

RESEARCH ARTICLE

A FACILE SYNTHESIS OF PALLADIUM CONTAINING METALLODENDRIMER BASED ON DIAZINE AND ITS APPLICATION AS A CATALYST.

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Abstract

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Key words:-Diazine. Aroyl chloride. phenylacetylene, Triaminopyrimidine, Metallodendrimer.

..... A palladium containing metallodendrimer has been directly prepared by the reaction of 2,4,6-Triaminopyrimidine (Diazine) with 4-methyl benzoyl chloride using (Ph₃P)₂PdCl₂ in DMF at 70 °C in good yields. The compound was characterized with IR, NMR, Mass and other spectroscopic methods while SEM and EDX showed the surface morphology and the presence of Palladium chloride of the compound. TG and DSC exhibited the good thermal stability of the metallodendrimer. The compound was found to be an effective homogeneous catalyst for the C-C cross-coupling reaction such as Heck and Sonogashira.

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Introduction:-

In the past two decades, the idea and synthesis of dendrimers have received increasing find out [1, 2] not only since of the aesthetically pleasing structures of these molecules but also as an event of their various applications in hostguest chemistry [3], material science [4], and membrane chemistry [5]. So far, two complementary methodologies [6, 7], the divergent and the convergent were implemented within the preparation of dendrimers.

Metallodendrimers are the unique magnificence of synthetic macromolecules having remarkably branched, three dimensional, nanoscale design with very low polydispersity and excessive functionality [8]. Active centre in a metallodendrimer may be situated in three extraordinary areas: (i) metallic atom as the dendrimer center, (ii) metal atoms within the dendrimer branches (iii) metallic atoms in the outer edge. Such as PAMAM dendrimers can coordinate different transition metals through their nitrogen atoms.

Metals able to coordinate with the PAMAM structure include among others Cu [9, 10] Au [11] Pd [12]Pt [13] Ag [14] Co[15] as well as bimetallic systems such as Pd-Au[16] and Pt-Ru[17].

Recently, metallodendrimers have been widely investigated in different fields, which includes molecular light harvesting, catalysts, liquid crystals, molecular encapsulation, and drug delivery [18]. The majority of the studies has been achieved in the field of catalysis where metals such as Cu (II), Rh (III), Ru (II), Pd (II), Fe (I) and Co (III) are used in the production of metallodendrimers. In addition to, metallodendrimer compounds have been prepared via click chemistry, employing Diels-Alder reactions [19], thiolene reactions [20], and azide-alkyne reactions [21, 22]. Here we report the synthesis and characterization of a new class of homogeneous Pd containing diazine-

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based metallodendrimer which have shown efficient catalytic activity in the Heck and Sonogashira crosscoupling reaction.

Experimental Section:

Unless in any other case noted, all reagents were reagent grade and used without further purification. Dehydrated DMF, DMSO, CH₃CN and THF were used as reaction solvent. Those solvents were bought from Aldrich and used as required. De-ionized water was used in the experiment in which required. The IR spectra was taken on a Shimadzu FTIR 8400S Fourier remodel Infrared Spectrophotometer (four hundred-4000 cm-1) with KBr pellets. ¹H NMR and ¹³C NMR spectra were recorded at 300 MHz and 75 MHz, respectively, on a JEOL AL 300/BZ tool as well as BRUKER DPX-400 MHz & 100 MHz spectrophotometer respectively. Chemical shifts was taken relative to TMS. Mass spectra (MS) was measured with the aid of the usage of AXIMA-CFR, Shimadzu/Kratos TOF Mass spectrometer. Scanning Electron Microscope (SEM) and power Dispersive X-ray (EDX) was taken on a Hitachi S-4800. Analytical thin layer chromatography (TLC) became silica gel 60 F 254 covered on 25 TCC aluminum sheets (20×20 cm). 2, 4, 6-triamino-1, 3, 5-diazine, 4-methyl benzoyl chloride and (Ph₃P)₂PdCl₂ were purchased from Sigma Aldrich and had been directly used without further purification. The thermal behavior of metallodendrimer was determined by a thermogravimetric analyzer (NETZSCH STA 449F3) from 26 to 600 °C. Elemental analyses were carried out with a Fisons EA 1108 CHNS-O apparatus. All TG and DSC facts had been received under a nitrogen environment by the use of aluminum oxide crucible at a heating fee of 10 °k/min and at a flow rate of 40 and 60 mL/min.

Synthesis of 2, 4, 6-Tris (di-4-methylbenzamido)-1, 3, 5-Diazine Palladium (II) chloride (3)

4-Methyl benzoyl chloride 2 (1.47 g, 9.54 mmol), $(Ph_3P)_2PdCl_2$ (0.11g, 10% mol) were sequentially added to a solution of 2, 4, 6-triamino-1, 3, 5-diazine 1 (0.2 g, 1.59 mmol) in DMF (10 mL). The solution was degassed and stirred at room temperature under a nitrogen atmosphere for 1 h and the reaction was continued for 5 h at 70 °C. The progress of the reaction was monitored by TLC. At the starting of the reaction, the mixture was turned into a clear solution and graduallyit turned into white solid. After completion of the reaction, distilled H₂O was added. After the removal of solvent, the product was washed with sodium hydrogen carbonate solution and purified by recrystallization by using ethanol and found the desired product 3.

White crystalline solid; yield: 90 %.; IR (KBr): v_{max} 3052.29, 2976.31, 1710.20, 1611.69, 1418.69, 1360.20 cm⁻¹.¹H NMR (300 MHz, CD₃OD): δ 7.80 (m, 12 H), 7.23 (m, 12 H), 4.96 (s, 1H) 2.3 (s, 18 H) ppm.¹³C NMR (75 MHz, CDCl3): δ 21.63, 129.28, 130.50, 131.28, 144.63 and 172.33 ppm. MALDI-TOF MS: m/z (%) = calcd. for C₅₂N₅H₄₃O₆ Pd₃Cl₆ 1365.90; found 1369.44 (100) [M]⁺, Anal. Calcd. (%) for C₅₂N₅H₄₃O₆ Pd₃Cl₆: C, 45.70; H, 3.17; N, 5.13. Found: C, 45.67; H, 3.10; N, 5.10.

Application of Pd-metallodendrimer 3 as a catalyst in the Sonogasira reaction:

Synthesis of 4-(2-phenylethynyl)phenol 14, [30]

4-Iodophenol (1 mmol), Pd-metallodendrimer 3 (1.5 mol%), CuI 0.5 mol% were kept in a R.B flask with phenylacetylene (1.2 mmol) under the nitrogen atmosphere and Et₃N (2 mL) as a base and CH₃CN (5 mL) as a solvent were added into the reaction flask. The resulting mixture was stirred at 60 $^{\circ}$ C temperatures for 3 hrs and the reaction was checked by TLC. Then the solvent was vaporized under reduced pressure and the residue obtained was purified by silica gel chromatography using ethyl acetate and hexane (4:1) and solid product was obtained, mp: 124-126 $^{\circ}$ C; ¹H-NMR (CDCl₃, 400 MHz): δ 5.08 (s, 1 H, OH); 6.75 (d, 2 H, *J*=8.8 Hz); 7.29-7.35 (m, 3 H); 7.43 (d, *J*=8.8, 2 H); 7.55 (d, *J*=8.8, 2 H). ¹³C NMR (100 MHz, CDCl₃): δ 93.93, 114.13, 115.30, 123.97, 128.47, 129.03, 133.93, 134.43, 159.51.

Synthesis of 1-(2-p-tolylethynyl)benzene, 15 [30]

Solid colourless product was obtained, mp: 70-72 °C (lit. 71 °C); ¹H NMR (400 MHz): δ 2.31(s, 3 H); 7.20 (d, 2 H, *J*= 8.8 Hz); 7.32 (t, 3 H, *J*= 5.6 Hz); 7.33 (d, 2 H, *J*=8.4 Hz); 7.54 (d, 2 H, *J*= 8.0 Hz). ¹³C NMR (100 MHz, CDCl₃): δ 92.51, 93.13, 120.20, 122.23, 128.27, 128.47, 128.97, 132.03, 133.93, 139.13.

Synthesis of 1-(2-(4-methoxyphenyl)ethynyl)benzene, 16 [31]

Solid white product was obtained, mp: 54-56 °C (lit. 57 °C); ¹H NMR (400 MHz): δ 3.71 (s, 3H); 6.88 (d, 2 H, *J*=8.8Hz); 7.33 (t, *J*=10.8, 3 H); 7.36 (d, 2 H, *J*=8.8 Hz); 7.44 (d, 2 H, *J*=8.0).

C NMR (100 MHz, CDCl₃): δ 55.51, 93.23, 113.23, 115.20, 123.37, 128.47, 129.47, 132.03, 133.93, 160.97.

Application of Pd-metallodendrimer 3 as a catalyst in the Heck reaction.

A combination of 4-Iodophenol (1 mmol) with styrene (1.2 mmol), Pd-metallodendrimer 3 (1.5 mol%) and triethylamine (1.2 mL) was stirred in DMF (5 mL) in an R.B flask under nitrogen environment. The solution was heated at 85 °C for 24 hrs. The advancement of the reaction was observed with the aid of TLC (n-hexane/ethyl acetate 1:1). After the achievement of the desired conversion of the reaction, the reaction mixture was evaporated to dryness under reduced pressure and the residue was turned into extracted with chloroform. The chloroform extract was washed with distilled water and dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. Then it was refined by silica gel column chromatography with n-hexane / ethyl acetate (3:1). Solid colourless trans stilbene, **22** [32] was found and melting point was 74-76 °C, IR (KBr): v_{max} 3027, 1600.35, 1496, 1452.24, 1319.36, 1267.27, 962.35, 909.25, 733.74. ¹H NMR (400 MHz, CDCl₃), δ 7.02 (s, 2 H), 7.35 (dd, 1 H, J=1.2 Hz, 7.2 Hz), 7.43 (dd, 4 H, *J*=9.2 Hz, 7.2 Hz), 7.63 (dd, 4H, *J*=1.2 Hz, 8.8 Hz). ¹³C NMR (100 MHz, CDCl₃): δ 126.56, 127.61, 128.11, 128.85, 137.46.

(E)-Methyl 3-o-tolylacrylate, 23 [32]

IR (KBr): v_{max} 2950.32, 1722.32, 1639.35, 1267.27, 1220.20, 1172.21, 980.30, 764.27. ¹H NMR (400 MHz, CDCl₃), δ 2.48 (s, 3 H); 3.84 (s, 3 H); 6.46 (d, 1 H, J=16.0 Hz); 7.35-7.68 (m, 3 H); 7.83-7.98 (m, 1 H); 8.33 (d, *J*=8.0 Hz, 1 H).

¹³C NMR (100 MHz, CDCl₃): δ 19.66, 51.56, 118.46, 126.17, 126.61, 130.11, 130.75, 133.56, 137.66, 142.46, 167.36.

Methoxy-4-styrylbenzene, 24 [32]

mp. 135-137 °C, IR (KBr): v_{max} 2960.74, 1601.35, 1511.24, 1319.35, 1251.27, 1179.75, 1031.15, 966.36, 812.25. ¹H NMR (400 MHz, CDCl₃), δ 3.88 (s, 3 H); 6.37 (d, 2 H, *J*=8.0 Hz); 6.57 (d, 1 H, *J*=16 Hz); 6.86 (d, 1 H, *J*=16 Hz); 6.39-6.29 (m, 1 H); 7.58 (t, 2 H, *J*=7.2 Hz); 7.94 (t, 4 H, *J*=9.2 Hz). ¹³C NMR (100 MHz, CDCl₃): δ 55.31, 114.29, 126.32, 126.76, 127.26, 127.86, 128.33, 128.77, 130.22, 137.34, 159.40.

Results and Discussion:-

Metallodendrimer (**3**) was synthesized by the reaction of 2,4,6-Triaminopyrimidine **1**(1.59 mmol) with 4-methyl benzoyl chloride **2** (9.54 mmol) in the presence of $(Ph_3P)_2PdCl_2$ (10 mol%) in anhydrous DMF at room temperature to 70 °C for 6 h under a nitrogen atmosphere (Scheme 1). The progress of reaction was monitored by thin layer chromatography (TLC) and after complete conversion of the reaction, purification of the solid reaction mixture by recrystallization gave the dendrimerized product **3** in 90% yield (Table 1, entry 1). PdCl₂ was also effective and provided **3** in 60% (entry 2). Since $(Ph_3P)_2PdCl_2$ was given more yield than PdCl₂, we selected $(Ph_3P)_2PdCl_2$ for the later optimization. The use of tetrahydrofuran as the solvent caused in low yields of **3**, because of the poor solubility of **3** (entry 3). DMSO also good solvent and gave **3** in 85% (entry 4). Increasing the amount of $(Ph_3P)_2PdCl_2$ from 10 to 20 mol% did not progress the final yield of **3**, the yield reduced due to the creation of a complex as a byproduct instead of the desired product (entry 5). The product was found to be soluble in all common organic solvents, and was characterized by IR, ¹H NMR, ¹³C NMR, and mass spectrometry.



Scheme 1

Entry	1	2	Pd complex	Solvent	Time	4
	(mmol)	(mmol)	(mol%)	(mL)	(h)	(%)
1	1.59	9.54	$(Ph_{3}P)_{2}PdCl_{2}$ (10)	DMF (10)	6	90
2	1.59	9.54	PdCl ₂ (10)	DMF (10)	6	60
3	1.59	9.54	$(Ph_{3}P)_{2}PdCl_{2}$ (10)	THF (10)	6	55
4	1.59	9.54	$(Ph_{3}P)_{2}PdCl_{2}$ (10)	DMSO (10)	6	85
5	1.59	9.54	$(Ph_3P)_2PdCl_2 (20)$	DMSO (10)	6	70

Table 1:-Optimization for Preparation of Metallodendrimer 3

The assignments of IR spectral bands most useful in establishing the structural identity of metal complexes. The strong IR peak of **3** confirmed the presence of required groups of the compound. The appearance of the signal in the range of 3000-3100 cm⁻¹ and 1680-1760 cm⁻¹ represented the C-H, C=O group respectively whereas a strong absorption band at 1580-1620 cm⁻¹ displayed C=N. The peak at 1300-1360, and 1250-1335 cm⁻¹ confirmed the presence of C=C and C-N group respectively. C-Cl stretching absorption was observed at 761.8 cm⁻¹. Here it's far remarkable that there's no band for N-H in the place approximately 3400–3250 cm-1 which turned into indicated that 1° amino group of triaminodiazine is transformed into 3° amido group. In ¹H NMR and ¹³C NMR spectra confirmed the preferred compound 3. Because of the formation of Pd-O coordinated bond, small adjustments within the aromatic area in comparison to starting materials indicated that metallic complexation has been achieved. There's no ¹H NMR peak for NH or NH₂ group, which confirmed the shape of compound **3**. The self-assembly procedure of the compound **3** was investigated with Pd (II) as the central metal ions, and this led to a well-designated four coordinated complex that was confirmed through MALDI-TOF MS (Figures S 1- S 6 in the Supporting Information).

The images of the compound (3) were taken in a Scanning Electron Microscope (SEM) at an accelerating voltage of 10 KV with magnifications ranging from 100 μ m-500 nm.SEM images of the compound 3 revealed that the formation of high component ratio randomly disbursed, entangled nanofibers. The length of the fibers is numerous μ M. Coordination between the ligand and Pd (II) fashioned "branches of a tree without leaves and cylindrical fiber-like shape for compound 3 (Fig 1). Every chain stacked with neighboring chain by way of π - π stacking interaction and shaped fibril morphology. The fibers are stabilized with the aid of π -stacking of the aromatic core of the ligands.



Figure 1:-SEM images of the compound 3



Figure 2:-TG and DSC curves of the compound 3

Metal detection or analysis of metallodendrimer has been accomplished through employing the energy Dispersive X-ray (EDX) method. From EDX evaluation, the existence of Palladium turned into properly detected and it was 4.10% of weight and 0.56% of atomic of the compound and chlorine was 0.82% of weight and 0.33% of atomic of the compound and chlorine was present as palladium chloride in our desired synthesized compound and the reaction was effective for the preparation of the required metallodendrimer **3**.

The thermal properties of the metallodendrimers, **3** was studied by TG and DSC at temperatures of 26 °C to 600°C under a nitrogen atmosphere (**figure 2**). The content of a particular component of metallodendrimer changes with its composition and structure and determined on the basis of the weight reduction of these components in the thermogravimetric graph. It was found from TG curve that actual weight reduction of the compound **3** from 185°C to 230 °C. The thermogram of TG for compound **3** showed two different stages of decomposition at 185°C to 230 °C, and the DSC values of the compound were nearly the same as that of TG values of the compound. In the DSC curve of **3** display the sharp endothermic curve above 185 °C representing the melting points. The primary decomposition stage confirmed 86.99% weight loss of compound **3**.

We have reported new homogeneous palladium containing metallodendrimer (3) based on diazine catalyst which is an air-stable and very much effective catalyst for the Heck, Sonoghasira coupling reactions. In order to evaluate the activities of our catalytic system, the reaction between iodobenzene and phenylacetylene was initially selected for the Sonoghasira coupling reaction in the presence of a catalytic amount of the Pd-metallodendrimer 3 as a homogeneous catalyst (**Scheme 2, Table 2**). The catalytic systems revealed different reactivity depending not only on the palladium precursor but also on the nature of the base and the solvent and temperature.





 Table 2:-Optimization of the Pd-metallodendrimer 3 catalyzed Sonogashira reaction between 4-iodophenol and phenylacetylene

Entry	Base	solvent	Time	Co-Catalyst CuI mol%	Catalyst (3) mol%	Yield%
1	KO ^t Bu	CH ₃ CN	3	-	1.0	63
2	Na ₂ CO ₃	CH ₃ CN	3	-	1.5	70

3	K ₂ CO ₃	DMF	3	-	1.0	75
4	Et ₃ N	DMF	2	1.0	1.5	90
5	K ₂ CO ₃	CH ₃ OH	24	2.0	-	-

t-BuOK, Na₂CO₃, and K₂CO₃ with CH₃CN or DMF as the solvent were appropriate bases to complete the Sonogashira coupling without using CuI at 70 °C for 3h with a yield higher than 60% (Table 2, entries 1–3). Copper salts are used as co-catalysts within the Sonogashira reaction, even though it makes the Sonogashira method air sensitive. Notwithstanding this drawback, copper salts in the presence of a base have been used notably for the formation of Cu-alkynyl species that transmetallate to palladium within the catalytic cycle. Due to investigate the effect of CuI as a catalyst, a blank experiment was performed in the absence of a palladium-metallodendrimer 3 catalyst revealed that no reaction happened even within the presence of CuI (2 mol%) at 24 hour (Table 2, entry 5). In the presence of Et₃N, DMF, Pd-metallodendrimer 3 (1.5 mol%) as well as CuI (1.0 mol%), the reaction was completed within two hours without any deleterious effects at the conversions with 90% yield (Table 2, entry 4). Therefore, the optimized reaction condition was found with 90% yield when 1.5 mol% of Pdmetallodendrimer 3 as a catalyst, 1.0 mol% CuI as a co-catalyst, Et₃N, and DMF were used under the nitrogen atmosphere at 70 °C at 2 hour (Table 2, Entry 4). After optimization, we achieved the catalytic activities with more electron-donating or greater sterically hindered aryl halide substrates. Good to remarkable conversions were acquired with the greater electron-donating or extra sterically hindered methyl and methoxy-substituted aryl halide substrates under the chosen reaction catalyzed by compound 3 after 2h (Scheme 3, Table 3, Entries 1-6)



 Table 3:-Sonogashira coupling reaction of different aryl chlorides with phenylacetylene catalyzed by Pdmetallodendrimer 3.

Entry	R	Х	product	Yield%
1	4, OH	4, I	14	90
2	5, OH	5, Br	14	80
3	6, CH ₃	6, I	15	94
4	7, CH ₃	7, Br	15	81
5	8, OCH ₃	8, I	16	95
6	9, OCH ₃	9, Br	16	80

Reaction conditions:

Aryl halide (1mmol), phenylacetylene (1.2 mmol), catalyst (1.5 mol%), base (1.2 mmol), solvent (5 mL), 70 °C, 2h, under nitrogen atmosphere, Yield% was calculated based on aryl halide.

Similarly, due to optimization the Heck reaction conditions, a series of reactions under various combinations of bases, solvents, and temperatures, using Pd-metallodendrimer 3 as a catalyst, was pursued. Iodobenzene and styrene were selected as the typical substrates in this coupling reaction and the outcomes have been presented in Scheme 4 (Table 4).





Entry	Time (h)	Base	Temp (°c)	solvent	Catalyst, 3	Yield (%)
					(mol%)	
1	24	NaOH	RT	CH ₃ CN	1.5	-
2	24	Na ₂ CO ₃	RT	DMSO	2.0	-
3	20	Et ₃ N	60	DMF	2.0	50
4	24	K_2CO_3	85	CH ₃ OH	1.5	60
5	26	KO ^t Bu	85	CH ₃ C ₆ H ₅	1.5	70
6	24	K_2CO_3	85	DMF	1.5	75
7	24	Et ₃ N	85	DMF	1.5	90

Reaction conditions: Iodobenzene (1 mmol), styrene (1.2 mmol), base (1.2 mmol), 24 hour, Temp. 85 °C, Yields% was calculated on the basis of iodobenzene.

The coupled product was not found, when the coupling reaction was started with using 1.5 mol % Pdmetallodendrimer 3 as a catalyst, with styrene (1.2 mmol), and Iodobenzene (1 mmol) in CH₃CN or DMSO (5 mL), and at room temperature in the presence of NaOH or Na₂CO₃ (1.2 equivalent) at 24 h (table 4, entries 1-2). Interestingly, the reaction confirmed the progress of 50% yield with 2 mol% of compound 3 in the presence of Et₃N and DMF at 60 °C at 20 h (**Table 4, entry 3**).Moreover, using other bases including K₂CO3, KO^tBu and in the presence of the solvents, methanol, toluene or DMF at 85 ⁰C, the coupling products were found above 60% yield (table 4, entries 4-6). The best result was found when 1.5 mol% of the catalytic system (3) and Et₃N, as a base, and solvent DMF were used under the nitrogen atmosphere at 85 ⁰C at 24 h for Heck coupling reaction (**Table 4, entry** 7).

Table 5:-Heck coupling reaction of different aryl chlorides with different olefins catalyzed by Pd-metallodendrimer

 3.

Entry	Aryl halides	Olefins	products	Yield%
1	17	20	22	90
2	18	CO ₂ Me 21	CO ₂ Me	95
3	H ₃ CO—Br 19	CO ₂ Me	H ₃ CO 24	92

Yield% was calculated based on aryl halide.

A wide variety of olefins and diversely substituted aryl halides were selected for cross-coupling to produce the corresponding 1, 2-disubstituted olefins. The results have been summarized in table 5. Though aryl bromides and aryl iodides performed nicely (**Table 5, entries 1-3**) under these optimized Heck reaction conditions. However, while compared to the iodo analogues with bromo analogues, a reduced reactivity was discovered in the case of the corresponding bromo derivatives and was found less yield % of the product.

Above all coupling products for Sonogasira and Heck reaction were analyzed by spectroscopic methods and compared with authentic spectra. (Figures S 07-S 12 and S 13-S 21 in the supporting information)

Conclusion:-

In summary, A novel palladium containing metallodendrimer 3 was prepared by the coordination reaction of 2,4,6-triaminopyrimidine (1) with 4-methyl benzoyl chloride (2). The complexation was clearly observed in ¹H NMR, ¹³C NMR, and mass spectra. SEM images of 3 revealed branches of the tree without leafs or cylindrical fiber. Thermal stability of the metallodendrimer 3 was determined by TG and DSC analysis which showed good thermal stability of the compound and can be stored in the white solid crystalline state for a long time at ambient temperature without decomposition. The homogeneous catalyst system showed several advantages including low catalyst loading, substrate tolerance, very good yields, green solvents, short reaction times and very simple procedure for synthesizing Heck and Sonogashira coupling reaction products that are biologically important in the various field. These outcomes signify a noteworthy development in the field of C-C bond formation reactions.

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Conflicts of Interest

The authors declare no conflicts of interest

Graphical abstract



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