

Calix Assisted Palladium Nanocatalyst: A Review

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ABSTRACT

The article reviews recent advances in c-c cross coupling area as calix protected palladium nanocatalyst. The extensive use of palladium complex as catalyst in the calix chemistry is newly emerging field which deals with Suzuki, Heck, Stille and Sonogashira cross coupling reactions. The brief survey of cross-coupling reactions also includes yield, catalyst loading, Recyclability



KEYWORDS: Calix, Palladium, Nanoparticles, Nanocatalyst, Coupling reactions

INTRODUCTION

Palladium Chemistry gain considerably interest form 19's sanctuary. Professor Richard Heck is considered as a father of Palladium catalysed coupling chemistry. His first initiation, Pd-catalysed vinylic substitution reactions with aryl halides published in 1972.^{1, 2} The award of the 2010 Nobel Prize in Chemistry applauded by chemists worldwide that is belonging for C-C cross coupling to Richard Heck, Ei-ichi Negishi³, and Akira Suzuki⁴.

After first and second generation of supramolecules, A third generation has been classified as calixarene which is cyclic tetramers synthesized using p-tert butyl phenol and formaldehyde.⁵ The calixarenes has mainly into two (1) hetero-calixarenes, in which hetero atoms such as O, N and S replace the bridge methylene group termed as oxacalixarene, azacalixarene, thiocalixarene⁶; and (2) heterocalixarenes, in which heterocyclic moieties such as resorcinol and pyrroles replace the phenolic unit termed as calix-resorcinol, calix-pyrrole⁷.

In the present review, the different platform of calixarene has been used for the preparation Pd-NPs as catalyst reservoirs for molecular palladium species in various carbon-carbon cross coupling reactions.

Why calixarene?

The calixarenes has been used for the preparations of metal nano-particles (MNPs) due to following properties. (1) Highly optimized upper rim and⁸ (2) Vigorously Modified

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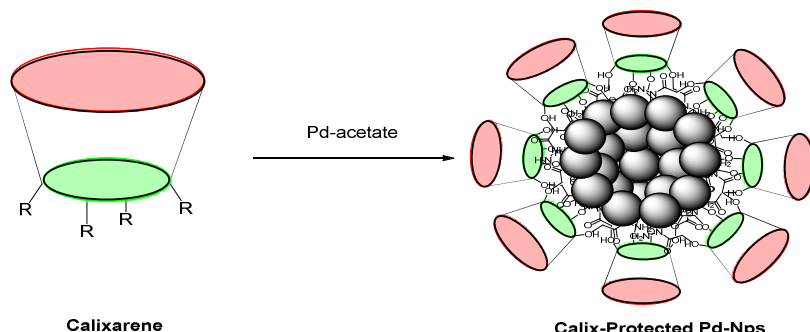
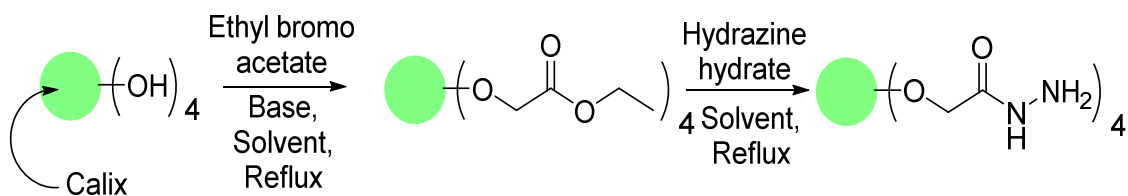
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Lower rim⁹. Calix has ability to stabilize and reduce metal into nano form. In calixarene metal Nanoparticle chemistry, the hydrazine hydrate plays a vital role for the formation of metal Nanoparticles.^{10, 11} The Nitrogen atom present on hydrazide functional group and oxygen atom on carbonyl group was the key inspiration for the functionalization. The hydrazine hydrate group improves the efficiency for of the preparation of nanoparticles. The presence of bridge group electrons and web-type calix system having hydrogen bonding through -NH group made it stabilize and reductive of Pd-NPs in water¹¹.

Synthesis of Palladium nanoparticles:

The synthesis calix-protected nanoparticles have been completed using two main steps. In the first step the synthesis of calixarene (Scheme 1) was initiated which followed by the preparation of palladium nanoparticles using palladium acetate at room temperature (Scheme 2). A calix solution in distilled water was prepared and added dropwise into the preheated solution of Palladium acetate in distilled water and heated the solution was vigorously stirred while heating for 5-7 hr. The formation of water-soluble PdNps and the complete reduction of PdAc in solution was confirmed by a gradual color change black from brown to brownish yellow, as well as by UV-visible spectroscopy, selected area electron diffraction (SAED) and transmission electron microscopy (TEM).



C-C Cross coupling reaction:

A Suzuki-Miyuara reaction¹¹⁻¹⁴ is the cross-coupling reaction of aryl halide with alkylboranes in the presence of base and catalyst (Scheme 3.1). A reaction between aryl halide and organo stannane reagent in the presence of Pd catalyst and base is termed as **Stille cross coupling reaction**¹¹ (Scheme 3.2). **A Heck reaction**^{11, 13-15} is recognized as the reaction of an unsaturated halide with an alkene in the presence of base and Pd catalyst to form a substituted alkene (Scheme 3.3). **Sonogashira Reaction**¹³ is recognized as the reaction of an unsaturated halide with an alkyne in the presence of base and Pd catalyst to form a substituted alkyne. (Scheme 3.4). The catalyst loading, base, solvent parameter has been taken as per following table 1.

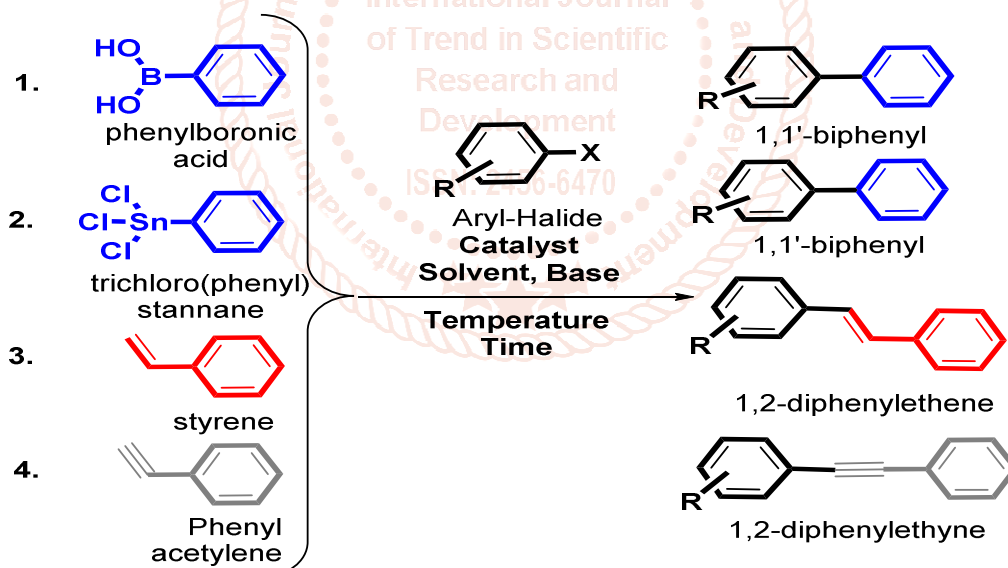


Table1 Parameter for the C-C cross coupling reactions

Sr. No	Pd-Nps	C-C-Cross Coupling Rea.	Catalyst (mmol)	Solvent: water	Base
1	TMRTH	Suzuki	1.2	1,4-dioxane	Na ₂ CO ₃
2	DHOC	Suzuki	0.007	DMF	Na ₂ CO ₃
		Sonogashira		NMP	Na ₂ CO ₃
		Heck		NMP	Na ₂ CO ₃
3	CPTH	Heck	0.008	NMP	Na ₂ CO ₃
4	OXDH	Suzuki	0.009	1,4-dioxane	Na ₂ CO ₃
		Heck		NMP	Na ₂ CO ₃
5	TPNH	Suzuki	0.009	1,4-dioxane	Na ₂ CO ₃
		Heck		Methanol	Na ₂ CO ₃
		Stille		1,4-dioxane	KOH

Outline:

The reported calix-protected PdNps was utilizing for the Suzuki, Stille, Heck and Sonogashira cross coupling reaction. The Calix-protected Nanoparticles are very efficient, high yield, less time consuming then fashioned catalyst and recyclable more than 5 cycles.

Table2 comparison of various PdNps

Sr. No	Type of NPs	TEM size	Catalytic activity	
			Reaction	Yield
1	TMRTH	5±2 nm	Suzuki	93-97
2	DHOC	5±2 nm	Suzuki	89-92
			Sonogashira	83-90
			Heck	87-95
3	CPTH	5±2 nm	Heck	90-96
4	OXDH	5±2 nm	Suzuki	92-98
			Heck	93-97
5	TPNH	4±2 nm	Suzuki	93-97
			Heck	94-98
			Stille	94-96

Reference

- [1] R. F. Heck and J. P. Nolley, *The Journal of Organic Chemistry*, 1972, 37, 2320-2322.
- [2] B. C. Barnard, *Platinum Metals Review*, 2008, 52, 38-45.
- [3] E.-i. Negishi, *Angewandte Chemie International Edition*, 2011, 50, 6738-6764.
- [4] A. Suzuki, *Angewandte Chemie International Edition*, 2011, 50, 6722-6737.
- [5] A. Zinke, E. Ziegler, E. Martinowitz, H. Pichelmayer, M. Tomio, H. Wittmann-Zinke and S. Zwanziger, *Berichte der Deutschen Chemischen Gesellschaft [Abteilung] B: Abhandlungen*, 1944, 264-272.
- [6] H. Kumagai, M. Hasegawa, S. Miyanari, Y. Sugawa, Y. Sato, T. Hori, S. Ueda, H. Kamiyama and S. Miyano, *Tetrahedron letters*, 1997, 38, 3971-3972.
- [7] B. König and M. H. Fonseca, *European Journal of Inorganic Chemistry*, 2000, 2000, 2303-2310.
- [8] C. Gutsche, *Monographs in Supramolecular Chemistry*, The Royal Society of Chemistry, Cambridge, 1989, 1.
- [9] J. Vicens and V. Böhmer, *Calixarenes: a versatile class of macrocyclic compounds*, Springer Science & Business Media, 2012.
- [10] A. R. Kongor, V. A. Mehta, K. M. Modi, M. K. Panchal, S. A. Dey, U. S. Panchal and V. K. Jain, *Topics in Current Chemistry*, 2016, 374, 28.
- [11] K. Modi, C. Patel, U. Panchal, A. Liska, A. Kongor, L. Jiri and V. Jain, *New Journal of Chemistry*, 2019, 43, 5611-5622.
- [12] U. Panchal, K. Modi, M. Panchal, V. Mehta and V. K. Jain, *Chinese Journal of Catalysis*, 2016, 37, 250-257.
- [13] V. Mehta, M. Panchal, A. Kongor, U. Panchal and V. Jain, *Catalysis Letters*, 2016, 146, 1581-1590.
- [14] M. Panchal, A. Kongor, V. Mehta, M. Vora, K. Bhatt and V. Jain, *Journal of Saudi Chemical Society*, 2018, 22, 558-568.
- [15] A. Kongor, M. Panchal, V. Mehta, K. Bhatt, D. Bhagat, D. Tipre and V. K. Jain, *Arabian journal of chemistry*, 2017, 10, 1125-1135.