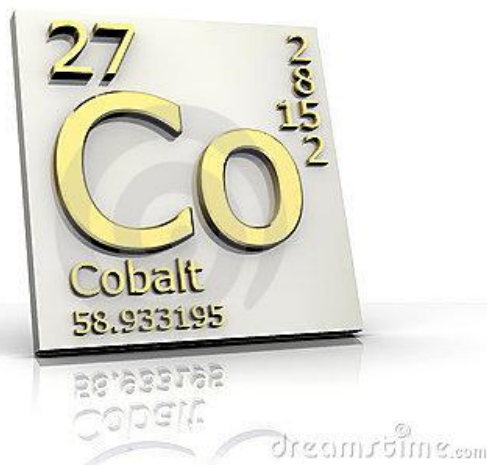


Department of Chemistry and Biochemistry, University of Bern

Topic review

Cobalt Catalysed Organic Reactions



*Group of
Prof. Philippe Renaud*

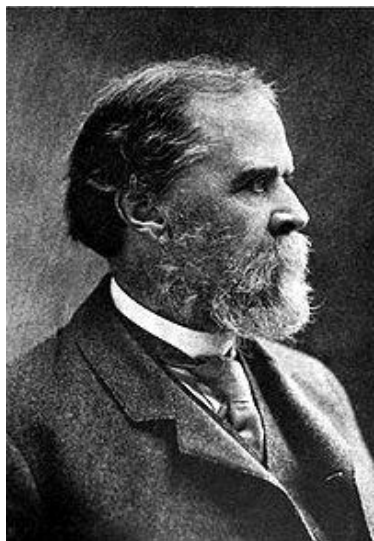
Andrey S. Kuzovlev

29.01.2015

- *‘ . . . we invite the attention of chemists to a class of salts which for beauty of form and color, and for abstract theoretical interest, are almost unequaled either among organic or inorganic compounds.’*

Wolcott Gibbs and Frederick Genth

“Researches of the ammoniacobalt bases”



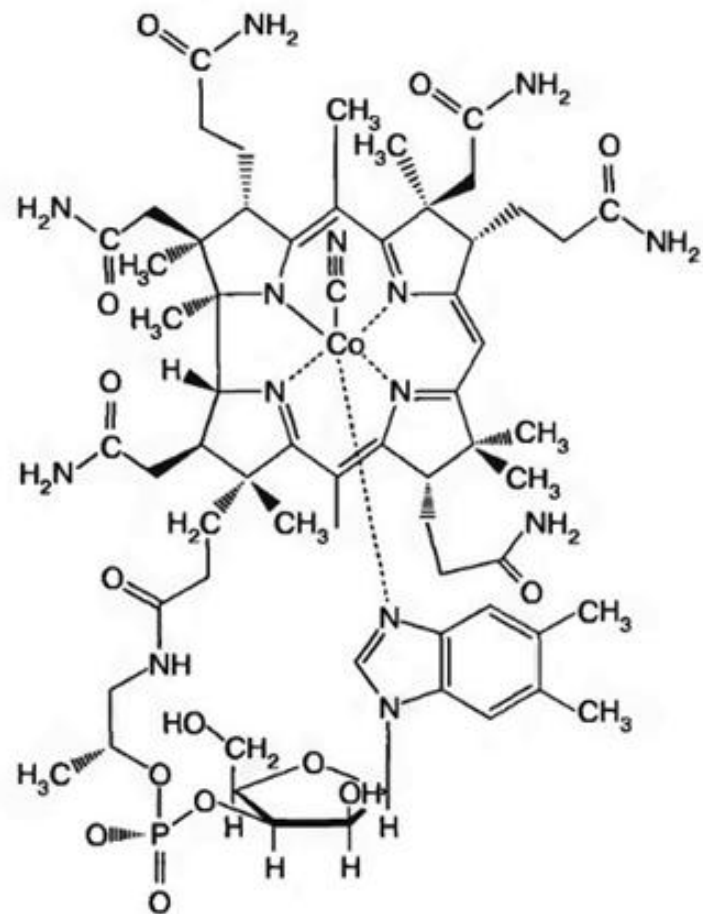
“Kobold” – Friendly Ghost

- Ancient Egyptians used cobalt ores to color glass more than 1300 B.C.E. (piece of such glass found in the tomb of Pharaoh Tutankhamen).
- Cobalt ores were also used to color Chinese pottery from the Tang (600–900 C.E.) and Ming (1350–1650 C.E.) dynasties.
- Elemental cobalt was first isolated by the Swedish chemist Georg Brandt in 1735.
- Espionage provided one of the earliest documented uses of cobalt compounds (invisible ink by the Paris-based American agent Silas Deane in 1776–1777).



Cobalt Coordination Compounds

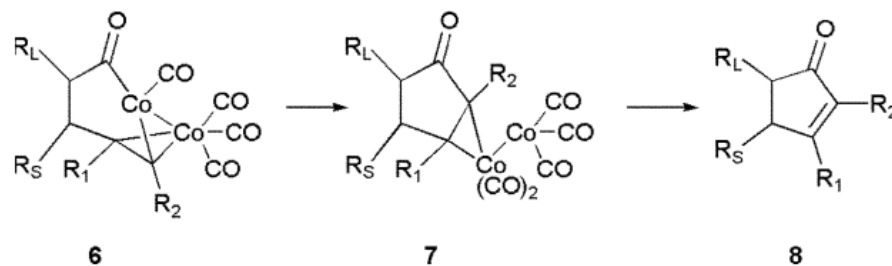
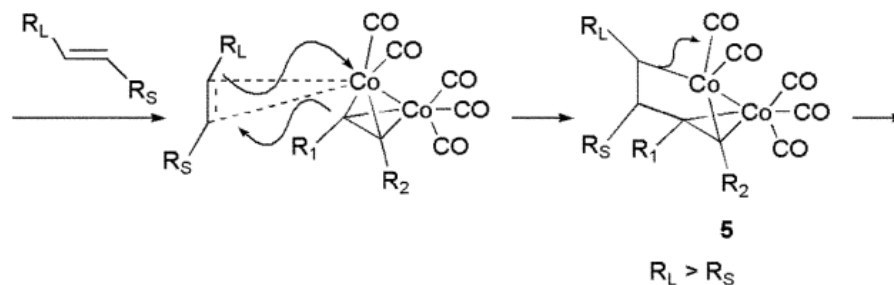
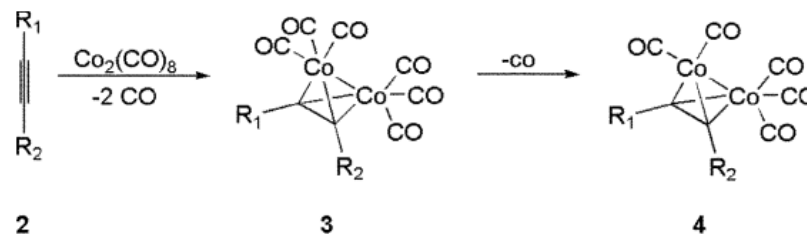
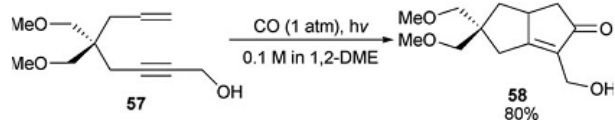
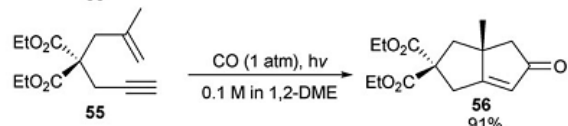
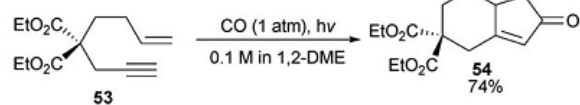
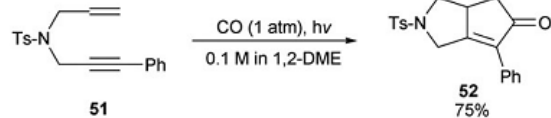
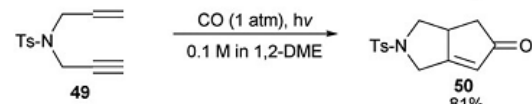
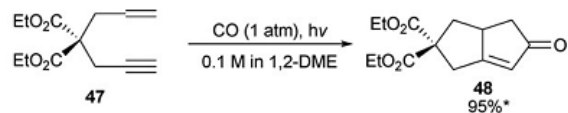
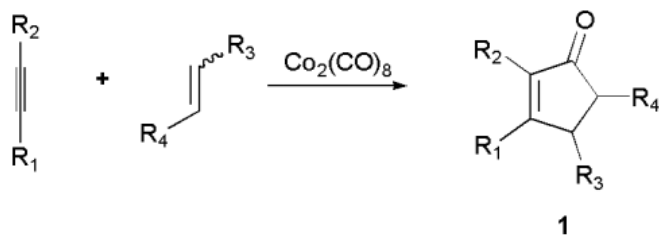
- A common oxidation state for simple compounds is +2, for coordination compounds +3
- Co(II) complexes: d^7 electron configuration, generally six- or four-coordinated, often high spin, distorted octahedral or tetrahedral geometries
- Co(III) complexes usually have a d^6 low-spin electronic configuration almost exclusively six-coordinated, with octahedral or distorted octahedral geometries
- Low oxidation state chemistry of cobalt is dominated by organometallic complexes containing C-donor ligands
- Vitamin B₁₂ contains five-coordinate Co(I) in a square pyramidal N₅ coordination environment



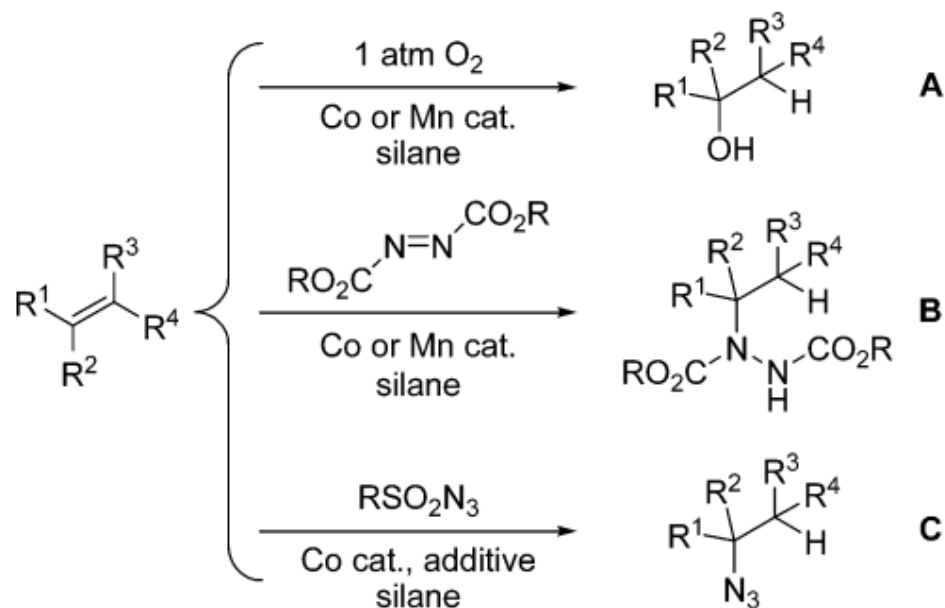
Contents

- *Pauson-Khand Reaction*
- *Hydroazidation and Hydrohydrazination*
- *Cyclizations:*
 - *Co(II)-Salen-Catalyzed Cyclopropanation*
 - *Co(II)-Porphyrin-Catalyzed Cyclopropanation*
 - *[6+2] Cycloaddition*
- *C-H-functionalization*
- *Formation of Unsymmetrical Biaryls*
- *Heck-Type Reaction*
- *Iodolactonization*

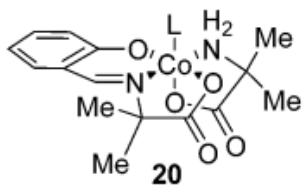
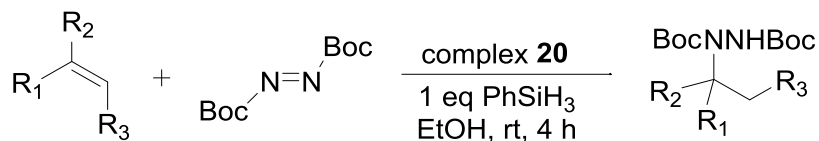
Pauson-Khand Reaction



Hydration, Hydrohydrazination, Hydroazidation



Hydrohydrazination

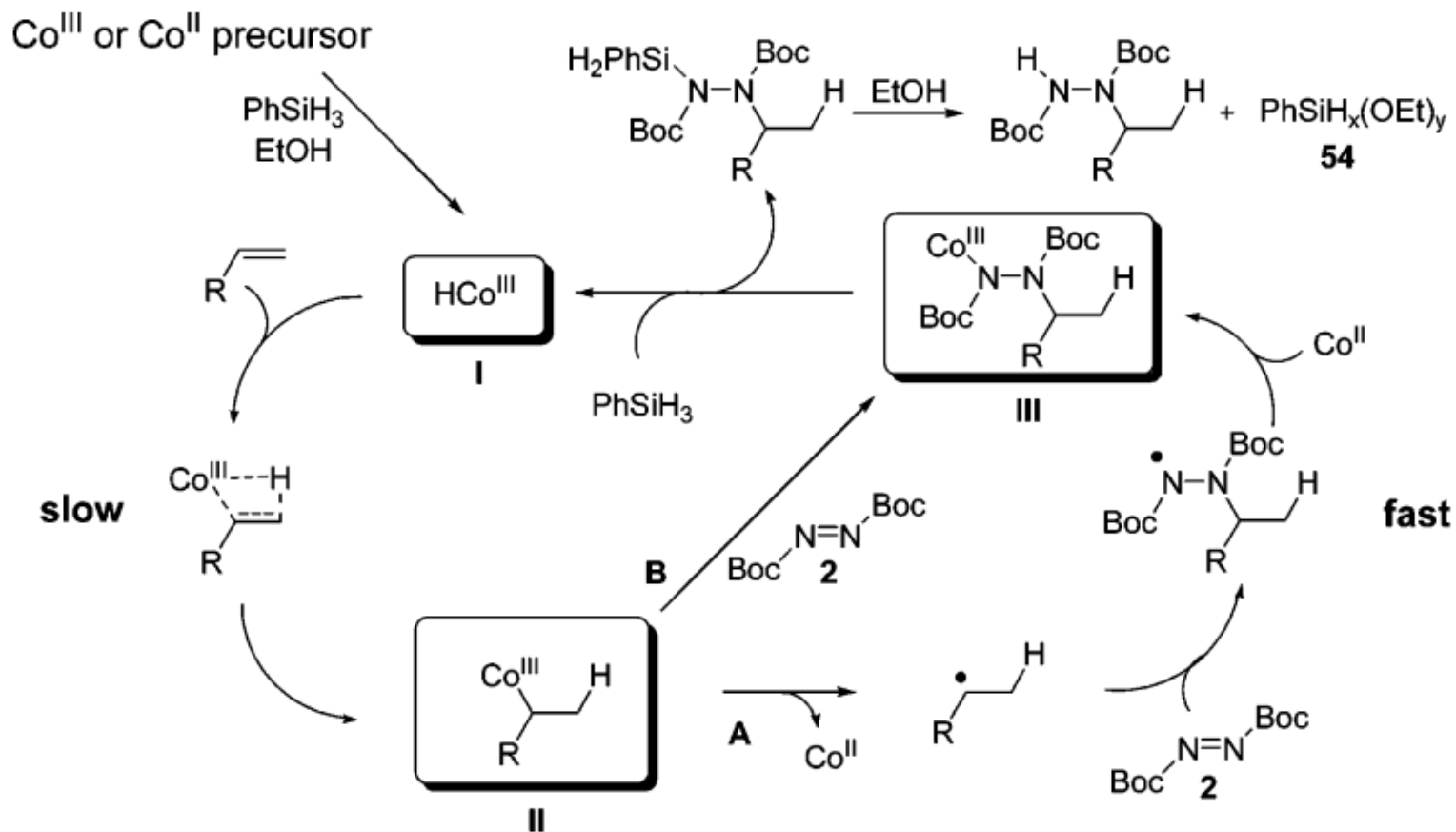


Key features

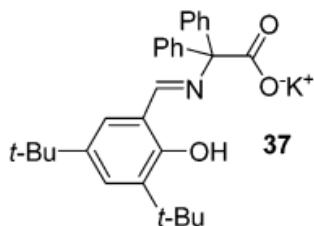
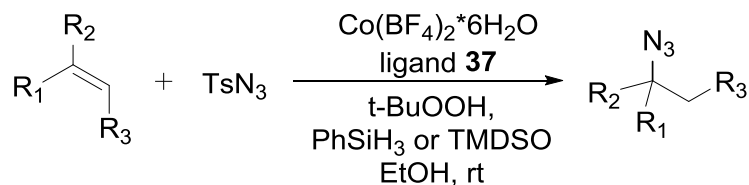
- High Markovnikov selectivity
- Strong activating effect of α -phenyl
- Large functional group tolerance

Entry	Alkene	Product	Yield (%)
1			73 (d.r. 1:1)
2			76
3			90
4		Polymerized	<5
5			60
6			74
7			66

Mechanism of Hydrohydrazination Reaction



Hydroazidation

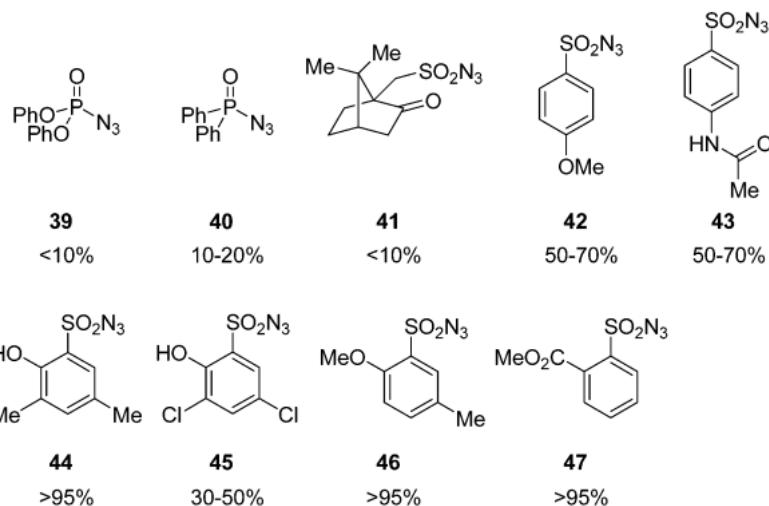
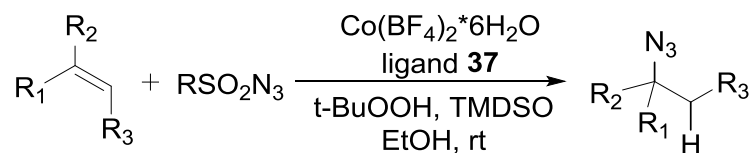


Limitations

- Substrate with stabilizing group in conjugation do not react
- Full conversion could not be obtained with di- and trisubstituted olefins

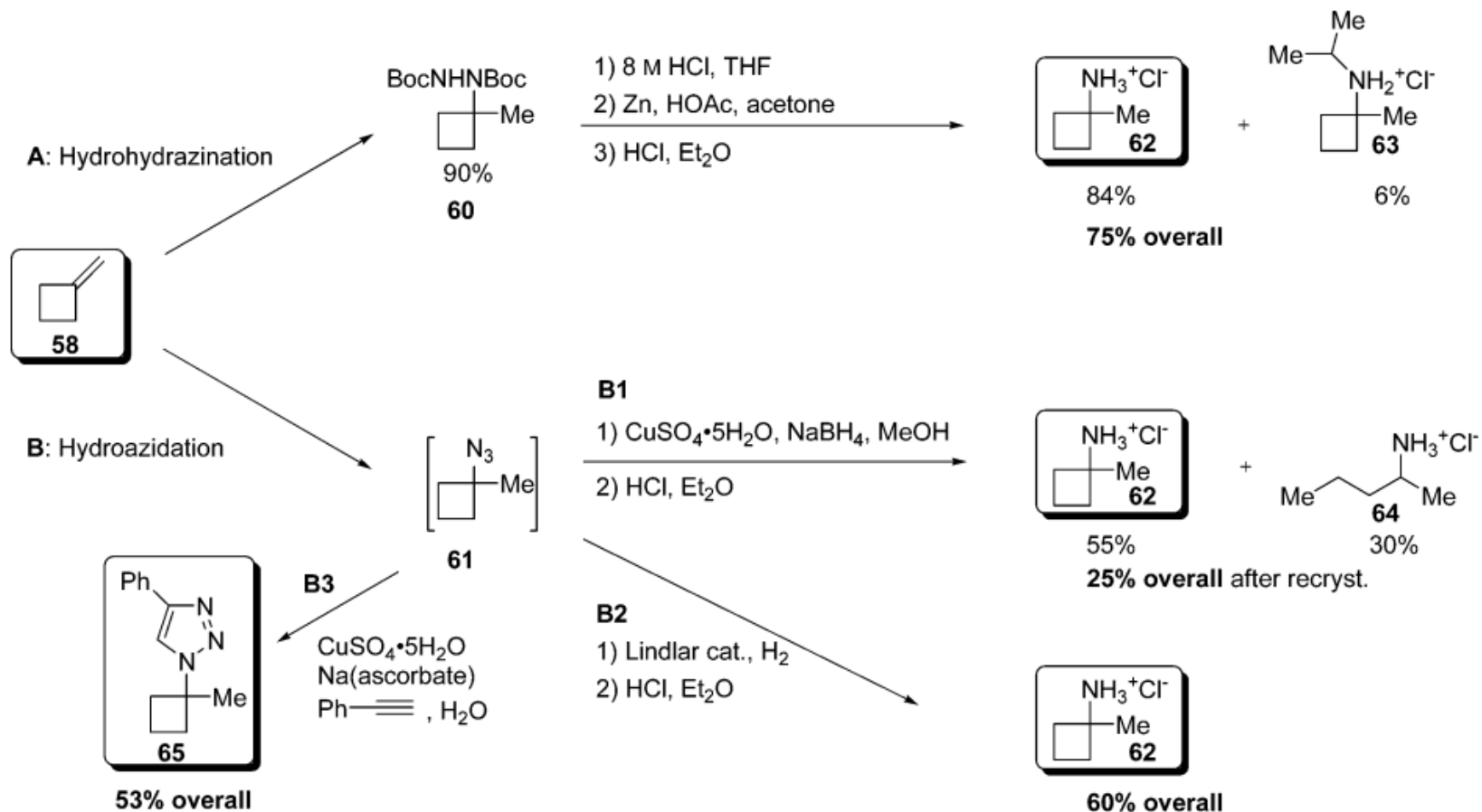
Entry	Alkene	Product	Yield (%) PhSiH ₃ /TMDSO
1			90 / 86
2			65 / 62
3			35 / 39
4			75 / 77
5			89 / 76
6			63 / 48

Hydroazidation



entry	alkene	product	Yield ^a with TsN ₃	Yield ^b with 46	Yield ^c with 47
1			86%	94%	91%
2			67%	19%	44%
3			39%	<20%	28%
4			58%	89%	91%
5			40%	64%	76%
6			48%	83%	79%

Hydrohydrazination and Hydroazidation for Amination

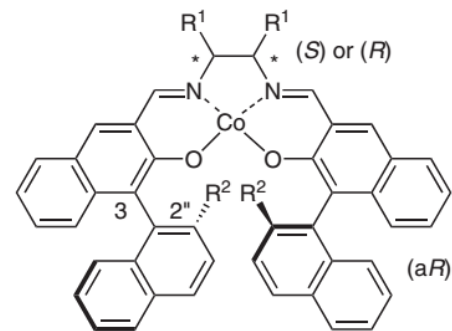
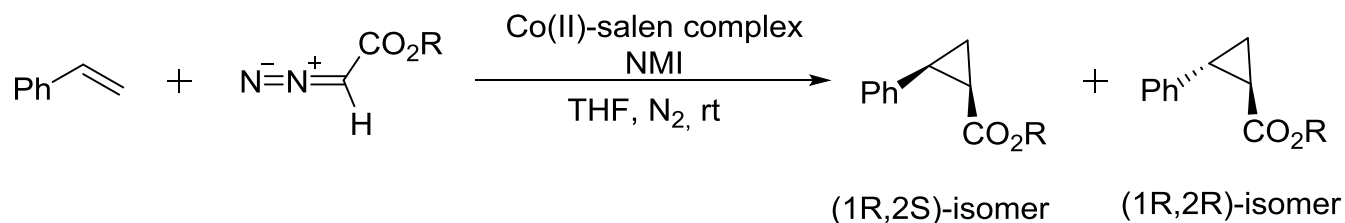


Hydrohydrazination, Hydroazidation

Conclusion

- New direct access to hydrazines and azides from olefins
- First successful use of an “oxido-reductive” approach for the hydroamination of unactivated olefins
- Key to successful hydroazidation:
 - using sulfonyl azides as nitrogen sources
 - Discovery of the activating effect of t-BuOOH
- Detailed mechanistic investigation (with catalytic cycle)was presented
- High yields under operationally simple reaction conditions

Co(II)-Salen-Catalyzed Cyclopropanation



- 9:** R¹, R¹ = -(CH₂)₄- (R), R² = Ph
10: R¹, R¹ = -(CH₂)₄- (S), R² = Ph
11: R¹ = H, R² = Ph
12: R¹, R¹ = -(CH₂)₄- (R), R² = Me

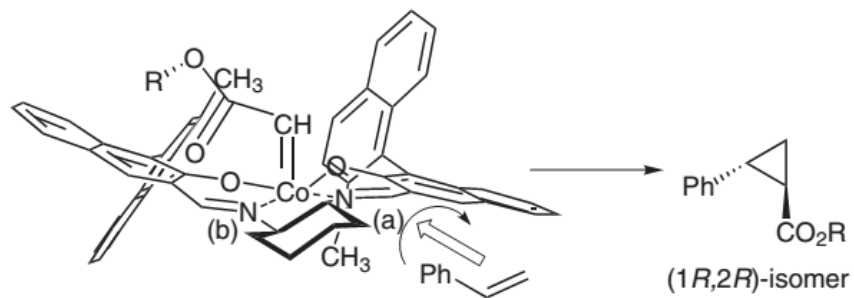
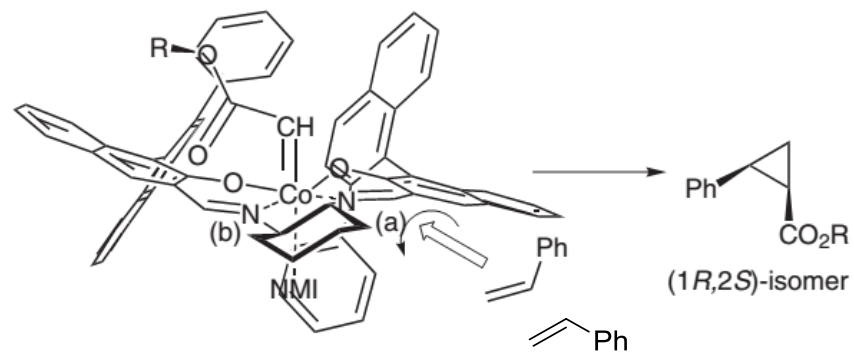
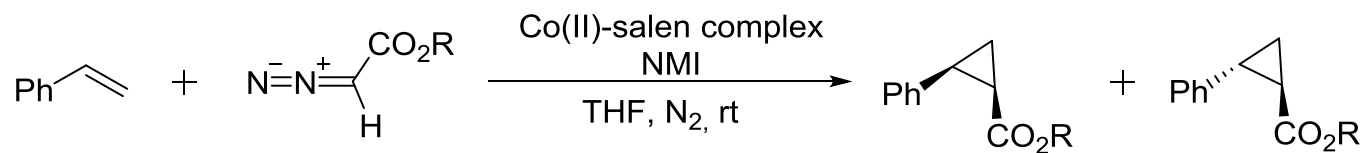
Entry	Cat.	THF/Styrene	R	Yield (%)	<i>cis:trans</i>	% ee (<i>cis</i>)
1 ^a	9	100/1	<i>t</i> -Bu	88	92:8	96 (1R, 2S)
2	9	100/1	<i>t</i> -Bu	89	98:2	98 (1R, 2S)
3	9	10/6	Et	quant	99:1	96 (1R, 2S)
4	9	10/1	<i>t</i> -Bu	90	98:2	98 (1R, 2S)
5	10	100/1	<i>t</i> -Bu	18	97:3	99 (1S, 2R)
6	11	10/1	<i>t</i> -Bu	25	97:3	2 (1S, 2R)
7	12	10/6	<i>t</i> -Bu	91	27:73	95 (1R, 2R) ^b
8	12	10/6	Et	quant	31:69	95 (1R, 2R) ^b

^a The reaction was carried out in the absence of NMI.

^b The ee of the *trans*-isomer.

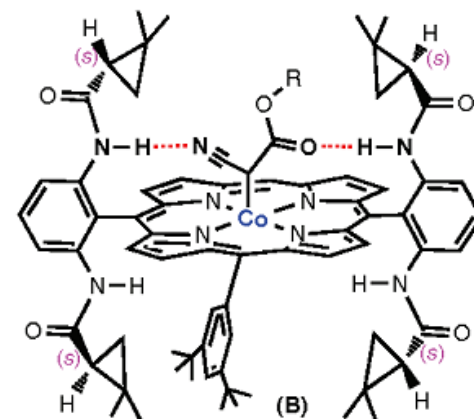
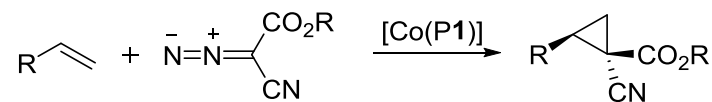
Tatsuya Uchida, Tsutomu Katsuki *Synthesis* **2006**, *10*, 1715-1723

Co(II)-Salen-Catalyzed Cyclopropanation

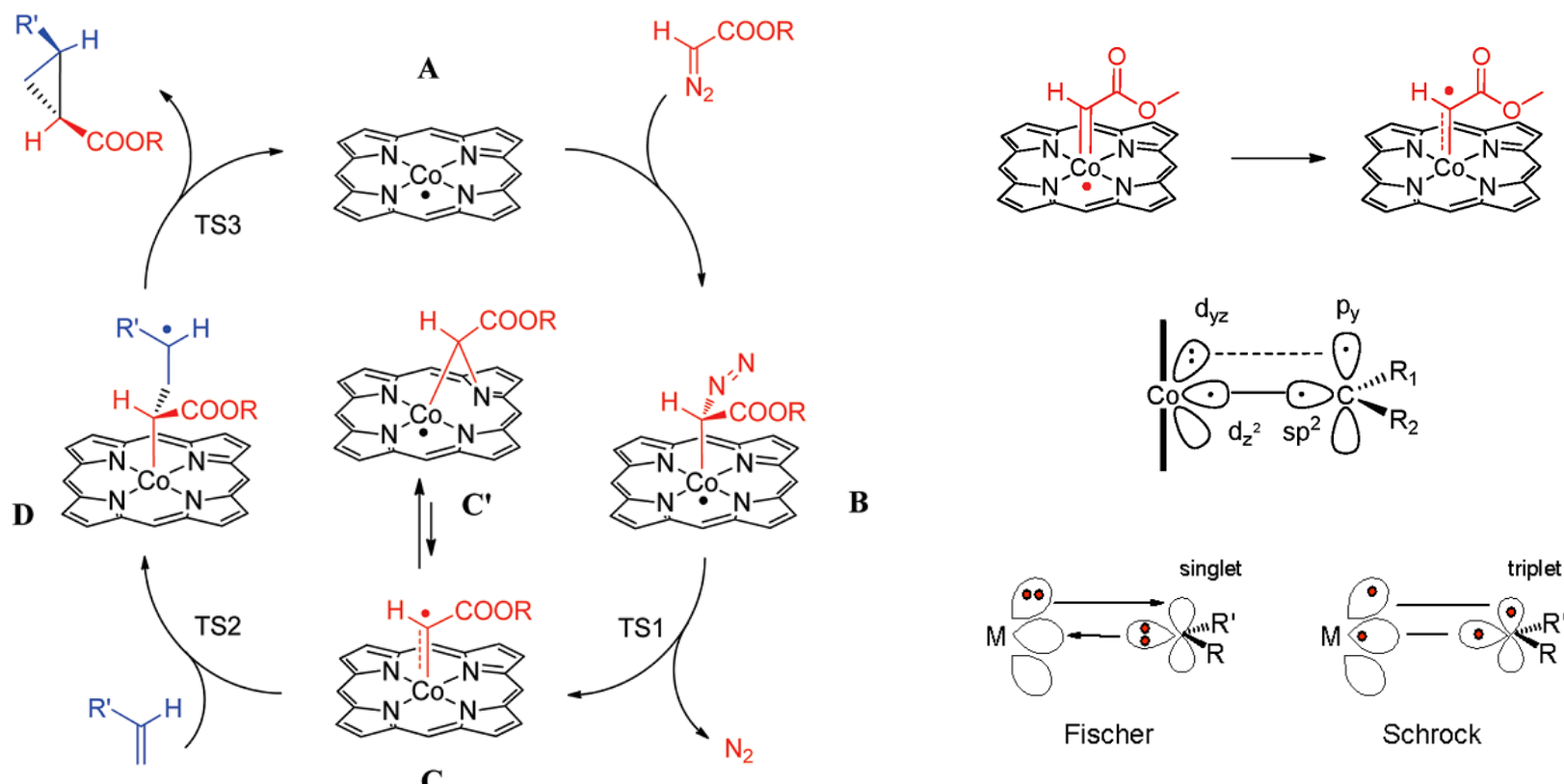


Co(II)-Porphyrin-Catalyzed Cyclopropanation

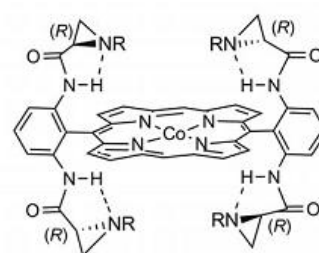
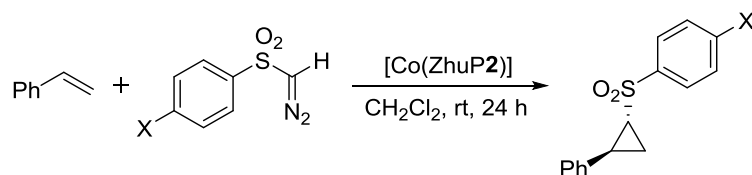
Entry	Cyclopropane	Yield (%)	E:Z	ee (%)	[α]
1		96	>99:1	98	(-)
2		88	>99:1	99	(-)
3		90	>99:1	98	(-)
4		90	>99:1	88	(-)
5		72	>99:1	82	(-)
6		72	>99:1	92	(-)
7		86	>99:1	82	(+)



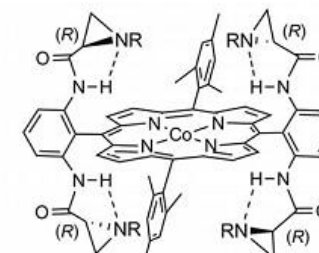
Co(II)-Porphyrin-Catalyzed Cyclopropanation 'Carbene Radical'



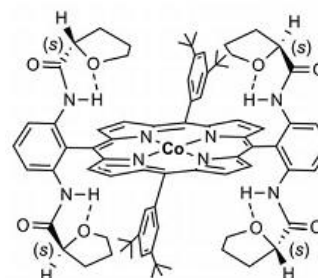
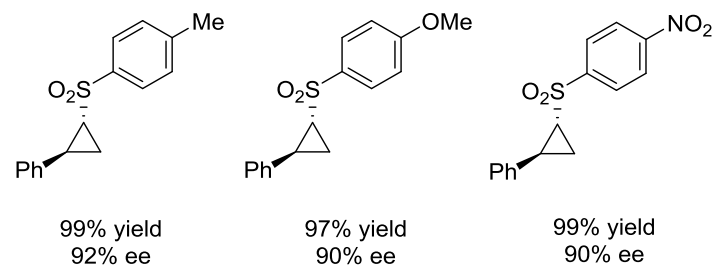
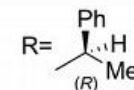
Co(II)-Porphyrin-Catalyzed Cyclopropanation



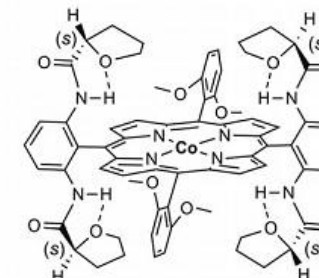
Co(GaoP1)
48% yield^[b], 19% ee^[c]



Co(GaoP2)
53% yield, 7% ee



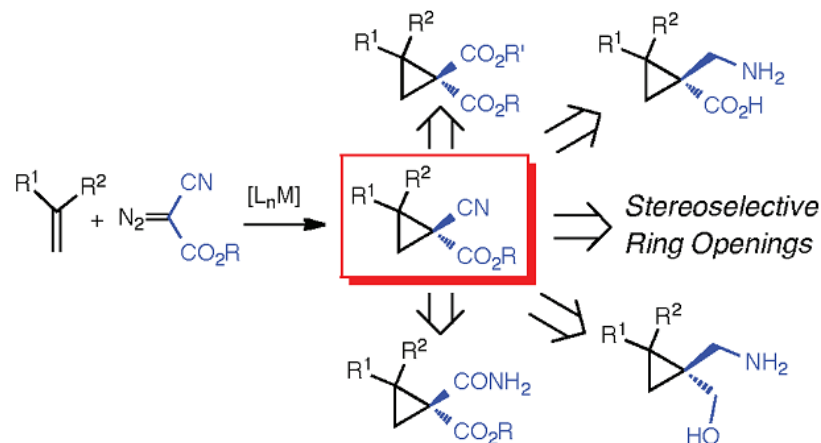
Co(ZhuP1)
30% yield, 54% ee



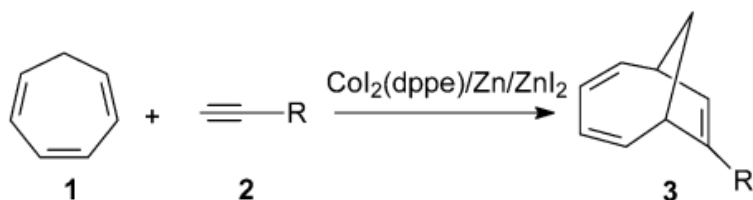
Co(ZhuP2)
99% yield, 92% ee

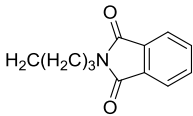
Co(II)-Porphyrin-Catalyzed Cyclopropanation Conclusion

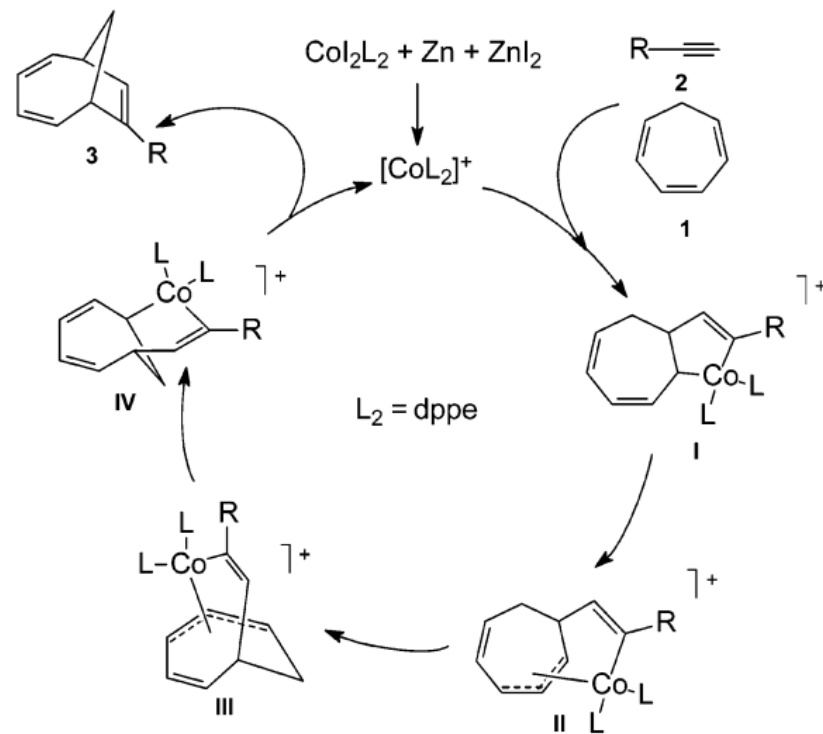
- One-electron-reduced Fisher-type carbene play a key role
- Rare example of the involvement of a ligand radical in organometallic catalysis
- High reactivity and diastereo- and enantioselectivity with acceptor/acceptor-substituted diazo reagents
- First example of metal-catalyzed asymmetric intermolecular cyclopropanation with diazosulfones
- Obtained nonracemic cyclopropanes a myriad of synthetic and biological applications



[6+2] cycloaddition

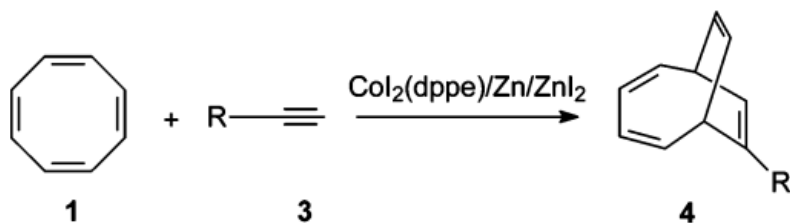


Entry	Ar	Yield/%
1	Ph	86
2	n-Bu	95
3	SiMe ₃	92
4	CH ₂ C(Me) ₂ CH ₂ Ac	96
5	CH ₂ CH ₂ OAc	83
6	(CH ₂) ₃ CN	90
7		82
8	CH ₂ SO ₂ Ph	50
9	CH ₂ SiMe ₃	65
10	CH ₂ OH	60

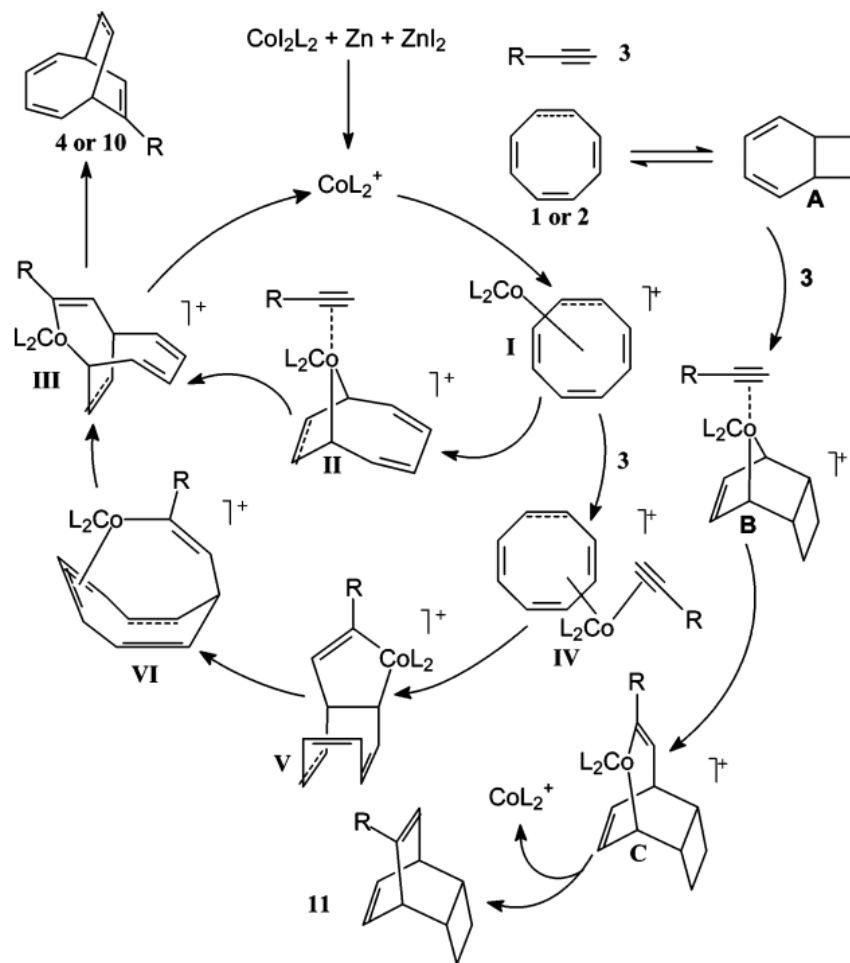


First enantioselective [6+2] cycloaddition
phenylacetylene to CHT with 91 % yield, 74 % ee

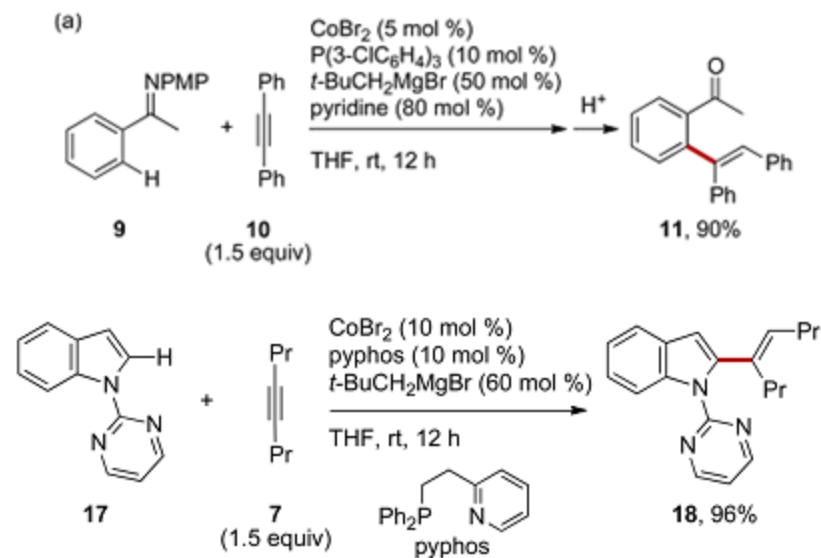
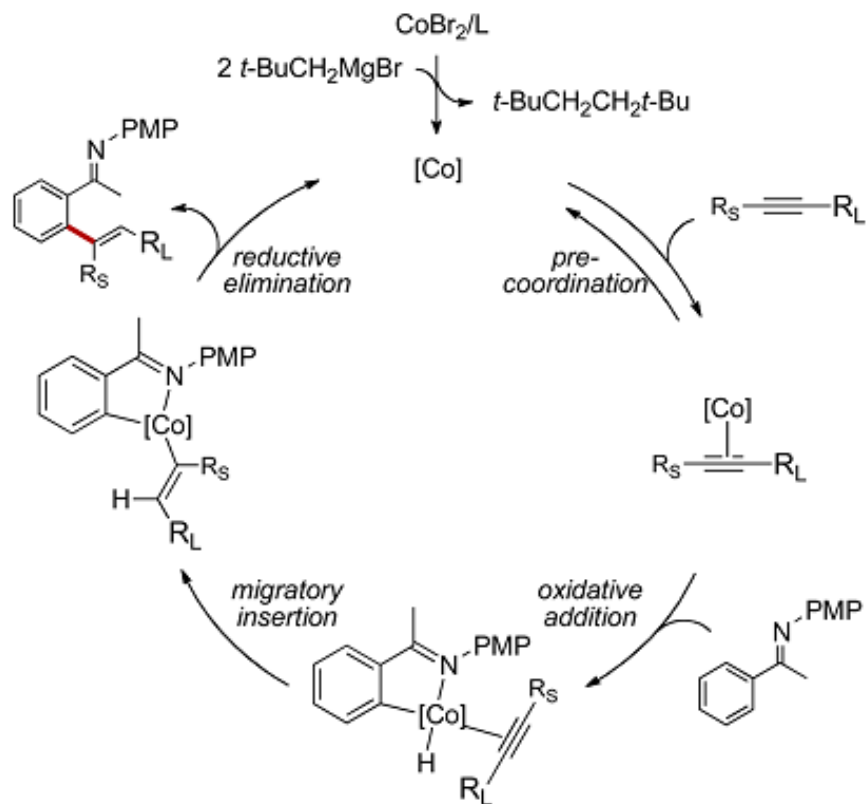
[6+2] cycloaddition



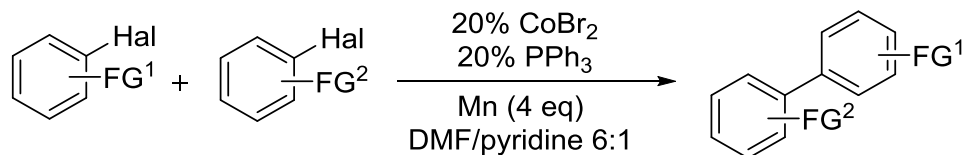
Entry	Ar	Yield/%
1	Ph	70
2	n-Bu	61
3	SiMe ₃	89
4	CH ₂ C(Me) ₂ CH ₂ Ac	75
5	CH ₂ CH ₂ OAc	56
6	(CH ₂) ₃ CN	88
7		94
8	CH ₂ SO ₂ Ph	71
9	CH ₂ OH	69



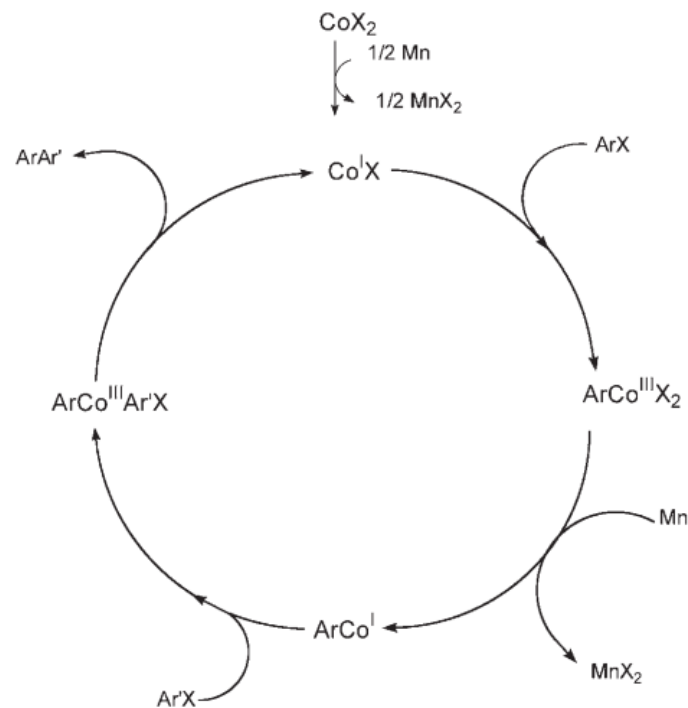
C-H – functionalization. Hydroarylation



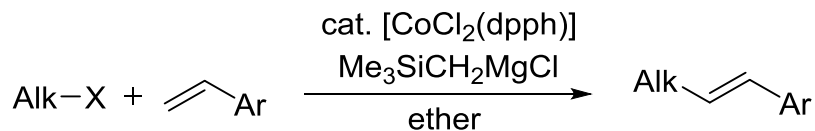
Formation of Aryl-Aryl(Heteroaryl) Compounds



Entry	Ar ¹ Hal	Ar ² Hal (HetArHal)	Ar ¹ -Ar ² Ar ¹ -HetAr (%)	Ar ² -Ar ² HetAr- HetAr (%)
1			88	10
2			84	6
3			72	10
4			73	24
5			60	17
6			94	2



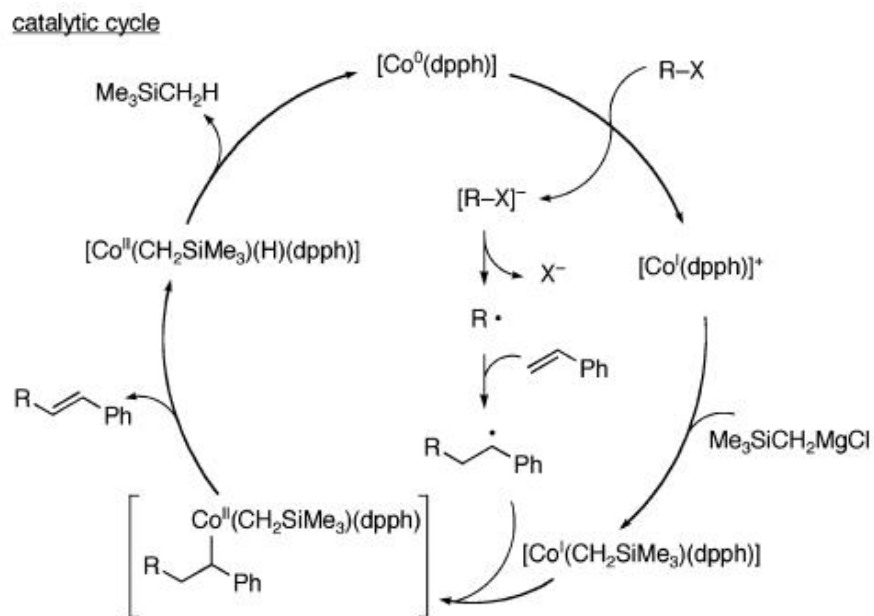
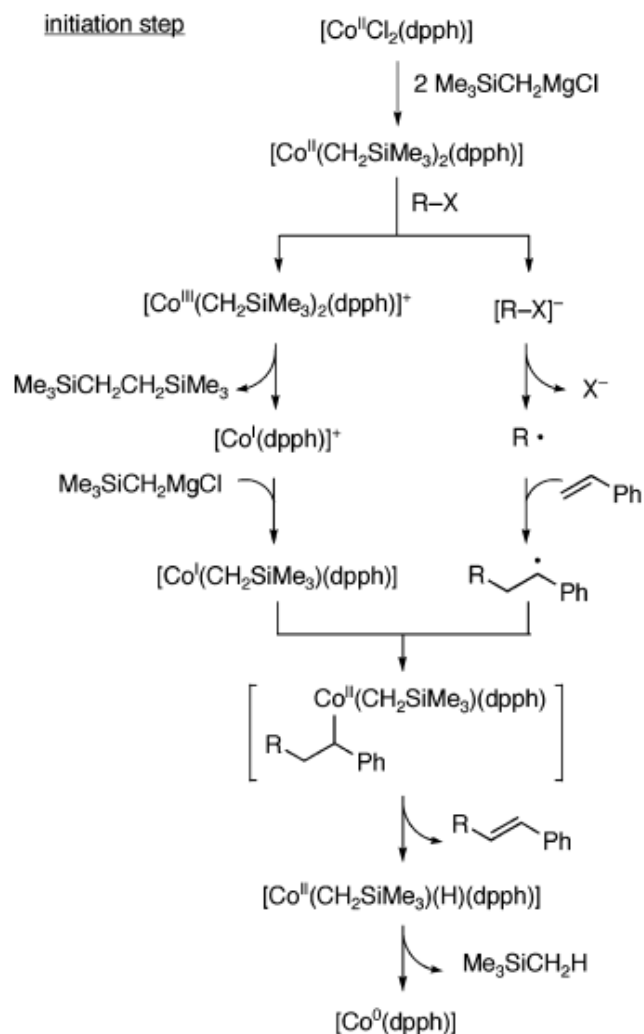
Cobalt-Catalyzed Heck-Type Reaction



Entry	Alk-X	Time/h	Temp//°C	Yield/%
1	n-C ₆ H ₁₃ CH(Br)CH ₃	8	20	73
2	n-C ₁₂ H ₂₅ Br	8	20	76
3	n-C ₁₂ H ₂₅ Br	3	35	71
4	n-C ₁₂ H ₂₅ I	3	35	57
5	n-C ₁₂ H ₂₅ Cl	3	35	74
6	Ad-Br	8	20	87
7	Ad-Cl	3	35	90
8	c-C ₆ H ₁₁ Cl	3	35	84
9	t-C ₄ H ₉ Br	8	20	11
10	t-C ₄ H ₉ Br	3	35	67
11	CH ₃ I	3	35	55

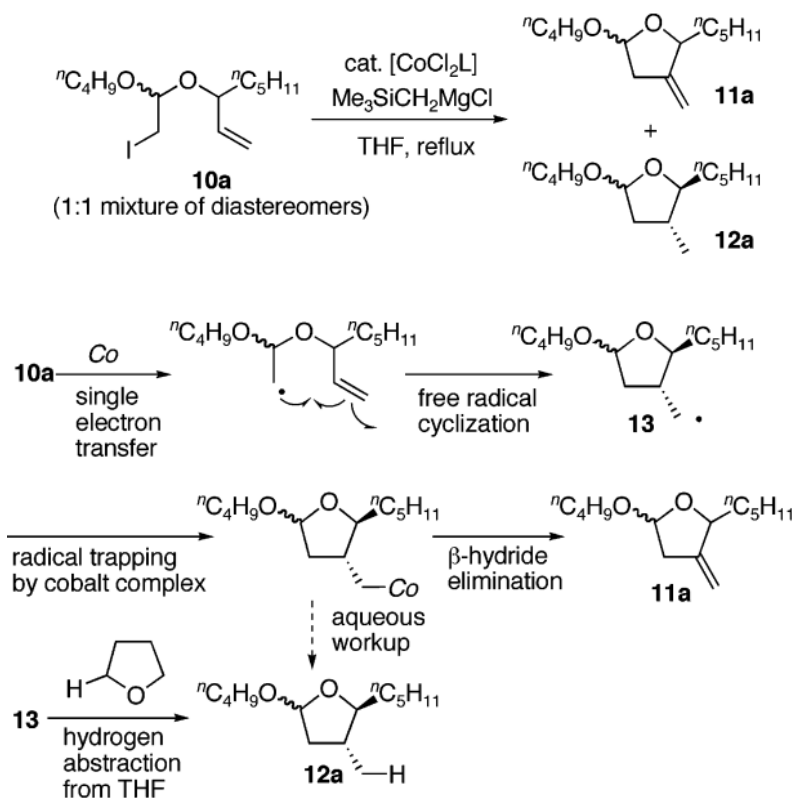
Entry	Ar	Yield/%
1	C ₆ H ₄ - <i>p</i> -Me	73
2	C ₆ H ₄ - <i>p</i> -Cl	76
3	C ₆ H ₄ - <i>m</i> -Cl	71
4	C ₆ H ₄ - <i>o</i> -Cl	57
5	C ₆ H ₄ - <i>p</i> -OMe	74
6	C ₆ H ₄ - <i>p</i> -CON(CH ₂ Ph) ₂	87
7	C ₆ H ₄ - <i>m</i> -CON(CH ₂ Ph) ₂	90
8	C ₆ H ₄ - <i>m</i> -COO-t-C ₄ H ₉	84

Cobalt-Catalyzed Heck-Type Reaction



Koichiro Oshima et al *J. Am. Chem. Soc.* **2006**, *128*, 8068-8077

Cobalt-Catalyzed Heck-Type Reaction. Cyclization

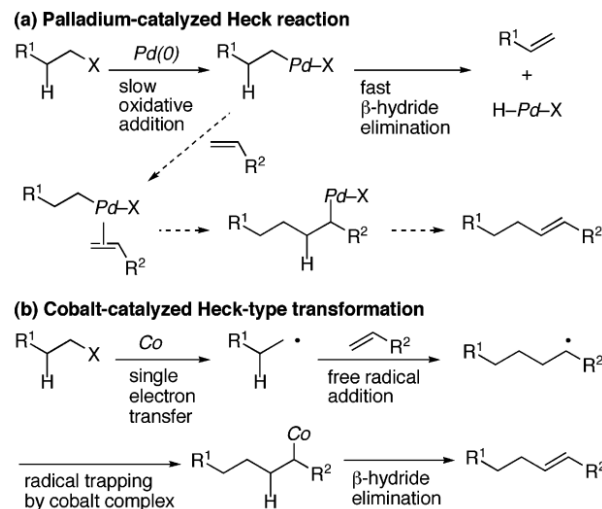


entry	substrate ^b	product	yield ^c
1	10b	11b	74% (67:33)
2	10c	11c	79%
3	10d	11d	94% (62:38)
4	10e	11e	91%
5	10f	11f	82%
6	10g	11g	82% (50:50)
7	10h	11h	58% with DPPB 66% with DPPP (63:37)

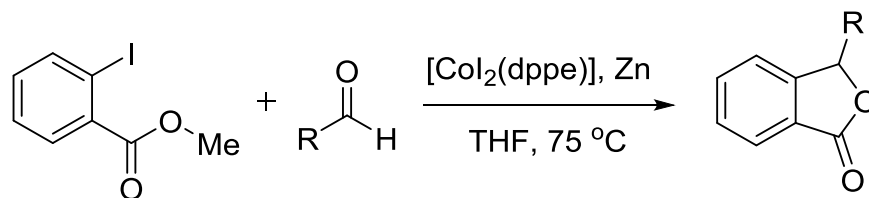
Cobalt-Catalyzed Heck-Type Reaction

Conclusions

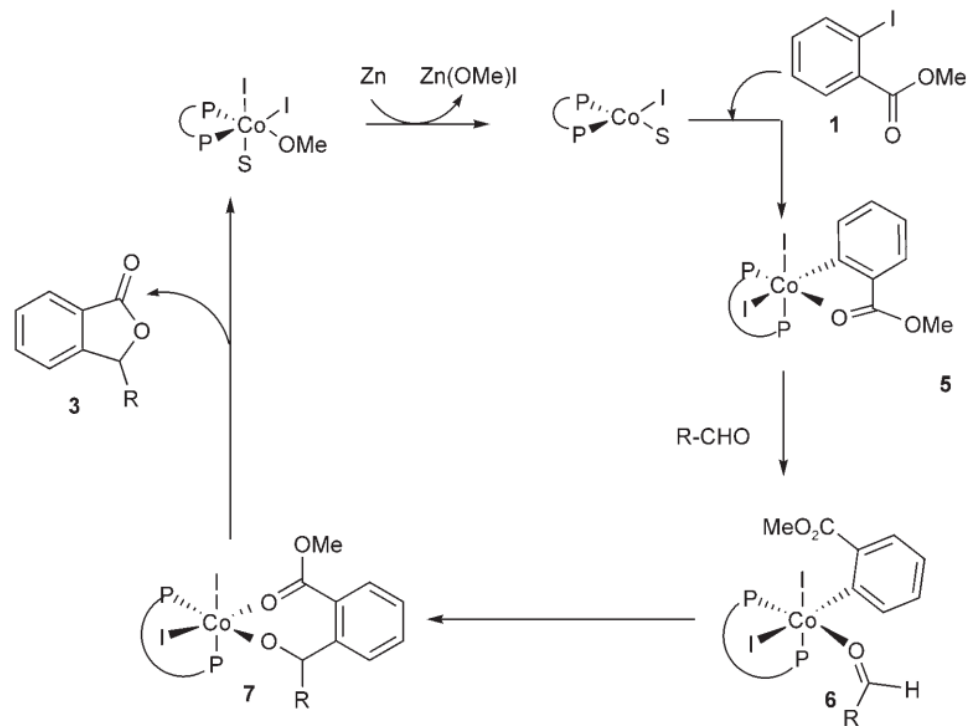
- $\text{CoCl}_2(\text{dpph})$ efficiently catalyzes a Heck-type reactions
- Mechanism is different from the palladium catalyzed one
- Reaction going via a radical pathway
- β -elimination is excluded
- Allowing to employ alkyl halides
- Procedure is simple and reaction tolerates a variety of functionalities
- Alkyl chlorides proved to be excellent alkyl sources in Heck-type reactions



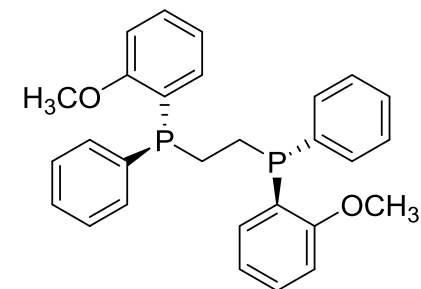
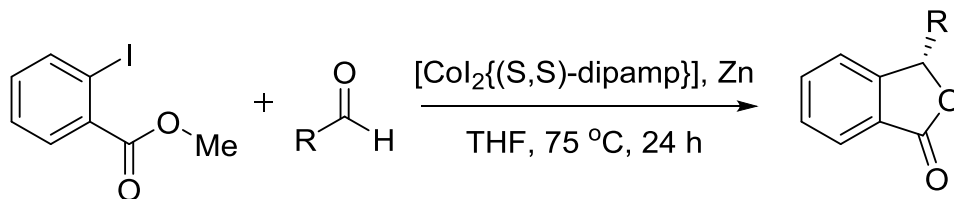
Cocyclization 2-iodobenzoates with aldehyde



Entry	Aldehyde	Yield (%)
1		94
2		92
3		94
4		86
5		90
6		50
7		60



Cocyclization 2-iodobenzoates with aldehyde



(S,S)-dipamp

Entry	Aldehyde	Yield (%)	ee
1		89	84
2		80	79
3		85	91
4		83	98
5		81	70

Conclusions

- First Co-catalyzed cocyclization 2-iodobenzoates with aldehyde
- Mild reaction conditions
- Inexpensive and efficient reaction
- High enantioselectivity

Conclusion

- Reactions are going under relatively mild conditions
- Powerful green low cost catalysts
- Low rates for β -hydride elimination pathway to compare with other metals
- High affinity to carbon-carbon π -bond, carbon-nitrogen π -bond
- Co-promoted various cycloadditions spanning from [2+1] to the [6+4]
- Small changes in the catalyst system or parameters such as solvent, ligand or concentrations lead to new unexpected results

*Thank you
for your attention!*

