Brief Communications

Iridium-catalyzed regiospecific allylation of dimethyl malonate in ionic liquids

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Allylation of dimethyl malonate with 1-(4-chlorophenyl)prop-2-enyl methyl carbonate in the presence of $[Pd(All)Cl]_2$, $[Rh(COD)Cl]_2$, $[Ir(COD)Cl]_2$ (COD is cycloocta-1,5-diene), and a chiral ferrocenyl-containing phosphite ligand based on (*R*)-BINOL (BINOL is 2,2′-dihydroxy-1,1′-binaphthyl) in CH_2Cl_2 gave a mixture of linear and branched cross-coupling products, the latter having a moderate optical purity (below 51%). The rhodium- and iridium-catalyzed reactions were very highly regioselective (regiospecific in the case of Ir), giving a branched product. In ionic liquids ([bmim][BF_4] and [bdmim][BF_4]) (bmim is 1-butyl-3-methylimidazolium and bdmim is 1-butyl-2,3-dimethylimidazolium), the Ir-catalyzed reaction regiospecifically afforded a branched product as a racemate. The same result was obtained with $[Ir(COD)Cl]_2$ as a catalyst; this reaction easily occurred in ionic liquids even without a base.

Key words: ionic liquid, allylation, metal complex catalysis, iridium, rhodium, palladium.

Conduction of reactions in ionic liquids (ILiq) is considered to be an approach of "green" chemistry because they are nonvolatile and nontoxic and recycling is possible.[1] In recent years, Pd-[2—5] and Ru-catalyzed allylation reactions[6] in ILiq have been reported. Here we studied regiospecific allylation in ILiq in the presence of iridium complexes.

When investigating the properties of imino phosphite **1** (prepared as described for ligands in Refs 7 and 8) as a chiral ligand (hereafter denoted as L*) in asymmetric synthesis catalyzed by transition metal complexes, we performed a comparative study of allylation of dimethyl malonate with allylic carbonate **2** in the presence of Pd, Rh, and Ir complexes generated *in situ* from ligand L* and the

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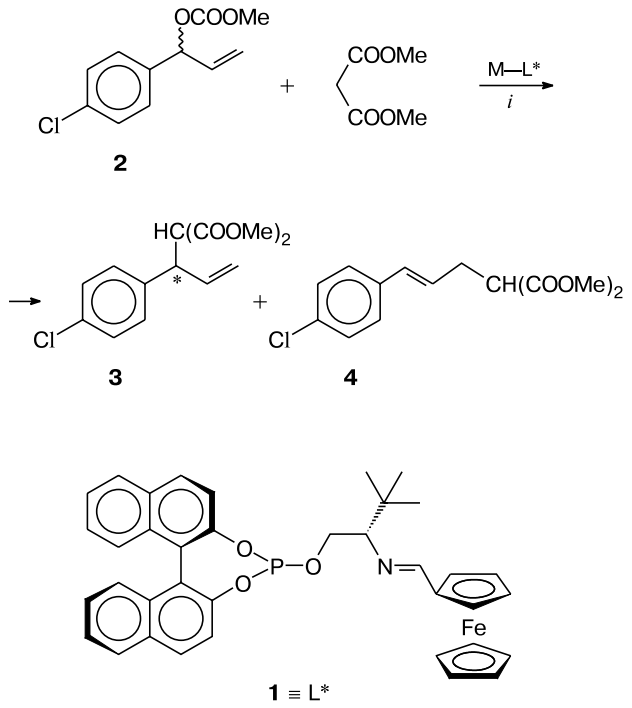
achiral complex precursors $[Pd(All)Cl]_2$, $[Rh(COD)Cl]_2$, and $[Ir(COD)Cl]_2$ (Table 1, entries *1—6*). The reaction can yield both branched isomer **3** and linear cross-coupling product **4** because of possible allylic rearrangement (Scheme 1).

Scheme 1



i. BSA, KOAc, 20 °C, 48 h.

The formation of isomer **3** was poorly enantioselective; the Pd-catalyzed reaction was not at all regioselective, while the catalysis by the Rh complex afforded product **3** with a high regioselectivity. In contrast, the Ir-catalyzed allylation regiospecifically yielded isomer **3** with a moderate optical purity (*ee* 51%).

The most efficient Ir-based catalytic system ($[Ir(COD)Cl]_2$—L*) was used to carry out allylation in ILiq, namely, 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]). Under these conditions, the reaction was also regiospecific but not enantioselective, giving isomer **3** (see Table 1, entry *7*). An analogous outcome was obtained in the presence of the complex $[Ir(COD)L^*]^+Cl^-$ (see Table 1, entry *8*). The formation of a racemate in the presence of an *a priori* chiral transition metal complex suggests that $[Ir(COD)L^*]^+Cl^-$ is not a complex responsible for catalysis. The reaction was successful with $[Ir(COD)Cl]_2$ as a catalyst containing no L* (see Table 1, entry *9*). It is known that ILiq similar to [bmim][BF_4], which contain in position 2 of the imidazolium ring a sufficiently acid hydrogen atom, can form carbene complexes with transition metals in the presence of bases (see Ref. 9 and references therein). One could thus assume that the true catalyst in all these cases is an achiral carbene complex formed from the starting iridium complex and ILiq. To exclude this possibility, we carried out allylation in the presence of the catalytic system $[Ir(COD)Cl]_2$—L* in ILiq that is incapable of forming carbene complexes, *viz.*, in 1-butyl-2,3-dimethylimidazolium tetrafluoroborate [bdmim][BF_4] (see Table 1, entry *13*). However, in this case too, the product was a racemate. This indicates that the chiral ligand L*, which allows an optically active product to be obtained in CH_2Cl_2, proved to be

Table 1. Catalytic allylation of dimethyl malonate with allylic carbonate **2**[a]

Entry	Precatalyst	M : L*	Solvent	Yield of **3** + **4** (%)	**3** : **4**	*ee* of **3** (%)
1	$[Pd(All)Cl]_2$—L*	1 : 1	CH_2Cl_2	92	52 : 48	34 (*R*)
2	$[Pd(All)Cl]_2$—L*	1 : 2	CH_2Cl_2	57	44 : 56	18 (*S*)
3	$[Rh(COD)Cl]_2$—L*	1 : 1	CH_2Cl_2	15	95 : 5	16 (*R*)
4	$[Rh(COD)Cl]_2$—L*	1 : 2	CH_2Cl_2	34	95 : 5	21 (*R*)
5	$[Ir(COD)Cl]_2$—L*	1 : 1	CH_2Cl_2	52	>99 : 1	51 (*R*)
6	$[Ir(COD)Cl]_2$—L*	1 : 2	CH_2Cl_2	88	99 : 1	45 (*R*)
7	$[Ir(COD)Cl]_2$—L*	1 : 2	[bmim][BF_4]	78	>99 : 1	0
8	$[Ir(COD)L^*]^+Cl^-$	—	[bmim][BF_4]	13	99 : 1	0
9	$[Ir(COD)Cl]_2$	—	[bmim][BF_4]	78	>99 : 1	—
10[b]	$[Ir(COD)Cl]_2$	—	[bmim][BF_4]	80	>99 : 1	—
11	$[Ir(COD)Cl]_2$	—	CH_2Cl_2	85	99 : 1	—
12[b]	$[Ir(COD)Cl]_2$	—	CH_2Cl_2	25	99 : 1	—
13	$[Ir(COD)Cl]_2$—L*	1 : 1	[bdmim][BF_4]	71	99 : 1	0
14	$[Rh(COD)L^*]^+BF_4^-$	—	[bdmim][BF_4]	14	88 : 12	6 (*R*)
15	$[Rh(COD)L^*]^+BF_4^-$	—	CH_2Cl_2	10	91 : 9	17 (*R*)

[a] COD is cycloocta-1,5-diene, bmim is 1-butyl-3-methylimidazolium, and bdmim is 1-butyl-2,3-dimethylimidazolium.

[b] The reactions were carried out in the absence of BSA/KOAc (BSA is *N*,*O*-bis(trimethylsilyl)acetamide).

an inefficient asymmetric inducer in the Ir-catalyzed allylation in ILiq. In support of this, ligand L* in the presence of the Rh complex in ILiq indeed acted as a chiral inducer, though being highly inefficient (see Table 1, entry *14*). However, its efficiency was low in CH_2Cl_2 as well (see Table 1, entry *15*).

Thus, the use of an Ir complex (even $[Ir(COD)Cl]_2$, one of the most accessible iridium complexes) as a catalyst makes it possible to regiospecifically obtain branched product **3** in the allylation under study. The reaction is equally successful both in the common organic solvent CH_2Cl_2 (see Table 1, entry *11*) and, when one is guided by the principles of green chemistry, in one of the least expensive and most accessible ILiq, namely, $[bmim][BF_4]$; note that the allylation in ILiq remains highly yielding even without a base (see Table 1, entry *10*).

Experimental

^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AMX-400 instrument (400.13 (^1H), 100.6 (^{13}C), and 162.0 MHz (^{31}P) with reference to Me_4Si (^1H and ^{13}C) and 85% H_3PO_4 in D_2O (^{31}P). Mass spectra were recorded on MSVKh TOF (MALDI) and Finnigan LCQ Advantage instruments (ESI).

(R_{ax},2″*S*)-2-{3″,3″-Dimethyl-2″-[(ferrocenylmethylidene)amino]butoxy}dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepine (1). The yield was 79%, a red powder. Found (%): C, 71.02; H, 5.59; N, 2.35. $C_{37}H_{34}FeNO_3P$. Calculated (%): C, 70.82; H, 5.46; N, 2.23. ^{31}P NMR ($CDCl_3$), δ_P: 142.5 (s). ^{13}C NMR ($CDCl_3$), δ_C: 162.0 (s, C=N); 148.9 (d, Ar, $^2J_{C,P}$ = 5.6 Hz); 147.5, 132.3, 131.6, 130.4, 129.9, 129.7, 128.3, 127.8, 126.7, 126.6, 126.0, 124.6, 124.3, 123.9, 122.8, 122.4, 122.1, 121.9, 121.7 (C_{Ar}); 81.6 (s, *ipso*-C_{Fc}); 79.5 (d, NCH, $^3J_{C,P}$ = 2.8 Hz); 70.9, 69.2, 68.9, 68.6, 68.1 (s, C_{Fc}); 65.7 (d, OCH_2, $^2J_{C,P}$ = 6.5 Hz); 33.2 (s, Bu^t); 27.2 (s, Me). ESI MS, *m/z* (I_{rel} (%)): 627 $[M]^+$ (2), 543 (100), 478 (73), 268 (25). MALDI MS, *m/z* (I_{rel} (%)): 628 $[M + H]^+$ (81), 544 (7), 314 (100), 268 (18).

Catalytic allylation of dimethyl malonate with carbonate 2 (general procedure). A solution of an appropriate precatalyst (0.01 mmol) and a ligand (0.02—0.04 mmol) in CH_2Cl_2 (5 mL) or ILiq (1.5 mL) was stirred for 40 min and then allylic substrate **2** (0.5 mmol) was added. The mixture was stirred for 20 min, whereupon dimethyl malonate (0.75 mmol), *N*,*O*-bis(trimethylsilyl)acetamide (BSA) (0.75 mmol), and KOAc (3 mg) were added. The reaction mixture was stirred at 20 °C for 48 h. After removal of the solvent or extraction of products from the ILiq with ethyl acetate followed by removal of the latter, the products were isolated by column chromatography (200×17 mm, silica gel, hexane—EtOAc (9 : 1)). The fraction consisting of a mixture of regioisomers **3** and **4** was concentrated and their ratio was determined by ^1H NMR spectroscopy ($CDCl_3$, 300 MHz). The optical yield of product **3** was determined by HPLC on a Daicel Chiralcel OD-H chiral column (220 nm, hexane : Pr^iOH = 93 : 7, 0.7 mL min^{-1}).

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