Literature presentation

C-C Bond Formation between Fischer Carbene Complex And Allylic Alcohols promoted by a $M(CO)_5$ Shift

Barluenga,J.; Rubio, E.; Lopez, J. A.; Tomas, M. *Angew. Chem. Int. Ed*. **1999**, 38(8), 1091

Universidad de oviedo, Spain

Kamikawa, K.; Uchida, K.; Furusho, M.; Uemura, M. et. *Org. Lett*. **2004**, 6(23), 4307

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November 11, 2004

Opportunities inCarbene Chemistry

…Again, the **flexibility** and/or **capriciousness** of many transition-metal complexes toward organic substrates becomes more than apparent…

---Jose Barluenga/Universidad de oviedo

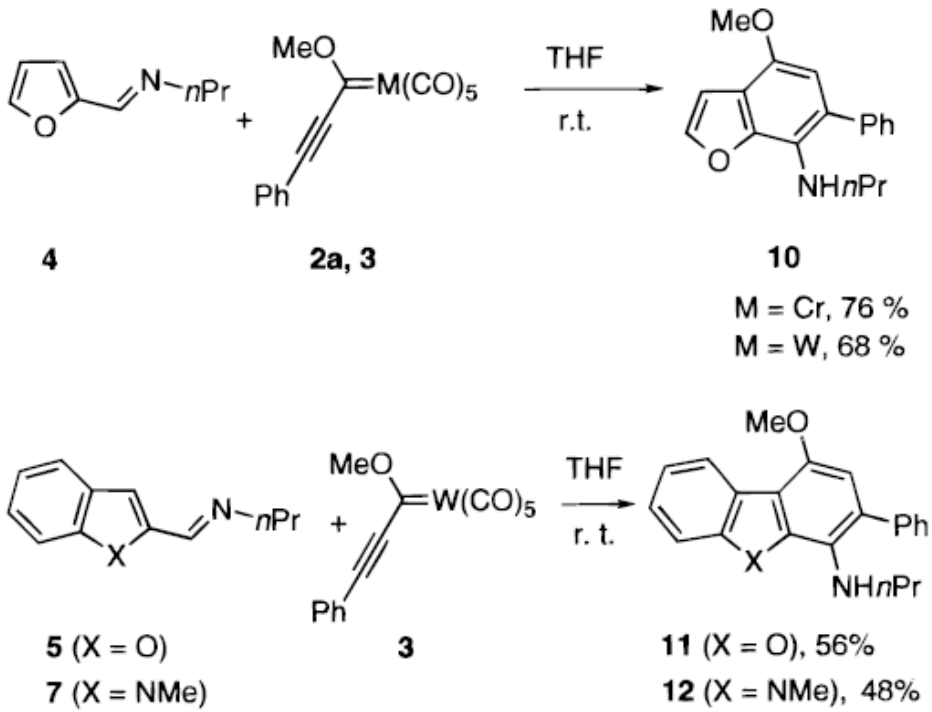
…These lead to **unexpected** C-H and C-C bond-forming reactions and might be regarded as a further **surprise** from Fischer carbene complexes….

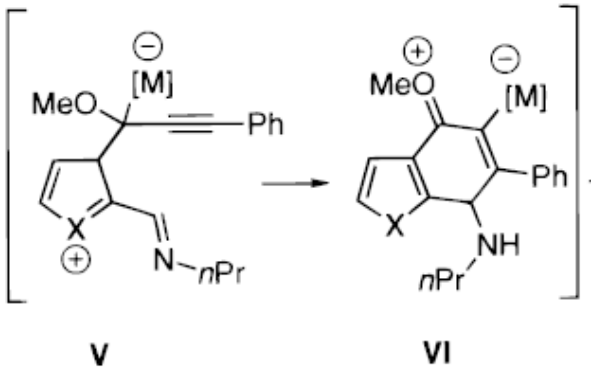
---Jose Barluenga/Universidad de oviedo

…**Surprisingly**, R-allyl *â*-phenyl propionate **6a** was obtained in 75% yield without formation of *â*-allyl *â*-phenyl propionate….

---Motokazu Uemura/Osaka Prefecture University

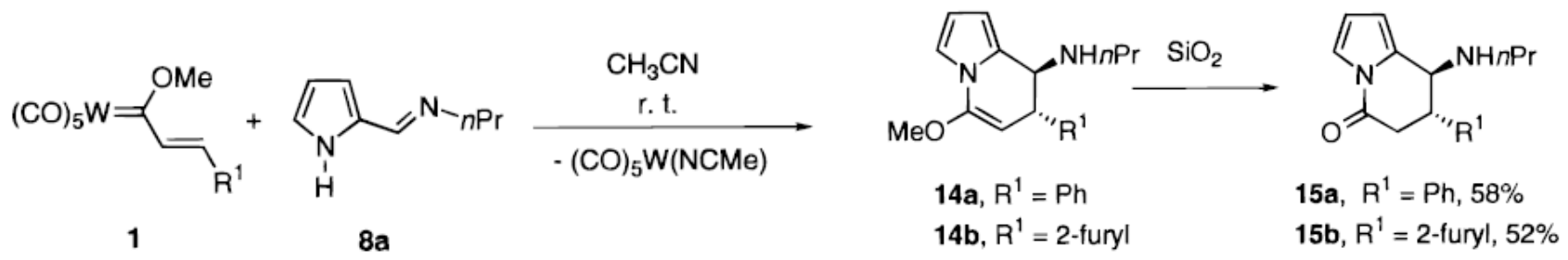
[3+3] Carbocyclization through [1,2]M(CO)$_5$ shift

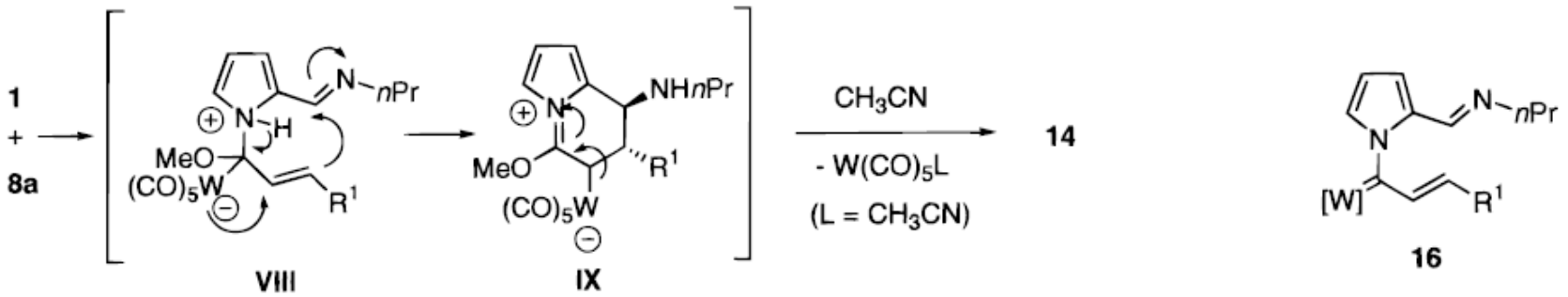




Barluenga, J.; Tomas, M. et. *J. Am. Chem. Soc.* **1999,** 121, 3065

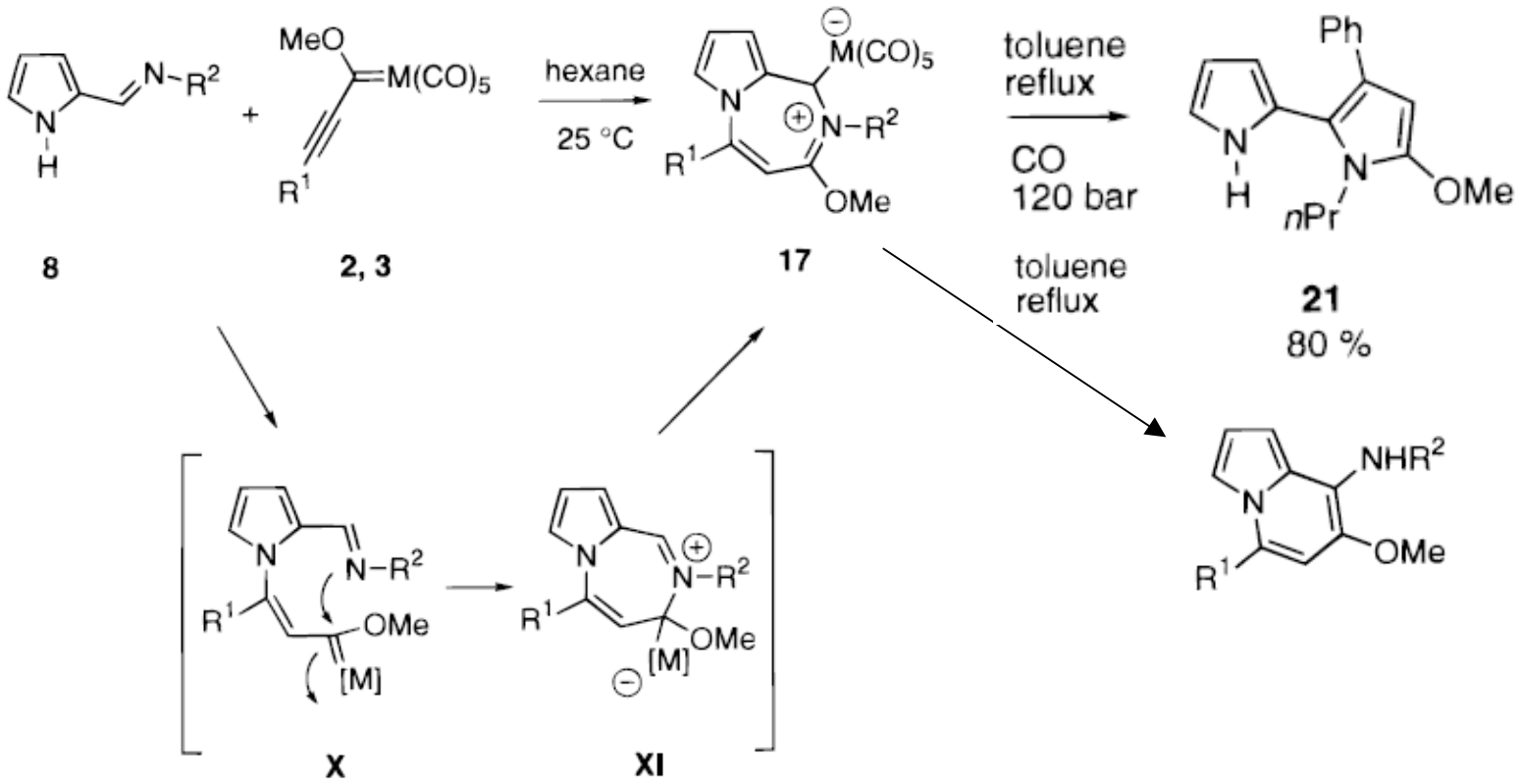
[3+3] Heterocyclization through [1,2]M(CO)$_5$ shift





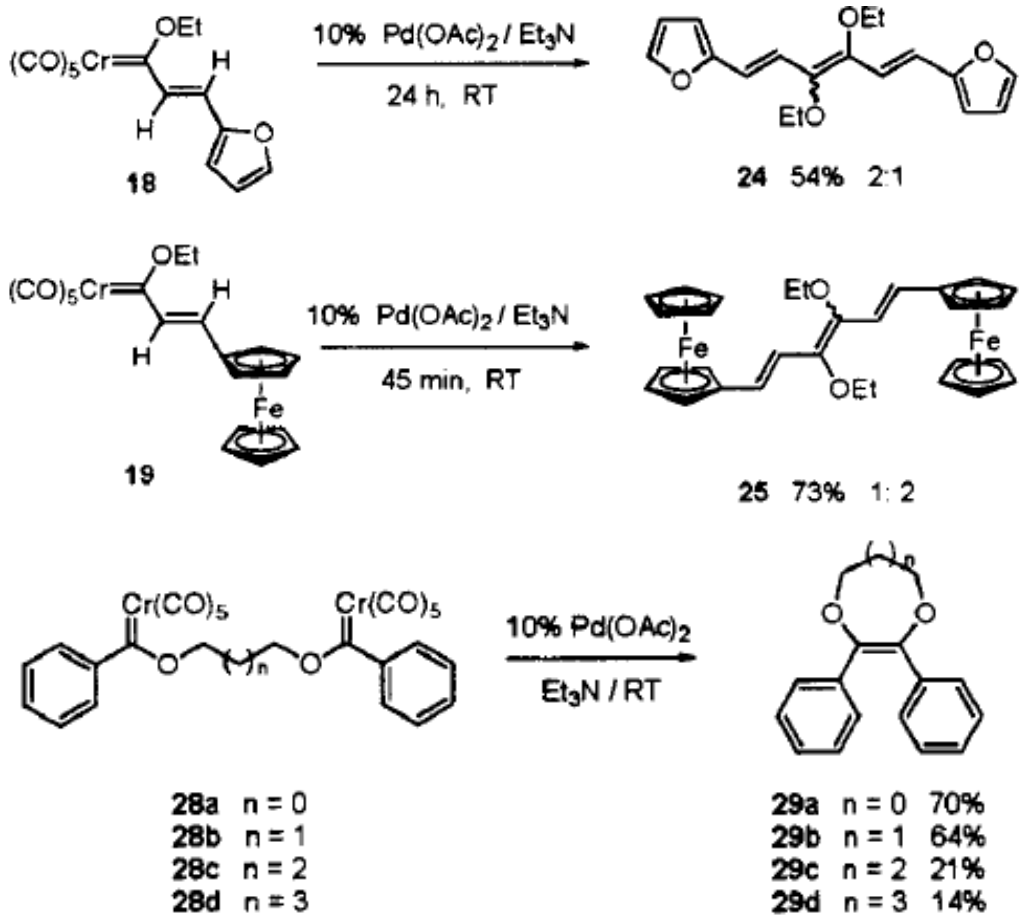
Barluenga, J.; Tomas, M. et. *J. Am. Chem. Soc.* **1999,** 121, 3065

[4+3] Heterocyclization through [1,3]$M(CO)_5$ shift



Barluenga, J.; Tomas, M. et. *J. Am. Chem. Soc.* **1999,** 121, 3065

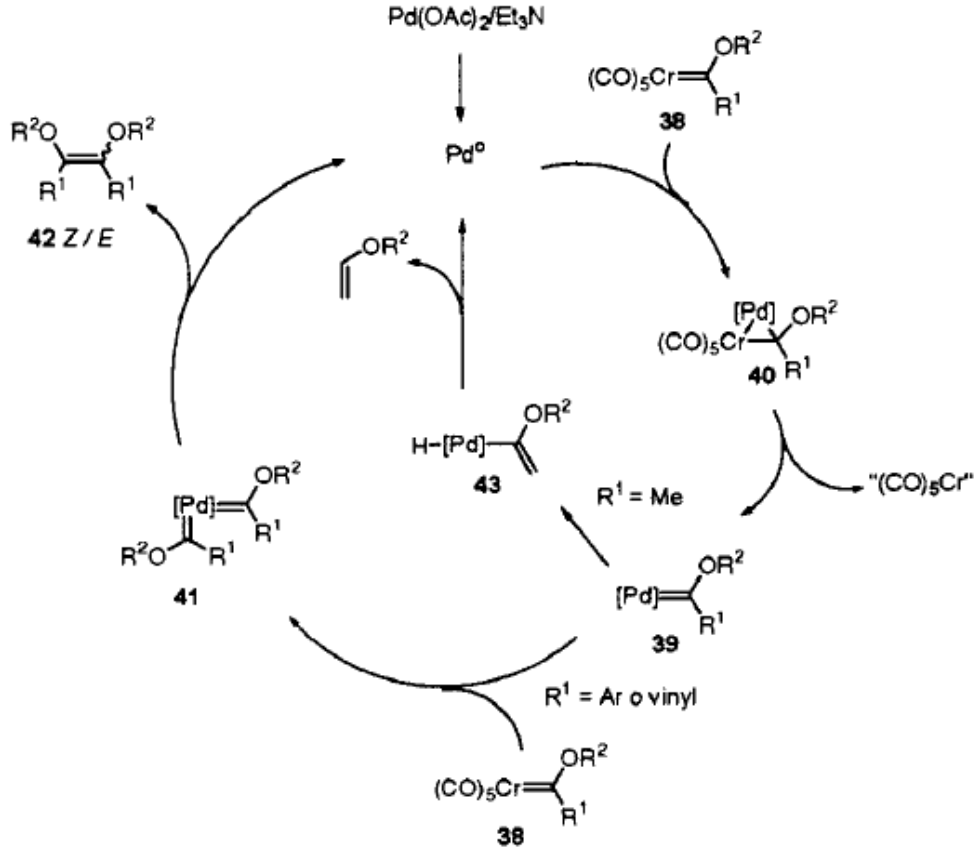
IntermolecularCarben Transfer



Sierra, M. A.; Del Amo, J. C.; Mancheno, M. J.; Gomez, M. *J. Am. Chem. Soc.,* **2001**, 123, 851-861

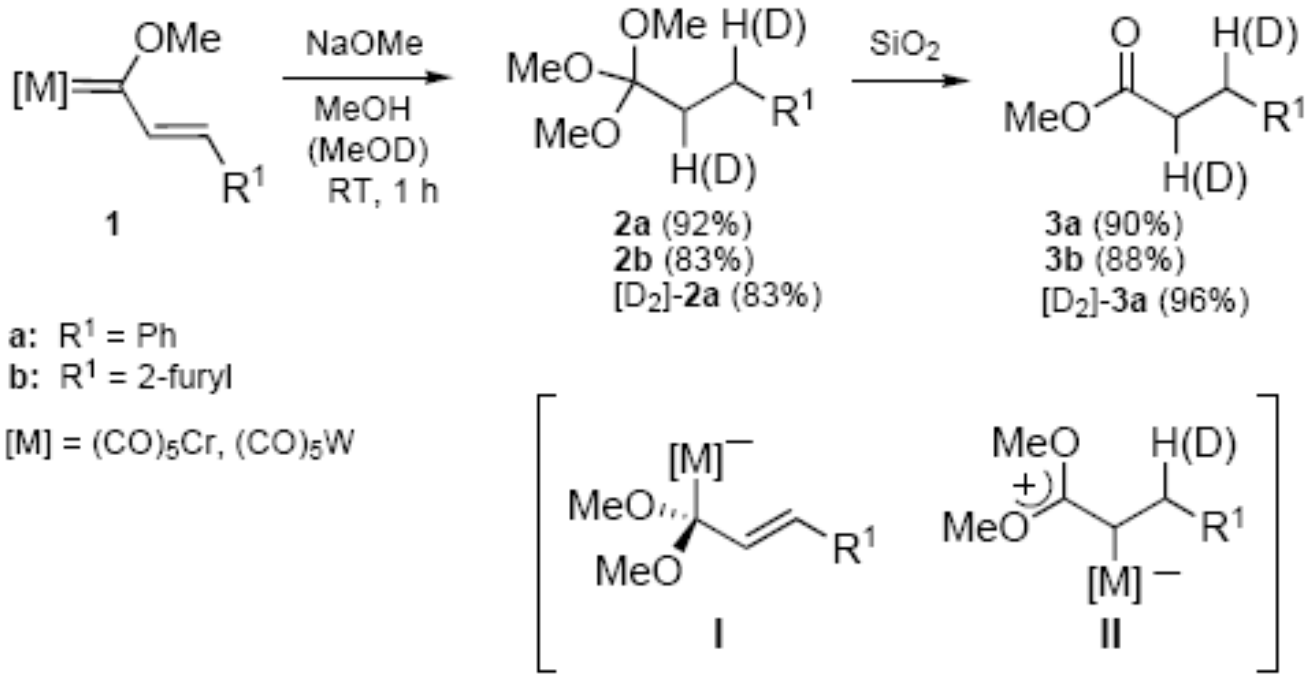
Proposed Mechanism for Intermolecular Carben Transfer

Scheme 8



Sierra, M. A.; Del Amo, J. C.; Mancheno, M. J.; Gomez, M. *J. Am. Chem. Soc.,* **2001**, 123, 851-861

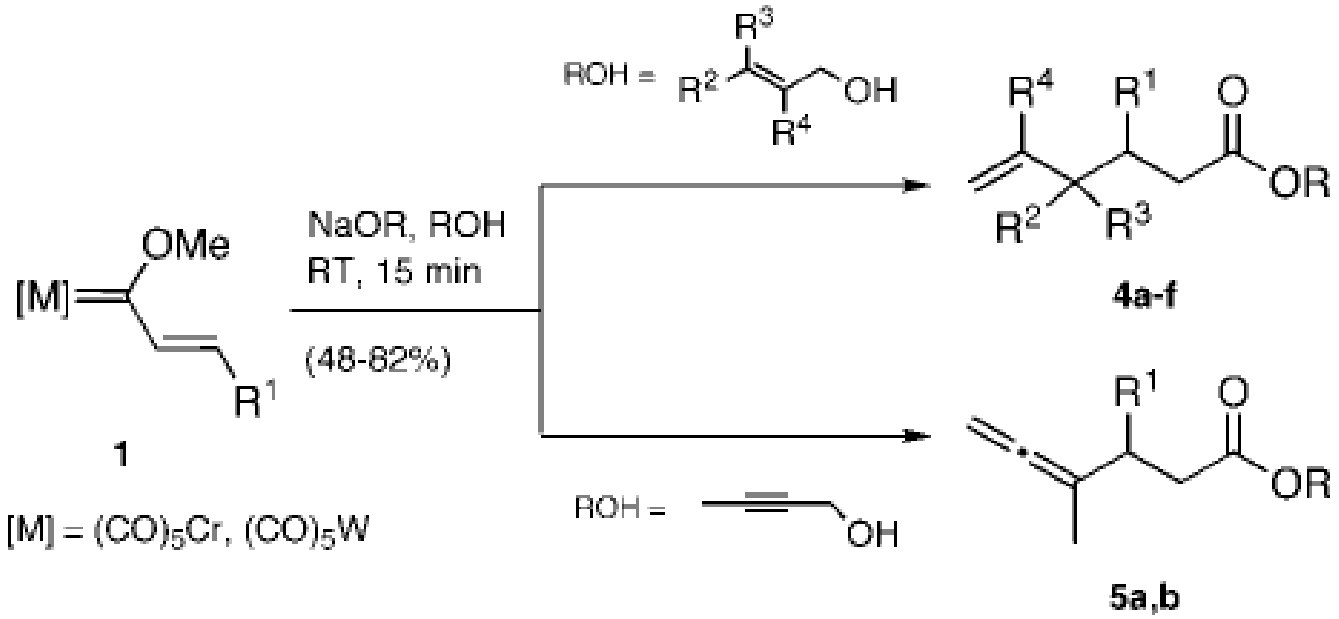
Reaction of CH_3ONa/CH_3OH with Fischer Carbene complex



Scheme 1. Reaction of sodium methoxide/methanol with Fischer alkenyl-carbene complexes. Formation of saturated orthoesters **2** and their hydrolysis products **3**.

Barluenga,J.; Rubio, E.; Lopez, J. A.; Tomas, M. *Angew. Chem. Int. Ed*. **1999**, 38(8), 1091

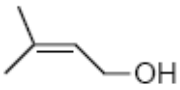
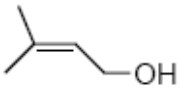
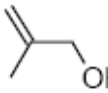
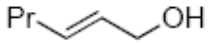
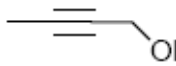
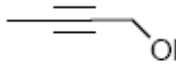
Reaction of allyl and propargyl alcohol with Fischer Carbene



Scheme 2. Reaction of allyl and propargyl alcohols with Fischer alkenyl-carbene complexes.

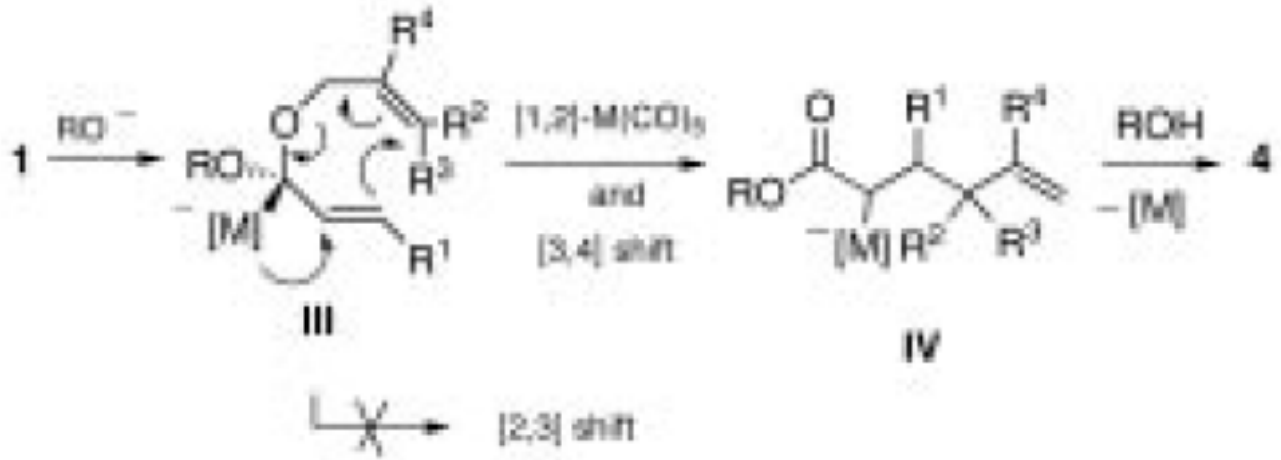
Reaction of allyl and propargyl alcohol with Fischer Carbene

Table 1. Reaction of carbene complexes with allylic and propargylic alcohols.

Entry	ROH	R^1	R^2	R^3	R^4	Product	Yield [%][a]
1		Ph	H	H	H	**4a**	82
2		2-Furyl	H	H	H	**4b**	76
3		Ph	Me	Me	H	**4c**	48
4		2-Furyl	Me	Me	H	**4d**	55
5		Ph	H	H	Me	**4e**	50
6		2-Furyl	Pr	H	H	**4f**[b]	71
7		Ph	–	–	–	**5a**	62
8		2-Furyl	–	–	–	**5b**	58

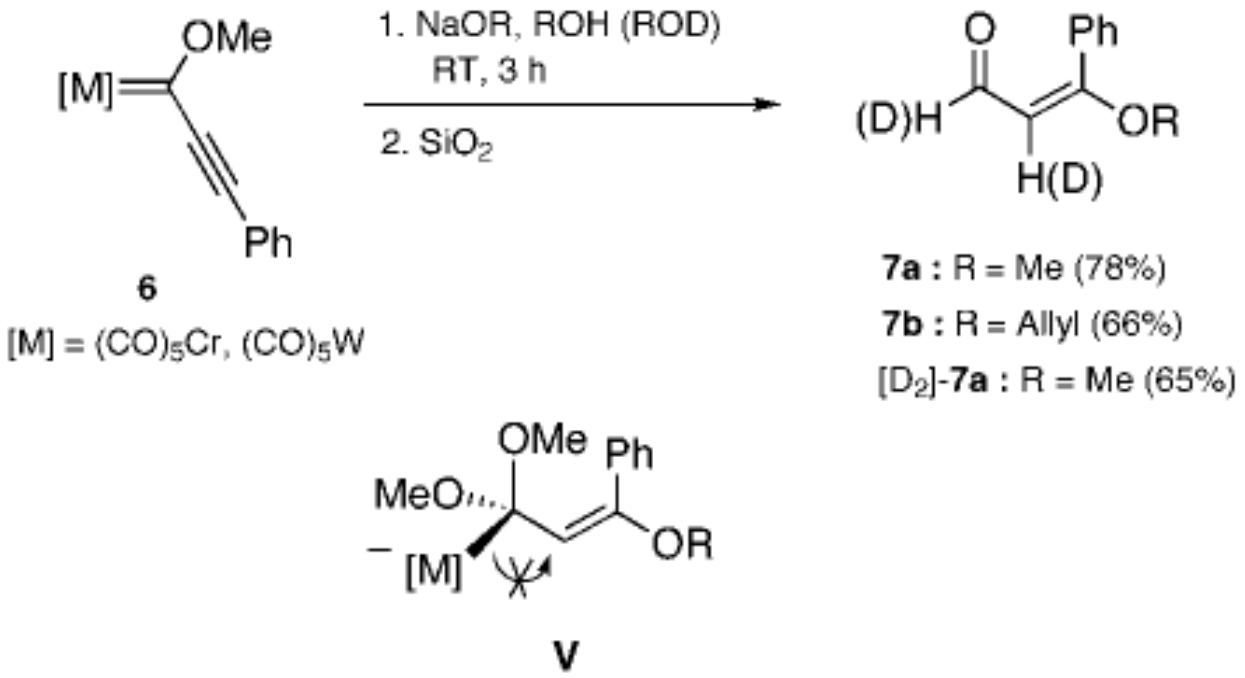
[a] Nonoptimized yields of purified isolated products. All yields refer to reactions with tungsten complexes. [b] Isolated as a 3:2 mixture of diastereoisomers.

Proposed mechanism



Scheme 3. Mechanism proposed for the rearrangement observed in the formation of **4**.

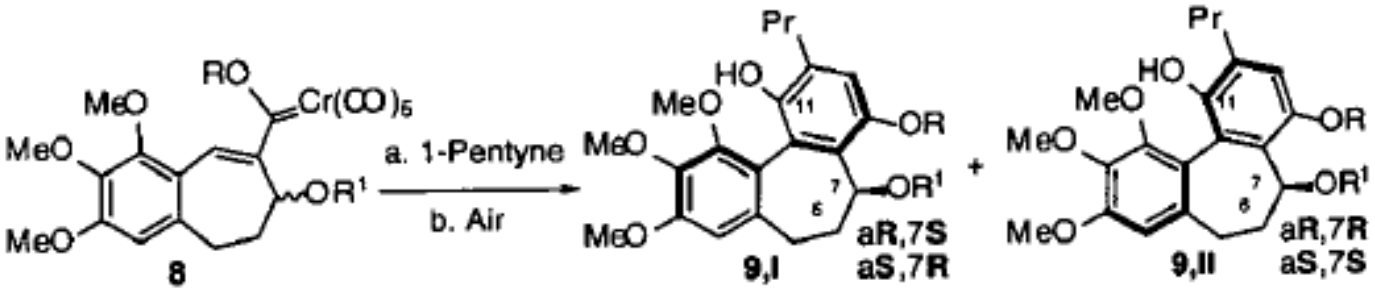
Support for the Reaction Pathway



Scheme 4. Reaction of alcohols with Fischer alkynylcarbene complexes.

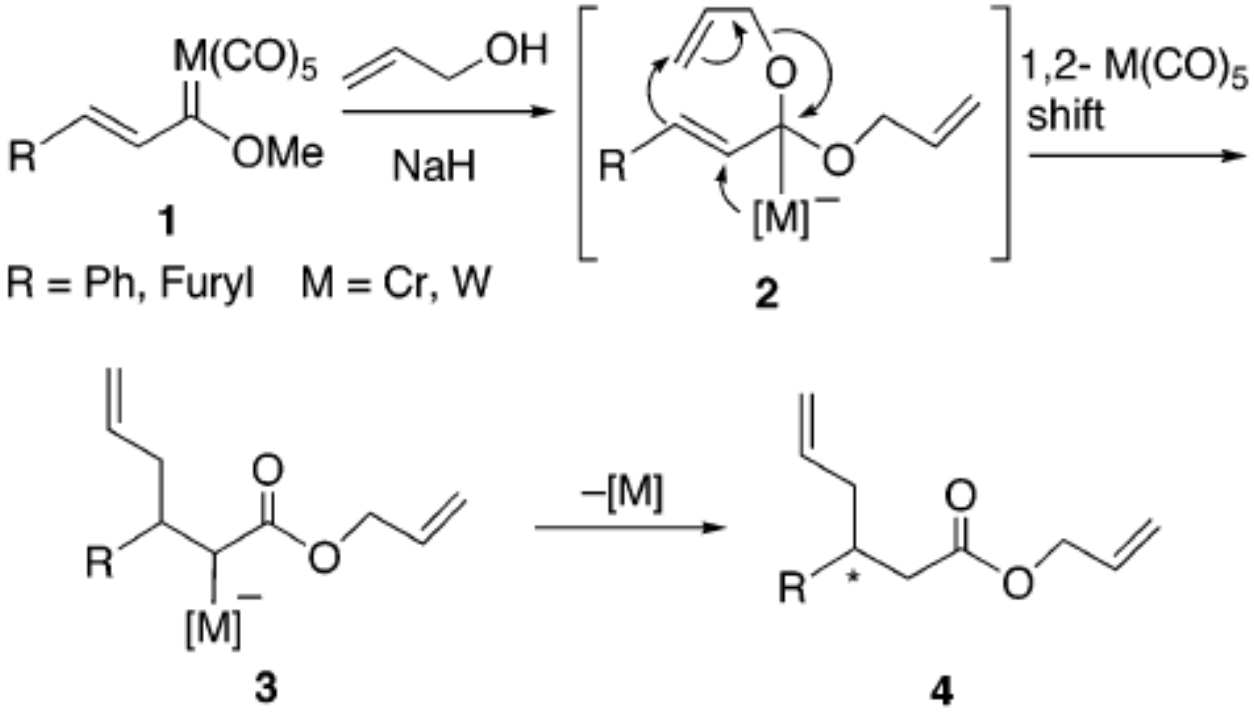
Chiral alpha,beta-unsaturated Fischercarbene complex

Table 2. Atropisomer-Selective Benzannulation of Carbene Complexes **8** with 1-Pentyne[a]



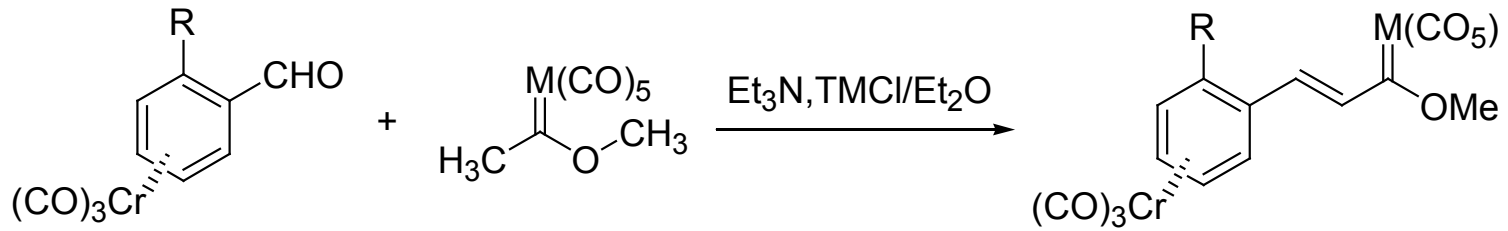
Vorogushin, A. V.; Wulff, W. D.; Hansen, H.-J. *J. Am. Chem. Soc*. **2002**, *124*, 6512-6513**.**

Scheme 1. [3,4]-Sigmatropic Rearrangement Promoted by [1,2]-Metal Shift Reported by Barluenga[4]



Barluenga,J.; Rubio, E.; Lopez, J. A.; Tomas, M. *Angew. Chem. Int. Ed*. **1999**, 38(8), 1091

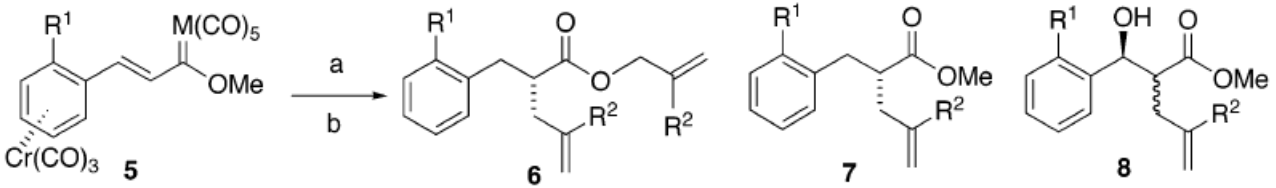
Preparation of binuclear unsaturated Fischer carbene complex



Kamikawa, K.; Uchida, K.; Furusho, M.; Uemura, M. et. *Org. Lett*. **2004**, 6(23), 4307

Reactions homobinuclear carbenecomplexes with allylic alcohols

Table 1. Reaction of Binuclear Carbene Complexes **5** with Allyl Alcohols[a]



5a; R^1 = H, M = Cr
5b; R^1 = OMe, M = Cr
5c; R^1 =Me, M = Cr
5d; R^1 = OPr-*i*, M = Cr

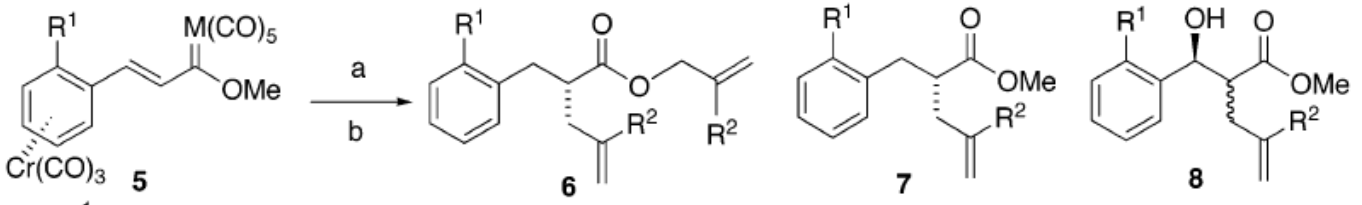
Alphabetical numbering for compounds **6**, **7** and **8** is as follows;
a: $R^1 = R^2 = H$; b: R^1 = OMe, R^2 = H; c: R^1 = OMe, R^2 = Me; d: R^1 = Me, R^2 = H; e: R^1 = O^{i}Pr, R^2 = H

entry	complex	temp (°C)	yield of **6** (%)	yield of **7** (%)	yield of **8** (%)	% ee[b] of **6** or **7**	anti/syn ratio[c] of **8**
1	**5a**	25	75				
2	**5b**	25	68			95	
3	**5b**	0		40	40	97	78/22
4	**5b**	25	85			72	
5	**5b**	0			45		83/17
6	**5c**	25	83			77	
7	**5c**	0		55	40	93	83/17
8	**5c**	−30		33	30	97	80/20
9	**5d**	0		10	51		85/15

[a] Reagents and conditions: (a) $CH_2{=}C(R^2)CH_2OH$, NaH, THF, under inert gas in a balloon; (b) $h\nu$−air, ether. [b] Determined by chiral HPLC (see Supporting Information for details). [c] Determined by integration of representative signals by ^{1}H NMR of the crude product.

Reactions heterobinuclear carbene complexes with allylic alcohols

Table 1. Reaction of Binuclear Carbene Complexes **5** with Allyl Alcohols[a]



5e; R^1 = H, M = W
5f; R^1 = OMe, M = W
5g; R^1 = Me, M = W
5h; R^1 = OPr-*i*, M = W

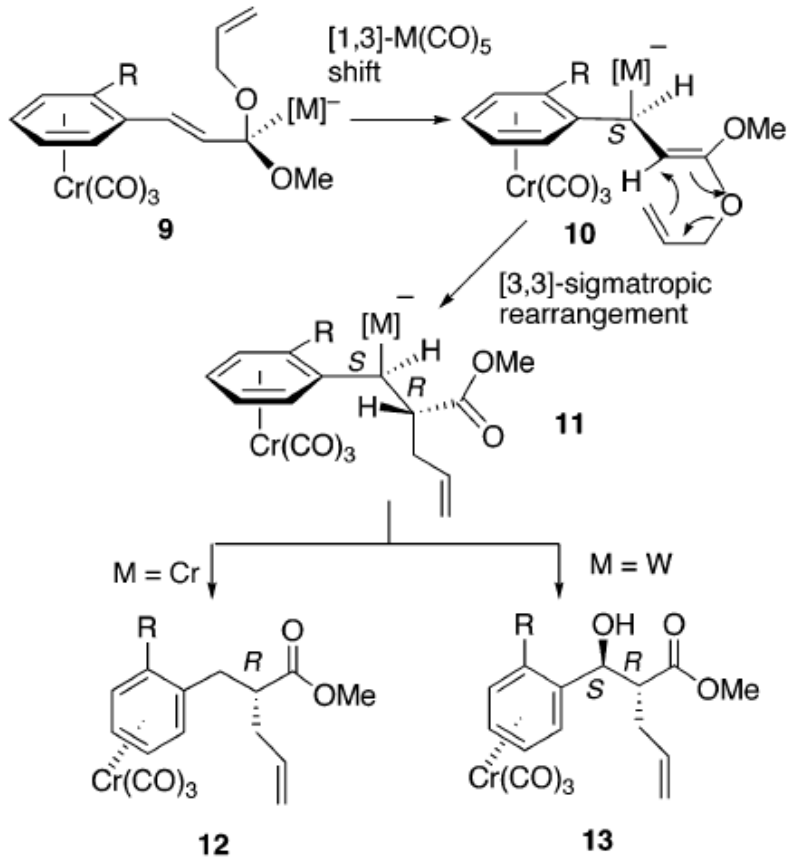
Alphabetical numbering for compounds **6**, **7** and **8** is as follows;
a: $R^1 = R^2$ = H; b: R^1 = OMe, R^2 = H; c: R^1 = OMe, R^2 = Me; d: R^1 = Me, R^2 = H; e: R^1 = O^{i}Pr, R^2 = H

entry	complex	temp (°C)	yield of **6** (%)	yield of **7** (%)	yield of **8** (%)	% ee[b] of **6** or **7**	anti/syn ratio[c] of **8**
10	**5e**	25		10	71		63/37
11	**5e**	−30			75		92/8
12	**5f**	−30			65		92/8
13	**5g**	−30			70		92/8
14	**5h**	−30			31		75/25

[a] Reagents and conditions: (a) CH_2=C(R^2)CH_2OH, NaH, THF, under inert gas in a balloon; (b) *hν*−air, ether. [b] Determined by chiral HPLC (see Supporting Information for details). [c] Determined by integration of representative signals by ^{1}H NMR of the crude product.

Proposed mechanism

Scheme 2. Proposed Mechanism



Conclusions

1. Stereoselective [3,3]-sigmatropic rearrangement of chiral binuclear R,*â*-unsaturated Fischer carbene complexes coulded be promoted by a 1,3-metal shift.
2. Reaction of chiral homobinuclear Fischer carbene complexes with allyl alcohol in the presence of base gave R-allyl esters in up to 97% ee.
3. Hheterobinuclear carbene complexes afforded *anti*-aldol-type products, R-allyl-*â*-hydroxy esters, in up to 92/8 dr.