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Synthesis and characterisation of PC$_{sp3}$P phosphine and phosphinite iridium complexes. Cyclometallation and dehydrogenation of a cyclohexyl ring†

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A cyclohexyl based pincer phosphine ligand undergoes cyclometalation with an iridium cyclooctadiene precursor to give a highly thermally stable iridium(III) complex where a C(sp³)–H bond has been oxidatively added. This iridium(III) hydride complex is reduced with potassium to give a terminal iridium(I) dinitrogen complex with no tendency to dimerization. The corresponding cyclohexyl phosphinite ligand undergoes reversible dehydrogenation to give the aromatic cyclometalated iridium(III) hydride complex together with 3 equivalents of dihydrogen.

Introduction

Pincer PCP complexes of iridium have received considerable attention as promising catalysts for dehydrogenation of alkanes,[1] alcohols,[2] secondary amines[3] and ammonia borane.[4] In addition, activation of small molecules, *e.g.* dinitrogen,[5] water,[6] carbon dioxide and carbon monoxide,[7] is an area that has been investigated with these types of complexes. All of the examples above have been executed with PC$_{sp2}$P pincer complexes, and examples of iridium complexes with PC$_{sp3}$P pincer ligands are more rare in the literature. Early examples by Shaw *et al.* concern ligands of [^{t}Bu$_2$(CH$_2$)$_2$CHR(CH$_2$)$_2$PtBu$_2$] type,[8] and also a tripodal phosphine ligand based on a cyclohexane ring has successfully been cyclometalated.[9] More recent examples include PCP ligands with a cycloheptatriene backbone and a chelating diphosphinite ligand containing a cyclopropyl group which have produced C$_{sp3}$–H activation.[10] Benzylic C–H activation with PCP ligands on iridium has also been reported.[11] Applications of PC$_{sp3}$P ligands in nickel(II) chemistry have been reported recently.[12]

In the course of the investigations of PC$_{sp2}$P iridium complexes for dehydrogenation of cycloalkanes it was found that dinitrogen has an inhibitory effect and this was attributed to a bridging dinitrogen complex.[5] Later, Goldman showed that there is dimer–monomer equilibrium in these systems and that the monomer dominates in a solution under dinitrogen.[13] Dinitrogen complexes of transition metals are interesting in their own right and they have been shown to be involved in ammonia production at low temperature.[14]

We have developed cyclohexyl based PC$_{sp3}$P ligands and we and others have shown that *cis*-1,3-bis-[(di-*tert*-butylphosphino)methyl]cyclohexane (**1**), Chart 1, undergoes cyclometalation when treated with palladium,[15] platinum[16] and rhodium[17] precursors. In this context we have also developed applications in Suzuki and Heck coupling reactions.[15,18] We were also interested in exploring these ligands in iridium chemistry and here we report the preparation and structural characterization of
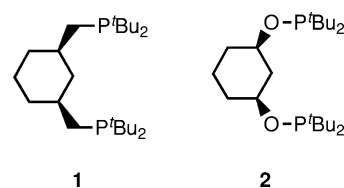

Chart 1

an aliphatic PCP iridium complex and the end-on monomeric dinitrogen complex formed upon reduction in a nitrogen atmosphere. The corresponding cyclohexyl phosphinite ligand, *cis*-1,3-Bis-(di-*tert*-butylphosphinito}cyclohexane (**2**), Chart 1, fails to undergo cyclometalation with palladium and platinum precursors,[15c,16a] and here we also report on an unusual aromatisation of a coordinated cyclohexyl ring. These results again underline that PC$_{sp2}$P and PC$_{sp3}$P ligands can display different chemistries.[19]

Experimental

General procedures and materials

All experiments were carried out under an atmosphere of nitrogen in a glove box or using high vacuum-line techniques. All non-deuterated solvents were vacuum-transferred directly to the reaction vessel from sodium/benzophenone ketyl. Ligands *cis*-1,3-Bis-(di-*tert*-butylphosphino)methyl}cyclohexane (**1**) and *cis*-1,3-Bis-(di-*tert*-butylphosphinito}cyclohexane (**2**) were prepared according to the literature.[15a,16] *cis*-1,3-cyclohexanediol was obtained from the commercially available *cis/trans* mixture using literature procedures.[20] All commercially available reagents were purchased from Sigma Aldrich and used as received. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Varian Unity INOVA 500 spectrometer working at 499.77 MHz (^{1}H). Chemical shifts are given in ppm downfield from TMS using residual solvent peaks (^{1}H-, ^{13}C NMR) or H$_3$PO$_4$ as reference. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad, v = virtual. Elemental analyses were performed by H. Kolbe, Mülheim an der Ruhr, Germany. Fast Atom Bombardment (FAB) mass spectroscopic data were obtained on a JEOL SX-102 spectrometer using 3-nitrobenzyl

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alcohol as matrix. The TGA was recorded on a TGA Q500 by heating the sample up to 500 °C with a slope of 10 °C/min.

Preparation of *trans*-[IrHCl{*cis*-1,3-Bis-(di-*tert*-butylphosphino)methyl}cyclohexane] (3). Phosphine **1** (0.502 g, 1.25 mmol) and [(COD)IrCl]$_2$ (0.419 g, 0.624 mmol) were dissolved in THF (15 cm^3) in a thick-walled Schlenk flask. The flask was sealed, placed in an oil bath (200 °C) and stirred for 2 h resulting in a dark brown solution. The THF was removed under vacuum and the dark brown semi-solid residue was treated with pentane (15 cm^3). The flask was sealed, heated to 120 °C and stirred for 20 min resulting in a dark brown solution. By storing the solution at −18 °C dark red prisms were formed overnight. Yield 0.486 g (62%). Anal. Calcd for C$_{24}$H$_{50}$ClIrP$_2$: C, 45.88; H, 8.02. Found: C, 46.93; H, 8.12. ^{1}H NMR (THF-d$_8$): δ 2.17–0.97 (m, Cy), 1.99 (td, J = 10.3, 2.84 Hz, 1H, *HC*–Ir), 1.35 (vt, J = 12.7 Hz, tBu), 1.32 (vt, J = 12.7 Hz, tBu), −43.0 (td, J = 11.9, 3.07 Hz). ^{13}C{^{1}H} NMR (THF-d$_8$): δ 54.5 (vt, J_{PC} = 15.1 Hz, CH), 37.2 (vt, J_{PC} = 20.6 Hz, *C*(CH$_3$)$_3$), 36.4 (d, $^2J_{CH}$ = 5.6 Hz, H*C*–Ir), 35.5 (vt, J_{PC} = 20.9 Hz, *C*(CH$_3$)$_3$), 35.0 (vt, J_{PC} = 17.7 Hz, *C*H$_2$CH$_2$CH), 34.3 (vt, J_{PC} = 25.1 Hz, P–*C*H$_2$), 29.8 (vt, J_{PC} = 5.1 Hz, C(*C*H$_3$)$_3$), 29.6 (vt, J_{PC} = 5,2 Hz, C(*C*H$_3$)$_3$), 28.0 (t, $^4J_{PC}$ = 1.6 Hz, CH$_2$*C*H$_2$CH$_2$). ^{31}P{^{1}H} NMR (THF-d$_8$): δ 64.6 (d, $^2J_{P-H}$ = 8.6 Hz). MS (FAB+) Found (Calcd): 592.2941 (592.2939) [M − HCl$^+$], 628.2711 (628.2706) [M$^+$].

Preparation of *trans*-[IrN$_2${*cis*-1,3-Bis-(di-*tert*-butylphosphino)}cyclohexane] (4). To a stirred toluene solution of **2** (0.10 g, 0.11 mmol) potassium (0.01 g, 0.25 mmol) was added and the mixture was heated to 120 °C in a nitrogen atmosphere overnight. The toluene was evaporated in vacuum and the orange solid was dissolved in hexane and filtered through a Celite® plug. Concentration of the hexane solution and cooling at −28 °C overnight afforded **4** as orange crystals. Yield: 0.061 g (62%). Anal. Calc for C$_{24}$H$_{49}$IrN$_2$P$_2$: C, 46.51; H, 7.97. Found: C, 46.37; H, 7.88; ^{1}H NMR (C$_6$D$_6$): δ 0.95 (t, J = 7.0 Hz, 2H, Cy), 0.98 (m, 2H, Cyl), 1.10 (t, J = 7.0 Hz, 1H, Cy) 1.20–1.50 (m, 36H, *t*-Bu), 1.6–2.10 (m, 6H, Cy and P–CH$_2$), δ 2.35 (m, 1H, Cy), δ 3.31 (bs, 1H, Cy). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 70.7 (s), 50.5 (vt, $^2J_{P-C}$ = 10.0 Hz, CH$_2$P), 35.2 (vt, $^2J_{P-C}$ = 12.5 Hz) and 34.8 (vt, $^2J_{P-C}$ = 10.0 Hz), 28.6, 27.6, 27.1 and 25.6 (s, CH$_3$, *t*-Bu) and 22.5 (s, CH$_2$, Cy). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 70.8 (s). IR (toluene-d$_8$): ν_{NN} = 2065 cm^{-1}.

Reaction of ligand 2 with [Ir(COD)Cl]$_2$. To a colourless solution of **2** (0.25 g, 0.62 mmol) in toluene (7 mL), [Ir(COD)Cl]$_2$ (0.21 g, 0.31 mmol) was added and the solution was heated to 180 °C overnight in a thick-walled Schlenk flask. The toluene solution was concentrated to 1 mL and refrigerated at −28 °C overnight affording red-brown X-ray quality crystals consistent with *trans*-[IrHCl{*cis*-1,3-Bis-(di-*tert*-butylphosphino)methyl}benzene] (5) as seen by ^{31}P and ^{1}H NMR spectroscopy. Yield: 0.31 g (91.2%).

Crystallography. Intensity data were collected at 100 (**3**) or 293 (**4** and **5**) K with an Oxford Diffraction Xcalibur 3 system using ω-scans and Mo-Kα (λ = 0.71073 Å).[21] Crystals of **4** are weak scatterers giving only 42% observed reflections out to Θ = 25°. CCD data were extracted and integrated using Crysalis RED.[22] The structures were solved using direct methods and refined by full-matrix least-squares calculations on F^2 using SHELXTL

**Table 1** Crystal data for **3**, **4** and **5**

	3	**4**	**5**
formula	C$_{24}$H$_{49}$ClIrP$_2$	C$_{24}$H$_{49}$IrN$_2$P$_2$	C$_{22}$H$_{39}$ClIrO$_2$P$_2$
fw	628.27	619.79	625.12
space group	*Pbca*	*Pbca*	*P*-1
a/Å	12.3722(2),	12.4022(3)	8.2429(5)
b/Å	15.0811(2)	15.3075(3)	12.2217(8)
c/Å	28.6246(4)	29.3338(7)	13.4226(8)
α/deg			100.461(5)
β/deg			95.623(5)
γ/deg			104.395(6)
V/Å^3	5340.96(13)	5568.9(2)	1273.38(14)
Z	8	8	2
D_{calcd}/g cm^{-3}	1.560	1.478	1.630
μ/mm^{-1}	5.228	4.922	5.488
θ range/deg	2.18–33.25	2.15–33.10	2.58–33.20
no reflns collected	50780	33522	13293
no of unique reflns	9705	4917	8453
$R(F)$ ($I > 2\sigma(I)$)^a	0.0414	0.0287	0.0358
$wR2(F^2)$ (all data)^b	0.1314	0.0456	0.0681
S^c	1.071	0.844	0.768
R_{int}	0.0575	0.0732	0.0360

^{a} $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. ^{b} $wR2 = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$. ^{c} $S = [\sum w(|F_o| - |F_c|)^2/(m-n)]^{1/2}$.

5.1.[23] Non-H atoms were refined with anisotropic displacement parameters. Hydrogen atoms were constrained to parent sites, using a riding model. Crystal data and details about data collection are given in Table 1.

Results and discussions

Heating a solution of **1** and 0.5 equivalents of bis(1,5-cyclooctadiene)diiridium(I) dichloride dimer ([(COD)IrCl]$_2$) in THF at 200 °C for 2 h, resulted in complex **3** (Scheme 1). No dihydrogen was needed to assist in the removal of COD. Similarly to the rhodium case, the reaction gives the iridium(III) chloro hydride product.[17]
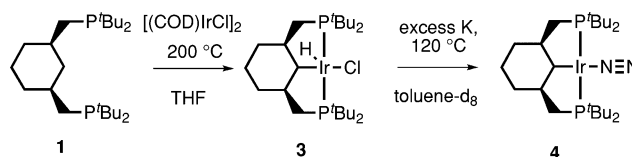
Scheme 1

The reaction could be monitored by means of ^{31}P{^{1}H} NMR spectroscopy. After stirring the solution of **1** and [(COD)IrCl]$_2$ at room temperature overnight the spectrum showed four peaks. One peak could be assigned to unreacted starting material and three peaks to two possible intermediates (Chart 2). One possible intermediate, **A**, where **1** presumably is a monodentate ligand, gives rise to two signals (δ = 21.1 and 29.4 ppm) with a 1:1 ratio. The other peak (δ = 30.0 ppm) we tentatively assigned to compound **B** in Chart 2. Here the phosphorus atoms are coordinated in a *cis* fashion to give an eight-membered chelate ring, making them magnetically equivalent. The reason why ring-closing in **A** is slow is probably that it requires a conformational change of the cyclohexyl ring from diequatorial (in the free ligand and **A**) to diaxial (in **B**).

By continuously heating the NMR tube at *ca.* 200 °C a new peak grew at δ = 64.6 ppm and it soon became the dominant
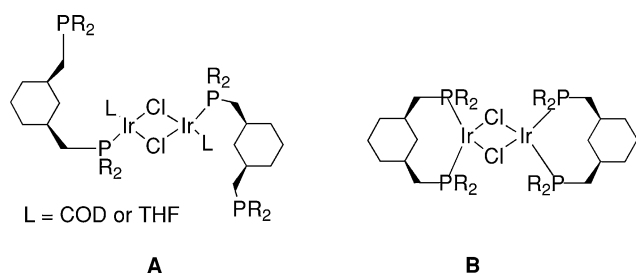
Chart 2

peak. All four phosphorus compounds exist simultaneously but there is no sign of any reversibility. An alternative C–H activation mechanism where ligand **1** is pseudo *ortho*-metallated was ruled out, since none of the intermediate signals are doublets; a doublet should arise as soon as C–H activation occurs due to P–H$_{hydride}$ coupling, as seen for the product (*vide infra*).

Complex **3** was isolated and characterised by multinuclear NMR spectroscopy and FAB-MS. As mentioned the ^{31}P{^{1}H} NMR spectra exhibits a doublet at 64.6 ppm, due to coupling with the hydride. In addition, the hydride is observed as a triplet of doublets ($\delta = -43.0$ ppm) in ^{1}H NMR spectroscopy with $^2J_{HP} = 11.9$ Hz and $^3J_{HH} = 3.07$ Hz. The *tert*-butyl methyl-protons are displayed as virtual triplets at 1.35 and 1.32 ppm respectively, showing that the two sides of the coordination plane are inequivalent. This is also manifested in the ^{13}C{^{1}H} NMR spectrum where the C–H activated carbon also is displayed as a doublet at 36.4 ppm with a coupling constant of 5.6 Hz to the hydride. The structure of complex **3** was unambiguously confirmed using X-ray crystallography. Burgundy-red prisms were grown from a pentane solution at −18 °C. A perspective view of the molecular structure is shown in Fig. 1, including selected bond distances and angles.

chelate ligand causes the two P atoms to bend away from the chloro ligand. The cyclohexyl ring has a chair conformation with small deviations from the normal cyclohexane bond angles.[24] It is aligned with the coordination plane and the three coordinating positions are equatorially oriented. The position of the hydride could not be refined in a reliable way, but there is some electron density in a transoid configuration (on the opposite side of the remaining C1–H1 bond) and this conclusion is also supported by the Cl1–Ir1–C1 angle; it bends towards the side of the C1–H1 bond. A transoid configuration is expected as a result of the oxidative addition of Ir1 to C1–H$_{eq}$.

The anthracene based iridium PCP complex reported by Kaska[25] is thermally stable in alkane solution up to 250 °C. This prompted us to study the thermal stability of the analogous complex **3** using TGA. It displays a weight loss corresponding to HCl at 220 °C in both air and nitrogen. At 250 °C in air and 300 °C in nitrogen, substantial thermal decomposition starts to occur rapidly and at 500 °C there is a total weight loss of 63% in air and of 89% in nitrogen. This again underlines the high thermal stability induced by the dichelating PCP ligand framework.

Heating complex **3** with an excess of potassium in toluene at 120 °C under an atmosphere of nitrogen turned the solution dark. The temperature is needed for the dissolution of potassium into the mixture. A ^{1}H NMR spectrum of the resultant mixture shows there is no signal in the hydride region and the ^{31}P NMR spectrum shows a single, new peak at 70.76 ppm. The product was soluble in hexane. Cooling the hexane solution at −28 °C or alternatively slowly evaporating the hexane at room temperature afforded complex **4** as orange crystals. The IR spectrum of the crystals in toluene-d$_8$ shows a strong band at 2065 cm^{-1} attributed to an N–N stretching frequency of a terminally bound dinitrogen. The crystals were analytically pure and a single crystal X-ray structure confirmed that **4** is a monomeric end-on dinitrogen complex in which Ir(I) has a distorted square planar geometry. A perspective view of the molecular structure is shown in Fig. 2, including selected bond distances and angles. There are no significant intermolecular interactions with atom N2.
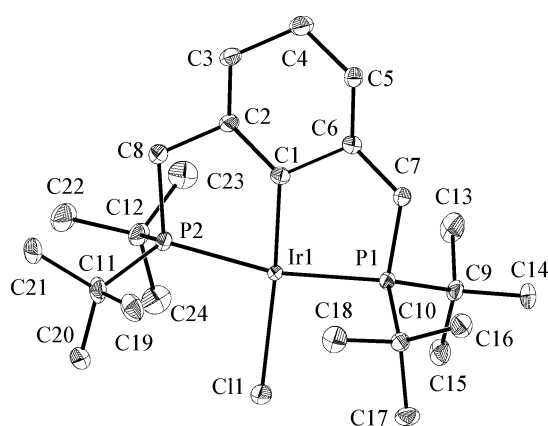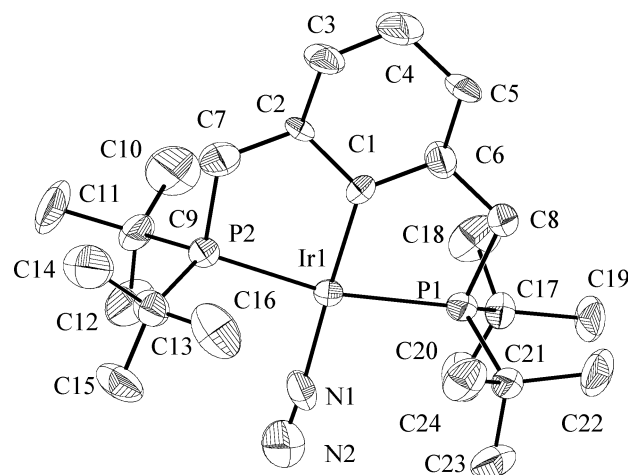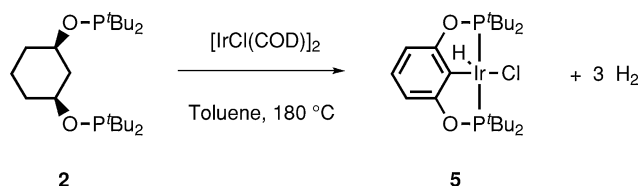

Fig. 1 DIAMOND drawing of compound **3** at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: Ir1–C1 2.094(5), Ir1–Cl1 2.4354(14), Ir1–P1 2.3059(12), Ir1–P2 2.3116(13), P1–Ir1–P2 166.74(5).

As seen from Fig. 1, **3** exhibits a distorted square-pyramidal (assuming the hydride is in an axial position) geometry. The axial position of the hydride is also supported by its high field chemical shift. Bond distances and angles are very close to the ones observed in the related aliphatic pincer complex [Ir{HCl}(^{t}Bu$_2$P(CH$_2$)$_2$CH(CH$_2$)$_2$P^{t}Bu$_2$)].[8] As usual, the bis-

Fig. 2 DIAMOND drawing of compound **4** at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: Ir1–C1 2.092(5), Ir1–N1 1.874(6), Ir1–P1 2.2960(17), Ir1–P2 2.2961(17), N1–N2 1.064(7), P1–Ir1–P2 165.67(6).

There are very few terminal Ir(I) complexes that have been crystallographically characterized, one of them being the aromatic analogue of **4**.[13,26] Comparing the Ir–N distances the shortest is found in **4** (Ir–N: 1.874(6) Å), indicating a lower *trans* influence of the cyclohexyl group as compared to both phenyl (Ir–N: 1.9471(21) Å) and a β-di-iminate ligand (Ir–N: 1.903(3) Å). The *trans* influence of dinitrogen is similar to chloride as indicated from the similar Ir–Cl distances observed in the structures of **3** and **4**, respectively. Based on the ν(N–N) the N–N bond in **4** is the weakest reported for a terminal iridium complex, indicating that the metal center in **4** is more π-basic than its aromatic analogue. Still, the N–N distance in the solid state is 1.064(7) Å, shorter than in free dinitrogen. This is most probably caused by libration of the N$_2$-ligand, a process that is known to give apparent bond distances that are too short.[27] Due to instrument problems we were unable to re-collect the data at low temperature. The aromatic analogue is involved in a monomer–dimer equilibrium, but in the present case there is no evidence for such behavior;[5,13] in solution **4** exclusively exists as a monomer. This could be due to steric reasons but an overlay plot of **4** and the corresponding aromatic monomer shows that there are small steric differences between the two. Probably the stronger interaction between N$_2$ and the metal centre in **4** (as seen from the shorter Ir–N distance) makes the coordinated dinitrogen so electron poor as to render it non-nucleophilic towards a second metal centre.

The phosphinite ligand **2** has earlier been shown to defy cyclometalation forming mononuclear *cis*-compounds or *trans*-spanning di-nuclear complexes with both palladium and platinum[15c,16] and we were interested in the possibility for cyclometalation with iridium. Heating a toluene solution of **2** with 0.5 equivalents of ([(COD)IrCl]$_2$) at 180 °C overnight indeed gave a cyclometalated product. Closer inspection of the ^{1}H NMR spectrum showed, however, that the previously reported aromatic compound **5** had formed, *cf.* Scheme 2. All spectroscopic data agreed with those reported in the literature[1b] and an X-ray analysis confirmed this, giving the molecular structure shown in Fig. 3. Bond distances and angles are close to the ones reported for the corresponding *p*-anisyl complex.[1b]

To us, this was a rather surprising result and we decided to study the reaction in more detail using NMR spectroscopy. This revealed that during the course of the reaction several hydride species are involved. Also, olefinic protons appeared corresponding to cyclohexene and cyclohexadiene fragments. The reaction is rather slow but eventually goes to completion with the formation of dihydrogen as the only visible by-product as seen by ^{1}H NMR spectroscopy. The reaction can be accelerated by the addition of a hydrogen acceptor. Thus, in the presence of 1.5 equivalents of phenylacetylene the reaction is over within 2 h instead of 14. Here the by-product is mainly ethylbenzene. It seems that the first two dehydrogenations are reversible and only with aromatisation
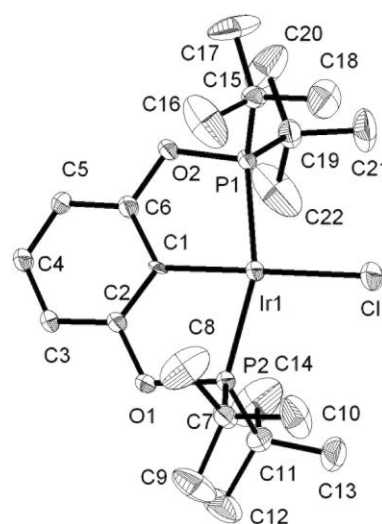

Fig. 3 DIAMOND drawing of compound **5** at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: Ir1–C1 2.000(3), Ir1–Cl1 2.3947(12), Ir1–P1 2.2897(10), Ir1–P2 2.2925(11), P1–Ir1–P2 159.90(4).

does the reaction become irreversible. Full dehydrogenation of cyclohexane has been reported for iridium before but always using a hydrogen acceptor.[1d,28]

Acknowledgements

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Scheme 2

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