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## PC(sp<sup>3</sup>)P pincer carbonyl complexes of iridium(i), and iridium(III)<sup>†</sup>

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The previously reported complex *trans*-[IrHCl(*cis*-1,3-bis-(di-*tert*-butylphosphino)methyl)cyclohexane] (**2**) forms the 18-electron carbonyl compound *anti*-[Ir(CO)HCl(*cis*-1,3-bis-((di-*tert*-butylphosphino)methyl)cyclohexane)] (**5a**) upon reaction with 1 atm CO. The structural isomer *syn*-[IrH(CO)Cl(*cis*-1,3-bis-((di-*tert*-butylphosphino)methyl)cyclohexane)] (**5b**) is obtained directly upon complexation of the ligand (**1**) with IrCl<sub>3</sub>·H<sub>2</sub>O in refluxing DMF. *syn*-**5b** is the first iridium aliphatic pincer complex with this orientation of the hydrogens and is the thermodynamically more stable isomer. Both compounds **5a** and **5b** afford the Ir(I) complex *trans*-[Ir(CO)(*cis*-1,3-bis-((di-*tert*-butylphosphino)methyl)cyclohexane)] (**4**) upon treatment with KO<sup>t</sup>Bu. Complex **4** was also synthesised in a more straightforward fashion from the previously known terminal nitrogen complex *trans*-[Ir(N<sub>2</sub>)(*cis*-1,3-bis-((di-*tert*-butylphosphino)-methyl)cyclohexane)] (**3**) under atmospheric CO. The complexes **4**, **5a** and **5b** were characterised spectroscopically and in the solid state. IR data point to a more electron rich metal centre as compared to the corresponding aromatic complexes.

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## Introduction

The chemistry of iridium PCP pincer-type complexes has been continuously developed over the last decades, mainly owing to their applications as active homogeneous catalysts in the dehydrogenation<sup>1</sup> of alkanes,<sup>2–6</sup> alcohols<sup>7,8</sup> and amine-boranes.<sup>9,10</sup> Oxidative additions and reductive eliminations are fundamental processes in these and many other catalytic transformations and stoichiometric reactions, and are highly influenced by the electronic properties of the metal centre.<sup>11</sup> In this aspect, the application of all-aliphatic pincer backbones is a relevant task, since the properties of a C(sp<sup>3</sup>)-compared to the more common C(sp<sup>2</sup>)-based PCP complexes might differ significantly due to electronic factors such as stronger *trans* influence by the metallated carbon and a metal centre with higher nucleophilicity.<sup>12</sup> Also, the hybridization is expected to influence the rate of any concerted reaction.<sup>13,14</sup> Carbon monoxide has been long known to coordinatively add to both PC(sp<sup>2</sup>)P<sup>15</sup> and PC(sp<sup>3</sup>)P-supported<sup>16</sup> iridium(III) complexes, and such iridium carbonyl complexes have later been found to be involved in catalytic transformations such as transfer hydrogenations of ketones<sup>8</sup> and olefin hydroformylation.<sup>17</sup> PCP iridium(I) carbonyl complexes are well known for benzene based pincer structures,<sup>7,18–22</sup> and have been reported to catalyse

the decarbonylation of 2-naphtaldehyde<sup>23</sup> and the partial deoxygenation of diols<sup>24</sup> and glycerol,<sup>25</sup> but there are no PC(sp<sup>3</sup>)P-supported iridium(I) carbonyl complexes reported to this date.

Here we report on the synthesis and interconversion of PC(sp<sup>3</sup>)P pincer carbonyl complexes with iridium(I) and iridium(III). The electronic properties of the PC(sp<sup>3</sup>)P pincer ligand is also probed using carbonyl stretching frequencies.

## Experimental section

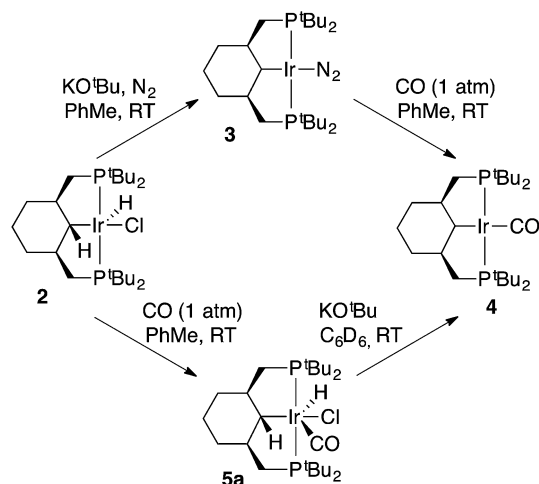
### General comments

All manipulations were performed under a nitrogen or argon atmosphere using standard Schlenk or glovebox techniques, except where noted. Solvents were purified by vacuum distillation from sodium/benzophenone ketyl radical. The ligand *cis*-1,3-bis-((di-*tert*-butylphosphino)methyl)cyclohexane, **1**, and the complexes **2** and **3** were prepared according to previously reported procedures,<sup>26,27</sup> cf. Scheme 1 for numbering. All other chemicals were purchased from commercial suppliers and used as received. <sup>1</sup>H-, <sup>13</sup>C and <sup>31</sup>P-NMR experiments were recorded on a Varian Unity INOVA 500 spectrometer, operating at 499.76 (<sup>1</sup>H), 125.68 (<sup>13</sup>C) and 202.31 (<sup>31</sup>P) MHz. For <sup>1</sup>H- and <sup>13</sup>C-NMR spectra, the residual solvent peak was used as an internal reference. <sup>31</sup>P-NMR spectra were referenced externally using 85% H<sub>3</sub>PO<sub>4</sub> at δ = 0 ppm. Multiplicities are abbreviated as follows: (s) singlet, (d) doublet, (t) triplet, (q) quartet, (m) multiplet, (br) broad, (v) virtual. IR spectra were obtained on a Bruker ALPHA FT-IR spectrometer. Elemental analyses were performed by H. Kolbe Microanalytisches Laboratorium, Mülheim an der Ruhr, Germany.

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<sup>†</sup> Electronic supplementary information (ESI) available: NMR spectra for **4**. Computational details. Crystal data for **4**, **5a** and **5b**. CCDC 1029323, 1029332 and 1029333. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4ra15562a





Scheme 1

### Crystallography

XRD-quality crystals of compounds **4**, **5a** and **5b** were obtained through recrystallization from toluene or hexane. Intensity data were collected with an Oxford Diffraction Excalibur 3 system, using  $\omega$ -scans and MoK $\alpha$  ( $\lambda = 0.71073$  Å) radiation.<sup>28</sup> The data were extracted and integrated using CrysAlis RED.<sup>28</sup> The structure was solved by direct methods and refined by full-matrix least-squares calculations on  $F^2$  using SHELXTL5.1.<sup>29</sup> Compound **4** formed small, weakly diffracting crystals, giving rise to a high  $R_{\text{int}}$ .<sup>30</sup> Non-H atoms were refined with anisotropic displacement parameters. Hydrogen atoms were constrained to parent sites, using a riding model. For **5a** and **5b** attempts were made to locate the hydride atoms. Although residual electron density could be located in the expected area *trans* to CO and Cl, respectively, all attempts to model this as a hydride failed, giving unreasonable distances and angles and negative isotropic thermal parameters. Molecular graphics were generated using CrystalMaker® 8.3.5.<sup>31</sup>

**Preparation of *trans*-[Ir(CO)(*cis*-1,3-bis-((di-*tert*-phosphino)methyl))-cyclohexane] (**4**).** Compound **3** (10.0 mg, 0.016 mmol) was dissolved in toluene (3 mL), and the solution was freeze-pump-thawed prior to addition of CO (1 atm). After stirring at room temperature for 1.5 h, the solvent was removed *in vacuo*, and the yellow solid residue was recrystallized from hexane. Yield: 7.8 mg (78%). <sup>1</sup>H-NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  2.32–2.27 (m,  $\text{PCH}_2\text{CH}$ , 2H), 2.22–2.19 (m, Cy, 2H), 2.02–1.98 (br m, Cy, 1H), 1.73–1.64 (m, Cy, 2H), 1.52 (tt,  $J = 4.0$  Hz,  $J = 13.5$  Hz,  $\text{PCH}_2\text{CH}$ , 2H), 1.48–1.42 (m, Cy, 1H), 1.32 (vt,  $J_{\text{PH}} = 13.0$  Hz,  $^t\text{Bu}$ , 18H), 1.26 (vt,  $J_{\text{PH}} = 13.0$  Hz,  $^t\text{Bu}$ , 18H), 1.19 (t,  $J = 11.0$ , HC–Ir, 1H), 0.95 (dq,  $J = 3.5$  Hz,  $J = 12.5$  Hz, Cy, 2H). <sup>13</sup>C{<sup>1</sup>H}-NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  194.8 (vt,  $J_{\text{PC}} = 15$  Hz, Ir–CO, 1C), 71.6 (vt,  $J_{\text{PC}} = 7.2$  Hz, HC–Ir, 1C), 50.3 (vt,  $J_{\text{PC}} = 19$  Hz,  $\text{PCH}_2$ , 2C), 36.9 (vt,  $J_{\text{PC}} = 25$  Hz, Cy, 2C), 36.4 (vt,  $J_{\text{PC}} = 21$  Hz,  $\text{C}(\text{CH}_3)_3$ , 2C), 35.8 (vt,  $J_{\text{PC}} = 22$  Hz,  $\text{C}(\text{CH}_3)_3$ , 2C), 34.9 (vt,  $J_{\text{PC}} = 19$  Hz, Cy, 2C), 29.8 (vt,  $J_{\text{PC}} = 5.6$  Hz,  $\text{C}(\text{CH}_3)_3$ , 6C), 29.7 (vt,  $J_{\text{PC}} = 5.2$  Hz,  $\text{C}(\text{CH}_3)_3$ , 6C), 27.7 (vt,  $J_{\text{PC}} = 2.8$  Hz,  $\text{CH}_2\text{CH}_2\text{CH}_2$ , 1C). <sup>31</sup>P{<sup>1</sup>H}-NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  81.8 (s). IR (NaCl/nujol)  $\nu_{\text{CO}} = 1917$   $\text{cm}^{-1}$ , (hexane)  $\nu_{\text{CO}} = 1920$   $\text{cm}^{-1}$ , ( $\text{CH}_2\text{Cl}_2$ )  $\nu_{\text{CO}} = 1896$   $\text{cm}^{-1}$ .

**Preparation of *anti*-[Ir(CO)HCl(*cis*-1,3-bis-((di-*tert*-butylphosphino)methyl))-cyclohexane] (**5a**).** Compound **2** (25.0 mg, 0.040 mmol) was dissolved in THF (3 mL), and the solution was freeze-pump-thawed prior to addition of CO (1 atm). A colour change from deep red to colourless was observed within seconds. After stirring at room temperature for 2 h, the solvent was removed *in vacuo*, and the white solid residue was recrystallized from hexane. Yield: 22.2 mg (85%). <sup>1</sup>H-NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  1.89–1.84 (m,  $\text{PCH}_2\text{CH}$ , 2H), 1.82–1.77 (br m, Cy, 2H + 1H), 1.61 (t,  $J = 10.5$  Hz, HC–Ir, 1H), 1.51–1.45 (br m,  $\text{PCH}_2\text{CH}$ , 2H + Cy, 1H), 1.41 (vt,  $J_{\text{PH}} = 13.0$  Hz,  $^t\text{Bu}$ , 18H), 1.37 (vt,  $J_{\text{PH}} = 13.0$  Hz,  $^t\text{Bu}$ , 18H), 1.12 (tt,  $J = 3.5$  Hz,  $J = 14.0$  Hz, Cy, 2H), 0.90 (dq,  $J = 4.0$  Hz,  $J = 13.0$  Hz, Cy, 2H), –8.59 (dt,  $J_{\text{HH}} = 1.5$  Hz,  $J_{\text{PH}} = 17.0$  Hz, Ir–H, 1H). <sup>13</sup>C{<sup>1</sup>H}-NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  226.7 (s, Ir–CO, 1C), 51.5 (vt,  $J_{\text{PC}} = 11$  Hz, CH–Ir, 1C), 37.8 (vt,  $J_{\text{PC}} = 27$  Hz,  $\text{PCH}_2$ , 2C), 36.8 (vt,  $J_{\text{PC}} = 21$  Hz, Cy, 2C), 36.2 (vt,  $J_{\text{PC}} = 23$  Hz,  $\text{C}(\text{CH}_3)_3$ , 2C), 33.9 (vt,  $J_{\text{PC}} = 17$  Hz,  $\text{C}(\text{CH}_3)_3$ , 2C), 32.7 (s, Cy, 2C), 30.8, (vt,  $J_{\text{PC}} = 3.2$  Hz,  $\text{C}(\text{CH}_3)_3$ , 6C), 30.6 (vt,  $J_{\text{PC}} = 3.0$  Hz,  $\text{C}(\text{CH}_3)_3$ , 6C), 27.8, (s,  $\text{CH}_2\text{CH}_2\text{CH}_2$ , 1C). <sup>31</sup>P{<sup>1</sup>H}-NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  50.2 (s). IR (ATR)  $\nu_{\text{CO}} = 1977$   $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{25}\text{H}_{51}\text{ClIrOP}_2$  (657.29): C, 45.68; H, 7.82. Found: C, 45.60; H, 7.65.

**Preparation of *syn*-[IrH(CO)Cl(*cis*-1,3-bis-((di-*tert*-butylphosphino)methyl))-cyclohexane] (**5b**).** *cis*-1,3-Bis-[(di-*tert*-butylphosphino)methyl]cyclohexane (**1**) (24.8 mg, 0.062 mmol) and  $\text{IrCl}_3 \cdot \text{H}_2\text{O}$  (18.6 mg, 0.062 mmol) was mixed with dry degassed DMF (4 mL) under a stream of  $\text{N}_2$ . The mixture was heated to 150 °C for 24 h. Upon cooling to RT a yellow precipitate came out of solution. The solvent was removed *in vacuo*, followed by repeated crystallisation from THF to afford **5b** as a pale yellow crystalline powder. Yield: 23.2 mg (54%). <sup>1</sup>H-NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  2.61–2.52 (m,  $\text{PCH}_2\text{CH}$ , 2H), 2.09–2.01 (m,  $\text{PCH}_2\text{CH}$ , 2H + Cy, 2H), 1.86–1.81 (m, Cy, 1H), 1.55 (vt,  $J_{\text{PH}} = 13.5$  Hz,  $^t\text{Bu}$ , 18H), 1.53–1.51 (m, Cy, 1H), 1.42 (t,  $J = 11.0$  Hz, HC–Ir, 1H), 1.15 (tt,  $J = 4.0$  Hz,  $J = 14.0$  Hz, Cy, 2H), 1.06 (vt,  $J_{\text{PH}} = 12.5$  Hz,  $^t\text{Bu}$ , 18H), 0.92 (dq,  $J = 3.5$  Hz,  $J = 13.0$  Hz, Cy, 2H), –18.7 (t,  $J_{\text{PH}} = 13.0$  Hz, Ir–H, 1H). <sup>31</sup>P{<sup>1</sup>H}-NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  56.4 (d,  $J_{\text{PH}} = 13.0$  Hz). IR (ATR)  $\nu_{\text{CO}} = 1989$   $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{25}\text{H}_{51}\text{ClIrOP}_2$  (657.29): C, 45.68; H, 7.82. Found: C, 45.59; H, 7.79.

## Results and discussion

We have earlier reported on the cyclometallation of ligand **1** with  $[\text{Ir}(\text{COD})\text{Cl}]_2$  to give *trans*-[IrHCl(*cis*-1,3-bis-((di-*tert*-butylphosphino)methyl)cyclohexane)] (**2**), and also on the reduction of this compound with metallic potassium under an  $\text{N}_2$  atmosphere at elevated temperatures, affording the Ir(I) terminal nitrogen complex **3**.<sup>26</sup> We here report an alternative synthesis of **3** from **2** under slightly milder conditions and in comparable yields, using KO<sup>*t*</sup>Bu (Scheme 1) as was previously reported by Milstein and Frech for the preparation of a naphthyl based PCP Rh(I)  $\eta^1\text{-N}_2$  complex.<sup>32</sup> Upon addition of CO to a degassed toluene solution of **3**, a colour change from orange to yellow was observed within minutes, consistent with what is expected upon substitution to a stronger  $\pi$ -acceptor ligand. Following this route, the Ir(I) carbonyl complex **4** was isolated and characterised by IR and NMR spectroscopy and the structure was confirmed by means of X-ray crystallography. It shows a characteristic carbonyl shift at 194.8 ppm in the <sup>13</sup>C-NMR



spectrum. Complex **4** failed to give satisfactory elemental analysis, possibly due to a limited stability at room temperature similarly to what was found for complex **3**. However, based on NMR spectra (see ESI†) it is essentially pure. The molecular structure of compound **4** is shown in Fig. 1, and the crystallographic data for the compounds **4–5** are given in Table 1. The structure adopts a distorted square planar geometry around iridium. While the angle between the PCP coordinated carbon and the carbonyl ligand is close to ideal ( $177.1^\circ$ ), the P–Ir–P angle is much more distorted ( $164.46^\circ$ ) due to the usual geometric constraints imposed by the chelating pincer arms. With respect to bond lengths and angles around iridium, complex **4** resembles its aromatic analogue very closely,<sup>7</sup> and, surprisingly, there is no substantial change of the Ir–CO or C–O distances (PC<sub>Ar</sub>P mean distances: Ir–CO =  $1.863 \text{ \AA}$ ; C–O =  $1.147 \text{ \AA}$ , **4**: Ir–CO =  $1.860(7) \text{ \AA}$ ; C–O =  $1.143(7)$ ); a similar observation was made regarding the Ir(I)–N<sub>2</sub> complexes where the aliphatic ligand was also observed to induce a small decrease in the N–N bond distance.<sup>26</sup> However, both the N<sub>2</sub><sup>−</sup> and current CO-ligands are subject to substantial libration,<sup>33</sup> an explanation that is unambiguous in the N<sub>2</sub>-case since the complex actually showed a shorter distance than in free N<sub>2</sub>. Therefore, a better measure of the electron density is the  $\nu_{\text{CO}}$  stretching frequency. In hydrocarbons this is  $1920 \text{ cm}^{-1}$  for **4** compared with  $1928 \text{ cm}^{-1}$  for the corresponding aromatic compound.<sup>34</sup> In dichloromethane the corresponding values are  $1896$  and  $1913 \text{ cm}^{-1}$ , respectively,<sup>35</sup> and overall this points to a more electron rich metal centre in **4** compared to the aromatic analogue, a trend that agrees with the observations of  $\nu_{\text{NN}}$  stretching frequencies for Ir(I)–N<sub>2</sub> complexes and CV-measurements for Ni(II) complexes.<sup>12c,26</sup>

Subjecting the deep red solution of complex **2** to  $1 \text{ atm CO}$  resulted in a colourless solution of the  $18$  electron complex **5a** within seconds. Treating a C<sub>6</sub>D<sub>6</sub> solution of **5a** with an excess of KO<sup>t</sup>Bu afforded reduction to the iridium(I) complex **4**, as confirmed by comparison with the NMR-spectrum of the isolated compound. The lower route is, however, slower and

Table 1 Crystallographic data for compounds **4–5**

	<b>4</b>	<b>5a</b>	<b>5b</b>
Formula	C <sub>25</sub> H <sub>49</sub> IrOP <sub>2</sub>	C <sub>25</sub> H <sub>50</sub> ClIrOP <sub>2</sub>	C <sub>25</sub> H <sub>50</sub> ClIrOP <sub>2</sub>
<i>F</i> <sub>w</sub>	619.78	656.24	656.24
Space group	<i>Pbca</i>	<i>P2</i> <sub>1</sub> / <i>n</i>	<i>Pbca</i>
<i>a</i> /Å	12.4581(9)	12.5453(2)	12.3770(2)
<i>b</i> /Å	15.3030(9)	15.2101(3)	15.3452(2)
<i>c</i> /Å	29.2263(16)	15.5649(3)	28.8663(4)
$\beta$ /deg	90	93.996(2)	90
<i>V</i> /Å <sup>3</sup>	5571.9	2962.80	5482.51
<i>Z</i>	8	4	8
<i>D</i> <sub>calcd</sub> /g cm <sup>−3</sup>	1.478	1.469	1.590
$\mu$ /mm <sup>−1</sup>	4.920	4.718	5.100
$\theta$ /range/deg	2.47–28.12	2.42–28.96	2.23–33.14
Reflns collected	90 480	70 507	39 527
Unique reflns	6596	7422	9768
<i>R</i> ( <i>F</i> ) [ <i>I</i> > 2σ( <i>I</i> )] <sup>a</sup>	0.0520	0.0332	0.0389
w <i>R</i> <sub>2</sub> ( <i>F</i> <sup>2</sup> ) (all) <sup>b</sup>	0.1167	0.1030	0.1221
<i>S</i> <sup>c</sup>	1.224	1.425	1.124
<i>R</i> <sub>int</sub>	0.126	0.0594	0.0317
CCDC	1029323	1029333	1029332

<sup>a</sup>  $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ . <sup>b</sup>  $wR_2 = [\sum w(|F_o| - |F_c|)^2/\sum(|F_o|)^2]^{1/2}$ . <sup>c</sup>  $S = [\sum w(|F_o| - |F_c|)^2/\sum(|F_o|)^2]^{1/2}$ .

slightly less clean than the synthesis starting from compound **3** (Scheme 1).

Refluxing ligand **1** and IrCl<sub>3</sub>·H<sub>2</sub>O in DMF gave a yellow solid material that was shown to be complex **5b**, an isomer of **5a** (Scheme 2). This type of cyclometallation where the solvent is the carbonyl source, was previously observed by Azerraf and Gelman in the formation of a dibenzobarrelene based PC(sp<sup>3</sup>)P iridium complex.<sup>8a,8c</sup>

The structural isomers **5a** and **5b** are clearly distinguishable by means of NMR-spectroscopy, most notably in the <sup>31</sup>P-NMR

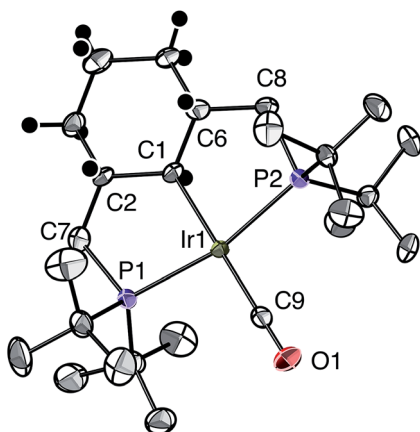


Fig. 1 Molecular structure of **4** at the 30% probability level. For clarity, hydrogen atoms are only depicted in the cyclohexyl ring. Selected bond lengths (Å) and bond angles (°) with estimated standard deviations: Ir1–C1 =  $2.143(6)$ , Ir1–C9 =  $1.860(7)$ , C9–O1 =  $1.143(7)$ , Ir1–P1 =  $2.3073(16)$ , Ir1–P2 =  $2.3060(15)$ , P1–Ir1–P2 =  $164.46(6)$ , C1–Ir–C9 =  $177.1(3)$ , Ir1–C9–O1 =  $179.1(7)$ , P1–Ir1–C1 =  $82.38(16)$ , P2–Ir1–C1 =  $82.14(16)$ .

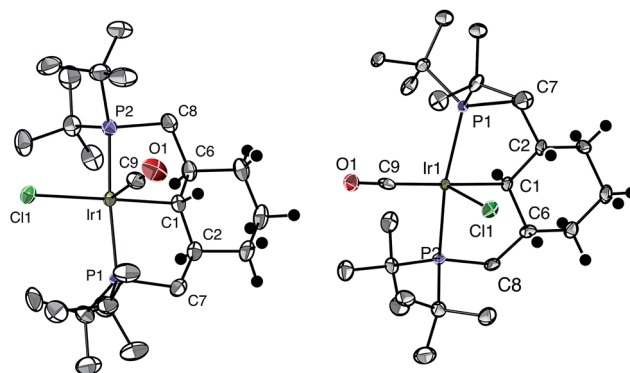


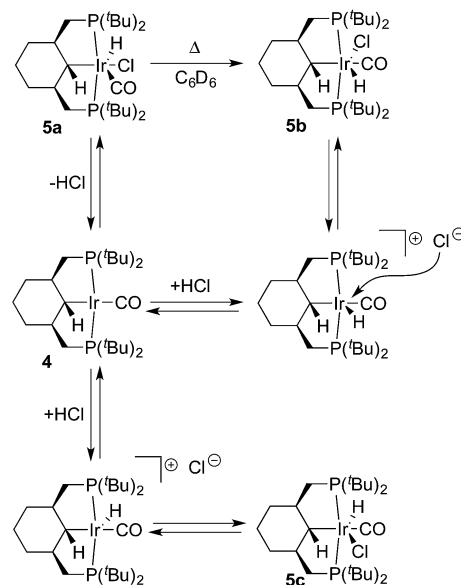
Fig. 2 Molecular structure of **5a** and **5b** at the 30% probability level. For clarity, hydrogen atoms are only depicted in the cyclohexyl ring. Selected bond lengths (Å) and bond angles (°) with estimated standard deviations: **5a**: Ir1–C1 =  $2.137(4)$ , Ir1–C9 =  $1.943(4)$ , C9–O1 =  $1.101(5)$ , Ir1–Cl1 =  $2.5374(10)$ , Ir1–P1 =  $2.3591(10)$ , Ir1–P2 =  $2.3643(10)$ , P1–Ir1–P2 =  $158.44(4)$ , C1–Ir–C9 =  $87.16(16)$ , Ir1–C9–O1 =  $173.7(4)$ , C1–Ir1–Cl1 =  $179.40(11)$ , P1–Ir1–Cl1 =  $95.53(4)$ , P2–Ir1–Cl1 =  $96.39(4)$ . **5b**: Ir1–C1 =  $2.159(4)$ , Ir1–C9 =  $1.909(5)$ , C9–O1 =  $1.111(6)$ , Ir1–Cl1 =  $2.5340(12)$ , Ir1–P1 =  $2.3578(11)$ , Ir1–P2 =  $2.3555(11)$ , P1–Ir1–P2 =  $161.82(4)$ , C1–Ir–C9 =  $174.72(18)$ , Ir1–C9–O1 =  $174.1(4)$ , C1–Ir1–Cl1 =  $90.49(12)$ , P1–Ir1–Cl1 =  $94.15(4)$ , P2–Ir1–Cl1 =  $94.44(4)$ .



shifts ( $\delta = 50.2$  ppm and  $56.4$  ppm respectively in  $C_6D_6$ ) and the  $^1H$ -NMR hydride shifts ( $\delta = -8.59$  ppm and  $-18.7$  ppm respectively in  $C_6D_6$ ), and both compounds are seemingly resistant towards isomerisation upon standing in solution at room temperature for several days. A significantly lower solubility of compound **5b** made attempts to obtain a satisfactory  $^{13}C$ -NMR spectrum of this compound unsuccessful. However, crystallographic and IR spectroscopic data clearly confirm the presence of a carbonyl ligand. The  $\nu_{CO}$  stretching frequencies for **5a** and **5b** are found at  $1977\text{ cm}^{-1}$  and  $1989\text{ cm}^{-1}$  respectively, which can be compared to the value reported for the aromatic analogue of **5a** ( $\nu_{CO} = 1985\text{ cm}^{-1}$ , KBr).<sup>15</sup> Thus, it is again clear that the electron density at iridium bonded to a  $C(sp^3)$ -carbon is higher than in an analogous aromatic complex. Also, the  $\pi$ -back donation is weaker *trans* to a  $\sigma$ -bonded carbon than *trans* to the hydride ligand. As expected the  $\nu_{CO}$  values in the Ir(III) complexes **5a** and **5b** are substantially higher than the value in the Ir(I) complex **4**.

The molecular structures of compound **5a** and **5b** are given in Fig. 2. Notably, the two isomers **5a** and **5b** have different orientations of their respective hydride ligands relative to the  $\alpha$ -hydrogen, as illustrated in Schemes 1 and 2. In case of **5a**, the hydride and  $\alpha$ -hydrogen are located *anti* to each other, while in **5b** they are *syn*. All previously reported  $PC(sp^3)P$  complexes with iridium<sup>26,36</sup> show an *anti* configuration and this seems to be the preferred outcome of a metallation involving a concerted oxidative addition process *via* a C–H  $\sigma$ -complex. This is therefore what is observed in the fast CO addition to **2** which has an *anti* configuration. Gelman observed that the quality of the DMF influenced the outcome of the cyclometallation reaction, affording a  $PC(sp^3)PIrH(CO)Cl$  complex in the presence of water and a  $PC(sp^3)PIr(CO)(Cl)_2$  complex in dry solvent,<sup>8c</sup> but **5b** is analogous to the complex reported in wet DMF, featuring the carbonyl ligand located in a *trans* position and the hydride and chloride both in *cis* position to the metallated PCP carbon, although DMF freshly distilled from  $CaH_2$  was used.

The observations by Gelman and the *syn* configuration of the hydride ligand and  $\alpha$ -hydrogen in **5b** probably means that the mechanism for formation of the cyclometallated species in DMF is not a simple C–H oxidative addition but involves several deprotonation/protonation steps. There was no tendency for isomerization of **5b**. Overall, this indicates that the *syn* configuration is thermodynamically more stable than the *anti* one and this is also in line with the higher density for **5b**. To test this hypothesis, we attempted isomerisation of **5a** to **5b** (Scheme 3). Indeed, when a solution of **5a** in  $C_6D_6$  was heated at  $90^\circ C$ , signals of **5b** appeared, together with very small amounts of **4** and another compound, which is characterized by a doublet at



Scheme 3

$57.6$  ppm in the  $^{31}P\{^1H\}$  NMR spectrum and a triplet at  $-18.78$  ( $J_{PH} = 11.8$  Hz) in the  $^1H$  NMR spectrum. Based on the similarity of the NMR signals of this new compound and those of **5b**, we tentatively ascribe it to the structure **5c**, *i.e.* the *anti* isomer with CO *trans* to the  $\sigma$ -C bond. After 36 h the reaction was complete and only **5b** together with traces of **4** was observed. These observations suggest that most likely the isomerisation of **5a** to **5b** proceeds *via* a reversible dehydrochlorination to give **4**, followed by protonation *syn* (to give **5b**) or *anti* (to give **5c**) with respect to the  $\alpha$ -CH of **4**.

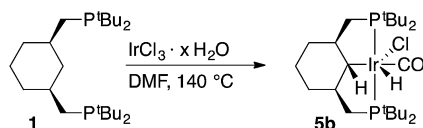
DFT calculations confirm the relative thermodynamic stability of **5a**, **5b** and **5c**. Thus, energies of **5a** and **5c** are almost equal, while complex **5b** is  $7.4$  kcal lower than **5a** and **5c** in agreement with experimental observations (see ESI† for details).

## Conclusions

In summary, we have described the synthesis of new cyclohexyl-based PCP carbonyl complexes with iridium(I) and iridium(III). As noted earlier, the  $C(sp^3)$  ligand gives a more electron rich metal complex than observed for the corresponding aromatic systems. Furthermore, we have, for the first time, isolated the thermodynamically more stable *syn* isomer of a  $PC(sp^3)P$  complex with iridium.

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Scheme 2





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