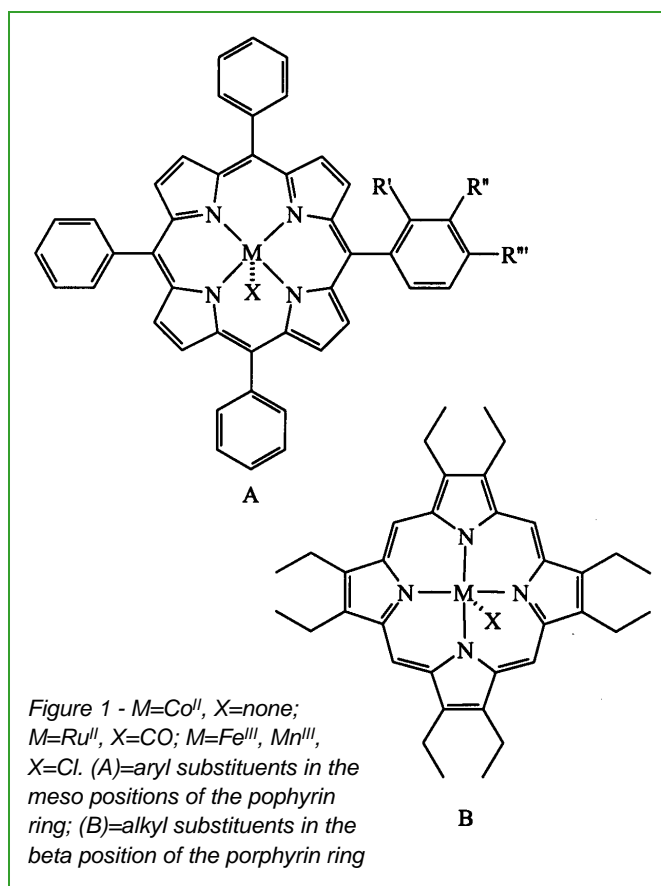# Carbon-nitrogen bond formation catalysed by metallo-porphyrins

by Sergio Cenini, Emma Gallo and Andrea Penoni

A survey of the amidation and amination reactions of unsaturated and saturated hydrocarbons catalysed by metallo-porphyrins is reported. Chloramine-T, $(p\text{-}CH_3C_6H_4SO_2NCl)^-Na^+$, and its derivatives, and organic azides, ArN_3, have been discussed as aminating agents, while the use of tosylimino derivatives, $ArSO_2N=IPh$, has been considered only when appropriate. The possible intermediates in these reactions have been discussed, on considering the nature of the products that can be obtained by reaction of these aminating agents with the metallo-porphyrin derivatives.

Figure 1 - M=Co^{II}, X=none; M=Ru^{II}, X=CO; M=Fe^{III}, Mn^{III}, X=Cl. (A)=aryl substituents in the meso positions of the pophyrin ring; (B)=alkyl substituents in the beta position of the porphyrin ring

Transition metal-mediated reactions that form and cleave the bonds of organic molecules are the foundation of homogeneous catalysis. The formation of carbon-hydrogen and carbon-carbon bonds by reductive elimination from a metal centre is now common. Catalytic hydrogenation of alkenes, hydroformylation, alkene arylation (Heck reaction) and cross-coupling processes are the most important examples that involve C-H and C-C bond formation.

The formation of carbon-heteroatom bonds by homogeneous, catalytic reactions is less common, and only recently this has become a very intense field of research. In particular, the formation of carbon-nitrogen bonds has attracted a great deal of interest, due to the importance in several fields of compounds containing this bond. Particularly useful are the metal-mediated catalytic hydroaminations of olefins and alkynes, which avoid production of by-products, like salts, generally observed in metal-catalysed amination of C-X derivativatives (X=halogen for example). However, known aminations of olefins often require stoichiometric use of transition metals and general methods for carrying out

aminations catalytically are not yet available. Works carried out in our laboratories have deeply investigated the catalytic carbonylation of aromatic nitro compounds, to give isocyanates, carbamates, ureas, allylic amines and heterocycles, to mention the most important products [1]. However, the rather drastic conditions required by these catalytic reactions (ca. 140-170 °C and 40-80 atm of carbon monoxide) precluded the application of this methodology to the synthesis of other complex, fine chemical products. We thus became interested in the use of other aminating agents such as Chloramine-T, $(p\text{-}CH_3C_6H_4SO_2NCl)^-Na^+\cdot3H_2O$, and organic azides, $R\,N_3$, for the synthesis of organic compounds

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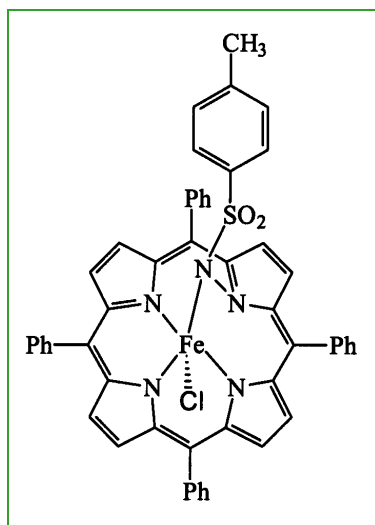*Figure 2 - Structure of the bridged nitrene complex, $Fe^{III}(TPP)(NTs)Cl$*

such as aziridines and allylammines, starting from olefins, and of amines and Schiff bases, starting from saturated hydrocarbons. It turned out that the best catalysts for these reactions are the porphyrin derivatives of transition metals.

These compounds have been succesfully applied in catalytic oxidation reactions [2]. On the other hand, amination reactions with reasonable good results have only been obtained until recently by using [*N*(*p*-tolylsulfonyl)imino]phenyliodinane, PhI=NTs (Ts=$SO_2C_6H_4CH_3$-*p*), and related derivatives as the nitrogen source [3]. However, this is in reality an amidation reaction, since these reagents can only be obtained starting from the corresponding sulfonamides. Metalloporphyrins are fascinating compounds from several points of view (Figure 1).

The synthesis and applications of metallo-porphyrin derivatives in catalytic reactions, was initiated having in mind the modeling of heme-containig enzymes which were able to catalyse various oxidation reactions [2]. For example cytochromes P450 react with single oxygen atom donors such as hydrogen peroxide with the intermediate formation of oxo ferryl complexes, which are the active species in the catalytic cycle and are formally equivalent to the Fe^V=O system. This system could be a (porphyrin radical cation)Fe^{IV}=O or a (porphyrin)Fe^{IV}=O complex with a free radical derived from a one-electron oxidation of a protein aminoacid close to the heme [2].

On considering that the oxo, M=O, imido, M=NR, and carbene, M=CR_2, species are isoelectronic, it is not surprising that metallo-porphyrin derivatives have been subsequently employed as shuttles of nitrene and carbene species to the substrate, from precursors such as PhI=NTs and diazoalkanes. The use of PhI=NTs as aminating agent is very popular and originates from the good results obtained by using PhIO as the single oxygen atom donor. Several nitrene complexes of transition metal porphyrin derivatives have been isolated and characterised by X-rays. Of these, the iron(III) complex, Fe(TPP)(NTs)Cl (TPP=dianion of the *meso*-tetraphenylporphyrin) requires some comments (Figure 2) [4]. The active intermediate in the iron porphyrins catalysed transfer of *N*-tosyl ni-

trene of PhI=NTs to alkenes or alkanes could be a Fe^V-nitrene complex, which has been never isolated nor characterised *in situ.* The only species that could be isolated was the bridged nitrene complex reported in Figure 2, resulting from the insertion of the *N*-tosyl moiety into a Fe-N bond of Fe(TPP)Cl. This species is a dead form of the intemediate active species, since it does not react with an olefin such as cyclooctene [4a]. However it is still active in catalysing alkene aziridination by PhI=NTs, and presumably under the catalytic conditions it is in equilibrium with the terminal, Fe^V-nitrene complex. Although the X-ray crystal structures of $Os^{VI}(TPP)(NTs)_2$ [5] and of $Os^{VI}(TPP)(NC_6H_4NO_2$-*p*$)_2$ [6] are known (both showing terminal imido ligands), the corresponding ruthenium complex, $Ru^{VI}(TPP)(NTs)_2$, has been reported without the crystal structure determination [3].

At room temperature, this last compound reacts readily with styrenes and norbornene to give the corresponding aziridines in stoichiometric reactions. Ruthenium(IV) paramagnetic mono nitrene complexes, Ru(TBPP)(NR) [TBPP=dianion of 5, 10, 15, 20-tetrakis(*p-ter*-butylphenyl) porphyrin; R=*p*-XC_6H_4, X=Me, H, Cl, I], have also been reported without the crystal structure determination [7].

Interestingly, they undergo facile imido transfer reactions with tertiary phosphines to give the corresponding phosphinimines, but no reaction was observed with alkenes. Electronwithdraving groups in the R substituents accelerate the reactions with phosphines. It seems, thus, that in the case of ruthenium complexes, the nitrene ligand must be activated by another imido ligand in the *trans* position or by a base like a phosphine, in order to have imido transfer reactions. However, the situation is more complex. By reaction of *p*-$NO_2C_6H_4N_3$ with Ru(TPP) (CO) in toluene, we have isolated the mono imido complex, Ru(TPP)(CO) (NC_6H_4-NO_2-*p*). This derivative proved to be very reactive, and attempted crystallizations from tetrahydrofuran, gave an immediate reaction with the solvent (Equation 1):

$$Ru(TPP)CO(NC_6H_4NO_2\text{-}p) + 2\ THF \rightarrow 2\ Ru(TPP)(CO)(THF) + p\text{-}NO_2C_6H_4N=NC_6H_4NO_2\text{-}p \tag{1}$$
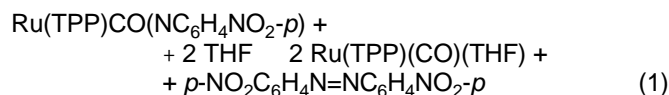
This complex readily reacts also with alkenes (Figure 3). More investigations are at the moment necessary, in order to clarify the conditions by which a ruthenium-imido species becomes reactive. One final point should also be consid-
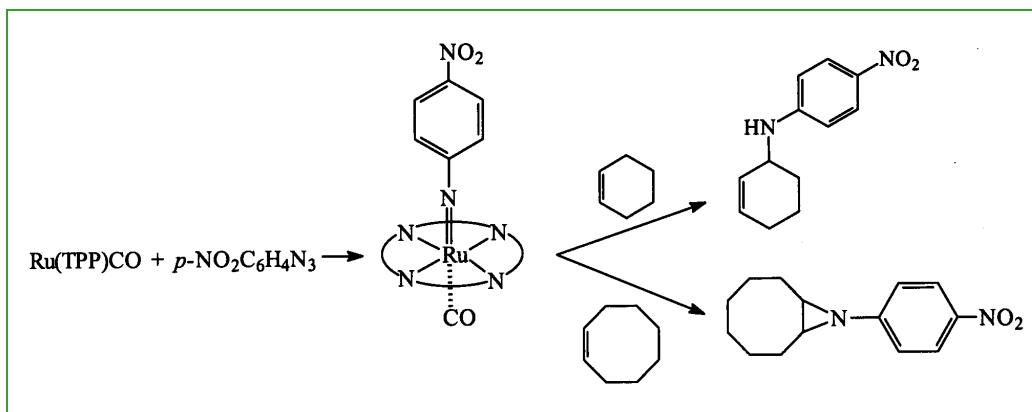

Figure 3 - Stoichiometric reactions or Ru(TPP)(CO) ($NC_6H_4NO_2$-p) with cyclohexene and cyclooctene to give the corresponding allylamine and aziridine respectively

ered. In transition metal porphyrin complexes, usually the metal lies in the plane of the porphyrin ring, a situation which by steric reasons favours a *trans* coordination of the entering ligands. Thus, in reactions like those reported in Figure 3 we should think to an external nucleophilic attack of the olefin to an electrophilic nitrogen atom of the imido ligand. This seems to be the case, since in the catalytic amination reactions of olefins with organic azides (see later), we have observed a reactivity which follows the order: p-NO$_2$C$_6$H$_4$N$_3$>p-ClC$_6$H$_4$N$_3$>p-OMeC$_6$H$_4$N$_3$.

However, highly substituted porphyrin derivatives exhibit significantly distorted, non planar conformation in the solid state, and chelating ligands can adopt a *cis* coordination at the metal centre. In early transition metal porphyrin derivatives, incorporation of small ions causes the porphyrin ring to ruffle to reduce the hole size and a *cis* coordination even of non chelating ligands can be observed [8].

Thus, labile intermediate species having this type of coordination cannot be excluded even for late transition metal porphyrin derivatives, particularly when the metal is in a high oxidation state.

Catalytic reactions

Comparison of the aminating agents

Tosylimino iodobenzene, PhI=NSO$_2$C$_6$H$_4$CH$_3$-p, and related derivatives, can be obtained by oxidation of PhI with peracetic acid, to give PhI(OAc)$_2$, and its subsequent reaction with the arylsulfonamides (Equation 2).

$$PhI(OAc)_2 \ + \ ArSO_2NH_2 \ \xrightarrow{\ KOH\ } \ PhI=NSO_2Ar \ + \ AcOK \qquad (2)$$
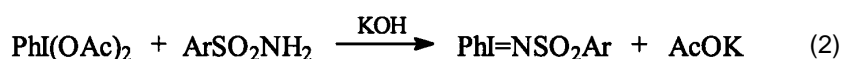
Thus it is not a reagent readily available and moreover it is a polymer, with I··········N or I··········O bridges, insoluble in the common solvents. This creates some problems, particularly for conducting experiments with a controlled quantity of reagents in solution. Chloramine-T, (p-CH$_3$C$_6$H$_4$SO$_2$NCl)$^-$ Na$^+$·3H$_2$O, has the structure reported in Figure 4.

Centrosymmetric dimers result from the bridging of sodium by water and from intradimer hydrogen bond (dotted lines). In addition, the sixth coordination site on each sodium is filled by the chlorine of an adjacent dimer (dashed lines). Thus, the best description of Chloramine-T is that its structure is close to that depicted in **B** rather than its more common representation **A**.
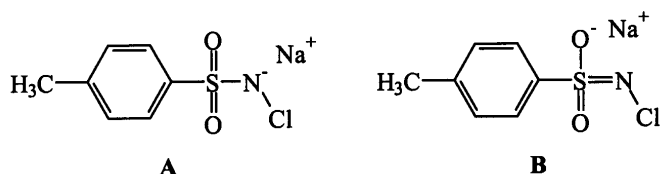
Chloramine-T is an inexpensive and commercial product, which can be redily obtained by reaction of tosylsulfonamide with NaClO, and it is formally the nitrogen analogue of sodium hypochlorite. However, not only it is rather insolu-
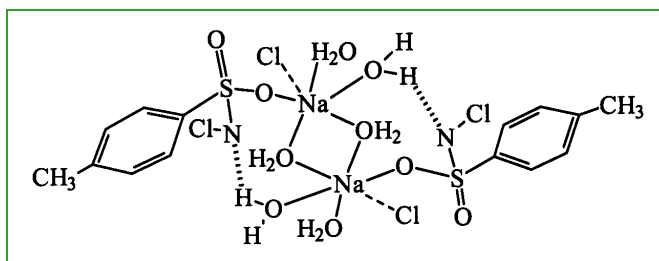
Figure 4 - Portion of the structure of Chloramine-T

ble in the common solvents, but also it crystallizes with three molecules of water and the catalytic reactions can be altered by the presence of humidity. This reagent can be dried by heating at 100 °C or by *vacuum* pumping in the presence of P$_4$O$_{10}$, but it should be kept in mind that it can explode [9]. We have eliminated all these problems by using an appropriate tetraalkylammonium salt of Chloramine-T [10] (Equation 3).

$$(3)$$
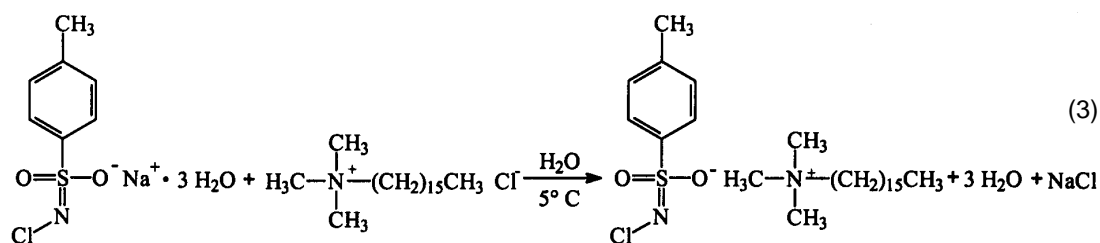
Of course, wih both tosyilimino iodobenzene and Chloramine-T only a tosylimino residue can be transferred to the substrate. The same happens when using tosylazide, p-CH$_3$C$_6$H$_4$SO$_2$N$_3$, as aminating agent. However, the family of the organic azides is very wide [11], and with these reagents real amination reactions can be realized. Even this class of compounds can be dangerous, particularly the aliphatic deri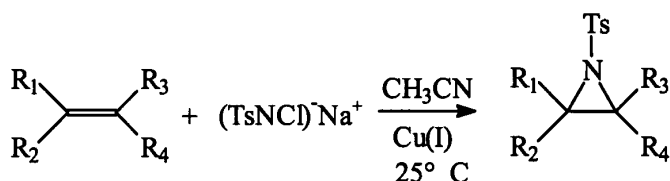vatives. The aryl azides as a class are reported to detonate if heated at temperatures higher than 100 °C, and should be treated as potentially liable to detonate, particularly in the presence of heavy metals or acids. For these reasons we avoided in general the use of liquid azides, which require a distillation for their purification.

The literature concerning the use of tosylimino iodobenzene and related derivatives as aminating agents is so abundant, that a rather long review should be necessary for an appropriate discussion of their catalytic amination reactions. In the following, we will mention them only when relevant for the discussion. The reader interested in this subject can find in [6] and [7] and in the reported literature, some of the most recent and relevant results obtained in this field.

Chloramine-T and related derivatives as aminating agents of olefins

The use of Chloramine-T as aminating agent of olefins has been mainly developed by Sharpless group. Anhydrous Chloramine-T reacts with selenium metal to give a reagent in solution which probably is the *bis*-imido compound, Se(NTs)$_2$ [9a]. It reacts with olefins to give allylic sulfonamides, and related sulfur species also effect allylic amination of olefins. Allylic amination and 1,2-diamination of mono and dienes with

a modified diiminoselenium reagent have also been carried out by replacement of the insoluble Chloramine-T with the more reactive and entirely soluble dichloroamine derivative, $NsCl_2$ (Ns=2-nosyl=o-$NO_2C_6H_4$ SO_2N) [12]. The use of the dichloroamine derivative resulted in a substantial process improvement. The stoichiometric reactions of several hydrocarbon substrates with an iron(II)chloride-Chloramine-T complex prepared *in situ* in anhydrous conditions, have been studied [13]. Tosylamination of adamantane and chlorination of mesitylene proceed in good yield, while naphthalene gives *N,N'-bis*(toluene-*p*-sulfonyl)-1,4-naphthoquinone diimine. A variety of olefinic substrates undergo both *cis* and *trans*-addition to the double bond as well as allylic functionalisation. Aziridation of alkenes proceeds successfully in moderate to good yields, using anhydrous Chloramine-T in acetonitrile in the presence of various copper(I) catalysts [14] (Equation 4).
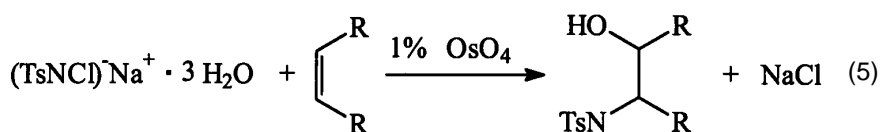
$$(TsNCl)^-Na^+ + \underset{R}{\overset{R}{\diagdown}} \xrightarrow{1\% \ OsO_4} \underset{TsN}{\overset{HO}{\diagup}}\underset{R}{\overset{R}{\diagup}} + NaCl \quad (5)$$

The reactions are carried out in the presence of 5Å powdered molecular sieves, and CuCl proved to be the best catalyst. The aziridination of *trans-beta*-methylstyrene proceeds stereospecifically to give the *trans* aziridine isomer. Chloramine-B ($C_6H_4SO_2NCl$)$^-Na^+$ and the 4-nosyl derivative (p-$NO_2C_6H_4$ SO_2NCl)$^-Na^+$ have also been used. Anhydrous Bromamine-T (TsNBr)$^-Na^+$ was shown to be a superior source of nitrene compared to Chloramine-T in the copper catalysed aziridination of olefins in CH_3CN with 5Å powdered molecular sieves [15]. The enhanced reactivity could be due to weaker nitrogen-bromine bond (weaker than nitrogen-chlorine) facilitating the formation of a copper-nitrenoid complex. With CuCl as catalyst, the aziridination of cyclohexene and styrene, which is carried out in 5 and 31% yields respectively with Chloramine-T, is improved with Bromamine-T giving the products in 55 and 48% yields. However, it has been recently reported that phenyltrimethylammonium tribromide (PhNMe$_3^+$Br$_3^-$, also known as PTAB) provides good to excellent yields of aziridines across a wide range of olefin classes, with Chloramine-T in acetonitrile [16].

Thus the role of bromine in the aziridination reaction with Bromamine-T could be more complex than supposed. By using CuOTf as catalyst in the aziridination of alkenes in CH_3CN, in the presence of the *n*-pentylimine of pyridine-2-carboxaldehyde as ligand, hydrate Cloramine-T could be used, and even in the absence of molecular sieves good yields (45-75%) have been obtained [17]. The reaction is slow (three days at room temperature). Tosylamide, $TsNH_2$, was the main by-product (12-25%).
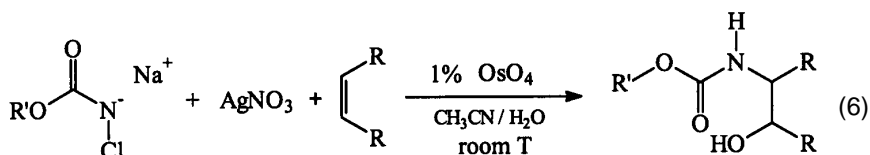
In spite of the presence of water and of the possible hydrolysis of the supposed copper-nitrene intermediate complex to give a metal-oxo species, no epoxide was observed among the products. However, with cyclohexene as the alkene the allylamine becomes the most abundant product

(22%), together with the aziridine (8%), while the obtained $TsNH_2$ was 64%. In the amination of tetraline, 46% of the tosylamidation product in the *alpha* position was obtained, with 54% of $TsNH_2$. It is rather peculiar the reason by which the *n*-alkylimine of pyridine-2-carboxaldehyde has been used as ligand. It has been supposed that it could be a better ligand than for example 2,2'-bipyridine for copper(I), since this happens for iron(II) [18]. Vicinal, *cis*-oxyamination of olefins by Chloramine-T hydrate has been effected in good yields by using OsO_4 as catalyst, at 60 °C and with a substrate to catalyst ratio of 100 [19] (Equation 5).

Probably, the imido derivative $OsO_3(NTs)$ is formed *in situ*. The procedure has been improved by conducting the reac-

$$(TsNCl)^-Na^+ \cdot 3H_2O + \underset{R_2}{\overset{R_1}{\diagup}}\!=\!\!\underset{R_4}{\overset{R_3}{\diagup}} \xrightarrow[Cu(I)]{\underset{25° \ C}{CH_3CN}} \underset{R_2}{\overset{R_1}{\diagup}}\overset{Ts}{\underset{}{\triangle}}\underset{R_4}{\overset{R_3}{\diagup}} + NaCl \quad (4)$$

tions in the presence of a phase transfer catalyst [20a]. The osmium-catalysed oxyamination of olefins has also been carried out in good yields by using *N*-chloro-*N*-argento carbamates generated *in situ* as aminating

$$R'O\overset{O}{\underset{}{\diagdown}}\underset{Cl}{\overset{}{N^-}}Na^+ + AgNO_3 + \underset{R}{\overset{R}{\diagup}} \xrightarrow[\substack{CH_3CN/H_2O \\ room \ T}]{1\% \ OsO_4} R'O\overset{O}{\underset{}{\diagdown}}\underset{HO}{\overset{H}{N}}\underset{R}{\overset{R}{\diagup}} \quad (6)$$

agents [20b] (Equation 6). The asymmetric aminohydroxylation of olefins in good yields and with high *e.e.* (70-80%) has been carried out by the Sharpless group by using Chloramine-T hydrate and $K_2OsO_2(OH)_4$ as catalyst, with ligands based on dihydroquinidine-phthalazine and dihydroquinine-phthalazine [21]. Smaller substituents on nitrogen facilitate the asymmetric aminohydroxylation of olefins [22]. By using anhydrous Chloramine-M, (CH_3SO_2NCl)$^-Na^+$, higher enantioselectivities, higher regioselectivities and better chemoselectivity (which principally means suppressing formation of the vicinal diol, sometimes a significant by-product) have been obtained. Methanesulfonamide is the major by-product and it is easily removed. *Alpha*, *beta*-unsaturated amides gave only racemic products in the reaction with Chloramine-T, $K_2OsO_2(OH)_4$ as catalyst and optically active ligands, but afforded excellent reactivity, giving high yields of the hydroxysulfonamide products, whether or not ligand was added [23]. Thus a ligand independent aminohydroxylation of *alpha*, *beta*-unsaturated amides was carried out, with only 1% mol of catalyst, 1.2 equivalents of (TsNCl)$^-Na^+\cdot3H_2O$, in CH_3CN/H_2O. Catalytic, asymmetric aminohydroxylation with amino-substituted heterocycles as nitrogen sources has been investigated, for the direct introduction of biomedically relevant heterocyclic substrates to olefins [24]. The enantioselective procedure for the vicinal addition of a hydroxy group and amino-substituted heterocycles to olefins, makes use of $K_2OsO_2(OH)_4$ in the presence of dihydroquinidine or dihydroquinine as catalyst, and of compounds such as **C** and related derivatives as aminating agents. Very
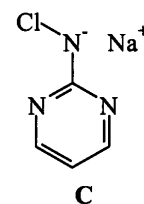
high *e.e.* have been obtained. With the exception of the OsO_4 catalysed hydroxyamination reactions of olefins with Chloramine-T, for which the intermediate formation of osmium-oxo-imido species is supported by the synthesis and properties of trioxoalkylimido and dioxobisalkylimido osmium (VIII) derivatives, the nature of the active species can only be supposed, without experimental evidences. On the other hand, as discussed in the introduction, porphyrin complexes of transition metals are likely candidates to give nitrene complexes by reaction with the proper precursor. In fact, by reaction of Fe(TPP)Cl with a tetraalkylammonium salt derived from Chloramine-T (see introduction) we have isolated the bridged nitrene complex, Fe(TPP)(NTs)Cl [10] (see Figure 2). We have then carried out a study of the amination of aliphatic olefins with the alkylammonium salt derived from Chloramine-T, catalysed by M(TPP)Cl complexes (M=Fe, Mn) (Equation 7). The reactions were not selective since mixtures of products were in general obtained with cyclic olefins (Table 1). The most important by-product of the reactions was $TsNH_2$ (40-

Table 1 - [a]Calculated with respect to the starting ammonium salt of Chloramine-T. [b]Reaction carried out for one hour, at reflux in dry CH_2Cl_2 (2 ml), with the olefin (5.5-7.5 ml), the aminating agent and the catalyst in a 2000:20:1 ratio

Olefin	Product	Yield%[a, b]	
		Fe(TPP)Cl	Mn(TPP)Cl
Cyclohexene	allylamine	18.7	22.1
	a-chloroamine	13.5	16.8
cyclooctene	allylamine	7.2	9.2
	aziridine	8.5	10.3
	a-chloroamine	5.4	8.1
cyclopentene	allylamine	15.4	19.1
	a-chloroamine	5.2	6.1

of any catalyst, gave the 1-chloro-2-sulfonamide derivative. On considering that the intermediate aziridine is at least in part converted into the corresponding *alpha*-chloramine, we can conclude that the yield of the products were comparable to those obtained by using tosylimino iodobenzene derivatives as aminating agents [25]. Good results have been obtained by using Ru(TPP)(CO) as catalyst in refluxing cyclohexene. The allylamine has been obtained in 67.2% yields, with 7.1% of the aziridine and 18.5% of $TsNH_2$. The same catalyst gave with styrene in refluxing benzene 34% of the corresponding aziridine.

Organic azides as aminating agents of hydrocarbons

The first report on the use of organic azides as aminating agents of olefins deals with the catalytic decomposition of benzenesulfonyl azide in cyclohexene solution at 84 °C, in the presence of copper powder [26].
A complex mixture of products was obtained: the amide (37%), the aziridine (15%), the enamine (17.5%) and the allylamine (3%). No reaction was observed

(7)
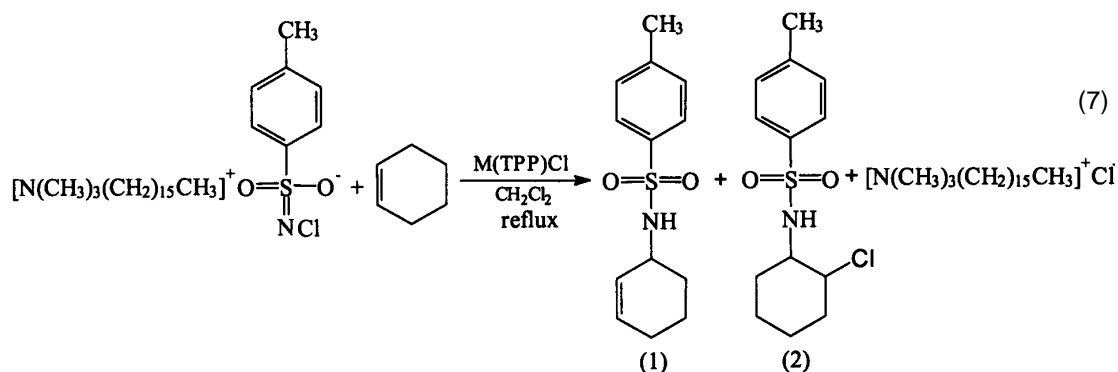
50%), even if the reactions were conducted in dry solvents, in the presence of molecular sieves and under a dinitrogen atmosphere.
By using the bridged nitrene complex, Fe(TPP)(NTs)Cl as catalyst in the amination of cyclohexene, no reaction was observed after 24 hours. The *alpha*-chloramine derivatives are probably derived by attack of the chloride ion of the alkylammonium salt present in solution to an intermediate aziridine. It is known that this reaction is favoured by electronwithdraving groups present as substituents at the nitrogen atom of the aziridine, and in fact the preformed aziridine of cyclohexene by reaction with the tetraalkylammonium salt derived from Chloramine-T in CH_3CN and in the presence of Mn(TPP)Cl or in the absence
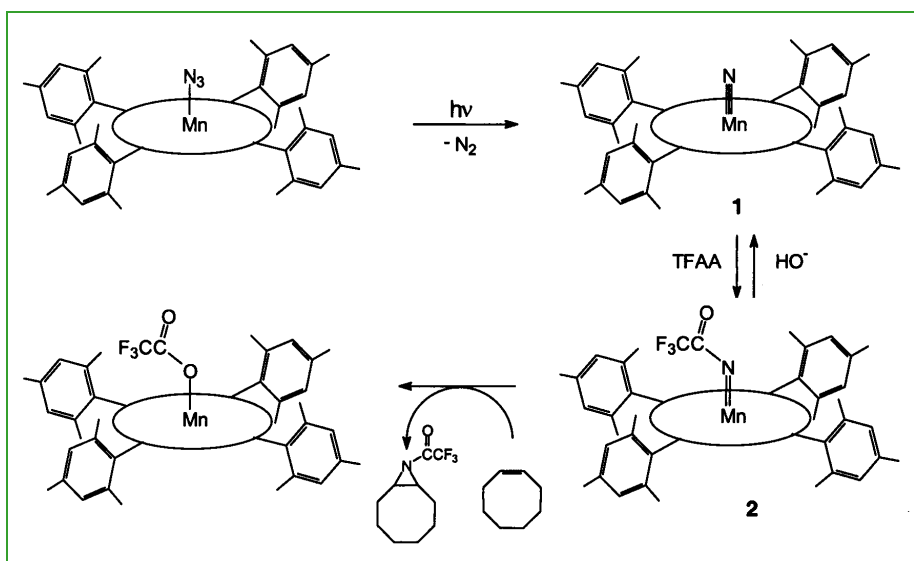

Figure 5 - *Synthesis of N-trifluoroacetyl aziridine of cyclooctene starting from $Mn(TPP)N_3$ and TFFA*
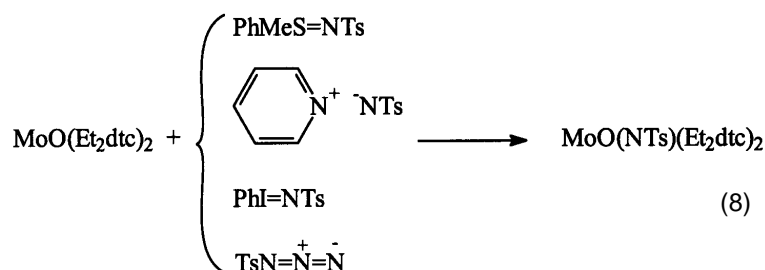
in the absence of copper and intermediate copper-azide and copper-nitrene species were suggested.

On the other hand, Groves first reported the use of an azido-manganese(III) porphyrin system, Mn(TMP)N$_3$ (TMP=meso-tetramesitylporphyrin dianion) for the stoichiometric synthesis of N-trifluoroacetyl aziridine of cis-cyclooctene with trifluoroacetic anhydride (TFFA) [27] (Figure 5). The key point is the irradiation of the azido complex in benzene, which affords a nitridomanganese(V) porphyrinato complex **1,** which by reaction with TFFA gives an acylimido manganese(V) trifluoroacetate derivative **2**. Compound **2** is the crucial intermediate able to transfer the imido ligand to the olefin. Overall, this sequence of reactions corresponds to the aziridination of cyclooctene by CF$_3$CON$_3$. Other nitridomanganese(V) complexes with Schiff bases as ligands were later used for the amination of electron-rich olefins, such as ketone silyl enol ethers to give the corresponding N-trifluoroacetylated alpha-amino ketones, of glycal substrates to give 2-amino sugars and of styrene to give the N-trifluoroacetyl amino alcohol [28].

The reaction of arylazides with chromium(II) porphyrin compounds leads to the production of paramagnetic imido complexes, Cr^{IV}(TPP)NAr, susceptible to hydrolysis to give Cr^{IV}(TPP)O [29]. These complexes undergo reaction with PPh$_3$, benzaldehyde, CS$_2$ and styrene leading to transfer of the imido group. With styrene the corresponding aziridine is formed. In a report by Holm, several compounds were found to function as imido group donors to a N,N'-diethyldithiocarbamate complex of molybdenum [30] (Equation 8).

Of these, PhI=NTs gave with styrene 96% yield of the corresponding aziridine, in few minutes at 25 °C, by using 5 mol % of CuOTf as catalyst , TsN$_3$ gave only 12% of the aziridine after 12 hours at 65 °C, while the other two compounds gave no reaction [31]. Thus tosylimino iodobenzene was the preferred reagent to be used as aminating agent of olefins. By using TsN$_3$ in refluxing cyclohexene to give the allylamine and with several transition metal porphyrin derivatives as catalysts, we obtained the results reported in

* M. Pizzotti, S. Quici, personal communication.

Table 2 - ^{a}Amination in cyclohexene t reflux with TsN$_3$ to give the allylamine; catalyst/azide=1/20. ^{b}Time required for the complete consumption of the azide. ^{c}Calculated with respect to the starting azide. ^{d}OEP=dianion of beta-octaethylporphyrin

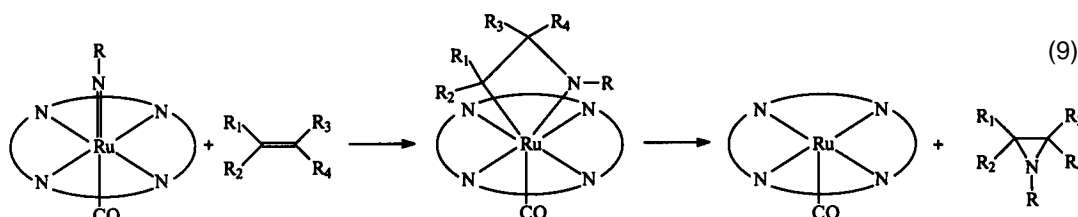| Catalyst	t (h)^b	allylamine (%)^c	p-toluenesulfonamide(%)^c
Co(TPP)	2.75	37.5	27.0
Co(p-OMeTPP)	4	23.6	37.2
Co(OEP)^d	4.8	22.9	36.9
Co(m-MeTPP)	4	26.3	24.6
Ru(TPP)CO	2.5	57.8	34.5
Ru(OEP)CO^d	8	15.4	37.9

Table 2. Ru(TPP)CO proved to be the best catalyst and in these conditions the yield of the allylamine was quite satisfactory. In the allylic amination of cyclohexene, by using Ru(TPP)CO as catalyst in CH$_2$Cl$_2$ at reflux, with molar ratios catalyst/ aminating agent/cyclohexene=1/20/2000, a comparison of the aminating ability of the tosyl derivatives has confirmed the superior performance of TsN=IPh (Table 3). However, in our hands other aromatic azides proved to be efficient reagents not only for the amination of olefins, but also of saturated C-H bonds, by using transition metal porphyrin derivatives as catalysts (see later). In particular, p-NO$_2$C$_6$H$_4$N$_3$ was very effective. In the amination of cyclohexene used as solvent to give the allylamine, with a catalyst/azide ratio of 1/50, Co(OEP) and Ru(TPP)CO catalysed a complete conversion of the azide in ca. one hour to give the product in 61% yield, with p-NO$_2$C$_6$H$_4$NH$_2$ as the main by-product [32]. In the blank experiment, only the corresponding aziridine was slowly formed and in low yield. With other olefins such as styrene and alpha-methylstyrene and with Ru(TPP)CO as catalyst, the formation of the corresponding aziridine in ca. 90% yield was observed.

In the reactions catalysed by Ru(TPP)CO, the intermediate formation of a ruthenium(IV) mono nitrene complex is likely (see Figure 3). However, the formation of a ruthenium(VI) bis nitrene complex can not be excluded [3, 32]. In the case of the cobalt-catalysed reactions the situation is more complex. The reaction between Co(TPP) and p-NO$_2$C$_6$H$_4$N$_3$, was run in a NMR tube and signals attributable to [Co(TPP)]$_2$ (p-NO$_2$C$_6$H$_4$N=NC$_6$H$_4$NO$_2$-p) were observed. Attempts to isolate and characterise this complex were unsuccesful because of the easy decoordination of the diazene moiety. Moreover, reactions of p-NO$_2$C$_6$H$_4$N$_3$ with cis and trans-3-heptene catalysed by Ru(TPP)CO gave the corresponding cis and trans aziridine respectively, although in low yields*. When the same reactions were carried out by using Co(TPP) as catalyst, mixtures of the aziridines were obtained and in very low yield. This seems to suggest that the intermediate ruthenium-nitrene complex gives a concerted reaction with the olefin, without the formation of radical species (Equation 9).

We have carried out a kinetic investigation on the reaction leading to the allylamine from cyclohexene and p-NO$_2$C$_6$H$_4$N$_3$, catalysed by Co(TPP). The reaction was followed by

$$MoO(Et_2dtc)_2 + \begin{cases} PhMeS=NTs \\ \text{[pyridine]} N^+ \ ^-NTs \\ PhI=NTs \\ TsN=\overset{+}{N}=\overset{-}{N} \end{cases} \longrightarrow MoO(NTs)(Et_2dtc)_2$$
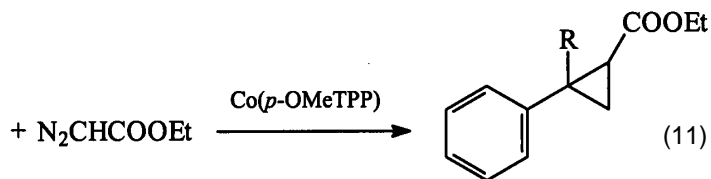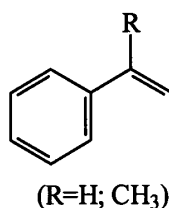
(8)

(9)

IR spectroscopy and it is first order in all the regents. The kinetic data indicates the existence of a reversible pre-equilibrium followed by a slow reaction and allows to exclude the slow, irreversible formation of an imido intermediate, followed by a fast reaction with the olefin. One possible reaction scheme is reported in Figure 6.

Works are in progress in order to clarify the nature of the reaction intermediates. By using Co(TPP) as catalyst in the amination in toluene as solvent of cyclohexene, we have observed that even small amounts of the Schiff base derived from benzaldehyde and *para*-nitroaniline were also formed. It soon became clear that the benzylic group of several hydrocarbons can be readily aminated with *p*-$NO_2C_6H_4N_3$ and Co(TPP) as catalyst. An example is reported in Equation 10.

$$ArN_3 + PhCH_3 \xrightarrow[-N_2]{Co(TPP)} PhCH_2NHAr \xrightarrow[ArN_3]{Co(TPP)} PhCHNAr + ArNH_2 + N_2 \quad (10)$$
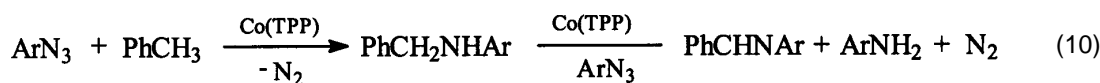
The first product is the benzylic, secondary amine. When the benzylic carbon does not bear a second hydrogen atom as in isopropylbenzene, the reaction stops at this stage. When a second hydrogen atom is present the reaction further proceeds, and a second molecule of the azide oxidises the amine to the corresponding Schiff base (Equation 9). We have confirmed this behaviour with compounds such as ethylbenzene, fluorene, *sec*-butylbenzene, tetrahydronaphthalene and dihydroanthracene. The catalytic amination of saturated C-H bonds is a reaction which has few precedents in the literature and it is of high synthetic value.

Very recently it has been reported that Ru(TPP)(NTs)$_2$ and related derivatives reacts in a stoichiometric way with adamantane, ethylbenzene and cumene to give the corresponding amides in good yields [3b]. With a chiral manganese(III)porphyrin complex the catalytic aziridination and amidation of styrene-type substrates with PhI=NTs has been realised with enantiomeric excess ranging from 43 to

68% [33]. The asymmetric amidation of saturated C-H bonds of ethylbenzene and ethylnaphthalenes with 45-58% *e.e.* has also been realised with chiral ruthenium(II) and manganese(III) porphyrin derivatives as catalysts [3c].

To the best of our knowledge, those reported in this review are the only examples of amination reactions in which a cobalt(II)-porphyrin catalyst has been successfully employed. We briefly also mention that these complexes are good catalysts even for the cyclopropanation reactions of styrene and *alpha*-methyl styrene, with ethyldiazoacetate (EDA) (Equation 11).

$$ \text{(R=H; CH}_3\text{)} + N_2CHCOOEt \xrightarrow{Co(p\text{-}OMeTPP)} \quad (11)$$

In CH_2Cl_2 at reflux, with catalyst/EDA/olefin ratios of 1/100/500, a quantitative conversion of EDA has been observed in 6-7 hours, with formation of the cyclopropane derivatives in a *trans/cis* ratio of ca. 80/20. In these reactions, porphyrin derivatives of ruthenium have been already employed as catalysts [34], while cobalt complexes with ligands different than porphyrins have only been used [35].
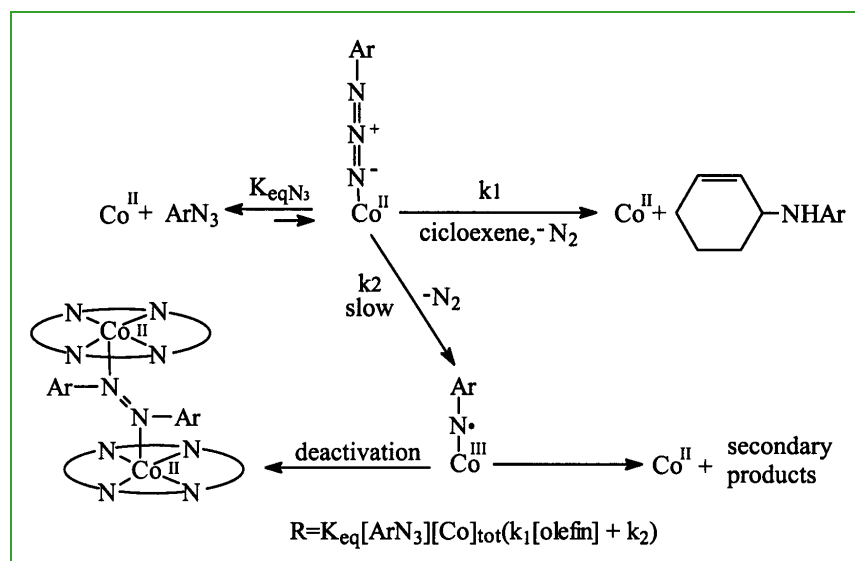

Figure 6 - Possible reaction scheme for the allylic amination of cyclohexene with p-$NO_2C_6H_4N_3$ catalysed by Co(TPP)

$$R = K_{eq}[ArN_3][Co]_{tot}(k_1[olefin] + k_2)$$

Conclusions

In this report we have discussed the use of reagents such as Chloramine-T and organic azides in the amination reactions of unsaturated and saturated hydrocarbons, catalysed by metallo-porphyrin derivatives. When relevant, a comparison has been made with the related amidation reactions, where imido precursors such as ArI=NTs have been used. We like to emphasize that the use of organic azides as aminating agents, considerably expands the number of organic products that can be catalytically obtained by this methodology, which can find interesting applications in the field of fine chemical syntheses. u

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Formazione del legame carbonio-azoto catalzzata da metallo-porfirine

Nell'articolo vengono discusse le reazioni di ammidazione e di amminazione di idrocarburi saturi ed insaturi catalizzate da metallo-porfirine. Viene ampiamente illustrato l'impiego di azidi organiche, ArN3, Cloramina-T, (p-CH$_3$C$_6$H$_4$SO$_2$NCl)$^-$Na$^+$, e suoi derivati come agenti amminanti, mentre l'uso di tosilimmino derivati, ArSO$_2$N=IPh, è preso in considerazione solo nei casi appropriati. Possibili intermedi per questo tipo di processi vengono discussi considerando la natura dei prodotti che si ottengono per reazione degli agenti amminanti stessi con derivati metallo porfirinici.