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PC(sp^3)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 $IrCl_3 \cdot H_2O$ 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(N_2){*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.

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[1] 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(sp^3)-compared to the more common C(sp^2)-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(sp^2)P-[15] and PC(sp^3)P-supported[16] iridium(III) complexes, and such iridium carbonyl complexes have later been found to be involved in catalytic transformations such as transfer hydrogenations of ketones[8] 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-naphtaldehyde[23] and the partial deoxygenation of diols[24] and glycerol,[25] but there are no PC(sp^3)P-supported iridium(I) carbonyl complexes reported to this date.

Here we report on the synthesis and interconversion of PC(sp^3)P pincer carbonyl complexes with iridium(I) and iridium(III). The electronic properties of the PC(sp^3)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. ^{1}H-, ^{13}C and ^{31}P-NMR experiments were recorded on a Varian Unity INOVA 500 spectrometer, operating at 499.76 (^{1}H), 125.68 (^{13}C) and 202.31 (^{31}P) MHz. For ^{1}H- and ^{13}C-NMR spectra, the residual solvent peak was used as an internal reference. ^{31}P-NMR spectra were referenced externally using 85% H_3PO_4 at $\delta = 0$ 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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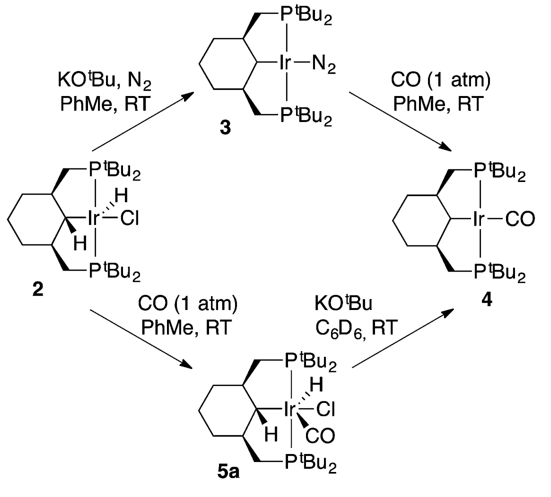
† Electronic supplementary information (ESI) available: NMR spectra for **4**. Computational details. Crystal data for **4**, **5a** and **5b**. CCDC 1029323, 1029332 and 1029333. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4ra15562a



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 ω-scans and MoKα ($\lambda = 0.71073$ Å) 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}H-NMR (C$_6$D$_6$): 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, $J = 4.0$ Hz, $J = 13.5$ Hz, PCH_2CH, 2H), 1.48–1.42 (m, Cy, 1H), 1.32 (vt, $J_{\text{PH}} = 13.0$ Hz, ^{t}Bu, 18H), 1.26 (vt, $J_{\text{PH}} = 13.0$ Hz, ^{t}Bu, 18H), 1.19 (t, $J = 11.0$, HC–Ir, 1H), 0.95 (dq, $J = 3.5$ Hz, $J = 12.5$ Hz, Cy, 2H). ^{13}C{^{1}H}-NMR (C$_6$D$_6$): δ 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_{PC} = 19 Hz, PCH$_2$, 2C), 36.9 (vt, $J_{\text{PC}} = 25$ Hz, Cy, 2C), 36.4 (vt, $J_{\text{PC}} =$ 21 Hz, C(CH$_3$)$_3$, 2C), 35.8 (vt, $J_{\text{PC}} = 22$ Hz, C(CH$_3$)$_3$, 2C), 34.9 (vt, $J_{\text{PC}} = 19$ Hz, Cy, 2C), 29.8 (vt, $J_{\text{PC}} = 5.6$ Hz, C(CH$_3$)$_3$, 6C), 29.7 (vt, $J_{\text{PC}} = 5.2$ Hz, C(CH$_3$)$_3$, 6C), 27.7 (vt, $J_{\text{PC}} = 2.8$ Hz, CH$_2$$CH_2CH_2$, 1C). ^{31}P{^{1}H}-NMR (C$_6$D$_6$): δ 81.8 (s). IR (NaCl/nujol) $\nu_{\text{CO}} = 1917$ cm^{-1}, (hexane) $\nu_{\text{CO}} = 1920$ cm^{-1}, (CH$_2$Cl$_2$) $\nu_{\text{CO}} = 1896$ 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}H-NMR (C$_6$D$_6$): δ 1.89–1.84 (m, PCH_2CH, 2H), 1.82–1.77 (br m, Cy, 2H + 1H), 1.61 (t, $J = 10.5$ Hz, HC–Ir, 1H), 1.51–1.45 (br m, PCH_2CH, 2H + Cy, 1H), 1.41 (vt, $J_{\text{PH}} = 13.0$ Hz, ^{t}Bu, 18H), 1.37 (vt, $J_{\text{PH}} = 13.0$ Hz, ^{t}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). ^{13}C{^{1}H}-NMR (C$_6$D$_6$): δ 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, PCH$_2$, 2C), 36.8 (vt, $J_{\text{PC}} = 21$ Hz, Cy, 2C), 36.2 (vt, $J_{\text{PC}} = 23$ Hz, C(CH$_3$)$_3$, 2C), 33.9 (vt, $J_{\text{PC}} = 17$ Hz, C(CH$_3$)$_3$, 2C), 32.7 (s, Cy, 2C), 30.8, (vt, $J_{\text{PC}} = 3.2$ Hz, C(CH$_3$)$_3$, 6C), 30.6 (vt, $J_{\text{PC}} = 3.0$ Hz, C(CH$_3$)$_3$, 6C), 27.8, (s, CH$_2$$CH_2CH_2$, 1C). ^{31}P{^{1}H}-NMR (C$_6$D$_6$): δ 50.2 (s). IR (ATR) $\nu_{\text{CO}} = 1977$ cm^{-1}. Anal. calcd for C$_{25}$H$_{51}$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 IrCl$_3$·H$_2$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}H-NMR (C$_6$D$_6$): 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, $J_{\text{PH}} = 13.5$ Hz, ^{t}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}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). ^{31}P{^{1}H}-NMR (C$_6$D$_6$): δ 56.4 (d, $J_{\text{PH}} = 13.0$ Hz). IR (ATR) $\nu_{\text{CO}} = 1989$ cm^{-1}. Anal. calcd for C$_{25}$H$_{51}$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 [Ir(COD)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^{t}Bu (Scheme 1) as was previously reported by Milstein and Frech for the preparation of a naphthyl based PCP Rh(I) η^1-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}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)–N_2 complexes where the aliphatic ligand was also observed to induce a small decrease in the N–N bond distance.[26] However, both the N_2- and current CO-ligands are subject to substantial libration,[33] an explanation that is unambiguous in the N_2-case since the complex actually showed a shorter distance than in free N_2. 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)–N_2 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 C_6D_6 solution of **5a** with an excess of KO^{t}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 slightly less clean than the synthesis starting from compound **3** (Scheme 1).

Refluxing ligand **1** and $IrCl_3 \cdot H_2O$ 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^3)P iridium complex.[8a,8c]

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

Table 1 Crystallographic data for compounds 4–5

	4	5a	5b
Formula	$C_{25}H_{49}IrOP_2$	$C_{25}H_{50}ClIrOP_2$	$C_{25}H_{50}ClIrOP_2$
F_w	619.78	656.24	656.24
Space group	*Pbca*	*P*2$_1$/*n*	*Pbca*
a/Å	12.4581(9)	12.5453(2)	12.3770(2)
b/Å	15.3030(9)	15.2101(3)	15.3452(2)
c/Å	29.2263(16)	15.5649(3)	28.8663(4)
β/deg	90	93.996(2)	90
V/Å^3	5571.9	2962.80	5482.51
Z	8	4	8
D_{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
$R(F)$ ($I > 2\sigma(I)$)^a	0.0520	0.0332	0.0389
wR_2(F^2) (all)^b	0.1167	0.1030	0.1221
S^c	1.224	1.425	1.124
R_{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} $S = [\sum w(|F_o| - |F_c|)^2/\sum(|F_o|)^2]^{1/2}$.

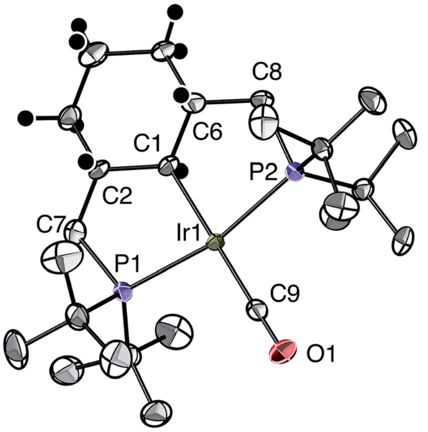


Fig. 1 Molecular structure of **4** at the 30% probability level. For clarity, hydrogen atoms are only depicted in the cyclohexyl ring. Selected bond lengths (Å) and bond angles (°) with estimated standard deviations: Ir1–C1 = 2.143(6), Ir1–C9 = 1.860(7), C9–O1 = 1.143(7), Ir1–P1 = 2.3073(16), Ir1–P2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

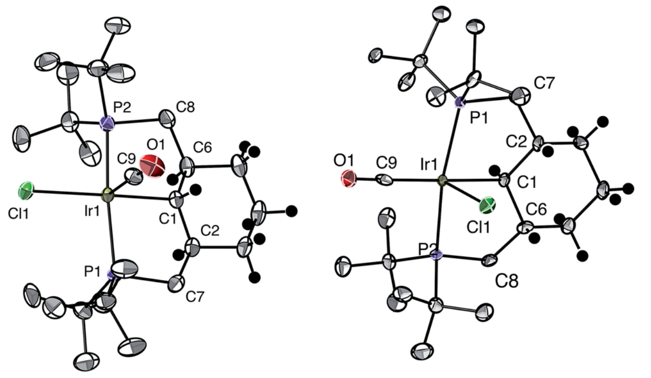
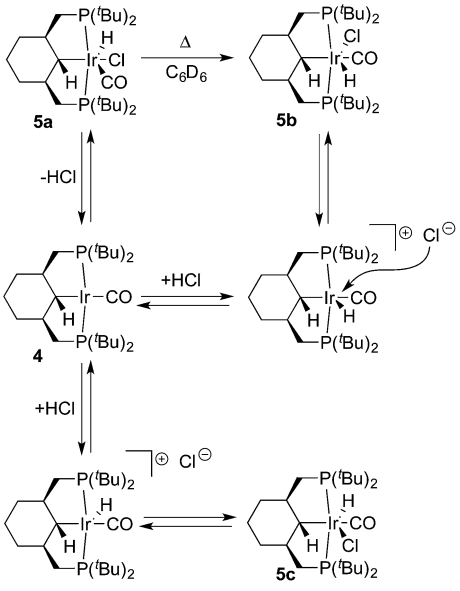


Fig. 2 Molecular structure of **5a** and **5b** at the 30% probability level. For clarity, hydrogen atoms are only depicted in the cyclohexyl ring. Selected bond lengths (Å) and bond angles (°) with estimated standard deviations: **5a**: Ir1–C1 = 2.137(4), Ir1–C9 = 1.943(4), C9–O1 = 1.101(5), Ir1–Cl1 = 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).

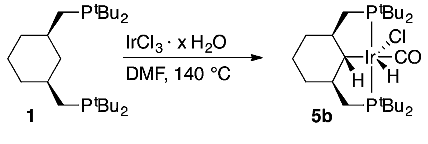
shifts ($\delta = 50.2$ ppm and 56.4 ppm respectively in C_6D_6) and the ^{1}H-NMR hydride shifts ($\delta = -8.59$ ppm and -18.7 ppm respectively in C_6D_6), and both compounds are seemingly resistant towards isomerisation upon standing in solution at room temperature for several days. A significantly 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** ($\nu_{CO} = 1985$ 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 °C, signals of **5b** appeared, together with very small amounts of **4** and another compound, which is characterized by a doublet at 57.6 ppm in the ^{31}P{^{1}H} NMR spectrum and a triplet at -18.78 ($J_{PH} = 11.8$ Hz) in the ^{1}H 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**.



Scheme 3



Scheme 2

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.

Acknowledgements

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