

Trispyrazolylborate Coinage Metals Complexes: Structural Features and Catalytic Transformations

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Dedicated to Professor Armando J.L. Pombeiro for his outstanding achievements in Coordination Chemistry and Catalysis

ARTICLE INFO

Article history:

Received 00 December 00

Received in revised form 00 January 00

Accepted 00 February 00

Keywords: Group 11 metal complexes;

Tris(pyrazolyl)borate; steric hindrance;

electronic features homogeneous

catalysis

ABSTRACT

Tris(pyrazolyl)borates (Tp^x) have become one of the most broadly used polydentate anionic ligands in coordination chemistry and catalysis since Trofimenko introduced them in 1966. Herein an overview of the main structural features of Group 11 metal complexes with Tp^x ligands are reviewed, as well as their catalytic properties, that can be controlled by ligand steric and electronic factors, a feature that can be exploited with this class of ligands that surpasses 200 members.

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1. Introduction.

Since Trofimenko introduced the anionic tris(pyrazolyl)borate (Tp^x , Figure 1) ligand in 1966, they have been extensively used in coordination or organometallic chemistry with most metals or metalloids of the periodic table [1]. In the case of coinage metal complexes, a number of studies within the classical coordination chemistry or the bioinorganic chemistry have appeared in the literature. These Group 11 metal coordination compounds can exhibit a certain structural diversity, leading to a number of advances in fundamental as well as in applied aspects. For instance, Tp^x ligands with alkyl or aryl substituents at the pyrazolyl ring are ideal for bioinorganic model building [2],[3], whereas a number of the catalytic reactions have also been described employing the Tp^xM core [4] containing copper or silver. Tp^x ligands are also named as scorpionates [1], due to the most common tridentate coordination mode, resembling the claws and tail of a scorpion. The substituents on the pyrazolyl ring or, at a lower extent, at the boron center, provides a platform that generates a number of different ligands with different steric and electronic properties that further affect at the metal center when coordinated.

Because of this, we have divided this review in two chapters, devoted to (i) the structural properties of coinage metal complexes with trispyrazolylborate ligands and (ii) the catalytic uses of such series of compounds. It is worth mentioning that we employ the rules proposed by Trofimenko to identify these ligands, generally represented by $\text{Tp}^{\text{R}^3, \text{R}^1, \text{R}^2}$, with several distributions being possible, the most frequent being the following: $\text{Tp}^{(\text{R}^2)}$, for a 3,5-disubstituted pyrazolyl with the same R group, $\text{Tp}^{\text{R}^3, \text{R}^1}$, for a 3,5-disubstituted pyrazolyl ring with different groups, $\text{Tp}^{\text{R}^3, 4, \text{R}^2}$, for a 3,4-disubstituted pyrazolyl group, and $\text{Tp}^{(\text{R}^2), \text{R}^2}$, for the same R group in positions 3 and 5, and a different R group in position 4. The first members of the series Tp and Tp* correspond to $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{H}$ and $\text{R}^1 = \text{R}^3 = \text{Me}$; $\text{R}^2 = \text{H}$. When a $\text{Tp}^{*, \text{R}}$ is employed, it corresponds to $\text{R}^1 = \text{R}^3 = \text{Me}$; $\text{R}^2 = \text{R}$.

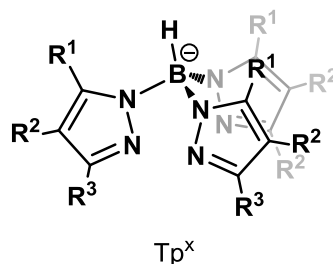


Figure 1. Generic trispyrazolylborate ligand (Tp^x).

2. Tris(pyrazolyl)borate Group 11 Metal Complexes: Structural Features.

With coinage metals, complexes bearing a Tp^x ligand usually contain the latter bonded by the three N-donors to the metal center. Only when a high steric pressure is exerted by the R^3 substituents (Figure 1), deviations from that common mode are observed. The steric pressure has been estimated on the basis of the cone and wedge angles, defined in Table 1, and calculated from structural data. Because of this, data is limited to a portion of Tp^x ligands but can provide qualitative explanations for structural trends or catalytic behaviors.

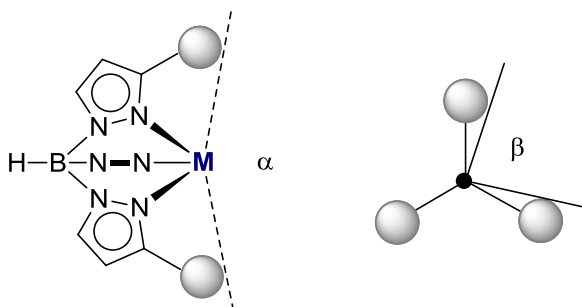


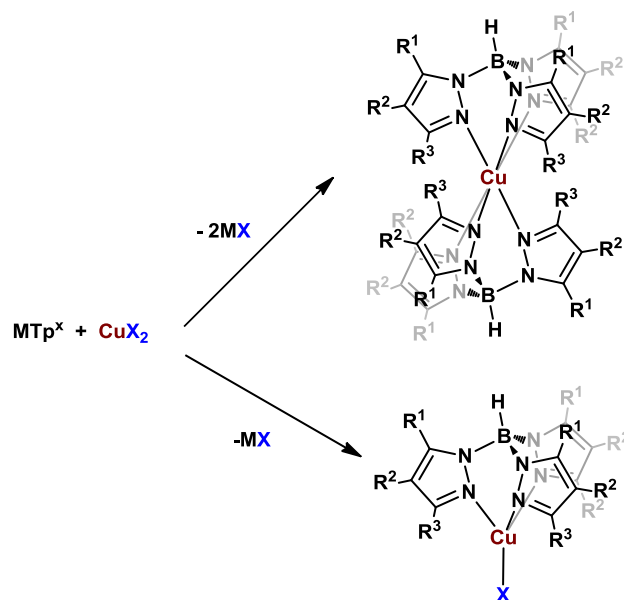
Table 1. Cone ($360-\alpha$) and wedge (β , drawn through the B-M axis) angles ($^\circ$) of some Tp^x ligands [1a].

Ligand	Cone angle ($360-\alpha$)	Wedge angle
Tp	183	70
Tp^*	239	67
$\text{Tp}^{\text{iBu, Me}}$	243	31
Tp^{iBu}	251	29

Tp ^{Cy}	281	53
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2.1 Copper complexes.

A quite large number of Cu(I) and Cu(II) complexes bearing Tp^x ligands have been described since the seminal work by Trofimenko. They are usually prepared by direct transmetalation reaction of [MTp^x] and a CuX or CuX₂ precursor. Complexes with Cu in +2 oxidation state were more common at the beginning of these investigations, since they do not need special precautions about the atmosphere employed, at variance with the unstable Cu(I) counterpart. The solid-state structure adopted by these complexes depends on both the substituents on the pyrazole rings and the oxidation state of the metal. Regarding Cu(II) derivatives, [Tp^xCuX] complexes bearing ligands with a low steric hindrance (R³ being small in volume) are quite unstable and rapidly convert into Tp₂M and MX₂ (Scheme 1a). On the other hand, sterically hindered Tp^x ligands [2i] as Tp^{tBu} [3h,5], Tp^{tBu,Me} [6], Tp^{Cy} [7] or Tp^{iPr2} [8], with bulky alkyl groups at the 3-position of the pyrazole rings, stabilize four-coordination [9] with respect to six-coordination numbers. This effect has been described as a “tetrahedral enforcer” [10]. For instance, in the case of the Tp^{tBu,Me} ligand the formation of six-coordinate sandwich complexes [(Tp^{tBu,Me})₂Cu] [6] is effectively inhibited, whereas for less bulky Tp^x ligands the corresponding six-coordinate complexes of the type [(Tp^x)₂Cu] are formed: [(Tp)₂Cu] [11], [(Tp^{*})₂Cu] [12] or [(Tp^{Br3})₂Cu] [13] among others [11d]. In some cases, moderately hindered Tp^{Cy}, Tp^{Ph} and Tp^{Ph2} ligands cleavage of the B–N bond has been reported [14]. Thus, the reaction of K[Tp^{Cy}] or K[Tp^{Ph2}] with one equivalent of CuCl₂ in CH₂Cl₂ leads to the formation of mixtures of [Tp^RCuCl] and [Tp^RCuCl(Hpz^R)] (R = Cy, 3,5-Ph₂). Also, treatment of Cu(BF₄)₂·6H₂O with one equivalent of K[Tp^{Ph}] in CH₂Cl₂ afforded [Cu(Hpz^{Ph})₄](BF₄)₂ in low yield as the only isolable product. These aspects may become crucial in some catalytic processes which involve the oxidation of copper(I) to copper(II).



Scheme 1. Generic complexes obtained from Cu(II) and Tp^x precursors.

With copper in its +1 oxidation state, dinuclear structures of composition $[\text{Tp}^x\text{Cu}]_2$ can be formed depending of the nature of the R^3 group. It is they case of $[\text{TpCu}]_2$ [15], $[\text{Tp}^*\text{Cu}]_2$ [15], $[\text{Tp}^{\text{Ph}2}\text{Cu}]_2$ [16], $[\text{Tp}^{\text{tBu}}\text{Cu}]_2$ [16], $[\text{Tp}^{\text{tBu,Me}}\text{Cu}]_2$ [6], $[\text{Tp}^{\text{tBu,iPr}}\text{Cu}]_2$ [17] and $[\text{Tp}^{\text{Ms}}\text{Cu}]_2$ [18] where the hydrotris(pyrazolyl)borate ligand acts as a bridge between the two metal ions. However, there is a certain structural diversity depending of the pyrazolyl substituents, as shown in Figure 2. The parent complex $[\text{TpCu}]_2$ displays a coordination geometry around the Cu(I) centres as a distorted tetrahedron, whereas the coordination number of copper is reduced to three for $[\text{Tp}^*\text{Cu}]_2$ and $[\text{Tp}^{\text{Ph}2}\text{Cu}]_2$, in a distorted trigonal planar arrangement. In the case of the bulkier $[\text{Tp}^{\text{tBu}}\text{Cu}]_2$, $[\text{Tp}^{\text{tBu,Me}}\text{Cu}]_2$, $[\text{Tp}^{\text{tBu,iPr}}\text{Cu}]_2$ or $[\text{Tp}^{\text{Ms}}\text{Cu}]_2$, the copper centres are two-coordinate and linear, with one of the pyrazolyl groups of each ligand remaining as non-coordinated. Additionally, in these systems it has been found that alkyl substitution at the 5-position of the pyrazolyl group in $[\text{Tp}^{\text{R,R'}}\text{Cu}]_2$ complexes may exert an effect in fluxional process, since $[\text{Tp}^{\text{tBu}}\text{Cu}]_2$ is fluxional on the NMR time scale at temperatures over -56°C , whereas $[\text{Tp}^{\text{tBu,Me}}\text{Cu}]_2$ shows a static ^1H NMR spectrum even at high temperature [6].

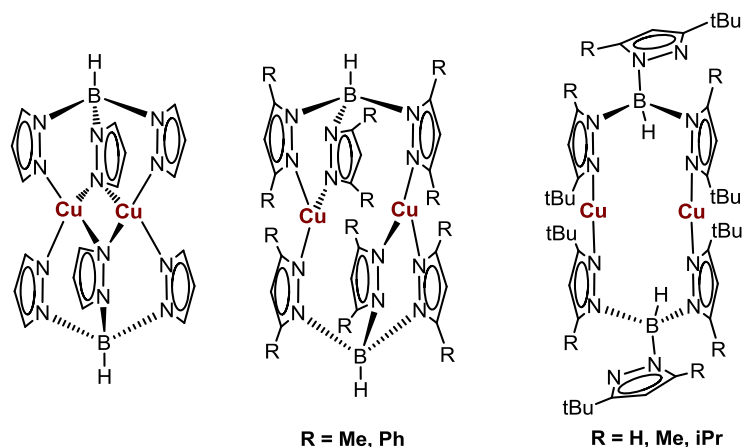
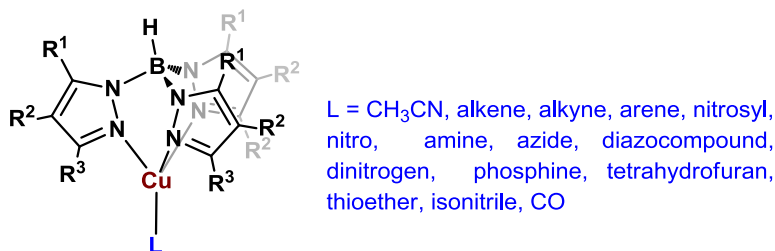


Figure 2. Structural variety of dinuclear compounds $[\text{Tp}^x\text{Cu}]_2$

Most of the mentioned dinuclear compounds react with donor ligands affording mononuclear complexes of general formula $[\text{Tp}^x\text{CuL}]$ (Figure 3). Compounds have been isolated with this fourth ligand being CH_3CN [3a, 19], alkene [20], alkyne [21], arene [18], nitrosyl [3l,o,p, 19a], nitro [3k], amine [22], azide [23], diazocompound [24], dinitrogen [25], phosphine [19d, 26], tetrahydrofuran [19a], thioether [27], isonitrile [28] or CO [20c]. The latter $[\text{Tp}^x\text{Cu}(\text{CO})]$ complexes deserve some comments since they have frequently been employed to estimate the electronic effects of the Tp^x ligands by examining the ν_{CO} value (Table 2). An array of values from ca. 2055 to 2137 cm^{-1} has been described (Table 2), the nature of the $\text{R}^1\text{-R}^3$ groups greatly influencing such values. Tp^x ligands bearing electron-withdrawing groups, such CF_3 or Br, results in electron-deficient copper(I) centers which lead to weak π -back bonding interaction with carbon monoxide, and, therefore, high ν_{CO} frequencies. To the contrary, alkyl-substituted $[\text{Tp}^x\text{Cu}(\text{CO})]$ complexes exhibit the low ν_{CO} values and, consequently, provide higher electronic density at the copper center. Similar trends have also been observed for a series of NO adducts [29].

Figure 3. [Tp^xCuL] adductsTable 2. ν_{CO} frequency values (cm⁻¹) for [Tp^xCu(CO)] complexes.

Complex	ν_{CO}	Reference	Complex	ν_{CO}	Reference
[TpCu(CO)]	2083	[30]	[Tp ^{CF3} Cu(CO)]	2100	[31]
[Tp [*] Cu(CO)]	2060	[15]	[Tp ^{CF3,1Ni} Cu(CO)]	2103	[20f]
[Tp ^{Ph2} Cu(CO)]	2086	[3i]	[Tp ^{CF3,2Ni} Cu(CO)]	2109	[20f]
[Tp ^{iPr2} Cu(CO)]	2056	[3i]	[Tp ^{C2F5} Cu(CO)]	2110	[32]
[Tp ^{tBu} Cu(CO)]	2069	[3h]	[Tp ^{C3F7} Cu(CO)]	2102	[32]
[Tp ^{tBu,Me} Cu(CO)]	2059	[33]	[Tp ^{CF3,4-RPh} Cu(CO)]	2120	[20i]
[Tp ^{tBu,iPr} Cu(CO)]	2057	[3a,33]	[Tp ^{Br3} Cu(CO)]	2110	[34]
[Tp ^{Cy,4Br} Cu(CO)]	2068	[35]	[F12-Tp ^{4Bo,3Ph} Cu(CO)]	2113	[20h]
[Tp ^{Ph,iPr} Cu(CO)]	2075	[33]	Tp ^{(CF3)2,Br} Cu(CO)	2125	[19f]
[Tp ^{Ms} Cu(CO)]	2079	[19a]	[Tp ^{(CF3)2} Cu(CO)]	2137	[36]
[Tp ^{CF3,CH3} Cu(CO)]	2109	[19a]			

Tp^xCu complexes bearing a carbene ligand have been detected in solution with a series of different Tp^x ligands. NMR studies revealed the existence of a correlation between the chemical shift of the carbene carbon nuclei bonded to copper in species [Tp^xCu=¹³C(Ph)(CO₂Et)] and the values of the ν_{CO} frequencies of the corresponding [Tp^xCu(CO)] complexes. Such correlation demonstrates the utility of both scales as tools to estimate the relative electron density at the copper center in this class of compounds. [24].

2.2 Silver complexes.

At variance with [Tp^xCu(I)] complexes, the number of examples of dinuclear complexes with silver is quite reduced: derivatives with Tp^{*}, Tp^{Br3} and Tp^{*,Br} have been characterized X ray diffraction as [Tp^xAg]₂ structures [37, 38, 39]. Complex [Tp^xAg]₂ showed a dimeric structure with each Tp^{*} ligand bridging both metals, albeit one Ag(I) is four coordinate whereas the other is two coordinate and nearly linear (Figure 4). The Ag...Ag distance was sufficiently short to propose a significant bonding interaction between the silver atoms. [Tp^{*}Ag]₂ and [Tp^{4Br}Ag]₂ showed a fluxional behaviour in solution, with a pyrazolyl ring exchange process occurring rapidly at 293 but not at 193 K, whereas [TpAg]₂ was not fluxional, even at room temperature [37]. The structures of [Tp^{Br3}Ag]₂ and [Tp^{*,Br}Ag]₂ shows a different coordination mode with each silver ion connected to two pyrazolyl rings of one Tp^x ligand and a third pyrazolyl ring of the other Tp^x ligand

(Figure 4), similarly to the structure of $[\text{Tp}^*\text{Cu}]_2$ (see Figure 2). In this case the Ag-Ag distance also falls in the range expected for the so-called argentophilic interactions. Trinuclear silver cationic complexes which contain a triangular $[\text{Ag}_3]^{3+}$ core has been isolated using Tp^{py} [40], Tp^{An} [41] or Tp^{Ms} [39] ligands. $[\text{Ag}_3(\text{Tp}^{\text{An}})_2]\text{ClO}_4$ showed the trinucleating bridging coordination mode for the Tp^{An} ligand shown in Figure 4, where each pyrazol of each Tp^{An} ligand coordinates to a distinct Ag(I) ion, leading to complex in which the Tp^{An} coordinates in a $\mu^3\text{-}\kappa^1\text{:}\kappa^1\text{:}\kappa^1$ -fashion. Each Ag center is dicoordinated with a nearly-linear geometry.

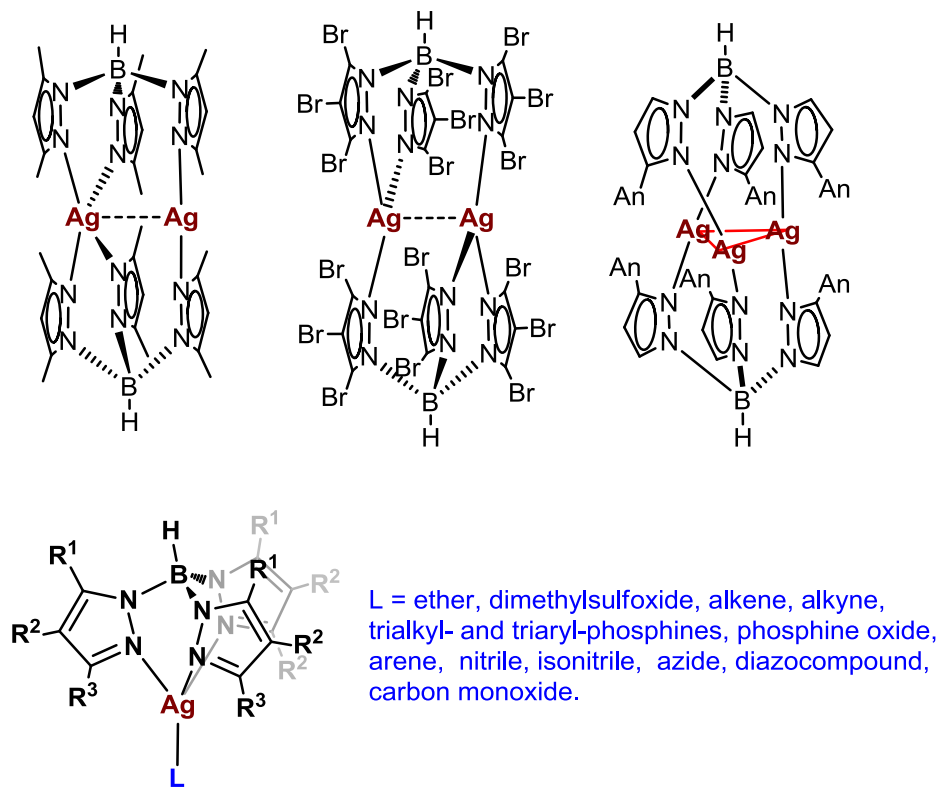


Figure 4. Top: Molecular structures of $[\text{Tp}^*\text{Ag}]_2$, $[\text{Tp}^{\text{Br}_3}\text{Ag}]_2$, and $[\text{Ag}_3(\text{Tp}^{\text{An}})_2]^+$. Bottom: mononuclear $[\text{Tp}^x\text{AgL}]$ complexes.

Mononuclear adducts of composition $[\text{Tp}^x\text{AgL}]$ adducts can be prepared by direct reaction of $[\text{MTp}^x]$ and a Ag(I) salt in the presence of the L ligand. In this manner a series of compounds has been prepared with L being ether [19f, 26b, 37c, 42], dimethylsulfoxide [43], alkene [20a,e,g,k,l, 42b,c, 44], alkyne [42b], trialkyl- and triaryl-phosphines [26e, 45], phosphine oxide [45c], arene [42b, 45c], nitrile [42b, 46], isonitrile [26e, 47], azide [23], diazocompound through carbonyl group coordination [48] or carbonyl [19f, 20c,k, 45c]. Albeit the κ^3 -coordination mode is the most common for Tp^x ligands in the $[\text{Tp}^x\text{AgL}]$ complexes, κ^2 -bonded silver Tp^x adducts are also known, particularly with RB- instead of HB- derivatives [20l, 47, 49].

Carbonyl complexes $[\text{Tp}^x\text{Ag}(\text{CO})]$ have also been described for a number of ligands. There is a particular feature with some of these compounds: with electron withdrawing substituents at the pyrazolyl rings, the $\nu(\text{CO})$ values surpass that of free CO, at variance with the copper analogs. This is the case of ligands $\text{Tp}^{(\text{CF}_3)_2}$, $\text{Tp}^{(\text{CF}_3)_2,\text{Br}}$ or a family of fully fluorinated hydrotrisindazolyborate ligands, among others [19f,h, 20c,k, 45c]. All of them provide carbonyl complexes with $\nu(\text{CO})$

around 2160 cm^{-1} , examples of the so-called non-classical metal-carbonyl complexes, as the result of a relatively low electron density at the silver center and the concomitant reduced Ag-CO π -back-bonding contribution.

2.3 Gold complexes.

In spite of the early reports, four decades ago, of the synthesis of $[\text{TpAuCl}_2]$, $[\text{Tp}^*\text{AuCl}_2]$ [50], and $[\text{TpAuMe}_2]$ [51] complexes, the development of gold-containing Tp^x ligands remains scarce when compared with the number of examples of the other members of Group 11. This lack of more complexes in the case of gold(III) has been justified by the high reducing power of the Tp^x anion [52]. The above $[\text{Tp}^x\text{AuX}_2]$ complexes display a square-planar geometry with Tp^x ligand coordinated by a κ^2 mode (Figure 5a). All these compounds showed fluxional behavior that was studied by variable-temperature NMR, indicating that there exists an exchange between coordinated and uncoordinated donor groups, consistent with the facile formation of pentacoordinate intermediates.

Gold(I) complexes have been isolated as $[\text{Tp}^x\text{AuL}]$ adducts with $L =$ phosphine [45a, 51], CO [20c, 53], ethylene [20c,h; 54] and isonitrile [53] ligands. Some of these adducts decomposed under light, or are very reactive, as the CO complexes. The $[\text{Tp}^x\text{AuL}]$ adducts featuring κ^3 -bonded scorpionates and rather rare and unstable, such as the mentioned carbonyl (Figure 5b). The isonitrile derivative (Figure 5c) displays a true $\text{N}_{\text{pyr}}\text{-Au}$ bond, whereas the bond distances from the metal center to the other two pyrazoles are significantly longer, the compound being considered with a dicoordinated, distorted linear geometry. $[\text{Tp}^x\text{Au(ethylene)}]$ compounds (Figure 5d) show trigonal planar coordination geometry around the metal bearing the ethylene ligand coordinated in a typical η^2 -fashion and the scorpionate in κ^2 -mode.

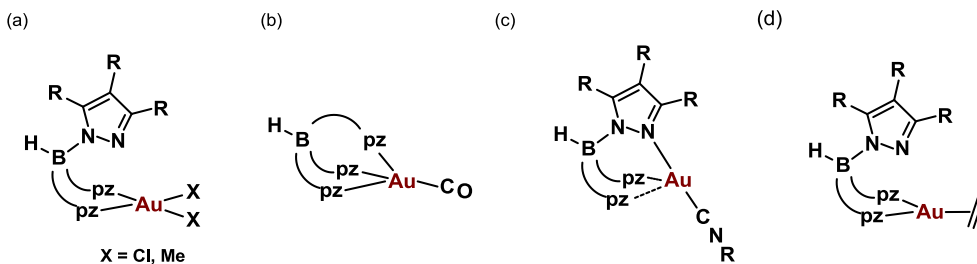


Figure 5. (a) $[\text{Tp}^x\text{AuX}_2]$ and (b) $[\text{Tp}^x\text{Au(ethylene)}]$ complexes structure.

The gold anionic complex $[\text{NBu}_4][\text{Au}_3(\text{o-C}_6\text{BrF}_4)_3(\text{Tp})]$ contains a $\mu^3\text{-}\kappa^1\text{:}\kappa^1\text{:}\kappa^1\text{-Tp}$ ligand and an asymmetrical trinuclear anionic fragment in which two of the three metals displays an aurophilic weak interaction [55] (Figure 6a). This interaction along with two unusual $\text{B-H}\cdots\text{Au}$ hydrogen bonds confer the anion a “basket” geometry. Indeed, the formation of the heterobimetallic complex $[\{\text{Pb}(\text{Tp})\}][\{\text{Au}_3(\text{o-C}_6\text{BrF}_4)_3(\text{Tp})\}]$ (Figure 6b) is explained by the encapsulation of a cationic Pb(II) moiety within the anionic trinuclear Au(I) fragment.

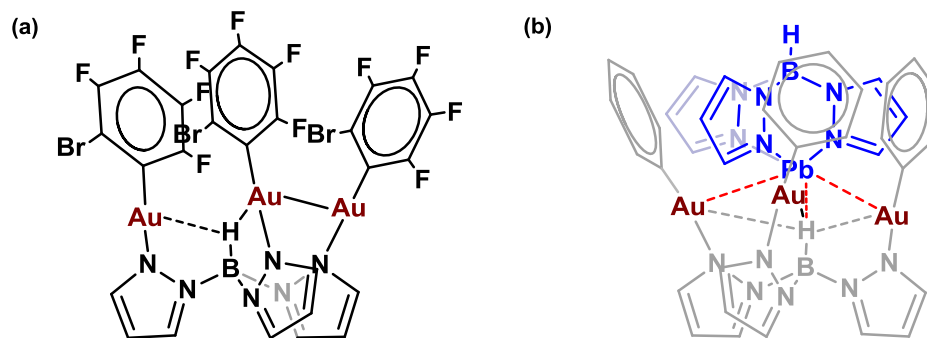


Figure 6. Structures of (a) $[\text{NBu}_4][\text{Au}_3(\text{o-C}_6\text{BrF}_4)_3(\text{Tp})]$ and (b) $[\{\text{Pb}(\text{Tp})\}]\{\text{Au}_3(\text{o-C}_6\text{BrF}_4)_3(\text{Tp})\}$. The aromatic substituents in the latter have been omitted for clarity.

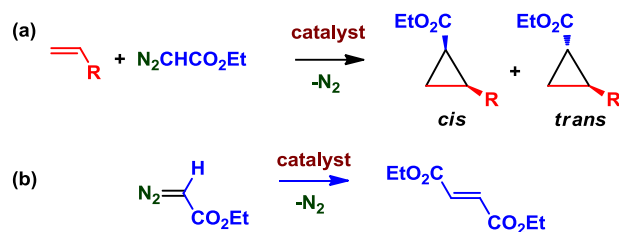
3. Tris(pyrazolyl)borate Group 11 Metal Complexes as Catalysts.

As described in the previous section, the tripodal Tp^x ligands, due to their structural and electronic features, display an important influence in the nuclearity, coordination number, geometry, and reactivity of the metal complex. These aspects are crucial since they determine the activity and selectivity of the metal compound as potential catalysts. Copper and silver complexes bearing Tp^x ligands have been employed as catalysts in different organic transformations: among them, the most developed reactions can be classified in two main types: carbene, nitrene and oxo transfer to saturated or unsaturated hydrocarbons and atom transfer radical additions to olefins (ATRA). The discovery of $[\text{Tp}^x\text{Au}(\text{I})]$ complexes for catalytic applications is yet to be done.

3.1 Addition reactions of carbene, nitrene and oxo groups to unsaturated substrates.

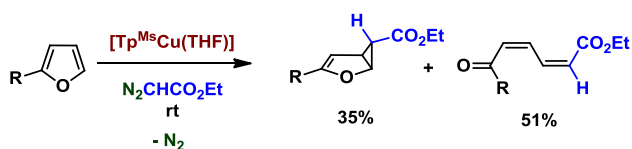
3.1.1 Cyclopropanation and cyclopropenation reactions.

The transfer of carbene groups from diazocompounds to olefins to yield cyclopropane products catalyzed by $[\text{Tp}^x\text{CuL}]$ catalysts (Scheme 2a) have been developed in the last three decades. First example was provided with complex $[\text{Tp}^*\text{Cu}(\text{CH}_2=\text{CH}_2)]$ as catalyst for the reaction of ethyl diazoacetate (EDA) with alkenes [56] in moderate to high yields, but low diastereoselection. This important issue [57] was overcome later using catalyst $[\text{Tp}^{\text{Ms}}\text{Cu}(\text{THF})]$, leading to the preferential formation of the *cis* cyclopropane: a 98:2 *cis:trans* ratio was reported with styrene and ethyl diazoacetate whereas other terminal olefins gave ca. 80:20 mixtures of *cis* and *trans* isomers. [58]. This catalyst was very selective toward olefin cyclopropanation, with very small amount of carbene-coupling products being observed (Scheme 2b). Styrene cyclopropanation was also achieved in a fluoruous medium catalyzed by the $[\text{Tp}^{\text{Br}_3}\text{Cu}(\text{NCMe})]$ complex, which allowed the recyclability of the catalyst for five times with constant yields and diastereoselectivities [59].



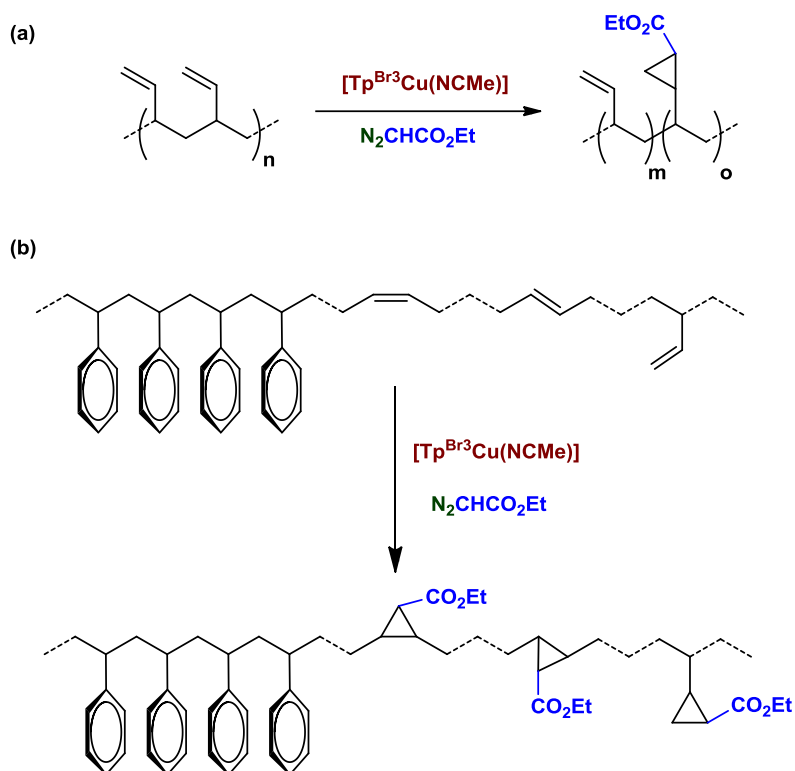
Scheme 2. (a) Olefin cyclopropanation of terminal olefins with ethyl diazoacetate. (b) Side reaction, coupling of ethyl diazoacetate.

As an extension of the previous reactions, furans have also been functionalized [60]. Thus, several $[\text{Tp}^x\text{CuL}]$ complexes were used as catalysts for the reaction of EDA with different furans (Scheme 3). The reactions afforded different cyclopropanes and dienes with ratios that depended on the Tp^x ligand employed, therefore inducing the control of the selectivity in the process. The reaction could be driven toward the latter upon treatment with elemental iodine. This methodology was applied to the synthesis of ostpanic acid as a practical example.



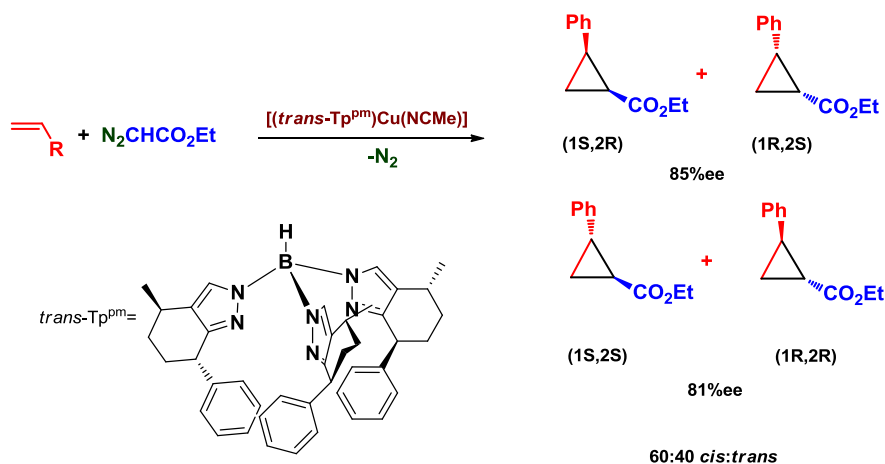
Scheme 3. Tp^xCu -catalyzed reaction of EDA with furans.

Macromolecules have also been modified with this strategy. Polybutadienes [61] (Scheme 4a) or styrene-butadiene rubbers [62] (Scheme 4b) rubbers were functionalized upon cyclopropanation of the olefinic groups of the polymeric chain. Importantly, the polar groups incorporated provided distinct properties regarding their potential use as adhesives, preserving the structure of the initial polymer.



Scheme 4. Functionalization of polymers by cyclopropanation of the C=C bonds.

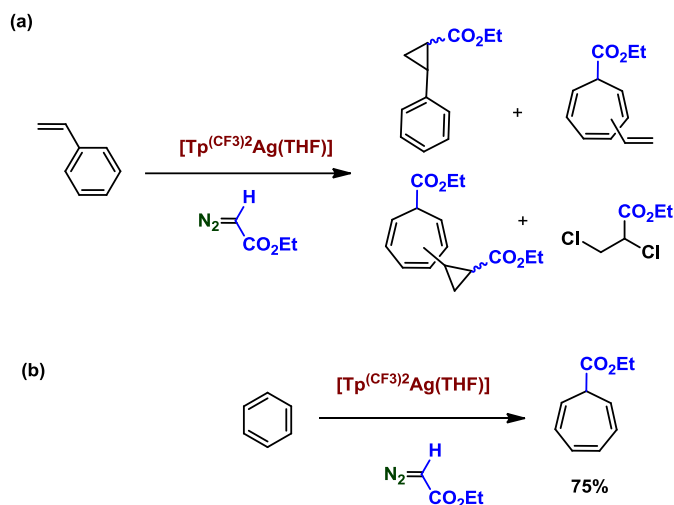
Asymmetric olefin cyclopropanation with diazocompounds has been achieved using a copper complex bearing the chiral *trans*-Tp^{pm} ligand as the catalyst with enantiomeric excesses in the 80–85% range for both *cis* and *trans* isomers in the reaction of styrene and EDA (Scheme 5) [19c]. Those results surpassed the *ee* reported for other chiral [Tp^xCu] complexes [63].



Scheme 5. Asymmetric cyclopropanation of styrene catalyzed by a copper complex bearing the chiral *trans*-Tp^{pm}.

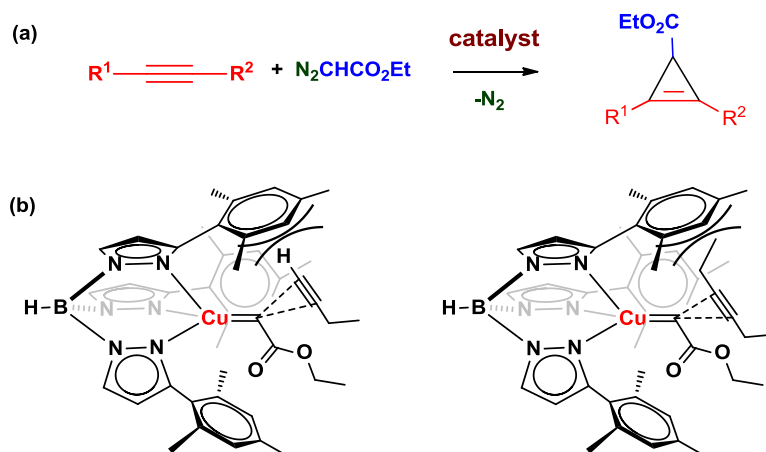
The activity of Tp^x-containing silver complexes in cyclopropane formation by carbene addition to arenes/alkenes has

also been studied. Complex $[\text{Tp}^{(\text{CF}_3)_2}\text{Ag}(\text{THF})]$ was reported as catalyst for the reaction of styrene and EDA [64]. In addition to the cyclopropanation of the alkene moiety, the Buchner reaction was also observed, leading to cycloheptatrienes (Scheme 6a). Moreover, the products from the insertion of the carbene into the C–Cl bond of dichloromethane were also formed (*vide infra*). With benzene as the substrate, a single cycloheptatriene product was obtained (Scheme 6b), in a reaction previously observed with the copper $[\text{Tp}^{\text{Br}_3}\text{Cu}(\text{NCMe})]$ complex [65].



Scheme 6. Reaction of styrene (a) or benzene (b) with EDA catalyzed by $[\text{Tp}^{(\text{CF}_3)_2}\text{Ag}(\text{THF})]$.

Alkynes have also been the subject of the reaction with ethyl diazoacetate in the presence of $[\text{Tp}^x\text{CuL}]$ catalysts, leading to their conversion into cyclopropenes (Scheme 7a) [66]. Curiously, one of the most active catalyst for the olefin cyclopropanations, $[\text{Tp}^{\text{Ms}}\text{Cu}(\text{THF})]$, afforded low yields in the case of the cyclopropanation of internal alkynes. Kinetic studies showed that the reaction of EDA with 1-hexyne using several Tp^xCu -catalysts was significantly slower for $\text{Tp}^x = [\text{Tp}^{\text{Ms}}\text{Cu}]$, followed by $[\text{Tp}^{\text{Ph}}\text{Cu}]$ and $[\text{Tp}^{\text{Br}_3}\text{Cu}]$ [21]. This trend correlated well with the stabilities of the $[\text{Tp}^x\text{Cu}(1\text{-hexyne})]$ adducts: those complexes favouring the formation of alkyne adducts display lower catalytic activities as the result of a certain decrease of the concentration of the catalytic species $[\text{Tp}^x\text{Cu}]$. The bulkiness of the tris(pyrazolyl)borate ligand also affects the catalyst chemoselectivity of the process. Thus, in the 1-hexyne cyclopropanation reaction catalyzed by $[\text{Tp}^{\text{Ms}}\text{Cu}]$, although slow, cyclopropene was obtained in moderate yields, whereas for 3-hexyne diethyl fumarate and maleate, from the dimerization reaction of EDA, were obtained as the major products. This behaviour was attributed to steric repulsions between the mesityl groups of the Tp^{Ms} ligand and 3-hexyne, which would prevent the approach of the alkyne to the carbene ligand and hindering the process of carbene transfer (Scheme 7b).

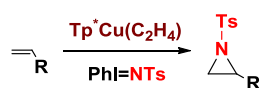


Scheme 7. (a) The alkyne cyclopropanation reaction. (b) Steric interactions between the mesityl groups of the Tp^{Ms} ligand and the alkyne during the carbene transfer step with 1-hexyne and 3-hexyne.

3.1.2 Nitrene transfer addition reactions.

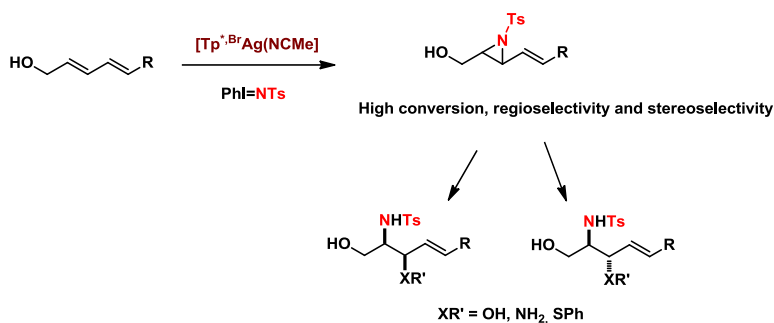
Transition-metal-catalyzed nitrene transfer reactions represents a convenient method for the formation of C–N bonds. In this process, a metallonitrene intermediate is generated in situ upon the appropriate selection of the catalyst and the nitrene precursor, in a process that is somewhat related to the carbene transfer reaction previously described. The coinage metals Cu, Ag, and Au have been reported to promote reactions involving nitrenes, with copper being by far the most extensively studied of these metals [4c]. The commonly employed nitrene sources are hypervalent I(III) compounds such as *N*-(*p*-toluenesulfonyl)imino phenyliodinane ($\text{PhI}=\text{NTs}$), *N*-halogenated sulfonamide salts (chloramine-T and bromamine-T), or organic azides.

In the case of tris(pyrazolyl)borate complexes, $[\text{Tp}^* \text{ML}]$ ($\text{M} = \text{Cu}, \text{Ag}$) have been described for these transformations. Complex $[\text{Tp}^* \text{Cu}(\text{C}_2\text{H}_4)]$ was reported for the olefin aziridination reaction [56], using PhINTs as the nitrene source (Scheme 8). Later studies showed that the electronic features of poly(pyrazolyl)borate ligands have a significant influence on the efficiency of the copper-catalyzed aziridination reaction, being the electron-deficient poly(pyrazolyl)borates complexes the most effective catalysts for these transformations [20b,67–68].



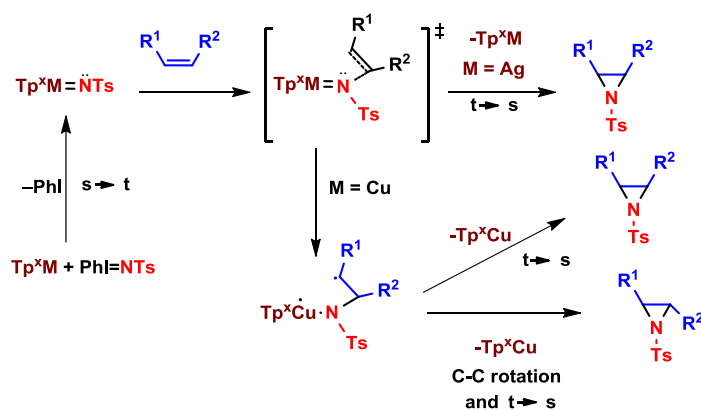
Scheme 8. Seminal report on the $\text{Tp}^* \text{Cu}$ -catalyzed olefin aziridination reaction.

With *E,E*-dien-1-ols as the substrates, the scope of this transformation was expanded providing a new route for the synthesis of sphingosines. The use of $[\text{Tp}^{*,\text{Br}} \text{Ag}(\text{NCMe})]$ as catalyst led to the preferential formation of the aziridine located vicinal to the OH group, that remained unaltered (Scheme 9). Also, the reaction occurred with complete stereoretention, at variance with the copper analogue as the catalyst. Further ring-opening strategies led to sphingosine derivatives reducing the previous reported routes [69].



Scheme 9. The selective aziridination of dien-1-ols and its use as a synthetic methodology.

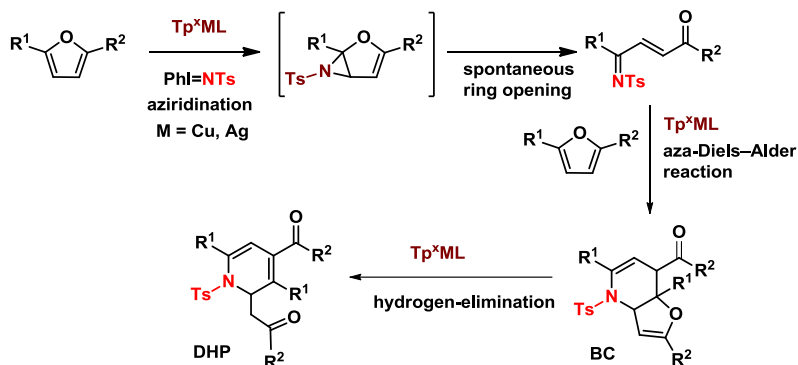
The mechanism of the above transformations has been studied on the basis of experimental probes and DFT calculations. These results led to the novel proposal that triplet and singlet pathways were both involved during the transformation, at variance with previous ideas that each catalytic system would occur through one or the other pathways [70]. The first step is the formation of a triplet metal-nitrene species, from which the first C-N bond is formed. At this stage, the reaction may lead to a radical intermediate, responsible of C-C rotation in some cases and loss of stereochemistry (copper route), or may jump into the singlet pathway through a MECP, excluding the possibility of C-C-rotation, that is the case of silver (Scheme 10).



Scheme 10. Proposed mechanism of the Tp^*M -catalyzed aziridination reaction.

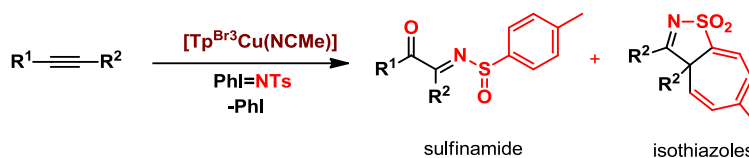
The nitrene addition reaction has been extended to furans as substrates. Thus, the reaction of the mono- or dialkyl-substituted furans with $\text{PhI}=\text{NTs}$, catalyzed by copper or silver tris(pyrazoly)borate complexes, lead to the formation of 1,2-dihydropyridines (Scheme 11) [71]. The best catalyst, in term of yields, was the $[\text{Tp}^{\text{Br}^3}\text{Cu}(\text{NCMe})]$ complex. The study of the mechanism revealed that this transformation starts with furan aziridination, sequentially followed by aziridine ring-opening, transimination reaction, inverse-electronic-demand aza-Diels-Alder reaction, and a final hydrogen elimination reaction. Importantly, the use of the asymmetric 2-methylfuran showed that there is an influence of the $[\text{Tp}^*\text{ML}]$ complex in the ratio of the products from the aza-Diels-Alder reaction (bicyclic compound **BC**) and its derivative from the hydrogen elimination (1,2-dihydropyridine, **DHP**): i) $\text{Tp}^{\text{M}^s}\text{Cu}(\text{NCMe})$ induced the quantitative formation of 1,2-dihydropyridine, whereas in the case of the $\text{Tp}^*-\text{}$, $\text{Tp}^{\text{Br}^3}-\text{}$, or $\text{Tp}^*-\text{Br}-\text{}$ copper catalysts, a certain amount of **BC** could be detected, ii) this selectivity was reversed by using silver instead of copper the complex Tp^*-BrAg provided a 90:10 ratio of bicyclic

compound and 1,2-dihydropyridine, respectively.



Scheme 11. Reaction of furans and PhI=NTs: synthesis of 1,2-dihydropyridines.

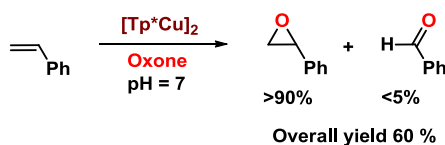
With alkynes as the substrates, a novel transformation has been described when reacted with PhI=NTs in the presence of catalytic amounts of $[\text{Tp}^{\text{Br}3}\text{Cu}(\text{NCMe})]$ [72]. Two products were isolated from the reaction mixture, and characterized as sulfenamides and isothiazoles (Scheme 12). The formation of the sulfenamides involves the rare reduction of the sulfone group to a sulfoxide, whereas the generation of isothiazoles involved the insertion of an alkyne carbon atom into the aromatic ring of the *N*-tosyl moiety. In the case of internal alkynes both compounds are obtained, whereas the use of terminal alkynes lead to the selective formation of the sulfenamide compounds. Other tris(pyrazolyl)borate derivatives were employed in this study but could not reach the activity of the $\text{Tp}^{\text{Br}3}$ derivative.



Scheme 12. Reaction of PhI=NTs and alkynes using $[\text{Tp}^{\text{Br}3}\text{Cu}(\text{NCMe})]$ as catalyst.

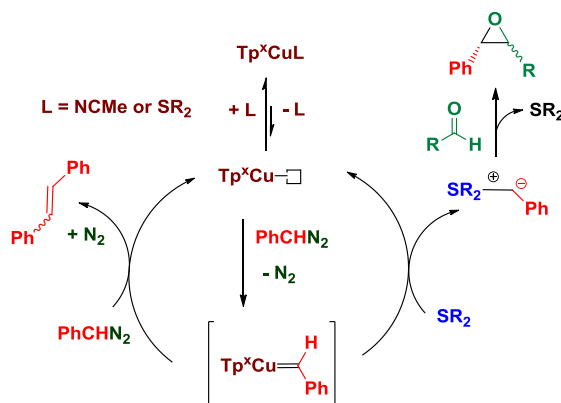
3.1.3 Epoxidation reactions.

The epoxidation of olefins catalyzed by transition metal complexes is an extensively studied research field. Although a plethora of epoxidation catalysts based on transition metals has been reported, there is only one example involving a $[\text{Tp}^*\text{M}]$ complex as the catalyst with M being a coinage metal. It is the case of $[\text{Tp}^*\text{Cu}]_2$, that promoted the conversion of styrene into styrene oxide using Oxone (potassium peroxymonosulfate) as the oxidizing agent (Scheme 13) [73]. In that contribution, the authors also described the use of silica gel-supported complex as heterogeneous catalysts [74] affording similar results, using water as solvent.



Scheme 13. Styrene epoxidation reaction using $[\text{Tp}^*\text{Cu}]_2$ as precatalyst.

An alternative method for the synthesis of epoxides consists of the reaction of an aldehyde with *in situ* generated sulfur ylides, the latter being formed from the transition metal-catalyzed decomposition of a diazo compound in the presence of catalytic amounts of a sulfide. $[\text{Tp}^x\text{CuL}]$ complexes, with organic sulfides as cocatalyst, catalyze the reaction of phenyldiazomethane and aldehydes affording the corresponding epoxides, with activities surpassing or similar to those of already reported rhodium-based systems [27] (Scheme 14). $[\text{Tp}^{\text{Br}^3}\text{Cu}(\text{NCCH}_3)]$ showed the highest catalytic activity among the copper(I) tris(pyrazolyl)borate complexes tested. The catalytic activity is controlled by electronic effects induced by the Tp^x ligand as well as by the stability of the $[\text{Tp}^x\text{Cu}(\text{SR}_2)]$ adducts. For instance, in the case of Tp^{Ms} as ligand, $[\text{Tp}^{\text{Ms}}\text{Cu}(\text{THT})]$ (THT = tetrahydrothiophene) and $[\text{Tp}^{\text{Ms}}\text{Cu}(\text{SMe}_2)]$ species could be isolated and characterized. Importantly, $[\text{Tp}^{\text{Ms}}\text{Cu}(\text{THF})]$ also showed high catalytic activities with *in situ* generated PhCHN_2 from benzaldehyde tosylhydrazone sodium salt at 60 °C in methyl tert-butyl ether as solvent, improving already reported methods with copper-based catalysts.

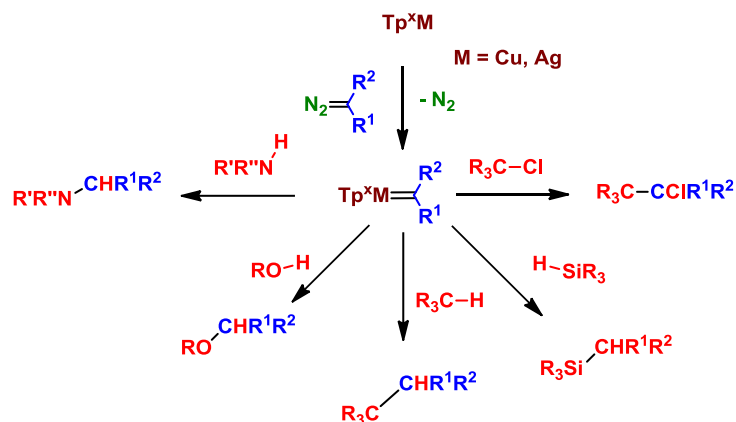


Scheme 14. Mechanistic proposed for the epoxidation of aldehydes catalyzed by Tp^xCuL and SR_2 .

3.2 Insertion reactions of carbene, nitrene and oxo groups into C-H and C-X bonds.

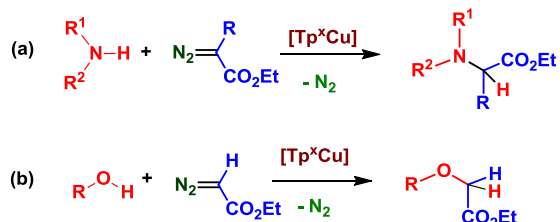
3.2.1 Carbene insertion reactions.

Metal-carbenes can serve as reactive intermediates for X-H group functionalization, allowing the control of the reaction course in terms of selectivity, in contrast to free carbenes. In the specific case of $[\text{Tp}^x\text{M}]$ ($\text{M} = \text{Cu}, \text{Ag}$), the electronic and structural features of Tp^x ligands play an important role in the ability of those complexes to catalyze X-H functionalization, not only of the highly polar N-H, O-H and C-Cl bonds, but also to the less nucleophilic C-H and Si-H bonds. (Scheme 15).



Scheme 15. Carbene insertion into saturated bonds catalyzed by $[\text{Tp}^x\text{ML}]$ ($\text{M} = \text{Cu}, \text{Ag}$) complexes.

Tp^xCu -complexes promote the insertion of diazo compounds into amine or amide N–H bonds [75] and alcohols O–H bonds [76] in very high yield and under very mild conditions. For amines, $[\text{Tp}^x\text{Cu}]$ complexes were tested with pyrrolidine as the probe and EDA. Quantitative conversions were observed in all cases, the difference being established in the time required for the completion of the reaction: 20 min for $[\text{Tp}^*\text{Cu}]_2$ and $[\text{Tp}^{\text{Cy}}\text{Cu}(\text{NCMe})]$, and 120 min for $[\text{Tp}^{\text{Ph}}\text{Cu}(\text{NCMe})]$ and $[\text{Tp}^{\text{Ms}}\text{Cu}(\text{THF})]$. The reaction of $\text{RC}(\text{N}_2)\text{CO}_2\text{Et}$ diazo compounds and amines, in the presence of catalytic amounts of $[\text{Tp}^*\text{Cu}]_2$, lead to the corresponding aminoacid derivatives in almost quantitative yields (Scheme 16a). In the case of alcohols, the same complexes catalyze the insertion of the carbene unit from EDA into the OH bond of saturated and unsaturated alcohols with very high degrees of chemoselectivity (high yields in ethers) and regioselectivity (for unsaturated alcohols, only the insertion products were obtained) (Scheme 16b). Interestingly, $[\text{Tp}^{\text{Ms}}\text{Cu}(\text{THF})]$ afforded the highest yields in the case of the saturated alcohols (92% for 1-butanol), but only modest in the case of allyl alcohol (40% yield). This behavior was later attributed to the formation of very stable $[\text{Tp}^{\text{Ms}}\text{Cu}(\text{olefin})]$ adducts [20e].



Scheme 16. Carbene insertion into N–H and O–H bonds catalyzed by Tp^xCuL complexes.

In contrast to the X–H bonds ($\text{X} = \text{O}$ and N), the less nucleophilic C–H and Si–H bonds requires a more electrophilic metal-carbene intermediate to achieve the carbene insertion. Seminal work with Tp^x -containing catalysts employed $[\text{Tp}^{\text{Ms}}\text{Cu}(\text{THF})]$, which only promoted the functionalization of the C–H bonds of cycloalkanes and the α -C–H bonds of cyclic ethers [77]. However, when moving to a Tp^x ligand with electron-withdrawing groups such as $[\text{Tp}^{\text{Br}_3}\text{Cu}(\text{NCMe})]$, secondary and tertiary sites of linear or branched alkanes were modified [34]. The relative steric effect of the hydrotris(pyrazolyl)borate ligands (Tp^x) has been rationalized on the basis of this alkane functionalization (Table 3),

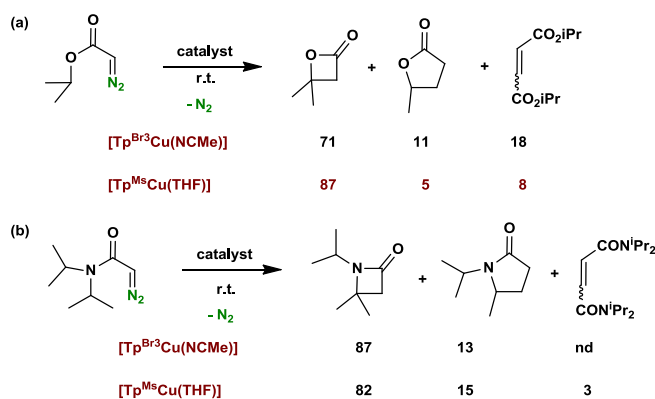
defining a relative steric parameter [78], using the relative percentages of functionalized products P₂ and P₃ (the primary sites remained unchanged) with a number of different catalyst differing in the Tp^x ligand. The validity of the model was tested in the styrene cyclopropanation reaction, the functionalization of the tertiary sites of pristane and the amidation of the aliphatic C–H bonds of cumene, finding good correlations between the regioselectivities of the processes and the SP_R values in all cases.

Table 3. The relative steric parameter (SP_R).

$\text{Pristane} \xrightarrow[\text{-N}_2]{\text{N}_2\text{CHCO}_2\text{Et}, [\text{Tp}^x\text{CuL}]}$
 $\text{P}_2 + \text{P}_3$

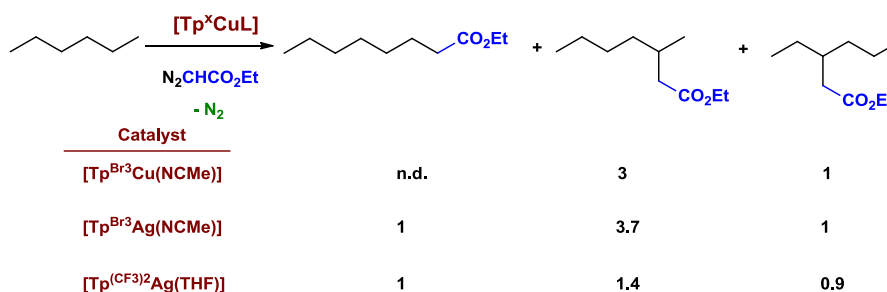
Tp ^x	R ¹	R ²	R ³	% P ₂	% P ₃	SP _R
Tp*	Me	H	Me	75	25	1,00
Tp ^{Br3}	Br	Br	Br	76	24	1,06
Tp ^{Ph,4Bn}	H	CH ₂ Ph	Ph	78	22	1,18
Tp ^{Cy}	H	H	Cy	80	20	1,33
Tp ^{Cy,4Br}	H	Br	Cy	80	20	1,33
Tp ^{Ph}	H	H	Ph	80	20	1,33
Tp ^{Ph,4Pr}	H	ⁿ Pr	Ph	83	17	1,63
Tp ^{Ms}	H	H	2,4,6-Me ₃ C ₆ H ₃	86	14	2,05

The [Tp^xCuL] complexes also catalyzed the intramolecular insertion of a carbene moiety into a C–H bond of the molecule also bearing the diazo group leading to the formation of lactams and lactones [79] (Scheme 17). Remarkably, the complexes bearing the ligands Tp^{Br3} and Tp^{Ms} provided activities and selectivities for these transformations comparable with or superior than the rhodium catalyst [Rh₂(OAc)₄]. The observation of higher yields in some cases with Tp^{Ms} as ligand was attributed to a higher protection of the transient metalcarbene intermediate. The difference in size of the Tp^x ligand also influenced the regioselectivity, when more than one reaction site was available (Scheme 17).

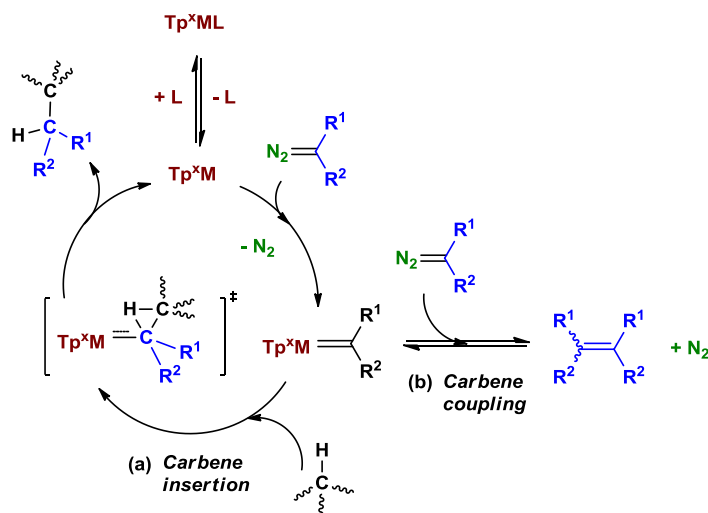


Scheme 17. Examples of the intramolecular C–H functionalization reaction by carbene insertion: (a) formation of lactones and (b) lactams.

The activation of primary sites in the intermolecular version of this transformation was first achieved with the silver complexes bearing electron-withdrawing ligands $[\text{Tp}^{\text{Br}^3}\text{Ag}(\text{NCMe})]$ [39c] and $[\text{Tp}^{(\text{CF}_3)_2}\text{Ag}(\text{THF})]$ [80]. For the sake of comparison with $[\text{Tp}^{\text{Br}^3}\text{Cu}(\text{NCMe})]$, Scheme 18 shows the activity and selectivity of these catalysts referred to *n*-hexane as substrate. Theoretical calculations carried out in order to explain the difference in reactivity showed that exist a much lower barrier for the silver catalysts [81]. The C–H functionalization reaction occurs with the formation of a metalcarbene intermediate that reacts with the alkane in a single, irreversible step where the regioselectivity is decided (Scheme 19).

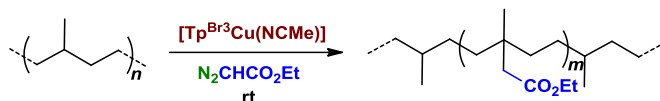


Scheme 18. Comparison of the functionalization of hexane with EDA catalyzed by $[\text{Tp}^{\text{X}}\text{M}]$ complexes.



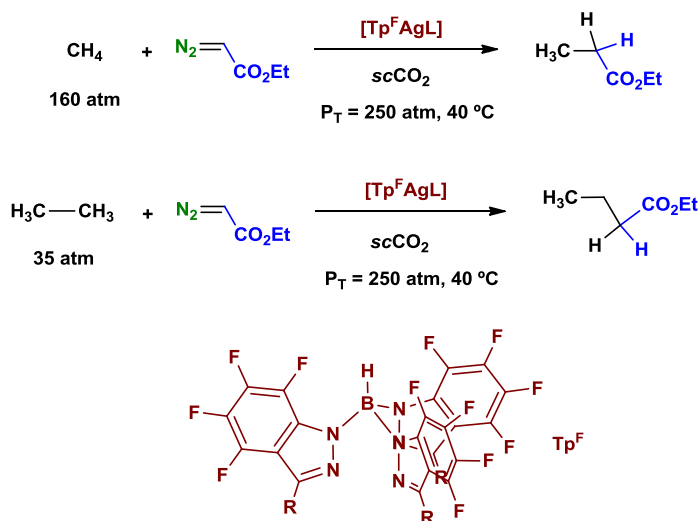
Scheme 19. (a) Mechanistic proposal for the alkane C–H bond functionalization by carbene insertion from diazo compounds catalyzed by a $[\text{Tp}^{\text{X}}\text{ML}]$ complex ($\text{M} = \text{Cu}, \text{Ag}$); (b) the formation of fumarate and/or maleate derivatives by carbene transfer from diazo compounds ($\text{R}^1, \text{R}^2 = \text{CO}_2\text{Et}$).

As an application of this methodology, polyolefins, such as polyethylene or polypropylene, have been functionalized by carbene insertion into C–H bonds with a preferential incorporation of the carbene moiety into the tertiary sites (Scheme 20) [82].



Scheme 20. Functionalization of polyolefin by carbene insertion catalyzed by [Tp^{Br}₃Cu(NCMe)].

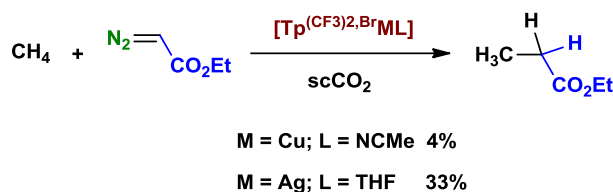
An important advance with use of [Tp^xML] catalyst in C-H functionalization was accomplished when fully fluorinated hydrotrisindazolylborates [83] were used as ligands, their [Tp^xAgL] catalysts showing excellent activities. Moreover, they could be employed in fluorous biphasic conditions, which allowed the separation of products and the recycling of the catalyst [42e]. But the most important achievement with these complexes has been the functionalization of the first members of the series of alkanes, from methane to butane, using supercritical carbon dioxide as the reaction medium. The catalyst and EDA were dissolved in the fluid mixture of supercritical carbon dioxide with the alkane [84] (Scheme 21). The presence of the fluorine atoms in the indazolyl groups increased the solubility of the silver complexes in the supercritical fluid. By this methodology, a significant amount of methane (and the other alkanes) reacted with the in situ generated metalcarbene, with no other C–H or C–X bond in the reaction mixture that could compete with the CH₄. Methane was converted into ethyl propionate in high turnover numbers (TON up to 750) at 40 °C and 250 atm.



Scheme 21. Functionalization of methane and ethane using [Tp^FAgL] catalysts in scCO₂ as the solvent.

The development of the new ligand Tp^{(CF₃)₂,Br} (hydrotris((3,5-bis(trifluoromethyl)-4-bromo)-pyrazol-1-yl)borate) allowed the preparation of its copper and silver complexes, both of them capable of inserting the carbene unit from EDA into the C–C bond of methane, in the first example of this transformation induced by copper [19f], also in a homogeneous

process that uses scCO_2 as the reaction medium (Scheme 22). The ν_{CO} values of the corresponding carbonyl adducts $[\text{Tp}^{(\text{CF}_3)_2, \text{Br}}\text{M}(\text{CO})]$, 2125 cm^{-1} ($\text{M} = \text{Cu}$) and 2167 cm^{-1} ($\text{M} = \text{Ag}$), indicated that both metal centers are highly electrophilic in nature. It is important to point out that when the copper catalyst was used for the functionalization of pentane, 2-methylbutane, and hexane in neat alkane or in scCO_2 , an increase in the regioselectivity toward the primary sites was observed in scCO_2 [85]. This different result was attributed to the interaction of the carbon dioxide molecules with the fluorine atoms of the ligand, with CO_2 molecules withdrawing electron density from the complex and thus enhancing the electrophilic nature of the metal center (Figure 7).



Scheme 22. First example of the catalytic modification of methane with copper under homogeneous conditions.

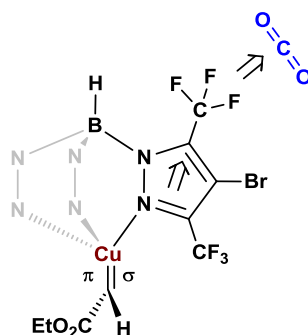
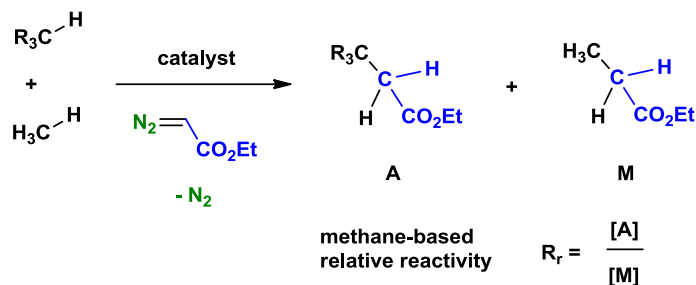


Figure 7. The electronic flux from the fluorine atoms to carbon dioxide.

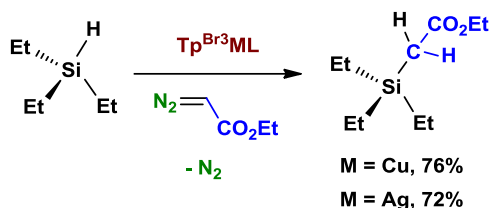
Unfortunately, in all cases mixtures of products were obtained when more than one type of C–H bond was available in the alkane, the design of selective catalyst toward primary sites yet remaining as a challenge in this strategy [86]. It is important to note that the mechanism of the EDA conversion to diethyl maleate and diethyl fumarate catalyzed by these complexes has also been proposed by computational studies [87].

A relevant application of these investigations consists of the measurement of the relative reactivities by competition experiments (Scheme 23) of a series of C–H bonds of a series of gaseous or liquid alkanes towards in situ generated electrophiles (copper-, silver-, or rhodium-carbenes), with methane as the reference [88].



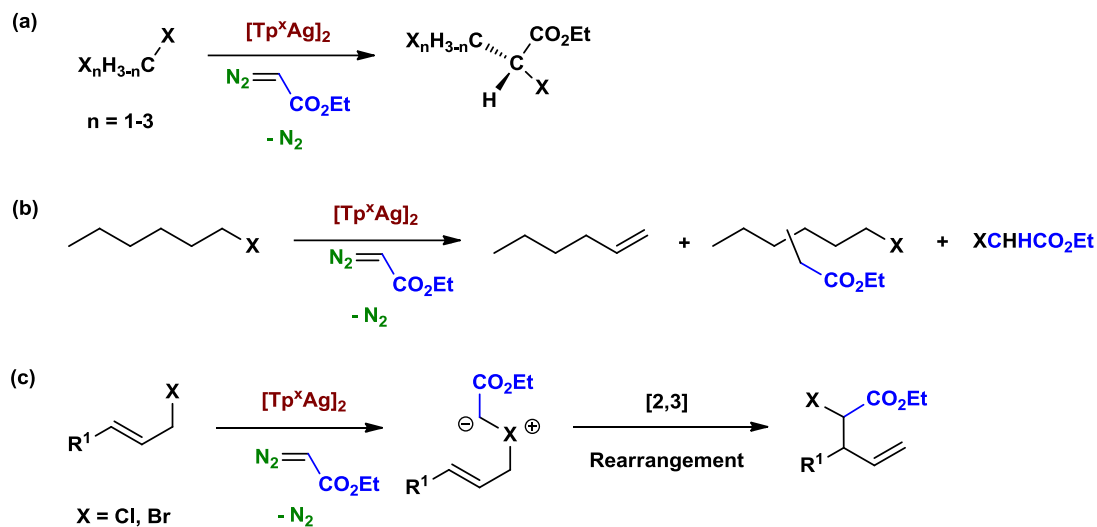
Scheme 23. The quantitative reactivity relative to methane (R_r) of higher alkanes.

As an extension of the above studies, the functionalization of Si–H bonds with EDA using the same strategy was addressed. The $\text{Tp}^{\text{Br}_3}\text{ML}$ ($\text{M} = \text{Cu}, \text{Ag}$) complexes catalyze this transformation with good yields, the silver case being the first example of such a reaction [89] (Scheme 24). Other diazo compounds were also tested: $\text{N}_2\text{C}(\text{Ph})\text{CO}_2\text{Et}$ displayed similar reactivity to that of EDA, whereas other $\text{N}_2\text{C}(\text{R})\text{CO}_2\text{Et}$ ($\text{R} = \text{Me}, \text{CO}_2\text{Et}$) afforded lower conversions.



Scheme 24. Intermolecular insertion of carbene from EDA into Si–H bonds.

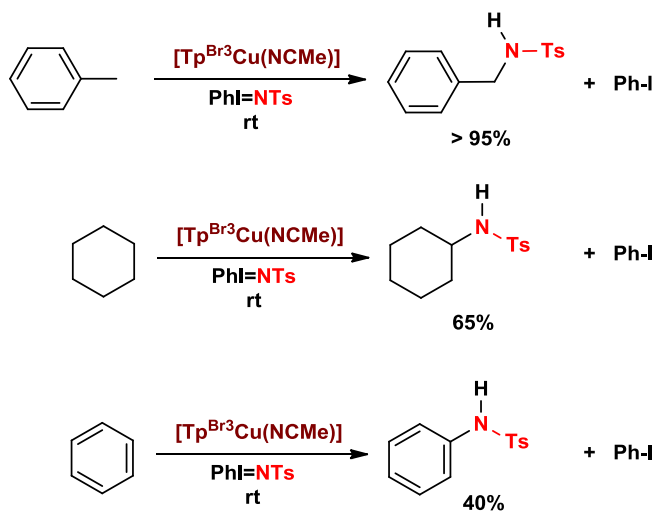
The highly electrophilic silver–carbene intermediates can also react with carbon–halogen bonds ($\text{X} = \text{Cl}$ and Br), even in the case of C–Cl bonds that are difficult to activate. This reaction was first reported with the $[\text{Tp}^{(\text{CF}_3)_2}\text{Ag}(\text{THF})]$ catalyst [90], later also demonstrated with the $\text{Tp}^{\text{Br}_3}\text{Ag}$ analogue. (Scheme 25a). The mechanistic studies showed that the reaction proceeded through the transfer of the carbene group to the halogen atom and the formation of an ylide which rearranged with the intermediacy of the silver center. The reaction was general for several polyhalomethanes and for haloalkanes. Interestingly, the dehydrohalogenation and the carbene insertion into C–H bonds reactions occurred for those bearing an alkyl chain, thus producing an olefin and haloacetate (Scheme 25b). A 2,3-sigmatropic rearrangement of ylide was observed in the case of unsaturated substrates (Scheme 25c) [91].



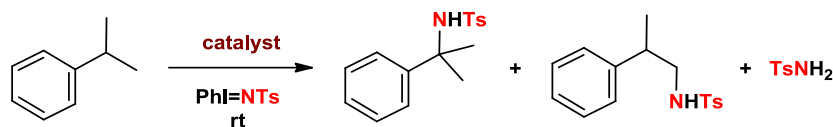
Scheme 25. Reaction of haloalkanes with ethyl diazoacetate catalyzed by $[Tp^xAg]$ complexes.

3.2.2 Nitrene insertion reactions.

$[Tp^xML]$ ($M = Cu, Ag$) complexes have shown to be active catalyst in the insertion of nitrene groups in Csp^2-H and Csp^3-H bonds. With $[Tp^{Br^3}Cu(NCMe)]$ as the catalyst, and $PhI=NTs$ as nitrene source, cyclohexane, benzene and alkylbenzenes were functionalized (Scheme 26) [92]. Interestingly, the functionalization of $C-H$ bonds at the β -carbon in substrates such as ethylbenzene or cumene were also observed [93] (Scheme 27). Thus, it was found that the Tp^* - and the Tp^{Br^3} -containing catalysts gave similar amounts of the two products from the reaction of $PhI=NTs$ and cumene, whereas the other two catalysts, containing the more sterically demanding Tp^{Cy} and Tp^{Ms} , provided higher amounts of the product derived from the insertion into the less hindered position, i.e., the primary sites. These results support the existence of an important steric effect in this reaction.



Scheme 26. The functionalization of alkylic or aromatic $C-H$ bonds by nitrene insertion catalyzed by $[Tp^{Br^3}Cu(NCMe)]$.

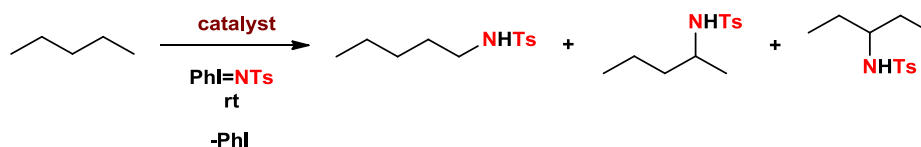


Catalyst

[Tp [*] Cu] ₂	13 (57)	9 (43)	78
[Tp ^{Cy} Cu(NCMe)]	11 (36)	19 (64)	70
[Tp ^{Ms} Cu(THF)]	1 (5)	16 (95)	83
[Tp ^{Br³} Cu(NCMe)]	30 (59)	20 (41)	50

Scheme 27. Reaction of PhI=NTs and cumene in the presence of [Tp^xCu] as the catalyst: yields (%) of the insertion products (regioselectivity percentage in brackets).

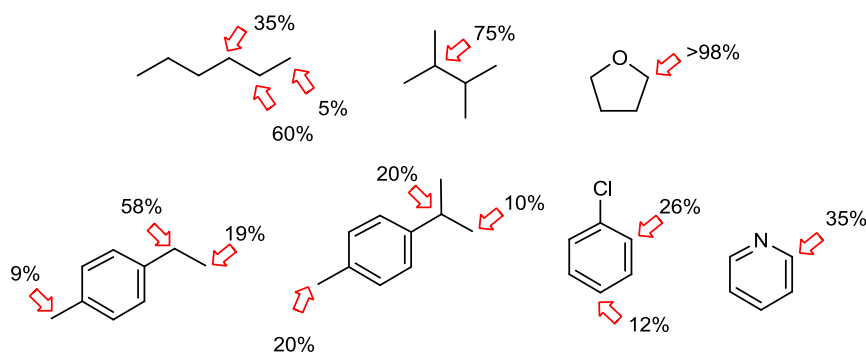
Unactivated alkanes, such as hexane or 2,3-dimethylbutane, have been also functionalized with [Tp^xAg] catalysts [94], the order of activity being Tp^{*,Br}Ag > Tp^{*}Ag ≥ Tp^{Ms}Ag > Tp^{Br³}Ag. Different regioselectivities were observed depending of the catalyst employed, in good accord with the implication of the metal center in the nitrene transfer step (Scheme 28). The [Tp^{Ms}Ag] catalyst provided the highest value of the primary site activation products.



<u>Catalyst</u>	<u>Yield</u>			
[Tp [*] Ag]	40	7	58	35
[Tp ^{*,Br} Ag]	65	10	59	31
[Tp ^{Ms} Ag]	40	15	53	32
[Tp ^{Br³} Ag]	15	n.d.	70	30

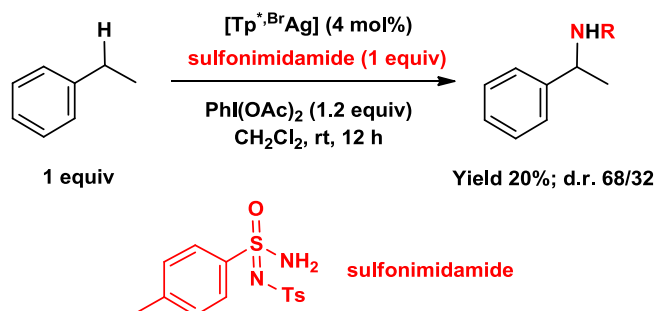
Scheme 28. Influence of the catalyst: yields (%) and regioselectivities (%) of the functionalization of pentane by nitrene insertion from PhI=NTs.

The main drawback of this methodology is the lack of selectivity, since mixtures of products are observed either with Csp²-H and Csp³-H bonds, as shown in Scheme 29.



Scheme 29. Regioselectivity of the functionalization of alkanes or arenes by nitrene insertion from PhI=NTs catalyzed by $[\text{Tp}^*,\text{BrAg}]$.

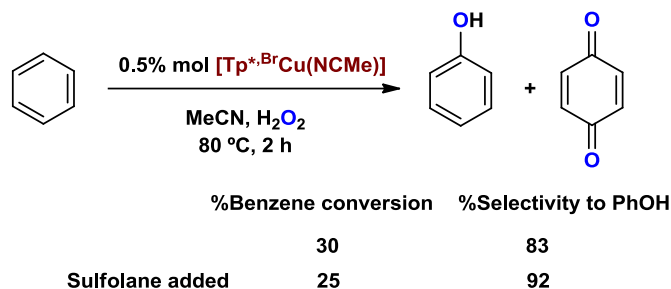
It is important to note that other nitrene sources such as mixtures of sulfonimidamide and $\text{PhI}(\text{OAc})_2$ have been also employed with these Tp^*ML catalysts [95] (Scheme 30), and compared with the $[\text{Rh}_2(\text{S-nta})_4]$ (nta: *N*-(1,8-naphthoyl)-alanine) catalyst. For benzylic sites, $[\text{Tp}^*,\text{BrAg}]_2$ induces similar conversions to the rhodium catalyst, although the latter affords excellent levels of diastereocontrol. The silver complex was more active for non-activated C-H bonds, such as pentane and other alkanes.



Scheme 30. Sulfonimidamide reagent for the silver-catalyzed C-H amination of ethylbenzene.

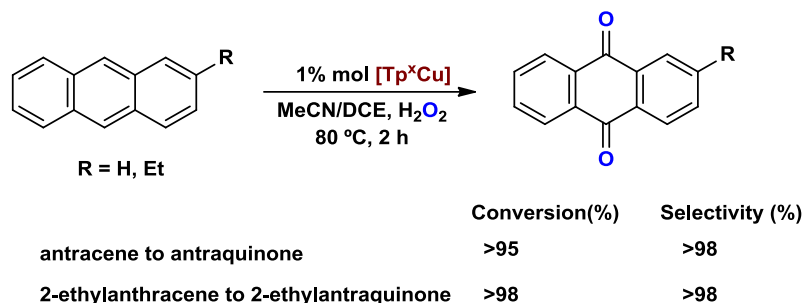
3.2.3 Oxo insertion reactions.

One of the goals in current chemistry is the direct oxidation of benzene into phenol with the aim of substituting the cumene process at the industrial level. Several $[\text{Tp}^*\text{Cu}]$ complexes have been tested toward the reaction of benzene and hydrogen peroxide as the oxidant and at moderate temperatures [96]. Those complexes afforded conversions within the 14–30% range and selectivities toward phenol in the interval 67–85% (benzoquinone accounting for the residual of the initial benzene). Remarkably, the conversion and selectivities were comparable to the reference iron-based systems. The best results were obtained with $[\text{Tp}^*,\text{BrCu}(\text{NCMe})]$ with a 92% selectivity at a 25% benzene conversion (Scheme 31), with sulfolane as additive. This system does not require the presence of an acidic medium and operates under mild conditions.



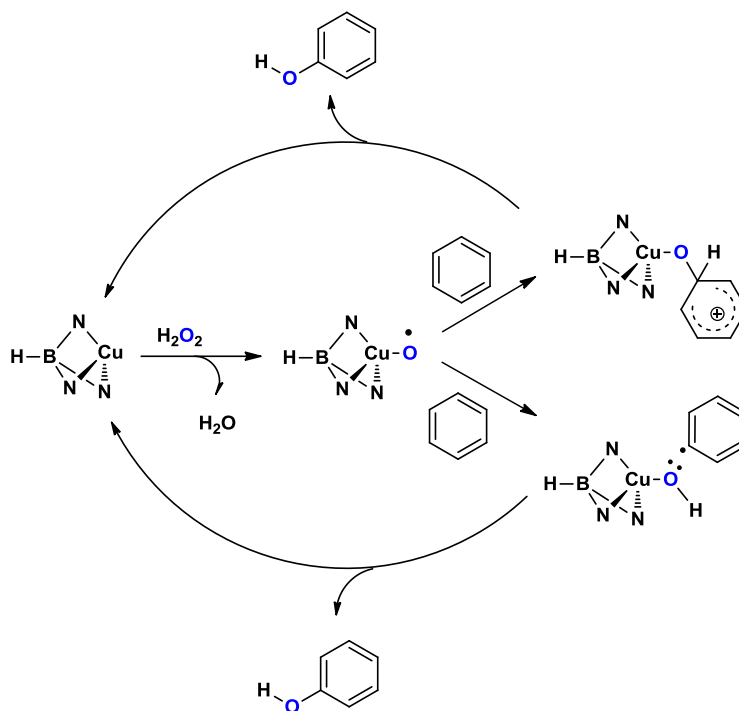
Scheme 31. The direct oxidation benzene with hydrogen peroxide catalyzed by $[\text{Tp}^{*,\text{Br}}\text{Cu}(\text{NCMe})]$.

The authors also applied this methodology to the oxidation of anthracene and 2-ethylanthracene. Four copper complexes bearing Tp^x ligands ($\text{Tp}^{*,\text{Br}}$, Tp^{Ms} , Tp^{Ph} and $\text{Tp}^{\text{Br}3}$) were employed as catalysts for this transformation, and afforded almost quantitative conversions into 9,10-antraquinones upon heating at 80 °C for 2 h (Scheme 32). Once again the $[\text{Tp}^{*,\text{Br}}\text{Cu}(\text{NCMe})]$ complex provided the best results: 98% isolated yields.



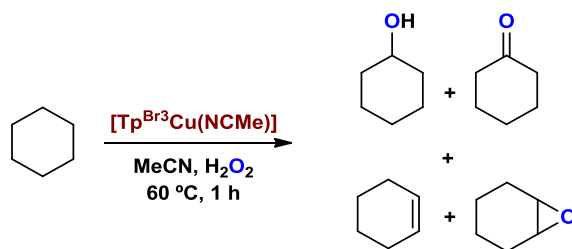
Scheme 32. The direct oxidation of aromatic C–H bonds of anthracene and 2-ethylanthracene with hydrogen peroxide catalyzed by $[\text{Tp}^x\text{Cu}]$ complexes.

Mechanistic studies of the above copper-catalyzed hydroxylation of benzene with high selectivity toward phenol showed the existence of two competitive pathways, with an unprecedented dual behavior of a copper-oxyl intermediate (Scheme 33) [97]. The $\text{Tp}^{*,\text{Br}}$ ligand remains as spectator in this reaction. Both pathways, the electrophilic substitution and the rebound (H-abstraction), contribute to the global transformation, albeit the former contributes in a larger extent.



Scheme 33. The two pathways leading to the formation of phenol from the common copper-oxyl intermediate.

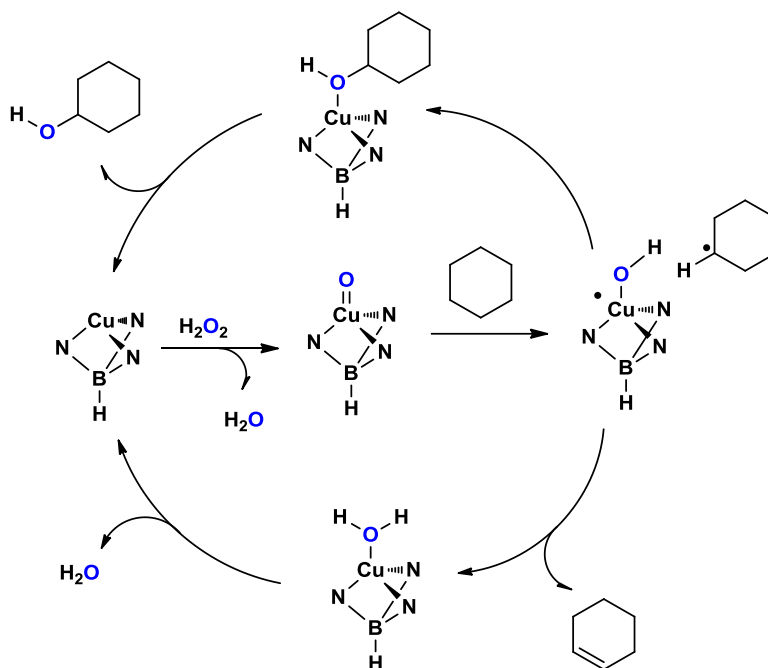
Alkanes have also been studied with the same catalytic system [98], showing that in addition to the oxidation of the C-H bonds, a second transformation is observed from which alkenes are formed through a dehydrogenation process (Scheme 34). The transformation took place under mild conditions, and the oxidant also operated as the sacrificial hydrogen acceptor, providing water as byproduct. Five Tp^xCu complexes were used for these studies, containing $\text{Tp}^{\text{Br}3}$, $\text{Tp}^{*\text{Br}}$, Tp^* , $\text{Tp}^{\text{Me}3}$ and Tp^{Ph} . In the case of cyclohexane as substrate, all the complexes tested led to the formation of the four products shown in Scheme 34, but in a different ratio, with the compounds derived from the dehydrogenation of cyclohexane, cyclohexene and cyclohexene oxide, as the minor products. The best conversions were obtained for $[\text{Tp}^{\text{Br}3}\text{Cu}(\text{NCMe})]$ as catalysts. In contrast to copper, the silver analogues proved to be non-active in these oxidation reactions. The reaction was also expanded to linear alkanes. Thus, the *n*-hexane provided ketones as the major products. The formation of 1-hexene was observed upon the dehydrogenation process, with other olefins being undetected in most cases.



Scheme 34. Products obtained in the Tp^xCu -catalyzed cyclohexane oxidation reaction with H_2O_2 .

The experimental data and DFT calculations suggested a competitive mechanism in which the hydroxylation and

dehydrogenation pathways are initiated from a common copper-oxyl intermediate (Scheme 35), excluding the participation of hydroxyl radicals derived from Fenton-like reaction mechanisms. The hydroxylation reaction takes place through a rebound mechanism, the radical intermediate also promotes the alternative dehydrogenation pathway. The theoretical study revealed that the coordination geometry around the metal center is tetrahedral during the whole catalytic cycle, with the Tp^x ligand bound to copper in a κ^3 fashion, therefore, the ligand is quite rigid along the pathway and seems to exert no influence in the reaction outcome.

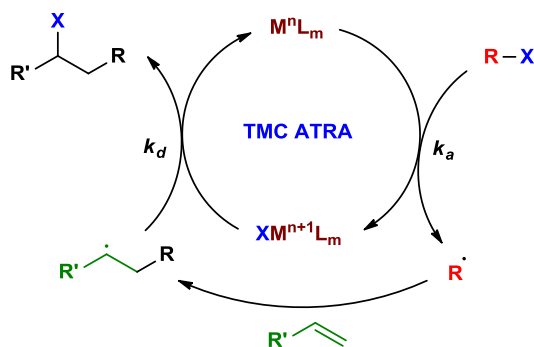


Scheme 37. Mechanistic proposal for the copper-catalyzed oxidation of cyclohexane showing the two competitive pathways.

3.3 Atom transfer radical reactions.

3.3.1 Atom transfer radical addition reactions.

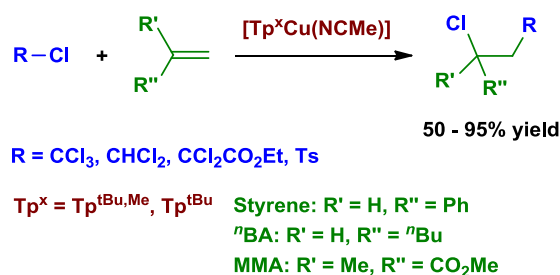
The anti-Markovnikov addition of HBr to olefins promoted by peroxides or light, known as Kharasch reaction [99], originates the transition metal-catalyzed atom-transfer radical reactions (TMC-ATR), which constitutes a versatile and effective method for C-C bond formation (Scheme 36) [100]. The process follows a radical pathway in which carbon-centered radicals (generated from halogenated alkanes) are added across alkenes to form 1:1 adducts. The reaction can be performed in both intermolecular and intramolecular fashion; the so-called atom-transfer radical addition (ATRA) and atom transfer radical cyclization (ATRC), respectively.



Scheme 38. Mechanism for transition metal-catalyzed atom-transfer radical addition reactions.

[$\text{Tp}^x\text{Cu(I)}$] complexes were described as very efficient catalysts for ATRA reactions of polyhalogenated alkanes to alkenes [32]. The addition of CCl_4 or CHCl_3 to several olefins proceeded under mild conditions with yields up to 95% (Scheme 37). The catalytic activity was enhanced when bulky Tp^x ligands, which avoid the formation of catalytically inert species such as $[\text{Tp}^x_2\text{Cu}]$. In addition, the use of electron-donating Tp^x ligands also improve the reactivity by facilitating the single electron transfer (SET) process from the metal center to the alkyl halide.

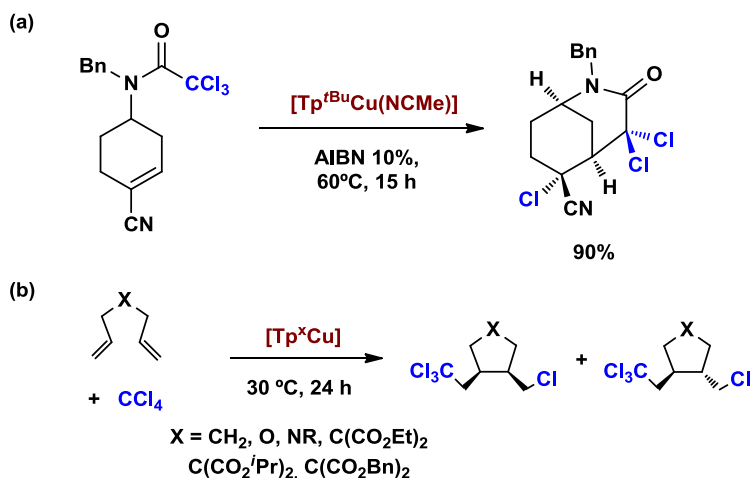
Among several bulky and electron-donating Tp^x ligands, Tp^{tBu} exhibits the best catalytic activity [101]. Interestingly, the addition of 20 eq. of acetonitrile improves the yield in the reaction of styrene with CCl_4 using a low catalyst loading (0.05 mol% [$\text{Tp}^{\text{tBu}}\text{Cu}(\text{NCMe})$]) without the participation of reducing agents. It was proposed that such additive increased the stability of catalytically active Cu(II) species, eliminating the catalyst deactivation. However, an excess of acetonitrile may block the access to catalytically active Cu(I) species, thus a fine tuning of the reaction conditions is needed. A complete mechanistic study was carried out for this transformation using Tp^xCu complexes as catalysts [19g].



Scheme 37. Atom transfer radical addition catalyzed by [Tp^xCu] complexes.

The intramolecular version of ATRA processes allows the synthesis of complex structures by the directed installation of a C-C bond. For example, the ATRC reactions catalyzed by [Tp^xCu] complexes established a new entry to 2-azabicyclo[3.3.1]nonanes [102], a framework found in many natural products. As shown in Scheme 38a, the reaction of trichloroacetamide tethered cyclohexenes, catalyzed by [$\text{Tp}^{\text{tBu}}\text{Cu}(\text{NCMe})$] with 2,2-azobis(2-methylpropionitrile) (AIBN) as reducing agent, yields the corresponding polyfunctionalized 2-azabicyclononanes. Interestingly, these polyfunctionalized products can be chemoselectively converted to other value-added compounds by working on the chlorine atoms.

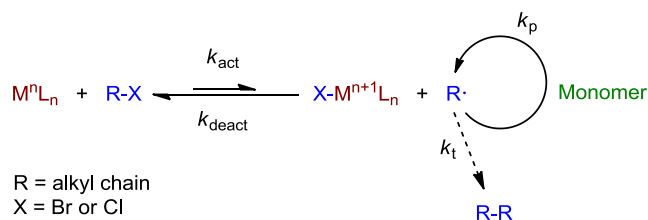
The inter- and intramolecular ATRA processes can be also combined in a radical-domino fashion. Thus, at least two C-C bonds can be generated in one step reaction with increasing of molecular complexity. For example, a process that involves a consecutive addition-cyclization of radical species was reported when reacting CCl_4 with various 1, ω -dienes, catalyzed by $[\text{Tp}^x\text{Cu}(\text{NCMe})]$ (Mg as reducing agent), leading to the corresponding five-membered hetero- and carbocycles in moderate to high yields (Scheme 40b) [103].



Scheme 38. (a) Atom transfer radical cyclization of trichloroacetamide tethered cyclohexenes and (b) atom transfer radical addition cyclization of CCl_4 to 1, ω -dienes catalyzed by $[\text{Tp}^x\text{Cu}]$ complexes.

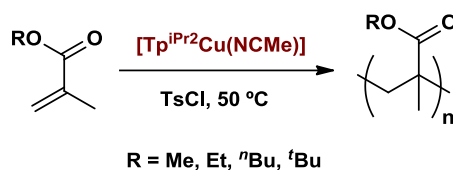
3.3.2 Atom transfer radical polymerization reactions.

Even when the addition of radicals to olefins in ATRA reactions is an outer-sphere process, the catalytic system can be designed for the consecutive C-C bond formation, controlled by the transition metal complex: this is the so-called atom transfer radical polymerization (ATRP) [104]. In this process, the alkyl halide acts as an initiator so that, mechanistically, the first stage of ATRP corresponds to an ATRA reaction. Next, chain propagation takes place by the reactivation of alkyl halide adduct formed and further reaction with the monomer (Scheme 39). To ensure a controlled “living” polymerization the activation and deactivation equilibrium must be shifted to the left, leading to a low concentration of alkyl radicals and avoiding radical-radical termination reactions. The efficiency of the ATRP catalyst depends on the nature of the metal and the design of the suitable ligand. Although most of the copper complexes employed in these systems are cationic, the use of soluble catalysts in organic reaction media was achieved with neutral $\text{Tp}^x\text{Cu}(\text{I})$ -complexes [105].



Scheme 39. Atom transfer radical polymerization.

The $\text{Tp}^*\text{Cu(I)}$ -containing catalyst for the ATRP of acrylates or styrene [105], resulted in high polydispersity indexes (PDI = 3.82–4.63), presumably due to the catalyst deactivation by the formation of non-reactive $[(\text{Tp}^*)_2\text{Cu}]$ complex. In contrast, the catalytic performance of the bulky $[\text{Tp}^{\text{tBu,Me}}\text{Cu}(\text{NCMe})]$ complex was superior; i.e. quite low PDI (1.14) were found for the polymerization methyl methacrylate (MMA). However, the activity of this complex was too low. For example, long reaction time (48 h) was needed to achieve 75% conversion for MMA or even no reaction was observed in the case of styrene. This result was attributed to the high steric hindrance of the ligand. Then, a subtle change in the ligand structure was introduced by using Tp^{iPr_2} ligand. The corresponding $[\text{Tp}^{\text{iPr}_2}\text{Cu}(\text{NCMe})]$ complex was found to be very efficient as catalyst for the ATRP of MMA with low value of PDI (1.09) (Scheme 40). The catalyst was also suitable for the polymerization of others methacrylates (EtMA, ethyl methacrylate; *n*-BuMA, *n*-butyl methacrylate; *t*-BuMA, *tert*-butyl methacrylate), as well as acrylates (MA, methyl acrylate; *n*-BA, *n*-butyl acrylate) and styrene.



Scheme 40. Atom transfer radical polymerization catalyzed by $[\text{Tp}^{\text{iPr}_2}\text{Cu}(\text{NCMe})]$.

4. Conclusions.

The role of Group 11 metal complexes bearing tris(pyrazolyl)borate in homogeneous catalysis have experienced a great development in the last two decades. The catalytic capabilities of the $[\text{Tp}^x\text{M}]$ complexes reported in the literature can be understood taking into consideration the electronic and structural features of those species. The versatility of these ligands in term of their design and, therefore, their metal complexes has allowed exploring a variety of catalytic systems, finding in some case novel transformations. Nevertheless, although great advances have been achieved in terms of activity and chemoselectivity, the control of the regioselectivity in most of the processes still remains a challenge. Additionally, examples of enantioselective catalysis are yet scarce, its development yet to be done in the incoming years.

Acknowledgments

We thank MINECO for Grant CTQ2017-82893-C2-1-R.

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