Synthesis, Characterisation and X-Ray Structure of Ferrocenyl N-Heterocyclic Carbene Complexes of Rhodium(I)

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Abstract

The synthesis, spectroscopic and structural characterization of Rh(I) ferrocenyl N-heterocyclic carbene complexes are described. The in situ deprotonation of the imidazolium salts with KOBu- and subsequent complexation to rhodium(I) proved to be an efficient route for their synthesis yielding good to excellent yields. The X-ray crystal structure of bromo(n^1,5-cyclooctadiene)(1-ferrocenyl-3-propyl-1H-imidazol-2-ylidene)rhodium(I) was obtained and reveals substitution disorder of a bromine and chlorine atom on Rh(1) in the ratio of 0.96:0.04.

Keywords: Ferrocenylimidazolium salts; Ferrocenyl N-heterocyclic carbene rhodium(I); X-Ray crystal structure

Introduction

Metal-NHC (NHC=N-heterocyclic carbenes) complexes were first reported independently in 1968 by Wanzalic and Ofele and the first stable carbene was isolated by Arduengo et al. in 1991 [1]. Since then, NHCs have proved to be a versatile class of ligands in a wide range of metal catalyzed organic transformations [2] and have gained considerable attention as spectator ligands in organometallic chemistry, especially as alternatives to phospine ligands in homogeneous catalysis [3].

The activity and selectivity of NHC complexes as catalysts can be enhanced by a change of the electronic and steric properties of the 1,3-imidazol-2-ylidene substituents. The substituents can also be used to introduce remote functional groups which can be used to immobilize the catalyst on solid support. While organic substituents have been extensively investigated, the ferrocenyl moiety has not enjoyed the same degree of attention. Sterically, the ferrocenyl moiety represents a relatively bulky group with a unique cylindrical shape and electronically, the powerful donor capacity of ferrocene might be advantageous for additional stabilization of the electron-deficient carbene moiety [4].

N-heterocyclic carbene complexes containing the ferrocenyl moiety were pioneered by Bildstein et al. in 1998. Since then a number of mono and bidentate ferrocenyl-NHC complexes have been reported, many with or without a spacer between the ferrocenyl and the NHC unit [4-11]. It was reported that when the ferrocenyl moiety is attached directly to the carbene, there is a substantial electron donation from the carbene to the metal centre compared to those with a spacer in between [4].

Horvath et al. have reported the synthesis and structural characterization of bis(carbene)gold(I)-ferrocenylphenyl complex [12]. The carbene complex was screened against the human HeLa cervix epitheloid carcinoma cell line, CoLo 320 DM, a human colon adenocarcinoma line, the Jurkat leukaemia cell line and the Jurkat leukaemia breast cancer cell line. It was active against Jurkat leukaemia and its activity was higher than that of cisplatin at lower concentrations.

Chiral ferrocenyl-NHC complexes have also been reported by Bolm et al. [7]. They synthesized a chiral N-heterocyclic carbene complex with an oxazolinyl-ferrocenyl substituent linked to rhodium-COD [7]. The compound showed high catalytic reactivity in the hydrosilylation of acetylene. Chung et al. [13] have synthesized a series of monodentate ferrocenyl-NHC complexes of rhodium and investigated them for catalytic reduction of 4-methylacetophenone. Although this transformation gave high overall yields (>99%), some of the complexes displayed low stereoselectivities. However, a 52% ee was achieved with a chiral C2-symmetric N-heterocyclic carbene complex [13].

In this work, the synthesis and characterization of various ferrocenyl NHC rhodium(I) complexes was carried out successful via the deprotonation of the ferrocenyl imidazolium salt by a base followed by subsequent complexation by the rhodium centre. Moderate to good yield were obtained. The compounds were characterized by NMR, FT-IR, mass spectrometry and a crystal structure of compound 3 was obtained.

Experimental Methods

All reactions, unless otherwise stated, were performed under an inert atmosphere of dry nitrogen. All reagents, except the ferrocenyl imidazolium salts, were purchased either from Sigma-Aldrich or Fluka and were used as received, unless otherwise stated. The ferrocenyl imidazolium salts were prepared by reacting ferrocenylimidazoles with alkyl halides as described previously. Solvents were freshly dried prior to reaction using standard drying procedures and stored over molecular sieves [14]. Melting points were recorded on an Electrothermal IA 900 series digital melting point apparatus and are uncorrected. Infrared spectra were recorded on a DigiLab FTS 3100 Excalibur HE spectrophotometer as KBr disks. 1H and 13C NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer as solutions in CDCl3 using TMS as an internal standard. Mass spectra were recorded on a VG-70SE mass spectrometer at the University of Witwatersrand in Johannesburg. X-ray analysis was done at the Ludwig-Maximilians University, Munich.

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Synthesis of ferrocenyl NHC-rhodium(I) [[(NHC)Rh(COD) X] complexes

General procedure: [Rh(cod)Cl] (1.0 eq.) and KOBu (2.2 eq.) were placed in a two-necked round-bottomed flask on a Schlenk line and THF (20 cm³) was added under an atmosphere of argon, and stirred for 45 minutes at room temperature. To this mixture was added the appropriate imidazolidine salt (2.2 eq.). The reaction mixture was stirred for 3 hours at room temperature, filtered and the filtrate concentrated under vacuum. The resulting residue was dissolved in dichloromethane and subjected to column chromatography using silica gel as stationary phase and dichloromethane as eluent. Removal of the solvent under reduced pressure provided the product.

Iodo(η⁵-1,5-cyclooctadiene)(1-ferrocenyl-3-methyl-1H-imidazol-2-ylidene)rhodium(I) (1):

[Brh(Cod)Cl]₂ (50 mg, 0.1 mmol); KOBu (25 mg, 0.223 mmol); 1-ferrocenyl-3-methyl-1H-imidazolium iodide (88 mg, 0.223 mmol). Yield (106 mg, 88%) of a yellow powder; m.p. 185-186°C; IR (KBr cm⁻¹): 3098, 2935, 2872, 2827, 1556, 1497, 1283, 1238, 1105, 832, 728; ¹H NMR (CDCl₃): 7.31 (1H, d, J 2.0, NCH=NCH), 6.95 (1H, d, J 2.0 NCH=NCH), 5.22 (2H, br, CH-COD), 4.37 (2H, br, C₂H), 4.29 (2H, br, C₂H), 4.26 (5H, s, C₂H), 3.47 (1H, m, CH-COD), 2.99 (1H, m, CH-COD), 2.26 (2H, m, CH-C₂-COD), 1.89 (2H, m, CH₂-COD); ¹³C NMR (CDCl₃): 182.90 [d, J 50.57, C(carbene)], 122.30, 121.83, 96.98, 95.67 (d, J 13C-C 7.03), 95.04 (d, J 13C-C 6.68), 72.09 (d, J 13C-C 14.05), 70.06 (d, J 13C-C 14.26), 69.79, 67.40, 65.77, 65.62, 61.26, 39.04, 32.63, 31.49, 29.69, 29.43; m/z (APCI) 477 (M⁺-1 100%).

Bromo(η⁵-1,5-cyclooctadiene)(1-ferrocenyl-3-propyl-1H-imidazol-2-ylidene)rhodium(I) (2):

[Brh(Cod)Cl]₂ (48 mg, 0.097 mmol); KOBu (24 mg, 0.213 mmol); 1-ferrocenyl-3-(propyl-2-yl)-1H-imidazolium bromide (79 mg, 0.213 mmol). Yield (71 mg, 73%) of a yellow powder; m.p. 242-243°C; IR (KBr cm⁻¹): 2929, 2870, 1501, 1485, 1230, 1123, 1039, 1009, 867, 725; ¹H NMR (CDCl₃): 7.32 (1H, d, J 2.0, NCH=NCH), 6.96 (1H, d, J 2.0 NCH=NCH), 5.15 (1H, m, CH-COD), 5.01 (1H, m, CH-COD), 4.32 (2H, t, J 1.5, C₂H), 4.26 (5H, s, C₂H), 4.21 (2H, t, J 1.5, C₂H), 3.25 (1H, m, CH-COD), 2.82 (1H, m, CH-COD), 2.27 (4H, m, CH₂-COD), 1.87 (4H, m, CH₂-COD), 1.52 (6H, t, J 9.5, CH₂); ¹³C NMR (CDCl₃): 181.86 (d, J 13C-C 50.57, C(carbene)), 122.65, 116.42, 97.66, 96.60 (d, J 13C-C 7.09), 96.46 (d, J 13C-C 7.18), 69.69, 69.40 (d, J 13C-C 14.42), 62.89, 65.81, 65.67, 33.23, 31.55, 29.36, 28.65, 23.51; m/z (APCI) 506 (M⁺-Br 100%).

Iodo(η⁵-1,5-cyclooctadiene)(3-ethyl-1-ferrocenyl-1H-imidazol-2-ylidene)rhodium(I) (3):

[Brh(Cod)Cl]₂ (41 mg, 0.083 mmol); KOBu (20.5 mg, 0.183 mmol); 1-ferrocenyl-3-propyl-1H-imidazolium iodide (68.5 mg, 0.183 mmol). Yield (51 mg, 52%) of a yellow powder; m.p. 205-206°C; IR (KBr cm⁻¹): 2931, 2869, 1569, 1499, 1407, 1291, 1105, 998, 868, 736; ¹H NMR (CDCl₃): 7.31 (1H, d, J 2.0, NCH=NCH), 6.96 (1H, d, J 2.0, NCH=NCH), 5.08 (2H, br, CH-COD), 4.43 (2H, br, C₂H), 4.25 (5H, s, C₂H), 4.22 (2H, br, C₂H), 3.19 (1H, m, CH-COD), 2.85 (1H, m, CH-COD), 2.25 (4H, br, CH₂-COD), 1.84 (6H, m, CH₂-COD + CH₃) 1.11 (3H, t, J 7.4, CH₃); ¹³C NMR (CDCl₃): 182.90 [d, J 50.57, C(carbene)], 122.14, 120.11, 97.52, 96.81 (d, J 13C-C 7.13), 96.34 (d, J 13C-C 6.98), 70.03 (d, J 13C-C 14.37), 67.92, 68.55 (d, J 13C-C 14.40), 68.26, 65.83, 65.69, 32.78, 32.77, 31.98, 31.04, 29.12, 28.99, 23.75, 11.59; m/z (APCI) 506 (M⁺-Br 100%).
2.25 (4H, m, CH<sub>2</sub>-COD) 1.89 (4H, m, CH<sub>2</sub>-COD), 1.52 (2H, m, CH<sub>2</sub>), 1.06 (3H, t J 7.3, CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>): 182.13 [d, J<sub>C(carbene)</sub> 49.06, C(carbene)], 122.0, 120.20, 97.23, 95.41 (d, J<sub>C(carbene)</sub> 7.10), 94.70 (d, J<sub>C(carbene)</sub> 6.89), 72.58 (d, J<sub>C(carbene)</sub> 14.17), 70.87 (d, J<sub>C(carbene)</sub> 14.19), 69.76, 67.59, 65.74, 65.60, 61.41, 51.69, 32.23, 31.26, 29.74, 29.37, 20.24, 13.96 m/z (APCI) 519 (M<sup>+</sup>-100%).

**Bromo(n<sup>1</sup>-1,5-cyclooctadiene)(3-benzyl-1-ferrocenyl-1H-imidazol-2-yldiene)rhodium(I) (6):**

![Image of complex](image)

[Rh(COD)Cl] (22.4 mg, 0.046 mmol); KOBu' (11.2 mg, 0.10 mmol); 3-benzyl-1-ferrocenyl-1H-imidazolium iodide (42.3 mg, 0.10 mmol). Yield (54 mg, 92%) of a yellow powder; m.p. 207-208°C; IR (KBr cm<sup>-1</sup>): 2932, 2875, 1650, 1500, 1407, 1231, 1118, 998, 870, 708; <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.43 (5H, m, ArH), 7.30 (1H, d, J 2.0, NCH=CHN), 6.78 (1H, d, J 2, NCH=CHN), 5.13 (2H, m, 2 × CH-COD), 4.34 (2H, br, C<sub>2</sub>H), 4.27 (5H, s, s C<sub>6</sub>H<sub>5</sub>), 4.24 (2H, br, C<sub>4</sub>H), 3.16 (1H, m, CH-COD), 2.92 (1H, m, CH-COD); <sup>13</sup>C NMR (CDCl<sub>3</sub>): 183.76 [d, J<sub>C(carbene)</sub> 50.57, C(carbene)], 136.22, 128.93, 128.46, 128.18, 128.34, 120.57, 97.32 (d, J<sub>C(carbene)</sub> 7.00), 96.47 (d, J<sub>C(carbene)</sub> 7.11), 70.28 (d, J<sub>C(carbene)</sub> 14.45), 69.78, 67.83, 68.92 (d, J<sub>C(carbene)</sub> 14.44), 68.14 65.90, 61.50, 32.51, 32.16, 29.19, 28.33; m/z (APCI) 553 (M<sup>+</sup>-Br 100%).

**Iodo(n<sup>1</sup>-1,5-cyclooctadiene)(1-ferrocenylphenyl-1-methyl-1H-imidazol-2-yldiene)rhodium(I) (7):**

![Image of complex](image)

[Rh(COD)Cl] (25 mg, 0.05 mmol); KOBu' (13.5 mg, 0.12 mmol); 1-ferrocenylphenyl-1-methyl-1H-imidazolium iodide (52.4 mg, 0.22 mmol). Yield (60 mg, 88%) of a yellow powder; m.p. 252-253°C; IR (KBr cm<sup>-1</sup>): 2933, 2875, 1529, 1459, 1413, 1243, 1106, 1077, 1002, 819, 728, 698; <sup>1</sup>H NMR (CDCl<sub>3</sub>): 8.13 (2H, d, J 18.3, ArH), 7.65 (2H, d, J 7.98, ArH), 7.17 (1H, d, J 1.9, NCH=CHN), 7.03 (1H, d, J 1.9, NCH=CHN), 5.19 (1H, m, CH-COD), 5.05 (1H, m, CH-COD), 4.76 (2H, br, C<sub>4</sub>H), 4.40 (2H, br, C<sub>4</sub>H), 4.09 (5H, s, s C<sub>6</sub>H<sub>5</sub>), 3.30 (1H, m, CH-COD), 2.77 (1H, m, CH-COD), 2.33 (2H, m, CH-COD), 2.13 (2H, m, CH-COD), 1.99 (2H, m, C<sub>6</sub>H<sub>5</sub>), 1.81 (4H, br, CH<sub>2</sub>-COD), 1.14 (3H, t, J 7.4, CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>): 182.33 [d, J<sub>C(carbene)</sub> 49.82, C(carbene)], 139.22, 138.12, 126.03, 124.71, 124.61, 121.35, 120.77, 97.04 (d, J<sub>C(carbene)</sub> 6.88), 96.90 (d, J<sub>C(carbene)</sub> 6.93), 84.04, 69.73, 69.48 (d, J<sub>C(carbene)</sub> 14.34), 68.92 (d, J<sub>C(carbene)</sub> 14.61), 66.62, 65.53, 53.23, 33.17, 31.73, 28.26, 28.75, 11.60; m/z (APCI) 581 (M<sup>+</sup>-Br 100%).

**Bromo(n<sup>1</sup>-1,5-cyclooctadiene)(1-ferrocenylphenyl)-3-propan-2-yl-1H-imidazol-2-ylidene)rhodium(I) (10):**

![Image of complex](image)

[Rh(COD)Cl] (25 mg, 0.05 mmol); KOBu' (13.5 mg, 0.12 mmol); 1-ferrocenylphenyl)-3-propan-2-yl-1H-imidazolium bromide (52 mg, 0.12 mmol). Yield (60 mg, 91%) as a yellow powder; m.p. 206-207°C; IR (KBr cm<sup>-1</sup>): 2935, 2875, 1529, 1459, 1413, 1243, 1106, 1077, 1002, 819, 728, 698; <sup>1</sup>H NMR (CDCl<sub>3</sub>): 8.13 (2H, d, J 18.3, ArH), 7.65 (2H, d, J 7.98, ArH), 7.17 (1H, d, J 1.9, NCH=CHN), 7.03 (1H, d, J 1.9, NCH=CHN), 5.19 (1H, m, CH-COD), 5.05 (1H, m, CH-COD), 4.76 (2H, br, C<sub>4</sub>H), 4.40 (2H, br, C<sub>4</sub>H), 4.09 (5H, s, s C<sub>6</sub>H<sub>5</sub>), 3.30 (1H, m, CH-COD), 2.77 (1H, m, CH-COD), 2.33 (2H, m, CH-COD), 2.13 (2H, m, CH-COD), 1.99 (2H, m, C<sub>6</sub>H<sub>5</sub>), 1.81 (4H, br, CH<sub>2</sub>-COD), 1.14 (3H, t, J 7.4, CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>): 182.33 [d, J<sub>C(carbene)</sub> 49.82, C(carbene)], 139.22, 138.12, 126.03, 124.71, 124.61, 121.35, 120.77, 97.04 (d, J<sub>C(carbene)</sub> 6.88), 96.90 (d, J<sub>C(carbene)</sub> 6.93), 84.04, 69.73, 69.48 (d, J<sub>C(carbene)</sub> 14.34), 68.92 (d, J<sub>C(carbene)</sub> 14.61), 66.62, 65.53, 53.23, 33.17, 31.73, 28.26, 28.75, 11.60; m/z (APCI) 581 (M<sup>+</sup>-Br 100%).
Results and Discussion

We have synthesized a series of ferrocenyl-NHC-Rh(I)(COD) (X) carbene complexes from appropriate ferrocenylimidazolium salts and [Rh(COD)Cl]2. The in situ deprotonation of the imidazolium salt with a base, and trapping the carbene with rhodium(I), was the synthetic route employed in the formation of the NHC complexes in this study. The dimeric chloro-bridged rhodium complex [Rh(COD)Cl]2, KOBu, and the corresponding imidazolium salts in THF under argon were stirred for 3h at room temperature. The resulting solution was concentrated and chromatographed on a column (silica gel, dichloromethane), affording the Rh-NHC complexes in good to excellent yields (Scheme 1).

The Rh-NHC complexes were characterized using IR, 1H NMR, 13C NMR, mass spectrometry and X-ray crystallography.

The 1H NMR and 13C NMR spectral data of the complexes, along with their assignments, are recorded in the experimental section. The 1H NMR spectra display two doublets at 7.0 and 7.2 ppm (J = 2.0), corresponding to the NCH=CHN unit of the imidazol-2-ylide. The spectra also reveal the disappearance of the C2(H) peak which normally appears at about 10 ppm for the imidazolium salts. The absence of the peak indicates that coordination to rhodium takes place at C(2). The signals of the protons of the bound imidazol-2-ylide ring appear at higher field than those of the unsubd ring, further indicating its coordination. From the 13C NMR spectrum, the four CH protons on the 1,5-cyclooctadiene (COD) ring are not equivalent (giving four signals at 5.15, 5.0, 3.25 and 2.9 ppm) which may be attributed to the spatial orientation of the COD.

A comparison of the 1H NMR chemical shifts of the N-ferrocenyl group of the imidazol-2-ylide with those of the 4-ferrocenylphenyl group assisted in the evaluation of the effect of a spacer group. There was a small difference in their chemical shift values which may be due to the presence of the spacer group between the imidazole-2-ylidene and ferrocene. In the absence of the spacer, the protons were shifted more to the presence of the spacer group assisted in the evaluation of the effect of a spacer group. There was a small difference in their chemical shift values which may be due to the presence of the spacer group between the imidazole-2-ylidene and ferrocene. In the absence of the spacer, the protons were shifted more upfield, implying some deshielding. However, this shift is insignificant, since the linking system is conjugated and a large chemical shift difference is not expected.

The 13C NMR spectrum shows the signal of the metalated carbon as a doublet between 181 and 183 (J$_{pp}$, C(carbene)). Other characteristic doublets were observed around at 95.90 (69.3, C(2)), 95.70 (69.5, C(7,7)), 71.51 (69.4, C(14,34)) and 71.17 (69.6, C(14,34)).

X-ray crystallography

X-ray diffraction data for the rhodium-NHC complex 3 was collected on an Oxford Xcalibur diffractometer with graphite-monochromated Mo Ka radiation at 173 (2) K. The collection method involved using a detector size of 0.3°. Data collection, data reduction and refinement were performed with the program CrystalsPro [15]. The crystal structures were solved by direct method, using the program SHELXS-97 [16]. Crystal structure refinement was carried out by SHELXL-97 [16]. Molecular graphics were generated by ORTEP-3 for Windows [17] and Mercury [18-21].

Scheme 1: Synthesis of ferrocenylimidazol-2-ylidene Rh(I)-NHC complexes.
The crystal structure of the rhodium complex 3 (Figure 1) was obtained with a single crystal grown from a mixture of dichloromethane and toluene. The ORTEP diagram of the molecule, showing its atom-numbering scheme, is shown in Figure 1. The complex crystallizes in the monoclinic space group P2₁/n with Z = 4. Least-squares refinement of the structure gave a final R factor of 0.0331. Details of crystal and structure refinement data are summarized in Table 2, while selected bond angles, bond lengths and torsion angles are listed in Table 1.

The structure exhibits a square planar geometry around the Rh(I) centre, with the imidazolylidene ring nearly perpendicular to the coordination plane as deduced from the torsional Br(1)-Rh(1)-C(1)-N(2) angles of -88.26(2)° and 93.07(2)°, respectively. The Rh-C(carbene) bond length of 2.0189(17) Å is in the range of a single bond. The average COD-Rh bond lengths are 2.1143 Å (trans to bromine) and 2.1571 Å (trans to imidazolylidene ring).

The X-ray determination of 3 was also useful as it reveals substitutional disorder of the bromine and chlorine atom on Rh(I) in the ratio of 0.96/0.04. The disorder arises from the reactants employed in the synthesis of Rh-NHC complex, 1-ferrocenyl-3-propyl-1H-imidazol-2-ylidene)rhodium(I). It is worthwhile to note that the yield of the compounds did not follow any particular pattern or depended on the substituent groups present. The simplicity, efficiency and milder conditions of this method makes it the synthetic route of choice for these reactions.

**Table 1:** Selected bond lengths (Å) and angles (°) of compound 3.

| Bond length         | Angle   |
|---------------------|---------|
| Rh(1)-C1            | 2.019(2)|
| Rh(1)-Br            | 2.516(3)|
| Rh(1)-C(17)         | 2.120(2)|
| Rh(1)-C(18)         | 2.109(2)|
| Rh(1)-C(21)         | 2.212(2)|
| Rh(1)-C(22)         | 2.203(2)|
| Rh(1)-C(1)          | 2.370(5)|
| N(1)-C(1)           | 1.368(2)|
| N(1)-C(3)           | 1.387(2)|
| N(2)-C(2)           | 1.379(2)|
| N(2)-C(4)           | 1.471(2)|
| N(1)-C(7)           | 1.427(2)|
| C(2)-C(3)           | 1.335(3)|
| Br(1)-Rh(1)-C(1)    | 90.66(5)|

**Table 2:** Crystal data and structure refinement for compound 3.

| Parameter                  | Value     |
|----------------------------|-----------|
| Empirical formula          | C₂₆H₂₅Br₃Cl₂FeN₃Rh |
| Formula weight             | 583.385   |
| Temperature (K)            | 173(2)    |
| Wavelength (Å)             | 0.71073   |
| Crystal system             | Monoclinic|
| Space group                | P2₁/n     |
| Unit cell dimensions       |           |
| a/Å                        | 10.295(3) |
| b/Å                        | 11.492(3) |
| c/Å                        | 19.119(5)|
| β/°                        | 107.565(5)|
| Volume (Å³)                | 2239.75(1)|
| Z                          | 4         |
| Density (calculated) g/cm³ | 1.7301(8) |
| Absorption coefficient (mm⁻¹) | 3.11   |
| F(000)                     | 1172      |
| Crystal size (mm³)         | 0.28 × 0.23 × 0.20 |
| Reflections measured       | 9834      |
| Reflections unique         | 4529[R(int) = 0.026] |
| Theta range for data collection (°) | 4.28-26.32 |
| Limiting indices           | -12<x<12 |
| -13<y<14                   | -16<z<23 |
| Goodness-of-fit on F²      | 0.9       |
| Data/restraints/parameters | 4529/0/268|
| Final R indices            | R1=0.260 |
| Largest diff. peak and hole (eÅ⁻³) | 0.516, -0.444 |

**Conclusion**

Novel ferrocenylimidazol-2-ylidene-rhodium complexes have been synthesized from ferrocenylimidazolium salts and [Rh(COD)Cl]₃. These carbene complexes have been characterized by IR, NMR, mass spectrometry and X-ray crystal structure analysis. The use of an in situ deprotonation method and trapping the resultant carbene with the rhodium metal centre proved efficient and straightforward.

**Supplementary Material**

CCDC 764293 contains the supplementary crystallographic data for compound 3. The data can be obtained free of charge.
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