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REVIEW COMMENTARY

RHODIUM(II)-CATALYZED AZIRIDINATIONS AND CH INSERTIONS WITH [*N*-(*p*-NITROBENZENESULFONYL)IMINO]PHENYLIODINANE

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The $[Rh_2(OAc)_4]$-catalyzed decomposition of NsN=IPh {[*N*-(*p*-nitrobenzenesulfonyl)imino]phenyliodinane} in the presence of olefins affords aziridines in yields of up to 85%. The aziridination of *cis*-hex-2-ene and *cis*-β-methylstyrene is stereospecific, but, *cis*-stilbene affords a 3:1 mixture of *cis*- and *trans*-aziridines in low yield. With chiral Rh(II) catalysts, optically active aziridines are formed having enantiomeric excesses of up to 73%. The NsN=IPh–$[Rh_2(OAc)_4]$ system is also efficient for the allylic amination of olefins and for insertion into CH bonds, activated by phenyl or oxygen substituents.

1. INTRODUCTION

Transition metal mediated reactions of carbenes have attracted considerable attention in recent years owing to the possibility of effecting asymmetric syntheses by means of appropriate chiral catalysts. Several efficient systems for a symmetric cyclopropanation have been designed involving decomposition of diazo compounds[1] or of iodonium ylides[2] by an appropriate transition metal catalyst bearing chiral ligands, mostly based on Cu,[3] Rh[4] or Ru.[5] In contrast, the analogous transition metal-catalyzed addition of nitrenes has been much less investigated. The first evidence of metal-catalyzed nitrene transfer from *p*-toluenesulfonyl azide to cyclohexene was reported in 1967.[6] Subsequent investigations in the area were carried out in connection with model studies on cytochrome P–450. The tosylamidation of cyclohexane and the intramolecular CH insertion of the nitrene moiety of [*N*-(2,5-diisopropylbenzenesulfonyl)imino]phenyliodinane in the presence of either an Fe(III)- or Mn(III)-porphyrin or $[Rh_2(OAc)_4]$ was investigated by Breslow and Gellman.[7,8] Groves and Takahashi[9] reported an example of stoichiometric nitrene transfer from an Mn(III)-porphyrin to an olefin. Mansuy *et al.*[10] developed a catalytic aziridination process based on Fe(III)- and Mn(III)-porphyrins using TsN=IPh{[*N*-(*p*-toluenesulfonyl)imino]phenyliodinane}.

The asymmetric aziridination was developed mainly by Evans and co-workers[11] and Conser and Jacobsen[12] with TsN=IPh and copper salts and bis(oxazoline) or salen ligands, respectively. The reactions proceeded with high yields and, in some cases, with exceptional enantioselectivities, producing aziridines with up to 98% enantiomeric excess (ee). The Cu-catalyzed asymmetric aziridination of styrene with TsN=IPh was also investigated by Lowenthal and Masamune,[13] albeit with less success. Other catalytic systems which have been investigated include CuOTf in conjunction with a trispyrazolylborate ligand[14] and Mn(salen) complexes[15,16] with TsN=IPh as nitrene precursor.

In the past, we had encountered remarkable success in enantioselective carbenoid reactions catalyzed with Doyle *et al.*'s chiral Rh(II) catalysts bearing pyrrolidone carboxylate or oxazolidinone ligands. Asymmetric inductions reaching the limits of detection were found in intramolecular cyclopropanations of allylic diazoacetates,[4] in intermolecular cyclopropenation of certain terminal acetylenes[17] and in intramolecular CH insertions of *meso*-alkyldiazoacetates.[18] We speculated, therefore, that the chiral Rh(II) carboxamidates might be equally successful in catalytic nitrene transfer. Nitrene transfer from TsN=IPh to olefins in the presence of $[Rh_2(OAc)_4]$ has been investigated by Evans and co-workers[11] in the past, but was found much less satisfactory than when carried out in the presence of Cu catalysts. Our initial effort, therefore, was directed towards improvement of the Rh(II)-catalyzed aziridination, in order to make it competitive with the Cu-catalyzed reaction.

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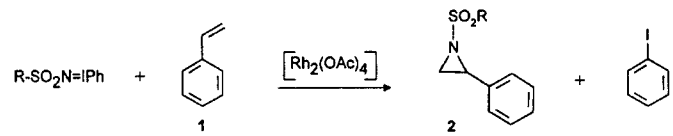
AZIRIDINATION OF OLEFINS

Extensive experiments for optimization of the aziridination of styrene (**1**) with TsN=IPh–[$Rh_2(OAc)_4$] involving variations of solvent and temperature were unsuccessful. The yields of aziridine (**2**) were significantly below those obtained with Cu(II) and never exceeded 60%. However, it was found that acceptable yields of aziridine (85% isolated yield) could be obtained when the nitrene precursor TsN=IPh was replaced with NsN=IPh (Table 1). Interestingly, however, the introduction of a second nitro group as in 2,4-$(NO_2)_2C_6H_3SO_2N$=IPh resulted in no further improvement (48%), and no aziridine was obtained when (*p*-$MeOC_6H_4SO_2N$=IPh) was used as a nitrene source. With [$Cu(acac)_2$] the yields of aziridine were always higher than with [$Rh_2(OAc)_4$], except for NsN=IPh. TsN=IPh was the ylide of choice for aziridination with [$Cu(acac)_2$]. Since some Rh(II)-catalyzed decomposition of NsN=IPh occurred under the conditions of aziridination, the olefin was always used in excess (5–20-fold; see Tables 1 and 2) over the ylide. Despite this, sulfonamide ($NsNH_2$) was formed as a secondary product, in particular with unreactive olefins. Formation of sulfonamide together with iodosylbenzene has been reported in the Fe(TPP)(Cl)- and Mn(TPP)(Cl)-catalyzed aziridination of stilbene. In these systems, metal-catalyzed epoxidation of stilbene by PhIO occurs.[10] However, no epoxides were found in the Rh(II)-catalyzed reactions.

The electronic substituent effect for styrene aziridination was determined by competition experiments using pairs of substituted styrenes (**1** and **1-X**) in 2–10-fold excess over NsN=IPh and with 2 mol% of [$Rh_2(OAc)_4$] with respect to NsN=IPh in CH_2Cl_2 at room temperature.[19] Competition constants (k_{rel}) were determined from the ratios of the aziridines (**2/2 – X**) as determined by ^{1}H NMR of the crude reaction mixture. A plot of $\log k_{rel}$ vs Hammetts σ^+ constants is shown in Figure 1. A ρ-value of −0·60 is obtained for the reaction, very close to that for Rh(II)-catalyzed addition of diazomalonate (and the corresponding iodonium ylide) to styrenes.[2]

The stereospecificity of the reaction was investigated with three olefins and afforded ambiguous results. *cis*-Hex-2-ene and *cis*-β-methylstyrene reacted in a fully stereospecific manner, producing the *cis*-aziridines in 54% and 82% yield, respectively. In both cases the absence of *trans* isomers in the reaction mixture was verified by comparison with an authentic sample of the corresponding *trans*-aziridine. In contrast, the aziridination of *cis*-stilbene proceeded very slowly and afforded a 77 : 23 mixture of *cis*- and *trans*-aziridine in only 18% yield. Both aziridines rearranged under the reaction conditions (see below), but since rearrangement of the *trans* isomer is faster, it follows that its formation under the conditions of aziridination is not due to isomerization of the *cis*-aziridine, but to a non-specific aziridination pathway. These results should be compared with those obtained in the Cu-catalyzed



Scheme 1.

Table 1. [$Rh_2(OAc)_4$]-catalyzed aziridination of styrene (**1**) with PhI=NSO_2R[a]

R	Catalyst	Yield of aziridine (%)	Time
Me	[$Cu(acac)_2$]	7	75 h
Me	[$Rh_2(OAc)_4$]	0	75 h
4-MeC_6H_5	[$Cu(acac)_2$]	95[b]	
4-MeC_6H_5	[$Rh_2(OAc)_4$]	59[c]	40 min
4-$MeOC_6H_5$	[$Cu(acac)_2$]	60	45 min
4-$MeOC_6H_5$	[$Rh_2(OAc)_4$]	0	35 min
4-$NO_2C_6H_5$	[$Cu(acac)_2$]	71[c]	14 h
4-$NO_2C_6H_5$	[$Rh_2(OAc)_4$]	85[c]	35 min
4-$NO_2C_6H_5$	none	0[c]	24 h
2,4-$(NO_2)_2C_6H_4$	[$Cu(acac)_2$]	58	100 min
2,4-$(NO_2)_2C_6H_4$	[$Rh_2(OAc)_4$]	48	135 min

[a] Conditions: styrene (5 mmol), ylide (1 mmol), catalyst (0·02 mmol), in CH_2Cl_2 (20 ml) for [$Rh_2(OAc)_4$] or CH_3CN (20 ml) for [$Cu(acac)_2$], room temperature. Ref. 19.
[b] Ref. 11.
[c] 20 mmol of styrene.

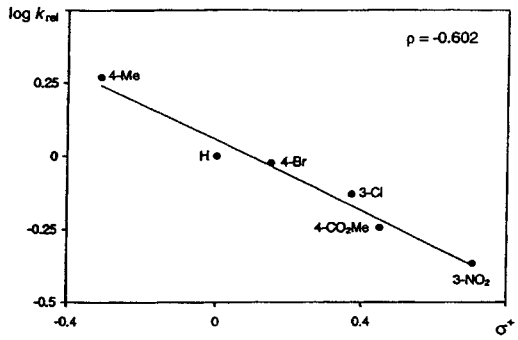


Figure 1. Hammett plot for $[Rh_2(OAc)_4]$-catalyzed addition of NsN=IPh to substituted styrenes. $\rho = -0{\cdot}6$

aziridination, which is fully stereospecific with oct-4-ene, partly stereospecific, depending on the counterion of the Cu catalyst, with *cis*-β-methylstyrene and still less stereospecific with *cis*-stilbene.

The extension of the aziridination to olefins of general structure encountered some difficulties. The yields were lower and aziridination was often accompanied by products of formal nitrene insertion into the α-position of the double bonds (see below). With hex-1-ene the yield dropped to 63% (Table 2) and *cis*- and *trans*-hex-2-ene afforded the corresponding aziridines in 54% and 27% yield, respectively. Steric hindrance may be a detrimental factor in these reactions, as evidenced for norbornene, which afforded only 4% of *exo*-aziridine when the reaction was carried out at room temperature. The yield increased to 29% in refluxing CH_2Cl_2. The aziridination of the electron-deficient ethyl acrylate proceeded very sluggishly, affording the aziridine in only 7% yield.

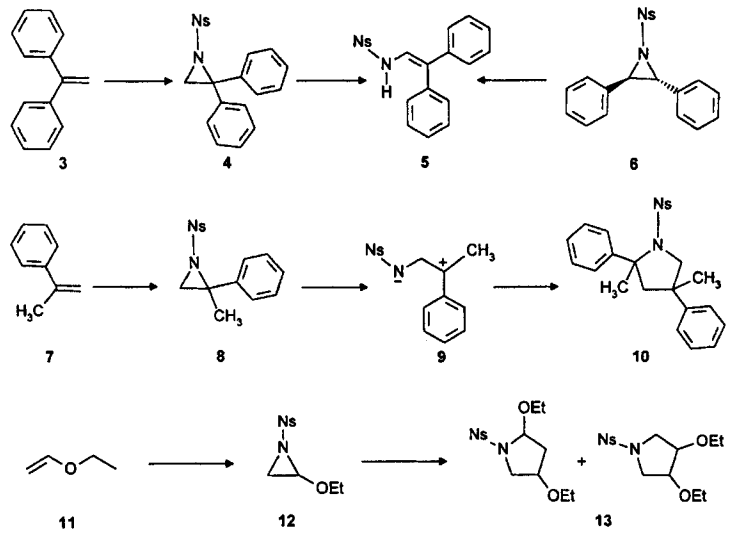
The aziridines derived from olefins having α-substituents capable of stabilizing charge underwent ring opening either upon exposure to $[Rh_2(OAc)_4]$ during the reaction or during work-up. Thus, aziridination of 1,1-diphenylethene (**3**) afforded a mixture of aziridine **4** and enamine **5** in a ratio depending on the reaction time and method of purification. In separate experiments it was found that pure **4** rearranges to **5** in the presence of $[Rh_2(OAc)_4]$ or on chromatography with SiO_2. The aziridine **6** derived from *trans*-stilbene, when exposed to $[Rh_2(OAc)_4]$ underwent ring opening accompanied by phenyl migration to the same enamine **5**. Ring opening accompanied by phenyl migration to **5** occurred also with the corresponding *cis*-diphenylaziridine but at a lower rate. The aziridination of α-methylstyrene (**7**) afforded no isolable aziridine **8**, but rather a pyrrolidine **10**, which must originate from ring opening of **8** to a dipolar species **9** which, in turn, is intercepted by a second molecule of **7**. The relative configuration of **10** was not determined, but is assumed to be *trans*. Similarly, ethyl vinyl ether (**11**) afforded no **12**, but rather a mixture of isomeric pyrrolidines **13** in 48% overall yield. No ring opening was observed, however, with vinyl acetate.[20]

The enantioselectivity of the aziridination was tested with styrene (**1**) and *cis*-β-methylstyrene (Table 3). Surprisingly, the catalysts most efficient for enantioselective cyclopropanation of olefins, such as $[Rh_2\{(2S)\text{-mepy}\}_4]$[21] or $[Rh_2\{(4R)\text{-phox}\}_4]$[22] produced aziridines with only low enantioselectivity. McKervey and co-workers' sulfonated rhodium prolinate[23] and Ikegami and co-workers' rhodium phthaloyl phenylalaninate[24]

Table 2. Aziridination of olefins with NsN=IPh, catalyzed by $[Rh_2(OAc)_4]$[a]

Olefin	Yield of aziridine (%)	Comments
Styrene	85	
Hex-1-ene	63	
Vinyl acetate	47	
Ethyl vinyl ether	0	Ring opening; see text
Ethyl acrylate	7	
Indene	40	
Norbornene	4	*exo* Isomer; 29% at 45 °C
Cyclohexene	4	70% insertion product; see below
trans-Hex-2-ene	27	Stereospecific
cis-Hex-2-ene	54	Stereospecific
trans-β-Methylstyrene	68	Stereospecific
cis-β-Methylstyrene	82	Stereospecific
trans-Stilbene	41	Stereospecific (+ 11% of **11**)
cis-Stilbene	14	4% of *trans*-aziridine
α-Methylstyrene	0	Ring opening; see below
1,1-Diphenylethene	65	Rearranges to enamine

[a]Conditions: 1 mmol of NsN=IPh, 20 mmol of olefin, 0·02 mmol of $[Rh_2(OAc)_4]$ in CH_2Cl_2 (10 ml) in presence of molecular sieves 4A (6·0 g), room temperature.[18]



Scheme 2.

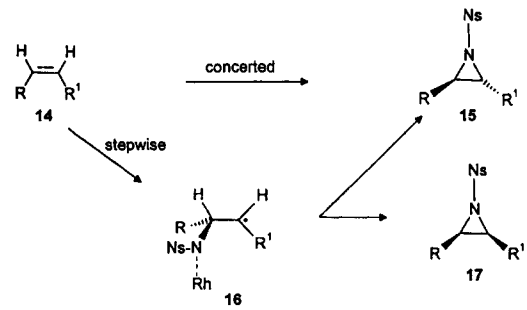
were equally unsatisfactory. So far, the best result has been achieved with the catalyst of Pirrung (rhodium bisnaphtholphosphate),[25] which afforded the aziridine of *cis*-β-methylstyrene with 80% yield and 73% *ee*. Further optimization of the catalyst structure is in progress.

Although the enantioselectivity of the Rh(II)-catalyzed aziridination is at present of limited preparative interest, it is mechanistically significant. It suggests that the nitrene transfer takes place in proximity of the metal, and that a free nitrene cannot be involved. A rhodium-complexed nitrene is a plausible intermediate, in analogy with metal nitrenes proposed for aziridinations catalyzed by Fe(TPP)(Cl), Mn(TPP)(Cl)[10] or Cu complexes.[11] The capacity of Rh(II) to form metal–carbene complexes as reactive intermediates is well documented.[26] The ρ-value of $-0{\cdot}60$ is consistent with the intermediacy of a moderately electrophilic intermediate. It compares favourably with the values for carbenoid addition of diazomalonate to styrene (**1**), carried out in the presence of Rh(II) ($\rho = -0{\cdot}47$) and Cu(I) ($\rho = -1{\cdot}12$) catalysts.[2] The [Cu(acac)$_2$]-catalyzed aziridination of styrenes (**1**) with NsN=IPh yields a preliminary value of $-0{\cdot}5$.[19] However, since the ρ-values for addition of dichlorocarbene to styrene (**1**) [$\rho = -0{\cdot}62$ (80 °C)[27]] and α-methylstyrene (**7**) [$\rho = -0{\cdot}38$ (0 °C)[28]] lie in the same range, it is difficult to draw final conclusions from the Hammett plots alone.

Table 3. Asymmetric induction in Rh(II)-catalyzed aziridination of styrene (**1**) and *cis*-β-methylstyrene

	Styrene		*cis*-β-Methylstyrene	
Catalyst	Aziridine yield (%)	*ee* (%)	Aziridine yield (%)	*ee* (%)
[Rh$_2$\{(2*S*)-mepy\}$_4$][a]	81	21		
[Rh$_2$\{(4*S*)-phox\}$_4$][b]	56	22		
[Rh$_2$\{(4*S*)-macim\}$_4$][c]	50	<10		
[Rh$_2$\{(2*S*)-bepy\}$_4$][d]	71	27	70	35
[Rh$_2$\{(*S*)-ptpa\}$_4$][e]	92	0		
[Rh$_2$\{psp\}$_4$][f]			70	<10
[Rh$_2$\{(R)-(−)-bnp\}$_4$][g]	74	55	80	73

[a] Ref. 21.
[b] Ref. 22.
[c] Ref. 18.
[d] Dirhodium tetrakisbenzyl-(2*S*)-pyrrolidinonecarboxylate. Ref. 31.
[e] Ref. 23.
[f] Ref. 24.
[g] Ref. 25.



Scheme 3.

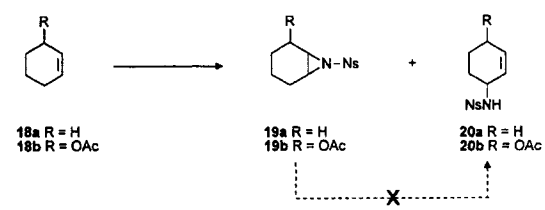
The stereospecific aziridination of hex-2-ene and β-methylstyrene, in turn, suggests that a free nitrene is not involved, since the latter should add at least in part unspecifically from the triplet ground state. The stereospecificity of the addition may be rationalized either by a concerted reaction of the *cis*-olefin **14** with the metal-complexed nitrene to afford the *cis*-aziridine **17**. However, a stepwise mechanism involving a radical intermediate (**16**), in which the rate of ring closure is faster than that for rotation around the single bond, could in principle also result in a stereospecific aziridination.[11,15] A dipolar intermediate would be more difficult to reconcile with the ρ-value, however. The *trans*-aziridine **15** then appears if the rates of ring closure and for bond rotation are competitive. The loss of stereospecificity in the aziridination of *cis*-stilbene is in favour of a stepwise mechanism. The radical lifetime should be enhanced with this compound owing to the possibility of delocalization of the unpaired electron, and rotation around the single bond will be faster than in less crowded olefins owing to the possibility of strain release. It is not clear, however, whether the stepwise mechanism applies to all olefins, or only to *cis*-stilbene.

INTERMOLECULAR NITRENE INSERTION INTO CH BONDS

One of the special features of the Rh(II)-catalyzed carbenoid reactions in comparison with the copper-catalyzed reactions is their preference for intramolecular CH insertions. Such intra- and even intermolecular insertions have been reported in the past for nitrenes generated in the presence of $[Rh_2(OAc)_4]$[8] or with Mn- and Fe-porphyrins.[29] Under our conditions, cyclohexene (**18a**) afforded a 70% yield of allylic insertion product (**20a**) together with only 4% of aziridine **19a**. In the series of cycloalkenes the selectivity for aziridination vs insertion, respectively, varies with the ring size as follows: cyclopentene, 20:80; cyclohexene, 5:95; cycloheptene 67:33; and cyclooctene, >99:1.[30] The products of allylic insertion of cycloalkenes may be formed not only by a true insertion process, but also by ring opening of an intermediate aziridine. In order to eliminate this possibility, 3-acetoxycyclohexene (**18b**) was exposed to the usual reaction conditions. The principal product, isolated in 43% yield as a mixture of stereoisomers, was identified as 3-acetoxy-6-*p*-nitrobenzenesulfonylaminocyclohexene (**20b**), together with a small amount of aziridine **19b**. Since **20b** cannot derive from **19b**, it follows that the reaction does indeed take place at the allylic position.

Intermolecular CH insertion (Table 4) also takes place in positions adjacent to aromatic rings and oxygen atoms. Tetralin, indan and ethylbenzene reacted at the α-position and afforded the corresponding insertion products in 51%, 69% and 50% yield, respectively. The yield dropped significantly with toluene and also, unexpectedly, with isopropylbenzene and diphenylmethane. The lower yield with toluene indicates that secondary CH bonds are more reactive than primary bonds, but the trend does not continue for tertiary CH bonds, which are in fact less reactive than the secondary bonds. In addition, while one phenyl group activates the CH bond, a second one exerts a deactivating effect. Tetrahydrofuran reacted selectively at the α-position, giving a 56% yield of insertion product. In contrast, hydrocarbons exhibited very low selectivity. Methylcyclopentane and methylcyclohexane afforded an inseparable mixture of insertion products but adamantane, surprisingly, reacted in high yield at the tertiary CH bonds (71%) and to only a very minor degree (5%) at the methylene groups.

The mechanism of the insertion reactions is not yet established. Insertion into the activated CH bond may be direct or may involve a sequence of hydrogen abstraction followed by radical recombination. The observed reactvities are compatible with both mechanisms. Steric hindrance or blockage of the coordination sites of the Rh(II) by phenyl groups may be responsible for the lower reactivity of 2-propylbenzene and diphenylmethane in comparison with ethylbenzene. The allylic amination of 1-deuterocyclohexene (**21**) with NsN=IPh–$[Rh_2(OAc)_4]$ was examined in order to gain insight into the mechanism of allylic amination. Direct CH insertion with **21** expectedly affords a 1:1 mixture of **22** and **23**. For a radical reaction, two isomeric radicals would be formed in a 1:1 ratio, and their colligation should afford **22**, **23** and **24** in a ratio of

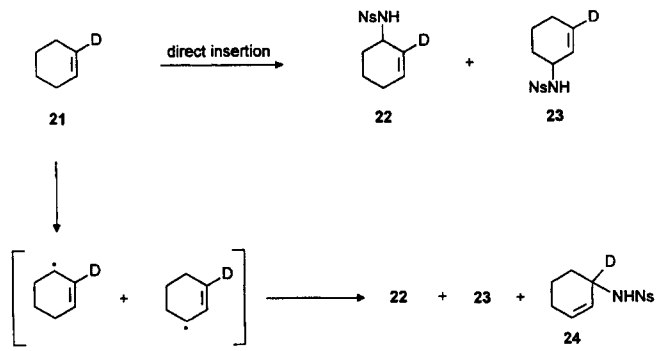


Scheme 4.

Table 4. Intermolecular CH insertion with NsN=IPh–$[Rh_2(OAc)_4]$[a]

Compound	α-insertion (%)	Comments
Cyclopentene	44	9% aziridine
Cyclohexene	70	4% aziridine
Cycloheptene	17	24% aziridine
Cyclooctene	0	54% aziridine
Toluene	3	
Ethylbenzene	50	
Isopropylbenzene	8	
Indan	69	
Tetralin	51	
Diphenylmethane	13	
Methylcyclopentane	16	Mixture of insertion products
Methylcyclohexane	18	Mixture of insertion products
Adamantane	71	5% insertion into secondary position
Cyclohexane	30	In CH_2ClCH_2Cl, reflux
Tetrahydrofuran	56	
Dioxane	39	
Benzyl methyl ether	78	Isolated as *N*-(*p*-nitrobenzenesulfonyl)benzimine

[a] Conditions: in CH_2Cl_2, room temperature, 20 equiv. of substrate, 1 equiv. of NsN=IPh, 0·02 equiv. of $[Rh_2(OAc)_4]$.



Scheme 5.

2 : 1 : 1. Analysis of the reaction mixture by ^1H and ^2H NMR spectrometry revealed the signals corresponding to **22** and **23** in a 1 : 1 ratio, together with a trace of **24**. This is consistent with direct insertion of the nitrene into the CH bond, or with a mechanism in which radical recombination is faster than reorientation of the radicals.

For both mechanisms, an enantioselective amination is in principle possible. Indeed, when indan was aminated in the presence of Pirrung's catalyst,[25] the product was enantioenriched with an *ee* of 31% (yield 71%). Further experiments towards improved understanding of the reaction mechanism and higher enantioselectivity are in progress.

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