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An Arbuzov-type reaction with the bis(alkynyl) iridium complex $[Cp^*Ir(L)(C{\equiv}CAr)_2]$

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ABSTRACT

The bis(alkynyl) iridium complexes $[Cp^*Ir(L)(C{\equiv}CAr)_2]$ undergo an Arbuzov-type reaction with phosphites to give four-membered iridacyclic phosphonates $[Cp^*Ir(L)\{C(Ar){=}C[P({=}O)(OR)_2]C{=}CHAr\}]$. These can isomerise to a five-membered iridafuran in the presence of a strong acid. In the absence of a phosphite, the bis(alkynyl) iridium complexes undergo acid-catalysed aerobic oxidation to form 1,2-diketone iridabenzofurans $[Cp^*Ir(L)\{C_6H_4\text{-}1,2\text{-}CH{=}CC({=}O)C({=}O)Ar\}]$. A common reaction pathway involving initial protonation and alkynyl migration is proposed.

1. Introduction

Bis(alkynyl) complexes are known for Cr [1], Mn [2], Fe [3], Ru [4], Os [5,4f,4g], Co [6], Rh [1a,b], Ir [7], Pd [8], Pt [8,9], Au [10], and Hg [11]. Much of this has been driven by interest in their potential as molecular wires and nonlinear optical materials, and their luminescent properties. Reports on their reactivity, on the other hand, are rather limited. They include simple nucleophilic substitution of an alkynyl in an osmium complex [4f], protonation of an anionic manganese complex to form an alkenylidene [2c], or of a ruthenium complex to form a butenenyl via C–C coupling between the two alkynyl ligands [4d], and acid catalysed hydrolysis of an alkynyl to a ketone in a ruthenium complex; this last reaction also gave a ruthenacycle [4c]. There are also examples of bis(alkynyl) complexes of platinum used in the synthesis of heteronuclear clusters [12].

Recently, we reported the synthesis of the bis(alkynyl) iridium complexes $[Cp^*Ir(CO)(C{\equiv}CAr)_2]$ and studied their reductive coupling in MeOH to the diyne complexes $[Cp^*Ir(CO)(ArC{\equiv}CC{\equiv}CAr)]$ [13]. In the course of those investigations, we attempted to measure the kinetics of that reaction for a phosphite derivative $[Cp^*Ir[P(OMe)_3](C{\equiv}CPh)_2]$, **1a-H**; an excess of $P(OMe)_3$ was used to suppress any dissociation of the phosphite ligand. We found, instead, that the kinetics deviated from that expected, i.e., a first-order reaction, which we eventually traced to a reaction between the bis(alkynyl) complex and the phosphite. We wish to report here the results of those investigations.

2. Discussion

The reaction of **1a-H** with $P(OMe)_3$ was found to afford a four-membered metallacyclic complex $[Cp^*Ir[P(OMe)_3]\{(Ph)C{=}C[P({=}O)(OMe)_2]C{=}CHPh\}]$, **2a-H**; the yield improved in the presence of acetic acid (isolated yields ~10–55%) (Scheme 1). The reaction was tolerant of variations to the substituents on the phenyl ring of the alkynyls, and of the ancillary ligand (L) on the iridium centre. It also proceeded with a different phosphite; the reaction of **2a-H** with $P(OEt)_3$ afforded $[Cp^*Ir[P(OMe)_3]\{C(Ph){=}C[P({=}O)(OEt)_2]C{=}CHPh\}]$, **2′a-H**, although the reaction proceeded differently with $P(OPh)_3$ and we have not attempted to identify the species formed.

In the presence of a strong acid, *viz.*, 37% aq HCl, the four-membered metallacycle **2a-H** isomerized to the ring expansion product **3a-H**; this isomerisation did not occur with acetic acid. In the absence of added phosphite, the complexes **1n-X** reacted with air/O_2 (and in the presence of CH_3COOH) to afford 1,2-diketone iridabenzofuran complexes with the general formula [Cp*Ir(L)

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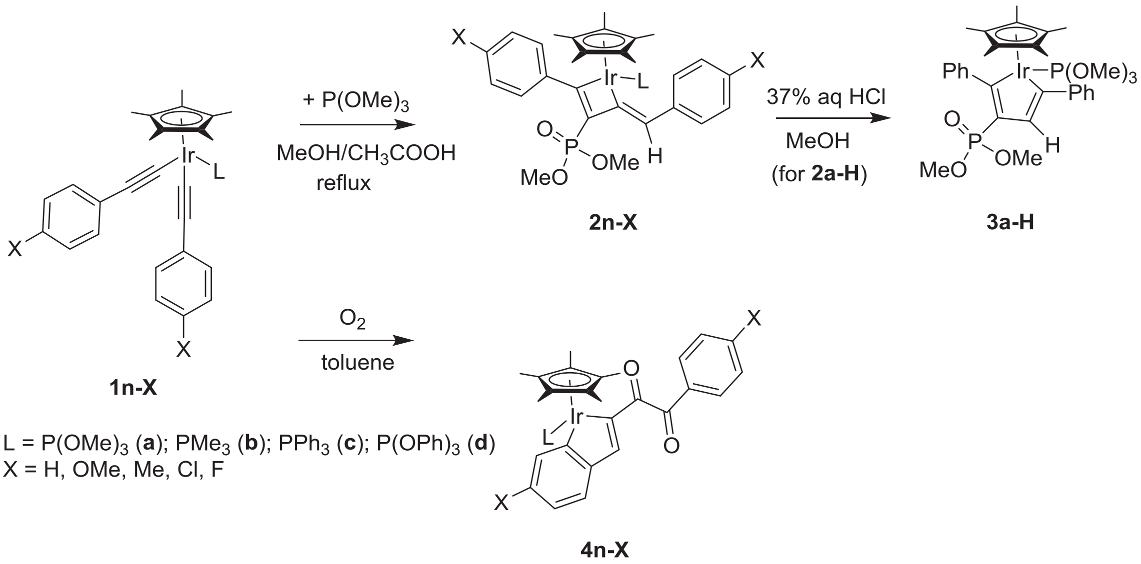

Scheme 1.

{C_6H_4-*1,2*-CH=CC(=O)C(=O)C_6H_4X-*p*}], **4n-X**; the isolated yields were modest (20–50%), although the ^1H NMR spectra of the reaction crude showed that the conversions were quantitative. All the products have been completely characterized spectroscopically and by elemental analyses, and the structures of **2a-H**, **3a-H** and **4c-H** have been confirmed by single-crystal X-ray crystallographic studies; the ORTEP plots are given in Figs. 1 to 3, respectively, together with selected bond parameters.

In all three structures, the metallacyclic rings are planar. The bond parameters are consistent with little delocalisation within the metallacycle. For example, the C=C double bond length range is 1.35–1.37 Å and the C(sp^2)-C(sp^2) single bond length range is 1.44–1.48 Å [14], while the Ir···C19 vector in **2a-H** is nonbonding at 2.650(3) Å. The Wiberg bond indices from a computational study on **2a-H** and **3a-H** are consistent with these, with values of ~1.7, 1.1 and 0.06, respectively (Fig. S4). The Ir–C bond lengths for the iridacycles (~2.06 Å) are rather shorter than an Ir–C single bond (~2.16) [15], and comparable to those in *N*-iridacyles (~2.03 Å) which exhibit Ir=C double bond character [16]; their bond indices are ~0.7 in **2a-H** and **3a-H**.

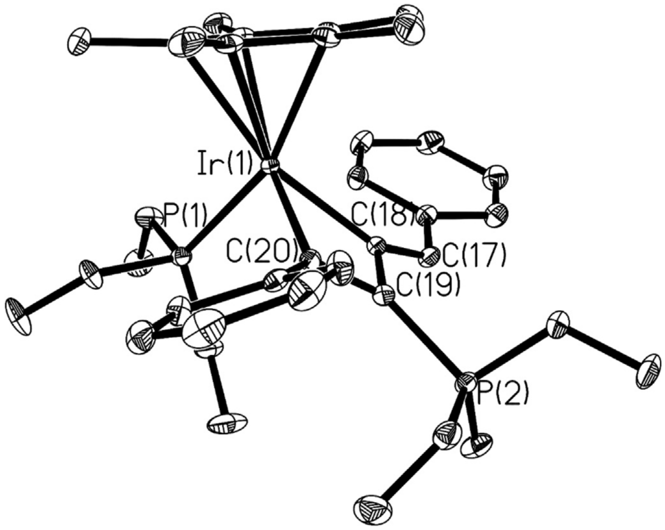

Fig. 1. ORTEP plot of **2a-H** (50% probability thermal ellipsoids). H atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ir1–C20 = 2.063(3); Ir1–C18 = 2.092(3); C18–C19 = 1.476(4); C19–C20 = 1.359(4); C19–P2 = 1.777(3); P2–O6 = 1.472(2); P2–O4 = 1.588(2); C17–C18 = 1.345(4); Ir1–P1 = 2.1909(7); C18–Ir1–C20 = 64.10(10); Ir1–C20–C19 = 99.37(19); C20–C19–C18 = 102.0(2); C19–C18–Ir1 = 94.24(17); Ir1–C18–C17 = 140.5(2); C20–C19–P2 = 132.6(2).

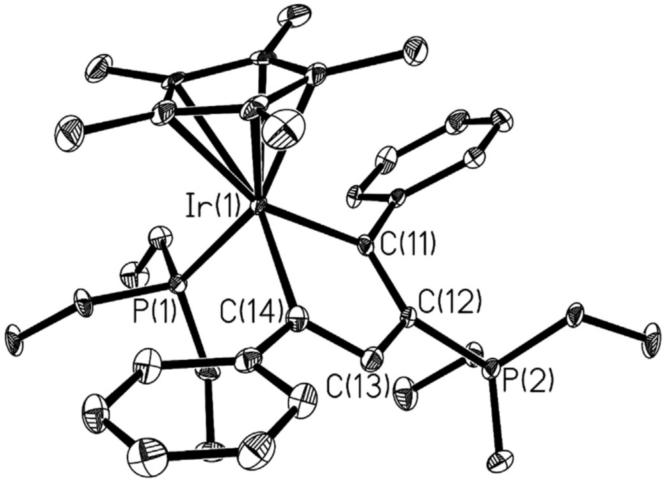

Fig. 2. ORTEP plot of **3a-H** (50% probability thermal ellipsoids). H atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ir1–C14 = 2.073(4); Ir1–C11 = 2.059(4); C11–C12 = 1.368(5); C12–C13 = 1.453(5); C13–C14 = 1.351(5); C12–P2 = 1.766(4); P2–O4 = 1.475(3); C14–C23 = 1.484(5); Ir1–P1 = 2.2001(10); C11–Ir1–C14 = 78.45(15); Ir1–C14–C13 = 115.4(3); C14–C13–C12 = 115.6(4); C13–C12–C11 = 114.9(3); C12–C11–Ir1 = 115.6(3); C12–C11–C15 = 121.1(3).

It is possible that the source of the O=$P(OMe)_2$ moiety is dimethyl phosphate, HP(=O)$(OMe)_2$, which may be formed under certain conditions from $P(OMe)_3$ [17]. This was excluded through an experiment in which HP(=O)$(OMe)_2$ was used in place of $P(OMe)_3$; no **2a-H** was obtained. The observations are consistent with the Arbuzov reaction, which involves the reaction of a trialkyl phosphite with an alkyl halide to form a phosphonate [18]. Organometallic variants of this reaction have been reported for Fe [19], Co [20], Ni [21], and Rh [22]. In those organometallic examples, the reactions involved attack at a metal-coordinated phosphite. Most often, a halide ion abstracted an alkyl group from a cationic