ELSEVIER

Journal of Molecular Catalysis A: Chemical 137 (1999) 135–146

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

Catalytic amination of unsaturated hydrocarbons: reactions of *p*-nitrophenylazide with alkenes catalysed by metallo-porphyrins

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Received 22 December 1997; accepted 9 March 1998

Abstract

Porphyrin derivatives of transition metals such as Ru(TPP)CO, Ru(OEP)CO and Co(OEP)(TPP = dianion of 5, 10, 15, 20-tetraphenylporphyrin, OEP = dianion of 2, 3, 7, 8, 12, 13, 17, 18-octaetylporphyrin) catalyse the reaction of *p*-nitrophenylazide with cyclohexene to give the corresponding allylamine in good yields. With other olefins such as cyclooctene, 1-octene, styrene and substituted styrenes the main product becomes the corresponding aziridine. The reaction of *p*-nitrophenylazide with Ru(TPP)CO has been investigated and the mechanism of the catalytic reactions is discussed.

Keywords: Alkenes; Amination; Organic azides; Metallo-porphyrins

1. Introduction

Transition metal mediated inter-molecular activation and functionalisation of C–H bonds is a topic of high current interest. A few methods have been reported in the literature, which afford an allylic amine by a C–H activation reaction [1–12]. Stoichiometric reactions have been performed employing sulphur and selenium imino compounds (RN = X = NR; X = S, Se) [1–4] or molybdenum oxaziridines [5,6]. A few catalytic processes have also been reported employing PhI = NTs (Ts = tosyl) [7,8], PhNHOH [9–12] or aromatic amines [13] as the nitrogen containing compound, but the turnovers numbers are quite low and the reaction with amine requires the presence of *tert*-butylhydroperoxide as oxidant. Very recently we have reported on the catalytic synthesis of allylic amines, employing a simple unactivated olefin such as cyclohexene, and an aromatic nitro compound as the aminating agent under CO pressure, in the presence of a ruthenium catalyst [14]. The selectivity of the reactions is high and the turnover numbers are higher than those reported for the most C–H activation reactions.

In recent years, the catalytic activity of porphyrin derivatives of transition metals has attracted a considerable attention [15]. In particular these complexes have been employed as catalysts for the

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1381-1169/99/$ - see front matter
PII: S1381-1169(98)00116-2

amination of alkenes to give allylamines and/or aziridines, but the aminating agents were limited to tosyliminoiodobenzene derivatives [7,8] or to the ammonium salt of Chloramine-T [16]. Thus the number of aminating agents is limited to tosyl derivatives.

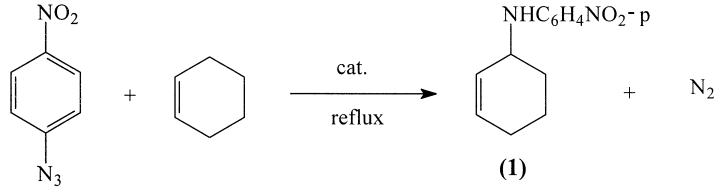
It has been recently reported that Cr(TPP)(TPP = dianion of 5, 10, 15, 20-tetraphenylporphyrin) reacts with tosylazide to give the corresponding nitrene complex, which is able to transfer the nitrene moiety to unsaturated substrates in stoichiometric reactions [17]. We thought thus possible to use porphyrin derivatives of transition metals as catalysts and organic azides as sources of the nitrene residue, in the catalytic amination of olefins. The results here reported have shown that this represents a simple procedure for the catalytic synthesis of allylamines or aziridines in a selective way, with a high turnover number and in mild conditions.

It is worth mentioning here that previous reactions of $TosN_3$ in cyclohexene in the presence of copper metal gave a complex mixture of products [18]. On the other hand TsN_3 proved to be less efficient than TsN = IPh, when it has been used with styrene as olefin and CuOTf as catalyst [19].

2. Results

2.1. Reactions with cyclohexene

The reactions of *p*-nitrophenylazide with cyclohexene at reflux, catalysed by several cobalt (II) and ruthenium (II) porphyrin derivatives, gave the corresponding allylamine in good yields (Eq. (1))(Table 1).



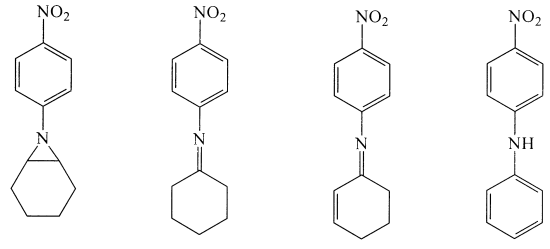
(1)

The main by-product of the reaction is *p*-nitroaniline. Small amounts of other-by-products have been identified as the corresponding aziridine (**2**), the imine of cyclohexanone (**3**) and the imine of cyclohex-1-en-2-one (**4**).

Table 1
Catalytic reactions of cyclohexene with *p*-nitrophenylazide

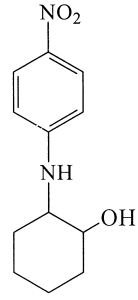
Catalyst[a,b]	*t* (h)[c]	Allylamine (**1**) (%)	*p*-Nitroaniline (%)	(**2**) (%)[d]	(**3**) (%)[d]	(**4**) (%)[d]
Co(TPP)	2.0	53.0	17.2	0.4	0.5	0.9
Co(TPMPP)	1.5	59.7	10.5	0.3	1.0	0.4
Co(TTP)	1.75	54.1	13.9	1.2	0.0	1.6
Co(OEP)	1.0	61.1	10.4	0.1	0.8	0.9
Ru(TPP)CO	0.75	61.5	15.6	0.1	0.7	0.3
Ru(OEP)CO	3.0	45.4	9.2	1.5	1.5	0.5

[a]Azide/catalyst = 50/1, in 10 ml of cyclohexene.
[b]TPP = dianion of 5, 10, 15, 20-tetraphenylporphyrin, TPMPP = dianion of 5, 10, 15, 20-tetrakis-*p*-methoxyphenylporphyrin, TTP = dianion of 5, 10, 15, 20-tetrakis-*meta*-tolylporphyrin, OEP = dianion of 2, 3, 7, 8, 12, 13, 17, 18-octaethylporphyrin.
[c]Time required to reach a complete conversion of the azide.
[d]See text.



(2) (3) (4) (5)

Traces of *p*-nitrophenylphenylamine (**5**) have also been observed. In the reaction catalysed by Ru(TPP)CO, 4.5% of a compound with a mass spectrum corresponding to (**6**) has been detected.



(6)

Unisolable and uncharacterizable materials correspond to the remaining, converted azide.

A series of reactions carried out in the experimental conditions of Table 1, but with a ratio azide/catalyst of 20, did not show substantial differences in the products distribution. Analogously, a reaction catalysed by Ru(TPP)CO with a ratio azide/catalyst of 75 was completed in 1.45 h, with a distribution of the products similar to the one reported in Table 1.

It is well known that organic azides can react with olefins even without the aid of a metal catalyst [20]. We have thus carried out a reaction in the conditions of Table 1, but in the absence of metal catalysts. The data reported in Table 2 show that only after 2.5 h of reaction a significant amount of aminated product is present. Nevertheless, the product is the corresponding aziridine (**2**) and not the allylamine. After 7 h of reaction, more than 30% of unreacted azide was still present.

It is worth noting that the *p*-nitroaniline present since the beginning of the reaction, is in part due to an impurity present in the starting azide and to a partial decomposition of the azide during the gas-chromatographic analysis.

Table 2
Reaction of cyclohexene with *p*-nitrophenylazide[a]

t (h)	Allylamine (**1**) (%)	Aziridine (**2**) (%)	*p*-Nitroaniline (%)
0.75	< 1	0.2	9.9
2.5	< 1	2.1	12.4
4.0	< 1	10.6	32.3
7.0[b]	< 1	22.4	46.0

[a] Reaction conditions as in Table 1, but in the absence of metal catalysts.
[b] Thirty-two percent of unreacted azide was still present.

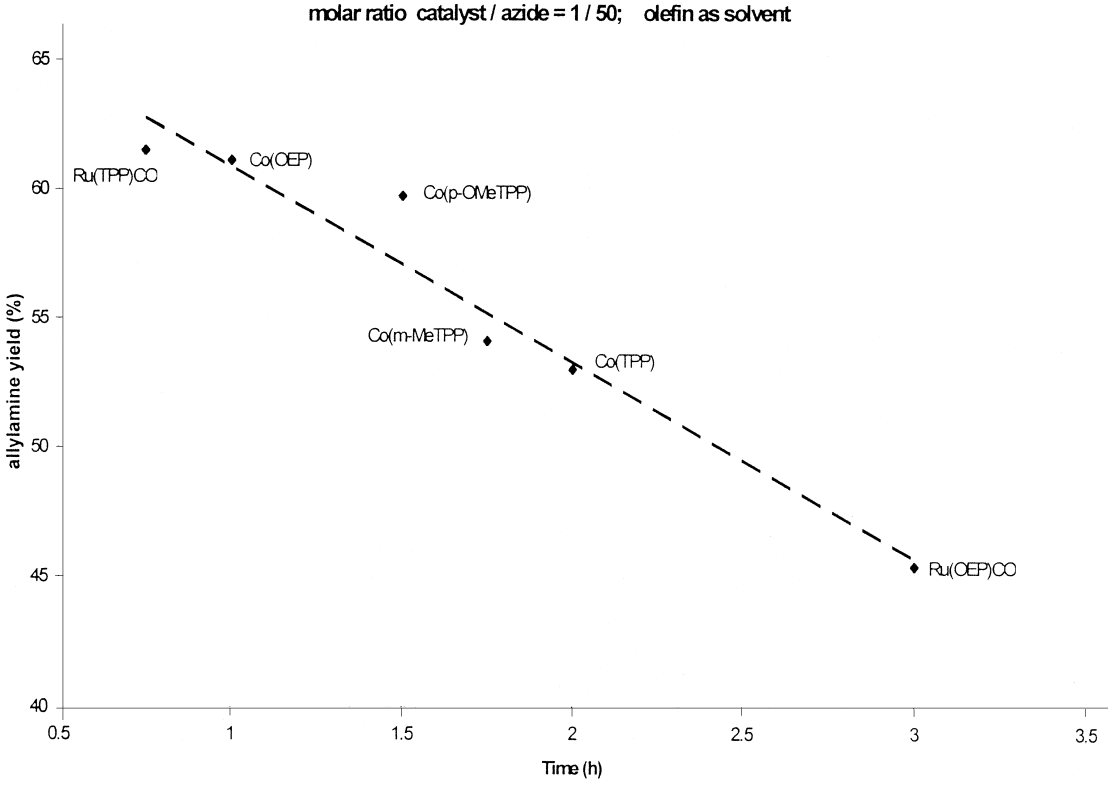


Fig. 1. Catalytic reactions of cyclohexene with *p*-nitrophenylazide (data taken from Table 1).

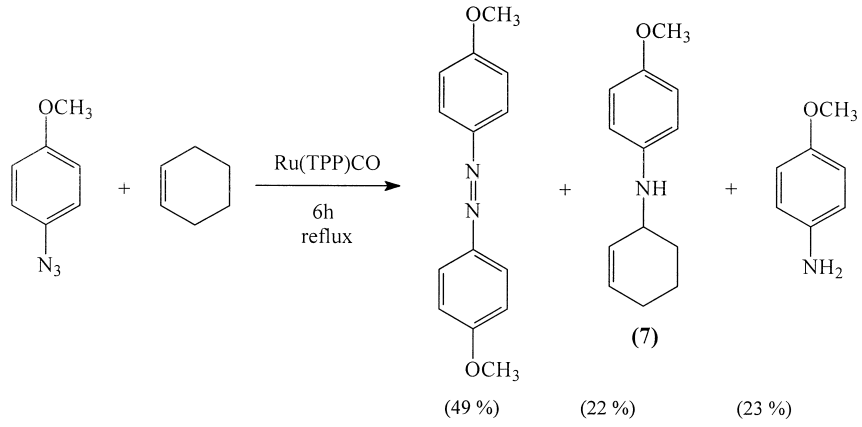
Plotting the time necessary to reach a complete conversion of the azide vs. the amount of the found allylamine (data taken from Table 1) a good, nearly linear correlation was obtained (Fig. 1). The most active catalysts are also the most selective. However while Ru(TPP)CO is a catalyst better than Ru(OEP)CO, Co(OEP) is more active and selective than Co(TPP). Thus at the moment it is not possible to speculate about the electronic effects of the porphyrin ligands on the activity and selectivity of the catalysts.

A long series of other metal complexes has also been tested as catalysts for the reaction of cyclohexene with *p*-nitrophenylazide. Compounds such as: Ti(TPP)O, V(TPP)O, Cr(TPP)Cl, Mn(TPP)Cl, Fe(TPP)Cl, Fe(TPP)CO(Py), Rh(TPP)Cl, Ni(TPP), Pd(TPP), Cu(TPP), Zn(TPP), Co(salen), $Co(acac)_2$, $[Rh(OAc)_2]_2$, $Rh(acac)_3$, $[Rh(OAc)(acac)]_2$ and $[RhCl(cyclooctene)_2]_2$ proved to be inactive in the reaction. [1] Similarly, negative results have been obtained with Lewis acids such as $TiCl_4$, $FeCl_3$, $AlCl_3$ and $BF_3 \cdot Et_2O$.

Thus the amination of cyclohexene with *p*-nitrophenylazide is not an easy reaction to be catalysed, and only the proper choice of the metal and the ligand allowed an efficient catalytic activity. This is probably related to the more or less easy interaction of the azide with the catalyst, and to the reactivity of the intermediate nitrene complex formed (see Section 3). The reaction is also sensitive to the nature of the azide employed. By conducting the amination reaction of cyclohexene with *p*-metho-

[1] Pd(TPP) derivative sample is thru the courtesy of Prof. M. Pizzotti and Dr. S. Quici.

xyphenylazide and Ru(TPP)CO as catalyst, the main product of the reaction was the corresponding azo derivative (Eq. (2)).



(2)

In the absence of Ru(TPP)CO, *p*-methoxyphenylazide gave only a small quantity of *p*-methoxyaniline after 8 h of reaction.

In the amination of cyclohexene with *p*-nitrophenylazide, the addition to the catalytic system in one to one ratio, of bases such as 1-methyl-imidazole, 2-methyl-benzimidazole and 4-*tert*-butyl-pyridine, resulted in a less efficient reaction (Table 3).

The ruthenium catalysts were particularly sensitive to the presence of the more basic ligands (1-MI and 2-MBI). The effect is less evident increasing the steric hindrance of the ligand (from 1-MI to 2-MBI), and decreasing the binding capability of the base (4-BP).

Moreover, the catalytic reaction is practically blocked by using a donor solvent such as tetrahydrofuran. The presence of bases is beneficial in the oxidation reactions catalysed by metallo-porphyrins [15,21]. In our case, the presence of donor ligands probably interferes with the formation of the catalytically active species, probably a bis-nitrene complex (see Section 3).

When the catalytic amination reaction of cyclohexene was carried out in a solvent such as benzene, some significant differences have been observed in the outcome of the reactions (Table 4).

Table 3
Catalytic reactions of cyclohexene with *p*-nitrophenylazide in the presence of bases[a]

Catalyst	Base[b]	*t* (h)	Allylamine (**1**) (%)	*p*-Nitroaniline (%)	(**2**) (%)[d]	(**3**) (%)[d]	(**4**) (%)[d]
Co(TPMPP)	2-MBI	2.5	51.8	16.7	4.7	3.8	1.5
Ru(TPP)CO	2-MBI	2.5[c]	15.3	10.3	7.7	6.9	5.7
Co(TPP)	2-MBI	2.5	41.0	19.2	4.4	3.0	7.9
Ru(TPP)CO	1-MI	2.5[c]	6.6	11.3	11.6	9.0	5.2
Co(TPMPP)	1-MI	2.5	46.6	13.9	6.9	4.4	1.3
Co(TPP)	1-MI	2.5	31.7	21.1	4.4	3.6	16.7
Ru(OEP)CO	1-MI	2.5[c]	3.8	19.9	1.9	0.5	0.2
Ru(TPP)CO	4-BP	2.5[c]	34.8	22.1	0.0	0.5	0.6
Co(TPMPP)	4-BP	2.5	49.8	27.4	0.0	0.0	1.9
Co(TPP)	4-BP	2.5	30.7	23.3	0.0	0.0	2.1

[a] Reaction conditions as in Table 1; catalyst/base ratio equal to one.
[b] 1-MI = 1-methylimidazole, 2-MBI = 2-methylbenzimidazole, 4-BP = 4-*tert*-buthylpyridine.
[c] Conversion of the azide not complete.
[d] See text.

Table 4
Catalytic reactions of cyclohexene with *p*-nitrophenylazide in benzene as solvent[a]

Catalyst	*t* (h)[b]	Allylamine (**1**) (%)	*p*-Nitroaniline (%)	Azo-derivative (%)	(**2**) (%)[c]	(**3**) (%)[c]	(**4**) (%)[c]
Co(TPP)	3	35.0	20.4	12.7	0.0	0.0	12.1
Co(TPMPP)	2.5	24.2	16.9	6.6	0.9	1.8	0.9
Ru(TPP)CO	1.5	26.8	13.2	4.6	0.1	1.0	0.4
Ru(OEP)CO	4.5	22.8	16.8	29.9	2.1	2.0	1.7

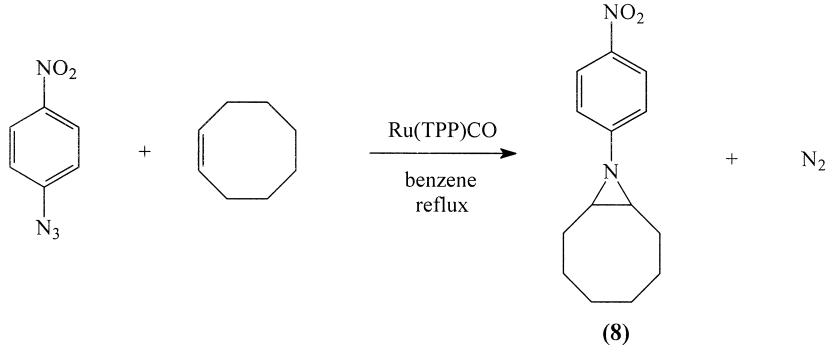
[a]Reactions carried out with a catalyst/azide ratio of 1/50, in 1 ml of cyclohexene and 9 ml of benzene.
[b]Time required to reach a complete conversion of the azide.
[c]See text.

As expected, the amount of allylamine decreases. The amount of *p*-nitroaniline increased with one exception (Ru(TPP)CO as catalyst). Surprisingly, significant quantities of the azo derivative, *p*-NO_2–$C_6H_4N{=}NC_6H_4$–NO_2-*p*, were also found. Probably in the presence of the solvent, the attack of the olefin on the intermediate nitrene complex is disfavoured, while the reaction with another molecule of the azide becomes competitive.

2.2. Reactions with other olefins

The ruthenium complex. Ru(TPP)CO, has been used as catalyst in the reactions of *p*-nitrophenylazide with other olefins.

By using cyclooctene as the olefin, at reflux in benzene, (catalyst:azide:olefin ratio of 1:250:2000), after 3 h of reaction 25% of the amination product has been obtained (Eq. (3)).

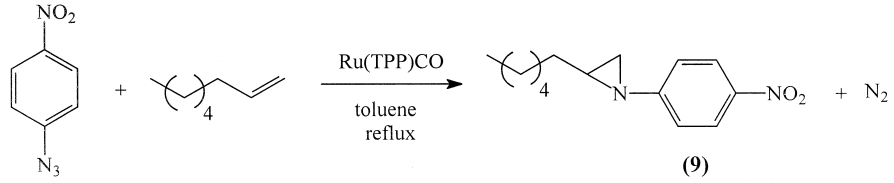


(8) (3)

Traces of *p*-nitroaniline and of the azo compound has been found as by-products.

In the absence of the catalyst only a small quantity of *p*-nitroaniline was found. It is interesting to note that in this case (and with the other olefins investigated, see below) the main amination product is the aziridine, while the allylamine is not found. This could be due to a different mechanism adopted by cyclohexene and cyclooctene in the attack to the intermediate nitrene complex [7,8]. However, it seems more probable that even in the case of cyclohexene the primary product is the corresponding aziridine which, for steric reasons, is unstable in the reaction conditions and rearranges to the allylamine. However, in this transformation the metal should be involved, since in the blank experiment carried out on cyclohexene (Table 2), we have observed the formation of the aziridine. The direct reaction between cyclohexene and *p*-nitrophenylazide should proceed through the intermediate formation of the corresponding triazoline, with subsequent loss of dinitrogen [20].

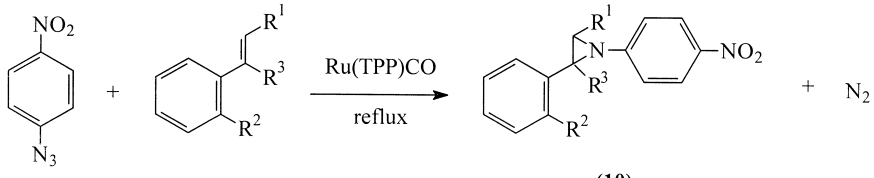
The catalytic reaction of 1-octene with *p*-nitrophenylazide, at reflux in toluene (catakyst:azide: olefin = 1:125:2000), gave after 3 h of reaction 29% of the aziridine and significant quantities of two isomers (Eq. (4)).



(9) (4)

p-Nitroaniline (32%) has also been detected among the products. The same reaction was carried out in the absence of the solvent, obtaining 41.2% of aminated products. Of these, 25% was the aziridine and 16% corresponds to two isomers of the allylamine. The blank experiment carried out on 1-octene showed the formation of only a small quantity of *p*-nitroaniline.

We have then studied a series of substituted styrenes as substrates (Eq. (5)):



(10)

(5)

	R^1	R^2	R^3
10 a	H	H	H
10 b	H	H	CH_3
10 c	CH_3	OH	H
10 d	CH_3	OCH_3	H

With 2-allylphenol ($R^1 = CH_3$, $R^2 = OH$, $R^3 = H$) as a mixture of *cis–trans* isomers in benzene at reflux (catalyst:azide:olefin = 1:125:130), after 1.5 h of reaction two isomers of the corresponding aziridine (32%) have been obtained, together with *p*-nitroaniline (40%) and the azo compound (10%). The blank experiment has shown that no amination product is formed after 2 h of reaction.

The formation of large amounts of *p*-nitroaniline is probably due to the presence of the phenolic group. When the same reaction was conducted on *trans*-anethole ($R^1 = CH_3$, $R^2 = OCH_3$, $R^3 = H$) (catalyst:azide:olefin = 1:115:120) at reflux in benzene for 2 h, a mixture of isomers of the aziridine was obtained (38%), together with *p*-nitroaniline (20%) and of the azo compound (15%). No amination product was obtained in the reaction carried out in the absence of the catalyst, for 4 h.

α-Methylstyrene ($R^1 = H$, $R^2 = H$, $R^3 = CH_3$) gave large quantities of amination products. For a reaction carried out for 30 min at reflux in toluene (catalyst:azide:olefin = 1:125:250), a total of 85.1% of amination products has been obtained (together with the expected aziridine two isomers are also present), while *p*-nitroaniline (6.4%) and the azo compound (6.2%) were also found.

The same experiment carried out with catalyst:azide:olefin = 1:125:2000, gave 92% of the amination products, while traces of *p*-nitroaniline and azo compound were also found.

The blank experiment carried out for 2.5 h, showed a small conversion of the azide, with formation of *p*-nitroaniline (60%) and of the aminated products (10%).

It is interesting to note that the absence of a substituent in the β-position in the α-methylstyrene allows the formation of large amounts of the amination products. On the contrary in *trans*-anethole, the methyl group in the β-position generates a steric hindrance for the insertion of the double bond in the metal nitrene system.

Finally, with the unsubstituted styrene ($R^1 = R^2 = R^3 = H$), the reaction carried out for 45 min at reflux in toluene (catalyst:azide:olefin = 1:125;250) gave 89% of the aziridine and traces of *p*-nitroaniline. The blank experiments gave results similar to those observed with α-methylstyrene.

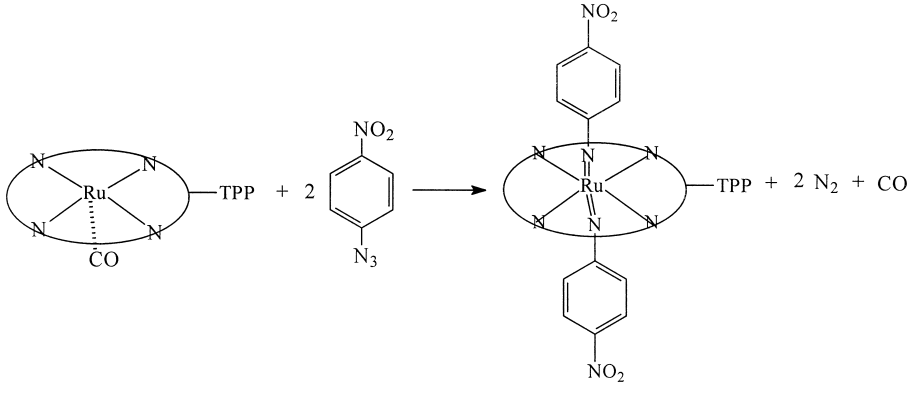
Attempts to carry out catalytic reactions on allyl alcohol and cyclopent-1-en-2-one, gave respectively only some *p*-nitroaniline or no reaction at all. Negative results were also obtained with *trans*-stilbene ($R^1 = C_6H_5$, $R^2 = R^3 = H$) (Eq. (5)), confirming the great influence of a substituent in β in the insertion reaction of the olefin in the metal–nitrene bond.

Good results were obtained with norbornene (90% of amination products). However the same result was obtained in the blank experiment, showing that the metal is not responsible for the outcome of the reaction.

3. Conclusions

Very recently it has been reported that tosyliminoiodobenzene reacts with Ru(TPP)CO(CH_3OH) to give the bis-nitrene complex, Ru(TPP)$(NTs)_2$ [22].

We have observed that even *p*-nitrophenylazide reacts with Ru(TPP)CO to give the analogous bis-nitrene complex, although in low yields (Eq. (6)) (see Section 4).



(6)

Various attempts to grow crystals of this compound suitable for an X-ray structural determination have been up to now unsuccessful.

The ruthenium (VI) bis-nitrene complex Ru(TPP)$(NTs)_2$, is able to transfer, in stoichiometric reactions, the imido group to styrenes to give the corresponding aziridines [22]. On the other hand it has been observed that the ruthenium (IV) mono-nitrene complex Ru(Porphyrin)(NAr) does not react with olefins [23]. It seems thus important to have two nitrene ligands in the *trans* positions in order to have an active catalytic species. Probably the two *trans* nitrene ligands (which can act as two or four electron donors) labilise each other.

In the present work we have observed that simple olefins such as cyclohexene, cyclooctene and 1-octene gave with *p*-nitrophenylazide comparable amounts of aminated products. Conjugated olefins such as styrene and α-methylstyrene gave higher quantities of aminated products, while electron poor olefins such as cyclopent-1-en-2-one do not enter in the catalytic cycle. We have also evidenced the importance of β-substituents in the styrene derivatives in generating steric hindrance in the attack of the olefin to the metal–nitrene bond. Finally, for the first time catalysts have been discovered able to activate in a relevant manner the azide in its reactions with olefins.

While the reactions carried out with the ruthenium catalysts probably have the bis-nitrene complex as the active species, no hypothesis can be formulated at the moment for the cobalt catalysts, and this will be the object of further studies.

4. Experimental

All reactions are carried out under an inert atmosphere of dinitrogen with magnetic stirring and all the operations are conducted in presence of molecular sieves to prevent interferences of water and dioxygen. Elemental analyses have been carried out on a Perkin Elmer 2400 CHN Elemental Analyzer. ^{1}H NMR spectra were obtained using a Brucker AC-200 (200 MHz) spectrometer.

Quantitative results for cyclohexene are carried out with a Perkin Elmer 8420 Capillary-Gas Chromatograph.

Solvents and cyclohexene were purified by distillation. Other olefins (cyclooctene, styrenes and 1-octene) and bases such as 2-MBI, 1-MI and 4-BP were furnished by Aldrich and used as received. *p*-Nitrophenylazide and *p*-methoxyphenylazide were prepared as described in literature [24,25]. Ru(TPP)CO, Ru(OEP)CO are prepared by a modification of a Tsutsui procedure [26], Co(TTP), Co(OEP), Co(TPP) and Co(TPMPP) are provided by Aldrich.

Porphyrins are prepared as reported by Adler et al. [27].

4.1. Catalytic reactions

4.1.1. p-Nitrophenylazide with various olefins

4.1.1.1. Cyclohexene. To cyclohexene used as solvent (10 ml) 44.2 mg (0.27 mmol) of *p*-nitrophenylazide and 5.4×10^{-3} mmol of catalyst in ratio azide/catalyst 50/1 were added and heated at reflux. The duration of the reaction depends on the nature of the catalyst (see Table 1). The reactions are carried out even in presence of solvents (benzene or toluene 9 ml) and 1 ml of cyclohexene (see Table 4). By chromatographic separation with flash-chromatography with eluent CH_2Cl_2/hexane 8/2 the product of allylic amination and *p*-nitroaniline were isolated as major derivatives.

4.1.1.2. Styrene. In a 50-ml flask in inert atmosphere 5.2 mg ($7 \cdot 10^{-3}$ mmol) of Ru(TPP)CO were added to 0.2 ml (1.75 mmol) of styrene in 10 ml of toluene. Finally 143.5 mg of *p*-nitrophenylazide (0.87 mmol) were added to the solution which was heated at reflux for 45 min.

The formation of amination products was verified with TLC using as eluent CH_2Cl_2/hexane 7/3.

We obtained the corresponding aziridine in a 89% yield. A side product of the reaction is *p*-nitroaniline derived by the decomposition of the azide.

The reaction mixture was purified by flash-chromatography with the same eluent used for the analysis.

4.1.1.3. α-Methylstyrene. In a 50-ml flask in inert atmosphere 3.8 mg of Ru(TPP)CO (5.1×10^{-3} mmol) were added to 0.17 ml (1.28 mmol) of α-methylstyrene in 10 ml of toluene. Finally 104.1 mg (0.64 mmol) of *p*-nitrophenylazide were added and the solution was heated at reflux for 30 min.

The formation of amination products was verified with TLC by using CH_2Cl_2/hexane 7/3 as eluent. After separation and purification by flash-chromatography with the same eluent used for the analysis we found 85.1% amination derivatives (aziridine and other isomers), 6.4% of *p*-nitroaniline and 6.2% of diazene.

The reaction was carried out even with catalyst:azide:α-methyl-styrene 1:125:2000 in 9 ml of toluene at reflux and in the same experimental conditions. About 92% of amination products was recovered after purification by flash-chromatography by using CH_2Cl_2/hexane 7/3 as eluent.

4.1.1.4. 2-Allylphenol. In a 50-ml flask in inert atmosphere 4.3 mg (5.9×10^{-3} mmol) of Ru(TPP)CO were added to 0.1 ml (0.77 mmol) of 2-allylphenol in 10 ml of benzene. A total of 122 mg of *p*-nitrophenylazide (0.74 mmol) were added to the solution which was heated at reflux for 1.5 h.

The formation of amination products was verified with TLC by using CH_2Cl_2/hexane 6/4 as eluent. After separation and purification by flash-chromatography with the same eluent used for the analysis, we obtained 32% of azirdination products isomers (44% yield of *p*-nitroaniline and 10% of diazene).

4.1.1.5. trans-Anethole. In a 50-ml flask in inert atmosphere 4.1 mg of Ru(TPP)CO (5.5×10^{-3} mmol) were added to 0.1 ml (0.66 mmol) of *trans*-anethole in 10 ml of benzene. Finally 104.8 mg (0.63 mmol) of *p*-nitrophenylazide were added and the solution was heated at reflux for 2 h.

The formation of amination products was verified with TLC by using CH_2Cl_2/hexane 6/4 as eluent. After separation and purification by flash-chromatography with the same eluent used for the analysis, we obtained 38% of aziridination products isomers (20% yield of *p*-nitroaniline and 15% of diazene).

4.1.1.6. Cyclooctene. A total of 188.6 mg (1.15 mmol) of *p*-nitrophenylazide were added to a solution of Ru(TPP)CO (3.4 mg)(4.6×10^{-3} mmol) in 10 ml of distilled benzene and 1.2 ml of cyclooctene (9.2 mmol) in an inert atmosphere and then heated at reflux for 3 h. Molecular ratio of catalyst:azide:olefin is 1:250:2000.

At the end we isolated some products and in particular the aziridine with a 25% yield. Purification of the products was made by flash chromatography by using CH_2Cl_2/hexane 8/2 as eluent.

4.1.1.7. 1-Octene. A total of 97 mg (0.59 mmol) of *p*-nitrophenylazide were added to a solution of 3.5 mg of Ru(TPP)CO (4.7×10^{-3} mmol) in toluene (9 ml) and 1.5 ml (9.4 mmol) of 1-octene.

The reaction was heated at reflux for 3 h and after cooling the solvent was dried in vacuo. The isolation and purification of the products was carried out by flash-chromatography by using CH_2Cl_2/hexane 6/4 as eluent. After purification we obtained 41.2% of aminated products (25.5% of the corresponding aziridine and 16.5% of allylamine) and 32% of *p*-nitroaniline.

The reaction was carried out even in absence of toluene in 1-octene neat. In this latter case we used 11.7 mg of Ru(TPP)CO, 119.8 mg of *p*-nitrophenylazide and 10 ml of 1-octene. The reaction was

heated at reflux for 45 min. After purification of the products we found 25% of aziridine, 16% of allylamine and 58% of *p*-nitroaniline.

4.1.1.8. p-Methoxyphenylazide with cyclohexene. To cyclohexene (10 ml), 40.23 mg (0.27 mmol) of *p*-methoxyphenylazide and 4 mg (5.4×10^{-3} mmol) of Ru(TPP)CO (molecular ratio, azide:catalyst = 50:1) were added and heated at reflux.

By chromatographic separation with flash-chromatography by using CH_2Cl_2/hexane 7/3 as eluent, allylamine (22%), *p*-methoxyaniline (23%) and diazene (49%) were recovered as major derivatives.

4.1.1.9. Reaction of Ru(TPP)CO with p-nitrophenylazide. Under an inert atmosphere 100 mg of Ru(TPP)CO (0.13 mmol) were added to a solution of *p*-nitrophenylazide 88.4 mg (0.54 mmol) in 15 ml of CH_2Cl_2. The reaction was heated at reflux for 2 h. After cooling and evaporation of the solvent, separation of the products was obtained by flash-chromatography (eluent CH_2Cl_2:toluene 1:1).

The derivative, obtained in low yields, was up to now characterized by elemental analysis and ^{1}H NMR spectroscopy.

Elemental analysis, found (calculated) C: 69.10% (68.22), H: 3.99% (3.68), N: 11.53% (11.36). ^{1}H NMR 200 MHz ($CDCl_3$, ppm): 8.64, 8H, s; 8.16, 4H, dd, $J = 3.1$, $J = 7.8$; 7.99, 4H, dd, $J = 3.1$, $J = 7.8$; 7.72, 20H, s.

Compound (**1**). ^{1}H NMR 200 MHz ($CDCl_3$, ppm): 8.07, 2H, d, $J = 8.8$ Hz; 6.54, 2H, d, $J = 8.8$ Hz; 5.89, 1H, d, $J = 5.2$ Hz; 5.75, 1H, d, $J = 5.2$ Hz; 4.67, 1H, broad, exchange with D_2O, NH; 4.11, 1H, s; range 2.1–1.6, 6 H, m. GC-Ms: 218, 190, 171, 143, 123, 103, 81.

Compound (**2**). ^{1}H NMR 200 MHz ($CDCl_3$, ppm): 8.08, 2H, d, $J = 8.8$ Hz; 6.99, 2H, d, $J = 8.8$ Hz; 2.45, 2H, s; range 2.2–1.8, 8H, m. GC-Ms: 218, 203, 189, 161, 149, 143, 103, 81.

Compound (**4**). ^{1}H NMR 200 MHz ($CDCl_3$, ppm): 8.20, 2H, d, $J = 7.2$ Hz; 6.80, 2H, d, $J = 7.2$ Hz; range 6.4–5.8, 2H, m; range 2.3–1.9, 6H, m. GC-Ms: 216, 202, 186, 151, 102, 94.

Compound (**7**). ^{1}H NMR 200 MHz ($CDCl_3$, ppm): 6.80, 2H, d, $J = 9.6$ Hz; 6.53, 2H, d, $J = 9.6$ Hz; 5.82, 1H, d, $J = 3$ Hz; 5.77, 1H, d, $J = 3$ Hz; 4.13, 1H, s; 3.75, 3H, s, OCH_3; 3.00, 1H, broad, exchange with D_2O, NH; range 2.1–1.7, 6H, m.

Compound (**8**). ^{1}H NMR 200 MHz ($CDCl_3$, ppm): 8.10, 2H, d, $J = 8.8$ Hz; 7.00 2H, d, $J = 8.8$ Hz; range 2.5–2.1, 4H, m; range 1.8–1.3, 10H, m. ^{13}C NMR 200 MHz: 162.5, s; 142.1, s; 125.8, d; 120.9, d; 44.9, d; range 27.6–27.0, t. GC-Ms: 246, 231, 217, 203, 189, 177, 164, 149, 130, 117, 103, 76.

Compound (**9**). ^{1}H NMR 200 MHz ($CDCl_3$, ppm): 8.11, 2H, d, $J = 7.3$ Hz; 7.02, 2H, d, $J = 7.3$ Hz; 2.17, 3H, m; range 1.5–1.1, 13 H, m, aliphatic. GC-Ms: 248, 219, 191, 177, 165, 151.

Compound (**10a**). ^{1}H NMR 200 MHz ($CDCl_3$, ppm): 8.17, 2H, d, $J = 9.2$ Hz; 7.37, 5H, s, aromatic; 7.09, 2H, d, $J = 9.2$ Hz; 3.25, 1H, q, $J = 3.2$ Hz; 2.25, 2H, m.

Compound (**10b**). ^{1}H NMR 200 MHz ($CDCl_3$, ppm): 8.05, 2H, d, $J = 8.8$ Hz; range 7.4–7.2, 5H, m, aromatic; 6.50, 2H, d, $J = 8.8$ Hz; 3.51, 2H, d, $J = 5.6$ Hz; 1.65, 3H, s. GC-Ms: 251, 240, 221, 204, 179, 149.

Compound (**10c**). ^{1}H NMR 200 MHz ($CDCl_3$, ppm): 8.09, 2H, d, $J = 8.8$ Hz; range 7.2–6.8, 4H, m, aromatic; 6.70, 2H, d, $J = 8.8$ Hz; 5.6, 1H, s, broad, exchange with D_2O, OH; 1.8, 2H, m; 1.30, 3H, m.

Compound (**10d**). ^{1}H NMR 200 MHz ($CDCl_3$, ppm): 8.11, 2H, d, $J = 8.8$ Hz; range 7.4–6.9, 4H, m, aromatic; 6.70, 2H, d, $J = 8.8$ Hz; 3.8, 3H, s; 1.8, 2H, m; 1.30, 3H, m.

Acknowledgements

We thank MURST 40% for financial support. We likewise thank Prof. M. Pizzotti and Dr. S. Quici for giving us a sample of the Pd(TPP) derivative.

References

[1] K.B. Sharpless, T. Hori, J. Org. Chem. 41 (1976) 176.
[2] K.B. Sharpless, T. Hori, L.K. Truesdale, C.O. Dietrich, J. Am. Chem. Soc. 98 (1976) 269.
[3] G. Kresze, H. Braxmeier, H. Munsterer, Org. Synth. 65 (1987) 159.
[4] T.J. Katz, S. Shi, J. Org. Chem. 59 (1994) 8297.
[5] L.S. Liebeskind, K.B. Sharpless, R.D. Wilson, J.A. Ibers, J. Am. Chem. Soc. 100 (1978) 7061.
[6] R.E. Moller, K.A. Jorgensen, J. Am. Chem. Soc. 115 (1993) 11814.
[7] J.P. Mahy, G. Bedi, P. Battioni, D. Mansuy, Tetrahedron Lett. 29 (1988) 1927.
[8] J.P. Mahy, G. Bedi, P. Battioni, D. Mansuy, J. Chem. Soc. Perkin Trans. 2 (1988) 1517.
[9] R.S. Srivastava, K.M. Nicholas, Tetrahedron Lett. 35 (1994) 8739.
[10] R.S. Srivastava, K.M. Nicholas, J. Org. Chem. 59 (1994) 5365.
[11] R.S. Srivastava, Y. Ma, R. Pankayatselvan, W. Dingens, K.M. Nicholas, J. Chem. Soc., Chem. Commun. (1992) 853.
[12] M. Johannsen, K.A. Jorgensen, J. Org. Chem. 60 (1995) 5979.
[13] R.S. Srivastava, K.M. Nicholas, J. Chem. Soc., Chem. Commun. (1996) 2335.
[14] S. Cenini, F. Ragaini, S. Tollari, D. Paone, J. Am. Chem. Soc. 118 (1996) 11964.
[15] F. Montanari, L. Casella (Eds.), Metalloporphyrins Catalysed Oxidations, Kluwer Academic Publishers, Dordrecht, 1994.
[16] S. Cenini, A. Penoni, S. Tollari, J. Mol. Catal. A Chemical 124 (1997) 109.
[17] B. Moubazaki, K.S. Murray, P.J. Nichols, S. Thomson, B.O. West, Polyhedron 13 (1994) 485.
[18] H. Kwart, A.A. Khan, J. Am. Chem. Soc. 89 (1967) 1951.
[19] D.A. Evans, M.M. Faul, M.T. Bilodeau, J. Am. Chem. Soc. 116 (1994) 2742.
[20] S. Patai, (Ed.), The Chemistry of the Azido Group, Interscience Publishers, London, 1971.
[21] J.P. Collmann, T. Kodadek, S.A. Raybuck, B. Meunier, Proc. Natl. Acad. Sci. USA 80 (1983) 7039.
[22] S.M. Au, W.H. Fung, M.C. Cheng, C.M. Che, S.M. Peng, Chem. Commun. (1997) 1665.
[23] W.H. Leung, T.S.M. Hun, H.W. Hou, K.Y. Wong, J. Chem. Soc., Dalton Trans. (1997) 237.
[24] G. Ribaldone, G. Caprara, G. Borsotti, Chim. Ind. 50 (1968) 1200.
[25] P.A.S. Smith, B.B. Brown, J. Am. Chem. Soc. 73 (1951) 2438.
[26] D.P. Rillema, J.K. Nagle, L.F. Barringer Jr, T.J. Meyer, J. Am. Chem. Soc. 103 (1981) 56.
[27] A.D. Adler, F.R. Longo, J.D. Finarelli, J. Goldmacher, J. Assour, L. Korsalgoff, J. Org. Chem. 32 (1967) 476.