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A Practical, Fast, and High-Yielding Aziridination Procedure Using Simple Cu(II) Complexes Containing N-Donor Pyridine-Based Ligands

Fabian Mohr, Seth A. Binfield, James C. Fettinger, and Andrei N. Vedernikov*

Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742

avederni@umd.edu

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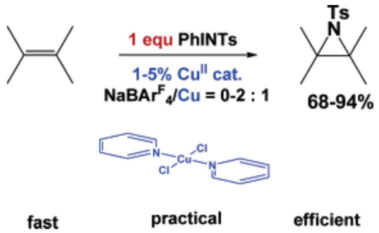

Four-coordinate dichlorocopper(II) complexes derived from di(2-pyridyl)methanes or pyridine itself exhibit high catalytic activity in aziridination of regular olefins with PhINTs in weakly coordinating chloroform in the presence of 1−2 equiv of $\mathrm{NaBAr^F_4}$ ($\mathrm{BAr^F_4}^-$ = tetra[3,5-di(trifluoromethyl)phenyl]-borate). High yields of aziridines exceeding 90% can be obtained with a 1:1 olefin/PhINTs ratio and 1−5 mol % catalyst loading for such reactive olefins as styrene, tri- and tetramethylethylene. For *cis*-cyclooctene, indene, methyl acrylate, methyl methacrylate, vinyl methyl ketone, *tert*-butylethylene, and neopentylethylene, as well as for 1-hexene and cyclopentene, yields of corresponding aziridines vary from 44% to 83%. The catalytic activity and efficiency of the reported copper complexes decrease moderately in the absence of $\mathrm{NaBAr^F_4}$.

Introduction

Aziridines are important synthetic intermediates in modern organic synthesis, which can be obtained, in particular, by reacting olefins with suitable sources of nitrenes such as iminoiodinanes.[1] The importance of the latter reaction steadily increases as more and more efficient catalytic routes are discovered.[2−10] High catalyst loadings (up to 5 mol %) and high olefin/PhINTs ratios (10−3) are still the most important limitations of currently employed protocols for olefin aziridination. These limitations are especially important when the olefinic substrate and/or catalyst are expensive. In addition to theoretical modeling[5] and experimental study[11−15] of the reaction mechanism, a better understanding of the structure−reactivity relationship for copper catalysts could contribute significantly to the solution of these problems. Until recently, most copper-based catalysts for olefin aziridination were prepared in situ and have rarely been structurally characterized,[13−16] thus making a systematic search of any structure−reactivity relationships difficult. Recently we have shown that copper complexes LCuX_n (X = Cl, OTf; n = 1, 2) containing the macrocyclic

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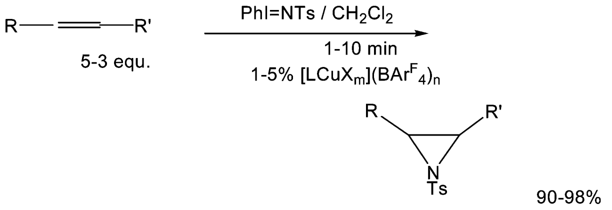
tripyridine ligand L = [2.1.1]-(2,6)-pyridinophane are very active catalysts for aziridination of a variety of olefins, allowing fast and high yielding reactions when 3−5 equiv of olefin per 1 equiv of PhINTs was used (eq 1):[17]

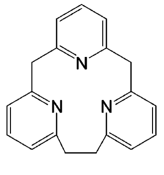


(1)

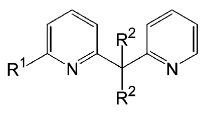
High activity of the catalysts was achieved in poorly coordinating dichloromethane solutions when the anionic ligands (X) were removed with NaBAr$^F{}_4$ (BAr$^F{}_4$ = tetrakis(3,5-di(trifluoromethyl)phenyl)borate) creating the coordinatively unsaturated cationic copper species [LCuX$_m$]$^{n+}$ ($n + m = 2$ or 1). Two factors, the coordination unsaturation that promotes faster coordination of PhINTs to copper and the macrocycle ring constraints that make the catalysts less vulnerable to oxidative degradation, may be responsible for the enhanced catalytic activity. In support of the latter idea copper complexes based on perbrominated hydridotris(pyrazolyl)borate were recently found to be very active in olefin aziridination.[6] In this work we show that the presence of a facially chelating ligand attached to copper is not a requirement for creating highly active catalysts and that coordinative unsaturation at copper alone can be responsible for the very high catalyst activity. Furthermore, we show here that simple BAr$^F{}_4$-*free* coordinatively unsaturated copper(II) complexes can serve as efficient aziridination catalysts when a 1:1 olefin/PhINTs ratio is used. In combination with the simplicity of preparation and low cost of the catalysts reported here, these results imply development of very practical and versatile catalytic systems.

Results and Discussion

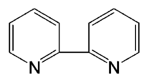
On the basis of the results from our previous work,[17,18] strong pentacoordinate copper(II) or tetracoordinate copper(I) complexes such as (η^3-L)CuCl$_2$ and (η^3-L)CuCl are poor catalysts for olefin aziridination. However, replacement of chloride by much more labile triflate ligands or removal of Cl with NaBAr$^F{}_4$ increases the catalytic activity significantly. At this point, it was reasonable to assume that four-coordinate copper(II) or thee-coordinate copper(I) complexes might be efficient catalysts for olefin aziridination in weakly coordinating solvents. Coordinating solvents such as acetonitrile are not compatible with low-coordinate copper species. Potentially four-coordinate copper(II) complexes of the type (L′)CuCl$_2$, where L′ denotes a bidentate N-donor ligand such as di(2-pyridyl)methane (dpm) or two pyridine ligands, can be considered as unsaturated analogues of (η^3-L)CuCl$_2$ in which one of the three pyridine rings as well as some or all of its alkylydene bridges have been removed.



L



R^1, R^2 = H **dpm**;
R^1 = Me, R^2 = H **Me-dpm**;
R^1 = H, R^2 = Me **dpp**;
R^1 = Cl, R^2 = H **Cl-dpm**;



dipy

Since dpm ligand contains potentially vulnerable benzylic CH bonds, its dimethylated analogue, 2,2-di(2-pyridyl)propane (dpp), was expected to be more robust toward highly oxidizing PhINTs. Similarly, as a result of the electron-withdrawing nature of the chlorine substituent, the benzylic CH bonds in (6-chloro-2-pyridyl)2-pyridylmethane (Cl-dpm) were expected to be of lower reactivity than those in dpm, whereas complexes derived from (6-methyl-2-pyridyl)2-pyridylmethane (Me-dpm) might be less robust. Pyridine (py) and dipyridyl (dipy) complexes with no benzylic CH bonds or bridging carbons at all might be of superior efficiency as compared with dpm-based copper complexes. Finally, for the reason of better solubility in reaction mixtures, a copper derivative of 4-*tert*-butylpyridine (*t*Bupy) was also included in our study. A series of (L′)CuCl$_2$ complexes, (dpm)CuCl$_2$,[19] (Me-dpm)CuCl$_2$,[20] (Cl-dpm)CuCl$_2$, (dpp)CuCl$_2$, (py)$_2$CuCl$_2$,[21] (dipy)CuCl$_2$,[22] and (*t*Bupy)$_2$CuCl$_2$, have been prepared, and their catalytic activity in olefin aziridination was studied in this work. A related cationic four-coordinate copper(I) analogue, [(Cl-dpm)$_2$Cu]$^+$[CuCl$_2$]$^-$, was also synthesized and tested to emphasize the effect of the metal coordination unsaturation on the catalytic activity. To determine the degree of coordination unsaturation of copper in these complexes, we analyzed results of their X-ray crystal structure determination.

Preparation and Solid-State Structure Characterization of Copper Catalysts. A series of copper(II) complexes of the type (L′)CuCl$_2$, where L′ = dpm, dpp, Me-dpm, Cl-dpm, dipy, (py)$_2$, and (*t*Bupy)$_2$, was prepared in 75−94% yield by reacting CuCl$_2$ with a 10% excess of ligand in THF or benzene. The resulting green or blue complexes were characterized by elemental analysis and, in the case of (Cl-dpm)CuCl$_2$ and [(Cl-dpm)$_2$Cu]$^+$[CuCl$_2$]$^-$, by X-ray crystallography. X-ray crystal structures of all of the other complexes studied here with the exception of (dpp)CuCl$_2$ and (*t*Bupy)$_2$CuCl$_2$ have been determined previously.[19−22] According to the data available, (dpm)CuCl$_2$ exists in a solid state as a bis(μ-chloro)-bridged dimer containing five-coordinate copper atoms in a distorted trigonal-bipyramidal environment.[19] We assume that the analogous (dpp)CuCl$_2$ complex has a similar dinuclear structure.

In contrast, (Me-dpm)CuCl$_2$ complex is monomeric with a copper atom that adapts highly distorted tetrahedral geometry presumably due to steric crowding caused by the *o*-methyl substituents.[20] Indeed, a similar metal coordination geometry was found by us for the chloro-

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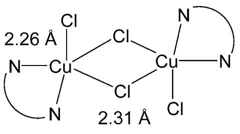
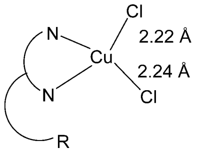
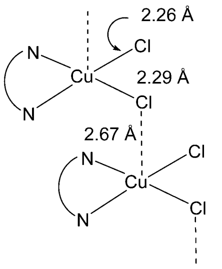


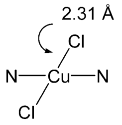
[(dpm)CuCl$_2$]$_2$



(Me-dpm)CuCl$_2$



[(dipy)CuCl$_2$]$_n$



(py)$_2$CuCl$_2$

analogue (Cl-dpm)CuCl$_2$[23] (see Figure 1 in Supporting Information).

The dichloro(dipyridyl)copper(II) complex (dipy)CuCl$_2$ containing the more compact dipy ligand compared to dpm is polymeric in the solid state with copper atoms linked by bridging chlorides.[22] The copper(II) pyridine complex, (py)$_2$CuCl$_2$, is monomeric and contains a four-coordinate planar copper atom.[21]

The product obtained by reacting copper(I) chloride and Cl-dpm taken in 1:1 ratio in dichloromethane turned out to be ionic with one copper atom in its cationic part being four-coordinate, in a highly distorted tetrahedral environment, (Cl-dpm)$_2$Cu$^+$ [24] (see Figure 2 in Supporting Information), and another copper atom in the anionic part being two-coordinate, CuCl$_2^-$.

Because the copper atom in the cationic part of this copper(I) complex forms much longer and therefore weaker bonds with the nitrogen atoms of the chloro-substituted pyridine fragments, N1 and N12, it is reasonable to expect relatively easy displacement of the chloropyridine fragments by stronger electron donors if such are present in solution.

Thus, according to the solid-state structure studies, we could expect that all (L′)CuCl$_2$ complexes investigated here might exhibit high catalytic activity in olefin aziridination in weakly coordinating solvents when NaBAr$^F_4$ is used to remove the chloride ligands. More importantly, we could also expect that the four monomeric four-coordinate copper(II) complexes, (Me-dpm)CuCl$_2$, (Cl-dpm)CuCl$_2$, (py)$_2$CuCl$_2$, and (*t*Bupy)$_2$CuCl$_2$ may be active aziridination catalysts in the absence of NaBAr$^F_4$. Dinuclear copper complexes (dpm)CuCl$_2$ and (dpp)CuCl$_2$ containing longer than regular and therefore weaker Cu−Cl bonds might also be active enough in NaBAr$^F_4$-free systems.

Finally, the Cl-dpm copper(I) complex synthesized contains both unsaturated and saturated copper(I) atoms and therefore might exhibit some catalytic activity.

Catalytic Olefin Aziridination in the PhINTs/Cu^x/NaBAr$^F_4$/CHCl$_3$ Systems. (a) Copper(II) Complexes. Catalytic studies with *cis*-cyclooctene as a test substrate showed that all (L′)CuCl$_2$ complexes at 5 mol % loading activated with 2 equiv of NaBAr$^F_4$ in chloroform solutions exhibited high catalytic activity at the 3:1 olefin/PhINTs ratio with almost quantitative yields of corresponding aziridines for the all the copper(II) catalysts. These results allowed us to decrease the olefin/PhINTs ratio to 1:1, which still gave high yields of corresponding reaction products (Table 1, entry 1). Yields ranging from 66% (dpm) to 86% (L′ = dpp and (tBupy)$_2$) are very similar to the results obtained with the macrocyclic [LCuX$_m$](BAr$^F_4$)$_n$ catalyst (87%).[17] Remarkably, one of the best results in entry 1 was obtained with the simplest catalyst used in this work, the dichlorodi(pyridine)copper(II) complex. It is also worth noting that the efficiency of the catalysts derived from dpm and tested here with *cis*-cyclooctene and other substrates increases in the same order as their expected ability to withstand oxidative degradation increases, L′: Me-dpm ≈ dpm < Cl-dpm ≈ dpp < (tBupy)$_2$ ≈ (py)$_2$. Interestingly, (dipy)CuCl$_2$ exhibited the same or slightly lower activity than dpm and Me-dpm complexes. Possible reason for this behavior may be lower solubility of the (dipy)CuCl$_2$ complex in chloroform caused by its polymeric nature.

To learn more about the scope and limitations of this catalytic system we studied other olefinic substrates containing one, two, three and four substituents, both activating (Ph, *o*-C$_6$H$_4$CH$_2$, Me, *n*-Bu, *t*-Bu, *neo*-Am, (CH$_2$)$_3$) and deactivating (COMe, COOMe), attached to the C═C bond. Aziridination of the most reactive of them, styrene, was performed in all of the dpm-based systems with indistinguishably high, almost quantitative yields in less than 1−2 min (Table 1, entry 2). Remarkably, as little as 1% of (py)$_2$CuCl$_2$-based catalyst was enough to obtain the same yield of aziridine though the reaction took more time.

High yields of aziridines exceeding 90% were also observed for tetra- (entry 3) and trimethylethylene (entry 4). Worse though still satisfactory performance was exhibited by indene (83%, entry 5), substrates with electron-withdrawing COOMe (methyl methacrylate, 69%, entry 6; methyl acrylate, 44%, entry 7) or COMe group (1-butene-2-one, 65%, entry 8), bulky *t*-Bu group (*tert*-butyl ethylene, 55%, entry 5), or alkyl groups with secondary allylic CH bonds,[7,17] cyclopentene (52%, entry 10) and 1-hexene (49%, entry 11). The importance of the presence of the electron-rich C═C bond in olefinic substrates is clearly evidenced, in particular, by the fact that methyl methacrylate performed much better than methyl acrylate. On the other hand, the steric effect of substituents directly attached to the C═C bond on its reactivity is evident when one compares the better performance of 4,4-dimethyl-1-pentene (67%, entry 12) with less bulky *neo*-pentyl group attached to the C═C bond and the worse performance of *tert*-butyl ethylene where the steric effect of the alkyl group is more pronounced.

(b) Copper(I) Complex. With *cis*-cyclooctene as a substrate we tested also the catalytic activity of Cl-dpm-derived copper(I) catalyst, [(Cl-dpm)$_2$Cu]$^+$[CuCl$_2$]$^-$, in the

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[23] Greenish crystals of (Cl-dpm)CuCl$_2$ (C$_{11}$H$_9$Cl$_3$CuN$_2$) are monoclinic, space group *C*2/*c*, with a = 21.008(16) Å, b = 8.111(7) Å, c = 15.895(13) Å, β = 99.683(13)°, V = 2670(4) Å^3 and Z = 8 at −100 °C. The full-matrix least-squares refinement on F^2 provided residuals R_1 = 0.0467, wR_2 = 0.1145 and GOF = 1.047 for 4266 reflections [$I > 2\sigma(I)$] and 191 variables.

[24] Yellowish crystals of [(Cl-dpm)$_2$Cu][CuCl$_2$]·CH$_2$Cl$_2$ (C$_{23}$H$_{20}$N$_4$Cl$_6$Cu$_2$) are centrosymmetric monoclinic, space group *P*21/*n* (No. 14) with a = 11.6293(15) Å, b = 13.7395(18) Å, c = 16.846(2) Å, β = 105.510(2)°, V = 2593.6(6) Å^3 and Z = 4 at −100 °C. The full-matrix least-squares refinement on F^2 provided residuals R_1 = 0.0341, wR_2 = 0.0833 and GOF = 1.050 for 4564 reflections [$I > 2\sigma(I)$] and 396 variables.

TABLE 1. Results of Olefin Aziridination with 1 equiv of PhINTs in the Presence of 5 mol % of (L′)CuCl$_2$ and 2 equiv of NaBAr^F$_4$ in CHCl$_3$ at 296 K

		yield of aziridine,[a] % (time, min)						
entry	substrate	dpm	dpp	Cl-dpm	Me-dpm	(py)$_2$	dipy	(tBupy)$_2$
1	*cis*-cyclooctene	66 (1)	82 (1)	83 (1)	67 (5)	83 (1)	73 (10)	86 (5)
2	styrene	95 (1)	95 (1)	98 (1)	93 (2)	97 (10)[b]	98 (5)	94 (2)
3	tetramethylethylene	76 (5)	81 (5)	91 (2)	75 (1)	94 (2)	50 (5)	85 (1)
4	trimethylethylene					90 (5)		94 (1)
5	indene					83 (5)		85 (2)
6	methyl methacrylate					69 (10)		56 (10)
7	methyl acrylate	35 (30)	45 (30)	45 (20)	38 (25)	44 (5)		32 (10)
8	1-butene-2-one					65 (8)		72 (8)
9	*tert*-butylethylene	49 (10)	60 (3)	63 (5)	31 (40)	55 (3)		50 (3)
10	cyclopentene					52 (5)		51 (5)
11	1-hexene					49 (10)		47 (10)
12	4,4-Dimethyl-1-pentene					67 (5)		65 (2)

[a] NMR yields on PhINTs. The isolated yields were 1−5% lower. [b] 1 mol % of catalyst.

TABLE 2. Results of Olefin Aziridination (n = 1 or 5 equiv) with PhINTs in the Presence of 5 mol % of (L′)$_2$CuCl$_2$ and NaBAr^F$_4$ (x = 0 or 1 equiv) in CHCl$_3$ at 296 K

		yield of aziridine,[a] % (time, min)					
		$n = 1; x = 1$	$n = 1; x = 0$				$n = 5; x = 0$
entry	substrate	(py)$_2$	dpm	Cl-dpm	Me-dpm	(py)$_2$	(py)$_2$
1	styrene	93 (5)	97 (20)	81 (5)	65 (20)	92 (5)	98 (5)
2	tetramethylethylene	84 (5)	51 (30)	67 (2)	55 (30)	68 (2)	70 (2)
3	trimethylethylene	88 (5)				71 (5)	98 (5)
4	*cis*-cyclooctene	73 (3)	50 (15)	57 (1)	36 (60)	62 (2)	98 (2)
5	indene	75 (7)				75 (12)	84 (30)
6	methyl methacrylate	68 (6)				72 (5)	65 (2)
7	methyl acrylate	69 (60)				33 (15)	72 (2)
8	1-butene-2-one	65 (9)				59 (20)	83 (5)
9	4,4-dimethyl-1-pentene	64 (5)				54 (5)	74 (4)
10	1-hexene	50 (5)				34 (9)	44 (9)
11	*tert*-butylethylene	30 (10)	21 (30)	19 (15)		31 (15)	39 (15)
12	cyclopentene	37 (5)				39 (6)	42 (6)

[a] NMR yields on PhINTs. The isolated yields were 1−5% lower.

presence of 2 equiv of NaBAr^F$_4$ and at the 3:1 olefin/PhINTs ratio. While the reaction set up under the same conditions was equally fast in the case of (Cl-dpm)CuCl$_2$ and [(Cl-dpm)$_2$Cu]$^+$[CuCl$_2$]$^-$ catalysts (1−2 min), the yield of aziridine obtained in the latter case was almost 20% lower. Assuming that the catalytic activity of the copper(I) catalyst may be due to the presence of low-coordinate copper anion CuCl$_2$$^-$ we tried pure CuCl + 1 equiv of NaBAr^F$_4$ system and observed only very slow reaction (120 min) with the aziridine yield of 50%. Therefore, the observed activity of the Cl-dpm copper(I) complex can be more likely ascribed to the cationic part of this copper(I) compound, which has relatively weak Cu-chloropyridine bonds and therefore can readily open up a coordination vacancy at the copper atom.

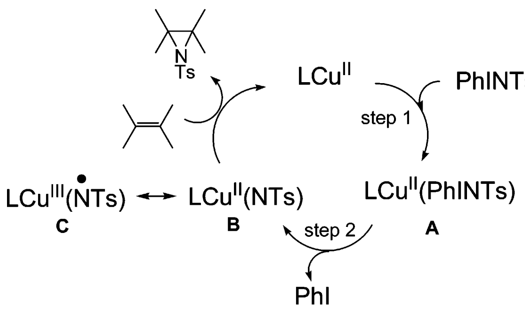
The catalytic results obtained here allowed us to conclude that simplified analogues of a previously reported macrocyclic copper complex systems[17] show almost the same level of catalytic activity. Thus, coordinative unsaturation of the copper atom is the most important attribute of a complex that is highly active in olefin aziridination with PhINTs in weakly coordinating solvents. This conclusion opens up the possibility for further developing highly active metal catalysts for this reaction. Though the dichlorodi(pyridine) copper(II) based systems reported here are good examples of such practical catalysts, the value of the catalytic systems described could be further increased if a similar level of catalytic activity were possible at a reduced content or in the absence of NaBAr^F$_4$.

Catalytic Olefin Aziridination in NaBAr^F$_4$-Poor and NaBAr^F$_4$-Free Systems. (a) Systems with 1 equiv of NaBAr^F$_4$. Results of the aziridination of styrene and tetra- and trimethylethylene given in Table 2 (column 3) show that in the presence of only 1 equiv of NaBAr^F$_4$ high yields of aziridines exceeding 84% can still be obtained for the three most reactive substrates with the (py)$_2$CuCl$_2$ catalyst (entries 1−3), whereas the results for *cis*-cyclooctene (73%, entry 4), indene (75%, entry 5), methyl methacrylate (68%, entry 6), methyl acrylate (69%, entry 7), 1-butene-2-one (65%, entry 8), 4,4-dimethyl-1-pentene (64%, entry 9), and 1-hexene (50%, entry 10) are less satisfactory. The performance of *tert*-butylethylene (30%, entry 11) and cyclopentene (37%, entry 12) is poor. The yields and/or reaction rates for all NaBAr^F$_4$-poor systems are slightly worse in comparison with systems activated with 2 equiv of NaBAr^F$_4$.

These results confirm again that the degree of coordination unsaturation of copper-based systems is an important factor determining their activity as aziridination catalysts. In accordance with this conclusion, the performance of the NaBAr^F$_4$-free systems including dpm- or pyridine-based catalysts was found to be lower.

(b) NaBAr^F$_4$-Free Systems. Reflected in longer reaction times (up to 60 min) and/or lower yields of aziridines

SCHEME 1



(up to 28%), this trend can be seen by comparing the effectiveness of the dpm, Cl-dpm, Me-dpm, and di(pyridine) dichlorocopper(II) complexes given in Tables 1 and 2 (columns 4−7). Despite the decreased efficiency, still high yields of aziridine of 92−97% can be obtained for styrene (entry 1). The yields with the $(py)_2CuCl_2$ complex as a catalyst (column 5) are still satisfactory for tetramethylethylene (68%, entry 2), trimethylethylene (71%, entry 3), *cis*-cyclooctene (62%, entry 4), indene (75%, entry 5), methyl methacrylate (72%, entry 6), 1-butene-2-one (59%, entry 8), and 4,4-dimethyl-1-pentene (54%, entry 9) substrates. The yields for three remaining substrates are poor and range from 31% to 39%.

To learn if we can improve yields of aziridines in this very simple and therefore attractive $NaBAr^F_4$-free catalytic system we changed the olefin/PhINTs ratio from 1:1 used everywhere in this work (all data in Table 1 and columns 3−7 in Table 2) to 5:1 (Table 2, last column). Modest (3−10%) to significant (36%, the case of *cis*-cyclooctene) yield increase was observed. These results imply that simple $(py)_2CuCl_2$ complex may be also efficient in olefin aziridination if greater than 1:1 olefin/PhINTs ratios are affordable (olefin substrate is cheap).

The differences in catalyst performance are clearly visible from the data given in Table 2 and follow the trends discussed for data in Table 1. In particular, $(py)_2CuCl_2$ complex performs better than other complexes for all substrates, while the Me-dpm complex is significantly less efficient. Another observation based on comparison of dpm and Me-dpm complexes is that the ability of a ligand to withstand oxidative degradation (L′ = dpm) might be more important in determining catalyst efficiency than monomeric structure (L′ = Me-dpm) of (L′)-$CuCl_2$ complexes. Thus, four-coordinate dichlorocopper(II) complexes alone can catalyze aziridination of activated olefins efficiently, and dichlorodi(pyridine)copper(II) complex in $CHCl_3$ solvent represents an active and inexpensive catalytic system for olefin aziridination with PhINTs.

Mechanistic Considerations. The use of low-coordinate copper species as aziridination catalysts for reactive olefinic substrates dramatically accelerates the otherwise slow PhINTs coordination to copper leading presumably to a soluble copper−iminoiodinane adduct **A** (Scheme 1, step 1) in a poorly coordinating solvent.

Coordination to the metal may be required for an intramolecular electron transfer leading to liberation of PhI and formation of a plausible highly reactive copper-nitrene adduct **B** (step 2). In general, the copper−nitrene adducts may be involved in a consecutive (as in the case of Cu^{II}−nitrene adducts)[25,26] or concerted (as in the case of Cu^I-nitrene adducts)[11,25] transfer to olefin. A consecutive nitrene transfer from the radical-like nitrene adduct **B** has been proposed for Cu^{II}-catalyzed reactions,[26] and this also may be the case of the copper−pyridinophane systems, which showed a partial loss of the initial C=C bond configuration.[3,17] We obtained a similar result in this work with isomerically pure *cis*-2-butene and PhINTs taken in the 5:1 ratio in the presence of 5% of $CuCl_2(py)_2$ and 2 equiv of $NaBAr^F_4$. The experiment showed fast and practically quantitative conversion of the olefin into the 4.7:1 mixture of the *cis*- and *trans*-isomeric 2,3-dimethyl-*N*-tosyl-aziridines and thus the partial loss of the olefin configuration.

To figure out if the radical-like behavior can be expected for nitrene adducts such as *trans*-$[CuCl(py)_2(NSO_2Ar)]^+$, which can form in PhINTs−$(py)_2CuCl_2$−$NaBAr^F_4$ systems as a result of chloride ligand abstraction with Na^+ and nitrene coordination to copper(II), or *trans*-$CuCl_2(py)(NSO_2Ar)$, which can form in $NaBAr^F_4$-free systems and be viewed as a result of pyridine ligand substitution by nitrene, we performed DFT calculations for two model intermediates, *trans*-$[CuCl(py)_2(NSO_2Ph)]^+$ (see Figure 3a in Supporting Information) and *trans*-$CuCl_2(py)(NSO_2Ph)$ (see Figure 3b in Supporting Information). The results of our DFT calculations show that both adducts have slightly distorted square planar geometry typical for d^8 metal complexes. The resonance structure **C**, $LCu^{III}(^\bullet NSO_2Ar)$, has an important contribution to the copper−nitrene adduct structure in both cases. Indeed, the Mulliken spin density distribution in the cationic complex is 1% on copper and 99% on the NSO_2-Ph ligand including 74% on the nitrene nitrogen and 2% on copper and 98% on the NSO_2Ph ligand including 75% on the nitrene nitrogen in the neutral complex as it is expected for the structure **C**. These results support one more time the idea of the consecutive nitrene transfer in the PhINTs−$(py)_2CuCl_2$−$NaBAr^F_4$ or PhINTs−$(py)_2CuCl_2$ systems.

Consistent with this statement is the fact that the catalyst resting state was always Cu^{II} as evidenced by the persistent bright green color of reaction mixtures resulted after the dissolution of PhINTs was complete (see Experimental Section for details of a sample aziridination experiment).

An attack of the adduct **B** on an olefinic substrate may be fast for reactive olefins whose reactivity in the systems studied here decreases in the order styrene > trimethylethylene, tetramethylethylene > *cis*-cyclooctene, indene > methyl methacrylate, 1-butene-2-one > 4,4-dimethyl-1-pentene. The nitrene transfer step may become rate-limiting for electron-poorer substrates (methyl acrylate) or substrates with sterically poorly accessible C=C bonds (*tert*-butylethylene). In the two latter cases resistance of a metal complex toward oxidative degradation and protection of a coordinated nitrene against other side reactions may be a key feature of an efficient catalytic system. More careful catalyst design is required to satisfy such reaction conditions.

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Conclusions

We have shown that unsaturated four-coordinate dichlorocopper(II) complexes are very active catalysts for aziridination of activated and regular olefins, which perform well at 1−5% loading when 1:1 olefin/PhINTs is used in chloroform solutions. An enhancement of their catalytic activity is observed in the presence of $NaBAr^F_4$. Thus, simple, cheap, and readily available four-coordinate copper(II) compounds such as $(py)_2CuCl_2$ can be recommended as efficient catalysts for aziridination of a variety of olefins in weakly coordinating solvents.

Experimental Section

Computational Details. Theoretical calculations including Mulliken spin population analysis in this work have been performed using density functional theory (DFT) method,[27] specifically functional PBE,[28] implemented in an original program package "Priroda".[29] In PBE calculations relativistic Stevens-Basch-Krauss (SBK) effective core potentials (ECP) [30−32] optimized for DFT calculations have been used. The basis set was 311-split for main group elements with one additional polarization p-function for hydrogen, additional two polarization d-functions for elements of higher periods. Full geometry optimization has been performed without constraints on symmetry. For all species under investigation frequency analysis has been carried out. All minima have been checked for the absence of imaginary frequencies.

(6-Chloro-2-pyridyl)(2-pyridyl)methane (Cl-dpm). An ice-cooled solution of 2-picoline (9.9 mL, 0.1 mol) in THF (40 mL) was treated with ^{n}BuLi (10 mL, 10 M solution in hexanes). After 30 min of stirring, a solution of 2,6-dichloropyridine (7.4 g, 0.05 mol) in THF (20 mL) was added, and the mixture was heated to reflux for 1 h. After cooling to room temperature the reaction mixture was hydrolyzed with water, and the organic phase was separated. The aqueous phase was extracted with Et_2O (3 × 20 mL) and the combined organic layers were dried (Na_2SO_4). After removal of the solvents the remaining dark oil was distilled in a vacuum to afford 6.5 g (64%) of Cl-dpm with a bp of 107−110° at 0.23 mmHg. ^1H NMR ($CDCl_3$, 400 MHz) 4.31 (s, 2H), 7.13 (dd, *J* = 1, 4 Hz, 1H), 7.17 (dd, *J* = 4, 7 Hz, 2H), 7.28 (dd, *J* = 1, 8 Hz, 1H), 7.55 (t, *J* = 8 Hz, 1H), 7.61 (dt, *J* = 2, 8 Hz, 1H), 8.55 (m, 1H); ^{13}C NMR ($CDCl_3$, 400 MHz) 46. 4, 121.6, 121.8, 121.9, 123.5, 136.6, 139.0, 149.4, 150.6, 158.5, 160.2; HRMS (FAB+) calcd for $C_{11}H_{10}N_2Cl$ *m/z* 205.0533, found *m/z* 205.0538.

Dichlorocopper(II) Complexes, (L′)CuCl₂. A suspension of $CuCl_2$ (0.100 g, 0.744 mmol) in THF or benzene (in the case of *t*Bupy ligand) (ca. 5 mL) was treated with a THF or benzene solution of the ligand (1.1 equiv), and the mixture was left for ca. 18 h. The resulting green or blue solids were isolated by filtration, washed well with THF or benzene and Et_2O, and dried. Thus obtained were

$(py)_2CuCl_2$: sky blue solid (yield 94%). Anal. Calcd for $C_{10}H_{10}N_2Cl_2Cu$ (292.7): C, 41.04; H, 3.44; N, 9.57. Found: C, 41.14; H, 3.42; N, 9.27.

$(dipy)CuCl_2$: turquoise solid (yield 93%). Anal. Calcd for $C_{10}H_8N_2Cl_2Cu$ (290.6): C, 41.33; H, 2.77; N, 9.64. Found: C, 41.24; H, 2.54; N, 9.29.

$(dpm)CuCl_2$: green solid (yield 85%). Anal. Calcd for $C_{11}H_{10}N_2Cl_2Cu$ (304.7): C, 43.37; H, 3.31; N, 9.19. Found: C, 43.56, H, 3.21; N, 8.87.

$(dpp)CuCl_2$: blue solid (yield: 82%). Anal. Calcd for $C_{13}H_{14}N_2Cl_2Cu$ (332.7): C, 46.93; H, 4.24, N, 8.42. Found: C, 46.73; H, 4.27; N, 8.02.

$(Cl\text{-}dpm)CuCl_2$: bright green solid (yield 75%). Anal. Calcd for $C_{11}H_9N_2Cl_3Cu$ (339.1): C, 38.96; H, 2.68; N, 8.26. Found: C, 38.56; H, 2.42; N, 7.90.

$(Me\text{-}dpm)CuCl_2$: lime green solid (yield 89%). Anal. Calcd for $C_{12}H_{12}N_2Cl_2Cu$ (318.7): C, 45.23; H, 3.80; N, 8.79. Found: C, 44.95; H, 3.76; N, 8.70.

$(tBupy)_2CuCl_2$: sky blue solid (yield 85%). Anal. Calcd for $C_{18}H_{26}N_2Cl_2Cu$ (404.9): C, 53.40; H, 6.47; N, 6.92. Found: C, 53.50; H, 6.32; N, 6.87.

(6-Chloro-2-pyridyl)(2-pyridyl)methane Copper(I) Complex, $[(Cl\text{-}dpm)_2Cu][CuCl_2]\ CH_2Cl_2$. A suspension of CuCl (0.100 g, 1.00 mmol) in dichloromethane (ca. 5 mL) was treated with a dichloromethane solution of (6-chloro-2-pyridyl)(2-pyridyl)methane (1.1 equiv), and the mixture was left for overnight. The resulting yellowish solid was isolated by filtration, washed well with Et_2O, and dried (yield 90%). ^1H NMR (CD_2Cl_2, 400 MHz) 4.41 (br s, 2H), 7.33 (br m, 1H), 7.40 (br d, *J* = 7.1 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.61 (br d, *J* = 7.6 Hz, 1H), 7.81 (t, *J* = 7.8 Hz, 1H), 7.86 (dt, *J* = 1.5, 7.8 Hz, 1H), 8.43 (br s, 1H). Anal. Calcd for $C_{23}H_{20}N_4Cl_6Cu_2$ (692.2): C, 39.91; H, 2.91; N, 8.09. Found: C, 40.52; H, 2.32; N, 8.27.

Aziridination Experiments. In a drybox the copper catalyst (10 μmol, 5 mol %) and $NaBAr^F_4$ if any (17.6 mg, 20 μmol or 8.9 mg, 10 μmol) were placed into a small sample vial equipped with a magnetic stirrer bar. The olefin (200 μmol) dissolved in $CDCl_3$ (0.5 mL) was added with stirring, and PhINTs (74.6 mg, 200 μmol) was introduced immediately. The reaction time was defined as the time required for all PhINTs to dissolve. All resulting reaction mixtures were ultimately bright green, leaving no doubt that the catalyst resting state is Cu^{II}.

The NMR yields on PhINTs were calculated from NMR integrals of the aziridine and iodobenzene resonances. In a number of cases we used also dichloromethane as an internal standard. The latter (5.0 μL) was added after the reaction was complete. In all the aziridination reactions iodobenzene liberated quantitatively based on PhINTs and therefore it could be considered and used as an "internal standard" by itself. To ensure that there is no errors associated with integration of the signals of aromatic and aliphatic protons due to significant difference in their relaxation times, when taking NMR spectra we used the NMR relaxation delay of 8.0 s. Greater values of the delay had no effect on the integral ratios.

To confirm the identity of the aziridine by ^1H NMR spectroscopy,[17,33] and in a few cases by ^{13}C NMR spectroscopy, and estimate its isolated yield, the reaction mixture was filtered through a short column filled with alumina and eluted with small amount of dichloromethane. This method allowed reliable separation of copper catalyst, any "inorganic" components of the reaction mixture and efficient purification of the aziridine. The NMR-pure aziridine was isolated from the filtrate after removal of solvent, unreacted olefin and iodobenzene under high vacuum. The yield of the isolated aziridine was no more than 5% lower compared with the NMR yield.

2-Acetyl-*N*-(*p*-toluenesulfonyl)-aziridine.[34] ^1H NMR ($CDCl_3$, 22 °C) δ: 2.00 (s, 3H), 2.39 (s, 3H), 2.42 (d, $^3J_{H-H}$ = 4.2 Hz, 1H), 2.72 (d, $^3J_{H-H}$ = 7.4 Hz, 1H), 3.21 (dd, $^3J_{H-H}$ = 4.2 Hz, $^3J_{H-H}$ = 7.4 Hz, 1H), 7.29 (d, $^3J_{H-H}$ = 8.4 Hz, 2H), 7.76 (d, $^3J_{H-H}$ = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 22 °C) δ: 21.8, 26.0, 32.0, 42.1, 128.3, 130.1, 134.0, 145.5.

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2-*neo*-Pentyl-*N*-(*p*-toluenesulfonyl)-aziridine. ^{1}H NMR ($CDCl_3$, 22 °C) δ: 0.90 (s, 9H), 1.25 (m, 1H), 1.45 (m, 1H), 1.94 (d, $^3J_{H-H} = 4.6$ Hz, 1H), 2.41 (s, 3H), 2.57 (d, $^3J_{H-H} = 7.0$ Hz, 1H), 2.78 (m, 1H), 7.30 (d, $^3J_{H-H} = 8.4$ Hz, 2H), 7.79 (d, $^3J_{H-H} = 8.4$ Hz, 2H). ^{13}C NMR ($CDCl_3$, 22 °C) δ: 21.7, 29.5, 30.7, 34.1, 37.7, 45.5, 128.1, 129.8, 135.4, 144.6.

Mixture of *cis*- and *trans*-2,3-Dimethyl-*N*-tosyl-aziridines.[17] In the experiment with 5% $CuCl_2(py)_2$, 2 equiv of $NaBAr^F_4$, and 5:1 olefin/PhINTs the ratio of the *cis*- and *trans*-isomeric products was 4.7:1.The reaction took ca. 5 min. Both NMR and isolated yields of the two aziridines on PhINTs are quantitative. ^{1}H NMR ($CDCl_3$, 22 °C) select peaks δ: 1.15 (vd, $^3J_{H-H} = 5.0$ Hz, 6H, Me, *cis*-aziridine), 1.40 (d, $^3J_{H-H} = 5.0$ Hz, 6H, Me, *trans*-aziridine), 2.70 (m, 2H, CH, *trans*-aziridine), 2.84 (m, 2H, CH, *cis*-aziridine).

Example of Aziridination of Tetramethylethylene with 1 equiv of PhINTs Catalyzed with 5% of $(py)_2CuCl_2$–$2NaBAr^F_4$. The dichlorodi(pyridine)copper(II) complex, $(py)_2CuCl_2$, (2.9 mg, 10 μmol, 5mol %) and $NaBArF_4$ (17.6 mg, 20 μmol) were placed into a vial with a magnetic stirrer bar. Tetramethylethylene (16.8 mg, 200 μmol) was weighed in a separate vial, diluted with 0.5 mL of $CDCl_3$, and added with stirring to the mixture above. Immediately after that PhINTs (74.6 mg, 200 μmol) was introduced. In 2 min all PhINTs dissolved to give clear green solution. UV–vis spectrum recorded immediately after that showed the presence of two broad bands at 736 and 846 nm, in the region typical for Cu^{II} compounds.[35] The liquid was transferred into a NMR tube, and the ^{1}H NMR spectrum was recorded. Yield based on the NMR integrals of the aziridine and iodobenzene liberated was 94% on PhINTs (an average of two experiments). To confirm the identity of the aziridine, the reaction mixture was filtered through a 2 cm column filled with alumina and eluted with 6 mL of dichloromethane. NMR-pure aziridine was isolated from the filtrate after removal of solvent, the unreacted olefin, and iodobenzene under high vacuum. Isolated yield 47.0 mg (93%).

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Supporting Information Available: Crystallographic experiments, description and full crystallographic details of (Cl-dpm)$CuCl_2$ and $[(Cl\text{-}dpm)_2Cu][CuCl_2]$ in CIF format; ^{1}H and ^{13}C NMR spectra of (Cl-dpm), 2-*neo*-pentyl-*N*-(*p*-toluenesulfonyl)aziridine and $[(Cl\text{-}dpm)_2Cu][CuCl_2]$; Cartesian coordinates and results of the Mulliken spin density calculations for *trans*-$[(py)_2CuCl(NSO_2Ph)]^+$ and *trans*-$(py)CuCl_2(NSO_2Ph)$; and electronic absorption spectrum of the sample reaction mixture. This material is available free of charge via the Internet at http://pubs.acs.org.

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