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Diastereoselective formation of chiral iridium hydrides containing the chiral P,N-chelate ligand (4*S*)-2-(2-(diphenylphosphino)phenyl)-4-isopropyl-1,3-oxazoline†

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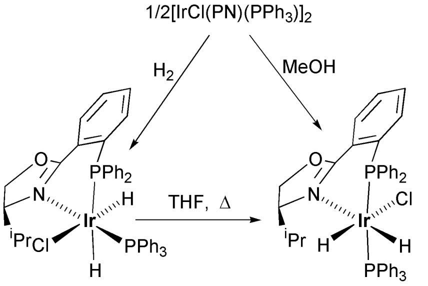
The iridium complex [Ir(μ-Cl)(PN)(PPh$_3$)]$_2$ (1) reacts with H$_2$ affording only the kinetic isomer *OC*-6-55-*C* of the dihydride [IrClH$_2$(PN)(PPh$_3$)] (2) and with methanol yielding, also exclusively, the thermodynamic isomer *OC*-6-53-*C* (2b) of the same dihydride; complex 2b has been characterised by X-ray diffractometric methods.

The knowledge of the factors that govern the stability of dihydrides and the control of their isomerization reactions are at the heart of the design of catalysts for asymmetric hydrogenation. In spite of this crucial role, only very recently it has been possible to spectroscopically detect catalytically active dihydrides containing chiral chelate ligands[1] and single-crystal X-ray structure determinations of such a type of chiral compounds are very scarce.[2] In this context, highly diasteroselective formation of chiral iridium dihydrides, one of the most efficient species for asymmetric hydrogenation,[3] is very rare.[2] We present here a very unusual case in which both the kinetically and the thermodynamically preferred dihydrides of a chiral PN containing iridium moiety are isolated and completely characterised. Thus, the oxidative addition of H$_2$ to the iridium(I) complex [Ir(μ-Cl)(PN)(PPh$_3$)]$_2$ (**1**)[4] (PN = (4*S*)-2-(2-(diphenylphosphino)phenyl)-4-isopropyl-1,3-oxazoline, Fig. 1) proceeds stereoselectively under kinetic control to form the dihydride [IrClH$_2$(PN)(PPh$_3$)] (*OC*-6-55-*C*, **2a**). On the other hand, reaction of **1** with MeOH affords, also selectively, the thermodynamically preferred dihydride isomer *OC*-6-53-*C* (**2b**).

Red solutions of the air-sensitive complex **1** in tetrahydrofuran (THF) turn yellow upon standing for some hours under hydrogen at room temperature and atmospheric pressure. From the resulting solution [IrClH$_2$(PN)(PPh$_3$)] (**2a**) can be isolated in good yield. The spectroscopic data[5] indicated the formation of only one diastereomer with $>99.5\%$ stereoselectivity. Complex **2a** is unstable in solution: in CHCl$_3$ it evolves to the dichloride [IrCl$_2$H(PN)(PPh$_3$)] (**3**, *OC*-6-52-*C*),[6] whereas, in THF or MeOH, it slowly isomerizes[7] to the *OC*-6-53-*C* (**2b**) isomer.

The high-field region of the ^{1}H NMR spectrum of **2a** consists of two signals corresponding to two different hydride ligands.[5] One of them (δ −9.40) displays a ddd pattern with one large ($^2J_{PH}$ = 162.9 Hz) and one short ($^2J_{PH}$ = 26.1 Hz) coupling constant (*trans* and *cis* to phosphorus, respectively). The second hydride (δ −22.16) possesses coupling constants which are typical for a hydride located *cis* to the two phosphorus and to one hydrogen atom.[8] The ^{31}P{^{1}H} NMR spectrum consists of an AX system with a coupling constant comparable to those previously reported for *cis* phosphorus ligands at iridium (J_{PAPX} = 7.6 Hz).[9] The hydride at δ −22.16 shows NOE with the H$_g$ and CH isopropyl oxazoline protons while the hydrogen at δ −9.40 only shows NOE with the latter. The structure of the *OC*-6-55-*C* isomer (**2a**) (Scheme 1) fit with all these spectroscopic data. Formally, this isomer is the result of the concerted *cis* addition of H$_2$ to an 'IrCl(PN)(PPh$_3$)' fragment, derived from complex **1**, along the P(PN)–Ir–Cl axis. It is of interest to point out that the diasteroselective formation of the *OC*-6-55-*C* isomer implies that the H$_2$ molecule efficiently discriminates between the two diastereofaces of the metallic fragment: H$_2$ approaches it from above of the molecular plane as it is shown in Fig. 2. Most probably, the presence of the PPh$_2$ phenyls, as well as, the oxazoline isopropyl group, precludes an interaction from below the molecular plane. Furthermore, *cis* addition along the P(PPh$_3$)–Ir–N axis was not observed.



2a (OC-6-55-C) **2b** (OC-6-53-C)

Scheme 1

On the other hand, stirring of complex **1** in methanol, at RT, caused the precipitation of a yellow solid that was isolated in excellent yield. Its solid state structure was determined by a single-crystal X-ray diffraction study.‡ This analysis (Fig. 3) revealed that this complex is the *OC*-6-53-*C* diastereomer of the dihydride [IrClH$_2$(PN)(PPh$_3$)] (**2b**). The coordination of the iridium is approximately octahedral, with *cis*-ligand-to-ligand angles between 84.34(18) and 97.70(17)° (excluding the hydride ligands). The long bond distances Ir–N (2.149(7) Å) and Ir–Cl (2.509(2) Å) are indicative of the strong *trans* influence of the hydride ligands. The hydride atoms were located in a difference-Fourier map with a low angle cut of data.

Its IR spectrum showed two bands at 2203 and 2152 cm^{-1}, which correspond to ν(Ir–H) vibrations of two terminal

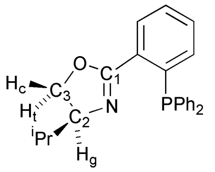


Fig. 1

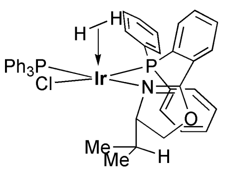


Fig. 2

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† Electronic supplementary information (ESI) available: selected analytical and spectroscopic data for **1**. See http://www.rsc.org/suppdata/cc/b2/b200518b/

DOI: 10.1039/b200518b

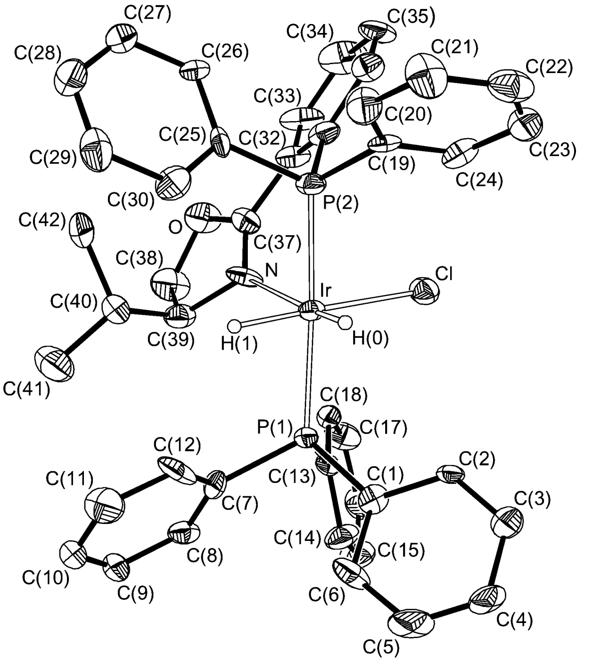
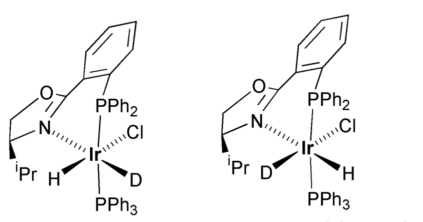


Fig. 3 X-Ray crystal structure of **2b** (ORTEP view, ellipsoids at 50% probability). Selected interatomic distances [Å] and angles [°]: Ir–N 2.149(7), Ir–P(1) 2.302(3), Ir–P(2) 2.268(3), Ir–Cl 2.509(2); N–Ir–P(1) 97.70(17), N–Ir–P(2) 84.34(18), P(2)–Ir–P(1) 174.55(11), N–Ir–Cl 90.7(2), P(1)–Ir–Cl 94.92(9), P(2)–Ir–Cl 90.10(9).

hydrides. The former lies in the range of Ir–H absorptions for *trans* to chloride hydrides.[10] Spectroscopic data[5] confirmed that the solid state structure is maintained in solution. Thus, the hydrides were also identified in solution by their characteristic ^{1}H NMR upfield shifts at δ −22.59 and −20.35. The H–H and P–H couplings correspond to mutually *cis* hydrides which are also located *cis* respect to the two phosphorus atoms of the molecule. Furthermore, NOE experiments indicated that the more shielded hydride occupies a *trans* position respect to the chlorine, whereas the other is *trans* to the nitrogen atom of the PN ligand. Additionally, the ^{31}P NMR spectrum consists of an AB system (δ_{PA}, 14.3, δ_{PB}, 13.7, J_{PAPB} = 389 Hz) confirming the *trans* arrangement of the two phosphorus atoms.[11]

Treatment of **1** with CH_3OD resulted in the precipitation of the monodeuterated complex [IrClDH(PN)(PPh$_3$)] (**2-d$_1$**).[5] While the organic part of the ^{1}H NMR spectrum of **2-d$_1$** matches the corresponding region of complex **2b**, the high field region of the spectrum consisted of a doublet of doublets centred at δ −20.31 (J = 18.7 and 15.8 Hz) and a pseudotriplet at δ −22.57 (J = 15.0 Hz). Selective decoupling experiments revealed that each hydride belongs to a different molecule, the observed constants being due to coupling to phosphorus nuclei. Both hydride signals together integrated for one hydrogen with a relative intensity of 65/35, the signal at δ −22.57 being the most intense one. Thus, isolated **2-d$_1$** consists of a mixture of two isomers in a 65/35, **2b-d$_1$/2b′-d$_1$** ratio. From the value of the hydride chemical shift we conclude that, in the major isomer the hydride occupies a *trans* position respect to the chlorine atom, whereas in the minor isomer the hydride is located *trans* to the PN nitrogen atom.

Interestingly, when compound **1** was stirred in CD_3OH a mixture of the isotopomers **2b-d$_1$** and **2b′-d$_1$** was obtained again, but now in the opposite **2b-d$_1$/2b′-d$_1$** = 35/65 ratio.[5] As expected, the dideuterated compound [IrClD$_2$(PN)(PPh$_3$)] (**2-d$_2$**)[5] was obtained by treating complex **1** in CD_3OD for 20 h. ^{2}H NMR data indicated that again, only the *OC*-6-53-*C* isomer is obtained (Fig. 4). The above results indicate that most probably the oxidative addition of methanol to complex **1** proceeds through an undetected Ir(III) hydrido-methoxo intermediate followed by the subsequent β-elimination from the methoxo group to give the final dihydride product.[12]



2b-d$_1$ (OC-6-63-C) **2b′-d$_1$** (OC-6-53-C)

Fig. 4

In summary, the dimer [Ir(μ-Cl)(PN)(PPh$_3$)]$_2$ readily activates methanol to give diastereoselectively the thermodynamically stable dihydride [IrClH$_2$(PN)(PPh$_3$)] (**2b**, *OC*-6-53-*C*). By direct hydrogenation of **1** with H_2 the kinetic diastereomer *OC*-6-55-*C* (**2a**) is also selectively obtained. The structures of the new complexes have been spectroscopically determined and by an X-ray crystallographic analysis of **2b**. Studies on detailed reactivity and on catalytic applications of the hydrides **2** are in progress in our laboratory.

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Notes and references

‡ *Crystal data* for **2b**·1/2CDCl$_3$: $C_{42}H_{41}ClIrNOP_2 \cdot 1/2CDCl_3$ M = 925.54; orthorhombic, space group I_{222}, a = 17.371(2), b = 18.477(3), c = 23.918(2), U = 7676.8(16) Å^3, Z = 8, D_c = 1.602 Mg m^{-3}, μ(Mo-Kα) = 3.771 mm^{-1}. Crystals suitable for X-ray diffraction were grown by slow diffusion of diethyl ether into a solution of **2b** in CDCl$_3$. 9427 reflections measured, 6722 unique (R_{int} = 0.0354). Final $wR(F^2)$ = 0.0780 (all data), Flack parameter[13] x = −0.026(12). CCDC reference number 177913. See http://www.rsg.org/suppdata/cc/b2/b200518b/for crystallographic data in CIF or other electronic format.

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4 Complex **1** has been prepared as a mixture of two isomers in a *ca.* 8:1, **1a**:**1b** ratio, by subsequent displacement of the olefin from [Ir(μ-Cl)(η^2-C$_8$H$_{14}$)$_2$]$_2$ by PN and PPh$_3$.

5 *Selected analytical and spectroscopic data* for the complexes: NMR data at room temperature in CDCl$_3$ (^{1}H: 300 MHz, SiMe$_4$. ^{31}P: 121 MHz, external 85% H$_3$PO$_4$ in D$_2$O; ^{13}C: 75 MHz, SiMe$_4$. For proton and carbon labelling, see Fig. 1). IR in Nujol mulls. **2a:** ^{1}H NMR: δ 4.72 (m, 1H; H$_g$), 4.35 (m, 2H; H$_c$, H$_t$), −9.40 (ddd, J 162.9, 26.1, 4.5 Hz, 1H; *trans* to P hydride), −22.16 (ddd, J 22.2, 10.2, 4.5 Hz, 1H; *trans* to Cl hydride). ^{31}P{^{1}H} NMR: δ 5.84 (d, J 7.6 Hz, PPh$_3$), 1.54 (d, PN). ^{13}C NMR: δ 161.13 (C$_1$), 80.58 (C$_2$/C$_3$), 66.78 (C$_3$/C$_2$). IR: 2185, 2056 cm^{-1} ($\nu_{Ir–H}$); Anal. Calc. for $C_{42}H_{41}ClIrNOP_2$: C, 58.23; H, 4.73; N, 1.62. Found: C, 58.60; H, 5.11; N, 1.72. **2b**: ^{1}H NMR: δ 3.91 (pdd, J 8.8, 3.3 Hz, 1H; H$_t$), 3.72 (pt, J 8.8 Hz, 1H; H$_c$), 3.05 (dm, J 8.8 Hz, 1H; H$_g$), −20.35 (ddd, J 18.7, 15.9, 8.1 Hz, 1H; *trans* to N hydride), −22.59 (ptd, J 14.7, 8.1 Hz, 1H; *trans* to Cl hydride). ^{31}P{^{1}H} NMR: δ 14.3, 13.7 (AB system, J_{AB} 389 Hz). ^{13}C NMR: δ 162.23 (C$_1$), 74.82 (C$_2$/C$_3$), 66.30 (C$_3$/C$_2$). IR: 2203, 2152 cm^{-1} ($\nu_{Ir–H}$). **2b-d$_1$:** ^{1}H NMR: δ −22.57 (pt, J_{PH} 15.0 Hz). ^{31}P{^{1}H} NMR: δ 13.6, 14.5 (AB system, J_{AB} 389 Hz). ^{2}H NMR: δ −19.97 (m). IR: 2253 cm^{-1} ($\nu_{Ir–H}$), 1572 cm^{-1} ($\nu_{Ir–D}$). **2b′-d$_1$**: ^{1}H NMR: δ −20.31 (dd, J_{PH} 15.8, 18.7 Hz). ^{31}P{^{1}H} NMR: δ 13.6, 14.5 (AB system, J_{AB} 389 Hz). ^{2}H NMR: δ −22.21 (m); IR: 2199 cm^{-1} ($\nu_{Ir–H}$), 1597 cm^{-1} ($\nu_{Ir–D}$). **2-d$_2$**: ^{31}P{^{1}H} NMR: δ 13.9, 14.4 (AB system, J_{AB} 386 Hz). ^{2}H NMR: δ −19.89 (m), −22.18 (m). IR: 1616, 1572 cm^{-1} ($\nu_{Ir–D}$).

6 Compound **3** can be obtained in good yield by reacting complex **1** with one equivalent of aqueous HCl in acetone.

7 Isomerization is complete after 13 h of treatment in boiling THF or 24 h of stirring in MeOH.

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