

## Transition metal complexes of NO<sub>x</sub>

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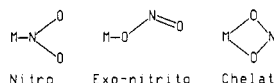
**Abstract** - The structure-reactivity relationships of organometallic nitrites and nitrates are summarized. The mechanism(s) of the reactions of these complexes, especially their oxygen-atom transfer reactions, are outlined with respect to their uses as catalysts and intermediate precursors.

### INTRODUCTION

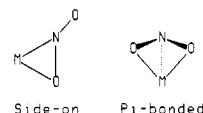
NO, NO<sub>2</sub>, and NO<sub>3</sub> complexes of transition metals comprise a class of materials with many potential uses as catalysts, as oxidants and as precursors to new and otherwise inaccessible compounds. As yet, much of this potential is unrealized because NO<sub>2</sub> and NO<sub>3</sub> 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).

### NO<sub>2</sub> COMPLEXES

Several general features of the NO<sub>2</sub> ligand are worth noting. NO<sub>2</sub><sup>-</sup> is a triatomic species with 18 valence electrons. It is isoelectronic with other ligands including SO<sub>2</sub> and




the allyl anion. Isomers  are known (refs. 6,7,8). By

analogy with SO<sub>2</sub> and the allyl ligand, two other isomeric forms,

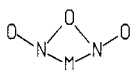


can be postulated. Neither form has been isolated, although some evidence for side-on and/or pi-NO<sub>2</sub> geometry has been obtained by photolysis of Co(NH<sub>3</sub>)<sub>5</sub>(NO<sub>2</sub>)<sup>2+</sup> (ref. 9). Recently, research on nickel (ref. 10) and cobalt (ref. 3) complexes has shown 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 <sup>15</sup>N NMR spectroscopy (ref. 3) (Table 1).

TABLE 1. Characteristic infrared bands and <sup>15</sup>N chemical shifts for MNO<sub>2</sub> isomers.

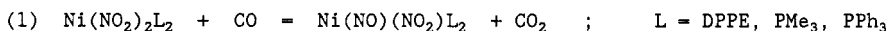
Vib. Frequency (cm <sup>-1</sup> )	ν <sub>N-O</sub> Asym.	ν <sub>N-O</sub> Symm.	δ <sub>NO2</sub>	ρ <sub>M-NO2</sub>	δ <sup>15</sup> N (ppm) vs. CH <sub>3</sub> NO <sub>2</sub>
	1390	1320	815	590	0-100
	1260	1200 1180	860	n.a.	180-230
	1400	1095	760	n.a.	230

In one of our early studies (ref. 11) using  $^{15}\text{N}$  substitution in *cis*- $\text{Fe}(\text{DEDTC})_2(\text{NO})(\text{NO}_2)$ , it was found that the  $\text{NO}$  and  $\text{NO}_2$  ligands undergo an intramolecular oxygen atom transfer reaction via a symmetric intermediate or transition state:

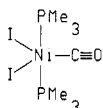


This widely quoted result prompted us (refs. 12,13,14) and others (refs. 15,16,17) to explore the use of the  $-\text{NO}_2$  ligands as oxidants in organic media. Tovrog *et al.* have shown that the closely related cobalt complexes of the type  $\text{CoNO}_x(\text{salen})$  catalyze the reactions between  $\text{O}_2$  and olefins through the reaction of the  $\text{NO}_2$  complex,  $\text{CoNO}_2(\text{salen})$ , with the olefin followed by the re-oxidation of  $\text{CoNO}(\text{salen})$  by  $\text{O}_2$  to  $\text{CoNO}_2(\text{salen})$ . Although several oxidized organic products were obtained, this series of reactions clearly established the potential for using the  $\text{MNO}/\text{MNO}_2$  couple as an oxidative catalyst. In his studies of cobalt complexes, Valenilla (ref. 3) found that the reactions between  $\text{O}_2$  and cyclohexene produced cyclohexene epoxide cleanly without the formation of other oxidized organic species.

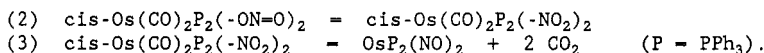
One of the first oxygen atom transfer reactions to  $\text{CO}$  to be investigated in any detail was the reaction of  $\text{NiNO}_2$  complexes with  $\text{CO}$  which produced a nickel nitrosyl complex and  $\text{CO}_2$  (ref. 12):



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

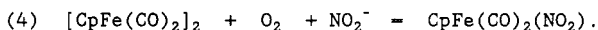


Since the reactions between  $\text{NO}_2^-$  and  $\text{CO}$  or alkenes do not take place in the absence of the transition metal, the role of the metal is critical for controlling these oxygen atom transfer reactions. The requirements thus far elucidated include: both the  $\text{NO}_2$  and  $\text{CO}$  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  $\text{NO}_2$  ligand responsible for oxidation was presented in a note by Roper (ref. 19) in his studies of the  $\text{OsP}_2(\text{CO})_2(\text{NO}_2)_2$  complexes. Roper found that the bis nitrito isomer rearranged to the bis nitro isomer before undergoing oxygen atom transfer to produce  $\text{CO}_2$  and the dinitrosyl complex:

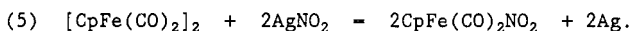


Most of the  $\text{NO}_2$  complexes which have thus far been isolated have amines or phosphines as co-ligands. Phosphine ligands are unsuited for oxidative catalysts because of the ease with which they are oxidized to phosphine oxides. Amine complexes are normally insoluble in organic solvents and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

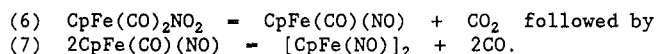
Only three organometallic  $\text{NO}_2$  complexes have been reported in the earlier literature (refs. 20,21,22). Angelici reported that a golden yellow compound thought to be  $\text{CpFe}(\text{CO})_2(\text{NO}_2)$  was formed from air oxidation of  $[\text{CpFe}(\text{CO})_2]_2$  in acidic solutions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



An oxygen atom transfer reaction between the  $\text{NO}_2$  and  $\text{CO}$  ligands of the type described in reaction 1 could account for the thermal instability of  $\text{CpFe}(\text{CO})_2(\text{NO}_2)$ . To address this question, Hansen prepared several new organometallic  $\text{NO}_2$  complexes of iron and ruthenium including  $\text{CpFeNO}_2$  (ref. 4).  $\text{CpFe}(\text{CO})_2\text{NO}_2$  was prepared using several synthetic strategies. The highest yields were obtained from the reaction of  $\text{AgNO}_2$  with  $[\text{CpFe}(\text{CO})_2]_2$ :



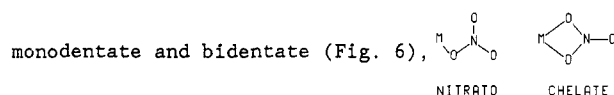
The compound decomposes above -30°C. Its structure was established as the nitro isomer by X-ray crystallography and by solution NMR spectroscopy. There was no evidence for the presence of any other isomer of the -NO<sub>2</sub> ligand. The compound decomposes at room temperature by a first order intramolecular transfer of an oxygen atom between the NO<sub>2</sub> and CO ligands to produce the hitherto unknown CpFe(CO)(NO) and CO<sub>2</sub>. 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)]<sub>2</sub>:



These new organometallic NO<sub>2</sub> 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.

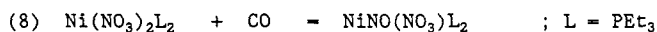
## NO<sub>3</sub> COMPLEXES

NO<sub>3</sub><sup>-</sup> 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,



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 NO<sub>3</sub><sup>-</sup>, 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)<sub>5</sub>(NO<sub>3</sub>) (ref. 26) to the relatively complicated species, RuH(NO<sub>3</sub>)(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (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.



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)<sub>5</sub>NO<sub>3</sub> have not yet been characterized structurally, several others have, including Cp<sub>2</sub>Ti(NO<sub>3</sub>)<sub>2</sub> and CpFe(CO)<sub>2</sub>(NO<sub>3</sub>). Structurally, these monodentate nitrate complexes have no unusual features associated with the M-ONO<sub>2</sub> 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 T<sub>c</sub> 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 NO<sub>x</sub> 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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