Transition metal complexes of NOx

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Abstract - The structure-reactivity relationships of organometallic nitrites and nitrates are summarized. The mechanism(s) of the reactions of these complexes, especially their oxygen-atom transfer reactions, are outlined with respect to their uses as catalysts and intermediate precursors.

INTRODUCTION

NOx, NO2, and NO3 complexes of transition metals comprise a class of materials with many potential uses as catalysts, as oxidants and as precursors to new and otherwise inaccessible compounds. As yet, much of this potential is unrealized because NOx and NO3 compounds which are soluble in organic media are relatively rare. On the other hand, a great many metal nitrosyl complexes have been reported (ref. 1), and the relationship between their chemical reactivity and their structural features is well documented and articulated by bonding arguments (ref. 2). In contrast, the bonding, structure, reactivity relationships in metal nitrites and nitrates have been little explored. Consequently, recent work in our laboratories has focussed on the synthesis and reactions of transition metal nitrites and nitrates that are soluble in organic solvents (refs. 3,4,5).

NO2 COMPLEXES

Several general features of the NO2 ligand are worth noting. NO2- is a triatomic species with 18 valence electrons. It is isoelectronic with other ligands including SO2 and the allyl anion. Isomers are known (refs. 6,7,8). By analogy with SO2 and the allyl ligand, two other isomeric forms, can be postulated. Neither form has been isolated, although some evidence for side-on and/or pi-NO2 geometry has been obtained by photolysis of Co(NH3)6(NO2)2+ (ref. 9). Recently, research on nickel (ref. 10) and cobalt (ref. 3) complexes has shown that the -O-N=O ligand has exo and endo conformations. The endo complexes have M-O distances that vary smoothly from non-bonded to chelated. While the geometry of these isomers in the solid state was determined by X-ray crystallography, their solution geometries have been established using infrared and 15N NMR spectroscopy (ref. 3) (Table 1).

<table>
<thead>
<tr>
<th>Ligand Geometry</th>
<th>Vib. Frequency (cm⁻¹)</th>
<th>( \nu_{N-\text{OAsym.}} )</th>
<th>( \nu_{N-\text{OSym.}} )</th>
<th>( \delta_{NO2} )</th>
<th>( \Delta_{M-NO2} )</th>
<th>( \delta^{15N} ) (ppm) vs. CH3NO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-NO2</td>
<td>1390</td>
<td>1320</td>
<td>815</td>
<td>590</td>
<td>0-100</td>
<td></td>
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<tr>
<td>exo-NO2</td>
<td>1260</td>
<td>1200</td>
<td>860</td>
<td>n.a.</td>
<td>180-230</td>
<td></td>
</tr>
<tr>
<td>endo-NO2</td>
<td>1400</td>
<td>1095</td>
<td>760</td>
<td>n.a.</td>
<td>230</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 1. Characteristic infrared bands and 15N chemical shifts for NO2 isomers.
In one of our early studies (ref. 11) using $^{15}\text{N}$ substitution in cis-Fe(DEDTG)(NO)(NO$_2$), it was found that the NO and NO$_2$ ligands undergo an intramolecular oxygen atom transfer reaction via a symmetric intermediate or transition state:

\[
\begin{array}{c}
\text{O} \quad \text{O} \\
\text{Fe} \quad \text{Fe}
\end{array}
\]

This widely quoted result prompted us (refs. 12,13,14) and others (refs. 15,16,17) to explore the use of the -NO$_2$ ligands as oxidants in organic media. Tovrog et al. have shown that the closely related cobalt complexes of the type CoNO$_x$(salen) catalyze the reactions between O$_2$ and olefins through the reaction of the NO$_2$ complex, CoNO$_x$(salen), with the olefin followed by the re-oxidation of CoNO(salen) by O$_2$ to CoNO$_2$(salen).

Although several oxidized organic products were obtained, this series of reactions clearly established the potential for using the MNO/MNO$_2$ couple as an oxidative catalyst. In his studies of cobalt complexes, Valenilla (ref. 3) found that the reactions between O$_2$ and cyclohexene produced cyclohexene epoxide cleanly without the formation of other oxidized organic species.

One of the first oxygen atom transfer reactions to CO to be investigated in any detail was the reaction of MNO$_2$ complexes with CO which produced a nickel nitrosyl complex and CO$_2$ (ref. 12):

\begin{equation}
\text{Ni(NO)}_2\text{L}_2 + \text{CO} \rightarrow \text{Ni(NO)(NO)}_2\text{L}_2 + \text{CO}_2 ; \quad \text{L} = \text{DPPE, PMe}_3, \text{PPh}_3
\end{equation}

Although the CO is not initially coordinated, this reaction is first order in CO and first order in complex for all L, and under all experimental conditions that were evaluated. This associative reaction clearly proceeds through formation of a five coordinate nickel carbonyl species analogous to NiI$_2$(CO)(PMe)$_3$ complex isolated and structurally characterized by M. Dartiguenave (ref. 18).

Since the reactions between NO$_2$ and CO or alkenes do not take place in the absence of the transition metal, the role of the metal is critical for controlling these oxygen atom transfer reactions. The requirements thus far elucidated include: both the NO$_2$ and CO ligands must be bound to adjacent coordination sites of the metal for the reaction to take place. Early evidence for the coordinative form of the NO$_2$ ligand responsible for oxidation was presented in a note by Roper (ref. 19) in his studies of the OsP$_2$(CO)$_2$(NO)$_2$ complexes. Roper found that the bis nitrito isomer rearranged to the bis nitro isomer before undergoing oxygen atom transfer to produce CO$_2$ and the dinitrosyl complex:

\begin{equation}
\text{cis-Os(CO)}_2\text{P}_2(-\text{ON=O})_2 = \text{cis-Os(CO)}_2\text{P}_2(-\text{NO})_2
\end{equation}

\begin{equation}
\text{cis-Os(CO)}_2\text{P}_2(-\text{NO})_2 = \text{OsP}_2\text{(NO)}_2 + 2\text{CO}_2 \quad (\text{P} = \text{PPh}_3).
\end{equation}

Most of the NO$_2$ complexes which have thus far been isolated have amines or phosphines as co-ligands. Phosphine ligands are unsuited for oxidative catalysts because of the ease with which they are oxidized to phosphine oxides. Amine complexes are normally insoluble in organic solvents and complexes of Schiff's bases produce numerous oxidation products from olefin oxidation. For these reasons, it was decided to explore organometallic complexes of NO$_2$.

Only three organometallic NO$_2$ complexes have been reported in the earlier literature (refs. 20,21,22). Angelici reported that a golden yellow compound thought to be CpFe(CO)$_2$(NO)$_2$ was formed from air oxidation of [CpFe(CO)$_2$] in acidic solutions of NO$_2$ but he was unable to characterize it because of rapid decomposition (ref. 22).

\begin{equation}
[CpFe(CO)$_2$] + \text{O}_2 + \text{NO}_2^- = CpFe(CO)$_2$(NO)$_2$.
\end{equation}

An oxygen atom transfer reaction between the NO$_2$ and CO ligands of the type described in reaction 1 could account for the thermal instability of CpFe(CO)$_2$(NO)$_2$.

To address this question, Hansen prepared several new organometallic NO$_2$ complexes of iron and ruthenium including CpFeNO$_2$ (ref. 4). CpFe(CO)$_2$NO$_2$ was prepared using several synthetic strategies. The highest yields were obtained from the reaction of AgNO$_2$ with [CpFe(CO)$_2$]$_2$:

\begin{equation}
[CpFe(CO)$_2$]$_2^2 + 2\text{AgNO}_2 = 2\text{CpFe(CO)$_2$NO}_2 + 2\text{Ag}.
\end{equation}
The compound decomposes above -30°C. Its structure was established as the nitro isomer by X-ray crystallography and by solution NMR spectroscopy. There was no evidence for the presence of any other isomer of the -NO₂ ligand. The compound decomposes at room temperature by a first order intramolecular transfer of an oxygen atom between the NO, and CO ligands to produce the hitherto unknown CpFe(CO)(NO) and CO₂. This new nitrosyl compound is also very reactive, decomposing with the loss of CO to form the known (ref.23) nitrosyl bridged dimer, [CpFe(NO)]₂:

(6) CpFe(CO)₂NO, = CpFe(CO)(NO) + CO₂ followed by
(7) 2CpFe(CO)(NO) = [CpFe(NO)]₂ + 2CO.

These new organometallic NO₃ complexes comprise a class of compounds whose chemical and physical properties afford new synthetic routes to other new materials which may have significant roles to play in catalysis.

\[
\text{NITRO COMPLEXES}
\]

NO₃⁻ is a tetraatomic species with a total of 24 electrons. It is planar and isoelectronic with the carbonate ion. Only two forms of monomeric nitrate complexes, monodentate and bidentate (Fig. 6), have been identified (refs. 24, 25 for example). Since the geometry of the nitrate ligand precludes it from being tridentate, and an N-bonded π complex is unlikely since there are no unshared pairs of electrons on the nitrogen atom of NO₃⁻, no other monomeric nitrate complexes are likely nor have any been found.

Nearly 30 organometallic nitrate complexes have been prepared (refs. 26-47) ranging from simple metal carbonyl derivatives such as Mn(CO)₅(NO₃) (ref. 26) to the relatively complicated species, RuH(NO₃)(CO)₂(PPh₃)₂ (ref. 41). However, most of these compounds have been prepared as extensions of halide complexes, and their reactions have been little explored. While oxygen atom transfer reactions have often been implicated for nitrate complexes, only one reaction has been confirmed (ref.29), but no detailed kinetic studies of these reactions have been reported.

(8) Ni(NO₃)L₂ + CO = NiNO(NO₃)L₂ ; L = PEt₃

Nitrate complexes of the early transition metals, Ti, Zr, and Hf are well-represented among nitrate complexes in contrast with the absence of nitrites. Although many nitrate complexes such as Mn(CO)₅NO₃ have not yet been characterized structurally, several others have, including Cp₂Ti(NO₃)₂ and CpFe(CO)₅(NO₃). Structurally, these monodentate nitrate complexes have no unusual features associated with the M-ONO₃ group. The bond lengths and angles are comparable to those found in other nitrate complexes, and the nitrate ligand produces little effect on the other ligands in the complex.

The recent use of mixtures of simple metal nitrates as precursors for high Tₘ superconductors (ref. 47), suggests that organometallic nitrates may have an important role to play in the development of these new materials.

**SUMMARY**

The wide range of reactions, structures, and properties of metal complexes of NO₃ provide the basis for their use as catalysts, oxidants, polymer precursors, and precursors for other compounds and materials. The diversity of the properties of these compounds makes them a fertile area for further research. Clearly, much remains to be done.

**Acknowledgements**

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