Short Communication

Studies on Five-coordinated $d^8$ Metal Ions. Part II*. The Displacement of 1,10-Phenanthroline by the Reaction of the Five-coordinate Cyanobis(1,10-phenanthroline)platinum(II) Cation with Cyanide

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In an earlier paper,\textsuperscript{1} it was shown that $[\text{Pt(phen)}_2]^{2+}$ rapidly adds cyanide giving the ion $[\text{Pt(phen)}_2(\text{CN})]^+$. In the solid state, as its nitrate salt, this ion has a square-pyramidal structure with an apical Pt--N bond which is 30\% longer than the basal Pt--N bonds. The platinum atom is displaced 0.0069 nm in the direction of the apical donor-atom, as predicted by theory for a five-coordinate, square-pyramidal $d^8$ complex with an apical bond which is longer and weaker than the basal bonds.\textsuperscript{2} Therefore, even for this system where the apically bonded donor group forms a part of a rigid chelate, the central atom is probably bonded to all five donor atoms and therefore does not necessarily contain a "half-bonded" $\eta^1$ chelate. The salt $[\text{PtCl(PEt}_3)_2(\text{phen})][\text{BF}_4]$ the cation of which has a similar structure and reactivity, was originally reported as containing a five-coordinate complex,\textsuperscript{3} but was later incorrectly (\textit{vide infra}) reformulated as a "half-bonded" system on the basis of the structure alone.\textsuperscript{4} It may also be relevant that in the $^{13}$C NMR spectra of $[\text{Pt(phen)}_2(\text{CN})]^+$,\textsuperscript{1} both in nitromethane and aqueous solution, the four halves of the phen ligands are equivalent on the NMR time-scale. The $J^{(195}\text{Pt}--^{13}\text{C})$ coupling constants of the peaks assignable to phen in the spectra are only between 5 and 15\% smaller than for $[\text{Pt(phen)}_2]^{2+}$. Thus, the Pt--N bonds, although presumably weaker in the five-coordinate complex than in $[\text{Pt(phen)}_2]^{2+}$, should not correspond to those of a system with only three Pt--N bonds and one "half-bonded" $\eta^1$ phen molecule, and still give such high values of $J(\text{Pt}--\text{C})$.

The present work is an attempt to use reactivity as an alternative means of characterizing the five-coordinate complex. An obvious choice of reaction was that between $[\text{Pt(phen)}_2]^{2+}$ and an excess of [CN]$^-$, which preliminary observation revealed to occur in two stages:

\begin{equation}
[\text{Pt(phen)}_2]^{2+} + [\text{CN}]^- \xrightarrow{k_1} [\text{Pt(phen)}_2(\text{CN})]^+ \tag{1}
\end{equation}

\begin{equation}
[\text{Pt(phen)}_2(\text{CN})]^+ + [\text{CN}]^- \xrightarrow{k_2} [\text{Pt(phen)(CN)}_2]^{2+} + \text{phen}\tag{2}
\end{equation}

The kinetics of reaction (1) were measured under standard acidic conditions (buffered with aqueous 0.05 mol $\text{LiC}_2\text{O}_4\text{H}_2$ and $\text{C}_2\text{O}_4\text{H}_2$), and these results are summarised in Table 1. The effect of pH upon this reaction will be the subject of a future publication;\textsuperscript{5} the rate law is:

\[
\text{Rate} = k_1[\{\text{Pt(phen)}_2\}]^{2+}[\text{CN}]^-;
\]

\[
k_1 = 1.87 \times 10^8 \text{ mol}^{-1} \text{ s}^{-1} \text{ (at } 25 \degree \text{C})
\]

\[
\Delta H_1^* = +11.3 \text{ kJ mol}^{-1}
\]

\[
\Delta S_1^* = -50 \text{ J mol}^{-1} \text{ K}^{-1}
\]

\footnote{Part 1. See Ref. 1.}

\footnote{1,10-Phenanthroline is abbreviated to phen throughout this Communication.}

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Table 1. Kinetic Data.

<table>
<thead>
<tr>
<th>Reaction (1) in 0.05 mol l(^{-1}) aqueous</th>
<th>T /°C</th>
<th>[Pt complex] /mol l(^{-1})</th>
<th>[KCN] range /10(^{-3}) mol l(^{-1})</th>
<th>No. of runs</th>
<th>(k_{av,obs}) /l mol(^{-1}) s(^{-1})</th>
<th>(k^a) /l mol(^{-1}) s(^{-1})</th>
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<td></td>
<td>17.1</td>
<td>1.15\times10^{-4}</td>
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<td>3.63</td>
<td>1.63(3)\times10^8</td>
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<td>18.9</td>
<td>2.04–4.09</td>
<td>2.04–4.09</td>
<td>7</td>
<td>3.92</td>
<td>1.60(2)\times10^8</td>
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<tr>
<td>K[C(_2)O(_4)]H(_2)C(_2)O(_4)H(_2)</td>
<td>22.6</td>
<td>2.98</td>
<td>6</td>
<td>5.70</td>
<td>1.86(15)\times10^8</td>
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<td></td>
<td>29.9</td>
<td>0.68–1.9</td>
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<td>1.97(6)\times10^8</td>
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<td>31.7</td>
<td>1.01–2.02</td>
<td>6</td>
<td>10.4</td>
<td>2.01(7)\times10^8</td>
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<tr>
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<td>33.6</td>
<td>1.31–3.5</td>
<td>6</td>
<td>13.8</td>
<td>2.31(17)\times10^8</td>
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</table>

<table>
<thead>
<tr>
<th>Reaction (2) in 0.10 mol l(^{-1}) methanolic</th>
<th>T /°C</th>
<th>[Pt complex] /mol l(^{-1})</th>
<th>[KCN] range /10(^{-3}) mol l(^{-1})</th>
<th>No. of runs</th>
<th>(k_{av,obs}) /l mol(^{-1}) s(^{-1})</th>
<th>(k^a) /l mol(^{-1}) s(^{-1})</th>
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<td>18.2</td>
<td>1.00\times10^{-5}</td>
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<td>13</td>
<td>2.95(7)</td>
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<td>23.2</td>
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<td>27.4</td>
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<td>2.3(2)</td>
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<td>30.1</td>
<td>1.9–7.7</td>
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<td>5.6(2)</td>
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<td>35.2</td>
<td>1.9–7.6</td>
<td>6</td>
<td>7.3(3)</td>
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</table>

\(^a\) The rate constants were obtained from the slope of a linear plot of pseudo-first-order rate constants versus [KCN]. The pseudo-first-order rate constants were calculated from logarithmic first-order plots which were linear for more than three half-lives. The reactions were monitored spectrophotometrically at 375 and 325 nm, respectively. \(^b\) A preliminary report of these data was given at the 13\(^{th}\) meeting of the Royal Society of Chemistry Inorganic Mechanisms Group, Cardiff, Great Britain, 1980. \(^c\) [Pt(phen)]\(_2\)[NO\(_3\)]\(_2\) was prepared according to Ref. 1. A freshly prepared solution of K[C\(_2\)N] (A.R. grade) was used. All reagent solutions were saturated with dinitrogen. The pH of the medium was ca. 1.7.

However, the product of the second reaction, (2), is virtually insoluble in water. Thus, the rate was measured in methanol (in the presence of a Na\(_2\)[B\(_4\)O\(_7\)]\(_{10}\)H\(_2\)O buffer), ensuring that the fraction of total cyanide which was protonated was a constant. The pK of HCN in methanol is not accurately known, so the rate law (but not \(k_2\)) could be established:

\[
\text{Rate}=k_2^c[(\text{Pt(phen)}_2\text{(CN)})^\text{+}][\text{CN}^-]
\]

In a constant ionic strength medium, sodium ethanoate (0.10 mol l\(^{-1}\)) in methanol with [KCN]\(>10^{-3}\) mol l\(^{-1}\), the HCN concentration can be ignored. From a study of the kinetics in this medium (Table 1), the rate law was explicitly:

\[
\begin{align*}
\text{Rate}&=k_2^d(\text{Pt(phen)}_2\text{(CN)})^\text{+}][\text{CN}^-]; \\
&=4.06 \text{ 1 mol}^{-1} \text{ s}^{-1} \text{ (at 25}°\text{C)} \\
&=\Delta H_2^\text{+}=39 \text{  kJ mol}^{-1} \\
&=\Delta S_2^\text{+}=\text{+105  J mol}^{-1} \text{ K}^{-1}
\end{align*}
\]

From these data, it can be seen that the rate constant for reaction (2) is in the range normally observed for nucleophilic substitution by cyanide in platinum(II) complexes.\(^b\,^7\) In contrast, the rate constant, \(k_1\), for the formation of the five-coordinate species is many orders of magnitude larger than \(k_2\), suggesting that no ligand displacement is involved. This argument is further supported by consideration of the activation parameters. \(\Delta H_2^\text{+}\), at 40 kJ mol\(^{-1}\), is typical of values for substitution reactions,\(^b\,^7\) whereas \(\Delta H_1^\text{+}\) is about one quarter of typical values (40–60 kJ mol\(^{-1}\))\(^b\,^7\) for such processes as:

\[
[\text{PtL}_3\text{X}^\text{+}]+\text{X}^-\rightarrow[\text{PtL}_3\text{X}^\text{+}]+\text{L}
\]

These data clearly support the proposition that no Pt–N bond is broken during reaction (1), thus arguing strongly against formulating species such as [Pt(phen)]\(_2\)(CN)]^+ and [PtCl(P\(_3\)\(_2\)(phen)]^+ as four-coordinate complexes containing \(\eta^1\)-phen. For some substitu-

tion reactions where phen is the leaving group, it has been suggested \(^8\) (on the basis of kinetic data) that “half-bonded” \(\eta^1\)-phen exists in intermediates, but the existence of such a species has never been demonstrated; the kinetic data described above remove the only possible argument which remained in support of such complexes.

It is of interest that the value of \(\Delta S^\# \) is in a range normally considered as typical for an associative reaction \(^6,7\) suggesting the formation of a six-coordinate activated complex, \([\text{Pt}(\eta^1\text{-phen})_2(\text{CN})_2] \). The displacement of phen from \([\text{Ir}(1,5\text{-cyclooctadiene})(\text{phen})]^+\) with 1,2-diaminoethane as the nucleophile has \(\Delta S^\# = -25 \text{ J mol}^{-1} \text{ K}^{-1} \). \(^9\) This reaction was described as a dissociative displacement of phen from the stable five-coordinate intermediate containing \(\eta^1\)-1,2-diaminoethane. The results presented here clearly indicate the possibility of an alternative interpretation of these results, viz. an associative mechanism with a six-coordinate activated complex. Both these reactions present examples of a reaction type which is not accord with Tolman’s rule (i.e. the number of electrons in the activated complex must be either sixteen or eighteen). \(^10\)

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