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Copper-Homoscorpionate Complexes as Very Active Catalysts for the Olefin Aziridination Reaction

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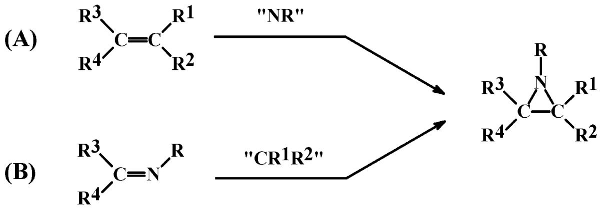
A series of complexes Tp^xCu (Tp^x = homoscorpionate ligand) have been tested as the catalysts for the olefin aziridination reaction using PhINTs as the nitrene source. Very high yields of aziridines have been obtained with a group of representative substrates, including nonactivated terminal olefins. The high activity of these catalysts has allowed the use of equimolar amounts of PhINTs and olefins, avoiding the requirement of excess olefin. In an effort to eliminate nondesired byproducts, chloramine-T has been employed as the nitrene source, in a reaction that produces sodium chloride as the sole residue, with high degrees of conversions also being obtained.

Introduction

Aziridine rings are useful substrates in organic chemistry due to their versatility as intermediates for the preparation of a number of products, ranging from amino acids to polymeric chains.[1] Several routes are known to lead to these strained rings, including stoichiometric[1] and catalytic processes. Among the latter, metal-free[1,2] and metal-based[3] procedures have been reported, although most of the recent work cited in the literature has concentrated on the use of transition metal complexes as catalysts for aziridine synthesis. This is mainly due to the potential of such catalysts to control the selectivity of the reaction, i.e., to induce some degree of enantio- or diastereomeric excess. Two different catalytic processes have led to the formation of aziridines (Scheme 1): the addition of a “NR” nitrene unit to a C−C double bond (alkene)[4−6]or alternatively the addition of a carbene unit “CR_2” to a C−N double bond (imine).[7] The former route (Scheme 1, A) has been extensively studied when compared with the latter (Scheme 1, B), and very efficient catalysts, based on different transition metals, have been reported, some of them inducing excellent degrees of enantioselection.[6c,d] With the exception of the seminal work by Kwart and Kahn,[4] and a few others, where tosyl azide was used as the nitrene source, the most employed reagent for the olefin aziridination reaction has been the iminoiodane PhI=NTs[8] (Ts = tosyl), for both achiral[5] and chiral[6] catalysts. Very recently, DuBois et al.[5j] have described the use of a rhodium-based catalyst for the olefin aziridination reaction using $H_2NSO_3CH_2CCl_3$ as the nitrene source ($PhI(OAc)_2$ and MgO were used as co-reagents). The experimental procedure for most systems generally supposes the use of 1−5% molar ratio of the catalyst with respect to the nitrene source, whereas the PhINTs:olefin ratio usually ranged from 1:5 to 1:10.

Scheme 1



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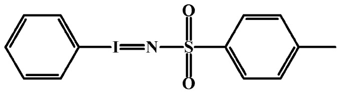
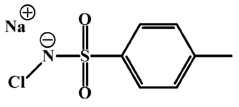
Despite the number of already known systems and their catalytic activities, there is still some work to be done in order to avoid the following drawbacks: (a) most of the catalysts display a low catalytic activity when linear, nonactivated (1-hexene, 1-octene); (b) the excess of olefin required is not acceptable for the conversion of expensive or rare substrates; (c) a high catalyst loading (5%) is usually needed for copper-based catalysts; and (d) the use of PhINTs supposes the formation of iodobenzene as a byproduct,with the subsequent low values of the atomic selectivity[9] for this process. In this sense, in recent years chloramine-T (*N*-chloro-*N*-sodium-*p*-toluenesulfonamide)[10] and related compounds have been screened as the nitrene source for this transformation: the main advantage of these reagents is the formation of an alkaline halide as byproduct. With these ideas in mind, the design of improved catalysts for the olefin aziridination reaction should meet the following requirements: (i) high performance for both activated (styrene, cyclooctene) and nonactivated (1-hexene, acrylates) olefins, (ii) no need of excess of olefin, and (iii) compatible with *environmental friendly* nitrene sources other than PhINTs. In this contribution we present the catalytic properties of some copper(I) complexes containing polypyrazolylborate[11] ligands toward the olefin aziridination reaction under the requirements underlined above.

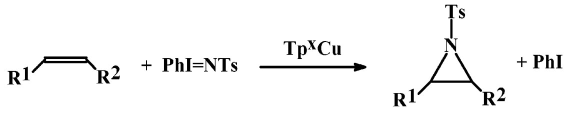


PhINTs



Chloramine-T

Results and Discussion



(1)

Ts = p-$CH_3C_6H_4SO_2$

Table 1. Olefin Aziridination[a] with Tp^{x}Cu Complexes as the Catalysts

entry	catalyst	styrene	*cis*-cyclooctene	1-hexene
1	Tp*Cu	>95	93	81
2	Tp^{Cy}Cu	>95	93	84
3	Tp^{Ph}Cu	>95	88	78
4	Tp^{Ms}Cu	>95	82	62
5	Tp^{Br3}Cu	>95	>95	91
6[b]	Tp^{Br3}Cu	85	69	54

[a] Cu:PhINTs:olefin, 0.025:0.5:5 (mmol). Yields determined by GC and NMR. [b] Experiment performed with 1% of the catalyst referred to PhINTs (Cu:PhINTs:styrene = 0.01:1:5).

Catalytic Activity of the Complexes Tp^{x}Cu toward Alkene Aziridination with PhINTs. A few years ago, we reported the use of the complex Tp*Cu-(C_2H_4)[12] as the catalyst for the olefin aziridination reaction. The emergence of a second generation of homoscorpionate Tp^x ligands with a variety of R^1-R^3 groups attached to the pyrazolyl rings has led us to test the catalytic capabilities of a series of Tp^{x}Cu complexes toward the nitrene transfer reaction to olefins (eq 1), therefore studying the influence that such groups might have on this transformation. The complexes Tp^{x}Cu have been prepared by direct reaction of the thalium or potassium salt of the Tp^x ligand and copper iodide. The catalytic experiments have been performed according to the following methodology. The catalyst and the olefin were dissolved in methylene chloride, under nitrogen, and in the presence of molecular sieves. The existence of adventitious water in the reaction mixture induces a well-known, nondesired side reaction: the formation of *p*-toluenesulfonamide, which diminished the yields in the aziridine. After a few minutes stirring, the nitrene source, PhI=NTs, was added in one portion, and the suspension (PhI=NTs is quite insoluble in methylene chloride) was stirred until the solid iminoiodane disappeared. Initially, a 1:10 PhI=NTs-to-olefin ratio was employed in this first screening. After filtration, the solution was investigated by GC, and later by NMR (after removal of volatiles), with the results shown in Table 1. The degrees of transformation induced by this family of catalysts were quantitative for styrene and very high for *cis*-cyclooctene. The less reactive 1-hexene was converted into the corresponding aziridine in variable yield, ranging from 62% obtained with Tp^{Ms}Cu to 91% provided by the perbromo ligand containing catalysts Tp^{Br3}Cu. This is a very interesting, unprecedented result since, as mentioned above, terminal, nonactivated olefins are usually quite unreactive toward this transformation. For example, a recent work with fluoro-containing homoscorpionate ligands provided 1-octene-derived aziridines in 28−34% yield, using a 5% catalyst loading and excess PhINTs with respect to the olefin.[13] However, this is not the only example with deactivated olefins. We have also studied the aziridination of methyl acrylate (CH_2CHCO_2Me) and methyl methacrylate ($CH_2C(Me)CO_2Me$) in the presence of Tp^{Br3}Cu as the catalyst. When a 1:5 PhINTs-to-olefin ratio was employed, using a 5% loading of catalyst, those olefins were converted into the corresponding aziridines in 39 and 68%, respectively. These degrees of conversions are quite high when compared with previous reports with other catalysts and clearly assess the potential of this family of catalysts for the olefin aziridination reaction.On the basis of those findings, we decided to decrease the catalyst ratio, with respect to the nitrene source, to 1%. The results obtained with the representative olefins employed (Table 1, entry 6) were quite good. As mentioned above, most of the reported catalysts required a 5% loading, with respect to PhINTs. An exception has been presented by Halfen and co-work-

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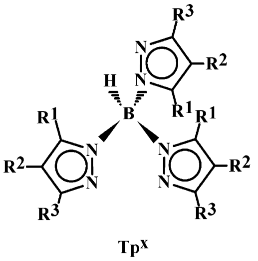
Table 2. Olefin Aziridination with $Tp^{Br3}Cu$ as the Catalyst with Equimolar Mixtures of Olefin and PhI=NTs

entry	catalyst:PhINTs	PhINTs:olefin	styrene	*cis*-coe[c]	1-hexene
1[a]	1:20	1:1	93	89	68
2[b]	1:40	1:1	93	90	71

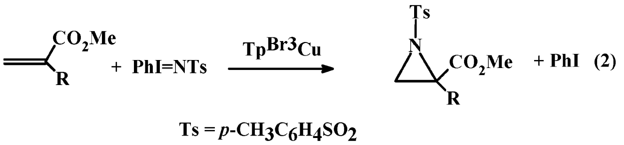
[a] Cu:PhINTs:olefin, 0.025:0.5:0.5 (mmol). [b] Cu:PhINTs:olefin, 0.025:1:1 (mmol). [c] *cis*-Cyclooctene.

Chart 1. Homoscorpionate Ligands Employed in this Work



Ligand	*R*^{1}	*R*^{2}	*R*^{3}
Tp*	CH_3	H	CH_3
Tp^{Cy}	H	H	C_6H_{11}
Tp^{Ph}	H	H	C_6H_5
Tp^{Ms}	H	H	mesytil
Tp^{Br3}	Br	Br	Br

ers[14] with the catalyst $[(^iPr_3TACN)Cu(O_2CCF_3)_2]$, which quantitatively converted styrene into its aziridine with only a 0.5% loading (10−20-fold excess of styrene). Lower yields were obtained with *cis*-cyclooctene and hexane (25−35% with 5% loading). Therefore, to our knowledge, the results in Table 1 for the less activated olefins such as *cis*-cyclooctene and 1-hexene find no precedent in the literature for such 1% catalyst loading.



Ts = *p*-$CH_3C_6H_4SO_2$
R = H, Me

Once the improvement of the catalytic activity was established, with respect to our original work with $Tp^*Cu(C_2H_4)$,[12] we decided to face the next drawback in aziridine catalytic synthesis, i.e., the need for excess olefin. As already mentioned, the high yields shown in Table 1 have been obtained using a 10-fold excess of olefin with respect to PhI=NTs. Given the exceptional activity of the perbromo catalyst, we have run similar reactions using *equimolar* mixtures of olefin and PhI=NTs, with the results shown in Table 2. Again, high yields were obtained for both styrene and *cis*-cycloctene, and also a quite high degree of transformation was observed for 1-hexene: it seems clear that the need for excess olefin is not required when using this copper-based catalyst. It is also interesting to note that we have carried out two sets of experiments (Table 2) varying the relative ratio of the catalyst and the reactants. However, no change in the yields was observed. We believe that this is due to the fact that the rate-limiting step for this transformation is the dissolution of the nitrene source, which is very slow. Because of this, in the range of catalyst concentration we have used, no differences were observed in terms of conversion yields. To confirm that in the observed catalytic activity the use of this system for preparative purposes is allowed, we have run a scale-up reaction with 2.5 mmol of PhINTs and 1 equiv of styrene, in the presence of 0.125 mmol of $Tp^{Br3}Cu$ (5% loading). An almost quantitative (>95%) yield was detected by NMR, and after workup, *N*-tosyl-2-phenylaziridine was isolated in 86% yield. Similar experiments with *cis*-cyclooctene and 1-hexene provided isolated solid of the corresponding aziridines in 82 and 62% yield, respectively. At this point, we can conclude that the $Tp^{Br3}Cu$ catalyst displays an exceptional catalytic activity for the olefin aziridination reaction, in such a way that (i) it provides high yields of aziridines even for linear, nonactivated α-olefins; (ii) low catalyst loading (1%) is enough for high conversions; and (iii) no excess of olefin is required, with equimolar mixtures of PhINTs and the alkenes being converted into aziridines in considerable yields. In no case have we detected any product derived from the insertion of the nitrene unit into a C−H bond. We have recently described[15] the catalytic insertion of NT groups from PhINTs into the C−H bonds of several substrates. However, it seems that the addition of this fragment into unsaturated C−C double bonds is more favored than the insertion into saturated C−H bonds: when cyclohexene was investigated, only the aziridine product was observed, with no evidence of the insertion product, despite the well-known reactivity of the allylic position toward this transformation.

Chloramine-T as the Nitrene Source. All the aforementioned problems usually detected in the already reported catalytic olefin aziridination systems can be avoided with the use of $Tp^{Br3}Cu$ as the catalyst, with the exception of the formation of iodobenzene as a byproduct. It would be desirable to eliminate such aromatic compounds from this system, or alternatively to generate a different, environmentally friendly byproduct. Such an alternative could be based on the use of chloramine-T (*N*-chloro-*N*-sodium-*p*-toluenesulfonamide), an affordable, cheap, commercial reagent that, after nitrene transfer, produces sodium chloride in addition to the desired aziridine. We have tested the catalytic capabilities of the perbromo-homoscorpionate copper complex toward this nitrene source, with the results shown in Table 3. At first, the experiment (entry 1) carried out under conditions similar to those employed with PhINTs has also provided the aziridines derived from styrene and cyclooctene in high yields. However, 1-hexene was only converted in 34% yield, in contrast to the ca. 90% conversion shown in Table 1 for $Tp^{Br3}Cu$ as the catalyst. To explain this difference, we must invoke the very low solubility of chloramines T in methylene chloride. As mentioned above, the dissolution of the nitrene source seems to be the rate-determining step in this process, and it seems that for chloramine-T this is even slower than in the case of PhINTs. Because of this, the neat concentration of chloramine-T in solution is very low, and only in the presence of

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Table 3. Olefin Aziridination with Tp^xCu as the Catalyst with Chloramine-T as the Nitrene Source

entry	catalyst/solvent	catalyst:chloramine-T[a]	chloramine T:olefin	styrene	*cis*-cyclooctene	1-hexene
1	$Tp^{Br3}Cu/CH_2Cl_2$	1:20	1:10	96	88	34
2	$Tp^{Br3}Cu/CH_2Cl_2$	1:20	1:1	53		
3	$Tp^{Br3}Cu/CH_2Cl_2$	1:40	1:1	55		
4	$Tp^{Br3}Cu/CH_2Cl_2$	1:20	1:20			51
5	Tp^*Cu/CH_2Cl_2	1:20	1:10	40		
6	Tp^*Cu/CH_3CN	1:20	1:5	90	90	30
7[b]	Tp^*Cu/CH_3CN	1:20	1:1	84 (78)[c]		

[a] Referred to 0.025 mmol of the catalyst:0.5 (mmol). [b] Scale-up experiment: 0.125 mmol of catalyst employed. [c] Isolated yield in parentheses.

activated olefins is the aziridination reaction favored instead of that of formation of tosylamine, with traces of water. The use of a higher olefin:chloramine-T ratio (entry 1 vs 4) led to the improvement of this yield. In any case, the degrees of conversions shown in Table 3 are quite good when compared with others in the literature. In a seminal work on the use of this reagent for aziridine formation with copper-based catalysts, Komatsu et al.[10g] reported 31 and 38% conversions for styrene and cyclooctene, respectively. Later, Taylor and co-workers[10e] presented, also with copper catalysts, a 74% yield for styrene aziridination. These and other examples[10] present a common factor: the reactions have been performed in acetonitrile, where chloramine-T is somewhat more soluble than in methylene chloride or other solvents. However, we have found that when using this solvent, a side reaction takes place in such a way that no aziridine nor tosylamine was detected: a unique species was detected by GC, but work to characterize this compound is still underway. Since this result was probably due to the enormous activity of the $Tp^{Br3}Cu$ catalyst, we decided to test the less reactive, according to data in Table 1, Tp^*Cu complex in acetonitrile (Table 3, entry 6). No side reaction was observed, and very high yields were obtained with styrene and cyclooctene (90%), again 1-hexene being transformed in only 30% yield. Thus, the activity of the readily available Tp^*Cu catalyst in acetonitrile with chloramine-T as the nitrene source is comparable to that of $Tp^{Br3}Cu$ in methylene chloride. In addition, it can be envisaged that the use of the appropriate solvent with the latter will probably allow the aziridination of nonactivated aziridines in high yields. The superior activity of the Tp^*Cu complex has been definitively demonstrated in the scale-up experiment (Table 3, entry 7). Using a 5% catalyst loading, an overall yield of 84% was detected at the end of the reaction, leading to the isolation of the aziridine in 78% yield, an excellent result considering the use of equimolar amounts of the nitrene source and the olefin.

In conclusion, we have found that the complexes Tp^x-Cu are very good catalysts for the aziridination of olefins. Particularly effective is the perbromo catalyst $Tp^{Br3}Cu$, which has provided very high yields of aziridines, even with equimolar mixtures of the olefin and PhINTs and low (1%) catalyst loading. The use of Tp^*Cu and chloramine-T also provided high yields of aziridines, in addition to avoiding of the formation of iodobenzene as the byproduct. Work aimed to improve this catalyst to operate under environmental friendly conditions is currently underway in our laboratory.

Experimental Section

General Procedures. All preparations and manipulations were carried out under an oxygen-free nitrogen atmosphere using conventional Schlenk techniques. The solvents were dried and degassed before use. NMR spectra were run with a Varian Mercury 400 MHz, using as solvent $CDCl_3$. GC analyses were recorded in a Varian CP-3800. Solvents were dried and degassed before use. The olefins and chloramine-T were purchased from Aldrich and employed without any further purification. Syntheses of the copper catalysts were carried out as reported previously.[16]

General Catalytic Experiment. The Tp^xCu complex and the olefin were dissolved in CH_2Cl_2 (20 mL), and molecular sieves were added to the stirred solution. PhINTs was then introduced in one portion, and the mixture was stirred for several hours, until no solid PhINTs was observed in the reaction mixture. The amounts of the copper catalyst, the olefin, and PhINTs are outlined in the footnotes of Tables 1 and 2. After the solution was filtered off, volatiles were removed under reduced pressure. An exact amount of 2-hexene (as standard) was then added to the crude product, and the mixture was dissolved in $CDCl_3$ to be investigated by ^1H NMR spectroscopy. By this procedure we estimate the aziridine/tosylamine ratio as well as the amount of PhINTs consumed. Investigation of the same sample by GC (TSD detector) allows the determination the response factor of those products, in order to use this technique for a set of catalytic experiments. The aziridines were characterized by comparison with reported spectroscopic data. Reported yields are referred to an average of, at least, two experiments. In the case of chloramine-T, an identical procedure was employed, using acetonitrile as the solvent.

Scale-up experiments were run in a similar manner, using a 1:20:20 ratio for [Cu]:[nitrene source]:[olefin], referred to 0.125 mmol of the catalyst. The perbromo catalyst was employed with PhINTs (80 mL of CH_2Cl_2 as the solvent), and Tp^*Cu was used with chloramine-T as the nitrene source (80 mL of acetonitrile as the solvent).

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