

Bimetallic Catalysis: Transition and Group 11 Metals

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Dong Group Literature Talk

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Overview

- Introduction
- Group Exchange
- C-C Bond Forming Reactions
 - Direct Arylation
 - Decarboxylative Cross-Coupling
 - The “Copper Effect” and Palladium
 - Gold and Palladium Synergy
 - Dissimilar Couples
- Conclusions

Which Metals?

- No Main Group, Only Transition or Group 11

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
Period 1	1 H																		2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne	
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe	
6	55 Cs	56 Ba	57-71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn	
7	87 Fr	88 Ra	89-103	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo	

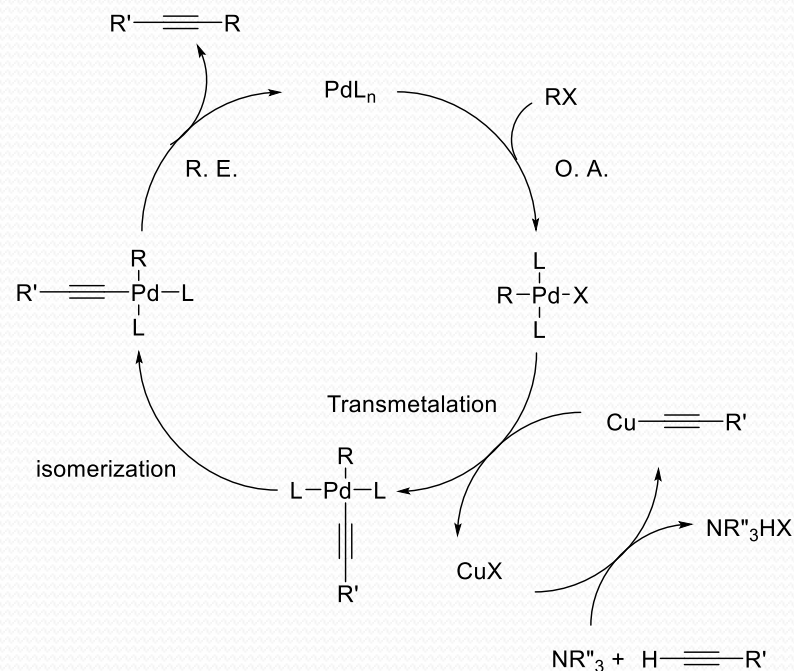
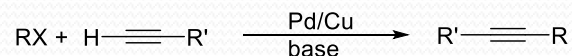
57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Why Do We Care?

- Transmetalation
 - If process is catalytic in both metals, two catalytic circles should exist, connected by a transmetalation step
 - Little is understood about transmetalation to this point, so difficult to predict
- Through this transmetalation step new complexes can be obtained that were previously impossible
- Taps into unique qualities and strengths of each metal, leading to unique reactivity and transformations

Well-Known Example

- Most well-known example is Sonogashira coupling
 - Uses catalytic palladium (TM) and copper (Group 11)
 - Two distinct catalytic cycles linked by transmetalation step

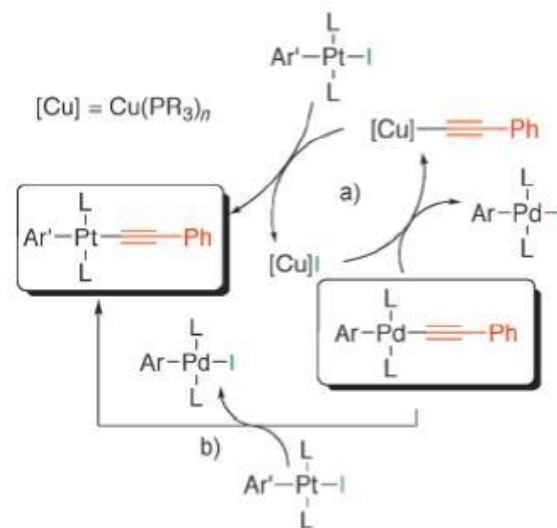
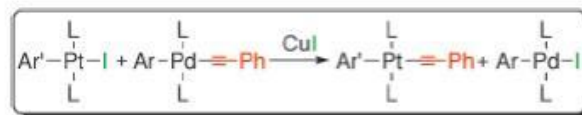
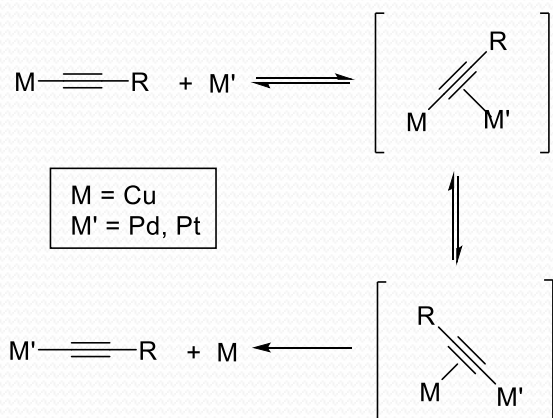


Group Exchange

- Types of organometallic exchange:
 - Halogen for carbon group
 - Carbon for carbon
 - Isomerization with transmetalation
 - Thermal decomposition with transmetalation
- Ligand exchange is essential in most organic reactions that utilize transition metal complexes

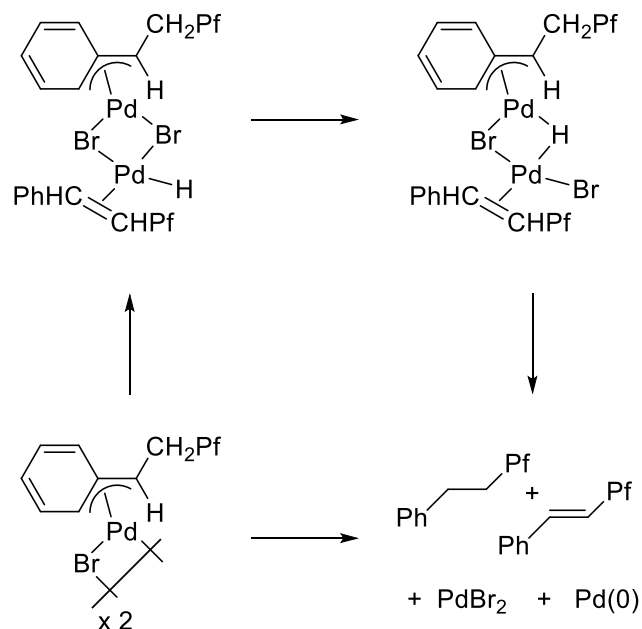
Halogen for Carbon Group Exchange: Alkynyl Transfer

- When reductive elimination does not occur, a stable organo-transition metal complex can be isolated
 - Good method for preparation of rigid-rod σ -bonded alkynyl polymers
 - Often transmetalation from copper to another metal due to ease of formation



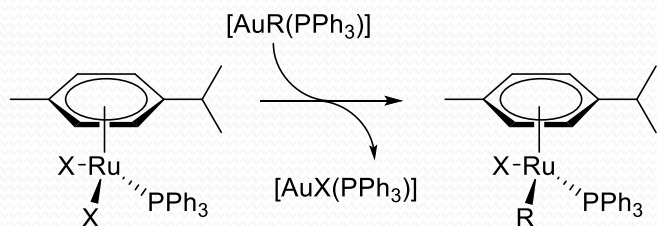
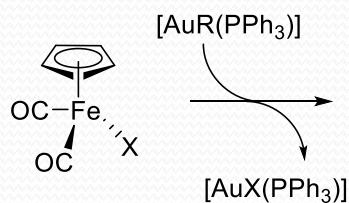
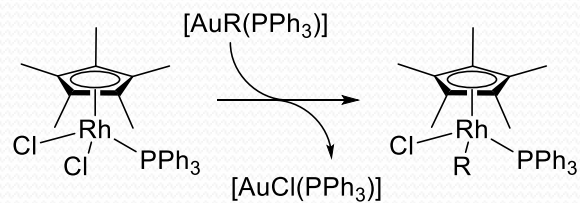
Halogen for Carbon Group Exchange: Ligand Disproportionation

- Hydrides can also participate

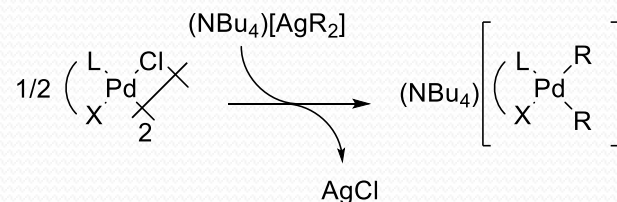


Halogen for Carbon Group Exchange: Gold and Silver Transmetalation

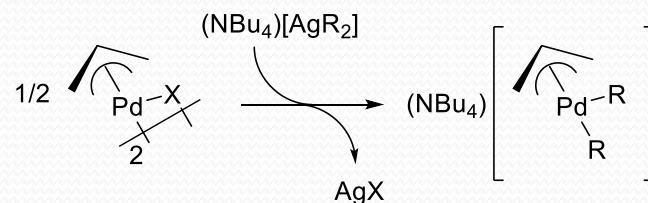
- Gold and silver complexes have been shown to transmetalate to other metal centers



R = 4-(OMe)C₄H₄, 4-(CF₃)C₄H₄, vinyl, Me



R = C₆Cl₂F₃; X^ΛL = C₆H₄(CH₂NMe₂)



R = C₆H₅, C₆Cl₂F₃

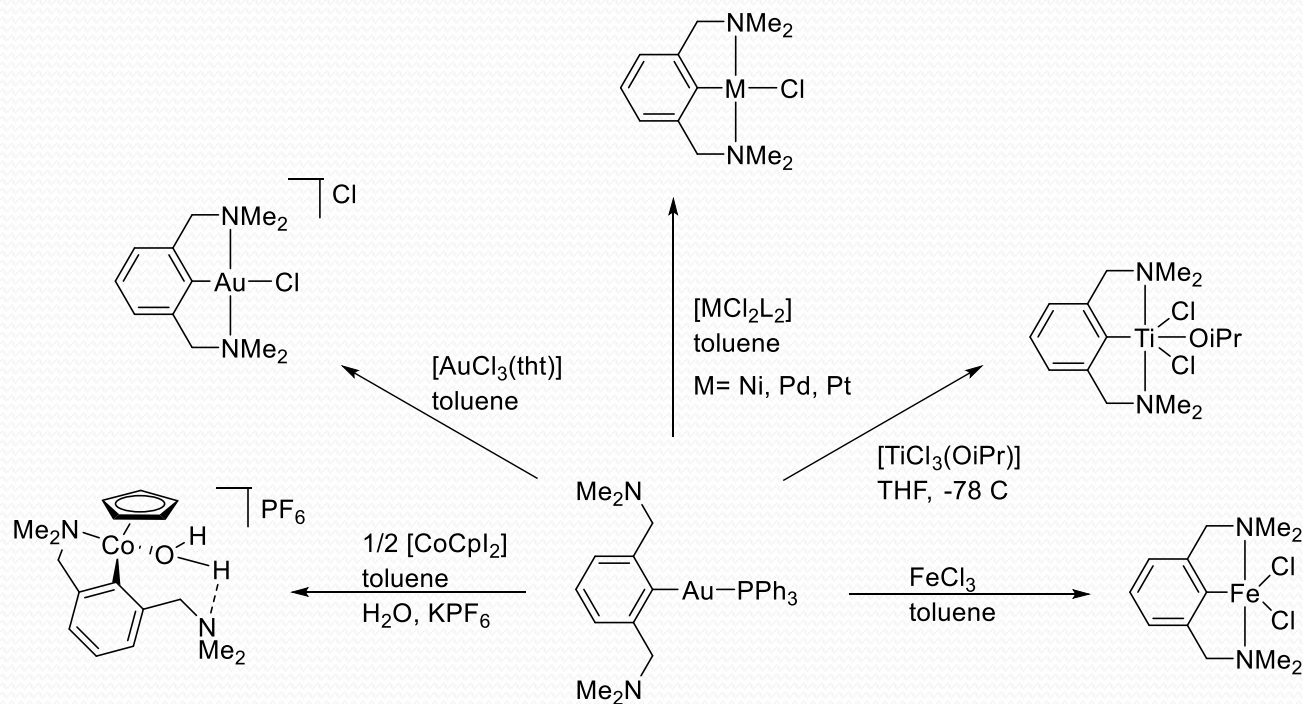
Blum, S.A., *Organometallics*, **2011**, 30, 1776.

Hashmi, A.S.K., *Organometallics*, **2011**, 30, 3457.

Weibel, J.M., *Chem. Rev.*, **2008**, 108, 3149.

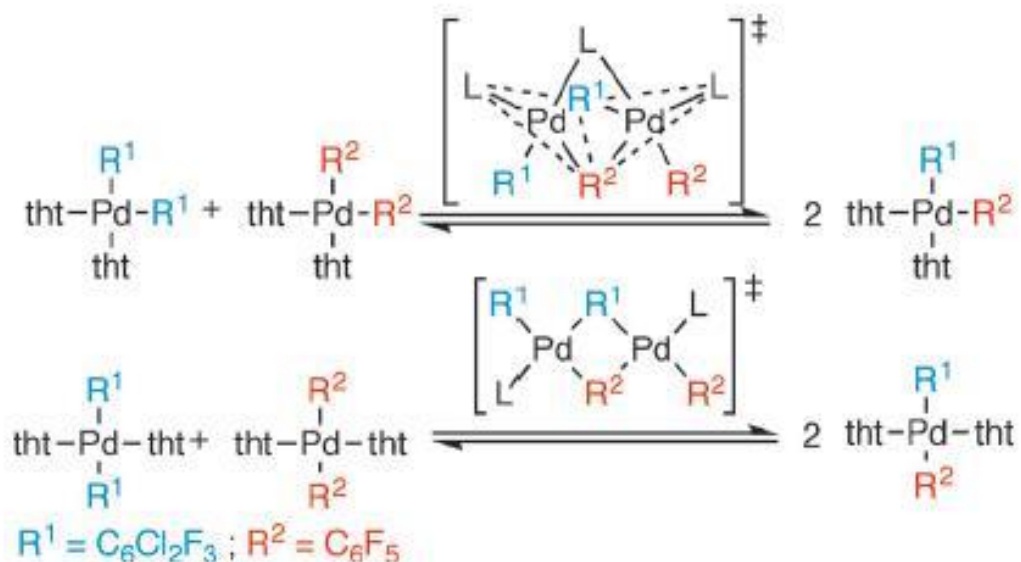
Halogen for Carbon Group Exchange: Gold and Silver Transmetalation

- Aryl-gold(I) complexes can be transmetalated to a variety of metals to give NCN pincer complexes



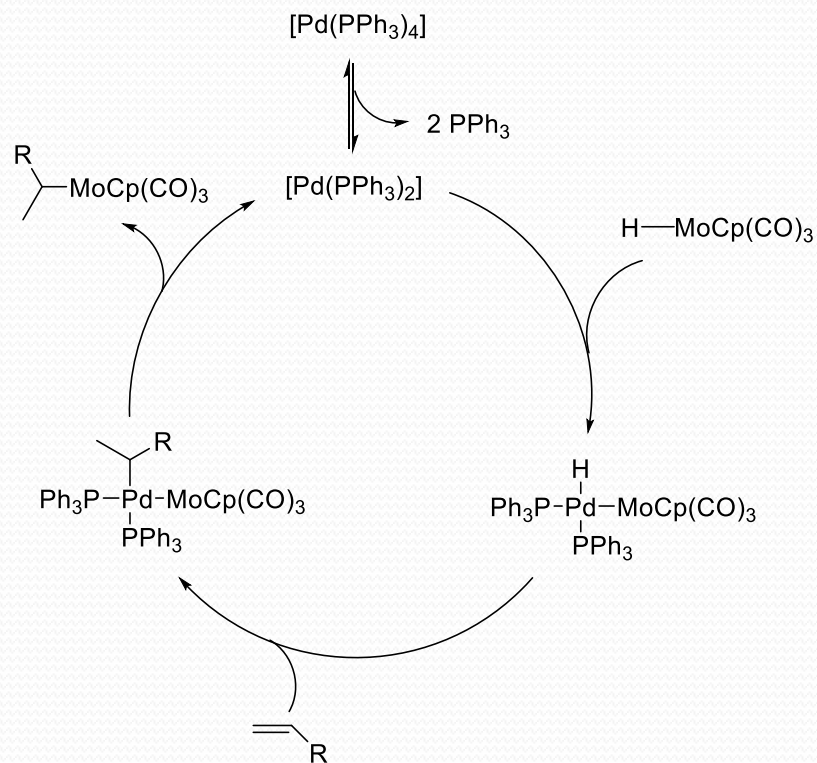
Carbon for Carbon Exchange?

- Carbon-for-carbon exchange may be taking place more often than observed



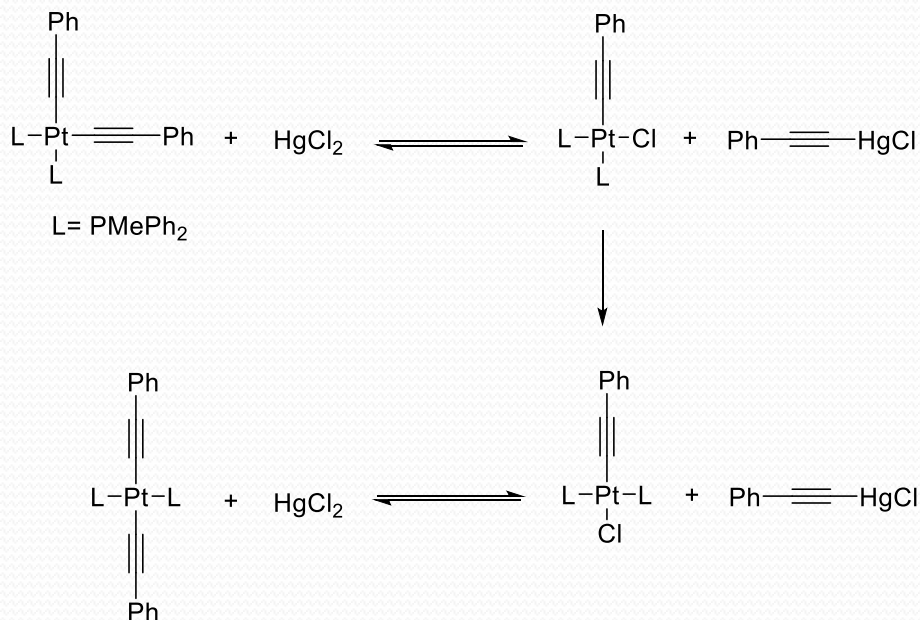
Carbon for Carbon Exchange

- Without Pd(o), no olefin insertion occurs to M-H bond

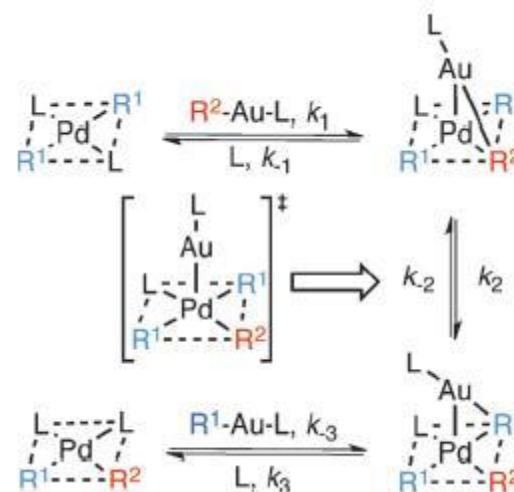


Isomerization Involving Transmetalation

- Cross showed isomerization of Pt ethynyl complexes via Hg catalysis

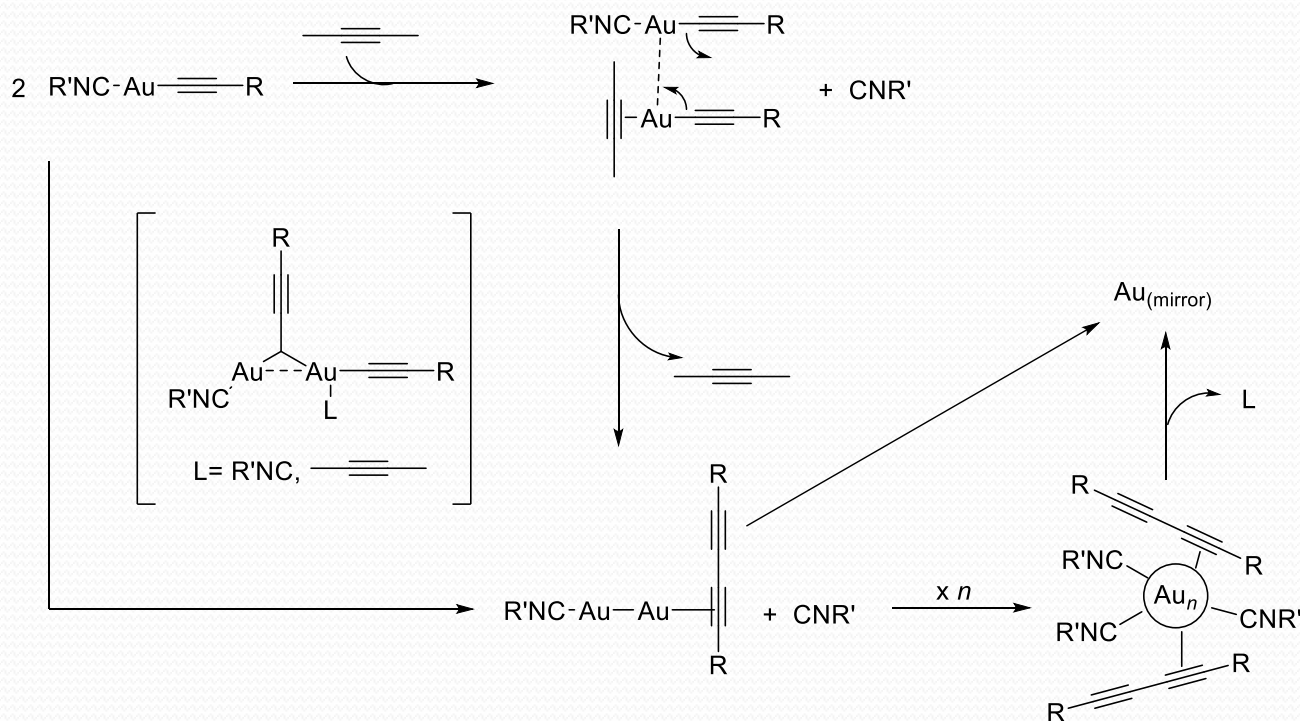


- Espinet showed isomerization of aryl Pd complexes via Au catalysis



Thermal Decomposition of Gold Complexes

- Decomposition of Au alkynyl complexes to produce nanoparticles

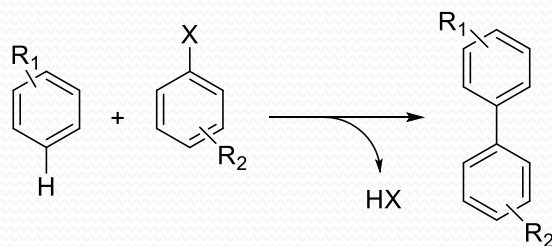


C-C Bond Forming Reactions

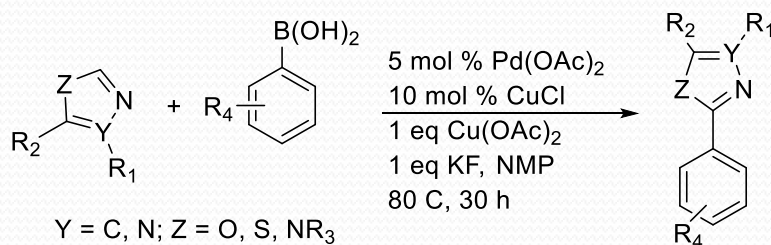
- Direct Arylation
- Decarboxylative Cross-Coupling
- Pd Catalysis and the “Copper Effect”
- Gold/Palladium Synergy
- Dissimilar TM Couples

C-H Activation: Direct Arylation

- Direct arylation is an economic and green approach that allows for minimization of byproducts

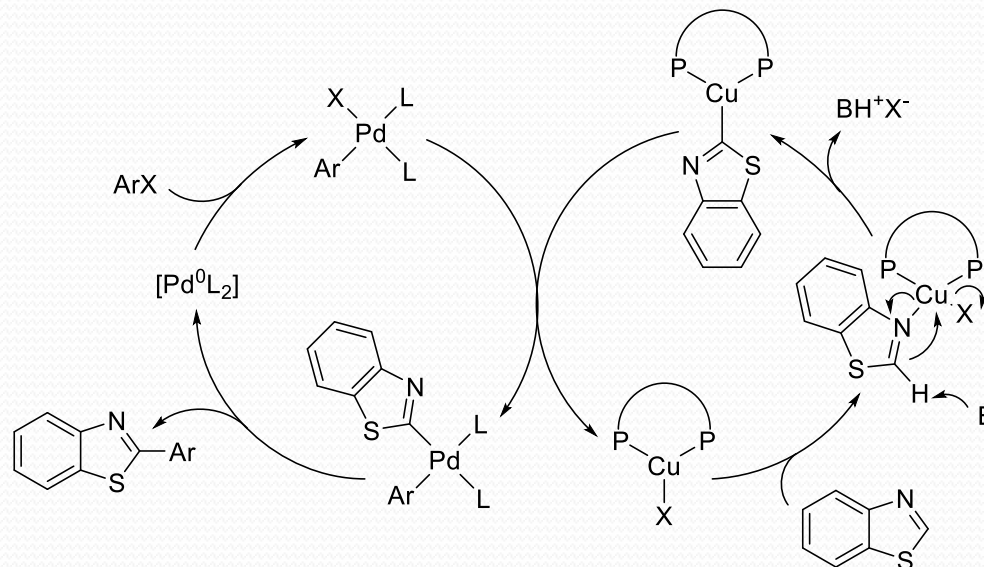
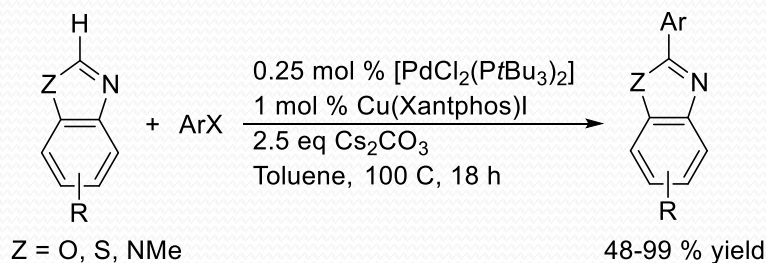


- You reported direct arylation of heteroarenes with aryl boronic acids



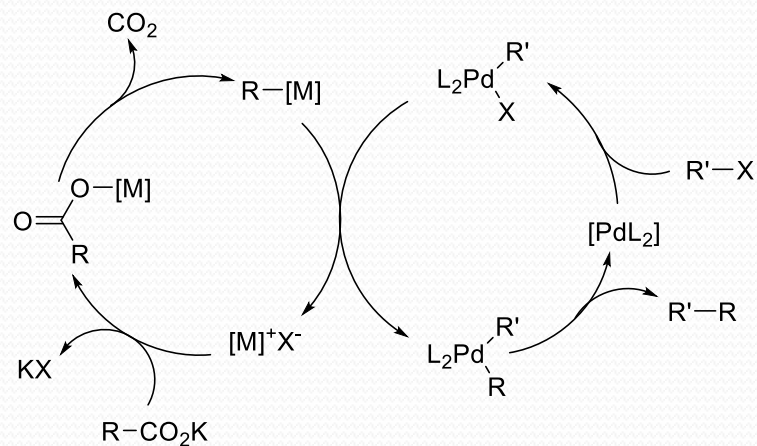
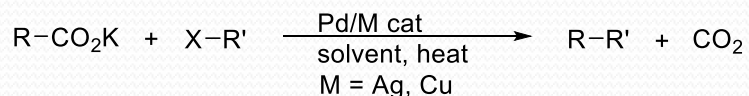
C-H Activation: Optimized Direct Arylation

- Huang reported direct arylation of heteroarenes with aryl halides



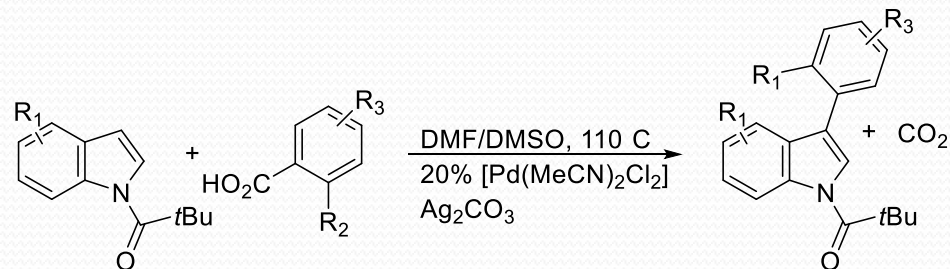
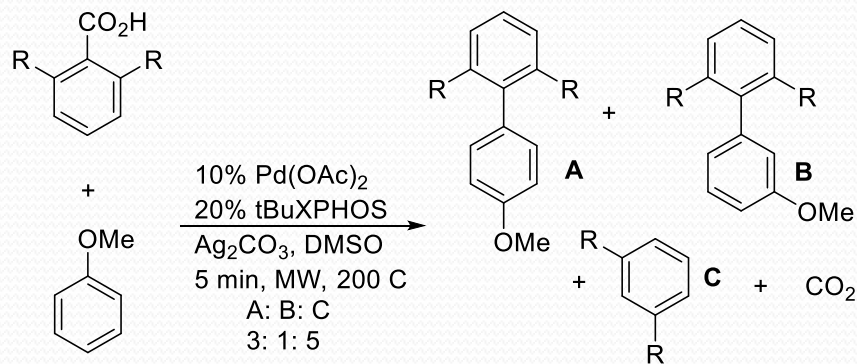
Decarboxylative Cross-Coupling

- Goossen showed Pd/ Cu or Ag catalyzed cross-coupling reaction from carboxylic acid salts



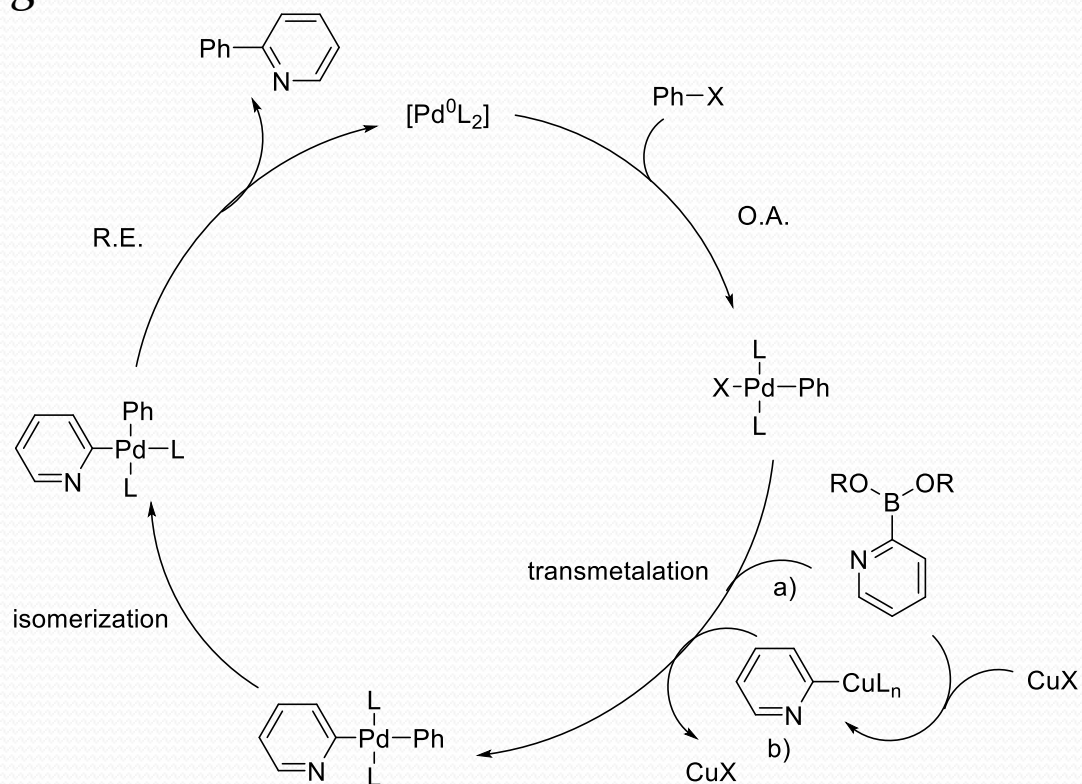
Goossen, L.J., *Science*, **2006**, 313, 662.
 Crabtree, R.H., *Chem. Commun.*, **2008**, 6312.
 Larrosa, I., *Org. Lett.*, **2009**, 11, 5506.

- Benzoic acids can be used directly, but need stoichiometric amounts of Ag



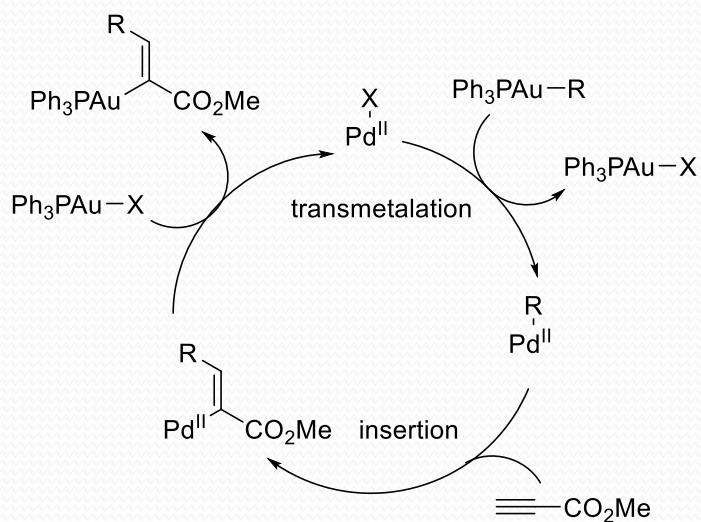
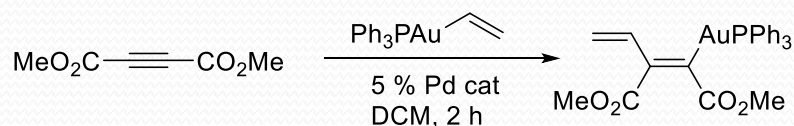
What is the “Copper Effect”?

- Reports have shown that Cu(I) salts can increase the rates of Pd catalyzed cross-couplings

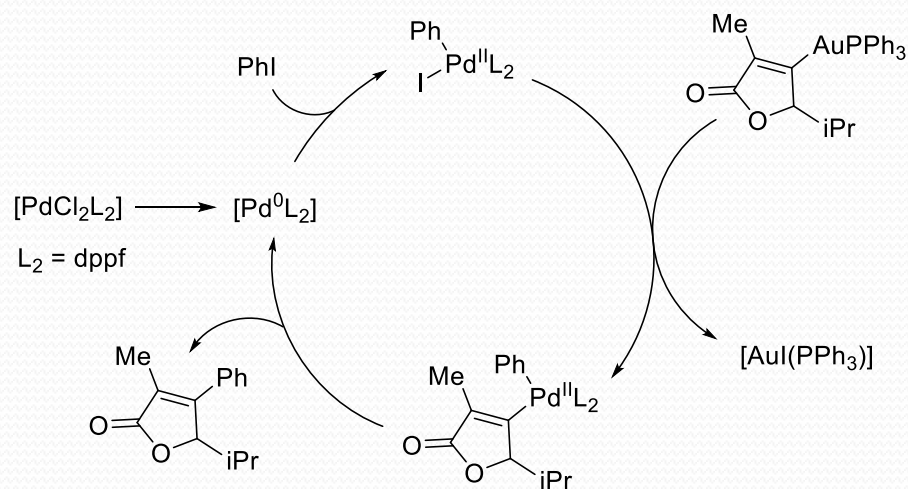


Gold and Palladium Synergy: Carboauration Reactions of Alkynes and Cross Coupling

- Blum formed *syn*-alkenyl gold complexes that were stable to H₂O and O₂



- Sarandeses showed Pd-catalyzed coupling of gold furanones with phenyl iodides

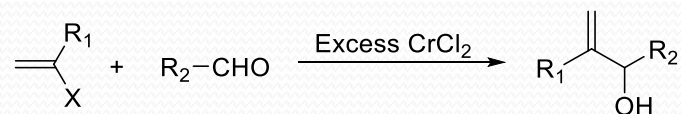


Blum, S.A., *Organometallics*, **2009**, *28*, 1275.

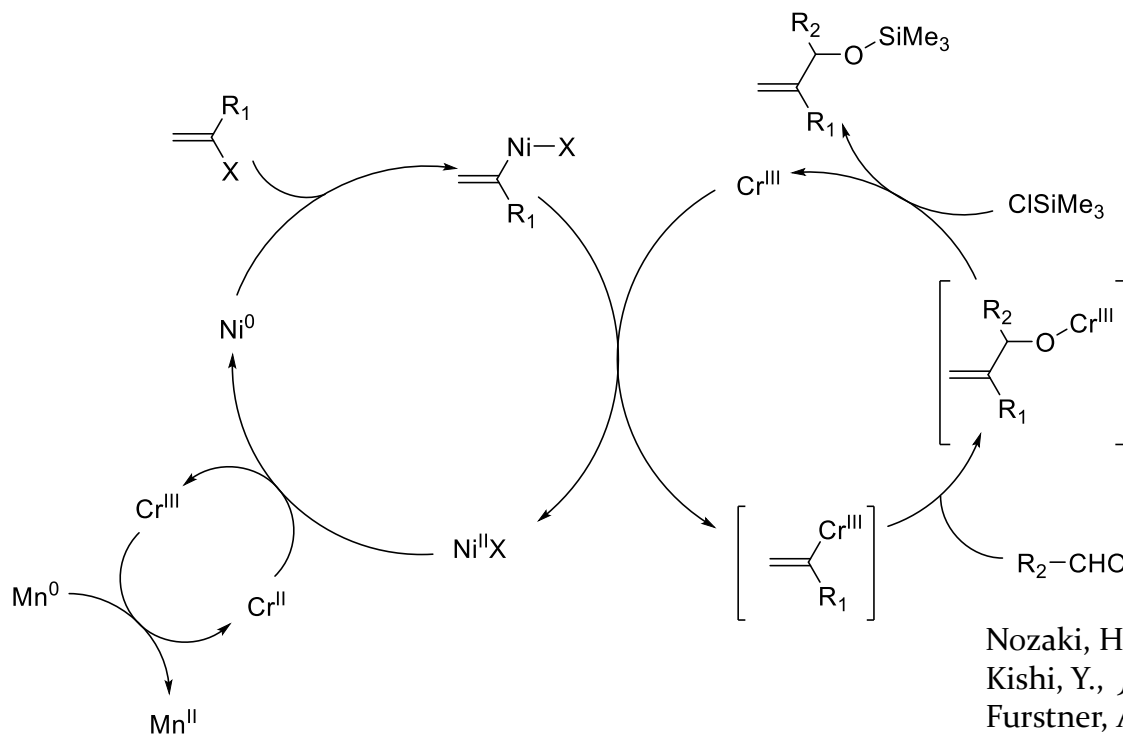
Sarandeses, L.A., *Chem. Eur. J.*, **2010**, *16*, 9905.

Dissimilar TM Couples: Cr/Ni-Catalyzed Vinylation of Aldehydes

- Nozaki originally thought only involved stoichiometric amounts of CrCl_2



- Fürstner/Shi made the reaction catalytic in Ni and Cr by adding Mn



Nozaki, H., *JACS*, **1977**, *99*, 3179.

Kishi, Y., *JACS*, **1986**, *108*, 5644.

Fürstner, A., *Chem. Rev.*, **1999**, *99*, 991.

Conclusions

- Bimetallic systems are growing in popularity due to their unique reactivity, but the field is still relatively young
- Pd(II)/Au(I) catalysis, especially, is being used more and more
- In the future, making more processes catalytic and more simple starting material synthesis will increase utility
- More mechanistic studies need to be done to allow predictions of reactivity

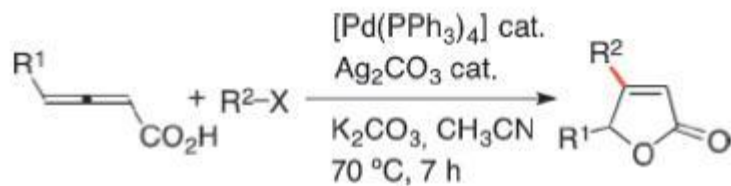
Thanks!



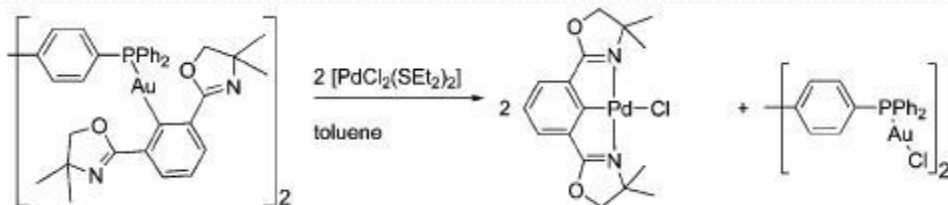
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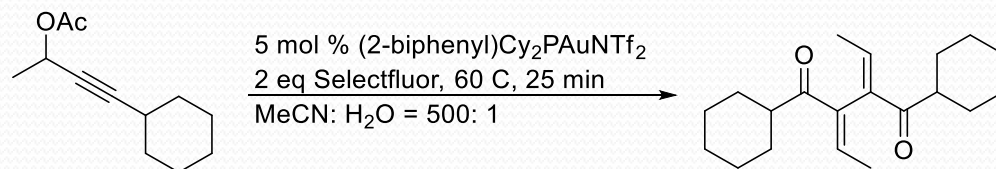
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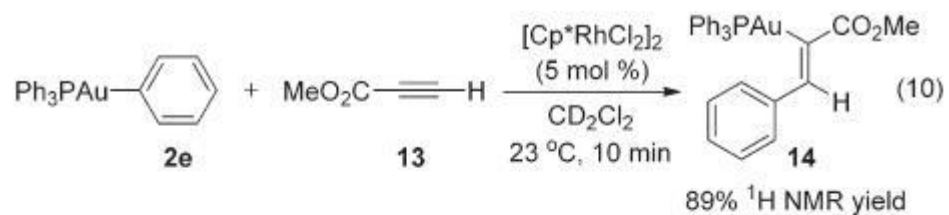
• B)



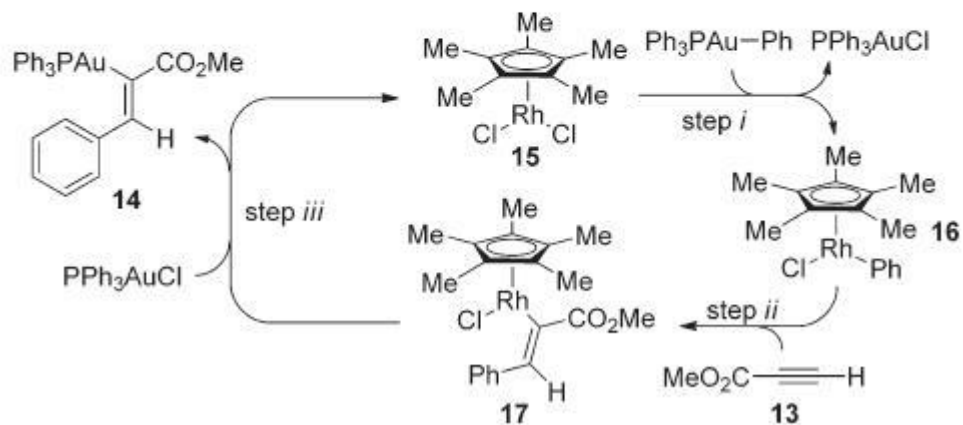
• C)



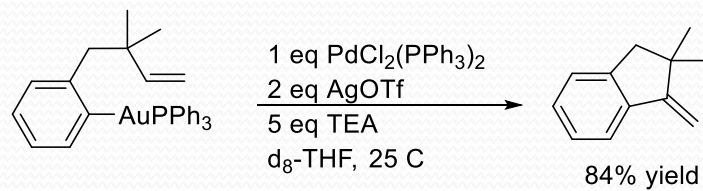
Question 2:



Proposed Mechanism:



Question 3:



Dissimilar TM Couples

- Chen and Ma showed Fe/Pd catalyzed synthesis of β -allylic substituted butenolides

