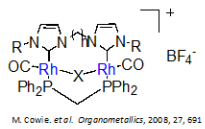
イリジウム錯体の配位空間を利用した生体機能分子の高効率合成反応の構築

研究代表者　福澤 信一　研究員

1. Introduction

・ Most of the complexes containing bis-NHCs are Chelating or Pincer structures

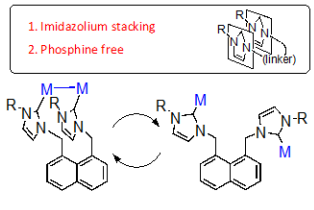
・ Few report : bis-NHC ligand and metal (1:2) bridging complexes



M. Cowie. *et al. Organometallics*, 2008, 27, 691

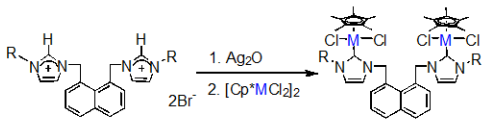
・ Synthesis of bis-NHC ligand and metal (1:2) bridging complex

1. Imidazolium stacking
2. Phosphine free



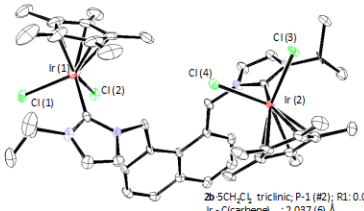
Methylnaphthalene bridging NHC

2. Synthesis of Complexes 2

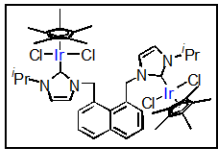


2a M=Ir , R=Me
2b M=Ir , R=^{i}Pr
2c M=Rh, R=Me

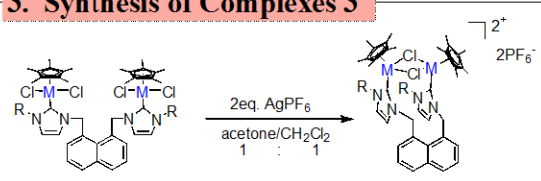
	R	M	yield (%)	^{13}C {^{1}H} NMR (ppm) (NCN)
2a	Me	Ir	75	179.9
2b	^{i}Pr	Ir	75	179.7
2c	Me	Rh	99	170.3 ($^1J_{C\text{-}Rh}$ = 56.4 Hz)



2b·5CH_2Cl_2 triclinic; P-1 (#2); R1: 0.0460
Ir - C(carbene) : 2.037 (6) Å
2.053 (5) Å



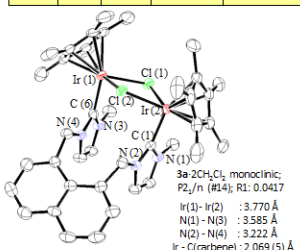
3. Synthesis of Complexes 3



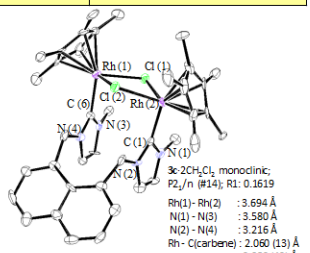
2a M=Ir , R=Me
2b M=Ir , R=^{i}Pr
2c M=Rh, R=Me

3a M=Ir , R=Me
3b M=Ir , R=^{i}Pr
3c M=Rh, R=Me

	R	M	yield (%)	^{13}C {^{1}H} NMR (ppm) (NCN)	^{31}P{^{1}H} NMR
3a	Me	Ir	78	157.0	–143.7 (sep, J_{PF} = 713 Hz, PF_6)
3b	^{i}Pr	Ir	76	158.0	–143.8 (sep, J_{PF} = 713 Hz, PF_6)
3c	Me	Rh	72	167.2 ($^1J_{C\text{-}Rh}$ = 58.8 Hz)	–143.7 (sep, J_{PF} = 713 Hz, PF_6)

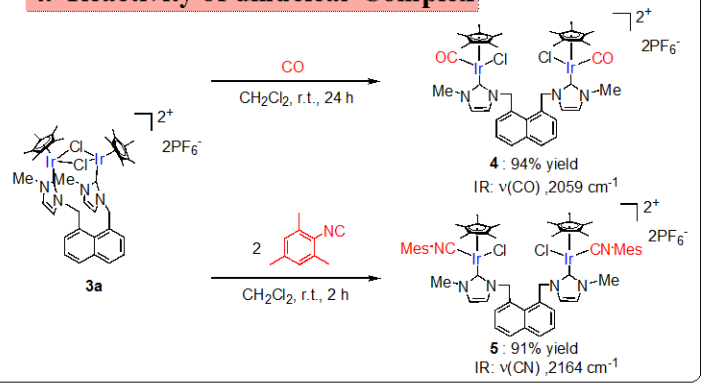


3a·2CH_2Cl_2 monoclinic;
$P2_1/n$ (#14); R1: 0.0417
Ir(1)- Ir(2) : 3.770 Å
N(1) - N(3) : 3.585 Å
N(2) - N(4) : 3.222 Å
Ir - C(carbene) : 2.069 (5) Å
2.059 (5) Å



3c·2CH_2Cl_2 monoclinic;
$P2_1/n$ (#14); R1: 0.1619
Rh(1)- Rh(2) : 3.694 Å
N(1) - N(3) : 3.580 Å
N(2) - N(4) : 3.216 Å
Rh - C(carbene) : 2.060 (13) Å
2.082 (12) Å

4. Reactivity of dinuclear Complex

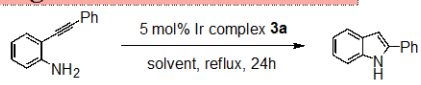


3a

4 : 94% yield
IR: ν(CO) ,2059 cm^{-1}

5 : 91% yield
IR: ν(CN) ,2164 cm^{-1}

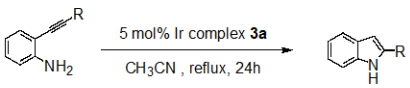
5. Screening of Reaction Condition[a]



entry	solvent	GC yield (%)
1	CH_3CN	73
2[b]	CH_3CN	52
3	CH_3CH_2CN	62
4	DCE	32
5	THF	15
6	1.4-dioxane	19
7	DMF	38
8	IPA	33

[a] Ir complex **3a** (0.0125 mmol), 2-phenylethynyl aniline (0.25 mmol), solvent (2 mL) were employed.
[b] Using Rh complex **3c**

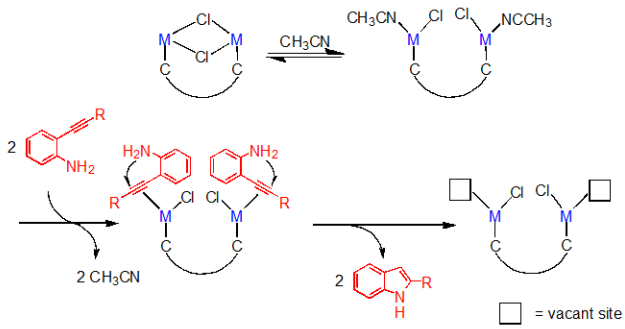
6. Intramolecular Hydroamination[a]



entry	R	isolated yield (%)
1	n-hex	80
2	cyclopropyl	75
3	CH_2Ph	69
4	*o*-$CH_3C_6H_4$	78
5	*m*-$CH_3C_6H_4$	70
6	*p*-$CH_3C_6H_4$	68
7	*p*-$MeOC_6H_4$	37
8	*p*-$CF_3C_6H_4$	24
9	*p*-$NO_2C_6H_4$	15
10	2-pyridyl	N.R.
11	2-thiophenyl	76

[a] Ir complex **3a** (0.0125 mmol), 2-aminophenyl alkynyl compound or alkynylamine (0.25 mmol), acetonitrile (2 mL) were employed.

7. Reaction Mechanism



□ = vacant site