Reactions of Nitric Oxide Coordinated to Transition Metals

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I. Introduction

The use of the nitroprusside ion, $[Fe(CN)_5(NO)]^{2-}$, as the basis of qualitative spot-test determination of SH^-, $SO_3{}^{2-}$ and a variety of organic compounds has a very long and distinguished history. However, only recently has it become clear that these tests involve reaction of the coordinated nitric oxide and that the characteristic colors produced must be associated with the chromophoric group $[Fe\{N(O)R\}]$, where R is sulfide, sulfite, or carbanion. Apart from the analytical use of this work, however, only scant attention has been paid to the reactions of coordinated NO. This contrasts with the great interest in the reactivity of coordinated carbon monoxide, which reflects the more apparent industrial significance of the latter.

Recently, there has been a considerable upsurge in the study of transition metal nitrosyls and the reactions of the nitrosyl ligand. This is partly due to the increase in understanding of the way in which NO binds to a metal, which is subtly different to the situation involving CO, principally because nitric oxide has an additional electron. Thus NO can function as an electron donor, giving NO^+, or an electron acceptor, giving NO^- and even $N_2O_2{}^{2-}$. Another stimulus to investigating NO reactivity has been the developments in pollution control, largely stemming from attempts to remove, or at least diminish the concentration of, NO in exhaust gases emitted by the internal combustion engine. Further interest has arisen from the possibility of producing organo-nitrogen compounds from nitric oxide in reactions assisted or moderated by transition metal catalysts. Apart from the synthesis of nitric acid and nitrosyl chloride, NO has, as yet, little major industrial significance. In Japan, however, caprolactam is synthesized commercially by photolysis of cyclohexene and NO, but reactions between other hydrocarbons and nitric oxide, with or without catalysts, have been barely investigated and have apparently not yet provided useful routes to bulk or specialist organic chemicals. However, coordinated NO exhibits a very wide range of chemical behavior, as we shall see, and it is inconceivable that significant industrial processes involving transition-metal-catalyzed reactions of NO will not ultimately be developed.

Before beginning a discussion of the known reactions of nitrosyl ligands, it is necessary to comment briefly on the bonding between nitric oxide and metals. The fine details of the M-N-O interaction are not the subject of this review, but for those interested in such background information, extensive discussions have been presented by Manoharan and Gray,[1] Fenske and DeKock,[2] Pierpont and Eisenberg,[3] Mingos,[4] Enemark and Feltham,[5] and Hoffmann and his co-workers.[6]

There are three principal bonding modes in nitrosyl complexes, all of which involve metal-to-nitrogen, rather than M-O-N, interaction: (i) terminal, linear M-N-O groups, (ii) terminal, bent M-N-O groups, and (iii) bridging NO groups. In the first of these it has almost become conventional (although in the view of this author and others[7] not necessarily correct) to regard the nitrosyl ligand as being bound to the metal formally as "NO^+".[8] In the second, when the bond angle is usually about 120°, the ligand can be represented as coordinated "NO^-".[9] There are theoretical arguments for and against these representations,[10] but they have certain distinct advantages, the principal one of which is ease of correlation with, and prediction of, reactivity.

There are relatively few nitrosyl complexes which have the bent M-N-O system, and it is not often easy to predict when such a situation will occur. Simple MO theories have been advanced to account of the existence of nonlinear M-N-O bonds, and Ibers, Hoffmann and their colleagues[6,11] have suggested a set of rules by which we can predict when such a bonding arrangement will occur.

The bending of the M-N-O group is of very considerable importance in understanding certain aspects of metal nitrosyl chemistry. Many nitrosyl carbonyl complexes undergo displacement of CO by other Lewis bases via an *associative* process[12] rather then the dissociative pathway exhibited by simple metal carbonyls. If one believes that the "18-electron rule" is obeyed by metal carbonyl compounds in the transition state, then conversion of linear M-N-O into bent M-N-O represents effectively the withdrawal of an electron pair from the metal to the rehybridized N atom of NO, so facilitating the accommodation at the metal of a lone pair of electrons associated with the incoming Lewis base. Such a situation is strongly implied by the structures of $[Co(diars)_2(NO)][ClO_4]_2$[13] and $[Co(diars)_2(NCS)(NO)][NCS]$, in which the Co-NO bond angle in the former is 179° and in the latter is 132°. It seems highly likely that in reactions where metal nitrosyl complexes may catalyze the

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TABLE I. Color Reactions of the Nitroprusside Anion

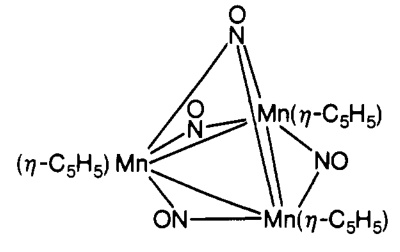
substrate	color	product (if known)[a]
SH^-, S^{2-}	red	$[Fe(CN)_5(NOS)]^{4-}$?
Se^{2-}	blue-green	$[Fe(CN)_5(NOSe)]^{4-}$?
Te^{2-}	black	$[Fe(CN)_5(NOTe)]^{4-}$?
mercaptans	purple-red	$[Fe(CN)_5\{N(O)SR\}]^{3-}$
$SO_3{}^{2-}$	deep red	$[Fe(CN)_5\{N(O)OSO_2\}]^{4-}$
$CH_3C(O)R$[b]	red	$[Fe(CN)_5\{N(O)CHCOR\}]^{4-}$ and $RC(O)CH{=}NOH$
$MeC(O)CH_2CO_2H$	red	
α-, β-, and γ-diketones	red	
RCH_2CN[c]	red	$RC({=}NOH)CN$
RCH_2NHCH_2R'	blue to violet[d]	
indole	violet	$[Fe(CN)_5(N_2OC_8H_6)]^{4-}$
α-methylindole	red	
thiourea and derivatives	red	
thiamine	green	
polyhydric phenols	green[d] or blue[e]	
m-$C_6H_4(NO_2)_2$	red-violet	

[a] Usually $[Fe(CN)_5(H_2O)]^{3-}$ unless otherwise stated. [b] R = Me, Ph, *p*-BrC_6H_4, $CH_2C({=}O)Me$. [c] Ph, *p*-$C_6H_4NO_2$, $C({=}O)OEt$. [d] In basic solution. [e] In acid solution.

oligomerization or dismutation of olefins, M–N–O bond angle bending may be a precursor to the essential activity of the system. However, in this review, such processes will not be discussed, since they do not involve chemical changes of the NO group per se.

In relation to the cobalt complexes mentioned above, we may note that in $[Co(diars)_2(NO)]^{2+}$, the NO group may be regarded formally as contributing three electrons to the metal, so that the "18-electron" configuration is attained. If this were to be the case in $[Co(diars)_2(NCS))NO)]^+$, the metal would have a "20-electron" configuration, which is virtually unknown in cobalt compounds. In the bent arrangement, the NO group formally contributes one electron, and so the "18-electron rule" is satisfied.

The nitrosyl group, like CO, can form bridges between two or three metal atoms. Both forms are exemplified in $[Mn_3(\eta^5\text{-}C_5H_5)_3(NO)_4]$ (1).[14] Similar bond arrangements probably occur



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on metal surfaces, but very little study has been made of the reactivity of the NO group in such situations which, admittedly, are relatively rare.

Within this review, the reactions of the nitrosyl ligand have been categorized into five sections, which represents an attempt to correlate reactivity with mechanism and the bonding modes of NO. Thus, the sections describing nucleophilic and electrophilic reactions can be related to the bonding modes $\{M(NO^+)\}$ and $\{M(NO^-)\}$, respectively. Reduction cannot be so readily categorized, but many disproportionation reactions could be represented as electrophilic attack upon coordinated NO by free NO, or nucleophilic attack upon the metal complex by CO. The last section contains a collection of many reactions which are not readily categorized, such as "insertion" processes and addition of certain types of hydrocarbons to bridging NO groups.

A number of discussions of certain aspects of the reactivity of coordinated NO have been published, and to be recommended are those of Swinehart,[15] Mašek,[16] Enemark and Feltham,[5] and Eisenberg and Meyer.[17] No discussion is given herein of the synthesis of nitrosyl complexes, but extensive reviews have been presented by Johnson and McCleverty,[18] Griffith,[19] Connelly,[20] and Caulton.[21]

II. Nucleophilic Attack

A. Nitroprusside Ion

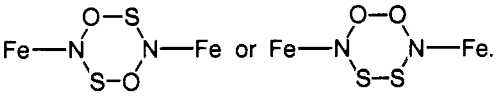
Although color tests using $[Fe(CN)_5(NO)]^{2-}$, e.g., the Gmelin reaction for identifying SH^-, the Boedeker test for sulfite, and others, have been known for many years, the chemistry of these reactions has only recently been elucidated. It is now clear that the majority of them can be described as nucleophilic attack upon the coordinated NO group, resulting either in the production of an unusual ligand bound to Fe(II), or in displacement of NO by another species, usually H_2O. Examples of the color reactions are summarized in Table I.

Swinehart has reviewed[15] the reactions of $[Fe(CN)_5(NO)]^{2-}$ with OH^-, SH^-, thiols, sulfite, ketones, and related species, and consequently this subject will not be dealt with here in great detail. However, partly for historical reasons and partly because the reactions of the nitroprusside ion are central to the development of the study of nucleophilic attack on transition metal nitrosyls, some discussion is appropriate in a separate section at the beginning.

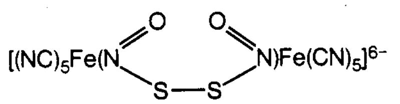
The rate of formation of $[Fe(CN)_5(NO_2)]^{4-}$ by hydroxide ion attack on $[Fe(CN)_5(NO)]^{2-}$ is first order in OH^- and nitroprusside ion concentration,[22] and careful electrochemical studies have shown[23] that $[Fe(CN)_5(N({=}O)OH)]^{3-}$ is a probable, but very short-lived, intermediate. Comparison of the rate of hydrolysis of nitroprusside ion with that of "free" NO^+ indicates that the metal strongly stabilizes the nitrosonium ion against nucleophilic attack by OH^-, and this modification of the properties of NO by coordination can be regarded as a central theme of this review.

High concentrations of acid are required to reconvert $[Fe(CN)_5(NO_2)]^{4-}$ to $[Fe(CN)_5(NO)]^{2-}$, which contrasts with the behavior of ruthenium complexes such as $[RuCl(bpy)_2(NO_2)]$. The analogous ruthenium and osmium pentacyanonitrosyls similarly afford $[M(CN)_5(NO_2)]^{4-}$ (M = Ru or Os) when treated[24] with OH^-.

Reaction of $[Fe(CN)_5(NO)]^{2-}$ with SH^- causes the formation of a purple-violet color, and with Na_2Se or Na_2Te it is reported that blue-green or black colors are generated.[25] Electrotitrations of the thiol reaction have been interpreted[26] in terms of the formation of $[Fe(CN)_5(N({=}O)SH)]^{3-}$ which, in basic media, readily forms $[Fe(CN)_5(NOS)]^{4-}$. However, as the result of more recent studies of the final products of this reaction, it has been suggested[27] that the nitrososulfide should be reformulated as $[Fe_2(CN)_{10}(N_2O_2S_2)]^{8-}$, possibly containing the groups



Certainly, the oxidative instability of sulfide would seem to lend support to the idea of S–S bond formation, but in the absence of definitive crystallographic data, either of these structural proposals would seem to be highly speculative. Indeed, one may wonder why



has not apparently been considered.

Alkaline solutions of mercaptans also give purple-red colorations with nitroprusside ion,[28] presumably involving the ion $[Fe(CN)_5(N({=}O)SR)]^{3-}$, and this type of reaction has been used to form the basis for a color test for cysteine[29] under mildly basic conditions.

Thioureas, particularly $(NH_2)_2CS$, $(Me_2N)_2CS$, and $(EtNH)_2CS$, react with $[Fe(CN)_5(NO)]^{2-}$ giving[25,28,30] adducts which, in the case of thiourea itself, have been formulated as $[Fe(CN)_5\{N(=O)SC(=NH)NH_2\}]^{3-}$. The true nature of this anion is unknown, but it evolves N_2 to give, possibly, $[Fe(CN)_5\{N(=O)NHC(=O)SH\}]^{3-}$ and then the blue $[(NC)_5Fe\{N(=O)NHC(=O)S\}Fe(CN)_5]^{7-}$. However, it seems equally likely that N_2 is evolved as the result of a "diazotization" of the coordinated thiourea and that the blue color produced could be due to $[Fe(CN)_5(NCS)]^{3-}$.

When nitroprusside ion is irradiated in the presence of aqueous thiocyanate, or when alkaline solutions of $[Fe(CN)_5(NO_2)]^{4-}$ containing NCS^- are acidified, the blue color mentioned above is produced.[31] A possible mechanism has been put forward:

$$\begin{tikzcd}[Fe(CN)_5(NO)]^{2-} + H_2O \arrow[r, "h\nu"] & {[Fe(CN)_5(OH_2)]^{3-} + NO^+} \arrow[d, "NCS^-"] \\ {[Fe(CN)_5(NO_2)]^{4-} + NCS^-} \arrow[r] & {[Fe(CN)_5(NCS)]^{4-} + NO_2^-}\end{tikzcd}$$

$$NO^+ + 2OH^- \longrightarrow NO_2^- + H_2O$$

$$[Fe(CN)_5(NCS)]^{4-} + HNO_2 \longrightarrow [Fe(CN)_5(NCS)]^{3-}$$

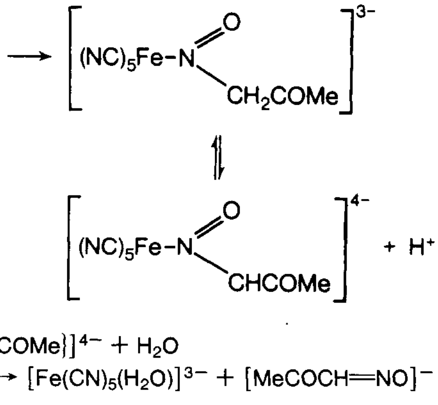
Proposals that intermediates such as $[Fe(CN)_5\{N(=O)(OH)(NCS)\}]^{4-}$ or $[Fe(CN)_5\{ON(=O)NCS\}]^{4-}$ (the unusual ligand being regarded as analogous to nitrate) are involved seem unlikely.

Reaction of nitroprusside ion with sulfite results in the formation of a deep red color and production of what appears to be the ion $[Fe(CN)_5\{N(=O)OSO_2\}]^{4-}$. This formulation is based on IR spectral studies,[33] and it has been suggested that the overall reaction may be similar to the first step in the Raschig synthesis of hydroxylamine, i.e., the formation of $[ONSO_3]^-$ from NO_2^- and SO_2/HSO_3^-. This reaction may be contrasted with that of "free" NO with alkaline metal sulfites, in which $[O_3SN_2O_2]^{2-}$ is formed.

Ketones and other species containing "acidic" protons (as in active methylene groups and certain aromatic compounds containing electron-withdrawing substituents) form colored solutions with $[Fe(CN)_5(NO)]^{2-}$ under basic conditions. The most carefully studied reaction is that involving acetone.[34] The red color produced initially rapidly fades, and the species $[Fe(CN)_5(H_2O)]^{3-}$ and $MeC(=O)CH=NOH$ can be recovered from the reaction mixture. The overall reaction scheme is thought to be as follows:

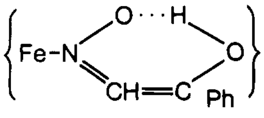
$$MeCOCH_3 + OH^- \longrightarrow [CH_2COMe]^- + H_2O$$

$$[Fe(CN)_5(NO)]^{2-} + [CH_2COMe]^-$$



$$[Fe(CN)_5\{N(=O)CHCOMe\}]^{4-} + H_2O \rightarrow [Fe(CN)_5(H_2O)]^{3-} + [MeCOCH=NO]^-$$

Salts of the type $[Fe(CN)_5\{N(=O)CHCOR\}]^{4-}$ have been isolated, and protonation of these compounds affords blue solutions which may contain $[Fe(CN)_5N(O)CH_2COR]^{3-}$ or $[Fe(CN)_5\{N(OH)=CHCOR\}]^{3-}$. With acetophenone, the blue protonated species which could be isolated[35] may contain the group i while the deprotonated (red) form may contain ii. Formaldehyde is



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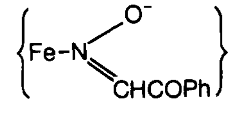


ii

believed[36] to react with nitroprusside ion giving another anion tentatively formulated as $[(NC)_5Fe\{N(OH)C(OH)N(=O)\}Fe(CN)_5]^{8-}$.

The reactions of $[Fe(CN)_5(NO)]^{2-}$ with ammonia[37] and aliphatic amines[38] have recently been investigated. In the pH range 11–12.5, ammonia reacts with nitroprusside ion giving $[Fe(CN)_5(NH_3)]^{3-}$ and NO_2^-, essentially via OH^- attack at the NO group. The nitro group so formed is displaced from the metal by water which, in turn and at relatively high ammonia concentrations, is replaced by NH_3. However, at very strong ammonia concentrations, N_2 is evolved, and it is to be assumed that this occurs by direct nucleophilic attack of NH_3 on the metal-bound NO group. Similar behavior occurs with primary aliphatic amines (RNH_2), the products including N_2 and ROH which are analogous to the products of the hydrolysis of alkyldiazonium salts. With secondary amines under similar conditions, however, it is believed that metal-bound *N*-nitrosamines are produced. In contrast, in liquid ammonia, NaNHPh reacts[39] with $[Fe(CN)_5(NO)]^{2-}$ affording $Na_4[Fe(CN)_5\{N(=O)NPh\}]$, but with NaNRR′, only $Na_3[Fe(CN)_5(NH_3)]$ could be isolated. In this last reaction, it must be presumed that RR′NNO is formed but is lost in the reaction mixture.

Many other compounds which may readily be deprotonated under basic conditions, e.g., indole, pyrrole, phenol, phenylhydrazine, and hydrazones (Table I), will also give colors when treated[15] with $[Fe(CN)_5(NO)]^{2-}$. Although the products of many of these reactions have not yet been characterized, it seems entirely likely that attack on the coordinated NO group by the N or O donor atom of the nucleophile would occur. With amines, we can anticipate the formation of *N*-nitroso complexes, as illustrated above, with phenols the generation of nitrito compounds, and perhaps, with phenylhdrazines and hydrazones, initial production of the group $[Fe\{N(=O)NHNHR\}]^{3-}$. Intermediates or products like these involving metals other than iron are discussed below.

B. Reactions of Other Nitrosyl Complexes with Nucleophiles

Attempts have been made, with varying success, to correlate the CO stretching frequency or stretching force constant in metal carbonyl complexes with reactivity of the coordinated CO groups toward nucleophilic attack. A similar approach in metal–nitrosyl chemistry has been adopted by Bottomley and his colleagues who propose[40] that metal nitrosyl compounds having $\nu(NO) > 1886\ cm^{-1}$ or, better, $f(NO) > 13.8$ mdyn $Å^{-1}$ will be susceptible to attack at the N atom by nucleophiles such as OH^-, OR^- (R = alkyl), NH_3, N_2H_4, NH_2OH, and N_3^- (see Table II). There seems to be a fair correlation, and the occasional exceptions to the rule may reflect inadequacies in the three-atom approximation used in calculating $f(NO)$, and/or the strong effect that the medium in which spectra have been recorded have on the value of $\nu(NO)$.

It is important to remember that the values of $f(NO)$ and $\nu(NO)$ are influenced by the electron density at the metal atom to which NO is bound. This density is, in turn, dependent on the oxidation state of the metal, the nature of and charge on the ligands, and the overall charge on the complex. As a consequence of Pauling's electroneutrality principle, metal atoms striving to become electrically neutral may disperse surplus charge either by oxidation or by back-donation to the ligands via suitable orbitals.

TABLE II. Reactions of Nitrosyl Complexes with Nucleophiles. Correlation of ν(NO) and *f*(NO) with Chemical Behavior

complex	$M(NO)^{n+}$	$\nu(NO)^a$	$f(NO)^b$	reagent	product
1. $[IrCl_5(NO)]^-$	4+	2006^c	16.0	a OH^-	$[IrCl_5(NO_2)]^{3-}$
				b NH_3	$[IrCl_5(NH_3)]^{2-}$, N_2
				c N_3^-	$[IrCl_5(H_2O)]^{2-}$, N_2, N_2O
				d NH_2OH	$[IrCl_5(H_2O)]^{2-}$, N_2O
$[IrBr_5(NO)]^-$	4+	1953^d	15.1	as above and	
				e N_2H_4	$[IrBr_3(N_2H_4)_3]$, 0.5 H_2O
2. $[IrCl_3(NO)(PPh_3)_2]^+$	4+	1945^d		OEt^-	$[IrCl_3\{N(=O)OEt\}(PPh_3)_2]$
3. $[Fe(CN)_5(NO)]^{2-}$	3+	1938^d	14.7	OH^-	$[Fe(CN)_5(NO_2)]^{4-}$
4. $[Ru(CN)_5(NO)]^{2-}$	3+	1927^c		OH^-	$[Ru(CN)_5(NO_2)]^{4-}$
5. $[Os(CN)_5(NO)]^{2-}$	3+	1904^c		OH^-	$[Os(CN)_5(NO_2)]^{4-}$
6. $[Ru(NH_3)_5(NO)]^{3+}$	3+	1925^d	14.6	a OH^-	$[Ru(NH_2)(NH_3)_4(NO)]^{2+}$, $[Ru(NH_3)_5(N_2)]^{2+}$, or $[Ru(NH_3)_5(NO_2)]^{2+}$ or $[Ru(NH_3)_4(NO)(OH)]^{2+}$
				b NH_3	$[Ru(NH_3)_4(NO)(OH)]^{2+}$, N_2O, N_2, or $[Ru(NH_3)_5(N_2O)]^{2+}$ or $[Ru(NH_3)_5(N_2)]^{2+}$
				c N_2H_4	$[Ru(NH_3)_5(N_2O)]^{2+}$ and/or $[Ru(NH_3)_5(N_2)]^{2+}$, $[Ru(NH_3)_5(N_3)]^{2+}$
				d NH_2OH	$[Ru(NH_3)_5(N_2O)]^{2+}$, N_2, N_2O
7. $[RuCl(bpy)_2(NO)]^{2+}$	3+	1927^e	14.5	a OH^-	$[RuCl(bpy)_2(NO_2)]$
				b $ArNH_2$	$[RuCl(bpy)_2(NNAr)]^{2+}$
				c N_3^- aq	$[RuCl(bpy)_2(H_2O)]^+$, N_2, N_2O
				d $C_6H_5NMe_2$	$[RuCl(bpy)_2\{N(O)C_6H_5NMe_2\}]^+$
8. $[Ru(NO)(NO_2)_2(OH)]^{2-}$	3+	1902^d	14.1	OH^-	$[Ru(NO_2)_5(OH)]^{4-}$
$[RuCl_5(NO)]^{2-}$	3+	1886^c	13.9		no reactions
9. $[Ru(diars)_2Cl(NO)]^{2+}$	3+	1876^c	13.8	a OH^-	$[Ru(diars)_2Cl(NO_2)]$
				b N_3^-	$[Ru(diars)_2Cl(N_3)[$, N_2, N_2O
				c N_2H_4	$[Ru(diars)_2Cl(N_3)]$
				d $PhNHNH_2$	$[Ru(diars)_2Cl\{N(O)NNHPh\}]$
				e NH_2OH	reaction, products not identified
$[Ru(NH_3)_4(NO)(OH)]^{2+}$	3+	1878^d	13.5		no reactions
$[Os(NH_3)_5(NO)]^{2+}$	3+	1885^d	13.4		no reactions
$[Os(NH_3)_4(NO)(OH)]^{2+}$	3+	1833^d	12.3		no reactions
$[Mo(NO)_2(S_2CNEt_2)_2]$	2+	1775, 1655^f		N_3^{-} ^{g}	$[Mo(NO)(S_2CNEt_2)_3]$, N_2O $[Mo(N_3)(NO)(DMSO)(S_2CNEt_2)_2]$
				NCO^-	$[Mo(NO)(S_2CNEt_2)_3]$, N_2O $[Mo(NCO)(NO)(DMSO)(S_2CNEt_2)_2]$

[a] In cm^{-1}; solvent as indicated. [b] In mdyn/Å. [c] Nujol mull. [d] Aqueous solution. [e] Acetone. [f] Chloroform. [g] In $(CH_3)_2SO$ solution.

Thus, in species such as $[Ir(NO)X_5]^{2-}$, the metal–NO unit has a high formal positive charge, $\{Ir(NO)\}^{4+}$, and the halide ligands are electronegative. Hence ν(NO) is quite high; there is little π donation from Ir to NO and so the nitrosyl ligand appears to retain residual positive charge. In the system *trans*-$[M(NH_3)_4(NO)(OH)]^{2+}$, the ligands are net σ donors and have no π-acceptor characteristics (saving NO), and the nitric oxide group is opposite a strong trans-influencing ligand in the octahedral complex. Hence, despite the positive charge on the compound, the metal must back-donate some charge to the NO group, thereby reducing its residual positive charge and, therefore, its attractiveness to nucleophiles.

The corollary of these arguments is, of course, that those compounds having particularly low values of ν(NO) and *f*(NO) should be susceptible to attack by electrophiles, and this point is discussed in a later section.

The reactions of some nitrosyl complexes with nucleophiles are summarized in Table II; nucleophilic reagents and products are listed together with appropriate values of ν(NO) or *f*(NO), and the formal charge on the M(NO) group is also given.

The reaction of $[Ru(NH_3)_5(NO)]^{3+}$ with OH^- (Table II, 6a) is more complicated than might be expected, since the products depend on hydroxide ion concentration. Thus, at 0.5 M $[Ru(NH_2)(NH_3)_4(NO)]^{2+}$ is formed, while at 5 M $[Ru(NH_3)_5(NO_2)]^{2+}$ is produced. Between 0.5 and 1.5 M, small amounts of $[Ru(NH_3)_5(N_2)]^{2+}$ are also generated. However, if $[Ru(NH_3)_5(NO)]^{3+}$ is heated with, or kept in prolonged contact with, OH^-, ammonia substitution occurs, and $[Ru(NH_3)_4(NO)(OH)]^{2+}$ is formed. Even at hydroxide concentrations as high as 10 M, there is no attack on the NO group of this dication. The occurrence of $[Ru(NH_3)_5(N_2)]^{2+}$ in alkaline solutions of $[Ru(NH_3)_5(NO)]^{3+}$ could be explained[42] by attack of either displaced NH_3 or $[Ru(NH_2)(NH_3)_4(NO)]^{2+}$ on the trication, giving the intermediates $[Ru(NH_3)_5\{N(=O)NH_2\}]^{2+}$ or $[(NH_3)_5Ru\{N(=O)NH_2\}Ru(NH_3)_4(NO)]^{5+}$ which would then dehydrate giving dinitrogen complexes.

The complexes $[Ru(bpy)_2(NO)X]^{2+}$,[43] $[Ru(diars)_2Cl(NO)]^{2+}$ (bpy = 2,2′-bipyridyl; diars = *o*-phenylenebis(dimethyl)arsine),[44] and $[Ir(NO)X_5]^{2-}$ [45] all react with OH^- to give the corresponding nitro complexes. While the equilibrium constant for the reaction $NO^+ + 2OH^- \rightarrow NO_2^- + H_2O$ is 2.3 × 10^{31} L^2 mol^{-2}, the corresponding constants for the conversion of $[Ir(NO)Cl_5]^{2-}$, $[Ir(NO)Br_5]^{2-}$, $[Fe(CN)_5(NO)]^{2-}$, and $[Ru(bpy)_2Cl(NO)]^{2+}$ are 6 × 10^{29}, 6.8 × 10^{27}, 1.5 × 10^6, and 1.6 × 10^9 L^2 mol^{-2}, respectively.[45] It is, of course, obvious that $[Ir(NO)X_5]^{2-}$ can be stable in solution only under acid conditions.

Alcoholysis of $[IrCl_3(NO)(PPh_3)_2]^+$ affords[46] $[IrCl_3\{N(=O)(OEt)\}(PPh_3)_2]$, and the alkyl nitrite can be displaced either by heating the complex or by treating it with CO, NH_3, or pyridine. In acid solution, $[IrCl_3\{N(=O)OEt\}(PPh_3)_2]$ reverts to the parent nitrosyl cation.

It may be noted that hydrolysis of the species $[M(NO)(NCMe)_2(PPh_3)_2]^{2+}$ (M = Rh or Ir) affords[47] hydroxy complexes $[M(NO)(OH)(PPh_3)_2]^+$, no nitro compounds being detected. Also, treatment of $[Fe(CO)_2(NO)(PPh_3)_2]^+$ or $[Mn(\eta^5\text{-}C_5H_5)(CO)(NO)(PPh_3)]^+$ with alkoxide ion gives[48] the carboalkoxy derivatives $[Fe\{C(=O)OR\}(CO)(NO)(PPh_3)_2]$ or $[Mn(\eta^5\text{-}C_5H_5)\{C(=O)OR\}(NO)(PPh_3)]$. However, consideration of the NO stretching frequencies of these complexes serves to emphasize the fact that positive charge on the complex does not, per se, facilitate attack at NO; the nitric oxide group must itself retain residual positive charge before nucleophilic addition will occur.

While the iridium complexes $[Ir(NO)X_5]^{2-}$ react instantaneously[45] with ammonia (Table II, 1b) giving $[Ir(NH_3)_5X]^{2-}$ and N_2, possibly via an unstable dinitrogen complex $[Ir(N_2)X_5]^{2-}$, the ruthenium complexes $[Ru(bpy)_2(NO)X]^{2+}$ and $[Ru(diars)_2Cl(NO)]^{2+}$ are converted by ammonia, and even some primary and secondary amines, into the corresponding nitro compounds, presumably via traces of water in the reactants.[43,44] In contrast, $[Ru(NH_3)_5(NO)]^{3+}$ reacts[49] at pH 10 with primary aliphatic amines (RNH_2, R = Me or Et) giving $[Ru(NH_3)_5(N_2)]^{2+}$ and ROH. It is thought that nucleophilic attack at the NO group, with subsequent proton loss, gives the intermediate metal diazenido species $[Ru(NH_3)_5(N_2R)]^{3+}$ which is hydrolyzed to afford the dinitrogen complex and the appropriate aliphatic alcohol. These reactions are comparable with those of $[Fe(CN)_5(NO)]^{2-}$ with aliphatic amines discussed previously,[38] and are analogous to the "diazotization" of primary aliphatic amines. They may also be compared with the behavior of other ruthenium nitrosyls toward aromatic amines (see below).

The blue-black polymeric compounds $[Cu(NO)X_2]_n$ (X = halide), which exist in equilibrium with CuX_2 and NO, react[50] with aliphatic amines also apparently via a modified "diazotization" reaction. Thus, for example, treatment of $PhCH_2CH_2NH_2$ in acetonitrile with $[Cu(NO)X_2]_n$, followed by addition of ethylenediamine and aqueous NaOH (presumably to remove Cu^{2+}), gave a mixture of $PhCH_2CHX_2$ (the main product), $PhCH_2CH_2X$, $PhCH_2CH_2OH$, and $PhCH_2CN$, together with NO, N_2O, and N_2. The yield of *gem*-dihalide could be increased, and displacement of NO eliminated, if the amine was complexed by CuX_2 prior to reaction with the nitrosyl polymer. There would appear to be at least three separate reactions in this system:

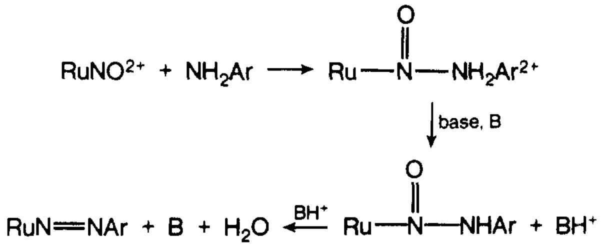
$$2RCH_2NH_2 + [Cu(NO)X_2]_n \rightarrow 2[RCH_2NH_2CuX_2] + 2NO$$

$$2RCH_2NH_2 + [Cu(NO)X_2]_n \rightarrow RCH_2X + RCH_2OH + N_2 + CuX + N_2O$$

$$2RCH_2NH_2 + [Cu(NO)X_2]_n \rightarrow 2RCHX_2 + 4CuX + 2N_2 + 2HCl + 2H_2O$$

The second of these reactions formally corresponds to the nitrosation of amine via an alkyldiazonium intermediate but, since reactions of amines with $NOBF_4$ give acetamides exclusively, Cu^{2+} would seem to be intimately involved in the denitrogenation of $RCH_2N_2^+$, perhaps by forming a complex. Support for this view comes from the observation that ethyl diazoacetate reacts with $CuCl_2$ giving ethyl dichloroacetate. The copper(II) nitrosyl halides also react with alcohols, secondary amines, azide ion, and ammonia giving, respectively, alkyl nitrites, R_2NNO, N_2 and N_2O, and N_2 and free CuX_2. Aromatic amines, when treated with $[Cu(NO)X_2]_n$, afford ArX and N_2 which, of course, is entirely analogous to conventional nitrosation of such amines, followed by treatment of the diazonium salts with halide.

The mechanism of the "diazotization" of p-$RC_6H_4NH_2$ (R = H, Me, or MeO) by $[Ru(bpy)_2Cl(NO)]^{2+}$, in which $[Ru(bpy)_2(N_2C_6H_4R)Cl]^{2+}$ is formed (Table II, 7b), has been investigated[51] in some detail. That the reaction must occur within the coordination sphere of the metal was elegantly demonstrated by the reaction of $[Ru(bpy)_2Cl(^{15}NO)]^{2+}$ with p-$MeOC_6H_4NH_2$, in which $[Ru(bpy)_2Cl(^{15}N^{14}NC_6H_4OMe)]^{2+}$ only was produced. The proposed mechanism involves several steps:

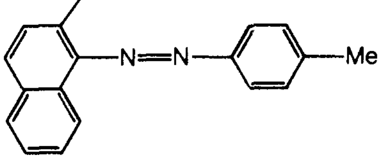


$$RuNO^{2+} + NH_2Ar \longrightarrow Ru{-}N(=O){-}NH_2Ar^{2+} \xrightarrow{\text{base, B}} Ru{-}N(=O){-}NHAr + BH^+$$

$$Ru{-}N(=O){-}NHAr + BH^+ \xrightarrow{BH^+} RuN{=}NAr + B + H_2O$$

There is convincing evidence to support this suggestion. For example, adducts formed between $[Ru(bpy)_2Cl(NO)]^{2+}$ and tertiary amines have been detected by IR spectroscopy, and impure $[Ru(bpy)_2Cl\{N(=O)NMe_2(C_6H_4Me)\}]^{2+}$ was isolated from a reaction with p-$MeC_6H_4NMe_2$. It seems highly likely that nitrosamines are generated as transient intermediates in the formation of ArN_2^+ via NO^+, and so related metal-coordinated species might be expected to be formed in the reaction with $[Ru(bpy)_2Cl(NO)]^{2+}$. Thus, if reaction with $ArNH_2$ was carried out in dichloromethane, rather than the more polar acetonitrile, nitrobenzene, DMF, or $(CH_3)_2SO$, $[Ru(bpy)_2Cl\{N(=O)NH_2Ar\}]^{2+}$ precipitated. The nitrosyl parent could be regenerated if this adduct was acidified, but when treated with K_2CO_3 in acetone, it afforded $[Ru(bpy)_2Cl\{N(=O)NHAr\}]^+$. Further careful acidification gave the diazotized product, $[Ru(bpy)_2Cl(N_2Ar)]^{2+}$.

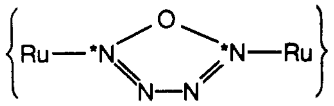
On treatment of $[Ru(bpy)_2Cl(N_2C_6H_4Me)]^{2+}$ with KI and β-naphthol, p-MeC_6H_4I and **2** were formed. On heating the diazonium complex in acetone, decomposition occurred and toluene was liberated.



2

The amines C_6H_5NRMe (R = H or Me) also react[52] with $[Ru(bpy)_2Cl(NO)]^{2+}$ but form nitrosoarene complexes, $[Ru(bpy)_2Cl\{N(=O)C_6H_4NRMe\}]^+$. The generation of such compounds must be competitive with diazotization, but in reactions involving primary aromatic amines, no evidence of aromatic nitrosation could be detected. The nitro complex $[Ru(bpy)_2\{N(=O)C_6H_4NRMe\}(NO_2)]^+$ could be converted by acid into $[Ru(bpy)_2\{N(=O)C_6H_4NRMe\}(NO)]^{3+}$ which would undergo further reaction with amine, affording $[Ru(bpy)_2\{N(=O)C_6H_4NRMe\}_2]^{2+}$. Phenoxide ion could also be nitrosylated in this way, although anisole was unreactive; there was no evidence for the formation of ArONO. These reactions, like the "diazotization" discussed above, also appear to occur within the coordination sphere of the metal, since ^{15}N was retained in the nitrosoarene complex when $[Ru(bpy)_2Cl(^{15}NO)]^{2+}$ was used.

The products of reaction of $[Ru(NH_3)_5(NO)]^{3+}$ with hydrazine hydrate are temperature dependent (Table II, 6c).[53] Thus, at low temperatures, providing that halide was present, a mixture of $[Ru(NH_3)_5(N_2O)]^{2+}$ and $[Ru(NH_3)_5(N_2)]^{2+}$ was formed in 10 s. After 3 min, however, strongly colored species had appeared, and it was thought possible that these contained Ru(III) azido complexes, e.g., $[Ru(NH_3)_5(N_3)]X_2$. These colored mixtures rapidly turned yellow and their IR spectra revealed the presence of $[Ru(NH_3)_5(N_2O)]^{2+}$ and $[Ru(NH_3)_5(N_2)]^{2+}$ as well as the azide. This behavior contrasts with that of $[Ru(diars)_2Cl(^{15}NO)]^{2+}$ which, when treated with N_2H_4, gives only $[Ru(diars)_2Cl(^{15}N^{14}N^{14}N)]$ (Table II, 9c).[54] That there is direct attack by hydrazine on the NO group of the nitrosyl ammine was demonstrated by the formation of $[Ru(NH_3)_5(^{14}N^{15}NO)]^{2+}$ and $[Ru(NH_3)_5(^{29}N_2)]^{2+}$ from $[Ru(NH_3)_5(^{15}NO)]^{3+}$ and $^{28}N_2H_4$. The mechanism of the reaction is not known in detail, but a likely intermediate must involve the group $[Ru\{N(=O)NH_2NH_2\}]^{3+}$ or, more probably, $[Ru\{N(=O)NHNH_2\}]^{2+}$ and/or $[Ru\{N(OH)=NNH_2\}]^{2+}$. Of relevance is the observation that $[Ru(diars)_2Cl(NO)]^{2+}$ reacts[54] with phenylhydrazine giving $[Ru(diars)_2Cl\{N(O)=NNHPh\}]$ (Table II, 9d). Loss of ammonia from the simple labeled hydrazine adduct would be expected to afford $[Ru(NH_3)_5(^{14}N^{15}NO)^{2+}$ provided that there was migration of the metal from the central to the terminal N atom of N_2O. Indeed, there is some precedent for such a type of rearrangement, since hydrazine attack on $[Fe(\eta^5\text{-}C_5H_5)(CO)_3]^+$ gives[55] $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(NCO)]$ via dehydration of the intermediate $[Fe(\eta^5\text{-}C_5H_5)(CO)_2\{C(=O)NHNH_2\}]$. Deprotonation and dehydration of an intermediate such as $[Ru(NH_3)_5\{^{15}N(OH)=NNH_2\}]^{2+}$ should give the Ru(II) species $[Ru(NH_3)_5(^{15}N^{14}N^{14}N)]^+$. That this latter species was not detected while its Ru(II) counterpart may have been present perhaps reflects the fact that the reactions were carried out in air. However, these suggestions do not explain the formation of the dinitrogen complexes. These could arise via attack on $[Ru(NH_3)_5(NO)]^{3+}$ either by free ammonia, generated by degradation of $[Ru(NH_3)_5\{N(=O)NHNH_2\}]^{2+}$, or by $[Ru(NH_2)(NH_3)_4(NO)]^{2+}$ as mentioned earlier.[42] Alternatively $[Ru(NH_3)_5(^{15}N^{14}N^{14}N)]^+$ could be attacked by $[Ru(NH_3)_5(^{15}NO)]^{3+}$ giving an intermediate containing the group



which could decompose giving both $[Ru(NH_3)_5(^{29}N_2O)]^{2+}$ and $[Ru(NH_3)_5(^{29}N_2)]^{2+}$. This hypothesis may be related to nitrosonium ion attack on $[Ru(diars)_2Cl(N_3)]$ in which $[Ru(diars)_2Cl(N_2)]^+$ is formed.[56]

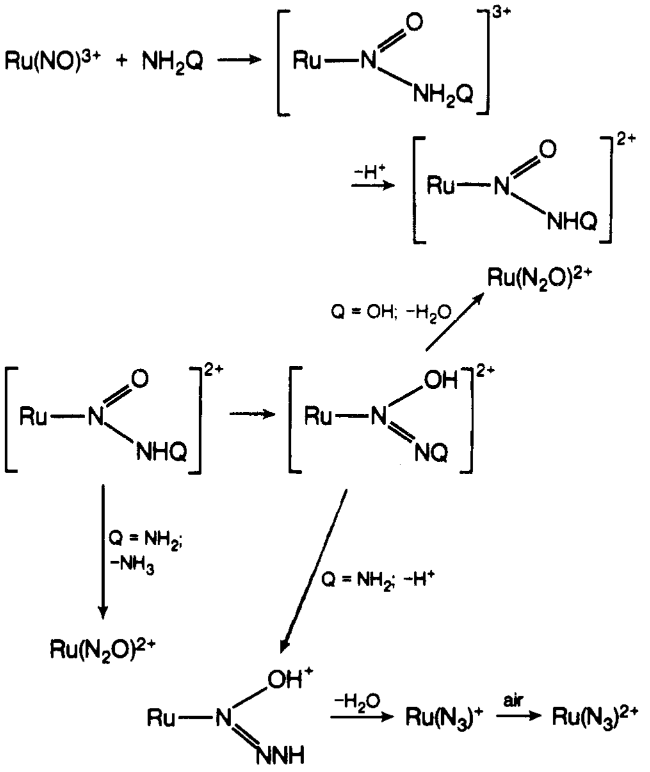
Hydroxylamine attack on $[Ru(NH_3)_5(^{15}NO)]^{3+}$ gives[53] $[Ru(NH_3)_5(^{15}N^{14}NO)]^{2+}$ (Table II, 6d). It may be recalled that HNO_2 reacts with hydroxylamine giving N_2O and water in a process initially involving[57] attack by NO^+, viz.

$$NO^+ + NH_2OH \rightarrow [ONNH_2OH]^+ \rightarrow [ONNHOH] + H^+$$

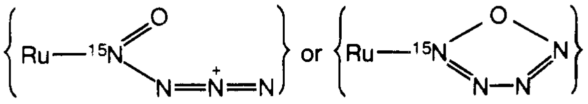
and so, in the ruthenium-moderated reaction, we might expect an intermediate such as $[Ru(NH_3)_5\{^{15}N(=O)NHOH\}]^{2+}$. Dehydration of this, like its hydrazine analogue, should ultimately give $[Ru(NH_3)_5(^{14}N^{15}NO)]^{2+}$, contrary to the experimental observations. However, it has been suggested that [ONNHOH] can undergo proton transfer to give [HON=NOH], hyponitrous acid, and the corresponding rearrangement in the ruthenium intermediate would afford $[Ru(NH_3)_5\{^{15}N(OH)=NOH\}]^{2+}$ which would be analogous to the O-protonated form of $[Ru(diars)_2Cl\{N(O)=NNHPh\}]$. Loss of water from the hyponitrous acid complex would then afford $[Ru(NH_3)_5(^{15}N^{14}NO)]^{2+}$, in the same way that dehydration of $[Ru(diars)_2Cl\{^{15}N(O)=NNH_2\}]$ is thought to give $[Ru(diars)_2Cl(^{15}N^{14}N^{14}N)]$.

The possibility that the mechanisms of reaction of $[Ru(NH_3)_5(NO)]^{3+}$ with hydrazines and hydroxylamine might involve a common type of intermediate, viz., $[Ru\{N(OH)=NQ\}]^{2+}$, where Q = OH or NHR, is very appealing. Certainly, the generation of azido and dinitrogen oxide species can be conveniently explained; see Scheme I. However, the origin of $[Ru(NH_3)_5(N_2)]^{2+}$ in the reactions with hydrazine deserves further investigation. This might involve studying the behavior of $[Ru(^{14}NH_3)_5(^{14}NO)]^{3+}$ and its ^{15}NO analogue with $^{15}NH_3$, trying to establish whether $^{14}NH_3/^{15}NH_3$ exchange takes place and at what rate, and confirming (or otherwise) the formation of $[Ru(^{14}NH_3)_5(^{29}N_2)]^{2+}$ and/or $[Ru(^{14}NH_3)_5(^{30}N_2)]^{2+}$ by direct attack of $^{15}NH_3$ on coordinated NO. This investigation should also reveal whether species such as $[Ru(^{14}NH_2)(^{14}NH_3)_4(^{14}NO)]^{2+}$ are a significant factor in the formation of N_2 complexes, since, in the presence of $^{15}NH_3$ presumably only $[Ru(^{14}NH_3)_5(^{28}N_2)]^{2+}$ could be formed from its reaction with $[Ru(^{14}NH_3)_5(^{14}NO)]^{3+}$. That $^{14}NH_3/^{15}NH_3$ exchange may not occur particularly rapidly can be deduced from observations[58] that $[Ru(NH_3)_6]^{3+}$ in strong base in the presence of $^{15}NH_3$ and air affords only $[Ru(NH_3)_5(^{14}NO)]^{3+}$ (*not* $[Ru(NH_3)_5(^{15}NO)]^{3+}$). This indicates that coordinated NH_3, which obviously has not undergone ammonia exchange, is oxidized by air under basic conditions to give coordinated NO. A further study with $[Ru(^{15}NH_3)_5(^{15}NO)]^{3+}$ and $^{28}N_2H_4$, provided that it could be firmly established that $^{14}NH_3$ complexes were not produced, would reveal whether the dinitrogen complex depends for its formation on $^{14}NH_3$ liberated from the intermediate $[Ru(^{15}NH_3)_5\{^{15}N(OH)=^{14}N^{14}NH_2\}]^{2+}$, in which case $[Ru(^{15}NH_3)_5(^{14}N^{15}NO)]^{2+}$ and $[Ru(^{15}NH_3)_5(^{29}N_2)]^{2+}$ would be the products. However, it must be recognized that if cyclic intermediates derived from azido species play a significant role in these reactions, then the above experiments may provide ambiguous results. Indeed, it is difficult to conceive of tests which would demonstrate unequivocally the existence of a cyclic or a noncyclic mechanism.

SCHEME I



Azide ion reacts with $[Ru(diars)_2Cl(^{15}NO)]^{2+}$ (Table II, 9b) giving[56] exclusively unlabeled $[Ru(diars)_2Cl(N_3)]$, and a 1:1 mixture of $^{28}N_2O$ and $^{14}N^{15}NO$ (*no* $^{15}N^{14}NO$ or $^{30}N_2O$). In earlier studies[59] of the reaction between NO^+ and N_3^-, it was suggested that the products, N_2 and N_2O, were formed via the intermediate N_4O, and such a species has apparently been isolated. Two metal-bound forms of this molecule have been proposed for the ruthenium-moderated reaction, viz.



Although no final conclusion about the precise mechanism has been reached, it is thought likely that the cyclic species is formed and is then displaced by more azide, giving unlabeled $[Ru(diars)_2Cl(N_3)]$. Decomposition of the cyclic N_4O via this route would give equal amounts of $^{14}N^{15}NO$ and $^{28}N_2O$ whereas degradation via the noncyclic intermediate would produce only $^{14}N^{15}NO$. If decomposition of N_4O took place while still bound to the metal, it would be expected that unequal amounts of $^{28}N_2O$ and $^{29}N_2O$ would be formed. The isolation of the complexes $[Ru(bpy)_2X(solvent)]^{+}$ [60] and $[IrBr_5(H_2O)]^{2-}$ [45] after treatment

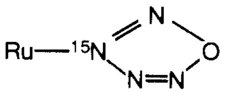
TABLE III. Compounds Which Undergo Electrophilic Attack at NO

complex	ν(NO)^a	reagent	products
$[Ru(NO)_2(PPh_3)_2]$	1665, 1615^b	HCl	$[RuH(NO)_2(PPh_3)_2]^+$, then $[RuCl_3(NO)(PPh_3)_2]$
		$PhCH_2Br$	$[RuBr(CO)(NO)(PPh_3)_2]$ and/or $[RuBr_2(CO)_2(PPh_3)_2]$, PhCH=NOH, PhCN, and $PhCONH_2$
		O_2	$[Ru(NO)(PPh_3)_2(NO_3)(O_2)]$
$[Ru(CO)(NO)(PPh_3)_2X]$, X = Cl	1592^b	O_2	$[Ru(NO)(PPh_3)_2(O_2)X]$
= NCS	1620^b		
$[Os(NO)_2(PPh_3)_2)$	1665, 1615^b	HCl	$[OsCl_2(NHOH)(PPh_3)_2]$
$[OsCl(CO)(NO)(PPh_3)_2]$	1565^c	HCl	$[OsCl_2(CO)(HNO)(PPh_3)_2]$
		O_2	$[OsCl(CO_3)(NO)(PPh_3)_2]$
$[Co(diars)_2(NO)]^{2+}$	1852^b	HBr	$[Co(diars)_2Br(HNO)]^{2+}$
$[Co(diars)_2Br(NO)]^+$	1665, 1550^b	HBr	$[Co(diars)_2Br(HNO)]^{2+}$
$[Co(NO)(salen)]$ (**3**)	1624^c	O_2/py	$[Co(NO_2)(salen)py]$
$[Co(NO)(acacen)]$ (**4**); X = O; R = Me	1690^b	O_2/py	$[Co(NO_2)(acacen)(py)]$
$[Co(NO)(SacSacen)$ (**4**); X = S; R = Me	1638^b	O_2/py	$[Co(NO_2)(SacSacen)(py)]$
$[Co(NO)(S_2CNMe_2)_2]$	1626^b	O_2/py	$[Co(NO_2)(S_2CNMe_2)_2(py)]$
$[Co(NH_3)_5(NO)]^{2+}$ (**8**)	1600^c	NO	$[Co_2(NH_3)_{10}(N_2O_2)]^{4+}$, **9**, and/or $[Co(NH_3)_5(OH)]^{2+}$ NO_2^-, and N_2O
$[Co(en)_2(NO)]^{2+}$	1660^c	O_2/MeCN	$[Co(NO_2)(en)_2(NCMe)]^{2+}$
$[Co(en)_2(NO)(MeOH)]Cl_2$	1611^b	NO	$[CoCl(NO_2)(en)_2]Cl + N_2O$
$[Co(NO)(DMGH)_2MeOH]$	1641^b	O_2/py	$[Co(DMGH)_2(py)(NO_2)]$ and $[Co(DMGH)_2(py)(NO_2]$
$[Co(NO)(CO)_3]$	1806^d	NO	$[Co(DMGH)_2(py)(NO_2)] + N_2O$
		NO/py	$[Co(N_3O_4)]_n$, **10** or **11**; or $[Co_4(NO)_8(NO_2)_3(N_2O_2)])$ **12**
$[Co(CO)_2(NO)X]^-$; X = Br	1767^e	$PhCH_2Br$	PhCH=NOH and $PhCH_2CO_2H$
X = I	1712^e		
$[Co(NO)(PPh_3)_3]$	1738^b	NO	$[Co(NO)_2(NO_2)(PPh_3)_2] + N_2O + N_2$ $PhCH_2Br$ PhCH=NOH, low yield
$[Rh(NO)(PPh_3)_3]$	1610^c	HCl (xs)	$[RhCl_3(NH_2OH)(PPh_3)_2]$
		$PhCH_2Br$	$[RhBr(CO)(PPh_3)_2]$ + PhCH=NOH (low yield)
$[RhCl_2(NO)(PPh_3)_2]$	1632^b	$PhCH_2Br$	$[RhCl_2Br(CO)(PPh_3)_2]$ + PhCH=NOH (low yield)
$[Ir(NO)(PPh_3)_3]$	1600^c	HCl (xs)	$[IrCl_3(NH_2OH)(PPh_3)_2]$ via $[IrH(NO)(PPh_3)_3]^+$
$[Ir(NO)_2(PPh_3)_2]^+$	1760^b, 1715	O_2	$[Ir(NO)(NO_3)(PPh_3)_2]^+$
$[IrCl_2(CO)(NO)(PPh_3)_2]$	1560^c, 1520	O_2	$[IrCl_2(CO)(NO_3)(PPh_3)_2]$
$[NiCl(NO)(diphos)]$	1735^d	O_2	$[NiCl(NO_2)(diphos)]$
$[Pt(NO)(NO_2)(PPh_3)_2]$	~1600^d	O_2	$[Pt(NO_3)(NO_2)(PPh_3)_2]$

[a] In cm^{-1}; in medium as indicated. [b] Nujol mull. [c] KBr disk. [d] CH_2Cl_2 soln. [e] diglyme solution.

of the appropriate nitrosyls with azide (Table II, 1c and 7c) is also consistent with dissociation of N_4O prior to its degradation.

It might be expected that azido complexes would react with NO^+ giving N_2 and N_2O via an intermediate very similar to that discussed above. These gaseous products, and $[Co(NH_3)_5(H_2O)]^{3+}$, are indeed obtained by nitrosation[61] of $[Co(NH_3)_5(N_3)]^{2+}$. However, nitrosonium ion attack upon *trans*-$[Ru(diars)_2Cl(^{15}N^{14}N^{14}N)]$ afforded[56] unequal amounts of *trans*-$[Ru(diars)_2Cl(^{29}N_2)]^+$ (ca. 80%) and *trans*-$[Ru(diars)_2Cl(^{28}N_2)]^+$ (ca. 20%); analysis of the gaseous products could not be made. It is clear from this last reaction at least that, because of the formation of different products, there can be no common intermediate in the reaction between $[Ru(NO)]^{3+}$ and N_3^- and $[Ru(N_3)]^{2+}$ and NO^+. However, for the latter system, a cyclic intermediate has been proposed, viz.



It must be presumed that $^{28}N_2O$ is eliminated preferentially from this species and that slow migration of the metal to an adjacent ^{14}N atom might occur in order to permit elimination of $^{29}N_2O$. The implication of this proposal is that degradation occurs while N_4O is bound to the metal atom. No reaction was detected between $[Ru(diars)_2Cl(N_2)]^+$ and NO^+ under the experimental conditions used for attack on the azide, and this indicated that once the dinitrogen species was formed, no subsequent reaction, giving the observed isotopic distributions, occurred.

Very few reactions of nitric oxide coordinated to elements of groups 4B to 7B have been reported. A rare exception to this concerns the behavior[62] of *cis*-$[Mo(NO)_2(S_2CNMe_2)_2]$ with azide and cyanate. Thus, in $(CH_3)_2SO$ in the dark, $[Mo(NO)(S_2CNMe_2)_3]$, $[Mo(NO)(S_2CNMe_2)_2(DMSO)X]$ (X = N_3 or NCO), and N_2O were formed. From results obtained with $Na^{15}N^{14}N^{14}N$, and by using gas analysis, it seems that the dinitrogen oxide produced in these reactions does not originate from the azide, but full details of this study have apparently not yet appeared.

III. Electrophilic Attack

It is reasonable to assume, following the arguments of Bottomley[40] about the relationship of ν(NO)/*f*(NO) to the susceptibility of coordinated NO toward nucleophilic attack, that species having particularly low values of ν(NO) would be liable to attack by electrophiles (Table III). Of course, the situation here is, in some sense, more complicated since low NO stretching frequencies are usually associated with relatively "electron-rich" metal complexes. Such complexes commonly contain metals in low oxidation states, and when this is coupled with coordinative unsaturation, then oxidative addition reactions are bound to compete with any process designed to involve the NO group.

A. Protonation of NO

It is very tempting to view the protonation of coordinated NO as a process induced by prior bending of the M–N–O bond angle. The phenomenon of bent M–N–O groups has been discussed earlier, and there is little necessity for additional comment here. However, the rehybridization of the nitrogen atom occasioned by conversion from linear M-N-O (sp) to bent M-N-O (sp^2) effectively places a lone pair of electrons on the N atom. This conversion could, in principle, be brought about by turning a conventional 18-electron nitrosyl complex (M-NO$^+$; bond angle 180°) into a transient 20-electron species. This could be achieved by association with a Lewis base, followed by M-N-O bond angle bending, thereby relieving the electronic excess at the metal. Hence, two electrons are removed from the metal and are given to the NO group (formally converting the system to M-NO$^-$), and the electron population of the metal is maintained at 18. This metal-NO electron-transfer process would be reversible and, of course, could be a concerted rather than a stepwise process. It is known,[12] however, that the above mechanism is implied by CO exchange in mixed metal carbonyl nitrosyl complexes which involves an associative process, whereas metal carbonyls themselves react via a dissociative pathway.

Although $[Co(diars)_2(NO)][ClO_4]_2$ is not protonated by $HClO_4$, when treated with HBr it affords[13] $[Co(diars)_2Br(HNO)]^{2+}$ (Br$^-$ behaving as a Lewis base). This reaction could be regarded in the following way:

$$[Co(diars)_2(NO)]^{2+} \xrightarrow{Br^-} [Co(diars)_2Br(NO)]^+$$

(20 e, linear Co-N-O)

$$[Co(diars)_2Br(HNO)]^{2+} \xleftarrow{H^+} [Co(diars)_2Br(NO)]^+$$

(18 e, bent Co-N-O)

Protonation of $[Co(diars)_2Br(NO)]^+$ also gives the HNO complex. It is clearly established from X-ray studies that $[Co(diars)_2(NO)]^{2+}$, an 18-electron system, has a linear Co-N-O bond, whereas $[Co(diars)_2(NCS)(NO)]^+$ has a Co-N-O bond angle of 132°.

Collman and Roper have investigated the reactions of nitrosyl complexes of Os, Rh, and Ir. Thus, $[Os(NO)_2(PPh_3)_2]$, where the Os-N-O bond angle is slightly distorted from linearity, reacts reversibly with 2 mol of HCl giving $[OsCl_2(NHOH)(NO)(PPh_3)_2]$. Similar treatment of $[OsCl(CO)(NO)(PPh_3)_2]$ is said to give $[OsCl_2(CO)(HNO)(PPh_3)_2]$, and if this species is treated with CO, HNO can be displaced forming $[OsCl_2(CO)_2(PPh_3)_2]$. In both of these reactions it is conceivable that intermediates containing bent Os-N-O groups could be formed by initial coordination of Cl$^-$. An alternative pathway could involve protonation of an NO group, thereby converting it from a three- to a two-electron donor, and producing a coordinatively unsaturated intermediate. Further protonation, to give the group Os-NHOH, would reduce the nitrogen-containing ligand further, to a one-electron donor. Thus, the reaction could be thought of as occurring in steps, e.g.

$$[Os(NO)_2L_2] + H^+ \rightarrow [Os(NO)(HNO)L_2]^+; \quad + X^- \rightarrow [Os(NO)(HNO)L_2X]$$

$$[Os(NO)(HNO)L_2X] + H^+ \rightarrow [Os(NO)(NHOH)L_2X]^+; \quad + X^- \rightarrow [Os(NO)(NHOH)L_2X_2]$$

Continuing protonation should lead, logically, to the production of hydroxylamine, i.e., $[Os(NO)(NH_2OH)L_2X_3]$, and although this has not been observed with the Os complex, related Rh[64] and Ir[64,65] nitrosyl compounds can be so reduced. It is, of course, an assumption that the addition of H$^+$ occurs initially at the N atom. Protonation could also occur at the oxygen atom, giving {M(NOH)}, and such ambivalence of behavior has a parallel in the protonation of aryl-diazenido complexes of platinum and rhenium (ArN$_2$ is electronically equivalent to NO). Thus, the species $[PtCl(NH{=}NPh)(PEt_3)_2]^+$ and $[ReCl_2(N{=}NHPh)(NH_3)(PMe_2Ph)_2]^+$ have been prepared[66] by the addition of H$^+$ to $[PtCl(N_2Ph)(PEt_3)_2]$ and $[ReCl_2(N_2Ph)(NH_3)(PMe_2Ph)_2]$, respectively. In the end, however, the site of protonation need not have any particular influence on the reduction of coordinated NO to hydroxylamine.

Although $[Ru(NO)_2(PPh_3)_2]$ is electronically equivalent to and isostructural with its Os analogue, its protonation by HCl proceeds differently and in two stages,[67] giving first $[RuH(NO)_2(PPh_3)_2]^+$ and then $[RuCl_3(NO)(PPh_3)_2]$ (the fate of the other NO group is not known). The reactions of $[M(NO)_2(PPh_3)_2]$ described so far were carried out in the absence of oxygen, but when protonation was accomplished in air, the hydroxy complexes $[M(NO)_2(PPh_3)_2(OH)]^+$ were formed. Apparently, this remarkable reaction has not been investigated in detail but is thought to involve a hydroperoxide intermediate.

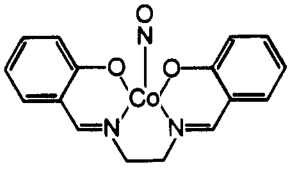
Treatment of $[M(NO)(PPh_3)_3]$ (M = Rh or Ir) with 2 mol of HCl afforded[65] $[MCl_2(NO)(PPh_3)_2]$, which contains bent M-N-O. However, with an excess of HCl, $[MCl_3(NH_2OH)(PPh_3)_2]$, together with some of the nitrosyl dichloride complex, was formed, and the hydroxylamine could be displaced by CO giving $[MCl_3(CO)(PPh_3)_2]$. Similar treatment of $[Co(NO)(PPh_3)_3]$ afforded only $[CoCl_2(NO)(PPh_3)_2]$ and $[CoCl_2(PPh_3)_2]$. It has been reported[63] that reaction of $[Rh(NO)(PPh_3)_3]$ with HCl afforded isomers of $[RhCl_3(NHO)(PPh_3)_2]$, but it has been suggested that these compounds may actually contain hydroxylamine. Attempts have been made[65] to identify the intermediates in the system $[M(NO)(PPh_3)_3]$/HCl (M = Rh or Ir). It is unlikely that $[MCl_2(NO)(PPh_3)_2]$ is one, since it does not react further with HCl, and the same appears to be true for $[MClH(NO)(PPh_3)_2]$. However, $[MH(NO)(PPh_3)_3]^+$, on further treatment with HCl, afforded the hydroxylamine complex, $[MCl_3(NH_2OH)(PPh_3)_2]$.

Finally, it is tempting to speculate on a possible relationship between the *formal* oxidation state of the metal, the electron density on the NO (which can be regarded *formally* as a neutral ligand), and the extent of protonation of the nitrosyl group. As the *formal* oxidation state in $[OsCl(CO)(NO)(PPh_3)_2]$, $[Os(NO)_2(PPh_3)_2]$, and $[Ir(NO)(PPh_3)_3]$ decreases from +1 to 0, and the d-orbital population increases from 7 to 9 (with concomitant back-donation to the NO), the number of protons which can be added to the nitrosyl ligand increases from 1 to 3, giving $[OsCl_2(CO)(HNO)(PPh_3)_2]$, $[OsCl_2(NO)(NHOH)(PPh_3)_2]$, and $[IrCl_3(NH_2OH)(PPh_3)_2]$, respectively.

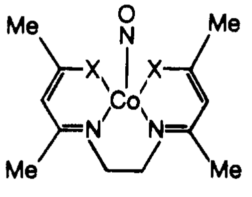
B. Oxygenation

Reactions of coordinated NO with oxygen can give either a nitrato or nitro/nitrito species, and in at least one case, a mixture of these has been found. The factors which favor formation of one product rather than the other are not yet understood.

Clarkson and Basolo observed[68] that nitrosylcobalt Schiff base complexes (**3** or **4**), $[Co(NO)(en)_2]^{2+}$ or $[Co(NO)(S_2CNMe_2)_2]$, reacted with O$_2$ in the presence of bases (pyridines, PBu$^n_3$, MeCN) giving nitro products, e.g.



3, [Co(NO)(salen)]

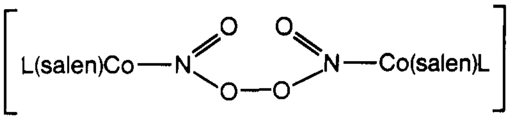


4, X = O, R = Me, Ph;
X = S, R = Me

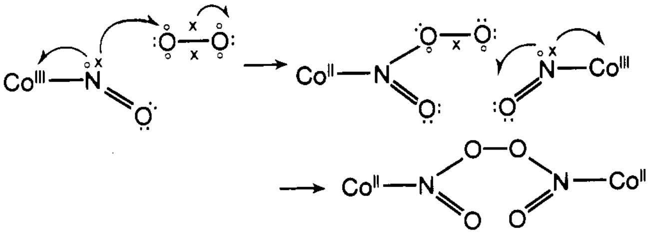
$$[Co(NO)(salen)] + pyr + 1/2O_2 \rightarrow [Co(NO_2)(salen)(pyr)]$$

$$[Co(NO)(en)_2]^{2+} + MeCN + 1/2O_2 \rightarrow [Co(NO_2)(en)_2(NCMe)]^{2+}$$

Similar oxygenation of NO occurs when $[NiCl(NO)(diphos)]$ is treated[69] with O$_2$ either in boiling DMF or under UV light in dichloromethane. Quantitative yields of the nitro product, [$NiCl(NO_2)$(diphos)], were obtained upon irradiation, but no reaction at all occurred in the dark. Kinetic studies of the reaction with, for example, [Co(NO)(salen)], were interpreted in terms of initial rapid formation of the electron-rich intermediate [Co(NO)(salen)L] (L = Lewis base). This could be formulated as a 20-electron system, i.e., containing {$Co^I(NO^+)$}, or more conventionally as having a bent Co-N-O bond, i.e., {$Co^{III}(NO^-)$}. Slow attack on this by oxygen was thought to give the peroxy-nitrate intermediate [Co{$N(O)O_2$}(salen)L] which was itself attacked by another molecule of [Co(NO)(salen)L] giving the dimer



This bimetallic intermediate can be formally described as containing peroxy-bridged dinitrogen tetroxide bound to Co(II), and support for such an intermediate comes from ESR spectral studies of the reaction involving [NiCl(NO)(diphos)]. The signals obtained both in solution and in frozen glasses within 1 min of oxygenation of the nickel nitrosyl are thought to be consistent with a d^9 Ni(I) species, formulated as [(diphos)ClNi{N(=O)-O—ON(=O)}NiCl(diphos)]. Formation of such an intermediate via a radical pathway can be visualized, using electron dot bonding representations to describe residual one-electron bonds, as follows:



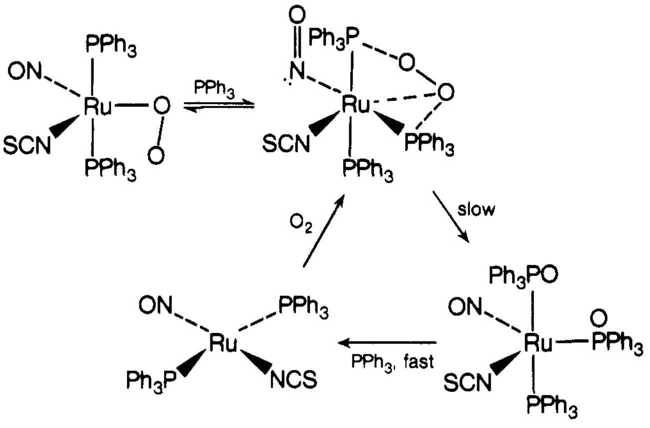
Homolytic fission of the peroxy link would then afford the expected nitro product. In its essential aspects, the mechanism proposed by Clarkson and Basolo parallels that suggested[70] for the gas-phase reaction of NO and O_2 in which the peroxy-nitrate intermediate, $NO(O_2)$, reacts further with NO, giving O=N—O—O—N=O which then homolytically dissociates to NO_2.

It has been reported[71] that [$Co(NO)(DMGH)_2(H_2O)$] (DMGH = dimethylglyoximate(1−)), reacts similarly, giving nitro products, but a reinvestigation of this reaction by Marzilli and his co-workers showed[72] that, if bases, e.g., pyridines, imidazole, or PPh_3, were present, greater than 50% conversion to the *nitrate* [$Co(NO_3)(DMGH)_2B$] occurred. The other products were the nitro species [$Co(NO_2)(DMGH)_2B$](<40%) and an unidentified compound (ca. 10%). No mechanism has been put forward for this reaction, but it was observed that (i) the formation constants of [$Co(NO)(DMGH)_2B$] were apparently much higher than those of the Schiff bases complexes **2** and **3**, and that (ii) ν(NO) for the dimethylglyoximato complex was higher than those of **2** and **3**. In this system it appears that base is necessary for oxygenation to occur, and we might reasonably expect some dependence of the rate of reaction on the basicity of B. After all, the mechanism is formally an electrophilic attack by O_2 on the nitrogen atom of the NO group, and strong bases would be expected to push more charge onto the nitric oxide ligand. However the actual enhancement of the rate of conversion of coordinated NO to NO_3/NO_2 caused by increasing the base strength was insubstantial.

The reactions of O_2 with triphenylphosphine ruthenium, osmium, rhodium, and iridium nitrosyl complexes have been only briefly reported. Thus, [$Ru(NO)_2(PPh_3)_2$], in the absence of acid, affords[67] [$Ru(NO)(NO_3)(O_2)(PPh_3)_2$] but, as previously mentioned, when acid is present, [$Ru(NO)_2(OH)(PPh_3)_2$]$^+$ is formed; the osmium analogue behaves similarly. While treatment of [$Ru(CO)(NO)(PPh_3)_2X$] (X = Cl or NCS) with oxygen gives[73] [$Ru(NO)(O_2)(PPh_3)_2X$] (the fate of the CO is unknown at present), its osmium analogue (X = Cl) is converted[74] to [$OsCl(CO_3)(NO)(PPh_3)_2$]. The complexes [$Ir(NO)_2(PPh_3)_2$]$^+$, [$IrCl_2(CO)(NO)(PPh_3)_2$] (and related mixed halide compounds), and [$Pt(NO)(NO_2)(PPh_3)_2$] also react with oxygen, giving [$Ir(NO)(NO_3)(PPh_3)_2$], [$IrCl_2(CO)(NO_3)(PPh_3)_2$],[75] and [$Pt(NO_3)(NO_2)(PPh_3)_2$],[69] respectively.

SCHEME II

$$[Ru(CO)(NO)(NCS)(PPh_3)_2] + O_2 \longrightarrow [Ru(NO)(NCS)(O_2)(PPh_3)_2] + CO$$



It is possible that *nitrato* species could arise directly from a peroxy-nitrato intermediate (i.e., [M{N(=O)OO}]), or by attack of such an intermediate on a nitro complex, giving a second transient species, e.g., [M{$N(=O)OON(O)_2$}M], which could then undergo O-O bond fission forming {$M(NO_2)$} and {$M(NO_3)$} species. However, in either case there must be rearrangement of the N and O atoms to give M-O-NOO and, in the absence of more detailed synthetic and kinetic studies, further speculation seems fruitless.

An interesting application of the oxygenation reaction is the catalytic conversion[73] of Ph_3P to Ph_3PO by [$Ru(CO)(NO)(NCS)(PPh_3)_2$]. The postulated mechanism for this process is given in Scheme II. The rate-determining step is thought to be O-atom transfer to the coordinated P atoms, giving the unstable phosphine oxide complex.

C. Other O-Atom Transfer Reactions

In a remarkable reaction, Feltham and his colleague[76] have shown that *trans*-[$Fe(^{15}NO)(^{14}NO_2)(S_2CNMe_2)_2$], prepared at −60 °C, isomerizes at 5 °C to its cis isomer and then slowly undergoes $^{14}N/^{15}N$ exchange, giving *cis*-[$Fe(^{14}NO)(^{15}NO_2)(S_2CNMe_2)_2$]. The reaction is first order in the cis isomer and is independent of solvent and of concentration of NO, NO_2, or NO_2^-; there is no evidence of a dissociative mechanism. Other reactions of [$Fe(NO)(NO_2)(S_2CNMe_2)_2$], shown below, occur at rates no faster than that observed for $^{14}N/^{15}N$ exchange:

$$cis\text{-}[Fe(^*NO)(NO_2)(S_2CNMe_2)_2] + NO \rightarrow [Fe(NO)(NO_2)(S_2CNMe_2)_2] + {}^*NO \ (22\ ^\circ C,\ CH_2Cl_2)$$

$$cis\text{-}[Fe(NO)(^*NO_2)(S_2CNMe_2)_2] + NO \rightarrow [Fe(NO)(NO_2)(S_2CNMe_2)_2] + {}^*NO$$

$$cis\text{-}[Fe(^*NO)(NO_2)(S_2CNMe_2)_2] + NO_2 \rightarrow [Fe(NO)(NO_2)(S_2CNMe_2)_2] + {}^*NO_2$$

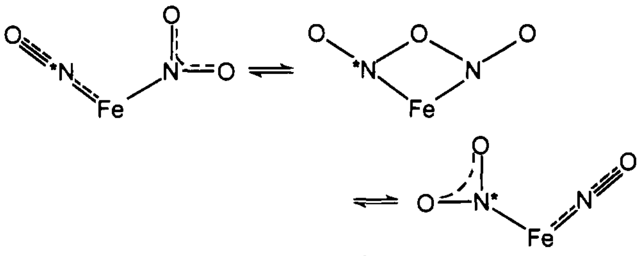
$$cis\text{-}[Fe(NO)(^*NO_2)(S_2CNMe_2)_2] + NO_2 \rightarrow [Fe(NO)(NO_2)(S_2CNMe_2)_2] + {}^*NO_2$$

These results are consistent with the process

TABLE IV. Nitrosylation of Benzyl Bromide by Transition Metal Nitrosyl Complexes

	organic products, %								
reaction system	$PhCH_2Br$	PhCH=NOH	PhCN	$PhCONH_2$	PhCHO	$PhCH_2OH$	$(PhCH_2)_2$	$PhCH_2NO_2$	Others
$PhCH_2Br$ + NO alone; toluene; 110 °C, 48 h	40.0		0.4		3.5	9.5		45.1	
$Ru(NO)_2(PPh_3)_2$ + CO; toluene; 110 °C, 48 h		9.0	17.2	77.0	5.4				
$Ru(NO)_2(PPh_3)_2$ + C_2H_4; toluene; 110 °C, 20 h			14.2	4.9	2.0		8.2		
$Ru(NO)_2\{P(OPh)_3\}_2$ + CO; toluene; 110 °C, 18 h	61.0	*a*	13.0		1.0	*a*		*a*	
$RhCl_2(NO)(PPh_3)_2$ + CO; toluene; 110 °C, 48 h	71.1		6.0	4.0	18.0	2.0			
$Rh(NO)(PPh_3)_3$ + CO; toluene; 110 °C, 20 h	19.5		18.4		11.2	9.4			*b*
$Co(NO)\{P(OEt)_3\}_3$ + CO; toluene; 110 °C, 30 h	76.0			3.5	3.1	5.9	6.5		

[a] Traces. [b] Substantial amounts of unidentified material.



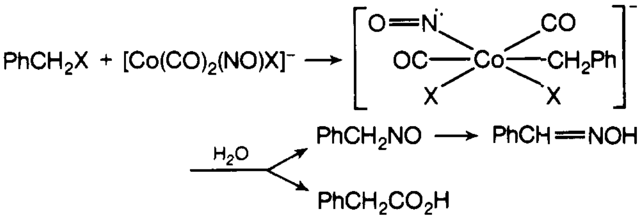
It is possible that the intermediate $[Fe(N_2O_3)(S_2CNMe_2)_2]$ dissociates, giving $[Fe(S_2CNMe_2)_2]$ and N_2O_3, with an equilibrium in favor of the intermediate itself. However, the structure of *cis*-$[Fe(NO)(NO_2)(S_2CNMe_2)_2]$, as determined crystallographically, reveals nothing particularly unusual about the compound. The Fe and two N atoms are coplanar and the Fe–NO_2 plane is orthogonal to the plane defined by these three atoms. It was suggested that deoxygenation by CO of nitrito and nitrato complexes of the heavy transition metals to give nitrosyl complexes could occur via O-atom transfer between NO_2^- or NO_3^- and CO bound to the metal.

Nitric oxide reacts with many metal nitrosyl compounds giving N_2O and either nitro or hyponitrito complexes. While these conversions could be regarded as electrophilic attack by free NO on coordinated NO, they are more conveniently dealt with in the section on homogeneous disproportionation and reduction of nitric oxide (V).

D. Formation of N–C Bonds

Treatment of $[Rh(NO)(PPh_3)_3]$ with benzoyl chloride gives,[64] eventually, $[RhCl(CO)(PPh_3)_2]$ and Ph_3P, possibly via the intermediate $[RhCl(COPh)(NO)(PPh_3)_2]$. This last species should have a bent Rh–N–O group, and might eliminate PhNO via a group transfer process, although no evidence of nitrosobenzene has been found. Similar treatment of $[Co(NO)(PPh_3)_3]$ affords $[Co(CO)(NO)(PPh_3)_2]$, chlorobenzene, and PPh_3. Denitrosylation of $[M(NO)(PPh_3)_3]$ (M = Rh or Ir) can also be effected by *p*-$MeC_6H_4SO_2Cl$, the products being $[MCl(PPh_3)_3]$ and (*p*-$MeC_6H_4SO_2)_2$; the corresponding cobalt nitrosyl is converted to a mixture of $[CoCl_2(PPh_3)_2]$ and $[CoCl(NO)(PPh_3)_2]$.

The carbonylate ion $[Co(CO)_2(NO)X]^-$ (X = Br or I) reacts[77] stoichiometrically with benzyl halides in acetone at 40–50 °C affording, after acidification and extraction, a residue consisting mainly of benzaldoxime (30–35% yield based on Co) and some phenylacetic acid (5–10%). The course of the reaction is not apparently affected by CO pressures up to 5 atm. Although mechanistic studies have not been reported, it is suggested that the reaction proceeds via oxidative addition of benzyl halide to be cobaltate anion:



In a more recent study, the reactions of benzyl bromide with neutral nitrosyl complexes in hydrocarbon solvents have been examined.[78] Benzyl bromide is a particularly convenient substrate, since, if it is converted to $PhCH_2NO$, it will readily tautomerize to PhCH=NOH, which is easily characterized. The most extensively investigated compound has been $[Ru(NO)_2(PPh_3)_2]$, which is relatively stable in solution and is easily prepared. This complex reacts smoothly with $PhCH_2Br$ under CO in refluxing toluene to give $[RuBr(CO)(NO)(PPh_3)_2]$ and $[RuBr_2(CO)_2(PPh_3)_2]$, the former appearing in the early stages of the reaction and being converted into the latter as the reaction proceeds. The organic products were identified as mainly PhCH=NOH, PhCN, and $PhCONH_2$, although smaller amounts of PhCHO and $PhCH_2OH$ were also detected (Table IV). It was established that optimal conversion of coordinated NO into aryl nitrogen compounds using $[Ru(NO)_2(PPh_3)_2]$ occurred at 110 °C after 48 h.

If this reaction is carried out under nitrogen or ethylene, instead of CO, the yield of free organonitrogen compounds is greatly decreased, and bibenzyl is also formed. However, the total nitrogen content of the system is accounted for by the isolation of $[RuBr_2(NCPh)_2(PPh_3)_2]$ and $[RuBr_3(NO)(PPh_3)_2]$.

Benzyl bromide reacts less efficiently with "free" NO in toluene under nitrogen or CO, giving $PhCH_2NO_2$ as the major product, a species *not* detected in the reactions with $[Ru(NO)_2(PPh_3)_2]$, together with small amounts of benzaldehyde and benzyl alcohol, and a trace of PhCN. It was established that $[Ru(NO)_2(PPh_3)_2]$ does not react with CO in toluene and that "free" NO does not react directly with toluene under the conditions of the experiments described above.

The most plausible explanation for these reactions seems to involve initial nucleophilic attack on benzyl bromide by a coordinated NO group (or electrophilic addition of $PhCH_2^+$ to the

SCHEME III

1. $[Ru(NO)_2(PPh_3)_2] + PhCH_2Br \rightarrow [RuBr(NO)\{N(=O)CH_2Ph\}(PPh_3)_2]$ (fast)
2. $[RuBr(NO)\{N(=O)CH_2Ph\}(PPh_3)_2] \rightarrow [RuBr(NO)\{N(OH)=CHPh\}(PPh_3)_2]$ (tautomerization)
3. $[RuBr(NO)\{N(OH)=CHPh\}(PPh_3)_2] \rightarrow [RuBr(NO)(NCPh)(PPh_3)_2] + H_2O$ (fast)
4. $[RuBr(NO)(NCPh)(PPh_3)_2] + CO \rightarrow [RuBr(CO)(NO)(PPh_3)_2] + PhCN$
5. $[RuBr(NO)\{N(OH)=CHPh\}(PPh_3)_2] + CO \rightarrow [RuBr(CO)(NO)(PPh_3)_2] + PhCH=NOH$ (slow)
6. $[RuBr(CO)(NO)(PPh_3)_2] + PhCH_2Br \rightarrow [RuBr_2(CO)\{N(OH)=CHPh\}(PPh_3)_2]$ (slow)
7. $[RuBr_2(CO)\{N(OH)=CHPh\}(PPh_3)_2] + CO \rightarrow [RuBr_2(CO)_2(PPh_3)_2] + PhCH=NOH$
8. $[RuBr_2(CO)\{N(OH)=CHPh\}(PPh_3)_2] \rightarrow [RuBr_2(CO)(NCPh)(PPh_3)_2] + H_2O$ (slow)
9. $[RuBr_2(CO)(NCPh)(PPh_3)_2] + CO \rightarrow [RuBr_2(CO)_2(PPh_3)_2] + PhCN$

coordinated NO group with concomitant attachment of Br^- to the metal). The overall process under CO is summarized in Scheme III.

Alternative pathways involving conventional oxidative addition, viz.

$$[Ru(NO)_2(PPh_3)_2] + 2PhCH_2Br \rightarrow [Ru(CH_2Ph)Br_2(NO)(PPh_3)_2] + PhCH_2NO$$

or

$$[Ru(NO)_2(PPh_3)_2] + PhCH_2Br \rightarrow [RuBr(CH_2Ph)(NO)(PPh_3)_2] + NO$$

can be dismissed since these could not account for the early formation of $[RuBr(CO)(NO)(PPh_3)_2]$, the failure to observe $\nu(NO)$ values commensurate with the presence of $\{Ru(NO)\}^{3+}$ species (>1800 cm^{-1}), the fairly rapid appearance of PhCN, the absence of acyl products derived from CO insertion into Ru–C bonds, and the fact that $PhCH_2NO_2$ (expected and usually found in reactions of "free" NO and $PhCH_2Br$) was not detected in the products of these denitrosylation reactions carried out under CO. Another possible intermediate, $[Ru(CH_2Ph)(NO)_2(PPh_3)_2]Br$, also seems unlikely since it proved impossible to isolate or obtain any evidence for the existence of $[Ru(NO)_2(PPh_3)_2R][BF_4]$ (R = Me or Et), analogous to $[Ru(NO)_2(PPh_3)_2X]^+$ (X = Cl or OH), in the reaction between $[Ru(NO)_2(PPh_3)_2]$ and $[R_3O][BF_4]$.

That $PhCH{=}NOH$ could be rapidly dehydrated in the presence of ruthenium nitrosyl complexes (e.g., reactions 3 and 8) was demonstrated by reaction of $[RuCl(NO)(PPh_3)_2]$ with $PhCH{=}NOH$ in refluxing toluene. Under nitrogen the yield of PhCN was almost quantitative, while under CO it was the major product, some hydrolysis products and unreacted oxime also being present. The lower yield of benzonitrile in the reaction under CO might be expected because of competition of oxime and CO for the site at the metal in the coordinatively unsaturated $[RuCl(NO)(PPh_3)_2]$ (cf. reactions 5 and 7). Reaction between $[RuCl(CO)(NO)(PPh_3)_2]$ and $PhCH_2Br$ under nitrogen in refluxing toluene is very slow, yielding mostly PhCHO (10%) and traces of PhCN and $[RuClBr(CO)_2(PPh_3)_2]$. This last observation is consistent with the view that $[Ru(NO)_2(PPh_3)_2]$ is rapidly converted into $[RuBr(CO)(NO)(PPh_3)_2]$ but that the latter only slowly forms $[RuBr_2(CO)_2(PPh_3)_2]$.

The occurrence of $PhCONH_2$, PhCHO, and $PhCH_2OH$ in the reaction products can be rationalized as arising from hydrolysis of PhCN, $PhCH{=}NOH$, and $PhCH_2Br$, respectively. Dehydration of $PhCH{=}NOH$ will generate sufficient water to accomplish these hydrolyses, and there is ample evidence of the metal-assisted hydration of nitriles to amides.

In the absence of CO, that is, under N_2 or ethylene, it is thought that $[Ru(NO)_2(PPh_3)_2]$ reacts with benzyl bromide according to reactions 1–3. After that point, the reactions in Scheme IV may occur. It may be noted that a mixture of benzyl bromide and $[RuBrCl(CH_2Ph)(NO)(PPh_3)_2]$ in refluxing toluene afforded small amounts of bibenzyl which is consistent with the proposed reactions 10 and 11.

SCHEME IV

10. $[RuBr(NO)(NCPh)(PPh_3)_2] + PhCH_2Br \rightarrow [RuBr_2(CH_2Ph)(NO)(PPh_3)_2] + PhCN$

11. $[RuBr_2(CH_2Ph)(NO)(PPh_3)_2] + PhCH_2Br \rightarrow [RuBr_3(NO)(PPh_3)_2] + (PhCH_2)_2$

12. $[RuBr(NO)(NCPh)(PPh_3)_2] + PhCH_2Br \rightarrow [RuBr_2\{N({=}O)CH_2Ph\}(NCPh)(PPh_3)_2]$

13. $[RuBr_2\{N({=}O)CH_2Ph\}(NCPh)(PPh_3)_2] \rightarrow [RuBr_2\{N(OH){=}CHPh\}(NCPh)(PPh_3)_2]$

14. $[RuBr_2\{N(OH){=}CHPh\}(NCPh)(PPh_3)_2] \rightarrow [RuBr_2(NCPh)_2(PPh_3)_2] + H_2O$ (slow)

From a comparison of the apparent reaction rates and the products obtained under CO and under either N_2 or ethylene, it seems that the role of CO is to facilitate the liberation of the nitrosobenzyl derivatives without generating compounds which are themselves significantly reactive. Indeed, the original intention of using CO was to deactivate $[RuBr(NO)(PPh_3)_2]$ which, we thought, might be formed in the reaction after elimination of $PhCH_2NO$. Further, it has been suggested that in the related reactions between $[Ru(NO)_2(PPh_3)_2]$ and halogens, in which $[Ru(NO)(PPh_3)_2X_3]$ is the final product, a likely intermediate is $[Ru(NO)(PPh_3)_2X]$. It is known that $[RuCl(NO)(PPh_3)_2]$ is extremely reactive toward oxidative addition, and such behavior might complicate the intended nitrosylation processes. Another significant point is that, under CO, no bibenzyl is formed, suggesting that, unlike the reactions in the absence of CO, radical processes are unimportant in the overall mechanism.

The behavior of other organic halides with $[Ru(NO)_2(PPh_3)_2]$ has also been briefly investigated. Thus, $PhCH_2Cl$, $PhCH_2CH_2Br$, PhBr, o-$C_6H_4(CH_2Br)_2$, and Pr^iBr effectively denitrosylate the ruthenium complex, although the organic products, other than those obtained from benzyl chloride, have not been characterized; PhCHMeBr does not react with $[Ru(NO)_2(PPh_3)_2]$. Under comparable conditions, benzyl chloride produced the same compounds as those obtained using the bromide, but in very much lower yields. This is quite consistent with the greater bond strength of the C–Cl vs. the C–Br bond.

Other nitrosyl complexes undergo denitrosylation with benzyl bromide, including $[Ru(NO)_2(diphos)]$, $[Ru(NO)_2\{P(OEt)_3\}_2]$, $[Rh(NO)(PPh_3)_3]$, $[RhCl_2(NO)(PPh_3)_2]$, and $[Co(NO)L_3]$ (L = PPh_3 or $P(OEt)_3$). In none of these reactions, however, are the yields of organonitrogen compounds ever comparable to those obtained with $[Ru(NO)_2(PPh_3)_2]$.

In what must be a closely related reaction, Schoonover and Eisenberg have shown[79] that $[Ru(\eta^3\text{-}C_3H_5)(NO)(PPh_3)_2]$ reacts with CO to give first the intermediate $[Ru(\eta^3\text{-}C_3H_5)(CO)(NO)(PPh_3)_2]$ and then $[Ru(CO)_3(PPh_3)_2]$ and (presumably) acrolein oxime. From spectral studies it is clear that the allyl group in the intermediate retains its η^3-bonding mode, the implication being that the Ru–N–O bond angle must be bent (unless the NO functions as a one-electron ligand, the 18-electron rule is violated in this intermediate). It is suggested that the ensuing coupling of the allyl and NO groups can be viewed as nucleophilic attack at the allyl C atom by coordinated NO^-, the sequence being facilitated by the presence of both groups within the coordination sphere of the metal. Such an unequivocal view of the behavior of the Ru–N–O group cannot be taken of the reactions of benzyl bromide with $[Ru(NO)_2(PPh_3)_2]$ since the coupling of carbon and nitrosyl N atoms can and does occur in the absence of CO. However, it is tempting to imagine that Ru–N–O bond angle bending might occur assisted either by association of the initial complex with CO, giving the transient $[Ru(CO)(NO)_2(PPh_3)_2]$, or by attachment of Br^-, and such a bending would undoubtedly make the N atom more nucleophilic.

These reactions may also be compared with the formation[80] of acrylonitrile in a heterogeneously catalyzed process involving propene and NO, and with the addition of NO to $[Ni(\eta^3\text{-}C_3H_5)Br]_2$ in which $[Ni(CH_2{=}CHCH{=}NOH)Br(NO)]$ is formed. In both of these latter processes, it is believed that prior coordination of NO to a metal followed by M–N–O bond angle bending must occur before formation of the C–N bond.

IV. Reduction

A. One-Electron Processes

Since the nitrosonium ion is reduced in a one-electron step to give neutral NO, it seems reasonable to expect that some metal complexes formally containing NO^+ should behave similarly. That is, on reduction, they should afford species formally containing $NO\cdot$.

Much has been written over the last 15 years or so about the one-electron reduction of $[Fe(CN)_5(NO)]^{2-}$ in water and other solvents and, until very recently, there has been some confusion about the nature of the reduction products. It is now clear that one-electron reduction, achieved by chemical, electrochemical, or radiolytic techniques, affords,[81] initially at least, the *brown* $[Fe(CN)_5(NO)]^{3-}$. This compound, described formally as containing Fe(II) and NO·, is labile, readily losing CN^- (presumably trans to the NO group) to give the *blue* $Fe^I(NO^+)$ species, $[Fe(CN)_5(NO)]^{2-}$.

Both of these anions have been isolated[82] as the salts of large organic cations and are paramagnetic but exhibit different ESR spectral signals.[83] From spectral and other studies, it seems quite clear that $[Fe(CN)_4(NO)]^{2-}$ is identical with those species previously formulated as $[Fe(CN)_5(NOH)]^{2-}$, with the possible exception of compounds generated[84] polarographically in acid solution. The structure of $[Et_4N]_2[Fe(CN)_4(NO)]$, determined crystallographically,[85] is remarkable in that the anion is square pyramidal with apical NO and a *linear* Fe-N-O group. Simple molecular orbital treatments of such five-coordinate species predict that $[Fe(CN)_4(NO)]^{2-}$ should be trigonal bipyramidal with equatorial NO, and this species is therefore a rare example of a pyramidal molecule *not* having a bent Fe-N-O bond angle.

Other nitrosyl complexes undergo a reversible one-electron reduction to give species containing, formally, coordinated NO·, viz.

$$[Cr(CN)_5(NO)]^{3-} + e^- \rightleftharpoons [Cr(CN)_5(NO)]^{4-} \quad (86)$$

$$[Ru(NH_3)_5(NO)]^{3+} + e^- \rightleftharpoons [Ru(NH_3)_5(NO)]^{2+} \quad (87)$$

$$[Ru(bpy)_2(NO)X]^{n+} + e^- \rightleftharpoons [Ru(bpy)_2(NO)X]^{(n-1)+} \quad (88)$$

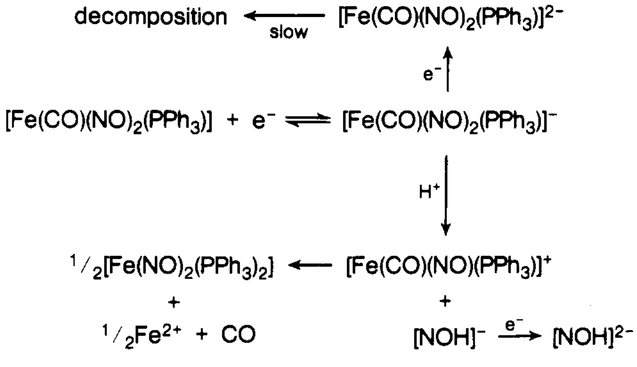
$$[Fe(NO)(S_2C_2R_2)_2]^- + e^- \rightleftharpoons [Fe(NO)(S_2C_2R_2)_2]^{2-} \quad (89)$$

The $E_{1/2}$ values for the reduction of $[Ru(bpy)_2(NO)X]^{n+}$ (X = Cl, N_3, or NO_2, $n = 2$; X = NH_3, pyr, or MeCN, $n = 3$)[88] are somewhat insensitive to the nature of X but are influenced by the nature of the solvent in which the electrochemical measurements were made. It is said that these observations are consistent with the view that electron transfer is occurring to and from a peripheral ligand rather than involving a metal d orbital. From spectral data (IR, NMR, Mössbauer) it seems quite reasonable that the nitrosyl group is the site of this electron transfer and that the NO group in $[Ru(bpy)_2(NO)X]^{n+}$ is behaving, as indicated earlier, as a modified nitrosonium ion.

In the dithiolene species, $[Fe(NO)(S_2C_2R_2)_2]^{n-}$ (R = CN or CF_3) and $[Fe(NO)(S_2C_6XY_3)_2]^{n-}$ (X = Me, Y = H; X = Y = Cl),[89] the situation is different in that the $E_{1/2}$ values are markedly dependent on the sulfur ligand substituents, suggesting that the redox orbital is not simply associated with the NO but is also strongly S-ligand in character. The related complexes $[Co(NO)(S_2C_2R_2)_2]^-$ also undergo one-electron reduction, but again the nature of the redox orbital is ambiguous and seems to be sulfur ligand based.

Similar comments can be made about the nature of the one-electron reduction processes involving[90] $[Fe(NO)_2(N\text{-}N)]$ and $[Co(CO)(NO)(N\text{-}N)]$ (N-N = 2,2′-bipyridyl, *o*-phenanthroline, or di-2-pyridyl ketone). Here, spectral studies indicate that $[Fe(NO)_2(N\text{-}N)]^-$ and $[Co(CO)(NO)(N\text{-}N)]^-$ should be described as radical anions where the unpaired electron is mainly localized in an orbital of (N-N) ligand character. However, polarographic reduction of $[Fe(CO)(NO)_2(PPh_3)]$[91] and $[Co(CO)_{3-x}(NO)(PR_3)_x]$ (x = 1 or 2; R = alkyl and/or aryl)[92] has been interpreted in terms of addition of an electron to coordinated NO^+, but the reduced species are unstable, viz. for Fe, see Scheme V.

SCHEME V

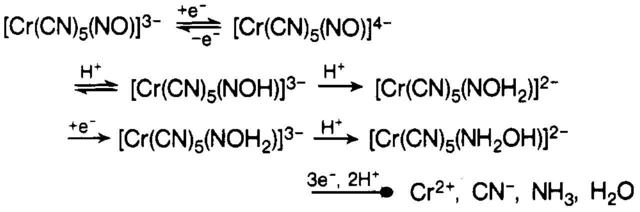


B. Multielectron Processes

The brown species $[Fe(CN)_5(NO)]^{3-}$ readily dissociates to give blue $[Fe(CN)_4(NO)]^{2-}$ which may itself be voltammetrically oxidized and reduced in reversible one-electron steps.[81] However, $[Fe(CN)_4(NO)]^{2-}$ further dissociates giving the electroinactive $[Fe(CN)_3(NO)]^{3-}$. These anions, together with $[Fe(CN)_3(NO)]^{4-}$, can be synthesized[82] by sodium metal reduction of the nitroprusside ion, $[Fe(CN)_5(NO)]^{2-}$, in liquid ammonia, and it is significant that under these conditions, the NO group remains intact. However, four-electron electrochemical reduction[84] of $[Fe(CN)_5(NO)]^{2-}$ in aqueous solution affords $[Fe(CN)_5(NH_2OH)]^{3-}$ in a three- or four-stage process.

Polarographic reduction of $[Mn(CN)_5(NO)]^{3-}$ (formally isoelectronic with $[Fe(CN)_5(NO)]^{2-}$) has been interpreted[93] in terms of an initial two-electron process giving $[Mn(CN)_5(NO)]^{5-}$, which then decomposes giving Mn^{2+}, CN^-, and either N_2 or NH_3. The course of the electrochemical reduction[86] of $[Cr(CN)_5(NO)]^{3-}$ is dependent on pH. Thus, in alkaline solution, a reversible one-electron process affords $[Cr(CN)_5(NO)]^{4-}$ which, it is suggested, corresponds to the formal reduction of Cr(I) to Cr(0), i.e., to the addition of an electron to a metal d orbital rather than to the NO group. However, as pH decreases, the electrode reaction becomes a two-electron process, and ultimately at pH <3, a second three-electron transfer is observed, the final products of the reduction being Cr^{2+}, CN^-, and NH_3. A mechanism, involving successive protonation of the NO group, has been suggested (Scheme VI).

SCHEME VI

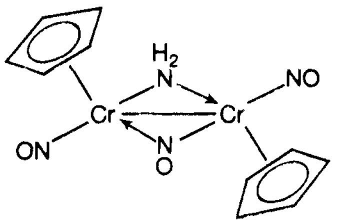


Treatment of $[Cr(NO)(H_2O)_5]^{2+}$ with Cr(II) in aqueous acid affords[94] hydroxylamine according to the equation:

$$2[Cr(NO)(H_2O)_5]^{2+} + 4[Cr(H_2O)_6]^{2+} + 2H_3O^+ \rightarrow 3[Cr(OH)(H_2O)_4]_2{}^{4+} + 2NH_3OH^+ + 6H_2O$$

This appears to be a two-electron reduction involving a binuclear intermediate. Reaction of $[Ru(NH_3)_5(NO)]^{3+}$ with chromous ion (>6 molar equiv) in acid solution gives,[95] in an apparent six-electron reduction, $[Ru(NH_3)_6]^{2+}$; i.e., coordinated NO is reduced to ammonia. With 1 molar equiv of Cr^{2+}, $[Co(NH_3)_5(NO)]^{2+}$ appears to dissociate, giving free NO and $[Cr(H_2O)_6]^{3+}$, but with smaller concentrations of Cr^{2+}, $[Cr(NO)(H_2O)_5]^{2+}$ is produced. Similar results are obtained[96] with $[Co(NO)(en)_2(H_2O)]^{2+}$, $[Co(H_2O)_6]^{2+}$, and $[Cr(NO)(H_2O)_5]^{2+}$ being formed perhaps via the intermediate $[Co(NOH)(en)_2(H_2O)]^{3+}$. In all of these reactions, the formation of a transient binuclear species, perhaps similar to those involved in the inner-sphere, electron-transfer reactions of the redox pairs Cr^{II}/Co^{III}, Cr^{II}/Cr^{III}, etc., would seem to be likely.

Borohydride ion attack upon $[Cr(\eta^5\text{-}C_5H_5)Cl(NO)_2]$ affords[97] a mixture of $[Cr(\eta^5\text{-}C_5H_5)(NO)_2]_2$ and $[Cr_2(\eta^5\text{-}C_5H_5)_2(NO)_3(NH_2)]$ (**5**). Reaction of *tert*-butyllithium with the dinitrosyl chloride affords[98] $[Cr_2(\eta^5\text{-}C_5H_5)_2(NO)_3N(OH)Bu^t]$, and similar treatment of $[Co(\eta^5\text{-}C_5H_5)(NO)]_2$ and $[Ni(^5\text{-}C_5H_5)(NO)]$ gives $[Co_3(\eta^5\text{-}C_5H_4R)_3(NO)_2]$ (R = H or Bu^t), $[Co_2(\eta^5\text{-}C_5H_4R)_2(\mu_2\text{-}NO)(\mu_2\text{-}NHBu^t)]$, $[Co_3(\eta^5\text{-}C_5H_4R)_3(\mu_3\text{-}NBu^t)_2]$, and $[Ni_3(\eta^5\text{-}C_5H_4R)_3(\mu_3\text{-}NBu^t)]$, respectively. Reaction of $[Co(NO)_2(PPh_3)_2]^+$ with BH_4^- is reported[99] to give $[Co(NO)(PPh_3)_3]$ and ammonia, and the corresponding diphos complex affords, in THF, [Co(NO)(diphos)(THF)]; the fate of the other NO group is unknown. Reduction of $[RhCl_2(NO)((PPh_3)_2]$ with $AlHBu^i_2$ in the presence of PPh_3 gives $[RhCl(PPh_3)_3]$ as the only identified product.[64]



5 (and/or the cis isomer)

In molten PPh_3, $[Fe(NO)_2Br]_2$ dissolves giving,[100] ultimately, $[Fe(NO)(PPh_3)_2Br_2]$, $[Fe(NO)_2(PPh_3)_2]$, Ph_3PO, and N_2. $[Fe(NO)_2I]_2$ behaves similarly with $P(C_6H_{11})_3$, but when $[Fe(NO)_3I]$ is treated with pyridine, $[Fe(pyr)_6](NO_2)I$, nitric oxide, and N_2 are produced. Treatment of the 1:1 adduct formed between $MoCl_5$ and NO with $PMePh_2$ affords[101] the phosphinimido species $[MoCl_4(N{=}PMePh_2)(OPMePh_2)]$ and $[MoCl_3(NH_2)(OPMe_2Ph)_2]$. It is believed that the latter complex is derived by hydrolysis of the former. Reduction of the coordinated NO in $[RuCl_5(NO)]^{2-}$, giving $[Ru_2N(OH)_5(H_2O)_5]\cdot nH_2O$, is achieved[102] using alkaline formaldehyde, while with $SnCl_2$ in HCl solution, $[Ru_2Cl_8N(H_2O)_2]^{3-}$, containing the group Ru=N—Ru, is produced.

There appear to be no instances where coordinated NO is reduced by hydrogen, but a number of nitrosyl complexes will hydrogenate alkenes in the presence of H_2.

C. Heterogeneous Reduction of NO

Although the reduction of NO from the exhaust gases of combustion processes has been of some interest for many years, only relatively recently have there been very significant developments in this area. The upsurge of research activity has occurred mainly as a result of U.S. government policy, as formulated by the Environmental Protection Agency (EPA) toward pollution of the atmosphere, particularly in urban areas, caused by exhaust gases emanating mainly from cars, trucks, and buses.

The major pollutants generated by the internal combustion engine are CO and NO, although unburnt hydrocarbons can also be a substantial nuisance, particularly in the formation of photochemical smog. Other pollutants of lesser but nonetheless significant importance are sulfur oxides, lead compounds, and halogens.

Nitric oxide is generated from N_2 and O_2, assisted by CO, in the post-flame combustion gas, viz.

$$CO + OH \rightarrow CO_2 + H;\ O_2 + H \rightarrow OH + O$$

$$N_2 + O \rightarrow NO + N;\ O_2 + N \rightarrow NO + O$$

Provided that these gases are present, the production of NO is dependent mainly on temperature and rises significantly as the heat increases.

The problems associated with the diminution and near-removal of CO, NO, and unburnt hydrocarbons in engine exhausts as seen from a mainly American viewpoint have been extremely well reviewed by Wei.[103] However, some aspects of the chemistry of CO and NO control must be included herein, since they involve the reactions of coordinated NO.

The removal of significant amounts of CO and unburnt hydrocarbons from vehicle exhausts, as required by EPA standards for cars produced in the U.S.A. after 1975, is achieved relatively satisfactorily by operating the engine with a lean air–fuel mixture (i.e., with air–fuel stoichiometries of greater than 14.7 by weight) and by using a secondary air inlet to the exhaust to complete the oxidation of CO to CO_2 over a catalyst. The oxidation catalysts (noble metals, base metal oxides of alloys, as pellets or coatings on ceramic supports, or as wire meshes) are poisoned by petrol additives containing Pb, S, and P, and these must be removed for effective long-life operation of the catalytic reactor (ideally 5 years or 50 000 miles).

The problem with NO has been much more difficult to solve and, indeed, there is very real doubt as to whether EPA requirements for 1978 can be met. Partial success is attained by operating the engine with a *rich* mixture (air:fuel ratio < 14.7) and by using spark retardation and exhaust gas recirculation to reduce the initial highest temperatures of the cylinder emissions (high gas temperatures lead to the destruction of the CO oxidation catalysts). The effect of these measures is to lower the operating effectiveness of the engine; e.g., the car becomes sluggish to drive, gasoline consumption goes up steeply (by up to 30%), and stalling and rough idling become prevalent. Even then there still remains a sufficient amount of NO which requires catalytic reduction. The engine may also be operated under very lean conditions, i.e., with air:fuel ratios $> 20{:}1$, in which case emitted NO_x and CO are greatly diminished, although the amount of unburnt hydrocarbons, which reaches a minimum at ratios of ca. 17:1, begins to increase slightly.

There are variations of this general principle, perhaps the most interesting being the simultaneous oxidation and reduction of exhaust gases in a situation where the amounts of air and fuel burnt are very strictly controlled to be within the stoichiometric ratio 14.7 ± 0.1. This control, however, presents some difficulties associated mainly with reliable and prolonged monitoring of oxygen in the exhaust gases emitted after catalytic treatment.

An inspection of the data published about the reactions of NO with CO/H_2 mixtures leaves an initial impression of a wealth of information at times conflicting and certainly confusing. This is, without doubt, a reflection of the enormous variety of catalyst formulations, preparations, and operating conditions of the experiments. The catalysts generally consist either of active components dispersed as microcrystallites on thermally stable and chemically inert supports such as alumina or aluminosilicates, ceramics (using materials such as cordierite, $Mg_2Al_4Si_5O_{18}$, spodumene, $LiAl(SiO_3)_2$, asbestos, $Mg_3(Si_2O_5)_2(OH)_2$, or metal oxide–metal mixtures), or of metallic wires, gauzes or screens (stainless steel or certain alloys). The active supported catalysts (i.e., those species dispersed on silicate media) may be derived from the "platinum metals" (Ru, Os, Rh, Ir, Pd, or Pt), copper, silver, or gold, mixtures of transition metal oxides (especially of the first-row elements) with each other or with certain p-block metal oxides, or from the p-block metal oxides alone. All-metal catalysts are usually alloys such as mixtures of Ni and Cu (on steel wire) or even more exotic combinations involving first, second, and third row transition elements with p-block metals such as Al. The reaction conditions must include the handling of gas velocities (in the range 0–300 000 vol/h) which vary rapidly and irregularly but occasionally remain steady, and temperatures that similarly oscillate, within the range ca. 0 to 1100 °C. Consequently, as already mentioned, it is often difficult to make comparisons of, and draw conclusions from, the enormous amount of experimental information that is derived from both rigorous laboratory conditions and "live" vehicle tests.

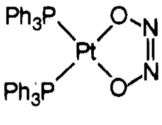
The decomposition of NO to its elements is thermodynamically favored to proceed to completion, but is kinetically very slow, even when catalyzed using presently known materials. Fortunately, the catalytic reduction of nitric oxide by CO and H_2 is relatively fast and, under the conditions being discussed, is the only effective way of eliminating NO.[103] However, bearing in mind that the exhaust gas will contain air, it is likely that oxygen will preferentially react with CO and H_2, thereby inhibiting NO reduction, although there are metal catalysts which can direct hydrogen to reduce NO even when oxygen is present. In practice, there must be an overall reducing atmosphere to effect removal of NO, and this appears to be incompatible with the oxidizing conditions necessary for the removal of CO!

However, the problem can be overcome, to a limited extent, by a dual catalytic system in which an engine is operated with a rich mixture to produce a net reducing exhaust gas (i.e., relative to the composition of gas obtained by burning stoichiometric air:fuel mixtures, CO_2, oxygen, and nitrogen concentrations are lowered while CO, hydrogen, water, and unburnt hydrocarbon concentrations are increased). This reducing gas mixture is then introduced to a catalyst converter which reduces NO using CO and H_2. The effluent gas from this process is then mixed with more air to provide net oxidizing conditions and is then passed through a second catalyst system to oxidize residual hydrocarbons and CO to CO_2 and water. Ammonia, often found as a byproduct of NO reduction (especially shortly after a cold-engine start), can unfortunately be reoxidized to NO in the second catalytic converter.

However, a number of interesting chemical facts emerge which are of relevance to the reactivity of coordinated NO. It is implicit that NO attaches itself initially to a metal atom at the catalyst surface, and that this attachment (i.e., coordination) induces and facilitates chemical reactivity not encountered in the gas phase. The following general points can be made.

(i) The most successful transition metal catalysts for oxidation and reduction are those containing the platinum metals, especially Pd, Pt, and Ru.[104] Under reducing conditions, Pd- and Pt-based compounds convert NO to NH_3, and the Pt-derived species are effective in simultaneous oxidation and reduction of exhaust gases using stoichiometric air:fuel mixtures. Ruthenium-based catalysts minimize NH_3 production and seem to be particularly effective in converting NO to N_2 in the presence of high concentrations of CO. Oxygen inhibits the reduction processes, but Ir-derived catalysts can achieve[105] significant conversion of NO to N_2 in the presence of quite high concentrations of O_2. Copper chromites (sometimes promoted by Ba^{2+} and other metals) and SnO_2/CuO mixtures are also effective[106] in the reduction of NO as well as oxidation of CO and hydrocarbons, but many catalysts are only capable of operating under relatively cool conditions (up to ca. 250 °C), being unable to withstand higher temperatures and attack by water vapor. Furthermore, while there may be a decrease in the amounts of NO and CO emitted by catalyst-treated exhaust gas, other pollutants may be generated as the results of degradation of the catalysts themselves. Ruthenium and chromium are particularly obnoxious in this respect, the former affording the volatile and extremely toxic RuO_4; production of metal carbonyls, likewise volatile and toxic, also occurs.

(ii) From IR spectal studies,[107,108] it seems that NO is adsorbed in three ways without dissociation at a metal site, as (coordinated) NO^+, NO^-, and as *cis*-$N_2O_2^{2-}$. There is also evidence to suggest that, under certain conditions, dissociative adsorption occurs; N–O bond dissociation must occur at some stage for any subsequent reaction to proceed. The existence of surface-bound *cis*-$N_2O_2^{2-}$ (hyponitrite) has been confirmed by IR spectroscopy using appropriate N-isotopic substitution. Thus, slow isotopic mixing of ^{14}NO and ^{15}NO, giving $^{15}N^{15}NO_2^{2-}$ and $^{14}N^{15}NO_2^{2-}$, was observed at −78 °C, and rapid mixing occurs at 25 °C. On chromium oxide supported on silica, chelating NO_2^- was also detected. These observations are of particular interest in three respects. First, it has been observed that NO reacts with cobalt(II) ammines or $Co(CO)_3(NO)$ under homogeneous conditions, giving, inter alia, complexes of *trans*-$N_2O_2^{2-}$ and μ-NO_2^- groups (see section V). Second, it has recently been established that $Pt(PPh_3)_2(N_2O_2)]$ (**6**), obtained by reaction of $[Pt(PPh_3)_3]$ with NO in solution, contains the *cis*-hyponitrito ligand. Third, NO reacts with a number of metal alkyls in solution affording the anion derived from *N*-alkyl-*N*-nitrosohydroxylamine (**7**) (see section V.A). Ir spectral studies also indicate[108] that NO reacts with CO at metal oxide surfaces giving adsorbed NCO^-, CO_3^{2-}, NO_2^-, NO_3^-, and N_2 as well as adsorbed CO and NO.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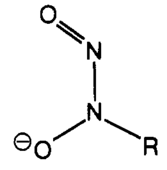
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Oxygen exchange reactions between $N^{18}O$ and bulk oxide in NiO and Fe_2O_3 have been observed.[111] These studies are very interesting since they show that oxide O exchanges with nitric oxide O atoms at temperatures far below those required for the dissociation of NO gas. Indeed, on nickel oxide, oxygen exchange is measurable at room temperature. There is no evidence that the exchange mechanism involves dissociative adsorption, but surface-bound NO_2^- has been observed in these systems. It has been suggested that NO_2^- exists in "dynamic exchange" with adsorbed NO, and this hypothesis may be related to the intramolecular O-atom exchange reactions undergone[76] by *cis*-$[Fe(NO)(NO_2)(S_2CNMe_2)_2]$ in solution (section III.C).

(iii) At relatively low temperatures (<500 °C) in the presence of hydrogen, water vapor, and relatively large concentrations of CO (i.e., low concentrations of NO), ammonia is generated on reduction, as well as some N_2 and N_2O.[105] The mechanisms whereby this occurs are speculative, but may involve surface-bound isocyanate:[112]

$$\text{M(metal atom site)} + \text{NO} \rightarrow \text{M–NO};\ \text{M} + \text{CO} \rightarrow \text{M–CO}$$

$$\text{M–NO} + \text{M} \rightarrow \text{M–N} + \text{M–O};\ \text{M–CO} + \text{M} \rightarrow \text{M–C} + \text{M–O}$$

$$\text{M–N} + \text{CO} \rightarrow \text{M–NCO};\ \text{M–C} + \text{NO} \rightarrow \text{M–CNO} \rightarrow \text{M–NCO}$$

$$\text{M–NCO} + 2H_2O \rightarrow \text{M–OH} + CO_2 + NH_3$$

The intermediacy of metal nitride species, M–N, has been implicated in the photochemical reaction of $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(NO)]$ with PPh_3 in solution, in which $[Mo(\eta^5\text{-}C_5H_5)(CO)(NCO)(PPh_3)_2]$ is formed[113] (in fact, it is implied in this work that the intermediate containing the Mo–N group should be regarded as a metallonitrene, but this is more a question of nomenclature rather than of mechanism). It is also known that azido complexes react with CO giving metal-bound isocyanate[114] and that such species can be hydrolyzed by acid giving CO_2 and NH_3 (it is not suggested that azido species are necessarily formed in reactions of NO with metal atoms on oxide surfaces; it is thought, however, that azides can react by loss of N_2 giving the very reactive intermediate M–N:).

It has recently been found[115] that noble metal or mixed Ni/Cu catalysts can convert mixtures of NO, CO, and H_2 into HCN and ammonium cyanate or its isomer urea. There is also growing evidence that a large amount of NO in automobile exhausts is converted into NH_4OCN.

Rhenium dioxide reacts[116] with NO in aqueous solution, giving $[Re(NO)(OH)_3$, perrhenate ion, and NH_4^+. Although the mechanism of this reaction is unknown, it seems clear that CO is unnecessary for the formation of ammonia from nitric oxide.

At higher temperatures than those referred to above, ammonia may be produced by direct reaction of surface N atoms, or of adsorbed NO with hydrogen:

$$\text{M-N} + H_2 \rightarrow \text{M-NH}_2 \text{ (followed by hydrolysis)}$$

$$\text{M-NO} + 2H_2 \rightarrow \text{M-NH}_2 + H_2O$$

$$2\text{M-NH}_2 + H_2 \rightarrow 2\text{M} + 2NH_3$$

There is no apparently analogous reaction which occurs in solution, but it may be recalled that some metal nitrosyl complexes react[98,99] with reducing agents such as $LiBu^t$, $LiAlH_4$, or $NaBH_4$ affording species which contain amido or imido bridges, and that $[RuCl_5(NO)]^{2-}$ may be reduced to a binuclear imido complex using selected reducing agents (preceding section IV.B).[102]

(iv) Nitrogen is generated as the main reduction product of NO by CO (with or without hydrogen) at moderate to high temperature. It may be formed[105] as the result of the combination of adjacent surface N atoms:

$$\text{M-N} + \text{M-N} \rightarrow 2\text{M} + N_2$$

by the thermal decomposition of surface amide (or imide), also via a two-site combination, or by reaction of amide with adsorbed NO:

$$2\text{M-NH}_2 \rightarrow 2\text{M} + N_2 + 2H_2$$

$$\text{M-NH}_2 + \text{M-NO} \rightarrow 2\text{M} + N_2 + H_2O$$

or by the decomposition of adsorbed dinitrogen oxide

$$\text{M-N} + \text{NO(g)} \rightarrow \text{M-NNO or M-ONN}$$

$$\text{M-NNO or M-ONN} + \text{M} \rightarrow \text{M-O} (+\text{M}) + N_2$$

Such reactions do not appear to have direct counterparts in solution coordination chemistry, but solid $[M(NO)_2Cl_2]_n$ (M = Mo or W), when heated at 340–350 °C, decomposes,[117] affording $MOCl_4$, MO_2Cl_2, M and N_2O, and N_2. The related complex $[MoCl_2(NO)_2(PPh_3)_2]$, when heated under CO_2, afforded dinitrogen, N_2O, and NO.

(v) The conversion of NO to N_2O seems to be a relatively minor pathway for most reactions based on Pt-metal catalysts.[105] However, dinitrogen oxide is formed together with N_2 on Cu (100 surfaces) and is the main product of the reaction of NO with CO over silver and gold-containing catalysts:[118,119]

$$\text{M-N} + \text{NO(g) (or M-(NO))} \rightarrow \text{M-NNO} (+ \text{M})$$

$$\text{M-NNO} \rightleftharpoons \text{M} + \text{NNO(g)}; \text{ M-NCO} + \text{NO(g)} \rightarrow \text{M} + \text{NNO} + CO_2$$

The low concentrations of N_2O formed over the platinum metals may be a reflection of the known ability of these compounds to decompose N_2O to oxide (M–O) and N_2. In comparing these results with homogeneous reactions of tertiary phosphine complexes of Ru, Os, Rh, and Ir, it should be noted that disproportionation of mixtures of NO and CO (stoichiometry 2:1) into N_2O and CO_2 can be achieved under relatively mild conditions. Also, NO will react with cobalt nitrosyl complexes affording cobalt-nitrito and -hyponitrito species, N_2O and N_2 (see section V.A). It is thought likely that hyponitrito intermediates are involved in these reactions.

It may be seen from the foregoing discussion that there are very many parallels between heterogeneous and homogeneous reactions of coodinated NO. Indeed, many of the processes which have only recently been described by solution chemists were demonstrated quite some time ago under heterogeneous conditions.

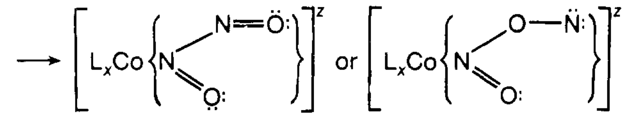
Some study has been made recently of the reactions of NO with NH_3 in cobalt- and copper-exchanged zeolites.[120] These systems appear to contain dinitrosyl cobalt and ammino–cobalt nitrosyl species, $[Co(NH_3)_n(NO)]^{2+}$, which, on treatment with NO/NH_3 mixtures, afford N_2O, N_2, and water. If the pressure of NO is kept low and the reaction temperature is less than 50 °C, N_2O formation is suppressed.

V. Homogeneous Disproportionation of NO

A. Reaction of Coordinated NO with Nitric Oxide

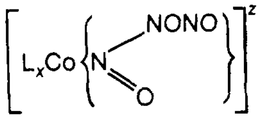
Treatment of either *cis*-$[Co(en)_2(NO)(MeOH)]Cl_2$ in methanol or $[Co(NO)(DMGH)_2(MeOH)]$ in methanol/pyridine mixtures with NO afforded *cis*-$[CoCl(NO_2)(en)_2]Cl$ or $[Co(NO_2)(DMGH)_2(py)]$, respectively, and N_2O. It has been suggested[121] that these reactions might occur via intermediates similar to those involved in the oxygenation of [Co(NO)(salen)] in pyridine, e.g.

$[L_xCo(NO)]^z$ + NO

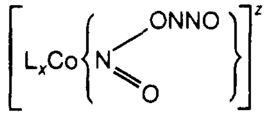


A B

Further attack of NO on the intermediate A would lead to the transient species



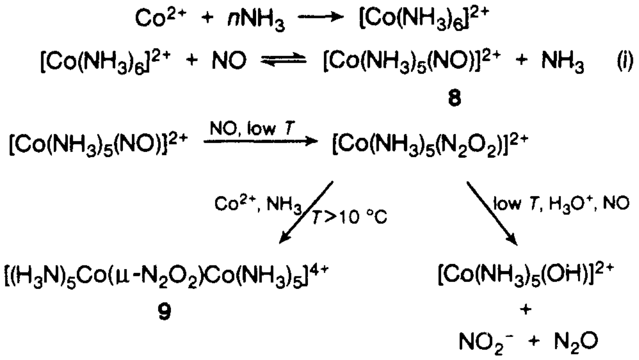
which might then be expected to break down giving $[L_xCo(solvent)]^z$, N_2O, and NO_2. This pathway is not particularly attractive since, in the ethylenediamine case, it would lead to the formation of labile Co(II) species which should react with NO/NO_2 mixtures giving both *cis*- and *trans*-chloronitrito products, and possible degradation of the en ligands, as has been observed elsewhere.[122] Alternatively, reaction of B with NO would give

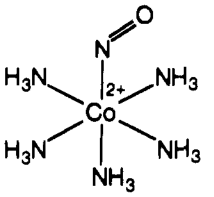


which could readily break up, with retention of the Co–N bond, giving the observed products, $[L_xCo(NO_2)]^z$ (the cis isomer in the en complex) and N_2O. However, there still remain some unsatisfactory aspects of this mechanism, and we shall return to this point at the end of the section.

These observations may be compared with the work of Gans,[123] who has shown that Co(II) ammines will react with NO, as shown in Scheme VII, to give various products whose formation is largely temperature dependent. It is suggested that the equilibrium i is the controlling factor in these reactions. At low temperatures, insufficient Co^{2+} is available for dimerization reactions, and only the black salt $[Co(NH_3)_5(NO)]^{2+}$ (**8**), which formally contains Co(III) and NO^-,[124] is produced. However, Gans felt it necessary to postulate the formation of $[Co(NH_3)_5(N_2O_2)]^{2+}$

SCHEME VII





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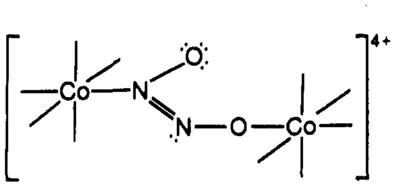


9

on further reaction of **8** with NO at low temperature, and this might be expected to hydrolyze giving Co(III) salts, nitrite ion, and N_2O (reactions not untypical of hyponitrite ion). However, at higher temperatures, $[Co(NH_3)_5(N_2O_2)]^{2+}$ reacts further with $[Co(NH_3)_6]^{2+}$ giving the asymmetrically bridged red dimer **9** which clearly contains hyponitrite.[125] This is obviously a competitive reaction, and total yields of **9** (maximized at ca. 30 °C) never exceeded ca. 25%.

In a probably related reaction,[126] $[Co(en)_2(NO_2)_2]^+$, in aqueous solution in the presence of NH_3 or RNH_2 (R = Me, Et or Bu^n), can catalytically convert NO into N_2 and N_2O. Both isomers of the Co(III) complex are effective, although the rate of consumption of NO is initially faster with the cis form. It has been suggested that one N-donor atom of an ethylenediamine ligand can be displaced by NO and that a nitro group may be abstracted by amine giving, ultimately, N_2. The further coordination of NO is envisaged, and the two NO groups would then disproportionate giving N_2O. In the light of discussions in section II.B and herein, this mechanistic view may need to be revised.

Treatment of the planar Rh(I) and Ir(I) complexes $[MClLQ_2]$ (M = Rh, L = CO, PPh_3 or $AsPh_3$, Q = PPh_3 or $AsPh_3$; M = Ir, L = N_2, Q = PPh_3) with NO free from NO_2 gave[127] $[MCl(NO)(NO_2)Q_2]$ and N_2O. The overall reaction could be represented as

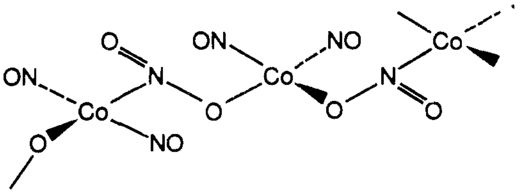
$$[MClLQ_2] + 4NO \rightarrow [MCl(NO)(NO_2)Q_2] + L + N_2O$$

Details of these reactions, and mechanistic comments, are sparse.

Cobalt carbonyl compounds react with NO to give[128] a number of interesting nitrosyl nitrite and hyponitrite complexes, depending on conditions.

$$\begin{aligned}&[Co_2(CO)_8] + NO\\&\rightarrow [Co(NO)_3]_n \quad \text{(difficult to confirm or identify species)}\\&\qquad +\\&\quad [Co(N_3O_4)]_n;\ n = \infty \text{ in the solid, } \mathbf{10}\\&\qquad\qquad n = 2 \text{ in solution, } \mathbf{11}\end{aligned}$$

$$\begin{aligned}&[Co(NO)(CO)_3] + NO \longrightarrow [Co(N_3O_4)]_n;\\&\qquad\qquad\qquad\qquad \mathbf{10} \text{ or } \mathbf{11}\\&\qquad\qquad\qquad\qquad + [Co_4(NO)_8(NO_2)_3(N_2O_2)]\\&\qquad\qquad\qquad\qquad\qquad\qquad \mathbf{12}\end{aligned}$$



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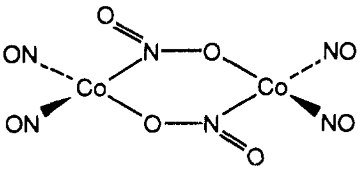

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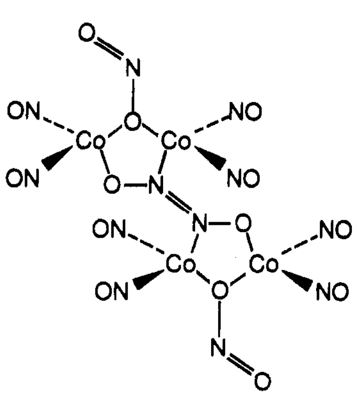


12

The phosphine complex $[Co(NO)(PPh_3)_3]$ behaves differently:[129]

$$[Co(NO)(PPh_3)_3] + 7NO \rightarrow [Co(NO)_2(NO_2)(PPh_3)] + 2Ph_3PO + 2N_2O + \tfrac{1}{2}N_2$$

This reaction is considered to be a metal-assisted disproportionation of NO into $NO^+NO_2^-$ and $\tfrac{1}{2}N_2$, and so the overall process can be split up into its apparent components:

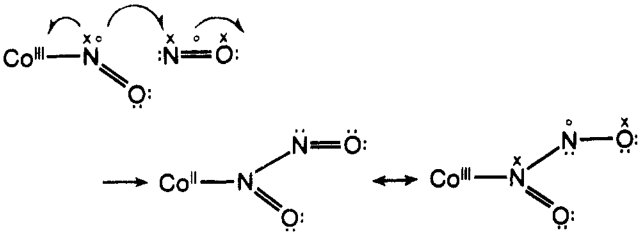
$$[Co(NO)(PPh_3)_3] + NO^+NO_2^- \rightarrow [Co(NO)_2(NO_2)(PPh_3)] + 2PPh_3$$

$$2PPh_3 + 4NO \rightarrow 2Ph_3PO + 2N_2O$$

The latter reaction is typical of the general behavior of nitric oxide when treated with tertiary phosphines.[130]

Nickel carbonyl derivatives also react with NO giving a variety of products.[131] Thus, nickel carbonyl itself, under pressure in a variety of solvents, affords species derived from $\{Ni(NO)\}^+$. In cyclohexane, $[Ni(NO)(NO_2)]_n$ and N_2O are formed, and in the presence of $NHEt_2$ and cyclopentadiene, $[Ni(\eta^5\text{-}C_5H_5)(NO)]$ could be produced. The species $[Ni(CO)_2(PPh_3)_2]$ reacts with pure NO in cyclohexane in a nearly 1:2 molar ratio giving $[Ni(NO)(OH)(PPh_3)_2]$ while, with NO containing traces of NO_2, $[Ni(NO)(NO_2)(PPh_3)_2]$ is formed together with N_2O. In *n*-pentane, a mixture of compounds is obtained, which can also be produced in the reaction between $[NiBr(NO)(PPh_3)_2]$ and $Ag_2N_2O_2$. It is possible that this mixture contains $[Ni_2(N_2O_2)(NO)_2(PPh_3)_4]$ and $[Ni_2(NO)_2O(PPh_3)_4]$, and a rational pathway to these various compounds can be proposed (Scheme VIII).

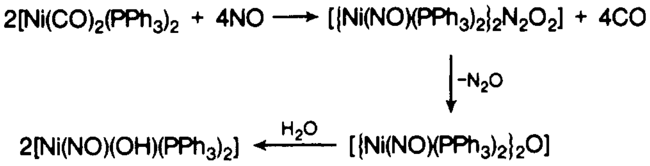
Returning to the question of mechanism, we may note that in all the reactions of "free" NO with coordinated NO, the products always include nitrites and N_2O, and occasionally hyponitrito derivatives. This can be no coincidence. Dealing first with the specific cases of the nitrosylation of cobalt ammine, ethylenediamine, and dimethylglyoxime nitrosyl complexes, we can devise a very attractive mechanism which picks up the implications of Gans' suggestions[123] for the formation of **8** and **9** from $[Co(NH_3)_6]^{2+}$, and also involves binuclear intermediates directly analogous to those proposed by Basolo and Clarkson[68] in the oxygenation of [Co(NO)(salen)]. Thus, as before, "free" NO would attack coordinated NO in what is effectively a *radical* process, giving the intermediate A:



A C

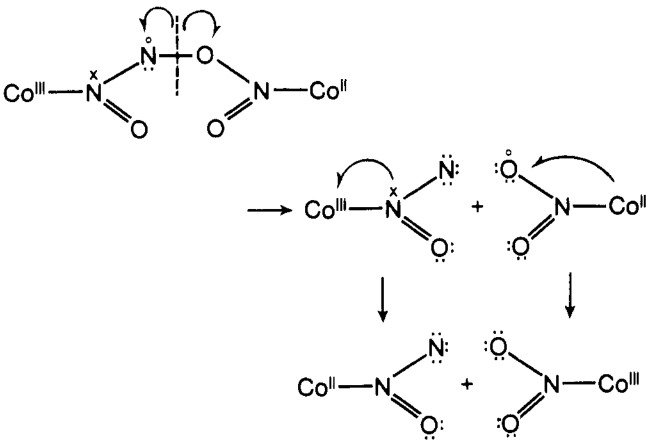
The species A could be described as a metal-based radical since it contains paramagnetic d^7 Co(II), but it can also be represented

SCHEME VIII

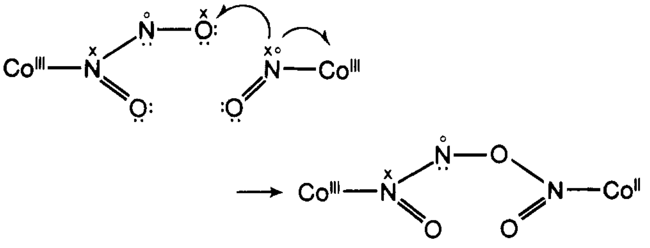


$$\begin{tikzcd} 2[Ni(CO)_2(PPh_3)_2] + 4NO \arrow[r] & [\{Ni(NO)(PPh_3)_2\}_2N_2O_2] + 4CO \arrow[d, "-N_2O"] \\ 2[Ni(NO)(OH)(PPh_3)_2] & [\{Ni(NO)(PPh_3)_2\}_2O] \arrow[l, "H_2O"'] \end{tikzcd}$$

SCHEME IX



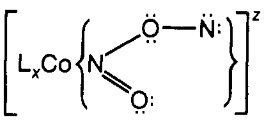
as its resonance hybrid, C, which is a ligand-based radical species, the electrons of importance being delocalized over the CoN_2O_2 π-orbital system. Reaction of C with $[L_xCo(NO)]^z$ again via one-electron processes, will give the bimetallic species D:



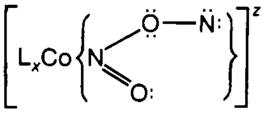
D

and homolytic fission of D about the N-O bond, as indicated, will give the species $[L_xCo(N_2O)]^z$ and $[L_xCo(NO_2)]^z$ (Scheme IX). We may expect N_2O to be only weakly bound to Co(II), and it will be readily displaced by NO, thus regenerating $[L_xCo(NO)]^z$. In such a mechanism, it is not necessary to invoke the autoxidation of a bridged hyponitrito complex, e.g., $[Cl(en)_2Co(\mu\text{-}N_2O_2)\text{-}Co(en)_2Cl]^{2+}$, to give the observed products, and, indeed, this is consistent with the stability of such species as $[CoCl(en)_2(NO)]^+$ in solution over a long period.

It may be seen that the key intermediate in Gans' scheme,[123] $[Co(NH_3)_5(N_2O_2)]^{2+}$, is apparently similar to the species represented as A and C above, and it may also be readily appreciated how **9**, with its asymmetric hyponitrito bridge, can be formed from $[Co(NH_3)_5(N_2O_2)]^{2+}$ and $[Co(NH_3)_6]^{2+}$. In this mechanism, the possible intermediate



has been discounted since it seems intrinsically unrealistic, and if it did exist, it would be so reactive that reaction products additional to those already observed would be expected. In the homolytic fission of D, N-N bond rupture would also give rise to



as well as regenerating $[L_xCo(NO)]^z$, and this path too has been disregarded.

An extension of these mechanistic ideas to the other systems described in this section is not so easy. The cobalt compounds discussed in detail above undergo their reactions with NO in protic solvents, and they contain ligands which may readily be deprotonated. Thus proton transfer may play an important part in these reactions and, indeed, the role of water in these processes has not been investigated and is therefore unknown. For species such as $[Co(NO)(CO)_3]$ in nonpolar, nonprotic solvents, reaction with NO could occur by a quite different pathway to that suggested above. However, it is very tempting to speculate that the formation of nitro-, nitrito-, and hyponitrito species may occur via a common mechanism involving one-electron transfer reactions. Indeed, it is already well established that many carbonyl complexes readily undergo electrochemical one-electron oxidations and reductions[131] and, in some cases, the radical anions and cations so produced have thermodynamic and kinetic stability. The addition of NO (as a one-electron donor) to a metal complex could occur with or without initial substitution of CO; e.g., $[Ni(CO)_2(PPh_3)_2]$ would form $[Ni(CO)_2(NO)(PPh_3)_2]$, a 19-electron species, or $[Ni(CO)(NO)(PPh_3)_2]$, a 17-electron compound. In a formal sense, assuming that the Ni-N-O bond angle is bent, i.e., that the nitric oxide is coordinated as NO^-, then these species contain d^9 Ni(I), and electron transfer within the Ni(I)/Ni(0) redox couple can be easily visualized. However, further experiments in this area are clearly needed before any definite conclusions about mechanism can be reached.

B. Reactions of NO with CO Catalyzed by Metal Complexes

Johnson and Bhaduri have shown[133] that $[Ir(NO)_2(PPh_3)_2]^+$ reacts with CO giving $[Ir(CO)_3(PPh_3)_2]^+$, CO_2, and N_2O, and that the tricarbonyl cation can be easily reconverted to the dinitrosyl precursor using NO under mild conditions, again generating CO_2 and N_2O. These reactions were immediately recognized as the basis of a possible homogeneous catalytic oxygen-transfer process:

$$2NO + CO \rightarrow CO_2 + N_2O$$

In 1974, Haymore and Ibers reported[134] their parallel and independent investigations of related reactions of iridium nitrosyl complexes, viz.

$$[IrBr(NO)_2(PPh_3)_2] + 3CO \rightarrow [IrBr(CO)_2(PPh_3)_2] + CO_2 + N_2O$$

$$[Ir_2(NO)_4(PPh_3)_2] + 8CO \rightarrow [Ir_2(CO)_6(PPh_3)_2] + 2CO_2 + 2N_2O$$

$$[IrCl(NO)(NO_2)(PPh_3)_2] + 4CO \rightarrow [IrCl(CO)_2(PPh_3)_2] + 2CO_2 + N_2O$$

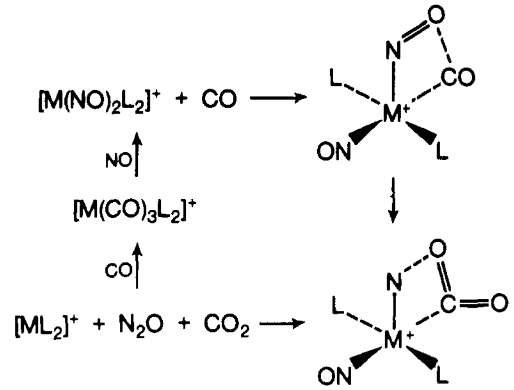
It was noticed by both groups of workers that the analogous rhodium complexes behaved similarly, and it was demonstrated[135,136] that $[Rh(NO)_2(PPh_3)_2][PF_6]$, its Ir analogue, $[IrBr(NO)_2(PPh_3)_2]$, $[Ir(CO)(PPh_3)_2(solvent)]^+$, and their Rh counterparts could catalyze, albeit slowly, the conversion of mixtures of NO and CO into N_2O and CO_2. While the compounds $[M(NO)_2(PPh_3)_2]$ (M = Ru and Os; isoelectronic with the Rh and Ir cations) reacted[137] extremely slowly with CO, giving carbon dioxide and dinitrogen oxide under pressure or UV light, the species $[Co(NO)_2(PPh_3)_2]^+$ and $[Fe(NO)_2(PPh_3)_2]$ failed to catalyze this reaction and, indeed, the iron complex undergoes substitution, affording $[Fe(CO)(NO)_2(PPh_3)]$ and $[Fe(CO)_2(NO)_2]$.

Reed and Eisenberg, also in 1974, observed[137] that ethanolic solutions of $RhCl_3\cdot nH_2O$ would catalyze the conversion of CO and NO into CO_2 and N_2O. Recently, it has been established[139]

TABLE V. Structural Data from the Species $[M(NO)_2(PPh_3)_2]^z$, A

M	z	∠P-M-P, deg	N-M-N, deg	M-N-O, deg
Rh	+1	116	158	159
Ir	+1	116	154	164
Co	+1	107	132	171, 171
Os	0	104	139	179, 174
Ru	0	104, 106	139, 140	178, 171 175, 168
Fe	0	112	124	178

SCHEME X



that this reaction also requires acid and water, and that the active catalyst appears to be $[Rh(CO)_2Cl_2]^-$.

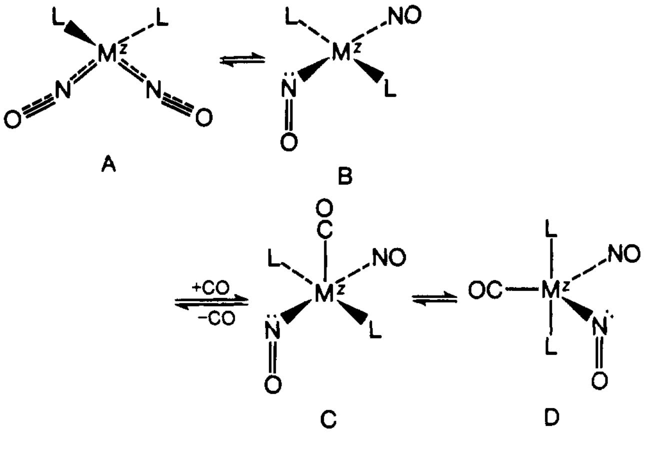
The complex $[Pt(PPh_3)_2(N_2O_2)]$ also reacts with CO giving[136] initially *cis*-$[Pt(CO)_2(PPh_3)_2]$, CO_2, and N_2O. The *cis*-dicarbonyl can be reconverted to the platinum *cis*-hyponitrite[6] using NO, but also readily rearranges to the unreactive $[Pt_3(CO)_3(PPh_3)_4]$. The overall process is not catalytic in the formation of CO_2 and N_2O.

Early speculation about the mechanism of disproportion of CO and NO by $[M(NO)_2(PPh_3)_2]^+$ led to a suggestion that the O-transfer process might involve a "metallo-nitrene" intermediate[133] (Scheme X). However, a number of more recent experiments indicate[135] that this pathway is unlikely. Thus, treatment of $[Ir(CO)(NO)(PPh_3)_2]$ with PPh_3 under UV light affords $[Ir(NCO)(PPh_3)_3]$. This reaction, designed to abstract an oxygen atom from NO giving the "metallo-nitrene", would appear to involve capture of the "naked" N atom by the adjacent CO, thereby forming isocyanate. A similar reaction would appear to occur[113] when $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(NO)]$ reacts photolytically with PPh_3. It would appear highly likely that, if a "metallo-nitrene" mechanism operates in these CO/NO disproportion reactions, then isocyanate intermediates should be present, and apparently they are not.

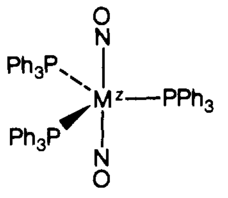
When equimolar mixtures of $[Rh(^{14}NO)_2(PPh_3)_2]^+$ and $[Rh(^{15}NO)_2(PPh_3)_2]^+$ are treated[135,136] with CO, $^{28}N_2O$, $^{29}N_2O$, and $^{30}N_2O$ are formed in the ratio 1:2:1. This nitrogen scrambling reaction does not appear to occur when CO is replaced by N_2, but under CO/^{15}NO mixtures, $[Rh(^{14}NO)_2(PPh_3)_2]^+$ again affords mixtures of the three dinitrogen oxides. However, there is no apparent exchange when $[Rh(^{14}NO)_2(PPh_3)_2]^+$ is treated with ^{15}NO for 6 h, but over a longer period some exchange does apparently take place. There is no evidence of PPh_3 dissociation from the dinitrosyl, giving the coordinatively unsaturated $[Rh(NO)_2(PPh_3)]^+$, and this is in apparent contrast to the behavior of $[Fe(NO)_2(PPh_3)_2]$ and $[Co(NO)_2(PPh_3)_2]^+$. However, it has been found that $[Ir(NO)_2(PPh_3)_2]^+$ reacts with L (PPh_3 or $AsPh_3$) giving $[Ir(NO)L_3]$ and releasing NO^+, while with the less bulky tertiary phosphines PMe_2Ph, $PMePh_2$ (L) or diphos (2L), $[IrL_4]^+$, phosphine oxide, Ph_3P, and N_2O are formed.

Taking these data into account, a proposed alternative to the "metallo-nitrene" mechanism is that the two NO groups can be coupled at the metal in $[M(NO)_2L_2]^z$ systems *before* oxygen abstraction takes place. This could arise via an intermediate, e.g., $[M(CO)(NO)_2L_2]^z$, as shown in Scheme XI. The polytopal rearrangement of A (18 e) ⇌ B (16 e) cannot be clearly demonstrated, but in other four-coordinate systems, planar ⇌ tetrahedral equilibrium are well established. The structures of the species A are severely distorted from ideal pseudotetrahedra (Table V) towards a trans-planar geometry, and this may well facilitate the rearrangement to B. Indeed, it has been suggested that the greater the distortion, the more facile will be the ultimate formation of C/D, since this distortion could be regarded as a manifestation of the extent to which M is back-donating charge to NO and of the readiness of M to accept a fifth ligand, e.g., CO. A correlation has been made[139] of the extent of distortion from tetrahedral geometry with the ability of $[M(NO)_2(PPh_3)_2]^z$ to catalyze the reduction of NO to N_2O, but this must be regarded with caution, since comparisons of solid-state structures with solution properties can be quite misleading.

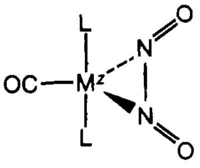
SCHEME XI



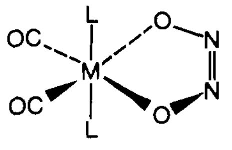
Being coordinatively unsaturated, B should readily accept CO giving pyramidal C which, since it contains "trans" NO groups, might be expected to be labile, losing NO and giving the 17-electron species $[M(CO)(NO)L_2]^z$ (M = Rh, z = +1). Such an intermediate could facilitate $^{14}NO/^{15}NO$ exchange reactions which *must* occur prior to formation of dinitrogen monoxide. In order that the NO groups can couple, they must presumably be mutually cis, and so there must be rearrangement of C to D, or some other similar five-coordinate species. It may be noted that treatment of A with bulky PPh_3 would give rise to sterically unfavorable forms of C/D. The three PPh_3 ligands would probably occupy equatorial sites in a form like D, thus giving the kinetically very labile *trans*-dinitrosyl, E. Hence, NO^+ could be readily lost, as observed. With sterically less demanding phosphines, the reaction would take a relatively normal course, leading to elimination of N_2O and formation of phosphine oxide (analogous to CO_2).



E

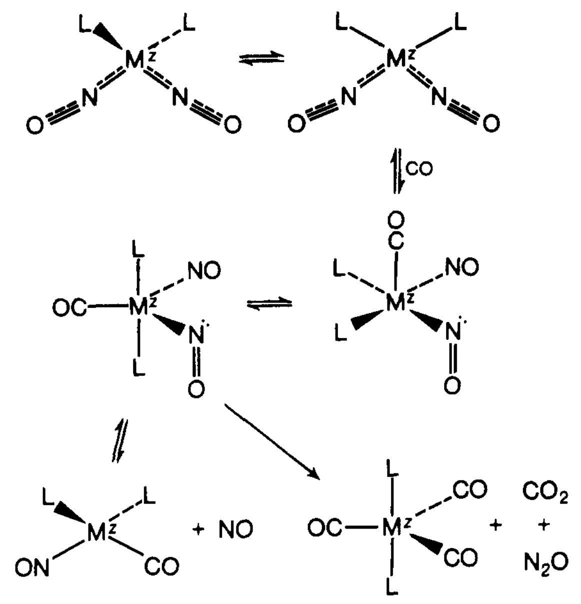


F



G

SCHEME XII



Once D is formed, coupling in the presence of CO might be expected to give a dinitrogen dioxide intermediate F, or possibly a hyponitrito species like G. The last can be related to $[Pt(PPh_3)_2(N_2O_2)]$ (**6**). Further reaction of the species containing coupled $(NO)_2$ with CO is then expected to give $[M(CO)_3L_2]^z$, N_2O, and CO_2, although no precise suggestions as to how this occurs have been made.

It must be observed that these proposals are largely conceptual since it has not been possible to detect or isolate any of the suggested intermediates. Indeed, some aspects of this mechanism are not very satisfactory: for example, the apparent necessity of B and C to be formed in order to explain exchange of $^{14}NO/^{15}NO$ prior to coupling giving dinitrogen monoxides. Why should CO not directly attack A, giving a five-coordinate intermediate with cis NO groups? Furthermore, displacement of one *neutral* NO group by CO as in the reaction

$$[Rh(NO)_2(PPh_3)_2]^+ + CO \rightarrow [Rh(CO)(NO)(PPh_3)_2]^+ + NO$$

is very unusual, although displacement of NO^+ is not uncommon. One might expect C (M = Rh, $z = +1$) to dissociate, giving $[Rh(CO)(NO)(PPh_3)_2]$. In relation to $^{14}NO/^{15}NO$ exchange via the proposed mononitrosyl carbonyl cation, it would be instructive to investigate the reaction between ^{15}NO or $^{15}NO^+$ and $[M(CO)(^{14}NO)(PPh_3)_2]$ (M = Rh or Ir).

A simplified representation of the conversion of CO and NO into CO_2 and N_2O is shown in Scheme XII. Here, isomerism of the tetrahedral $[M(NO)_2L_2]^z$ precursor to the planar intermediate occurs via a digonal twist.

The conversion of $[M(CO)_3L_2]^z$ into $[M(NO)_2L_2]^z$ with concomitant formation of CO_2 and N_2O has not been considered in any detail mechanistically. However, it has been suggested[136] that the first step requires dissociation of CO, and that the coordinatively unsaturated $[M(CO)_2L_2]^z$ will accept NO giving $[M(CO)_2(NO)L_2]^z$. Further CO dissociation and NO addition would give $[M(CO)(NO)_2L_2]^z$, which then reacts with NO according to the equation:

$$[M(CO)(NO)_2L_2]^z + 2NO \rightleftharpoons [M(NO)_2L_2]^z + N_2O + CO_2$$

In the context of these reactions, Eisenberg and Meyer have pointed out[17] that it is impossible to say whether species containing cis NO groups can exist as $\{M(NO^+)(NO^-)\}$, $\{M(O{=}N{-}N{=}O)\}$ or $\{M(ON{=}NO)\}$, and whether these formulations are relevant to a ground, excited, or transition state. Is it possible that N_2O_2 species are formed via processes similar to those suggested in the previous section (V.A) and that the production of CO_2 and N_2O parallels that of NO_2^- and N_2O?

The reaction of $RhCl_3 \cdot nH_2O$ in ethanol with mixtures of CO and NO has also been extensively studied.[138] It is clear that the first step in the eventual catalytic conversion of CO/NO mixtures into CO_2 and N_2O is the reduction of the Rh(III) salt to $[Rh(CO)_2Cl_2]^-$. It has been conclusively demonstrated that this carbonylate ion is the active catalyst necessary for the production of CO_2 and N_2O, and that H_3O^+ is an essential cocatalyst.

Treatment of the orange-yellow $[Rh(CO)_2Cl_2]^-$ with NO/CO mixtures (4:3 molar ratio) affords a green intermediate, believed to be $[Rh(CO)Cl_2(NO)_2]^-$, together with N_2O and CO_2. This species, which may be formed according to the equation

$$[Rh(CO)_2Cl_2]^- + 4NO \rightarrow [Rh(CO)Cl_2(NO)_2]^- + N_2O + CO_2$$

and which has not been isolated, is formally isoelectronic with $[Rh(CO)(NO)_2(PPh_3)_2]^+$ (C/D) discussed previously. However, if the relative concentration of NO is increased in this reaction, the dark red $[RhCl_2(NO)_2]^-$ is formed, again with N_2O and CO_2:

$$[Rh(CO)_2Cl_2]^- + 6NO \rightarrow [RhCl_2(NO)_2]^- + 2N_2O + 2CO_2$$

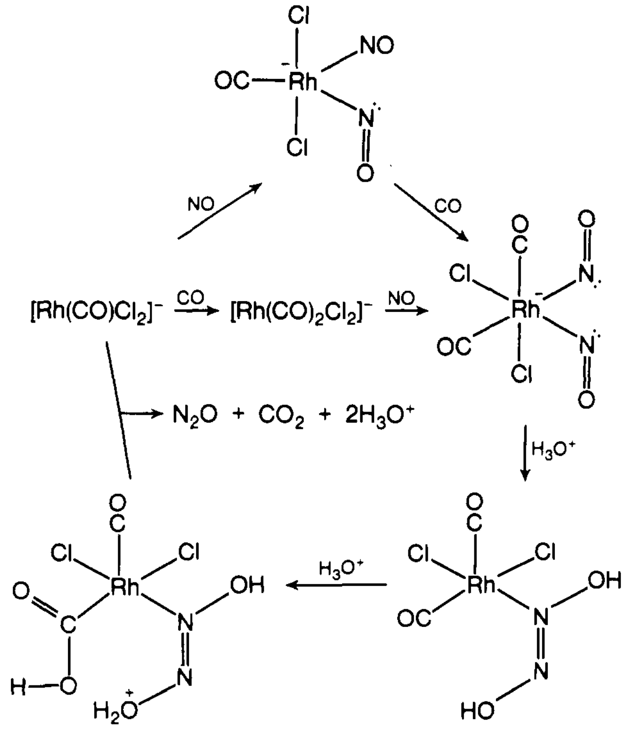
The dinitrosyl anion can continue to reduce NO, albeit slowly, but its treatment with CO causes reversion to $[Rh(CO)_2Cl_2]^-$:

$$[RhCl_2(NO)_2]^- + 3CO \rightarrow [Rh(CO)_2Cl_2]^- + CO_2 + N_2O$$

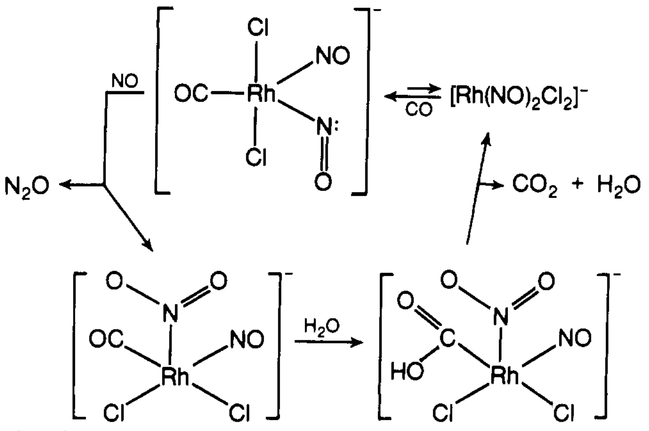
Hence a catalytic cycle can, in principle, be established with $[Rh(CO)Cl_2(NO)_2]^-$ as the key intermediate, and according to kinetic studies, its formation must be the rate-determining step. However, in the cycle proposed, $[Rh(CO)Cl_2(NO)_2]^-$ must be able to react with CO *and* with NO under acid-catalyzed conditions, giving N_2O and CO_2. Thus Schemes XIII and XIV, which seem reasonably consistent with the experimental facts, have been devised.

In Scheme XIII it is again proposed that the two NO groups couple, but to give hyponitrite ion. It may be recalled that both $[Co(NH_3)_5(NO)]^{2+}$ and $[Co(CO)_3(NO)]$ react with NO giving hyponitrite ion, and that $[Pt(PPh_3)_2(N_2O_2)]$ reacts with CO giving N_2O and CO_2. Not a great deal is known about the coordination

SCHEME XIII



SCHEME XIV



chemistry of hyponitrito complexes, but treatment of the Pt(II) compounds $[Pt(PPh_3)_2(N_2O_2)]$, $[Pt(en)_2(N_2O_2)]$, and $[\{Pt(dien)\}_2(N_2O_2)]_2^{2+}$ with acid leads to the release of N_2O.[140] The proposed formation of nitrito intermediates in Scheme XIV during the reaction of $[RhCl_2(CO)(NO)_2]^-$ with NO is also not unexpected in view of the results obtained from studies of the disproportionation of NO by authentic nitrosyl complexes (section V.A). In this respect, $[IrBr(NO)_2(PPh_3)_2]$, which reacts[134] with NO giving $[IrBr(NO)(NO_2)(PPh_3)_2]$ and N_2O and probably contains one bent Ir–N–O group, is formally isoelectronic with $[RhCl_2(CO)(NO)_2]^-$.

In a series of reactions[141] analogous to, but not identical with, the Wacker process for the oxidation of ethylene to acetaldehyde, mixtures of $PdCl_2$, $CuCl_2$, or CuCl in aqueous HCl can catalyze the formation of CO_2 and N_2O from CO and NO. The overall reactions seem to be

$$Pd^{2+} + CO + H_2O \rightarrow Pd^0 + CO_2 + 2H^+$$

$$Pd^0 + 2CuCl_2 \rightarrow Pd^{2+} + 2CuCl_2^-$$

$$Pd^0 + 2NO + 2H^+ \rightarrow Pd^{2+} + N_2O + H_2O$$

$$2CuCl_2^- + 2NO + 2H^+ \rightarrow 2CuCl_2 + N_2O + H_2O$$

The oxidation of CO to CO_2 proceeds more rapidly than the reduction of NO to N_2O, and it is thought that binuclear Pd^{II}–Cl–Cu^I and Pd^{II}–Cl–Pd^0 species may be active catalysts in the system. It is also believed that palladium hyponitrite intermediates play an important role in these reactions. In this connection, the observation[142] that the insoluble polymeric $[Pd(NO)Cl]_n$ reacts with HCl giving N_2O, Pd^{2+}, and Pd^0 species is intriguing.

The involvement of hyponitrites in the disproportionation of NO has also been invoked[143] in the Cu(I)-catalyzed reduction of NO by Sn(II) in aqueous acid. The products, depending on the concentrations of the metal ions, are N_2O or hydroxylamine, and the kinetic results have been interpreted in terms of intermediates such as $[CuCl_2(N_2O_2)(SnCl_3)]^{2-}$ and $[\{CuCl_2(SnCl_3)\}_2(N_2O_2)]^{4-}$.

In ethanolic solutions of $RhCl_3$, NO disproportionates[144] giving N_2O and ethyl nitrite. A proposal has been made that a species containing $Rh^{III}(NO^+)(NO^-)$ is formed and that OEt^- attacks the "NO^+" while the proton is added to "NO^-". Displacement of the coordinated HNO is thought to occur with dimerization and formation of N_2O and H_2O. However, it has been observed by Meyer and Eisenberg[138] that $[RhCl_2(NO)_2]^-$ slowly converts NO into dinitrogen oxide, and it has been demonstrated that $[Rh(CO)_2Cl_2]^-$ in ethanolic HCl consumes 22 mol of NO per Rh atom, with concomitant production of 2 mol of CO_2 and 6 mol of N_2O. Hence, if the initial stoichiometric conversion according to the equation

$$[Rh(CO)_2Cl_2]^- + 6NO \rightarrow [RhCl_2(NO)_2]^- + 2N_2O + 2CO_2$$

actually occurs, then the mole ratio of NO to N_2O is consistent with slow catalysis of the reaction

$$16NO + 8EtOH \rightarrow 4N_2O + 8EtONO + 4H_2O$$

However, no attempt has apparently been made to identify ethyl nitrite in these reactions.

Nitric oxide is quantitatively converted[145] into N_2O by reaction with $[Ti(\eta^5\text{-}C_5H_5)_2Cl]_2$, but with $[Ti(\eta^5\text{-}C_5H_5)_2]$, the polymeric $[Ti(\eta^5\text{-}C_5H_5)_2(NO)]_n$ is formed. However, NO may be reduced to N_2 and cyanate by reaction with $[Ti(\eta^5\text{-}C_5H_5)_2(CO)_2]$:

$$[Ti(\eta^5\text{-}C_5H_5)_2Cl]_2 + 2NO \rightarrow [Ti(\eta^5\text{-}C_5H_5)_2Cl]_2O + N_2O$$

$$[Ti(\eta^5\text{-}C_5H_5)_2] + NO \rightarrow [Ti(\eta^5\text{-}C_5H_5)_2(NO)]_n$$

$$2[Ti(\eta^5\text{-}C_5H_5)_2(CO)_2] + NO \rightarrow [Ti(\eta^5\text{-}C_5H_5)_2(NCO)] + [Ti(\eta^5\text{-}C_5H_5)O]_n + 3CO$$

$$3[Ti(\eta^5\text{-}C_5H_5)_2(CO)_2] + 3NO \rightarrow [Ti(\eta^5\text{-}C_5H_5)_2(NCO)] + 2[Ti(\eta^5\text{-}C_5H_5)O]_n + 4CO + CO_2 + N_2$$

Some of these bis(cyclopentadienyl)titanium species also react with N_2O, viz.

$$2[Ti(\eta^5\text{-}C_5H_5)_2] + N_2O \rightarrow [Ti(\eta^5\text{-}C_5H_5)_2]_2O + N_2$$

$$[Ti(\eta^5\text{-}C_5H_5)_2(CO)_2] + N_2O \rightarrow [Ti(\eta^5\text{-}C_5H_5)O]_n + N_2 + 2CO$$

$$[Ti(\eta^5\text{-}C_5H_5)_2(CO)_2] + 2N_2O \rightarrow [Ti(\eta^5\text{-}C_5H_5)O]_n + CO + CO_2 + 2N_2$$

No detailed mechanisms for these interesting reactions have been presented as yet, but it is possible that two metal sites are involved in a coupling reaction leading to a bridging hyponitrito intermediate.

In another reaction believed to proceed via a hyponitrite intermediate, N_2O has been produced[146] photolytically from coordinated NO in *cis*-$[Mo(NO)_2(S_2CNR_2)_2]$. The postulated reaction pathway is:

$$[Mo(NO^3)_2(\eta^2\text{-}S_2CNR_2)_2] \overset{h\nu}{\rightleftharpoons} [Mo(NO^3)(NO^1)(\eta^2\text{-}S_2CNR_2)_2]$$

(NO^3 and NO^1 represent three- and one-electron
donor ligands, respectively)

$$[Mo(NO^3)_2(\eta^2\text{-}S_2CNR_2)_2] + [Mo(NO^3)(NO^1)(\eta^2\text{-}S_2CNR_2)_2] \rightarrow [(ON^3)(\eta^2\text{-}R_2NCS_2)_2Mo\{N(O)N(O)\}Mo(\eta^2\text{-}S_2CNR_2)_2(NO^3)]$$

$$[\{Mo(NO^3)(\eta^2\text{-}S_2CNR_2)_2\}_2(N_2O_2)] \rightarrow 2[Mo(NO)(S_2CNR_2)_2] + N_2O + O$$

$$[Mo(NO^3)_2(\eta^2\text{-}S_2CNR_2)_2] \rightarrow [Mo(NO^3)_2(\eta^2\text{-}S_2CNR_2)(\eta^1\text{-}S_2CNR_2)]$$

$$[Mo(NO)(S_2CNR_2)_2] + [Mo(NO^3)_2(\eta^2\text{-}S_2CNR_2)(\eta^1\text{-}S_2CNR_2)] \rightarrow [Mo(NO^3)(\eta^2\text{-}S_2CNR_2)_3] + [Mo(NO)_2(S_2CNR_2)]$$

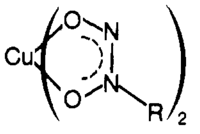
$$[Mo(NO)_2(S_2CNR_2)] \rightarrow S_2CNR_2 + N_2O + MoO \xrightarrow{O} MoO_2$$

It is of significance that NO coupling occurs apparently without the assistance of an external ligand, e.g., CO or NO. The proposed binuclear dithiocarbamato species may be analogous to $[\{Mo(diars)Cl_2(NO)\}_2(N_2O_2)]$ which is formed when *cis*-$[Mo(diars)Cl_2(NO)_2]$ is allowed to stand[147] in methanol.

VI. Other Reactions

A. NO Insertion Reactions

Although this class of reaction may not obviously fit within a discussion of reaction of coordinated NO, there is a strong possibility that intermediates containing metal–NO bonds are involved in the formation of "inserted" products. One of the earliest recognized reactions of NO with a transition metal compound was discovered and reported by Frankland[148] in 1856. This was the insertion of NO into a zinc–carbon bond, giving species of the type $[Zn\{ONN(R)O\}_2]$ (R = alkyl). This reaction appears to be general for main-group metal alkyls, since similar compounds containing $[ONN(R)O]^-$ are obtained upon nitrosylation of Grignard reagents,[149] cadmium,[150] aluminum[151] and even some boron alkyls.[152] Hydrolysis of some of these compounds, followed by treatment of the aqueous extract with Cu^{2+}, affords the copper(II) complexes of *N*-nitroso-*N*-alkylhydroxylaminate (**13**). These species are entirely analogous to the copper(II) complex of *N*-nitrosophenylhydroxylamine (cupferron), and reactions of group 2 alkyls with NO provide a convenient route to the alkyl analogues of cupferron. Aryl compounds, such as MgPhBr and BPh_3, also react with NO, but the products are not as simple as those obtained from the corresponding alkyls, and may be mixtures.



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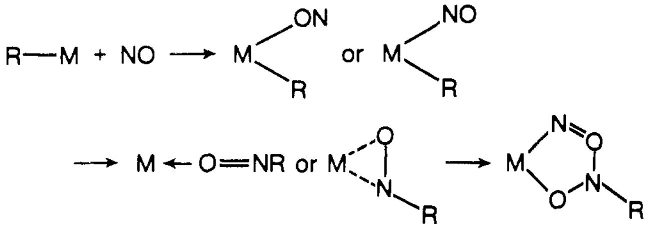
Reaction of $[ZnPr^n_2]$ with NO initially affords[150] $[ZnPr^n\{ONN(Pr^n)O\}]_n$ which, on hydrolysis, releases propane (1 mol) and $[Zn\{ONN(Pr^n)O\}_2]$. On standing, it slowly autoxidizes to $[Zn(OPr^n)\{ONN(Pr^n)O\}]_n$.

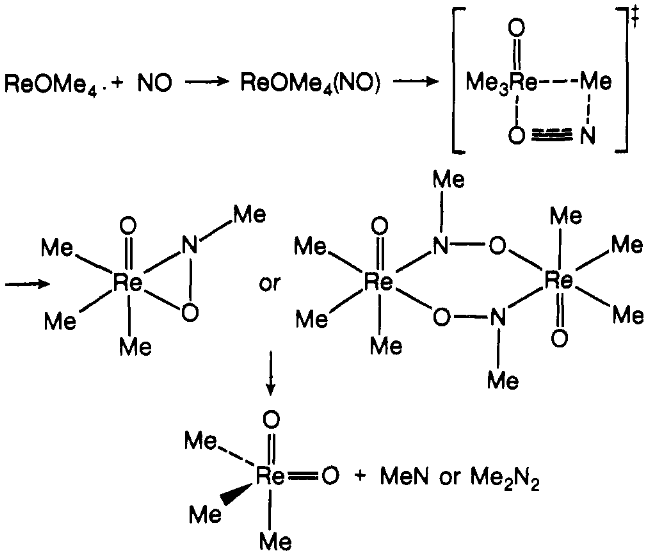
More recent work has revealed that d^0 transition metal alkyls will behave similarly with NO. Thus WMe_6,[153] MMe_2Cl_3, and MMe_3Cl_2 (M = Nb or Ta)[154] afford $[WMe_4\{ONN(Me)O\}_2]$, $[MCl_3\{ONN(Me)O\}_2]$, and $[MMeCl_2\{ONN(Me)O\}_2]$, respectively. The structures of the tungsten complex and $[TaMeCl_2\{ONN(Me)O\}_2]$ have been determined crystallographically, and the chelating nature of the nitroso hydroxylaminato ligand has been confirmed. Five moles of NO is absorbed[155] per mole of $[Zr(CH_2Ph)_4]$ in solution, and although no single product could be identified, it seems extremely likely that species containing $[ONN(CH_2Ph)O]^-$ are formed. The η-cyclopentadienyl complexes $[M(\eta^5\text{-}C_5H_5)_2XY]$ (M = Ti, X = Cl, Y = Me; M = Zr, X = Cl or Me, Y = Me) and $[Ti(\eta^5\text{-}C_5H_5)Me_3]$ likewise afford[156] $[M(\eta^5\text{-}C_5H_5)X\{ONN(Me)O\}]$ and $[Ti(\eta^5\text{-}C_5H_5)Me\{ONN(Me)O\}_2]$; it is thought that the hydroxylaminato ligand is monodentate in some of these compounds.

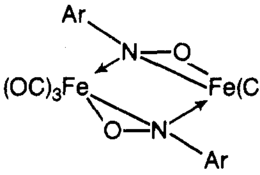
No detailed mechanistic studies have been made of these reactions. However, it has been suggested[150] that, with group 2 and 3 metal species at least, NO could act as a Lewis base and bind to the metal via the O atom. Group migration and further addition of NO to the paramagnetic alkylnitroso derivatives so formed should then lead to the observed product, e.g.



There are, at present, no IR spectral data to support the view that NO binds conventionally or unconventionally to any of these metals mentioned above, although such species might be very short-lived. Also, there is no definitive X-ray structural evidence that NO can bind to a metal via the O atom, although such an interaction between a Lewis acid and bridging NO, analogous to those between bridging CO and AlR_3 or BF_3,[157] could occur. There is, however, precedent for the formation of RNO complexes. Thus nitrosobenzene forms[158] a 1:1 adduct with Fe(II) phthalocyanin, and reaction of $[Pd(PBu^t_3)_2]$ with PhNO affords[159] $[Pd(PhNO)(PBu^t_3)_2]_3$ in which the three Pd atoms are linked via N–O bridges. The species $[Fe(CO)_3(ArNO)]_2$ (**14**) are also well established.[160] The compound $[NiPh(NO)(PPh_3)_2]$ can be obtained[161] by reaction of $[Ni(NO)(PPh_3)_2X]$ with LiPh and, on decomposition, is thought to give $[Ni(PhNO)(PPh_3)_2]$ which may be analogous to the formally isoelectronic azobenzene complex $[Ni(PhN_2Ph)(PPh_3)_2]$.[162] Also, $ReOMe_4$ reacts[163] with NO giving *cis*-ReO_2Me_3 in a series of steps which apparently involve an unstable mono- or binuclear rhenium complex containing MeNO (Scheme XV).

SCHEME XV

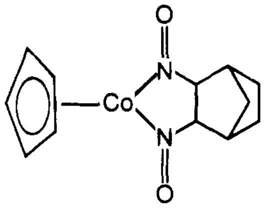




14

It is striking that the dimerization of NO with incorporation of an alkyl group seems to occur predominantly with d^0 and d^{10} metal alkyls. There is obvious scope for further exploration of this area.

Nitric oxide displaces CO from $[Co(\eta^5\text{-}C_5H_5)(CO)_2]$ giving[164] the nitrosyl-bridged species $[Co(\eta^5\text{-}C_5H_5)(\mu\text{-}NO)]_2$. This compound reacts with strained ring olefins, e.g., norbornene, under NO affording deep red adducts of the type **15**. Among the olefins which form species like **15** are derivatives of norbornene and norbornadiene, and while dicyclopentadiene also forms an adduct, addition occurs only at the strained ring, giving **16**. Only with the diolefin **17** is a dicobalt adduct formed. Although no reactions with acetylenes or noncyclic but "activated" olefins have been reported, it seems that transient red colors were formed when $[Co(\eta^5\text{-}C_5H_5)(\mu\text{-}NO)]_2$ was treated with NO and ethylene.



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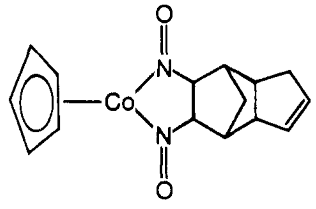

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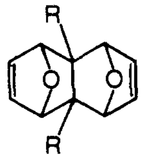


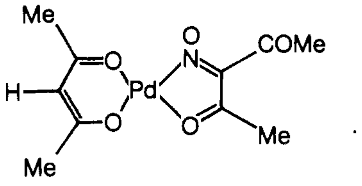
17

In benzene solution under 2 atm of NO, $[Pd(acac)_2]$ is converted[165] first into $[Pd(acac)(C_5H_6NO_3)]$ (**18**) and later into $[Pd(C_5H_6NO_3)_2]$ (**19**). From spectral studies and independent syntheses via reaction of $[PdCl_4]^{2-}$ with $(MeCO)_2C{=}NOH$ ($C_5H_6NO_3H$), it was established that the compounds **18** and **19**

TABLE VI. Reaction of [Co(NO)(DMGH)$_2$] with Acceptor Complexes

acceptor	products
[NiCl$_2$(PPh$_3$)$_2$]	[NiCl(NO)(PPh$_3$)$_2$] in equilibrium with acceptor
[CoCl$_2$(PPh$_3$)$_2$]	[Co(NO)$_2$(PPh$_3$)$_2$]$^+$
[CoCl$_2$(NO)(PPh$_3$)$_2$]	
[RhCl(PPh$_3$)$_3$]	[Rh(NO)(PPh$_3$)$_3$] + [RhCl$_2$(NO)(PPh$_3$)$_2$]
[Rh(CO)H(PPh$_3$)$_3$]	[Rh(CO)(NO)(PPh$_3$)$_2$] + traces of [Rh(NO)(PPh$_3$)$_3$]
[RuCl$_2$(PPh$_3$)$_3$]	[RuCl$_3$(NO)(PPh$_3$)$_2$] + [Ru(NO)$_2$(PPh$_3$)$_2$]
[RuHCl(PPh$_3$)$_3$]	[Ru(NO)$_2$(PPh$_3$)$_2$] and sometimes [RuCl$_3$(NO)(PPh$_3$)$_3$]
[RuH(NO)(PPh$_3$)$_3$]	
[RuCl(NO)(PPh$_3$)$_2$]	
[FeCl$_2$(PPh$_3$)$_2$]	[Fe(NO)$_2$(PPh$_3$)$_2$]
[Fe(base)H(diphos)$_2$]$^+$	[Fe(NO)$_2$(diphos)] [a]
[FeClH(diphos)$_2$] [b]	[Fe(NO)(diphos)$_2$]$^+$ + [Fe(NO)$_2$(diphos)]
[FeCl$_2$(diphos)]	[Fe(NO)(diphos)$_2$]$^+$ + [Fe(NO)$_2$(diphos)]

[a] diphos = Ph$_2$PCH$_2$CH$_2$PPh$_2$. [b] In the presence of PF$_6$$^-$.



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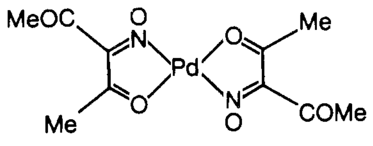


19

contain the chelating 3-hydroxyiminopentane-2,4-dionato ligand. **19** can also be prepared from [Pd(NO$_2$)$_4$]$^{2-}$ and acetylacetone, and it has been suggested that the complex described as [Pd(C$_5$H$_7$N$_2$O$_2$)$_2$], obtained[166] by reaction of [Pd(acac)$_2$] with KNO$_2$ and NH$_4$OAc, should be reformulated as **19**.

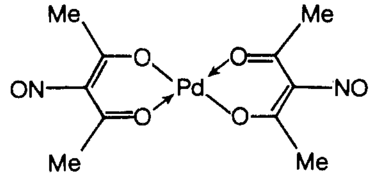
The reaction with NO described above is not strictly an insertion process. Bearing in mind that formation of **18** and **19** via this route seems to be acid catalyzed, the following steps for the conversion of [Pd(acac)$_2$] into **18** have been proposed:[165]

$$[\mathrm{Pd(acac)_2}] + \mathrm{H^+} \rightarrow [\mathrm{Pd(acac)}]^+ + \mathrm{Hacac}$$

$$\mathrm{Hacac} + 2\mathrm{NO} \rightarrow \mathrm{C_5H_6NO_3H} + 1/2\mathrm{H_2N_2O_2}$$

$$[\mathrm{Pd(acac)}]^+ + \mathrm{C_5H_6NO_3H} \rightarrow \underset{\mathbf{17}}{[\mathrm{Pd(acac)(C_5H_6NO_3)}]} + \mathrm{H^+}$$

It is, of course, possible that NO is oxidized to NO$^+$ under acid conditions, and that the nitrosonium ion attacks the 3-C atom of the β-diketone. It is well known that electrophiles will attack metal acetylacetonato complexes in this way. Thus, an intermediate could be **20** which could isomerize to the (presumably) thermodynamically more stable form, **19**.



20

B. Other Reactions

A number of reactions have been described in which NO can be transferred from one metal atom to another. The most extensively investigated system[167] is that of [Co(NO)(DMGH)$_2$], and a selection of the trans nitrosylations achieved is given in Table VI. Where metal chlorides are used as the NO acceptor, the cobalt-containing product is usually [CoCl(DMGH)$_2$L] (L is a Lewis base generally associated with the initial acceptor). It is thought that the majority of these reactions involve transfer of neutral NO, with prior dissociation in a ligand-mediated process. In other words, some analogies can be drawn between the behavior of [Co(NO)(DMGH)$_2$] and *p*-MeC$_6$H$_4$SO$_2$N(NO)Me, the latter being particularly effective in converting transtion metal carbonyl hydrides into the corresponding isoelectronic nitrosyls, e.g.

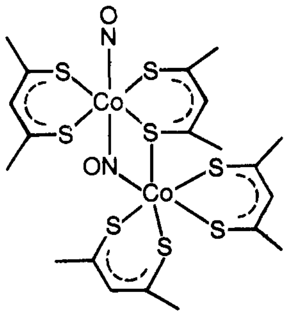
$$[\mathrm{Mn(CO)_5H}] + p\text{-}\mathrm{MeC_6H_4SO_2N(NO)Me} \rightarrow [\mathrm{Mn(CO)_4(NO)}] + p\text{-}\mathrm{MeC_6H_4SO_2NHMe} + \mathrm{CO}$$

The exchange of NO$^+$ and X$^+$ or NO$^-$ and X$^-$ does not seem to be implicated in the reactions of the cobalt dimethylglyoximate. However, in the reaction with [Fe(NO)(diphos)$_2$]$^+$, transfer of NO$^-$ is implied, giving [Fe(NO)$_2$(diphos)] and [Co(DMGH)$_2$(diphos)]$^+$.

Other nitrosyl complexes can behave similarly. Thus, in organic solvents, [Ru(NO)$_2$(PPh$_3$)$_2$] reacts with [CoCl(DMGH)$_2$(PPh$_3$)] according to the equation

$$[\mathrm{Ru(NO)_2(PPh_3)_2}] + 3[\mathrm{CoCl(DMGH)_2(PPh_3)}] \rightarrow [\mathrm{RuCl_3(NO)(PPh_3)_2}] + [\mathrm{Co(NO)(DMGH)_2}] + 2[\mathrm{Co(DMGH)_2}]$$

The ruthenium dinitrosyl also reacted with [RuCl$_2$(PPh$_3$)$_3$] giving [RuCl$_3$(NO)(PPh$_3$)$_2$] and [RuCl(NO)(PPh$_3$)$_2$]. In aqueous solution a number of nitrosyl complexes, when treated with reducing agents such as Cr(II), undergo ligand as well as electron exchange, as described in section IV.B. The five-coordinate [Co(NO)(SacSac)$_2$] (HSacSac = dithioacetylacetone) disproportionates[168] in solution giving [Co(NO)$_2$(SacSac)] and [Co(SacSac)$_3$]; a possible intermediate is **21**.



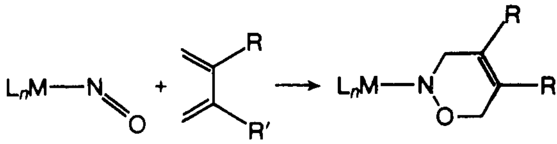
21

Finally, radiolysis of [Ru(NH$_3$)$_5$(NO)]$^{3+}$ in aqueous *tert*-butyl alcohol affords[169] the species [Ru(NH$_3$)$_5${N(=O)CH$_2$C(Me)$_2$(OH)}]$^{2+}$, which can be regarded as a ruthenium(II) alkylnitroso or Ru(III) nitroxide complex. Mechanistically, the product can be thought of as having been formed via reaction of the radical ·CH$_2$C(Me)$_2$OH, itself produced by OH· radical attack upon *tert*-butyl alcohol, with [Ru(NH$_3$)$_5$(NO)]$^{2+}$, formed from the interaction of the trication with H atoms or aquated electrons. The importance of [Ru(NH$_3$)$_5$(NO)]$^{2+}$ as an intermediate in radical reactions involving the corresponding trication has been underlined[170] in a study of the behavior of [Ru(NH$_3$)$_5$(NO)]$^{3+}$ with CO$_2$$^-$ and [Me$_2$COH]·. The dication is the initial product, from which the trans NH$_3$ ligand is displaced by H$_2$O giving a catalyst for the reduction of unreacted substrate. The final product of these reactions is *trans*-[Ru(NH$_3$)$_4$(NO)(OH)]$^{2+}$, and there is no evidence for attack on the NO group. However, attack by ·CH$_2$C(Me)$_2$OH on the nitroprusside ion is reported[81] to give [Fe(CN)$_5${N(=O)CH$_2$C(Me)$_2$OH}]$^{3-}$.

VII. Conclusion

Throughout this review, an attempt has been made to explain the reactivity of the NO group in terms of plausible mechanisms. In some cases this is clearly successful, but it can be readily seen that there are a number of areas where further work is necessary. This is especially true in the field of atom transfer reaction discussed in sections III.B, V.A, and V.B. A nagging problem remains as to why the nitrosyl ligand can be converted in one case to NO_2^- and in another to NO_3^- and even in one situation into both, and how two NO groups are converted into $N_2O_2^{2-}$, rather than O=N—N=O.

The formation of N-C bonds from nitrosyl complexes will remain a fascinating and potentially highly rewarding area of endeavour. Detailed studies of the insertion of NO into metal-alkyl bonds obviously demands further investigation. However, one class of reactions so far not studied[171] is cycloaddition, e.g.



Complexes such as $[Ni(\eta^5\text{-}C_5H_5)(NO)]$ and species containing bent M-N-O groups might be expected to undergo such reactions. Obviously, one driving force behind such studies is the hope of finding industrially significant reactions. However, it must be borne in mind that any process involving NO must be more than just competitive with one involving NH_3, since nitric oxide is produced by oxidation of ammonia!

Finally, it must be noted that there are very few reported reactions of nitric oxide bound to transition metals of groups 4, 5, 6, and 7. This must surely be accidental, since there seems to be no simple theoretical reason why NO should be "deactivated" by binding to such metals. Indeed, there is a very extensive chemistry of the dinitrogen ligand bound to Ti, Zr, Mo, W, and Re, and it has been demonstrated[172] that $[Mo(N_2H)(diphos)_2X]$ is a likely intermediate in the stepwise protonation of $[Mo(N_2)_2(diphos)_2]$, and that N_2H-containing species are implicated in the reduction of dinitrogen to ammonia and hydrazines by Mo and W phosphine complexes. The ligand N_2H is isoelectronic with NO, and it is inconceivable that reactions like the alkylation of N_2 and/or N_2R will not be paralleled by species such as the known $[Mo(NO)(diphos)_2X]$.[172]

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