

Reversible α -elimination in the conversion of N-CH₃ to N-CH=Ir by double C-H activation

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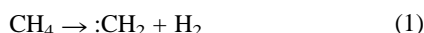
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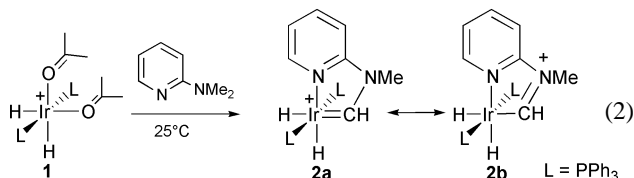
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2-Dimethylaminopyridine (pyNMe₂; py = 2-pyridyl) reacts with [H₂Ir(OCMe₂)₂L₂]⁺ (L = PPh₃) to give a cyclic carbene complex [H₂Ir(=CHN(Me)py)L₂]⁺ via an oxidative addition, reversible α -elimination sequence.

The conceptual conversion of eqn. (1) is highly endothermic ($\Delta H = 111$ kcal mol⁻¹, triplet; 119 kcal mol⁻¹, singlet). If the carbene is sufficiently stabilized by a metal fragment and by π -donor heteroatom substitution in the α -position (Fischer carbene), however, such a conversion becomes thermodynamically allowed. For example, both alkene to carbene¹⁻³ and THF to carbene^{4,5} rearrangements of this sort are known, but elevated temperatures may be required for satisfactory rates.⁴⁻⁵

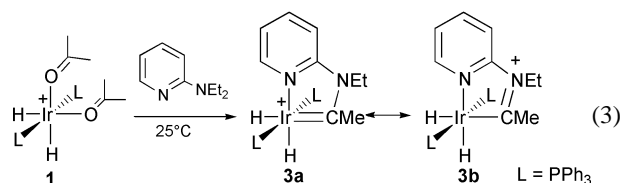


We now report a room-temperature route for the title reaction [eqn. (2)] via the activation of two geminal C-H bonds and liberation of H₂.



We find that 2-dimethylaminopyridine (pyNMe₂, 1 equiv.) reacts with [IrH₂(OCMe₂)₂L₂]⁺BF₄⁻ **1** in CH₂Cl₂ at 25 °C to give the cyclic heteroatom-stabilized carbene complex **2** (25 °C, 15 min, 78%), by a net reaction that resembles eqn. (1).[†] The identity of the product follows from the ¹H NMR spectrum, in particular the appearance of a low-field singlet of intensity 1H at δ 11.71 assigned to the CH=Ir proton. The NMe group of intensity 3H appears as a singlet at δ 3.50. The two inequivalent hydrides (1H each) resonate at δ -9.98 and δ -17.78 as triplets of doublets (²J_{PH} 16, ²J_{HH'} 4 Hz), indicating each is *cis* to the two phosphines. The ¹³C NMR shows a low-field resonance at δ 155.9 characteristic of Fischer carbenes.

The reaction is also possible for 2-diethylaminopyridine (pyNEt₂, 1 equiv.) to give the analogous product **3** (25 °C, 15 min, 80%), shown in eqn. (3). The spectral data for **3** is similar



to that for **2**, in particular, the ¹H NMR spectrum shows high-field resonances at δ -10.80 and δ -17.92, characteristic of terminal iridium(III) hydrides. The two hydrides (²J_{PH} 17 Hz, ²J_{HH'} 4 Hz) are mutually coupled and coupled to the PPh₃ ligands. The formation of **3** was also confirmed by a crystal structure determination (Fig. 1).[‡] The Ir-C distance of 2.018 Å is consistent with predominant single bond character while the C-N bond distance of 1.322 Å indicates some multiple bond

character as expected from the resonance form **3b** generally preferred by Fischer carbenes. Even with β -hydrogen atoms available, we see only the α -elimination product **3**. Preferred α -vs. β -elimination in metal alkyls has been reported.^{6,7}

The evidence discussed below suggests formation of **2** proceeds by initial C-H bond activation, perhaps to form an intermediate H₂ complex **5**. Loss of H₂ leads to an alkyl, **6**, which then rearranges to the observed carbene **2**, by α -elimination (Scheme 1).

Formation of an agostic C-H...M bond is typical in complexes related to **1**. For example, the known 2,6-di-

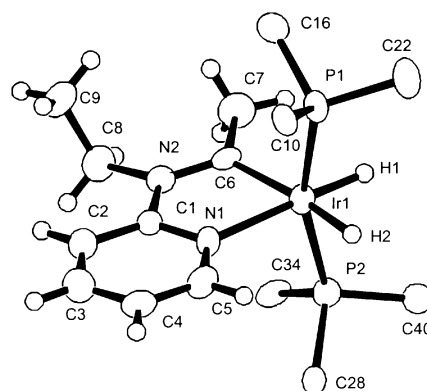
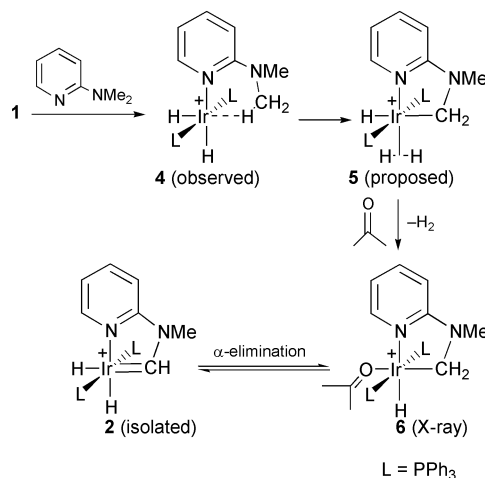
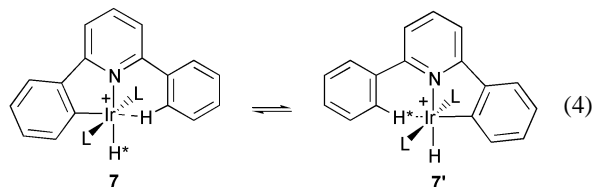


Fig. 1 An ORTEP view of the cation of [Ir(PPh₃)₂(pyNEtC-MeH₂)]BF₄·CH₂Cl₂ **3**. Selected bond lengths (Å): Ir(1)-C(6) 2.018(5), Ir(1)-N(1) 2.142(4), N(2)-C(1) 1.410(6), N(2)-C(6), 1.332(7). Only the *ipso* carbons of PPh₃ are shown for clarity. The ligand H atoms are in calculated positions. The hydrides were refined with Ir(1)-H(1) 1.43(5) Å and Ir(1)-H(2) 1.47(5) Å, no doubt shortened by systematic error.

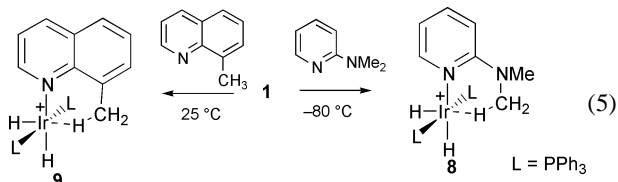


Scheme 1

phenylpyridine species **7**,⁸ is fluxional [eqn. (4)] via a pathway analogous to that of Scheme 1. To probe the formation of a



possible agostic C–H...M intermediate **4** in the present case, we treated **1** in CD₂Cl₂ with pyNMe₂ at low temperature and monitored the reaction by ¹H NMR. At –80 °C, a new species, **8**, is seen that is too reactive to isolate [eqn. (5)]. After 40 min



at 0 °C, it converts to **2**. Comparison of **8** with the fully characterized, stable material **9**, made via the route of eqn. (5),⁹ shows very close ¹H NMR spectral similarities, suggesting **8** has the agostic structure, **4**, shown in Scheme 1. For example, the inequivalent hydrides resonate as a pair of signals (**8**, δ –20.69, δ –29.84; **9**, δ –19.20, δ –28.60) coupled both to two *cis* phosphines (**8**, ²*J*_{PH} 17 Hz; **9**, ²*J*_{PH} 15 Hz) and to each other (**8**, ²*J*_{HH'} 7 Hz; **9**, ²*J*_{HH'} 8 Hz).

Net loss of H₂ occurs and free H₂ was detected (δ 4.2) in the ¹H NMR spectrum of the reaction mixture. After loss of H₂ to generate a vacant site *cis* to the newly formed iridium alkyl, an α-elimination gives the final product.

Reversible α-elimination is rare,⁶ but remarkably, this process is facile in this system. Dissolving the carbene **2** in acetone rapidly gives **6** by reversal of the α-elimination step. The Ir–H of the product **6** resonates as a triplet at δ –16.14 (²*J*_{PH} 14 Hz). This colorless alkyl complex was crystallized from acetone–diethyl ether and characterized by a crystal structure (Fig. 2). The equilibration of **2** and **6** was further probed by ¹H NMR. The colorless alkyl complex **6** dissolved in fresh CD₂Cl₂ at 25 °C with loss of acetone to give the yellow carbene **2** within seconds. In a typical case, **6**:**2** occur as a 1:1 ratio (integration

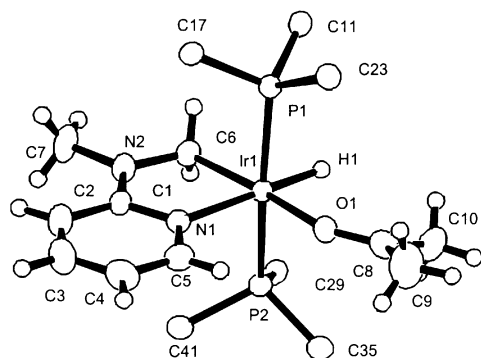


Fig. 2 An ORTEP view of the cation of [Ir(PPh₃)₂(pyNMeCH₂)(Me₂CO)(H)]BF₄·Me₂CO, **6**. Selected bond lengths (Å) are: Ir(1)–C(6) 2.072(5), Ir(1)–N(1), 2.126(4), N(2)–C(1) 1.338(7), N(2)–C(6) 1.480(7). The ligand H atoms and the hydride are shown in calculated positions.

of the hydride peaks). Incremental addition of acetone to the solution then led to displacement of the equilibrium in favor of **6**. For example, when 2 and 3 equivalents of acetone were added, the mole ratio of **6**:**2** became 2:1 and 3.3:1, respectively.

Several factors may make the rearrangement of the agostic species (**8**) to the carbene (**2**) thermodynamically favorable, in contrast with the highly endothermic base case of eqn. (1). The metal complexation stabilizes the carbene but this is not sufficient on its own, as shown by the failure of the agostic 8-methylquinoline species **9** to convert to the corresponding carbene, a species that is as yet unknown. Heteroatom stabilization by the adjacent amino group is clearly an important stabilizing factor. In addition, carbene **2** can be considered as a metallacycle with 10 π-electrons, which could in principle benefit from aromatic stabilization.

In summary, we have a rare double C–H activation route that provides a mild and fast synthetic method to generate chelating Fischer carbene complexes.

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Notes and references

† *Synthesis*: **2**: the BF₄ salt of **1** (280 mg, 0.3 mmol) was dissolved in degassed CH₂Cl₂ (4 mL) and 2-dimethylaminopyridine (37 mg, 0.3 mmol) was added. The resulting clear yellow solution was stirred for 15 min. Slow addition of diethyl ether (*ca.* 10 mL) gave a light yellow precipitate. The solution was then filtered and the light yellow powder was washed with diethyl ether (15 mL) and dried *in vacuo* to give pure **2**. Yield: 217 mg (78%). Complex **3** can be prepared similarly by treating **1** with 1 equiv. of 2-diethylaminopyridine. Satisfactory analytical and spectroscopic data were obtained for **2** and **3**.

‡ *Crystal data*: **3**: IrCl₂P₂F₄N₂C₄₄BH₄₄, pale yellow crystals, *M* = 1036.74, triclinic; space group *P* $\bar{1}$ (no. 2), *a* = 11.8113(4), *b* = 12.6330(5), *c* = 16.5025(7) Å, α = 100.210(2), β = 107.894(2), γ = 101.536(2), *V* = 2219.4(2) Å³, *Z* = 2; *D*_c = 1.551 g cm^{–3}; *T* = 183 K, λ(Mo–K_α) = 0.71069 Å, Nonius KappaCCD; no. reflections [*I* > 3.0σ(*I*)] = 6997; *R* = 0.043, *R*_w = 0.042, GOF = 1.34.

6: IrP₂F₄O₂N₂C₄₉BH₅₂; colorless crystals, *M* = 1041.93; monoclinic, space group *P*2₁/*n* (no. 14), *a* = 14.4246(6), *b* = 14.7760(6), *c* = 22.8912(7) Å, β = 107.342(2)°, *V* = 4657.2(3) Å³, *Z* = 4; *D*_c = 1.49 g cm^{–3}; *T* = 183 K, λ(Mo–K_α) = 0.71069 Å, Nonius KappaCCD; no. reflections [*I* > 3.0σ(*I*)] = 5722; *R* = 0.032, *R*_w = 0.034; GOF = 0.81.

CCDC 182/1870. See <http://www.rsc.org/suppdata/cc/b007679f/> for crystallographic files in .cif format.

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