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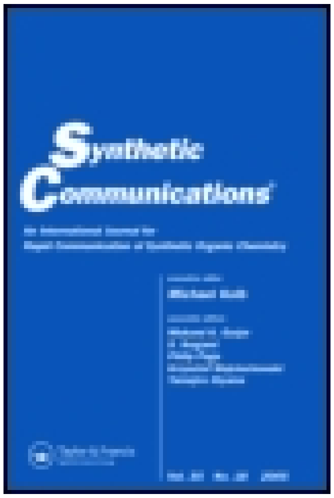

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Phosphine Free Tetradentate Salicylaldimine Ligand Complexed with Palladium: First Application in Heck Reactions

Rahul S. Kalhapure [a] , Thirumala Govender [b] & Krishnacharya G. Akamanchi [a]

[a] Department of Pharmaceutical Sciences and Technology , Institute of Chemical Technology, Matunga , Mumbai , IndiaCurrent address: Discipline of Pharmaceutical Sciences, School of Health Sciences, University of KwaZulu-Natal, Private Bag X54001, Durban 4000, South Africa.

[b] Discipline of Pharmaceutical Sciences, School of Health Sciences, University of KwaZulu-Natal , Durban , South Africa

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Phosphine Free Tetradentate Salicylaldimine Ligand Complexed With Palladium: First Application In Heck Reactions

Rahul S. Kalhapure[1], Thirumala Govender[2], Krishnacharya G. Akamanchi[1]

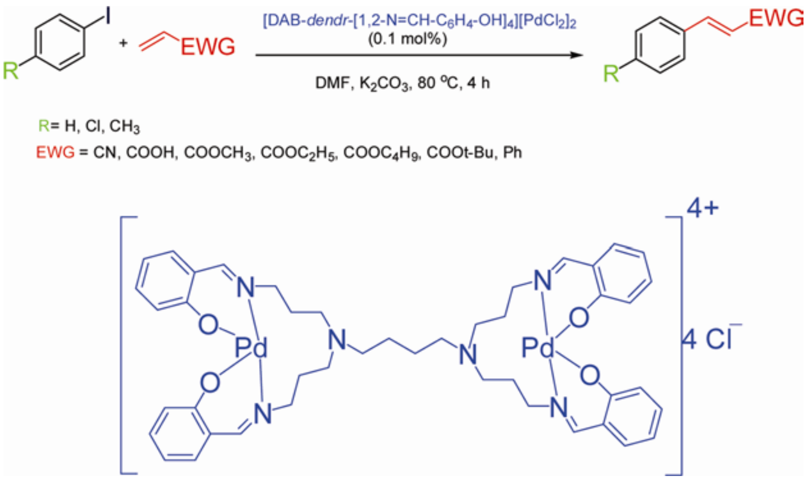
[1]Department of Pharmaceutical Sciences and Technology, Institute of Chemical Technology, Matunga, Mumbai, India [2]Discipline of Pharmaceutical Sciences, School of Health Sciences, University of KwaZulu-Natal, Durban, South Africa

Current address: Discipline of Pharmaceutical Sciences, School of Health Sciences, University of KwaZulu-Natal, Private Bag X54001, Durban 4000, South Africa.

Correspondence author E-mail: kgap@rediffmail.com

Abstract

Heck reactions were carried out using phosphine free tetradentate salicylaldimine ligand complexed with $PdCl_2$ under mild reaction conditions, short reaction time and low palladium loading. All aryl iodides underwent coupling reactions with olefins giving corresponding *trans*-products with good to high yield whereas aryl bromides gave very low yields and aryl chlorides failed to react.



KEYWORDS: Heck reactions; salicylaldimine; palladium chloride; aryl halides; olefins

INTRODUCTION

With a high potential for exploitability of useful features such as enhanced performance when compared to mononuclear complexes, ability to combine the best properties of homogeneous and heterogeneous catalysts in one system, stable macromolecular structures making them suitable for isolation via ultra-filtration thus providing the potential for catalyst recycling[1] dendrimeric ligands based metal catalysts, the metallodendrimers have recently attracted attention. Their exploitation is mainly aimed at reducing the amount of Pd required and high performance of the catalysts. Reactions which are catalyzed by using metallodendrimers include Heck reaction[2], Suzuki-Miyaura reaction,[3a] oxidation,[3b,c] polymerization,[1a,b] Sonogashira reaction,[4] hydroformylation, C-C coupling metathesis,[3d,5] and epoxide ring opening.[6]

Heck reaction, a widely used reaction in synthesis of various substituted olefins, dienes and natural products, is one of the most important palladium catalyzed reactions in organic chemistry for which several homogeneous and heterogeneous protocols have been reported in literature.[7,8] Most of the reported protocols employ Pd, an expensive metal, as catalyst in relatively large amounts and use of large amount also results in presence of residual metal in the product creating environmental concerns.[8a,b] Ligands play an important role in Heck reaction by increasing the solubility of metal, minimizing the palladium loading, yielding catalyst with high turnover number and high reactivity[8c] and in this context dendritic ligands have caught a good attention. Few examples are Reetz's dendritic phosphine, DAB-*dendr*-$[N(CH_2PPh_2)_2]_{16}$, bearing P-centres on the periphery co-ordinated to Pd catalysts,[9] DAB-G1(impyr-$PdCl_2$)$_4$ catalyst,[2] Pd(II)-phosphine complexes modified poly(ether imine) PETIM dendrimers,[10] palladium nanoparticle cored G3 dendrimer,[11] iminophosphine DAB-*dendr*-[1,2-($NCHC_6H_4PPh_2$)]$_{32}$, DAB-32-*imiphos*, and corresponding aminophosphine, DAB-*dendr*-[1,2-($NHCH_2$-$C_6H_4PPh_2$)]$_{32}$, DAB-32-*amiphos*, i.e. two dendrimeric *P, N*-ligands,[12] G4 PAMAM dendrimer encapsulated Pd^0 nanoparticles,[13] dendritic nanoreactor prepared by incorporating Pd^0 nanoparticles into poly (propylene imine) [PPI] dendrimer, and PPI dendrimer covalently functionalized with per fluorinated polyether chains on their periphery.[14] G1 and G2 dendrimeric salicylaldimine ligands based on PPI dendrimer scaffolds have been synthesized for preparation of multinuclear nickel complexes and evaluated in polymerization of norbornene.[1a] However these ligands have not been so far used for preparation of Pd complexes and screened for Heck reaction. In the present work we synthesized the same PPI tetradentate ligand [DAB-*dendr*-[1,2-N=CH-C_6H_4-OH]$_4$] and successfully prepared Pd(II) complex **1** (Fig. 1) and employed for Heck coupling reactions.

RESULTS AND DISCUSSION

DAB-*dendr*-[1, 2-N=CH-C_6H_4-OH]$_4$ Pd (II) complex **1** having two catalytic sites was prepared by using $PdCl_2(CH_3CN)_2$ and refluxing in CH_3CN for 24 h to ensure the completion of reaction. The IR spectra of **1** showed shift in ν (C=N) and ν (C- O) stretching frequencies from 1627 cm^{-1} and 1275 cm^{-1} to 1621 cm^{-1} and 1313 cm^{-1} respectively ensuring the formation of complex, and mass spectrometry and elemental analysis confirmed the molecular formula.

Previously dendrimers with two to sixty Pd atoms have been prepared either by complexation or entrapment.[2,10,11,13] Two Pd atoms were complexed with G1 PETIM dendrimer[10] but in the form of phosphine ligand. We for the first time complexed two Pd atoms with tetradentate DAB-*dendr*-[1,2-N=CH-C_6H_4-OH]$_4$ ligand without any phosphine as phosphine free conditions for Pd catalyzed reactions are preferred because of adverse environmental effects associated with phosphines.[12]

Heck coupling reactions between iodobenzene and methyl acrylate as model substrates were attempted using **1** and the results are summarized in Table 1. Reactions were carried out in different solvents such as toluene, CH_3CN, acetone, acetone-water (1:1), water and DMF with 1 mol% of **1** and K_2CO_3 as a base and at different temperatures. Reaction did not proceed in acetone, acetone-water (1:1) mixture and water (entry 4-6, Table 1), whereas in toluene and CH_3CN reaction did proceed but gave low yields (10-17%) (entry 1-3, Table 1). Best results were obtained in DMF and at reaction temperature of 80 ^oC giving very high yield in 4 h (entry 8, Table 1). Amount of **1** was reduced up to 0.1 mol% keeping other reaction conditions same and noticed no significant change in yield (entry 10, Table 1). Therefore for further studies DMF was chosen as solvent with catalyst amount of 0.1 mol% and reaction temperature of 80 ^oC.

To study the scope of the methodology, reactions were carried out using different substrates and results are presented in Table 2. All of the olefins gave good to excellent yields except acrylamide (entry 8, Table 2), which did not show any reaction. In all cases only *trans* isomer was obtained and none of the *cis* isomer or any other by-product could be observed by TLC or ^{1}H NMR spectra. In case of acrylic acid esters it was noticed that going from methyl to *t*-butyl esters resulted in slight decrease in yield (entry 3-6, Table 2). Styrene also reacted well but yield was comparatively less (entry 7, Table 2). Failure of acrylamide to react (entry 8, Table 2) was attributed to deactivation of catalyst by complexation with amide group. This conclusion is supported by carrying out reactions with methyl acrylate in presence of acrylamide and acetamide and in both the cases reaction did not proceed. Reactions with *p*-chloroiodobenzene and *p*-methyliodobenzene were equally facile but slightly lower yields were obtained with *p*-methyl- compared to *p*-chloroiodobenzenes (entry 9-12, Table 2).

Attempts to carry out reaction on aryl chlorides were unsuccessful while reaction with aryl bromides gave poor yield (entry 13 and 14, Table 2). A control reaction using only equivalent amounts of $PdCl_2$ as catalyst with no ligand gave < 3% yield.

To assess the standing of **1** with respect to other metallodendrimers, literature data is compiled in Table 3. Metallodendrimers with palladium loading in the range of 0.2 to 8 mol % have been used for 5 mmol of iodobenzene in evaluating Heck reactions whereas in our case 0.2 mol % of Pd loading was sufficient to give almost the same yield as that of the best catalyst but in short time (entry 1 and 5, Table 3) showing superiority of **1**.

CONCLUSION

In conclusion we have developed a new phosphine free tetradentate palladium complex-[DAB-*dendr*-[1,2-N=CH-C_6H_4-OH]$_4$] [$PdCl_2$]$_2$ for efficient Heck reaction. The catalyst is superior with respect to less amount of Pd requirement to achieve the same yield under similar reaction conditions in comparison with known methods utilizing metallodendrimers.

EXPERIMENTAL

Bis(acetonitrile)dichloropalladium (II), 1,4-diaminobutane, iodobenzene were obtained from Aldrich and used as received. All other chemicals were purchased from local chemical suppliers and used without any purification. IR spectra were recorded on FT-IR RX1 PerkinElmer instrument. ^{1}H NMR spectra were recorded on JEOL MY-60 operating at 60 MHz instrument. Chemical shifts are given as parts per million (ppm) downfield from tetramethylsilane (TMS) in δ units. Electrospray ionization (ESI)- mass spectra (MS) was recorded by using Agilent 6524 Q-TOF accurate Mass LC MS/MS system, Agilent (USA). Melting points were determined with Veego melting point apparatus having stirred paraffin bath. Silica gel # 60-120 was used for column chromatography and Thin Layer Chromatography (TLC) was performed using Merck Silica gel 60 F254 Plates.

Synthesis Of DAB-*Dendr*-(NH_2)$_4$[15]

DAB-*dendr*-(NH_2)$_4$ was prepared by some modifications in the reported method.[15]

DAB-*dendr*-(CN)$_4$: To a solution of diaminobutane (100 mmol, 8.81 g) in 100 ml of water was added acrylonitrile (800 mmol, 42.45 g) drop wise with stirring. The reaction mixture was heated at 80 °C for 1 h. Excess of acrylonitrile was removed as a water azeotrope under vacuum using rotary evaporator to get the product (29.7 g, 99%) as residue. This product was characterized by FT-IR and NMR. DAB-*dendr*-$(NH_2)_4$: To a hydrogenation vessel, filled with Raney Nickel catalyst (4 g), NaOH (65 mmol, 2.6 g) and methanol (100 ml) was added DAB-*dendr*-$(CN)_4$ (66.6 mmol, 20 g) dissolved in methanol (100 ml) and the mixture was hydrogenated at 100 psi at ambient temperature for 8 h. Reaction mixture was filtered through a bed of celite to remove Raney Nickel and filtrate was concentrated under vacuum. Crude product obtained was dissolved in dry acetone and filtered to remove NaOH. Acetone layer was concentrated in vacuo to get the colorless oil (20.44 g, 97%). This G1 PPI was used without further purification.

Preparation Of Ligand DAB-*Dendr*-[1,2-N=CH-C_6H_4-OH]$_4$:[1a]

Salicylaldehyde (12.6 mmol, 1.54 mL) was added to a mixture of DAB-$(NH_2)_4$ (3.2 mmol, 1g) and dry toluene (25 mL) under N_2 atmosphere. Mixture was stirred at room temperature for 72 h. Solvent was evaporated in vacuo leaving a yellow oil. Dichloromethane (20 mL) followed by petroleum ether (40 mL) were added and the mixture was kept at -4 °C for 72 h. Yellow precipitate obtained was recovered by filtration, washed with cold petroleum ether and air dried. Yield 2 g (85%). mp 65-67 °C (Lit 66-68 °C). IR (KBr): $\nu = 3082, 1627, 1394, 1275\ cm^{-1}$. ^1H NMR (60 MHz, $CDCl_3$): $\delta = 1.41$ (4 H, m), 1.99 (8 H, m), 2.40-2.62 (12 H, m), 3.69 (8 H, t), 6.83 (4 H, m), 7.16-7.26 (12 H, m), 8.32 (4 H, s). MS (ESI): m/z = 733.45.

Preparation Of [DAB-*Dendr*-[1,2-N=CH-C_6H_4-OH]$_4$][Pdcl$_2$]$_2$ 1

A mixture of ligand (1 mmol, 0.73 g) and $PdCl_2.(CH_3CN)_2$ (2 mmol, 1.037 g) in CH_3CN (15 mL) was refluxed under N_2 atmosphere for 24 h. The solvent was removed under vacuum using rotary evaporator. Orange colored solid residue obtained was washed with cold methanol and dried in oven at 100 ^oC for 1 h, Yield 1.20 g (83%). mp 183 ^oC (dec). IR (KBr): $\nu =$ 2926, 1621, 1313 cm^{-1}. MS (ESI): $m/z = 1083.8$ $[M^+]$. Anal Calcd for $C_{44}H_{54}Cl_4N_6O_5Pd_2$: C, 47.97; H, 4.94; N, 7.63. Found: C, 48.04; H, 5.06; N, 7.26.

General Procedure For Heck Reaction

Aryl halide (5 mmol), olefin (10 mmol), K_2CO_3 (5 mmol) and **1** (0.1 mol%) were taken in DMF (10 mL) in a sealed tube (25 mL) fitted with a Teflon cap under N_2 atmosphere and mixture was heated with stirring at 80 ^oC for 4 h, cooled to room temperature and solvent evaporated under reduced pressure on rotary evaporator. The residue was extracted using EtOAc (3 x 10 mL), dried over Na_2SO_4 and the solvent was removed on a rotary evaporator. The crude residue obtained was purified by column chromatography on silica gel, 60-120 mesh (petroleum ether–EtOAc, 98:2).

SUPPORTING INFORMATION

Supplemental data for this article can be accessed on the publisher's website.

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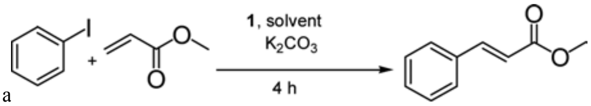
Table 1 Optimization of reaction conditions for Heck



reaction[a]

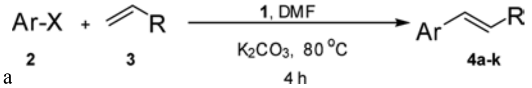
Entry	Amount of **1** in mol%	Solvent	Temperature °C	Yield[b](%)
1	1	PhMe	110	17
2	1	PhMe	80	12
3	1	CH_3CN	80	10
4	1	Acetone	60	n.r.
5	1	Acetone-H_2O (1:1)	80	n.r.
6	1	H_2O	80	n.r.
7	1	DMF	120	92
8	1	DMF	80	94
9	0.1	DMF	120	89
10	0.1	DMF	80	90

[a]Reaction conditions: Iodobenzene (5 mmol), methyl acrylate (10 mmol), K_2CO_3 (5 mmol), **1**, solvent (10 mL), reaction time 4 h, in a sealed tube under N_2 atmosphere.

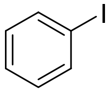
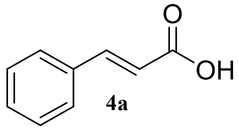
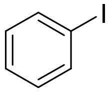
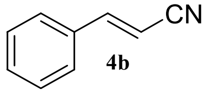
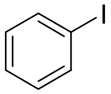
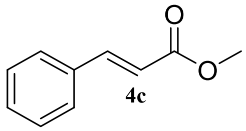
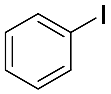
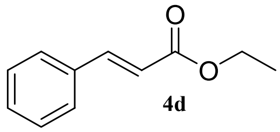
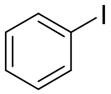
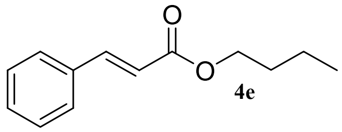
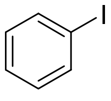
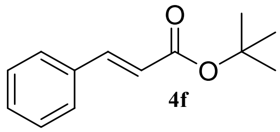
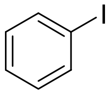
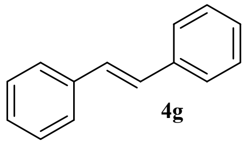
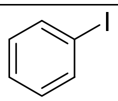
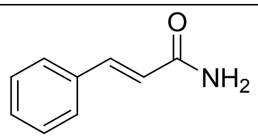
[b]Isolated yield.

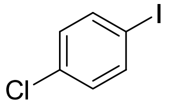
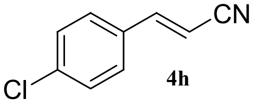
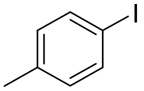
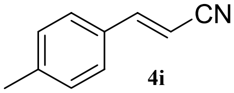
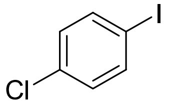
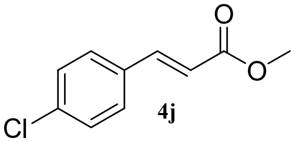
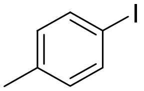
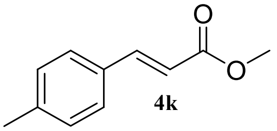
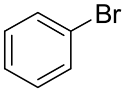
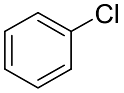
n.r. = no reaction

Table 2: Heck reactions using [DAB-*dendr*-[1,2-N=CH-C_6H_4-OH]$_4$] $[PdCl_2]_2$] complex



1[a]

Entry	Ar-X	R	Product	Yield[b](%)
1		COOH	 **4a**	88
2		CN	 **4b**	84
3		$COOCH_3$	 **4c**	94
4		$COOC_2H_5$	 **4d**	86
5		COO*n*-C_4H_9	 **4e**	82
6		COO*t*-Bu	 **4f**	75
7		C_6H_5	 **4g**	78
8		$CONH_2$		n.r.

9		CN	 **4h**	88
10		CN	 **4i**	82
11		$COOCH_3$	 **4j**	93
12		$COOCH_3$	 **4k**	85
13		$COOCH_3$	**4c**	04
14		$COOCH_3$	**4c**	n.r.

[a]Reaction conditions: Aryl halide (5 mmol), olefin (10 mmol), K_2CO_3 (5 mmol), **1** (0.1 mol%), DMF (10 mL), temperature 80 °C, reaction time 4 h, in a sealed tube under N_2 atmosphere.

[b] Isolated yield.

n.r. = no reaction

Table 3 Comparison of different metallodendrimer catalysts with catalyst 1 for Heck reaction between iodobenzene and methyl acrylate

Entry	Catalyst	Pd loading (mol%)	Temperature (^oC)	Time (h)	Yield (%)	Reference
1	DAB-G1 (impyr)-($PdCl_2$)$_4$	0.96	82	8	96	2
2	G1 PETIM metallodendrimer	2-0.2	140	4	69	10
3	G2 PETIM metallodendrimer	4-0.4	140	4	56	10
4	G3 PETIM metallodendrimer	8-0.8	140	4	54	10
5	[DAB-*dendr*-[1,2-N=CH-C_6H_4-OH]$_4$] [$PdCl_2$]$_2$**1**	0.2	80	4	94	This work

Figure 1. Structure of [DAB-*dendr*-[1,2-N=CH-C_6H_4-OH]$_4$] [PdCl_2]$_2$] complex **1**