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Synthesis and Reactivity of Cationic Iridium Amino-Carbenes Derived from Terminal Alkynes and 2-Aminopyridines

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*Abstract: The reaction of a terminal alkyne (RCCH) and 2-aminopyridine (R'C₅NH₃NH₂) with the dinuclear species [Cp*IrCl₂]₂ afforded cationic aminocarbene derivatives Cp*Ir(Cl)[=C(CH₂R)NHC₅NH₃R'] via a hydroamination and a ligand substitution. The reaction pathway has been examined through computational studies.*

Introduction

Even though several methodologies have been developed,¹ nucleophilic attack at the α -carbon of a vinylidene intermediate is one of the best and most attractive synthetic routes to transition metal carbenes. Transition metal vinylidenes are susceptible to a wide number of nucleophiles, including amines,^{2,3} water,⁴ alcohols,⁵ thiols,⁶ phosphines,⁷ and even fluoride.⁸ A large variety of Fischer-type transition metal carbenes have been made available using this methodology, including, alkoxy-,⁵ thio-,⁶ and aminocarbene.³ We have also recently utilized this method towards the synthesis of a variety of orthometallated iridium aminocarbene derivatives, with the reaction of [Cp*IrCl₂]₂ (**1**) with a terminal alkyne (**2**) and an aniline as the nucleophile.

In this report, we wish to report our attempt at extending this methodology to the use of a 2-aminopyridine (**3**) as the nucleophile. Two possible products, of structure **I** or **II**, may be expected *a priori* (Figure 1), and the outcome should be dictated by the feasibility of C-H activation versus ligand substitution. Literature on transition metal aminocarbenes having the aminopyridine moiety is extensive for ruthenium.³ There is, however, much less work carried

out with iridium and those mainly involved double C-H activation of the corresponding N-alkyl-2-aminopyridines.^{1a,9}

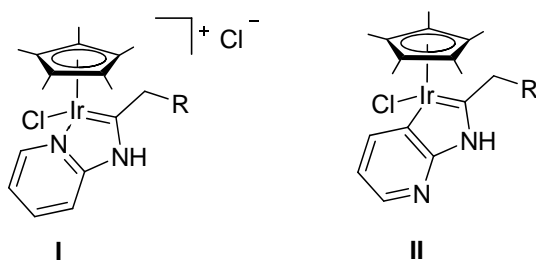
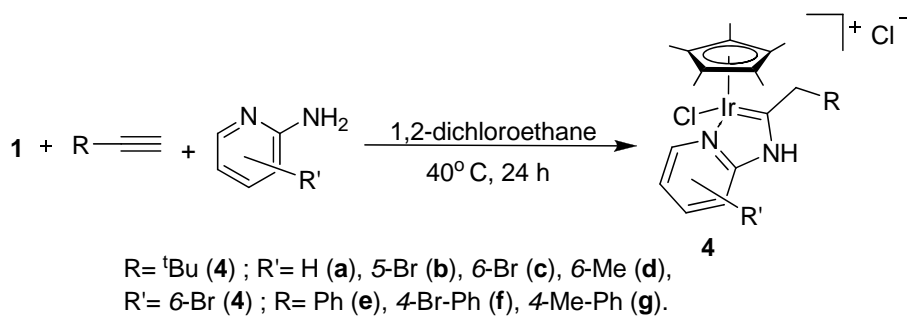


Figure 1. Possible products from the reaction of $[\text{Cp}^*\text{IrCl}_2]_2$ (**1**) with a terminal alkyne (**2**) and a 2-aminopyridine (**3**).

Results and discussion

The reaction of **1** with a terminal alkyne **2** and a 2-aminopyridine **3** afforded an iridium aminocarbene complex of the type $[\text{Cp}^*\text{Ir}(\text{=C}(\text{NHC}_5\text{NH}_3\text{R}')(\text{CH}_2\text{R}))\text{Cl}]\text{Cl}$ (**4.Cl**) in 59-82% yields (Scheme 1). A wide variety of aminopyridines and terminal alkynes can be employed; the reaction proceeded smoothly with both aliphatic and aromatic terminal alkynes but failed to afford aminocarbenes with internal alkynes (diphenyl acetylene and prop-1-ynylbenzene), and both electron-withdrawing and -donating substituents on the 2-aminopyridine can be tolerated.



Scheme 1

The products have all been characterised completely spectroscopically and analytically and, in the case of **4c.Cl**, by a single-crystal X-ray crystallographic study as well; an ORTEP plot of the cation **4c** is shown in Figure 2. Similar iridacycles which have been

structurally characterised include $\text{Tp}^{\text{Ph}}\text{Ir}(\text{H})(=\text{CH}-\text{NMePy})$,^{9a} $[\text{Ir}(\text{H})_2\{\text{C}(\text{Me})\text{NEtPy}\}(\text{PPh}_3)_2]^+$,^{9b} and $[\text{Ir}(\text{H})_2\{\text{C}(\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph})\text{NMePy}\}(\text{PPh}_3)_2]^+$.^{9c} The ^1H NMR spectra of the aminocarbene complexes were characterised by two doublet resonances arising from the diastereotopic CH_2 protons, and a resonance at ~ 242 ppm in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra which was typical for a transition metal carbene.

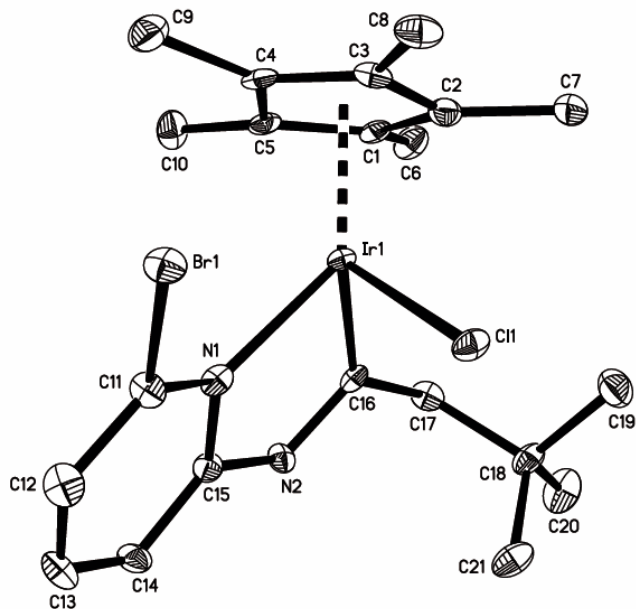
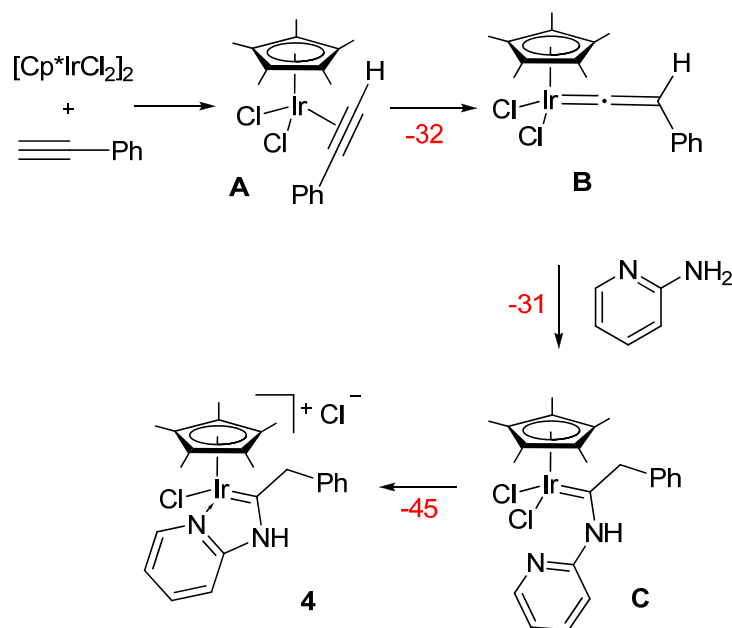


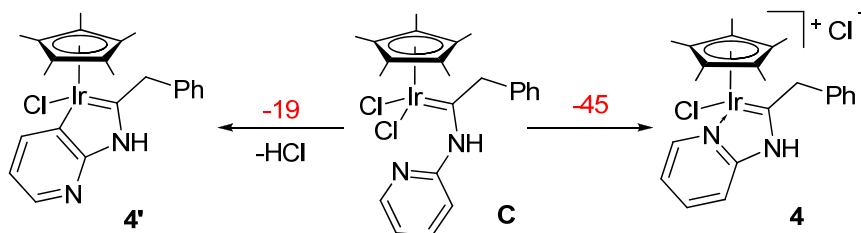
Figure 2. ORTEP plot (50% probability thermal ellipsoids) showing the molecular structure of the cation **4c**. H atoms are omitted for clarity.

The proposed reaction pathway to **4** (Scheme 2) is similar to that which we have proposed earlier for the orthometallated aminocarbene complexes, and differs only for the final step;^{3j} the Gibbs free energy (in kJ mol^{-1}) for each step has also been evaluated computationally with DFT and are also shown.



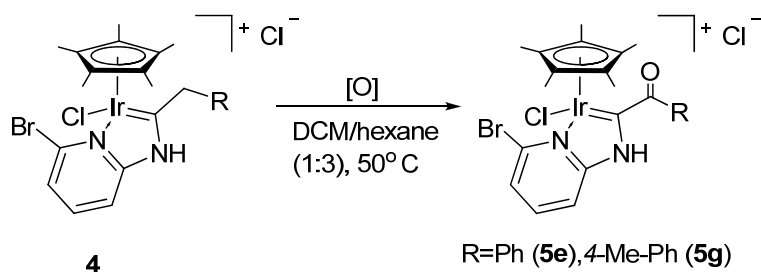
Scheme 2

Deuterium labelling experiments involving phenylacetylene-*d* with **1** and 2-amino-6-bromopyridine, and phenylacetylene with **1** and 2-amino-6-bromopyridine in the presence of D_2O , afforded **4e** with none and two deuterium, respectively, incorporated at the diastereotopic CH_2 protons. This is consistent with the alkyne-vinylidene rearrangement from **A** to **B** via intermolecular proton transfer with adventitious water. Nucleophilic attack by the aniline functionality at the vinylidene α -carbon followed by proton transfer would afford the aminocarbene intermediate **C**. From there, ligand displacement of a chloride by the pyridyl-N would result in **4**; the alternative orthometallation to afford the neutral aminocarbene **4'** that was observed with aniline,^{3j} is energetically less favourable (Scheme 3). An alternative pathway which we have also examined computationally involved the formation of a cationic intermediate early in the pathway, in which binding of the alkyne followed displacement of a chloride. The energetics for this pathway were comparable to that outlined above and hence could not be confidently excluded, but such a pathway may not be favoured in a relatively non-polar environment such as that employed here.



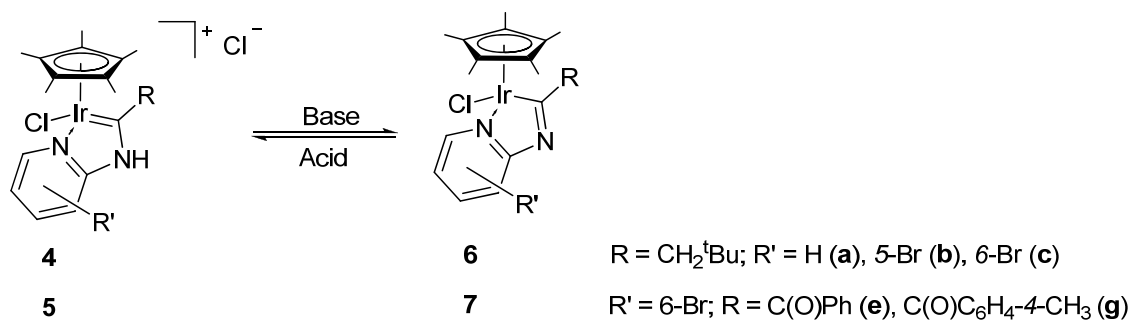
Scheme 3

It was also found that **4** which contains a benzylic group α to the carbene moiety was susceptible to aerial oxidation to form complexes **5**; those with aliphatic substituents, such as **4c**, were resistant to oxidation under similar conditions (Scheme 4). These oxidation products have also been characterised completely, and in the case of **5e.Cl**, by a single-crystal X-ray structural study as well.



Scheme 4

In both **4** and **5**, the NH proton is expected to be acidic. Indeed, the treatment with triethylamine afforded the neutral cyclometallated species **6** and **7**, respectively (Scheme 3). The reaction is reversible as treatment of **6** with HBF_4 afforded $[\text{Cp}^*(\text{Cl})\text{Ir}=\text{C}(\text{CH}_2^t\text{Bu})\text{NHPy}]\text{BF}_4$ **4c.BF₄**; the chloride salt, **4c.Cl**, could be obtained by treatment with conc HCl.

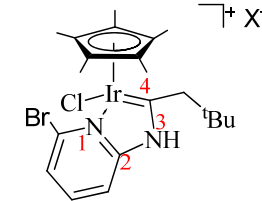
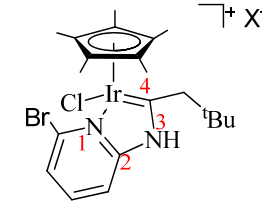
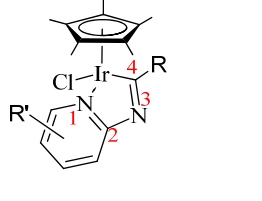
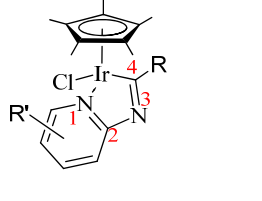
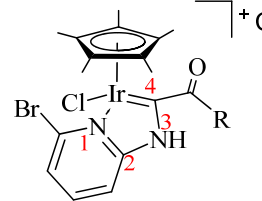
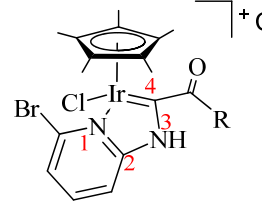


Scheme 5

Besides **4c.Cl** and **5e.Cl**, the complexes **4c.BF₄**, **5g.Cl**, **6b** and **7e**, have also been characterised crystallographically. Selected bond parameters for the six structures are given in Table 1.

The Ir-C(4) bond lengths in the cationic species are comparable or shorter than the corresponding bond length in the orthometallated aminocarbenes,^{3j} and hence are clearly indicative of Ir=C double bond character. The corresponding bond in the neutral species (**6b** and **7e**) is longer but not appreciably so, suggesting some double bond character as well. Indeed, the C-N bond lengths for all six crystals show similar variations, suggesting similar delocalisation of electrons about the metallacycles. This is corroborated by the ¹³C NMR spectra which show a distinct downfield peak at ~ 225 – 245 ppm for all the complexes in this study, both cationic and neutral. The structures of **5e**, **5g** and **7e** suggest that the ketone functionality in these complexes is not conjugated to the metallacycle; the dihedral angle between the Ir-C(4)-N(3) and C(4)-C=O planes range from about 68° to 79°. However, the infrared spectroscopic data ($\nu_{\text{C=O}}$ are 1659, 1654, 1653 and 1651 cm⁻¹ for **5e**, **5g**, **7e** and **7g**, respectively, compared to 1686 cm⁻¹ in acetophenone) suggests that in solution, there is conjugation.

Table 1: Selected bond parameters for **4c.Cl**, **4c.BF₄**, **5e**, **5g**, **6b** and **7e**. The two sets of values given for **5e** and **5g** are for the two crystallographically independent molecules found in the crystals.

	4c.Cl	4c.BF₄	6b	7e	5e	5g
Bond parameters	 $\text{X} = \text{Cl}(\mathbf{c}), \text{BF}_4(\mathbf{c}')$	 $\text{X} = \text{Cl}(\mathbf{c}), \text{BF}_4(\mathbf{c}')$	 $\text{R} = \text{CH}_2^t\text{Bu}; \text{R}' = 5\text{-Br} (\mathbf{6b})$ $\text{R} = \text{COPh}; \text{R}' = 6\text{-Br} (\mathbf{7e})$	 $\text{R} = \text{CH}_2^t\text{Bu}; \text{R}' = 5\text{-Br} (\mathbf{6b})$ $\text{R} = \text{COPh}; \text{R}' = 6\text{-Br} (\mathbf{7e})$	 $\text{R} = \text{Ph} (\mathbf{e}), p\text{-tolyl} (\mathbf{g})$	 $\text{R} = \text{Ph} (\mathbf{e}), p\text{-tolyl} (\mathbf{g})$
Bond lengths / Å						
Ir-Cl	2.379(2)	2.385(2)	2.388(2)	2.3998(13)	2.392(2) 2.403(2)	2.3923(18) 2.3951(19)
Ir-N(1)	2.118(8)	2.120(7)	2.060(6)	2.113(5)	2.121(7) 2.130(7)	2.142(6) 2.124(6)
Ir-C(4)	1.990(10)	1.967(9)	2.002(8)	2.015(6)	1.971(8) 1.969(9)	1.978(8) 1.981(8)
N(1)-C(2)	1.359(12)	1.340(10)	1.361(10)	1.369(7)	1.353(11) 1.345(11)	1.347(9) 1.370(9)
N(3)-C(2)	1.382(13)	1.391(12)	1.382(11)	1.388(7)	1.397(11) 1.384(11)	1.380(10) 1.383(10)
N(3)-C(4)	1.332(12)	1.338(11)	1.320(10)	1.284(7)	1.324(11) 1.309(11)	1.323(9) 1.315(9)
Bond angles / degree						
N(1) – Ir – C(4)	77.9(3)	78.3(3)	76.2(3)	75.0(2)	76.7(3) 76.3(3)	77.0(3) 76.8(3)
C(2) - N(3) - C(4)	120.9(8)	118.9(7)	112.7(7)	112.6(5)	118.6(7) 117.3(8)	119.5(6) 118.5(7)
N(1) - C(2) - N(3)	112.2(8)	114.0(7)	116.9(7)	117.4(5)	112.1(7) 114.0(7)	113.3(7) 113.2(6)
N(3) – C(4) - Ir	114.6(7)	114.8(6)	120.1(6)	122.2(4)	117.4(6) 118.5(6)	116.3(6) 117.7(6)

Conclusion

In this report, we have described a synthetic route to cationic aminocarbene complexes of iridium(III) by the reaction of **1** with aminopyridines and terminal alkynes. They can undergo reversible deprotonation at the NH moiety, and those containing a benzylic group at the metallacycle can readily undergo aerial oxidation. These are characteristic of electron delocalisation within, and hence aromaticity in, the metallacycle and is also corroborated by the structural and NMR parameters for these complexes.

Experimental Section

General. All reactions and manipulations, except for TLC separations, were performed under argon by using standard Schlenk techniques. All other reagents were from commercial sources and used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL ECA400 or ECA400-SL NMR spectrometer as CDCl_3 solutions; chemical shifts reported were referenced against the residual proton signals of the solvent at 7.26 and 77.24 ppm for ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR respectively. ESI/MS were recorded in EI mode on a MATLQCQ spectrometer. High resolution mass spectra (HRMS) were recorded in ESI mode on a Waters UPLC-Q-TOF mass spectrometer. $[\text{Cp}^*\text{IrCl}_2]_2$, **1**, was prepared according to the published method.¹⁰ Elemental analyses were performed by the microanalytical laboratory in NTU.

Reaction of **1** with alkyne and 2-aminopyridine.

In a 50 mL carius tube, dichloroethane solution (5 mL) of $[\text{Cp}^*\text{IrCl}_2]_2$ (40 mg, 50 μmol), 3,3-dimethyl-1-butyne (125 μl , 1 mmol) and 2-aminopyridine (10 mg, 100 μmol) was stirred at 40 $^\circ\text{C}$ for 24 h. The reaction solvent was then removed under reduced pressure, followed by recrystallization from dichloromethane / diethyl ether gave pure **4a.Cl** (45 mg, 80%).

Aerial oxidation of 4e.Cl and 4g.Cl

In a 50 mL round-bottomed flask, **4e.Cl** (20 mg, 29.7 μmol) was dissolved in dichloromethane (5 mL) and hexane (15 mL) and the reaction was left to reflux in the open at 50 °C overnight. The solvent was then removed under reduced pressure, followed by recrystallization from dichloromethane / diethyl ether gave pure **5e.Cl** (15 mg, 74%).

Reversible deprotonation of 4

To a solution of **4a.Cl** (20 mg, 34.8 μmol) in dichloromethane (5 ml) was added triethylamine (6 μl , 42 μmol) and stirred at RT for 15 min, filtered through silica gel and the solvent was evaporated under reduced pressure to afford pure **6a**. Similar procedure was used for **6b** and **6c**. The reversible protonation of **6c** (20 mg, 32.5 μmol) in dichloromethane (5 ml) with $\text{HBF}_4 \cdot \text{OEt}_2$ (5 μl , 39 μmol) afforded **4c.BF₄** (22 mg, 96%).

X-ray crystallographic studies. Crystals were grown from dichloromethane/hexane solutions and mounted on quartz fibres. X-ray data were collected on a Bruker AXS APEX system, using Mo $K\alpha$ radiation, with the SMART suite of programs.¹¹ Data were processed and corrected for Lorentz and polarization effects with SAINT,¹² and for adsorption effects using SADABS.¹³

The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. Hydrogen atoms were placed in calculated positions and refined with a riding model. There were two formula units per asymmetric unit for **5e.Cl** and **5g.Cl**. Dichloromethane solvates were found in the crystals of **4c.Cl**, **5e.Cl** and **5g.Cl**. For the latter two crystals, four sites were found for the solvates, which were modelled with various occupancies, and with **5e.Cl**, one of the solvate was modelled as disordered with two alternative positions for one of the Cl atoms. The crystal of **4c.BF₄** showed disorder of the anion which was modelled with two alternative sites for each of the F atoms, with occupancies of 0.7 and 0.3, respectively. The crystal of **6b** exhibited

disorder of the CH₂^tBu group, which was modelled with two alternative sites with their occupancies summed to unity. Appropriate restraints on the bond and thermal parameters were placed on all the disordered parts. All non-hydrogen atoms were given anisotropic displacement parameters in the final model.

Computational studies. The reaction energetics was studied using DFT theory utilising the Becke's three parameter hybrid function,¹⁴ and Lee-Yang-Parr's gradient-corrected correlation function (B3LYP).¹⁵ The LanL2DZ (Los Alamos Effective Core Potential Double- ζ) basis set together with an *f* polarisation function was employed for the Ir atom, and the 6-311+G(2d,p) basis set for all the other atoms. Spin-restricted calculations were used for geometry optimization, and harmonic frequencies were then calculated to characterize the stationary points as equilibrium structures with all real frequencies, and to evaluate zero-point energy (ZPE) corrections. All calculations were performed using the Gaussian 09 suite of program.¹⁶

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Supporting Information Available: Crystallographic data in CIF format, experimental details and characterisation for the complexes, and optimised geometry of all computed structures. Ordering information is given on any current masthead page.

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