

Shi Group

Dehydrogenation of alkanes by pincer-ligated metal complexes

Alkane dehydrogenation by pincer-Iridium complexes

Dehydrogenation of alkanes by pincer complexes of metals other than Iridium

Dehydrogenation of substrates containing heteroatoms

Tandem reactions involving alkane dehydrogenation

Alkane dehydrogenation by pincer-Iridium complexes

Alkane dehydrogenation

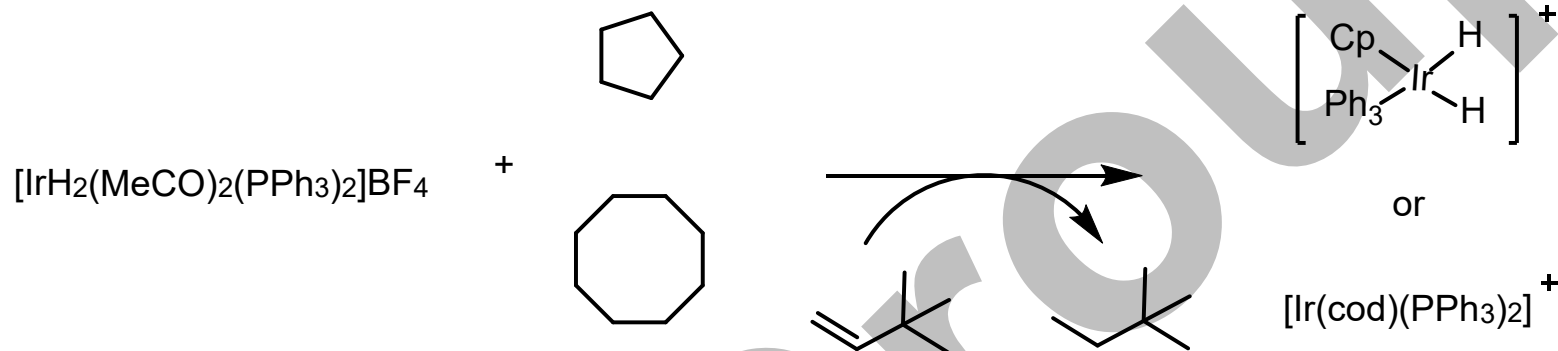
Variations of pincer-Iridium complexes

Mechanism

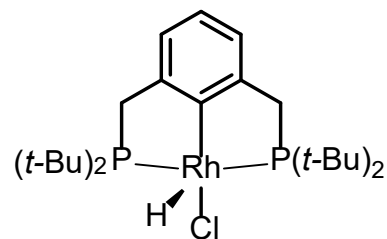
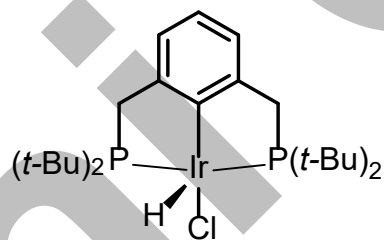
Alkane Dehydrogenation



Variations of pincer-Iridium complexes

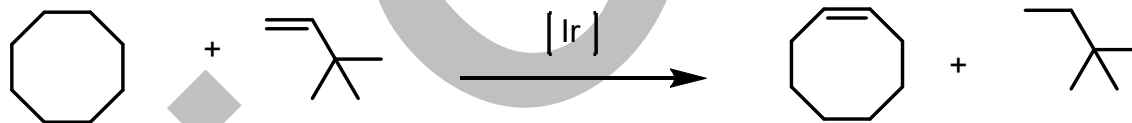
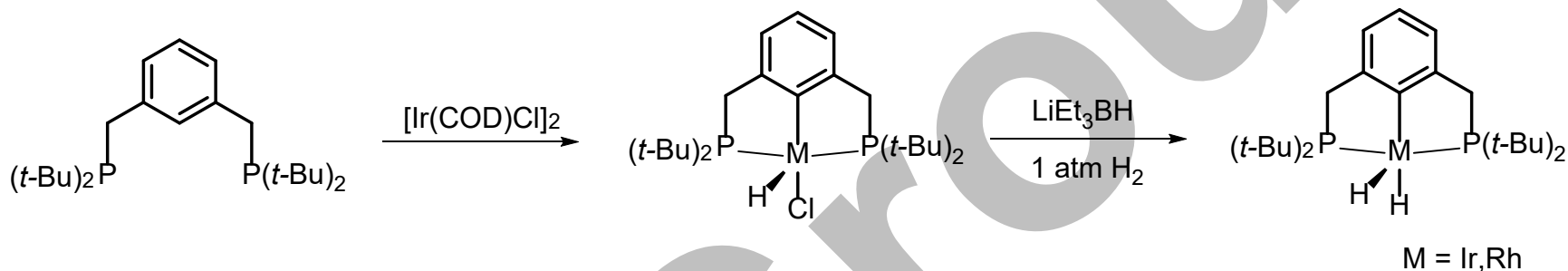


Crabtree, R. H. *J. Am. Chem. Soc.* **1979**, *101*, 7738



Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1020

Variations of pincer-Iridium complexes

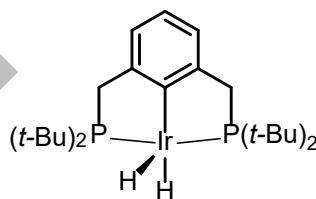


100 °C: 20.5 TONs/h; 150 °C: 82 TONs/h; 200 °C: 12 TONs/min

Kaska, W. C.; Jensen, C. M. *Chem. Commun.* **1996**, 2083

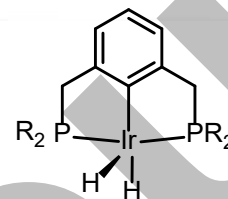
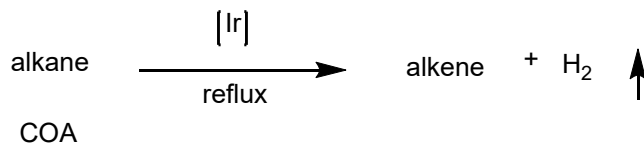
Variations of pincer-Iridium complexes

substrate	time (h)	T (°C)	products (TONs)
cyclohexane	1	150	cyclohexane(44),benzene(54),tba(211)
cyclohexane	0.5	200	cyclohexane(86),benzene(77),tba(310)
methylcyclohexane	1	150	methylcyclohexenes (41),toluene (11), tba (105)
methylcyclohexane	1	200	methylcyclohexenes (70),toluene (54), tba (310)
methylcyclohexane	120	150	methylcyclohexenes (67),toluene (65), tba (310)
decalin	72	150	octahydronaphthalenes (69), naphthalene (7), tetrahydronaphthalene (16),tba (159)
decalin	1	200	octahydronaphthalenes (24), naphthalene (4), tetrahydronaphthalene (8),tba (71)



Jensen, C. M. *J. Am. Chem.Soc.* **1997**, *119*, 840

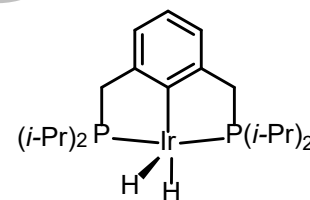
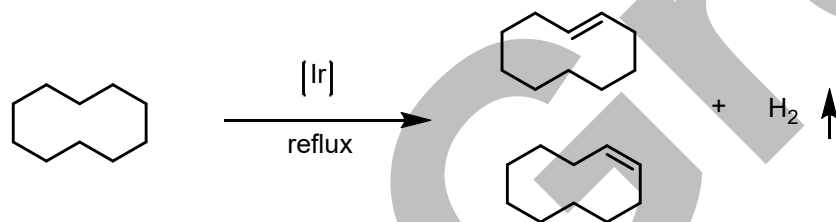
Variations of pincer-Iridium complexes



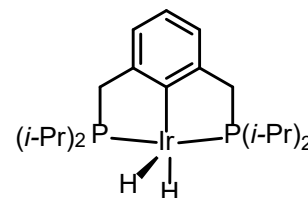
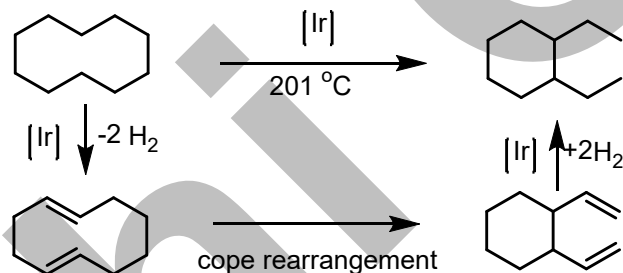
R = *i*-Pr or *t*-Bu

150 °C, 94 TONs/h

Kaska, W. C.; Jensen, C. M.; Goldman, A. S. *Chem. Commun.* **1997**, 2273.

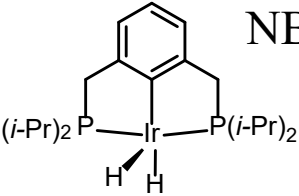
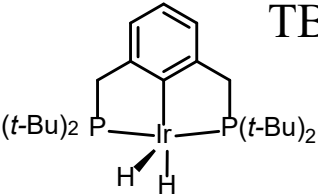


200 °C, 20 h 863 TONs



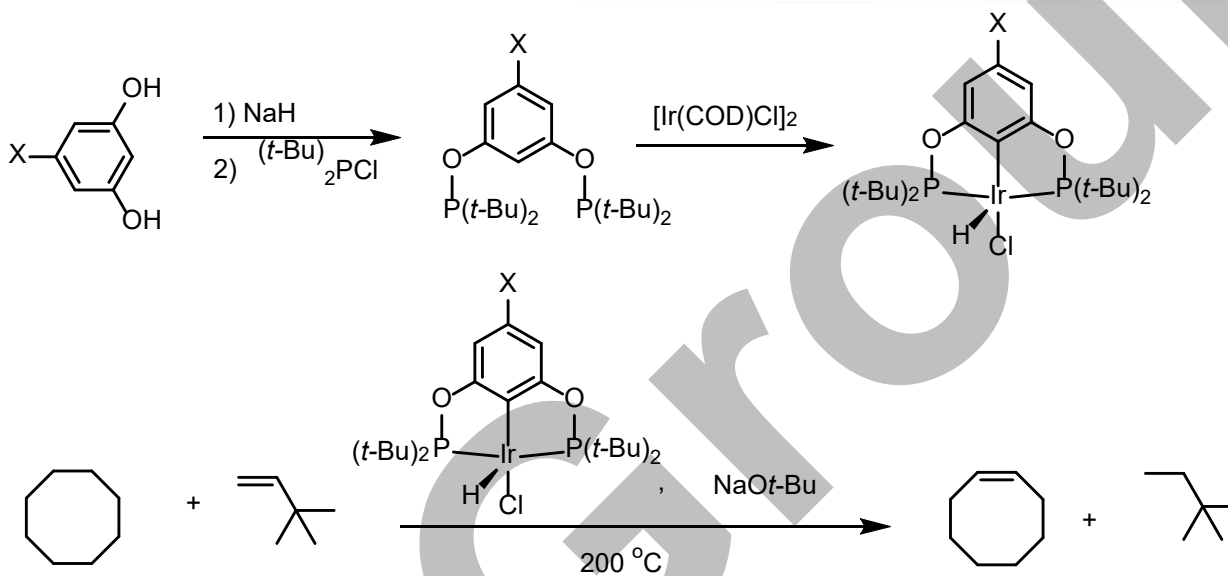
Goldman, A. S. *Chem. Commun.* **1999**, 655

Variations of pincer-Iridium complexes

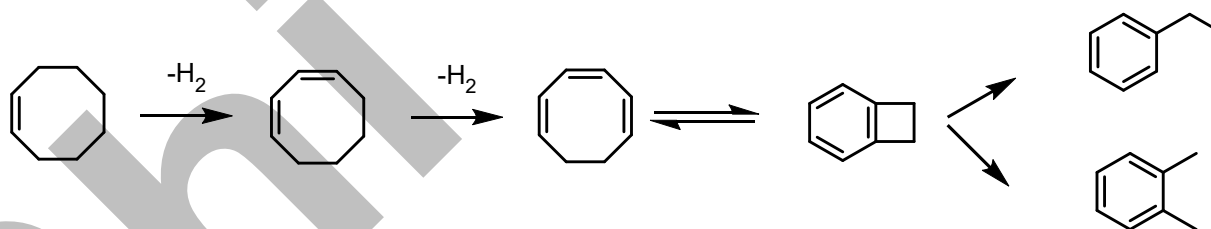
cat	accep	min	1-oct	trans-2	cis-2	others	total	%
 NBE	5	11	0.5	0.6	0	12	91	
	10	23	4	3	0	30	76	
	30	40	45	43	3	132	30	
	60	6	82	40	63	208	3	
 TBE	6	10	0	0	0	10	>90	
	15	18	19	8	0	45	40	
	30	20	41	20	0	81	25	
	60	28	47	26	0	91	20	

Goldman, A. S. *J. Am. Chem. Soc.* **1999**, *121*, 4086

Variations of pincer-Iridium complexes



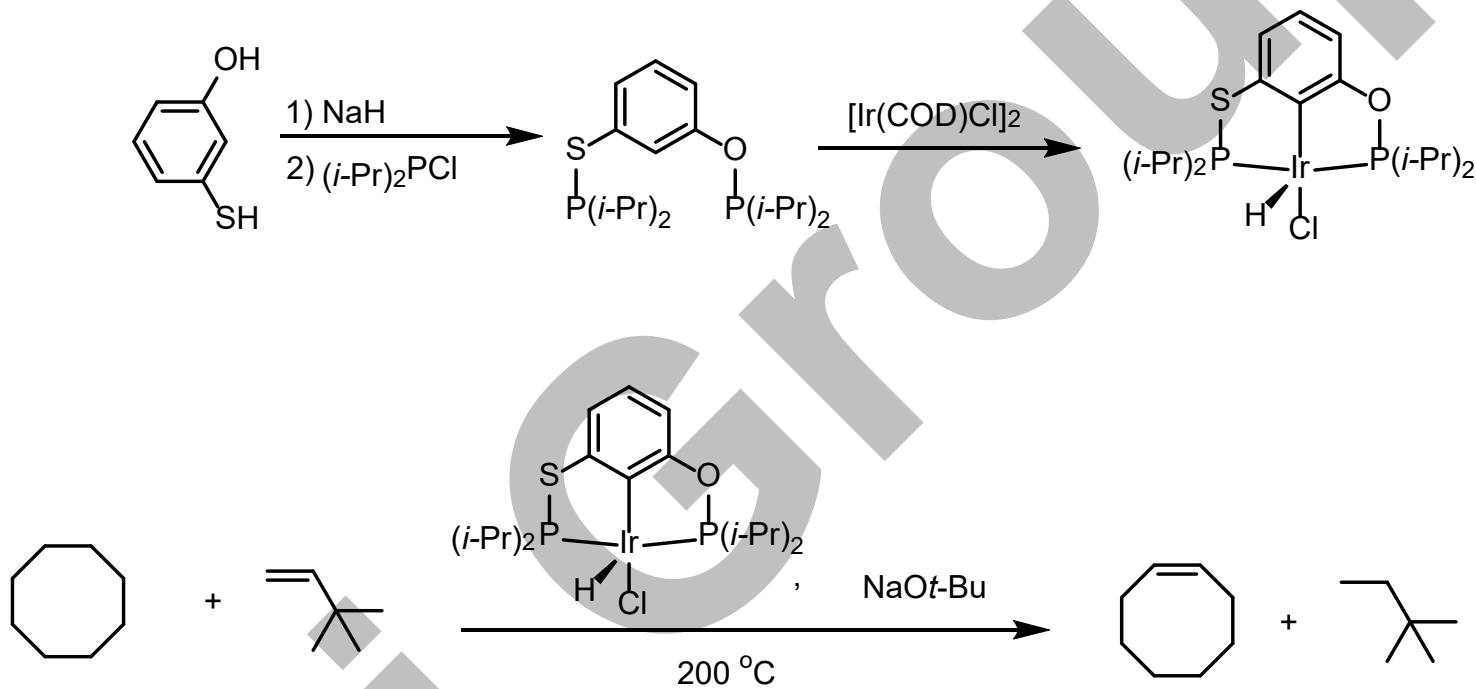
X = MeO, Me, H, F, C₆F₅, Ar^F



200 °C, 900 h 2000 TONs

Brookhart, M. *J. Am. Chem. Soc.* **2004**, *126*, 1804

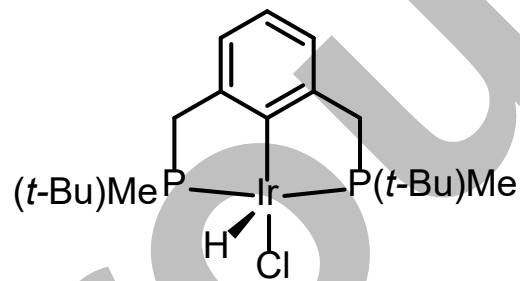
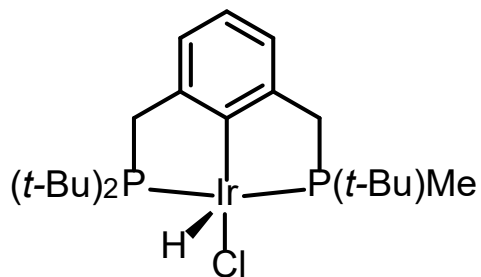
Variations of pincer-Iridium complexes



200 °C, 900 h 6000 TONs

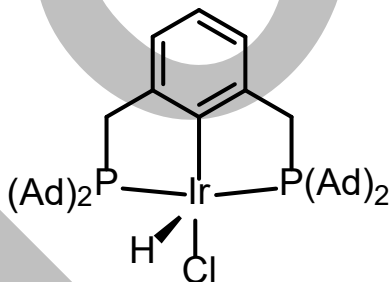
Huang, Z. *Angew. Chem. Int. Ed.* 2014, 53, 1390

Variations of pincer-Iridium complexes



COA/TBE: 150 °C, 5 h, 980 TONs ; (*i*Pr⁴PCP) Ir : 96 TONs ; (*t*Bu⁴PCP)Ir : 208 TONs

Goldman, A. S. *Organometallics* **2010**, 29, 2702

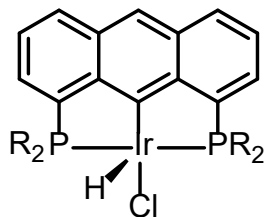


Ad = adamantyl

no acceptor

Goldman, A. S. *Organometallics* **2009**, 28, 5432

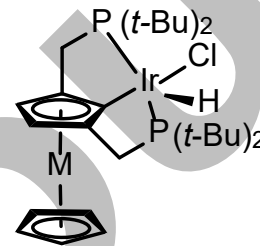
Variations of pincer-Iridium complexes



R = *i*-Pr, *t*-Bu

COA/TBE: < (*t*Bu₄PCP)Ir

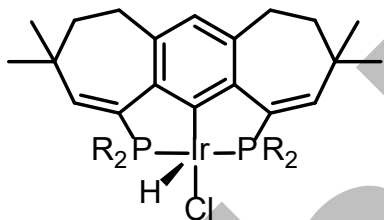
Hall, M. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 3596



M = Fe, Ru

COA/TBE: 180 °C, 8 h, 3300 TONs

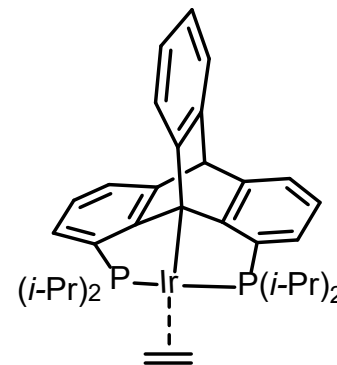
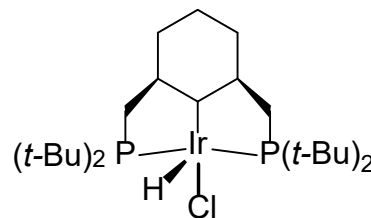
Koridze, A. A. *Organometallics* **2006**, *25*, 5466



R = *i*-Pr, Cy, Ph

COA/TBE: 230 °C, 24 h, 4820 TONs

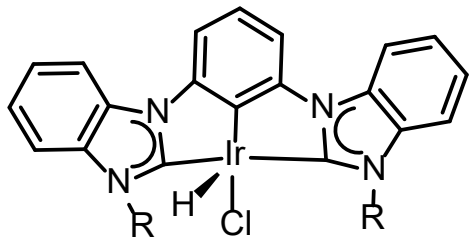
Yamamoto, Y. *Chem. Eur. J.* **2013**, *19*, 10672



n-octane/TBE, best 3300 TONs; poor

Wendt, O. F. *Polyhedron* **2014**, *84*, 63

Variations of pincer-Iridium complexes

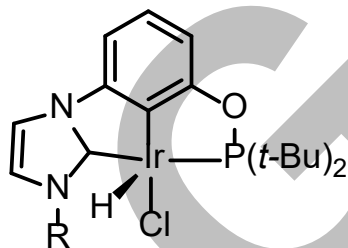
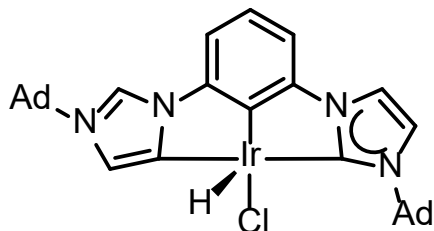


R = mesityl, 3,5-xylyl, 3,5-di-bubtylphenyl

Chianese, A. R. *Organometallics* **2010**, *29*, 3019

Chianese, A. R. *Organometallics* **2014**, *33*, 473

no acceptor/decane, 97 TONs

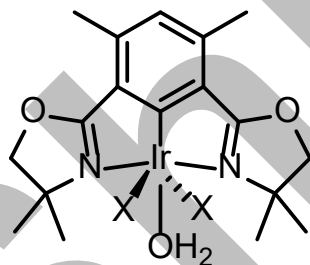


R = Me, *t*-Bu

Braunstein, P. *Organometallics* **2011**, *31*, 2606

Braunstein, P. *Dalton Trans.* **2012**, *41*, 636

very poor

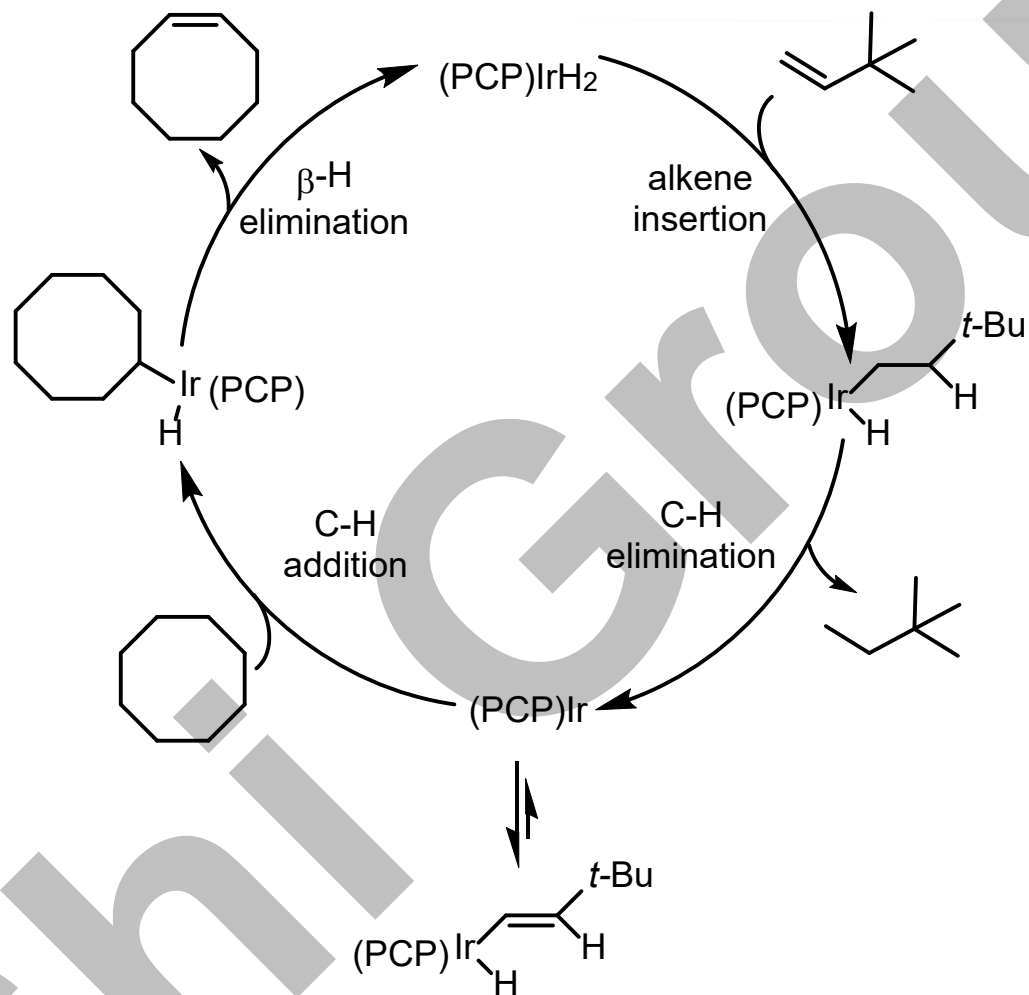


X = OAc

Goldberg, K. I. *Organometallics* **2013**, *32*, 1579

equivalent

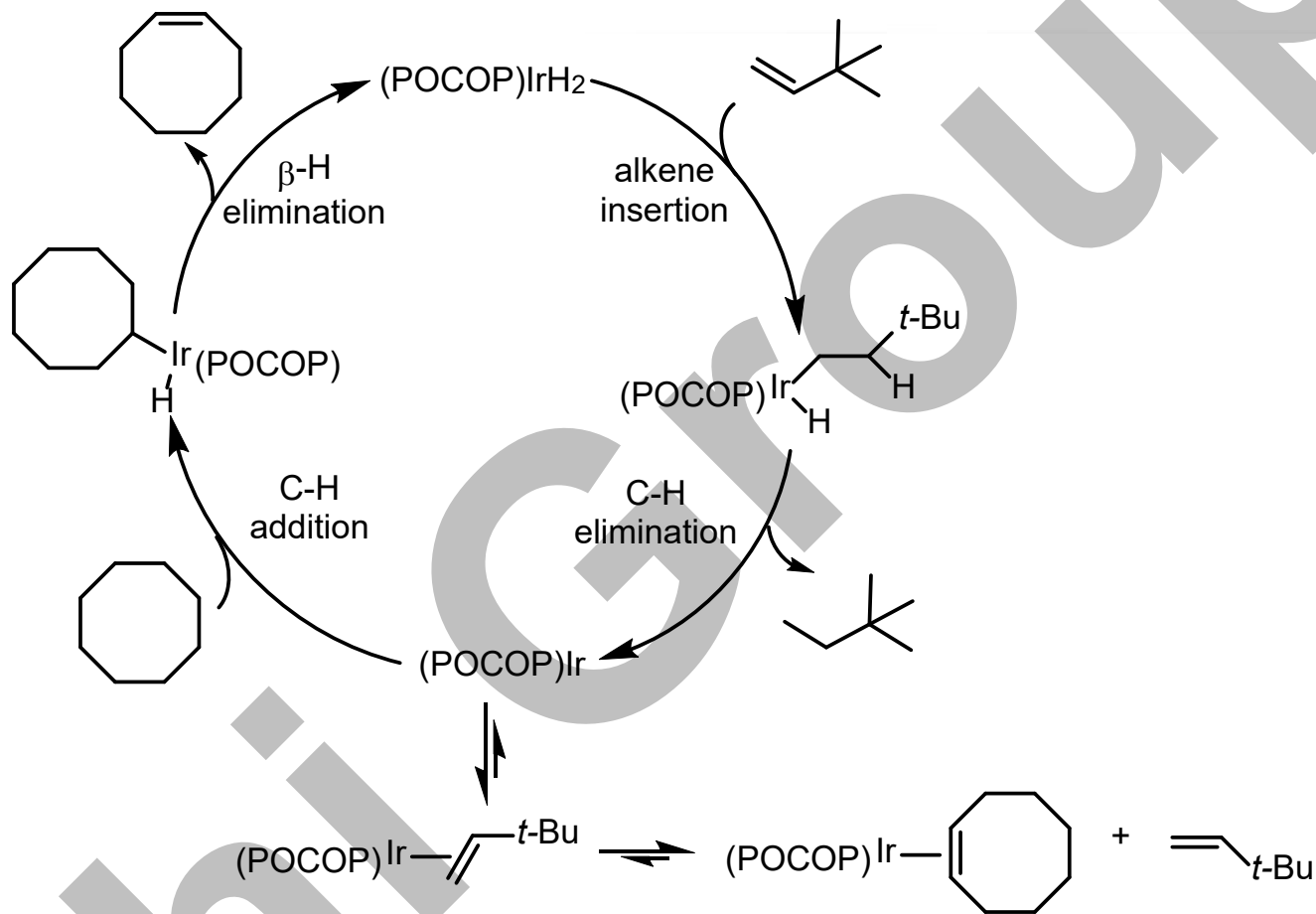
Mechanism



Goldman, A. S. *J. Am. Chem. Soc.* **2000**, *122*, 11017

Goldman, A. S. *J. Am. Chem. Soc.* **2003**, *125*, 7770

Mechanism



$t\text{Bu}^4\text{POCOP}: 157.5^\circ$; $t\text{Bu}^4\text{PCP}: 164.5^\circ$

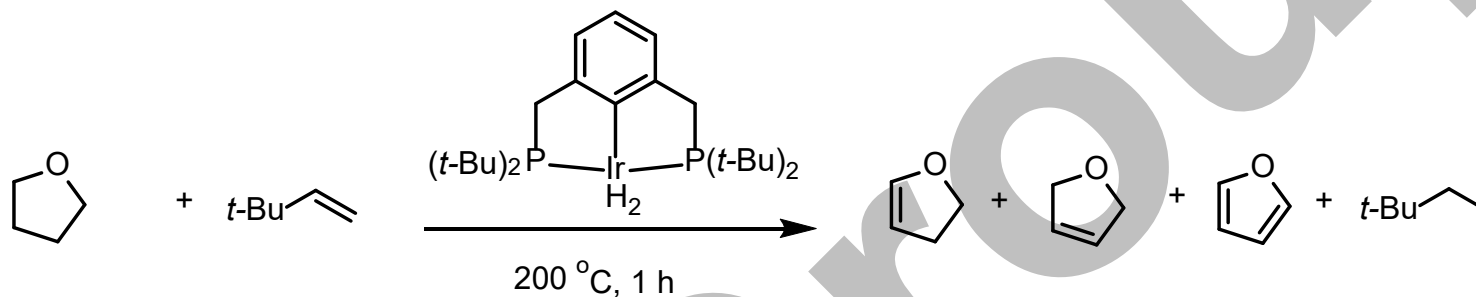
Jensen, C. M. *Inorg. Chim. Acta.* **2004**, *357*, 2953

Dehydrogenation of substrates containing heteroatoms

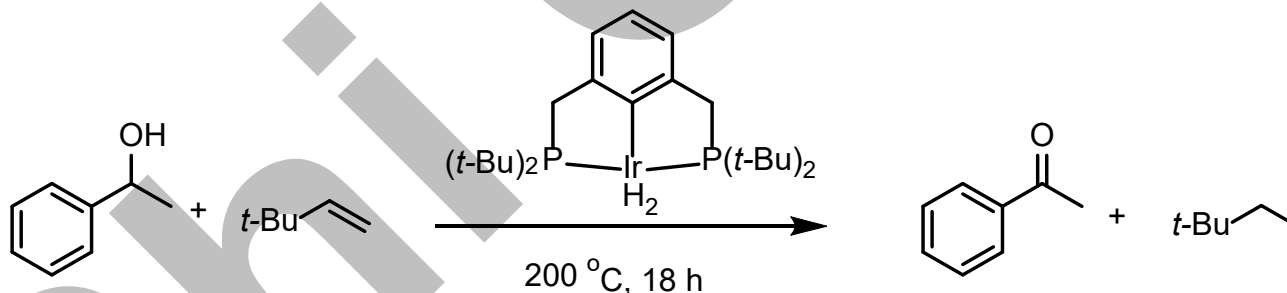
Dehydrogenation of substrates containing oxygen atoms

Dehydrogenation of substrates containing nitrogen atoms

Dehydrogenation of substrates containing oxygen atoms

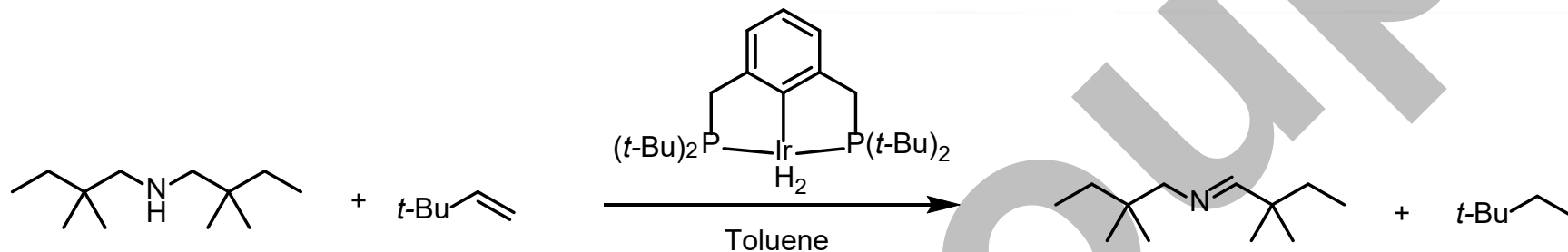


Kaska, W. C.; Jensen, C. M. *Chem. Commun.* **1996**, 2083

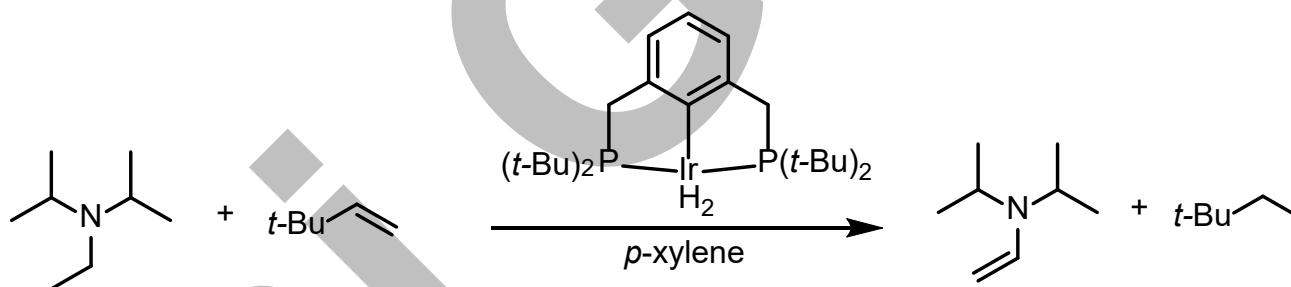


Jensen, C. M. *Can. J. Chem.* **2001**, 79, 823

Dehydrogenation of substrates containing nitrogen atoms

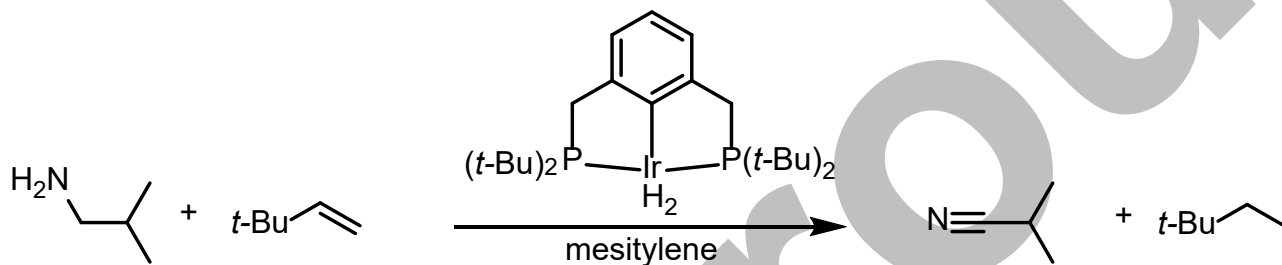


Jensen, C. M. *J. Mol. Catal. A:Chem.* **2002**, *189*, 119



Goldman, A. S. *Chem. Commun.* **2003**, 2060

Dehydrogenation of substrates containing nitrogen atoms



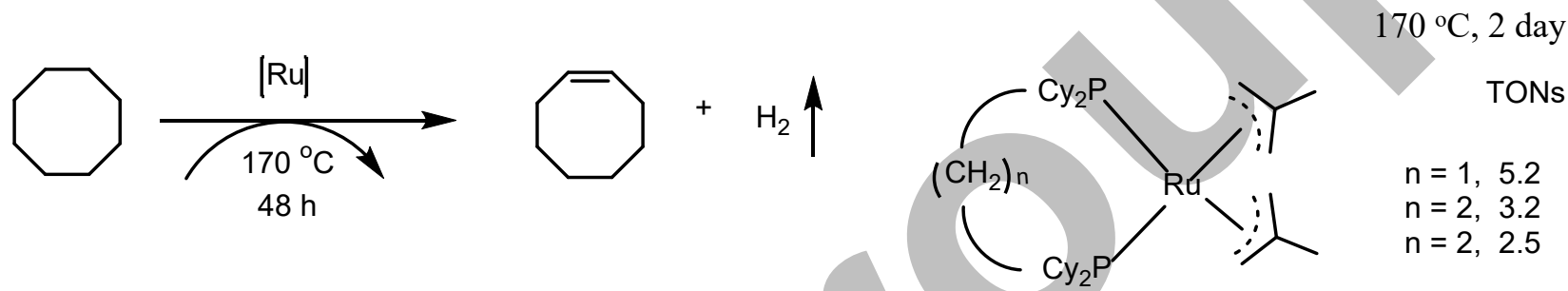
Brookhart, M. *Organometallics* **2008**, 27, 2036

Dehydrogenation of alkanes by pincer complexes of metals other than Iridium

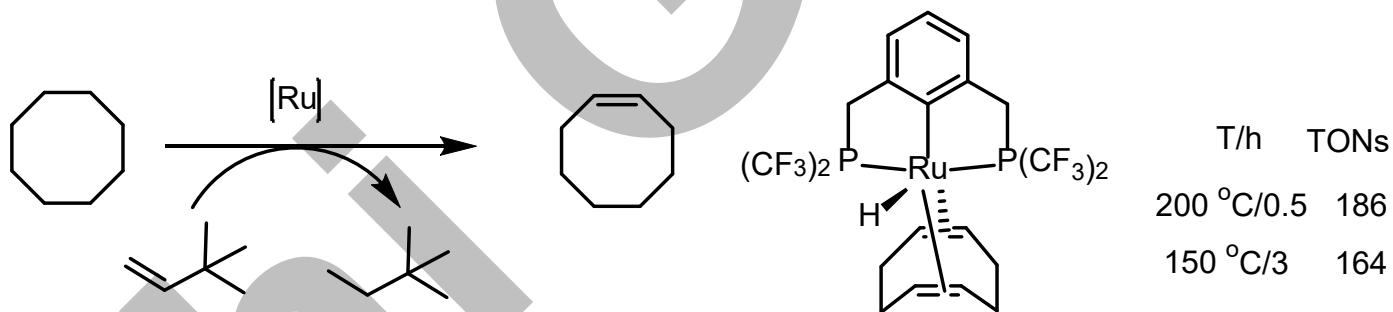
Alkane dehydrogenation by pincer- Ruthenium complexes

Alkane dehydrogenation by pincer-Rhodium complexes

Alkane dehydrogenation by pincer- Ruthenium complexes



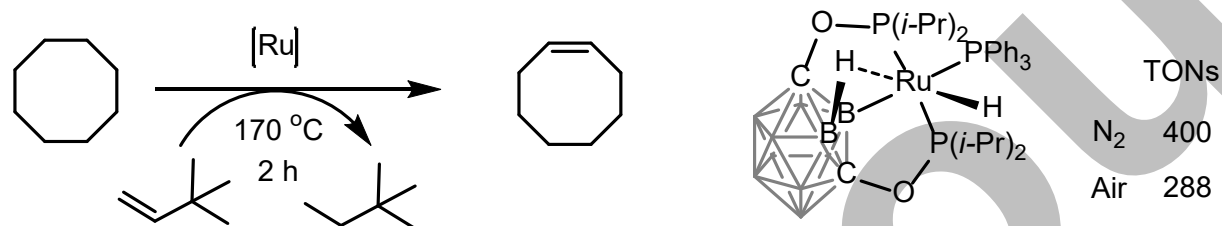
Leitner, W. *Organometallics* **1999**, *18*, 3316



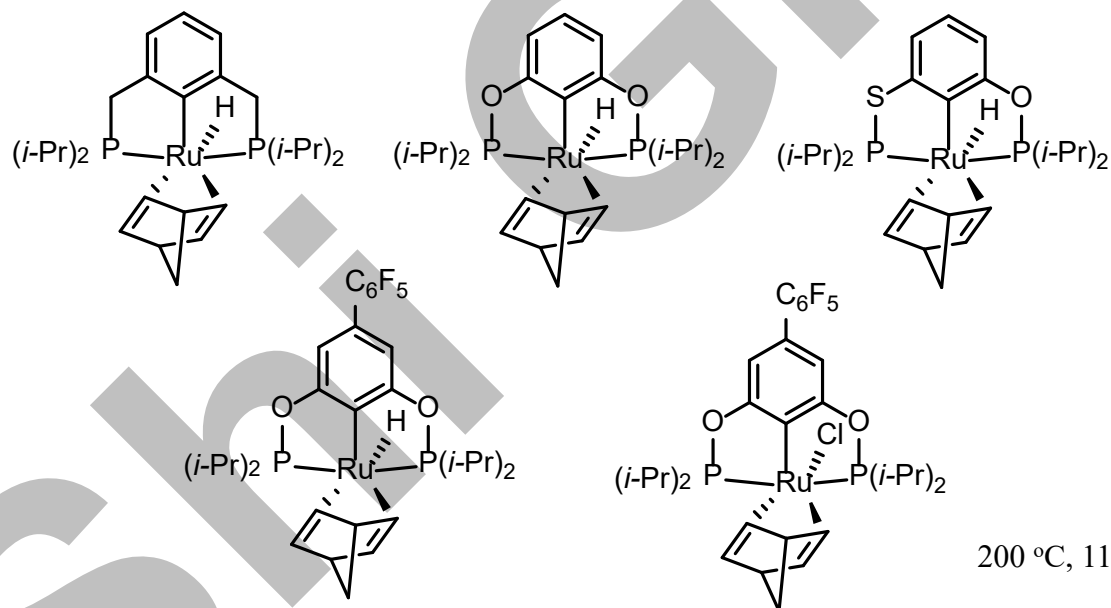
200 °C unstable, 30 min, decomposition
not sensitive to nitrogen, oxygen, water

Roddick, D. M. *Organometallics* **2011**, *30*, 5133

Alkane dehydrogenation by pincer- Ruthenium complexes



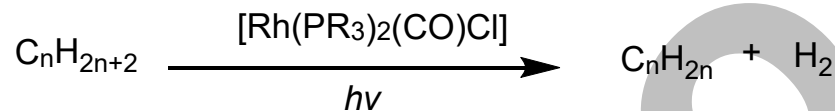
Popov, A. A.; Peryshkov, D. V. *Chem. Sci.* **2017**, *8*, 5399.



$200\text{ }^\circ\text{C}$, 1130 TOs/h but only 260 TOs after 24 h

Huang, Z. *Organometallics* **2016**, *35*, 181

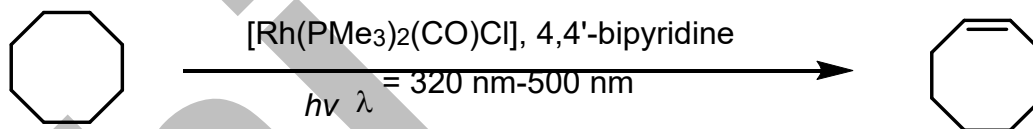
Alkane dehydrogenation by pincer-Rhodium complexes



$n = 7$ or 8 , $\text{R} = \text{Me}$, Et , or Ph

60-90 °C TOF: 795/h

Saito, Y. *J. Chem. Soc. Chem. Commun.* **1988**, 161



Beller, M. *Angew. Chem. Int. Ed.* **2014**, 53, 6477

Tandem reactions involving alkane dehydrogenation

Alkane metathesis

Alkyl group cross-metathesis

Alkane-alkene coupling reactions

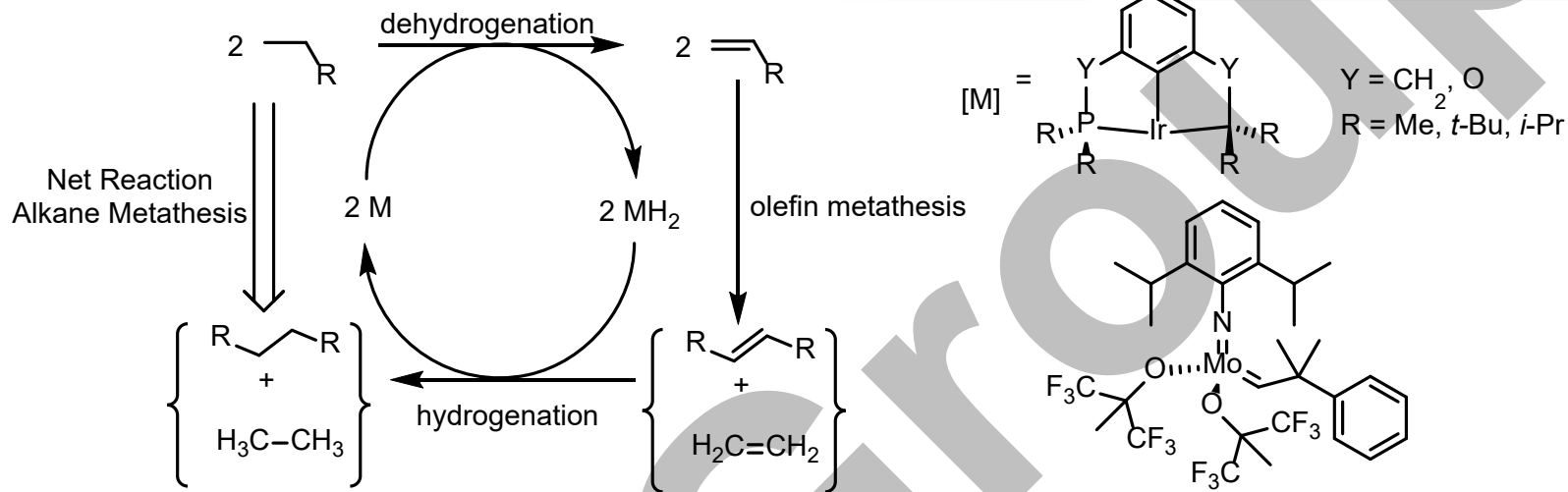
Dehydroaromatization

Aryl-alkyl coupling reactions

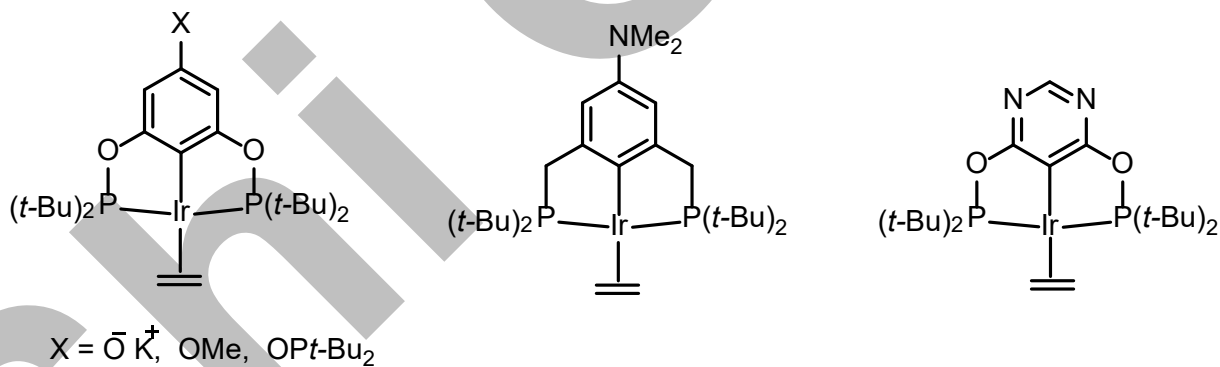
Silylation of alkanes

Borylation of alkanes

Alkane metathesis



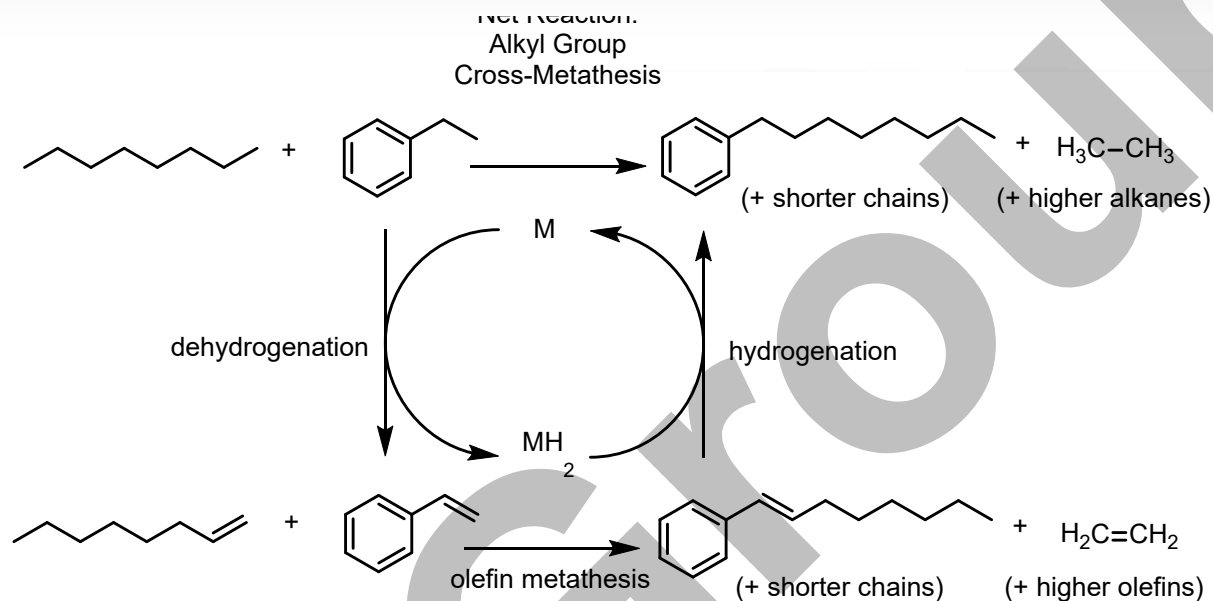
Goldman, A. S.; Brookhart, M. *Science* **2006**, *312*, 257



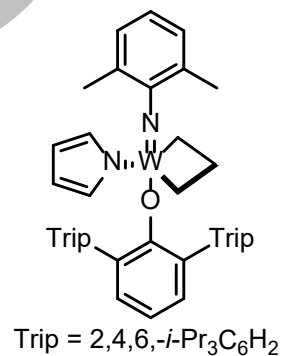
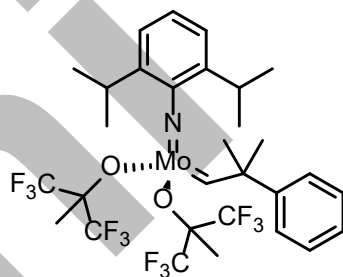
Goldman, A. S.; Brookhart, M. *Adv. Synth. Catal.* **2009**, *351*, 188

Goldman, A. S.; Brookhart, M. *Adv. Synth. Catal.* **2010**, *352*, 125

Alkyl group cross-metathesis

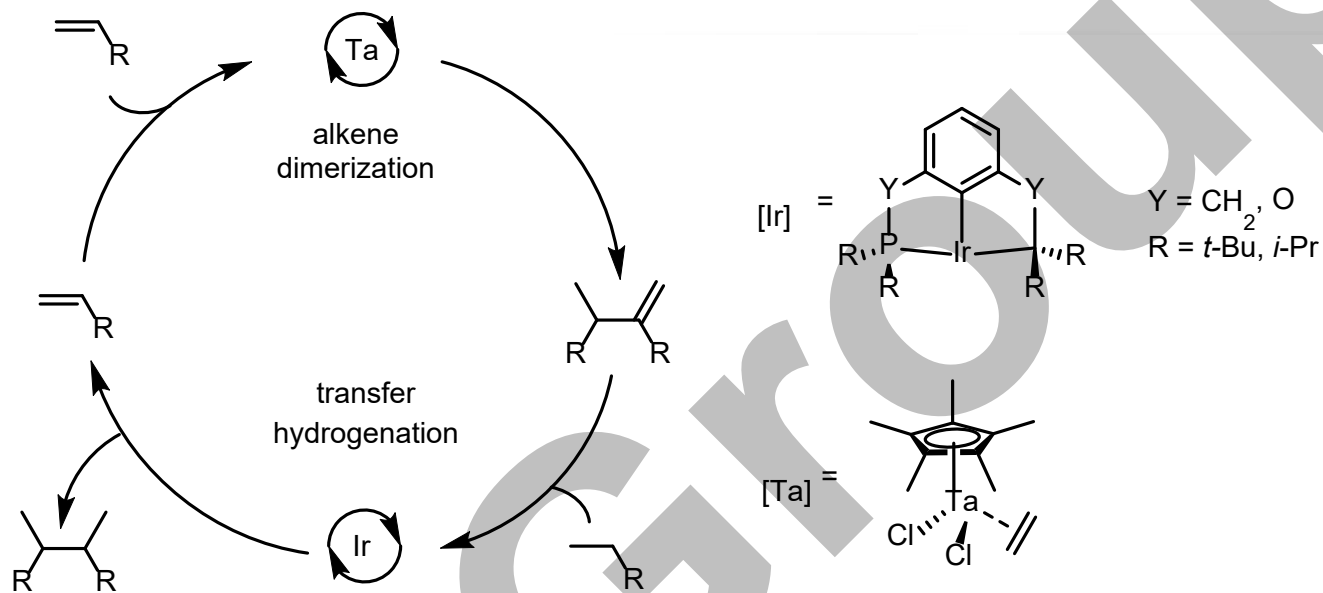


olefin metathesis catalysts:



Schrock, R. R.; Goldman, A. S. *J. Am. Chem. Soc.* **2013**, 135, 12572

Alkane-alkene coupling reactions



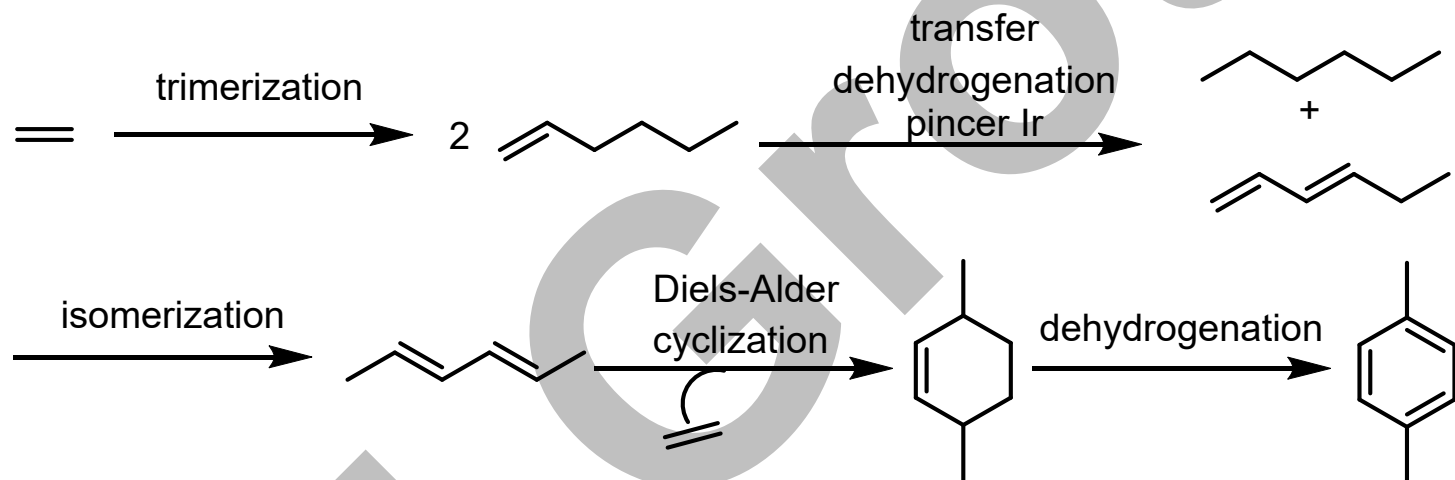
Net Reaction Alkane-Alkene Coupling



Bercaw, J. E. *J. Am. Chem. Soc.* **2013**, *135*, 10302

Bercaw, J. E. *Organometallics* **2014**, *33*, 3353

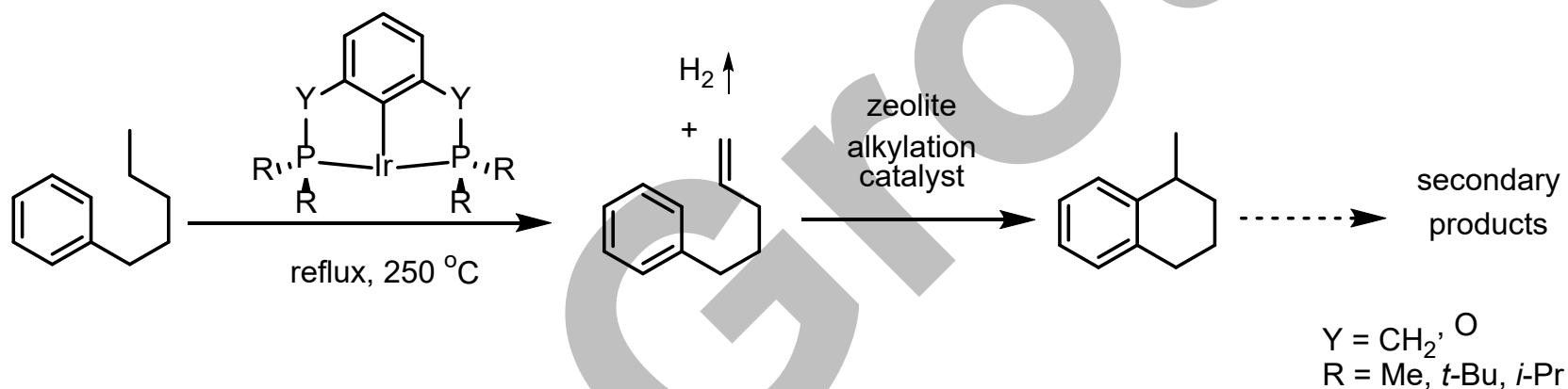
Dehydroaromatization



Brookhart, M. *J. Am. Chem. Soc.* **2012**, *134*, 15708

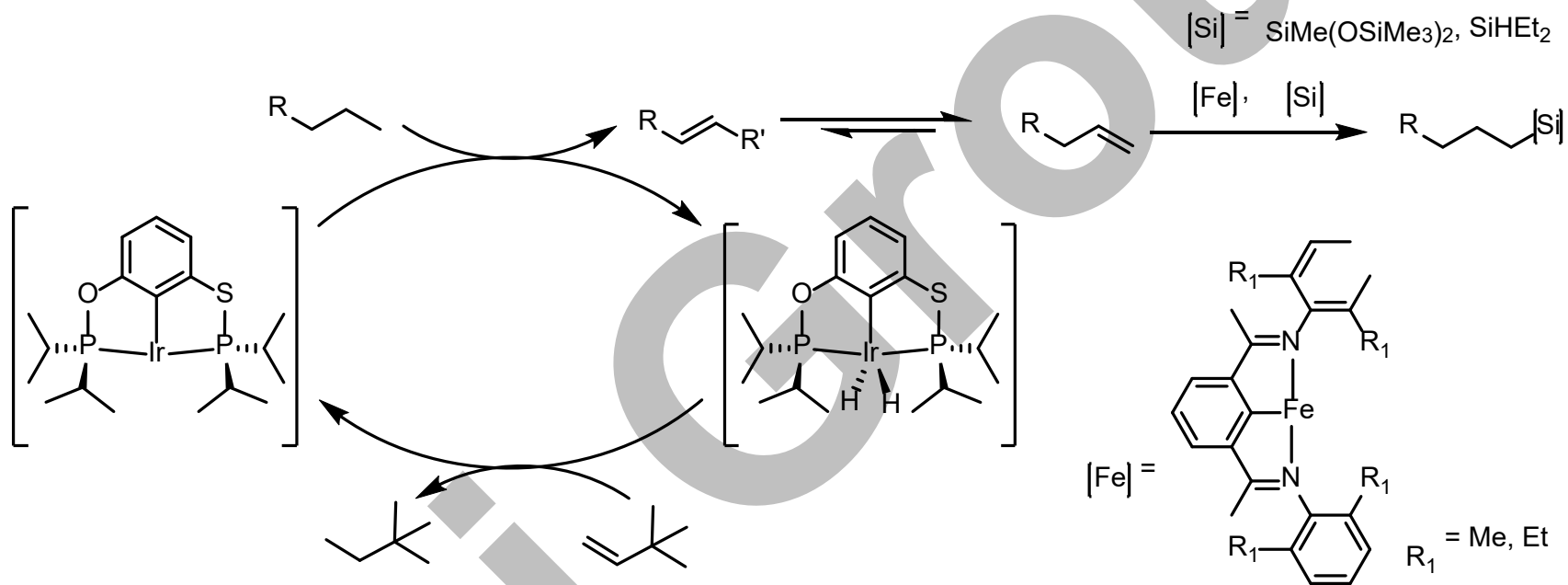
Brookhart, M. *ACS Catal.* **2013**, *3*, 1768

Aryl-alkyl coupling reactions



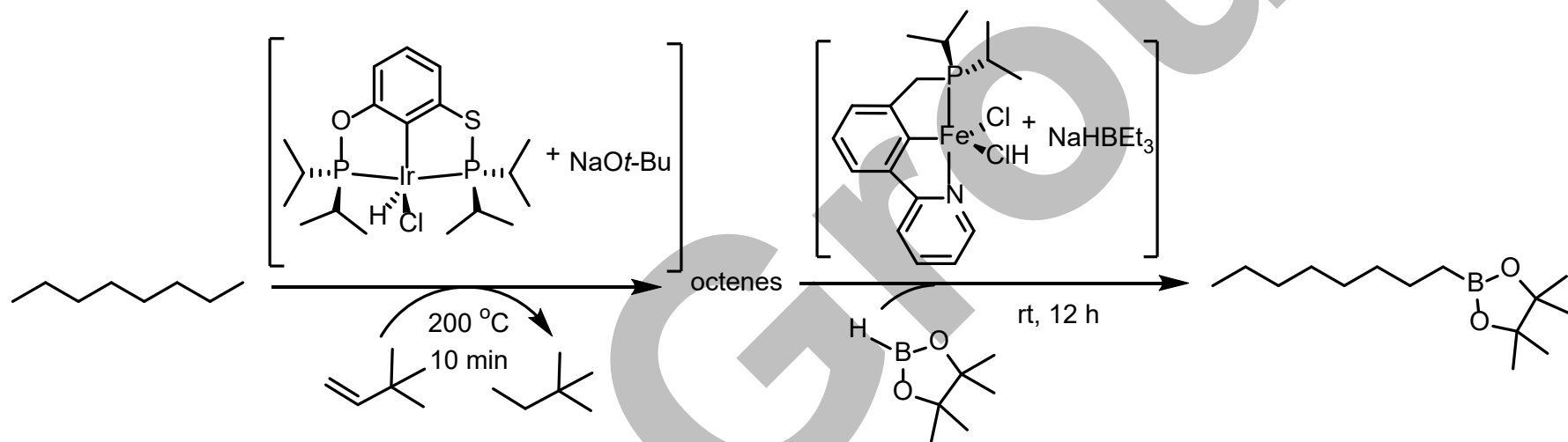
Goldman, A. S. *ACS Catal.* **2016**, *6*, 2836

Silylation of alkanes



Huang, Z. *Nat. Chem.* **2016**, *8*, 157

Borylation of alkanes



Huang, Z. *Nat. Chem.* **2016**, *8*, 157

Thanks !

Shi Group