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Synthesis and Characterization of New Sandwiched and multi Decker Palladium Organometallic Compounds of alkylated S-Indacene

Abstract

A synthesis of mono nuclear bis indacene mono metal compound of type [L-M-L] where (L is 2,6-diethyl-4,8-dimethyl-1,5-dihydro-*s*-indacene, M=Pd. Pd-bis (η^5-2,6-diethyl-4,8-dimethyl-1,5-dihydro-*s*-indaceneide) [Pd (Ic'H)$_2$], and the oligomeric form of this compound is successfully prepared. The prepared compound is of the type [L-M-L-M-L-M-L] where M= Pd and L =-2,6-diethyl-4,8-dimethyl-1,5-dihydro-*s*-indaceneide)}] [Ic'Pd(μ-Ic') Pd (μ-Ic')PdIc'] the reaction yields a almost quantitative yield. The synthesized compounds were characterized by NMR (^{1}H and ^{13}C), and elemental analysis. The spectroscopic data reveals the formation Multidecker compound. This oligomer is further subjected to catalytic property study

Keywords: palladium organometallics, s-indacene, multidecker, sandwich**.**

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1. Introduction

The organometallic chemistry of palladium is one of the most widespread and different fields of transition metal organometallic chemistry [1-6]. Palladium catalysts help in the transformations that cannot be readily achieved using classical techniques. The importance of the palladium is that most of the organic reactions which use palladium compounds involve the inter-conversion of palladium (II) and palladium (0) that is between the d^8 and d^{10} electronic states. This occurs as the reaction order usually involves oxidative addition to, or reductive elimination from. [7]. the current race in the research is to increases the efficiency of the yield by using the catalysts. These organo palladium compounds are very important in synthetic chemistry, for example the oxidative coupling or cyclization [8-12], carbon-carbon bond formation, the Suzuki coupling [13-15] The Negishi reaction is the Pd-catalyzed cross-coupling [16-18].Coupling between alkyl zinc reagent and 2-iodoimidazole also illustrates that primary aliphatic alkyl groups can be effectively cross-coupled using palladium catalyst. The palladium catalysed carbon-carbon bond formation in the literature also reported [19].

The fused ring molecules such as s-indacene, shows drastic efficiency for promoting the interactions between different redox centers because of its unique nature of pi extend conjugation and delocalization [24-25]. The palladium organometallic complexes derived from s-indacene is expected to exhibit more efficient catalytic activity due to ''cooperative effect'' between the s-indacene and

palladium. In order to increase the efficiencyfurther we planned to construct the oligomeric form of the $[L\text{-}M\text{-}L]_3$ type with M as a palladium.

However main difficulty of the preparation of the oligomeric form of this organometallic compounds is that the decrease in the solubility, because the increase in the ligand oligomeric units [22], it has been reported that the presence of alkyl groups in spacer ligand will increase the solubility of the compounds [23] therefore in this part of our research we are preparing the new organometallic compounds derived from the 2, 6-diethyl-4, 8-dimethyl-1, 5-dihydro-*s*-indacene with the metal center Palladium. Preparation of palladium bridged organometallic compounds such as Pd-bis (η^5-2,6-diethyl-4,8-dimethyl-1,5-dihydro-*s*-indaceneide) $[Pd(Ic'H)_2]$ and [Pd-bis{Ic'Pd-(μ:η^5:η^5-2,6-diethyl-4,8-dimethyl-1,5-dihydro-*s*-indaceneide)}] [Ic'Pd(μ-Ic')Pd(μ-Ic')PdIc'],the synthesis of the complexes is for further study to determine the what extent electron withdrawing and or electron withdrawing and effect on catalytic activity or catalytic properties.

2. Methods and materials

All reagents were Aldrich products, solvents are dried by the method prescribed in the book authored by purine [26]. Nuclear Magnetic Resonance (NMR) spectra of the ligand were taken in the deuterated chloroform deuterated DMSO, and deuterated toluene (C_7D_8), Nuclear Magnetic Resonance (NMR) the NMR samples of the organometallic compounds were prepared inside a dry chamber, and the tubes were sealed with septa. The deuterated solvents used were pre-dried using the usual techniques for this purpose. The ^1H and ^{13}C NMR spectra were recorded on a Bruker Advanced 400 spectrometer.

The ligand, 2,6-diethyl-1,5-dihydro-4,8-dimethyl-s-indacene was synthesized by employing the 8 reported method by Manriquez *et.al* [**27**] the synthetic route is shown in scheme 1.

Scheme 1

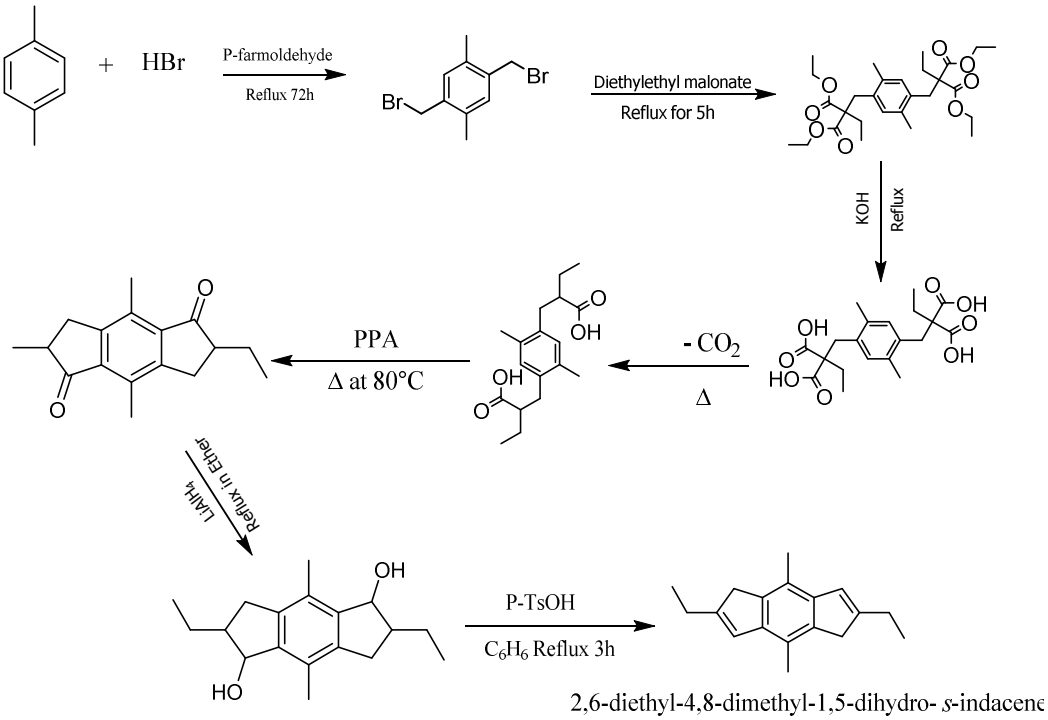

Figure 1: Synthetic route of 2,6-diethyl-4,8-dimethyl-1,5-dihydro-s-indacene.

2.2 Synthesis of organometallic compounds

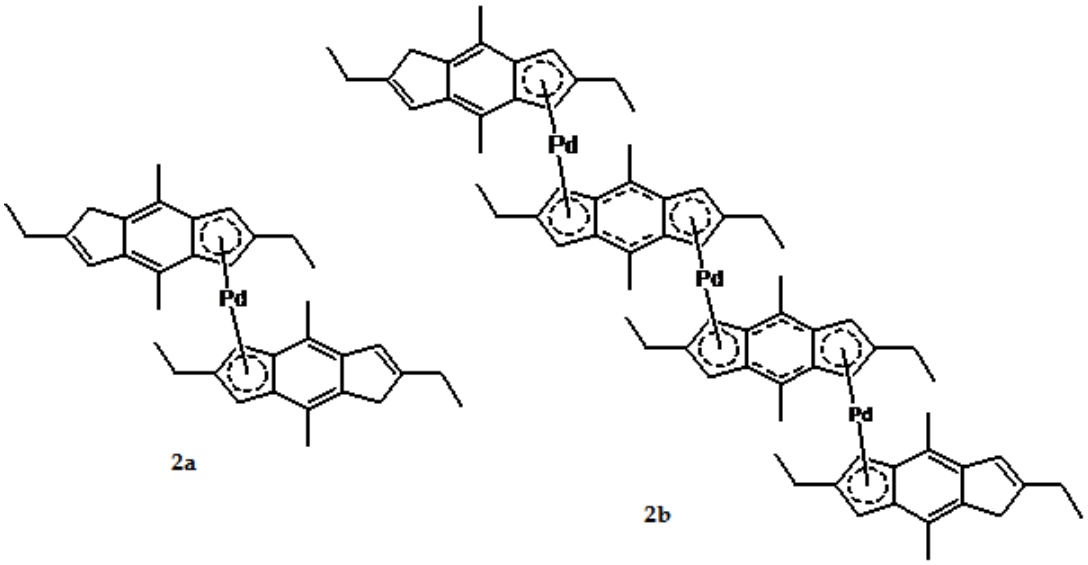

Figure 2: Compound 2a Pd-bis(η^5-2,6-diethyl-4,8-dimethyl-1,5-dihydro-*s*-indaceneide) [Pd(Ic′H)$_2$], and 2b[Pd-bis{Ic′Pd-(μ:η^5:η^5-2,6-diethyl-4,8-dimethyl-1,5-dihydro-*s*-indaceneide)}] [Ic′Pd(μ-Ic′)Pd(μ-Ic′)PdIc′]

2.2.1Synthesis of organometallic compound 2a, L-Pd-L type (L=2,6-diethyl-4,8-dimethyl-1,5-dihydro-*s*-indacene M=Pd)

A n-BuLi solution (2M in hexane, 1.0496 mL, 2.097 mmol) was slowly added to a 2,6-diethyl-4,8-dimethyl-1,5-dihydro-*s*-indacene solution (0.50 g, 2.097 mmol) in 20 mL of THF at -18^{0}C. The mixture was stirred for 1 h at room temperature, obtaining the respective monolithiated ligand. The resulting solution was cooled down to -18^{0}C and a palladium acetate solution (0.2354g, 1.0577 mmol) in 30 mL of THF was added dropwise and stirred for 1 h. The mixture was stirred for 2 h at room temperature prior to remove the solvent under reduced pressure; the remaining solid was washed with toluene and filtered off to remove the insoluble Lithium acetate salt. Black solid unstable to air (0.31 g, 0.65 mmol) was obtained, with a 68% yield. Anal. Calc. for $C_{36}H_{40}Pd$: C, 74.39; H, 6.93 %. Found: C, 80.65; H, 7.62%.^{1}H-NMR (400 MHz, DMSO-d6): δ 0.95 (t, J = Hz, 12H), 2.44 (s, 12H), 1.36 (q, J = Hz, 8H), 3.42 (s, 4H), 5.50 (s, 4H), 6.52 (s, 2H), .

2.2.2 Synthesis of organometallic compound 2b, L_4-Pd_3 type. (L=2,6-diethyl-4,8-dimethyl-1,5-dihydro-*s*-indacene, M=Pd)

In 100ml Schlenk flask dissolved 0.61g of 2a (1.048 mmol) in 20 mL of THF cooled to -18^{0}C added 0.5242ml solution of n-BuLi (2M in hexane 0.0671g 1.048M) was added slowly with the help of cannula, stirred the solution 1 hour at room temperature. Cool the monolithiated ligand to -18^{0}C and added slowly a solution of palladium acetate 0.1177g (0.524M) removed the cooling bath after 1 hour and the solution stirred for 2 hours at room temperature. The solvent is removed under vacuum added 20ml of toluene and filtered to remove the lithium acetate. The black solid unstable to air was obtained with a yield 60%Elemental Anal. Calc. for$C_{72}H_{82}Pd_3$: C, 68.27; H, 6.52. Found: C,68.20; H, 6.47%.

^{1}H-NMR(400 MHz, DMSO-d6): δ 0.27 (t, J = Hz, 12H), 0.98(t-12H),2.54 (s, 24H), 1.65 (q, J = Hz, 8H), 1.78 (q, J = Hz, 8H), 5.20 (s, 12H), 6.60 (s, 2H), 3.43 (s, 4H), 0.98 (t, J = Hz, 12H), .

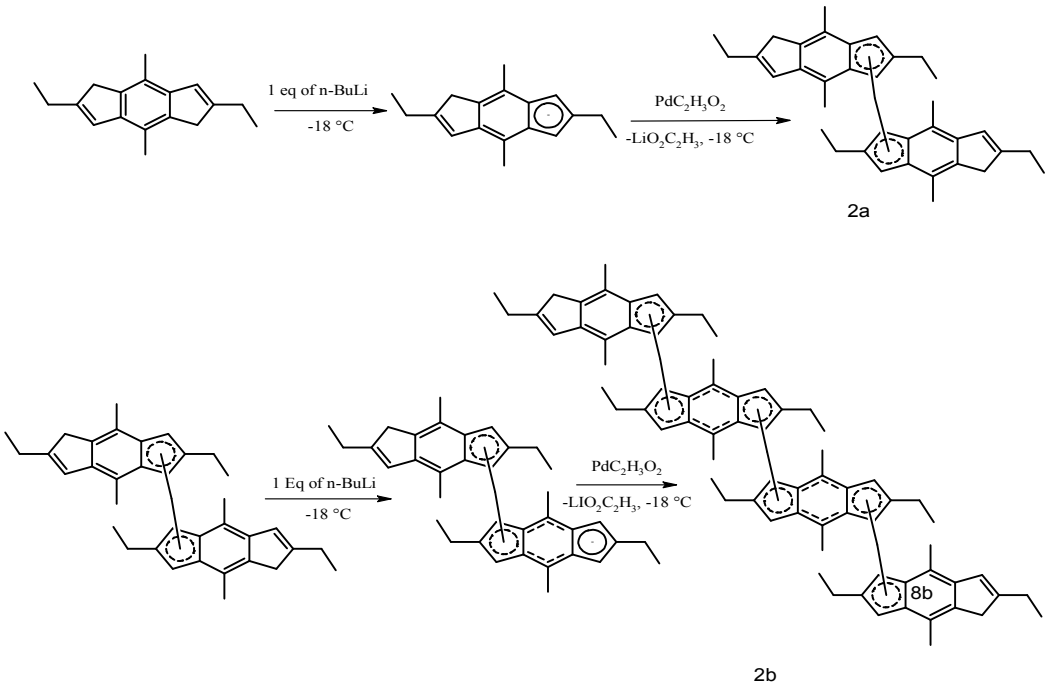

Figure 3: Reaction path way of the preparation of organometallic compounds by a salt elimination method.

3. Results and discussion

The synthesis of the ligand was achieved by the method described in the literature [27] and the organometallic compounds are prepared easily by methods described in the literature [28-31], these organometallic compounds are synthesized step by step, firstly prepared the palladium mono nuclear compound followed by the reaction with 2,6-diethyl-4,8-dimethyl-1,5-dihydro-*s*-indacene with one equivalent mole of the base n-BuLi produces corresponding mononuclear anion by abstracting a proton from the more acidic proton of the ligand that is in 3 or 7 position, to this mono lithiated salt, the palladium acetate in THF was added slowly at -18^{o}C. Then the compound **2a** is produced in good yield about 80%. Further, the **2a** is dissolved in the minimum quantity of the solvent THF and cooled this to -18^{o}C and add 1 equivalent mole of n-BuLi give the monolithiated salt of **2a** stirred the reaction mixture for 1hour at room temperature, and simultaneously dissolve the palladium acetate in an another flask. Again cool the monolithiated salt of Pd-bis(η^5-2,6-diethyl-4,8-dimethyl-1,5-dihydro-*s*-indaceneide) [Pd(Ic'H)$_2$] to -18^{o}C and transferred the palladium acetate solution. after complete addition the reaction is stirred additional 2h at room temperature. The solid is dissolved in pentane and filtered to remove un dissolved impurity and lithium acetate, the pentane is evaporated under vacuum the black solid is obtained as **2b**.the the synthesis of this type of the analog has been reported in the previous literature with 2,4,6,8-tetramethyl-1,5-dihydro-s-indacene,i.e. at position of 2,6 with a methyl group with iron[32],.These compounds also show the low solubility in the tetrahydrofuran,dichloromethane , chloroform, and shows the moderate solubility in the toluene and benzene. We have taken the NMR spectra of these compounds in the toluene. these compounds are highly unstable to air and moisture, because it does not obey the 18e rule, these compounds are 22 electron system, the 12e from the ligand and palladium donates 10e so the sum of the electrons are 22, more ever the polymeric systems of this compound also 22 electron system while the iron analogues are 18e system and these type of compounds with iron are stable in air and moisture for some time. The compound **2a** is achieved by treating the ligand with a base n-BuLi. One equivalent mole gives the mono lithiated salt of the ligand, then, after purification of the compound **2a** this will take as a starting material for the compound **8b** NMR spectra obtained for **2b** show the shifts in the peaks for

ethyl groups attached at 2, 6 position, clearly reveals that then formation of tetra Decker palladium complex (**2b**) the proton NMR of compound **2a** and **2b** is shown in table 1.

Table 1: The above table shows the HNMR spectra of the sandwich and multi-decker organometallic compound 2a and 2b.

^{1}HNMR	**2a**	**2b**
$C_{(1,3,5,7)}$-H	5.50	5.20
$C_{(4,8)}$-H	2.34,2.42,2.56	2.41,2.56,2.66
$C_{(2,6)}$-H (CH_2)	1.36	1.65,1.78
$C_{(2,6)}$-H (CH_3)	0.29, 0.95,	0.27,0.98
$C_{(5,5')}$-H	3.42	3.43
$C_{(7,7')}$-H	6.52	6.6

The major peak shifts were observed for ethyl groups. The ethyl group present 2a shows two peaks for CH_2 and CH_3 where as in **2b** there are four peaks for CH_2 and CH_3 because its experience different chemical environment. The ethyl groups experience the different magnetic field because of the nature of the molecule. This show the complex confirmation of the multi-decker complex.

4. Conclusion

We have successfully synthesized and characterized the sandwich and tetra decker decker organometallic compounds of the palladium by spectroscopic techniques. The synthesised compounds are considered for further study of its catalytic and electrochemical behaviour

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