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Polymer-Supported Chiral-at-Metal Lewis Acid Catalysts

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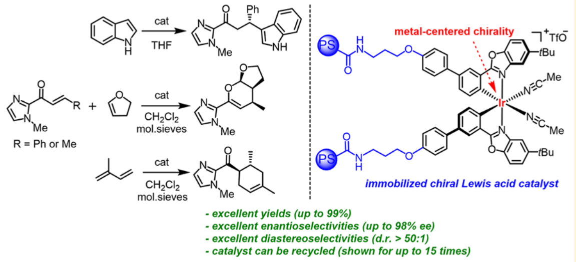
Supporting Information

ABSTRACT: The covalent immobilization of a chiral-at-metal bis-cyclometalated iridium(III) catalyst on a solid support is reported, and its catalytic activity has been investigated. As a catalyst immobilization strategy, a catalyst precursor was tethered to polystyrene macrobeads through an ester or amide linkage and subsequently converted to the immobilized active chiral Lewis acid by treatment with a Brønsted acid. The amide-linked catalyst displays high robustness and can be recycled multiple times without deterioration of enantioselectivity and only a gradual loss of catalytic activity. Chiral Lewis acid activity was demonstrated as an example for the enantioselective Friedel−Crafts alkylation of indole with an α,β-unsaturated 2-acyl imidazole and for the enantioselective Diels−Alder reactions of an α,β-unsaturated 2-acyl imidazole with 2,3-dihydrofuran or isoprene.



Immobilized chiral catalysts constitute an important repertoire for the asymmetric synthesis of chiral compounds.[1−3] In addition to the aspect of simplicity of catalyst recovery and recycling, solid-supported catalysts have also found increasing applications in continuous flow processes.[4] Many straightforward methods exist for the generation of solid-supported asymmetric catalysts.[5] In the case of metal-based asymmetric catalysts, one chiral or achiral ligand is typically immobilized and the complete catalyst finally assembled through the addition of metal salts or metal complex precursors. The direct immobilization of entire chiral organometallic catalysts or related precatalysts is less established. Several groups formed polymer-supported chiral organometallic catalysts by copolymerization with metal-containing monomers.[6] Davies reported the straightforward and general immobilization of chiral dirhodium catalysts by direct coordination of the dirhodium catalysts through one of their vacant axial coordination sites to a pyridine-functionalized resin.[7] Nomura and Richards synthesized a solid-supported chiral palladacycle through ligand exchange with a triphenylphosphine-funcationalized resin.[8] Here, we use a strategy in which a catalyst precursor is immobilized on polystyrene[9] through a covalent tether and subsequently converted to the immobilized active chiral Lewis acid by treatment with a Brønsted acid.

We have recently introduced a new class of chiral-at-metal Lewis acid catalysts in which an iridium(III)[10] or rhodium(III)[11] is bis-cyclometalated with 5-*tert*-butyl-2-phenylbenzoxazole or the corresponding benzothiazole derivatives in addition to two exchange-labile acetonitriles. Despite all ligands being achiral, the complexes can adopt a metal-centered Λ (left-handed propeller) or Δ configuration (right-handed propeller). We and others have shown that such complexes are excellent chiral catalysts for a variety of transformations, ranging from enolate chemistry, conjugate additions, and asymmetric transfer hydrogenations to asymmetric photoredox reactions.[10−12] Here, we report the immobilization of one member of this class of chiral-at-metal catalysts on polystyrene (Figure 1) through an ester or amide linkage, and we demonstrate for the enantioselective Friedel−Crafts alkylation of indole with an α,β-unsaturated 2-acyl imidazole and for the enantioselective Diels−Alder reactions of an α,β-unsaturated 2-acyl imidazole with 2,3-dihydrofuran or isoprene that these immobilized catalysts retain a high catalytic activity with excellent stereoselectivities and can be recycled multiple times.

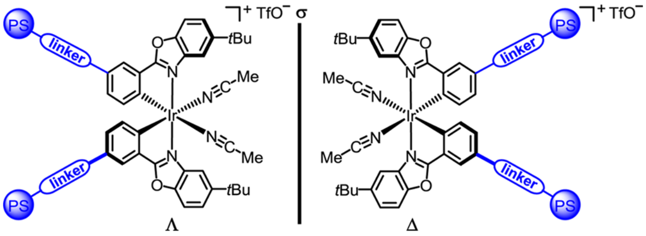


Figure 1. Polymer-supported chiral-only-at-metal iridium Lewis acid catalysts synthesized and investigated in this study (Λ and Δ enantiomers are shown).

Synthesis and Characterization of the Resin-Bound Catalysts. The synthesis is shown in Scheme 1. Accordingly, $IrCl_3 \cdot 3H_2O$ was bis-cyclometalated with 5-*tert*-butyl(3-bromophenyl)phenylbenzoxazole (**1**) followed by a reaction with the chiral salicylthiazoline (*S*)-**2**[10a,13] to generate the two diastereomers Λ-(*S*)-**Ir1** and Δ-(*S*)-**Ir1** as single enantiomers which were resolved by regular silica gel chromatography. The absolute metal-centered configuration was assigned by CD spectroscopy through comparison with published nonbromi-

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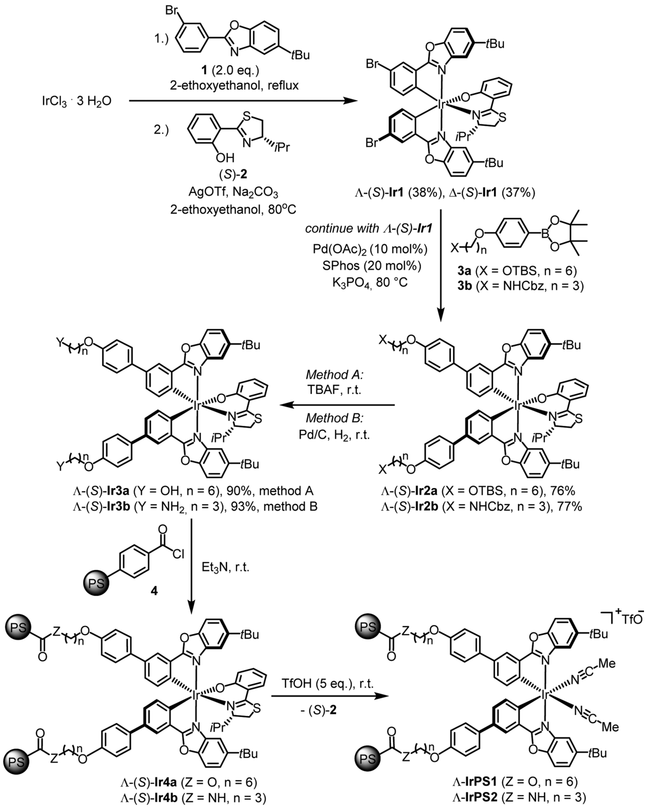
Scheme 1. Synthesis of Polymer-Supported Catalysts[a]



[a] Abbreviations: TBS = *tert*-butyldimethylsilyl, Cbz = *N*-carboxybenzyl.

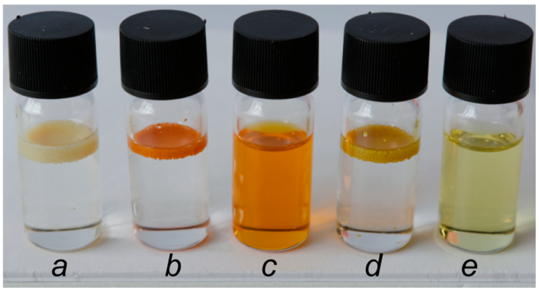
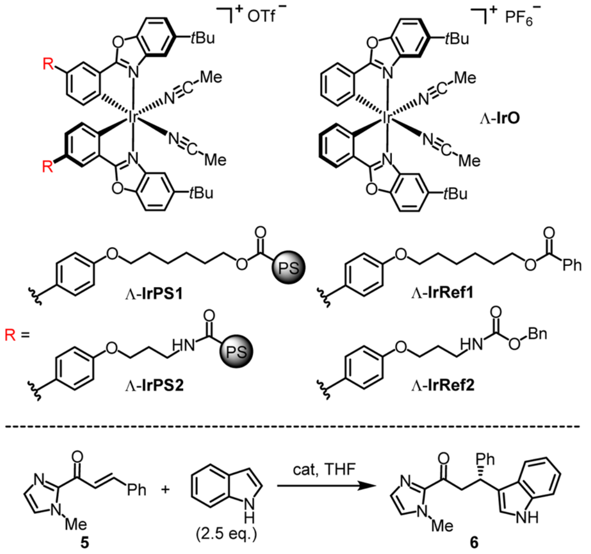


Figure 2. Visualization of iridium complex immobilization on polystyrene: (a) benzoyl chloride polystyrene resin (**4**); (b) resin-bound Λ-(*S*)-**Ir4a**; (c) homogeneous complex Λ-(*S*)-**Ir2a**; (d) resin-bound catalyst Λ-**IrPS1**; (e) homogeneous catalyst Λ-**IrRef1**. All samples are in CH_2Cl_2.

nated analogues.[10a] In the subsequent key step, the individual brominated diastereomers were cross-coupled with suitable boronic esters in order to introduce the linker unit.[14,15] For example, Λ-(*S*)-**Ir1** was reacted with the boronic ester **3a** or **3b** in the presence of $Pd(OAc)_2$, the ligand SPhos[16] (20 mol %), and K_3PO_4 at 80 °C to afford the complex Λ-(*S*)-**Ir2a** (76%) or Λ-(*S*)-**Ir2b** (77%), respectively. Next, protecting groups were removed to provide Λ-(*S*)-**Ir3a** (TBS removal with TBAF, 90%) containing a primary alcohol and Λ-(*S*)-**Ir3b** (Cbz removal with H_2 and Pd/C, 93%) containing a primary amine. Initially, Merrifield resin[5] with benzyl chloride as the reactive group was attempted for application to our system but the harsh basic conditions required for efficient attachment proved incompatible with our Ir(III) complexes. Therefore, these complexes were reacted with a functionalized polystyrene resin (**4**) (macroporous 200−400 μm) containing benzoyl chloride (0.5−2.0 mmol/g)[17] as the reactive functional group in the presence of Et_3N to afford the polymer-supported ester-linked complex Λ-(*S*)-**Ir4a** and the polymer-supported amide-linked complex Λ-(*S*)-**Ir4b**. The conversion was followed by monitoring the consumption of Λ-(*S*)-**Ir3a** or Λ-(*S*)-**Ir3b** using mesitylene as an internal standard (see the Supporting Information for more details). Loadings of 0.043 mmol/g were reached for the ester-linked complex Λ-(*S*)-**Ir4a** and 0.162 mmol/g for the amide-linked complex Λ-(*S*)-**Ir4b**. Furthermore, the immobilization was indicated visually by a change in color of the resin (Figure 2). Finally, the polystyrene-tethered active catalysts Λ-**IrPS1** and Λ-**IrPS2** were generated by replacing the auxiliary ligand with two acetonitriles upon treatment with trifluoromethanesulfonic acid in $MeCN/CH_2Cl_2$ (1/1) for 2 h, filtered, washed, and dried. The released salicylthiazoline (*S*)-**2** was reisolated in 93% and 95% yields for Λ-**IrPS1** and Λ-**IrPS2**, respectively.[10d]

Enantioselective Catalysis and Catalyst Recycling. The catalytic activities of the polymer-supported catalysts Λ-**IrPS1** and Λ-**IrPS2** were evaluated using the Friedel−Crafts alkylation of indole with the α,β-unsaturated 2-acyl imidazole **5** (Table 1).

Table 1. Enantioselective Friedel−Crafts Addition of Indole to *α*,*β*-Unsaturated 2-Acyl Imidazole 5 Catalyzed by Homogeneous and Immobilized Ir(III) Catalysts[a]



entry	catalyst[b]	*T* (°C)	*t* (h)	conversn (%)[c]	ee (%)[d]
1	Λ-**IrO** (1.0)	room temp	16	98	93 (*R*)
2	Λ-**IrPS1** (1.0)	room temp	72	70	97 (*R*)
3[e]	Λ-**IrPS1** (3.0)	40	48	91	96 (*R*)
4	Λ-**IrPS2** (1.0)	room temp	72	75	97 (*R*)
5	Λ-**IrPS2** (3.0)	40	48	>99	95 (*R*)
6	Δ-**IrPS2** (1.0)	room temp	72	76	97 (*S*)
7	Λ-**IrRef1** (1.0)	room temp	44	>99	98 (*R*)
8	Λ-**IrRef2** (1.0)	room temp	41	>99	97 (*R*)

[a] Reaction conditions unless specified otherwise: imidazole **5** (0.15 mmol), indole (0.38 mmol), and catalyst (1.0 or 3.0 mol %) in 0.2 mL of THF were stirred at the indicated temperature under an atmosphere of nitrogen. [b] Catalyst loadings provided in parentheses (mol %). [c] Conversion determined by ^1H NMR. [d] Determined by chiral HPLC analysis. [e] Increased reaction volume of 0.4 mL of THF was used in order to immerse all of the resin.

Interestingly, in comparison to the homogeneous catalyst Λ-**IrO**,[10a] the immobilized catalysts Λ-**IrPS1** and Λ-**IrPS2** provide higher enantioselectivities while featuring lower catalytic activities in comparison to the homogeneous catalysts. The slightly lower conversion observed for Λ-**IrPS1** (entry 3) in comparison to Λ-**IrPS2** (entry 5) can be attributed to the lower concentration required for immersing all of the resin Λ-**IrPS1**. Overall, the somewhat reduced catalytic activity of the immobilized catalysts in comparison to their homogeneous counterparts can be compensated by increasing the catalyst loading, extending the reaction time, and raising the temperature to 40 °C (entries 1−5). As expected, the mirror-image resin-bound catalyst Δ-**IrPS2** provides almost identical results but with opposite enantioselectivity (entry 6). Importantly, the higher enantioselectivities observed for Λ-**IrPS1**, Λ-**IrPS2**, and Δ-**IrPS2** can be traced back to the linker itself, as demonstrated for the homogeneous reference catalysts Λ-**IrRef1** and Λ-**IrRef2**, which are modified with analogous linker units (entries 7 and 8).

Finally, we investigated catalyst recycling with the polystyrene-immobilized complexes Λ-**IrPS1** and Λ-**IrPS2**. Table 2 reveals that Λ-**IrPS1** decreases its catalytic activity for the Friedel−Crafts reaction of indole with imidazole **5** to around 50% after four recyclings during the fifth run. In contrast, Λ-**IrPS2** retains 95% of its catalytic activity during the fifth run. This might be attributed to the more robust amide linkage in Λ-**IrPS2** in comparison to the more hydrolytically labile ester linkage in Λ-**IrPS1**. Interestingly, the catalysts can be recycled and run multiple times (for at least 15 cycles) without affecting enantioselectivities for the Friedel−Crafts reaction of indole with imidazole **5**. Overall, these results demonstrate that the amide-linked catalyst Λ-**IrPS2** is superior to Λ-**IrPS1**. Even after 10 further runs, enantioselectivity for the Friedel−Crafts reaction of indole with imidazole **5** is unchanged at 96% ee; when the reaction temperature in increased to 50 °C, full conversion is reached after 72 h (see the Supporting Information for details).

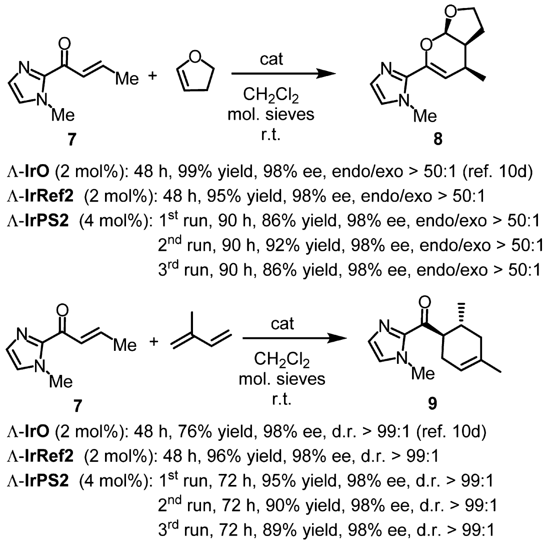
Table 2. Recycling Experiments with Immobilized Catalysts for Enantioselective Friedel−Crafts Alkylation[a]

	Λ-IrPS1		Λ-IrPS2	
	conversn (%)[b]	ee (%)[c]	conversn (%)[b]	ee (%)[c]
1st run	91	96	>99	95
2nd run	92	96	>99	96
3rd run	80	97	>99	96
4th run	47 (88)[d]	96 (96)[d]	>99	96
5th run	47 (80)[e]	96 (96)[e]	95	96
15th run	n.a.	n.a.	>99[f]	96[f]

[a] Reaction conditions: imidazole **5** (0.15 mmol), indole (0.38 mmol), and catalyst (3 mol %) in 0.2 mL (Λ-**IrPS2**) or 0.4 mL of THF (Λ-**IrPS1**) were stirred 48 h at 40 °C under nitrogen. n.a. = not applied. [b] Conversion determined by ^{1}H NMR. [c] Determined by chiral HPLC analysis. [d] Conversion and ee after 96 h are given in parentheses. [e] Conversion and ee after 112 h are given in parentheses. [f] Conversion and ee after 72 h at 50 °C.

Finally, we investigated the enantioselective Diels−Alder reactions of an *α*,*β*-unsaturated 2-acyl imidazole **7** with 2,3-dihydrofuran or isoprene catalyzed by the immobilized catalyst Λ-**IrPS2** (Scheme 2). Accordingly, the reaction of **7** with 2,3-dihydrofuran catalyzed by 4 mol % of Λ-**IrPS2** provided the formation of the dihydropyran **8** in a yield of 86% and with excellent enantio- (98% ee) and diastereoselectivities (endo/exo > 50/1). Furthermore, the Diels−Alder reaction of 2-acyl imidazole **7** with isoprene provided the desired product **9** with high enantio- and diastereoselectivity. Overall, the immobilized catalyst Λ-**IrPS2** provides the same enantio- and diastereoselectivity in comparison to the homogeneous counterparts Λ-**IrO** and Λ-**IrRef2** but needs to be used at twice the catalyst loading (4 versus 2 mol %). We also demonstrated that the immobilized catalyst Λ-**IrPS2** could be recycled and used for two additional runs without loss of catalytic activity and enantioselectivity for both reactions.

Scheme 2. Enantioselective Diels−Alder Reactions of *α*,*β*-Unsaturated 2-Acyl Imidazole 7 with 2,3-Dihydrofuran or Isoprene Catalyzed by Homogeneous and Immobilized Catalysts



Λ-**IrO** (2 mol%): 48 h, 99% yield, 98% ee, endo/exo > 50:1 (ref. 10d)
Λ-**IrRef2** (2 mol%): 48 h, 95% yield, 98% ee, endo/exo > 50:1
Λ-**IrPS2** (4 mol%): 1st run, 90 h, 86% yield, 98% ee, endo/exo > 50:1
2nd run, 90 h, 92% yield, 98% ee, endo/exo > 50:1
3rd run, 90 h, 86% yield, 98% ee, endo/exo > 50:1

Λ-**IrO** (2 mol%): 48 h, 76% yield, 98% ee, d.r. > 99:1 (ref. 10d)
Λ-**IrRef2** (2 mol%): 48 h, 96% yield, 98% ee, d.r. > 99:1
Λ-**IrPS2** (4 mol%): 1st run, 72 h, 95% yield, 98% ee, d.r. > 99:1
2nd run, 72 h, 90% yield, 98% ee, d.r. > 99:1
3rd run, 72 h, 89% yield, 98% ee, d.r. > 99:1

In conclusion, we here reported the successful covalent immobilization of a chiral-at-metal iridium Lewis acid catalyst on a polystyrene resin through two different linkers. In particular, the amide-linked catalyst is very robust and can be recycled multiple times without affecting enantioselectivity for the Friedel−Crafts reaction of indole with an *α*,*β*-unsaturated 2-acyl imidazole and for the enantioselective Diels−Alder reactions of an *α*,*β*-unsaturated 2-acyl imidazole with 2,3-dihydrofuran and isoprene. A somewhat reduced catalytic activity in comparison to the homogeneous catalyst can be compensated by increasing the reaction temperature, reaction time, and catalyst loading. Interestingly, it was also found that the linker itself leads to an increase in enantioselectivity, revealing that the functionalization of the cyclometalated ligand at the phenyl moiety provides opportunities to affect the asymmetric induction. This work will pave the way for using chiral-at-metal Lewis acid catalysts in flow chemistry applications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00016.

Synthetic details, analytical data, HPLC traces, and NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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