzi ligation.[118]

Numerous simple Suzuki condensation using iodo- or bromoazobenzene derivatives and an arylboronic acid in a presence of Pd(PPh$_3$)$_4$/sodium (hydrogeno)carbonate,[119–123] or Pd(OAc)$_2$/sodium carbonate[114,125] were successfully achieved in organic or organic/water solvents. For example, azobenzene derivatives possessing terminal phenylenebiuret hydrogen-bonding groups including Suzuki reaction as the final synthetic step were described (Scheme 25).[126]
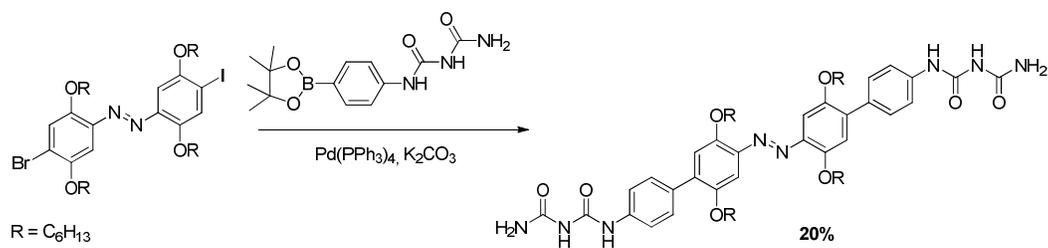
Scheme 25 Suzuki coupling for the azobenzene phenylenebiuret synthesis.[126]

Another example is the applications *in vivo*, where substitution in all four diazo-ortho-position allowed the isomerization with red light, and so the better penetrating of light for photoisomerization through tissues. This coumpound synthesized *via* Suzuki reaction (Fig. 3) underwent slow reduction by reduced glutathione, meaning that only extracellular or short-term intracellular use were possible in vivo.[127]

R = Cl or H
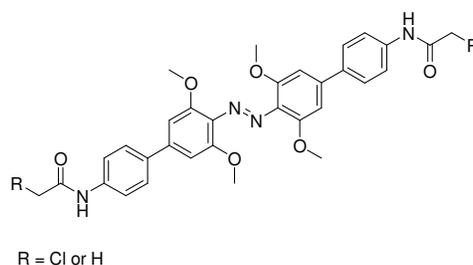
Fig. 3 Red-shifted azobenzene molecules.[127]

When two chromophores with different light-induced isomerization are included in one molecule, it can lead to light-motioned molecule as will. For example, the rotaxane described by Tian and co-workers possessed an azobenzene moiety with a E→Z isomerization wavelength of 380 nm (Z→E at 450 nm) whereas the stillbene had a E→Z isomerization wavelength of 280 nm (Z→E at 313 nm).[128] The link between the two moieties (Fig. 4 labeled in grey) was obtained by Suzuki coupling (Pd(OAc)$_2$, Na$_2$CO$_3$).

linked by Suzuki coupling
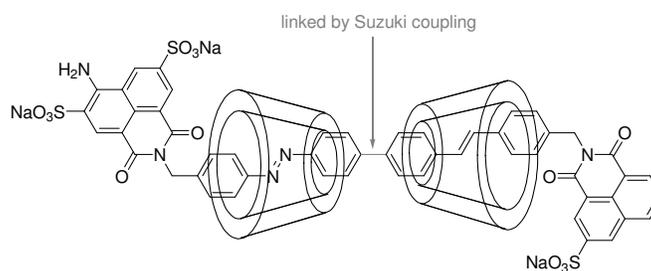
Fig. 4 Rotaxane synthesis.[128]

When dihalogenoazobenzenes are involved, polymers or macrocycles can be synthesized by pallado-coupling method. For example, in 2000, Masuda's group reported the synthesis of polymers having azobenzene units in the main chain by utilizing the Pd-catalyzed Suzuki coupling (Scheme 26a).[129] The conjugated polymers were prepared by coupling 1,3-

propanediol diesters of 1,4-phenylenediboronic acids with 4,4'-diiodoazobenzenes in quantitative yields. Another example is the formation of macromolecular "Accordions" by Suzuki coupling (Scheme 26b).[130]

a.

R_1 = H or C_6H_{13}
R_2 = H or C_6H_{13}

89% to 100%[129]

b.

nd [130]
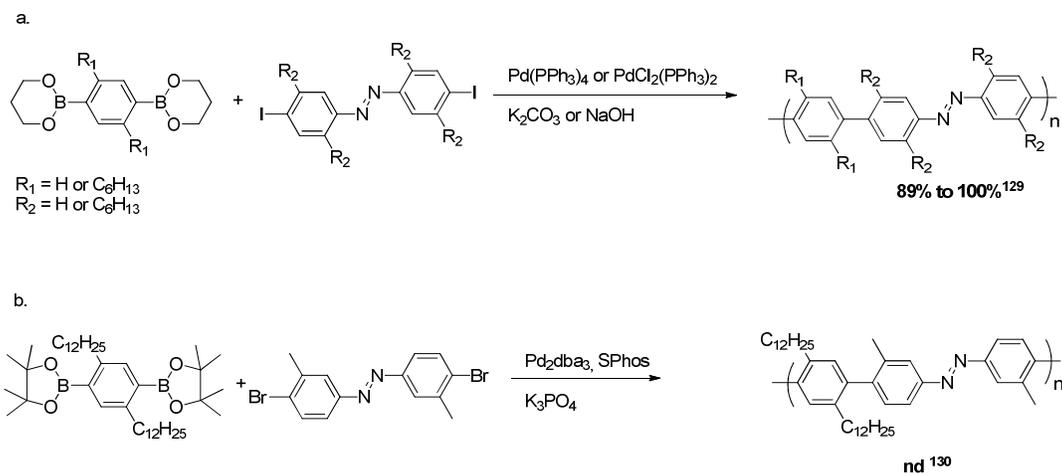
Scheme 26 Suzuki coupling for the polymerization of azobenzene.

Still in the polymer domain, a fluorene- and azobenzene-containing conjugated polymer has been successfully synthesized[131,132] using Suzuki polycondensation (Scheme 27a black and grey resp.). One year later, monodisperse conjugated polymer particles with incorporated light-switchable azobenzene moieties using a Suzuki-Miyaura dispersion polymerization under sonication and heating were described (Scheme 27b).[133] After a classical dibromoazobenzene formation by Mills reaction, the Suzuki-Miyaura coupling was performed with diboronic acid propandiol ester of fluorene derivative and Pd(PPh$_3$)$_4$ with PVPVA/Triton X45. This surfactant was used to disperse the particles properly.

a.

R = C₁₂H₂₅ or C₆H₁₂Br
X = I or Br

$R = C_{12}H_{25}$ or $C_6H_{12}Br$
$X = I$ or Br

R' =

76%[131] or **68%**[132]

b.

$R = C_8H_{17}$
$X = Br, Y = H$
$X = H, Y = Br$

R' =

or

40% to 65%[133]
depending on the purification cycles
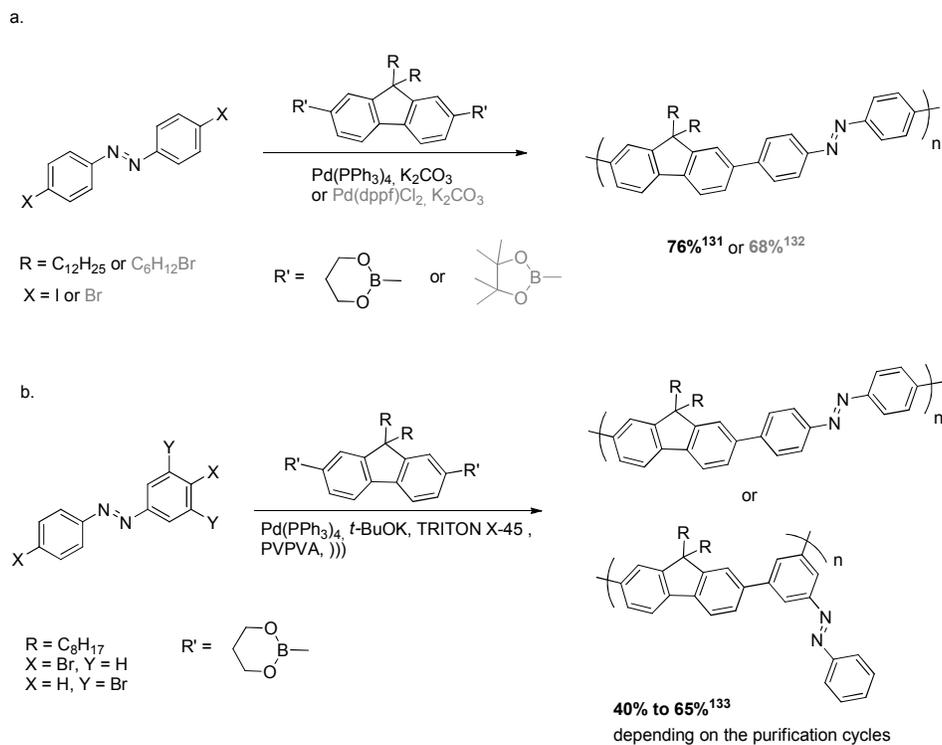
Scheme 27 Suzuki polycondensation.

Dihalogenated azobenzene can also lead to self-assemble macrocycle, as described by Yamamura, Okazaki and Nabeshima.[134] Suzuki coupling led the authors to obtain the desired azobenzene-linked biscatecholate ligand (Scheme 28). This ligand in presence of boron or titanium entities gave ring- and cage-shaped complexes.

$B(OH)_2$

Na_2CO_3
$Pd(PPh_3)_4$

72%
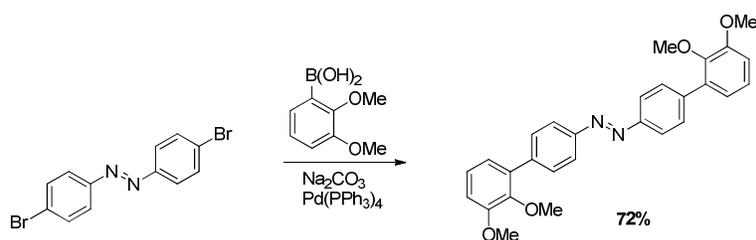
Scheme 28 Suzuki coupling for the formation of biscatecholate ligand.[134]

In cross-coupling reactions, azobenzenes therefore usually act as electrophiles, which greatly limits the scope of the reaction. But the boronic moiety can be also hold by the chromophore. For example, pallado-coupling to synthesize several tripod-shaped oligo(*p*-phenylene)s with legs composed of two phenylene units was reported. An azobenzene chromophore group was present on the functional arm.[135] To accomplish the synthesis of one of the tripod desired, they prepared the

paranitroazo derivative. And the coupling of this boronic ester with the precursor was carried out in presence of Pd(PPh$_3$)$_4$

as catalyst and Na$_2$CO$_3$ as the base (Scheme 29).
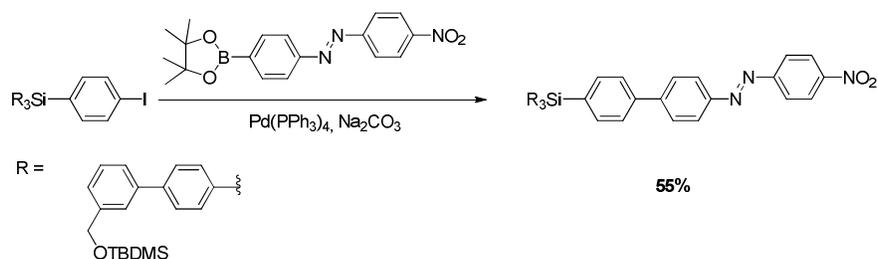
Scheme 29 Tripod-shaped oligo(*p*-phenylene) synthesis containing an azo moiety.[135]

Competing Knoevenagel reaction (route 2) to Suzuki route (route 1) to obtain their dendron precursor (Scheme 30),

Müllen and co-workers found that the palladium-catalyzed coupling sequence furnished pure product in good yield (93% *vs*

53%) because it avoided the production of a large number of side-products.[136]
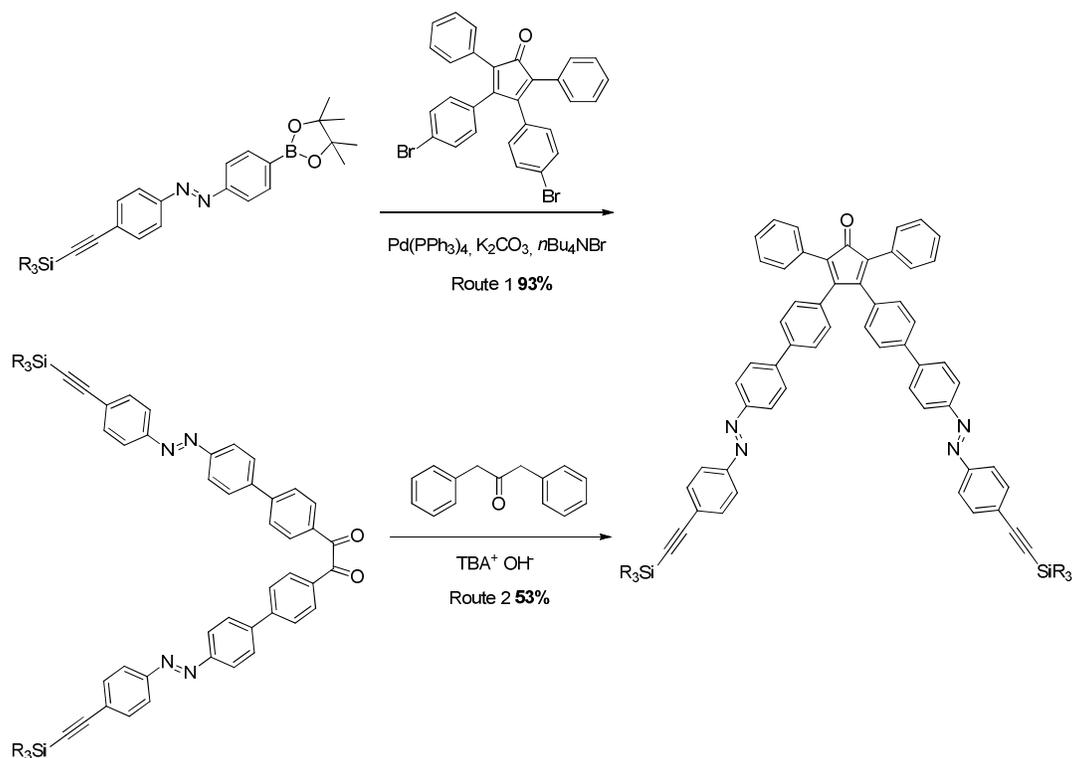
Scheme 30 Suzuki route *vs* Knoevenagel reaction to obtain dendron precursor.[136]

Instead of a boronic acid, Suzuki coupling reaction can employ an azobenzene trifluoroborate.[135] This method was applied for attaching an azobenzene moiety onto aryl and vinyl iodides. After an azobenzene boronic ester converted into its trifluoroborate derivative, the Suzuki cross coupling was performed yielding the reached compound in 59% (Scheme 31).[137] It is noticeable that to map the functional group compatibility of this reaction they have employed the azobenzene trifluoroborate with a variety of vinylic and aromatic iodides yielding the corresponding products in 41 to 72% yield.[137]
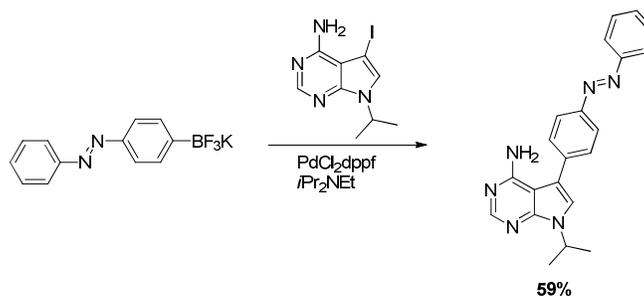
Scheme 31 Suzuki coupling on azobenzene triflouruborate derivative.[137]

Stille coupling was described very few times on azobenzenes. We can cite the study of Staubitz and co-workers on stannylated azobenzenes showing that these molecules can be used as nucleophilic components in Stille cross-coupling reactions with aryl bromides in yields from 70 to 93% (Scheme 32).[138]
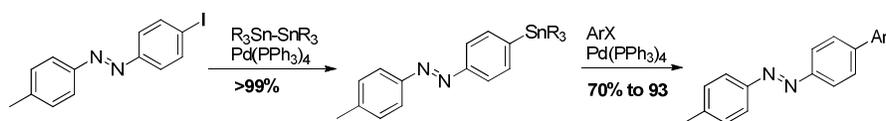
Scheme 32 Stille Coupling with azobenzene as nucleophile.[138]

A part from Suzuki and Stille couplings, Sonogashira coupling can be performed when a halogen is held by the aromatic ring. And among reactants, trimethylsilyl- or triisopropylsilylacetylene is a usefull tool for the Sonogashira cross-coupling functionalization of azobenzenes.[139–143] However 2,2-methylbut-3-yn-2-ol followed by a deprotection step is also described in literature[144,145] as in the following example (Scheme 33).

Scheme 33 Sonogashira coupling with 2,2-methylbut-3-yn-2-ol.[144]

More complex alkynes can also be used.[146] For example, Zarwell and Rück-Braun synthesized a tripod azobenzene-linker-conjugate by cross coupling, using tetrakis triphenylphosphine palladium (Pd[0]) and copper iodide with triethylamine, a commonly used base[147,148] in 61% yield (Scheme 34).[149] It is noticeable that in some conditions, the coupling and reduction of azobenzene can furnish hydrazines,[77] the acetylene acting as a proton donor.

Scheme 34 Sonogashira coupling for the formation of tripod azobenzene-linker-conjugate.[149]

Complexity can be also held by the azobenzene reactant. Almost none of the azobenzene emit light because of a radiationless deactivation process such as photoisomerization, Kano, Kawashima and co-workers have synthesized borylazobenzene and reported the intense fluorescence properties upon irradiation. Fluorescent borylazobenzene constructions went through Sonogashira coupling (Scheme 35).[150]

Scheme 35 Borylazobenzene functionalization.[150]

Other bases than triethylamine can also be used. Thus, Mohamed Ahmed and Mori described a Sonogashira coupling with aqueous ammonia (Scheme 36), a base which is tolerable for the reaction of aryl iodides or terminal alkynes bearing an

azobenzene group.[151] It is noticeable that without ammonia, the reaction failed, suggesting that the presence of an amino

group on the aryl halide could not substitute the ammonia.

R = (CH₃)₃Si, 4-NC-C₆H₄, *t*-Bu, C₆H₁₃
X = C₇H₁₅, H
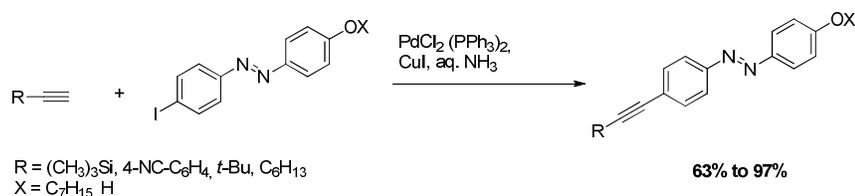
Scheme 36 Sonogashira coupling with aqueous ammonia.[151]

Dihalogeno-compounds can be used as reactant, as Tanaka's group functionalized an azobenzene to a chromogenic

host compound (Fig. 5a),[152] or Reed, Tour and co-workers for their oligomers precursors (Fig. 5b).[153] It is important to note

that none of the hydrazo product was obtained.
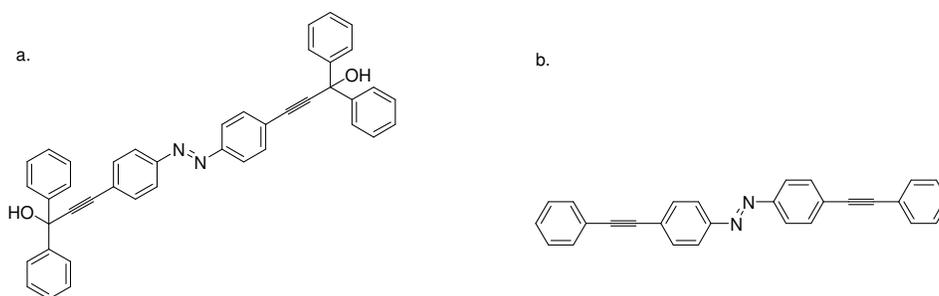
Fig. 5a Tanaka[152] and **Fig. 5b** Reed, Tour[153] molecules obtained by bis-Sonogashira coupling.

Since, multi Sonogashira couplings can lead to oligomers or polymers. For example, ethynyl-linked azobenzene

molecular wires were reported (Fig. 6).[154]
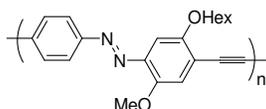
Fig. 6 Ethynyl-Linked Azobenzene Molecular Wires.[154]

In 2013, synthesis and photoresponse of helically folded polymers bearing an azobenzene moiety in the main chain was

successfully performed by Sonogashira coupling polymerization of D-hydroxyphenylglycine-derived monomer with 3,3'- and

4,4'-diethynylazobenzenes (Scheme 37).[155] Same manipulation have already been performed by the same group in 2011 but

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with the cross coupling on meta-position of the same aromatic ring.[156] Again, the diethynylazobenzenes involved were synthesized by Sonogashira coupling with trimethylsilylacetylene followed by deprotection.
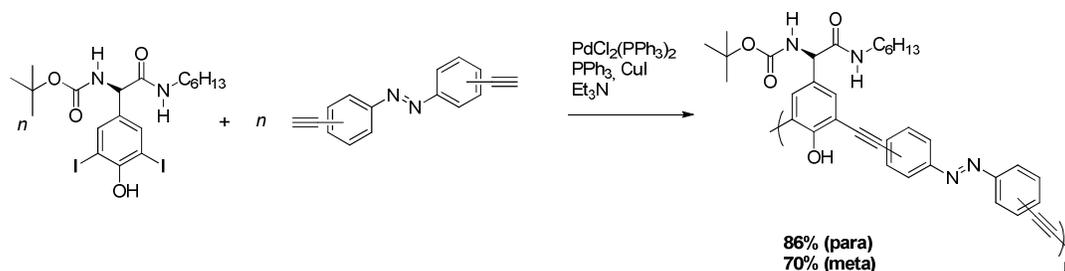
Scheme 37 Sonogashira coupling for the formation of helical polymer.[155,156]

3.3. Rhodium catalysis

For the formation of benzotriazole derivatives, a sequential rhodium-catalyzed amidation and oxidation in one pot was described. The best first step of the synthesis was achieved using tosyl azide in the presence of $[Cp*RhCl_2]_2$ with $AgNTf_2$[157] (Scheme 38) or $AgSbF_6$.[158] Same year, Jia and Han did the same manipulation demonstrating the ortho regioselectivity of the reaction and the plausible reaction mechanism was published.[158,159]
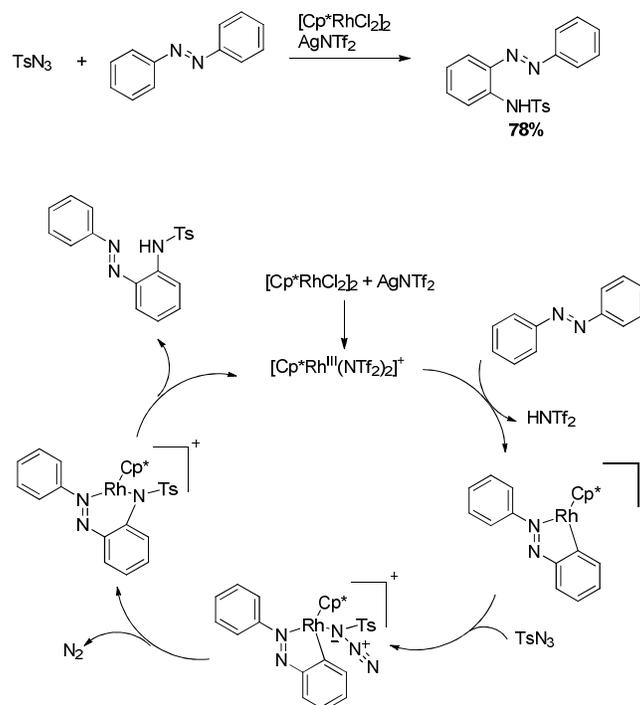
Scheme 38 Rhodium-catalyzed sulfamidation of azobenzene.[158]

Another example is the formation of indazoles by reaction of azobenzene with rhodium catalyst [Cp*RhCl$_2$]$_2$ and AgSbF$_6$.[160] The proposed reaction pathway for 2H-indazole synthesis is given below (Scheme 39). It begins with the C-H activation of azobenzene, followed by the addition of the aldehyde. Nucleophilic substitution followed by the aromatization gave the authors their reached product.
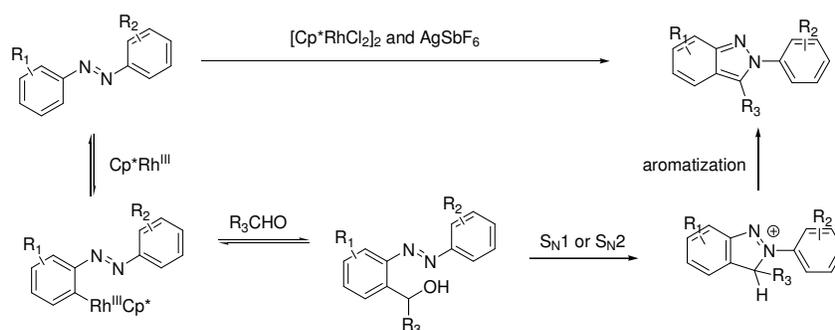
Scheme 39 Indazole synthesis from azobenzene derivative.[160]

3.4. Nickel catalysis

Part from complexation, only reductive cleavage of azobenzene into its aniline or derivative by Raney nickel or porous nickel was described in literature and especially concerning kinetics.[161,162] Diphenylhydrazine can also be obtained depending on the temperature set to the reaction.[163] Instead of Raney nickel, silica gel supported nickel[164] or nickel-containing mesoporous silicate molecular sieve catalyst can be used.[165] Furhtermore, the NiMCM-41 catalyst tested was also found to be reusable with keeping good to very good yields of the reaction. As an example, azobenzene was cleaved into aniline in 91% yield -1st run- to 89% yield -6th run- (Scheme 40).

R = R$_1$ = H, 4-Cl, 3-Br, 3-CH$_3$, 4-CH$_3$, 4-OCH$_3$ from 91% yield -1st run- to 89% yield -6th run-
R = H, R$_1$ = 4-NH$_2$
R = H, R$_1$ = 3-CH$_3$
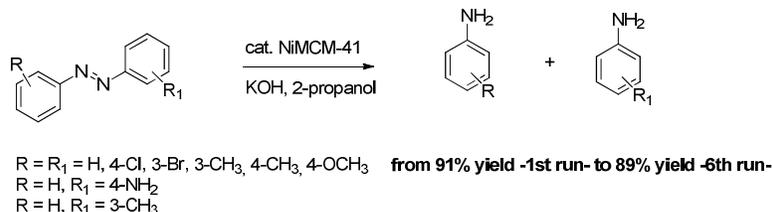
Scheme 40 Mesoporous silicate molecular sieve catalysis.[165]

4. Catalytic transformations involving azobenzene as promoter

4.1. Catalytic transformation involving azobenzene as promoter

Even if papers have been published on the synthesis of azo-containing phosphanes as potential catalytic promoters, few described their application in organometallic catalysis,[166,167] organocatalysis or on their catalytic application in water.

4.1.1. Organo-catalysis

As organocatalysis application, azobenzene-based thiourea catalysts can control the catalytic activity by the use of light. The conceptual design of the systems relies on the inactivation by an intramolecular hydrogen bonding, only on the *cis*-form.[168] Organo-catalysis proved to be more efficient in the dark (96% yield *vs* 21% at 365 nm), as expected by the authors (Scheme 41).
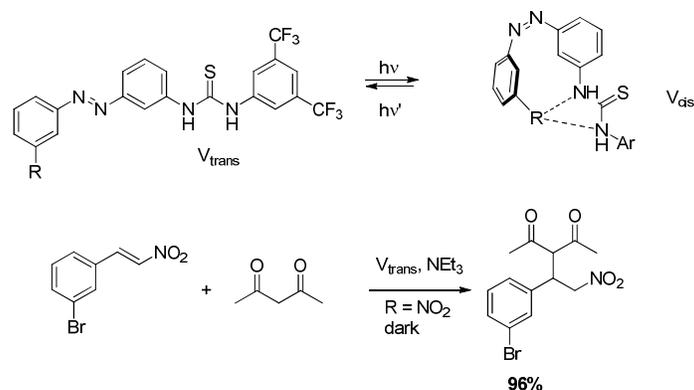
Scheme 41 ON-OFF organo-catalysis.[168]

Another example is given by Viehmann and Hecht who synthesized a photoswitchable guanidine catalyst (Fig. 7), beginning with the azobenzene formation from Mills reaction with Oxone®. However, if the catalyst underwent reversible photochromic properties it seemed to be inactive in the Ring Opening Polymerization of lactide.[89]
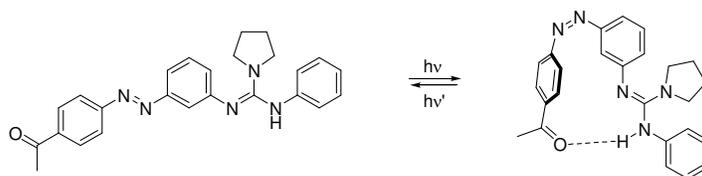
Fig. 7 Photoswitchable guanidine catalyst.[89]

4.1.2. Micellar catalysis

Surfactant can enhance the reactivities in water,[169] azobenzene ones could have the same properties but with a synthetic product recovery facilitated. For example, our group performed micellar catalysis using an azobenzenic surfactant and applied this to the Pd-catalyzed Tsuji–Trost reaction in water (Scheme 42).[170] Same organopalladed reaction was performed with a mixture of amphiphilic phosphanes (Scheme 42)[171] with or without randomly-modified β-cyclodextrins (RAME-β-CD). Without cyclodextrins, heptane/water was used for the reaction, whereas with these macromolecules, the reaction was performed in pure water. The addition of cyclodextrins in the aqueous compartment improved the phosphane-based aggregate dynamics, resulting in an increase in the catalytic performances.[172]
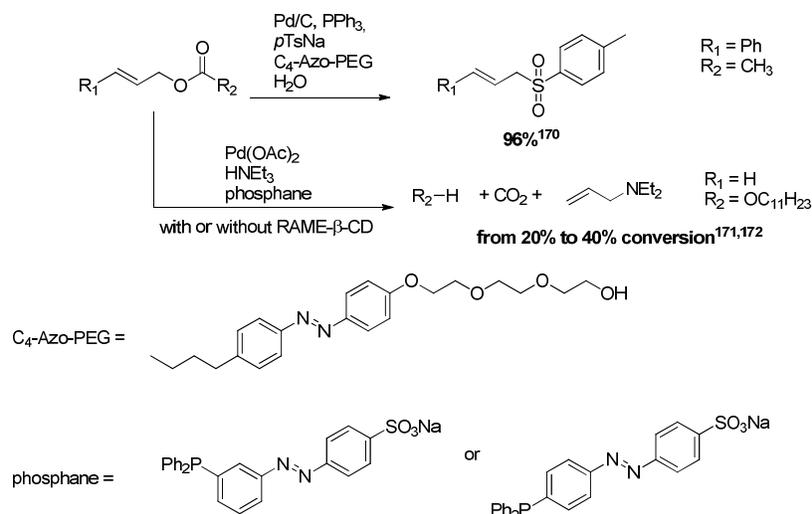
Scheme 42 Tsuji-Trost reactions in presence of azobenzene surfactants/phosphanes.

Another example was described as a new azobenzene, also used to enhance the yield the model reaction tested (Scheme 43).[139] BABTGA was then synthesized in 12 steps, beginning with a Mills reaction of butylaniline, followed by a Sonogashira coupling, a click reaction and an oxidation of the D-glucose moiety to its corresponding glucuronic acid. If aniline acetylation works in water, the recovery of the product, as well as the yields obtained are not as good as in the presence of the surfactant. Moreover, and most importantly, we demonstrated the impact of the surfactant isomerization on the good recovery of the acetanilides formed.
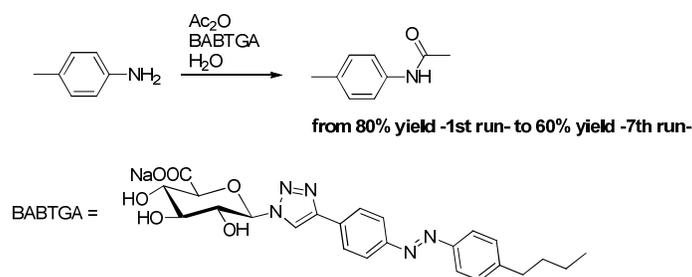
Scheme 43 Aniline acetylation in water enhanced by BABTGA.[139]

5. Conclusion

Azobenzene family is still extensively used in various applications such as light-controlled molecular brake,[74] molecular electronic devices[153] or even photoswitching azo compounds in vivo with red light.[127] Most of the strategies employed to obtain azobenzene derivatives via diazo coupling used phenol derivatives as electron-donnor moieties. However,

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substitution of in-situ HNO_2 was reported for the syntheses of diazo compounds. Reductive dimerization was described starting from nitroaryls in presence of various reductants: Zn,[68] Mg,[69] H_2/Pt or H_2/Au,[70,71] KOH[72] and complex hydrides.[74,75] Moreover, oxidative dimerizations were reported starting from anilines using conventional oxidants such as $KMnO_4$/$CuSO_4$,[76,77] MnO_2,[79] air or O_2,[80-83] m-CPBA.[84]

Part from diazo syntheses, metal complexations for the preparation of azobenzene metallocycles were studied including Pd, Ni or Rh atoms.[100-113] Pallado-catalysis using azobenzenes as reactant was the most developed in literature. Amongst the various works, Pd-catalysed C-H functionalization,[114-116] phosphinylation,[118] Suzuki,[119-137] Stille[138] or Sonogashira[139-156] couplings were described. In the case of Suzuki reaction, azobenzene derivatives were used both as halogenated compounds[119-125,127-134] or as borates.[126,135-137] Moreover, rhodium and nickel catalysis were reported in few papers, including 1,2-addition and azobenzene clivage into aniline.[157-165]

Finally, azobenzene was also used as core for reaction promoter, especially in photochromic micellar catalysis in water. In this topic, all the works were reported by our group, and concerned Tsuji-Trost catalysis or amidation.[139,166-172]

In the future, new methodologies for azobenzene production and especially with green reactants, solvents, or alternative technologies will be a challenge for synthetic organic chemists. Application of azobenzenes either as reactant or promoter will allow paving the way for catalysis, science and technology.

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Estelle Leonard

Estelle Léonard received her Ph.D in 2007 from University of Nancy (France) in the field of superbasic organometallic systems. After a first postdoctoral position in Birmingham University (UK) on catalyst design and noble metals catalysis, she moved to a second one in Le Mans University (France). Her research focused on photocontroled wettability using azobenzenes. She joined ESCOM engineer school of chemistry of Compiègne (France) and her current work in UTC (team TIMR) includes (photocontroled) micellar catalysis and radical chemistry in water.

Floriane Mangin

Floriane Mangin received her engineering masters' degrees in chemistry in 2011 from the Graduate School of Organic and Inorganic Chemistry in Compiegne (ESCOM) and from the University of Montpellier. In 2015, she obtained her Ph.D. from the University of Technology of Compiegne under the supervision of Professor Len. Her work was focused on the study of photochromic surfactants for an application in micellar catalysis and on the development of a new eco-friendly methodology using radical chemistry in aqueous media for the preparation of new maleimides derivatives and new surfactants.

Carole Villette

Carole Chevrin received her Ph.D in 2005 from the University of Reims (France) in the field of organometallic catalysis followed by a postdoctoral position in multi-steps synthesis of active compounds at the University of Orléans (France). After 2 years as temporary assistant professor, at the Universities of Cergy –Pontoise, in the field of total synthesis, and Lille, in the field of formulation, respectively, she became assistant professor at ESCOM (France). Her research is focused on catalysis applied to biomass and preparation of bio-based materials.

Muriel Billamboz

Muriel Billamboz received her Ph.D in 2008 from the University of Lille (France) in the field of organic and medicinal chemistry. She then worked as research engineer in a leading pharmaceutical industry at the pilot plant. After that she moved to another chemical industry as project leader in the field of process development. She finally joined the ESCOM engineer school of chemistry in Compiègne

(France). Her current work deals with the valorization of biomass thanks the use of alternative technologies, including micellar catalysis and radical chemistry in water.

Christophe Len

Prof. Dr. Christophe Len received his Ph.D. in 1995 from the Université de Picardie Jules Verne (UPJV) followed by a post-doctoral fellow at the University of Hull (England). In 1997, he became assistant Professor at UPJV and was promoted to full Professor in 2004 at the Université de Poitiers (France). In 2010, he moved as full Professor at the Université de Technologie de Compiègne – UTC (France). He has published 120 original publications and review articles, 3 chapters and 6 patents. Among recent awards and recognition to his scientific career, he was promoted Honorary Professor of the University of Hull, England (2012-2018) and Honorary Life Fellow of *Indian Society of Chemists and Biologists (ISCB, 2014)*. His current research explores organic chemistry and catalysis applied to biomass.