

# A gallium hydride as an oxidizing agent: direct synthesis of Ir(V) complexes via Ga-H bond activation

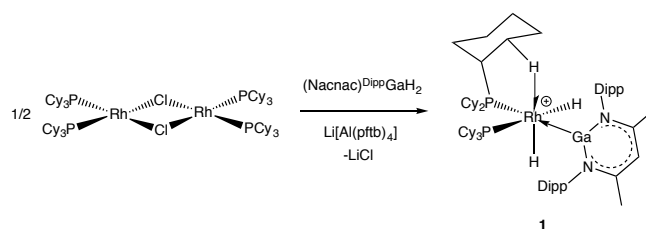
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**Abstract:** Reactions of the  $\beta$ -diketiminate stabilized gallium dihydride (Nacnac)<sup>Dipp</sup>GaH<sub>2</sub> with chelating Ir(I) bis(phosphine) precursors under an H<sub>2</sub> atmosphere are shown to provide a simple route to Ir(V) complexes stabilized by strongly  $\sigma$ -donating hydrides and the carbene-like (Nacnac)<sup>Dipp</sup>Ga donor. Characterization of these systems as seven-coordinate Ir(V) tetrahydride species is supported by single crystal X-ray and neutron diffraction, and by  $T_1$  NMR measurements. By contrast related systems featuring more sterically demanding (non-chelating) ancillary ligands are better described in terms of a bis(hydride) dihydrogen [L<sub>3</sub>Ir(H)<sub>2</sub>(H<sub>2</sub>)]<sup>+</sup> formulation and a formal Ir(III) oxidation state.

## Introduction

The oxidative activation of E-H bonds at late transition metal centres represents a key fundamental step in numerous catalytically important processes.<sup>[1]</sup> Within group 13 systems, for example, the cleavage of B-H bonds in this way is implicit in metal-mediated processes leading to the hydroboration of C=E multiple bonds, and to the borylation of unactivated hydrocarbons.<sup>[2]</sup> As such, the coordination of B-H bonds and their activation to give metal (boryl)hydride species is well precedented.<sup>[3,4]</sup> Much less common are processes involving the simultaneous activation of two E-H bonds at a transition metal centre to give a *d*/hydride complex stabilized by a formally neutral two-electron element-ylidene ligand.<sup>[5-7]</sup> Net transformations of this type have also been reported leading to the formation of Fischer carbene complexes [L<sub>n</sub>M=C(OR)R'] from ethers H<sub>2</sub>C(OR)R', but the mechanistic pathways adopted typically involve oxidative addition of a single C-H bond followed by a  $\beta$ -hydrogen transfer step.<sup>[8]</sup> Recently we have been examining the activation of E-H bonds in  $\beta$ -diketiminate ('Nacnac') stabilized group 13 hydrides, (Nacnac)<sup>Dipp</sup>EH<sub>2</sub> [E = Al, Ga; (Nacnac)<sup>Dipp</sup> = HC(MeCDippN)<sub>2</sub>],<sup>[9]</sup> and have described a pathway for the simultaneous activation of both E-H bonds through interaction with 12-electron cationic rhodium

fragments.<sup>[6c,7d]</sup> Thus, depending on the HOMO energy of the [(R<sub>3</sub>P)<sub>2</sub>Rh]<sup>+</sup> fragment, the extent of metal back-bonding into the EH<sub>2</sub> fragment can be minimal [resulting in the formation of an essentially unstretched 16-electron  $\kappa^2$ -H<sub>2</sub>Ga(Nacnac) complex], or more significant, leading to lengthened Ga-H and contracted Rh-H/Rh-Ga bonds. In the case of the [(Cy<sub>3</sub>P)<sub>2</sub>Rh]<sup>+</sup> system, the strongly electron-donating and non-chelating nature of the phosphine ligand set means that complete activation is achieved to generate a Rh(III) gallylene dihydride (**1**; Scheme 1).<sup>[6c]</sup>



**Scheme 1.** Double Ga-H activation at Rh(I) to give a gallylene-stabilized Rh(III) dihydride [counter-anion omitted for clarity; pftb = OC(CF<sub>3</sub>)<sub>3</sub>].<sup>[6c]</sup>

Given that the (Nacnac)<sup>Dipp</sup>GaH<sub>2</sub> molecule can therefore act not only as a source of two hydrides, but also of a strongly  $\sigma$ -donating gallylene ligand,<sup>[10]</sup> we wondered whether it could be employed to deliver a simple synthetic approach to late metal complexes featuring even higher oxidation states. Accordingly, related chemistry utilizing iridium precursors was investigated, with the aim of probing whether Ir(V) systems could be accessed directly from Ir(I) complexes.<sup>[11]</sup> A range of cationic iridium bis(phosphine) complexes was targeted, allowing for variation in the electronic and steric profiles of the P-donors, with a view to probing the factors underpinning the viability of this approach.

## Results and Discussion

The reactions of (Nacnac)<sup>Dipp</sup>GaH<sub>2</sub><sup>[12]</sup> with [Ir(dppp)(COD)][BAR<sup>f</sup><sub>4</sub>] and [Ir(dcyce)(COD)][Al(pftb)<sub>4</sub>]<sup>[13]</sup> under H<sub>2</sub> (ca. 4 bar) cleanly yield cyclooctane, together with cationic complexes of empirical composition [Ir(dppp)(H)<sub>4</sub>{Ga(Nacnac)<sup>Dipp</sup>}]<sup>+</sup>[BAR<sup>f</sup><sub>4</sub>]<sup>-</sup> (**2-dppp**) and [Ir(dcyce)(H)<sub>4</sub>{Ga(Nacnac)<sup>Dipp</sup>}]<sup>+</sup>[Al(pftb)<sub>4</sub>]<sup>-</sup> (**2-dcyce**), respectively [Scheme 2; Ar<sup>f</sup> = C<sub>6</sub>H<sub>3</sub>(CF<sub>3</sub>)<sub>2</sub>-3,5; pftb = OC(CF<sub>3</sub>)<sub>3</sub>]. Both compounds have been characterized by a combination of NMR spectroscopy, ESI mass spectrometry, elemental microanalysis and X-ray crystallography, with **2-dcyce** additionally being investigated by neutron diffraction studies.

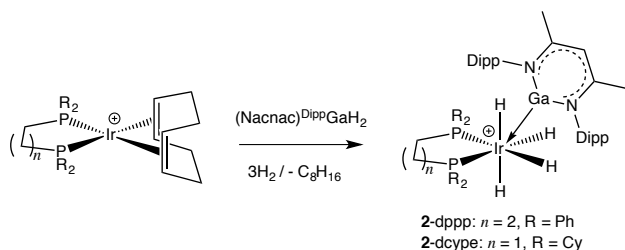
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Supporting information for this article (further spectroscopic data  
and neutron diffraction details; DFT run files) is given via a link at  
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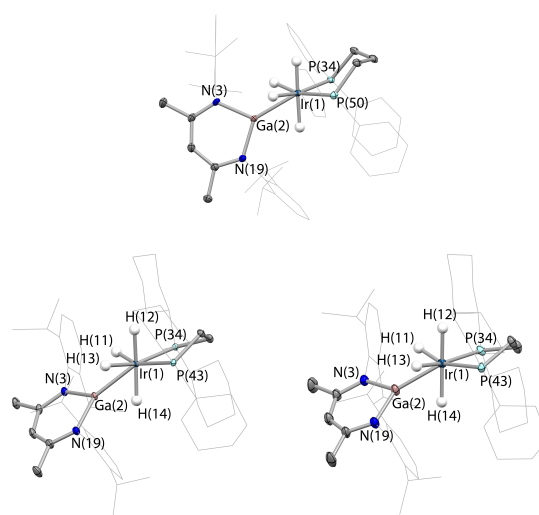


**Scheme 2.** Formation of **2-dppp** and **2-dcype** from  $(\text{Nacnac})^{\text{Dipp}}\text{GaH}_2$  and  $\text{Ir(I)}$  precursors in the presence of dihydrogen (anions omitted for clarity).

The ESI-MS spectrum of each compound shows a single peak envelope for the molecular ion and is indicative of the uptake of an additional molecule of  $\text{H}_2$ , compared to the chemistry observed for  $[\text{Rh}(\text{dppp})(\text{COD})]^+$  and  $[\text{Rh}(\text{dcype})(\text{COD})]^+$ .<sup>[6c]</sup> The presence of *four* iridium-bound hydrogens in each case is also consistent with the respective  $^1\text{H}$  NMR spectra, which show sharp, well-resolved upfield triplets integrating to 4H (**2-dppp**:  $\delta_{\text{H}} = -11.67$  ppm,  $^2J_{\text{HP}} = 7.3$  Hz; **2-dcype**:  $\delta_{\text{H}} = -13.24$  ppm,  $^2J_{\text{HP}} = 7.3$  Hz). Both resonances undergo minimal broadening even on cooling to 198 K, indicating either a highly symmetrical structure, or one that allows for very facile fluxional inter-conversion between Ir-H environments.

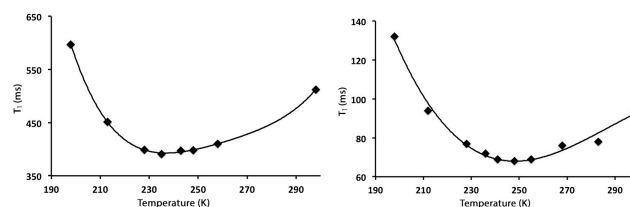
Single crystals of both **2-dppp** and **2-dcype** could be obtained suitable for X-ray crystallography. In each case these studies reveal a solid-state structure (Figure 1) consistent with the presence of four Ir-H units, as suggested by NMR/ESI-MS measurements. Thus, **2-dppp** and **2-dcype** both feature an approximately octahedral arrangement of the chelating phosphine and four hydrides at the iridium centre, with two hydrides being located *trans* to the phosphine donors and the other two *cis* to the phosphines (and mutually *trans*). Additionally, a  $\text{Ga}(\text{Nacnac})^{\text{Dipp}}$  unit caps one face of the octahedron defined by three of the hydride ligands. As such, the  $\text{IrP}_2\text{Ga}$  heavy atom skeleton deviates somewhat from planarity [sum of angles at  $\text{Ir(1)} = 352.2^\circ$ ].

Inspection of the X-ray structures also shows that the  $\text{M-Ga-C}$  angle is close to linear in each case, as is commonly observed for metal complexes featuring the (carbene-analogue)  $\text{Ga}(\text{Nacnac})^{\text{Dipp}}$  ligand [ $\angle\text{Ir(1)-Ga(2)-C(17)} = 172.1^\circ$  (**2-dppp**),  $172.9^\circ$  (**2-dcype**)]. The Ir-Ga bond lengths [ $\text{Ir(1)-Ga(2)} = 2.3389(5)$  Å (**2-dppp**),  $2.3419(4)$  Å (**2-dcype**)] are, if anything, even shorter than the Rh-Ga bond length in the rhodium complex **1** [ $2.368(1)$  Å], and are therefore strongly suggestive of direct Ir-Ga bonding, given that related  $\sigma$ -complexes featuring bridging hydrogens, typically feature much longer M-Ga contacts (e.g.  $2.538(1)$  Å for  $[(\text{dppp})\text{Rh}\{\kappa^2\text{-H}_2\text{Ga}(\text{Nacnac})^{\text{Dipp}}\}]^+$ ).<sup>[6c]</sup> However, taking into account the difficulty in locating hydrogen atoms in the vicinity of heavy metal atoms using X-ray techniques,<sup>[14]</sup> and the rapid fluxionality observed for **2-dppp**/**2-dcype** in solution, we sought to obtain more reliable characterization of the hydrogen-containing ligands through a combination of single crystal neutron diffraction and NMR-derived  $T_1$  relaxation times.



**Figure 1.** Molecular structures (upper) of **2-dppp** as determined by X-ray diffraction, and (lower) of **2-dcype** as determined by X-ray (left) and neutron diffraction (right). Anion and most H-atoms omitted, and aryl/Cy substituents shown in wireframe format for clarity; displacement ellipsoids shown at the 40% probability level. Key bond lengths (Å) and angles ( $^\circ$ ): **2-dppp**:  $\text{Ir(1)-Ga(2)} 2.3389(5)$ ,  $\text{Ga(2)-N(3)} 1.917(3)$ ,  $\text{Ga(2)-N(19)} 1.904(3)$ ,  $\text{Ir(1)-P(50)} 2.3204(10)$ ,  $\text{Ir(1)-P(34)} 2.3093(10)$ ,  $\text{P(34)-Ir(1)-P(50)} 90.69(4)$ ,  $\text{Ir(1)-Ga(2)-C(17)} 172.1$ ,  $\text{P(50)-Ir(1)-Ga(2)} 131.60(3)$ ,  $\text{P(34)-Ir(1)-Ga(2)} 129.84(3)$ . **2-dcype**: (from X-ray)  $\text{Ir(1)-Ga(2)} 2.3419(4)$ ,  $\text{Ir(1)-P(34)} 2.3205(8)$ ,  $\text{Ir(1)-P(43)} 2.3367(8)$ ,  $\text{Ga(2)-N(3)} 1.929(3)$ ,  $\text{Ga(2)-N(19)} 1.922(3)$ ,  $\text{P(34)-Ir(1)-P(43)} 84.56(3)$ ,  $\text{Ga(2)-Ir(1)-P(34)} 128.39(2)$ ,  $\text{Ga(2)-Ir(1)-P(43)} 135.40(2)$ ; (from neutron)  $\text{Ir(1)-H(11)} 1.64(1)$ ,  $\text{Ir(1)-H(12)} 1.58(1)$ ,  $\text{Ir(1)-H(13)} 1.66(1)$ ,  $\text{Ir(1)-H(14)} 1.73(1)$ .

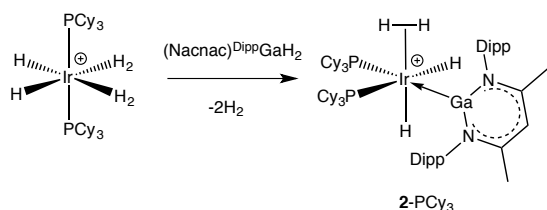
Measurement of the spin-lattice relaxation time  $T_1$  [or more strictly  $T_1(\text{min})$ , the minimum as a function of temperature] has proved to be an informative method for differentiating between classical metal hydrides and  $\eta^2$ -dihydrogen complexes.<sup>[15,16]</sup> The relaxation times measured at a range of temperatures for **2-dppp** and **2-dcype** (Figure 2 and supporting information) yield  $T_1(\text{min})$  values (at 500 MHz) of 391 ms for **2-dppp**, and 336 ms for **2-dcype** (at 235 and 243 K, respectively). For comparison, the distinct hydride and dihydrogen ligands in the complex  $[\text{IrH}(\text{H}_2(\text{bq})(\text{PPh}_3)_2)]^+$  ( $\text{bq} = 7,8\text{-benzoquinolate}$ ) show contrasting  $T_1$  values of 390 and 30 ms at 188 K and 500 MHz.<sup>[17]</sup> Fluxional species undergoing hydride/dihydrogen exchange also tend to show shorter  $T_1(\text{min})$  values, e.g. 29 ms for  $[\text{Ir}(\text{H})(\text{H}_2)(\eta^2\text{-S}_2\text{CH})(\text{PCy}_3)_2]^+$  (at 400 MHz).<sup>[18]</sup> These measurements therefore suggest that **2-dppp** and **2-dcype** are best formulated as  $\text{Ir(V)}$  complexes featuring four terminal hydride ligands.



**Figure 2.** Graphs of  $T_1$  relaxation times (at 500 MHz) for **2-dppp** (left) and **2-dcype** (right) as a function of temperature (line included as guide to the eye). The values of  $T_1(\text{min})$  derived from these data are 391 and 68 ms, respectively.

In the case of **2-dcype**, this assertion is given further support by the results of neutron crystallography (Figure 1). Thus, the geometric arrangement of the metal-bound hydrogen atoms suggested by X-ray measurements is corroborated (two *trans* to the phosphine ligands, two mutually *trans*), and the associated metrics are best interpreted in terms of four classical hydride donors. The Ir-H distances [1.58(1) – 1.73(1) Å] are as expected for (terminal) iridium-bound hydrides,<sup>[19]</sup> while the H...H and Ga...H separations [shortest contacts: 2.05(1) and 2.09(1) Å, respectively] are markedly longer than would be expected for a dihydrogen or GaH-containing  $\sigma$ -complex.<sup>[6c,20]</sup>

Further support for the formulation of **2-dppp** and **2-dcype** as Ir(V) tetrahydride complexes comes from the contrasting behaviour demonstrated by the closely related *bis*(tricyclohexylphosphine) complex **2-PCy<sub>3</sub>**. This system [which is most conveniently synthesized via an alternative synthetic route utilizing the Ir(III) precursor [Ir(PCy<sub>3</sub>)<sub>2</sub>(H)<sub>2</sub>(H<sub>2</sub>)<sub>2</sub>][BAR<sup>f</sup><sub>4</sub>] (Scheme 3),<sup>[21]</sup> has an analogous composition to **2-dppp** and **2-dcype**, featuring four metal-bound hydrogens. However, spectroscopic, structural and chemical properties suggest that, in this case, a formulation as an Ir(III) bis(hydride) dihydrogen complex is most appropriate.

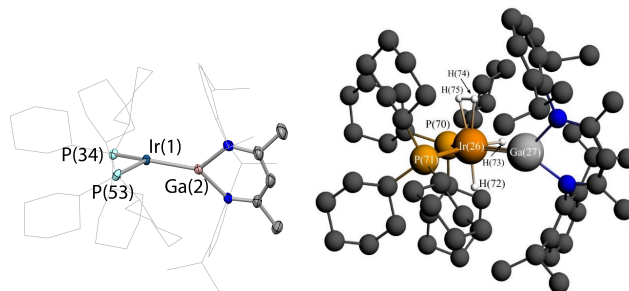


**Scheme 3.** Formation of **2-PCy<sub>3</sub>** from (NacNac)<sup>Dipp</sup>GaH<sub>2</sub> and [Ir(PCy<sub>3</sub>)<sub>2</sub>(H)<sub>2</sub>(H<sub>2</sub>)<sub>2</sub>][BAR<sup>f</sup><sub>4</sub>] (anions omitted for clarity).

In common with **2-dppp** and **2-dcype**, the <sup>1</sup>H NMR spectrum of **2-PCy<sub>3</sub>** features a single upfield resonance integrating to 4H (at  $\delta_{\text{H}} = -11.89$  ppm). While this signal is significantly broader than the hydride signals of either **2-dppp** or **2-dcype**, and cooling leads to further broadening, it is not possible even at 198 K to resolve distinct resonances corresponding to different H-atom environments. That said, a value for  $T_1(\text{min})$  of 68 ms can be measured (at 248 K) which is significantly shorter than those obtained for either **2-dppp** or **2-dcype** (391 and 336 ms, respectively). The value obtained for **2-PCy<sub>3</sub>** is more consistent with a dihydride/dihydrogen formulation (*i.e.* [Ir<sup>III</sup>(H)<sub>2</sub>(H<sub>2</sub>)]), being similar to those measured for fluxional group 9 hydride/dihydrogen systems, *e.g.* [Ir(H)(H<sub>2</sub>)( $\eta^2$ -S<sub>2</sub>CH)(PCy<sub>3</sub>)<sub>2</sub>]<sup>+</sup> (29 ms), [TpRh(PPh<sub>3</sub>)(H<sub>2</sub>)(H)][BAR<sup>f</sup><sub>4</sub>] (21 ms).<sup>[18,22,23]</sup> Consistently, **2-PCy<sub>3</sub>** undergoes rapid exchange with D<sub>2</sub> - in notable contrast to **2-dppp** or **2-dcype** (which undergo much slower exchange over a period of several days). HD is immediately evident in the <sup>1</sup>H NMR spectrum of **2-PCy<sub>3</sub>/D<sub>2</sub>** and the mixed IrH<sub>3</sub>D and IrH<sub>2</sub>D<sub>2</sub> isotopologues can be observed after several minutes, which show isotopic perturbations in the chemical shift of  $\Delta\delta = 80$  ppb and 150 ppb, respectively (see supporting information). These values are in line with the magnitude of isotopic perturbations observed in other iridium hydride/dihydrogen complexes.<sup>[18,22,23]</sup>

Finally, it is noteworthy that the ESI-MS spectrum of **2-PCy<sub>3</sub>** does not reveal a peak envelope corresponding to the molecular ion [M]<sup>+</sup> (in contrast to **2-dppp** or **2-dcype**) but rather for [M-2H]<sup>+</sup>, in line with the facile loss of H<sub>2</sub>. Consistently, solid samples of **2-PCy<sub>3</sub>** decompose upon extended exposure to vacuum, and single crystals could therefore be obtained only by carrying out the synthesis in concentrated fluorobenzene solution and layering the reaction mixture with hexane, without further manipulation.

The molecular structure of **2-PCy<sub>3</sub>** determined crystallographically is shown in Figure 3. Unfortunately, it was not possible to locate the iridium-bound hydrogens definitively, and suitable crystals for neutron diffraction analysis could not be obtained. However, the heavy atom skeleton reveals a number of significant differences compared to those of **2-dppp** and **2-dcype**. Thus, (i) the coordination sphere comprising the phosphorus atoms of the two PCy<sub>3</sub> donors and the Ga centre of the Ga(NacNac)<sup>Dipp</sup> ligand is close-to-planar [sum of angles at Ir(1) = 357.4°], and (ii) two very different P-Ir-Ga angles are observed [103.1(1) and 144.4(1)°]. By contrast, in the structures of both **2-dppp** and **2-dcype**, these two angles are essentially identical [*e.g.* 131.6(1) and 129.8(1)° for **2-dppp**], and the IrP<sub>2</sub>Ga skeleton is non-planar. The structure of **2-PCy<sub>3</sub>** is more reminiscent of the Rh(III) system **1** (Scheme 1),<sup>[6c]</sup> which also features a planar arrangement of the heavy atom skeleton, and disparate P-Rh-Ga angles [107.5(1) and 146.4(1)°]. Both compounds can be described in terms of an octahedral metal geometry featuring a meridional arrangement of PCy<sub>3</sub> and gallylene ligands. In the case of **1**, the coordination sphere is completed by a pair of *cis*-hydride donors, with a  $\sigma$ -bonded ligand (in this case an agostic C-H) in the sixth coordination site. A similar structure is postulated for **2-PCy<sub>3</sub>**, featuring analogous positioning of two (classical) hydrides, and an H<sub>2</sub> molecule acting as the  $\sigma$ -type ligand (Scheme 3 and Figure 3).

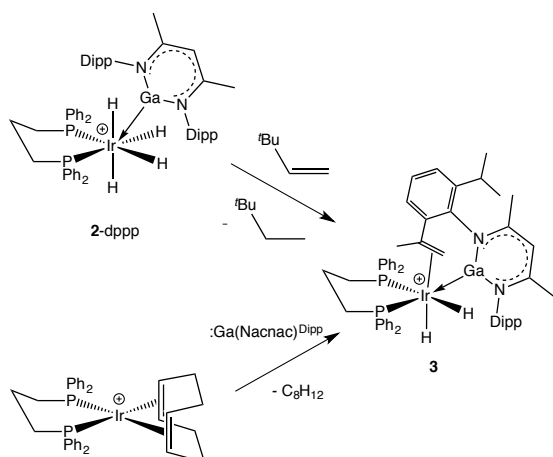


**Figure 3.** **2-PCy<sub>3</sub>**: the heavy atom skeleton of the cationic component as determined by X-ray crystallography (left), and the corresponding DFT-calculated structure (right). For X-ray structure: anion and most hydrogen atoms omitted, and aryl/Cy substituents shown in wireframe format for clarity; displacement ellipsoids shown at the 40% probability level. Key bond lengths (Å) and angles (°): Ir(1)-Ga(2) 2.3877(7), Ga(2)-N(3) 1.968(5), Ga(2)-N(20) 1.931(5), Ir(1)-P(34) 2.2611(14), Ir(1)-P(53) 2.3900(14), P(34)-Ir(1)-P(53) 109.87(3), Ir(1)-Ga(2)-C(18) 174.61, P(53)-Ir(1)-Ga(2) 103.13(4), P(34)-Ir(1)-Ga(2) 144.37(4).

This hypothesis has been tested by DFT calculations: optimization of the structure of **2-PCy<sub>3</sub>** from a range of starting

points invariably generates the same minimum energy geometry (Figure 3). The optimized structure not only reproduces the key features of the heavy atom skeleton, but also suggests the presence of two mutually *cis* hydride ligands with little residual interaction between them [ $d(\text{H}\cdots\text{H}) = 2.23 \text{ \AA}$ ], with a side-on bound  $\text{H}_2$  ligand completing the coordination sphere. The latter features an H-H separation of  $0.83 \text{ \AA}$ , suggestive of an essentially unstretched, weakly bound  $\text{H}_2$  ligand.<sup>[24]</sup> The facile loss of  $\text{H}_2$  from **2-PCy<sub>3</sub>** – for example under vacuum – is therefore readily understood.

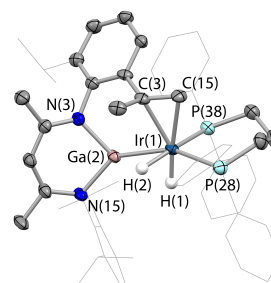
By contrast, for both **2-dppp** and **2-dcype**, formal reduction back to Ir(III) via  $\text{H}_2$  loss requires the use of chemical hydrogen scavenger. The reaction of **2-dppp** with excess TBE (tert-butylethylene, 3,3-dimethylbut-1-ene) results in the clean formation of a product in which *four* hydrogen atoms have been lost, as shown by ESI-MS. However, the presence of upfield resonances in the  $^1\text{H}$  NMR spectrum indicates that the product is not a simple Ir(I) product such as  $[\text{Ir}(\text{dppp})\{\text{Ga}(\text{NacNac})^{\text{Dipp}}\}]^+$ , but instead retains iridium-bound hydride ligands. A combination of NMR and X-ray crystallography has established the identity of this species as the Ir(III) complex  $[\text{Ir}(\text{dppp})(\text{H})_2\{\text{Ga}(\text{NacNac})^{\text{Dipp}}\}][\text{Al}(\text{pftb})_4]$  (**3**), in which one of the isopropyl groups of the (NacNac)<sup>Dipp</sup> substituents has undergone dehydrogenation to form an alkene which is tethered to the Ir centre (Scheme 4).



**Scheme 4.** Synthesis of alkene-tethered Ir(III) gallylene complex **3** from either Ir(V) or Ir(I) starting materials.

An X-ray crystallographic study of **3** (Figure 4) reveals a distorted octahedral geometry at iridium, with the coordination of the phosphine ligands and gallylene moiety augmented by the tethered alkene and two hydrides (which were located in the difference Fourier map and refined isotropically). One hydride is located *cis* to both phosphine donors, while the other is *trans* to one phosphine arm and *cis* to the other. The Ir-Ga distance [ $2.3488(8) \text{ \AA}$ ] is only slightly longer than that in **2-dppp** [ $2.3389(5) \text{ \AA}$ ] despite the lower oxidation state of iridium, an observation which may in part be due to the geometric constraints imposed by the alkene tether. The Ir-Ga- $\gamma\text{C}$  unit is

also distorted somewhat from the linearity [ $150.2(2)^\circ$ ]; the canting of the heterocycle towards the alkene suggests that constraints imposed by the tether may again be responsible. The alkene function itself is coordinated in familiar side-on fashion to Ir(1) with similar Ir-C bond lengths [ $2.334(8)$ ,  $2.263(7) \text{ \AA}$ ], and the C-C bond length [ $1.388(11) \text{ \AA}$ ] is clearly indicative of multiple bond character.



**Figure 4.** Molecular structure of **3** as determined by X-ray diffraction. Anion and most hydrogen atoms omitted, and aryl substituents shown in wireframe format for clarity; displacement ellipsoids shown at the 40% probability level.

Key bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ): Ir(1)-Ga(2)  $2.3488(8)$ , Ga(2)-N(3)  $1.932(6)$ , Ga(2)-N(15)  $1.916(6)$ , Ir(1)-P(28)  $2.315(2)$ , Ir(1)-P(38)  $2.339(2)$ , Ir(1)-C(3)  $2.334(8)$ , Ir(1)-C(15)  $2.263(7)$ , C(3)-C(15)  $1.388(1)$ , Ir(1)-Ga(2)-C(13)  $150.22$ , P(28)-Ir(1)-P(38)  $94.77(8)$ , P(28)-Ir(1)-Ga(2)  $152.28(6)$ , P(38)-Ir(1)-Ga(2)  $106.03(6)$ .

From an NMR perspective, there is a significant increase in the complexity of the Dipp signals on formation of **3** from **2-dppp**, consistent with the reduction of symmetry in the product. In addition, two mutually coupled doublets are observed for the alkene C-H protons ( $\delta_{\text{H}} = 2.68, 3.55 \text{ ppm}$ ,  $^2J_{\text{HH}} = 12.8 \text{ Hz}$ ), with a singlet at  $\delta_{\text{H}} = 1.71 \text{ ppm}$  being assigned to the remaining unactivated methyl group of the  $-\text{MeC}=\text{CH}_2$  moiety. The metal-bound hydrides are in slow exchange on the NMR timescale at room temperature and give rise to coupling patterns consistent with their crystallographically determined positions (Figure 4). H(2) is observed as an apparent doublet of triplets ( $\delta_{\text{H}} = -14.28 \text{ ppm}$ ), resulting from a large coupling to the *trans* phosphine ( $^2J_{\text{PH}} = 103.6 \text{ Hz}$ ) and much smaller, essentially equivalent couplings to  $\text{P}_{\text{cis}}$  and H(1) ( $^2J_{\text{PH}}/^2J_{\text{HH}} = 5.0 \text{ Hz}$ ). H(1) gives rise to a well-resolved triplet of doublets ( $\delta_{\text{H}} = -12.70 \text{ ppm}$ ), resulting from coupling to the two *cis* phosphines ( $^2J_{\text{PH}} = 12.0 \text{ Hz}$ ) and to H(2) ( $^2J_{\text{HH}} = 5.0 \text{ Hz}$ ). No coalescence of these hydride signals is observed on heating a fluorobenzene solution to  $75^\circ\text{C}$ , suggesting a relatively high barrier to exchange. Two mutually coupled doublets are observed for the inequivalent phosphorus nuclei in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\delta_{\text{P}} = -11.1, -5.0 \text{ ppm}$ ,  $^2J_{\text{PP}} = 13.7 \text{ Hz}$ ).

There is ample precedent for the dehydrogenation of pendant alkyl groups at low-coordinate late transition metal centres, resulting in the formation of a coordinated alkene moiety; such chemistry been described for a range of ligands including NHCs,<sup>[25]</sup> phosphines,<sup>[26]</sup> and even  $\beta$ -diketiminates,<sup>[27]</sup> incorporating isopropyl, cyclopentyl or cyclohexyl substituents. Mechanistically, such chemistry typically proceeds via oxidative addition of a C-H bond at a coordinatively/electronically unsaturated

metal centre, followed by  $\beta$ -hydride elimination. In the case of **3**, it is conceivable that a similar mechanism might be in operation, following initial abstraction of two equivalents of  $H_2$  from **2**-dppp by TBE. C-H oxidative addition and subsequent  $\beta$ -hydride elimination would be expected to be extremely facile at a putative three-coordinate 14-electron Ir(I) species of the type  $[Ir(dppp)\{Ga(NacNac)^{Dipp}\}]^+$ . To probe the potential involvement of such an intermediate, we therefore examined the direct reaction of the Ga(I) species  $:Ga(NacNac)^{Dipp}$  with  $[Ir(dppp)(COD)]^+_{[28]}$ . Although this reaction requires heating to 85°C to proceed to completion (presumably due to the need to displace the chelating COD ligand in the absence of  $H_2$ ), the product was confirmed by multinuclear NMR and ESI-MS to be identical to that obtained from **2**-dppp/TBE (Scheme 4, lower). As such, it is possible that a short lived Ir(I) gallylene species of the type  $[Ir(dppp)\{Ga(NacNac)^{Dipp}\}]^+$  might act as an intermediate in the observed dehydrogenation chemistry.

## Conclusions

From our synthetic studies it appears – in the cases of **2**-dppp and **2**-dcype at least – that Ir(V) systems can be formed through the combined oxidative activation of H-H and Ga-H bonds at Ir(I), with the strong  $\sigma$ -donating properties of the gallylene ligand presumably contributing to the stabilization of the product. The fact that under similar reaction conditions, the use of the same ancillary ligands leads to the formation of Rh(I) or Rh(III) systems,<sup>[6c]</sup> reflects established trends in the redox properties of the group 9 metals.<sup>[29]</sup>

In the case of rhodium, the nature of the product obtained depends largely on the electronic properties of the  $[(R_3P)_2Rh]^+$  unit.<sup>[6c]</sup> Factors leading to a higher HOMO energy (e.g. more strongly  $\sigma$ -donating phosphines, or wider P-M-P angles) bring about enhanced back-bonding into the  $GaH_2$   $a_1$  symmetry  $\sigma^*$  orbital, and hence greater oxidative Ga-H bond activation. In the case of the iridium chemistry described here – for which either an Ir(III) or Ir(V) product is obtained – the primary reactivity discriminators (in terms of the metal/ligand framework) appear to be steric rather than electronic. Thus, the strongly donating  $PCy_3$  and dcype donors give contrasting results in terms of formal iridium oxidation state, while the two bidentate systems (dppp and dcype) – although very different electronically – give rise to similar (narrow) P-Ir-P angles [**2**-dppp: 90.69(4)°; **2**-dcype: 84.56(3); cf. **2**- $PCy_3$ : 109.87(3)°] and to similar Ir(V) products. The idea that the formation of seven-coordinate Ir(V) species from six-coordinate Ir(III) via oxidative addition might be promoted by reducing the steric demands of the ancillary donors (e.g. by chelation) finds support in computational studies reported by Hall and co-workers.<sup>[30]</sup> As such, the Ir(III) formulation for the *bis*(tricyclohexylphosphine) system is entirely consistent with the wider P-Ir-P angle and greater steric demands of its ancillary ligand set.

## Experimental Section

### General considerations

All manipulations were carried out using standard Schlenk line or dry-box techniques under an atmosphere of argon. With the exception of fluorobenzene and 1,2-difluorobenzene, solvents were degassed by sparging with argon and dried by passing through a column of the appropriate drying agent using a commercially available Braun SPS; fluorobenzene and 1,2-difluorobenzene were dried by refluxing over calcium hydride, distilled, sparged and stored over activated molecular sieves. NMR spectra were measured in  $CD_2Cl_2$  which was stored over molecular sieves, and stored under argon in a Teflon valve ampoule. NMR samples were prepared under argon in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves.  $^1H$  and  $^{13}C$  NMR spectra were recorded on Varian Mercury-VX-300 or Bruker AVII-500 spectrometers and referenced internally to residual protio-solvent ( $^1H$ ) or solvent ( $^{13}C$ ) resonances and are reported relative to tetramethylsilane ( $\delta$  = 0 ppm).  $^{11}B$  and  $^{27}Al$  NMR spectra were referenced with respect to  $BF_3 \cdot OEt_2$  and  $Al(H_2O)_6^{3+}$ , respectively. Chemical shifts are quoted in  $\delta$  (ppm) and coupling constants in Hz. Elemental analyses were carried out at London Metropolitan University. Starting materials  $(NacNac)^{Dipp}GaH_2$ ,<sup>[12]</sup>  $(NacNac)^{Dipp}Ga$ ,<sup>[28]</sup>  $[IrH\{PCy_2(\eta^2-C_6H_6)\}\{PCy_2(\eta^3-C_6H_5)\}][BAR^f_4]$ ,<sup>[31]</sup>  $[Ir(dppp)(COD)][BAR^f_4]$  and  $[Ir(dcype)(COD)][Al(pftb)_4]$ <sup>[13]</sup> were prepared by literature procedures.

### Syntheses of novel compounds

**$[Ir(dppp)(H)_4\{Ga(NacNac)^{Dipp}\}][BAR^f_4]$  (**2**-dppp):**  $[Ir(dppp)(COD)][BAR^f_4]$  (0.100 g, 0.063 mmol) and  $(NacNac)^{Dipp}GaH_2$  (0.056 g, 0.115 mmol) were dissolved in 1,2-difluorobenzene (10 mL) in an ampoule fitted with a J. Young's valve. The solution was placed under  $H_2$  (ca. 4 atm), and stirred at room temperature for 12 h. Volatiles were then removed *in vacuo*, and the resulting solid washed with pentane (3 x 5 mL) and dried *in vacuo* to yield a pale yellow powder (0.083 g, 67%). Pale yellow crystals suitable for X-ray diffraction were obtained by layering a concentrated fluorobenzene solution with hexane at room temperature. Elemental microanalysis: calc. for  $C_{88}H_{83}N_2F_{24}P_2GaIrB$ : C 53.95% H 4.27% N 1.43%; meas. C 53.66% H 4.31% N 1.44%.  $^1H$  NMR (500 MHz, dichloromethane- $d_2$ , 298 K):  $\delta_H$  -11.67 (4H, t,  $^2J_{HP}$  = 7.3 Hz, IrH), 0.73 (12H, d,  $^3J_{HH}$  = 6.5 Hz,  $CH_3$  of Dipp  $^iPr$ ), 1.09 (12H, d,  $^3J_{HH}$  = 6.5 Hz,  $CH_3$  of Dipp  $^iPr$ ), 1.65 (2H, m,  $PCH_2CH_2$  of backbone), 2.01 (6H, s,  $CH_3$  of  $\beta$ -diketiminato backbone), 2.59 (4H, m,  $PCH_2$  of backbone), 2.67 (4H, sept,  $^3J_{HH}$  = 6.5 Hz, CH of Dipp  $^iPr$ ), 5.68 (1H, s,  $\gamma$ -CH), 7.02 - 7.31 (20H, m, CH of PPh), 7.33 (4H, d,  $^3J_{HH}$  = 8.0 Hz, *m*-CH of Dipp), 7.56 (4H, s, *p*-CH of  $[BAR^f_4]$ ), 7.61 (2H, t,  $^3J_{HH}$  = 8.0 Hz, *p*-CH of Dipp), 7.72 (8H, s, *o*-CH of  $[BAR^f_4]$ ).  $^{13}C\{^1H\}$  NMR (126 MHz, dichloromethane- $d_2$ , 298 K):  $\delta_C$  19.9 ( $PCH_2CH_2$  of backbone), 24.3 ( $CH_3$  of Dipp  $^iPr$ ), 24.4 ( $CH_3$  of Dipp  $^iPr$ ), 26.0 ( $CH_3$  of  $\beta$ -diketiminato backbone), 29.5 (CH of Dipp  $^iPr$ ), 33.9 (apparent triplet,  $^1J_{CP}/^3J_{CP}$  = 21.2 Hz,  $PCF_2$ ), 101.8 ( $\gamma$ -CH), 118.0 (*p*-CH of  $[BAR^f_4]$ ), 125.2 (q,  $^1J_{CF}$  = 271 Hz,  $CF_3$  of  $[BAR^f_4]$ ), 125.4 (*m*-CH of Dipp), 128.8 (t,  $J$  = 5.4 Hz, *m*-CH of PPh), 129.1 (*p*-CH of Dipp), 129.4 (q,  $^2J_{CF}$  = 24.3 Hz, *m*-CH of  $[BAR^f_4]$ ), 131.1 (*p*-CH of PPh), 133.0 (t,  $J$  = 28.6 Hz, *ipso*-C of PPh), 133.3 (t,  $J$  = 5.5 Hz, *o*-CH of PPh), 135.4 (*o*-CH of  $[BAR^f_4]$ ), 138.6 (*o*-C of Dipp), 143.7 (*ipso*-C of Dipp), 162.3 (q,  $^1J_{CB}$  = 49.2 Hz, *ipso*-C of  $[BAR^f_4]$ ), 173.4 (CN).  $^{31}P\{^1H\}$  NMR (162 MHz, dichloromethane- $d_2$ , 298 K):  $\delta_P$  -13.6 (s).  $^{11}B\{^1H\}$  NMR (128 MHz, dichloromethane- $d_2$ , 298 K):  $\delta_B$  -6.5.  $^{19}F$  NMR (376 MHz, dichloromethane- $d_2$ , 298 K):  $\delta_F$  -62.8. IR (KBr disc,  $\nu_{IR}/cm^{-1}$ ): 1805 (s), 1860 (s), 1890 (s). ESI-MS (cation): 1095 ( $[M]^+$ , 100%); accurate mass: calc. 1095.3967, meas. 1095.3967. Crystallographic data:  $C_{88}H_{83}N_2F_{24}P_2GaIrB$   $M_r$  = 1959.29, monoclinic,  $P2_1/n$ ,  $a$  = 16.1135(1),  $b$  = 13.3706(1),  $c$  = 40.7195(4) Å,  $\beta$  = 99.951(1)°,  $V$  = 8640.92(12) Å<sup>3</sup>,  $Z$  = 4,  $\rho_c$  = 1.506 Mg m<sup>-3</sup>,  $T$  = 150 K,  $\lambda$  = 1.54180 Å, 17871 independent reflections  $[R(int)$  = 0.022], used in all calculations.

$R_1 = 0.0429$ ,  $wR_2 = 0.1053$  for  $I > 2\sigma(I)$ , and  $R_1 = 0.0438$ ,  $wR_2 = 0.1057$  for all unique reflections. Max./Min. residual electron densities 2.95 and -1.81 e Å<sup>-3</sup>.

**[Ir(dcybe)(H)<sub>4</sub>(Ga(NacNac)<sup>Dipp</sup>)] [Al(pftb)<sub>4</sub>] (2-dcybe):** [Ir(dcybe)(COD)] [Al(pftb)<sub>4</sub>] (0.300 g, 0.18 mmol) and (NacNac)<sup>Dipp</sup>GaH<sub>2</sub> (0.104 g, 0.21 mmol) were dissolved in 1,2-difluorobenzene (5 mL) in an ampoule fitted with a J. Young's valve. The solution was placed under ca. 4 atm H<sub>2</sub> and stirred for 12 h. Volatiles were then removed *in vacuo* and the resulting oily, yellow solid washed with hexane (2 x 10 mL). The resulting solid was then extracted into minimal 1,2-difluorobenzene and layered with hexane. Storage at room temperature yielded pale yellow crystals suitable for X-ray diffraction. (Yield: 0.220 g, 60%). Elemental microanalysis: calc. for C<sub>71</sub>H<sub>93</sub>AlF<sub>36</sub>GalrN<sub>2</sub>O<sub>4</sub>P<sub>2</sub>, C 41.13% H 4.52% N 1.35%; meas. C 40.76% H 4.51% N 1.34%. <sup>1</sup>H NMR (500 MHz, dichloromethane-d<sub>2</sub>, 298 K): δ<sub>H</sub> -13.24 (4H, t, <sup>2</sup>J<sub>HP</sub> = 7.3 Hz, IrH), 0.41 (4H, m, PCH<sub>2</sub> of ligand backbone), 1.00-1.72 (44H, m, Cy), 1.23 (12H, d, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, CH<sub>3</sub> of Dipp 'Pr), 1.30 (12H, d, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, CH<sub>3</sub> of Dipp 'Pr), 1.96 (6H, s, CH<sub>3</sub> of β-diketiminato backbone), 2.89 (4H, sept, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, CH of Dipp 'Pr), 5.43 (1H, s, γ-CH), 7.29 (4H, d, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, m-CH of Dipp), 7.40 (2H, t, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, p-CH of Dipp). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, dichloromethane-d<sub>2</sub>, 298 K): δ<sub>C</sub> 24.2 (CH<sub>3</sub> of Dipp 'Pr), 24.2 (CH<sub>3</sub> of Dipp 'Pr), 26.3 (d, <sup>2</sup>J<sub>CP</sub> = 10.6 Hz, C<sup>2,6</sup>-Cy), 27.2 (m, PCH<sub>2</sub> of phosphine backbone), 27.3 (CH<sub>3</sub> of β-diketiminato backbone), 28.3 (Cy), 29.2 (Cy), 29.7 (CH of Dipp 'Pr), 35.6 (d, <sup>1</sup>J<sub>CP</sub> = 31.5 Hz, C<sup>1</sup>-Cy), 79.5 (br, C(CF<sub>3</sub>)<sub>3</sub> of [Al(pftb)<sub>4</sub>]), 102.1 (γ-CH), 121.9 (q, <sup>1</sup>J<sub>CF</sub> = 292.6 Hz, CF<sub>3</sub> of [Al(pftb)<sub>4</sub>]), 125.4 (m-CH of Dipp), 129.5 (p-CH of Dipp), 139.6 (ipso-C of Dipp), 143.6 (o-C of Dipp), 173.5 (CN). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, dichloromethane-d<sub>2</sub>, 298 K): δ<sub>P</sub> 58.5. <sup>27</sup>Al NMR (104 MHz, dichloromethane-d<sub>2</sub>, 298 K): δ<sub>Al</sub> 34.7. <sup>19</sup>F NMR (376 MHz, dichloromethane-d<sub>2</sub>, 298 K): δ<sub>F</sub> -75.4. ESI-MS (cation): 1105 ([M]<sup>+</sup>, 100%); accurate mass: calc. 1105.5688, meas. 1105.5775. Crystallographic data: (X-ray) C<sub>71</sub>H<sub>93</sub>AlF<sub>36</sub>GalrN<sub>2</sub>O<sub>4</sub>P<sub>2</sub>, M<sub>r</sub> = 2073.33, triclinic, P-1, a = 10.9728(2), b = 18.8785(3), c = 20.1116(4) Å, α = 87.1887(14), β = 86.5517(15), γ = 87.3844(13)°, V = 4149.76(13) Å<sup>3</sup>, Z = 2, ρ<sub>c</sub> = 1.659 Mg m<sup>-3</sup>, T = 150 K, λ = 1.54180 Å. 17158 independent reflections [R(int) = 0.026], used in all calculations. R<sub>1</sub> = 0.0401, wR<sub>2</sub> = 0.1084 for I > 2σ(I), and R<sub>1</sub> = 0.0412, wR<sub>2</sub> = 0.1093 for all unique reflections. Max./min. residual electron densities 2.04 and -1.67 e Å<sup>-3</sup>. (neutron) 7533 independent reflections; 4868 with I > 2σ(I). R<sub>1</sub> = 0.0992, wR<sub>2</sub> = 0.0799 for I > 2σ(I), and R<sub>1</sub> = 0.1650, wR<sub>2</sub> = 0.1217 for all unique reflections. Max. and min. residual difference densities: 1.44 and -1.08 Fermi/Å<sup>3</sup>.

**[Ir(PCy<sub>3</sub>)<sub>2</sub>(H)<sub>2</sub>(H<sub>2</sub>)(Ga(NacNac)<sup>Dipp</sup>)] [BAR<sup>f</sup><sub>4</sub>] (2-PCy<sub>3</sub>):** [Ir(PCy<sub>3</sub>)<sub>2</sub>(H)<sub>2</sub>(H<sub>2</sub>)<sub>2</sub>] [BAR<sup>f</sup><sub>4</sub>] was formed *in situ* by the hydrogenation (at room temperature and ca. 4 atm pressure) of [IrH{PCy<sub>2</sub>(η<sup>2</sup>-C<sub>6</sub>H<sub>5</sub>)}{PCy<sub>2</sub>(η<sup>3</sup>-C<sub>6</sub>H<sub>5</sub>)}] [BAR<sup>f</sup><sub>4</sub>] (0.200 g, 0.124 mmol) in fluorobenzene solution (3.5 mL). After stirring for 45 min, the resulting solution was opened to an argon atmosphere and rapidly transferred onto solid (NacNac)<sup>Dipp</sup>GaH<sub>2</sub> (0.061 g, 0.124 mmol). After stirring for 15 min (during which time a cloudy yellow solution was formed), the reaction mixture was filtered, layered with hexane and stored at room temperature, producing pale yellow crystals that were suitable for X-ray diffraction. Yield: 0.091 g, 37 %. Elemental microanalysis: calc. for IrP<sub>2</sub>GaN<sub>2</sub>AlO<sub>4</sub>F<sub>36</sub>C<sub>81</sub>H<sub>109</sub>: C 44.03% H 4.97 % N 1.27 % meas. C 44.79% H 5.02% N 1.22%. <sup>1</sup>H NMR (400 MHz, dichloromethane-d<sub>2</sub>, 298 K): δ<sub>H</sub> -11.89 (4H, br t, IrH), 1.08 - 1.93 (66H, m, Cy), 1.19 (12H, d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, CH<sub>3</sub> of Dipp 'Pr), 1.38 (12H, d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, CH<sub>3</sub> of Dipp 'Pr), 1.89 (6H, s, CH<sub>3</sub> of β-diketiminato backbone), 2.93 (4H, sept, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, CH of Dipp 'Pr), 5.41 (1H, s, γ-CH), 7.34 (4H, d, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, m-CH of Dipp), 7.41 (2H, t, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, p-CH of Dipp), 7.58 (4H, s, p-CH of [BAR<sup>f</sup><sub>4</sub>]), 7.75 (8H, s, o-CH of [BAR<sup>f</sup><sub>4</sub>]). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, dichloromethane-d<sub>2</sub>, 298 K): δ<sub>C</sub> 24.8 (CH<sub>3</sub> of Dipp 'Pr), 25.5 (CH<sub>3</sub> of Dipp 'Pr), 26.7 (C<sup>4</sup>-Cy), 25.6 (CH<sub>3</sub> of β-

diketiminato backbone), 28.0 (d, <sup>2</sup>J<sub>CP</sub> = 10.1 Hz, C<sup>2,6</sup>-Cy), 30.1 (CH of Dipp 'Pr), 30.3 (C<sup>3,5</sup>-Cy), 39.3 (d, <sup>1</sup>J<sub>CP</sub> = 24.2 Hz, C<sup>1</sup>-Cy), 103.4 (γ-CH), 118.1 (p-CH of [BAR<sup>f</sup><sub>4</sub>]), 125.2 (q, <sup>1</sup>J<sub>CF</sub> = 274 Hz, CF<sub>3</sub> of [BAR<sup>f</sup><sub>4</sub>]), 125.5 (m-CH of Dipp), 129.2 (p-CH of Dipp), 129.4 (q, <sup>2</sup>J<sub>CF</sub> = 29.4 Hz, m-CH of [BAR<sup>f</sup><sub>4</sub>]), 135.4 (o-CH of [BAR<sup>f</sup><sub>4</sub>]), 141.4 (o-C of Dipp), 143.7 (ipso-C of Dipp), 162.4 (q, <sup>1</sup>J<sub>CB</sub> = 50.1 Hz, ipso-C of [BAR<sup>f</sup><sub>4</sub>]), 172.4 (CN). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, dichloromethane-d<sub>2</sub>, 298 K): δ<sub>P</sub> 16.4 (s). <sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz, dichloromethane-d<sub>2</sub>, 298 K): δ<sub>B</sub> -6.5. <sup>19</sup>F NMR (376 MHz, dichloromethane-d<sub>2</sub>, 298 K): δ<sub>F</sub> -62.8. ESI-MS (cation): 1241 ([M-2H]<sup>+</sup>, 100%); accurate mass: calc. 1241.6942, meas. 1241.6746. Crystallographic data: C<sub>97</sub>H<sub>116</sub>BF<sub>24</sub>GalrN<sub>2</sub>P<sub>2</sub>, M<sub>r</sub> = 2103.68, monoclinic, P2<sub>1</sub>/n, a = 17.9237(2), b = 13.2726(2), c = 42.5997(5) Å, β = 97.2962(10)°, V = 10052.2(2) Å<sup>3</sup>, Z = 4, ρ<sub>c</sub> = 1.390 Mg m<sup>-3</sup>, T = 150 K, λ = 1.54180 Å. 20875 independent reflections [R(int) = 0.034], used in all calculations. R<sub>1</sub> = 0.0694, wR<sub>2</sub> = 0.1750 for I > 2σ(I), and R<sub>1</sub> = 0.0744, wR<sub>2</sub> = 0.1782 for all unique reflections. Max./min. residual electron densities 3.06 and -3.02 e Å<sup>-3</sup>.

**[Ir(dppp)(H)<sub>2</sub>(Ga(NacNac)<sup>Dipp</sup>)] [Al(pftb)<sub>4</sub>] (3):** *Method A:* A solution of 2-dppp (0.150 g, 0.077 mmol) and TBE (0.0485 mL, 0.386 mmol) in 1,2-difluorobenzene (5 mL) was stirred for 48 h at 85 °C in an ampoule fitted with a J. Young's valve. The solution was allowed to cool to room temperature and volatiles removed *in vacuo*. The resulting yellow oil was washed with pentane (3 x 5 mL) and dried *in vacuo* to give a yellow powder. Pale yellow crystals suitable for X-ray diffraction were obtained by layering a concentrated fluorobenzene solution with pentane and storage at room temperature. (Yield: 76 mg, 51%). *Method B:* A solution of [Ir(dppp)(COD)] [Al(pftb)<sub>4</sub>] (0.100 g, 0.060 mmol) and Ga(NacNac)<sup>Dipp</sup> (0.035 g, 0.072 mmol) in 1,2-difluorobenzene was stirred for 24 h at 85 °C in an ampoule fitted with a J. Young's valve. The reaction mixture was cooled to room temperature and volatiles removed *in vacuo*. The resulting yellow oil was washed with pentane (3 x 5 mL) and dried *in vacuo* to give a yellow powder. <sup>1</sup>H and <sup>31</sup>P NMR data matched that of the crystalline product obtained via Method A and were consistent with >90% conversion to product. Elemental microanalysis: calc. for C<sub>72</sub>H<sub>67</sub>AlF<sub>36</sub>GalrN<sub>2</sub>O<sub>4</sub>P<sub>2</sub>, C 42.00% H 3.28% N 1.36%; meas. C 42.46% H 3.19% N 1.22%. <sup>1</sup>H NMR (500 MHz, dichloromethane-d<sub>2</sub>, 298 K): δ<sub>H</sub> -14.28 (1H, dt, <sup>2</sup>J<sub>PH(trans)</sub> = 103.6 Hz, <sup>2</sup>J<sub>PH(cis)</sub><sup>2</sup>J<sub>HH</sub> = 5.0 Hz, IrH), -12.69 (1H, dt, <sup>2</sup>J<sub>PH(cis)</sub> = 12.0 Hz, <sup>2</sup>J<sub>HH</sub> = 5.5 Hz, IrH), 0.73, 0.86, 0.87, 1.16, 1.23, 1.34 (18H, d, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, 6 x CH<sub>3</sub> of Dipp 'Pr), 1.27 (2H, m, PCH<sub>2</sub>CH<sub>2</sub>), 1.71 (3H, s, H<sub>2</sub>C=C(CH<sub>3</sub>)), 2.15 (6H, 2 x s overlapping, 2 x CH<sub>3</sub> of β-diketiminato backbone), 2.68 (1H, d, <sup>2</sup>J<sub>HH</sub> = 12.8 Hz, H<sub>2</sub>C=C(CH<sub>3</sub>)), 2.76 (4H, m, PCH<sub>2</sub>), 2.91 - 3.03 (2H, 2 x overlapping septets, 2 x CH of Dipp 'Pr), 3.07 (1H, sept, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, CH of Dipp 'Pr), 3.55 (1H, d, <sup>2</sup>J<sub>HH</sub> = 12.8 Hz, H<sub>2</sub>C=C(CH<sub>3</sub>)), 5.65 (1H, s, γ-CH), 6.54 - 7.70 (26H, m, overlapping CH of Dipp and PPh). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, dichloromethane-d<sub>2</sub>, 298 K): δ<sub>C</sub> 18.2 (apparent t, <sup>2</sup>J<sub>CP</sub> = 2.8 Hz, PCH<sub>2</sub>CH<sub>2</sub>), 21.1, 23.7, 24.3, 24.4, 24.8, 25.3, 25.6 (2 x CH<sub>3</sub> of β-diketiminato backbone, 6 x CH<sub>3</sub> of Dipp 'Pr), 27.2 (dd, J = 29.0 Hz, J = 3.8 Hz, PCH<sub>2</sub>), 28.2 (CH of Dipp 'Pr), 28.6 (d, J = 30.2 Hz, PCH<sub>2</sub>), 29.0, 30.4 (2 x CH of Dipp 'Pr), 32.8 (CH<sub>2</sub>=C(CH<sub>3</sub>)), 52.2 (d, J = 2.5 Hz, CH<sub>2</sub>=C(CH<sub>3</sub>)), 79.5 (br, C(CF<sub>3</sub>)<sub>3</sub> of [Al(pftb)<sub>4</sub>]), 87.1 (d, J = 2.5 Hz, CH<sub>2</sub>=C(CH<sub>3</sub>)), 102.2 (γ-CH), 121.9 (q, <sup>1</sup>J<sub>CF</sub> = 292.6 Hz, CF<sub>3</sub> of [Al(pftb)<sub>4</sub>]), 115.4 - 144.6 (ArC of Dipp and PPh), 167.8 (CN), 170.3 (CN). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, dichloromethane-d<sub>2</sub>, 298 K): δ<sub>P</sub> -11.1 (d, <sup>2</sup>J<sub>PP</sub> = 13.7 Hz), -5.0 (d, <sup>2</sup>J<sub>PP</sub> = 13.7 Hz). <sup>27</sup>Al NMR (104 MHz, dichloromethane-d<sub>2</sub>, 298 K): δ<sub>Al</sub> 34.7. <sup>19</sup>F NMR (376 MHz, dichloromethane-d<sub>2</sub>, 298 K): δ<sub>F</sub> -75.4. ESI-MS (cation): 1091 ([M]<sup>+</sup>, 100%); accurate mass: calc. 1091.3654, meas. 1091.3566. Crystallographic data: C<sub>72</sub>H<sub>67</sub>AlF<sub>36</sub>GalrN<sub>2</sub>O<sub>4</sub>P<sub>2</sub>, M<sub>r</sub> = 2059.13, orthorhombic, P<sub>2</sub>ca, a = 19.45530(10), b = 20.55400(10), c = 42.0117(2) Å, V = 16799.82(14) Å<sup>3</sup>, Z = 8, ρ<sub>c</sub> = 1.628 Mg m<sup>-3</sup>, T = 150 K, λ = 0.71073 Å. 19107 independent reflections [R(int) = 0.035], used in all calculations. R<sub>1</sub> = 0.0744, wR<sub>2</sub> = 0.1536 for I > 2σ(I), and R<sub>1</sub> = 0.1030, wR<sub>2</sub> = 0.1830

for all unique reflections. Max./min. residual electron densities 2.42 and -1.56 e Å<sup>-3</sup>.

### Crystallography

X-ray data for compounds **2**-dppp, **2**-dcype, **2**-PCy<sub>3</sub> and **3** were collected on a Nonius KappaCCD or Oxford Diffraction SuperNova diffractometer at 150 K. Data collection and reduction were carried out using Collect and Denzo/Scalepack or CrysAlis, respectively, structure solution using either Sir92, Superflip or SHELXS86, and refinement using CRYSTALS.<sup>[32]</sup> Single-crystal neutron diffraction data were collected using the KOALA instrument on TG3, a thermal neutron guide at ANSTO.<sup>[33a]</sup> from 13 images obtained immediately prior to reactor shutdown at the end of cycle. Data were extracted using LAUEG and merged R<sub>merg</sub> 0.10(6) for 5323 reflections greater than 4σ.<sup>[33b]</sup> Complete details of all structures are contained within the respective CIFs (see Supporting Information) which have additionally been deposited with the CCDC.

### Computational Method

DFT calculations were carried out using the Amsterdam Density Functional (ADF 2013) software package.<sup>[34a,b]</sup> Calculations were performed using the Volko-Wilk-Nusair local density approximation with exchange from Becke,<sup>[34c]</sup> and correlation functions from Perdew (BP).<sup>[34d]</sup> Slater-type orbitals were used for the triple zeta basis set with an additional set of polarization functions (TZP).<sup>[34e]</sup> The large frozen core basis set approximation was applied with no molecular symmetry. General numerical integration was 6.

### Acknowledgements

This work was supported by the EPSRC (studentship to J.A.B.A.); ANSTO is thanked for the allocation of discretionary neutron beam-time on KOALA to proposal DB3706 and a further allocation to proposal P3932. We thank Dr Amber Thompson (Oxford Chemistry) for assistance with crystallography.

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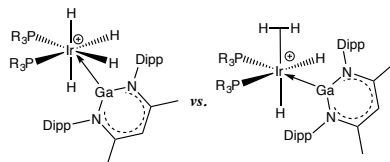
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Reactions of  $(\text{Nacnac})^{\text{Dipp}}\text{GaH}_2$  with chelating Ir(I) bis(phosphine) precursors provide a simple route to Ir(V) complexes stabilized by strongly  $\sigma$ -donating hydrides and the carbene-like  $(\text{Nacnac})^{\text{Dipp}}\text{Ga}$  donor. Related systems featuring more sterically demanding ancillary ligands, by contrast, are better described in terms of a bis(hydride) dihydrogen  $[\text{Ir}(\text{H})_2(\text{H}_2)]$  formulation and a formal Ir(III) oxidation state.



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**A gallium hydride as an oxidizing agent: direct synthesis of Ir(V) complexes via Ga-H bond activation**