Control of proton transfer by hydrogen bonding in the protonated forms of the binucleophilic complex [{η⁵-$C_5H_4CH(CH_2)_4NMe$}Ir(PPh_3)H_2]

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Proton transfer reactions between both nucleophilic sites of a dihydrido iridium complex containing the 4-*N*-methylpiperidylcyclopentadienyl ligand and their dependance with the hydrogen bonding ability of the solvent medium are studied by NMR.

Proton transfer reactions in organometallic and bioinorganic chemistry are of fundamental interest and recent reviews deal with their thermodynamic, kinetic or mechanistic aspects.[1,2] In this context, considerable attention has been focussed on the protonation or deprotonation of transition metal hydrides and on the role of dihydrogen and hydrogen-bonded complexes as possible intermediates. It is widely recognized that hydrogen bonding, in its conventional aspect,[3,4] plays a fundamental role on proton transfer reactions.[5] It may also be supposed to play a decisive role in its non-conventional aspect, *i.e.* as a weak intramolecular hydrogen–hydrogen attractive interaction between a conventional hydrogen-bond donor and a transition metal hydride.[6]

The nucleophilic character of the iridium dihydride complex [(η⁵-C_5H_5)Ir(PR_3)H_2] has been used during the past few years to prepare new cationic polyhydrides displaying in ^{1}H NMR quantum mechanical exchange couplings.[7] The recent synthesis of a piperidino-substituted cyclopentadienyl ligand[8,9] gives the opportunity to prepare an iridium dihydride containing a second nucleophilic site and convenient to study both the possibility of hydrogen bonding and the dynamics of proton transfer.

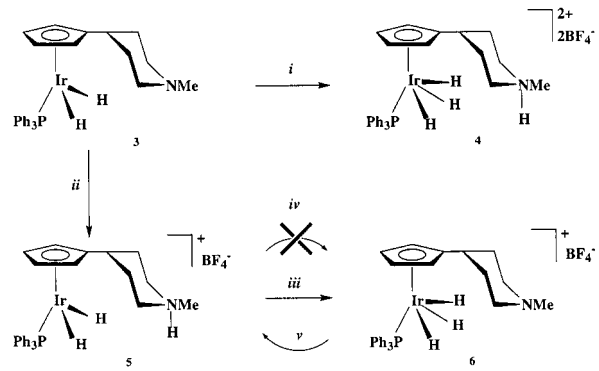
The new dihydrido iridium complex [(η⁵-C_5H_4pip)Ir(PPh_3)H_2] **3**, [pip = *N*-methylpiperidyl, $CH(CH_2)_4NMe$] has been prepared by usual methods starting from the salt Na(C_5H_4pip) recently described, and involving the intermediate preparation of the bis(ethylene) and diiodide iridium complexes [(η⁵-C_5H_4pip)Ir(C_2H_4)$_2$] **1** and [(η⁵-C_5H_4pip)Ir(PPh_3)I_2] **2**.

For the three complexes, **1**–**3**, the ^{1}H NMR spectra show respectively AA′BB′ (**1**) or AA′BB′X (**2** and **3**) patterns in the range δ 4.50–5.50 for the Cp protons, a sharp resonance at δ *ca.* 2.2 for the methyl group linked to nitrogen and second order signals in the range δ 1.2–3.0 for piperidyl ring protons. Electron saturation in **1**–**3** rules out the coordination of the piperidyl nitrogen to the metal as in the parent rhodium complex [(η⁵-C_5H_4pip)Rh(C_8H_{14})$_2$].[8]

The equivalent hydrides of **3** resonate at δ −17.52 (CD_2Cl_2, 293 K, J_{PH} 30.2 Hz) in the ^{1}H NMR and the ν_{Ir-H} vibrations appear at 2128 cm^{-1} in the IR spectrum (KBr pellet), in the terminal Ir–H region. Protonation of **3** was first carried out in the presence of 2 equiv. of $HBF_4{\cdot}Et_2O$. The reaction leads to the expected dicationic species **4** resulting from the protonation of both amino and metal dihydrido nucleophilic sites as shown in Scheme 1.

The formation of an ammonium group is revealed (^{1}H NMR) by the appearance of a new broad signal in the low-field region at δ 8.75 (CD_2Cl_2, 293 K), and by a down-field shift of the methyl resonance of the methylpiperidyl group which appears in **4** as a doublet centered at δ 2.92 ($^3J_{HH}$ 4.2 Hz). The IR spectrum exhibits new absorption bands at 2950 cm^{-1} attributed to the ν_{N-H} vibration of the ammonium group and in the ν_{Ir-H} region at 2029 cm^{-1} (KBr pellet). In the ^{31}P{^{1}H} NMR spectrum, the diprotonation of **3** is accompanied by an up-field shift of the phosphorus nucleus of the PPh_3 ligand, from δ 13.25 for the starting material to δ 7.20 for the diprotonated product **4**. The high-field ^{1}H NMR spectrum exhibits, at room temperature, a new doublet centered at δ −12.26 (CD_2Cl_2, J_{P-H} 6.6 Hz). As in the case of the cyclopentadienyl parent iridium cations [(η⁵-C_5H_5)Ir(PR_3)H_3^+],[7] this signal is highly temperature dependent and decoalesces (≈ 11.7 kcal mol^{-1}) at lower temperature into an AB_2X spin system (δ_A −12.73, δ_B −11.55) displaying large temperature dependent $J_{H_A-H_B}$ coupling constants *i.e.* 278 Hz at 183 K and 446 Hz at 203 K, attributed to quantum mechanical exchange couplings.

Acidification at room temperature of **3** in CH_2Cl_2 with slightly less than 1 equiv. of $HBF_4{\cdot}Et_2O$ gave the trihydride monocation **6** (Scheme 1) in which only the iridium hydride was protonated. This complex differs from the diprotonated product **4** mainly in that it exhibits neither the typical ammonium resonance in the low-field region of the ^{1}H NMR nor the ν_{N-H} vibration in the IR. The other spectroscopic data are somewhat similar to those observed for **4**. Typically, the ^{31}P{^{1}H} NMR spectrum exhibits a singlet at δ 7.80 (CD_2Cl_2). The ^{1}H NMR spectrum in the high-field region exhibits a broad resonance centered at δ −12,36 which decoalesces by decreasing the temperature into typical resonances for a AB_2 spin system (^{1}H{^{31}P}) characterized, as previously observed for the diprotonated derivative, by large and highly temperature dependant $J_{H_a-H_b}$ coupling constants, *i.e.* 295 Hz at 183 K, 368 Hz at 193 K, 464 Hz at 203 K and 634 Hz at 213 K. These coupling constants are slightly larger than those measured for the dication **4** at similar temperatures. According to recent observations,[10] this could suggest some degree of hydrogen-bonding interaction between the hydride ligands and the piperidyl nitrogen lone pair. This Ir(H)$_3$···N≡hydrogen-bonding interaction could also rationalize, (i) the observation in complex **6** of a slightly higher



Scheme 1 Summary of the reactions run in the NMR tube; i, $HBF_4{\cdot}Et_2O$ (2 equiv.), CD_2Cl_2, 293 K; ii, $HBF_4{\cdot}Et_2O$ (1 equiv.), CD_2Cl_2, 193 K; iii, 293 K; iv, in presence of THF or PPh_3O (10%), 293 K; v, addition of THF, 293 K.

energy barrier for the classical site to site proton exchange in the $[Ir(H)_3^+]$ group than in complex **4** and (ii) the low-field shift of the methyl resonance of the methylpiperidyl group which appears at δ 2.80 in **6** (instead of δ 2.20 and 2.92, respectively, observed for the starting material and complex **4**), although the added proton is clearly coordinated to the iridium atom.

^{1}H NMR monitoring demonstrates that the initial step of the protonation of **3** at 183 K with 1 equiv. of $HBF_4{\cdot}Et_2O$ consists in the quantitative formation of a piperidinium group observed at δ 12.3 (br) the dihydrido iridium part of the molecule being unchanged. The methyl resonance, which appears at δ 2.91 is downfield shifted, whereas the characteristic signals of the cyclopentadienyl protons and of the hydrido ligands are very similar to those observed for **3** *i.e.* two multiplets at δ 5.02 and 4.85 for the cyclopentadienyl protons and a broad doublet at δ −17.56 (J_{HP} 29.6 Hz) for the hydrides. When the reaction mixture is quickly warmed up to room temperature over a few minutes and then cooled again at 183 K, it is possible to follow by ^{1}H NMR the disappearance of the broad piperidinium resonance at δ 12.3 and of the hydride resonance at δ −17.56 and the growth of the characteristic signals of the trihydrido monocation **6**. The migration of the added proton from the piperidyl to the iridium dihydrido groups is not reversible.

When the protonation of **3** by 1 equiv. of $HBF_4{\cdot}Et_2O$ is carried out in presence of THF in the ratio THF/CD_2Cl_2 = 10/90, the initial step remains the protonation of the piperidyl group to give **5** but the migration of the added proton to give **6** is not observed. However, instead of proton transfer, ^{1}H NMR studies at various temperatures and various concentrations reveal an interesting intramolecular proton exchange process between the piperidyl amino group and iridium (Fig. 1). The coalescence was reached at 293 K (200 MHz) and ΔG^* at coalescence temperature of this purely kinetic phenomenon can be estimated[11] at 12 kcal mol^{-1}.

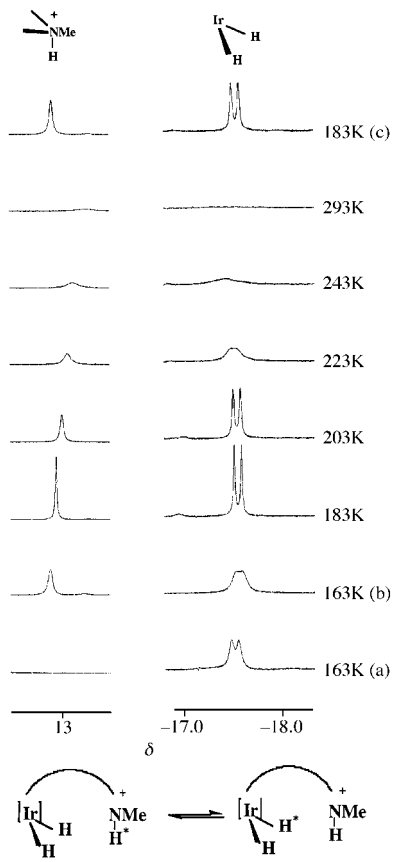


Fig. 1 Temperature dependance of the ^{1}H NMR spectra (CD_2Cl_2, 400 MHz), in the high- and low-field regions, in the presence of THF, (a) of the starting material **3** at 163 K, (b) after addition of 1 equiv. of $HBF_4{\cdot}Et_2O$ at 163 K, (c) after increasing progressively the temperature from 163 to 293 K and then cooling to 183 K.

This indicates a thermodynamic stabilization of the dihydrido piperidinium form **6** for the monoprotonated product which probably involves a weak hydrogen-bonding interaction between oxygen lone-pair of THF and the piperidinium proton. Furthermore, the observation of proton exchange with a low activation energy, involves a spatial proximity of both nucleophilic sites. This proximity could be explained by the existence of non-conventional intramolecular Ir–H···H–N hydrogen bonds such as those recently described by the groups of Crabtree[12,13] and Morris.[14]

As complementary experimental facts, it is of interest (i) that the addition of few drops of THF to a CD_2Cl_2 solution of the trihydrido cation **6** causes the immediate and total reverse transfer of the proton from the iridium hydride to the piperidyl sites to give **5** which experiences the low barrier exchange process described above and (ii) that the addition of $OPPh_3$, a weak base having a great capacity for formation of hydrogen bond,[15] to **6** causes again the total reverse transfer of the proton but the piperidinium species so obtained was stabilized to such an extent that the exchange of proton was not observed in the experimental conditions used.

In conclusion, we describe the synthesis of a new series of piperidylcyclopentadienyl iridium hydride complexes. We demonstrate that the kinetic site of protonation is the amino group of the piperidyl moiety whereas the thermodynamic one is dependent on the intermolecular hydrogen bonds present in the medium. In the absence of hydrogen bonding to solvent, the product of protonation at Ir is the thermodynamically stable one. The products of protonation at Ir and at N have similar stability in THF which allows the observation of an intramolecular proton transfer process and the product of protonation at N is the most stable in the presence of $OPPh_3$ owing to the formation of strong hydrogen bonds. This therefore further demonstrates the importance of hydrogen bonding for controlling the reactivity of hydrido organometallic complexes.

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