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Note

The reaction of $[Cp^*IrCl_2]_2$ with 2-methyl-1-butene-3-yne: Formation of a η^3-tetraenyl transition metal complex

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ABSTRACT

Reaction of the dimeric species $[Cp^*IrCl_2]_2$ 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.

1. 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 $[Cp^*IrCl_2]_2$, **1**, with terminal alkynes in the presence of water, alcohols or anilines afforded carbonyl alkyl complexes $[Cp^*IrCl(CO)(CH_2R)]$ via C≡C bond cleavage, alkoxycarbene complexes $[Cp^*IrCl_2(=C(OR')CH_2R)]$,3[e] or aminocarbene complexes $[Cp^*Ir(Cl)\{=C(CH_2R')NHC_6H_3R\}]$ 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.

2. 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 Fig. 1.

The head-to-head C–C coupling reaction is in contrast to that with terminal alkynes in which the C≡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 analogs are η^3-butadienyl and η^3-allylic complexes, examples of the former being relatively rare [7]; a chromium complex, $[(mesityl)Cr(CO)_2(CH_2CHC=CH_2)][BF_4]$, had only been synthesized and structurally characterized recently [7n].

Complex **2** has also been characterized crystallographically; there were two crystallographically independent molecules found and the ORTEP plot showing the structure for one of the molecules is given in Fig. 2. The tetraenyl ligand is bonded to the metal center 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

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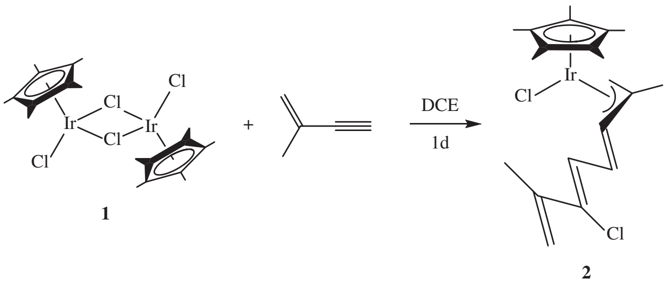

Scheme 1. The reaction of **1** with 2-methyl-1-butene-3-yne.

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 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.

The reaction depicted in Scheme 1 appeared to work with 1-ethynyl-1-cyclohexene, an enyne containing an internal alkene functionality, to give the analog **2a**; the ^{1}H NMR spectrum of the crude mixture showed two characteristic doublets for the alkenic protons (δ_H 6.94 and 6.39 ppm, $^3J_{HH}$ = 9.8 Hz) similar to those observed for **2** (δ_H 6.96 and 6.53 ppm, $^3J_{HH}$ = 11 Hz). However, an attempt at purification by TLC led to decomposition. The reaction also appeared to proceed with the bromo analog of **1**, *viz.*, $[Cp^*IrBr_2]_2$, **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 ^{1}H NMR spectroscopic data) to be the analog 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 ^{1}H 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.

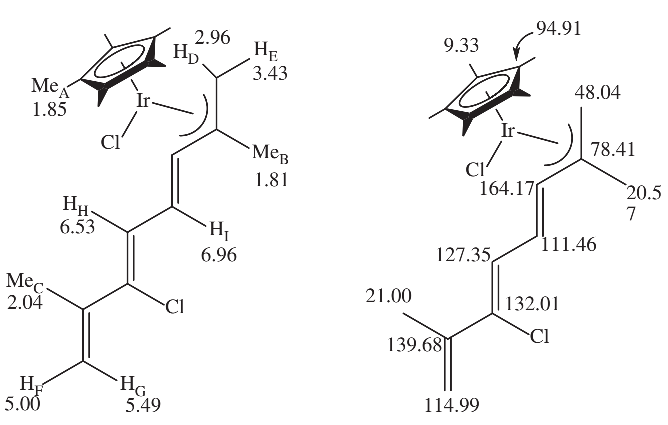

Fig. 1. ^{1}H (left) and ^{13}C (right) NMR assignments for **2**.

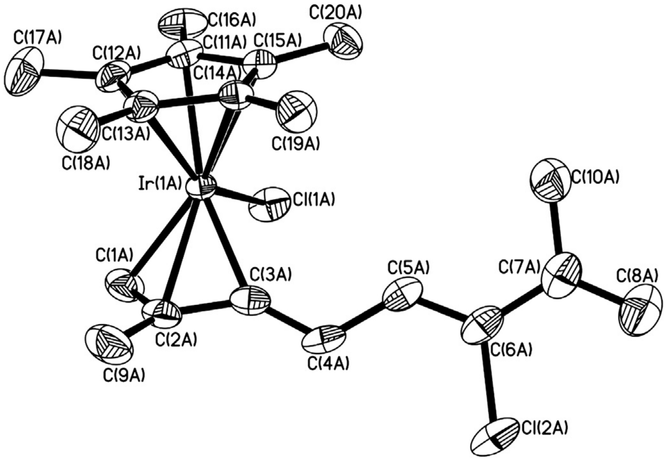

Fig. 2. ORTEP plot (50% probability thermal ellipsoids) showing the molecular structure and atomic numbering scheme for molecule **A** of complex **2**. Selected bond lengths (Å) and angles (°): Ir(1A)–C(1A) = 2.185(4); Ir(1A)–C(2A) = 2.175(4); Ir(1A)–C(3A) = 2.043(4); C(1A)–C(2A) = 1.420(6); C(2A)–C(3A) = 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 first step (**A**–**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 (Fig. 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–η^3 hapticity shift similar to that reported for similar complexes [7a], may have been the driving force for the reaction.

3. Concluding remarks

We have reported here our discovery that the reaction of $[Cp^*IrCl_2]_2$ 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.

4. Experimental

4.1. 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