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**Phil Baran Running a Nickel-
catalyzed Decarboxylative
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Professor Phil Baran | 26

May 2020 Pd And Ni Catalyzed

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Abstract. A variety of unsaturated thioethers have been subjected to cross-coupling reactions with functionalized zinc reagents in the presence of a transition-metal catalyst.

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Three different catalytic systems based on Pd (OAc)₂ or [Ni (acac)₂] and the ligands S-Phos or DPE-Phos gave the best results.

N-Heterocyclic thioethers based on a pyridine, pyrimidine, pyrazine,

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pyridazine, triazine,
benzothiazole, benzoxazole,
pyrrole, or quinazoline
ring, as well as
thiomethylacetylenes ...

*Pd- and Ni-Catalyzed
Cross-Coupling Reactions of*

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

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Several reactions entering or 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

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

The Suzuki-Miyaura reaction
is a cornerstone method for
sp²-sp² cross-coupling in

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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 advances, ligand development

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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 Suzuki-Miyaura
sp²-sp² cross-coupling: a
head ...*

Pd-catalyzed cross-coupling
reactions between R₁M and
various organic halides R₂X
(R=allyl, propargyl, benzyl,

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acyl, alkenyl, alkynyl,
aryl; listed in approximate
order of 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.

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

...

Pd/PtBu₃-catalyzed Negishi
chain-growth

polycondensation have

recently been reported to

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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 polycondensations)

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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 ...

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

...

(2014). Pd- and Ni-catalyzed cross-coupling reactions in the synthesis of organic electronic materials.

Science and Technology of

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Advanced Materials: Vol. 15,
No. 4, 044201.

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

...

Organic molecules and
polymers with extended π -

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are appealing as advanced electronic materials, and have already found practical applications in thin-film transistors, light emitting diodes, and chemical sensors. Transition metal (TM)-catalyzed cross-

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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

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affords tetra- and penta-substituted 1,3-dienes that would otherwise be difficult to access and tolerates electron-rich and -poor substituents, heterocycles, an aryl bromide, and a pinacol boronate ester.

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

...

A large portion of Ni-
catalyzed cross-coupling
reactions proceeding through
radical pathways employ

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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:

$\text{RC}\equiv\text{CH}$: sp: R-X: sp³ sp²:

Pd and Cu: requires base

Negishi coupling: 1977: R-Zn-

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X: sp³, sp², sp: R-X: sp³
sp²: Pd or Ni: Stille cross
coupling: 1978: R-SnR³: sp³,
sp², sp: R-X: sp³ sp²:
Pd: Suzuki reaction: 1979: R-
B(OR)₂: sp²: R-X: sp³ sp²:
Pd or Ni: requires base
Murahashi coupling: 1979 R-

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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*

The scope of the hydrometala

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tion-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

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of the carbonylation-cross-coupling tandem process first reported in 1978 .

A genealogy of Pd-catalyzed cross-coupling - ScienceDirect

Cross-coupling Reaction of

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Alkyl Halides With Grignard
Reagents Catalyzed by Ni,
Pd, or Cu Complexes With Pi-
Carbon Ligand(s) - PubMed.
Transition metal-catalyzed
cross-coupling reactions of
organic halides and pseudo-
halides containing a C-X

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(X = I, Br, Cl, OTf, OTs, etc.) with organometallic reagents are among the most important transformations for carbon-carbon bond formation between a variety of sp , $sp(2)$, and $sp(3)$ -hybridized ...

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*Cross-coupling Reaction of
Alkyl Halides With Grignard*

...

Cross-coupling reaction of
alkyl halides with grignard
reagents catalyzed by Ni,
Pd, or Cu complexes with pi-

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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-

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Reactions in The
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
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*cross-coupling reactions in
the ...*

Nickel- and palladium-
catalyzed cross-coupling
reactions have attracted
wide attentions, while
ligand-controlled
selectivity in these

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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 development

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of new catalyst systems to
control reaction
selectivity.

*Recent advances in
theoretical studies on
ligand ...*

Scheme 3 depicts two

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plausible catalytic cycles for Ni- and Pd-catalyzed cross-coupling reactions employing tertiary alkyl nucleophiles. While it is likely that such a Pd-catalyzed process would proceed via the Pd(0)-Pd(II)

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catalytic cycle that is well-established for cross-coupling reactions, 1 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-

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Miyaura cross-coupling of N-acetyl-amides have been explored with density functional theory calculations. The reaction of the two catalysts shares a similar process that contains oxidative addition

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to break the N-C(O) bond and
transmetalation with the
Ar'B(OH)₂ reagent.

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