Journal of Organometallic Chemistry 696 (2011) 2870–2876

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Cationic iridium complexes of the Xantphos ligand. Flexible coordination modes and the isolation of the hydride insertion product with an alkene

Ashley J. Pontiggia, Adrian B. Chaplin, Andrew S. Weller*

Department of Chemistry, Inorganic Chemistry Laboratory, University of Oxford, Oxford, OX1 3QR, UK

ARTICLE INFO

Article history:
Received 14 January 2011
Received in revised form
28 January 2011
Accepted 28 January 2011

Keywords:
Iridium
Phosphine
Pincer
X-ray
Hydride
Xantphos

ABSTRACT

Reaction of the Ir(I)–Xantphos complex [Ir(κ^2–Xantphos)(COD)][BAr$^F_4$] (Xantphos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene, Ar^F = C$_6$H$_3$(CF$_3$)$_2$) with H$_2$ in acetone or CH$_2$Cl$_2$/MeCN affords the Ir(III)–hydrido complexes [Ir(κ^3–Xantphos)(H)$_2$(L)][BAr$^F_4$], L = acetone or MeCN, whereas in non-coordinating CH$_2$Cl$_2$ solvent dimeric [Ir(κ^3–Xantphos)(H)(μ-H)]$_2$[BAr$^F_4$]$_2$ is formed. A common intermediate in these reactions that invokes a (σ, η^2-C$_8$H$_{13}$) ligand is reported. Addition of excess tert-butylethene (tbe) to [Ir(κ^3–Xantphos)(H)$_2$(MeCN)][BAr$^F_4$] results in insertion of a hydride into the alkene to form [Ir(κ^3–Xantphos)(MeCN)(CH$_2$CH$_2$C(CH$_3$)$_3$)(H)][BAr$^F_4$], an Ir(III) alkyl–hydrido-Xantphos complex. This reaction is reversible, and heating (80 °C) results in the reformation of [Ir(κ^3–Xantphos)(H)$_2$(MeCN)][BAr$^F_4$] and tbe. These complexes have been characterised by NMR spectroscopy, ESI-MS and single-crystal X-ray diffraction. They show variable coordination modes of the Xantphos ligand: *cis*-κ^2–*P,P*, *fac*–κ^3–*P,O,P* and *mer*-κ^3–*P,O,P* with the later coordination mode like that found in related PNP–pincer complexes.

1. Introduction

Transition-metal complexes involving tridentate "pincer" ligands, especially with the later transition metals, are an important class of materials as they mediate many interesting, and contemporary, transformations such as the activation of E–H bonds [1–4]. Within the complexes of group 9 metals, those with formally neutral PNP-type ligands (Chart 1) are distinct from (formally anionic) PCP-type ligands as they often result in an overall positive charge on the metal centre. In this regard they are similar to POP-type ligands such a DPEphos and Xanthphos that have found application in a number of catalytic process, especially carbonylation reactions such as hydroformylation [5–7]. Xantphos (Chart 1) is a particularly interesting comparison, as it is relatively rigid and thus might be expected to coordinate in a manner similar to PNP–ligands [8,9]. However well-characterised P,O,P–κ^3–coordination modes of Xantphos are, surprisingly, rare, there being only a handful of fully characterised examples [8–12]. The P,P–κ^2–coordination mode (*i.e.* with the O–donor atom not bound) is far more common. We have recently reported upon this unusual κ^3 coordination mode using Rh-based systems, *e.g.* **A** [13], and were interested in extending this to iridium to afford complexes that are directly analogues to Ir–PNP systems that have found much recent application in C–H activation chemistry [14–18]. We report here a preliminary study into their synthesis and reactivity.

2. Results and discussion

Complex **1** [Ir(κ^2–Xantphos)(COD)][BAr$^F_4$] (COD = 1,5-cyclooctadiene, Ar^F = C$_6$H$_3$(CF$_3$)$_2$) that is the precursor to the studies reported here is readily synthesised by addition of Xantphos to [Ir(COD)Cl]$_2$ in CH$_2$Cl$_2$ solvent in the presence of the halide abstracting agent Na[BAr$^F_4$] Scheme 1. X-ray quality crystals of dark orange **1** allowed for the solid-state structure to be determined, as shown in Fig. 1. This demonstrates a pseudo-square planar environment around the Ir(I) centre with *cis* phosphines and an oxygen atom that is not coordinated with the metal (Ir1···O1, 2.544(2) Å). Although the coordination environment is distorted somewhat from being ideal square planar, with the Ir–P distances differing by 0.1 Å and the COD ligand twisted [planes defined by P1–Ir1–P2 and the Ir1–centroid(C1,C2)–centroid(C5,C6) 21.99(3)°] the cation approximates to C$_s$ symmetry in the solid-state. Other *cis*-κ^2–Xantphos complexes have been structurally characterised [10,19–22]. In contrast to the solid-state structure, in solution the ^{1}H NMR spectrum of **1** shows equivalent methyl protons (δ 1.75, 6H) at room temperature and a single alkene COD environment (*δ* 3.85, 4H), *i.e.* apparent C$_{2v}$ symmetry. The ^{31}P {^{1}H} spectrum shows a singlet at *δ* 14.26 demonstrating equivalent phosphine environments. These data are consistent with rapid inversion of the

* Corresponding author.
E-mail address: andrew.weller@chem.ox.ac.uk (A.S. Weller).

0022-328X/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2011.01.036

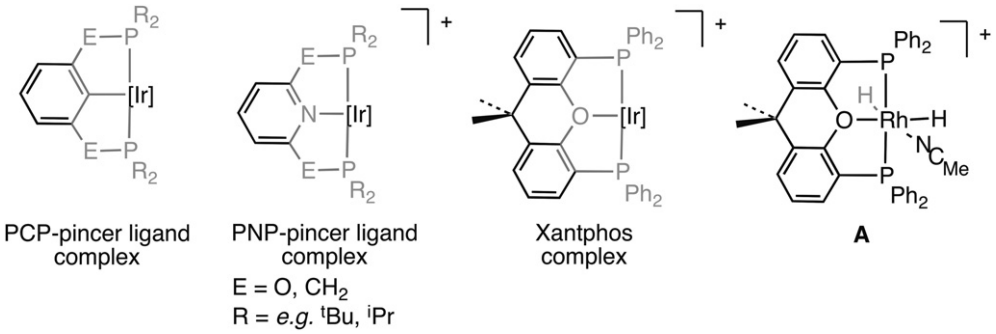


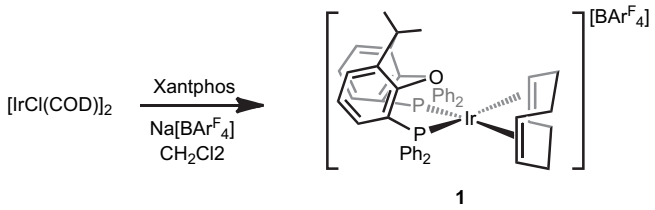
Chart 1.

Xantphos ligand on the NMR timescale in solution, possibility *via* a κ^3–intermediate [12]. Similar NMR data are observed for the analogous Rh–norbornadiene complex [13].

Addition of hydrogen (~4 atm) to **1** in d_6-acetone solution resulted in a colour change from orange to colourless, and ultimately (24 h) affords the dihydride complex [Ir(κ^3–Xantphos)(H)$_2$(acetone)][BAr$^F_4$], **3**, and the hydrogenation of COD to cyclooctane (COA). Initially formed, however, is an intermediate, spectroscopically characterised *in situ* as the monohydrido complex [Ir(κ^3–Xantphos)(H)(σ, η^2-C_8H_{13})][BAr$^F_4$] **2** (Scheme 2). The ^{1}H NMR spectrum of the reaction mixture after 10 min shows this intermediate to be the dominant species in solution. Two alkene peaks at δ 4.94 and 4.24 that integrate each to 1H relative to [BAr$^F_4$] and a doublet of doublets at δ −7.28 (dd, 1H) that shows *cis* couplings to the phosphines (J(PH) = 17.9, 27.5 Hz) are observed. This hydride signal collapses into a singlet on decoupling ^{31}P. Two Xantphos methyl environments are observed (δ 1.99, 1.41). The alkene peaks correlate with each another (COSY) and also to signals at 84.4 and 76.3 in the ^{13}C{^{1}H} NMR spectrum (HSQC) which lie in the region associated with bound alkene ligands. A relatively high frequency signal in the ^{1}H NMR spectrum (δ 3.58) does not couple with the alkene peaks (COSY) and shows a strong correlation to a carbon signal at 16.1. This carbon signal is also the lowest frequency one in the 13{1H} NMR spectrum and shows no correlation to other protons, suggesting an Ir–*CH*R$_2$ group. The ^{31}P {^{1}H} spectrum shows a pair of AB-roofed doublets (δ 7.4, 3.2) with a magnitude of coupling constant that demonstrates *trans*-orientated phosphines (J(PP) = 288 Hz). ESI-MS (ElectroSpray Ionisation-Mass Spectrometry) demonstrates the dominant parent ion at m/z = 881.267 ([IrC$_{47}$H$_{46}$P$_2$O$_1$]$^+$ calc. 881.265) that fits the suggested formulation. These data are fully consistent with partial hydrogenation of COD to form a (σ, η^2-C_8H_{13}) ligand. These data also argue against alternative formulations as an allyl [23–25] or vinyl[17] ligands. The formation of a σ, η^2-C_8H_{13} ligand from insertion of a hydride into a coordinated COD ligand has been reported previously [26,27].

Over a period of 24 h compound **2** smoothly converts to a new compound, characterised as [Ir(κ^3–Xantphos)(H)$_2$(acetone)][BAr$^F_4$], **3**. The ^{31}P {^{1}H} spectrum of **3** shows a single environment at δ 32.26 as a singlet, while two hydride environments are observed in the ^{1}H NMR spectrum at δ −26.01 and −26.90, both of which are doublets of triplets, collapsing to doublets on decoupling ^{31}P. The coupling constants show *cis* ^{1}H–^{31}P coupling (J(PH) = 13.8 and 14.0 Hz respectively), with no *trans* coupling observed. Inequivalent Xantphos methyl protons (δ 1.99 and 1.77) and free C_8H_{16} (δ 1.52) were also observed. There is no indication of any COD alkene or allyl signals in the range δ 3–5. These data point towards a structure for **3** as shown in Scheme 2. We assign the remaining coordination site to be occupied by a molecule of solvent (acetone). Similar structures have been reported for Rh [13] and Ru [8] Xantphos complexes while the close chemical shift of the hydrides points to a similar *trans* donor atom (*i.e.* O) for each. Strong peaks observed by ESI-MS at m/z = 831.208 ([IrC$_{42}$H$_{40}$O$_2$P$_2$]$^+$ calc. 831.213) and 773.168 ([M]$^+$ − acetone, calc. 773.171) support this formulation. We were unable to isolate crystalline samples of either **2** or **3** and thus neither a solid-state structural determination nor microanalytical data were obtained. Nevertheless spectroscopic and ESI-MS data are unequivocal for their determination.

Repeating the hydrogenation in very weakly-coordinating solvent CD_2Cl_2 with an added 2 eq of MeCN (per **1**) led to the formation of a new colourless complex [Ir(κ^3–Xantphos)(H)$_2$(MeCN)][BAr$^F_4$] **4** after 24 h, which was characterised by NMR spectroscopy, ESI-MS, and a single-crystal X-ray diffraction experiment (Scheme 3). The NMR data of **4** are very similar to those



Scheme 1.

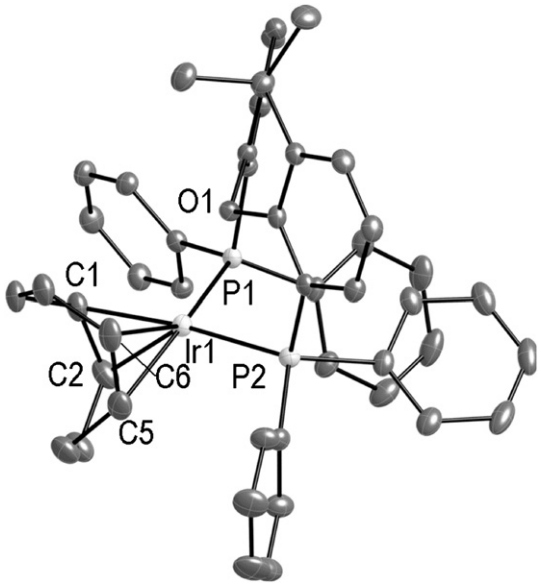


Fig. 1. The molecular crystal structure of the cationic portion of **1**, only the major disordered component of the COD ligand shown. Hydrogen atoms and anion are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level. Selected bond distances (Å): Ir1–P1, 2.3258(8); Ir1–P2, 2.4209(9); Ir1–C1, 2.161(4); Ir–C2, 2.161(4); Ir1–C5, 2.300(4); Ir1–C6, 2.208(4); Ir···O1, 2.544(2). Selected angle (°): P1–Ir1–P2, 101.22(3).