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Synthesis and Characterization of Sandwiched and Multidecker Iron Organometallic Compounds of 2, 6-diethyl-4, 8-dimethyl-1, 5-dihydro-*s*-Indacene

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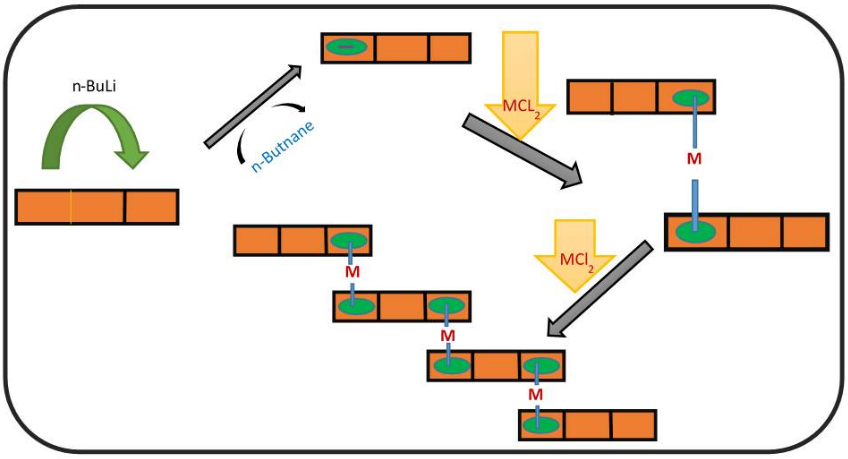
ABSTRACT

*Synthesis and characterization sandwich and multidecker iron organometallic complexes are achieved by employing the partially alkylated s-indacene, the synthesis of new organometallics are based on 2, 6-diethyl-4, 8-dimethyl-1, 5-dihydro-s-indacene**(Ic'H_2)**, the synthesis of multidecker organometallic compounds of type L_4M_3 where L refers to the partially alkylated ligand and M to the transition metal. The compound L_4M_3 was obtained in a good yield. All complexes reported were characterized by means of ^1H, ^{13}C NMR, elemental analysis,*

Graphical Abstract



Highlights:

- Multideck organometallic synthesis was carried out.
- Synthesized organometallic complexes were characterized by spectroscopic techniques.
- Synthesized complex may have the applicability in the field of magnetic materials and or conductivity applications.

Keywords: Ethyl-indacene, Organometallics, Multidecker complex's.

INTRODUCTION

Since ferrocene was first obtained as the product of attempts to synthesize Fulvalene by the coupling of cyclopentadienylmagnesium bromide over iron (III) chloride, [1] a great deal of research effort has been expended on the study of bis (η5-cyclopentadienyl)- metal complexes. One of the rich areas of metallocene study has been that of linked metallocenes; Organic modifications to cyclopentadienyl-type ligands and to metallocenes themselves have permitted the construction of a range of molecules comprising more than one metallocene unit.

Much of the interest in these species has been concerned with the nature of interactions between metal centres. A number of potential applications for metallocene systems with intermetallic interactions may be envisaged. For example, doping of appropriately linked metallocene polymers may lead to interesting low-dimensional conductors. In a partially oxidized poly (ferrocenylene) one would expect, by analogy, with various mono oxidized biferrocenes, distinct Fe (II) and Fe (III) sites between which electron transfers can take place leading to semi conductivity through a hopping mechanism. Indeed several studies have focused on the oxide cation products of poly (ferrocenylene). [2, 3] Hypothetical polymers in which fused-ring ligands alternate with metal atoms have been described by Burdett 5 (with the ligand being naphthalene) and by Manrıquez and Roman [6] (pentalene, *s*-indacene) as shown in figure 1. Extrapolating from the properties of small molecule analogues (*vide infra*), such polymers should give access to much more strongly delocalized conductors than poly (ferrocenylene). However, it was experimentally not achieved till today.

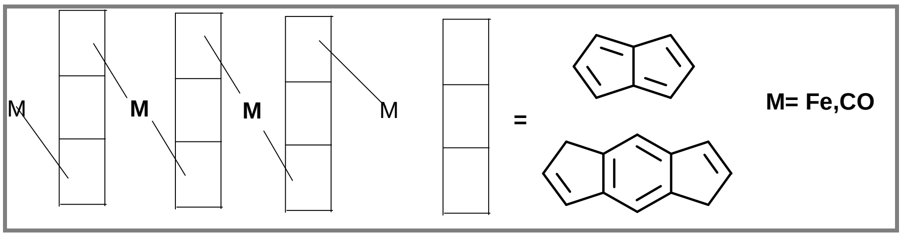


Figure 1. Hypothetical polymer based on pentalene or s-indacene system metallocene polymers.

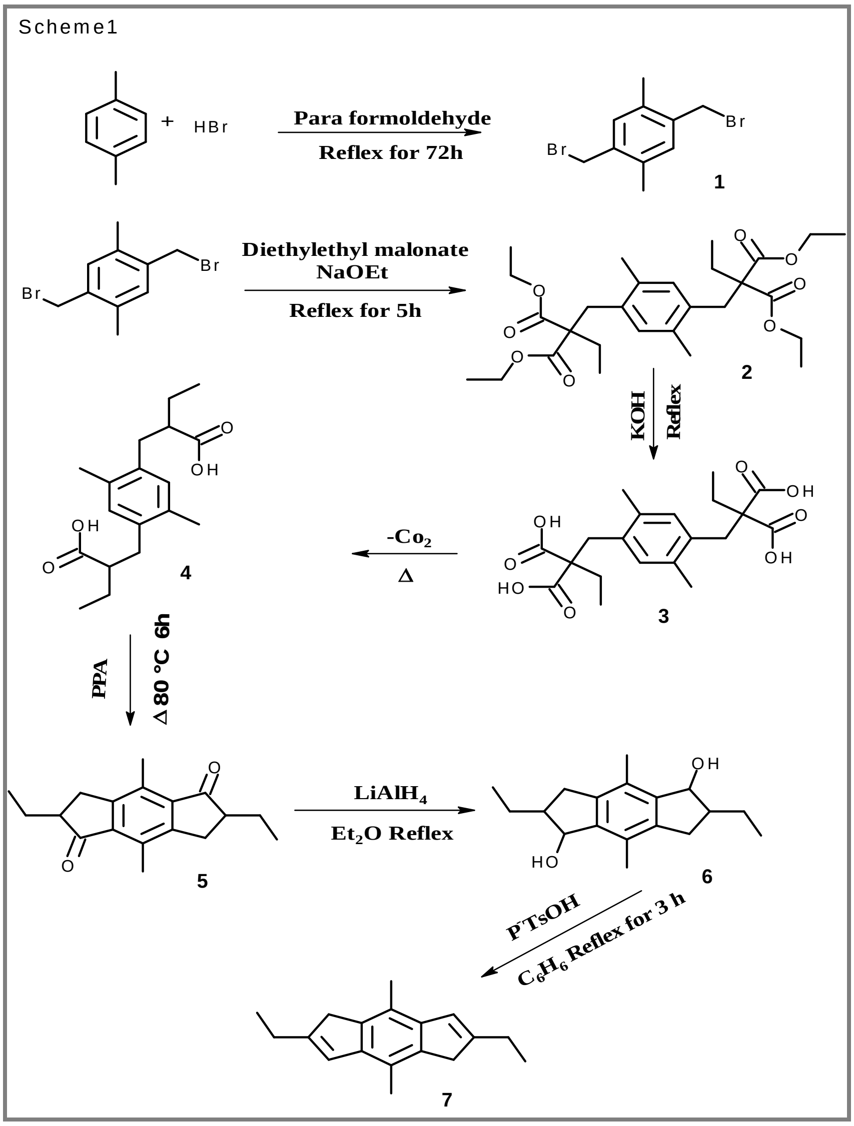
There are examples of linked metallocenes with significant anti ferromagnetic interactions between metal centres. [6] appropriate design of the linking groups to maximize the super exchange, combined with the use of two alternating metals with different spins, could lead to a ferrimagnet [7]. Molecular materials which undergo a spin-crossover are another area of current interest where magnetic phenomena can be described. an example of a double-spin crossover has been found in the metallocene-like triple-decker {Cp*CrP5CrCp*}+X- (X = PF6, SbF6) and one can speculate that other examples might be found by extending the chemistry of fused-ring bridged binuclear metallocenes, which have triple-decker-like orbital schemes, to metals other than Fe, Co, and Ni. Several studies have centred on the use of binuclear metallocenes for third-order nonlinear optical properties. Other species for second-order properties could be imagined where the interaction between a metallocene donor and a metallocenium acceptor is important. In this paper, we are reporting one such attempt to synthesize the multi decker organometallic complex derived from partially alkylated s-Indacene system.

MATERIALS AND METHODS

All reagents were Aldrich products, solvents are dried by the method prescribed in the book authored by purine [8, 9] .Nuclear Magnetic Resonance (NMR) spectra of the ligand was 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, the tubes were sealed with septa. The deuterated solvents used were pre-dried using the usual techniques for this purpose. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Advanced

400 spectrometer and these spectra were internally referenced using residual resonances of the nuclei. Infrared Spectroscopy (FT-IR) the samples of the organometallic compounds were prepared inside a dry chamber, using Nujol as a solvent. For the organic compounds KBr disks were used. The FT-IR spectra were recorded using a Parkin Elmer spectrophotometer in the range 250-4000 cm^{-1}. Melting points were measured in the Thiele tube apparatus.

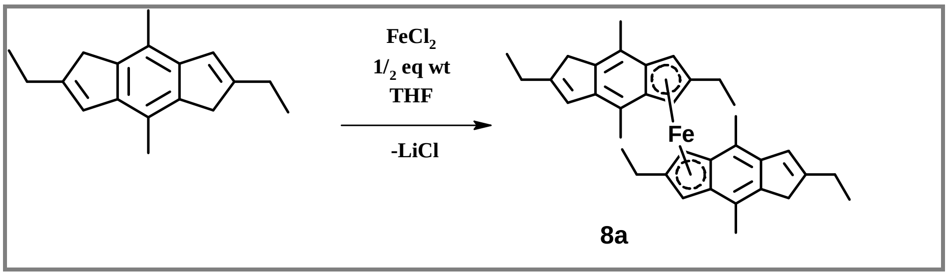
The ligand, 2,6-diethyl-1,5-dihydro-4,8-dimethyl-s-indacene was synthesized by employing the reported method by Manriquez *et.al* [10] the synthetic route is shown in scheme 1.



Scheme 1. synthetic route of 2,6-diethyl-4,8-dimethyl-1,5-dihydro-*s*-indacene.

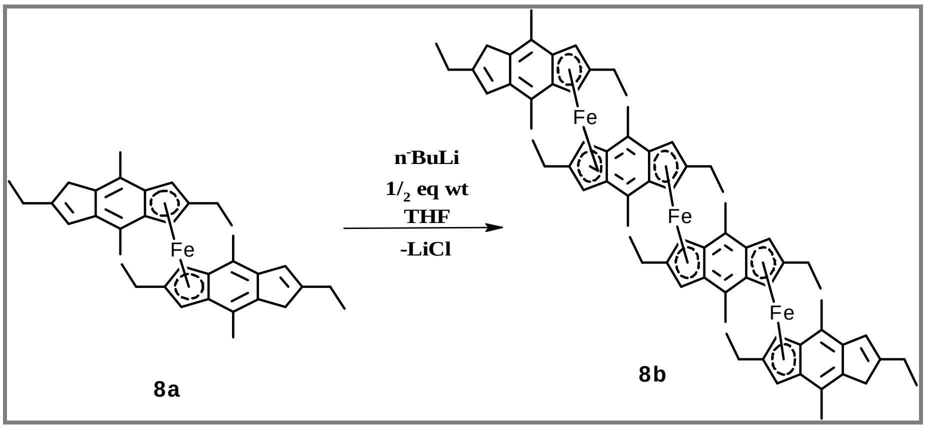
Synthesis of the organometallic compounds

Synthesis of L-Fe-L organometallic compound (L=2,6-diethyl-4,8-dimethyl-1,5-dihydro-*s*-indacenyl): 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°C. The mixture was stirred for 1 h at room temperature, obtaining the respective mono lithiated ligand. The resulting solution was cooled down to -18 °C, and a ferrous chloride anhydrous ($FeCl_2$) solution (0.1332g, 1.0477 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 chloride salt. Dark brown solid unstable to air were obtained, with a 80% yield (Scheme 2). Molecular weight 530.56368g Anal. Calc. for $C_{36}H_{42}Fe$: C, 81.50; H, 7.98. Found: C, 80.65; H, 7.62%. ^{1}H-NMR (C_6D_6,dppm):0.93 (3H, $C_{(6)}$–CH_3),1.88 (3H, $C_{(6)}$–CH_2),1.96 (3H, $C_{(2,4)}$–CH_3), 2.03 (3H, $C_{(4)}$–CH_3), 2.27 (3H, $C_{(8)}$–CH_3), 2.49(2H,$C_{(5)}$H), 4.46 (2H, $C_{(1,3)}$H), , 6.33 (2H, $C_{(7,7)}$H); ^{13}C NMR (C_6D_6, d ppm): 10.8 ($C_{(6)}$–CH_3), 12.0 ($C_{(8)}$–CH_3), 12.3 ($C_{(4)}$–CH_3), 19.0 ($C_{(2)}$–CH_3), 40.3 ($C_{(5)}$), 68.9 ($C_{(1,3)}$), 88.6($C_{(2)}$), 90.5 ($C_{(12)}$), 90.8 ($C_{(11)}$), 116.9 ($C_{(4)}$), 121.2 ($C_{(9)}$), 122.9 ($C_{(7)}$), 139.0 ($C_{(8)}$).



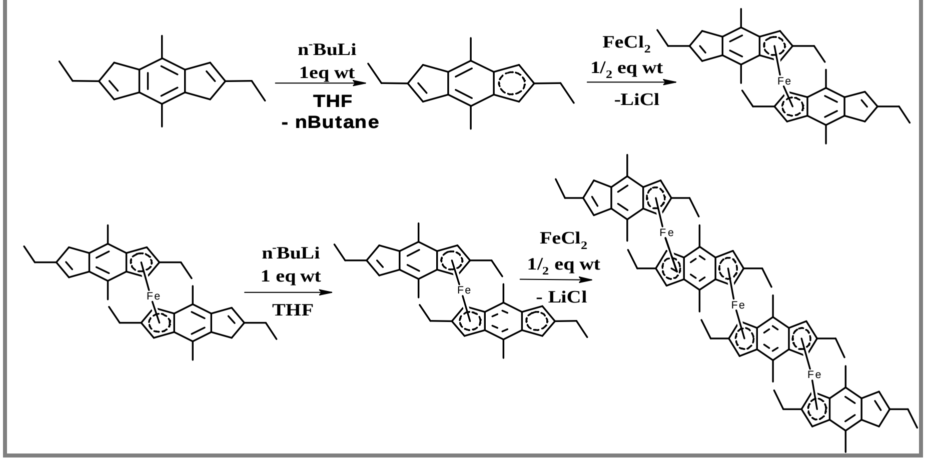
Scheme 2. the preparation of Fe-bis(η^5-2,6-diethyl-4,8-dimethyl-1,5-dihydro-*s*-indaceneide) [Fe(Ic'H)$_2$] organometallic

Synthesis of L_4-Fe_3 organometallic compound (L=2,6-diethyl-4,8-dimethyl-1,5-dihydro-*s*-indacene: In 100 mL Schlenk flask dissolved 0.5g of 8a (0.942 mmol) in 20 mL of THF cooled to-78°C added 0.4715 mL solution n-BuLi (2 M in hexane 0.06036 g 0.942 mmol) was added slowly with the help of cannula, stirred the solution 1 h at room temperature. Cool the monolithiated complex to -18°C and added slowly a solution of ferrous chloride anhydrous ($FeCl_2$) 0.0598 g (0.471 mmol), after complete addition removed the cooling bath, the solution is stirred for 2 h at room temperature. The solvent is removed under vacuum, added 20 mL of toluene and filtered to remove the lithium chloride and the black solid unstable to air yields 60% (Scheme 3 and 4). Molecular weight 1114.95 g, Molecular Formula: $C_{72}H_{82}Fe_3$Anal. Calc. for $C_{72}H_{82}Fe_3$: C, 77.49; H, 7.38. Found: C, 77.51; H, 7.41%. ^{1}HNMR (C_7D_8,dppm):0.287(3H,$C_{(2,6)}CH_3$), 0.957(3H,$C_{(2,6)}CH_3$),1.189(2H,$C_{(2,6)}$ CH_2),1.365 (2H, $C_{(2,6)}$–CH_2), 2.111(3H,$C_{(4,8)}$–CH_3),2.305(H,$C_{(4,8)}$–CH_3),2.421(1H,$C_{(7)}$–CH), 5.2(2H,C $_{(1,3)Fe}$– CH), 6.678 (2H,$C_{(5)}$–CH_2), ^{13}C NMR (C_7D_8, dppm): 12.38(C_6-CH_2-**CH_3**), 13.74($C_{4,8}$-**CH_3**), 23.57(C_6-**CH_2**-CH_3), 28.95($C_{1,5}$),38.73($C_{1,5}$-CH_2-**CH_3**), 86.16(C_2)123.0($C_{3,7}$), 124.0($C_{4,8}$),126.83(C_6), 127.73($C_{9,11}$), 136.41(C_8).



Scheme 3. The synthesis of multidecker organometallic compound.[Fe-bis{Ic*Fe-(μ:η^5:η^5-2,6-diethyl -4,8-dimethyl-1,5-dihydro-*s*-indaceneide)}][Ic*Fe(μ-Ic')Fe(μ-Ic')FeIc*].

Scheme 4:



Scheme 4. The synthetic route of organometallic compounds with intermediates.

RESULTS AND DISCUSSION

The synthetic route to substituted s-indacene, consists of seven reactions which form substituted 1,5-dihydro-s-indacenes, (scheme 1) . This route has quantitatively good yields, making it suitable for the synthesis of these fused ring systems. The first step of this process is the bromomethylation of p-xylene, yielding an almost quantitative yield of the 2,5-bis(bromomethyl)-1,4-dimethylbenzene, which is formed by a mixture of formaldehyde and hydrobromic acid,. The reason why this reaction has such a remarkable yield is due to the initial methyl groups in the xylene starting reagent, which prevents other unwanted secondary reactions, unlike those reported in the past [11-17].

The second step employs an alkylated diethyl malonate reagent, which will determine the desired alkyl group to be placed in positions 2 and 6 in the final product. In this step only primary ethyl substituted malonates may be used, the suitable alkyl diethyl malonate is deprotonated using *in-situ* formed ethoxide for base. The tetra ester product **2** is easily formed by a nucleophilic substitution over the brominated carbon of product **1**. In this case the importance of an inert atmosphere and anhydrous solvent throughout the whole process in order to have good yields. Reaction 4 is a simple ester hydrolysis in aqueous potassium hydroxide, followed by the addition of aqueous hydrochloric acid. This reaction is complete within 48 hours of solvent reflux, even if the tetra ester has dissolved before this time. This is done to ensure that all four ester groups have reacted; following the hydrolysis, a decarboxylation is done in a strict inert atmosphere to prevent air from oxidizing the mixture. The starting solid is heated to 190°C when a strong evolution of carbon dioxide occurs easily together with the formation of a brownish liquid corresponding to the respective diacid. Product **4** dissolves readily in ethyl ether to form a yellow solution. It is imperative to have product **4** completely pure. Trace amounts of water plus small amounts of the precursors decrease the yield of compound **5** drastically.

The formation of the diketone 5 is achieved by the reaction of polyphosphoric acid (PPA) on **4**. By undergoing a region selective symmetrical cyclization to give the corresponding diketone by means of an acyl intermediate, common in many processes involving PPA [18], next steps include the formation of 3,7-diols, 6 , together with the acidic intramolecular dehydration of these diols, which must at all times be degassed and handled with dried solvents in an inert atmosphere. The reduction of the keto groups into alcohols by LiAlH4 proceeds easily and with good yield, forming a total of four chiral carbon atoms which leads to several diastereisomers, making the characterization by means of any spectroscopic method extremely difficult, so for this step FTIR is taken for the conversion of diketone to diol that is disappearing of C=O 1698 cm^{-1} and a peak appears at 3300 that corresponds to OH of the diol 6.

The intramolecular dehydration of the diols proceeds in toluene with *para*-toluene sulphonic acid gives the final title productin this step *para*-toluenesulphonic acid must be completely dry to increase reaction rates.

While the synthesis of organometallic are carried out by salt elimination strategy, in this synthesis avoiding the air and moisture is necessary. Hence the reaction was carried out under nitrogen atmosphere and the used solvents were completely dried. The acidic proton of the ligand in 3 and 7 positions is reacted by simply treating with n-BuLi. This produces the anionic ligand, the mono and di anion can be achieved by reacting 1or 2 equivalent ratio of the base respectively.

The ligand is dissolved in the minimum amount of the THF solvent and the solution is cooled down to -18c and the n-BuLi is added slowly to the cool solution of the ligand , after complete addition removed the cooling bath and starred the solution for 1h at room temperature to complete the reaction this mono anionic ligand again cooled to the -18^{o}C and the solution of anhydrous ferrous chloride dissolved in the THF added with help of cannula after the addition, the cooling bath is removed and starred the solution for 2 h at room temperature form the brown colored solution the solvent is removed under vacuum the dark brown sold will appears then added toluene to dissolve the organometallic compound and filtered to remove the undissolved impurities and LiCl. After evaporation of toluene in rotary evaporator the solid is characterized and then this is taken as a stating material for the preparation of multidecker organometallic compound (8b) for this the same procedure follows as for compound 8a. Mono lithiated of 8a is produced when an equivalent mole of n-BuLi added. Then half equivalent mole of ferrous chloride is added and stirred for 2h and the solvent was vacuum evaporated, the dark brown solid is then dissolved in the toluene filtered to remove the lithium chloride. The toluene is evaporated under vacuum produces the dark brown solid of 8b.

The synthesized ligand and organometallic compounds are characterized by NMR spectroscopy the NMR characterization of the compounds is taken in the pure form. The peak shifting in the proton NMR spectra of the multidecker organometallic compound 8b, the shift in the peaks takes place when the protons environments are different. in the compound 8a there is no peaks splitting become the protons are in the same environment while compound 8b there are different environment i.e. the ethyl groups in the ligand experience the different environment centre 2 s-indacene are same and the first and last indacene ligands different, the first and last ligand have only one side eta bond while in the centre 2 ligands have two pentane rings forms 2 eta bonds so the ethyl substituents experiences different energy.

APPLICATION

The type of organometallic complexes reported here is having the intermetallic interactions. Due to this type of interactions, various applications, like, low dimensional conductors and semiconductors. Appropriate manipulation of spin crossover of this type of material will also lead to the ferrimagnet. This magnetic property may be used in the data storage devises.

CONCLUSION

We have successfully synthesized the oligomer like metallocenes with high delocalized property. This has a several potential application in the area of material synthesis with magnetic and or conducting properties. The spectroscopic data reveals the formation of the complexes. However still we have to address the solubility problem in these types of compounds. Presently we are looking an alternative way for synthesis of such molecule.

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