Iridium Pincer Complexes

Effect of Ligands on the Lewis Acidity of the Metal and the Binding of N-Bases to Iridium Pincer Complexes


Abstract: The coordination of pyridine (Py) and benzonitrile (PhCN) to benzene based pincer hydridochlorides [(PCP)IrH(Cl)] (1), [(POCOP)IrH(Cl)] (2), [(EtO(O)C-POCOP)IrH(Cl)] (3), and [(PCN)IrH(Cl)] (4) was studied spectroscopically and computationally to deduce the ligand influence. The variable temperature NMR (1H, 31P, 15N) and UV/Visible spectroscopic measurements revealed preferential coordination of these N-donor ligands in the apical position of 1–4 and gave the formation enthalpies for the hexacoordinate complexes, which follow the order: 1 ≈ 4 > 3 > 2. This order nicely agrees with the order of Lewis acidity obtained for these complexes in DFT calculations. The orbital and electron density distribution analysis were performed at the DFT/M06 theory level for 1–4 and a series of p-substituted PCP-based hydridochlorides. The increasing Lewis acidity of iridium [as a maximum energy, $V_{S,max}$ of molecular electrostatic potential (MEP)] correlates with decreasing basicity of Cl-ligand (as MEP minimum, $V_{S,min}$) as well as with Hammett $\sigma_p$ parameters of $p$-substituents. Importantly, these properties are conserved upon conversion into the corresponding dihydrides, as shown on the example of 1 and 4.

Introduction

Complexes of transition metals based on 1,3-bis[(di-tert-butylphosphanyl)methyl]benzene (PCP) are known to be effective catalysts for various processes.[1] Among them, ($\kappa^3$-PCP-pincer)-ligated iridium systems are preferred for transfer dehydrogenation and acceptorless dehydrogenation catalysis.[2] As a result of extensive studies, different modifications of the original ($\kappa^3$PCP) ligand complex have been developed,[3] which include the use of different donor groups instead of phosphane, the introduction of the electron-donating or electron-withdrawing substituents to the aromatic backbone, or replacement of the CH$_2$ bridges by oxo- or other linkers.[4]

Pincer-supported iridium hydridochlorides are typically used only as precursors for di- or tetrahydrides or even 14-electron monovalent [pincer]Ir species, which found extensive use as catalysts for alkane dehydrogenation, dehydrogenative coupling, and other reactions.[3,5] However recent studies bring evidence that hydridochlorides can be directly used in transfer dehydrogenation or amine-boranes dehydrogenation.[6]

In the latter reaction the pre-catalyst activation is shown to involve hexacoordinate complexes in which iridium center serves as a Lewis acid interacting with borohydride fragment and chloride ligand – as a basic site interacting with NH-proton.[6a,6b] The aim of this work is to access experimentally the influence of pincer’s properties (steric and electronic) on the Lewis acidity of the core metal and on the stability of hexacoordinate iridium complexes. For this purpose, we chose classic PCP-based hydridochloride complex 1, the POCOP-based complexes 2 and 3 as well as the recently described[6a] less hindered derivative of complex 1, bearing the pyrazole substituent instead of one -CH$_2$P$_2$Bu$_3$ arm (4, Scheme 1). Variable temperature studies by NMR and UV/Vis spectroscopy allowed to deduce the structure of their hexacoordinate adducts with pyridine (Py) and benzonitrile (PhCN) and to estimate relative stability of these complexes showing preferential coordination of N-ligands in the apical position (trans to the hydride ligand; designated here as isomers a). DFT calculations were performed at the M06 theory level for these complexes as well as for the series of para-substituted PCP-based complexes and their nitrile adducts to get details of the orbital composition and electron density distribution, which underpin the complexes bifunctional reactivity as proton acceptor and Lewis acid.

Results and Discussion

Binding of Pyridine

Recently, we have shown that the interaction of [(PCP)IrH(Cl)] (1) with pyridine yields instantaneously and quantitatively hexacoordinate complexes 1-Py$_a$ and 1-Py$_b$ (Scheme 2,
Table 1. Selected NMR parameters (chemical shifts in [ppm], spin-spin coupling constants J in Hz) for pentacoordinate hydridochlorides 1–4 and their complexes with pyridine (in CD2Cl2 at 200 K).

<table>
<thead>
<tr>
<th>Complex</th>
<th>1H</th>
<th>31P{1H}</th>
<th>15N[a]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(PCP)IrH(Cl) (1)</td>
<td>–43.40</td>
<td>66.70</td>
<td>–</td>
</tr>
<tr>
<td>(PCP)IrH(Cl)(Py) (1·Py_a)</td>
<td>–21.64</td>
<td>46.10</td>
<td>–138.7</td>
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<tr>
<td>(PCP)IrH(Cl)(Py) (1·Py_b)</td>
<td>–22.69</td>
<td>50.10</td>
<td>–149.5</td>
</tr>
<tr>
<td>(POCOP)IrH(Cl) (2)</td>
<td>–41.34</td>
<td>175.48</td>
<td>–</td>
</tr>
<tr>
<td>(POCOP)IrH(Cl)(Py) (2·Py_a)</td>
<td>–21.25</td>
<td>154.43</td>
<td>–136.0</td>
</tr>
<tr>
<td>(POCOP)IrH(Cl)(Py) (2·Py_b)</td>
<td>–22.69</td>
<td>153.55</td>
<td>–</td>
</tr>
<tr>
<td>(EtOC(O)-POCOP)IrH(Cl) (3)</td>
<td>–40.74</td>
<td>176.78</td>
<td>–</td>
</tr>
<tr>
<td>(EtOC(O)-POCOP)IrH(Cl)(Py) (3·Py_a)</td>
<td>–20.90</td>
<td>56.25</td>
<td>–233[e]</td>
</tr>
<tr>
<td>(EtOC(O)-POCOP)IrH(Cl)(Py) (3·Py_b)</td>
<td>–23.55</td>
<td>153.55</td>
<td>–221[e]</td>
</tr>
<tr>
<td>(PCN)IrH(Cl) (4)</td>
<td>–39.71</td>
<td>56.25</td>
<td>–138.1</td>
</tr>
<tr>
<td>(PCN)IrH(Cl)(Py) (4·Py_a)</td>
<td>–23.55</td>
<td>153.55</td>
<td>–221[e]</td>
</tr>
<tr>
<td>(PCN)IrH(Cl)(Py) (4·Py_b)</td>
<td>–24.70</td>
<td>153.55</td>
<td>–233[e]</td>
</tr>
</tbody>
</table>

[a] δN = –167 ppm for free pyridine. [b] Data from ref.[7] [c] Not observed because of low concentration. [d] At room temperature. [e] Assigned on the base of 1H-15N HMBC (see Figure S2).

Table 1.[7] At room temperature the pyridine binding is also quantitative in the case of pyrazolate-containing complex 4 (no signals of the starting material 4 are observed in NMR spectra), but not in the case of [(POCOP)IrH(Cl)] (2) and [(EtOC(O)-POCOP)IrH(Cl)] (3). For these complexes the equilibrium (Scheme 2) shifts to the right with the temperature decrease. The amount of 2·Py increases from 81.9 % at 270 K to ≈ 99 % at 200 K, while the amount of 3·Py increases from 92.2 % at 270 K to ≈ 99 % at 240 K.

Scheme 2. Formation of two isomers upon the sixth ligand binding.

The apical coordination of the ligand in isomers a was confirmed by using 15N-labeled pyridine, which gives a hydrido-15N splitting of ca 18 Hz for the corresponding hydrido resonances (Table 1). The resonances of 1·Py_a - 3·Py_a appear as pseudo-quartets at low temperatures (Figure 1, Figure S1), whereas for 4·Py_a it is a pseudo-triplet (Figure 2); all because of $2J_{NH} \approx 2J_{PH}$ (Table 1). Such a strong effect evidences the coordination of pyridine trans to the hydride ligand.[7,8] The dissociative exchange is evident from the broadening of the hydride resonances of apical isomers at room temperature (Figure 1, Figure 2). The apical isomers a are predominant for both 2·Py and 3·Py, the isomers ratio being 24.9:1 and 23.2:1, respectively, at 210 K decreasing to 17.8 and 18.7 at 270 K (Table S1). This is quite different from 2.5:1 ratio observed for 1·Py_a/1·Py_b or 5:1 ratio found 4·Py_a/4·Py_b that could be the result of different steric protection of iridium centers in 1–4. Another interesting point is that coalescence temperature for the resonance of isomer a is lower for 4·Py_a (220 K) than for 1·Py_a (260 K). That supports stronger pyridine binding to 1 than for 4.

Figure 1. Variable temperature 1H NMR spectra (600 MHz, hydride region) for (POCOP)IrH(Cl)(Py) (2·Py) obtained in situ by addition of 1 equiv. pyridine-15N to [(POCOP)IrH(Cl)] (2, c = 0.01M) in CD2Cl2.

Binding of Benzonitrile

Careful VT NMR measurements for all four pincer complexes 1–4 revealed that hexacoordinate species 1·PhCN – 4·PhCN formed in the reaction with benzonitrile also exist as two isomers with apical (a) and equatorial (b) coordination of PhCN (Scheme 2). The behavior of their signals in 1H and 31P NMR spectra resembles that of the resonances of pyridine-containing complexes 1·Py – 4·Py thus allowing the signals assignment (Table 2). The hydride signals of minor isomers b are well resolved at all temperatures, whereas those of isomers a are nar-
row only at low temperatures (190–220 K), broadening into a
baseline with the temperature increase (Figure 3, Figures S3, S4).
The major signals in $^{31}\text{P}^\text{1H}$ NMR spectra appear as
singlets with the same temperature behavior as that of $\delta_{\text{H}}$
$1\cdot\text{PhCN}_a$ – $3\cdot\text{PhCN}_a$ (Figures S5–S7). The values of the $^{2}J_{\text{PH}}$
coupling constants determined for these nitrile complexes are
similar to those of the starting 5-coordinate complexes and are
consistent with cis hydride-phosphorus ligand arrangements
in both apical (a) and equatorial (b) isomers.

Table 2. Selected NMR parameters (chemical shifts in [ppm], spin-spin
coupling constants $J$ in Hz) for benzonitrile complexes $1\cdot\text{PhCN}$ - $4\cdot\text{PhCN}$ (in
$\text{CD}_{2}\text{Cl}_{2}$ at 200 K).

<table>
<thead>
<tr>
<th></th>
<th>$^{1}\text{H}$</th>
<th>$^{31}\text{P}^\text{1H}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[(\text{PCP})\text{IrH(Cl)(L)}]$</td>
<td>$1\cdot\text{PhCN}_a$</td>
<td>$-19.61$ ($\delta_{\text{H}} = 14.1$)</td>
</tr>
<tr>
<td>$[(\text{PCP})\text{IrH(Cl)(L)}]$</td>
<td>$1\cdot\text{PhCN}_b$</td>
<td>$-22.21$ ($\delta_{\text{H}} = 14.8$)</td>
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<tr>
<td>$[(\text{POCOP})\text{IrH(Cl)(PhCN)}]$</td>
<td>$2\cdot\text{PhCN}_a$</td>
<td>$-15.87$ ($\delta_{\text{H}} = 14.6$)</td>
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<tr>
<td>$[(\text{POCOP})\text{IrH(Cl)(PhCN)}]$</td>
<td>$2\cdot\text{PhCN}_b$</td>
<td>$-21.45$ ($\delta_{\text{H}} = 14.6$)</td>
</tr>
<tr>
<td>$[(\text{EtOC(O)-POCOP})\text{IrH(Cl)(PhCN)}]$</td>
<td>$3\cdot\text{PhCN}_a$</td>
<td>$-19.60$ ($\delta_{\text{H}} = 14.5$)</td>
</tr>
<tr>
<td>$[(\text{EtOC(O)-POCOP})\text{IrH(Cl)(PhCN)}]$</td>
<td>$3\cdot\text{PhCN}_b$</td>
<td>$-20.95$ ($\delta_{\text{H}} = 14.5$)</td>
</tr>
<tr>
<td>$[(\text{POCOP})\text{IrH(Cl)(PhCN)}]$</td>
<td>$4\cdot\text{PhCN}_a$</td>
<td>$-22.53$ ($\delta_{\text{H}} = 20.7$)</td>
</tr>
<tr>
<td>$[(\text{POCOP})\text{IrH(Cl)(PhCN)}]$</td>
<td>$4\cdot\text{PhCN}_b$</td>
<td>$-24.28$ ($\delta_{\text{H}} = 20.7$)</td>
</tr>
</tbody>
</table>

Figure 2. $^{1}\text{H}$ NMR spectra (600 MHz, hydride region) for $[(\text{PCP})\text{IrH(Cl)(Py)}]$ ($4\cdot\text{Py}$) obtained in situ by addition of 1 equiv. pyridine-$^{15}\text{N}$ to $[(\text{PCP})\text{IrH(Cl)(Py)}]$ in $\text{CD}_{2}\text{Cl}_{2}$.

Figure 3. Variable temperature $^{1}\text{H}$ NMR spectra (300 MHz, hydride region) for $[(\text{EtOC(O)-POCOP})\text{IrH(Cl)(PhCN)}]$ ($3\cdot\text{PhCN}$) obtained in situ by addition of 1 equiv. benzonitrile to $[(\text{EtOC(O)-POCOP})\text{IrH(Cl)}]$ ($3\cdot\text{L}$) in $\text{CD}_{2}\text{Cl}_{2}$ (c = 0.02 M).

The different relative stability of benzonitrile complexes is
qualitatively reflected in the temperatures at which their signals
become visible in the NMR spectra. Whereas PCP based complex
$1\cdot\text{PhCN}$ (its isomer $1\cdot\text{PhCN}_b$ is visible already at room
temperature, the signals of its POCOP analogues appear only at
230 K (complex 2$\cdot\text{PhCN}$) and 240 K (complex 3$\cdot\text{PhCN}$) (Figure 3, Figures S3–S7). As already observed for pyridine complexes, the
complexation equilibrium shifts toward $1\cdot\text{PhCN}$ – $3\cdot\text{PhCN}$ with
cooling. Simultaneously the isomers ratio $a:b$ increases with
temperature decrease, being about 15:1 for $1\cdot\text{PhCN}$, 12.5:1 for
3$\cdot\text{PhCN}$ and 8.3:1 for 2$\cdot\text{PhCN}$ at 230 K (Table S1).

The strongest benzonitrile binding is observed for
$[(\text{PCP})\text{IrH(Cl)(Py)}]$, which forms hexacoordinate complex $4\cdot\text{PhCN}$ quantitatively already at room temperature. The $^{1}\text{H}$ and $^{31}\text{P}$ signals of the starting hydridochloride $4$ disappear upon addition of an equimolar amount of PhCN and simultaneously new reso-
nances of $4\cdot\text{PhCN}_a$ and $4\cdot\text{PhCN}_b$ appear in the spectra in
1:1 ratio (Figure 4). The signals broadening due to the fast disso-
ciative exchange is observed at r.t., but as in all other cases the
resonances sharpen upon cooling. The position of hydride sig-
nal of $4\cdot\text{PhCN}_a$ is strongly temperature dependent, it drifts to
lower field with the temperature decrease and becomes sharp
only below 220 K (Figure 4). In contrast, the hydride resonance
of $4\cdot\text{PhCN}_b$ resolves into sharp doublet already at 270 K and changes its position only slightly between 270 and 200 K.

Thermodynamics of Hexacoordinate Complexes

Stability of the hexacoordinate complexes $1\cdot\text{L}$ - $3\cdot\text{L}$ was estimated using the quantitative UV/Vis measurements. The start-
ing pentacoordinate hydride complexes $1$ - $4$ are red and their
UV/Visible spectra feature three rather wide overlapping bands
at ca. 420–510 nm (Figures S8–S10, Table 3) belonging to d$^{10}$
transitions of three lone electron pairs. These bands shift to low
wavenumbers on going from $1$ to $3$, i.e. with lowering of the
ligand electron donating ability.

As all hexacoordinate complexes are colorless, the ligands
addition to $1$ - $3$ leads to the fading of the original color and
lowering of the UV/Vis bands intensities (Figure 5). The latter
was used to quantify the amount of the hexacoordinate com-
plex formed at different temperatures. Using the isomers $a:b$
ratio determined by integration of the corresponding hydride
signals in $^{1}\text{H}$ NMR (vide supra) allowed calculations of the for-
mation constants $K$ for each isomer$^{34}$ and, ultimately, of forma-
tion enthalpy, $\Delta H^\circ$, and entropy, $\Delta S^\circ$ (Table 4; Figures S11–S15).

Inspection of the data obtained (Table 4) shows that for all
the complexes studied the isomers $a$ are thermodynamically
more preferred, featuring more negative formation enthalpies
than isomers $b$. Experimental $\Delta S^\circ$ values for complexes with
PhCN are as expected for a reaction going from two to one
particle and in good agreement with computationally predicted
values (vide infra). For pyridine, they are almost twice lower
than for PhCN. For similar L (PhCN or Py) stability of isomers
$1:b$ increases with $\Delta H^\circ$ and its reactivity toward N-donor ligands. The introduction of
electron accepting EtOC(O)-group in the
phosphorus pentoxide decreases the Lewis acidity of iridium center
and its reactivity toward N-donor ligands. The introduction of
electron accepting EtOC(O)-group in the para-position of cyclo-
Figure 4. Variable temperature $^1$H (400 MHz, hydride region; left) and $^{31}$P($^1$H) NMR spectra (162 MHz, right) of [(PCN)IrH(Cl)(PhCN)] (4·PhCN) obtained in situ by addition of 1 equiv. PhCN to 4 in CD$_2$Cl$_2$.

Table 3. Parameters of absorption bands in electronic spectra of 1–4 in CH$_2$Cl$_2$ (band maxima $\lambda$ in nm, molar extinction coefficients $\varepsilon$ in M$^{-1}$ cm$^{-1}$) at room temperature.

<table>
<thead>
<tr>
<th></th>
<th>$\lambda_1$</th>
<th>$\varepsilon_1$</th>
<th>$\lambda_2$</th>
<th>$\varepsilon_2$</th>
<th>$\lambda_3$</th>
<th>$\varepsilon_3$</th>
<th>$\lambda_4$ [eV]$^{[a]}$</th>
<th>$E_{\text{LUMO}}$ $^{[b]}$</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>434</td>
<td>1011</td>
<td>485</td>
<td>872</td>
<td>511</td>
<td>778</td>
<td>2.56</td>
<td>–1.39</td>
</tr>
<tr>
<td>2</td>
<td>430</td>
<td>2544</td>
<td>476</td>
<td>2667</td>
<td>511</td>
<td>2094</td>
<td>2.61</td>
<td>–1.57</td>
</tr>
<tr>
<td>3</td>
<td>426</td>
<td>2676</td>
<td>467</td>
<td>3051</td>
<td>500</td>
<td>2198</td>
<td>2.66</td>
<td>–1.83</td>
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<tr>
<td>4 $^{[a]}$</td>
<td>427</td>
<td>222</td>
<td>480</td>
<td>183</td>
<td>512</td>
<td>70</td>
<td>2.58</td>
<td>–1.49</td>
</tr>
</tbody>
</table>

$^{[a]}$ In toluene. $^{[b]}$ In kcal/mol.

DFT Studies

In order to get a deeper insight into the origin of the experimentally observed trends we performed DFT calculations for five-coordinate hydridochlorides 1–4 and a series of para-substituted PCP-based complexes 5–10 (Scheme 3), EtOC(O)-substituent in complex 3 was modeled by MeOC(O)-. The geometry optimization was followed by the orbital and electron density distribution analysis. To characterize quantitatively the Lewis acidity of complexes 1–10 we optimized their adducts with CH$_3$CN as a model base. The thermochemical data obtained (Table S2) are in qualitative agreement with the experimental values obtained for [(pincer)IrH(Cl)(NCPh)] complexes.

The orbital analysis revealed that HOMOs of all complexes are located on the chloride ligand, the HOMO energy varying in the relatively narrow range of $-6.06 \div -5.13$ eV (Table 5). The LUMOs are the iridium d-orbitals, located perpendicular to the pincer plane and thus having impacts from both Ir atom and hydride ligand (Figure 6). The exception is the p-NO$_2$ complex 7 where LUMO is located on the NO$_2$ group, whereas the Ir-based orbital is LUMO+1. Since the observed UV/Vis transitions have d-d$^*$ nature, and HOMO and LUMO have a complex composition (Table 5) we chose LUMO energies as a reasonable

Table 4. Thermodynamic parameters ($\Delta H^\circ$, $\Delta S^\circ$) and formation constants $K$ at 190 and 290 K for complexes 1-L – 3-L.

<table>
<thead>
<tr>
<th>L</th>
<th>isomer</th>
<th>$\Delta H^\circ$ [kcal/mol]</th>
<th>$\Delta S^\circ$ [cal/mol K]</th>
<th>$K_{190} \times 10^{-4}$ L/mol</th>
<th>$K_{290}$ L/mol</th>
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</thead>
<tbody>
<tr>
<td>[(PCP)IrH(Cl)(L)] (1-L)</td>
<td>PhCN</td>
<td>a</td>
<td>–16.8</td>
<td>–47</td>
<td>84000</td>
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<tr>
<td></td>
<td></td>
<td>b</td>
<td>–8.4</td>
<td>–18</td>
<td>59</td>
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<tr>
<td>[(POCOP)IrH(Cl)(L)] (2-L)</td>
<td>PhCN</td>
<td>a</td>
<td>–7.3</td>
<td>–24</td>
<td>0.13</td>
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<tr>
<td></td>
<td></td>
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<tr>
<td></td>
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<td>a</td>
<td>–5.7</td>
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<td>[(EtOOCC-POCOP)IrH(Cl)(L)] (3-L)</td>
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<td>–23</td>
<td>1300</td>
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<td>b</td>
<td>–9.4</td>
<td>–24</td>
<td>31</td>
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</table>
Table 5. Computed parameters characterizing the impact of hydride and iridium into HOMO and LUMO, the orbitals energies, MEP extrema energies (\(V_{\text{S,max}}\) and \(V_{\text{S,min}}\)) and formation energies of hexacoordinate complexes with MeCN for hydridochlorides 1–10.

<table>
<thead>
<tr>
<th>Complex No.</th>
<th>Substituent</th>
<th>(\sigma_p)^{[a]}</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
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<tbody>
<tr>
<td>1</td>
<td>(\sigma_p)</td>
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<td>0.78</td>
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<td>0.32</td>
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<tr>
<td>2</td>
<td>(\sigma_p)</td>
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<td>1.39</td>
<td>1.57</td>
<td>1.83</td>
<td>1.49</td>
<td>1.49</td>
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<td>(\sigma_p)</td>
<td>3</td>
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<tr>
<td>(\Delta E_{\text{eq}}) (MeCN)^{[d]}</td>
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<td>7.3</td>
<td>7.8</td>
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<td>11.7</td>
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<td>(\Delta E_{\text{ap}}) (MeCN)^{[d]}</td>
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</table>


descriptor for experimental UV/Vis data. Indeed, for complexes 1–4 there is a correlation of the energy of the \(\lambda_2\) transition with LUMO energies (Table 3).

The molecular electrostatic potential (MEP) minima, \(V_{\text{S,min}}\), are also located on the Cl ligand in complexes 1, 4–10 and possess two extrema points (Figure 8), which correspond to the two occupied p-orbitals. This is in good agreement with the experimentally observed hydrogen bonding of alcohols and –NH\(_2\) to chloride.\(^{[7,10]}\) The introduction of COOMe and NO\(_2\) substituents (complexes 3, 7, 8) expectedly decreases the chloride basicity (see \(V_{\text{S,min}}\) in Table 5), and the global MEP minima in these complexes are located on the substituents’ oxygen atoms. Another interesting point is that POCOP complexes 2, 3 feature only one MEP minimum on the Cl atom. This corresponds to the big difference in the orbital shape of HOMO-3, in which chloride ligand p-orbital is engaged in the \(\pi\)-system of POCOP-ligand of 2 in contrast to POCOP complex 1 (Figure 7).

The local MEP maxima characterize the depletion of electron density and thus could be used to estimate the Lewis acidity of a particular center. In complexes 1–10 the MEP maxima are found near the Ir–H line perpendicular to the pincer (PCP) plane. They are located close to the hydride ligand and at the empty coordination place (near Ir atom, opposite to hydride; Figure 8) coinciding with the LUMO location (Figure 6).
Figure 7. HOMO-3 of complexes 2 (left) and 1 (right) as isosurface at 0.06 a.u. Hydrogen atoms of tBu substituents and an aromatic ring are removed, tBu ligand shown as a wireframe.

Thus, the substitution in the aromatic ring affects both basicity of chloride and acidity of the metal center, yielding a good linear correlation of $V_{S,\text{max}}$ vs. $V_{S,\text{min}}$ for PCP-supported complexes ($R^2 = 0.99$; Figure 9). The strongest electron accepting group NO$_2$ gives maximum depletion of electron density, making the chloride the least basic in the series and concomitantly leading to the highest $V_{S,\text{max}}$ values meaning the most acidic iridium. On the other end of the basicity row is the complex 1, and its $p$-MeO-substituted congener 9 with close $V_{S,\text{min}}$ and $V_{S,\text{max}}$ values (Figure 9, Table 5). Interestingly, the change in the “flanking” bridges (CH$_2$ for O) or introduction of pyrazolate arm sets complexes 2–4 off this trend line. That can be explained by the above-mentioned engagement of chloride $p$-orbitals in pincer’s π-system leading to a decrease of $V_{S,\text{min}}$.

Since the dehydrogenation reactions catalyzed by pincer iridium complexes involve dihydrides and hydridochlorides are rather the catalyst precursors,[4a,4e,4f,6] we have also tested the electron density distribution in [(PCP)IrH$_2$] and [(PCN)IrH$_2$] complexes (Figure S16).[11] Notably, the conversion of 1 and 4 into the corresponding dihydrides does not cause substantial transformation of their MEP. The most important feature found for the complexes of original square pyramidal geometry at iridium with the hydride in the apical position is the conservation of the MEP minimum at the trans-to-C ligand (Figure S17) with nearly the same $V_{S,\text{min}}$ value (compare −45.41 (Cl) vs. −41.13 (H) in [(PCP)IrH(X)] and −48.67 (Cl) vs. −47.33 (H) in [(PCN)IrH(X)]).

The hydride ligands in the so-called T-shaped complexes (with H–Ir–H angle 180°) have slightly lower basicity ($V_{S,\text{min}} = −39.55$ for [(PCN)IrH$_2$] and −30.62 for [(PCP)IrH$_2$]), but at the same time these complexes are characterized by much higher Lewis acidity of Ir atom ($V_{S,\text{max}} = 40.91$ for [(PCN)IrH$_2$] and 36.69 for [(PCP)IrH$_2$]). These values are in agreement with comparable (or even higher) initial reaction rates of dehydrogenation observed in the presence of hydridochlorides in comparison to dihydrides.[6b,12]
Experimental data on the enthalpies of pyridine and benzonitrile binding to symmetric PXCP complexes 1–3 (X = CH₂, O) change in the order 1 > 3 > 2 (vide supra), which is the same as the order of their $V_{S,\text{max}}$ values. Accordingly, the computed formation energy of apical complexes with MeCN are also in a good agreement with the experiment and $\Delta E_{\text{ap}}$ vs. $V_{S,\text{max}}$ correlation (Figure 10) shows the same trend as $V_{S,\text{max}}$ vs. $V_{S,\text{min}}$ (Figure 9). All the PCP-based hydridochlorides 1, 4–10 show linear $\Delta E_{\text{ap}}$ vs. $V_{S,\text{max}}$ Correlation (Figure 10) with the strongest complex formed by the most acidic p-NO₂ derivative 7. The POCOP-based complexes 2 and 3 form the weakest adducts with the bases (with $\Delta E_{\text{ap}}$ being more negative for 3), as was shown experimentally.

**Figure 10.** Computed formation energies of apical complexes with MeCN ($\Delta E_{\text{ap}}$ in kcal/mol) vs. MEP maximum energy ($V_{S,\text{max}}$ in kcal/mol).

Assessment of the complexation energies for equatorial isomers b shows that for each ligand they are less energetically preferred than apical isomers a (Table 5). The energy difference $\Delta \Delta E = \Delta E_{\text{eq}} - \Delta E_{\text{ap}}$ exhibits very minor variation with the ligand, changing between 2.4 and 2.8 kcal/mol, with the exception for complexes 2-CH₃CN ($\Delta E = 4.4$ kcal/mol) and 4-CH₃CN ($\Delta E = 1.0$ kcal/mol). Such minimal energy gap between apical and equatorial complexes formed from [(PCN)Ir(H(Cl))] explains the isomers ratio determined from the NMR data for 4-PhCN complex (vide supra). It can be also evoked for the explanation of two reaction pathways of amine-boranes dehydrogenation, which feature very close energetic parameters.[6a]

According to previous DFT calculations,[4c,13] the MeO-MePCP and MePOCOP ligands (with tert-butyls at phosphorus substituted by less demanding methyls) show effects in the same directions, disfavoring, relative to the parent PCP ligand, the addition of C–H and H–H bonds to the 16e dihydrido complexes [(pincer)IrH₂]. This effect has been attributed to the increased π-donation from the methoxy or phosphinito groups to aryl that disfavors addition to the IrIII dihydrides.[13] However, the addition of these bonds (heterolytic splitting) is different from the binding of nitrogen bases since the former requires (back) donation from the metal whereas the latter relies on its Lewis acidity (the electron density deficiency). In this sense our data on the interaction with pyridine and nitriles are more in line with the trends deduced from the $V_{C,\text{O}}$ values of the [(pincer)Ir(CO)] adducts: the MeO-PCP complexes are more electron-rich than the parent PCP complexes, whereas the POCOP complexes appear to be more electron-poor.[13] Our data for PCP-series also show a correlation of $V_{S,\text{min}}$ and $V_{S,\text{max}}$ with Hammett $\sigma_p$ constants[14] of the $p$-substituents (Table 5, Figure S18) with the most electron-rich 9 [$\sigma_p$(MeO) = −0.27] and the most electron-deficient 7 [$\sigma_p$(NO₂) = 0.78] located at their termini.

The largest apical-equatorial energy difference ($\Delta \Delta E = \Delta E_{\text{eq}} - \Delta E_{\text{ap}}$) found for unsubstituted POCOP complex 2 is probably related not only to electronic but to steric factors as well. In this study we considered only the tBu₂P complexes in which bulky tert-butyl groups impose substantial steric protection to iridium center. The importance of their effect was elegantly proved in the recent study of H₂ addition to [(tBuPOCOP)Ir(CO)] and [(tBuPCP)Ir(CO)] with $R = ^t\text{Bu}$ and $i\text{Pr}$ at phosphorus.[13] Furthermore, according to Roy and Paul[16] substituted amine boranes cannot bind to the apical site of [(tBuPOCOP)IrH₂] due to steric hindrance, whereas the equatorial binding is unfavorable energetically. This is in line with the observed absence of catalytic activity of this complex in BH₃NHMe₂ dehydrogenation in contrast to very efficient reaction for BH₃NH₂.[17] In agreement with these computational findings our experimental data show the dominance of the apical isomers for complexes of 2 and 3 with pyridine and PhCN.

**Conclusions**

Variable temperature spectroscopic studies of pyridine (Py) and benzonitrile (PhCN) coordination to benzene based pincer hydridochlorides 1–4, which have square pyramidal geometry at iridium with the chloride in the pincer ligand plane, revealed preferential coordination of these N-donor ligands in the apical position. Such preference is reflected by both the ratio of hexacoordinate isomers formed and their formation enthalpy values obtained from combined UV/Vis and NMR data, which change in the order: [(PCP)Ir(H(Cl))(L)] > [(PCN)Ir(H(Cl))(L)] > [(EtOOC-POCOP)Ir(H(Cl))(L)] > [(POCOP)Ir(H(Cl))(L)]. Thus, these data can be used as the experimental estimate of the metal Lewis acidity. Another, in *silico*, approach is the analysis of the electron density distribution in the parent pentacoordinate hydridochloride complexes. The DFT calculations revealed a good correlation of maximum energy of MEP, $V_{S,\text{max}}$ with energies of MeCN complexation, suggesting $V_{S,\text{max}}$ can be taken as the computational measure of Lewis acidity within families of related compounds. The increase of the iridium Lewis acidity correlates with the decreasing basicity of Cl-ligand (as MEP minimum, $V_{S,\text{min}}$) as well as with Hammett $\sigma_p$ parameters of $p$-substituent in the PCP-benzene ring. Importantly, these properties are conserved upon conversion into the corresponding dihydrides, as shown on the example of 1 and 4, that explains the same activity of [(pincer)Ir(H(Cl))] and [(pincer)IrH₂] complexes in amine-boranes dehydrogenation. The ease of in situ dihydride formation opens the possibility of using the hydridochlorides, which are more stable and more convenient in handling, as pre-catalysts in a variety of catalytic reactions involving hydrogen atom transfer, as already exemplified in the literature. Altogether our data illustrate the importance of different factors in the pincer ligand...
design: how the change in the “flanking” bridges (e.g., substitution of CH₃ for O) sets the framework properties and the substitution in the aromatic ring fine-tunes them. Lower $V_{s,max}$ and $V_{s,min}$ values of POCOP complexes explain their better activity in alkanes dehydrogenation that involves breaking and forming of weakly polarized bonds via 14e/16e iridium species. Amineboranes feature more polarized bonds and thus their dehydrogenation relies on 16e/18e iridium complexes and higher electron density (more negative $V_{s,min}$) of the basic site is important for breaking NH-bond at the rate-limiting step. The trends revealed herein could be used for the design of complexes of other metals as potential catalysts for dehydrogenation/dehydrocoupling reactions and beyond.

**Experimental Section**

All reactions were carried out under an argon atmosphere using standard Schlenk techniques. Solvents were carefully dried by conventional methods and distilled under argon before use. The high purity PhCN and Py (b.p. 114–116 °C) were distilled under argon. Metal hydridochloride complexes [(PCP)IrH(Cl)] (1),[(PCP)-IrH(II)] (2) and [(EtOC(O)-POCOP)IrH(Cl)] (3)[18] and (IPCN)IrH(Cl) (4)[64] were prepared following the published procedures. The 15N-labelled pyridine was prepared from 15NH₄Cl (Sigma–Aldrich).[19] 1H-15N HMBC NMR spectra were recorded with a Bruker Avance 300 spectrometer at different temperatures (200–300 K). The resonances were calibrated relative to the external solvent peaks (1H) or referred to external 85 % H₃PO₄ (31P). The 1H-15N HMBC NMR spectra were recorded with a Bruker Avance 600 FT-NMR spectrometer (15N spectra were referred to MeNO₂). All N–H coupling constants were obtained with 15N-labelled pyridine. The samples for NMR were prepared with c = 0.02M. UV/Vis spectra were recorded at different temperatures (190–300 K) on Varian Cary 50 spectrometer using CaF₂ cells (d = 0.1 cm). Home-modified cryostat Carl Zeiss Jena was used for VT UV/Vis measurements. Hexacoordinate complexes with L = Py and PhCN were obtained in situ by addition of the equimolar amount of L to dichloromethane solution of 0.02M. UV/Vis spectra were recorded at different temperatures.”

**Acknowledgments**

This work was supported by the Russian Science Foundation (grant no. 14-13-00801) and the Ministry of Science and Higher Education of the Russian Federation (AAP, AVP, VAK, ESS). The synthesis of 15N-pyridine was performed within the RUDN University Program 5-100. The contribution of the Center of molecular composition studies of INEOS RAS is gratefully acknowledged.

**Keywords:** Iridium · Pincer complexes · Lewis acids · Lewis bases · Density functional calculations · Catalytic efficiency
Iridium Pincer Complexes

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Effect of Ligands on the Lewis Acidity of the Metal and the Binding of N-Bases to Iridium Pincer Complexes

The coordination of pyridine and benzonitrile to benzene based pincer hydridochlorides [(PCP)IrH(Cl)] (1), [(POCOP)IrH(Cl)] (2), [(EtO(O)C-POCOP)IrH(Cl)] (3), and [(PCN)IrH(Cl)] (4) was studied to deduce the ligand influence. The order of their experimental formation enthalpies: 1 ≈ 4 > 3 > 2, nicely agrees with the order of Lewis acidity obtained by DFT calculations. The effect of a p-substituent in the PCP ligand can be similar to the switch to the POCOP ligand.

DOI: 10.1002/ejic.201801341