

SYNTHETIC METHODS IN TRANSITION METAL NITROSYL CHEMISTRY

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ABBREVIATIONS

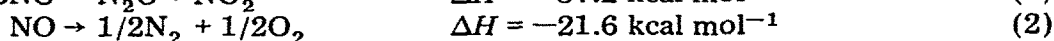
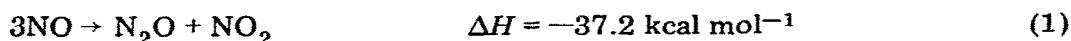
bipy	bipyridyl
COD	cyclo-octadiene
Cp	C_5H_5
das	<i>o</i> -phenylenebis(dimethylarsine)
DMG	dimethylglyoximate
dppe	1,2-bis(diphenylphosphino)ethane
en	ethylenediamine
L	ER_3 with E = P, As, Sb
N_4	any macrocyclic tetradentate amine
<i>o</i> -phen	<i>o</i> -phenanthroline
PPP	$\text{PhP}[(\text{CH}_2)_3\text{PPh}_2]_2$

Ph, ϕ	C_6H_5
RBpy ₃	tris-pyrazoylborate
SacSac	dithio-acetyiacetonate
tol	toluene
TPP	tetraphenylporphine dianion

A. INTRODUCTION

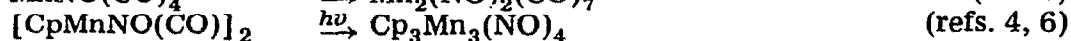
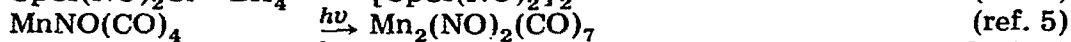
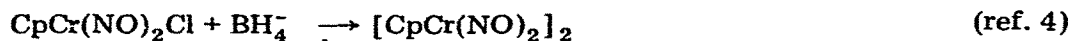
If inorganic chemistry could be said to suffer by comparison with organic chemistry, then this must be due in part to the lack of rational and general synthetic methods in the inorganic domain. This is of course due to the fact that inorganic chemistry encompasses such a variety of elements, but the 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 chemistry¹, structure² and bonding³ 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.



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,

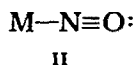
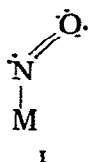


since they do not increase the number of nitrosyl groups per metal, are not covered. Also excluded are reactions of coordinated NO, which necessarily lead *away* from nitrosyl complexes. However, Section C describes reactions of coordinated ligands which produce the nitrosyl group. As a result, this 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.



(a) Simple adduct formation, $\text{ML}_n + x\text{NO} \rightarrow \text{M}(\text{NO})_x\text{L}_n$

(1) $x = 1$

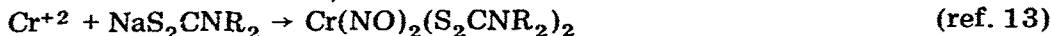
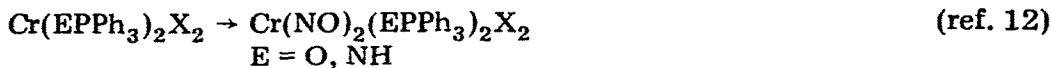
This type of reaction is expected when ML_n is either a 17- or 15-electron complex, lacking one or three electrons from the inert gas configuration (IGC). The following are examples (NO is assumed to be a reactant throughout Section B, (i)).



Numerous examples of this last reaction are known, with "chel" being a dithiocarbamate, dithiolate¹⁰, 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.



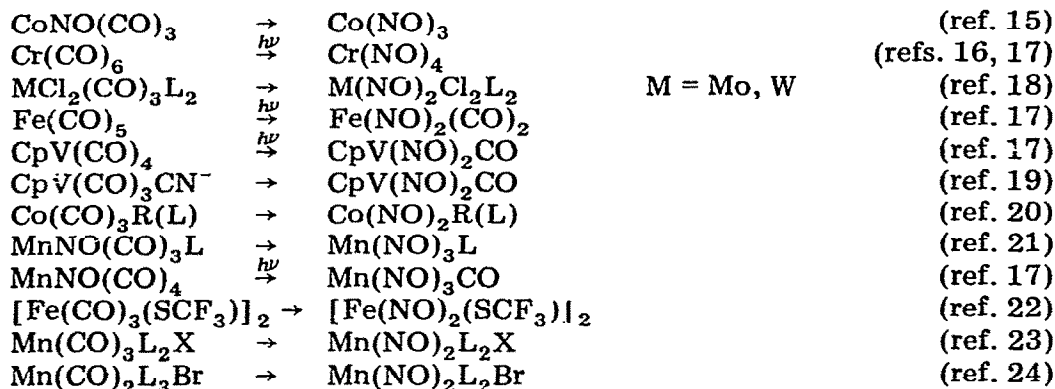
(2) $x = 2$ 

Although this second reaction is run without isolation of intermediates, it conceivably represents addition of NO to $\text{Cr}(\text{S}_2\text{CNR}_2)_2$.

Recent work has shown that the complex claimed to be $\text{Fe}(\text{NO})_2(\text{S}_2\text{CNEt}_2)_2$ is actually a nitro-nitrosyl complex¹⁴.

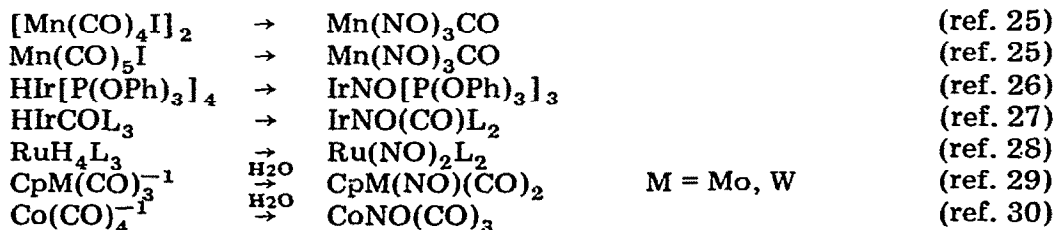
(b) *Substitution*, $\text{ML}_n + x\text{NO} \rightarrow \text{M}(\text{NO})_x\text{L}_m + (n-m)\text{L}$

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.



(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.



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

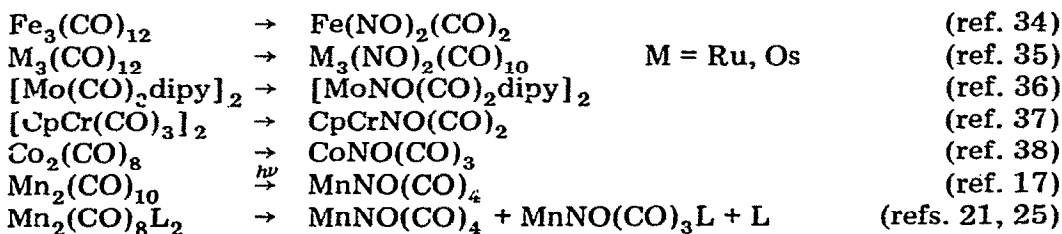
It is useful to consider the preparation of CpNiNO



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 complexes³². The reaction of $\text{Ni}(\text{C}_3\text{H}_5)_2$ with NO offers an attractive possible route to the unknown binary nitrosyl $\text{Ni}(\text{NO})_2$. A similar statement applies to $\text{M}(\text{C}_3\text{H}_5)_3$, $\text{M} = \text{Rh, Ir}$.

NO displaces one CO and one hydride from $[(\text{HO})\text{M}(\text{CO})_3\text{H}]_4 \cdot 4\text{H}_2\text{O}$, $\text{M} = \text{Mo, W}$. Addition of OPPh_3 allows isolation of $[\text{Mo}(\text{OH})(\text{CO})_2\text{NO}]_4 \cdot 4(\text{OPPh}_3)$. 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 donor³³.

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

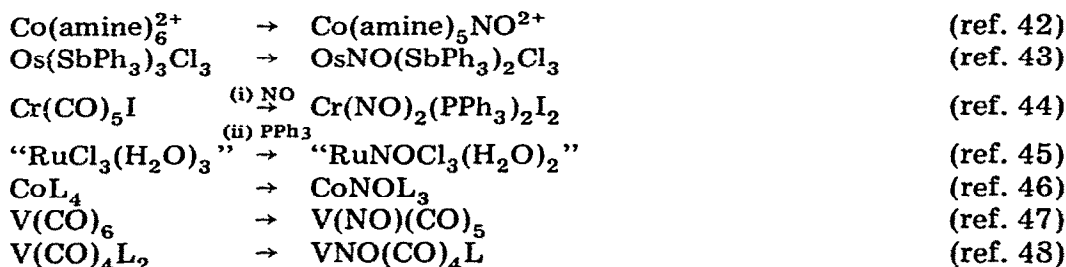


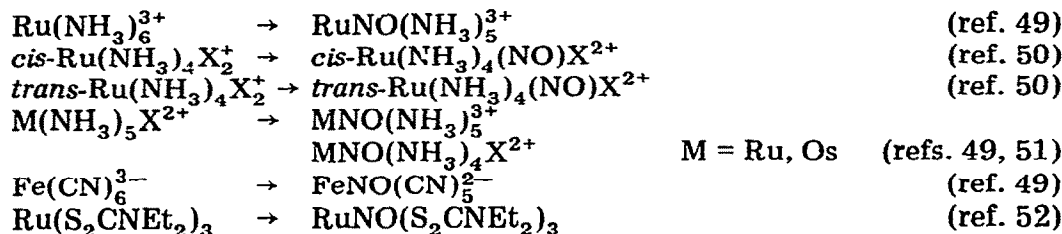
Formation of metal-metal single or multiple bonds is also possible.



The Fe-Fe distance of 2.326 Å in $[\text{CpFeNO}]_2$ is consistent with a double bond between these atoms⁴⁰.

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.



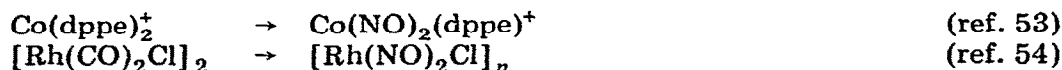


This last complex has been shown to contain one monodentate dithiocarbamate *cis* to the nitrosyl group.

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.

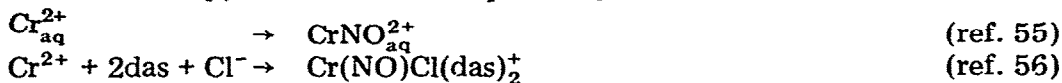


This behavior may account for the following reactions.



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.



Dithionite reduces $\text{Cr}(\text{NO})\text{Cl}(\text{das})_2^+$ to diamagnetic $\text{Cr}(\text{NO})\text{Cl}(\text{das})_2$.

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



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.

$\text{Ni}[\text{P}(n\text{-Bu})_3]_2\text{X}_2$ reacts in a complex manner depending upon the halogen⁵⁸. When X is Cl, an apparent reduction by NO produces $\text{NO}^+\text{NiL}_2\text{Cl}_2^-$. The bromo analog produces a mixture of this paramagnetic anion and a five-coordinate adduct $\text{Ni}(\text{NO})\text{Br}_2[\text{P}(n\text{-Bu})_3]_2$. Reaction of the iodo complex is interpreted as producing $[\text{Ni}(\text{NO})(\text{I})\text{P}(n\text{-Bu})_3]_2$. The latter presumably forms as a result of partial oxidation by NO of $\text{P}(n\text{-Bu})_3$ to the phosphine oxide. In fact, earlier workers⁵⁹ isolated only $\text{NiCl}_2(\text{OPET}_3)_2$ from the action of NO on $\text{NiCl}_2(\text{PET}_3)_2$ emphasizing the importance of careful control of stoichiometry in reactions of nitric oxide.

$\text{Rh}(\text{PPh}_3)_3\text{Cl}$ and $\text{Rh}(\text{PPh}_3)_2\text{COCl}$ 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. Hughes⁶⁰ reported the production of $\text{Rh}(\text{NO})(\text{NO}_2)(\text{PPh}_3)_2\text{Cl}$ from the reaction of $\text{Rh}(\text{PPh}_3)_2\text{COCl}$ 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. $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ 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 $\text{Rh}(\text{NO})_2(\text{PPh}_3)_2\text{Cl}$. Later papers correct this error, and discuss various attempts to separate components of the product mixture by crystallization.

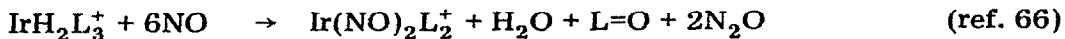
The work of Kiji et al.⁶² provides the best method for isolating pure $\text{RhNO}(\text{NO}_2)(\text{PPh}_3)_2\text{Cl}$ uncomplicated by the "isomeric" mixture noted by Hughes. Excess PPh_3 added to $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ prior to reaction with NO results in production of a solid with a single NO stretching frequency. These workers also claim to separate Hughes' product mixture into green $\text{RhNO}(\text{NO}_2)(\text{PPh}_3)_2\text{Cl}$ 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 $\text{Ir}(\text{PPh}_3)_3\text{Cl}$ reacts with NO to produce a pale brown material identified⁶³ as $\text{IrNO}(\text{NO}_2)(\text{PPh}_3)_2\text{Cl}$.

The reaction of RuCl_2L_3 with NO is solvent dependent. In chloroform the product is (quantitatively) $\text{RuNOCl}_3\text{L}_2$, indicating attack on solvent by the possible intermediate $\text{RuNOCl}_2\text{L}_n$. When halogen is unavailable from other sources (e.g. in acetone or benzene), halogen redistribution (disproportionation) occurs to produce⁶⁴ $\text{RuNOCl}_3\text{L}_2$ and $\text{Ru}(\text{NO})_2\text{L}_2$.

$\text{ML}_{3,4}$ with $\text{M} = \text{Pt}, \text{Pd}$ 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 $\text{ML}_2(\text{N}_2\text{O}_2)$, contain a hyponitrite ligand⁶⁵.

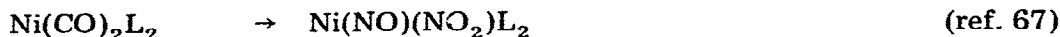
Oxidation of phosphine always must be considered.



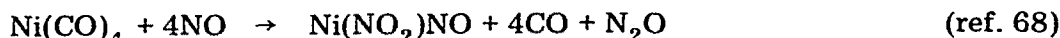
It is stated⁵⁹ that NO reacts with $\text{FeCl}_2(\text{PR}_3)_2$ to give only "inseparable mixtures".

Solutions of OsCl_6^{2-} absorb NO, but the primary reaction product is uncharacterized⁴³. Addition of phosphines, arsines or stibines produces $\text{OsNOCl}_3\text{L}_2$, 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.

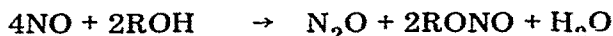


Here the identity of the oxygen deficient product (N_2O ?) was not investigated. The reaction of NO with Ni(CO)_4 has been more completely characterized.



In both of these cases the complex $\text{Ni(NO)}_2\text{L}$ ($\text{L}=\text{CO}, \text{PR}_3$), which is at least formally a possible product, is not observed.

$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ was initially reported to react with NO at room temperature in ethanol⁶⁹. 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 $\text{RhNOCl}_2(\text{PPh}_3)_2$. Further recent study⁷⁰ of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in ethanol shows conclusively that catalytic disproportionation of NO takes place according to the following reaction.



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

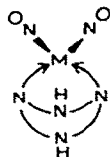
This reaction prompts visions of using the electronic "mismatch" of NO (a three-electron donor) and any 16-electron metal complex to advantage in a catalytic cycle for the purpose of reducing nitric oxide. It is precisely this incompatibility which is required to prevent formation of a stable complex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



It has been reported⁶² that the reaction mixture from NO treatment of RhClL_3 (which contains $\text{RhNO(NO}_2\text{)L}_2\text{Cl}$), 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 categorization of reactions of NO with 16-electron compounds, the reported⁷³ $[\text{RhNO(O}_2\text{CCH}_3)_2]_2$ deserves reinvestigation. $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4$ 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 $\text{MNOCl}_2(\text{PPh}_3)_2$ where $\text{M} = \text{Rh}, \text{Ir}$. The iridium compound has been characterized crystallographically⁷⁴.

It is claimed that $\text{Ru}(\text{CO})\text{MFIxDME}$ (MFIxDME is mesoporphyrin IX dimethyl ester) reacts with "slightly more than 2 equivalents of nitric oxide" to produce $\text{Ru}(\text{NO})_2\text{MFIxDME}$. 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" complex⁷⁶ of general formula $\text{Ru}(\text{NO})_2\text{L}_2$,



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.

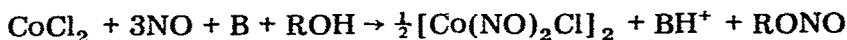
Another explanation is also worthy of consideration. Feltham¹⁴ has shown that the product of the reaction of $\text{FeNO}(\text{S}_2\text{CNR}_2)_2$ with NO is not the $\text{Fe}(\text{NO})_2(\text{S}_2\text{CNR}_2)_2$ originally claimed, but rather $\text{FeNO}(\text{NO}_2)(\text{S}_2\text{CNR}_2)_2$. This product results from NO_2 impurity which is often present in old pressurized metal containers of NO. It is likely that the purported $\text{Fe}(\text{NO})_2(\text{SacSac})_2$, prepared similarly, is really a nitro nitrosyl⁷⁷. Being mixtures, these materials all exhibit two nitrosyl stretching frequencies, as would a dinitrosyl complex.

(c) Reductive nitrosylation

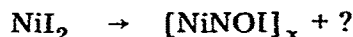
The unpaired electron on nitric oxide occupies a π^* orbital. As might be expected for an antibonding electron, ionization is a relatively facile process; NO has an ionization potential⁷⁸ of 9.26 eV . One might predict that NO could function as a stoichiometric reducing agent and this behavior has been observed⁷⁹.



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 $\text{Co}(\text{NO})_2$ -(*p*-toluidine)₂⁺ salts. This reaction was later rediscovered⁸¹ 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 ($\text{Co}^{2+} + 2\text{NO}$) undergoes a one-electron reduction in the reaction, and since the reducing agent was identified as NO, the reaction was termed reductive nitrosylation.



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

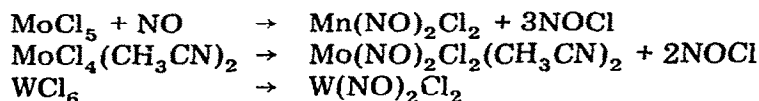


The conditions under which one gets simple replacement (i.e. CoNOL_5^{2+}) relative to reductive nitrosylation have been investigated⁸³.

The reaction of $\text{Co}(\text{S}_2\text{PF}_2)_2$ and nitric oxide produces⁸⁴ $\text{Co}(\text{NO})_2(\text{S}_2\text{PF}_2)_2$. 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 $\text{CpCr}(\text{NO})_2\text{Cl}$. Nitric oxide is presumed to be the reducing agent in this reaction⁸⁵.

The higher halides of molybdenum and tungsten also undergo reductive nitrosylation under mild conditions in aprotic solvents⁸⁶⁻⁸⁸

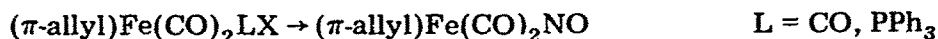


These reactions bear a striking similarity to the carbonylation⁸⁹ of RhCl_3



Finally, chloroferric tetraphenylporphyrin reversibly forms a weak *adduct* with NO in aprotic solvents; addition of alcohol precipitates the product of reductive nitrosylation⁹⁰, $\text{FeNO}(\text{TPP})$. $\text{MnCl}(\text{TPP})$ undergoes the same transformation. In contrast with the iron case, where nitrogenous base is not required, $\text{MnCl}(\text{TPP})$ is only reduced upon addition of base and the six-coordinate complex $\text{MnNO}(\text{TPP})(\text{base})$ results. The manganese complex contains a linear nitrosyl group^{11,91}. Fe^{III} hemoglobin likewise undergoes reductive nitrosylation in aqueous solution⁹².

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}.



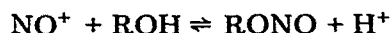
Although the reaction solvent is not mentioned, it is probable that it was a hydrocarbon. In this case NOX is probable as the oxidized product. It is then remarkable that the product complex is stable to nitrosyl halide.

An extremely brief report⁹⁴ 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 disproportionation 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} .

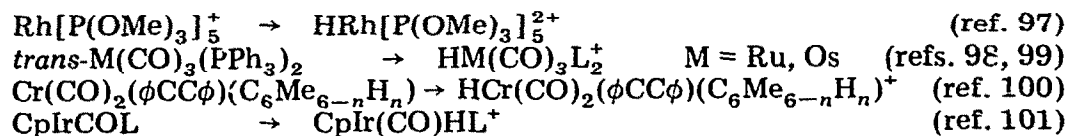
(ii) NO^+

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 solvents⁹⁵. Acetone appears to react with these salts and, surprisingly, they are slightly soluble in benzene, producing colored solutions⁹⁶. 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



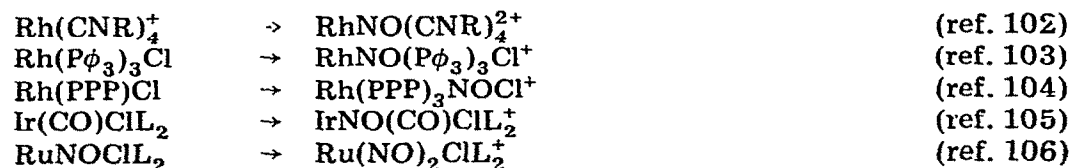
which is actually a synthetic route to alkyl nitrites. Since this is an equilibrium reaction, it is possible that NO^+ may still be the reactive species even in alcohol. Alternatively (see Section B(viii)), RONO may effect the nitrosation. Care must be taken to consider possible reactions of the metal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



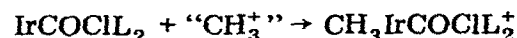
$\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ is not protonated under these conditions^{98,99} nor is CpMCOL where¹⁰¹ $\text{M} = \text{Co, Rh}$. It has been suggested that this is indicative of increasing transition metal basicity down a group.

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

(a) Addition



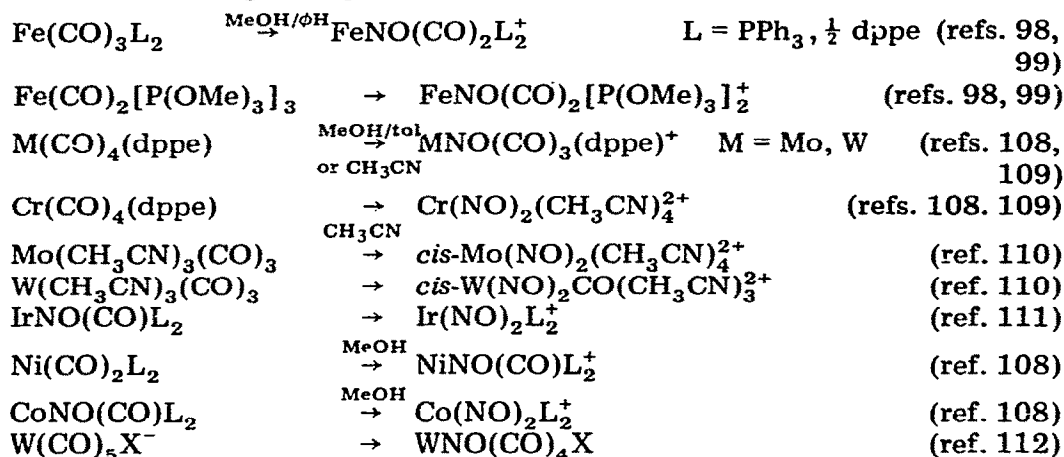
It is probably worth noting the formal similarity of these reactions to those involving the addition of CH_3^+ (via $\text{CH}_3\text{OSO}_2\text{F}$ or Me_3O^+) to square planar complexes¹⁰⁷.



(b) Substitution

A more common occurrence is ligand substitution by NO^+ . Carbon monox-

ide is often the ligand replaced.

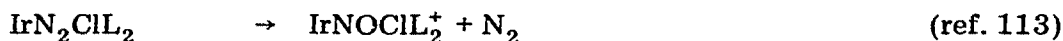


The last reaction proceeds in only low yield for molybdenum pentacarbonyl halide anions, and fails for the chromium analog.

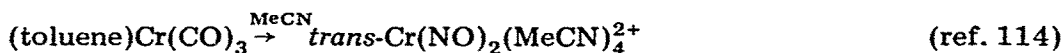
Phosphine substitution has also been observed.



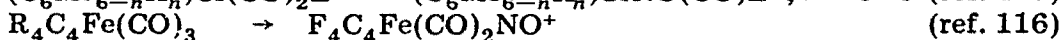
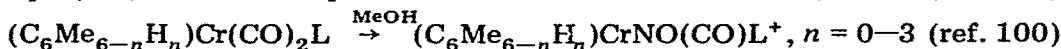
In contrast to the reaction of NO^+ with IrCOCIL_2^{105} , nitrogen is displaced from IrN_2CIL_2 .



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



or leave it intact.



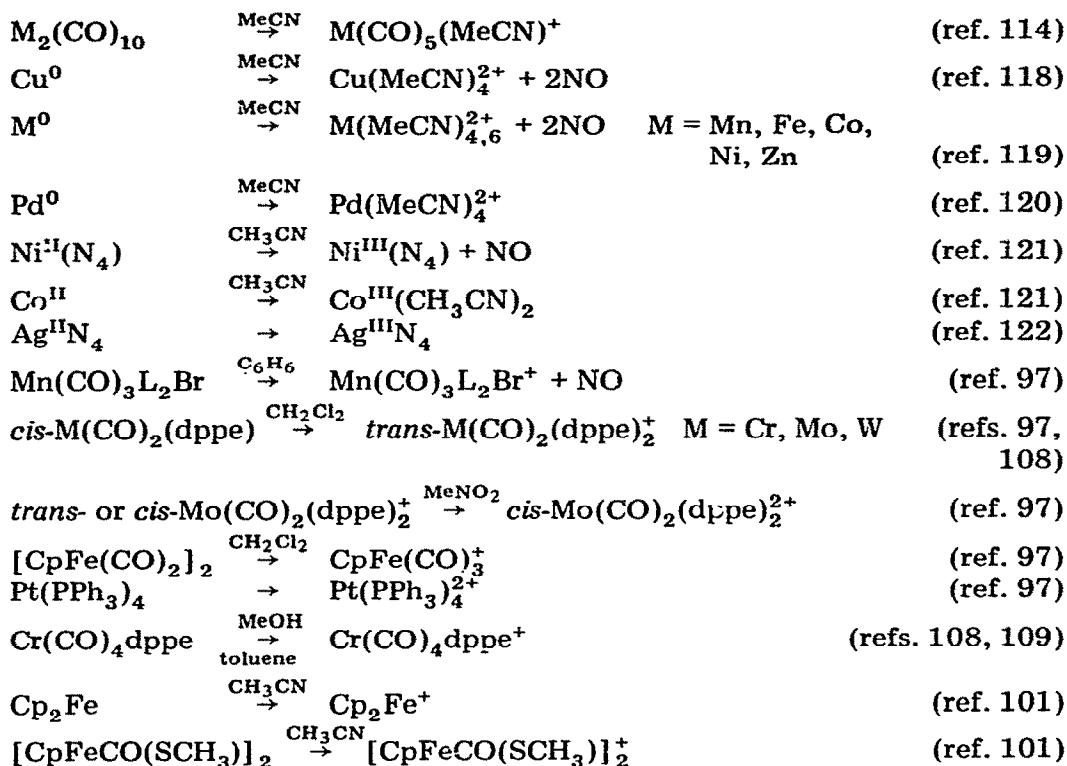
The effect of NO^+ on metal clusters has been little studied. Disruption of the cluster has been observed.



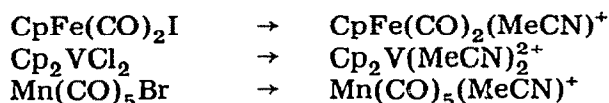
$\text{Os}_3(\text{CO})_9(\text{PPh}_3)_3$ fails to produce cationic nitrosyls on treatment with NO^+ ; only cationic carbonyls are produced. In acetonitrile, both the ruthenium and osmium species give carbonyls; the reaction is thus critically solvent dependent¹¹⁷.

Some warning must be added to this consideration of NO^+ as a nitrosylating

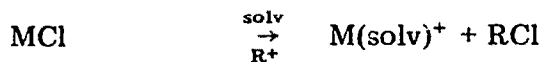
reagent. NO^+ in many instances functions simply as a one-electron oxidizing agent. The reduced form of NO^+ is listed if it was determined.



Finally, halogen abstraction has been observed in acetonitrile¹⁰¹.

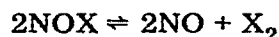


Although the nitrogen containing product has not been identified (NOX?), the reaction bears a striking similarity to halogen abstraction by alkylating agents such¹²³ as Me_3O^+ or MeOSO_2F .



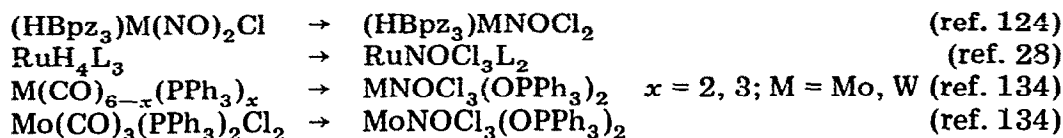
(iii) NOX

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.

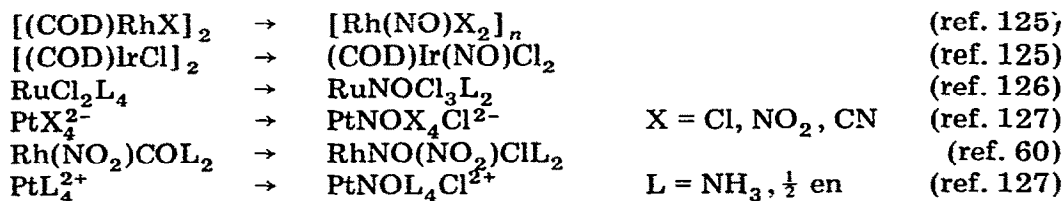


Several possible examples of oxidative addition by elemental halogens have

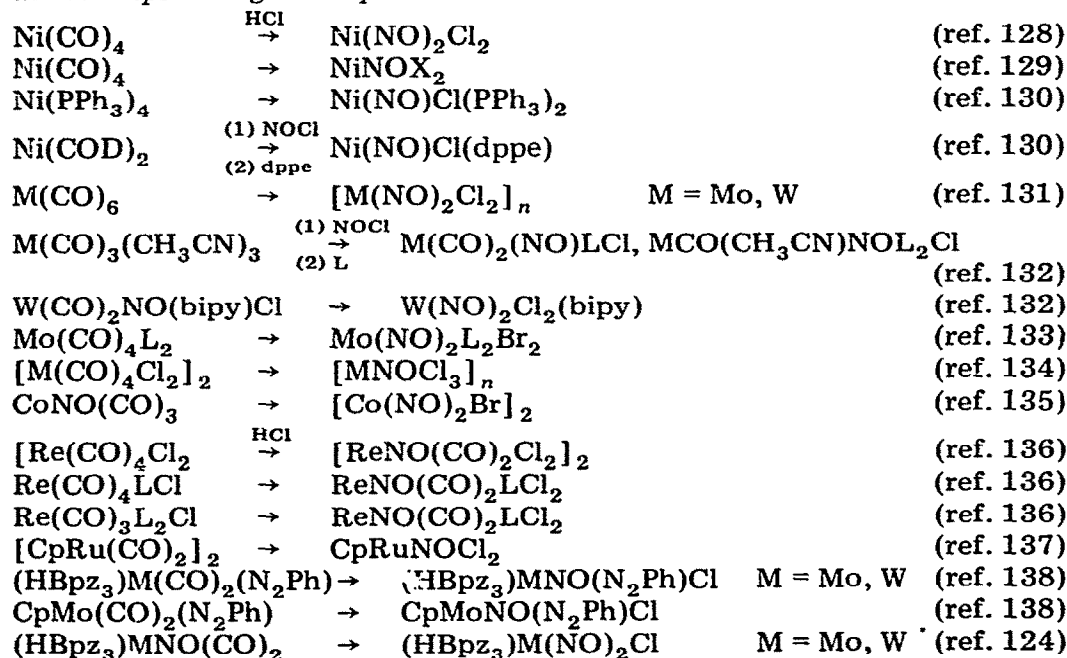
been reported in reactions with NOX. (NOX is assumed as a reagent throughout this section).



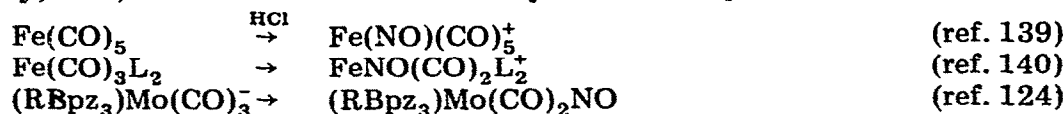
Oxidative addition may occur to coordinatively unsaturated substrates.



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



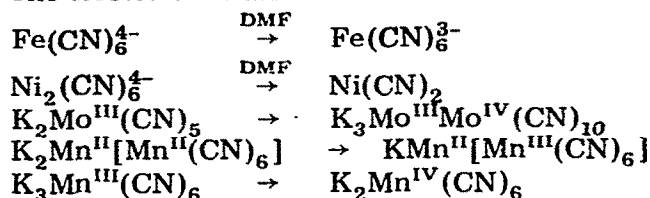
Under certain circumstances the halide of NOX does not coordinate; formally, then, NO^+ has been added and only one CO is replaced.



Nitrosyl chloride, under pressure or at 1 atm, converts $\text{Fe}(\text{CO})_5$ to $\text{Fe}(\text{NO})_2(\text{CO})_2$ in respectable yield. The reaction must be run under conditions deficient in NOCl , necessitating separation of $\text{Fe}(\text{NO})_2(\text{CO})_2$ from unreacted $\text{Fe}(\text{CO})_5$. If the reaction is performed stoichiometrically, the yield of $\text{Fe}(\text{NO})_2(\text{CO})_2$ declines to near zero. The fate of the chlorine (COCl_2 , FeCl_3 ?) was not reported¹⁴¹.

Connelly¹⁴² makes reference to the fact NOCl almost always displaces the hydrocarbon moiety from olefin complexes (e.g. $\text{C}_8\text{H}_8\text{Fe}(\text{CO})_3$). This is consistent with the decreased stability of olefin complexes of metals in higher oxidation states.

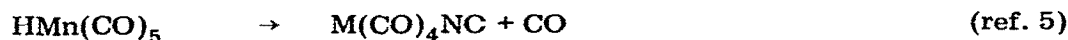
Cyano complexes appear to be simply oxidized, NOCl functioning as a one-electron oxidant¹⁴³.



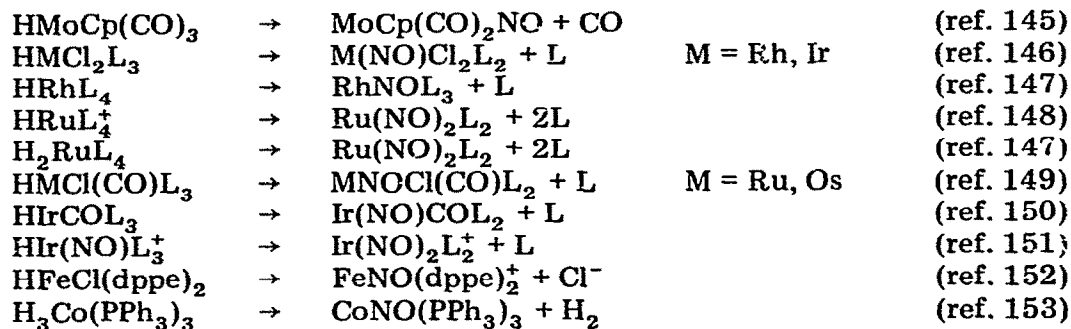
Nitrosyl chloride oxidized $\text{MX}_2(\text{PR}_3)_2$ complexes of cobalt and nickel to $\text{MX}_3(\text{PR}_3)_2$, this being one of the few routes to phosphine complexes¹⁴⁴ of Ni^{III} .

(iv) *N*-nitrosoamides

N-nitrosoamides such as *N*-methyl-*N*-nitroso-urea 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 $\text{Mn}(\text{CO})_4\text{NO}$ involves CO displacement.



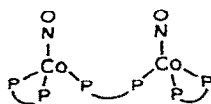
Other examples abound (nitroso sulfonamide RNO is assumed as a reagent).



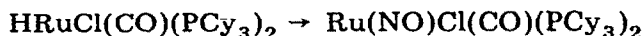
The last reaction is unique as an example of the elimination of molecular hydrogen subsequent to NO/H interchange.

H_3IrL_2 reacts with RNO in the presence of NO to produce the dimer $[\text{Ir}(\text{NO})_2\text{L}]_2$. The nitric oxide oxidizes phosphine liberated in the reaction. In its absence, half of the iridium is found⁵⁷ as IrNOL_3 .

In an attempt to inhibit ligand extrusion, and thereby produce a bent nitrosyl complex, $\text{HCo}(\text{dppe})_2$ was reacted with the nitrososulfonamide. It was anticipated that the chelate effect would prevent dissociation of phosphine. The reaction actually produces $\text{Co}_2(\text{NO})_2(\text{dppe})_3$ in high yield. The structure of this dimer was established to be that shown below using ^{31}P NMR¹⁵³.

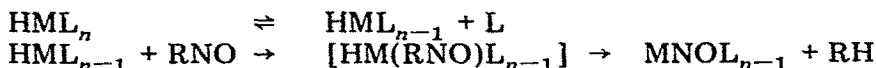


The only reaction in which ligand extrusion is not observed involves a tricyclohexylphosphine (PCy_3) complex.

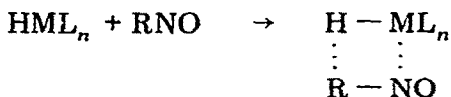


Here it is the reagent hydride complex which is unusual (PPh_3 forms $\text{HRuCl}(\text{CO})(\text{PPh}_3)_3$); coordinative unsaturation of the PCy_3 complex presumably results from the steric constraints of the bulky phosphine¹¹⁷.

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



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



Evidence for the first mechanism comes from the observation that the nitrosoamide reacts readily with $\text{OsHCl}(\text{CO})\text{L}_3$, while the relatively substitution-inert $\text{OsHCl}(\text{CO})_2\text{L}_2$ does not react¹⁵¹.

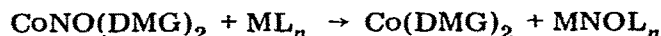
In a related but nevertheless distinct reaction, $\text{Pt}(\text{PPh}_3)_4$ reacts with CF_3NO by what is apparently oxidative addition to give $\text{Pt}(\text{PPh}_3)_2(\text{CF}_3)(\text{NO})$ (ref. 54). Nitrosobenzene, however, reacts with $\text{PdCl}_2(\phi\text{CN})_2$ to produce a rare example of intact, coordinated nitrosobenzene, $\text{PdCl}_2(\phi\text{NO})_2$ (ref. 154).

(v) Coordinated NO

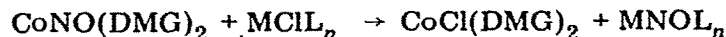
A reaction of substantial synthetic utility developed out of the observation that $\text{CcCH}_3(\text{DMG})_2$, where DMG is the monoanion of dimethylglyoxime,

will transfer a methyl group to square planar Co^{II} complexes. The complexes $\text{CoNO}(\text{tet})$, 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. $\text{CoNO}(\text{DMG})_2$, which has excellent solubility characteristics, has been found to transfer NO to a variety of metal complexes¹⁵⁵.

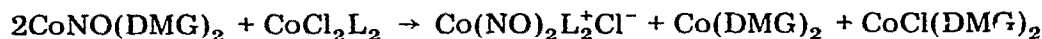
Two general types of behavior can occur. "Simple nitrosyl transfer" describes the transfer of NO from $\text{CoNO}(\text{DMG})_2$.



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.



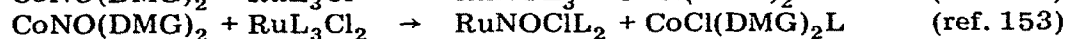
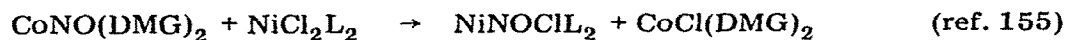
In an attempt to detect simple nitrosyl transfer, CoCl_2L_2 was chosen as substrate. The observed reaction is



$\text{CoNOCl}_2\text{L}_2$, if it is produced at all, evidently reacts even faster than CoCl_2L_2 with $\text{CoNO}(\text{DMG})_2$. This was verified independently¹⁵⁵.



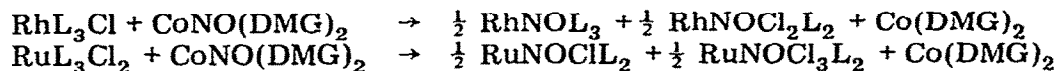
Nitrosyl halogen interchange occurs as follows.



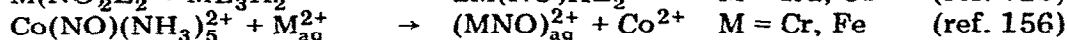
In the latter two reactions a characteristic of $\text{CoCl}(\text{DMG})_2$ manifests itself. This complex can halogenate low-valent nitrosyl complexes. The following reaction was verified independently.



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



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



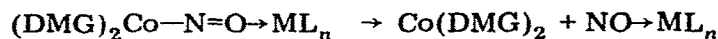
The limitations of nitrosyl transfer reactions are presently unknown. We have unsuccessfully attempted to produce a copper nitrosyl from CuClL_3 and

$\text{CoNO}(\text{DMG})_2$. 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 complexes⁹ and the structurally characterized oxygen bridge in $(\text{H}_3\text{N})_5\text{Co}(\text{O}_2)\text{Co}(\text{NH}_3)_5^{5+}$, it is possible that nitrosyl transfer occurs through the terminal



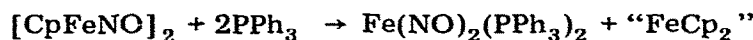
oxygen. An isonitrosyl would then be the initial product; rearrangement to the nitrosyl would follow in a manner analogous to that observed for cyanide-mediated electron transfer¹⁵⁷.



An analogous mechanism has been postulated for nitrosyl-mediated electron transfer from $\text{CoNO}(\text{en})_2\text{H}_2\text{O}^{2+}$ to¹⁵⁸ $\text{Cr}(\text{H}_2\text{O})_6^{2+}$.

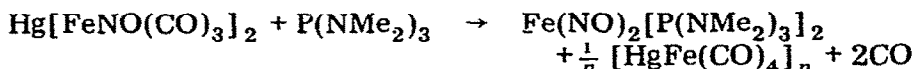
$\text{CoNO}(\text{SacSac})_2$, where SacSac is dithioacetylacetonate, spontaneously "disproportionates" at room temperature in solution, undergoing transfer of both the nitrosyl and SacSac to produce equimolar $\text{Co}(\text{SacSac})_3$ and⁹ $\text{Co}(\text{NO})_2(\text{SacSac})$.

Triphenyl phosphine reacts with $[\text{CpFeNO}]_2$ to produce $\text{Fe}(\text{NO})_2(\text{PPh})_2$ in 78% yield according to the following reaction⁴⁰.

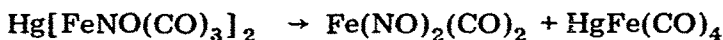


Ferrocene was not actually an observed product; only polymeric material was formed. This reaction barely qualifies as nitrosyl transfer, however, since $[\text{CpFeNO}]_2$ contains symmetrically bridging nitrosyl groups⁴⁰.

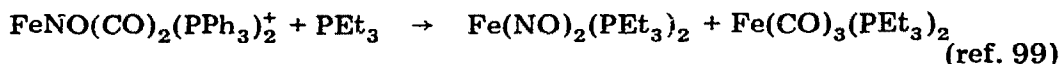
Phosphine substitution may also promote nitrosyl transfer in isolated instances



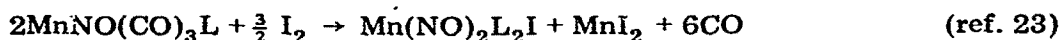
This overall reaction may only be an expression of the tendency of $\text{Hg}[\text{FeNO}(\text{CO})_3]_2$ itself to undergo nitrosyl transfer on heating¹⁵⁹

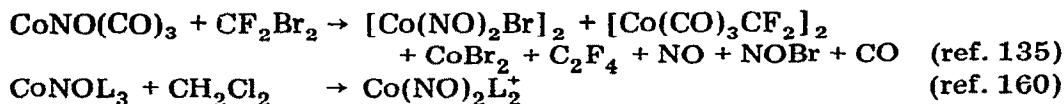


Brief mention is also given to the following reaction.

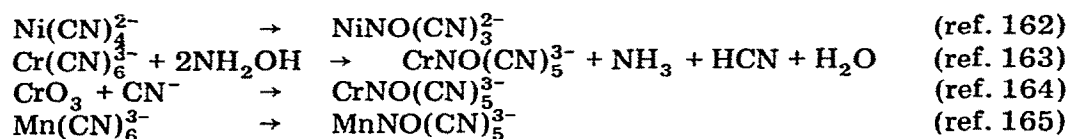


Transfer of the nitrosyl group has been observed to occur during oxidative addition.



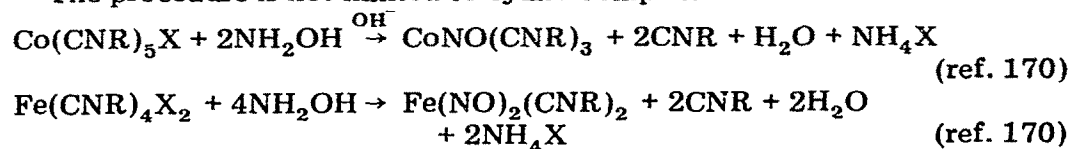
*(vi) NH₂OH*

The redox chemistry of hydroxylamine is complex and varied. Depending upon the pH, NH₃, NH₄⁺, N₂ or N₂O may be produced¹⁶¹. 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 (NH₂OH and OH⁻ are assumed reagents throughout this section).

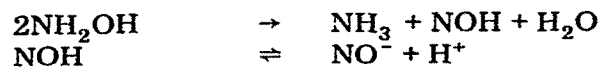


Molybdate, cyanide and base react with hydroxylamine to yield MoNO-(CN)₅⁴⁻ salts¹⁶⁶. The conflicting reports concerning the constitution of this anion were settled crystallographically. The complex is also accessible directly from Mo(CN)₆⁴⁻ (ref. 167). Ammonium vanadate (NH₄VO₃), cyanide and base react with hydroxylamine to produce a vanadium nitrosyl, originally formulated erroneously as VNO(CN)₅⁵⁻. This has now been characterized structurally¹⁶⁸ as VNO(CN)₅³⁻. When this reaction is performed under H₂S, the product is claimed to be K₄V(CN)₆NO·H₂O; although the CN and NO stretching frequencies closely resemble those of VNO(CN)₅³⁻, the cell constants differ and the compound is diamagnetic¹⁶⁹. Nitroprusside, FeNO(CN)₅²⁻, 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.



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

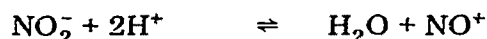


Basic conditions are suggested to be required to displace the second reaction towards "NO⁻". The production of NH₃ has been quantitated for the reaction of Ni(CN)₄²⁻, proving that only half of the hydroxylamine nitrogen is converted to the nitrosyl group¹⁶².

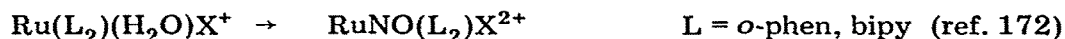
Further study of the generality and mechanism of this reaction is a potentially fertile area. One approach might be to examine reactions of coordinated hydroxylamine, although few such complexes have been characterized. One example, $\text{Pt}(\text{NH}_2\text{OH})_4^{2+}$, is stable in basic solution and may be isolated as the hydroxide salt. It is actually made by reduction of Pt^{IV} with hydroxylamine in basic solution¹⁷¹. 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.

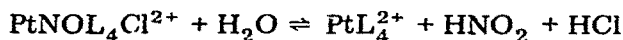


In attempting to categorize reported nitrosylation reactions there is some difficulty in distinguishing reactions of the above type (attack of NO^+ , generated by acidic solutions of nitrite salts, on metal complexes) from coordination of NO_2^- followed by oxide abstraction (Section C(i)). Godwin and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



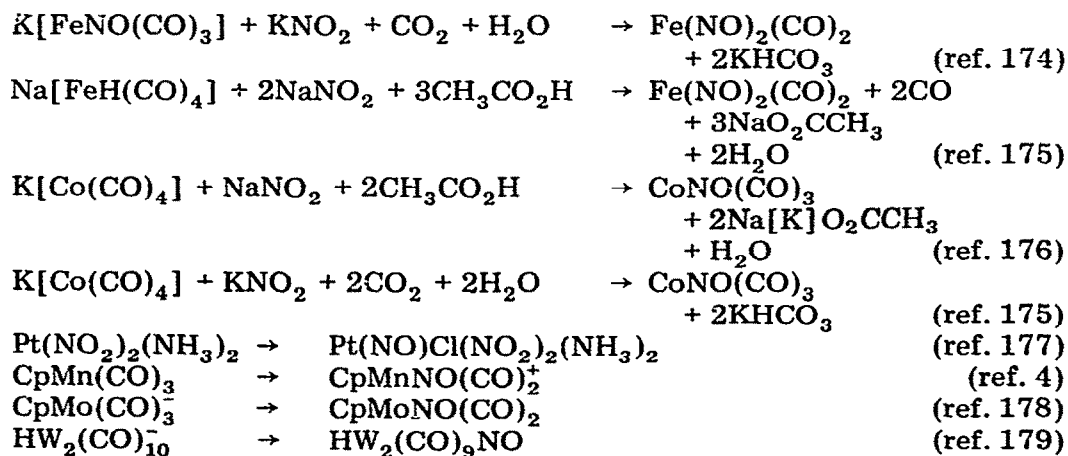
In this case, no reaction by nitrite (in the absence of added H^+) is observed in one hour; the nitrosylation reaction, on the other hand, is instantaneous.

The equilibrium



has been studied quantitatively for $\text{L} = \text{NH}_3, \frac{1}{2} \text{ en}$. K values from 10^{-5} to 10^{-6} indicate that an aqueous solution $2 \times 10^{-2} M$ 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 chloride¹⁷³.

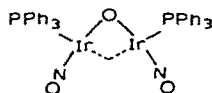
Other reactions of this type include the following.



$\text{Ru}(\text{NH}_3)_6^{2+}$ is unaffected by sodium nitrite, but nitrite and HCl produce¹⁸⁰ $\text{RuNO}(\text{NH}_3)_5^{3+}$. 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 $\text{Ru}(\text{NH}_3)_6^{3+}$ may be the first step in this reaction¹⁸¹. Note that this product contrasts markedly with the superficially similar reaction¹⁸² of NO_2^-/H^+ with $\text{OsN}_2(\text{NH}_3)_5^{2+}$ to produce $\text{Os}(\text{N}_2)_2(\text{NH}_3)_4^{2+}$.

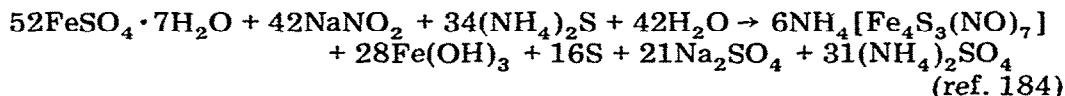
Addition of aqueous NaNO_2 to a solution of $\text{CpMn}(\text{CO})_2\text{NO}^+$ results in vigorous foaming. Ultraviolet irradiation of this solution produced a poorly soluble material of formula¹⁷⁸ $[\text{CpMn}(\text{NO})_2]_n$. Both bridging and terminal nitrosyls are suggested in the infrared. Analogous treatment of $\text{CpFe}(\text{CO})_3^+\text{HCl}_2^-$ gave an ill-defined nitrosyl complex¹⁷⁸.

$[\text{IrNO}(\text{PPh}_3)]_2\text{O}$ has been obtained from $\text{IrCO}(\text{PPh}_3)_2\text{Cl}$ and sodium nitrite in benzene/alcohol. The initial product was not isolated; reaction with oxygen yields the observed product, whose structure provides firm evidence



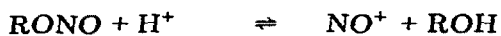
for a metal-metal bond. A complete understanding of this unusual reaction awaits publication of full experimental details¹⁸³.

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

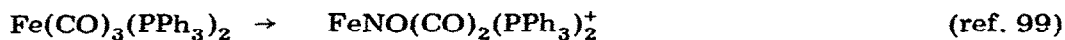


(viii) *RONO*

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



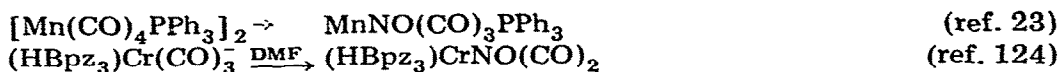
The following reaction was carried out by adding the metal complex to a solution of isopentyl nitrite and HPF_6 in benzene/methanol.



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



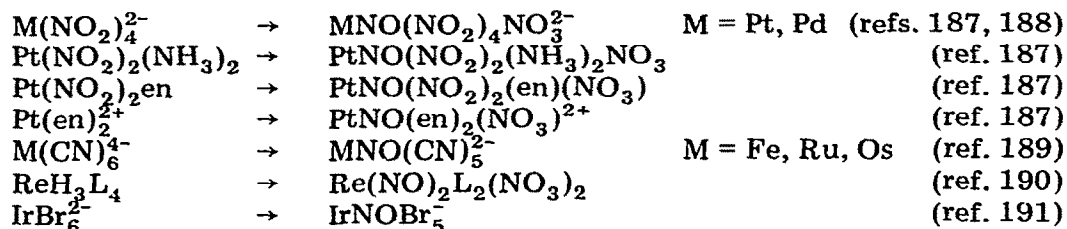
Some applications of alkyl nitrites in aprotic solvents have been noted.



Trifluoroacetyl nitrite converts $\text{CpMo}(\text{CO})_3^-$ into $\text{CpMo}(\text{CO})_2\text{NO}$ in 10% yield¹⁷⁸.

(ix) HNO_3

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^- .



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, $\text{CpMnNO}(\text{CO})_2^+$ has been made in low yield from the reaction of $\text{CpMn}(\text{CO})_3$ with nitric acid¹⁹².

The unit RuNO^{3+} is formed by the action of HCl and HNO_3 on¹⁹³ RuO_4 . However, boiling $\text{Ru}(\text{NH}_3)_6^{2+}$ in concentrated nitric acid produces $\text{Ru}(\text{NH}_3)_6(\text{NO}_3)_3$ and not a nitrosyl complex¹⁸⁰.

It is consistently claimed that ruthenium displays an extraordinary affinity for the nitrosyl group. For example¹⁹³, "ruthenium is unique in that it forms more nitrosyl complexes than any other element". "The $\text{Ru}(\text{NO})$ 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 $\text{RuNO}(\text{base})_2\text{Cl}_3$ and their number is based in part on the variety of bases employed. An equally lengthy list of complexes of form $\text{NiNOCl}(\text{base})_2$ could be compiled. If one chooses to judge the affinity of Ru for NO on the basis of the rate of reaction of

"RuCl₃ · 3H₂O" with NO in ethanol, then ruthenium is unexceptional. Co^{II} reacts much more rapidly.

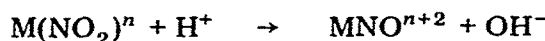
There is a claim¹⁹⁴ that CpMo(CO)₃NH₃⁺ reacts with sodium nitrate and HCl to produce CpMo(NO)₂Cl in low yield. However, in view of the fact that this was an attempt to produce the dinitrogen complex CpMo(CO)₃N₂⁺, the report may be a misprint, sodium *nitrite* being the reagent.

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 NO₂, 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 (N₂, N₃, N₂O, NH₂OH) 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

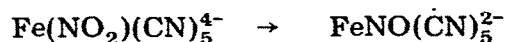
The general transformation considered in this section is the following



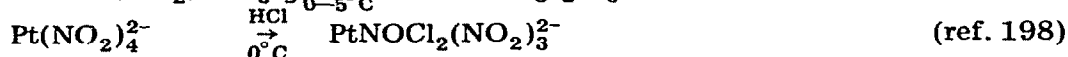
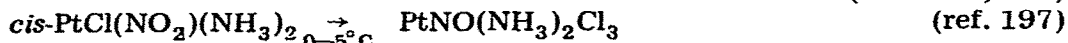
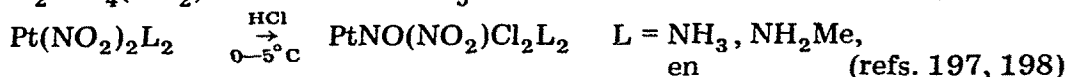
The nitro—nitrosyl interconversion has been thoroughly studied for amine complexes of¹⁹⁵ RuNO_x.



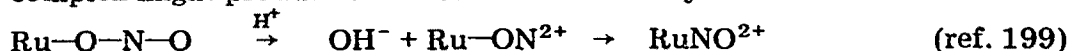
The reversibility of this reaction was established and an equilibrium constant measured for RuNO(bipy)₂Cl²⁺. Oxide ion could also be removed with SnCl₄ and BF₃, demonstrating that nitro—nitrosyl interconversion can also be effected under aprotic conditions. Nitroprusside is similarly obtainable¹⁹⁶.



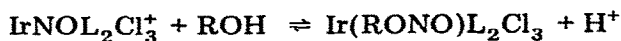
The following reactions exemplify this method



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.



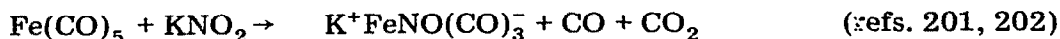
Reed and Roper have reported the related interconversion of an alkyl nitrite complex.



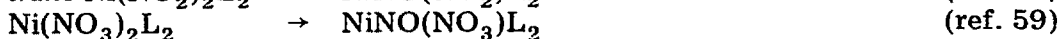
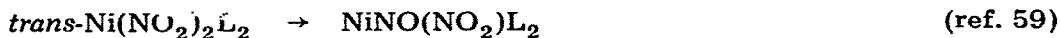
The mode of coordination of the alkyl nitrite ligand is unknown and therefore the mechanistic details of alkoxide removal remain to be explored²⁰⁰.

(ii) *Oxygen atom abstraction*

Carbon monoxide liberated from $\text{Fe}(\text{CO})_5$ reduces nitrite and nitrosyl² in the preparation of $\text{FeNO}(\text{CO})_3^-$.

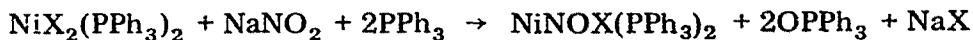


Gaseous carbon monoxide is reported to reduce nitrite and nitrate coordinated to nickel.



The nitrate complex with $\text{L} = \text{PEt}_3$ is tetrahedral, indicating that stereochemistry is not a determining factor in this reaction. The reaction proceeds under very mild conditions (25°C , 1 atm $\cdot \text{CO}$).

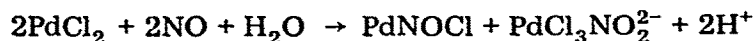
Phosphine is oxidized to phosphine oxide as nitrite is reduced to the nitrosyl group in a remarkably clean reaction²⁰³.



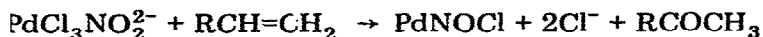
This reaction occurs only in tetrahydrofuran, and does not take place when the phosphine is $\text{P}(n\text{-Bu})_3$. It may also be that nitrite abstracts oxygen to form nitrate in this reaction. The reaction also proceeds satisfactorily²⁰⁴ in the presence of $\text{CH}_3\text{C}(\text{CH}_2\text{PR}_2)_3$ to produce the cation $\text{NiNO}[\text{CH}_3\text{C}(\text{CH}_2\text{PR}_2)_3]^+$.

The nitrosyl group has been introduced into the complexes $\text{M}(\text{NO})_2\text{L}_2$ ($\text{M} = \text{Ru, Os}$) by a unique series of reactions²⁰⁵. Although this is not the most convenient route to $\text{Ru}(\text{NO})_2\text{L}_2$, it is certainly the most interesting. Sodium nitrite replaces both chloride groups in $\text{MCl}_2(\text{CO})_2\text{L}_2$ in dimethylformamide. The initially formed dinitrito complex isomerizes to the dinitro complex, which then undergoes spontaneous oxygen transfer to produce $\text{M}(\text{NO})_2\text{L}_2$. 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 $\text{MCl}_2(\text{CO})_2\text{L}_2$, oxygen transfer may be an intramolecular process. This reaction certainly deserves further study.

Finally, ethylene has been used to abstract oxygen from nitrite²⁰⁶. 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.

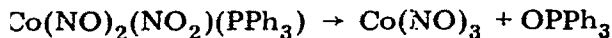


Complete conversion of Pd^{II} to PdNOCl was effected by abstracting oxygen from the nitro salt with a terminal olefin.



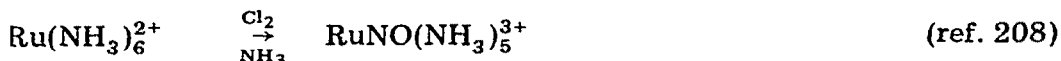
This insoluble PdNOCl has been only poorly characterized. It exhibits an extremely broad nitrosyl stretching vibration, typical of polymeric nitrosyl halides. Attempts at producing soluble derivatives using NH_3 or CN^- gave only Pd^{II} and N_2O . Triphenylphosphine and bipyridyl similarly displace PdNO .

An attempt to produce $\text{Co}(\text{NO})_3$ by oxygen atom abstraction was unsuccessful²⁰⁷.



(iii) Others

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

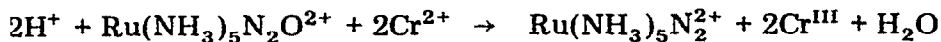


The authors speculate that chlorine may oxidize aqueous ammonia to NO_2 in the presence of ruthenium amines. Disproportionation of NO_2 to NO^+ and NO_2^- or direct attack of NO_2 on $\text{Ru}(\text{NH}_3)_6^{2+}$ might then produce the observed product.

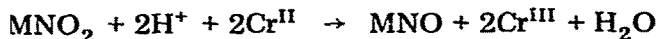
In a related fragmentary report, 0.1 *M* perchloric acid reacts with aqueous solutions of Ru^{III} ammine complexes to produce complexes containing the RuNO^{3+} unit²⁰⁹. Production of nitrosyl complexes is accompanied by reduction of ClO_4^- to Cl^- , and coordination of perchlorate has been suggested 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 $\text{RuN}_3\text{Cl}(\text{das})_2$ react with oxygen only in the presence of light to produce $\text{RuCl}(\text{NO}_2)(\text{das})_2$. Although a nitrene intermediate was suggested²¹⁰, attempts to trap such a species with cyclohexene failed. Ultraviolet irradiation of $\text{CpMoNO}(\text{CO})_2$ and PPh_3 in benzene produces²¹¹ some $\text{CpMo}(\text{CO})(\text{PPh}_3)_2\text{NCO}$. 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 observed²¹².



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



Reduction of RuNOCl_3 with SnCl_2 in hydrochloric acid gives an array of products, one of which involves deoxygenation of the nitrosyl group²¹³. This product, $\text{K}_3[\text{Ru}_2\text{N}(\text{H}_2\text{O})_2\text{Cl}_8]$, 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.

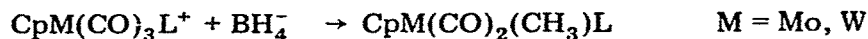


The controlled oxidation of oxygen-free nitrogenous ligands in general deserves further study.

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



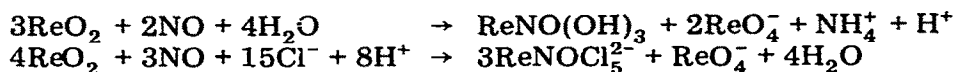
The yield is only 1%, however^{214,215}. The reaction of $\text{Co}(\text{NO})_2\text{L}_2^+$ with BH_4^- in tetrahydrofuran is reported to occur with evolution of ammonia¹⁰⁸. This reaction is analogous to the reported reduction of coordinated CO to CH_3 by borohydride in water/benzene. In this way $\text{CpReNO}(\text{CO})_2^+$ is converted²¹⁶ to $\text{CpReNO}(\text{CO})(\text{CH}_2\text{OH})$. When this reaction is performed in tetrahydrofuran, the reduction proceeds²¹⁷ all the way to $\text{CpReNO}(\text{CO})\text{CH}_3$. An earlier precedent for the reduction of coordinated CO exists²¹⁸.



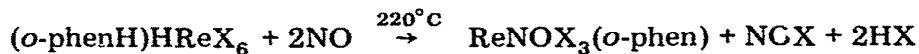
In view of the successful execution of these reactions, reduction of coordinated nitrite and nitrate with hydridic (or metallic) reducing agents should be investigated.

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 both²¹⁹ the presence or the absence of HCl.

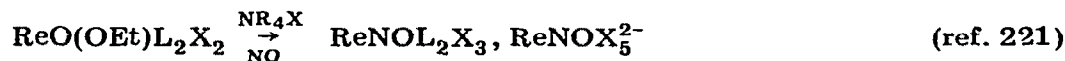


The production of NH_4^+ was established quantitatively. The reaction has also been carried out in the solid state^{219,220}.



NOX production in the first reaction was assayed quantitatively.

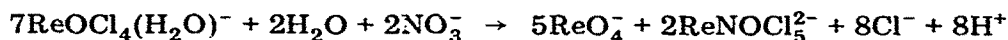




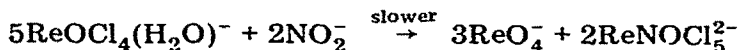
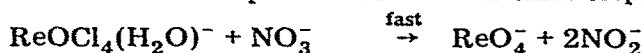
The yield in the first of these reactions is 60%, suggesting that reductive nitrosylation and not disproportionation is taking place.

Finally, $\text{ReH}_3(\text{PPh}_3)_4$ reacts in ethanol with halide ion and NO to produce²²¹ $\text{Re}(\text{NO})_2(\text{PPh}_3)_2\text{X}$. This nitrosyl complex is also formed by the reaction of an ethanolic solution of $\text{ReO}(\text{OEt})\text{L}_2\text{X}_2$ and NO.

Casey and Murmann²²² report a careful study of the related reaction of $\text{ReOCl}_4(\text{H}_2\text{O})^-$ with NO_3^- in 10 M HCl. The net reaction, observed under conditions deficient in nitrate, is



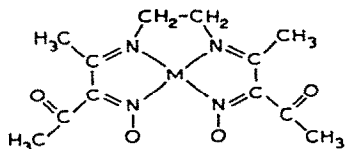
No, N_2 , N_2O , NO_2 or Cl_2 is produced. This formulation conceals the fact that the reaction proceeds in two distinct steps.



These reactions were verified independently.

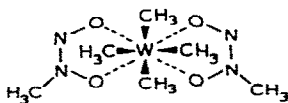
D. CAVEAT

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 isonitrosoacetyl-acetone complexes^{223,224}.

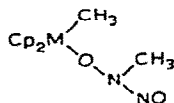


Nitric oxide formally inserts in the C—H bond of $(\pi\text{-allyl})\text{NiBr}$ to produce an α,β -unsaturated oxime complex²²⁵ of NiNOBr .

Uncontrolled amounts of nitric oxide react with hexamethyltungsten to produce $\text{W}(\text{CH}_3)_4[\text{N}(\text{O})\text{—N}(\text{O})\text{CH}_3]_2$ where each *N*-methyl-*N*-nitrosohydroxylamine group functions as a bidentate ligand²²⁶.



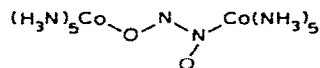
NO insertions into metal—carbon bonds may be rather general. The product of the action of NO on $\text{Cp}_2\text{M}(\text{CH}_3)_2$ where M = Ti or Zr has been identified as



An analogous reaction occurs²²⁷ with $\text{Cp}_2\text{Zr}(\text{Cl})(\text{CH}_3)$.

Pell and Armor²²⁸ investigated the reaction of $\text{Ru}(\text{NH}_3)_6^{3+}$ with NO in basic solution. The product is $\text{RuN}_2(\text{NH}_3)_5^{2+}$. When ^{15}NO is employed, the product is labeled as $\text{Ru}^{14}\text{N}^{15}\text{N}$. 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 metal²²⁹. The chelate nitrogen preferentially undergoes "nitrosoamidation" even in the presence of ammonia or alkylamines in the coordination sphere. The nitrosated chelate, formulated $\text{N}(\text{NO})\text{C}_2\text{H}_4\text{NH}_2^-$, 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*- $\text{PtCl}_2(\text{en})_2^{2+}$ both react, as does $\text{Pt}(\text{en})_3^{4+}$, 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 salt²³⁰ $[\text{Co}_2(\text{N}_2\text{O}_2)(\text{NH}_3)_{10}] \text{X}_4$.



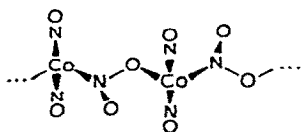
The conditions influencing the yields of this dimer relative to that of $\text{CoNO}(\text{NH}_3)_5\text{X}_2$, the black salt, have been investigated, but direct interconversion of these two species has not been observed⁴². $\text{K}_3\text{CoNO}(\text{CN})_5$ has been similarly identified as a hyponitrite 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 complex²³³. Finally, on standing, the vibrational spectrum of $\text{Mo}(\text{NO})_2(\text{das})_2\text{Cl}_2$ changes in a manner consistent with the formation of a hyponitrite-bridged dimeric cation²³⁴.

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 dimer²³⁵ $\text{Cp}_2\text{Mn}_2(\text{NO})_3(\text{NO}_2)$. Similarly, *mer*- OsCl_3L_3 reacts²³⁶ with nitric oxide and zinc to produce $\text{OsNO}(\text{NO}_2)\text{Cl}_2\text{L}_2$ and $\text{OsNO}(\text{NO}_2)\text{ClL}_3^+$. The bent CoNO^{2+} group is attacked by nitric oxide to form the coordinated nitro group⁸³, CoNO_2^{2+} and N_2O .

The synthesis of $\text{Co}(\text{NO})_3$ reported in Section B(i) is not as simple as it

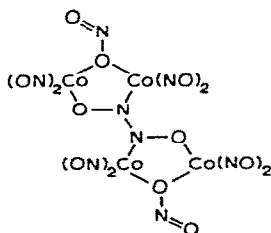
might first appear. Working independently under slightly different conditions, two groups of workers produced different compounds.

Working at room temperature in hexane, Srouse and Swanson produced an oxygen-rich material of formula CoN_3O_4 which possesses a polymeric, nitrite-bridged structure in the solid state²³⁷. The oxygen-poor product was not identified but other workers²³⁸ have suggested that it may be N_2O based on the

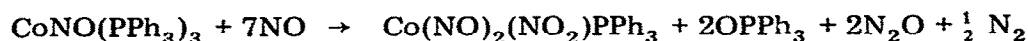


tendency of NO to disproportionate at higher temperatures and pressures.

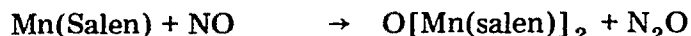
Using a unique "inverted J" shaped reactor, still a third nitro nitrosyl was produced²³⁸. This was characterized crystallographically as $\text{Co}_4(\text{NO})_8(\text{NO}_2)_2 \cdot (\text{N}_2\text{O}_2)$ and contains both nitrite (as a bridging group) and bridging hyponi-



trite. $\text{CoNO}(\text{PPh}_3)_3$ is unstable to nitric oxide at room temperature, undergoing a complex redox reaction²³⁹.



The high stability of the oxide-bridged dimeric product may account for the oxidation²⁴⁰ of $\text{Mn}(\text{Salen})$.



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

E. ACKNOWLEDGEMENTS

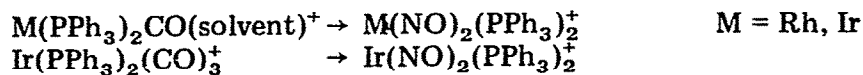
This review, and some of the original work described here, was supported by the Petroleum Research Fund, administered by the American Chemical Society, and by the National Science Foundation under grant GP-38641X.

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 observed²⁴¹.

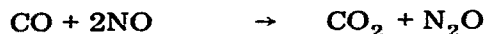


Structural details of $\text{Mn}(\text{NO})_2[\text{P}(\text{OMe})_2\text{Ph}]_2\text{Cl}$, the product of the reaction of *mer, trans*- $\text{Mn}(\text{CO})_3[\text{P}(\text{OMe})_2\text{Ph}]_2\text{Cl}$ with NO, have been reported²⁴². The structure is based on a trigonal bipyramid with apical phosphorus ligands.

Predictably (see text), $\text{IrN}_2(\text{PPh}_3)_2\text{Cl}$ reacts with NO in a complex manner.



Catalysis of the reaction



by $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ in ethanol or $\text{Ru}(\text{NO})_2(\text{PPh}_3)_2$ in benzene at 25°C has been reported²⁴³. Some metal dinitrosyl complexes have been cited as being particularly effective in catalyzing this reaction²⁴¹. Thus, while $\text{M}(\text{NO})_2(\text{PPh}_3)_2\text{Br}$ and $\text{M}(\text{NO})_2(\text{PPh}_3)_2^+$ (M = Rh, Ir) are active, $\text{IrNO}(\text{PPh}_3)_2\text{Br}_2$, $\text{Co}(\text{NO})_2(\text{PPh}_3)_2\text{Br}$ and $\text{Co}(\text{NO})_2(\text{PPh}_3)_2^+$ are not.

Section B(i)(c)

Reductive nitrosylation of a CH_2Cl_2 solution of MoCl_5 in the presence of PPh_3 produces $\text{Mo}(\text{NO})_2\text{Cl}_2(\text{OPPh}_3)_2$. The complex $\text{MoNOCl}_3(\text{OPPh}_3)_2$ was observed to be an intermediate by infrared spectroscopy and isolated²⁴⁴.

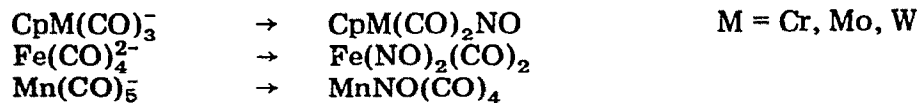
Section B(ii)

A brief review of NO^+ salts as synthetic reagents has appeared²⁴⁵. The effect of solvent is considered in detail, and the need for careful drying of solvents is emphasized.

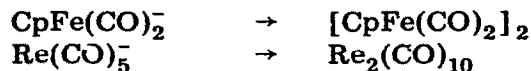
NOPF_6 reacts with $\text{CpW}(\text{CO})_2\text{NO}$ to produce $\text{CpW}(\text{NO})_2\text{CO}^+$ in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ at -78°C . The product is somewhat unique in that the carbonyl group is substitution labile²⁴⁶.

Section B(iii)

Several metal carbonyl anions react with NOCl without coordination of the halogen²⁴⁷.



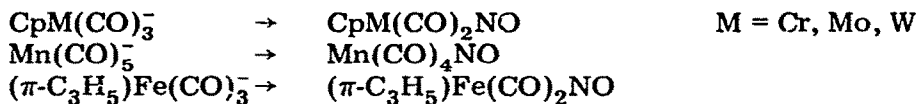
However, more nucleophilic anions act as reducing agents towards NOCl ²⁴⁷.



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

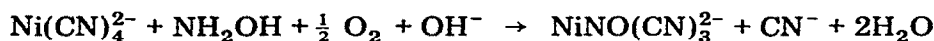
Section B(iv)

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⁺.

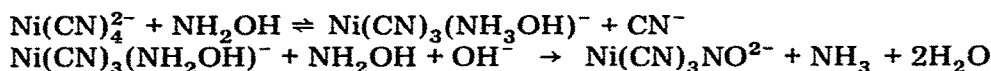


Section B(vi)

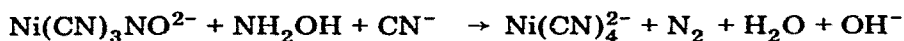
A kinetic study of the reaction of hydroxylamine with Ni(CN)₄²⁻ in basic solution has appeared²⁴⁹. In the presence of oxygen, the stoichiometry is



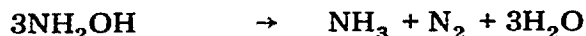
No ammonia is produced. The suggested mechanism involves a pre-equilibrium in which hydroxylamine replaces cyanide. Deprotonation of coordinated hydroxylamine, followed by oxidation of the resultant NiNO(CN)₃⁴⁻ by O₂, completes the reaction. Subsequent oxidation of NiNO(CN)₃²⁻ makes this an unattractive 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



Rather more than one mole of NH₃ is produced per Ni(CN)₃NO²⁻ detected. This is attributed to the following side reaction.



Molecular nitrogen was detected and, in the presence of excess NH₂OH, the major reaction is the nickel-catalyzed conversion of hydroxylamine to nitrogen and ammonia.

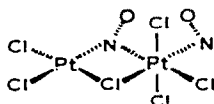


The common theme of this work is that NO⁻ is probably not a reactant (see text). In both instances inhibition by cyanide and catalysis by cyanide scavengers was cited as evidence for preliminary coordination of hydroxylamine.

Section B(vii)

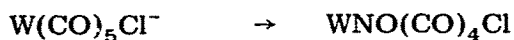
Equimolar sodium nitrite and K₂PtCl₄ react in aqueous ¹Cl. Addition of

Et_4NCl crystallizes a green salt whose actual formula was established crystallographically as $(\text{Et}_4\text{N})_2[\text{Pt}_2(\text{NO})_2\text{Cl}_6]$. The dimeric anion contains both four- and six-coordinate platinum and inequivalent (bent terminal and bridging) nitrosyl groups²⁵⁰.



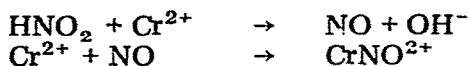
The relationship of this compound to those described in refs. 173 and 177 is unclear. More perplexing is the fact that the crystal actually studied does not have the composition (elemental analysis) of the bulk sample from which it was selected.

Acidification of metal carbonyl anions in the presence of nitrite ion is under study²⁴⁷.



This offers a promising new route to nitrosyl clusters.

A kinetic study²⁵¹ indicates that production of $\text{CrNO}_{\text{aq}}^{2+}$ from NO_2^- in acid solution does not involve NO^+ . The following mechanism was suggested.



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 products²⁵¹.



Section D

Insertion of NO into metal-methyl bonds occurs with Me_2MCl_3 and Me_3MCl_2 ($\text{M} = \text{Nb}, \text{Ta}$). The products are $\text{MCl}_3[\text{ON}(\text{Me})\text{NO}]_2$ and $\text{MeMCl}_2[\text{ON}(\text{Me})\text{NO}]_2$, 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 cleanly²⁵². Two salts of formula $\text{K}_6[\text{Co}_2(\text{CN})_{10}(\text{N}_2\text{O}_2)] \cdot n\text{H}_2\text{O}$, which are claimed to be isomeric with that produced by others^{231,232}, were studied by vibrational spectroscopy²⁵³. The following structures were suggested.



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