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PC(sp³)P pincer carbonyl complexes of iridium(I), and iridium(III)†

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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 IrCl₃·H₂O 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*t*Bu. Complex **4** was also synthesised in a more straightforward fashion from the previously known terminal nitrogen complex *trans*-[Ir(N₂){*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 dehydrogenation¹ of alkanes,^{2–6} alcohols^{7,8} and amine-boranes.^{9,10} 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.¹¹ In this aspect, the application of all-aliphatic pincer backbones is a relevant task, since the properties of a C(sp³)-compared to the more common C(sp²)-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.¹² Also, the hybridization is expected to influence the rate of any concerted reaction.^{13,14} Carbon monoxide has been long known to coordinatively add to both PC(sp²)P¹⁵ and PC(sp³)P-supported¹⁶ iridium(III) complexes, and such iridium carbonyl complexes have later been found to be involved in catalytic transformations such as transfer hydrogenations of ketones⁸ and olefin hydroformylation.¹⁷ PCP iridium(I) carbonyl complexes are well known for benzene based pincer structures,^{7,18–22} and have been reported to catalyse

the decarbonylation of 2-napthaldehyde²³ and the partial deoxygenation of diols²⁴ and glycerol,²⁵ but there are no PC(sp³) P-supported iridium(I) carbonyl complexes reported to this date.

Here we report on the synthesis and interconversion of PC(sp³)P pincer carbonyl complexes with iridium(I) and iridium(III). The electronic properties of the PC(sp³)P pincer ligand is also probed using carbonyl stretching frequencies.

Experimental section

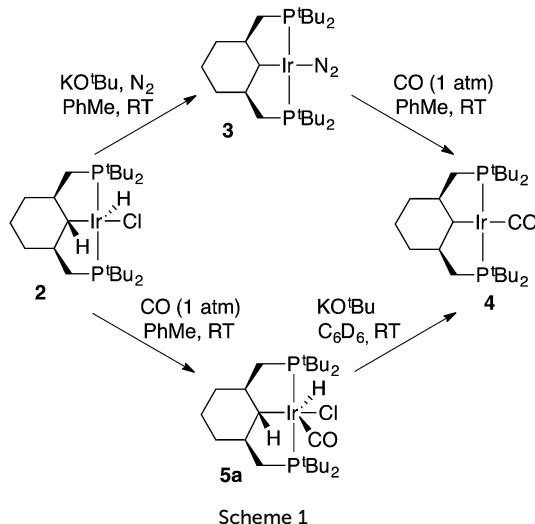
General comments

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,^{26,27} cf. Scheme 1 for numbering. All other chemicals were purchased from commercial suppliers and used as received. ¹H-, ¹³C and ³¹P-NMR experiments were recorded on a Varian Unity INOVA 500 spectrometer, operating at 499.76 (¹H), 125.68 (¹³C) and 202.31 (³¹P) MHz. For ¹H- and ¹³C-NMR spectra, the residual solvent peak was used as an internal reference. ³¹P-NMR spectra were referenced externally using 85% H₃PO₄ 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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† 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





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 ω -scans and MoK α ($\lambda = 0.71073 \text{ \AA}$) radiation.²⁸ The data were extracted and integrated using CrysAlis RED.²⁸ The structure was solved by direct methods and refined by full-matrix least-squares calculations on F^2 using SHELXTL5.1.²⁹ Compound **4** formed small, weakly diffracting crystals, giving rise to a high R_{int} .³⁰ 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® 8.3.5.³¹

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%). $^1\text{H-NMR}$ (C_6D_6): δ 2.32–2.27 (m, PCH_2CH , 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, $J = 4.0 \text{ Hz}$, $J = 13.5 \text{ Hz}$, PCH_2CH , 2H), 1.48–1.42 (m, Cy, 1H), 1.32 (vt, $J_{\text{PH}} = 13.0 \text{ Hz}$, ^1Bu , 18H), 1.26 (vt, $J_{\text{PH}} = 13.0 \text{ Hz}$, ^1Bu , 18H), 1.19 (t, $J = 11.0 \text{ Hz}$, HC–Ir, 1H), 0.95 (dq, $J = 3.5 \text{ Hz}$, $J = 12.5 \text{ Hz}$, Cy, 2H). $^{13}\text{C}\{^1\text{H}\}$ -NMR (C_6D_6): δ 194.8 (vt, $J_{\text{PC}} = 15 \text{ Hz}$, Ir–CO, 1C), 71.6 (vt, $J_{\text{PC}} = 7.2 \text{ Hz}$, HC–Ir, 1C), 50.3 (vt, $J_{\text{PC}} = 19 \text{ Hz}$, PCH_2 , 2C), 36.9 (vt, $J_{\text{PC}} = 25 \text{ Hz}$, Cy, 2C), 36.4 (vt, $J_{\text{PC}} = 21 \text{ Hz}$, $\text{C}(\text{CH}_3)_3$, 2C), 35.8 (vt, $J_{\text{PC}} = 22 \text{ Hz}$, $\text{C}(\text{CH}_3)_3$, 2C), 34.9 (vt, $J_{\text{PC}} = 19 \text{ Hz}$, Cy, 2C), 29.8 (vt, $J_{\text{PC}} = 5.6 \text{ Hz}$, $\text{C}(\text{CH}_3)_3$, 6C), 29.7 (vt, $J_{\text{PC}} = 5.2 \text{ Hz}$, $\text{C}(\text{CH}_3)_3$, 6C), 27.7 (vt, $J_{\text{PC}} = 2.8 \text{ Hz}$, $\text{CH}_2\text{CH}_2\text{CH}_2$, 1C). $^{31}\text{P}\{^1\text{H}\}$ -NMR (C_6D_6): δ 81.8 (s). IR (NaCl/nujol) $\nu_{\text{CO}} = 1917 \text{ cm}^{-1}$, (hexane) $\nu_{\text{CO}} = 1920 \text{ cm}^{-1}$, (CH_2Cl_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%). $^1\text{H-NMR}$ (C_6D_6): δ 1.89–1.84 (m, PCH_2CH , 2H), 1.82–1.77 (br m, Cy, 2H + 1H), 1.61 (t, $J = 10.5 \text{ Hz}$, HC–Ir, 1H), 1.51–1.45 (br m, PCH_2CH , 2H + Cy, 1H), 1.41 (vt, $J_{\text{PH}} = 13.0 \text{ Hz}$, ^1Bu , 18H), 1.37 (vt, $J_{\text{PH}} = 13.0 \text{ Hz}$, ^1Bu , 18H), 1.12 (tt, $J = 3.5 \text{ Hz}$, $J = 14.0 \text{ Hz}$, Cy, 2H), 0.90 (dq, $J = 4.0 \text{ Hz}$, $J = 13.0 \text{ Hz}$, Cy, 2H), –8.59 (dt, $J_{\text{HH}} = 1.5 \text{ Hz}$, $J_{\text{PH}} = 17.0 \text{ Hz}$, Ir–H, 1H). $^{13}\text{C}\{^1\text{H}\}$ -NMR (C_6D_6): δ 226.7 (s, Ir–CO, 1C), 51.5 (vt, $J_{\text{PC}} = 11 \text{ Hz}$, CH–Ir, 1C), 37.8 (vt, $J_{\text{PC}} = 27 \text{ Hz}$, PCH_2 , 2C), 36.8 (vt, $J_{\text{PC}} = 21 \text{ Hz}$, Cy, 2C), 36.2 (vt, $J_{\text{PC}} = 23 \text{ Hz}$, $\text{C}(\text{CH}_3)_3$, 2C), 33.9 (vt, $J_{\text{PC}} = 17 \text{ Hz}$, $\text{C}(\text{CH}_3)_3$, 2C), 32.7 (s, Cy, 2C), 30.8, (vt, $J_{\text{PC}} = 3.2 \text{ Hz}$, $\text{C}(\text{CH}_3)_3$, 6C), 30.6 (vt, $J_{\text{PC}} = 3.0 \text{ Hz}$, $\text{C}(\text{CH}_3)_3$, 6C), 27.8, (s, $\text{CH}_2\text{CH}_2\text{CH}_2$, 1C). $^{31}\text{P}\{^1\text{H}\}$ -NMR (C_6D_6): δ 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 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%). $^1\text{H-NMR}$ (C_6D_6): δ 2.61–2.52 (m, PCH_2CH , 2H), 2.09–2.01 (m, PCH_2CH , 2H + Cy, 2H), 1.86–1.81 (m, Cy, 1H), 1.55 (vt, $J_{\text{PH}} = 13.5 \text{ Hz}$, ^1Bu , 18H), 1.53–1.51 (m, Cy, 1H), 1.42 (t, $J = 11.0 \text{ Hz}$, HC–Ir, 1H), 1.15 (tt, $J = 4.0 \text{ Hz}$, $J = 14.0 \text{ Hz}$, Cy, 2H), 1.06 (vt, $J_{\text{PH}} = 12.5 \text{ Hz}$, ^1Bu , 18H), 0.92 (dq, $J = 3.5 \text{ Hz}$, $J = 13.0 \text{ Hz}$, Cy, 2H), –18.7 (t, $J_{\text{PH}} = 13.0 \text{ Hz}$, Ir–H, 1H). $^{31}\text{P}\{^1\text{H}\}$ -NMR (C_6D_6): δ 56.4 (d, $J_{\text{PH}} = 13.0 \text{ Hz}$). 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 N_2 atmosphere at elevated temperatures, affording the Ir(i) terminal nitrogen complex **3**.²⁶ We here report an alternative synthesis of **3** from **2** under slightly milder conditions and in comparable yields, using KO^1Bu (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.³² 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 π -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 $^{13}\text{C-NMR}$



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°), the P–Ir–P angle is much more distorted (164.46°) 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,⁷ and, surprisingly, there is no substantial change of the Ir–CO or C–O distances (PC_{Ar}P mean distances: Ir–CO = 1.863 Å; C–O = 1.147 Å, **4**: Ir–CO = 1.860(7) Å; C–O = 1.143(7)); a similar observation was made regarding the Ir(i)–N₂ complexes where the aliphatic ligand was also observed to induce a small decrease in the N–N bond distance.²⁶ However, both the N₂- and current CO-ligands are subject to substantial libration,³³ an explanation that is unambiguous in the N₂-case since the complex actually showed a shorter distance than in free N₂. Therefore, a better measure of the electron density is the ν_{CO} stretching frequency. In hydrocarbons this is 1920 cm^{−1} for **4** compared with 1928 cm^{−1} for the corresponding aromatic compound.³⁴ In dichloromethane the corresponding values are 1896 and 1913 cm^{−1}, respectively,³⁵ 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 ν_{NN} stretching frequencies for Ir(i)–N₂ complexes and CV-measurements for Ni(II) complexes.^{12c,26}

Subjecting the deep red solution of complex **2** to 1 atm CO resulted in a colourless solution of the 18 electron complex **5a** within seconds. Treating a C₆D₆ solution of **5a** with an excess of KO'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

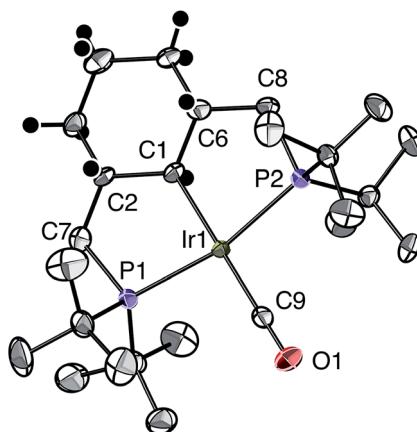


Fig. 1 Molecular structure of **4** at the 30% probability level. For clarity, hydrogen atoms are only depicted in the cyclohexyl ring. Selected bond lengths (Å) and bond angles (°) with estimated standard deviations: Ir1–C1 = 2.143(6), Ir1–C9 = 1.860(7), C9–O1 = 1.143(7), Ir1–P1 = 2.3073(16), Ir1–P2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

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

	4	5a	5b
Formula	C ₂₅ H ₄₉ IrOP ₂	C ₂₅ H ₅₀ ClIrOP ₂	C ₂₅ H ₅₀ ClIrOP ₂
<i>F</i> _w	619.78	656.24	656.24
Space group	<i>Pbca</i>	<i>P2₁/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)
β /deg	90	93.996(2)	90
<i>V</i> /Å ³	5571.9	2962.80	5482.51
<i>Z</i>	8	4	8
<i>D</i> _{calcd} /g cm ^{−3}	1.478	1.469	1.590
μ /mm ^{−1}	4.920	4.718	5.100
θ /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>)) ^a	0.0520	0.0332	0.0389
<i>wR</i> ₂ (<i>F</i> ²) (all) ^b	0.1167	0.1030	0.1221
<i>S</i> ^c	1.224	1.425	1.124
<i>R</i> _{int}	0.126	0.0594	0.0317
CCDC	1029323	1029333	1029332

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

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

Refluxing ligand **1** and IrCl₃·H₂O 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 Azerra and Gelman in the formation of a dibenzobarrelene based PC(sp³)P iridium complex.^{8a,bc}

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

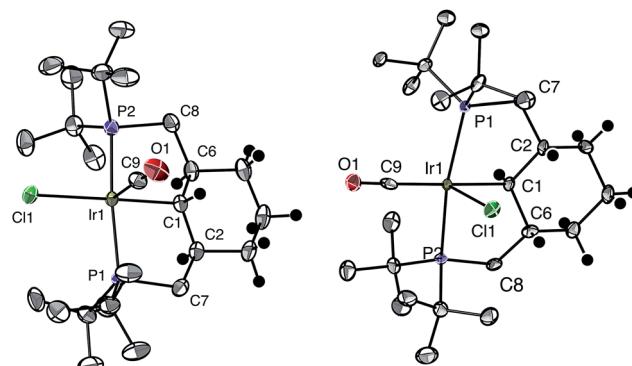
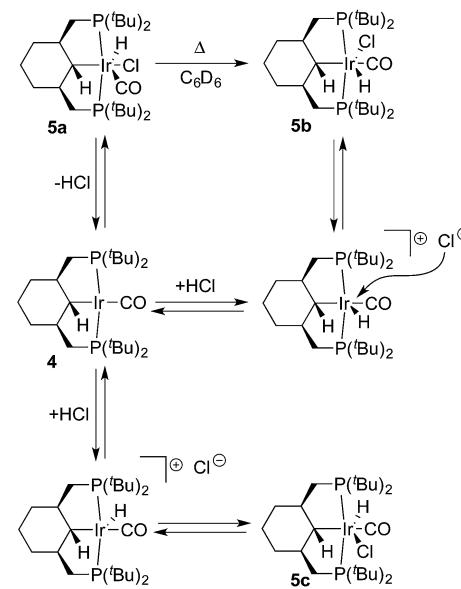


Fig. 2 Molecular structure of **5a** and **5b** at the 30% probability level. For clarity, hydrogen atoms are only depicted in the cyclohexyl ring. Selected bond lengths (Å) and bond angles (°) with estimated standard deviations: **5a**: Ir1–C1 = 2.137(4), Ir1–C9 = 1.943(4), C9–O1 = 1.101(5), Ir1–Cl1 = 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 ν_{CO} stretching frequencies for **5a** and **5b** are found at 1977 cm^{-1} and 1989 cm^{-1} respectively, which can be compared to the value reported for the aromatic analogue of **5a** ($\nu_{CO} = 1985\text{ cm}^{-1}$, KBr).¹⁵ 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 π -back donation is weaker *trans* to a σ -bonded carbon than *trans* to the hydride ligand. As expected the ν_{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 α -hydrogen, as illustrated in Schemes 1 and 2. In case of **5a**, the hydride and α -hydrogen are located *anti* to each other, while in **5b** they are *syn*. All previously reported $PC(sp^3)P$ complexes with iridium^{26,36} 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 σ -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,^{8c} 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 α -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 $90\text{ }^\circ C$, signals of **5b** appeared, together with very small amounts of **4** and another compound, which is characterized by a doublet at



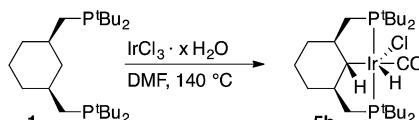
Scheme 3

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 σ -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 α -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.



Scheme 2

Acknowledgements

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