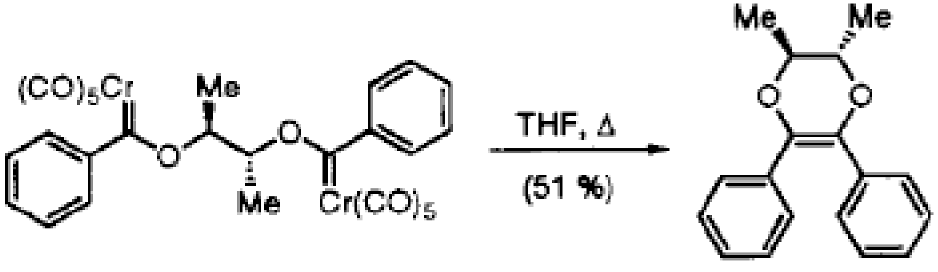
None-group VI Metal Catalyzed Reactions of Fischer Carbene Complexes through Transmetallation

presented by: Jie Huang

Feburary 5, 2004

1. Jose Barluenga et al. *J. Am. Chem. Soc.*, **2004**, 126, 470-471---------------**Ni, Cu, Rh**
2. Miguel A. Sierra et al. *J. Am. Chem. Soc.*, **2001**, 123, 851-861---------------**Pd**
3. Rudolf Aumann et al. *Eur. J. Org. Chem.,* **1999**, 2545-2561-------------------**Rh, Cu**
4. Koichi Narasaka et al. *Chemistry Letters* **1999**, 75-76---------------------------**Pd**

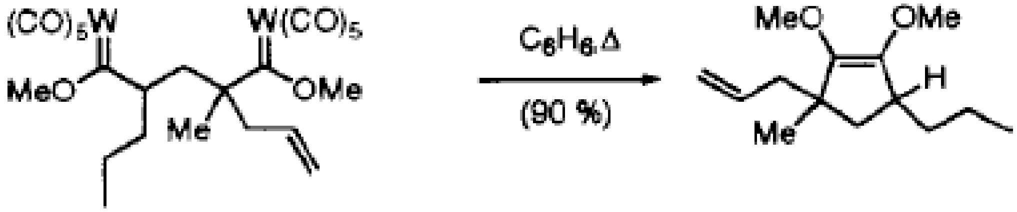
Self-Dimerization Catalyzed by Pd $(OAc)_2$



1

3

Wulff *JACS* **1996**, 2166



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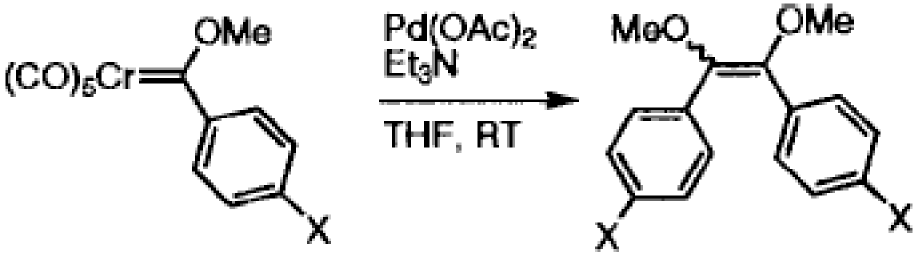
4

Macomber *Organometallics* **1988**, 2072



1a X = H
1b X = Br

2a E/Z 2:1 (53 %)
2b E/Z 2:1 (62 %)

$Rh_2(OAc)_4$ not effective

Miguel A. Sierra et al. *J. Am. Chem. Soc.*, **1998**, 120, 6812-6813

Self-Dimerization of Complexes 10

10a M = Cr, X = H, R = Me
10b M = Cr, X = Br, R = Me
10c M = W, X = H, R = Et

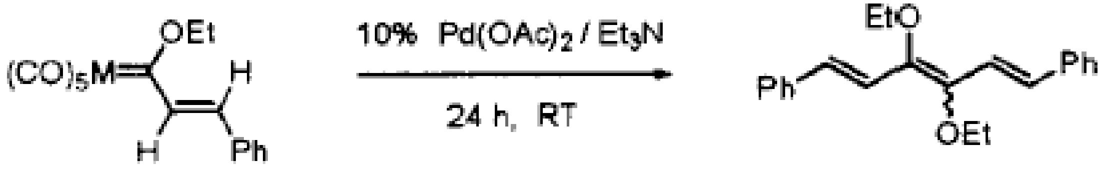
11a X = H, R = Me
11b X = Br, R = Me
11c X = H, R = Et

Table 1. Self-dimerization of Complexes **10**

entry	compd	catalyst (load)[a]/additive	solvent	T	reaction time (h)[b]	**11** E/Z[c]	yield (%)
1	**10a**	$Pd(OAc)_2$ (10%)/Et_3N	THF	rt	1.0	2:1	53
2	**10a**	$Pd(OAc)_2$ (2%)/Et_3N	THF	rt	12.0	4:1	58
3	**10a**	$Pd(OAc)_2$ (10%)/Et_3N/PPh_3 (30%)[a]	THF	rt	0.75	2.5:1	65
4	**10a**	$Pd(OAc)_2$ (10%)/Et_3N/$AsPh_3$ (30%)[a]	THF	rt	1.5	3.6:1	72
5	**10a**	$Pd(OAc)_2$ (10%)/Et_3N/$SbPh_3$ (30%)[a]	THF	rt	3.0	2:1	52
6	**10a**	$Pd(OAc)_2$ (10%)/Et_3N	THF	0 °C	2.0	2.5:1	48
7	**10a**	$Pd(OAc)_2$ (10%)/Et_3N	hexane	rt	20.0	2.4:1	50
8	**10a**	$Pd(OAc)_2$ (10%)/Et_3N	C_6H_6	rt	4.0	2.2:1	63
9	**10a**	$Pd(OAc)_2$ (10%)/Et_3N	Et_2O	rt	8.0	2.6:1	57
10	**10a**	$Pd(OAc)_2$ (10%)/Et_3N	MeCN	rt	0.25	2:1	94
11	**10a**	$Pd(OAc)_2$ (10%)/Et_3N	CH_2Cl_2	rt	1.5	2.2:1	68
12	**10a**	Pd(C) (5%)	THF	rt	21.0	5.1:1	49
13	**10a**	$Pd_2(dba)_3 \cdot CHCl_3$ (5%)	THF	rt	5.0	2.1:1	80
14	**10a**	$PdCl_2(PPh_3)_2$ (5%)/Et_3N	THF	rt	1.25	2.7:1	64
15	**10a**	$PdCl_2(MeCN)_2$ (5%)/Et_3N	THF	rt	0.75	2:1	72
16	**10b**	$Pd(OAc)_2$ (10%)/Et_3N	THF	rt	1.0	2:1	62
17	**10b**	$Pd(PPh_3)_4$ (3%)	THF	rt	2.5	2:1	55
18	**10b**	$Pd(PPh_3)_4$ (0.6%)	THF	rt	18.0	2:1	40
19	**10c**	$Pd(OAc)_2$ (10%)/Et_3N	THF	rt	5.0	1:1	46

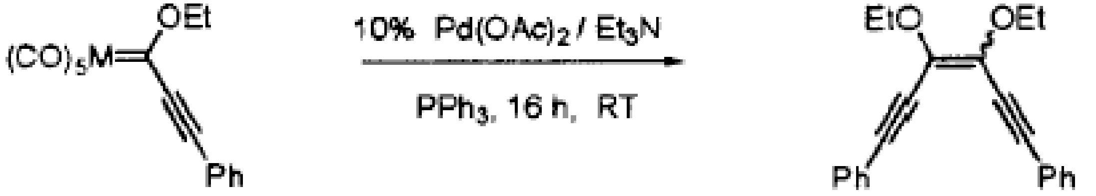
[a] Referred to the carbene complex. [b] The reactions were followed by TLC until complete disappearance of the spot corresponding to the starting carbene complex. [c] Determined by integration of the signals corresponding to the MeO-groups in the ^{1}H NMR spectra of the crude reaction mixtures. Each experiment was repeated at least twice and the value given is the average of both experiments.

Polyene-conjugated System Formation



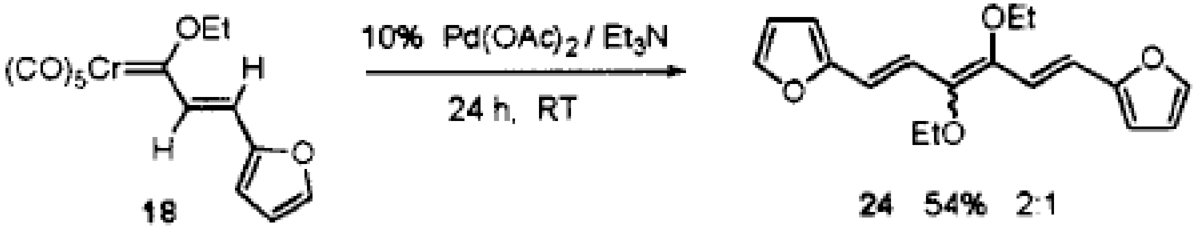
16a M = Cr
16b M = W

22 From **16a** 53 % 2:1
From **16b** 50 % 1:1



17a M = Cr
17b M = W

23 From **17a** 51 % 2:1
From **17b** 32 % 1:1



18

24 54% 2:1

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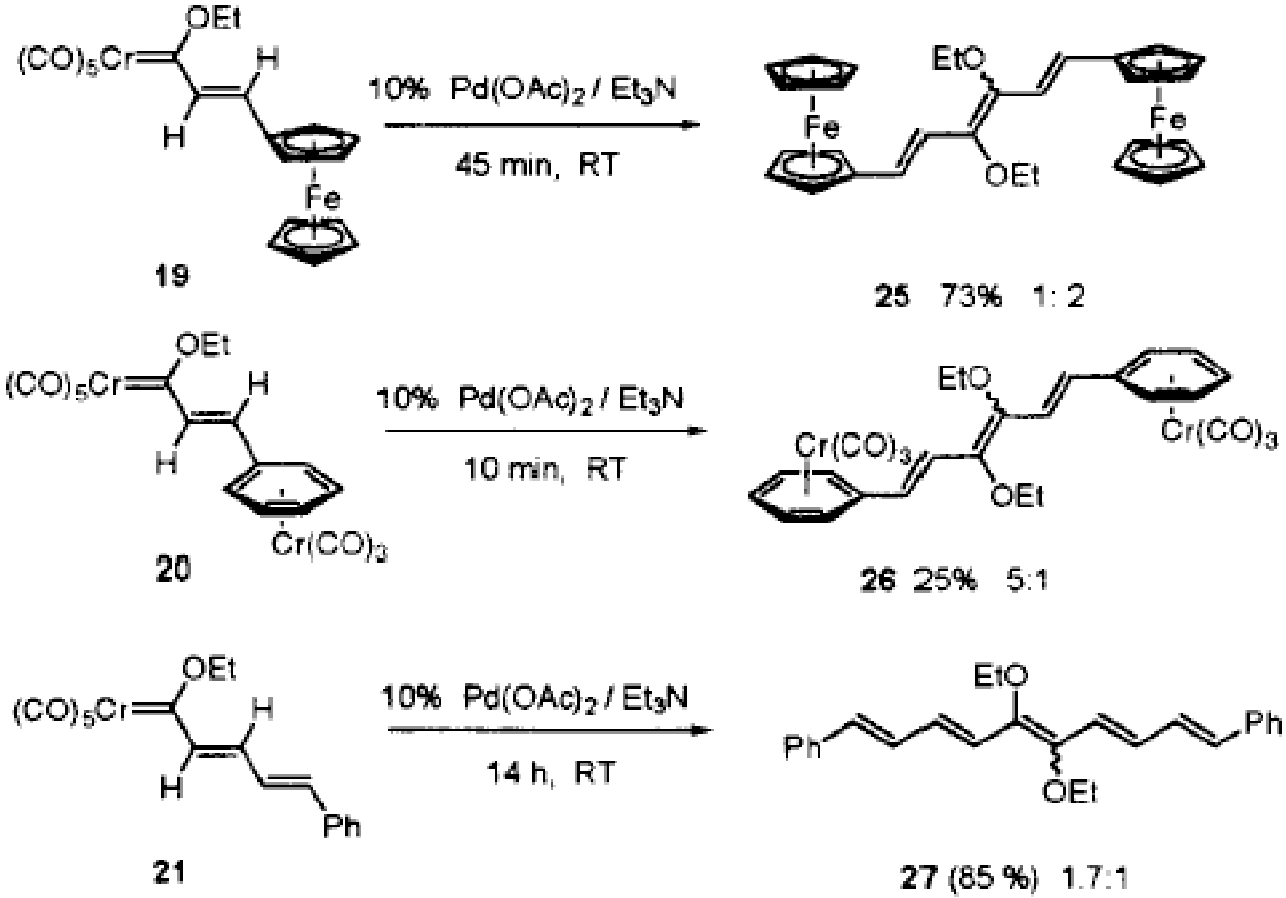
Polyene-conjugated System Formation



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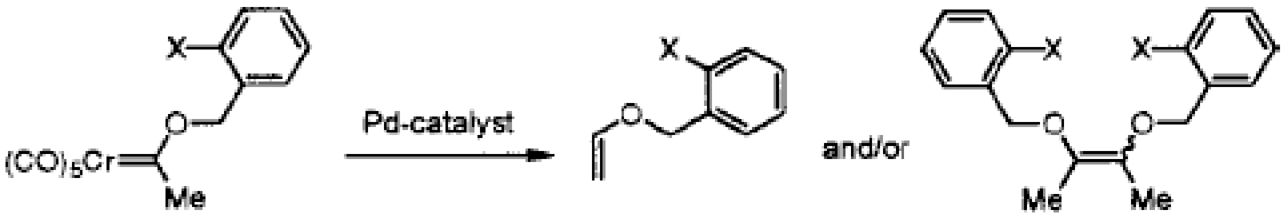
Reaction of Complexes 12



12a X = H
12b X = Me

13a X = H
13b X = Me 65%

14a X = H 70 %

Table 2. Reaction of Alkyl-Substituted Carbene Complexes **12** with Different Pd-Catalysts

entry	compound	catalyst (10%)[a] /additive	reaction time (h)[b]	**13/14**[c]	**14** *E/Z*[d]	yield (%)
1	**12a**	$Pd(OAc)_2/Et_3N$	1	100:0	–	–[e]
2	**12a**	$Pd(PPh_3)_4$	20	0:100	1.1:1	87
3	**12a**	Pd(C)	20	0:100	1.3:1	70
4	**12a**	$Pd_2(dba)_3{\cdot}CHCl_3$	5	0:100	1.9:1	76
5	**12a**	$PdCl_2(PPh_3)_2/Et_3N$	3	5:95	1.3:1	72
6	**12a**	$PdCl_2(MeCN)_2/Et_3N$	1	8:92	1.1:1	78
7	**12b**	$Pd(OAc)_2/Et_3N$	1	100:0	–	65

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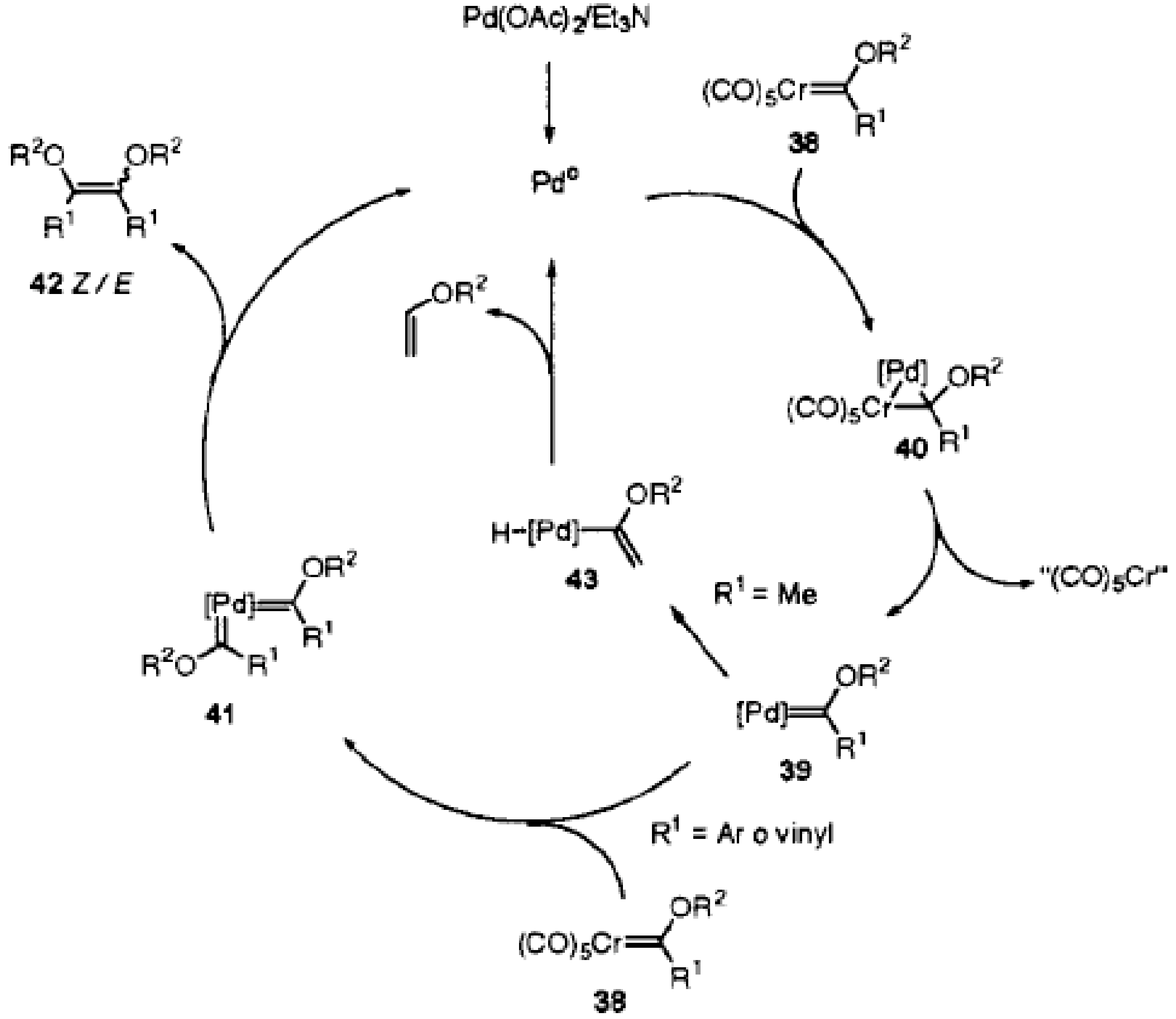
Scheme 8



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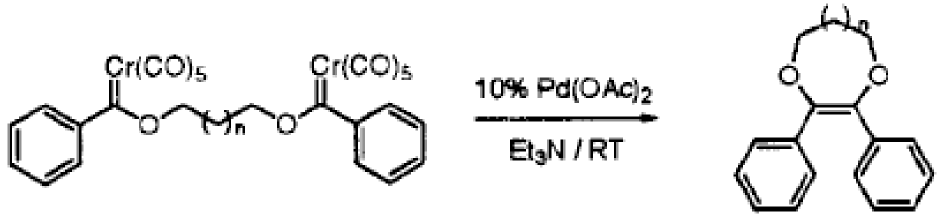
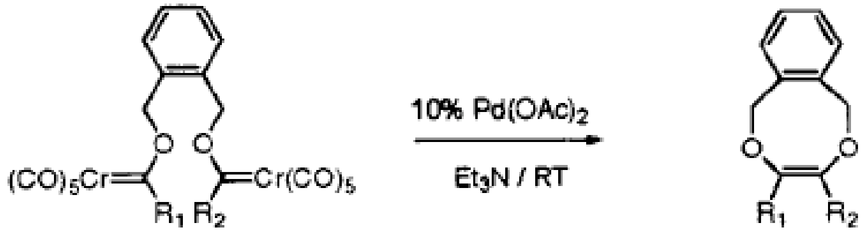
Intramolecular Dimerization to Form Cyclic Compounds



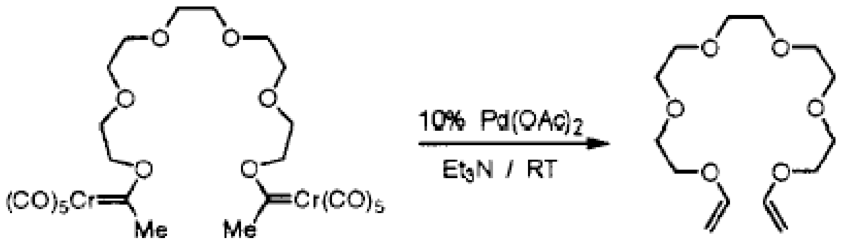
28a n = 0
28b n = 1
28c n = 2
28d n = 3

29a n = 0 70%
29b n = 1 64%
29c n = 2 21%
29d n = 3 14%



30a $R_1 = R_2 = Ph$
30b $R_1 = R_2 = Me$
30c $R_1 = Ph; R_2 = Me$

31a $R_1 = R_2 = Ph$ 54%
31b $R_1 = R_2 = Me$ 52%
31c $R_1 = Ph; R_2 = Me$ 53%



35

36 85%

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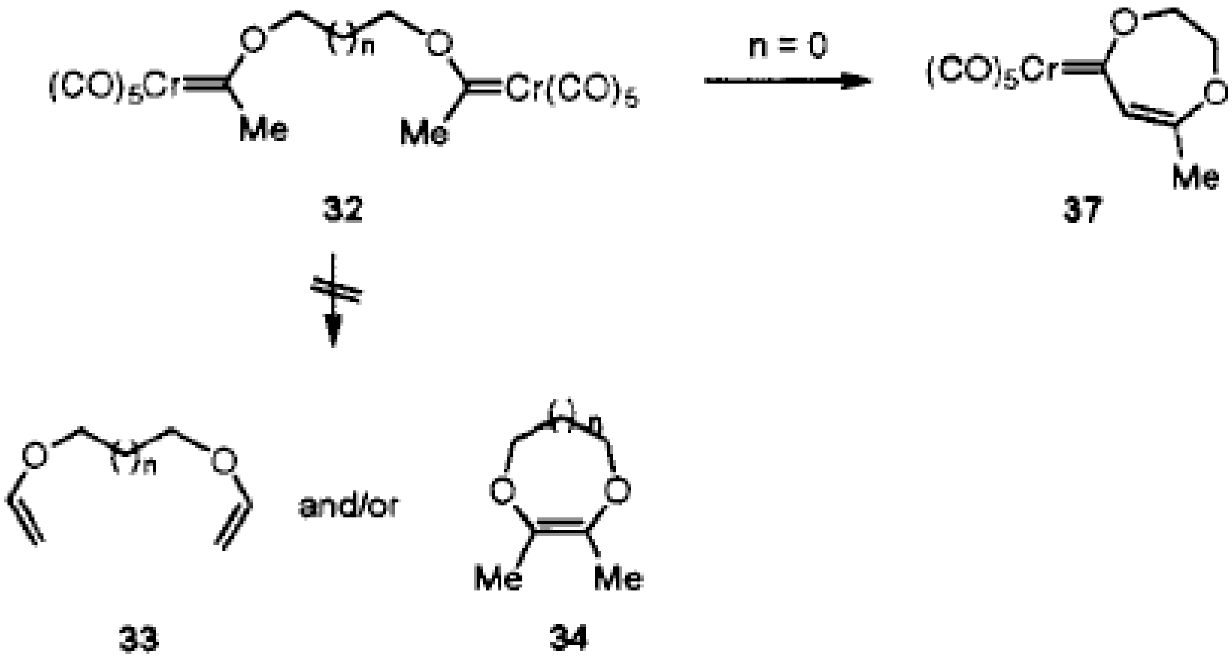
A Different Process

Scheme 7



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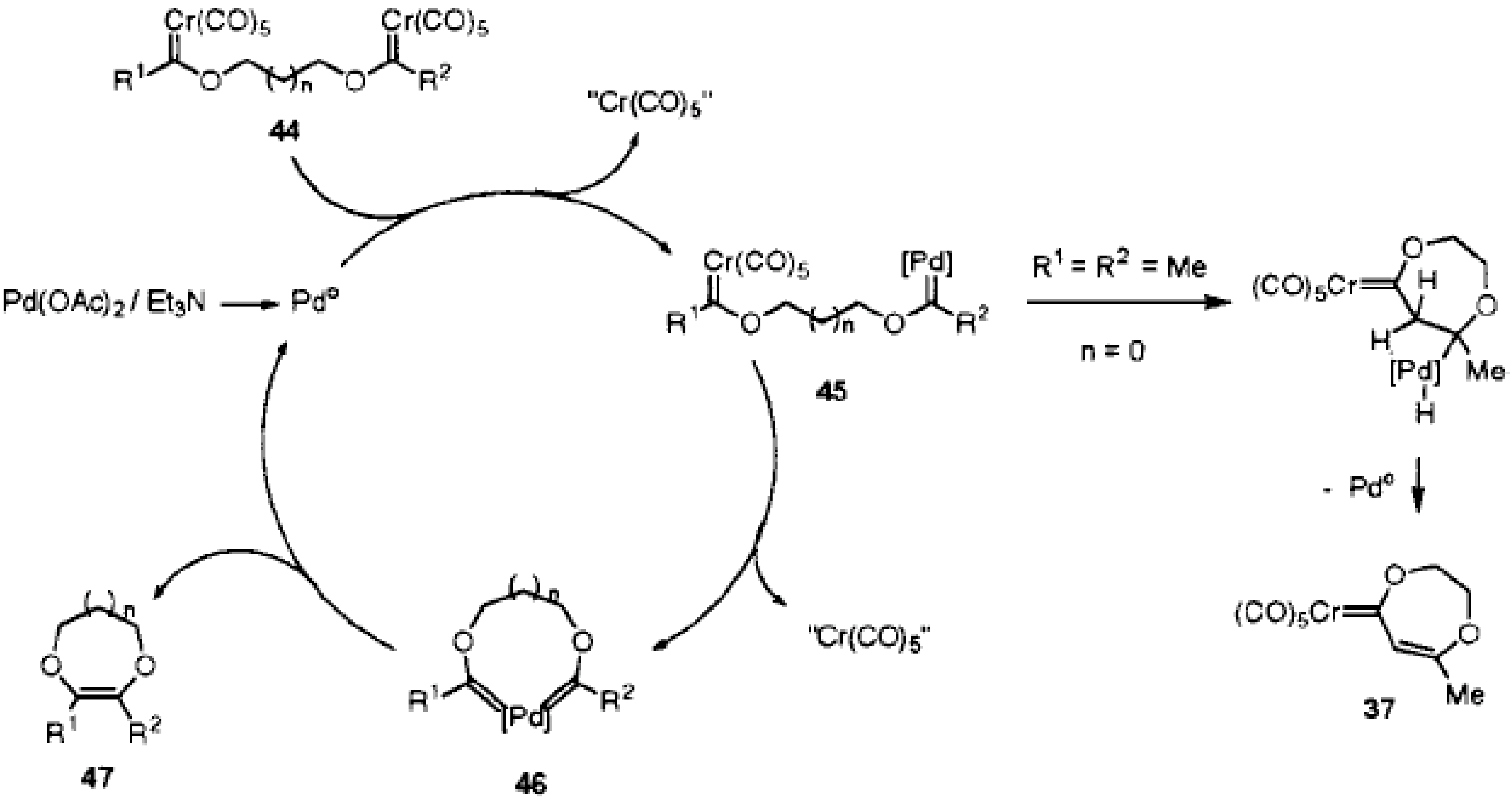
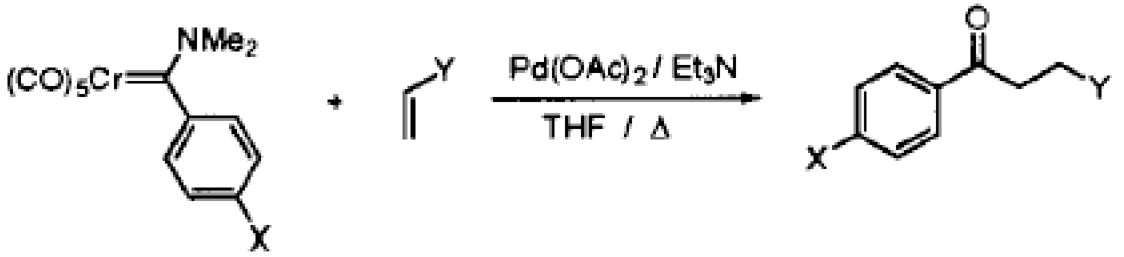


Miguel A. Sierra et al. *J. Am. Chem. Soc.*, **2001**, 123, 851-861

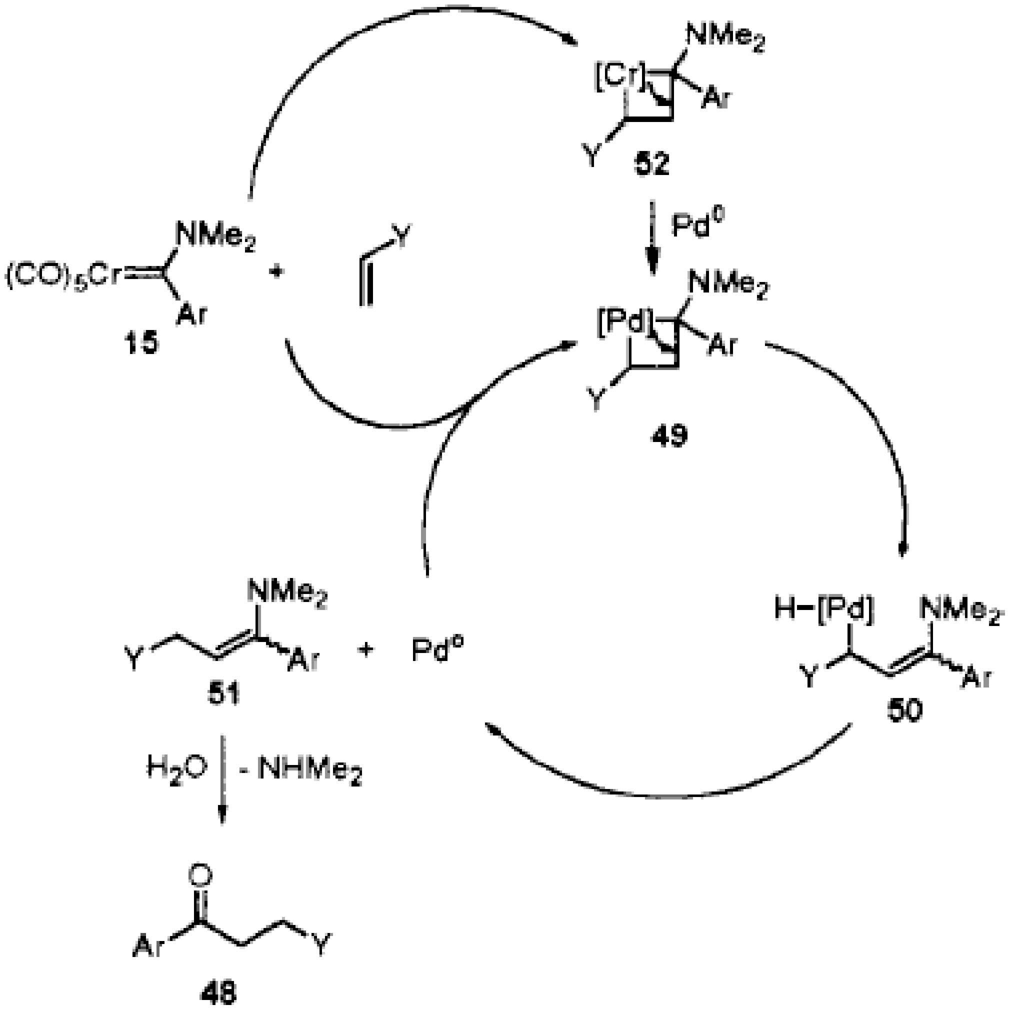
Pd Catalyzed Reaction of Aminocarbene Complexes



15a X = H
15b X = Br

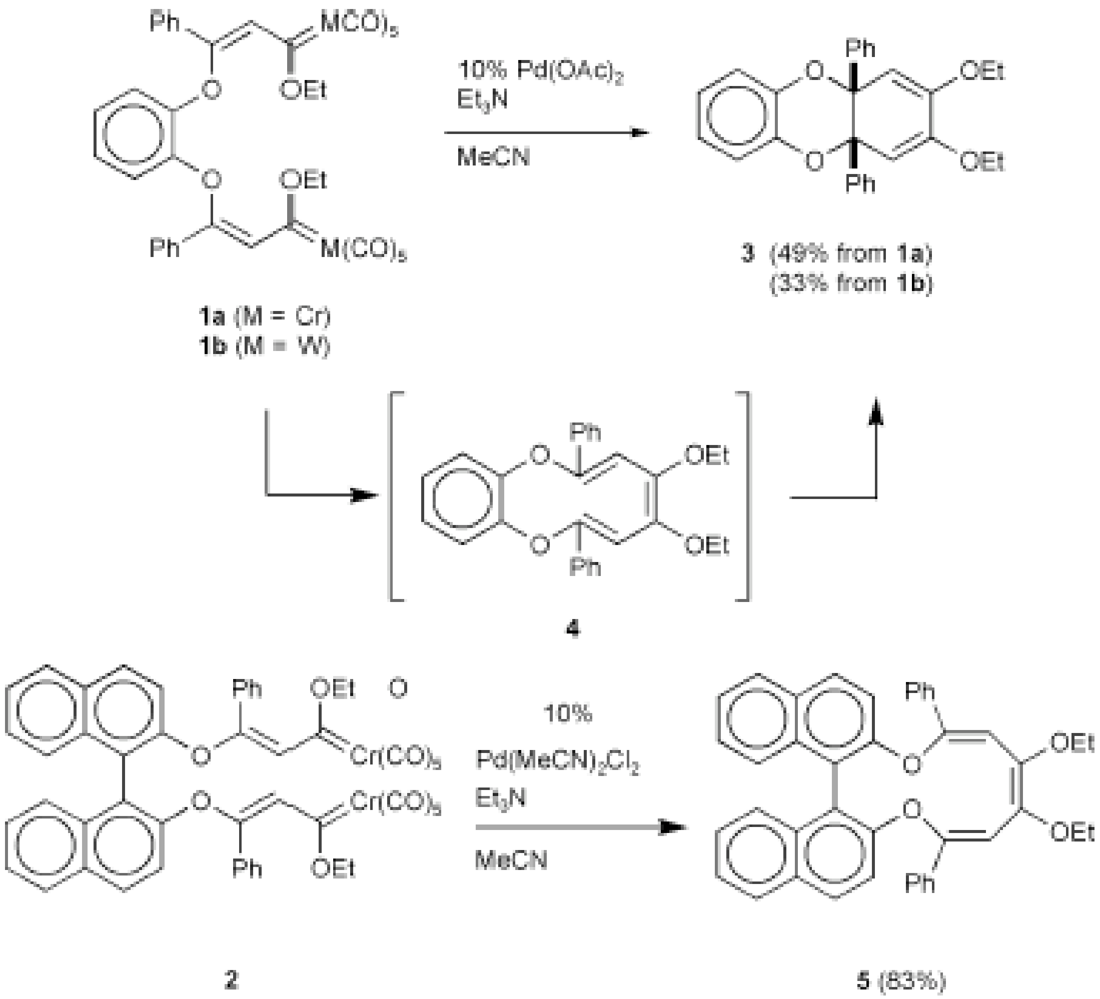
48a X = H, Y = COOMe (80%)
48b X = Br, Y = COOMe (75%)
48c X = Br, Y = CN (40%)

Miguel A. Sierra et al. *J. Am. Chem. Soc.*, **2001**, 123, 851-861

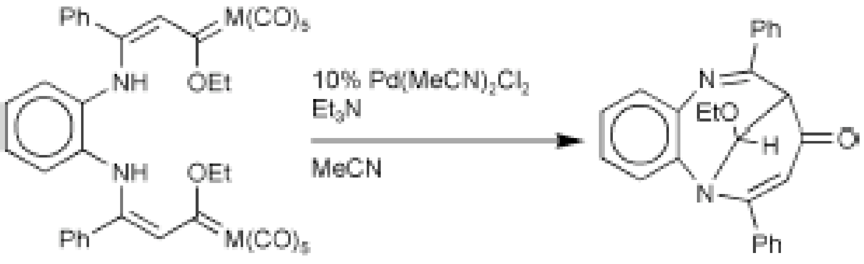


Miguel A. Sierra et al. *J. Am. Chem. Soc.*, **2001**, 123, 851-861

Pd Catalyzed Tandem Cyclization Process on Group VI bis-carbene Complexes



Miguel A. Sierra et al. *Chem. commun.*, **2002**, 1842-1843



1c M = Cr
1b M = W

6 (from **1c**, 62%)
(from **1d**, 23%)

Scheme 2

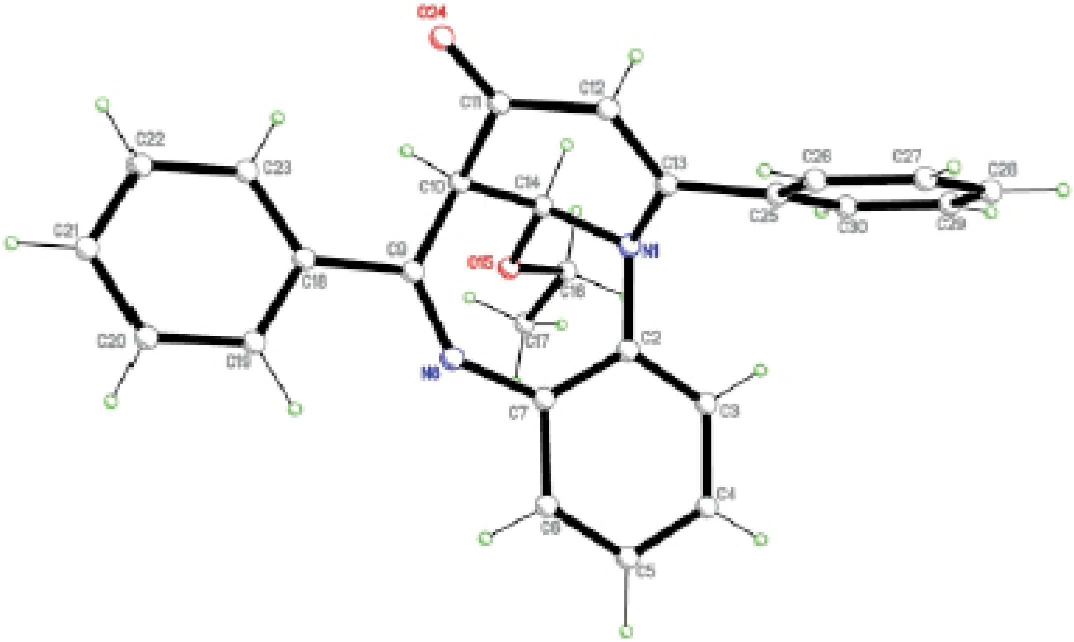
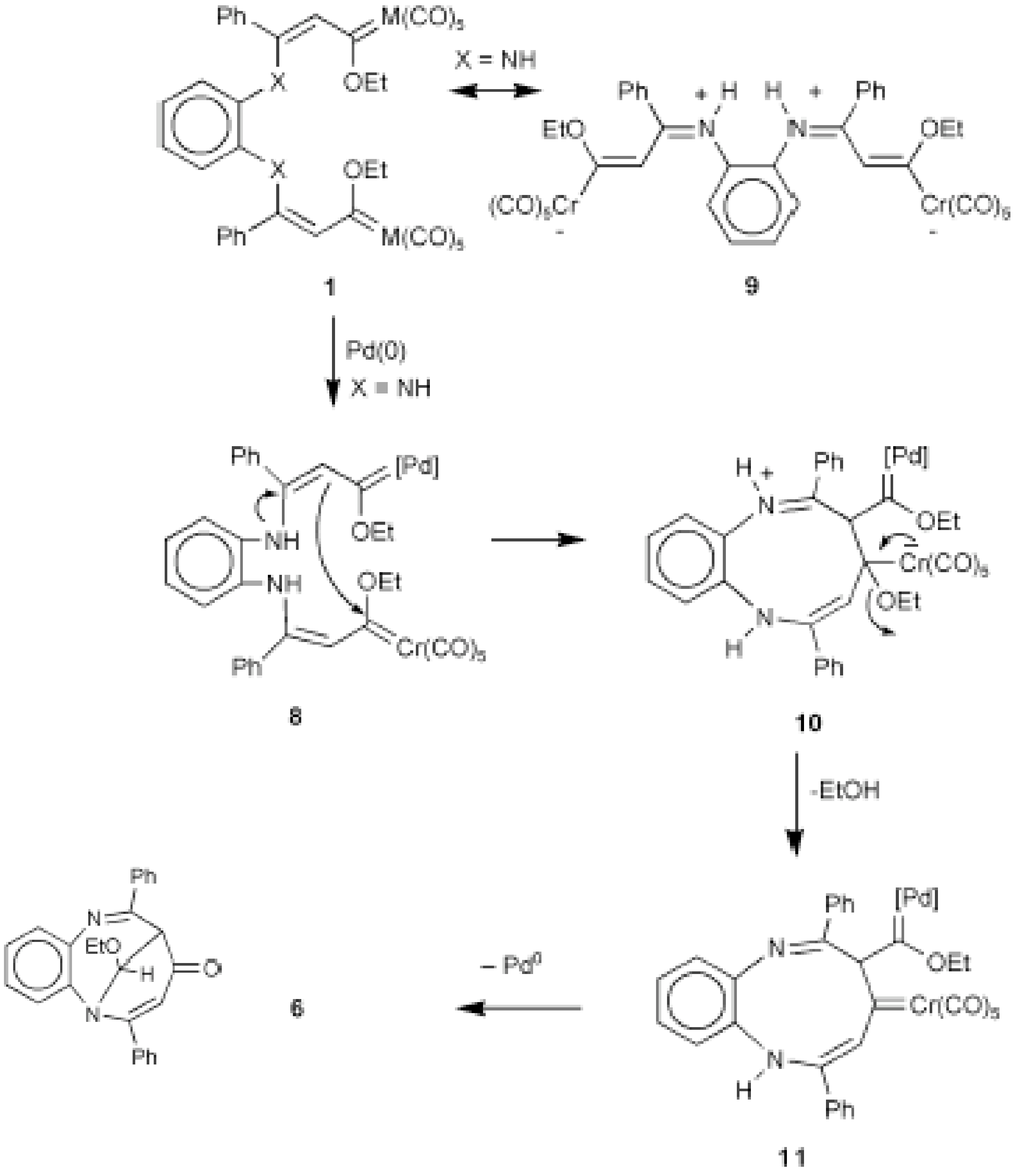


Fig. 1 Crystal structure for compound **6** obtained from **1c**.



Ph
M(CO)5
X
OEt
X
OEt
Ph
M(CO)5
1
X = NH
Ph
+ H
H +
Ph
EtO
N
N
OEt
(CO)5Cr
-
Cr(CO)5
-
9
Pd(0)
X = NH
Ph
[Pd]
NH
OEt
NH
OEt
Ph
Cr(CO)5
8
H +
Ph
[Pd]
N
OEt
Cr(CO)5
OEt
N
H
Ph
10
-EtOH
Ph
[Pd]
N
OEt
Cr(CO)5
N
H
Ph
11
– Pd0
Ph
N
EtO
H
O
N
Ph
6

Rearrangement of Chromium Allyloxy(aryl)carbene Complexes Catalyzed by Pd(0)

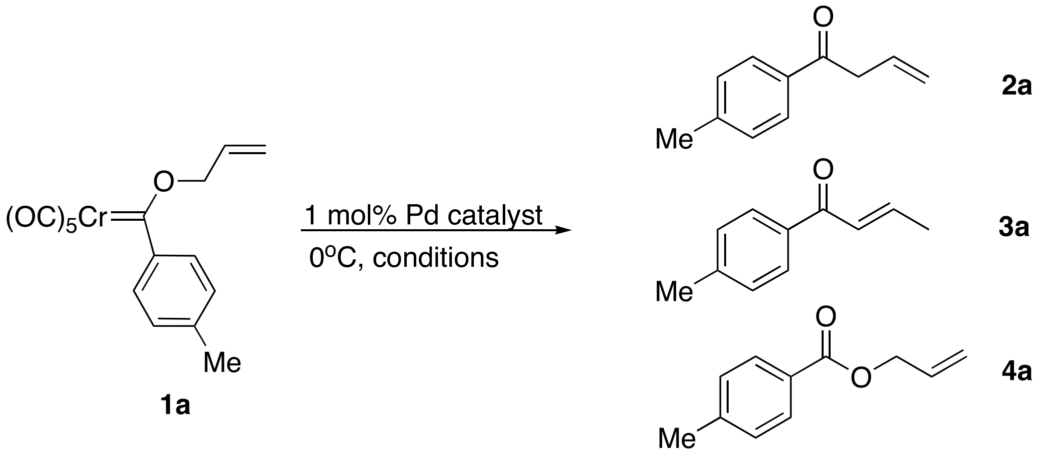


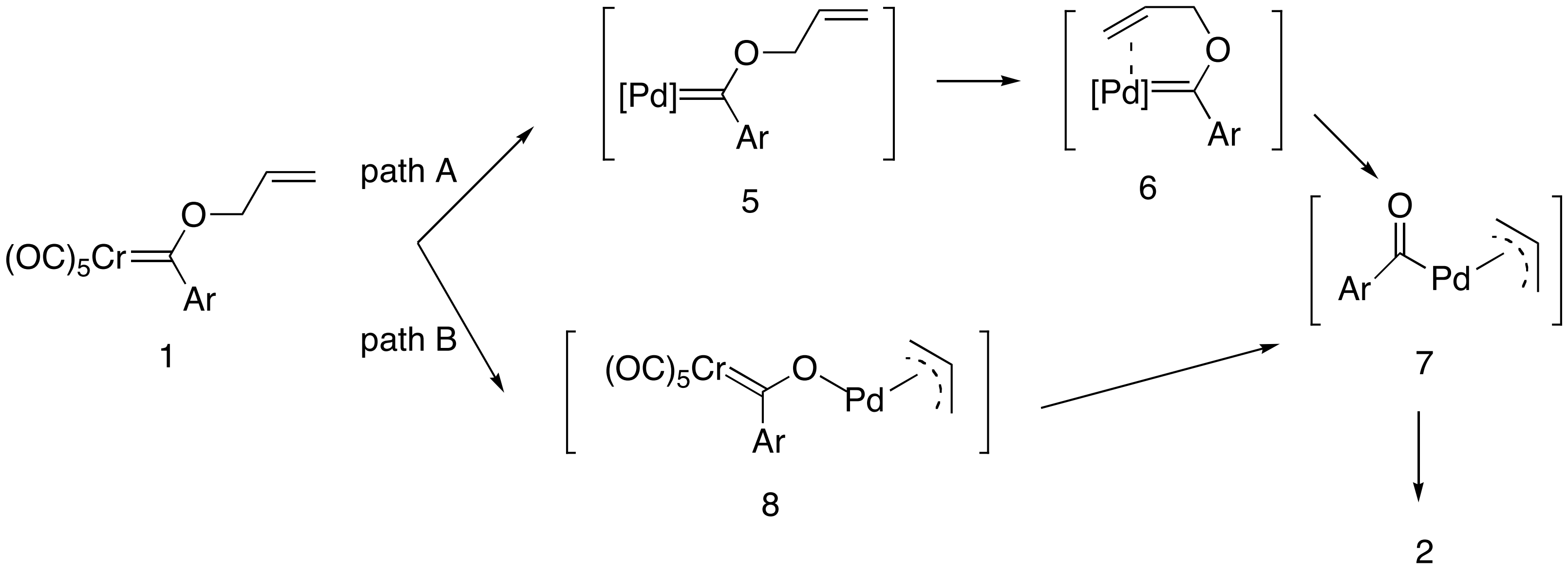
Table. Reaction conditions of Pd catalyzed reaction of **1a**

Entry	Catalyst	Solvent	Atm.	Time/h	Yields/%		
					2a	**3a**	**4a**
1	$Pd(PPh_3)_4$	Toluene	Ar	2	0	38	4
2	$Pd(PPh_3)_4$	THF	Ar	5	19	0	9
3[a]	$Pd(PPh_3)_4$	THF	CO	2.5	35	29	3
4	$Pd(PPh_3)_4$	CH_2Cl_2	Ar	6	33	6	17
5	$Pd(PPh_3)_4$	CH_2Cl_2	CO	17	71	0	4
6	$Pd(OAc)_2$	CH_2Cl_2	CO	1	42	0	2
7	$PdCl_2(PhCN)_2$	CH_2Cl_2	CO	1	47	4	4
8	$PdCl_2(dppf)$	CH_2Cl_2	CO	24	34	0	6
9	$Pd(dba)_2$	CH_2Cl_2	CO	1	6	13	0

[a] room temperature

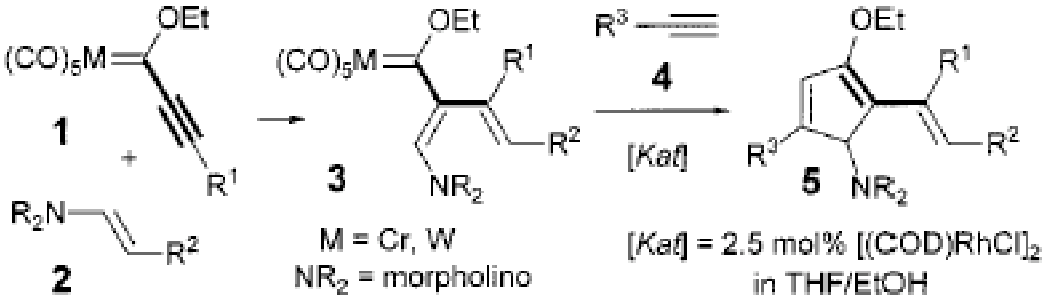
Koichi Narasaka et al. *Chemistry Letters* **1999**, 75-76

Plausible Mechanisms



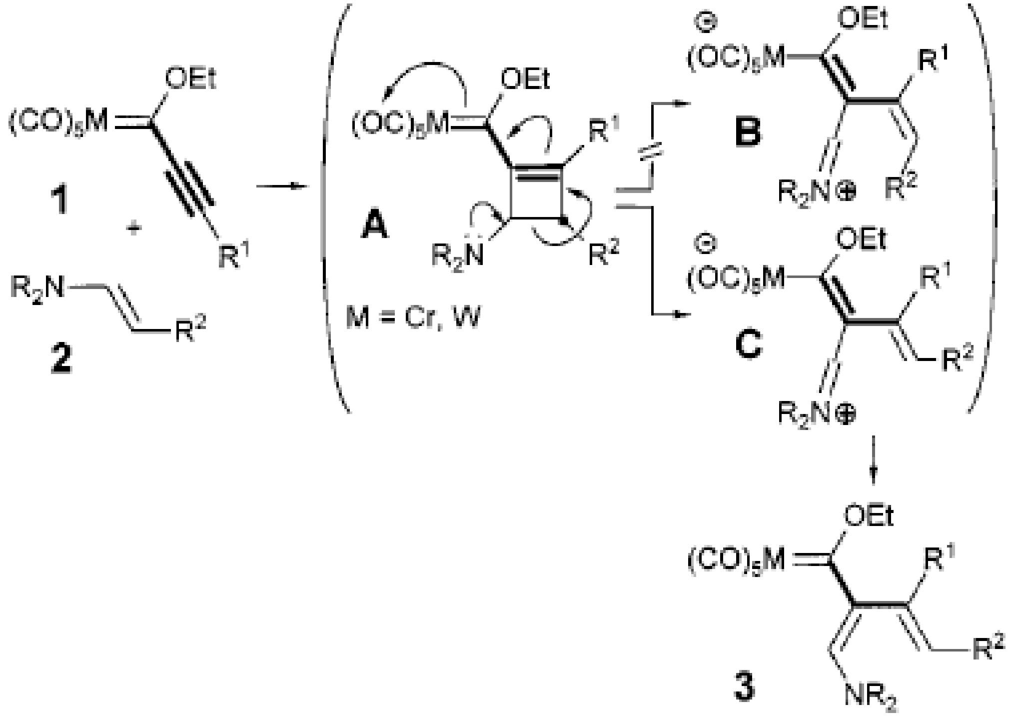
Koichi Narasaka et al. *Chemistry Letters* **1999**, 75-76

Rh-Catalyzed Vinyl Cyclopentadiene Formation: Type A



M = Cr, W
NR$_2$ = morpholino

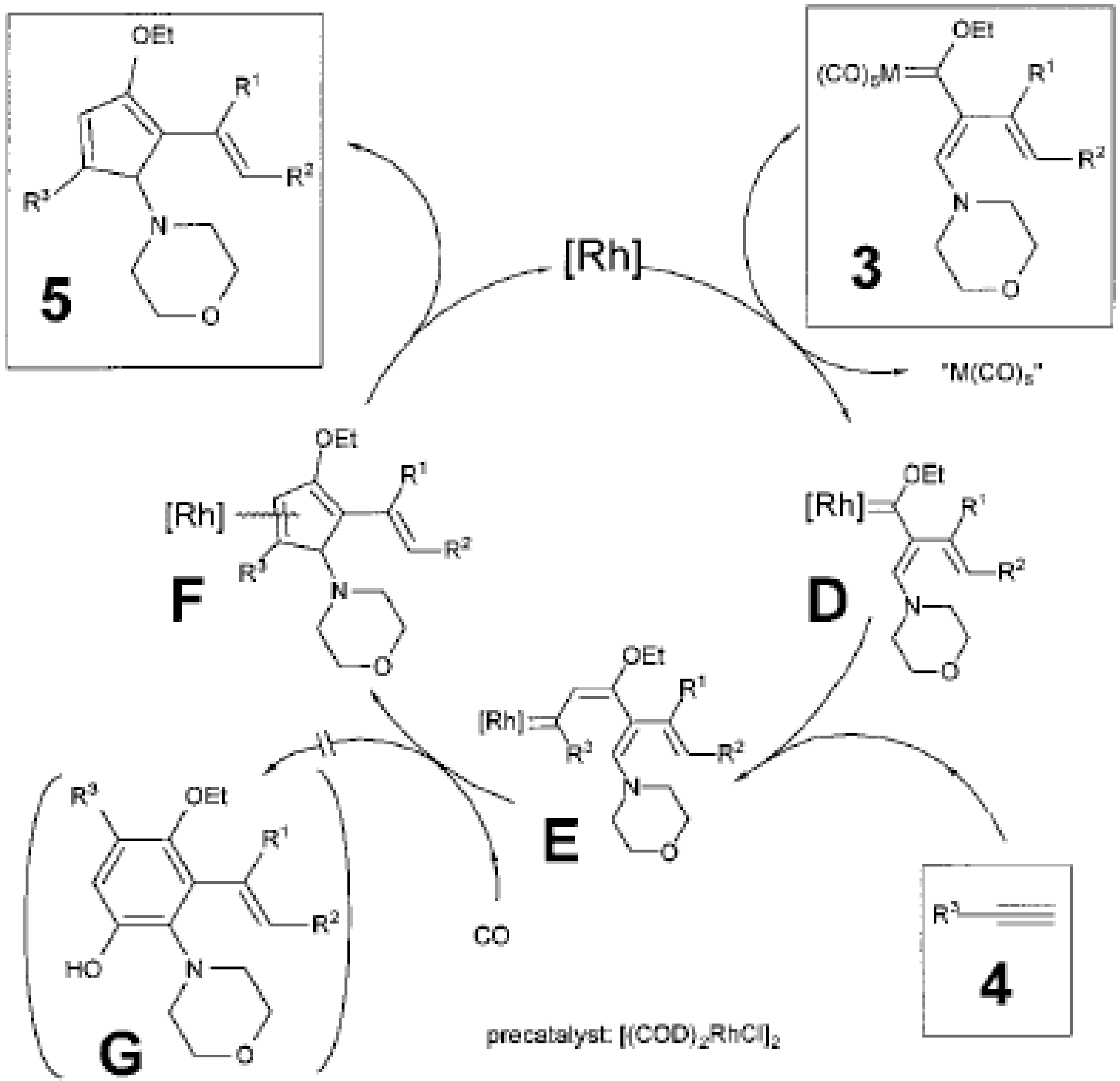
[*Kat*] = 2.5 mol% [(COD)RhCl]$_2$ in THF/EtOH



M = Cr, W

Rudolf Aumann et al. *Eur. J. Org. Chem.,* **1999**, 2545-2561

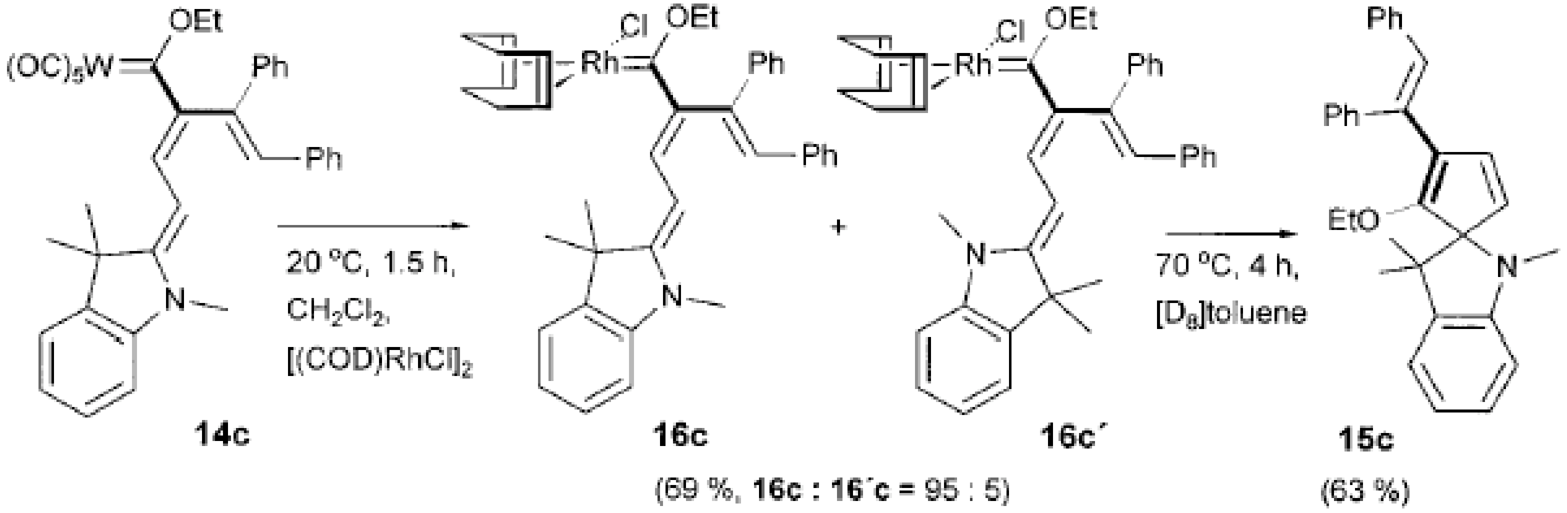
Rh-Catalyzed Vinyl Cyclopentadiene Formation



precatalyst: [(COD)$_2$RhCl]$_2$

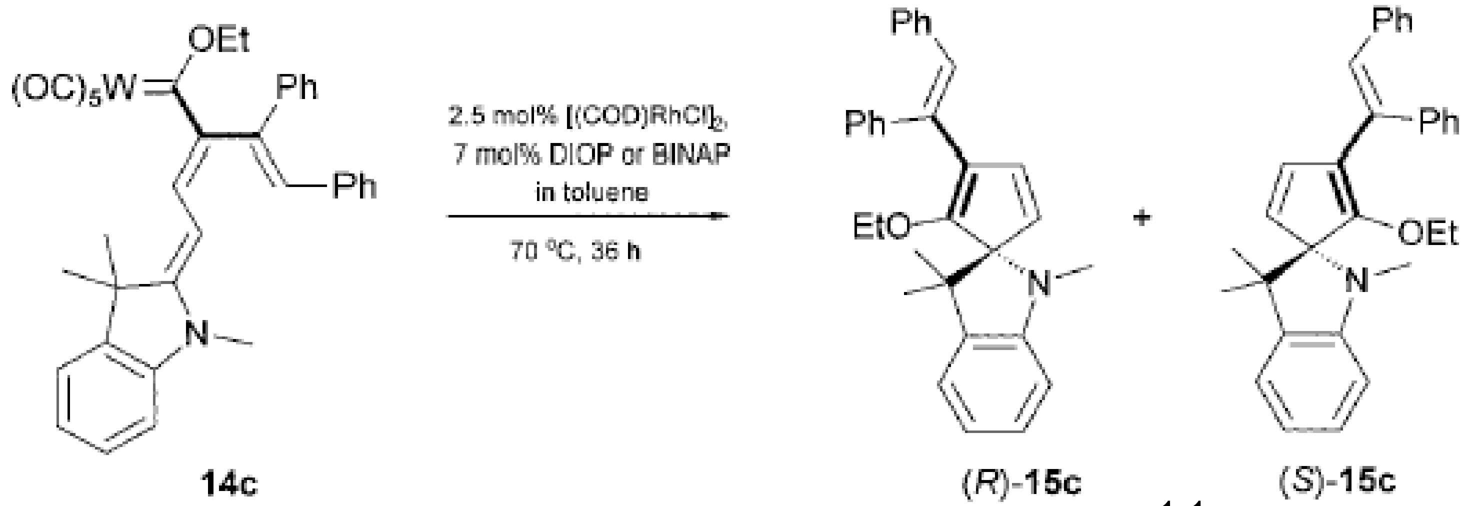
Scheme 4. Rhodium-catalyzed generation of cyclopentadienes **5** from cross-conjugated metallahexatrienes **3**

Experimental Proof: Preparation and Characterization of 16C



Rudolf Aumann et al. *Organometallic.,* **2001**, 3574-3581

Scheme 6. Attempted Chiral Induction by a Rhodium-Catalyzed π-Cyclization



1:1

Reaction of 14C in the presence of 5 mol % CuI and
7 mol % (-)-sparteine, 14 mol % (+)-methoxyproline, or 14 mol % (+)-1-phenylethylamine
in toluene or 1,2-dichloroethane afforded 15C after 12-16 h at 70°C, but no enatioselectivity was observed

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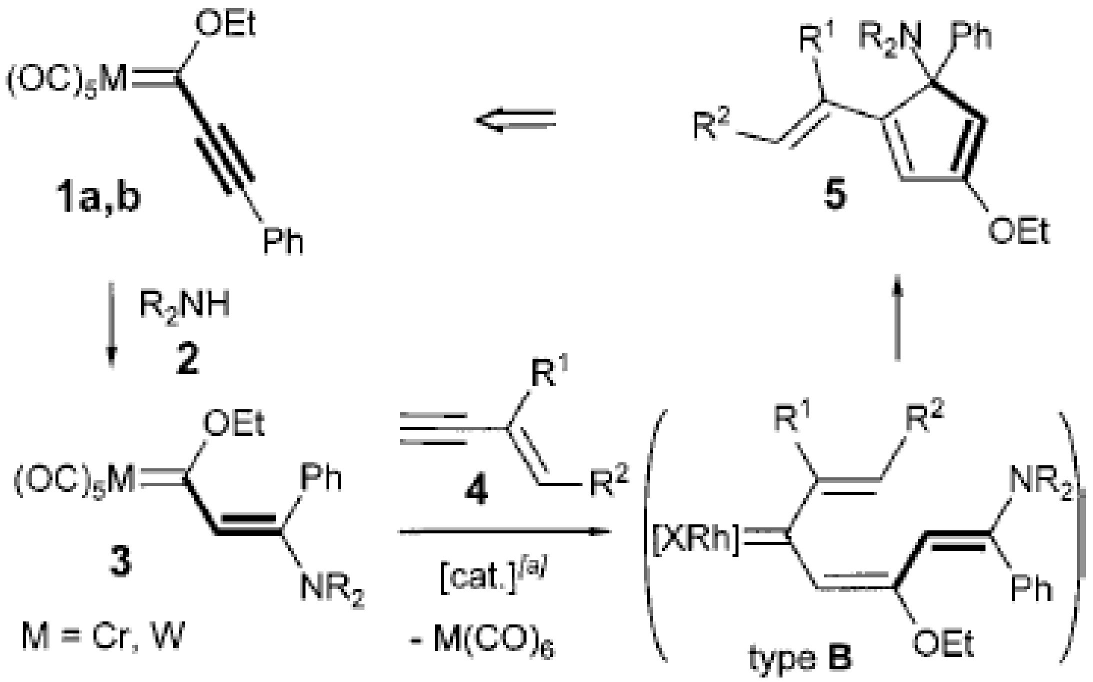
Rh-Catalyzed Vinyl Cyclopentadiene Formation: Type B



[a] [cat.] = 2 mol % $RhCl_3 \cdot 3H_2O$ in THF/MeOH (4:1); 20 °C.

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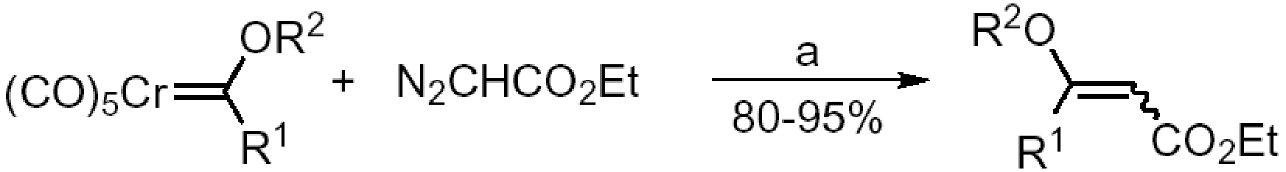
Chromium-Copper Exchange of Fischer Carbene Complexes

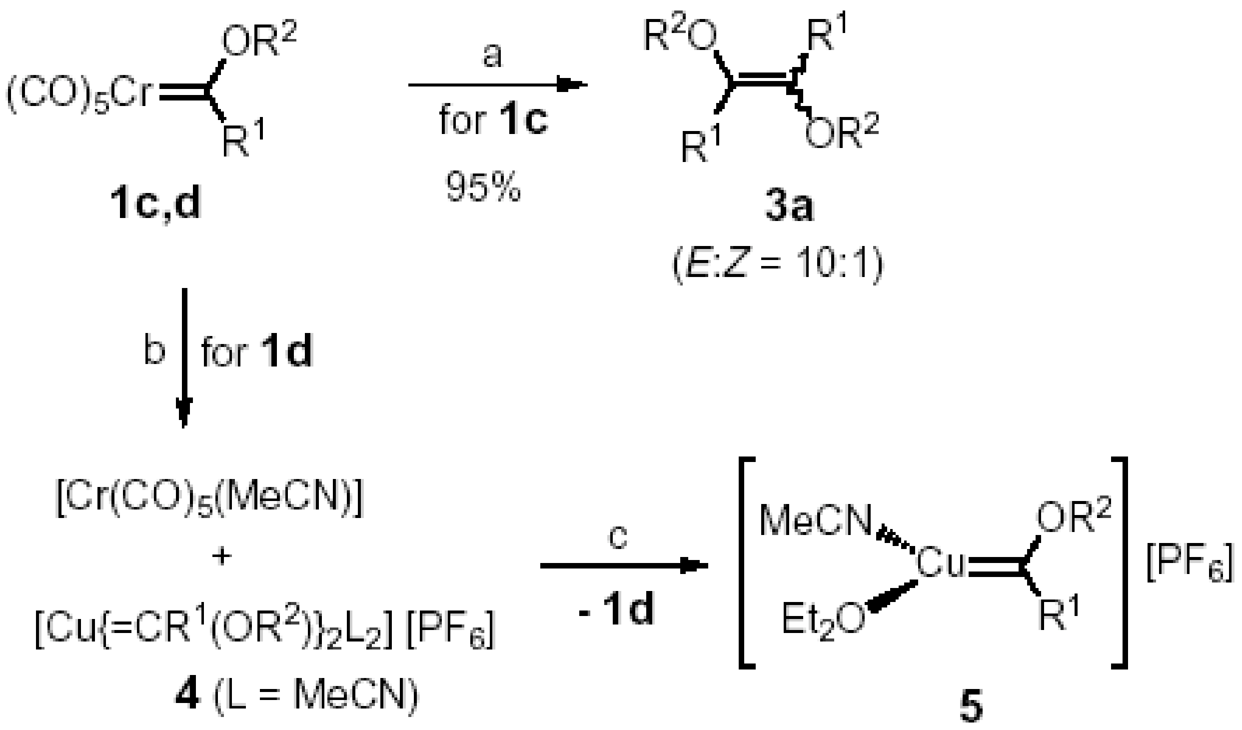


1a-d **2a-d**

	R^1	R^2
1a:	Ph	Me
1b:	Bu	Me
1c:	(*E*)-CH=CH-2-furyl	Me
1d:	(*E*)-CH=CH-2-furyl	(1R, 2S, 5R)-menthyl

a: 15 mol % CuBr, THF, 25°C,
E:Z = 1:1 (R^2 = Me)
E:Z > 30:1 (R^2 = (1R, 2S, 5R)-menthyl)

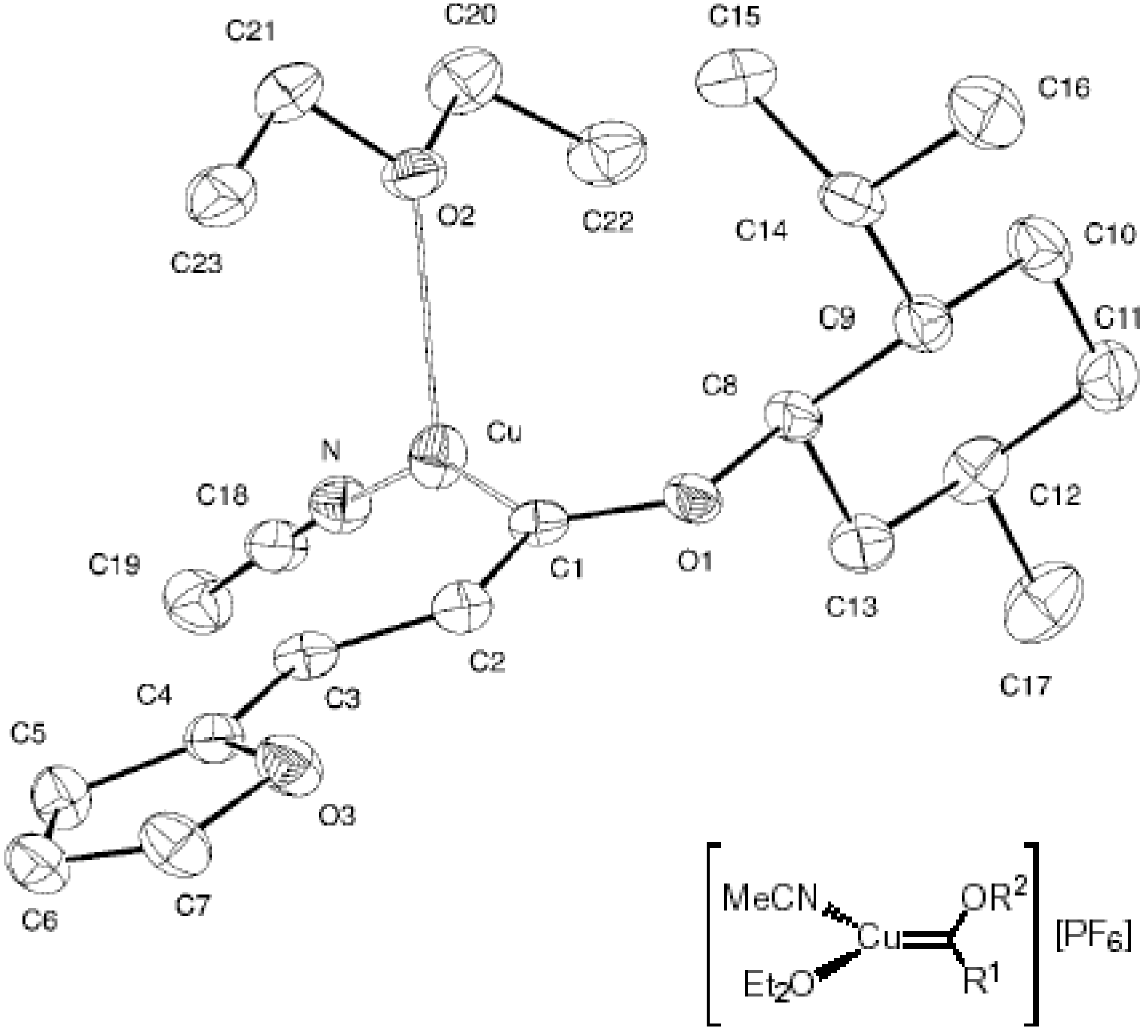
Jose Barluenga et al. *Angew.Chem. Int. Ed.*, **2001**, 42, 3392-3394



	R^1	R^2
1c:	(*E*)-CH=CH-2-furyl	Me
1d:	(*E*)-CH=CH-2-furyl	(1R, 2S, 5R)-menthyl
3a:	(*E*)-CH=CH-2-furyl	Me

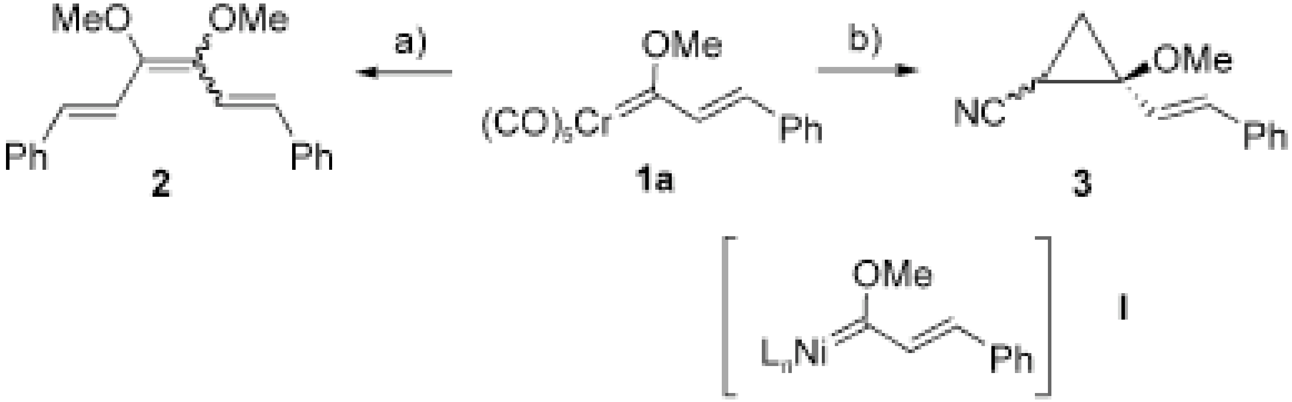
a: 15 mol % $[Cu(MeCN)_4][PF_6]$ CH_2Cl_2, 25°C, 95%
b: 50 mol % $[Cu(MeCN)_4][PF_6]$ CH_2Cl_2, 25°C
c: crystallization from CH_2Cl_2/Et_2O (1:5 v/v), -20°C, 50% (35% recovery of **1d**)

Jose Barluenga et al. *Angew.Chem. Int. Ed.*, **2001**, 42, 3392-3394


C21
C20
C15
C16
C23
O2
C22
C14
C10
C9
C11
C8
Cu
N
C18
C12
C19
C1
O1
C13
C2
C17
C4
C3
C5
O3
C6
C7
MeCN
Cu
OR2
Et2O
R1
[PF6]

5

Ni(0)-Mediated Dimerization and Cyclopropanation Reactions of Chromium Fischer Carbene Complexes



Scheme 1. Ni^0-catalyzed dimerization and cyclopropanation of chromium carbene complex **1a**. Reagents and conditions: a) $[Ni(cod)_2]$ (10 mol%), THF, 25 °C, 2 h, 90%; b) acrylonitrile, $[Ni(cod)_2]$ (10 mol%), MeCN, 25 °C, 3 h, 85 %.

Neither reaction occurs in the absence of nickel catalyst at RT

Jose Barluenga et al. *Angew.Chem. Int. Ed.*, **2003**, 42, 3008-3011

Ni(0)-Mediated [3+2+2] Cyclization of Chromium Fischer Carbene Complexes and Alkynes

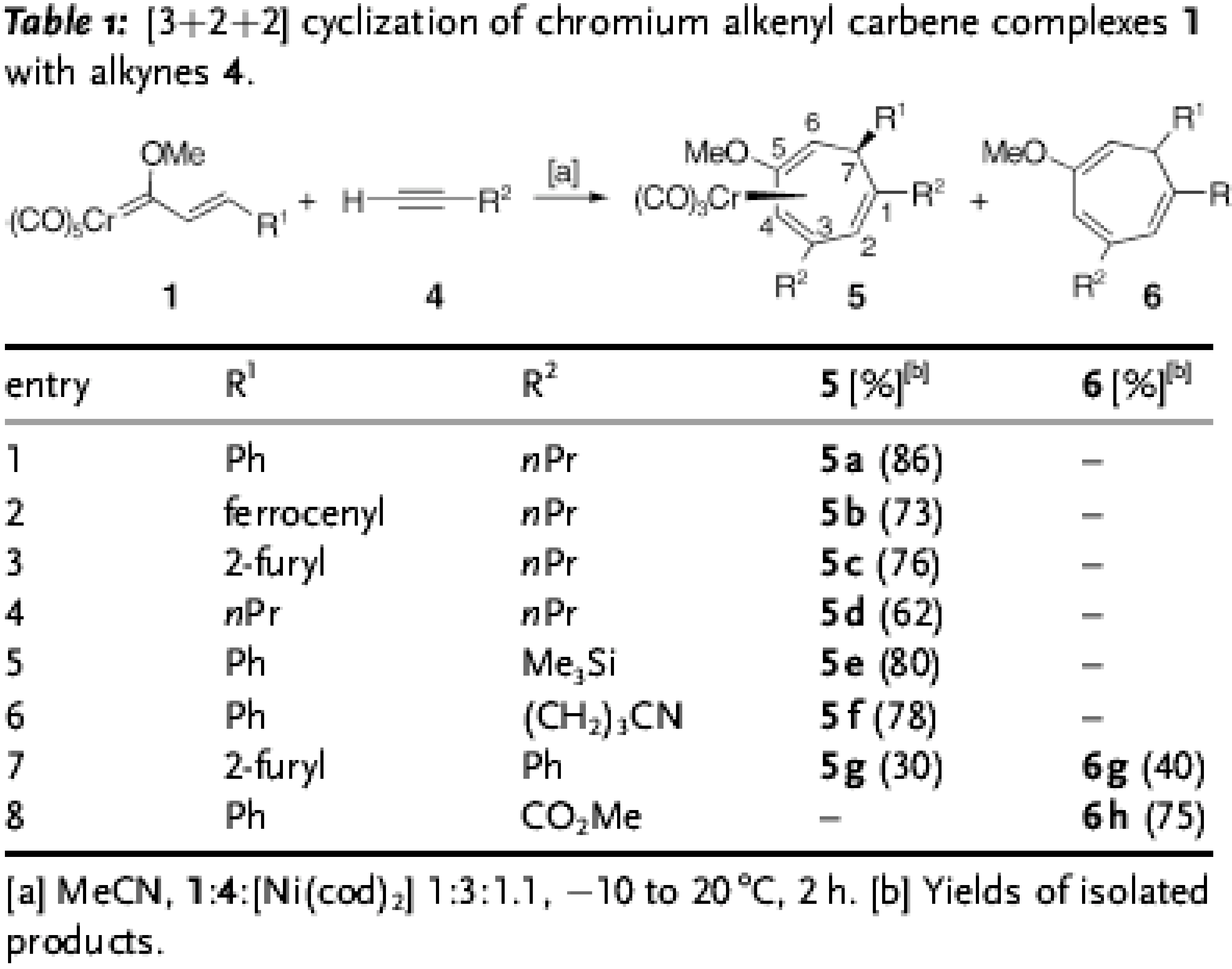


Table 1: [3+2+2] cyclization of chromium alkenyl carbene complexes **1** with alkynes **4**.

entry	R^1	R^2	**5** [%][b]	**6** [%][b]
1	Ph	*n*Pr	**5a** (86)	–
2	ferrocenyl	*n*Pr	**5b** (73)	–
3	2-furyl	*n*Pr	**5c** (76)	–
4	*n*Pr	*n*Pr	**5d** (62)	–
5	Ph	Me_3Si	**5e** (80)	–
6	Ph	$(CH_2)_3CN$	**5f** (78)	–
7	2-furyl	Ph	**5g** (30)	**6g** (40)
8	Ph	CO_2Me	–	**6h** (75)

[a] MeCN, **1**:**4**:[Ni(cod)$_2$] 1:3:1.1, −10 to 20 °C, 2 h. [b] Yields of isolated products.

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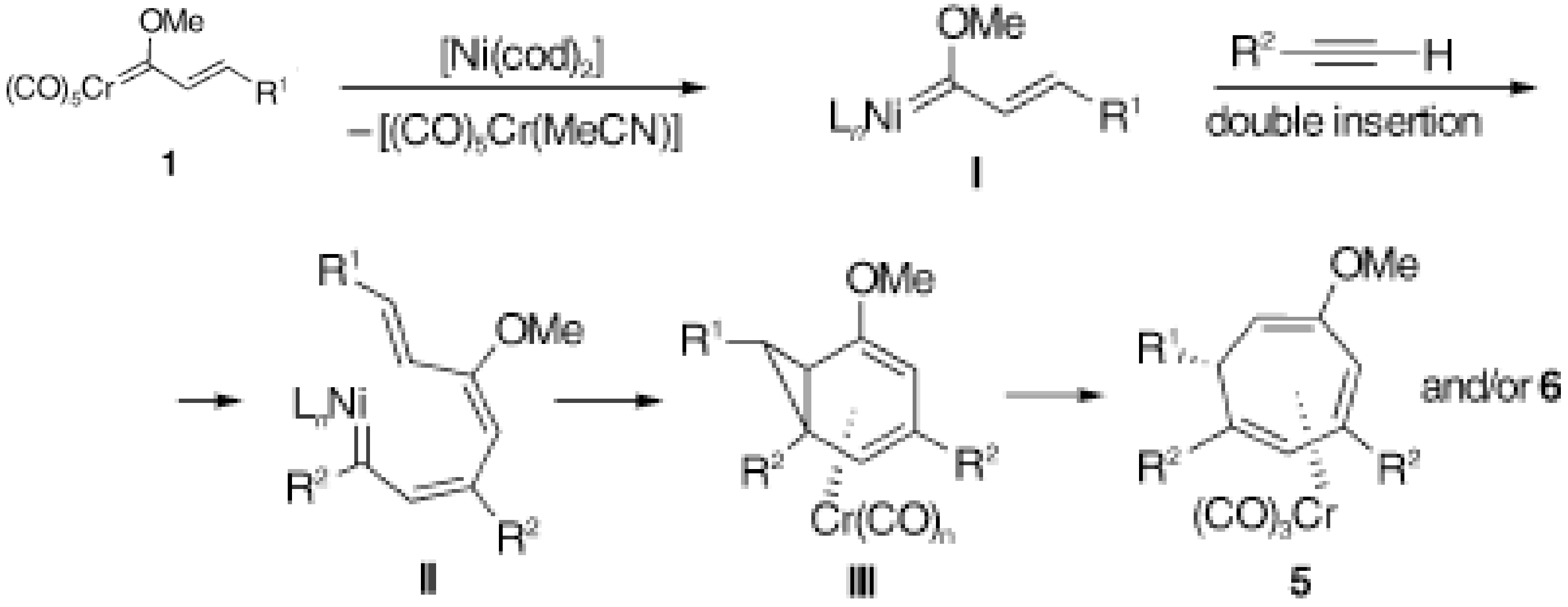

Scheme 2. Proposed mechanism for the formation of **5** and **6**.

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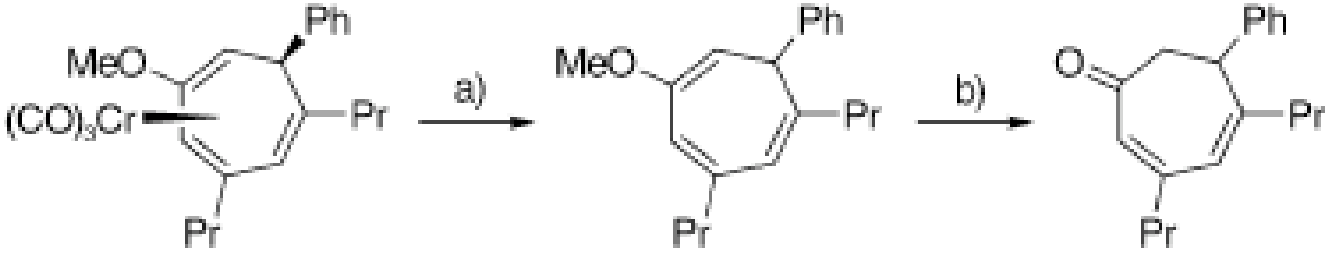

5a **6a** **9**

Scheme 3. Decomplexation of **5a** and hydrolysis of **6a**. Reagents and conditions: a) CO (35 bar), MeCN, 25 °C, 48 h, quantitative; b) 1 N HCl, THF, 25 °C, 2 h, 95%.

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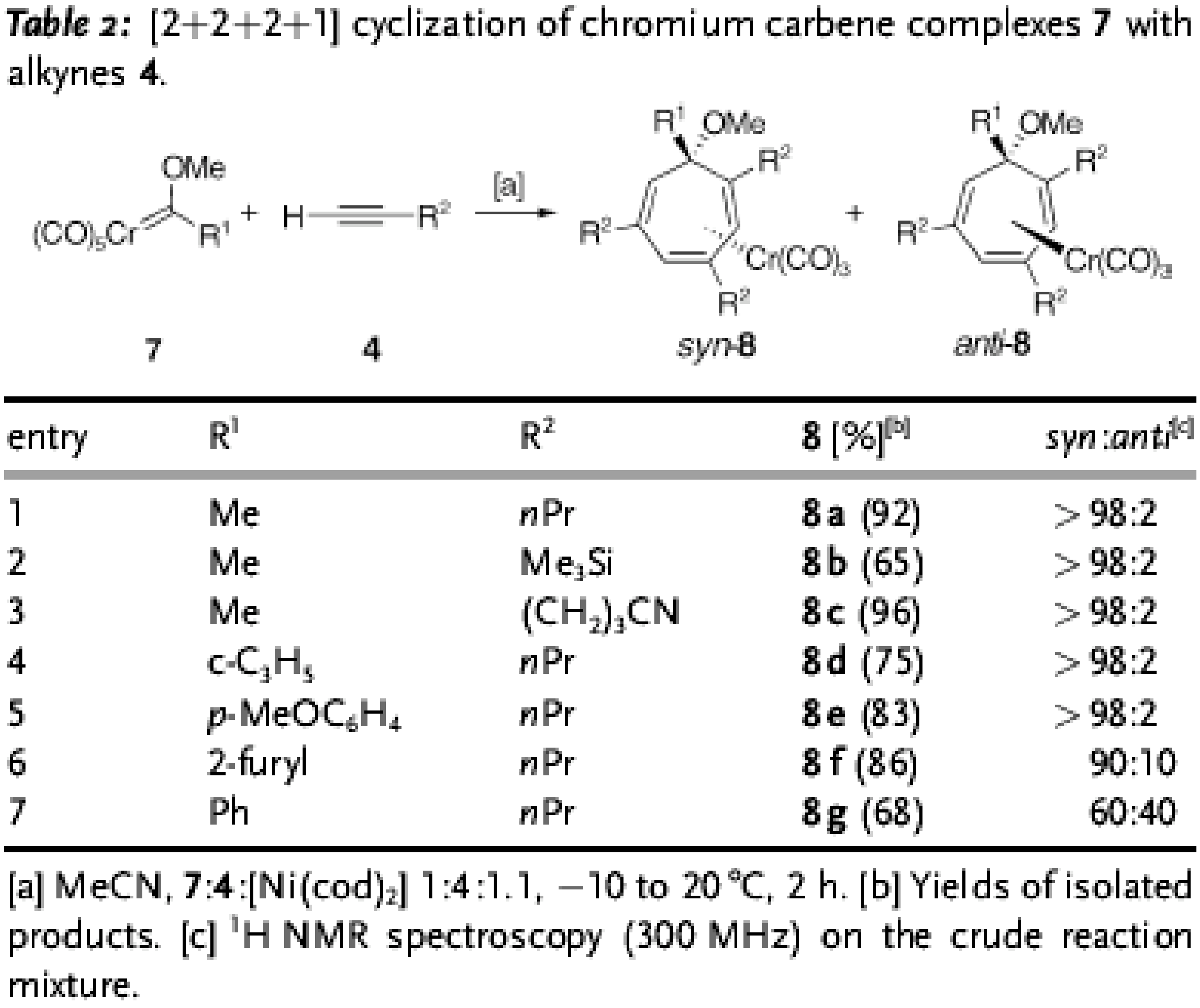

Table 2: [2+2+2+1] cyclization of chromium carbene complexes **7** with alkynes **4**.

entry	R^1	R^2	**8** [%][b]	*syn*:*anti*[c]
1	Me	*n*Pr	**8a** (92)	>98:2
2	Me	Me_3Si	**8b** (65)	>98:2
3	Me	$(CH_2)_3CN$	**8c** (96)	>98:2
4	c-C_3H_5	*n*Pr	**8d** (75)	>98:2
5	*p*-$MeOC_6H_4$	*n*Pr	**8e** (83)	>98:2
6	2-furyl	*n*Pr	**8f** (86)	90:10
7	Ph	*n*Pr	**8g** (68)	60:40

[a] MeCN, **7**:**4**:[Ni(cod)$_2$] 1:4:1.1, −10 to 20 °C, 2 h. [b] Yields of isolated products. [c] ^{1}H NMR spectroscopy (300 MHz) on the crude reaction mixture.

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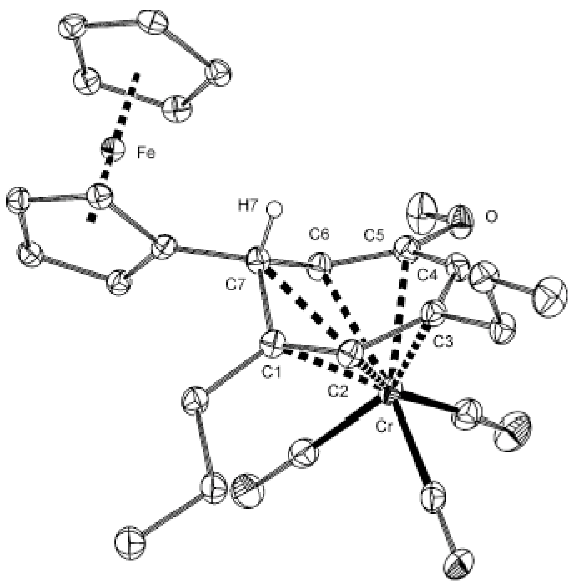
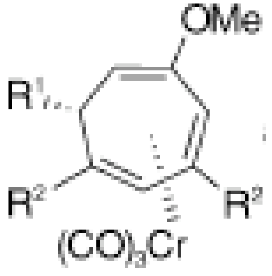
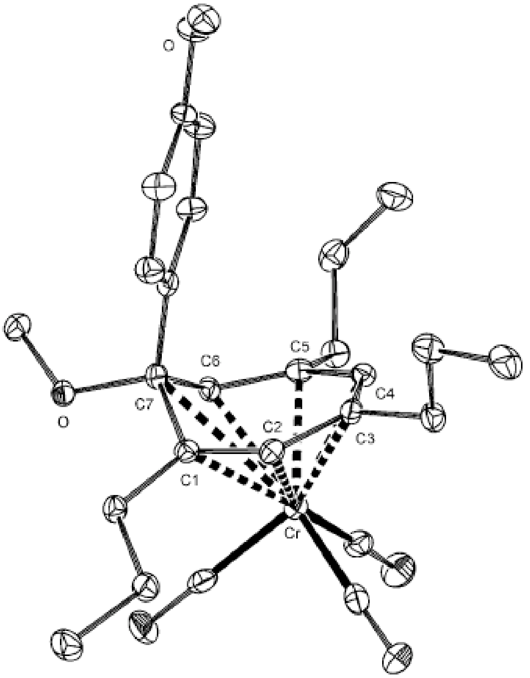


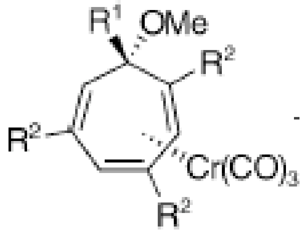


5

5b:

R^1=ferrocenyl,
R^2=*n*pr



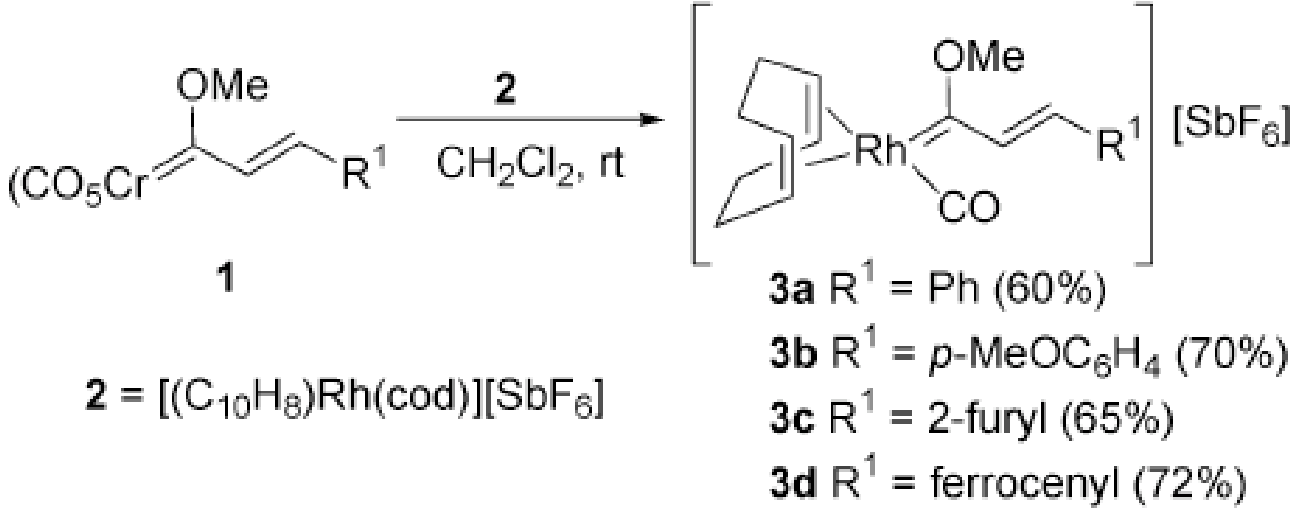


8e:

R^1=*p*-MeOC_6H_4,
R^2=*n*pr

New Fischer Carbene Complexes of Rhodium (I)

Scheme 1. Synthesis of Cationic Carbonyl Rhodium(I) Carbene Complexes **3a**−**d**



2 = [(C$_{10}$H$_8$)Rh(cod)][SbF$_6$]

3a R^1 = Ph (60%)
3b R^1 = *p*-MeOC$_6$H$_4$ (70%)
3c R^1 = 2-furyl (65%)
3d R^1 = ferrocenyl (72%)

The solid-state structure of 3b could be determined by a single-crystal analysis

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Scheme 2. [3 + 2] Cyclization of Carbenes **3a−c** with 1-Pentyne

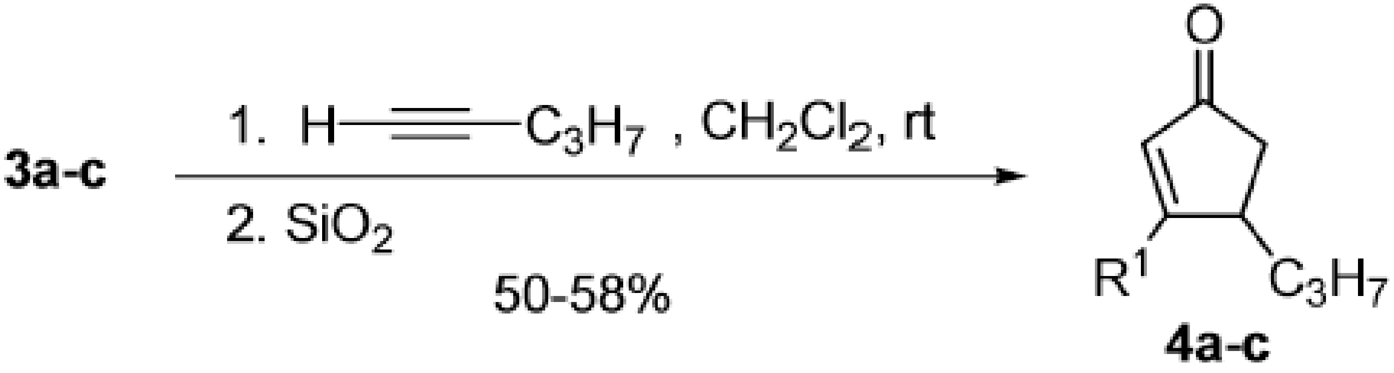

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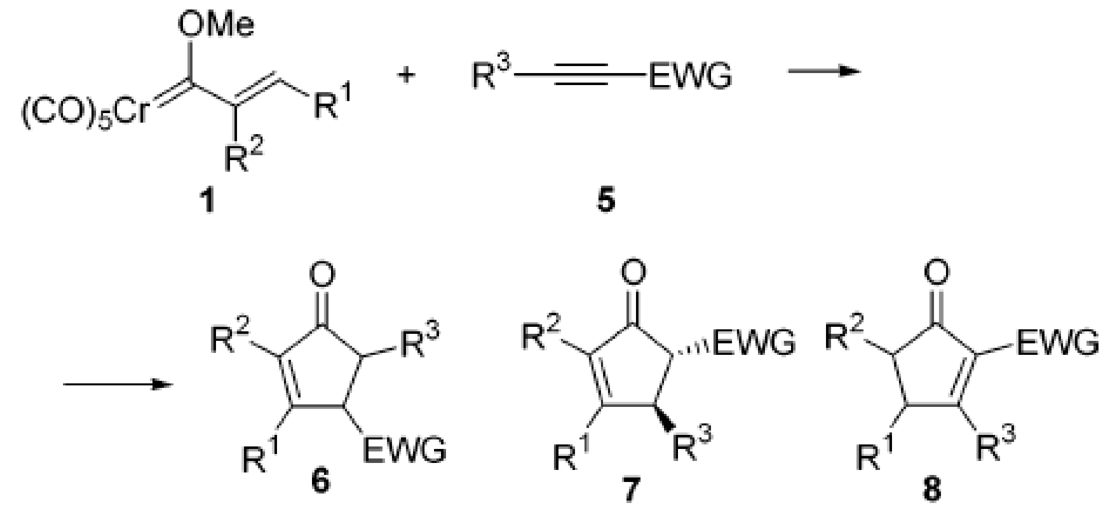
Table 1. Rh-Catalyzed [3 + 2] Cyclization of Alkenyl Chromium Carbene Complexes with Electron-Poor Alkynes[a]



entry	R^1	R^2	R^3	EWG	compd (yield, %)[b]
1	Ph	H	H	COOMe	**6a** (75)
2	*p*-$MeOC_6H_4$	H	H	COOMe	**6b** (81)
3	2-furyl	H	H	COOMe	**6c** (88)
4	ferrocenyl	H	H	COOMe	**6d** (71)
5	*n*-Bu	H	H	COOMe	**6e** (70)
6	$-CH_2CH_2CH_2O-$		H	COOMe	**6f** (89)
7	2-furyl	H	H	COMe	**6g** (64)
8	2-furyl	H	Ph	COOEt	**7a** (75)
9	2-furyl	H	1-cyclohexenyl	COOMe	**7b** (85)
10	2-furyl	H	Me	COOMe	**8** (81)

[a] Reagents and conditions: [(naphthalene)Rh(cod)][SbF_6] (10 mol %), CH_2Cl_2, 25 °C, 12−36 h, and then chromatographic workup. [b] Yields of isolated products.

Scheme 3. Proposed Mechanism for the [3 + 2] Cyclization