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SYNTHETIC METHODS IN TRANSITION METAL NITROSYL CHEMISTRY

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CONTENTS

ABBREVIATIONS

bipy	bipyridyl
COD	cyclo-octadiene
Cp	C_5H_5
das	*o*-phenylenebis(dimethylarsine)
DMG	dimethylglyoximate
dppe	1,2-bis(diphenylphosphino)ethane
en	ethylenediamine
L	ER_3 with E = P, As, Sb
N_4	any macrocyclic tetradentate amine
o-phen	*o*-phenanthroline
PPP	$PhP[(CH_2)_3PPh_2]_2$

Ph, ϕ	C_6H_5
$RBpy_3$	tris-pyrazoylborate
SacSac	dithio-acetyiacetonate
tol	toluene
TPP	tetraphenylporphine dianion

A. INTRODUCTION

If inorganic chemistry could be said to suffer by comparison with organic chemistry, then this must be due in part to the lack of rational and general synthetic methods in the inorganic domain. This is of course due to the fact that inorganic chemistry encompasses such a variety of elements, but the point remains that inorganic synthesis badly needs organization and a framework of tentative principles upon which further work may be hung. It is in this spirit that this review is offered.

The structure, bonding and reactivity of coordinated NO and CO have long been considered as strictly analogous. Recently it has become clear that nitric oxide can bond to metals in modes not yet observed for CO. The chemistry[1], structure[2] and bonding[3] of nitrosyl complexes have been reviewed. This review will focus on another difference between NO and CO, one of which is of great practical importance. The great majority of metal carbonyl syntheses are based on the use of carbon monoxide itself. Excess CO is seldom detrimental in these reactions, and high-pressure high-temperature conditions are always available for kinetically sluggish transformations. In contrast, these latter conditions are seldom tolerable with nitric oxide due to its thermodynamic instability (eqns. (1), (2)) and its tendency to function as an oxidizing agent.

$$3NO \rightarrow N_2O + NO_2 \qquad \Delta H = -37.2 \text{ kcal mol}^{-1} \qquad (1)$$
$$NO \rightarrow 1/2N_2 + 1/2O_2 \qquad \Delta H = -21.6 \text{ kcal mol}^{-1} \qquad (2)$$

These limitations have motivated the development of new approaches for introducing NO into metal complexes. Particularly attractive amongst these are methods which avoid entirely the use of nitric oxide. It is the purpose of this review to summarize all methods available for introducing the nitrosyl functionality into coordination complexes. Mechanistic data and speculation are included in the hope of stimulating further work directed towards a fuller understanding of the reactions of metal nitrosyls. Older, less well-known synthetic methods (Sections B (vi), C (ii)) are particularly attractive for further study. The generality of such reactions remains unexplored, yet these may offer routes to presently unknown nitrosyls.

In view of the stated purpose of this review, we specifically exclude substitution and bridge-splitting reactions on preformed nitrosyl complexes, as well as oxidative additions and reductive eliminations of metal nitrosyls, unless these involve a net increase in the number of NO ligands. Thermal or reductive condensation reactions,

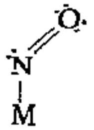
$$CpCr(NO)_2Cl + BH_4^- \rightarrow [CpCr(NO)_2]_2 \qquad \text{(ref. 4)}$$
$$MnNO(CO)_4 \xrightarrow{h\nu} Mn_2(NO)_2(CO)_7 \qquad \text{(ref. 5)}$$
$$[CpMnNO(CO)]_2 \xrightarrow{h\nu} Cp_3Mn_3(NO)_4 \qquad \text{(refs. 4, 6)}$$

since they do not increase the number of nitrosyl groups per metal, are not covered. Also excluded are reactions of coordinated NO, which necessarily lead *away* from nitrosyl complexes. However, Section C describes reactions of coordinated ligands which producte the nitrosyl group. As a result, this section is in no way a comprehensive review of extant nitrosyl complexes. Finally, since there is no fundamental difference between the synthesis of inorganic and organometallic nitrosyls, such a distinction will not be maintained in this review.

B. EXTERNAL SOURCES OF THE NITROSYL GROUP

(i) Nitric oxide

As a preliminary to this section, a statement concerning "electron counting" rules appropriate to the nitrosyl group is required. In considering a reaction of some metal complex with NO, the most useful rules will be those appropriate to the neutral diatomic molecule. Thus, we shall assume that the reagent NO functions as either a one-electron (I) or a three-electron (II) donor when it adds to or substitutes on a metal complex.



I

M—N≡O:

II

(a) Simple adduct formation, $ML_n + xNO \rightarrow M(NO)_xL_n$

(1) $x = 1$

This type of reaction is expected when ML_n is either a 17- or 15-electron complex, lacking one or three electrons from the inert gas configuration (IGC). The following are examples (NO is assumed to be a reactant throughout Section B, (i)).

$Cr(NR_2)_3$	→	$CrNO(NR_2)_3$	(ref. 7)
$CoCl_2L_2$	→	$CoNOCl_2L_2$	(ref. 8)
$Co(chel)_2$	→	$CoNO(chel)_2$	(ref. 9)

Numerous examples of this last reaction are known, with "chel" being a dithiocarbamate, dithiolate[10], dimethylglyoxime or a Schiff base or porphyrin. Several have been characterized crystallographically as containing bent CoNO groups.

A related reaction occurs for complexes of Fe^{II}. Since the FeNO moiety is bent in the complexes produced, the reaction represents conversion of a 14-electron species into a 15-electron species.

$Fe(chel)_2$	→	$FeNO(chel)_2$	(ref. 11)

(2) $x = 2$

$Cr(EPPh_3)_2X_2$	$\rightarrow$	$Cr(NO)_2(EPPh_3)_2X_2$ $E = O, NH$	(ref. 12)
$Cr^{+2} + NaS_2CNR_2$	$\rightarrow$	$Cr(NO)_2(S_2CNR_2)_2$	(ref. 13)

Although this second reaction is run without isolation of intermediates, it conceivably represents addition of NO to $Cr(S_2CNR_2)_2$.

Recent work has shown that the complex claimed to be $Fe(NO)_2$-$(S_2CNEt_2)_2$ is actually a nitro—nitrosyl complex[14].

(b) Substitution, $ML_n + xNO \rightarrow M(NO)_xL_m + (n-m)L$

Here one is guided by the principle that, in an 18-electron complex, a one-electron donor ligand (halide, alkyl, metal—metal bond) will be replaced by a bent nitrosyl, a three-electron donor by a linear nitrosyl, etc. More generally, Z two-electron donors are replaced by $(2Z)/3$ nitrosyls.

$CoNO(CO)_3$	$\rightarrow$	$Co(NO)_3$		(ref. 15)
$Cr(CO)_6$	$\xrightarrow{h\nu}$	$Cr(NO)_4$		(refs. 16, 17)
$MCl_2(CO)_3L_2$	$\rightarrow$	$M(NO)_2Cl_2L_2$	M = Mo, W	(ref. 18)
$Fe(CO)_5$	$\xrightarrow{h\nu}$	$Fe(NO)_2(CO)_2$		(ref. 17)
$CpV(CO)_4$	$\xrightarrow{h\nu}$	$CpV(NO)_2CO$		(ref. 17)
$CpV(CO)_3CN^-$	$\rightarrow$	$CpV(NO)_2CO$		(ref. 19)
$Co(CO)_3R(L)$	$\rightarrow$	$Co(NO)_2R(L)$		(ref. 20)
$MnNO(CO)_3L$	$\rightarrow$	$Mn(NO)_3L$		(ref. 21)
$MnNO(CO)_4$	$\xrightarrow{h\nu}$	$Mn(NO)_3CO$		(ref. 17)
$[Fe(CO)_3(SCF_3)]_2$	$\rightarrow$	$[Fe(NO)_2(SCF_3)]_2$		(ref. 22)
$Mn(CO)_3L_2X$	$\rightarrow$	$Mn(NO)_2L_2X$		(ref. 23)
$Mn(CO)_2L_3Br$	$\rightarrow$	$Mn(NO)_2L_2Br$		(ref. 24)

(1) Replacement of a one-electron donor. No examples of this reaction type are known.

(2) Replacement of ligand(s) equivalent to three electrons. The reactions are predictably straightforward when the reagent metal complex is coordinatively saturated.

$[Mn(CO)_4I]_2$	$\rightarrow$	$Mn(NO)_3CO$		(ref. 25)
$Mn(CO)_5I$	$\rightarrow$	$Mn(NO)_3CO$		(ref. 25)
$HIr[P(OPh)_3]_4$	$\rightarrow$	$IrNO[P(OPh)_3]_3$		(ref. 26)
$HIrCOL_3$	$\rightarrow$	$IrNO(CO)L_2$		(ref. 27)
RuH_4L_3	$\rightarrow$	$Ru(NO)_2L_2$		(ref. 28)
$CpM(CO)_3^{-1}$	$\xrightarrow{H_2O}$	$CpM(NO)(CO)_2$	M = Mo, W	(ref. 29)
$Co(CO)_4^{-1}$	$\xrightarrow{H_2O}$	$CoNO(CO)_3$		(ref. 30)

These last two reactions, carried out in protic solvents, may occur by attack of NO on the conjugate acid (hydride).

It is useful to consider the preparation of CpNiNO

$Cp_2Ni \rightarrow CpNiNO$ (ref. 31).

as a reaction of this type. This involves idealization of one cyclopentadienyl ring in nickelocene as being π-allylic in nature. It is reported that NO displaces allyl groups from allyl nickel complexes[32]. The reaction of $Ni(C_3H_5)_2$ with NO offers an attractive possible route to the unknown binary nitrosyl $Ni(NO)_2$. A similar statement applies to $M(C_3H_5)_3$, M = Rh, Ir.

NO displaces one CO and one hydride from $[(HO)M(CO)_3H]_4 \cdot 4H_2O$, M = Mo, W. Addition of $OPPh_3$ allows isolation of $[Mo(OH)(CO)_2NO]_4 \cdot 4(OPPh_3)$. The phosphine oxide does not coordinate to the metal, but merely hydrogen bonds to the hydroxyl protons. The structure, which contains no metal—metal bonds, consists of a tetrahedron of four metals and an interpenetrating tetrahedron of four triply bridging hydroxyl groups. Each metal is also bound to two COs and one NO, all terminal. The inert gas configuration is achieved considering OH to be a five-electron donor[33].

In metal clusters, substitution reactions with NO are somewhat more complex owing to the possibility of cleaving metal—metal bonds.

$Fe_3(CO)_{12}$	$\rightarrow$	$Fe(NO)_2(CO)_2$		(ref. 34)
$M_3(CO)_{12}$	$\rightarrow$	$M_3(NO)_2(CO)_{10}$	M = Ru, Os	(ref. 35)
$[Mo(CO)_2dipy]_2$	$\rightarrow$	$[MoNO(CO)_2dipy]_2$		(ref. 36)
$[CpCr(CO)_3]_2$	$\rightarrow$	$CpCrNO(CO)_2$		(ref. 37)
$Co_2(CO)_8$	$\rightarrow$	$CoNO(CO)_3$		(ref. 38)
$Mn_2(CO)_{10}$	$\xrightarrow{h\nu}$	$MnNO(CO)_4$		(ref. 17)
$Mn_2(CO)_8L_2$	$\rightarrow$	$MnNO(CO)_4 + MnNO(CO)_3L + L$		(refs. 21, 25)

Formation of metal—metal single or multiple bonds is also possible.

$CpCo(CO)_2$	$\rightarrow$	$[CpCoNO]_2$	(ref. 39)
$[CpFe(CO)_2]_2$	$\rightarrow$	$[CpFeNO]_2$	(ref. 40)
$[Ru(CO)_2I_2]_n$	$\rightarrow$	$[RuNOI_2]_n$	(ref. 41)

The Fe—Fe distance of 2.326 Å in $[CpFeNO]_2$ is consistent with a double bond between these atoms[40].

Finally, if the precursor complex deviates from the inert gas configuration by one electron, an 18-electron shell can be achieved by substitution of a two-electron donor.

$Co(amine)_6^{2+}$	$\rightarrow$	$Co(amine)_5NO^{2+}$	(ref. 42)
$Os(SbPh_3)_3Cl_3$	$\rightarrow$	$OsNO(SbPh_3)_2Cl_3$	(ref. 43)
$Cr(CO)_5I$	$\xrightarrow[(ii)\ PPh_3]{(i)\ NO}$	$Cr(NO)_2(PPh_3)_2I_2$	(ref. 44)
"$RuCl_3(H_2O)_3$"	$\rightarrow$	"$RuNOCl_3(H_2O)_2$"	(ref. 45)
CoL_4	$\rightarrow$	$CoNOL_3$	(ref. 46)
$V(CO)_6$	$\rightarrow$	$V(NO)(CO)_5$	(ref. 47)
$V(CO)_4L_2$	$\rightarrow$	$VNO(CO)_4L$	(ref. 48)

$Ru(NH_3)_6^{3+}$	→	$RuNO(NH_3)_5^{3+}$		(ref. 49)
cis-$Ru(NH_3)_4X_2^+$	→	*cis*-$Ru(NH_3)_4(NO)X^{2+}$		(ref. 50)
trans-$Ru(NH_3)_4X_2^+$	→	*trans*-$Ru(NH_3)_4(NO)X^{2+}$		(ref. 50)
$M(NH_3)_5X^{2+}$	→	$MNO(NH_3)_5^{3+}$		
		$MNO(NH_3)_4X^{2+}$	M = Ru, Os	(refs. 49, 51)
$Fe(CN)_6^{3-}$	→	$FeNO(CN)_5^{2-}$		(ref. 49)
$Ru(S_2CNEt_2)_3$	→	$RuNO(S_2CNEt_2)_3$		(ref. 52)

This last complex has been shown to contain one monodentate dithiocarbamate *cis* to the nitrosyl group.

Complexities arise when the precursor metal complex lacks an even number (usually two) of electrons from the IGC. Under these circumstances, several modes of reaction are possible. Two nitrosyl groups may substitute, producing a coordinatively saturated species.

$$ML_n \rightarrow M(NO)_2L_{n-2} + 2L$$

This behavior may account for the following reactions.

$Co(dppe)_2^+$	→	$Co(NO)_2(dppe)^+$	(ref. 53)
$[Rh(CO)_2Cl]_2$	→	$[Rh(NO)_2Cl]_n$	(ref. 54)

This rhodium complex is only poorly characterized owing to its insolubility. In addition, different groups, working under different conditions, have produced solids with the same apparent formula but different infrared spectra.

Alternatively, a 17-electron complex may result.

Cr_{aq}^{2+}	→	$CrNO_{aq}^{2+}$	(ref. 55)
$Cr^{2+} + 2das + Cl^-$	→	$Cr(NO)Cl(das)_2^+$	(ref. 56)

Dithionite reduces $Cr(NO)Cl(das)_2^+$ to diamagnetic $Cr(NO)Cl(das)_2$.

Substitution of a one-electron donor such as hydrogen may result in the formation of a metal—metal bond.

H_3IrL_2	→	$[Ir(NO)_2L]_2$	(ref. 57)

This dimer has no bridging groups and an Ir—Ir distance of 2.717 Å.

Often, however, reaction of NO with a coordinatively unsaturated complex results in a redox reaction, sometimes reducing the metal and other times in the form of a disproportionation of NO itself.

$Ni[P(n\text{-}Bu)_3]_2X_2$ reacts in a complex manner depending upon the halogen[58]. When X is Cl, an apparent reduction by NO produces $NO^+NiL_2Cl_2^-$. The bromo analog produces a mixture of this paramagnetic anion and a five-coordinate adduct $Ni(NO)Br_2[P(n\text{-}Bu)_3]_2$. Reaction of the iodo complex is interpreted as producing $[Ni(NO)(I)P(n\text{-}Bu)_3]_2$. The latter presumably forms as a result of partial oxidation by NO of $P(n\text{-}Bu)_3$ to the phosphine oxide. In fact, earlier workers[59] isolated only $NiCl_2(OPEt_3)_2$ from the action of NO on $NiCl_2(PEt_3)_2$ emphasizing the importance of careful control of stoichiometry in reactions of nitric oxide.

$Rh(PPh_3)_3Cl$ and $Rh(PPh_3)_2COCl$ are similarly "incompatible" with NO in terms of the inert gas formalism. Predictably, then, the nature of these reactions has been the source of considerable controversy. Hughes[60] reported the production of $Rh(NO)(NO_2)(PPh_3)_2Cl$ from the reaction of $Rh(PPh_3)_2$-COCl in benzene or chloroform. Although the NO_2 group was established to be N-bonded, two NO stretching frequencies were observed; "isomers" were suggested to be present. $Rh(PPh_3)_3Cl$ in chlorobenzene produces the same product. N_2O was detected as a reaction product, and it was suggested that the complexes catalyze disproportionation of NO to NO_2 and N_2O.

Kukushkin et al.[61] published a series of reports on this same reaction. These suffer from erroneous claims on the existence of a complex of formula $Rh(NO)_2(PPh_3)_2Cl$. Later papers correct this error, and discuss various attempts to separate components of the product mixture by crystallization.

The work of Kiji et al.[62] provides the best method for isolating pure $RhNO(NO_2)(PPh_3)_2Cl$ uncomplicated by the "isomeric" mixture noted by Hughes. Excess PPh_3 added to $Rh(PPh_3)_3Cl$ prior to reaction with NO results in production of a solid with a single NO stretching frequency. These workers also claim to separate Hughes' product mixture into green $RhNO(NO_2)$-$(PPh_3)_2Cl$ and a brown material which exhibits the second NO stretching frequency. This was suggested to be a halide-bridged oligomer with NO as one ligand. Suppression of this product in the presence of added phosphine (which is readily oxidized by NO) is consistent with this suggestion. The details of this reaction remain obscure; further study is required.

It was briefly noted that $Ir(PPh_3)_3Cl$ reacts with NO to produce a pale brown material identified[63] as $IrNO(NO_2)(PPh_3)_2Cl$.

The reaction of $RuCl_2L_3$ with NO is solvent dependent. In chloroform the product is (quantitatively) $RuNOCl_3L_2$, indicating attack on solvent by the possible intermediate $RuNOCl_2L_n$. When halogen is unavailable from other sources (e.g. in acetone or benzene), halogen redistribution (disproportionation) occurs to produce[64] $RuNOCl_3L_2$ and $Ru(NO)_2L_2$.

$ML_{3,4}$ with M = Pt, Pd reacts with NO in a unique fashion. Initially, the products were erroneously characterized as nitrosyl complexes, but it is now thought that the products of stoichiometry $ML_2(N_2O_2)$, contain a hyponitrite ligand[65].

Oxidation of phosphine always must be considered.

$$IrH_2L_3^+ + 6NO \rightarrow Ir(NO)_2L_2^+ + H_2O + L{=}O + 2N_2O \qquad \text{(ref. 66)}$$

It is stated[59] that NO reacts with $FeCl_2(PR_3)_2$ to give only "inseparable mixtures".

Solutions of $OsCl_6^{2-}$ absorb NO, but the primary reaction product is uncharacterized[43]. Addition of phosphines, arsines or stibines produces $OsNOCl_3L_2$, but this does not prove (or disprove) the existence of "$OsNOCl_3$" in view of the known reducing tendency of group V bases. The question of the nature of the immediate product of NO and OsX_6^{-2} also bears on the reaction of NO with commercial "$RuCl_3$ hydrate", which is known to contain Ru^{IV}. Reductive nitrosylation (see the next section) may be involved.

Some coordinatively saturated complexes undergo equally complex reactions with NO.

$Ni(CO)_2L_2 \rightarrow Ni(NO)(NO_2)L_2$ (ref. 67)

Here the identity of the oxygen deficient product (N_2O?) was not investigated. The reaction of NO with $Ni(CO)_4$ has been more completely characterized.

$Ni(CO)_4 + 4NO \rightarrow Ni(NO_2)NO + 4CO + N_2O$ (ref. 68)

In both of these cases the complex $Ni(NO)_2L$ (L=CO, PR_3), which is at least formally a possible product, is not observed.

$RhCl_3 \cdot 3H_2O$ was initially reported to react with NO at room temperature in ethanol[69]. Although the solution color changed and an ESR signal was detected in the solution, removal of solvent yielded a solid residue which exhibited no nitrosyl stretching frequency. Curiously, addition of PPh_3 to the above solution yields a solid which exhibits two nitrosyl stretching frequencies. Elemental analysis indicates this solid is a mixture. One of the NO stretching frequencies is identical with that of $RhNOCl_2(PPh_3)_2$. Further recent study[70] of $RhCl_3 \cdot 3H_2O$ in ethanol shows conclusively that catalytic disproportionation of NO takes place according to the following reaction.

$$4NO + 2ROH \rightarrow N_2O + 2RONO + H_2O$$

Under conditions of constant volume 0.02 *M* $RhCl_3$ turns over approximately twelve NO/Rh in two hours at 25°C.

This reaction prompts visions of using the electronic "mismatch" of NO (a three-electron donor) and any 16-electron metal complex to advantage in a catalytic cycle for the purpose of reducing nitric oxide. It is precisely this incompatibility which is required to prevent formation of a stable complex which effectively "poisons" the catalyst. The most attractive reaction of this sort is

$$2CO + 2NO \rightarrow 2CO_2 + N_2$$

It has been reported[62] that the reaction mixture from NO treatment of $RhClL_3$ (which contains $RhNO(NO_2)L_2Cl$), upon treatment with CO under pressure, results in loss of coordinated NO and NO_2 with the production of a carbonyl complex. Two other groups[71,72] have reported preliminary observations on the catalytic reaction of CO and NO, and this area is likely to see intense activity in the near future.

If there is any predictive value to the present catagorization of reactions of NO with 16-electron compounds, the reported[73] $[RhNO(O_2CCH_3)_2]_2$ deserves reinvestigation. $Rh_2(O_2CCH_3)_4$ requires a metal—metal bond if it is to be diamagnetic. Thus, reaction with NO must break the metal—metal bond even if the adduct contains a bent RhNO moiety. One predicts that this NO adduct will undergo gross structural modification, since it is valence-isoelectronic with monomeric $MNOCl_2(PPh_3)_2$ where M = Rh, Ir. The iridium compound has been characterized crystallographically[74].

It is claimed that Ru(CO)MPIXDME (MPIXDME is mesoporphyrin IX dimethyl ester) reacts with "slightly more than 2 equivalents of nitric oxide" to produce $Ru(NO)_2$MPIXDME. Elemental analysis was acceptable for this formulation and a parent peak was observed in the mass spectrum. This compound is sufficiently anomalous to justify reinvestigation, however. This may actually be a "sitting-atop" complex[76] of general formula $Ru(NO)_2L_2$,

where each L represents a nitrogen lone pair. This requires that the two uncoordinated porphyrin nitrogen atoms actually be protonated and that the RuNO groups approximate a linear geometry. The observed nitrosyl stretching frequencies in this complex (1786 and 1838 cm^{-1}) may be rather high for such a structure, however.

Another explanation is also worthy of consideration. Feltham[14] has shown that the product of the reaction of $FeNO(S_2CNR_2)_2$ with NO is not the $Fe(NO)_2(S_2CNR_2)_2$ originally claimed, but rather $FeNO(NO_2)(S_2CNR_2)_2$. This product results from NO_2 impurity which is often present in old pressurized metal containers of NO. It is likely that the purported $Fe(NO)_2(SacSac)_2$, prepared similarly, is really a nitro nitrosyl[77]. Being mixtures, these materials all exhibit two nitrosyl stretching frequencies, as would a dinitrosyl complex.

(c) Reductive nitrosylation

The unpaired electron on nitric oxide occupies a π^* orbital. As might be expected for an antibonding electron, ionization is a relatively facile process; NO has an ionization potential[78] of 9.26 eV. One might predict that NO could function as a stoichiometric reducing agent and this behavior has been observed[79].

$$NO + MF_6 \rightarrow NO^+MF_6^- \qquad M = Mo, Tc, Re, Ru, Os, Ir, Pt$$

Jackson et al.[80] studied the reaction of nitric oxide with alcoholic solutions of Co^{2+} in the presence of amines. In contrast to the behavior noted in Section B(i) for ammonia and primary amines, *p*-toluidine forms $Co(NO)_2$-(*p*-toluidine)$_2^+$ salts. This reaction was later rediscovered[81] under other circumstances, and an investigation of the stoichiometry proved that a proton acceptor (alkoxide or amine) is required but additional ligand is not. Since the group (Co^{2+} + 2NO) undergoes a one-electron reduction in the reaction, and since the reducing agent was identified as NO, the reaction was termed reductive nitrosylation.

$$CoCl_2 + 3NO + B + ROH \rightarrow \tfrac{1}{2}[Co(NO)_2Cl]_2 + BH^+ + RONO$$

The reaction also occurs with $FeCl_2$, and possibly NiI_2 (ref. 82).

$NiI_2 \rightarrow [NiNOI]_x + ?$

The conditions under which one gets simple replacement (i.e. $CoNOL_5^{2+}$) relative to reductive nitrosylation have been investigated[83].

The reaction of $Co(S_2PF_2)_2$ and nitric oxide produces[84] $Co(NO)_2$-(S_2PF_2). Although the fate of the second difluorodithiophosphate ligand was not determined, this reaction may represent reductive nitrosylation.

Cyclopentadienyl chromium dichloride reacts with NO to produce $CpCr(NO)_2Cl$. Nitric oxide is presumed to be the reducing agent in this reaction[85].

The higher halides of molybdenum and tungsten also undergo reductive nitrosylation under mild conditions in aprotic solvents[86–88]

$MoCl_5 + NO \rightarrow Mn(NO)_2Cl_2 + 3NOCl$
$MoCl_4(CH_3CN)_2 \rightarrow Mo(NO)_2Cl_2(CH_3CN)_2 + 2NOCl$
$WCl_6 \rightarrow W(NO)_2Cl_2$

These reactions bear a striking similarity to the carbonylation[89] of $RhCl_3$

$RhCl_3 + CO \rightarrow [Rh(CO)_2Cl]_2 + COCl_2$

Finally, chloroferric tetraphenylporphyrin reversibly forms a weak *adduct* with NO in aprotic solvents; addition of alcohol precipitates the product of reductive nitrosylation[90], FeNO(TPP). MnCl(TPP) undergoes the same transformation. In contrast with the iron case, where nitrogenous base is not required, MnCl(TPP) is only reduced upon addition of base and the six-coordinate complex MnNO(TPP)(base) results. The manganese complex contains a linear nitrosyl group[11,91]. Fe^{III} hemoglobin likewise undergoes reductive nitrosylation in aqueous solution[92].

Two groups have independently reported the ability of NO to replace carbon monoxide and one halogen in a reaction which appears to qualify as reductive nitrosylation[32,93].

$(\pi\text{-allyl})Fe(CO)_2LX \rightarrow (\pi\text{-allyl})Fe(CO)_2NO \qquad L = CO, PPh_3$

Although the reaction solvent is not mentioned, it is probable that it was a hydrocarbon. In this case NOX is probable as the oxidized product. It is then remarkable that the product complex is stable to nitrosyl halide.

An extremely brief report[94] describes an apparently general method of forming metal nitrosyls. Nitric oxide is passed through a hot suspension of the hydrated metal oxide in aqueous HCl. A heterogeneous system is claimed to be essential, there being no reaction with soluble chloro complexes. Thus, if the hydrated metal oxide is soluble in aqueous HCl, a mixture of NO and HCl gases is passed through an ethanolic suspension of the hydrated metal oxide. It is suggested that a disproportionastion of NO to NO^+ and NO^- is involved, indicating that this may actually be a reductive nitrosylation. Metals employed are Re^{IV}, Mo^{IV}, Pd^{IV}, Mn^{IV}, V^{IV} and Co^{III}.

(ii) NO^+

The salts of NO^+X^- (X being a non-coordinating anion such as BF_4^-, PF_6^- or HSO_4^-) provide a source of NO^+, the nitrogen oxide isoelectronic with carbon monoxide. The physical properties of these salts, in particular their hydrolytic sensitivity, were enumerated early, and acetonitrile and nitromethane suggested as suitably passive solvents[95]. Acetone appears to react with these salts and, surprisingly, they are slightly soluble in benzene, producing colored solutions[96]. These latter solutions may contain charge transfer complexes.

Early applications of NO^+ salts to metal nitrosyl syntheses utilized alcohols as solvents; these workers were apparently unaware of the solvolysis reaction

$$NO^+ + ROH \rightleftharpoons RONO + H^+$$

which is actually a synthetic route to alkyl nitrites. Since this is an equilibrium reaction, it is possible that NO^+ may still be the reactive species even in alcohol. Alternatively (see Section B(viii)), RONO may effect the nitrosation. Care must be taken to consider possible reactions of the metal complex with H^+, however. For example, all of the following protonations occur with NO^+ in the presence of methanol.

$Rh[P(OMe)_3]_5^+ \rightarrow HRh[P(OMe)_3]_5^{2+}$ (ref. 97)
trans-$M(CO)_3(PPh_3)_2 \rightarrow HM(CO)_3L_2^+$ M = Ru, Os (refs. 98, 99)
$Cr(CO)_2(\phi CC\phi)(C_6Me_{6-n}H_n) \rightarrow HCr(CO)_2(\phi CC\phi)(C_6Me_{6-n}H_n)^+$ (ref. 100)
$CpIrCOL \rightarrow CpIr(CO)HL^+$ (ref. 101)

$Fe(CO)_3(PPh_3)_2$ is not protonated under these conditions[98,99] nor is CpMCOL where[101] M = Co, Rh. It has been suggested that this is indicative of increasing transition metal basicity down a group.

As with CO, NO^+ may react in two distinct ways: addition or substitution (NO^+ is assumed as a reagent throughout this section).

(a) Addition

$Rh(CNR)_4^+ \rightarrow RhNO(CNR)_4^{2+}$ (ref. 102)
$Rh(P\phi_3)_3Cl \rightarrow RhNO(P\phi_3)_3Cl^+$ (ref. 103)
$Rh(PPP)Cl \rightarrow Rh(PPP)_3NOCl^+$ (ref. 104)
$Ir(CO)ClL_2 \rightarrow IrNO(CO)ClL_2^+$ (ref. 105)
$RuNOClL_2 \rightarrow Ru(NO)_2ClL_2^+$ (ref. 106)

It is probably worth noting the formal similarity of these reactions to those involving the addition of CH_3^+ (via CH_3OSO_2F or Me_3O^+) to square planar complexes[107].

$$IrCOClL_2 + \text{"}CH_3^+\text{"} \rightarrow CH_3IrCOClL_2^+$$

(b) Substitution

A more common occurrence is ligand substitution by NO^+. Carbon monoxide is often the ligand replaced.

$Fe(CO)_3L_2 \xrightarrow{MeOH/\phi H} FeNO(CO)_2L_2^+$ L = PPh_3, $\frac{1}{2}$ dppe (refs. 98, 99)

$Fe(CO)_2[P(OMe)_3]_3 \rightarrow FeNO(CO)_2[P(OMe)_3]_2^+$ (refs. 98, 99)

$M(CO)_4(dppe) \xrightarrow[\text{or } CH_3CN]{MeOH/tol} MNO(CO)_3(dppe)^+$ M = Mo, W (refs. 108, 109)

$Cr(CO)_4(dppe) \xrightarrow[CH_3CN]{} Cr(NO)_2(CH_3CN)_4^{2+}$ (refs. 108, 109)

$Mo(CH_3CN)_3(CO)_3 \rightarrow$ *cis*-$Mo(NO)_2(CH_3CN)_4^{2+}$ (ref. 110)

$W(CH_3CN)_3(CO)_3 \rightarrow$ *cis*-$W(NO)_2CO(CH_3CN)_3^{2+}$ (ref. 110)

$IrNO(CO)L_2 \rightarrow Ir(NO)_2L_2^+$ (ref. 111)

$Ni(CO)_2L_2 \xrightarrow{MeOH} NiNO(CO)L_2^+$ (ref. 108)

$CoNO(CO)L_2 \xrightarrow{MeOH} Co(NO)_2L_2^+$ (ref. 108)

$W(CO)_5X^- \rightarrow WNO(CO)_4X$ (ref. 112)

The last reaction proceeds in only low yield for molybdenum pentacarbonyl halide anions, and fails for the chromium analog.

Phosphine substitution has also been observed.

$MNOL_3 \rightarrow M(NO)_2L_2^+$ M = Rh, Ir (ref. 111)

In contrast to the reaction of NO^+ with $IrCOClL_2$[105], nitrogen is displaced from IrN_2ClL_2.

$IrN_2ClL_2 \rightarrow IrNOClL_2^+ + N_2$ (ref. 113)

In the presence of coordinated cycloolefins, NO^+ may replace the hydrocarbon

$(toluene)Cr(CO)_3 \xrightarrow{MeCN}$ *trans*-$Cr(NO)_2(MeCN)_4^{2+}$ (ref. 114)

or leave it intact.

$CpM(CO)_3 \rightarrow CpMNO(CO)_2^+$ M = Mn, Re (refs. 114, 115)

$CpM(CO)L \xrightarrow{MeOH} CpMNOL^+$ M = Co, Rh (ref. 101)

$(C_6Me_{6-n}H_n)Cr(CO)_2L \xrightarrow{MeOH} (C_6Me_{6-n}H_n)CrNO(CO)L^+$, $n = 0$—3 (ref. 100)

$R_4C_4Fe(CO)_3 \rightarrow F_4C_4Fe(CO)_2NO^+$ (ref. 116)

The effect of NO^+ on metal clusters has been little studied. Disruption of the cluster has been observed.

$Ru_3(CO)_9(PPh_3)_3 \xrightarrow{CH_2Cl_2/Et_2O} RuNO(CO)_2(PPh_3)_2^+$ (refs. 98, 117)

$Os_3(CO)_9(PPh_3)_3$ fails to produce cationic nitrosyls on treatment with NO^+; only cationic carbonyls are produced. In acetonitrile, both the ruthenium and osmium species give carbonyls; the reaction is thus critically solvent dependent[117].

Some warning must be added to this consideration of NO^+ as a nitrosylating reagent. NO^+ in many instances functions simply as a one-electron oxidizing agent. The reduced form of NO^+ is listed if it was determined.

$M_2(CO)_{10} \xrightarrow{MeCN} M(CO)_5(MeCN)^+$ (ref. 114)

$Cu^0 \xrightarrow{MeCN} Cu(MeCN)_4^{2+} + 2NO$ (ref. 118)

$M^0 \xrightarrow{MeCN} M(MeCN)_{4,6}^{2+} + 2NO$ M = Mn, Fe, Co, Ni, Zn (ref. 119)

$Pd^0 \xrightarrow{MeCN} Pd(MeCN)_4^{2+}$ (ref. 120)

$Ni^{II}(N_4) \xrightarrow{CH_3CN} Ni^{III}(N_4) + NO$ (ref. 121)

$Co^{II} \xrightarrow{CH_3CN} Co^{III}(CH_3CN)_2$ (ref. 121)

$Ag^{II}N_4 \rightarrow Ag^{III}N_4$ (ref. 122)

$Mn(CO)_3L_2Br \xrightarrow{C_6H_6} Mn(CO)_3L_2Br^+ + NO$ (ref. 97)

cis-$M(CO)_2(dppe) \xrightarrow{CH_2Cl_2}$ *trans*-$M(CO)_2(dppe)_2^+$ M = Cr, Mo, W (refs. 97, 108)

trans- or *cis*-$Mo(CO)_2(dppe)_2^+ \xrightarrow{MeNO_2}$ *cis*-$Mo(CO)_2(dppe)_2^{2+}$ (ref. 97)

$[CpFe(CO)_2]_2 \xrightarrow{CH_2Cl_2} CpFe(CO)_3^+$ (ref. 97)

$Pt(PPh_3)_4 \rightarrow Pt(PPh_3)_4^{2+}$ (ref. 97)

$Cr(CO)_4dppe \xrightarrow[toluene]{MeOH} Cr(CO)_4dppe^+$ (refs. 108, 109)

$Cp_2Fe \xrightarrow{CH_3CN} Cp_2Fe^+$ (ref. 101)

$[CpFeCO(SCH_3)]_2 \xrightarrow{CH_3CN} [CpFeCO(SCH_3)]_2^+$ (ref. 101)

Finally, halogen abstraction has been observed in acetonitrile[101].

$CpFe(CO)_2I \rightarrow CpFe(CO)_2(MeCN)^+$

$Cp_2VCl_2 \rightarrow Cp_2V(MeCN)_2^{2+}$

$Mn(CO)_5Br \rightarrow Mn(CO)_5(MeCN)^+$

Although the nitrogen containing product has not been identified (NOX?), the reaction bears a striking similarity to halogen abstraction by alkylating agents such[123] as Me_3O^+ or $MeOSO_2F$.

$$MCl \xrightarrow[R^+]{solv} M(solv)^+ + RCl$$

(iii) NOX

The covalent nitrosyl halides NOX generally react by simple oxidative addition in spite of the fact that they exist as part of the following equilibrium.

$$2NOX \rightleftharpoons 2NO + X_2$$

Several possible examples of oxidative addition by elemental halogen have been reported in reactions with NOX. (NOX is assumed as a reagent throughout this section).

$(HBpz_3)M(NO)_2Cl$	$\rightarrow$	$(HBpz_3)MNOCl_2$		(ref. 124)
RuH_4L_3	$\rightarrow$	$RuNOCl_3L_2$		(ref. 28)
$M(CO)_{6-x}(PPh_3)_x$	$\rightarrow$	$MNOCl_3(OPPh_3)_2$	$x = 2, 3$; M = Mo, W	(ref. 134)
$Mo(CO)_3(PPh_3)_2Cl_2$	$\rightarrow$	$MoNOCl_3(OPPh_3)_2$		(ref. 134)

Oxidative addition may occur to coordinatively unsaturated substrates.

$[(COD)RhX]_2$	$\rightarrow$	$[Rh(NO)X_2]_n$		(ref. 125)
$[(COD)IrCl]_2$	$\rightarrow$	$(COD)Ir(NO)Cl_2$		(ref. 125)
$RuCl_2L_4$	$\rightarrow$	$RuNOCl_3L_2$		(ref. 126)
PtX_4^{2-}	$\rightarrow$	$PtNOX_4Cl^{2-}$	X = Cl, NO_2, CN	(ref. 127)
$Rh(NO_2)COL_2$	$\rightarrow$	$RhNO(NO_2)ClL_2$		(ref. 60)
PtL_4^{2+}	$\rightarrow$	$PtNOL_4Cl^{2+}$	L = NH_3, $\frac{1}{2}$ en	(ref. 127)

When reaction occurs with coordinatively saturated complexes, each NOX added displaces ligands equivalent to four electrons.

$Ni(CO)_4$	$\xrightarrow{HCl}$	$Ni(NO)_2Cl_2$		(ref. 128)
$Ni(CO)_4$	$\rightarrow$	$NiNOX_2$		(ref. 129)
$Ni(PPh_3)_4$	$\rightarrow$	$Ni(NO)Cl(PPh_3)_2$		(ref. 130)
$Ni(COD)_2$	$\xrightarrow[(2)\ dppe]{(1)\ NOCl}$	Ni(NO)Cl(dppe)		(ref. 130)
$M(CO)_6$	$\rightarrow$	$[M(NO)_2Cl_2]_n$	M = Mo, W	(ref. 131)
$M(CO)_3(CH_3CN)_3$	$\xrightarrow[(2)\ L]{(1)\ NOCl}$	$M(CO)_2(NO)LCl$, $MCO(CH_3CN)NOL_2Cl$		(ref. 132)
$W(CO)_2NO(bipy)Cl$	$\rightarrow$	$W(NO)_2Cl_2(bipy)$		(ref. 132)
$Mo(CO)_4L_2$	$\rightarrow$	$Mo(NO)_2L_2Br_2$		(ref. 133)
$[M(CO)_4Cl_2]_2$	$\rightarrow$	$[MNOCl_3]_n$		(ref. 134)
$CoNO(CO)_3$	$\rightarrow$	$[Co(NO)_2Br]_2$		(ref. 135)
$[Re(CO)_4Cl_2$	$\xrightarrow{HCl}$	$[ReNO(CO)_2Cl_2]_2$		(ref. 136)
$Re(CO)_4LCl$	$\rightarrow$	$ReNO(CO)_2LCl_2$		(ref. 136)
$Re(CO)_3L_2Cl$	$\rightarrow$	$ReNO(CO)_2LCl_2$		(ref. 136)
$[CpRu(CO)_2]_2$	$\rightarrow$	$CpRuNOCl_2$		(ref. 137)
$(HBpz_3)M(CO)_2(N_2Ph)$	$\rightarrow$	$(HBpz_3)MNO(N_2Ph)Cl$	M = Mo, W	(ref. 138)
$CpMo(CO)_2(N_2Ph)$	$\rightarrow$	$CpMoNO(N_2Ph)Cl$		(ref. 138)
$(HBpz_3)MNO(CO)_2$	$\rightarrow$	$(HBpz_3)M(NO)_2Cl$	M = Mo, W	(ref. 124)

Under certain circumstances the halide of NOX does not coordinate; formally, then, NO^+ has been added and only one CO is replaced.

$Fe(CO)_5$	$\xrightarrow{HCl}$	$Fe(NO)(CO)_3^+$	(ref. 139)
$Fe(CO)_3L_2$	$\rightarrow$	$FeNO(CO)_2L_2^+$	(ref. 140)
$(RBpz_3)Mo(CO)_3^-$	$\rightarrow$	$(RBpz_3)Mo(CO)_2NO$	(ref. 124)

Nitrosyl chloride, under pressure or at 1 atm, converts $Fe(CO)_5$ to $Fe(NO)_2(CO)_2$ in respectable yield. The reaction must be run under conditions deficient in NOCl, necessitating separation of $Fe(NO)_2(CO)_2$ from unreacted $Fe(CO)_5$. If the reaction is performed stoichiometrically, the yield of $Fe(NO)_2(CO)_2$ declines to near zero. The fate of the chlorine ($COCl_2$, $FeCl_3$?) was not reported[141].

Connelly[142] makes reference to the fact NOCl almost always displaces the hydrocarbon moiety from olefin complexes (e.g. $C_8H_8Fe(CO)_3$). This is consistent with the decreased stability of olefin complexes of metals in higher oxidation states.

Cyano complexes appear to be simply oxidized, NOCl functioning as a one-electron oxidant[143].

$Fe(CN)_6^{4-}$	$\xrightarrow{DMF}$	$Fe(CN)_6^{3-}$
$Ni_2(CN)_6^{4-}$	$\xrightarrow{DMF}$	$Ni(CN)_2$
$K_2Mo^{III}(CN)_5$	$\rightarrow$	$K_3Mo^{III}Mo^{IV}(CN)_{10}$
$K_2Mn^{II}[Mn^{II}(CN)_6]$	$\rightarrow$	$KMn^{II}[Mn^{III}(CN)_6]$
$K_3Mn^{III}(CN)_6$	$\rightarrow$	$K_2Mn^{IV}(CN)_6$

Nitrosyl chloride oxidized $MX_2(PR_3)_2$ complexes of cobalt and nickel to $MX_3(PR_3)_2$, this being one of the few routes to phosphine complexes[144] of Ni^{III}.

(iv) N-nitrosoamides

N-nitrosoamides such as *N*-methyl-*N*-nitrosourea and *N*-methyl-*N*-nitroso-*p*-toluene sulfonamide react with a variety of metal hydrides to produce metal nitrosyls and, presumably, the parent amide. This reaction replaces a hydrogen atom (formally a one-electron donor) by the nitrosyl group. Although this might be expected to produce a bent nitrosyl complex, it is consistently found that extrusion of a two-electron donor ligand accompanies this reaction. Linear nitrosyl complexes result. For example, the original synthesis of $Mn(CO)_4NO$ involves CO displacement.

$HMn(CO)_5$	$\rightarrow$	$M(CO)_4NC + CO$	(ref. 5)

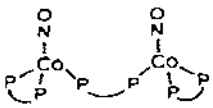
Other examples abound (nitroso sulfonamide RNO is assumed as a reagent).

$HMoCp(CO)_3$	$\rightarrow$	$MoCp(CO)_2NO + CO$		(ref. 145)
$HMCl_2L_3$	$\rightarrow$	$M(NO)Cl_2L_2 + L$	M = Rh, Ir	(ref. 146)
$HRhL_4$	$\rightarrow$	$RhNOL_3 + L$		(ref. 147)
$HRuL_4^+$	$\rightarrow$	$Ru(NO)_2L_2 + 2L$		(ref. 148)
H_2RuL_4	$\rightarrow$	$Ru(NO)_2L_2 + 2L$		(ref. 147)
$HMCl(CO)L_3$	$\rightarrow$	$MNOCl(CO)L_2 + L$	M = Ru, Os	(ref. 149)
$HIrCOL_3$	$\rightarrow$	$Ir(NO)COL_2 + L$		(ref. 150)
$HIr(NO)L_3^+$	$\rightarrow$	$Ir(NO)_2L_2^+ + L$		(ref. 151)
$HFeCl(dppe)_2$	$\rightarrow$	$FeNO(dppe)_2^+ + Cl^-$		(ref. 152)
$H_3Co(PPh_3)_3$	$\rightarrow$	$CoNO(PPh_3)_3 + H_2$		(ref. 153)

The last reaction is unique as an example of the elimination of molecular hydrogen subsequent to NO/H interchange.

H_3IrL_2 reacts with RNO in the presence of NO to produce the dimer $[Ir(NO)_2L]_2$. The nitric oxide oxidizes phosphine liberated in the reaction. In its absence, half of the iridium is found[57] as $IrNOL_3$

In an attempt to inhibit ligand extrusion, and thereby produce a bent nitrosyl complex, $HCo(dppe)_2$ was reacted with the nitrososulfonamide. It was anticipated that the chelate effect would prevent dissociation of phosphine. The reaction actually produces $Co_2(NO)_2(dppe)_3$ in high yield. The structure of this dimer was established to be that shown below using ^{31}P NMR[153].



The only reaction in which ligand extrusion is not observed involves a tricyclohexylphosphine (PCy_3) complex.

$$HRuCl(CO)(PCy_3)_2 \rightarrow Ru(NO)Cl(CO)(PCy_3)_2$$

Here it is the reagent hydride complex which is unusual (PPh_3 forms $HRuCl(CO)(PPh_3)_3$); coordinative unsaturation of the PCy_3 complex presumably results from the steric constraints of the bulky phosphine[117].

Nothing is presently known about the mechanism of this reaction. One can envision coordination of the nitroso compound (RNO) on a coordinatively unsaturated species.

$$HML_n \rightleftharpoons HML_{n-1} + L$$
$$HML_{n-1} + RNO \rightarrow [HM(RNO)L_{n-1}] \rightarrow MNOL_{n-1} + RH$$

or a four-center transition state with ligand elimination as a subsequent step.

$$HML_n + RNO \rightarrow \begin{matrix} H - ML_n \\ \vdots \quad\ \vdots \\ R - NO \end{matrix}$$

Evidence for the first mechanism comes from the observation that the nitrosoamide reacts readily with $OsHCl(CO)L_3$, while the relatively substitution-inert $OsHCl(CO)_2L_2$ does not react[151].

In a related but nevertheless distinct reaction, $Pt(PPh_3)_4$ reacts with CF_3NO by what is apparently oxidative addition to give $Pt(PPh_3)_2(CF_3)(NO)$ (ref. 54). Nitrosobenzene, however, reacts with $PdCl_2(\phi CN)_2$ to produce a rare example of intact, coordinated nitrosobenzene, $PdCl_2(\phi NO)_2$ (ref. 154)

(v) Coordinated NO

A reaction of substantial synthetic utility developed out of the observation that $CoCH_3(DMG)_2$, where DMG is the monoanion of dimethylglyoxime, will transfer a methyl group to square planar Co^{II} complexes. The complexes CoNO(tet), where tet represents a Schiff base or porphyrin, have been characterized structurally as square-based pyramids with apical bent nitrosyl groups. The nitrosyl—cobalt bond is mainly sigma in character as is the methyl—cobalt bond. $CoNO(DMG)_2$, which has excellent solubility characteristics, has been found to transfer NO to a variety of metal complexes[155].

Two general types of behavior can occur. "Simple nitrosyl transfer" describes the transfer of NO from $CoNO(DMG)_2$.

$$CoNO(DMG)_2 + ML_n \rightarrow Co(DMG)_2 + MNOL_n$$

Since Co^{II} is a potential halogen acceptor, halogen transfer is a possible secondary reaction. In this case, the net reaction is formally "NO/halogen interchange", or a type of redistribution reaction.

$$CoNO(DMG)_2 + MClL_n \rightarrow CoCl(DMG)_2 + MNOL_n$$

In an attempt to detect simple nitrosyl transfer, $CoCl_2L_2$ was chosen as substrate. The observed reaction is

$$2CoNO(DMG)_2 + CoCl_2L_2 \rightarrow Co(NO)_2L_2^+Cl^- + Co(DMG)_2 + CoCl(DMG)_2$$

$CoNOCl_2L_2$, if it is produced at all, evidently reacts even faster than $CoCl_2L_2$ with $CoNO(DMG)_2$. This was verified independently[155].

$$CoNO(DMG)_2 + CoNOCl_2L_2 \rightarrow Co(NO)_2L_2^+Cl^- + CoCl(DMG)_2$$

Nitrosyl halogen interchange occurs as follows.

$$CoNO(DMG)_2 + NiCl_2L_2 \rightarrow NiNOClL_2 + CoCl(DMG)_2 \quad \text{(ref. 155)}$$
$$CoNO(DMG)_2 + RhL_3Cl \rightarrow RhNOL_3 + CoCl(DMG)_2 \quad \text{(ref. 153)}$$
$$CoNO(DMG)_2 + RuL_3Cl_2 \rightarrow RuNOClL_2 + CoCl(DMG)_2L \quad \text{(ref. 153)}$$

In the latter two reactions a characteristic of $CoCl(DMG)_2$ manifests itself. This complex can halogenate low-valent nitrosyl complexes. The following reaction was verified independently.

$$RhNOL_3 + 2CoCl(DMG)L \rightarrow RhNOCl_2L_2 + 2Co(DMG)_2L + L \quad \text{(ref. 153)}$$

Thus nitrosyl halogen interchange may produce, in a stoichiometric fashion, a mixture of metal ntirosyls.

$$RhL_3Cl + CoNO(DMG)_2 \rightarrow \tfrac{1}{2}\, RhNOL_3 + \tfrac{1}{2}\, RhNOCl_2L_2 + Co(DMG)_2$$
$$RuL_3Cl_2 + CoNO(DMG)_2 \rightarrow \tfrac{1}{2}\, RuNOClL_2 + \tfrac{1}{2}\, RuNOCl_3L_2 + Co(DMG)_2$$

The following examples show that nitrosyl transfer reactions are not limited to $CoNO(DMG)_2$.

$$M(NO)_2L_2 + ML_3X_2 \rightarrow 2M(NO)XL_2 \quad M = Ru, Os \quad \text{(ref. 71b)}$$
$$Co(NO)(NH_3)_5^{2+} + M_{aq}^{2+} \rightarrow (MNO)_{aq}^{2+} + Co^{2+} \quad M = Cr, Fe \quad \text{(ref. 156)}$$

The limitations of nitrosyl transfer reactions are presently unknown. We have unsuccessfully attempted to produce a copper nitrosyl from $CuClL_3$ and

$CoNO(DMG)_2$. It might tentatively be concluded from the above reactions that coordinative unsaturation is required of the nitrosyl acceptor, but this is yet untested.

Several of these reactions appear to be clean enough for kinetic studies. In view of the isoelectronic relationship of cobalt nitrosyls and iron dioxygen complexes[9] and the structurally characterized oxygen bridge in $(H_3N)_5Co(O_2)Co(NH_3)_5^{5+}$, it is possible that nitrosyl transfer occurs through the terminal

oxygen. An isonitrosyl would then be the initial product; rearrangement to the nitrosyl would follow in a manner analogous to that observed for cyanide-mediated electron transfer[157].

$$(DMG)_2Co{-}N{=}O{\rightarrow}ML_n \rightarrow Co(DMG)_2 + NO{\rightarrow}ML_n$$

An analogous mechanism has been postulated for nitrosyl-mediated electron transfer from $CoNO(en)_2H_2O^{2+}$ to[158] $Cr(H_2O)_6^{2+}$.

$CoNO(SacSac)_2$, where SacSac is dithioacetylacetonate, spontaneously "disproportionates" at room temperature in solution, undergoing transfer of both the nitrosyl and SacSac to produce equimolar $Co(SacSac)_3$ and[9] $Co(NO)_2(SacSac)$.

Triphenyl phosphine reacts with $[CpFeNO]_2$ to produce $Fe(NO)_2(PPh)_2$ in 78% yield according to the following reaction[40].

$$[CpFeNO]_2 + 2PPh_3 \rightarrow Fe(NO)_2(PPh_3)_2 + \text{"}FeCp_2\text{"}$$

Ferrocene was not actually an observed product; only polymeric material was formed. This reaction barely qualifies as nitrosyl transfer, however, since $[CpFeNO]_2$ contains symmetrically bridging nitrosyl groups[40].

Phosphine substitution may also promote nitrosyl transfer in isolated instances

$$Hg[FeNO(CO)_3]_2 + P(NMe_2)_3 \rightarrow Fe(NO)_2[P(NMe_2)_3]_2 + \tfrac{1}{n}[HgFe(CO)_4]_n + 2CO$$

This overall reaction may only be an expression of the tendency of $Hg[FeNO(CO)_3]_2$ itself to undergo nitrosyl transfer on heating[159]

$$Hg[FeNO(CO)_3]_2 \rightarrow Fe(NO)_2(CO)_2 + HgFe(CO)_4$$

Brief mention is also given to the following reaction.

$$FeNO(CO)_2(PPh_3)_2^+ + PEt_3 \rightarrow Fe(NO)_2(PEt_3)_2 + Fe(CO)_3(PEt_3)_2 \quad \text{(ref. 99)}$$

Transfer of the nitrosyl group has been observed to occur during oxidative addition.

$$2MnNO(CO)_3L + \tfrac{3}{2} I_2 \rightarrow Mn(NO)_2L_2I + MnI_2 + 6CO \quad \text{(ref. 23)}$$

$CoNO(CO)_3 + CF_2Br_2 \rightarrow [Co(NO)_2Br]_2 + [Co(CO)_3CF_2]_2 + CoBr_2 + C_2F_4 + NO + NOBr + CO$ (ref. 135)

$CoNOL_3 + CH_2Cl_2 \rightarrow Co(NO)_2L_2^+$ (ref. 160)

(vi) NH_2OH

The redox chemistry of hydroxylamine is complex and varied. Depending upon the *p*H, NH_3, NH_4^+, N_2 or N_2O may be produced[161]. The use of hydroxylamine in the synthesis of metal nitrosyls, which has been neglected in recent times, utilizes hydroxylamine in the basic solution. The net transformation is replacement of X^- by NO^-. The main application has been to cyano complexes (NH_2OH and OH^- are assumed reagents throughout this section).

$Ni(CN)_4^{2-} \rightarrow NiNO(CN)_3^{2-}$ (ref. 162)

$Cr(CN)_6^{3-} + 2NH_2OH \rightarrow CrNO(CN)_5^{3-} + NH_3 + HCN + H_2O$ (ref. 163)

$CrO_3 + CN^- \rightarrow CrNO(CN)_5^{3-}$ (ref. 164)

$Mn(CN)_6^{3-} \rightarrow MnNO(CN)_5^{3-}$ (ref. 165)

Molybdate, cyanide and base react with hydroxylamine to yield $MoNO(CN)_5^{4-}$ salts[166]. The conflicting reports concerning the constitution of this anion were settled crystallographically. The complex is also accessible directly from $Mo(CN)_6^{4-}$ (ref. 167). Ammonium vanadate (NH_4VO_3), cyanide and base react with hydroxylamine to produce a vanadium nitrosyl, originally formulated erroneously as $VNO(CN)_5^{5-}$. This has now been characterized structurally[168] as $VNO(CN)_5^{3-}$. When this reaction is performed under H_2S, the product is claimed to be $K_4V(CN)_6NO \cdot H_2O$; although the CN and NO stretching frequencies closely resemble those of $VNO(CN)_5^{3-}$, the cell constants differ and the compound is diamagnetic[169]. Nitroprusside, $FeNO(CN)_5^{2-}$, the best known cyano nitrosyl, has not been produced in this way, presumably owing to the lack of a suitable precursor cyano complex.

The procedure is not limited to cyano complexes.

$Co(CNR)_5X + 2NH_2OH \xrightarrow{OH^-} CoNO(CNR)_3 + 2CNR + H_2O + NH_4X$ (ref. 170)

$Fe(CNR)_4X_2 + 4NH_2OH \rightarrow Fe(NO)_2(CNR)_2 + 2CNR + 2H_2O + 2NH_4X$ (ref. 170)

The source of the nitrosyl group in these reactions has been attributed to the following sequence of the purely formal reactions[162,170].

$$2NH_2OH \rightarrow NH_3 + NOH + H_2O$$
$$NOH \rightleftharpoons NO^- + H^+$$

Basic conditions are suggested to be required to displace the second reaction towards "NO^-". The production of NH_3 has been quantitated for the reaction of $Ni(CN)_4^{2-}$, proving that only half of the hydroxylamine nitrogen is converted to the nitrosyl group[162].

Further study of the generality and mechanism of this reaction is a potentially fertile area. One approach might be to examine reactions of coordinated hydroxylamine, although few such complexes have been characterized. One example, $Pt(NH_2OH)_4^{2+}$, is stable in basic solution and may be isolated as the hydroxide salt. It is actually made by reduction of Pt^{IV} with hydroxylamine in basic solution[171]. Here, however, the absence of a nitrosyl complex as product may reflect on the instability of nitrosyl complexes of Pt^{II}.

(vii) NO_2^-/H^+

The reaction which underlies this method is the following equilibrium.

$$NO_2^- + 2H^+ \rightleftharpoons H_2O + NO^+$$

In attempting to categorize reported nitrosylation reactions there is some difficulty in distinguishing reactions of the above type (attack of NO^+, generated by acidic solutions of nitrite salts, on metal complexes) from coordination of NO_2^- followed by oxide abstraction (Section C(i)). Godwin and Meyer have successfully distinguished between these (NO_2^-/H^+ is assumed as a reagent throughout this section) in the following reaction.

$$Ru(L_2)(H_2O)X^+ \rightarrow RuNO(L_2)X^{2+} \qquad L = o\text{-phen, bipy} \quad \text{(ref. 172)}$$

In this case, no anation by nitrite (in the absence of added H^+) is observed in one hour; the nitrosylation reaction, on the other hand, is instantaneous.

The equilibrium

$$PtNOL_4Cl^{2+} + H_2O \rightleftharpoons PtL_4^{2+} + HNO_2 + HCl$$

has been studied quantitatively for $L = NH_3, \frac{1}{2}$ en. K values from 10^{-5} to 10^{-6} indicate that an aqueous solution 2×10^{-2} M in the platinum nitrosyl and 0.2 M in H^+ is 15–20% hydrolyzed. These nitrosyl complexes generally dissolve in water with loss of NO and one chloride[173].

Other reactions of this type include the following.

$$K[FeNO(CO)_3] + KNO_2 + CO_2 + H_2O \rightarrow Fe(NO)_2(CO)_2 + 2KHCO_3 \quad \text{(ref. 174)}$$

$$Na[FeH(CO)_4] + 2NaNO_2 + 3CH_3CO_2H \rightarrow Fe(NO)_2(CO)_2 + 2CO + 3NaO_2CCH_3 + 2H_2O \quad \text{(ref. 175)}$$

$$K[Co(CO)_4] + NaNO_2 + 2CH_3CO_2H \rightarrow CoNO(CO)_3 + 2Na[K]O_2CCH_3 + H_2O \quad \text{(ref. 176)}$$

$$K[Co(CO)_4] + KNO_2 + 2CO_2 + 2H_2O \rightarrow CoNO(CO)_3 + 2KHCO_3 \quad \text{(ref. 175)}$$

$$Pt(NO_2)_2(NH_3)_2 \rightarrow Pt(NO)Cl(NO_2)_2(NH_3)_2 \quad \text{(ref. 177)}$$

$$CpMn(CO)_3 \rightarrow CpMnNO(CO)_2^+ \quad \text{(ref. 4)}$$

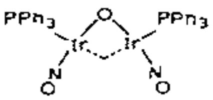
$$CpMo(CO)_3^- \rightarrow CpMoNO(CO)_2 \quad \text{(ref. 178)}$$

$$HW_2(CO)_{10}^- \rightarrow HW_2(CO)_9NO \quad \text{(ref. 179)}$$

$Ru(NH_3)_6^{2+}$ is unaffected by sodium nitrite, but nitrite and HCl produce[180] $RuNO(NH_3)_5^{3+}$. Although these observations provide evidence for attack on the metal complex by some form of the nitrous acid equilibrium mixture, some recent evidence suggests that oxidation to $Ru(NH_3)_6^{3+}$ may be the first step in this reaction[181]. Note that this product contrasts markedly with the superficially similar reaction[182] of NO_2^-/H^+ with $OsN_2(NH_3)_5^{2+}$ to produce $Os(N_2)_2(NH_3)_4^{2+}$.

Addition of aqueous $NaNO_2$ to a solution of $CpMn(CO)_2NO^+$ results in vigorous foaming. Ultraviolet irradiation of this solution produced a poorly soluble material of formula[178] $[CpMn(NO)_2]_n$. Both bridging and terminal nitrosyls are suggested in the infrared. Analogous treatment of $CpFe(CO)_3^+$ HCl_2^- gave an ill-defined nitrosyl complex[178].

$[IrNO(PPh_3)]_2O$ has been obtained from $IrCO(PPh_3)_2Cl$ and sodium nitrite in benzene/alcohol. The initial product was not isolated; reaction with oxygen yields the observed product, whose structure provides firm evidence



for a metal—metal bond. A complete understanding of this unusual reaction awaits publication of full experimental details[183].

Finally, there is the preparation of Roussin's black salt, which involves NO_2^- under acidic conditions. Only a ninteenth century German chemist of the classic mould would have the fortitude to conceive of (or attempt to balance) such a reaction.

$$52FeSO_4\cdot 7H_2O + 42NaNO_2 + 34(NH_4)_2S + 42H_2O \rightarrow 6NH_4[Fe_4S_3(NO)_7] + 28Fe(OH)_3 + 16S + 21Na_2SO_4 + 31(NH_4)_2SO_4 \quad \text{(ref. 184)}$$

(viii) RONO

As noted (Section B(ii)), reactions with NO^+ in protic solvents are linked by the following equilibrium to reactions of alkyl nitrites.

$$RONO + H^+ \rightleftharpoons NO^+ + ROH$$

The following reaction was carried out by adding the metal complex to a solution of isopentyl nitrite and HPF_6 in benzene/methanol.

$$Fe(CO)_3(PPh_3)_2 \rightarrow FeNO(CO)_2(PPh_3)_2^+ \quad \text{(ref. 99)}$$

Reaction of alcoholic solutions of metal halides with phosphines and *n*-pentyl nitrite produce nitrosyls, possibly via hydride intermediates.

M^{III}	$\rightarrow$	$MNOCl_3L_2$	M = Ru, Os	(ref. 185)
M^{III}	$\rightarrow$	$MNOCl_2L_2$	M = Rh, Ir	(ref. 186)

Some applications of alkyl nitrites in aprotic solvents have been noted.

$[Mn(CO)_4PPh_3]_2$	$\rightarrow$	$MnNO(CO)_3PPh_3$	(ref. 23)
$(HBpz_3)Cr(CO)_3^-$	$\xrightarrow{DMF}$	$(HBpz_3)CrNO(CO)_2$	(ref. 124)

Trifluoroacetyl nitrite converts $CpMo(CO)_3^-$ into $CpMo(CO)_2NO$ in 10% yield[178].

(ix) HNO₃

After executing the synthesis of a transition metal complex, especially one containing a low-valent metal, one has a natural aversion to performing a subsequent "reaction" in concentrated nitric acid. In fact one seldom thinks of this except as a mode of decomposing the complex in preparation for some wet chemical analysis. Nevertheless, nitric acid has sometimes been employed in introducing the nitrosyl group. The identity of the nitrosating agent in concentrated nitric acid remains obscure. Some of the following have the appearance of oxidative addition by $NO^+NO_3^-$.

$M(NO_2)_4^{2-}$	$\rightarrow$	$MNO(NO_2)_4NO_3^{2-}$	M = Pt, Pd	(refs. 187, 188)
$Pt(NO_2)_2(NH_3)_2$	$\rightarrow$	$PtNO(NO_2)_2(NH_3)_2NO_3$		(ref. 187)
$Pt(NO_2)_2en$	$\rightarrow$	$PtNO(NO_2)_2(en)(NO_3)$		(ref. 187)
$Pt(en)_2^{2+}$	$\rightarrow$	$PtNO(en)_2(NO_3)^{2+}$		(ref. 187)
$M(CN)_6^{4-}$	$\rightarrow$	$MNO(CN)_5^{2-}$	M = Fe, Ru, Os	(ref. 189)
ReH_3L_4	$\rightarrow$	$Re(NO)_2L_2(NO_3)_2$		(ref. 190)
$IrBr_6^{2-}$	$\rightarrow$	$IrNOBr_5^-$		(ref. 191)

This is the method of choice for producing nitroprusside.

Generally, the reaction is useful only for producing nitrosyl complexes of metals in their highest oxidation state for obvious reasons. However, $CpMnNO(CO)_2^+$ has been made in low yield from the reaction of $CpMn(CO)_3$ with nitric acid[192].

The unit $RuNO^{3+}$ is formed by the action of HCl and HNO_3 on[193] RuO_4. However, boiling $Ru(NH_3)_6^{2+}$ in concentrated nitric acid produces $Ru(NH_3)_6$-$(NO_3)_3$ and not a nitrosyl complex[180].

It is consistently claimed that ruthenium displays an extraordinary affinity for the nitrosyl group. For example[193], "ruthenium is unique in that it forms more nitrosyl complexes than any other element". "The Ru(NO) group is extraordinarily stable, ... and it is exceedingly difficult to break the ruthenium—nitrosyl bond by normal chemical substitution or oxidation—reduction methods". As the nitrosyl chemistry of other metals develops, these statements appear to pale. The large number of ruthenium nitrosyl complexes reflects more on effort expended (ruthenium is a fission product) than on stability. The majority of complexes are of the form $RuNO(base)_2Cl_3$ and their number is based in part on the variety of bases employed. An equally lengthy list of complexes of form $NiNOCl(base)_2$ could be compiled. If one chooses to judge the affinity of Ru for NO on the basis of the rate of reaction of

"$RuCl_3 \cdot 3H_2O$" with NO in ethanol, then ruthenium is unexceptional. Co^{II} reacts much more rapidly.

There is a claim[194] that $CpMo(CO)_3NH_3^+$ reacts with sodium nitrate and HCl to produce $CpMo(NO)_2Cl$ in low yield. However, in view of the fact that this was an attempt to produce the dinitrogen complex $CpMo(CO)_3N_2^+$, the report may be a misprint, sodium *nitrite* being the reagent.

C. REACTIONS OF COORDINATED LIGANDS

In this category we place all transformations of coordinated ligands which product the MNO moiety. The preponderant reaction of this type involves oxygen abstraction from coordinated NO_2, either as oxygen atoms (Section C(ii)) or as oxide ion (Section C(i)). One instance is reported where coordinated nitrate is converted to coordinated nitrosyl, but there are no cases where other nitrogenous ligands (N_2, N_3, N_2O, NH_2OH) undergo this transformation. There exists one example which may involve conversion of coordinated ammonia to a nitrosyl group (Section C(iii)).

(i) Oxide ion abstraction

The general transformation considered in this section is the following

$$M(NO_2)^n + H^+ \rightarrow MNO^{n+2} + OH^-$$

The nitro—nitrosyl interconversion has been thoroughly studied for amine complexes of[195] $RuNO_x$:

$$cis\text{-}Ru(NO_2)(L_2)X \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} cis\text{-}RuNO(L_2)X^{2+} \qquad L = o\text{-phen, bipy}$$

The reversibility of this reaction was established and an equilibrium constant measured for $RuNO(bipy)_2Cl^{2+}$. Oxide ion could also be removed with $SnCl_4$ and BF_3, demonstrating that nitro—nitrosyl interconversion can also be effected under aprotic conditions. Nitroprusside is similarly obtainable[196].

$$Fe(NO_2)(CN)_5^{4-} \rightarrow FeNO(CN)_5^{2-}$$

The following reactions exemplify this method

$$K_2IrBr_4(NO_2) \xrightarrow{HBr} KIrNOBr_5 \qquad \text{(ref. 191)}$$

$$Pt(NO_2)_2L_2 \xrightarrow[0-5^\circ C]{HCl} PtNO(NO_2)Cl_2L_2 \qquad L = NH_3, NH_2Me, \text{en} \qquad \text{(refs. 197, 198)}$$

$$cis\text{-}PtCl(NO_2)(NH_3)_2 \xrightarrow[0-5^\circ C]{} PtNO(NH_3)_2Cl_3 \qquad \text{(ref. 197)}$$

$$Pt(NO_2)_4^{2-} \xrightarrow[0^\circ C]{HCl} PtNOCl_2(NO_2)_3^{2-} \qquad \text{(ref. 198)}$$

Interestingly, both nitro and nitrito linkage isomers react with acid to produce ruthenium nitrosyls. A kinetic study of the reaction with the nitrito complex might produce evidence for an isonitrosyl intermediate.

$$Ru{-}O{-}N{-}O \xrightarrow{H^+} OH^- + Ru{-}ON^{2+} \rightarrow RuNO^{2+} \qquad \text{(ref. 199)}$$

Reed and Roper have reported the related interconversion of an alkyl nitrite complex.

$$IrNOL_2Cl_3^+ + ROH \rightleftharpoons Ir(RONO)L_2Cl_3 + H^+$$

The mode of coordination of the alkyl nitrite ligand is unknown and therefore the mechanistic details of alkoxide removal remain to be explored[200].

(ii) Oxygen atom abstraction

Carbon monoxide liberated from $Fe(CO)_5$ reduces nitrite and nitrosyl in the preparation of $FeNO(CO)_3^-$.

$$Fe(CO)_5 + KNO_2 \rightarrow K^+FeNO(CO)_3^- + CO + CO_2 \qquad \text{(refs. 201, 202)}$$

Gaseous carbon monoxide is reported to reduce nitrite and nitrate coordinated to nickel.

$$\textit{trans}\text{-}Ni(NO_2)_2L_2 \rightarrow NiNO(NO_2)L_2 \qquad \text{(ref. 59)}$$
$$Ni(NO_3)_2L_2 \rightarrow NiNO(NO_3)L_2 \qquad \text{(ref. 59)}$$

The nitrate complex with L = PEt_3 is tetrahedral, indicating that stereochemistry is not a determining factor in this reaction. The reaction proceeds under very mild conditions (25°C, 1 atm·CO).

Phosphine is oxidized to phosphine oxide as nitrite is reduced to the nitrosyl group in a remarkably clean reaction[203].

$$NiX_2(PPh_3)_2 + NaNO_2 + 2PPh_3 \rightarrow NiNOX(PPh_3)_2 + 2OPPh_3 + NaX$$

This reaction occurs only in tetrahydrofuran, and does not take place when the phosphine is $P(n\text{-}Bu)_3$. It may also be that nitrite abstracts oxygen to form nitrate in this reaction. The reaction also proceeds satisfactorily[204] in the presence of $CH_3C(CH_2PR_2)_3$ to produce the cation $NiNO[CH_3C(CH_2PR_2)_3]^+$.

The nitrosyl group has been introduced into the complexes $M(NO)_2L_2$ (M = Ru, Os) by a unique series of reactions[205]. Although this is not the most convenient route to $Ru(NO)_2L_2$, it is certainly the most interesting. Sodium nitrite replaces both chloride goups in $MCl_2(CO)_2L_2$ in dimethylformamide. The initially formed dinitrito complex isomerizes to the dinitro complex, which then undergoes spontaneous oxygen transfer to produce $M(NO)_2L_2$. Both CO_2 and $OPPh_3$ are identifiable products, indicating that oxygen transfer to phosphine and CO are competitive processes. Since there is no evidence for ligand dissociation by $MCl_2(CO)_2L_2$, oxygen transfer may be an intramolecular process. This reaction certainly deserves further study.

Finally, ethylene has been used to abstract oxygen from nitrite[206]. In a study of catalyst function in the Wacker process, Smidt and Jira found that aqueous $PdCl_2$ reacts with NO in the presence of HCl as follows.

$$2PdCl_2 + 2NO + H_2O \rightarrow PdNOCl + PdCl_3NO_2^{2-} + 2H^+$$

Complete conversion of Pd^{II} to PdNOCl was effected by abstracting oxygen from the nitro salt with a terminal olefin.

$$PdCl_3NO_2^{2-} + RCH{=}CH_2 \rightarrow PdNOCl + 2Cl^- + RCOCH_3$$

This insoluble PdNOCl has been only poorly characterized. It exhibits an extremely broad nitrosyl stretching vibration, typical of polymeric nitrosyl halides. Attempts at producing soluble derivatives using NH_3 or CN^- gave only Pd^{II} and N_2O. Triphenylphosphine and bipyridyl similarly displace NO.

An attempt to produce $Co(NO)_3$ by oxygen atom abstraction was unsuccessful[207].

$$Co(NO)_2(NO_2)(PPh_3) \rightarrow Co(NO)_3 + OPPh_3$$

(iii) Others

Coordinated ammonia is converted to coordinated nitrosyl in a poorly understood chlorination reaction.

$$Ru(NH_3)_6^{2+} \xrightarrow[NH_3]{Cl_2} RuNO(NH_3)_5^{3+} \qquad \text{(ref. 208)}$$

The authors speculate that chlorine may oxidize aqueous ammonia to NO_2 in the presence of ruthenium ammines. Disproportionation of NO_2 to NO^+ and NO_2^- or direct attack of NO_2 on $Ru(NH_3)_6^{2+}$ might then produce the observed product.

In a related fragmentary report, 0.1 *M* perchloric acid reacts with aqueous solutions of Ru^{III} ammine complexes to produce complexes containing the $RuNO^{3+}$ unit[209]. Production of nitrosyl complexes is accompanied by reduction of ClO_4^- to Cl^-, and coordination of perchlorate has been suggested as an initial step in the reaction. Several nitrosyl complexes are produced, but yields are not reported. Nevertheless, this reaction warrants further study.

Dichloromethane solutions of $RuN_3Cl(das)_2$ react with oxygen only in the presence of light to produce $RuCl(NO_2)(das)_2$. Although a nitrene intermediate was suggested[210], attempts to trap such a species with cyclohexene failed. Ultraviolet irradiation of $CpMoNO(CO)_2$ and PPh_3 in benzene produces[211] some $CpMo(CO)(PPh_3)_2NCO$. This, too, was suggested to arise by deoxygenation of coordinated NO to produce a nitrene which subsequently captures CO. This raises the general question of whether deoxygenation of nitrate or nitrite with phosphines or olefins might be effected photochemically. Such reactions remain unexplored.

Oxygen abstraction from coordinated N_2O has been observed[212].

$$2H^+ + Ru(NH_3)_5N_2O^{2+} + 2Cr^{2+} \rightarrow Ru(NH_3)_5N_2^{2+} + 2Cr^{III} + H_2O$$

It may be profitable to attempt to exploit reducing agents such as chromous ion, zinc metal or V^{II} in a similar manner.

$$MNO_2 + 2H^+ + 2Cr^{II} \rightarrow MNO + 2Cr^{III} + H_2O$$

Reduction of $RuNOCl_3$ with $SnCl_2$ in hydrochloric acid gives an array of products, one of which involves deoxygenation of the nitrosyl group[213]. This product, $K_3[Ru_2N(H_2O)_2Cl_8]$, is also produced by reduction of $RuNOX_5^{2-}$ with formaldehyde or SnX_2. The reverse of this reaction, the selective oxidation of metal nitride complexes to metal nitrosyls, is as yet unobserved.

$$M{\equiv}N\colon \rightarrow M{-}N{\equiv}O\colon$$

The controlled oxidation of oxygen-free nitrogenous ligands in general deserves further study.

Reduction by hydrides of coordinated NO to coordinated ammonia has also been observed.

$$CpCr(NO)_2Cl + BH_4^- \rightarrow Cp_2Cr_2(NO)_3NH_2$$

The yield is only 1%, however[214,215]. The reaction of $Co(NO)_2L_2^+$ with BH_4^- in tetrahydrofuran is reported to occur with evolution of ammonia[108]. This reaction is analogous to the reported reduction of coordinated CO to CH_3 by borohydride in water/benzene. In this way $CpReNO(CO)_2^+$ is converted[216] to $CpReNO(CO)(CH_2OH)$. When this reaction is performed in tetrahydrofuran, the reduction proceeds[217] all the way to $CpReNO(CO)CH_3$. An earlier precedent for the reduction of coordinated CO exists[218].

$$CpM(CO)_3L^+ + BH_4^- \rightarrow CpM(CO)_2(CH_3)L \qquad M = Mo, W$$

In view of the successful execution of these reactions, reduction of coordinated nitrite and nitrate with hydridic (or metalic) reducing agents should be investigated.

The syntheses of rhenium nitrosyls defy categorization in terms of the present analysis. This is in part due to the common choice of Re^{IV} as starting material, which is in turn dictated by its ready availability. No information is presently available on reactions of nitrosylating reagents with trimeric ReX_3.

A common reaction of Re^{IV} and gaseous nitric oxide involves disproportionation of the metal in the presence of NO. The unit $ReNO^{3+}$ is produced in aqueous solution in both[219] the presence or the absence of HCl.

$$3ReO_2 + 2NO + 4H_2O \rightarrow ReNO(OH)_3 + 2ReO_4^- + NH_4^+ + H^+$$
$$4ReO_2 + 3NO + 15Cl^- + 8H^+ \rightarrow 3ReNOCl_5^{2-} + ReO_4^- + 4H_2O$$

The production of NH_4^+ was established quantitatively. The reaction has also been carried out in the solid state[219,220].

$$(o\text{-phenH})HReX_6 + 2NO \xrightarrow{220^\circ C} ReNOX_3(o\text{-phen}) + NOX + 2HX$$

$$Ag_2ReCl_6 \xrightarrow{300^\circ C} ReNOCl_3$$

NOX production in the first reaction was assayed quantitatively.

$$ReBr_5^{2-} \underset{HBr,\ NO}{\xrightarrow{NR_4Br}} ReNOBr_5^{2-} \qquad \text{(ref. 221)}$$

$$ReBr_5L^- \underset{NO}{\xrightarrow{NR_4Br}} ReNOBr_5^{2-} \qquad \text{(ref. 221)}$$

$$ReO(OEt)L_2X_2 \xrightarrow[NO]{NR_4X} ReNOL_2X_3, ReNOX_5^{2-}$$ (ref. 221)

The yield in the first of these reactions is 60%, suggesting that reductive nitrosylation and not disproportionation is taking place.

Finally, $ReH_3(PPh_3)_4$ reacts in ethanol with halide ion and NO to produce[221] $Re(NO)_2(PPh_3)_2X$. This nitrosyl complex is also formed by the reaction of an ethanolic solution of $ReO(OEt)L_2X_2$ and NO.

Casey and Murmann[222] report a careful study of the related reaction of $ReOCl_4(H_2O)^-$ with NO_3^- in 10 *M* HCl. The net reaction, observed under conditions deficient in nitrate, is

$$7ReOCl_4(H_2O)^- + 2H_2O + 2NO_3^- \rightarrow 5ReO_4^- + 2ReNOCl_5^{2-} + 8Cl^- + 8H^+$$

No, N_2, N_2O, NO_2 or Cl_2 is produced. This formulation conceals the fact that the reaction proceeds in two distinct steps.

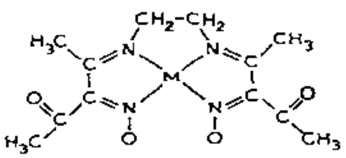
$$ReOCl_4(H_2O)^- + NO_3^- \xrightarrow{fast} ReO_4^- + 2NO_2^-$$

$$5ReOCl_4(H_2O)^- + 2NO_2^- \xrightarrow{slower} 3ReO_4^- + 2ReNOCl_5^{2-}$$

These reactions were verified independently.

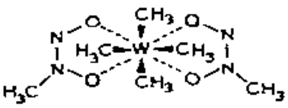
D. CAVEAT

The reactions cataloged to this point result in the coordination of a nitrosyl group to a metal. As mentioned in the introduction, nitric oxide contrasts to carbon monoxide in its ability to participate in unusual (or undesirable) side reactions involving attack on coordinated ligands. Nitric oxide is known to oxidize readily even relatively stable phosphines (e.g. PPh_3) to the corresponding phosphine oxide. Although cobalt Schiff base complexes cleanly add NO, the corresponding Ni, Cu and Pd complexes give isonitrosoacetylacetonate complexes[223,224].

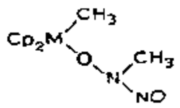


Nitric oxide formally inserts in the C—H bond of (π-allyl)NiBr to produce an α,β-unsaturated oxime complex[225] of NiNOBr.

Uncontrolled amounts of nitric oxide react with hexamethyltungsten to produce $W(CH_3)_4[N(O)—N(O)CH_3]_2$ where each *N*-methyl-*N*-nitrosohydroxylamine group functions as a bidentate ligand[226].



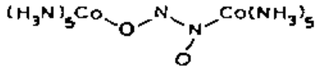
NO insertions into metal—carbon bonds may be rather general. The product of the action of NO on $Cp_2M(CH_3)_2$ where M = Ti or Zr has been identified as



An analogous reaction occurs[227] with $Cp_2Zr(Cl)(CH_3)$.

Pell and Armor[228] investigated the reaction of $Ru(NH_3)_6^{3+}$ with NO in basic solution. The product is $RuN_2(NH_3)_5^{2+}$. When ^{15}NO is employed, the product is labeled as $Ru^{14}N^{15}N$. In a related series of reactions, nitrosation of coordinated alkylamines have been demonstrated. Aqueous solutions of ethylenediamine complexes of Pt^{IV} react with nitrite salts with nitrosation of the chelate nitrogen in preference to the metal[229]. The chelate nitrogen preferentially undergoes "nitrosoamidation" even in the presence of ammonia or alkylamines in the coordination sphere. The nitrosated chelate, formulated $N(NO)C_2H_4NH_2^-$, is formed with release of protons. It is suggested that only one nitrogen per chelate can be derived since mono-, bis- and tris-ethylenediamine complexes react with no more than one, two or three moles of NO_2^-, respectively. *cis*- and *trans*-$PtCl_2(en)_2^{2+}$ both react, as does $Pt(en)_3^{4+}$, but the stereochemistry of nitrosation is unknown. Proton (or, better, ^{13}C) magnetic resonance would presumably answer these questions easily.

Coupling of two MNO moieties to form a dimer bridged by the hyponitrite ($ONNO^{2-}$) group has been observed. This structural unit has been definitively identified in the red salt[230] $[Co_2(N_2O_2)(NH_3)_{10}]X_4$.

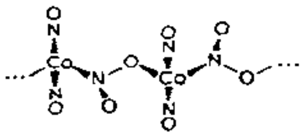


The conditions influencing the yields of this dimer relative to that of $CoNO(NH_3)_5X_2$, the black salt, have been investigated, but direct interconversion of these two species has not been observed[42]. $K_3CoNO(CN)_5$ has been similarly identified as a hyponitrite complex[231,232]. Cp_2Ti reacts with nitric oxide to produce an insoluble material exhibiting Ti—O and N=N stretching frequencies; this has been suggested to be a polymeric hyponitrite-bridged complex[233]. Finally, on standing, the vibrational spectrum of $Mo(NO)_2$-$(das)_2Cl_2$ changes in a manner consistent with the formation of a hyponitrite-bridged dimeric cation[234].

The oxidation of coordinated NO to the coordinated nitro group is another possible consequence of indiscriminate use of gaseous nitric oxide. This is apparently the origin of the new dimer[235] $Cp_2Mn_2(NO)_3(NO_2)$. Similarly, *mer*-$OsCl_3L_3$ reacts[236] with nitric oxide and zinc to produce $OsNO(NO_2)$-Cl_2L_2 and $OsNO(NO_2)ClL_3^+$. The bent $CoNO^{2+}$ group is attacked by nitric oxide to form the coordinated nitro group[83], $CoNO_2^{2+}$ and N_2O.

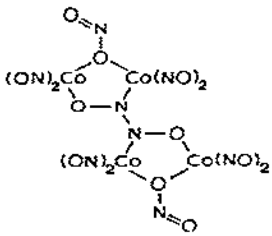
The synthesis of $Co(NO)_3$ reported in Section B(i) is not as simple as it might first appear. Working independently under slightly different conditions, two groups of workers produced different compounds.

Working at room temperature in hexane, Strouse and Swanson produced an oxygen-rich material of formula CoN_3O_4 which possesses a polymeric, nitrite-bridged structure in the solid state[237]. The oxygen-poor product was not identified but other workers[238] have suggested that it may be N_2O based on the



tendency of NO to disproportionate at higher temperatures and pressures.

Using a unique "inverted J" shaped reactor, still a third nitro nitrosyl was produced[238]. This was characterized crystallographically as $Co_4(NO)_8(NO_2)_2$·(N_2O_2) and contains both nitrite (as a bridging group) and bridging hyponi-



trite. $CoNO(PPh_3)_3$ is unstable to nitric oxide at room temperature, undergoing a complex redox reaction[239].

$$CoNO(PPh_3)_3 + 7NO \rightarrow Co(NO)_2(NO_2)PPh_3 + 2OPPh_3 + 2N_2O + \tfrac{1}{2} N_2$$

The high stability of the oxide-bridged dimeric product may account for the oxidation[240] of Mn(Salen).

$$Mn(Salen) + NO \rightarrow O[Mn(salen)]_2 + N_2O$$

However, in view of the recent synthesis of MnNO(TPP)(base), it seems likely that a comparable complex may exist for salicaldehydeethylenediimine, but that it readily undergoes attack by excess nitric oxide.

E. ACKNOWLEDGEMENTS

This review, and some of the original work described here, was supported by the Petroleum Research Fund, administered by the American Chemical Society, and by the National Science Foundation under grant GP-38641X.

F. APPENDIX

The following represent recent reports, current to July, 1974, organized in accord with the sequence shown in the contents.

Section B(i)(b)

The following substitution reactions have been observed[241].

$M(PPh_3)_2CO(solvent)^+ \rightarrow M(NO)_2(PPh_3)_2^+$ M = Rh, Ir
$Ir(PPh_3)_2(CO)_3^+ \rightarrow Ir(NO)_2(PPh_3)_2^+$

Structural details of $Mn(NO)_2[P(OMe)_2Ph]_2Cl$, the product of the reaction of *mer, trans*-$Mn(CO)_3[P(OMe)_2Ph]_2Cl$ with NO, have been reported[242]. The structure is based on a trigonal bipyramid with apical phosphorus ligands.

Predictably (see text), $IrN_2(PPh_3)_2Cl$ reacts with NO in a complex manner.

$$IrN_2(PPh_3)_2Cl + 4NO \rightarrow IrNO(NO_2)(PPh_3)_2Cl + N_2 + N_2O$$

Catalysis of the reaction

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

by $RhCl_3 \cdot xH_2O$ in ethanol or $Ru(NO)_2(PPh_3)_2$ in benzene at 25°C has been reported[243]. Some metal dinitrosyl complexes have been cited as being particularly effective in catalyzing this reaction[241]. Thus, while $M(NO)_2$-$(PPh_3)_2Br$ and $M(NO)_2(PPh_3)_2^+$ (M = Rh, Ir) are active, $IrNO(PPh_3)_2Br_2$, $Co(NO)_2(PPh_3)_2Br$ and $Co(NO)_2(PPh_3)_2^+$ are not.

Section B(i)(c)

Reductive nitrosylation of a CH_2Cl_2 solution of $MoCl_5$ in the presence of PPh_3 produces $Mo(NO)_2Cl_2(OPPh_3)_2$. The complex $MoNOCl_3(OPPh_3)_2$ was observed to be an intermediate by infrared spectfoscopy and isolated[244]

Section B(ii)

A brief review of NO^+ salts as synthetic reagents has appeared[245]. The effect of solvent is considered in detail, and the need for careful drying of solvents in emphasized.

$NOPF_6$ reacts with $CpW(CO)_2NO$ to produce $CpW(NO)_2CO^+$ in CH_2Cl_2/CH_3CN at −78°C. The product is somewhat unique in that the carbonyl group is substitution labile[246]

Section B(iii)

Several metal carbonyl anions react with NOCl without coordination of the halogen[247].

$CpM(CO)_3^- \rightarrow CpM(CO)_2NO$ M = Cr, Mo, W
$Fe(CO)_4^{2-} \rightarrow Fe(NO)_2(CO)_2$
$Mn(CO)_5^- \rightarrow MnNO(CO)_4$

However, more nucleophilic anions act as reducing agents towards NOCl[247].

$CpFe(CO)_2^- \rightarrow [CpFe(CO)_2]_2$
$Re(CO)_5^- \rightarrow Re_2(CO)_{10}$

This mode of reaction has been observed previously for cyanide complexes (see text).

Section B(iv)

A significant new variant on the use of *N*-methyl-*N*-nitrosotoluenesulfonamide has been reported[247,248]. This nitrosoamide reacts with some metal carbonyl anions as a formal source of NO^+.

$CpM(CO)_3^- \rightarrow CpM(CO)_2NO$ M = Cr, Mo, W
$Mn(CO)_5^- \rightarrow Mn(CO)_4NO$
$(\pi\text{-}C_3H_5)Fe(CO)_3^- \rightarrow (\pi\text{-}C_3H_5)Fe(CO)_2NO$

Section B(vi)

A kinetic study of the reaction of hydroxylamine with $Ni(CN)_4^{2-}$ in basic solution has appeared[249]. In the presence of oxygen, the stoichiometry is

$$Ni(CN)_4^{2-} + NH_2OH + \tfrac{1}{2}\,O_2 + OH^- \rightarrow NiNO(CN)_3^{2-} + CN^- + 2H_2O$$

No ammonia is produced. The suggested mechanism involves a pre-equilibrium in which hydroxylamine replaces cyanide. Deprotonation of coordinated hydroxylamine, followed by oxidation of the resultant $NiNO(CN)_3^{4-}$ by O_2, completes the reaction. Subsequent oxidation of $NiNO(CN)_3^{2-}$ makes this an unattractive synthetic procedure. The reaction in the absence of oxygen is slower and kinetically less tractable, but preferable from a synthetic standpoint. The following mechanism is proposed

$$Ni(CN)_4^{2-} + NH_2OH \rightleftharpoons Ni(CN)_3(NH_3OH)^- + CN^-$$
$$Ni(CN)_3(NH_2OH)^- + NH_2OH + OH^- \rightarrow Ni(CN)_3NO^{2-} + NH_3 + 2H_2O$$

Rather more than one mole of NH_3 is produced per $Ni(CN)_3NO^{2-}$ detected. This is attributed to the following side reaction.

$$Ni(CN)_3NO^{2-} + NH_2OH + CN^- \rightarrow Ni(CN)_4^{2-} + N_2 + H_2O + OH^-$$

Molecular nitrogen was detected and, in the presence of excess NH_2OH, the major reaction is the nickel-catalyzed conversion of hydroxylamine to nitrogen and ammonia.

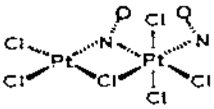
$$3NH_2OH \rightarrow NH_3 + N_2 + 3H_2O$$

The common theme of this work is that NO^- is probably not a reactant (see text). In both instances inhibition by cyanide and catalysis by cyanide scavengers was cited as evidence for preliminary coordination of hydroxylamine.

Section B(vii)

Equimolar sodium nitrite and K_2PtCl_4 react in aqueous HCl. Addition of

Et_4NCl crystallizes a green salt whose actual formula was established crystallographically as $(Et_4N)_2[Pt_2(NO)_2Cl_6]$. The dimeric anion contains both four- and six-coordinate platinum and inequivalent (bent terminal and bridging) nitrosyl groups[250].



The relationship of this compound to those described in refs. 173 and 177 is unclear. More perplexing is the fact that the crystal actually studied does not have the composition (elemental analysis) of the bulk sample from which it was selected.

Acidification of metal carbonyl anions in the presence of nitrite ion is under study[247].

$$W(CO)_5Cl^- \rightarrow WNO(CO)_4Cl$$

This offers a promising new route to nitrosyl clusters.

A kinetic study[251] indicates that production of $CrNO^{2+}_{aq}$ from NO_2^- in acid solution does not involve NO^+. The following mechanism was suggested.

$$HNO_2 + Cr^{2+} \rightarrow NO + OH^-$$
$$Cr^{2+} + NO \rightarrow CrNO^{2+}$$

This emphasizes the potential complexity of reactions using NO_2^-/H^+.

Section B(ix)

Chromous ion reacts with nitric acid to produce three metal-containing products[251].

$$4Cr^{II} + HNO_3 + H^+ \rightarrow CrNO^{2+} + Cr^{3+} + Cr_2(OH)_2^{4+}$$

Section D

Insertion of NO into metal—methyl bonds occurs with Me_2MCl_3 and Me_3MCl_2 (M = Nb, Ta). The products are $MCl_3[ON(Me)NO]_2$ and $MeMCl_2$-$[ON(Me)NO]_2$, respectively. The crystal structure of the tantalum methyl dichloro compound was determined. Further insertion into the last methyl group of this compound does not proceed cleanly[252]. Two salts of formula $K_6[Co_2(CN)_{10}(N_2O_2)] \cdot nH_2O$, which are claimed to be isomeric with that produced by others[231,232], were studied by vibrational spectroscopy[253]. The following structures were suggested.

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