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Allylic Amination and Aziridination of Olefins by Aryl Azides Catalyzed by Co^{II}(tpp): A Synthetic and Mechanistic Study

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Co^{II}(tpp) catalyzes the reaction of aromatic azides (ArN_3) with nonactivated olefins to yield allylic amines or aziridines in moderate-to-good yields. The chemoselectivity of the catalytic reaction is particularly high. Depending on the substrate employed, allylic amines or aziridines can be obtained. The reaction mechanism was investigated, and the reaction proceeds through reversible coordination of the aryl azide to the Co^{II}–porphyrin complex. The often postulated "nitrene" complex is not an intermediate in this reaction. The kinetics for the allylic amination is first order in azide, Co(tpp), and olefin. For the aziridination, the kinetics is again first order in azide and catalyst, but we observed a first-order dependence of the rate on α-methylstyrene only up to an olefin concentration of 6.9 M. An inhibiting role of the competitively formed 1-(4-nitrophenyl)-5-methyl-5-phenyl-1,2,3-triazoline was identified. The triazoline was shown to reversibly coordinate to Co(tpp), which blocks the free coordination site necessary for the catalytic reaction to proceed, and is it responsible for the catalyst deactivation in the aziridination reaction of α-methylstyrene by 4-nitrophenyl azide.

Introduction

Among the many different feasible catalytic transformations, C–C, C–O, and C–N bond-forming reactions have received special attention, and consequently, they have had a particularly high impact on both academic and industrial research.[1] This is due to the versatility of these methodologies for the construction of important structural motifs. For organic synthesis, the introduction of nitrogen functional groups is as important as that of oxygen functional groups.[2] Although reactions for introducing these functional groups include isoelectronic activated species and their reaction patterns are analogous (i.e., aziridination vs. epoxidation and sulfimidation vs. sulfoxidation), nitrogen-atom transfer reactions have been studied far-less frequently.[3] This is partly due to the lack of appropriate nitrogen sources, as opposed to oxidants, which are available in a wide variety of forms. Thus, it has been out of necessity that the synthetic methods that have been developed for the oxidative formation of the C–N bond have been of type usually distinct than those suitable for oxidative C–O bond formation. Catalytic aziridination and C–N bond-forming reactions have been slow to develop, so much that it is still fair to say that no truly general method for direct catalytic C–N bond formation exists.

Iminophenyliodinanes[4] have been extensively employed as nitrogen sources in the last few years, but several problems are strictly related to their use.[5] The synthetic procedure to obtain these molecules does not allow the preparation of a large class of starting materials, the side product of the reaction is iodobenzene, and, last but not least, the sulfonyl group is always introduced in the aminated compound. It is worth noting that iminoiodinane compounds can be also prepared in situ from the corresponding sulfonylamine and diacetoxyiodobenzene[6] or iodosylbenzene.[7] Alternative nitrene sources such as chloramine-T[8] or bromamine-T[9] have been employed to overcome some of the limitations associated with the use of iminoiodinane compounds. To get over the problem of the limited solubility of these compounds in the commonly employed organic solvents and to avoid the presence of trace amounts of water that inevitably contaminates these last starting materials, some years ago we considered an alkylammonium salt of *N*-chloro-*p*-toluensulfonamide as an aminating agent.[10] Very recently, us and Katsuki and coauthors published two reviews on the use of azide compounds as a nitrogen source for atom-efficient and ecologically benign nitrogen-atom-transfer reactions.[11,12] In particular, Katsuki obtained interesting results with the use of tosylazide as a nitrene precursor even in enantioselective reactions by using chiral ruthenium Schiff base complexes as catalysts.

Organic azides are the precursors of the nitrene moiety [RN] and the only side product of the decomposition is

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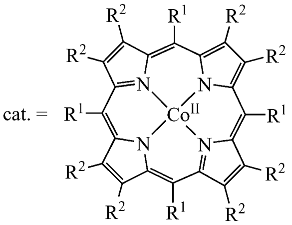
molecular nitrogen. For this reason, they can be considered atom-efficient nitrogen-atom-transfer agents. Organic azides, depending on the experimental conditions and the nature of the metal and the azide, can react with the metal complex to give a metal–imido species or a metal–azide adduct. The formation of a metal–nitrogen bond can occur with coordination of the terminal nitrogen Nγ or Nα atom or by oxidative addition of the azido group. To predict the coordinating mode of the organic azide it is important to remember that the nitrogen in the α position is more basic than the terminal unsubstituted one. Among azides, aromatic azides present several advantages: (i) They can be easily synthesized from the corresponding substituted anilines by a simple procedure. (ii) They allow an N-aryl group to be introduced into the molecule when it is necessary. (iii) They are stable enough to be safely handled in the laboratory.

In our ongoing study on amination reactions catalyzed by transition metals,[13,14] we recently reported the use of aromatic azides in the amination of unsaturated hydrocarbons catalyzed by ruthenium[14–16] and cobalt[17,18] porphyrin complexes. The metal coordination mode of the porphyrin complexes renders them a unique class of catalysts for N-group transfer reactions,[19] and indeed, the first transition-metal complexes that showed good activity as catalysts in aziridination reactions were metalloporphyrins.[20] Cobalt porphyrin complexes have been recently shown to be competent catalysts in the aziridination reaction of alkenes by employing bromamine-T[21] or diphenylphosphoryl azide[22] as the aminating agents. The same authors also reported the use of cobalt–porphyrin complexes as catalysts for intramolecular C–H amination with arylsulfonyl azides.[23]

We reported that cobalt(II) porphyrin complexes are able to activate aromatic azides for the amination of the C–H bond of saturated organic compounds under mild conditions to give secondary amines and imines (Scheme 1).[24,25]

We report herein that cobalt(II) tetraphenylporphyrinate, Co(tpp) (tpp = dianion of tetraphenylporphyrin), can be used as a catalyst for the selective aziridination or amination of the allylic C–H bond of alkenes depending on the nature of the substrate employed. Particular attention was given to the understanding of the mechanism of such reactions with the aim to be able to direct the catalytic cycle towards the formation of the desired product.

$$\mathrm{ArCH_2R + Ar'N_3 \xrightarrow{cat.} ArC(R){=}NAr' + ArC(R)(H)\text{-}NHAr' + Ar'NH_2 + N_2}$$



Co(tpp): R^1 = Ph, R^2 = H
Co(*p*-MeOtpp): R^1 = *p*-$MeOC_6H_4$, R^2 = H
Co(*p*-Cltpp): R^1 = *p*-ClC_6H_4, R^2 = H
Co(oep): R^1 = H, R^2 = Et

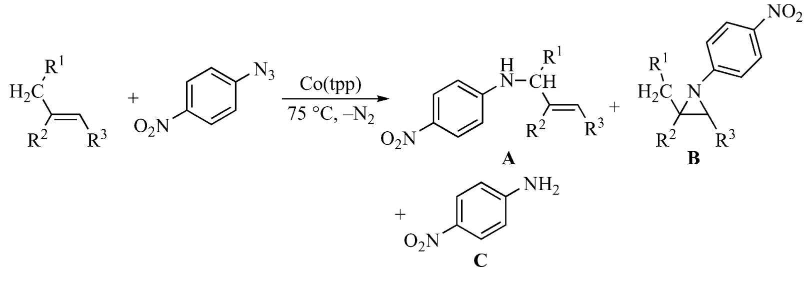
Scheme 1. Benzylic amination reactions catalyzed by Co^{II} porphyrin complexes.[24]

Results and Discussion

The reaction of 4-nitrophenyl azide with olefins in benzene at 75 °C can be efficiently catalyzed by Co(tpp) to give the corresponding allylic amines (**A**) or aziridines (**B**), depending on the substrate used, in moderate-to-good yields (Scheme 2, Table 1). 4-Nitroaniline (**C**) was always observed among the products. Whereas several selective catalysts for the aziridination reaction were recently reported, the selective insertion of nitrenoids into the allylic C–H bond has been explored only to a lower extent.[26] Much work is needed to understand the mechanism of the alkene activation. In the present study, we chose four substrates with allylic C–H bonds that can undergo allylic amination and compared them with styrene and α-methylstyrene, which are commonly employed in aziridination reactions. All reactions reported in Table 1 were carried out in a 1:1 volume mixture of the olefin and benzene at 75 °C in order to have comparable results.

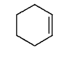
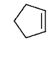
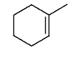
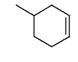
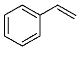
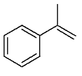
When cyclohexene was employed as the substrate (Table 1, entry 1), allylic amine **1** was formed in good yields (60% isolated yield) in 6 h. The only byproduct formed in this reaction was 4-nitroaniline (39%) and no trace of aziridine **2** was ever detected. Aziridine **2** is the only aminated olefin-based product that is obtained from the uncatalyzed reaction (see "Mechanistic Studies"). When the same catalytic reaction was repeated in refluxing neat cyclohexene (b.p. 83 °C) we again isolated allylic amine **1** in 60% yield and in just 3 h.

In contrast, in the catalytic reaction with cyclopentene, at complete conversion of the starting azide, allylic amine **3** was obtained in low yield (9%; Table 1, entry 2) and a nearly equal amount of aziridine **4** (11%) was formed together

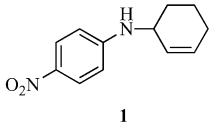


Scheme 2. Amination reactions catalyzed by Co(tpp).

Table 1. Amination reactions of alkenes with 4-nitrophenyl azide (ArN_3) catalyzed by Co(tpp).[a]

Entry	Olefin	t / h	Conv. / %[b]	A[c] (Yield / %)	B[c] (Yield / %)	C[c] (Yield / %)
1		6	>99	**1** (60)	**2** (–)	(39)
2		7	>99	**3** (9)	**4** (11)	(69)
3[d]		12	99	**6** + **7** (47)	–	(50)
4[e]		15	>99	**9** + **10** (47)	–	(48)
5[f]		8	>99	–	**11** (15)	(54)
6[f]		8	70	–	**12** (38)	(11)

[a] Experimental conditions: Co(tpp) (32 mg, 0.048 mmol) in benzene (15 mL) and the olefin (15 mL) at 75 °C; Co(tpp)/ArN_3, 4:50. [b] Conversion of the starting azide. [c] Isolated yield. [d] Mixture of two diastereoisomers in 55:45 ratio. [e] Mixture of four diastereoisomers in 58:21:15:6 ratio. [f] Co(tpp): 8 mg (0.012 mmol) was used; Co(tpp)/ArN_3, 1:50.



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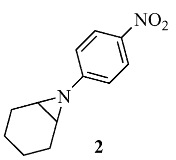
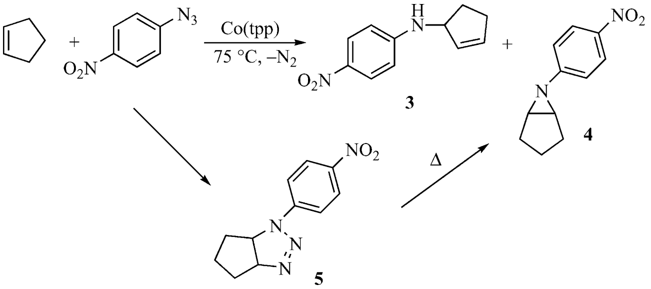


2

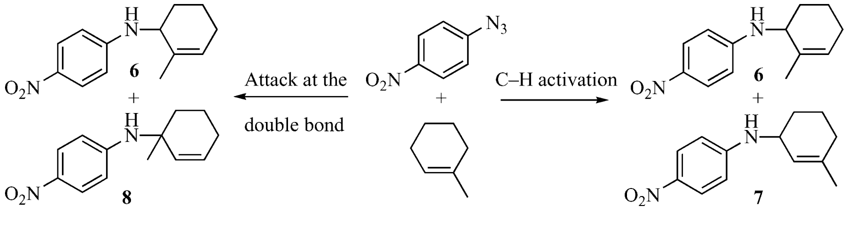
with 4-nitroaniline (69%). It should be pointed out that at 75 °C, the 1:1 mixture of cyclohexene and benzene is below the reflux temperature of both solvents, whereas the same consideration does not hold with the use of cyclopentene, which has a boiling point of 44–46 °C. We know that the temperature has a strong influence on the product distribution and on the catalytic activity of Co(tpp) in this reaction. In fact, when 4-nitrophenyl azide was treated in refluxing cyclopentene in the absence of the catalyst, complete conversion was observed in 5 h, and the only aminated olefin-based product obtained was triazoline **5** (41%), which was fully characterized (Scheme 3). The rest of the starting azide was again recovered as 4-nitroaniline (see Supporting Information). Triazoline **5** is not stable upon heating over 50 °C and readily looses dinitrogen to yield the aziridine. This can easily explain the loss of selectivity observed in the catalytic reaction conducted in refluxing cyclopentene/benzene, 1:1. Two competitive reactions occur at the same time: on the one side, there is the Co(tpp)-catalyzed reaction yielding allylic amine **3**, whose rate is decreased by the fact that the temperature is lower than 75 °C, and on the other side, there is the uncatalyzed reaction giving triazoline **5**, which is readily converted into aziridine **4** by effect of the increased temperature with respect to boiling cyclopentene.



Scheme 3. Reaction between cyclopentene and 4-nitrophenyl azide in the presence or absence of Co(tpp).

To understand whether electrophilic attack of the azide occurs at the double bond (with aziridine formation followed by a β C–H insertion reaction[27] to yield the allylic amine) or directly at the allylic C–H bond, two differently substituted cyclohexenes were chosen as substrates for the catalytic reactions, namely, 1-methylcyclohexene and 4-methylcyclohexene. From the reaction with 1-methylcyclohexene one could expect to obtain two different sets of diastereoisomers if the attack occurs at one or the other position (Scheme 4).

The catalytic reaction, upon complete conversion of the starting azide, yielded 47% of allylic amines **6** and **7** in a 45:55 ratio, as determined by ^1H NMR spectroscopy. No trace of allylic amine **8** was observed (Table 1, entry 3). It should be pointed out that, similarly to what was observed for the radical reactions, the attack at the endocyclic CH_2 is faster than attack at the exocyclic CH_3 and no trace of aminated products derived from CH_3 activation were detected. A similar result was obtained from the reaction with 4-methylcyclohexene (Table 1, entry 4). In this case, the re-



Scheme 4. Possible outcome of the Co(tpp)-catalyzed reaction between 1-methylcyclohexene with 4-nitrophenyl azide depending on the attack site.

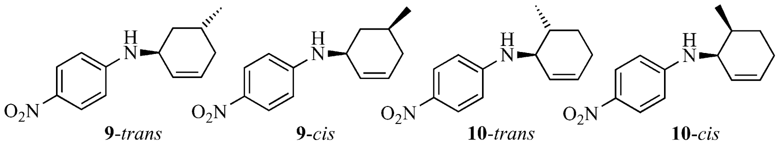
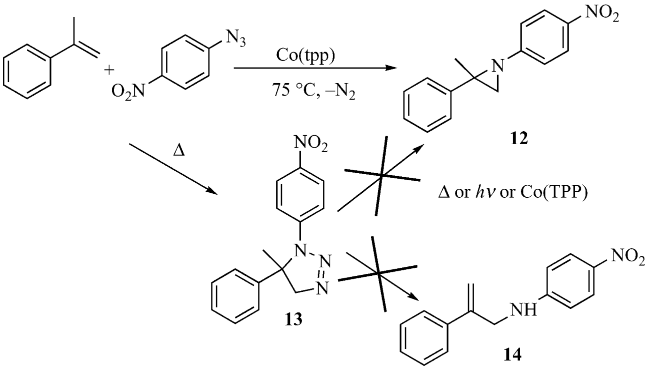


Figure 1. Allylic amines obtained from the catalyzed reaction between 4-methylcyclohexene and 4-nitrophenyl azide.

action yielded a mixture of four diastereoisomers in a global 47% yield in a 58:21:15:6 ratio. By comparison with the ^{1}H NMR spectra reported in the literature,[28] the major products were determined to be **9**-*trans* and **9**-*cis* (Figure 1); the minor products were determined to be **10**-*trans* and **10**-*cis* derived from the other possible nitrene insertion into the more-hindered allylic C–H bond. In both cases, products derived from attack at the double bond were not observed, and we can conclude that allylic amine formation occurs by attack of the olefin to the cobalt-coordinated azide (see also Mechanistic Studies).

When linear alkenes such as 1-octene were employed in the present system, no reaction occurred. Conjugated dienes also failed to react. In contrast, when styrene, which has no allylic C–H bonds, was employed as a substrate, the reaction product was the corresponding aziridine **11**, albeit in low yields (Table 1, entry 5). A similar result was obtained with α-methylstyrene, even if in principle this olefin could also give the allylic amine (Table 1, entry 6). In this case, together with aziridine **12** (38%), 1-(4-nitrophenyl)-5-methyl-5-phenyl-1,2,3-triazoline (**13**, 30%) was obtained (Scheme 5). This particular triazoline is surprisingly stable, as already reported by us some years ago.[15] Its formation and the importance this compound has on the overall catalytic cycle will be further discussed in the mechanistic studies reported below. Once formed, **13** is not converted into **12** by Co(tpp) under the reaction conditions. We can also exclude the formation of 4-nitro-*N*-(2-phenylallyl)aniline (**14**), which was synthesized by an independent route with a methodology reported recently in our laboratory (see Supporting Information).[29] This latter compound was never detected among the products of the catalytic reactions and remains unchanged under the reaction conditions.



Scheme 5. Reaction between α-methylstyrene and 4-nitrophenyl azide in the presence or absence of Co(tpp).

No reaction was observed with other styrenes such as β-methylstyrene, *cis*-stilbene, *trans*-stilbene, and 1,1-diphenylethylene. These results suggest that steric hindrance at the olefinic substrate represents a major obstacle to the catalytic reactivity. Different results were obtained with 1,2-dihydronaphthalene and 1,2-dihydro-4-phenylnaphthalene: in these cases, the only aminated products obtained were the benzylic amines derived from disproportionation reactions of the starting olefins. These results will be the subject of a forthcoming paper.

Mechanistic Studies

Uncatalyzed Reaction

The uncatalyzed reaction between aromatic azides and double bonds leading to the formation of 1,2,3-Δ^2-triazolines was reported almost a century ago.[30] Nonactivated double bonds give very slow reactions, and the triazoline in most cases is not stable enough to be isolated. The aziridine is obtained instead, although often in low yields. For example, in our hands, the reaction of 4-nitrophenyl azide in refluxing cyclohexene gave complete conversion of the starting azide in 16 h to yield aziridine **2** with 70% selectivity (the rest of the azide was transformed into 4-nitroaniline). It should be pointed out that the aziridine is not an intermediate in our catalytic reaction. No reaction was observed if a catalytic amount of Co(tpp) was added to a stirred solution of aziridine **2**, and if this last compound is added to a catalytic run, it is recovered unaffected at the end of the reaction (see Supporting Information).

Kinetic Studies

To clarify the mechanism of the amination reactions we performed a kinetic study. The reaction between 4-nitrophenyl azide and cyclohexene catalyzed by Co(tpp) was followed by IR spectroscopy by monitoring the intensity of the 2120 cm^{-1} absorption of the azide. All reactions were conducted at 75 °C and showed an excellent first-order dependence of the rate on the azide concentration ($R^2 > 0.99$ for all reactions, see Supporting Information). The kinetics is also first order with respect to Co(tpp). We can rule out any term independent from the catalyst in the reaction rate, as the fitting for the plot of $k_{\text{obs.}}$ versus the concentration of Co(tpp) can be forced to pass through the origin without affecting the R^2 value (R^2 = 0.99; Figure S1, Supporting Information). In other words, the uncatalyzed reaction mentioned in the previous paragraph is so slow under the conditions of the kinetic measurements not to be observable at all. A first-order dependence was finally observed with respect to cyclohexene, but in this case, the straight line in the plot of $k_{\text{obs.}}$/[Co(tpp)] versus the olefin concentration showed an intercept on the axis of the reaction rate (Figure 2). This indicates the presence of an olefin-independent reaction. Such a reaction between the aryl azide and the cobalt complex has indeed been independently observed, as detailed in the following.

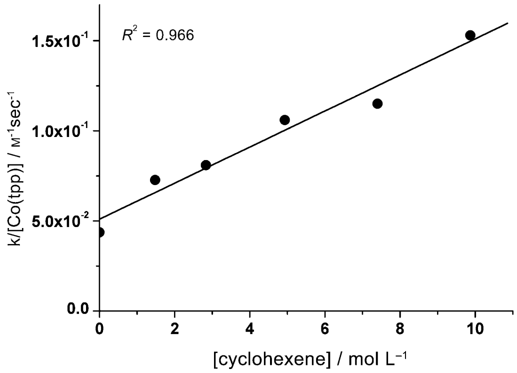


Figure 2. Dependence of the rate of the allylic amination on the concentration of cyclohexene.

Because the reaction products are different, a kinetic study was also performed by employing 4-nitrophenyl azide and α-methylstyrene as the substrate and Co(tpp) as the catalyst. The kinetics is again first-order in azide ($R^2 > 0.98$ for all reactions) and catalyst concentrations (see Supporting Information). However, a first-order dependence of the rate on the concentration of α-methylstyrene was observed only up to an olefin concentration of 6.9 M (90% v/v in benzene). In neat α-methylstyrene, the reaction rate is lower than it would be expected (Figure 3). We previously observed an analogous outcome when studying the catalytic activity of Ru(tpp)(CO) for this reaction.[15] In that case, an inhibiting role of the competitively formed triazoline was identified. The triazoline was shown to coordinate to ruthenium, which blocks the free coordination site necessary for the catalytic reaction to proceed. An analogous explanation is likely to be involved here, and this possibility was investigated by performing further spectroscopic studies.

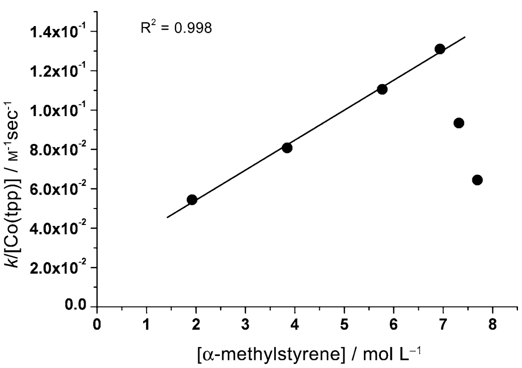


Figure 3. Dependence of the aziridination rate on the concentration of α-methylstyrene.

More information on the reactivity of the aryl azide complexes could be gained by kinetic experiments run with a different azide. When employing 4-methoxyphenyl azide, we observed a sharp decrease in the reaction rate, which indicates that the presence of an electron-donating group on the azide slows down the reaction. This data is consistent with electrophilic behavior of the coordinated azide in the transition state, as expected.

UV Studies

We next monitored the catalytic reactions by UV/Vis spectroscopy in order to shed some light on the products that are formed during the catalytic cycle. The UV/Vis spectral changes for the reaction of 4-nitrophenyl azide with cyclohexene catalyzed by Co(tpp) are shown in Figure 4.

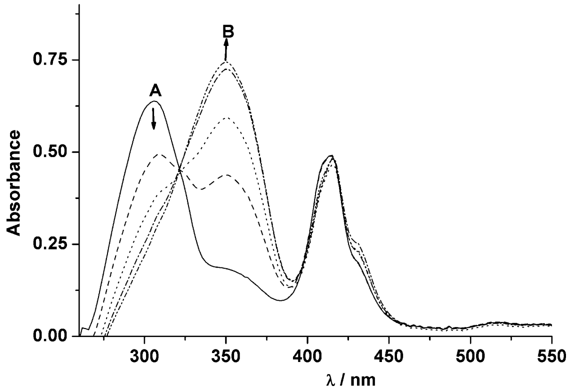


Figure 4. UV/Vis spectral changes during the reaction of 4-nitrophenyl azide (6.2×10^{-1} mmol) with cyclohexene (30 mL) in the presence of Co(tpp) (4.1×10^{-2} mmol) at 84 °C. Scans were taken at 30-min intervals. **A** = $4\text{-}NO_2C_6H_4N_3$; **B** = **1**.

The presence of the isosbestic point at 322 nm indicates that the conversion of the starting aryl azide (**A**) into allylic amine (**B**) **1** occurs without the accumulation of any long-lived intermediate. We already showed that aziridines cannot be intermediates in the synthesis of allylic amines. The present result not only supports this view, but also indicates that no other intermediate is observed along the reaction pathway.

We next looked at the UV/Vis spectral changes in the aziridination reaction. The spectral changes for the reaction of 4-nitrophenyl azide (6.1×10^{-1} mmol) with α-methylstyrene (90% v/v in benzene, 6.933 M, 30 mL) catalyzed by Co(tpp) (4×10^{-4} M) at 75 °C are reported in Figure 5. Un-

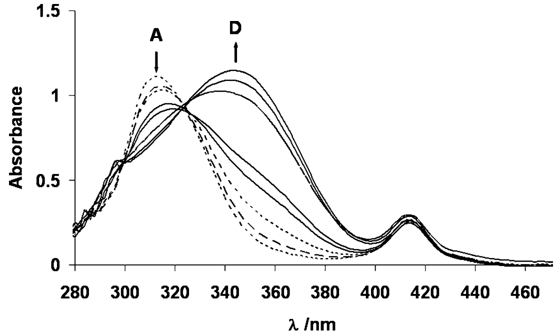


Figure 5. UV/Vis spectral changes during the reaction of 4-nitrophenyl azide (6.1×10^{-1} mmol) with α-methylstyrene (90% v/v in benzene, 30 mL) in the presence of Co(tpp) (1.2×10^{-2} mmol) at 75 °C. Scans were taken at 1-h intervals. **A** = $4\text{-}NO_2C_6H_4N_3$; **D** = **12** + **13**.

der these conditions, we observed the disappearance of the starting azide (**A**) (λ = 312 nm) with the simultaneous formation of aziridine **12** (λ = 341 nm) and triazoline **13** (λ = 350 nm), which resulted in a broadened signal around 345 nm (**D**). After 10 h, the conversion of the starting azide was quantitative and we could isolate aziridine **12** (43%) and triazoline **13** (50%).

During the catalytic reaction, the Soret band of Co(tpp) (λ = 413 nm) remains unchanged. We can thus exclude the formation of a long-lived Co^{III} intermediate, because in this case a considerable redshift of the Soret band would be expected (λ = 430 nm).[31] In contrast, the presence of a pentacoordinate Co(tpp) complex cannot be ruled out, as in this case no significant shift is observed. To be able to understand the changes at the metal center during the reaction, we next looked at the stoichiometric reactions of Co(tpp) with both the olefin and the azide. No UV/Vis observable shifts were observed with cyclohexene or α-methylstyrene. When the stoichiometric reaction between Co(tpp) and 4-nitrophenyl azide was monitored by UV/Vis we observed the disappearance of the ArN_3 signal at 312 nm and the appearance of a new signal at 344 nm (Figure 6). The Soret band of Co(tpp) at such a concentration goes out of range. When the reaction with 4-nitrophenyl azide was repeated employing substoichiometric amounts of Co(tpp) (mol ratio = 10) the free diazene $[4\text{-}(NO_2)C_6H_4N{=}NC_6H_4\text{-}4\text{-}(NO_2)]$ could be detected (λ = 336 nm) as the major reaction product (see Supporting Information).[24] Finally, examination of the reaction of Co(tpp) with 4-nitrophenyl diazene $[4\text{-}(NO_2)C_6H_4N{=}NC_6H_4\text{-}4\text{-}(NO_2)]$ by UV/Vis spectroscopy indicates that the same final product is obtained when either the azide or the diazene is employed as starting material.

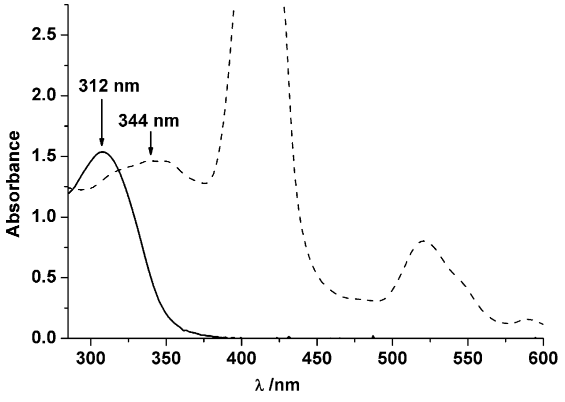
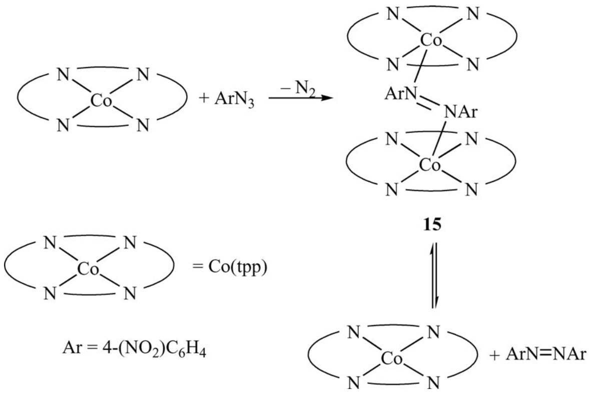


Figure 6. UV/Vis spectra of 4-nitropenhyl azide (solid line, λ_{max} = 312 nm) and that of the product of the stoichiometric reaction between Co(tpp) (0.15 mmol) and 4-nitrophenyl azide (0.16 mmol) in benzene (30 mL) at 75 °C after the complete consumption of the starting azide (dashed line, λ_{max} = 344 nm).

NMR Spectroscopic Studies

If Co(tpp) is treated with an excess amount of olefin, such as cyclohexene or α-methylstyrene, in C_6D_6 no significant shift in the ^1H NMR signals is observed. In contrast, as already reported by us,[24] when the stoichiometric reaction between Co(tpp) and 4-nitrophenyl azide was conducted at 60 °C in C_6D_6 new signals were observed in the ^1H NMR spectrum that cannot be attributed to any known compound, but again are identical to those of the product obtained by reaction of Co(tpp) with $4\text{-}(NO_2)\text{-}C_6H_4N{=}NC_6H_4\text{-}4\text{-}(NO_2)$. All the above reported data, together with the observation of only one set of resonances for the aryl groups of the diazene moiety of this complex, which indicates high symmetry, lead us to formulate the identity of the final product as $[Co(tpp)]_2(ArN{=}NAr)$ [**15**; Ar = $4\text{-}(NO_2)C_6H_4$] (Scheme 6). A similar complex that has an unsubstituted diazene (HN=NH) group bridging two ruthenium–porphyrin complexes has been reported.[32] Unfortunately, any attempt to grow single crystals suitable for X-ray diffraction always gave the Co(tpp) complex without any coordinated ligand.



Scheme 6. Proposed reaction product obtained from the reaction of Co(tpp) with 4-nitrophenyl azide.

The reaction between the azide and Co(tpp) was repeated in C_6D_6 in the presence of the spin-trap compound tempo (2,2,6,6-tetramethyl-1-piperidine-*N*-oxide), and the spectroscopic changes of the products were monitored by ^1H NMR spectroscopy. The signals due to paramagnetic Co^{II}(tpp) gradually disappeared to give rise to a diamagnetic cobalt(III) complex. Because there is no reaction between the Co–porphyrin complex and tempo in the absence of the azide, and because the addition of tempo does not have a marked effect on the reaction of Co(tpp) with $4\text{-}(NO_2)\text{-}C_6H_4N{=}NC_6H_4\text{-}4\text{-}(NO_2)$, this result suggests that the unpaired spin density of the Co(tpp) complex is partly localized on the azide nitrogen atoms in an intermediate complex.

In order to investigate the role of complex **15** in the synthesis of allylic amines, a series of catalytic reactions in C_6D_6 at 60 °C with increasing amounts of cyclohexene were monitored by ^1H NMR spectroscopy. First, we performed the reaction between equimolar amounts of 4-nitrophenyl azide and cyclohexene in the presence of stoichiometric Co(tpp). Only complex **15** was formed and allylic amine **2** was not present in the final mixture. When the reaction was repeated by employing a 1:10:170 ratio of Co(tpp)/azide/olefin, the azide signals disappeared in 9 h and allylic amine **2** was formed together with aniline (see Supporting Information). Complex **15**, in contrast, was not formed during the catalytic cycle, because of the great excess of cyclohexene.

Similar results were obtained by following the ^{1}H NMR spectral changes of a catalytic reaction of 4-nitrophenyl azide with α-methylstyrene in the presence of Co(tpp). In this latter case, by employing CH_2Cl_2 as an internal standard in a sealed tube (see Experimental Section), a clean first-order dependence on the reaction rate with respect to the azide was observed {Co(tpp)/azide/olefin, 1:10:50; in C_6D_6 at 75 °C, $k_{obs.}/[Co] = 4.29 \times 10^{-2}\ \text{M}^{-1}\ \text{sec}^{-1}$}. At the end of the reaction, we measured a 49% yield of aziridine **12** together with triazoline **13** (12%) and 4-nitroaniline (21%). The rest of the starting azide was converted into an unidentified product.

We next examined the effect of triazoline **13** on Co(tpp). A remarkable shift was observed in C_6D_6 at room temperature on the ^{1}H NMR resonances of both the Co–porphyrin moiety and the organic molecule (Figure 7). Unfortunately any attempt to grow crystals suitable for X-ray structural characterization of the coordination complex between Co(tpp) and the triazoline met with failure, and again only Co(tpp) was recovered. This is probably due to a very weak coordination. A similar Ru(tpp)(L)CO complex (L = **13**) was already reported by us.[15]

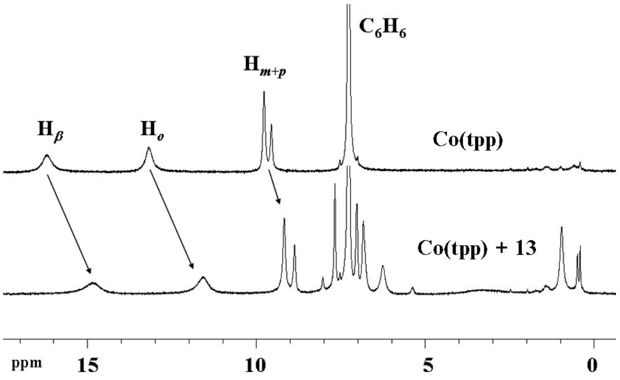


Figure 7. ^{1}H NMR spectra of Co(tpp) (upper line) and Co(tpp) + **13** (lower line) in C_6D_6. Arrows evidence the shifts of the signal of the protons of the porphyrin skeleton (H_β = tpp pyrrolic protons; H_o = tpp *ortho* aromatic protons; H_{m+p} = tpp *meta* and *para* aromatic protons).

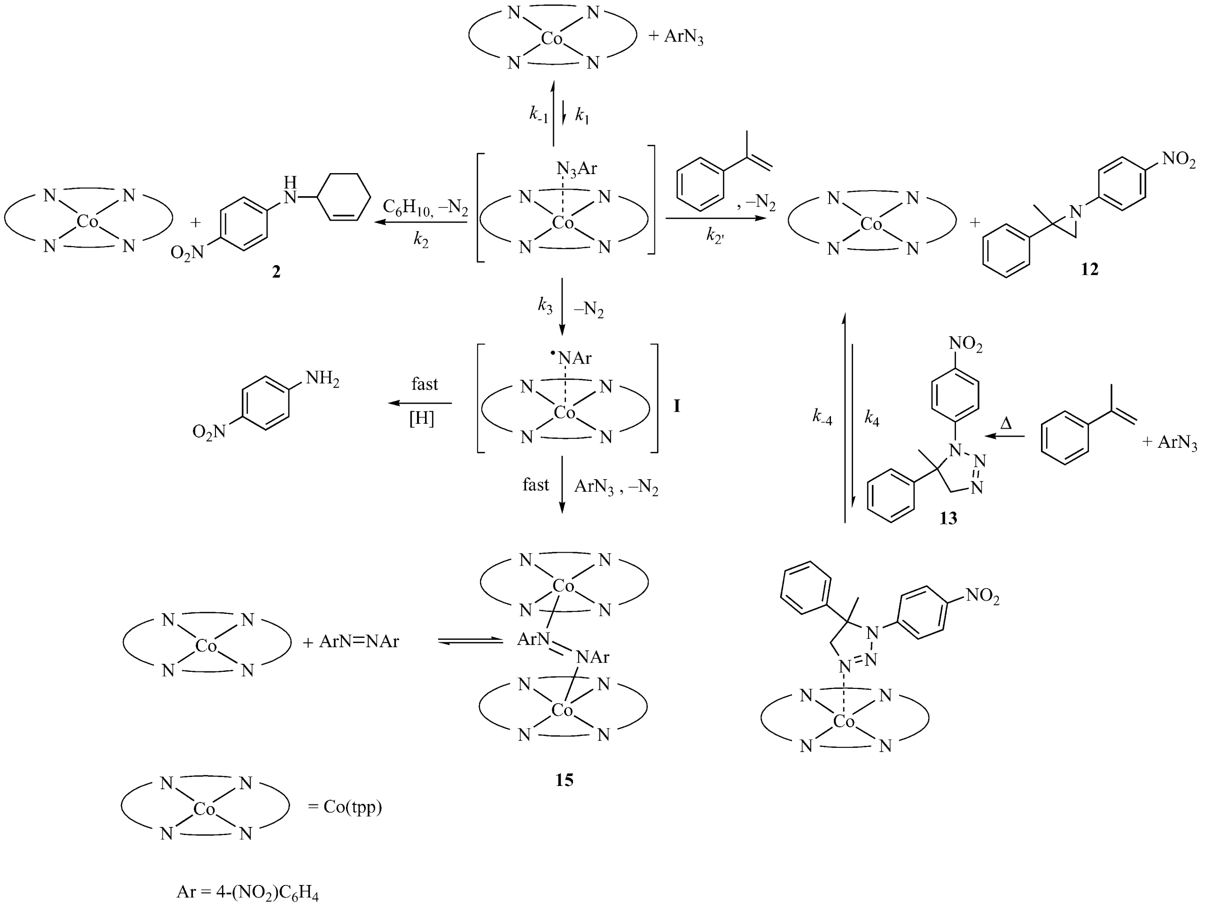
Even if the coordination of the triazoline moiety to Co(tpp) appears to be weak, its effect on the catalytic aziridination and allylic amination reactions is not negligible. In fact, when the catalytic reaction of 4-nitrophenyl azide with α-methylstyrene in the presence of Co(tpp) was repeated in the presence of **13** [Co(tpp)/**13**/azide/olefin, 1:5.8:10:50; in C_6D_6 at 75 °C] the reaction rate was slower than in its absence ($k_{obs.}/[Co] = 3.36 \times 10^{-2}\ \text{M}^{-1}\ \text{sec}^{-1}$ vs. $k_{obs.}/[Co] = 4.29 \times 10^{-2}\ \text{M}^{-1}\ \text{sec}^{-1}$). When the same reaction was repeated in the presence of a different triazoline, namely, 1-(4-methoxyphenyl)-5-methyl-5-phenyl-1,2,3-triazoline (**16**), no effect on the reaction rate was observed ($k_{obs.}/[Co] = 4.34 \times 10^{-2}\ \text{M}^{-1}\ \text{sec}^{-1}$; see Supporting Information). It should be noted that this last triazoline containing an electron-donating substituent on the aryl ring is less stable than **13**, and it is probably transformed during the catalytic reaction. No reaction between 4-methoxyphenyl azide and **13** was observed in the presence of Co(tpp). The coordination of **13** to the catalyst was observed even in the allylic amination of cyclohexene. The reaction rate measured by monitoring the disappearance of the azide ^{1}H NMR signals of a catalytic reaction of 4-nitrophenyl azide with cyclohexene catalyzed by Co(tpp) [Co(tpp)/azide/olefin, 1:10:50; in C_6D_6 at 75 °C] in the presence of **13** (5 equiv.; $k_{obs.}/[Co] = 1.76 \times 10^{-2}\ \text{M}^{-1}\ \text{sec}^{-1}$) is considerably slower than in its absence ($k_{obs.}/[Co] = 4.83 \times 10^{-2}\ \text{M}^{-1}\ \text{sec}^{-1}$; see Supporting Information).

Reaction Mechanism

It is widely accepted that aryl azides can generate metal–nitrene (imido) intermediates in the presence of a suitable metal ion. We already showed that cobalt(II) porphyrin complexes are able to activate aromatic azides for the amination of C–H bonds of saturated organic compounds under mild conditions to give secondary amines and imines, without the intermediate formation of a metal–nitrene.[24] All the kinetic data reported above support, even in the present case, the occurrence of a reversible interaction between Co(tpp) and the arylazide, as proposed in Scheme 7.

The equilibrium associated to k_1 and k_{-1} in Scheme 7 is shifted to the side of the reactants, in accord with the fact that the intermediate complex between Co(tpp) and the aryl azide is not observable. This complex can either react with cyclohexene to yield the allylic amine or loose dinitrogen in an unimolecular reaction to afford an intermediate, formulated as a true imido complex (**I**, Scheme 7), as already suggested for benzylic C–H activation.[24] We propose the imido complex to be responsible not only for the formation of diazene, but also for that of aniline for several reasons: (i) Aniline formation occurs by hydrogen abstraction, very likely from cyclohexene. Such hydrogen-abstraction reactions are typically performed by radical species and odd-electron species **I** is the most likely responsible for it. (ii) Although diazene is formed in the absence of cyclohexene, it was only obtained in trace amounts in the presence of the latter. This suggests that both aniline and diazene are derived from the same intermediate, which reacts with cyclohexene at a much faster rate than that with an azide molecule. (iii) If aniline is derived from reaction of **I**, then its formation should be inhibited by an increase in the concentration of cyclohexene. In contrast, the selectivity should not be altered if both the allylic amine and aniline originate from the azido complex. Although a detailed study of the effect on the selectivity of the cyclohexene concentration was not performed, the allylic amine selectivity in neat cyclohexene is indeed higher than that in a 50:50 mixture of cyclohexene/benzene.[17] It should be considered that even in the absence of cyclohexene, the decomposition of the azide in the presence of Co(tpp) leads to the formation of aniline as a byproduct, and we cannot exclude that its formation during the catalytic reaction may occur by other routes.

Note that any mechanism in which the aminating species is the imido complex can be completely excluded by the



Scheme 7. Proposed reaction mechanism for the allylic amination and aziridination reactions.

available data. Indeed, the formation of such a complex cannot be an equilibrium, and so only two possibilities exist for the kinetics of the reaction: either the rate of formation of the imido complex is slow relative to that of its subsequent reaction with the olefin, or it is fast. In the former case, the kinetics should be zero order in the olefin concentration. In the second, the kinetics should be zero order in the azide, and the imido complex should be spectroscopically observable. The available data are clearly not compatible with either alternative.

Application of the steady-state approximation to the intermediate arylazide–Co^{II}porphyrin complex leads, in the case of allylic amination of cyclohexene, to Equation (1):

$$V = -d[\mathrm{ArN_3}]/dt = [\mathrm{Co}][\mathrm{ArN_3}]k_1(k_2[\mathrm{C_6H_{10}}] + k_3)/(k_2[\mathrm{C_6H_{10}}] + k_3 + k_{-1}) \qquad (1)$$

From this equation we can note the following: (i) The term [Co] refers to the actual concentration of free Co(tpp). However, because both the azido complex and the imido complex are present in very-low concentrations, in practice, this term is coincident with the total cobalt concentration. Note that this would not always be true in the case of the aziridination reaction, where the concentration of the triazoline adduct is not negligible in some cases. (ii) If $k_{-1} >> k_2[\mathrm{C_6H_{10}}]$, then the kinetics would become first order in cyclohexene concentration. The fact that this is indeed what is observed indicates that this condition is met in the present system. Note that this was not the case for the related benzylic amination reactions. Equation (1) can thus be simplified to give Equation (2):

$$V = -d[\mathrm{ArN_3}]/dt = [\mathrm{Co}][\mathrm{ArN_3}]k_1\ (k_2[\mathrm{C_6H_{10}}] + k_3)/(k_3 + k_{-1}) \qquad (2)$$

(iii) Equation (2) may be further simplified in case either $k_2[\mathrm{C_6H_{10}}] >> k_3$ or $k_3 >> k_2[\mathrm{C_6H_{10}}]$. However, the experimental results clearly show that neither case occurs. This is clearly indicated by the positive slope and positive (and not negligible) intercept in the rate versus $[\mathrm{C_6H_{10}}]$ plot (Figure 2).

A similar reaction mechanism can be proposed even for the aziridination reactions. In this case, however, we should consider that the kinetics of the triazoline formation (see Supporting Information) indicate that at high olefin concentration **13** is formed at a rate that is competitive with that of the catalytic reaction and that this last compound can reversibly coordinate to Co(tpp) (Scheme 7). The equilibrium constant, $K_{\mathrm{eq.}} \approx 3.6 \times 10^{-2}\ \mathrm{mol\,L^{-1}}$, for the complex formation was calculated by ^{1}H NMR titration, which demonstrates that even if the equilibrium is shifted toward the reactants, the complex is formed even for low concentrations of **13** (see Supporting Information). Any attempt to isolate the complex in the solid state, however, failed due to the low solubility of Co(tpp) relative to that of the newly formed complex. The formation of this complex reduces the active catalyst amount and consequently the reaction rate, which thus explains the effect observed when the solution contains more than 90% (v/v) of α-methylstyrene (see Figure 3).

In a manner similar to the intermediate coordination of the azide proposed in Scheme 7, a mechanism that involves N-bound tosylimidoioninane-adduct formation as the active intermediate in the Mn^{III} corrole catalyzed aziridination reaction, in route to the Mn^{V} imido product, was recently unambiguously demonstrated in elegant work by Abu-Omar and coworkers.[33] Structurally related iodoimine adducts have also been proposed on a kinetic ground as the active intermediates in both the Mn/salen-catalyzed sulfimidation of sulfides[34] and in the Mn/porphyrin-catalyzed aziridination of olefins.[35]

Conclusions

In this paper we reported a new catalytic system for the aziridination and allylic amination of nonactivated olefins. The mechanistic aspects of the catalytic cycle of both reactions were deeply investigated and the unusual aspects were explained. Yields of the catalytic reactions are moderate to good, and kinetic and mechanistic data allowed us to propose a reasonable mechanism. In particular, we showed that in the present system, the often-postulated cobalt–imido complexes are not the intermediates in the catalytic amination reactions. The selectivity of the present Co(tpp) system is particularly high. Depending on the substrate employed, allylic amines or aziridines can be obtained.

Experimental Section

General Procedures: Unless otherwise stated, all operations were carried out under an atmosphere of purified dinitrogen by using modified Schlenk techniques. Solvents were dried and distilled before use by standard methods. Benzene, cyclohexene, cyclopentene, α-methylstyrene, and 1-octene were distilled from sodium and stored under dinitrogen. The synthesis of 4-nitrophenyl azide,[36] 4-nitrophenyldiazene,[37] 1-(4-nitrophenyl)-5-methyl-5-phenyl-1,2,3-triazoline (**13**),[15] tetraphenylporphyrin ($tppH_2$),[38] and Co(tpp)[39] were carried out as reported in the literature. ^1H and $^{13}C\{^1H\}$ NMR spectra were obtained with Bruker Avance 300-DRX or Avance 400-DRX spectrometers. Chemical shifts (ppm) are reported relative to TMS. Infrared spectra were recorded with a BIO-RAD FTS spectrophotometer. UV/Vis spectra were recorded with an Agilent 8453E instrument. Elemental analyses and mass spectra were recorded in the analytical laboratories of Milan University. All other starting materials were commercial products and used as received, unless otherwise reported.

Caution: Like hydrogen azide, many other azides are also explosive substances that decompose with the release of nitrogen through the slightest input of external energy, for example, pressure, impact, or heat, but this is not the case for the aryl azides employed in the present study.[40]

Catalytic Allylic Amination of Olefins by Co(tpp): 4-Nitrophenyl azide (100 mg, 0.61 mmol) was added to a solution of Co(tpp) (32 mg, 0.048 mmol) in a 1:1 volume mixture of the desired olefin and benzene (30 mL). The resulting red solution was heated at 75 °C until total consumption of the aryl azide (IR absorbance: $\tilde{\nu} = 2121\ cm^{-1}$, <0.03) was observed. The final mixture was evaporated to dryness in vacuo, and the products were separated by flash chromatography (*n*-hexane/ethyl acetate, see Table 1 and Supporting Information). The reaction of 4-nitrophenyl azide (0.62 mmol) in the presence of Co(tpp) (0.041 mmol) in cyclohexene (30 mL) at 84 °C was followed by UV/Vis spectroscopy. Spectra were taken at 30-min intervals. An isosbestic point at $\lambda = 322$ nm was observed.

Catalytic Aziridination of Olefins by Co(tpp): 4-Nitrophenyl azide (101 mg, 0.62 mmol) was added to a solution of Co(tpp) (8.0 mg, 0.012 mmol) in a 1:1 mixture of the desired olefin and benzene (30 mL). The resulting red solution was heated at 75 °C until total consumption of the aryl azide (IR absorbance: $\tilde{\nu} = 2121\ cm^{-1}$, <0.03) was observed. The final mixture was evaporated to dryness in vacuo, and the products were isolated by flash chromatography (*n*-hexane/CH_2Cl_2, see Table 1 and Supporting Information). The reaction of 4-nitrophenyl azide (0.61 mmol) in the presence of Co(tpp) (0.012 mmol) in α-methylstyrene (90% v/v in benzene, 30 mL) at 75 °C was followed by UV/Vis spectroscopy. Spectra were taken at 1-h intervals.

^1H NMR and UV/Vis Spectroscopic Analysis of $[Co(tpp)]_2(p\text{-}NO_2C_6H_4N{=}NC_6H_4NO_2\text{-}p)$ (15)

^1H NMR: Co(tpp) (10.3 mg, 0.015 mmol) and 4-nitrophenyl azide (2.7 mg, 0.015 mmol) were dissolved in C_6D_6 (1 mL) at 60 °C. The disappearance of the aryl azide was monitored by recording a ^1H NMR spectrum every 5 min. The absorptions due to Co(tpp) shift during the reaction. The final spectrum shows signals at: ^1H NMR (300 MHz, C_6D_6, 60 °C): $\delta = 15.64$ (br. s, 8 H), 12.92 (br. s, 8 H), 9.56 (m, 12 H), 7.82 (m, 4 H), 7.41 (m, 4 H) ppm. The ^1H NMR spectrum is identical to that of the product obtained by reaction of Co(tpp) (17.3 mg, 0.026 mmol) with 4-nitrophenyldiazene (3.7 mg, 0.013 mmol) in C_6D_6 (1 mL) at 60 °C.

UV/Vis: The reaction mixture of Co(tpp) (100 mg, 0.15 mmol) and 4-nitrophenyl azide (25.7 mg, 0.16 mmol) in benzene (30 mL) was heated at 80 °C until complete consumption of the aryl azide (UV/Vis signal at 312 nm) was observed. The UV/Vis signal at 344 nm attributed to complex **15** was observed.

Reaction of Co(tpp) with 4-Nitrophenyl Azide in the Presence of tempo Followed by ^1H NMR Spectroscopy: tempo (18.5 mg, 0.116 mmol) dissolved in C_6D_6 (0.1 mL) was added to a solution of Co(tpp) (5.1 mg, 0.0076 mmol) in C_6D_6 (0.5 mL). The solution was heated at 60 °C inside the NMR probe for 10 min [no changes in the chemical shift of the signals of the paramagnetic Co^{II}(tpp) were observed], then 4-nitrophenyl azide (13.3 mg, 0.081 mmol) dissolved in C_6D_6 (0.1 mL) was added, and the resulting red solution was heated at 60 °C inside the probe. A ^1H NMR spectrum was recorded every 5 min until complete consumption of the aryl azide. The signals due to paramagnetic Co^{II}(tpp) gradually disappeared to give rise to a new diamagnetic cobalt(III) complex. ^1H NMR (300 MHz, C_6D_6): $\delta = 9.17$ (s, 8 H), 8.15 (m, 8 H), 7.63 (m, 12 H), 1.18 (s, ca. 12 H, CH_3 tempo) ppm. Others signals due to the tempo moiety are too broadened to be attributed without uncertainty.

Reaction of Co(tpp) with 13 Followed by ^1H NMR Spectroscopy: Compound **13** (2.0 mg, 0.0075 mmol) was added to a solution of Co(tpp) (5.2 mg, 0.0076 mmol) in C_6D_6 (0.75 mL). A ^1H NMR spectrum was recorded after 5 min at room temperature. The ^1H NMR spectrum is reported in Figure 7. Among all the signals, the proton resonances at: ^1H NMR (300 MHz, C_6D_6): $\delta = 15.1$ (br. s, 8 H), 11.7 (br. s, 8 H), 9.1 (m, 12 H) ppm can be attributed to the Co(tpp) moiety.

Typical Procedures for the Determination of the Reaction Kinetics with Respect to the Azide

^{1}H NMR: Co(tpp) (2.3 mg, 0.0034 mmol) was dissolved in C_6D_6 (0.8 mL) in an NMR tube. The substrates (see Supporting Information for details) and CH_2Cl_2 (6 µL) were added, the tube was sealed under N_2, and then the sample was heated to 75 °C inside the probe. A ^{1}H NMR spectrum was recorded every 5 min.

IR: The rate constants of the reactions were measured by monitoring the change in absorbance of the band at 2121 cm^{-1} of 4-nitrophenylazide. The first-order rate constants k_{obs} were obtained by linear fits of $\ln(A/A_o)$ versus time according to the equation $\ln(A/A_o) = -k_{obs} \times t$, where A_o and A are the initial absorbance and the absorbance at the time t. For all reactions, the R^2 value is larger than 0.990.

Allylic Amination Reaction of Cyclohexene

i) Determination of the Kinetics Order with Respect to 4-Nitrophenyl Azide: Co(tpp) (13.5 mg, 0.020 mmol) was dissolved in cyclohexene (15 mL) with 4-nitrophenyl azide (53.4 mg, 0.33 mmol), and the resulting red solution was immersed in an oil bath preheated at 75 °C. The consumption of the aryl azide was monitored by recording an IR spectrum every 15 min.

ii) Determination of the Kinetics Order with Respect to Co(tpp): Co(tpp) was dissolved in cyclohexene (30 mL) with 4-nitrophenyl azide (100 mg, 0.61 mmol), and the resulting red solution was immersed in an oil bath preheated at 75 °C following the consumption of the aryl azide. An IR spectrum was recorded every 15 min. The same reaction was repeated four times with four different amounts of Co(tpp) (7.1 mg, 0.0102 mmol; 13.6 mg, 0.0201 mmol; 27.8 mg, 0.0414 mmol; 34.1 mg, 0.0508 mmol).

iii) Determination of the Kinetics Order with Respect to Cyclohexene: Co(tpp) (27 mg, 0.040 mmol) was dissolved in the solvent mixture (30 mL) with 4-nitrophenyl azide (100 mg, 0.61 mmol), and the resulting red solution was immersed in an oil bath preheated at 75 °C. The consumption of the aryl azide was monitored by recording an IR spectrum every 15 min. The same reaction was repeated six times with different ratios of the cyclohexene/benzene solvent mixture (30:0, 22.5:7.5, 15:15, 8.6:21.4, 4.5:25.5, 0:30 mL).

Aziridination Reaction of α-Methylstyrene

i) Determination of the Kinetics Order with Respect to 4-Nitrophenyl Azide: Co(tpp) (8.6 mg, 0.013 mmol) was dissolved in α-methylstyrene/benzene (1:3, 30 mL) with 4-nitrophenyl azide (101.4 mg, 0.618 mmol), and the resulting red solution was immersed in an oil bath preheated at 75 °C. The consumption of the aryl azide was monitored by recording an IR spectrum every 15 min.

ii) Determination of the Kinetics Order with Respect to Co(tpp): Co(tpp) was dissolved in α-methylstyrene/benzene (1:3, 30 mL) with 4-nitrophenyl azide (100 mg, 0.61 mmol), and the resulting red solution was immersed in an oil bath preheated at 75 °C following the consumption of the aryl azide. An IR spectrum was recorded every 15 min. The same reaction was repeated four times with four different amount of Co(tpp) (8.6 mg, 0.013 mmol; 16.8 mg, 0.025 mmol; 24.5 mg, 0.037 mmol; 32.8 mg, 0.049 mmol).

iii) Determination of the Kinetics Order with Respect to α-Methylstyrene: Co(tpp) (8.6 mg, 0.013 mmol) was dissolved in the solvent mixture (30 mL) with 4-nitrophenyl azide (100 mg, 0.61 mmol), and the resulting red solution was immersed in an oil bath preheated at 75 °C. The consumption of the aryl azide was monitored by recording an IR spectrum every 15 min. The same reaction was repeated six times with different ratios of the α-methylstyrene/benzene solvent mixture (30:0, 28.5:1.5, 27:3, 22.5:7.5, 15:15, 7.5:22.5 mL).

Supporting Information (see footnote on the first page of this article): Representative experimental procedures and characterization data and kinetic graphics.

Acknowledgments

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