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The (Porphyrin)ruthenium-Catalyzed Aziridination of Olefins Using Aryl Azides as Nitrogen Sources

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Aryl azides have been used as atom-efficient nitrene transfer reagents in the (porphyrin)ruthenium-catalyzed amination of olefins. Several azides, olefins and [Ru(porphyrin)CO] complexes were tested to investigate the scope and limits of the reaction. Quantitative yields and short reaction times were achieved by using terminal olefins and aryl azides bearing electron-withdrawing groups on the aryl moiety. The reactions were influenced by steric factors. Internally disubstituted olefins exhibited a lower reactivity and tri- and tetrasubstituted olefins did not react at all. A very high turnover number (TON) for the [Ru(TPP)CO] (TPP = tetraphenylporphyrin dianion) catalyzed amination of α-methylstyrene by *p*-nitrophenyl azide was obtained.

Introduction

The development of new methods for the direct and selective synthesis of organonitrogen compounds represents an important goal for both academia and industry. Aziridines exhibit various biological properties,[1–3] and they are useful building blocks in organic synthesis[4–10] due to easy opening of the three-membered ring.[11–15] Two of the most effective routes for the synthesis of this class of compound are the carbene transfer reaction to imines[16–20] and the nitrene transfer to olefins.[4] The direct aziridination of unsaturated hydrocarbons has been extensively studied by employing [*N*-(arylsulfonyl)imino]phenyliodinane compounds [PhI=N(SO_2)Ar][21–26] as nitrogen sources which can be prepared in situ from the corresponding sulfonylamine and iodosylbenzene[27] or (diacetoxyiodo)benzene.[28–31] It should be noted that by using these synthetic procedures the side-product of the reaction is iodobenzene, and a sulfonyl group is always introduced into the aminated compound. To overcome some of the limitations associated with the use of iminoiodinane compounds, alternative nitrene sources such as chloramine-T[32–35] or bromamine-T[36–39] have been employed. In any case, the *N*-protecting group is a sulfonyl derivative.

In the last few years the use of organic azides RN_3 as nitrogen sources has been explored due to the high synthetic versatility of this class of molecules. The lability of the N^{α}–N^{β} bond of the N_3 group allows the generation of a nitrene [RN] with the ecofriendly molecular nitrogen being the only reaction side-product. Therefore, organic azides can be considered as atom-efficient nitrene transfer reagents. Nitrene transfer from RN_3 to an organic substrate can be performed by thermal[40] or photochemical activation,[41,42] but very often the chemoselectivity of the reaction is low. On the other hand, the presence of transition-metal catalysts can drive the amination reaction to the desired product under milder conditions. Recently, several reviews on the use of organic azides as nitrogen sources in amination reactions have been published.[43–46] Very interesting results were achieved by using tosyl azide,[45,47–50] 2-(trimethylsilyl)ethanesulfonyl azide[51] and diphenylphosphoryl azide[52] as nitrene precursors even in enantioselective reactions.

In the last few years we have reported on the use of aryl azides as aminating agents. They represent very convenient reagents because (i) they can be easily synthesized from the corresponding substituted anilines by a simple procedure, (ii) they allow the introduction of a great variety of *N*-aryl groups into the molecule and (iii) they are stable enough to be safely handled in the laboratory. Moreover, it is important to point out that the aryl group on the aziridine nitrogen atom should be considered as part of the molecule that can play an important role in further aziridine rearrangements.[53,54]

Aryl azides react with benzylic C–H bonds to form amines and imines,[55,56] with conjugated dienes to give *N*-aryl-2-vinylaziridines[54] and with styrenes to form *N*-arylaziridines.[57] The amination reactions of benzylic com-

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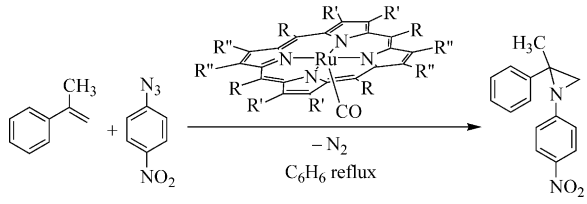
pounds are catalyzed by [Co(porphyrin)] complexes and the aziridination reactions are efficiently catalyzed by [Ru(porphyrin)CO] complexes.

Herein we report a full account of our synthetic results on the amination of olefins by aryl azides catalyzed by carbonyl(porphyrin)ruthenium complexes. A preliminary communication on this reaction, mainly concerning the mechanistic aspects of the reaction, has already been published.[57] The effect of the coordination sphere of the ruthenium atom on the catalytic activity has been investigated in detail. To extend the scope of the reaction, we have also studied the effect of different functional groups on the azide and the olefin on the reaction efficiency.

Results and Discussion

To study the effect on the catalytic activity of the electronic and/or steric behaviour of different substituents on (porphyrin)ruthenium complexes, the reaction between α-methylstyrene and *p*-nitrophenyl azide was carried out in the presence of several catalysts (Scheme 1, Table 1).



Scheme 1. Aziridination reaction of α-methylstyrene by *p*-nitrophenyl azide catalyzed by [Ru(porphyrin)CO] complexes.

Table 1. Aziridination reaction of α-methylstyrene by *p*-nitrophenyl azide catalyzed by [Ru(porphyrin)CO] complexes **1**–**13**.[a]

Entry	Catalyst	R	R′	R″	Time [h][b]	Selectivity [%][c]
1	**1**	C_6H_5	H	H	0.75	99
2	**2**	C_6H_5	Br	H	0.5	98
3	**3**	C_6H_5	Ph	H	0.5	99
4	**4**	H	Et	Et	1.5	96
5	**5**	4-$CF_3C_6H_4$	H	H	0.5	98
6	**6**	4-$CH_3OCOC_6H_4$	H	H	0.75	93
7	**7**	4-ClC_6H_4	H	H	1	95
8	**8**	4-*n*BuC_6H_4	H	H	1	99
9	**9**	4-FC_6H_4	H	H	1.5	98
10	**10**	4-*t*BuC_6H_4	H	H	1.5	94
11	**11**	3,5-$(CF_3)_2C_6H_3$	H	H	1	97
12	**12**	2,4,6-$(CH_3)_3C_6H_2$	H	H	2	95
13	**13**	4-$CH_3OC_6H_4$	H	H	2	88

[a] General procedure for the reaction: catalyst (1.20×10^{-2} mmol) in refluxing benzene (30 mL), molar ratio catalyst/azide/olefin = 1:50:250. [b] Time required for complete conversion of the starting azide. [c] Determined by ^{1}H NMR (2,4-dinitrotoluene used as the internal standard) on complete conversion of the starting azide.

All catalysts employed for the reactions reported in this study were dried in vacuo at 120 °C for 3 h before use. This procedure had been shown earlier to be effective in removing all coordinated water without decomposing the catalyst.[58] In fact, if the sample was not dried at a high temperature, a decrease in the reaction rate was observed owing to the presence of variable amounts of the less active [Ru(porphyrin)CO(H_2O)] complex.

As reported in Table 1, the presence of β-substituted pyrrolic moieties in the tetraphenylporphyrin skeleton yielded high aziridine selectivities in short reaction times (Entries 2 and 3, Table 1). It is important to point out that if a hydrogen atom is present in the *meso*-porphyrin position, as in the case of [Ru(OEP)CO] (**4**) (OEP = octaethylporphyrin dianion) (Entry 4, Table 1), this positive catalytic effect is suppressed. Complex **4**, with flexible ethyl groups, is probably able to stack more efficiently than (*meso*-substituted porphyrin)ruthenium complexes, thus reducing the access of organic substrates to the active metal centre. The effect of the ethyl groups on the overall packing of (porphyrin)-ruthenium complexes has already been reported.[59]

Several *para*-substituted *meso*-arylporphyrins were also tested. Although precise kinetic measurements were not taken at this stage, it is apparent that electron-withdrawing groups on the *meso*-aryl moiety accelerate the reaction. However, if substituents are placed at the *meta* or *ortho* positions of the *meso*-aryl groups, steric effects also become evident. In fact, the rate of the reaction catalyzed by **11** (Entry 11, Table 1) is lower than may have been expected based on the high electron-withdrawing power of the two CF_3 groups. Not surprisingly, complex **12**, which is deactivated both electronically and sterically, is a less active catalyst. The catalytic behaviour of the methoxy-substituted (porphyrin)ruthenium complex **13** (Entry 13, Table 1) deserves special comment.

It is common for a catalytic cycle to be negatively affected by the presence of a coordinating group, such as OCH_3, which can compete with the organic substrate for the metal centre. Therefore, it is not surprising that the rate of the **13**-catalyzed reaction is lower than those observed by using catalysts containing non-coordinating electron-donating groups (Entries 8 and 10, Table 1).

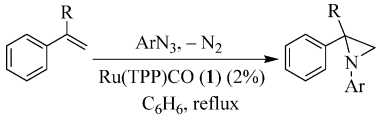
In order to mimic the effect of a methoxy group linked to an aryl ring, such as that present in the ruthenium complex **13**, the **1**-catalyzed reaction between *p*-nitrophenyl azide and α-methylstyrene was carried out in the presence of 4-methylanisole by using a catalytic molar ratio **1**/azide/4-methylanisole/olefin of 1:50:50:250. The consumption of the azide was monitored by IR spectroscopy, measuring the intensity of the 2121 cm^{-1} absorption of the N_3 group. The A/A_0 vs. time dependence of the [Ru(TPP)CO]-catalyzed reactions of *p*-nitrophenyl azide with α-methylstyrene in the presence or absence of 4-methylanisole was measured. The reaction rate was 2.5 times lower when 4-methylanisole was added to the reaction mixture, which indicates competition for the ruthenium centre between the methoxy group of 4-methylanisole and the N_3 group of the aryl azide.

We then investigated the reactivity of different aryl azides by using styrene or α-methylstyrene as olefins and [Ru(TPP)-CO] (**1**) as the catalyst (Scheme 2, Table 2). [Ru(TPP)CO] was chosen because it is the synthetically most accessible of the complexes found to have a high catalytic activity.

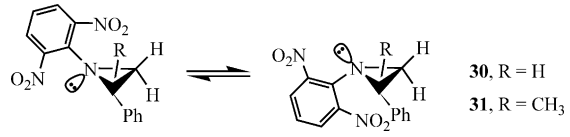
Table 2. Aziridination reactions of styrene and α-methylstyrene by different aryl azides catalyzed by **1**.[a]

Entry	Ar	R = H			R = CH_3		
		Time [h][b]	Selectivity [%][c]	Product	Time [h][b]	Selectivity [%][c]	Product
1	4-$O_2NC_6H_4$	1.2	99	**14**	0.75[d]	99[d]	**15**
2	4-ClC_6H_4	2	90	**16**	1	95	**17**
3	4-BrC_6H_4	2	95	**18**	1.5	94	**19**
4	4-NCC_6H_4	2	94	**20**	1	99	**21**
5	4-$CH_3OC_6H_4$	4	69	**22**	6	54	**23**
6	4-$CH_3C_6H_4$	4	40	**24**	2.5	30	**25**
7	4-*t*BuC_6H_4	4	90	**26**	4	96	**27**
8	2-$O_2NC_6H_4$	3.2	93	**28**	3	91	**29**
9	2,6-$(O_2N)_2C_6H_3$	3.5	99[e]	**30**	3.5	90[f]	**31**
10	3,5-$(CF_3)_2C_6H_3$	1	99	**32**	0.5	97	**33**
11	3,5-$Cl_2C_6H_3$	1.3	96	**34**	1	93	**35**
12	3,4,5-$(CH_3O)_3C_6H_2$	3	85	**36**	2.5	90	**37**

[a] General procedure for the reaction: **1** (9.0 mg, 1.20×10^{-2} mmol) in refluxing benzene (30 mL); molar ratio **1**/azide/olefin = 1:50:250. [b] Time required for complete conversion of the starting azide. [c] Determined by ^{1}H NMR (2,4-dinitrotoluene was used as the internal standard). [d] These data, already present in Table 1 (Entry 1), are reported here for a better comparison of the experimental results. [e] The ^{1}H NMR spectrum showed the presence of both 1,2-*trans*/*cis* isomers in a ratio of 83:17. [f] Only the 1,2-*trans* isomer was obtained.



Scheme 2. Aziridination reactions of styrene and α-methylstyrene by different aryl azides catalyzed by **1**.



Scheme 3. The pyramidal inversion of the nitrogen atom in compounds **30** and **31**.

The data reported in Table 2 suggest that the results depend on both the electronic and the steric characteristics of the azide. In general, the presence of electron-withdrawing groups on the aryl moiety of the azide is responsible for high aziridine selectivities and short reaction times. The best results were observed by using *para*- or *meta*-substituted aryl azides (Entries 1–4 and 10 and 11, Table 2). The use of *ortho*-substituted aryl azides (Entries 8 and 9, Table 2), in which the N_3 group is sterically hindered, resulted in longer reaction times. It is worth noting that the 1,2-*trans* and -*cis* isomers of compound **30** are observable as separate products in a ratio of 83:17 in the ^{1}H NMR spectrum. The pyramidal inversion of the aziridine nitrogen atom is a very well-known process,[60] and usually the interconversion occurs at room temperature because the energy barrier is relatively small (ca. 25 kJ/mol). But if, for any reason, the energy barrier increases, it would be possible to isolate both the *cis* and *trans* isomers. The steric hindrance around the *N*-aryl group in the case of **30** probably increases the barrier to *cis*/*trans* inversion of the aziridine nitrogen atom relative to those of the other aziridines reported in Table 2 (Scheme 3).[6] The reaction of 2,6-$(O_2N)_2$-$C_6H_3N_3$ with α-methylstyrene yielded only the 1,2-*trans* isomer **31** (Entry 9, Table 2).

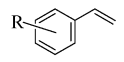
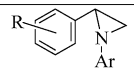
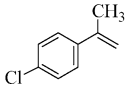
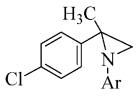
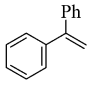
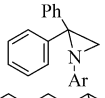
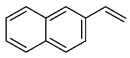
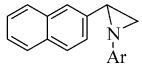
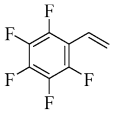
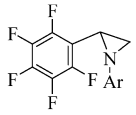
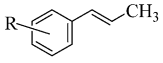
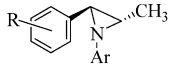
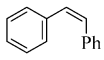
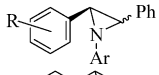
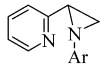
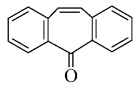
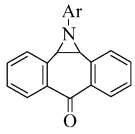
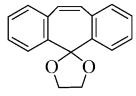
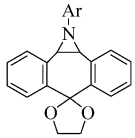
The correlation observed between the electronic characteristics of the aryl azides and the synthetic results reveals the electrophilic role of the azide in the catalytic cycle. Furthermore, as reported in Table 2, α-methylstyrene always exhibited better reactivity than styrene. This could be due to the presence of the methyl group at the α position of the double bond which can stabilize the transient positive charge density formed during the nucleophilic attack of the azide by the olefin.

On the other hand, the presence of an electron-donating group in the *para* position of the aryl group (Entries 6 and 7, Table 2) is responsible for longer reaction times and a decrease in aziridine selectivity. When the electron-donating group is also a coordinating one, such as the methoxy group (Entries 5 and 12, Table 2), this negative effect is enhanced for all the reasons illustrated above. This effect is more pronounced with 4-$CH_3OC_6H_4N_3$ than with 3,4,5-$(CH_3O)_3$-$C_6H_2N_3$ due to the better coordinating capability of an unhindered methoxy group compared with three adiacent ones. When the aziridination reaction was performed with 4-$CH_3OC_6H_4N_3$ and 4-$CH_3C_6H_4N_3$ (Entries 5 and 6, Table 2), the corresponding aniline was the major by-product of the reaction.

The amination reactions of styrene and α-methylstyrene were also performed in the presence of **1** with non-aromatic azides such as benzoyl azide, trimethylsilyl azide and triphenylmethyl azide. With benzoyl azide the corresponding aziridine was formed only in trace amounts. No reaction was observed by employing the other two azides which confirms the electrophilic role of the azide.

In order to extend the scope of the reaction, we employed *p*-nitrophenyl azide to aminate, in the presence of **1**, several olefins. The reactions that gave positive results are reported in Table 3; with tri- or tetrasubstituted olefins such as (*E*)-β-methyl-β-nitrostyrene, 2-methyl-1-phenyl-1-propene, α-methylstilbene and tetraphenylethylene, no reaction was observed.

Table 3. Aziridination reaction of different olefins by *p*-nitrophenyl azide catalyzed by **1**.[a]

Entry	Olefin	Product		Time [h][b]	Selectivity [%][c]
1			**38**, R = 4-CH_3	0.75	93
			39, R = 3-Cl	1.35	98
			40, R = 4-Cl	1.2	97
2			**41**	0.75	96
3			**42**	0.75	95
4			**43**	1	89
5			**44**	6	92
6			**45**, R = H	4.5	54
			46, R = 4-CH_3O	1.25	92
7[d]			**47**	32	33
8			**48**	3	85
9			**49**	2	95
10			**50**	16	48

[a] General procedure for the reaction: **1** (9.0 mg, 1.20×10^{-2} mmol) in refluxing benzene (30 mL); molar ratio **1**/*p*-nitrophenyl azide/olefin = 1:50:250. [b] Time required for complete conversion of the starting azide. [c] Determined by ^{1}H NMR (2,4-dinitrotoluene was used as the internal standard). [d] The ^{1}H NMR spectrum showed the presence of both 2,3-*cis*/*trans* isomers in a ratio of 3:1.

The reaction efficiency depended on both the electronic and the steric characteristics of the olefins. The best catalytic results were observed by using terminal styrenes bearing electron-donating substituents either at the α position of the double bond (Entry 1, Table 1 and Entries 2 and 3, Table 3) or on the aryl moiety (Entry 1, Table 3, compound **38**), which again indicates the electrophilic role of the azide in the reaction. This hypothesis is in agreement with the very low reactivity of the electron-deficient 2,3,4,5,6-pentafluorostyrene (Entry 5, Table 3).

On the other hand, the presence of substituents on the β-carbon atom of the double bond (Entries 6 and 7, Table 3) produces a lowering of the yields and longer reaction times for steric reasons. It should be noted that **46** is formed in good yield and in a short reaction time in spite of the presence of a methyl group on the β-carbon atom and of a methoxy group on the aryl moiety (Entry 6, Table 3). This experimental result suggests that in this case the electron-donating capability of the methoxy group strongly promotes the reaction and balances the negative catalytic effect arising from the presence of steric hindrance on the double bond and of a coordinating group on the aryl moiety.

In accord with the poor reactivity of internal olefins, the aziridine of (*Z*)-stilbene was obtained in a low yield and after a very long reaction time (Entry 7, Table 3); again the aniline is the by-product of the reaction. The lack of stereospecificity of the reaction between *p*-nitrophenyl azide and (*Z*)-stilbene indicates a two-step mechanism, which allows isomerization to proceed, rather than a concerted nitrogen atom transfer (Entry 7, Table 3).[23,61] Nevertheless, with (*E*)-β-methylstyrenes, the aziridination reaction is stereospecific probably because, in the stepwise process, the rate of ring closure is fast relative to the rate of C^{α}–C^{β} bond rotation (Entry 6, Table 3).

The reaction of 2-vinylpyridine with *p*-nitrophenyl azide occurred in 3 h with an aziridine selectivity of 85% despite the presence of a coordinating pyridine unit (Entry 8, Table 3). In this case, the inhibiting effect is probably not significant because of the low accessibility of the pyridine nitrogen atom. In fact, if 4-vinylpyridine, in which coordination is sterically not inhibited, was used as the unsaturated substrate, no reaction would be observed.

In contrast with the low reactivity of (*Z*)-stilbene, 5-dibenzosuberenone reacted with *p*-nitrophenyl azide to yield

Table 4. Optimization of the catalyst loading of **1** for the reaction of α-methylstyrene with *p*-nitrophenyl azide.[a]

Entry	**1** [mol-%]	Molar ratio **1**/azide/olefin	Time [h][b]	Conversion [%][c]	Selectivity [%][d]	TON
1	2	1:50:250	1	100	99	50
2	0.4	1:250:1250	4	100	97	250
3	0.2	1:500:2500	6	96.5	95	482
4	0.1	1:1000:5000	10	96.5	95	965
5	0.04	1:2500:12500	25	92.5	92	2300

[a] General procedure for the reaction: catalyst **1** was refluxed in benzene (60 mL) with α-methylstyrene (0.8 mL, 6.15 mmol) and *p*-nitrophenyl azide (200 mg, 1.22 mmol). [b] Time required for the reported conversion of the starting azide. [c] Determined by IR spectroscopy measuring the absorbance of the azide band at 2121 cm^{-1}. [d] Determined by ^1H NMR (2,4-dinitrotoluene was used as the internal standard).

the corresponding aziridine with a high selectivity in a short time (Entry 9, Table 3). We presume that the presence of a conjugated carbonyl group can drive the reaction and that a different mechanism is involved.[62] As a matter of fact, when the carbonyl group of 5-dibenzosuberenone was protected as a cyclic ketal (Entry 10, Table 3), the reaction slowed down considerably and also the selectivity dropped. Compound **50** has only been characterized in solution because it hydrolyzed to **49** during attempts to purify it by chromatography in the presence of Et_3N in the eluent (see Exp. Sect.). Since the reaction had been performed to provide mechanistic information rather than to obtain a new compound, no further attempt to isolate pure **50** was made.

Overall, the trends in reactivity observed with different olefins strongly point to an *end-on* approach of the olefin towards the electrophilic aminating species. This is also in full agreement with the higher reactivity of aryl azides bearing electron-withdrawing groups and the better catalytic performances of (porphyrin)ruthenium complexes having electron-withdrawing substituents.

Figure 1 shows a plausible transition state for the reaction which accounts for all the experimental observations discussed.

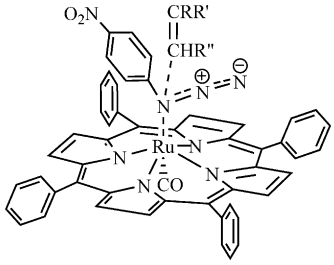


Figure 1. Proposed transition state for the aziridination reaction catalyzed by **1**.

We propose the formation of an azido(porphyrin)ruthenium(II) adduct, [(ArN_3)Ru^{II}(porphyrin)(CO)], instead of an imido(porphyrin)ruthenium(IV) complex, [ArN=Ru^{IV}(porphyrin)(L)],[51,63] obtained by N_2 loss from a metal azide adduct on the basis of a preliminary kinetic study that indicated that the first step of the reaction is an equilibrium and not an irreversible step. Any attempt to spectroscopically observe the species [(ArN_3)Ru(TPP)(CO)] failed. Evidence that an imidometal complex is not always the group transfer reagent has already been provided by the amination of benzylic groups and by the aziridination of styrenes catalyzed by [Co^{II}(porphyrin)][55,56] and [Mn^{III}(corrole)][64] complexes, respectively.

The pocket conformation of the azide moiety prevents a close approach of the whole hydrocarbon molecule and accounts for the effect that the steric hindrance of the R′′ group has on the reaction rate and selectivity. We do not discuss the mechanistic aspects of this reaction in this paper because we are still investigating them, and a complete study will be reported in a following paper.[65]

All the catalytic reactions described up to now in this paper were carried out with 2 mol-% catalyst. Although this is a suitable amount on a laboratory scale, a lower catalyst loading would be preferable for industrial applications. We have thus studied the effect of decreasing amounts of catalyst on the aziridination reaction between *p*-nitrophenyl azide and α-methylstyrene catalyzed by **1** taken as a model case. The results are reported in Table 4.

Although the selectivity was reduced at high catalytic ratios, 92% selectivity in the aziridine was observed even when only 0.04 mol-% of catalyst was employed (Entry 5, Table 4). It is important to point out that, to the best of our knowledge, the resulting turnover number (TON) of 2300 is the highest value reported for the intermolecular aziridination of olefins[31,50,51,66] and is compatible with an application in the fine chemicals industry.

Conclusions

We have investigated the synthetic applicability of aryl azides as nitrogen sources for the aziridination of olefins. Data collected indicate that by using this methodology a wide range of aziridines can be obtained as it is possible to introduce several functional groups onto both the azide and the olefin. In several cases the high selectivity achieved allows the aziridine to be obtained as the only reaction product, which confirms the atom efficiency of the reaction. It is important to point out that the large turnover number of 2300 observed in one case also minimizes the problems associated with catalyst recovery and allows the reaction crude to be used for further aziridine modifications. The presence of different substituents on the nitrogen atom and at other positions in the ring allows the aziridines reported in this paper to be employed in the synthesis of organic compounds of biological importance.[9] Further studies will be directed towards this goal.

Experimental Section

General: ^{1}H NMR spectra were recorded with an Avance 300-DRX Bruker instrument operating at 300 MHz for ^{1}H, at 75 MHz for ^{13}C and at 282 MHz for ^{19}F and with an Avance 400-DRX Bruker instrument operating at 400 MHz for ^{1}H and at 100 MHz for ^{13}C. Chemical shifts (ppm) are reported relative to TMS. The ^{1}H NMR signals of compounds described in the following have been assigned by COSY and NOESY techniques. Assignments of the resonances in the ^{13}C NMR spectra were made by using the APT pulse sequence, HSQC and HMQC techniques. Infrared spectra were recorded with a BIO-RAD FTS or with a Varian Scimitar FTS 1000 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. Unless otherwise specified, all reactions were carried out under nitrogen by employing standard Schlenk techniques and magnetic stirring. Solvents were dried prior to use by standard procedures and stored under nitrogen. All starting materials were commercial products and were used as received unless otherwise reported. Aryl azides,[67–69] *meso*-tetraphenylporphyrins,[70,71] β-substituted *meso*-tetraphenylporphyrins[72,73] and their ruthenium complexes,[54,74,75] were synthesized according to methods reported in the literature or by using minor modifications of them. [Ru(OEP)(CO)] (Aldrich) was used as received. The purity of the azides and olefins employed was checked by GC-MS or ^{1}H NMR analyses. The [Ru(porphyrin)(CO)] complexes employed were kept under vacuum at 120 °C for 3 h prior to use. The collected analytical data for *N*-(4-chlorophenyl)-2-phenylaziridine (**16**)[76] and *N*-(4-cyanophenyl)-2-phenylaziridine (**20**)[77] are in agreement with those reported in the literature.

Synthesis of [Ru(β-Ph$_4$TPP)(CO) (3)]: [$Ru_3(CO)_{12}$] (30.0 mg, 4.69×10^{-5} mol) and β-Ph$_4$TPPH$_2$[73] (50.2 mg, 5.47×10^{-5} mol) were dissolved in dry toluene (30 mL), and the resulting purple solution was refluxed under nitrogen for 18 h. Oxidation of the crude by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)[78] followed by solvent evaporation and purification by flash chromatography on silica (eluent *n*-hexane/dichloromethane, 8:2) yielded pure [Ru(β-Ph$_4$TPP)(CO)] (37.2 mg, 65%). ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 8.24 (s, 4 H, H$^\beta$), 7.75–7.68 (m, 8 H, H$_{Ar}$), 7.19–6.78 (m, 32 H, H$_{Ar}$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = 147.7 (C), 146.7 (C), 142.1 (C), 141.5 (C), 139.2 (C), 135.6 (CH), 135.0 (CH), 132.6 (CH), 132.2 (CH), 127.4 (CH), 127.1 (CH), 126.8 (CH), 126.3 (CH), 126.1 (CH), 125.6 (CH), 123.3 (C) ppm. $C_{69}H_{44}N_4ORu$ (1046.2): calcd. C 79.22, H 4.24, N 5.36; found C 79.60, H 4.42, N 5.11. IR (neat, ATR cell): $\tilde{\nu}$ = 1955 (CO), 1006 (oxidation marker) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (logε_M) = 419 (5.2), 538 (4.4) nm. MS (ESI): *m*/*z* = 1069 [M + Na]$^+$.

General Procedure for Catalytic Reactions: In a typical run, the catalyst (1.20×10^{-2} mmol) and the azide (6.10×10^{-1} mmol) were added to a solution of the olefin (3.08 mmol) in dry benzene (30 mL). The reaction solution was then refluxed by using a preheated oil bath. The consumption of the azide was monitored by TLC up to the point that its spot was no longer observable, and then by IR spectroscopy measuring the characteristic azide absorbance in the region 2095–2130 cm^{-1}. The reaction was considered to be finished when the absorbance of the azide measured was below 0.03 (using a 0.5 mm thick cell). The solution was then concentrated to dryness and analyzed by ^{1}H NMR with 2,4-dinitrotoluene as an internal standard. The residue was purified by flash chromatography on deactivated silica using 10% Et_3N in the eluent (*n*-hexane/ethyl acetate) during the packing of the column. All the reaction times, azide conversions and aziridine selectivities are reported in Tables 1, 2, and 3. Analytical data for compounds **14**–**49** are reported in the Supporting Information.

Cyclic Ethyl Ketal of 5*H*-Dibenzo[*a*,*d*]cyclohepten-5-one: 5*H*-Dibenzo[*a*,*d*]cyclohepten-5-one (506 mg, 2.45 mmol) was refluxed in toluene (50 mL) with ethylene glycol (10 mL, 180 mmol) and *p*-toluenesulfonic acid (51 mg, 0.270 mmol) for 10 h. During the reaction, the Dean–Stark apparatus was used for continuous removal of the water. Then the reaction mixture was washed with water (3×10 mL), and the solvents were evaporated to dryness to yield the title compound (550 mg, 90%). ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.96–7.93 (m, 2 H, Ar*H*), 7.46–7.36 (m, 6 H, Ar*H*), 7.14 (s, 2 H, CH_2), 4.17 (br., 2 H, CH_2), 3.82 (br., 2 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = 138.5 (C), 133.7 (C), 131.5 (CH), 129.8 (CH), 128.4 (CH), 128.1 (CH), 124.4 (CH), 66.0 (CH_2), 64.0 (CH_2) ppm. $C_{17}H_{14}O_2$ (250.3): calcd. C 81.58, H 6.64; found C 80.35, H 6.49. MS (EI): *m*/*z* = 250 [M$^+$].

Kinetic Measurements: Complex **1** (9.1 mg, 12.3 μmol), *p*-nitrophenyl azide (101.1 mg, 0.617 mmol) and α-methylstyrene (400 μL, 3.08 mmol) were added to benzene (30 mL) in a Schlenk flask under N_2. The solution was stirred for 1 min to dissolve all the reagents, and then a sample (0.2 mL) was withdrawn for IR analysis. The consumption of the azide was monitored by IR spectroscopy, measuring the azide absorbance at 2121 cm^{-1}, by withdrawing samples of the solution at regular times. The absorbance of the azide was below 1% of the starting value after 1.5 h. The reaction was repeated in the presence 4-methylanisole. Complex **1** (9.0 mg, 12.1 μmol), *p*-nitrophenyl azide (99.5 mg, 0.607 mmol), 4-methylanisole (80 μL, 0.635 mmol) and α-methylstyrene (400 μL, 3.08 mmol) were added to benzene (30 mL) in a Schlenk flask under N_2. The procedure reported above was followed. The absorbance of the azide was below 1% of the starting value after 4 h (the graphics are reported in the Supporting Information).

Supporting Information (see footnote on the first page of this article): Analytical data for all reaction products and kinetic graphics.

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