

Chem Soc Rev

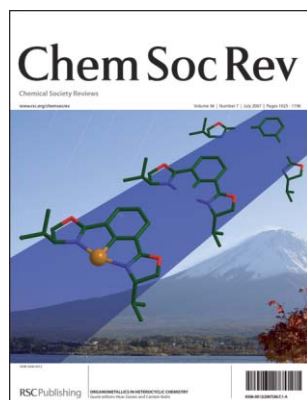
Chemical Society Reviews

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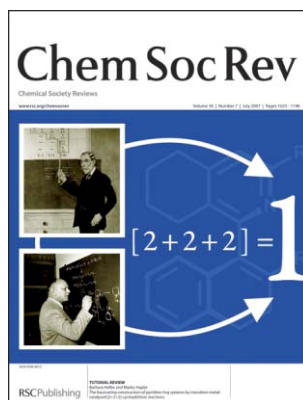
IN THIS ISSUE

ISSN 0306-0012 CODEN CSRVR 36(7) 1025–1196 (2007)



Cover

See Hisao Nishiyama, page 1133. Bisoxazoliny benzenes assembled from benzene and substituted oxazolines provide N,C,N-pincers for transition metal complexes exhibiting high catalytic activity. Image reproduced by permission of Hisao Nishiyama from *Chem. Soc. Rev.*, 2007, 36, 1133.



Inside cover

A long way to go: From the first discovery by Sir William Ramsay (above: photo reproduced by permission of RSC-LIC) that pyridine could be made by the reaction of acetylene and HCN in a red hot iron tube over the beginning of the catalytic era by Walter Reppe (below: photo reproduced by permission of BASF, Ludwigshafen), now even chiral pyridines can be made selectively by [2+2+2] cycloaddition. Image reproduced by permission of Barbara Heller and Marko Hapke from *Chem. Soc. Rev.*, 2007, 36, 1085.

CHEMICAL SCIENCE

C49

Drawing together the research highlights and news from all RSC publications, *Chemical Science* provides a 'snapshot' of the latest developments across the chemical sciences showcasing newsworthy articles, as well as the most significant scientific advances.

Chemical Science

July 2007/Volume 4/Issue 7

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EDITORIAL

1035

Organometallics in heterocyclic chemistry

Huw Davies and Carsten Bolm

Guest editors Huw Davies and Carsten Bolm introduce the reviews in this themed issue of *Chemical Society Reviews* on Organometallics in Heterocyclic Chemistry.



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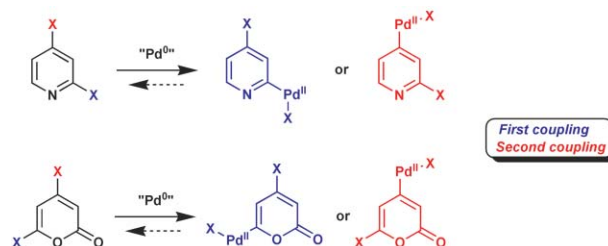
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1036

Regioselective (site-selective) functionalisation of unsaturated halogenated nitrogen, oxygen and sulfur heterocycles by Pd-catalysed cross-couplings and direct arylation processes

Ian J. S. Fairlamb*

Regioselective Pd-catalysed cross-couplings of poly-halogenated unsaturated heterocycles are discussed. The origin of the regioselectivity derives from a more favourable oxidative addition step.

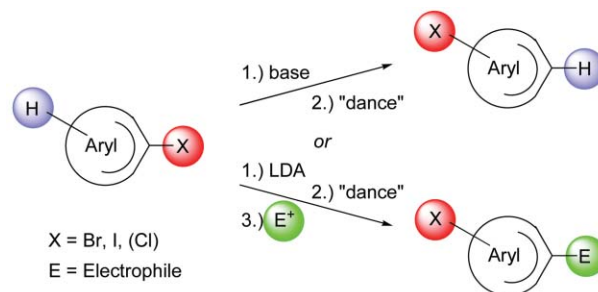


1046

Halogen dance reactions—A review

Michael Schnürch, Markus Spina, Ather Farooq Khan, Marko D. Mihovilovic and Peter Stanetty*

Halogen Dance (HD) reactions are a useful tool for synthetic chemists as they enable access to positions in aromatic and heteroaromatic systems for subsequent functionalization which are often difficult to address by other methods, hence, allowing entry to versatile scaffolds.

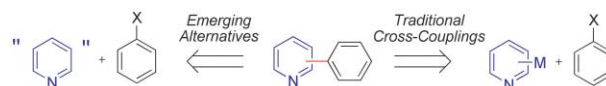


1058

Applications of and alternatives to π -electron-deficient azine organometallics in metal catalyzed cross-coupling reactions

Louis-Charles Campeau and Keith Fagnou*

This tutorial review highlights and discusses the innovations that facilitate the synthesis of azine-containing biaryls using azine organometallics with a focus on the pyridine containing biaryls.

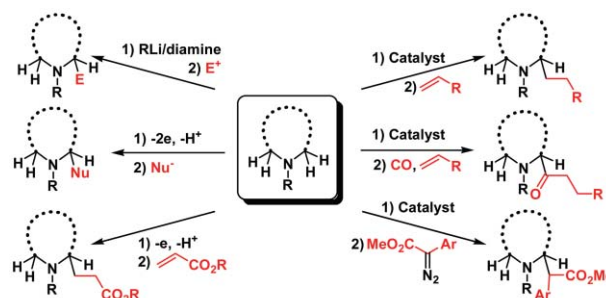


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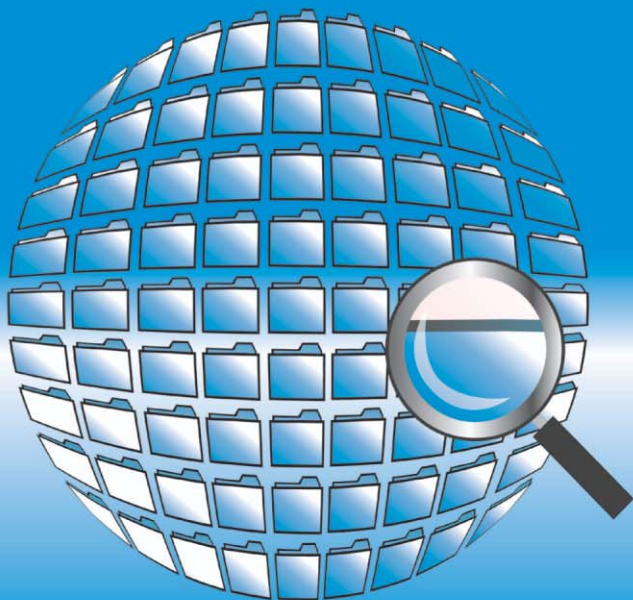
Direct sp^3 C–H bond activation adjacent to nitrogen in heterocycles

Kevin R. Campos*

Activation of sp^3 C–H bonds adjacent to nitrogen in heterocycles is an attractive transformation that is emerging as practical method in organic synthesis.



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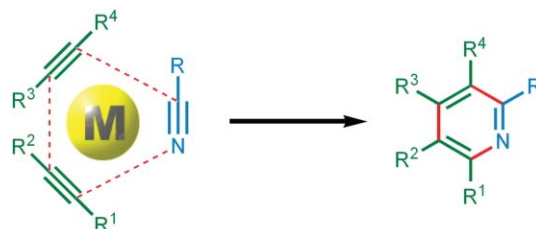
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1085

The fascinating construction of pyridine ring systems by transition metal-catalysed [2 + 2 + 2] cycloaddition reactions

Barbara Heller* and Marko Hapke*

Mechanisms and exciting recent developments in the application of transition metal-catalysed [2 + 2 + 2] cycloaddition reactions in the synthesis of achiral and chiral pyridines are presented.

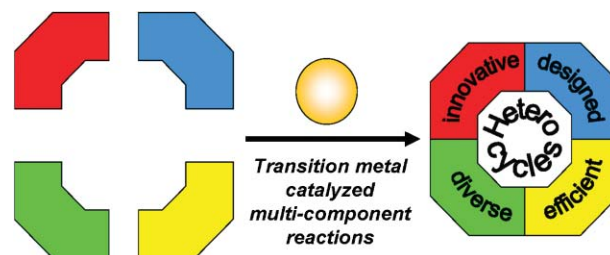


1095

Multi-component syntheses of heterocycles by transition-metal catalysis

Daniel M. D'Souza and Thomas J. J. Müller*

Transition-metal catalysis paves new diversity oriented alleys to the realm of heterocycles by domino, sequential, and consecutive multi-component reactions.

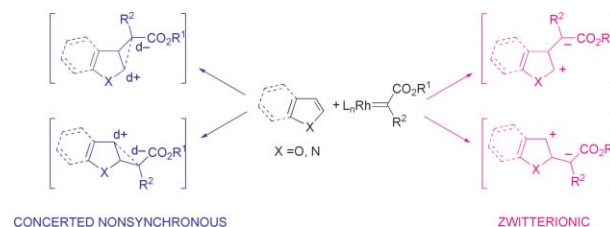


1109

Intermolecular reactions of electron-rich heterocycles with copper and rhodium carbenoids

Huw M. L. Davies* and Simon J. Hedley

This *tutorial review* describes the reactions of the electron-rich heterocycles pyrrole, furan, indole and benzofuran with copper and rhodium carbenoids and presents a mechanistic rationale for the range of products that can be formed.

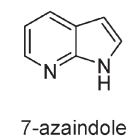
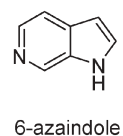
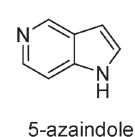
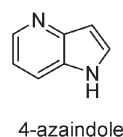


1120

Organometallic methods for the synthesis and functionalization of azaindoles

Jinhua J. Song,* Jonathan T. Reeves, Fabrice Gallou, Zhulin Tan, Nathan K. Yee and Chris H. Senanayake

In this *tutorial review*, we have surveyed the recent development of organometallic chemistry-based methods for the synthesis of the azaindoles which have found wide applications in medicinal and material sciences.



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Raffaele P. Bonomo *et al.*, *Dalton Trans.*, 2007, 1400

Electrochemical behaviour of mononuclear Fe(III) complexes as models for oxygenases: reactivity of Fe(II) species electrochemically formed *in situ* toward dioxygen

Nakédia M. F. Carvalho *et al.*, *Dalton Trans.*, 2007, 1023

Copper(II) cyclam-based complexes for radiopharmaceutical applications: synthesis and structural analysis

Jon D. Silversides *et al.*, *Dalton Trans.*, 2007, 971

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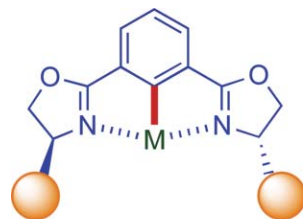
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1133

Synthesis and use of bisoxazoliny-phenyl pincers

Hisao Nishiyama

Synthetic methods to prepare bisoxazoliny-phenyl (Phebox) derivatives and their transition-metal complexes are summarized. Several applications to homogeneous and asymmetric catalysis with chiral Phebox metal complexes have also been reviewed.



Ligand synthesis
Complex synthesis
Reactivity
Catalytic applications
Asymmetric catalysis

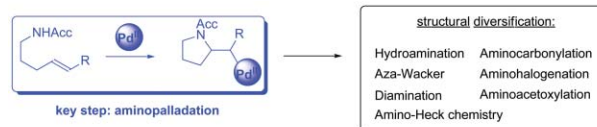
M = Rh, Pt, Pd, Ni etc.

1142

Intramolecular aminopalladation of alkenes as a key step to pyrrolidines and related heterocycles

Ana Minatti* and Kilian Muñiz*

All from just one initial step: after installing a nitrogen heterocyclic core through a catalytic aminopalladation reaction, broad structural diversification can be accomplished by varying the subsequent reaction conditions.

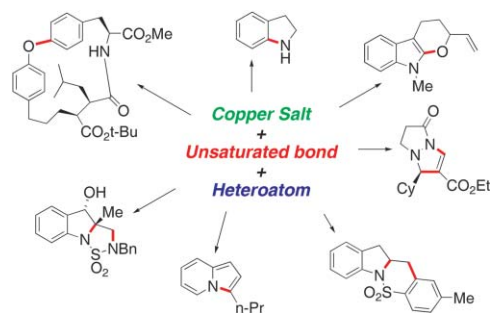


1153

Heterocycle synthesis by copper facilitated addition of heteroatoms to alkenes, alkynes and arenes

Sherry R. Chemler* and Peter H. Fuller

Copper salts facilitate the synthesis of heterocycles using a myriad of reaction mechanisms. This *tutorial review* summarizes recent developments in this area including the use of ligands to aid in catalysis and asymmetric catalysis.



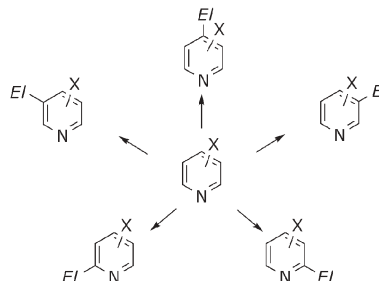
CRITICAL REVIEWS

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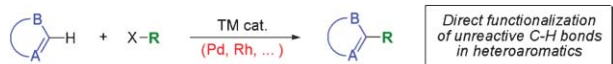
Pyridine elaboration through organometallic intermediates: regiochemical control and completeness

Manfred Schlosser* and Florence Mongin

Pharmaceutical research needs pyridine building blocks garnished with uncommon substituent patterns. This *critical review* explains how whole families thereof can be made with little effort, and targets as a readership, researchers generally oriented toward organic synthesis and in particular those active in the life sciences area.



1173




Direct transition metal-catalyzed functionalization of heteroaromatic compounds

Ilya V. Seregin and Vladimir Gevorgyan*

Progress made in C–H activation methods for direct functionalization of heterocyclic molecules, invaluable building blocks for pharmaceutical chemistry and material science, is summarized.

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