



## Alkyl dehydrogenation in iridium tri-cyclopentyl phosphines

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### ABSTRACT

The iridium cyclooctadiene complex incorporating a tricyclopentyl phosphine ligand (PCyp<sub>3</sub>), Ir(η<sup>2</sup>:η<sup>2</sup>-C<sub>8</sub>H<sub>12</sub>)(PCyp<sub>3</sub>)Cl, has been prepared. Removal of the chloride from this complex using Na[BAr<sup>F</sup><sub>4</sub>] [Ar<sup>F</sup> = C<sub>6</sub>H<sub>3</sub>(CF<sub>3</sub>)<sub>2</sub>] in CH<sub>2</sub>Cl<sub>2</sub>/arene solvent results in dehydrogenation (C–H activation followed by β–H transfer) of one of the alkyl phosphine rings and formation of the complexes [Ir(η<sup>6</sup>-C<sub>6</sub>H<sub>5</sub>X){PCyp<sub>2</sub>(η<sup>2</sup>-C<sub>5</sub>H<sub>7</sub>)}] [BAr<sup>F</sup><sub>4</sub>] (X = H, F) which contain a hybrid phosphine–alkene ligand. These complexes are formed alongside another product (5–20% yield) that has been identified as [Ir(η<sup>2</sup>:η<sup>2</sup>-C<sub>8</sub>H<sub>12</sub>){PCyp<sub>2</sub>(η<sup>2</sup>-C<sub>5</sub>H<sub>7</sub>)}] [BAr<sup>F</sup><sub>4</sub>], which can be prepared in high yield by an alternative, and slightly modified, route. This complex is with a minor isomer that has been tentatively identified as [Ir(η<sup>2</sup>:η<sup>3</sup>-C<sub>8</sub>H<sub>11</sub>)(H){PCyp<sub>2</sub>(η<sup>2</sup>-C<sub>5</sub>H<sub>7</sub>)}] [BAr<sup>F</sup><sub>4</sub>], which results from allylic C–H activation of cyclooctadiene. Addition of H<sub>2</sub> to [Ir(η<sup>2</sup>:η<sup>2</sup>-C<sub>8</sub>H<sub>12</sub>){PCyp<sub>2</sub>(η<sup>2</sup>-C<sub>5</sub>H<sub>7</sub>)}] [BAr<sup>F</sup><sub>4</sub>] and its isomer in arene solvent (C<sub>6</sub>H<sub>5</sub>X, X = F, H) forms the dihydrido η<sup>6</sup>-arene Ir(III) complexes [Ir(H)<sub>2</sub>(η<sup>6</sup>-C<sub>6</sub>H<sub>5</sub>X)(PCyp<sub>3</sub>)] [BAr<sup>F</sup><sub>4</sub>]. In contrast, hydrogenation in CH<sub>2</sub>Cl<sub>2</sub> alone results in the formation of Ir(H)<sub>2</sub>(PCyp<sub>3</sub>){η<sup>6</sup>-(C<sub>6</sub>H<sub>3</sub>(CF<sub>3</sub>)<sub>2</sub>)BAr<sup>F</sup><sub>3</sub>} in which the [BAr<sup>F</sup><sub>4</sub>]<sup>−</sup> anion is now acting as a ligand through one of its aryl rings. The fluorobenzene complex [Ir(H)<sub>2</sub>(η<sup>6</sup>-C<sub>6</sub>H<sub>5</sub>F)(PCyp<sub>3</sub>)] [BAr<sup>F</sup><sub>4</sub>] can be cleanly converted to [Ir(η<sup>6</sup>-C<sub>6</sub>H<sub>5</sub>F){PCyp<sub>2</sub>(η<sup>2</sup>-C<sub>5</sub>H<sub>7</sub>)}] [BAr<sup>F</sup><sub>4</sub>] by addition of the hydrogen acceptor *tert*-butylethene (tbe).

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## 1. Introduction

Hybrid phosphine–alkene ligands are receiving increased attention due to the role that they play in homogeneous catalysis, given the enhanced selectivity and reactivity that they promote when complexed with a metal centre [1]. Examples include: dehydrogenative silylation [2], functionalisation of nitrogen heterocycles *via* C–H activation [3], hydrogenation of imines [4], 1,4-addition reactions [5,6], Suzuki–Miyaura reactions [7] and allylic substitutions [8]. Such ligands can be prepared *via* standard chemical routes, but an attractive alternate methodology is to prepare the ligands *in situ* by a dehydrogenation procedure, which also furnishes an active metal complex with the ligand of interest. Indeed it has recently been demonstrated by Ellman, Bergman and co-workers that *in situ* dehydrogenation of cyclic phosphines can lead to a significantly more active and stable catalysts for C–H activation reactions [3]. Dehydrogenation of coordinated ligands is well established, and examples involving Ru [9], Rh [3,10–12], Re [13], Os [14], Ir [11,12,15] and Pt [16] have been reported. We, concurrently but independent to Sabo-Etienne and co-workers, have reported upon the late transition-metal chemistry of tricyclopentyl

phosphine, PCyp<sub>3</sub> [17,18], that can undergo dehydrogenation when complexed with a metal, to form phosphine–alkene ligands pre-organised on Ru [19,20] or Rh [6,21–23] centres (*e.g.* Scheme 1). In some cases the dehydrogenation is fully reversible, in that addition of H<sub>2</sub> hydrogenates the double bond to form a phosphine with a saturated backbone, which can then itself undergo dehydrogenation to re-establish the phosphine–alkene ligand coordinated to the metal centre [20–22]. Gr utzmacher and co-workers have also reported reversible dehydrogenation in cyclic phosphine systems complexed with iridium (Scheme 1) [24].

We report here an extension to our recent studies using rhodium–PCyp<sub>3</sub> materials to encompass iridium complexes. Low valent iridium complexes are known to be active alkane dehydrogenation catalysts [25] and we anticipated that dehydrogenation of the cyclic alkyl group in PCyp<sub>3</sub> would occur readily, leading to Ir(I) complexes containing a hybrid phosphine–alkene ligand.

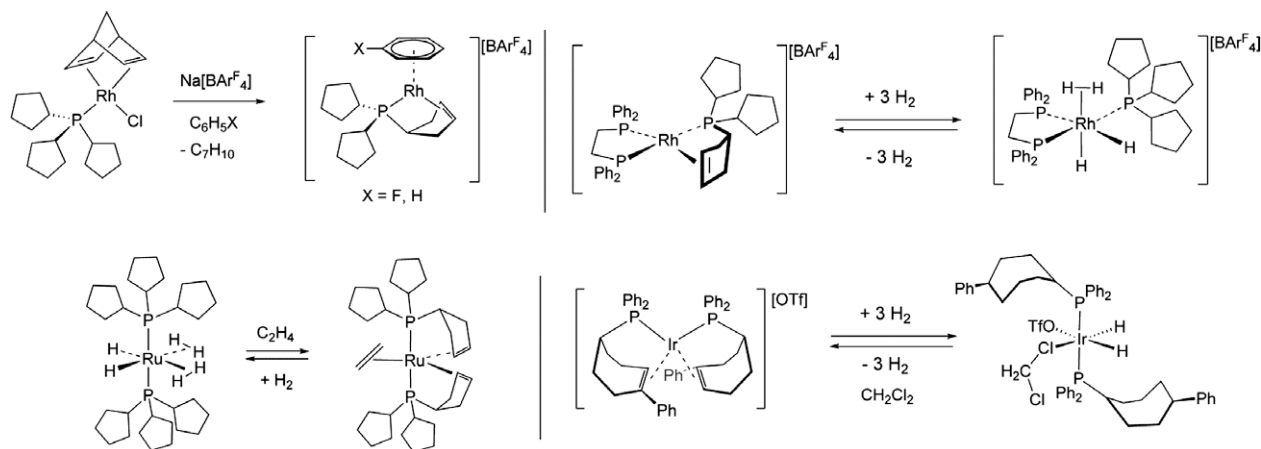
## 2. Results and discussion

We have previously reported that removal of the chloride ligand in Rh(nbd)Cl(PCyp<sub>3</sub>) using Na[BAr<sup>F</sup><sub>4</sub>] {nbd = norbornadiene, Ar<sup>F</sup> = C<sub>6</sub>H<sub>3</sub>(CF<sub>3</sub>)<sub>2</sub>} results in dehydrogenation of one of the PCyp<sub>3</sub> alkyl groups, with norbornadiene acting as a sacrificial hydrogen acceptor. If this reaction is performed in an arene solvent, such

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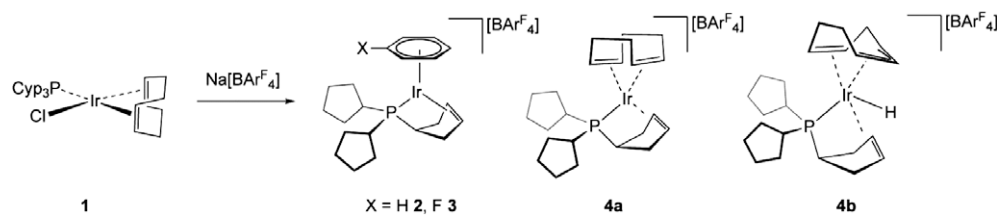


**Scheme 1.** Selected examples of alkyl dehydrogenation in PCyp<sub>3</sub> and related complexes of Rh [31], Ru [29] and Ir [24].

as C<sub>6</sub>H<sub>5</sub>F, an arene adduct is formed, e.g. [Rh(η<sup>6</sup>-C<sub>6</sub>H<sub>5</sub>F){PCyp<sub>2</sub>(η<sup>2</sup>-C<sub>5</sub>H<sub>7</sub>)}][BARF<sub>4</sub>], (Scheme 1). By contrast, in CH<sub>2</sub>Cl<sub>2</sub>, where there is little stabilisation available from the solvent, a rare example of a complex with a coordinated [BARF<sub>4</sub>]<sup>-</sup> anion is formed, Rh{PCyp<sub>2</sub>(η<sup>2</sup>-C<sub>5</sub>H<sub>7</sub>)}{η<sup>6</sup>-(C<sub>6</sub>H<sub>3</sub>(CF<sub>3</sub>)<sub>2</sub>)BARF<sub>3</sub>}, in which the metal's coordination sphere is completed by an η<sup>6</sup>-π-interaction from the anion [23]. Following the same protocol, addition of Na[BARF<sub>4</sub>] to the new, but straightforwardly synthesised, complex Ir(η<sup>2</sup>:η<sup>2</sup>-C<sub>8</sub>H<sub>12</sub>)Cl(PCyp<sub>3</sub>) (**1**) resulted in the formation of three new compounds in a variable ratio that depended on the solvent used. These compounds have been identified by NMR spectroscopy and X-ray crystallography as [Ir(η<sup>6</sup>-C<sub>6</sub>H<sub>5</sub>X){PCyp<sub>2</sub>(η<sup>2</sup>-C<sub>5</sub>H<sub>7</sub>)}][BARF<sub>4</sub>] (X = H, **2**, or F, **3**) and the isomeric pair [Ir(η<sup>2</sup>:η<sup>2</sup>-C<sub>8</sub>H<sub>12</sub>){PCyp<sub>2</sub>(η<sup>2</sup>-C<sub>5</sub>H<sub>7</sub>)}][BARF<sub>4</sub>] (**4a**) and [IrH(η<sup>2</sup>:η<sup>3</sup>-C<sub>8</sub>H<sub>11</sub>){PCyp<sub>2</sub>(η<sup>2</sup>-C<sub>5</sub>H<sub>7</sub>)}][BARF<sub>4</sub>] (**4b**) (Scheme 2).

In benzene/CH<sub>2</sub>Cl<sub>2</sub> solvent complex **2** is formed in 95% relative yield compared to **4a/b**, but could not be isolated in bulk form away from traces of **4a/b** by recrystallisation. The <sup>1</sup>H NMR spectrum of **2** shows a coordinated benzene ligand, δ 6.31, and an alkene that comes from dehydrogenation of the cyclopentyl ligand, δ 3.76, in a 6:2 relative integral ratio. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum shows a single environment, at δ 68.4, while the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum is in full accord with the <sup>1</sup>H NMR spectrum, showing signals due to coordinated arene, free anion, and the phosphine-alkene ligand. A solid-state structure of **2** (Fig. 1) as determined by

a single crystal X-ray diffraction study confirms that dehydrogenation of one of the PCyp<sub>3</sub> alkyl rings has occurred, as well as coordination of the benzene solvent to give a formally Ir(I), 18-electron, metal centre. The bond lengths and angles around the metal centre are unremarkable, and not dissimilar to those reported for [Rh(η<sup>6</sup>-C<sub>6</sub>H<sub>5</sub>X){PCyp<sub>2</sub>(η<sup>2</sup>-C<sub>5</sub>H<sub>7</sub>)}][BARF<sub>4</sub>] (X = H, F) [22]. Dissolution of the bulk crystalline sample showed that it was also contaminated with **4a/4b** which clearly co-crystallises with **2**. This was also confirmed by an ESI-MS of the crystalline material dissolved in CH<sub>2</sub>Cl<sub>2</sub>. Similarly, complex **3** could not be produced free of **4a/4b** by this method (80:20 relative ratio), but an alternative synthetic route produces **3** pure (*vide infra*) which allows for complete characterisation. The <sup>1</sup>H NMR spectrum for **3** is broadly similar to **2** and shows a coordinated fluorobenzene ligand [δ 6.47 (4H), 5.90 (1H)]. In the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum the coordinated fluorobenzene is indicated by resonances observed at δ 141.7, 94.7, 88.7 and 82.9. Three resonances appear as doublets of doublets [<sup>19</sup>F and <sup>31</sup>P coupling] while the one at δ 88.7 is simply a doublet and can also be correlated to the integral 1-H resonance in the <sup>1</sup>H NMR spectrum at δ 5.90. It is thus assigned to the *para*-{CH} group on the arene. The coordinated, dehydrogenated, cyclopentene ring is observed in the <sup>1</sup>H NMR spectrum at δ 3.81 (2-H) and in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum as a singlet at δ 45.8, with no <sup>31</sup>P-<sup>13</sup>C coupling being observed. Finally, the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum displays a single environment, at δ 69.2, that shows coupling to <sup>19</sup>F [(FP) 2.2 Hz], a



solvent	arene adduct	4a/4b
CH <sub>2</sub> Cl <sub>2</sub> / C <sub>6</sub> H <sub>6</sub>	95	5 §
C <sub>6</sub> H <sub>5</sub> F	80	20 §
CH <sub>2</sub> Cl <sub>2</sub>	-	35 *
CH <sub>2</sub> Cl <sub>2</sub> / COD	-	75 *

§ by NMR spectroscopy \* isolated yield of **4a/4b**

**Scheme 2.** Synthesis of **2**, **3** and **4a/4b**.

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