

## Synthesis and Application of Bis[1,2-(4-aryl-2-alkyl-1H-inden-1-yl)]Ethane as an Efficient Ligand for Preparation of Olefin Polymerization Catalysts

V. Lotfi<sup>\*1</sup>, B. Emamgholi<sup>2</sup>, S. T. Bahrami<sup>3</sup>, E. Poorakbar<sup>4</sup>

<sup>1</sup> Department of Chemistry, Faculty of Sciences, University of Tehran, Tehran, Islamic Republic of Iran

<sup>2</sup> Department of Chemistry, Faculty of Sciences, Imam Khomeini International University, Qazvin, Islamic Republic of Iran

<sup>3</sup> Department of Chemistry, Faculty of Sciences, Islamic Azad University, Qaemshahr Branch, Qaemshahr, Islamic Republic of Iran

<sup>4</sup> Department of Biology, Faculty of Sciences, University of Payame Noor, Tehran, Islamic Republic of Iran

Received: 22 November 2017 / Revised: 1 July 2018 / Accepted: 8 August 2018

### Abstract

In this study, a class of bis-1,2-(4-aryl-2-alkyl-1H-inden-1-yl) ethane was synthesized and characterized by spectroscopic methods such as <sup>1</sup>HNMR, <sup>13</sup>CNMR, melting point and FTIR. bis-1,2-(4-aryl-2-alkyl-1H-inden-1-yl) ethane was synthesized by the reaction of butyllithium, arylindenes and dibromoethane in a facile, one-pot strategy. It's shown that these methods have a wide scope to afford libraries of aryl-substituted indenenes. The prepared compounds was then applied as a ligand for the fabrication of a number of metal complexes which can be used as catalyst for the polymerization of the olefins.

**Keywords:** Organometallic Compound; Metallocene; Bis-arylalkyl Ethane Ligand; Catalysis.

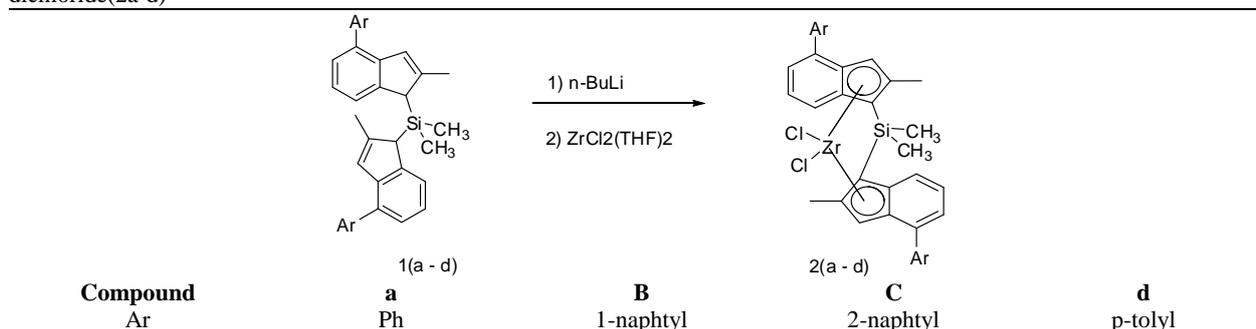
### Introduction

Metallocene family is an important class of organometallic compounds. Metallocenes generally consist of a central metal which is bonded to two cyclopentadienyl anions. [1,2] This class of organometallic compounds have wide applications in several occasions, such as organic catalysis [3-5] super capacitors, [6] batteries, [7] and Ziegler-Natta olefin polymerization catalysis [8]. Based on the importance of metallocenes in several applications specially as catalysts and also in industries, so many researches have been focused on the synthesis of advanced structures from this compounds. Indene is a benzene ring fused to

a five membered ring, and is an appropriate choice to be used as a ligand for metallocenes. Recently significant advances has been observed in R-olefin polymerization catalyst chemistry: particularly the stereochemical control of polypropylene synthesis using metallocene-based catalysts. These compounds having indene systems as subunits are well known as  $\alpha$ -olefin polymerization catalysts [9]. Spaleck, et al described bridged zirconocene catalysts possessing indene systems (Table 1, 2a-d) which yield highly isotactic polypropylene when used with methylaluminumoxane as a cocatalyst [10].

Starting with compound 1 bearing various functional groups on it, showed that the effectiveness of the

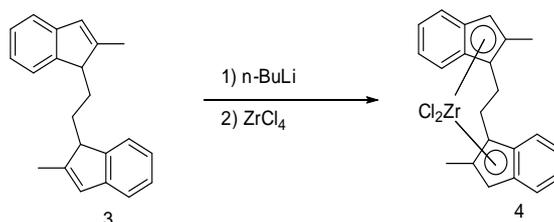
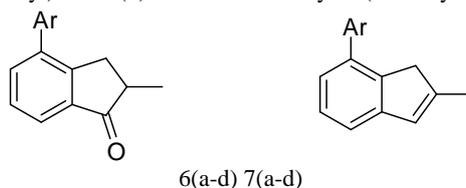
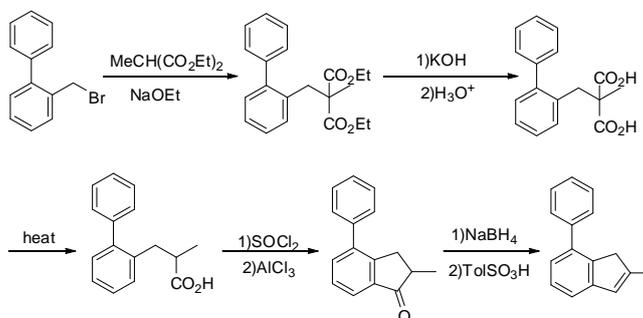
\* Corresponding author: Tel: +982166897089; Fax: +982163340191; Email: v.lotfi.k@gmail.com

**Table 1.** Dimethylbis (2-alkyl-4-arylindenyl)silane(1a-d) and [Dimethylsilanediylbis (2-alkyl-4-arylindenyl)]-zirconium dichloride(2a-d)

ligands strongly depends on the position and electronic effects of the substituents. The activities of the synthesized metallocenes as catalyst is a function of various factors including electronic and steric effect. Extensive studies of the relationship between metallocene structure and activity/stereoselectivity of the respective propylene polymerization catalysts showed that, in the general case, the best results are observed for advanced zirconocenes of structure (2) involving a dimethylsilanediyl-bis(indenyl) chelating

ligand bearing methyl in position 2 and aryl in position 4 of the indenyl fragments [11]. The activity of the catalyst (2a) in polymerization reactions was tested. The results showed that the product contained 775 kg ppm within average molecular weight of 729,000 g/mol polymer and its isotacticity 95/2 with the melting point of 157°C [12,13].

In 2001, Ewen et al suggested a new ligand containing an ethylene bridge located between the two indenyl rings. Catalysts prepared by this ligand family

**Scheme 1.** 1,2-Bis(2-methylindenyl)ethane(3) and rac-Ethanedylbis(2-methylindenyl) zirconium Dichloride(4)**Scheme 2.** 2-methyl-4-aryl-1-indanone(6a-d) and 2-methyl-4-aryl-1H-indene(7a-b)**Scheme 3.** synthesis steps of 2-methyl-7-phenyl-1H-indene.

are shown in Scheme 1. They were used for the polymerization reaction and the product contained 118 kg.ipp/mmol with an average molecular weight of 300,000 g/mol polymer. The product also showed isotacticity 78/5 with the polymer melting point of 150°C [14].

Substituted aryliindanones (6a-d) and aryliindenes (7a-d) are other significant ligands, which are used for the synthesis of active compounds in the preparation of metallocene complexes. In particular, substituted aryliindanones and aryliindenes can be exploited to prepare bridged chiral metallocenes which are of great importance as highly active catalysts in olefin polymerization.

In 1994, Spaleck, et al. disclosed the synthesis of aryliindanones and aryliindenes through the following methods [12].

Industrial application of this ligand leads to challenges for shortening of the synthetic paths as an important parameter from the economical view point. In this research we focus on providing a novel method for the synthesis of bis-1,2-(4-aryl-2-alkyl-1H-inden-1-yl) Ethane as the catalyst ligand. However, Important intermediates such as 2-methyl-4-aryl-1H-indene and 2-methyl-4-aryl-1-indanone that are used for the synthesis of the ligand have successfully been prepared. Hereby we offer a new method for the synthesis of the mentioned ligands. The catalytic activity of the catalyst was investigated in polymerization reactions.

## Materials and Methods

### Solvents and reagents

All chemicals were purchased from Sigma, Fluka, Merck, Aldrich and Yantai Suny Chem. International Co., Ltd. We used commercial solid reagents without further purification. Solvents were distilled and dried prior to use according to standard practices; water was doubly distilled. Liquid reactants were distilled prior to use. before using THF and diglyme, they were dried by refluxing under argon over sodium wire and distilled directly. Column chromatography was performed on silicagel 60 (Merck, grain size 0.063-0.2 mm) and *n*-hexane as eluant. All reactions were carried out under an atmosphere of argon in oven-dried glassware with magnetic stirring.

### Instrumentation

The FT-IR spectra were measured on a Bruker-Tensor 270 spectrophotometer as KBr disks as smears between salt plates. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a Bruker FT-400 MHz spectrometer with CDCl<sub>3</sub> as solvent while chemical shifts are presented as

delta-values expressed in ppm referenced to CHCl<sub>3</sub> residue at 7.25 and 78 ppm, respectively at room temperature. The mass spectra obtained with a GC-Mass Agilent quadrupole mode 5973N instrument, operating at 70 eV. Elemental analyses were carried out with an Elementor Vario EL. III instrument.

### General procedure for the synthesis of alkylferrocene

A solution of acid chloride (63 mmol) in 30 ml dry dichloromethane was added to a suspension of anhydrous aluminium chloride (8.41 g, 63 mmol) in 30 ml dry dichloromethane and then the mixture was stirred at 5 °C for 1h under argon gas. The solution of aluminium chloride, acid chloride complex was added dropwise in 30 min to a solution of ferrocene (11.16 g, 60 mmol) in 100 ml dry dichloromethane at 0 °C. The mixture was heated to room temperature and stirred for 16 h. A solution of NaBH<sub>4</sub> (2.38 g, 63 mmol) in 25 ml diglyme was then added dropwisely to the purple reaction mixture at -5 °C. An orange solution was formed and stirred at 0 °C for 1 h. Then the mixture was hydrolyzed with addition of 20 mL water while maintaining its temperature at less than 10° C. The mixture is allowed to be separated by settling and the organic phase is then withdrawn. The aqueous phase is extracted with 3 times 30 ml of dichloromethane and then all the organic phases are combined. The organic layer was washed with 50 ml of brine and next dichloromethane was distilled under atmospheric pressure. The diglyme and the residual ferrocene are distilled at reduced pressure approximately 20 mm Hg and at a column head temperature of 85°-95° C. Also, the alkylferrocene derivatives were distilled at a more reduced pressure, less than 5 mm Hg.

#### Ethyl ferrocene (**1b**)

From 4.95 g acetylchloride, 11.43 g of light brown liquid was obtained in 89% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): 1.16-1.19 (t, 3H, CH<sub>3</sub>), 2.32-2.37 (q, 2H, FcCH<sub>2</sub>), 3.99-4.16 (m, 9H, Fc).

#### Propyl ferrocene (**1c**)

From 5.83 g propionylchloride, 11.63 g of light brown liquid was obtained in 85% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): 0.93-0.96 (t, 3H, CH<sub>3</sub>), 1.49-1.58 (m, 2H, CH<sub>2</sub>CH<sub>3</sub>), 2.31-2.35 (t, 2H, FcCH<sub>2</sub>), 4.05-4.15 (m, 9H, Fc).

From 10.04 g ferrocene, 17.63 g of orange liquid was obtained in 89% yield. FT-IR (KBr, cm<sup>-1</sup>): 3084 (Cp-H), 2938 (C-H), 1648, 1455 (C=C), 1312 (CH<sub>2</sub>-Cl), 1025 (Cp), 815 (C-Cl), 496 (Cp-Fe); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): 1.62-1.66 (m, 4H, CpCH<sub>2</sub>CH<sub>2</sub>), 1.76-1.82 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>Cl), 2.33-2.37 (t, 4H, Cp-CH<sub>2</sub>), 3.53-3.56 (t, 4H, CH<sub>2</sub>Cl), 3.98 (d, 4H, j=1.4 Hz, CH<sub>2</sub>C<sub>5</sub>H<sub>4</sub>), 4.00 (d, 4H, j=1.4 Hz, CH<sub>2</sub>C<sub>5</sub>H<sub>4</sub>); <sup>13</sup>C NMR

(100 MHz, CDCl<sub>3</sub>, ppm): 27.38 (CpCH<sub>2</sub>CH<sub>2</sub>), 27.61 (CH<sub>2</sub>CH<sub>2</sub>Cl), 31.28 (CpCH<sub>2</sub>), 43.97 (CH<sub>2</sub>Cl), 67.59, 66.83 (Cp), 87.42 (C<sub>1,1'</sub> Cp); m/z (EI): 368 (64.26% [M]<sup>+</sup>), 366 (100% [M]<sup>+</sup>), 91 (14.82% [CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Cl]<sup>+</sup>); Anal. Calc. for: C<sub>18</sub>H<sub>24</sub>Cl<sub>2</sub>Fe (367.141): C, 58.89; H, 6.59; Fe, 15.21. Found: C, 57.12; H, 6.39; Fe, 15.05%.

#### General procedure for Synthesis of 3-(2-halophenyl)-2-methylpropanenitrile (8a-8b)

A solution of *n*-BuLi (36.2 mmol, 14.5 ml) in hexane was added to a solution of *i*-Pr<sub>2</sub>NH (34.5 mmol, 6 ml) in 100 mL of THF at -78°C under Ar atmosphere. After 5 min, a solution of propionitrile (90 mmol, 6.4 ml) in THF was added. The reaction mixture was stirred at -78°C for 1 h, after which a solution of 2-halobenzyl bromide (36 mmol) in 40 mL of THF was added at once and the reaction mixture was stirred with warming to room temperature for about 1.5 h, then diluted with water and extracted with ether. The ethereal extracts were dried with Na<sub>2</sub>SO<sub>4</sub>, the solvent was evaporated, and the residue was separated by column chromatography on silica gel with hexane-ethylacetate (98:2) as eluant.

#### 3-(2-bromophenyl)-2-methylpropanenitrile (8a): Isolated yield 87% (0.49 g, from 0.625 g of 2-bromobenzyl bromide) of

Anal. Calc. for C<sub>17</sub>H<sub>16</sub>O : C, 53.52 ; H, 4.45  
<sup>1</sup>HNMR(CDCl<sub>3</sub>): δ ( ppm) 1.36-1.42 (3H, d, -CH<sub>3</sub>) , 3.02-3.05( 3H, m, -CH<sub>2</sub>- , -CH-CN ) , 7.13-7.58( 4H, m, -Ph ).  
<sup>13</sup>CNMR(CDCl<sub>3</sub>): 16.79 (-CH<sub>3</sub>), 24.94 (-CH-), 39.26 (-CH<sub>2</sub>-), 121.18 (-CN), 128.08, 130.50, 132.04, 135.37, 123.37, 126.76 (-Ph).

#### 3-(2-chlorophenyl)-2-methylpropanenitrile (8b)

General procedure for synthesis of 9a-d:

2.25 g (10 mmol) of 3-(2-bromophenyl)-2-methylpropanenitrile (8), 11 mmol of arylboronic acid and 2.33 g (22 mol) of sodium carbonate were placed in 40 ml of dimethoxyethane and 10 ml of water in the reaction vessel, the mixture was degassed a number of times and saturated with argon. 50 mg (0.2 mmol) of palladium acetate and 0.1 g (0.4 mmol) of triphenylphosphine (TPP) were added and the reaction mixture was stirred for 2 hours at 80° C. After addition of 50 ml of water, the mixture was extracted 3 times with 50 ml of diethyl ether, the ether phase was washed twice with 50 ml of water each time and dried over magnesium sulfate. Removal of the solvent gave product of 9(a-d) [1].

#### Synthesis of 3-([1,1'-biphenyl]-2-yl)-2-methylpropanenitrile (9a): Isolated yield 85% (0.47 g, from 0.56 g of 3-(2-bromophenyl)-2-methylpropanenitrile)

Anal. Calc. for C<sub>17</sub>H<sub>16</sub>O : C, 86.97 ; H, 6.79;  
<sup>1</sup>HNMR(CDCl<sub>3</sub>): δ ( ppm) 1.10-1.12 ( 3H, d, -CH<sub>3</sub> ) 2.51-2.6 ( 1H, m, -CH-CN ) , 2.8-3.02 (2H, m, -CH<sub>2</sub>- ) , 7.25-7.43 ( 9H, m, Arom. H ); <sup>13</sup>CNMR(CDCl<sub>3</sub>): 16.82 (-CH<sub>3</sub>), 25.56 (-CH-), 36.20 (-CH<sub>2</sub>-), 121.59 (-CN ), 126.20, 126.28, 126.74, 126.78, 127.40, 128.03, 128.10, 128.90, 128.93, 129.42, 130.53, 131.52, 133.43, 153.07; MS : 221(M)<sup>+</sup>, 167(M -C<sub>3</sub>H<sub>4</sub>N)<sup>+</sup>

#### 2-methyl-3-(2-(naphthalen-1-yl)phenyl)propanenitrile(9b): Isolated yield 89% (0.61 g, from 0.56 g of 3-(2-bromophenyl)-2-methylpropanenitrile)

Anal. Calc. for C<sub>17</sub>H<sub>16</sub>O : C, 88.52 ; H, 6.25;  
<sup>1</sup>HNMR(CDCl<sub>3</sub>): δ ( ppm) 1.01-1.02 ( 3H, d, -CH<sub>3</sub> ) 2.44-2.53 ( 1H, m, -CH-CN ) , 2.67-2.81 (2H, m, -CH<sub>2</sub>- ) , 7.27-7.94 ( 11H, m, Arom. H ); <sup>13</sup>CNMR(CDCl<sub>3</sub>): 16.72(-CH<sub>3</sub>), 25.71(-CH-), 36.66(-CH<sub>2</sub>-), 124.94(-CN), 124.23, 124.61, 124.76, 125.00, 126.09, 126.23, 126.95, 127.01, 127.07, 127.33, 128.12, 128.79, 130.03, 130.14, 134.68, (Arom. C); MS : 271(M)<sup>+</sup>, 217(M -C<sub>3</sub>H<sub>4</sub>N)<sup>+</sup>

#### 2-methyl-3-(2-(naphthalen-2-yl)phenyl)propanenitrile(9c): Isolated yield 86% (0.58 g, from 0.56 g of 3-(2-bromophenyl)-2-methylpropanenitrile)

Anal. Calc. for C<sub>17</sub>H<sub>16</sub>O : C, 88.47 ; H, 6.29;  
<sup>1</sup>HNMR(CDCl<sub>3</sub>): δ ( ppm) 1.07-1.09 ( 3H, d, -CH<sub>3</sub> ) 2.56-2.61 ( 1H, m, -CH-CN ) , 2.93-3.01 (2H, m, -CH<sub>2</sub>- ) , 7.26-7.91 ( 11H, m, Arom. H ); <sup>13</sup>CNMR(CDCl<sub>3</sub>): 16.76(-CH<sub>3</sub>), 25.68(-CH-), 36.27(-CH<sub>2</sub>-), 125.18(-CN), 126.27, 126.28, 126.75, 126.85, 126.88, 126.98, 127.01, 128.94, 129.69, 132.23, 133.125, 137.55, 141.17, (Arom. C); MS : 271(M)<sup>+</sup>, 217(M -C<sub>3</sub>H<sub>4</sub>N)<sup>+</sup>

#### 2-methyl-3-(4'-methyl-[1,1'-biphenyl]-2-yl)propanenitrile(9d): Isolated yield 88% (0.52 g, from 0.56 g of 3-(2-bromophenyl)-2-methylpropanenitrile)

Anal. Calc. for C<sub>17</sub>H<sub>16</sub>O : C, 86.67 ; H, 7.02;  
<sup>1</sup>HNMR(CDCl<sub>3</sub>): δ ( ppm) 1.10-1.11(3H, d, -CH<sub>3</sub>) , 2.41(3H, d, -CH<sub>3</sub>), 2.51-2.59(1H, m, -CH-CN) , 2.83-3.01(2H, m, -CH<sub>2</sub>-) , 7.16-7.33(8H, m, Arom.H); <sup>13</sup>CNMR(CDCl<sub>3</sub>): 16.63(-CH<sub>3</sub>), 20.16(-CH-), 25.48(CH<sub>3</sub>-phenyl), 36.24(-CH<sub>2</sub>-), 121.68(-CN), 124.54, 126.17, 126.55, 127.80, 127.88, 128.10, 128.89, 129.52, 133.51, 135.95, 137.05, 141.128, (Arom. C); MS : 235(M)<sup>+</sup>, 181(M -C<sub>3</sub>H<sub>4</sub>N)<sup>+</sup>

General procedure for synthesis of 6a-d:

The nitrile is heated under reflux conditions with a dilute acid such as dilute hydrochloric acid. giving rise

to the corresponding carboxylic acid amixture of 0.148mol of (9a-d) and 125g of 50%(w/w) sulphuric acid in 250-ml round-bottomed flask under reflux for 3 hours and was allowed to cool. The solution was saturated with ammonium sulphate and extracted with 150ml portions of ether, dry the ethereal extracts was dried with anhydrous sodium sulphate(vogel).

**Method A: Using chlorosulfonic acid.**

To 1 mmol of the carboxylic acid was added 3.0 mL of chlorosulfonic acid. The solution was stirred for 1 h at 0°C. At the end of reaction, the mixture was quenched in 5 mL of ice-cold water and extracted with 2 x 5 mL of dichloromethane. The combined organic layers were washed with 5 mL of NaHCO<sub>3</sub> solution and dried over Na<sub>2</sub>SO<sub>4</sub>. Dichloromethane was removed under reduced pressure to furnish indanones. All analytical data were obtained without any further purification[7].

**Method B: Using thionyl chloride and aluminm trichloride**

A solution of 5.8 g (24.2 mmol) of carboxylic acid in 6 ml (83 mmol) of thionyl chloride was stirred at room temperature for 18 hours. Excess thionyl chloride was distilled off. To remove trace of thionyl chloride, 10ml of dry toluene was added and removed in vacuo three times. The acid chloride was taken up in 15 ml of toluene and added dropwise at 10° C. to a suspension of 4.8 g (36.3 mol) of AlCl<sub>3</sub> in 40 ml of toluene. When the addition was complete, the mixture was refluxed for a further 3 hours. The reaction mixture was poured into 50 g of ice and acidified to pH 1 by means of concentrated aqueous HCl. The organic phase was separated off, the aqueous phase was then extracted three times with 100 ml of Et<sub>2</sub>O in each case. The combined organic phases were washed with saturated aqueous NaHCO<sub>3</sub> solution and saturated aqueous NaCl solution and then dried (MgSO<sub>4</sub>), giving 5.4 g (93%) of 6a, which was reacted further without further purification. [2]

**Method C: Using polyphosphoric acid**

In a 25-ml flask 1g (5mmol) of carboxylic acid and 10g of polyphosphoric acid were added and the resulting mixture was heated in an oil bath to 120-140 ° C. when the contents of the flask initially reached the reaction temperature stirred vigorously to ensure thorough mixing of the reactants. After 2 hours the reaction mixture was allowed to cool and 10 ml of water. Then the organic product was extracted with ether, washed with water and driedover magnesium sulphate(vogel).

**Synthesis of 2-methyl-4-phenyl-1-indanone(6a): Isolated yield 86% (0.48 g, from 0.55 g of 9a) of colorless oil**

Anal. Calc. for C<sub>17</sub>H<sub>16</sub>O: C, 86.55; H, 6.43; <sup>1</sup>HNMR(CDCl<sub>3</sub>): δ (ppm) 1.27-1.32(3H ,d , -CH<sub>3</sub>), 2.64-2.84(2H , m , -CH<sub>2</sub>-), 3.37-3.50 (1H , m , -CH-), 7.27-7.80(8H , m , Arom.H).

**2-methyl-4-(1-naphthyl)-1-indanone(6b): Isolated yield 79% (0.54 g, from 0.68 g of 9b) of colorless oil**

Anal. Calc. for C<sub>17</sub>H<sub>16</sub>O: C, 88.47; H, 6.09; <sup>1</sup>HNMR(CDCl<sub>3</sub>): δ (ppm) 1.22-1.25(3H ,d , -CH<sub>3</sub>), 2.34-2.69(2H , m , -CH<sub>2</sub>-), 2.98-3.12(1H , m , -CH-), 7.26-7.59(10H , m , Arom.H).

**2-methyl-4-(2-naphthyl)-1-indanone(6c): Isolated yield 80% (0.544 g, from 0.68 g of 9c) of colorless oil**

Anal. Calc. for C<sub>17</sub>H<sub>16</sub>O: C, 88.45; H, 6.04; <sup>1</sup>HNMR(CDCl<sub>3</sub>): δ ( ppm) 1.31-1.33(3H ,d , -CH<sub>3</sub>), 2.73-2.83(2H , m , -CH<sub>2</sub>-), 3.44-3.50(1H , m , -CH-), 7.26-7.59(10H , m , Arom.H).

**2-methyl-4-(4-methylphenyl)-1-indanone(6d): Isolated yield 88% (0.52 g, from 0.59 g of 9d) of colorless oil**

Anal. Calc. for C<sub>17</sub>H<sub>16</sub>O: C, 86.46; H, 6.84; <sup>1</sup>HNMR(CDCl<sub>3</sub>): δ ( ppm) 1.30-1.31( 3H, d, -CH<sub>3</sub>), 2.40(3H, s, CH<sub>3</sub>-phenyl), 2.68-2.80(2H, m, -CH<sub>2</sub>-), 3.39-3.45(1H, m, -CH -), 7.16-7.33(7H, m, Arom. H).

*General procedure for synthesis of 7a-d:*

2.3 mmol of arylindanones dissolved in 4.5 ml of THF/MeOH (2:1), and 0.128 g (3.4 mmol) of sodium borohydride added in portions at 0° C with stirring. The reaction mixture was stirred for a further 18 hours and poured into ice, concentrated HCl pH 1 The mixture was extracted several times with Et<sub>2</sub>O. The organic layer was washed with saturated aqueous NaHCO<sub>3</sub> solution and NaCl and then dried over MgSO<sub>4</sub>. The solvent was removed in vacuum, and the crude product, without further purification, was taken up in 10 ml of toluene, 0.02 g of p-toluene sulfonic acid were added, and the mixture was refluxed for 2 hours. The reaction mixture was washed with saturated aqueous NaHCO<sub>3</sub> solution, and the solvent was removed in vacuum. The crude product was purified by filtration through 5 g of silica gel (hexane/CH<sub>2</sub>Cl<sub>2</sub>), giving arylindenes as a colorless oil. 60 [8]

**2-methyl-7-phenyl indene (7a):Isolated yield 90% (0.42 g, from 0.5 g of 6a) of colorless oil**

Anal. Calc. for C<sub>16</sub>H<sub>14</sub>: C, 93.63; H,6.29; <sup>1</sup>HNMR(CDCl<sub>3</sub>): δ (ppm) 2.04( 3H , S , -CH<sub>3</sub> ), 3.27-3.28(2H, d, - CH<sub>2</sub> -), 6.44,6.58(1H, S, -C=CH - vinyl,

isomer), 7.16-7.44(8H, m, Arom.H).

**2-Methyl-7-(1-naphthyl) indene (7b): Isolated yield 91% (0.538g, from 0.625 g of 6b) of yellow oil**

Anal. Calc. for  $C_{20}H_{16}$ : C, 93.82; H, 6.39;  $^1\text{HNMR}(\text{CDCl}_3)$ :  $\delta$  (ppm) 2.05-2.06(3H, d,  $-\text{CH}_3$ ), 2.99-3.41(2H, d,  $-\text{CH}_2-$ ), 6.10, 6.57(1H, s,  $-\text{C}=\text{CH}-$  vinyl, isomer), 7.26-7.96(10H, m, Arom.H).

**2-Methyl-7-(2-naphthyl) indene (7c): Isolated yield 87% (0.512g, from 0.625g of 6c) of yellow oil**

Anal. Calc. for  $C_{20}H_{16}$ : C, 93.85; H, 6.35;  $^1\text{HNMR}(\text{CDCl}_3)$ :  $\delta$  (ppm) 2.19-2.20(3H, d,  $-\text{CH}_3$ ), 3.44-3.47(2H, d,  $-\text{CH}_2-$ ), 6.76, 6.83(1H, s,  $-\text{C}=\text{CH}-$  vinyl, isomer), 7.29-8.21(10H, m, Arom.H).

**2-Methyl-7-(4-methylphenyl) indene (7d): Isolated yield 95% (0.484 g, from 0.542 g of 6a) of colorless oil**

Anal. Calc. for  $C_{17}H_{16}$ : C, 92.85; H, 7.24;  $^1\text{HNMR}(\text{CDCl}_3)$ :  $\delta$  (ppm) 2.20(3H, s,  $-\text{CH}_3$ ), 2.47(3H, s,  $\text{CH}_3$ -phenyl), 3.42-3.44(2H, d,  $-\text{CH}_2-$ ), 6.60, 6.67(1H, s,  $-\text{C}=\text{CH}-$  vinyl, isomer), 7.18-7.55(7H, m, Arom.H).

General procedure for synthesis of 5a-d:

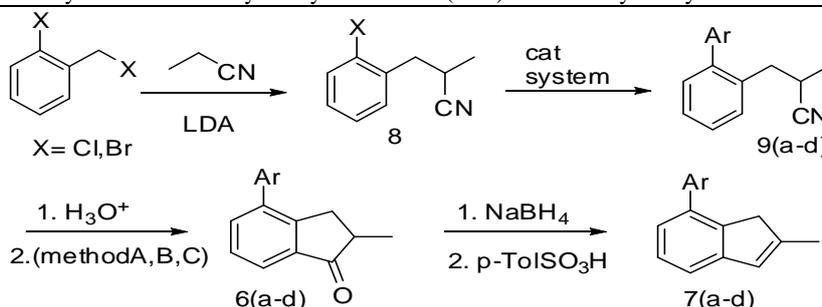
**1,2-Bis(2-methyl-4-phenylindenyl)ethane (5a)**

0.96 ml (2.4 mmol) of a 2.5M solution of butyllithium in hexane added at room temperature under argon to a solution of 2.4 mmol of arylindenes (7a-d) in 5 ml of THF. The mixture was stirred at 60° C. for 2 hours, and cooled to -78° C., 0.225 g (1.2 mmol) of dibromoethane added, and the mixture was warmed to room temperature 18 hours. The reaction mixture was washed with 5 ml of  $\text{H}_2\text{O}$ , the solvent was removed in vacuum, and the residue was chromatographed on 5 g of silica gel (hexane/ methylene chloride 9:1), giving (5%) of (5a-d) as a yellow oil [8].

### Results and Discussion

Due to the structure of the catalysts with different ligands indene bridge possesses sufficient capacity, and performs the reaction with a good selectivity. Industrial application of such ligand is used to shorten the synthetic pattern as an important parameter to be considered in industrial production. In this research, focus has been directed to provide a novel method for the synthesis of bis-1,2-(4-aryl-2-alkyl-1H-inden-1-yl) Ethane as ligand. A novel method for synthesis of 2-methyl-4-phenyl-1H-indene and 2-methyl-4-phenyl-1-

**Table 2.** synthesis of 2-methyl-4-aryl-1-indanone(6a-d) and 2-methyl-4-aryl-1H-indene (7a-b)

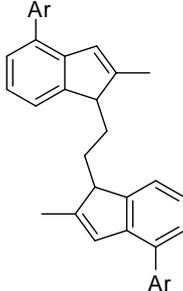


Compound	a	B	C	d
Ar	Ph	1-naphtyl	2-naphtyl	p-tolyl

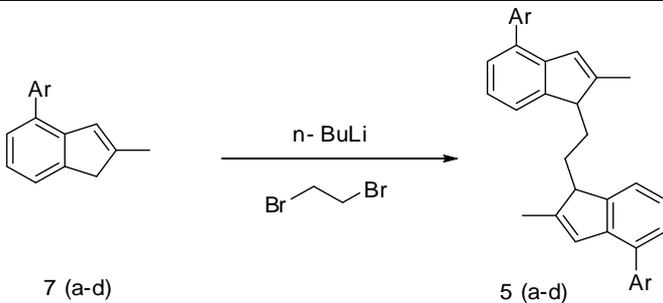
**Table 3.** synthesis of 2-methyl-4-aryl-1-indanone(6a-d) and 2-methyl-4-aryl-1H-indene by different catalysts

Catalyst System <sup>a</sup>	X=Cl	X= Cl	X=Br
	Catalyst a	Catalyst b	Catalyst c
9a (yield %)	85	75	88
9b (yield %)	79	71	85
9c (yield %)	75	65	82
9d (yield %)	73	62	82
Method	$\text{ClCO}_3\text{H}$	$\text{SOCl}_2, \text{AlCl}_3$	PPA
6a (yield %)	98	95	62
6b (yield %)	96	94	57
6c (yield %)	93	90	50
6d (yield %)	88	85	45

<sup>a</sup> catalyst a:  $\text{ArB}(\text{OH})_2, \text{Pd}_2(\text{dba})_3, \text{P}(\text{t-Bu})_3, \text{CS}_2\text{CO}_3, \text{dioxane}$ ; catalyst b:  $\text{ArB}(\text{OH})_2, \text{Benzyle DABCO}, (\text{n-Bu})_4\text{NBr}, \text{DMF}$ ; catalyst c:  $\text{ArB}(\text{OH})_2, \text{Pd}(\text{OAc})_2, \text{Ph}_3\text{P}, \text{Na}_2\text{CO}_3, \text{H}_2\text{O-DME}$ .

**Table 4.** Synthesis of 1,2-Bis(2-methyl-4-aryindenyl)ethane


Compound	a	B	C	d
Ar	Ph	1-naphthyl	2-naphthyl	p-tolyl

**Table 5.** Synthesis of bis-1,2-(4-aryl-2-alkyl-1H-inden-1-yl) Ethane as ligand


Compound	a	B	c	d
Ar	Ph	1-naphthyl	2-naphthyl	p-tolyl

indanone which are important intermediates in the synthesis of this ligand has been developed. For this purpose a solution of *n*-BuLi in hexane was added to a solution of *i*-Pr<sub>2</sub>NH in THF at -78°C and then propionitrile added to the reaction mixture. After this, a solution of *o*-bromobenzyl bromide in THF was added at once and 2-bromo- $\alpha$ -methylbenzene propanenitrile (compound **8**) was obtained. The product was introduced in Suzuki cross coupling reaction to produce the compound **9(a-d)**. The compounds **9(a-d)** was hydrolyzed in acid conditions and then was objected in cyclization reaction in the presence of PPA. The reduction of the product with NaBH<sub>4</sub> and dehydration of corresponding alcohols resulted in compound **7(a-d)** in 75-87% overall yields.

In this study 1,2-Bis(2-methylindenyl)ethane, was used as ligand and was applied in polymerization reaction. The resulting polymer properties, including average molecular weight, isotacticity, and polymer melting point improved. We succeeded in the synthesis of ligand **5(a-d)**, demonstrated in the Table 4.

Substituted bis-1,2-(4-aryl-2-alkyl-1H-inden-1-yl) Ethane is important for preparing active compounds in the fields of metallocene complexes. In particular, this

ligand can be used to prepare bridged chiral metallocenes which are of great importance as highly active catalysts in  $\alpha$ -olefin polymerization. The catalyst properties can be influenced in a targeted manner by variation of the ligand system, (**5a-d**) by substitution. This makes it possible to achieve the desired degree of change in the polymer yield, the tacticity or the melting point of the polymers. The ligand systems used for these highly active metallocenes are prepared from the corresponding indenenes which are in turn obtained from indanones which are substituted in the appropriate positions; arylindenenes are synthesized from commercially available precursors or precursors known in the literature [5].

Finally using *n*-butyl lithium, and 1,2-Dibromo ethane, ligand bis-1,2-(4-aryl-2-alkyl-1H-inden-1-yl) Ethane was synthesized.

### Conclusion

In this work, we have developed convenient strategies for the synthesis of 2-methyl-4-aryl-1H-indanone (**6a-d**) and 2-methyl-4-aryl-1H-indene (**7a-b**) and related important ligands to obtain metallocenes derivatives. The presently described preparation method

offer some advantages over previous method. For instance, it uses cheaper reagent than the general method which consumes same starting materials in last step and has higher total yields.

### References

1. Ren W., Zi G., Fang D.C., and Walter M. D.. Thorium Oxo and Sulfido Metallocenes: Synthesis, Structure, Reactivity, and Computational Studies. *J. Am. Chem. Soc.*, **133** (33):13183–13196 (2011).
2. Yang P., Pageni P., Kabir M. P., Zhu T., and Tang Ch.. Metallocene-Containing Homopolymers and Heterobimetallic Block Copolymers via Photoinduced RAFT Polymerization. *Organomet. Chem.* **813**: 95-102 (2016).
3. Brintzinger H.H., Fischer D., Mülhaupt R., Rieger B., and Waymouth R.M.. Stereospecific Olefin Polymerization with Chiral Metallocene Catalysts. *Angewandte Chemie International Edition*, **34**: 1143-1170 (1995).
4. Zuccaccia C., Tensi L., Kuhlman R.L., A.P. Gies Jr., and Macchioni A. C–H Activation and Olefin Insertion as Sources of Multiple Sites in Olefin Polymerization Catalyzed by CpAlkylHf(IV) Complexes. *ACS Catal.* **7**(1): 563-567 (2017).
5. Bahadorikhalili S., Ma'mani L., Mahdavi H., and Shafiee A.. Copper supported  $\beta$ -cyclodextrin functionalized PEGylated mesoporous silica nanoparticle-graphene oxide hybrid: An efficient and recyclable nano-catalyst for straightforward synthesis of 2-arylbenzimidazoles and 1, 2, 3-triazoles. *Microporous Mesoporous Mater.* **262**:207-216(2018).
6. Mao X., Simeon F., Achilleos D.S., Rutledge G.C. and Hatton T.A., Metallocene/carbon hybrids prepared by a solution process for supercapacitor applications. *J. of Mat. Chem. A* **42**: 13120-13127(2013).
7. Rahimzadeh G., Bahadorikhalili S., Kianmehr E., and Mahdavi M.. Ionic liquid-functionalized magnetic nanostructures as an efficient catalyst for the synthesis of 6H-chromeno [4, 3-b] quinolin-6-ones. *Molec. Divers.* **21**(3), pp.597-609(2017).
8. Ding Y., Zhao Y., Li Y., Goodenough J.B. and Yu G., An all-aqueous redox flow battery with unprecedented energy density. *Energy Environ. Sci. EES* **10**: 491-497 (2017).
9. Fei Zh., Pattanasattayavong P., Han Y, Schroeder B.C., Yan F., Joseph Kline R., Anthopoulos T. D. and Heeney M.. Influence of Side-Chain Regiochemistry on the Transistor Performance of High-Mobility, All-Donor Polymers. *J. Am. Chem. Soc.* **136**:10460-10469 (2014).
10. Zhao W., Yan Q., Tsutsumi K. and Nomura K.. Catalytic one-pot synthesis of end-functionalized poly(9,9'-di-n-octyl-fluorene vinylene)s by acyclic diene metathesis (ADMET) polymerization using ruthenium-carbene catalysts *Organometallics* **35**: 1895-1905 (2016).
11. Spaleck W., Kueber F., Winter A., Rohrmann J., Bachmann B., Antberg M., Dolle V., Paulus E. The Influence of Aromatic Substituents on the Polymerization Behavior of Bridged Zirconocene Catalysts. *Organometallic* **13**: 954-963 (1994).
12. Stehling U., Diebold J., Kirsten R., Roell W., Brintzinger H.H., Juengling S., Muehlhupt R., Langhauser F. ansa-Zirconocene Polymerization Catalysts with Anelated Ring Ligands - Effects on Catalytic Activity and Polymer Chain Length . *Organometallics* **13**: 964-970 (1994).
13. Ewen J. A., Elder M. J., Raghava Reddy B.. U. S. patent US6262199B (2001).
14. Kriffl C.B., Goeres M., Volker E., Frankfurt F., Andreas W. US Patent, PatentNumber US0033076 (2005).
15. Pletnev A.A. and Larock R.C.. Carbopalladation of Nitriles: Synthesis of Benzocyclic Ketones and Cyclopentenones via Pd-Catalyzed Cyclization of  $\omega$ -(2-Iodoaryl)alkanenitriles and Related Compounds. *J. Org. Chem.* **67**: 9428-9438 (2002).
16. Kim J., Shokova E., Tafeenko V. and Kovalev V.. (CF<sub>3</sub>CO)<sub>2</sub>O/CF<sub>3</sub>SO<sub>3</sub>H-mediated synthesis of 1,3-diketones from carboxylic acids and aromatic ketones. *Beilstein J. Org. Chem.* **10**: 2270–2278 (2014).
17. Oberursel F.K., Eppsteiffaunus B.B., Walter S.. US Patent, Patent Number US6051727A (2000).