特異なカルベン配位子を有する安定かつ高反応性なニッケル錯体触媒の開発

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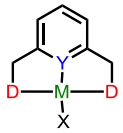
1. Introduction

◆ Complexes of Pincer-type Ligands

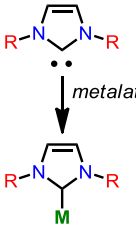


Y = C, N
D = PR_2, NR_2, OR, SR

➢ This complexes are formed the **hard structure** by *a central M-C σ-bond* and *two coordinate bonds*.

➢ Easy to **fine tuning**.

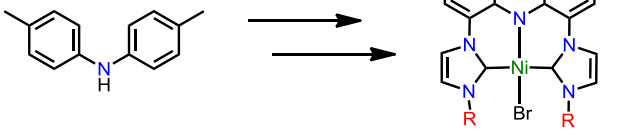
◆ *N*-Heterocyclic Carbene (NHC)



➢ Formed the **hard bond** to transition metals.

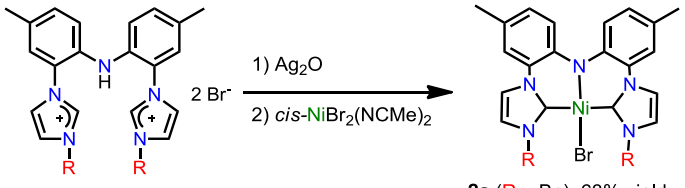
➢ **Strong electron donor ability**

This Work



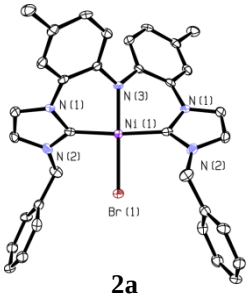
2a (R = Bn)
2b (R = *n*-Bu)

2. Synthesis of Ni Complexes 2



1

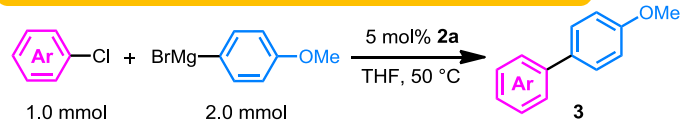
2a (R = Bn) 63% yield
2b (R = *n*-Bu) 51% yield



2a

Crystal System : monoclinic
Space Group : *C*2/c (#15)
Z value : 4
Residuals : *R*1 = 0.0580
Ni-C(carbene) : 1.902(3) Å
Br-Ni-C(carbene) : 92.63(11)˚
N-Ni-C(carbene) : 87.37(11)˚
Br-Ni-N : 180.0˚

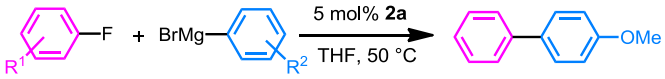
3. Kumada Cross Coupling Reaction



1.0 mmol　2.0 mmol　**3**

Entry	Ar	3	Time (h)	Isolated Yield (%)
1	Ph	**3a**	24	89[a]
2	*o*-MeC_6H_4	**3b**	48	87
3	*p*-$CF_3C_6H_4$	**3c**	67	38
4	1-naphthyl	**3d**	44	95
5	3-pyridyl	**3e**	19	90
6	3-thiophenyl	**3f**	26	22

[a] GC yield.



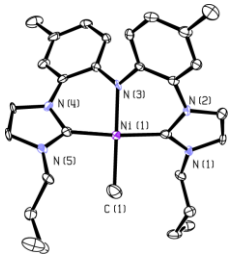
1.0 mmol　2.0 mmol　**3a**

R^1 = H　R^2 = *p*-OMe　74% yield / 65 h
R^1 = *p*-OMe　R^2 = H　53% yield / 75 h

4. Synthesis of Ni Complexes 4

2b

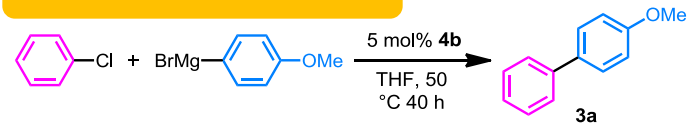
4a (R = Me) 40% yield
4b (R = *p*-$MeOC_6H_4$) 91% yield[a]
[a] Including by-product



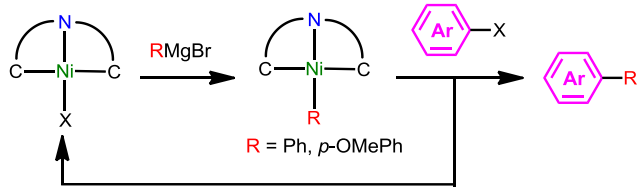
4a

Crystal System : triclinic
Space Group : *P*$\bar{1}$ (#2)
Z value : 2
Residuals : *R*1 = 0.0945

5. Reaction Mechanism



3a
35% yield



R = Ph, *p*-OMePh