Recent Examples of Cobalt-catalyzed Cross-coupling Reactions of Alkyl Halides

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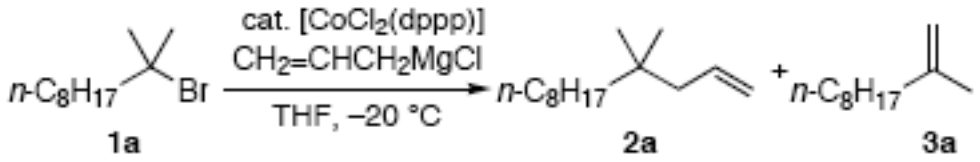
January 20th, 2006

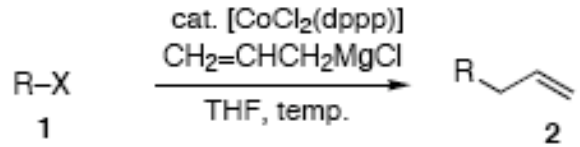
Cobalt-catalyzed Cross-coupling of Tertiary Halides



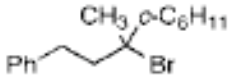
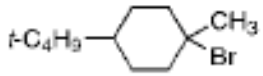
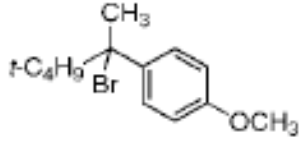
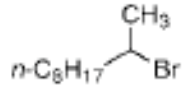
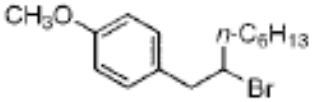
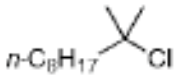
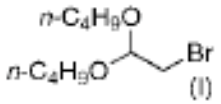
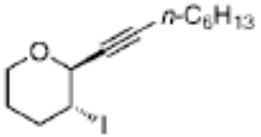
1a 2a 3a

- yields: 90% of **2a** and 8% of **3a**
- background reaction gives no allylation product

Tsuji, T.; Yorimitsu, H.; Oshima, K. *Angew. Chem., Int. Ed.,* **2002**, *41*, 4137-4139



1 2

1		Temperature [°C]	Yield of 2 [%]
	**1b**	−20	83
	**1c**[a]	0	76[b]
	**1d**	−20	73[c]
	**1e**	0	57
	**1f**	−20	84
	**1g**	0	30
(I)	**1g-I**	−40	82
	**1a-Cl**	20	31
	**1h**	0	49
(I)	**1h-I**	−40	82
	**1i-I**	−40	76[d]

[a] *trans*/*cis* = 87/13. [b] *trans*/*cis* = 82/18. [c] DPPE was used. [d] *trans*/*cis* = 86/14.

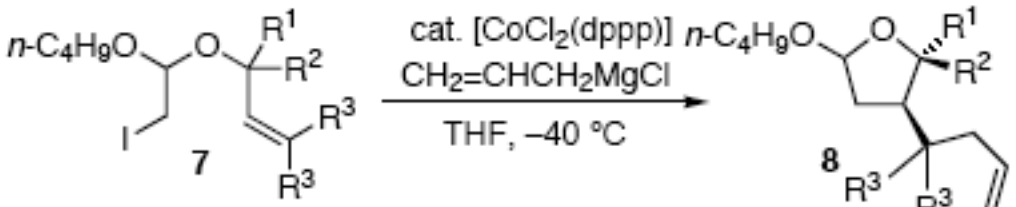
The Scope of

Cobalt-phosphine-catalyzed

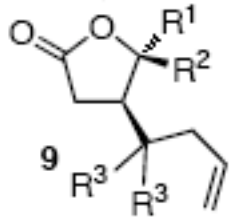
Cross-coupling

Reaction

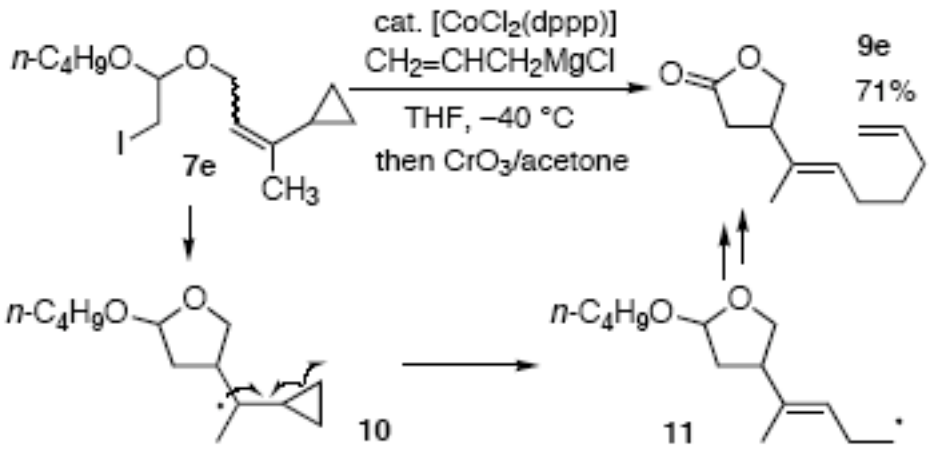
Cobalt-catalyzed Cyclization of Iodoacetals



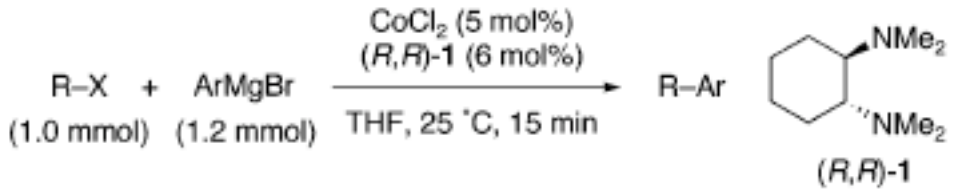
	R^1	R^2	R^3	Yield of **9** [%]
7a	H	H	H	77
7b	CH_3	CH_3	H	100
7c	H	H	CH_3	98
7d	*n*-C_5H_{11}	H	H	77



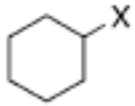
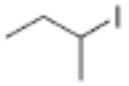
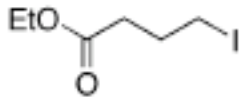
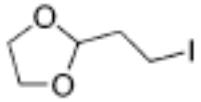
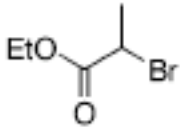
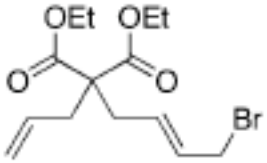
Cobalt-catalyzed Reaction to Give Ring Opening Product



Cobalt-diamine complex as a Catalyst for Coupling of Alkyl Halides with Arylmagnesium Reagents

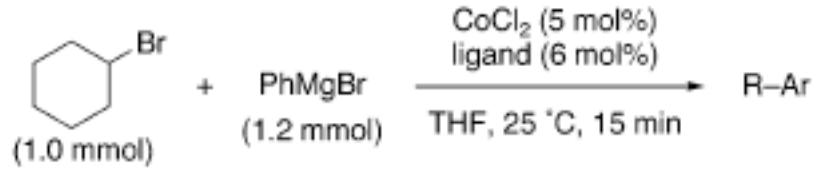


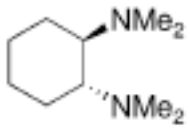
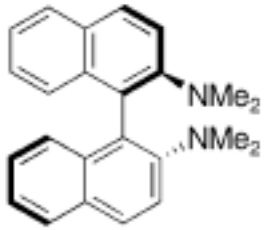
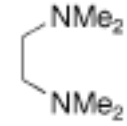
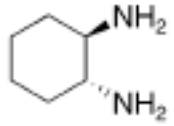
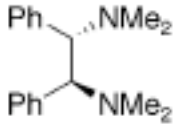
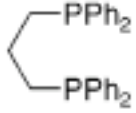
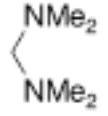
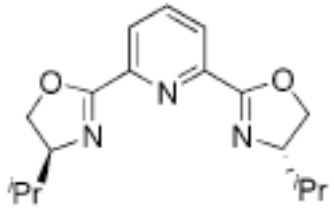
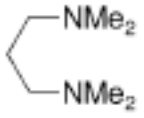
Ohmiya, H.; Yorimitsu, H.; Oshima, K. *J. Am. Chem. Soc.,* **2006**, *128*, ASAP articles

entry	R–X	Ar	R–Ar
1		Ph	95 (X=I)
2		Ph	95(X=Br)[a]
3		2-naphthyl	93 (X=Br)
4	$^{n}C_8H_{17}$–X	Ph	99 (X=I)
5		Ph	80 (X=Br)
6		Ph	10 (X=Cl)
7		2-MeC_6H_4	99 (X=I)
8		2-thienyl	86 (X=I)
9		1-phenylvinyl	72 (X=I)[b]
10		Ph	73
11		4-$MeOC_6H_4$	87
12		Ph	91
13		Ph	86
14		Ph	88
15		Ph	56[c]

[a] When the reaction was performed on a 10 mmol scale, an 87% yield of the product was obtained. [b] $CoCl_2$ (10 mol %) and (*R*,*R*)-**1** (36 mol %) were used. [c] No cyclopentane ring was observed.

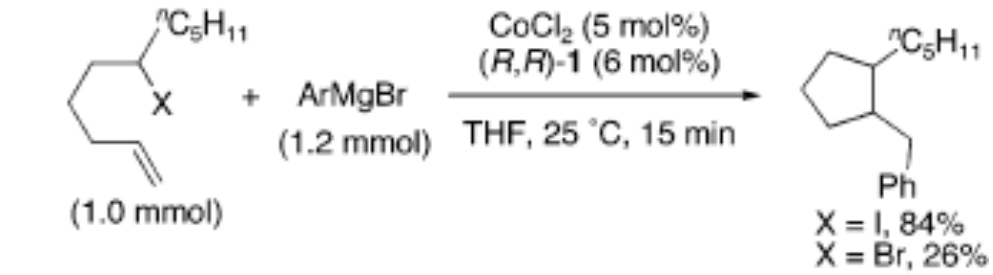
Cobalt-diamine Catalyzed Cross-coupling Reaction

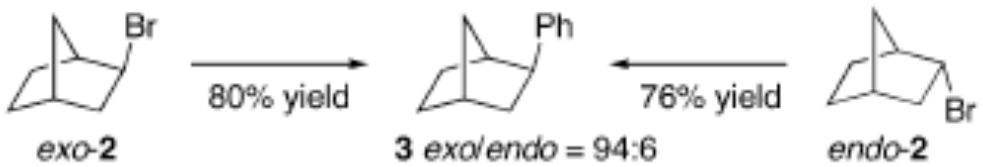


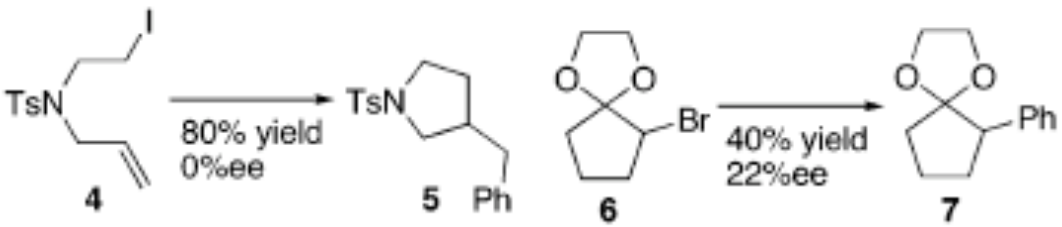
entry	ligand	yield /%	entry	ligand	yield /%
1		95	6		<1
2		43	7		<1
3		76	8		<1
4		<1	9		<1
5		<1			

Ligand Effect

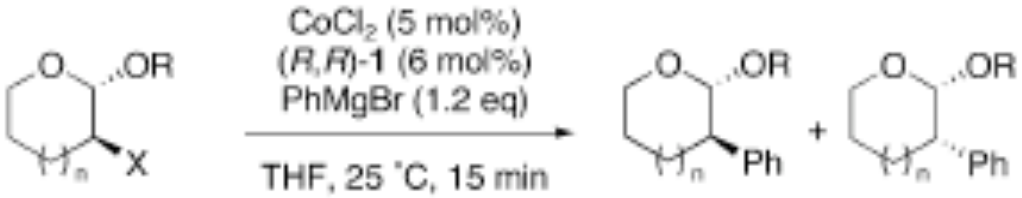
Justification of the Existence of Carbon-centered Radicals







Diastereoselective Cross-coupling of Halo Acetals



entry	n	X	R	yield	trans/cis
1	1	I	Me	83%	51:49
2	1	I	^{i}Pr	81%	60:40
3	0	Br	Me	82%	95:5
4	0	Br	^{i}Pr	80%	96:4

Total Synthesis of AH13205