Literature Presentation

Chiral Olefin Ligands

New Spectators in Asymmetric Catalysis

Glorius, F. *Angew. Chem. Int. Ed.* **2004**, 43, 3364-3366

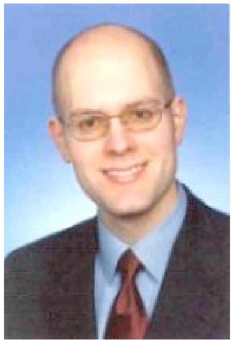
Fischer, C.; Suzuki, T.; Carreira, E. M. *J. Am. Chem. Soc.* **2004**, 126, 1628

Hu, Gang

Michigan State University

June 24, 2004

Dr. Frank Glorius



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Education and Research Experience

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Education and Research Experience

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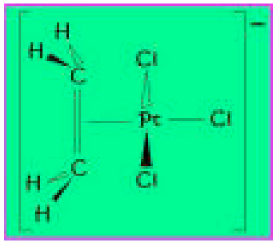
1992, Postdoc fellow, CIT, Peter Dervan

1992-1997, CIT, 1996, associate professor, 1997, full professor

1998-, ETH Zurich, full professor

Olefin as ligand in transition metal complex

Zeise's salt: K[$PtCl_3(C_2H_4)$]



The role of olefin ligand in a reaction:

(1) Dissociate from the metal or
undergo chemical conversion

(2) Spectator

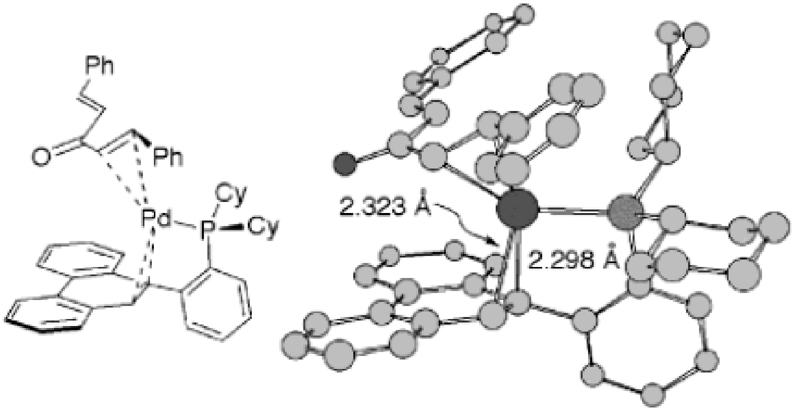


Figure 2. X-ray crystal structure of **3a**/Pd(dba).

Yin, J.; Rainka, M. P.; Zhang, X-X.; Buchwald, S. *J. Am. Chem. Soc*. **2002**, 124, 1162

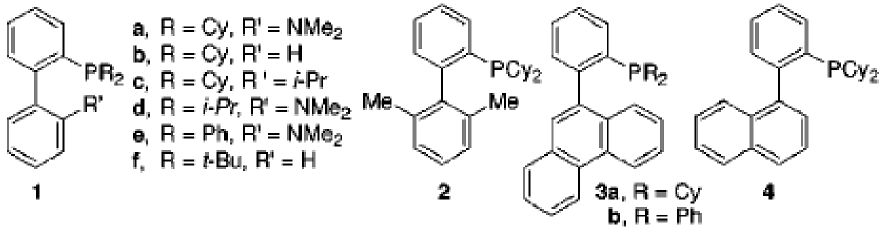
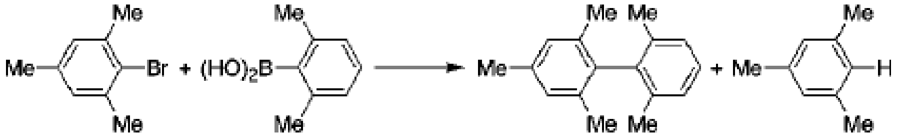


Figure 1. Hindered biarylphosphines.

Table 1. Ligand Effects in the Coupling of Hindered Substrates[a]



entry	ligand	conv (%)	biaryl (%)[b]	biaryl/Ar–H
1	**1a**	47	33	2.3
2	**1b**	20	10	0.9
3	**1c**	74	40	1.9
4	**1d**	68	34	1.6
5	**1e**	49	25	1.3
6	**1f**	21	<1	<0.3
7	**2**	56	48	5.0
8	**3a**	100	91	10
9	**3a**[c]	57	50	7.4
10	**4**[c]	20	16	4.1

[a] Reaction conditions: 1.0 equiv of ArBr, 1.4 equiv of Ar′B(OH)$_2$, 3.0 equiv of K_3PO_4, toluene, 2 mol % Pd$_2$(dba)$_3$, 8 mol % ligand, 110 °C, 17−24 h. [b] GC yield. [c] 0.5 mol % Pd$_2$(dba)$_3$, 1.2 mol % ligand used.

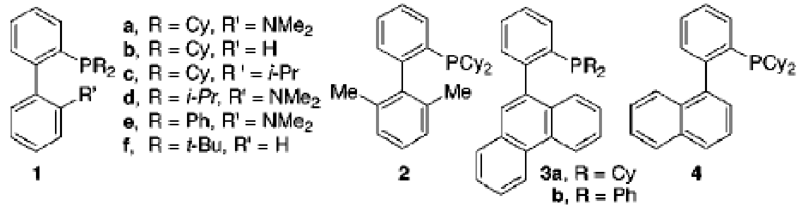
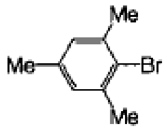
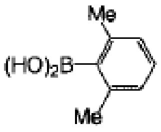
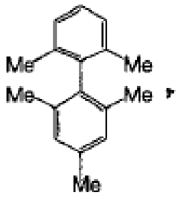
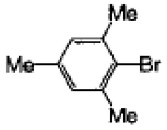
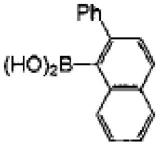
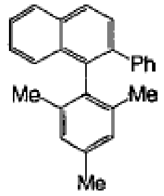
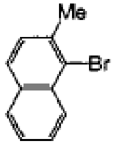
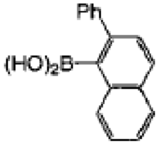
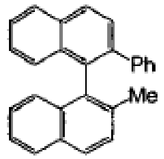
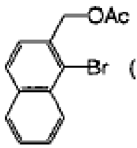
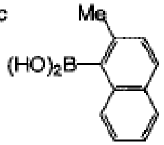
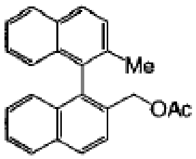
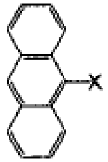
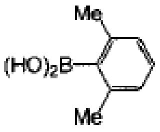
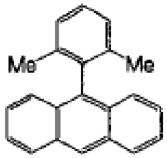
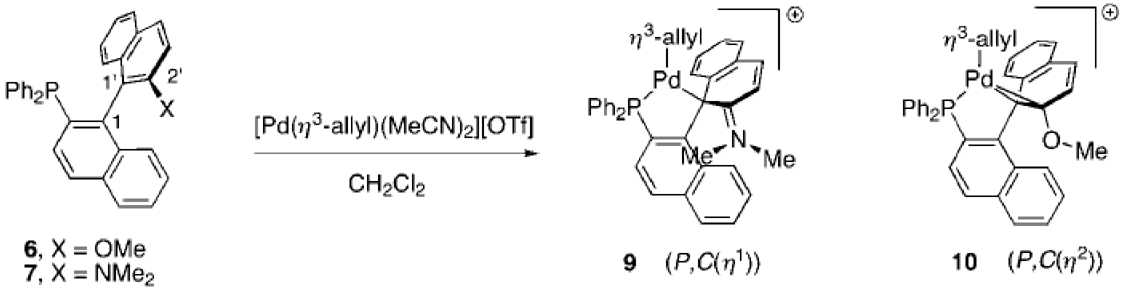


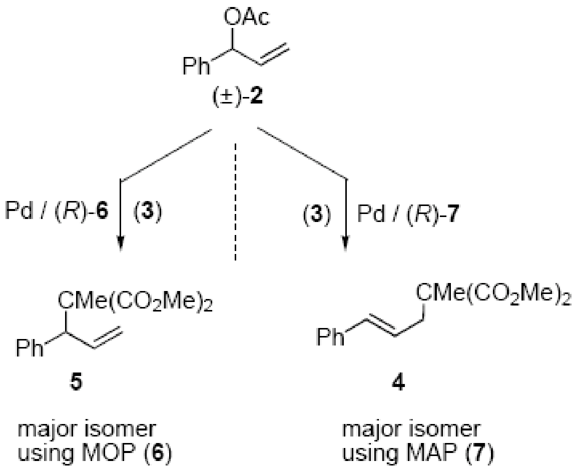
Figure 1. Hindered biarylphosphines.

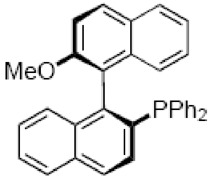
Table 2. Hindered Suzuki Couplings Using Biaryl-Based Ligands[a]

Entry	ArBr	Ar'B(OH)$_2$	Product	L	mol% Pd/ L	Yld, %
1				**3a**	4/8	82
2				**3b**	4/8	$70^{b,c,d}$
3				**3b**	2/4	$90^{b,c}$
4				**3a**	4/8	98
5 (Br) 6 (Cl)				**3a** **3a**	1/1.2 1/1.2	$80^{b,c}$ $82^{b,c}$

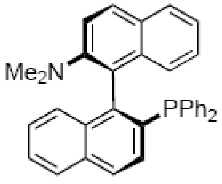


Scheme 1. Preparation of cationic MAP and MOP allylpalladium complexes (+)-**9** and (+)-**10**.



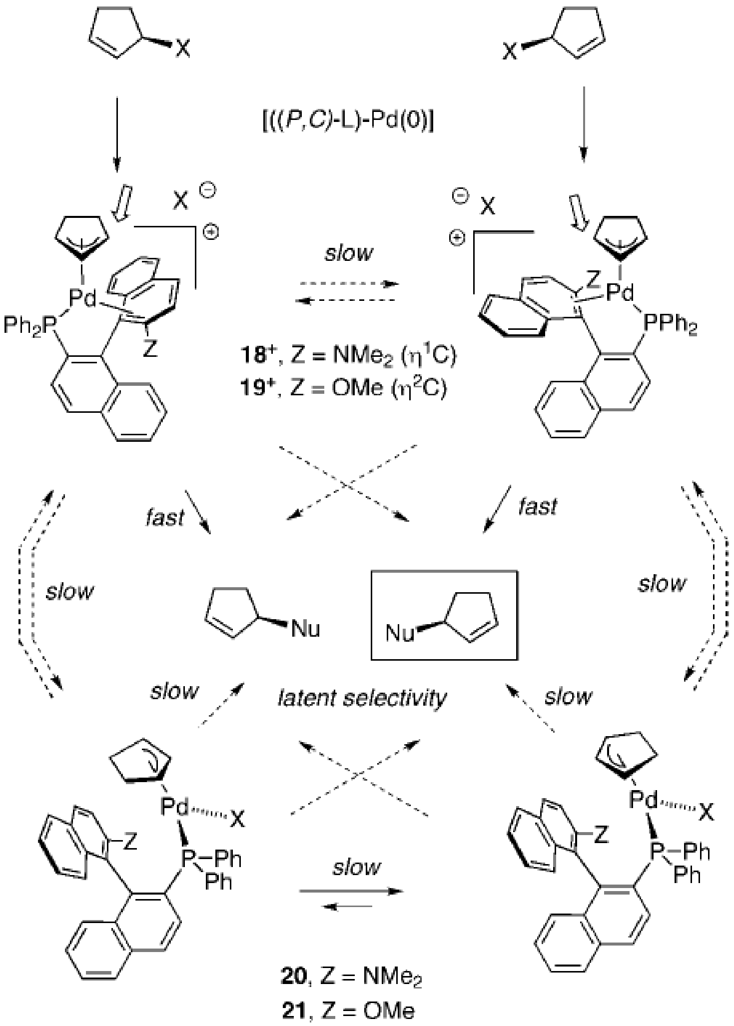


(*R*)-MOP, (*R*)-**6**



(*R*)-MAP, (*R*)-**7**

Lloyd-Jones, G. C.; Kocovsky, P. et al. *Chem. Eur. J.* **2000**, 6, 4348

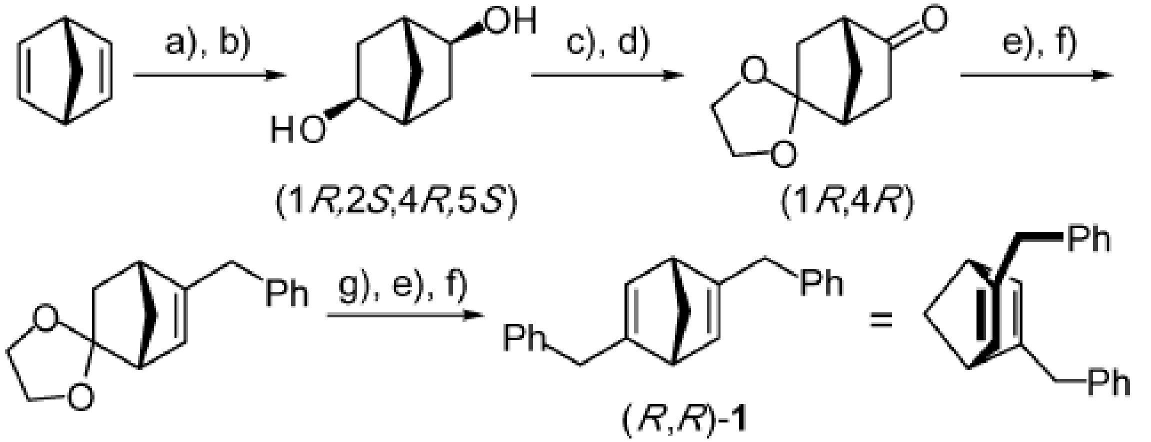


18$^+$, Z = NMe$_2$ (η^1C)
19$^+$, Z = OMe (η^2C)

20, Z = NMe$_2$
21, Z = OMe

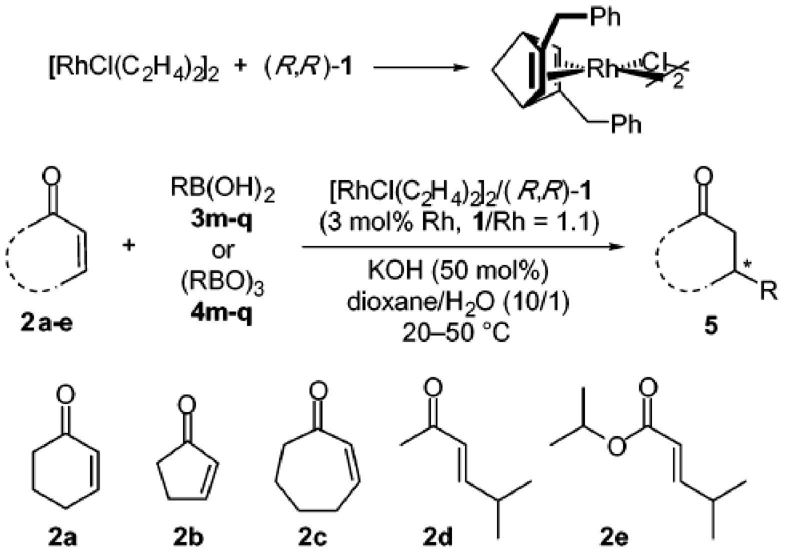
X = $O_2C(tBu)$ or Cl

[2.2.1] diene ligand in asymmetric catalysis



[a] Reagents and conditions: a) $HSiCl_3$, $[PdCl(\pi\text{-}C_3H_5)]_2$/(*R*)-MeO-MOP (0.1 mol % Pd), 0 °C. b) i) MeOH, Et_3N; ii) H_2O_2, KHF_2, THF/MeOH. c) Me_2SO, $(COCl)_2$, Et_3N, CH_2Cl_2. d) $HOCH_2CH_2OH$, TsOH. e) i) LDA, THF; ii) Tf_2Npy-2. f) $PhCH_2MgBr/Et_2O$, $PdCl_2(dppf)$ (1 mol %). g) dil HCl/THF.

Hayashi, T.; Ueyama, K.; Tokunaga, N.;. Yoshida, K. et al. *J. Am. Chem. Soc.* **2003**, 125, 11508



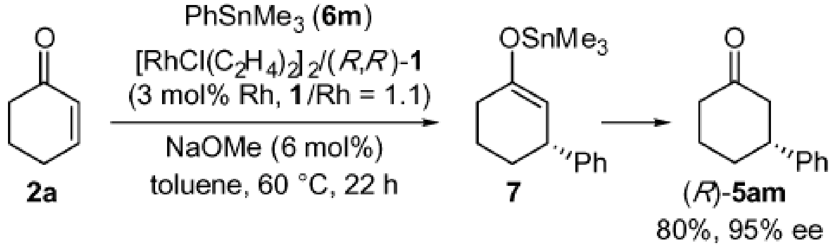
[a] R = Ph (**m**), 3-MeOC$_6$H$_4$ (**n**), 4-MeOC$_6$H$_4$ (**o**), 4-MeC$_6$H$_4$ (**p**), 3-ClC$_6$H$_4$ (**q**), 4-CF$_3$C$_6$H$_4$ (**r**), 4-FC$_6$H$_4$ (**s**), 2-naphthyl (**t**), (*E*)-*n*-C$_5$H$_{11}$CH=CH (**u**).

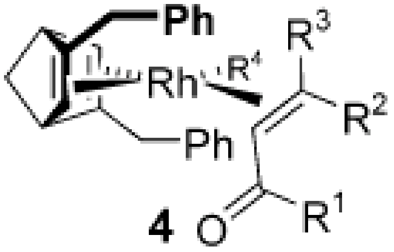
Table 1. Asymmetric 1,4-Addition of Organoboron Reagents RB(OH)$_2$ (**3**) or (RBO)$_3$ (**4**) to α,*β*-Unsaturated Ketones and Esters **2** Catalyzed by [RhCl(C$_2$H$_4$)$_2$]$_2$/(*R*,*R*)-**1**[a]

entry	**2**	**3** or **4**	temp (°C)	time (h)	yield[b] (%) of **5**	% ee[c]
1	**2a**	**3m**	30	1	94 (**5am**)	96 (*R*)
2[d]	**2a**	**3m**	20	3	85 (**5am**)	96 (*R*)
3	**2a**	**3m**	40	1	94 (**5am**)	95 (*R*)
4	**2a**	**4n**	30	1	92 (**5an**)	97 (*R*)
5	**2a**	**4o**	30	1	89 (**5ao**)	95 (*R*)
6	**2a**	**4p**	30	1	88 (**5ap**)	96 (*R*)
7	**2a**	**4q**	50	1	92 (**5aq**)	93 (*R*)
8	**2a**	**3r**	50	1	90 (**5ar**)	99 (*R*)
9	**2a**	**4s**	50	1	91 (**5as**)	97 (*R*)
10	**2a**	**4t**	30	1	96 (**5at**)	96 (*R*)
11	**2a**	**3u**	50	1	73 (**5au**)	88 (*R*)
12	**2b**	**4m**	50	1	88 (**5bm**)	88 (*R*)
13[e]	**2b**	**3u**	50	1	78 (**5bu**)	96 (*R*)
14	**2c**	**3m**	50	1	81 (**5cm**)	90 (*R*)
15	**2d**	**3m**	30	3	81 (**5dm**)	97 (*R*)
16	**2e**	**4m**	50	1	73 (**5em**)	92 (*R*)

[a] The reaction was carried out with enone **2** (0.30 mmol), boron reagent **3** or **4** (0.60 mmol), [RhCl(C$_2$H$_4$)$_2$]$_2$ (3 mol % Rh), (*R*,*R*)-**1** (**1**/Rh = 1.1/1.0), and 1.5 M aq KOH (0.10 mL) in dioxane (1.0 mL). [b] Isolated yield by silica gel chromatography. [c] Determined by HPLC analysis with chiral stationary phase columns: Daicel Chiralcel OD-H for **5am**, **5an**, **5ar**, **5at**, **5cm**, **5dm**, and **5em**; OB−H for **5bm**; AD for **5ao**, **5ap**, **5aq**, and **5as**; and AS for **5au** and **5bu**. [d] The ratio of **3m**/**2a** is 1.3/1.0. [e] The amount of the rhodium catalyst is 10 mol %.

Model to rationalize the stereochemical outcome





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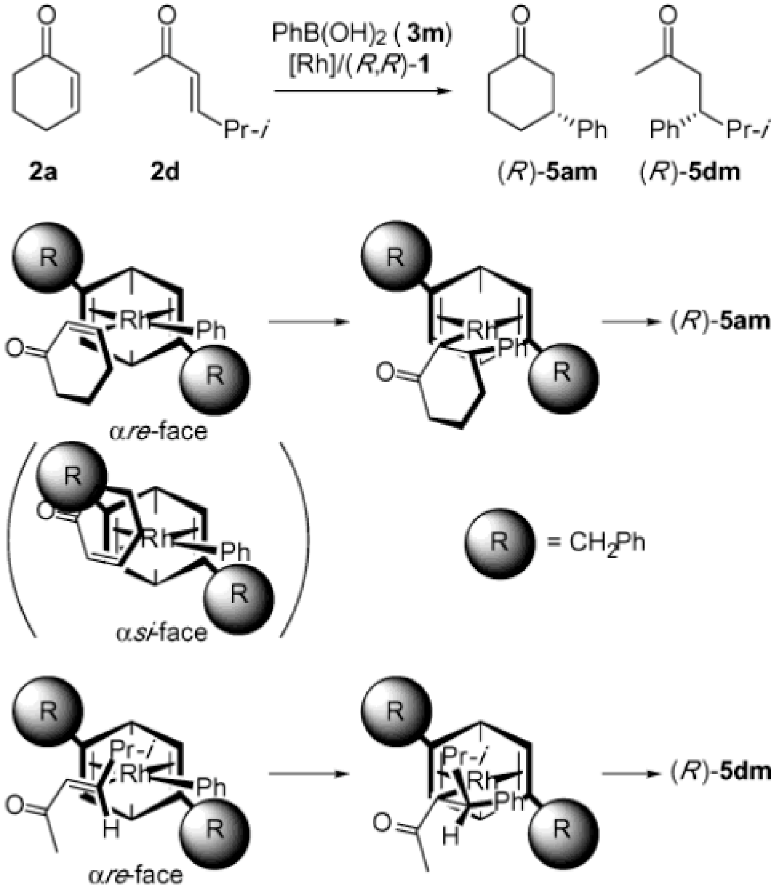
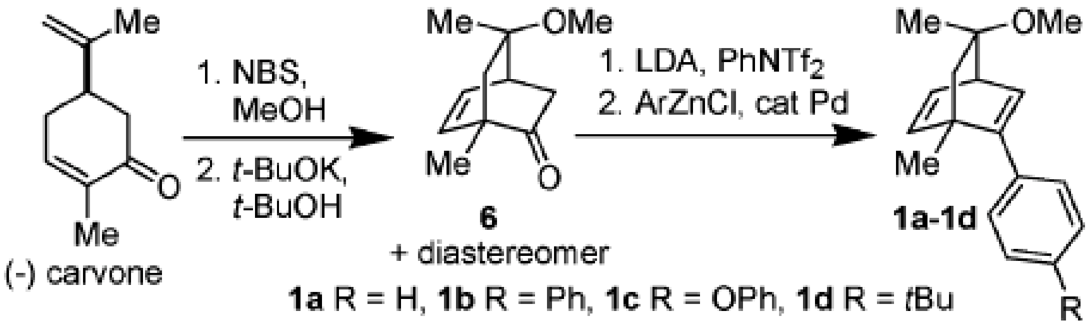
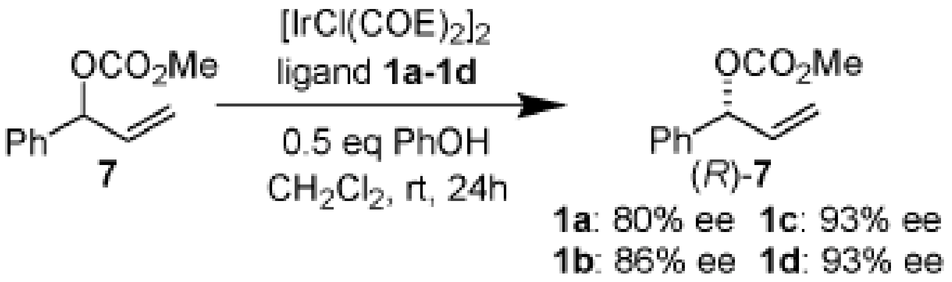
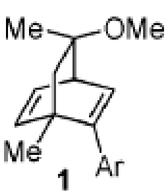


[2.2.2] diene ligand in asymmetric catalysis

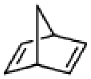




Fischer, C.; Defieber, C.; Suzuki, T.; Carreira, E. M. *J. Am. Chem. Soc.* **2004**, 126, 1628



1



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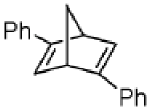
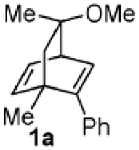


(±)-**5**



1a

Not working in this reaction

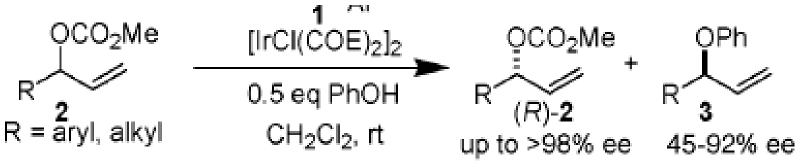


Table 1. Kinetic Resolution of Allylic Carbonates (Scheme 1)[a]

entry	R	yield/% (%)[b]	ee/% [c]
1	C_6H_5	32 (72)	93
2	2-naphthyl	33 (81)	94
3	1-naphthyl	28 (78)	90
4	$(3\text{-MeO})C_6H_4$	37 (87)	97
5	$(4\text{-Br})C_6H_4$	38 (88)	97
6	$(4\text{-Cl})C_6H_4$	39 (87)	91
7	$(4\text{-F})C_6H_4$	34 (82)	85
8	$(3\text{-Br})C_6H_4$	40 (90)	88
9	$(4\text{-CF}_3)C_6H_4$	37 (83)	96
10	$(4\text{-NO}_2)C_6H_4$	45 (94)	95
11	$(4\text{-CO}_2\text{Me})C_6H_4$	46 (91)	80
12	$(3\text{-Me})C_6H_4$	39 (89)	80
13	$(4\text{-Me})C_6H_4$	28 (78)	87
14	cC_6H_{11}	30 (68)	>98
15	$BnOCH_2$	32 (77)	84

[a] Reactions conducted with 1.5 mol % $[IrCl(COE)_2]_2$, 3.6 mol % **1d** and 0.5 mmol **2** in 3 mL of CH_2Cl_2. [b] The combined yield of recovered optically active carbonate and optically active phenyl ether in parentheses. [c] ee was determined by chiral HPLC; the absolute configuration has been established as (*R*) for entries 1, 3, and 6. For details see Supporting Information.

Conclusions:

1. **As a consequence of chelation, dienes with the proper geometry can form intriguingly complex which may result in catalyst with enhanced stability, selectivity and catalytic activity.**
2. **Bidentate ligands consisting of an alkene unit and another coordination element, as indicated by Rh and Ir complexes should become a valuable class of ligands with new catalytic properties.**