



## Synthesis of 1-(2-Indenylethyl) Pyrrolidine and its Transition Metal Complexes

Gloria Ukalina Obuzor and Brian L. Booth

Department of Pure and Industrial Chemistry

University of Port Harcourt, Port Harcourt, Rivers State

Department of Chemistry

University of Manchester Institute of Science and Technology

Manchester, England, M60 1qd, UK.

### ABSTRACT

The ligand 1-(2-indenylethyl)pyrrolidine was synthesized and fully characterized (IR, NMR, Mass Spec. and Micro Analysis). The complex 1-(2-indenylethyl)pyrrolidinetitanium dichloride (IV) was synthesized in 72% yield by the reaction of the Grignard reagent of the new ligand 1-(2-indenylethyl)pyrrolidine with  $TiCl_3 \cdot 3THF$  followed by oxidation with  $AgCl$  while 1-(2-indenylethyl)pyrrolidinezirconium dichloride complex was synthesized in 38% yield by the reaction of the lithium salt of the new ligand 1-(2-indenylethyl)pyrrolidine and  $ZrCl_4 \cdot 2THF$ . Both complexes were not soluble in most organic solvents for fully characterization. However, Mass spec. gave the molecular masses and the fragmentation pattern of the metal complexes.

### INTRODUCTION

There has been increasing interest in the development of the chemistry of ansa-metallocene-based systems since the report of a new generation of group IV bent metallocenes containing bridged cyclopentadienyl ligands suitable as olefin polymerization catalysts to produce high-density polyethylenes, isotactic and syndiotactic polyolefins [1,2]. Replacement of cyclopentadienyl ring hydrogens by various substituents has been shown to result in significant changes in both steric and electronic effects on the metal centers [3]. In addition to the *ansa* complexes particular efforts have been made to synthesize cyclopentadienyl rings with pendent donor group acting as a bidentate ligand bonded to the metal center, where one three-electron amido group occupies the site of one of the cyclopentadienyl rings of the ansa complex [4, 5]. While preliminary studies on the structure-activity relationship of these novel catalyst have appeared [6, 7] thorough understanding of the various effects caused by the ligand periphery remains unachieved. Based on the significant difference of indenyl ligands, a linked amido-indenyl ligand has been successfully prepared.

The limited stability of mono(indenyl)titanium complexes was expected to be improved by the introduction of a five-membered ring immobilized nitrogen linked to the indenyl by an ethylene bridge. Metallation of these ligands would give us new types of metal complexes whose activity as Ziegler-Natta catalysts for the polymerization of ethylene could be explored.

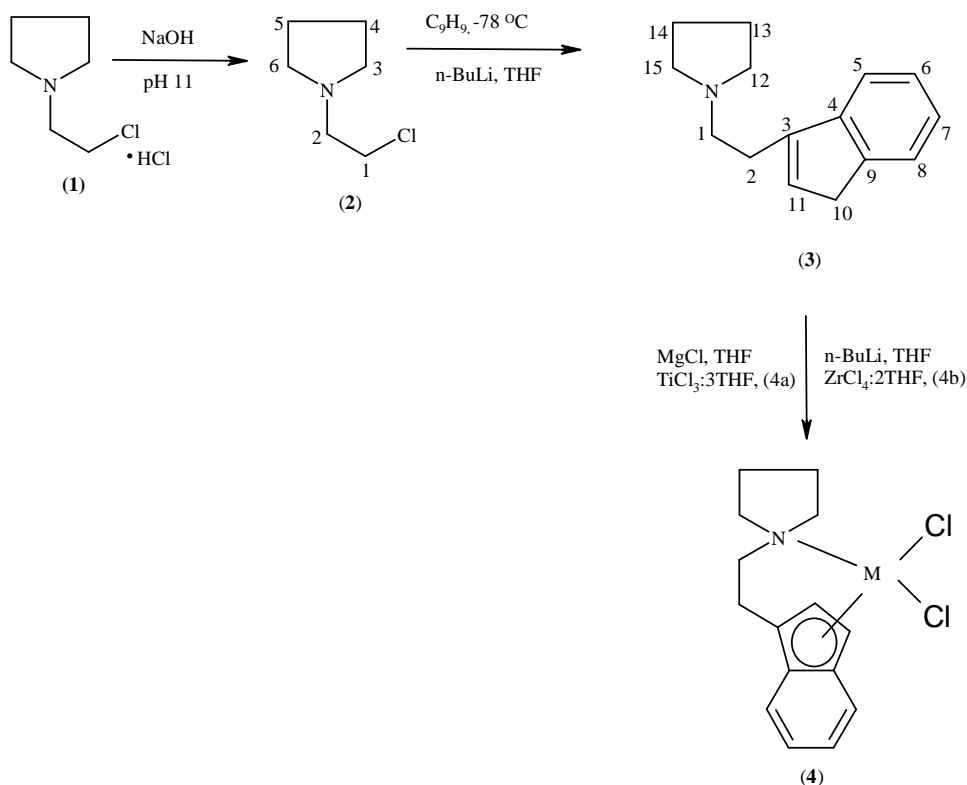
### MATERIALS AND METHODS

N/B: Moisture- and air sensitive compounds were handled under an argon atmosphere using Schlenk techniques. Diethyl ether was distilled from benzophenone ketyl. The NMR, IR and Mass. Spec. were done at The University of Manchester, Manchester, England.

#### Preparation of 1-(2-chloroethyl)pyrrolidine (2).

1-(2-Chloroethyl)pyrrolidine hydrochloride (20.0g, 118mmol) (1) was dissolved in water and neutralized with aqueous sodium hydroxide to pH 11. The solution was extracted with dichloromethane, washed with water, dried ( $MgSO_4$ ) and concentrated. Distillation under vacuum afforded the product (2) as colourless oil, (15.0g, 96% yield) b.p.115-116.5 °C (2mm Hg).  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  1.4 (s, 4H,  $H_4$ ), 2.2 (s, 4H,  $H_3$ ), 2.4 (t, 2H, J 15Hz,  $H_1$ ) 3.2 (t, 2H, J 15Hz,  $H_2$ ) ppm.  $^{13}C$  NMR (70MHz,  $CDCl_3$ )  $\delta$  22.9 ( $C_4$ ), 41.0 ( $C_2$ ), 53.9 ( $C_3$ ), 57.2 ( $C_1$ ) ppm. IR  $\nu_{max}$  (neat)

3450s, 2960s, 2690s, 2595s, 2490m, 1460s (C-N str.), 1400w, 1410w, 760w (C-Cl), 680w (C-Cl)  $\text{cm}^{-1}$ . [Found: C, 54.1; H, 8.8; N, 10.2; Cl, 26.9.  $M_{134}$ .  $\text{C}_6\text{H}_{12}\text{NCl}$  requires C, 53.9; H, 9.0; N, 10.4; Cl, 26.6 MS(FAB)m/z 135(M+1) 96%]



### Synthesis of 1-(2-indenylethyl)pyrrolidine (3) and its complexes

(I)

#### Preparation of 1-(2-indenylethyl)pyrrolidine (3) [8].

To a flame-dried, three-necked, round-bottom flask (250ml) was added freshly distilled indene (6.5ml, 56mmol) in THF (50ml) (under argon) cooled to  $-78^\circ\text{C}$  for 30 min and n-butyllithium (22.5ml of 2.5M solution in hexane, 56mmol) was added drop-wise to the solution, which turned yellow. The mixture was stirred for a further 1hr at  $-78^\circ\text{C}$ . 1-(2-chloroethyl)pyrrolidine (2) (5.0g, 38mmol) in THF (20ml) was cannulated into the reaction mixture and was allowed to warm to room temperature then stirred for 18 hr. The mixture was hydrolyzed with water and the aqueous layer was extracted with diethyl ether. The combined ether layers were dried ( $\text{MgSO}_4$ ) and concentrated. The crude oil (8.1g, 92%) was fractionally distilled under vacuum (in a sand-bath) to give the product (3) as a light brown oil (6.6g, 3.0mmol, 82% yield); b.p.  $219\text{--}223^\circ\text{C}$  (1.0mm).  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ )  $\delta$  1.7 (s, 4H,  $\text{H}_{13}$  and  $\text{H}_{14}$ ), 2.5 (s, 4H,  $\text{H}_1$  and  $\text{H}_2$ ), 2.63 (s, 4H,  $\text{H}_{12}$  and  $\text{H}_{15}$ ), 3.2 (s, 2H,  $\text{H}_{10}$ ), 6.1 (s, 1H,  $\text{H}_{11}$ ), 7.0-7.4 (m, 4H, aromatic) ppm.  $^{13}\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ )  $\delta$  23.7 ( $\text{C}_{13}$  and  $\text{C}_{14}$ ), 27.8 ( $\text{C}_2$ ), 37.9 ( $\text{C}_{10}$ ), 54.4 ( $\text{C}_{12}$  and  $\text{C}_{15}$ ), 55.3 ( $\text{C}_1$ ), 119.0 ( $\text{C}_5$ ), 124.2 ( $\text{C}_8$ ), 124.7 ( $\text{C}_6$ ), 124.9 ( $\text{C}_7$ ), 126.4 ( $\text{C}_{11}$ ), 142.7 ( $\text{C}_3$ ), 144.4 ( $\text{C}_4$ ), 145.4 ( $\text{C}_9$ ). IR  $\nu_{\text{max}}$  (neat) 3070w, 3020w, 2960s, 2790s, 1457m, 1400w, 1350w, 1150w, 1130w  $\text{cm}^{-1}$ . [Found: C, 84.6; H, 9.2; N, 6.8  $M_{214}$ .  $\text{C}_{15}\text{H}_{19}\text{N}$  requires C, 84.5; H, 8.9; N, 6.6. MS (FAB) m/z 215(M+1)98%].

#### Preparation of 1-(2-indenylethyl)pyrrolidinetitanium dichloride (IV) (4a) using $\text{TiCl}_3 \cdot 3\text{THF}$ and 1-(2-indenylethyl)pyrrolidinemagnesium chloride [9]

In a 250ml round-bottom Schlenk flask fitted with a reflux condenser, isopropylmagnesium chloride (6.4ml of 2.0 solution in ether, 13mmol) was syringed in. The ether was removed under vacuum to leave colourless oil. A toluene/THF mixture (4:1 v/v ratio, 40.0ml) was added followed by 1-(2-

indenylethyl)pyrrolidine (**3**) (3.0g, 14mmol) in toluene/THF (10ml). The solution was heated to reflux. After refluxing for 2 days, the solution was cooled and the volatile materials were removed under reduced pressure. The light yellow solid residue was slurried in dry pentane (50ml) and filtered under argon to leave a light yellow powder which was washed with dry pentane (50ml) and dried under reduced pressure and argon to give (1.2g, 22%) of the expected compound as a light yellow powder and recovered starting material (**3**) (1.6g, 76%) after the pentane was evaporated.

1-(2-indenylethyl)pyrrolidinemagnesium chloride (1.0g, 40mmol) in THF (5ml) in a two-necked 250ml Schlenk flask fitted with a sintered tube attached to a three-necked flask (stirring) was charged with  $\text{TiCl}_3 \cdot 3\text{THF}$  (0.57g, 40mmol) suspended in THF (5ml) under argon, and this resulted in a colour change from pale blue to deep purple. After 15 min.,  $\text{AgCl}$  (0.57g, 40mmol) was added to the solution and it turned green. After 1.5 hr, the THF was removed under reduced pressure to leave a green solid (0.42g). The green solid was slurried with toluene (20ml), filtered and the toluene was removed under reduced pressure. TLC (hexane/ethyl acetate 3:1) showed two very close spots. The green solid was not soluble for NMR analysis. MS(FAB)m/z gave peaks at 160( $\text{C}_{11}\text{H}_{12}\text{O}$ )17%, 205( $\text{C}_4\text{H}_8\text{NOTiCl}_2$ ) 213( $\text{C}_{11}\text{H}_{19}\text{N}$ )17%, 259( $[\text{C}_4\text{H}_8\text{N}]_2\text{TiCl}_2$ )<sup>+</sup>40%, 313(20%), 331( $[\text{C}_{15}\text{H}_{19}\text{NTiCl}_2]$ )60%, 332( $[\text{C}_{15}\text{H}_{19}\text{NTiCl}_2]$ )<sup>+</sup>51%

#### (IV) Preparation of 1-(2-indenylethyl)pyrrolidinezirconium dichloride (**4b**) Using $\text{ZrCl}_4 \cdot 2\text{THF}$ [10]

A solution of 1-(2-indenylethyl)pyrrolidine (**3**) (5.0g, 24mmol) in THF (50ml) was cooled to  $-78^\circ\text{C}$  and was treated drop-wise by syringe with a solution of n-butyllithium (9.6ml of 2.5M solution in hexane, 24mmol) in THF (50ml) over 40 min period. The bright yellow solution was stirred for 1 hr and was then warmed to room temperature before being cannulated into a constant-addition dropping funnel and the solution was diluted to 100ml. A solution of  $\text{ZrCl}_4 \cdot 2\text{THF}$  (9.0g, 24mmol) in THF (25ml) was cannulated into a second constant-addition dropping funnel and the solution was diluted to 100ml. The two solutions were simultaneously added drop-wise to a 1-litre three-necked flask containing THF (250ml) maintained at  $25^\circ\text{C}$  over a 3 hr period. The resultant solution was stirred for 18 hr. Solvent was removed under reduced pressure. Diethyl ether (2 x 20ml) was used to slurry the yellow residue and was also removed under reduced pressure to ensure complete removal of THF. The dry residue was slurried with diethyl ether (50ml), filtered and washed with dry diethyl ether (50ml). The yellow solid obtained was washed successively with aqueous HCl (4N, 2 x 20ml),  $\text{H}_2\text{O}$  (2 x 20ml), EtOH (2 x 20ml), and ether (20ml) and was dried under argon to give yellow solid (38%). TLC analysis (hexane/diethyl ether 2:1) showed it to contain two spots at an  $R_F$  value of 0.44 for the starting material and a second spot at an  $R_F$  value of 0.41. The solid was not soluble enough for NMR analysis initially but later became soluble in  $\text{D}_2\text{O}$  to give the  $^1\text{H}$  NMR spectrum of starting material (**3**). MS(FAB)m/z of the yellow solid gave peaks at 116( $\text{C}_6\text{H}_{12}\text{N}$ )46%, 161( $\text{C}_{11}\text{H}_{13}\text{O}$ )25%, 213( $\text{C}_{15}\text{H}_{19}\text{N}$ )25%, 301( $[\text{C}_4\text{H}_8\text{N}]_2\text{ZrCl}_2$ ) 392( $\text{C}_{15}\text{H}_{19}\text{NZrCl}_2$ )40%, and 393( $\text{C}_{15}\text{H}_{19}\text{NZrCl}_2$ )<sup>+</sup>78%.

## RESULTS AND DISCUSSION

An aqueous solution of 1-(2-chloroethyl)pyrrolidine hydrochloride (**1**) was neutralized with sodium hydroxide solution at pH 11 to give the free base (**2**) in 96% yield after extraction and distillation in a sand-bath (b.p.  $115\text{--}116^\circ\text{C}/2\text{mm Hg}$ ). Compound (**2**) was fully characterized by  $^1\text{H}$  and  $^{13}\text{C}$ , IR, Microanalysis and Mass Spectroscopy. When the free base (**2**) was caused to react with indenyllithium initially at  $-78^\circ\text{C}$  and then at room temperature for 18hr [9] the desired new product 1-(2-indenyl)pyrrolidine (**3**) was obtained in 82% yield as a light brown oil which was purified by distillation in a sand-bath (b.p.  $219\text{--}223^\circ\text{C}/1\text{ mm Hg}$ ). The IR (neat) spectrum showed bands at 2960s (C-H str.), 1457m, 1400w (C-N str.)  $\text{cm}^{-1}$ . The  $^1\text{H}$  NMR spectrum gave a singlet at  $\delta 1.70$  ppm integrating for four protons for the  $(\text{CH}_2\text{CH}_2)$  ( $\text{H}_{13}$  and  $\text{H}_{14}$ ), a singlet at  $\delta 2.5$  ppm for the four protons of the  $\text{N}(\text{CH}_2)_2$  ( $\text{H}_1$  and  $\text{H}_2$ ) group, a singlet at  $\delta 2.63$  ppm integrating for four protons of the  $\text{CH}_2\text{NCH}_2$  ( $\text{H}_{12}$  and  $\text{H}_{15}$ ), and a singlet at  $\delta 3.2$  ppm for the two protons of  $\text{H}_{10}$ . The olefinic proton ( $\text{H}_{11}$ ) is a singlet at  $\delta 6.1$  ppm while the aromatic protons were multiplet between  $\delta 7.0\text{--}7.4$  ppm. The  $^{13}\text{C}$  NMR spectrum showed thirteen lines with the carbons of the aromatic ring between  $119.0\text{--}124.9$  ppm and the three quaternary carbons between  $142.7\text{--}145.4$  ppm. The microanalysis and mass spectrum confirmed a molecular mass of 213 a.m.u and a molecular formula of  $\text{C}_{15}\text{H}_{19}\text{N}$ .

A good yield (72%, **4a**) was achieved by the treatment of the Grignard salt of (**3**) with  $\text{TiCl}_3 \cdot 3\text{THF}$  in THF, which gave a deep purple reaction solution. Oxidation by the addition of one equivalent of  $\text{AgCl}$  to the reaction solutions, which presumably contains 1-(2-indenyl) pyrrolidinetitanium caused the solution to become green. The green oil gave rise to air-sensitive yellow oil that congeals on exposure to air but stable (remained green) in toluene under argon in Schlenk tube. Sublimation gave purple haze and charred oil while all attempts of crystallization failed because the solids obtained dissolved once out of solvent; du Plooy *et. al.* [11] experienced similar difficulty. The NMR spectra could not be obtained because the oil was not soluble in most NMR organic solvents [12] but mass spectrum of (**4a**) green oil was obtained as  $\text{MS}(\text{FAB})m/z$  213( $\text{C}_{11}\text{H}_{19}\text{N}$ )17%, 259( $[\text{C}_4\text{H}_8\text{N}]_2\text{TiCl}_2$ )<sup>+</sup>40%, 313(20%), 332( $[\text{C}_{15}\text{H}_{19}\text{N}]\text{TiCl}_2$ )51%.

The reaction of the lithium salt of (**3**) with  $\text{ZrCl}_4 \cdot 2\text{THF}$  gave bright yellow oil (38%, **4b**). Their <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra could not be obtained because the oil was not soluble in most NMR organic solvents but eventually, the <sup>1</sup>H spectrum ( $\text{D}_2\text{O}$ ) gave signals of the starting material while mass spectrum of the bright yellow oil gave peaks at  $\text{MS}(\text{FAB})m/z$  116( $\text{C}_6\text{H}_{12}\text{N}$ )46%, 161( $\text{C}_{11}\text{H}_{13}\text{O}$ )25%, 213( $\text{C}_{15}\text{H}_{19}\text{N}$ )25%, 301( $[\text{C}_4\text{H}_8\text{N}]_2\text{ZrCl}_2$ ) 392( $\text{C}_{15}\text{H}_{19}\text{NZrCl}_2$ )40% and 393( $\text{C}_{15}\text{H}_{19}\text{NZrCl}_2$ )<sup>+</sup>78%.

#### ACKNOWLEDGEMENT:

My thanks go to Association of Commonwealth Universities for the Sponsorship and Scholarship that made this research work possible.

#### REFERENCE

- [1] Amor, F and Okuda, J. (1996). Linked amido-indenyl complexes of Titanium. *Journal of Organometallic Chemistry* 520: 245-248.
- [2] Vassilyev, O; Panarello, A and Khinast, J.G. (2005). Enantioselective Hydrogenations with Chiral Titanocenes. *Molecules*, 10: 587-619
- [3] Bercaw, J. E.; Marvich, R. H.; Bell, L. G. and Hans Brintzinger, H (1972). Titanocene as an intermediate in Reactions involving molecular hydrogen and Nitrogen, *JOACS* 94 (4): 1219.
- [4] Möhring, P. C. and Coville, N. J (2005). Group 4 metallocene polymerisation catalysts: quantification of ring substituent steric effects. *Coordination Chemistry Reviews*, 479: 18-35.
- [5] Junseong L.; Youngkyu, D and Youngjo K. (2007). Facile synthesis and X-ray structures of (g5- $\text{C}_5\text{Me}_5$ ) $\text{Ti}(\text{OArF})_3$  ( $\text{OArF}=\text{OC}_6\text{F}_5$ ,  $\text{OCH}_2\text{C}_6\text{F}_5$ , and  $\text{OCH}_2\text{C}_6\text{F}_2\text{H}_3$ ) . *J. Organometallic Chemistry* 692: 3593–3598
- [6] Jutzi, D. J. and Simeling, U (1995). Cyclopentadienyl] Titanium and Zirconium Complexes *J. Organometallic Chemistry* 500: 175.
- [7] Christoffers, J.; Werner, T; Baro, A and Fischer, P. (2004). Synthesis of a tin-functionalized cyclopentadiene derivative. *Journal of Organometallic Chemistry* 689:3550–3555
- [8] Aparna, K; Ferguson, M and Ronald Cavell, G (2000) A Monomeric Samarium Bis(Iminophosphorano) Chelate Complex with a Sm=Bond. *J. Am. Chem. Soc.*, 122 (4), pp 726–727
- [9] Ciruelos, S.; Cuenca, T.; Gómez, R.; Gómez-Sal, P.; Manzanero, A.; Royo, P (1996). Synthesis and Reactivity of [(Amidosilyl) cyclopentadienyl] Titanium and Zirconium Complexes *Organometallics*, 15: 5577.
- [10] Richardson, W. E. and Smith, C. H. (2008) Synthesis of novel alkyl-aryl polyamide. *Journal of the American Oil Chemists' Society*, 11: 206-210.
- [11] du Plooy, K. E.; Moll, U.; Wocadlo, S.; Massa, W. and Okudo, J (1995). Coordination Properties of novel tridentate. Cyclopentadienyl Ligands in Titanium and Zirconium Complexes. *Organometallics*, 14: 3129-3131
- [12] Wells, N. J.; Huffman, N. C. and Caulton, K. G (1981). Monocyclopentadienyl Zirconium(IV) complexes. *Journal of Organometallic Chemistry*, 213: C17-C20.