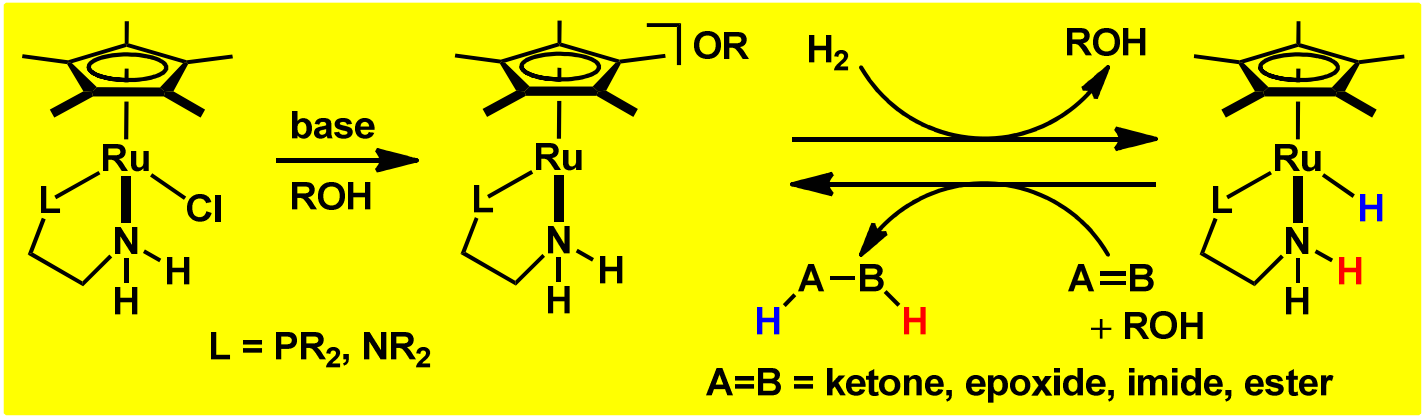
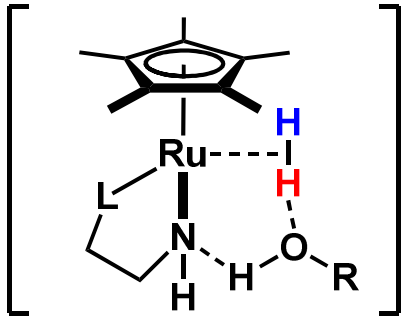
1Da-02

新規トリフリルアミドテザー型Cp'Ru錯体の合成と反応性

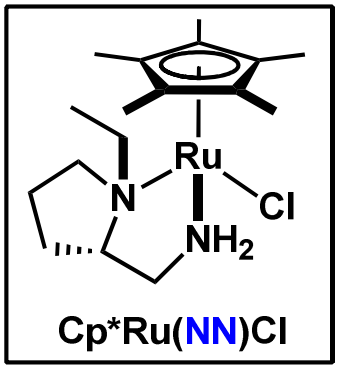
（東工大院理工・九大先導研）〇坂本直紀・遠藤慶徳・
伊藤正人・碇屋隆雄

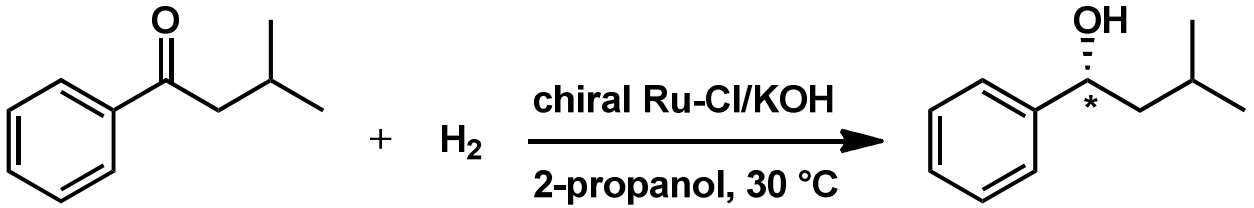
BIFUNCTIONAL CHIRAL Cp*Ru CATALYSTS FOR ASYMMETRIC HYDROGENATION





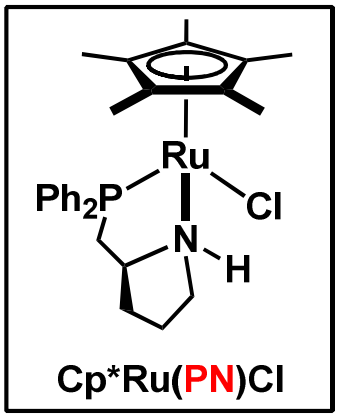
chiral Cp*Ru catalyst

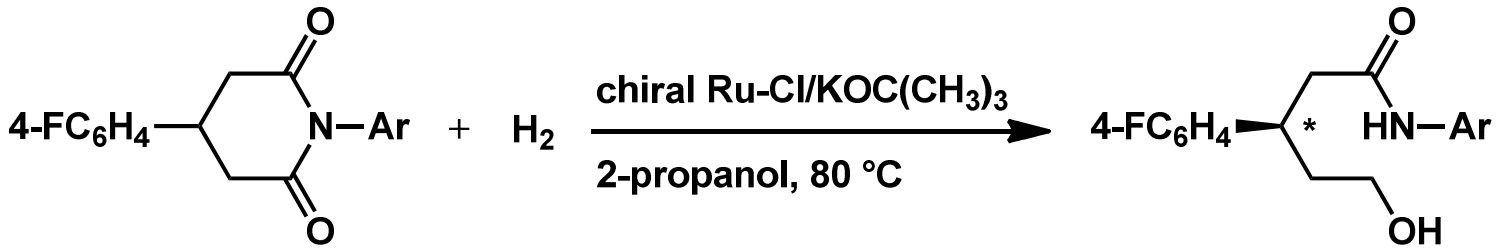




98% yield, 95% ee

Organometallics **2001,** *20,* 379–381.

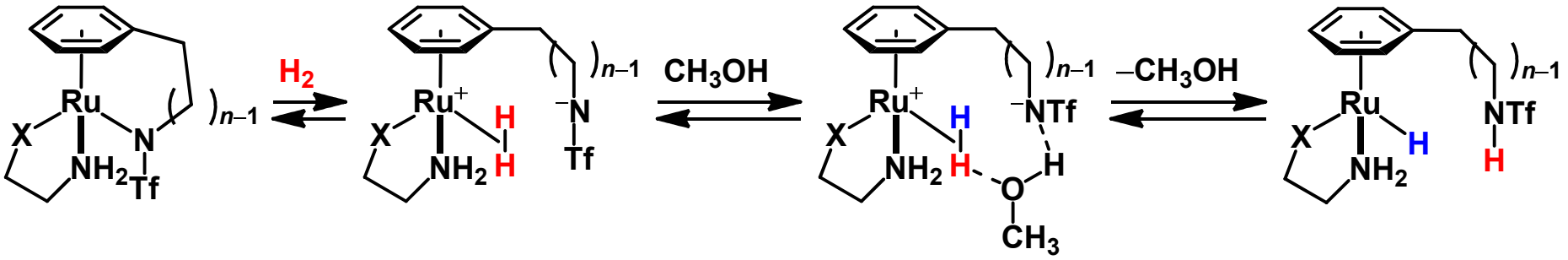




>99% yield, 98% ee

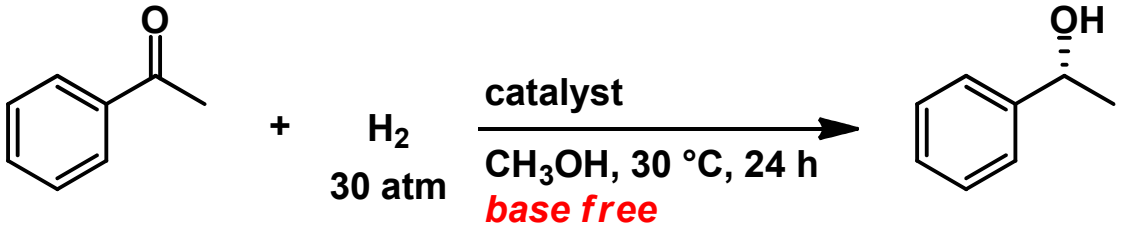
J. Am. Chem. Soc. **2007,** *129,* 290–291.
J. Am. Chem. Soc. **2010,** *132,* 11414–11415.

BASE-FREE TETHERED BIFUNCTIONAL HYDROGENATION CATALYSTS



Organometallics **2008,** *27,* 6053-6055.

Asymmetric hydrogenation of ketone



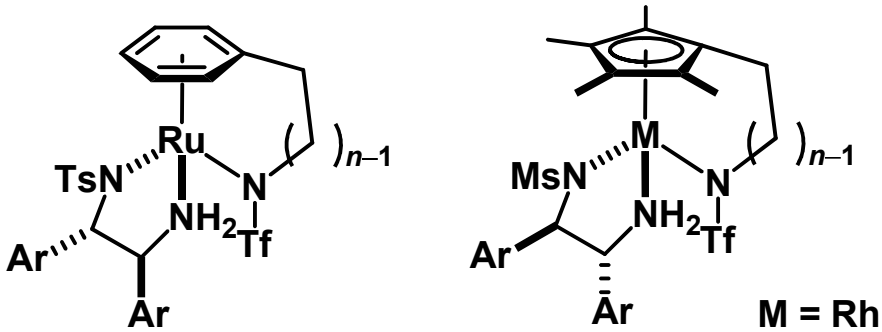
S/C = 100, [ketone] = 0.25 M

M	*n*	yield, %[a]	ee, %[b]
Ir	2	37	94
	3	53	86
	4	96	93

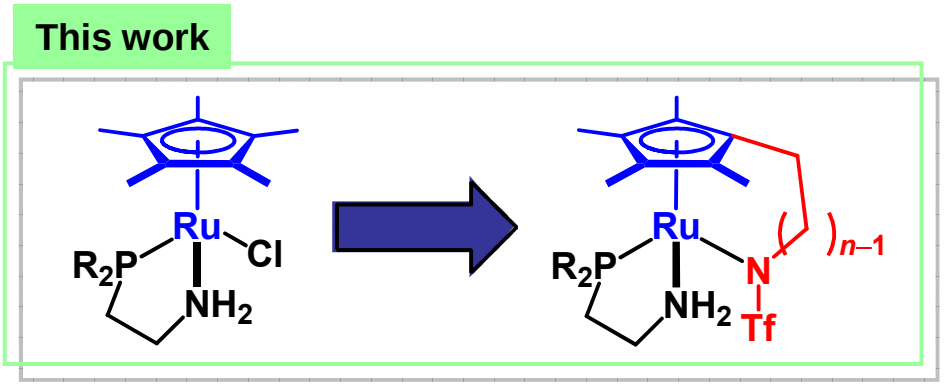
[a] ^{1}H NMR analysis, [b] HPLC analysis

Organometallics **2010,** *29,* 2397-2399.

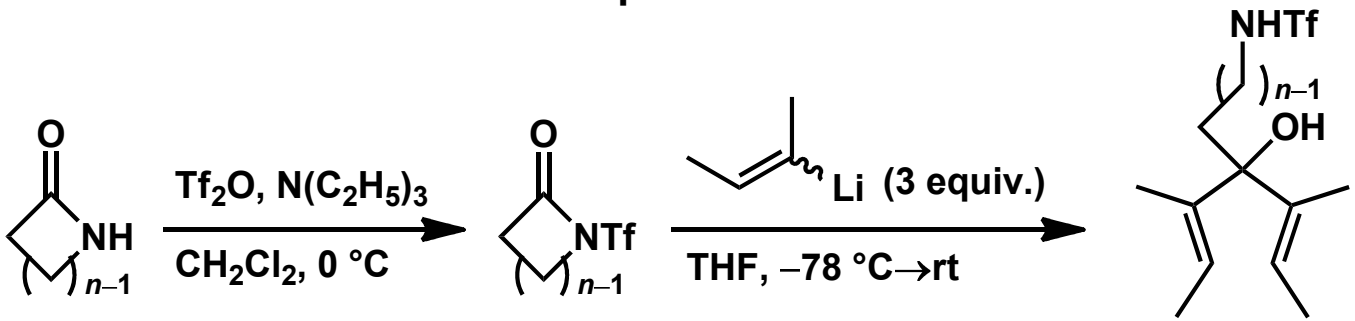
catalyst



This work

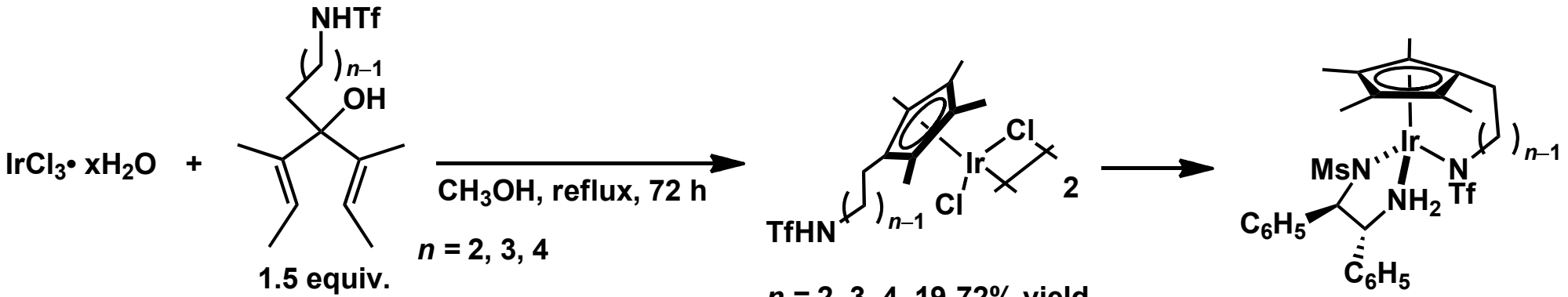


SYNTHESIS OF TETHERED Cp*Ir COMPLEXES



n = 3 25% yield
n = 4 68% yield

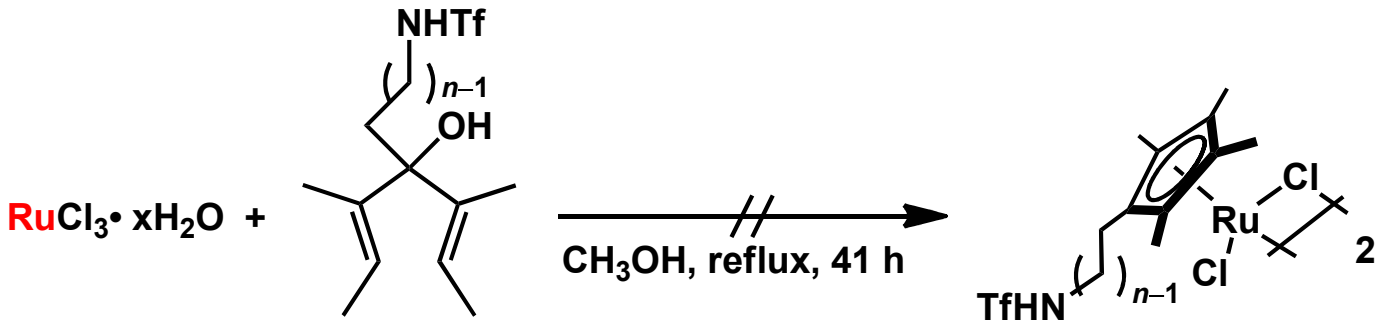
n = 3 36% yield
n = 4 53% yield



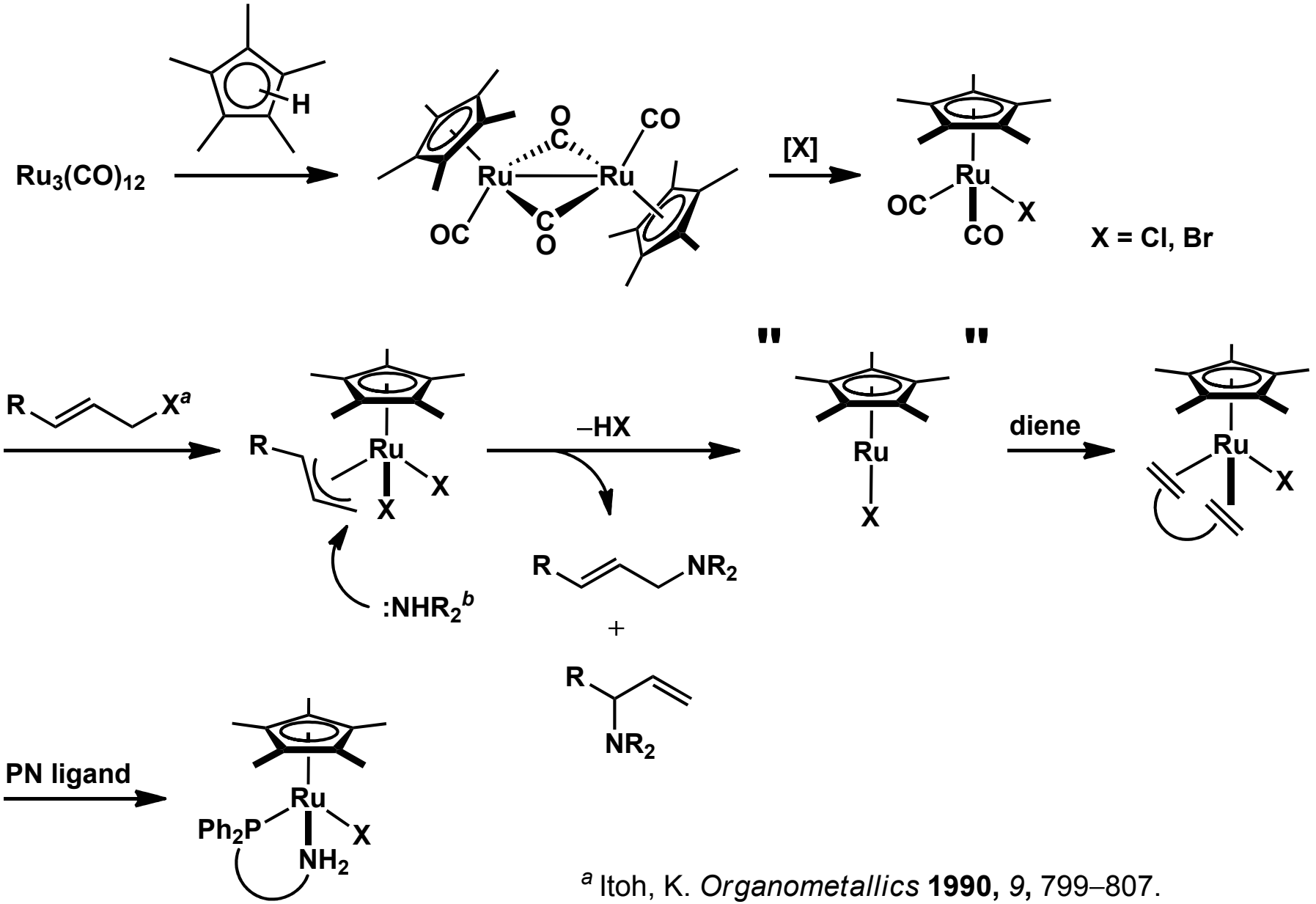
n = 2, 3, 4 19-72% yield

n = 2, 3, 4 85-90% yield

Organometallics **2010,** *29,* 2397-2399.



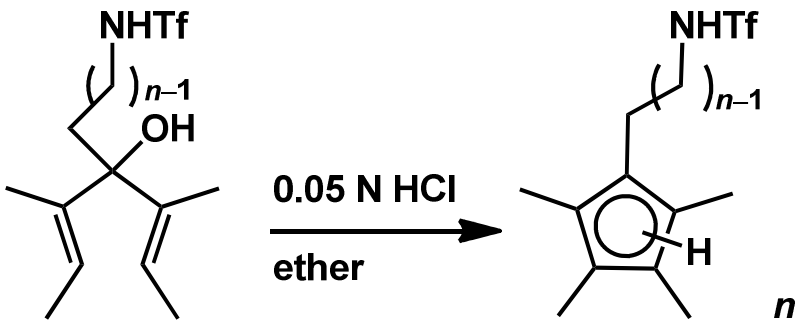
SYNTHETIC STRATEGY OF Cp*Ru(PN)X FROM $Ru_3(CO)_{12}$



[a] Itoh, K. *Organometallics* **1990,** *9*, 799–807.

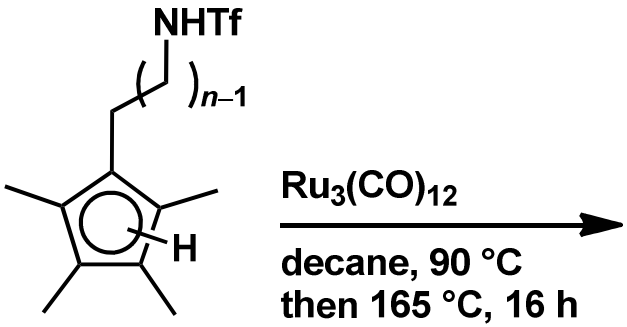
[b] Kondo, T.; Mitsudo, T. *Organometallics* **1995,** *14,* 1945–1953.

SYNTHESIS OF Ru CARBONYL COMPLEXES BEARING TETHERED LIGAND (1)



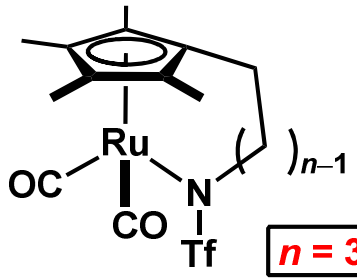
n = 3, 4

Organometallics **2010,** *29,* 2397-2399.



1.25 equiv./Ru

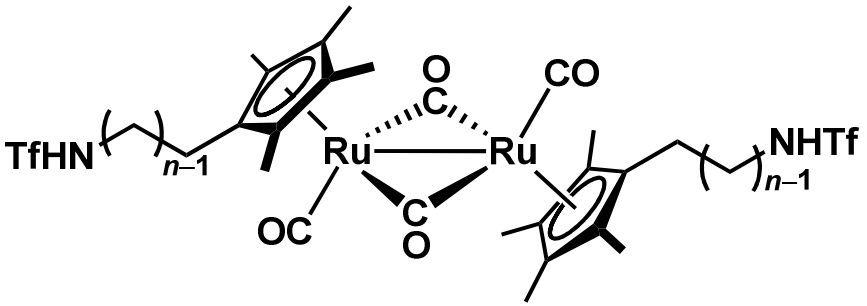
(dichlorobenzene solution)



n = 3 48% yield

^{19}F NMR (δ, $CDCl_3$)
–73.3 (s, SO_2CF_3)

IR (cm^{-1}, KBr)
2034
1992

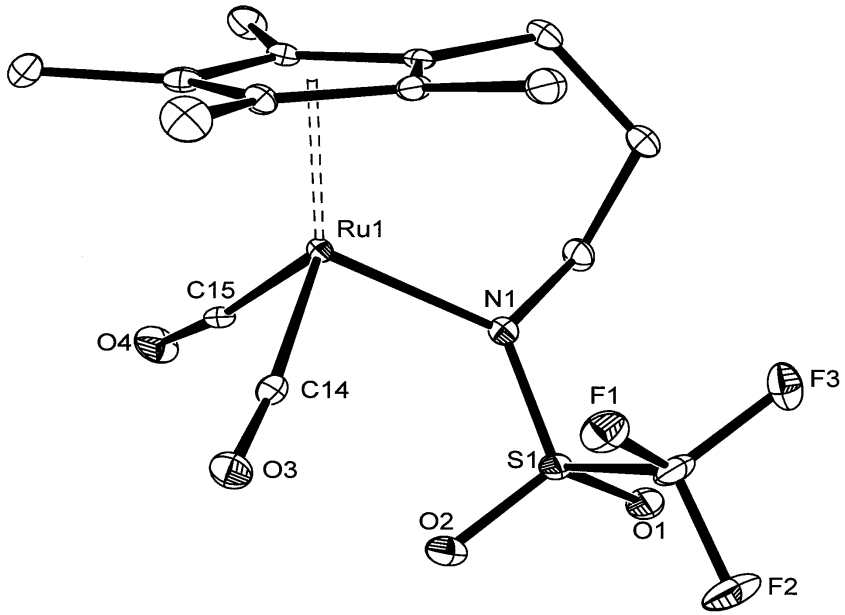


n = 4 66% yield

^{19}F NMR (δ, $CDCl_3$)
–77.2 (s, SO_2CF_3)

IR (cm^{-1}, KBr)
1929
1736

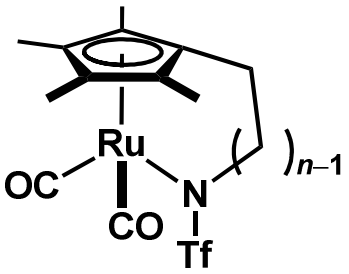
SYNTHESIS OF Ru CARBONYL COMPLEXES BEARING TETHERED LIGAND (2)



n = 3

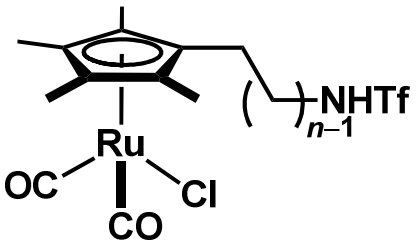
$\bar{P}1$ (#2)
*R*1 = 0.0471
*wR*2 = 0.1475

Ru—N	2.155(4)
C(14)—O(3)	1.138(6)
C(15)—O(4)	1.134(7)
Ru—N—C	117.5(3)
S—N—C	117.6(3)
Ru—N—S	124.9(2)
Total	360.0°



1 M HCl in Et_2O (2 equiv.)

Et_2O, rt, 1 h



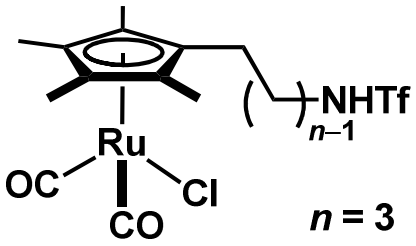
n = 3 96% yield

^{19}F NMR (δ, $CDCl_3$)
–73.3 (s, SO_2CF_3)

^{19}F NMR (δ, $CDCl_3$)
–77.1 (s, SO_2CF_3)

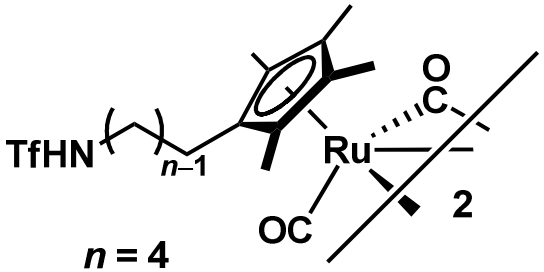
^{1}H NMR (δ, $CDCl_3$)
5.07 (br, 1H, N*H*Tf)

SYNTHESIS OF π–ALLYL COMPLEX



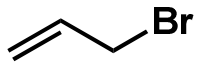
n = 3

or



n = 4

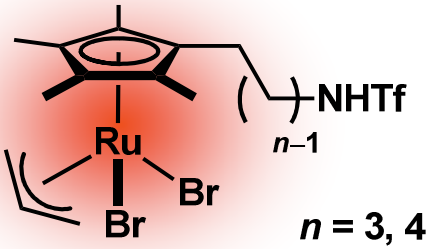
\+



100 equiv./Ru

with periodic evacuation

CH_2Cl_2, 140 °C, 15 h

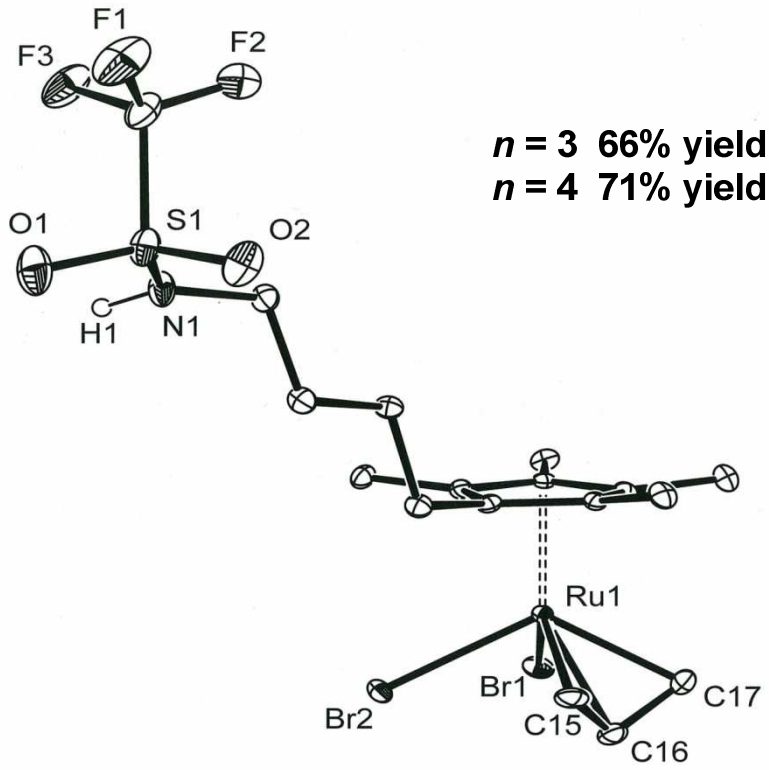


n = 3, 4

dark red crystals

For Cp*Ru analogue:
Itoh, K. *Organometallics* **1990,** *9,* 799–807.

^{1}H NMR (δ , $CDCl_3$) (*n* = 4)
1.63 (br, 2H, $CH_2CH_2CH_2CH_2NHTf$)
1.63 (br, 2H, $CH_2CH_2CH_2CH_2NHTf$)
1.74 (s, 6H, CH_3)
1.79 (s, 6H, CH_3)
2.12 (br, 2H, $CH_2CH_2CH_2CH_2NHTf$)
2.28 (d, 2H, $^3J_{HH}$ = 10.4 Hz, anti-CH_2CHCH_2)
3.37 (br, 2H, $CH_2CH_2CH_2CH_2NHTf$)
4.30 (d, 2H, $^3J_{HH}$ = 6.1 Hz, syn-CH_2CHCH_2)
4.79 (br, 1H, N*H*Tf)
5.19–5.27 (m, 1H, CH_2CHCH_2)



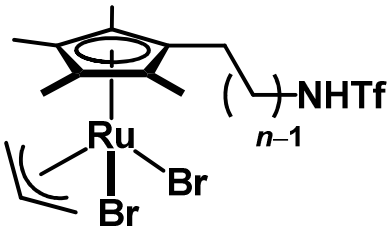
n = 3 66% yield
n = 4 71% yield

^{19}F NMR (δ, $CDCl_3$)
–77.0 (s, SO_2CF_3)
–76.9 (s, SO_2CF_3)

$P2_1/c$ (#14)
*R*1 = 0.0353
w*R*2 = 0.0938

n = 4

REACTIONS OF π–ALLYL COMPLEX



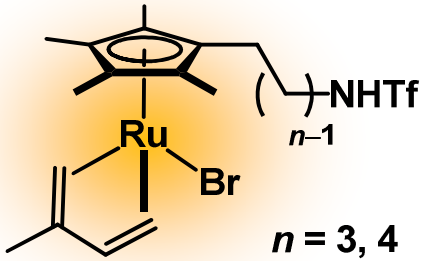
n = 3, 4

+ $NH(CH_3)_2$ (2.0 M solution in THF)

2 equiv.

isoprene (2 equiv.)

THF, –78 °C then rt, 17 h



n = 3, 4

orange oil

n = 3 quantitative

n = 4 45% yield (isolated yield)

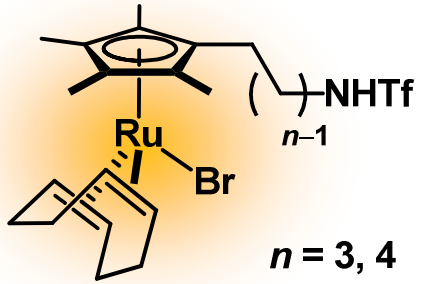
^{19}F NMR (δ, $CDCl_3$)

–77.1 (s, SO_2CF_3)

–77.1 (s, SO_2CF_3)

COD (2 equiv.)

THF, –78 °C then rt, 17 h



n = 3, 4

orange powder

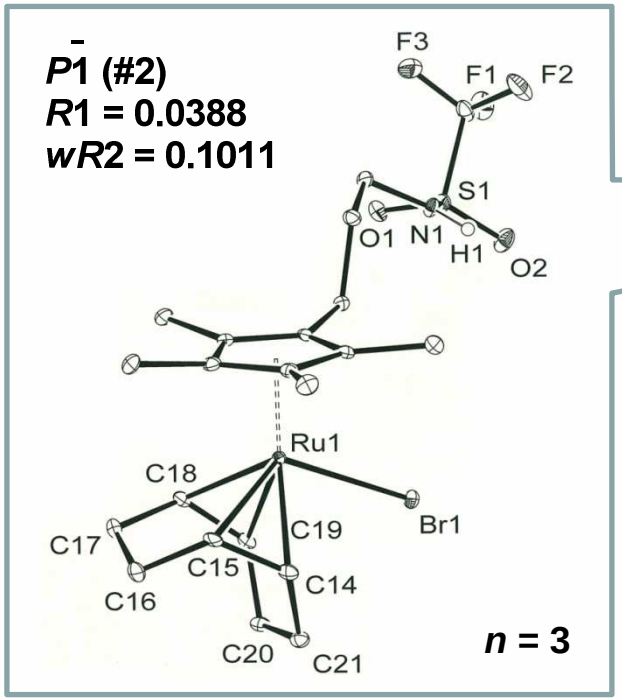
n = 3 79% yield

n = 4 65% yield (isolated yield)

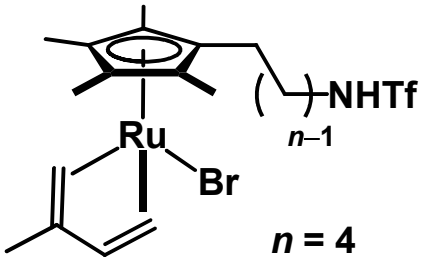
^{19}F NMR (δ, CD_2Cl_2)

–77.6 (s, SO_2CF_3)

–77.7 (s, SO_2CF_3)



SYNTHESIS OF TETHERED DIENE COMPLEX

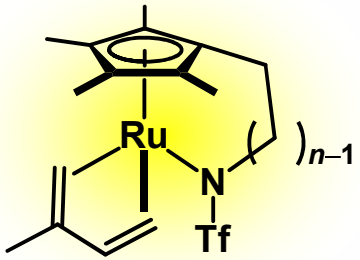


n = 4

^{19}F NMR (δ, $CDCl_3$)
–77.1 (s, SO_2CF_3)

Ag_2CO_3 (0.6 equiv.)

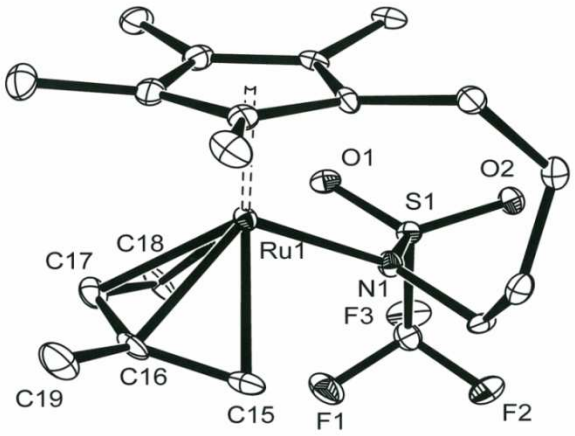
CH_2Cl_2, rt, 13.5 h



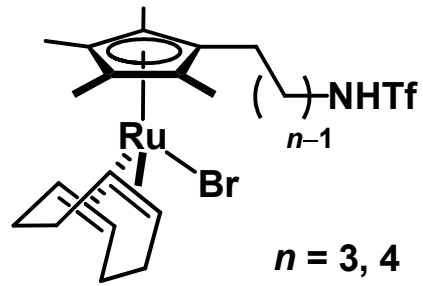
yellow powder
79% yield

^{19}F NMR (δ, $CDCl_3$)
–73.7 (major) (br, SO_2CF_3)
–73.4 (minor) (br, SO_2CF_3)

^{1}H NMR (δ, $CDCl_3$)
1.35 (s, 3H, $C_5(CH_3)_4$)
1.52 (s, 3H, $C_5(CH_3)_4$)
1.63 (s, 3H, $C_5(CH_3)_4$)
2.00 (s, 3H, $C_5(CH_3)_4$)



Pbca (#61)
*R*1 = 0.0677
w*R*2 = 0.1452



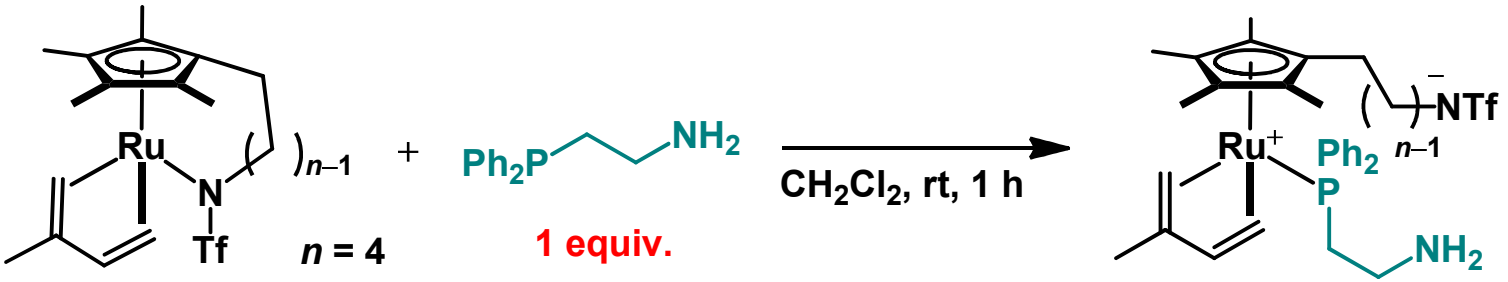
n = 3, 4

Ag_2CO_3 (0.6 equiv.)

CH_2Cl_2, rt, 23.5 h

complicated

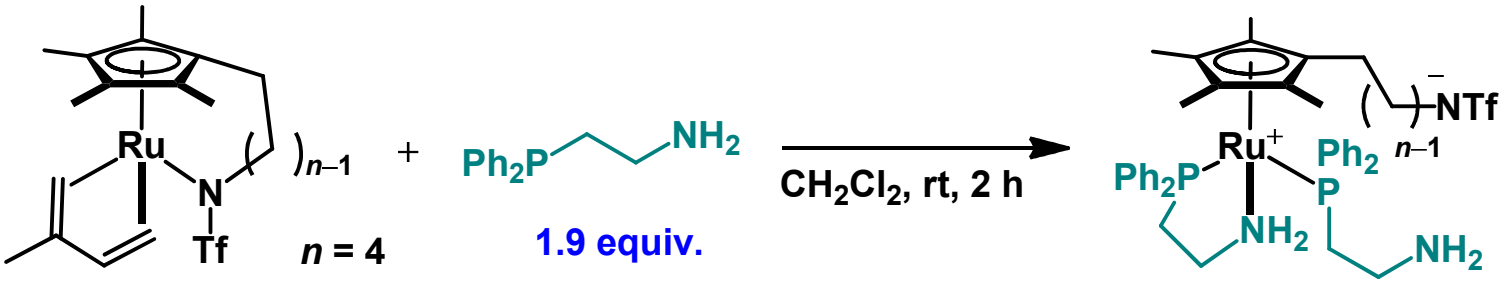
SYNTHESIS OF PN COMPLEX (1)



^{19}F NMR (δ, $CDCl_3$)
–73.7 (major) (br, SO_2CF_3)
–73.4 (minor) (br, SO_2CF_3)

^{19}F NMR (δ, CD_2Cl_2)
–76.1 (s, SO_2CF_3)

^{31}P{^{1}H} NMR (δ, CD_2Cl_2)
59.9 (s)

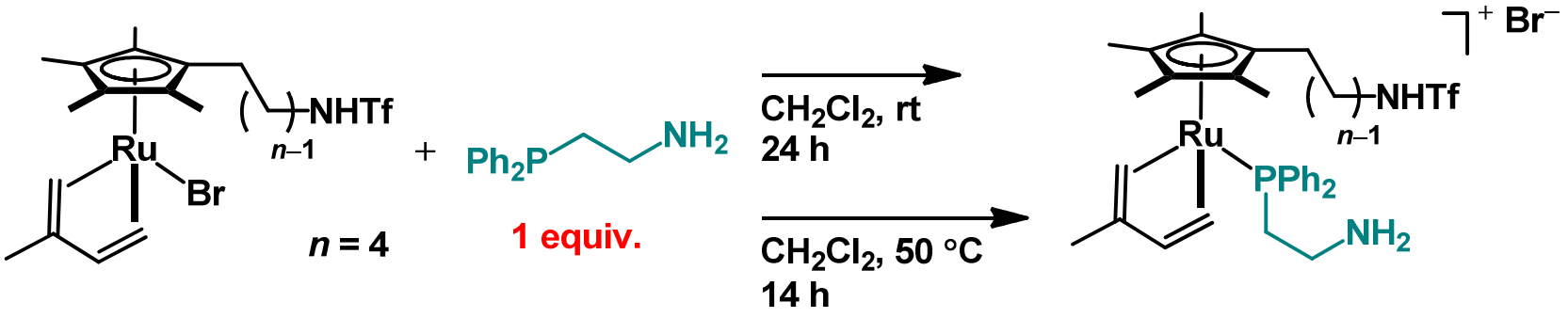


^{19}F NMR (δ, $CDCl_3$)
–76.4 (s, SO_2CF_3)

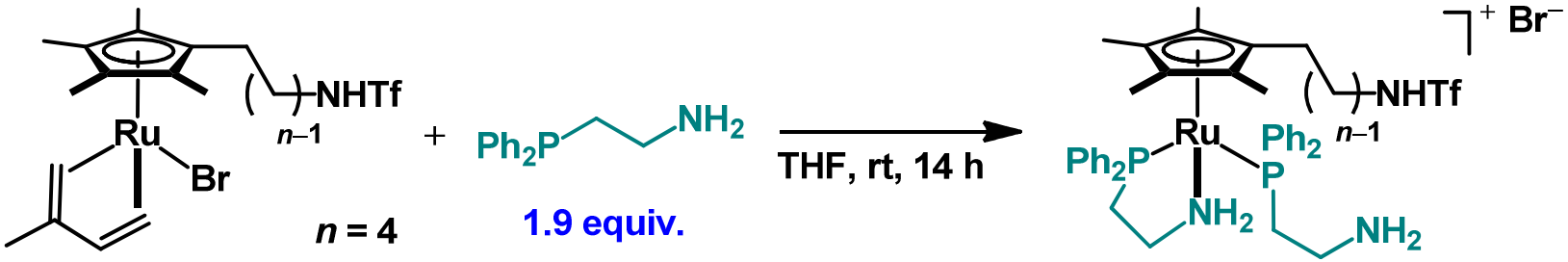
^{31}P{^{1}H} NMR (δ, $CDCl_3$)
40.4 (d, J = 33.3 Hz)
57.2 (d, J = 35.1 Hz)

^{1}H NMR (δ, $CDCl_3$)
1.28 (s, 3H, $C_5(CH_3)_4$)
1.38 (s, 3H, $C_5(CH_3)_4$)
1.57 (s, 3H, $C_5(CH_3)_4$)
1.78 (s, 3H, $C_5(CH_3)_4$)

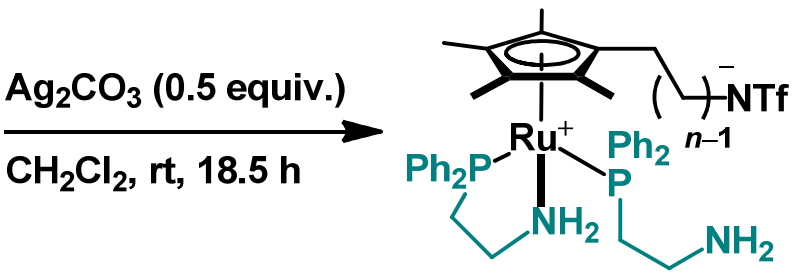
SYNTHESIS OF PN COMPLEX (2)



^{19}F NMR (δ, CD_2Cl_2)	$^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2)	^1H NMR (δ, CD_2Cl_2)
–77.7 (s, SO_2CF_3)	59.6 (s)	1.64 (s, 6H, $C_5(CH_3)_4$)
		1.71 (s, 6H, $C_5(CH_3)_4$)

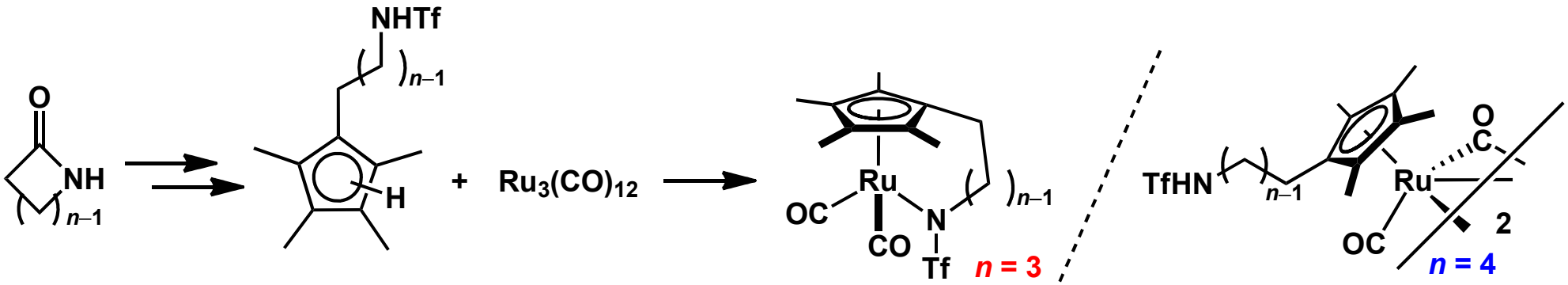


^{19}F NMR (δ, $CDCl_3$)	$^{31}P\{^1H\}$ NMR (δ, $CDCl_3$)	^1H NMR (δ, $CDCl_3$)
–77.1 (s, SO_2CF_3)	40.0 (d, J = 35.2 Hz)	1.18 (s, 3H, $C_5(CH_3)_4$)
	56.8 (d, J = 35.2 Hz)	1.48 (s, 3H, $C_5(CH_3)_4$)
		1.55 (s, 3H, $C_5(CH_3)_4$)
		1.77 (s, 3H, $C_5(CH_3)_4$)

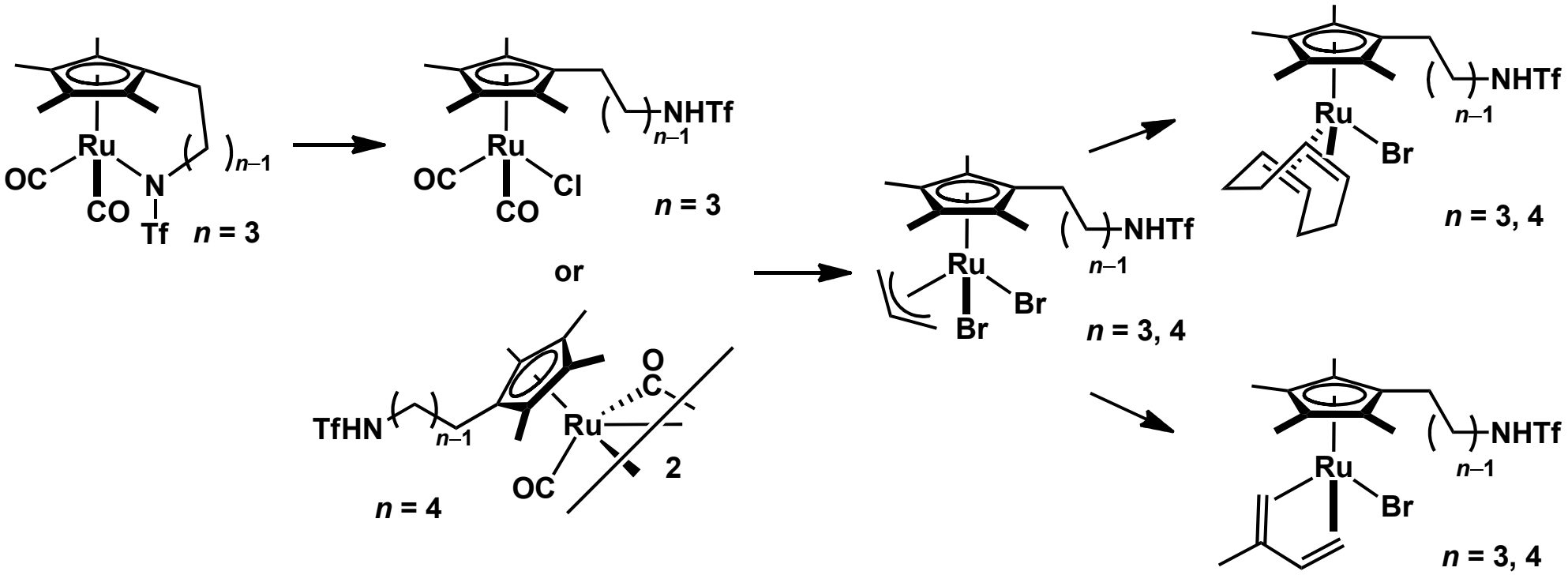


SUMMARY (1)

Synthesis of Ru carbonyl complexes



Synthesis of Ru diene complexes



SUMMARY (2)

Reaction of Ru isoprene complex with PN ligand