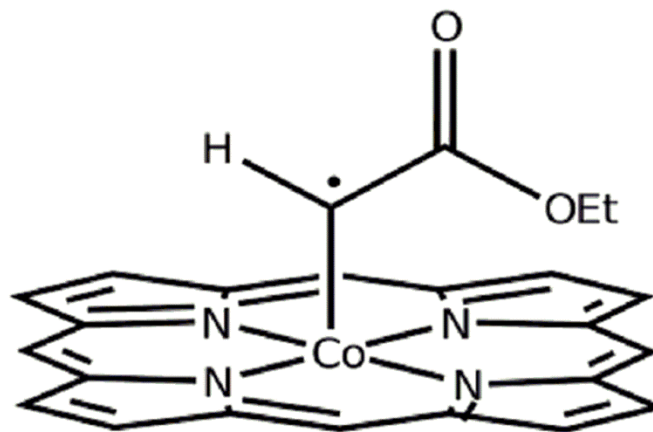
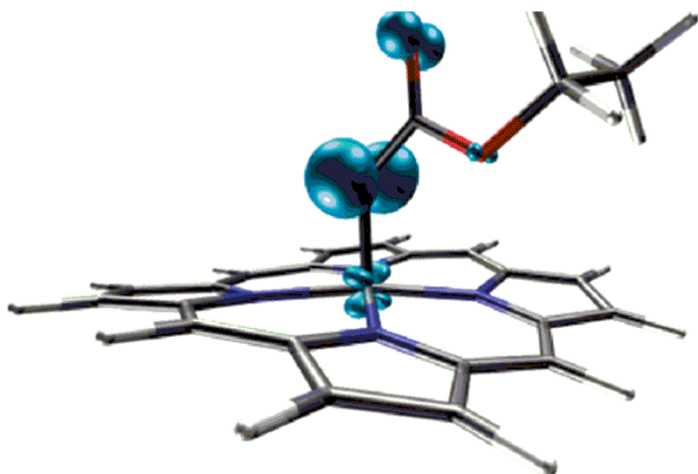


# The reactivity of 9 metal complex (II) and the new activated species, Metal carbene radical By Bas de Bruin

~Application to form Metal carbene radical not via diazo compounds~



H, L, Woodcock *Organometallics* 2011, 30, 2739

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2.1. Metal carbene radical

2.2. Application

2.3. My desired reaction

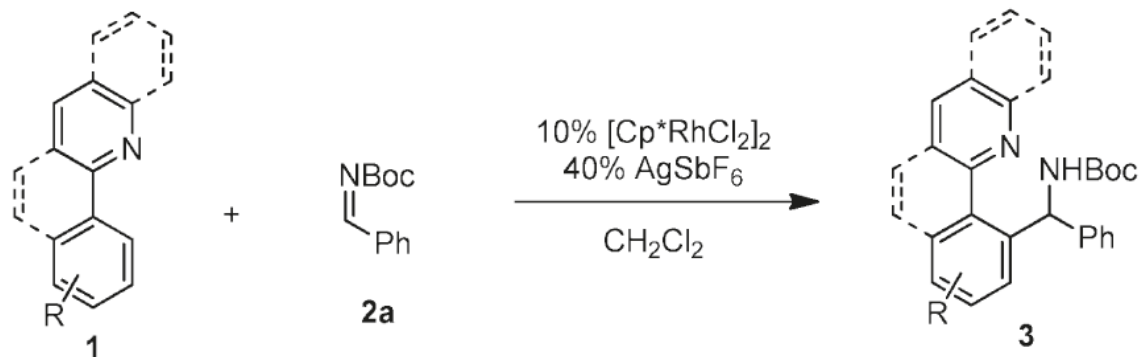
2012/10/13 Kato (M2)

# 1. Metal or Ligand Radicals? -intro-

Rh, Ir as diamagnetic complexes ~C-H bond activation by Rh(III) and Ir(III)~

## Rhodium(III)-Catalyzed Arylation of Boc-Imines

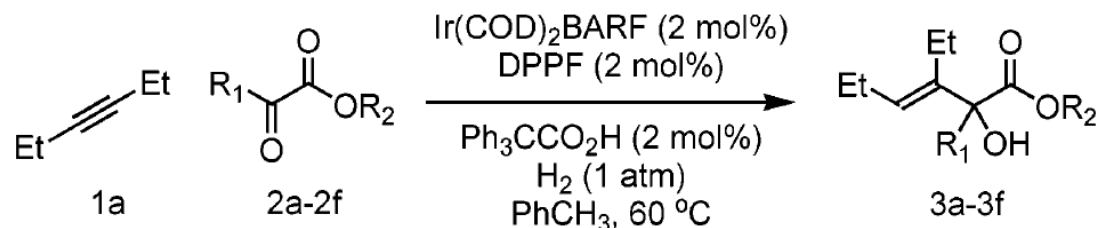
Bergman, R. G et al., JACS, 2011, 133, 1248



Rh, Ir as diamagnetic complexes ~H-H bond activation by Rh(I)~

## Enantioselective Direct Reductive Coupling via Rh cat. Asymmetric Hydrogenation

M, J. Krische, JACS, 2006, 128, 718



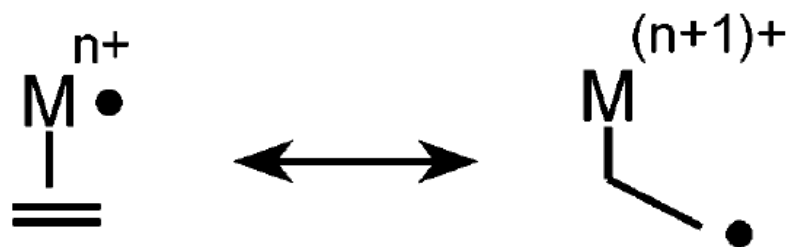
the reaction using Rh, Ir(I,III) cat. mainly was reported, much less is known of the structure, reactivity and physical properties of their of their paramagnetic analogs

# 1. Metal or Ligand Radicals? -intro-

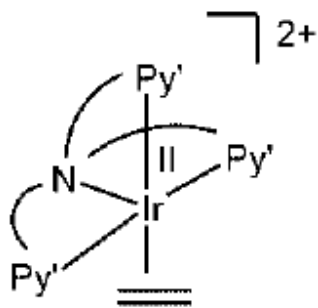
Bas de Bruin, JACS, 2005, 127, 1895

**Paramagnetic complex : low-spin 17- or 19-VE (valence electron) species with the unpaired spin-density located at the metal**

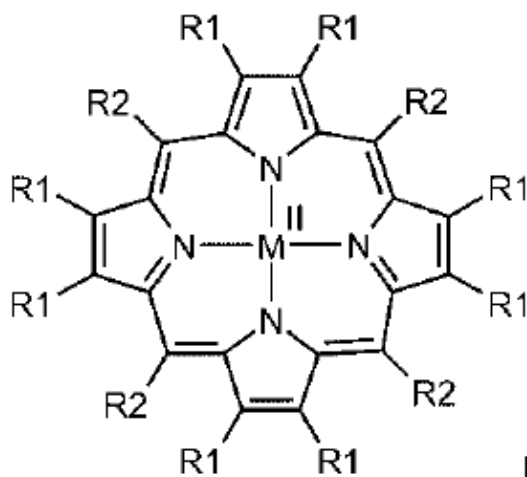
If complexes containing d-accepting ligands such as CO and olefins.....  
leaving the metal in the usual 16- or 18-VE closed-shell configuration



Bas de Bruin, Eur. J. Inorg. Chem. 2007, 211

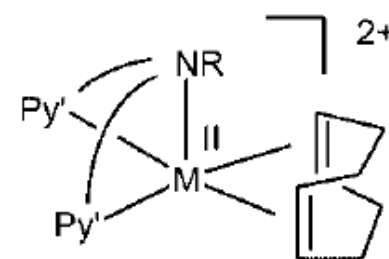


$\text{N}_4$ -Ligand  $\text{Ir}^{\text{II}}$  Complexes



$[\text{M}^{\text{II}}(\text{por})]$   
Por.-Ligand  $\text{Ir}^{\text{II}}$  Complexes

$\text{M} = \text{Rh, Ir}$



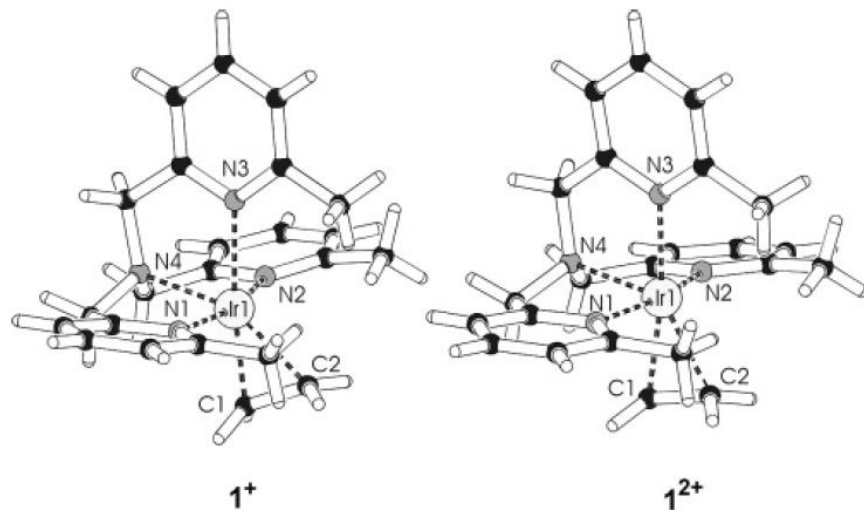
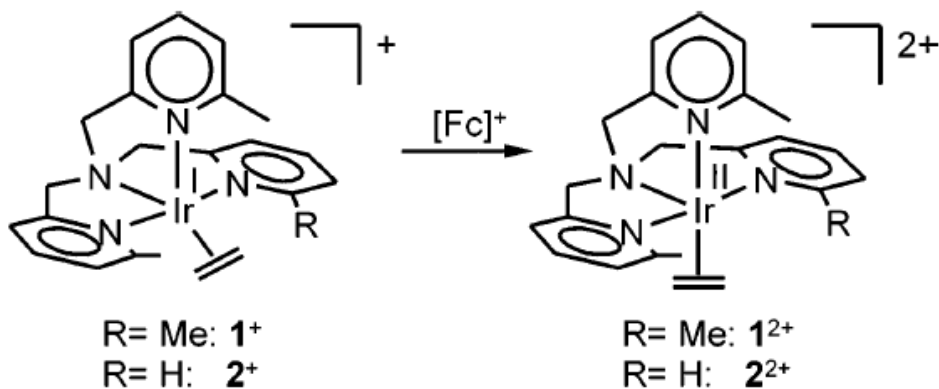
$\text{N}_3$ -Ligand  $\text{Ir}^{\text{II}}$  Complexes

$\text{M} = \text{Rh, Ir}$

# 1. Metal or Ligand Radicals?

## 1.1. N<sub>4</sub>-Ligand M<sup>II</sup> Complexes.

Bas de Bruin, Organometallics 2002, 21, 4312



[Fc]=ferrocenium hexafluorophosphate (Fc(PF<sub>6</sub>))

weakening of the Ir-ethene interaction by oxi.

	1 <sup>+</sup> [(Me <sub>3</sub> tpa)Ir(ethene)] <sup>+</sup>	1 <sup>2+</sup> [(Me <sub>3</sub> tpa)Ir(ethene)] <sup>2+</sup>
Ir1-C1	2.042 (9)	2.136 (6)
Ir1-C2	2.143 (9)	2.149 (6)
Ir1-N1	2.075 (7)	2.071 (5)
Ir1-N2	2.043 (8)	2.062 (5)
Ir1-N3	2.260 (7)	2.136 (5)
Ir1-N4	2.154 (8)	2.146 (5)
Ir1-N5		
C1-C2	1.451 (13)	1.380 (9)
O5-N5		
C1-Ir1-N3	173.3 (3)	172.0 (2)
C2-Ir1-N3	132.8 (3)	150.2 (2)
N5-Ir1-N3		
Ir1-N5-O5		

1<sup>+</sup> is distorted trigonal bipyramid

1<sup>2+</sup> is square pyramidal  
due to the olefin moves to a position  
trans to the third pyridine group

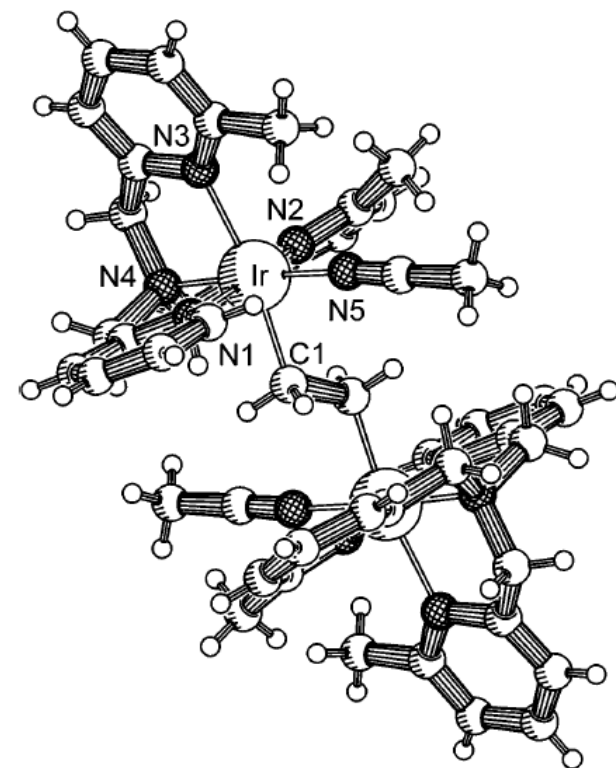
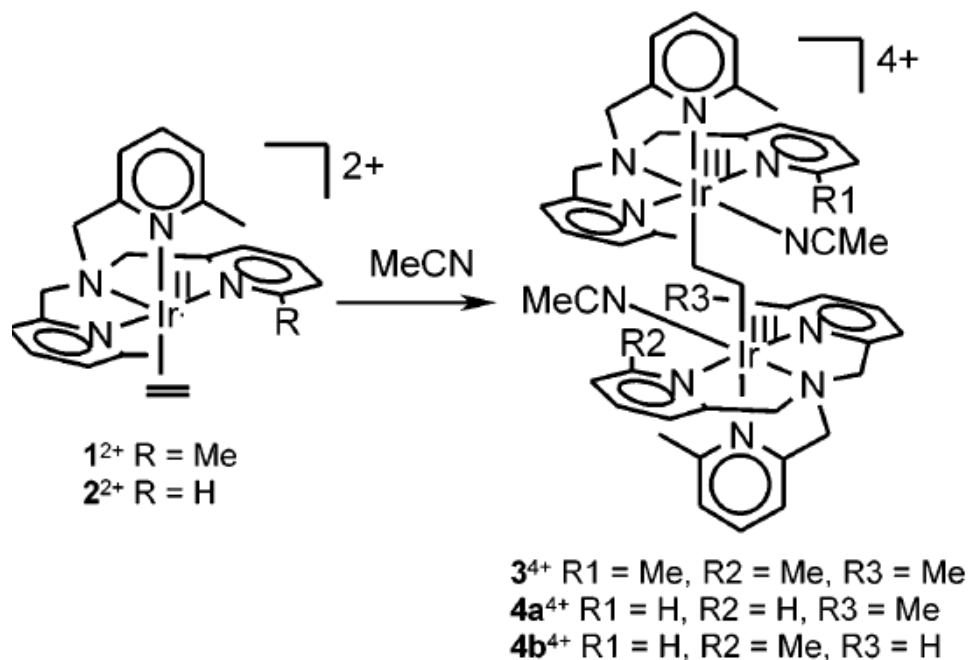
π back donation decrease by oxi.

# 1. Metal or Ligand Radicals?

## 1.1. N<sub>4</sub>-Ligand M<sup>II</sup> Complexes.

Formation of Ethylene Bridged Dinuclear Species in Acetonitrile

X-ray structure of 4b<sup>4+</sup>.



No reaction in weakly coordinating solvents such as acetone

The reactivity with MeCN of 2<sup>2+</sup> increased over the more hindered analogue 1<sup>2+</sup>

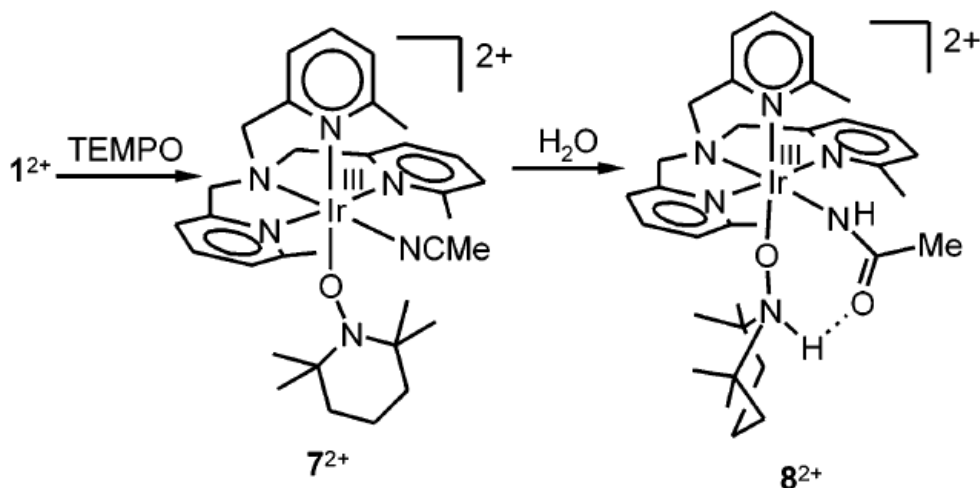


an associative step in the reaction mechanism, either as the ratelimiting step or in a (concentration limiting) pre-equilibrium

# 1. Metal or Ligand Radicals?

## 1.1. N<sub>4</sub>-Ligand M<sup>II</sup> Complexes.

### Formation of 7<sup>2+</sup> from 1<sup>2+</sup> and TEMPO



### X-ray structure of 8<sup>2+</sup>.

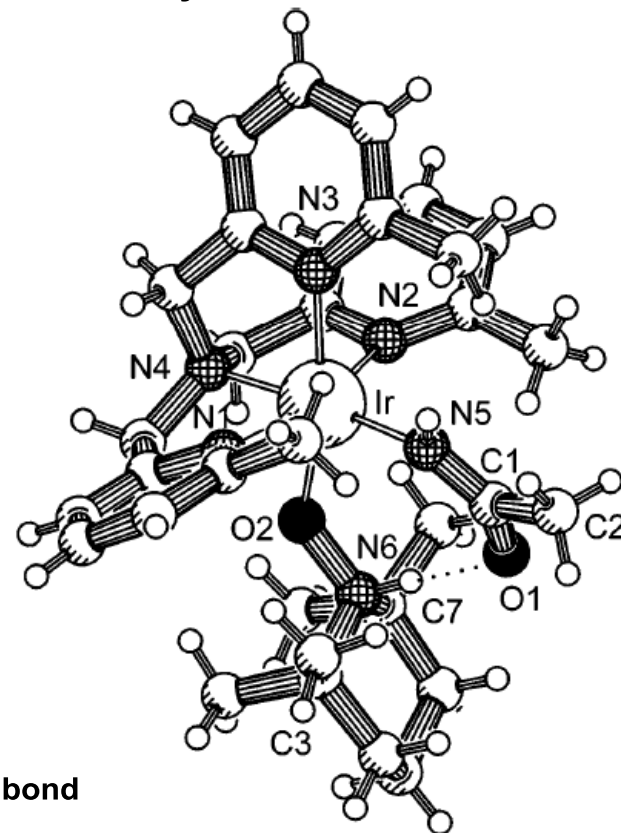


Table 5. Selected Bond Lengths (Å) and Angles (deg) of 8<sup>2+</sup>

8 <sup>2+</sup>	
Ir1–N1	2.113 (5)
Ir1–N2	2.101 (3)
Ir1–N3	2.131 (9)
Ir1–N4	2.055 (9)
Ir1–N5	2.073 (5)
N6–H–O2	1.423 (6)
C1–N5	1.310 (7)
C1–C2	1.514 (2)
C1–O1	1.263 (2)
N6...O1	2.646
O1...O2	3.333
Ir1–N5–C1	138.25 (16)
Ir1–O2–N6	129.10 (11)
C2–C1–N5	117.7 (7)
C2–C1–O1	117.9 (0)
N5–C1–O1	124.3 (2)
C3–N6–C7	116.7 (2)
C3–N6–O2	109.5 (9)
C7–N6–O2	109.4 (1)

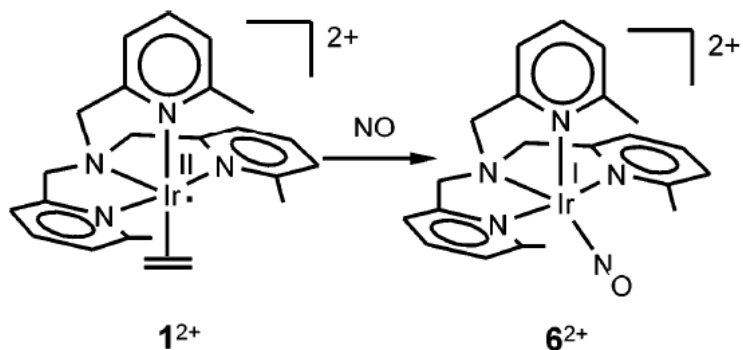
feature of reduced N-O bond

$\eta^1$ -non-reduced N-O bond : 1.265(7)

8<sup>2+</sup>: This fragment should be regarded as an N-protonated TEMPO anion coordinated to Ir<sup>III</sup> rather than an organic radical coupled to an Ir<sup>II</sup> metalloradical. Transition metal  $\eta^1$ -complexes with reduced TEMPO ligands are rare

# 1. Metal or Ligand Radicals?

## 1.1. N<sub>4</sub>-Ligand M<sup>II</sup> Complexes.



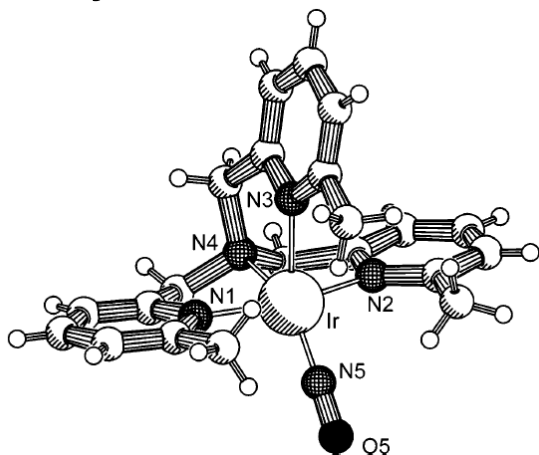
the structure of  $6^{2+}$  is fairly similar to that of  $1^{+}$

Ir-N5-O5: 174.5 °C  $\Rightarrow$  NO act as 1e reductant

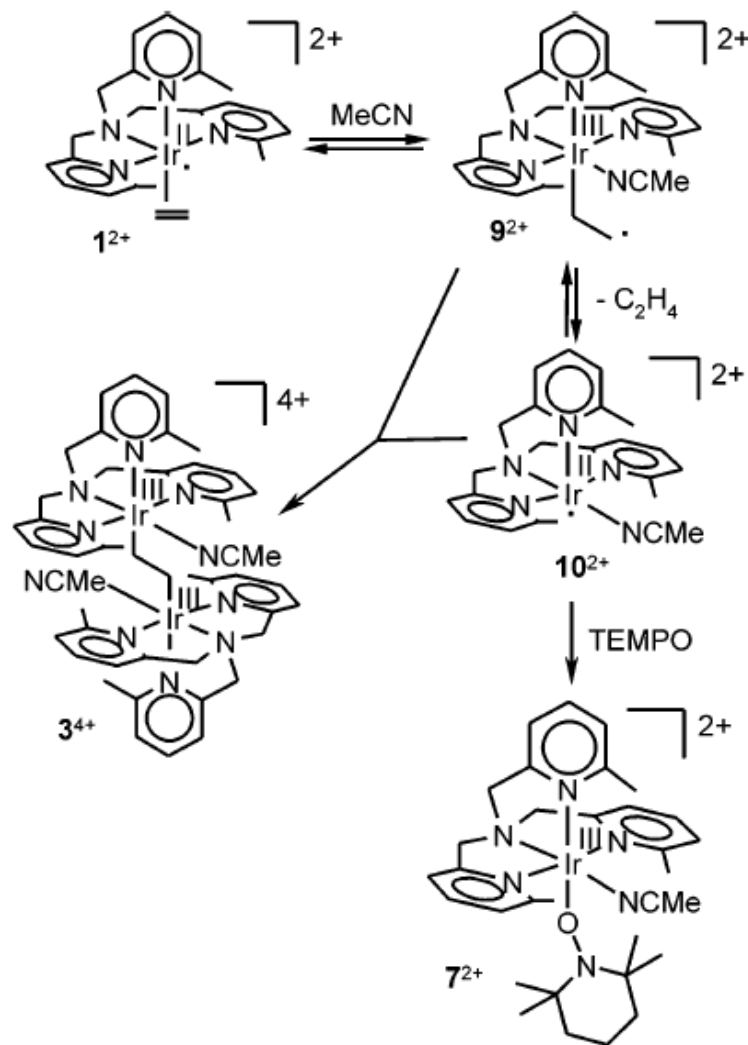
NO act as 1e reductant : isoelectronic with CO

NO act as 1e oxidant : isoelectronic with  $^1\text{O}_2$

### Xray of $6^{2+}$



### Proposed Mechanism



dimerization of  $9^{2+}$  and reaction of  $9^{2+}$  with Tempo was not observed.



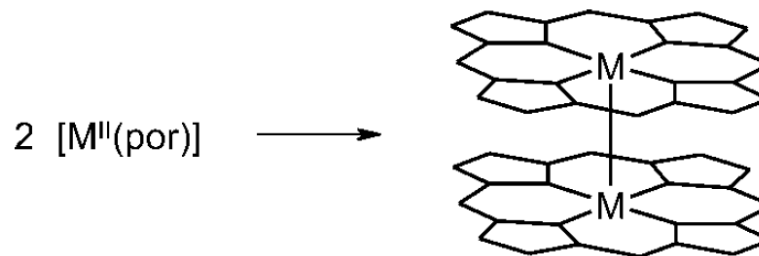
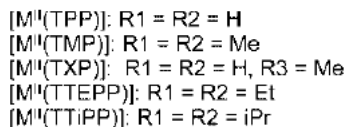
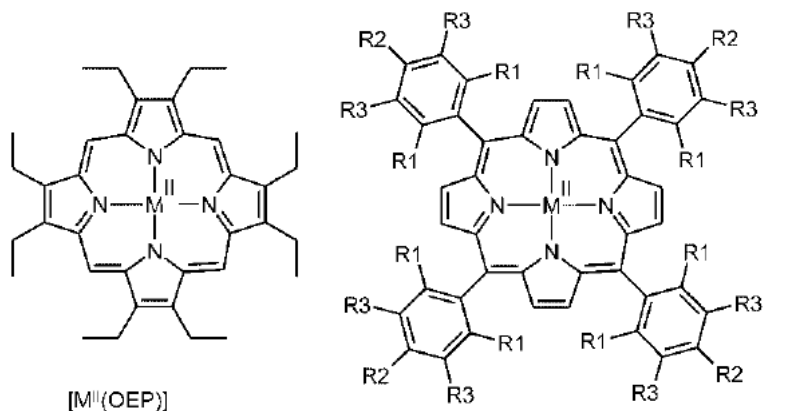
the density of  $9^{2+}$  should be low

# 1. Metal or Ligand Radicals?

## 1.2. Por.-Ligand M<sup>II</sup> Complexes.

### Structure of Neutral 17-VE M<sup>II</sup>(alkene)(por) Radicals

#### Porphyrinato Rh<sup>II</sup> and Ir<sup>II</sup> complexes



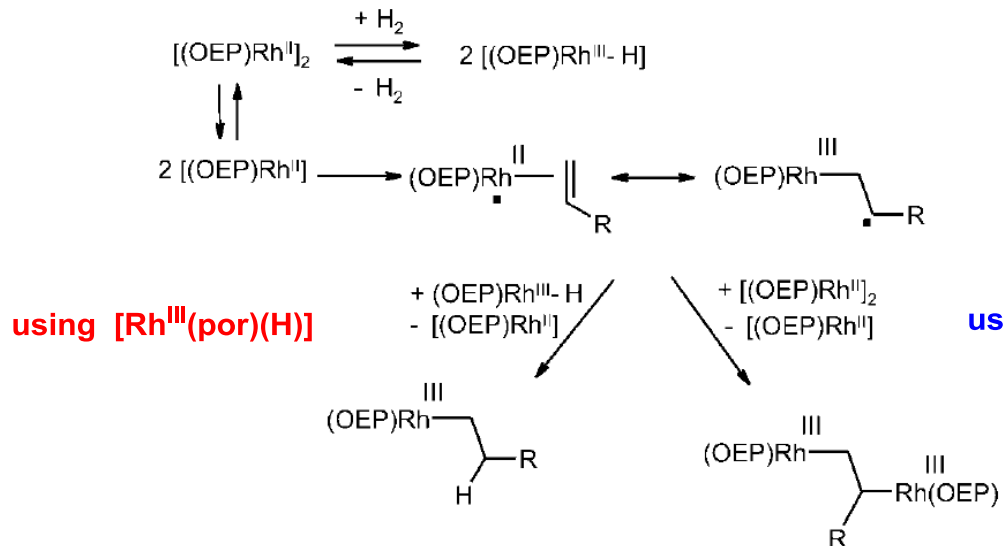
Size: TTiPP > TTEPP > TMP > TXP > TTP > TPP > OEP

By TXP in por. of the size, dimerization

Cobalt(II) porphyrins are invariably monomeric species

#### Reactivity of $[Rh^{II}(por)]$ and $[Rh^{III}(por)(H)]$ towards alkenes

J Halpern, JACS, 1985, 107, 4333



$[Rh^{II}(por)]$  species have low affinity toward alkenes and high reactivity



# 1. Metal or Ligand Radicals?

## 1.2. Por.-Ligand M<sup>II</sup> Complexes.

### Activation of unstrained aliphatic carbon-carbon bonds

K, S, Chan, J. Chem. Soc., Dalton Trans., 2001, 510

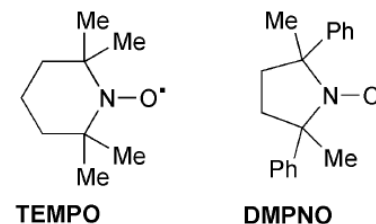
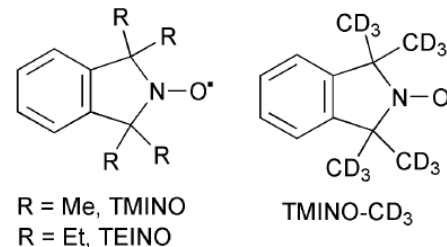
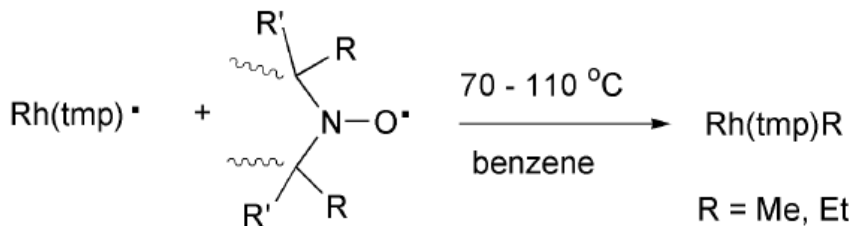
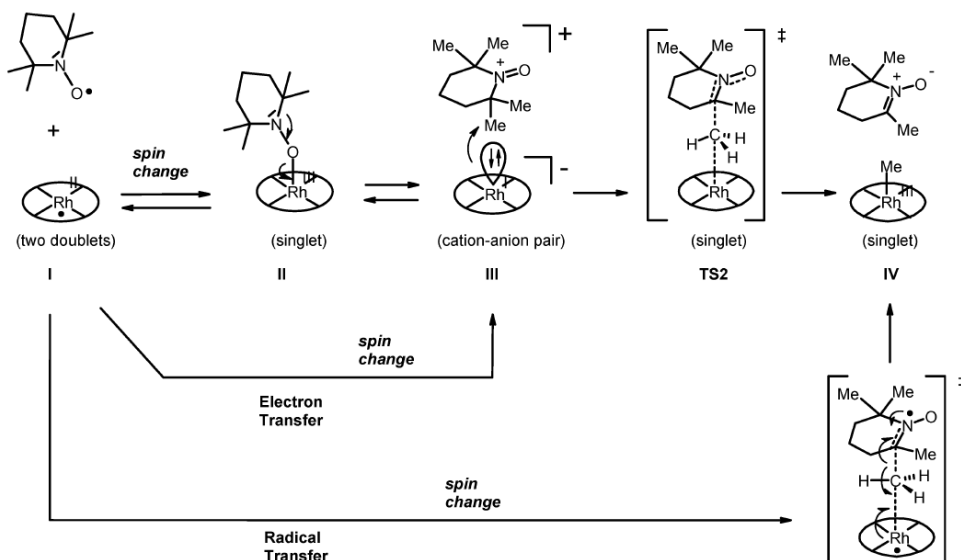


Fig. 1 Structures of nitroxides.

Entry	Nitroxide	Temperature/ °C	Time/h	Yield of Rh(tmp)R (%)
1	TMINO	70	4	73
2	TMINO-CD <sub>3</sub>	70	4	68
3	TEMPO	70	4	68
4	DMPNO	110	46	86
5	TEINO	110	40	40

### Carbon-Carbon Bond Activation of 2,2,6,6-Tetramethyl-piperidine-1-oxyl

Bas de Bruin et al., JACS, 2008, 130, 2051



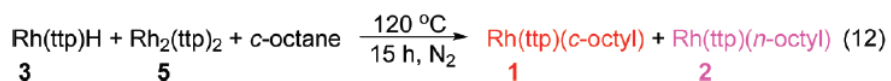
**both pathways are consistent with the experimental kinetic data**

# 1. Metal or Ligand Radicals?

## 1.2. Por.-Ligand M<sup>II</sup> Complexes.

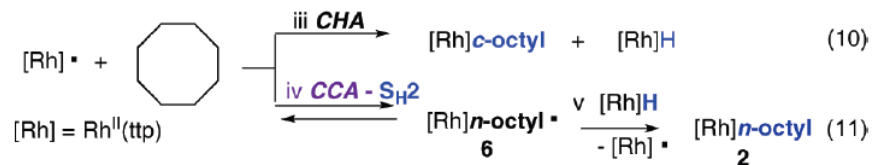
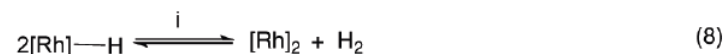
### Metalloradical-Catalyzed Aliphatic Carbon-Carbon Activation of Cyclooctane

K, S, Chan, JACS, 2010, 132, 6920



Entry <sup>a</sup>	3:5	Yield 1 (%)	Yield 2 (%)	Total yield (%)
1 <sup>b</sup>	1:0	0	21	21
2	2:1	60	18	78
3	5:1	53	26	79
4	10:1	0	73	73

CCA catalyzed by [Rh<sup>I</sup>]



### Summary 1

Stability:  $[(\text{N}_4\text{-ligand})\text{M}^{\text{II}}(\text{ethene})]^{2+} \gg [(\text{por})\text{M}^{\text{II}}(\text{ethene})]$

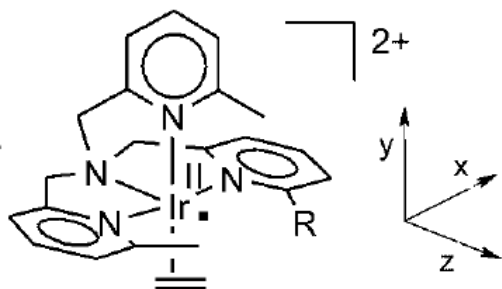
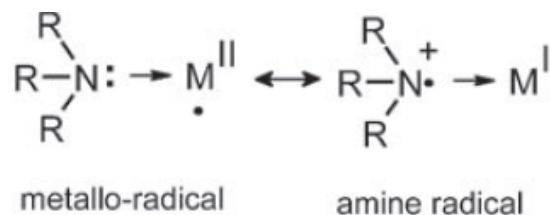
Reactivity:  $[(\text{N}_4\text{-ligand})\text{M}^{\text{II}}(\text{ethene})]^{2+} \ll [(\text{por})\text{M}^{\text{II}}(\text{ethene})]$

Why the reactivity is so different ?

# 1. Metal or Ligand Radicals?

## Stabilization by Aminyl Radical

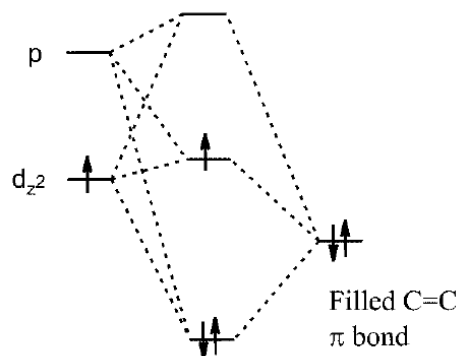
Bas de Bruin, Chem. Eur. J. 2007, 13, 3386



2+ X-Ray for R = Me

1. DFT spin density plots reveal that the spin density is substantially delocalized over the N<sub>amine</sub> donor (15~18%) and the metal (73~78%).
2. The pyridylmethyl groups shield the vacant position trans to the amine

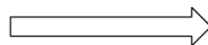
## Activation of [M<sup>II</sup>(por)] Reactivity



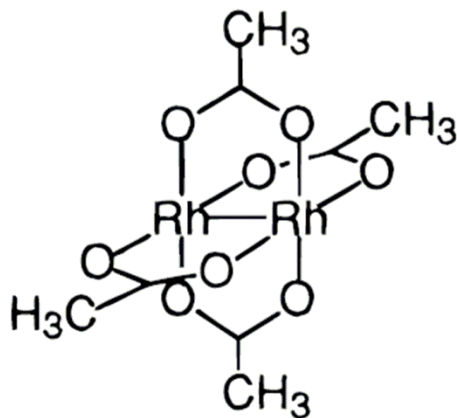
The planar [M<sup>II</sup>(por)] species have the half-filled  $d_z^2$  orbital and the higher lying empty p orbital available for alkene  $\rightarrow$  metal  $\sigma$  bonding, further are involved with the alkene fragment sensitive to radical reactions.

## 2. New activated species ~intro~

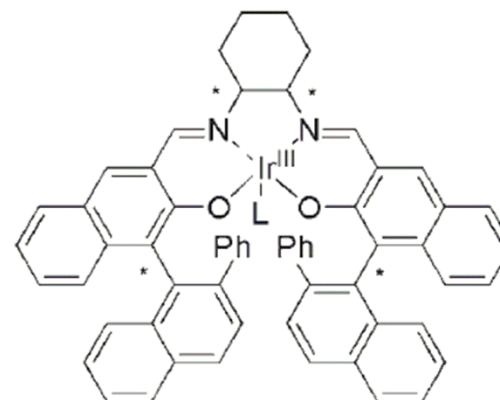
the case of general 9 metal carbenoid



formation of Fisher carbenoid  
careful of carbene dimerization



Doyle-type dinuclear, acetate-bridged,  
Rh(II)-Rh(II) species



- 1: (*aR,R*), L=CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>  
5: (*aR,S*), L=CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>  
6: (*aR,R*), L=C<sub>6</sub>H<sub>5</sub>

mononuclear diamagnetic Ir(III) catalysts



C-H activation, cyclopropanation etc..

P. Doyle et al, Chem. Rev. 1998, 98, 911



mainly regioselective cyclopropanation

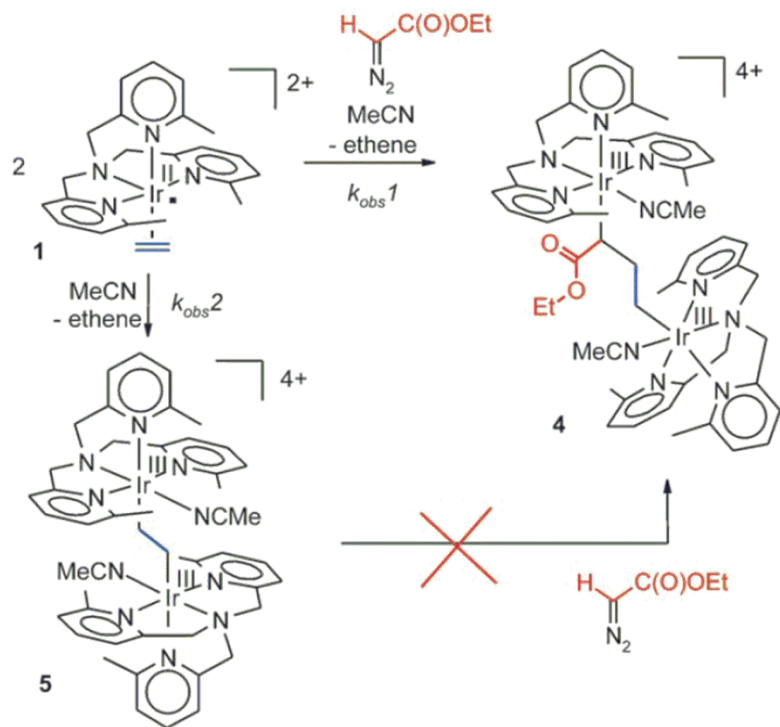
Katsuki et al, ACIE. 2007, 46,3889

**But, the reactivity of both mononuclear (diamagnetic) M(I) and mononuclear (paramagnetic) M(II) complexes (M=Rh,Ir) towards diazo compounds has received almost no attention !!!**

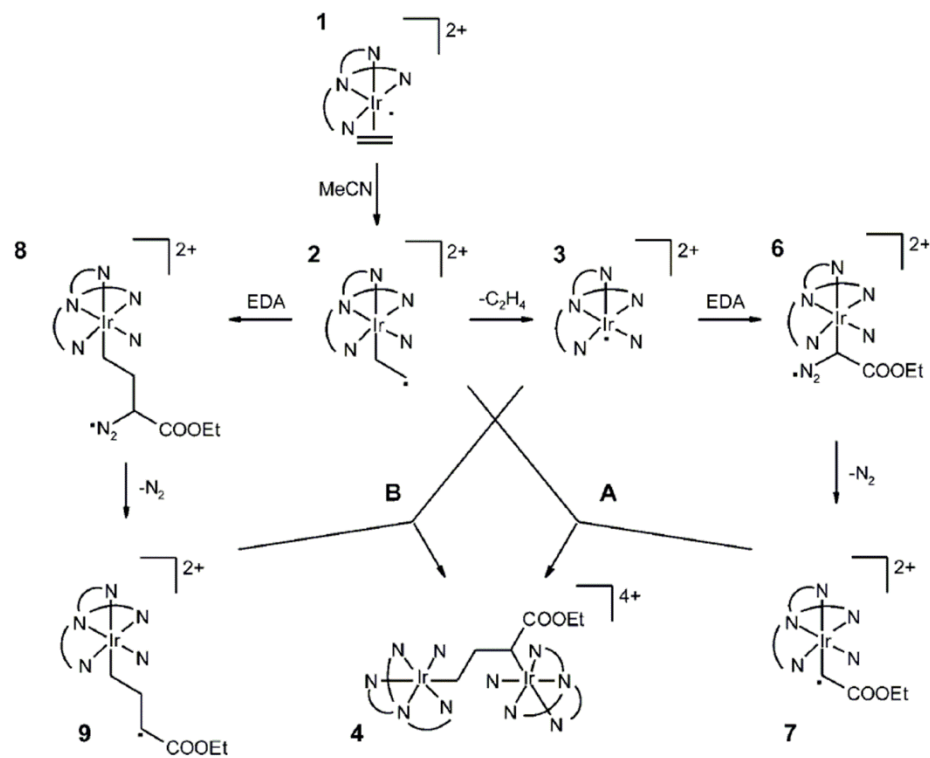
## 2. New activated species using diazo compound

### 2.1. Metal carbene radical

#### Ir(II) ethene complex with Diazo compounds

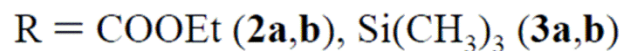
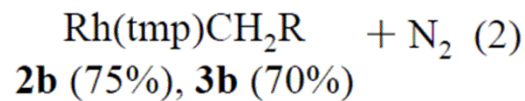
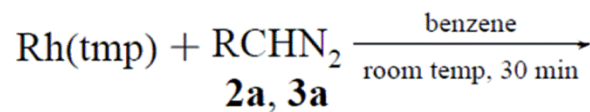


#### Conceivable pathways to the species **4**



#### Rh Por. with Diazo compounds

K, S, Chan, Organometallics 2007, 26, 679



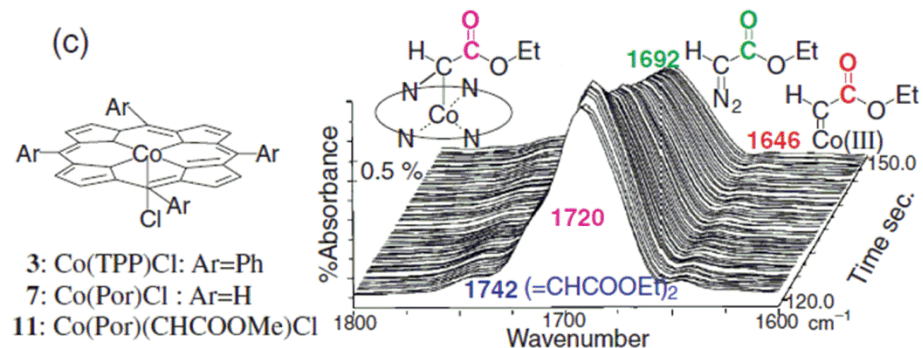
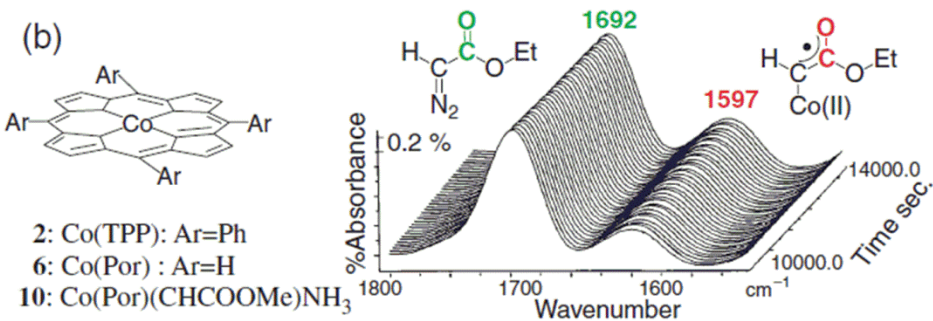
## 2. New activated species using diazo compound

### 2.1. Metal carbene radical

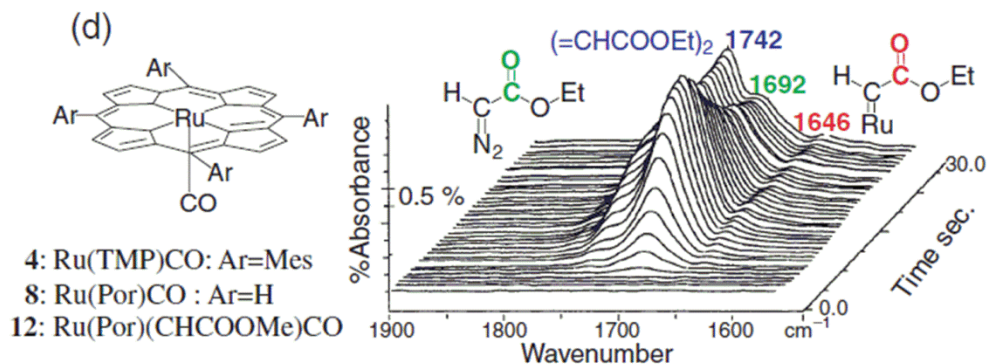
#### Co Por. with Diazo compounds

#### FT-IR and Theoretical Analysis of the Characteristic Bonding of Co porphyrin

T, Yamada et al, chem lett, 2004, 140



$\nu_{C=O} (N_2CHCO_2Me) : 1692-1694 \text{ cm}^{-1}$   
normal Carbenod complex :  $1646 \text{ cm}^{-1}$   
abnormal Carbenod complex :  $1597 \text{ cm}^{-1}$   
diethyl maleate and fumarate :  $1742 \text{ cm}^{-1}$



Co-carbene complexes were significantly shifted ca.  $50 \text{ cm}^{-1}$  downward



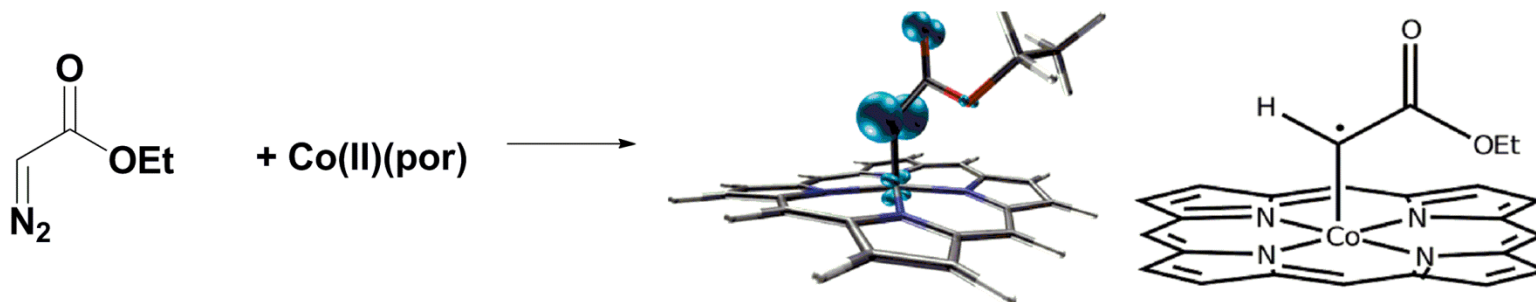
the surplus electron was delocalized between the carbene carbon and carbonyl group

## 2. New activated species using diazo compound

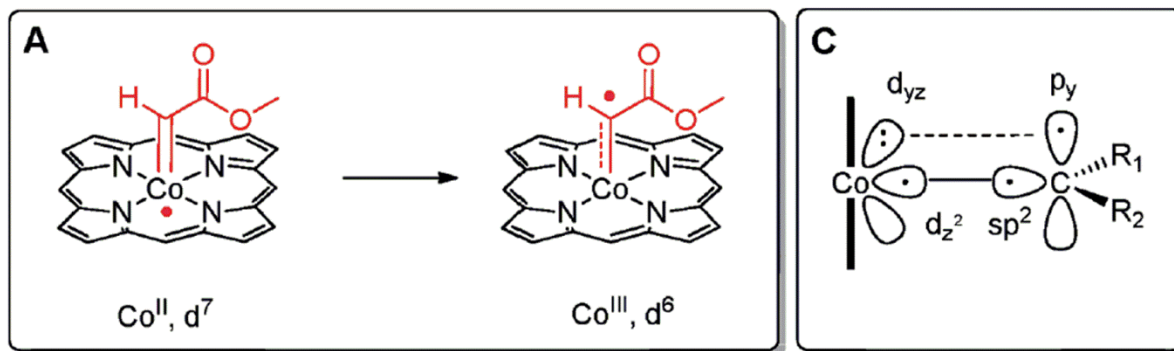
### 2.1. Metal carbene radical

Carbene radicals was proposed by Bruin

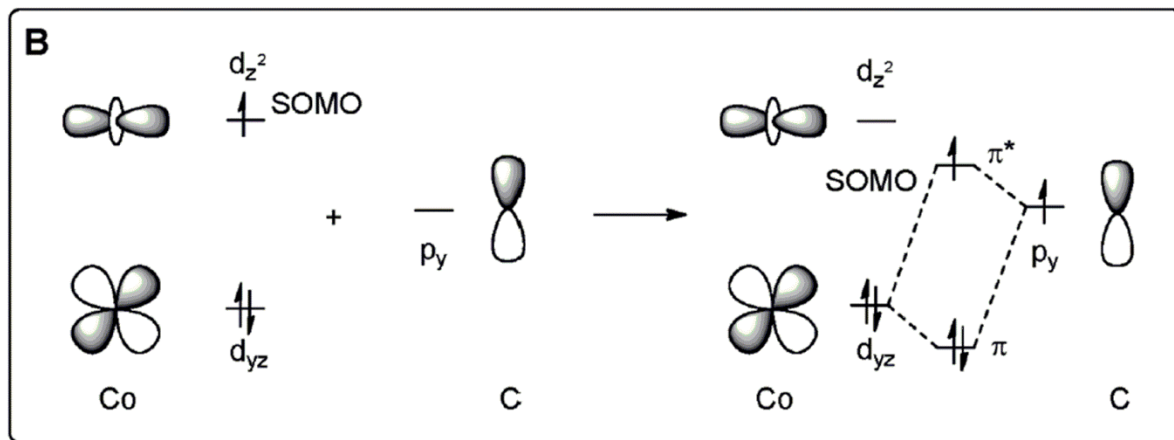
Bas de Bruin, JACS, 2010, 132, 10891



Redox noninnocent behavior of carbenes coordinated to  $\text{Co(por)}$  species explained by a simplified MO bonding



**A, B as singlet carbene:**  
intramolecular electron transfer from  
cobalt to the carbene



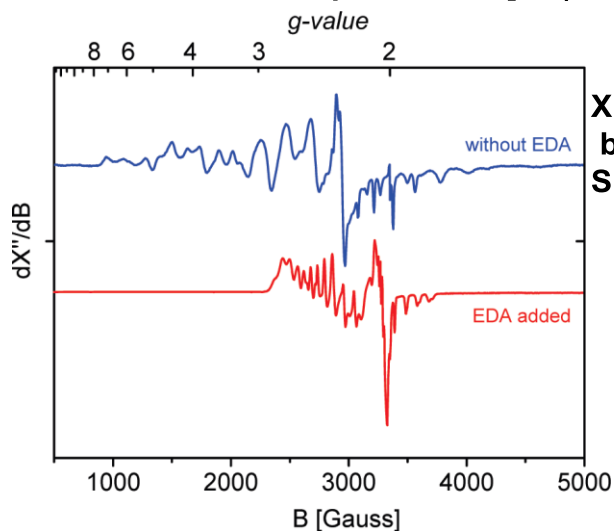
**C as triplet carbene:** Formation of a  $\text{Co-C}$   $\sigma$ -bonding pair from the unpaired electrons in the cobalt  $d_{\sigma}$  orbital and unpaired electron in the  $p_y$  orbital

## 2. New activated species using diazo compound

### 2.1. Metal carbene radical

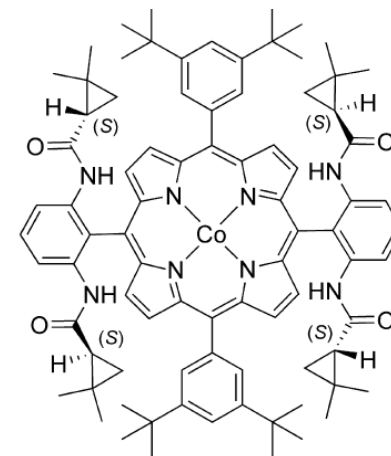
#### EPR Spectroscopy

X-band EPR spectrum of [Co(3,5-Di<sup>t</sup>Bu-ChenPhyrin)]



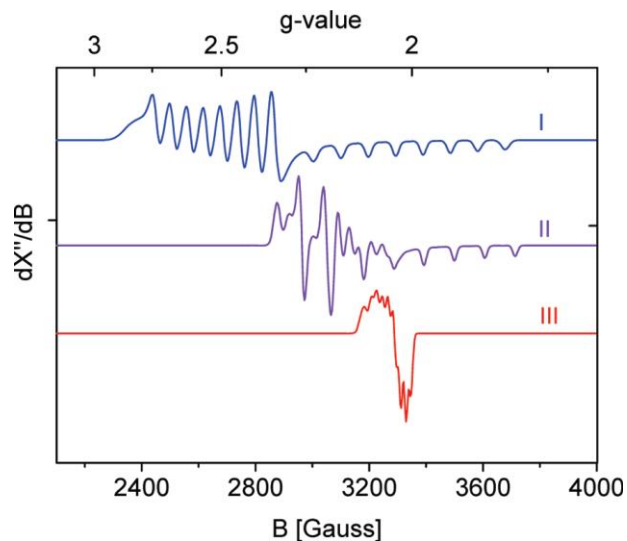
X-band EPR spectrum of [Co(3,5-Di<sup>t</sup>Bu-ChenPhyrin)] before (top) and after (bottom) addition of EDA. Spectra were recorded in frozen toluene at 40 K.

indicating the presence of 2-3 paramagnetic cobalt species



Co(3,5-Di<sup>t</sup>Bu-ChenPhyrin)

#### Individual components I, II, and III contributing to the EPR spectrum



a mixture of three species I, II, and III in a rough ratio of 5:1:0.8 as derived from the spectral simulations



## 2. New activated species using diazo compound

### 2.1. Metal carbene radical

#### EPR Spectroscopy

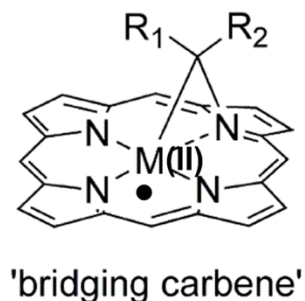
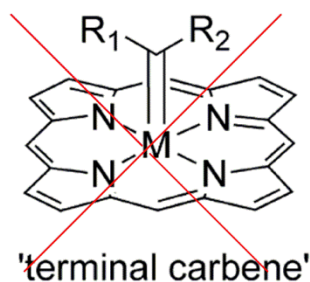
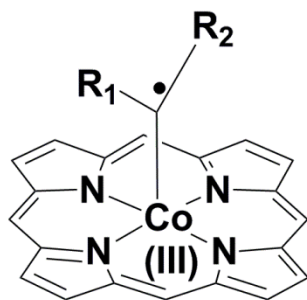
**Table 1.** Experimental<sup>a</sup> and DFT Calculated<sup>b</sup> EPR Parameters<sup>c</sup>

	$g_x$	$g_y$	$g_z$	$A_x^{\text{Co}}$	$A_y^{\text{Co}}$	$A_z^{\text{Co}}$	$A_x^{\text{H}}$	.	$A_z^{\text{H}}$
<b>I<sup>a</sup></b> Co(TPP)(H <sub>2</sub> O) <sup>e</sup>	2.558 2.505	2.520 2.505	2.004 2.014	255 265	208 265	270 315	— —	— —	— —
<b>II<sup>a</sup></b> Co( <i>por</i> )(CHCOOMe) 'bridging carbene' <sup>b</sup>	2.228 2.332	2.120 2.183	2.005 2.070	110 -39	115 234	300 491	— —	— —	— —
<b>III<sup>a</sup></b> Co( <i>por</i> )(CHCOOMe) 'terminal carbene' <sup>b</sup>	2.060 2.010	2.048 2.002	2.030 1.975	40 -67	56 -19	nr <sup>d</sup> 6	160 -77	40 -50	nr <sup>d</sup> -13

<sup>a</sup> Parameters from spectral simulations. <sup>b</sup> Orca, b3-lyp/TZVP. <sup>c</sup> Hyperfine couplings in MHz. <sup>d</sup> nr = not resolved. <sup>e</sup> Taken from reference 24.

**Free radical :  $g=2.00232$**

**A is in proportion to lone pair density**



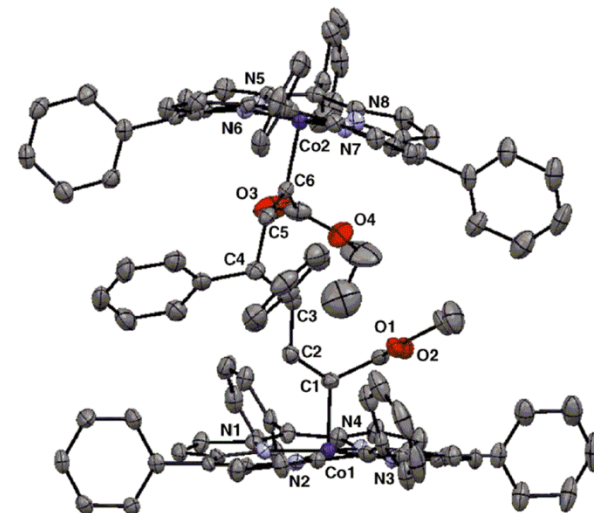
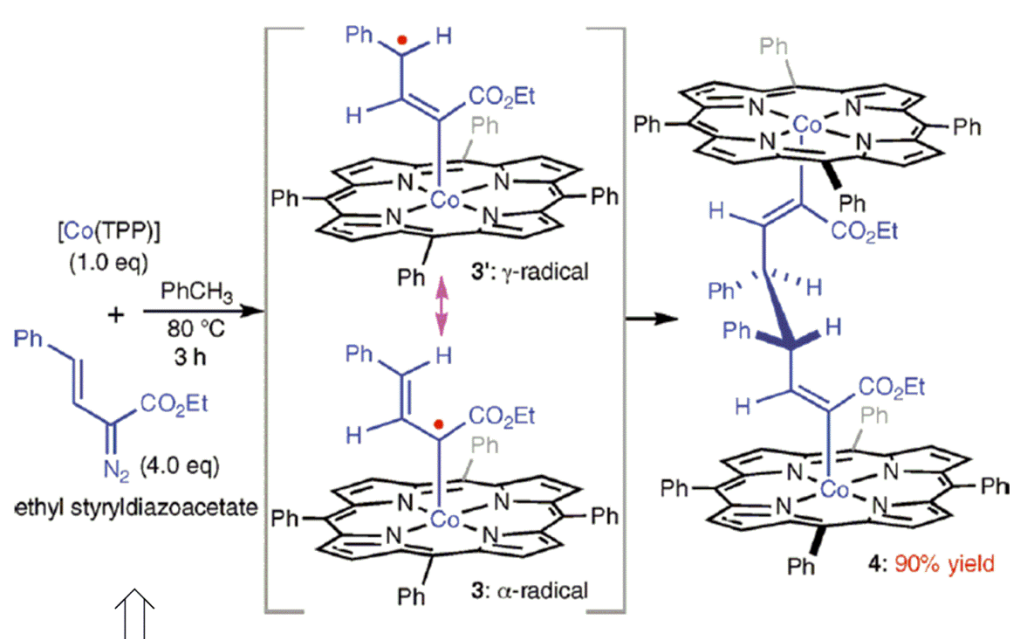
**the bridging carbene and terminal carbene exist in dynamic equilibrium with each other in solution**

## 2. New activated species using diazo compound

### 2.1. Metal carbene radical

Bas de Bruin, X, P, Zhang, JACS, 2011, 133, 8518

#### Homodimerization via C-C Bond Formation

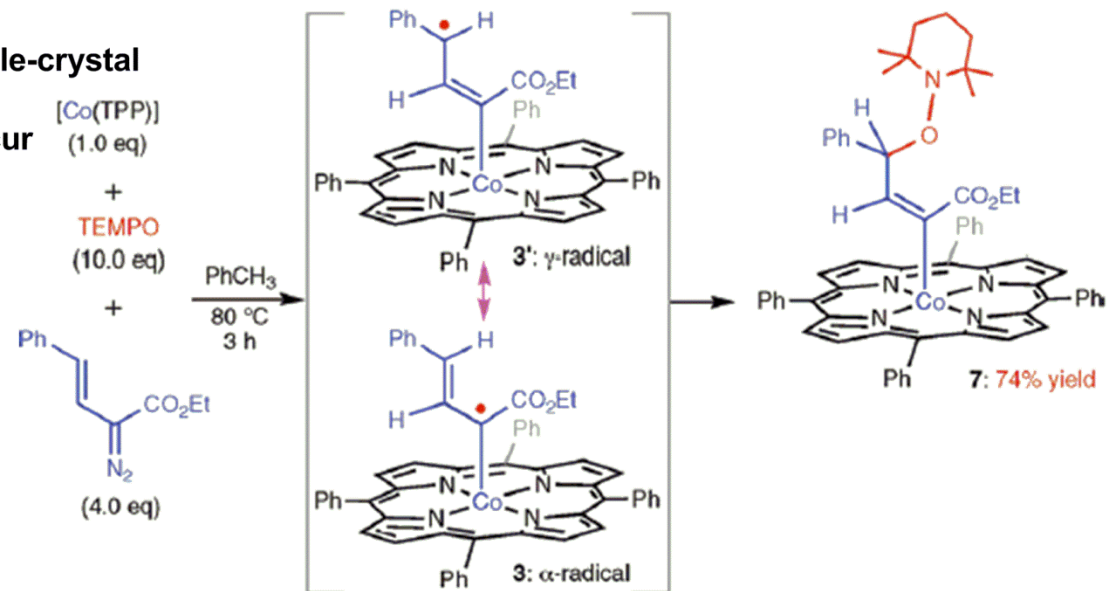


#### Trapping by TEMPO

The detailed structure of 4 was unveiled by single-crystal X-ray diffraction.

C-H abstraction at  $\alpha,\gamma$ -C from toluene didn't occur

The structure of 7 was unveiled by NMR and MS



## 2. New activated species using diazo compound

### 2.1. Metal carbene radical

First report of using cobalt(II) porphyrin complexes for cyclopropanation reactions

S, Cenini, Eur. J. Inorg. Chem. 2003, 1452

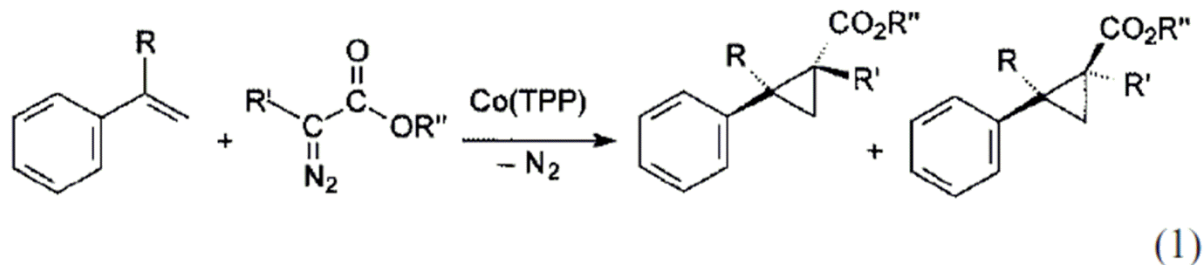


Table 1. Reactions of EDA with olefins catalyzed by Co<sup>II</sup>(porphyrin)

Entry <sup>[a]</sup>	Substrate	Catalyst	<i>t</i> /h <sup>[b]</sup>	Cyclopropane yield% <sup>[c]</sup>	<i>trans/cis</i> ratio <sup>[d]</sup>
1	styrene	Co(TPP)	21	62 (1)	85:15
2	styrene	Co( <i>p</i> -ClTPP)	22	99 (1)	75:25
3	styrene	Co( <i>p</i> -OMeTPP)	22	80 (1)	76:24
4	styrene	Co(OEP)	24	71 (1)	83:17
5	1,1-diphenylethylene	Co(TPP)	7	99 (3)	–
6	1,1-diphenylethylene	Co( <i>p</i> -ClTPP)	10	88 (3)	–
7	1,1-diphenylethylene	Co( <i>p</i> -OMeTPP)	19	85 (3)	–
8	1,1-diphenylethylene	Co(OEP)	20	65 (3)	–
9	$\alpha$ -methylstyrene	Co(TPP)	19	95 (5)	70:30
10	$\alpha$ -methylstyrene	Co( <i>p</i> -ClTPP)	17	91 (5)	75:25
11	$\alpha$ -methylstyrene	Co( <i>p</i> -OMeTPP)	20	72 (5)	77:23
12	$\alpha$ -methylstyrene	Co(OEP)	21	65 (5)	85:15

**In the control, diethyl maleate reacts with Co(TPP) to give the corresponding cyclopropane in low yields. there has never been reported with other catalytic systems based on metal-porphyrin complexes!!**

## 2. New activated species using diazo compound

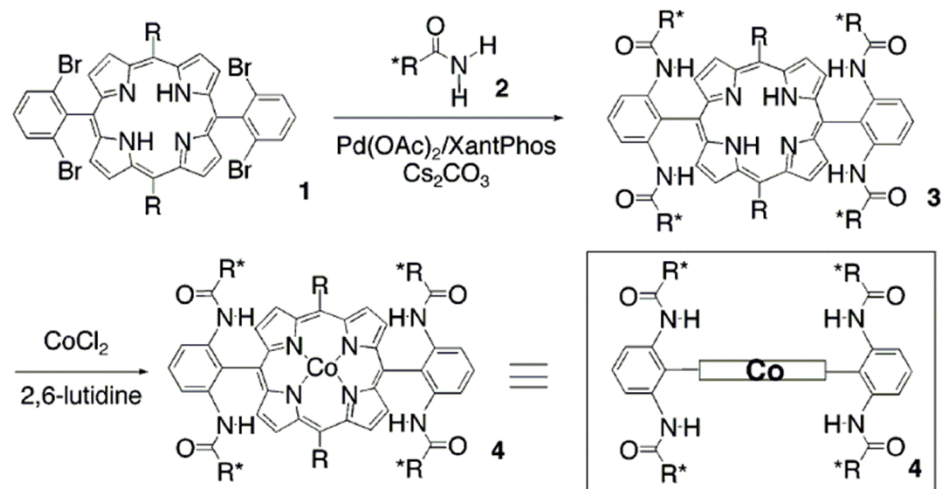
### 2.1. Metal carbene radical

X, P, Zhang, J. Org. Chem. 2003, 68, 8179 -First asymmetric cyclopropanation using Co Por.

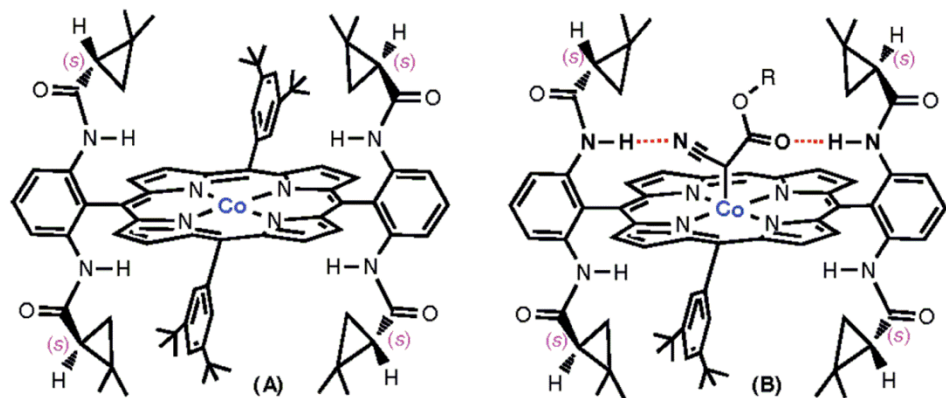
X, P, Zhang, JACS, 2004, 126, 14718 -Ligand improvement

X, P, Zhang, JACS, 2010, 132, 12796- Great Stereoselective Cyclopropanation

#### scheme : synthesis of Chiral Cobalt Porphyrin



#### Effect of stabilization by hydrogen bond



⇐ stabilized metallocarbene intermediate  
bring about good regioselectivity

[Co(P1)]  
(P1 = 3,5-Di<sup>t</sup>Bu-ChenPyrin)

Potential Double H-Bonding Interaction  
in Postulated Carbene Complex of [Co(P1)]<sup>a</sup>

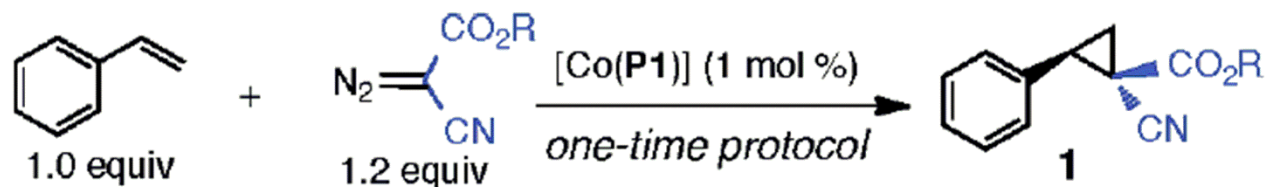
<sup>a</sup>For clarity, the 3,5-di-<sup>t</sup>-Bu-phenyl group in the back of the ligand is omitted.

## 2. New activated species using diazo compound

### 2.1. Metal carbene radical

#### Asymmetric Cyclopropanation with olefin

Performed in one-time fashion for 24 h using 1 mol % [Co(P1)] under N<sub>2</sub> with 1.0 equiv of styrene and 1.2 equiv of R-cyanodiazooacetates.



entry	R	solvent	temp (°C)	yield (%) <sup>b</sup>	E:Z <sup>c</sup>	ee (%) <sup>d</sup>
1	Et	CH <sub>2</sub> Cl <sub>2</sub>	25	99	84:16	62
2	Et	C <sub>6</sub> H <sub>5</sub> Cl	25	92	84:16	66
3	Et	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	25	99	81:19	71
4	Et	C <sub>6</sub> H <sub>5</sub> Me	25	94	85:15	70
5	Et	<i>n</i> -C <sub>6</sub> H <sub>14</sub>	25	99	88:12	74
6	<i>t</i> -Bu	<i>n</i> -C <sub>6</sub> H <sub>14</sub>	25	89	>99:1	91
7	<i>t</i> -Bu	<i>n</i> -C <sub>6</sub> H <sub>14</sub>	0	83	>99:1	95
8	<i>t</i> -Bu	<i>n</i> -C <sub>6</sub> H <sub>14</sub>	-20	96	>99:1	98

Co cat. is durable to various solvent!!

previous report : diazoacetate, Diazosulfones,  $\alpha$ -nitrodiazoacetates as diazo reagents

## 2. New activated species using diazo compound

### 2.1. Metal carbene radical

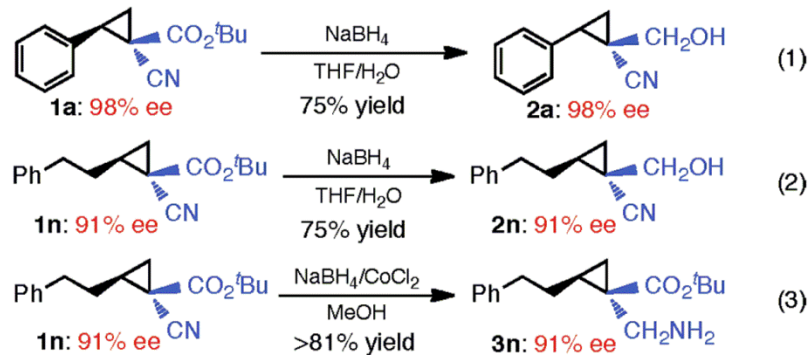
#### Great substrate scope

entry	cyclopropane	yield (%) <sup>b</sup>	E:Z <sup>c</sup>	ee (%) <sup>d</sup>	[α] <sup>e</sup>
<i>electron-rich and -poor aromatic olefins</i>					
1		96	>99:1	98	(-)
2 <sup>g</sup>		88	>99:1	99	(-)
3 <sup>g</sup>		81	>99:1	98	(-)
4 <sup>g</sup>		90	>99:1	98	(-)
5 <sup>h</sup>		73	>99:1	99	(-) <sup>f</sup>
<i>electron-deficient nonaromatic olefins</i>					
6 <sup>i</sup>		90	>99:1	88	(-)
7 <sup>i</sup>		79	>99:1	92	(-)
8 <sup>j</sup>		99	>99:1	87	(-)
9 <sup>k</sup>		72	>99:1	82	(-)
10 <sup>j</sup>		81	>99:1	92	(-)
11 <sup>j</sup>		99	72:28	82	(-)

#### simple aliphatic and electron-rich olefins

12 <sup>l</sup>		86	>99:1	≥96 <sup>n</sup>	(-)
13 <sup>l</sup>		72	>99:1	≥92 <sup>n</sup>	(-)
14 <sup>l</sup>		90	>99:1	91	(-)
16 <sup>m</sup>		97	>99:1	71	(+)
17 <sup>l</sup>		86	>99:1	82	(+)
18 <sup>l</sup>		80	>99:1	88	(-)

#### transformation

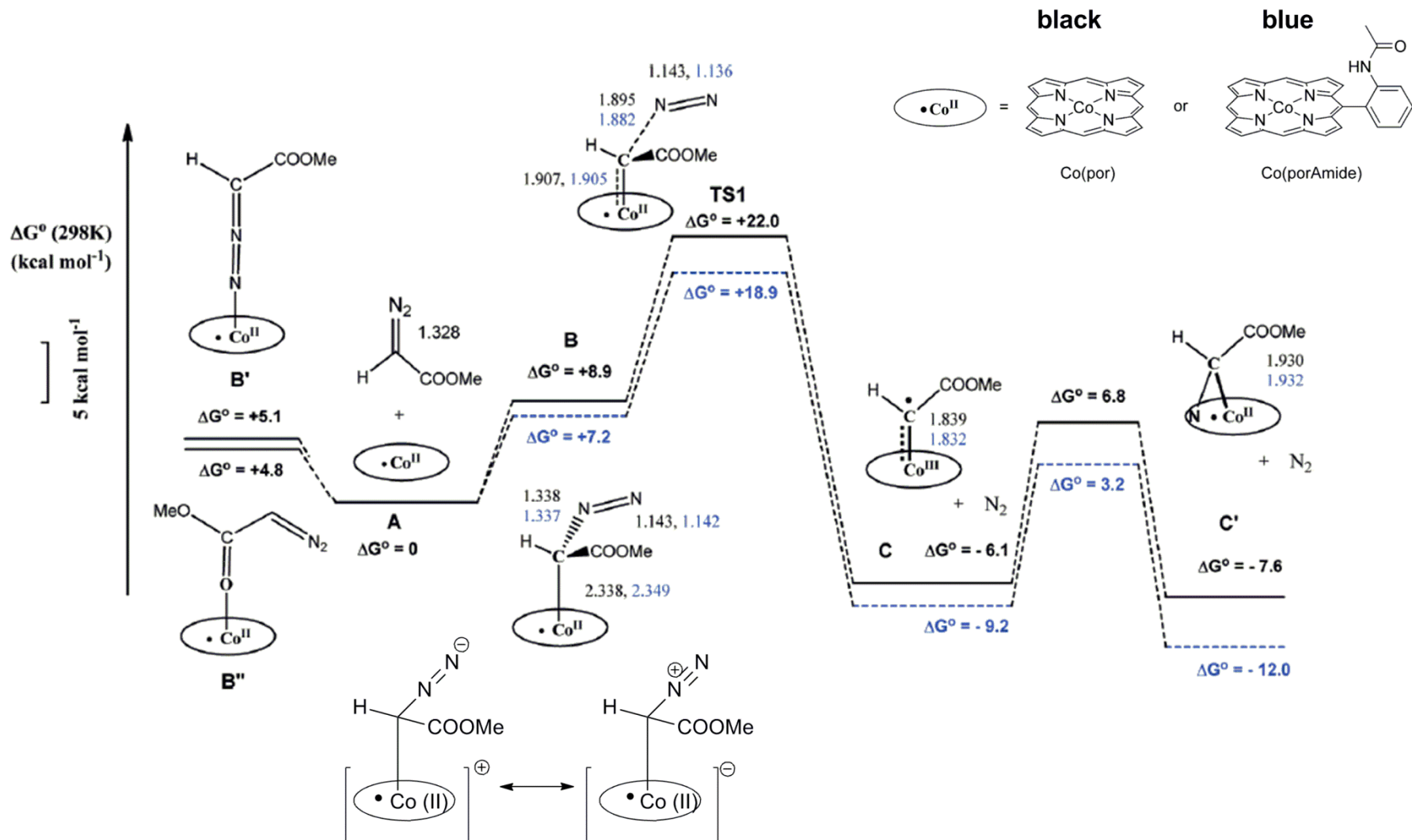


## 2. New activated species using diazo compound

### 2.1. Metal carbene radical

#### Formation of the Carbene Complexes by DFT calculation

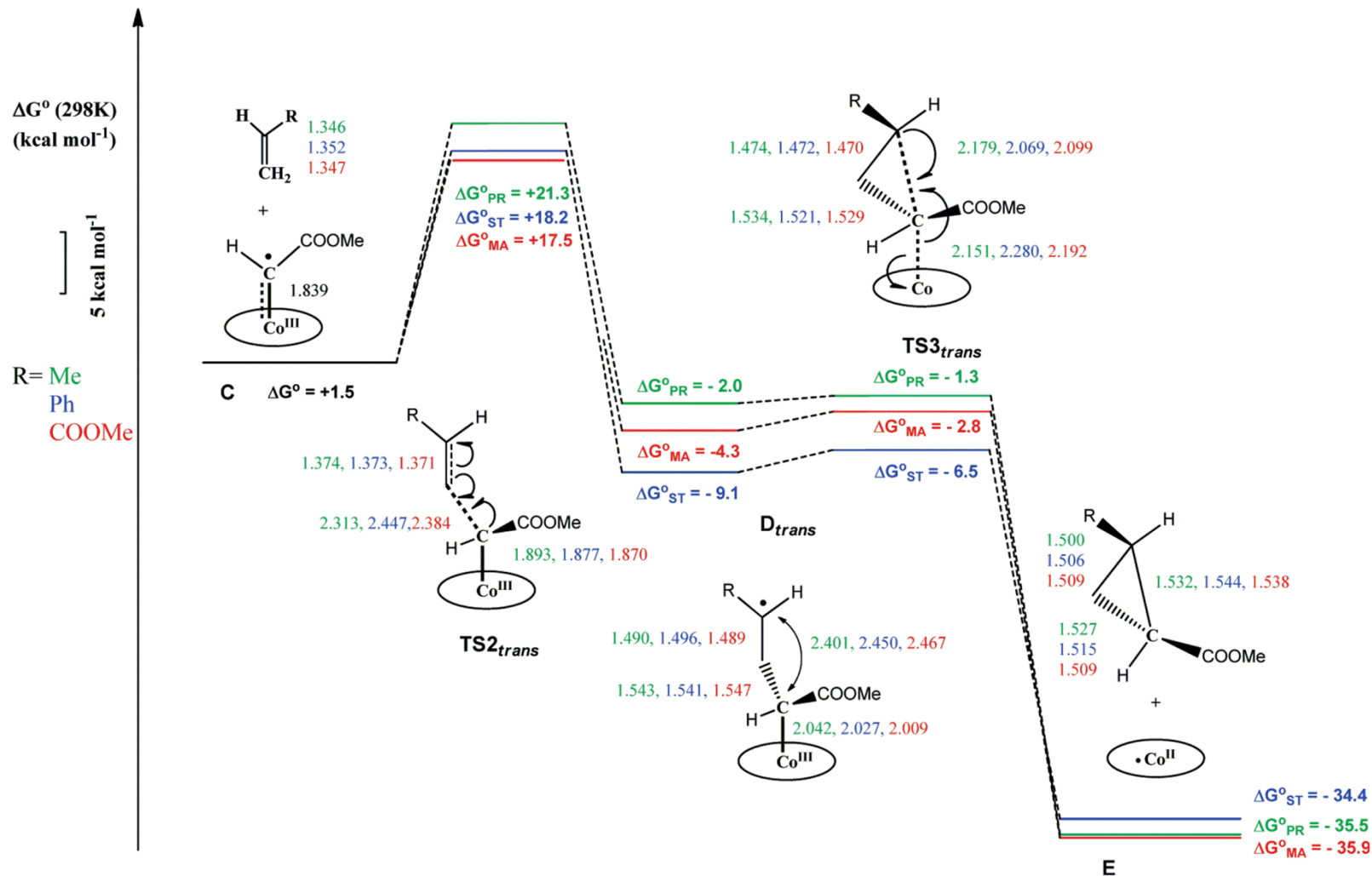
The calculated free energies for the reaction of MDA with Co(por) and Co(porAmide)



## 2. New activated species using diazo compound

### 2.1. Metal carbene radical

#### Computed pathways for trans-cyclopropanation



the diastereoselectivity of cyclopropanation is predetermined in the C-C bond-forming transition state TS2.

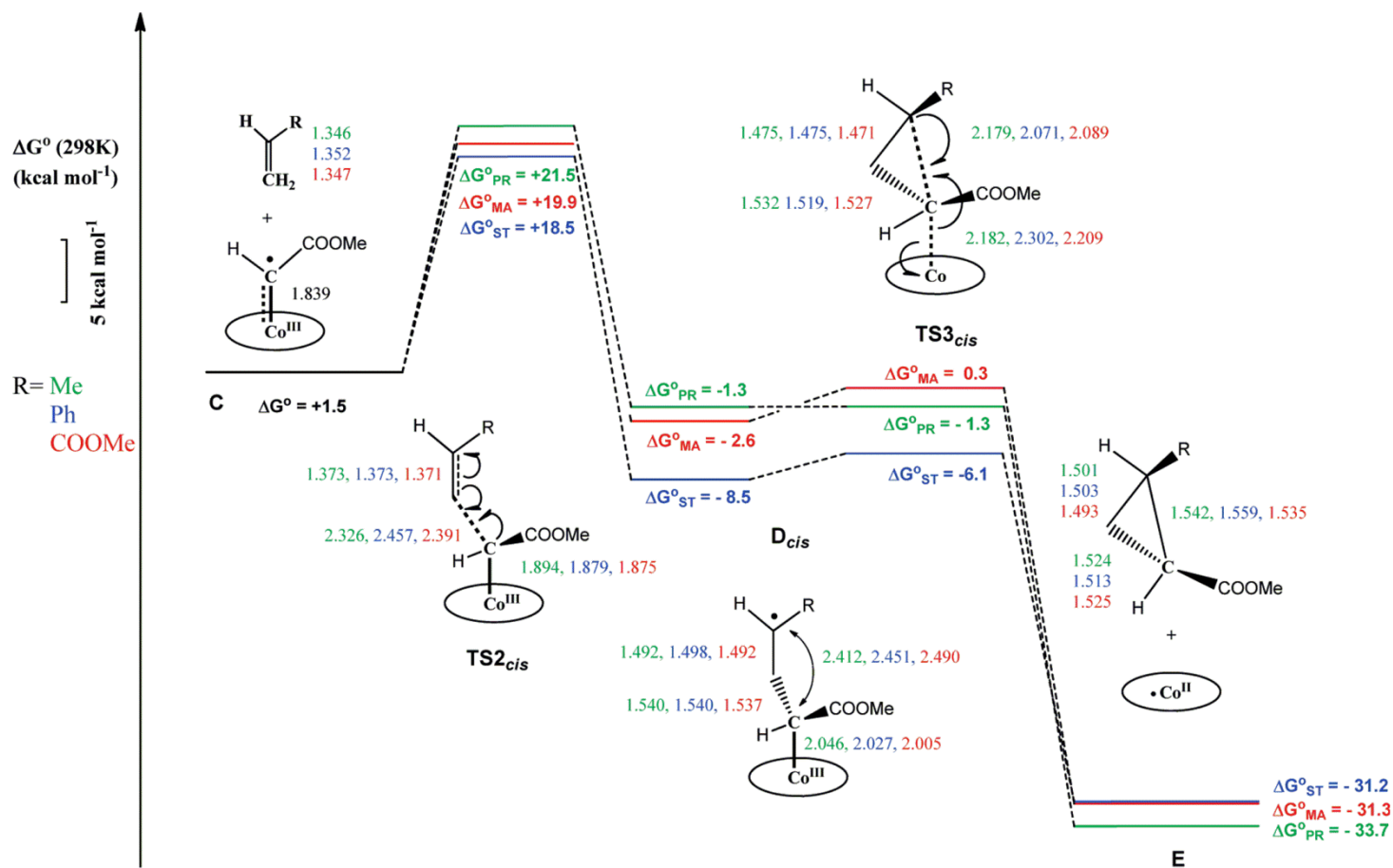
because the barrier for rotation of a C-C bond in propane is about 3 kcal/mol



## 2. New activated species using diazo compound

### 2.1. Metal carbene radical

#### Computed pathways for cis-cyclopropanation



#### Calculated and Experimental trans:cis Ratios

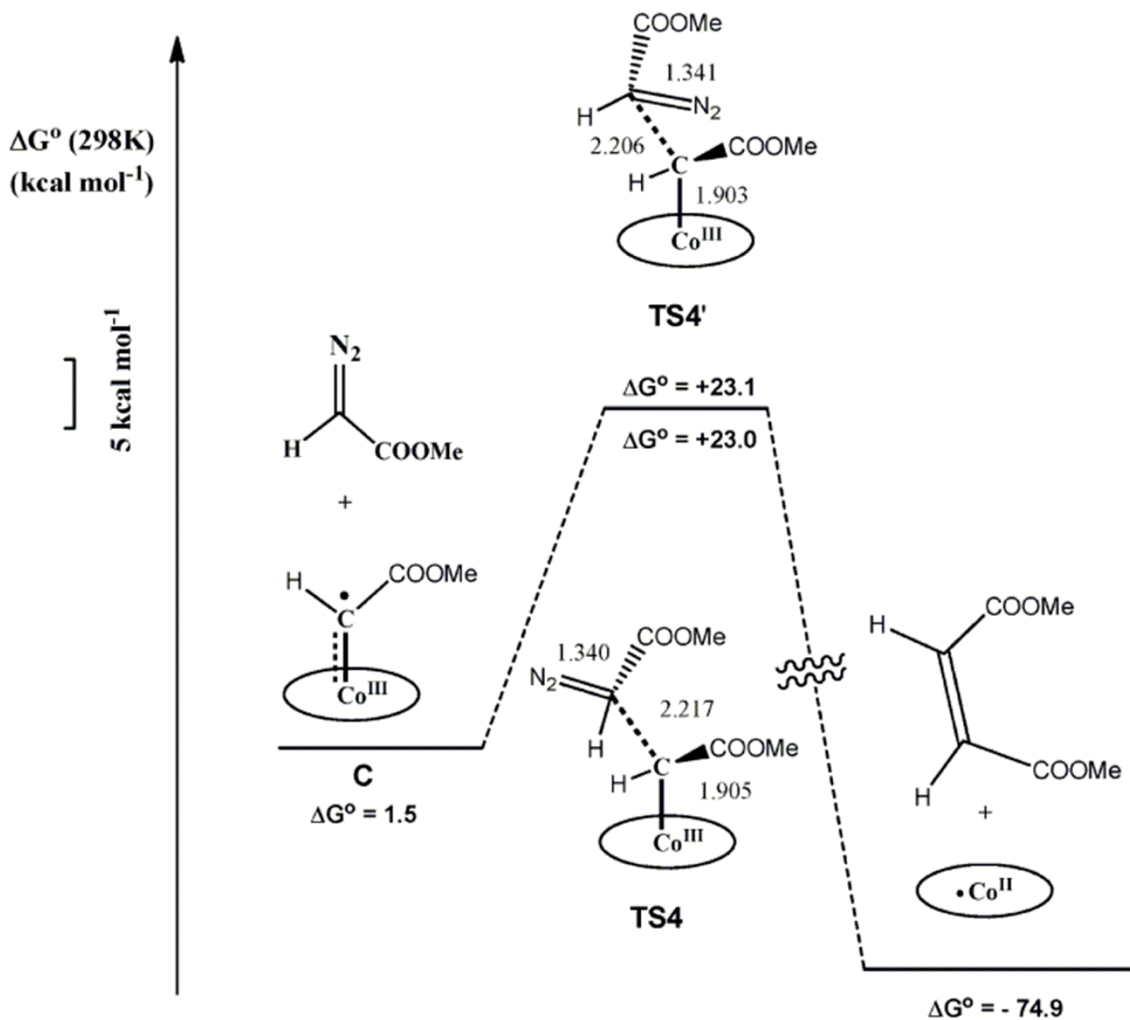
olefin	$\Delta G_{trans}$	$\Delta G_{cis}$	trans:cis	expt.
methyl acrylate	17.5	19.9	98:02	99:01 <sup>a</sup>
styrene	18.2	18.5	68:32	75:25 <sup>b</sup>
propene	21.3	21.5	55:45	n.d.

<sup>a</sup> Co<sup>II</sup>(3,5-Di<sup>t</sup>Bu-ChenPhyrin), ref 4d. <sup>b</sup> Co<sup>II</sup>(TPP), ref 4a.

## 2. New activated species using diazo compound

### 2.1. Metal carbene radical

#### Suppression of Side-Product Formation by Carbene Dimerization



One of the advantages of using Coll(por) catalysts for cyclopropanation is their markedly suppressed carbene dimerization activity

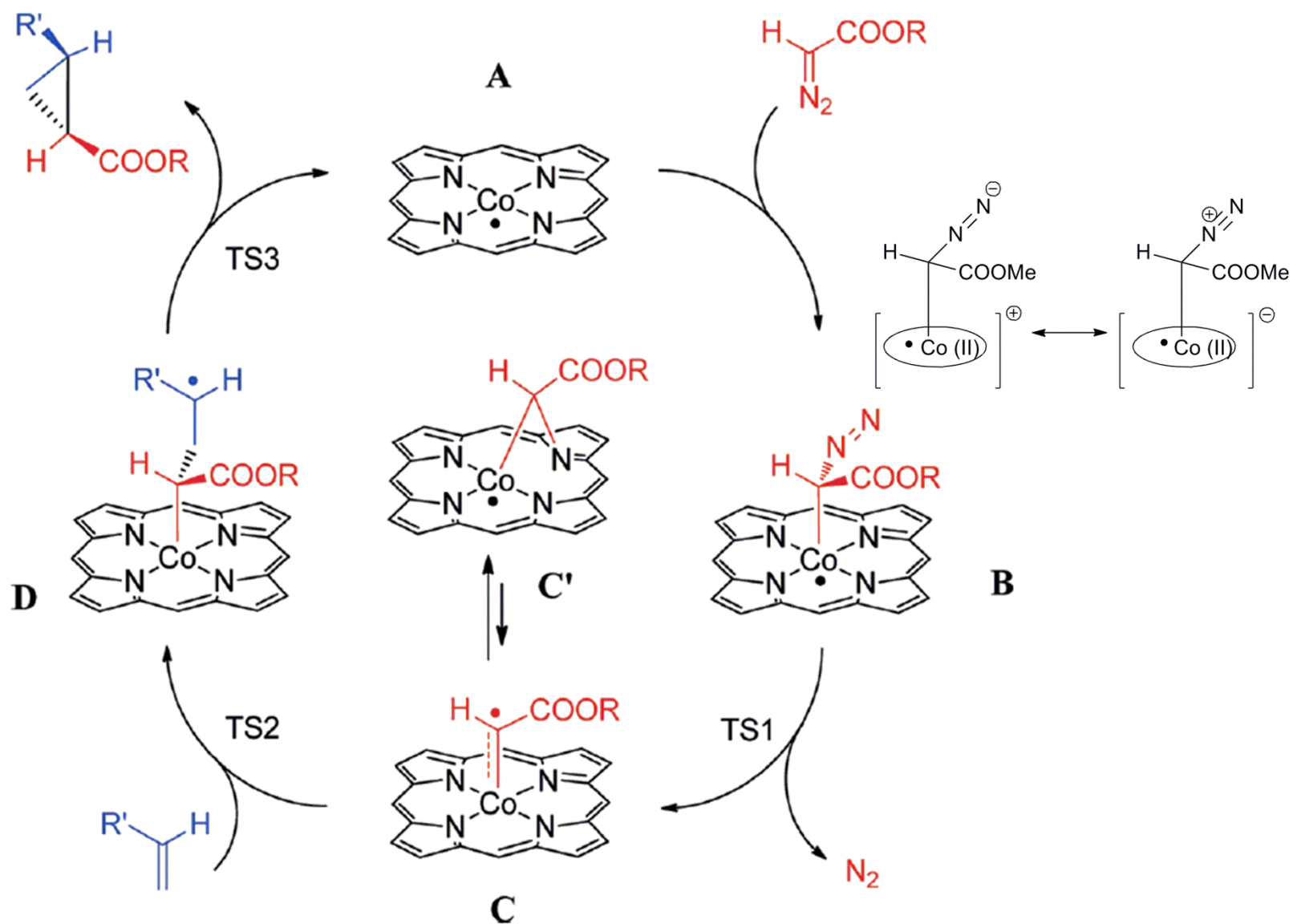


the calculated barrier for dimer formation is higher than the barriers for radical addition of C to olefin due to the steric influence between the porphyrin ring and the attacking diazoacetate, carbene dimerization is expected to be suppressed

## 2. New activated species using diazo compound

### 2.1. Metal carbene radical

#### Reaction mechanism



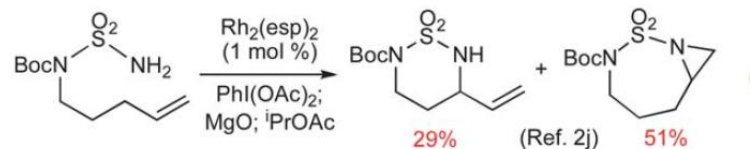
## 2. New activated species using diazo compound

### 2.2. Application

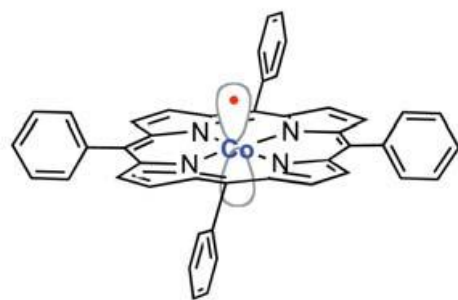
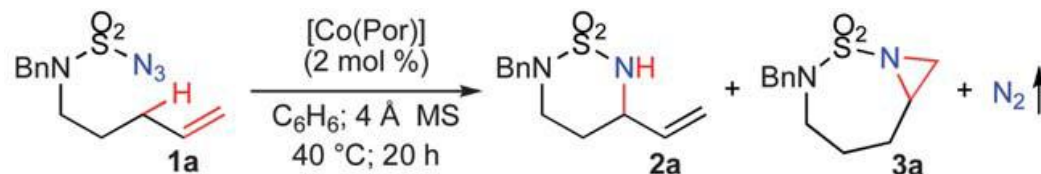
#### Application to amination - Chemoselective intramolecular allylic C-H amination

Chem. Sci., 2011, 2, 2361, X, P, Zhang

The amination of Du Bois - selectivity is low.....

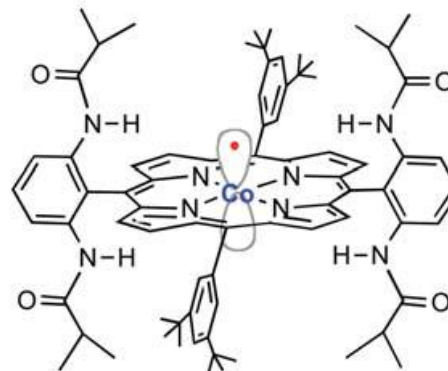


#### The amination using Metal carbene radical



$[\text{Co}(\text{TPP})]$

yield: 43%; **2a/3a**: > 99/1



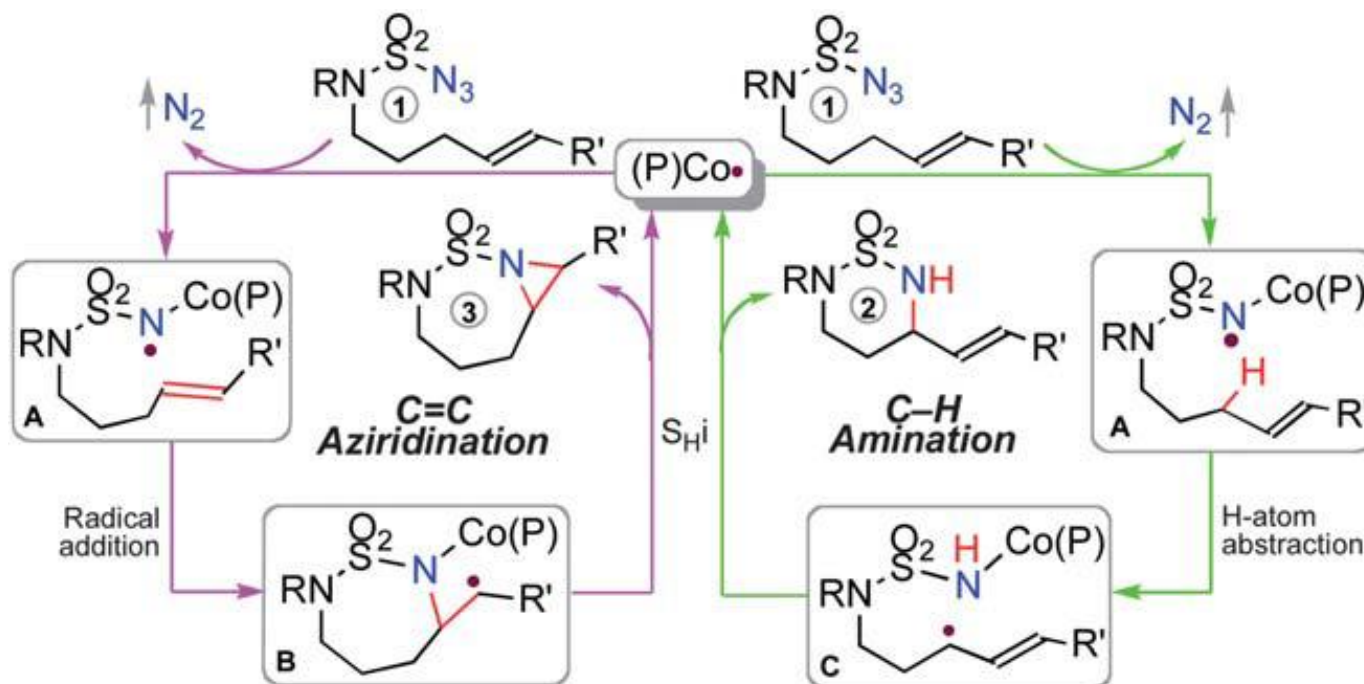
$[\text{Co}(\text{P1})]$  (P1: 3,5-Di $t$ Bu-IbuPhyrin)

yield: 99%; **2a/3a**: > 99/1

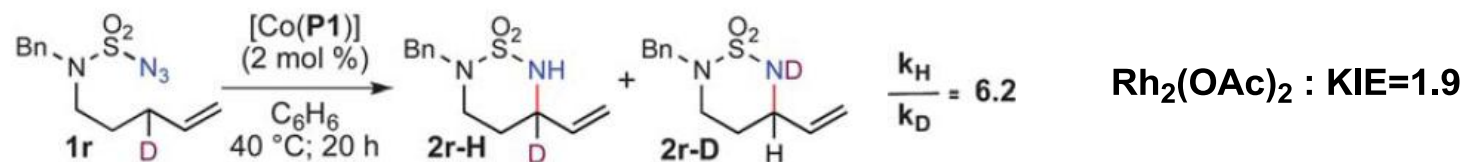
## 2. New activated species using diazo compound

### 2.2. Application

#### Reaction mechanism



#### The study of KIE



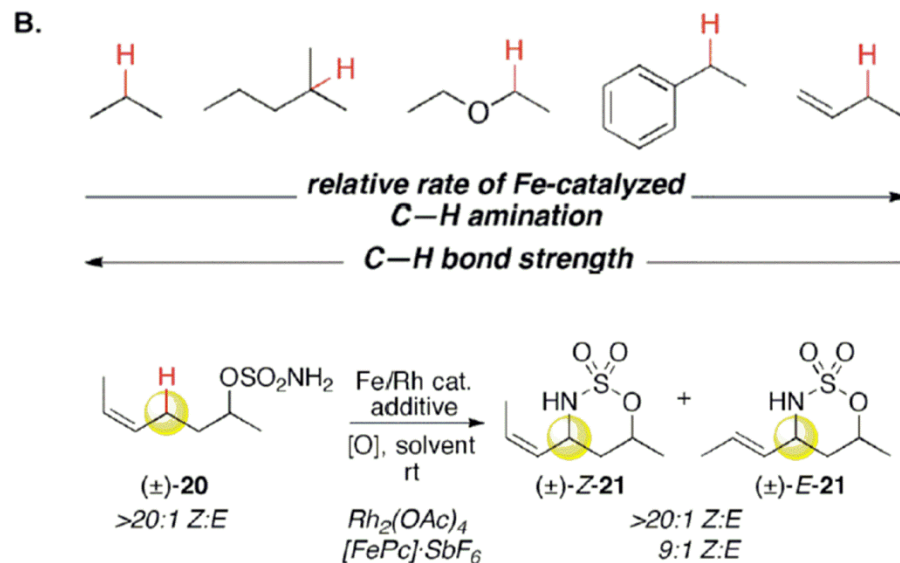
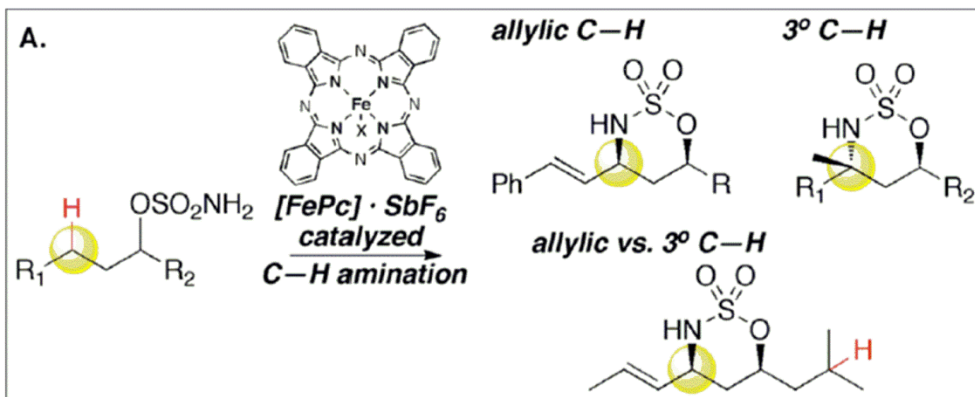
## 2. New activated species using diazo compound

### 2.2. Application

#### Formation of Nitrene Radical -another metal-

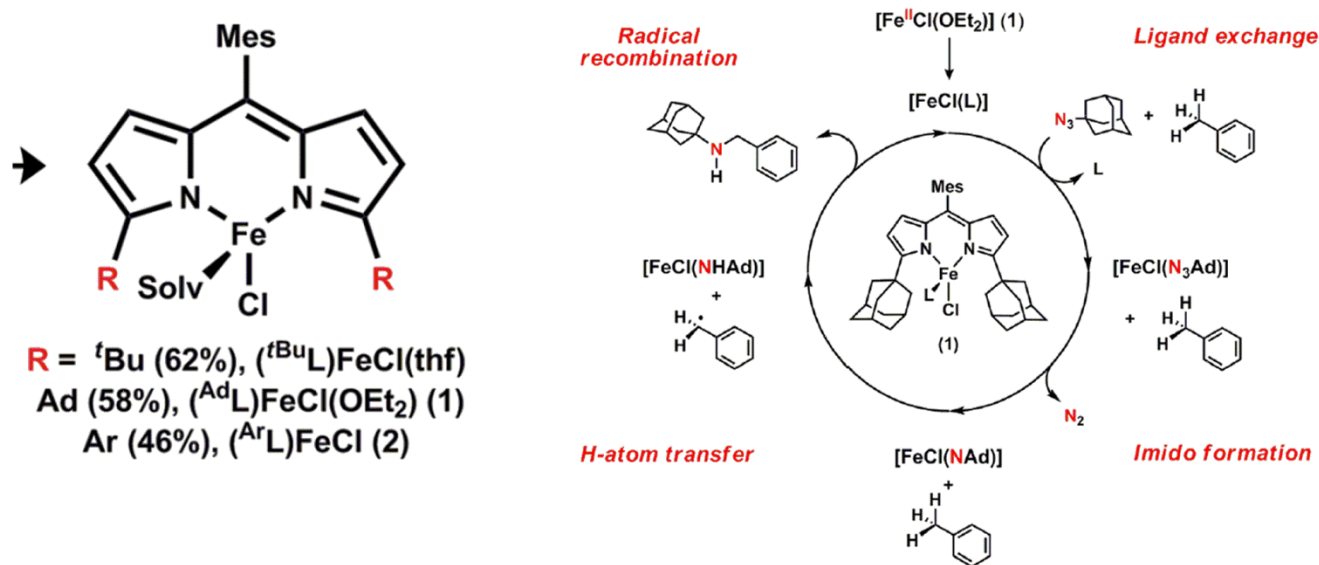
#### Iron-catalysed Intramolecular Allylic C-H Amination

M. C. White, JACS, 2012, 134



#### Catalytic C-H Bond Amination from High-Spin Iron Imido Complexes

T, A. Betley, JACS, 2011, 133, 4917



toluene to its perdeuterio analogue : KIE=12.8

## 2. New activated species using diazo compound

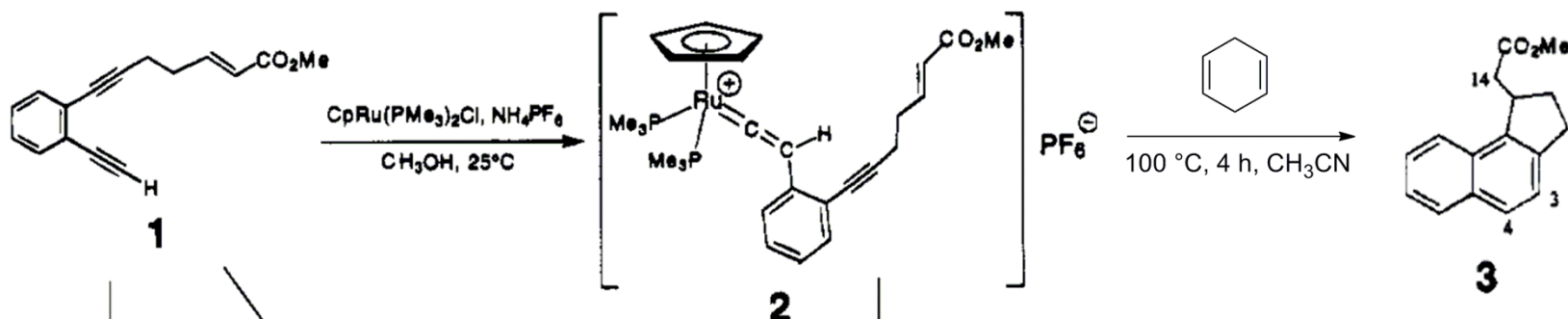
### 2.3. My desired reaction

Using Carbene radical and Carbenoid, most problematic point is.....via diazo compounds !!

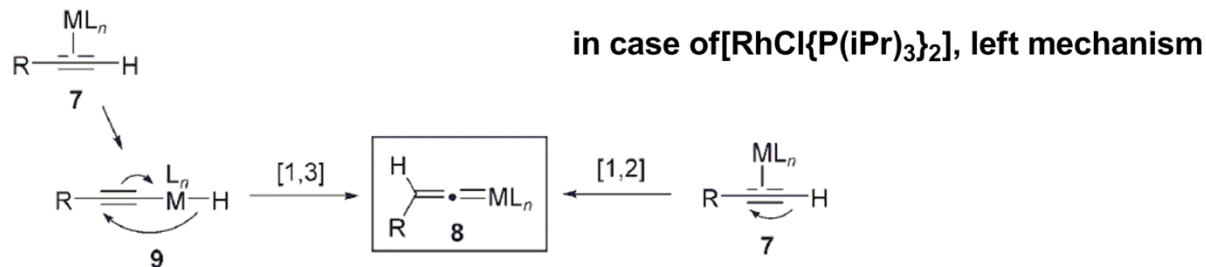
the other approach of carbenoid formation

### Metal Vinylidenes through transition-metal activation of terminal alkynes

M. G. Finn, JACS. 1995,117, 8045



### Mechanism



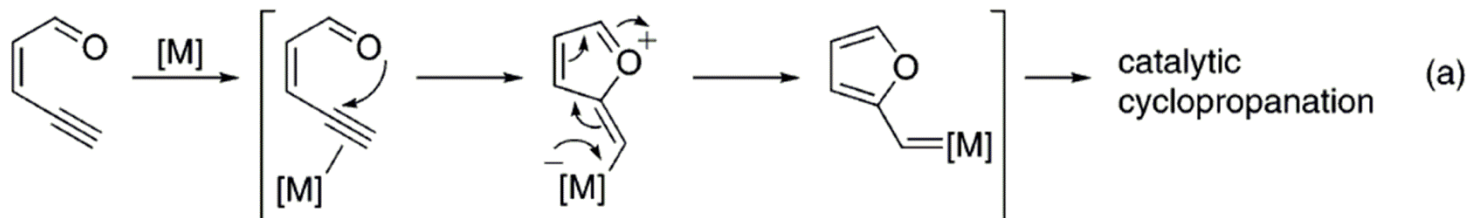
## 2. New activated species using diazo compound

### 2.3. My desired reaction

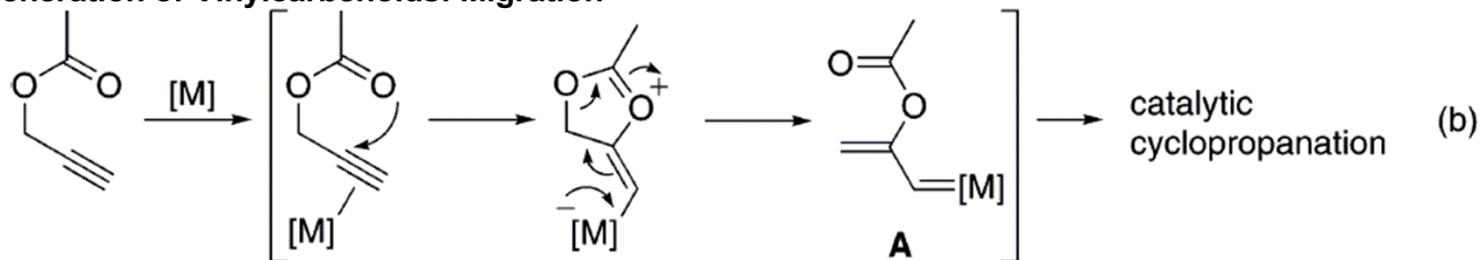
the other approach of carbenoid formation

#### 1: Generation of Furyl and Pyrrolyl Carbenoids: Cyclization

S, Uemura, J. Org. Chem. 2003, 68, 8505

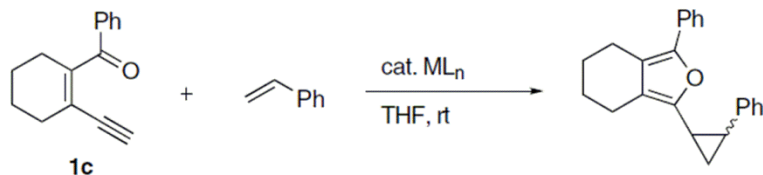


#### 2: Generation of Vinylcarbenoids: Migration



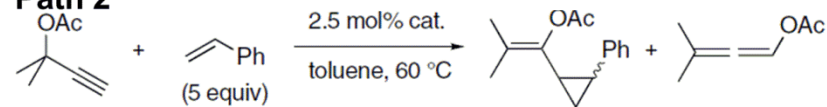
#### Path 1

Scheme 5



cat. (5 mol%)	time	yield ( <i>cis:trans</i> )
Cr(CO) <sub>5</sub> (THF)	14 h	85% (74:26)
Mn(CO) <sub>5</sub> Br	24 h	21% ( 9:91)
[( <i>p</i> -cymene)RuCl <sub>2</sub> ] <sub>2</sub>	2 h	85% (33:67)
[Rh(OAc) <sub>2</sub> ] <sub>2</sub>	1 h	93% ( 8:92)
PtCl <sub>2</sub>	1 h	81% (23:77)

#### Path 2



entry	cat.	time	yield	<i>cis:trans</i>	allene
1	[RuCl <sub>2</sub> (CO) <sub>3</sub> ] <sub>2</sub>	18 h	86%	80:20	5%
2 <sup>a</sup>	[RuCl <sub>2</sub> (CO) <sub>3</sub> ] <sub>2</sub>	18 h	99%	87:13	0%
3	[Rh(OCOCF <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub>	30 min	trace	—	99%
4	[IrCl(cod)] <sub>2</sub>	18 h	37%	70:30	7%
5 <sup>b</sup>	AuCl <sub>3</sub>	10 min	63%	79:21	26%
6	PtCl <sub>2</sub>	1 h	93%	78:22	7%
7 <sup>a</sup>	PtCl <sub>2</sub>	10 h	74%	80:20	23%

<sup>a</sup> In ClCH<sub>2</sub>CH<sub>2</sub>Cl at 50 °C. <sup>b</sup> 1 mol% of AuCl<sub>3</sub> was used at room temperature.

But this method is only applied to terminal alkyne



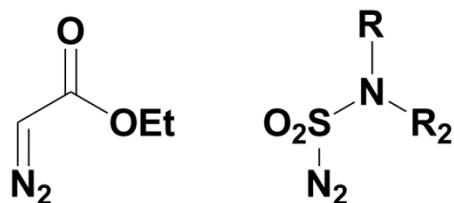
## 2. New activated species using diazo compound

### 2.3. My desired reaction

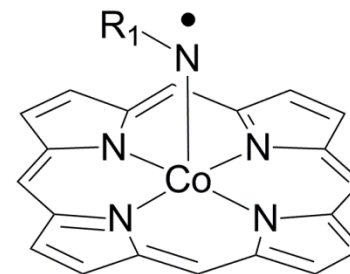
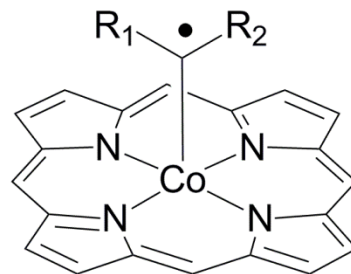
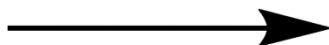
#### Summary 2

Application so far

Nucleophilic character via a stepwise radical process



+ Co(II)(por)

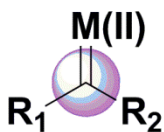


Cyclopropanation

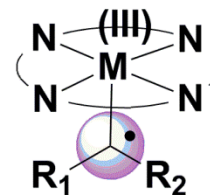


C-H amination

Difference between Fisher-Carbenoid and M-C radical



Fisher-Carbenoid



M-C radical

M=Co

electronic number

6

7

characteristic

electrophilic, competitive

nucleophilic, stepwise

generation

via diazocompound

via diazocompound

Acknowledgement to Komatsu, Kimura, Sonobe