PHOSPHINE-FREE TETRADENTATE SALICYLALDIMINE LIGAND COMPLEXED WITH PALLADIUM: FIRST APPLICATION IN HECK REACTIONS

Rahul S. Kalhapure,1 Thirumala Govender,2 and Krishnacharya G. Akamanchi1

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

GRAPHICAL ABSTRACT

Abstract Heck reactions were carried out using phosphine-free tetradentate salicylaldimine ligand complexed with PdCl₂ 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 excellent yields, whereas aryl bromides gave very poor yields and aryl chlorides failed to react.

Keywords Aryl halides; Heck reactions; olefins; palladium chloride; salicylaldimine

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The present affiliation for Rahul S. Kalhapure is Discipline of Pharmaceutical Sciences, School of Health Sciences, University of KwaZulu-Natal, Durban, South Africa.

Address correspondence to Krishnacharya G. Akamanchi, Department of Pharmaceutical Sciences and Technology, Institute of Chemical Technology, Matunga, Mumbai 400019, India. E-mail: kgap@rediffmail.com

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INTRODUCTION

Because of their high potential for useful features such as enhanced performance over mononuclear complexes, ability to combine the best properties of homogeneous and heterogeneous catalysts in one system, and stable macromolecular structures that make them suitable for isolation via ultrafiltration and thus provide potential for catalyst recycling, dendrimeric ligand–based metal catalysts (metallodendrimers) have recently attracted attention. Their exploitation is mainly aimed at reducing the amount of Pd required and high performance of the catalysts. Reactions catalyzed by using metallodendrimers include the Heck reaction, Suzuki–Miyaura reaction, oxidation, polymerization, Sonogashira reaction, hydroformylation, C-C coupling metathesis, and epoxide ring opening.

The 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. Most of the reported protocols employ Pd, an expensive metal, as catalyst in relatively large amounts and use of these large amount also results in residual metals in the products, creating environmental concerns. Ligands play an important role in the Heck reaction by increasing the solubility of metal, minimizing the palladium loading, and yielding catalysts with high turnover number and high reactivity. In this context dendritic ligands have received attention. A few examples are Reetz’s dendritic phosphine, DAB-dendr-[N(CH2PPh2)2]16, bearing P-centers on the periphery coordinated to Pd catalysts, DAB-G1(impyr-PdCl2)4 catalyst, Pd(II)-phosphine complexes modified poly(ether imine) PETIM dendrimers, palladium nanoparticle cored G3 dendrimer, iminophosphine DAB-dendr-[1,2-(NCHC6H4PPh2)]32, DAB-32-imiphos, and corresponding aminophosphine, DAB-dendr-[1,2-(NHCH2-C6H4PPh2)]32, DAB-32-amiphos, i.e., two dendrimeric P, N-ligands, G4 PAMAM dendrimer encapsulated Pd0 nanoparticles, dendritic nanoreactor prepared by incorporating Pd0 nanoparticles into poly(propylene imine) (PPI) dendrimer, and PPI dendrimer covalently functionalized with perfluorinated polyether chains on the periphery. 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. However, these ligands have not been used so far for preparation of Pd complexes and screened.

Figure 1. Structure of [DAB-dendr-[1,2-\(N=CH-\text{C}_6\text{H}_4\text{OH}\)]_4\[\text{PdCl}_2\]_2] complex 1.
for Heck reaction. In the present work we synthesized the same PPI tetradsentate
ligand [DAB-dendr-[1,2-N=CH-C6H4-OH]4], successfully prepared the Pd(II)
complex 1 (Fig. 1), and employed it for Heck coupling reactions.

RESULTS AND DISCUSSION

DAB-dendr-[1,2-N=CH-C6H4-OH]4 Pd (II) complex 1, having two catalytic
sites, was prepared by using PdCl2(CH3CN)2 and refluxing in CH3CN for 24 h to
ensure the completion of the reaction. The infrared (IR) spectra of 1 showed shifts
in ν (C=N) and ν (C-O) stretching frequencies from 1627 and 1275 cm⁻¹ to 1621
and 1313 cm⁻¹ respectively, ensuring the formation of the complex, and mass spec-
trometry and elemental analysis confirmed the molecular formula.

Previously, dendrimers with 2 to 60 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. For the first time we com-
plexed two Pd atoms with tetradsentate DAB-dendr-[1,2-N=CH-C6H4-OH]4 ligand
without any phosphine. 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. Reac-
tions were carried out in different solvents such as toluene, CH3CN, acetone, acet-
one–water (1:1), water, and dimethylformamide (DMF) with 1 mol% of 1 and
K2CO3 as a base and at different temperatures. Reaction did not proceed in acetone,
acetone–water (1:1) mixture, or water (entries 4–6, Table 1), whereas in toluene and
CH3CN the reaction did proceed but gave poor yields (10–17%) (entries 1–3, Table 1).

| Entry | Amount of 1 (mol%) | Solvent | Temperature (°C) | Yieldb (%) |
|-------|-------------------|---------|-----------------|------------|
| 1     | 1                 | PhMe    | 110             | 17         |
| 2     | 1                 | PhMe    | 80              | 12         |
| 3     | 1                 | CH3CN   | 80              | 10         |
| 4     | 1                 | Acetone | 60              | n.r.       |
| 5     | 1                 | Acetone–H2O (1:1) | 80 | n.r.   |
| 6     | 1                 | H2O     | 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         |

aReaction conditions: Iodobenzene (5 mmol), methyl acrylate (10 mmol), K2CO3 (5 mmol), 1, solvent
(10 mL), reaction time 4 h, in a sealed tube under N2 atmosphere.
bIsolated yield.
Note. n.r., no reaction.
The best results were obtained in DMF and at reaction temperature of 80 °C, giving very good yield in 4 h (entry 8, Table 1). Amount of \( \text{I} \) was reduced up to 0.1 mol\%, keeping the other reaction conditions the same, and we 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 °C.

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 thin-layer chromatography (TLC) or \(^1\)H NMR spectra. In the case of acrylic acid esters it was noticed that going from methyl to \( t \)-butyl esters resulted in a slight decrease in yield (entries 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 the presence of acrylamide and acetamide and in both the cases the reaction did not proceed. Reactions with \( p \)-chloriodobenzene and \( p \)-methyliodobenzene were equally facile but slightly lower yields were obtained with \( p \)-methyl- compared to \( p \)-chloriodobenzenes (entries 9–12, Table 2).

Attempts to carry out the reaction on aryl chlorides were unsuccessful whereas reaction with aryl bromides gave poor yields (entries 13 and 14, Table 2). A control reaction using only equivalent amounts of \( \text{PdCl}_2 \) as catalyst with no ligand gave <3\% yield. To assess the standing of \( \text{I} \) 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 shorter time (entry 1 and 5, Table 3), showing the superiority of \( \text{I} \).

**CONCLUSION**

In conclusion we have developed a new phosphine-free tetradentate palladium complex \([\text{DAB-dendr-[1,2-N=CH-C}_6\text{H}_4\text{-OH]}_4][\text{PdCl}_2]\) for efficient Heck reaction. The catalyst is superior because less Pd is required to achieve the same yield under similar reaction conditions in comparison with known methods utilizing metallodendrimers.

**EXPERIMENTAL**

Bis(acetonitrile)dichloropalladium (II), 1,4-diaminobutane, and 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 a FT-IR RX1 Perkin-Elmer instrument. \(^1\)H NMR spectra were recorded on a Jeol MY-60 instrument operating at 60 MHz. Chemical shifts are given as parts per million (ppm) downfield from tetramethylsilane (TMS) in \( \delta \) units. Electrospray ionization (ESI)–mass spectra (MS) was recorded using an Agilent 6524 Q-TOF Mass LC MS/MS system (Agilent, USA). Melting points were determined
Table 2. Heck reactions using [DAB-dendr-[1,2-N=CH-C₆H₄-OH]₄[PdCl₂]₂] complex 1a

| Entry | Ar-X | R       | Product | Yield (%) |
|-------|------|---------|---------|-----------|
| 1     | COOH | 4a      |         | 88        |
| 2     | CN   | 4b      |         | 84        |
| 3     | COOCH₃ | 4c   |         | 94        |
| 4     | COOC₂H₅ | 4d |         | 86        |
| 5     | COO-n-C₄H₉ | 4e |         | 82        |
| 6     | COO-t-Bu | 4f |         | 75        |
| 7     | C₆H₅ | 4g      |         | 78        |
| 8     | CONH₂ | 4h      |         | n.r.      |
| 9     | CN   | 4h      |         | 88        |

(Continued)
with a Veego melting-point apparatus having a stirred paraffin bath. Silica gel (60–120 mesh) was used for column chromatography and thin-layer chromatography (TLC) was performed using Merck silica-gel 60 F254 plates.

### Synthesis of DAB-dendr-(NH$_2$)$_4$

DAB-dendr-(NH$_2$)$_4$ was prepared by some modifications in the reported method.$^{15}$ Acrylonitrile (800 mmol, 42.45 g) was added dropwise to a solution of

### Table 2. Continued

| Entry | Ar-X | R | Product | Yield$^b$ (%) |
|-------|------|---|---------|--------------|
| 10    | ![Image](image1.png) | CN | ![Image](image2.png) | 82           |
| 11    | ![Image](image3.png) | COOCH$_3$ | ![Image](image4.png) | 93           |
| 12    | ![Image](image5.png) | COOCH$_3$ | ![Image](image6.png) | 85           |
| 13    | ![Image](image7.png) | COOCH$_3$ | 4c | 04           |
| 14    | ![Image](image8.png) | COOCH$_3$ | 4c | n.r.         |

$^a$Reaction conditions: Aryl halide (5 mmol), olefin (10 mmol), K$_2$CO$_3$ (5 mmol), I$_2$ (0.1 mol%), DMF (10 mL), temperature 80°C, reaction time 4 h, in a sealed tube under N$_2$ atmosphere.

$^b$Isolated yield.

Note. n.r., no reaction.

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

| Entry | Catalyst | Pd loading (mol%) | Temperature (°C) | 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     | 4–0.3             | 140              | 4        | 56        | 10        |
| 4     | G3 PETIM metallodendrimer     | 8–0.8             | 140              | 4        | 54        | 10        |
| 5     | [DAB-dendr-[1,2-N=CH-C$_6$H$_5$-OH]$_4$][PdCl$_2$]$_2$I | 0.2               | 80               | 4        | 94        | This work |

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diaminobutane (100 mmol, 8.81 g) in 100 ml of water 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-<i>dendr</i>-(CN)<sub>4</sub> (66.6 mmol, 20 g) dissolved in methanol (100 ml) was added to a hydrogenation vessel filled with Raney nickel catalyst (4 g), NaOH (65 mmol, 2.6 g), and 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 the filtrate was concentrated under vacuum. The crude product obtained was dissolved in dry acetone and filtered to remove NaOH. The 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-<i>dendr</i>-[1,2-N=CH-C<sub>6</sub>H<sub>4</sub>-OH]<sub>4</sub><sup>[1a]</sup>**

Salicylaldehyde (12.6 mmol, 1.54 mL) was added to a mixture of DAB-(NH<sub>2</sub>)<sub>4</sub> (3.2 mmol, 1 g) and dry toluene (25 mL) under N<sub>2</sub> atmosphere. The mixture was stirred at room temperature for 72 h. The 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. A 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): ν = 3082, 1627, 1394, 1275 cm<sup>−1</sup>. <sup>1</sup>H NMR (60 MHz, CDCl<sub>3</sub>): δ = 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): <i>m/z</i> = 733.45.

**Preparation of [DAB-<i>dendr</i>-[1,2-N=CH-C<sub>6</sub>H<sub>4</sub>-OH]<sub>4</sub>][PdCl<sub>2</sub>]<sub>2</sub> 1**

A mixture of ligand (1 mmol, 0.73 g) and PdCl<sub>2</sub>·(CH<sub>3</sub>CN)<sub>2</sub> (2 mmol, 1.037 g) in CH<sub>3</sub>CN (15 mL) was refluxed under N<sub>2</sub> 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 an oven at 100 °C for 1 h, yield 1.20 g (83%), mp 183 °C (dec). IR (KBr): ν = 2926, 1621, 1313 cm<sup>−1</sup>. MS (ESI): <i>m/z</i> = 1083.8 [M<sup>+</sup>]. Anal. calcd. for C<sub>44</sub>H<sub>54</sub>Cl<sub>4</sub>N<sub>6</sub>O<sub>5</sub>Pd<sub>2</sub>: 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<sub>2</sub>CO<sub>3</sub> (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<sub>2</sub> atmosphere and the mixture was heated with stirring at 80 °C for 4 h and cooled to room temperature. The solvent was evaporated under reduced pressure on a rotary evaporator. The residue was extracted using EtOAc (3 × 10 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>, 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).
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SUPPORTING INFORMATION

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

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