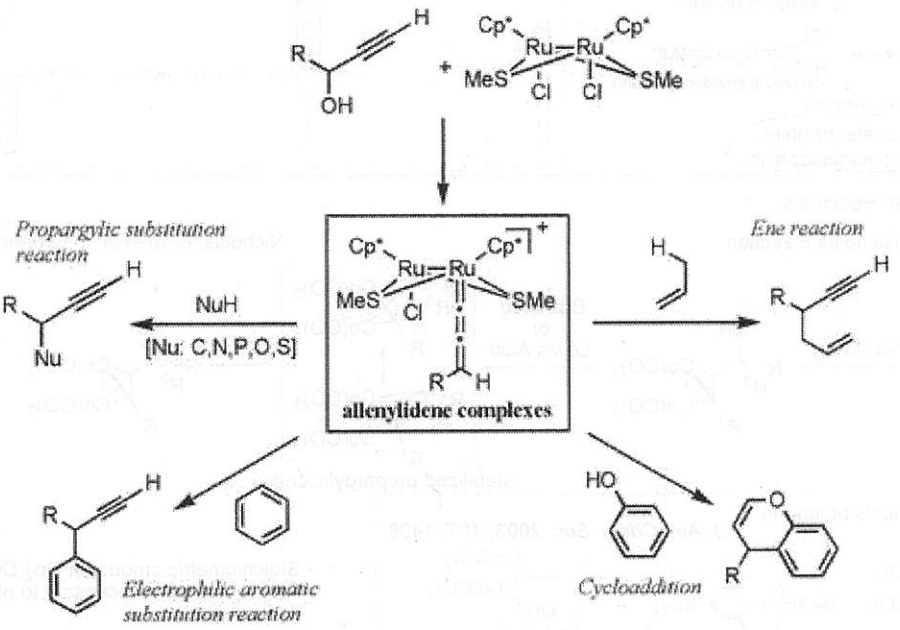
090930
Sho Takechi (M2 part)

Transition Metal-Allenylidene and Nitiride Complexes in Catalytic Reactions -metal-ligand multiple bonds-

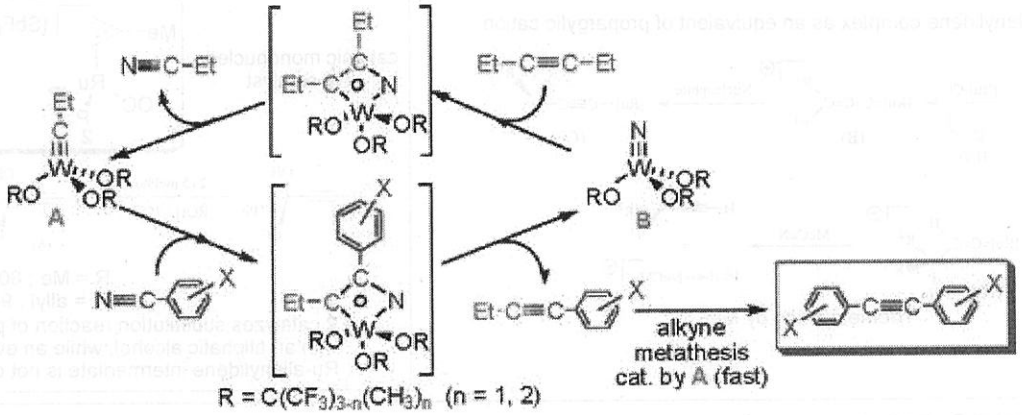
1. Catalytic Reactions Involving Allenylidene Complexes as Intermediate

Sulfur bridged di-Ru Catalyst



2. Catalytic Reactions Involving Nitride Complexes as intermediate

Catalytic Nitrile-Alkyne Cross-Metathesis



-Contents-

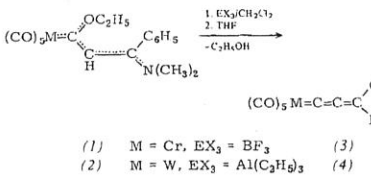
1. Catalytic Reactions involving Allenylidene Complexes as Intermediate

1-1. Background

• The isolation of the first allenylidene complexes

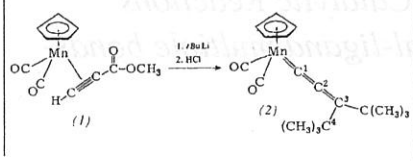
Fischer, E. O. *et al. Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 623.
Berke, H. *Angew. Chemie. Int. Ed. Engl.* **1976**, *15*, 624.

Fischer



(1) M = Cr, EX_3 = BF_3 (3)
(2) M = W, EX_3 = $Al(C_2H_5)_3$ (4)

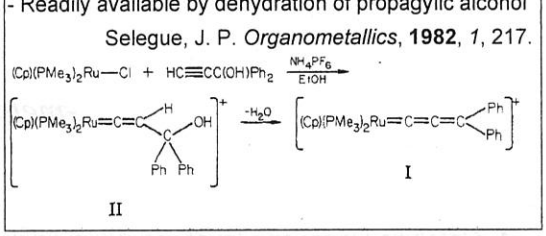
Berke



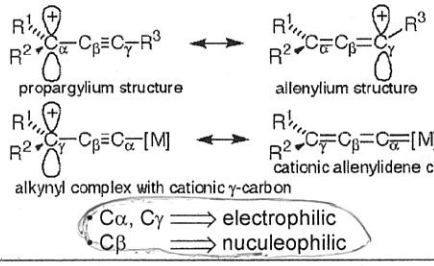
(1) (2)

- Readily available by dehydration of propagylic alcohol

Selegue, J. P. *Organometallics*, **1982**, *1*, 217.



II I



Analysis of the Electronic Structures of the Complexes $Os(\eta^5\text{-}C_5H_5)Cl(C{=}C{=}CH_2)(PH_3)$ (13), $[Os(\eta^5\text{-}C_5H_5)(C{=}C{=}CH_2)(PH_3)_2]^+$ (14), and $[Os(\eta^5\text{-}C_5H_5)(C{=}C{=}CH_2)(CO)(PH_3)]^+$ (15)'

Distribution of the LUMO on the C Atoms of the Allenylidene (%)

	C_α	C_β	C_γ
13	24	5	30
14	24	5	31
15	28	3	33

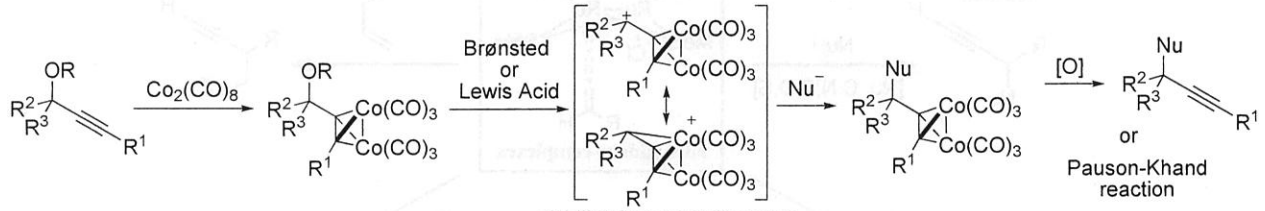
Distribution of the HOMO on the C Atoms of the Allenylidene (%)

	C_α	C_β	C_γ
13	4	22	0
14	4	25	0
15	5	23	0

• Propargylic Substitution Reactions

Traditional method : Nicholas Reaction

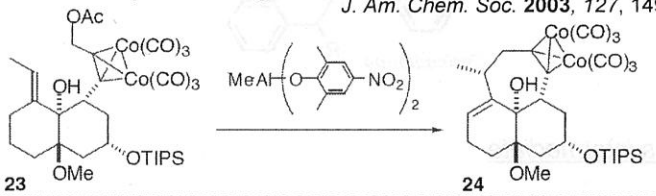
Nicholas, K. M.et al. *J. Organomet. Chem.* **1972**, *44*, C2



stabilized propargylic cation

ex.) Tanino's total synthesis of ingenol

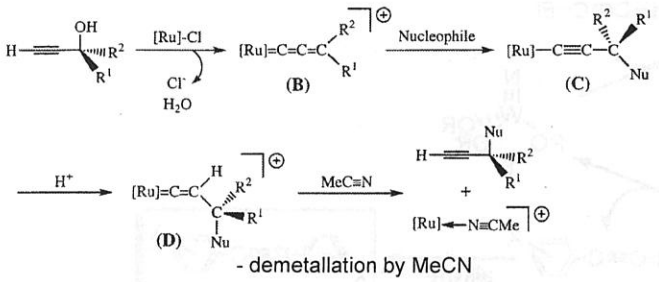
J. Am. Chem. Soc. **2003**, *127*, 1498.



23 24

- Stoichiometric amount of $Co_2(CO)_8$ is wasted.
- Sevral steps are necessary to obtaine propagylic derivatives.

- Cationic Ru-allenylidene complex as an equivalent of propargylic cation.

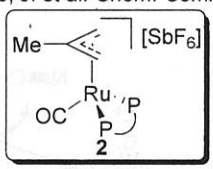


- demetallation by MeCN

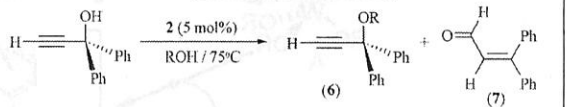
- Catalytic propargylic substitution reaction by cationic mono-Ru catalyst

Gimeno, J. et al. *Chem. Commun.* **2004**, 2716.

cationic mononuclear Ru catalyst



P P = dppf



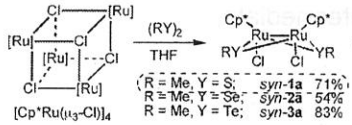
R = Me : 80%/10% (6/7)
R = allyl : 94%/4% (6/7) etc.

- **2** catalyzes substitution reaction of propargylic alcohol with an aliphatic alcohol, while an evidence for a Ru-allenylidene intermediate is not obtained.

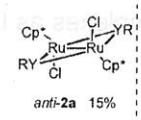
1-2. Sulfur bridged di-Ru Catalyst

• Preparation of chalcogen-bridged di-Ru catalyst

Y. Nishibayash, S. Uemura et al. *Organometallics* **2004**, *23*, 26.

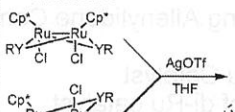


R = Me, Y = S;	*syn*-**1a**	71%
R = Me, Y = Se;	*syn*-**2a**	54%
R = Me, Y = Te;	*syn*-**3a**	83%
R = Et, Y = S;	*syn*-**1b**	62%
R = Et, Y = Se;	*syn*-**2b**	79%
R = Et, Y = Te;	*syn*-**3b**	80%
R = ^{n}Pr, Y = S;	*syn*-**1c**	78%
R = ^{n}Pr, Y = Se;	*syn*-**2c**	50%
R = ^{i}Pr, Y = S;	*syn*-**1d**	85%
R = ^{i}Pr, Y = Se;	*syn*-**2d**	43%

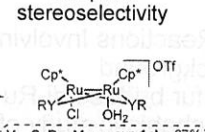


anti-**2a** 15%
anti-**2b** 79%
anti-**2c** 50%

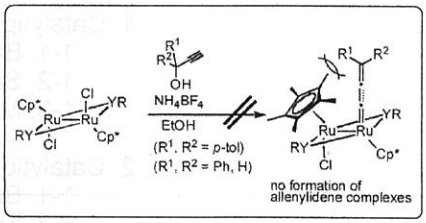
syn & anti mixuture



complete stereoselectivity



Y = S, R = Me;	*syn*-**1a'**	87%
Y = S, R = Et;	*syn*-**1b'**	80%
Y = S, R = ^{i}Pr;	*syn*-**1c'**	88%
Y = S, R = ^{i}Pr;	*syn*-**1d'**	91%
Y = Se, R = Me;	*syn*-**2a'**	89%
Y = Se, R = Et;	*syn*-**2b'**	96%
Y = Se, R = ^{n}Pr;	*syn*-**2c'**	89%
Y = Se, R = ^{i}Pr;	*syn*-**2d'**	86%
Y = Te, R = Me;	*syn*-**3a'**	72%
Y = Te, R = Et;	*syn*-**3b'**	93%

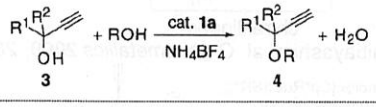


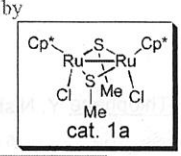
- *Anti* -catalyst is ineffective against propargylic substitution reactions.

• Propagylic substitution reactions

Y. Nishibayashi, M. Hidai et al. *J. Am. Chem. Soc.* **2000**, *122*, 11019.

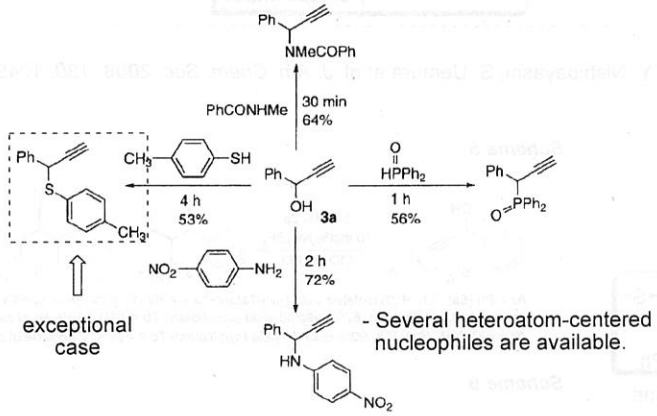
Table 1. Propargylic Substitution Reactions Catalyzed by [Cp*RuCl(μ_2-SMe)$_2$RuCp*Cl] (**1a**)[a]



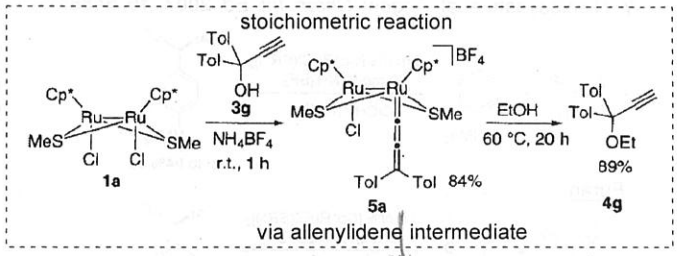


run		R^1, R^2	R	time	yield of 4[b]	
1	**3a**	Ph, H	Et	15 min	**4aa**	88
2	**3a**	Ph, H	Me	15 min	**4ab**	84
3	**3a**	Ph, H	^{i}Pr	15 min	**4ac**	91
4	**3b**	Fc, H	Et	60 min	**4b**	88
5	**3c**	^{n}C$_5$H$_{11}$, H	^{i}Pr	15 min	**4c**	75
6[c]	**3d**	$-(CH_2)_5-$	Et	30 min	**4d**	57
7[c]	**3e**	$-(CH_2)_4-$	Et	30 min	**4e**	54
8	**3f**	Ph, Ph	Et	20 h	**4f**	62
9	**3g**	*p*-Tol, *p*-Tol	Et	20 h	**4g**	61
10[d]	**3a**	Ph, H	Ph	60 min	**4ad**	65
11[d]	**3a**	Ph, H	R*1[e]	60 min	**4ae**	80
12[d]	**3a**	Ph, H	R*2[f]	60 min	**4af**	92
13[d]	**3a**	Ph, H	R*3[g]	60 min	**4ag**	69
14[d]	**3a**	Ph, H	R*4[h]	60 min	**4ah**	43

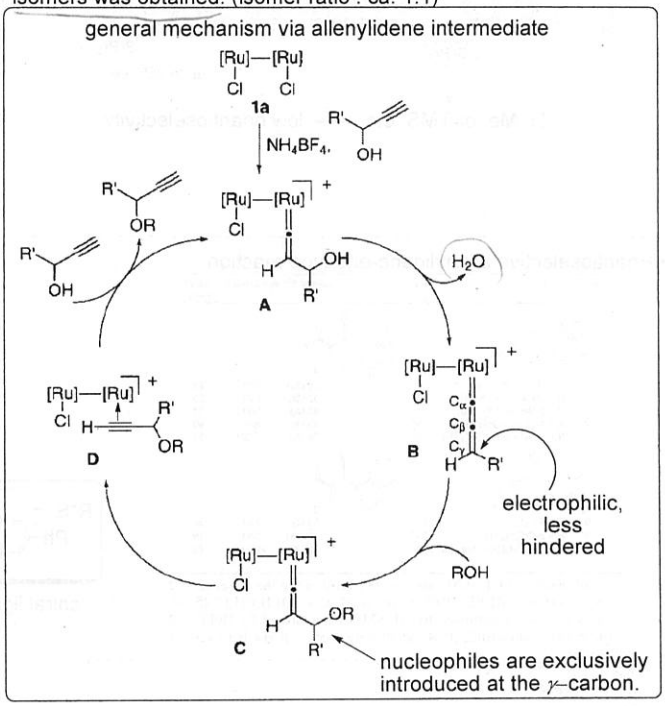
[a] All the reactions of **3** (0.60 mmol) were carried out in the presence of **1a** (5 mol %) and NH_4BF_4 (10 mol %) in alcohol (15 mL) at 60 °C. [b] Isolated yield. [c] At room temperature. [d] Reactions were carried out with **3a** (0.60 mmol) and alcohol (3.0 mmol) in $ClCH_2CH_2Cl$ (15 mL). [e] R*1 = (*S*)-$CH_2CH(Me)Et$. [f] R*2 = (*S*)-$CH_2CH(Me)Ph$. [g] R*3 = (*S*)-$CH(Me)Ph$. [h] R*4 = (*S*)-$CH(Me)Et$.



[a] All the reactions were carried out with **3a** (0.60 mmol) and nucleophiles (3.0 mmol) in the presence of **1a** (5 mol %) and NH_4BF_4 10 %mol) in $ClCH_2CH_2Cl$ (15 mL) at 60 °C.

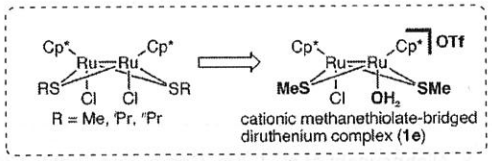


- when chiral alcohols were used, a mixture of two diastereomeric isomers was obtained. (isomer ratio : ca. 1:1)

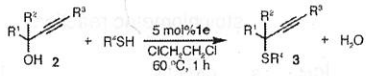


⟹ Exceptional Case : Sulfur-Centered Nucleophiles

M. Hidai, S. Uemura et al. *J. Am. Chem. Soc.* **2002**, *124*, 15172.

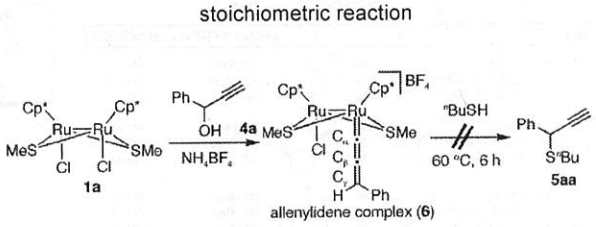


not only terminal alkyne but also internal alkyne are available.



run	propargylic alcohol	thiol	yield of **3**, %[b]
1	**2a**, R^1 = Ph, R^2 = H, R^3 = Ph	R^4 = Ph	**3ad**, 70
2	**2a**, R^1 = Ph, R^2 = H, R^3 = Ph	$R^4 = CH_2CH_2CO_2Me$	**3ae**, 92
3	**2a**, R^1 = Ph, R^2 = H, R^3 = Ph	$R^4 = CH_2CH_2CH_2Cl$	**3af**, 90
4[c]	**2a**, R^1 = Ph, R^2 = H, R^3 = Ph	$R^4 = CH_2CH_2OH$	**3ag**, 52
5	**2b**, $R^1 = Ph_2C{=}CH$, R^2 = H, R^3 = Ph	R^4 = ^{n}Bu	**3ba**, 96
6	**2c**, R^1 = PhC≡C, R^2 = H, R^3 = Ph	R^4 = ^{n}Bu	**3ca**, trace
7	**2d**, R^1 = Ph, R^2 = H, R^3 = ^{n}Bu	R^4 = ^{n}Bu	**3da**, 87
8	**2d**, R^1 = Ph, R^2 = H, R^3 = ^{n}Bu	$R^4 = CH_2CH_2CHMe_2$	**3db**, 90
9	**2e**, R^1 = Ph, R^2 = H, R^3 = ^{n}hexyl	R^4 = ^{n}Bu	**3ea**, 83
10	**2f**, R1 = Ph, R^2 = H, R^3 = ^{t}Bu	R^4 = ^{n}Bu	**3fa**, 86
11	**2f**, R^1 = Ph, R^2 = H, R^3 = ^{t}Bu	$R^4 = CH_2CH_2CHMe_2$	**3fb**, 87
12	**2g**, R^1 = *p*-MeC_6H_4, R^2 = H, R^3 = Ph	R^4 = ^{n}Bu	**3ga**, 90
13	**2g**, R^1 = *p*-MeC_6H_4, R^2 = H, R^3 = Ph	$R^4 = CH_2CH_2CHMe_2$	**3gb**, 92
14	**2h**, R^1 = Ph, R^2 = Me, R^3 = Ph	R^4 = ^{n}Bu	**3ha**, 84

[a] All the reactions of **2** (0.30 mmol) with thiol (1.50 mmol) were carried out in the presence of **1e** (0.015 mmol) in $ClCH_2CH_2Cl$ (8 mL) at 60 °C for 1 h. [b] Isolated yield. [c] 10 mol % of **1e** was used.

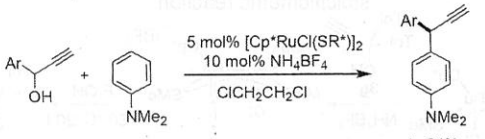


-Not via allenylidene intermediate.

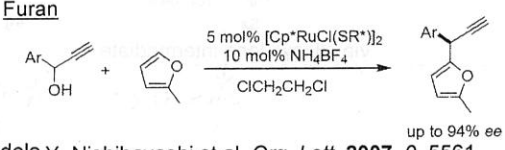
- Nicholas type activation by coordination of acetylene unit of propargylic alcohols on the diruthenium site?

• Enantioselective Friedel-Crafts Reactions

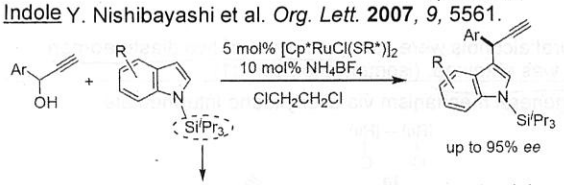
Y. Nishibayashi et al. *Angew. Chem. Int. Ed.* **2007**, *46*, 6488.



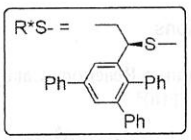
Furan



Indole Y. Nishibayashi et al. *Org. Lett.* **2007**, *9*, 5561.

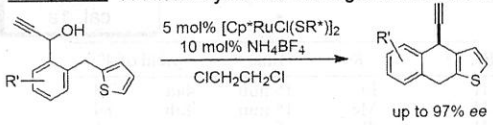


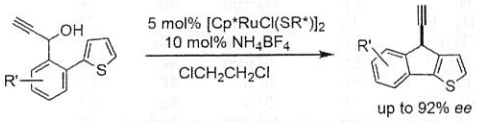
H, Me, or TMS, etc. ⟶ low enantioselectivity

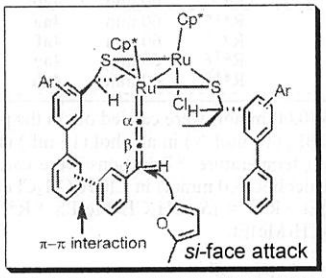


chiral ligand

Thiophene Y. Nishibayashi et al. *Organometallics* **2009**, *28*, 2920.





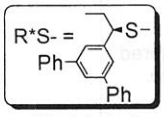


• Enantioselective allenylidene-ene type reaction

Y. Nishibayashi, S. Uemura et al. *J. Am. Chem. Soc.* **2008**, *130*, 10498.

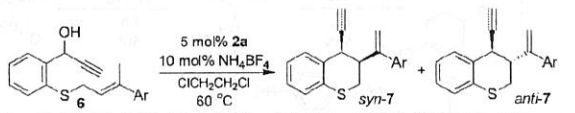
run	1	time (h)	yield of 3[b] (%)	syn-3/anti-3[c]	ee of syn-3[d]
1	R = H, Ar = Ph (**1a**)	6	85 (**3a**)	17/1	93
2	R = 4-Me, Ar = Ph (**1f**)	6	92 (**3f**)	14/1	90
3	R = 6-Me, Ar = Ph (**1g**)	6	93 (**3g**)	17/1	92
4	R = 4-Cl, Ar = Ph (**1h**)	5[e]	85 (**3h**)	8/1	90
5	R = H, Ar = *p*-MeC$_6$H$_4$ (**1i**)	7[e]	78 (**3i**)	23/1	93
6	R = Ph (**1j**)	23	68 (**3j**)	33/1	96
7	R = *p*-ClC$_6$H$_4$ (**1k**)	24[e]	72 (**3k**)	33/1	99
8	R = CH$_2$CH$_2$CH=CMe$_2$ (**1l**)	24	63 (**3l**)	>99/<1	88

[a] All reactions of **1** (0.20 mmol) were carried out in the presence of **2** (0.01 mmol) and NH_4BF_4 (0.02 mmol) at 60 °C in $ClCH_2CH_2Cl$ (5 mL). [b] Isolated yield. [c] Determined by ^1H NMR. [d] Determined by HPLC. [e] **2** (0.02 mmol) and NH_4BF_4 (0.04 mmol) were used. [f] $ClCH_2CH_2Cl$ (20 ml) was used.



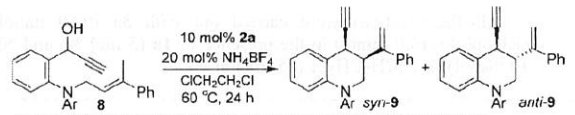
chiral ligand

Scheme 5



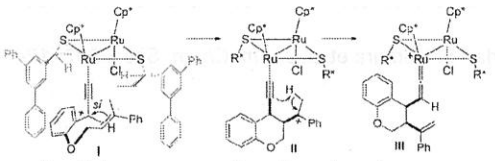
Ar = Ph (**6a**), 5 h, 91% isolated yield (*syn*-**7a**/*anti*-**7a** = >99/<1), 89% *ee* of *syn*-**7a**
Ar = *p*-MeC$_6$H$_4$ (**6b**); 2 h, 87% isolated yield (*syn*-**7b**/*anti*-**7b** = 17/1), 88% *ee* of *syn*-**7b**
Ar = *p*-ClC$_6$H$_4$ (**6c**); 6 h, 90% isolated yield (*syn*-**7c**/*anti*-**7c** = >99/<1), 86% *ee* of *syn*-**7c**

Scheme 6



Ar = Ph (**8a**); 65% isolated yield (*syn*-**9a**/*anti*-**9a** = 14/1), 98% *ee* of *syn*-**9a**
Ar = *p*-MeC$_6$H$_4$ (**8b**); 45% isolated yield (*syn*-**9b**/*anti*-**9b** = 20/1), 94% *ee* of *syn*-**9b**
Ar = *p*-ClC$_6$H$_4$ (**8c**); 80% isolated yield (*syn*-**9c**/*anti*-**9c** = 13/1), 95% *ee* of *syn*-**9c**

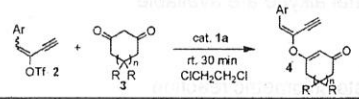
Scheme 3



allenylidene-ene reaction via a stepwise process.

• Vinylic substitution reactions via butatrienylideneintermediates

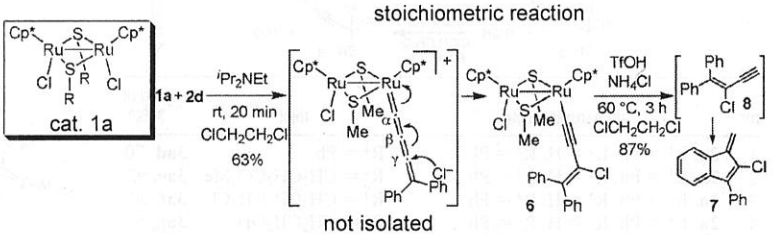
Y. Nishbayashi *et al. J. Am. Chem. Soc.* **2008**, *130*, 2908.

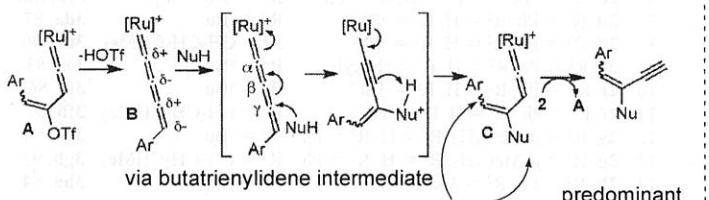


run	2[b]	3	4	yield of 4,(%)[c]	isomer ratio (*E*/*Z*)[d]
1	Ar = Ph (**2a**)	3a		91 (**4aa**)	>99/<1
2	Ar = *p*-MeC$_6$H$_4$ (**2b**)	3a		87 (**4ba**)	>99/<1
3	Ar = *p*-ClC$_6$H$_4$ (**2c**)	3a		86 (**4ca**)	>99/<1
4	Ar = Ph (**2a**)	3b		82[e] (**4ab**)	>99/<1
5	Ar = *p*-MeC$_6$H$_4$ (**2b**)	3b		55[e] (**4bb**)	>99/<1
6	Ar = *p*-ClC$_6$H$_4$ (**2c**)	3b		42[e] (**4cb**)	>99/<1
7	Ar = Ph (**2a**)	3c		88 (**4ac**)	>99/<1
8	Ar = *p*-MeC$_6$H$_4$ (**2b**)	3c		84 (**4bc**)	>99/<1
9	Ar = *p*-ClC$_6$H$_4$ (**2c**)	3c		77 (**4cc**)	>99/<1
10	OTf **2d**	3a		84 (**4da**)	>99/<1
11	OTf **2e**	3a		89 (**4ea**)	>99/<1
12	Ar = Ph (**2a**)	3d		93 (**4ad**)	98/2

[a] All reactions of **2** (0.30 mmol) with **3** (0.90 mmol) were carried out in the presence of **1a** (0.009 mmol) in $ClCH_2CH_2Cl$ (8 mL) at room temperature for 30 min. [b] The isomer ratio is shown in Supporting Information. [c] Isolated yield. [d] Determined by ^1H NMR. [e] The reaction was carried out in the presence of **1a** (0.015 mmol) for 1 h.

stoichiometric reaction



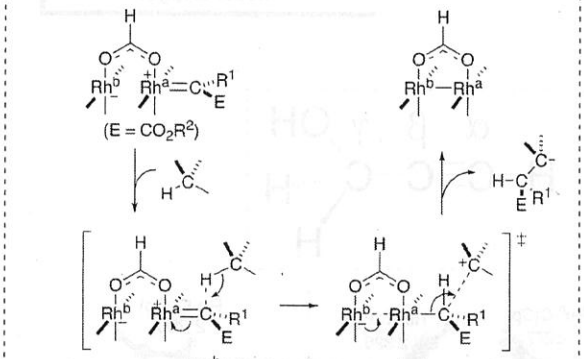


1-3. Mechanisticl study of Dimetallic Effects in Propargylic Substitution Reaction

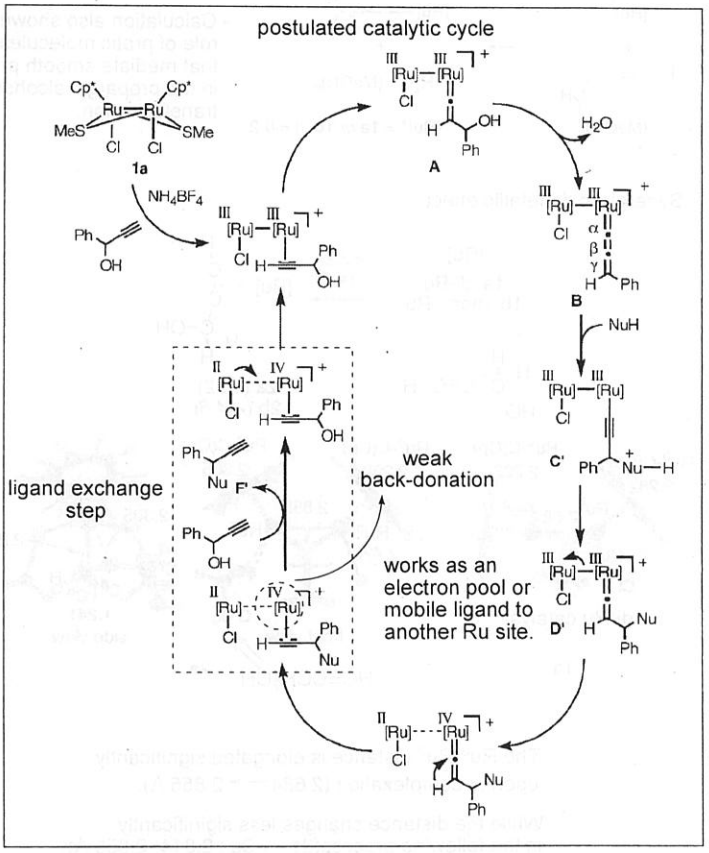
- Nishibayashi et al. proposed di-Rh type mechanism.

Y. Nishibayashi, M. Hidai, S. Uemura et al. *Organometallics* **2004**, *20*, 5177.

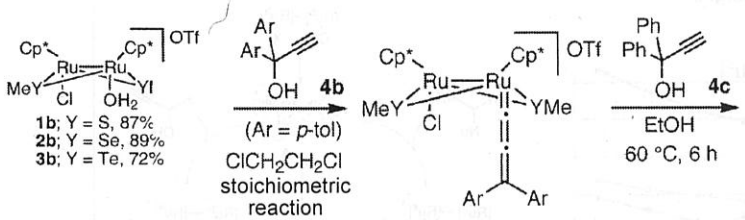
cf.) C-H Insertion of Alkane with Dirhodium Carbene Complexs

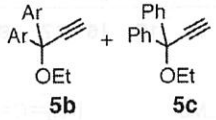


- Rh^b atom acts as an electron ***donor*** to the Rh^a atom in the C-H insertion step.



-Experimental results





Y = S, 38% (**5b**) and 70% (**5c**)
Y = Se, 49% (**5b**) and 70% (**5c**)
Y = Te, <5% (**5b**) and <10% (**5c**)

- in the tellurolate case, either the step of a nucleophilic attack on C_γ in the allenylidene moiety of 3c doesn't proceed smoothly or the ligand exchange with another propargylic alcohol does not occur readily.

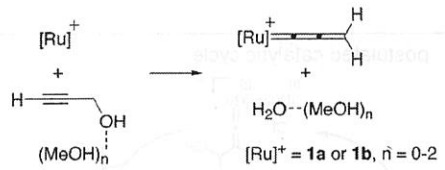
- cyclic voltammograms of 1b and 2b revealed two reversible waves at $E_{1/2}$ = + 0.58, + 1.15 V and $E_{1/2}$ = + 0.53, + 1.11 V, respectively, assignable to the redox couples [Ru^{III}/Ru^{IV}] and [Ru^{IV}/Ru^{IV}].
- in contrast, the cyclic voltammogram of 3b exhibited one irreversible wave at E_p = + 1.91V.

⟹

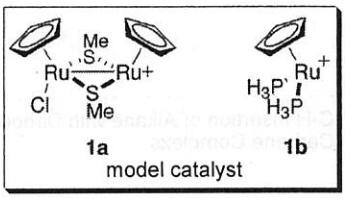
- the oxidation (namely, an electron transfer) of 1b and 2b proceeds more smoothly than that of 3b.
- the higher oxidation state of Ru^{IV} reducing the back-donation ability from the Ru to the coordinatede alkyne moiety.

• Theoretical Study by DFT Calculation

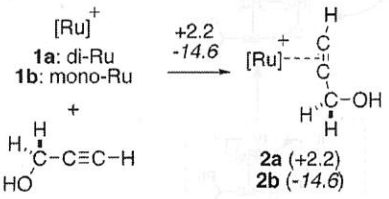
E, Nakamura *et al. J. Am. Chem. Soc.* **2005**, *127*, 9428.

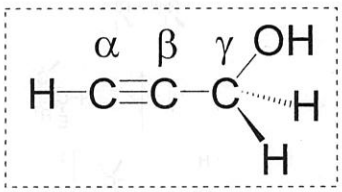


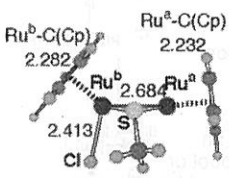
- Calculation also showed the important role of protic molecules (e.g., MeOH) that mediate smooth proton transfer in the propargyl alcohol-allenylidene transformation.

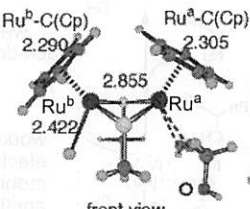


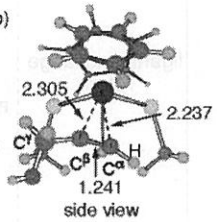
- Synergistic dimetallic effect

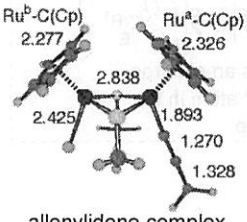


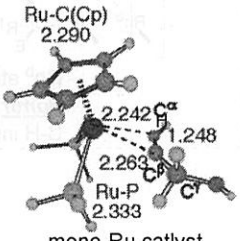






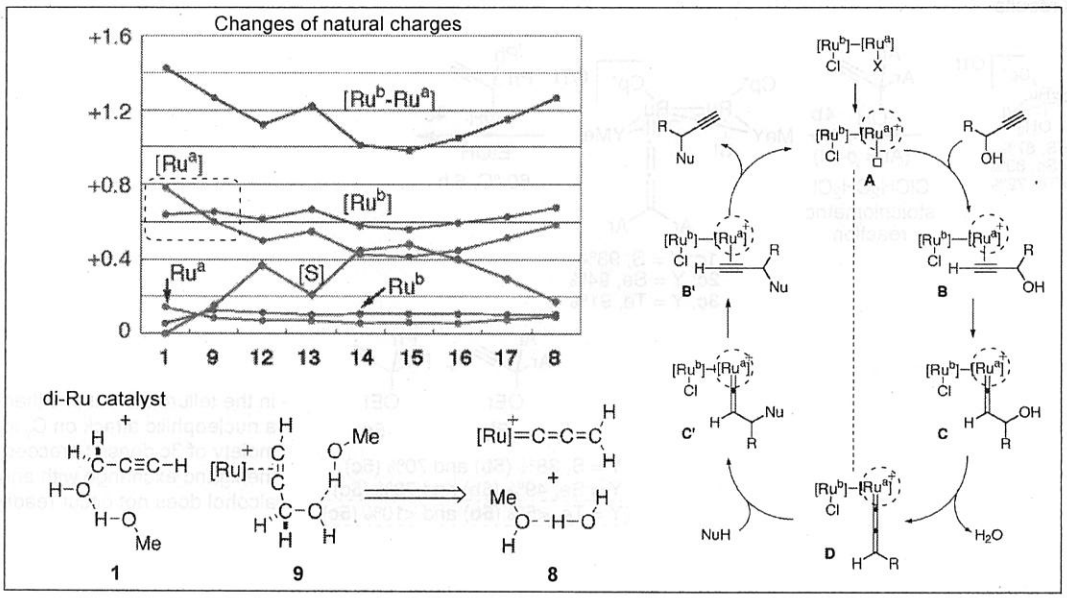




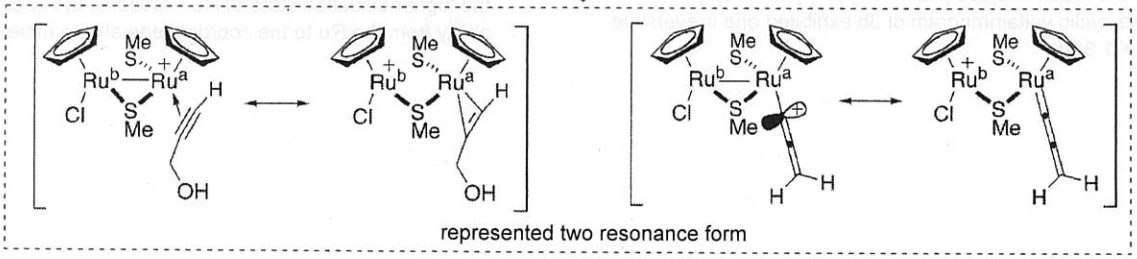


- The Ru^a-Ru^b distance is elongated significantly upon π-complexation (2.684 ⟶ 2.855 Å).
- While the distance changes less siginificantly in the following process(2a⟶8a : 2.814~2.855 Å).

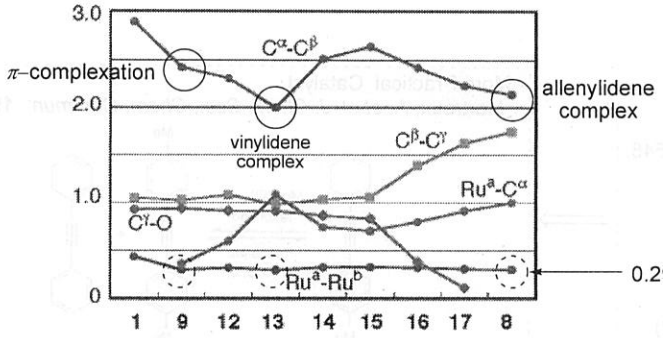
C^α-C^β bond length : (**2a**: 1.241 Å, **2b**: 1.248 Å)
C^β-C^α-H angle : (**2a**: 155.8°, **2b**: 154.7°)
C^α-C^β-C^γ angle : (**2a**: 161.3°, **2b**: 154.6°)
⟹ These results indicate **weaker back-donation** in the di-Ru system.



- The $[Ru^a]$ fragment is less positeive than the $[Ru^b]$ fragment throughout the reaction pathway (except 1), while the valence formalism indicates a positive charge at the $[Ru^a]$ moiety.



• Wiberg Bond Analysis

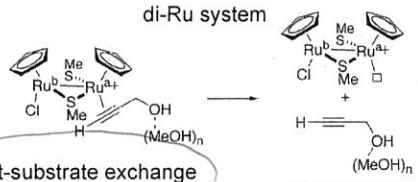


- Ru^a-Ru^b bond becomes weaker when there is back-donation from the Ru^a atom.

0.29~0.32 (from **9** to **8**)

- Product-substrate exchange step (catalyst turnover step)

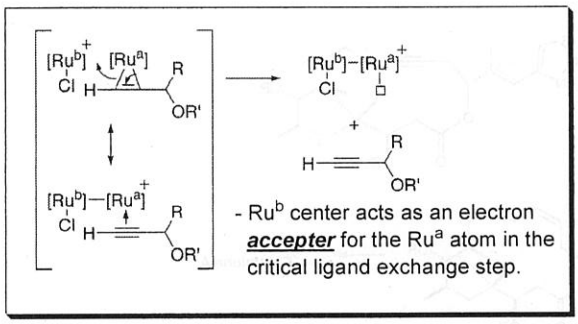
di-Ru system



- Product-substrate exchange can readily take place in this di-Ru system.

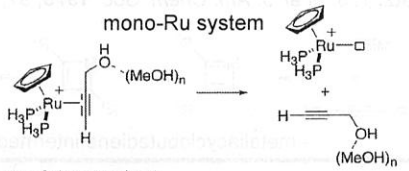
ΔG = -2.2 (n = 0)
-2.0 (n = 1)
+1.9 (n = 2)

why?



- Ru^b center acts as an electron ***accepter*** for the Ru^a atom in the critical ligand exchange step.

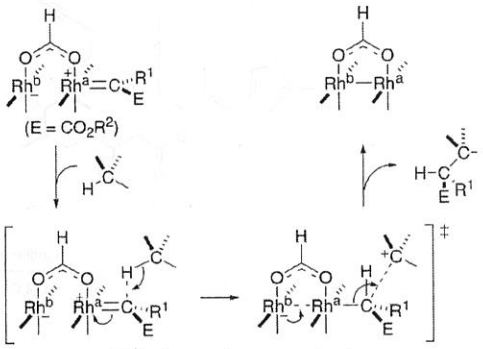
mono-Ru system



- Smooth exchange of the product with the substrate on the mono-Ru center is difficult.

ΔG = +14.6 (n = 0)
+20.4 (n = 1)
+20.5 (n = 2)

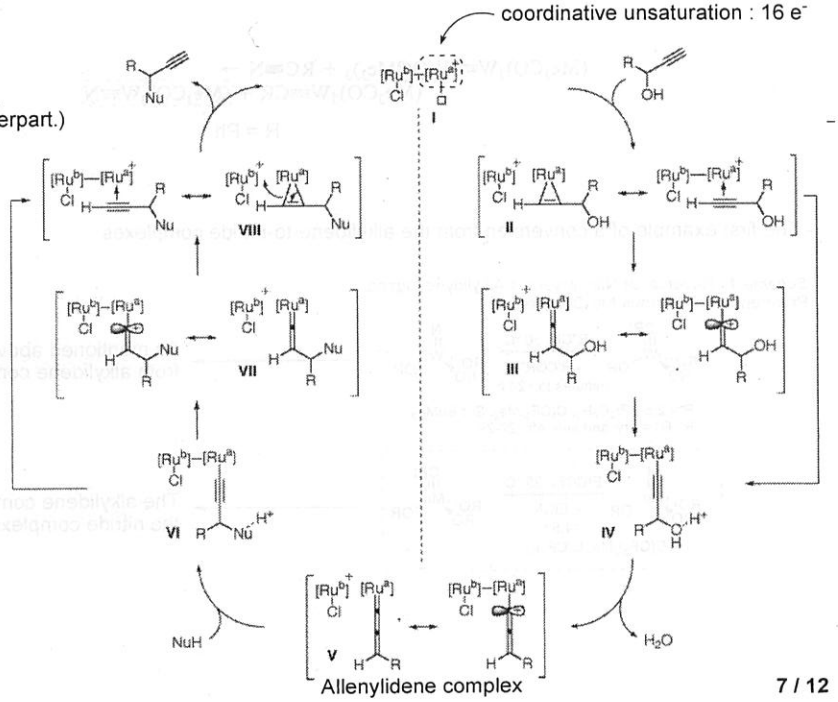
Once again...



- Rh^b atom acts as an electron ***donor*** to the Rh^a atom in the C-H insertion step.

- The energy loss due to coordinative unsaturation can be compensated by reinforcement of the Ru-Ru bond. (such an effect is unavailable in the monoruthenium counterpart.)

- In the ligand dissociation step, the Ru^b center accepts electrons from the Ru^a center, which have been offered for the back-donation in the π-complex.



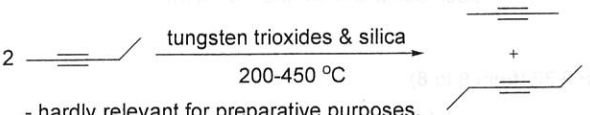
2. Catalytic Reactions Involving Nitride Complexes as intermediate

2-1. Background

Classical Catalyst System for Alkyne Metathesis

- The First Effective Alkyne Metathesis Catalyst

Bailey, G. C. *et al. Chem. Commun.*, **1968**, 1548.

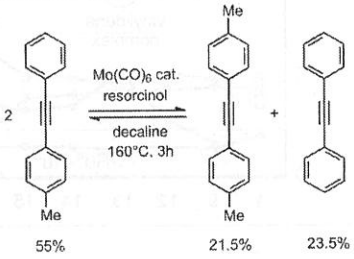


- hardly relevant for preparative purposes.

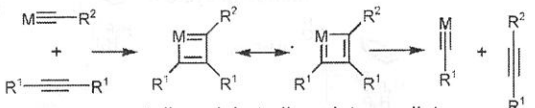
(mole ratio : 1.0 to 1.2)

- More Practical Catalyst

Mortreux, A. *et al. J. Chem. Soc., Chem. Commun.*, **1974**, 786.



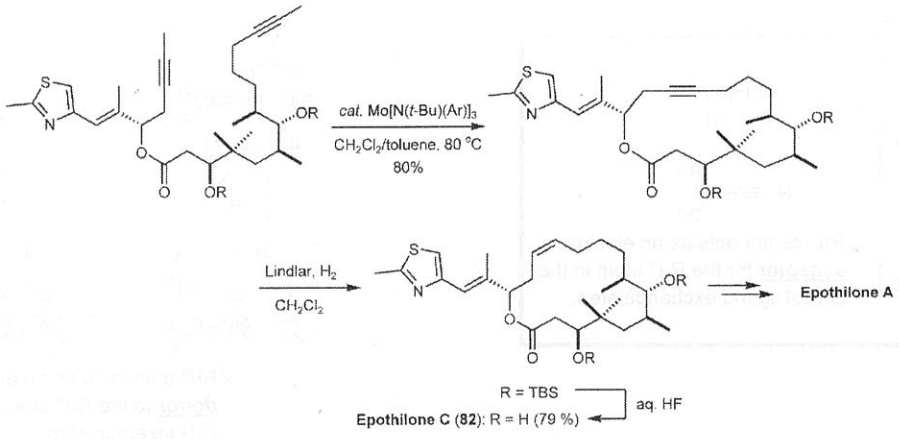
Katz. T. J. *et al. J. Am. Chem. Soc.* **1975**, *97*, 1592.



- metallacyclobutadiene intermediate.

- An example of the application to the natural product synyhesis

A. Fürstner et al. *Chem Commun.* **2001**, 1057.



- Precedents for the alkylidene-to-nitiride conversion

Schrock, R. R. et al. *J. Am. Chem. Soc.* **1982**, *104*, 4291.

$$(Me_3CO)_3W{\equiv}W(OCMe_3)_3 + RC{\equiv}N \rightarrow (Me_3CO)_3W{\equiv}CR + (Me_3CO)_3W{\equiv}N$$

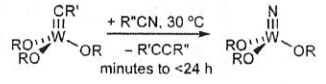
R = Ph

- irreversible reaction.

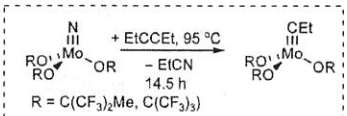
- The first example of a conversion from the alkylidene-to-nitride complexes

Johnson, M. J. et al. *J. Am. Chem. Soc.* **2006**, *128*, 9614.

Scheme 1. Reversal of Nitride versus Alkylidyne Ligand Preference in W versus Mo Complexes



R = 2,6-*i*-$Pr_2C_6H_3$, $C(CF_3)Me_2$, Si-*t*-$BuMe_2$
R', R" = aryl and see refs. 27-29



R = $C(CF_3)_2Me$, $C(CF_3)_3$)

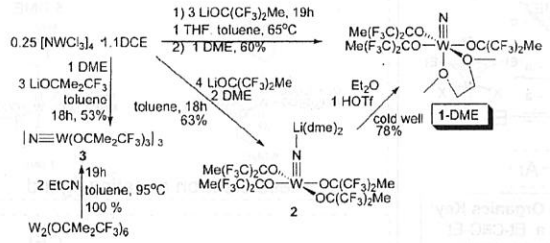
As mentioned above, the formation of nitride species from alkylidene complexes and nitrile is well-known process.

The alkylidene complexes are formed irreversibly from the nitride complexs, but with a large activation barrier.

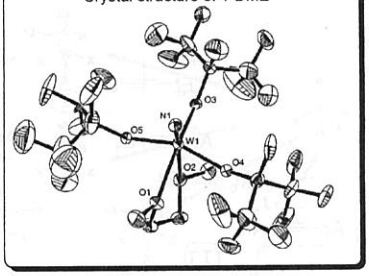
2-2. Tungsten-nitride complexes

Johnson, M. J. et al. *J. Am. Chem. Soc.* **2007**, *129*, 3800.
J. Am. Chem. Soc. **2008**, *130*, 8984.

Scheme 3. Syntheses of Tungsten-Nitride Complexes

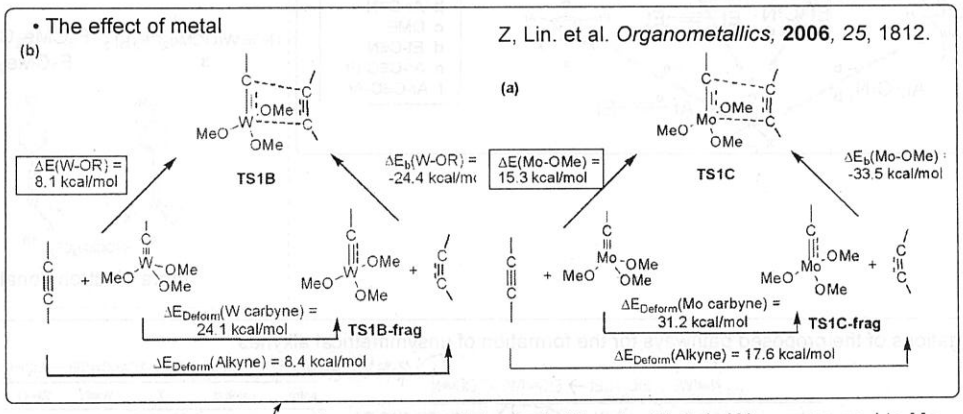


Crystal structure of 1-DME

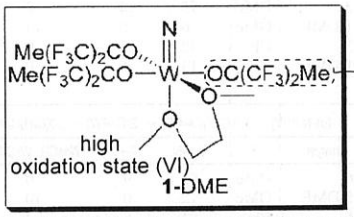


• The effect of metal

Z, Lin. et al. *Organometallics*, **2006**, *25*, 1812.



- the greater spatial extent of the d orbitals in W as compared to Mo should lead to a diminished barrier to metalacycle formation for W complexes.



- weaker donor ligand favors the formation of an alkylidyne relative to the nitride.

- Lewis acidity of the W center increases.

• The effect of ligand (in case of Mo)

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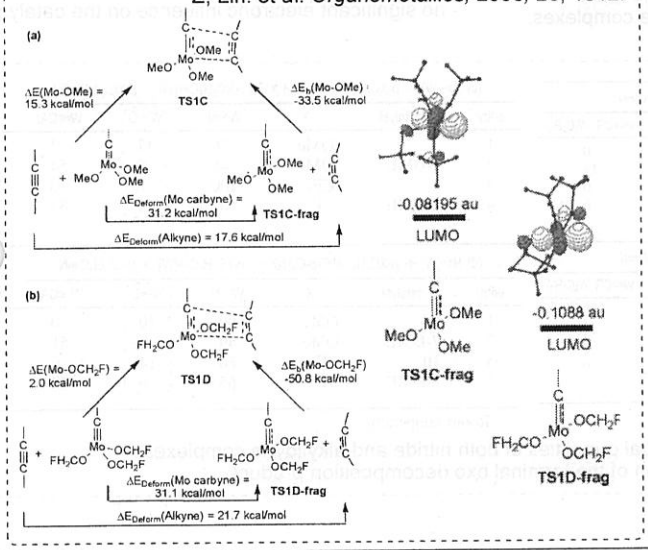
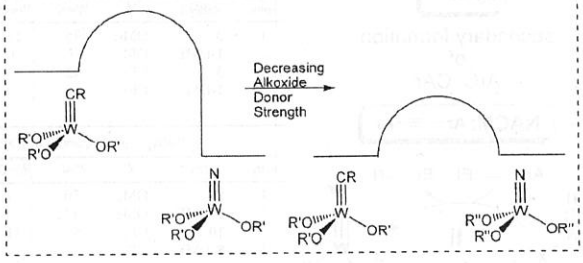
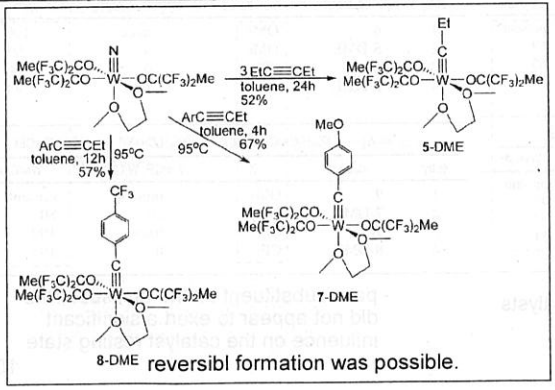


- for an identical set of ancillary ligands, there is a greater positive at the metal center in the nitride complex than in the alkylidyne complex.

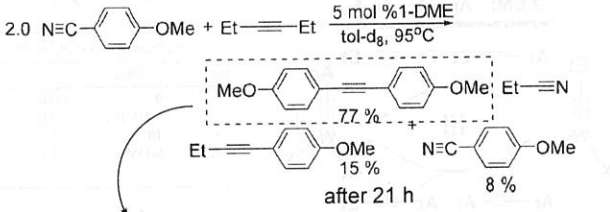
• Impact of alkoxide on relative energies of alkylidyne and nitride complexes.



2-3. Catalytic nitrile-alkyne cross-metathesis

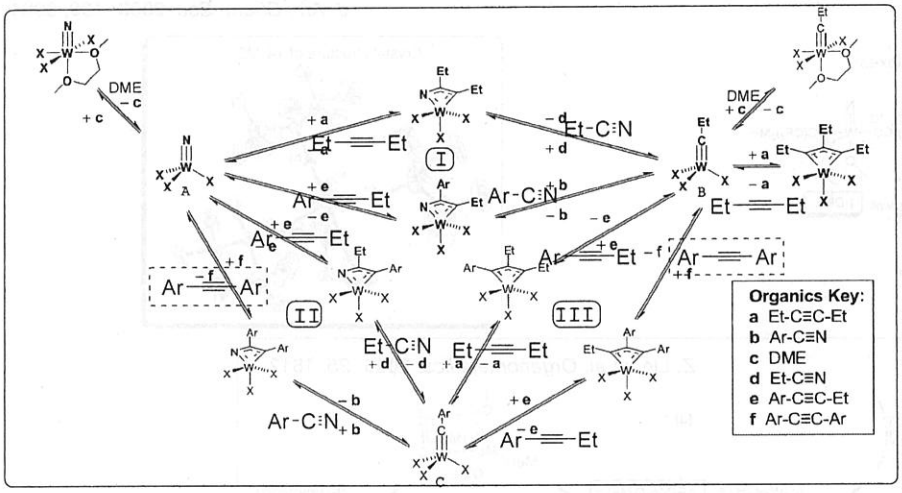


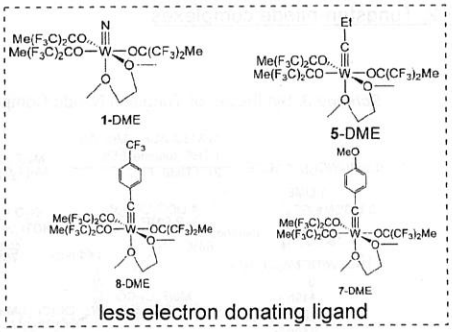
reversibl formation was possible.

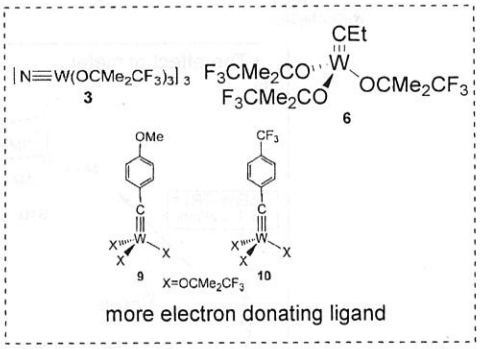


symmetrical diaryl alkyne was the major product.

• Three possible cycles for formatioon of symmetrical alkyne





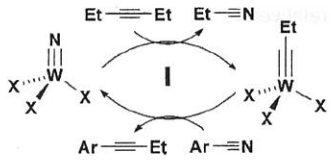


• Stoichiometrric investigations of the proposed pathways for the formation of unsymmetrical alkynes

Cycle I

formation of ArC≡CEt from ArC≡N

NACM: Ar—≡—Et



(a) N≡[W] + EtC≡CEt → EtC≡[W] + EtC≡N

entry	catalyst	W≡N	W=O	W≡CR, W(C$_3$R$_3$)
1	**3**	63	26	9
2	**1**-DME[a]	0	0	100

(b) N≡[W] + EtC≡CEt ← EtC≡[W] + EtC≡N

entry	catalyst	W≡N	W=O	W≡CR, W(C$_3$R$_3$)
1	**6**	89	11	0
2	**5**-DME	28	0	72

(c) N≡[W] + *p*-XC$_6$H$_4$C≡CEt → EtC≡[W] + *p*-XC$_6$H$_4$C≡N

entry	catalyst	X	W≡N	W=O	W≡CR, W(C$_3$R$_3$)	W≡CAr
1	**3**	OMe	75	14	0	9
2	**1**-DME	OMe	6	0	14	80
3	**3**	CF_3	42	33	0	25
4	**1**-DME	CF_3	13	0	0	87

(d) N≡[W] + *p*-XC$_6$H$_4$C≡CEt ← EtC≡[W] + *p*-XC$_6$H$_4$C≡N

entry	catalyst	X	W≡N	W=O	W≡CR, W(C$_3$R$_3$)	W≡CAr
1	**6**	OMe	60	9	0	25
2	**5**-DME	OMe	12	0	10	78
3	**6**	CF_3	64	5	4	19
4	**5**-DME	CF_3	13	0	0	87

[a] Room temperature.

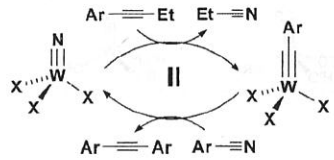
- use of the less electron donating $OC(CF_3)_2Me$ ligand leads to preferential formation of alkylidyne or benzylidyne complexes.
- reversible for both catalysts.

- no significant electronc influence on the catalyst

Cycle II

secondary formation of ArC≡CAr

NACM: Ar—≡—Ar



(a) N≡[W] + *p*-XC$_6$H$_4$C≡CEt → *p*-XC$_6$H$_4$C≡[W] + EtC≡N

entry	catalyst	X	W≡N	W=O	W≡CAr	W≡CR, W(C$_3$R$_3$)
1	**3**	OMe	75	14	9	0
2	**1**-DME	OMe	6	0	80	14
3	**3**	CF_3	42	33	25	0
4	**1**-DME	CF_3	13	0	87	0

(b) N≡[W] + *p*-XC$_6$H$_4$C≡CEt ← *p*-XC$_6$H$_4$C≡[W] + EtC≡N

entry	catalyst	X	W≡N	W=O	W≡CAr	W≡CR, W(C$_3$R$_3$)
1	**9**	OMe	70	7	14	0
2	**7**-DME	OMe	42	0	39	19
3	**10**	CF_3	61	11	21	0
4	**8**-DME	CF_3	17	0	83	0

(c) N≡[W] + *p*-XC$_6$H$_4$C≡C-*p*-C$_6$H$_4$X → *p*-XC$_6$H$_4$C≡[W] + *p*-XC$_6$H$_4$C≡N

entry	catalyst	X	W≡N	W=O	W≡CAr
1	**3**	OMe	76	17	7
2	**1**-DME[a]	OMe	46	0	54
3	**3**	CF_3	100	0	0
4	**1**-DME	CF_3	67	0	33

(d) N≡[W] + *p*-XC$_6$H$_4$C≡C-*p*-C$_6$H$_4$X ← *p*-XC$_6$H$_4$C≡[W] + *p*-XC$_6$H$_4$C≡N

entry	catalyst	X	W≡N	W=O	W≡CAr
1	**9**	OMe	90	10	0
2	**7**-DME	OMe	49	0	51
3	**10**	CF_3	86	14	0
4	**8**-DME	CF_3	65	0	35

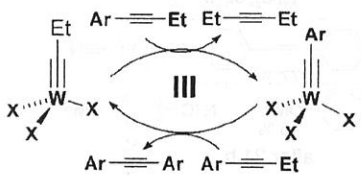
[a] Room temperature.

- the use of **1**-DME affords substantial quantities of both nitride and alkylidyne complexes at equilibrium, without the formation of the terminal oxo decomposition product.

Cycle III

formation/consumption of ArC≡CAr

ACM: Ar—≡—Ar



(a) EtC≡[W] + *p*-XC$_6$H$_4$C≡CEt → *p*-XC$_6$H$_4$C≡[W] + EtC≡CEt

entry	catalyst	X	W≡CR, W(C$_3$R$_3$)	W≡CAr
1	**6**	OMe	present	present
2	**5**-DME	OMe	31	69
3	**6**	CF_3	35	65
4	**5**-DME	CF_3	21	79

(b) EtC≡[W] + *p*-XC$_6$H$_4$C≡CEt ← *p*-XC$_6$H$_4$C≡[W] + EtC≡CEt

entry	catalyst	X	W≡CR, W(C$_3$R$_3$)	W≡CAr
1	**9**	OMe	present	present
2	**7**-DME	OMe	52	48
3	**10**	CF_3	33	67
4	**8**-DME	CF_3	49	51

(c) EtC≡[W] + *p*-XC$_6$H$_4$C≡C-*p*-C$_6$H$_4$X → *p*-XC$_6$H$_4$C≡[W] + *p*-XC$_6$H$_4$C≡CEt

entry	catalyst	X	W≡CR, W(C$_3$R$_3$)	W≡CAr
1	**6**	OMe	trace	100
2	**5**-DME	OMe	6	93
3	**6**	CF_3	0	100
4	**5**-DME	CF_3	16	84

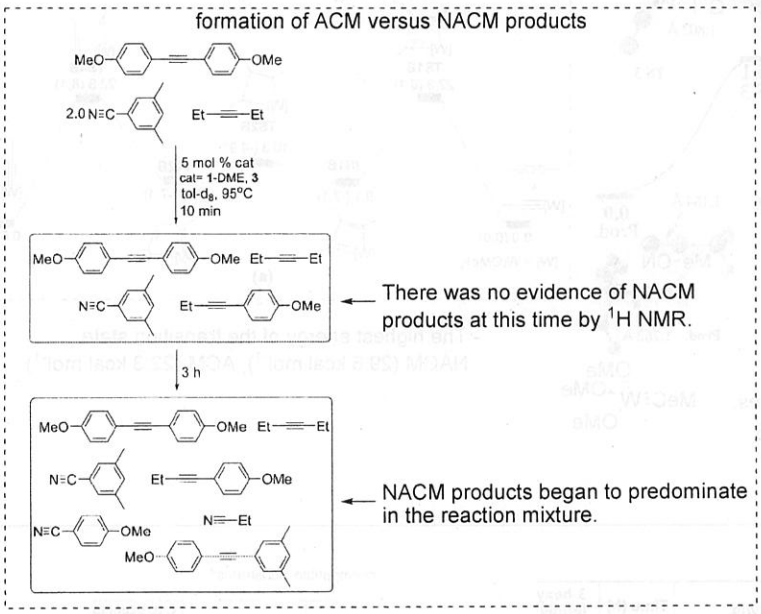
(d) EtC≡[W] + *p*-XC$_6$H$_4$C≡C-*p*-C$_6$H$_4$X ← *p*-XC$_6$H$_4$C≡[W] + *p*-XC$_6$H$_4$C≡CEt

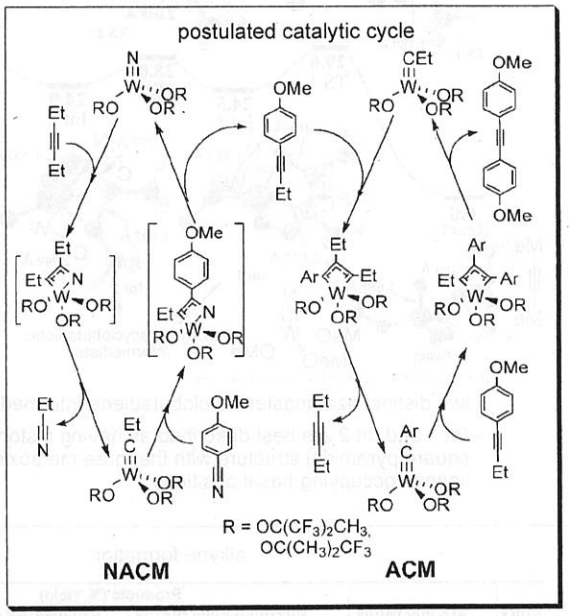
entry	catalyst	X	W≡CR, W(C$_3$R$_3$)	W≡CAr
1	**9**	OMe	present	present
2	**7**-DME	OMe	20	80
3	**10**	CF_3	trace	100
4	**8**-DME	CF_3	0	100

- the favored resting state of the catalysts was the benzylidyne complex.

- para-substituent on the aryl substrate did not appear to exert a significant influence on the catalyst resting state.

- The large difference in reaction rate between NACM and ACM at room temperture implicates ACM as the primary process by which the symmetrical alkyne is formed over NACM. (i.e., the symmetrical diaryl alkyne is formed principally via cycle III and not cycle II, at least in the case of ligation by $OC(CF_3)_2Me$.)
- In case of 3, the alkylidyne complexes required for ACM are present in only very small quantities, but in case of 1-DME, a much larger fraction of the catalyst exists in the alkylidyne form, thus favoring rapid ACM.

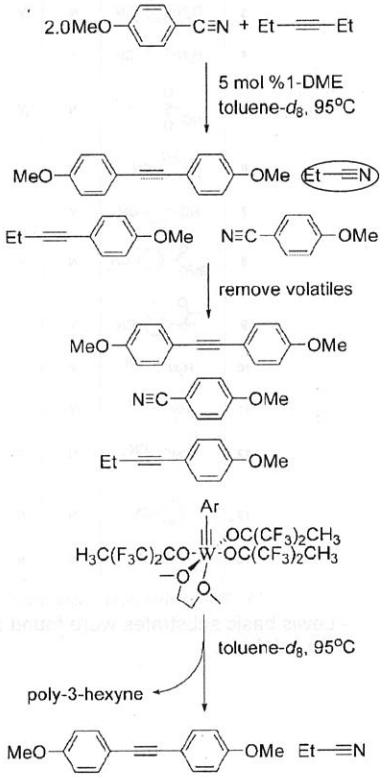




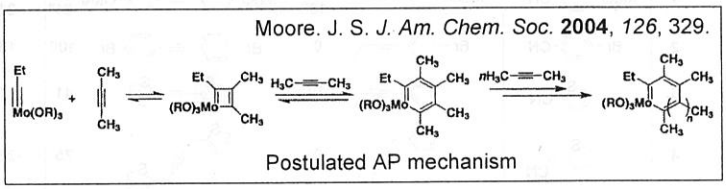
• Preferntial formation of symmetrical alkynes

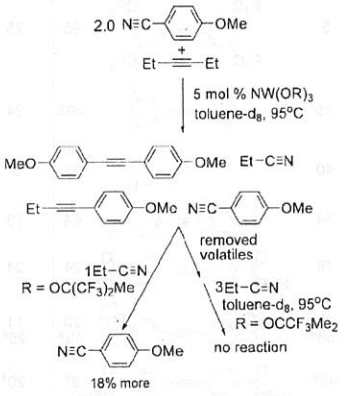
Alkyne Polymerization

- AP is known to compete with AM in some systemes.

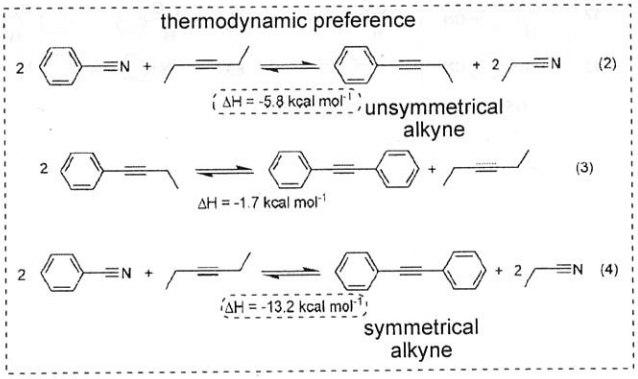


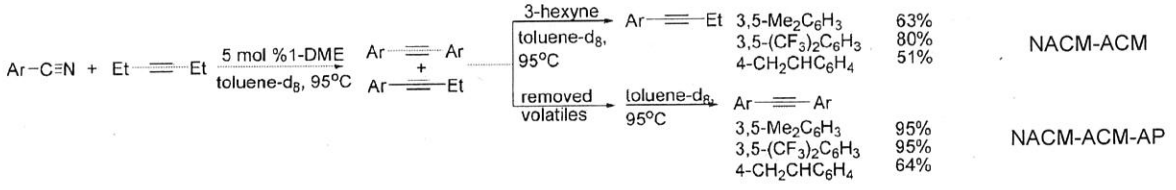
- simple removal of volatiles from the system, followed by heating toluene often allows the unsymmetrical alkyne to be metathesized into the symmetrical alkyne and 3-hexyne.
- 3-hexyne is removed from the system by polymerization or evacuation.



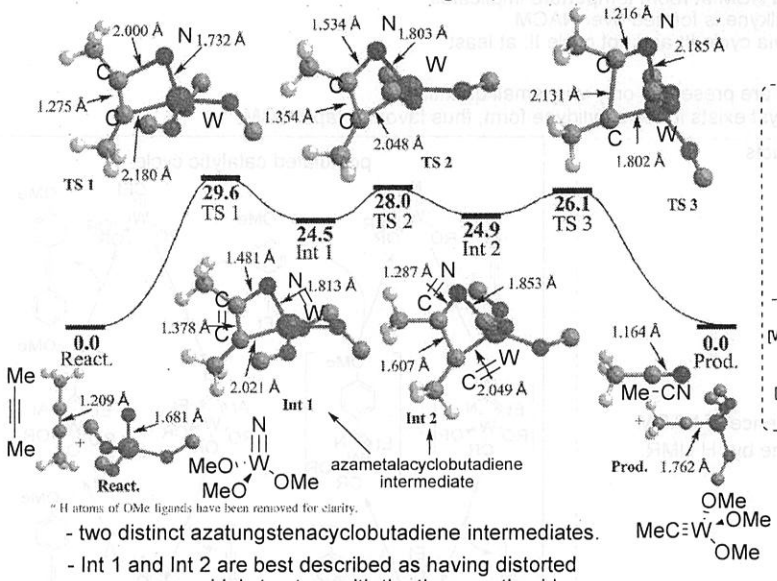


- In case of 1-DME, the "back reaction" of the alkynes ArC≡CEt and ArC≡CAr with EtCN occurred.





• Calculated structure and relative Gibbs energies (kcal mol-1) for nitride-alkylidyne interconversion in a model system



" H atoms of OMe ligands have been removed for clarity.

- two distinct azatungstenacyclobutadiene intermediates.
- Int 1 and Int 2 are best described as having distorted square pyramidal structure with the three methoxide ligands occupying basal positions.

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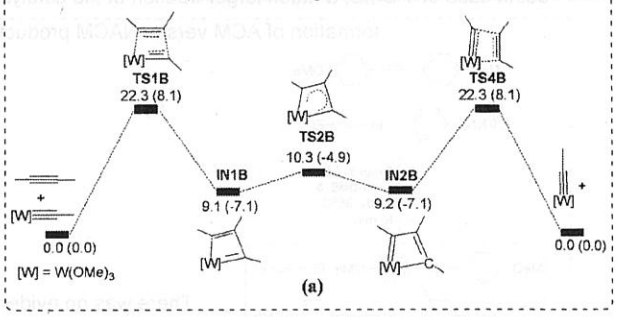
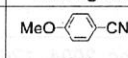
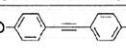
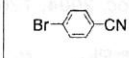
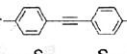
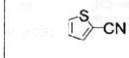
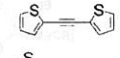
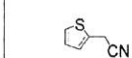
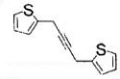
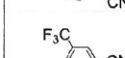
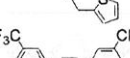
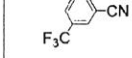
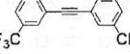
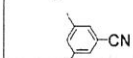
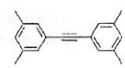
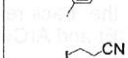
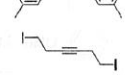
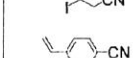
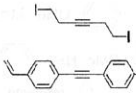
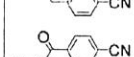
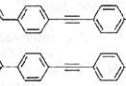
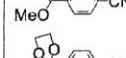
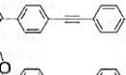
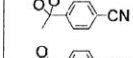
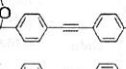
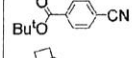
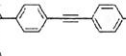


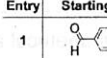
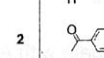
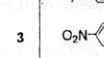
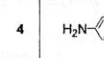
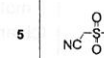
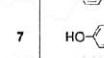
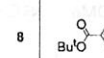
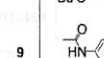
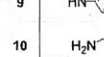
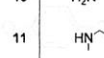
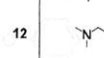
- The highest energy of the transition state NACM (29.6 kcal mol^{-1}), ACM (22.3 kcal mol^{-1})

alkyne formation

Entry	Starting Nitrile	Products (% Yield) Unsymmetrical Alkyne	Products (% Yield) Symmetrical Alkyne	Time (h)	3-hexy (equiv)
1		11 18[a]	 81 61[a]	8 31[a]	1.0 1.0[a]
2		0	 100	15	2.0
3		19	 41	11	2.0
4		0	 75	22	2.0
5		5	 95	25	2.0
6		<5	 >95	24	2.0
7		40	 33	6	2.0
8		34	 64	13	1.6
9		76	 24	24	3.0
10		19 58[a]	 23 12[a]	11 25[a]	1.0 1.0[a]
11		43[a]	 6[a]	20[a]	2.0[a]
12		4 25[a]	 0 0[a]	12 25[a]	1.0 1.0[a]
13		69	 13	18	2.0

95 °C, toluene. [a] catalyst = 3.

Incompatible Substrates[a]

Entry	Starting Nitrile	Cat. Decomp. 1-DME	Cat. Decomp. 5
1		N	Y
2		Y	
3		N	Y
4		Y	
5		N	Y
6		Y	
7		Y	
8		N	Y
9		Y	
10		Y	
11		Y	
12		N	Y
13		N	N
14		N	N

" Y: This catalyst form is deactivated.

- Lewis basic substrates were found to deactivate the catalysts.