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## Chlorotrimethylsilane (TMSCl): an efficient siliconbased Lewis acid mediator in allylic alkylation using a diethylzinc reagent<sup>†</sup>

Wen-Hui Deng, Fei Ye, Xing-Feng Bai, Li Li,\* Tao Song, Yun-Long Wei and Li-Wen Xu\*

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Chlorotrimethylsilane (TMSCI) was a highly efficient catalyst in the allylic alkylation of 1,3-diaryl-2-propenyl acetates with a diethylzinc reagent, in which various 1,3-diaryl-2-propenyl acetates are efficiently transferred to 1,3-diarylpent-1-enes in good to excellent yields.

Organosilicon compounds present key structural features in a plethora of non-naturally occurring molecules, and they are important reagents, catalysts, or substrates in organic synthesis.1 Especially in the past few decades, silicon-based Lewis acid has occupied an important position in catalysis and tremendous progress has been achieved in the application of silicon-based Lewis acids in organic synthesis.2 The behavior of these silicon-based Lewis acids were suggested primarily by the tendency of the silicon atom to expand its valence shell, giving rise to five- or six-coordinate intermediates, which allows one to consider organosilicon compounds as Lewis acids to promote organic transformations.3 Furthermore, silicon-based Lewis acids offer some advantages over traditional metal-based Lewis acid and Brønsted acid. For example, silicon-based Lewis acids are compatible with many synthetically valuable C-nucleophiles and heteroatoms, such as silvl enol ethers, indium or cupratesbased organometallic reagents, Grignard reagents, phosphines, and carbamates.<sup>4</sup> Among many commercial available siliconbased Lewis acids, chlorotrimethylsilane (TMSCl) is one of the most useful reagents or activators in catalytic organic reactions, such as conjugate addition,<sup>5</sup> multi-component reactions,<sup>6</sup> Pictet-Spengler reaction,7 aza-Michael additions,8 etherification of aldehydes,9 cross-aldol condensation,10 nucleophilic addition,11 Friedel-Crafts reaction,12 and other transformations.13 However, its direct use as a silicon-based Lewis acid catalyst in organic reactions is rarely reported.14 As an extension of our

previous studies on TMSCI-mediated and -catalyzed organic transformations, herein we reported a mild and convenient procedure for TMSCI-catalyzed allylic alkylation of 1,3-diaryl-2-propenyl acetate with diethylzinc reagent.

In recent years, catalytic allylic alkylation of organometallic reagents has received much attention and several methods have been developed for regioselective allylation of organolithium compounds, alkyl Grignard and alkylzinc reagents under copper catalysis or stoichiometric cuprates derived from these organometallic reagents.<sup>15-19</sup> Nevertheless, the scope of allylic substrates providing the desired carboncarbon bond formation remains limited to allyl halides and allylic picolinates as well as the use of metal catalysts in most cases. In addition, in many cases an excess of organometallic reagent as well as stoichiometric copper salt is required, which is particularly undesirable from the standpoint of modern organic synthesis.

Although the copper-catalyzed asymmetric allylic alkylations with organometallic reagents are known,<sup>16-19</sup> it seemed that an allylic substitution of 1,3-diphenylallyl acetate with organozinc reagent as well as the synthesis of 1,3-diarylpent-1-enes could be developed. Interestingly, during our work on the development of catalytic alkylation of organozinc reagent, we observed unexpectedly that chlorotrimethylsilane (TMSCl) was a highly efficient catalyst in the allylic alkylation of 1,3-diaryl-2-propenyl acetates with diethylzinc reagent. To the best of our knowledge, the subject of catalytic ability of TMSCl in copper-free allylic alkylation has not been reported to date.

Initially, we commenced the investigation by testing the copper-catalyzed allylic substitution of 1,3-diphenylallyl acetate with organozinc reagent (Et<sub>2</sub>Zn) in the presence of chiral phosphine ligands. Beside famous BINAP (2,2'-bis(diphenyl-phophino)-1,1'-binaphthyl), a C<sub>2</sub>-axially chiral monophosphine L2 {Ph-NNP: (1-(2-benzylnaphthalen-1-yl)naphthalen-2-yl)-diphenylphosphine} and L3 prepared from Ar-BINMOL,<sup>20</sup> have been brought to light after their successful application in asymmetric catalysis. As illustrated in Table 1, unfortunately, the copper catalyst system derived from Cu(OTf)<sub>2</sub> and BINAP



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Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education, College of Material, Chemistry and Chemical Engineering, Hangzhou Normal University, Hangzhou 311121, P. R. China. E-mail: liwenxu@hznu.edu.cn; licpxulw@yahoo.com; Fax: +86 2886 5135; Tel: +86 2886 8915

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Entry	Cat.	Ligand	TMSCl (eq.)	Temperature	Time (h)	Yield <sup>b</sup> (%)
1	Cu(OTf).	L1	0	-20 °C	36	<5
2	$Cu(OTf)_2$	L1	2.0	-20 °C	10	×5 80
3	$Cu(OTf)_2$	L2	2.0	−20 °C	10	90
4	$Cu(OTf)_2$	L3	2.0	−20 °C	18	>99
5	$Cu(OTf)_2$	L3	0	−20 °C	36	<5
6	$[Pd(\eta^3 - C_3H_3)Cl]_2$	L3	2.0	-20 °C	10	40
7	$Ni(acac)_2$	L3	2.0	$-20$ $^{\circ}C$	10	60
8	_	_	2.0	-20 °C	12	>99
9	_	_	1.0	RT	4	94
10	_	_	0.5	RT	5	95
11	_	_	0.2	RT	9	96
12	_	_	0.2	RT	12	$50^{c}$
13	_	_	0.2	RT	12	$30^d$
14	_	_	0.2	RT	12	$<5^{e}$

<sup>*a*</sup> Reaction conditions: 1 mol% of transition metal catalyst, 1 mmol of 1,3diphenylallyl acetate (1a), Et<sub>2</sub>Zn (1.0 M solution in hexane; 2.0 equiv. for entries 1–8 and 1.5 equiv. for 9–14), 2.0 equiv. TMSCl, and 2 mol% of racemic ligand or chiral ligand (L1–L3), at -20 °C. <sup>*b*</sup> Isolated yields after flash column chromatography. <sup>*c*</sup> The reaction was performed in THF. <sup>*d*</sup> The reaction was performed in DCM. <sup>*e*</sup> The reaction was performed in toluene.

almost has no activity for the allylic substitution (Entry 1 of Table 1, <5% yield). It should be mentioned that allylic alkylation of 1,3-diaryl-2-propenyl acetates with diethylzinc reagent was not occurred under catalyst-free reaction. Despite these negative results, we decided to investigate the effect of additive on the catalytic allylic alkylation of 1,3-diphenylallyl acetate with diethylzinc reagent. Inspired by Alexakis's copper catalysis in the allylic alkylation of allylic chloride and allylic bromide,17 we hypothesized that the addition of chlorotrimethylsilane (TMSCl) would be beneficial to the in situ formation 3-chloro-1,3-diphenylprop-1-ene and then accelerated the allylic alkylation of Et<sub>2</sub>Zn due to the cooperative catalytic activity of Cu(OTf)<sub>2</sub> and TMSCl. As shown in Scheme 1, in our preliminary hypothesis, 1,3-diphenylallyl acetate could be converted to high reactive 3-chloro-1,3-diphenylprop-1-ene in the presence of TMSCl under the catalytic reaction conditions,<sup>21</sup> which would led to the formation of key  $\pi$ -allylcopper intermediate (IV) after the oxidative addition of copper source.<sup>22</sup> Meanwhile, it has been revealed that TMSCl could activated Cu(OTf)2 and other Lewis acid catalysts in many organic transformations.5-13



Scheme 1 The hypothesis of TMSCl-mediated copper-catalyzed allylic substitution of organometallic reagents (M-R): double roles of TMSCl as reactive reagent and silicon-based Lewis acid catalyst.

Fortunately, when 2.0 equiv. of TMSCl was added to the reaction mixture using Cu(OTf)<sub>2</sub> as catalyst, the allylic alkylation proceeded smoothly and the yield of desired product 2a was dramatically improved to 80% (Entry 2). However, when chiral (R)-BINAP was used as ligand, there was no enantioselectivity. Next, we examined our ligands that designed and prepared recently20 in this copper-catalyzed allylic alkylation of 1,3-diphenylallyl acetate with organozinc reagent (Et<sub>2</sub>Zn) in the presence of 2.0 equiv. of TMSCl. As expectedly, the reaction proceeded smoothly to give the desired 2a in higher yield (Entry 3 and 4). Nevertheless, the enantioselectivity was not detected under both the reaction conditions. Notably, the absence of TMSCl was also led to no reaction when ligand L3 was used in this case (Entry 5). Comparably and interestingly, we found that both the palladium and nickel catalysts gave inferior activity in this reaction. More meaningfully, the allylic alkylation of 1,3-diphenylallyl acetate with organozinc reagent (Et<sub>2</sub>Zn) proceeded better in the presence of TMSCl without any catalysts and ligands (Entry 8). These reaction results showed that these transition metal catalysts and chiral ligands disturbed the interaction between TMSCl and substrates to some extent. Further evaluations of the amount of TMSCl highlighted the crucial role of this silicon-based Lewis acid in achieving high yield with 1.5 equiv. Et<sub>2</sub>Zn. As shown in Table 1 (Entries 9–11), the use of 20 mol% of TMSCl as catalyst or mediator gave rise to excellent yield in 9 hours at room temperature (Entry 11). By changing the diethylether (Et<sub>2</sub>O) to other solvents (Entries 12-14), such as THF, DCM, or toluene, we observed an obvious decrease of yield. Especially, TMSCl did not promote this reaction in toluene (Entry 14). Notably, a longer time was needed when 10 mol% of TMSCl was used in this reaction, and some unexpected and unidentified byproducts were detected in this case.

Having established the utilization of 20 mol% TMSCl in diethylether at room temperature as the optimized conditions to perform the allylic alkylation reaction, we next extended allylic coupling of organozinc reagent ( $Et_2Zn$ ) with various 1,3-diarylallyl acetates (Table 2). As can be seen, the process can tolerate a variety of common functional 1,3-diarylallyl acetates (**1a–k**) with  $Et_2Zn$ . The allylic alkylation of  $Et_2Zn$  with 1,3-diarylallyl acetates (**1a–k**), bearing either electron-donating groups or electron-

Table 2	2	TMSCl-mediated	allylic	alkylation	of	organozinc	reagent
(Et <sub>2</sub> Zn)	wi	th various 1,3-diar	ylallyl a	acetates <sup>a</sup>			



2	<i>p</i> -Br	<i>p</i> -Br	2 <b>b</b> : 96
3	<i>p</i> -Ме	<i>p</i> -Ме	<b>2c:</b> 94
4	<i>p</i> -Cl	<i>p</i> -Cl	<b>2d</b> : 96
5	p-CF <sub>3</sub>	p-CF <sub>3</sub>	<b>2e:</b> 56
6	<i>p</i> -Cl	Н	<b>2f:</b> 97 <sup>c</sup>
7	Н	<i>p</i> -Cl	<b>2g:</b> 97 <sup>c</sup>
8	<i>p</i> -Br	Н	<b>2h</b> : 94 <sup><i>c</i></sup>
9	Н	<i>p</i> -Br	<b>2i</b> : 91 <sup>c</sup>
10	Н	<i>p</i> -Ме	<b>2j:</b> 98 <sup><i>c</i></sup>
11	<i>р</i> -Ме	Н	<b>2k:</b> 95 <sup>c</sup>

<sup>*a*</sup> Reaction conditions: 1 mmol of 1,3-diarylallyl acetates (1), 1.5 equiv. Et<sub>2</sub>Zn (1.0 M solution in hexane), and 20 mol% of TMSCl, in Et<sub>2</sub>O, at room temperature. <sup>*b*</sup> Isolated yields after flash column chromatography. <sup>*c*</sup> The total yield of two isomers. It was difficult to be separated by flash column chromatography. The ratio of two isomers is almost 1 : 1–1.3 : 1.

withdrawing groups on their aromatic rings proceeded smoothly in good to excellent yields. Unfortunately, an obvious limitation at the present stage of this method is the selectivity is low because the reactions with unsymmetrical 1,3-diarylallyl acetates (1f-k) containing two different substituents on aromatic rings would lead to a mixture of regioisomeric products (Entries 6–11, 2f-k). Nevertheless, these reaction results may suggest that the allylic addition involves the formation a  $\pi$ -allyl or carbenium intermediate.

For further investigation on the scope of this type allylic substrates for TMSCl-promoted allylic alkylation of  $Et_2Zn$ , two different substrates **3** and **4** were synthesized from 1,3-diphenylprop-2-en-1-ol though silylation and allylic amidation.<sup>22</sup> However, when **3** or **4** was employed in this reaction, desired product **2a** was not detected. It may be due to low leaving abilities of the silicon-based group and benzamide group. Thus, treatment of TMSCl with allylic substrate **3** or **4** did not furnish the formation of a reactive intermediate, including  $\pi$ -allyl or carbenium intermediate (Scheme 2).



Scheme 2 The evaluation of TMSCI-mediated allylic substitution of TBDPS-protected allylic substrate and allylic amide.

As shown in Table 1, although the application of chiral phosphine ligands was unsuccessfully in the preparation of optically pure 1,3-diphenylpent-1-ene, further exploration led to the determination of TMSCl-promoted allylic alkylation of organozinc reagent for the facile preparation of 1,3-diarylpent-1-enes. To gain access to the asymmetric version of TMSCl-promoted allylic alkylation of Et<sub>2</sub>Zn with 1,3-diphenylallyl acetate, a chiral starting material **1a** with 39% ee was prepared by our synthetic method reported recently.<sup>20c</sup> The stereochemistry of allylic substitution was examined next. Unfortunately, as shown in Scheme 3, the desired product **2a** was obtained with no enantiomeric excess.

Based on these studies and previous findings on allylic alkylation of organometallic reagents,15 a mechanism of the TMSCl-promoted allylic alkylation of Et<sub>2</sub>Zn with 1,3-diarylallyl acetates could be proposed in Scheme 4. The initial step of present reaction can take place through possible activation of 1,3-diarylallyl acetate by Lewis acidic TMSCl, and the corresponding carbenium intermediate (II) was formed.<sup>23</sup> It was also supported by the reaction result of catalytic allylic alkylation of chiral 1,3-diphenylallyl acetate (39% ee) with diethylzinc reagent (Scheme 3). Then the attack Et<sub>2</sub>Zn to the corresponding carbenium intermediate (II) was occurred as rate determining step.<sup>23a</sup> In the final step, elimination of EtZnCl and subsequent reaction with TMSOAc from this nucleophilic addition gives the final product 2a and began new cycle of silicon-based Lewis acid catalyst. In the controlled experiment, we have ever used strong Lewis acidic ZnCl<sub>2</sub> as catalyst in this reaction that only trace



**Scheme 3** TMSCl-mediated allylic alkylation of chiral 1,3-diphenylallyl acetate (39% ee) with diethylzinc reagent.



 $\label{eq:scheme 4} \begin{array}{l} \mbox{Proposed mechanism for the allylic alkylation of $Et_2$Zn with $1,3$-diarylallyl acetate.} \end{array}$ 

product was obtained, which maybe support the formation of carbenium intermediate was promoted by powerful TMSCl.<sup>2</sup> Although the mechanism of the TMSCl-mediated allylic alkylation of 1,3-diaryl-2-propenyl acetates with diethylzinc reagent has not been well established, it is potentially very useful and simple synthetic methods because various 1,3-diaryl-2-propenyl acetates are efficiently transferred to 1,3-diarylpent-1-enes in good to excellent yields.

In summary, we have disclosed that chlorotrimethylsilane (TMSCl) was a highly efficient catalyst in the allylic alkylation of 1,3-diaryl-2-propenyl acetates with diethylzinc reagent. In this reaction, various 1,3-diaryl-2-propenyl acetates are efficiently transferred to 1,3-diarylpent-1-enes in good to excellent yields. A plausible mechanism for this reaction involves the formation of carbenium intermediate activated by silicon-based Lewis acid. Although allylic alkylation of allylic substrates with organometallic reagents has been reported with copper catalysis, this is the first example that the simple silicon-based Lewis acid, TMSCl, could be applied in the intermolecular allylic alkylation of organozinc reagent. Additionally, the use of organosilicon compounds as catalyst opens up the possibility of performing the reaction of organometallic compounds with silicon-based Lewis acids. Further investigations in this direction are currently underway.

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