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Synthesis and Characterization of Ferrocenyl-N-heterocyclic Carbenes

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Carbenes containing ferrocenyl substituents are interesting target compounds due to the stereoelectronic influence of the ferrocenyl group in terms of steric protection, electron-donation and reversible redox chemistry. In this paper synthetic approaches to novel ferrocenyl-N-heterocyclic carbenes are summarized and their ^{1}H NMR spectroscopic structural properties are discussed. The synthesis of these ferrocenyl-N-heterocyclic carbenes ligands involves the reaction of the alcohol 1-(ferrocenyl)ethanol successively with N-methylimidazol, N-butyl-imidazol and N,N-carbonyldimidazole in glacial acetic acid.

Key Words: Carbene, N-Heterocyclic carbene, Ferrocene.

INTRODUCTION

In contrast to Fischer and Schrock type carbenes, novel ferrocenyl-N-heterocyclic carbenes (**Scheme-I**) are extremely stable, inert ligands when complexed. Until the year 1960, it has been thought that carbenes were too reactive to be isolated, this thwarted widespread efforts to investigate carbene chemistry. The reactivity and stability of N-heterocyclic carbenes was reported by Wanzlick[1]. Wanzlick and Schonherr[2] reported the first application of novel ferrocenyl-N-heterocyclic carbenes as ligands for metal complexes. Surprisingly, the field of novel ferrocenyl-N-heterocyclic carbenes as ligands in transition metal chemistry remained dormant for almost 23 years.

Scheme-I: General formula of N-heterocyclic carbene

Over the past 40 years[3], N-heterocyclic carbenes[4] have blossomed into a class of ligands that have proven to be useful for a broad range of transition metals[5,6]. As strong, two-electron donors, they generally coordinate to metals in a fashion that is analogous to phosphines[7] however, in many instances, they often produce complexes

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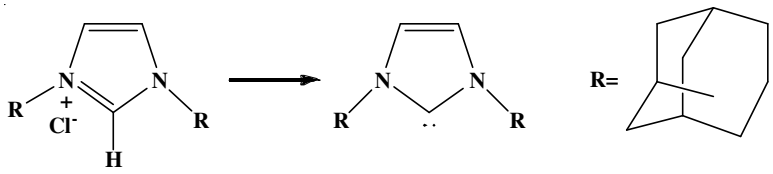
which are more thermally-stable[8] and/or exhibit higher catalytic activities[5]. novel ferrocenyl-N-heterocyclic carbenes are often the ligand of choice for applications ranging from metal-mediated catalysis to organometallic materials[5,9].

N-Heterocyclic carbenes are stable singlet carbenes and are strong σ-donors that can stabilize both early and late transition metals. Their reactivities is comparable to any other classical two electron donors such as phosphines, amines or ethers. They coordinate strongly to late transition metals and heavy main group elements, but are also known to bind to early transition metals and the lanthanoids. The first stable N-heterocyclic carbine (**Scheme-II**) was isolated and characterize by Arduengo *et al.*[10]. This discovery led to an avalanche of investigations concerning this powerful class of ligands,



Scheme-II: NHC as reported by Arduengo *et al.*[10]

During the1990s, novel ferrocenyl-N-heterocyclic carbenes gain popularity as ligands and research continues toward isolable novel ferrocenyl-N-heterocyclic carbenes. Due to their unique properties, they became a privileged group of catalytically useful ligands rivalling the classical cyclopentadienyl and phosphine ligands[11].

Novel ferrocenyl-N-heterocyclic carbenes are most frequently prepared *via* deprotonation of the corresponding imidazolium salt with NaH in a mixture of liquid ammonia and THF. This route is suitable for novel ferrocenyl-N-heterocyclic carbenes with a large range of N-substituents. These ligands have successfully been tested in different C-C-coupling reactions.

EXPERIMENTAL

All chemicals were of reagent grade, purchased from Aldrich Chemical Co., Sigma Chemical Co. or Fisher Chemical Co. and were used without further purification except as noted below. Solvents were purified according to standard methods[12].

All reactions were conducted under argon. Alumina for chromatography was spence's grade UG1 100 mesh, which had been neutralized with ethyl acetate and dried at 150 °C. Solutions were dried over anhydrous magnesium sulphate and evaporated under reduced pressure using a rotary evaporator.

^{1}H NMR spectra were recorded on Bruker DPX 200 (200 MHz) spectrometers. All ^{1}H NMR spectra are reported in ppm relative to the central line of the triplet for $CDCl_3$ at 77.0 ppm.

Synthesis: 1-(Ferrocenyl)ethanol (**1**) was obtained from acetylferrocene according to literature procedures[13]. Acetylferrocene was obtained by acetylation of ferrocene using Freidel-Crafts reaction[14].

Ferrocenyl-1-(N-methylimidazolium)chloride (2): 1-(Ferrocenyl)ethanol (299 mg, 1.3 mmol), N-methyl-imidazol (156.0 mg, 1.9 mmol) and 3 mL of glacial acetic acid were introduced, under argon, into a tube of schlenk. The resulting mixture was stirred at room temperature for 12 h and was then evaporated using a vacuum pump. LiCl (0.17 g, 4.0 mmol) and 5.0 mL of dry ethanol was then added and the reaction mixture left, under stirring, for another 2 h at room temperature. After evaporation of the solvents, 20 mL of dichloromethane was then added and the reaction mixture was filtered on a cellulose acetate bed. The filtrate was then concentrated under reduced pressure using a rotary evaporator. The obtained product was purified on a column chromatography using CH_2Cl_2/MeOH (10/1) as eluent. The first fraction when evaporated yielded 1-ferrocenyl(N-methylimidazolium)-chloride (86 mg, 20 %) as a thick brown oil.

^{1}H NMR (200 MHz; $CDCl_3$ δ ppm): 1.97 (m, 3:00, CH_2-CH_3); 3.50 (m, 3:00, N-CH_3); 4.09 (m, 2:00, C_P); 4.25 (S, 5:00, C_P); 4.25 (m, 2:00, C_P); 5.88 (S, 1:00, CH_2 C_P); 6.99 (S, 1:00, HC=C, Im+); 7.16 (S, 1H, HC=C, Im+); 11.02 (S, 1:00, imidazol).

Ferrocenyl-1-(N-butylimidazolium)chloride (3): 1-Ferrocenyl(N-butyl-imidazolium)chloride (**3**) (103.63 mg, 22 %) was obtained, as a thick brown oil, following the same procedure as described for 1-ferrocenyl(N-methylimidazolium)-chloride (**2**) using 1-(ferrocenyl)ethanol (299 mg, 1.3 mmol), N-buthylimidazol (231.8 mg, 1.9 mmol) and 6.3 mL of glacial acetic.

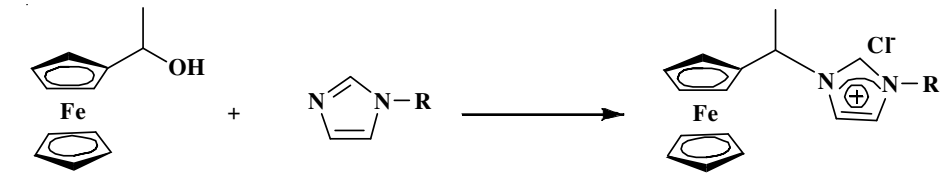
^{1}H NMR (200 MHz; $CDCl_3$ δ ppm): 1.87 (T, 3:00, CH_3); 2.0-2.2 (m, 9:00, CH_3-CH and CH_2) 4.24 (S, 5:00, C_P); 4.28 (m, 2:00, C_P); 4.36 (m, 2:00, C_P); 5.9 (S, 1:00, CH (Me)) ; 7.20 (m, 1:00, HC=C, Im+); 7.3 (m, 1:00, HC=C, Im+); 10.9 (S, 1:00, imidazol).

1-(1-Ferrocenylethyl)-1*H*-imidazole (4): Into a round bottom flask equipped with a cooling agent, was added under atmosphere of argon, 1-(ferrocenyl)ethanol (230 mg, 0.8 mmol), N,N-carbonyldimidazole (162 mg, 1 mmol) and 10 mL of dried dichloromethane. The mixture was refluxed for 1 h, it was then cooled to room temperature and 50 mL of ether was added, the resulting mixture was washed twice with 50 mL of 20 % aqueous solution of phosphoric acid. The pH of the aqueous phase is adjusted at 5 by addition of a 1 M NaOH aqueous solution and extracted with dichloromethane. The combined dichloromethane extracted was dried over anhydrous sodium sulfate and evaporated to yield a small amount of thick brown oil.

^{1}H NMR (200 MHz; $CDCl_3$ δ ppm): 1.24-1.44 (D, 3:00, CH_3); 4.14-4.30 (m, 9:00, FC); 4.46 (S, 2:00, CH_2); 7.18 (S, 1:00, CH); 8.16 (S, 1:00, CH).

RESULTS AND DISCUSSION

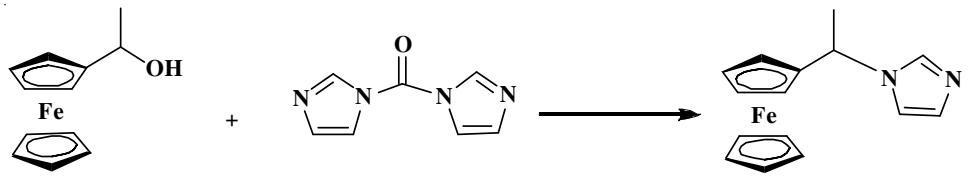
Reaction of the 1-(ferrocenyl)ethanol (**1**) with N-methyl- and N-butyl-imidazol in glacial acetic acid gave successively the expected 1-ferrocenyl(N-methyl-imidazolium)chloride (**2**) and 1-ferrocenyl(N-butylimidazolium)chloride (**3**) as illustrated by the following reaction.



1

2, R = Me
3, R = Bu

We also obtained 1-(1-ferrocenylethyl)-1*H*-imidazole (**4**) from the reaction of 1-ferrocenylethanol (**1**) and N,N-carbonyldimidazole.



1 **4**

Conclusion

The synthesis and ^{1}H NMR characterization of three different ferrocenyl-N-heterocyclic carbenes ligands have been described. The synthetic procedure involves the reaction of the alcohol 1-(ferrocenyl)ethanol successively with N-methyl-imidazol, N-butylimidazol and N,N-carbonyldimidazole. The yield of the three ferrocenyl-NHC's is about 22 %.

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