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The [Ru(CO)(porphyrin)]-Catalyzed Synthesis of *N*-Aryl-2-vinylaziridines

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[Ru(CO)(porphyrin)] complexes have been found to catalyze the direct aziridination of conjugated dienes by aryl azides with high chemoselectivity, to provide *N*-aryl-2-vinylaziridines. To determine the scope of the reaction, several hydrocarbons and azides were tested. The reactions between 2,3-dimethylbuta-1,3-diene and aryl azides bearing electron-withdrawing groups in the *para* or *meta* positions in their aryl moieties occur very efficiently in short times, while the selectivities of the aziridinations are governed by the steric hindrances of the double bonds, so lower yields are registered with sterically encumbered 1,4-disubstituted dienes, though it is worth noting that the aziridination of *trans*,*trans*-1,4-diphenylbuta-1,3-diene was stereospecific and that only one isomer was obtained. The aza-[3,3]-Claisen rearrangement of 2-isopropenyl-2-methyl-*N*-(4-nitrophenyl)aziridine to produce the corresponding 2,5-1*H*-benzo[*b*]azepine is also reported.

Introduction

Vinylaziridines are useful building blocks in organic synthesis thanks to the simultaneous presence of both an aziridine ring and a double bond. The versatility of vinylaziridines is due to ring-opening[1–4] or ring-expansion[5–8] reactions that are responsible for the formation of both natural and non-natural products such as alkaloids,[9–11] β-lactams,[12,13] and allylamines.[14–16]

Most of the reported synthetic routes to 2-vinylaziridines – which include ring-closure of amino alcohols,[17,18] aminolysis of epoxides,[5,15] aziridination of allylic carbonates,[19] and functionalization of aziridines[20] – require several steps. Reactions between imines and ylides[21–28] represent one of the best studied methodologies for the production of vinylaziridines, but can only be applied with activated imines in which an electron-withdrawing group, such as *p*-tolylsulfonyl (tosyl), diphenylphosphanyl (DPP), or 2-(trimethylsilyl)ethylsulfonyl (SES), is bound to the nitrogen atom.[23] Therefore, to synthesize *N*-aryl- or *N*-alkyl-2-vinylaziridines, it is necessary either to enhance the reactivity of the imines by adding a Lewis acid[25] to activate the C=N bond, or to use more reactive ylides.[21,22] In any event, a synthetic limitation of this methodology is the strong base used to generate the ylide, which could be incompatible with several functional groups. As a matter of fact, the *N*-aryl-2-vinylaziridines reported in the literature always have an unsubstituted phenyl group on the aziridine nitrogen and a trimethylsilyl group on a vinylic position.

An alternative synthetic strategy, the direct aziridination of dienes by treatment with nitrido complexes[29] or PhI=NTs,[30,31] occurs with low regio- and chemoselectivities.

Widespread use of vinylaziridines is hampered not only by the lack of efficient and general routes for their preparation but also by the difficulties encountered in their purification. The chemical stability of a vinylaziridine largely depends on the nature of the substituent on its aziridine nitrogen,[32–35] with reactivity towards nucleophiles being promoted by the presence of an electron-withdrawing group on the nitrogen atom[3,34] whereas a rearrangement frequently occurs when a *N*-aryl group is present in the molecule.[36,37]

Organic azides[38] – in particular sulfonyl[39,40] and aryl azides[41,42] – represent a versatile class of aminating agents. They can be regarded as atom-efficient nitrogen atom transfer agents because their decomposition generates the nitrene functionality and molecular nitrogen as the only side product.

The uncatalyzed intramolecular azide-olefin cycloaddition reaction provides several *N*-heterocyclic compounds by vinylaziridine formation,[41–43] but the analogous intermolecular reactions occur with control over regioselectivity only in the presence of metal complexes.

We have recently reported that aryl azides are effective aminating agents for styrenes, to form *N*-arylaziridines,[44] and for benzylic C–H bonds, to form amines and imines.[45,46] The aziridination reaction is catalyzed by [Ru(CO)(TPP)] (**1**; TPP = dianion of tetraphenylporphyrin),

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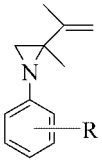
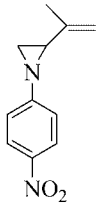
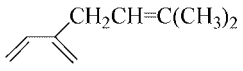
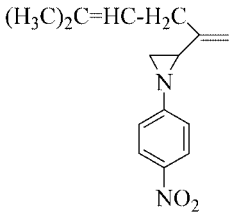
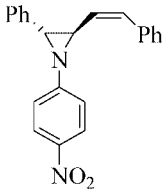
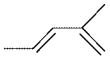
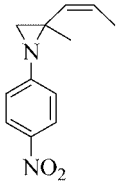
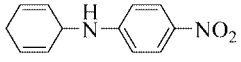
whereas the amination of benzylic compounds is catalyzed by [Co^{II}(porphyrin)] complexes.

In order to extend the scope of our methodology we have investigated [Ru(CO)(porphyrin)] complex-catalyzed reactions between aryl azides and conjugated dienes to synthesize *N*-aryl-2-vinylaziridines. Here we report the results of this study, together with the aza-[3,3]-Claisen rearrangement of 2-isopropenyl-2-methyl-*N*-(4-nitrophenyl)aziridine to the corresponding 2,5-1*H*-benzo[*b*]azepine.

Results and Discussion

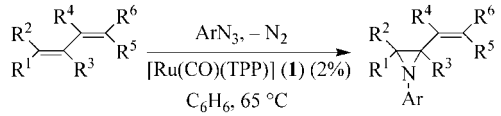
As already discussed in the Introduction, there are very few available methods for the production of *N*-aryl-2-vinylaziridines, and to the best of our knowledge this is the first time that this class of aziridines has been synthesized in good yields by [Ru(CO)(porphyrin)]-catalyzed intermolecular additions of aryl azides to 1,3-dienes without thermolysis or photolysis of the azides.[37,47,48]

Table 1. Aziridination of conjugated dienes catalyzed by [Ru(CO)(TPP)] (**1**).[a]

Entry	Substrate	Product		Time (h)	Yield (%)[b,c]
1			**2a**, R = 4-NO_2	4	99 (77)
			2b, R = 4-Cl	4	95 (60)
			2c, R = 3,5-$(CF_3)_2$	1.5	99 (66)
			2d, R = 4-Br	6	60[d]
			2e, R = 4-OCH_3	15	15 (traces)
			2f, R = 4-CN	11	99 (70)
2			**3**	12	35[e] (10)
3			**4**	10	61 (20)
4			**5**	3	40 (25)
5			**6**	8	82 (35)
6			**7**	15	65 (54)

[a] General procedure for the aziridination: **1** (10.0 mg, $1.30 \cdot 10^{-2}$ mmol) in benzene (30 mL) at 65 °C; mol ratios **1**/ArN_3/diene = 1:50:250. [b] Determined by ^{1}H NMR (1-chloro-4-nitrobenzene as an internal standard) at complete conversion of the starting azide. [c] The number in parentheses is the yield of the isolated product, purified by flash chromatography on deactivated silica with use of 10% Et_3N in *n*-hexane during the packing of the column. [d] All attempts to obtain pure **2d** failed. [e] The reaction was run in a pressure tube at 65 °C. The selectivity in **3** was 70% with respect to the converted azide (50%).

The aryl azides and the dienes that have been tested in the catalytic system illustrated in Scheme 1 are reported in Table 1.



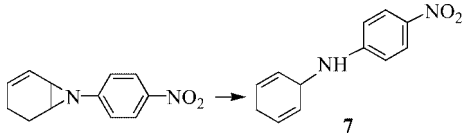
Scheme 1. Synthesis of *N*-aryl-2-vinylaziridines.

The reactions between 2,3-dimethylbuta-1,3-diene and different azides (Table 1, Entry 1) proceeded with high yields in short reaction times with use of aryl azides bearing electron-withdrawing groups in the *para* or *meta* positions in their aryl groups (Table 1, products **2a**, **2c**). The reaction between 2,3-dimethylbuta-1,3-diene and 4-cyanophenyl azide afforded the corresponding vinylaziridine in a 99% yield but required a longer reaction time (Table 1, product **2f**), which may be due to the presence of a coordinating group capable of competing with the $-N_3$ moiety for the ruthenium atom and thus partly inhibiting the catalytic reaction. As expected, the presence of an electron-donating and coordinating group such as $-OCH_3$, (Table 1, product **2e**) resulted in a longer reaction time and a lowering of the yield.

When the diene is not symmetric, the aziridine moiety is always formed on the less sterically hindered double bond (Table 1, Entries 2, 3), while when the diene is 1,3-disubstituted, the aziridine ring is formed on the double bond with the unsubstituted terminal carbon atom (Table 1, Entry 5). The reaction between isoprene and 4-nitrophenyl azide was run in a pressure tube at 65 °C, due to the low boiling point of this diene. Lower yields were registered with a sterically encumbered 1,4-disubstituted diene (Table 1, Entry 4), although the reaction did occur with a *trans* selectivity and with retention of the geometry of the unreacted double bond. It is worth noting that most of the reported procedures normally give *cis*-vinylaziridines or mixtures of *cis*- and *trans*-vinylaziridines[23] and also that the aziridination of an isolated double bond by a nitrene source is not always stereospecific.[30,49–54] In view of the importance that a stereospecific azidirination of 1,4-disubstituted diene may have, it is intended to test other substrates.

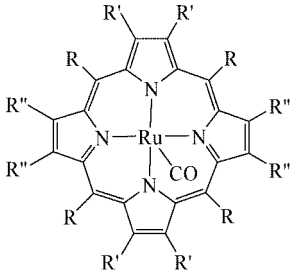
As already discussed in the Introduction, *N*-aryl-2-vinylaziridines are unstable on silica gel because of ring-opening reactions, so the purification procedure causes a lowering of the yields, as reported in Table 1.

Our methodology does not allow the preparation of aziridines of unconjugated or cyclic dienes. The ^1H NMR spectra of reaction mixtures of hexa-1,5-diene or cycloocta-1,3-diene with 4-nitrophenyl azide, run at complete conversion of the starting azide, show the presence of mixtures of products, which do not appear to include the desired aziridines. On the other hand, the reaction between cyclohexa-1,3-diene and 4-nitrophenyl azide afforded the allylamine **7** (Table 1, Entry 6) instead of the corresponding vinylaziridine. Komatsu[24] and co-authors reported the synthesis of the *N*-tosyl-2-vinylaziridine of cyclohexadiene by a very different strategy some years ago. It should be noted that the published methodology is based on the use of a stoichiometric amount of a nitrido-manganese complex in the presence of Ts_2O. We propose that the formation of **7** could be due to rearrangement of the initially formed *N*-aryl-2-vinylaziridine, which should be more prone to this kind of reaction than the corresponding *N*-tosyl-2-vinylaziridine (Scheme 2).[36,37]



Scheme 2.

At this stage it was of interest to investigate the influence of the electronic and/or steric behavior of different [Ru(porphyrin)] complexes on the formation of vinylaziridines, and so we synthesized the catalysts shown in Figure 1.



[Ru(CO)(TPP)] (**1**): R = C_6H_5; R' = R" = H
[Ru{4-(CF_3)TPP}(CO)] (**9**): R = 4-$(CF_3)C_6H_4$; R' = R" = H
[Ru{3,5-$(CF_3)_2$TPP}(CO)] (**10**): R = 3,5-$(CF_3)_2C_6H_3$; R' = R" = H
[Ru(4-*n*BuTPP)(CO)] (**11**): R = 4-*n*BuC_6H_4; R' = R" = H
[Ru(CO)(TMOP)] (**12**): R = 4-$(OCH_3)C_6H_4$; R' = R" = H
[Ru(β-Br_4-TPP)(CO)] (**13**): R = C_6H_5; R' = Br, R" = H
[Ru(CO)(OEP)] (**14**): R = H; R' = R" = Et
[Ru(CO)(TMP)] (**15**): R = 2,4,6-$(CH_3)_3C_6H_2$; R' = R" = H
[Ru(CO)(2,6-Cl_2TPP)] (**16**): R = 2,6-$Cl_2C_6H_3$; R' = R" = H

Figure 1. [Ru(porphyrin)] complexes used as catalysts.

The catalytic activities of all the complexes were tested in the model reaction between 2,3-dimethylbuta-1,3-diene and 4-nitrophenyl azide to give **2a**, and the obtained results are reported in Table 2.

The most evident trend that emerges from the analysis of the collected data (Table 2) is that the introduction of substituents on the *ortho* or *meta* positions in the *meso*-aryl moieties in the porphyrin rings reduces both reaction rate and selectivity, independently of the electronic nature of the group introduced (cf Table 2, Entry 1 with Entries 3, 8, 9). Thus, at least in these cases, a clear predominance of steric over electronic effects is observed. The introduction of substituents into the *para*-positions of the aryl rings, on the other hand, has only a small effect on reaction rate and selectivity (Table 2, Entries 1, 2, 4). An exception to this small sensitivity to electronic effect is represented by complex **12** (Table 2, Entry 5), although in this case the low activity and selectivity may be due to the coordinating ability

Table 2. Synthesis of **2a** catalyzed by the complexes reported in Figure 1.[a]

Entry	Catalyst	Time [h]	Conversion [%][b]	Selectivity [%][c]
1	**1**	4	100	99
2	**9**	2.5	100	99
3	**10**	24	66	70
4	**11**	4	100	99
5	**12**	10	95	70
6	**13**	3	100	99
7	**14**	10	100	75
8	**15**	25	95	60
9	**16**	24	65	55

[a] General procedure for the aziridination: catalyst ($1.30 \cdot 10^{-2}$ mmol) in benzene (30 mL) at 65 °C; mol ratio catalyst/ArN_3/diene = 1:50:250. [b] Determined by IR by following the consumption of the azide ($\tilde{\nu}N_3$ = 2121 cm^{-1}). [c] Determined by ^1H NMR (1-chloro-4-nitrobenzene as an internal standard) after complete conversion of the starting azide.

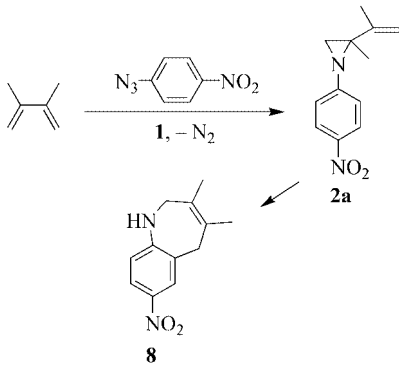
of the methoxy group. The same kind of effect has been noted when an azide possessing a methoxy group in the *para* position is used, as discussed above. It is also worth noting that unpublished data from our group have shown that ethereal solvents such as THF completely inhibit the catalytic reaction. A small effect on the reaction rate and selectivity is also observed upon the introduction of four bromine atoms into the β-positions in the pyrrolic group (Table 2, Entry 6). A quite different kind of porphyrin complex, [Ru(CO)(OEP)] (**14**), was less effective than most aryl-substituted catalysts.

In order to optimize the synthetic methodology in the test case of the aziridination of 2,3-dimethylbuta-1,3-diene with 4-nitrophenyl azide we lowered the amount of the catalyst and, after 9 h at 65 °C with use of a **1**/ArN_3/diene mol ratio of 1:400:2000, we obtained a 90% yield of **2a**. Note that under these experimental conditions we observed the presence of the byproduct 2,5-1*H*-benzo[*b*]azepine (**8**), formed by an aza-[3,3]-Claisen rearrangement of the 2-vinylaziridine.[5,13,36,37]

To avoid the formation of benzoazepines and to obtain 2-vinylaziridines in good yields, the reaction must be run for no longer than the time necessary for the consumption of the azide. The crude product must be purified rapidly and the purified product must be stored at ≤ 4 °C.

It should be noted that even the loss of product observed during the purification by flash chromatography is due to partial aza-[3,3]-Claisen rearrangements of 2-vinylaziridines to 2,5-1*H*-benzo[*b*]azepines, which occur to some degree despite the use of deactivated silica. It may be pointed out that the purification of vinylaziridines on silica gel not previously treated with Et_3N produces complete conversion into the corresponding benzoazepines. No better results were obtained by use of neutral alumina or Florisil instead, or by sublimation of the vinylaziridines from the reaction mixtures after removal of the solvent. The sublimation temperature is too high to afford acceptable yields of purified product and the formation of benzoazepines was observed even in this case.

The observed rearrangement can be turned to advantage. Indeed, our methodology allows the isolation of 2,5-1*H*-benzo[*b*]azepines when the reaction between a diene and an aryl azide is run for a long time: (*Z*)-3,4-dimethyl-7-nitro-2,5-dihydro-1*H*-benzo[*b*]azepine (**8**), for example, was obtained in a 50% yield when the reaction between 2,3-dimethylbuta-1,3-diene and 4-nitrophenyl azide was run for 20 h under the same experimental conditions as reported in Table 1 for the synthesis of **2a** (Scheme 3). The only other reaction product was as yet unconverted **2a**.



Scheme 3. Synthesis of (*Z*)-3,4-dimethyl-7-nitro-2,5-dihydro-1*H*-benzo[*b*]azepine (**8**).

^1H NMR analysis of the reaction between 2,3-dimethylbuta-1,3-diene and 4-nitrophenyl azide revealed **8** to be the only reaction product when the **1**/ArN_3/diene ratio was 1:20:70 and the catalyst was 13 times more concentrated (Figure 2).

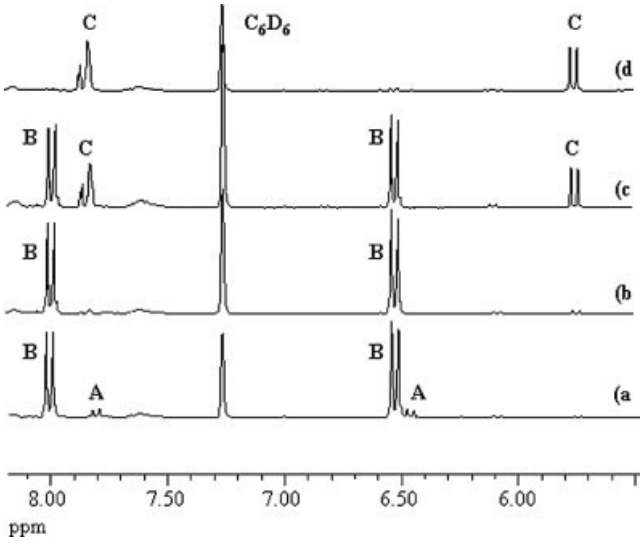


Figure 2. ^1H NMR spectra of reaction mixtures involving 2,3-dimethylbuta-1,3-diene and 4-nitrophenyl azide in the presence of **1**. a) registered after 10 min, b) after 20 min, c) after 2 h, and d) after 17 h. A: Aromatic signals of 4-nitrophenyl azide. B: Aromatic signals of **2a**. C: Aromatic signals of **8**.

Figure 2 also shows that, under these experimental conditions, compound **8** was formed only after the complete consumption of the aryl azide. Preliminary results show that the same methodology can also be applied to the synthesis of 1*H*-benzo[*b*]azepines of myrcene and *trans*-2-meth-

ylpenta-1,3-diene. A more extensive investigation of this rearrangement reaction is in progress and the results will be reported in a following paper.

Conclusions

In conclusion, we report a method to produce *N*-aryl-2-vinylaziridines in a one-step reaction by use of aryl azides and conjugated dienes in the presence of [Ru(CO)(porphyrin)] complexes as catalysts. The reaction times and the aziridination selectivity are governed more by steric than electronic properties of the porphyrin ring. With our optimized purification procedure we were in some cases able to isolate these unstable products in good yields. However, it must be considered that the crude products can be used for further reactions without any purification when vinylaziridines are obtained in quantitative yields. Moreover, it should be emphasized that high yields can also be obtained with a 0.25% mol amount of the catalyst **1**.

Experimental Section

General: ^{1}H NMR spectra were recorded on an Advance 300 DRX Bruker instrument, operating at 300 MHz for ^{1}H and at 75 MHz for ^{13}C, and on an Advance 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 below have been attributed by COSY and NOESY techniques. Assignments of the resonances in ^{13}C NMR were made with the aid of the APT pulse sequence, HSQC, and HMQC techniques. Infrared spectra were recorded on a BIO-RAD FTS-7 spectrophotometer. Elemental analyses and mass spectra were recorded in the analytical laboratories of Milan University. Unless otherwise specified, all reactions were carried out under nitrogen with use of standard Schlenk techniques and magnetic stirring. Solvents were dried prior to use by standard procedures and stored under nitrogen. 4-Nitrophenyl azide,[55] 4-chlorophenyl azide,[55] 4-bromophenyl azide,[55] 4-methoxyphenyl azide,[55] 4-cyanophenyl azide,[55] and 3,5-bis(trifluoromethyl)-phenyl azide[55] were synthesized by methods reported in the literature. The complexes [Ru(CO)(porphyrin)] [porphyrin = TPP,[56] 4-(CF_3)TPP,[56] 3,5-(CF_3)$_2$TPP,[57] 4-*n*BuTPP,[56] TMOP,[56] TMP,[56] 2,6-(Cl)$_2$TPP][56] (TPP = dianion of tetraphenylporphyrin) were synthesized by the literature methods. [Ru(CO)(OEP)] (Aldrich) was used as received.

2-Isopropenyl-2-methyl-*N*-(4-nitrophenyl)aziridine (2a): Complex **1** (10.0 mg, $1.30\cdot10^{-2}$ mmol) and 4-nitrophenyl azide (100 mg, $6.09\cdot10^{-1}$ mmol) were added to a dry benzene solution (30 mL) of 2,3-dimethylbuta-1,3-diene (0.34 mL, 3.05 mmol). The resulting red solution was stirred at 65 °C in a preheated oil bath for 4 h, the consumption of the aryl azide being monitored by TLC until the corresponding spot was no longer observable and then by IR spectroscopy. The reaction was considered to be finished when the absorbance of the azide band at 2121 cm^{-1} in the IR spectrum of the solution, measured in a 0.5 mm thick cell, was at or below 0.03. The obtained solution was evaporated to dryness and analyzed by ^{1}H NMR with 1-chloro-4-nitrobenzene as the internal standard (99% yield). The residue was purified by flash chromatography on deactivated silica with use of Et_3N in *n*-hexane (10%) during the packing of the column (*n*-hexane/EtOAc 10:0→7:3) (77% yield).

Synthesis of 2a with Use of Different Catalysts: In a typical run, [Ru(CO)(porphyrin)] ($1.30\cdot10^{-2}$ mmol) and *p*-nitrophenyl azide (100 mg, $6.09\cdot10^{-1}$ mmol) were added to a solution of 2,3-dimethylbuta-1,3-diene (0.34 mL, 3.05 mmol) in dry benzene (30 mL). The resulting red solution was stirred at 65 °C in a preheated oil bath and the conversion of the azide was determined by measuring the absorbance of the azide band at 2121 cm^{-1} in the IR spectrum of the solution. The reaction mixture was then evaporated to dryness and analyzed by ^{1}H NMR with 1-chloro-4-nitrobenzene as the internal standard to determine the reaction selectivity (see Table 2). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.16 (d, ^3J = 9.0 Hz, 2 H, Ar*H*), 6.93 (d, ^3J = 9.0 Hz, 2 H, Ar*H*), 5.15 (s, 1 H, C=CH_{trans}), 5.02 (s, 1 H, C=CH_{cis}), 2.62 (s, 1 H, N–CH_{anti}), 2.14 (s, 1 H, N–CH_{syn}), 1.83 (s, 3 H, C=CCH_3), 1.22 (s, 3 H, CH_3) ppm. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 8.01 (d, ^3J = 9.0 Hz, 2 H, Ar*H*), 6.50 (d, ^3J = 9.0 Hz, 2 H, Ar*H*), 5.14 (s, 1 H, C=CH_{trans}), 4.98 (s, 1 H, C=CH_{cis}), 2.25 (s, 1 H, N–CH_{anti}), 1.71 (s, 3 H, C=CCH_3), 1.65 (s, 1 H, N–CH_{syn}), 0.93 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 157.6, 145.7, 142.7, 125.5, 120.6, 113.3, 46.8, 40.6, 19.7, 19.0 ppm. MS (EI) *m*/*z* (%): 218 [M]$^+$, 203 (73) [M – CH_3]$^+$, 157 (100) [M – CH_3 – NO_2]$^+$. Anal. calcd. (%) for $C_{12}H_{14}N_2O_2$ (218.26): C 66.04, H 6.47, N 12.84; found: C 66.02, H 6.82, N 12.53.

***N*-(4-Chlorophenyl)-2-isopropenyl-2-methylaziridine (2b):** 4-Chlorophenyl azide (93 mg, $6.06\cdot10^{-1}$ mmol) and **1** (10.0 mg, $1.30\cdot10^{-2}$ mmol) were added to a dry benzene solution (30 mL) of 2,3-dimethylbuta-1,3-diene (0.34 mL, 3.05 mmol) in a procedure identical to that described for the aziridine **2a**. The resulting red solution was stirred at 65 °C in a preheated oil bath for 4 h, 95% NMR yield, 60% isolated yield. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.16 (d, ^3J = 8.7 Hz, 2 H, Ar*H*), 6.57 (d, ^3J = 8.7 Hz, 2 H, Ar*H*), 5.18 (s, 1 H, C=CH_{trans}), 5.00 (s, 1 H, C=CH_{cis}), 2.21 (s, 1 H, N–CH_{anti}), 1.77 (s, 3 H, C=CCH_3), 1.59 (s, 1 H, N–CH_{syn}), 0.93 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ = 149.9, 146.9, 129.2, 127.1, 122.2, 112.3, 45.0, 39.6, 19.5, 18.0 ppm. Anal. calcd. (%) for $C_{12}H_{14}ClN$ (207.70): C 69.39, H 6.79, N 6.74; found: C 69.02, H 6.88, N 6.53.

***N*-[3,5-Bis(trifluoromethyl)phenyl]-2-isopropenyl-2-methylaziridine (2c):** 3,5-Bis(trifluoromethyl)phenyl azide (166 mg, $6.51\cdot10^{-1}$ mmol) and **1** (10 mg, $1.30\cdot10^{-2}$ mmol) were added to a dry benzene solution (30 mL) of 2,3-dimethylbuta-1,3-diene (0.38 mL, 3.36 mmol) in a procedure identical to that described for the aziridine **2a**. The resulting red solution was stirred at 65 °C in a preheated oil bath for 1.5 h, 99% NMR yield, 66% isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.45 (s, 1 H, Ar*H*), 7.26 (s, 2 H, Ar*H*), 5.15 (s, 1 H, C=CH_{trans}), 5.01 (s, 1 H, C=CH_{cis}), 2.59 (s, 1 H, N–CH_{anti}), 2.11 (s, 1 H, N–CH_{syn}), 1.83 (s, 3 H, C=CCH_3), 1.18 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 152.6, 145.7, 132.6 ($^2J_{C,F}$ = 33.0 Hz, *C*–CF_3), 123.7 ($^1J_{C,F}$ = 270.9 Hz, *C*F_3), 120.8, 115.5, 113.2, 46.5, 40.5, 19.6, 18.7 ppm. MS (EI) *m*/*z*: 309 [M]$^+$, 294 (100) [M – CH_3]$^+$. Anal. calcd. (%) for $C_{14}H_{13}F_6N$ (309.25): C 54.37, H 4.24, N 4.53; found: C 53.99, H 3.98, N 4.33.

***N*-(4-Bromophenyl)-2-isopropenyl-2-methylaziridine (2d):** 4-Bromophenyl azide (118 mg, $5.96\cdot10^{-1}$ mmol) and **1** (10.0 mg, $1.30\cdot10^{-2}$ mmol) were added to a dry benzene solution (30 mL) of 2,3-dimethylbuta-1,3-diene (0.34 mL, 3.05 mmol) in a procedure identical to that described for the aziridine **2a**. The resulting red solution was stirred at 65 °C in a preheated oil bath for 6 h, 60% NMR yield. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.30 (d, ^3J = 8.4 Hz, 2 H, Ar*H*), 6.52 (d, ^3J = 8.4 Hz, 2 H, Ar*H*), 5.18 (s, 1 H, C=CH_{trans}), 5.00 (s, 1 H, C=CH_{cis}), 2.21 (s, 1 H, N–CH_{anti}), 1.76 (s, 3 H, C=CCH_3), 1.58 (s, 1 H, N–CH_{syn}), 0.93 (s, 3 H, CH_3) ppm.

2-Isopropenyl-*N*-(4-methoxyphenyl)-2-methylaziridine (2e): 4-Methoxyphenyl azide (91.0 mg, $6.11\cdot10^{-1}$ mmol) and **1** (10.0 mg, $1.30\cdot10^{-2}$ mmol) were added to a dry benzene solution (30 mL) of 2,3-dimethylbuta-1,3-diene (0.34 mL, 3.05 mmol) in a procedure identical to that described for the aziridine **2a**. The resulting red solution was stirred at 65 °C in a preheated oil bath for 15 h, 15% NMR yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.87 (d, ^3J = 9.0 Hz, 2 H, Ar*H*), 6.99 (d, ^3J = 9.0 Hz, 2 H, Ar*H*), 5.08 (s, 1 H, C=CH_{trans}), 4.93 (s, 1 H, C=CH_{cis}), 3.75 (s, 3 H, OCH_3), 2.89 (s, 1 H, N–CH_{anti}), 2.42 (s, 1 H, N–CH_{syn}), 1.83 (s, 3 H, C=CCH_3), 1.09 (s, 3 H, CH_3) ppm. MS (EI) *m*/*z*: 203 $[M]^+$, 188 (100) $[M - CH_3]^+$, 172 (40) $[M - OCH_3]^+$, 157 (32) $[M - CH_3 - OCH_3]^+$.

4-(2-Isopropenyl-2-methylaziridin-1-yl)benzonitrile (2f): 4-Cyanophenyl azide (88.0 mg, $6.11\cdot10^{-1}$ mmol) and **1** (10.0 mg, $1.30\cdot10^{-2}$ mmol) were added to a dry benzene solution (30 mL) of 2,3-dimethylbuta-1,3-diene (0.34 mL, 3.05 mmol) in a procedure identical to that described for the aziridine **2a**. The resulting red solution was stirred at 65 °C in a preheated oil bath for 11 h, 99% NMR yield, 70% isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.53 (d, ^3J = 9.0 Hz, 2 H, Ar*H*), 6.92 (d, ^3J = 9.0 Hz, 2 H, Ar*H*), 5.13 (s, 1 H, C=CH_{trans}), 4.99 (s, 1 H, C=CH_{cis}), 2.56 (s, 1 H, N–CH_{anti}), 2.08 (s, 1 H, N–CH_{syn}), 1.82 (s, 3 H, C=CCH_3), 1.18 (s, 3 H, CH_3) ppm. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.18 (d, ^3J = 8.4 Hz, 2 H, Ar*H*), 6.49 (d, ^3J = 8.4 Hz, 2 H, Ar*H*), 5.13 (s, 1 H, C=CH_{trans}), 4.98 (s, 1 H, C=CH_{cis}), 2.21 (s, 1 H, N–CH_{anti}), 1.71 (s, 3 H, C=CCH_3), 1.59 (s, 1 H, N–CH_{syn}), 0.89 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ = 155.2, 146.1, 133.2, 121.1, 119.8, 112.8, 105.1 (*C*N), 45.8, 39.7, 19.4, 18.3 ppm. Anal. calcd. (%) for $C_{13}H_{14}N_2$ (198.27): C 78.75, H 7.12, N 14.13; found: C 78.52, H 7.38, N 13.87.

2-Isopropenyl-*N*-(4-nitrophenyl)aziridine (3): This reaction was run in a pressure tube under nitrogen. 4-Nitrophenyl azide (40 mg, $2.44\cdot10^{-1}$ mmol) and **1** (3.6 mg, $5\cdot10^{-3}$ mmol) were added to a dry benzene solution (10 mL) of isoprene (0.12 mL, 1.07 mmol), the resulting red solution was stirred at 65 °C in a preheated oil bath for 12 h, the obtained solution was evaporated to dryness, and the residue was analyzed by ^{1}H NMR with 1-chloro-4-nitrobenzene as the internal standard. The selectivity of the reaction was 70% with respect to the converted azide (50%). The residue was purified by flash chromatography on deactivated (10% Et_3N in *n*-hexane) silica gel (*n*-hexane/CH_2Cl_2 = 8:2) (10% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.15 (d, ^3J = 9.0 Hz, 2 H, Ar*H*), 7.05 (d, ^3J = 9.0 Hz, 2 H, Ar*H*), 5.21 (s, 1 H, C=CH_{trans}), 5.06 (s, 1 H, C=CH_{cis}), 2.74 (dd, ^3J = 3.3 Hz, ^3J = 6.3 Hz, 1 H, N–C*H*), 2.50 (d, ^3J = 3.3 Hz, 1 H, N–CH_{anti}), 2.29 (d, ^3J = 6.3 Hz, 1 H, N–CH_{syn}), 1.76 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 161.3, 143.1, 142.2, 125.6, 120.9, 114.1, 44.9, 34.3, 18.3 ppm. MS (EI) *m*/*z*: 204 $[M]^+$, 189 (52) $[M - CH_3]^+$, 157 (63) $[M - H - NO_2]^+$, 143 (100) $[M - CH_3 - NO_2]^+$. Anal. calcd. (%) for $C_{11}H_{12}N_2O_2$ (204.23): C 64.69, H 5.92, N 13.72; found: C 64.42, H 5.61, N 13.95.

2-(5-Methyl-1-methylenehex-4-enyl)-*N*-(4-nitrophenyl)aziridine (4): 4-Nitrophenyl azide (100 mg, $6.09\cdot10^{-1}$ mmol) and **1** (10 mg, $1.30\cdot10^{-2}$ mmol) were added to a dry benzene solution (30 mL) of myrcene (0.55 mL, 3.23 mmol) in a procedure identical to that described for the aziridine **2a**. The resulting red solution was stirred at 65 °C in a preheated oil bath for 10 h, 61% NMR yield, 20% isolated yield. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.96 (d, ^3J = 9.0 Hz, 2 H, Ar*H*), 6.52 (d, ^3J = 9.0 Hz, 2 H, Ar*H*), 5.31 (m, 1 H, C*H*), 5.26 (s, 1 H, C=CH_{trans}), 5.03 (s, 1 H, C=CH_{cis}), 2.29–2.25 (m, 3 H, CH_2 overlapping with C*H*), 2.10 (m, 2 H, CH_2), 2.01 (d, 1 H, N–CH_{anti}), 1.77 (m, 4 H, CH_3 overlapping with N–CH_{syn}), 1.65 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ = 160.8, 146.3, 143.3, 132.1, 125.3, 124.4, 120.4, 112.0, 43.7, 34.9, 32.7, 27.3, 26.0, 17.9 ppm. Anal. calcd. (%) for $C_{16}H_{20}N_2O_2$ (272.35): C 70.56, H 7.40, N 10.29; found: C 70.19, H 7.68, N 10.03. MS (EI) *m*/*z*: 272 $[M]^+$, 203 (95) $[M - CH_2CHC(CH_3)_2]^+$, 157 (65) $[M - CH_2CHC(CH_3)_2 - NO_2]^+$.

***N*-(4-Nitrophenyl)-*trans*-2-phenyl-3-[(*E*)-styryl]aziridine (5):** 4-Nitrophenyl azide (107 mg, $6.52\cdot10^{-1}$ mmol) and **1** (10 mg, $1.30\cdot10^{-2}$ mmol) were added to a dry benzene solution (30 mL) of *trans,trans*-1,4-diphenylbuta-1,3-diene (670 mg, 3.25 mmol) in a procedure identical to that described for the aziridine **2a**. The resulting red solution was stirred at 65 °C in a preheated oil bath for 3 h, 40% NMR yield, 25% isolated yield. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 7.95 (d, ^3J = 9.0 Hz, 2 H, Ar*H*), 7.45–7.10 (m, 10 H, Ph), 6.66 (d, ^3J = 9.0 Hz, 2 H, Ar*H*), 6.57 [d, ^3J = 15.8 Hz, 1 H, C=C(Ph)*H*], 5.50 (dd, ^3J = 15.8 Hz, ^3J = 9.4 Hz, 1 H, PhC=C*H*), 3.21 [d, ^3J = 2.5 Hz, 1 H, N–C(Ph)*H*], 3.11 (dd, ^3J = 9.4 Hz, ^3J = 2.5 Hz, 1 H, N–C*H*) ppm. ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ = 156.3, 143.8, 137.8, 136.6, 136.0, 129.9, 129.2, 129.1, 127.0, 126.8, 126.7, 125.3, 125.0, 120.6, 51.8, 49.3 ppm. MS (EI) *m*/*z*: 342 $[M]^+$, 220 (40) $[M - C_6H_4NO_2]^+$. Anal. calcd. (%) for $C_{22}H_{18}N_2O_2$ (342.40): C 77.17, H 5.30, N 8.18; found: C 76.85, H 5.68, N 7.93.

2-Methyl-*N*-(4-nitrophenyl)-2-[(*E*)-propenyl]aziridine (6): 4-Nitrophenyl azide (110 mg, $6.71\cdot10^{-1}$ mmol) and **1** (10 mg, $1.30\cdot10^{-2}$ mmol) were added to a dry benzene solution (30 mL) of *trans*-2-methylpenta-1,3-diene (0.37 mL, 3.23 mmol) in a procedure identical to that described for the aziridine **2a**. The resulting red solution was stirred at 65 °C in a preheated oil bath for 8 h, 82% NMR yield, 35% isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.13 (d, ^3J = 9.0 Hz, 2 H, Ar*H*), 6.91 (d, ^3J = 9.0 Hz, 2 H, Ar*H*), 5.83 [dq, ^3J = 14.0 Hz, ^3J = 6.5 Hz, 1 H, C=C(CH$_3$)-*H*], 4.97 (d, ^3J = 14.0 Hz, 1 H, CH_3C=C*H*), 2.41 (s, 1 H, N–CH_{anti}), 2.36 (s, 1 H, N–CH_{syn}), 1.71 (d, ^3J = 6.5 Hz, 3 H, C=CCH_3), 1.39 (s, 3 H, CH_3) ppm. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 8.01 (d, ^3J = 9.0 Hz, 2 H, Ar*H*), 6.47 (d, ^3J = 9.0 Hz, 2 H, Ar*H*), 5.61 [dq, ^3J = 15.5 Hz, ^3J = 6.6 Hz, 1 H, C=C(CH$_3$)*H*], 4.90 (dq, ^3J = 15.5 Hz, ^4J = 1.8 Hz, 1 H, CH_3C=C*H*), 1.91 (s, 1 H, N–CH_{anti}), 1.89 (s, 1 H, N–CH_{syn}), 1.57 (dd, ^3J = 6.6 Hz, ^4J = 1.8 Hz, 3 H, C=CCH_3), 1.13 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ = 157.5, 142.8, 132.8, 128.0, 125.1, 120.5, 43.1, 41.5, 19.7, 18.0 ppm. MS (EI) *m*/*z*: 216 $[M - 2 H]^+$, 201 (100) $[M - 2 H - CH_3]^+$, 155 (85) $[M - 2 H - CH_3 - NO_2]^+$. Anal. calcd. (%) for $C_{12}H_{14}N_2O_2$ (218.26): C 66.04, H 6.47, N 12.84; found: C 66.11, H 6.78, N 12.53.

Cyclohexa-2,5-dienyl-(4-nitrophenyl)amine (7): 4-Nitrophenyl azide (112 mg, $6.83\cdot10^{-1}$ mmol) and **1** (10 mg, $1.30\cdot10^{-2}$ mmol) were added to a dry benzene solution (30 mL) of cyclohexa-1,3-diene (0.32 mL, 3.41 mmol) in a procedure identical to that described for the aziridine **2a**. The resulting red solution was stirred at 65 °C in a preheated oil bath for 15 h, 65% NMR yield, 54% isolated yield. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 8.09 (d, ^3J = 9.0 Hz, 2 H, Ar*H*), 6.60 (d, ^3J = 9.0 Hz, 2 H, Ar*H*), 6.03–5.99 (m, 2 H, C*H*), 5.86–5.80 (m, 2 H, C*H*), 4.63 (m, 1 H, N–C*H*), 4.56 (br s, 1 H, N*H*), 2.74–2.73 (m, 2 H, CH_2) ppm. ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ = 152.5, 138.5, 128.1, 127.0, 125.1, 111.8, 46.5, 26.6 ppm. MS (EI) *m*/*z*: 216 $[M]^+$, 188 (100) $[M - C_2H_4]^+$. Anal. calcd. (%) for $C_{12}H_{12}N_2O_2$ (216.24): C 66.65, H 5.59, N 12.95; found: C 66.95, H 5.89, N 13.03.

(Z)-3,4-Dimethyl-7-nitro-2,5-dihydro-1*H*-benzo[*b*]azepine (8)

Method A: Complex **1** (10.0 mg, $1.30\cdot10^{-1}$ mmol) and 4-nitrophenyl azide (110 mg, $6.71\cdot10^{-1}$ mmol) were added to a dry benzene solution (30 mL) of 2,3-dimethylbuta-1,3-diene (0.42 mL, 3.71 mmol),

the resulting red solution was stirred at 65 °C in a preheated oil bath for 20 h, the reaction mixture was then evaporated to dryness, and the residue was analyzed by ^{1}H NMR with 1-chloro-4-nitrobenzene as an internal standard. Product **8** was obtained in a 50% NMR yield; the only other reaction product was as yet incompletely converted **2a**.

Method B: Complex **1** (40.0 mg, 0.06 mmol) and 4-nitrophenyl azide (150 mg, 0.92 mmol) were added to a dry benzene solution (30 mL) of 2,3-dimethylbuta-1,3-diene (0.43 mL, 3.77 mmol) and the resulting red solution was stirred at 65 °C in a preheated oil bath for 16 h, the conversion of the intermediately formed vinylaziridine **2a** into the benzoazepine **8** being monitored by TLC until its spot was no longer observable. The reaction mixture was then evaporated to dryness and the residue was purified by flash chromatography on silica gel (*n*-hexane/EtOAc 9:1→4:6) (60% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.93 (d, ^3J = 8.8 Hz, 1 H, Ar*H*), 7.87 (s, 1 H, Ar*H*), 5.61 (d, ^3J = 8.8 Hz, 1 H, Ar*H*), 3.58 (s, 1 H, N*H*), 3.22 (d, ^3J = 4.8 Hz, 2 H, NH–CH_2), 3.00 (s, 2 H, CH_2), 1.50 (s, 3 H, CH_3), 1.49 (s, 3 H, CH_3) ppm. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.96 (dd, ^3J = 9.0 Hz, ^4J = 2.4 Hz, 1 H, Ar*H*), 7.91 (br s, 1 H, Ar*H*), 5.66 (d, ^3J = 9.0 Hz, 1 H, Ar*H*), 3.63 (br s, 1 H, N*H*), 3.26 (d, ^3J = 6.4 Hz, 2 H, NH–CH_2), 3.04 (s, 2 H, CH_2), 1.54 (br s, 6 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 152.2, 132.7, 126.3, 125.7, 124.0, 120.7, 114.6, 47.2, 38.7, 18.4, 18.1 ppm. Anal. calcd. (%) for $C_{12}H_{14}N_2O_2$ (218.26): C 66.04, H 6.47, N 12.84; found: C 66.01, H 6.21, N 12.69.

Ru(β-Br$_4$-TPP)(CO) (13): $Ru_3(CO)_{12}$ (65.6 mg, $1.03\cdot10^{-1}$ mmol) and β-Br$_4$-TPPH$_2$[58] (71.2 mg, $7.71\cdot10^{-2}$ mmol) were dissolved in dry toluene (20 mL), the reaction mixture was heated at reflux for 6 h, and the resulting orange solution was evaporated to dryness under reduced pressure. The purple residue was purified by flash chromatography on silica with ethyl acetate/*n*-hexane 2:8 as eluent (54.5 mg, 70%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.46 (s, 4 H, H_β), 8.03–8.00 (m, 8 H, H_o), 7.79–7.68 (m, 12 H, H_m, H_p) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 146.8, 141.8, 138.1, 134.9, 134.2, 133.8, 128.6, 127.5, 127.2, 124.3, 122.4 ppm. IR (Nujol): $\tilde{\nu}$ = 1959 cm^{-1} (CO), 1013 cm^{-1} (oxidation marker). UV/Vis (CH_2Cl_2): λ_{max} (log ε_M) = 417 (5.4), 538 (4.3), 573 nm (3.9). Anal. calcd. (%) for $C_{45}H_{24}Br_4N_4ORu$ (1053.8): C, 51.11; H, 2.29; N, 5.30; found: C 51.38, H 2.05, N 5.52.

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