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Phil Baran Running a
Nickel-catalyzed
Decarboxylative Alkyl-
Alkyl Cross-coupling
~~Pd-catalyzed Cross
Coupling Reactions;
Olefin Metathesis,~~

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~~Prof. Reiser, Lect 17~~

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Cruel and Unusual
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General Principles of
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Transition metal
catalyzed cross
coupling Proton Guru
Practice V.4:

Palladium Catalyzed
Coupling Reactions
Studies in Natural
Product Synthesis |
Professor Phil Baran |
26 May 2020 Pd And
Ni Catalyzed Cross
Abstract. A variety of
unsaturated
thioethers have been

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subjected to
cross coupling
reactions with
functionalized zinc
reagents in the
presence of a
transition metal
catalyst. Three
different catalytic
systems based on Pd
(OAc)₂ or [Ni (acac)
₂] and the ligands
S Phos or
DPE Phos gave the

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best results.

N Heterocyclic
thioethers based on a
pyridine, pyrimidine,
pyrazine, pyridazine,
triazine,
benzothiazole,
benzoxazole, pyrrole,
or quinazoline ring,
as well as
thiomethylacetylenes

...

Pd and

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Ni Catalyzed
Cross Coupling
Reactions of ...

This Perspective
presents an overview
on recent
experimental and
computational
studies on the off-
cycle reactions of
palladium- and nickel-
catalyzed cross-
couplings. Several
reactions entering or

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leaving the catalytic cycle have been characterized, including the activation of Pd(II) precatalysts by H-shift and the deactivation of Ni(II) precatalysts by comproportionation.

Designing Pd and Ni Catalysts for Cross-Coupling Reactions ...

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The Suzuki–Miyaura reaction is a cornerstone method for sp^2 – sp^2 cross-coupling in industry. There has been a concerted effort to enable the use of Ni catalysis as an alternative to Pd in order to mitigate cost and improve sustainability.

Despite significant

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Advances, ligand development for Ni-catalyzed Suzuki–Miyaura cross-coupling remains underdeveloped when compared to Pd and, as a consequence, ligands for Ni-catalyzed processes are typically taken from the Pd arena.

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Ni vs. Pd in
Catalyzed Cross
Suzuki–Miyaura
Coupling
sp²–sp² cross-
coupling: a head ...

Pd-catalyzed cross-
coupling reactions
between R¹M and
various organic
halides R²X (R=allyl,
propargyl, benzyl,
acyl, alkenyl, alkynyl,
aryl; listed in
approximate order of

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reactivity). The catalytic cycle in scheme 1 serves as a reasonable model for other cross-coupling reactions mediated by Pd, Ni [25–27], and other TMs.

Pd- and Ni-catalyzed cross-coupling reactions in the ...
Pd/PtBu₃-catalyzed Negishi chain-growth

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polycondensation
have recently been
reported to produce
polyfluorenes with
molecular weights of
up to 120 kDa
(scheme 16), with
exceptionally high
catalyst turnover
numbers (TON > 200
000, the highest
reported to date for
TM-catalyzed cross-
coupling

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polycondensations)
and turnover
frequencies (TOFs up
to 280 s^{-1}). These
remarkable catalytic
efficiencies can result
in TONs and TOFs
that are two orders of
magnitude higher
than that of step-
growth ...

Pd- and Ni-catalyzed
cross-coupling

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reactions in the ...
(2014). Pd- and Ni-
catalyzed cross-
coupling reactions in
the synthesis of
organic electronic
materials. Science
and Technology of
Advanced Materials:
Vol. 15, No. 4,
044201.

Pd- and Ni-catalyzed
cross-coupling

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reactions in the ...

Organic molecules
and polymers with
extended -

conjugation are

appealing as

advanced electronic

materials, and have

already found

practical applications

in thin-film

transistors, light

emitting diodes, and

chemical sensors.

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Transition metal
(TM)-catalyzed cross-
coupling
methodologies have
evolved over the past
four decades into one
of the most powerful
and versatile
methods for C-C
bond ...

Pd- and Ni-catalyzed
cross-coupling
reactions in the ...

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The coupling is catalyzed by a combination of (5,5-bis(trifluoromethyl)-2,2'-bipyridine)NiBr₂ and (1,3-bis(diphenylphosphino)propane)PdCl₂ in the presence of a zinc reductant. This method affords tetra- and penta-substituted 1,3-dienes that would

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Otherwise be difficult to access and tolerates electron-rich and -poor substituents, heterocycles, an aryl bromide, and a pinacol boronate ester.

Multimetallic Ni- and Pd-Catalyzed Cross-Electrophile ...

A large portion of Ni-

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And Ni catalyzed cross-coupling reactions proceeding through radical pathways employ bidentate and tridentate N-ligands, including bipyridine (bpy), bioxazoline (biOx), terpyridine (terpy), and pyridine-bioxazoline (py-box) (see Figure 1Biii in main text).

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Mechanisms of Nickel-
Catalyzed Cross-
Coupling Reactions

Pd or Ni: requires
base Sonogashira

coupling: 1975:

RC CH: sp: R-X: sp 3

sp 2: Pd and Cu:

requires base Negishi

coupling: 1977: R-Zn-

X: sp 3, sp 2, sp: R-X:

sp 3 sp 2: Pd or Ni:

Stille cross coupling:

1978: R-SnR 3: sp 3,

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sp 2, sp: R-X: sp 3 sp

2: Pd: Suzuki reaction:

1979: R-B(OR) 2: sp 2:

R-X: sp 3 sp 2: Pd or

Ni: requires base

Murahashi coupling:

1979 R-Li sp 2, sp 3: R-

X sp 2: Pd or Ru

Hiyama coupling:

1988: R-SiR 3: sp 2: R-

X: sp 3 sp 2

Cross-coupling
reaction - Wikipedia

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The scope of the hydrometalation–cross-coupling tandem process was substantially expanded by (i) the discovery of the Pd- or Ni-catalyzed cross-coupling of alkenylzirconium derivatives during the 1977–1978 period, and (ii) the development of the c

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Arboalumination–cross-coupling tandem process first reported in 1978.

Reactions In

A genealogy of Pd-catalyzed cross-coupling -

ScienceDirect

Cross-coupling

Reaction of Alkyl

Halides With

Grignard Reagents

Catalyzed by Ni, Pd,

Where To
Download Pd
or Cu Complexes
With Pi-Carbon
Catalyzed Cross
Ligand(s) - PubMed.
Coupling
Transition metal-
catalyzed cross-
coupling reactions of
The
organic halides and
pseudo-halides
containing a C-X
bond (X = I, Br, Cl,
OTf, OTs, etc.) with
organometallic
reagents are among
the most important

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transformations for
carbon-carbon bond
formation between a
variety of sp , $sp(2)$,
and $sp(3)$ -hybridized ...

The

Cross-coupling
Reaction of Alkyl
Halides With
Grignard ...

Cross-coupling
reaction of alkyl
halides with grignard
reagents catalyzed by

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Ni, Pd, or Cu

complexes with pi-
carbon ligand(s).

Terao J , Kambe N Acc

Chem Res ,

41(11):1545-1554, 01

Nov 2008

Pd- and Ni-catalyzed
cross-coupling
reactions of ...

Pd- and Ni-catalyzed
cross-coupling
reactions in the

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And Ni
Catalyzed Cross
Coupling
Reactions in
The

synthesis of organic
electronic materials
July 2014 Science and
Technology of
Advanced Materials
15(4):044201

(PDF) Pd- and Ni-
catalyzed cross-
coupling reactions in
the ...

Nickel- and palladium-
catalyzed cross-
coupling reactions

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have attracted wide attentions, while ligand-controlled selectivity in these reactions are still elusive, and calculations can help obtain possible catalytic cycles to generate different products and provide insights into key factors of selectivity, which facilitates the

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development of new
catalyst systems to
control reaction
selectivity.

Reactions In

Recent advances in
theoretical studies on
ligand ...

Scheme 3 depicts two
plausible catalytic
cycles for Ni- and Pd-
catalyzed cross-
coupling reactions
employing tertiary

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alkyl nucleophiles.

While it is likely that such a Pd-catalyzed process would proceed via the Pd(0)–Pd(II) catalytic cycle that is well-established for cross-coupling reactions, the Ni-catalyzed cycle is not so clearly defined. Since multiple stable oxidation states are ...

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The Use of Tertiary
Alkylmagnesium

Nucleophiles in Ni ...

The mechanisms and
origins of selectivity

in the Pd-catalyzed
nondecarbonylative

and Ni-catalyzed
decarbonylative

Suzuki-Miyaura cross-
coupling of N-acetyl-

amides have been

explored with density

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functional theory
calculations. The
reaction of the two
catalysts shares a
similar process that
contains oxidative
addition to break the
N-C(O) bond and
transmetalation with
the Ar'B(OH)₂
reagent.

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Catalyzed Cross Coupling Reactions In The