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The Reaction of [Cp*IrCl₂]₂ with 2-Methyl-1-butene-3-yne: Formation of a η^3 -Tetraenyl Transition Metal Complex

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Key words: Iridium; η^3 -tetraenyl; conjugated enyne; C-C coupling

Abstract

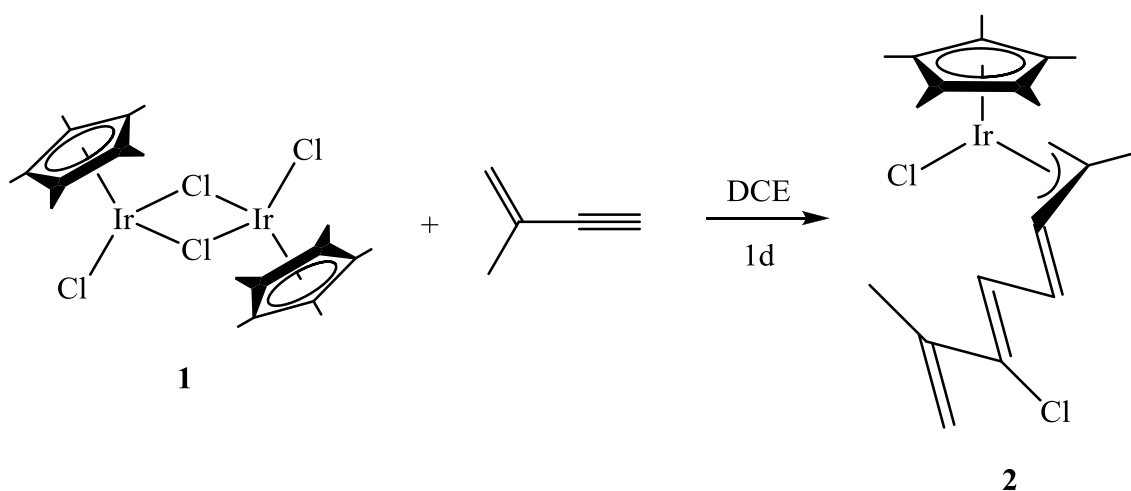
Reaction of the dimeric species [Cp*IrCl₂]₂ with 2-methyl-1-butene-3-yne results in C-C bond formation between two alkyne molecules and their coordination to an iridium center to form a complex containing a η^3 -tetraenyl ligand. The reaction pathway has been studied experimentally and computationally.

Introduction

The chemistry of half-sandwich iridium complexes with terminal alkynes that has been reported include hydration,¹ hydrosilylation,² C≡C bond cleavage in the presence of water,³ and insertion into a metal-hydride/halide bond.⁴ In particular, we have found that the reaction of [Cp*IrCl₂]₂, **1**, with terminal alkynes in the presence of water, alcohols or anilines afforded carbonyl alkyl complexes [Cp*IrCl(CO)(CH₂R)] via C≡C bond cleavage, alkoxy-carbene complexes [Cp*IrCl₂(=C(OR')CH₂R)],^{3e} or aminocarbene complexes [Cp*Ir(Cl){=C(CH₂R')NHC₆H₃R}] via a hydroamination and an orthometallation,⁵ respectively. In addition, we have also recently reported the formation of an iridafuran from the reaction of **1** with a C=O conjugated alkyne.⁶ In contrast to this, we found that the reaction of **1** with a C=C conjugated alkyne (enyne), resulted in the formation of an iridium complex containing a η^3 -tetraenyl functionality. We wish to report here our studies on this reaction.

Results and Discussion

The reaction of **1** with 2-methyl-1-butene-3-yne afforded complex **2**, which was the result of the head-to-head coupling of two units of the enyne, in 85% yield (Scheme 1). Complex **2** has been completely characterized; assignments of the ^1H and ^{13}C resonances have been made with the aid of ^1H NOESY, HMBC and HMQC experiments, and are given in Figure 1.



Scheme 1

The head-to-head C-C coupling reaction is in contrast to that with terminal alkynes in which the $\text{C}\equiv\text{C}$ bond was cleaved in the presence of water,⁴ as well as with C=O conjugated alkynes in which there was head-to-tail coupling of the alkyne units.⁶ The C-C coupled ligand is technically a η^3 -tetraenyl ligand and appears to be, to our knowledge, the first such example. The closest analogues are η^3 -butadienyl and η^3 -allylic complexes, examples of the former being relatively rare;⁷ a chromium complex, [(mesityl)Cr(CO)₂(CH₂CHC=CH₂)] [BF₄], had only been synthesized and structurally characterized recently.^{7ⁿ}

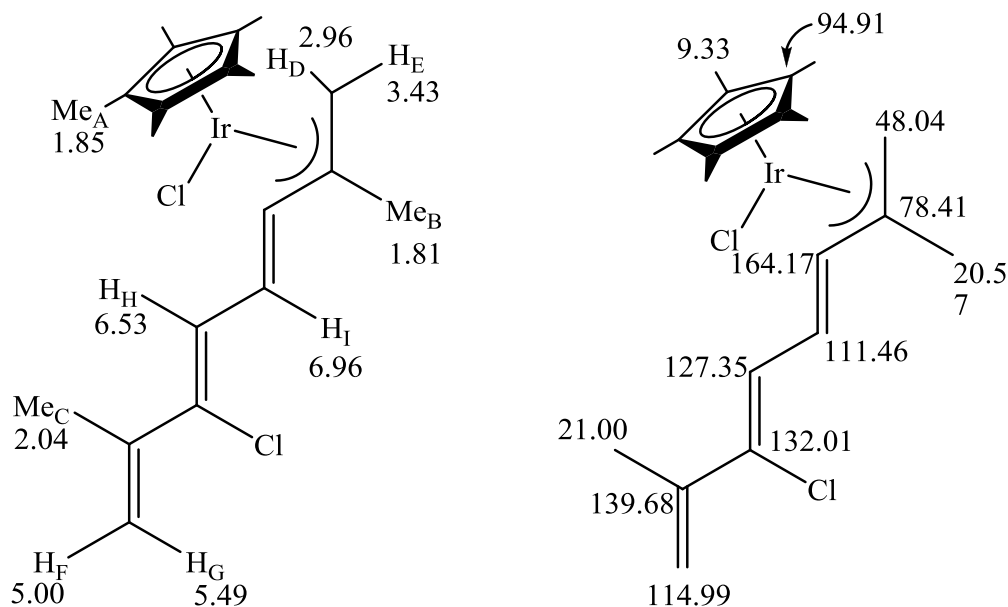


Figure 1. ^1H (left) and ^{13}C (right) NMR assignments for **2**.

Complex **2** has also been characterised crystallographically; there were two crystallographically independent molecules found and the ORTEP plot showing the structure for one of the molecules is given in Figure 2. The tetraenyl ligand is bonded to the metal centre much like an allyl moiety, in a more or less symmetrical, *exo* fashion; the Ir-C distances for this range from 2.030(4) to 2.190(4) Å, while the C-C bond distances of the allyl moiety range from 1.408(6) to 1.420(6) Å. The *exo* triene unit is bent away from the iridium and out of the C(1)-C(2)-C(3) plane, and the bond parameters are as may be expected; the C=C double bonds range in lengths from 1.331(6) to 1.345(7) Å, and the C-C single bonds (along the main tetraenyl chain) range in lengths from 1.434(6) to 1.463(7) Å, consistent with delocalization along the triene. This triene fragment is, however, not conjugated to the allyl moiety; the dihedral angle between the the C(1)-C(2)-C(3) and C(3)-C(4)-C(5) planes is 58.5° and 44.7° for molecules A and B, respectively.

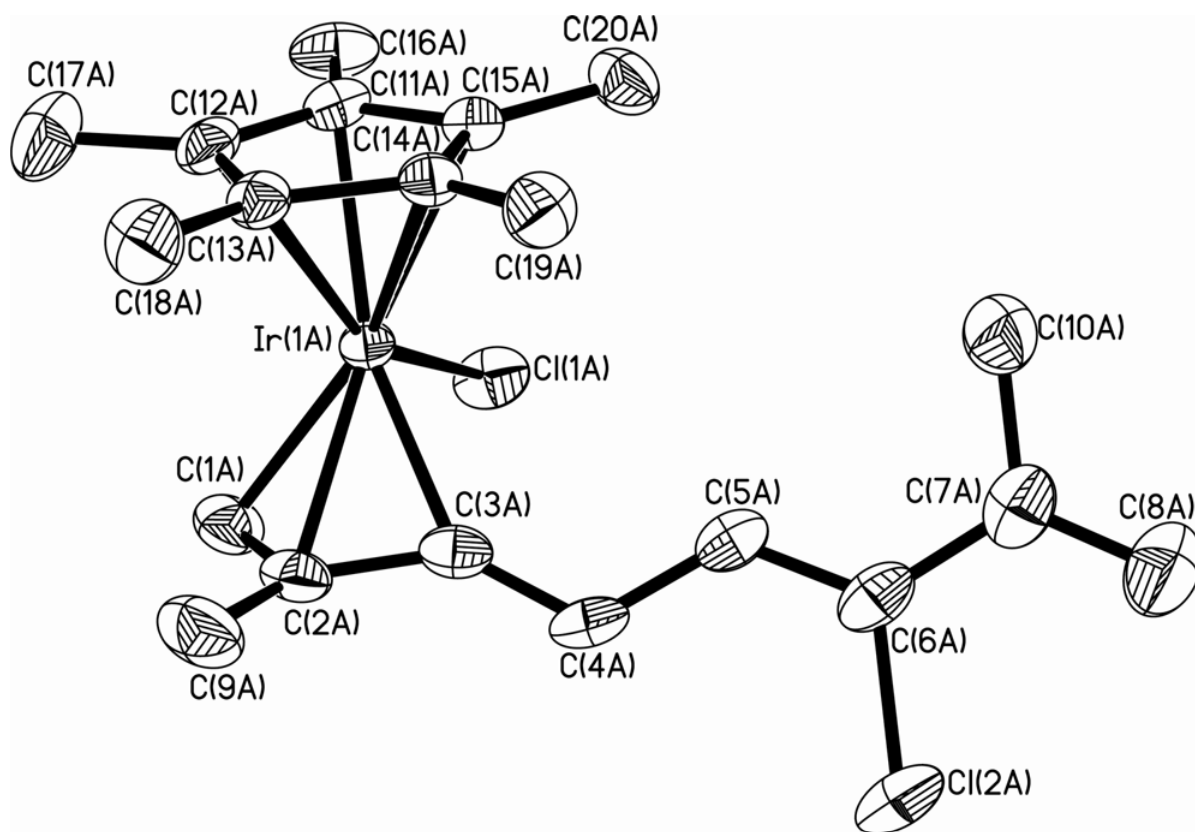


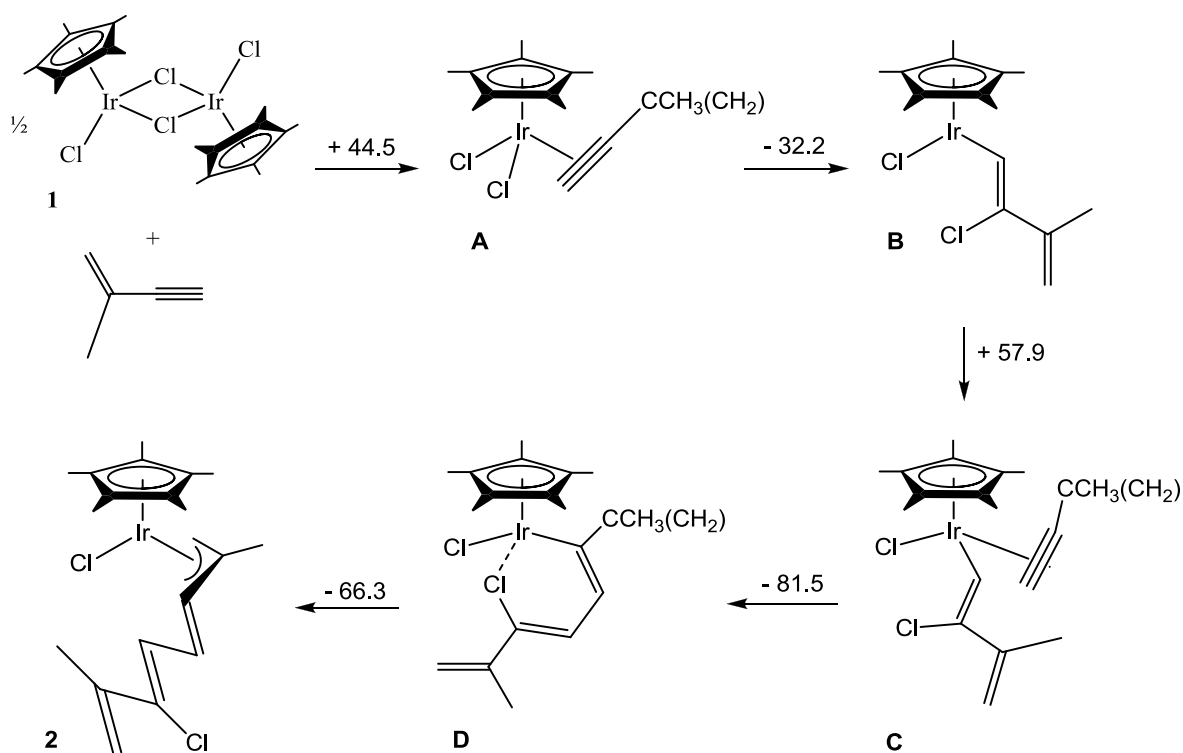
Figure 2. ORTEP plot (50% probability thermal ellipsoids) showing the molecular structure and atomic numbering scheme for molecule A of complex **2**. Selected bond lengths (Å) and angles (°): Ir(1A)-C(1A) = 2.185(4); Ir(1A)-C(2A) = 2.175(4); Ir(1A)-C(3A) = 2.043(4); C(1A)-C(2A) = 1.420(6); C(2A)-C(3A) = 1.412(6); C(3A)-C(4A) = 1.331(6); C(4A)-C(5A) = 1.434(6); C(5A)-C(6A) = 1.343(6); C(6A)-C(7A) = 1.463(7); C(7A)-C(8A) = 1.335(7); C(7A)-C(10A) = 1.492(7); C(1A)-C(2A)-C(3A) = 115.2(4); C(2A)-C(3A)-C(4A) = 142.6(4); C(3A)-C(4A)-C(5A) = 122.3(4); C(4A)-C(5A)-C(6A) = 128.5(4); C(5A)-C(6A)-C(7A) = 126.3(4); C(6A)-C(7A)-C(8A) = 123.6(5).

The reaction depicted in Scheme 1 appeared to work with 1-ethynyl-1-cyclohexene, an enyne containing an internal alkene functionality, to give the analogue **2a**; the ^1H NMR spectrum of the crude mixture showed two characteristic doublets for the alkenic protons (δ_{H} 6.94 and 6.39 ppm, $^3J_{\text{HH}} = 9.8$ Hz) similar to those observed for **2** (δ_{H} 6.96 and 6.53 ppm, $^3J_{\text{HH}} = 11$ Hz). However, an attempt at purification by TLC led to decomposition. The reaction

also appeared to proceed with the bromo analogue of **1**, viz., [Cp*IrBr₂]₂, **1'**; it reacted with 2-methyl-1-buten-3-yne to give two products in a 1:1 ratio; Cp*Ir(CO)(Br)₂, **3'**, and a compound deduced (on the basis of the ¹H NMR spectroscopic data) to be the analogue of **2** in which both chlorine atoms have been replaced with bromine atoms (**2b**). On the other hand, the reaction failed with 2-methyl-1-hexen-3-yne, an enyne containing an internal alkyne functionality, and with isoprene. These results indicated that a terminal alkyne, but not a terminal alkene, functionality was required.

No intermediates were observed when the formation of **2** was monitored by ¹H NMR spectroscopy; only resonances ascribable to **1**, **2** or unreacted enyne were observed. An attempt at cross coupling of a C=C conjugated alkyne with a non-conjugated alkyne was also unsuccessful, and a reaction involving **1** with two equivalents each of 2-methyl-1-buten-3-yne and phenylacetylene resulted only in equal amounts of **2** and unreacted **1** after workup (which removed the unreacted phenylacetylene).

The tentative reaction pathway for the formation of **2** which we are proposing is depicted in Scheme 2; the structures shown are of intermediates, with geometries optimized using density functional theory (DFT). The free energies (in kJ mol⁻¹) for the reaction steps have been computed and are also given.



Scheme 2

The first step (**A** to **B**) is similar to that which we have proposed for the reaction of **1** with C=O conjugated alkynes, and involves a *1,2*-insertion of the alkyne into the Ir-Cl bond.⁶ If this step involves an ionic pathway, then it may account for the failure of 2-methyl-1-hexen-3-yne to react; the decreased electrophilicity of the alkyne group due to the presence of the additional electron donating ethyl group. A second alkyne insertion (via intermediate **C**) into the Ir-C bond results in the intermediate **D**. The optimized geometry of **D** shows the chlorine atom on the organic ligand interacting via a dative bond with the iridium center and thus maintaining an 18-electron configuration there (Figure 3). The step from **C** to **D** involves a *2,1*- rather than a *1,2*-insertion and is presumably reversible; the latter would have given an intermediate which cannot lead to a complex with a η^3 -bonding mode, and the final step involving a η^1 to η^3 hapticity shift similar to that reported for similar complexes,^{7^a} may have been the driving force for the reaction.

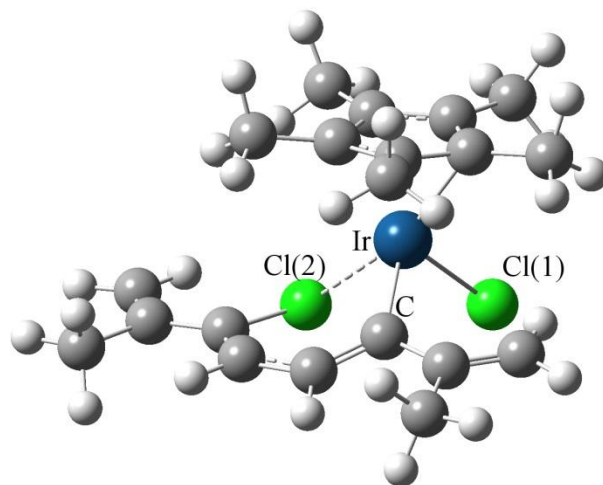


Figure 3. Optimized geometry for intermediate **D**. Selected bond distances [\AA] and angles [deg]: Ir-Cl(1), 2.425; Ir-Cl(2), 2.591; Ir-C, 2.069; Cl(1)-Ir-C, 94.3; Cl(2)-Ir-C, 84.4; Cl(1)-Ir-Cl(2), 80.3.

Concluding Remarks

We have reported here our discovery that the reaction of $[\text{Cp}^*\text{IrCl}_2]_2$ with the conjugated enyne 2-methyl-1-butene-3-yne resulted in C-C bond formation between two enyne molecules to form a complex containing the novel η^3 -tetraenyl ligand. This reaction appears to work with conjugated enynes containing either an internal, or a terminal, alkene functionality but the alkyne functionality must be terminal. A reaction pathway has also been proposed. We believe that such complexes may be available for other metal systems, and that the methodology may have general applicability.

Experimental

General Procedures. All reactions and manipulations were performed under argon using standard Schlenk techniques. Solvents were purified, dried, distilled, and stored under argon prior to use, except for 1,2-dichloroethane, which was used as supplied. IR spectra were acquired as CH_2Cl_2 solutions. ^1H NMR spectra were recorded on a Bruker ACF300 or

AV300 NMR spectrometer as CDCl₃ solutions; chemical shifts reported were referenced against the residual signals of the solvent. Mass spectra were obtained on a Finnigan MAT95XL-T spectrometer in a 3NBA matrix (FAB) or a Finnigan MAT LCQ spectrometer with MeOH as solvent (ESI). All elemental analyses were performed by the microanalytical laboratory at NUS. [Cp*IrCl₂]₂, **1**, and [Cp*IrBr₂]₂, **1'**, were prepared according to their published methods.^{8,9} All other reagents were from commercial sources and used without further purification.

Reaction of 1 with 2-methyl-1-butene-3-yne. A dichloroethane solution (3 ml) of **1** (36.3 mg, 45.6 μmol) and 2-methyl-1-butene-3-yne (36 μL, 0.38 mmol) was stirred at room temperature for 20 minutes. The solvent was then removed under reduced pressure and the residue obtained was dissolved in a minimum amount of dichloromethane and chromatographed on silica gel TLC plates. ¹H NMR analysis of the crude mixture showed almost quantitative formation of **2**, with a small amount of Cp*Ir(CO)(Cl)₂, **3**. Elution with hexane/CH₂Cl₂ (1/1, v/v) yielded **2** as a yellow solid. Yield = 41 mg, 85%.

Data for **2**: ¹H NMR (δ, CDCl₃): 1.85 (s, 15H, Cp*), 1.81 (s, 3H, Me_B), 2.04 (s, 3H, Me_C), 2.96 (s, 1H, H_D), 3.43 (s, 1H, H_E), 5.00 (s, 1H, H_F), 5.49 (s, 1H, H_G), 6.53 (d, 1H, ³J_{HH} = 10.02 Hz, H_H), 6.96 (d, 1H, ³J_{HH} = 10.02 Hz, H_I). ¹³C NMR (δ, CDCl₃): 164.17 (s, C₃), 139.68 (s, C₇), 132.01 (s, C₆), 127.35 (s, C₅), 114.99 (s, C₈), 111.46 (s, C₄), 94.91 (s, Cp*), 78.41 (s, C₂), 48.04 (s, C₁), 21.00 (s, C₁₀), 20.57 (s, C₉), 9.33 (s, Cp*, CH₃). FAB-MS: 530 [M]⁺, 495 [M-Cl]⁺. Anal. Calcd for C₂₀H₂₇Cl₂Ir: C, 45.28; H, 5.13. Found: C, 45.63; H, 5.12.

Data for **3**: ¹H NMR (δ, CDCl₃): 1.94 (s, 15H, Cp*).

Repeating this procedure with isoprene or 2-methyl-1-hexen-3-yne resulted in only unreacted **1** after 2 d.

A similar procedure was employed for the reaction of [Cp*IrBr₂]₂, **1'** with 2-methyl-1-butene-3-yne. ¹H NMR spectroscopic analysis of the remaining orange-red residue showed

the presence of unreacted **1'**, **3'** and signals which could be interpreted to belong to **2b**, in a 1:2:2 ratio.

Data for **2b**: ^1H NMR (δ , CDCl_3): 1.83 (s, 3H, CH_3), 1.88 (s, 15H, Cp^*), 2.04 (s, 3H, CH_3), 3.27 (s, 1H), 3.30 (s, 1H), 5.04 (s, 1H), 5.48 (s, 1H), 6.68 (d, 1H, =CH), 6.86 (d, 1H, =CH)

Data for **3'**: ^1H NMR (δ , CDCl_3): 2.02 (s, 15H, Cp^*)

Reaction of 1 with 1-ethynyl-1-cyclohexene. To a solution of **1** (20 mg, 0.025 mmol) in dichloroethane (2 ml) was added 1-ethynyl-1-cyclohexene (20 μL , 0.17 mmol). The orange solution was stirred at room temperature for 1 h after which the orange solution turned wine red. All volatiles were removed under reduced pressure. ^1H NMR analysis of the remaining reddish residue showed a complex spectrum containing two major unidentified singlets in the Cp^* region at 1.71 and 1.90 ppm and two sets of alkene doublets at 6.38 ($J = 9.8$ Hz) and 6.93. The unidentified Cp^* signal and the alkene signals would be expected of the target complex **2a**. The crude mixture was subjected to TLC separation using DCM as the eluent. A deep purple band ($R_f \sim 0.5$) was observed, but slowly turned colourless on the plate, presumably due to decomposition. No identifiable products could be recovered.

Attempted cross coupling reaction of 1 with a mixture of 2-methyl-1-buten-3-yne and phenylacetylene. To a carius tube containing dried 4 Å molecular sieves (7 pieces) were added **1** (10 mg, 0.0126 mmol), dichloromethane (2 ml), 2-methyl-1-buten-3-yne (5 μL , 0.053 mmol) and phenylacetylene (6 μL , 0.055 mmol). The orange mixture was stirred at room temperature for 1 d after which all volatiles were removed under reduced pressure. ^1H NMR analysis of the remaining orange residue showed signals attributed to unreacted **1** and **2** in a 1:1 ratio.

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 $\text{Mo K}\alpha$ radiation, at 223 K with the SMART suite of programs.¹⁰ Data were

processed and corrected for Lorentz and polarization effects with SAINT¹¹ and for adsorption effects using SADABS.¹² The structure was solved by direct methods followed by difference maps to complete the structure. Hydrogen atoms were placed in calculated positions and refined with a riding model. All non-hydrogen atoms were given anisotropic displacement parameters in the final model.

Table 1. Crystal data and structure refinement for **2**.

Empirical formula	C ₂₀ H ₂₇ Cl ₂ Ir
Formula weight	530.52
Crystal system	Monoclinic
Space group	P2 ₁ /c
a, Å	8.3579(3)
b, Å	34.3148(13)
c, Å	14.1156(5)
β, deg	91.3810(10)
Volume, Å ³	4047.2(3)
Z	8
Density (calculated), Mg/m ³	1.741
Absorption coefficient, mm ⁻¹	6.860
F(000)	2064
Crystal size, mm ³	0.38 x 0.22 x 0.06
Reflections collected	61016
Independent reflections	11809 [R(int) = 0.0433]
Max. and min. transmission	0.6837 and 0.1802
Data / restraints / parameters	11809 / 0 / 429
Goodness-of-fit on F ²	1.166
Final R indices [I > 2σ(I)]	R1 = 0.0367, wR2 = 0.0731
R indices (all data)	R1 = 0.0437, wR2 = 0.0755
Largest diff. peak and hole, e.Å ⁻³	2.093 and -1.211

Computational studies. The computational studies were carried out using density function theory (DFT), utilising the Becke's three parameter hybrid function¹³ and Lee-Yang-Parr's gradient-corrected correlation function¹⁴ (B3LYP). The basis set used was the LANL2DZ (Los Alamos Effective Core Potential Double- ζ) augmented with an *f* polarization function,¹⁵ for the iridium atom, and 6-311+G(2d,p) for the light atoms. Spin-restricted calculations were used for structural optimization, harmonic frequency calculations and to evaluate zero-point energy (ZPE) corrections. Optimized geometries were characterized as equilibrium structures with all real frequencies. All calculations were performed using the Gaussian 09 suite of program.¹⁶

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Supplementary material: CCDC 932282 contains the supplementary crystallographic data for **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Crystal and refinement data, and 2D-NMR spectra for **2**, and optimized geometry of computed structures.

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