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Iridium-Catalyzed Enantioselective Allylic Alkylation using Chiral Phosphoramidite Ligand Bearing an Amide Moiety

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Abstract: New chiral phosphoramidites with an amide moiety were used for iridium-catalyzed asymmetric allylic alkylation reactions. The best results were obtained with a ligand bearing an oxazolidinone moiety. The reaction of cinnamyl acetate with diethyl sodiomalonate without the use of lithium chloride gave the branched product with 94% *ee*.

Keywords: allylic substitution; asymmetric catalysis; C–C bond formation; iridium; phosphoramidites

Introduction

Asymmetric allylic alkylation is one of the most powerful tools for constructing a new chiral center *via* a carbon-carbon bond-forming reaction from an achiral substrate or a racemic substrate.[1] A challenging topic in this area is the regio- and enantioselective allylic alkylation of unsymmetrical substrates. In 1997, we first reported that $[Ir(cod)Cl]_2$ and triphenylphosphite comprised an efficient catalyst system for the allylic alkylation reaction of terminally monosubstituted allylic acetates to give a branched product with high selectivity.[2] We also reported on the highly branched product-selective allylic amination in 2001.[3] Based on our results, iridium-catalyzed asymmetric allylic alkylation has been explored.[4,5,6] Helmchen and co-workers reported the first example of iridium-catalyzed asymmetric allylic alkylation using a chiral oxazolinyl-phosphine ligand.[4a]

Chiral phosphoramidite ligands have become important in transition metal-catalyzed asymmetric synthesis.[7] Helmchen first used binaphthol-based phosphoramidites for iridium-catalyzed enantioselective allylic alkylation.[4b] Alexakis and co-workers improved the enantioselectivity (up to 98% *ee*) of allylic alkylation by using a relatively bulky phosphoramidite ligand bearing a chiral bis[1-(*o*-methoxyphenyl)-ethyl]amine moiety.[5] Although the enantioselectivity is high, the following limitations still need to be overcome: (1) a stoichiometric amount of LiCl is needed for high regio- and enantioselectivity. The reaction without LiCl gave considerably lower regio- and enantioselectivity. For example, the reaction of cinnamyl carbonate with dimethyl sodiomalonate without LiCl gave products in 31% yield with 65% branched product-selectivity.[5d] The enantioselectivity was 44% *ee*. The development of a reaction without LiCl is desired.[8] (2) The reaction of acetates is quite slow. For example, it took 18 h to complete the reaction of cinnamyl acetate with dimethyl sodiomalonate even in the presence of LiCl.[4d] The development of an efficient reaction of acetates is desired. The enantioselective allylic amination and etherification using a similar phosphoramidite ligand were reported by Hartwig and co-workers.[9] The binaphthol-based phosphoramidite ligand bearing a chiral bis(1-arylethyl)amine moiety has been successfully used for enantioselective allylic substitution. It has three chiral elements that are derived from binaphthol and bis(1-arylethyl)amine.[4d–f,h–l,5,6,9] New ligands are still needed to expand the scope and enhance the selectivity of allylic substitution. We designed a novel phosphoramidite $P(OR)_2$(amide) ligand. The planarity of the amide group strongly contributes to a more rigid chiral conformation. Furthermore, such a phosphoramidite ligand is expected to act as a chiral bidentate ligand through coordination of the carbonyl oxygen and phosphorus atom to the central metal (Figure 1).

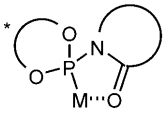


Figure 1. Chiral phosphoramidate ligand as a bidentate ligand.

To the best of our knowledge, there has been only one previous example of a chiral phosphoramidite with an amide moiety: the rhodium-catalyzed enantioselective hydrogenation of enones using the phosphoramidite ligand prepared from 1,1′-bi-2-naphthol and ε-caprolactam.[10] We describe here the iridium-catalyzed enantioselective allylic alkylation using a newly prepared chiral phosphoramidite bearing an amide moiety. Enantioselectivities of up to 94% *ee* were achieved by the reaction of acetates without the use of LiCl.

Results and Discussion

The chiral phosphoramidite ligands **L1**–**L9** were prepared from 1,1′-bi-2-naphthol and amides in two steps. A chiral phosphorochloridite was formed from phosphorus trichloride and 1,1′-bi-2-naphthol, and then coupled with an amide to give the corresponding chiral phosphoramidite (Figure 2). X-ray analyses of ligands **L1** and **L3** clearly show the planar framework of the amide group. ORTEP drawings of **L1** and **L3** are shown in Figure 3 and Figure 4, respectively. The torsion angle of P–N–C=O is 9.9° in **L1** and 10.5° in **L3**, which shows that these four atoms lie in nearly the same plane in both cases.

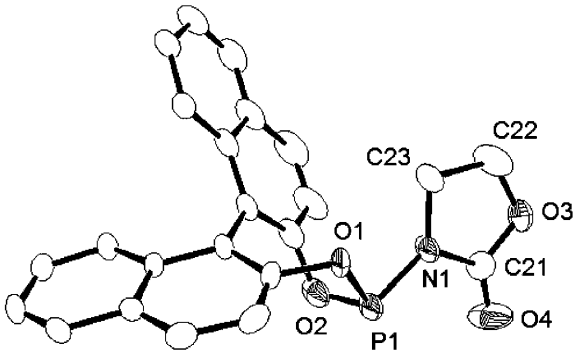


Figure 3. ORTEP drawing of **L1**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths (Å), angles (deg), and torsion angles (deg): P1–O1, 1.654(3); P1–O2, 1.617(5); P1–N1, 1.715(4); O1–P1–O2, 99.76(17); O1–P1–N1, 92.57(19); O2–P1–N1, 102.7(2); P1–N1–C21, 120.2(3); P1–N1–C23, 128.9(3); C21–N1–C23, 110.6(4); N1–C21–O3, 110.2(5); N1–C21–O4, 126.2(5); O3–C21–O4, 123.5(5); P1–N1–C21–O4, 9.9(13).

The efficiency of ligands **L1**–**L9** was examined for the reaction of cinnamyl acetate (**1a**) with diethyl sodiomalonate in the presence of 2 mol% of $[Ir(cod)Cl]_2$ and 4 mol% of ligand. The best ligand for the reaction was **L1**, which had an oxazolidinone moiety. The alkylated product was obtained in 94% yield with 93% *ee* (*S*) without LiCl (Table 1, entry 1).[11] The reaction was complete in 1.5 h at room temperature. The use of LiCl in the reaction

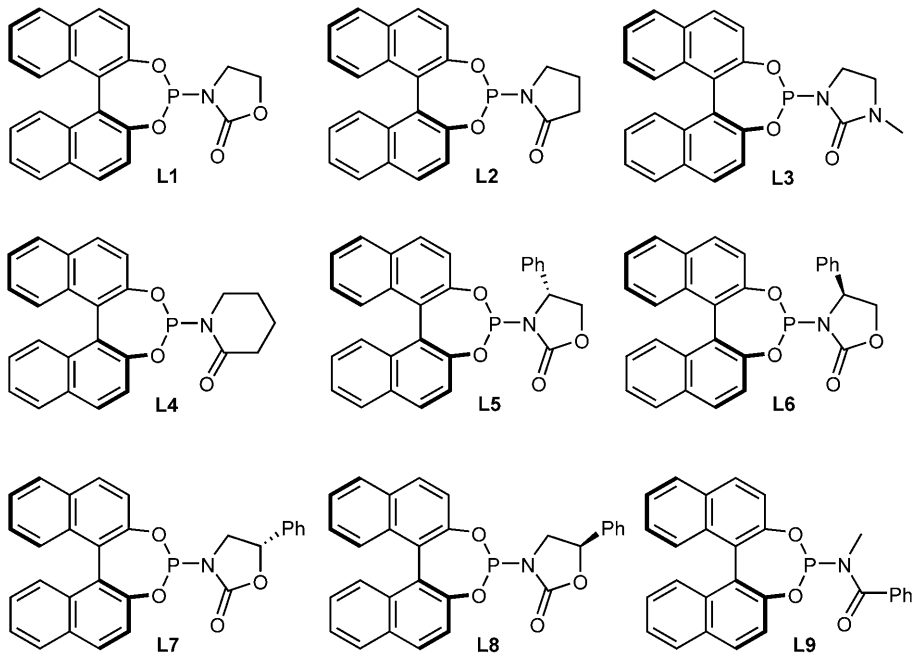


Figure 2. Newly prepared chiral phosphoramidite ligands.

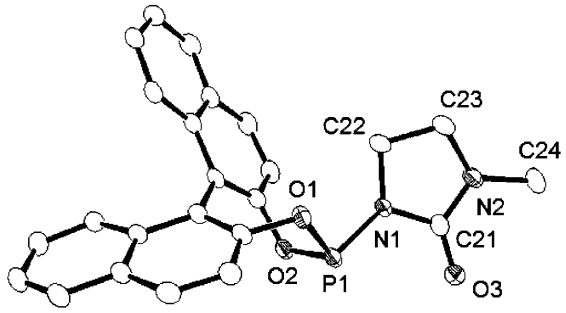
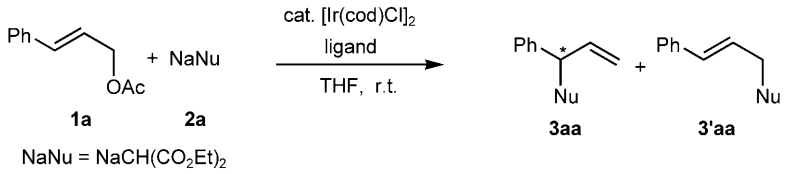


Figure 4. ORTEP drawing of **L3**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths (Å), angles (deg), and torsion angles (deg): P1–O1, 1.6537(11); P1–O2, 1.6394(12); P1–N1, 1.6768(13); O1–P1–O2, 99.00(6); O1–P1–N1, 94.27(7); O2–P1–N1, 105.47(7); P1–N1–C21, 119.82(11); P1–N1–C22, 130.21(11); C21–N1–C22, 109.68(12); N1–C21–N2, 108.10(14); N1–C21–O3, 125.03(15); N2–C21–O3, 126.86(16); P1–N1–C21–O3, 10.5(2).

with **L1** did not increase the regio- or enantioselectivity, and did not accelerate the reaction (entry 3). The use of NaHMDS or LiHMDS as a base instead of NaH decreased the yields and enantioselectivities (entries 4 and 5). Replacement of the oxygen atom in the oxazolidinone moiety with a carbon or nitrogen atom led to almost the same level of regio- and enantioselectivities given by **L1** (entries 6–9). With **L2** and **L3**, LiCl slightly improved the enantioselectivity. The enantioselectivity given with **L2** derived from pyrrolidinone was 90% *ee* (entry 6). The use of LiCl increased the enantioselectivity to 93% *ee* (entry 7). Ligand **L3** derived from *N*-methylimidazolidinone was slightly less effective than **L1**. The reaction gave a product in 89% *ee* (entry 8). The use of LiCl increased the enantioselectivity to 94% *ee* (entry 9). A six-membered ring amide moiety was far less effective

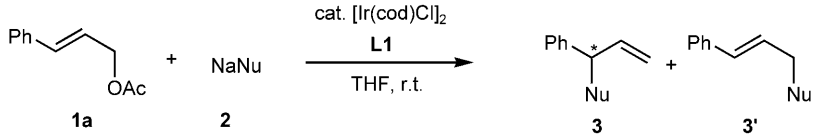
Table 1. Reactions of allylic acetate (**1a**) with diethyl sodiomalonate (**2a**) in the presence of $[Ir(cod)Cl]_2$ and phosphoramidite ligand (**L1**–**L9**).[a]



Entry	Ligand	Additive	Time [h]	Yield [%][b]	**3aa/3′aa**[c]	*ee* [%][d]
1	**L1**	none	1.5	94	>99/1	93 (*S*)
2[e]	**L1**	none	5	88	>99/1	94 (*S*)
3	**L1**	LiCl	1.5	91	>99/1	93 (*S*)
4[f]	**L1**	none	4	86	>99/1	80 (*S*)
5[g]	**L1**	none	24	23	96/4	6 (*R*)
6	**L2**	none	2	96	>99/1	90 (*S*)
7	**L2**	LiCl	2	97	>99/1	93 (*S*)
8	**L3**	none	1	98	>99/1	89 (*S*)
9	**L3**	LiCl	0.5	97	>99/1	94 (*S*)
10	**L4**	none	48	37	94/6	28 (*S*)
11	**L4**	LiCl	16	88	97/3	23 (*S*)
12	**L5**	none	7	89	91/9	39 (*S*)
13	**L5**	LiCl	24	56	75/25	33 (*S*)
14	**L6**	none	24	83	81/19	37 (*S*)
15	**L6**	LiCl	24	48	75/25	50 (*S*)
16	**L7**	none	2.5	97	>99/1	91 (*S*)
17	**L7**	LiCl	2	97	>99/1	93 (*S*)
18	**L8**	none	3	98	99/1	91 (*S*)
19	**L8**	LiCl	2	94	99/1	91 (*S*)
20	**L9**	none	4	96	93/7	16 (*S*)
21	**L9**	LiCl	4	94	78/22	55 (*S*)

[a] All reactions of **1a** (1 mmol) with diethyl sodiomalonate (**2a**) (2 mmol), which was prepared from diethyl malonate and NaH, were carried out in the presence of $[Ir(cod)Cl]_2$ (0.02 mmol), and ligand (**L1**–**L9**, P/Ir = 1) in THF (5 mL) at room temperature.
[b] Isolated yields.
[c] Determined by ^{1}H NMR.
[d] Determined by HPLC analysis using Chiralcel OJ-H.
[e] 0.08 mmol of **L1** was used.
[f] NaHMDS was used instead of NaH.
[g] LiHMDS was used instead of NaH.

Table 2. Reactions of cinnamyl acetate (**1a**) with various sodiomalonates (**2**) in the presence of $[Ir(cod)Cl]_2$ and **L1**.[a]



Entry	NaNu	Additive	Time [h]	Yield [%][b]	**3/3′**[c]	*ee* [%][d]
1	$NaCH(CO_2Et)_2$ (**2a**)	none	1.5	94	>99/1	93 (*S*)
2	$NaCH(CO_2Et)_2$ (**2a**)	LiCl	1.5	91	>99/1	93 (*S*)
3	$NaCH(CO_2Me)_2$ (**2b**)	none	2	94	>99/1	89 (*S*)[e]
4	$NaCH(CO_2Me)_2$ (**2b**)	LiCl	1	94	>99/1	93 (*S*)[e]
5	$NaCMe(CO_2Me)_2$ (**2c**)	none	24	77	94/6	75
6	$NaCMe(CO_2Me)_2$ (**2c**)	LiCl	24	59	91/9	62
7	$NaC(allyl)(CO_2Me)_2$ (**2d**)	none	48	39	93/7	45
8	$NaC(allyl)(CO_2Me)_2$ (**2d**)	LiCl	48	28	93/7	69

[a] All reactions of **1a** (1 mmol) with sodiomalonate (**2**) (2 mmol), which was prepared from malonate and NaH, were carried out in the presence of $[Ir(cod)Cl]_2$ (0.02 mmol), and ligand (**L1**, P/Ir = 1) in THF (5 mL) at room temperature.
[b] Isolated yields.
[c] Determined by ^1H NMR.
[d] Determined by HPLC analysis using chiral column.
[e] The absolute configuration was determined by comparison of the value of the optical rotation with that reported in the literature.[5d]

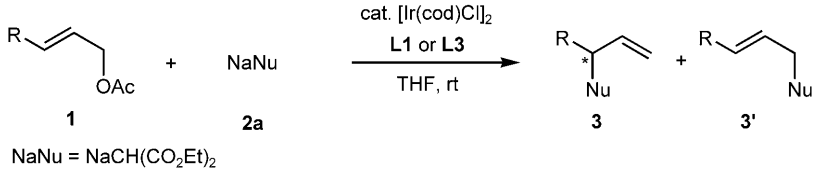
than a five-membered ring amide moiety. With **L4** prepared from δ-valerolactam, the yield and enantioselectivity were considerably decreased (entries 10 and 11). Although ligands **L5**–**L8** had two chiral centers, **L1** was better than **L5**–**L8**. Ligands **L5** and **L6** were not effective in the reaction, while reactions using **L7** and **L8** gave 91% *ee* (entries 12–19). The stereochemistry of the product **3aa** was the same when **L5**–**L8** were used (entries 12–19). The stereochemistry of the binaphthol moiety in the ligand determined the stereochemistry of the product. The use of LiCl in the reaction with **L7** improved the enantioselectivity by only 2% (entry 17). With **L8**, LiCl did not improve the enantioselectivity (entries 18 and 19). The ligand **L9** bearing an acyclic amide moiety was less effective than **L1** (entries 20 and 21).

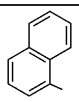
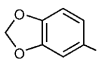
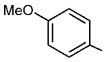
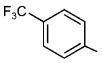
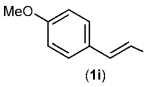
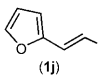
Asymmetric allylic alkylations of cinnamyl acetate (**1a**) with various sodiomalonates (**2**) in the presence of catalytic amounts of $[Ir(cod)Cl]_2$ and **L1** are summarized in Table 2. The reaction with diethyl sodiomalonate (**2a**) without LiCl was slightly more enantioselective than that with dimethyl sodiomalonate (**2b**) without LiCl (entries 1 and 3). The use of LiCl in the reaction with dimethyl sodiomalonate (**2b**) improved the enantioselectivity by only 4% (entry 4). The reaction using α-substituted sodiomalonates (**2c–d**) decreased the yields and the regio- and enantioselectivities (entries 5–8).

The results of the reactions of various allylic acetates (**1**) with diethyl sodiomalonate (**2a**) using **L1** or **L3** are shown in Table 3. These reactions were performed in the absence or presence of LiCl. Ligand **L1** led to better enantioselectivity than **L3**, except for the reaction of 3-(1-naphthyl)-2-propenyl acetate (**1b**). All of the reactions without LiCl were highly branched product-selective and were complete within 2 h at room temperature. The use of LiCl did not improve the rate or regioselectivity in any case. LiCl had only a slight effect on enantioselectivity. With **L1**, the maximum increase in enantioselectivity with the use of LiCl was only 11% (entries 17 and 18). With **L3**, the maximum increase was 15% (entries 29, 30. 37, and 38). The reaction of 3-(2-naphthyl)-2-propenyl acetate (**1c**) was more enantioselective than that of 3-(1-naphthyl)-2-propenyl acetate (**1b**) (entries 5–12). The substituent on the aromatic ring affected the enantioselectivity. The reaction of 3-(4-trifluoromethyphenyl)-2-propenyl acetate (**1g**) gave a lower enantioselectivity than that of a substrate substituted by an electron-rich aromatic ring, such as **1d–1f** (entries 25–28). 2,4-Dienyl acetates (**1h–1j**) reacted with diethyl sodiomalonate to give the branched products (**3ha–3ja**) in good yields with good enantioselectivities (entries 29–40).[4e,f,h]

Construction of a chiral all-carbon-substituted quaternary carbon center on an allylic site is a challenging problem in enantioselective allylic alkylation.[12] We examined the allylic alkylation of (*E*)-3-phenyl-2-butenyl acetate. Branched-product selective allylic alkylation gives a product bearing a chiral all-carbon-substituted quaternary carbon center. The reaction of (*E*)-3-phenyl-2-butenyl acetate in refluxing THF for 48 h gave no alkylated product with a quantitative recovery of the starting material. The carbonate was

Table 3. Reactions of various allylic acetates (**1**) with diethyl sodiomalonate (**2a**) in the presence of $[Ir(cod)Cl]_2$ and ligand (**L1** or **L3**).[a]



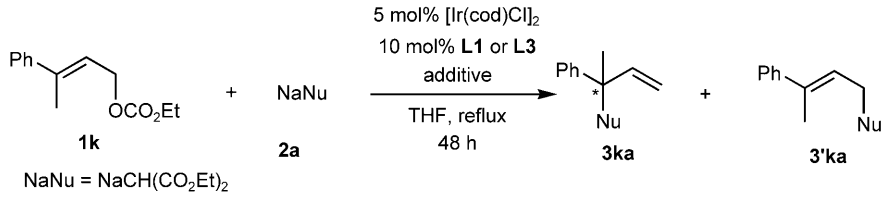
Entry	R	Ligand	Additive	Time [h]	Yield [%][b]	**3/3′**[c]	*ee* [%][d]
1	 (1a)	**L1**	none	1.5	94	>99/1	93 (*S*)
2		**L1**	LiCl	1.5	91	>99/1	93 (*S*)
3		**L3**	none	1	98	>99/1	89 (*S*)
4		**L3**	LiCl	0.5	97	>99/1	94 (*S*)
5	 (1b)	**L1**	none	1	88	>99/1	72
6		**L1**	LiCl	0.5	94	>99/1	80
7		**L3**	none	1	93	>99/1	81
8		**L3**	LiCl	0.5	94	>99/1	81
9	 (1c)	**L1**	none	1.5	84	>99/1	89
10		**L1**	LiCl	1.5	88	>99/1	89
11		**L3**	none	1	94	>99/1	80
12		**L3**	LiCl	1	92	>99/1	93
13	 (1d)	**L1**	none	1	95	>99/1	87
14		**L1**	LiCl	1	95	>99/1	89
15		**L3**	none	1	91	>99/1	87
16		**L3**	LiCl	0.5	94	>99/1	94
17	 (1e)	**L1**	none	1	85	>99/1	84
18		**L1**	LiCl	1	92	>99/1	91
19		**L3**	none	1	84	>99/1	77
20		**L3**	LiCl	0.5	83	>99/1	92
21	 (1f)	**L1**	none	1	91	>99/1	90
22		**L1**	LiCl	0.5	90	>99/1	89
23		**L3**	none	1	89	>99/1	88
24		**L3**	LiCl	0.5	95	>99/1	93
25	 (1g)	**L1**	none	1	90	>99/1	79
26		**L1**	LiCl	1	87	>99/1	77
27		**L3**	none	1	92	>99/1	78
28		**L3**	LiCl	1	95	>99/1	87
29	 (1h)	**L1**	none	2	85	>99/1	72
30		**L1**	LiCl	1	83	>99/1	83
31		**L3**	none	1.5	90	>99/1	71
32		**L3**	LiCl	1.5	90	>99/1	80
33	 (1i)	**L1**	none	1.5	74	>99/1	72
34		**L1**	LiCl	1.5	74	>99/1	79
35		**L3**	none	1.5	80	>99/1	64
36		**L3**	LiCl	1.5	76	>99/1	78
37	 (1j)	**L1**	none	1.5	82	>99/1	72
38		**L1**	LiCl	1	84	>99/1	83
39		**L3**	none	1.5	82	>99/1	70
40		**L3**	LiCl	1	87	>99/1	81

[a] All reactions of **1** (1 mmol) with diethyl sodiomalonate (**2a**) (2 mmol), which was prepared from diethyl malonate and NaH, were carried out in the presence of $[Ir(cod)Cl]_2$ (0.02 mmol), and ligand (**L1** or **L3**, P/Ir = 1) in THF (5 mL) at room temperature.

[b] Isolated yields.

[c] Determined by ^{1}H NMR.

[d] Determined by HPLC analysis using chiral column.



ligand	additive	yield (%)	3ka/3'ka	*ee* (%)
L1	none	30	59/41	10
L1	LiCl	17	66/34	21
L3	none	62	78/22	12
L3	LiCl	60	77/23	15

Scheme 1.

more reactive than the acetate. The reaction of (*E*)-3-phenyl-2-butenyl ethyl carbonate (**1k**) gave the branched product **3ka** in low yield (Scheme 1).

To obtain insight into the mechanism, we examined the ^{31}P NMR spectrum of a 1:2 mixture of $[Ir(cod)Cl]_2$ and **L1** in THF-d_8. The chemical shift of **L1** was 140.3 ppm, while the spectrum of a 1:2 mixture of $[Ir(cod)Cl]_2$ and **L1** showed only one singlet peak at 111.2 ppm. This result indicated that a single iridium species coordinated by one molecule of **L1** was formed.

Two plausible transition states of the nucleophilic attack to π-allyliridium intermediates are shown in Figure 5. Ligand **L1** acts as a bidentate ligand. The phosphorus atom and carbonyl oxygen atom in **L1** coordinate to iridium to form five-membered ring chelation, which leads to a stable chiral structure. The efficiency of **L1** is due to the planarity of the amide group and bidentate coordination. The phosphorus atom coordinates with the iridium *trans* to the substituted allylic terminus to deliver sodiomalonate at the substituted allylic terminus. Considering that the absolute configuration of alkylated product was (*S*) when **L1** was used as a ligand, transition state A seems to be more favorable than transition state B. The steric repulsion between a naphthyl moiety and a hydrogen of the terminal allylic carbon suggests that transition state B is less favored.

Conclusions

In summary, we have prepared new chiral phosphoramidites with an amide framework, and found that these phosphoramidites were useful ligands for iridium-catalyzed asymmetric allylic alkylation. Further synthetic applications and investigations of mechanistic details are currently in progress.

Experimental Section

General

^{1}H, ^{13}C, and ^{31}P NMR spectra were measured on a JEOL JNM-ECP 500 A spectrometer using Me_4Si and phosphoric acid as an internal standard. Samples were dissolved in $CDCl_3$. GC analyses were performed on a Shimadzu GC-14B using 3.2 mm × 2 m glass columns packed with 5% OV-17 on 60/80 mesh Chromosorb WAW-DMCS. The products were purified by column chromatography on 63–210 mesh silica gel (Kanto Kagaku; Silica Gel 60N). Optical rotations were measured on a Jasco P-1020 Polarimeter. High-resolution mass spectra were obtained with a JEOL Mstation JMS-700.

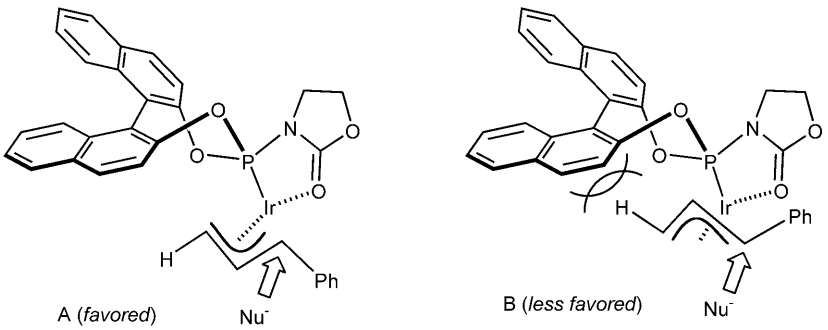


Figure 5. Two plausible transition states of the nucleophilic attack to π-allyliridium intermediates.

Materials

All reagents and solvents were dried and purified before use by the usual procedures. (*S*)-1,1′-Bi-2-naphthol, phosphoryl chloride, 2-oxazolidinone, 2-pyrrolidinone, 2-piperidinone, (*R*)-(−)-4-phenyl-2-oxazolidinone, (*S*)-(+)-4-phenyl-2-oxazolidinone, and maleimide were purchased. *N*-Methyl-2-imidazolidinone,[13] (*R*)-5-phenyl-2-oxazolidinone,[14] and (*S*)-5-phenyl-2-oxazolidinone[14] were prepared as described in the literature. 3-Substituted-2-propen-1-ols were prepared as described in the literature.[3a] $[Ir(cod)Cl]_2$ was prepared as described in the literature.[15] (*E*)-3-Phenyl-2-butenyl ethyl carbonate (**1k**) was prepared from acetophenone in three steps.[16]

Synthesis of Chiral Phosphoramidite Ligands

A typical experimental procedure for the synthesis of chiral phosphoramidite ligands (**L1**–**L9**) is described below. Into a two-necked flask with a stirring bar was placed (*S*)-(−)-1,1′-bi-2-naphthol (1.43 g, 5.0 mmol). The flask was evacuated and filled with argon. PCl_3 (8.0 mL) was added to the flask. The reaction mixture was heated under reflux temperature (70 °C) overnight to form the phosphorochloridite. Excess PCl_3 was removed by azeotropic distillation with toluene at 140 °C. To a stirred solution of 2-oxazolidinone (434 mg, 5.0 mmol) in anhydrous THF (30 mL) was added triethylamine (2.0 mL) at 0 °C, and to this was added the solution of phosphorochloridite in anhydrous THF (3 mL). After being stirred at room temperature for 40 h, the reaction mixture was filtered on Florisil. Recrystallization from CH_2Cl_2/*n*-hexane gave phosphoramidite **L1**; yield: 957 mg (2.4 mmol, 48%); $[\alpha]_D^{28}$: +491.9 (*c* 1.00, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.64 (ddd, J = 10.1, 8.7 and 6.9 Hz, 1H), 3.55 (ddd, J = 10.1, 8.7 and 6.9 Hz, 1H), 4.14 (ddd, J = 8.7, 8.7 and 6.9 Hz, 1H), 4.19 (ddd, J = 8.7, 8.7 and 6.9 Hz, 1H), 7.25–7.53 (m, 8H), 7.94–8.03 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 42.4, 42.5, 64.57, 64.58, 120.7, 121.03, 121.04, 123.00, 123.02, 123.7, 123.8, 125.38, 125.40, 126.57, 126.63, 126.7, 126.8, 128.41, 128.45, 130.5, 131.0, 131.1, 131.7, 132.42, 132.43, 132.61, 132.62, 148.0, 148.30, 148.34, 159.0, 159.2; ^{31}P NMR (202 MHz, $CDCl_3$): δ = 138.2: HR-MS: m/z = 401.0804, calcd for $C_{23}H_{16}NO_4P$ (M^+): 401.0817.

L3; yield: 40%; $[\alpha]_D^{23}$: +351.9 (*c* 0.21 $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.50 (ddd, J = 9.6, 9.2 and 6.9 Hz, 1H), 2.83 (s, 3H), 3.12 (ddd, J = 9.2, 8.7 and 6.4 Hz, 1H), 3.16 (ddd, J = 9.2, 8.7 and 6.4 Hz, 1H), 3.34 (ddd, J = 9.6, 9.2 and 6.4 Hz, 1H), 7.21–7.30 (m, 3H), 7.37–7.51 (m, 5H), 7.90–7.98 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 30.3, 38.96, 39.01, 46.3, 121.2, 121.3, 121.4, 122.96, 122.98, 123.79, 123.83, 125.0, 125.1, 126.30, 126.33, 126.7, 126.8, 128.3, 128.4, 130.2, 130.7, 130.9, 131.5, 132.4, 132.5, 132.63, 132.64, 148.7, 149.0, 149.1, 160.3, 160.5; ^{31}P NMR (202 MHz, $CDCl_3$): δ = 140.6; HR-MS: m/z = 414.1129, calcd. for $C_{24}H_{19}N_2O_3P$ (M^+): 414.1133.

X-Ray Crystallographic Studies of L1

Colorless crystals of **L1** suitable for X-ray analysis were obtained by recrystallization from CH_2Cl_2/*n*-hexane. A single crystal was mounted using liquid paraffin to a 0.4–0.5 mm cryoloop (Hampton Research) and used for data collection. All measurements were made on a Bruker APEX II CCD area detector with graphite monochromated Mo-Kα radiation. Details of crystal and data collection parameters are summarized in the Supporting Information. The structure was solved by direct methods SHELXS-97 and refined by full-matrix least-squares against F^2 using SHELXL-97 software.[17] Crystallographic data for **L1**: $C_{23}H_{16}NO_4P$, fw = 401.34, hexagonal, $P6_5$, a = 15.251(3) Å, c = 15.465(4) Å, V = 3115.2(11) Å^3, Z = 6, 17135 reflections measured, 4785 unique (R_{int} = 0.0780), R_1 = 0.0923, wR_2 = 0.2325, GOF = 1.362. CCDC 687334 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

X-Ray Crystallographic Studies of L3

Colorless crystals of **L3** suitable for X-ray analysis were obtained by recrystallization from CH_2Cl_2/*n*-hexane. A single crystal was mounted using liquid paraffin to a 0.4–0.5 mm cryoloop (Hampton Research) and used for data collection. All measurements were made on a Bruker APEX II CCD area detector with graphite monochromated Mo-Kα radiation. Details of crystal and data collection parameters are summarized in supporting information. The structure was solved by direct methods SHELXS-97 and refined by full-matrix least-squares against F^2 using SHELXL-97 software.[17] Crystallographic data for **L3**: $C_{24}H_{19}N_2O_3P$, fw = 414.38, orthorhombic, $P2_12_12_1$, a = 7.9277(16) Å, b = 14.406(3) Å, c = 17.957(4) Å, V = 2050.8(7) Å^3, Z = 4, 10611 reflections measured, 4436 unique (R_{int} = 0.0556), R_1 = 0.0398, wR_2 = 0.0661, GOF = 1.493. CCDC 687335 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Asymmetric Allylic Alkylation

A typical procedure of asymmetric allylic alkylation is described below. A flask was charged with $[Ir(cod)Cl]_2$ (14.2 mg, 0.02 mmol) and **L1** (16.5 mg, 0.04 mmol). The flask was evacuated and filled with argon. To the flask were added THF (2.5 mL) and cinnamyl acetate (187.8 mg, 1.07 mmol). Diethyl sodiomalonate was prepared in another flask. To the flask which contained a THF (2.5 mL) solution of sodium hydride (60% in oil, 83.4 mg, 2.1 mmol) was added diethyl malonate (360.7 mg, 2.3 mmol) at 0 °C. A THF solution of sodium malonate was added to the reaction mixture. The mixture was stirred at room temperature for 2 h. The progress of the reaction was monitored by GLC. After the reaction was complete, to the mixture was added saturated aqueous NH_4Cl, and the aqueous layer was extracted with ether. The combined organic layers were dried with Mg_2SO_4. The solvent was evaporated under vacuum. Column chromatography of the residue gave **3aa** as a colorless oil (*n*-hexane/AcOEt = 95/5); yield: 278.1 mg (1.01 mmol, 94%). The *ee* value was determined by HPLC analysis with a Chiralcel OJ-H column [eluent: *n*-hexane/ethanol = 99/1, flow rate: 0.5 mL min^{-1}, column temperature: 35 °C, retention time: 25.75 min (*S*) and 29.23 min (*R*)]. $[\alpha]_D^{24}$: −26.2 (*c* 1.01, $CHCl_3$) [94% *ee* (*S*)]. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.98 (t, J = 7.3 Hz, 3H), 1.27 (t, J = 7.3 Hz, 3H), 3.83 (d, J = 11.0 Hz, 1H), 3.89–3.98 (m, 2H),

4.10 (dd, $J=11.0$ and 8.2 Hz, 1H), 4.21 (q, $J=7.3$ Hz, 2H), 5.08 (d, $J=10.1$ Hz, 1H), 5.12 (d, $J=17.0$ Hz, 1H), 6.00 (ddd, $J=17.0$, 10.1 and 8.2 Hz, 1H), 7.21–7.30 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=13.7$, 14.1, 49.6, 57.4, 61.2, 61.5, 116.4, 127.0, 128.0 (2C), 128.5 (2C), 137.9, 140.0, 167.4, 167.8.

Supporting Information

Experimental procedures, compound characterization data, crystal structure analysis, and NMR spectra are available in the Supporting Information.

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