Palladium (I) chemistry

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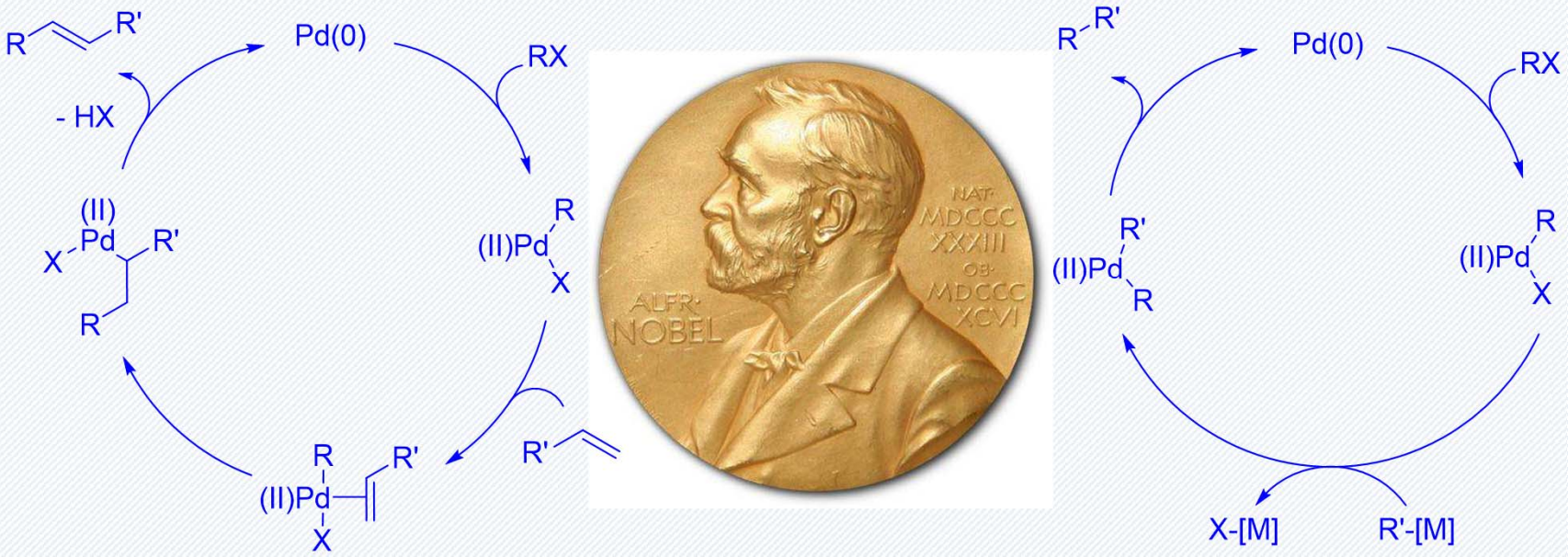
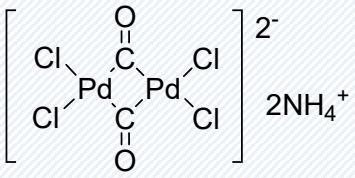
Student : Wei-Feng Zheng
2019/05/24

Contents

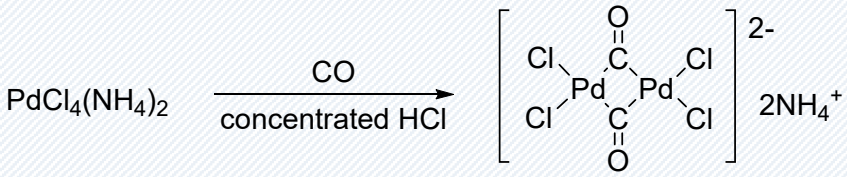


Nobel Prize in Chemistry 2010

The first preparation of **dinuclear Pd (I)**

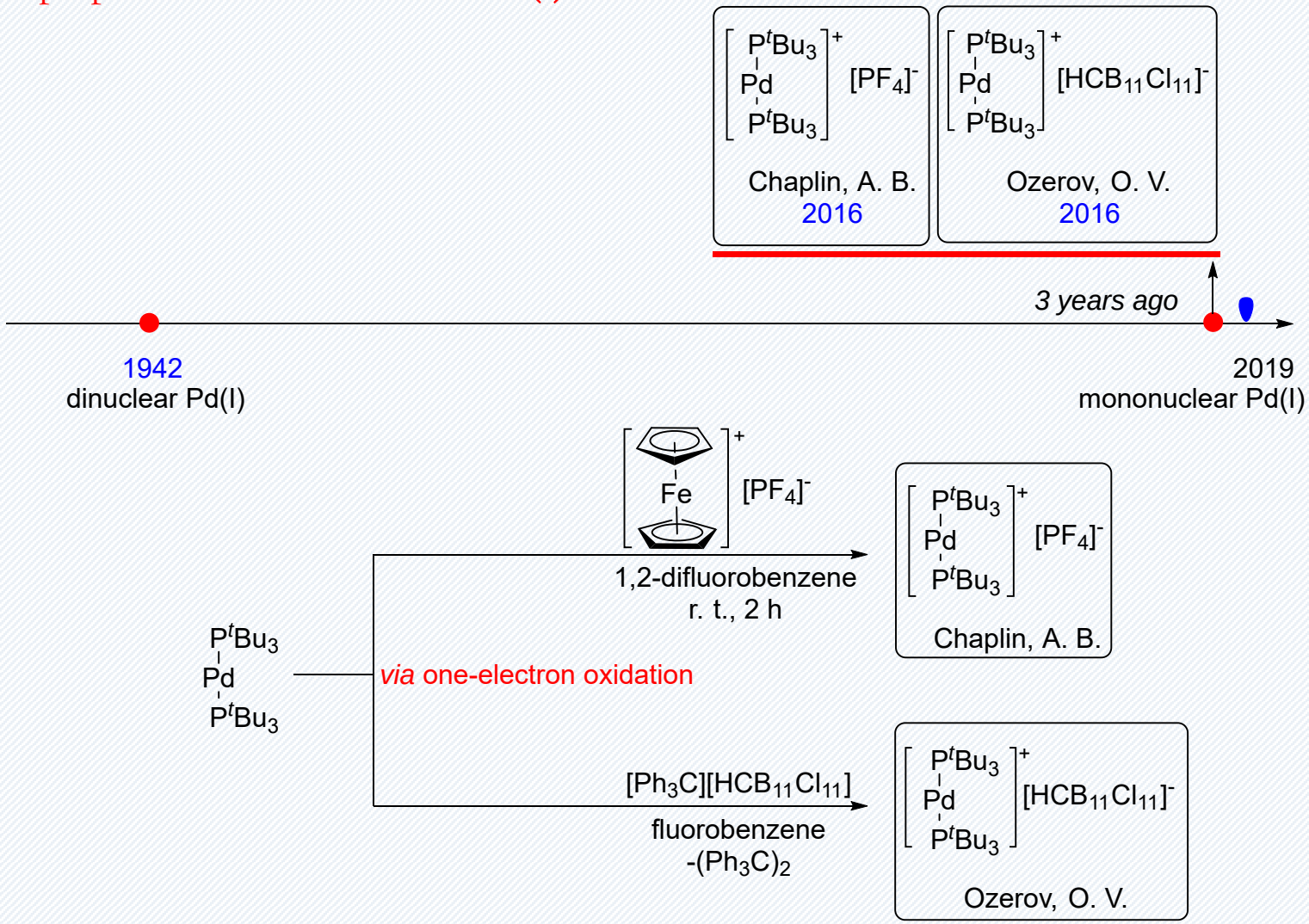


Meilakh, E.
1942



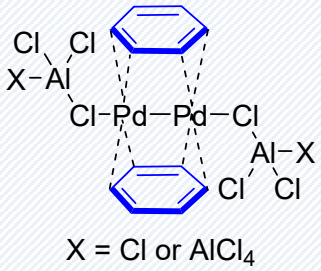
First preparation: Meilakh, E. and coworkers, *Dorzady Akad. Nazth S.S.S.R.* **1942**, *36*, 171.
Assigned the structure by IR spectra: Goggin, P. L. and coworkers, *J. Chem. Soc. Dalton Trans.* **1974**, *0*, 534.
X-ray crystallographic: Goggin, P. L. and coworkers, *J. Chem. Soc. Dalton Trans.* **1981**, *0*, 1077.

The first preparation of **monomeric Pd (I)**



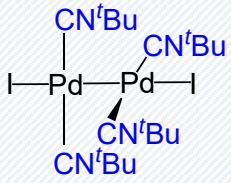
Chaplin, A. B. and coworkers, *Angew. Chem. Int. Ed.* **2016**, *55*, 3754.
Ozerov, O. V. and coworkers, *Chem* **2016**, *1*, 902.

The first preparation of different kinds dinuclear Pd (I)

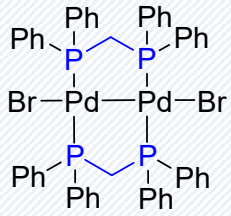


X = Cl or $AlCl_4$

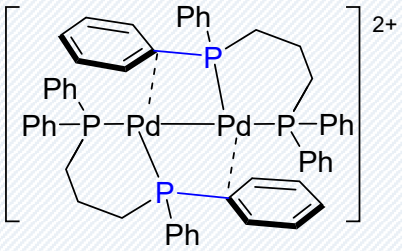
Allegra, G.
1965



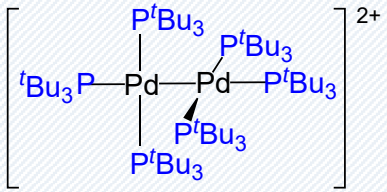
Otsuka, S.
1971



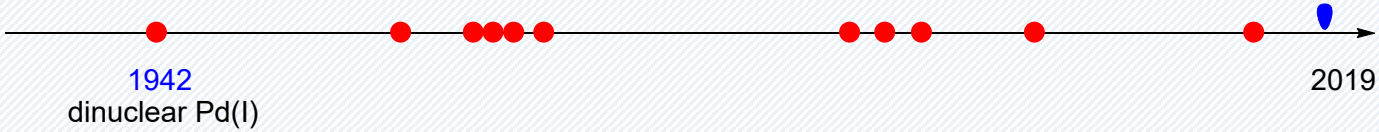
Colton, R.
1973

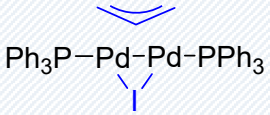


Leeuwen, P. W. N. W.
1992

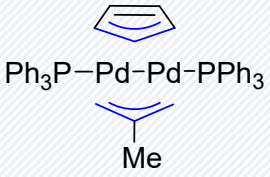


Girolami, G. S.
1994

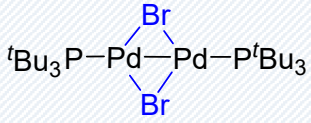




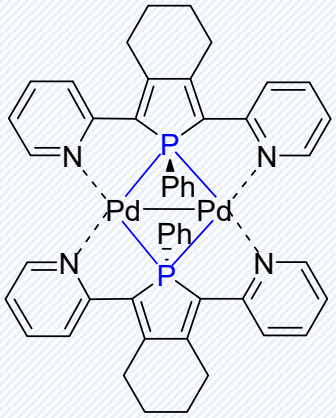
Yamazaki, H.
1972



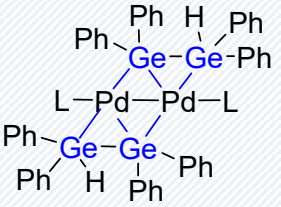
Werner, H.
1975



Mingos, D. M.
1996

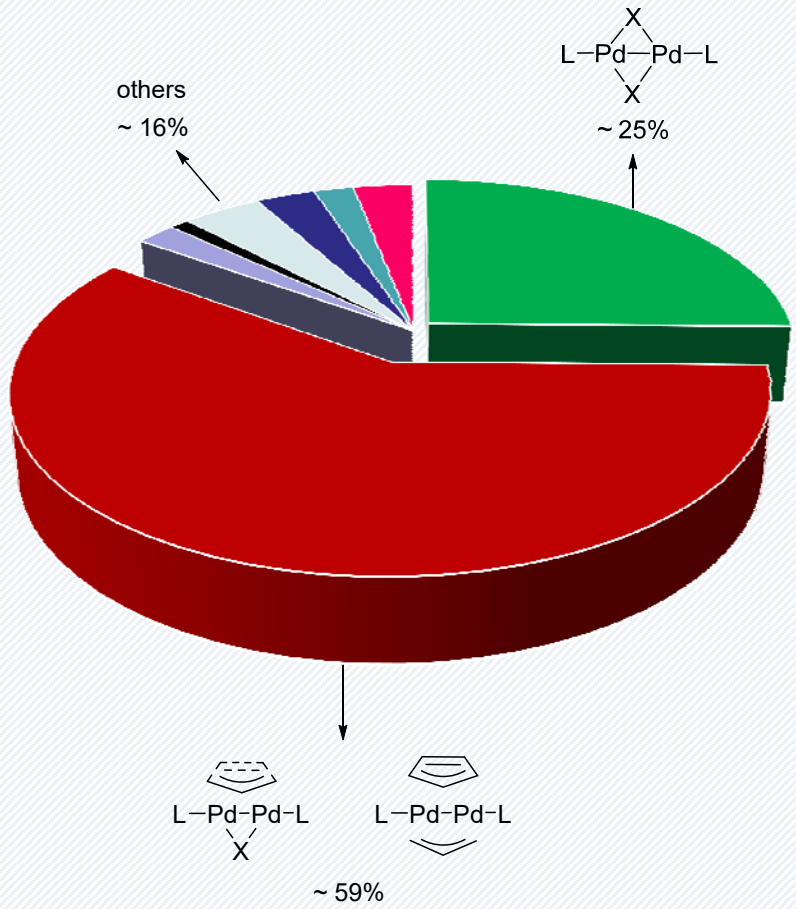


Réau, R.
2001



Osakada, K.
2015

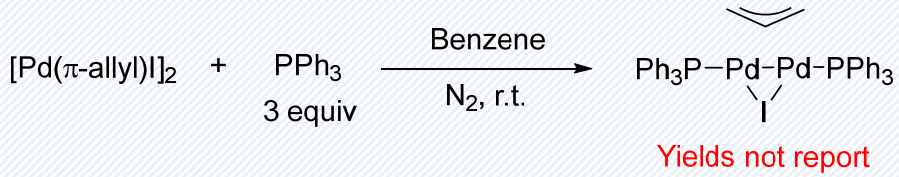
The proportion of Pd (I) species



2. Synthesis of dinuclear Pd (I) complexes

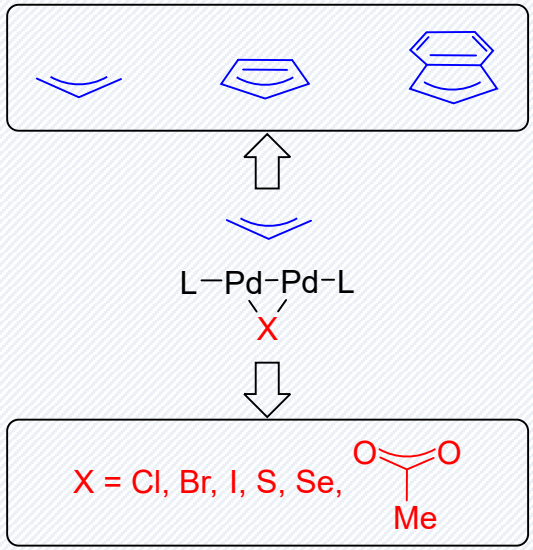
The first example of (μ-allyl)(μ-X)Pd_2L_2

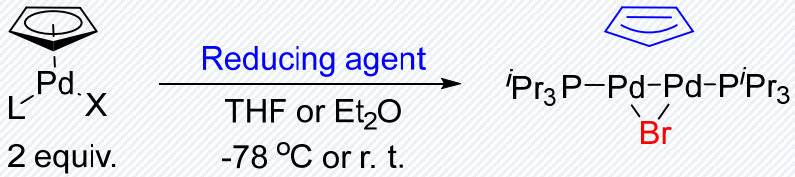
The first preparation of μ-η^3-allyl dipalladium (I)



Yields not report

Yamazaki, H. and coworkers, *Acta Crystallogr.* **1972**, *B 28*, 899.



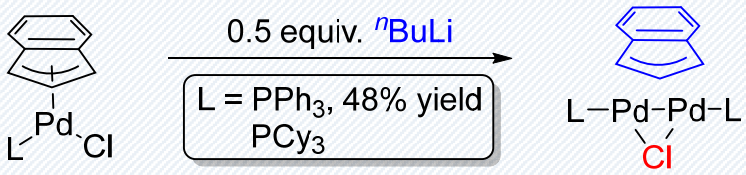


yields: L = P^{i}Pr$_3$; X = Cl, Br (82%), I

L = PPh$_3$ (91%), PCy$_3$ (83%); X = Br

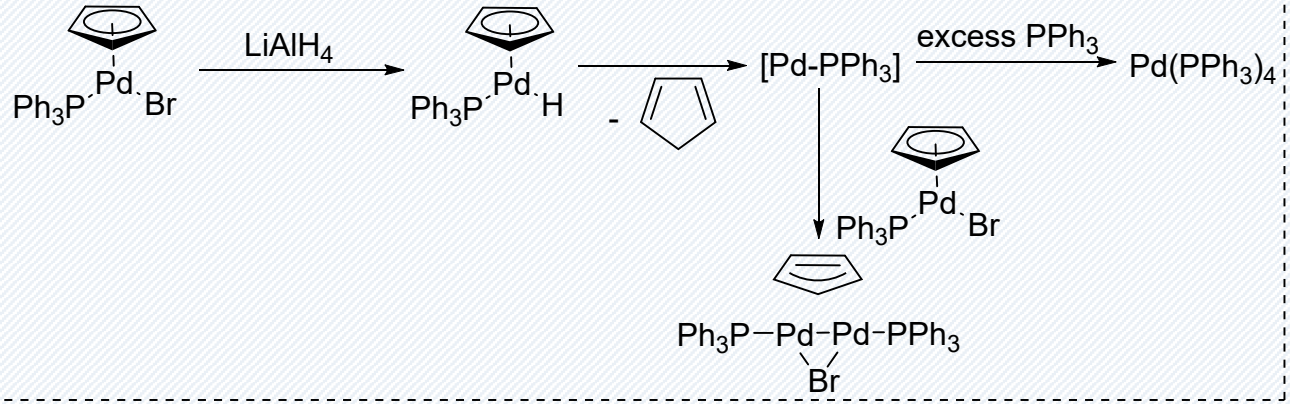
Reducing agent: Mg, Sodium amalgam, ^{n}BuMgBr, LiAlH$_4$, LiAlH(O^{t}Bu)$_3$, NaBH$_4$

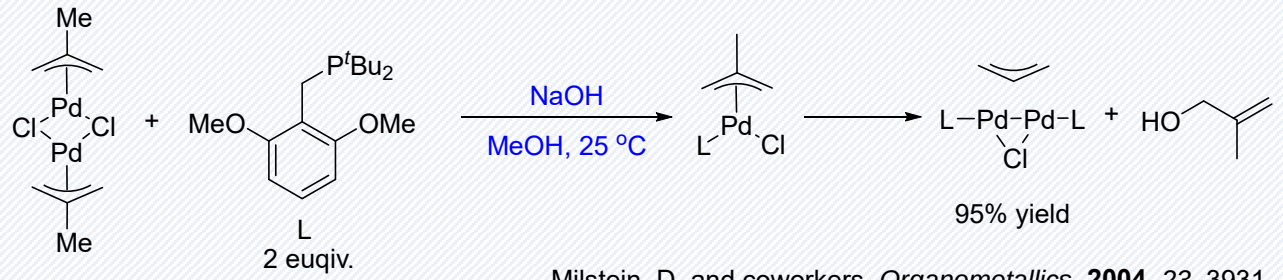
Felkin, H. and coworkers, *J. Organomet. Chem.* **1977**, *129*, 429.



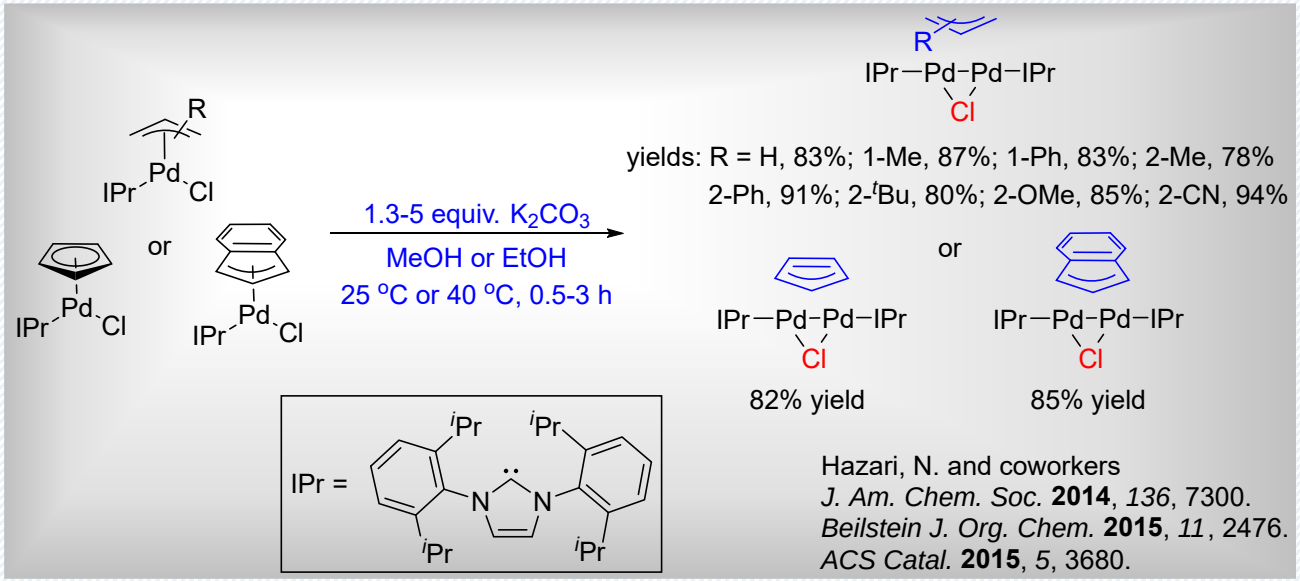
Zargarian, D. and coworkers, *J. Am. Chem. Soc.* **2006**, *128*, 6508.

Proposed mechanism



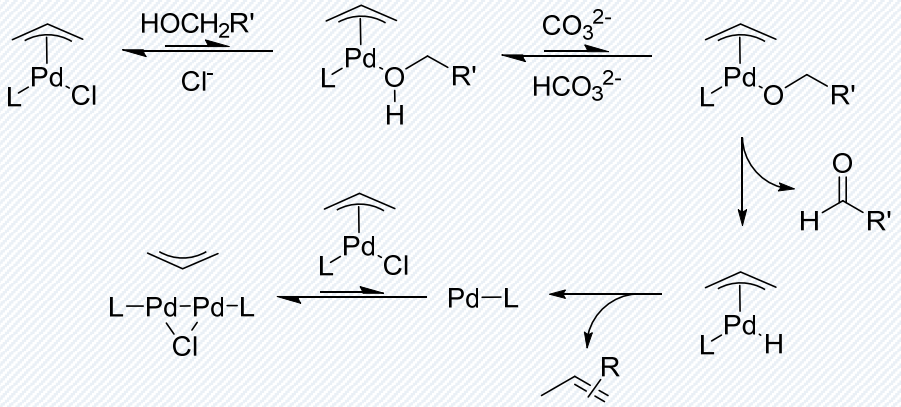


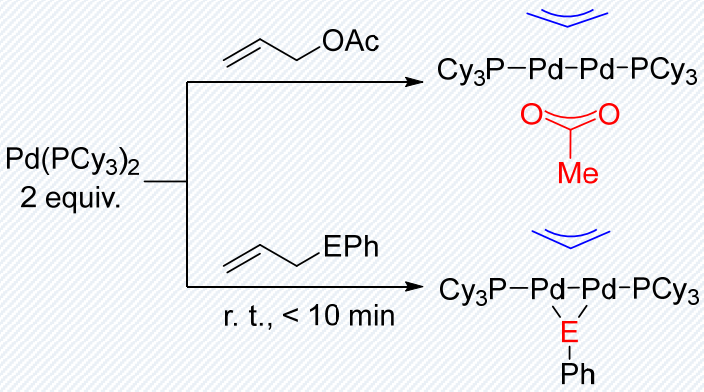
Milstein, D. and coworkers, *Organometallics*, **2004**, *23*, 3931.



Hazari, N. and coworkers
J. Am. Chem. Soc. **2014**, *136*, 7300.
Beilstein J. Org. Chem. **2015**, *11*, 2476.
ACS Catal. **2015**, *5*, 3680.

Proposed mechanism

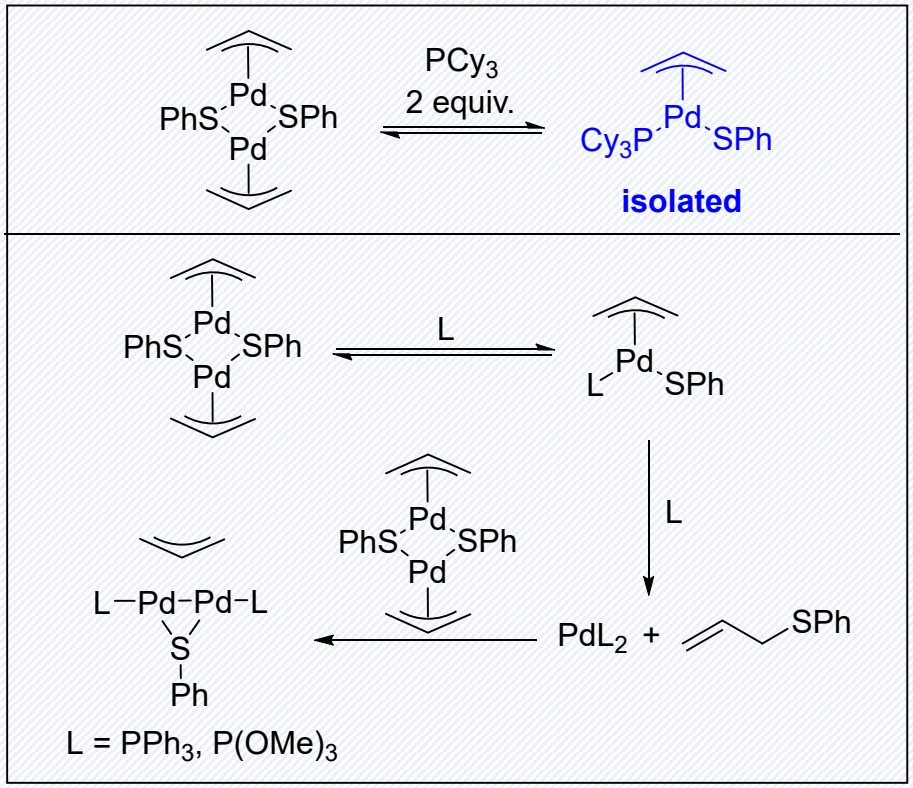




Yields not report

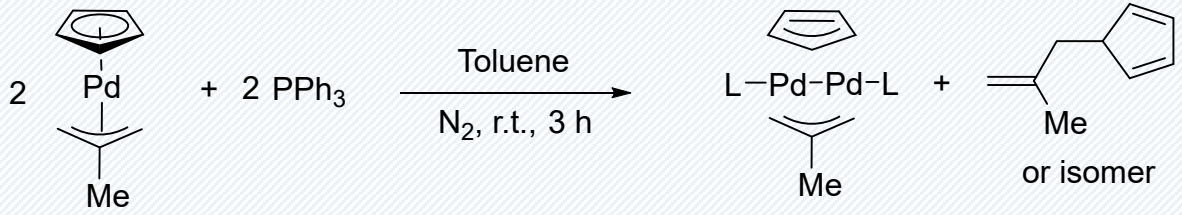
E = S, 85% yield
E = Se, 28% yield

Yamamoto, A. and coworkers
J. Am. Chem. Soc. **1981**, *103*, 5600.
Chem. Lett. **1983**, 1725.



Kurosawa, H. and coworkers, *Organometallics*, **1995**, *14*, 5450.

The first preparation of Cp-allyl sandwich dipalladium (I)

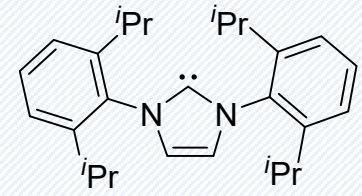


L = PPh_3 (85% yield), $P(OMe)_3$, $P(OC_6H_5)_3$

Werner, H. and coworkers, *Angew. Chem. Int. Ed.* **1975**, *14*, 185.

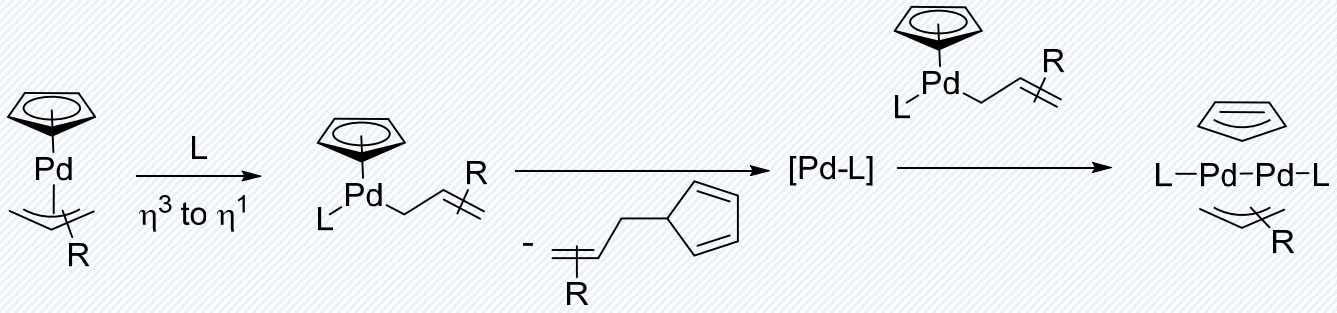
L = PEt_3 (76% yield), **IPr** (50% yield)

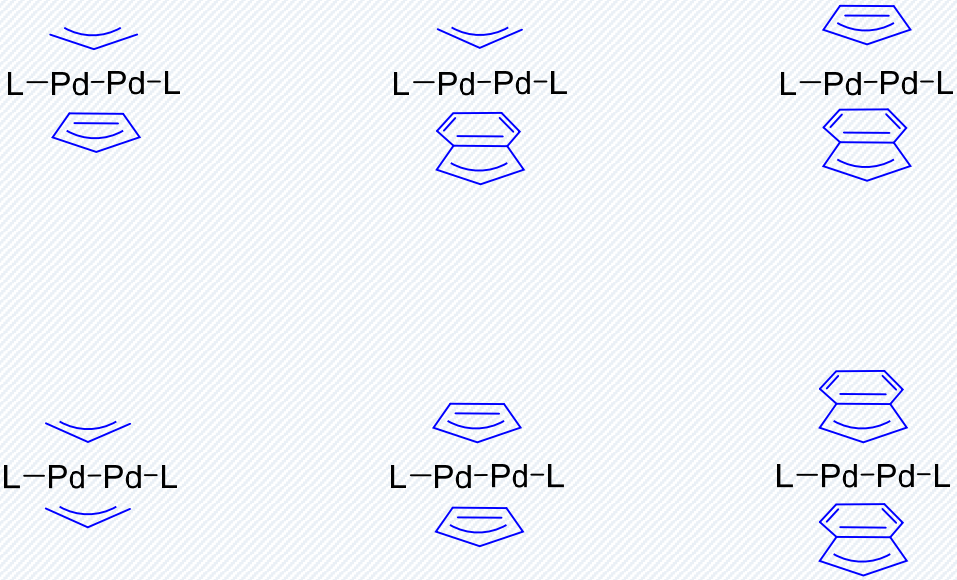
IPr =

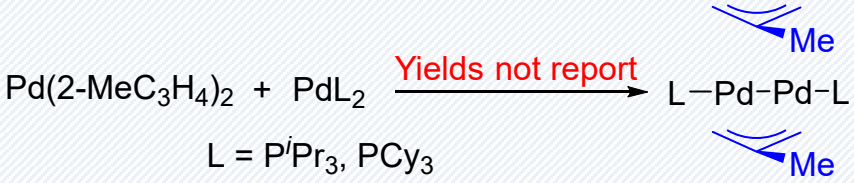


Hazari, N. and coworkers, *Organometallics* **2013**, *32*, 4223.

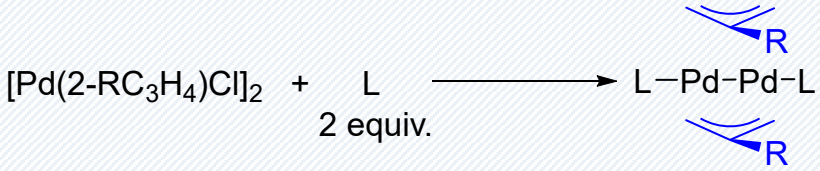
Proposed mechanism




L–Pd–Pd–L
L–Pd–Pd–L
L–Pd–Pd–L
L–Pd–Pd–L
L–Pd–Pd–L
L–Pd–Pd–L

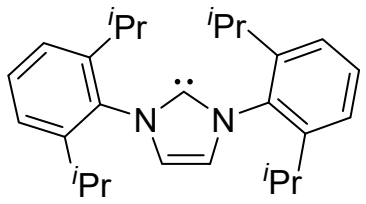


Werner, H. and coworkers, *J . Organomet. Chem.* **1979**, *179*, 421.

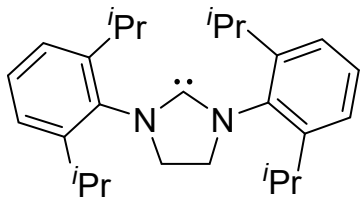


yields: R = H; L = PMe_3 (75%), PEt_3 (79%), PPh_3 (57%),
IPr (40%), **SIPr** (84%), **IMes**(42%), **IiPr** (39%),
R = Me; L = PMe_3 (52%), PEt_3 (84%), PPh_3 (67%), **IPr** (29%)

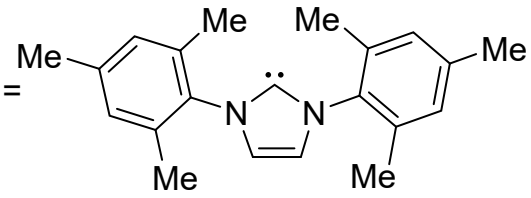
IPr =



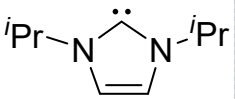
SIPr =



IMes =

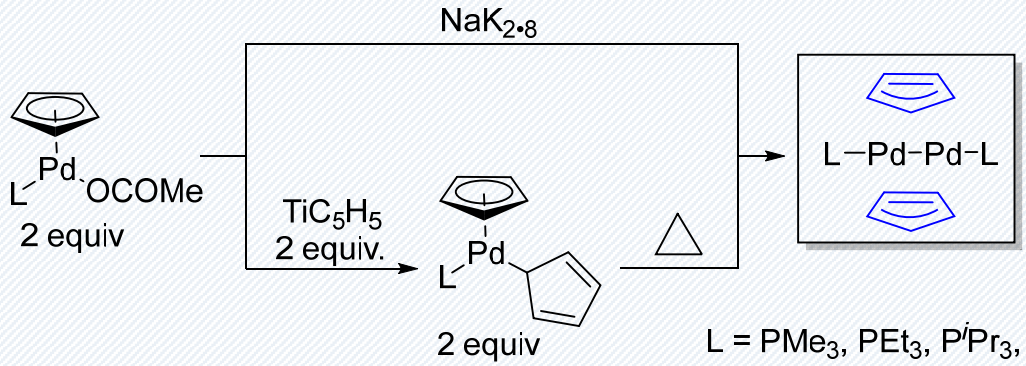


IiPr =



Jolly, P. W. and coworkers, *Angew. Chem. Int. Ed.* **1985**, *24*, 283.

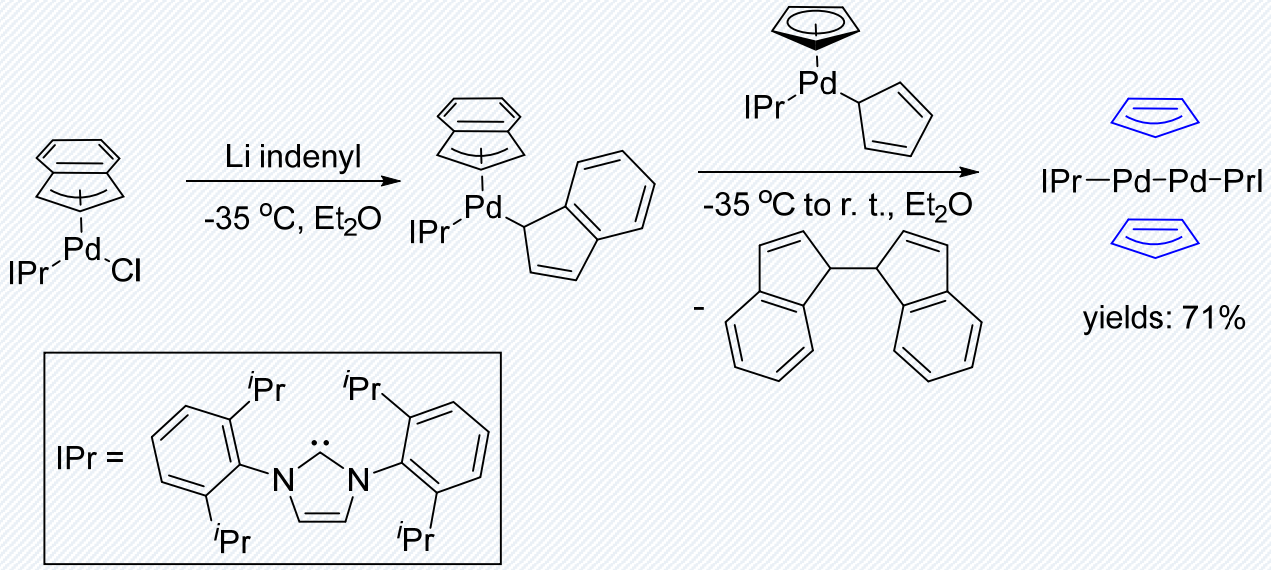
Hazari, N. and coworkers, *J. Am. Chem. Soc.* **2011**, *133*, 3280.



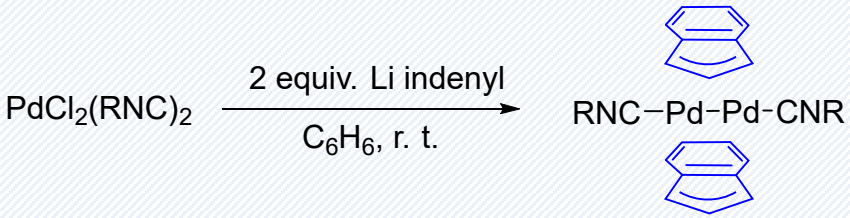
L = PMe_3, PEt_3, P^iPr_3, PPh_3

yields: 40-60%

Werner. H, and coworkers, *Angew. Chem. Int. Ed.* **1979**, *18*, 948.

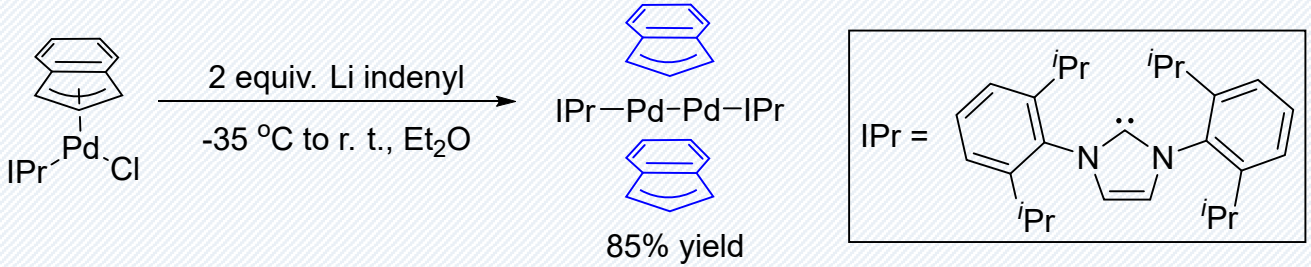


Hazari, N. and coworkers, *Organometallics* **2013**, *32*, 5114.

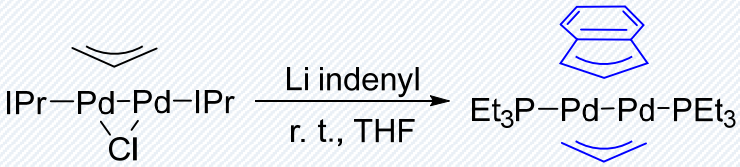


yield: R = ^{t}Bu, 2,6-$Me_2C_6H_3$ (62%), 2,4,6-$Me_3C_6H_2$
2,4,6-$^{t}Bu_3C_6H_2$ (51%)

Kobayashi, K. and coworkers, *J. Organomet. Chem.* **1991**, *410*, C25.

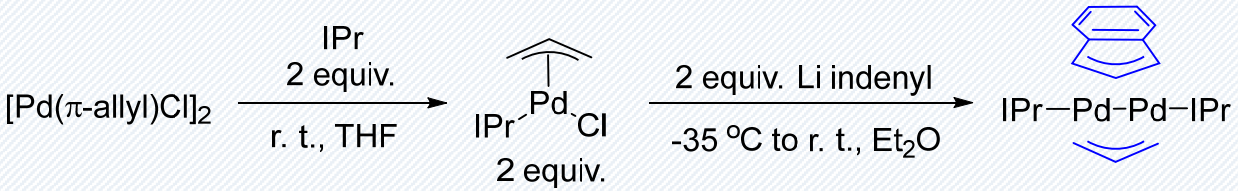


Hazari, N. and coworkers, *Organometallics*, **2013**, *32*, 5114.



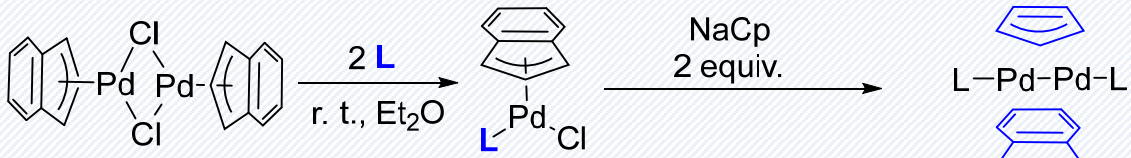
yield: 68%

Hazari, N. and coworkers, *Organometallics* **2013**, *32*, 4223.



yield: 78%

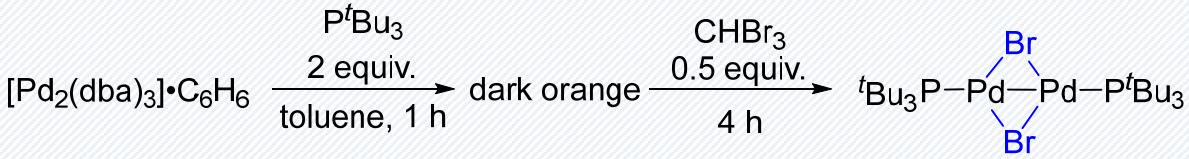
Hazari, N. and coworkers, *Organometallics* **2013**, *32*, 5114.



yields: L = PEt_2 (38%)
IPr (not report)

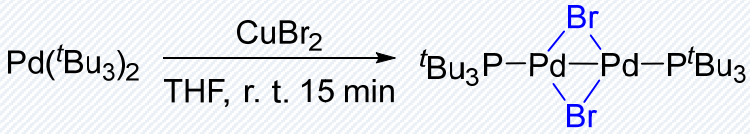
Hazari, N. and coworkers, *Organometallics* **2013**, *32*, 4223.

The first example of $(\mu\text{-X})_2Pd_2L_2$



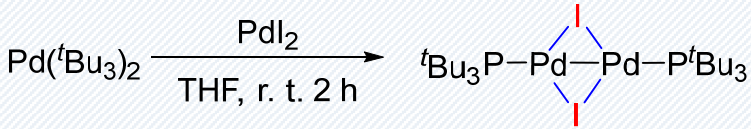
green
18% yield

Mingos, D. M. and coworkers, *J. Chem. Soc. Dalton. Trans.* **1996**, 4313.



50% yield

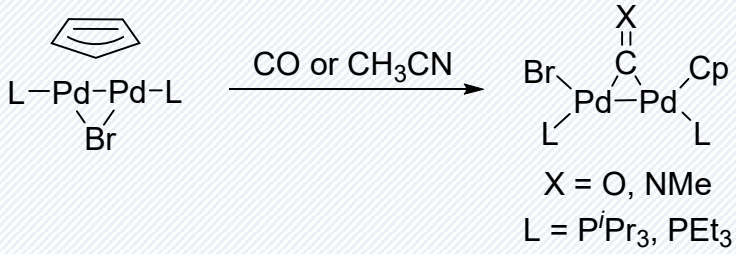
Schoenebeck, F. and coworkers, *Angew. Chem. Int. Ed.* **2012**, *51*, 7226.

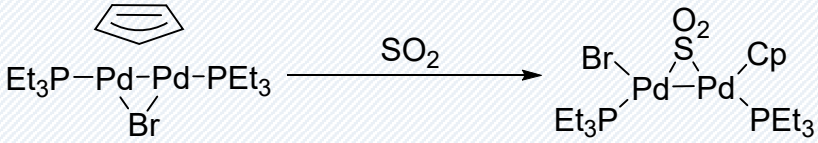


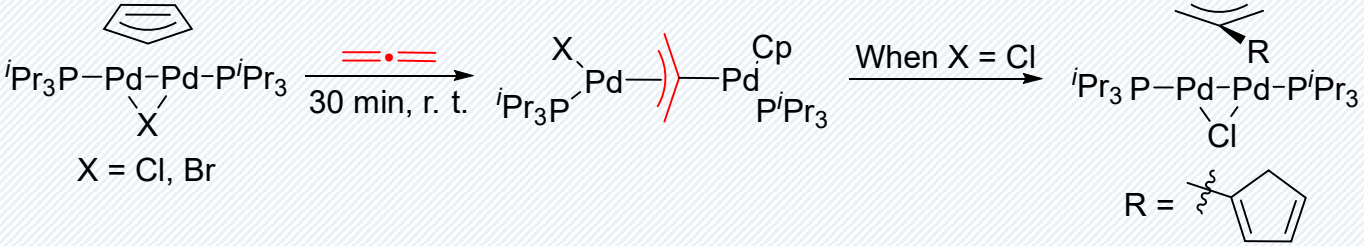
97% yield

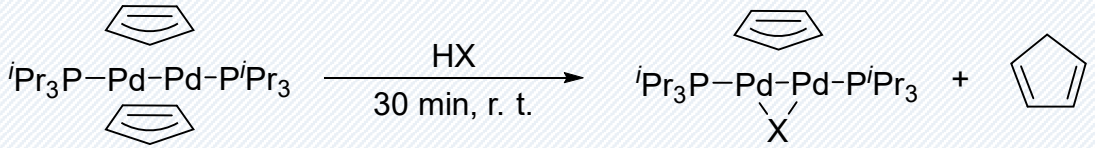
Schoenebeck, F. and coworkers, *Angew. Chem. Int. Ed.* **2015**, *54*, 10322.

3. Reactions involving dinuclear Pd (I) complexes

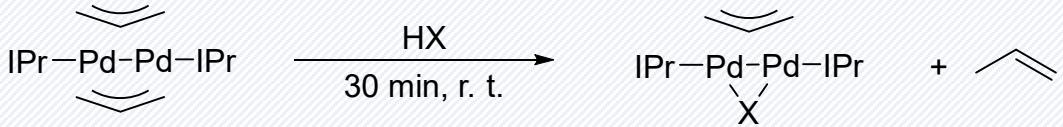

L–Pd–Pd–L
Br
CO or CH3CN
X
C
Br
Cp
Pd–Pd
L
L
X = O, NMe
L = PiPr3, PEt3


Et3P–Pd–Pd–PEt3
Br
SO2
O2
S
Br
Cp
Pd–Pd
Et3P
PEt3

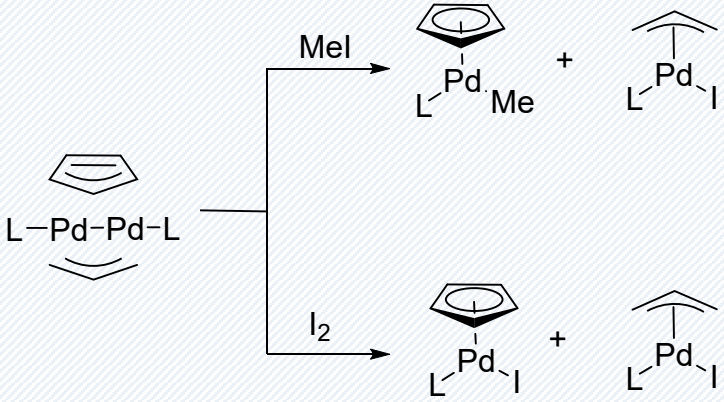

iPr3P–Pd–Pd–PiPr3
X
X = Cl, Br
30 min, r. t.
X
Pd
iPr3P
Cp
Pd
PiPr3
When X = Cl
R
iPr3 P–Pd–Pd–PiPr3
Cl
R =



X = SPh, OAc

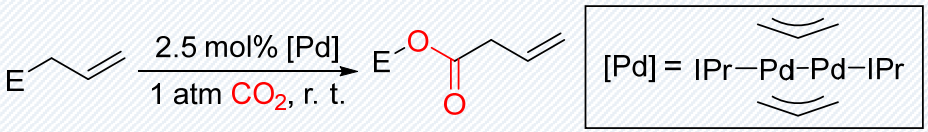


X = SPh, Cl, OAc

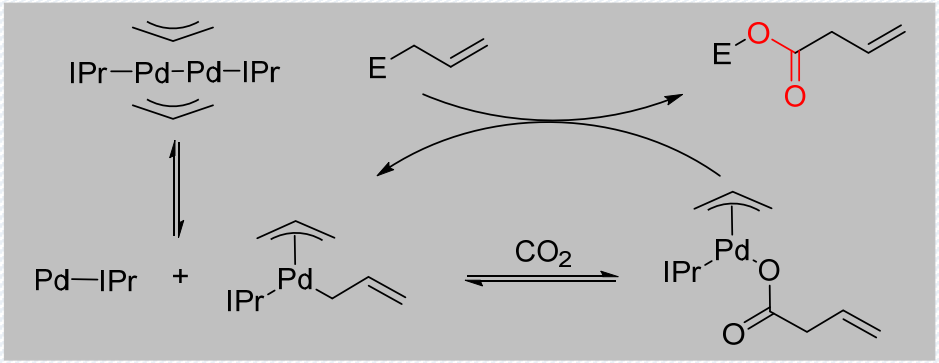


R = Me; L = PMe_3, PPh_3, P(O-*o*-Tol)$_3$
R = ^{t}Bu; PPh_3, P(O-*o*-Tol)$_3$

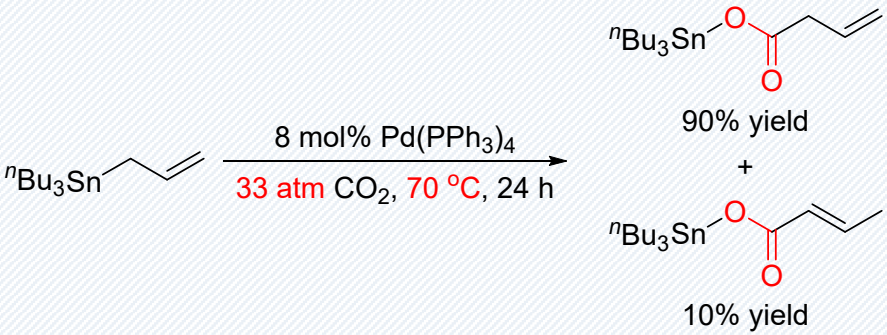
R = Me; L = PMe_3, P(O-*o*-Tol)$_3$
R = ^{t}Bu; PPh_3



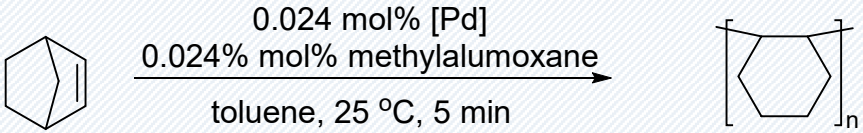
Substrate	Time (h)	NMR yield (%)
Me_3Sn(2-methylallyl)	20	79
$^nBu_3Sn$(2-methylallyl)	24	80
Me_3Sn(allyl)	26	70
$^nBu_3Sn$(allyl)	24	82
(pinaco)B(allyl)	26	60
(pinaco)B(2-methylallyl)	55	81



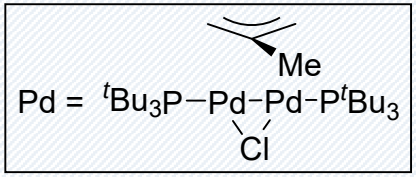
Hazari, N. and coworkers, *Chem. Commun.* **2011**, *47*, 1069.

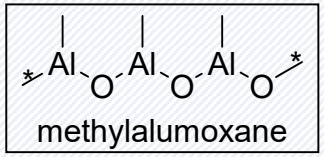


Nicholas, K. M. and coworkers, *J. Am. Chem. Soc.* **1997**, *119*, 5057.

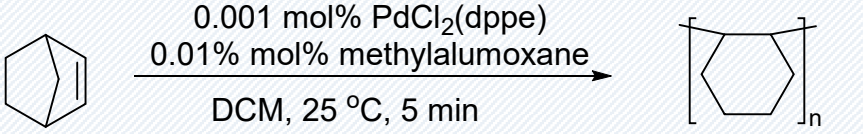


100% convertion



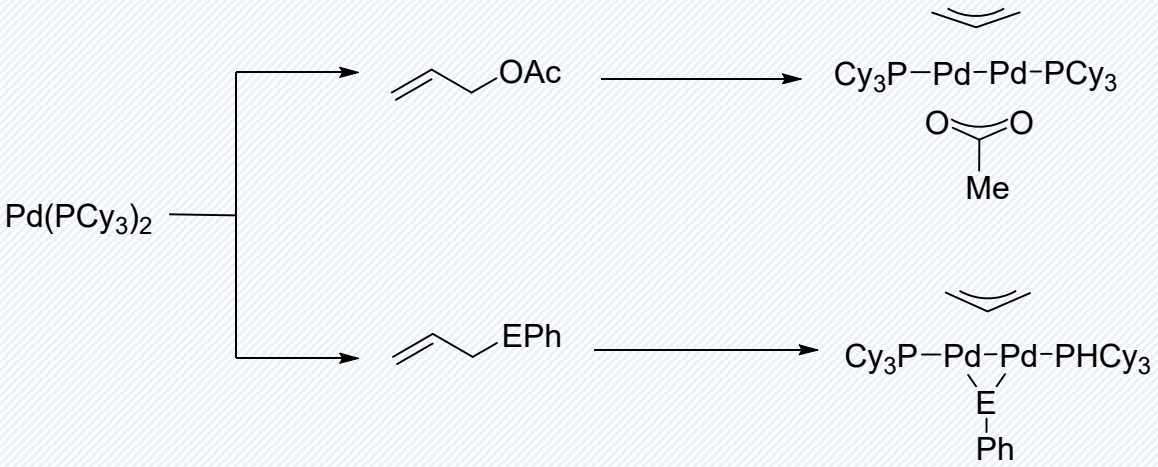


Zhang, L. and coworkers, *Organometallics* **2010**, *29*, 5766.

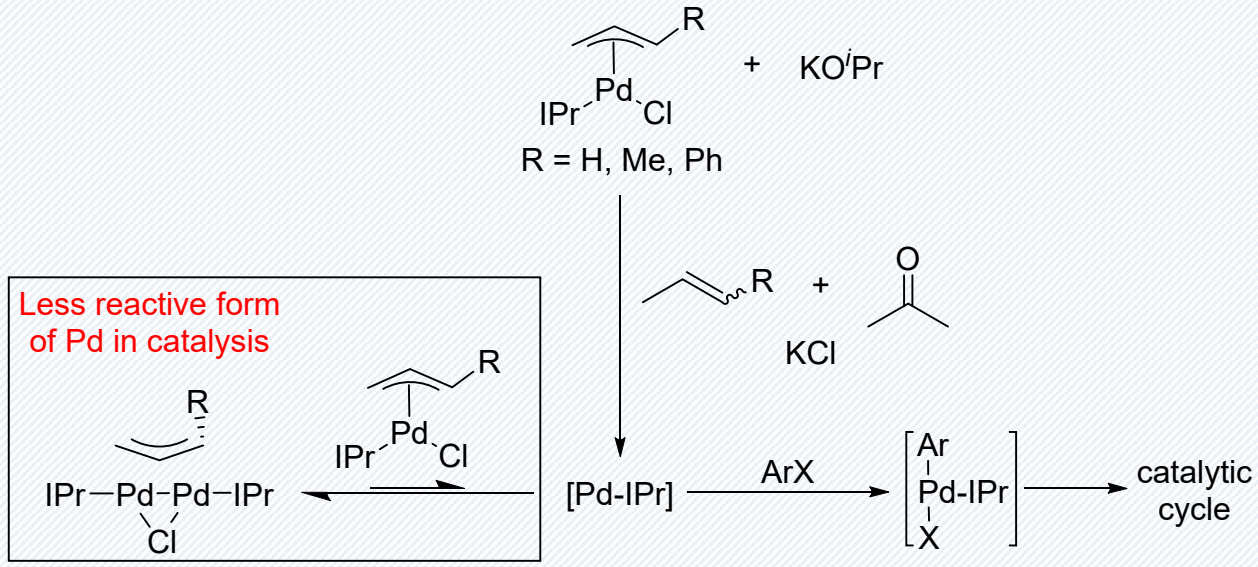


2.2% convertion

Janiak, C and coworkers, *Macromol. Rapid Commun.* **2002**, *23*, 16.

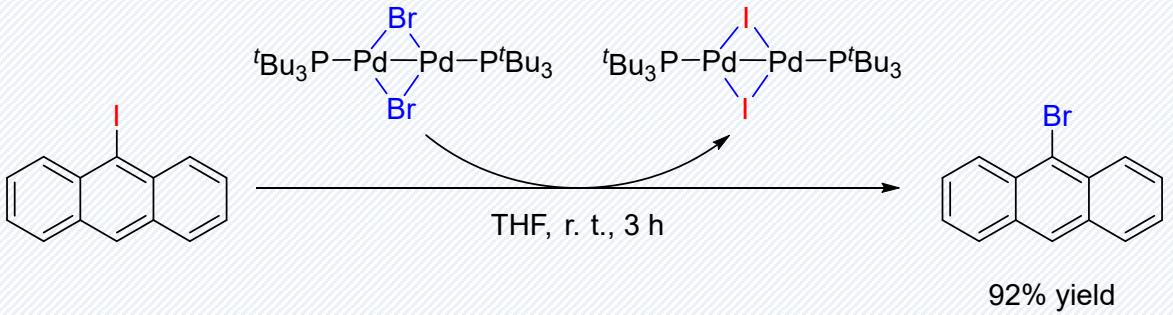


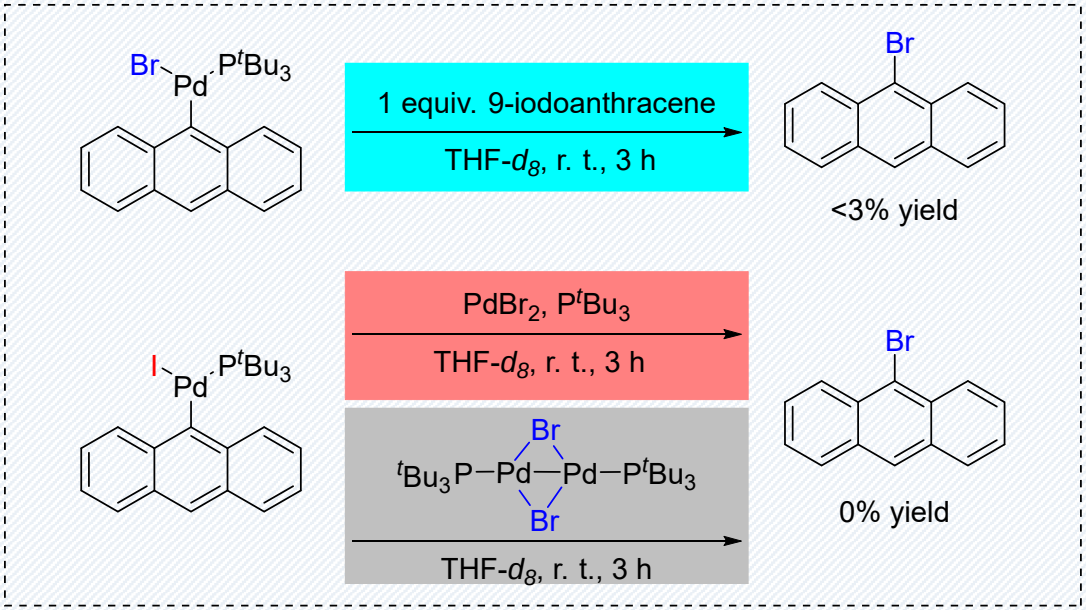
Yamamoto, A. and coworkers, *J. Am. Chem. Soc.* **1981**, *103*, 5600.

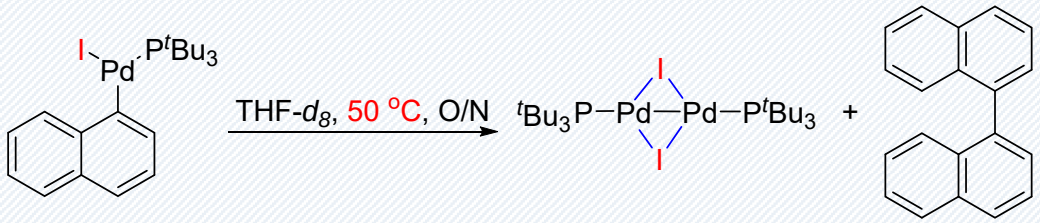


Hazari, N. and coworkers, *J. Am. Chem. Soc.* **2014**, *136*, 7300.

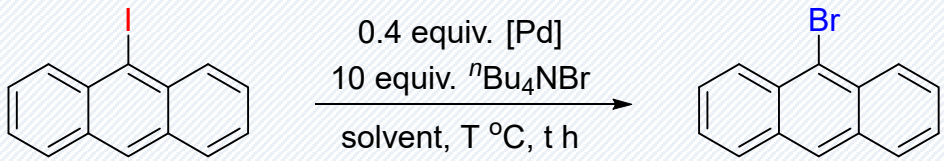
I/Br halogen exchange



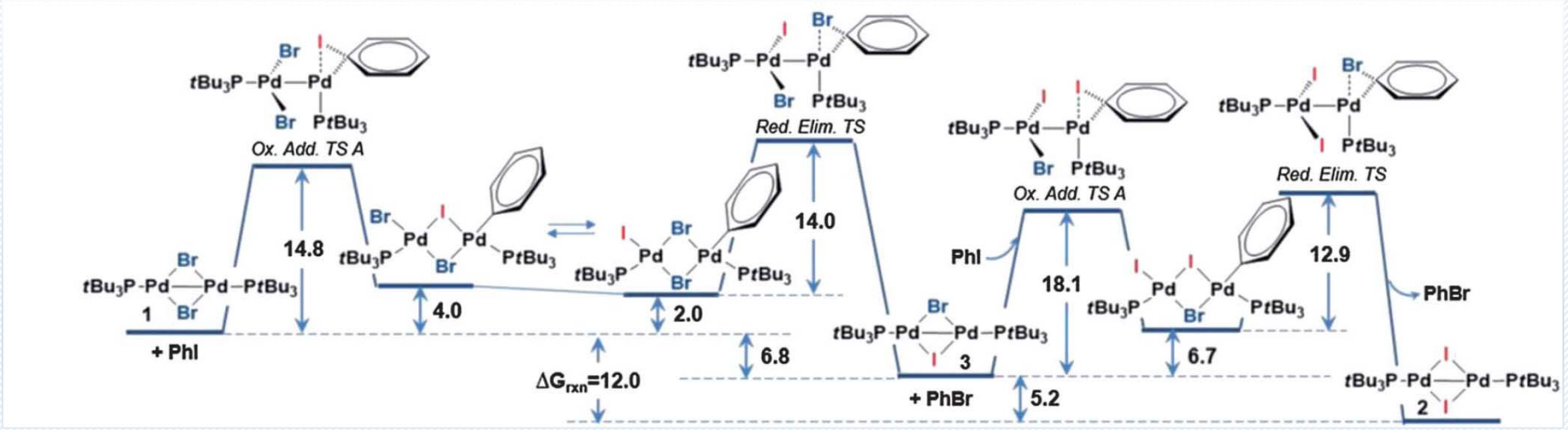


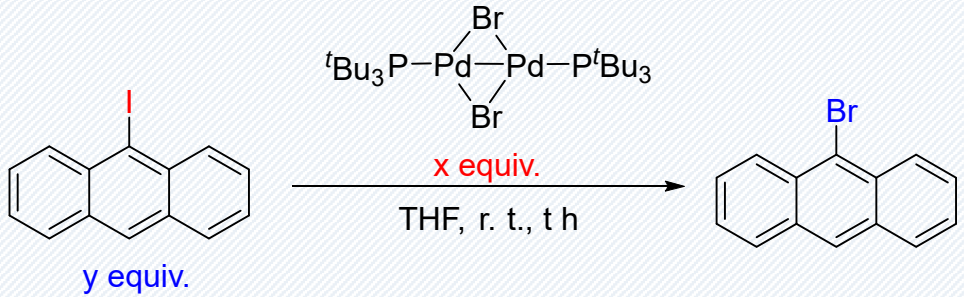


Schoenebeck, F. and coworkers, *Chem. Sci.* **2013**, *4*, 4434.



entry	[Pd]	solvent	T (°C)	t (h)	yield (%)
1	$Pd_2(dba)_3$ / P^tBu_3	THF	25	19	1
2	$Pd_2(dba)_3$ / P^tBu_3	THF	25	48	5
3	$Pd_2(dba)_3$ / P^tBu_3	toluene	35	42	0
4	$Pd_2(dba)_3$ / P^tBu_3	toluene	35	42	8
5	$Pd(P^tBu_3)_2$	THF	25	19	3
6	$Pd(P^tBu_3)_2$	toluene	25	42	0
7	$Pd(P^tBu_3)_2$	toluene	35	42	7





entry	x equiv.	y equiv.	t (h)	yield (%)
1	1	4	1.5	57
2	2	4	1.5	64
3	1	0.5	0.5	28
4	1	1	0.5	25

0% yield

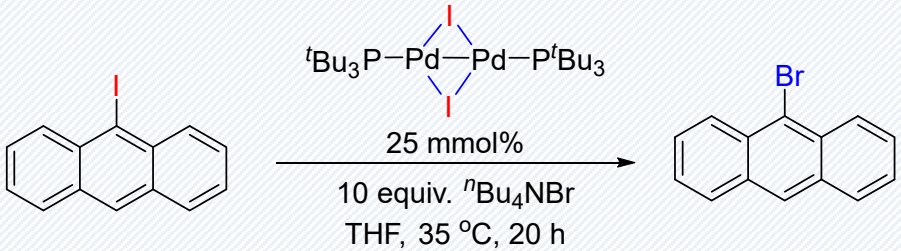
conditions A

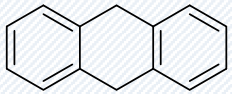
0.4 equiv. [Pd]
1 equiv. *iso*-propyl iodide
10 equiv. $^{n}Bu_4NBr$
toluene, 35 °C, 16 h

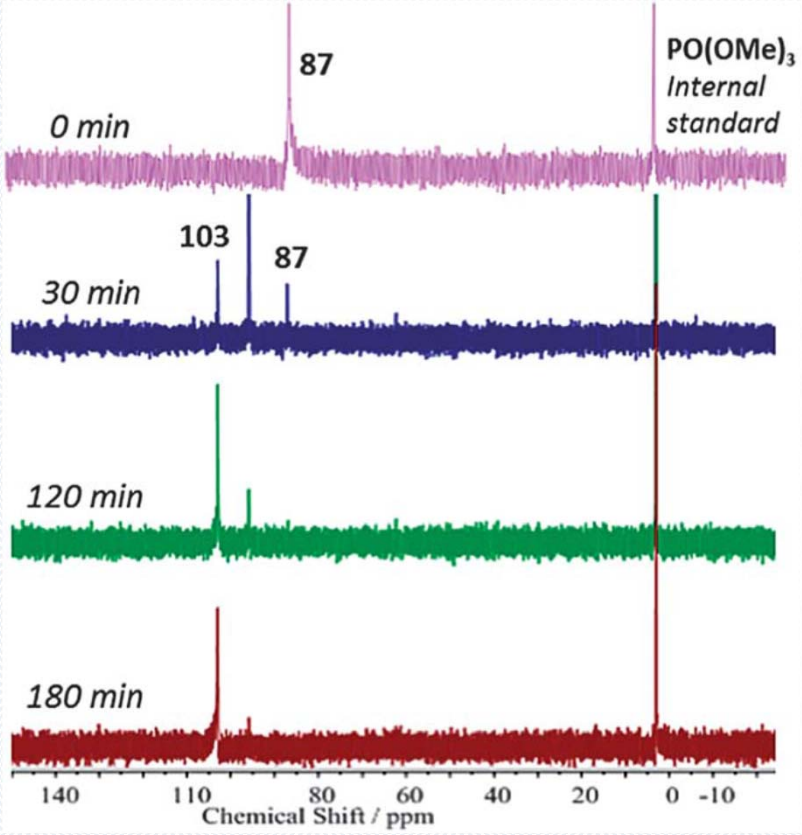
conditions B

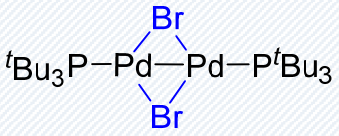
10 mol% AIBN
10 mol% ^{n}BuSnH
10 equiv. $^{n}Bu_4NBr$
benzene, 80 °C, 16 h

[Pd] = $Pd(P^{t}Bu_3)_2$ or $Pd(PPh_3)_4$

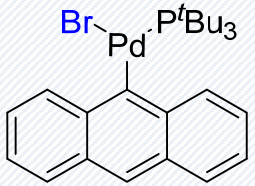


entry	change in conditions	yield (%)
1	/	62
2	 :THF = 1:1 instead of THF	74
3	8.8 equiv.  was added	77

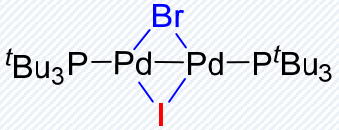




87 ppm



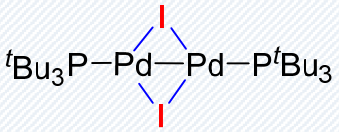
71 ppm



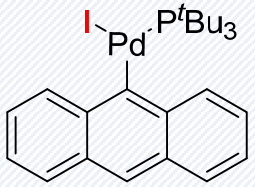
97 ppm

PtBu3

64 ppm

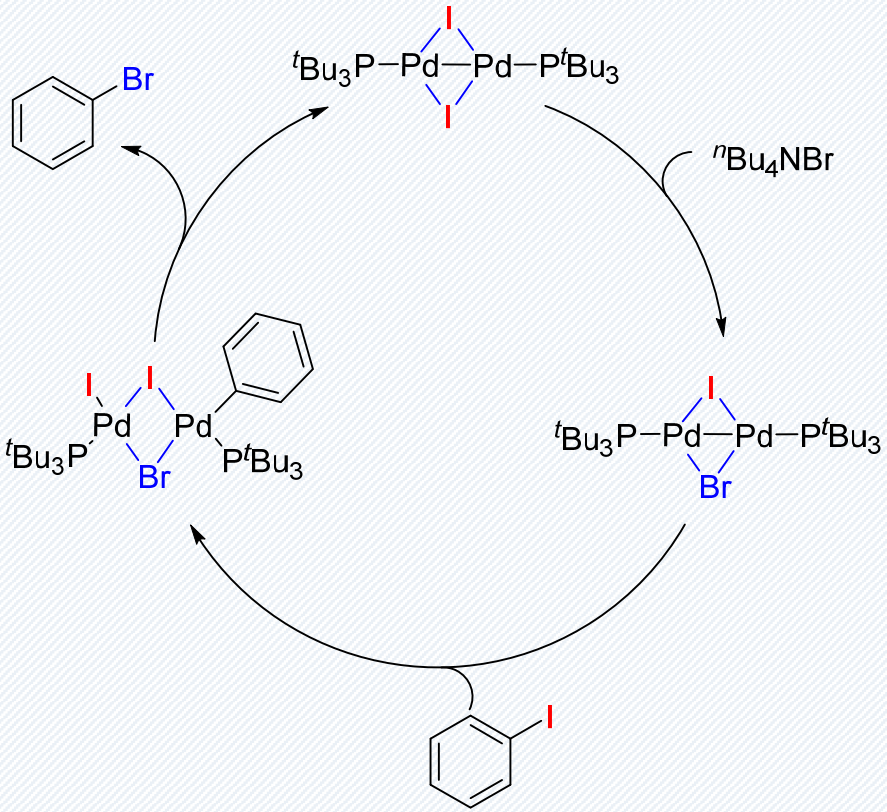


103 ppm



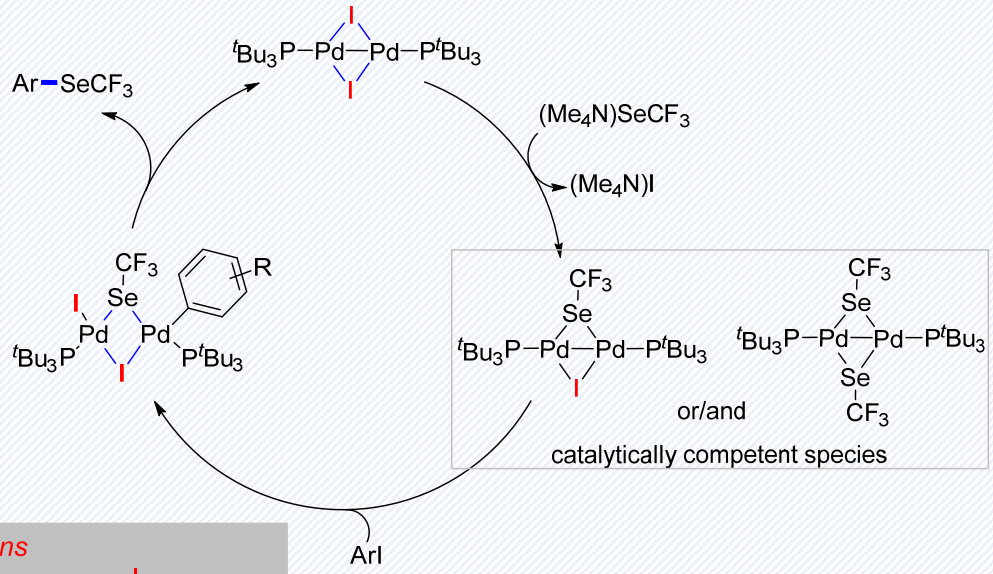
62 ppm

Proposed mechanism



C-$SeCF_3$ coupling

(The first catalytic method to convert aryl iodides into the corresponding $ArSeCF_3$)

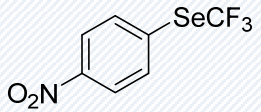


Conditions

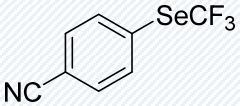
5 mol% $^tBu_3P–Pd–Pd–P^tBu_3$

in toluene, 40-60 °C, 24 h

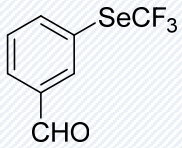
Air-, moisture-, and thermally-stable



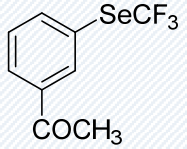
84% yield



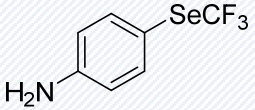
99% yield



49% yield

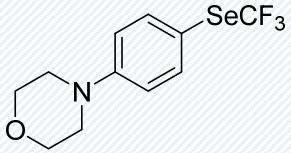


48% yield

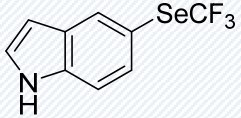


95% yield

93% yield

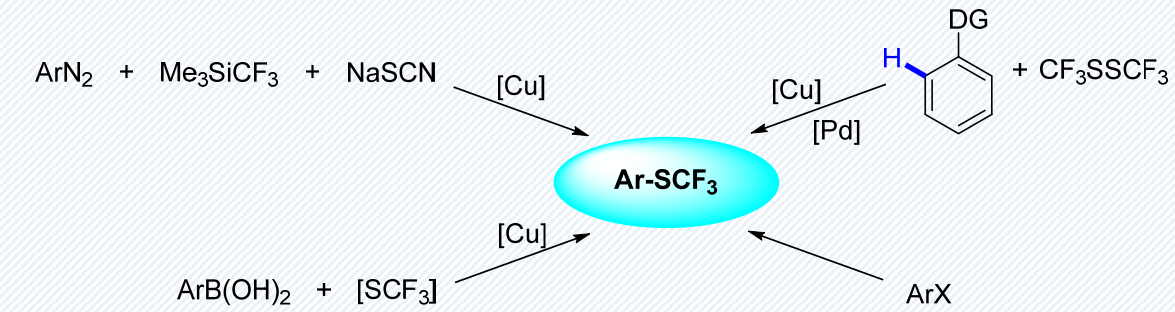


95% yield



94% yield

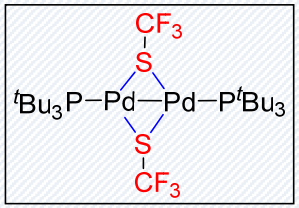
Schoenebeck, F. and coworkers, *Angew. Chem. Int. Ed.* **2015**, *54*, 10322.



Conditions

5 mol% $^{t}Bu_3P–Pd(I)_2–Pd–P^{t}Bu_3$

in toluene, 80 °C, 12-15 h

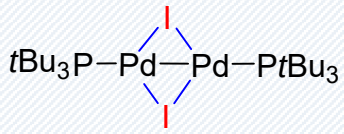


Schoenebeck, F. and coworkers, *Angew. Chem. Int. Ed.* **2015**, *54*, 6809.

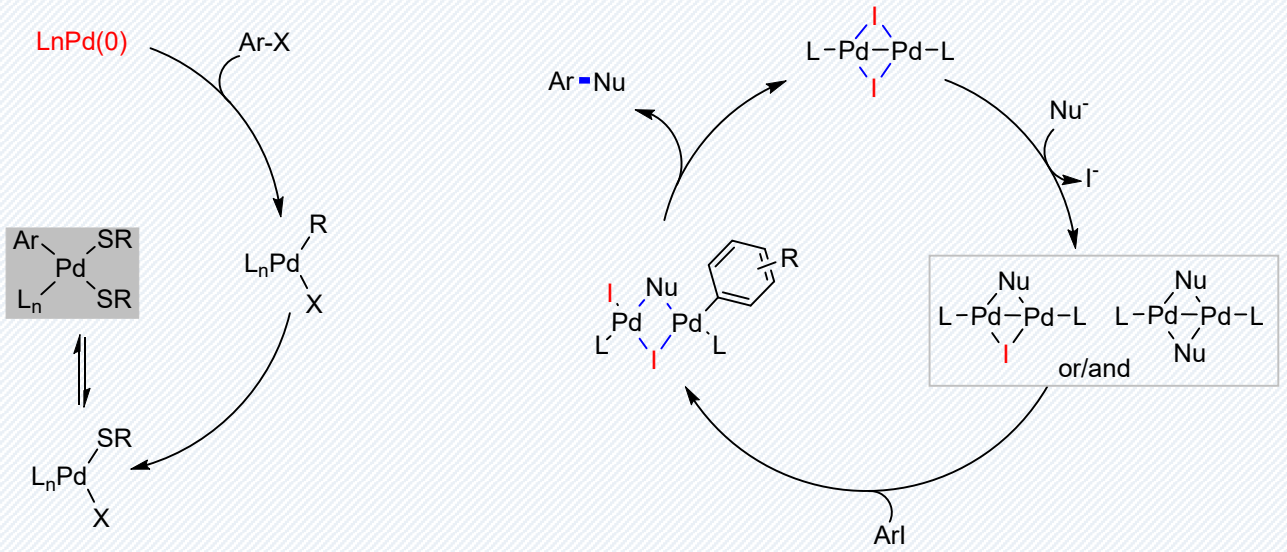
LnPd(0)

- *Air-sensitive*
- *Strategies for recovery:*
  - polyethylene-bound Pd
  - metal scavengers
  - specialized cindition (biphasic, ionic liquids, supercritical CO_2)
- Poisonous Pd ate complexes
- No chemoselectivity in C-Br vs C-OTf vs C-Cl

vs.

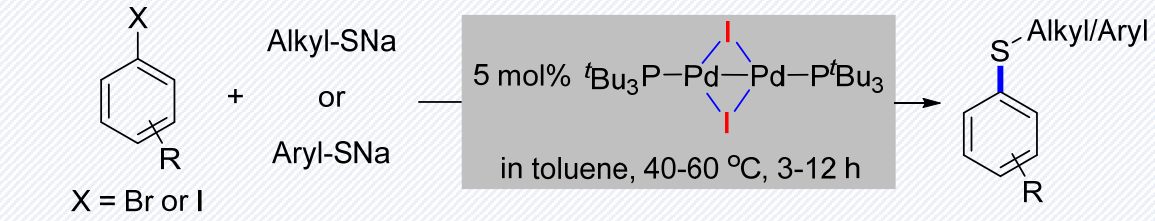


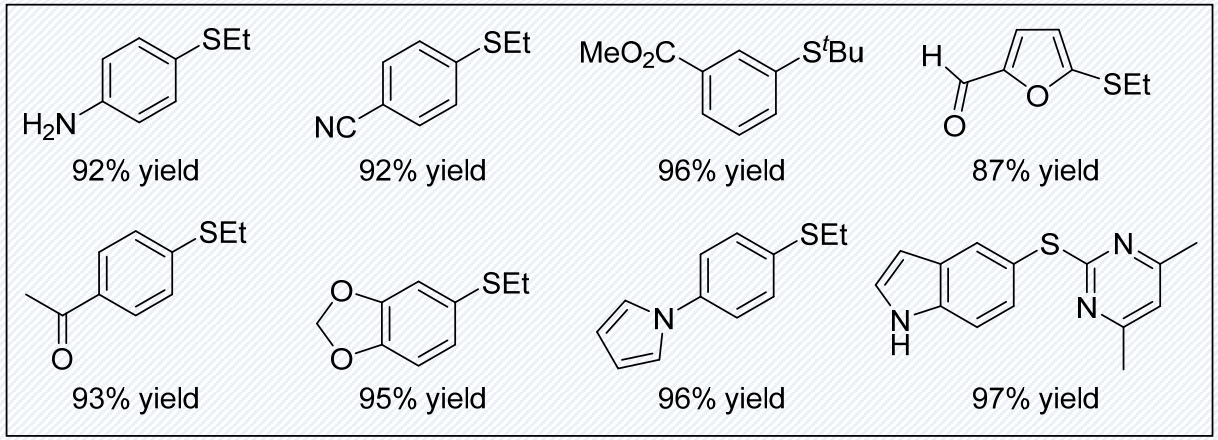
- Robust & air-stable
- Straightforward recovery
- Pd(I) catalysis cycles
- Avoidance of poisonous complexes from Pd(II) I/SR exchange at oxidation state (I).
- Chemoselectivity in C-Br

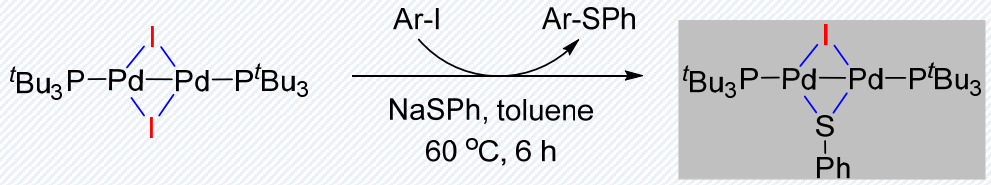


- Challenge in Pd(I): electron-rich nucleophiles could potentially reducing the Pd(I) entity to Pd(0)

Schoenebeck, F. and coworkers, *Angew. Chem. Int. Ed.* **2018**, *57*, 12425.

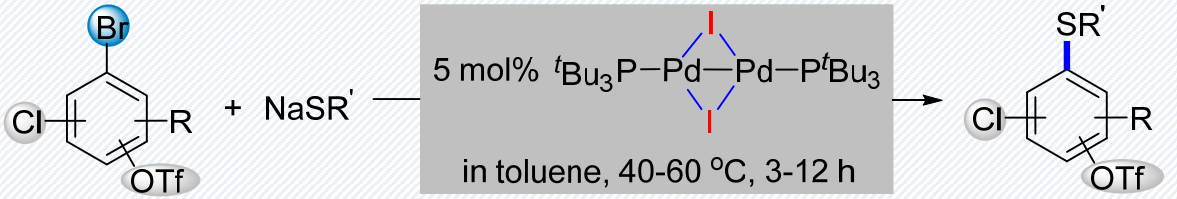


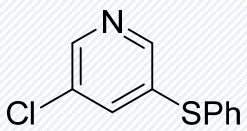




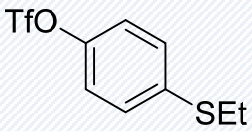
81% recovery

[Yield of Ar-SPh]
1st cycle: 88%
2nd cycle: 99%
3rd cycle: 98%
4th cycle: 97%
5th cycle: 93%

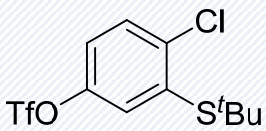




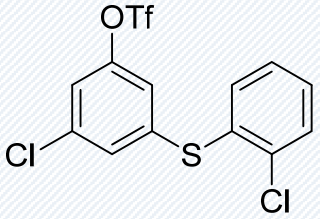
93% yield



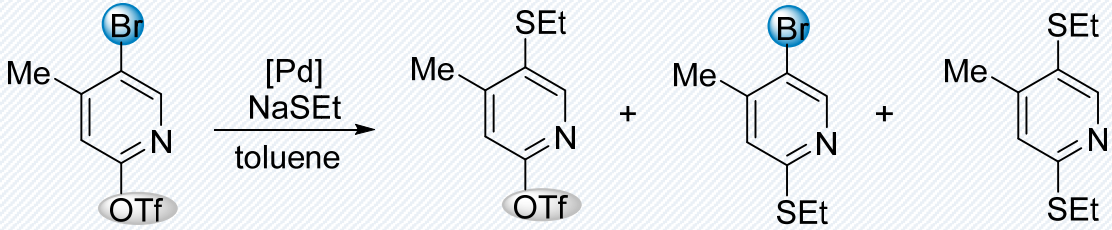
94% yield



91% yield



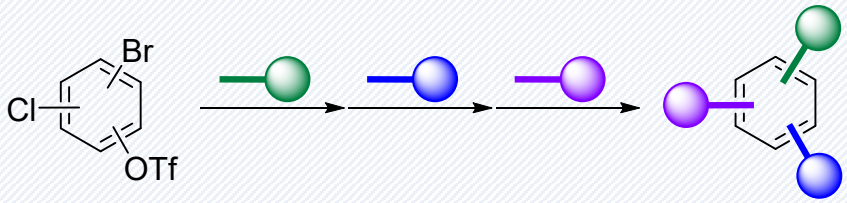
92% yield



1 mol% Pd_2dba_3 / DPEphos T = 100 °C, 2 h, 4% recovery	trace	88% yield	8% yield
5 mol% [Pd(I) Br-dimer] T = 60 °C, 12 h, 80% recovery	20% yield	0% yield	0% yield
5 mol% [Pd(I) I-dimer] T = 60 °C, 12 h, 2% recovery	98% yield	0% yield	0% yield

C-C coupling

Rapid & Fully Selective Functionalization ?



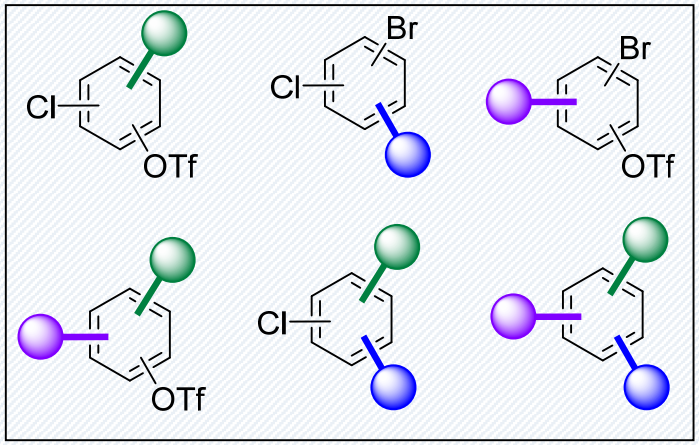
Library of diversely & densely functionalized arenes !

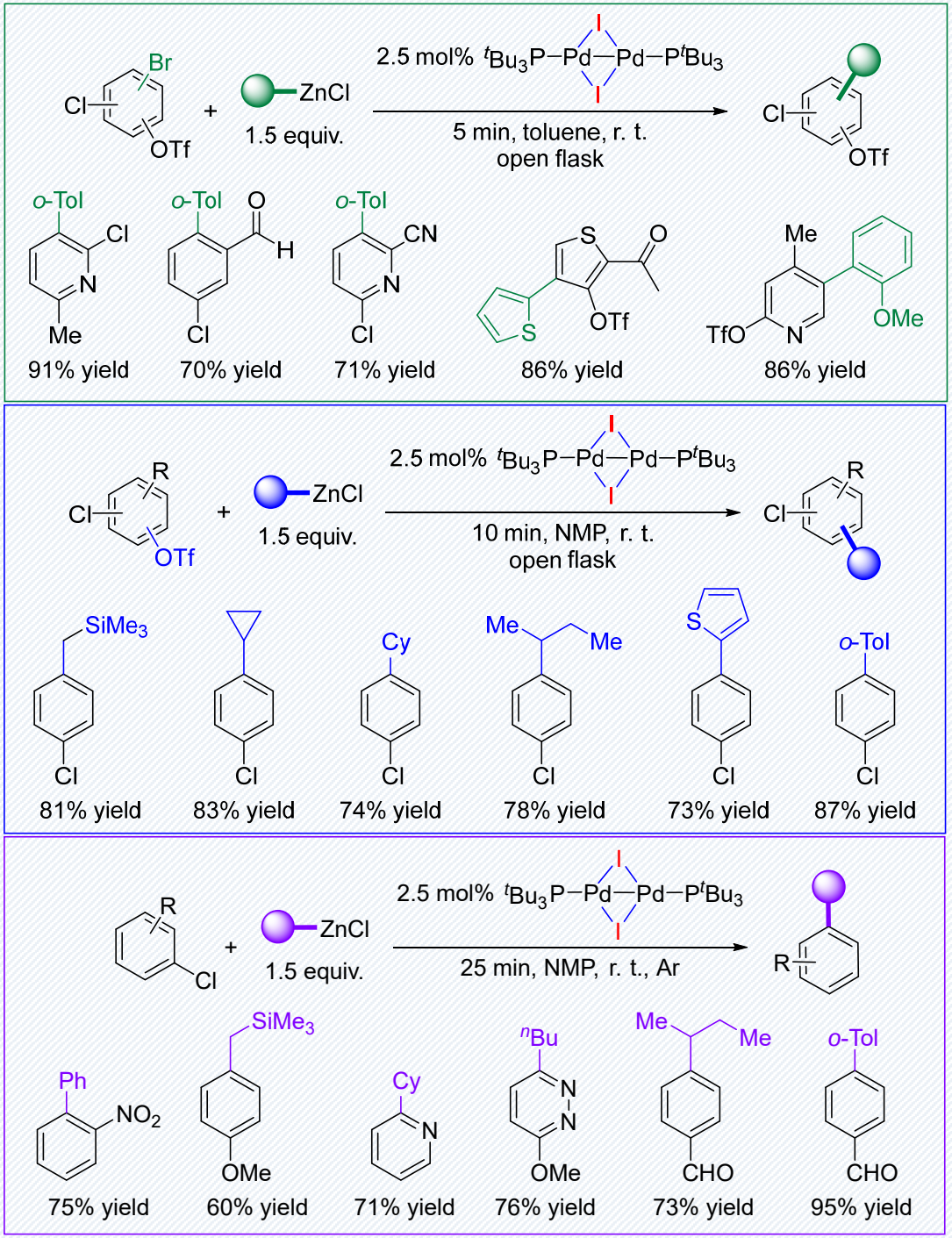
Site selectivity in **Pd(0)** reaction depends on:

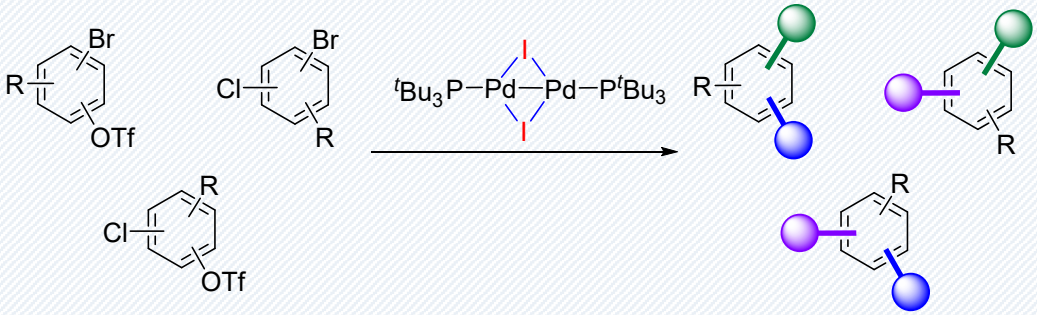
- Pd catalyst / ligand
- Steric and electronic of substrate
- Additive, solvent

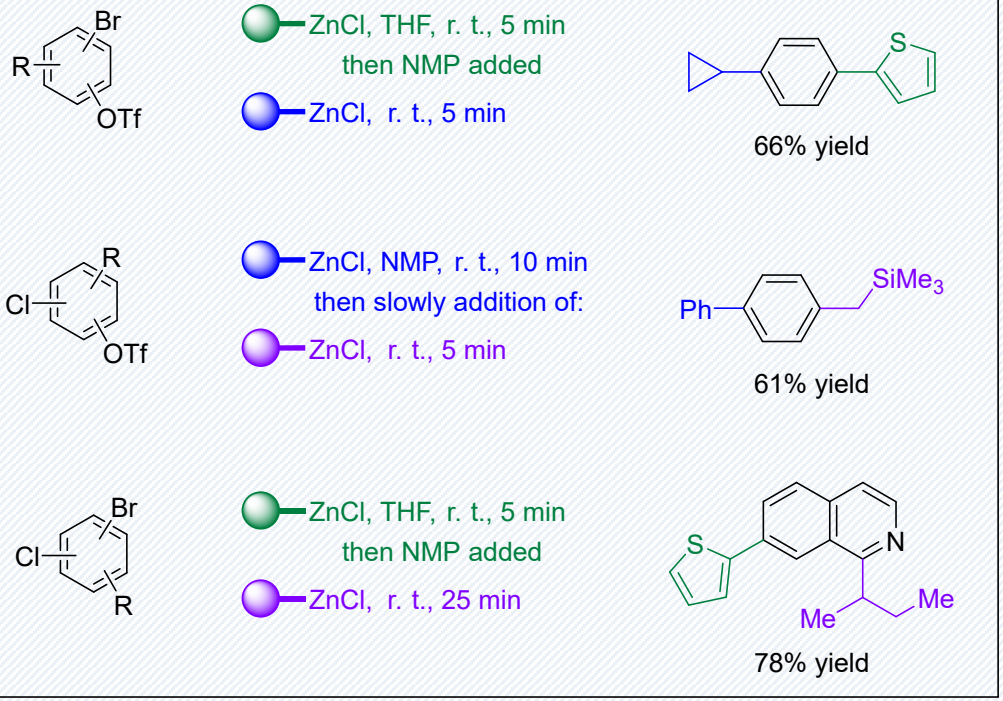
Challenges:

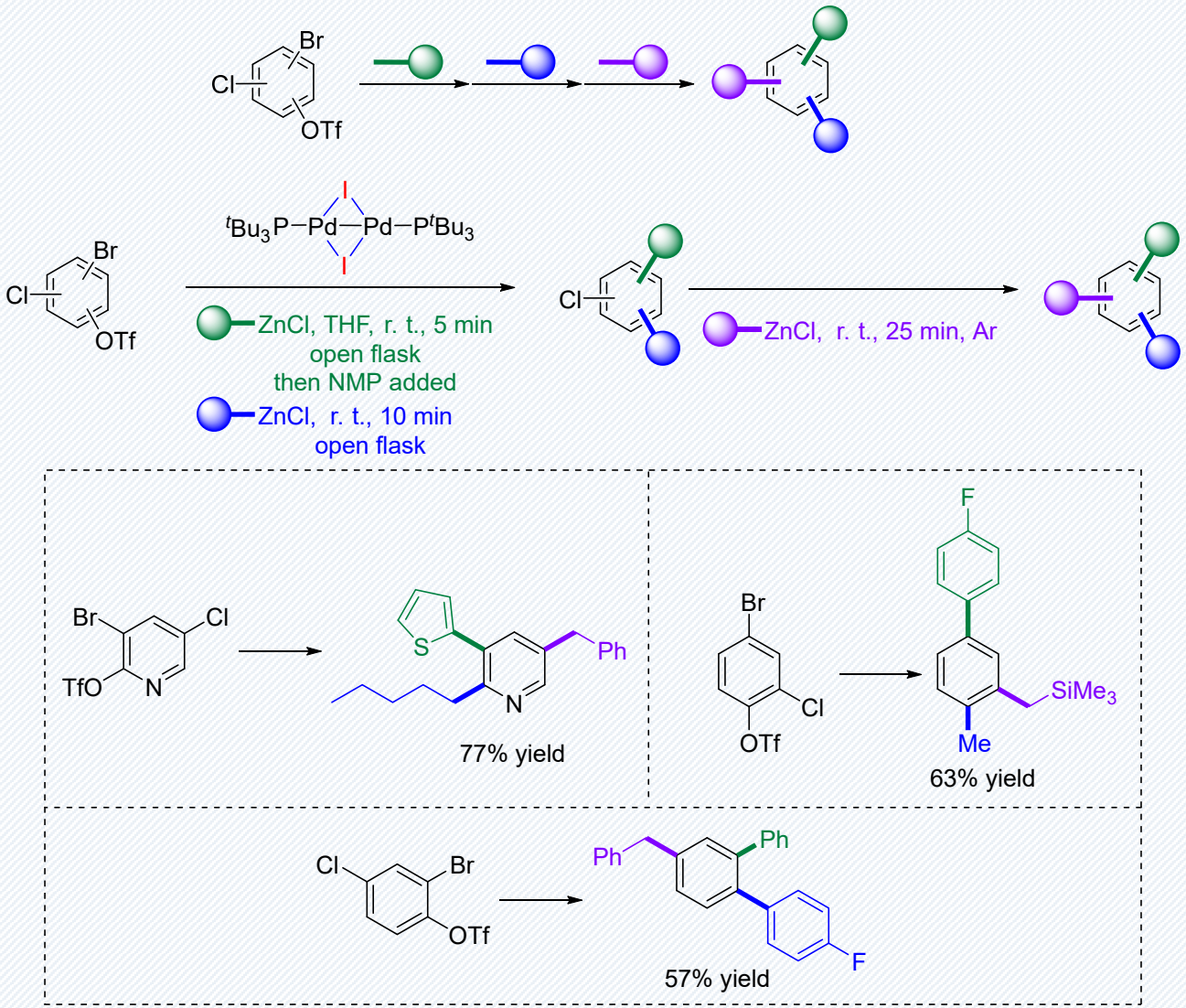
- Unpredictable
- Usually resulting complex
- No alkylation (β-H elimination)
- Air-sensitive
- Long reaction time and high temperature




Br
Cl
OTf
+
ZnCl
1.5 equiv.
2.5 mol% tBu3P–Pd–Pd–PtBu3
5 min, toluene, r. t.
open flask
Cl
OTf
o-Tol
Cl
N
Me
91% yield
o-Tol
O
H
Cl
70% yield
o-Tol
CN
N
Cl
71% yield
S
O
S
OTf
86% yield
Me
TfO
N
OMe
86% yield
R
Cl
OTf
+
ZnCl
1.5 equiv.
2.5 mol% tBu3P–Pd–Pd–PtBu3
10 min, NMP, r. t.
open flask
Cl
R
SiMe3
Cl
81% yield
Cl
83% yield
Cy
Cl
74% yield
Me
Me
Cl
78% yield
S
Cl
73% yield
o-Tol
Cl
87% yield
R
Cl
+
ZnCl
1.5 equiv.
2.5 mol% tBu3P–Pd–Pd–PtBu3
25 min, NMP, r. t., Ar
R
Ph
NO2
75% yield
SiMe3
OMe
60% yield
Cy
N
71% yield
nBu
N
N
OMe
76% yield
Me
Me
CHO
73% yield
o-Tol
CHO
95% yield


Br
R
OTf
Br
Cl
R
^{t}Bu$_3$P–Pd–Pd–P^{t}Bu$_3$
I
I
R
R
Cl
R
OTf
R

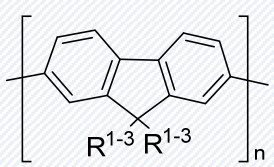

Br
R
OTf
ZnCl, THF, r. t., 5 min
then NMP added
ZnCl, r. t., 5 min
S
66% yield
R
Cl
OTf
ZnCl, NMP, r. t., 10 min
then slowly addition of:
ZnCl, r. t., 5 min
Ph
SiMe$_3$
61% yield
Br
Cl
R
ZnCl, THF, r. t., 5 min
then NMP added
ZnCl, r. t., 25 min
S
N
Me
Me
78% yield



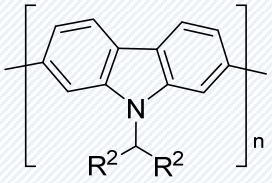
Schoenebeck, F. and coworkers, *Angew. Chem. Int. Ed.* **2018**, *57*, 12573.

Polymerization reaction

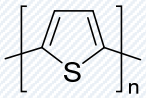
Polymers in material applications



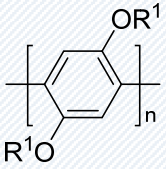
Polyfluoene
transistor, LEDs



Polycarbazole (PCz)



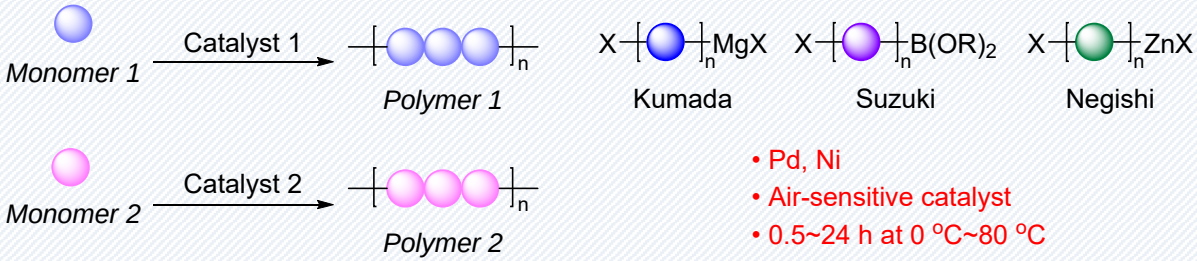
Polythiophene
organic field effect
transistors (OFETs)
solar cells



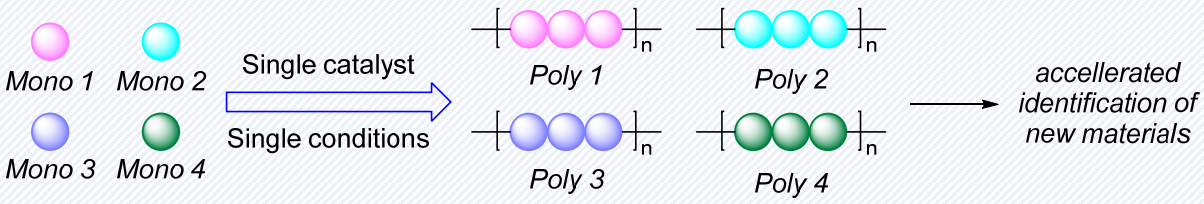
Poly(*p*-phenylene) PPP
photovoltatic cells

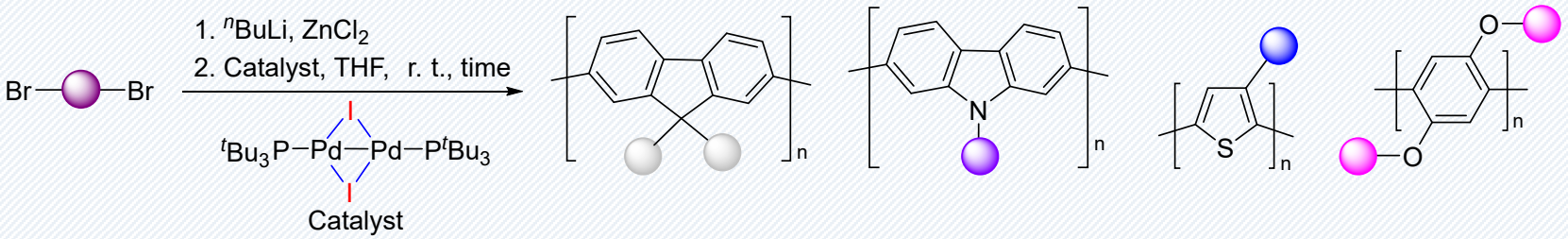
R^1 = 2-ethylhexyl, R^1 = octyl , R^3 = 4-hexyloxyphenyl

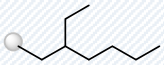
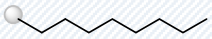
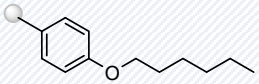
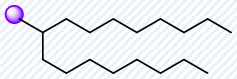
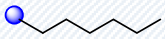
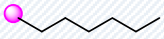
Current approach ♦ *specific catalyst for single polymer*



Vision ♦ *simple conditions for many polymers*

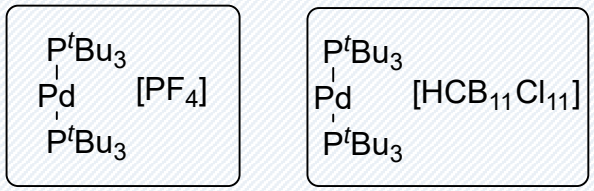


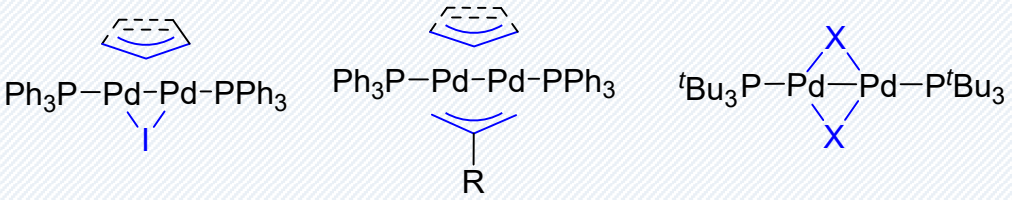


polymer	entry	catalyst loading (%)	time (min)	M_n (Kg/mol)	M_w (Kg/mol)	PDI	note
	1	0.5	0.5	24.3	52.3	2.15	open flask
	2	0.005	30	51.0	98.9	1.94	
	3	0.005	20 h	53.1	123.1	2.32	$Pd(CH_3CN)_2Cl_2$ P^tBu_3
	4	0.5	30	13.1	23.8	1.82	open flask
	5	0.005	30	15.4	25.8	1.66	
	6	0.5	1	44.3	80.1	1.80	
	7	0.5	2	23.1	43.2	1.86	
	8	0.5	0.5	9.3	18.0	1.94	open flask
	9	0.5	1	5.9	7.2	1.20	

Schoenebeck, F. and coworkers, 10.1002/anie.201903765

4. Summary



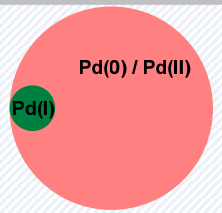


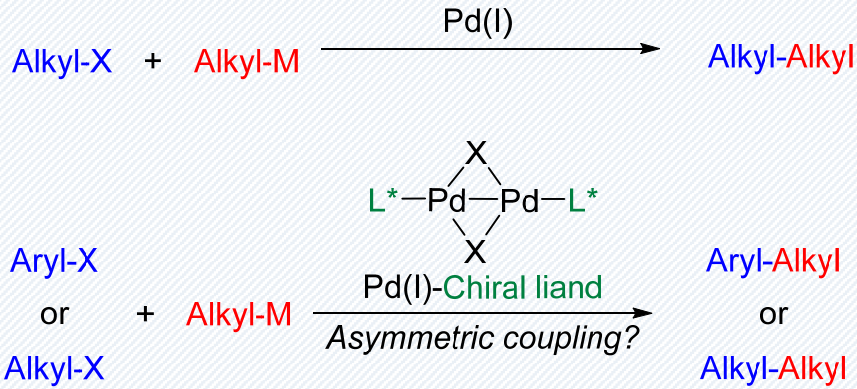
Pd(I)

- Air-stable
- Moisture stable
- Thermally stable
- High chemoselectivity in cross-coupling reaction
- Limited nucleophilic scope

Pd(0) / Pd(II)

- Wide range of reaction types
- Commercial available





Thanks for your attention !