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Note

Solvent influence in the formation of normal and abnormal carbene complexes in reactions of imidazolium salts with $[Ir(H)_2(PPh_3)_2(OCMe_2)_2]BF_4$

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ABSTRACT

Abnormal and normal carbene complexes are formed in reactions of 2-pyridylmethylimidazolium salts with $[Ir(H)_2(PPh_3)_2(OCMe_2)_2]BF_4$ at room temperature in tetrahydrofuran (THF) or dichloromethane (CH_2Cl_2). Reactions in THF lead to the formation of abnormal carbene (C-5 bound), while reactions in CH_2Cl_2 lead to formation of normal carbene (C-2 bound).

1. Introduction

N-heterocyclic carbenes (NHC's) have become ligands of great interest in homogeneous catalysis and organometallic chemistry [1–6]. All of the examples before 2001 involved binding through the C-2 position (normal carbene), the same position as in the free carbene isolated by Arduengo et al. [7]. Since the first publications on the binding of the metal via the C-5 position (abnormal carbene) [8], there has been increasing interest in this abnormal binding mode [9,10]. It is now clear that abnormal carbenes have good potential as ligands since they are much stronger electron donors than their normal counterparts [11].

Since the discovery of the abnormal carbene, mechanistic work was done to make clearer how this unusual product is formed. Crabtree et al. [12] showed that the normal and abnormal carbenes formed from the reaction with $Ir(H)_5(PPh_3)_2$ occur via different paths, C2 (N path) and C5 (An path) depending on the anion involved. Tight ion pairing between the cationic complex and the anion were invoked to account for the different outcomes. In this note, we show that the reaction is also solvent dependent. Again outer sphere interactions are invoked, but in this case, the solvent is proposed to be involved in favoring or disfavoring tight ion pairing.

Three main synthetic methods have been utilized to make the carbene complexes. These include, formation of the free carbene via a strong base, then complexation with the metal [1–5]. This procedure always gives the normal carbene (C-2) due to the stability of the free carbene at that position [7,13]. The second is reaction with Ag salts to give the silver NHC, followed by transmetallation, which can give either normal or abnormal carbenes [11,14,15]. The most atom-efficient, in view of the absence of coreactant base or silver salt, is the CH activation method. This method was developed in Crabtree's lab with $Ir(H)_5(PPh_3)_2$ as a metal precursor and refluxing THF as a solvent. This method leads to formation of either normal or abnormal carbene complexes (Scheme 1) [16].

2. Experimental

2.1. General methods

N-butyl-*N*′-(2pyridylmethyl) imidazolium bromide (**1b**) [16], *N*-isopropyl-*N*′-(2pyridylmethyl) imidazolium bromide (**1a**) [16] and $[Ir(H)_2(PPh_3)_2(OCMe_2)_2]BF_4$ (**2**) [17], were prepared according to literature methods; all other reagents are commercially available and were used as received. Br/BF_4^- anion exchange was accomplished by stirring the Br imidazolium salt with $AgBF_4$ in acetone at RT and overnight.

2.2. Typical synthesis

A mixture of **1b** (16 mg, 0.053 mmol), **2** (50 mg, 0.054 mmol) and if used $NaHCO_3$ (15 mg, 0.18 mmol) in 7 mL of CH_2Cl_2 or THF were stirred at 25 °C for 35 min. If $NaHCO_3$ was used, the solution was filtered through celite or sand and added to about 50 mL pentane. The off-white solid immediately precipitated and was filtered

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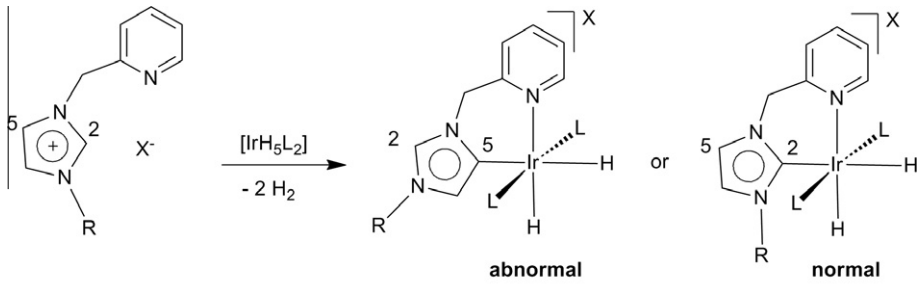


Scheme 1. CH activation method to abnormal or normal carbenes using $Ir(H)_5(PPh_3)_2$.

off and dried. Typical yield: 40–45 mg (74–83%). Full spectroscopic data for **3** [12] and **4** [16] has been published. We are including representative ^{1}H NMR spectra for abnormal and normal carbenes.

2.3. Representative ^{1}H NMR spectra

^{1}H NMR for **3b** ($CDCl_3$, 298 K): δ 7.90 (d, 1H, H_{py}), 7.63 (d, 1H, H_{py}), 7.52 (m, 1H, H_{py}), 7.51 (d, 1H, H_{im}), 7.31–7.16 (m, 30H, H_{py}, H_{ph}), 6.34 (d, 1H, H_{im}), 6.15 (t, 1H, H_{py}), 4.86 (s, 2H, CH_2), 2.87 (m, 2H, CH_2), 0.90 (m, 4H, CH_2, CH_2), 0.62 (t, 3H, CH_3), −11.17 (dt, 1H, Ir-H), −20.97 (dt, 1H, Ir–H)

^{1}H NMR for **4b** ($CDCl_3$, 298 K): δ 8.71 (s, 1H, NCHN), 8.19 (d, 1H, H_{py}), 7.37–7.15 (m, 32H, H_{py}, H_{ph}), 6.07 (t, H_{py}), 5.03 (s, 1H, H_{im}), 4.72 (s, 2H, CH_2), 3.63 (t, 1H, CH_2), 1.47 (m, 2H, CH_2), 1.17 (m, 2H, CH_2), 0.90 (t, CH_3), −10.89 (dt, Ir–H), −19.61 (dt, Ir–H).

2.4. Acid conversion

A 1:1 mixture of **4** and 54% wt HBF_4 in CH_2Cl_2 was stirred at RT for 2 h.

3. Results and discussion

This note reports an even simpler synthetic pathway to these unusual carbene complexes. This method was previously used to synthesize a normal carbene complex for mechanistic studies [12], but we now discuss it and its extensions in more detail in this note. The novel point is the presence of mild base, incapable of direct deprotonation of an imidazolium salt, that nevertheless allows room temperature reaction leading to formation of either abnormal or normal carbene complexes from $[Ir(H)_2(PPh_3)_2(OCMe_2)_2]BF_4$ (**2**) by reaction with the popular pyridine-substituted imidazolium salts, in this case with an isopropyl or n-butyl wingtip group (**1a or b**). The reaction yields following results (Scheme 2).

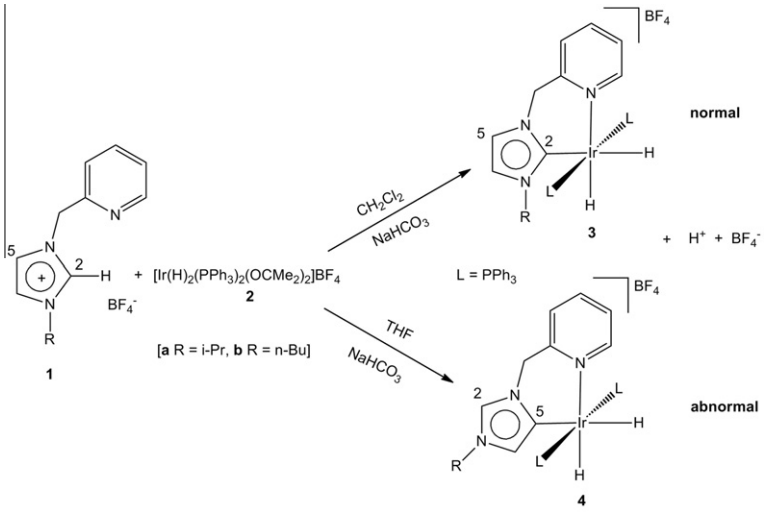
Both products were isolated and are extremely stable in air for prolonged periods of time. When the iridium precursor is reacted with the imidazolium ligand in CH_2Cl_2, at RT for 35 min, normal carbene is observed. If this solution is left standing, the normal carbene starts to decompose. When the same reaction is performed in THF, the mixture of abnormal and normal carbene is observed. In addition, it was noticed that if this reaction mixture was left standing, it undergoes conversion of the abnormal into the normal carbene. The reaction equation shows that there is one equivalent of H^+ BF_4^- formed during the reaction, as written in Scheme 2. It was our belief that this internal acid was the catalyst for the conversion, of the abnormal carbene into normal carbene, and for the decomposition of the normal carbene. In CH_2Cl_2, this conversion occurs readily, however in THF the conversion slows down due to the buffering of the acid by the large excess of THF. When sodium bicarbonate is added as a reactant in order to neutralize the internal acid, the reaction still leads to the formation of the normal carbene in CH_2Cl_2 but now leads to formation of only abnormal carbene in THF.

It is no doubt the low solubility of sodium bicarbonate in CH_2Cl_2 is preventing abnormal carbene formation after 35 min. However, if the reaction is followed in an NMR tube, then the abnormal carbene is detected, but the complete conversion to normal carbene occurs within minutes. In THF, the added base slows down the conversion of the abnormal carbene to normal carbene. This is likely due to the increased solubility of the base in the THF, in addition to the ability of THF to buffer the acid. Separate experiments in which an abnormal carbene was reacted with one equivalent HBF_4 in CH_2Cl_2 (overnight) led to the complete conversion of the abnormal to normal carbene (Scheme 3). In addition abnormal carbene did not convert to normal carbene without acid even after heating at 100 °C in trifluorotoluene, so our conclusion is that the acid is necessary for the conversion.

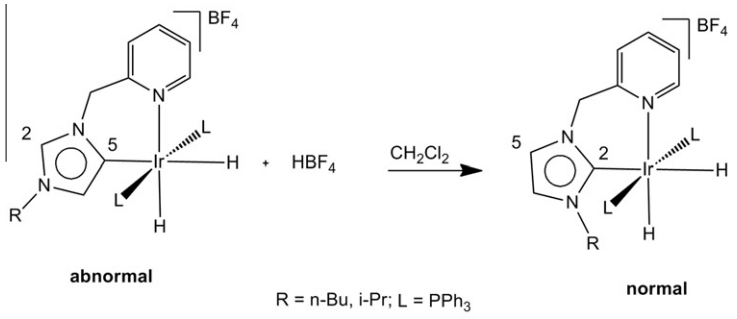
Conversion of the normal to abnormal carbene does not occur under similar conditions with or without acid. This is a good indication that the normal carbene is the thermodynamic product.

Both products were identified using ^{1}H NMR ($CDCl_3$) by comparison with literature data [12,16]. Experience of having isolated both products in previous research has provided us with a simple NMR "fingerprint" for each product. When distinguishing between the normal and abnormal carbenes the most telling are the imidazolium H signals. In the abnormal carbene complexes, the imidazolium hydrogens are in sufficiently different environments, thus their chemical shift difference is greater than 3 ppm. The normal carbenes have a much more similar chemical shift, differing only by about 1 ppm. Comparing the imidazolium signals from normal carbene (**3**) and abnormal carbene (**4**), shows that the two imidazolium H's of normal carbene have signals at 6.34 and 7.51 ppm. Abnormal carbene shows two signals at 5.03 and 8.71 ppm. This provides clear evidence of different binding modes in the two complexes. A more detailed look at the NMR data of the two complexes can be found in previous research papers [12,16].

This reaction requires that the ligands have a covalently-attached pyridine wingtip group. Reactions in which free pyridine and free imidazolium salts were added in a 1:1 mixture for reaction with iridium precursor (**2**) led only to the binding of pyridine to the metal, the imidazoluim salt persisted unchanged. It seems likely that in the reaction of Scheme 2, the pyridine moiety binds to the metal first, which brings the imidazolium salt close to the metal, the two acetone groups being easily displaced with any pyridine. What happens next is unclear, but one feasible mechanism, includes C–H bond cleavage, and then the dissociation of H^+. No trace of the ion effect seen in the previous reaction with $Ir(H)_5(PPh_3)_2$ is present here, the product being independent of the anion originally present in the imidazolium salt. One explanation could be that the bicarbonate ion replaces the original anions



Scheme 2. New CH activation method to abnormal or normal carbenes using $[Ir(H)_2(PPh_3)_2(OCMe_2)_2]BF_4$.



Scheme 3. Acid catalyzed conversion of the abnormal carbene to normal carbene.

present in the imidazolium salt, so that the original anions are irrelevant. However, when a coordinating anion like bromine is used, the reaction leads to a mixture of products, none of which could have been identified as either normal or abnormal carbenes.

4. Conclusions

$Ir(H)_5(PPh_3)_2$ was previously shown to be a very efficient metal precursor for the N-heterocyclic carbene complexes, but it is now clear that $[Ir(H)_2(PPh_3)_2(OCMe_2)_2]BF_4$ can be an even better precursor. All the reactions are performed in air, with wet solvents and at 25 °C. It is especially interesting, and potentially very useful to see that just by changing a solvent, and a common solvent at that, one can produce normal or abnormal carbene complex.

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