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An investigation of the Lewis acid mediated 1,3-dipolar cycloaddition between *N*-benzyl-*C*-(2-pyridyl)nitrone and allylic alcohol. Direct entry to isoxazolidinyl *C*-nucleosides †

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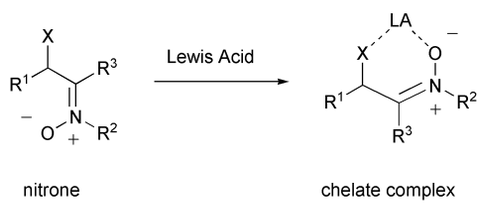
The cycloaddition reaction of *N*-benzyl *C*-(2-pyridyl) nitrone with allylic alcohol has been carried out to obtain the corresponding 2-benzyl-3-(2-pyridyl)-5-hydroxymethylisoxazolidine. The influence of Lewis acids in the reaction has been studied and a complete 3,5-regioselectivity and *cis* diastereoselectivity was observed when the reaction was carried out with 1.0 equiv of AgOTf, $[Ag(OClO_3)(PPh_2Me)]$ or $Zn(OTf)_2$. Insight into the mechanism of the reaction has been obtained by isolating and characterizing (X-ray) the intermediate complexes. Also, a model based on both experimental and theoretical results is proposed.

Introduction

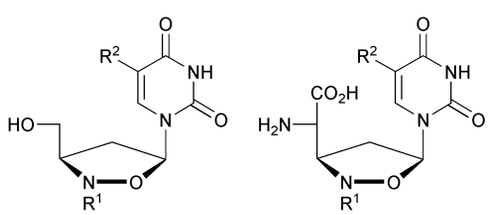
The 1,3-dipolar cycloaddition of nitrones with alkenes is a powerful synthetic method that has found numerous applications in the synthesis of a variety of carbon frameworks.[1] Several laboratories have focused on the development of Lewis acid reagents to modulate the selectivity of the reaction.[2] Such a modulation can be achieved either by complexation of the dipolarophile[3] (typically, in cycloadditions with electron-poor alkenes) or by nitrone activation[4] through previous complexation.[5] For the latter it has been observed that the presence of a coordinating group at the alpha position is needed to achieve the desired complexation (Scheme 1). Usually, such a coordinating group consists of a carbonyl moiety (ester or ketone), and typically, several cycloaddition reactions of carbonyl conjugated nitrones with allylic alcohols have been reported to show high selectivities when activated with several Lewis acids.[6] However, the coordinating group X, can also be part of a heterocyclic ring, thus increasing the range of nitrones which can be used as suitable substrates.[7]



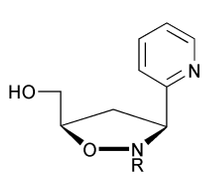
Scheme 1

As part of our continuing efforts to develop novel strategies for preparing heterocyclic nucleosides[8] (*i.e.* nucleoside analogues in which the furanose ring has been replaced by a different heterocyclic ring),[9] we have investigated the applicability of 1,3-dipolar cycloaddition reactions of nitrones to the synthesis of isoxazolidinyl nucleosides.[10] We now wish to report our findings on Lewis acid modulated cycloadditions leading to interesting isoxazolidinyl *C*-nucleoside analogues **1**.[11] In this context, several *C*-nucleosides with different hetero- and carbocyclic rings have been found to possess promising biological activities.[12]

Compound **1** (R = Bn) can be easily obtained in one step by a cycloaddition reaction between the corresponding 2-pyridyl nitrone and allylic alcohol, and using the appropriate Lewis acid. In this paper we also present a detailed study of that reaction, including isolation and full characterization of the intermediate complexes.[13] A theoretical study, at a semi-empirical (PM3) level, of the reaction has also been carried out.



isoxazolidinyl nucleosides



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Results and discussion

The *N*-benzyl-*C*-(2-pyridyl)nitrone **2** employed for the present investigation was obtained by condensation of 2-formylpyridine and *N*-benzylhydroxylamine.[14] The results of the reaction illustrated in Scheme 2 are collected in Table 1.

Cycloaddition of **2** with allylic alcohol took seven days in acetone at reflux to give a 70 : 30 mixture of *cis* and *trans* adducts, respectively (entry 1). On the other hand, the addition of silver salts (entries 2 and 3) only afforded the *cis* isomer with notable increasing of the rate of the reaction. With Zn salts, only in the case of $Zn(OTf)_2$ an even higher effect was observed

† Electronic supplementary information (ESI) available: optimized geometries (PDB format). See http://www.rsc.org/suppdata/ob/b3/b304112c/

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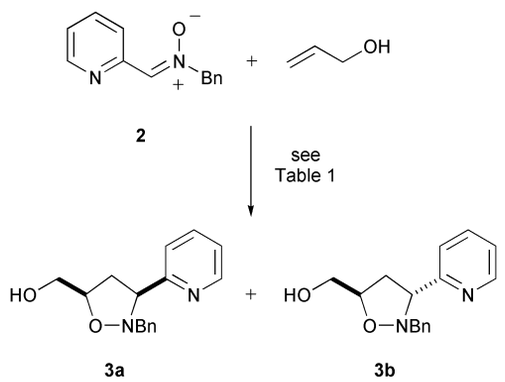
Table 1 Cycloadditions of nitrone **2** with allylic alcohol[a]

Entry	Lewis acid	Time (days)	*cis* : *trans*[b]	Yield[c] (%)
1	None	7	70 : 30	90
2	AgOTf	3.5	>95 : 5[d]	100
3	$[Ag(OClO_3)PPh_2Me]$	5	>95 : 5[d]	92
4	$Zn(OTf)_2$	3	>95 : 5[d]	100
5	$ZnBr_2$	5	>95 : 5[d]	100

[a] Reactions carried out on a 1 mmol scale; nitrone–Lewis acid–dipolarophile 1 : 1 : 10. [b] The diastereomeric ratio was determined by integration of the appropriate signals. [c] Yield of the mixture of diastereomers after purification by column chromatography. [d] Only one isomer was detected by ^1H and ^{13}C NMR.

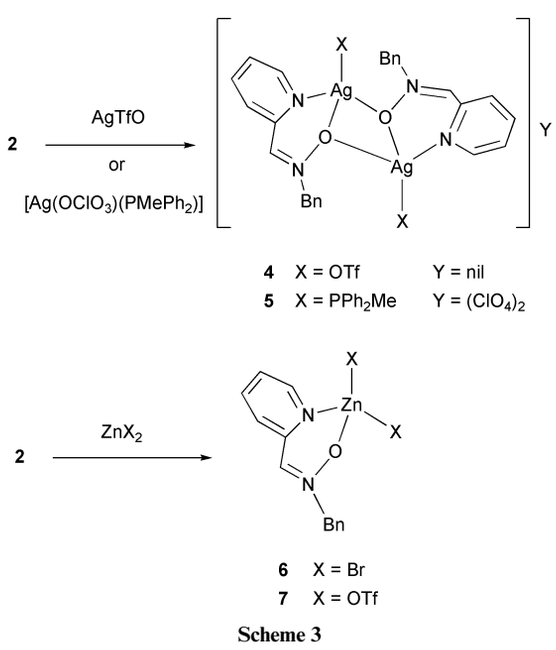


Scheme 2

(entry 4), the addition of $ZnBr_2$ (entry 5) leading to a slower reaction; in both cases only the *cis* isomer was obtained. This behaviour is in good agreement with the results of previously reported Lewis acid promoted cycloaddition reactions with allylic alcohols.[6] Thus, carrying out the reaction in the presence of 1.0 equiv of $Zn(OTf)_2$ the *cis* adduct **5a** was obtained in quantitative yield as a single isomer.

Isolation and characterization of intermediate complexes

In order to obtain information concerning the structures of the intermediate nitrone–metal complexes, nitrone **2** was treated in the absence of the dipolarophile with $[Ag(OClO_3)(PPh_2Me)]$, AgTfO, $ZnBr_2$ and $Zn(OTf)_2$ (Scheme 3). Complexes **4**–**7** were isolated and characterized by spectroscopic methods (see



Scheme 3

Experimental section). In addition nitrone **2** and complexes **5** and **6** were submitted to a single-crystal X-ray structure analysis[15] which allowed the complete structural identification.[16]

Thus, silver complexes **4** and **5** were obtained as white solids when 2-PyBN **2** was added to a diethyl ether solution of the corresponding silver(I) salts AgTfO and $[Ag(OClO_3)(PPh_2Me)]$, respectively. Their IR spectra showed absorptions that can be assigned to covalent triflate groups[17] in the case of **4** and ionic[18] perchlorate for **5**. The presence of covalent triflate groups was confirmed by $^{19}F\{^1H\}$ NMR, spectra in which a singlet at −77.5 ppm, characteristic of OSO_2CF_3 groups, was observed.[19]

The ^1H NMR spectra exhibit a downfield displacement of the nitrone resonances in both cases, owing to the coordination to the metallic centre. The $^{31}P\{^1H\}$ NMR of **5** displayed a doublet of doublets as a consequence of the ^{107}Ag (51.82% isotopic abundance) and ^{109}Ag (48.18%) nucleus coupling. The LSIMS mass spectra (nitrobenzyl alcohol as matrix) of **4** showed the parent peak with loss of one triflate molecule at *m*/*z* (%) = 787 (10) which confirmed the proposed dinuclear formulation. In the case of **5** only fragmentation peaks are observed.

The molecular structure of complex **5** is shown in Fig. 1. The molecule consists of two *N*-benzyl-*C*-(2-pyridyl) nitrone phosphine silver(I) molecules connected through the oxygen atom from the nitrone. In each unit the nitrone is acting as a chelate ligand through both N,O heteroatoms. The geometry around the silver is tetrahedral distorted with bond angles of 146.9(2)°, N(1)–Ag–P and 88.66(19), O(1)–Ag–O(1′). Bond lengths and angles in the nitrone molecule are similar to those found in the free nitrone.[16] Thus, the distances in the N–O and N=C units in **7** are 1.309(8) and 1.295(11) Å respectively and 1.300(3) and 1.299(3) Å in **2**. Only a small variation is observed in the C–N distance from 1.488(3) in the free nitrone to 1.535(11) Å in the silver complex. There are two different Ag–O bond lengths in the molecule: Ag–O(1) = 2.381(5) and Ag–O(1′) = 2.510(6) Å. This fact has been observed in other dinuclear silver(I) derivatives with bridging oxygen ligands.[20] The Ag–N and Ag–P distances of 2.306(7) and 2.338(2) Å respectively are similar to those found in the literature.[21] On the basis of this structure and the mass spectrum of complex **4**, we can propose a similar dinuclear disposition with covalent triflates for this complex.

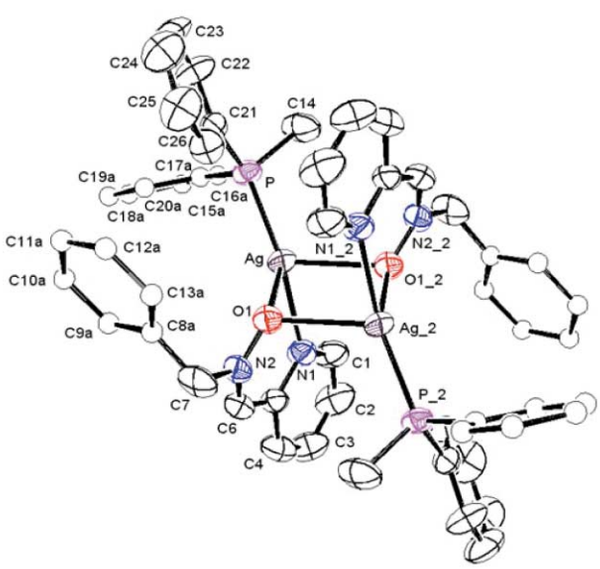


Fig. 1 ORTEP diagram of complex **5**. Displacement ellipsoids drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Complexes **6** and **7** can be isolated as air-stable solids. The presence of covalent triflate in **7** can be confirmed by IR and $^{19}F\{^1H\}$ NMR spectra. The ^1H NMR spectra in both complexes show a downfield displacement when compared with the

free nitrone as occurred in silver compounds. As stated above the structure of complex **6** was confirmed by X-ray diffraction. The molecule (Fig. 2) shows a tetrahedral distorted disposition for the metallic centre [N(1)–Zn–Br(1) = 106.62(11)°, O–Zn–Br(2) = 113.43(10)°]. The distances in the nitrone skeleton are similar to those found in the free nitrone, however, the bond angle N(2)–C(6)–C(5) of 128.2(4)° is slightly larger than that found in **2** [N–C–C = 126.3(2)°], which can be assigned to the formation of the chelate. In addition, it should be mentioned that the distance between the zinc atom and the bromine *trans* to the pyridine [Zn–Br(1) = 2.3641(8) Å] is 0.034 Å larger than between the zinc atom and the bromine *trans* to the oxygen from the N–O group [Zn–Br(2) = 2.3300(8) Å]. This situation has been also observed in N,O-chelating aldehyde zinc complexes four-, five- or even six-coordinated.[22]

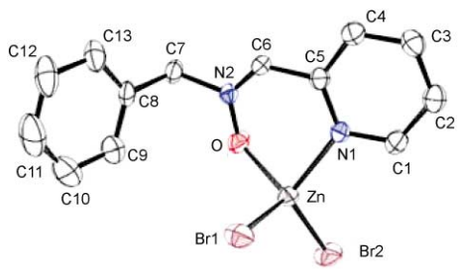
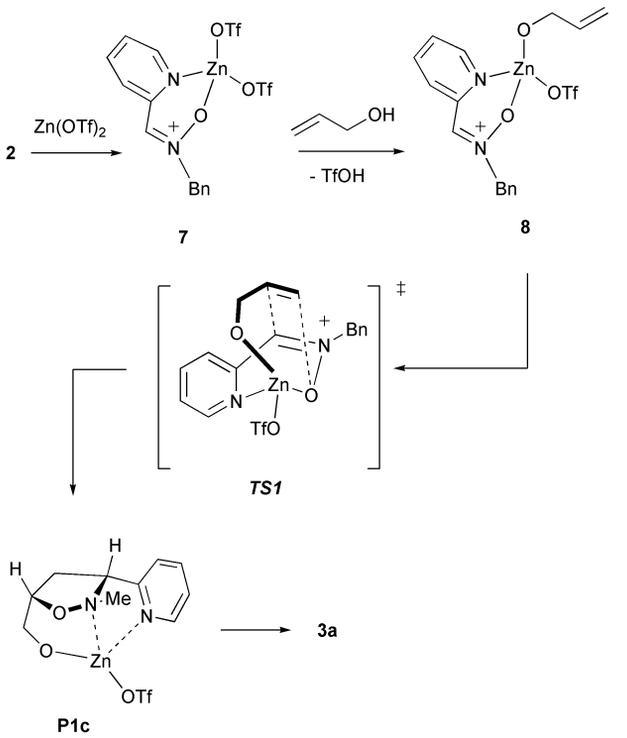


Fig. 2 ORTEP diagram of complex **6**. Displacement ellipsoids drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

To confirm that complexes **4**–**7** were real intermediates of the reactions they were dissolved in acetone and treated with the corresponding dipolarophiles. In all reactions the obtained results were identical to those observed when the Lewis acid was added directly to the reaction as indicated above. Moreover, once compounds **4**–**7** were identified, it was possible to isolate them from the reaction mixtures after short periods of time (less than 6 h), thus confirming the *in situ* formation of such complexes.

At this point it is reasonable to speculate on the coordination of allylic alcohol in the complex as a function of the number of ligands. Thus, for the reaction in the presence of $Zn(OTf)_2$, it is possible to invoke substitution of a triflate group by the allylic alcohol giving rise to the reactive intermediate **8** (Scheme 4). This intermediate immediately evolves to give complex **P1c** which, after work-up, affords the final *cis* adduct **3a**.

According to this mechanism, only an *exo* approach is possible and thus the complete *cis* selectivity is rationalized with transition state **TS1**. A similar process may be invoked for activation with silver salts. In that case, however, the allylic alcohol might dissociate complexes **4** and **5** to form the corresponding intermediates with similar structure to **8**.



Scheme 4

Mechanistic considerations

The validity of the hypothesis outlined in Scheme 4 was tested by carrying out semiempirical calculations (PM3) of the whole process.[23] Semiempirical methods are intended for studying large and complicated molecular systems of interest for which a complete application of the *ab initio* methods is generally prohibitive in terms of computational effort.[24] Furthermore, when several mechanisms can be invoked for related processes the problem of determining the operating mechanism in each case can be most conveniently and economically tackled following a semiempirical approach at the first stages of the computational study, considering the limitations of the underlying approximations.[25] All calculations were performed with the MOPAC package[26] using the PM3 method.[27] The only simplification was the replacement of the *N*-benzyl group by a methyl group. The potential energy surfaces (PESs) for the studied processes have been calculated in detail. Thus, calculation of the whole reaction path profiles starting from the optimized geometry of the nitrone was carried out. Critical points have been located without any geometry restriction and have been characterized through the calculation of the force constants matrix by ensuring that they correspond to minima or saddle points on the PES; *i.e.*, they have zero or one and only one imaginary frequency, respectively. For transition structures the C–C and C–O distances represent the reaction coordinates. All the reaction paths have been checked by tracing the intrinsic reaction coordinate (IRC)[28] from the transition structure to the lower energy structures it connects. In all cases, it could be verified that the transition states proceed from the reactants and give rise to the products. Optimized geometries (in PDB format) of all stationery points are available from the supplementary material. †

Firstly, we have investigated the reaction promoted by zinc(II) triflate outlined in Scheme 4. The formation of complex **7** from nitrone **2** is exothermic (−20.81 kcal mol^{-1}) and it takes place without energy barrier. After nucleophilic substitution of a triflate group by allylic alcohol, complex **8** is formed. The formation of **8** is endothermic (by 7.06 kcal mol^{-1}) which is in agreement with the fact that energy must be given to the reaction (it only works at reflux, lower temperatures affording rather low conversion rates or no reaction at all).

The only possible transition state **TS1** for the intramolecular reaction was located. The IRC analysis showed as starting and final points of the reaction the corresponding complex **8** and product **P1c**, respectively. The energies (kcal mol^{-1}) of the corresponding stationary points are given in Table 2 and the optimized structures are shown in Fig. 3.

Alternatively, it is also possible to consider an external delivery of the allylic alcohol to the complex **7** as illustrated in Scheme 5.

In this case, it might even become apparent that, in the *exo* approach, an opportunity for coordination between zinc and allylic alcohol may emerge, such a possibility has been rejected by calculations. Hence, a tetracoordinated zinc atom is always preferred. The two possible transition structures **TS2x** and **TS2n** corresponding to *exo* and *endo* attacks, respectively were located. The energy values for reactants (complex **7** and allylic

Table 2 Heats of formation (PM3) of the reagents, starting complexes, transition structure and product for the intramolecular path shown in Scheme 4

	Energy (kcal mol^{-1})	Relative energy to reactants
2	43.47	
$Zn(OTf)_2$	−438.63	
Allylic alcohol	−31.30	
7	−415.97	−20.81[a]
8	−183.14	−16.85[b]
TS1	−137.46	42.42[c]
P1c	−213.69	−30.83[c]

[a] The energy of the reactants has been calculated as the sum of that of the nitrone and zinc(II) triflate, *i.e.*: −395.16 kcal mol^{-1}. [b] The energy of the reactants has been calculated as the sum of that of the nitrone, zinc(II) triflate and allylic alcohol, from which the energy corresponding to a molecule of triflic acid (−260.33 kcal mol^{-1}) has been subtracted, *i.e.*: −166.13 kcal mol^{-1}. [c] Complex **8** has been considered as the starting point.

Table 3 Heats of formation (PM3) of the reagents, starting complexes, transition structure and product for the intramolecular path shown in Scheme 4

	Energy (kcal mol^{-1})	Relative energy to reactants[a]
7	−415.97	
Allylic alcohol	−31.30	
TS2x	−404.49	42.78
TS2n	−405.85	41.42
P2c	−485.83	−38.56
P2t	−486.42	−39.15

[a] The energy of the reactants has been calculated as the sum of complex **7** and allylic alcohol, *i.e.*: −447.27 kcal mol^{-1}.

alcohol), transition structures and diastereomeric products are given in Table 3. The optimized structures for transition structures and final adducts are shown in Fig. 4. In this case, the preferential formation of the *cis* adduct (from an *exo* attack) is not well-predicted although close values are obtained for the addition by the two channels.

For the purpose of comparison, the complete profiles of the two approaches are shown in Fig. 5. The compared energy values are, in all cases, relative values. Admittedly, the energy

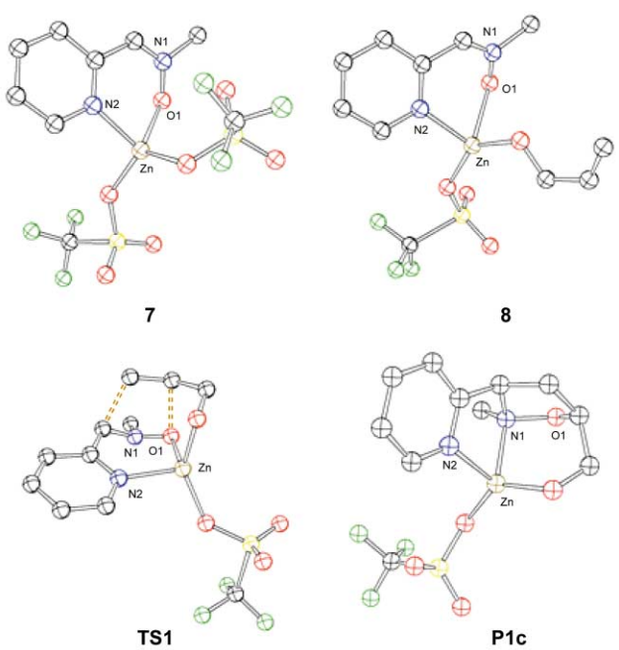
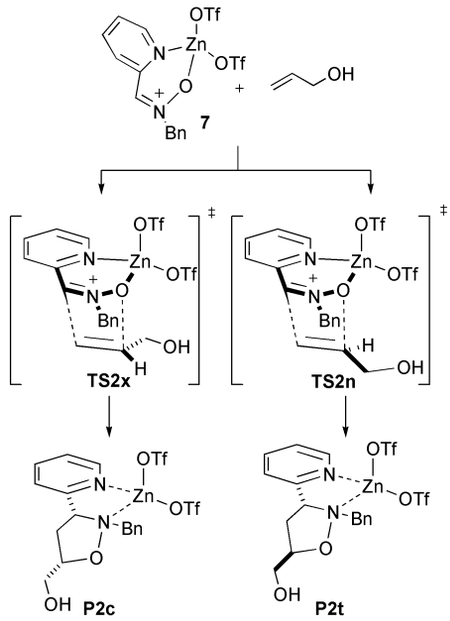


Fig. 3 Optimized structures of complexes, transition state and product for the intramolecular path depicted in Scheme 4 (hydrogen atoms have been omitted for clarity).



Scheme 5

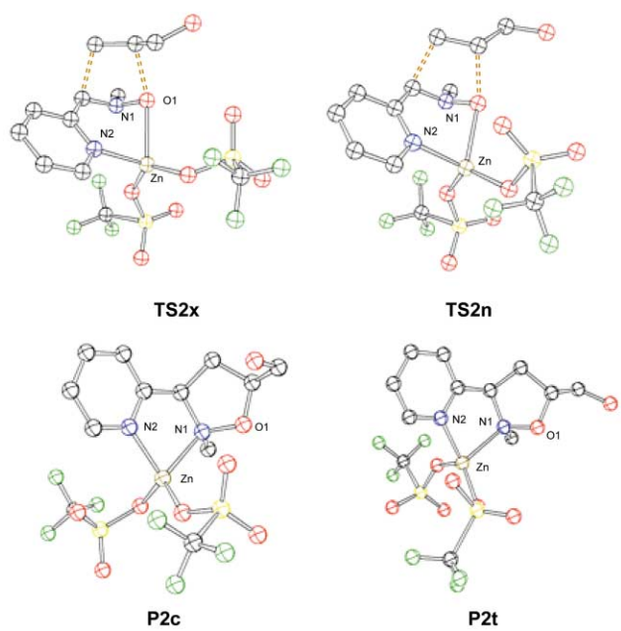


Fig. 4 Optimized structures of complexes, transition state and product for the intramolecular path depicted in Scheme 5 (hydrogen atoms have been omitted for clarity).

values for the two approaches are too close and fall into the range of the experimental error (less than 5 kcal mol^{-1}) considering that the reaction is carried out in acetone at reflux (*ca*. 330 K). However, the fact that only one isomer is obtained supports the hypothesis of the intramolecular mechanism, since the values found for the TS's corresponding to the intermolecular mechanism predict mixtures of isomers. These results clearly indicate that semiempirical calculations are not precise enough to describe the system and higher level calculations should be made in order to evaluate quantitatively the energetic differences.

Conclusions

In summary, we have demonstrated that the intermediate complexes formed in the cycloaddition of *N*-benzyl-*C*-(2-pyridyl) nitrone with allylic alcohol when metals complexes are added to promote the reaction, can be isolated and characterized by X-ray crystallography. It has also been shown that the com-

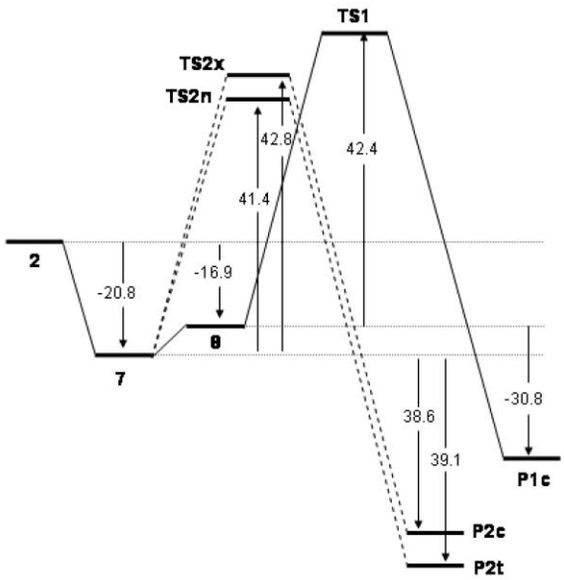


Fig. 5 Reaction profiles for both intra- (continuous line) and intermolecular (dotted line) paths illustrated in Schemes 4 and 5, respectively. See notes of Tables 2 and 3 for definitions of relative energies in each case.

plexes are real intermediates of the reaction. The semiempirical study of the reaction does not agree with the experimental observations. However, intramolecular cycloadditions remain as a possibility since it has been demonstrated that it is energetically possible. Although an intermolecular approach is predicted, the energy differences should not be considered quantitatively due to both limitations of the method and the proximity of energy values for a reaction carried out at 330 K. The extension of the method leading to asymmetric induction is currently the object of intensive investigation.

Experimental

General methods

The reaction flasks and other glass equipment were heated in an oven at 130 °C overnight and assembled in a stream of Ar. All reactions were monitored by TLC on silica gel 60 F254; the position of the spots was detected with 254 nm UV light or by spraying with one of the following staining systems: 50% methanolic sulfuric acid, 5% ethanolic phosphomolybdic acid and iodine. Preparative centrifugally accelerated radial thin-layer chromatography (PCAR-TLC) was performed with a Chromatotron® Model 7924 T (Harrison Research, Palo Alto, CA, USA) and with solvents that were distilled prior to use; the rotors (1 or 2 mm layer thickness) were coated with silica gel Merck grade type 7749, TLC grade, with binder and fluorescence indicator (Aldrich 34,644–6) and the eluting solvents were delivered by the pump at a flow-rate of 0.5–1.5 mL min^{-1}. Melting points were uncorrected. ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded on a Varian Unity or on a Bruker 300 instrument in $CDCl_3$. Elemental analysis were performed on a Perkin Elmer 240B microanalyzer. Pyridyl nitrone **2** was prepared as described.[16]

[(3*S**,5*R**)-2-Benzyl-3-pyridin-2-ylisoxazolidin-5-yl]methanol 3a and [(3*R**,5*R**)-2-benzyl-3-pyridin-2-ylisoxazolidin-5-yl]-methanol 3b

Without Lewis acid. To a solution of the nitrone **2** (0.212 g, 1 mmol) in acetone (10 mL) was added allylic alcohol (0.58 g, 10 mmol) and the resulting mixture was heated at reflux under Ar atmosphere for seven days. The solvent was evaporated and the products ratio was established by NMR analysis. The residue was purified by preparative, centrifugally accelerated, radial, thin-layer chromatography (Chromatotron®).

With Lewis acid. To a 0.1 M solution of the nitrone **2** (0.212 g, 1 mmol) in acetone (10 mL) was added the corresponding metal complex (1 mmol). The resulting mixture was stirred at ambient temperature for 15 min and then allylic alcohol (0.58 g, 10 mmol) was added and the mixture was heated at reflux under Ar atmosphere for the time indicated in Table 1. The solvent was evaporated and the products ratio was established by NMR analysis. The residue was purified by preparative, centrifugally accelerated, radial, thin-layer chromatography (Chromatotron®).

3a: (0.265 g, 98%; Table 1, entry 4); oil (Found: C, 71.3; H, 6.5; N, 10.6. Calc. for $C_{16}H_{18}N_2O_6$: C, 71.1; H, 6.7; N, 10.4%). $\delta_H(CDCl_3)$ 2.53 (dt, 1H, *J* 12.9 and 5.6 Hz, H_{4a}), 2.88 (dt, 1H, *J* 12.9 and 8.6 Hz, H_{4b}), 3.52 (br s, 1H, ex. D_2O, CH_2OH), 3.67 (dd, 1H, *J* 4.8 and 12.0 Hz, CH_2OH), 3.81 (dd, 1H, *J* 2.6 and 12.0 Hz, CH_2OH), 3.93 (d, 1H, *J* 13.5 Hz, NCH_2Ph), 3.99 (d, 1H, *J* 13.5 Hz, NCH_2Ph), 4.19 (dd, 1H, *J* 5.6 and 8.6 Hz, H_3), 4.49 (m, 1H, H_5), 7.16 (m, 1H, PyH_5), 7.39 (m, 1H, PyH_3), 7.40 (m, 5H, Ph), 7.63 (m, 1H, PyH_4), 8.50 (m, 1H, PyH_6). $\delta_C(CDCl_3)$ 36.6 (C_4), 60.2 (NCH_2Ph), 63.7 (CH_2OH), 64.0 (C_3), 69.8 (C_5), 121.7 (PyC_5), 122.4 (PyC_3), 127.1 (PhCH), 128.1 (PhCH × 2), 128.6 (PhCH × 2), 136.9 (PyC_4), 137.0 (PhC), 148.7 (PyC_6), 159.9 (PyC_2).

3b: (0.073 g, 27%; Table 1 entry 1); oil (Found: C, 70.9; H, 6.4; N, 10.2. Calc. for $C_{16}H_{18}N_2O_6$: C, 71.1; H, 6.7; N, 10.4%). $\delta_H(CDCl_3)$ 2.61 (m, 2H, H_{4a} and H_{4b}), 3.58 (dd, 1H, *J* 4.8 and 11.7 Hz, CH_2OH), 3.60 (br s, 1H, ex. D_2O, CH_2OH), 3.72 (dd, 1H, *J* 2.9 and 11.7 Hz, CH_2OH), 3.93 (d, 1H, *J* 13.5 Hz, NCH_2Ph), 3.99 (d, 1H, *J* 13.5 Hz, NCH_2Ph), 4.11 (t, 1H, *J* 7.4 Hz, H_3), 4.28 (m, 1H, H_5), 7.12 (m, 1H, PyH_5), 7.29 (m, 5H, Ph), 7.54 (m, 1H, PyH_3), 7.62 (m, 1H, PyH_4), 8.48 (m, 1H, PyH_6). $\delta_C(CDCl_3)$ 38.3 (C_4), 61.1 (NCH_2Ph), 63.7 (CH_2OH), 64.0 (C_3), 70.9 (C_5), 122.5 (PyC_5), 124.4 (PyC_3), 127.3 (PhCH), 128.3 (PhCH × 2), 129.0 (PhCH × 2), 137.0 (PyC_4), 137.1 (PhC), 149.4 (PyC_6), 160.2 (PyC_2).

[Ag(OTf)(2-PyBN)]$_2$ 4

To a diethyl ether solution (20 mL) of nitrone **2** (2-PyBN) (0.042 g, 0.2 mmol) under Argon atmosphere was added [AgOTf] (0.042 g, 0.2 mmol). A solid precipitated immediately which was filtered off and washed with diethyl ether (2 × 5 mL) to give 0.071 g, (75%) as a white solid. Mp 116 °C (from diethyl ether) (Found: C, 35.49; H, 2.75; S, 6.61. Calc. for $C_{28}H_{24}N_4O_8Ag_2F_6S_2$: C, 35.84; H, 2.58; S, 6.83%). IR(Nujol): *ν* (C=N) 1593, *ν* (TfO) 1290, 1237, 1167 cm^{-1}. δ_H(acetone-d_6): 5.23 (s, 4H), 7.30–7.35 (m, 6H), 7.50–7.65 (m, 6H), 8.15 (dt, 2H, *J* 1.0 and 7.8 Hz), 8.49 (s, 2H), 8.75–8.85 (m, 4H). δ_F(acetone-d_6) −77.5 (s). δ_C(acetone-d_6) 76.6, 130.4, 131.0, 133.8, 134.0, 134.4, 135.0, 139.0, 139.6, 144.5, 154.6, 157.5, 210.8. *m*/*z* (LSISM+) 787 (10%) $[M - TfO]^+$; 575 (8) $[M - TfO - (2\text{-PyBN})]^+$; 531 (33) $[Ag(2\text{-PyBN})_2]^+$, 319 (100) $[Ag(2\text{-PyBN})]^+$.

[Ag(2-PyBN)(PPh_2Me)]$_2$(ClO_4)$_2$ 5

To a diethyl ether solution (20 mL) of nitrone **2** (2-PyBN) (0.042 g, 0.2 mmol) under an argon atmosphere was added [Ag($OClO_3$)(PPh_2Me)] (0.081 g, 0.2 mmol). After 12 h of stirring the obtained solid was filtered off and washed with diethyl ether (2 × 5 mL) to give **5** (0.109 g, 88%) as a white solid. Mp: 172 °C (from diethyl ether) (Found: C, 51.40; H, 3.99; N, 2.10. Calc. for $C_{54}H_{52}N_2O_{10}Ag_2Cl_2P_2$: C, 51.41; H, 4.23; N, 2.26%). IR(Nujol): *ν* (C=N) 1599, *ν* (ClO_4) 1097, 624 cm^{-1}. $\delta_H(CDCl_3)$ 1.93 (d, 6H, *J* 7.6 Hz), 5.24 (s, 4H), 5.29–5.53 (m, 36H), 7.72 (s, 2H), 8.17–8.20 (m, 4H). $\delta_P(CDCl_3, -60\ °C)$ −2.8 (dd, $J(^{107}Ag–P)$ 734 Hz, $J(^{109}Ag–P)$ 846 Hz). $\delta_C(CDCl_3)$ 13.1, 13.4, 71.8, 125.5, 128.8, 129.2, 129.3, 129.8, 131.0, 131.1, 132.3, 132.5, 132.7, 134.6, 139.3. *m*/*z* (LSISM+) 518 (83%)

$[Ag(2\text{-PyBN})(PPh_2Me)]^+$; 507 (60) $[Ag(PPh_2Me)_2]^+$; 307 (100) $[AgPPh_2Me]^+$.

$[ZnBr_2(2\text{-PyBN})]$ 6 and $[Zn(OTf)_2(2\text{-PyBN})]$ 7

To an acetone solution (20 mL) of nitrone **2** (2-PyBN) (0.042 g, 0.2 mmol) under an argon atmosphere was added $ZnBr_2$ (0.045 g, 0.2 mmol) or $Zn(TfO)_2$ (0.073 g, 0.2 mmol). After 4 h of stirring the solution was concentrated under pressure and the residue was triturated with diethyl ether to give a white solid which was filtered off and washed with diethyl ether (2 × 5 mL).

6: (0.075 g, 85%). white solid; mp:249–250 °C (from diethyl ether) (Found: C, 35.50; H, 2.60; N, 6.64. Calc. for $C_{13}H_{12}N_2OBr_2Zn$: C, 35.73; H, 2.77; N, 6.41%). IR(Nujol): ν (C=N) 1617 cm^{-1}. δ_H(acetone-d_6) 5.40 (s, 2H), 7.41–7.45 (m, 3H), 7.60–7.64 (m, 2H), 8.00 (t, 1H, *J* 6.2 Hz), 8.07 (d, 1H, *J* 7.8 Hz), 8.41 (dt, 1H, *J* 1.7 and 7.8 Hz), 8.76 (d, 1H, *J* 4.5 Hz), 8.80 (s, 1H). δ_C(acetone-d_6) 149.6, 141.2, 137.8, 132.8, 130.0, 129.5, 129.1, 128.4, 71.2. *m*/*z* (LSISM+) 567 (37%) $[M - Br + (2\text{-PyBN})]^+$; 355 (66) $[M - Br]^+$.

7: (0.104 g, 90%). white solid; mp 253–255 °C (from diethyl ether) (Found: C, 31.69; H, 2.28; N, 4.50; S, 11.12. Calcd. for $C_{15}H_{12}N_2O_7F_6S_2Zn$: C, 31.31; H, 2.10; N, 4.87; S, 11.14%). IR(Nujol): ν (C=N) 1617, ν (TfO) 1288, 1246, 1188 cm^{-1}. δ_H(acetone-d_6) 5.37 (s, 2H), 7.42–7.52 (m, 5H), 7.83 (t, 1H, *J* 6.6 Hz), 8.04 (d, 1H, *J* 7.5 Hz), 8.40 (t, 1H, *J* 7.8 Hz), 8.78 (br s, 2H). δ_C(acetone-d_6) 150.6, 150.5, 147.6, 141.5, 138.0, 133.2, 130.9, 130.9, 130.1, 129.5, 128.4, 71.1. δ_F(acetone-d_6) −74.6 (s). *m*/*z* (LSISM+) 637 (100%) $[M - TfO + (2\text{-PyBN})]^+$; 425 (42) $[M - TfO]^+$.

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