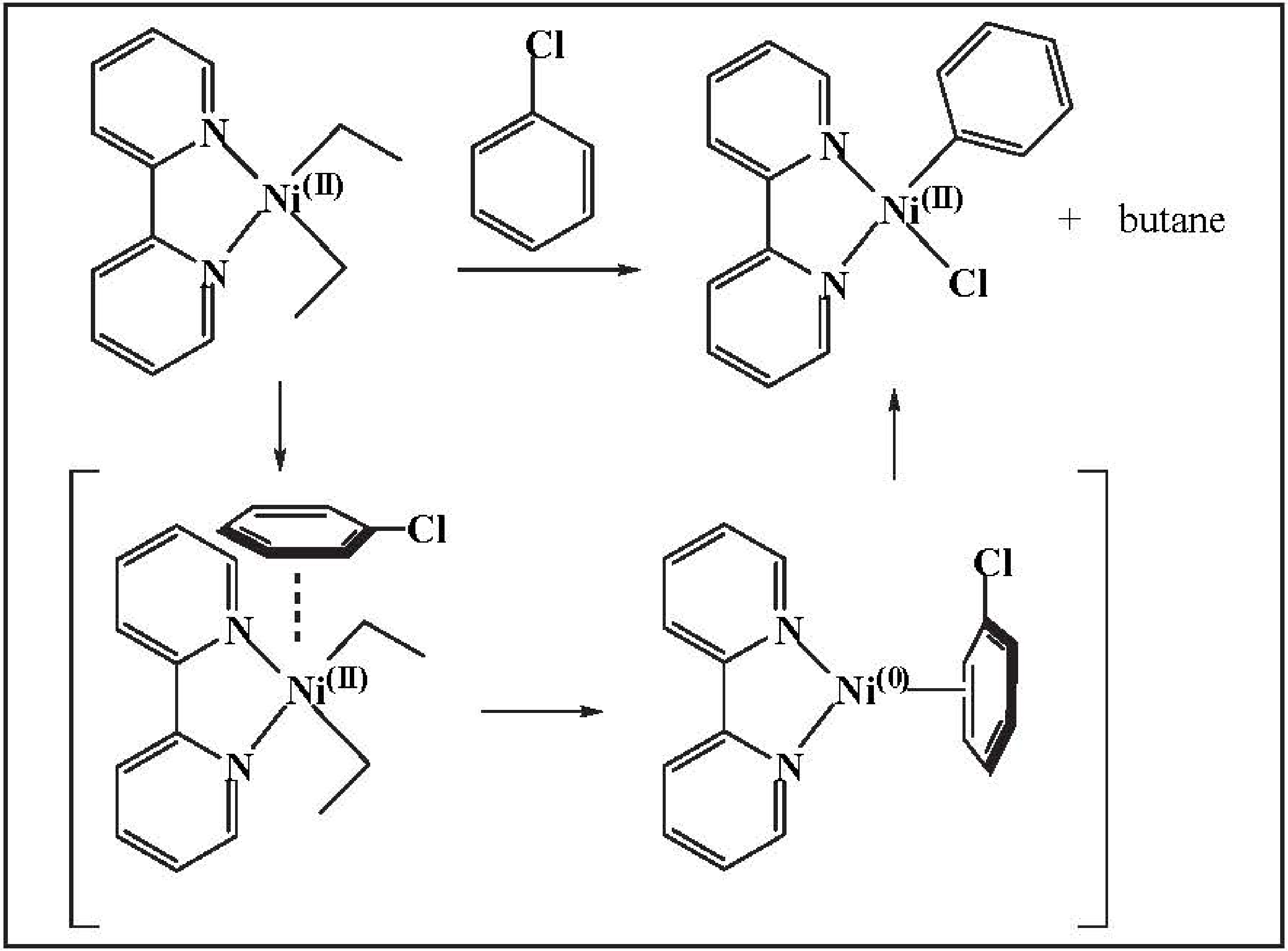
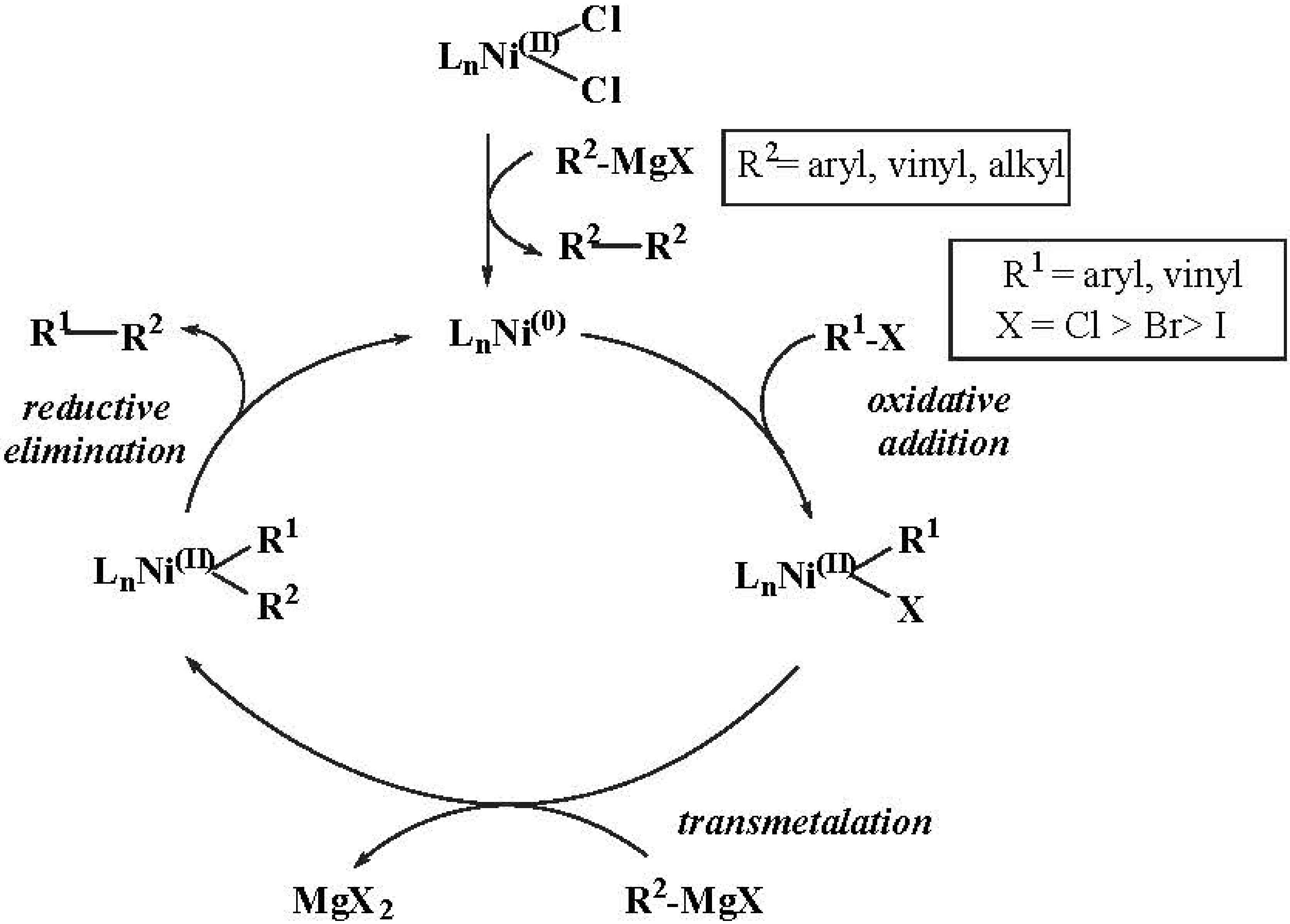
Reductive elimination/Oxidative addition: Yamamoto *JOMC* **1970** (24) C63. "Preparation of a phenyl-nickel complex, phenyl (dipyridyl)nickel chloride, an olefin dimerization catalyst.




$L_nNi^{(II)}Cl_2$
R^2-MgX
R^2—R^2
R^2 = aryl, vinyl, alkyl
R^1 = aryl, vinyl
X = Cl > Br> I
$L_nNi^{(0)}$
R^1—R^2
reductive elimination
R^1-X
oxidative addition
$L_nNi^{(II)}(R^1)(R^2)$
$L_nNi^{(II)}(R^1)(X)$
transmetalation
MgX_2
R^2-MgX

For this Kumada coupling reaction, the following product distributions were obtained using two different ligands, PPh_3(n = 2) and a chelating ligand dppf.

1. Propose a mechanism how these products were made.
2. Explain why the two ligands lead to different results.

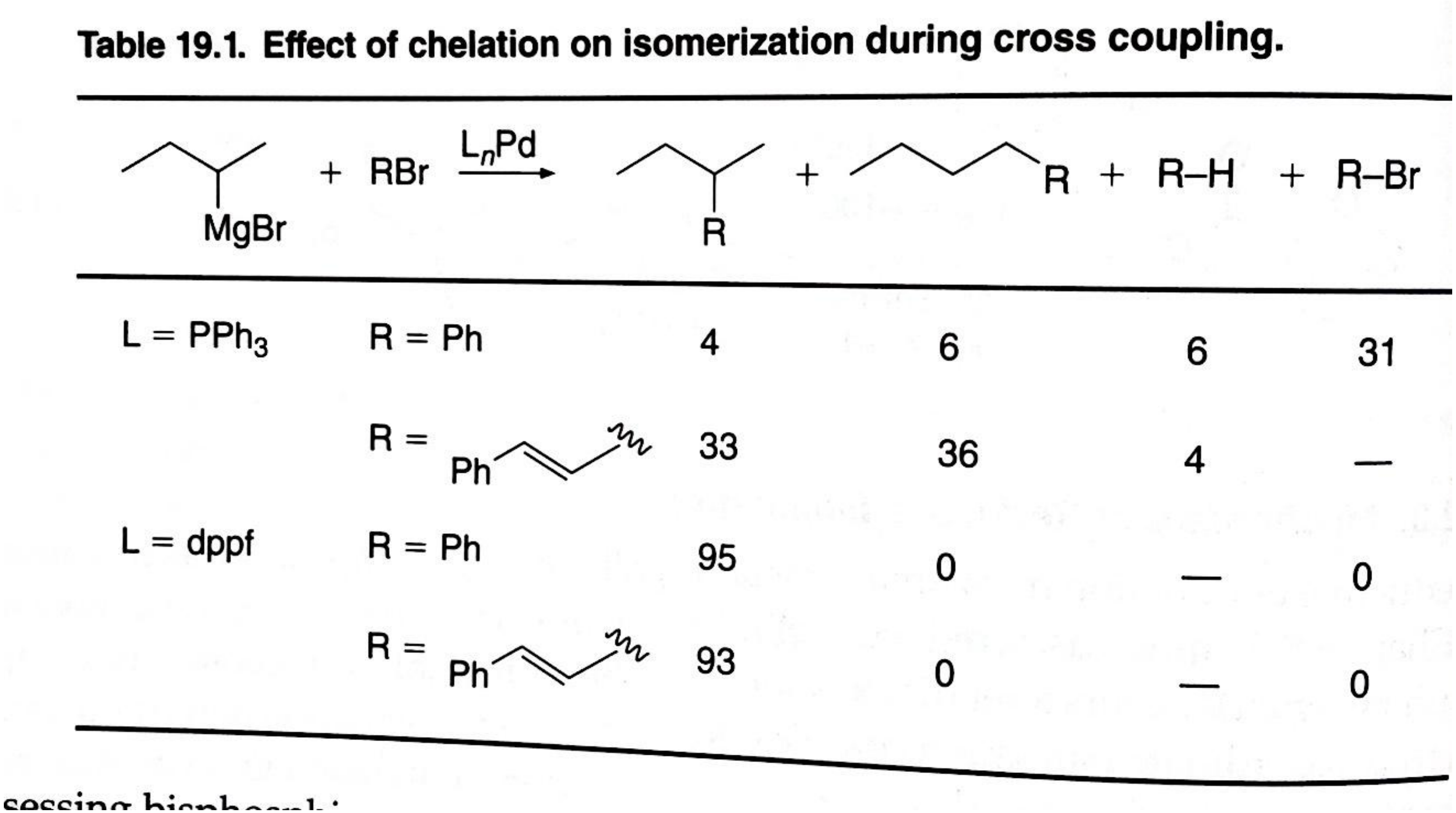
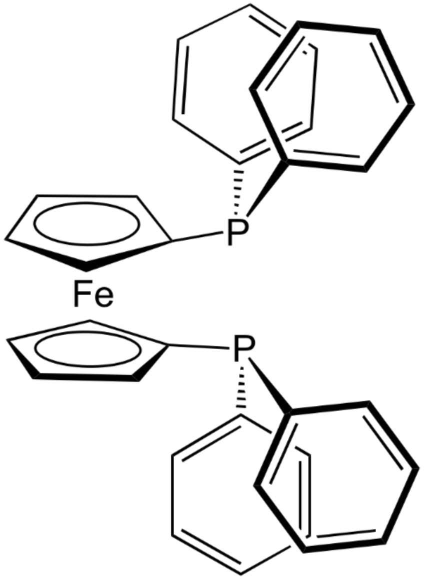


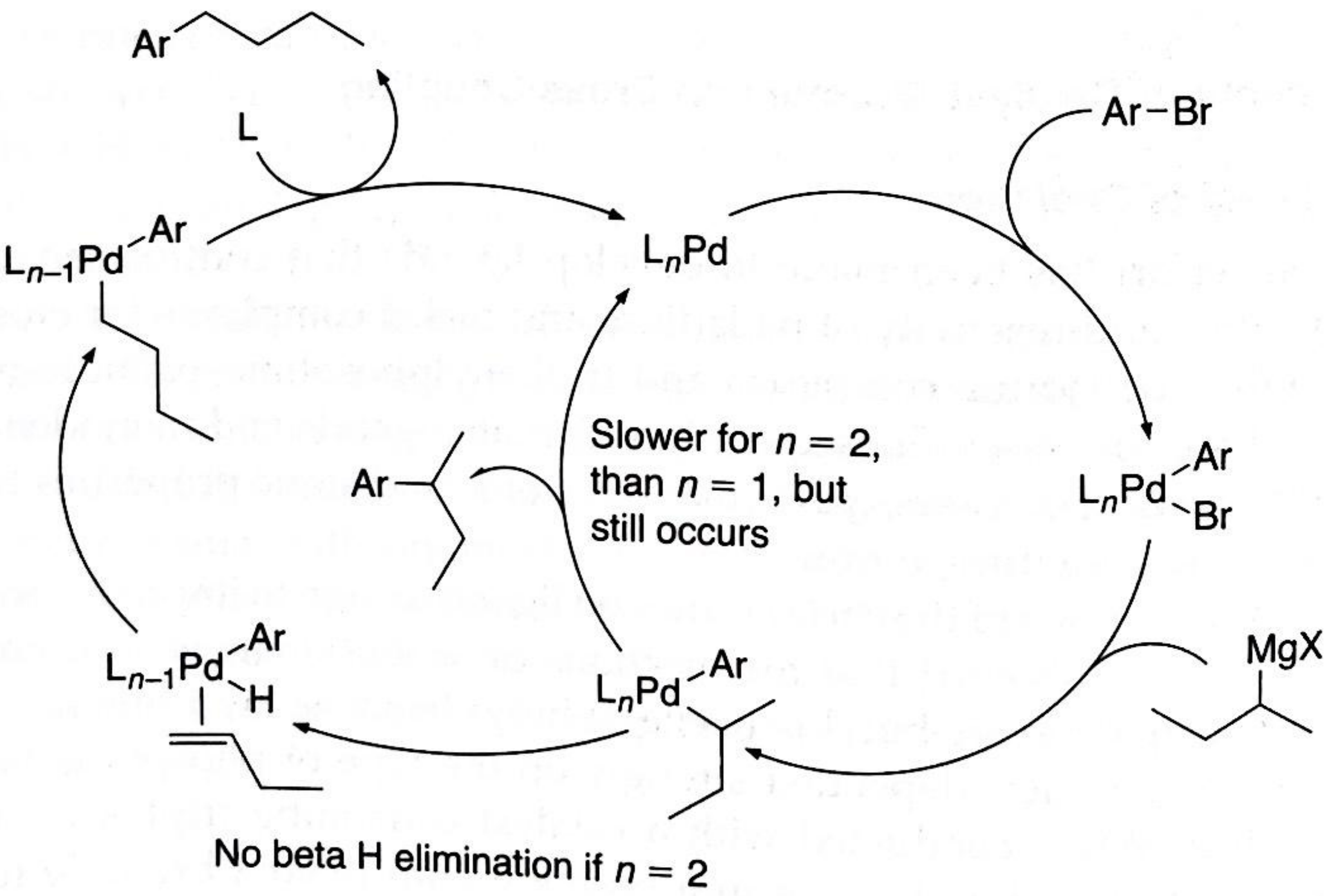
Table 19.1. Effect of chelation on isomerization during cross coupling.

MgBr	+ RBr $\xrightarrow{L_nPd}$	R	+ R	+ R–H	+ R–Br
L = PPh_3	R = Ph	4	6	6	31
	R = Ph	33	36	4	—
L = dppf	R = Ph	95	0	—	0
	R = Ph	93	0	—	0

sessing bisphosph

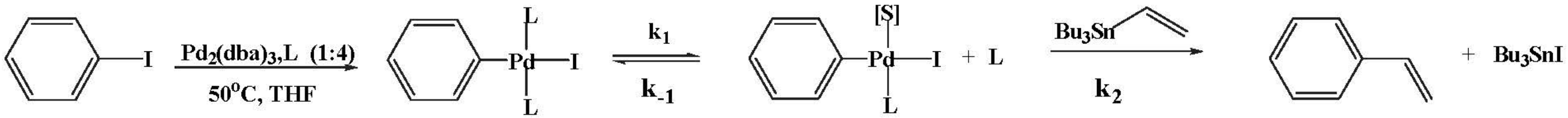


dppf


Ar
L
Ar−Br
$L_{n-1}Pd$ Ar
L_nPd
Slower for $n = 2$, than $n = 1$, but still occurs
Ar
L_nPd Ar Br
MgX
$L_{n-1}Pd$ Ar H
L_nPd Ar
No beta H elimination if $n = 2$

Scheme 19.7

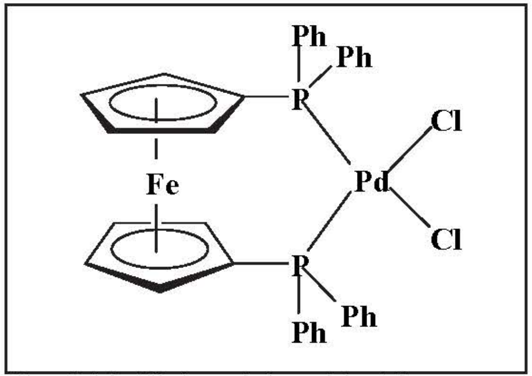
Kinetics studies support a mechanism involving fast oxidative addition followed by a rate-determining transmetalation event which requires initial solvent/ligand exchange. This predissociation event is disfavored thermodynamically with strong donor ligands such as PPh_3, and more favored with weak donor ligands such as $AsPh_3$.



1

2

Suzuki: Ligand Effects for Csp^3-Csp^2 couplings



dppf, bis(diphenylphosphino)ferrocene

$PdCl_2$(dppf) is often found to be a superior catalyst for Suzuki cross coupling reactions between boron-alkyl derivatives (possessing β-hydrogens) and vinyl/aryl halides/triflates. This ligand is thought to favor reductive elimination vs. competitive β-hydride elimination for at least two reasons:

· The bidentate phosphine ligand enforces a *cis* geometry between the alkyl and vinyl/aryl substituents; this *cis* geometry is required for reductive elimination

· The large bite angle for this bidentate phosphine ligand results in a smaller angle between the alkyl and vinyl/aryl substituents. Recall that minimization of the angle between two metal-bound substituents is thought to promote reductive elimination event by increasing orbital overlap:

Suzuki *JACS* **1989** (111) 314
see also **Hayashi** *JACS* **1984** (106) 158; **Brown** *Inorg. Chimica Acta*, **1994** (220) 249.
Danishevsky *ACIEE* **2001** (40) 4544.

Why 3-coordinate and 5-coordinate are faster in reductive elimination than 4- and 6-coordinate?

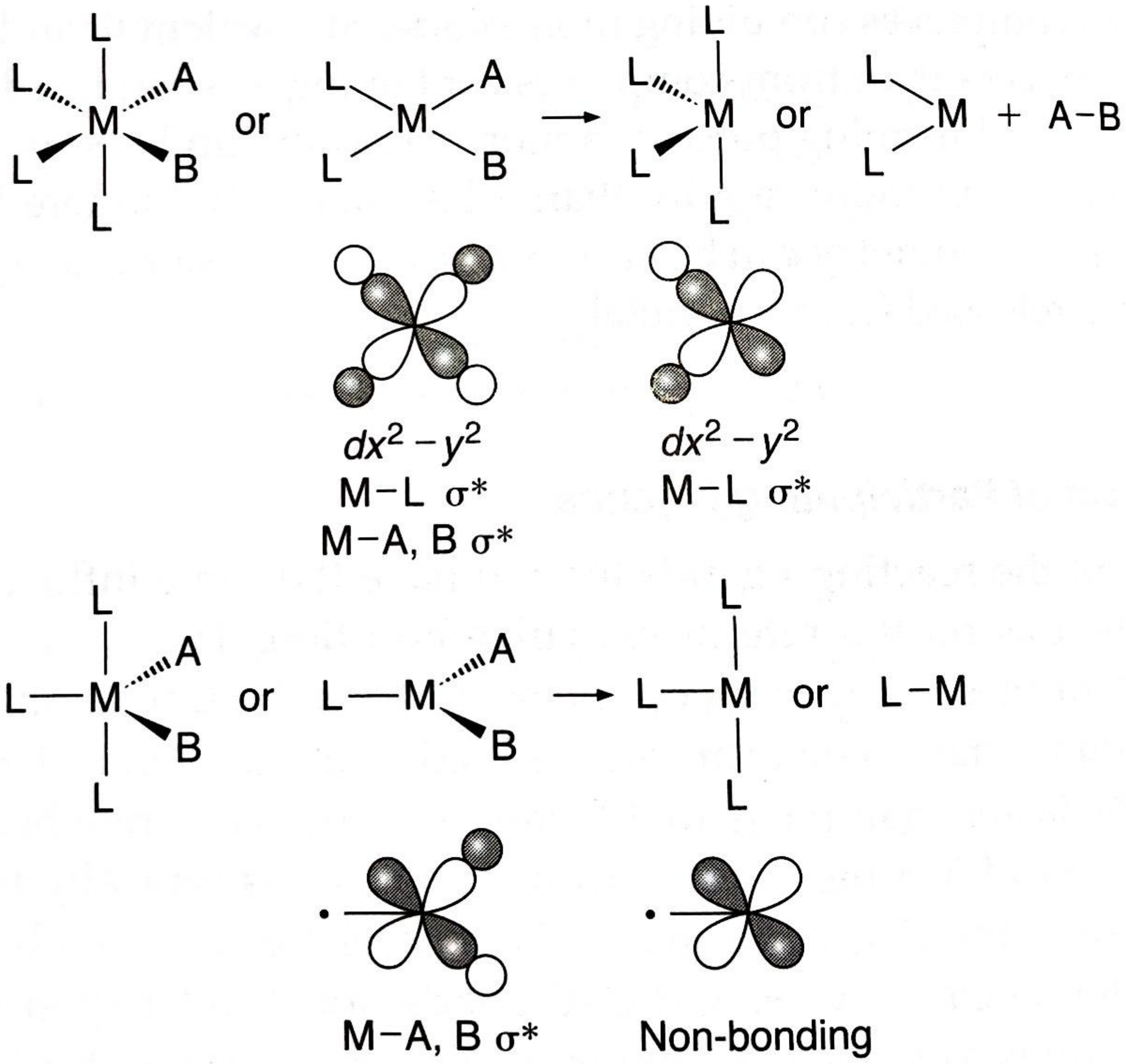


Figure 8.1.
The origin of the relative rates for reductive elimination from complexes with odd and even coordination numbers.