

# Dehydrogenation of Alkanes

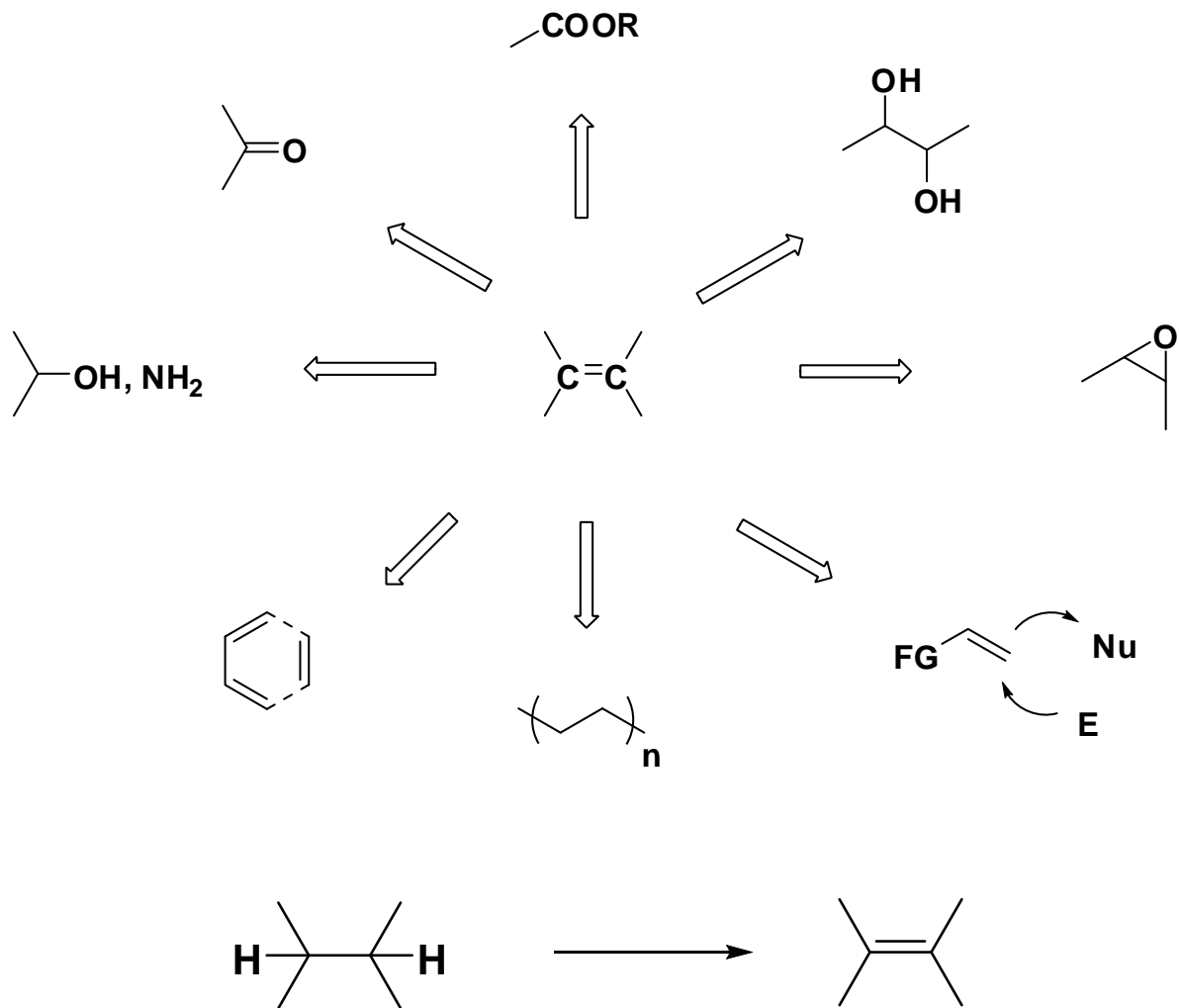
Zhiqian “Wallace” Wang

02-08-2012

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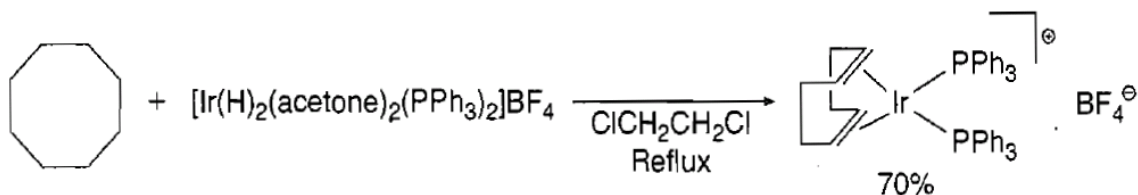
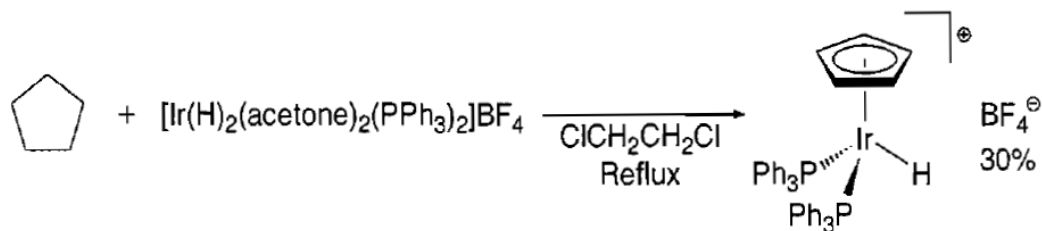
- Introduction
- Dehydrogenation of Alkanes by Pincer Iridium Complexes
- Alkane Metathesis
- Dehydrogenation Involving Heteroatoms
- Conclusion

# Introduction: Dehydrogenation of Alkanes

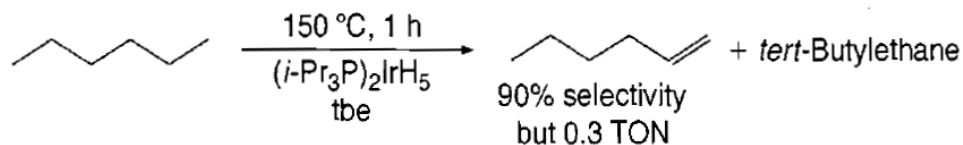
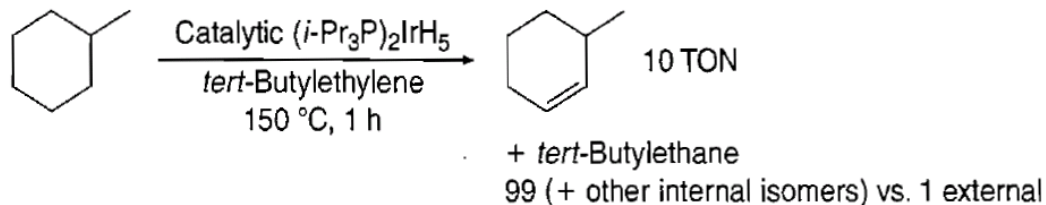
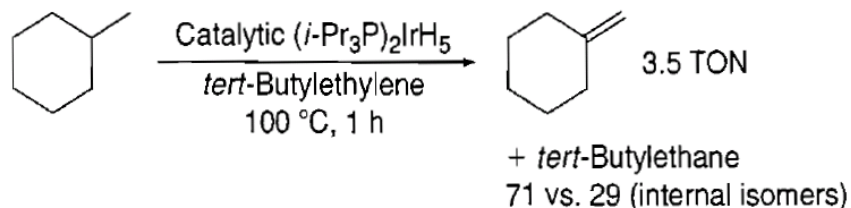


# Early Work: From 1970s

Crabtree:

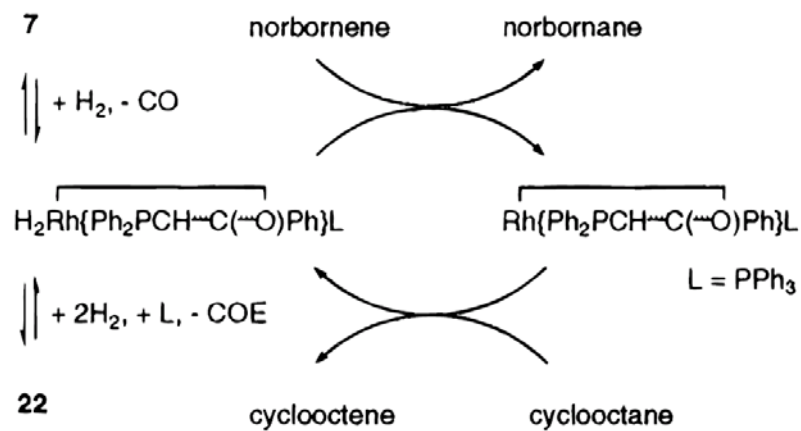
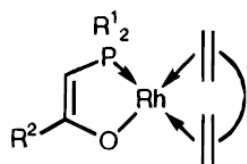
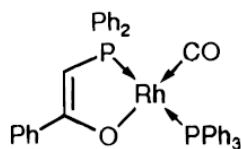
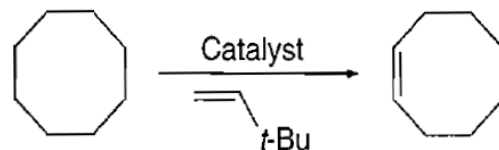


Felkin:



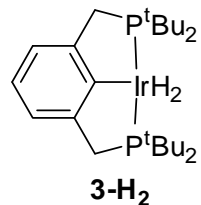
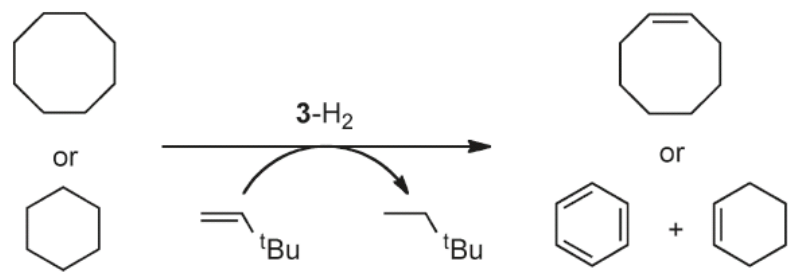
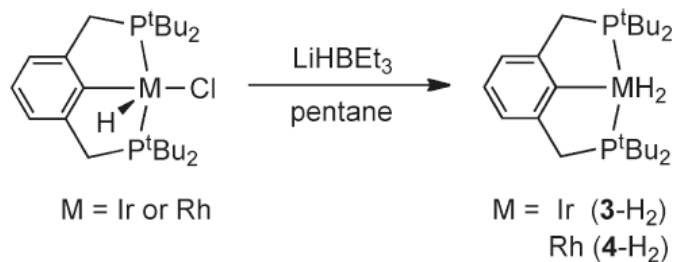
Crabtree: Catalyst =  $[\text{Ir}(\text{PR}_3)_2(\kappa^2\text{-O}_2\text{CC}_2\text{F}_5)_2\text{H}_2]^+$  R = Cy or  $\text{C}_6\text{H}_4\text{CF}_3$   
 35 turnovers with acceptor; 35 turnovers without acceptor in open reflux

Felkin: Catalyst =  $(i\text{-Pr}_3\text{P})_2\text{IrH}_5$ ,  $[(p\text{-FC}_6\text{H}_4)_3\text{P}]_2\text{IrH}_5$ , or  $[(p\text{-FC}_6\text{H}_4)_3\text{P}]_3\text{RuH}_4$   
 45–70 turnovers with acceptor

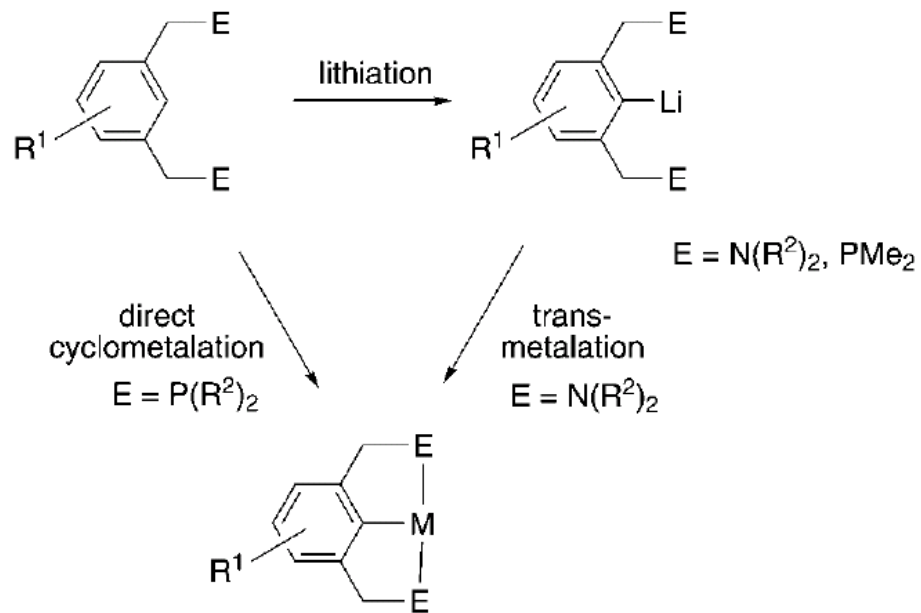


# Dehydrogenation of Alkanes by Pincer Iridium Complexes

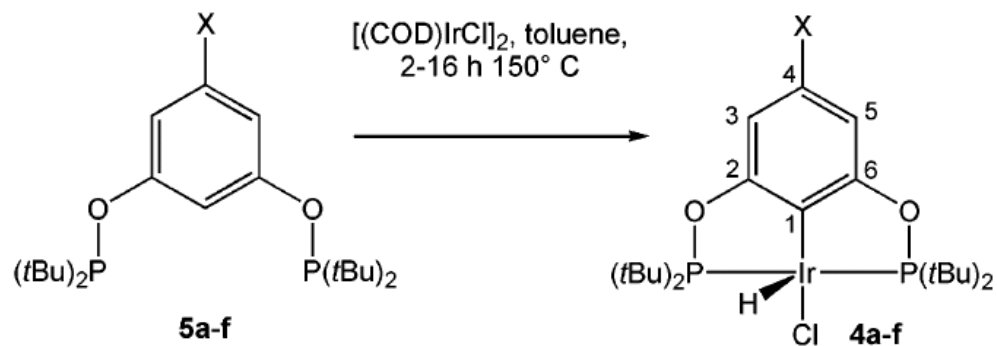
1996: Jensen



82 turnovers/h at 150°C, 12 turnovers/min at 200°C  
no observable decomposition over one week at 200°C



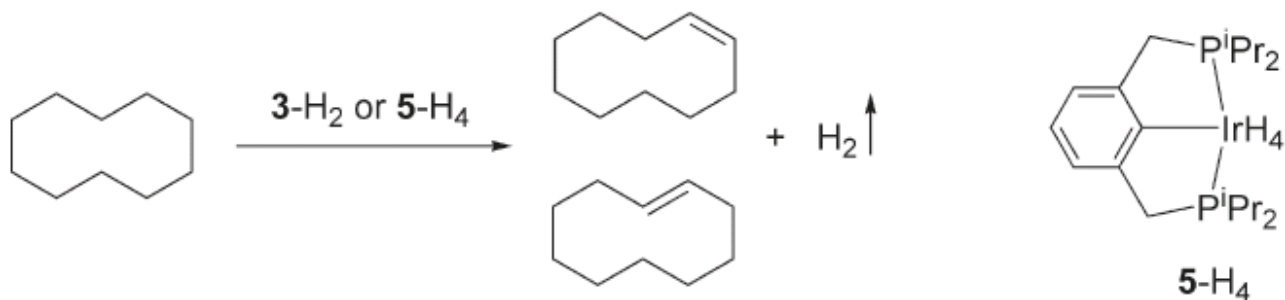
Angew. Chem. Int. Ed. 2001, 40, 3750 - 3781



J. AM. CHEM. SOC. 2004, 126, 1804-1811

# The first example of efficient acceptorless dehydrogenation

Goldman:



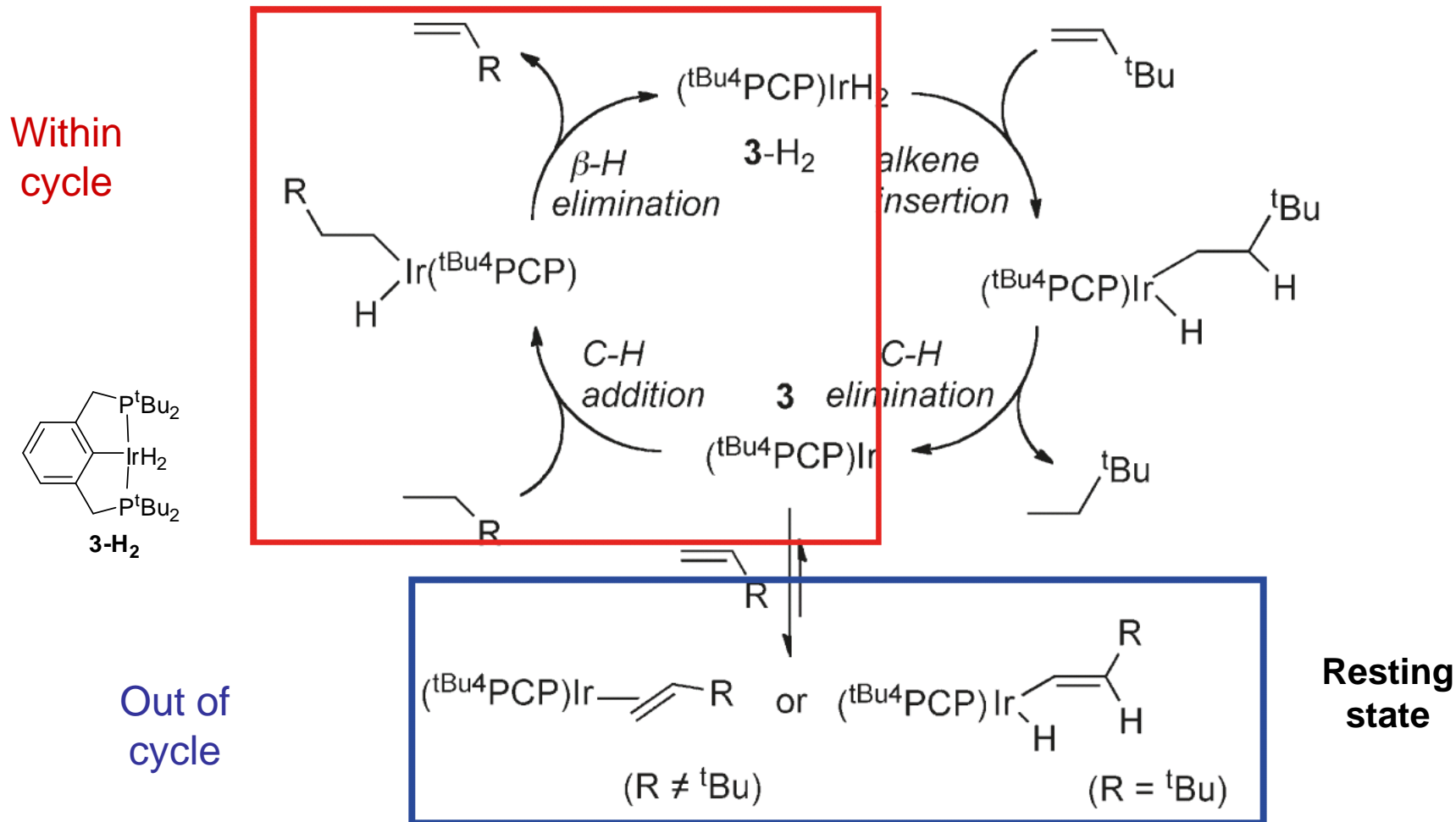
**close to 1000 turnovers**

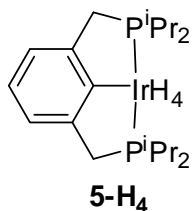
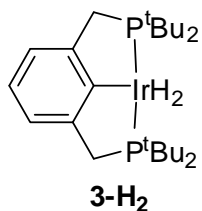
Chem. Commun. 1997, 2273

Chem. Commun. 1999, 655



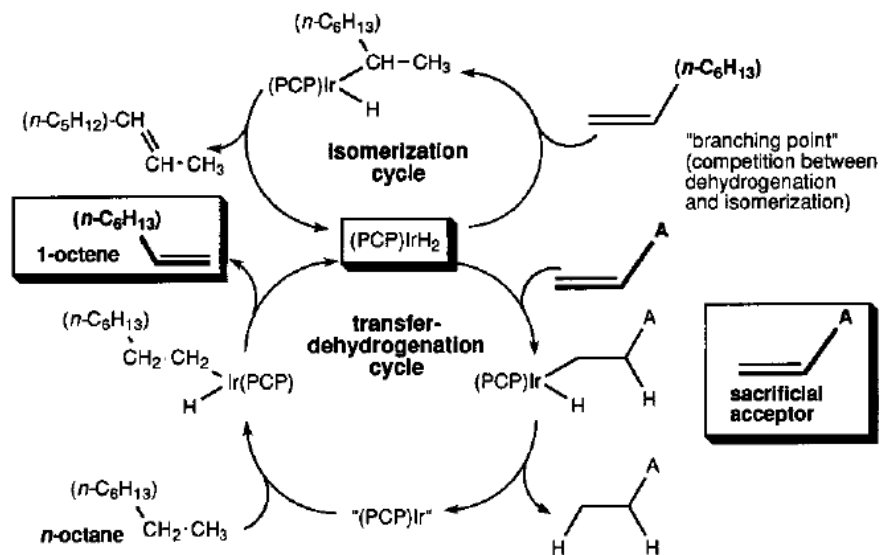
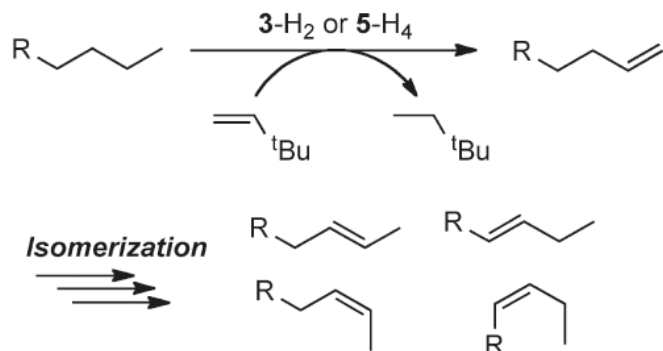
# Scheme 1. Proposed Mechanism of *n*-Alkane/TBE Transfer Dehydrogenation by 3-H<sub>2</sub>





Catalysts 3 and 5 show high kinetic selectivity for dehydrogenation of the terminal position of *n*-alkanes to give  $\alpha$ -olefins. This regioselectivity holds great promise with respect to the formation of valuable  $\alpha$ -olefins and products derived from them in tandem catalytic systems.

## But --- isomerization



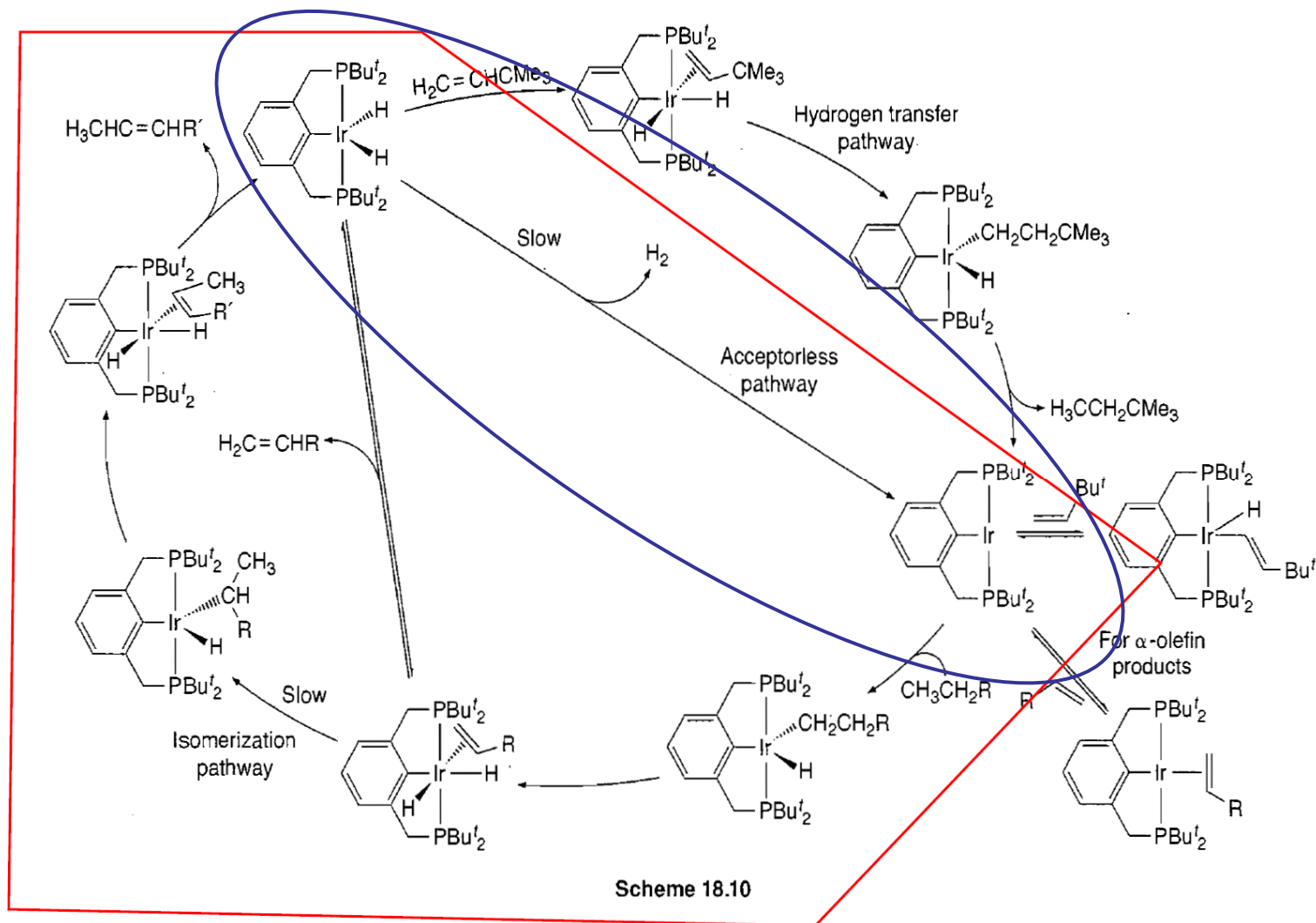
**Figure 1.** Proposed mechanism of both transfer-dehydrogenation of *n*-octane and octene-isomerization catalyzed by the (PCP)Ir catalysts.

**Table 1.** Octene Distributions (Concentrations in mM) from Transfer-Dehydrogenation of *n*-Octane Catalyzed by **1** or **2** Using Various Hydrogen Acceptors. All Runs Conducted at 150 °C with 1.0 mM Catalyst in *n*-Octane Solution

cat <sup>a</sup>	accep	min	1-oct	<i>trans</i> - <b>2</b>	<i>cis</i> - <b>2</b>	other	total	%
<b>2</b>	nbe <sup>b</sup> 0.2 M	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
<b>2</b>	nbe 0.5 M	5	8	0	0	0	8	>90
		10	19	2	1	0	22	87
		30	59	56	40	0	154	38
		60	59	105	71	3	238	25
<b>2</b>	tbe <sup>c</sup> 0.5 M	5	21	3	3	0	27	78
		10	27	6	6	0	40	68
		30	44	65	45	1	155	28
		60	41	103	78	19	250	16
<b>2</b>	1-dec 0.5 M	10	10	0	0	0	10	>90
		30	43	31	21	0	95	45
		60	10	64	40	13	134	8
<b>1</b>	tbe 0.2 M	6	10	0	0	0	10	>90
		15	18	19	8	0	45	40
		30	20	41	20	0	81	25
		60	18	47	26	0	91	20
<b>1</b>	nbe 0.5 M	15	23	4	2	0	29	79
		30	27	7	3	0	37	73
		60	30	15	5	0	50	60
<b>1</b>	1-dec <sup>d</sup> 0.5 M	15	13	0	0	0	13	>95
		30	34	1	0.6	0	36	95
		60	74	7	4	0	86	87
		90	94	9	9	0	111	84
		120	97	32	14	0	143	68

<sup>a</sup> cat = catalyst; accep = acceptor; 1-oct = 1-octene; other = (other octenes + 2 × [dienes]); % = 100 × [1-octene]/total. <sup>b</sup> Norbornene. <sup>c</sup> *t*-Butylethene. <sup>d</sup> 1-Decene.

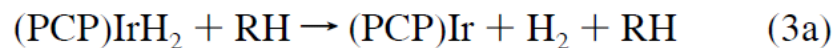
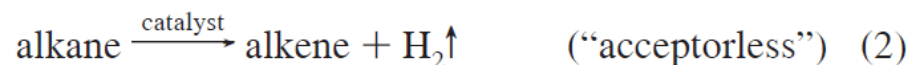
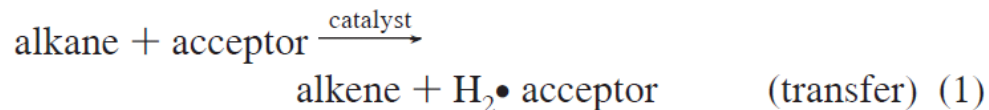
# Mechanism of (PCP)Ir-Catalyzed Acceptorless Dehydrogenation of Alkanes



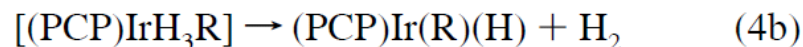
Rate determine step :  $\text{H}_2$  loss

## A Combined Computational and Experimental Study

2002: Karsten Krogh-Jespersen\* and Alan S. Goldman\*

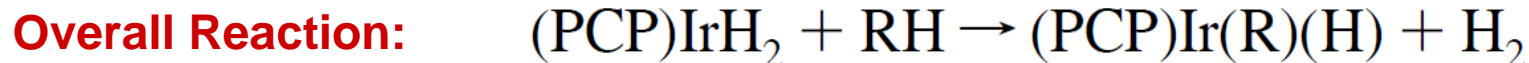


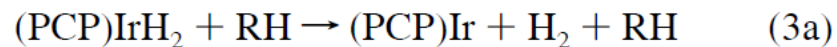
**Dissociative (D) pathway**



**Associative (A) pathway**

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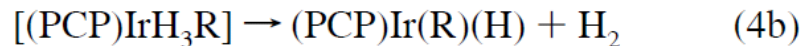




Dissociative (*D*) pathway

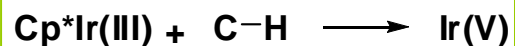
Ir(I) pathway is not accessible in the Cp\*Ir case, and the alternative of  $\sigma$ -bond-metathesis by Cp\*Ir(III) was calculated to be less favorable than the Ir(V) pathway

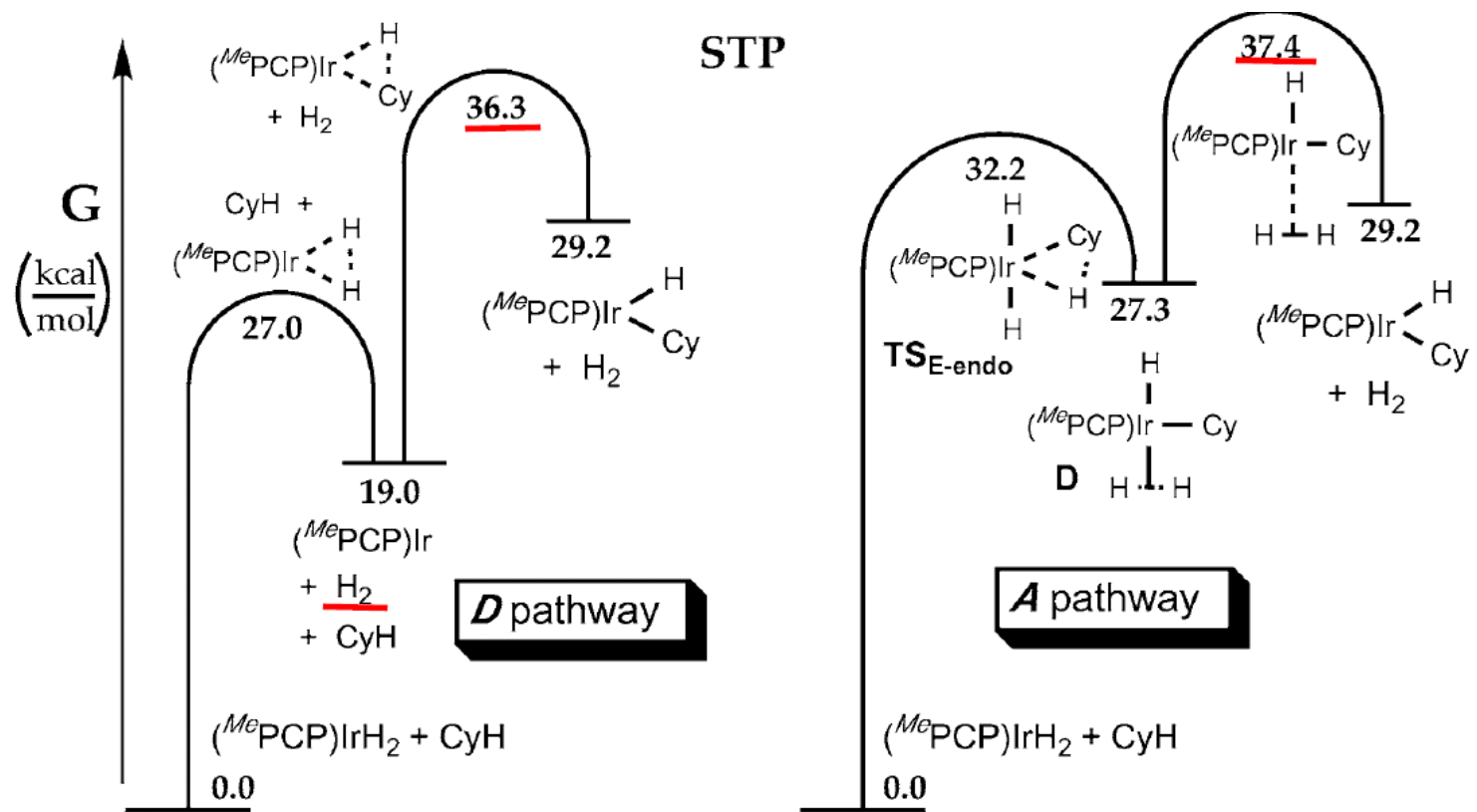
*Vs.*



Associative (*A*) pathway

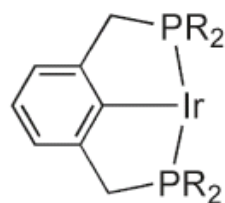
**Bergman & Hall:**



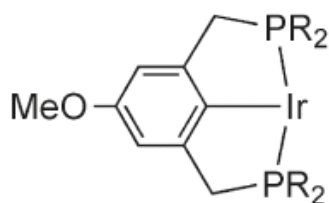


high entropy under these conditions of the free H<sub>2</sub> molecule

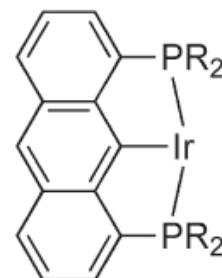
A wide range of modified PCP pincer ligands with varying electronic and steric properties have been explored synthetically and computationally



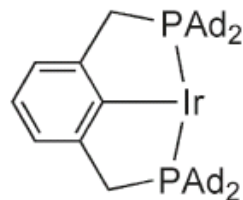
R = <sup>t</sup>Bu (3)  
iPr (5)



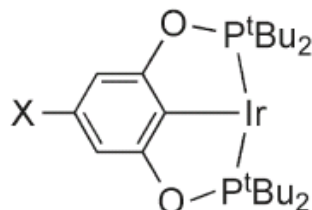
R = <sup>t</sup>Bu (6a)  
iPr (6b)



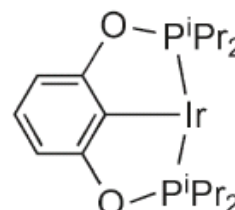
R = <sup>t</sup>Bu (7a)  
iPr (7b)



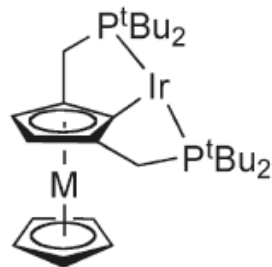
8  
Ad = 1-adamantyl



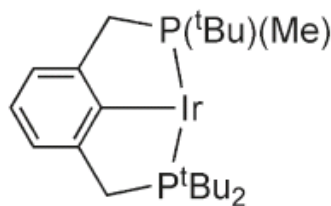
X = H (9a)  
3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (9b)



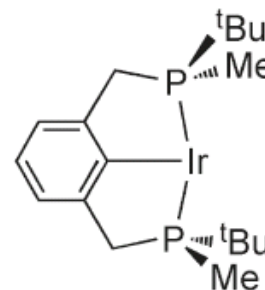
10



M = Fe (11)  
Ru (12)



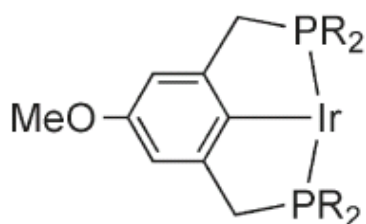
13



14



## (R4PCP)Ir

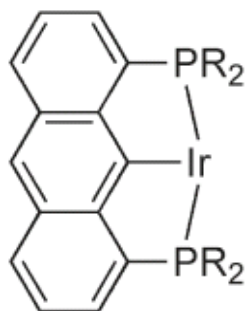


R = <sup>t</sup>Bu (6a)

<sup>i</sup>Pr (6b)

The **p-methoxy-substituted** complex (MeO-<sup>t</sup>Bu4PCP)IrH<sub>2</sub> (6a-H<sub>2</sub>) gave a 2-3-fold increase in turnovers for acceptorless dehydrogenation of cyclodecane as compared to 3-H<sub>2</sub>.

The **sterically less bulky** (MeO-<sup>i</sup>Pr4PCP)IrH<sub>4</sub> (6b-H<sub>4</sub>) was extremely effective in the acceptorless dehydrogenation of cyclodecane, with a total of 3050 turnovers obtained after 72 h under reflux conditions (201 °C)



R = <sup>t</sup>Bu (7a)

<sup>i</sup>Pr (7b)

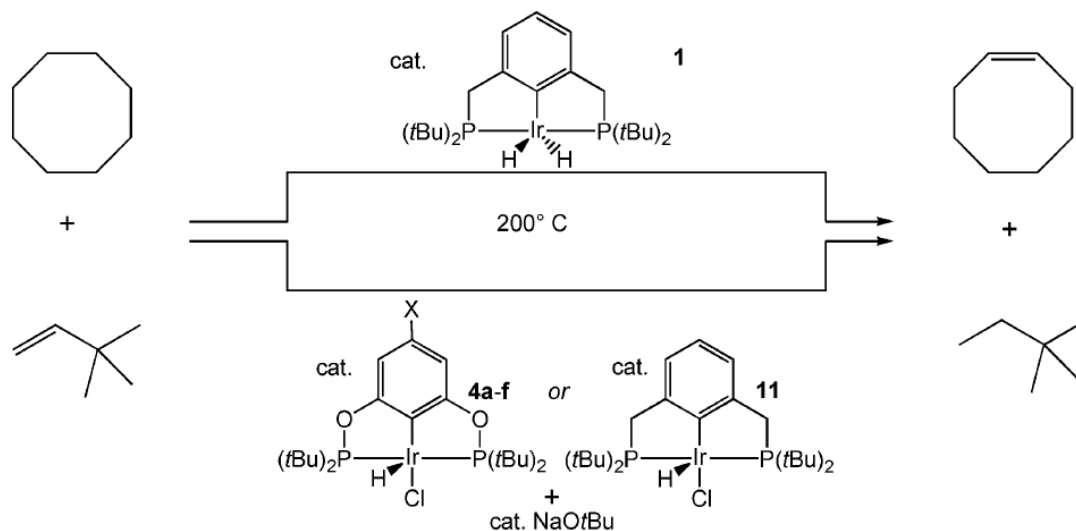
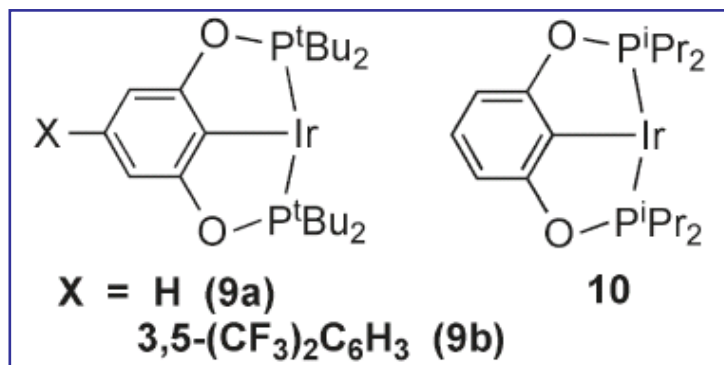
Thermally **very stable**:

Complex 7a-H<sub>2</sub> tolerated reaction temperatures up to **250 °C**

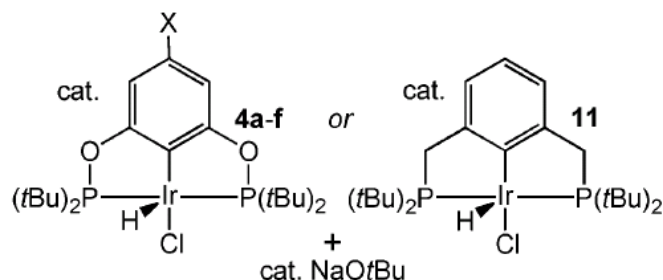
Complex 7a-H<sub>2</sub> significantly **less reactive** than 3-H<sub>2</sub> under comparable conditions

# One of the most notable modifications of the PCP ligand: Brookhart and Jensen

(R<sub>4</sub>POCOP)Ir



	X
<b>4a</b>	MeO
<b>4b</b>	Me
<b>4c</b>	H
<b>4d</b>	F
<b>4e</b>	C <sub>6</sub> F <sub>5</sub>
<b>4f</b>	Ar <sup>F</sup>



	X
<b>4a</b>	MeO
<b>4b</b>	Me
<b>4c</b>	H
<b>4d</b>	F
<b>4e</b>	C <sub>6</sub> F <sub>5</sub>
<b>4f</b>	Ar <sup>F</sup>

**Table 1.** TONs for the Transfer Dehydrogenation of COA and TBE Catalyzed by **4a–f** and **11** Plus NaOtBu Obtained at 200 °C and the COE:1,3-COD Product Ratio<sup>a</sup>

	<b>4</b> ( <i>p</i> -X=)						
	<b>a</b> MeO	<b>b</b> Me	<b>c</b> H	<b>d</b> F	<b>e</b> C <sub>6</sub> F <sub>5</sub>	<b>f</b> Ar <sup>F</sup>	<b>11</b> H
8 min	806	811	922	840	1150	1162	156
(COE/COD) <sup>b</sup>	(100/0)	(100/0)	(99/1)	(99/1)	(94/6)	(94/6)	(100/0)
31 min	1226	1087	1194	1108	1401	1424	198
(COE/COD) <sup>b</sup>	(93/7)	(95/5)	(93/7)	(93/7)	(90/10)	(89/11)	(100/0)
178 min	1564	1356	1514	1380	1699	1735	216
(COE/COD) <sup>b</sup>	(86/14)	(87/13)	(86/14)	(85/15)	(83/17)	(82/18)	(100/0)
918 min	1674	1413	1512	1465	1863	1893	212
(COE/COD) <sup>b</sup>	(83/17)	(87/13)	(86/14)	(85/15)	(80/20)	(79/21)	(100/0)
2398 min	1904	1484	1583	1530	2041	2070	227
(COE/COD) <sup>b</sup>	(81/19)	(86/14)	(84/16)	(84/16)	(78/22)	(76/24)	(100/0)
6170 min	2017	1488	1609	1605	2175	2186	230
(COE/COD) <sup>b</sup>	(78/22)	(86/14)	(83/17)	(83/17)	(75/25)	(75/25)	(100/0)
20 305 min	2047	1485	1603	1633	2170	2210	230
(COE/COD) <sup>b</sup>	(78/22)	(85/15)	(83/17)	(82/18)	(75/25)	(75/25)	(100/0)

<sup>a</sup> Average of three runs, based on conversion of TBE determined by <sup>1</sup>H NMR, 3030 TO = 100% conversion, all reactions performed under an argon atmosphere. <sup>b</sup> Determined by <sup>1</sup>H NMR, the sum of COE and COD double bonds equals TON of TBE within 2% difference.

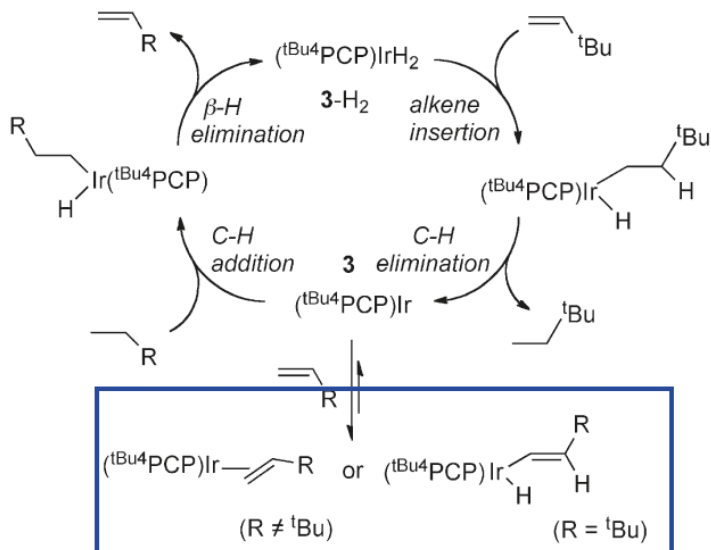
(R<sub>4</sub>PCP)Ir

Vs.

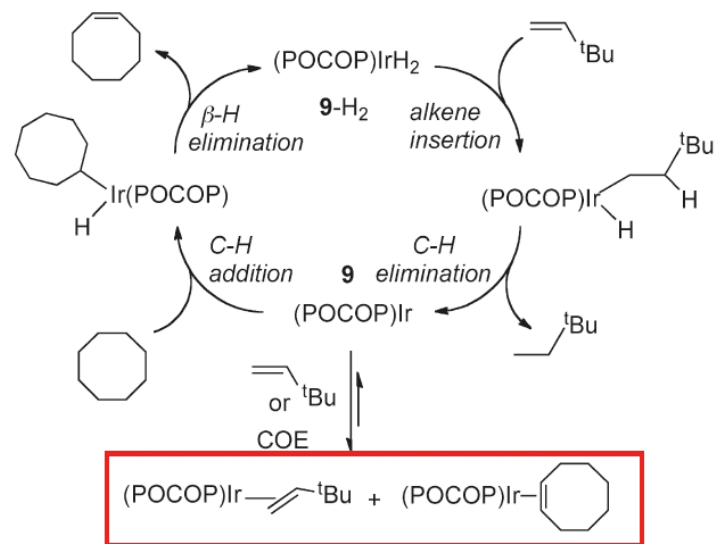
(R<sub>4</sub>POCOP)Ir

(tBu<sub>4</sub>PCP)Ir reversibly reacts with TBE to give a **vinyl C-H addition Product**  
(tBu<sub>4</sub>POCOP)Ir forms a **π-coordinated complex**

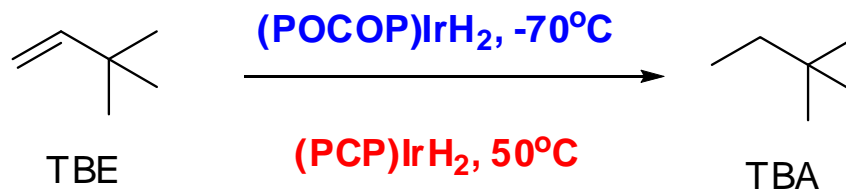
Scheme 1. Proposed Mechanism of *n*-Alkane/TBE Transfer Dehydrogenation by 3-H<sub>2</sub>



Scheme 3. Proposed Mechanism of COA/TBE Transfer Dehydrogenation by 9



Alkene hydrogenation by 9b-H<sub>2</sub> is much more facile than by 3-H<sub>2</sub>



## Geometric Differences:

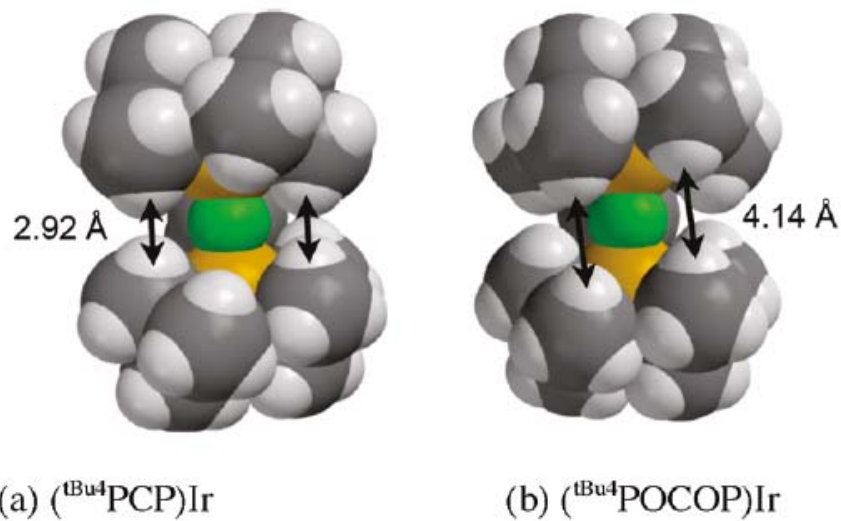
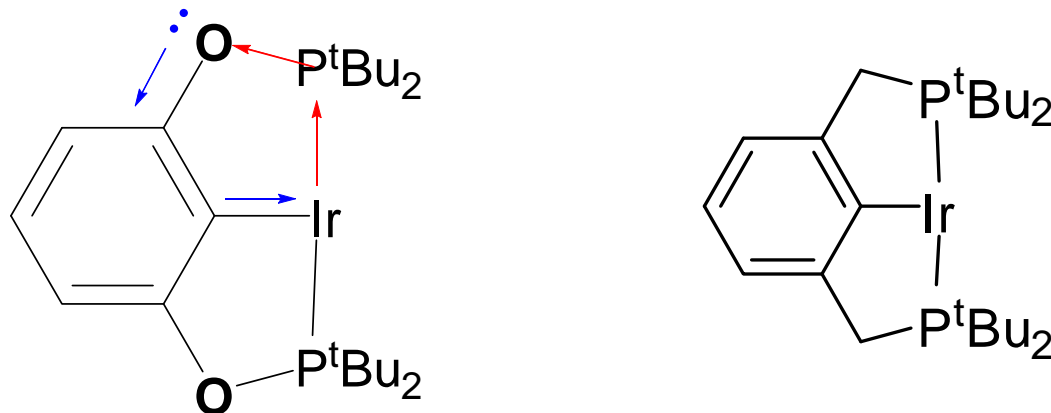


Figure 3. Geometric comparisons between (<sup>t</sup>Bu<sub>4</sub>PCP)Ir and (<sup>t</sup>Bu<sub>4</sub>POCOP)Ir (DFT-optimized structures).<sup>65,76</sup>

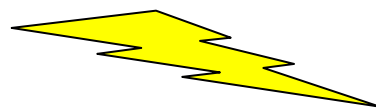
**(POCOP)Ir is much less sterically hindered than that of (PCP)Ir**

## Electronic Differences:



The iridium center in 9a is calculated to be very slightly more electron-rich than that in 3

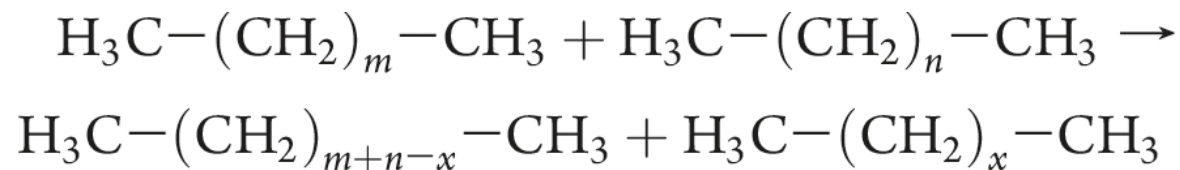
**Geometric**



**Electronic**

## Alkane Metathesis : disproportionation or molecular distribution

potential applications in fuel and bulk chemical production



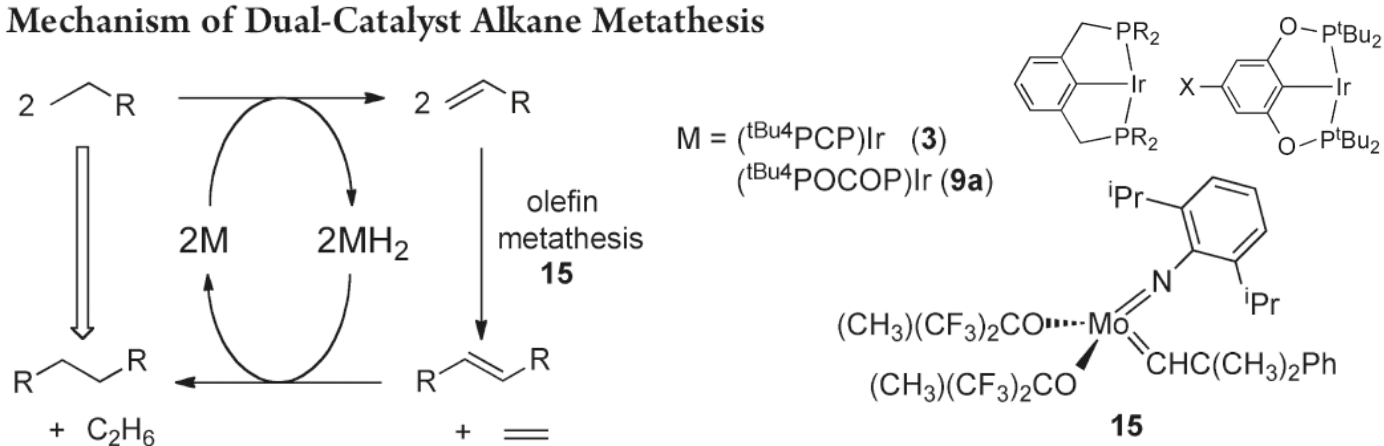
1973 Burnett and Hunghe

Platinum/alumina : alkane transfer-dehydrogenation catalyst

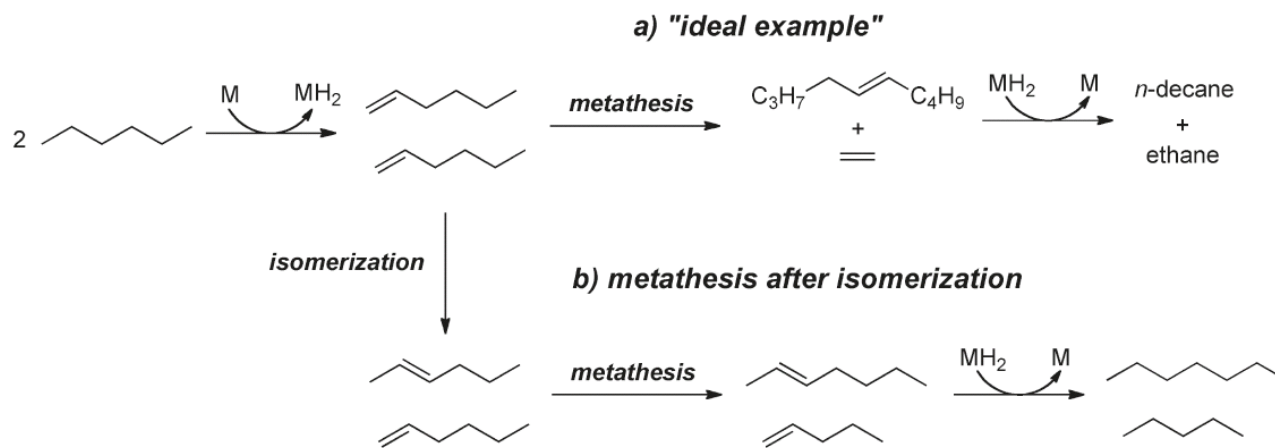
Tungsten oxide/silica: metathesis of resulting olefins

# 2006 Goldman and Brookhart

## Proposed Mechanism of Dual-Catalyst Alkane Metathesis

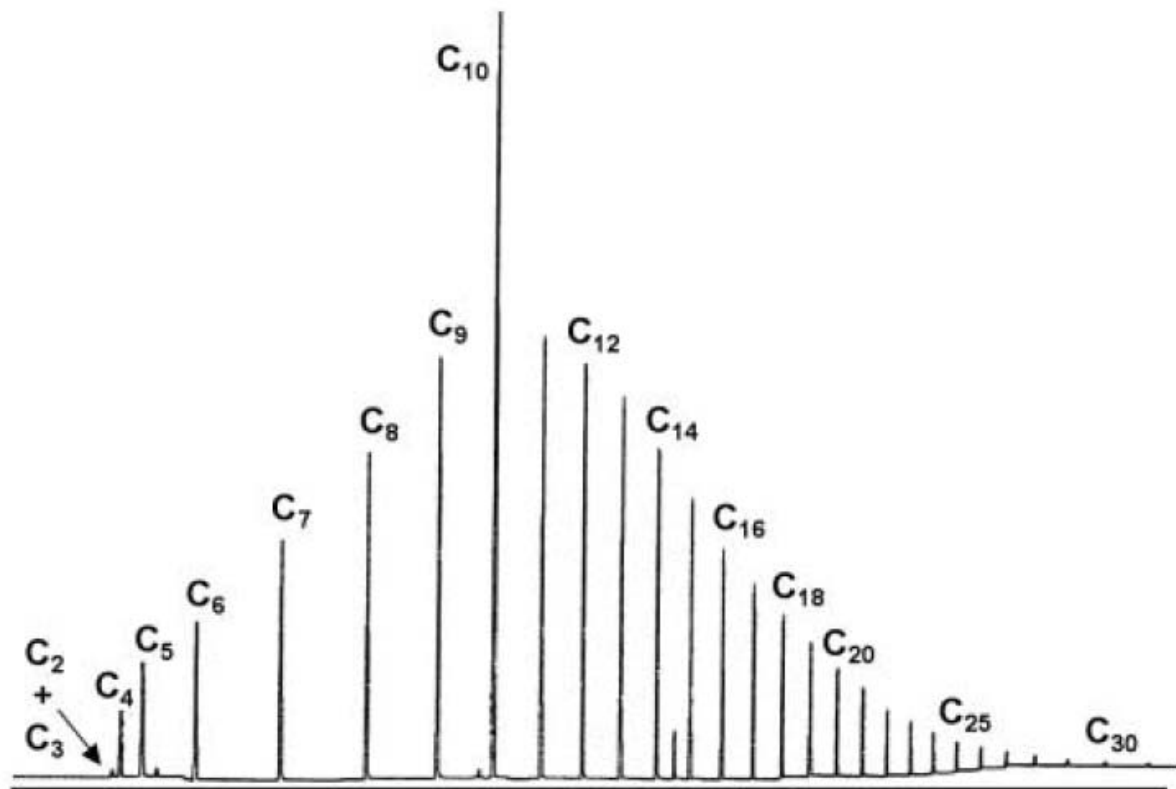


Scheme 5. Product Formation Pathways for *n*-Hexane Metathesis: (a) Ideal Pathway To Produce *n*-Decane and Ethane Selectively, (b) Possible Pathway for Formation of *n*-Pentane and *n*-Heptane





**Fig. 4.** GC trace of product mixture resulting from the metathesis of *n*-decane (solvent) by **2b**-H<sub>4</sub> and Re<sub>2</sub>O<sub>7</sub>/Al<sub>2</sub>O<sub>3</sub> after 9 days at 175°C (see Table 3).



How to avoid secondary metathesis, which decreases the overall selectivity

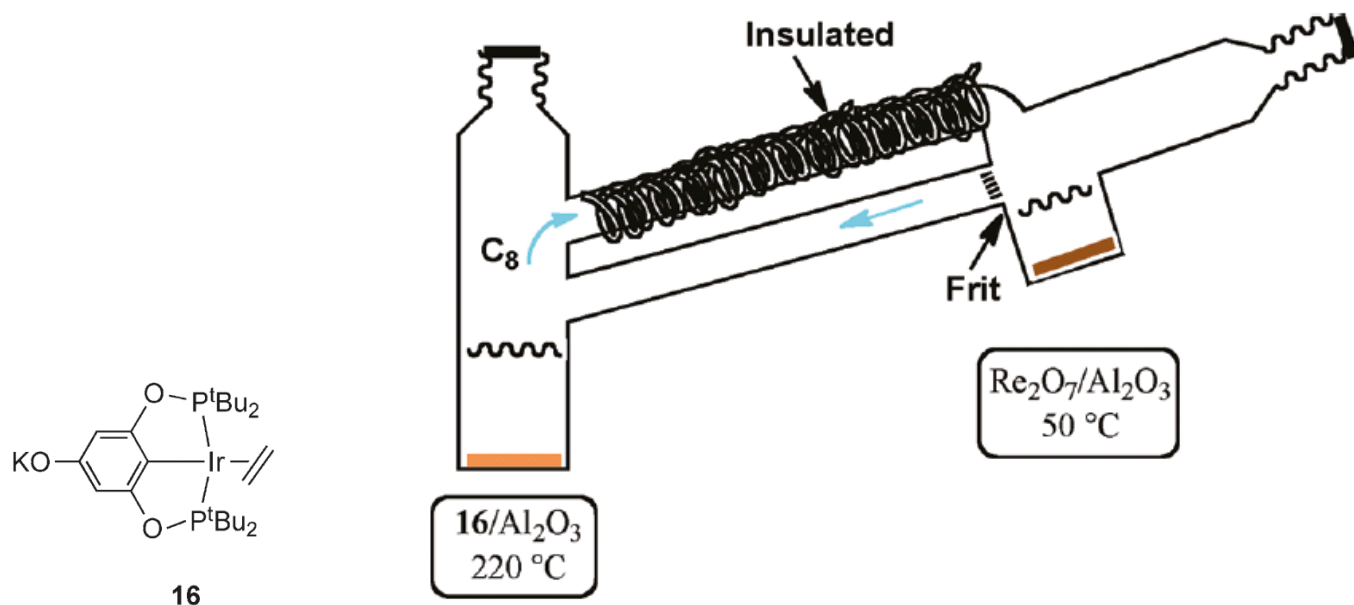
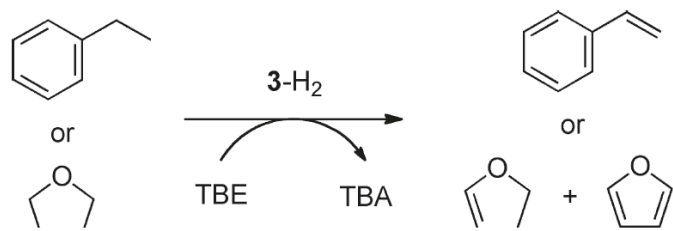


Figure 5. Two-pot system for alkane metathesis.

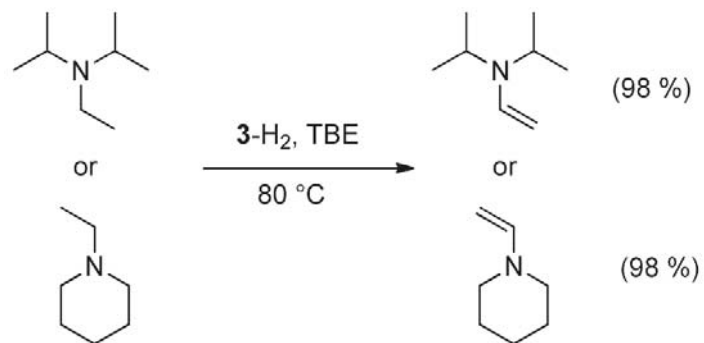
During n-octane metathesis using the two-pot apparatus, the only observed products of secondary metathesis were very small quantities of n-C<sub>15</sub>H<sub>32</sub> and n-C<sub>16</sub>H<sub>34</sub>

## Dehydrogenation Involving Heteroatoms:

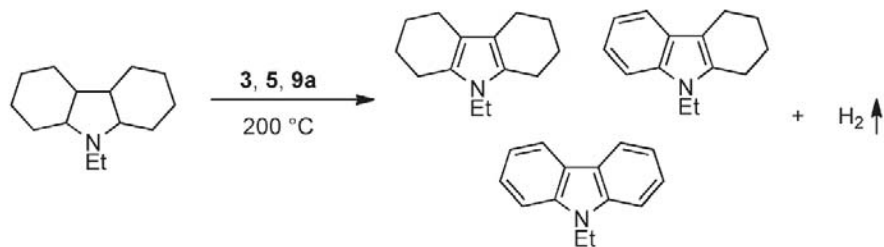
Kaska and Jensen



Goldman

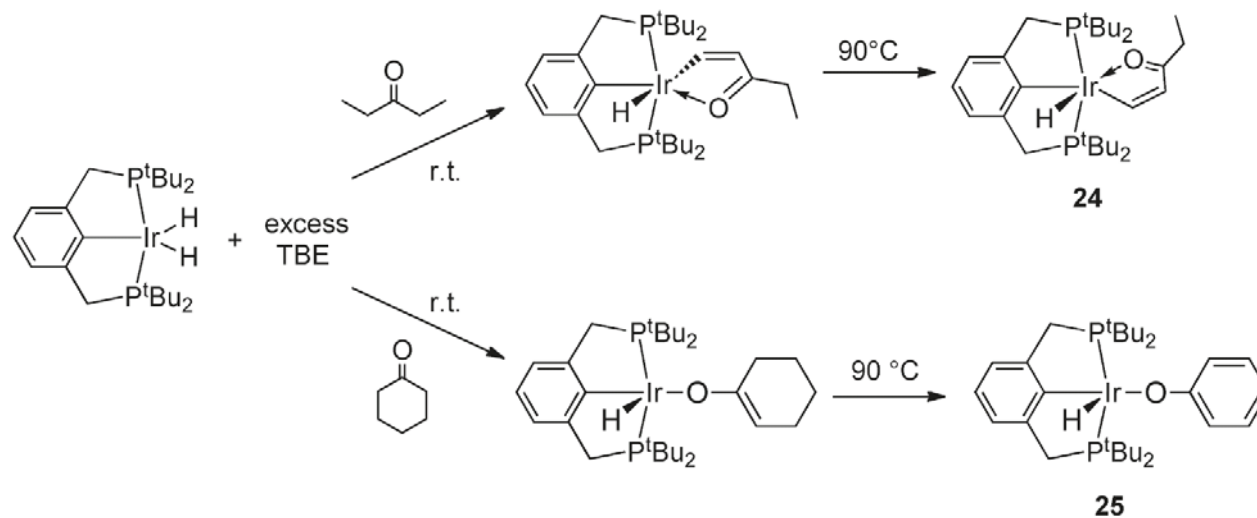


Jensen

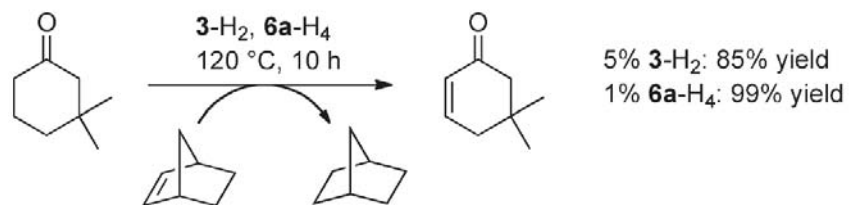


# Goldman

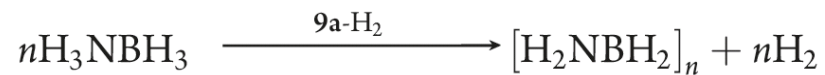
## Dehydrogenation of 3-Pentanone and Cyclohexanone



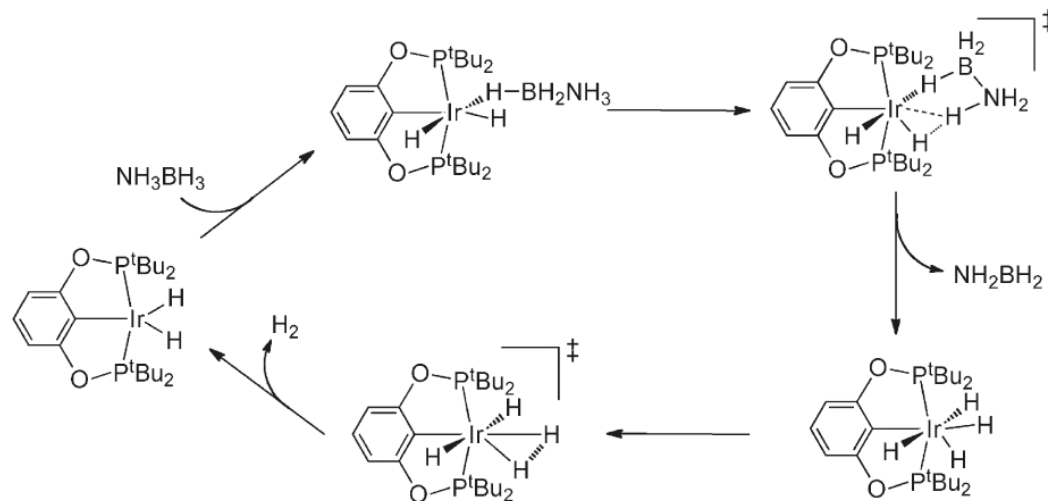
only stoichiometric reactions were observed



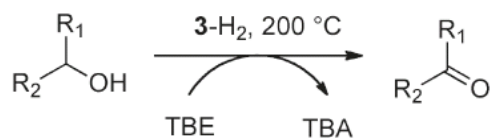
# Dehydrogenation of Amine-Boranes



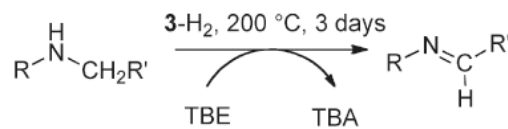
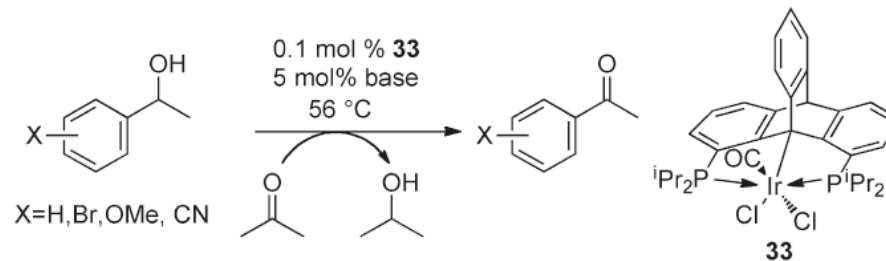
## Proposed Mechanism of Ammonia–Borane Dehydrogenation by 9a-H<sub>2</sub>



# Dehydrogenation of C-N and C-O Linkages

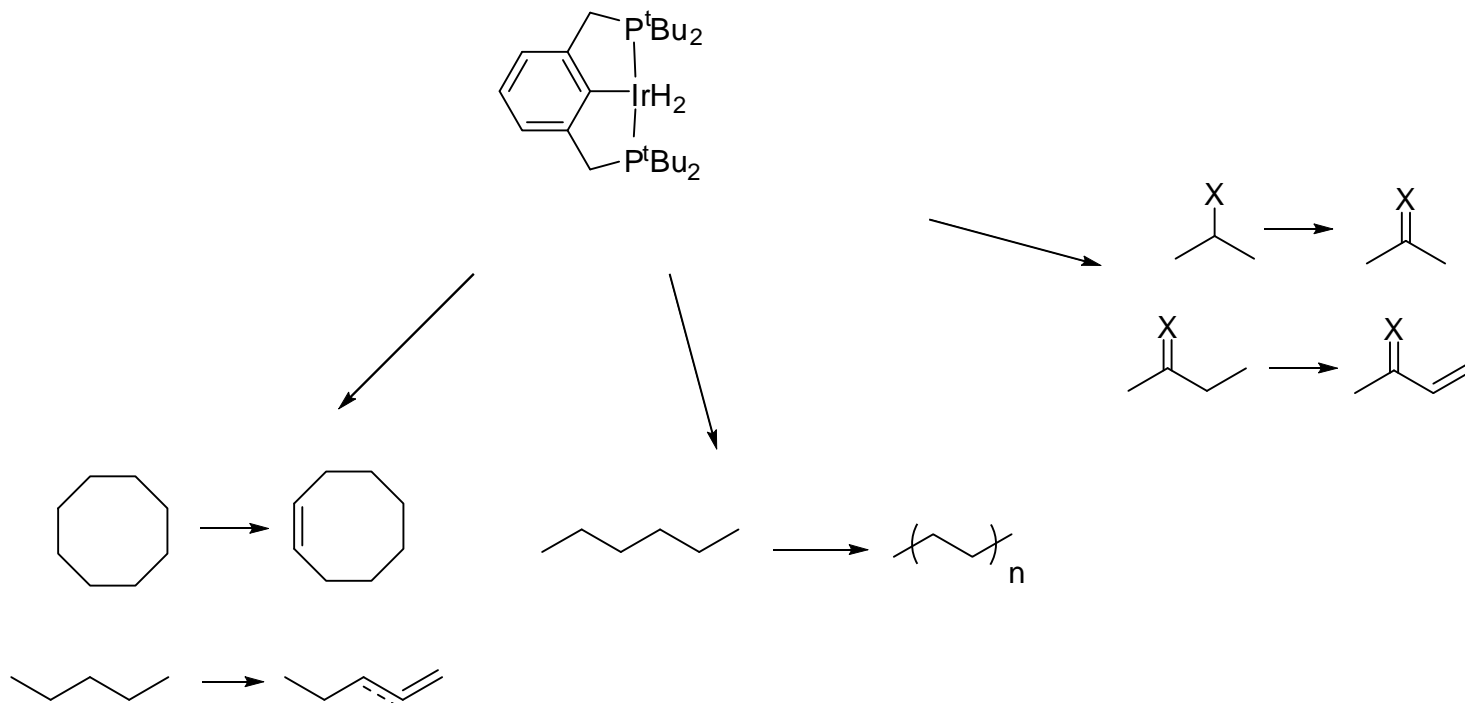


Substrate	Product	Yield
		> 99 %
		> 99 %
		> 99 %



Product	Yield
	72 %
	77 %
	53 %

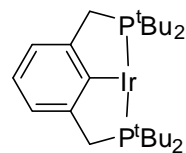
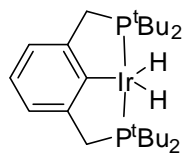
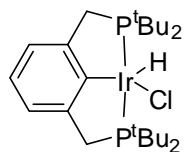
# Conclusion



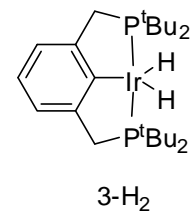
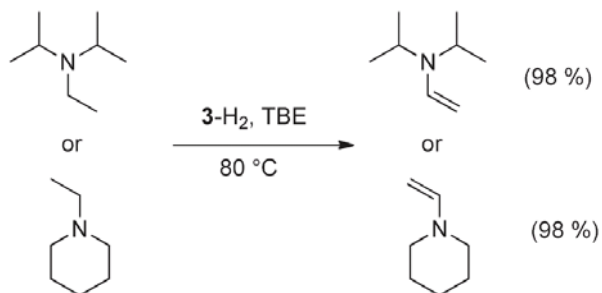
**Thanks**



Count valence electrons for each complex:



Why these reactions have such a selectivity?



Propose a mechanism of following reaction: no need to explain selectivity of product a and b

