Theoretical Mechanistic Evaluation of Palladium, Nickel, and Copper Catalysts in Suzuki–Miyaura Cross-Coupling

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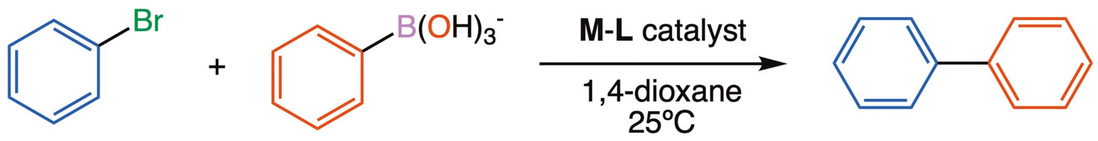
INTRODUCTION

This work focuses on the mechanistic analysis of the Suzuki–Miyaura coupling, a key reaction in the formation of carbon-carbon bonds.[1] To improve the sustainability of catalytic processes, the replacement of palladium-based catalysts by nickel and copper analogues, which are more accessible and cheaper, has been investigated. The aim is to compare the reactivity and efficiency of these three metals with generic phosphine and carbene ligands.[2]



M

Pd(0)

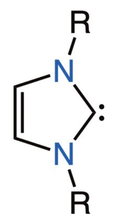
Ni(0)

Cu(I)Br

L

PMe_3

$P(CF_3)_3$



R = Me (NHC)

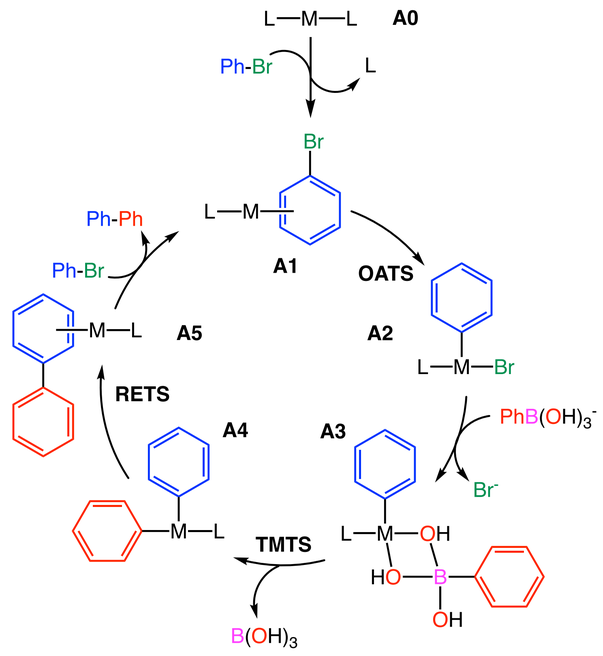
R = CF_3 ($NHC\text{-}CF_3$)

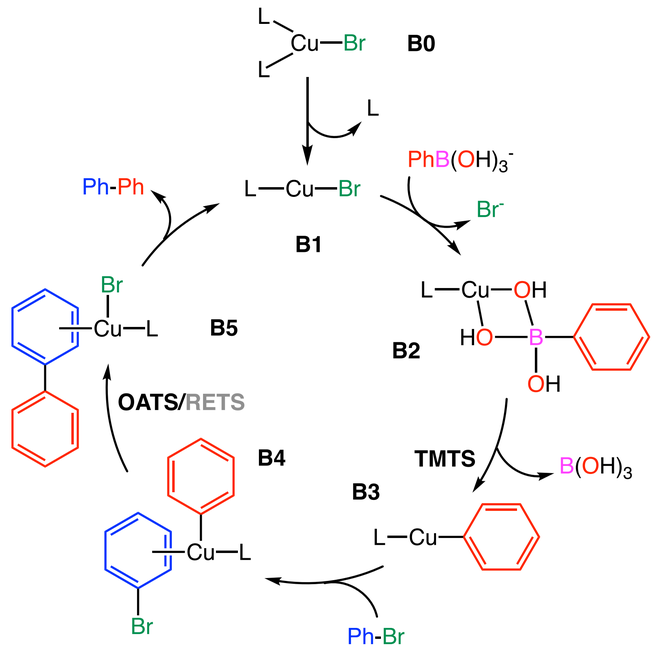
[1] Miyaura, N.; Yamada, K.; Suzuki, A. *Tetrahedron Letters,* **1979**, *20*, 3437-3440

[2] Gómez-Mudarra, F. A.; Aullón, G.; Jover, J. *Advances in Inorganic Chemistry*, **2024**, 84, 219–258

REACTION MECHANISM

The reaction involves the coupling of phenyl bromide and phenylboronic acid, catalyzed by palladium(0) or nickel(0) complexes (left) and copper(I) (right), in the presence of a base. The process consists of three key steps: oxidative addition, transmetalation and reductive elimination for palladium and nickel. For the copper catalyst the steps are: transmetalation, oxidative addition/reductive elimination.



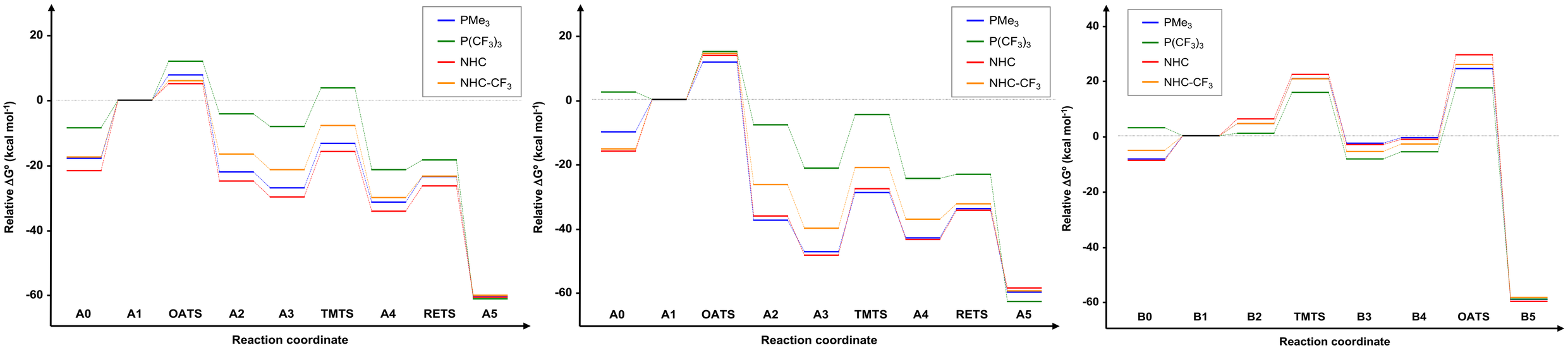


RESULTS

PALLADIUM(0) CATALYST

NICKEL(0) CATALYST

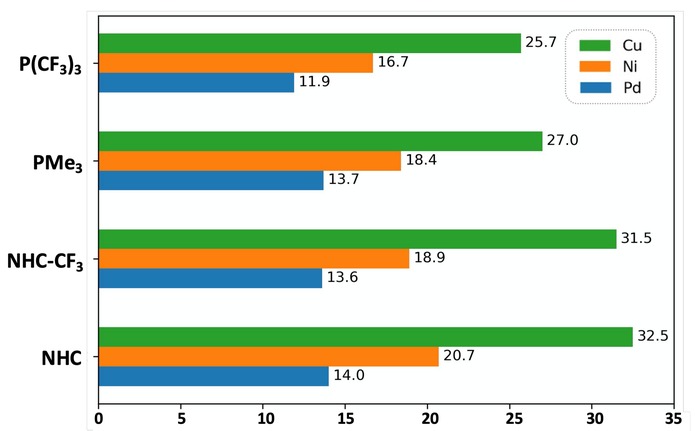
COPPER(I) CATALYST



Palladium(0) catalyst exhibits the lowest activation barriers for the studied reaction, with values around 14 kcal mol^{-1} for all ligands except $P(CF_3)_3$, showing an activation barrier of 11.9 kcal mol^{-1}.

Nickel(0) catalyst exhibits activation barriers ranging from 16 to 21 kcal mol^{-1}, with values of 16.7 kcal/mol for the $P(CF_3)_3$ and 18.4 kcal mol^{-1} with PMe_3 ligand.

Copper(I) catalyst exhibits the highest activation barriers, ranging from 25 to 33 kcal mol^{-1}. The most efficient being 25.7 kcal mol^{-1} for the $P(CF_3)_3$ and 27.0 kcal mol^{-1} for the PMe_3 ligand.



SUPPORTING INFORMATION

The complete published work can be accessed through the following QR code.

METHODOLOGY

All calculations were carried out with the Gaussian16 package, functional B3LYP and implicit description of 1,4-dioxane as solvent (PCM/SMD).

The basis sets for geometry optimization are 6-31G* for all atoms except Pd, Ni, and Cu, for which SDD with ECP has been used. Single point calculations to obtain Gibbs energies at 25°C have been carried out using the def2-TZVPPD basis set for all atoms.

Tight convergence criteria, ultrafine grids and Grimme's D3 dispersion were employed.

FUNDINGS

Ayuda PRE2019-091164 financiada por MCIN/AEI 10.13039/501100011033 y por FSE invierte en tu futuro

Structures of Excellence María de Maeztu program (CEX2021-001202-M)

CONCLUSIONS

Palladium-based systems continue to be the most efficient for the Suzuki–Miyaura reaction, but nickel and copper catalysts offer a more sustainable alternative due to their greater availability and lower cost.

The higher activation barrier observed in copper systems indicates that further research is needed to optimize their performance.