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Asymmetric Catalysis |*Hot Paper*|

Immobilized Catalysts for Iridium-Catalyzed Allylic Amination: Rate Enhancement by Immobilization

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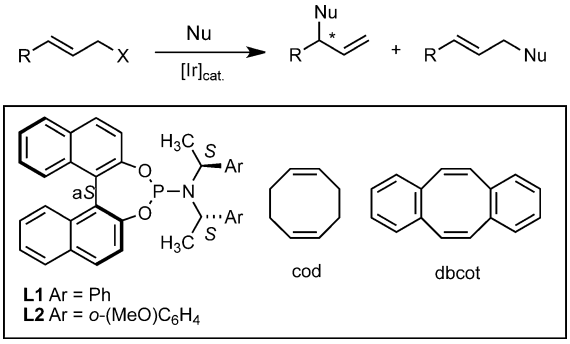
Dedicated to Professor Lixin Dai, Shanghai Institute of Organic Chemistry, on the occasion of his 90th birthday

Abstract: The first immobilized catalyst for Ir-catalyzed asymmetric allylic aminations is described. The catalyst is a cationic (π-allyl)Ir complex bound by cation exchange to an anionic silica gel support. Preparation of the catalyst is facile, and the supported catalyst displayed considerably enhanced activity compared with the parent homogeneous catalyst. Up to 43 consecutive amination runs were possible in recycling experiments.

Introduction

The Ir-catalyzed asymmetric allylic substitution (Scheme 1) has been developed to a useful level of applicability.[1] The current best catalysts are prepared from complexes [{Ir(cod)Cl}$_2$] (cod = cycloocta-1,5-diene) or [{Ir(dbcot)Cl}$_2$] (dbcot = dibenzocyclooctatetraene) by reaction with phosphoramidites, for example **L1**[2] or **L2**.[3] Upon treatment with base, cyclometallation[4] is effected to give complexes that are schematically described in Scheme 2.[1c,5] Of these, the (π-allyl)Ir complexes **C1**–**C3** are particularly convenient single-species catalysts that have mainly been employed in the work leading to this article.

Unfortunately, current catalysts are not very active; typically, 1–4 mol% catalyst is required and catalyst recovery has not been explored systematically.[6] So far, attempts to reduce the catalyst loading were only partially successful.[7] In our own work, a limit of 0.4 mol% was reached for alkylations[8] and aminations;[9] however, reaction times of more than 100 h were required at this loading. In contrast to commonly employed procedures in which the nucleophile is used in excess, during the development of an allylic esterification it was necessary to employ an excess of the allylic component;[10] surprisingly, reactions could be completed within a few hours, even with 0.2 mol% catalyst. Nevertheless, in the case of a precious-metal catalyst, loading of less than 0.1 mol% appears desirable for applications, even on a multigram scale. An obvious way to meet this demand is catalyst immobilization. Herein, we are pleased to report the development of the first immobilized Ir catalyst for allylic aminations. Allylic aminations have found numerous applications in syntheses of biologically active compounds, in particular alkaloids.[11]



Scheme 1. Iridium-catalyzed allylic substitution.

Immobilization often yields a catalyst with low activity, and special efforts and additional steps in ligand synthesis, as well as specific expertise in polymer chemistry, are required. These disadvantages are offset by facile recovery of the catalyst upon multiple uses.[12] In the area of asymmetric allylic substitution, a considerable body of work with Pd catalysts has been assembled by the groups of Uozumi and, earlier, Hayashi.[13] These authors developed chiral phosphanes bound to amphiphilic polymers as catalysts, which gave rise to very high enantioselectivity with water as solvent at a typical catalyst loading of 5 mol%. However, the number of consecutive runs with a given catalyst was reported as only three.[13d] Pd complexes were formed in situ on the polymer. Characterization of such catalysts is very difficult. In work by our own group with a similar approach, using polyethyleneglycol-bound PHOX ligands, we were discouraged by the fact that the maximum number of consecutive runs was only six, and deactivation of the catalyst could not be prevented.[14]

Our approach to the development of a supported catalyst for the Ir-catalyzed allylic substitution was guided by the mechanism of the allylic substitution; the presently accepted catalytic cycle is summarized in Scheme 2.[1c,15] Of the various intermediates, cationic (π-allyl)Ir complexes **C** are excellent catalysts and are readily available.[16] This suggested immobiliza-

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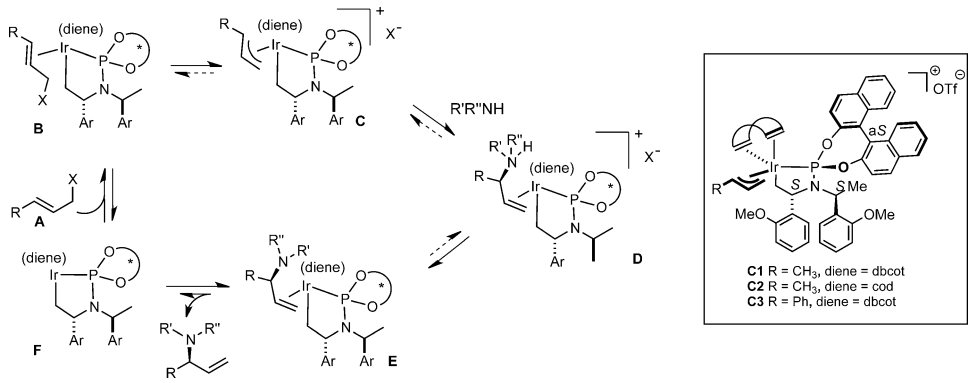


Scheme 2. Catalytic cycle of an allylic amination using a cationic (π-allyl)Ir complex (**C**) as catalyst. Grey areas: species bound to a cation exchanger; **C1**–**C3**: complexes used in the present investigation.

tion on a cation exchange material, which leads to the following scenario (cf. Scheme 2).

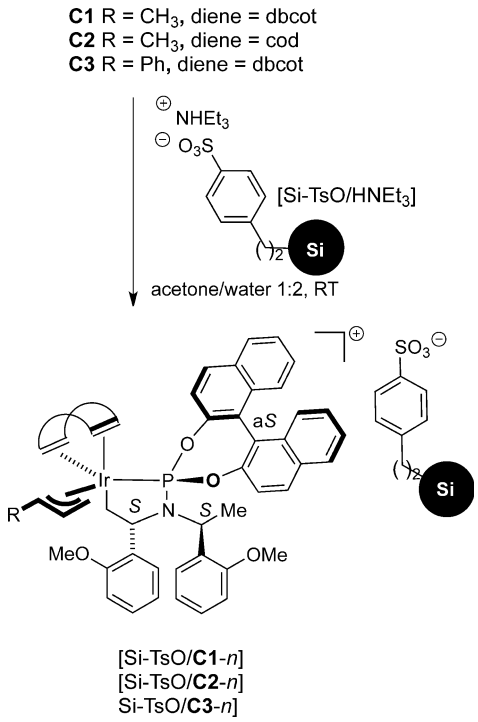
Complex **C** is loaded on to the solid support by ion exchange; reaction with a nucleophile is expected to yield charged olefin complex **D**, which is deprotonated to give uncharged complex **E**, which can leave the solid support and dissociate into product and the putative 16 valence-electron complex **F**. The reaction of the latter complex with the allylic substrate is fast and reversible.[1c,17] The concentration of **F** is small, and this species has so far not been observed experimentally. Complex **E** constitutes the resting state of the reaction, if the amine nucleophile is used in excess as in usually employed procedures. Our approach requires binding of a cationic catalytic species after completion of the reaction. Accordingly, an excess of the allylic component is required to form (π-allyl)Ir complex **C**, which has been found by NMR investigation to be a resting state if the allylic component is used in excess.[15,16] Note that the charged complex **D** is not suitable for capture because it is prone to react back to complex **C**; that is, it gives rise to equilibration that finally yields the linear allylation product.

Work with solid supported catalysts likely requires manipulations under air. For this reason, we chose catalysts containing dbcot as ancillary ligand (Scheme 2). These are known to allow allylic substitutions in air, which is not possible with the corresponding cod complexes.[18]

Results and Discussion

Preparation of the immobilized catalysts

The choice of the support was inspired by the recent work of Borrè et al. on ring closing metathesis;[19] the authors used a pyridinium-tagged Ru catalyst in conjunction with a silica gel-based cation exchanger containing carbon-bound *p*-ethylphenylsulfonic acid (Si-TsOH "Biotage", 0.59 mmol g^{-1}). We also used this ion exchanger and first prepared various alkali and ammonium salts, which were reacted with the Ir complexes. Optimal results were obtained with a triethylammonium salt, which is easily available by treatment of the ion exchanger with triethylamine. Loading of the Ir complex was performed by suspending the ammonium salt in a solution of a crotyl complex **C1**–**3**, in acetone (Scheme 3); upon addition of water, the silica gel became yellow within a few minutes, and the previously light-yellow supernatant became colorless. The amount of bound Ir complex was assessed by determining the amount of crotyl complex recovered from the supernatant. Samples of silica gel with contents of 10–70 μmol crotyl complex per gram were prepared.

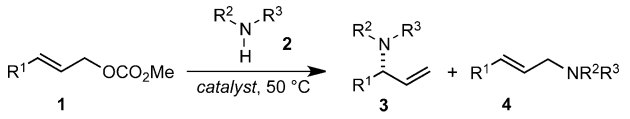


Scheme 3. Preparation of supported catalysts by reaction of (π-allyl)Ir complexes with an ammonium salt of a silica gel bound *p*-ethylbenzenesulfonic acid (*n* = amount of complex per gram of supported catalyst).

Determination of the content of Ir complex on the support after its use as catalyst was carried out by cation exchange, which involved treatment of the supported catalyst with a solution of LiOTf, followed by quantitative analysis of liberated **C1**–**C3** by NMR spectroscopic analysis. Compared with methods based on the determination of metal content, for example by ICP-MS,[19] the recovery of the Ir complex is advantageous because deterioration, for example by oxidation at phosphorus, is taken into account.

Allylic amination under homogeneous conditions

A representative set of reactants were chosen for testing (Scheme 4). Results obtained under standard reaction conditions, using either 2.32 or 0.42 mol% catalyst, are presented in Table 1. Reaction times of 1–3 h were required with 2.32 mol% catalyst; reaction times at low loading of 0.42 mol% were markedly longer (38–55 h). Selectivities were also lower than obtained at the higher catalyst loading, except for the regioselectivity of the reaction with benzylamine (entries 7 and 8 in Table 1). The reactions did not furnish useful results with 0.1 mol% catalyst. The influence of the solvent was tested with isopropanol, tetrahydrofuran (THF), and toluene at catalyst loading of 0.42 mol% (entries 2–4 in Table 1). Though there were no significant differences in reactions times, the enantiomeric excesses of the product were lower in toluene and isopropanol than in THF. Notably, when aniline was used as nucleophile (entries 9 and 10 in Table 1) it was necessary to add a base (NEt_3) that was stronger than aniline to avoid reducing the regioselectivity through rearrangement of the branched product **3** into the linear isomer **4**.[20] This procedure worked well in conjunction with 2.32 mol% catalyst; however, it failed with a loading of 0.42 mol%, which induced preferential formation of the linear isomer (branched/linear (b/l) ratio 15:85).



1 a R^1 = Ph, **b** R^1 = Me, **c** R^1 = CH_2OCPh_3
2 a R^2 = Bn, R^3 = Me, **b** R^2 = Bn, R^3 = H, **c** R^2 = Ph, R^3 = H, **d** R^2R^3NH = benzimidazole, **e** R^2 = R^3 = Bn
3,4 aa R^1 = Ph R^2 = Bn, R^3 = Me, **ba** R^1 = Me, R^2 = Bn, R^3 = Me, **ab** R^1 = Ph R^2 = Bn, R^3 = H, **ac** R^1 = R^2 = Ph, R^3 = H, **ad** R^1 = Ph, R^2R^3NH = benzimidazole, **ae** R^1 = Ph, R^2 = R^3 = Bn, **ce** R^1 = CH_2OCPh_3, R^2 = Bn, R^3 = Bn

Scheme 4. Ir-catalyzed allylic aminations.

Table 1. Allylic aminations according to Scheme 4 under homogeneous conditions: influence of catalyst loading.[a] Bn = benzyl, Tr = trityl.

Entry	R^1 of **1**	**2**	Solvent	*ent*-**C1** [mol%]	*t* [h]	Yield [%][b]	b/l[c]	*ee* [%][d]
1	Ph	MeN(H)Bn	THF	2.32	1.2	89	93:7	96
2	Ph	MeN(H)Bn	THF	0.42	38	63	93:7	98
3	Ph	MeN(H)Bn	toluene	0.42	41	65	95:5	80
4	Ph	MeN(H)Bn	*i*PrOH	0.42	38	68	94:6	82
5	Me	MeN(H)Bn	THF	2.32	1.3	88	96:4	91[e]
6	Me	MeN(H)Bn	THF	0.42	47	76	90:10	72[e]
7	Ph	H_2NCH_2Ph	THF	2.32	1.1	80	79:21	94
8	Ph	H_2NCH_2Ph	THF	0.42	49	80	97:3	74
9	Ph	H_2NPh	THF[f]	2.32	1.6	86	94:6	97
10	Ph	H_2NPh	THF[f]	0.42	43	<17[g]	15:85	94
11	Ph	benzimidazole	THF	2.32	3	89	98:2	97
12	Ph	benzimidazole	THF	0.42	55	35	97:3	93
13	Ph	$HNBn_2$	THF	2.32	1.9	88	97:3	98
14	Ph	$HNBn_2$	THF	0.42	53	62	70:30	97
15	CH_2OTr	$HNBn_2$	THF	2.32	2	75	95:5	97
16	CH_2OTr	$HNBn_2$	THF	0.42	55	66	69:31	78

[a] Reaction conditions: carbonate **1** (0.65 mmol), nucleophile **2** (0.5 mmol), catalyst, solvent (0.6 mL), stirred, 50 °C. [b] Isolated yield of the branched product **3**. [c] Branched/linear ratio, determined by ^1H NMR spectroscopic analysis of the crude product. [d] Determined by HPLC analysis. [e] Determined by GC analysis using a chiral stationary phase. [f] Reaction was performed with NEt_3 (1.0 equiv) as additive. [g] Purity ca. 80%.

Allylic aminations using immobilized catalysts: catalyst activity

The reaction of carbonate **1 a** with *N*-methyl-benzylamine (**2 a**) was used as a model in exploratory experiments with immobilized catalysts (Table 2, entries 1–11). To our surprise, reactions were generally faster than those carried out under homogeneous conditions. A catalyst loading of 0.1 mol% sufficed for successful preparative amination runs. However, a limit was reached at a loading of 0.05 mol%, which gave rise to only 19% yield over a period of 36 h (entry 6 in Table 2). The influence of the following reaction variables was found: 1) The rate of the amination reaction was slow upon use of a supported catalyst prepared in situ from the triethylammonium salt [SiTsO/$HNEt_3$] and complex *ent*-**C1** (entry 7 in Table 2). 2) A mixture of *ent*-**C1** and unmodified silica gel gave a catalyst with low activity (entry 8 in Table 2). 3) At low catalyst loading, the influence of the solvent on rate as well as enantioselectivity was small (cf. entries 3, 9, and 10 in Table 2); in contrast, under homogeneous conditions, enantioselectivity was found to be strongly dependent on the solvent (Table 1, entries 2–4). These observations indicate that the superiority of the supported catalyst over the homogeneous catalyst at low-catalyst loading is due to the microenvironment provided by the support. Furthermore, an effect due to adsorption of a reactant on silica gel is unlikely, because with the highly polar solvent isopropanol, the reaction rate should decrease compared with that obtained with toluene. 4) A supported catalyst derived from the cod complex **C2** gave similar results to that derived from the dbcot complex **C1** (entry 11 in Table 2).

The substrate scope of the allylic amination promoted by immobilized catalysts is apparent from Table 2, entries 12–23. Again, results were generally superior to those achieved under homogeneous conditions (Table 1). The regioselectivity with aniline as nucleophile is particularly remarkable. Under otherwise identical conditions, the homogeneous catalyst gave rise to the linear product at 0.42 mol% catalyst loading (Table 1,

Table 2. Substrate scope of allylic aminations according to Scheme 4 using immobilized catalysts.[a]

Entry	R^1 of **1**	**2**	Solvent	Catalyst [mol%][b]	*t* [min]	Yield (conversion) [%][c]	b/l[d]	*ee* [%][e]
1	Ph	MeN(H)Bn	THF	2.32	10	89	98:2	98
2	Ph	MeN(H)Bn	THF	0.8	66	84	94:6	96
3	Ph	MeN(H)Bn	THF	0.42	84	81 (92)	93:7	99
4	Ph	MeN(H)Bn	THF	0.22	75	84	94:6	94
5	Ph	MeN(H)Bn	THF	0.11	180	87	94:6	97
6	Ph	MeN(H)Bn	THF	0.05	2200	19	81:19	n. d.
7	Ph	MeN(H)Bn	THF	0.42[f]	540	87 (100)	94:6	95
8	Ph	MeN(H)Bn	THF	0.42[g]	1380	59 (69)	92:8	98
9	Ph	MeN(H)Bn	toluene	0.42	30	87 (96)	97:3	97
10	Ph	MeN(H)Bn	*i*PrOH	0.42	60	83 (88)	96:4	91
11	Ph	MeN(H)Bn	THF[k]	0.42	120	84 (98)	94:6	94
12	Me	MeN(H)Bn	THF	2.32	15	91	97:3	92
13	Me	MeN(H)Bn	THF	0.42	72	89	92:8	93
14	Ph	H_2NCH_2Ph	THF[h]	2.32	35	82	97:3	97
15	Ph	H_2NCH_2Ph	THF[i]	0.42	45	86	99:1	86
16	Ph	H_2NPh	THF[h]	2.32	40	83	94:6	97
17	Ph	H_2NPh	THF[h]	0.42	120	73	80:20	97
18	Ph	benzimidazole	THF[j]	2.32	90	86	97:3	98
19	Ph	benzimidazole	THF[i]	0.42	150	76	79:21	69
20	Ph	$HNBn_2$	THF[h]	2.32	30	83	88:12	98
21	Ph	$HNBn_2$	THF[i]	0.42	90	83	84:16	98
22	CH_2OTr	$HNBn_2$	THF[h]	2.32	40	79	94:6	97
23	CH_2OTr	$HNBn_2$	THF[i]	0.42	180	73	85:15	94

[a] Reaction conditions: carbonate **1** (0.65 mmol), nucleophile **2** (0.5 mmol), catalyst, solvent (0.6 mL), shaken at 50 °C. [b] [Si-TsO/*ent*-**C1**–38.9 μmol g^{-1}] and [Si-TsO/*ent*-**C1**–10.6 μmol g^{-1}] were used in reactions with 2.32 and 0.42 mol% catalyst, respectively. [c] Conversion (the sum of **3** and **4**) was determined by ^{1}H NMR spectroscopic analysis of the crude product by using an internal standard; yield of isolated branched product **3**. [d] Branched/linear ratio, determined by ^{1}H NMR spectroscopic analysis of the crude product. [e] Determined by chiral HPLC or by GC analysis (entries 12 and 13). [f] Reaction was performed with **1a** (0.50 mmol), *ent*-**C1** (0.42 mol%), and [Si-TsO/$HNEt_3$] (200 mg) as additive. [g] Reaction was performed with **1a** (0.50 mmol), *ent*-**C1** (0.4 mol%) and silica gel (200 mg) as an additive. [h] Additive NEt_3 (1.0 equiv). [i] Additive NEt_3 (0.5 equiv). [j] Additive NEt_3 (2.0 equiv). [k] The supported catalyst was prepared from complex **C2** to give [Si-TsO/C2-10.5 μmol g^{-1}].

with generally high enantiomeric excess and regioselectivity were possible in THF (Figure 2A). Regioselectivity is characterized here by Seebach's ds value;[21] that is, the percentage of the major regioisomer. The first ≈20 runs required a reaction time of only 10 min; up to run 33, conversion was complete within 3 h, and selectivities were undiminished, although the yield of the final run was moderate (57% of **3a**).

Leaching was determined for aliquots of the supported catalyst; these were treated with LiOTf to recover the complex **C3**. The recovered material was characterized with respect to purity and amount by ^{31}P NMR spectroscopic analysis. The results are presented in Figure 2B. By using THF as solvent, the average recovery of pure complex **C3** along runs 1–30 was 98% per run. It is apparent that catalyst loss per run increases slightly with the number of runs. Thus, the number of possible consecutive runs is limited by leaching of the catalytically active Ir complex.

entry 10), whereas the supported catalyst furnished the branched isomer (Table 2, entry 17). With a view to the catalytic cycle given in Scheme 2, this result indicates that proton removal from species **D** is faster at the support than in solution.

Rate profiles are presented in Figure 1. Comparison of reaction times at 50% conversion indicates that, at a loading of 0.42 mol%, the reaction promoted by the supported catalyst is faster than the reaction under homogeneous conditions by a factor of 24. Fitting of the curves assuming formation of the products according to a first order rate equation gave a factor of 33.

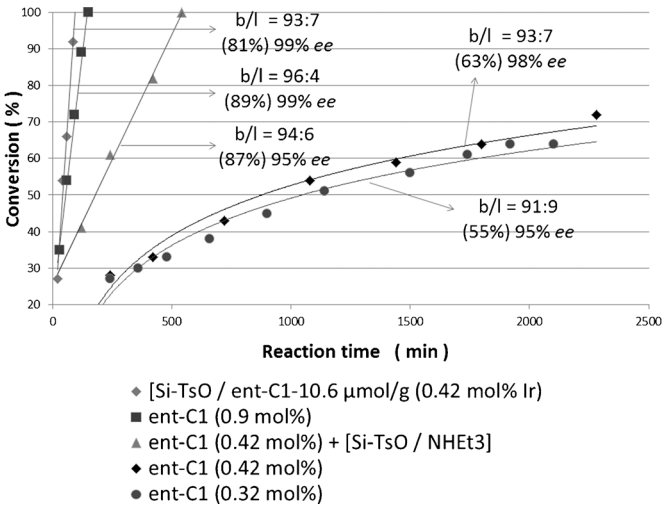


Figure 1. Kinetic profiles of reactions of **1a** with **2a** promoted with homogeneous and immobilized catalysts (solvent: THF). Reaction conditions: a solution of carbonate **1a** (0.65 mmol), nucleophile **2a** (0.5 mmol) and catalyst in solvent (0.6 mL) was reacted at 50 °C. Conversion was measured by GC analysis using hexamethylbenzene as internal standard (see the Supporting Information).

Recycling of immobilized catalysts and catalyst loss

Recyclability is of prime importance for an immobilized catalyst. We have investigated this aspect by using the reaction of carbonate **1a** with *N*-methyl-benzylamine (**2a**) (cf. Scheme 4). Note that although complex **C1** is the initial catalyst, during the reaction **C1** is transformed into complex **C3**, which constitutes the resting state and is recovered (cf. Scheme 2). THF and toluene were used as solvents. First a high catalyst loading of 2.4 mol% was employed. Up to 33 consecutive aminations

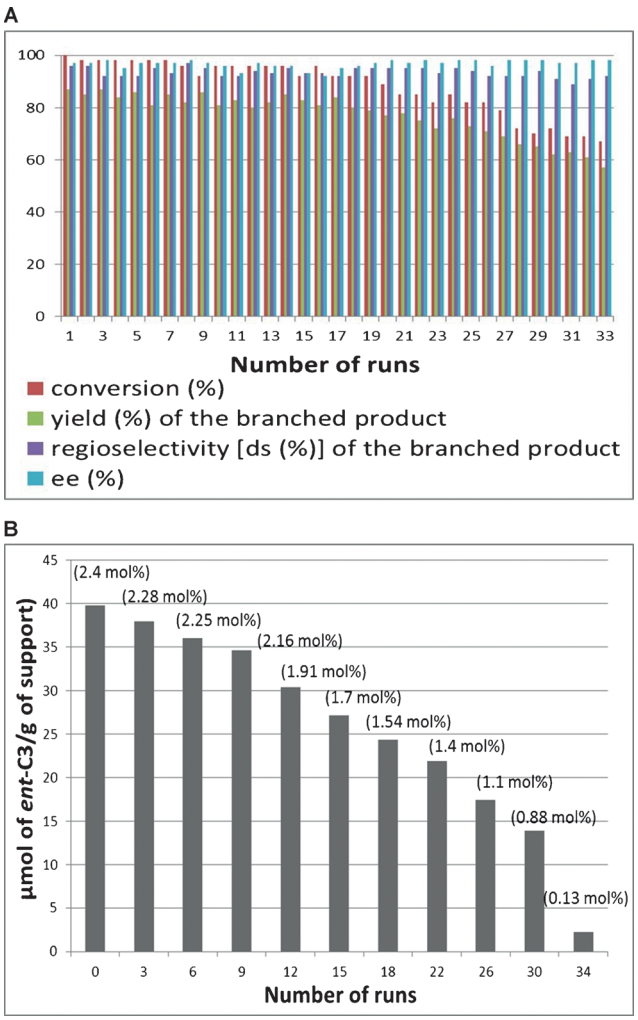


Figure 2. Yields and selectivities achieved in consecutive reactions of **1a** with **2a**; initial catalyst loading: 2.4 mol%, solvent: THF, initial catalyst: [Si-TsO/*ent*-**C1**-39.8 µmol g^{-1}]. A) Conversion, yield and selectivities. The ds value is used as a measure of regioselectivity. B) Amount of catalyst on support (µmol *ent*-**C3** per gram of support) and loading (mol%) for every third amination run (solvent THF).

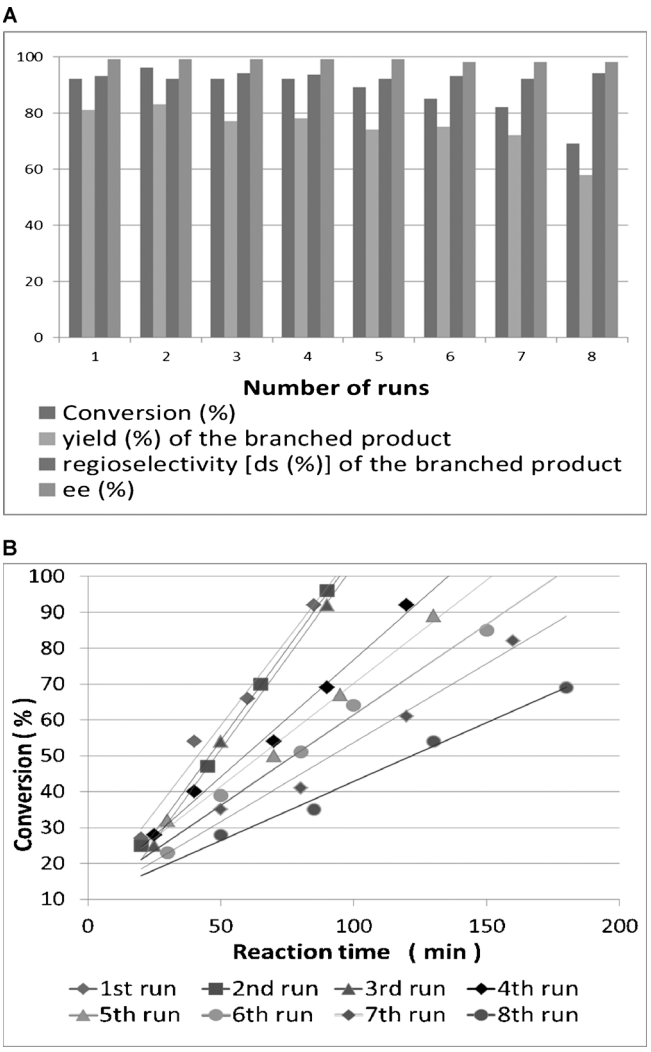


Figure 3. Consecutive reactions of **1a** (0.65 mmol) with **2a** (0.5 mmol), initial catalyst loading of 0.42 mol% (solvent: THF, initial catalyst: [Si-TsO/ent-C1–10.6 µmol g^{-1}]). A) Conversion, yield and selectivities. B) Kinetic profiles (conversion was determined by GC analysis using an internal standard, cf. Figure 1).

A second recyclability test was performed with a catalyst loading of 0.42 mol% and THF as solvent. It was possible to carry out eight consecutive runs without change of regio- or enantioselectivity (Figure 3). Yields of more than 70% were achieved up to run seven. In another set of consecutive reactions, 11 runs were achieved with more than 80% yield up to run 10 (see the Supporting Information). Reaction rate profiles are given in Figure 3B.

Loss of catalyst is expected to be a function of solvent polarity. In case of predominant electrostatic bonding of the catalyst to the support, loss of the catalyst is expected to decrease upon lowering of solvent polarity. Accordingly, we have studied another series of consecutive reactions of carbonate **1a** with amine **2a** using toluene as solvent (Figure 4). Indeed, 43 runs were accomplished at catalyst loading of 2.4 mol%; yields were high up to the 30th run (Figure 4A). Recovery of 98.4% of *ent*-**C3** per run was achieved over 41 runs (Figure 4B). As with solvent THF, catalyst loss per run increased with the number of runs. This result indicates that several processes contribute to loss of catalyst.

The "split test"[22] can be used to detect whether a catalytically active species is present in the solution phase during a reaction catalyzed with a solid catalyst. This test was conducted as follows. The standard allylic reaction of **1a** with **2a** was carried out by using [D_8]THF as solvent and catalyst loading of 2.32 mol%. After conversion of 70% had been reached, a sample of the supernatant was filtered into an NMR tube and analyzed by ^{1}H NMR spectroscopy. A very slow reaction was found at 50 °C (6% conversion over a period of 45 h), whereas the reaction in the flask with immobilized catalyst reached 96% conversion within 10 min.[23] This result is interesting with respect to the mechanism of the allylic substitution (cf. Scheme 2). Allylic amination is usually carried out with an excess of the amine; in that case, the uncharged olefin complex **E** is found as resting state. This complex does not bind to the support and would be lost in consecutive runs. As pointed

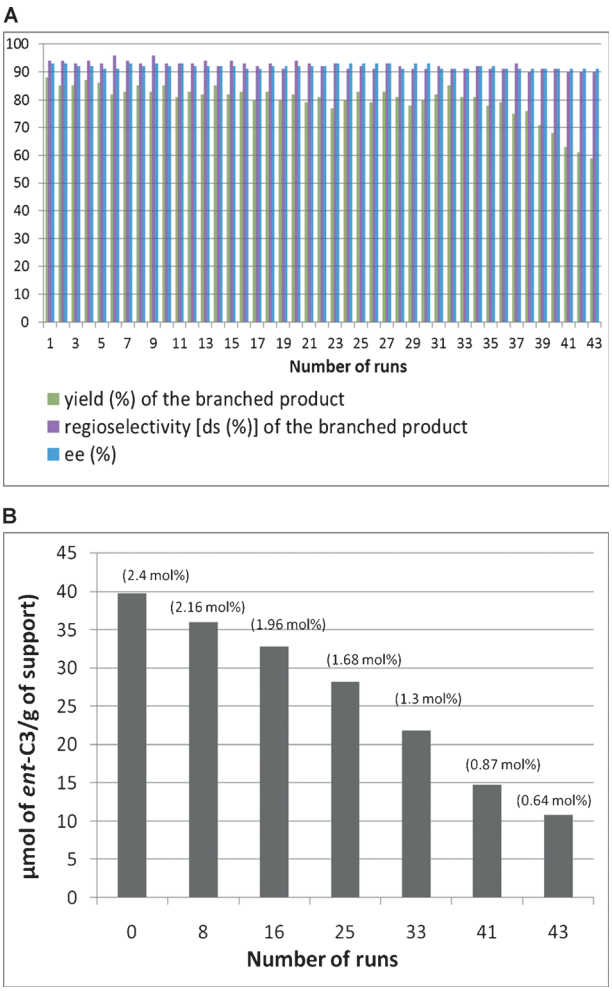


Figure 4. Consecutive reactions of **1a** with **2a**, initial catalyst loading of 2.4 mol% (solvent: toluene, initial catalyst: [Si-TsO/**C1**-39.8 µmol g^{-1}]). A) Yield and selectitivities. B) Amount of catalyst on support (µmol *ent*-**C3** per gram of support) and loading (mol%) for every third amination run (solvent toluene).

out above, we used an excess of the allylic electrophile to ensure that allyl complex **C** constitutes the resting state, because the rate of the steps **E**→**C** (via **B** and **C**) is higher than that of the steps **C**→**D**→**E**. The fact that residual catalytic activity persists in solution demonstrates that olefin complex **E** is present in low concentration. This type of product inhibition is likely the reason for leaching.

Conclusions

The asymmetric Ir-catalyzed allylic amination is an established reaction, which has found numerous applications. Still problematic is the currently employed catalyst loading of 1–4 mol% of iridium. In an effort to substantially reduce catalyst loading, we have investigated catalysts immobilized by ionic bonding. Stable cationic (π-allyl)Ir complexes are readily available, and they are useful single-species catalysts. The supported catalysts were prepared by binding these species to a modified silica gel by cation exchange. The supported catalysts displayed considerably enhanced activity compared with the parent homogeneous catalysts. Up to 43 consecutive amination runs were possible in recycling experiments. Preparation of the catalysts is facile.

Experimental Section

General methods

For spectroscopic and other measurements, as well as chromatographic methods, see the Supporting Information. All reactions were carried out under an atmosphere of argon in glassware that was washed several times with demineralized water and dried. Most reactions were carried out by using complexes **C1** or *ent*-**C1**. Only these complexes are included in the general procedures; experiments using **C2** or **C3** are presented in the tables and the text. When working with supported catalysts, magnetic stirring was avoided. The standard reaction vessel was a Schlenk tube with an externally attached magnet (see the Supporting Information). This was moved by a magnetic stirrer. Anhydrous THF, diethyl ether, toluene, dichloromethane, and acetonitrile were purchased from Sigma–Aldrich (Chromasolv) and taken from a solvent purification system (MBraun, MB SPS-800, filter material: MB-KOL-A, MB-KOL-M; catalyst: MB-KOL-C). Amine nucleophiles were distilled prior to use. Silica gel containing carbon-bound *p*-ethylbenzenesulfonic acid [ISOLUTE Si-TsOH (SCX-3), 0.59 mmol g^{-1}] was purchased from Biotage GB Ltd.[24] Ir-complexes **C1**, **C2**, and **C3** (and enantiomers) were prepared as reported.[16,5] The syntheses and spectroscopic data of the following allylic substrates and branched allylic amines have been reported: **1a**,[25] **1b**,[25] **1c**,[26] **3ab**,[4] **3ac**,[4] **3ad**,[27] and **3ae**.[28]

Preparation of [Si-TsO/$NHEt_3$]: general procedure (GP1)

Si-TsOH ("Biotage", 1.8 g, 0.59 mmol g^{-1}) was mixed with excess NEt_3 (15 mL) by slow rotation in a rotary evaporator over a period of 8 h at RT. The excess of NEt_3 was then removed carefully by using a syringe, and the silica gel was dried under vacuum at RT for 48 h.

Preparation of supported catalysts [Si-TsO/C1-*n*]: general procedure (GP2)

See Scheme 3 for formulas and designation. In an oven-dried Schlenk tube (washed several times with distilled water to remove inorganic salts), a suspension of [Si-TsO/$NHEt_3$] (see GP1) in a solution of **C1** in acetone (degassed) was shaken by hand for 3 min under an atmosphere of argon at RT. Distilled water (degassed) was then added and shaking was continued for a further 5 min. At this point, the solid phase became yellow and the supernatant became colorless. The supernatant was then removed carefully by using a syringe, and the silica gel was washed successively with degassed acetone (3×2 mL) and degassed *n*-hexane (3×2 mL). Finally, the silica gel was dried under vacuum at RT overnight to give the supported catalyst. The combined liquid phases were filtered through a short silica gel column to recover the excess of **C1**. The amount of **C1** on the solid support was determined by the difference between the initial and recovered amounts of **C1**.

Preparation of [Si-TsO/C1–10.6 µmol per g of support]

According to GP2, [Si-TsO/$NHEt_3$] (1.0 g) was treated with a solution of **C1** (15 mg, 12.5 µmol) in acetone/water (1:2, 5.1 mL). The supported catalyst was washed with acetone and *n*-hexane and dried

overnight in high vacuum to obtain [Si-TsO/**C1**–10.6 μmol per g of support].

Preparation of [Si-TsO/*ent*-C1–38.9 μmol per g of support]

According to GP2, [Si-TsO/$NHEt_3$] (1.0 g) was treated with a solution of *ent*-**C1** (63.3 mg, 52.8 μmol) in acetone/water (1:2, 10 mL). The supported catalyst was washed with acetone and *n*-hexane, and dried overnight in high vacuum to obtain [Si-TsO/*ent*-**C1**–38.9 μmol per g of support].

Allylic amination using a nonsupported catalyst: general procedure (GP3)

In a dried Schlenk tube, a solution of **C1** (0.42–2.32 mol%) in an appropriate solvent (0.6 mL) was prepared under an argon atmosphere. Carbonate **1** (0.65 mmol), and possibly a base (NEt_3, 0.5–1.0 equiv, unless otherwise indicated) were then added, and the mixture was stirred for 5 min at RT. Amine **2** (0.5 mmol) and possibly hexamethylbenzene (0.5 mmol) as an internal standard were added, and the reaction mixture was stirred at 50 °C. Conversion was monitored by TLC (petroleum ether/ethyl acetate; $KMnO_4$). When complete conversion of the nucleophile was reached, the reaction mixture was concentrated in vacuo. The ratio of regioisomers as well as final conversion were determined by ^{1}H NMR spectroscopic analysis of the crude product. The residue was then subjected to flash chromatography on silica gel (petroleum ether/ethyl acetate) to give the corresponding pure branched and linear products. For the determination of kinetic profiles (Figure 1), samples were analyzed by GC using hexamethylbenzene as internal standard (see the Supporting Information for details).

Allylic amination using a supported catalyst [Si-TsO/C1-*n*]: general procedure (GP4)

In a heat-gun-dried Schlenk tube (free of soluble inorganic salts), a suspension of [Si-TsO/**C1**-*n*], carbonate **1** (1.3 equiv), and possibly a base (NEt_3, 0.5–2.0 equiv) in anhydrous degassed solvent (0.5–1.4 M) was shaken for 5 min at RT under an argon atmosphere. Amine **2** (1 equiv) and possibly hexamethylbenzene (1 equiv) as an internal standard were added and the vessel was shaken at 50 °C until TLC (petroleum ether/ethyl acetate; $KMnO_4$] as well as GC-MS monitoring showed complete conversion of the amine. The reaction mixture was further shaken at RT for 5 min, then the supernatant was removed carefully by using a syringe, and the residue was washed with anhydrous degassed solvent (4×3 mL) and dried. The combined liquids were concentrated in vacuo, and the ratio of regioisomers as well as final conversion were determined by ^{1}H NMR spectroscopic analysis of the crude product. The residue was subjected to flash chromatography on silica gel (petroleum ether/ethyl acetate) to give the pure branched and linear product. For the determination of kinetic profiles (Figure 1), samples were analyzed by GC using hexamethylbenzene as internal standard (see the Supporting Information for details).

Catalyst deactivation was assessed by recovery of a catalytically active (π-allyl)Ir complex. This was carried out for aminations with the substrate **1a**, which gives rise to complex **C3** as resting state. The amount of **C3** contained in the recovered catalyst was determined as follows. An aliquot of the supported catalyst (50 mg) was suspended in acetone/water (1:1, 1 mL), and LiOTf (10 mg) was added. The resultant mixture was shaken for 1 h at RT under an argon atmosphere and was then filtered through a pad of cotton. The filtrate was concentrated under reduced pressure, and the residue was dissolved in THF (5 mL). The solution was dried with anhydrous Na_2SO_4, filtered, and the solvent was removed in vacuo. Quantitative ^{31}P NMR spectroscopic analysis was carried out with [D_8]THF as solvent and **C1** as internal standard.

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Keywords: allylic compounds · amination · asymmetric catalysis · iridium · supported catalysts

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