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The influence of strong acidic proton donors on the reactivity of $H_2Ir(CO)Cl(PPh_3)_2$ with D_2

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Dedicated to Professor Renato Ugo on the occasion of his 65th birthday

Abstract

The interaction of the complex $H_2Ir(CO)Cl(PPh_3)_2$ with various proton donors of increasing acidity, namely 2,2,2-trifluoro ethanol (TFE), 1,1,1,3,3,3-hexafluor-2-propanol (HFIP), perfluoro *tert*-butylalcohol (PFTB) and trifluoroacetic acid (TFA), has been investigated. The gradual proton downfield shift of the hydride *trans* to the chlorine, in the presence of increasing amounts of the proton donors, and the T_1 measurements have shown that the chlorine ligand is the basic counterpart in the hydrogen bond interaction. This intermolecular hydrogen bond influences the reactivity of the complex and particularly the H_2/D_2 exchange process. The $HDIr(CO)Cl(PPh_3)_2$ isotopomer obtained by reacting $H_2Ir(CO)Cl(PPh_3)_2$ with D_2 in dichloromethane is formed in greater amount when one of the proton donors is added to the reaction mixture; furthermore the stronger the acid, the larger the amount of HDIr isotopomer formed.

Keywords: Intermolecular hydrogen bond; Iridium; Vaska complex; Perfluorurated alcohols

1. Introduction

In recent years, numerous observations dealing with intra- and intermolecular hydrogen bonds between organometallic complexes and organic proton donors have been reported. In fact, an organometallic complex offers several basic counterparts [1–6] for the interaction with the proton donors, namely d-electrons of the metal centre, electron lone pairs on ligands atoms such as halogens or oxygens of carbonyls and nitrosyls, aromatic rings π-electrons. Interestingly, the hydride ligands can also behave as the basic site of interaction with proton donors. Such an interaction is called 'di-hydrogen bond' or 'unconventional hydrogen bond' [4,7–16] and it has been demonstrated that it can contribute significantly to the stabilisation of organometallic structures in mononuclear complexes. Moreover, the formation of an intermolecular 'unconventional' H···H interaction has been demonstrated to precede the formation of a non-classical di-hydrogen complex [17–20] and the protonation of the metal centre [21–25]. It has also been shown that it can influence the reactivity of the organometallic system [26–28]. The variety of basic sites available on organometallic complexes may lead to competition between different sites of interaction.

The low interaction enthalpy of intermolecular hydrogen bonding is not expected to give noteworthy

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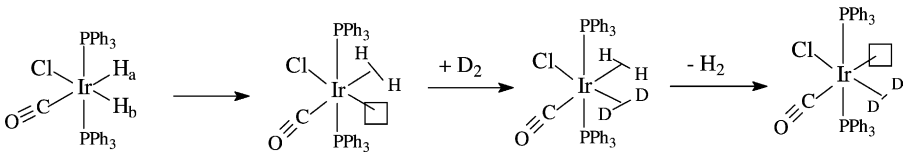


Scheme 1.

perturbations of the electronic distribution on the metal complex. In spite of this, Shubina and co-workers have recently found that the interaction between OsHCl(CO)(P^tBu_2Me)$_2$ [29] and perfluorurated alcohol—involving the chlorine ligand of the organometallic complex—increases the insaturation on the metal centre. The formation of the adduct can be monitored by IR spectroscopy as new bands appear relating to different stretching frequencies of the CO ligand. The possibility of modifying the electronic properties of organometallic complexes by means of intermolecular hydrogen bonding interactions appears very appealing as it may provide new routes to control the reactivity of a given organometallic complex.

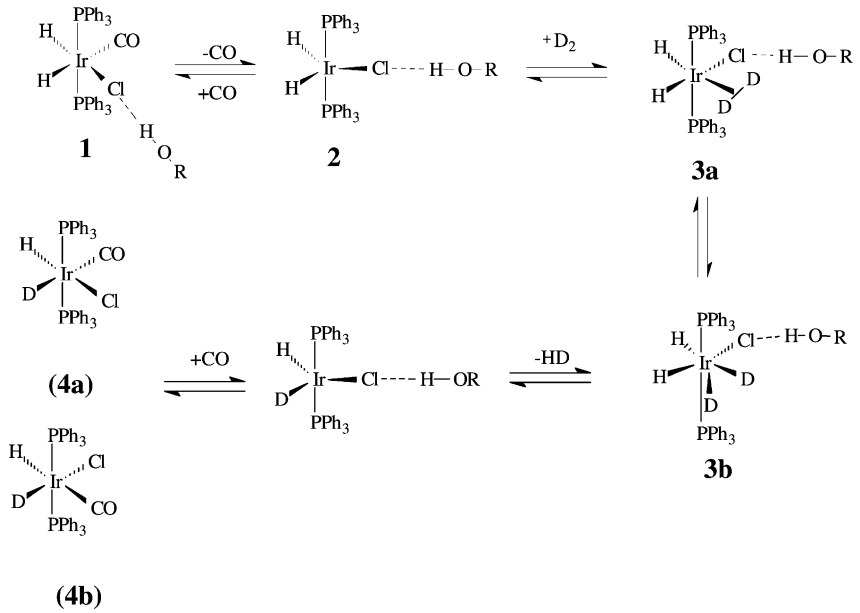
In this paper, we show that the variation induced by intermolecular hydrogen bonds modifies the reactivity of the $H_2Ir(CO)Cl(PPh_3)$ complex towards D_2 exchange.

The $Ir(CO)Cl(PPh_3)_2$ complex, well known as Vaska's compound [30], shows reversible hydrogen co-ordination, either in solution and in the solid state.

Furthermore, it was observed that this complex catalyses the formation of HD from H_2/D_2 mixtures [31].

The formation of the HD and the corresponding $HDIr(CO)Cl(PPh_3)_2$ implies the addition of a D_2 molecule to the coordinatively saturate $H_2Ir(CO)$-$Cl(PPh_3)_2$ complex and therefore a mechanism was suggested that implies the expansion of the Ir co-ordination sphere from 6 to 8 ligands.

In this paper, we report our observations on how the H/D exchange process at the iridium centre (Schemes 1 and 2) is affected by the presence of proton donors of increasing acidity.



Scheme 2.

2. Experimental

The Vaska's complex $Ir(CO)Cl(PPh_3)_2$ was purchased from Aldrich and hydrogenated in a CH_2Cl_2 solution.

The complexes $Ir(CO)Br(PPh_3)_2$ and $Ir(CO)I(PPh_3)_2$ were synthesised as previously reported [32]. The ^1H NMR spectra were recorded on a JEOL EX 400 spectrometer at a proton resonance of 400 MHz.

The samples for D_2/H_2 exchange were prepared as follows: 0.5 ml of a 14 mM CD_2Cl_2 solution of $H_2Ir(CO)Cl(PPh_3)_2$ was introduced into a screw cap NMR tube with a PTFE/silicone valve, degassed and exposed to 1 atm of D_2 at 77 K. The tube was then thawed, shaken and warmed up to 323 K in order to speed up the exchange process that is slow at RT. ^1H NMR spectra were recorded every 30 min. The H_2/D_2 exchange experiments have been repeated using HFIP, PFTB and trifluoroacetic acid (TFA) in equimolar amounts with respect to the complex.

3. Results and discussion

3.1. Characterisation of the interaction between $H_2Ir(CO)Cl(PPh_3)_2$ and perfluorurated alcohols

To a 14 mmol CD_2Cl_2 solution of $H_2Ir(CO)Cl(PPh_3)_2$ increasing amounts of a series of perfluorurated organic compounds were added. 2,2,2-Trifluoro ethanol (TFE), 1,1,1,3,3,3-hexafluor-2-propanol (HFIP), perfluoro *tert*-butylalcohol (PFTB) and trifluoroacetic acid (TFA) have been used as strong proton donors. For each of them, the concentration was gradually increased up to 17 mmol.

^1H NMR spectra of solutions with different [alcohol]/$[H_2Ir]$ ratios were recorded at temperatures from 297 to 213 K. As can be seen in Fig. 1, the increase of [ROH]/$[H_2Ir]$ ratios causes a gradual shift to low frequencies of the hydride *trans* to the chlorine ligand, whereas no change in the chemical shift is observed on the signal of the hydride *cis* to chlorine atom. The trend of the hydride shift as a function of [ROH] is not linear, and in the case of TFA a maximum value is obtained when the complex and the acid are in nearly equimolar amounts. This observation allows us to rule out the hypothesis that the hydride drift is due to changes in the solvent properties upon addition of acid.

The addition of increasing amounts of the same proton donors has also been carried out on two analogues namely: $H_2Ir(CO)Br(PPh_3)_2$ and $H_2Ir(CO)I(PPh_3)_2$. With the bromine containing derivative the shift ($\Delta\delta$) of the hydride *trans* to the halogen is much smaller than that observed with Cl and is almost zero with the I containing complex.

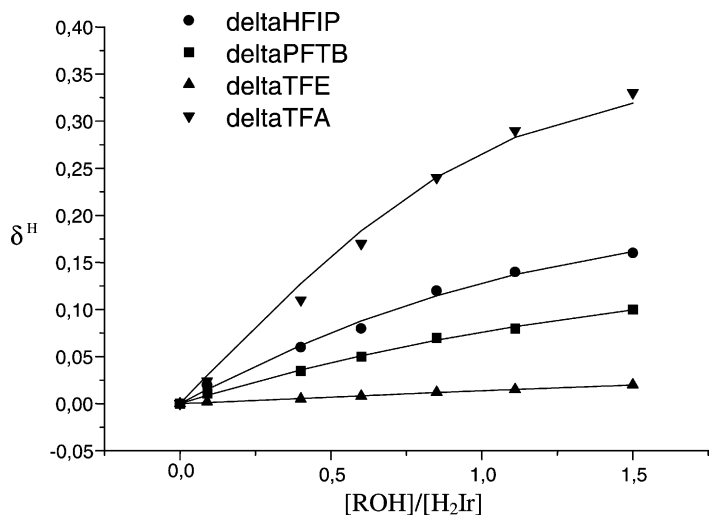


Fig. 1. Variation of hydride chemical shift (−18.5 ppm) reported as a function of the addition of: TFE (upward triangles), HFIP (circles), PFTB (squares), TFA (downward triangles). The ratios [ROH]/$[H_2Ir]$ are: 0, 0.09, 0.4, 0.6, 0.85, 1.11, 1.15, respectively.

Moreover, lowering the temperature from 297 to 213 K does not lead to a further frequency shift of this hydride resonance.

The behaviour of the OH resonance of the perfuorurated alcohols as a function of the [HA]/[H_2Ir] ratio reflects that of the hydrides, but the downfield shift is more evident. This finding is indicative of a direct involvement of the hydroxylic proton in the hydrogen bond with the complex whereas the smaller effect observed for the *trans* hydride resonance suggests that the latter ligand does not act as the basic counterpart in the formation of the hydrogen bond. Unfortunately, the broadening of the OH resonance prevents an exact determination of the δ values. With the HFIP (which shows the narrowest peak) there is a downfield shift from 3.22 to 4.19 ppm when the [ROH]/[H_2Ir] ratio goes from 0 to 1.5. Differently from that was observed for the hydride resonance, in this case upon decreasing the temperature a further shift to higher frequencies (Fig. 2) of the OH signal has been observed.

The complex H_2Ir exhibits three possible basic counterparts to the formation of H-bonds, namely the chlorine, the carbonyl and the hydride ligand.

The di-hydrogen Ir$H\cdots$HOR interaction would result in a considerable decrease of the longitudinal relaxation time of the hydride resonance due to the contribution of the $H\cdots H$ dipolar interaction [33,34]. Another contribution to the shortening of T_1 should arise from the increased weight (longer τ_c) and steric hindering of the adduct with respect to the free complex. The H–H dipolar contribution can be determined by considering the difference between the T_1 of the hydride measured in the presence of deuterated and non-deuterated alcohol. The T_1 difference thus obtained at 213 K (the temperature that corresponds to the minimum in the plot of T_1 versus temperature) is 15 ms. The interprotonic distance responsible for such a T_1 difference has been evaluated using the following equation [35]:

$$\left(\frac{1}{T_1}\right)_{H_2Ir\cdots DOR} - \left(\frac{1}{T_1}\right)_{H_2Ir\cdots HOR} = \frac{3}{10}\left(\frac{\mu_0}{4\pi}\right)^2 {}^2\gamma_H^4 \frac{1}{r^6}\tau_c \left[\frac{1}{1+\varpi_0^2\tau_c^2} + \frac{4}{1+4\varpi_0^2\tau_c^2}\right] \quad (1)$$

At the temperature where T_1 reaches its minimum, the value of $\omega_0\tau_c$ is 0.62 [35], the calculation of the interproton distance r is then straightforward and a value of 3.5 Å was obtained. This value is far from the hydrogen bond distances that are in the range of 1.7–2.3 Å. This result therefore unambiguously rules out the occurrence of a non-conventional $H\cdots H$ bond and suggests that the basic site of the interaction is the chlorine ligand.

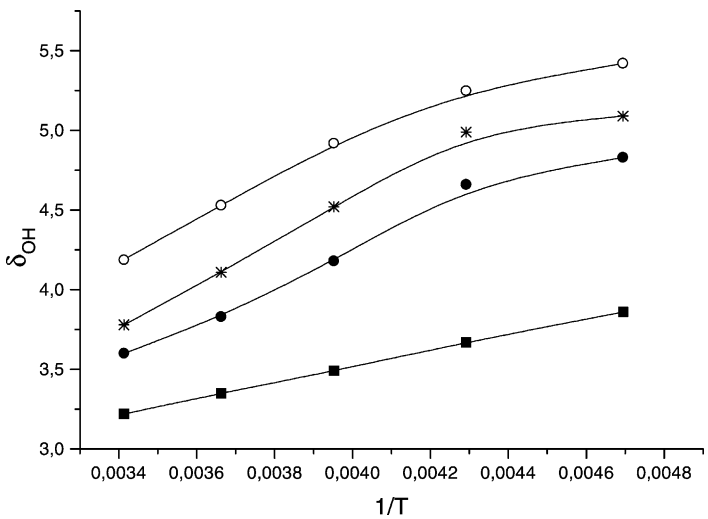


Fig. 2. Hydroxyl chemical shift (δ_{OH}) of HFIP at different temperatures (25, 0, −20, −40 and −60 °C) and variable [HFIP]/[H_2Ir] ratios: it varies from 0 (squares) to 0.5 (open circles) to 1 (stars) to 1.5 (filled circles).

3.2. Calculation of the equilibrium constants

Taking into account that the formation of the adduct is reversible and that this process is fast on the NMR time scale, the observed chemical shifts for the hydride and the alcohol resonances correspond to weighted averages of the shifts for the "free" and for the bound species according to equation:

$$\delta_{obs} = \delta_{free}\frac{[H_2Ir]}{[H_2Ir]_0} + \delta_{bound}\frac{[H_2Ir\cdots HOR]}{[H_2Ir]_0}$$

From this equation and keeping in mind that the relative percentages of free and bounded species depend on the equilibrium constant (K_f), we can obtain the formation constant (K_f) [36] of the H-bonding adduct by interpolating the hydride chemical shift at different [HOR]/[H_2Ir] ratios according to the following equation:

$$\left(\frac{1}{\delta_H^{bond}}\right)^2 y^2 x + \frac{1}{\delta_H^{bond}} yx\left(1 + x + \frac{1}{K_f\,[H_2Ir]_0}\right) + x = 0$$

where $x = [HOR]_0 / [H_2Ir]_0$ and $y = \delta_H^{obs} - \delta_H^{free}$

The K_f values reported in Table 1 were obtained at RT. Surprisingly, in spite of their relative acidities, PFTB shows a smaller equilibrium constant than HFIP. A possible explanation relies on the competition between the formation of the adduct and the self association process of the alcohol.

Table 1
K_f values of the strong proton donors at RT

	K_f
TFE	1.08×10^1
HFIP	3.10×10^2
PFTB	1.25×10^2
TFA	4.62×10^2

Further support for this explanation has been gained by IR spectroscopy. We have recorded the IR spectra of 6 and 20 mM solutions of HFIP in CH_2Cl_2 and compared them with the IR spectrum of an equimolar solution of HFIP and H_2Ir (Fig. 3). One can see that upon increasing the concentration of the alcohol from 6 to 20 mM a broad band appears, besides the band of the free alcohol (3578 cm^{-1}) at 3325 cm^{-1} due to the self association process. When the H_2Ir complex is present in an equimolar amount with respect to the alcohol, this broad band drifts to about 3288 cm^{-1}. This means that, in this case, the interaction with the complex—although weaker than the self association—is preferred. The frequency difference between the free

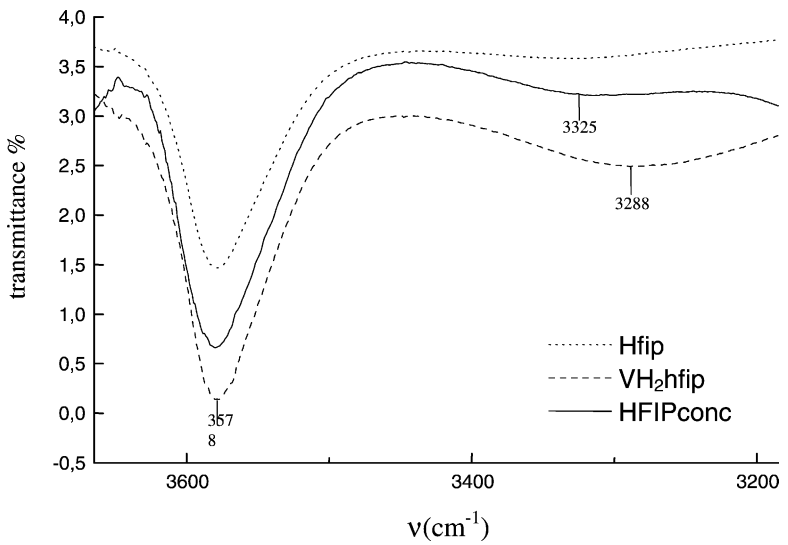


Fig. 3. IR spectra of: 6 mmol solution of HFIP in dichloromethane (dotted line), 20 mmol solution of the same alcohol (solid line) and equimolar solution of $H_2Ir(CO)Cl(PPh_3)_2$ and HFIP (dashed line).

and the bound OH allows the estimation of the hydrogen bonding enthalpy by means of the empirical equation suggested by Iogansen et al. [37].

$$-\Delta H^{\circ} = \frac{18\Delta\nu_{OH}}{\Delta\nu^{\circ}_{OH} + 720}$$

The obtained interaction enthalpy is 5.17 kcal mol^{-1}.

Conversely while the IR spectra of PFTB show the self association band also at very low concentrated solutions, the addition of the complex does not effect the position of this band. This indicates that self association is thermodynamically preferred to the interaction with the complex in the case of PFTB while the opposite behaviour occurs in the case of HFIP.

3.3. Reactivity of $H_2Ir(CO)Cl(PPh_3)_2$ with D_2

The substitution of hydrides with deuterium nuclei requires the formation of a co-ordination vacancy on the metal centre: dihydride to di-hydrogen tautomerization allows the addition of a deuterium molecule to iridium as reported in Scheme 1. This mechanism can account only for the formation of the $D_2Ir(CO)Cl(PPh_3)_2$ complex, if one can rule out the possibility of an expansion of the iridium co-ordination sphere from 6 to 8. Another reaction mechanism has to be invoked to explain the formation of the mixed HDIr isotopomer.

The reaction of D_2 with $H_2Ir(CO)Cl(PPh_3)_2$ can be conveniently followed by recording ^{1}H NMR spectra of the hydride region. The mixed isotopomer HDIr shows an isotopic shift in the hydride region, in fact its resonance is separated of 15 ppb from the H_2Ir one (Fig. 4): this allows a direct assessment of the actual amounts of the two isotopomers.

The concentration of the third isotopomer (D_2Ir) has been obtained from the difference between the integral of the aromatic region (that does not change during the reaction) and the hydride region integral. The three species are reported as a function of reaction time in Fig. 5. It is worth to note that neither H_a nor H_b is preferred in the replacement with D, as both (4a) and (4b) species (Scheme 2) are formed in equal amount.

The effect of intermolecular hydrogen bonding on the formation of the three species was evaluated by adding equimolar amounts of TFE, HFIP and PFTB to H_2Ir solutions and performing the same D_2 exchange experiment.

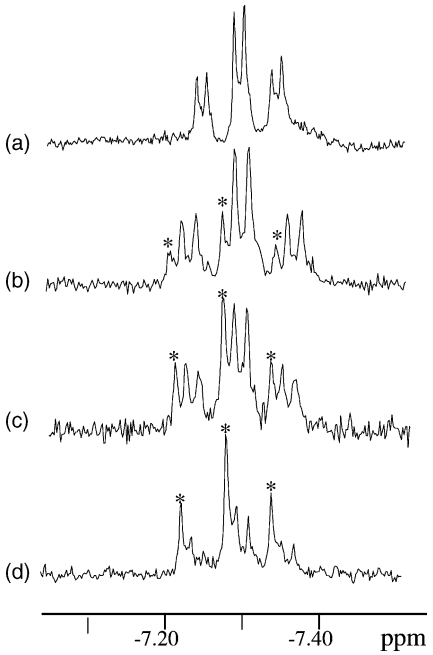


Fig. 4. ^{1}H NMR signal of the hydride *trans* to the CO ligand during the exchange reaction of the hydrogenated complex with D_2: (A) $t = 0$, (B) $t = 1$ h, (C) $t = 3$ h, (D) $t = 4.5$ h. The hydride resonances of the $HDIr(CO)Cl(PPh_3)_2$ isotopomer are indicated with the symbol (∗).

We have noticed that in all cases the maximum amount of the mixed isotopomer HDIr is reached after about 210 min but it is greater when the constant of the adduct formation (K_f) increases. In fact, the sample containing an equimolar amount of HFIP produces an amount of HDIr that is almost twice that observed without the alcohol (Fig. 6). At the same time, we do not observe any change in the rate of formation of D_2Ir that mainly derives from the more active mechanism of H_2/D_2 exchange depicted in Scheme 1.

In other words, the interaction with the alcohol molecules decreases the activation barrier of the second exchange mechanism, this however is much less active than the former mechanism which implies the elimination of H_2 and the addition of a D_2 molecule.

The addition of a much stronger proton donor such as TFA yields to a further enhanced effect on the amount of HDIr produced in the reaction of H_2Ir with D_2. In this case, the reaction was carried out at 303 K instead of 323 K because it was noted that a higher temperature causes the oxidative addition of the acid

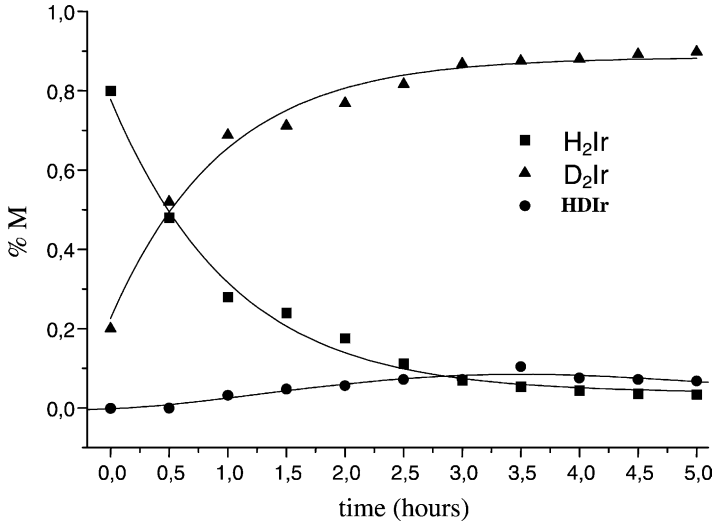


Fig. 5. $H_2Ir(CO)Cl(PPh_3)_2$ (squares), $HDIr(CO)Cl(PPh_3)_2$ (circles) and $D_2Ir(CO)Cl(PPh_3)_2$ (triangles) formed during the reaction of $H_2Ir(CO)Cl(PPh_3)_2$ with D_2 in CD_2Cl_2 without alcohol addition. The $HDIr(CO)Cl(PPh_3)_2$ isotopomer reaches its maximum value (10%) in 3 h and 30 min.

molecule to the complex $Ir(CO)Cl(PPh_3)_2$ thus yielding to the stable $H(CF_3COO)Ir(CO)Cl(PPh_3)_2$ compound. As shown in Fig. 7, the mixed isotopomer HDIr reaches a maximum value of about 10%, when the perfluorurated acid TFA is used. Furthermore the rate of the D_2Ir formation is considerably decreased in the presence of TFA thus indicating a higher activity of the second mechanism.

The relationship between the amounts of HDIr formed and the strength of intermolecular hydrogen bond shed light on the relative importance of the mechanistic pathway shown in Scheme 2. In fact, the

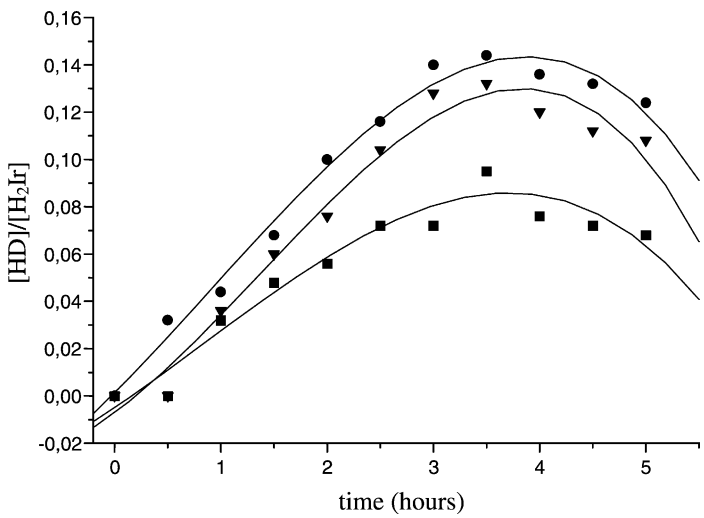


Fig. 6. $HDIr(CO)Cl(PPh_3)_2$ formed during the reaction of the hydrogenated Vaska complex with D_2: without alcohol addition (squares), with PFTB (triangles) and with HFIP (circles). The maximum is reached after 3 h and 30 min and is equal to: 8, 13 and 14%, for without alcohol addition, with PFTB and with HFIP, respectively.

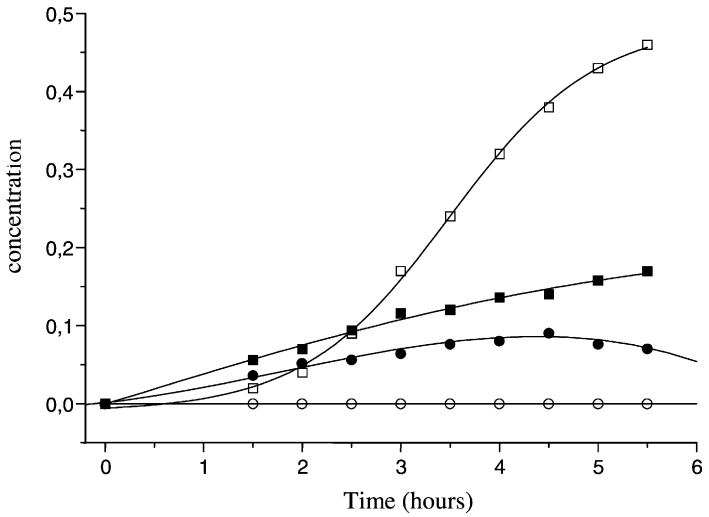


Fig. 7. Concentration of $D_2Ir(CO)Cl(PPh_3)_2$ (squares) and $HDIr(CO)Cl(PPh_3)_2$ (circles) at 313 K with HFIP (open symbols) and with trifluoroacetic acid (filled symbols). In this case, it is evident that the activation of mechanism leads to the formation of the mixed isotopomer; in fact, it is not observed at all with the alcohol.

increased amount of HDIr as a consequence of the interaction with H^+ donors cannot be rationalised considering a mechanism based on the expansion of the co-ordination sphere. Actually, it implies an enhanced cleavage of the CO ligand. In fact, the labilisation of the CO ligand on the hydrogenated Vaska complex has been recently observed by Duckett et al. using *para*-hydrogen [38]. The hydrogen bond interaction between chlorine and H^+ decreases the electronic charge on the metal and, consequently, the d–π* back donation to the CO: in this way, the CO ligand is labilised and the activation barrier to the formation of the mixed isotopomer HDIr is decreased.

4. Conclusions

The obtained results unambiguously show that (1) there is a strong intermolecular hydrogen bond between the perfluorurated proton donors and the chloride ligand in $H_2Ir(CO)Cl(PPh_3)_2$. (2) The minor structural and electronic effects associated with the formation of the intermolecular hydrogen bond affect the reactivity of the iridium centre due to this interaction causing an overall decrease of the electronic charge at the metal centre. This is responsible for the decreased d–π* back donation resulting in an increase in the lability of the CO ligand. Studying the reactivity of the hydrogenated Vaska complex with D_2 we have observed that the formation of the mixed isotopomer $HDIr(CO)Cl(PPh_3)_2$ proceeds through the reaction pathway shown in Scheme 2 whose activation energy is decreased by the formation of an intermolecular hydrogen bond through the Cl ligand with strongly acidic proton donors such as perfluorurated alcohols and trifluoroacetic acid.

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