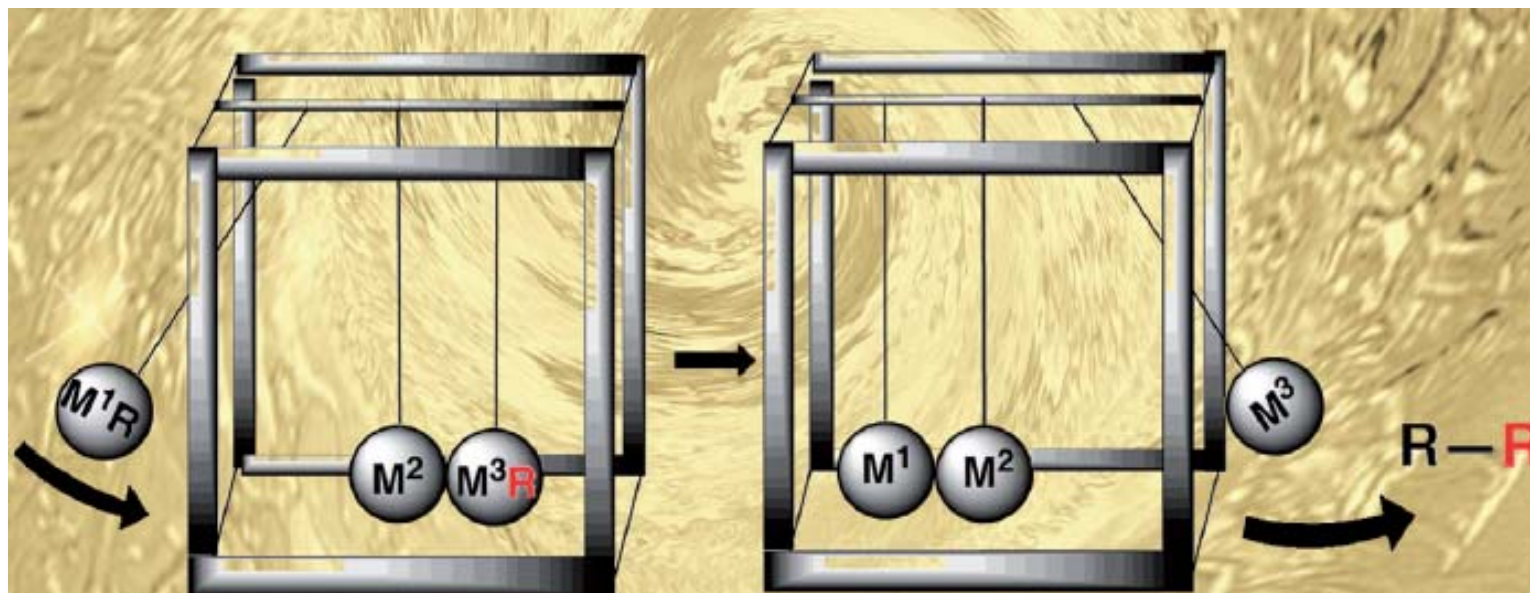


Bimetallic catalysed C–C Coupling and Other Reactions using Transition Metals



Reporter: Xinjin Li

Sep 7th, 2015

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1 Introduction

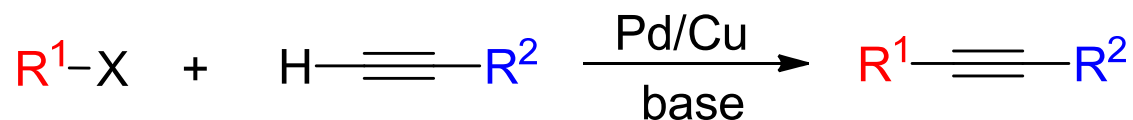
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1. Introduction

Bimetallic catalysis refers to homogeneous processes in which two transition metals cooperate in a synthetic process (often a C–C coupling) and their actions are connected by a transmetalation step.



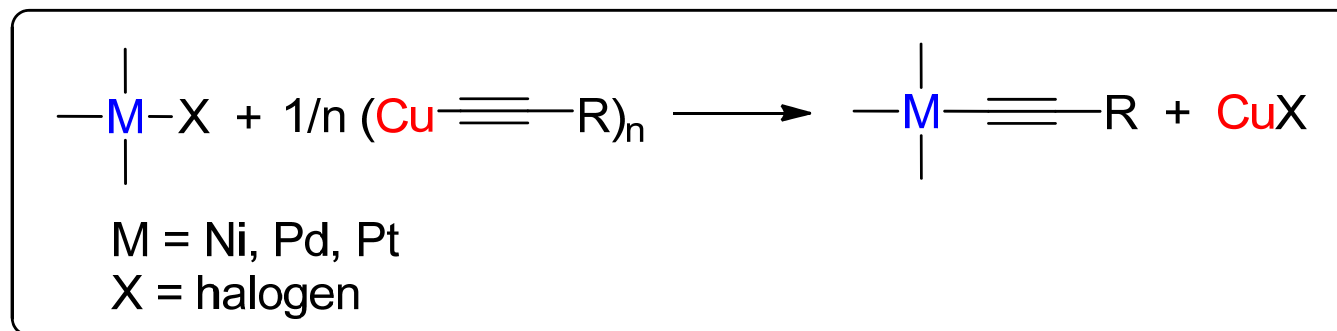
Scheme 1. Sonogashira coupling

Pérez-Temprano, M. H.; Casares, J. A; Espinet, P. *Chem. Eur. J.* **2012**, *18*, 1864.

2. Group Exchange between Organometallic Complexes

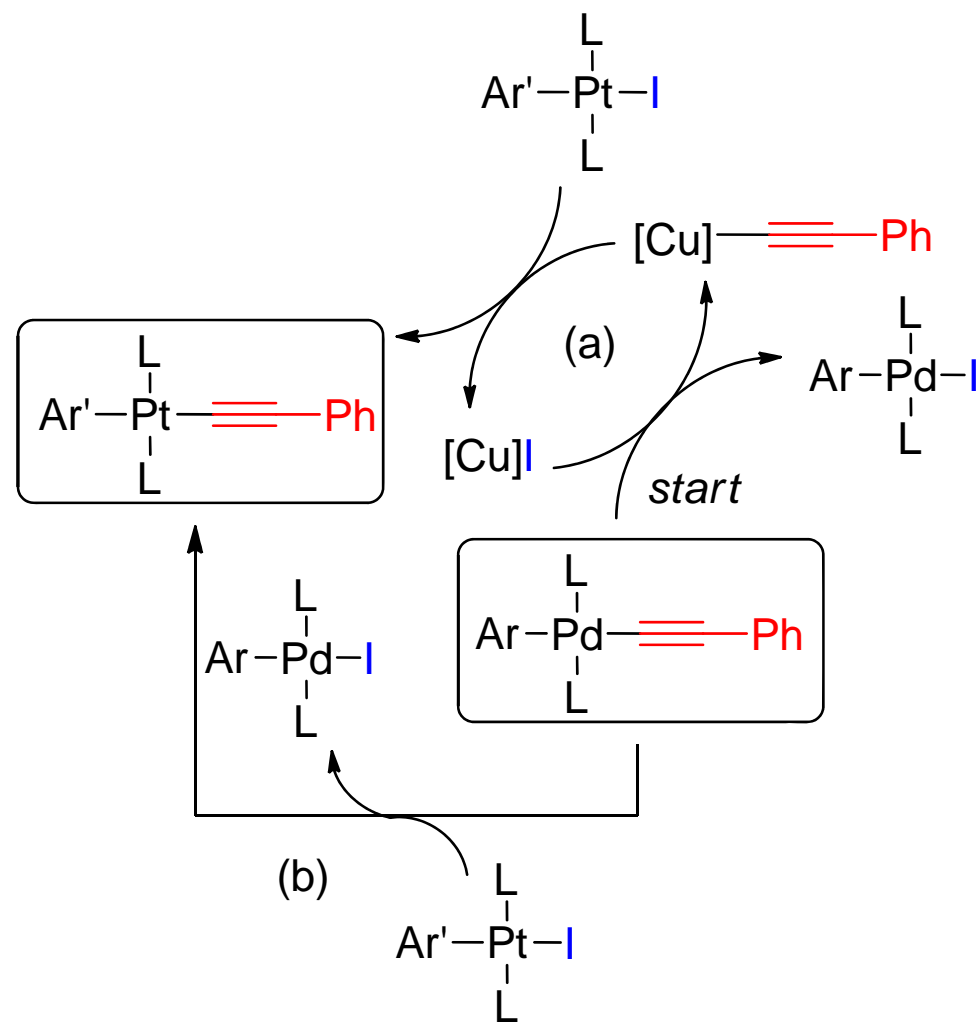
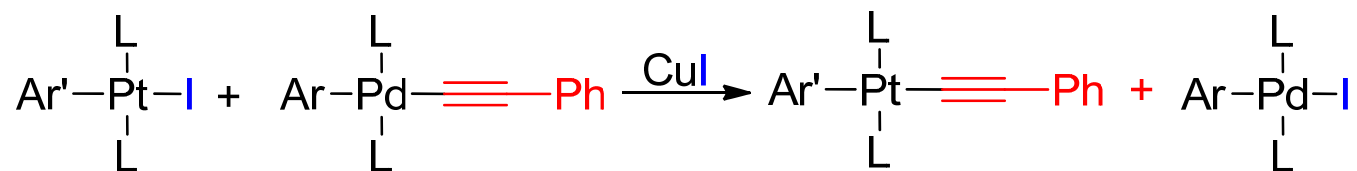
Group transfers are essential in most organic reactions assisted by transition metal complexes, and can be classified according to the type of ligand exchange and bond involved: halogen for organic group and carbon for carbon exchange.

Halogen for organic group exchange: In a catalytic process, transmetalation of an organic group to a halogen–transition-metal complex is eventually followed by a reductive elimination, giving a R1–R2 cross-coupling product. However, when the reductive elimination fails and the transmetalated complex is stable, the exchange is a new method for preparing organo-transition-metal complexes.



Scheme 2. Alkynyl transfer from Cu to other metals

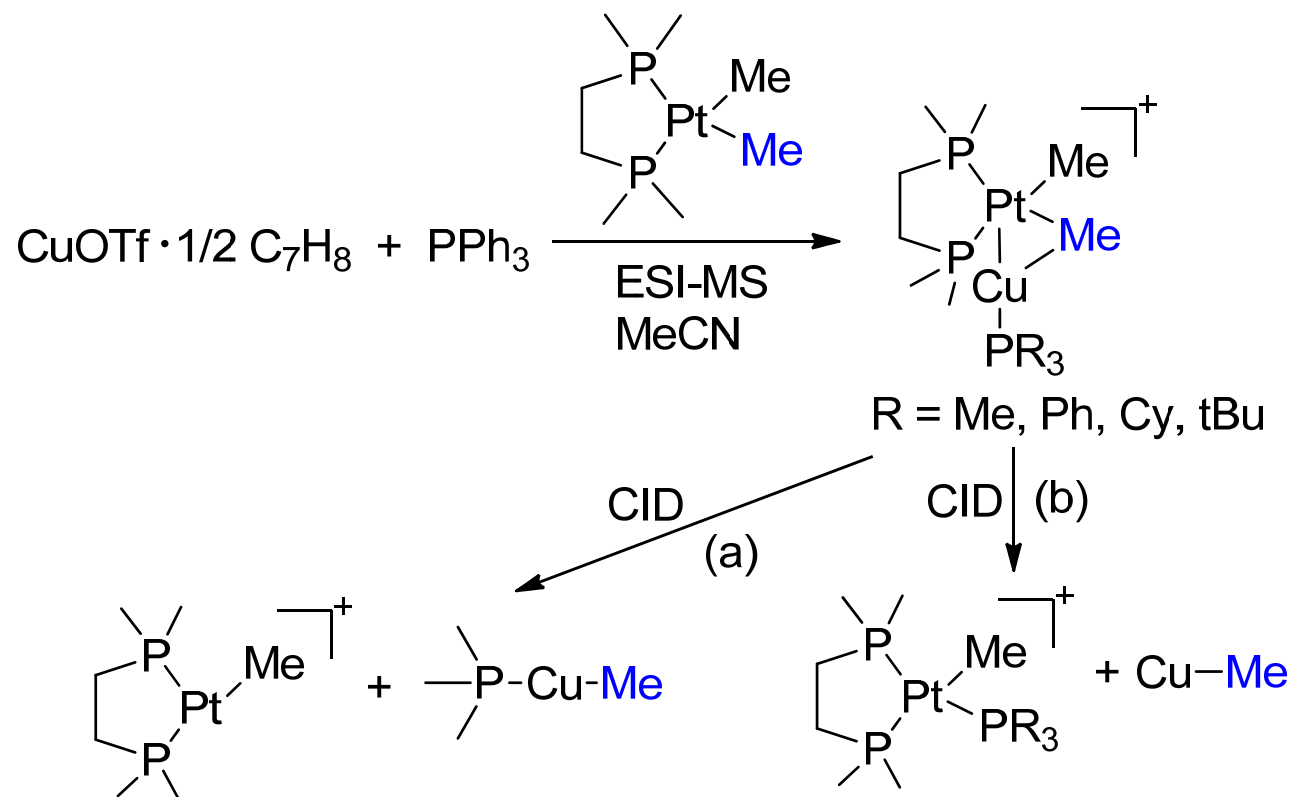
Osakada, K.; Yamamoto, T. *Coord. Chem. Rev.* **2000**, 198, 379.



Scheme 3. Cu^I-mediated alkyne transfer from Pd^{II} to Pt^{II}

Osakada, K.; Yamamoto, T. *Organometallics* **1997**, *16*, 5354.

Pseudohalide for organic group exchange

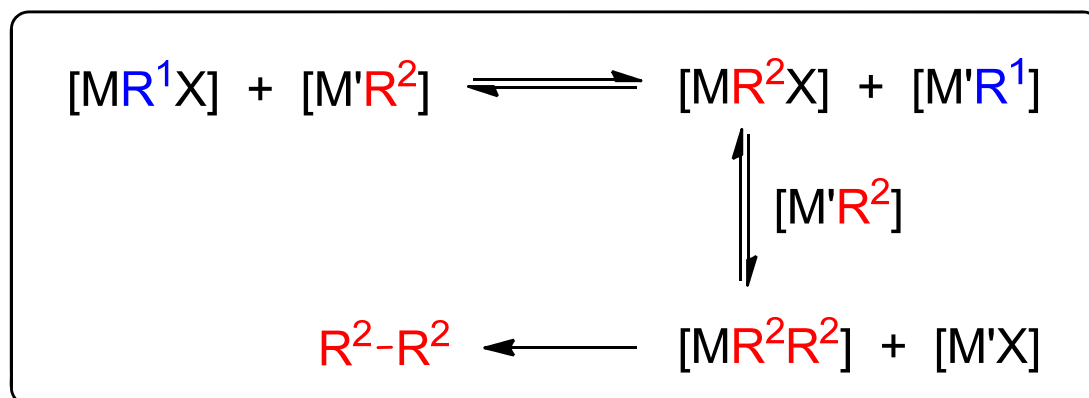


Scheme 4. Transmetalation from Pt^{II} to Cu^I

Moret, M.-E.; Serra, D.; Bach, A.; Chen, P. *Angew. Chem. Int. Ed.* **2010**, *49*, 2873.

2. Group Exchange between Organometallic Complexes

Carbon for carbon exchange: Reports on carbon for carbon exchange using non-main-group arylating agents are unusual. In fact, unobserved carbon for carbon exchanges might be more common than expected.

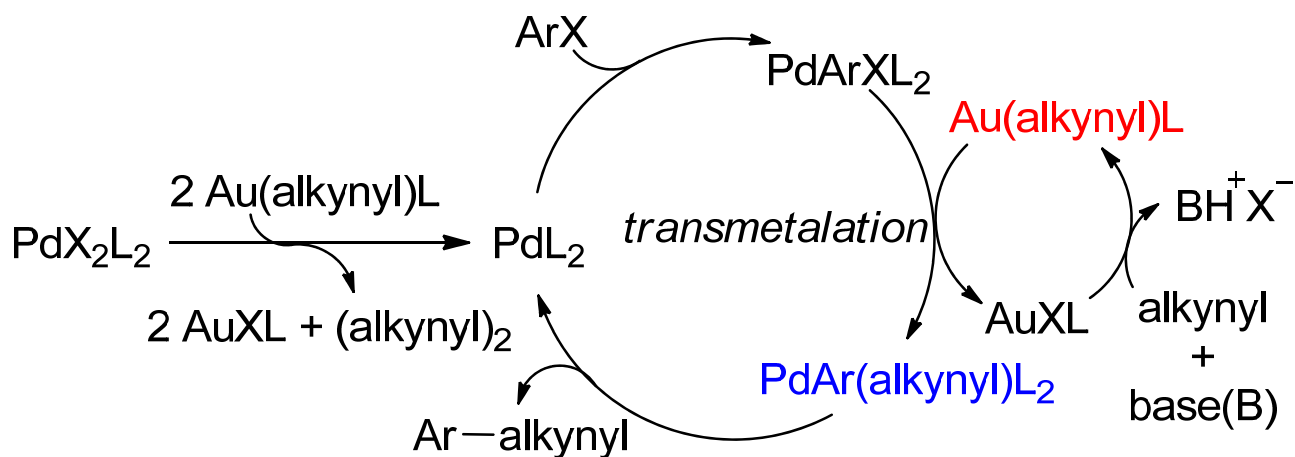


Scheme 5. A plausible mechanism of formation of undesired homocoupling products

Casares, J. A.; Espinet, P.; Fuentes, B.; Salas, G. *J. Am. Chem. Soc.* **2007**, *129*, 3508.

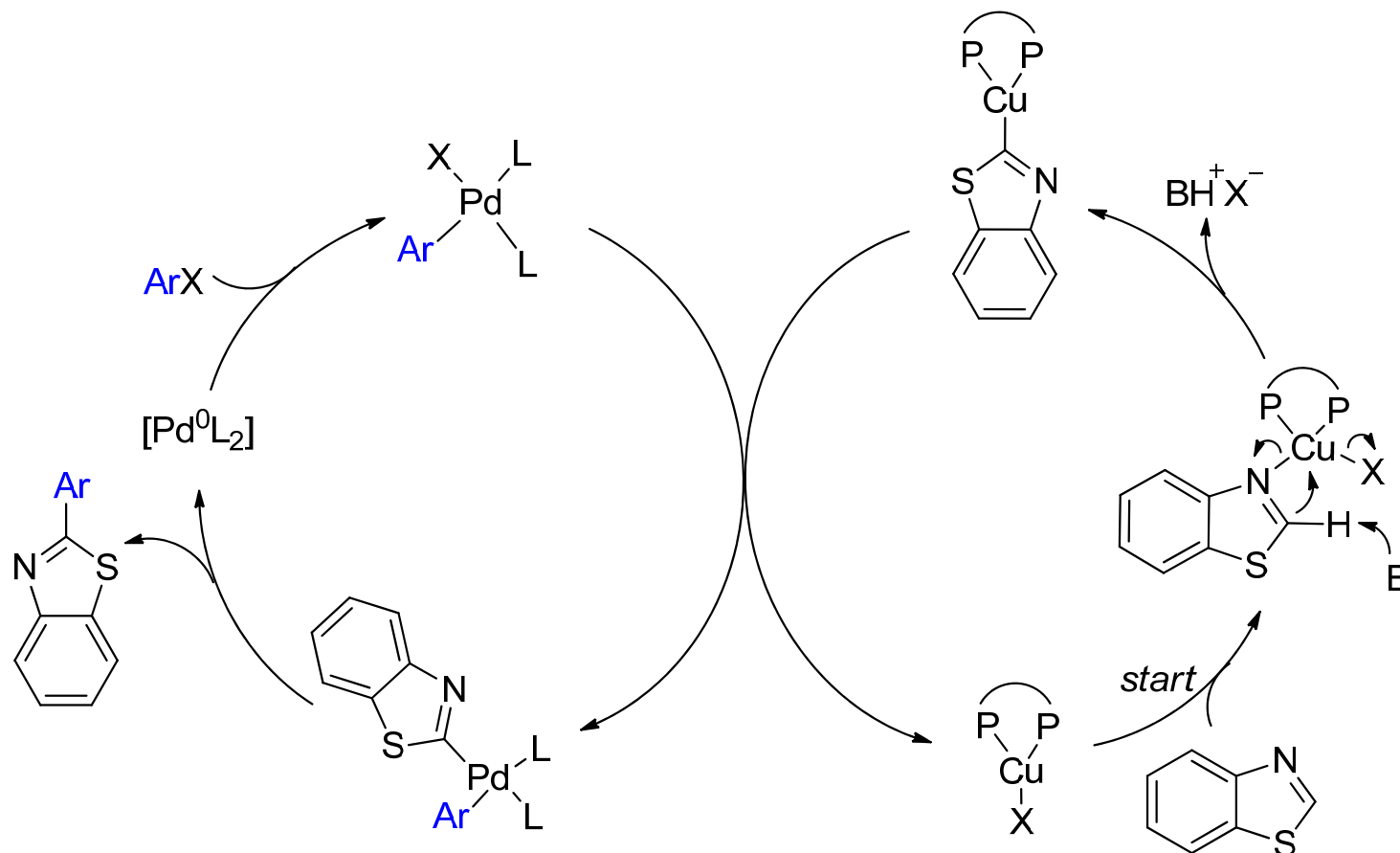
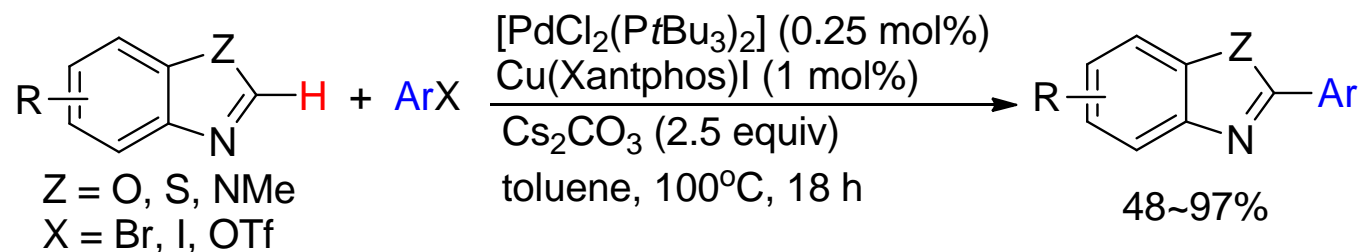
3. Bimetallic Catalysis in C–C bond Forming Reaction

Bimetallic catalysis involving C–H activation: The role of one of the metals is to activate a C–H bond and then to transfer this organic group to a second metal and that completes the catalytic cycle.



Scheme 6. Mechanistic proposal correcting the so-called “Pd-free Sonogashira reaction”

Lauterbach, T.; Espinet, P. and et al. *Org. Lett.* **2010**, *12*, 3006.

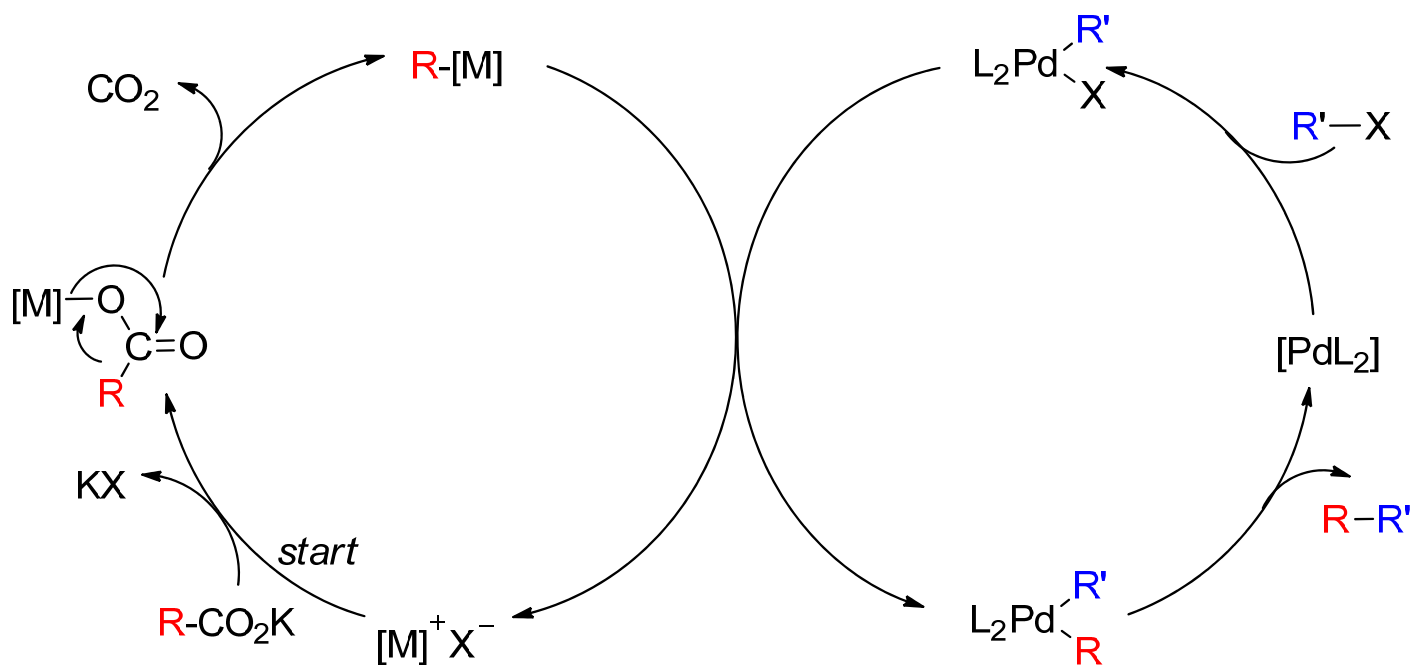
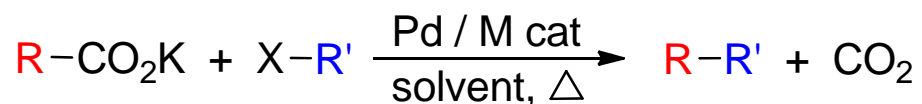


Scheme 7. Pd/Cu double-co-catalytic mechanism in the direct arylation of heteroarenes

Huang, J.; Chan, J. and et al. *J. Am. Chem. Soc.* **2010**, *132*, 3674.

Decarboxylative cross-coupling processes

A copper(I) or a silver(I) catalyst mediates the extrusion of CO₂ from carboxylic acid salts, while a palladium complex catalyzes the coupling of the resulting carbon nucleophiles with carbon electrophiles.

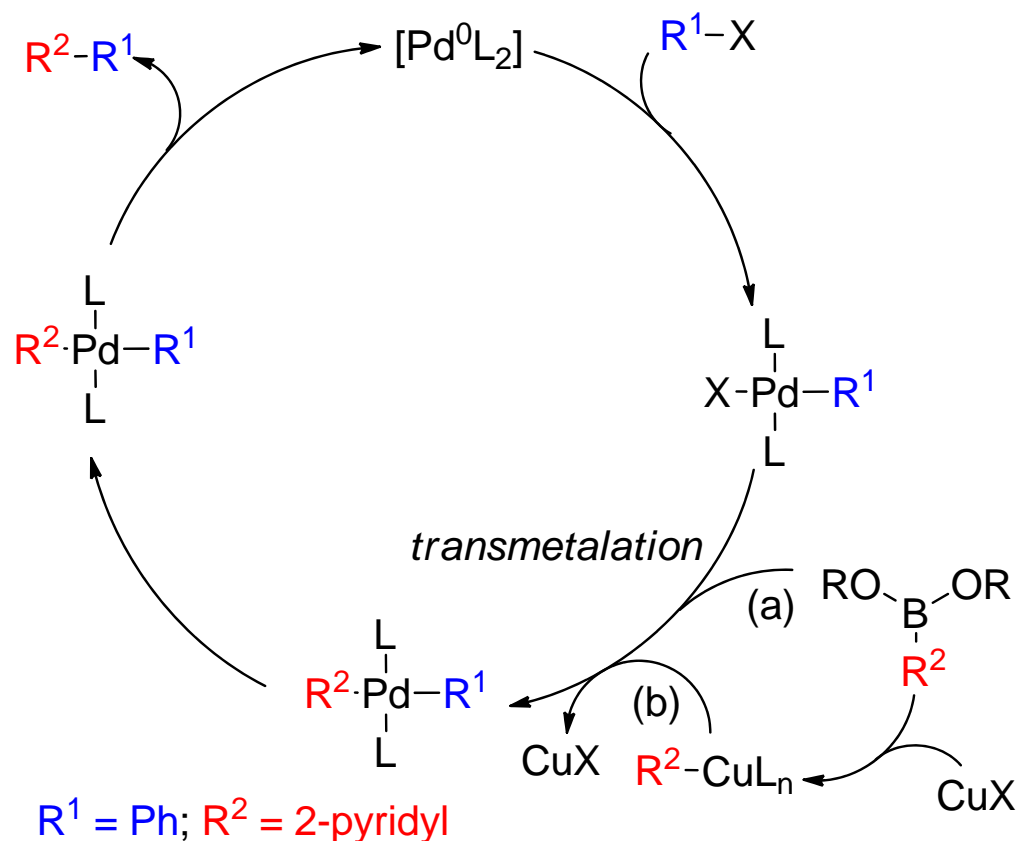


Scheme 8. Pd/M decarboxylative cross-coupling process (M=Ag, Cu)

Goossen, L. J.; Deng, D.; Levy, L. M. *Science* **2006**, 313, 662.

“Copper effect” in Suzuki coupling reaction

With the exception of Sonogashira and Stille reactions, copper effects in bimetallic catalysis have been reported less frequently.

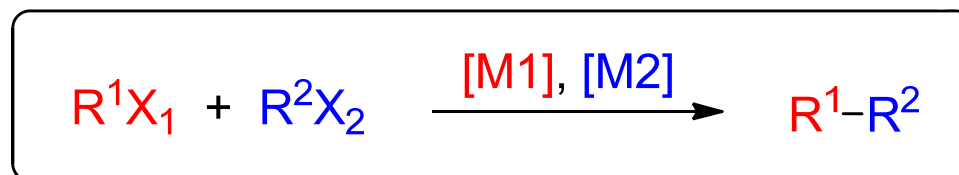


Scheme 9. Proposed organocopper-mediated transmetalation in a Suzuki catalytic cycle

Deng, J. Z.; Paone, D. V and et al. *Org. Lett.* **2009**, *11*, 345.

Bimetallic catalysed cross-Ullmann reaction

Compared to all the above examples involving only one metal catalyst undergoing oxidative addition, the bimetallic catalysed cross-Ullmann reaction (the cross-coupling of two different aryl electrophiles) is highly challenging.

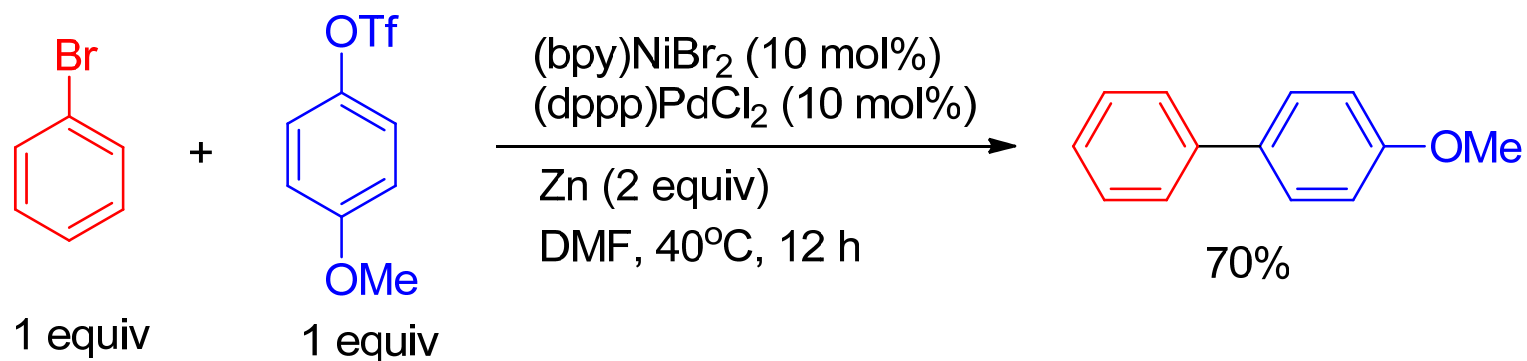
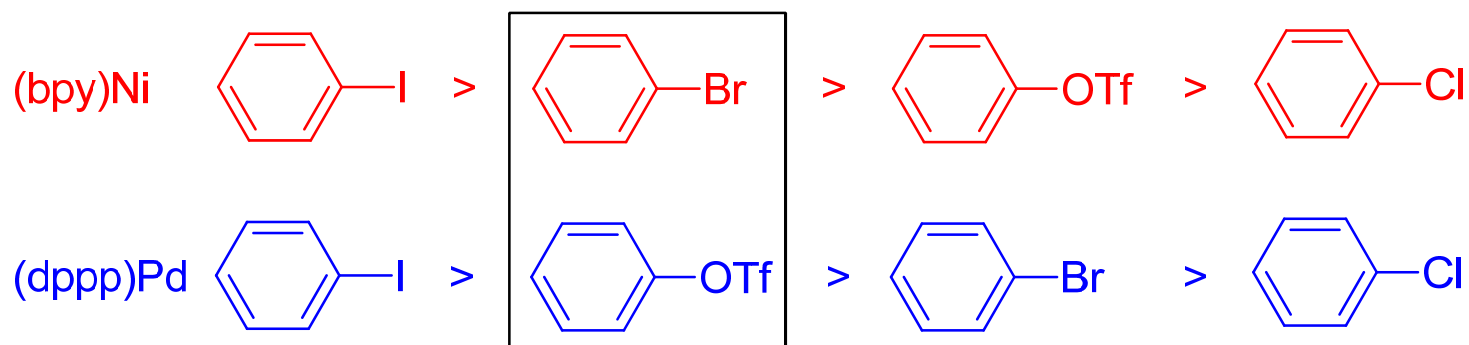


- ✦ Each of the two catalysts activated only one of the two substrates.
- ✦ Selective transmetallation could be achieved.
- ✦ The catalysts were redox compatible.

Ackerman, L. K. G.; Lovell, M. M.; Weix, D. J. *Nature*, **2015**, 524, 454.

Multimetallic catalysed cross-coupling of aryl bromides with aryl triflates

Relative reactivity of catalysts



Ackerman, L. K. G.; Lovell, M. M.; Weix, D. J. *Nature*, **2015**, 524, 454.

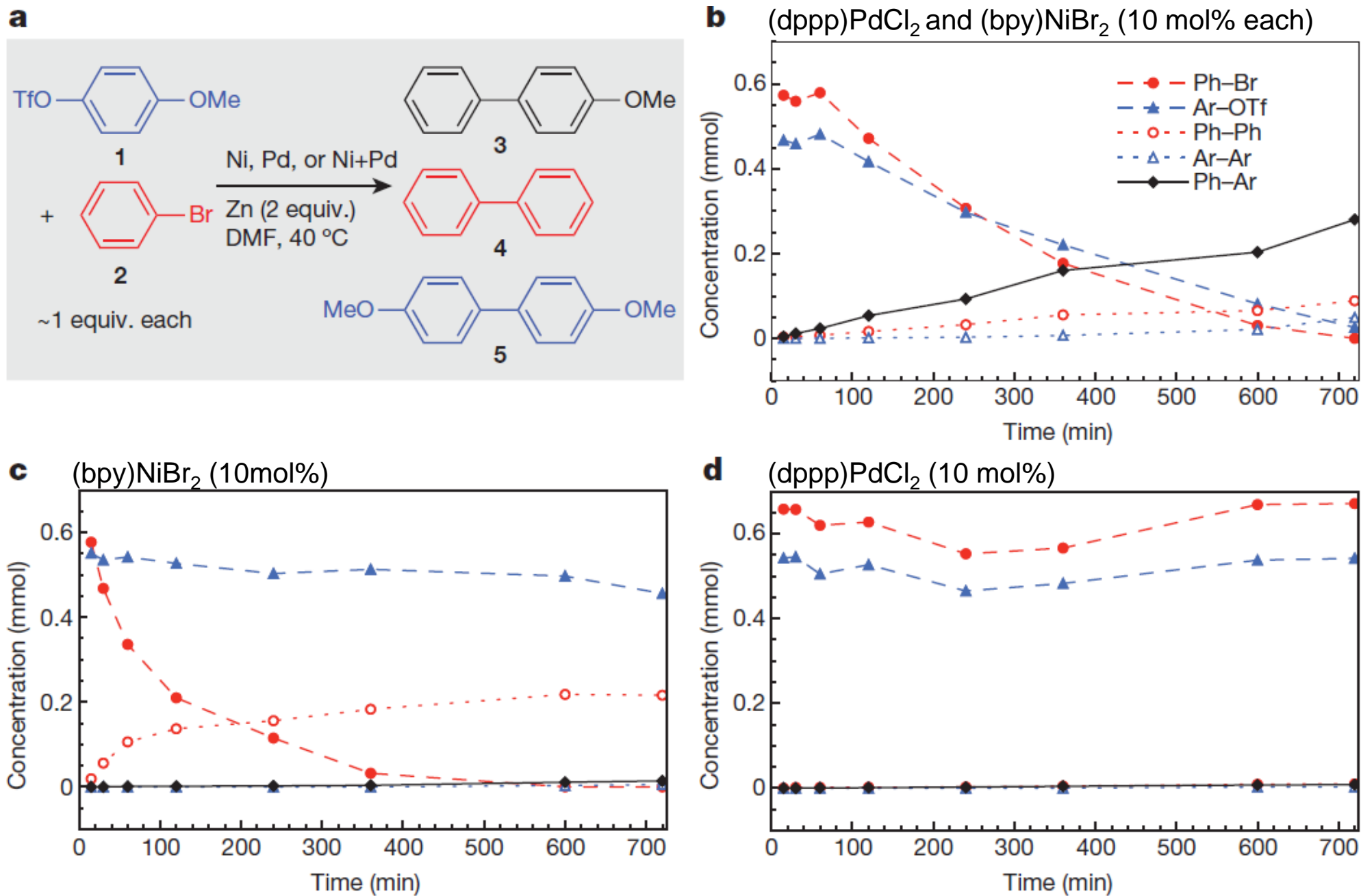


Fig.1 Selectivities of nickel and palladium catalysts.

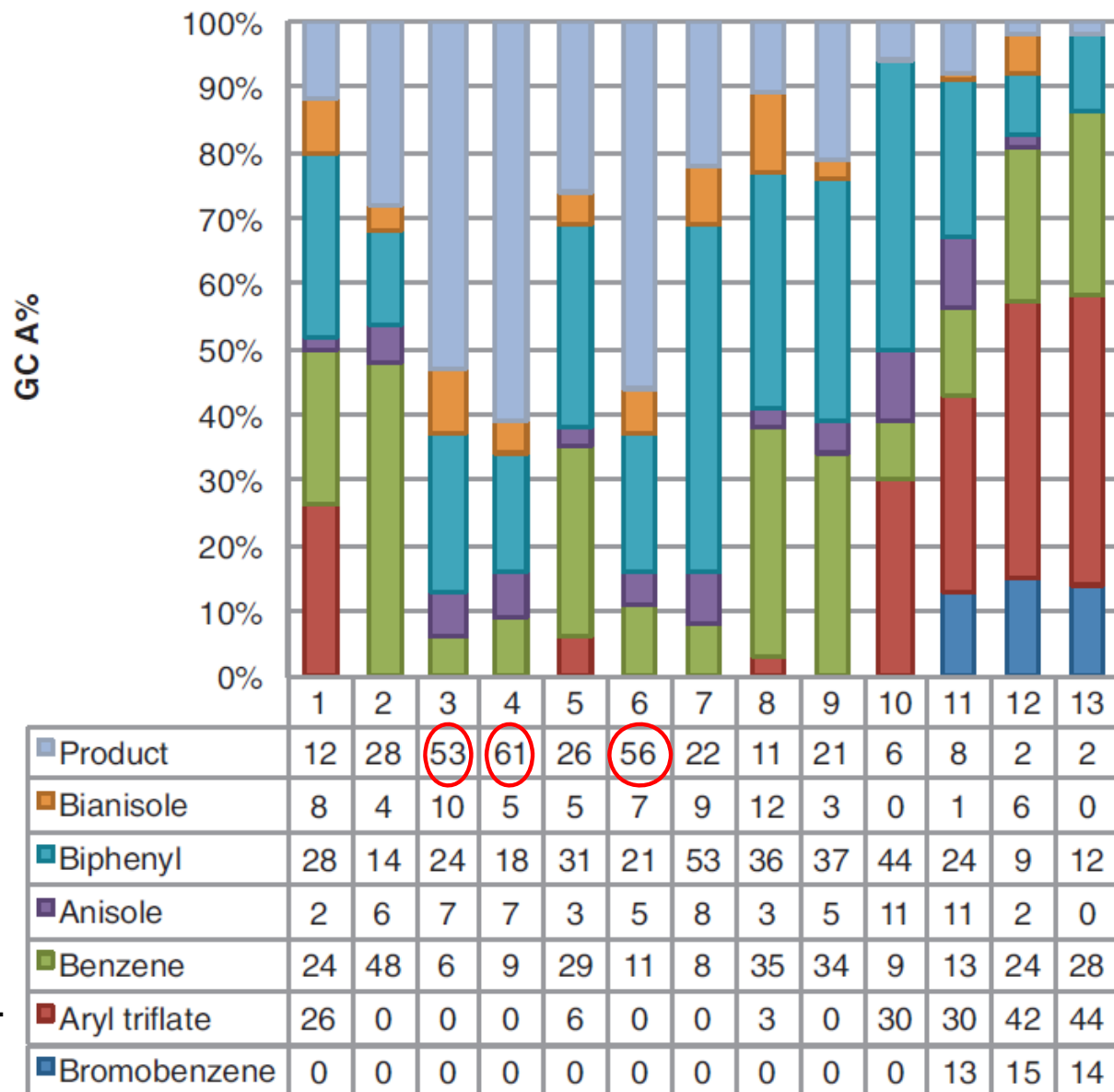
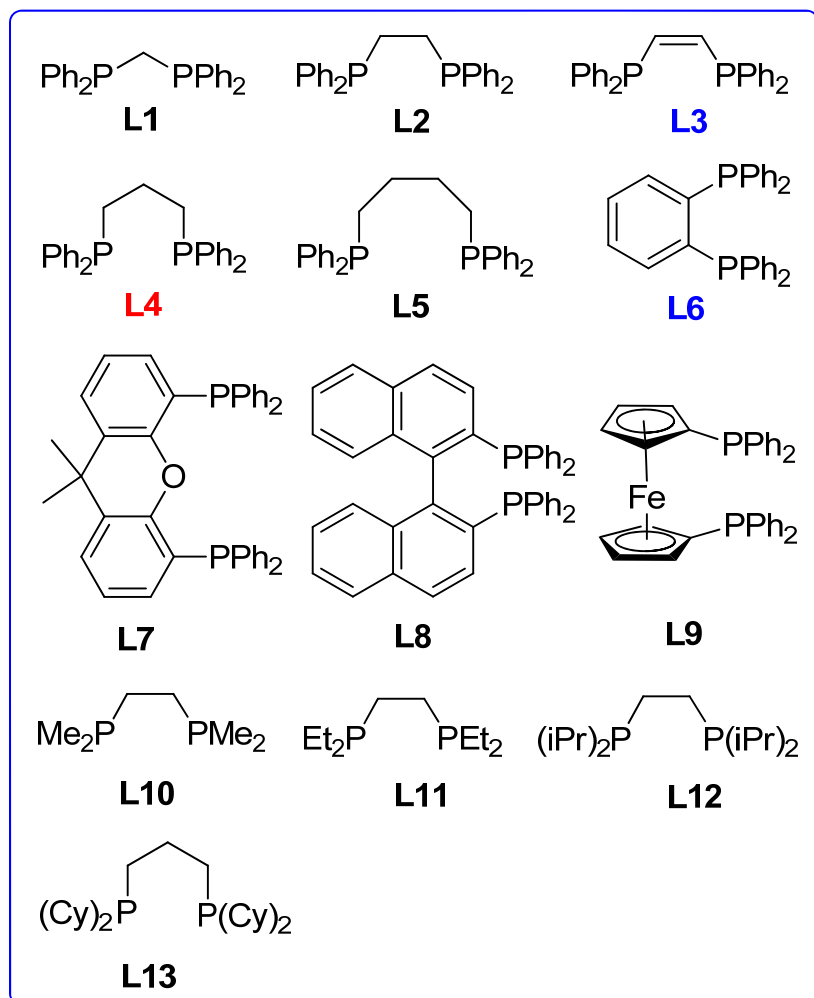
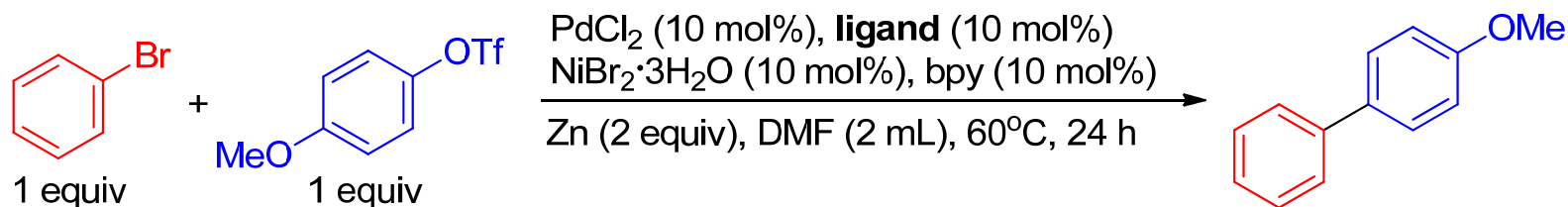


Fig.2 Varying ligands on the palladium catalyst.

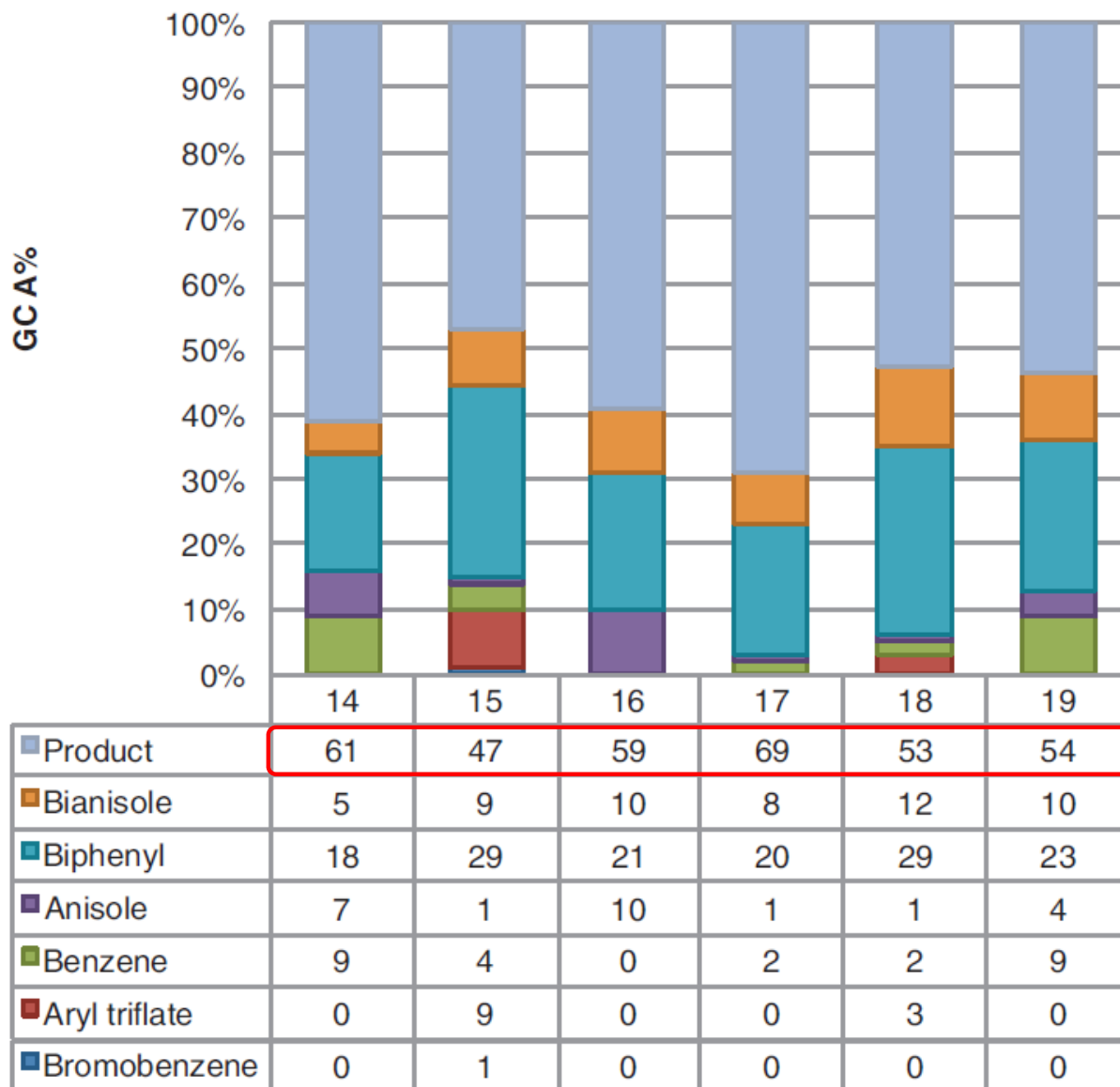
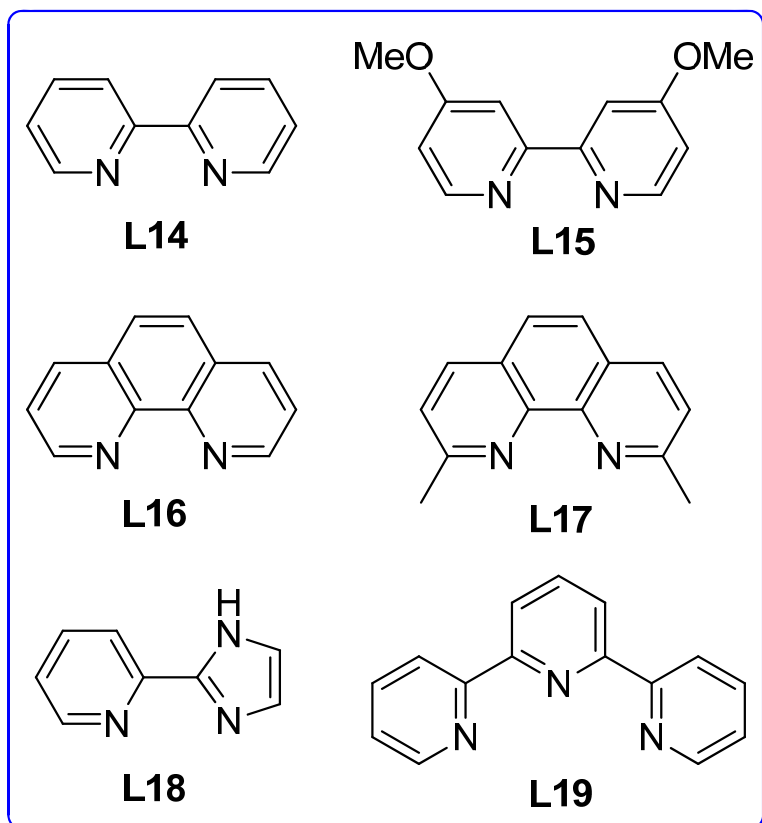
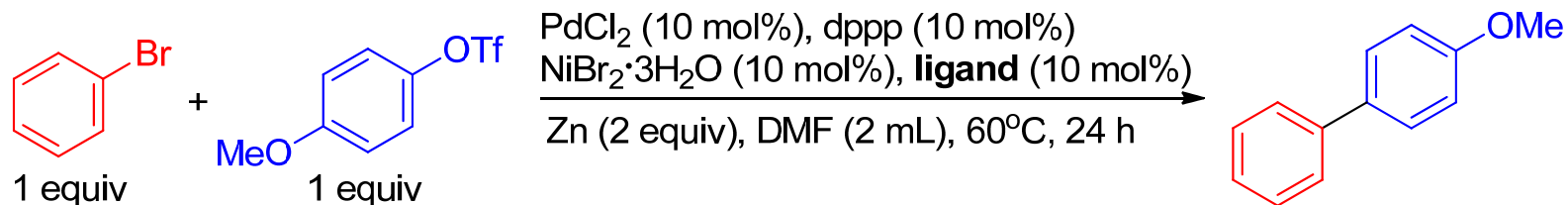
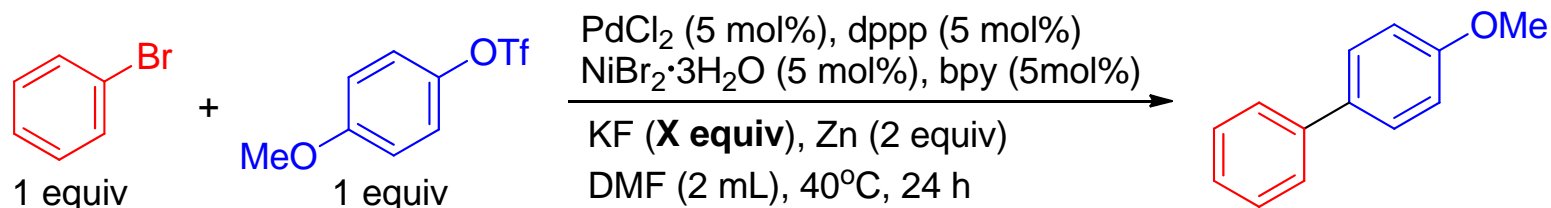


Fig. 3 Varying ligands on the nickel catalyst.



Equiv KF	t (h)	PhBr Remaining (% yield)	ArOTf Remaining (% yield)
0	11	30	38
	24	5	10
0.2	11	35	36
	24	20	28
0.5	11	13	15
	24	0	1
1	11	0	9
	24	0	0
2	11	1	0
	24	0	0
3	11	0	0
	24	0	0

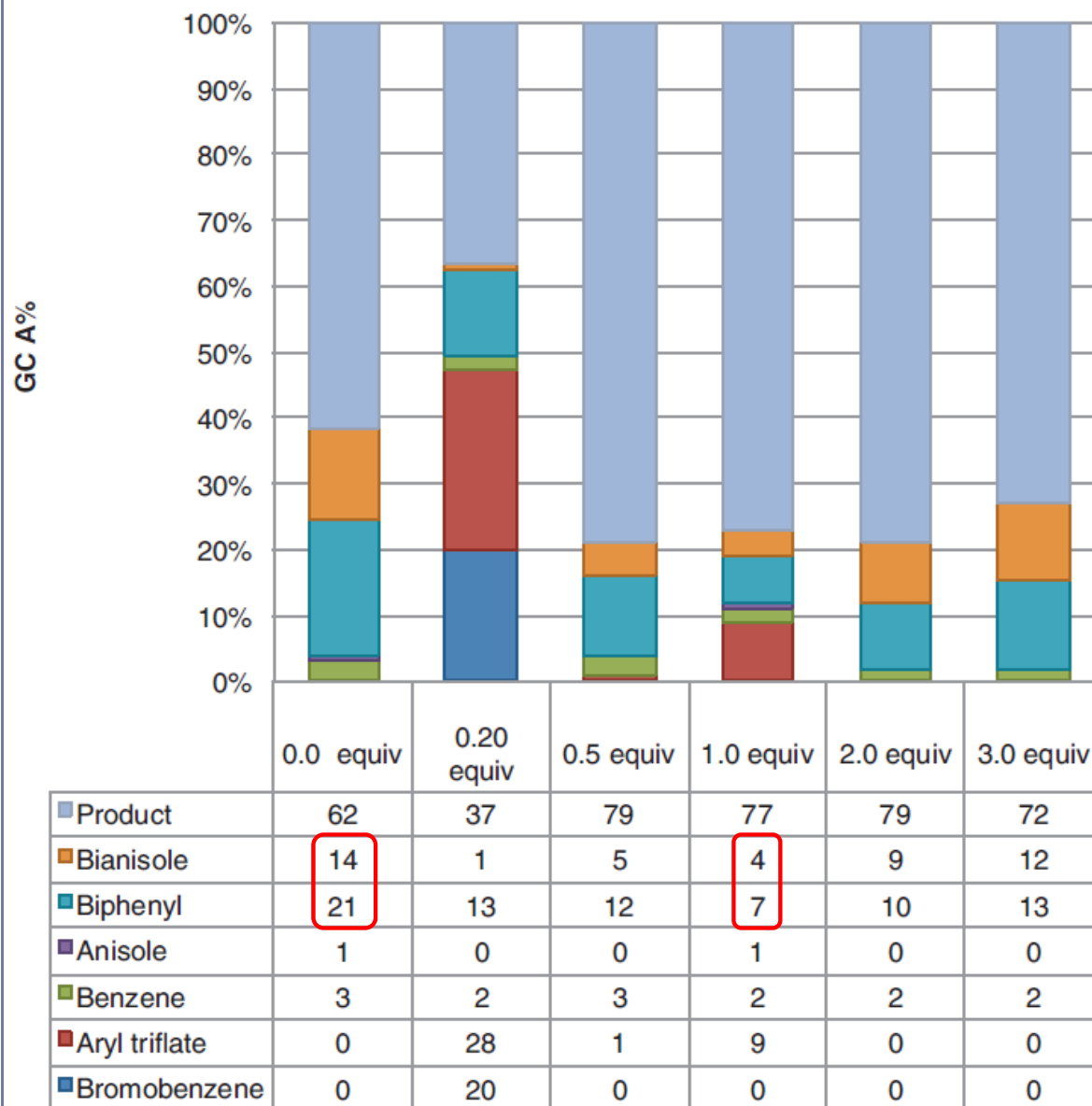
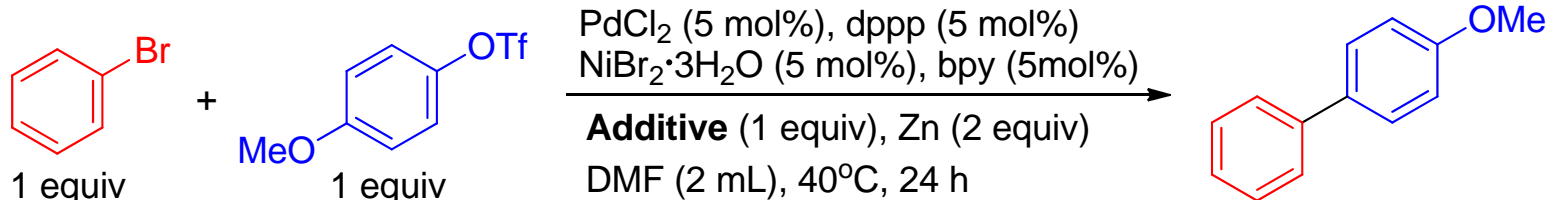


Fig. 4 The effect of KF on the selectivity of the multimetal-catalysed cross-Ullmann reaction.



Additive	t (h)	PhBr Remaining (% yield)	ArOTf Remaining (% yield)
No Salt	3	42	47
	24	5	10
KF	3	30	31
	24	0	0
LiF	3	39	39
	24	0	3
CsF	3	3	37
	24	0	11
KI	3	5	37
	24	0	0
KBr	3	0	23
	24	0	2
KOAc	3	2	26
	24	0	0

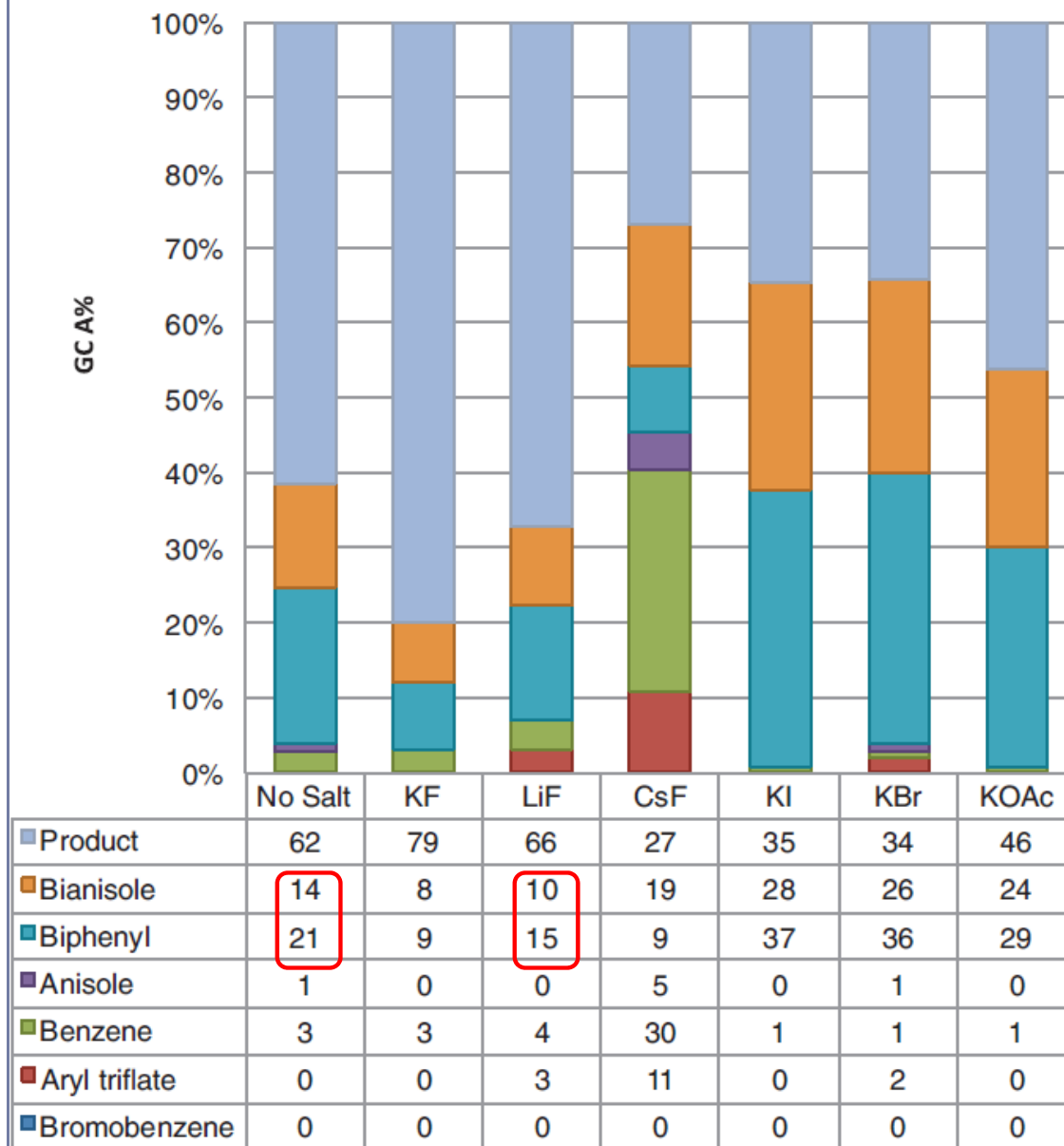
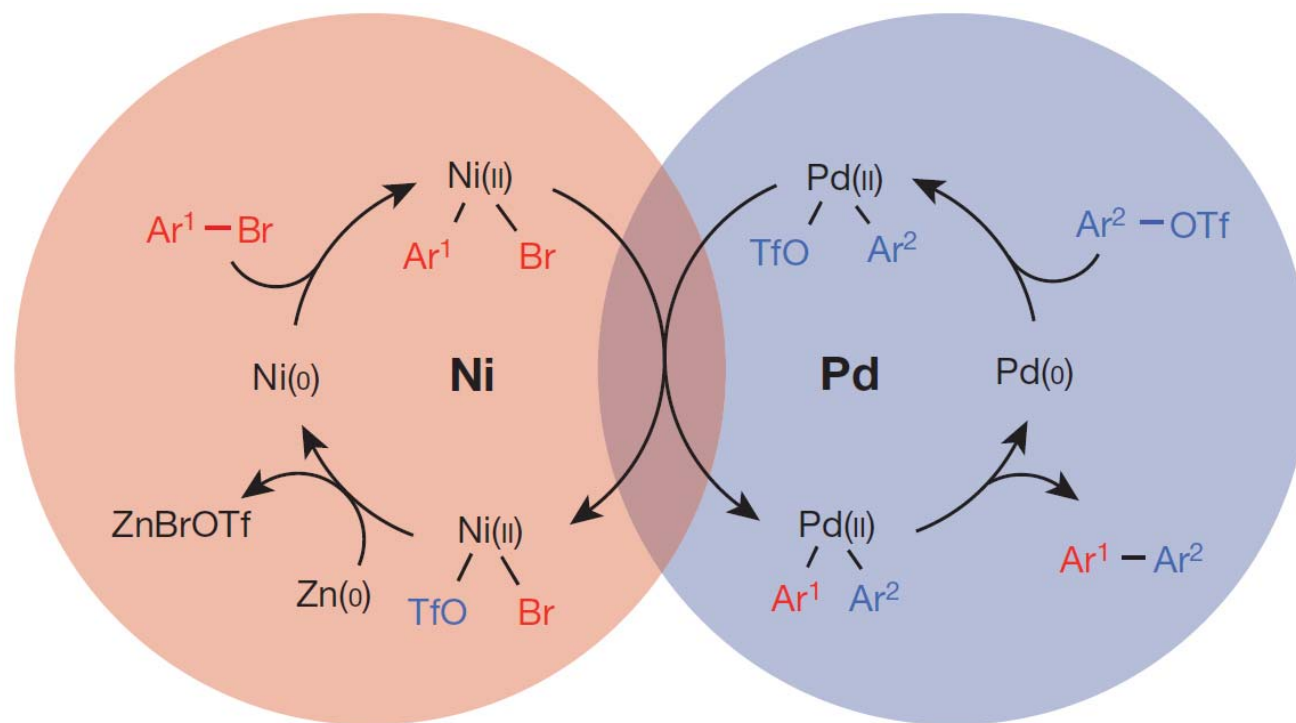


Fig. 5 The effect of additive on the selectivity of the multimetal-catalysed cross-Ullmann reaction.

Multimetallic catalysed cross-coupling of aryl bromides with aryl triflates



Scheme 10. A general cross-Ullmann reaction catalysed by a combination of nickel and palladium.

Ackerman, L. K. G.; Lovell, M. M.; Weix, D. J. *Nature*, **2015**, *524*, 454.

Summary and Outlook

- (1) New methods to form C–C bonds using bimetallic systems (Pd/Cu, Pd/Au, Pd/Ni couples) have emerged, but it is also to develop other less well-behaved metal combinations.
- (2) It is important to understand the exchange of ancillary ligands, and the relative rates.
- (3) In the near future, new processes, particularly the catalytic versions of processes are hoped.

Thanks for your attention!