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N-Metallacycles from [Cp*MX₂]₂ and Alkynylpyridines: Synthesis, Reaction Pathway and Aromaticity

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ABSTRACT: The reaction of [Cp*MX₂]₂ (M = Rh or Ir, X = Cl, Br or I) with alkynylpyridines afforded halogen-substituted *N*-metallacyclic complexes. The reaction pathway has been examined through deuterium labeling and other experiments and computational studies, and is proposed to proceed via halide dissociation followed by attack at the alkyne. These *N*-metallacycles exhibit aromaticity, and undergo Sonogashira coupling reactions.

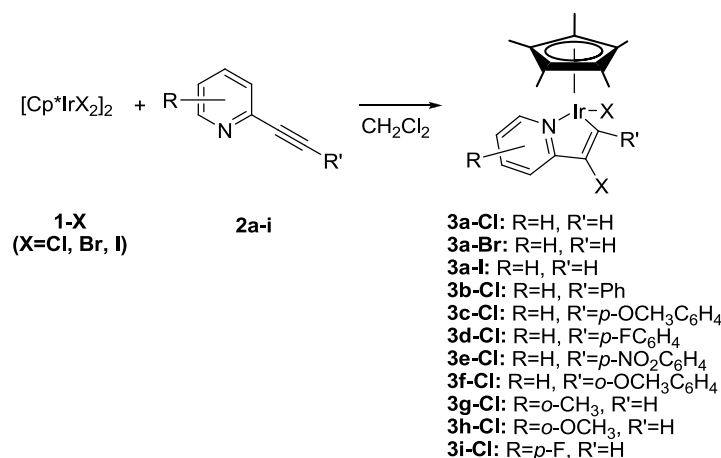
Introduction

Cyclometalated complexes have attracted interests because of their involvement in many carbon-carbon,¹ and carbon-heteroatom,² bond forming reactions, often under relatively mild conditions. More recently, *N*-metallacyclic complexes especially those of iridium, have been demonstrated to promote the oxidation of water to oxygen,³ selective C-H bond oxidation,⁴ conversion of alkanes to alkenes,⁵ and transfer hydrogenation of ketones and amines.⁶ Conjugated metallacyclic complexes, in particular, are also of interest as they are known to display structural and spectroscopic characteristics of aromaticity,⁷ and a wide variety of aromatic metallacycles have been synthesised and their physical and chemical properties investigated over the years.⁸

A variety of synthetic methodologies to metallacycles have been developed. These include ortho C-H activation of aromatic amines,⁹ or imines,¹⁰ transmetalation,¹¹ often involving the use of additives such as a base,¹² an acid,¹³ or a silver salt.¹⁴ In the course of our investigations into the chemistry of the complex [Cp*MX₂]₂, **1**, we have serendipitously uncovered a simple, one-pot route to a class of aromatic *N*-iridacycles.

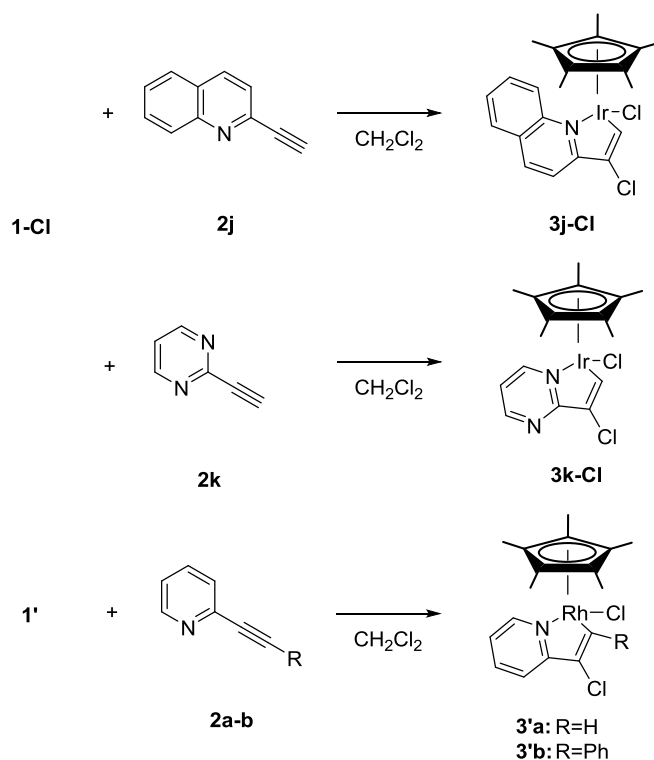
Results and discussion

The reaction between **1** and an alkynylpyridine **2** afforded the *N*-iridacyclic complexes **3** in essentially quantitative yields (Scheme 1). This reaction works well with both terminal and internal alkynes, and the electronic properties of R and R' do not show much effect on the yield.



Scheme 1

The reaction could also work with other halogeno-derivatives (**3a-Br** and **3a-I**), starting from $[\text{Cp}^*\text{IrX}_2]_2$ ($\text{X} = \text{Br}$ or I), and could also be extended to other N-heterocycles with a similar structural motif, such as quinoline and pyrimidine. Similar N-rhodacyclic complexes could also be synthesized starting from $[\text{Cp}^*\text{RhCl}_2]_2$, **1'** (Scheme 2).



The products **3** have been characterized spectroscopically and analytically, and the structure of **3a-Cl** has been confirmed by a single-crystal X-ray diffraction study; the ORTEP plot showing the molecular structure, together with selected bond parameters, are shown in Figure 1.

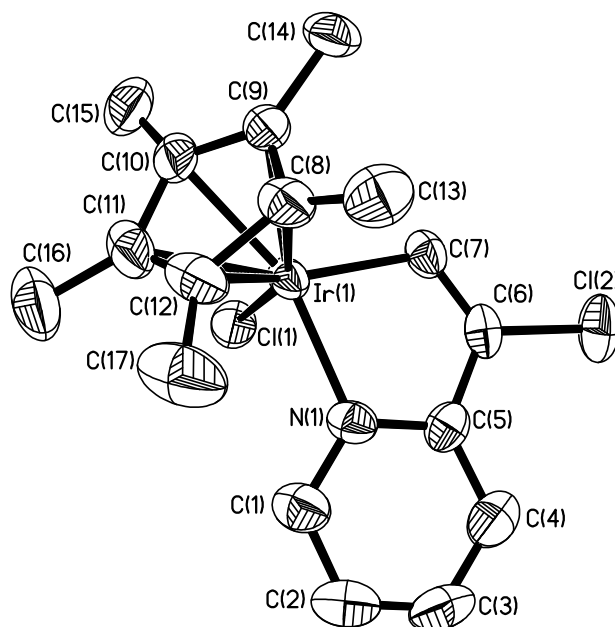
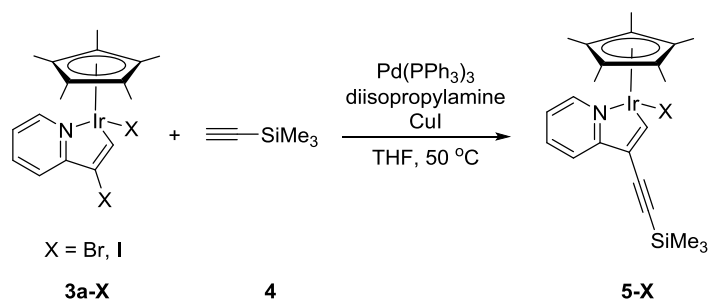


Figure 1. ORTEP plot of **3a-Cl**. All H atoms have been omitted. Thermal ellipsoids are plotted at the 50% probability level. Selected bond lengths (Å) and angles (°): Ir(1)-Cl(1) = 2.3997(12); Ir(1)-C(7) = 2.036(4); Ir(1)-N(1) = 2.077(4); C(6)-C(7) = 1.313(6); C(5)-C(6) = 1.440(6); C(5)-N(1) = 1.358(6); C(7)-Ir(1)-N(1) = 77.62(17).

The Ir-C bond length of the metallacycle is rather short (Ir(1)-C(7) = 2.036(4) Å) and is comparable to that in similar *N*-iridacyclic compounds, and suggests some Ir=C double bond character.¹⁵ This would also suggest that there is delocalisation of electrons within the metallacycle and hence some degree of aromaticity. Consistent with this is that, for all the complexes **3** in this study, the resonance for the proton on the metallacycle is highly deshielded ($\delta_{\text{H}} \sim 8.5\text{-}9.2$ ppm). This can be compared to the more upfield shift reported for an α -CH of a vinyl group in transition metal vinyl complexes ($\delta_{\text{H}} = 5.84$ ppm).¹⁶ We do note, however, that the differences in the C-C bond lengths within the ring of **3a-Cl** (C(6)-C(7) = 1.313(6) Å and C(5)-C(6) = 1.440(6) Å) suggests the dominance of one resonance structure.

A useful feature of the complexes **3** is the presence of a halogen substituent on the metallacycle. This allows for further synthetic elaboration. For instance, we have found that we can carry out Sonogashira coupling reactions to afford alkyne-substituted analogues (Scheme 3).



Scheme 3

Aromaticity studies

Besides the structural and NMR characteristics mentioned above, the aromaticity of the metallacycle is also indicated by the computationally optimized structure of **3a-Cl**, which possesses a π -type molecular orbital, the HOMO-28, which is delocalized over both the pyridine ring and the 5-membered iridacycle (Figure 2).

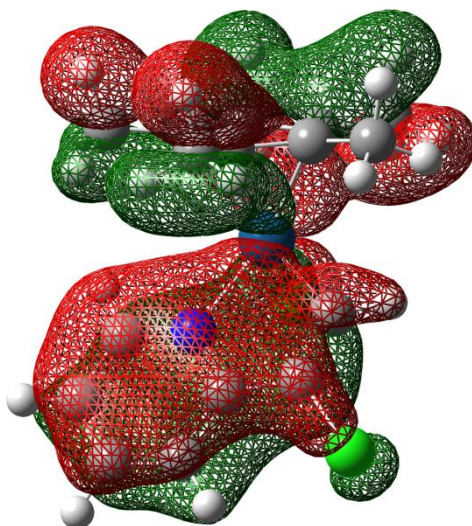
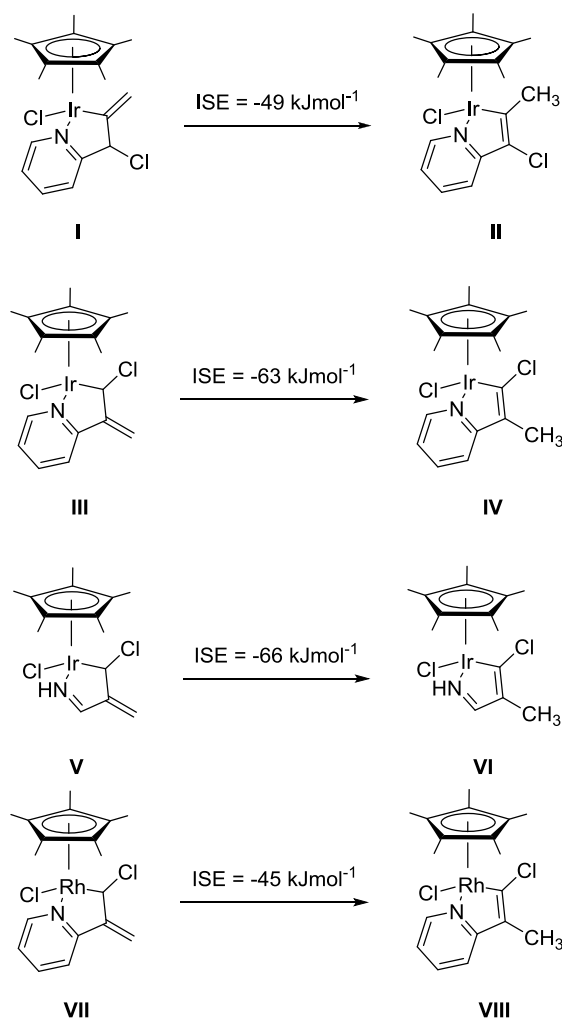


Figure 2. Computed HOMO-28 of **3a-Cl** showing delocalisation of the orbital within the pyridine and *N*-iridacycle.

We also examined the use of two different computational methods to verify the aromaticity of the metallacycle. The first of these is the isomerisation stabilization energy (ISE) proposed by Schleyer and co-workers.¹⁷ This involves computation of the total energy difference between two species - the proposed aromatic system and its nonaromatic exocyclic methylene isomer, such as those shown in Scheme 4. A negative ISE indicates the presence of a stabilization which may be regarded as aromatic stabilization energy (ASE) on

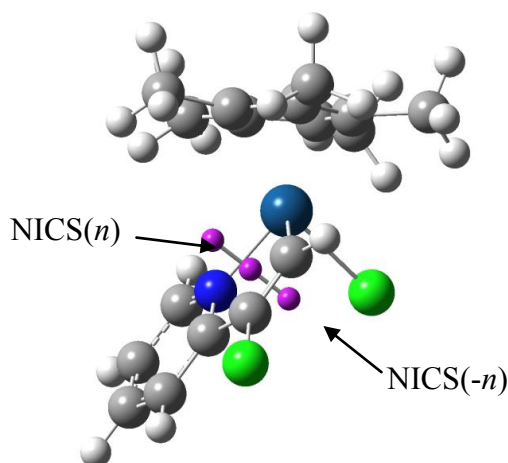
moving from the non-aromatic complex **I**, **III**, **V** and **VII** to the aromatic derivative **II**, **IV**, **VI** and **VIII**. The ISE from complex **I** to **II** is not appropriate for an assessment of the aromaticity within the metallacyclic ring as the ene functionality in **I** is not conjugated with the pyridine ring. We have thus calculated the ISE for complex **III** and similar analogues in which the location of the Cl has to be, unfortunately, different from that in the complexes **3**. The figures indicate the presence of aromaticity in the iridacyclic system, which are about two-thirds that of pyrrole (-63 and -92 kJ mol⁻¹, respectively); the rhodium analogue has a slightly lower value (-45 kJ mol⁻¹). In contrast to organic systems, for example, pyrrole and indole (-92 and -197 kJ mol⁻¹, respectively), however, the presence of the 6-membered pyridine ring does not help to further stabilise the iridacycle (-63 and -66 kJ mol⁻¹ for **II** and **IV**, respectively).



Scheme 4

The second measure of aromaticity is the nucleus independent chemical shift (NICS),¹⁸ in which the absolute magnetic shielding at the centre of the ring is computed. A negative NICS value indicates aromaticity, while a positive value indicates antiaromaticity. In order to reduce the influence of the σ bonding framework, NICS values calculated are at points some distance from the plane of the ring.¹⁹ Some groups have recommended scanning the NICS values over a range of distances for more complicated systems, arguing that the use of a single NICS value may not be adequate.²⁰ Our calculations on both complexes **I** and **II** gave negative values (Table S2), which was unexpected since there should not be any aromaticity in the metallacycle of **I**, as corroborated by the ISE calculations. We have also calculated the values of NICS(n) and NICS(- n), with n ranging from 0 to 3Å, for the complex **3a-Cl** (Table 1). While the NICS(n) values were dependent on the distance of Bq from the geometric centre of the ring, such a trend was not observed for the NICS(- n) values. We have attributed this to Bq approaching the Cl atom for the NICS(- n) values. For such complexes therefore, NICS may not be a good indicator of aromaticity.

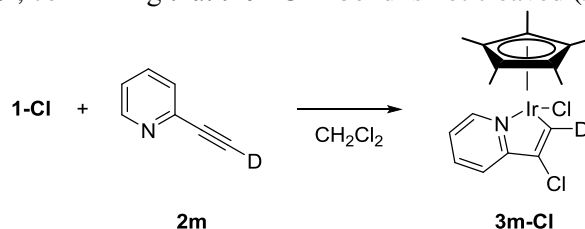
Table 1. NICS values of **3a-Cl** calculated at various distance from the centre of the metallacyclic plane. The position of Bq, at which the NICS value is calculated, is indicated by the purple sphere.



Distance of Bq from the geometric centre (n Å)	NICS (n)	NICS(0)	NICS($-n$)
0.5	-5.7	-9.3	-10.8
1.0	-3.1	-9.3	-9.3
1.5	-1.9	-9.3	-7.9
2.0	-1.2	-9.3	-7.9
2.5	-0.9	-9.3	-8.8
3.0	-0.8	-9.3	-7.3

Reaction pathway

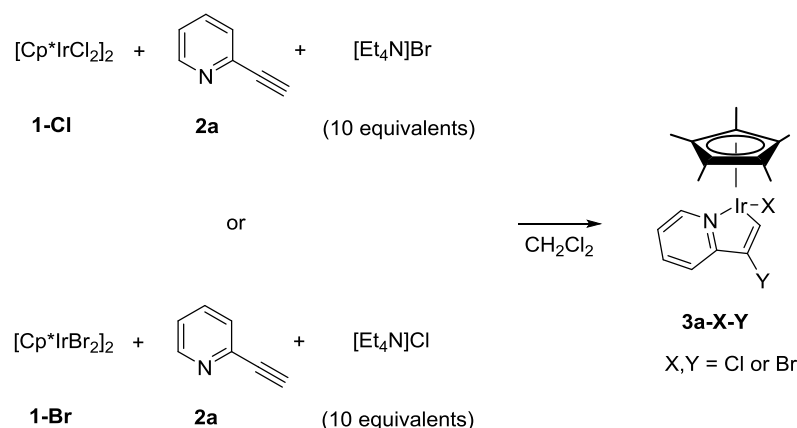
An isotopic labelling experiment with *d*1-alkynylpyridine **2m**, shows that the deuterium is incorporated into the iridacycle **3m-Cl**, confirming that the $\equiv\text{C-H}$ bond is not cleaved (Scheme 5).



Scheme 5

To verify if the Cl on the metallacyclic ring is the result of external attack by a dissociated chloride or via an intramolecular transfer, two NMR-scale reactions were carried out: (1) The reaction of **1-Cl** with **2a** in the presence of 10 equivalents (wrt **1-Cl**) of $[\text{Et}_4\text{N}]\text{Br}$, and (2) the reverse reaction of **1-Br** with **2a** in the presence of 10 equivalents (wrt **1-Br**) of $[\text{Et}_4\text{N}]\text{Cl}$. Each of the reactions gave all the four possible products **3a-X-Y** (X, Y = Cl or Br) but in different ratios (Table 2 and Figure S2).

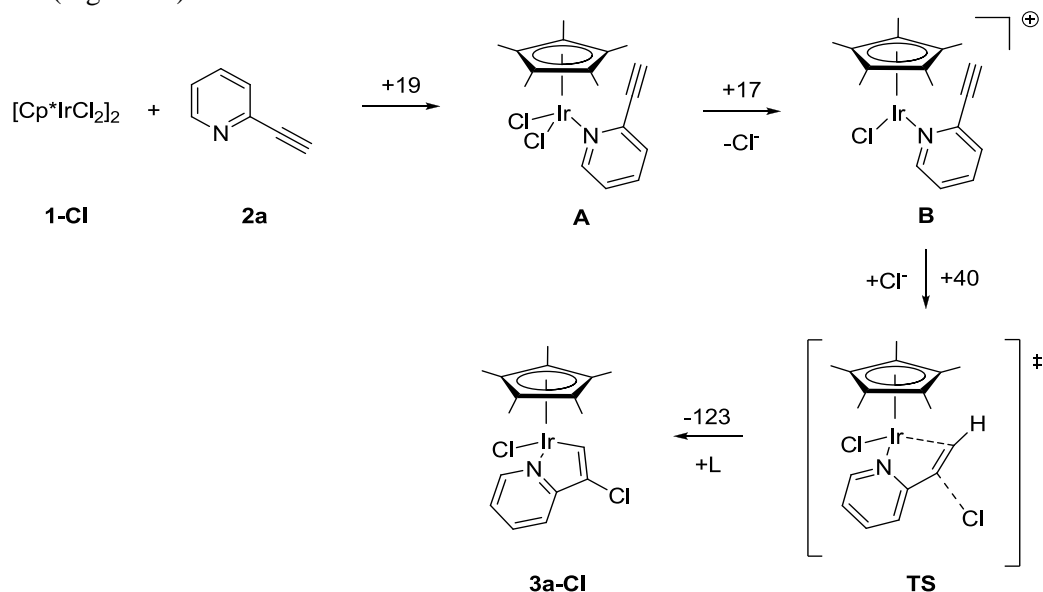
Table 2. Ratio of products from the reactions of **1-X** with **2a** in the presence of 10 equivalents (wrt **1-X**) of $[\text{Et}_4\text{N}]\text{Y}$ (X, Y = Cl or Br).



Reaction	3a-Cl-Cl	3a-Br-Cl	3a-Cl-Br	3a-Br-Br
(1) 1-Cl + 2a + $[\text{Et}_4\text{N}]\text{Br}$	1.0	0.9	3.7	3.7
(2) 1-Br + 2a + $[\text{Et}_4\text{N}]\text{Cl}$	1.0	0.2	0.6	0.1

The observations were not consistent with an intramolecular halide transfer and point instead to external attack by halide. Such halide ion functionalization of alkynes to form metallacycles has been reported.²¹ The possibility of halide exchange in the dimeric reactant prior to subsequent reaction with **2a** was ruled out; although the reaction of **1-Cl** with four equivalents of [Et₄N]Br led rapidly (< ½ h) to the formation of **1-Br**, the reverse reaction did not proceed even overnight. This suggests that **1-Br** is more stable than **1-Cl**. On the other hand, the ratios of **3a-Cl-Y:3a-Br-Y** obtained for the reactions in Table 2 (~1:1 and 5:1 for reactions 1 and 2, respectively) point clearly to the preference for a Cl over a Br ligand in the mononuclear products. We have also verified this through the reaction of Cp*Ir(py)(Cl)₂ with five equivalents of [Et₄N]Br, which afforded Cp*Ir(py)(Cl)₂, Cp*Ir(py)(Br)(Cl) and Cp*Ir(py)(Br)₂ in a ratio of 1:3:2 while the reverse reaction of Cp*Ir(py)(Br)₂ with five equivalents of [Et₄N]Cl afforded only Cp*Ir(py)(Cl)₂ and Cp*Ir(py)(Br)(Cl) in a ratio of 4:1 (Figure S2). These latter observations can also account for the fact that the ratio of **3a-X-Cl: 3a-X-Br** for reaction 2 in Table 1 is not simply the reverse of that in reaction 1; the greater tendency for Cl⁻ to displace metal-bound Br⁻ from a mononuclear intermediate in reaction 2 would lead to a larger proportion of **3a-X-Br** than may be expected from a simple reversal of reaction 1. That the reaction did not require a dimeric intermediate was ruled out through the observation that **3a-Cl** was also obtained from the reaction of Cp*Ir(py)(Cl)₂ with **2a**. Attempt to exploit this reaction to obtain non-halogen substituted analogues have not been successful so far - reactions of **1-Cl** and **2a** in a large excess of NaOMe or NH₄OH gave only **3a**; no MeO or OH-substituted analogues were observed.

On the basis of the above, we have proposed the reaction pathway shown in Scheme 6. The Gibbs free energy for the various steps has been computed with density functional theory and the computed energies (in kJ mol⁻¹) are also given. For this pathway, the PCM model with CH₂Cl₂ as the reaction solvent was used in the computation. The initial binding of the nitrogen to the iridium metal centre led to the formation of **A**, followed by the dissociation of a chloride anion. External attack by chloride on the C-C moiety led to the formation of the final product. We have modeled the transition state (**TS**) for this last step, which lies +40 kJ mol⁻¹ above **B** (Figure S3).



Scheme 6

Concluding remarks

In this study, we have reported a facile synthetic route to *N*-iridacycles from the reaction of alkynylpyridines with the readily available dinuclear species [Cp*MX₂]₂. A reaction pathway involving dissociation of a halide ion followed by external attack on the alkyne moiety has been proposed on the basis of experimental and computational studies. We have also demonstrated that these complexes can be further derivatized at the metallacycle via Sonogashira coupling; they are almost certainly susceptible to other similar coupling reactions as well. The aromaticity of the metallacycles has been verified by a number of methods, among which our results suggest that nucleus independent chemical shifts are not good indicators for such complexes.

Experimental Section

General. All reactions and manipulations, except for TLC separations, were performed under an argon atmosphere by using standard Schlenk techniques. Solvents used were of AR grade. The starting materials **1**,²² **1'**,²³ and **1-X** (X = Br, I),²⁴ were prepared according to published methods. All other chemicals were from commercial sources and used as supplied without further purification. ¹H and ¹³C{¹H} NMR spectra were recorded on a 300 or 400 NMR spectrometer. Chemical shifts reported are with respect to the residual ¹H resonance in CDCl₃. High resolution mass spectra (HRMS) were recorded in ESI mode on a TOF mass spectrometer.

Reaction of 1 with the alkynylpyridines. In a typical reaction, to a solution of **1-Cl** (20 mg, 25 μmol) in dichloromethane (3 mL) was added **2a** (5.1 μL, 50 μmol). The reaction mixture was stirred for 3 h, and the solvent was then removed under reduced pressure to afford **3a-Cl** as a dark brown solid.

An analogous procedure was used for all the other complexes. The yields, ¹H NMR and ¹³C NMR data are collected in Table 3.

Sonogashira coupling reaction. A mixture of complex **3a-Br** (40 mg, 0.068 mmol), Pd(PPh₃)₄ (2mg, 2 mol%), CuI (1 mg, 2 mol%), diisopropylamine (10 μL) and trimethylsilylacetylene (15 μL, 0.075 mmol) in THF (5 mL) was heated to 50 °C for 18h. The mixture was filtered and solvent was removed under vacuum. The crude product was purified by TLC using Hex/DCM (1:3, v/v) as eluent and a yellow band **5-Br** was isolated. An analogous procedure was used for the reaction of complex **3a-I** and trimethylsilylacetylene.

Data for **5-Br**: ¹H NMR (δ, CDCl₃): 0.24 (s, 9H, CH₃), 1.84 (s, 15H, Cp*), 6.85-6.89 (m, 1H, aromatic), 7.52-7.61 (m, 2H, aromatic), 8.49 (d, 1H, ²J_{HH} = 5.7 Hz, aromatic), 9.65 (s, 1H, Ir-C=). HRMS: 529.1779; calc for [M-Br+H]⁺: 529.1777. Yield: 3.6 mg (9%).

Data for **5-I**: ¹H NMR (δ, CDCl₃): 0.24 (s, 9H, CH₃), 1.84 (s, 15H, Cp*), 6.85-6.89 (m, 1H, aromatic), 7.51-7.61 (m, 2H, aromatic), 8.50 (d, 1H, ²J_{HH} = 5.7 Hz, aromatic), 9.66 (s, 1H, H-C=). HRMS: 529.1711; calc for [M-I+H]⁺: 529.1722. Yield: 5.7 mg (13%).

Deuterium labelling experiment. Complex **1-Cl** (0.025 mmol, 20 mg) and **2m** (0.05 mmol, 5 μL) was dissolved in DCE (2 mL) and the mixture was stirred at rt for 18 h. Excess solvent was removed under reduced pressure to yield **3m-Cl**.

Data for **3m-Cl**: ¹H NMR (δ, CDCl₃): 1.74 (s, 15H, Cp*), 7.01-7.05 (m, 1H, aromatic), 7.55 (d, 1H, J = 7.8 Hz, aromatic), 7.61-7.65 (m, 1H, aromatic), 8.47 (d, 1H, J = 5.5 Hz, aromatic), 8.61 (s, 0.09H, H-C=, 90% deuteration).

Halide exchange reaction. In a typical reaction, to a solution of **1-Cl** (15 mg, 19 μmol) and NEt₄Br (40 mg, 0.19 mmol) in dichloromethane (3 mL) was added **2a** (4 μL, 38 μmole). The reaction mixture was stirred for 1 h, and the solvent was then removed under reduced pressure. The crude ¹H NMR spectrum showed the presence of **3a-Cl-Cl**, **3a-Cl-Br**, **3a-Br-Cl** and **3a-Br-Br**.

An analogous procedure was used for the other salts.

Crystallographic Studies. A diffraction quality crystal of **3a-Cl** was grown by slow diffusion of hexane into a dichloromethane solution and then mounted onto a quartz fiber. X-ray data were collected on a Bruker AXS APEX system, using Mo Kα radiation, at 223 K with the SMART suite of programs.²⁵ Data were processed and corrected for Lorentz and polarization effects with SAINT,²⁶ and for absorption effects with SADABS.²⁷ Structural solution and refinement were carried out with the SHELXTL suite of programs.²⁸ The structure was solved by direct methods to locate the iridium atom, followed by difference maps for the light, non-hydrogen atoms. Hydrogen atoms were placed in calculated positions and refined with a riding model.

Table 3. Yields, HRMS, ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data for **3**.

Product	Alkyne	Yield	HRMS	^1H NMR (δ , CDCl_3)	$^{13}\text{C}\{^1\text{H}\}$ NMR data
3a-Cl¹	2a	25 mg, 99%	Found: 467.0989 Calc $[\text{M-Cl+H}]^+$: 467.0992	1.73 (s, 15H, Cp*), 7.01-7.04 (m, 1H, aromatic), 7.54 (d, 1H, $J = 7.9$ Hz, aromatic), 7.61-7.65 (m, 1H, aromatic), 8.47 (d, 1H, $J = 5.3$ Hz, aromatic), 8.61 (s, 1H, H-C=).	9.2 (CH ₃ , Cp*), 89.3 (C, Cp*), 120.6, 121.2, 124.4, 137.8, 151.3, 164.0 (C&CH, aromatic), 165.3 (Ir-C=).
3a-Br	2a	29 mg, 99%	Found: 511.0471 Calc $[\text{M-Br+H}]^+$: 511.0487	1.76 (s, 15H, Cp*), 6.94-6.97 (m, 1H, aromatic), 7.60-7.63 (m, 2H, aromatic), 8.46 (d, 1H, $J = 5.7$ Hz, aromatic), 8.94 (s, 1H, H-C=).	9.4 (CH ₃ , Cp*), 89.5 (C, Cp*), 110.4, 120.9, 121.6, 137.8, 151.8, 164.5 (C&CH, aromatic), 169.9 (Ir-C=).
3a-I	2a	34 mg, 99%	Found: 559.0348 Calc $[\text{M-I+H}]^+$: 559.0349	1.82 (s, 15H, Cp*), 6.79-6.82 (m, 1H, aromatic), 7.54-7.57 (m, 1H, aromatic), 7.67-7.69 (m, 1H, aromatic), 8.46 (d, 1H, $J = 5.6$ Hz, aromatic), 9.51 (s, 1H, H-C=).	9.9 (CH ₃ , Cp*), 90.0 (C, Cp*), 120.2, 123.5, 137.7, 152.7, 165.9 (C&CH, aromatic), 180.3 (Ir-C=).
3b-Cl	2b	29 mg, 99%	Found: 543.1298 Calc $[\text{M-Cl+H}]^+$: 543.1305	1.42 (s, 15H, Cp*), 7.01-7.05 (m, 1H, aromatic), 7.20 (t, 1H, $J = 7.4$ Hz, aromatic), 7.35 (t, 2H, $J = 7.8$ Hz, aromatic), 7.49 (d, 2H, $J = 7.2$ Hz, aromatic), 7.64-7.68 (m, 2H, aromatic), 8.52 (d, 1H, $J = 5.6$ Hz, aromatic).	8.5 (CH ₃ , Cp*), 89.3 (C, Cp*), 119.9, 120.9, 120.9, 126.2, 127.2, 127.4, 128.4, 132.0, 137.5, 146.0, 150.8, 165.0 (C&CH aromatic), 174.9 (Ir-C=).
3c-Cl	2c	30 mg, 99%	Found: 573.1408 Calc $[\text{M-Cl+H}]^+$: 573.1411	1.42 (s, 15H, Cp*), 3.84 (s, 3H, OCH ₃), 6.89 (d, 2H, $J = 8.8$ Hz, aromatic), 6.99-7.03 (m, 1H, aromatic), 7.48 (d, 2H, $J = 8.8$ Hz, aromatic), 7.62-7.66 (m, 2H, aromatic), 8.50 (d, 1H, $J = 5.6$ Hz, aromatic).	8.6 (CH ₃ , Cp*), 55.2 (OCH ₃), 89.4 (C, Cp*), 112.5, 120.7, 129.1, 137.5, 138.6, 150.7, 158.1, 165.1 (C&CH aromatic), 175.1 (Ir-C=).
3d-Cl	2d	30 mg, 99%	Found: 561.1201 Calc $[\text{M-Cl+H}]^+$: 561.1211	1.42 (s, 15H, Cp*), 7.02-7.08 (m, 3H, aromatic), 7.48-7.52 (m, 2H, aromatic), 7.65-7.66 (m, 2H, aromatic), 8.52 (d, 1H, $J = 5.6$ Hz, aromatic).	8.9 (CH ₃ , Cp*), 89.4 (C, Cp*), 114.0, 114.2, 121.0, 121.1, 129.2, 129.3, 137.6, 150.8, 164.9 (C&CH aromatic), 173.5 (Ir-C=).
3e-Cl	2e	30 mg, 98%	Found: 588.1144 Calc $[\text{M-Cl+H}]^+$: 588.1156	1.43 (s, 15H, Cp*), 7.09-7.13 (m, 1H, aromatic), 7.63-7.65 (m, 2H, aromatic), 7.70-7.71 (m, 2H, aromatic), 8.21-8.23 (m, 2H, aromatic), 8.56 (d, 1H, $J = 5.6$ Hz, aromatic).	8.6 (CH ₃ , Cp*), 89.4 (C, Cp*), 121.4, 121.6, 121.8, 122.9, 127.9, 137.8, 145.9, 150.9, 153.7, 164.2 (C&CH aromatic), 170.5 (Ir-C=).

¹ Anal. Calcd for C₁₇H₂₀C₁₂NIr: C, 40.72; H, 4.02; N, 2.79. Found: C, 40.70; H, 4.27; N, 2.55.

3f-Cl	2f	29 mg, 97%	Found: 573.1401 Calc [M-Cl+H] ⁺ : 573.1411	1.43 (s, 15H, Cp*), 3.85 (s, 3H, OCH ₃), 6.91-7.01 (m, 3H, aromatic), 7.17-7.22 (m, 1H, aromatic), 7.52-7.54 (m, 1H, aromatic), 7.58-7.69 (m, 2H, aromatic), 8.50 (d, 1H, <i>J</i> = 7.6 Hz, aromatic)	8.5 (CH ₃ , Cp*), 53.5 (OCH ₃), 89.6 (C, Cp*), 109.8, 120.3, 120.7, 127.2, 128.0, 135.6, 137.4, 150.7, 154.5, 164.7 (C&CH aromatic), 171.3 (Ir-C=).
3g-Cl	2g	38 mg, 98%	Found: 481.1140 Calc [M-Cl+H] ⁺ : 481.1148	1.68 (s, 15H, Cp*), 2.96 (s, 3H, CH ₃), 7.06 (d, 1H, ² <i>J</i> _{HH} = 7.2 Hz, aromatic), 7.36 (d, 1H, <i>J</i> = 7.5 Hz, aromatic), 7.47-7.50 (m, 1H, aromatic), 8.56 (s, 1H, H-C=).	9.5 (CH ₃ , Cp*), 27.4 (CH ₃), 89.2 (C, Cp*), 117.5, 120.2, 137.8 (C&CH aromatic), 164.8 (Ir-C=).
3h-Cl	2h	26 mg, 98%	Found: 497.1100 Calc [M-Cl+H] ⁺ : 497.1098	1.72 (s, 15H, Cp*), 4.00 (s, 3H, OCH ₃), 6.51-6.54 (m, 1H, aromatic), 7.17-7.20 (m, 1H, aromatic), 7.58-7.63 (m, 1H, aromatic), 8.57 (s, 1H, H-C=).	9.7 (CH ₃ , Cp*), 57.3 (OCH ₃), 89.3 (C, Cp*), 101.1, 113.2, 125.1, 140.8, 163.2, 164.2 (C&CH aromatic), 165.6 (Ir-C=).
3i-Cl	2i	25 mg, 98%	Found: 485.0911 Calc [M-Cl+H] ⁺ : 485.0898	1.74 (s, 15H, Cp*), 7.40-7.46 (m, 1H, aromatic), 7.52-7.57 (m, 1H, aromatic), 8.37-8.39 (m, 1H, aromatic), 8.57 (s, 1H, H-C=)	9.1 (CH ₃ , Cp*), 89.5 (C, Cp*), 121.2, 121.2, 125.2, 125.4, 139.3, 139.6, 155.7, 158.2, 160.7, 164.3 (C&CH aromatic), 164.3 (Ir-C=).
3j-Cl	2j	27 mg, 98%	Found: 517.1133 Calc [M-Cl+H] ⁺ : 517.1148	1.70 (s, 15H, Cp*), 7.51-7.54 (m, 1H, aromatic), 7.67-7.75 (m, 3H, aromatic), 8.01 (d, 1H, <i>J</i> = 8.7 Hz, aromatic), 8.41 (d, 1H, <i>J</i> = 8.7 Hz, aromatic), 8.98 (s, 1H, H-C=).	9.5 (CH ₃ , Cp*), 90.1 (C, Cp*), 118.6, 125.4, 126.2, 126.4, 128.1, 128.6, 130.8, 138.8, 146.0, 165.0 (C&CH aromatic), 172.2 (Ir-C=).
3k-Cl	2k	29 mg, 99%	Found: 468.0923 Calc [M-Cl+H] ⁺ : 468.0944	1.74 (s, 15H, Cp*), 7.00-7.04 (m, 1H, aromatic), 8.59-8.70 (m, 2H, aromatic), 9.16 (s, 1H, H-C=).	9.2 (CH ₃ , Cp*), 90.0 (C, Cp*), 116.7, 123.0, 158.4, 158.5, 171.3 (C&CH aromatic), 172.5 (Ir-C=)
3'a²	2a	20 mg (98%)	Found: 377.0428 Calc [M-Cl+H] ⁺ : 377.0418	1.67 (s, 15H, Cp*), 7.08-7.12 (m, 1H, aromatic), 7.51 (d, 1H, <i>J</i> = 8.0 Hz, aromatic), 7.70-7.74 (m, 1H, aromatic), 8.56 (d, 1H, <i>J</i> = 5.2 Hz, aromatic), 8.60 (s, 1H, H-C=)	9.3 (CH ₃ , Cp*), 96.2 (d, ¹ <i>J</i> _{RhC} =6.18 Hz, C, Cp*), 120.9, 121.2, 137.8, 151.0 (C&CH, aromatic), 178.8 (d, ¹ <i>J</i> _{RhC} =35.14 Hz, Rh-C=).
3'b	2b	24 mg, 99%	Found: 453.0734 Calc [M-Cl+H] ⁺ : 453.0731	1.37 (s, 15H, Cp*), 7.08-7.12 (m, 1H, aromatic), 7.19-7.23(m, 1H, aromatic), 7.32-7.36 (m, 2H, aromatic), 7.59-7.61 (m, 2H, aromatic), 7.64-7.66 (m, 1H, aromatic), 7.71-7.75(m, 1H, aromatic), 8.74 (d, 1H, <i>J</i> = 5.2 Hz).	8.8 (CH ₃ , Cp*), 96.4 (d, ¹ <i>J</i> _{RhC} =6.61 Hz, C, Cp*), 120.9, 121.0, 126.3, 127.1, 127.7, 137.6, 144.8, 150.8, 163.6 (C&CH aromatic), 186.8 (d, ¹ <i>J</i> _{RhC} =32.96 Hz, Rh-C=).

² Anal. Calcd for C₁₇H₂₀C₁₂NRh: C, 49.54; H, 4.89; N, 3.40. Found: C, 50.05; H, 5.29; N, 2.99.

Computational studies. Geometry optimizations were carried out by DFT utilizing Becke's three-parameter hybrid function,²⁹ and Lee, Yang, and Parr's gradient-corrected correlation function (B3LYP).³⁰ The LANL2DZ (Los Alamos effective core potential double- ζ) basis set, together with an f polarization function,³¹ was employed for the Ir atom; the 6-311+G(2d,p) basis set was used for all the other atoms. For calculations involving solvated species, the polarized continuum model (PCM) using dichloromethane as the solvent was employed to approximate a solvent field. 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. The transition state was characterised with one imaginary frequency which corresponded to the expected reaction trajectory. NICS(l) was evaluated by placing a ghost atom (Bq) at the geometric mean of the ring atoms, and NICS(n) and NICS(- n) with Bq at n Å above and below the geometric centre, respectively (Table 1). The NICS values are the isotropic chemical shifts of the respective Bq's. All calculations were performed using the Gaussian 09 suite of programs.³²

Supporting information

Crystallographic data of **3a-Cl** in CIF format, experimental details and characterization for the complexes, details of deuterium labelling experiments, and of computational studies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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