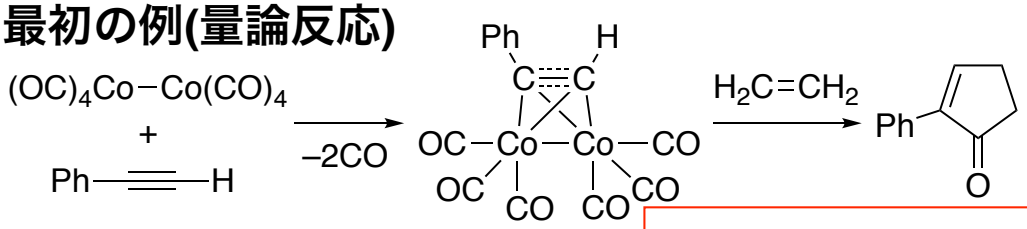
触媒的環化反応

2021年度
有機金属化学第10回

Pauson-Khand反応 ([2+2+1]付加環化反応)

最初の例(量論反応)



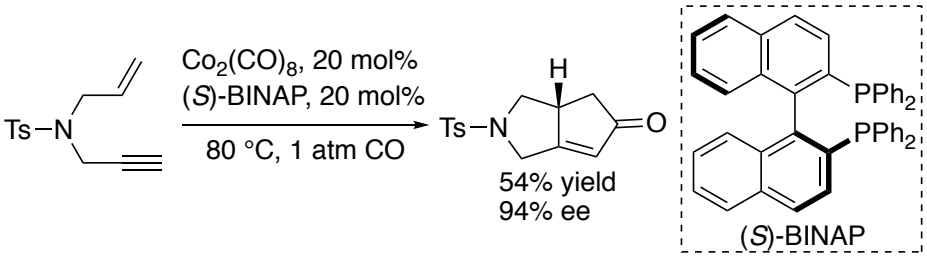
Pauson, P. L.; Khand, I. U., *Ann. N. Y. Acad. Sci.* **1977,** *295*, 2-14.

初期の触媒反応の例

Khand, I. U.; Knox, G. R.; Pauson, P. L.; Watts, W. E.
Foreman, M. I., *J. Chem. Soc., Perkin Trans. 1* **1973**, 977-981.

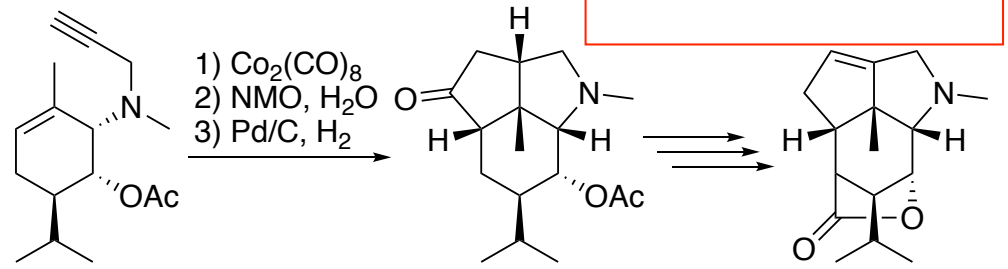
Rautenstrauch, V.; Mégard, P.; Conesa, J.; Küster, W.
Angew. Chem. Int. Ed. Engl. **1990,** *29*, 1413-1416.

ホスフィン添加で効率向上＆不斉化



Hiroi, K.; Watanabe, T.; Kawagishi, R.; Abe, I.
Tetrahedron Asym. **2000,** *11*, 797-808.

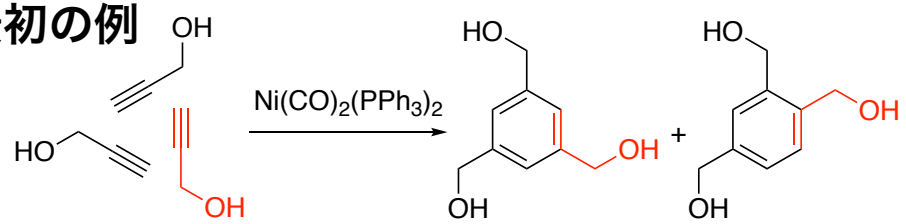
アルカロイド合成への応用



Cassayre, J.; Zard, S. Z., *J. Am. Chem. Soc.* **1999,** *121*, 6072-6073.

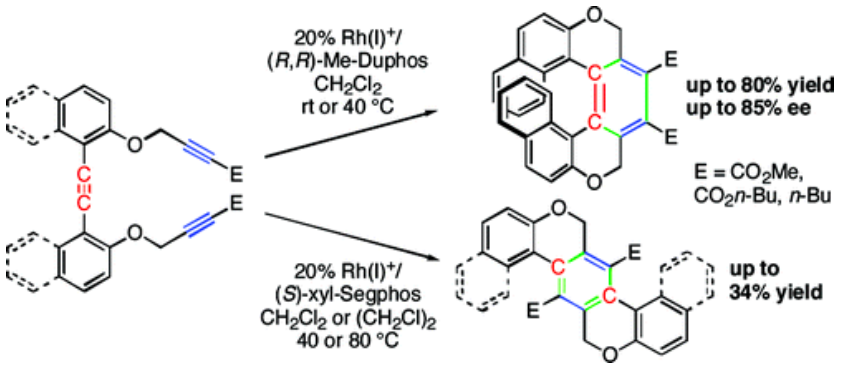
アルキン三量化反応 ([2+2+2]付加環化反応)

最初の例



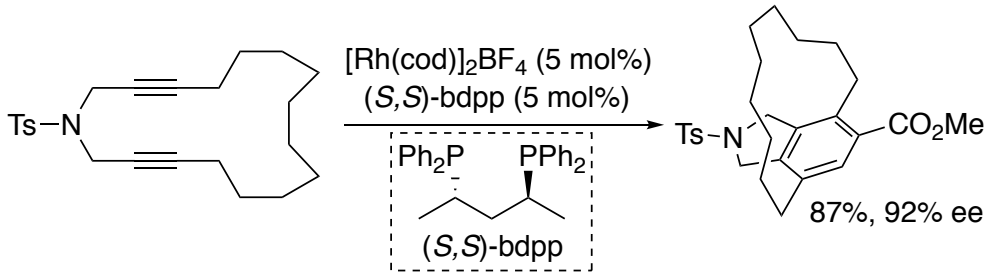
Reppe, W.; Schwecknediek, W. J.
Justus Liebigs Ann. Chem. **1948,** *560*, 104-116.

ヘリセン合成への応用



Tanaka, K.; Kamisawa, A.; Suda, T.; Noguchi, K.; Hirano, M.
J. Am. Chem. Soc. **2007,** *129*, 12078-12079.

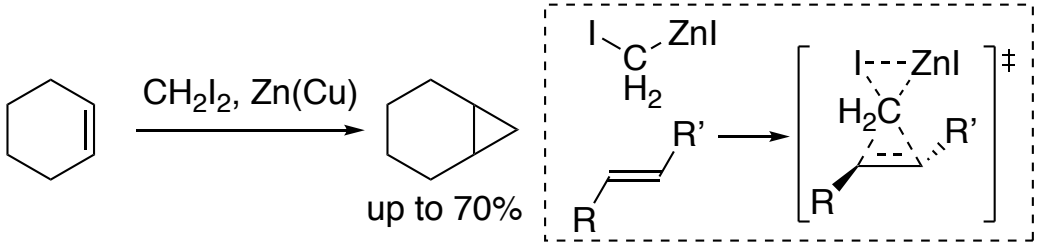
軸不斉シクロファン合成への応用



Araki, T.; Noguchi, K.; Tanaka, K.
Angew. Chem. Int. Ed. **2013,** *52*, 5617-5621.

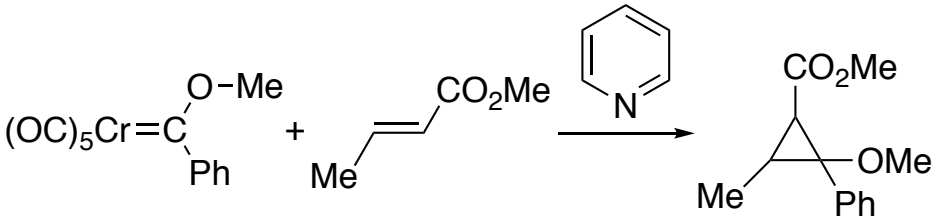
カルベン錯体の反応

最初の報告



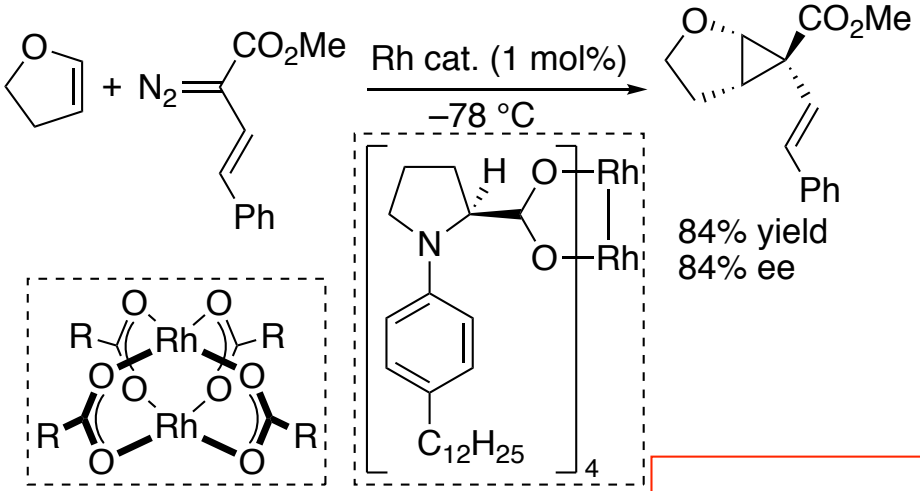
Simmons, H. E.; Smith, R. D., *J. Am. Chem. Soc.* **1958,** *80*, 5323-5324.

有機金属錯体を用いる最初の報告



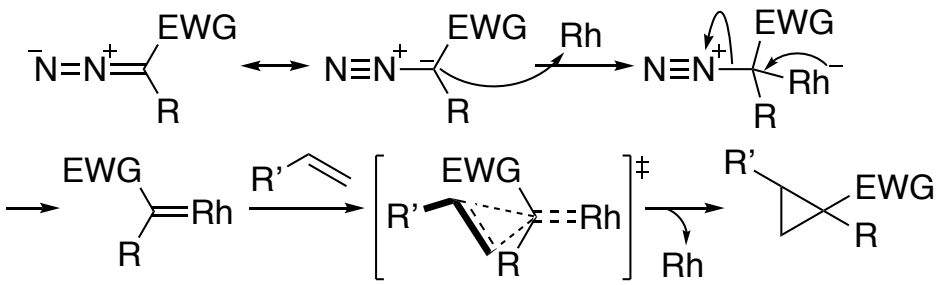
Fischer, E. O.; Dötz, K. H., *Chem. Ber.* **1970,** *103*, 1273-1278.

触媒的不斉シクロプロパン化



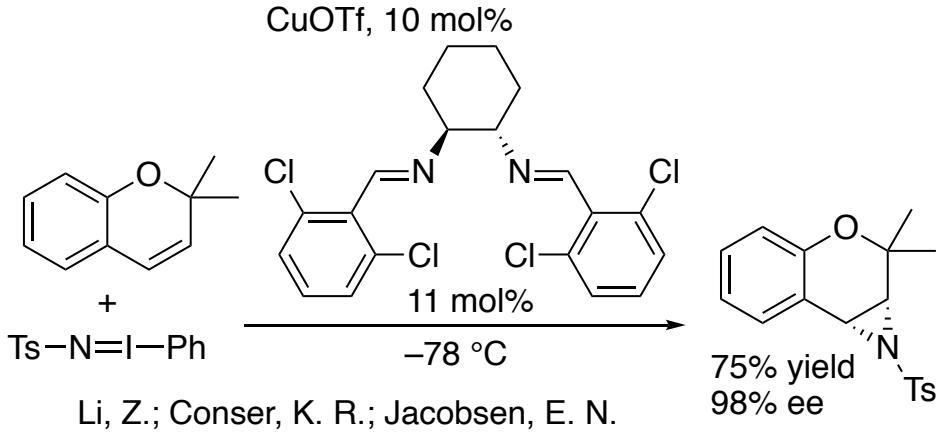
Davies, H. M. L.; Bruzinski, P. R.; Lake, D. H.; Kong, N.;
Fall, M. J., *J. Am. Chem. Soc.* **1996,** *118*, 6897-6907.

Rh触媒シクロプロパン化の反応機構



Nowlan, D. T.; Gregg, T. M.; Davies, H. M. L.; Singleton, D. A.
J. Am. Chem. Soc. **2003,** *125*, 15902-15911.

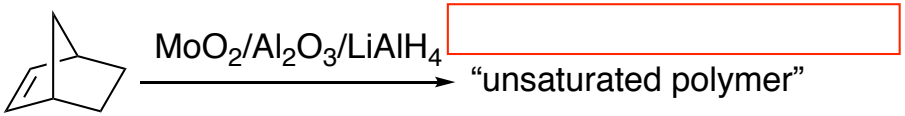
nitrene transferによる触媒的アジリジン化

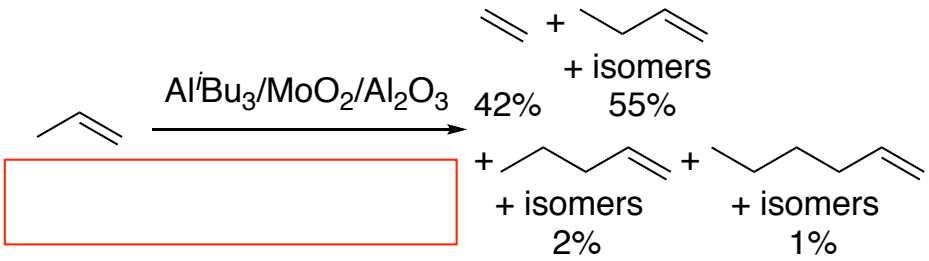


Li, Z.; Conser, K. R.; Jacobsen, E. N.
J. Am. Chem. Soc. **1993,** *115*, 5326-5327.

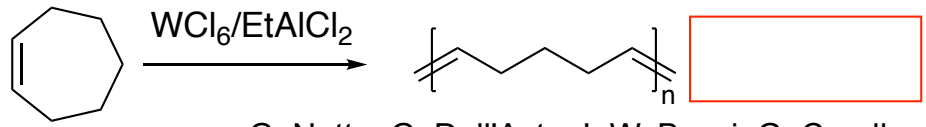
カルベン錯体の反応：オレフィンメタセシス

最初の報告



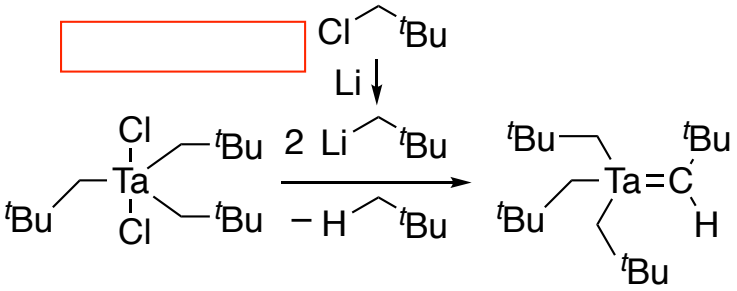


H.S. Eleuterio , Ger. Pat. **1960,** 1072811.
Banks, R. L.; Bailey, G. C.
Ind. Eng. Chem. Prod. Res. Dev. **1964,** *3*, 170-173.



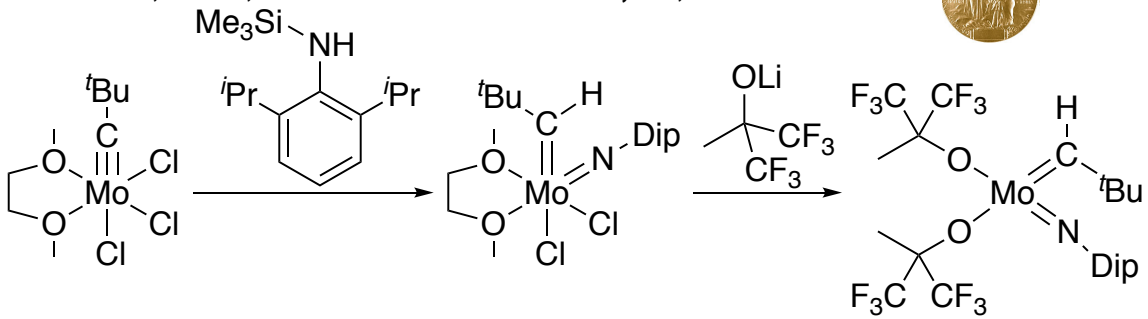
G. Natta, G. Dall'Asta, I. W. Bassi, G. Carella,
Makromol. Chem., **1966,** *91,* 87-106.

構造の明確なアルキリデン錯体の合成



Richard Schrock
Nobel Prize 2005

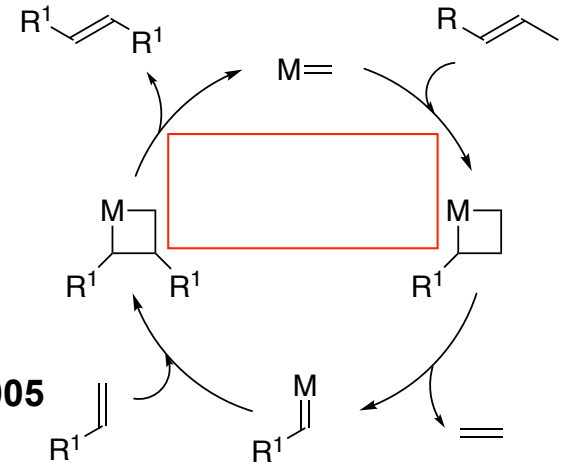
Schrock, R. R., *J. Am. Chem. Soc.* **1974,** *96*, 6796-6797.



Murdzek, J. S.; Schrock, R. R., *Organometallics* **1987,** *6*, 1373-1374.

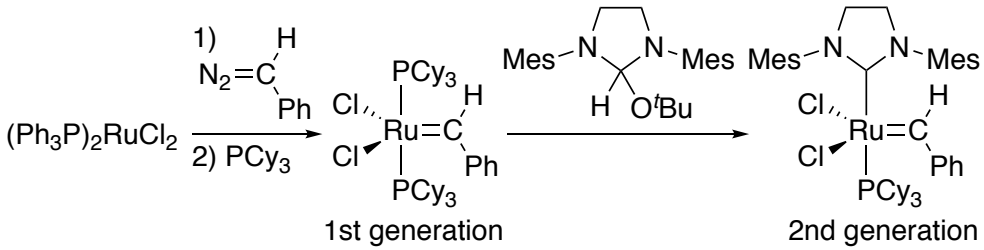
反応機構

Yves Chauvin
Nobel Prize 2005



P. J. L. Hérisson, Y. Chauvin, *Makromol. Chem.*, **1971,** *141,* 161-176.
J.-P. Soufflet, D. Commereuc, Y. Chauvin, *C. R. Hebd. Seances Acad. Sci. Série C*, **1973,** *276,* 169-171.

官能基許容性の高いRu錯体



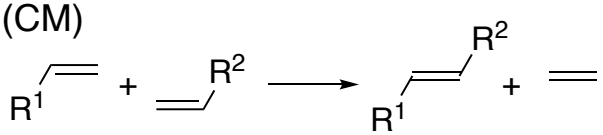
Robert Grubbs
Nobel Prize 2005

Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H.
Angew. Chem. Int. Ed. Engl. **1995,** *34*, 2039-2041.
Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H.
Org. Lett. **1999,** *1*, 953-956.

カルベン錯体の反応：オレフィンメタセシスの応用

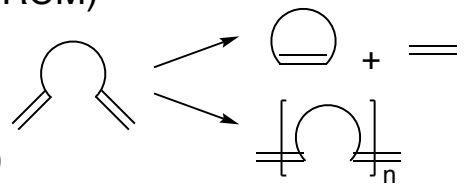
反応形式の分類

cross metathesis (CM)

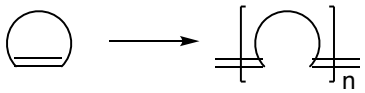


ring-closing metathesis (RCM)

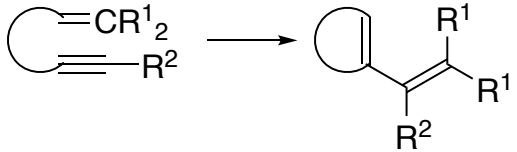
acyclic diene metathesis polymerization (ADMET)



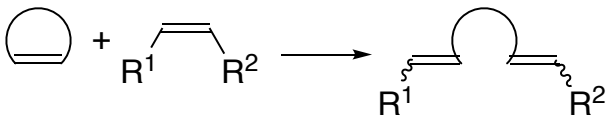
ring-opening metathesis polymerization (ROMP)



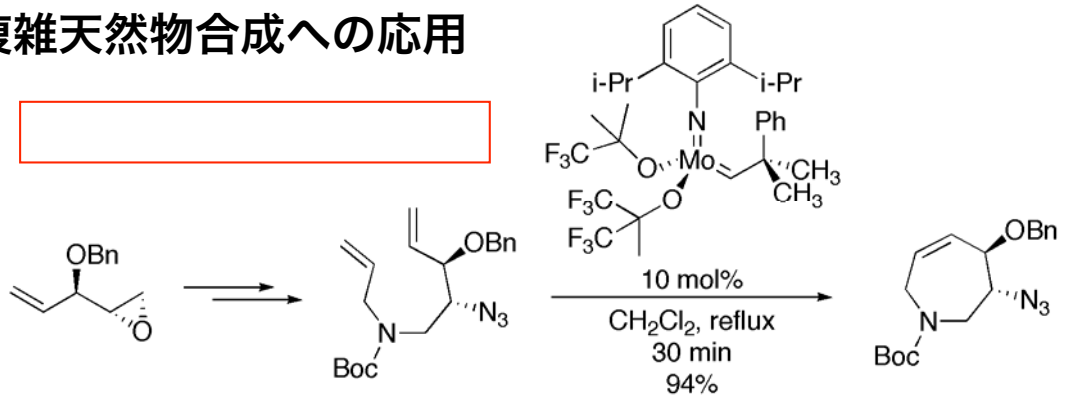
eneyne metathesis (EYM)



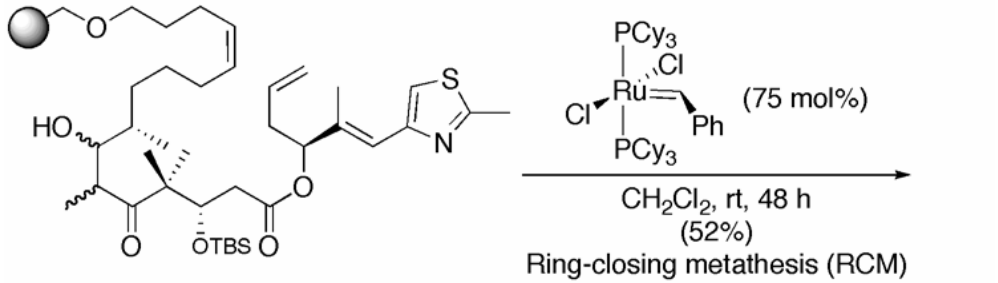
ring-opening cross metathsis (ROCM)

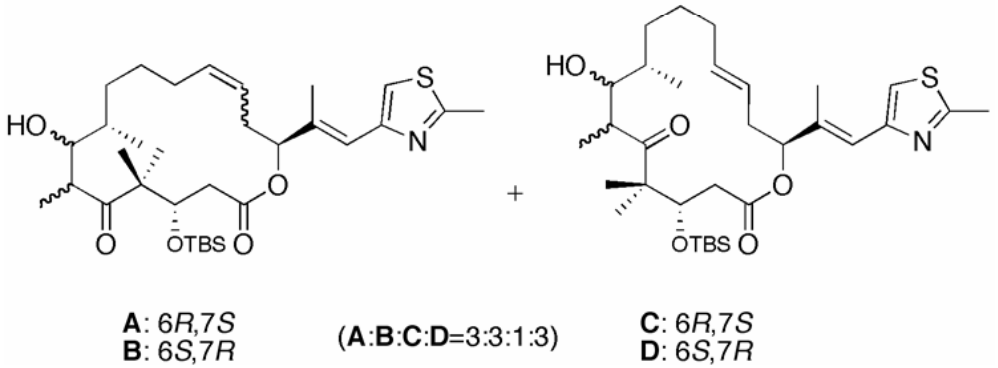


複雑天然物合成への応用



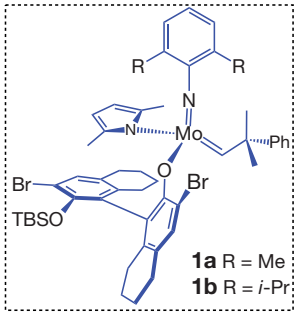
Fürstner, A.; Thiel, O. R., *J. Org. Chem.* **2000,** *65*, 1738-1742.

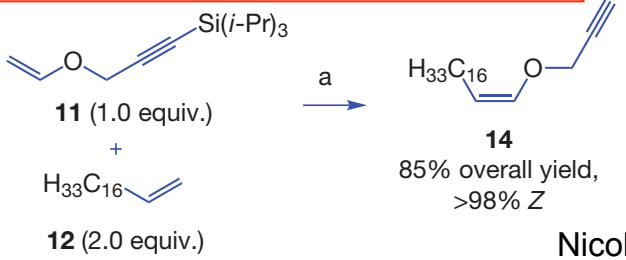




Nicolaou, K. C.; Winssinger, N.; Pastor, J.; Ninkovic, S.; Sarabia, F.; He, Y.; Vourloumis, D.; Yang, Z.; Li, T.; Giannakakou, P.; Hamel, E., *Nature* **1997,** *387*, 268.

Z-選択的クロスメタセシス



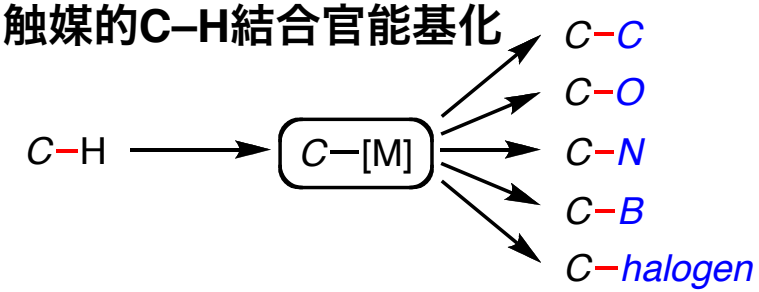


Meek, S. J.; O'Brien, R. V.; Llaveria, J.; Schrock, R. R.; Hoveyda, A. H., *Nature* **2011,** *471*, 461.

触媒的C–H結合官能基化

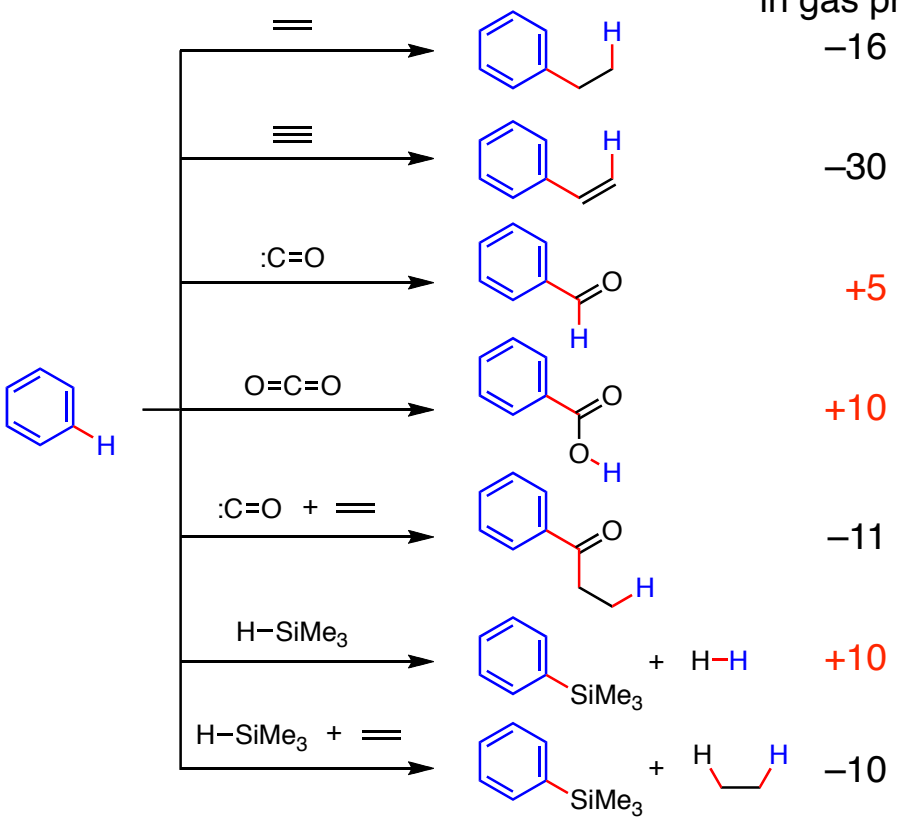
thanks to prof. Nakao@Kyoto

触媒的C–H結合官能基化



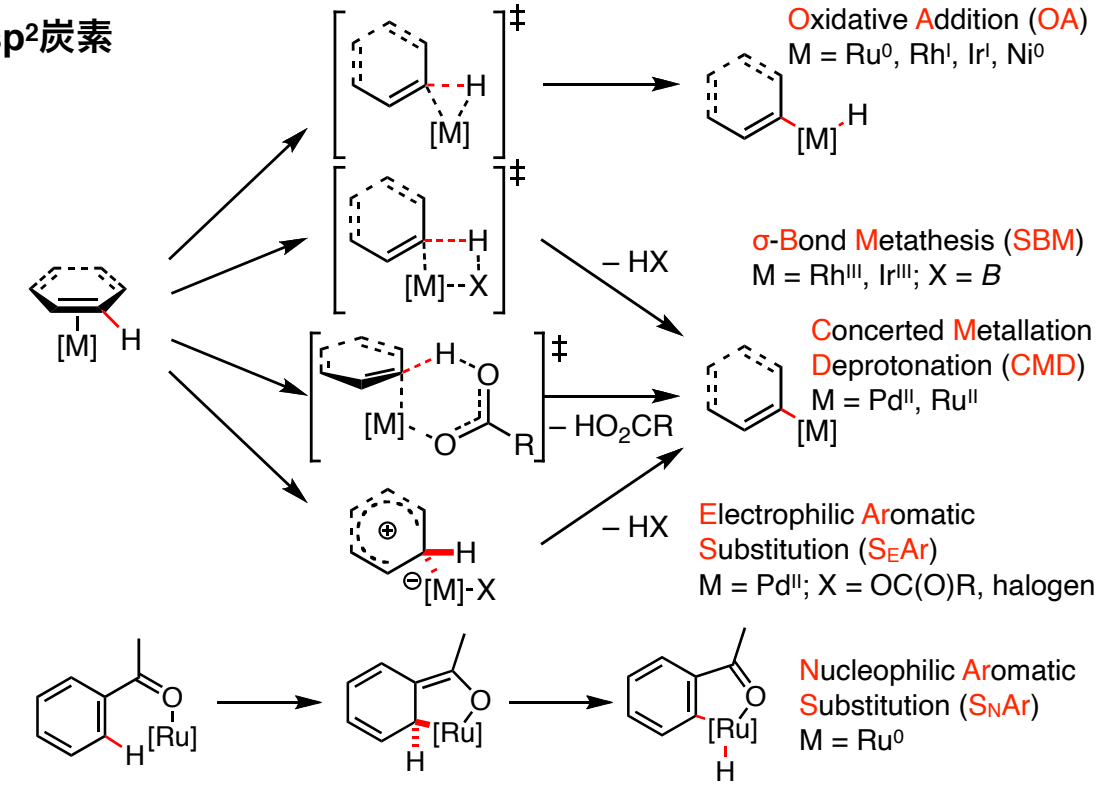
C–H 結合の活性化段階に金属 (M) が関与し,
C–M 結合を有する中間体を経由して進行する触媒反応.

C–H結合官能基化の熱力学

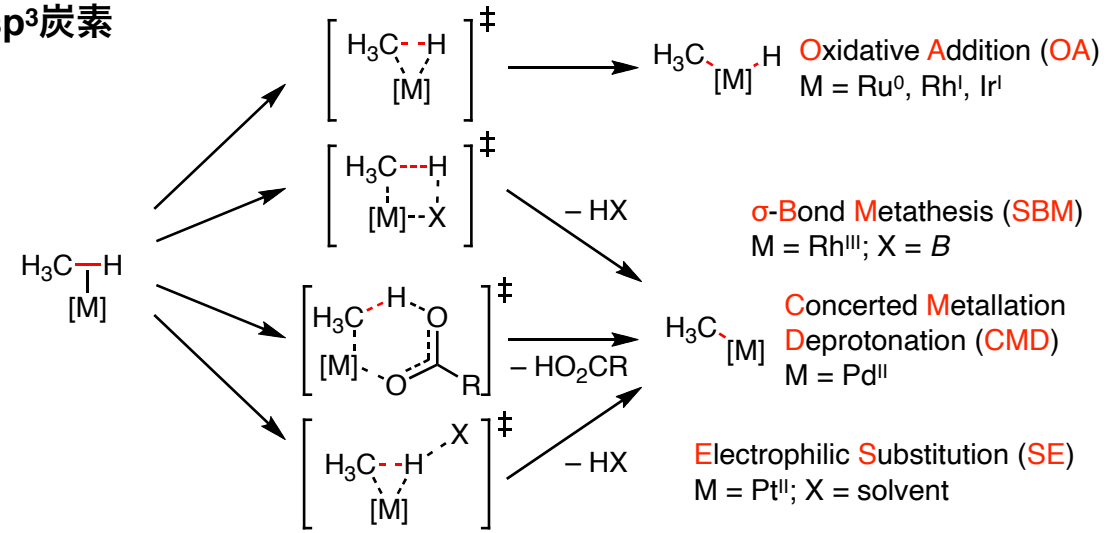


C–H結合切断メカニズム

sp²炭素



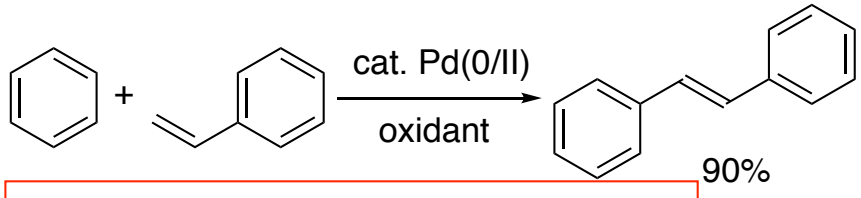
sp³炭素



触媒的C–H結合官能基化

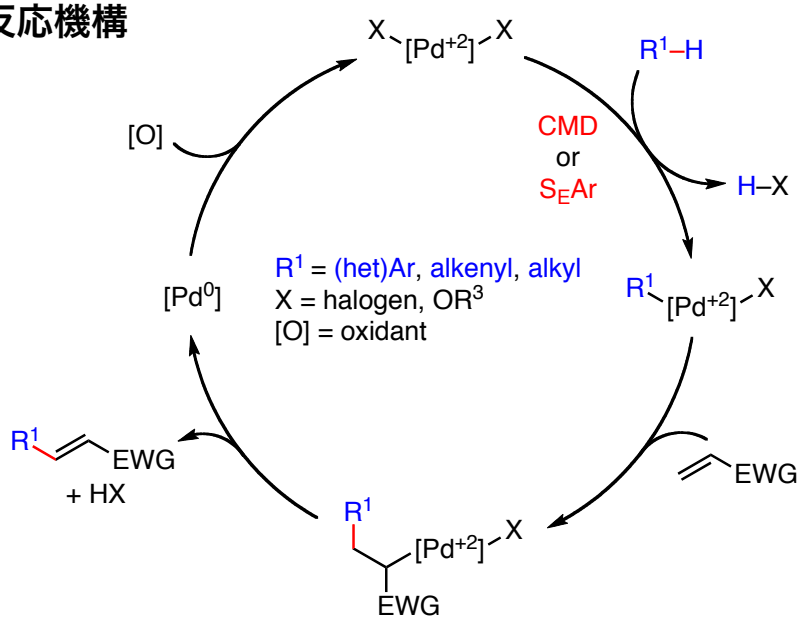
thanks to prof. Nakao@Kyoto

芳香族化合物の触媒的アルケニル化(S_EAr経由)

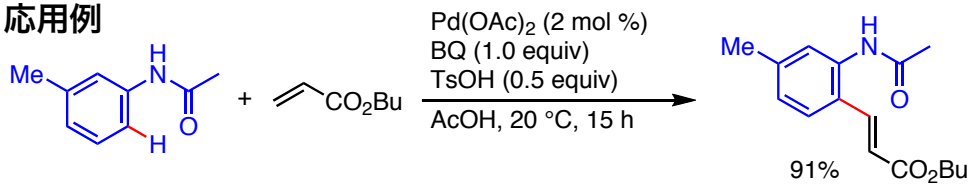


Fujiwara, Y.; Moritani, I.; Danno, S.; Asano, R.; Teranishi, S. *J. Am. Chem. Soc.* **1969,** *91*, 7166-7169.

反応機構

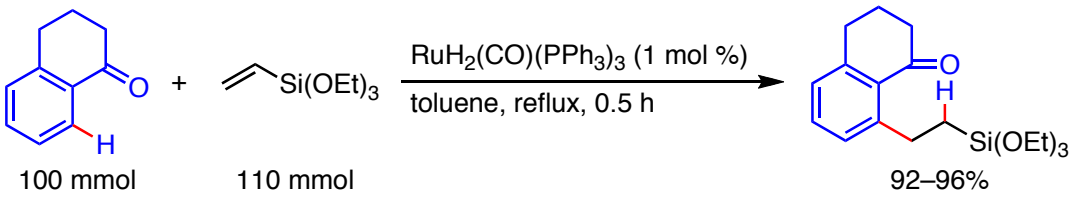


応用例



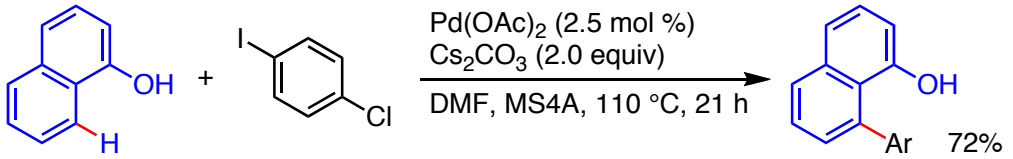
Boele, M. D. K.; van Strijdonck, G. P. F.; de Vries, A. H. M.; Kamer, P. C. J.; de Vries, J. G.; van Leeuwen, P. W. N. M., *J. Am. Chem. Soc.* **2002,** *124*, 1586-1587.

芳香族化合物の触媒的アルキル化(OA or S_NAr経由)



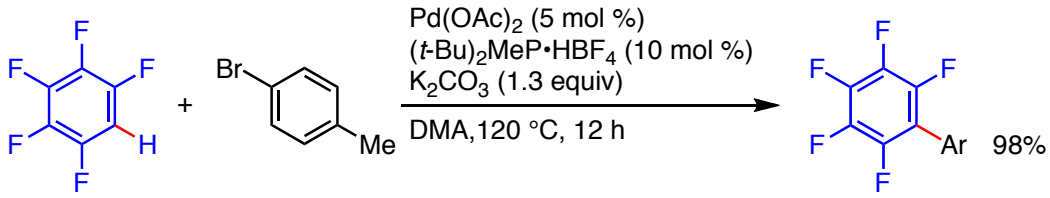
Murai, S.; Kakiuchi, F.; Sekine, S.; Tanaka, Y.; Kamatani, A.; Sonoda, M.; Chatani, N., *Nature* **1993,** *366*, 529-531.

求電子剤とのカップリング



Satoh, T.; Kawamura, Y.; Miura, M.; Nomura, M., *Angew. Chem. Int. Ed. Engl.* **1997,** *36*, 1740-1742.

Zaitsev, V. G.; Daugulis, O., *J. Am. Chem. Soc.* **2005,** *127*, 4156-4157.

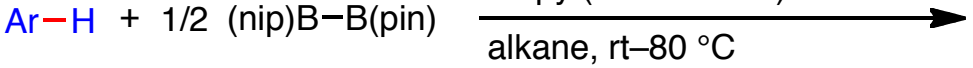


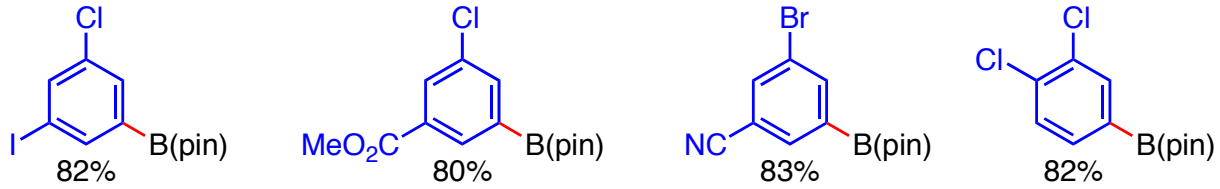
Lafrance, M.; Rowley, C. N.; Woo, T. K.; Fagnou, K., *J. Am. Chem. Soc.* **2006,** *128*, 8754-8756.

触媒的C–H結合官能基化

thanks to prof. Nakao@Kyoto

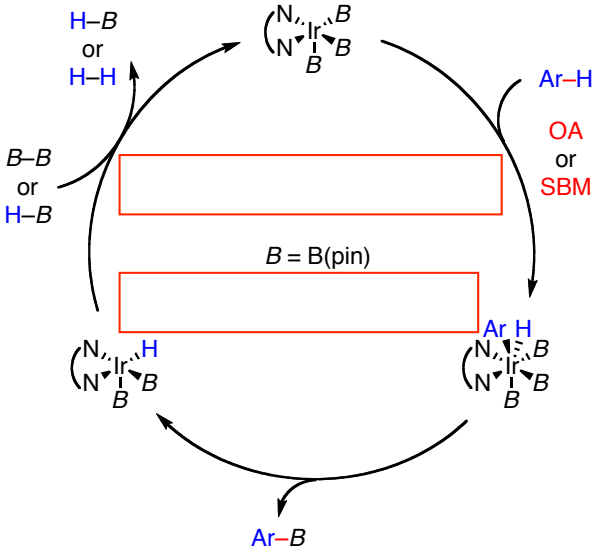
ベンゼン環C–Hホウ素化





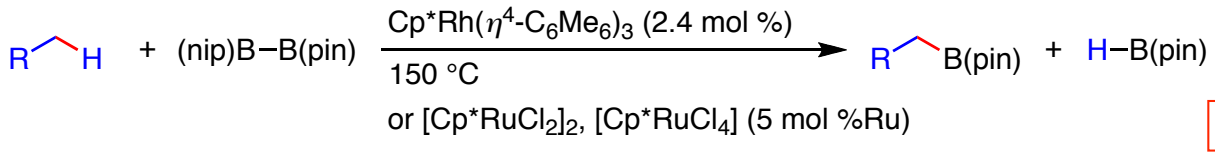
Ishiyama, Miyaura, Hartwig, et al. *Angew. Chem. Int. Ed.* **2002**, *41*, 3056;
Marder, et al. *Chem. Commun.* **2005**, 2172; Hartwig, et al. *J. Am. Chem. Soc.* **2008**, *130*, 7534.
Ishiyama, Miyaura, et al. *Chem. Commun.* **2010**, 159.

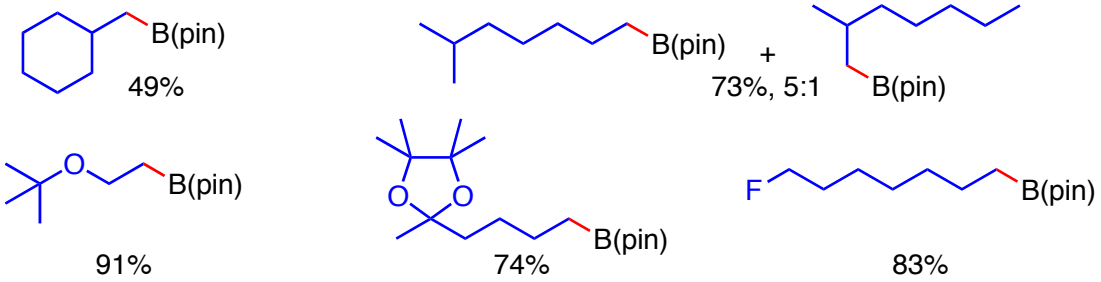
反応機構



Ishiyama, Miyaura, Hartwig, et al. *J. Am. Chem. Soc.* **2002**, *124*, 390;
J. Am. Chem. Soc. **2005**, *127*, 14263; Sakaki, et al. *J. Am. Chem. Soc.* **2003**, *125*, 1611

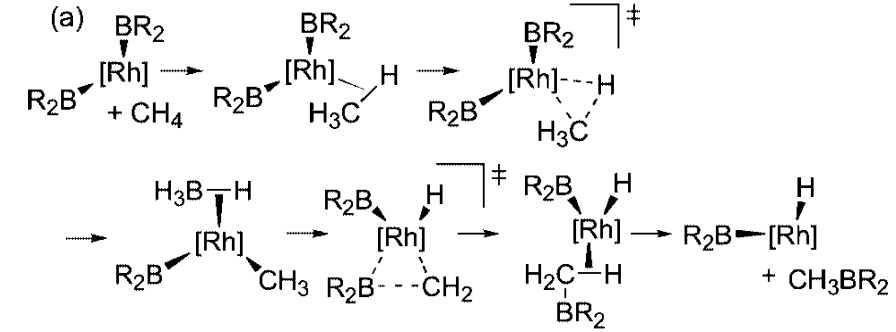
C(sp³)–Hホウ素化





Hartwig, et al. *Science* **2000**, *287*, 1995; *J. Am. Chem. Soc.* **2003**, *125*, 858;
J. Am. Chem. Soc. **2004**, *126*, 15334; *J. Am. Chem. Soc.* **2006**, *128*, 13684.

反応機構



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