Axial ligand substitution reactions of ruthenium (II) dimethylglyoxime complexes

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Received 30 June 1988; revised and accepted 10 November 1988

Kinetics of ligand substitution reactions of six-coordinated Ru(II) macrocyclic complexes of the following type have been investigated:

\[(\overline{L})\text{Ru}(\text{DMGH})_2(L) + X \rightarrow (\overline{L})\text{Ru}(\text{DMGH})_2(X) + L\]

where “\(\overline{L}\)” and “\(L\)” are either both triphenylphosphine ligands or methylimidazole and triphenylphosphine ligands, respectively. The nucleophile “\(X\)” is either Melm, Im, py, pip, P(OBu)\(_3\), or Tmic. In all cases, with the exception of Tmic as a nucleophile, the reaction mechanism is strictly dissociative (D). The reaction proceeds through the formation of a five-coordinate intermediate which possesses little or no ability to discriminate between different nucleophiles. In the case of Tmic, the rate data can be fitted by a dissociative “1_d” or an Associative “1.a” interchange mechanism.

In the present work we report a study of axial ligand substitution reactions of \(\overline{L}\)Ru(\text{DMGH})_2(L) complexes with nucleophiles \(X\), where “\(\overline{L}\)” and “\(L\)” are either both P\(_3\) ligands or Melm, and P\(_3\) ligands respectively, and \(X = \text{Im, Melm, py, pip, Tmic and/or P(OBu)}_3\) for \(\overline{L} = \overline{P}\).

Materials and Methods

All the chemicals used were analytical grade reagents. The complexes Ru(\text{DMGH})_2(P\(_3\))\(_2\), Ru(\text{DMGH})_2(Melm)(P\(_3\))\(_2\) and Ru[P\(_3\)]Cl\(_2\) were prepared according to standard literature method. The purity of these compounds was checked by comparison of their spectra with published ones and by elemental analyses. 1-Methylimidazole (Melm) (Aldrich) was distilled from KOH prior to use. Tributylphosphite [P(OBu)\(_3\)] (Aldrich) and dimethylglyoxime (Analar) were used without further purification. Toluene (Aldrich) was freshly distilled from CaH\(_2\) before use. Pyridine (py), piperidine (pip) and tosyl-methyl-isocyanide (Tmic) were Aldrich reagents and used without further purification.

*Ligand abbreviations: DMGH = dimethylglyoximate; P\(_3\) = triphenylphosphine; Im = imidazole; Melm = 1-methylimidazole; py = pyridine; pip = piperidine; Tmic = tosyl-methyl-isocyanide; P(OBu)\(_3\) = tri-\(n\)-butylphosphite.*

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Kinetics

All reactions were routinely run in serum-capped nitrogen purged cuvettes and monitored by visible spectroscopy, using an Aminco DW-2a UV-Vis spectrophotometer or Perkin-Elmer Hitachi 340 recording spectrophotometer. Temperatures were maintained by circulating water through a thermostatable cell holder using a Lauda circulator (K-21R). Solutions were thermostated for approximately 15 min prior to measurements. Temperatures were directly read from a temperature reading device attached to the cell holder. The slower reactions were followed by periodically scanning the spectrum at a series of time intervals over the wavelength range 320-800 nm. The faster reactions were monitored at an absorbance maximum or minimum and the absorbance was recorded continuously as a function of time. The chart speeds were adjusted to suit the rate of the reaction. Reaction solutions were prepared by injecting 10-150 μL of the ligand (either neat or as a toluene solution) into the serum-capped cell containing the thermostated solution of the complex, using a Hamilton gas-tight syringe. Concentrations of the complexes were in the range $7 \times 10^{-5} - 2 \times 10^{-4} \text{mol dm}^{-3}$. Reactions were carried out under pseudo-first-order conditions keeping the ligand concentration at least 10 times greater than the complexes concentration. All reactions were followed until constancy in absorbance was obtained. The observed pseudo-first-order rate constants were calculated from plots of $\ln((A_w - A_p)/(A_w - A_i))$ versus time, where $A_w$, $A_i$, and $A_p$ are the absorbances at times zero, $t$ and infinity respectively. These plots were drawn in triplicate; the reproducibility of the separate runs was typically within ±5% or less. Activation parameters were obtained from a linear fit of the $\ln(k/T)$ versus $1/T$ data.

Results and Discussion

The reactions studied can be categorized as follows:

$$\text{Ru(DMGH)}_2(\text{Po}_3)_2 + X = \text{Ru(DMGH)}_2(\text{Po}_3)X$$

where $X = \text{Melm, Im, py, pip and Tmic}$.  

$$\text{Ru(DMGH)}_2(\text{Po}_3)(\text{Melm}) + \text{Melm} = \text{Ru(DMGH)}_2(\text{Melm})_2 + \text{Po}_3$$

$$\text{Ru(DMGH)}_2(\text{Po}_3)(\text{MeIm}) + \text{Po}_3 = \text{Ru(DMGH)}_2(\text{Po}_3)_2 + \text{MeIm}$$

Thus for the compound Ru(DMGH)$_2$(Po$_3$)MeIm we were able to study the forward and reverse reactions in which one Melm substitutes one Po$_3$ and vice versa. All the reactions were studied under pseudo-first-order conditions by maintaining a sufficiently large excess of the substituting ligand. Under these conditions all reactions yielded first-order plots for at least three half-lives. In all cases studied, with the exception of $X = \text{Melm}$, the reactions was followed to the formation of the mixed complex only. In the case of $X = \text{Melm}$, the reaction was continued till the formation of bis-Melm complex. Complete spectral scans in a number of representative runs gave spectral curves that maintained one or more isosbestic points throughout the reaction. Fig. 1 gives spectral scans for the reaction of Ru(DMGH)$_2$(Po$_3$)$_2$ with Melm in toluene at 70.5±0.3°C. The kinetic data were analyzed at a wavelength corresponding to the region of maximum change. All experiments were done in triplicate.

Table 1 gives kinetic data for axial ligation of Ru(DMGH)$_2$(Po$_3$)$_2$ in which the substituting ligands were Melm, py, Im, POBu$_3$ and pip. The reactions were studied at 70.5, 80.0 and 90.0°C and monitored at the $\lambda_{max}$ given in Table1. The table also gives the positions of the isosbestic points observed in each case. The dependence of the rate constants on the concentrations of the entering nucleophile at a given temperature was also
Table 1—Axial ligand substitution rate data for the reaction:

\[(\text{PO}_3)\text{Ru(DMGH)}_2(\text{PO}_3) + X = (\text{PO}_3)\text{Ru(DMGH)}_2X + \text{PO}_3\]

in toluene

<table>
<thead>
<tr>
<th>X</th>
<th>Temp. °C</th>
<th>(k; \text{s}^{-1})</th>
<th>(\lambda_{\text{max}}, \text{nm})</th>
<th>Isosbestic point, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeIm</td>
<td>70.5</td>
<td>(8.93 \times 10^{-5})</td>
<td>396</td>
<td>375</td>
</tr>
<tr>
<td></td>
<td>80.0</td>
<td>4.3 \times 10^{-4}</td>
<td>342,371</td>
<td></td>
</tr>
<tr>
<td></td>
<td>90.0</td>
<td>1.34 \times 10^{-3}</td>
<td>378</td>
<td></td>
</tr>
<tr>
<td>Py</td>
<td>70.5</td>
<td>(6.63 \times 10^{-5})</td>
<td>390</td>
<td></td>
</tr>
<tr>
<td></td>
<td>80.0</td>
<td>3.58 \times 10^{-4}</td>
<td>371</td>
<td></td>
</tr>
<tr>
<td></td>
<td>90.0</td>
<td>1.15 \times 10^{-3}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Im</td>
<td>70.5</td>
<td>6.6 \times 10^{-5}</td>
<td>399</td>
<td>378</td>
</tr>
<tr>
<td></td>
<td>80.0</td>
<td>3.86 \times 10^{-4}</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>90.0</td>
<td>1.31 \times 10^{-3}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>POBu(_3)</td>
<td>70.5</td>
<td>(8.67 \times 10^{-5})</td>
<td>338</td>
<td>317,354,415</td>
</tr>
<tr>
<td></td>
<td>80.0</td>
<td>3.28 \times 10^{-4}</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>90.0</td>
<td>9.74 \times 10^{-4}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pip</td>
<td>70.5</td>
<td>1.21 \times 10^{-4}</td>
<td>410</td>
<td>390</td>
</tr>
<tr>
<td></td>
<td>80.0</td>
<td>4.2 \times 10^{-4}</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>90.0</td>
<td>1.06 \times 10^{-3}</td>
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</tr>
</tbody>
</table>

\(\lambda_{\text{max}}\) for Ru(DMGH)\(_2\)(PO\(_3\))\(_2\) occurred at 362 nm.

Table 2—Activation parameters for axial ligand substitution reactions of Ru(DMGH)\(_2\)(PO\(_3\))\(_2\)

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Nucleophile &quot;X&quot;</th>
<th>(\Delta H)(_\text{f}), kJ mol(^{-1})</th>
<th>(\Delta S)(_\text{f}), JK(^{-1})mol(^{-1})</th>
<th>(\Delta G)(_\text{f}), kJ mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(DMGH)(_2)(PO(_3))(_2) Melm</td>
<td>141.4</td>
<td>87.9</td>
<td>115.1</td>
<td></td>
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<tr>
<td>Py</td>
<td>134.7</td>
<td>69.0</td>
<td>114.2</td>
<td></td>
</tr>
<tr>
<td>Im</td>
<td>156.1</td>
<td>128.9</td>
<td>117.6</td>
<td></td>
</tr>
<tr>
<td>POBu(_3)</td>
<td>125.9</td>
<td>42.7</td>
<td>113.4</td>
<td></td>
</tr>
<tr>
<td>pip</td>
<td>112.5</td>
<td>7.1</td>
<td>110.5</td>
<td></td>
</tr>
<tr>
<td>Ru(Fe[POBu(_3)](_2)) Melm</td>
<td>117.2</td>
<td>96.2</td>
<td>88.3</td>
<td></td>
</tr>
</tbody>
</table>


studied. It was found that the concentration of the entering ligand had little or no effect on the rate constants and that the rate constants calculated were within the range of experimental error of one another. In addition, it was found that the nature of the nucleophile had no effect on the observed rate constants.

Table 2 lists the thermodynamic parameters calculated for these processes. The magnitude of the activation enthalpies and entropies and the insensitivity of the rate to the nature or concentration of the nucleophile "X" clearly demonstrate that the reaction mechanism is dissociative and that the five-coordinate intermediate possesses little or no ability to discriminate between nucleophiles. The rate behaviour of this system thus follows a simple dissociative \((D)\) mechanism of the form:

\[(\text{PO}_3)\text{Ru(DMGH)}_2(\text{PO}_3) \xrightarrow{k_1} (\text{PO}_3)\text{Ru(DMGH)}_2 + \text{PO}_3\]

\[(\text{PO}_3)\text{Ru(DMGH)}_2 + X \xrightarrow{k_2} (\text{PO}_3)\text{Ru(DMGH)}_2X\]

The PO\(_3\) ligand in the trans position is reported to extenuate its effect on the kinetics of ligand substitution. For such a mechanism, the observed pseudo-first order rate constant, neglecting the reverse reaction, is given by:

\[k_{\text{obs}} = \frac{k_1 k_3 [X]}{k_2 [\text{PO}_3] + k_3 [X]}\]

In this study, all reactions were carried out with large excess of the entering ligand X and negligible concentration of PO\(_3\). Under these conditions, the above expression reduces to:

\[k_{\text{obs}} = k_1\]

This implies that the pseudo-first order rate constant corresponds to the rate constant for the dissociation of PO\(_3\).

Addition of Melm, Im, POBu\(_3\) and pip to Ru(DMGH)\(_2\)(PO\(_3\))\(_2\) produces the mixed complexes. The position of the observed spectral band maximum (Table 1) is shifted towards higher energy for the POBu\(_3\) mixed complex while the shift occurs towards lower energy for the Melm, py, Im and pip mixed complexes. This is attributed to the \(\sigma\)-donor-\(\pi\)-acceptor characteristics of the POBu\(_3\) ligand in comparison to the \(\sigma\)-donor properties only of the remaining ligands.

The net effect of the \(\pi\)-acceptor characteristics of POBu\(_3\) is its ability to accept electron density from filled \(t_2g\) orbitals of metal thus reducing the ease of charge transfer from Ru to (DMGH). On the other hand, Melm, py and pip, with only \(\sigma\)-donor properties, would increase such charge transfer. The order of the energy shift for the mixed complexes follows the sequence: POBu\(_3\) > PO\(_3\) > py; Melm; Im. It, thus, follows that POBu\(_3\) is a better \(\pi\)-acceptor than PO\(_3\).

The reaction of the mixed complex Ru(DMGH)\(_2\)(PO\(_3\))(Melm) with PO\(_3\) to produce the bis-PO\(_3\) complex was investigated at 80°-90°C under pseudo-first order conditions. The concentration of PO\(_3\) was varied by a factor of 10 with no effect on the calculated rate constant, which is indicative of a dissociative mechanism. Table 3 gives...
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the kinetic data obtained for this system. These data together with those obtained for the reaction of Ru(DMGH)2(P03)2 with Melm afford the calculation of the equilibrium constant for the reaction:

\[
\text{Ru(DMGH)}_2(\text{P0}_3) + \text{Melm} \rightleftharpoons \frac{K}{\text{Ru(DMGH)}_2(\text{Po}_3 \cdot \text{Melm}) + \text{P0}_3} \quad \ldots \quad (8)
\]

The values of the equilibrium constant calculated are respectively 3 and 1 at 80° and 90°C. This means that synergic π-bonding occurs in the mixed complex with the result that triphenylphosphine is extremely inert to Melm. In addition to the above kinetic data, the reaction of the mixed complex, Ru(DMGHh(P03)(Melm), was investigated with respect to substitution of the second P03 with Melm at 90°C. Only a value of \(6.4 \times 10^{-5} \text{s}^{-1}\) was obtained for the pseudo-first order rate constant. This value is slower by a factor of 600 than either the rate of substitution of the first P03 in the bis-P03 complex or the Melm in the mixed complex (MeIm)Ru(DMGH)2(Melm). These data are also suggestive of the \(\text{trans}\) deactivation characteristics of Melm relative to P03 and lend additional support to the synergic π-bonding effect in the mixed complex. Similar behaviour was also observed by Sweigart et al.5 for Ru(II)-bis-phthalocyanine aduct.

Kinetic data for the reaction of Tmic with Ru(DMGH)2(P03)2 at 70°C are given in Table 4. The reaction was studied under pseudo-first order conditions and the Tmic concentrations were varied by a factor of 6, and monitored at \(\lambda = 387\) nm. The observed pseudo-first order rate constants gave a linear relationship (Eq. 9) with the Tmic concentration,

\[
k_{\text{obs}} = k[T\text{mic}] \quad \ldots \quad (9)
\]

where \(k\) represents the second-order rate constant and has a value of \(8.05 \times 10^{-5} \text{mol}^{-1} \text{dm}^3 \cdot \text{s}^{-1}\). In the concentration range studied, this behaviour of Tmic is unlike that observed for the other ligands studied in this work. Such a behaviour is similar to that observed for axial substitution in Ru-phthalocyanine complex.

The rate data can be interpreted on the basis of a dissociative interchange mechanism of the type:

\[
(P03)\text{Ru(DMGH)}_2(P03) + \text{Tmic} \rightleftharpoons K_1 (P03)\text{Ru(DMGH)}_2(P03)\text{Tmic} \quad \ldots \quad (10)
\]

\[
(P03)\text{Ru(DMGH)}_2(P03)_2\text{Tmic} \rightleftharpoons K_2 (P03)\text{Ru(DMGH)}_2(P03)\text{Tmic} \quad \ldots \quad (11)
\]

### Table 3 — Axial ligand substitution rate data for the reactions:

<table>
<thead>
<tr>
<th>Nucleophile</th>
<th>Temp., °C</th>
<th>(k, s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PO3</td>
<td>80.0</td>
<td>(1.43 \times 10^{-4})</td>
</tr>
<tr>
<td>PO3</td>
<td>90.0</td>
<td>(1.0 \times 10^{-3})</td>
</tr>
<tr>
<td>Melm</td>
<td>90.0</td>
<td>(6.4 \times 10^{-5})</td>
</tr>
</tbody>
</table>

The \(k\) values are the average of three experiments.

### Table 4 — Axial ligand substitution rate data for the reaction:

\[(P03)\text{Ru(DMGH)}_2(P03) + \text{Tmic} = (P03)\text{Ru(DMGH)}_2(\text{Tmic}) + P03 \quad \ldots \quad (12)
\]

The reaction was monitored at 387 nm. The value for \(k_2K\) from linear least squares fit was found to be equal to \(8.05 \times 10^{-5} \text{mol}^{-1} \text{dm}^3\).

\[
k_{\text{obs}} = \frac{k_2k_1[T\text{mic}]}{1 + K_1[T\text{mic}]} \quad \ldots \quad (13)
\]

For \(K_1[T\text{mic}] \ll 1\), equation (13) reduces to:

\[
k_{\text{obs}} = k_2K_1[T\text{mic}] \quad \ldots \quad (14)
\]

The slope of the \(k_{\text{obs}}\) versus Tmic plot gives the value of \(k_2K_1\). Inclusion of the equilibrium process involving outer-sphere complex formation with PO3, in the interchange process (Eq. 15),

\[
(P03)\text{Ru(DMGH)}_2(\text{Tmic}) + \text{PO3} \rightleftharpoons (P03)\text{Ru(DMGH}2(\text{Tmic})\text{...PO3} \quad \ldots \quad (15)
\]

yields the rate constant expression (16),

\[
k_{\text{obs}} = \frac{k_2K_1[T\text{mic}]}{1 + K_1[T\text{mic}]} + K_2[PO3] \quad \ldots \quad (16)
\]

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which reduces to (14) under the condition
\[ 1 \gg K_1[Tmic] + K_2[P0_3]. \]
The inclusion of (15) into the mechanism gives a more elaborate form of the
\[ I_d \] mechanism, in which the overall rate can be equally affected by the competition of (P0_3) and
(Tmic) for the highly reactive coordinatively-un saturated intermediate (P0_3)Ru(DMGH)₂, as well as by competition of (P0_3) and (Tmic) to form outer-sphere complexes with (P0_3)Ru(DMGH)₂(P0_3).

Alternatively, an associative interchange mechanism can be proposed. In this latter case the set of equations is identical with equations 10-16. The essential difference between the two mechanisms is the form of the activated complex. In the first, it is primarily a five-coordinate intermediate, whereas in the second a seven-coordinate activated complex is proposed. The present data do not allow us to distinguish between the two pathways. The behaviour is quite similar to that observed for a number of amine complexes of cobalt(III)^{19,20}. In addition, similar behaviour was reported^{21-23} for the reaction of CH₃Co(DMGH)₂ pip with Lewis bases such as CS₂, (MeO)₂PO and (n-Bu)₃PO. In this system, strong hydrogen bonding occurs upon addition of Lewis base leading to a stabilization of the outer-sphere complex.

The dissociative interchange \[ I_d \] mechanism proposed for the reaction of Tmic can also be invoked for the remaining ligands studied in this work. The high concentration of ligands used for Melm, Im, pip, py and POBu₃ may account for the independence of the observed rate of the ligand concentration, meaning that in these systems we were working at the limiting concentration range in which the factor \( K[X] \gg 1 \). Such high concentration of the ligands were necessary to overcome the slow rate of the reaction.

References