

# Asymmetric Carbon-Carbon Bond Forming Reactions Catalysed by Metal(II) Bis(oxazoline) Complexes Immobilized using Supported Ionic Liquids

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**Abstract:** A series of bis(oxazoline) metal(II) complexes has been supported on silica and carbon supports by non-covalent immobilisation using an ionic liquid. The catalytic performance of these solids was compared for the enantioselective Diels–Alder reaction between *N*-acryloyloxazolidinone and cyclopentadiene and the Mukaiyama-aldol reaction between methyl pyruvate and 1-methoxy-1-trimethylsilyloxypropene. In both reactions the enantioselectivity was

strongly influenced by the choice of support displaying enantioselectivities (*ee* values) up to 40% higher than those conducted under homogeneous reaction conditions.

**Keywords:** asymmetric catalysis; Diels–Alder reaction; ionic liquids; Mukaiyama-aldol reaction; supported catalysts

## Introduction

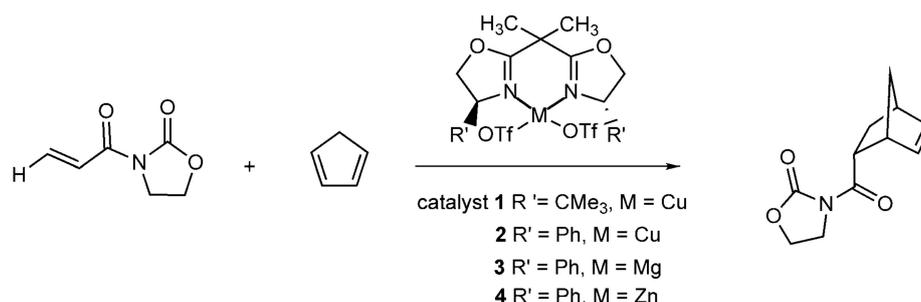
The development of heterogeneous catalysts able to promote enantioselective organic reactions is a field of growing interest. A major advantage of the use of a heterogeneous catalyst for reactions is the ease with which it can be recovered and subsequently reused. Some of the most widely used methods to immobilize expensive catalysts, such as those based on metal bis(oxazoline) complexes include covalent grafting of the ligand<sup>[1,2,3]</sup> or electrostatic immobilisation of the metal anion.<sup>[4]</sup> Although covalent grafting has been the more successful technique, this methodology often results in lower activity and selectivity compared with the analogous homogeneous reactions.<sup>[5]</sup> These changes may be due to modifications in the structure of the catalyst and the conformational preference of the chiral ligand; however, the nature of the support effect is not well understood.

In order to alleviate these problems, immobilisation without covalent bonding has been developed. This method utilises a thin film of ionic liquid containing

the homogeneous catalyst immobilised on a high surface area support material (Table 1). The resulting catalyst behaves similarly to those found under homogeneous reaction conditions due to the solvation of the metal complex by the ionic liquid with the reac-

**Table 1.** Surface area and pore volume for the silica and carbon supports.

Support/Ionic Liquid	Surface area [m <sup>2</sup> g <sup>-1</sup> ]	Average pore diameter [nm]	Pore volume [cm <sup>3</sup> g <sup>-1</sup> ]
SI1032	273	14.2	0.97
MCM-41	1011	2.5	1.07
SBA-15	995	3.4	1.29
Carbon Nano Tubes (CNT)	206	9.3	0.51
Graphite	11	5.4	0.02
Activated Carbon (AC)	767	2.7	0.59
Theoretical surface area of a monolayer of [C <sub>2</sub> mim][NTf <sub>2</sub> ]	540		



**Scheme 1.** The Diels–Alder reaction between *N*-acryloyloxazolidinone and cyclopentadiene using 10 mol% M(II) bis(oxazoline) catalysts.

tion taking place in the thin liquid film. *Supported ionic liquid phase* (SILP) catalysis has been the subject of a number of reviews<sup>[6]</sup> and has been reported to effectively immobilise homogeneous catalysts for use in hydroformylations,<sup>[7]</sup> carbonylations,<sup>[8]</sup> hydrogenations,<sup>[9]</sup> hydroaminations,<sup>[10]</sup> Heck and Suzuki–Miyaura reactions.<sup>[11]</sup>

Asymmetric metal-catalysed SILP-mediated reactions have been limited to hydrogenations,<sup>[12]</sup> oxidations,<sup>[13]</sup> cyclopropanations<sup>[14]</sup> and Mukaiyama-aldol<sup>[15]</sup> reactions. In all cases, immobilisation of the chiral complexes onto silica using an ionic liquid resulted in similar *ee* values and conversions compared with the same reactions conducted under homogeneous conditions. In contrast, moderate to poor *ee* values were observed for the bis(oxazoline)-Cu(II)-catalysed Diels–Alder reaction between *N*-acryloyloxazolidinone (**1**) and cyclopentadiene (Scheme 1) when immobilised onto silica using SILP technology despite high *ee* values being obtained under homogeneous conditions in the ionic liquid.<sup>[16]</sup> This paper reports on the general applicability of SILP metal-bis(oxazoline) catalysts for asymmetric Diels–Alder and Mukaiyama-aldol reactions.

## Results

### Diels–Alder Reaction

Table 2 summarises the results of a comparative study of the Diels–Alder reaction (Scheme 1) catalysed by a series of copper(II), magnesium(II) and zinc(II) triflate-based chiral Lewis acids (10 mol%) in homogeneous conditions at room temperature in dichloromethane, diethyl ether and [C<sub>2</sub>mim][NTf<sub>2</sub>]. A comparison with the competing racemic reaction conducted in the absence of catalyst was also undertaken. Interestingly in the molecular solvents, the non-metal-catalysed reaction showed significant conversions which, in some cases, were comparable with those of the metal-catalysed reactions. However, in the ionic liquid, the non-metal-catalysed reaction showed poor conversion probably due to the high rates of diene polymerisation. In [C<sub>2</sub>mim][NTf<sub>2</sub>], all the metal-catalysed reactions showed complete conversion within 1 min at room temperature; with *ee* values higher than the analogous reactions conducted in dichloromethane. Overall, the *ee* values found in diethyl ether were poor ( $\leq 22\%$ ) when compared with reactions performed in either dichloromethane or [C<sub>2</sub>mim][NTf<sub>2</sub>]. The increased enantioselection found in the ionic liquid is partly due to the fact that the

**Table 2.** Comparison of homogeneous Diels–Alder reaction conducted in dichloromethane, diethyl ether and [C<sub>2</sub>mim][NTf<sub>2</sub>]<sup>[a]</sup> using a series of 10 mol% Cu(II), Mg(II) and Zn(II) bis(oxazoline) catalysts. Enantioselectivities determined on the *endo* isomer.

Catalyst	CH <sub>2</sub> Cl <sub>2</sub> <sup>[b]</sup>			Et <sub>2</sub> O <sup>[b]</sup>			[C <sub>2</sub> mim][NTf <sub>2</sub> ] <sup>[c]</sup>		
	% conv.	% <i>endo</i>	% <i>ee</i>	% conv.	% <i>endo</i>	% <i>ee</i>	% conv.	% <i>endo</i>	% <i>ee</i>
–	56	87	–	40	88	–	12	86	–
1	78	88	70 ( <i>S</i> )	32	87	14 ( <i>S</i> )	100	89	90 ( <i>S</i> )
2	44	82	16 ( <i>S</i> )	38	80	15 ( <i>R</i> )	100	88	19 ( <i>R</i> )
3	61	80	50 ( <i>S</i> )	49	80	22 ( <i>S</i> )	100	92	80 ( <i>R</i> )
4	100 <sup>[c]</sup>	83	4 ( <i>S</i> )	44	80	7 ( <i>R</i> )	100	85	20 ( <i>R</i> )

<sup>[a]</sup> Reactions conducted at 25 °C in 5 cm<sup>3</sup> of molecular solvent and 2 cm<sup>3</sup> of [C<sub>2</sub>mim][NTf<sub>2</sub>].

<sup>[b]</sup> Conversions recorded after 15 min.

<sup>[c]</sup> Conversion recorded after 1 min.

**Table 3.** Comparison of the Lewis acid-catalysed Diels–Alder reaction under SILP reaction conditions in diethyl ether.

Entry	Support	Catalyst <b>1</b>		Catalyst <b>2</b>		Catalyst <b>3</b>		Catalyst <b>4</b>	
		% conv. <sup>[a,b]</sup>	% <i>ee</i> <sup>[c]</sup>						
1	SI1302	100	87 ( <i>S</i> )	100	8 ( <i>R</i> )	100	66 ( <i>R</i> )	100	22 ( <i>R</i> )
2	MCM-41	100	95 ( <i>S</i> )	100	16 ( <i>R</i> )	100	70 ( <i>R</i> )	100	53 ( <i>R</i> )
3	SBA-15	100	96 ( <i>S</i> )	100	17 ( <i>R</i> )	100	72 ( <i>R</i> )	100	32 ( <i>R</i> )
4	AC	94	0	29	0	66	51 ( <i>R</i> )	100	0
5	CNT	100	92 ( <i>S</i> )	100	3 ( <i>R</i> )	100	65 ( <i>R</i> )	100	37 ( <i>R</i> )
6	Graphite	100	85 ( <i>S</i> )	100	2 ( <i>R</i> )	100	25 ( <i>R</i> )	100	56 ( <i>R</i> )

<sup>[a]</sup> Conversion at 20°C recorded after 3 min.

<sup>[b]</sup> Determined by HPLC.

<sup>[c]</sup> *endo ee* determined by HPLC.

contribution from the uncatalysed racemic reaction is minimised. However, the exception to this is Zn(II) bis(oxazoline) catalyst **4** which also shows complete conversion after 1 min in both dichloromethane and ionic liquid. Therefore, the differences in *ee* observed with respect to the choice of solvent are not solely due to the competing background racemic reaction but could also be due to changes in the catalyst geometry. In ionic liquids, the high concentration of ions could encourage chelation of the anions to the metal centre which are known to dissociate to some degree in molecular solvents.<sup>[4e,17]</sup> This non-dissociation in ionic liquids would result in the reaction proceeding *via* an octahedral rather than a tetrahedral complex. Interestingly, for all the catalysts **2–4**, a reversal of configuration was found in dichloromethane compared with ionic liquid which would be consistent with a change in catalyst geometry. A similar concept was proposed by Carbone et al. to account for the switch in configuration for Diels–Alder reactions conducted in the presence of coordinating solvents.<sup>[18]</sup>

Immobilisation of catalysts **1–4** using the ionic liquid onto a range of silica and carbon supports was performed by wet impregnation. For the supported catalysts, the performance for the Diels–Alder reaction was studied using diethyl ether as the solvent due to its low rate of reaction for all the homogeneous catalysts. In addition, [C<sub>2</sub>mim][NTf<sub>2</sub>] has a low solubility in diethyl ether compared with dichloromethane and thus reducing the possibility of ionic liquid/catalyst leaching. Table 3 summarises the results for the SILP-catalysed Diels–Alder reaction. In all cases the configurations were identical to those obtained under homogeneous ionic liquid conditions. With the exception of activated carbon (AC), all SILP catalysts showed complete conversion after 3 min under the present conditions. SILP catalysts supported on AC showed lower activity and/or enantioselectivities for all catalysts examined. For most supports, the SILP catalysts **2** and **3** showed comparable or slightly lower *ee* values to those found under homogeneous ionic liquid conditions demonstrating the applicability of

SILPs to these systems. Small increases in *ee* of up to 6% were observed for catalyst **1** in the case of MCM-41, SBA-15 and CNT supported materials. In contrast, with the exception of AC supported SILP catalysts, Zn(II) bis(oxazoline) catalyst **4** showed significant increases in *ee* from 2–36% on immobilisation compared with the homogeneous ionic liquid reaction. Although the non-covalent immobilisation of bis(oxazoline) complexes, for example, by using supported ionic liquid phase methodologies, is believed to reduce conformational differences between the homogeneous and heterogeneous systems the results from Table 3 show that this is not always the case. Immobilisation can have beneficial effects on selectivity, for example, as well as providing a method to separate the catalyst and the reaction mixture easily. Therefore, the influence of the support on the reaction was further analysed by varying the support to ionic liquid mass ratio.

The results for the MCM-41 and graphite supported systems for catalysts **1–4** are shown in Table 4 and Table 5, respectively, for the Diels–Alder reaction as a function of the IL:support ratio used. Herein, the standard SILP preparation procedure was employed with 10 mol% catalyst with respect to the dieneophile loaded onto 0.05 g, 0.10 g and 0.20 g of each support using 0.15 g of ionic liquid, that is, 25 wt%, 40 wt% and 57 wt% support being used. For comparison, Table 4 and Table 5 also include the results from the biphasic IL–Et<sub>2</sub>O (0.15 g/5 cm<sup>3</sup>) reaction (0 wt%), i.e., where no support was present, and the catalyst was immobilised onto the support (0.1 g) in the absence of ionic liquid (denoted 100 wt%). With the exception of catalyst **2** which performed poorly throughout, the presence of an ionic liquid thin film was found to be crucial in obtaining high enantioselectivities and activity. In the absence of ionic liquid significant drops in *ee* were observed. Interestingly, the MCM-41 SILP based catalysts **1–3** showed comparable or little change in *ee* as a function of the ionic liquid loading between 0–57 wt%. For MCM-41 SILP catalyst **4**, all supported systems showed significantly higher *ee*

**Table 4.** Ionic liquid/MCM-41 support effects on catalysed Diels–Alder reaction under heterogeneous reaction conditions in diethyl ether.

Entry	Support [wt%]	Catalyst 1		Catalyst 2		Catalyst 3		Catalyst 4	
		% conv. <sup>[a,b]</sup>	% ee <sup>[c]</sup>						
1	0	100	90 ( <i>S</i> )	100	19 ( <i>R</i> )	100	80 ( <i>R</i> )	100	46 ( <i>R</i> )
2	25	100	92 ( <i>S</i> )	100	16 ( <i>R</i> )	100	77 ( <i>R</i> )	100	42 ( <i>R</i> )
3	40	100	95 ( <i>S</i> )	100	17 ( <i>R</i> )	100	70 ( <i>R</i> )	100	53 ( <i>R</i> )
4	57	100	90 ( <i>S</i> )	100	16 ( <i>R</i> )	100	68 ( <i>R</i> )	100	48 ( <i>R</i> )
5	100	83	66 ( <i>S</i> )	100	21 ( <i>R</i> )	100	37 ( <i>R</i> )	22	2 ( <i>S</i> )

<sup>[a]</sup> Conversion at 20 °C after 3 min.

<sup>[b]</sup> Determined by HPLC.

<sup>[c]</sup> *endo ee* and configuration determined by HPLC.

<sup>[d]</sup> 0.100 g of support used (??where??).

**Table 5.** Ionic liquid/graphite support effects on catalysed Diels–Alder reaction under heterogeneous reaction conditions in diethyl ether.

Entry	Support [wt%]	Catalyst 1		Catalyst 2		Catalyst 3		Catalyst 4	
		% conv. <sup>[a,b]</sup>	% ee <sup>[c]</sup>						
1	0	100	90 ( <i>S</i> )	100	19 ( <i>R</i> )	100	80 ( <i>R</i> )	100	46 ( <i>R</i> )
2	25	100	88 ( <i>S</i> )	100	12 ( <i>R</i> )	55	30 ( <i>S</i> )	100	43 ( <i>R</i> )
3	40	100	85 ( <i>S</i> )	100	17 ( <i>R</i> )	100	25 ( <i>S</i> )	100	56 ( <i>R</i> )
4	57	100	80 ( <i>S</i> )	100	18 ( <i>R</i> )	82	17 ( <i>S</i> )	100	12 ( <i>R</i> )
5	100 <sup>[d]</sup>	100	42 ( <i>S</i> )	100	21 ( <i>R</i> )	100	37 ( <i>S</i> )	22	2 ( <i>S</i> )

<sup>[a]</sup> Conversion at 20 °C after 3 min.

<sup>[b]</sup> Determined by HPLC.

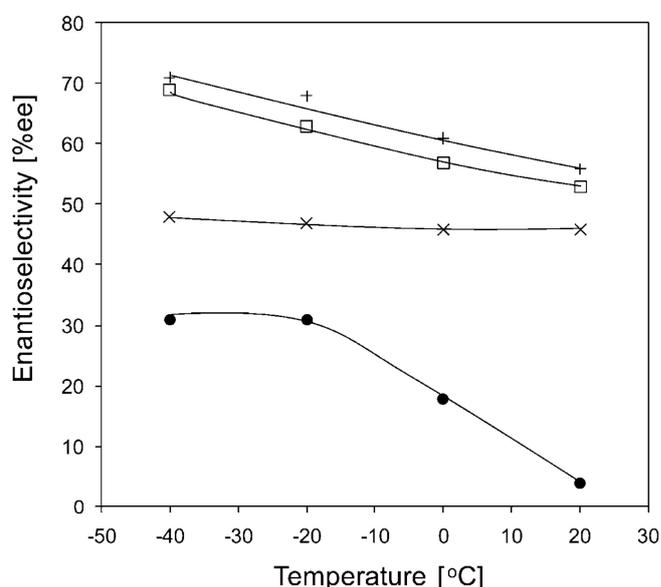
<sup>[c]</sup> *endo ee* and configuration determined by HPLC.

<sup>[d]</sup> 0.100 g of support used.

values compared with the biphasic ionic liquid–diethyl ether reaction. In contrast, graphite SILP based catalysts **3** and **4** showed large variations in *ee* with the IL:support ratio. For the MCM-41 support, the absence of IL will result in an increase in exposure of surface silanol groups increasing the rate of the silica-catalysed racemic reaction and a drop in *ee*. In the case of graphite the poor *ee* in the absence of IL maybe associated with other surface heteroatoms facilitating the non-metal-catalysed reaction.

The support to IL mass ratio has been shown to have a significant effect for other SILP catalysed reactions. Riisager et al. observed that the performance of the Rh-catalysed hydroformylation using propene was strongly linked to ionic liquid loading on the silica support.<sup>[8a]</sup> In addition, following optimisation of the acidic chloroaluminate SILP catalyst for a slurry phase Friedel–Crafts alkylation of cumene, a critical ionic liquid loading value was found to be necessary to overcome the neutralisation of the chloroaluminate with the surface silanol groups on the silica.<sup>[19]</sup>

The effect of temperature was also studied for catalyst **4** immobilised on MCM-41 and graphite SILP catalysts and compared with homogenous reactions conducted in IL and dichloromethane (Figure 1). Com-



**Figure 1.** Variation in *endo % ee* as a function of temperature on the for the Zn(II) bis(oxazoline)-catalysed homogeneous Diels–Alder reaction in dichloromethane (●) and the biphasic mixture [C<sub>2</sub>mim][NTf<sub>2</sub>] + diethyl ether (×) and the heterogeneous SILP catalysed Diels–Alder reaction supported on graphite (+) and supported on MCM-41 (□).

plete conversions were noted for all reactions run below room temperature after 3 min. Unsurprisingly, decreasing the temperature resulted in an increase in *ee* for both the SILP catalysts and the homogeneous reaction conducted in dichloromethane. At  $-40^{\circ}\text{C}$ , reactions using graphite and MCM-41 SILP systems resulted in *ee* values of 71% and 69%, respectively, which are significantly higher than that obtained when using dichloromethane (31% *ee* at  $-40^{\circ}\text{C}$ ). Surprisingly, lowering the temperature in the biphasic IL/ $\text{Et}_2\text{O}$  reaction showed no increase in *ee*. A homogeneous comparison of catalyst **1** in ionic liquid at low temperature was impossible due to the high viscosity of the reaction media; however, an *ee* of 25% was observed in the analogous homogeneous reaction conducted at  $0^{\circ}\text{C}$ .

Recycle experiments were also performed using catalysts **1** and **4** supported on MCM-41, SBA-15, CNT and graphite and monitored after 3 min conversion (Table 6). The use of MCM-41 maintained excellent conversion with a slight decrease in *ee* upon recycle. Although the carbon supported catalysts also showed excellent conversion upon recycle, a more marked decrease in *ee* was observed. Analysis of the supernatant and product following recycle showed that, for all the supports studied, the metal leaching was below 0.01 mol% by ICP per reaction and HPLC analysis showed that ligand leaching was below the detection limit. The decrease in enantioselectivity on recycle was, therefore, attributed to the build up of cyclopentadiene dimer<sup>[20]</sup> on the support surface as has been previously observed in other SILP catalysed Diels–Alder reactions.<sup>[16]</sup> This proposal was supported by the fact that the addition of cyclopentadiene dimer (1.5 molar equivalents with respect to substrate) to

the ethereal layer of fresh MCM-41 and CNT SILP catalyst **1** led to little change in the conversion but a marked decrease in *ee* from 95% to 8% for MCM-41 and from 85% to 3% *ee* for graphite supported SILP catalyst **1**.

Supported homogeneous catalysts have been reported previously for similar enantioselective Diels–Alder reactions. Rechavi and Lemaire<sup>[21,22]</sup> used a covalently-supported ligand based on IndaBOX for the same Diels–Alder reaction. Using this silica grafted ligand with  $\text{Cu}(\text{ClO}_4)_2$ , an *ee* of 92% at  $-78^{\circ}\text{C}$  was reached although the *ee* dropped to 81% at room temperature. O’Leary et al.<sup>[23]</sup> immobilised catalyst **2** onto chromatographic silica through electrostatic interactions and the same Diels–Alder reaction conducted at  $-50^{\circ}\text{C}$  resulted in an *ee* of 57% at 43% conversion. In contrast, Xiao and Li also studied electrostatic immobilisation of **2** onto silica where up to 93% *ee* at 83% conversion over 8 h was observed for a similar Diels–Alder reaction between cyclopentadiene and *N*-crotonoyloxazolidinone.<sup>[24]</sup> Recently, *ee* values greater than 95% were recorded with moderate conversion (30–60%) under homogeneous conditions for the same Diels–Alder reaction (Scheme 1) using a palladium-based BINAP catalyst and a range of ionic liquids.<sup>[25]</sup> While there has been extensive use of oxides as supports in enantioselective catalysis, with the exception of asymmetric keto ester hydrogenations involving a surface chiral modifier,<sup>[26]</sup> the use of carbon-based supports has been limited. Baleiz et al. anchored a chiral vanadium salen complex to various supports in order to develop a recyclable catalyst for the enantioselective cyanosilylation of benzaldehyde.<sup>[27]</sup> Therein, an 85% *ee* was obtained when the catalyst was immobilised onto silica, which compared favourably with the analogous homogeneous reactions 89% *ee*. In contrast, grafting the vanadium complex onto single walled nanotubes (SWNTs) resulted in a modest 66% *ee*. Even lower *ee* values (48%) were achieved when the complex was anchored onto activated carbon. These poor *ee* values were attributed to the significant amount of heteroatoms on the surface and, in the case of AC, ill-defined structure of the support. To the best of our knowledge the present MCM-41 or SBA-15 SILP system using catalyst **1** has the highest reported *ee* with complete conversion using a supported catalyst system for this particular Diels–Alder reaction and is able to achieve these results at room temperature. Moreover, for the Zn-based catalyst system, the increase in *ee* on immobilisation is the largest reported to date compared with that found in the homogeneous IL reaction. Furthermore, the use of a supported ionic liquid provides reasonable *ee* of up to 56% for Zn(II)-based catalysts of this type for the first time.

**Table 6.** Recycle of the Diels–Alder reaction catalysed by catalysts **1** and **4** conducted in diethyl ether under SILP reaction conditions at room temperature.

Catalyst	Support (0.1 g)	Cycle	% conv. <sup>[a,b]</sup>	% <i>ee</i> <sup>[c]</sup>
<b>1</b>	MCM-41	1	100	95
		2	100	93
		3	95	91
	Graphite	1	100	85
		2	100	77
		3	97	74
<b>4</b>	MCM-41	1	100	53
		2	100	51
		3	100	50
	Graphite	1	100	56
		2	100	55
		3	97	49

<sup>[a]</sup> Conversion recorded after 3 min at  $20^{\circ}\text{C}$ .

<sup>[b]</sup> Determined by HPLC.

<sup>[c]</sup> *endo ee* determined by HPLC.

**Table 7.** Comparison of Lewis acid catalysed Mukaiyama-aldol reaction under homogeneous and heterogeneous reaction conditions in different solvents.

Entry	Support	Solvent	Time [min]	Catalyst 1		Catalyst 2		Catalyst 4	
				% conv. <sup>[a,b]</sup>	% ee <sup>[c]</sup>	% conv. <sup>[a,b]</sup>	% ee <sup>[c]</sup>	% conv. <sup>[a,b]</sup>	% ee <sup>[c]</sup>
1	–	CH <sub>2</sub> Cl <sub>2</sub>	15	43 <sup>e</sup>	82 (S)	67	47 (S)	100	4 (S)
2	–	Et <sub>2</sub> O	15	32	80 (S)	8	61 (S)	44	7 (R)
3	–	IL	1	100	90 (S)	100	60 (S)	100	20 (R)
4	SI1302 <sup>[d]</sup>	IL/Et <sub>2</sub> O	5	100	86 (S)	100	73 (S)	100	21 (R)
5	MCM-41 <sup>[d]</sup>	IL/Et <sub>2</sub> O	5	100	88 (S)	100	71 (S)	100	24 (R)
6	SBA-15 <sup>[d]</sup>	IL/Et <sub>2</sub> O	5	100	89 (S)	100	73 (S)	100	23 (R)
7	AC <sup>[d]</sup>	IL/Et <sub>2</sub> O	5	100	53 (S)	100	70 (S)	0	
8	CNT <sup>[d]</sup>	IL/Et <sub>2</sub> O	5	100	86 (S)	100	68 (S)	100	25 (S)
9	Graphite <sup>[d]</sup>	IL/Et <sub>2</sub> O	5	100	87(S)	100	76 (S)	100	3 (S)

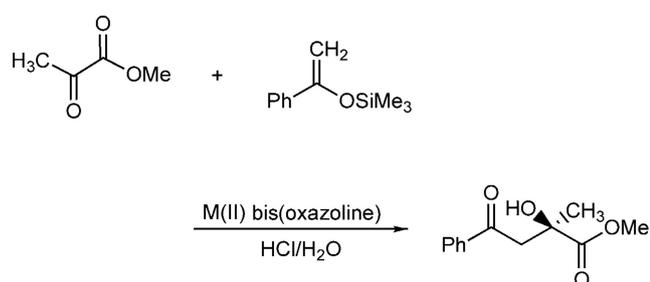
<sup>[a]</sup> Conversion at 20 °C.

<sup>[b]</sup> Determined by HPLC.

<sup>[c]</sup> ee determined by HPLC.

<sup>[d]</sup> Time taken for maximum conversion.

<sup>[e]</sup> 91% selectivity to the desired product.



**Scheme 2.** The Mukaiyama-aldol condensation reaction between methyl pyruvate and 1-phenyl-1-trimethylsiloxyethene using 10 mol% M(II) bis(oxazoline) catalysts.

## Mukaiyama-Aldol Reaction

Table 7 summarises the results of a comparative study of the Mukaiyama-aldol reaction (Scheme 2) catalyzed by a series of copper(II) and zinc(II) triflate based chiral Lewis acids (10 mol%) in homogeneous conditions at room temperature in various solvents (entries 1–3). For Cu catalysts **1** and **2**, and Zn catalyst **4**, increasing conversions followed the trend Et<sub>2</sub>O < CH<sub>2</sub>Cl<sub>2</sub> ≪ IL. It should be noted at this point that there was no reaction was observed for the analogous Mg(II) catalyst **3**.

Typically, complete conversions were achieved within 1 min at room temperature with catalysts **1**, **2** and **4** in the ionic liquid, whereas in dichloromethane and diethyl ether moderate to good conversions were only achieved after 15 min. Interestingly, all the catalysts gave a markedly higher ee in ionic liquid compared with dichloromethane and, in most cases, diethyl ether. Exceptionally, no improvement in ee was obtained on comparing the ionic liquid and diethyl ether for catalyst **2**.

Although catalyst **1** in ionic liquids produced the highest ee, a by-product, identified by <sup>1</sup>H NMR spectroscopy as 3-hydroxy-1,3-diphenylbutan-1-one, was consistently formed in ~9% yield. Interestingly, this by-product was only generated during reactions conducted in ionic liquid with catalyst **1** and there was no evidence for its formation with any other catalyst/solvent system. This by-product results from a Mukaiyama-aldol reaction between 1-phenyl-1-trimethylsiloxyethene and acetophenone generated *via* hydrolysis.

Reactions using catalysts **1**, **2** and **4** immobilised using the ionic liquid on silica and carbon supports were also performed. All silica supports showed complete conversion and 100% selectivity to the Mukaiyama-aldol product under SILP conditions for all catalysts. In contrast with the Diels–Alder reaction reported herein, a minimal change in ee was observed for the three catalysts. The conversions and ee values were more varied for the reaction catalysed by SILP catalysts supported on carbon. For example, with catalyst **1** only 53% ee was observed compared with 86% and 87% ee obtained with CNT and graphite. For the SILP based Zn catalyst on AC no conversion was noted and a poor ee was observed with graphite.

## Discussion

The large variation in ee upon change of oxide support or support to IL mass ratio may indicate that the confinement of the catalyst and/or reactants within the support is important.<sup>[28]</sup> Caplan et al. showed that surface confinement could be observed in the carbonyl-ene reaction between methylenecyclopentene and ethyl glyoxylate.<sup>[29]</sup> Therein, impregnation of a [Cu(BOX-Ph)]<sup>2+</sup> in a zeolite Y utilising the ‘ship in a bottle’ methodology showed a 93% ee compared with

57% *ee* obtained in the analogous homogeneous reaction. A similar enhancement in *ee* was also observed in the epoxidation of  $\alpha$ -methylstyrene. Encapsulation of an Mn(salen) complex in MCM-22 resulted in an increased *ee* of 91% in comparison with 51% *ee* obtained for the homogeneous reaction.<sup>[30]</sup> A surface effect was also observed for a laponite exchanged [Cu(BOX-Ph)][OTf]<sub>2</sub> catalyst in the Mukaiyama-aldol reaction between 2-(trimethylsilyloxy)furan and methyl 2-oxo-2-phenylacetate. The immobilisation resulted in a reversal of the *anti/syn* selectivity coupled with an increase in the *ee* from 16%, for the homogeneous reaction, to 90% *ee*, for the supported reaction.<sup>[31]</sup> Structuring within the support may also play a role even in graphite-based catalysts which have large layer spacing. These spaces could be filled by ionic liquid forming a highly ordered lamellar type structure.<sup>[32]</sup> In addition, imidazolium-based ionic liquids have been used to functionalise CNTs,<sup>[33,34]</sup> for example, which produce soft functional materials with assembled structures<sup>[35]</sup> and are suitable for enantioselective catalysis. Although a large change in *ee* was observed little change in *endo* selectivity was found on moving from molecular solvent to ionic liquid to SILP systems. The fact that the confinement of the catalyst within the pore has no significant effect on the *endo/exo* selectivity is surprising if the pore/ionic liquid structure is influencing the structure of the catalyst/reactant complex to the extent that the change in *ee* indicates.

As well as catalyst confinement, another possible explanation for the marked changes in *ee*, in particular the increased *ee* found for MCM-41, SBA-15 and CNT (Table 2, entries 7, 10, 12) compared with the homogeneous reaction (Table 2, entry 3), is the change in thermal conductivity obtained when these supports are combined with ionic liquids. Cooling is regularly used in enantioselective reactions to improve the *ee* and stabilize the catalyst in the most selective form. Therefore, for exothermic reactions, local heating can cause lower *ee* values and by increasing the thermal conductivity of the medium this effect may be reduced. Recent studies have shown that when CNTs are combined with ionic liquids, the thermal conductivity can increase by up to 37% compared with the pure ionic liquid and may contribute to the increased *ee* observed.<sup>[36]</sup> This effect has been observed in the gas-phase hydrogenation of 1,3-cyclohexadiene catalysed by Rh[(nbd)(PPh<sub>3</sub>)] [BF<sub>4</sub>]. Therein, the use carbon nanofibres compared with a range of oxides led to an improvement in selectivity.<sup>[37]</sup> This support effect was attributed to the support with the highest thermal conductivity providing the most effective sink for the energy released.

## Conclusions

For the majority of reaction systems studied, SILP catalysis was found to show significantly higher activities and *ee* values compared with the corresponding homogeneous reactions conducted in dichloromethane. Although the presence of an ionic liquid thin film was crucial in enabling high *ee* values to be obtained, little reduction in activity was found compared with the homogeneous reactions conducted in ionic liquid, thereby significantly reducing the amount of ionic liquid required. In some instances the non-covalent immobilisation of bis(oxazoline) complexes using SILP methodologies can reduce conformational differences between the homogeneous and heterogeneous systems. However, contrasting conversions and *ee* values were also observed demonstrating strong support effects. This support effect was found to be independent of catalyst, reaction or support/IL loading and highlights the complex nature of heterogeneous catalysis even with SILP systems.

## Experimental Section

Unless otherwise stated all reagents (*ex* Aldrich) were used as received. Diethyl ether and dichloromethane were dried and degassed prior to use. 1-Ethyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}imide ([C<sub>2</sub>mim][NTf<sub>2</sub>]) was prepared in house using standard literature methods<sup>[38]</sup> and, after drying for 24 h at 60°C under a high vacuum whilst stirring, was found to contain <0.13 wt% water, determined by Karl-Fischer analysis, and <10 ppm halide, determined by suppressed ion chromatography. Silica supports, MCM-41 and SBA-15, were synthesised using standard literature methods.<sup>[39,40]</sup> Silica supports, SI1302, SI10010 and SI10645, were obtained from GRACE Davison. All silica supports were calcined at 400°C prior to use. Carbon nanotubes were obtained from Bayer Material Science. Activated carbon and graphite were used as received from Aldrich. Table 1 summarises the BET surface areas and pore volumes for each of the supports used and the theoretical surface area for a monolayer of ionic liquid.

The *endo* selectivity and conversions for the Diels–Alder reaction were determined by <sup>1</sup>H NMR and HPLC and the *ee* values based on the *endo* isomer were calculated from the HPLC profile using a Chiralcel OD-H column (hexane:propan-2-ol, 90:10, flow rate 1 cm<sup>3</sup> min<sup>-1</sup>). The retention times of the *endo* enantiomers were major (*S*)-enantiomer, *t*<sub>R</sub> 25.5 min, and minor (*R*)-enantiomer, *t*<sub>R</sub> 28.6 min. All data from the Diels–Alder reactions were averaged over three runs.

The selectivity and conversions were for the Mukaiyama-aldol reactions were determined by <sup>1</sup>H NMR and HPLC and the *ee* values were calculated from the HPLC profile using a Chiralcel OD-H column (hexane:propan-2-ol, 96:4, flow rate 1 cm<sup>3</sup> min<sup>-1</sup>). The retention times of the *endo* enantiomers were major (*R*)-enantiomer, *t*<sub>R</sub> 20.1 min, and

minor (*S*)-enantiomer,  $t_R$  23.8 min. All data from the Mukaiyama-aldol reactions were averaged over three runs.

### General Procedure for the Homogeneous Lewis Acid-Catalyzed Diels–Alder or Mukaiyama–Aldol Reactions in Molecular Solvents

A flame-dried Schlenk flask was charged with ligand (0.011 mmol), metal(II) triflate (0.010 mmol, 10 mol%) and dichloromethane (5 cm<sup>3</sup>) and the resulting solution stirred at room temperature for 3 h to afford a clear green solution. Thereafter, *N*-acryloyloxazolidinone (0.0143 g, 0.1 mmol) was added followed by freshly distilled cyclopentadiene (50  $\mu$ L). For the Mukaiyama-aldol reaction, methyl pyruvate (0.0102 g, 0.1 mmol) followed by (0.0243 g, 0.12 mmol) of 1-phenyl-1-trimethylsiloxyethene. The reaction mixture was stirred at the desired temperature for the specified amount of time and then diluted with 5 cm<sup>3</sup> of 1:1 ethyl acetate:hexane.

Following concentration of the Diels–Alder reaction mixture, the crude adduct was dissolved in 5 cm<sup>3</sup> of diethyl ether and filtered through a small plug of silica gel to afford unpurified product and analysed directly.

Following concentration of the Mukaiyama-aldol reaction mixture, the residual oil was redissolved in THF (5 cm<sup>3</sup>) and the corresponding silyl-adduct was hydrolysed by stirring for 1 h using 2M HCl (10 cm<sup>3</sup>). The THF was removed under vacuum and the keto-alcohol was extracted from the aqueous by washing with Et<sub>2</sub>O (3  $\times$  5 cm<sup>3</sup>). The crude product was analysed directly.

For reactions conducted in diethyl ether, the catalyst was activated in dichloromethane which was then removed under vacuum followed by addition of diethyl ether (5 cm<sup>3</sup>) and stirred for 30 min after which the substrates were added. Both the Diels–Alder and Mukaiyama-aldol reactions were worked up as previously described to afford the unpurified products which were analysed directly.

### General Procedure for the Homogeneous Lewis Acid-Catalyzed Diels–Alder and Mukaiyama–Aldol Reactions in 1-Ethyl-3-methylimidazolium Bis[(trifluoromethyl)sulfonyl]imide ([C<sub>2</sub>mim][NTf<sub>2</sub>])

A flame-dried Schlenk flask was charged with ligand (0.011 mmol) and metal(II) triflate (0.010 mmol, 10 mol%). To this was added dichloromethane (5 cm<sup>3</sup>) and [C<sub>2</sub>mim][NTf<sub>2</sub>] (3.00 g, 2 cm<sup>3</sup>) and the resulting solution was stirred at room temperature for 5 min. Dichloromethane was then removed under high vacuum for one hour leaving the active catalyst dissolved in the ionic liquid. Thereafter, the Diels–Alder or Mukaiyama-aldol substrates were added. The resulting mixture was stirred at room temperature for the specified amount of time after which the ionic liquid was extracted with diethyl ether (3  $\times$  5 cm<sup>3</sup>) in air. Both the Diels–Alder and Mukaiyama-aldol reactions were worked up as previously described to afford the unpurified products which were analysed directly.

### General Procedure for the Liquid-Liquid Biphasic Lewis Acid-Catalyzed Diels–Alder Reactions in [C<sub>2</sub>mim][NTf<sub>2</sub>]/Diethyl Ether

A flame-dried Schlenk flask was charged with ligand (0.011 mmol) and metal(II) triflate (0.010 mmol, 10 mol%). To this was added dichloromethane (5 cm<sup>3</sup>) and [C<sub>2</sub>mim][NTf<sub>2</sub>] (0.15 g, 0.23 cm<sup>3</sup>) and the resulting solution stirred at room temperature for 5 min. Dichloromethane was then removed under high vacuum for one hour leaving the active catalyst dissolved in the ionic liquid. Thereafter, diethyl ether (5 cm<sup>3</sup>) was added followed by the Diels–Alder substrates. The resulting mixture was stirred at the desired temperature for the specified amount of time after which the diethyl ether was removed and the remaining ionic liquid was extracted with diethyl ether (2  $\times$  5 cm<sup>3</sup>) in air. The Diels–Alder products were worked up as previously described to afford the unpurified products which were analysed directly.

### General Procedure for the Heterogeneous Lewis Acid-Catalyzed Reactions in Diethyl Ether

A flame-dried Schlenk flask was charged with ligand (0.011 mmol), metal(II) triflate (0.010 mmol, 10 mol%) and dichloromethane (5 cm<sup>3</sup>) and the resulting solution stirred at room temperature for 3 h. To the resulting green solution was added support (0.1 g) and for catalysts using a supported ionic liquid film, 0.1 cm<sup>3</sup> of ionic liquid was also added. After stirring for 20 min, the dichloromethane was removed under vacuum for one hour to afford a free flowing powder after which the flask was charged with diethyl ether (5 cm<sup>3</sup>) followed by the addition of substrates. The reaction mixture was stirred at room temperature for the specified amount of time after which the silica was extracted with diethyl ether (3  $\times$  5 cm<sup>3</sup>) in air. Both the Diels–Alder and Mukaiyama-aldol reactions were worked up as previously described to afford the unpurified products which were analysed directly.

### Procedure for Recycle of the Heterogeneously Catalysed Reactions

The silica/ether slurry solution was left to settle in order to separate the phases after which the ethereal layer was removed by pipette and the silica was further extracted with diethyl ether (2  $\times$  5 cm<sup>3</sup>). After extraction fresh diethyl ether (5 cm<sup>3</sup>) was added to the silica and the resultant slurry was charged with further portions of either Diels–Alder or Mukaiyama-aldol substrates.

It should be noted that for reactions conducted in dichloromethane, prior to addition of reagents, the time required to form the active catalyst is critical to achieving reproducible catalyst performance. As reported by Evans et al.<sup>[41]</sup> a 3 h complexation time is typically required to achieve consistent results. In contrast, for reactions conducted in the ionic liquid, the catalyst performance does not depend on the metal-ligand complexation time and reproducible *ee* values and conversions were obtained after aging/complexation for only 5 min.

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