Chapter 14

Double Cyclometalation: Implications for Carbon-Hydrogen Oxidative Addition With PCP Pincer Compounds of Iridium

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Treatment of 4-X-C₆H₄-2,6-(CH₂P'^Bu₂)₂ (X = H (1), NO₂ (2), MeO (3)) with IrCl₃.nH₂O in 2-propanol/water generates the corresponding cyclometalated pincer chlorohydrido iridium complexes (1a – 3a). In the case of 3, a second intramolecular oxidative addition reaction of one of the t-butyl C-H bonds to the Ir(III) center, followed by the reductive elimination of H₂, gives the novel doubly metalated compound 3b, which is stable to air and water. Comparative electrochemical studies of 1a and 3a establish an equilibrium between the pincer chlorohydrido compound and the doubly metalated complexes 1b, 3b and H₂. A square scheme can be used to describe the relationship between the redox couples and solution equilibria. Interestingly the oxidation product 1b⁺ undergoes a faster follow-up reaction as 3b⁺. The unusual stability of the doubly metalated complex was supported by DFT calculations at different levels of theory on model compounds.
Introduction

Meridional, anionic or neutral tri-dentate ligands (1,2) are often called pincer compounds (3). Although these ligands were first reported in the 1970’s (4,5), their design has been recently expanded to include a variety of donor atoms and spacer backbones (6). Specifically, the ligands contain donor atoms that are able to coordinate a central atom in a trans fashion. Moreover, these donor atoms are anchored to spacer groups as a backbone. If the backbone is rigid, and/or planar, metal complexation can generate a thermally very stable system (7). The popularity of the ligands has increased because they have favorable properties when treated with transition metal compounds (8). The ligands can have variable bite angles which can control the steric environment and the shape of the frontier orbitals, they can synthetically self-assemble different metals (8,9), and they have catalytic potential (10,11).

Over the years many research groups have exploited the synthesis and chemistry of various (PCP)[M] pincer metal complexes ([M] = Rh, Ir, Ru, Pt fragments) (8), e.g. the complexation of C₆H₄-1,3-(CH₂P₂Bu₂)₂ to a metal fragment generates two internal five-membered metallacycles and in the case of a d⁵ Ir(III) metal center a square-pyramidal coordination geometry (8). One of the catalytic pathways for which such complexes show considerable promise, is alkane dehydrogenation, in particular, with anthraphos (PCP)Ir(III)H₂ (7) and (PCP)Ir(III)H₂ compounds (11). Theoretical calculations seem to be controversial, whether an associative or a dissociative mechanism is operative (7, 12-14). Consequently, an investigation of a model methoxy-functionalized PCP system is reported in this account in order to ascertain the importance of electronic and steric factors in the oxidative addition reactions of these complexes (15,16).

Results

Intramolecular C-H oxidative addition to Ir(III)

The pincer ligands 1 (4), 2 (17), and 3 (15) (Chart 1) have been synthesized according to procedures which have been described in the literature. The pincer complex 2a (Scheme 1) was prepared in an analogous way as 1a (4) by heating a 2-propanol/water solution of 2 in the presence of IrCl₃:nH₂O to 80 °C. As revealed by NMR spectroscopy and X-ray structure analysis the red complex 2a forms a square-pyramidal arrangement of the iridium bound atoms with the hydride in the apical position (17). Thus the structure is fully compatible with that of 1a (Scheme 1).
In contrast to this, treatment of the methoxy functionalized ligand 3 with IrCl$_3$·nH$_2$O in 2-propanol/water gave a reaction mixture from which deep red crystals were isolated and identified as the doubly cyclometalated Ir(III) complex 3b (Scheme 1). In addition, 3a was also present in the reaction mixture. Changing to a non-polar reaction medium by treating 3 with stoichiometric amounts of [Ir(COE)$_2$Cl]$_2$ in toluene also leads to reaction mixtures which contain both 3a and 3b. The ratio of 3a : 3b varies with reaction time and temperature and the amount of hydrogen present in the system. Thus, if hydrogen is allowed to escape from the reaction mixture, only 3b is observed. On the other hand, if 3b is treated with hydrogen, 3a is formed exclusively. This behavior indicates that the chlorohydrido complex 3a is in equilibrium with the doubly cyclometalated complex 3b + H$_2$. The deep red complex 3b can be handled and stored under air for weeks and melts at 200 °C without decomposition.

The oxidative addition of one t-butyl C-H bond to the iridium in 3a causes the formation of an additional four-membered ring and the loss of any symmetry in the molecule. Thus the $^3$P{H} NMR spectrum of 3b shows two doublets at $\delta$ 50.8 and 9.8 which are assigned to P'Bu$_2$ and P'Bu, respectively. The large phosphorus-phosphorus coupling of 351.1 Hz agrees with the mutual trans position of the two phosphine groups. Three resonances, which are split by the interaction with the corresponding adjacent phosphorus nucleus, are observed for the intact t-butyl groups in the $^1$H and $^{13}$C{H} NMR spectra. The resonance of the metal bound CH$_2$ group is shifted to $\delta$ -6.7 in the $^{13}$C{H} NMR spectrum and is split into a doublet of doublets by a large and a small phosphorus carbon interaction. There is no indication of either hydride or hydrogen weakly bound to iridium in the $^1$H NMR spectra at different temperatures.

The stereochemistry of 3b was established by an X-ray structure analysis in the solid state and is compatible with the structure shown in Scheme 1 (15).
Scheme 1

L = CO (e,h); NH₃ (f,i); CH₃CN (g,j)
X = H (1); NO₂ (2); OMe (3)
Complex 3b crystallizes in the monoclinic space group $P2_1/n$. The coordination geometry around iridium is best described as distorted square-pyramidal. The iridium atom deviates only by 0.016 Å from the basal plane. Interestingly, the bond lengths and angles involving the atoms in this plane are comparable to those found for 2a (15,17). Due to the constraints of the four-membered ring the two Ir-P distances differ considerably. The four-membered ring is located nearly perpendicular to the basal plane.

Note when a sample of 2a is stored over a longer period of time (> 9 months) it is completely converted into 2b (18).

**Reactivity of complexes 3a,b**

Reactions of complexes 3a,b are presented in Scheme 1. Treatment of solutions of either 3a or 3b in THF with NaNH under a hydrogen atmosphere gives iridium tetrahydride 3c in nearly quantitative yield. If the solvent is removed under vacuum or by a stream of argon the iridium dihydride 3d is obtained exclusively. The hydrides 3c,d (15,16) were characterized by their NMR spectra which are fully compatible with those of the analogous PCP pincer complexes 1c,d (19,20).

Different products are observed when the deep red solutions of 3a and 3b in benzene are treated with carbon monoxide, ammonia and acetonitrile, respectively. In all cases the color changes immediately to pale red (3f,g; 3i,j) or even off white solutions (3e, 3h). The spectroscopic data of the complexes 3e-j agree with the structures displayed in Scheme 1 and in the case of 3e are compatible with those reported for \(\text{C}_6\text{H}_3\text{H}_2\text{H}_2\text{CH}_2\text{P}(\text{Me})_2\text{Ir}-(\text{CO})(\text{H})\text{Cl} (1e)\) (4). The structure of 3h was established by an X-ray analysis (Figure 1). The AB pattern in the $^{31}\text{P}$-$^1\text{H}$ NMR spectra, the number of resonances and their multiplicities in the $^1\text{H}$ and $^{13}\text{C}$-$^1\text{H}$ NMR spectra of the complexes 3h-j are comparable with those of the educt 3b and demonstrate that the four-membered ring is maintained. Characteristic absorptions in the infrared are observed at 1987 cm$^{-1}$ (3e) and 1990 cm$^{-1}$ (3h) for the CO stretching vibration.

In summary these investigations demonstrate that bonding of any donor ligand at 3b is preferred at the empty coordination side trans to the CH$_2$ group. Stable complexes (3h, 3i) are formed depending on the donor ligand. The CH$_3$CN molecule is only weakly bound which prevents the isolation of 3j. It can be concluded from this that the weak donor H$_2$ coordinates, in the back reaction of 3b + H$_2$, to the empty coordination site before the final conversion to 3a takes place.

**Electrochemical studies**

The redox properties of 1a, 3a and 3b were investigated by cyclic voltammetric experiments in a dichloromethane/tetra-$n$-butylammonium
hexafluorophosphate 0.1 M electrolyte at a Pt-electrode at various scan rates. All compounds are oxidized at potentials a few hundred mV positive of the ferrocene standard potential (22).

The electrochemical behavior of 3a and 3b was already described qualitatively (15). While 3b exhibits a reversible one-electron wave, which indicates oxidation to a Ir(IV) complex 3b$^+$ and re-reduction of the latter species (Figures 2a,b), chlorohydride 3a shows a more complicated voltammetric signal (Figures 2c,d).

The overlapping oxidation peaks at slow scan rates $v$ and the variation of the reverse peaks with $v$ indicate that oxidation of 3a follows a square-scheme in which two electron transfers and two chemical equilibrium reactions are coupled (23,24). Comparison of the cyclic voltammograms of 3a and 3b suggests that the current/potential curves are easily explained if 3a is in equilibrium with 3b$^+$ + H$_2$. Then 3b gives rise to the peak couple at ≈ 0.18 V vs. the ferrocene standard, while 3a undergoes one-electron oxidation at ≈ 0.27 V. In the oxidized state, we find an equilibrium between 3a$^+$ and 3b$^+$ + H$_2$.

The experimental curves were modelled with the DigiSim simulation program (25) and the data could be reproduced under the assumption that the equilibrium in the Ir(III) state is in favor of 3a (in accordance with the observations discussed in earlier paragraphs of this paper), while it is shifted to the side of 3b$^+$ in the Ir(IV) state. Thus, electron transfer allows switching of the relative stabilities of the chlorohydrido and the doubly cyclometalated complex. Moreover, the computer simulations indicate that 3b$^+$ undergoes a slow follow-up reaction to form an electroinactive product X (Scheme 2a). Details of the simulations and a quantitative discussion will be published separately (26).
Figure 2. Experimental voltammograms (circles) and computer simulations (lines) of 3a (c = 0.2 mM) and 3b (c = 0.6 mM) in CH$_2$Cl$_2$. a) 3b, v = 100 mV, b) 3b, v = 2 V/s, c) 3a, v = 100 mV/s, d) 3a, v = 2 V/s.
Qualitatively, the cyclic voltammograms of 1a (Figure 3) are similar to those of 3a in particular as regards overlapping of the oxidation signals and the behavior of the reduction peaks. However, in accordance with the electron-donating properties of the methoxy substituent in 3a, 1a is oxidized at considerably higher potentials than 3a. Furthermore, the intensity of the oxidation signal is enhanced in 1a as compared to the case of 3a.

The simulations of the voltammograms indicate the presence of a further oxidation step starting from the species C$^+$ formed as a product of the follow-up reaction of 1b$^+$ (Scheme 2b). A reaction to species D$^{2+}$ had to be included into the calculations. The identity of species C$^+$, C$^{2+}$, and D$^{2+}$ is not yet defined. However, possibly the additional oxidation step leads to an Ir(V) complex. Thus the oxidation current increases over that expected from the square scheme (Scheme 2a).
Quantum Chemical Calculations

The unusual finding of the stable complex 3b prompted us to perform density functional calculations at various levels of theory for the model compounds shown in Figure 4 as well as for complex 3b presented in Scheme 1. Because X-ray structures of the square-pyramidal complex 2a and the doubly metalated complex 3b have been reported (17), experimental and theoretical data for the two types of structures represented by 3a and 3b can be compared. In the case of the model complexes only one t-butyl group was retained during the calculations, the other three groups were replaced by hydrogen atoms in order to reduce the computational effort. The geometric structures of 2a’,b’,k’ and 3a’,b’,k’ were optimized in the local density approximation (SVWN (27)) as well as with the gradient-corrected B3LYP (27) hybrid functional. For this purpose, the effective core potential SDD (27) and LACVP* (28) basis sets were applied using the programs Gaussian 98 (27), Jaguar (28) and Titan (29). In the case of 3b, structure optimizations were performed at the SVWN/LACVP* and B3LYP/LACVP* levels of approximation.

The relative thermodynamical stabilities of the model complexes are presented in Figure 4. Almost parallel trends in the theoretical energy differences are obtained for the methoxy and the nitro compounds. All computational procedures predict the square-pyramidal chlorohydrido complexes 2a’, 3a’ to be most stable. The structures 2k’, 3k’ are higher in energy by ca. 16 to 30 kcal/mol, depending on whether the SVWN or the B3LYP approach is applied. The B3LYP method leads to pronounced larger energy differences (Figure 4).
The doubly cyclometalated 2b' and 3b' (+ H₂) are predicted to be highest in energy: they are energetically less stable than 2a', 3a' by about 34 (2a', B3LYP/LACVP*) to 39 kcal/mol (3a', SVWN/SDD(f)). Here, higher relative energies are obtained in the SVWN approximation.

In the case of 2k', 3k' the bonding of the two hydrogen atoms to iridium may be best described as η²-coordinated H₂. The calculated H-H and Ir…Hav. distances in these complexes drastically depend on the computational approach. At the SVWN level of theory longer H-H bonds (0.883 to 0.902 Å) and shorter Ir … Hav. distances (1.769 to 1.807 Å) are obtained as compared to the B3LYP calculations (H-H: 0.789 to 0.799 Å, Ir … Hav.: 1.905 to 1.930 Å). In any case, the H-H distances in 2k', 3k' are longer than the theoretical bond length predicted for the H₂ molecule (0.743 (B3LYP/LACVP*) and 0.763 Å (SVWN/LACVP*),

Figure 4. Computed thermodynamic stabilities (kcal/mol) for the model complexes (--- SVWN, ---- B3LYP).
respectively). Likewise, the Ir--Hav. distances in these complexes are much longer than the Ir-H bonds in 2a', 3a' (1.555 (B3LYP/SDD(f), 2a') to 1.587 Å (SVWN/LACVP*, 3a')). These remarkable differences in structural features for 2k', 3k' as obtained by the SVWN and B3LYP methods, respectively, correspond to the trends in the relative energies (Figure 4). The SVWN approximations predict 2k', 3k' to be closer in energy to 2a', 3a' as compared to the B3LYP results. On the other hand, the B3LYP energies are closer to those obtained for complexes 2b', 3b' (+ H2) than the energies calculated at the SVWN level of theory (Figure 4).

Relevant structural parameters of 3b as obtained by X-ray diffraction and density functional calculations (B3LYP/ LACVP*, SVWN/LACVP*) have been compared (15). The same distorted square-pyramidal coordination geometry around iridium as observed in the experiment is predicted by the computational procedures. The overall agreement between the experimental crystal structure and the gas-phase structures as calculated for 3b by both theoretical procedures is very good. The energy profile displayed in Figure 4 agrees with that one calculated for the intermolecular C-H activation by \{C6H1-2,6-(CH2PttBu2)2\}IrH2 (12,13).

**Discussion**

Complex 3b is the result of two consecutive intramolecular C-H bond activations (Scheme 1) (30,31). We had previously shown that in the case of the PCP pincer complex \{Bu2PCH2CH2CHCH2CH2PttBu2\}IrH2 there is an equal ease with which t-buty! and the ligand backbone C-H bonds can be activated (32). In contrast to this all experimental and theoretical data agree with the phenyl iridium bond formation being preferred over the t-buty! C-H activation in the case of 3b. This way a bis-chelate with two thermodynamically stable internal five-membered rings is generated. The analogy to the Thorpe-Ingold effect, where geminal dialkyl groups enhance ring closure, was emphasized by Shaw (5,33). The formation of the phenyl iridium bond occurs first, despite the greater number of methyl C-H bonds, because this bond is stronger than the cyclometalated alkyl iridium bond from the t-buty! group (34). Thus, calculations sustain the observation that 2a', 3a' are thermodynamically the most stable complexes.

Interestingly enough, the oxidative addition of a C-H bond of one of the t-buty! groups to the metal center in complexes of the type 1a to generate an isolable complex has not been reported before. For this reason, it is difficult to explain why 3b, with two cyclometalated bonds and easily melting at 200 °C, forms at all, since the calculations show that it is thermodynamically less stable than 3a and 3k' (Figure 4). Furthermore, why is this reaction not observed for 1a?

The most likely attack of a t-buty! methyl C-H bond is at the free coordination site opposite to the hydride ligand in 3a. This will generate a seven
coordinate Ir(V) dihydride chloride complex, which rearranges to give the Ir(III) dihydrogen complexes $3k'$, $3k''$. Although $3k'$ was not observed spectroscopically, its theoretical existence was demonstrated by quantum chemical calculations (Figure 4). Comparable $\eta^2$-$H_2$ complexes are well established (35). As demonstrated by the electrochemical studies, complex $3b + H_2$ is in equilibrium with $3a$, the equilibrium being on the side of the chlorohydrido complex $3a$. This explains why there is no indication of an $\eta^2$-$H_2$ complex in the $^1H$ NMR spectra. The loss of $H_2$ from $3k'$ leads to the thermodynamically least stable product $3b$. This is only achieved if $H_2$ is allowed to escape from the reaction mixture, which renders the overall process irreversible. Moreover, this is consistent with the observation that the presence or absence of hydrogen in the reaction mixture regulates the amounts of $3a$ and $3b$ regardless of different solvents and temperatures during the reaction. Thus, if $H_2$ is added to pure $3b$, the hydrochloride complex $3a$ is formed exclusively. In this case the attack of hydrogen will occur at the empty coordination site, which is trans to the iridium bound CH$_2$ group, and the $\eta^2$-$H_2$ complex $3k'$ will be formed. In order to reductively eliminate the $t$-butyl C-H bond, the dihydrogen complex has to rearrange to give a Ir(V) dihydride intermediate with at least one hydride ligand cis to the CH$_2$ group bound to iridium. This is the microscopic reverse of the $t$-butyl C-H activation (vide infra). That the empty coordination site trans to the CH$_2$ group is easily accessible to donor ligands was demonstrated by the reaction of $3b$ with CO, ammonia and acetonitrile which gave the complexes $3h$-$j$.

The electrochemical data indicate that one-electron transfer oxidation of both 1a and 3a reverses the stability of the two central species related to C-H activation by the Ir-PCP-pincer complexes. While the open chlorohydride form is favored in the Ir(III) oxidation state, after oxidation the doubly-cyclometalated species prevailed. In contrast to 3a, however, where the one-electron oxidation product $3b'$ of the square scheme reacts only slowly, 1b$^+$ quickly undergoes further transformation. This leads to further oxidation and might be a reason why the intramolecular C-H insertion product was never observed when working with unsubstituted 1a.

**Conclusion**

The isolation and X-ray crystal structure of $3b$ shows that pincer complexes with pendant P'BuC$_2$ groups can undergo thermally stable multiple C-H insertion reactions by consecutive cyclometalations. The experimental data reveal that in solution there is an equilibrium between $3a$ and $3b + H_2$ which implies C-H oxidative addition via an Ir(V) oxidation state. Loss of hydrogen is the thermodynamic driving force for the isolation of $3b$. Electrochemical oxidation accelerates the C-H activation via an Ir(IV) state. Although our calculations show hardly any differences in the case of 2a, 2b and 3a, b a more detailed analysis of substituent effects in pincer complexes display a reduced reactivity
of \([\{X-C_6H_2-2,6-(CH_2PMe_2)_2\}Ir]\) fragment towards C-H bonds when going from \(X = \text{MeO} > \text{H} > \text{NO}_2\) (16) which is in agreement with the results discussed here.

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References