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Intermolecular Alkene Aziridination: An Original and Efficient $Cu^{I}\cdots Cu^{I}$ Dinuclear Catalyst Deriving from a Phospha-Amidinate Ligand

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Mononuclear and dinuclear Cu^{I} complexes **1** and **2** derived from the phospha-amidinate ligands $[tBu_2P(NSiMe_3)_2]^-$ and $[Ph_2P(NSiMe_3)_2]^-$, respectively, have been evaluated in the catalytic aziridination of olefins using PhI=NTs (Ts = *p*-tolylsulfonyl) as the nitrene source. Dinuclear complex **2** featuring bridging NPN ligands and weak Cu···Cu interactions proved to be a robust and efficient catalyst. Aziridines could be obtained in good to excellent yields for a broad range of alkenes within 12 h at room temperature using 5 mol-% Cu and 1.2 to 2.4 equiv. PhINTs with respect to the alkene. Complex **2** performed best with styrenes and methyl acrylate. The presence of weak Cu···Cu interactions in **2** is uncommon in catalytic aziridination reactions, and some interesting parallels with the widespread dinuclear Rh(II) catalysts can be drawn.

Introduction

Aziridines are highly reactive and versatile synthons for the preparation of nitrogen-containing compounds.[1] Similarly to epoxides, they readily undergo ring-opening reactions with a wide range of nucleophiles, and this has led to numerous applications in natural product synthesis and medicinal chemistry.[2] Besides their transformation into 1,2-difunctionalized scaffolds, aziridines have also shown rich reactivity in ring-expansion reactions, giving straightforward access to various five- and six-membered rings.[1,3]

Although aziridines can be classically prepared by functional group manipulations starting from epoxides, amino alcohols, or azido alcohols,[1,2] most modern methods rely on two types of transition-metal-catalyzed group-transfer reactions: (i) the addition of carbenes or ylids to imines; and (ii) the transfer of nitrenes to alkenes.[4] The latter approach, referred to as *catalytic aziridination*, has attracted considerable interest over the last two decades. In particular, significant efforts have been made to develop new efficient nitrene precursors and transition metal catalysts to generate the key metallanitrene intermediates. Nowadays, the most commonly used nitrene source is certainly the iminoiodinane PhI=NTs (Ts = *p*-tolylsulfonyl),[5] although various alternative functional groups have been shown to also be competent.[6] In terms of catalysts, most studies are performed with dirhodium(II) tetracarboxylates $[Rh_2(O_2CR)]_2$ and related systems.[7] But copper complexes also occupy a prominent position, and are becoming more and more frequently used in natural product synthesis, medicinal chemistry and materials science.[8]

Following the pioneering discovery of D. A. Evans et al. in the early 1990s that simple and inexpensive Cu^{I} and Cu^{II} salts catalyze alkene aziridination under relatively mild conditions,[9] a broad range of copper complexes have been studied.[10,11] The structure of the copper catalyst was shown to have a great influence, and the use of ancillary ligands has allowed the catalytic performance to be modulated in terms of both activity and selectivity. Mostly, *N*-based polydentate ligands have been used in such catalytic aziridination reactions, and Scheme 1 shows representative examples of the ligands that have been investigated. These studies have resulted in significant progress being made, and some very efficient catalytic systems have been described.[10b,10d,10f,10h,11c–11e] However, most of the reported systems use relatively high catalytic loadings (up to 10 mol-%) and/or large excess of alkenes (often 5 to 10 equiv.). These remain significant drawbacks of Cu-catalyzed aziridination with iminoiodanes, and further studies seeking to develop new efficient catalysts are thus warranted. As for ourselves, we became interested in Cu complexes derived from $[R_2P(NR')_2]^-$ ligands.

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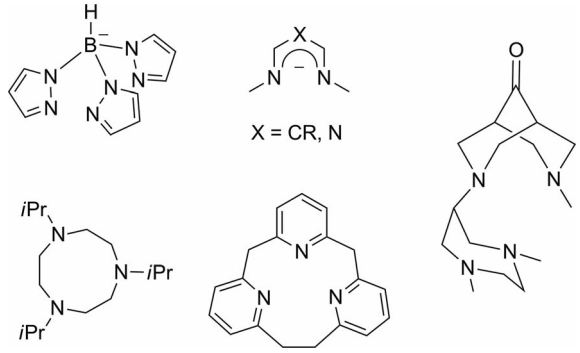


Scheme 1. Representative *N*-based polydentate ligands that have been investigated in Cu-catalyzed aziridination.

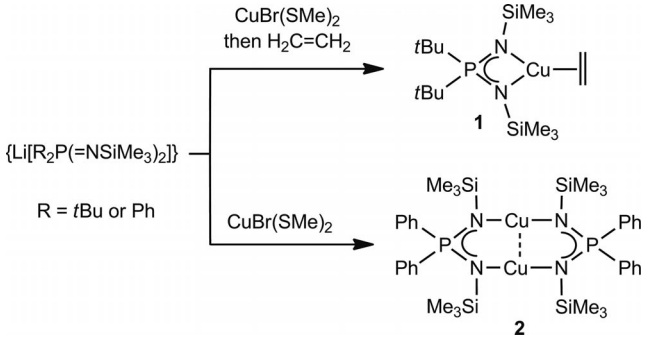
These NPN ligands are phosphorus analogs of the extensively used amidinates $[RC(NR')_2]^-$,[12] and can thus be referred to as phospha-amidinates.[13] They are readily accessible[14] and show versatile coordination properties[15] including to Cu.[16,17] Most remarkably, Hofmann[16] prepared the ethylene-Cu^I complex $\{Cu[tBu_2P(NSiMe_3)_2](H_2C{=}CH_2)\}$ (**1**) and used it to identify for the first time a Cu carbene complex relevant to catalytic cyclopropanation.[18] But to the best of our knowledge, NPN Cu complexes have not been investigated in aziridination to date. It is noteworthy that bridging rather than chelate coordination has also been observed with such NPN ligands. Despite differing from **1** only in the nature of the substituents at phosphorus, the $\{Cu[Ph_2P(NSiMe_3)_2]\}_2$ complex **2** described by Müller[17] adopts a dinuclear structure with weak Cu···Cu interactions in the solid state. Phospha-amidinate ligands thus offer the opportunity to evaluate both mononuclear and dinuclear NPN Cu^I complexes. To date, only a few polynuclear Cu complexes have been investigated in catalytic aziridination. Morales and Pérez[19] have studied a dinuclear Cu^I complex deriving from tris(thiocyanatomethyl)mesitylene, while Biffis and co-workers[20] have investigated di- and trinuclear Cu^I complexes bridged by bis- and tris-NHC (*N*-heterocyclic carbene) ligands.

In this paper, we report the first study of phospha-amidinate Cu complexes in catalytic aziridination. The mononuclear vs. dinuclear structure of complexes **1** and **2** has been analyzed in detail, and their catalytic performance has been evaluated. The dinuclear species **2** proved to be a robust and efficient catalyst. It performed best with styrenes and methyl acrylate, giving very good yields of the corresponding aziridines. The presence of weak Cu···Cu interactions is uncommon in catalytic aziridination, and some interesting parallels with the widespread dinuclear Rh(II) catalysts can be drawn.

Results and Discussion

Synthesis and Structure of Cu^I Complexes $\{Cu[tBu_2P(NSiMe_3)_2](H_2C{=}CH_2)\}$ (1) and $\{Cu[Ph_2P(NSiMe_3)_2]\}_2$ (2)

Cu^I complex **1** was prepared following the procedure described by Hofmann et al.[16] in 1999. The $tBu_2P(NSiMe_3)(NHSiMe_3)$ pro-ligand, obtained by a double Staudinger reaction between tBu_2PH and N_3SiMe_3,[14b] was lithiated with *n*BuLi. After reaction with $CuBr(SMe_2)$ in pentane followed by ethylene bubbling, complex **1** was obtained as white crystals upon crystallization at –30 °C (65% yield; Scheme 2). The structure of **1** was confirmed by complete NMR analysis, all data being consistent with those reported previously.[16]



Scheme 2. Synthesis of the NPN-Cu^I complexes **1** and **2**.

A similar procedure was then used to prepare a related complex featuring Ph instead of *t*Bu groups at phosphorus. Complex **2** was prepared by Müller et al.[17] in 2000 using a different strategy, and its structure was confirmed by X-ray crystallography. Here, we treated the lithium salt of $Ph_2P(NSiMe_3)(NHSiMe_3)$[15b,15c] with $CuBr(SMe_2)$ in pentane, and proceeded with NMR characterization. The appearance of a unique set of ^{31}P and ^{29}Si NMR signals [^{31}P: δ = 23.2 (s) ppm; ^{29}Si: δ = –6.5 (d, J = 8.0 Hz) ppm] indicated the clean formation of a symmetrical compound. In this case, bubbling ethylene induced no change in the NMR spectra, and complex **2** was isolated as white crystals (75% yield) after filtration and cooling to –30 °C for 3 d. Its molecular structure was unambiguously confirmed by X-ray diffraction analysis.

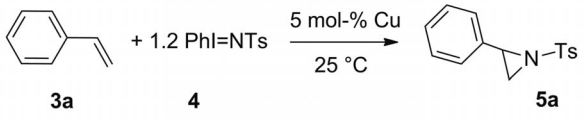
According to X-ray diffraction data, complexes **1** and **2** adopt mononuclear and dinuclear structures, respectively, in the solid-state. This difference clearly has to do with whether or not ethylene is present in the coordination sphere of Cu, and it also reveals the subtle influence of the substituents at phosphorus on the coordination properties of the NPN ligands. The sterically demanding *t*Bu groups induce wide C–P–C and acute N–P–N bond angles (Thorpe–Ingold effect), and thereby favor chelate coordination in complex **1** [C–P–C: 111.89(13)° and N–P–N: 104.33(12)°].[16] In contrast, the Ph groups are less bulky, and lead to more acute CPC and wider NPN bond angles, so that bridging coordination is preferred in complex **2** [C–P–C: 105.1(2)° and N–P–N: 115.8(2)°].[17] Remarkably, the distance between the two copper atoms in the dinuclear complex **2** [2.621(1) Å] is much shorter than that found by Morales and Pérez in the complex derived from tris(thiocyanatomethyl)mesitylene [2.936(2) Å],[19] and actually falls within the typical range associated with weak d^{10}···d^{10}, so-called metallophilic interactions.[21,22]

The two related NPN Cu^I complexes show markedly different chemical behavior. Complex **1** proved to be extremely sensitive, and decomposed rapidly both in solution and in the crystalline state in the absence of an ethylene atmosphere. In contrast, solution and solid-state samples of complex **2** showed no sign of decomposition over several days at room temperature. The lack of reaction with ethylene suggests that **2** is not prone to dissociation, and actually retains its dimeric structure in solution. To confirm this hypothesis, ^{1}H DOSY NMR experiments were carried out on both complexes **1** and **2**.[23] For mononuclear ethylene complex **1**, a diffusion coefficient of $D = 7.6 \times 10^{-11}$ $m^2 s^{-1}$ was found in $CDCl_3$ solution at 22 °C. Complex **2** gave a significantly lower value, $D = 4.7 \times 10^{-11}$ $m^2 s^{-1}$, under the same conditions. The corresponding hydrodynamic radii R_H (8.37 Å for **2** vs. 5.30 Å for **1**), as estimated from the Stokes–Einstein equation,[24] unambiguously indicate that the difference in nuclearity between complexes **1** and **2** is maintained in solution.

Styrene Aziridination Promoted by NPN Cu^I Complexes 1 and 2

Having synthesized NPN Cu^I complexes **1** and **2**, we were eager to evaluate their catalytic properties in olefin aziridination. For this study, iminophenyliodinane PhI=NTs **4** was chosen as the nitrene source.[5] First, we focused on styrene (**3a**) as a model substrate, and tested various solvents (Table 1). The reactions were performed at 25 °C, and the catalyst loading was set at 5 mol-% in Cu to enable a comparison between the mononuclear and dinuclear complexes. Large excesses of olefins (5 to 10 equiv. with respect to the nitrene source) are often used in catalytic aziridination reactions to achieve high yields. This is a real limitation on a preparative scale, and so we decided to use nearly equimolar quantities of styrene and the iminoiodinane (actually 1.2 equiv. of PhI=NTs with respect to styrene). The use of apolar solvents such as benzene gave good results with both catalysts (Table 1, entries 1 and 2). Aziridine **5a** was obtained in high yields within a few hours. Mononuclear complex **1** was clearly more efficient than dinuclear complex **2** under these conditions (97 vs. 82% yield after 12 h). This difference probably stems from solubility issues. Indeed, complex **1** is very soluble in benzene,[25] whereas **2** forms suspensions even at dilute concentrations. In contrast, complex **2** out-performed **1** in chlorinated solvents (Table 1, entries 3–5). With **2**, aziridine **5a** was obtained in quantitative yield in dichloromethane or chloroform, whereas **1** was not able to achieve conversions higher than 70%, probably due to catalyst degradation. The use of coordinating solvents proved detrimental in our case:[26] acetonitrile significantly lowered the catalytic activity of complex **2**, and tetrahydrofuran completely shut down the process (Table 1, entries 6 and 7).

Table 1. Cu-catalyzed aziridination of styrene (**3a**).



3a **4** **5a**

Entry[a]	Cat.	Solvent	*t* (h)	Yield (%)[b]
1	**1**	C_6D_6	12	97 (92)[c]
2	**2**	C_6D_6	12	82 (78)[c]
3	**1**	CD_2Cl_2	12	70
4	**2**	CD_2Cl_2	12	99
5	**2**	$CDCl_3$	12	99
6	**2**	CH_3CN-d_3	24	19
7	**2**	THF-d_8	24	0

[a] All experiments were performed under an argon atmosphere starting from 0.2 mmol styrene (0.1 M solution). [b] Yields were determined by ^{1}H NMR spectroscopy. [c] Yields after 3 h given in parentheses.

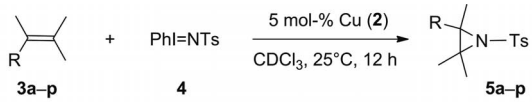
These first catalytic runs showed that mononuclear and dinuclear NPN Cu^I complexes both catalyze the aziridination of styrene at room temperature. Dinuclear complex **2** clearly gives the best compromise: it is much more stable than mononuclear complex **1**, and it performs very efficiently in chlorinated solvents (quantitative conversion of styrene within 12 h). Compound **2** is a rare example of a dinuclear Cu complex that shows activity in this transformation;[19,20] the presence of weak Cu···Cu interactions is very uncommon in catalytic aziridination reactions. We were thus very interested in further evaluating the catalytic performance of **2**.

Scope of the Intermolecular Aziridination Catalyzed by NPN Dinuclear Cu^I Complex 2

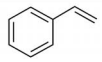
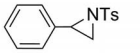
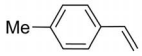
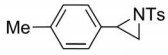
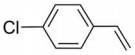
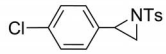
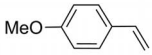
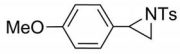
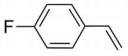
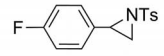
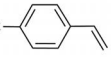
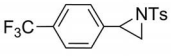
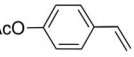
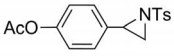
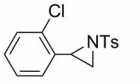
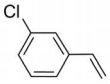
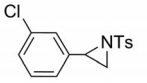
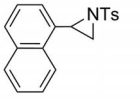
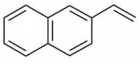
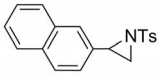
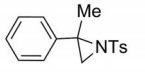
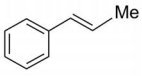
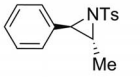
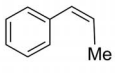
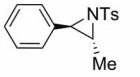
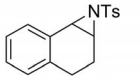
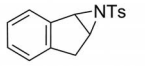
The catalytic activity of complex **2** towards a broad range of styrenic substrates was evaluated (Table 2). Aziridination of *para*-substituted styrenes **3b–d** (*p*-Me, Cl, MeO) proceeded in 68–75% yield (Table 2, entries 2–4) under the optimal conditions identified for styrene (5 mol-% Cu, $CDCl_3$, 25 °C, 12 h, 1.2 equiv. PhI=NTs). These rather modest yields can be explained by the formation of *p*-toluenesulfonamide $TsNH_2$ (as confirmed by ^{1}H NMR spectroscopy and GC-MS), as the result of undesirable hydrolysis of the nitrene source in solution. To improve the efficiency of the catalytic process, the amount of iminoiodinane was increased to 2.4 equiv. Gratifyingly, *para*-substituted styrenes **3b–d** were then converted into the corresponding aziridines (i.e., **5b–d**) in much higher yields (88–92%).

Under these conditions, complex **2** was successfully used in the aziridination of a wide variety of substrates, including functionalized ones. As shown in Table 2, entries 5–7, **2** efficiently promotes the aziridination of *para*-substituted styrenes bearing fluorinated (*p*-F, F_3C) and ester (*p*-AcO) moieties. It is noteworthy that the aziridines were obtained in very high yields (84–95%), regardless of the electron-donating or accepting nature of the *para*-substituent of the styrenic substrates. The catalytic system was also compatible

Table 2. Aziridination of styrenic olefins **3a**–**p** catalyzed by the dinuclear Cu complex **2**.[a]



3a–p **4** **5a–p**

Entry	Olefin		Aziridine		Equiv. PhI=NTs	Yield (%)[b]
1		**3a**		**5a**	1.2	99
2		**3b**		**5b**	1.2 2.4	68 92
3		**3c**		**5c**	1.2 2.4	68 92 (77)[c]
4		**3d**		**5d**	1.2 2.4	75 88
5		**3e**		**5e**	2.4	95
6		**3f**		**5f**	2.4	88
7		**3g**		**5g**	2.4	84
8		**3h**		**5h**	2.4	72
9		**3i**		**5i**	2.4	89
10		**3j**		**5j**	2.4	88
11		**3k**		**5k**	2.4	99
12		**3l**		**5l**	2.4	33
13		**3m**		**5m**	2.4	52
14		**3n**		**5m**	2.4	52
15		**3o**		**5o**	2.4	62
16		**3p**		**5p**	2.4	74

[a] Experiments were performed at room temperature under an argon atmosphere starting from 0.2 mmol olefin (0.1 M in $CDCl_3$). [b] Yields were determined by ^1H NMR spectroscopy. [c] Isolated yield from a reaction carried out with 1 mmol olefin.

and proceeded efficiently with *ortho*- and *meta*-substituted substrates. Chloro-substituted styrenes **3h** and **3i** were converted into the corresponding aziridines (i.e., **5h** and **5i**) in 72 and 89% yields, respectively (Table 2, entries 8 and 9). Very good results were also obtained with 1- and 2-vinylnaphthalenes (**3j** and **3k**; Table 2, entries 10 and 11; 88 and 99% yields of the respective aziridines).

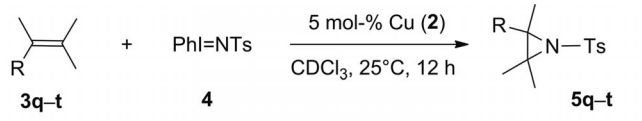
The influence of substitution at the reactive C=C double bond was then investigated. Methylstyrene was chosen as substrate since its *gem*, *trans*, and *cis* isomers are all commercially available. In addition, β-methylstyrenes offer the opportunity to probe the stereoselectivity of aziridination, and thereby to gain some mechanistic insight. A mixture of diastereomers is usually obtained starting from either the *E* or *Z* alkene, with ratios depending on the catalytic system used.[9b,10b,10e,10i,11b,11f] A modest yield of 33% was obtained in the aziridination of *α*-methylstyrene **3l** (Table 2, entry 12), indicating a strong deleterious effect of geminal substitution. Steric factors probably impede the formation of the quaternary center in the corresponding aziridine. β-*E*-Methylstyrene **3m** gave a slightly higher but still modest yield of 52% (Table 2, entry 13). Remarkably, the reaction proceeded with complete stereoselectively to give the corresponding *trans* aziridine (i.e., **5m**) exclusively.[27] Under the same conditions, β-*Z*-methylstyrene **3n** also provided a single aziridine in 52% yield (Table 2, entry 14), but surprisingly, this was again identified as *trans* aziridine **5m**. ^1H NMR spectroscopic analysis of the crude reaction mixture indicated that the formation of **5m** was accompanied by a complete isomerization of the unreacted substrate. According to control experiments, the isomerization of **3n** into its more thermodynamically stable *E* isomer **3m** did not occur in the presence of dinuclear Cu complex **2** alone, but required the presence of PhI=NTs. Under these conditions, $Z \rightarrow E$ isomerization of β-methylstyrene took place very easily and much more quickly than aziridination. From a mechanistic viewpoint, metal-catalyzed alkene aziridination reactions typically involve metallanitrene intermediates, and proceed by concerted or radical stepwise pathways.[28] Based on the complete retention of stereochemistry observed upon aziridination of β-*E*-methylstyrene **3m**, we surmise that a concerted pathway operates in our case.

The aziridination of cyclic β-substituted styrenes was then investigated. With 3,4-dihydronaphthalene **3o** and indene **3p** (Table 2, entries 15 and 16), $Z \rightarrow E$ isomerization is inherently prevented, and the corresponding aziridines (i.e., **5o**,**p**) were obtained in relatively good yields (62 and 74%, respectively). The complete chemoselectivity observed in these reactions is worth mentioning. Despite the presence of activated C–H bonds (in allylic and/or benzylic positions), no products arising from C–H amination were detected.[29]

Finally, the encouraging results obtained with styrenic substrates prompted to us to assess the efficiency of complex **2** towards unactivated alkenes (Table 3). Modest yields in the range of 20–43% were obtained with 1-hexene (**3q**), cyclohexene (**3r**), and cyclooctene (**3s**) (Table 3, entries 1–3), indicating that linear and cyclic aliphatic olefins are rela-

tively poor substrates. But once again, it is remarkable that complete chemoselectivity in favor of aziridination over C–H amination was observed, particularly for **3r**. This stands in stark contrast with the fact that mixtures of aziridines and allylic amines are typically obtained with Cu[10b,10e] as well as Rh[7] complexes. Finally, complex **2** showed very good reactivity towards methyl acrylate (**3t**), giving the corresponding aziridine **5t** in 89% yield (Table 3, entry 4). This transformation holds particular synthetic interest as functionalized aziridine **5t** gives ready access to α- and β-amino acids.[2,30]

Table 3. Cu-catalyzed aziridination of aliphatic alkenes **3q**–**s** and methyl acrylate (**3t**).[a]



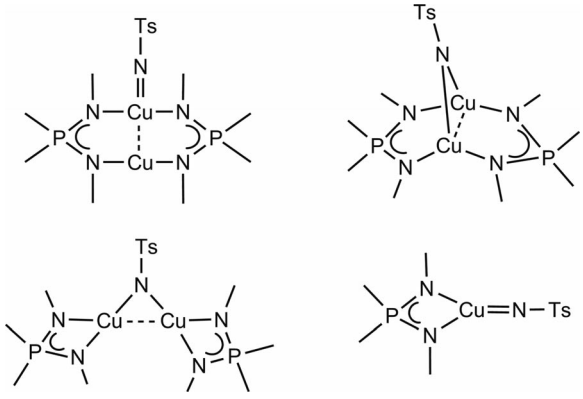
Entry	Olefin		Aziridine		Equiv. PhI=NTs	Yield (%)[b]
1		**3q**		**5q**	1.2	39
2		**3r**		**5r**	1.2	20
3		**3s**		**5s**	2.4	43
4		**3t**		**5t**	1.2	89

[a] Experiments were performed at room temperature under an argon atmosphere starting from 0.2 mmol olefin (0.1 M in $CDCl_3$). [b] Yields were determined by ^1H NMR spectroscopy.

Conclusions

In conclusion, the first evaluation of NPN Cu complexes in catalytic aziridination is reported. Phospha-amidinates $[R_2P(NR')_2]^-$ readily form Cu^I complexes such as $\{Cu[tBu_2P(NSiMe_3)_2](H_2C{=}CH_2)\}$ **1** and $\{Cu[Ph_2P(NSiMe_3)_2]\}_2$ **2**. The bulky *t*Bu groups favor chelate coordination of the NPN ligand in **1** (mononuclear complex), whereas the less sterically demanding Ph groups lead to bridging coordination in **2** (dinuclear complex). Both complexes have been shown to be competent catalysts for the aziridination of styrene with iminoiodinane PhI=NTs as nitrene source. Dinuclear complex **2** clearly gives the best compromise. It is a robust and efficient catalyst for the aziridination of a broad range of substrates, in particular styrene derivatives and methyl acrylate.

From this work, phospha-amidinates appear to be a promising yet relatively underexplored class of *N*-based ligands.[15b–15d,15f] The presence of weak Cu···Cu interactions in the dinuclear complex **2** is also remarkable. To date, essentially only mononuclear Cu complexes have been used in catalytic aziridination reactions. These results draw some interesting parallels with the widely used dinuclear Rh(II) catalysts, in which the central Rh–Rh bond clearly plays a major role.[31] It is conceivable that the dinuclear, weakly bonded Cu···Cu structure of **2** behaves somewhat similarly, and enables some cooperativity between the two metal centers.[32] The participation of mononuclear copper species cannot be excluded, but the dinuclear species seems to be highly favored with the phospha-amidinate ligand $[Ph_2P(NSiMe_3)_2]^-$. At this stage, it is clearly not possible to give a detailed mechanistic picture for these aziridination reactions, and the precise structure of the key metallanitrene intermediate remains unclear. Based on the few nitrene/carbene dinuclear complexes proposed or eventually even characterized with copper and rhodium,[18b,33,34] several structures can be envisioned, with terminal or bridging coordination of the nitrene moiety (Scheme 3).



Scheme 3. Conceivable structures for the key metallanitrene intermediate involved in aziridination reactions catalyzed by **2**.

Future work will seek to gain some mechanistic insight and further explore the catalytic properties of such NPN copper complexes in aziridination and related nitrene-transfer reactions.

Experimental Section

General Methods: All reactions were performed using standard Schlenk techniques under an argon atmosphere. Solvents were dried and distilled prior to use (Et_2O and THF over sodium, pentane and dichloromethane over CaH_2). All organic reagents were obtained from commercial sources and used as received. [CuBr(SMe$_2$)] was purchased from Sigma–Aldrich. $\{Cu[tBu_2P(NSiMe_3)_2](CH_2{=}CH_2)\}$ (**1**)[16] and $\{Li[Ph_2P(NSiMe_3)_2]\}$[15b,15c] were prepared according to literature procedures. ^{31}P, ^1H, and ^{13}C NMR spectra were recorded with Bruker Avance 300, 400, and 500 spectrometers. ^{31}P, ^{28}Si, ^1H, and ^{13}C chemical shifts are expressed with a positive sign, in parts per million, relative to external 85% H_3PO_4 and Me_4Si. ^1H DOSY NMR experiments were recorded with a Bruker Avance 500 spectrometer equipped with a 5 mm triple resonance inverse Z-gradient probe. All chemical shifts are relative to TMS and samples were prepared in $CDCl_3$. All diffusion measurements were made using the stimulated echo pulse sequence with bipolar gradient pulses. The shape of the gradients was square. The diffusion delay (Δ) was fixed at 100 ms, and the gradient pulse duration (δ) at 2 ms. The recycle delay was adjusted to 3 s, and the strength of the gradient was varied in 16 increments (from 5 to 95%) in a linear ramp.

Synthesis of Homo-Bimetallic Complex {Cu[$Ph_2P(NSiMe_3)_2$]}$_2$ (2): A mixture of {Li[$Ph_2P(NSiMe_3)_2$]} (192 mg, 0.80 mmol) and [CuBr(SMe_2)] (115 mg, 1.04 mmol, 1.3 equiv.) was stirred in dried pentane (30 mL) under an argon atmosphere at room temperature for 4 h. Then the solution was filtered to remove the lithium salts and the excess of the Cu-precursor. The solution was concentrated to 10 mL and kept at –30 °C for 72 h. The white crystals formed were isolated by simple filtration, and product **2** (201 mg, 75%) was isolated as a white powder. $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6, 0 °C): δ = 23.1 (s) ppm. $^{29}Si\{^1H\}$ NMR (59.6 MHz, C_6D_6, 0 °C): δ = –5.5 (d, $J_{Si,P}$ = 8.0 Hz) ppm. ^1H NMR (300 MHz, C_6D_6, 0 °C): δ = 7.63 (ddd, J = 9.5, 3.4, and 1.7 Hz, 4 H, HPh_2P), 7.10 (br., 1 H, HPh_2P), 7.03–6.96 (m, 5 H, HPh_2P), 0.02 (s, 18 H, $SiMe_3$) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, 0 °C): δ = 139.4 [d, $^1J_{C,P}$ = 113.7 Hz, $C_{ipso}Ph_2P$], 132.3 (d, $^3J_{C,P}$ = 10.1 Hz, $C_{meta}Ph_2P$), 130.4 (d, $^4J_{C,P}$ = 2.8 Hz, $C_{para}Ph_2P$), 127.9 (d, $^2J_{C,P}$ = 12.2 Hz, $C_{ortho}Ph_2P$), 4.6 (d, $^3J_{C,P}$ = 3.6 Hz, $SiMe_3$) ppm.

Crystal-Structure Determination of Complex 2: Data were collected using an oil-coated shock-cooled crystal with a Bruker-AXS Kappa APEXII Quazar diffractometer with Mo-K_α radiation (λ = 0.7103 Å). Phi and omega scans were used. Semi-empirical absorption corrections were used.[35] The structure was solved by direct methods (SHELXS97)[36] and refined using the least-squares method on F^2 with SHELXL97.[37] All non-H atoms were refined with anisotropic displacement parameters. The H atoms were refined isotropically at calculated positions using a riding model with their isotropic displacement parameters constrained to be equal to 1.5 times the equivalent isotropic displacement parameters of their pivot atoms for terminal sp^3 atoms and 1.2 times for all other carbon atoms. The new set of X-ray data has been deposited to the Cambridge Crystallographic Data Centre (improved resolution quality): CCDC-901290. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal Data for 2: $C_{36}H_{56}Cu_2N_4P_2Si_4$, M_r = 846.25, monoclinic, space group $C2/c$, a = 18.4120(8), b = 12.5009(5), c = 19.6122(8) Å, β = 106.200(2)°, V = 4334.8(3) Å^3, Z = 4, $\rho_{calcd.}$ = 1.297 g cm^{-3}, $F(000)$ = 1776, T = 193(2) K, crystal size 0.60 × 0.16 × 0.12 mm^3, 46915 reflections collected (6629 independent, R_{int} = 0.0207), $\theta \leq$ 30.55°, 223 parameters, R_1 [$I > 2\sigma(I)$] = 0.0247, wR_2 (all data) = 0.0770, largest diff. peak and hole: 0.307 and –0.329 e Å^{-3}.

Typical Procedure for the Intermolecular Alkene Aziridination: Inside the glove-box under an argon atmosphere, a Schlenk tube was charged with the catalyst (5 mol-%), the alkene (0.2 mmol), and the solvent (2 mL). After stirring for 1 min, PhI=NTs (1.2 or 2.4 equiv.) was added in one portion. The mixture was stirred at room temperature for 12 h under an argon atmosphere. The reaction mixture was then directly analyzed by ^1H NMR spectroscopy.

Supporting Information (see footnote on the first page of this article): Experimental procedures and NMR spectra of complex **2** and compound **5c**.

Acknowledgments

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