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# Group 9 complexes of an N-heterocycle carbene bearing a pentafluorobenzyl substituent: attempted dehydrofluorinative coupling of cyclopentadienyl and N-heterocycle carbene ligands

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Dedicated to Prof. Dick Chambers on the occasion of his 70th birthday.

#### Abstract

Treatment of *N*-methylimidazole with pentafluorobenzyl bromide produces 1-pentafluorobenzyl-3-methylimidazolium bromide (1), which reacts with silver(I) oxide to give the N-heterocycle carbene (NHC) complex 1-pentafluorobenzyl-3-methylimidazolin-2-ylidene silver(I) bromide (2). Complex 2 acts as a carbene transfer reagent giving the complexes  $[(\eta^5-C_5Me_5)MCl_2(NHC)]$  (3a, M = Rh; 3b M = Ir) on reaction with  $[(\eta^5-C_5Me_5)MCl(\mu-Cl)]_2$ . An attempt to use intramolecular dehydrofluorinative coupling methodology to link the carbene and the pentamethylcyclopentadienyl ligands of  $[(\eta^5-C_5Me_5)RhCl(CN'Bu)(NHC)]BF_4$  was unsuccessful. © 2004 Elsevier B.V. All rights reserved.

Keywords: Imidazole; N-heterocycle carbene; Dehydrofluorinative carbon-carbon coupling

### 1. Introduction

N-heterocycle carbenes (NHCs) are strong  $\sigma$ -donors that, in some cases, have been found to be more effective ligands for organometallic catalysts than other two electron donor ligands, such as phosphines [1–4]. Increasingly, chelating ligands containing one or more NHC units and another functionality are finding importance [5]. Although complexes of  $\eta^5$ -cyclopentadienyl ligands are exceedingly common and important in organometallic chemistry, a complex containing a chelating  $\eta^5$ ,  $\kappa$ C-cyclopentadienyl-NHC ligand is yet to be reported. We have developed a convenient route to cationic rhodium and iridium complexes of chelating tri- and bi-functional cyclopentadienylphosphine ligands [6]. This route involves the intramolecular dehydrofluorinative coupling of coordinated  $\eta^5$ pentamethylcyclopentadienyl and phosphine ligands. The latter must bear a fluorinated aryl group susceptible to nucleophilic attack at an ortho position, such as pentafluorophenyl or tetrafluoropyridyl [6-8]. The development of such an approach to ligands containing an NHC functionality would obviate the problematic synthesis of a non-coordinated cyclopentadienyl-NHC ligand and its complexation. We therefore sought to investigate the possibility of using the intramolecular dehydrofluorinative coupling to prepare a cationic complex of a group 9 metal containing a chelating cyclopentadienyl-NHC ligand. Here we report the synthesis of pentamethylcyclopentadienyl rhodium and iridium complexes of an NHC bearing a pentafluorobenzyl substituent and the attempted intramolecular dehydrofluorinative carbon-carbon coupling of the two ligands.

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#### 2. Results and discussion

The pentafluorobenzyl-substituted imidazolinium salt **1** was prepared in 87% yield by treatment of *N*-methylimidazole with pentafluorobenzyl bromide in dichloromethane (Scheme 1). Salt **1** was characterized by elemental analysis and NMR spectroscopy, and the cation by mass spectrometry. As expected the <sup>1</sup>H NMR spectrum exhibits five resonances. The imidalozinium methylene and ethylene, benzyl and methyl hydrogen resonances occur at  $\delta$  10.81, 7.67, 7.61, 5.85 and 4.12, respectively, which are similar to those of the non-fluorinated analogue [2]. The three expected fluorine resonances occur at  $\delta$  –142.85, –153.51 and –161.79, which are assigned to *ortho, para* and *meta* fluorine atoms, respectively.

Silver NHC complexes, which are readily prepared from imidazolium salts and silver(I) oxide, act as NHC transfer reagents [1], removing the need to prepare free carbenes which are highly sensitive to moisture. The silver complex **2** was prepared by treatment of **1** with silver(I) oxide and isolated in 71% yield. The <sup>1</sup>H NMR spectrum of **2** exhibited only two higher frequency resonances indicative of the loss of the ring methylene hydrogen atom, and is consistent with the spectra of similar silver NHC complexes [9]. Attempts to characterize **2** by mass spectrometry were unsuccessful, and the formulation as a salt is based on that of the other silver NHC complexes [1,9,10]. Although **2** was not obtained analytically pure it was found amenable to further reaction and was used without further purification.

Treatment of the rhodium and iridium dimers  $[(\eta^5 C_5Me_5$ )MCl( $\mu$ -Cl)]<sub>2</sub> with 2 gave the NHC complexes 3a and 3b in 95 and 90% yield, respectively. The complexes displayed similar NMR spectra. The two heterocycle hydrogen resonances are at ca.  $\delta$  7.0 and 6.5 with a mutual coupling of ca. 2 Hz, and the methyl and pentamethylcyclopentadienyl hydrogen resonances occur at ca.  $\delta$  4.0 and 1.7, respectively. The methylene hydrogen atoms are diastereotopic and give broadened doublet resonances at ca.  $\delta$  6.0 and 5.5, with mutual coupling of ca. 15 Hz. These resonances sharpen on cooling and broaden on warming. The data are consistent with restricted rotation about the M-C(NHC) bond and a conformation of the carbene ligand with  $Cp^{\dagger}$ -Rh-C-N angles of ca.  $\pm 90^{\circ}$  (Fig. 1) leading to the nonequivalence of the methylene hydrogen atoms. Simple molecular models reveal that steric reasons can explain the preference for this conformation and the restricted rotation. Studies of other NHC complexes have revealed that any restriction of rotation is for steric reasons alone [9,11]. Variable temperature NMR spectra of 3a and 3b were recorded in order to obtain the energy barriers to rotation,





 $\Delta G^{\ddagger}$ , about the M–C(NHC) bonds. Significant broadening of the benzyl resonances was observed in the <sup>1</sup>H NMR spectra up to 323 K (at a spectrometer frequency of 300 MHz), but the coalescence temperatures could not be reached in CDCl<sub>3</sub>. Unfortunately the compounds were insufficiently soluble in toluene, even at elevated temperature, for their NMR spectra to be recorded. A minimum value of  $\Delta G^{\ddagger}$  of 62 kJmol<sup>-1</sup> for both complexes was obtained from the spectra in CDCl<sub>3</sub> [12–14]. Values of  $\Delta G^{\ddagger}$  of 60 kJ mol<sup>-1</sup> upwards have been obtained for four coordinate group 9 metal(I) benzyl-NHC complexes with ligands less bulky than  $\eta^5$ -pentamethylcyclopentadienyl [9]. The *ortho, para* and *meta* fluorine resonances occur at ca.  $\delta$  –141, –152 and –160, respectively, showing that rotation about the C–C<sub>6</sub>F<sub>5</sub> bond is not hindered.

Treatment of complex 3a with *t*-butylisonitrile in the presence of an excess of sodium tetrafluoroborate gave the salt 4, in 75% yield (Scheme 1). The identity of the salt was confirmed by elemental analysis, and that of the cation by mass spectrometry. The IR spectrum exhibits  $\nu(C=N)$  at  $2200 \text{ cm}^{-1}$ , which is the same as that of  $[(\eta^5 C_5Me_5$ )RhCl<sub>2</sub>(CN<sup>*t*</sup>Bu)] [15]. The <sup>1</sup>H and <sup>19</sup>F NMR spectra are also consistent with this formulation, but show the presence of two isomers in a ca. 1:1 ratio. The <sup>19</sup>F spectra show two pairs of resonances for the ortho, para and meta fluorine atoms. The <sup>1</sup>H NMR spectrum exhibits three broadened singlets at  $\delta$  3.93, 1.84 and 1.60 assigned to the N-methyl, pentamethylcyclopentadienyl and butyl hydrogen atoms, and six resonances in the region  $\delta$  5.0–7.5, with a total integration of four hydrogen atoms relative to that of three for the *N*-methyl resonance, which can be assigned to the NCH<sub>2</sub> and HCCH hydrogen atoms. The data are consistent with the two pairs of enantiomers shown in Scheme 1. These arise from the stereogenic rhodium atom and rotamers from the restriction of the rotation about the M-C(NHC) bond. It is presumed that it is the bulk of the <sup>t</sup>Bu group that increases  $\Delta G^{\ddagger}$  significantly relative to **3a**.

In an attempt to induce dehydrofluoroinative carboncarbon coupling of the pentamethylcyclopentadienyl and NHC ligands salt **4** was treated with proton sponge. No reaction was observed by NMR over several days or at elevated temperatures (up to 323 K).

#### 3. Conclusion

Pentafluorobenzyl-substituted NHC complexes of rhodium and iridium have been conveniently prepared by the use of a silver transfer reagent. In both complexes there is restricted rotation about the M–C bond, which is proposed to arise from the bulk of the ligands. A cation was generated from the neutral rhodium complex by abstraction of a chloride and addition of <sup>*t*</sup>butylisonitrile. No intramolecular dehydrofluorinative coupling was observed on addition of proton sponge. The restricted rotation about the M–C bond may account for the lack of reaction, since this may prevent the pentafluorophenyl group from adopting a conformation necessary for the reaction. Further investigations into the intramolecular dehydrofluorinative coupling of pentamethylcyclopentadienyl to NHC ligands are in progress.

#### 4. Experimental

#### 4.1. Instrumentation

The <sup>1</sup>H and <sup>19</sup>F NMR spectra were recorded in CDCl<sub>3</sub> using a Bruker DPX300 or DRX500 spectrometer. <sup>1</sup>H (300.01 or 500.13 MHz) were referenced internally using the residual protio solvent resonance relative to SiMe<sub>4</sub> ( $\delta$  0) and <sup>19</sup>F (282.26 MHz) externally to CFCl<sub>3</sub> ( $\delta$  0). All chemical shifts are quoted in  $\delta$  (ppm), using the high frequency positive convention, and coupling constants in Hz. Infrared spectra were recorded on a Perkin-Elmer RX.1 FT-IR spectrophotometer. Mass spectra were recorded on a VG Autospec X-series mass spectrometer. Elemental analyses were performed by A.S.E.P., The School of Chemistry, Queen's University Belfast.

### 4.2. Materials

*N*-methylimidazole, benzyl chloride, silver(I) oxide and <sup>*t*</sup>butylisonitrile (Aldrich) were used as supplied.  $[(\eta^5-C_5Me_5)MCl(\mu-Cl)]_2$  (M = Rh or Ir) were prepared as previously described [16].

# *4.3. 1-Pentafluorobenzyl-3-methylimidazolium bromide* (1)

Pentafluorobenzyl bromide (3.92 g, 15.0 mmol) was added to *N*-methylimidazole (1.23 g, 15.0 mmol) in dichloromethane (100 cm<sup>3</sup>) and the solution left at ambient temperature for 20 h, after which time the colourless solid that formed was collected by filtration and washed with toluene (2 × 10 cm<sup>3</sup>). Concentration of the filtrate produced more solid, which was treated as before. The product was obtained as a colourless crystalline solid (4.37 g, 87.4%). Anal. Calcd. for C<sub>11</sub>H<sub>8</sub>N<sub>2</sub>BrF<sub>5</sub>·0.5CH<sub>2</sub>Cl<sub>2</sub>: C, 35.8%; H, 2.35%; N, 7.3%. Found C, 36.9%; H, 2.7%; N, 7.7%. LSIMS: 263 ( $M^+$ ), 245 ([M - F + H]<sup>+</sup>), 181 ([C<sub>6</sub>F<sub>5</sub>CH<sub>2</sub>]<sup>+</sup>). HRLSIMS:  $C_{11}H_8F_5N_2$  requires 263.06077; found:  $M^+$  263.06014. <sup>1</sup>H NMR:  $\delta$  10.81 (1H, s, NCHN), 7.67 (1H, s, HCCH), 7.61 (1H, s, HCCH), 5.85 (2H, s, NCH<sub>2</sub>), 4.12 (3H, s, NCH<sub>3</sub>). <sup>19</sup>F NMR:  $\delta$  –142.85 (2F, s, F<sub>o</sub>), –153.51 (1F, s, F<sub>p</sub>), –161.79 (2F, s, F<sub>m</sub>).

# 4.4. 1-Pentafluorobenzyl-3-methylimidazolin-2-ylidene silver(I) bromide (2)

Silver oxide (0.15 g, 0.65 mmol) was added to **1** (0.21 g, 0.61 mmol) in dichloromethane (100 cm<sup>3</sup>) and the mixture stirred in the absence of light at ambient temperature for 2 h. The reaction mixture was filtered through celite, which was then washed with dichloromethane (2 × 10 cm<sup>3</sup>). The combined filtrate and washings were concentrated by rotary evaporation to yield a pale yellow solid (0.41 g, 70.7%). Complex **2** was not characterized by elemental analysis, but its identity is confirmed by complexes **3a**, **3b** and **4**. <sup>1</sup>H NMR:  $\delta$  7.26 (1H, s, HCCH), 7.02 (1H, s, HCCH), 5.46 (2H, s, NCH<sub>2</sub>), 3.87 (3H, s, NCH<sub>3</sub>). <sup>19</sup>F NMR:  $\delta$  -140.84 (2F, s, F<sub>o</sub>), -151.12 (1F, s, F<sub>p</sub>), -159.92 (2F, s, F<sub>m</sub>).

## 4.5. $\eta^5$ -Pentamethylcyclopentadienylrhodium(1pentafluorobenzyl-3-methylimidazolin-2-ylidene) dichloride (**3a**)

A solution of  $[{(\eta^5-C_5Me_5)RhCl(\mu-Cl)}_2]$  (0.068 g, 0.11 mmol) and 2 (0.10 g, 0.11 mmol) in dichloromethane (100 cm<sup>3</sup>) was left at an ambient temperature for 15 h. The reaction mixture was filtered through celite, which was washed with dichloromethane (20 cm<sup>3</sup>). The combined filtrate and washings were concentrated by rotary evaporation to give an orange oil, which was recrystallized from chloroform to yield an orange solid (0.06 g, 95.2%). Anal. Calcd. for C<sub>21</sub>H<sub>22</sub>Cl<sub>2</sub>N<sub>2</sub>Rh·0.5CHCl<sub>3</sub>: C, 40.9%; H, 3.6%; N, 4.4%. Found C, 41.2%; H, 3.75%; N, 4.6%. LSIMS: 535  $[M - Cl]^+$ . HRLSIMS: C<sub>21</sub>H<sub>22</sub>N<sub>2</sub>ClF<sub>5</sub>Rh requires 535.04467; found:  $M^+$  535.04730. <sup>1</sup>H NMR:  $\delta$  7.01 [1H, d, <sup>3</sup>*J*(HH) 2.0, *H*CCH'], 6.58 [1H, d, <sup>3</sup>*J*(HH) 2.0, HCCH'], 6.06 [1H, d, <sup>2</sup>*J*(HH) 14.6, NC*H*H'], 5.49 [1H, d, <sup>2</sup>*J*(HH) 14.6, NCHH'], 4.06 (3H, s, NCH<sub>3</sub>), 1.68 (15H, s, C<sub>5</sub>CH<sub>3</sub>). <sup>19</sup>F NMR:  $\delta - 140.96$  (2F, m, F<sub>o</sub>), -151.73 [1F, t, <sup>3</sup>J(FF) 21.6,  $F_n$ ], -160.35 (2F, m,  $F_m$ ).

## 4.6. $\eta^5$ -Pentamethylcyclopentadienyliridium-(1-pentafluorobenzyl-3-methylimidazolin-2-ylidene) dichloride (**3b**)

A solution of  $[\{(\eta^5-C_5Me_5)IrCl(\mu-Cl)\}_2]$  (0.12 g, 0.15 mmol) and 2 (0.14 g, 0.16 mmol) in dichloromethane (100 cm<sup>3</sup>) was left at an ambient temperature for 3 h. The mixture was filtered through celite, which was washed with dichloromethane (2 × 10 cm<sup>3</sup>). The solvent was removed from the combined filtrate and washings by rotary evaporation to give a yellow oil, which was recrystallized from chloroform to yield a yellow solid (0.18 g, 90%). Anal.

Calcd. for C<sub>21</sub>H<sub>22</sub>N<sub>2</sub>Cl<sub>2</sub>F<sub>5</sub>Ir.CHCl<sub>3</sub>: C, 33.9%; H, 3.0%; N, 3.6%. Found C, 34.0%; H, 2.65%; N, 3.8%. HRLSIMS: C<sub>21</sub>H<sub>22</sub>N<sub>2</sub>ClF<sub>5</sub><sup>193</sup>Ir requires 625.10211; found:  $M^+$  625.10487. <sup>1</sup>H NMR:  $\delta$  6.93 [1H, d, <sup>3</sup>*J*(HH) 1.9, *H*CCH'], 6.50 [1H, d, <sup>3</sup>*J*(HH) 1.9, HCCH'], 6.05 [1H, d, <sup>2</sup>*J*(HH) 15.4, NCHH'], 5.47 [1H, d, <sup>2</sup>*J*(HH) 15.4, NCHH'], 3.99 (3H, s, NCH<sub>3</sub>), 1.66 (15H, s, C<sub>5</sub>CH<sub>3</sub>). <sup>19</sup>F NMR:  $\delta$  –141.19 (2F, m, F<sub>o</sub>), -151.88 [1F, t, <sup>3</sup>*J*(FF) 20.4, F<sub>p</sub>], -160.54 (2F, m, F<sub>m</sub>).

# 4.7. [η<sup>5</sup>-Pentamethylcyclopentadienylrhodium-(1-pentafluorobenzyl-3-methylimidazolin-2-ylidene) <sup>t</sup>butylisonitrilechloride]tetrafluoroborate (4)

Complex 3a (0.10 g, 0.185 mmol) was treated with tertbutylisocyanide (0.015 g, 0.175 mmol) and NaBF<sub>4</sub> (0.18 g, 1.73 mmol) in a solution of dichloromethane  $(30 \text{ cm}^3)$  and methanol (20 cm<sup>3</sup>). After stirring for 1 h, the solvent was removed by rotary evaporation and the product extracted into dichloromethane. The solvent was removed from the filtrate by rotary evaporation to yield a yellow solid (0.09 g, 75%). Anal. Calcd. for C<sub>26</sub>H<sub>31</sub>N<sub>3</sub>BClF<sub>9</sub>Rh: C, 44.25%; H, 4.4%; N, 5.95%. Found C, 43.5%; H, 4.4%; N, 5.6%. HRLSIMS: C<sub>26</sub>H<sub>31</sub>N<sub>3</sub>ClF<sub>5</sub>Rh requires 618.11817; found:  $M^+$  618.11495. <sup>1</sup>H NMR:  $\delta$  7.35 (1H, br s, HCCH), 7.26 (1H, br s, HCCH), 6.77 (2H, br s, HCCH), 6.12 [1H, br d, <sup>3</sup>*J*(HH) 16.7, NCHH'], 5.36 (2H, br m, NCH<sub>2</sub>), 5.09 [1H, br d, <sup>3</sup>*J*(HH) 16.7, NCH*H*'], 3.93 (3H, br s, NCH<sub>3</sub>), 1.84 (15H, br s, C<sub>5</sub>CH<sub>3</sub>), 1.60 (9H, br s, <sup>t</sup>Bu). <sup>19</sup>F NMR: δ – 141.15 (2F, d, J 21.5, F<sub>o</sub>), -141.82 (2F, d, J 15.6, F<sub>o</sub>), -151.25 (1F, s, F<sub>p</sub>), -152.00 (1F, s, F<sub>p</sub>), -153.01 (1.6F, s,  ${}^{10}\text{BF}_4^-$ ), -153.07 $(6.4F, s, {}^{11}BF_4^-), -160.25 (2F, m, F_m), -161.14 (2F, m, F_m).$  $\nu$ (C=N) 2200 cm<sup>-1</sup>.

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