Synlett Account

Transition-Metal-Catalyzed Cross-Coupling with Non-Diazo Carbene Precursors

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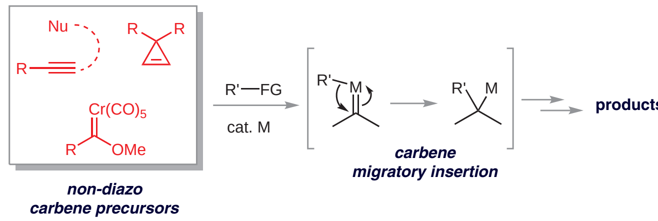

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Abstract Transition-metal-catalyzed cross-coupling reactions through metal carbene migratory insertion have emerged as powerful methodology for carbon–carbon bond constructions. Typically, diazo compounds (or in situ generated diazo compounds from *N*-tosylhydrazones) have been employed as the metal carbene precursors for this type of cross-coupling reactions. Recently, cross-coupling reactions employing non-diazo carbene precursors, such as conjugated ene-yne-ketones, allenyl ketones, alkynes, cyclopropenes, and Cr(0) Fischer carbenes, have been developed. This account will summarize our efforts in the development of transition-metal-catalyzed cross-coupling reactions with these non-diazo carbene precursors.

Key words cross-coupling, catalysis, carbene migratory insertion, metal carbene, C–C bond formation

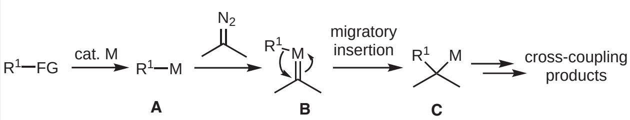
1 Introduction

N

A

B B

C



FG = H, Cl, Br, I, [B], [Si] ...

M = Pd, Cu, Rh, Ir, Ni ...

Scheme 1 Cross-coupling reactions based on metal carbene migratory insertion

Scheme 2 Generation of a metal carbene from ene-yne-ketone

2 Cross-Coupling with Ene-yne-ketones, Allenyl Ketones, and Alkynes

2 **3** **7**

tert

Z *E* **4**

5

9

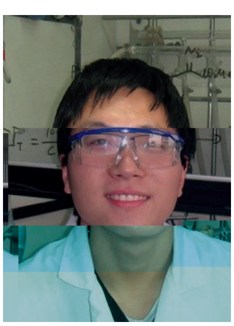
10

11

11

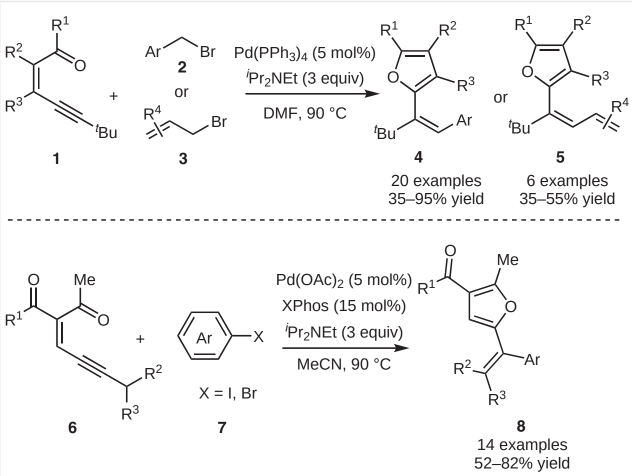
12 β

Biographical Sketches

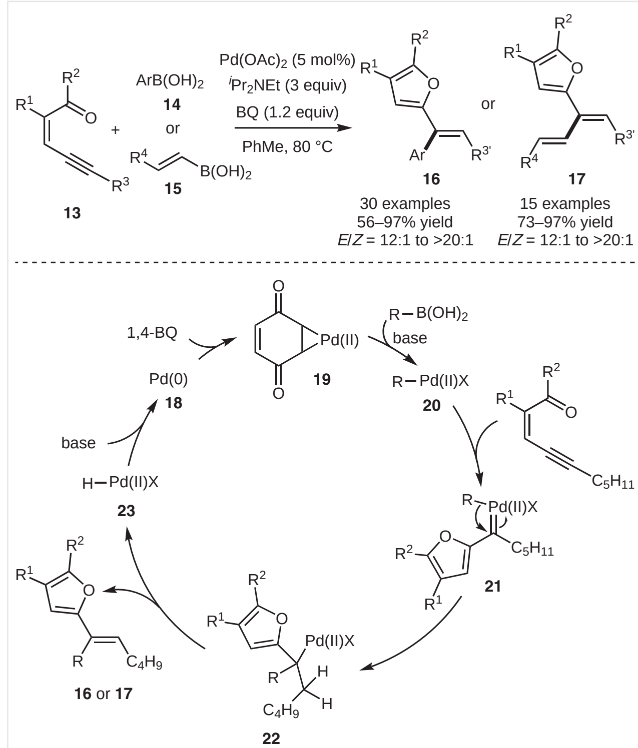


Kang Wang was born in Shandong Province. He obtained his B.S. degree in 2013 at the School of Chemistry and Chemical Engineering at Shandong University. He then became a graduate student in Jianbo Wang's group at Peking University. He obtained his Ph.D. degree in July 2018. The research of his Ph.D. thesis focused on transition-metal-catalyzed cross-coupling with chromium(0) Fischer carbene complexes.

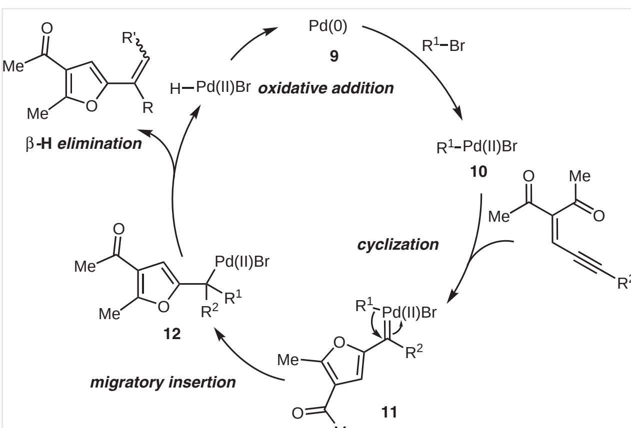
Jianbo Wang received his B.S. degree from Nanjing University of Science and Technology in 1983 and his Ph.D. from Hokkaido University (under the supervision of Prof. H. Suginome) in 1990. He was a postdoctoral associate at the University of Geneva from 1990 to 1993 (with Prof. C. W. Jefford) and University of Wisconsin-Madison from 1993 to 1995 (with Prof. H. E. Zimmerman and F. A. Fahien). He began his academic career at Peking University in 1995. His research interests have been focused on catalytic metal carbene transformations.



Scheme 3 Palladium-catalyzed cross-coupling of conjugated ene-yne-ketones with benzyl or allyl halides



Scheme 5 Palladium-catalyzed oxidative coupling reaction of conjugated ene-yne-ketones with organoboronic acids



Scheme 4 Proposed mechanism of palladium-catalyzed cross-coupling of conjugated ene-yne-ketones with halides

13 **14** **15**

E Z

E

18

19

20

21

21 **22**

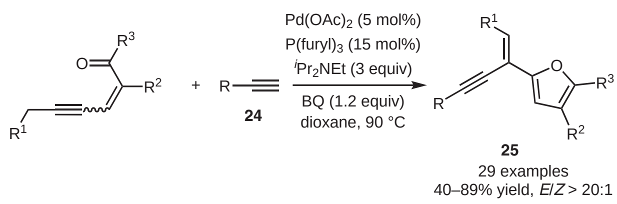
β

18

β

24

25



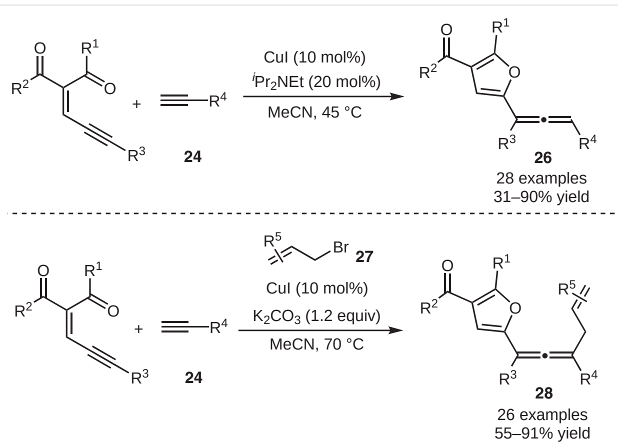
Scheme 6 Palladium-catalyzed oxidative coupling of ene-yne-ketones with terminal alkynes

24

26

28

27



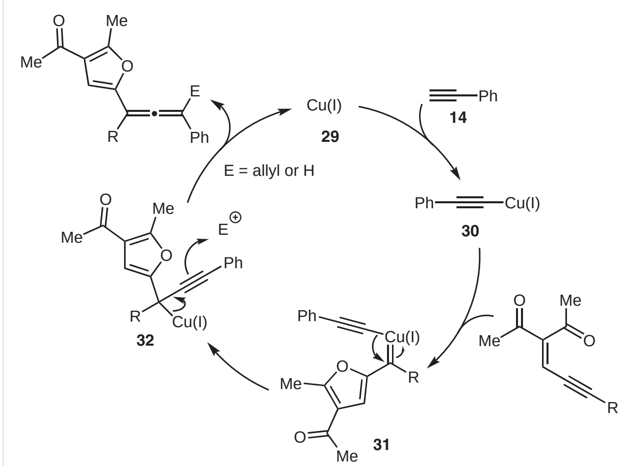
Scheme 7 Cu(I)-catalyzed coupling of ene-yne-ketones with terminal alkynes

30
29

31
30 **31**

32

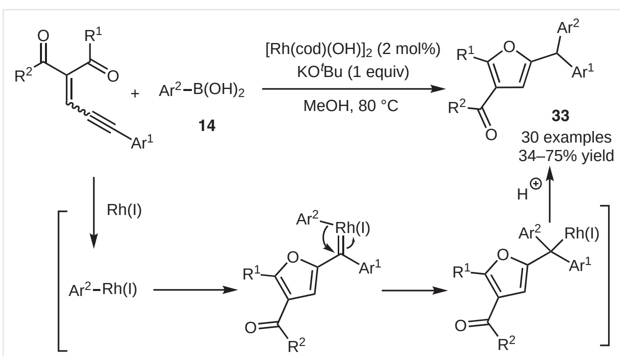
32



Scheme 8 Proposed reaction mechanism for Cu(I)-catalyzed cross-coupling of an ene-yne-ketone with an alkyne

β

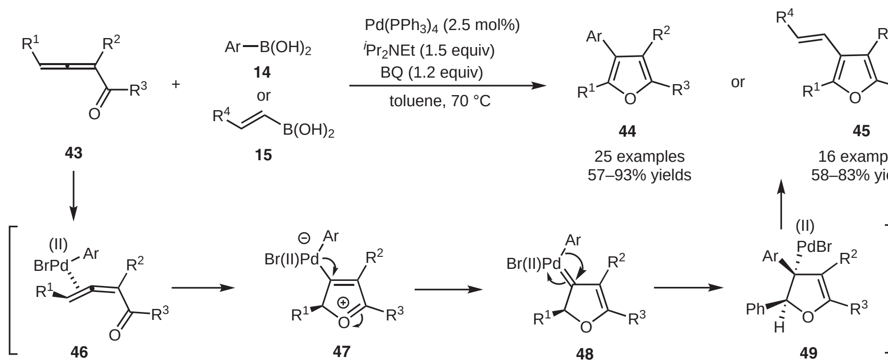
33



Scheme 9 Rh(I)-catalyzed cross-coupling of an ene-yne-ketone with arylboronic acid

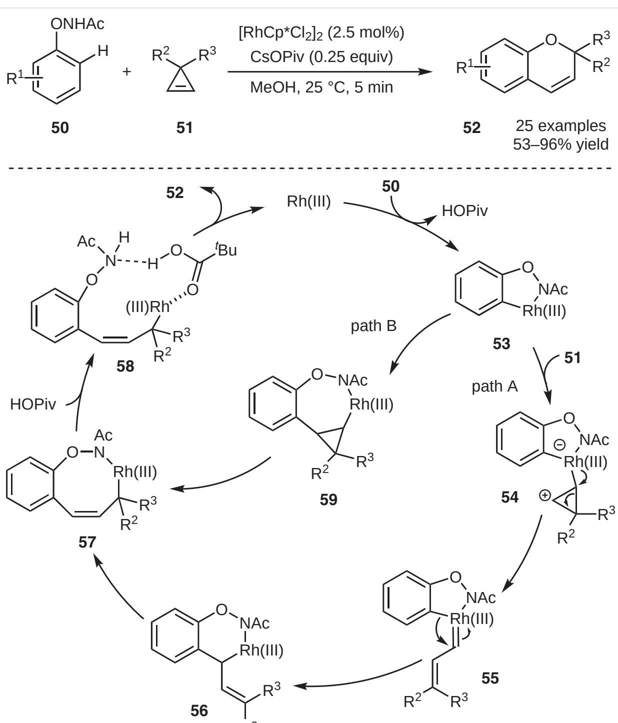
α

α



Scheme 12 Palladium-catalyzed oxidative cross-coupling of allenyl ketone with aryl- or vinylboronic acid

N
H
52
53 β
54
55



Scheme 13 Rh(III)-catalyzed cross-coupling of cyclopropene with *N*-phenoxyacetamide

57
58 *H*
59 β
57
60
61
E Z
E
62
62
63
β
62
63
β
65 **65'**
β **61**

4 Palladium-Catalyzed Cross-Coupling with Chromium(0) Fischer Carbenes

66

67

Scheme 15 Transition-metal-catalyzed carbene transfer reactions of chromium(0) Fischer carbene complexes

Scheme 16 Transition-metal-catalyzed cross-coupling with chromium(0) Fischer carbene

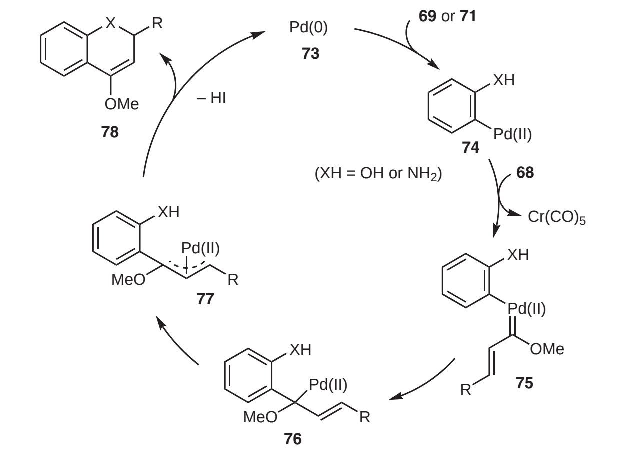
68

69

75

75 **77**

78



Scheme 18 Proposed mechanism for palladium-catalyzed [3+3] annulation of vinyl chromium(0) Fischer carbenes

80

79

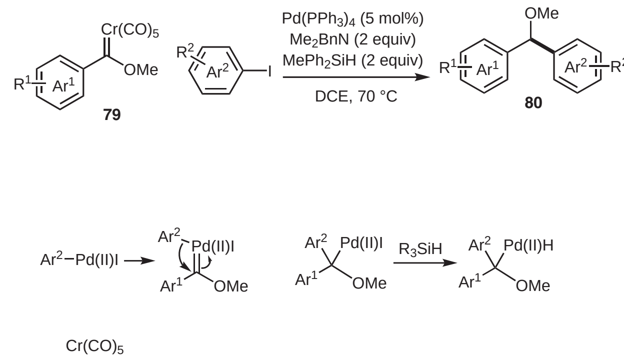
A

B

81

82

ρ



Scheme 19 Palladium-catalyzed reductive coupling reactions of aryl chromium(0) Fischer carbenes with aryl iodides

IM2

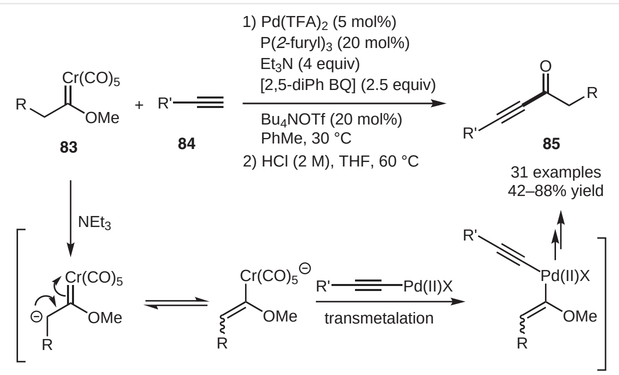
TS1

TS2 **IM4**

84

83

β



Scheme 21 Palladium-catalyzed oxidative coupling reaction of alkyl chromium(0) carbene with terminal alkyne

5 Conclusion

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